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Detecting the Dzyaloshinskii–Moriya interaction by means of pulsed EPR spectroscopy

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ABSTRACT

The Dzyaloshinskii–Moriya (DM) interaction is induced by the spin–orbit interaction with an antisymmetric component in the exchange coupling. We have examined a possibility to detect the DM interaction as well as the non-secular part of the dipolar interaction for weakly-coupled systems by analyzing relaxation processes from the double to single quantum coherence by pulsed EPR measurement. Numerical simulation for two and three spin-1/2 systems indicates that the proposed measurement has a capability to determine the signs of the DM interactions that are important to distinguish spins in a uniform field from in a staggered field.

Understanding the dynamics of spins in solids is clearly a noble and important issue in the condensed matter physics and chemistry. It is therefore not surprising that a tremendous amount of experimental and theoretical efforts has been made to explore the dynamical behavior of the spin system. Recently, the chiral order of magnetic spins in molecular based materials [1], inorganic materials [2–5], and semiconductor nanostructures [6,7] has attracted much attention because of its unique anisotropic features [8]. The key feature of these materials is the Dzyaloshinskii–Moriya (DM) interaction between the neighboring spins $\widehat{\mathbf{S}}_i$ and $\widehat{\mathbf{S}}_{i+1}$, which is induced by the spin–orbit interaction with an antisymmetric component in the exchange coupling and is expressed as $\mathbf{D}\cdot(\widehat{\mathbf{S}}_i\times\widehat{\mathbf{S}}_{i+1})$, where $\mathbf{D}$ is the coupling constant [9,10].

For $S=1/2$ antiferromagnetic spin chain, the DM interactions are classified into two kinds [11]; one is the uniform DM interaction $(\sum_i \mathbf{D}\cdot(\widehat{\mathbf{S}}_i\times\widehat{\mathbf{S}}_{i+1}))$ [12,13], and the other is the staggered DM interaction $(\sum_i(-1)^i\mathbf{D}\cdot(\widehat{\mathbf{S}}_i\times\widehat{\mathbf{S}}_{i+1}))$ [14,15]. In the latter case, a gyromagnetic (g) tensor may be staggered. While efforts have been made to identify the DM interactions by measuring the continuous wave electron paramagnetic resonance (CW EPR) spectra of forbidden transitions between the singlet ground state and the triplet excited state of the spin gap systems which is allowed by the DM interaction [16–18], it is not easy to determine the DM parameter due to the weakness of the coupling strength.

In this Letter, we explore a possibility to detect the DM interactions by means of pulsed EPR spectroscopy techniques. In particular, we focus on the different relaxation dynamics caused by the uniform and staggered DM interactions.

There are several varieties of pulsed EPR methods for detecting electron–electron couplings to determine structures of biological molecules [25], such as DEER (double electron–electron resonance) [19,20], '2 + 1' pulse train [21,22], and DQ (double quantum) EPR [23,24]. In those methods we assume the high-field approximation for spins in solids, where the spins are weakly coupled and pulsed EPR techniques are used to manipulate the spin density operator. We thus propose the pulsed EPR spectroscopy utilizing the double quantum coherence (DQC) to extract the effects of the DM interaction, as well as the non-secular part of the dipolar interaction.

It will be shown that the difference between the uniform and the staggered DM interactions can clearly be seen from this measurement when the system is nearly parallel to the static magnetic field.

Note that although here we restricted our discussions for two and three spin cases, the present detection scheme may be applicable to a multispin system, where the collective excitations, such as spin waves, play essential roles. This is because energy scale of the collective excitations is very small compared with the Zeeman energy and we can separate EPR spectra from the collective excitations.

We consider N-spin system in a chain with the Zeeman term $\mu_B\widehat{\mathbf{S}}_i\mathbf{g}_i\mathbf{H}$ described by the Hamiltonian,

$$\widehat{H}=\widehat{H}_0+\widehat{H}_1=\sum_i^N\widehat{H}_{0i}+\sum_i^{N-1}\widehat{H}_{1i}, \tag{1}$$

where

$$\widehat{H}_{0i}/\hbar=\mu_B\widehat{\mathbf{S}}_i\mathbf{g}_i\mathbf{H}/\hbar \tag{2}$$

and

$$\widehat{H}_{1i}/\hbar=\widehat{\mathbf{S}}_i\mathbf{J}\widehat{\mathbf{S}}_{i+1}+b\left\{\widehat{\mathbf{S}}_i\cdot\widehat{\mathbf{S}}_{i+1}-\frac{3}{r^3}(\widehat{\mathbf{S}}_i\cdot\mathbf{r})(\widehat{\mathbf{S}}_{i+1}\cdot\mathbf{r})\right\}+(\pm1)^i\mathbf{D}\cdot(\widehat{\mathbf{S}}_i\times\widehat{\mathbf{S}}_{i+1}). \tag{3}$$

