

# Merging–splitting and suppression–enhancement in magnetic resonance lines of highly polarized exchange-coupled nonequivalent spins

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We use Green's functions to study the frequencies and strengths of magnetic resonance lines in a system of highly polarized exchange-coupled inequivalent spins of a solid. We find that comparison of the results with the NMR pattern for two silver isotopes coupled by the Ruderman–Kittel interaction and with the EPR pattern for  $\text{Cu}^{2+}$  ions occupying magnetically inequivalent positions in the lattice and coupled by the exchange interaction yields good agreement in ultralow magnetic fields. © 1994 American Institute of Physics.

## 1. INTRODUCTION

In addition to the ordinary dipole–dipole interaction, magnetic nuclei of a metal are coupled by the Ruderman–Kittel (RK) interaction,<sup>1</sup> which constitutes an indirect interaction of nuclear spins with each other via conduction electrons, and which is predominant in heavy metals. Knowledge of the coupling constant  $J$  of the RK interaction is of great interest as a source of valuable information about the electron band structure. NMR methods are often used to determine  $J$ . At low spin polarizations, however, all quantities measured by magnetic resonance methods in magnetically disordered samples (only this case is considered below) are proportional to the squares of the local fields, and there is no way to find the sign of the RK coupling constant. At high spin polarizations the measured quantities also contain the first power of  $J$ . Knowing the sign of  $J$  is not only of general interest for materials science but makes it possible to determine whether the nuclear ordering achieved at lower spin temperatures, is ferromagnetic or antiferromagnetic. In view of this, the magnetic resonance (MR) of highly polarized nuclear spins of metals is of special interest. The signs and values of the coupling constants in the exchange interaction of the highly polarized electron spins of paramagnetic ions can also be effectively observed in EPR experiments, and the nature of ordering, as the temperature decreases, can be predicted.

Exchange coupling and the RK interaction, which is similar in notation, commute with the components of the total magnetization of equivalent spins, so that in this case they cause the well-known exchange narrowing of MR lines.<sup>2</sup> But if the highly polarized spins are not equivalent, these interactions can lead to significant changes in the frequencies and strengths of MR lines. Interacting inequivalent spins are similar to two coupled oscillators, whose partial frequencies must be close enough for the interaction to produce appreciable effects. Hence the isotopes of metals with close gyromagnetic ratios (such as  $^{107}\text{Ag}$  and  $^{109}\text{Ag}$  in silver and  $^{203}\text{Tl}$  and  $^{205}\text{Tl}$  in thallium) and magnetically inequivalent ions in paramagnetic salts are extremely suitable objects

for studying exchange interactions via MR methods. With paramagnetic salts there is the possibility of varying the difference in the Larmor frequencies by rotating the sample in relation to the direction of the constant magnetic field.

This problem has been studied by a group of Finnish researchers<sup>3,4</sup> working with NMR at extremely low spin temperatures and a group of Japanese researchers<sup>6</sup> working with EPR in ultrahigh constant magnetic fields (the special experimental conditions are dictated by the need to operate with highly polarized spins). Briefly, their results are as follows:

(a) As the spin polarizations increased, a single NMR line split into two.

(b) At low spin polarizations, MR lines tend to merge. For one thing, as the experimenter brought the Larmor frequencies together, the MR lines merged before the Larmor frequencies became equal.

(c) A suppression–enhancement of magnetic lines was observed: the strengths of the MR lines did not correspond to the relative concentrations of the two spin species.

The theoretical interpretation of the spectrum by Oja, Annala, and Takano<sup>5</sup> was based on the Kubo–Tomita method of moments,<sup>7</sup> which is valid when the square of the difference of the partial frequencies,  $(\omega_{ab}^0)^2$ , is much larger than the square of the coupling constant,  $(J/\hbar)^2$ . As a result the most interesting region, where the lines begin to overlap, dropped out of the picture. To describe the suppression–enhancement effect, Hakonen, Nummila, and Vuorinen<sup>4</sup> and Oja, Annala, and Takano<sup>5</sup> used the molecular field method, which is incapable of taking into account the effect of merging lines caused by spin fluctuations. Kuroda, Motokawa, and Date<sup>6</sup> used the molecular field method to describe both suppression–enhancement and line splitting, with the spin polarization assumed to be 100%, although in some experiments it was much lower. Hence although the molecular field method can be used for any  $(\omega_{ab}^0)^2$ -to- $(J/\hbar)^2$  ratio, line merging dropped out of the picture. The case of an arbitrary  $(\omega_{ab}^0)^2$ -to- $(J/\hbar)^2$  ratio has also been studied in the theoretical papers of Tomita *et al.*<sup>8</sup> and Hamano and Shibata.<sup>9</sup> Tomita *et al.*<sup>8</sup> used equations for the first and second Green's functions, while Hamano and Shibata<sup>9</sup> used equations for the

