Quantum theory of nuclear spin dynamics in diamond nitrogen-vacancy center

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We develop a quantum theory for a variety of nuclear spin dynamics such as dephasing, relaxation, squeezing, and narrowing due to the hyperfine interaction with a generic, dissipative electronic system. The first-order result of our theory reproduces and generalizes the nonlinear Hamiltonian for nuclear spin squeezing [M. S. Rudner et al., Phys. Rev. Lett. 107, 206806 (2011)]. The second-order result of our theory provides a good explanation to the experimentally observed 13C nuclear spin bath narrowing in diamond nitrogen-vacancy center [E. Togan et al., Nature 478, 497 (2011)].

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Diamond nitrogen-vacancy (NV) center is a leading platform for quantum computation and sensing at the nanoscale [1–7]. An important advantage of the NV center is the long electron spin coherence time [8], which is ultimately limited by the noise from the randomly fluctuating 13C nuclei in ultrapure samples [9]. To protect the NV spin coherence, dynamical decoupling [10, 11] has achieved remarkable success in prolonging the NV spin coherence time [12] for an ultrashort duration (~ T2) around the refocusing point. To achieve persistent coherence protection, especially for multiple coupled spins, a promising approach is to suppress the nuclear spin noise by narrowing the nuclear spin bath distribution. This approach has been widely explored and successfully demonstrated in semiconductor quantum dots [13–22].

Recently the dynamics of nuclear spins in NV centers is attracting increasing interest. Experimentally, hyperfine induced nuclear spin decoherence and relaxation [11, 23–32] have been studied and 13C nuclear spin bath narrowing has been observed [32]. Theoretically, despite many works on the nuclear spin dynamics induced by the isotropic contact hyperfine interaction (HFI) with electrons in quantum dots, most of them are not directly applicable to the NV center, because the NV spin decoherence is dominated by the anisotropic dipolar HFI with 13C nuclei. The dipolar HFI does not conserve the total spin and leads to very different electron-nuclear coupled dynamics, e.g., the widely used Fermi golden rule approach does not fully capture the nuclear spin relaxation under quasi-resonant optical pumping when the HFI is anisotropic [34, 35]. Up to now, only the dynamics of a few nuclei strongly coupled to the NV center has been treated, either by direct numerical modelling [23–27] or by rate equations to describe the incoherent relaxation of the nuclear spin population, with the rate obtained either phenomenologically [30, 33] or from the Fermi golden rule [26]. By contrast, narrowing of the many weakly coupled 13C nuclei, the dominant source of NV spin decoherence, has not been addressed theoretically. The experimentally observed narrowing of 13C nuclei in NV center [33] is consistent with a theoretical prediction in semiconductor quantum dots [36], but the specific physical mechanism remains unclear.

In this letter, we develop a quantum theory for the nuclear spin dynamics induced by general HFI with a dissipative electronic system. This theory has three distinguishing features compared with previous works. First, instead of treating only the incoherent nuclear spin relaxation [31, 35], it include both the diagonal population and the off-diagonal coherence and can describe a variety of nuclear spin dynamics such as dephasing [28], squeezing [37], and dynamic polarization and narrowing [13–22, 36]. This is highly desirable given the recent advances of electron-nuclei hybrid quantum registers [38–40]. Second, instead of treating the entire HFI as a perturbation [41], it treats the longitudinal HFI non-perturbatively, the key to nuclear spin narrowing [34] and squeezing [37]. Third, without resorting to large electron-nuclear energy mismatch and weak optical excitation [36], it only assumes the electron-induced nuclear spin dynamics to be much slower than the electron damping and is applicable to many electron-nuclear coupled systems, such as single [32, 44] and double [45, 49] quantum dots including quadrupolar interactions [50, 51], as well as NV centers [23, 35]. We exemplify this theory in two paradigmatic examples. The first-order result reproduces and generalizes the nonlinear Hamiltonian responsible for nuclear spin squeezing as proposed in Ref. [37]. The second-order result provides a good explanation to the observed 13C nuclear spin narrowing [33] in NV center.

We consider many nuclear spins {I(N)} coupled to a generic, dissipative electron system. The nuclear Hamiltonian $H_N$ may include the Zeeman term and quadrupolar effect. The electron Hamiltonian includes multiple energy levels and external control such as optical/microwave pumping. We always work in an appropriate electron rotating frame and the nuclear spin interaction picture, and decompose the total Hamiltonian $\hat{H}(t)$ into the time-independent electron part $\hat{H}_e$, the longitudinal HFI $\hat{K}$ that commutes with $\hat{H}_N$ and hence induces no nuclear spin flip between different eigenstates of $\hat{H}_N$, and the transverse HFI $V(t)$ that flips the nuclear
spins. The coupled system obeys $\dot{\rho}(t) = -i[\hat{H} + \hat{K} + \hat{V}(t), \rho(t)] + L_c \rho(t)$, with $L_c \equiv \sum_\mu \Gamma_\mu \hat{D} [[f]] (i) \hat{\rho}$ for the electron damping in the Lindblad form $\hat{D}[\hat{L}] \hat{\rho} \equiv \hat{L} \hat{\rho} \hat{L}^\dagger - (\hat{L}^\dagger \hat{L}, \hat{\rho})/2$. Here we focus on the electron-induced nuclear spin dynamics and leave the direct nuclear spin interactions and the intrinsic nuclear spin damping to the end of our discussion.

To derive a closed equation of motion for the nuclear spin state $\dot{\rho}(t) \equiv Tr_c \dot{\rho}(t)$, we employ the adiabatic approximation to eliminate the fast electron motion. We introduce the complete nuclear spin basis set $|m\rangle \equiv \otimes_j |m_j\rangle$ as the common eigenstates of $\hat{H}_N$ and $\hat{K}$ with $\hat{K}|m\rangle = K_m|m\rangle$, where $K_m$ is an electron operator, e.g., $K_m = \hat{S}_z h_m$ for the contact HFI $\hat{S} \cdot \sum_k a_k \hat{I}_k \equiv \hat{S} \cdot \hat{h}$, with $h_m \equiv \langle m| \hat{h}_z |m\rangle$ being the nuclear field. The $(m,n)$th block $\dot{\rho}^{(m,n)}(t) \equiv \langle m| \dot{\rho}(t) |n\rangle$ of $\dot{\rho}$ obeys

$$\dot{\rho}^{(m,n)}(t) = L_{mn} \rho^{(m,n)}(t) - \frac{i}{2} \left[ \rho^{(m,m)}(t), \hat{K}_{n,m} \right] - i \langle m| \hat{V}, \rho|n\rangle,$$

where $\hat{K}_{n,m} \equiv \hat{K}_m - \hat{K}_n$ and $L_{mn}(\bullet) \equiv -i[\hat{H}_N, \bullet] + L_c(\bullet)$ with $\hat{H}_n \equiv \hat{H} + (K_m + K_n)/2$. Tracing over the electron yields the evolution of $\rho^{(m,n)}(t) \equiv \langle m| \hat{h}_z |n\rangle$:

$$\rho^{(m,n)}(t) = \frac{1}{2} \left[ \hat{K}_{n,m}, \rho^{(m,n)}(t) \right] - i Tr_c \langle m| \hat{V}, \rho|n\rangle.$$