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Here, $\mathbf{H}$, $\mathbf{r}$, $\mathbf{J}$, and $b = \mu_0 g^2 \mu_B^2 / 4\pi\hbar r^3$ are the magnetic fields, the inter-electron vector, the antiferromagnetic Heisenberg coupling, and the dipolar coupling, respectively. Assuming the static field is applied in the z direction, we let the Zeeman term be

$$\mu_B \hat{\mathbf{S}}_i \mathbf{g}_i \mathbf{H}/\hbar \equiv \omega_{ix}\hat{S}_{ix} + \omega_{iy}\hat{S}_{iy} + \omega_i \hat{S}_{iz}. \tag{4}$$

We also rewrite the exchange interaction as

$$\begin{aligned}\hat{\mathbf{S}}_i \mathbf{J} \hat{\mathbf{S}}_{i+1} =& J\hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_{i+1} + J_{xy}(\hat{S}_{ix}\hat{S}_{i+1y} + \hat{S}_{iy}\hat{S}_{i+1x}) \\ &+ J_{xz}(\hat{S}_{ix}\hat{S}_{i+1z} + \hat{S}_{iz}\hat{S}_{i+1x}) + J_{yz}(\hat{S}_{iy}\hat{S}_{i+1z} + \hat{S}_{iz}\hat{S}_{i+1y}).\end{aligned} \tag{5}$$

For simplicity, we choose the vector $\mathbf{D}$ to be directed along the x axis and consider only the nearest-neighbor interactions. Since D_x and D_y play a similar role in relaxation processes, we can apply the same argument for D_y.

To begin with, we discuss the time evolution of a two-particle system of spin 1/2 described by Eq. (1) for the pulse sequence in Fig. 1. Here, the order of coherence p is the difference in magnetic quantum numbers ΔM and the double-, single-, and zero-quantum coherences (DQC, SQC, and ZQC) correspond to $|p| = 2$, 1, 0, respectively.

In a system with coupled electron spins, DQC can be created by the sequence $\pi/2 - \tau/2 - \pi - \tau/2 - \pi/2$, which is known as the DQC generator [26], where $\tau = \pi/|J + b(1 - 3\cos^2\theta)|$ with the phase cycle $[(x,x,x) - (y,y,y) + (-x,-x,-x) - (-y,-y,-y)]$. Note that while this phase cycle suppresses all of the pathways that yield SQC and ZQC, this cannot eliminate SQC and ZQC in the equilibrium state. Thus, the existence of initial SQC and ZQC weakens the signal intensity.

If the system is in $-\hat{S}_z$ at first, the DQC state immediately after the third pulse is expressed as

$$\hat{\rho}(0) = -2\hat{S}_{1x}\hat{S}_{2y} - 2\hat{S}_{1y}\hat{S}_{2x}, \tag{6}$$

which is undetectable by the quadrature detection. However, the DM interaction as well as the non-secular part of the dipolar, exchange, and Zeeman interactions can create detectable SQC excitations via forbidden coherence (FC) pathways since all of them consist of *one* creation or annihilation operator only. While this transition causes the undesired relaxation in the allowed DQ EPR measurement, we extract the dynamical information of the above-mentioned four interactions from the relaxation in the present measurement.

Although the non-secular hyperfine coupling assumes the same form as the anisotropic Zeeman interaction for the electron spin operators, the non-secular hyperfine coupling is much smaller than the anisotropic Zeeman interaction and therefore we ignore the hyperfine coupling.

