Symmetry relations in phase-sensitive magnetic-resonance spectroscopy

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We have found symmetry relations which are generally applicable to most signals of phase-sensitive magnetic-resonance spectroscopy. One of them is a kind of reciprocal relation connecting the signals before and after magnetic-field reversal, and is based on a symmetry property of a system under an antiunitary transformation: time reversal. The relation tells us that the phase of a signal is closely related to the behavior of the signal when a static magnetic field is reversed. Another is a relation which originates from a symmetry property under a unitary transformation. From this, we can obtain information on a geometrical symmetry of a system. Some phenomena of phase-sensitive magnetic-sublevel spectroscopy are exemplified. The usefulness of these relations is also discussed.

I. INTRODUCTION

Many kinds of spectroscopic techniques have been devised and used in order to investigate the magnetic resonance in gases and solids [1–3]. The standard NMR and electron-spin resonance (ESR) techniques are now widely used in many fields of science. Also optical techniques have been extensively used because of their high sensitivity. Population differences between magnetic sublevels can be greatly enhanced from their thermal equilibrium values by optical pumping [3], and an optical photon is sensitively detectable.

Optical methods for a magnetic resonance detection may be classified into two categories as follows.

One method is to detect a change of the sublevel population associated with the magnetic resonance. The magnetic resonance is detected by the change of the intensity or polarization of a transmitted or fluorescent light. Conventional optical-rf double resonance [4], optical hole burning [5], optically detected coherent transients [6], photon-echo nuclear double resonance (PENDOR) [7], and so on are involved.

Another method is to detect sublevel coherence. In techniques such as quantum beats (QB) [8] [QB echo, QB free induction decay, synchronized QB (echo) [10]), and coherent Raman beat (CRB) [9], sublevel coherence is optically created and detected, whereas the Raman heterodyne technique [11,12] consists of an optical detection of rf-induced sublevel coherence.

Rather generally adopted in the methods of the latter category is phase-sensitive detection (PSD). It has provided us with additional information on sublevel resonance. Not only can we know about the resonance frequency but also about whether the signal we observe is the in-phase or out-of-phase response to the excitation. In this sense we call these phase-sensitive magnetic-resonance spectroscopies (PSMRS). Of course the standard NMR spectroscopy often makes use of PSD technique as well. In some cases this phase-selectivity is quite

important [13].

In this paper we report on fundamental relations which we have discovered for signals of PSMRS in general. One of these is a kind of reciprocal relation connecting the signals before and after magnetic-field reversal, and is closely related to time-reversal symmetry [14]. Another is a symmetry relation which is based on a symmetry property of the system under a unitary transformation. These relations have not been reported so far by others in spite of the simple form and generality. They can be powerful means for analyzing the signal of PSMRS which often shows complicated behaviors just because of the additional information on a phase of the signal.

In Sec. II we define a system and derive the relations. Clear examples of the relations are given and discussed in Sec. III. The utility of the relations is mentioned in Sec. IV.

II. SYMMETRY RELATION

In this section we define a system which is treated in this paper and derive the symmetry relations.

We consider the Hamiltonian $H(\mathbf{a})$ which depends on a set of parameters $\mathbf{a}$ $(a_1, a_2, \ldots, a_M)$. M is an integer. The eigenvalues $E_k(\mathbf{a})$ and eigenvectors $|\phi_k(\mathbf{a})>$ also depend parametrically on $\mathbf{a}$;

$$H(\mathbf{a})|\phi_k(\mathbf{a})\rangle = E_k(\mathbf{a})|\phi_k(\mathbf{a})\rangle \quad (k = 1, 2, \ldots, N) .$$

N is an integer. We restrict ourselves to the nondegenerate case:

$$E_k(\mathbf{a})\langle E_l(\mathbf{a}) \quad \text{if } k \langle l \ (k,l = 1, 2, \ldots, N) .$$