The above two equations contain four time scales: electron evolution and damping on the time scale $T_e$ as driven by $L_{mn}$, nuclear spin precession on the time scale $T_{coh}$ in the electron mean field $\langle \hat{K}_{n,m} \rangle$ and $\langle \hat{V}(t) \rangle$, nuclear spin dephasing on the time scale $T_2$ due to $\hat{K}_{n,m}$ fluctuation, and nuclear spin relaxation on the time scale $T_1$ due to $\hat{V}(t)$ fluctuation. Any dynamics much slower than $T_e$ can be adiabatically singled out. For specificity, we consider $T_e \ll T_{coh}, T_1, T_2$ and single out the full dynamics of $\dot{\rho}(t)$ on the coarse grained time scale $\Delta t \gg T_e$.

To apply the adiabatic approximation, we identify $\dot{\rho}(t)$ as the slow variable and other matrix elements of $\dot{\rho}$ as fast variables. We treat $L_{mn}$ exactly and regard $\hat{K}_{n,m}$ and $\hat{V}(t)$ as first-order small quantities. Carrying out the adiabatic approximation to successively higher orders (see Sec. A of [52]) gives the nuclear spin dynamics order by order $\dot{\rho} = (\dot{\rho}) + (\dot{\rho})_2 + \cdots$. The first-order dynamics

$$(\dot{\rho}^{(m,n)})_1 = \frac{1}{2} \left[ \hat{K}_{n,m}, \rho^{(m,n)}(t) \right] - i Tr_c \langle m| \hat{V}, \rho|n\rangle,$$

(1)

describes nuclear spin precession in the electron mean fields, which in turn depends on the nuclear field via $(\dot{\rho}^{(m,n)})_1 = Tr_c (\dot{\rho}^{(m,n)} P_{mn})$. Here $\rho_0(t) = \sum_m \langle m| \rho^{(m,m)}(t) |m\rangle$ is the zeroth-order approximation to $\dot{\rho}(t)$ and $\dot{P}_{mn}$ is the electron steady state determined by $L_{mn} P_{mn} = 0$ and $Tr_c \dot{P}_{mn} = 1$. For $\langle \hat{p}(t)| \hat{V}(t)|m\rangle = V^{(p,m)} e^{-i\varepsilon_{pm} t}$ [53], the second-order adiabatic approximation gives the nuclear spin relaxation

$$(\dot{\rho}^{(m,m)})_2 = \sum_p (W_{m-p} \rho^{(p,p)}(p,p) - W_{p-m} \rho^{(m,m)}(p,p)),$$

(2)

by the fluctuation of $\hat{V}(t)$, where the transition rate

$$W_{p-m} = 2 \Re \int_0^\infty e^{-i\varepsilon_{pm} t} Tr_c \hat{V}^{(p,m)} e^{L_{m} t} \hat{V}^{(p,m)} \dot{P}_{mn} dt$$

(3)

is a generalized non-equilibrium fluctuation-dissipation relation and reduces to Refs. 34, 37$^*$ when $\hat{V}(t)$ is linear in $\{I_n\}$. For the off-diagonal coherences, we have

$$(\rho^{(m,n)})_2 = - \left( \Gamma^p_{m,n} + \frac{1}{2} \sum_p (W_{p-n}|m + W_{p-m}|n) \right) \rho^{(m,m)},$$

(4)

where we have neglected a second-order energy correction and electron-mediated nuclear spin interactions, and

$$\Gamma^p_{m,n} = \Re \int_0^\infty Tr_c \dot{K}_{m,n} e^{L_{m} t} K_{m,n} \dot{P}_{mn} dt$$

(5)

is the pure dephasing induced by the fluctuation of $\dot{K}_{m,n} = \dot{K}_n - \langle \dot{K}_{n,m} \rangle$. The expression for $W_{p-m}$ is slightly modified [52], but it reduces to $W_{p-m}$ when the difference between $\hat{K}_m$ and $\hat{K}_n$ is neglected. In this case Eqs. (2) and (3) reduce to generalized Lindblad master equation with nonlinear dependence of nuclear spin precession, dephasing, and relaxation on the nuclear field. This is the origin of nonlinear nuclear spin effects such as squeezing and narrowing. The above equations follow from perturbative treatment of both $\hat{K}_{n,m}$ and $\hat{V}(t)$ on the time scale $\Delta t \gg T_e$. If we focus on nuclear spin relaxation on the time scale $\Delta t \gg T_e$, we can treat $\hat{K}_{n,m}$ exactly and still derive Eqs. (2) and (3) (see Sec. B of [52]), with $L_{pm}$ replaced with $L_{pm} = L_{pm} + i\{\cdots, \hat{K}_{p,m}\}/2$ in Eq. (3).

Now we discuss the nuclear spin transition rate beyond the widely used Fermi golden rule by evaluating Eq. (3) analytically via a perturbative expansion of

$$\int_0^\infty e^{i\varepsilon_{pm} t} \dot{C}_{p,m} dt = - (\hat{H} + i\omega)_{p,m}^\dagger \equiv - \hat{G} (\text{with subscripts suppressed for brevity})$$

for this purpose, we divide $\hat{L} = -i[\hat{H}, \bullet] + L_c(\bullet)$ into the unperturbed part $\hat{L}^d$ and the perturbation $\hat{L}^{nd}$,

$$\hat{L}^d(\bullet) \equiv -i[\hat{H}^d, \bullet] - \frac{1}{2} \langle \hat{\Gamma}, \bullet \rangle,$$

(6a)

$$\hat{L}^{nd}(\bullet) \equiv -i[\hat{H}^{nd}, \bullet] + \sum_{f,i} \gamma_{f,i} |f\rangle \langle i| \bullet,$$

(6b)

where $\hat{H}^d = \sum_i \varepsilon_i |i\rangle \langle i| (\hat{H}^{nd})$ is the diagonal (off-diagonal) part of $\hat{H}$, the self-energy $-\langle \hat{\Gamma}, \bullet \rangle/2$ and the quantum jump $\sum_f \gamma_{f,i} |f\rangle \langle i| \bullet$ are the diagonal and off-diagonal part of $\hat{L}_c$, respectively, with $\hat{\Gamma} \equiv \sum_i \Gamma_i |i\rangle \langle i|$, and $\Gamma_i \equiv \sum_f \gamma_{f,i}$ the total dephasing rate of $|i\rangle$. For $||\hat{L}^{nd} \equiv \varepsilon_{pm}|| \gg ||\hat{L}^{nd}||$, we use Dyson equation $\hat{G} = \hat{G}^d - \hat{G}^d \hat{L}^{nd} \hat{G}$ with $\hat{G}^d \equiv (\hat{L}^d + i\omega)^{-1}$ to obtain

$$W_{p-m} \approx -2 \Re Tr_c \hat{V}^{(p,m)}(\hat{G}^d - \hat{G}^d \hat{L}^{nd} \hat{G}^d) \hat{V}^{(p,m)} \dot{P}_{mn},$$