The conversion from DQC to SQC in the evolution period can readily be verified by the power series expansion of the spin density operator

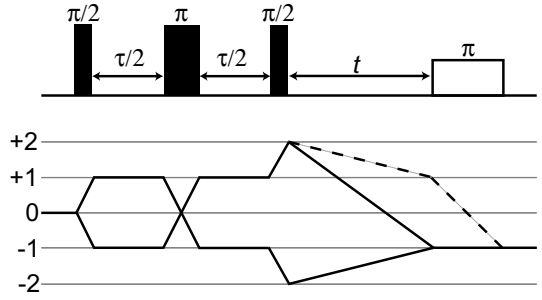

Fig. 1. Pulse sequence and related coherence transfer pathways. The fourth selective π pulse converts the coherence order of either of two spins in the dashed pathway as $p = +1 \rightarrow -1$.

$$\hat{\rho}(t) = \hat{\rho}(0) - \mathrm{i}t\hat{\mathscr{L}}\hat{\rho}(0) - \frac{t^2}{2}\hat{\mathscr{L}}^2\hat{\rho}(0) + \cdots, \tag{7}$$

where $\hat{\mathscr{L}}$ is the Liouvillian of Eq. (1): $\hat{\mathscr{L}}\hat{\rho} = (\hat{H}\hat{\rho} - \hat{\rho}\hat{H})/\hbar$. Since the commutator $\hat{\rho}(0)$ with $2\hat{S}_{1y}\hat{S}_{2z} - 2\hat{S}_{1z}\hat{S}_{2y}$ yields the detectable SQC $\hat{S}_{1y} - \hat{S}_{2y}$, we find the signal in the lowest order is proportional to D_x. Furthermore, the z component of the DM interaction cannot excite SQC since it is only a flip-flop term. Although the present analysis holds only for a short time, this suffices to illustrate a role of the DM interaction. Below, we utilize the response function approach to discuss longer time period.

In conventional EPR measurements, the intensity of signal from the forbidden transitions is of the order of α^2 and approximately 10^{-8} smaller than from the allowed transitions in the high field region [27], while the intensity of the present pulse measurement is of the order of α, where $\alpha \simeq \|\hat{H}'_{1i}\|/\|\hat{H}_{0i}\|$ and $\|\hat{H}_{ji}\|$ $(j = 0, 1)$ stands for the norm of the Hamiltonians of spin i. Here, $\hat{H}_{0i}$ is given by Eq. (2), which leads to $\|\hat{H}_{0i}\| = \mu_B g_i H/2$ and $\hat{H}'_{1i}$ is now expressed as

$$\begin{aligned}\hat{H}'_{1i}/\hbar =& \omega_{ix}\hat{S}_{ix} + \omega_{iy}\hat{S}_{iy} + b(C + D) + (\pm 1)^i D_x(\hat{S}_{iy}\hat{S}_{i+1z} - \hat{S}_{iz}\hat{S}_{i+1y}) \\ &+ (\pm 1)^i D_y(\hat{S}_{iz}\hat{S}_{i+1x} - \hat{S}_{ix}\hat{S}_{i+1z}),\end{aligned} \tag{8}$$

where C and D are the dipolar interactions, which contain only one creation or annihilation operator, expressed in the polar coordinates as [28]

$$C = -\frac{3}{2}(\hat{S}_i^+\hat{S}_{i+1z} + \hat{S}_{iz}\hat{S}_{i+1}^+)\sin\theta\cos\theta\mathrm{e}^{-\mathrm{i}\phi}, \tag{9}$$

and

$$D = -\frac{3}{2}(\hat{S}_i^-\hat{S}_{i+1z} + \hat{S}_{iz}\hat{S}_{i+1}^-)\sin\theta\cos\theta\mathrm{e}^{\mathrm{i}\phi}. \tag{10}$$

Here, θ is the angle between the z axis and $\mathbf{r}$, and ϕ is the azimuthal angle. They are experimentally changeable parameters that make possible to determine the sign of the DM interaction.

Likewise, the intensity of CW EPR absorption between the singlet ground state and the triplet excited states of the spin gap systems is proportional to D^2 [29], which corresponds to α^2. On the other hand, the detection scheme proposed in this Letter is proportional to D and therefore the resulting spectra reflect the sign of the DM interaction.