density matrix. Both groups, however, used idealized models of paramagnets; besides, their equations cannot be used to describe the experimental data of Refs. 3–6.

The goal of the present work is to develop a theory that will make it possible to describe merging–splitting and suppression–enhancement within a broad range of  $J^2(\hbar\omega_{ab}^0)^2$  values and compare the results with experimental data. To this end we use the method of two-time retarded Green's functions with allowance for the third Green's functions.

## 2. CALCULATING THE SPECTRUM

Suppose that we have a constant magnetic field  $H$  and we place in it exchange-coupled spins of two species with Larmor frequencies  $\omega_a$  and  $\omega_b$ . To this end we write the Hamiltonian of such a system in the form

$$\mathcal{H} = -\hbar\omega_a I_a^z - \hbar\omega_b I_b^z - \sum_{i,j} J_{ij} \mathbf{I}_{ai} \mathbf{I}_{bj}, \quad (1)$$

where  $\omega_a = \gamma_a H$  and  $\omega_b = \gamma_b H$  in the case of nuclear spins with gyromagnetic ratios  $\gamma_a$  and  $\gamma_b$ ,  $\mathbf{I}_a$  and  $\mathbf{I}_b$  are the spin operators of species  $a$  and  $b$ , and the Zeeman energies of the spins are assumed to be considerably higher than the energy of the RK interaction. We wish to find the precession frequency spectrum of this spin system. We introduce the Fourier transforms of the main (first) two-time retarded Green's functions:<sup>10</sup>

$$G_1^{aa} = \langle\langle I_{ai}^+ | I_a^- \rangle\rangle_\omega, \quad G_1^{ab} = \langle\langle I_{ai}^+ | I_b^- \rangle\rangle_\omega, \\ G_1^{ba} = \langle\langle I_{bi}^+ | I_a^- \rangle\rangle_\omega, \quad G_1^{bb} = \langle\langle I_{bi}^+ | I_b^- \rangle\rangle_\omega,$$

where

$$\langle\langle A|B \rangle\rangle_\omega = \frac{1}{2\pi} \int_{-\infty}^{\infty} \theta(t-t') \langle [A(t), B(t')] \rangle \\ \times \exp\{i\omega(t-t')\} d(t-t'), \quad (2)$$

$$\theta(x) = \begin{cases} 1 & \text{if } x > 0, \\ 0 & \text{if } x < 0, \end{cases}$$

and  $\langle \dots \rangle$  stands for the average with an equilibrium statistical operator.

We write the chain of equations for the Fourier transforms of the Green's functions according to the formula<sup>10</sup>

$$\omega \langle\langle A|B \rangle\rangle_\omega = \frac{i}{2\pi} \langle [A, B] \rangle + \langle\langle [A, \mathcal{H}] | B \rangle\rangle_\omega. \quad (3)$$

If we limit ourselves to the third Green's functions, the chain has the following explicit form:

$$(\omega - \omega_a) G_1^{aa} = \frac{i}{\pi} \langle a \rangle + \frac{\bar{a}}{\hbar} (G_2^{aa} - G_2^{ba}),$$

$$(\omega - \omega_a) G_1^{ab} = -\frac{\bar{a}}{\hbar} (G_2^{bb} - G_2^{ab}),$$

$$(\omega - \omega_b) G_1^{bb} = \frac{i}{\pi} \langle b \rangle + \frac{\bar{a}}{\hbar} (G_2^{bb} - G_2^{ab}),$$

$$(\omega - \omega_b) G_1^{ba} = -\frac{\bar{a}}{\hbar} (G_2^{aa} - G_2^{ba}), \quad (4)$$

