Sharp reversals of steady-state nuclear polarisation as a tool for quantum sensing

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The polarisation dynamics of nuclear spins weakly coupled to an NV center is highly sensitive to the parameters of the microwave control and the nuclear Larmor frequency. What is commonly regarded as a challenge, we propose here as a resource for quantum sensing. By varying a single experimental parameter in a suitable set-up, i.e., the Rabi frequency of a continual microwave driving or the nuclear Larmor frequency, we predict periodic reversals of the steady-state polarisation of the nuclear spin. Crucially, interference between the transverse and longitudinal dipolar interaction of electron and nuclear spins results in remarkably sharp steady-state polarisation reversals of nuclear spins within only a few tens of Hz change in the nuclear Larmor frequency. Our method is particularly robust against imperfections such as decoherence of the electron spin and the frequency resolution of the sensor is not limited by the coherence time $T_2$ of the electron sensor.

Introduction — The negatively charged nitrogen-vacancy (NV) defect center in diamond has been studied extensively over the past decade for nanoscale sensing \cite{1,2} and, more recently, as a source for nuclear spin hyperpolarisation. Both applications benefit from the ability to prepare the electron spin of the NV sensor in a pure state by short, microsecond long, laser pulses which achieve over 95\% of electron spin polarisation. Microwave control schemes can then transfer this electron spin polarisation to a nearby ensemble of nuclear spins even at ambient condition \cite{3,11}.

Many dynamic nuclear polarization (DNP) protocols have been developed and applied over the past several decades, starting from continuous microwave irradiation \cite{12} to more efficient pulsed schemes \cite{13,14}. Common to these continuous wave protocols is the use of a long microwave pulse to match the Larmor frequency of the nuclear spins to the electronic Rabi rotation in the frame of reference of the microwave drive, a condition that is known as a Hartmann-Hahn resonance \cite{15}. It has been noticed that, owing to the weak electron-nuclear interaction, even a small detuning from this resonance can have a significant effect on the polarization transfer dynamics. This renders these schemes strongly dependent on the intensity and frequency of the microwave drive as well as the nuclear Larmor frequency. Considerable efforts are being expended to address this challenge for example with the development of polarisation techniques that are less sensitive to precise resonance conditions \cite{16}.

In this work we are adopting a radically different point of view and instead of regarding this strong parameter sensitivity of the polarisation dynamics as a challenge we will explore it as a resource for novel nuclear spin sensing schemes. To this end we investigate the steady-state polarisation in the off-resonant case in which the microwave Rabi frequency is far detuned from the nuclear Larmor frequency. In this regime we observe reversals of the steady-state nuclear spin polarisation that are periodic in the applied Rabi frequency of the microwave drive or the nuclear Larmor frequency. Crucially, we find remarkably sharp steady-state nuclear spin polarisation reversals and build-ups within only a few tens of Hz change in the nuclear Larmor frequency. These sharp polarisation reversals are induced by the interference between the transverse and longitudinal dipolar coupling components of electron and nuclear spins, can be applied for quantum sensing and useful for atomic-scale nuclear spin imaging \cite{17,18,20}.

In sensing applications at room temperature relaxation and decoherence processes of the NV electron spin typically limit spectral resolution and sensitivity in protocols that are based on long Ramsay sequences. In such situations a quantum memory needs to be used for improving the resolution \cite{21,22} which is experimentally challenging. The sensing scheme that we propose here does not rely on direct measurements of the nuclear Larmor frequency in a Ramsay setup but rather on population measurements of the nuclear spin in steady state. As a consequence the coherence time of the NV center does not limit the spectral resolution in our set-up.