We set that this Hamiltonian is to be transformed by some unitary or antiunitary transformation T into $H(\mathbf{b})$,

$$TH(\mathbf{a})T^{-1} = H(\mathbf{b}) , \tag{1}$$

where $\mathbf{b}$ is another set of parameters $b_1, b_2, \ldots, b_M$. Then we can obtain the following results:

$$E_k(\mathbf{b}) = E_k(\mathbf{a}) \tag{2}$$

and

$$|\phi_k(\mathbf{b})\rangle = T|\phi_k(\mathbf{a})\rangle \tag{3}$$

apart from an arbitrary phase factor [14].

Before going to the next case, let us consider a special case. T is an antiunitary transformation K: time reversal, and $\mathbf{a}$ is an externally applied static magnetic field $\mathbf{H}$. In this case we have the following relation:

$$KH(\mathbf{H})K^{-1} = H(-\mathbf{H}) . \tag{4}$$

That is, $\mathbf{b} = -\mathbf{H}$. This can be derived from the fact that any system has to retain time-reversal symmetry when we include a source of the magnetic field [15]. Then we obtain in this case

$$E_k(-\mathbf{H}) = E_k(\mathbf{H}) \tag{5}$$

and

$$|\phi_k(-\mathbf{H})\rangle = K|\phi_k(\mathbf{H})\rangle . \tag{6}$$

Now we consider the mechanism of the PSMRS. It can be divided into two stages. The first is the creation of the magnetic-sublevel coherence. Various kinds of processes are considered [16]. In principle any degree of multiphoton process can be considered for a multilevel
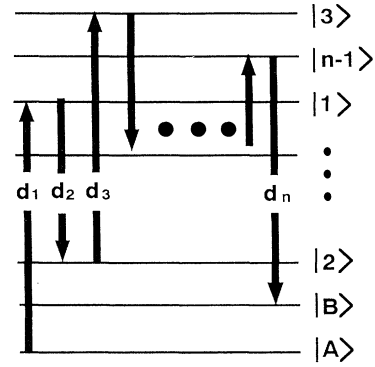

FIG. 1. Schematic diagram of a particular n-photon process to create the coherence between levels $|A\rangle$ and $|B\rangle$. Each one-photon process is here assumed to be a resonant one to the particular transition. d_k is the transition operator responsible for the $|k-1\rangle\leftrightarrow|k\rangle$ transition.

system. The process is described by a density operator of the system. We consider the sublevels $|A\rangle$ and $|B\rangle$ and set that the coherence between them is created by an n-photon process (see Fig. 1). We now start with the following nth-order perturbation solution for the density matrix element [17]:

$$\rho_{AB}^{*(n)}(t) = \left[\frac{i}{\hbar}\right]^n \left[\int_0^t dt_1 \int_0^{t_1} dt_2 \cdots \int_0^{t_{n-1}} dt_n \langle A|[\ldots[[\rho^*(0),H_1^*(t_n)],H_1^*(t_{n-1})],\ldots,H_1^*(t_1)]|B\rangle\right]_{\text{av}}, \tag{7}$$

where $\rho_{AB}^{*(n)}(t)$ is the nth-order density matrix element and $H_1^*(t)$ is the interaction Hamiltonian (an asterisk denotes that the quantity is in the interaction picture). $[\ ]_{\text{av}}$ is a statistical average to incorporate relaxation effects. If we set that $A, B_1, B_2, \ldots, B_n$ are an arbitrary set of operators, we have the following relation [18]:

$$[\ldots[[A,B_1],B_2],\ldots,B_n] = \sum_{N_1,N_2,\ldots,N_n=0}^1 (-B_n)^{N_n}(-B_{n-1})^{N_{n-1}} \cdots (-B_1)^{N_1} A (B_1)^{1-N_1}(B_2)^{1-N_2} \cdots (B_n)^{1-N_n}$$

$$= \sum_{N_1,N_2,\ldots,N_n=0}^1 \left\{\prod_{l=n}^1 (-B_l)^{N_l}\right\} A \left\{\prod_{m=1}^n (B_m)^{1-N_m}\right\} . \tag{8}$$

