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To cite this article: Seungjoo Nah 2016 Mater. Res. Express 3 075008

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Dynamic nuclear polarization in diamond

Seungjoo Nah
Samsung Electronics, Yongin, Gyeonggi 17113, Korea
E-mail: seungjoo.nah@gmail.com

Keywords: NV centers, dynamic polarization, long-life coherence, dephasing, fast-phonon transitions

Abstract
We study the dynamic nuclear polarization of nitrogen-vacancy (NV) centers in diamond through optical pumping. The polarization is enhanced due to the hyperfine interaction of nuclear spins as applied magnetic fields vary. This is a result of the averaging of excited states due to fast-phonon transitions in the excited states. The effect of dephasing, in the presence of a vibronic band, is shown to have little effect during the dynamic polarization.

1. Introduction
Negatively charged nitrogen-vacancy (NV) centers in diamond are a promising candidate for solid-state quantum computation. Due to the long-life coherence of nuclear spin, optical coherent mapping of nuclear spin onto the electronic spin states of NV centers at room temperature, has attracted intensive research aimed at developing solid state systems for the study of spintronics and quantum computation. NV centers can be spin-polarized by optical pumping via intersystem states which transfers nonzero electronic spin of the excited states $S_1^z = \pm 1$ to $S_0^z = 0$ of the ground states. This is used to initialize the NV center in experiments. It is known that the nuclear spin of the NV centers can be polarized via hyperfine coupling of the electron/nuclear spin through Level Anti-Crossing (LAC) of sub-levels in the excited states at the magnetic field $B = 512$ gauss, see equation (10) below [7–9]. This provides a method for controlling the nuclear spin of the NV centers by varying magnetic fields during optical cycling between the ground and the excited states. LAC is the result of averaged states between two orbital branches $E_X$ and $E_Y$ in the excited states $3E$ due to fast-phonon mediated transitions $R \sim 1$ THz, see figure 1.

Although it is estimated that LAC is a result of the phonon-mediated transitions inducing the population transfer between the two branches, it has yet to be treated analytically [1]. In this paper, we analytically investigate the averaging in the excited states via the fast phonon-mediated transitions between the two branches and dynamic nuclear polarization of the NV centers in diamond, which is enhanced through LAC.

This paper is organized as follows. In section 2, we describe the excited states model of the NV centers and show the averaging in the excited states due to the fast phonon-mediated transitions. In section 3, we derive the master equations for the whole systems during optical cycling, and in section 4 we discuss the results and the dynamic nuclear polarization of the NV centers.

2. Model: excited states and averaging due to phonon transitions
The excited state Hamiltonian of the NV centers in diamond is

$$H_{\text{ex}} = H^+ \oplus H^- + H_{\text{int}} + H_{\text{bath}},$$

with a phonon-bath Hamiltonian $H_{\text{bath}}$. The first and the second terms, $H^+$ and $H^-$, represent the NV centers corresponding to the two orbital branches $E_X$ and $E_Y$ respectively, including the Zeeman splitting and the hyperfine interaction but neglecting the nuclear Zeeman splitting

$$H^\pm = D_{\text{eo}} S_x^\pm + H_{\text{zm}} + H_{\text{HF}},$$

where the zero-field energy splitting $D_{\text{eo}}^\pm$ corresponds to the two orbital branches.
The Zeeman splitting due to the applied magnetic field $B$ is

$$H_{zm} = g \mu_B B S_z$$

for electronic spin projection operator $S_z$ along the symmetric axis of the NV centers [2]. Here, $g \approx 2$ is the electron $g$ factor [4, 6] and $\mu_B$ the Bohr magneton.

The hyperfine interaction via electronic/nuclear spin flip is

$$H_{HF} = A_s^L S_z I_z + \frac{A_{es}}{2} (S_+ I_- + \text{H.c.}),$$

where $S_z$ is the electronic spin raising operator and $I_z$ is the nuclear spin lowering operator (H.c. is short for Hermitian conjugate of the first term in parenthesis above). The reported values of the hyperfine couplings are $A_s^L/A_{es} = -57.8/-59.2$ MHz for $^{13}N$ [9].

The interaction in equation (1) represents a weak coupling between the phonon-bath and the NV centers. Assuming weak interaction and a Markovian approximation in the bath, we project out the bath in equation (1) to derive the master equations of the system of the NV centers [17, 18].