The model — We start by considering an isolated spin pair formed by an NV center and a nuclear spin $i$ with gyromagnetic ratio $\gamma_n$. Their interaction can be described by the dipole-dipole coupling $H_{\text{int}} = S_z \cdot A_i \cdot I_i$, where $A_i = (a_{i\parallel}, a_{i\perp})$ is the hyperfine vector with $a_{i\parallel}$ and $a_{i\perp}$, denotes the related coupling components paral-
one can go to rotating frame with a nuclear spin. The coupling parameter is \((a_\parallel, a_\perp) = (2\pi)(40, 10) \text{ kHz}\). The nuclear spin is initially in a fully mixed state \(\rho_0 = \frac{1}{2}\) and the total evolution time is 11 ms. Up: Pulse sequences in our scheme. Bottom: (a) The steady-state polarisation changes with the reset time, \(\omega_n = (2\pi)15 \text{ kHz}, \Omega = (2\pi)200 \text{ kHz}\). (b) The steady-state polarisation changes with the Rabi frequency of the driving, \(\omega_n = (2\pi)15 \text{ kHz}\). The blue line presents \(t_\text{sw} = 11 \mu s\) and the red dashed line shows \(t_\text{sw} = 22 \mu s\). (c) Periodical steady-state polarisation shows up as well as the sharp reversals with the change of nuclear Larmor frequency of nuclear spin \(\Omega\). The coupling parameter is \((a_\parallel, a_\perp)\) and the microwave dressed states \(\{\pm\}\) define \(\sigma_z = \frac{1}{2}(|+\rangle\langle+| - |−\rangle\langle−|)\). We assume \(h = 1\) as customary and the Hamiltonian of the model is given by

\[
H'_{\text{tot}} = \Omega x + \omega_n I_z + \sigma_\parallel (a_\parallel I_ \parallel + a_\perp I_\perp),
\]

one can go to rotating frame with \(H_0 = \Omega x + \omega_n I_z\) and

\[
H_{\text{in}} = a_\perp (e^{i\Delta t} \sigma_+ I_+ + e^{-i\Delta t} \sigma_- I_-) + a_\parallel e^{i\Omega t} I_ \parallel \sigma_ + + H.C.,
\]

in which \(\Delta_\perp = \Omega \pm \omega_n\).

The NV spin is initialised to the ground state by green laser illumination and transferred to state \(|−\rangle\) by using a microwave-\(\pi/2\) pulse. We follow the basic cycles for nuclear spin polarisation, namely an iteration between evolution according to Hamiltonian \((1)\) followed by reinitialisation of the electron spin to \(|−\rangle\). The density matrix of the system evolves according to

\[
\rho_n(t + t_{\text{re}}) \rightarrow \text{Tr}_e[U(t_{\text{re}})](\rho_n(t) \otimes |−\rangle\langle−|)U^\dagger(t_{\text{re}}))
\]

\(\text{Tr}_e\) presents the trace over the electron and \(\rho_n\) is the density matrix of nuclear spins in the system. All the numerical simulations are implemented by using Eq. \((3)\), the reset of the NV to the state \(|−\rangle\) every \(t_{\text{re}}\) introduces an effective interaction time in each cycle and \(U(t_{\text{re}}) = e^{-iH'_{\text{tot}}t_{\text{re}}}\).

When \(\omega_n \sim 2k\pi/t_{\text{re}}\) \((k = 1, 2, ...),\) one can do an expansion on a detuning \(\delta = \omega_e - 2k\pi/t_{\text{re}}\) \((\delta t_{\text{re}} \ll 1\) and \(k = 1\) is chosen for simplification) the time evolution operator is given by \(U_{\text{tot}} = U_0U_{\text{int}} = e^{-iH_{\text{tot}}t_{\text{re}}}e^{−i\delta t_{\text{re}}}[iH_{\text{tot}}dt]\) with \(e^{-iH_{\text{tot}}t_{\text{re}}} = e^{-i\omega_n t_{\text{re}}}e^{i\omega_{\text{int}} t_{\text{re}}}}\). According to the second-order expansion, the master equation is given by

\[
\rho_n(t + t_{\text{re}}) = \sum_{j,k=\pm} |C_j I_j^x + C_k I_k^x + C_k^* I_k^y| \rho_n(t) + \text{(D}[I_j] + \mathcal{M}_j[I_k] + \mathcal{M}[I_j])\rho_n(t),
\]