From the response function approach [30], the intensity of signal is easily shown to be of the order of α for the pulse sequence in Fig. 1. We consider a two-particle system of spin 1/2 with the Hamiltonian of the form

$$\hat{H} = \hat{H}_0 + \hat{H}'_1, \tag{11}$$

where

$$\hat{H}_0/\hbar = \omega_1\hat{S}_{1z} + \omega_2\hat{S}_{2z}, \tag{12}$$

and

$$\hat{H}'_1/\hbar = D_x(\hat{S}_{1y}\hat{S}_{2z} - \hat{S}_{1z}\hat{S}_{2y}). \tag{13}$$

The time-dependent density operator is expanded in powers of $\hat{H}'_1$ to obtain the linear response function

$$\begin{aligned}S^{(1)}(t) =& \mathrm{i}\langle\langle\hat{S}^+|\mathrm{e}^{-\mathrm{i}\hat{\mathscr{L}}_0 t}\hat{\mathscr{L}}'_1|\hat{\rho}(0)\rangle\rangle \\ =& D_x(-\mathrm{i}\cos\omega_1 t + \sin\omega_1 t + \mathrm{i}\cos\omega_2 t - \sin\omega_2 t).\end{aligned} \tag{14}$$

Since $\alpha \simeq D_x/\omega_i$, the intensity of this signal is of the order of α. Furthermore, we can verify that the intensity of forbidden transitions is of order α^2

$$S^{(1)}(t) = 0, \tag{15}$$

$$\begin{aligned} S^{(2)}(t) &= -\langle\langle \widehat{S}^{+}|\mathrm{e}^{-\mathrm{i}\hat{\mathscr{L}}_0 t_2}\,\hat{\mathscr{L}}'_1\mathrm{e}^{-\mathrm{i}\hat{\mathscr{L}}_0 t_1}\,\hat{\mathscr{L}}'_1|\widehat{S}_y\rangle\rangle \\ &= D_x^2\{(-\mathrm{i}\cos\omega_1 t_2 + \sin\omega_1 t_2 - \ \mathrm{i}\cos\omega_2 t_2 + \sin\omega_2 t_2) \\ &\quad\times\cos(\omega_1-\omega_2)t_1 - (\cos\omega_1 t_2 + \mathrm{i}\sin\omega_1 t_2 + \cos\omega_2 t_2 \\ &\quad + \mathrm{i}\sin\omega_2 t_2)\sin(\omega_1-\omega_2)t_1\}. \end{aligned} \tag{16}$$

In a similar fashion, we can prove that the z component of the DM interaction cannot excite SQC since all orders of response functions equal to zero.

The signal from the SQC created by the DM interaction, $\widehat{S}_{1y}-\widehat{S}_{2y}$, is 0 for the quadrature detection, because $\mathrm{Tr}[\widehat{S}^{+}(\widehat{S}_{1y}-\widehat{S}_{2y})]=0$. Thus, a selective π_x pulse for either of two spins immediately before the detection is necessary to detect the DM interaction as shown in Fig. 1. Since the fourth pulse in Fig. 1 applies only in the high-field region, we have to employ the strong EPR field against the exchange coupling. This limits the applicability of the proposed pulsed EPR technique to the weakly-coupled spin systems. A possible candidate is the quantum dot system, in which we can modify the strength of spin–spin interactions. Biological molecules may be another candidate although no attempt has been made to find the DM interaction in such a system so far.

In order to demonstrate the present detection scheme closely and to analyze the relaxation mechanism precisely, we have to include longitudinal and transverse relaxations as well as inhomogeneous broadening processes. We calculate the EPR spectra for the given pulse sequence using a quantum master equation for nearly Gaussian–Markovian noise bath [31], which is an extension of the stochastic Liouville equation [32]. We assume that the Hamiltonian $\widehat{H}$ defined by Eq. (1) is coupled to the harmonic heat-bath. The total Hamiltonian is then expressed as

$$\widehat{H}_{\ \mathrm{tot}} = \widehat{H} + \hat{V}\sum_j c_j\hat{x}_j + \sum_j\left(\frac{\hat{p}_j^2}{2m_j}+\frac{1}{2}m_j\omega_j^2\hat{x}_j^2\right), \tag{17}$$

where $\hat{x}_j, \hat{p}_j, m_j$, and ω_j are the coordinate, momentum, mass, and frequency of the jth bath oscillator, respectively. The operator $\hat{V}$ is the system part of the coupling described by the creation and annihilation operators $\widehat{S}^{+}$ and $\widehat{S}^{-}$. In this Letter, we assume a nearly Gaussian–Markovian noise bath defined by an Ohmic spectral distribution with a Lorentzian cutoff,