The master equations of the system density matrix can be written in terms of two variables (fast and slow variables, see below) due to the block diagonalized structure of the unperturbed basis $|S_n, I_z\rangle$ of electronic/nuclear spin projection onto the symmetric axis of the NV centers in diamond in the order of $|m_S, m_I\rangle = \{|+, 1\rangle, |+, 1\rangle, |-, 1\rangle, |-, 1\rangle, |0, 1\rangle, |0, 1\rangle\}$ for $^{13}N$ by assuming perfect alignment of the applied magnetic field $B$ along the symmetric axis of the NV centers. This is well-defined at high strain in diamond, [3] and as a consequence of the negligible coherence between the two branches according to the Markovian approximation, the master equations of the two branches are ($\hbar = 1$)

$$\dot{\rho}^\pm = -i[H^\pm, \rho^\pm] - R \rho^\pm + R \rho^\mp,$$

where $R$ is the rate of phonon transitions between the two branches, see figure 1.

Separation of slow/fast variables in equation (5) as $\rho = \rho^+ + \rho^-$ and $\tilde{\rho} = \rho^+ - \rho^-$ to isolate the phonon related terms reads

$$\dot{\rho} = -i[\tilde{H}, \rho] - i[\tilde{H}, \tilde{\rho}],$$

$$\dot{\tilde{\rho}} = -i[\tilde{H}, \tilde{\rho}] - i[\tilde{H}, \rho] - 2R\tilde{\rho},$$

where $\tilde{H} = (H^+ - H^-)/2$ and $\tilde{H} = (H^+ + H^-)/2$ accordingly. It should be noted that the fast transition rate $R \sim 1$ THz appears only in the second equation while the resonant frequency of the first equation is of the order of a few GHz.

The fast variables approach quasi-equilibrium in a short time due to large $R$, resulting in

$$\tilde{\rho} \approx -i[\tilde{H}, \rho]/2R,$$

which is the source of the dephasing in the excited states due to the fast-phonon mediated transitions between the two branches [1]. This can be shown by constructing an augmented matrix of $2d$-dimension from the $d$-dimensional matrix, the second term of equation (6b) on the right hand side, then diagonalizing the augmented matrix and showing the eigenvalues of the matrix are negligible in comparison with $R$. The augmented matrix has a form of

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Figure 1. Electronic excited states of the NV centers: two spin-triplet branches $E_x$ and $E_y$, and the phonon-mediated transition $R$ between the two branches, which is to be averaged in this paper.
\[ F = \begin{pmatrix} A & 0 & 0 \\ 0 & B & 0 \\ 0 & 0 & C \end{pmatrix}. \]  

(8)

For \(^{15}\text{N}\), \(d = 6\), and hence \(\text{dim}(F) = 12\). This structure remains intact when optical cycling between the ground and the excited states is included in section 3, since the optical transition is spin–conserving. Each sub-matrix in the block-diagonalized matrix, equation (8), can be rearranged to have a structure of, for instance,

\[ A = i \begin{pmatrix} 0 & 0 & a & -a \\ 0 & 0 & -a & a \\ a & -a & \omega & 0 \\ -a & a & 0 & -\omega \end{pmatrix}, \]

where \(a\) and \(\omega\) are of the order of or less than GHz at given strain in diamond, corresponding to hyperfine coupling and resonant frequency, respectively. For the sub-matrix, there exists a similarity transformation \(T_\mu\), i.e. such that, for example, \(T_\mu^* A T_\mu^{-1} = \hat{D}_\mu\), with \(\text{max} \{ D_\mu \} \ll R\) (see also Ref. [1] for detail). Thus, the equations of the fast variables equation (6a) reach quasi-equilibrium equation (7), accounting for leading order in \(R\).

Substitution of the relation equation (7) into equation (6a) reads

\[ \dot{\rho} = -i[H, \rho] - [\hat{H}, [\hat{H}, \rho]]/2R. \]  

(9)

For slow variables \(\bar{\rho}\), corresponding to the averaged level states in the excited states with the introduction of dephasing due to phonons, the second term on the right hand side above has not received any attention in NV centers until recently [1]. The result of this consideration is equivalent to averaging the excited state Hamiltonian

\[ \Pi_{\text{es}} = \bar{D}_{\text{es}} S_z^2 + H_{\text{int}} + H_{\text{bath}}, \]  

(10)

which is explained empirically in several experimental papers [5, 6, 7, 9] with the averaged energy splitting \(\Pi_{\text{es}} = 1.42\text{GHz}\) between \(m_S = \pm 1\) and \(m_S = 0\) in the excited states. This is the origin of LAC at 512 gauss (\(\omega \approx 1.42\text{GHz}\)).

