Low field nuclear polarization using Nitrogen Vacancy centers in diamonds

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It was recently demonstrated that bulk nuclear polarization can be obtained using Nitrogen Vacancy (NV) color centers in diamonds, even at ambient conditions. This is based on the optical polarization of the NV electron spin, and using several polarization transfer methods. One such method is the NOVEL sequence, where a spin-locked sequence is applied on the NV spin, with a microwave power equal to the nuclear precession frequency. This was performed at relatively high fields, to allow for both polarization transfer and noise decoupling. As a result, this scheme requires accurate magnetic field alignment in order to preserve the NV properties. Such a requirement may be undesired or impractical in many practical scenarios. Here we present a new sequence, termed the refocused NOVEL, which can be used for polarization transfer (and detection) even at low fields. Numerical simulations are performed, taking into account both the spin Hamiltonian and spin-decoherence, and we show that, under realistic parameters, it can outperform the NOVEL sequence.

Dynamic Nuclear Polarization (DNP) 1 has gained renewed interest in recent years 2, 3 due to its ability to dramatically increase the signals in nuclear magnetic resonance spectroscopy (NMR) and imaging (MRI) experiments. This relies on polarization transfer from electrons to their neighboring nuclei via microwave (MW) irradiation. The DNP process is typically performed at cryogenic temperatures, in order to gain high initial electron Boltzmann polarization. An alternative approach is to use high non-equilibrium polarization 4, 5, allowing high polarizations to be achieved even at ambient conditions. It was recently demonstrated that Nitrogen-Vacancy (NV) color centers in diamonds 6–8 can be used as such a polarization source, based on the ability to polarize the NV electronic S = 1 spin to its |0⟩ ground state using optical illumination with 532 nm green light. Such an NV based polarization source offers many advantages: it allows fast electron polarization; it is extremely stable; it can be used in combination with coherent polarization schemes due to the NV spin long coherence times 9; and it relies on a relatively simple experimental setup. Nevertheless, polarization transfer to nuclei outside of the diamond itself still poses many challenges. It was also shown that nuclear polarization can improve NV based measurements, by increasing the NV spin free evolution/Ramsey coherence time 10.

NV based polarization of 13C nuclei in the diamond can be achieved using the NOVEL (nuclear orientation via electron spin locking) scheme 11, 12, allowing for nuclear sensing 10 and bulk polarization 13. During this sequence a spin-lock 14 (SL) is applied on the NV spin with a SL Rabi frequency equal to the nuclear Larmor frequency, resulting in the rotating-frame/lab-frame Hartmann-Hahn polarization transfer condition. These NV based experiments were performed at relatively high fields (around 5000 Gauss) to allow for efficient SL noise decoupling together with the Hartmann-Hahn condition. This relatively high magnetic field requires precise alignment of the field direction to that of the NV axis, in order to allow for the laser induced NV spin polarization to take place. NV based polarization transfer was also obtained using an aligned magnetic field of 514 Gauss 15, for which NV-nuclear state mixing occurs in the excited state, or at arbitrarily aligned fields, but based on the interaction of the NV to its close neighboring 13C nuclei 16.

In this article we present a method for coherent polarization transfer to remote nuclei (and therefore possibly also to nuclei outside of the diamond) at low fields (≪ 500 Gauss), for which field alignment is less demanding. This can be of importance for nuclear polarization applications in which field alignment is undesired or impractical, possibly including the use of nano-diamonds.

The sequence presented here, is shown schematically in Fig. 1. It is composed of three parts: (1) initialization, which includes a laser pulse for NV polarization and spin state detection, and a π 2 preparation pulse; (2) the

Figure 1. Schematic representation of the refocused-NOVEL sequence, as described in the main text.
refocused-NOVEL (rNOVEL) sequence, which is composed of $N$ repetitions of two SL pulses of duration $\frac{\tau_s}{2}$, separated by a $\pi$ pulse of the same phase (unlike the re-focused continuous-wave decoupling sequence [17] [18]); and (3), a detection $\frac{\pi}{4}$ pulse, which can be added with different phases for optical detection of the NV polarization.

In order to describe the effect of this sequence we can consider a simple model spin system composed of the $S = 1$ NV electron, limited to its $|0\rangle, |1\rangle$ subspace, and a spin $I = \frac{1}{2}$ nucleus. The Hamiltonian of this system in the electronic rotating frame is given, assuming ideal $\pi$ pulses for simplicity, by [14]:

$$H = \Delta_e S_z - \omega_0 I_z + A_{||} S_x I_x + \frac{1}{2} S_z (A_+ I^+ + A_- I^-) + b(t) S_z + \frac{1}{\sqrt{2}} \Omega_{SL} S_x + \sum_{k=1,3,5,...} N \delta(t - \frac{1}{2} k \tau) \pi_x.$$  

(1)

The above Hamiltonian includes the off resonance irradiation on the electronic spin, $\Delta_e$; the nuclear Larmor precession frequency $\omega_0$; the secular and pseudo-secular terms of the hyperfine interaction, $A_{||}$ and $A_\perp$; external pure dephasing noise, $b(t)$; and the MW irradiation term, given by the SL term with an amplitude of $\Omega_{SL}$ and the ideal $\pi_x$ pulses.

