Dynamic Frequency Shift in NV^- Center in Diamond

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April 16, 2024

Abstract

Sensor applications of negatively charged nitrogen vacancy (NV^- center in diamond are now in practical use, yet for finer sensitivity, a comprehensive understanding of various kinds of sources that cause detrimental relaxation and damping is still required. During the course of theoretical study regarding this, we found that Gaussian white noise with the zero-mean has a substantial effect, which manifests itself in a period of free induction decay (FID) oscillation. This effect is experimentally detectable through comparison with zero-field splitting fixed by, e.g., optically detected magnetic resonance (ODMR). The result is corroborated by a different analytical framework, Lindblad master equation. Our finding in FID oscillation period, or an equivalent energy shift, is concluded to fall into a class of dynamic frequency shift.

1 Introduction

Since usefulness of color centers in diamond was recognized, extensive studies regarding these have been continued. Among others, a nitrogen vacancy center with an excess electron, NV^-, is the most promising one. It is now used as sensors and other applications, to name a few, for local magnetic fields [1, 2, 3, 4], electron [5] and viscous [6] flows in graphene, temperature [7, 8, 9], and even vortexes in cuprate high-temperature superconductors [10]. One of the reasons behind this ability lies in its long relaxation times even at room temperature. Aiming at finer sensitivity, further effort mainly in terms of material science has been made to obtain clean and high-purity samples, which are expected to be ideal for longer relaxation times. However, as shown in the counter-intuitive example that ultra long relaxation time was reported in a system with phosphorus intentionally-doped [11], underlying physics regarding relaxation phenomena is not crystal clear, and a comprehensive understanding of various sources that cause relaxation and damping is highly required. As such, NV^{-1} is still an ideal and unique test bed to study, in particular, non-equilibrium open quantum physics, and

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along this line, the inhomogeneous relaxation time, T_2^*, of NV^- has been studied as a typical example of relaxation times. While primary interests lie in what sources as noise dominate relaxation phenomena and how, in the course of the study, we theoretically find that anisotropic noise with the zero-mean can bring about an energy shift in non-trivial manner, which is the main result of this work.

The relaxation time T_2^* characterizes free induction decay (FID) and Ramsay fringe. In spite of many advanced theoretical and computational methods to discuss the relaxation time [12, 13], its core can be captured by simply considering an effective model of a two-level system, or a spin $1/2$, in a fictitious magnetic field along z-direction whose *amplitude* fluctuates, and in this case, pure dephasing part of T_2^* is focused. The modeling is verified by the following consideration [14].

An NV^- center, where direction toward N- from V-sites is taken as z axis, locally has $\mathrm{C}_{3\mathrm{v}}$ point group symmetry. An electronic ground state of NV^- is known to be $S = 1$ triplet states, whose behavior is described by an $S = 1$ spin Hamiltonian respecting the symmetry. The most general Hamiltonian for the triplet state up to the second order of spin operators can be read as [14] (Zeeman term against an externally applied magnetic field is omitted in order to avoid unnecessary confusion in the later discussion)

$$H = (d_0 + \xi)S_z^2 + -\Pi_x(S_xS_y + S_yS_x) - \Pi_y(S_x^2 - S_y^2), \tag{1}$$

where $\vec{S} = (S_x, S_y, S_z)$ are $S = 1$ operators, and S_z is diagonal with its eigenvalues $m = \{+1, 0, -1\}$. In the Hamiltonian, $d_0 \approx 2.87$GHz is zero-field splitting, and the other terms with *constants*, ξ and $\Pi_{x,y}$, represent contribution from local lattice deformation and electric field induced by intrinsic charge density fluctuation. Diagonalize the Hamiltonian and pick up the lower two energy states, then it is equivalent to a two-level system in a fictitious *static* magnetic field.