3. Master equations: whole system

The Hamiltonian of the whole system, as a result of averaging the excited state branches (see equation (10)) and adding the ground states, reads

\[ H = \Pi_{\text{es}} \oplus H_{\text{gs}} + H_{\text{int}} + H_{\text{bath}}. \]  

(11)

Here, we have to consider two types of bath in the whole system

\[ H_{\text{bath}} = H_{\text{ph}} \oplus H_{\text{pt}}, \]  

(12)

where \(H_{\text{ph}}\) describes the phonon-sideband and \(H_{\text{pt}}\) corresponds to the photon during optical cycling between the ground and the excited states [10, 11, 12, 13]. Accordingly, \(H_{\text{int}}\) consists of two types of the interactions corresponding to the two baths, assuming weak interaction with the NV centers.

The ground state Hamiltonian \(H_{\text{gs}}\) has a similar structure with that of the averaged excited states

\[ H_{\text{gs}} = D_{\text{gs}} S_z^2 + g\mu_B BS_z \]

\[ + A_{\text{gs}}^z S_z I_z + A_{\text{gs}}^\perp (S_y I_y + \text{H.c.}), \]

(13)

but \(D_{\text{gs}} = 2.87\text{GHz}\) and \(A_{\text{gs}}^z/A_{\text{gs}}^\perp = 2.3/2.7\text{MHz}\) for \(^{15}\text{N}\) [8, 9]. It is known that the electron \(g\) factor of the ground states is close to that of the excited states, \(g \approx 2\) [4, 6]. The master equations of the whole system are given by tracing out the bath, as done in section 2 [14, 17–19] (\(h = 1\))

\[ \dot{\rho} = -i[H, \rho] + \mathcal{R}(\rho), \]  

(14)

where the second term on the right hand side represents the relaxation processes of the optical cycling through the phonon sideband, \(H_{\text{int}}\). We adopted a Markovian approximation in the bath of photon and phonon sideband.

Here, we briefly discuss the adiabatic elimination of the phonon-sideband states \(\sigma_{mn}^{1\perp}\) (superscripts related to the NV center states while subscripts to the phonon-states) [17, 19]. For instance,

\[ \sigma_{mn}^{1\perp} = -i\omega_{\text{mn}} \sigma_{mn}^{1\perp} - R_\sigma \sigma_{mn}^{1\perp} + k_\sigma \rho_{\phi}, \]

(15)

where \(\omega_{\text{mn}}\) is the resonant frequency between two phonon-sideband states, \(R_\sigma\) is the decay rate of the phonon-sideband state onto the NV center states, and \(k_\sigma\) is the absorption coefficients, see figure 2. This results in decreasing the magnitude of the coherence transfer between the ground states \(^2\text{A}_2\) and the excited states \(^2\text{E}\) via the phonon sideband, since \(k \ll 1\) [15, 16]. Meanwhile, the populations are
satisfying the conservation of populations transfer during the optical cycling. This does not bring a noticeable change in the final results of this paper, shown below in figure 3.

3.1. Excited state
The master equations for the excited states population $^3E$ after the averaging are (here, we labels diagonal terms $\rho_i$ instead of $\rho_{ii}$, except for off-diagonal components)

$$
\dot{\rho}_i = -\gamma_i \rho_i + \alpha_0 \sigma_i + \alpha_a \sigma_5
$$

$$
\dot{\rho}_2 = -\gamma_2 \rho_2 + \alpha_0 \sigma_2 + \alpha_a \sigma_6 + i a (\rho_{25} - \rho_{52})
$$

$$
\dot{\rho}_3 = -\gamma_3 \rho_3 + \alpha_0 \sigma_3 + \alpha_a \sigma_5 + i a (\rho_{36} - \rho_{63})
$$

