Nonsecular resonances for the coupling between nuclear spins in solids

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Spin-spin relaxation in solid-state nuclear-magnetic resonance in strong magnetic fields is normally described only with the help of the secular part of the full spin-spin interaction Hamiltonian. This approximation is associated with the averaging of the spin-spin interaction over the fast motion of spins under the combined action of the static and the radio-frequency (rf) fields. Here, we report a set of conditions (nonsecular resonances) when the averaging over the above fast motion preserves some of the nonsecular terms entering the full interaction Hamiltonian. These conditions relate the value of the static magnetic field with the frequency and the amplitude of the rf field. When the above conditions are satisfied, the effective spin-spin interaction Hamiltonian has an unconventional form with tunable parameters. This tunable Hamiltonian offers interesting possibilities to manipulate nuclear spins in solids and can shed new light on the fundamental properties of the nuclear-spin-spin relaxation phenomenon.

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I. INTRODUCTION

The experimental technique of nuclear magnetic resonance (NMR) has long established itself as a versatile tool for microscopic investigations of matter. One major source of microscopic information in NMR is the spin-spin relaxation. In solids, the description of NMR spin-spin relaxation requires averaging the full Hamiltonian of the nuclear-spin-spin interaction over the fast spin rotations induced by strong external magnetic fields. The present paper theoretically predicts a set of resonant conditions for solid-state NMR experiments leading to an unconventional form of the averaged interaction Hamiltonians.

We consider nuclear-spin-spin interactions in the presence of a static magnetic field and a continuously applied *rotating* radio-frequency (rf) field in the regime when the two fields have comparable values, while both of them are still much larger than the local fields with which nuclear spins affect each other. Such a setting is realizable experimentally. However, it implies the use of smaller-than-typical static fields and, therefore, a certain sacrifice in terms of the signal intensity. In a typical NMR experiment, the rf field may be large in comparison with the local fields, but it is still much smaller than the static field. This typical setting for strong continuously applied rf fields was originally considered by Redfield[1] and, subsequently, was discussed in NMR textbooks.[2,3] In such a case, the averaged interaction Hamiltonian is obtained from the full Hamiltonian with the help of a two-step truncation procedure.[1] The first step is to eliminate all interaction terms that do not commute with the Zeeman Hamiltonian for the static magnetic field.[4] The second step is to make the transformation into the rotating reference frame where the rf field appears static and then to further truncate the interaction Hamiltonian by eliminating all the terms that do not commute with the Zeeman Hamiltonian for the effective magnetic field in the rotating frame.

When the static and the rf fields are comparable to each other, the validity of the above two-step truncation becomes questionable because the spin motions caused by both fields fall on the same time scale. The full interaction Hamiltonian then needs to be averaged over the above two motions simultaneously rather than in two independent steps. In this paper, we show that, in the case of a purely rotating rf field (as opposed to the case of a linearly polarized rf field), such a single-step averaging can be performed rigorously without requiring the rf field to be smaller than the static field. We find that such a single-step procedure generically reproduces the results of Redfield's two-step truncation, but the reason for this agreement lies not in the perturbation theory but in the ergodic character of the single-spin dynamics driven by the static and the rf fields. We also find that, in certain special cases, which we call "nonsecular resonances," the averaged spin-spin interaction Hamiltonian includes other terms in addition to the outcome of Redfield's truncation procedure. In the case of the single-spin species, the nonsecular resonances appear when the rf-field frequency is matched with certain multiples or simple fractions of the Larmor frequency corresponding to the effective magnetic field in the rotating reference frame. In the case of two different spin species, the sums and the differences of the two effective Larmor frequencies also appear in some of the nonsecular resonance conditions. These resonances are nonsecular in the sense that the corresponding time-averaged interaction Hamiltonians do not conserve the total Zeeman energy associated with the external fields in either the laboratory or the rotating reference frame. The nonsecular resonances may have a range of applications, such as, e.g., nuclear cross polarization or molecular structure determination.

It is worth noting that analogous selective recoupling of the spin-spin interaction is extensively used[5–9] in the context of the magic angle spinning (MAS) technique of NMR where it recovers a part of the standard truncated Hamiltonian after that Hamiltonian is suppressed by the spinning of the sample. The MAS recoupling schemes match the frequency of the spin nutation[5] or the frequency of the rf pulses[7–9] with the multiples of the sample spinning frequency. In the present paper, recoupling takes place at a more basic level: It recovers a part of the *full* spin-spin interaction Hamiltonian lost in the standard truncation procedure. The nonsecular resonances described below have nothing to do with sample spinning. However, they are best observable and, probably, most useful in combination with MAS.

In a broader context, our results could have been obtained in the framework of the averaged Hamiltonian theory,[10] e.g., in its application to the low-field NMR,[11] but to the best of our knowledge, it has never been attempted, perhaps because of the nonperturbative character of the problem. The role of the nonsecular terms was, however, discussed in the context of the phenomenon of nuclear-spin super-radiance.[12,13]

The rest of this paper is organized as follows. We give the general formulation of the problem in Sec. II, introduce our single-step truncation procedure in Sec. III, present the results of this truncation with the identification of the nonsecular resonances in Sec. IV, and then discuss a possible experimental test and possible applications of the nonsecular resonances in Sec. V.

II. GENERAL FORMULATION

We consider a lattice of nuclear spins in a static magnetic field pointing along the z axis, $\boldsymbol{H}_0 \equiv (0,0,H_0)$, irradiated by an rf field rotating in the x-y plane with frequency ω, $\boldsymbol{H}_1(t) \equiv (H_1 \cos\omega t, H_1 \sin\omega t, 0)$. We limit ourselves to the case of the magnetic dipole spin-spin interaction, which is, typically, dominant in solids. The full Hamiltonian[2,3] is

$$\mathcal{H} = \mathcal{H}_z + \mathcal{H}_{\text{rf}} + \mathcal{H}_D, \tag{1}$$

where

$$\mathcal{H}_z = -H_0 \sum_i^N \gamma_i I_{iz}, \tag{2}$$

$$\mathcal{H}_{\text{rf}} = -\boldsymbol{H}_1(t) \cdot \sum_i^N \gamma_i \boldsymbol{I}_i, \tag{3}$$

and

$$\mathcal{H}_D = \sum_{i<j}^N J_{ij} \left[\boldsymbol{I}_i \cdot \boldsymbol{I}_j - \frac{3(\boldsymbol{I}_i \cdot \boldsymbol{r}_{ij})(\boldsymbol{I}_j \cdot \boldsymbol{r}_{ij})}{r_{ij}^2} \right]. \tag{4}$$

Here, $J_{ij} = \frac{\gamma_i \gamma_j \hbar^2}{r_{ij}^3}$ are the coupling constants, $\boldsymbol{I}_i \equiv (I_{ix}, I_{iy}, I_{iz})$ are the operators of the nuclear spin of the ith lattice site, γ_i is the gyromagnetic ratio of that spin, $\boldsymbol{r}_{ij} \equiv (r_{ij,x}, r_{ij,y}, r_{ij,z})$ are the displacement vectors between two lattice sites i and j, and N is the number of spins. The characteristic time of a single-spin motion induced by the Hamiltonian $\mathcal{H}_D$ can be estimated as $T_2 = \hbar (\sum_j J_{ij}^2)^{-1/2}$. The variable T_2 is also to be referred to as the transverse relaxation time. The time scale of nuclear-spin relaxation due to the coupling to electrons or phonons is to be denoted as T_1 (longitudinal relaxation time). We further introduce the Larmor frequencies $\Omega_{0i} = \gamma_i H_0$ and the nutation frequencies $\omega_{1i} = \gamma_i H_1$. In the following, we drop lattice index i in the gyromagnetic ratio and use the notations $\gamma \equiv \gamma_i$, $\Omega_0 = \gamma H_0$, $\omega_1 = \gamma H_1$, etc., when not dealing with the interactions of nonequivalent (unlike) spins explicitly.