As a Hamiltonian describes unitary time evolution of a given system, some "noise" is necessary to describe pure dephasing. For the purpose, the constants in the Hamiltonian, ξ and $\Pi_{x,y}$, are allowed to fluctuate around their certain mean values, by regarding the parameters in Eq, (1) as stochastic variables [14]. Since NV^- centers in most cases lie at room temperature, thermal lattice fluctuation and accompanied charge fluctuation are naturally considered as its origin. However introduction of such a fluctuation in the Hamiltonian turns itself into time dependent one. In this course, the eigenvalue problem delivered by the static Hamiltonian might lose its firm ground. The idea of the authors of Ref. [14] is that, by considering a snapshot of the time dependent Hamiltonian, the stochastic effect is incorporated as fluctuation of energy difference between the two states in the effective two-level system. The system obtained is thus equivalent to a spin 1/2 in fictitious *fluctuating* magnetic field, $B_z(t)$. The analysis of T_2^* on the basis of this model unveiled qualitatively different behavior of T_2^* against an externally applied magnetic field, depending on which parameter's fluctuation in the Hamiltonian dominates, and showed agreement with experiments [14].

The essentials of Ref. [14] are to assume that the influence of stochastic variables in the Hamiltonian can be read as fluctuation of the energy levels derived by diagonalizing the snapshot Hamiltonian. Here, being fueled by its success and reviewing the work, we notice that a margin still remains in this procedure: not only diagonal components in the effective two-level system, or energy levels, but also off-diagonal components in diagonalized snapshot Hamiltonian can also be considered as stochastic variables, which have the zero-means. This corresponds to encompassing vacuum fluctuation of fictitious in-plane magnetic fields in the effective two-level system. To examine consequences of this extension, below we consider a spin 1/2 system in a fictitious magnetic field whose direction fluctuates as well as amplitude, and show that the in-plane vacuum fluctuation brings about an energy shift, or an equivalent frequency shift as an experimentally detectable effect. This frequency shift falls into a class of dynamic frequency shift defined below.

2 Theory

2.1 stochastic model

Consider dynamics of a spin 1/2 exposed to a fictitious fluctuating magnetic field, $\vec{B}(t) = \{B_\mu(t)\}$ ($\mu = x, y, z$), which is assumed to involve Gaussian white noise with the mean values $(\overline{B_x(t)}, \overline{B_y(t)}, \overline{B_z(t)}) = (0, 0, d_0)$ and fluctuation amplitude γ_μ. A connection of γ_z to the parameters in the original Hamiltonian, Eq. (1), can be postulated as in Ref.[14], while ones of γ_x and γ_y can not, even though their origins could be traced back to the parameters in the original Hamiltonian. This is because these two parameters describe fluctuation around the zero off-diagonal components of the matrix already diagonalized, where dependence of $\gamma_{x,y}$ on the parameters in the Hamiltonian is unseen. Therefore γ_x and γ_y are phenomenologically treated, and the values of γ_μ's are reasonably assumed to be different from each other, partly because of an intrinsic symmetric property. Here we would like to emphasize, in advance, that it is unequality of γ_x and γ_y which plays an essential role in this work.

A two-component state vector, $|\psi(t)\rangle$, obeys ($\hbar = 1$)

$$i\frac{\partial}{\partial t}|\psi(t)\rangle = \frac{1}{2}\vec{B}(t) \cdot \vec{\sigma}|\psi(t)\rangle, \tag{2}$$

with usual Pauli matrix, $\vec{\sigma}$. Introducing Bloch vector, defined by $\vec{r} = (x, y, z) \equiv \langle\psi(t)|\vec{\sigma}/2|\psi(t)\rangle$, the dynamics is equivalently described by Bloch equation

$$\frac{d}{dt}\vec{r} = \vec{B}(t) \times \vec{r} = \begin{pmatrix} 0 & -B_z(t) & B_y(t) \\ B_z(t) & 0 & -B_x(t) \\ -B_y(t) & B_x(t) & 0 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}, \tag{3}$$

where the matrix in Eq. (3) is simply denoted by $M(t)$.