$$(\omega - \omega_a) G_2^{aa} = I_2 + \frac{R_2 G_{3a}}{\hbar},$$

$$(\omega - \omega_a) G_2^{bb} = I_2 + \frac{R_2 G_{3b}}{\hbar}, \quad (\omega - \omega_a) G_2^{ab} = \frac{R_2 G'_{3a}}{\hbar},$$

$$(\omega - \omega_b) G_2^{ba} = \frac{R_2 G'_{3b}}{\hbar},$$

where

$$\langle a \rangle \equiv \langle I_{ai}^z \rangle, \quad \langle b \rangle \equiv \langle I_{bi}^z \rangle, \quad I_2 = \frac{i}{\pi} \langle a \rangle \langle b \rangle,$$

$$\bar{a} = \sum_j J_{ij} R_2 = \frac{1}{a} \sum_{jk} J_{ij} J_{ik}, \quad (5)$$

$$G_2^{aa} = \langle\langle I_{bj}^z I_{ai}^+ | I_a^- \rangle\rangle_\omega, \quad G_2^{ab} = \langle\langle I_{bj}^z I_{ai}^+ | I_b^- \rangle\rangle_\omega,$$

$$G_2^{bb} = \langle\langle I_{ai}^z I_{bj}^+ | I_b^- \rangle\rangle_\omega, \quad G_2^{ba} = \langle\langle I_{ai}^z I_{bj}^+ | I_a^- \rangle\rangle_\omega.$$

The system of equations (4) is an open chain of equations for the first and second Green's functions. (In view of their complexity we do not write the third Green's functions.) To identify the first-order frequency shifts in the very first equations, we introduce, following Refs. 11 and 12, the cumulant, or semi-invariant, Green's functions  $\langle A|B \rangle$  in addition to the ordinary Green's functions, the relation between the two being

$$\langle\langle A|B \rangle\rangle = \langle A|B \rangle,$$

$$\langle\langle A_1 B_1 | B \rangle\rangle = \langle A_1 \rangle \langle A_2 | B \rangle + \langle A_2 \rangle \langle A_1 | B \rangle + \langle A_1 A_2 | B \rangle, \quad (6)$$

etc. (these relations remain valid in the frequency representation). Using this method, we reduce the second and third Green's functions to the first and second cumulant functions and ignore the third cumulant Green's function, which vanishes in the zeroth approximation. Retaining only the corresponding first functions (with the same upper indices) in the equations for the second Green's functions, we arrive at the following closed system of equations:

$$(\omega - \omega_a^0) G_1^{aa} + \frac{\bar{a}}{\hbar} \langle a \rangle G_1^{ba} = \frac{i}{\pi} \langle a \rangle + \frac{\bar{a}}{\hbar} (K_2^{aa} - K_2^{ba}),$$

$$(\omega - \omega_a^0) G_1^{ab} + \frac{\bar{a}}{\hbar} \langle a \rangle G_1^{bb} = \frac{\bar{a}}{\hbar} (K_2^{ab} - K_2^{bb}),$$

$$(\omega - \omega_b^0) G_1^{ba} + \frac{\bar{a}}{\hbar} \langle b \rangle G_1^{aa} = \frac{i}{\pi} \langle b \rangle - \frac{\bar{a}}{\hbar} (K_2^{aa} - K_2^{ba}),$$

$$-(\omega - \omega_b^0) G_1^{bb} + \frac{\bar{a}}{\hbar} \langle b \rangle G_1^{ab} = -\frac{\bar{a}}{\hbar} (K_2^{ab} - K_2^{bb}), \quad (7)$$

$$(\omega - \omega_a^0) K_2^{aa} = \frac{\delta_a^2}{\bar{a}\hbar} G_1^{aa}, \quad (\omega - \omega_b^0) K_2^{ba} = \frac{\delta_a^2}{\bar{a}\hbar} G_1^{ba},$$

$$(\omega - \omega_a^0)K_2^{ab} = \frac{\delta_b^2}{\bar{a}\hbar} G_1^{ab}, \quad (\omega - \omega_b^0)K_2^{bb} = \frac{\delta_a^2}{\bar{a}\hbar} G_1^{bb},$$

where  $K$  denotes cumulant Green's functions, and

$$\omega_a^0 = \omega_a + \langle b \rangle \frac{\bar{a}}{\hbar}, \quad \omega_b^0 = \omega_b + \langle a \rangle \frac{\bar{a}}{\hbar},$$

$$\delta_b^2 = \sum_j J_{ij}^2 [ \langle (I_{bj}^z)^2 \rangle - \langle (I_{bj}^z) \rangle^2 ],$$

$$\delta_a^2 = \sum_j J_{ij}^2 [ \langle (I_{aj}^z)^2 \rangle - \langle (I_{aj}^z) \rangle^2 ].$$