(7)
where $G^d(\bullet) = i \sum_{j'j} |j'\rangle \langle j| / z_j'z_j$ with $z_j'z_j \equiv \varepsilon_j' - \varepsilon_j - \omega - i(\Gamma_j' + \Gamma_j)/2$. As an example, for $V^{(p,m)} = \lambda |j\rangle \langle j| (f \neq i)$, substituting Eqs. (6) into Eq. (7) gives $W_{pe-m}$ as the sum of the Fermi golden rule contribution $W_{pe-m}^{\text{golden}} = 2\pi |\lambda|^2(\sum |P_{m,m}|^2)/(\varepsilon_j - \varepsilon_i - \omega)$ and the quantum coherent contribution $W_{pe-m}^{\text{coh}} = 2\pi |\lambda|^2 \sum |i|\sum |j| |\rho_{m,m}|^2/(\varepsilon_j - \varepsilon_i - \omega)$.

The above theory is applicable to many situations to describe a variety of electron-induced nuclear spin dynamics. With the dependence of $\mathcal{L}_{m,n}$ and hence $P_{m,n}$ on $K_m$ and $K_n$ neglected, Eqs. (15) describe the independent dynamics of individual nuclear spins [23]. Including these dependences allow us to describe correlated nuclear spin dynamics, such as squeezing [37] by Eq. (1) and these dependences allow us to describe correlated nuclear spin squeezing, as pioneered in Ref. [37], with a semi-

driven by the Hamiltonian $\hat{K}_n = \frac{1}{2}\sum_n (|\psi^n\rangle \langle \psi^n| + |\psi^n\rangle \langle \psi^n|)$, where

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where $\gamma \equiv 1/(12 \text{ns})$, $\gamma_{s2} \sim \gamma/120$, and $\gamma_{cc} \sim \gamma/800$ are obtained by fitting the fluorescence data [33].

The first-order dynamics in Eq. (1) gives

$$(\hat{p}^{(m,n)})_1 = -i (h_{m,n} (\hat{S}_{z})_{m,n} - h_n (\hat{S}_{z})_{n,m}) p^{(m,n)}$$

for strong electron damping $1/T_e \gg |h_{m,n} - h_n|$, where $h_{m,n} = \langle m| \hat{h} |n\rangle$. This is equivalent to $\hat{p} = -i [\hat{p}, \hat{H}_{\text{eff}}]$ driven by the Hamiltonian $\hat{H}_{\text{eff}} = h_{z} (\hat{S}_{z})_{h_{z}}$ with $\langle \hat{S}_{z} \rangle_{h_{z}} = \sum_m |m\rangle \langle m| \langle \hat{S}_{z} \rangle_{m,m}$. Such electron-induced nonlinear nuclear spin Hamiltonian could lead to nuclear spin squeezing, as pioneered in Ref. [37], with a semi-

phenomenological derivation of $\hat{H}_{\text{eff}}$ for the electron under ESR. Here our first-order result provides an alternative, microscopic derivation for general electron pumping.

Finally, we apply the theory to explain the $^{13}$C nuclear spin narrowing observed in NV center under coherent population trapping (CPT) at low temperature [33]. The NV states consist of a $A$ subsystem ($|\pm 1\rangle$ and $|A_1\rangle$) and a two-level subsystem ($|0\rangle$ and $|E_g\rangle$), both under resonant optical pumping (Fig. 1). Under two-photon resonance (i.e., when $|\pm 1\rangle$ are degenerate), the bright state $|b\rangle$ of the $A$ subsystem is pumped into $|A_1\rangle$, which decays into (and is trapped in) the dark state $|d\rangle$. However, the CPT efficiency is degraded by the off-resonant optical excitation of $|d\rangle$ into $|A_2\rangle$. In the rotating frame of the two lasers, the NV Hamiltonian $\hat{H}_n$ consists of the ground-state Zeeman splitting $g_e \mu_B B S_g^z \equiv \omega_e S_g^z$, laser detuning $\Delta [A_2] / \Delta [A_2]$ for $|\pm 1\rangle \rightarrow |A_2\rangle$ excitation, optical pumping $\omega_N / \sqrt{2} (|A_1\rangle \langle b| + i |A_2\rangle \langle d| + h.c.) + (\omega_e / 2) (|E_g\rangle \langle 0| + h.c.)$, and the strain term $\xi (|d\rangle \langle d| - |b\rangle \langle b|)$ (see [33] or Sec. C of [52]). The excited states undergo spontaneous emission within each subsystem, non-radiative decay between different subsystems, and pure dephasing $\gamma_p$ for each excited state. Since $\gamma_s \gg \gamma_{cc}$, the population of the excited states is mostly in $|E_g\rangle$.

The NV ground and excited state spins $\hat{S}_g$ and $\hat{S}_e$ are coupled to the on-site $^{14}$N nucleus $\hat{I}_0$ via contact HFI $A_g \hat{S}_g \cdot \hat{I}_0 + A_s \hat{S}_e \cdot \hat{I}_n$, where $A_e \approx 40$ MHz [54], and $A_s \approx 2.2$ MHz [52]. The total NV spin $\hat{S} \equiv \hat{S}_g + \hat{S}_e$ is coupled to the surrounding $^{13}$C nuclei $\{\hat{I}_n\}$ via dipolar HFI $\sum_{n=1}^{N} \hat{S}_g \cdot \hat{A}_n \cdot \hat{I}_n$. For small magnetic field, $\hat{I}_0$ is quantized along the N-V axis ($z$ axis) by the mean field $A_g (\hat{S}_g) + A_s (\hat{S}_e)$, which is constant along the $z$ axis and fast oscillating in the $xy$ plane. Similarly, the $n$th $^{13}$C nucleus $\hat{I}_n$ is quantized along $\hat{e}_z \cdot \hat{A}_n$ by the mean field $\langle \hat{S} \rangle \cdot \hat{A}_n$. For convenience, we introduce local Cartesian coordinates $\{e_{n,x}, e_{n,y}, e_{n,z}\}$ for the $n$th $^{13}$C nucleus with $e_{n,z} = e_z \cdot \hat{A}_n |e_z \cdot \hat{A}_n|$ and decompose the HFI into the longitudinal part $\hat{K} = \hat{S}_g \cdot \hat{I}_0$ and the transverse part $\hat{L}_n$

$$\hat{V} \equiv (A_g \hat{S}_g \cdot \hat{I}_0 + A_s \hat{S}_e \cdot \hat{I}_0) \cdot \hat{I}_{n,1} + \sum_{n=1,2,\ldots,N} \hat{S}_1 \cdot \hat{A}_n \cdot \hat{I}_{n,1}$$

for strong electron damping $1/T_e \gg |h_{m,n} - h_n|$, where $h_{m,n} = \langle m| \hat{h} |n\rangle$. This is equivalent to $\hat{p} = -i [\hat{p}, \hat{H}_{\text{eff}}]$ driven by the Hamiltonian $\hat{H}_{\text{eff}} = h_{z} (\hat{S}_{z})_{h_{z}}$ with $\langle \hat{S}_{z} \rangle_{h_{z}} = \sum_m |m\rangle \langle m| \langle \hat{S}_{z} \rangle_{m,m}$. Such electron-induced nonlinear nuclear spin Hamiltonian could lead to nuclear spin squeezing, as pioneered in Ref. [37], with a semi-