Substituting $\rho^*(0)$ and $H_1^*(t_k)$ for A and B_k $(k=1,2,\ldots,n)$ in the above, we obtain from Eq. (7) the following expression:

$$\rho_{AB}^{*(n)}(t) = \sum_{N_1,N_2,\ldots,N_n=0}^1 \left[\frac{i}{\hbar}\right]^n \left[\int_0^t dt_1 \int_0^{t_1} dt_2 \cdots \int_0^{t_{n-1}} dt_n \langle A| \left\{\prod_{l=n}^1 [-H_1^*(t_l)]^{N_l}\right\}\rho^*(0)\left\{\prod_{m=1}^n [H_1^*(t_m)]^{1-N_m}\right\}|B\rangle\right]_{\text{av}} . \tag{9}$$

This is somewhat different from that in Ref. [19].

Here we express explicitly $H_1^*(t)$ as

$$H_1^*(t) = \sum_{k=1}^n h_k^*(t) = \sum_{k=1}^n \{-\mathbf{d}_k^* \cdot \mathbf{A}_k(t)\}$$

$$= \sum_{k=1}^n (-\mathbf{d}_k^* \cdot \mathbf{e}_k)A_k(t) = \sum_{k=1}^n [-d_k^* A_k(t)] ,$$

where $A_k(t)$ represents the electromagnetic field, and $d_k^* = \exp(iH_0t/\hbar)d_k\exp(-iH_0t/\hbar)$ the corresponding transition operator. We shall treat only the cases where

$\mathbf{d}_k$ is an electric or magnetic dipole operator and the polarization of the electromagnetic field ($\mathbf{A}_k$), expressed by a unit vector $\mathbf{e}_k$, is a linear polarization. And we treat a particular n-photon process where each one-photon process involved is resonant or near resonant to a particular transition as follows (see Fig. 1):

$$|A\rangle \underset{h_1^*}{\leftrightarrow}|1\rangle \underset{h_2^*}{\leftrightarrow}|2\rangle \underset{h_3^*}{\leftrightarrow} \cdots \underset{h_{n-1}^*}{\leftrightarrow} |n-1\rangle \underset{h_n^*}{\leftrightarrow}|B\rangle . \tag{10}$$

We shall derive, in the following, symmetry relations for this n-photon process.

Then the transition matrix element for the $|k-1\rangle \leftrightarrow |k\rangle$ transition can be written as follows:

$$\langle k-1|H_1^*(t)|k\rangle = \langle k-1|h_k^*(t)|k\rangle$$
$$= \langle k-1|-d_k^* A_k(t)|k\rangle$$
$$= \langle k-1|-d_k|k\rangle A_k^*(t) ,$$

where $A_k^*(t) = A_k(t)\exp[i(E_{k-1}-E_k)t/\hbar]$. After simple but long calculations we can obtain the formula

$$\rho_{AB}^{*(n)}(t) = i^n \mu_{AB}^{(n)} f^{(n)}(t) , \tag{11}$$

where

$$\mu_{AB}^{(n)} = \langle A|d_1|1\rangle \langle 1|d_2|2\rangle \cdots \langle n-1|d_n|B\rangle ,$$

$$f^{(n)}(t) = \left[\int_0^t dt_1 \int_0^{t_1} dt_2 \cdots \int_0^{t_{n-1}} dt_n g^{(n)}(t_1,t_2,\ldots,t_n)\right]_{av} ,$$

$$g^{(n)}(t_1,t_2,\ldots,t_n) = \hbar^{-n} \sum_{k=0}^n (-1)^k \sum_{\substack{0 \le p_i \langle p_{i+1} \le n , \\ 0 \le q_i < q_{i+1} \le n}}' A_1^*(t_{p_k}) A_2^*(t_{p_{k-1}}) \cdots A_k^*(t_{p_1})$$

$$\times \rho_{kk}^*(0) A_{k+1}^*(t_{q_1}) A_{k+2}^*(t_{q_2}) \cdots A_n^*(t_{q_{n-k}}) .$$

