Theory of nuclear spin dephasing and relaxation by optically illuminated nitrogen-vacancy center

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Abstract
Dephasing and relaxation of the nuclear spins coupled to the nitrogen-vacancy (NV) center during optical initialization and readout is an important issue for various applications of this hybrid quantum register. Here we present both an analytical description and a numerical simulation for this process, which agree reasonably with the experimental measurements. For an NV center under cyclic optical transition, our analytical formulas not only provide a clear physical picture, but also allow control of the nuclear spin dissipation by tuning an external magnetic field. For more general optical pumping, our analytical formulas reveal a significant contribution to the nuclear spin dissipation due to electron random hopping into/out of the $m = 0$ (or $m = \pm 1$) subspace. This contribution is not suppressed, even under saturated optical pumping and/or vanishing magnetic field, thus providing a possible solution to the puzzling observation of nuclear spin dephasing in zero perpendicular magnetic field Dutt et al (2007 Science 316 1312). It also implies that enhancing the degree of optical spin polarization of the nitrogen-vacancy center can reduce the effect of optically induced nuclear spin dissipation.

1. Introduction

The diamond nitrogen-vacancy (NV) center [1] is a leading platform for various quantum technologies such as quantum communication, quantum computation, and nanoscale sensing [2–8]. The electronic spin of the NV center and a few surrounding nuclear spins form a hybrid quantum register [9–11]. Important advantages of this solid-state quantum register include the long electron and nuclear spin coherence time [12], the capability of high-fidelity initialization, coherent manipulation, and projective readout of the electronic/nuclear spins [5, 13] and even the entire quantum register [11, 14, 15] by optical and microwave (or radio frequency) illumination. In the dark, the coherence time of the nuclear spin qubit could reach a few milliseconds [2]. However, during the optical illumination for initialization and readout [2, 8, 14, 16–18], the dissipative spontaneous emission and non-radiative decay of the NV electron generates substantial noise in the nuclear spin qubits through hyperfine interaction (HFI), which significantly shortens the nuclear spin coherence time and degrades the control precession. This has motivated widespread interest in using the NV center electron to engineer nuclear spin dissipation [16, 17].

In the past few years, many studies [16, 17, 19–21] have been devoted to optically induced nuclear spin dissipation, including the dephasing process as characterized by the $T_2$ time and the relaxation process as characterized by the $T_1$ time. Generally, both $T_1$ and $T_2$ originate from the random fluctuation of the NV electron under optical illumination, which falls into two categories: one involves the flip of the NV electron spin and the other does not. The former is usually strongly suppressed by the large energy splitting of the NV electron unless the NV electron is tuned to the ground state or excited state level anticrossing [19, 21]. The latter is energetically more favorable and dominates the nuclear spin $T_1$ and $T_2$ times in many situations, as confirmed by a series of experiments [2, 12, 17]. In particular, in [2], Dutt et al measured the $T_2$ of a strongly coupled $^{13}$C...
nuclear spin due to the latter mechanism under illumination of a 532 nm laser. They found that with decreasing non-axial magnetic field (i.e., the magnetic field component perpendicular to the N–V symmetry axis), the dephasing rate 1/T₂ decreases significantly and remains finite at vanishing non-axial magnetic field. The subsequent theoretical investigation of this experiment was carried out in the framework of a phenomenological spin-fluctuator model [16]. This work successfully explains the magnetic field dependence of the observed T₂ time and gives an intuitive understanding for the optically induced nuclear spin dissipation: the generation of a rapidly fluctuating effective magnetic field on the nuclear spins by the optically induced random hopping of the electron between different states. When the hopping is sufficiently fast and hence the noise correlation time is sufficiently short, the nuclear spin dissipation could be suppressed [16] in a way similar to the motional narrowing effect in NMR spectroscopy in liquids. This effect has been successfully used to significantly increase the nuclear spin coherence time [12]. Despite this remarkable success, the spin-fluctuator model still suffers from three drawbacks. First, its analytical form is qualitative, while obtaining quantitative results requires numerical simulations. This not only complicates the calculation, but also smears the underlying physical picture. Second, the various parameters in this model are phenomenological, i.e., they are not directly related to the physical parameters of the NV center, but instead are obtained from fitting the experimental data. This precludes straightforward guidance on controlling the nuclear spin dissipation by tuning various experimental parameters. Third, the origin of the experimentally observed finite zero-field dephasing [2] remains not very clear, except for some qualitative arguments. Very recently, a room-temperature experiment by Dreau et al. [17] further suggested that under a magnetic field along the N–V axis and illumination of a 532 nm laser, the latter mechanism (i.e., the one that does not involve the flip of the NV electron) could be very important for the nuclear spin T₁ time. There, a qualitative formula was used to fit the measured T₁ time versus the external magnetic field along the N–V axis, but a quantitative understanding remains absent.

To bridge the gap between experimental observation and theoretical understanding, we present both a two-level toy model and a more realistic seven level model to account for the nuclear spin dephasing and relaxation induced by an optically illuminated NV center at room temperature. In addition to numerical simulations, we also provide analytical expressions for the dephasing rate and relaxation rate. They clearly reveal the dependence of the nuclear spin dephasing and relaxation on various model parameters, which are all experimentally measurable.

In the following, we begin with the simplest case in which a single cyclic transition (e.g., between the ground and excited m = 0 states) of the NV center is optically driven. Our analytical expressions for the nuclear spin dephasing and relaxation provide a quantitative description and a physically transparent interpretation that substantiates the previous analytical (but qualitative) and numerical results [16]. They also demonstrate the possibility to control the nuclear spin dissipation by tuning the magnetic field [16]. Next we consider the more realistic seven level model with general optical illumination of the NV center, incorporating finite non-radiative decay between m = 0 and m = ±1 subspaces. Our numerical results agree well with the experimental measurements [17]. Our analytical results shows that random hopping between the m = 0 (or m = ±1) triplet states and the metastable singlet of the NV center could significantly contribute to nuclear spin dissipation. This contribution is not suppressed under saturated optical pumping and remains finite even in zero non-axial magnetic field. This provides a possible solution to the puzzling observation of nuclear spin dephasing in zero magnetic field [2]. The analytical formulas for the nuclear spin dissipation in terms of HFI tensors also allow us to measure the HFI tensor for the excited electron state, which is usually smeared by the short electron spontaneous emission lifetime.

2. Two-level fluctuator model: analytical results

2.1. Model

To begin with, we present a microscopic theory for the decoherence of an arbitrary nuclear spin Û (e.g., 13C, 15N, or 14N) by the electron of the NV center undergoing optically induced cyclic transition |g⟩ → |e⟩, e.g., |g⟩ = |0⟩ and |e⟩ = |E⟩ in the widely used setup for single-shot readout of the electron spin at low temperature [14, 22]. At room temperature, most experiments use a 532 nm laser to excite the phonon sideband and more than one excited states of the NV center should be included (to be discussed in the next section). In this case, the two-level model only provides a qualitative description and the excited state |e⟩ in this model should be understood as the phonon sideband of the NV excited states. In the rotating frame, the electron dynamics is governed by the Liouville superoperator $L_e(\cdot) \equiv -i[H_e, (\cdot)] + \sum_{\alpha} \gamma_\alpha D(L_\alpha)(\cdot)$, where

$$\hat{H}_e = \Delta \hat{\sigma}_{e} + \frac{\Omega_e}{2} (\hat{\sigma}_{e} + \text{h.c.})$$
is the electron Hamiltonian, \( \hat{\sigma}_{ij} \equiv |j\rangle \langle i| \), \( \Delta \) is the detuning of the optical pumping, and \( \gamma_{e} \) is the rate of the optical dissipation process \( \hat{L}_{e} \) in the Lindblad form \( \mathcal{D} \hat{L}_{e} \). Here we include the spontaneous emission \( \hat{L} = \hat{\sigma}_{ee} \) of the excited state \(|e\rangle\) with rate \( \gamma_{e} \approx 1/(11 \text{ ns}) \) and the pure dephasing \( \hat{L} = \hat{\sigma}_{e} \) of the excited state \(|e\rangle\) with rate \( \gamma_{e} \), which has a strong temperature dependence, from a few tens of MHz at low temperature up to 10^7 MHz at room temperature [23, 24]. Including the electron–nuclear HFI \( (\hat{S}_{x} \cdot A_{x} + \hat{S}_{z} \cdot A_{z}) \equiv \hat{F} \cdot \hat{I} \) and the nuclear spin Zeeman term \( \gamma_{N} \hat{B} \cdot \hat{I} \) \( (\gamma_{N} = -10.705 \text{ kHz m}^{-1} \) is the C nuclear gyromagnetic ratio) under a magnetic field \( \hat{B} \), the electron–nuclear coupled system obeys

\[
\dot{\rho} = \mathcal{L}_{e} \rho - i \left[ \left( \hat{F} + \gamma_{N} \hat{B} \right) \cdot \hat{I}, \rho \right]
\]

(1)

in the rotating frame of the pumping laser.

There are two contributions to the nuclear spin dissipation. One involves the flip of the electron spin and hence is strongly suppressed by the large electron–nuclear energy mismatch away from the NV center ground state and excited state anticrossings. The other does not flip the electron spin and hence is energetically favorable in most situations. In our analytical derivation, we neglect the former contribution by dropping the off-diagonal electron spin flip terms in \( \hat{F} \) and only keep the diagonal part: \( \hat{F} \approx \hat{\sigma}_{ee} \omega_{e} + \hat{\sigma}_{e} \omega_{e} \), where \( \omega_{e} = \langle g | \hat{S}_{z} | g \rangle \cdot A_{x} \) and \( \omega_{e} = \langle e | \hat{S}_{z} | e \rangle \cdot A_{x} \). The second term of equation (1) describes the precession of the nuclear spin with angular frequency \( \gamma_{N} \hat{B} + \omega_{e} \) and \( \gamma_{N} \hat{B} + \omega_{e} \), respectively, conditioned on the electron state being \(|g\rangle\) and \(|e\rangle\).