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Finally, we apply the theory to explain the $^{13}$C nuclear spin narrowing observed in NV center under coherent population trapping (CPT) at low temperature [33]. The NV states consist of a $A$ subsystem ($|\pm 1\rangle$ and $|A_1\rangle$)
wardly from the perturbation formula Eq. (7). The transition rate \( W_{m_1 \rightarrow m} = W_{m \rightarrow m_1} \) for \( ^{14}\text{N} \) from \( |\mathbf{m}\rangle \) to \( |\mathbf{m} \pm 1\rangle \) \( \propto \hat{I}_m \hat{I}_m \) is dominated by the following contributions from different NV transitions: \( A_g^2 \chi_g P_{E_x,E_y} \) from \( |0\rangle \rightarrow |\pm 1\rangle \) and \( A_c^2 \sum_f f \chi_f P_{E_x,E_y} \) from \( |E_y\rangle \rightarrow |f\rangle \), where \( P_{E_x,E_y} \equiv \langle E_y | \hat{P}_{m,m} | E_y \rangle \) is the population on \( |E_y\rangle \), \( f \) runs over \( A_1, A_2, E_1, E_2 \) states, \( \chi_g \equiv (\gamma + 2\gamma_{ce})/D_{ax}^2 \), and \( \chi_f \equiv (1/4)(\Gamma_f + \gamma_{ce})/(\varepsilon_{E_y} - \varepsilon_f)^2 \), with \( \varepsilon_f \) the energy of \( |f\rangle \) in the laboratory frame. These transition rates differ from the phenomenological expression \( A_c P_{E_x,E_y} \) in Ref. [33], which only considers the \(^{14}\text{N} \) flip by the NV transition \( |E_y\rangle \rightarrow |A_1\rangle \). Similarly, the transition rate \( W_{m_1 \pm 1 \rightarrow m} \) of the \( n \)th \(^{13}\text{C} \) nucleus from \( |\mathbf{m}\rangle \) to \( |\mathbf{m} \pm 1_n\rangle \) \( \propto \hat{I}_m \hat{I}_m \) is dominated by the following contributions: \( \chi_g (|A_n,+,\rangle - |A_n,-\rangle)^2 P_{E_x,E_y}/8 \) from \( |0\rangle \rightarrow |\pm 1\rangle \), \( |A_n,-\rangle^2 (\chi_A + \chi_E) P_{E_x,E_y}/2 \) from \( |E_y\rangle \rightarrow |A_1\rangle, |E_1\rangle \), and \( |A_n,+,\rangle^2 (\chi_A + \chi_E) P_{E_x,E_y}/2 \) from \( |E_y\rangle \rightarrow |A_2\rangle, |E_2\rangle \), where \( A_{n,b} = e_{n,b} \cdot \hat{A}_n \cdot \hat{E}_m \). Since \( P_{E_x,E_y} \) consists of the dominant CPT term \( P_{E_x,E_y}^{(0)} \equiv \hat{P}_{m,m} (\hat{c}_m^2 + \hat{d}_m^2) \) and a small correction \( \chi \equiv (\gamma + 2\gamma_{ce})/4(\Delta^2 (\gamma + \gamma_{s1})) \) from the off-resonant excitation \( |d\rangle \rightarrow |A_2\rangle \), all the nuclear spin transition rates \( \propto P_{E_x,E_y} \) are minimized at the two-photon resonance \( \delta_m = 0 \), where \( \eta_1 = \gamma_{ce}/\gamma_{s1} \) and \( \delta_0 \) is the intrinsic width of the CPT dip (see Sec. D of [32]). Therefore, although much more involved, the weak-field nuclear spin dynamics in the NV center is similarly to that in quantum dot under a strong magnetic field [30]. The differences are (i) different \(^{13}\text{C} \) nuclei are narrowed about different local axis; (ii) NV ground and excited states all contribute to the nuclear spin flip and narrowing; (iii) off-resonant excitation \( |d\rangle \rightarrow |A_2\rangle \) limits the narrowing efficiency, as suggested in Ref. [33] and discussed below.

The steady state is obtained by solving Eq. (2), where \( n \) runs over \( |\mathbf{m} \pm 1_k\rangle \) with \( k = 0,1,\cdots,N \). The nuclear spin interactions and intrinsic relaxation that are neglected up to now is included by adding a \(^{14}\text{N} \) depolarization rate \( \gamma_\mathbf{n} \) to \( W_{m_1 \pm 1 \rightarrow m} \) and \(^{13}\text{C} \) depolarization rate \( \gamma_c \) to \( W_{m \pm 1 \rightarrow m} \) (\( n \geq 1 \)). The calculated steady state population of \(^{14}\text{N} \) on \( |m_0\rangle \) agrees with the experiment [Fig. 2(b)]. At the optimal \( \Omega_A \) corresponding to maximal population, the calculated \(^{14}\text{N} \) narrowing time \( \sim 200 \mu s \) also agrees reasonably with the experimental value \( \sim 353\pm34 \mu s \). We further confirm that the decrease of the population at large \( \Omega_A \) arises from the off-resonant excitation \( |d\rangle \rightarrow |A_2\rangle \), as suggested in Ref. [33].