This paper is limited to the regime $\Omega_0, \omega_1 \gg 1/T_2 \gg 1/T_1$. The first of these inequalities implies the separation of the time scales between the fast motion due to the external fields and the slow motion due to the spin-spin interaction. The second inequality allows us to consider the nuclear spins as isolated from the environment. As mentioned in the Introduction, the theoretical analysis in the literature,[1–3] so far, was limited by the additional inequality $H_1 \ll H_0$ (i.e., $\omega_1 \ll \Omega_0$). Our main focus is on the regime $H_1 \sim H_0$. However, also, for a range of situations satisfying the inequality $H_1 \ll H_0$, the nonsecular resonances obtained below will imply important observable effects.

III. TRUNCATION PROCEDURE

We calculate the effective spin-spin interaction Hamiltonian by averaging the full interaction Hamiltonian $\mathcal{H}_D$ over the fast spin motion induced by the terms $\mathcal{H}_z + \mathcal{H}_{\text{rf}}$. In the Heisenberg representation, this fast motion is described by the following equation for each of the spins:

$$\frac{d\boldsymbol{I}_i}{dt} = \boldsymbol{I}_i \times \gamma \boldsymbol{H}(t), \tag{5}$$

where $\boldsymbol{H}(t) = \boldsymbol{H}_0 + \boldsymbol{H}_1(t)$. The above equation is linear in terms of spin operators (I_{ix}, I_{iy}, I_{iz}) and, therefore, its predictions are essentially the same as those for the classical spins, in which case, (I_{ix}, I_{iy}, I_{iz}) would be simply three numbers. Despite the linearity of Eq. (5), it is not solvable analytically either classically or quantum mechanically for an arbitrary time-dependent $\boldsymbol{H}(t)$. However, for the specific time dependence considered in this paper, the solution is facilitated by the transformation from the laboratory reference frame into the reference frame rotating around the z axis with frequency ω. The equations of motion in the rotating frame have the same form as Eq. (5) but with time-independent effective magnetic field $\boldsymbol{H}_e = (H_1, 0, H_0 + \omega/\gamma)$. (The x axis in the rotating frame coincides with the direction of the rf field.) The corresponding Larmor frequency is

$$\Omega_e = \gamma H_e = \text{sgn}(\gamma) \sqrt{\omega_1^2 + (\Omega_0 + \omega)^2}. \tag{6}$$

Thus, the motion of a spin in the laboratory frame can be characterized as the Larmor precession with frequency Ω_e around the direction of $\boldsymbol{H}_e$, which itself rotates with frequency ω around the z axis.

Our formal procedure for averaging $\mathcal{H}_D$ consists of the transformation into the reference frame that follows the fast spin rotation induced by Eq. (5). In that reference frame, each spin would be motionless if the full Hamiltonian included only $\mathcal{H}_z + \mathcal{H}_{\text{rf}}$. Such a transformation is time-dependent. As a result, the Hamiltonian $\mathcal{H}_D$ expressed in the new spin coordinates acquires some quickly oscillating interaction coefficients, which we then average out.

The above procedure may, at first sight, appear equivalent to the one introduced by Redfield.[1–3] The difference, however, is that Redfield did not define the entire transformation and then average the resulting Hamiltonian over time but rather used the Zeeman-energy-conservation criterion of Van Vleck[4] to separately average the Hamiltonians obtained at the intermediate steps of this transformation. Such an independent averaging of the intermediate Hamiltonians is justifiable by the perturbation theory arguments[1] only when $\Omega_0 \gg \omega_1$. In general, the first transformation step makes some terms in the interaction Hamiltonian periodically time-dependent, but since the frequency Ω_e is comparable with the oscillation frequency of these time-dependent terms, one cannot straightforwardly eliminate these terms. It turns out that, in the case of $\Omega_0 \sim \omega_1$, the spin motions associated with the intermediate

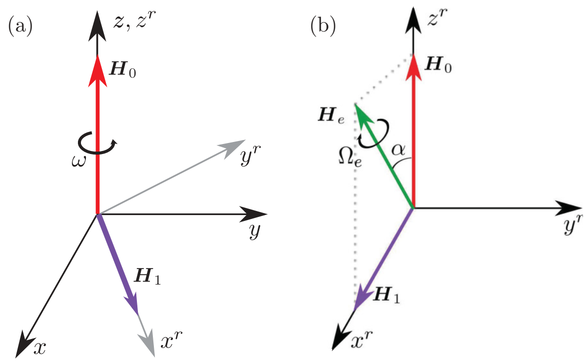

FIG. 1. (Color online) (a) Illustration of the transformation from the laboratory reference frame (x,y,z) to the rotating reference frame (x^r,y^r,z^r)—Eq. (7). (b) Illustration for the transformation from the rotating reference frame (x^r,y^r,z^r) to the tilted-rotating and then double-rotating reference frames—Eqs. (8) and (10).

transformation steps may be correlated, and thus, the averaging over them cannot be performed independently.

The overall transformation into the reference frame that follows the motion induced by Eq. (5) can be decomposed into three simple transformations visualized in Fig. 1. The first transformation is from the laboratory frame to the reference frame rotating with the rf field,

$$U_\omega = \begin{pmatrix} \cos(\omega t) & \sin(\omega t) & 0 \\ -\sin(\omega t) & \cos(\omega t) & 0 \\ 0 & 0 & 1 \end{pmatrix}. \tag{7}$$

The second transformation is from the rotating to the "tilted-rotating" reference frame where the z axis coincides with the direction of $\boldsymbol{H}_e$,

$$U_\alpha = \begin{pmatrix} \cos\alpha & 0 & -\sin\alpha \\ 0 & 1 & 0 \\ \sin\alpha & 0 & \cos\alpha \end{pmatrix}, \tag{8}$$

with

$$\alpha = \operatorname{arccot}\left[\frac{\Omega_0 + \omega}{\omega_1}\right], \tag{9}$$

admitting values in the range $[0,\pi]$.

Finally, the third transformation is into the "double-rotating" reference frame precessing around $\boldsymbol{H_e}$ with frequency $-\Omega_e$,

$$U_{\Omega_e} = \begin{pmatrix} \cos(\Omega_e t) & -\sin(\Omega_e t) & 0 \\ \sin(\Omega_e t) & \cos(\Omega_e t) & 0 \\ 0 & 0 & 1 \end{pmatrix}. \tag{10}$$

The effective magnetic field in this reference frame is equal to zero. The explicit implementation of transformation (10) before performing the time averaging of $\mathcal{H}_D$ formally discriminates our treatment from that of Redfield.[1–3]

We denote the axes in the double-rotated reference frame as $\{x',y',z'\}$ and the corresponding spin projections as $\boldsymbol{I}'_i \equiv (I'_{ix},I'_{iy},I'_{iz})$. The spin coordinates in the laboratory reference frame can now be expressed as

$$\boldsymbol{I}_i = U_\omega^{-1} U_\alpha^{-1} U_{\Omega_e}^{-1}\, \boldsymbol{I}'_i. \tag{11}$$

The substitution of Eq. (11) into Eq. (4) allows us to reexpress the interaction Hamiltonian $\mathcal{H}_D$ in terms of $\boldsymbol{I}'_i$ and then to average the interaction coefficients in the resulting expression.