If both spin species have  $I = \frac{1}{2}$  and the same polarization  $p = \tanh(\hbar\bar{\omega}/2kT)$ , where  $\bar{\omega} = (x_a\gamma_a + x_b\gamma_b)H$ , with  $x_a$  and  $x_b$  the relative concentrations of the two spin species, we have

$$\langle a \rangle = \frac{x_a p}{2}, \quad \langle b \rangle = \frac{x_b p}{2}, \quad \delta_b^2 = \frac{x_b(1-x_b p^2)}{4} \sum_j J_{ij}^2,$$

$$\delta_a^2 = \frac{x_a(1-x_a p^2)}{4} \sum_j J_{ij}^2.$$

Since exchange interactions are short-range, each spin interacts only with its nearest neighbors, so that in what follows we put  $\sum_j J_{ij}^2 = zJ^2$  and  $\bar{a} = zJ$ , where  $z$  is the number of nearest neighbors.

In looking for the spectrum we can reduce the number of equations in (7) by adding them pairwise and obtaining equations for the functions  $G_1^a = G_1^{aa} + G_1^{ab}$ ,  $K_2^a = K_2^{aa} + K_2^{ab}$ , etc. Then for the spectrum we obtain a fourth-order equation, i.e., in the general case Eqs. (7) describe a four-frequency spectrum. We simplify Eqs. (7) by replacing  $\omega$  with  $\omega_{a,b}^0$  so that we get the difference  $\omega_{ab}^0 = \omega_a^0 - \omega_b^0$ . Then

$$K_2^{aa} = \frac{\delta_b^2}{\hbar\bar{a}\omega_{ab}^0} G_1^{aa}, \quad K_2^{ba} = \frac{\delta_b^2}{\hbar\bar{a}\omega_{ab}^0} G_1^{ba},$$

$$K_2^{ab} = -\frac{\delta_b^2}{\hbar a\omega_{ab}^0} G_1^{ab}, \quad K_2^{bb} = \frac{\delta_b^2}{\hbar\bar{a}\omega_{ab}^0} G_1^{bb}. \quad (8)$$

Indeed, in the equations for the second Green's functions the right-hand side is nonzero because  $J$  is nonzero. If  $J=0$ , then all  $K$ 's vanish. Hence it is natural to introduce the dimensionless parameter  $\varepsilon = J/\hbar\omega_{ab}^0$  and assume that Eqs. (8) are valid. Then

$$(\omega - \bar{\omega}_a^0)G_1^{aa} + \frac{\bar{a}}{\hbar} \langle a \rangle G_1^{ba} = \frac{i}{\pi} \langle a \rangle,$$

$$(\omega - \bar{\omega}_a^0)G_1^{ab} + \frac{\bar{a}}{\hbar} \langle a \rangle G_1^{bb} = 0,$$

$$(\omega - \bar{\omega}_b^0)G_1^{bb} + \frac{\bar{a}}{\hbar} \langle b \rangle G_1^{ab} = \frac{i}{\pi} \langle b \rangle,$$

$$(\omega - \bar{\omega}_b^0)G_1^{ba} + \frac{\bar{a}}{\hbar} \langle b \rangle G_1^{aa} = 0, \quad (9)$$

where

$$\bar{\omega}_a^0 = \omega_a^0 - \frac{\delta_b^2}{\hbar^2\omega_{ab}^0}, \quad \bar{\omega}_b^0 = \omega_b^0 + \frac{\delta_a^2}{\hbar^2\omega_{ab}^0} \quad (10)$$

act as the partial frequencies of the two oscillators.<sup>1)</sup> Equations (8) provide a kind of decoupling method, the validity of which, like that of all decoupling methods, can be verified by comparing the results with the experimental data.