Time profiles of FID of a two-level system are described by $x(t)$ and $y(t)$ in this usage. With a time-ordering operator $\mathcal{T}$, the formal solution of this equation can be written as

$$\vec{r}(t) = \mathcal{T} \exp\left[\int_0^t M(t')dt'\right]\vec{r}_0, \tag{4}$$

for a certain initial state $\vec{r}_0 \equiv (x_0, y_0, z_0)$ at $t = 0$. To deal with the time-ordering operator, we follow the method given in Ref. [15]. Divide the full-time evolution from

$t' = 0$ to $t' = t$ into a series of time slices with width Δ, which is finally taken by the limit of $\Delta \to 0$. Since the noises are assumed to be white, those belonging to different time slices are uncorrelated, and the matrix is regarded as "constant" during the thin time slice Δ. Taking ensemble average, denoted by overbar, the solution can then be written as

$$\vec{r}(t) = \left[\overline{\exp(M\Delta)}\right]^{t/\Delta} \vec{r}_0. \tag{5}$$

A series expansion with respect to Δ gives $\overline{\exp[M\Delta]} = M_{xyz} + O(\Delta^3)$, where

$$M_{xyz} = \begin{pmatrix} 1 - \left(\frac{\gamma_y}{2} + \frac{\gamma_z}{2}\right)\Delta & -d_0\Delta & 0 \\ d_0\Delta & 1 - \left(\frac{\gamma_z}{2} + \frac{\gamma_x}{2}\right)\Delta & 0 \\ 0 & 0 & 1 - \left(\frac{\gamma_x}{2} + \frac{\gamma_y}{2}\right)\Delta \end{pmatrix}. \tag{6}$$

In the derivation, the mean values, $\overline{B_x(t)} = \overline{B_y(t)} = 0$ and $\overline{B_z(t)} = d_0$, and the second order correlations

$$\overline{B_\mu(t)B_{\nu\neq\mu}(t)} = 0, \quad \overline{B_\mu^2(t)} = \frac{\gamma_\mu}{\Delta}, \tag{7}$$

are substituted. The last condition is consistent with white noise in time slice with width Δ. Taking the limit $\Delta \to 0$, the solution turns to

$$\vec{r}(t) = \left[M_{xyz}\right]^{t/\Delta} \vec{r}_0 \xrightarrow{\Delta\to 0} \exp\left[-N_{xyz}t\right] \vec{r}_0, \tag{8}$$

where

$$N_{xyz} = \begin{pmatrix} \frac{1}{2}\left(\gamma_y + \gamma_z\right) & d_0 & 0 \\ -d_0 & \frac{1}{2}\left(\gamma_x + \gamma_z\right) & 0 \\ 0 & 0 & \frac{1}{2}\left(\gamma_x + \gamma_y\right) \end{pmatrix}. \tag{9}$$

The final form of $z(t)$ is immediately obtained as

$$z(t) = \exp\left(-\frac{\gamma_x + \gamma_y}{2} t\right) z_0, \tag{10}$$

where $z_0 = 0$ is usually prepared after $\pi/2$ pulse injection. As for $x(t)$ and $y(t)$, let Ω be a real constant as

$$\Omega = \sqrt{16d_0^2 - (\gamma_x - \gamma_y)^2}, \tag{11}$$

whose reality comes from a reasonable assumption that, for NV^- center, $d_0 > \gamma_{x,y,z}$. Then the final solutions are represented as

$$\begin{pmatrix} x(t) \\ y(t) \end{pmatrix} = \exp\left[-N_{xy}t\right] \begin{pmatrix} x_0 \\ y_0 \end{pmatrix}, \tag{12}$$

where the matrix exponential is

$$\exp\left[-N_{xy}t\right] = \exp\left(-\frac{\gamma_{\text{all}}}{4}t\right)\left[N_{xy}^{(1)}\cos\left(\frac{\Omega}{4}t\right) + N_{xy}^{(2)}\sin\left(\frac{\Omega}{4}t\right)\right], \tag{13}$$

with

$$N_{xy}^{(1)} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \tag{14}$$

$$N_{xy}^{(2)} = \frac{1}{\Omega}\begin{pmatrix} \gamma_x - \gamma_y & -4d_0 \\ 4d_0 & -\gamma_x + \gamma_y \end{pmatrix}, \tag{15}$$

$$\gamma_{\text{all}} = \gamma_x + \gamma_y + 2\gamma_z. \tag{16}$$

Note that both matrices, $N_{xy}^{(1,2)}$, are regular as their determinants are identically unity. From these equations, FID signal shows sinusoidal oscillation with exponential decay, whose relaxation time characterized by γ_{all} corresponds to T_2^*. The in-plane vacuum fluctuation $\gamma_{x,y}$, as expected, additively contributes to the relaxation constant, whose amount is half of that of longitudinal fluctuation γ_z.