The full time-dependent form of $\mathcal{H}_D$ in the double-rotated reference frame is rather long. It can be found in the Supplemental Material in Ref. 14 together with the implementation of the time-averaging procedure. Below, we exemplify this procedure by one typical term and then, in the next section, present only the resulting time-averaged expressions for $\mathcal{H}_D$.

The term we have chosen as an example originates from the calculation for equivalent (like) spin species discussed in the next section. It has the form

$$a_{ij}(t) c(\boldsymbol{r}_{ij}) I'_{ix} I'_{jx}, \tag{12}$$

where $c(\boldsymbol{r}_{ij})$ is some function of the relative displacement between the two nuclei, and

$$a_{ij}(t) = \cos^2(\omega t)\cos^2(\Omega_e t). \tag{13}$$

The time-averaged value of the above coefficient is calculated as follows:

$$\langle a_{ij}\rangle = \lim_{\tau\to\infty}\frac{1}{2\tau}\int_{-\tau}^{\tau} a_{ij}(t)dt = \begin{cases} \frac{1}{4}, & \text{if} \quad \omega \neq \pm\Omega_e, \\ \frac{3}{8}, & \text{if} \quad \omega = \pm\Omega_e. \end{cases} \tag{14}$$

In the above case, $\langle a_{ij}\rangle = \frac{1}{4}$ is what one obtains by the standard two-step truncation procedure outlined in the Introduction, whereas, in the case of $\omega = \pm\Omega_e$, there is an extra contribution associated with the fact that $\langle\cos^2(\omega t)\cos^2(\Omega_e t)\rangle \neq \langle\cos^2(\omega t)\rangle\langle\cos^2(\Omega_e t)\rangle$.

The question then arises, what happens if, in an experiment, the actual values of H_0, H_1, and ω are such that one of the nonsecular resonance conditions is satisfied approximately but not exactly. In such a case, the Hamiltonian-averaging procedure needs to be modified. Below, we illustrate this modification for the resonant condition $\omega = -\frac{1}{2}\Omega_e$, but the expression for the resulting correction to the averaged Hamiltonian is applicable to all other nonsecular resonances.

In the chosen example, the mismatch of the resonant condition can be parametrized with the help of the variable $\Delta\Omega_e$ defined by the equation $\omega = -\frac{1}{2}(\Omega_e + \Delta\Omega_e)$. Now, we modify the last step of the transformation to the double-rotated reference frame [Eq. (10)] by changing the value of the rotation frequency from Ω_e, given by Eq. (6), to $\Omega_e + \Delta\Omega_e$. In the modified double-rotated reference frame, the averaged interaction Hamiltonian obtained in Sec. IV A for the nonsecular resonance $\omega = -\frac{1}{2}\Omega_e$ is exactly valid, but, in addition, since $\Omega_e + \Delta\Omega_e$ is different from Ω_e, the effective magnetic field is different from zero, which then gives rise to the following additional term:

$$\Delta\mathcal{H} = \Delta\Omega_e \sum_i I'_{iz}. \tag{15}$$

When $\Delta\Omega_e \gg 1/T_2$, such a term suppresses the effect of the resonant nonsecular terms given in the next section. This is, of course, expected for a significant departure from the nonsecular resonance conditions. When $\Delta\Omega_e \sim 1/T_2$, the above term still suppresses the effect of the nonsecular terms but only partially, and this partial suppression is on the same order of magnitude as the suppression caused by the secular interaction terms (to be explained in Sec. IV A). In such a

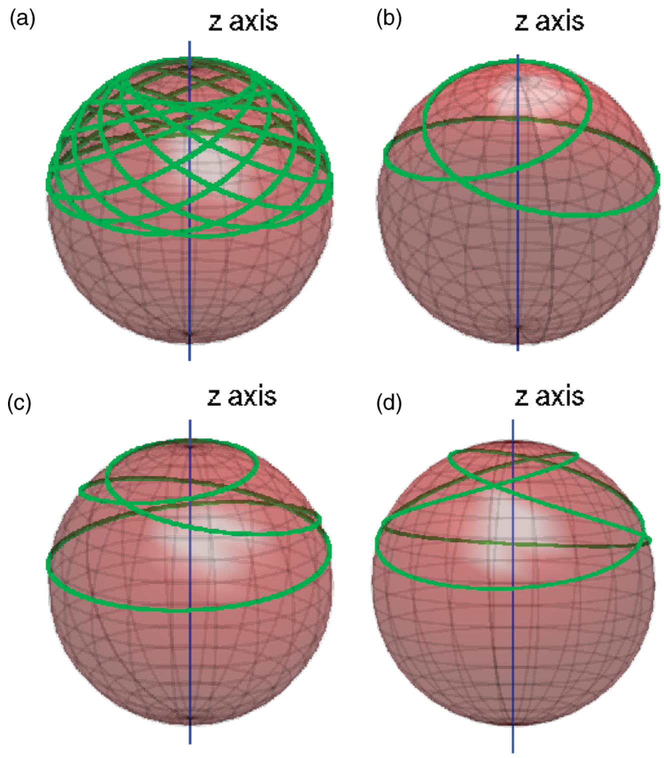

FIG. 2. (Color online) Examples of trajectories of a single classical spin under the combined action of the static and the rf magnetic fields: (a) general case, open ergodic trajectory; (b) $\omega = -\Omega_e$, closed trajectory; (c) $\omega = -2\Omega_e$, closed trajectory; (d) $\omega = \frac{1}{2}\Omega_e$, closed trajectory.

case, the term (15) should simply be included in the averaged Hamiltonian together with the secular terms and the resonant nonsecular terms.

The above considerations imply that, in a generic case, when the strength of the secular terms can be estimated as $\hbar/T_2$, the nonsecular resonance conditions cannot be resolved experimentally with accuracy much better than $\pm 1/T_2$. However, if the secular terms are suppressed by other means, then the experimental resolution is limited by the strength of the nonsecular terms themselves. Thus, if the strength of the nonsecular terms is much smaller than $\hbar/T_2$, then the nonsecular resonances can be resolved with proportionally better accuracy.

In the present case, as in several other contexts associated with nuclear-spin dynamics[15–21] and beyond,[22] the properties of the classical limit can be exploited to gain quantitative insight into the behavior of a quantum system, which, as such, may be far from the classical limit. Let us, therefore, think about the averaging procedure presented in this section in terms of classical spin trajectories. The typical situation corresponds to an irrational value of the ratio ω/Ω_e. In this case, the trajectory of a classical spin that follows Eq. (5) is open and ergodic on the spin sphere as illustrated in Fig. 2(a). Averaging over such trajectories leads to the standard two-step truncation result. If ω/Ω_e is a rational number, then the individual spin trajectories become closed, and one can suspect that the averaging result is different from the irrational case. In reality, however, almost all rational values of ω/Ω_e lead to the same averaging results as the irrational values. In the case of like spins, the only exceptions are $\omega/\Omega_e = \{\pm 1/2, -1, -2\}$—see Figs. 2(b)–2(d). The fact that no other rational numbers appear in this set is related to the fact that the interaction Hamiltonian $\mathcal{H}_D$ is of the second order in terms of spin variables. If higher-order spin couplings were involved, e.g., of the form $I_{ix} I_{jx} I_{ky}$, then other ratios with absolute values, such as 1/3 or 3 may also appear in the above set.