Equations (9) yield a biquadratic equation for the spectrum. Thus, the method of decoupling provided by Eqs. (8) reduces the number of spectral frequencies to two. Since these two frequencies agree with the two MR lines observed experimentally,<sup>3-6</sup> we restrict our discussion to them. In the future we plan to examine a more complicated situation in which a multitude of MR peaks is observed.<sup>13</sup> Equations (10) lead to the following spectrum of exchange-coupled inequivalent spins:

$$\bar{\omega}_{a,b} = \frac{1}{2}(\bar{\omega}_a^0 + \bar{\omega}_b^0) \pm \left\{ \frac{1}{4}(\bar{\omega}_a^0 - \bar{\omega}_b^0)^2 + (\bar{a})^2 \langle a \rangle \langle b \rangle \right\}^{1/2}. \quad (11)$$

If the first term in the braces is considerably greater than the second, we can write the spectrum (assuming that  $\bar{\omega}_a^0 - \bar{\omega}_b^0 > 0$ ) as

$$\bar{\omega}_a \approx \omega_a^0 - \frac{x_b(1-x_b p^2)z}{4\omega_{ab}^0} \left( \frac{J}{\hbar} \right)^2 + \frac{x_a x_b p^2 z^2}{4\omega_{ab}^0} \left( \frac{J}{\hbar} \right)^2, \quad (12)$$

$$\bar{\omega}_b \approx \omega_b^0 - \frac{x_a(1-x_a p^2)z}{4\omega_{ab}^0} \left( \frac{J}{\hbar} \right)^2 - \frac{x_a x_b p^2 z^2}{4\omega_{ab}^0} \left( \frac{J}{\hbar} \right)^2.$$

The second terms on the right-hand sides of Eqs. (12) describe the merging of the spin frequencies due to spin fluctuations, and the third terms describe their repulsion. Equations (12) are consistent with the theoretical result of Oja, Annala, and Takano,<sup>5</sup> with the difference that their fluctuation terms contain the factor  $1-p^2$  instead of  $1-x_b p^2$  and  $1-x_a p^2$ .

We now calculate the critical value  $p_m$  of the spin polarization, i.e., the value of  $p$  above which the MR lines split in any field, however weak. To this end we write the difference of spin frequencies as

$$\bar{\omega}_a - \bar{\omega}_b = \omega_{ab}^0 \left\{ \left[ 1 - \frac{((1-p^2 + 2x_a x_b p^2)z)}{4(\omega_{ab}^0)^2} \left( \frac{J}{\hbar} \right)^2 \right]^2 \right. \\ \left. + \frac{x_a x_b p^2 z^2}{(\omega_{ab}^0)^2} \left( \frac{J}{\hbar} \right)^2 \right\}^{1/2}.$$

If  $\bar{\omega}_a - \bar{\omega}_b > \omega_{ab}^0$ , the MR lines are always split, with the result that the  $p_m$  is fixed by the condition that  $\bar{\omega}_a - \bar{\omega}_b = \omega_{ab}^0$ . Ignoring terms of order  $J^4(\hbar\omega_{ab}^0)^{-4}$ , we get

$$p_m = \pm (1 + 2x_a x_b (z-1))^{-1/2}, \quad (13)$$

where the plus and minus correspond to positive and negative spin polarizations. The condition for the lines to merge is

$$\bar{\omega}_a - \bar{\omega}_b \approx \Gamma, \quad (14)$$

where  $\Gamma$  is the halfwidth at half-height of the resonance lines (we have in mind the case where the widths are the same).

### 3. CALCULATING ABSORPTION SIGNALS

The energy absorbed by the spins from a variable field polarized parallel to the  $x$  axis (and hence the observed MR signal) is proportional to the imaginary part of the complex magnetic susceptibility. First we calculate the total susceptibility  $\chi_{xx} = \chi'_{xx} - i\chi''_{xx}$  by the formula<sup>10</sup>

$$\chi_{xx} = -2\pi i \langle \langle M_x | M_x(t) \rangle \rangle_\omega. \quad (15)$$