in which \(\mathcal{D}[I_\parallel] \rho_n = \pm g_{\parallel} g_{\text{int}} I_\parallel I_\perp \rho_n + \rho_n I_\perp I_\parallel - 2I_\parallel \rho_n I_\parallel, \mathcal{M}_\parallel[I_\parallel] \rho_n = g_{\parallel} g_{\text{int}} I_\parallel I_\perp \rho_n + \rho_n I_\perp I_\parallel - I_\parallel \rho_n I_\parallel, \mathcal{M}_\perp[I_\perp] \rho_n = 2g_{\parallel} g_{\text{int}} I_\parallel I_\perp \rho_n + \rho_n I_\perp I_\parallel - 2I_\parallel \rho_n I_\parallel, \mathcal{M}[I_j] \rho_n = -2g_{j\parallel} g_{\text{int}} I_\parallel \rho_n I_\parallel.\)

The detailed expansion and defined terms in Eq. \((4)\) are given in SM 27.

When \(|\delta| \gg |C_x|, |C_y|, ..., |g_{j\parallel} g_{\text{int}}|\), the steady state polarisation of the system is given by \(\rho_s^{\text{ss}} \approx N_c^x \frac{1}{\sqrt{2}} |+\rangle\langle+| + |−\rangle\langle−| (\text{with the normalized coefficent} N_c^x, \text{see SM 27}).\) The steady state polarisation of the nuclear spin is determined by the competition between the dissipation items \(\mathcal{D}[I_\parallel] + \mathcal{D}[I_\perp].\) Therefore, by controlling the Rabi frequency of MW driving \(\Omega\) (Fig. 1), the reset time \(t_{\text{re}}\) or the nuclear Larmor frequency (Fig. 1a, b and c)), the effective dissipation rates are shifted and periodical reversals of the nuclear steady state polarisation are shown. Namely, the nuclear polarisation reversals arise from the imbalance between effective flip-flop rate from \(\sigma_+ I_+ + \sigma_- I_-\) and flip-flop rate from \(\sigma_\parallel I_\parallel + \sigma_\perp I_\perp,\) which is similar to the polarisation reversals in Ref. 28. These also fit well with Fermi golden rules by calculating the transition probabilities between \(|−\rangle\leftrightarrow|+\rangle\) (flip-flop) and \(|−\rangle\leftrightarrow|+\rangle\) (flip-flip) 27 and our numerical simulations in Fig. 1 (a, b and c).

Sharp polarisation reversals for quantum sensing

When \(\omega_n \sim 2\pi/t_{\text{re}}\) and \(|\delta|\) is comparable to \(|C_x|, |C_y|, ..., |g_{j\parallel} g_{\text{int}}|\), reversals of the positive and negative steady-state polarisation \(2I_\parallel\) of the NV spin is built-up by using negative steady-state polarisation states \(|−\rangle\) around the same nuclear Larmor frequency, (see Fig. 1c and d). Additionally, there
are similar characters of steady-state polarisation of z-direction and x-direction, as shown in Fig. 1d and Fig. 2c, the reversal point of steady-state polarisation $\langle 2I_z \rangle$ is coincide with the trough of the negative steady-state polarisation $\langle 2I_z \rangle$ built-up and linewidths are the same. These phenomenons arise from interference between the transverse and longitudinal dipolar interaction of electron and nuclear spins. Notice that the transversal interactions $\sigma_x a_x I_t^x$ do not commute with longitudinal interaction $\sigma_x a_x I_t^z$, there are several interference items of $I_x$, $I_y$ and $I_z$ in the second-order expansion of the time-dependent evolution operator $Te^{-i \int_0^t \text{H}_{\text{tot}} dt}$, as well as $M_{I_j}[I_k]$ and $M[I_z]$ in the second-order expansion of the master equation. These interference items are negligible when $|\delta| \gg |C_x|, |C_y|, ..., |g_x g_z^2|$, but play key roles when $|\delta|$ is comparable to $|C_x|, |C_y|, ..., |g_x g_z^2|$, details are given in SM [27].