Here $\sum'$ means that the summation is restricted to the cases $p_i \ne q_j$, and we have assumed that the initial density operator $\rho^*(0)$ has only diagonal matrix elements. We can therefore obtain

$$\rho_{AB}^{(n)}(t) = \langle A|\exp(-iH_0t/h)\rho^{*(n)}(t)\exp(+iH_0t/h)|B\rangle$$
$$= i^n \mu_{AB}^{(n)} f^{(n)}(t)\exp(i\omega_{AB}t) , \tag{12}$$

where $\omega_{AB} = (E_B-E_A)/\hbar$ is an angular frequency of the sublevel resonance. Because of Eq. (2) the absolute value and even the sign of ω_{AB} are definitely determined. We must note that $f^{(n)}(t)$ is in general a complex quantity because of the phase factors in $A_k^*(t)$. But we here treat the case that these phase factors cancel out and $f^{(n)}(t)$ is a real constant. This is because we are to observe a phase-sensitive signal using the electromagnetic fields whose relative phase relations are definitely fixed.

The next is the detection stage of the sublevel coherence. This is done by a coherent Raman process. An excitation of the system where sublevel coherence exists results in the creation of a Raman light which is coherently related to the excitation (see Fig. 2). The density operator for the coherent Raman process can be calculated in the similar way, and is described in detail in Refs. [11,20]. We generally expect, therefore, that the signals can be
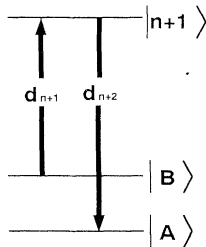

FIG. 2. Schematic diagram of a coherent Raman process to detect the coherence between levels $|A\rangle$ and $|B\rangle$. The transition between levels $|B\rangle$ and $|n+1\rangle$ is here assumed to be resonant.

written in the form

$$I_s(t) = \alpha \, \mathrm{Re}[i^p \sigma^{(p)}\exp(i\omega_{AB}t)] . \tag{13}$$

Here α is a real number, and $\sigma^{(p)}$ is a product of the transition matrix elements relevant to the creation and detection of the sublevel coherence:

$$\sigma^{(p)} = \mu_{AB}^{(n)} \langle B|d_{n+1}|n+1\rangle \langle n+1|d_{n+2}|A\rangle$$
$$= \prod_{k=1}^p \langle k-1|d_k|k\rangle , \tag{14}$$

where $p = n+2$ and $|0\rangle = |p\rangle = |A\rangle$ and $|n\rangle = |B\rangle$. This quantity depends on the static magnetic field. It is, in general, a complex number and determines the phase of the signal, as is readily known from Eq. (13).

Now we shall derive symmetry relations of the signal, or of the quantity $\sigma^{(P)}$ using the above relations.

First we derive a symmetry relation which is related to the antiunitary transformation: time reversal. The transformation property of d_k with respect to time reversal is [14]

$$Kd_kK^{-1} = (-1)^{D_k}d_k , \tag{15}$$

where D_k is 1 if d_k is a magnetic dipole operator and 0 if d_k is an electric dipole operator.