IV. RESULTS

In this section, we present the time-averaged Hamiltonians separately for the couplings of like spins (Sec. IV A) and unlike spins (Sec. IV B). Like spins have the same gyromagnetic ratios and, hence, the same Larmor frequencies. Unlike spins have different gyromagnetic ratios and different Larmor frequencies. The Hamiltonians referring to the above two cases are marked by superscripts l and u, respectively. The details of the calculations can be found in Ref. 14.

A. Like spins

Away from the nonsecular resonances, our averaging procedure reproduces the standard truncated Hamiltonian for like spins,[3]

$$\mathcal{H}^l_{D0} = \sum_{i<j}^{N} J_{ij} \frac{1}{2}(3\cos^2\alpha - 1)\left(1 - \frac{3r_{ij,z}^2}{r_{ij}^2}\right) \times \left[I'_{iz} I'_{jz} - \frac{1}{2}(I'_{ix} I'_{jx} + I'_{iy} I'_{jy})\right], \tag{16}$$

where α is given by Eq. (9).

As already mentioned in Sec. III, the averaged Hamiltonian contains additional coupling terms in the case of nonsecular resonances associated with ratios $\omega/\Omega_e = \{\pm 1/2, -1, -2\}$. According to Eq. (6), these ratios translate into the following expressions for ω in terms of Ω_0 and ω_1:

$$\omega = -\Omega_e : \omega = -\frac{\omega_1^2 + \Omega_0^2}{2\Omega_0}, \tag{17}$$

$$\omega = -2\Omega_e : \omega = \frac{-4\Omega_0 \pm 2\sqrt{\Omega_0^2 - 3\omega_1^2}}{3}, \tag{18}$$

$$\omega = \pm\frac{1}{2}\Omega_e : \omega = \frac{\Omega_0 \pm \sqrt{4\Omega_0^2 + 3\omega_1^2}}{3}. \tag{19}$$

The upper (lower) sign before the square root in Eq. (19) corresponds to the upper (lower) sign of the resonant condition $\omega = \pm\frac{1}{2}\Omega_e$. In the case of Eq. (18), both signs before the square root are realizable for the same condition $\omega = -2\Omega_e$ as long as $|\Omega_0| \geqslant \sqrt{3}|\omega_1|$. When the value of ω following from Eq. (17), (18), or (19) is negative, this indicates that frequency vector $\boldsymbol{\omega}$ is antiparallel to $\boldsymbol{H}_0$. The resonance conditions $\omega = \Omega_e$ and $\omega = 2\Omega_e$ are absent in the above list because, after the substitution of Ω_e given by Eq. (6), they give no real-valued solutions for ω.

Now, we list the corresponding averaged Hamiltonians,

$$\omega = -\Omega_e: \mathcal{H}^l_{D1} = \mathcal{H}^l_{D0} + \sum_{i<j}^{N} J_{ij} \left\{ \frac{3}{8}(\cos\alpha - 1)^2 \left[\frac{r^2_{ij,y} - r^2_{ij,x}}{r^2_{ij}} (I'_{ix}I'_{jx} - I'_{iy}I'_{jy}) + \frac{2\, r_{ij,x} r_{ij,y}}{r^2_{ij}} (I'_{ix}I'_{jy} + I'_{iy}I'_{jx}) \right] \right.$$

$$\left. + \frac{3}{2}(\cos 2\alpha - \cos\alpha) \left[-\frac{r_{ij,x} r_{ij,z}}{r^2_{ij}} (I'_{ix}I'_{jz} + I'_{iz}I'_{jx}) + \frac{r_{ij,y} r_{ij,z}}{r^2_{ij}} (I'_{iy}I'_{jz} + I'_{iz}I'_{jy}) \right] \right\}, \tag{20}$$

$$\omega = -2\Omega_e: \mathcal{H}^l_{D2} = \mathcal{H}^l_{D0} + \sum_{i<j}^{N} J_{ij}\, \frac{3}{4}\,[\sin 2\alpha - 2\sin\alpha] \left[\frac{r_{ij,x} r_{ij,z}}{r^2_{ij}} (I'_{ix}I'_{jx} - I'_{iy}I'_{jy}) - \frac{r_{ij,y} r_{ij,z}}{r^2_{ij}} (I'_{ix}I'_{jy} + I'_{iy}I'_{jx}) \right], \tag{21}$$

$$\omega = \pm\frac{1}{2}\Omega_e : \mathcal{H}^l_{D3} = \mathcal{H}^l_{D0} + \sum_{i<j}^{N} J_{ij}\, \frac{3}{8}[\sin 2\alpha \pm 2\sin\alpha] \left[\frac{r^2_{ij,y} - r^2_{ij,x}}{r^2_{ij}} (I'_{ix}I'_{jz} + I'_{iz}I'_{jx}) \mp \frac{2\, r_{ij,x} r_{ij,y}}{r^2_{ij}} (I'_{iy}I'_{jz} + I'_{iz}I'_{jy}) \right]. \tag{22}$$

The upper (lower) sign of the resonance condition of Eq. (22) corresponds to the upper (lower) sign in the expression for $\mathcal{H}^l_{D3}$.

We note that the standard truncated Hamiltonian $\mathcal{H}^l_{D0}$ conserves the z' projection of the total spin polarization $\sum_i I'_{iz}$ in the double-rotating reference frame. This total spin component still relaxes on the time scale on the order of T_1 because of the interaction with electronic spins or phonons. We call this "normal longitudinal relaxation." In contrast, the nonsecular terms appearing in Eqs. (20)–(22) do not conserve $\sum_i I'_{iz}$, which means that all three projections of the total spin polarization decay to zero in both the double-rotating and the laboratory reference frames on a time scale, which is, in general, much faster than T_1. We call this "anomalous longitudinal relaxation."

The nonsecular terms in Eqs. (20)–(22) are comparable with $\mathcal{H}^l_{D0}$ when $H_1 \sim H_0$. In such a case, the time scale of the anomalous longitudinal relaxation is expected to be on the order of T_2, which is clearly much faster than T_1. Therefore, the nonsecular resonances should be readily identifiable in an experiment of the type proposed in Sec. V A.

In the case of $H_1 \ll H_0$, the nonsecular terms can still induce the anomalously fast longitudinal relaxation, but this case requires a more detailed discussion. We first note that all nonsecular terms in Eqs. (20)–(22) are equal to zero when $\alpha = 0$, which, according to Eq. (9), corresponds to $H_1 = 0$. When $H_1 \ll H_0$, the nonsecular terms are much smaller than the terms in $\mathcal{H}^l_{D0}$ in agreement with the standard truncation result of Redfield.[1–3] The values of the α-dependent prefactors of the nonsecular terms in the Hamiltonians (20)–(22) are plotted as functions of H_1/H_0 in Fig. 3 for $H_1/H_0 \leqslant 0.5$. The strongest of these terms are on the order of H_1/H_0. They correspond to the resonances $\omega \approx \Omega_0$ and $\omega \approx -2\Omega_0$ obtained from Eq. (18) with a plus sign and Eq. (19) with a minus sign, respectively, in the limit $H_1/H_0 \to 0$. (In our sign convention, the usual single-spin NMR resonance is located at $\omega \approx -\Omega_0$.)

In general, the nonsecular terms linear in H_1/H_0 should induce a longitudinal relaxation on the time scale on the order of $T_2(H_0/H_1)^2$, which can still be much shorter than T_1 and, thus, can represent a clear indication of a nonsecular resonance. The above estimate is of the second order in terms of H_0/H_1 because the first-order effect of the nonsecular terms should be averaged out by the spin motions due to the much stronger secular terms. In view of this consideration, the observability of the nonsecular resonances can be significantly improved by suppressing the secular Hamiltonian $\mathcal{H}^l_{D0}$. If this is performed, the time scale of the longitudinal relaxation induced by the nonsecular terms can be estimated as $T_2(H_0/H_1)$, i.e., it becomes much faster.