In the above equations, our main result is included: a period of the oscillation, τ, is found to be also influenced by the in-plane vacuum fluctuation, in the form $|\gamma_x - \gamma_y|$, as

$$\tau = \frac{2\pi}{\Omega/4} = 4\frac{2\pi}{\sqrt{16d_0^2 - (\gamma_x - \gamma_y)^2}}. \tag{17}$$

Since the off-diagonal components in Eq. (2) are stochastic variables with the zero-means, substantial effects in energy are, at first sight, not expected. However, Eq. (17) indicates that the in-plane fluctuation causes an energy, or frequency shift. The point of interest is that a condition of non-zero γ_x and γ_y is not sufficient, and unequality of the two is required to obtain the finite contribution.

We claim that the effect caused by the anisotropic in-plane vacuum fluctuation is experimentally detectable. When an oscillation period of FID shows a deviation from the one obtained by zero-field splitting, the origin of it can be ascribed to the vacuum fluctuation effect discussed here. In previous studies, the oscillation period in FID is considered to be solely determined by zero- field splitting d_0, whose value is ~ 2.87 GHz, measured by e.g. ODMR at zero external magnetic field. Since ODMR is free from the frequency shift induced by the in-plane vacuum fluctuation, careful FID measurements can unveil the effects as a difference of the period from the conventional value $2\pi/d_0$.

The system addressed above is omnipresent [16, 17], and indeed often referred to as Abragam model in literature [18]. However most of the previous studies conventionally assumed $\gamma_x = \gamma_y$. Once this equality is imposed, the effect due to the in-plane vacuum fluctuation in frequency shift disappears, as in Eq. (17). In this respect, our finding is thought to stem from a property given by the condition of $\gamma_x \neq \gamma_y$, detail of which is described in latter section.

One might think that the substantial effect from the in-plane vacuum fluctuation as in the form of frequency shift is an artifact of naive mathematical handling of equations.

Therefore in order to corroborate the results, we demonstrate below that the identical solutions are obtained within the framework of master equation with Lindblad form, which is one of the most-established methods for open quantum physics [12, 13].

2.2 Equivalent Lindblad equation

Consider a phenomenological Lindblad master equation for a density operator ρ of a general two-level system

$$\frac{d\rho}{dt} = -i[H,\rho] + \sum_{\mu=x,y,z}\left(L_\mu \rho L_\mu^\dagger - \frac{1}{2}L_\mu^\dagger L_\mu \rho - \frac{1}{2}\rho L_\mu^\dagger L_\mu\right), \tag{18}$$

where Hamiltonian, describing unitary time evolution, is $H = (d_0/2)\sigma_z$, while Lindblad operators, characterizing relaxation processes, are given by $\{L_\mu\} = (\sqrt{\gamma_\mu}/2)\sigma_\mu$ with phenomenological relaxation constants γ_μ. The equivalence of the treatment in the last subsection and that with Eq.(18) is demonstrated by agreement of their explicit solutions.

From the Lindblad equation Eq.(18), analytical solutions of $S_{\mu=x,y,z}(t) \equiv \mathrm{Tr}[\rho(t)\sigma_\mu]$ for an initial condition $(S_x(t=0), S_y(t=0), S_z(t=0)) = (\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta) \equiv (x_0, y_0, z_0)$ on the Bloch sphere are straightforwardly obtained as

$$\begin{aligned} S_x(t) &= \sin\theta \exp\left[-\frac{\gamma_x+\gamma_y+2\gamma_z}{4}t\right] \\ &\quad\times\left[\cos\phi\cosh\left(\frac{\sqrt{\left(\gamma_x-\gamma_y\right)^2-16d_0^2}}{4}t\right)\right. \\ &\quad\left.+\frac{(\gamma_x-\gamma_y)\cos\phi-4d_0\sin\phi}{\sqrt{\left(\gamma_x-\gamma_y\right)^2-16d_0^2}}\sinh\left(\frac{\sqrt{\left(\gamma_x-\gamma_y\right)^2-16d_0^2}}{4}t\right)\right], \end{aligned} \tag{19}$$