A most important observation is the narrowing of the \(^{13}\text{C} \) nuclei, manifested as the narrowing of the CPT dip of the NV fluorescence (\( \times \) steady state NV population on \( |E_y\rangle \) [33]). To compare with the experiment, we first obtain the nuclear spin steady state \( \rho_{ss} \) under the experimentally used magnetic field \( \omega_e = g_e B = 0.18 \text{ MHz} \) and then calculate the \( \rho_{ss} \)-averaged population \( \sum_m \rho_{ss} (m,m) \langle E_y | \hat{P}_{m,m} (\omega_e) | E_y \rangle \) and the post-selected population

\[
\sum_m \rho_{ss} (m,m) \langle E_y | \hat{P}_{m,m} (\omega_{re}) | E_y \rangle
\]

under the readout magnetic field \( \omega_{re} = g_e B_r \), where \( C(\langle E_y | \hat{P}_{m,m} (\omega_{re}) | E_y \rangle) \) is the average number of collected photons in the conditioning window. When normalized to unity at large \( \omega_{re} \), the calculated populations agree with the experimental fluorescence [Fig. 2(b)]. To gain a clear understanding of the narrowing, we neglect \(^{14}\text{N} \), replace the dipolar HFI tensor \( \hat{A}_n \) by a uniform one \( A_0 \delta_{ee} + A_1 (\delta_{ee} + \omega_e) \), set \( \omega_e = 0 \), and use the Fokker-Planck equation [34][33] to obtain the distribution \( \rho_{ss} (h) \equiv \Omega \delta (\hat{h}_C - h) \rho_{ss} \) of the \(^{13}\text{C} \) nuclear field \( \hat{h}_C = A_1 \sum_n \hat{I}_n \):

\[
p_{ss} (h) \propto \left( 1 + \frac{R}{R + \Gamma_{dep} (h^2 + \delta^2_0)} \right) e^{-h^2/(2\sigma_{eq}^2)}
\]

where \( \sigma_{eq} = \sqrt{N A_1}/2 \) is the fluctuation of \( \hat{h}_C \) in thermal equilibrium, \( R = \sum_f f \chi_f A_1^2 P_0 (1 - 2\chi) \) is the typical \(^{13}\text{C} \) spin-flip rate, \( \Gamma_{dep} = \gamma_c + \gamma_R \) is the total \(^{13}\text{C} \) depolarization rate due to the intrinsic depolarization (rate \( \gamma_c \)) and off-resonant excitation \( |A_2\rangle \), and \( \delta_0 = \sqrt{\Gamma_{dep}/(R + \Gamma_{dep})} \delta_0 \). Since \( R \gg \Gamma_{dep} \) under typical experimental conditions, the Lorentzian factor \( 1/(h^2 + \delta^2_0) \) creates a sharp peak in \( p_{ss} (h) \) around \( h = 0 \) with a typical width \( \delta_0 \ll \delta_0 \). This makes the steady-state fluctuation \( \sigma = (\langle \hat{h}_C^2 \rangle - \langle \hat{h}_C \rangle^2)^{1/2} \) of \( \hat{h}_C \) with respect to \( p_{ss} (h) \) much smaller than \( \sigma_{eq} \), corresponding to \(^{13}\text{C} \) spin bath narrowing. Equation (11) also suggests that the narrowing would be degraded when \( \Omega_A \) exceeds an optimal value due to the increase of \( \delta_0 \) and hence \( \delta_0 \) (by power broadening) and \( \Gamma_{dep} \) (by off-resonant excitation \( |d\rangle \rightarrow |A_2\rangle \)). Without the strain and for small depolarization \( \gamma_c \), we can obtain the optimal narrowing analytically as \( (\sigma/\sigma_{eq})_{\min} \approx \left( \eta_{s1} / (\pi \eta^2_{s1}) \right)^{1/4} \sqrt{\sigma_{eq} / \Delta} \), which is achieved at \( \delta_0 = (\sqrt{2} \sigma_{eq}) \approx (P_0 \gamma_{c}/(2R \eta_{s1}))^{1/4} (\Delta \eta_{s1} / \sigma_{eq})^{1/2} \) with \( \eta_{s1} = \Gamma_{A_1} A_{1} (\gamma + \gamma_{s1})^2 \). We find numerically that the strain has very small influence on the optimal narrowing, although it has some affect at low pump power.

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[52] Note1, see supplementary material for derivation of Eqs. (1)–(5) (Sec. A), exact treatment of the longitudinal HFI \( \hat{K} \) (Sec. B), summary of the NV Hamiltonian under coherent population trapping (Sec. C), and analytical expression for the NV steady state \( \hat{P}_{m,m} \) (Sec. D).

[53] Note2, when \( \langle p|\hat{V}(t)|m \rangle \) oscillates at multiple widely separated frequencies compared with the nuclear spin relaxation and dephasing rates, the contributions from different frequency components are additive.

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[56] Note3, as \( \hat{S}_z^e \) and \( \mathbf{S}_\perp \) exhibit vanishingly small low-frequency fluctuation, the term \( \propto \hat{S}_z^e \) in \( \hat{K} \) and \( (\mathbf{S}_\perp \cdot \mathbf{A}_n \cdot \mathbf{e}_{n,z}) \hat{I}_n^z \) in \( \hat{V} \) induce negligibly small nuclear spin dephasing compared with the term \( \propto \hat{S}_z^g \) in \( \hat{K} \) and hence is neglected.
Supplementary materials for “Quantum theory of nuclear spin dynamics in diamond nitrogen-vacancy center”

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The following sections provide background information related to specific topics of the main text. Section A provides a detailed derivation of Eqs. (1)-(5) of the main text. Sec. B provides an exact treatment of the longitudinal hyperfine interaction (HFI) $\hat{K}$ and derive Eqs. (2) and (3) of the main text. Sec. C summarizes the NV Hamiltonian under the experimental condition [1] of coherent population trapping. Sec. D provides analytical expressions for the steady NV state $\hat{P}_{\text{m.m}}$.

A. Derivation of nuclear spin equations of motion

The starting point is

$$\dot{\rho}^{(m,n)} = \mathcal{L}_{m,n} \rho^{(m,n)} - \frac{i}{2} \{[\hat{\rho}^{(m,n)}, \hat{K}^{(m,n)}], \rho^{(m,n)}\} - \frac{i}{2} \{[\hat{\rho}^{(m,n)}, \hat{V}], \rho^{(m,n)}\}.$$

On the coarse grained time scale $T_c \ll \Delta t \ll T_{\text{coh}}, T_1, T_2$, the trace $\rho^{(m,n)} \equiv \text{Tr}_e \hat{\rho}^{(m,n)}$ is slowly varying, while other elements of $\rho^{(m,n)}$ almost instantaneously follow the trace $\rho^{(m,n)}$. Thus we treat the nuclear spin density matrix elements $|\rho^{(m,n)}|$ (zeroth-order quantities) as slow variables and other variables as fast variables and identify $K_{m,n}$ and $\hat{V}$ as first-order small quantities. Correspondingly, we decompose $\hat{\rho} = \hat{\rho}_0 + \hat{\rho}_1 + \cdots$, where $\hat{\rho}_k$ is a kth-order small quantity. Note that the trace of $[\hat{\rho}_0]$ is the slow variable $\bar{\rho} = \text{Tr}_e \hat{\rho}_0$, while other elements of $\hat{\rho}_0$ are fast variables. For consistency, for $k = 1, 2, \cdots$, we require $\text{Tr}_e \hat{\rho}_k = 0$, so $\hat{\rho}_k$ are fast variables.

Since we always work in the nuclear spin interaction picture, any nuclear spin evolution is caused by the HFI with the electron. Thus the zeroth-order dynamics vanishes: $(\dot{\rho})_0 = 0$.