The suppression of $\mathcal{H}^l_{D0}$ makes the observable effects of the nonsecular resonances more dramatic not only in the limit of $H_1 \ll H_0$, but also in the general case of $H_1 \sim H_0$. It can be realized, for example, as follows.

A given nonsecular resonance imposes a constraint on the three parameters H_0, H_1, and ω, which leaves the freedom to impose one additional relationship. This freedom can be used to impose the magic angle condition $1 - 3\cos^2\alpha = 0$. However, this condition together with any of the like-spin nonsecular resonances fixes the ratio H_1/H_0 to be on the order of 1, which means that it cannot be used if the experiment is limited to the regime $H_1 \ll H_0$.

Another resource for suppressing $\mathcal{H}^l_{D0}$ is to exploit the spatially dependent factor $1 - \frac{3r^2_{ij,z}}{r^2_{ij}}$. For example, if the

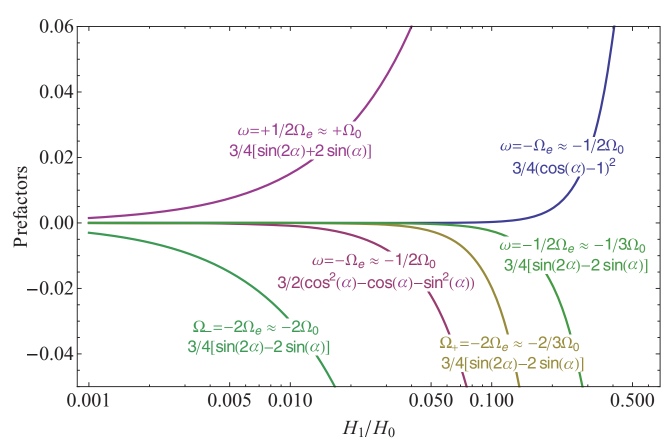

FIG. 3. (Color online) Plots of the α-dependent prefactors of the nonsecular terms in the like-spin Hamiltonians (20)–(22) as functions of the ratio H_1/H_0 for $H_1 < 0.5H_0$. The legend for each line indicates the corresponding resonant condition and the α dependence of the prefactor being plotted. Each resonant condition is given both in its exact form, Eqs. (17)–(19), and in the approximate form for the case $H_1 \ll H_0$. The conditions $\omega_+ = -2\Omega_e$ and $\omega_- = -2\Omega_e$ correspond to the nonsecular resonances (18) with signs (+) or (−), respectively.

nonsecular resonances are to be investigated in CaF_2, where ^{19}F nuclei form a simple cubic lattice, it is better to use the static field along the [111] direction of that lattice. In such a case, $1 - \frac{3r_{ij,z}^2}{r_{ij}^2} = 0$ for all six nearest neighbors of each spin, i.e., the secular interaction with these neighbors is suppressed, whereas, the nonsecular terms remain large.

Of course, the most effective way to suppress the secular interactions for all pairs of interacting spins is to use the MAS technique.[3] This technique completely averages out all factors $1 - \frac{3r_{ij,z}^2}{r_{ij}^2}$ when $\cos^2\Theta = 1/3$, where Θ is the magic angle between the spinning axis and the static magnetic field. Spinning at the magic angle, however, does not completely average out the factors $r_{ij,y}^2 - r_{ij,x}^2$, $r_{ij,x}r_{ij,y}$, or $r_{ij,x}r_{ij,z}$ that enter the nonsecular interaction terms.

B. Unlike spins

In this subsection, we consider coupling between two unlike spin species. We will use lattice index i to label one of these species and index j to label the other. We reintroduce the labeling of gyromagnetic ratios γ_i and γ_j and the corresponding Larmor frequencies $\Omega_{0i} = \gamma_i H_0$ and $\Omega_{0j} = \gamma_j H_0$. The two spin species are now to be described in two different double-rotated reference frames. The effective Larmor frequencies Ω_{ei}, Ω_{ej} and the corresponding tilting angles α_i, α_j are then defined by adding the indices i or j to variables Ω_e, Ω_0, ω_1, and α in Eqs. (6) and (9).

As in the case of like spins, our averaging procedure for unlike spins recovers the standard truncated Hamiltonian[3] away from the nonsecular resonances,

$$\mathcal{H}_{D0}^u = \sum_{\langle i,j\rangle} J_{ij}\frac{1}{2}[3\cos\alpha_i\cos\alpha_j - \cos(\alpha_i - \alpha_j)] \times \left(1 - \frac{3r_{ij,z}^2}{r_{ij}^2}\right) I'_{iz}I'_{jz}, \tag{23}$$

where the sum $\sum_{\langle i,j\rangle}$ includes all pairs of unlike spins.

It should be mentioned here, that, in the very special cases of $\gamma_i = -\gamma_j$ and $\omega = 0$, the secular Hamiltonian $\mathcal{H}_{D0}^u$ should also include the so-called "double-flip" terms $I'_{i+}I'_{j+}$ and $I'_{i-}I'_{j-}$, where $I'_{i\pm} = I'_{ix} \pm I'_{iy}$, etc. These terms are preserved by the averaging because their counterparts $I_{i+}I_{j+}$ and $I_{i-}I_{j-}$ in the original full Hamiltonian (1) now conserve the Zeeman energy. This case can be mapped onto a somewhat unusual problem of like spins by changing the sign of all y- and z-spin projections for one of the two spin species, e.g., $I_{jy} \to -I_{jy}$ and $I_{jz} \to -I_{jz}$. However, when $\omega \neq 0$, the two spin species in the transformed problem will experience rf fields rotating in the opposite directions, which means that the transformed problem is not equivalent to the problem of like spins in a single-rotating field.

Another special case is $\gamma_j \to 0$. It implies that the terms of type $I_{iz}I_{j\pm}$ in the full Hamiltonian (1) become secular, and, as a result, terms $I'_{iz}I'_{j\pm}$ may appear in $\mathcal{H}_{D0}^u$. Such a limit is not realizable physically in the case of magnetic dipole interaction because $\gamma_j = 0$ simultaneously suppresses the interaction itself.

The above special cases should be kept in mind in the analysis of the parameter dependence of the nonsecular resonances.

There exist two kinds of unlike nonsecular resonances, namely, the resonances involving the motion of only one spin species and the resonances involving both spin species. The resonances of the first kind are the following:

$$\omega = -\Omega_{ei}: \omega = -\frac{\omega_{1i}^2 + \Omega_{0i}^2}{2\Omega_{0i}}, \tag{24}$$

$$\omega = \pm\frac{1}{2}\Omega_{ei}: \omega = \frac{-\Omega_{0i} \pm \sqrt{4\Omega_{0i}^2 + 3\omega_{1i}^2}}{3}, \tag{25}$$

and those obtained from Eqs. (24) and (25) by replacing index i with index j. The resonances of the second kind are

$$\omega = (-1)^n \tfrac{1}{2}(\Omega_{ei} \pm \Omega_{ej}), \tag{26}$$

$$\omega = (-1)^n(\Omega_{ei} \pm \Omega_{ej}), \tag{27}$$

where variable n takes values 0 or 1 and, thus, controls the sign in front of the entire expression. Resonant conditions (26) and (27) lead to fourth-order polynomial equations with respect to ω, which, in principle, can be solved analytically. However, in view of the cumbersome character of the resulting formulas, we chose to investigate the solutions numerically. Several plots illustrating the character of these solutions are presented in Fig. 4 and further in Fig. 5 of the Appendix. As evident from these plots, it cannot be guaranteed that each of the eight conditions envisioned by Eqs. (26) and (27) is realizable for a given set of values of γ_i, γ_j, H_0, and H_1. For example, if $\gamma_i,\gamma_j > 0$, then no value of ω exists that would satisfy the condition $\omega = 1/2(\Omega_{ei} + \Omega_{ej})$.