Through careful calculations, near the anomalous points $\omega_n \sim 2\pi/t_{\text{re}}$, the related items of the steady polarisation in z-direction $\langle 2I_z \rangle$ could be simplified as

$$\rho_{ss}^z \simeq N_e [\frac{\delta - \omega_{\text{an}}}{\delta - \omega_{\text{an}}} | \downarrow_i \rangle \langle \downarrow_i | + | \uparrow_i \rangle \langle \uparrow_i |],$$

in which a small detuning is defined as $\delta = \omega_n - 2\pi/t_{\text{re}}$. Therefore, the reversal points is shifted from $2\pi/t_{\text{re}}$ by $\frac{\omega_{\text{an}}^2}{2\omega_n}$ (see Fig. 2) and the linewidth of the spectra, namely the frequency resolution of the anomalous steady state polarisation reversal is approximated to be $a_{ss}^2 t_{\text{re}}$, which fits the numerical simulations in Fig. 2. We take steady-state polarisation $\langle 2I_z \rangle$ in z-direction as an example to illustrate the characters of these reversal points, because characters of steady-state polarisation of z-direction and x-direction are quite similar.

There are several characters of these reversal points.
The calculation of the worst-case asymptotic convergence is not related to the MW driving and transversal coupling. Converging of the system at the trough is shown in Fig. 4.

The nuclear spin converges to steady-state polarisation when NV resets are applied every $t_{re} = 44 \mu s$ with $(a_\perp, a_\parallel) = (2\pi)(4,0.5) \text{ kHz}$, $\omega_n = (2\pi)22.64 \text{ kHz}$ and $\Omega = (2\pi)2 \text{ kHz}$ (the red line). (a) The other lines are different from the red one with $\Omega = (2\pi)1 \text{ kHz}$ (the black dotted line), $a_\perp = (2\pi)2 \text{ kHz}$ (the blue dashed line). (b) The red line is the same as the one in (a). The blue dashed one is different from the red one with $a_\parallel = (2\pi)0.25 \text{ kHz}$, while the black dotted line is with $t_{re} = 22 \mu s$.

i) They are periodically shown up via the shift of the Larmor frequency of nuclear spin and very sensitive to the shift. ii) With the given reset time of the electron spin, the shift of the reversal points from $2\pi/t_{re}$ depends on the transverse coupling, and the frequency linewidth of the spectra is determined by the longitudinal dipolar coupling, as shown in Fig. 2. iii) It is quite robust. The electron spin is reinitialized every tens of $\mu s$, which makes the steady polarisation built-up not sensitive to electron spin decoherence, as shown in Fig. 3a. The scheme works when the reset time is within the decoherence time of the NV center and the linewidth is not related to the NV center decoherence.

All these features make our scheme has potential applications for quantum sensing. Specifically, we detect the steady-state polarisation signal of nuclei located in close proximity to the NV center. The electron spin of the NV center can be optically initialized and read out by using laser illumination. One can have the nuclear spins to be polarised in the off-resonant case with the NV resets, then read out the steady-state polarisation reversal points to spectrally resolve nearby signals, we expose the sensor to two closed nuclear spins with slightly different frequencies. As shown in Figure 3c and d, both frequency components can be clearly achieved in the resulting spectrum even though the Larmor frequencies are only 50 Hz apart. The sensing is related to the steady state of the target nuclear spin which makes the sensing is robust to electron spin decoherence.

Conclusion — In conclusion, we show the remarkable results of periodic steady state polarisation reversals and built-ups when a nuclear spin interacts with a periodically reinitialised electron spin. Based on these steady state polarisation reversal points, we provide a new method for quantum sensing, particularly robust against imperfections such as decoherence from the electron spin, with the resolution of the sensor not being limited by the decoherence time $T_2$ of the electron sensor.

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