1. First-order dynamics

The first-order evolution $(\dot{\rho}^{(m,n)})_1$ of the slow variable $\rho^{(m,n)} = \langle m | \hat{\rho}^{(m,n)} | n \rangle$ is obtained from Eq. (2) by replacing $\hat{\rho}(t)$ with $\hat{\rho}_0(t)$, i.e., the solution to the zeroth-order version of Eq. (1):

$$\dot{\rho}_0^{(m,n)} = \mathcal{L}_{m,n} \rho_0^{(m,n)}.$$

The trace of this equation gives $\dot{\rho}^{(m,n)} = 0$, i.e., we solve for the fast variables contained in $\dot{\rho}_0^{(m,n)}$ as functions of the slow variables $\rho^{(m,n)}$, which are regarded as fixed. Coarse-graining for an interval $T_c \ll \Delta t \ll T_{\text{coh}}, T_1, T_2$ or equivalently calculating the steady-state solution gives $\dot{\rho}_0^{(m,n)}(t) = \dot{\rho}_0^{(m,n)}$, where $\hat{P}_{m,n} = \hat{P}_{n,m}$ is the time-independent electron steady state as determined by $\mathcal{L}_{m,n} \hat{P}_{m,n} = 0$ and $\text{Tr}_e \hat{P}_{m,n} = 1$. By replacing $\hat{\rho}(t)$ with $\hat{\rho}_0(t) = \sum_{m,n} |m\rangle \langle n | \hat{\rho}_0^{(m,n)}(t)$ in Eq. (2), we obtain $(\dot{\rho}^{(m,n)})_1$ as given by Eq. (1) of the main text.

2. Second-order dynamics

The second-order evolution $(\dot{\rho}^{(m,n)})_2$ of the slow variable $\rho^{(m,n)}$ is obtained from Eq. (2) by replacing $\hat{\rho}(t)$ with $\hat{\rho}_1(t)$, the solution to the first-order version of Eq. (1):

$$(\dot{\rho}^{(m,n)}_0)_1 + \dot{\rho}^{(m,n)}_1 = \mathcal{L}_{m,n} \rho^{(m,n)}_1 - \frac{i}{2} \{[\rho^{(m,n)}_0, \hat{K}^{(m,n)}], \rho^{(m,n)}_0\} - \frac{i}{2} \{[\rho^{(m,n)}_0, \hat{V}], \rho^{(m,n)}_0\},$$
where \((\rho_0^{(m,n)})_1 = P_{m,n}(\hat{\rho}^{(m,n)})_1\) comes from the first-order evolution \((\hat{\rho}^{(m,n)})_1\). Substituting into the above equation and coarse-graining for an interval \(1/\gamma_s \ll \Delta t \ll T_{coh}, T_1, T_2\) (or equivalently calculating the steady-state solution) gives

\[
\dot{\rho}_{0}^{(m,n)} = i\sum_{p} \left[ (L_{m,n} + i\omega_{m,p})^{-1}(\dot{V}^{(m,p)}P_{p,n} - \langle \dot{V}^{(m,p)} \rangle_{p,n}P_{m,n}) \right] p_{p,n} + \sum_{p} \left[ (L_{m,n} + i\omega_{m,p})^{-1}(\dot{V}^{(m,p)}P_{p,n} - \langle \dot{V}^{(m,p)} \rangle_{p,n}P_{m,n}) \right] p_{p,n}
\]

as a function of the slow variables \(\{p_{p,n}\}\). Here \(L_{m,n}^{-1} = \int_0^\infty e^{-L_{m,n} dt} dt\) and \((L_{m,n} + i\omega_{m,p})^{-1} \equiv -\int_0^\infty e^{-(L_{m,n} + i\omega_{m,p}) dt} dt\), and we have assumed that \(\dot{V}^{(m,n)}(t) = \langle \dot{V}^{(m,p)}(t) \rangle_{p,n} \) oscillates at a single frequency \(\omega_{m,n}\). We can verify the consistent condition \(\dot{\rho}_{0}^{(m,n)} = 0\). Then replacing \(\dot{\rho}(t)\) with \(\rho_1(t)\) in Eq. (2) gives the desired second-order nuclear spin evolution.

For \(m = n\), neglecting the coupling of the nuclear spin population \(p^{(m,m)}\) to nuclear spin coherences \(p^{(p,q)}\) \((p \neq q)\), which amounts to neglecting the small second-order corrections to the transverse mean field \(\langle \dot{V}(t) \rangle\) and electron-mediated nuclear spin interactions (they induce nuclear spin diffusion and depolarization, which will be included phenomenologically at the end of the derivation), we obtain the nuclear spin relaxation Eq. (2) in the main text. The transition rate from \(\{m\}\) to \(\{p\}\) induced by \(\dot{V}(t)\) is

\[
W_{p-m} = -2 \text{Re} \text{Tr}_r \dot{V}^{(m,p)}(L_{p,m} + i\omega_{p,m})^{-1}(\dot{V}^{(p,m)}P_{m,m} - \langle \dot{V}^{(p,m)} \rangle_{m,m}P_{m,m}).
\]

Using \((L_{p,m} + i\omega_{p,m})^{-1}\hat{P}_{p,m} = \hat{P}_{p,m}/(i\omega_{p,m})\), the contribution from the second term \(\propto \hat{P}_{p,m}\) is \((2/\omega_{p,m}) \text{Im}(\dot{V}^{(m,p)}P_{m,m})\). Since \(\{p\}\) and \(\{m\}\) differs only by a single nuclear spin flip, the difference between \(P_{m,m}\) and \(P_{p,m}\) are negligible and we recover Eq. (3) in the main text.

For \(m \neq n\), neglecting the coupling of \(p^{(m,n)}\) to other variables, which amounts to neglecting the small second-order corrections to the transverse mean field and the electron-mediated nuclear spin interaction, we obtain

\[
\dot{\rho}_1^{(m,n)} = -i\left[ \delta\hat{\rho}_{m,n}^{(2)} - \delta\hat{\rho}_{n,m}^{(2)} \right] p_{p,n} - \frac{\sum_p (W_{p-m} + W_{m-p})}{2} p_{p,n},
\]

where \(\delta\hat{\rho}_{m,n}^{(2)}\) is given by Eq. (5) of the main text and

\[
\delta\hat{\rho}_{m,n}^{(2)} = -\sum_p \text{Im} \text{Tr}_r \dot{V}^{(m,p)}(L_{p,m} + i\omega_{p,m})^{-1}(\dot{V}^{(p,m)}P_{m,m} - \langle \dot{V}^{(p,m)} \rangle_{m,m}P_{m,m}),
\]

\[
W_{p-m} = -2 \text{Re} \text{Tr}_r \dot{V}^{(m,p)}(L_{p,n} + i\omega_{p,m})^{-1}(\dot{V}^{(p,m)}P_{m,m} - \langle \dot{V}^{(p,m)} \rangle_{m,m}P_{m,m}).
\]