The time-averaged Hamiltonians corresponding to the nonsecular resonances (26) and (27) are the following:

$$\omega = -\Omega_{ei}: \mathcal{H}_{D1}^u = \mathcal{H}_{D0}^u + \sum_{\langle i,j\rangle} J_{ij}\frac{3}{2}[\cos(\alpha_i + \alpha_j) - \cos\alpha_j]\left[-\frac{r_{ij,x}r_{ij,z}}{r_{ij}^2}I'_{ix}I'_{jz} + \frac{r_{ij,y}r_{ij,z}}{r_{ij}^2}I'_{iy}I'_{jz}\right], \tag{28}$$

$$\omega = \pm\frac{1}{2}\Omega_{ei}: \mathcal{H}_{D2}^u = \mathcal{H}_{D0}^u + \sum_{\langle i,j\rangle} J_{ij}\frac{3}{4}[\sin\alpha_j(\cos\alpha_i \pm 1)]\left[\frac{r_{ij,y}^2 - r_{ij,x}^2}{r_{ij}^2}I'_{ix}I'_{jz} \mp \frac{2r_{ij,x}r_{ij,y}}{r_{ij}^2}I'_{iy}I'_{jz}\right], \tag{29}$$

$$\omega = (-1)^n(\Omega_{ei} \pm \Omega_{ej}): \mathcal{H}_{D3}^u = \mathcal{H}_{D0}^u + \sum_{\langle i,j\rangle} J_{ij}\frac{3}{4}[\sin(\alpha_i + \alpha_j) \pm (-1)^n\sin\alpha_i + (-1)^n\sin\alpha_j] \times\left[\frac{r_{ij,x}r_{ij,z}}{r_{ij}^2}(I'_{ix}I'_{jx} \mp I'_{iy}I'_{jy}) + (-1)^n\frac{r_{ij,y}r_{ij,z}}{r_{ij}^2}(\pm I'_{ix}I'_{jy} + I'_{iy}I'_{jx})\right], \tag{30}$$

$$\omega = (-1)^n \frac{1}{2}(\Omega_{ei} \pm \Omega_{ej}) : \mathcal{H}_{D4}^u = \mathcal{H}_{D0}^u + \sum_{\langle i,j \rangle} J_{ij} \frac{3}{8}[\cos \alpha_i + (-1)^n][\cos \alpha_j \pm (-1)^n]$$
$$\times \left[\frac{r_{ij,y}^2 - r_{ij,x}^2}{r_{ij}^2} (I'_{ix} I'_{jx} \mp I'_{iy} I'_{jy}) - (-1)^n \frac{2 r_{ij,x} r_{ij,y}}{r_{ij}^2} (\pm I'_{ix} I'_{jy} + I'_{iy} I'_{jx}) \right]. \tag{31}$$

The upper (lower) sign of the nonsecular resonances of Eqs. (30) and (31) corresponds to the upper (lower) signs in the corresponding Hamiltonians. In the case of a small mismatch of the above resonant conditions, the additional term (15) for

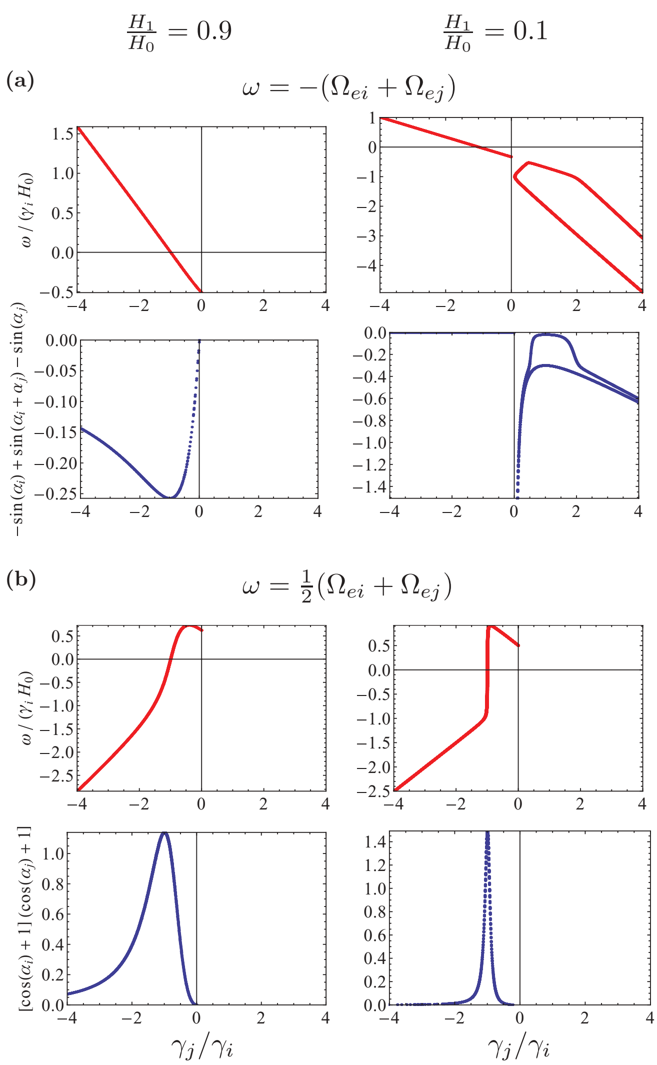

FIG. 4. (Color online) Examples of nonsecular resonances for unlike spins. Plots of the resonant values of ω and the prefactors in the nonsecular Hamiltonians (30) and (31) as functions of γ_j/γ_i for two resonant conditions indicated above the respective plots. All examples presented are obtained numerically for either $H_1/H_0 = 0.9$ or $H_1/H_0 = 0.1$. Each column of plots corresponds to the ratio H_1/H_0 indicated above it. The plot lines consist of the actual computed points and, thus, in some cases, have the appearance of dotted lines. The results for $H_1/H_0 = 0.1$ are qualitatively representative of the limit $H_1 \ll H_0$. The analogous plots for the six remaining resonant conditions associated with Eqs. (30) and (31) are given in the Appendix.

one or both spin species should be included. In the case of resonances (30) and (31), one, in fact, has the freedom of distributing the mismatch between the two spin species.

The standard truncated Hamiltonian (23) conserves both $\sum_i I'_{iz}$ and $\sum_j I'_{jz}$, whereas, each of the nonsecular Hamiltonians (28)–(31) violates the above conservation for at least one of the two spin species. We observe, however, that the total z' polarization of both spin species, i.e., $\sum_i I'_{iz} + \sum_j I'_{jz}$, is still conserved by the nonsecular Hamiltonians given by Eq. (30) for $\omega = \pm(\Omega_{ei} - \Omega_{ej})$ and by Eq. (31) for $\omega = \pm\frac{1}{2}(\Omega_{ei} - \Omega_{ej})$ because the terms in these Hamiltonians have the character of the so-called "flip-flops."