We can next transfer to the interaction frame of the ideal $\pi$ pulses. This is given, for an even $N$, by a unitary transformation of the form $U(t) = e^{i \frac{1}{2} \sum_k \delta(t' - k \tau) S_x dt}$. The resulting Hamiltonian is then given by:

$$H' = s(t) [\Delta_e + A_{||} I_z + \frac{1}{2} (A_+ I^+ + A_- I^-) + b(t)] S_z - \omega_0 I_z + \Omega_{SL} S_x,$$

$$s(t) = \begin{cases} 1, & 0 \leq \text{mod} (t, 2 \tau) < \frac{\tau}{2} \\ -1, & \frac{\tau}{2} \leq \text{mod} (t, 2 \tau) < \frac{3\tau}{2} \\ 1, & \frac{3\tau}{2} \leq \text{mod} (t, 2 \tau) < 2\tau \end{cases}.$$  

(2)

$s(t)$ is a periodic square wave, with a frequency of $\omega_f = \pi/\tau$ (as in CPMG [19] and similar sequences) which can be expended in terms of a Fourier Series:

$$s(t) = \sum_k s_k e^{ik\omega_f t},$$

$$s_k = 2(-1)^{\frac{k+1}{2}} \frac{\pi k}{\omega_f},$$  

(3)

with $k = \pm1, \pm3, ...$.

In order to simplify the form of $H'$, we can transfer to a rotating frame in $S_x$, with a frequency of $k'\omega_f$. Assuming that $\omega_f \gg |\Delta_e + \frac{1}{2} A_{||} + b(t)|, |A_\perp|$ (at all times), we can neglect all the $k \neq k'$ time-dependent terms. As such, the Hamiltonian can be written as:

$$H^R \approx s_k' [\Delta' S_z + \frac{1}{2} (A_+ I^+ + A_- I^-) S_z] - \omega_0 I_z + \Omega_k S_x,$$

(4)

where $\Delta' = \Delta_e + A_{||} + b(t)$, and $\Omega_k = \Omega_{SL} - k'\omega_f$. This reduces the Hamiltonian to a familiar form, with $\Delta'$ and $\Omega_k$ serving as effective detuning and irradiation terms on the $S$ spin. As such, $\Delta'$ will have little effect on the spin dynamics when $s_k' \Delta' \ll \Omega_k$, resulting in a decoupling of the undesired off resonance and noise effects. In addition, when $\Omega_k \approx \pm \omega_n$, with $\omega_n = \omega_0 + \frac{1}{2} A_{||}$ to first order (see supplementary material (SM)), the NOVEL Hartmann-Hahn condition is met, and the $A_{||}$ part of the hyperfine interaction will result in polarization transfer between the electron and nucleus [12] (See SM). Higher $k'$ values will lead to higher quenching of the interactions, resulting in narrower resonance conditions, lower dephasing and slower polarization transfer. We note that in the extreme case of $\Omega_{SL} = 0$ or $\omega_f \rightarrow 0$ (i.e no $\pi$ pulses) these conditions are identical to the ones used for CPMG based sensing [20] and spin-lock/NOVEL experiments, respectively.

In order to demonstrate these conditions and their effects on the spin system, we performed numerical simulations on a system composed of an NV and a single $^{13}$C nucleus, with $A_{||} = 30$ kHz, $A_\perp, \Delta_e = 40$ kHz, and an external field of 80 Gauss. The NV and nuclear polarizations, $\langle S_z \rangle(t) = \langle 0 | \rho(t) | 0 \rangle - \langle -1 | \rho(t) | -1 \rangle$ and $\langle I_x \rangle(t) = 2Tr(I_x \rho(t))$ respectively, were calculated using the Liouville von-Neumann equation,

$$\frac{\partial \rho}{\partial t} = -i[H, \rho],$$  

(5)

where $H$ is given in Eq. [1] When dephasing noise was considered, a bath modeled by an Ornstein-Uhlenbeck process was considered, with a correlation time $\tau_c$, and an interaction strength $\Delta_{noise}$ with the NV. This is described in more detail in the SM, based on Ref. [21].