For the kth transition matrix element we obtain

$$\langle k-1|d_k|k\rangle(-\mathbf{H}) = \langle k-1(-\mathbf{H})|d_k|k(-\mathbf{H})\rangle$$
$$= [\langle k-1(\mathbf{H})|K^{-1}]d_k[K|k(\mathbf{H})\rangle]$$
$$= [\langle k-1(\mathbf{H})|(K^{-1}d_kK)|k(\mathbf{H})\rangle]^*$$

from Eq. (6) and antilinearity of K [14]. And finally from Eq. (15) we obtain

$$\langle k-1|d_k|k\rangle(-\mathbf{H}) = (-1)^{D_k}[\langle k-1(\mathbf{H})|d_k|k(\mathbf{H})\rangle]^*$$
$$= (-1)^{D_k}[\langle k-1|d_k|k\rangle(\mathbf{H})]^* . \tag{16}$$

Therefore from the definition of $\sigma^{(p)}$ [Eq. (14)] we obtain

the relation

$$\sigma^{(p)}(-\mathbf{H})=(-1)^{\sum\limits_{k=0}^{p} D_k}[\sigma^{(p)}(\mathbf{H})]^* .$$ (17)

This is one of the main results of this paper. This is a kind of reciprocal relation in that it connects the signals before and after the magnetic-field reversal. For the process where $\sum_{k=0}^{p} D_k$ is odd, for example, the signal changes its sign for magnetic-field reversal if $\sigma^{(p)}$ is real, and does not change its sign if $\sigma^{(p)}$ is purely imaginary. That is, it tells us that the phase of the PSMRS signal is closely related to the change of the signal with magnetic-field reversal. For Raman heterodyne signals (RHS) in Pr^{3+}:LaF_3 a restricted form of this relation was obtained by using the explicit expressions of the wave functions, and has been called a general symmetry law [20]. But we have here derived the relation from a more general point of view: time-reversal symmetry, regardless of the detailed character of the system.

It can be said, from the viewpoint of the time-reversal symmetry, that in the absence of a magnetic field the Kramer's theorem [14] holds, and in the presence of a magnetic field the reciprocal relation [Eq. (17)] holds for the signal of PSMRS.

Next we shall derive a symmetry relation for $\sigma^{(p)}$ which is originated from a symmetry property of the system under a unitary transformation U. We assume that the transformation property of d_k with respect to U can be written in the form

$$U d_k U^{-1}=(-1)^{D_k'} d_k ,$$ (18)

where D_k' takes a value of 1 or 0 depending on the nature of d_k. Then in a similar way we can obtain another important result of this paper:

$$\sigma^{(p)}(\mathbf{b})=(-1)^{\sum\limits_{k=0}^{p} D_k'}\sigma^{(p)}(\mathbf{a})$$ (19)

using Eqs. (6) and (18).

It must be noted that whenever a signal is obtained including the quantity $\sigma^{(p)}$ in its expression, with or without the use of the coherent Raman process, the signal should have symmetry properties resulting from the symmetry relations of $\sigma^{(p)}$ [21].

The restriction on polarizations of the electromagnetic fields is needed for the requirement that Eq. (15) must hold. In cases of arbitrary polarizations we are able to find symmetry relations between the signals with different polarizations. We shall treat circular polarizations, for example, and set that

$$d_k^{(\pm)}=\mathbf{d}_k \cdot \mathbf{e}^{(\pm)} ,$$ (20)

where $\mathbf{e}^{(\pm)}$ is a unit vector representing the $\sigma_\pm$ polarization, respectively. Then we have, instead of Eq. (15), the following transformation property of $d_k^{(\pm)}$ with respect to time reversal:

$$K d_k^{(\pm)} K^{-1}=(-1)^{D_k} d_k^{(\mp)} .$$ (21)

Therefore we obtain, instead of Eq. (17), the relation

$$\sigma_{(\pm)}^{(p)}(-\mathbf{H})=(-1)^{\sum\limits_{k=0}^{p} D_k}[\sigma_{(\mp)}^{(p)}(\mathbf{H})]^* ,$$ (22)

where $\sigma_{(\pm)}^{(p)}$ represents the product of the transition matrix elements for the electromagnetic field with the $\sigma_\pm$ polarization.