Allowing for the fact that  $M_x = \gamma_a I_a^x + \gamma_b I_b^x$ , we can write Eq. (15) as

$$\chi_{xx} = \chi_{aa} + 2\chi_{ab} + \chi_{bb}, \quad (16)$$

where

$$\begin{aligned} \chi_{aa} &= -\frac{1}{2}N\pi i \gamma_a^2 G_1^{aa}, & \chi_{bb} &= -\frac{1}{2}N\pi i \gamma_b^2 G_1^{bb}, \\ \chi_{ab} &= -\frac{1}{2}N\pi i \gamma_a \gamma_b G_1^{ab}. \end{aligned} \quad (17)$$

By the system of equations (10) the first Green's functions are

$$\begin{aligned} G_1^{aa} &= -\frac{i\bar{\omega}_b^0 \langle a \rangle}{\pi(\omega - \bar{\omega}_a)(\omega - \bar{\omega}_b)}, \\ G_1^{bb} &= -\frac{i\bar{\omega}_a^0 \langle b \rangle}{\pi(\omega - \bar{\omega}_a)(\omega - \bar{\omega}_b)}, \\ G_1^{ab} &= G_1^{ba} = -\frac{izJ \langle a \rangle \langle b \rangle}{\pi(\omega - \bar{\omega}_a)(\omega - \bar{\omega}_b)}. \end{aligned} \quad (18)$$

We now calculate  $\chi''_{xx}$ . To this end we replace  $\omega$  with  $\omega - i\Gamma$ , introducing the damping  $\Gamma$ . Using the identity

$$\frac{1}{(\omega - \bar{\omega}_a)(\omega - \bar{\omega}_b)} \equiv \frac{1}{\bar{\omega}_a - \bar{\omega}_b} \left( \frac{1}{\omega - \bar{\omega}_a} - \frac{1}{\omega - \bar{\omega}_b} \right),$$

we can write  $\chi''_{xx}$  as a sum of terms resonant at the frequencies  $\bar{\omega}_a$  and  $\bar{\omega}_b$ :

$$\begin{aligned} \chi''_{xx} &= \chi''_{aa}(\bar{\omega}_a) \left( 1 + 2 \frac{\chi''_{ab}(\bar{\omega}_a)}{\chi''_{aa}(\bar{\omega}_a)} + \frac{\chi''_{bb}(\bar{\omega}_a)}{\chi''_{aa}(\bar{\omega}_a)} \right) \\ &+ \chi''_{bb}(\bar{\omega}_b) \left( 1 + 2 \frac{\chi''_{ab}(\bar{\omega}_b)}{\chi''_{bb}(\bar{\omega}_b)} + \frac{\chi''_{aa}(\bar{\omega}_b)}{\chi''_{bb}(\bar{\omega}_b)} \right), \end{aligned} \quad (19)$$

where

$$\begin{aligned} \chi''_{aa}(\bar{\omega}_a) &= \frac{\gamma_a N \langle a \rangle \Gamma(\omega - \bar{\omega}_b^0)}{2Z}, \\ \chi''_{bb}(\bar{\omega}_a) &= \frac{\gamma_b N \langle b \rangle \Gamma(\omega - \bar{\omega}_a^0)}{2Z}, \\ \chi''_{ab}(\bar{\omega}_a) &= -\frac{\gamma_a \gamma_b N \langle a \rangle \langle b \rangle \Gamma}{2Z}, \end{aligned} \quad (20)$$

with  $Z = (\bar{\omega}_a - \bar{\omega}_b)[(\omega - \bar{\omega}_a)^2 + \Gamma^2]$ , and similarly for the terms resonant at the frequency  $\bar{\omega}_b$ .

Equations (20) show that if the frequency of the external field equals the partial frequencies of the  $b$ -spins ( $\omega = \bar{\omega}_b^0$ ), the susceptibility  $\chi''_{aa}(\bar{\omega}_a)$  vanishes. This phenomenon is well-known in the theory of oscillations<sup>14</sup> by the name of

dynamic damping of one of the coupled oscillators. Replacing  $\omega$  in the numerators of Eqs. (20) with the corresponding resonance frequency, we get

$$\begin{aligned} \chi''_{xx} &= \frac{\gamma_a^2 N \langle a \rangle \Gamma(\bar{\omega}_a - \bar{\omega}_b^0)(1 - \eta_a)^2}{2Z} \\ &+ \frac{\gamma_b^2 N \langle b \rangle \Gamma(\bar{\omega}_a - \bar{\omega}_b^0)(1 + \eta_b)^2}{2Z}, \end{aligned} \quad (21)$$