When \( \omega_{e} = \omega_{e} \), the optically induced random hopping of the electron between \(|g\rangle\) and \(|e\rangle\) gives rise to random fluctuation of the nuclear spin precession frequency and hence nuclear spin dissipation: the fluctuation of the precession frequency orientation (magnitude) leads to nuclear spin relaxation (pure dephasing) [16]. Below, we derive analytically a closed equation of motion of the nuclear spin to describe these effects.

### 2.2. Lindblad master equation for nuclear spin

The time scale for the optically pumped two-level NV center to reach its steady state is

\[ \gamma_{N} \approx 1/(2R + \gamma_{e}) < 12 \text{ ns}, \]

where \( R = 2\pi (\Omega_{0}/2)^{2} \delta \left( \left( \gamma_{N} + \gamma_{e} / 2 \right) / 2 \right) \) is the optical pumping rate from \(|g\rangle\) to \(|e\rangle\) and \( \delta \left( x \right) = \left( \gamma_{N} / \pi \right) / \left( x^{2} + \gamma_{N}^{2} / 4 \right) \) is the broadened \( \delta \)-function. Due to the large dephasing rate \( \gamma_{e} \), the pumping rate can be approximated as \( R = \Omega_{0}^{2} / \gamma_{e} \). When \( \gamma_{N} \) is much shorter than the time scale of the nuclear spin dissipation, we can regard the NV center as always in its steady state \( \hat{P} \) as determined by \( \mathcal{L}_{e} \hat{P} = 0 \), e.g., the steady state populations in \(|e\rangle\) and \(|g\rangle\) are \( P_{e} = R/(2R + \gamma_{e}) \) and \( P_{g} = 1 - P_{e} \), respectively. Then we treat the dissipative NV center as a Markovian system [25] and use Born–Markovian approximation to derive a Lindblad master equation for the reduced density matrix of the nuclear spin \( \hat{\rho}(t) \equiv \mathcal{T}_{e} \hat{P}(t) \) (see appendix A for details):

\[
\dot{\rho} = -i \left[ \hat{\omega} \cdot \hat{I}, \rho \right] + 2 \Gamma_{e} \mathcal{D} \left[ \hat{L}_{e} \right] \hat{\rho} + \Gamma_{a} \mathcal{D} \left[ \hat{L}_{a} \right] \hat{\rho} + \Gamma_{a} \mathcal{D} \left[ \hat{L}_{a} \right] \hat{\rho},
\]

(2)

where \( \hat{\omega} = \gamma_{N} \hat{B} + P_{g} \omega_{g} + P_{e} \omega_{e} \) is the average precession frequency that defines the nuclear spin quantization axis \( \hat{e}_{Z} \equiv \hat{\omega} / |\hat{\omega}| \). The last three terms describe the nuclear spin dissipation in the tilted cartesian coordinate

\[
e_{X} = e_{x} \sin \varphi - e_{y} \cos \varphi,
\]

\[
e_{Y} = \cos \varphi \cos \theta e_{x} + \sin \varphi \sin \theta e_{y},
\]

\[
e_{Z} = |\hat{\omega}| / \sin \theta \cos \varphi e_{x} + |\hat{\omega}| / \sin \sin \varphi e_{y} + \cos \theta e_{z},
\]

(3a)

(3b)

(3c)

where \( \theta(\varphi) \) is the polar (azimuth) angle of \( \hat{\omega} \) in the conventional coordinate \( (e_{x}, e_{y}, e_{z}) \) with \( e_{z} \) along the N–V symmetry axis. The different vectors are shown schematically in figure 1(a). The nuclear spin dissipation includes pure dephasing (the second term of equation (2)) due to the fluctuation of \( \hat{L}_{a} \) and relaxation [the last two terms of equation (2)], with \( \hat{L}_{e} \equiv \hat{F}_{e} \pm i \hat{F}_{T} \) due to the fluctuation of \( \hat{L}_{e} \equiv \hat{F}_{e} \pm i \hat{F}_{T} \). Typically the nuclear spin level splitting \( |\hat{\omega}| \ll \gamma_{N}, \gamma_{e} \), so we obtain

\[
\Gamma_{a} = \frac{\pi^{2}}{2T} |(\omega_{e} - \omega_{g})|_{Z}^{2},
\]

\[
\Gamma_{e} = \frac{\pi^{2}}{4T} |(\omega_{e} - \omega_{g})|_{Z}^{2},
\]

(4a)

(4b)

where \( O_{e} \equiv O_{X} e_{X} + O_{Y} e_{Y} \) is the component perpendicular to the nuclear spin quantization axis, \( T = 1/(R + 1/(\gamma_{N} + R)) \) is the duration of one electron hopping cycle (excitation time 1/R and de-excitation time 1/(\gamma_{N} + R)), and

\[
\gamma_{e} = \frac{\sqrt{R + \gamma_{N} \omega_{g} + \pi \gamma_{f}^{2} \delta(\gamma_{N}^{2} + \gamma_{e}^{2}) / (2R + \gamma_{e})}}{R + \gamma_{N}} \approx \frac{\sqrt{2}}{R + \gamma_{N}} \approx \frac{\sqrt{2}}{2R + \gamma_{N}} \approx \frac{\sqrt{2}}{2R + \gamma_{N}}.
\]

(5)
is the uncertainty of the electron dwell time in the excited state in each hopping cycle. Here the last step of equation (5) holds at room temperature, where $\gamma_0 \sim 10^7$ MHz is much larger than the typical $\gamma_p$, $R$, and $\Delta$.

### 2.3. Physical picture

Equations (2)–(5) not only provide a quantitative and analytical description for the dissipative nuclear spin dynamics due to an optically pumped NV center, but also have a physically transparent interpretation that substantiates the previous analytical (but qualitative) and numerical results [16]. For example, the pure dephasing rate in equation (4a) is directly connected to the nuclear spin phase diffusion process by the optically induced random hopping of the electron between the ground state $|g\rangle$ and the excited state $|e\rangle$ [16]. To clearly see this, let us consider the phase accumulation of the nuclear spin during an interval $[0, t]$. Suppose that during this interval, the electron undergoes $N$ hopping cycles, and that during the $k$th cycle, the electron stays in $|g\rangle$ for an interval $\tau_k$, so the total dwell times in $|g\rangle$ and $|e\rangle$ are $\tau = \sum_{k=1}^N \tau_k$ and $t - \tau$, respectively, and the nuclear spin accumulates a phase factor $e^{-i(\omega_g^0 B_z \tau - i(\omega_g^0 + \omega_e^0) t)}$. For $t \gg T$, the number of hopping cycles $N \approx t/T \gg 1$, i.e., $\tau$ is the sum of many random variables $\{\tau_k\}_k$, so $\tau$ obeys a Gaussian distribution centered at $P_e t$ with a standard deviation $\sqrt{N} \tau$, where $\tau$ is the rms fluctuation of each $\tau_k$. Averaging the phase factor over this Gaussian distribution gives $e^{-\frac{1}{2} \sigma^2} e^{-i \gamma_0 t}$, where $\Gamma_0$ coincides with equation (4a) as long as $\gamma_0$ is given in equation (5), e.g., at room temperature, for weak pumping $R \ll \gamma_0$, the uncertainty $\tau \approx \sqrt{2 \gamma_0 t}$ of the dwell time in $|e\rangle$ is dominated by the uncertainty in the spontaneous emission, while for saturated pumping, $\tau_e \approx 1/(\sqrt{2} R)$ is strongly suppressed by the rapid optically induced transition between $|e\rangle$ and $|g\rangle$. The relaxation rate $\Gamma_0$ in equation (4b) can be understood in a similar way.

Analytical results for equations (4) provide a microscopic basis for the previous model [16] and experimental observations [2, 12, 26], e.g., they clearly show the initial increase of the dissipation rates $\Gamma_p$, $\Gamma_\xi \propto R$ under weak pumping $R \ll \gamma_0$ and the motional narrowing $\Gamma_p$, $\Gamma_\xi \propto 1/R$ under saturated pumping $R \gg \gamma_0$. The former arises from the increase of $T$ with decreasing $R$ under weak pumping, while the latter comes from both the decrease of $\tau_e \sim 1/R$ and $T \sim 1/R$ under saturated pumping. Our analytical formulas also demonstrate the possibility [16] to control $\Gamma_\nu$ and $\Gamma_\eta$ by using the magnetic field to tune the nuclear quantization axis $e_\eta \propto \omega_0$, e.g., if we tune $e_\eta$ to be perpendicular (parallel) to $\omega_\eta = \omega_0$, then we can eliminate nuclear spin pure dephasing (relaxation). Interestingly, the sum rule

$$\Gamma_\nu + \Gamma_\eta + \Gamma_\xi = \frac{\tau_e^2}{27} |\omega_\eta - \omega_\xi|^2$$

suggests that reducing $\Gamma_\nu$ ($\Gamma_\xi$) inevitably increases $\Gamma_\eta$ ($\Gamma_\xi$) and it is impossible to suppress $\Gamma_\eta$ and $\Gamma_\xi$ simultaneously, unless $\omega_\eta = \omega_\xi$. The condition $\omega_\eta = \omega_\xi$ is satisfied when the $^{13}$C nucleus spin is sufficiently far away from the NV center and hence couples to the NV ground state and excited states through the same dipolar hyperfine interaction. In this case, equation (4) shows that the nuclear spin dissipation totally vanishes, simply because the nuclear spin precession frequency is not randomized by the optically induced electron hopping.
2.4. Connection to experimental observations

Equation (2) describes the dissipative evolution of the nuclear spin in the tilted coordinate \((e_x, e_y, e_z)\) with \(e_z \propto \bar{\omega}\). From equation (2), we obtain the Bloch equations

\[
\begin{align*}
\dot{\langle \hat{I}_z \rangle} &= -\frac{\langle \hat{I}_x \rangle}{T_2}, \\
\dot{\langle \hat{I}_x \rangle} &= \left( i \bar{\omega} - \frac{1}{T_2} \right) \langle \hat{I}_x \rangle, 
\end{align*}
\]

(7a) for the average nuclear spin \(\langle \hat{I}(t) \rangle \equiv Tr \hat{I} \rho(t)\), where \(T_1 = 1/(\Gamma_+ + \Gamma_-)\) and \(T_2 = 1/((\Gamma_0 + \Gamma_1 + \Gamma_2)/2)\). Then the sum rule in equation (6) implies \(1/T_2 + 1/(2T_1) \propto |\omega_0 - \omega_i|^2\), i.e., tuning the magnetic field can prolong the \(T_1\) time (\(T_2\) time) at the cost of reducing the \(T_2\) time (\(T_1\) time).