$$J(\omega) = \frac{\hbar\eta}{\pi}\frac{\gamma^2\omega}{\omega^2+\gamma^2}, \tag{18}$$

where η and γ represent the strength of the system-bath coupling and the width of the spectral distribution of the bath, respectively. If we further assume the high temperature bath, $\beta\hbar\gamma \ll 1$, we can derive the hierarchy of equations for the reduced density operator by tracing over the bath degrees of freedom as

$$\begin{aligned} \frac{\partial}{\partial t}\hat{\rho}_n(t) &= -\left(\frac{\mathrm{i}}{\hbar}\widehat{H}^{\times}+n\gamma\right)\hat{\rho}_n(t) - \frac{\mathrm{i}}{\hbar}\hat{V}^{\times}\hat{\rho}_{n+1}(t) \\ &\quad - \frac{\mathrm{i}n}{\hbar}\hat{\Theta}_0\hat{\rho}_{n-1}(t) - \hat{\Gamma}\{\hat{\rho}_n(t)-\hat{\rho}_n^{\mathrm{eq}}\} \quad (n=1,2,\cdots), \end{aligned} \tag{19}$$

where

$$\hat{\Theta}_0 \equiv \frac{\eta\gamma}{\beta}\left(\hat{V}^{\times} - \ \mathrm{i}\frac{\beta\hbar\gamma}{2}\hat{V}^{\circ}\right), \tag{20}$$

and we set in $\hat{\Theta}_0\hat{\rho}_{n-1}(t)/\hbar = 0$ for $n=0$. In Eqs. (19) and (20), we have introduced the hyperoperator notations for any operator $\hat{O}$: $\hat{V}^{\times}\hat{O} \equiv \hat{V}\hat{O} - \hat{O}\hat{V}$ and $\hat{V}^{\circ}\hat{O} \equiv \hat{V}\hat{O} + \hat{O}\hat{V}$. To include the effect of the homogeneous broadening arising from the natural radiative damping, we have added the longitudinal (T_1-type) and transverse (T_2-type) relaxation processes, expressed as

$$\hat{\Gamma}\hat{O} \equiv \Gamma\sum_i(\widehat{S}_i^{+}\widehat{S}_i^{-}\hat{O} + \hat{O}\widehat{S}_i^{+}\widehat{S}_i^{-} - 2\widehat{S}_i^{-}\hat{O}\widehat{S}_i^{+}). \tag{21}$$

The above set of equations of motion may be regarded as a generalization of the Kubo's stochastic Liouville equation [33] and if we set $\beta\to 0$ with keeping $\eta = \Delta^2/\beta$, the above equations reduce to the stochastic Liouville equation, where Δ and γ correspond to the amplitude and the inverse correlation time of a noise, respectively. Note that although Eq. (19) can handle a finite temperature system, we have to include low temperature correction terms if the heat-bath is in a low temperature system, where quantum effects play an important role [34]. The hierarchy of equations, Eq. (19), continues to the infinity, but we can safely truncate the hierarchy for large N by the following terminator:

$$\begin{aligned} \frac{\partial}{\partial t}\hat{\rho}_N(t) &= -\left(\frac{\mathrm{i}}{\hbar}\widehat{H}^{\times}+N\gamma\right)\hat{\rho}_N(t) - \frac{1}{\gamma\hbar^2}\hat{V}^{\times}\hat{\Theta}_0\hat{\rho}_N(t) \\ &\quad - \frac{\mathrm{i}N}{\hbar}\hat{\Theta}_0\hat{\rho}_{N-1}(t) - \hat{\Gamma}\{\hat{\rho}_N(t)-\hat{\rho}_N^{\mathrm{eq}}\}, \end{aligned} \tag{22}$$

where N is chosen to satisfy $(N+1)\gamma \gg \omega_1$. The operator $\hat{V}$ in Eq. (19) can be any form, but here we set $\widehat{V} = \sum_i \widehat{S}_{iz} \equiv \widehat{S}_z$ to include the pure dephasing effects. For the fast modulation limit $\gamma\to\infty$, the effects which arise from these terms can be regarded as the T_2^{*} process due to random local strain fields (spin–phonon coupling) in solids.