where

$$\begin{aligned} \eta_a &= \frac{\gamma_a x_b p \bar{a}}{\gamma_b 2\hbar} \\ &\times \left\{ \frac{\bar{\omega}_a^0 - \bar{\omega}_b^0}{2} + \left[ \frac{(\bar{\omega}_a^0 - \bar{\omega}_b^0)^2}{4} + (\bar{a})^2 \langle a \rangle \langle b \rangle \right]^{1/2} \right\}^{-1}, \end{aligned} \quad (22)$$

$$\eta_b = \eta_a \frac{\gamma_a^2 x_a}{\gamma_b^2 x_b}. \quad (23)$$

For  $\bar{\omega}_a^0 \bar{\omega}_b^0$ , Eq. (22) can be written as

$$\eta_a = \frac{\gamma_b x_b p z J}{\gamma_a \hbar ((\bar{\omega}_a^0 - \bar{\omega}_b^0))} [1 + (1 + \sigma)^{1/2}]^{-1}.$$

The quantity  $\sigma = x_a x_b p^2 z^2 (J/\hbar)^2 / (\bar{\omega}_a^0 - \bar{\omega}_b^0)^2$  is known in the theory of oscillations<sup>14</sup> as the coherence of two coupled oscillators. Equation (21) describes suppression–enhancement in MR signals from two spin species with coefficients  $\eta_b$  and  $\eta_a$ , respectively. Equations (21) and (22) show that for positive  $p$  and  $J$ , i.e., with a tendency toward ferromagnetic alignment, the high-frequency line is suppressed and the low-frequency enhanced; for  $J$ , i.e., with a tendency toward antiferromagnetic alignment, the high-frequency line is enhanced and the low-frequency suppressed. For negative  $p$ , suppression–enhancement is reversed.<sup>4</sup> For tight coherence ( $\sigma \gg 1$ ) the following approximate equalities hold:

$$\begin{aligned} (1 - \eta_a)^2 &\approx \left( \frac{\gamma_a x_a^{1/2} - \text{sgn}(\bar{a}p) \gamma_b x_b^{1/2}}{\gamma_b x_b^{1/2}} \right)^2, \\ (1 + \eta_b)^2 &\approx \left( \frac{\gamma_b x_b^{1/2} + \text{sgn}(\bar{a}p) \gamma_a x_a^{1/2}}{\gamma_b x_b^{1/2}} \right)^2. \end{aligned} \quad (24)$$

We see that for  $ap > 0$ , the  $a$ -mode is optical and the  $b$ -mode acoustic; for  $ap < 0$  the converse is true.

### 4. COMPARISON WITH EXPERIMENTAL DATA

The theoretical results for the merging–splitting and suppression–enhancement effects obtained above were compared with the experimental data of Oja, Annala, and Takano<sup>3</sup> and Hakonen, Nummala, and Vuorinen,<sup>4</sup> who observed both effects in silver atoms at positive and negative spin temperatures, respectively. High resolution of the NMR lines of two silver isotopes, <sup>107</sup>Ag and <sup>109</sup>Ag, in an external magnetic field of 0.8 mT (Ref. 4) made it possible to use the simplified formulas (12) to find  $J$ . Comparison of the frequency difference given by (12) with the experimental data yields two