The above Bloch equations have simple solutions \(\langle \hat{I}_z(t) \rangle = \langle \hat{I}_z(0) \rangle e^{-t/T_1}\) and \(\langle \hat{I}_x(t) \rangle = e^{i\tilde{\omega}t} \langle \hat{I}_x(0) \rangle\). However, nuclear spin initialization and measurement are usually performed in the conventional coordinate \((e_x, e_y, e_z)\) with \(e_z\) along the N–V axis, so \(T_1\) and \(T_2\) will be mixed in the observed signals. For example, Dutta et al. [2] initialized a strongly coupled \(^{13}\)C nuclear spin-1/2 (hereafter referred to as \(^{13}\)C\(_B\)), according to the notation of Gali [27]), into the eigenstate \((|+\rangle + |\downarrow\rangle)/\sqrt{2}\) of \(\hat{I}_z\), let it evolve freely for an interval \(\tau\), and then measured \(\hat{I}_z\) through a \(\pi/2\) pulse \(e^{-i\phi/2}\) followed by a fluorescence readout of \(\hat{I}_z\) via the NV center. According to equation (3), the measured signal \(\langle \hat{I}_z(t) \rangle = \sum_{\alpha=+,-,0} e_{\alpha} \cdot \langle e_{\alpha} \rangle \langle \hat{I}_z(t) \rangle\) consists of a non-oscillatory term \(e^{-\tilde{\omega}t} \sin^2 \theta \cos^2 \varphi/2\) that decays with a time scale \(T_1\) and an oscillatory term \(e^{-\tilde{\omega}t} (1 - \cos^2 \varphi \sin^2 \theta) \cos(|\tilde{\omega}|t)/2\) that decays with a time scale \(T_2\). The oscillating feature has been observed experimentally [2]. When the nuclear spin quantization axis \(e_z\) is parallel to the initial state polarization direction \(e_x\), i.e., \(\theta = \pi/2\) and \(\varphi = 0\), the oscillatory feature disappears.

At room temperature, when the magnetic field is along the \(z\) axis, the optical transition is spin conserving. The cyclic transition between the ground state \(|g\rangle = |0\rangle\) and excited state \(|e\rangle \equiv |0\rangle_{0}\) does not contribute to nuclear spin dissipation since \(\omega_0 = \omega_x = 0\). When \(B\) deviates from the \(z\) axis, its transverse component \(B_x = B_y = B_z e_z\) mixes the \(m = 0\) sublevels and the \(m = \pm 1\) sublevels, so that \(\omega_0 = -(2\gamma_0/D_{00}) B_x \cdot A_x + \omega_x = -28.025\) MHz \(m^{-1}\) is the zero-field splitting in the NV ground (excited) state and \(\gamma_0 = 28.025\) MHz \(m^{-1}\) is the gyromagnetic ratio of the NV electron. This can be understood as a hyperfine enhancement of the nuclear spin g-factor [14] (see the next section for more detailed discussion). As a result, the nuclear spin dissipation rates \(\Gamma_0\) and \(\Gamma_2\) are proportional to \(|B_x|^2\). This dependence agrees with the experimental observation by Dutta et al. [2, 16], who measured the \(T_2\) time of a strongly coupled \(^{13}\)C nuclear spin (referred to as a \(^{13}\)C\(_B\) nucleus) under illumination of a 532nm laser and a non–axial magnetic field. However, the two-level fluctuator model significantly overestimates the magnitude of the measured \(T_2\) time. For this nucleus, the HFI tensor has been obtained from \textit{ab initio} calculations [27] as

\[
A_x^{({^{13}\text{C}}_B)} \approx \begin{bmatrix} -8 & 0 & -0.7 \\ 0 & -8.99 & 0 \\ -0.7 & 0 & -8.00 \end{bmatrix} \text{MHz},
\]

(8a)

\[
A_y^{({^{13}\text{C}}_B)} \approx \begin{bmatrix} -3.78 & 0.19 & -1.47 \\ 0.19 & -5.83 & 0.22 \\ -1.47 & 0.22 & -4.12 \end{bmatrix} \text{MHz},
\]

(8b)

From this HFI tensor and the experimentally used non–axial magnetic field \(-65\text{G}\), we estimate \(|\omega_x - \omega_0| \sim 0.3\text{MHz}|\). Under optical pumping rate \(R = \gamma_0\) (the experimental condition [2]), the two-level fluctuator model (equation (4a)) gives \(T_2 \approx 1/\Gamma_0 \approx 250\) \(\mu\text{s}\), which is two orders of magnitudes larger than the experimental value \(\sim 1\) \(\mu\text{s}\). This large discrepancy suggests that the leakage from the \(m = 0\) subspace to the \(m = \pm 1\) subspace may play an important role in determining the nuclear spin dissipation. In the next section, we shall demonstrate that the small leakage from the \(|0\rangle\) subspace to the \(|\pm 1\rangle\) subspace could introduce additional contributions that may dominate the nuclear spin dissipation.

3. Seven-level fluctuator model: numerical and analytical results

3.1. Model

Now we consider general optical pumping of the NV center at room temperature, incorporating the finite non-radiative decay rate between \(m = 0\) and \(m = \pm 1\) subspaces. In this case, the electron–nuclear coupled system still obeys equation (1). The only difference is that now the Liouville superoperator \(\mathcal{L}_e\) for the optically pumped NV center includes seven energy levels: the ground triplet \(|m\rangle |g\rangle \equiv |m\rangle |0\rangle\) (i.e., \(|0\rangle\), \(|\pm 1\rangle\)), the excited triplet \(|m\rangle |e\rangle \equiv |m\rangle |0\rangle\) (i.e., \(|0\rangle\), \(|\pm 1\rangle\)), and the metastable singlet \(|S\rangle\), where \(|g\rangle \langle e\rangle\) denotes the ground (excited) orbital state. The unitary part of \(\mathcal{L}_e\) is described by a seven-level NV Hamiltonian
where $\Delta$ is the optical detuning, $\hat{H}_{gs} = D_{gs}\hat{S}_{x,gs} + \gamma_{e}\hat{B} \cdot \hat{S}_{e}$ and $\hat{H}_{es} = D_{es}\hat{S}_{x,es} + \gamma_{e}\hat{B} \cdot \hat{S}_{e}$ describe, respectively, the ground state triplet with zero-field splitting $D_{gs} = 2.87\text{GHz}$ and the excited state triplet with zero-field splitting $D_{es} = 1.41\text{GHz}$. The dissipative part of $L_{c}$ includes various dissipation processes between the seven levels of the NV center as sketched in figure 1(b): the spontaneous emission from the excited orbital $|e\rangle$ to the ground orbital $|g\rangle$ with rate $\gamma_{eg} = 1/(12\text{ns})$ [28], the non-radiative decay from $|\pm 1_e\rangle$ to the metastable singlet $|S\rangle$ with rate $\gamma_{1} \approx \gamma_{eg}$ followed by the non-radiative decay from $|S\rangle$ to $|0_g\rangle$ with rate $\gamma_{eg} = 1/(143\text{ns})$ [29], the leakage from $|0_g\rangle$ to $|\pm 1_e\rangle$ with equal rates $\gamma_{1} \ll \gamma_{eg}$ and the orbital dephasing of the excited state $\hat{L} = \hat{\sigma}_{x,gs}$ with rate $\gamma_{\text{orb}} \approx 10^{7}\text{MHz}$ [23, 24].

In most of the experimental optical readout and initialization of the NV center at room temperature, the NV center ground state is excited to the electron–phonon sideband states by an off-resonance 532 nm green laser. Therefore, a completely microscopic model should include the vibrational sidebands and the dynamic Jahn–Teller effect of the NV center. However, such a model would be very complicated. Here our simplified model implicitly includes these effects as long as the excited state $|e\rangle$ is identified as the electron–phonon hybridized states.

As discussed in the previous section, there are two processes contributing to nuclear spin dissipation. The one involving the electron spin flip is strongly suppressed away from the NV center ground state and excited state level anticrossing. Thus, in our analytical derivation below, we consider the other process that does not change the electron spin state, i.e., we drop the off-diagonal electron spin flip terms in $\hat{F}$ and only keep the diagonal part. The magnetic field component $B_{T} \equiv B_{e}e_{z} + B_{e}e_{r}$, perpendicular to the N–V axis ($z$ axis) slightly shifts the electron levels and mixes the electron states from $|m_{g}\rangle$ and $|m_{e}\rangle$ to $|\bar{m}_{g}\rangle$ and $|\bar{m}_{e}\rangle (m = 0, \pm 1)$. For $\gamma_{e}|B_{T}| \ll D_{gs}, D_{es}$, the level shift can be safely neglected, but the state mixing has a nontrivial influence on the diagonal part of $\hat{F}$, i.e., we need to keep the terms diagonal in the mixed basis $|\bar{m}_{g}\rangle$ and $|\bar{m}_{e}\rangle$:

$$\hat{F} \approx \sum_{m} \left( \hat{\sigma}_{x,0}a_{m} \left( \bar{m}_{g}\right) \hat{S}_{z,gs} \bar{m}_{e}\right) \cdot A_{m} + \hat{\sigma}_{x,1}a_{m} \left( \bar{m}_{g}\right) \hat{S}_{z,es} \bar{m}_{e}\cdot A_{m}.$$