III. EXEMPLIFICATION

A. Two-level NMR signal

We first consider NMR of a two-level system ($|1\rangle$ and $|2\rangle$) [1]. This may be the simplest case for PSMRS. For simplicity we shall treat the case of just resonance and no relaxation in a pulse NMR. We consider the situations depicted in Figs. 3(a) and 3(b). The signal is proportional to a time derivative of a particular component of the magnetic moment.

The signal in a single-coil configuration [Fig. 3(a)] is expressed as

$$I_s(t)=\alpha\frac{d}{dt}\langle d_x\rangle=\alpha\frac{d}{dt}(\langle 1|d_x|2\rangle\rho_{21}+\text{c.c.}) .$$

α is a real number. After an application of a $\pi/2$ pulse ρ_{12} takes a value of

$$i\frac{\langle 1|d_x|2\rangle}{2|\langle 1|d_x|2\rangle|}\exp(i\omega_H t) .$$

This corresponds to the case of full coherence (v component of the Bloch vector $(u,v,w)=1$. [See Eq. (A10) in Ref. [20].] Therefore we obtain the expression:

$$I_s(t)=\alpha'\text{Re}[i^2\sigma_{SC}^{(2)}\exp(i\omega_H t)] ,$$ (23)

where $\omega_H=(E_2-E_1)/\hbar$ and α' is a real number, and
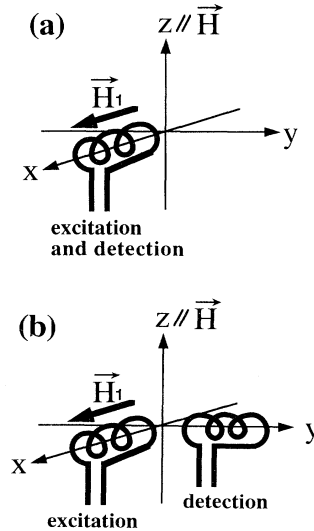

(a)

(b)

FIG. 3. Geometrical configuration of a phase-sensitive detection of NMR for a two-level system. (a) is a single-coil configuration and (b) the cross-coil one. It should be noted that the axes x, y, and z are fixed in the laboratory frame, not in the rotating frame.

$$\sigma_{SC}^{(2)} = \langle 1|d_x|2 \rangle \langle 2|d_x|1 \rangle = |\langle 1|d_x|2 \rangle|^2 \quad \text{real} . \tag{24}$$

In a cross-coil configuration [Fig. 3(b)], we obtain the following result in a similar way:

$$I_s(t) = \alpha \frac{d}{dt} \langle d_y \rangle = \alpha' \text{Re}[i^2 \sigma_{CC}^{(2)} \exp(i\omega_H t)] , \tag{25}$$

where

$$\sigma_{CC}^{(2)} = \langle 1|d_x|2 \rangle \langle 2|d_y|1 \rangle \quad \text{pure imaginary} . \tag{26}$$

And now we know that the reciprocal relation [Eq. (17)] in these NMR two-level cases takes the form

$$\sigma^{(2)}(-\mathbf{H}) = [\sigma^{(2)}(\mathbf{H})]^* \tag{27}$$

because a magnetic dipole transition is responsible both for the creation and detection of the two-level coherence: $D_1 = D_2 = 1$. Therefore from Eqs. (24) and (26) we obtain the following results:

$$\sigma_{SC}^{(2)}(-\mathbf{H}) = \sigma_{SC}^{(2)}(\mathbf{H}) , \tag{28}$$

$$\sigma_{CC}^{(2)}(-\mathbf{H}) = -\sigma_{CC}^{(2)}(\mathbf{H}) . \tag{29}$$

That is to say that the signal in the cross-coil configuration changes its sign under magnetic-field reversal, and that in the single coil does not.