$$\begin{aligned} S_y(t) &= \sin\theta \exp\left[-\frac{\gamma_x+\gamma_y+2\gamma_z}{4}t\right] \\ &\quad\times\left[\sin\phi\cosh\left(\frac{\sqrt{\left(\gamma_x-\gamma_y\right)^2-16d_0^2}}{4}t\right)\right. \\ &\quad\left.-\frac{(\gamma_x-\gamma_y)\sin\phi-4d_0\cos\phi}{\sqrt{\left(\gamma_x-\gamma_y\right)^2-16d_0^2}}\sinh\left(\frac{\sqrt{\left(\gamma_x-\gamma_y\right)^2-16d_0^2}}{4}t\right)\right], \end{aligned} \tag{20}$$

$$S_z(t) = \cos\theta\exp\left[-\frac{\gamma_x+\gamma_y}{2}t\right]. \tag{21}$$

In particular, when $|\gamma_x - \gamma_y| < 4d_0$, using a real constant as before, $\Omega = \sqrt{16d_0^2 - (\gamma_x-\gamma_y)^2}$, above results are summarized as

$$\begin{pmatrix} S_x(t) \\ S_y(t) \end{pmatrix} = \exp\left[-\frac{\gamma_{\rm all}}{4}t\right]$$
$$\times \begin{pmatrix} \cos\left(\frac{\Omega t}{4}\right) + \frac{\gamma_x-\gamma_y}{\Omega}\sin\left(\frac{\Omega t}{4}\right) & -\frac{4d_0}{\Omega}\sin\left(\frac{\Omega t}{4}\right) \\ \frac{4d_0}{\Omega}\sin\left(\frac{\Omega t}{4}\right) & \cos\left(\frac{\Omega t}{4}\right) - \frac{\gamma_x-\gamma_y}{\Omega}\sin\left(\frac{\Omega t}{4}\right) \end{pmatrix} \begin{pmatrix} x_0 \\ y_0 \end{pmatrix}, \tag{22}$$

and

$$S_z(t) = \exp\left[-\frac{\gamma_x+\gamma_y}{2}t\right] z_0. \tag{23}$$

These are identical with Eqs.(12) and (10), respectively. By this agreement, we can say that the frequency shift caused by the anisotropic in-plane vacuum fluctuation γ_x and γ_y is now on firm ground.

3 Discussion

3.1 role of anisotropy in in-plane vacuum fluctuation

The peculiarity of $\gamma_x \neq \gamma_y$ can be ascribed to an algebraic property of the Hamiltonian and the Lindblad operators in Eq.(18). For the two operators, the following commutation relation

$$\left[[H,\rho], \sum_{\mu=x,y,z} \gamma_\mu \left(L_\mu \rho L_\mu^\dagger - \frac{1}{2} L_\mu^\dagger L_\mu \rho - \frac{1}{2} \rho L_\mu^\dagger L_\mu \right) \right] \propto d_0(\gamma_x - \gamma_y), \tag{24}$$

holds [19], meaning that any non-zero component of the matrix commutator is proportional to $d_0(\gamma_x - \gamma_y)$. This commutation relation indicates that only when $\gamma_x = \gamma_y$, the evolution induced by the Lindblad operators is invariant under a rotation around the z axis, latter of which is induced by the Hamiltonian. We can expect that this non-commutativity is the origin of the frequency shift appeared in FID oscillation period, and if it is the case, the shift should be referred to as dynamic frequency shift, by the definition of the shift [20, 21]. This expectation is indeed supported by the following analysis.