$$
\dot{\rho}_4 = -\gamma_4 \rho_4 + \alpha_0 \sigma_4 + \alpha_a \sigma_6
$$

$$
\dot{\rho}_5 = -\gamma_5 \rho_5 + \alpha_0 \sigma_5 + \alpha_0 (\sigma_1 + \sigma_2) + i a (\rho_{52} - \rho_{25})
$$

$$
\dot{\rho}_6 = -\gamma_6 \rho_6 + \alpha_0 \sigma_6 + \alpha_0 (\sigma_3 + \sigma_4) + i a (\rho_{63} - \rho_{36}),
$$

with the ground state density matrix $\sigma$, $a = A_0 \omega / \sqrt{2}$, and an optical excitation/decay rate $\alpha_i/\gamma_i$. The small spin-mixing during optical excitation reported in the experiment is reflected on the terms having $\alpha_a$. See below 3.2 for $\gamma_i$, and $\gamma_c$. 

![Figure 2. Diagram of energy v.s. configuration coordinate of the NV centers in the Frank-Condon approximation: transitions between the ground (lower quasi-parabola) and the excited (upper quasi-parabola) states due to photons (line) and phonons (dash), respectively. The phonon-sideband ($\sigma_{nm}^{\omega}$), see equation (15) for example, is represented in dense lines on the parabolas, see Ref. [13] for detail.](image)

![Figure 3. Dynamic nuclear polarization of the NV centers $^{13}N$ as a function of the applied magnetic field during the optical cycling: two maxima at 512 G and at 1028 G, corresponding to LACs of the excited and the ground states, respectively, are seen.](image)
The off-diagonal components relevant to the above equations due to the hyperfine interaction are
\[
\dot{\rho}_{25} = -(\overline{\omega}_{25} + \tau + \overline{\omega}_{25}^2/2R)\rho_{25} + i\alpha (\rho_2 - \rho_5) + \alpha_k \sigma_{25},
\]
\[
\dot{\rho}_{36} = -(\overline{\omega}_{36} + \tau + \overline{\omega}_{36}^2/2R)\rho_{36} + i\alpha (\rho_3 - \rho_6) + \alpha_k \sigma_{36},
\]
(18)
where \(\tau = (\gamma_0 + \gamma_2)/2\). For the averaged frequency in the excited states, \(\overline{\omega}_{ij} = (\omega_{ij}^+ + \omega_{ij}^-)/2\). In the meantime, \(\overline{\omega}_{ij} = (\omega_{ij}^+ - \omega_{ij}^-)/2\) represents the dephasing due to the fast phonon transition \(R\) between the two branches, see equation (7). The processes via the phonon-side band, see equation (15), are reflected on \(\alpha_k = k\lambda_0\) where \(k = \{0, 1\}\) for the absorption coefficients \(\alpha_0\) of spin-conserving transitions during optical pumping.

3.2. Intersystem state
The intersystem state, see Ref. [3], \(^1\)A\(_1\) of the electronic spin-selective transitions with the rate \(\gamma'\) from the excited states \(|m_S = \pm 1\rangle\) reads
\[
\dot{\rho}_1 = -\Gamma \rho_1 + \gamma' (\rho_1 + \rho_3),
\]
\[
\dot{\rho}_3 = -\Gamma \rho_3 + \gamma' (\rho_2 + \rho_4),
\]
(19)
where \(\rho_1\) and \(\rho_3\) are the populations corresponding to the nuclear spin up and down, and \(\Gamma\) is the decay rate of the intersystem states. As known, the selective transition is used to initiate the NV centers through optical pumping [3, 5]. At this point, it should be noted that \(\gamma_+ = \gamma_0 + \gamma' + \gamma_6\) and \(\gamma_- = \gamma_0 + 2\gamma_6\) for the decay rates in the excited states, where \(\gamma'\) is a spin-selective transition rate from the electronic spin \(S_z = \pm 1\) in excited states to the intersystem states \(^1\)E and \(\gamma_6\) is a small electronic spin mixing (see, equation (20)) [3].