We can also derive Eqs. (28) and (29) from the consideration of a unitary transformation property of the system. If we make the transformation U of π rotation about the x axis, then the direction of the static magnetic field is reversed ($\mathbf{a} = \mathbf{H}$, $\mathbf{b} = -\mathbf{H}$), and

$$Ud_x U^{-1} = +d_x \quad \text{thus } D_k' = 0$$

$$Ud_y U^{-1} = -d_y \quad \text{thus } D_k' = 1 .$$

And now we know that the symmetry relation [Eq. (19)] gives the same results as Eqs. (28) and (29).

These results can be inferred from a behavior of the motion of the Bloch vector. This is because the situation considered here is quite simple. We would not be able to obtain an intuitive understanding in more complicated systems.

B. RHS of nuclear quadrupole resonance

We next consider RHS of nuclear quadrupole resonance in the presence of a static magnetic field in Pr^{3+}:LaF_3 [11,20]. Since the Raman heterodyne technique is a detection of sublevel coherence created by one-rf-photon process via a two-photon coherent Raman scattering process, RHS should be expressed as a special case of Eq. (13) in the form

$$I_s(t) = \alpha \, \text{Re}[i^3 \sigma^{(3)} \exp(i\omega_{AB} t)] . \tag{30}$$

Now we know that the reciprocal relation [Eq. (17)] of RHS takes the form

$$\sigma^{(3)}(-\mathbf{H}) = -[\sigma^{(3)}(\mathbf{H})]^* \tag{31}$$

because a magnetic dipole transition is responsible for the creation of sublevel coherence and two electric dipole transitions for the detection: $D_1 = 1$, $D_2 = D_3 = 0$.

This relation was exemplified in detail in Ref. [20] and so we do not mention it further here.

We shall here discuss in detail the symmetry relation [Eq. (19)] based on a unitary transformation property of the system. We take the transformation operator U as π rotation about the C_2 axis. We set again that the z axis is parallel to the C_2 axis as in Fig. 6 in Ref. [20]. Then the transformation property of the system is

$$UH(\mathbf{H}(\vartheta,\varphi))U^{-1} = H(\mathbf{H}(\vartheta,\varphi+\pi)) , \tag{32}$$

where ϑ and φ indicate the direction of the externally applied magnetic field. That is,

$$\mathbf{a} = (\vartheta,\varphi) , \quad \mathbf{b} = (\vartheta,\varphi+\pi) .$$

Now we know that the symmetry relation [Eq. (19)] takes the form

$$\sigma^{(3)}(\vartheta,\varphi+\pi) = (-1)^{D_1'} \sigma^{(3)}(\vartheta,\varphi) . \tag{33}$$

Here $D_2' = D_3' = 0$. The value of D_1' is determined from the transformation property of rf transition operators as follows:

$$Ud_x U^{-1} = -d_x \quad \text{thus } D_1' = 1 ,$$

$$Ud_y U^{-1} = -d_y \quad \text{thus } D_1' = 1 ,$$

$$Ud_z U^{-1} = +d_z \quad \text{thus } D_1' = 0 .$$

We therefore obtain the following symmetry relations:

$$\sigma^{(3)}(\vartheta,\varphi+\pi) = +\sigma^{(3)}(\vartheta,\varphi) \quad \text{if } \mathbf{H}_1 \| C_2 ,$$

$$\sigma^{(3)}(\vartheta,\varphi+\pi) = -\sigma^{(3)}(\vartheta,\varphi) \quad \text{if } \mathbf{H}_1 \perp C_2 .$$

These properties are, of course, originated from the C_2 site symmetry of Pr^{3+} site. We note that the geometrical interpretation in Ref. [20] is nothing but a result of the symmetry relation of Eq. (19).