Up to the first order of the small quantities $|\gamma_{e}B_{T}|/D_{gs}$ and $|\gamma_{e}B_{T}|/D_{es}$, we obtain (hereafter $|m_{g/e}\rangle$ stands for $|\bar{m}_{g/e}\rangle$):

$$\langle 0_{g}\left| \hat{S}_{z}\right| 0_{e}\rangle \approx -\frac{2\gamma_{e}B_{T}}{D_{gs}},$$

$$\langle 0_{g}\left| \hat{S}_{z}\right| 0_{e}\rangle \approx -\frac{2\gamma_{e}B_{T}}{D_{es}},$$

$$\langle \pm 1_{g}\left| \hat{S}_{z}\right| \pm 1_{e}\rangle \approx \pm e_{z} + \frac{\gamma_{e}B_{T}}{D_{gs}},$$

$$\langle \pm 1_{g}\left| \hat{S}_{z}\right| \pm 1_{e}\rangle \approx \pm e_{z} + \frac{\gamma_{e}B_{T}}{D_{es}}.$$

The terms proportional to $B_{T}$ lead to hyperfine enhancement of the nuclear spin g-factor [2], e.g., the term $\hat{\sigma}_{0,0}\langle 0_{e}\left| \hat{S}_{z}\right| 0_{e}\rangle \cdot A_{e}$ in $\hat{F}$ can be written as $\hat{\sigma}_{0,0}\gamma_{e}|B_{T}| \left[ -2\gamma_{e}A_{e} D_{gs}\gamma_{e}B_{T} \right]$, where $\left[ \ldots \right]$ is the correction to the nuclear gyromagnetic ratio by the HFI conditioned on the electron being in $|0_{e}\rangle$. Since $\gamma_{eg}|B_{T}| \ll D_{gs}, D_{es}$, the hyperfine enhancement terms in $\langle \pm 1_{g}\left| \hat{S}_{z}\right| \pm 1_{e}\rangle$ and $\langle \pm 1_{g}\left| \hat{S}_{z}\right| \pm 1_{e}\rangle$ can be safely dropped, so that

$$\hat{F} \approx \hat{S}_{x,gs}b_{gs} + \hat{S}_{x,es}b_{es} + \hat{\sigma}_{0,0}a_{e} + \hat{\sigma}_{0,0}a_{e},$$

where $a_{g} = -(2\gamma_{e}/D_{gs})B_{T} \cdot A_{e}$ and $a_{e} = -(2\gamma_{e}/D_{es})B_{T} \cdot A_{e}$ and $b_{g/e} = e_{z} A_{g/e}$.

Now the second term of equation (1) describes the nuclear spin precession conditioned on the electron state: the precession frequency is $\gamma_{eg}B_{gs} \pm b_{g} \left( \gamma_{eg}B_{gs} \pm b_{g} \right)$ when the electron state is $|\pm 1_{e}\rangle$ or $|\pm 1_{e}\rangle$, $|\pm 1_{e}\rangle$, or $\gamma_{eg}B_{gs} \pm a_{g} \left( \gamma_{eg}B_{gs} \pm a_{g} \right)$ when the electron state is $|0_{g}\rangle$ or $|0_{g}\rangle$. The optically induced hopping of the electron between different states randomizes the precession frequency and leads to nuclear spin dissipation [16]. Below we derive analytically a closed equation of motion of the nuclear spin to describe these effects.

### 3.2. Lindblad master equation for nuclear spin

The time scale $\tau_{NV} = 1/\min(\gamma_{eg}, R)$ for the seven-level NV center to reach its steady state is determined by the time scale of the slowest process: the non-radiative decay rate from $m = 0$ subspace to $m = \pm 1$ subspaces if the optical pumping is strong, or the optical pumping rate $R$ from the ground orbital to the excited orbital if the optical pumping is weak. When $\tau_{NV}$ is much shorter than the time scale $\tau_{0}$, $\tau_{1}$ of the nuclear spin dissipation, we can follow exactly the same procedures as used in the previous section to derive the Lindblad master equation for the nuclear spin density matrix and the Bloch equation for the average nuclear spin angular momentum. The
former (latter) has exactly the same form as equation (2) (equation (7)) and describes the nuclear spin dissipation in the tilted cartesian coordinate \((\mathbf{e}_x, \mathbf{e}_y, \mathbf{e}_z)\) with \(\mathbf{e}_y \equiv \hat{\omega}/|\hat{\omega}|\) (see equation (3)) and 
\[ \hat{\omega} = \gamma_{1B} \mathbf{B} + P_0 \mathbf{a}_e + P_0 \mathbf{a}_s, \]
where \(P_0\) and \(P_0\) are the steady state populations of the NV center on \(|0_e\rangle\) and \(|0_s\rangle\).

The detailed expression for the steady state populations is given in appendix A.

Now we discuss the analytical expressions for the nuclear spin pure dephasing rate \(\Gamma_\varphi\) and relaxation rate \(\Gamma_{\pm}\).

The former comes from the fluctuation of \(\tilde{F}_2\) between zero frequency, while the latter comes from the fluctuation of \(\tilde{F}_3 \pm i\gamma_G\) at the nuclear spin level splitting \(|\hat{\omega}|\). Since \(\hat{\mathbf{F}}\) is a linear combination of \(\hat{S}_{xG}, \hat{S}_{yG}, \hat{S}_{zG}, \hat{\delta}_{10,0},\) and \(\hat{\delta}_{01,0}\), the fluctuation of \(\tilde{F}_2\) and \(\tilde{F}_3\) involves cross-correlations among these four operators. Fortunately, due to the large orbital dephasing at room temperature, the optical pumping rate from the ground orbital to the excited orbital is nearly independent of the spin state and the coherence between electron states can be neglected. This allows us to neglect the cross correlation between \(\{\hat{S}_{yG}, \hat{S}_{zG}\}\) and \(\{\hat{\delta}_{10,0}, \hat{\delta}_{01,0}\}\) (see appendix B for details). So \(\Gamma_{\varphi}\) and \(\Gamma_{\pm}\) are the sum of the contributions \(\Gamma_{\psi}^{(1)}, \Gamma_{\varphi}^{(1)}\) from the fluctuation of \(\hat{S}_{xG}, \hat{S}_{zG}\) associated with the \(m = \pm 1\) subspace and the contributions \(\Gamma_{\psi}^{(0)}, \Gamma_{\varphi}^{(0)}\) from the fluctuation of \(\hat{\delta}_{10,0}, \hat{\delta}_{01,0}\) associated with the \(m = 0\) subspace. Unless explicitly specified, hereafter we consider the situation \(|\hat{\omega}| \ll R, \gamma_{1B}\) which is satisfied for weak hyperfine interaction or strong optical pumping. In this case, the dependence of the nuclear spin relaxation rate on \(|\hat{\omega}|\) can be neglected.

Under the above condition, the contribution from \(m = \pm 1\) subspace is

\[ \Gamma_{\psi}^{(1)} = \frac{2p_{1\pm}}{\gamma_{1\pm}} \sqrt{\left( b_{xG} + b_{xG} \frac{\gamma_{1\pm} + \gamma_{1\pm} + r}{r} \right)^2 - b_{yG} \cdot b_{yG} \frac{\gamma_{1\pm}^2}{r}}, \quad (9) \]

\[ \Gamma_{\varphi}^{(1)} \approx \frac{p_{1\pm}}{\gamma_{1\pm}} \sqrt{\left( b_{xG} + b_{xG} \frac{\gamma_{1\pm} + \gamma_{1\pm} + r}{r} \right)^2 - \left( b_{yG} \cdot b_{yG} \frac{\gamma_{1\pm}^2}{r} \right)}, \quad (10) \]

where \(p_{1\pm}\) is the steady-state population of the electron state \(|\pm\rangle\). Formally \(\Gamma_{\psi}^{(1)}\) and \(\Gamma_{\varphi}^{(1)}\) are independent of the magnetic field, but actually the components \(b_{xG}, b_{xG}, b_{yG}, b_{yG}, b_{yG}, b_{yG}\) defined in the tilted coordinate \(\mathbf{e}_x, \mathbf{e}_y, \mathbf{e}_z\) (see equations (3)), which in turn depends on the magnetic field. Importantly, \(\Gamma_{\psi}^{(1)}\) and \(\Gamma_{\varphi}^{(1)}\) do not vanish even in zero magnetic field. This provides a possible solution to the puzzling observation of nuclear spin dephasing in zero magnetic field [2], which has been speculated to be due to the orbital fluctuation of the NV center in the excited state [16].

Equations (9) and (10) exhibit four features. First, \(\Gamma_{\psi}^{(1)}\) and \(\Gamma_{\varphi}^{(1)}\) do not vanish when \(b_{xG} = b_{xG}\) and \(a_{\pm} = a_{\pm}\) as opposed to the two-level fluctuator model (equation (4)). This is because in the two-level fluctuator model, the electron only hops between \(|g\rangle\) (with nuclear spin precession frequency \(\gamma_{1B} \mathbf{B} + a_{\pm}\)) and \(|e\rangle\) (with nuclear spin precession frequency \(\gamma_{1B} \mathbf{B} + a_{\pm}\); when \(a_{\pm} = a_{\pm}\), the electron hopping does not randomize the nuclear spin precession, so there is no nuclear spin dissipation. By contrast, in the seven-level fluctuator model, the electron can hop between energy levels, each of which corresponds to a different nuclear spin precession frequency (see the discussion at the end of the previous subsection). Therefore, even if the nuclear spin is coupled to the NV excited state and ground state through the same hyperfine interaction, the dissipation process still exists. This conclusion is different from the expectation [14, 18] that the decoherence comes from the hyperfine difference between the excited state and ground state. The nuclear spin dissipation vanishes only when all these precession frequencies are equal, i.e., when \(a_{\pm} = a_{\pm}, a_{\pm} = b_{xG} = b_{xG} = 0\). Second, \(\Gamma_{\psi}^{(1)}\) and \(\Gamma_{\varphi}^{(1)}\) are proportional to the electron population \(P_{1\pm} = P_{1\pm} \propto \gamma_{1\pm} \) in the \(|\pm\rangle\) level, which vanishes when the leakage rate \(\gamma_{1\pm}\) from \(m = 0\) subspace to \(m = \pm 1\) subspace vanishes. Third, under weak pumping \(R \ll \gamma_{1V}, \gamma_{1V}\) we have \(\Gamma_{\psi}^{(1)}, \Gamma_{\varphi}^{(1)} \propto 1/R\) increasing with decreasing pumping strength, until the pumping is too weak for the Markovian assumption \(\gamma_{1V} \ll T_1, T_2\). Based on which our analytical formulas are derived, to remain valid. Upon further decrease of the pumping strength, the NV center becomes a non-Markovian bath and the nuclear spin dissipation rates would show a maximum and then decrease (see the next subsection for further discussion). Finally, under saturated optical pumping, \(\Gamma_{\psi}^{(1)}\) and \(\Gamma_{\varphi}^{(1)}\) are saturated instead of being suppressed:

\[ \Gamma_{\psi}^{(1)} \approx 2 \times \frac{\eta^2}{2T} \left( b_{xG} + b_{xG} \frac{2}{2} \right)^2, \quad (11a) \]

\[ \Gamma_{\varphi}^{(1)} \approx 2 \times \frac{\eta^2}{4T} \left( b_{xG} + b_{xG} \frac{2}{2} \right)^2, \quad (11b) \]

where \(T \equiv 2/\gamma_{1\pm} + 1/\gamma_{1\pm} \) is the average duration of one electron hopping cycle, \(\eta \equiv 2/\gamma_{1\pm}\) is the uncertainty of the dwell time at the \(|±\rangle\) level, and the prefactor 2 accounts for the contribution from the \(m = +1\) and \(m = -1\) subspaces.