We first consider a two-spin system to illustrate the effects of the positive and negative DM interaction in the EPR spectra. The parameters in Eq. (1) are set to be $\omega_1 = 100$ GHz, $\omega_2 = 1.01\omega_1$, $\omega_{ix}=\omega_{iy}=0.01\omega_i$ $(i=1,2)$, $J=b=0.001\omega_1$, $J_{xy} = J_{xz} = J_{yz} = 0.001J$, and $D_x = 0.01J$ since the DM interaction is of the order $(\Delta g/g)J$ [10], where g is the gyromagnetic ratio and Δg is its deviation from the value for a free electron. For simplicity, we choose $\phi = 0$ rad. The system-bath coupling parameters are set by $\gamma = 0.001\omega_1$ and $\eta = 2.4\times10^{-4}\omega_1$, corresponding to the inhomogeneous limit. Γ in Eq. (21) is $5\times10^{-6}\omega_1$, corresponding to $T_1 = 200$ ns and $T_2 = 100$ ns, and the temperature of the bath is 200 K. The number of hierarchy N we employed is at most $N=30$. The accuracy of calculations can be easily checked by changing N. We consider ideal pulses that neglect the effect of pulse duration.

Fig. 2A depicts the real part of the signal for (a) the positive DM interaction $(+\mathbf{D}\cdot(\mathbf{S}_1\times\mathbf{S}_2))$, (b) the negative DM interaction $(-\mathbf{D}\cdot(\mathbf{S}_1\times\mathbf{S}_2))$, and (c) the non-DM interaction $(\mathbf{D}=0)$ for $\theta=0$ rad. The peaks around 101 and 201 GHz arise from SQC and DQC, respectively. Around 201 GHz, (a) and (b) appear in an opposite manner reflecting the sign of the DM interactions, whereas (c) bisects (a) and (b). These results indicate that the signal is proportional to α, demonstrating the ability to determine the sign of the DM interaction. The linewidths of the peaks are attributed to the inhomogeneous lifetime T_2^{*} that is taken into account by the hierarchal formalism, while the T_1 and T_2 relaxations play a minor role in the linewidths.

Contrary to the case of $\theta=0$, the non-secular dipolar contribution becomes prominent for θ near $\pi/4$, because the non-secular dipolar interaction can also excite the SQC through FC pathways for nonzero θ.

Fig. 2B shows the signal at $\theta=\pi/4$, where the non-secular dipolar contribution reaches maximum. The major contribution of the signals arises from the non-secular part of the dipolar interaction and the difference between the positive and negative DM interactions diminishes. Thus we can use the angle $\theta=\pi/4$ to estimate the strength of the non-secular part of the dipolar interaction, while $\theta=0$ is used to study a role of the DM interactions.

We then present the real part of EPR spectra for a three-particle system with $\omega_3=\omega_1$. The other parameters are the same as in Fig. 2A. Depending on the signs of the DM interactions $\pm\mathbf{D}\cdot(\mathbf{S}_1\times\mathbf{S}_2)\pm\mathbf{D}\cdot(\mathbf{S}_2\times\mathbf{S}_3)$, there are four cases of the signs in the three particle system. Fig. 3 shows the signal for (a) the uniform DM interaction