Fig. 2 depicts the resonance conditions of this sequence, with the NV and nuclear polarizations plotted as a function of the sequence periodicity $\omega_f$ and the SL power $\Omega_{SL}$. This was performed using $N = 60$ and without dephasing noise, $b(t) = 0$. Changes in $\langle S_z \rangle$ (Fig. 2a) occur around $\Omega_{SL} = k\omega_f$ and $k\omega_f \pm \omega_n$ (with $\omega_n/2\pi \approx 0.1$ MHz). The former originates from the off resonance term and $A_{||}$, and can result in polarization inversion, but not in nuclear polarization; the latter originates from $A_{||}$, and results in NV-nuclear polarization transfer, as seen by the change in $\langle I_x \rangle$ (Fig. 2b). Far from these conditions the state of the NV and nuclear polarizations remain unchanged. We note that the sign of $\langle S_z \rangle$ and $\langle I_x \rangle$ can be inverted by changing the relative phase of the final $\pi/4$ pulse or of the rNOVEL pulses with respect to the initial $\pi/4$ pulse, respectively.
A more convenient form of the experiment is to sweep \( \Omega_{SL} \) and \( N \) with a fixed \( \tau \) value (in analogy with the NOVEL sequence), resulting in discrete changes of the total experiment time \( T = \tau N \). This is shown in Fig. 3(a,b), where the values of \( \langle S_z \rangle \) and \( \langle I_z \rangle \) are plotted, respectively, using an rNOVEL sequence with \( \tau = 2 \mu s \) (\( \omega_J/2\pi = 0.25 \) MHz). The resonance conditions are centered around \( \Omega_{SL} = 0.25, 0.75, 1.25 \) MHz for the \( k = 1, 3, 5 \) conditions, respectively, with the nuclear polarization transfer conditions separated by \( \omega_n \) from it (as was described above, and as marked in the figure). As expected, the reduction in the \( s_k \) values for higher \( k \) conditions (Eqs. 3-4) results in slower oscillations and narrower resonance conditions. A simulation of a regular NOVEL experiment is shown in Fig. 3(c,d) for comparison. This was performed using the same parameters as the rNOVEL, but omitting the \( \pi \) pulses. Here, the resonance conditions are centered around \( \Omega_{SL} = 0 \), with faster oscillations and broader conditions than in the rNOVEL case.

So far we did not consider the effects of dephasing noise. We next introduce this using parameters measured for shallow NVs with a depth of about 3 nm from the diamond surface [22]. This is given by fast and slow noise components, characterized by \( \tau_c \) of 11 and 150 \( \mu s \), and with \( \Delta_{noise} = 0.5 \) MHz used in both cases. The resulting NV and nuclear polarizations are plotted in Fig. 4 using the same spin system as before, for the rNOVEL (a,b) and NOVEL (c,d) sequences. Note the change in \( \langle I_z \rangle \) color-scale when compared to Figs. 2 and 3. In the NOVEL case, the low \( \Omega_{SL} \) power needed to polarize the nucleus is insufficiently strong to remove the effect of the decoherence noise. This results in a loss of NV polarization, leading to only \( \sim 6\% \) maximal polarization. In the rNOVEL sequence the effect of the noise on the NV polarization is reduced with \( k \), as can be seen in Fig. 4(a.) when comparing the different \( k \) conditions. This results in as much as \( \sim 13\% \) nuclear polarization, a factor of 2 higher than for the NOVEL case, but still lower than in the ideal scenario, in which noise was not considered (Fig. 3). We stress that the enhanced polarization, as well as the narrow spectral response, are the significant advantages of rNOVEL compared to NOVEL, and constitute the main results of this work. Enhanced polarization could clearly benefit various applications, such as in sensing [20] and cooling [10], and the high spectral resolution could contribute to selective addressing [23].

The limited nuclear polarization, as shown in Fig. 3,
In real systems the NV can interact with many nuclei, including the NV’s \(^{14/15}\)N nucleus. The strong hyperfine interaction with the latter will result in undesired off-resonance terms. These can be avoided by adding \(^{14/15}\)N pre-polarization \([24]\) or pre-saturation to the initialization step. In addition, the interaction with many remote nuclei will result in faster polarization transfer from the NV to the nuclei, leading to higher NV polarization loss in a single cycle. This will limit the amount of nuclear polarization that can be transferred within a single cycle of the sequence, requiring multiple cycles for substantial nuclear polarization. In addition, this can increase the feasibility of NV based detection of nuclear polarization, even in noisy spin systems. For this goal polarization - depolarization super cycles can be used, by alternating the phase of the initial \(\pi/2\) pulse phase \((y, y)\) or the rNOVEL pulses \((x, x)\) \([10]\).

While in principle the rNOVEL sequence can work at high fields, it will have disadvantages when compared with the NOVEL sequence. In particular, at high fields different re-coupling conditions can overlap, complicating the interpretation of the resulting signals. The lower limit on the field originates from the reduced separation between the noise and polarization conditions, and from the loss of nuclear polarization axis (see SM). Possible effects of the external field strength and alignment on the decoherence of the spin system must also be considered \([24]\).

Finally, the effects of MW imperfections were not considered here. These may be reduced using alternating phase rNOVEL sequences, in analogy with the CPMG variations such as XY-4 and XY-8 \([26, 27]\), or by continuous SL phase/power modulation \([28, 29]\).

To conclude, we presented here the refocused-NOVEL sequence, which is capable of both nuclear polarization and improved noise decoupling when compared with the NOVEL sequence. This can be used even at low fields, where precise field alignment is not needed, and where the NOVEL sequence is limited due to low noise decoupling. The basic spin dynamics of the rNOVEL sequence was explained and demonstrated using numerical simulations, and we described how it can be used to tune the amount of noise decoupling, at the cost of reduced NV-nuclear polarization transfer rate. Future studies of this sequence will include experimental realization, with the goal of creating nuclear polarization at low fields.

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