Equations (11) can be understood as follows. First, under strong pumping, the hopping time between the ground orbital and the excited orbital is negligibly small, so the \(m = +1\) (or \(m = -1\)) subspace effectively becomes a single energy level with nuclear spin precession frequency \(\gamma_{1B} \mathbf{B} + (b_{xG} + b_{xG})/2\) (or
\( \gamma_0 B = \frac{(b_x + b_z)}{2} \). Second, the duration \( T \approx 1/\gamma_2 \) of one hopping cycle is ultimately limited by the slowest process: the non-radiative decay from \( m = 0 \) to \( m = \pm 1 \) subspace. Therefore, equations (11) correspond to an effective two-level fluctuator model (cf. equations (4)): one state is the \( m = +1 \) (or \( m = -1 \)) subspace with nuclear spin precession frequency \( \gamma_N B + (b_x + b_z)/2 \) (or \( \gamma_N B - (b_x + b_z)/2 \)) and the other is the subspace outside \( m = \pm 1 \), which produces a nuclear spin precession frequency \( \gamma_N B \). Although strong optical pumping suppresses the randomization of the nuclear spin precession due to spin-conserving electron hopping between the ground orbital and excited orbital inside the \( m = +1 \) (or \( m = -1 \)) subspace, there is an extra contribution due to the random electron hopping in and out of the \( m = +1 \) (or \( m = -1 \)) subspace.

The contributions from the \( m = 0 \) subspace involve \( a_x \) and \( a_z \), in quadratic form, so \( \Gamma^{(0)}_{\psi}, \Gamma^{(0)}_{\pm} \propto |B_1|^2 \) increases significantly with the magnetic field components perpendicular to the N–V axis. Due to the finite leakage from \( m = 0 \) into \( m = \pm 1 \) subspace, the analytical expressions for \( \Gamma^{(0)}_{\psi} \) and \( \Gamma^{(0)}_{\pm} \) are very tedious (see appendix B), so here we discuss the limits of weak pumping and strong pumping. Under weak pumping, \( \Gamma^{(0)}_{\pm} \approx 1/R \) decrease with increasing pumping strength (this behavior does not persist down to \( R \ll 1/T_1 \) or \( 1/T_2 \), where our Markovian assumption does not hold). Under strong optical pumping, they are saturated:

\[
\begin{align*}
\Gamma^{(0)}_{\psi} &= \frac{\gamma_0^2}{2T} \left( \frac{a_x + a_z}{2} \right)^2, \\
\Gamma^{(0)}_{\pm} &= \frac{\gamma_0^2}{4T} \left( \frac{a_x + a_z}{2} \right)^2,
\end{align*}
\]

where

\[
\gamma_0 = \sqrt{2} \gamma_2 T \sqrt{\frac{2}{\gamma_1} + \frac{1}{\gamma_1^2} + \frac{1}{2\gamma_1^2} - \gamma_{N} \frac{1}{\gamma_1}}
\]

is the uncertainty of the time for the electron dwelling in the \( m = 0 \) subspace. Similar to the contributions from the \( m = \pm 1 \) subspace, under strong optical pumping, the contributions from the \( m = 0 \) subspace correspond to an effective two-level fluctuator model: one is the \( m = 0 \) subspace with nuclear spin precession frequency \( \gamma_N B + (a_x + a_z)/2 \), the other is the subspace outside \( m = 0 \), which produces a nuclear spin precession frequency \( \gamma_N B \).

When the leakage from \( m = 0 \) subspace to \( m = \pm 1 \) subspace is neglected (i.e., \( \gamma_2 = 0 \)), the steady-state populations in the \( m = \pm 1 \) subspace vanish, corresponding to perfect optical initialization of the NV center into the state \( |0\rangle \). In this case, we have \( \Gamma^{(1)}_{\psi} = \Gamma^{(1)}_{\pm} = 0 \) and

\[
\begin{align*}
\Gamma^{(0)}_{\psi} &= \frac{P_0 P_{\psi}}{2R + \gamma_1} (a_{+,Z} - a_{-,Z})^2, \\
\Gamma^{(0)}_{\pm} &\approx \frac{1}{2R + \gamma_1} \frac{P_0 P_{\psi}}{P_0 + P_{\psi}} (a_{+,+} - a_{-,+})^2,
\end{align*}
\]

where \( P_0 = 1 - P_\psi = R/(2R + \gamma_1) \). This recovers the room-temperature two-level fluctuator model (equations (4)) and (5), which can be easily understood: since the population is trapped in the \( m = 0 \) subspace, the fluctuation of the nuclear spin precession frequency could only come from the difference between \( a_+ \) and \( a_- \).

Below we discuss two situations: (i) the magnetic field is along the N–V axis (\( z \) axis); (ii) the magnetic field is perpendicular to the N–V axis (\( z \) axis).

### 3.3. Magnetic field along N–V axis (\( z \) axis)

When the magnetic field is along the N–V symmetric axis (\( z \) axis), we have \( a_+ = a_- = 0 \), so the average precession frequency \( \omega = \gamma_0 B \) is along the –\( z \) axis, and the tilted axis (\( e_1, e_\psi, e_2 \)) can be chosen as \( (e_x, -e_y, e_z) \). Since \( a_+ = a_- = 0 \), only \( m = \pm 1 \) subspace contributes to nuclear spin dissipation: \( \Gamma_{\psi} = \Gamma^{(1)}_{\psi} \) and \( \Gamma_{\pm} = \Gamma^{(1)}_{\pm} \) (see equations (9) and (10)).

To begin with, we demonstrate the validity of our analytical formulas equations (9) and (10) by comparing them with the exact numerical results from directly solving the electron–nuclear coupled equations of motion (equation (1)). We estimate the typical nuclear spin dissipation time \( \sim T_1, T_2 \ll \tau_{NV} \) for \(^{13}C_0\). In this case, the NV center is a highly non-Markovian bath beyond the description of our analytical formulas. To see how our analytical formulas become progressively applicable when going from the non-Markovian regime to the Markovian regime, we manually scale down \( A_\psi \) and \( A_\pm \) by a factor \( \eta = 1, 10, \) and 100 to decrease the nuclear spin dissipation. Figures 2(a) and (b) show three features: (i) Both the exact results (dashed lines) and our analytical results (solid lines) tend to saturate at large \( R \), even for very strong HFI (\( \eta = 1 \)), where the NV center is highly non-Markovian. (ii) With increasing \( \eta \) and/or optical pumping rate \( R \), the nuclear spin dissipation rates \( 1/T_1 \) decrease and/or the electron dissipation rate \( 1/\tau_{NV} \) increases, thus our analytical results begin to agree.
with the exact numerical results. (iii) For successively small $R$, the analytical dissipation rates $1/T_{1,2}$ (solid lines) tend to diverge, while the numerical results (dashed lines) exhibit a maximum value $\sim 1/\gamma_{NV}$. This is because at sufficiently small $R$, the time scale of the NV dissipation $\gamma_{NV} \sim 1/R$ is longer than the nuclear spin dissipation and the NV center becomes a non-Markovian bath. In this case, the electron-induced nuclear spin dissipation rates $1/T_{1}$ and $1/T_{2}$ are upper limited by the electron dissipation rate $\sim 1/\gamma_{NV}$.

In figures 2(c) and (d), both the exact numerical results (dashed lines) and our analytical formulas (solid lines) show that the nuclear spin dissipation rates $1/T_{1,2}$ increase rapidly with increasing leakage rate $\gamma_{m}$ from the $m = 0$ to $m = 1$ subspaces, due to the rapid increase of the population $P_{m}$. (see equations (9) and (10)). When $\gamma_{m} = 0$, the population $P_{m} = 0$, so our analytical formulas give vanishing nuclear spin dissipation rates, while the exact numerical results give extremely small dissipation rates. This residual dissipation comes from the process involving the electron spin flip, which has been neglected in our theory since it is strongly suppressed by the large electron–nuclear energy mismatch away from the ground state and excited state anticrossing. Nevertheless, for extremely small $\gamma_{m} (=\gamma_{m}/1000)$, it is responsible for the small difference between the analytical results (blue solid line) and the exact numerical results (blue dashed line) at large optical pumping rate in figure 2(d).

In [17], Dreau et al. measured the dependence of the $^{13}$C nuclear spin $T_{1}$ time on the magnetic field along the N–V axis under illumination of a 532 nm laser at room temperature. In the following, we consider this situation and compare our theoretical results with available experimental data [17].

For the nuclear spin dephasing time $T_{2}$ in figure 3(a), away from the ground state and excited level anticrossing of the NV center (indicated by arrows in figure 3(a)), our analytical formulas agree well with the exact numerical results, whether or not the electron spin flip terms in $\mathbf{F}$ are included. This indicates that the contribution involving the electron spin flip is negligibly small compared with the contribution not involving the electron spin flip.