### B. Exact treatment of longitudinal hyperfine interaction \(\hat{K}\)

For the nuclear spin relaxation time \(T_1\) much longer than the electron damping time \(T_e\), we can adiabatically single out the dynamics of \(\{p^{(m,m)}\}\) on the coarse-grained time scale \(T_c, T_{coh}, T_2 \ll \Delta t \ll T_1\) by treating both \(L_{m,n}\) and \(\hat{K}^{(m,n)}\) exactly and \(\dot{V}\) as a perturbation. The slow variables are \(\{p^{(m,m)}\}\) and others are fast variables. The zeroth-order steady state solution \(\rho_0^{(m,n)} \equiv 0\) \((m \neq n)\), so the first-order slow variable dynamics \((\hat{\rho}_1^{(m,n)})_1 = 0\). The first-order steady-state solution is determined from

\[
\dot{\rho}_1^{(m,n)} = \sum_{n} \left[ (L_{m,n} + i\omega_{m,p})^{-1}(\dot{V}^{(m,p)}P_{p,n} - \langle \dot{V}^{(m,p)} \rangle_{p,n}P_{m,n}) \right] p_{p,n} + \sum_{n} \left[ (L_{m,n} + i\omega_{m,p})^{-1}(\dot{V}^{(m,p)}P_{p,n} - \langle \dot{V}^{(m,p)} \rangle_{p,n}P_{m,n}) \right] p_{p,n}
\]

as

\[
\dot{\rho}_1^{(m,n)} = i\sum_{n} \left[ (L_{m,n} + i\omega_{m,p})^{-1}(\dot{V}^{(m,p)}P_{p,n} - \langle \dot{V}^{(m,p)} \rangle_{p,n}P_{m,n}) \right] p_{p,n} - \frac{\sum_{n} (W_{p-m} + W_{m-p})}{2} p_{p,n},
\]

where \(L_{m,n}^\bullet \equiv L_{m,n} - i\left[ \hat{K}^{(m,n)} \right]/2\). Replacing \(\dot{\rho}(t)\) in Eq. (2) with \(\dot{\rho}_1(t)\) and neglecting the coupling of \(p^{(m,m)}\) to nuclear spin coherences gives Eqs. (2) of the main text, with the transition rate

\[
W_{p-m} = 2 \text{Re} \int_0^\infty e^{i\omega_{p,m} t} \text{Tr}_r \dot{V}^{(m,p)} e^{i\omega_{p,m} t} \dot{V}^{(p,m)} \rho_{m,m}.
\]

obtained from Eq. (3) of the main text by replacing \(L_{p,m}^\bullet\) with \(L_{p,m}\). In the perturbation limit, we have \(L_{p,m}^\bullet \approx L_{p,m}\) and recovers Eq. (3) of the main text.
The NV Hamiltonian for the coherent population trapping (CPT) experiment has been discussed in [1]. Here we reproduce it with greater detail using our own notations. The NV states of relevance include 3 ground triplet states $|0\rangle$ (energy 0), $|\pm 1\rangle$ (energy $D_{gg}$), 6 excited triplet states $|E_1\rangle, |E_2\rangle$ (energy $E_{e1} = e_{E1}; |E_1\rangle, |E_2\rangle$ (energy $E_{e2} = e_{E2}; |A_1\rangle$ (energy $e_{A1}; |A_2\rangle$ (energy $e_{A2}$), and one metastable singlet $|S\rangle$ (energy $E_S$). A linearly polarized laser with electric field $E_1 e^{-i\omega_1 t}/2 + c.c.$ and frequency $\omega_1 = e_{A1} - D_{gg}$ resonantly excites the ground states $|\pm 1\rangle$ to the excited state $|A_1\rangle$ and, at the same time, off-resonantly excited $|\pm 1\rangle$ to the excited state $|A_2\rangle$ with detuning $\Delta = e_{A2} - e_{A1}$. Another linearly polarized laser with electric field $E_2 e^{-i\omega_2 t}/2 + c.c.$ and frequency $\omega_2 = E_{e2}$ resonantly excites $|0\rangle$ to $|E_2\rangle$. The relevant optical transition matrix element of the electric dipole operator $d \equiv -e r$ are $\langle A_1 | d | \pm 1 \rangle = \pm d_{a,E} e_{a} / (2 \sqrt{2})$, $\langle A_2 | d | \pm 1 \rangle = i d_{a,E} e_{a} / (2 \sqrt{2})$, and $\langle E_2 | d | 0 \rangle = d_{a,E} e_{a} / \sqrt{2}$, where $e_{a} \equiv e_{x} \pm i e_{y}$ and $d_{a,E}$ is the reduced matrix element of the electric dipole moment [2]. Thus the laser coupling Hamiltonian

$$\hat{H}_l(t) = \frac{\Omega_A}{\sqrt{2}}(\hat{\sigma}_{A_1,b} + i \hat{\sigma}_{A_1,d}) e^{-i \omega_1 t} + \frac{\Omega_A e^{-i \omega_2 t}}{2} \hat{\sigma}_{E_1,0} + h.c..$$

where we have defined $\hat{\sigma}_{ij} = \hat{\sigma}_{ij} \equiv |i\rangle \langle j|$. Thus the strain term gives rise to ground state Zeeman term $g_{z\mu} B S_{z} \equiv \omega_{z} S_{z}$. The latter includes small corrections to the energy splitting between $|\pm 1\rangle$ and couples $|+1\rangle$ and $|1\rangle$ through $\hat{H}_{\text{strain}} = -\xi_{z} \hat{\sigma}_{z} + \hat{\sigma}_{\text{str}}$, where $\xi_{z} = \langle c_{x}^2 + c_{y}^2 \rangle / 2$. The field Hamiltonian includes

$$\hat{H}_{l}(t) = \frac{\Omega_A}{\sqrt{2}}(\hat{\sigma}_{A_1,b} + i \hat{\sigma}_{A_1,d} + h.c.) + \frac{\Omega_A^2}{2} \hat{\sigma}_{E_1,0} + \hat{\sigma}_{0,E}. \label{eq:CPT-Hamiltonian}$$

We further include an additional magnetic field $B$ along the $z$ (N-V) axis and uniaxial strain with effective ground strain fields $\xi_{\perp}, \xi_{\parallel}$. The former gives rise to ground state Zeeman term $g_{z\mu} B S_{z} \equiv \omega_{z} S_{z}$. The latter includes small corrections to the energy splitting between $|\pm 1\rangle$ and couples $|+1\rangle$ and $|1\rangle$ through $\hat{H}_{\text{strain}} = -\xi_{z} \hat{\sigma}_{z} + \hat{\sigma}_{\text{str}}$, where $\xi_{z} = \langle c_{x}^2 + c_{y}^2 \rangle / 2$. The field Hamiltonian includes

$$\hat{H}_{l}(t) = \frac{\Omega_A}{\sqrt{2}}(\hat{\sigma}_{A_1,b} + i \hat{\sigma}_{A_1,d} + h.c.) + \frac{\Omega_A^2}{2} \hat{\sigma}_{E_1,0} + \hat{\sigma}_{0,E} \tag{3} \label{eq:CPT-Hamiltonian-simplified}$$