The abstract algebraic property in Eq. (24) turns more explicit once the master equation is given in a matrix form. From Eq. (18), a set of differential equations for each component of the density matrix, $\rho_{ij} \equiv \langle \phi_i | \rho | \phi_j \rangle$ ($\{i, j\} = \{1, 2\}$), is written as

$$\frac{d}{dt} \begin{pmatrix} \rho_{11}(t) \\ \rho_{12}(t) \\ \rho_{21}(t) \\ \rho_{22}(t) \end{pmatrix} = \left(M_{xyz}^H + M_{xyz}^L \right) \begin{pmatrix} \rho_{11}(t) \\ \rho_{12}(t) \\ \rho_{21}(t) \\ \rho_{22}(t) \end{pmatrix}, \tag{25}$$

where

$$M^H_{xyz} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & -id_0 & 0 & 0 \\ 0 & 0 & +id_0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}, \tag{26}$$

$$M^L_{xyz} = \begin{pmatrix} -\frac{\gamma_x+\gamma_y}{4} & 0 & 0 & \frac{\gamma_x+\gamma_y}{4} \\ 0 & -\frac{\gamma_x+\gamma_y+2\gamma_z}{4} & \frac{\gamma_x-\gamma_y}{4} & 0 \\ 0 & \frac{\gamma_x-\gamma_y}{4} & -\frac{\gamma_x+\gamma_y+2\gamma_z}{4} & 0 \\ \frac{\gamma_x+\gamma_y}{4} & 0 & 0 & -\frac{\gamma_x+\gamma_y}{4} \end{pmatrix}. \tag{27}$$

In these equations, M^H_{xyz} characterizes unitary evolution, while M^L_{xyz} relaxation. These matrices do not commute when $d_0(\gamma_x - \gamma_y) \neq 0$, as

$$\left[M^H_{xyz}, M^L_{xyz}\right] = d_0(\gamma_x - \gamma_y) \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & -i/2, & 0 \\ 0 & i/2, & 0, & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}. \tag{28}$$

This is a representation of Eq.(24) in case of the present Hamiltonian and Lindblad operators.

The origin of this non-commutativity comes from the $(2,3)$ and $(3,2)$ components of M^L_{xyz}, both of which are proportional to $\gamma_x - \gamma_y$. This statement turns more obvious by comparing with a different master equation. Take the most typical textbook example [22], a Lindblad master equation with $H = (d_0/2)\sigma_z$ and the Lindblad operator $\{L_{\mu=\pm,z}\} = (\sqrt{\gamma_+}/2)\sigma_+, (\sqrt{\gamma_-}/2)\sigma_-, (\sqrt{\gamma_z}/2)\sigma_z\}$, where $\sigma_\pm \equiv (1/2)(\sigma_x \pm \sigma_y)$. This equation describes photon emission and absorption with phase relaxation. In the same manner as Eq. (25), two matrices in a set of differential equations in the present case, $M^H_{\pm z} + M^L_{\pm z}$, are $M^H_{\pm z} = M^H_{xyz}$ and

$$M^L_{\pm z} = \begin{pmatrix} -\frac{\gamma_-}{4} & 0 & 0 & \frac{\gamma_+}{4} \\ 0 & -\frac{\gamma_++\gamma_-+4\gamma_z}{8} & 0 & 0 \\ 0 & 0 & -\frac{\gamma_++\gamma_-+4\gamma_z}{8} & 0 \\ \frac{\gamma_-}{4} & 0 & 0 & -\frac{\gamma_+}{4} \end{pmatrix}, \tag{29}$$

which now commute: $[M^H_{\pm z},\ M^L_{\pm z}] = 0$. From this comutativity, an FID oscillation period derived from the master equation with H and $\{L_{\pm,z}\}$ is in turn anticipated to be free from the dynamic frequency shift. To see this, solutions of $(S_x(t), S_y(t), S_z(t))$ for the master equation with initial condition $(S_x(0), S_y(0), S_z(0)) = (\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta)$, should be given. They are readily obtained as

$$S_x(t) = \exp\left[-\frac{\gamma_+ + \gamma_- + 4\gamma_z}{8}t\right]\cos(d_0 t + \phi)\sin\theta, \tag{30}$$

$$S_y(t) = \exp\left[-\frac{\gamma_+ + \gamma_- + 4\gamma_z}{8}t\right]\sin(d_0 t + \phi)\sin\theta, \tag{31}$$