In deriving equation (10) for the nuclear spin relaxation rates, we have neglected the small nuclear spin level splitting $|\omega|$. When this term is included, the nuclear spin relaxation rates $\Gamma_{m}$ as given in equation (A.2) depend explicitly on $|\omega|$. For weak hyperfine interaction such that $|\omega| \gg |\gamma_{N} B|$, the nuclear spin relaxation rates show a Lorentzian dependence on the magnetic field $\Gamma_{m} \propto 1/([\mathbf{B}^2 + \delta_{B}^2])$ with a characteristic width

$$\delta_{B} = \frac{R^2}{\sqrt{(2R + \gamma_{1})^2 + 2(R + \gamma_{1})(\gamma_{1} + \gamma_{2})}}.$$
Under saturated pumping, as is usually used for optical readout, this width $\sim g_I/|\gamma_N| \sim 500$ mT. By contrast, the contribution involving the electron spin flip also has a Lorentzian dependence on the magnetic field, but with a much smaller characteristic width $\sim g_e/|\gamma_N| \sim 1$ mT. The magnetic field dependence of the relaxation time of the $^{13}$C nucleus has been measured by Dreau et al \cite{17}. They found that the anisotropic components $A_{g_{xx}} = A_{g_{yy}}$ and $A_{g_{zz}} = A_{g_{yy}}$ of the ground state HFI significantly contribute to the nuclear spin relaxation. The component $A_{g_{zz}}$ has been measured to be 0.25 MHz, while the other components are not clear. Here we assume $A_e = A_g$ with isotropic diagonal components $A_{g_{xx}} = A_{g_{yy}} = A_{g_{zz}} = 0.25$ MHz and a small anisotropic component $A_{g_{x,y}} = A_{g_{y,z}} = 1.5$ kHz and $A_{g_{x,z}} = A_{g_{y,z}} = 0$. Figure 3(b) shows that the exact numerical results obtained by directly solving equation (1) agree well with the experimentally measured $T_1$ time \cite{17}. As discussed previously, the exact results contain two contributions: the one not involving the electron spin flip (which is treated by our analytical formulas) and the one involving the electron spin flip (which is not treated by our analytical formulas). Figure 3(b) shows that our analytical formulas provide an accurate description of the former contribution, although in the present case the latter contribution dominates because of the much larger isotropic HFI $\sim 0.25$ MHz compared with the anisotropic HFI $\sim 1$ kHz. Finally, for the nuclear spin at lattice O as reported in the supplement of \cite{17}, it has a much shorter relaxation time $\sim 40$ ms at 200 mT. Such a short relaxation time is obviously dominated by the mechanism of equation (10), from which we estimate the anisotropic HFI component of this nuclear spin to be $\sim 20$ kHz.

3.4. Magnetic field perpendicular to N–V axis

Without losing generality, we consider the magnetic field $B = B_y e_y$ along the $y$ axis of the conventional coordinate. In this case, the precession frequencies $a_y = -(2g_B B_y D_0) e_y \cdot A_g$ and $a_x = -(2g_B B_z D_0) e_y \cdot A_g$ are proportional to the magnetic field. The nuclear spin precession frequency $\bar{\omega} \equiv g_N B + P_0 a_x + P_0 a_x$ deviates from the $z$ axis. In this case, both $\Gamma_{y,y}^{(0)}$, $\Gamma_{z,z}^{(0)}$ (see equations (9) and (10)) from the $m = \pm 1$ subspace and $\Gamma_{y,z}^{(0)}$, $\Gamma_{z,y}^{(0)}$ from the $m = 0$ subspace are nonzero. For $\Gamma_{y,y}^{(0)}$ and $\Gamma_{z,z}^{(0)}$, the quantities $b_{y,z}$, $b_{z,y}$, etc are defined in the tilted coordinate $e_x$, $e_y$, $e_z \equiv \bar{\omega}/|\bar{\omega}|$ that differs from the conventional coordinate ($e_x$, $e_y$, $e_z$).

First, we compare our analytical formulas for the nuclear spin $1/T_1$ and $1/T_2$ to the exact numerical results from directly solving the electron–nuclear coupled equations of motion (equation (1)). To see how our analytical formula becomes progressively applicable when going from the non-Markovian regime to the Markovian regime, we start from the strongly coupled nuclear spin $^{13}$C$_0$ and downscale its HFI tensors $A_g^{(3)}$ and $A_e^{(3)}$ (see equations (8)) by a factor $\eta = 1$, 10, and 100 to decrease the nuclear spin dissipation. The nuclear spins $1/T_2$ and $1/T_1$ shown in figure 4 show very similar behaviors to the case when the magnetic field is along the $N$–$V$ axis (cf figure (2)), including the saturation at high optical pumping rate $R$ and the improved agreement between the analytical results and the numerical results with increasing $\eta$ and/or $R$. In particular, figures 4(c) and (d) show that $1/T_2$ increases rapidly with the leakage rate $\gamma_{y,z}$ indicating that in addition to the contributions $\Gamma_{y,y}^{(0)}$ and $\Gamma_{z,z}^{(0)}$ from the $m = \pm 1$ subspace, the contributions $\Gamma_{y,z}^{(0)}$ and $\Gamma_{z,y}^{(0)}$ from the $m = 0$ subspace also increase with $\gamma_{y,z}$. For $\gamma_{y,z} = 0$, the nuclear spin dissipation becomes very slow. In this case, the contribution from the processes involving electron spin flip (not included in our analytical treatment) is no longer negligible. This leads to the discrepancy between the analytical results (black solid lines) and the numerical results (black dotted lines) in figure 4(d).
Finally we set the scale factor $\eta = 1$ and compare our theoretical results with available experimental data. In [2], Dutt et al measured the dependence of the decay rate of the nuclear spin precessing signal on the non-axial magnetic field under optical illumination of a 352 nm laser. In this case, the strong HFI makes the NV center a highly non-Markovian bath, so our analytical theory only provides a qualitative description for the nuclear spin dissipation. Since $A_{x/y}(^{3}C_{h})$ and $A_{x/y}(^{3}C_{e})$ (see equations (8)) are approximately isotropic, $a_{x}$ and $a_{y}$ are almost along the y axis while $b_{x}$ and $b_{y}$ are approximately along the e axis. For relatively large $B_{y}$, the magnetic field term $\gamma_{N}B_{y}e_{y}$ and the HFI contribution $a_{x} = B_{y}e_{y}$ dominate the average nuclear spin precession frequency $\bar{\omega}$, so the nuclear spin quantization axis $e_{y} \propto \bar{\omega}$ is almost along the y axis. Since $a_{x}$ and $a_{y}$ ($b_{x}$ and $b_{y}$) are nearly parallel (perpendicular) to $e_{y}$, the $m = 0$ ($m = \pm 1$) subspace mainly contributes to the nuclear spin pure dephasing (relaxation), so that $\Gamma_{y} \approx \Gamma_{y}^{(0)}$ increases quadratically with the magnetic field, while $\Gamma_{y} \approx \Gamma_{y}^{(1)}$ is nearly independent of the magnetic field. In other words, we expect the nuclear spin $1/T_{2}$ to increase appreciably with $B_{y}$ and the nuclear spin $1/T_{1}$ to be nearly independent of $B_{y}$, as confirmed in figure 5(a). According to the Bloch equation equation (7), since the experimentally used initial states are eigenstates of $\hat{I}_{z}$ and $\hat{I}_{x}$, their decay time is largely determined by $T_{2}$. Indeed, for $B_{y} \gg 1$ mT, figure 5(a) shows reasonable agreement between the numerically calculated $1/T_{2}$ and the experimentally measured decay time of different initial states. Note that the two-fold degenerate $1/T_{2}$ corresponds to identical decay of $\langle \hat{I}_{z} \rangle$ and $\langle \hat{I}_{y} \rangle$ (see figure 5(d)). By contrast, for $B_{y} \rightarrow 0$, the average nuclear spin precession frequency $\bar{\omega}$ is dominated by a small term $\langle \hat{S}_{x} \rangle_{b_{x}} + \langle \hat{S}_{z} \rangle_{b_{y}}$ along the z axis (neglected in our analytical treatment). In this case, the fluctuation of $b_{y}$ and $b_{x}$ of the $m = \pm 1$ subspace mainly contributes to nuclear spin pure dephasing, while the fluctuation of $a_{x}$ and $a_{y}$ of the $m = 0$ subspace mainly contributes to nuclear spin relaxation. Correspondingly, in figure 5(a), the nuclear spin relaxation $1/T_{1} \propto B_{y}^{2}$ vanishes at $B_{y} = 0$, while the nuclear spin $1/T_{2}$ is two-fold degenerate, corresponding to near identical decay of $\langle \hat{I}_{x} \rangle$ and $\langle \hat{I}_{y} \rangle$ (see figure 5(a)). Due to the switch of the nuclear spin quantization axis at intermediate magnetic field $B_{y} \sim 1$ mT, the association of the solid line with $1/T_{1}$ and the dashed lines with $1/T_{2}$ in figure 5(a) near the crossover region is meaningless.

4. Conclusion

We have presented a numerical and analytical study of the nuclear spin dephasing and relaxation induced by an optically illuminated NV center at room temperature. When the NV center undergoes a single cyclic transition,
our analytical results provide a physically transparent interpretation that substantiates the previous results \cite{16} and demonstrate the possibility to control the nuclear spin dissipation by tuning the magnetic field \cite{16}. For general optical illumination of an NV center incorporating finite non-radiative decay, our numerical results agree with the experimental measurements \cite{17}. Our analytical results suggests that the random hopping in and out of the $m_\ell = 0$ (or $m_\ell = \pm 1$) triplet states of the NV center could significantly contribute to nuclear spin dissipation. This means that increasing the spin polarization degree of the NV center would effectively suppress the optically induced dissipation process. This contribution referred to here is not suppressed under saturated optical pumping and provides a possible solution to the puzzling observation of nuclear spin dephasing in zero magnetic field \cite{2}.