In the basis $|b\rangle, |d\rangle, |0\rangle$, we have $S_{z} \equiv \hat{\sigma}_{b,d} + \hat{\sigma}_{d,b}$ and $\hat{\sigma}_{-} = e^{2i\phi} (\hat{\sigma}_{d,b} - \hat{\sigma}_{b,d} + \hat{\sigma}_{b,d} - \hat{\sigma}_{d,b}) / 2$. Thus the strain term

$$\hat{H}_{\text{strain}} = -\xi_{z} \langle \hat{\sigma}_{d,b} \rangle (\hat{\sigma}_{d,b} \cos(\Theta + 2\phi) - i \xi_{\perp} (\hat{\sigma}_{d,b} \sin(\Theta + 2\phi)$$

and the Zeeman term $\omega_{z} S_{z} \equiv \omega_{z} (\hat{\sigma}_{d,b} + \hat{\sigma}_{b,d})$ couples inducing between the dark state and the bright state. The strain-induced coupling is minimized by choosing $2 \phi = \pi \tag{1}$, such that

$$\hat{H}_{l} = \xi_{\perp} (\hat{\sigma}_{d,b} - \hat{\sigma}_{b,d}) + \omega_{z} (\hat{\sigma}_{d,b} + \hat{\sigma}_{b,d}) + \Delta \hat{\sigma}_{A_1,A_2} + \xi_{\perp} \hat{\sigma}_{A_1,b} + i \hat{\sigma}_{A_1,d} + h.c.) + \frac{\Omega_A^2}{2} \hat{\sigma}_{E_1,0} + \frac{\Omega_A^2}{2} \hat{\sigma}_{0,E} \tag{3}$$

D. Analytical expressions for steady NV state

The NV steady state $\hat{P}_{m,m}$ (denoted by $\hat{P}$ for brevity) is determined by $\mathcal{L}_{m,m} \hat{P} = 0$ and $\text{Tr}_{e} \hat{P} = 1$, where $\mathcal{L}_{m,m}(\bullet) \equiv -i[\hat{H}_{l} + \hat{S}_{z} h_{m} \langle \bullet \rangle] + \mathcal{L}_{e} \langle \bullet \rangle$ and $\hat{H}_{l} + \hat{S}_{z} h_{m} = \hat{H}_{l} w_{0} - w_{a} \sigma_{a} + h_{m}$. Straightforward calculation gives

$$P_{S,S} = \frac{2 \gamma_{s}}{\gamma_{s} + \gamma_{e}} P_{e=E},$$

$$P_{0,0} = \left(1 + \frac{\gamma + 2 \gamma_{e}}{W_{E}} \right) P_{e=E},$$

$$\gamma_{s} P_{S,S} = \gamma_{s} P_{A_{1},A_{1}} + \gamma_{s} P_{A_{2},A_{2}},$$

$$P_{b,b} = \eta_{1} \left(1 + \frac{\gamma_{e}}{\gamma_{s} + \gamma_{e}} \right) P_{e=E},$$

$$P_{b,b} = \eta_{1} \left(1 + \frac{\gamma_{e}}{\gamma_{s} + \gamma_{e}} \right) P_{e=E},$$

$$P_{e=E} = \frac{1}{\eta_{1}} \left(1 + \frac{\gamma_{e}}{\gamma_{s} + \gamma_{e}} \right) P_{e=E}.$$
where $W_E \equiv \Omega_E^2 / \Gamma_A$ is the resonant optical transition rate between $|0\rangle$ and $|E\rangle$, $W_A = \Omega_A^2 / \Gamma_A$ is the resonant optical transition rate from $|\pm 1\rangle$ to $|A_1\rangle$, and $\eta_1 \equiv \gamma_{ce}/\gamma_s$. We treat the off-resonant $|\pm 1\rangle \rightarrow |A_2\rangle$ excitation perturbatively. Up to zeroth order, near the two-photon dark resonance (small $\delta_m$), we neglect $O(\delta_m^4)$ and higher order terms and obtain

$$
P_{E,E}^{(0)} = P_0 \frac{\delta_m^2}{\delta_m^2 + \delta_0^2},
$$

$$
P_{A_1, A_1}^{(0)} = 2\eta_1 P_{E,E}^{(0)},
$$

$$
P_{d,d}^{(0)} \approx 1 - \left(2 + \frac{\gamma + 2\gamma_{ce}}{W_E}\right) P_{E,E}^{(0)},
$$

where

$$
P_0 \approx \frac{1}{\eta_2} + 2\eta_1 \frac{\gamma^2}{W_A} + \frac{\gamma^2}{W_E}.
$$

$$
\delta_0^2 \approx \frac{\eta_1 \eta_2}{4} \frac{W_A^2 - 8W_2 \xi_2 / \Gamma_A + 4\xi^2}{\eta_1 \eta_2 + \frac{W_2}{\gamma^2} \left(1 + \frac{\eta_2}{2} \frac{\gamma^2}{W_E}\right)},
$$

with $\eta_2 \equiv \gamma_s / (\gamma + \gamma_{ce})$ and we have used $\xi_2 \ll \Gamma_s$, and $\eta_1 \ll 1$. Note that only $|E\rangle, |0\rangle$, and $|d\rangle$ are significantly populated, while the populations on $|S\rangle, |b\rangle, |A_1\rangle$ are much smaller than that on $|E\rangle$ since $\gamma_{ce} \ll \gamma, \gamma_s, \gamma_{s1}, \gamma$. The leading order correction from the off-resonant excitation to $|A_2\rangle$ are

$$
P_{E,E}^{(2)} \approx \frac{1}{2\eta_1} \frac{W_A}{\gamma + \gamma_s} P_{d,d}^{(0)},
$$

$$
P_{A_1,A_1}^{(2)} = \frac{W_A}{\gamma + \gamma_s} P_{d,d}^{(0)},
$$

$$
P_{A_2,A_2}^{(2)} = \frac{W_A}{\gamma + \gamma_{s1}} P_{d,d}^{(0)},
$$

where $W_A = (\Omega_A^2 / 2) \Gamma_A / \Delta^2$ is the off-resonant transition rate from $|\pm 1\rangle$ to $|A_2\rangle$ and we have used $\gamma_{s2} \ll \gamma, \gamma_s$. Now, with the off-resonant excitation from $|d\rangle$ to $|A_2\rangle$, the populations on the excited states no longer vanish even on two-photon resonance $\delta_m = 0$. As suggested in Ref. [1], this off-resonant excitation limits the efficiency of nuclear spin cooling and narrowing. Under saturated pumping $W_E \gg \gamma$, we have $P_{d,d}^{(0)} \approx 1 - 2P_{E,E}^{(0)}$.

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