C. Synchronized QB signal of $\Delta m = 2$ coherence

We briefly discuss a recent experiment of a synchronized QB spectroscopy using cesium vapor performed by Mishina, Fukuda, and Hashi [10]. The energy level diagram and the geometrical configuration are shown in Figs. 22 and 23 of Ref. [10]. In that experiment the polarimeter was effectively used, so in this case the signal expression becomes

$$I_s(t) = \alpha \, \text{Re}[E_0(\mathbf{E}_s \cdot \mathbf{e}_y)]$$
$$= \alpha' \, \text{Re}[i^4 \sigma^{(4)} \exp(i\omega_{AB} t)] , \tag{34}$$

where

$$\sigma^{(4)} = \langle 1|d_p|3 \rangle \langle 3|d_p|2 \rangle \langle 2|d_x|3 \rangle \langle 3|d_y|1 \rangle \tag{35}$$

and α and α' is a real constant, and $d_p = \mathbf{d} \cdot \mathbf{e}_p$ ($\mathbf{e}$ is a unit vector expressing the polarization of the pumping light and $\mathbf{d}$ is an electric dipole operator).

Now we know that the reciprocal relation [Eq. (19)] of the synchronized QB spectroscopy is expressed as

$$\sigma^{(4)}(-\mathbf{H}) = [\sigma^{(4)}(\mathbf{H})]^* . \tag{36}$$

because all the transition operators are electric dipole allowed $(D_1 = D_2 = D_3 = D_4 = 0)$. We consider here the cases where $d_p = d_x$ or $d_p = d_y$ for simplicity. In both cases $\sigma^{(4)}(\mathbf{H})$ becomes pure imaginary, and so from the reciprocal relation [Eq. (36)] we obtain

$$\sigma^{(4)}(-\mathbf{H}) = -\sigma^{(4)}(\mathbf{H}) . \tag{37}$$

That is to say that the signal must change its sign under magnetic-field reversal. This sign reversal is actually observed [10].

IV. UTILITY OF SYMMETRY RELATION

We here mention the utility of the above mentioned symmetry relations [Eqs. (17) and (19)]. It is true that in a simple case these relations can be readily known by a simple consideration without any use of these symmetry relations. In a complicated system often encountered in a solid-state spectroscopy [2] (such as RHS in Pr^{3+}:LaF_3 [11]), however, the symmetry properties are by no means self-evident. Of course, if one can obtain the exact expression of the signal, it automatically incorporates these relations. But we can rarely obtain the exact expression even for simpler systems. For complicated systems these symmetry relations become guiding principles for analyzing the PSMRS signals.

As is readily known from the expression, these relations hold for a particular multiphoton process. Different processes may lead to different symmetry relations in general. From the behavior of the signal, therefore, one can know what kind of process is actually responsible for the observed signal. Slight deviation of the signal behavior from that expected for a particular process suggests that the observed signal should have contributions from some other processes.

The phase of a rf magnetic field at the sample position is often difficult to know in cryogenic systems, for example. The reciprocal relation can give this information because the signal phase is closely related to the behavior of the signal with magnetic-field inversion.

Just as in the case of Pr^{3+}:LaF_3 the symmetry properties of the signals reflect the symmetry property of the system (in that case, C_2 site symmetry of the Pr^{3+} site). Therefore one can obtain the information on the circumstance, or the site symmetry, of the ions and atoms through their PSMRS signals.

[1] See, for example, A. Abragam, *The Principles of Nuclear Magnetism* (Oxford Univ. Press, London, 1961).

[2] See, for example, R. M. Macfarlane and R. M. Shelby, in *Spectroscopy of Crystals Containing Rare Earth Ions*, edited by A. A. Kaplyanskii and R. M. Macfarlane (North-Holland, Amsterdam, 1987).

[3] See, for example, W. Happer, Rev. Mod. Phys. **44**, 169 (1972).

[4] J. Brossel and F. Bitter, Phys. Rev. **86**, 308 (1952); B. Cagnac, Ann. Phys. (Paris) **6**, 467 (1960); see also *Spectroscopy of Crystals Containing Rare Earth Ions* (Ref. [2]), p. 67.

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