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Appendix A. Lindblad master equation of nuclear spin

Here we derive a closed equation of motion for the nuclear spin from the coupled equation of motion equation (1), where $\mathcal{L}_c$ is the Liouville superoperator of the two-level or seven-level NV model. First, we calculate the steady state density matrix $\hat{\mathcal{P}}$ of the NV center from $\mathcal{L}_c \hat{\mathcal{P}} = 0$. For the two-level model, the steady state populations on $|e\rangle$ and $|g\rangle$ are $P_e = R/(2R + \gamma_\ell)$ and $P_g = 1 - P_e$, where $R = 2\pi (\Omega_0/2)^2\delta((\gamma + \gamma_\ell)/2)(\Delta)$ is the optical transition rate from $|g\rangle$ to $|e\rangle$ and $\delta^{\gamma_\ell}(x) = (\gamma_\ell/\pi)/(x^2 + \gamma_\ell^2)$ is the broadened $\delta$-function. For the seven-level model at room temperature, because the optical detuning is much larger than the spin energy splitting, the spin-conserving optical transition rates from the ground orbital $|g\rangle$ to the excited orbital $|e\rangle$ are all equal to $R$ for different spin states. The steady-state population on $|\ell\rangle$ is

Figure 5. (a) Nuclear spin $1/T_1$ (solid line) and $1/T_2$ (dashed lines) from numerically solving equation (1) compared with the experimentally measured decay for the initial state being an eigenstate of $\hat{I}_x$ (squares) and $\hat{I}_y$ (triangles). (b)-(d) show the dissipative evolution under (b) $B_y = 0.1$ mT, (c) $B_y = 2$ mT, and (d) $B_y = 10$ mT for the initial state being an eigenstate of $\hat{I}_z$ (solid line), $\hat{I}_y$ (dashed line), and $\hat{I}_x$ (dotted line). The parameters are $R = 6.4$ MHz and $\gamma_\ell = \gamma_0/30$. 
\[ P_{0_z} \approx \frac{R + \gamma_1 + 2\gamma_2}{2R + \gamma_1 + 2\gamma_2} \left( \frac{2R + \gamma_1 + 2\gamma_2}{\gamma_1} + \frac{R}{\gamma_1} \right) \]

The populations on other NV levels are

\[ P_{0_1} \approx \frac{R}{R + \gamma_1 + 2\gamma_2} P_{0_z}, \]

\[ P_{\pm 1} \approx \frac{R + \gamma_1 + \gamma_2}{R + \gamma_1 + 2\gamma_2} \approx \frac{\gamma_2}{\gamma_1} P_{0_z}, \]

and \[ P_3 \approx (2\gamma_1/\gamma_2)P_{\pm 1}. \] When the leakage from the \( m = 0 \) subspace to the \( m = \pm 1 \) subspaces are neglected by setting \( \gamma_2 = 0 \), we have \( P_{\pm 1} = P_{\pm 1} = P_3 = 0 \) and \( P_0 = 1 - P_0 = R/(2R + \gamma_1) \), which recovers the two-level fluctuator model.

Second, we decompose the HFI into the mean-field part \( \langle \mathbf{F}_r \rangle \cdot \mathbf{I} \) and the fluctuation part \( \langle \mathbf{F} - \langle \mathbf{F}_r \rangle \rangle \cdot \mathbf{I} \equiv \mathbf{F} - \langle \mathbf{F}_r \rangle \), where the nuclear spin density matrix is the nuclear spin precession frequency \( \gamma_1 \) and the nuclear spin dephasing rate due to the interaction \( \mathbf{F} \) is the average Knight field from the NV center, e.g., \( \langle \mathbf{F}_r \rangle = P_g \omega_g + P_e \omega_e \) for the two-level model and \( \langle \mathbf{F}_r \rangle = P_g a_x + P_0 a_z \) for the seven-level model. Under this decomposition, equation (1) becomes

\[ \dot{\rho} = \mathcal{L}_r \rho - \frac{i}{2} \left[ \mathcal{J} \cdot \mathbf{I}, \rho \right] - \frac{i}{2} \left[ \mathbf{F} \cdot \mathbf{I}, \rho \right], \tag{A.1} \]

where \( \mathcal{J} \equiv \gamma_0 \mathbf{B} + \langle \mathbf{F}_r \rangle \) is the total magnetic field that defines the nuclear spin quantization axis. Consequently, the nuclear spin dephasing and relaxation should be defined in the cartesian frame \( (e_x, e_y, e_z) \), where \( e_z \equiv \mathcal{J}/|\mathcal{J}|. \)

Third, we decompose \( \mathbf{F} - \langle \mathbf{F}_r \rangle \) into the sum of the longitudinal part \( \mathbf{F}_l \mathbf{L} \) and the transverse part \( \mathbf{F}_t \mathbf{T} \), where the nuclear spin density matrix is the nuclear spin precession frequency \( \omega \) and equation (2) for the nuclear spin density matrix \( \dot{\rho}(t) = \mathcal{L}_r \rho(t) \), where

\[ \Gamma_e = \text{Re} \left[ \int_0^{+\infty} \text{Tr} \mathbf{F}_z \left( e^{\omega \mathbf{L} t} \mathbf{P} \right) dt \right] \equiv \text{Re} \langle \mathbf{F}_z; \mathbf{P} \rangle_0 \]

is the nuclear spin pure dephasing rate due to the fluctuation of \( \mathbf{F}_z \) at zero frequency, and

\[ \Gamma_\pm = \frac{1}{2} \text{Re} \left[ \int_0^{+\infty} \text{Tr} \mathbf{F}_z \left( e^{(\omega + \gamma_1)\mathbf{L} t} \mathbf{P} \right) dt \right] \equiv \frac{1}{2} \text{Re} \langle \mathbf{F}_z; \mathbf{P} \rangle_\pm = |\omega|, \]

is the nuclear spin-flip rate due to the fluctuation of \( \mathbf{F}_z \) at the nuclear spin precession frequency \( |\omega| \), and

\[ \langle \mathbf{\tilde{a}}; \mathbf{\tilde{b}} \rangle_{\omega} \equiv \int_0^{+\infty} \text{Tr} \mathbf{\tilde{a}}(\omega + \nu)\mathbf{\tilde{b}}\mathbf{\tilde{P}}dt = -\text{Tr} \mathbf{\tilde{a}}(\mathbf{\mathcal{L}}_r - i\nu)^{-1} \mathbf{\tilde{b}}\mathbf{\tilde{P}} \]

is the steady-state correlation at frequency \( \omega \) between the fluctuation \( \mathbf{\tilde{a}} \equiv \mathbf{\tilde{a}} - \text{Tr} \mathbf{\tilde{a}} \mathbf{\tilde{P}} \) and the fluctuation \( \mathbf{\tilde{b}} \equiv \mathbf{\tilde{b}} - \text{Tr} \mathbf{\tilde{b}} \mathbf{\tilde{P}}. \)

For the seven-level NV model, we have

\[ \mathbf{\tilde{F}}_z = b_{g,z} \mathbf{\tilde{S}}_{g,z} + b_{e,z} \mathbf{\tilde{S}}_{e,z} + a_{g,z} \partial_{0,y} + a_{e,z} \partial_{0,y}, \]

\[ \mathbf{\tilde{F}}_\pm = b_{g,\pm} \mathbf{\tilde{S}}_{g,\pm} + b_{e,\pm} \mathbf{\tilde{S}}_{e,\pm} + a_{g,\pm} \partial_{0,y} + a_{e,\pm} \partial_{0,y}, \]

where \( \mathbf{\tilde{O}} \equiv \text{Tr} \mathbf{\tilde{P}} \) is the fluctuation part of electron operator \( \mathbf{\tilde{O}}, a_{g,e,\pm} \equiv a_{g,e} \pm i\partial_{0,y} \) and \( b_{g,e,\pm} \equiv b_{g,e} \pm i\partial_{0,y} \), etc. We can verify that the group \( \mathbf{\tilde{S}}_{g,\pm}, \mathbf{\tilde{S}}_{e,\pm} \) and the group \( \partial_{0,y}, \partial_{0,y} \) have vanishing cross-correlation, so \( \Gamma_\pm = \Gamma_\pm^{(1)} + \Gamma_\pm^{(0)} \) and \( \Gamma_e = \Gamma_e^{(1)} + \Gamma_e^{(0)} \) can be written as the sum of the contributions from the \( m = \pm 1 \) subspaces:

\[ \Gamma_\pm^{(1)} = \text{Re} \left( \left| b_{g,e} \right|^2 \langle \mathbf{\tilde{S}}_{g,\pm}; \mathbf{\tilde{S}}_{g,\pm} \rangle_0 + \left| b_{e,e} \right|^2 \langle \mathbf{\tilde{S}}_{e,\pm}; \mathbf{\tilde{S}}_{e,\pm} \rangle_0 \right) \]

\[ + b_{g,e} b_{e,e} \left( \langle \mathbf{\tilde{S}}_{g,\pm}; \mathbf{\tilde{S}}_{g,\pm} \rangle_0 + \langle \mathbf{\tilde{S}}_{e,\pm}; \mathbf{\tilde{S}}_{e,\pm} \rangle_0 \right) \]

\[ \Gamma_\pm^{(0)} \approx \frac{1}{2} \text{Re} \left( \left| b_{g,\pm} \right|^2 \langle \mathbf{\tilde{S}}_{g,\pm}; \mathbf{\tilde{S}}_{g,\pm} \rangle_\pm + \left| b_{e,\pm} \right|^2 \langle \mathbf{\tilde{S}}_{e,\pm}; \mathbf{\tilde{S}}_{e,\pm} \rangle_\pm \right) \]

\[ + \frac{1}{2} \text{Re} \left( b_{g,\pm} b_{e,\pm} \left( \langle \mathbf{\tilde{S}}_{g,\pm}; \mathbf{\tilde{S}}_{g,\pm} \rangle_\pm + \langle \mathbf{\tilde{S}}_{e,\pm}; \mathbf{\tilde{S}}_{e,\pm} \rangle_\pm \right) \right) \]
and the contributions from the \( m = 0 \) subspaces:

\[
\Gamma_{\phi}^{(0)} = \text{Re} \left( a_{rZ}^2 \left\langle \hat{\sigma}_{0,0}; \hat{\sigma}_{0,0} \right\rangle_0 + a_{rZ}^2 \left\langle \hat{\sigma}_{0,0}; \hat{\sigma}_{0,0} \right\rangle_0 \right) \\
+ \text{Re} \left( a_{rZ} a_{eZ} \left\langle \hat{\sigma}_{0,0}; \hat{\sigma}_{0,0} \right\rangle_0 + \left\langle \hat{\sigma}_{0,0}; \hat{\sigma}_{0,0} \right\rangle_0 \right),
\]

\[
\Gamma_{\phi}^{(0)} \approx \frac{1}{2} \frac{1}{\text{Re} \left( a_{rZ} \right)} \left[ \left| a_{eZ} \right|^2 \left\langle \hat{\sigma}_{0,0}; \hat{\sigma}_{0,0} \right\rangle_0 + \left| a_{eZ} \right|^2 \left\langle \hat{\sigma}_{0,0}; \hat{\sigma}_{0,0} \right\rangle_0 \right] \\
+ \frac{1}{2} \text{Re} \left( a_{rZ} a_{eZ} \left\langle \hat{\sigma}_{0,0}; \hat{\sigma}_{0,0} \right\rangle_0 + \left\langle \hat{\sigma}_{0,0}; \hat{\sigma}_{0,0} \right\rangle_0 \right),
\]