3.3. Ground state
The master equations of the ground states population \(^1\)A\(_2\), employing the same numeric labeling with that of the excited states, \(|m_S, m_I\rangle\), is similar in structure to that of the excited states, except for the additional contributions of the intersystem states to \(\{0, \uparrow \text{ or } \downarrow\ \rangle (\sigma_5\text{ and } \sigma_6, \text{see below})\)
\[
\dot{\sigma}_1 = -\alpha \sigma_1 + \gamma_0 \rho_4 + \gamma_6 \sigma_5 + \gamma_6 \sigma_5 + i\beta (\sigma_{25} - \sigma_{52}),
\]
\[
\dot{\sigma}_2 = -\alpha \sigma_2 + \gamma_0 \rho_2 + \gamma_6 \sigma_5 + i\beta (\sigma_{25} - \sigma_{52}),
\]
\[
\dot{\sigma}_4 = -\alpha \sigma_4 + \gamma_0 \rho_4 + \gamma_6 \sigma_5 + i\beta (\sigma_{25} - \sigma_{52}) + \Gamma \rho_1,
\]
\[
\dot{\sigma}_5 = -\alpha \sigma_5 + \gamma_0 \rho_5 + \gamma_6 \sigma_5 + \gamma_6 \sigma_5 + i\beta (\sigma_{25} - \sigma_{52}) + \Gamma \rho_1,
\]
\[
\dot{\sigma}_6 = -\alpha \sigma_6 + \gamma_0 \rho_6 + \gamma_6 \sigma_5 + \gamma_6 \sigma_5 + i\beta (\sigma_{25} - \sigma_{52}) + \Gamma \rho_1,
\]
(20)
where the ground state hyperfine coupling \(b = A_0^\perp/\sqrt{2}\) and the decay constant \(\alpha = \alpha_0 + \alpha_6\) in terms of the spin-conserving and the small spin-mixing rates, respectively. For clarity, we named the ground state density matrix \(\sigma\).

The relevant off-diagonal components of the ground states are
\[
\dot{\sigma}_{25} = -(i\omega_{25} + \alpha) \sigma_{25} + i\beta (\sigma_{52} - \sigma_{25}),
\]
\[
\dot{\sigma}_{36} = -(i\omega_{36} + \alpha) \sigma_{36} + i\beta (\sigma_{56} - \sigma_{36}),
\]
(21)
where the ground state resonant frequency \(\omega_{ij}^\perp\) is in consideration of secular terms. The terms \(\gamma_k = k\lambda_0\) with \(k = \{0, 1\}\) originate from the transition through the phonon-side band, equation (15), same as that of the excited state equations. Comparison of equation (18) with equation (21) contrasts the effect of the phonon-mediated transitions between the two branches \(E_X\) and \(E_Y\) in the excited states in the course of the averaging.

4. Discussion
Arriving at the results of averaging in the excited states, equation (10), we now understand the observed LAC at \(\overline{\omega}_{36} \approx 0\) when \(B = 512\) gauss in the excited states observed in the experiments. Then, we see the dynamic nuclear polarization by numerically finding the steady state solutions of the master equations of the whole system during the optical pumping for known values, [3] except for \(\gamma_6 = \gamma_6^{\text{manson}}/3\), equations (17)–(21). Since there are two LACs corresponding to both the ground (at \(\omega_{56}^\perp \approx 0\) when \(B = 1028\) gauss) and the excited states, we expect two peaks in the nuclear polarization, as seen in figure 3 by varying the magnetic field, although the origin of two LACs are different. When \(\overline{\omega}_{ij} \sim \sqrt{R\overline{\tau}}\), the effect of the dephasing in equation (18) is comparable to that of the decoherence rates, which accelerates the decoherence in the excited states. See [1] for a report of the simple two-sublevel structure in the excited states.

Instead of the bare basis \(|m_S, m_I\rangle_{\text{bare}}\) employed in section 2, the exact basis \(|m_S, m_I\rangle_{\text{exact}}\) of the NV center Hamiltonian \(H = H_0 \oplus H_{\text{ex}} + H_{\text{m}} + H_{\text{HF}}\) will be an interesting set to study the averaging and the spin-
mixing to address the same effects, most of all, analyzing the results of the phonon-mediated transitions in view of the exact basis. In addition, the dephasing originating via the phonon-sideband casts important questions relevant to the decoherence which attract further study by way of a polaron transformation \[20\] and/or the master equation approach \[21\] adopted in the study of resonant energy transfer (RET).

To conclude, we showed the averaging due to the fast phonon in the excited states and the dynamic nuclear polarization of the NV centers as a function of the applied magnetic field during optical cycling.

References