In general, the nonsecular Hamiltonians (24)–(27) are comparable to the standard truncated Hamiltonian (23) when H_1 is comparable to H_0—see the plots in Fig. 4 for $H_1/H_0 = 0.9$. If $H_1 \ll H_0$, then the nonsecular terms are normally small because Eq. (9) gives the values of α_i and α_j either close to 0 or to π—Figs. 5(c), 5(d), and 5(f) for $H_1/H_0 = 0.1$.

However, as the plots in Figs. 4 and 5(a), 5(b), and 5(e) for $H_1/H_0 = 0.1$ indicate and our approximate calculations confirm, there are interesting and potentially useful exceptions when the angle-dependent prefactors of the nonsecular Hamiltonians remain comparable to 1, even though $H_1 \ll H_0$. The first exception corresponds to the condition $\gamma_j/\gamma_i \approx -1$ for the nonsecular resonances $\omega = \pm 1/2(\Omega_{ei} - \Omega_{ej})$ and $\omega = 1/2(\Omega_{ei} + \Omega_{ej})$. In these cases, the nonsecular terms in Hamiltonians (31) remain large as long as $|\gamma_j/\gamma_i + 1| \lesssim H_1/H_0$. [In the case of resonance $\omega = 1/2(\Omega_{ei} + \Omega_{ej})$, one should also be mindful of adding the secular double-flip contribution mentioned after Eq. (23).] This group of resonances can, thus, be exploited for pairs of nuclei satisfying the condition $\gamma_i \approx -\gamma_j$, such as, e.g., ^{129}Xe and ^{23}Na. The second exception corresponds to the condition of $\gamma_j/\gamma_i \approx 0$ (or $\gamma_i/\gamma_j \approx 0$) for the resonances $\omega = \pm(\Omega_{ei} + \Omega_{ej})$. The corresponding nonsecular Hamiltonians (30) are large as long as $|\gamma_j/\gamma_i| \lesssim H_1/H_0$. These nonsecular resonances can be very useful for the purposes of cross polarization when the gyromagnetic ratio of one of the two nuclei is much smaller than the other.

Finally, we mention that, as in the case of like spins, the suppression of the secular interaction terms between unlike spins by matching the magic angle condition or by the MAS technique is an additional resource for observing the nonsecular resonances. The only difference in the present case is that the magic angle condition involves two angles: $3 \cos \alpha_i \cos \alpha_j - \cos(\alpha_i - \alpha_j) = 0$.

V. DISCUSSION

A. Experimental realizability

The standard truncated Hamiltonians (16) and (23) conserve the z' projection of the total spin polarization for each of the available spin species in their respective double-rotated reference frames. The most obvious qualitative effect of the nonsecular Hamiltonians is that they do not conserve this total z' projection for at least one of the spin species. This difference can be tested experimentally. In the case of like spins, it leads to the anomalously fast longitudinal relaxation discussed in Sec. IV A. In the case of unlike spins, it may, in addition, lead to an anomalous cross-polarization effect.

To be specific, a possible way to observe the anomalous longitudinal relaxation can consist of the following steps: (i) polarizing the system in the static magnetic field, (ii) turning on the rf field (preferably, adiabatically) to match one of the nonsecular resonance conditions, (iii) waiting enough time for the additional interaction terms to relax $\sum_i I'_{iz}$ (the waiting time should still be much shorter than T_1), and finally, (iv) suddenly turning off the rf field. No free-induction decay signal should be observable in this case. In contrast, away from the nonsecular resonances, a free-induction decay signal of finite intensity should always be observable for waiting times on the order of T_1.

The requirements for the above kind of experiments are the following: (1) The static and the rf fields should be strong enough to ensure $\Omega_0,\omega_1 \gg 1/T_2$. (2) As discussed in the context of Eq. (15), the nonsecular resonances should be matched to an accuracy of roughly $\frac{1}{T_2}$. (3) The static and the rf magnetic fields should be relatively homogeneous, otherwise, the non-secular-resonance conditions cannot be satisfied over the entire sample. (4) The strength of the resonantly coupled terms must be such that the time scale associated with the anomalous relaxation of the longitudinal magnetization is faster than T_1 (see the end of Sec. IV A). (5) Finally, in the case of $H_1 \sim H_0$, a real circularly polarized rf field should be used, as performed, e.g., in Ref. 23.

Now, we discuss the observability of the nonsecular resonances in the NMR setting that uses a linearly polarized rf field in the regime of $H_1 \ll H_0$. The latter condition extends to the experiments in larger static fields, which means stronger NMR signals.

The Hamiltonian averaging procedure used in this paper cannot be straightforwardly extended to linearly polarized rf fields because a closed analytical solution for the spin motion is not available in such a case. In particular, the usual assumption that one can neglect one of the two counter-rotating components contributing to the linearly polarized rf field is not justified when $H_1 \sim H_0$. However, when $H_1 \ll H_0$, the case of the linearly polarized rf field should be treatable by combining our truncation procedure with the perturbation expansion.[2,24] In this limit, the presence of two rotating components may lead to additional nonsecular resonances, but the resonances obtained in the present paper for a single-rotating component of the same frequency should also be present. We further expect that the same nonsecular resonance in the rotating and the linearly polarized settings is generically characterized by the same nonsecular Hamiltonian when the leading order of the expansion of this Hamiltonian in terms of H_1/H_0 is linear (see the discussion in Sec. IV A). At small values of H_1/H_0, the nonsecular resonances, satisfying the above linearity requirement, are also the strongest and, thus, the most promising in terms of experimental observation. In fact, the low-field NMR relaxation study of protons in ice reported in Ref. 25 may have observed such a nonsecular resonance as a secondary peak, appearing in that paper in Fig. 7(a).

In the above context, we finally note that an experiment with small linearly polarized fields should avoid the interplay with the secondary single-spin resonances described by Winter.[2,26]

In addition to the possibility of using stronger static fields and linearly polarized rf fields, the regime of $H_1 \ll H_0$ has two other advantages. First, the rf-field homogeneity requirement is less stringent when $H_1 \ll H_0$ because what matters is the homogeneity of the effective frequencies Ω_{ei} for which the leading rf-field contribution is only on the order of $(H_1/H_0)^2$. Second, in the case when the secular part of the interaction is externally suppressed, the smallness of H_1/H_0 implies that the nonsecular resonances can be resolved with higher accuracy (see the discussion in Sec. III).

B. Possible applications

1. Fundamental studies of spin-spin relaxation

Perhaps, the most direct use of the tunable Hamiltonians (20)–(22) and (28)–(31) is to conduct fundamental experimental studies of nuclear-spin-spin relaxation in solids, which is still not completely understood, in a much broader range of parameters than those accessible with the standard truncated Hamiltonians.

2. Cross polarization

In the case of unlike spins, the nonsecular Hamiltonians (30) and (31) for the resonances $\omega = \pm(\Omega_{ei} - \Omega_{ej})$ and $\omega = \pm\frac{1}{2}(\Omega_{ei} - \Omega_{ej})$ can be used to cross polarize different spin species. As mentioned in Sec IV B, these Hamiltonians contain flip-flop terms $I'_{ix}I'_{jy} - I'_{iy}I'_{jx}$ and $I'_{ix}I'_{jx} + I'_{iy}I'_{jy}$, which can transfer polarization from one spin species to the other. Such a transfer would require an rf field rotating with a single frequency as opposed to the standard Hartmann-Hahn cross-polarization routine,[27] which involves two rf-field frequencies. The two spin species can also be cross polarized, albeit less efficiently, using the transient effect of the double-flip terms $I'_{ix}I'_{jy} + I'_{iy}I'_{jx}$ and $I'_{ix}I'_{jx} - I'_{iy}I'_{jy}$ for resonances $\omega = \pm(\Omega_{ei} + \Omega_{ej})$ and $\omega = \pm\frac{1}{2}(\Omega_{ei} + \Omega_{ej})$. The suppression of the secular terms by either the magic angle condition or the MAS technique as discussed in Sec. IV B, can enhance the efficiency of both the flip-flop-based and the double-flip-based cross-polarization processes. In the latter case, this enhancement should be particularly significant.