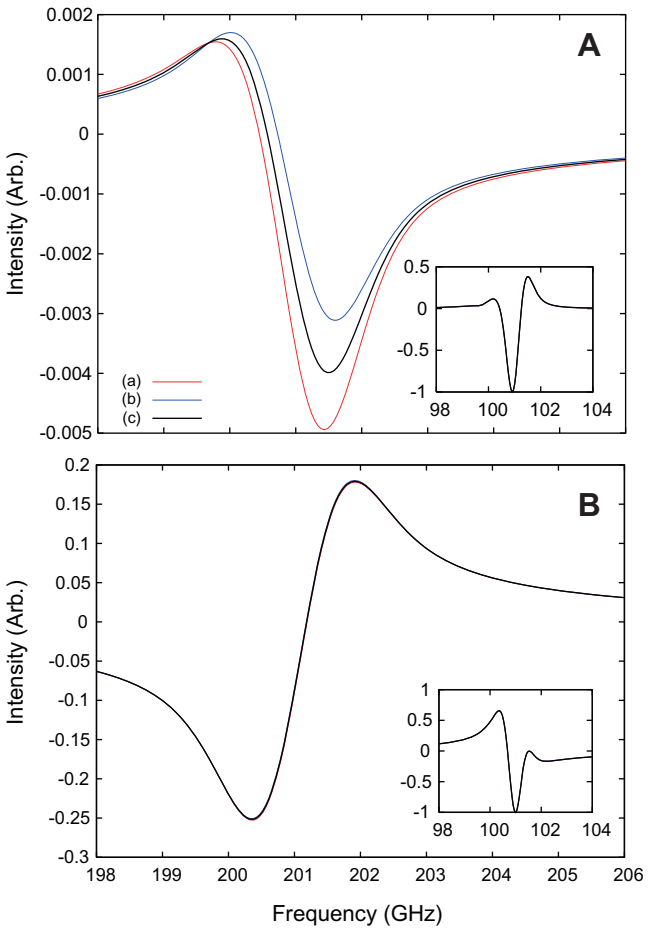

Fig. 2. Simulated EPR frequency spectra of the DQC for a two-particle system with (A) $\theta = 0$ and (B) $\theta = \pi/4$ by the pulse sequence shown in Fig. 1. (A) Illustrated the distinction among the (a) positive, (b) negative, and (c) non-DM interaction for $\theta = 0$, but not for $\theta = \pi/4$. Insets show the spectra of the SQC. The normalization of EPR spectra is such that the maximum at (a) in (A) is unity. (B) The spectra with $\theta = \pi/4$ represents the non-secular dipolar interaction, which affects the distinction.

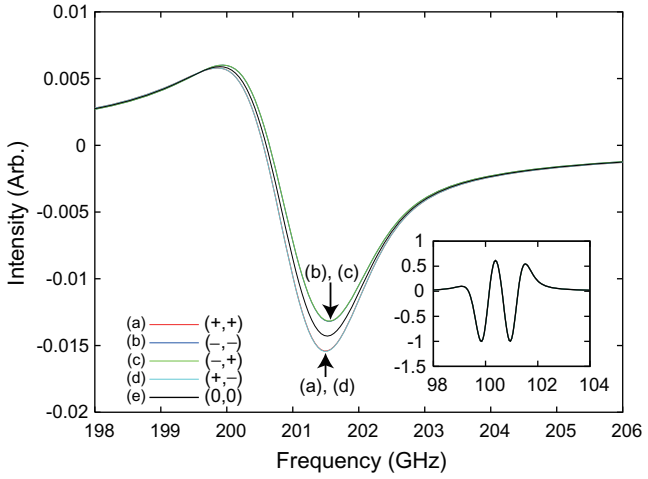

Fig. 3. Simulated EPR frequency spectra for a three-particle system with $\theta = 0$, illustrating the distinction between the (a) uniform $(+,+)$ or (d) negative-staggered $(+,-)$ and (b) negative-uniform $(-,-)$ or (c) staggered $(-,+)$ DM interactions. The signal for (e) the non-DM interaction (0,0) almost bisects (a) or (d) and (b) or (c). Insets show the spectra of the SQC. The normalization is such that the maximum at (a) is unity.

$(+,+)$, (b) the negative-uniform DM interaction $(-,-)$, (c) the staggered DM interaction $(-,+)$, and (d) the negative-staggered DM interaction $(+,-)$. The signal for (e) the non-DM interaction $(0,0)$ almost bisects (a) or (d) and (b) or (c). The spectra (a) or (d) and (b) or (c) exhibit distinctive features although the difference between (a) and (d) or (b) and (c) is hardly noticeable. The present scheme therefore can provide useful information to clarify the sign of the DM interactions, although we cannot separate all four cases of the signs. Note that here we assumed uniform g tensor. If g tensor is staggered, however, we can distinguish all of the four cases (not shown).

In conclusion, we have demonstrated a method to detect the DM interaction, as well as the non-secular part of the dipolar interaction by analyzing the relaxation processes from DQC to SQC using a pulsed EPR technique as illustrated in Fig. 1. The present technique can also provide the information on the staggered DM interactions for a three-particle system, although we need a staggered g tensor to distinguish the four cases of the signs. Even though the intensity in the forbidden transitions is much weaker than that in the allowed transitions and the other interactions can interfere with the different spectra, the pulsed EPR spectroscopy has potential to detect the DM interaction by measuring the relaxation of DQC.

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