Using the analytical expressions for the above correlation functions in Appendix B, we obtain \( \Gamma_{\phi}^{(1)} \) as equation (9) and

\[
\Gamma_{\phi}^{(1)} = \frac{P_{1F}}{\gamma_{11}} \left( \left| \omega \right| \right) \left( 1 + \frac{R + \gamma_1 + \gamma_1}{R} \right) \\
+ \frac{P_{1F}}{\gamma_{11}} \left( \left| \omega \right| \right) \frac{R + \gamma_1 + \gamma_1}{R} \left( 1 - \frac{\left| \omega \right|^2}{R} \right),
\]

where

\[
f (\omega) = \frac{R^2 \gamma_{11}^2}{R^2 \gamma_{11}^2 + \left( 2R + \gamma_1 \right)^2 + 2 \left( R + \gamma_1 \right) \gamma_{11} + \gamma_{11}^2} \omega^2 + \omega^4.
\]

**Appendix B. Steady-state correlation functions**

Here we use the equation of motion method to evaluate the eight correlation functions. For example, the correlation function \( \left\langle \hat{\sigma}_{0,0}; \hat{\sigma}_{0,0} \right\rangle_0 \) can be written as \(- \text{Tr} \hat{\sigma}_{0,0} \hat{X} = -X_{0,0}\), where \( \hat{X} \equiv \mathcal{L}_r \hat{\sigma}_{0,0} \hat{P} \) obeys \( \text{Tr} \hat{X} = 0 \) and \( X_{ij} \equiv \left\langle i | \hat{X} | j \right\rangle \). The large orbital dephasing rate \( \gamma_j \sim 10^7 \text{ MHz} \) allows us to neglect the off-diagonal coherence of the electron and only keep the diagonal populations \( R \equiv \left\langle \hat{P} \right\rangle \). The equations of motion of \( X_{ij} \) are obtained by taking the \( (i, j) \) matrix element of \( \mathcal{L}_r \hat{X} = \hat{\sigma}_{0,0} \hat{P} \). We find that the equations of motion of the diagonal (off-diagonal) elements of \( \hat{X} \) involve the off-diagonal (diagonal) elements. By eliminating the off-diagonal elements in favor of the diagonal elements, we obtain

\[
\begin{align*}
\gamma_1 X_{0,0} + (\gamma_1 + R) X_{0,0} &= R X_{0,0} = P_0 \left( 1 - P_0 \right), \\
\gamma_0 X_{S,S} + (\gamma_0 + R) X_{0,0} &= R X_{0,0} = P_0 \left( 1 - P_0 \right), \\
\gamma_0 X_{S,S} + \gamma_1 X_{-1,-1} + X_{1,1} &= P_1 \left( 1 - P_1 \right), \\
\gamma_1 X_{-1,-1} + R X_{-1,-1} &= R X_{-1,-1} = P_{-1} \left( 1 - P_{-1} \right), \\
\gamma_1 X_{1,1} + R X_{1,1} &= R X_{1,1} = P_{-1} \left( 1 - P_{-1} \right), \\
\gamma_1 X_{-1,1} + R X_{-1,1} &= P_{-1} \left( 1 - P_{-1} \right), \\
\gamma_1 X_{1,-1} + R X_{1,-1} &= P_{-1} \left( 1 - P_{-1} \right), \\
\gamma_1 X_{0,0} + R X_{0,0} &= R X_{0,0} = P_0 \left( 1 - P_0 \right),
\end{align*}
\]

where \( \Delta_{ij} \) is the energy difference between the electron state \( |i\rangle \) and \( |j\rangle \) in the rotating frame of the pumping laser. Solving the above equations gives the correlation function \( \left\langle \hat{\sigma}_{0,0}; \hat{\sigma}_{0,0} \right\rangle_0 = -X_{0,0} \), as
\begin{align*}
\langle \delta_{\phi_0,0} \delta_{\phi_0,0} \rangle_0 &= \frac{P_0 P_0}{1 + \eta} \left( \frac{1}{1 + \eta} \left( 1 - \frac{2 \gamma_2/R}{2R + \gamma_1} \right) + \frac{\eta}{R} \right) \\
&\quad + \frac{P_0}{1 + \eta} \left( \frac{1 - P_0 - P_0}{2R + \gamma_1} \right) \left( \frac{1}{R} + \frac{\gamma_1}{2R + \gamma_1} \right) \left( \frac{R + \gamma_1}{\gamma_1} \right) + \frac{1}{2R + \gamma_1} \\
&\quad + \frac{P_0}{1 + \eta} \left( \frac{1 - P_0 - P_0}{2R + \gamma_1} \right) \left( \frac{1}{R} + \frac{\gamma_1}{2R + \gamma_1} \right) \left( \frac{R + \gamma_1 + 2 \gamma_2}{\gamma_1} \right) + \frac{1}{2R + \gamma_1} \\
&\quad + \frac{P_0}{1 + \eta} \left( \frac{1 - P_0 - P_0}{2R + \gamma_1} \right) \left( \frac{1}{R} + \frac{\gamma_1}{2R + \gamma_1} \right) \left( \frac{R + \gamma_1 + 2 \gamma_2}{\gamma_1} \right) + \frac{1}{2R + \gamma_1}.
\end{align*}

where $\eta = 2 \gamma_2/(\gamma_1 + 2R + 2 \gamma_2)/(\gamma_2(2R + \gamma_1))$ is a dimensionless constant much smaller than unity since $\gamma_2 \ll \gamma_\phi$. Using the same method, the other correlation functions are obtained as:

\begin{align*}
\langle \delta_{\phi_0,0}(t) \delta_{\phi_0,0}(0) \rangle_0 &= \frac{P_0 P_0}{1 + \eta} \left( \frac{1}{1 + \eta} \left( 1 - \frac{2 \gamma_2/R}{2R + \gamma_1} \right) + \frac{\eta}{R} \right) \\
&\quad + \frac{P_0}{1 + \eta} \left( \frac{1 - P_0 - P_0}{2R + \gamma_1} \right) \left( \frac{1}{R} + \frac{\gamma_1}{2R + \gamma_1} \right) \left( \frac{R + \gamma_1 + 2 \gamma_2}{\gamma_1} \right) + \frac{1}{2R + \gamma_1} \\
&\quad + \frac{P_0}{1 + \eta} \left( \frac{1 - P_0 - P_0}{2R + \gamma_1} \right) \left( \frac{1}{R} + \frac{\gamma_1}{2R + \gamma_1} \right) \left( \frac{R + \gamma_1 + 2 \gamma_2}{\gamma_1} \right) + \frac{1}{2R + \gamma_1}.
\end{align*}

Similarly, the correlation functions at finite frequency are obtained as:

\begin{align*}
\langle \hat{S}_{x,z}: \hat{S}_{x,z} \rangle_0 &= \frac{2(R + i \omega)}{R \gamma_1 + i \omega(\gamma_1 + \gamma_1 + 2R)} P_{-1,1} \\
\langle \hat{S}_{y,z}: \hat{S}_{y,z} \rangle_0 &= \frac{2(R + \gamma_1 + i \omega)}{R \gamma_1 + i \omega(2R + \gamma_1)} P_{-1,1} \\
\langle \hat{S}_{x,z}: \hat{S}_{y,z} \rangle_0 &= \frac{2R}{R \gamma_1 + i \omega(2R + \gamma_1)} P_{-1,1} \\
\langle \hat{S}_{x,z}: \hat{S}_{x,z} \rangle_0 &= \frac{2(R + i \omega)}{R \gamma_1 + i \omega(2R + \gamma_1)} P_{-1,1}.
\end{align*}

When the leakage from the $m = 0$ subspace to the $m = \pm 1$ subspace is neglected by setting $\gamma_2 = 0$ (and hence $\eta = 0$), only the populations $P_0$ and $P_0$ are nonzero, so only the first term in the above expressions survives:

\begin{align*}
\langle \delta_{\phi_0,0} \delta_{\phi_0,0} \rangle_0 &= \langle \delta_{\phi_0,0}(t) \delta_{\phi_0,0}(0) \rangle_0 = -\langle \delta_{\phi_0,0}(t) \delta_{\phi_0,0}(0) \rangle_0 \\
&= -\left\langle \delta_{\phi_0,0}(t) \delta_{\phi_0,0}(0) \right\rangle_0 = \frac{P_0 P_0}{2R + \gamma_1},
\end{align*}

which give equation (13) of the main text. For saturated pumping, we have

\begin{align*}
\langle \delta_{\phi_0,0} \delta_{\phi_0,0} \rangle_0 &= \langle \delta_{\phi_0,0} \delta_{\phi_0,0} \rangle_0 \\
&= \langle \delta_{\phi_0,0} \delta_{\phi_0,0} \rangle_0 = \frac{\gamma_0^2}{8T}
\end{align*}

and hence equation (12) of the main text.
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