$$S_z(t) = \exp\left[-\frac{\gamma_+ + \gamma_-}{4}t\right]\left(\cos\theta - \frac{\gamma_+ - \gamma_-}{\gamma_+ + \gamma_-}\right) + \frac{\gamma_+ - \gamma_-}{(\gamma_+ + \gamma_-)}, \tag{32}$$

and indeed, the period of the sinusoidal behavior is solely fixed by d_0. Although the two Lindblad equations with $\{L_{x,y,z}\}$ and with $\{L_{\pm,z}\}$ seem to be equivalent from the view points of Lie algebra [23], the relaxation processes described by each are qualitatively different. Accordingly, the Lindblad equation with $\{L_{x,y,z}\}$ considered in the last section is not a cosmetic change of the Lindblad equation with $\{L_{\pm,z}\}$, and the difference between these two are crucial. From these consideration, we conclude that the frequency shift in FID oscillation period due to $\gamma_x \neq \gamma_y$ originates from the non-commutativity, Eq.(24) and that the shift is dynamic frequency shift [20, 21].

The Lindblad form of Eq.(18), which was phenomenologically introduced, reminds us similarity with a relaxation process of depolarization, but it is not exactly the case. Usually, the process is described by Lindblad master equation with $d_0 = 0$ and $\gamma_x = \gamma_y = \gamma_z$ in Eq.(18) [25, 24]. Possible generalization to address the case of $d_0 \neq 0$ and unequality of three relaxation constants was discussed in Refs. [19, 26]. In these studies, microscopic derivation was performed of the Lindblad master equation to describe *generalized* depolarization, starting from a model Hamiltonian consisting of a two-level system and three independent boson bathes [26]. However in these studies, $\gamma_x = \gamma_y$ was finally obtained. This result still survives even when coupling constants of the two-level system and each of three boson bathes with Ohmic spectral functions are different, and thereby we call Eq.(18) phenomenological. Since there is a crucial difference between $\gamma_x = \gamma_y$ and $\gamma_x \neq \gamma_y$ cases, as shown above, construction of a microscopic model system which yields the Lindblad form with $\gamma_x \neq \gamma_y$ through a conventional manner, is in need as a future work from the view point of open quantum physics.

3.2 overdamped fluctuating field

In discussions so far, a condition $4d_0 > |\gamma_x - \gamma_y|$ is throughout assumed. The following two subsections mention the results when $0 < 4d_0 \leq |\gamma_x - \gamma_y|$, as a complement.

Since formulation in Sec.2.1 maintains generality to some extents, it is applicable to any case equivalent to a two-level system in a fluctuating magnetic field, like superconducting charge qubit[27], and ion trap [28], to name a few. Let the scheme be applied to a certain system where $0 < 4d_0 < |\gamma_x - \gamma_y|$ is somehow satisfied. Then the solutions, $\tilde{x}(t)$ and $\tilde{y}(t)$, are now given as

$$\begin{pmatrix} \tilde{x}(t) \\ \tilde{y}(t) \end{pmatrix} = \exp\left[-\tilde{N}_{xy} t\right] \begin{pmatrix} \tilde{x}_0 \\ \tilde{y}_0 \end{pmatrix}, \tag{33}$$

where

$$\exp[-\tilde{N}_{xy} t] = \exp\left(-\frac{\gamma_{\rm all} + \Gamma}{4} t\right) \tilde{N}_{xy}^{(1)} + \exp\left(-\frac{\gamma_{\rm all} - \Gamma}{4} t\right) \tilde{N}_{xy}^{(2)}, \tag{34}$$

$$\tilde{N}_{xy}^{(1)} = \frac{1}{2\Gamma} \begin{pmatrix} \Gamma - (\gamma_x - \gamma_y) & 4d_0 \\ -4d_0 & \Gamma + (\gamma_x - \gamma_y) \end{pmatrix}, \tag{35}$$