3. Structure determination

The use of solid-state NMR for determining the structures of complex molecules involves MAS decoupling between nuclear spins followed by selective recoupling.[28,29] The nonsecular resonances obtained in this paper can, possibly, be used at the latter stage. As discussed in Sec. V A, the regime $H_1 \ll H_0$ may provide both the sufficient intensity and the sufficient frequency resolution for such experiments. If successful, such a method will not require the recoupling sequence to be adjusted to the sample spinning frequency. It will also have an added benefit of the nontrivial spatial dependence in the nonsecular Hamiltonians as compared to the

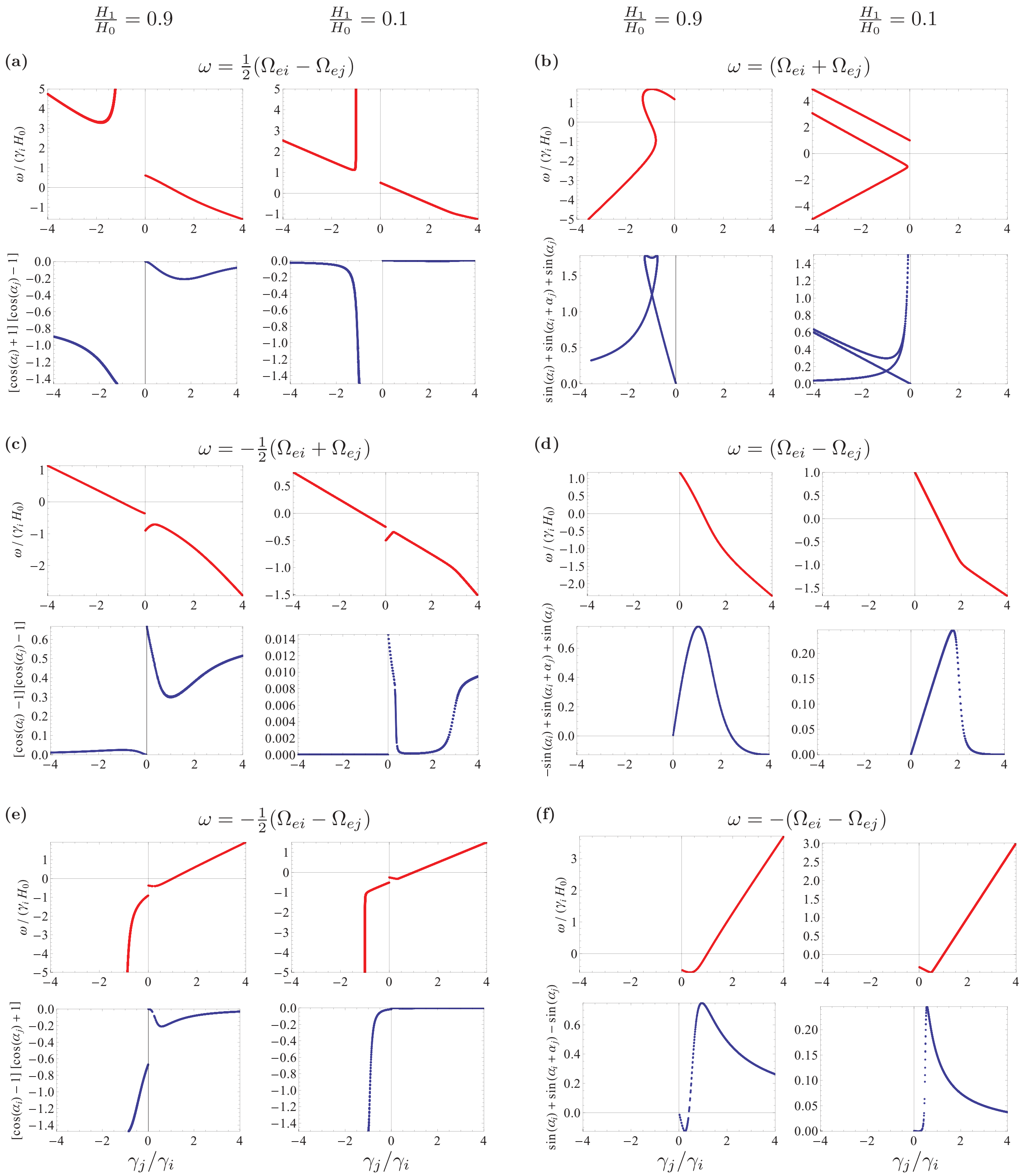

FIG. 5. (Color online) Examples of nonsecular resonances for unlike spins. Plots of the resonant values of ω and the prefactors in the nonsecular Hamiltonians (30) and (31) as functions of γ_j/γ_i for the resonant conditions indicated above the respective plots. All examples presented are obtained numerically for either $H_1/H_0 = 0.9$ or $H_1/H_0 = 0.1$. Each column of plots corresponds to the ratio H_1/H_0 indicated above it. The plot lines consist of the actual computed points and, thus, in some cases, have the appearance of dotted lines. The results for $H_1/H_0 = 0.1$ are qualitatively representative of the limit $H_1 \ll H_0$. The content of this figure together with Fig. 4 covers all eight resonant conditions associated with Eqs. (30) and (31).

usual secular interactions. This dependence can be converted into additional structure information for oriented samples.

To summarize, the nonsecular resonances for like and unlike spins amount to a new resource for manipulating nuclear spins, and, therefore, are likely to be useful for various NMR applications. However, the condition of applying a high-amplitude rf field for a rather long time may be challenging to realize in practice.

VI. CONCLUSION

In this paper, we theoretically described the properties of nonsecular resonances associated with the appearance of nonsecular terms in the time-averaged Hamiltonians of nuclear-spin-spin interactions in solids in the presence of strong rotating rf fields. Our analysis indicates that, under certain conditions, the effect of the nonsecular interaction terms should be particularly well observable. We have also discussed the extension of our findings for the case of linearly polarized rf fields. Finally, we discussed how the nonsecular resonances considered in this paper can be used for manipulating nuclear spins in various NMR applications.

Beyond NMR, the results of this paper apply to the mathematically equivalent problems, involving two interacting two-level systems, e.g., q bits, driven by an external rotating field.

Note added. After submitting this paper, we became aware of the preprint of a closely related paper[30] where a similar nonsecular resonance phenomenon was discovered under the name of "entanglement resonances." The analysis in Ref. 30 is based on the numerical solution of a two-spin-1/2 Floquet problem with a linearly polarized periodic magnetic field. As we expected, the leading resonances reported in Ref. 30 for the case of small linearly polarized oscillating fields agree with the like-spin resonances obtained in the present paper for the case of small-rotating rf fields [cf. Eqs. (17)–(19) of this paper and Fig. 2(b) of Ref. 30].

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APPENDIX: PLOTS OF NONSECULAR RESONANCES FOR UNLIKE SPINS

This appendix contains the collection of plots (Fig. 5) for the six-out-of-eight nonsecular resonances described by Eqs. (30) and (31) that were not included in Fig. 4.

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