$$\tilde{N}_{xy}^{(2)} = \frac{1}{2\Gamma} \begin{pmatrix} \Gamma + (\gamma_x - \gamma_y) & -4d_0 \\ 4d_0 & \Gamma - (\gamma_x - \gamma_y) \end{pmatrix}, \tag{36}$$

and a real constant $\Gamma = \sqrt{(\gamma_x - \gamma_y)^2 - 16d_0^2}$. These solutions show monotonic exponential decays without oscillation, which correspond to an overdamped case in a classical harmonic oscillator. Marked contrast to the case in Sec.2.1 can be seen in a matrix property: determinants of both $\tilde{N}_{xy}^{(1),(2)}$ are null, while those of $N_{xy}^{(1),(2)}$ in Eq.(13) are identically unity. Thus after applying $\pi/2$ pulse and set such an initial condition $(x_0, y_0, 0)$ as

$$\left[\Gamma - (\gamma_x - \gamma_y)\right] x_0 + 4dy_0 = 0, \tag{37}$$

or

$$\left[\Gamma + (\gamma_x - \gamma_y)\right] x_0 - 4dy_0 = 0, \tag{38}$$

the motion of the Bloch vector, $(\tilde{x}(t), \tilde{y}(t), \tilde{z}(t) = 0)$, is determined by a solely $\tilde{N}_{xy}^{(2)}$ term when Eq.(37) is satisfied since $\tilde{N}_{xy}^{(1)}(x_0, y_0)^T = 0$, or by solely $\tilde{N}_{xy}^{(1)}$ term when Eq.(38) is satisfied, since $\tilde{N}_{xy}^{(2)}(x_0, y_0)^T = 0$, where the superscript T denotes transpose of the column vector. In the former case, the longest relaxation time in this system, apart from whether this should be termed T_2^* or not, is expected [15].

3.3 possible exceptional points

In addition to the algebraic difference between Lindblad equations with $\{L_{x,y,z}\}$ and $\{L_{\pm,z}\}$, there is another qualitative difference in matrices $M_{xyz}^H + M_{xyz}^L$ and $M_{\pm z}^H + M_{\pm z}^L$, under the condition $d_0 \neq 0$. While both matrices have rank three in common, due to constraint of $\mathrm{Tr}\rho = 1$, a striking contrast is that $M_{xyz}^H + M_{xyz}^L$ can have an exceptional point, but $M_{\pm z}^H + M_{\pm z}^L$ not. Indeed, four eigenvalues of $M_{xyz}^H + M_{xyz}^L$ are

$$\left\{0, -\frac{\gamma_x + \gamma_y}{2}, -\frac{1}{4}\left(\gamma_{\mathrm{all}} \pm i\Omega\right)\right\}, \tag{39}$$

while, those of $M_{\pm z}^H + M_{\pm z}^L$ are

$$\left\{0, -\frac{\gamma_+ + \gamma_-}{4}, -\frac{\gamma_+ + \gamma_- + 4\gamma_z}{8} \pm id_0\right\}. \tag{40}$$

For the former, when $\Omega = 0$, or $4d_0 = |\gamma_x - \gamma_y|$, the eigenvalues degenerate and, at the same time, corresponding eigenvectors coalease. This corresponds to a critical damping condition for a simple classical harmonic oscillator. On the other hand, in the later case it will not happen. The role of exceptional points in Lindblad type master equation recently draws considerable attention [29, 30]. Studies along this line should be of interest.

4 Conclusion

We theoretically studied dynamic frequency shift which is expected to be observed in NV^- center in diamond through FID measurement. Our analytical method was primarily based on an extension of the procedure in Ref.[14], and novelty over it was an introduction of anisotropic in-plane vacuum fluctuation. The result was corroborated by a master equation with phenomenological Lindblad form, which corresponds to full-fledged depolarization process. The origin for the shift to manifest itself lies in the non-commutative property, whose explicit presentation is given in terms of the master equation. The findings in this work would stimulate experimental researchers in NV center community and also pose such a fundamental question as a microscopic model construction for the interesting Lindblad form.

The author thanks T. Teraji, Y. Masuyama, C. Shinei and T. Yamaguchi for their inputs on NV^- from an experimental side, and M. Arai for his valuable comments.

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