values:  $J/h = -28.5$  Hz and  $J/h = 24$  Hz. (Note that by calculating the coherence  $\sigma$  of two spin species with these values of  $J$ , we get  $\sigma = 0.33$  and  $\sigma = 0.24$ , respectively, which supports the use of the approximate formulas (12).) Both values of  $J$  were used to calculate the relative NMR line strengths. Good quantitative agreement with the experimental data can be obtained using  $J/h = -28.5$  Hz, which is close to the absolute value  $|J/h| = 26.5$  Hz measured by Poirereaud and Winter.<sup>15</sup> The value  $J/h = -28.5$  Hz also gives a good description of the frequency and strength pattern of the NMR lines observed by Oja, Annala, and Takano.<sup>3</sup> Moreover, the same value was used to find the spectrum in a 0.2 mT field (Ref. 4), where the general formula (11) should be used. At  $p = -0.286$  the frequencies obtained were  $\nu_a = 418$  Hz and  $\nu_b = 379$  Hz, and at  $p = -0.683$  the frequencies were  $\nu_a = 488$  Hz and  $\nu_b = 370$  Hz. The explanation for the fact that in the 0.2 mT field only one line was observed is that the susceptibility ratio  $\chi_a''/\chi_b''$  amounts to only 2%. Thus, the NMR spectrum in the 0.2 mT field is not a single exchange-merged line in which the two spin species act as one species, as assumed by Hakonen, Nummila, and Vuorinen.<sup>4</sup> (Note that the critical polarization for silver obtained by Eq. (13),  $p_m = -0.39$ , is essentially the same as that listed in Ref. 5.) A slight degradation in the agreement of  $\nu_b$  with the experimental data is apparently due to the fact that the decrease in the separation of partial frequencies makes the spectral formula (11) less attractive. Note that the spectral formulas we obtained proved unsuitable for describing the NMR spectrum of thallium.<sup>16</sup> The exceptionally high value of  $J$  in thallium (37.5 kHz according to Karimov and Shchegolev<sup>17</sup>) would seem to put this case beyond the scope of our approach.

Merging-splitting and suppression-enhancement have also been observed in a system of exchange-coupled electron spins.<sup>6</sup> The samples were four salts with paramagnetic  $\text{Cu}^{2+}$  ions, which can occupy two magnetically inequivalent positions in the lattice. Kuroda, Motokawa, and Date<sup>6</sup> conducted their experiment as follows. Special coils were used to generate magnetic field pulses up to 0.5 MOe. Spin transitions in such fields were induced by a 337- $\mu\text{m}$  HCN laser. The distance between the Zeeman frequencies was measured by rotating the sample relative to the direction of the "constant" magnetic field. An EPR spectrum consisting of two lines was observed, with the two lines merging at certain angles. Molecular field theory was used to process the experimental results. For  $(\text{NH}_4)_2\text{CuCl}_4 \cdot 2\text{H}_2\text{O}$  (chlorine salt), the only salt examined here,  $J = 0.12$  K was obtained (according to independent experimental data,<sup>18</sup> this value is 0.24 K; we note that by  $J$  the authors of Ref. 6 mean a quantity half the one in the present paper or in Refs. 3–5). To compare our formulas with the experimental data of Ref. 6, we must replace  $J$  with  $2J$ ,  $p$  with  $|p|$ ,  $\gamma_a h$  with  $g_2 \beta$ , and  $\gamma_b h$  with  $g_1 \beta$ , where  $\beta$  is the Bohr magneton. We must also take into account the following difference between EPR in paramagnetic salts and NMR in metals. With silver nuclei each of the 12 nearest neighbors of the chosen spin may turn out to be the  $^{109}\text{Ag}$  isotope with a probability  $x_a$  or the  $^{107}\text{Ag}$  isotope with a probability  $x_b$ . But in the case of chlorine salt, which has a bcc structure, the ions occupying (a) the centers of cubes, and (b) the vertices of cubes are mag-

netically inequivalent. An ion occupying the center of a cube is surrounded by eight "vertex" ions, and an ion occupying a vertex of a cube is surrounded by eight "central" ions. Thus, in the given case  $x_a = x_b = 1$  and  $z = 8$ .

Because the experiment setup of Ref. 6 differs from that of Refs. 3 and 4, in our formulas we must pass from resonance frequencies  $\bar{\omega}_{a,b}$  to resonant fields. The latter are solutions of the equation

$$h\nu = g_m \beta H + |p| z J \pm \left( \frac{\Delta g^2 \beta^2 H^2}{4} + p^2 z^2 J^2 - (1-p^2) z J^2 + \frac{(1-p^2)^2 z^2 J^4}{\Delta g^2 \beta^2 H^2} \right)^{1/2}, \quad (25)$$

where we have retained the notation of Ref. 6:  $g_m = \frac{1}{2}(g_1 + g_2)$ ,  $\Delta g = g_2 - g_1$ , and  $\nu$  is the laser frequency. That a spectrum consisting of two lines was observed in the experiment suggests that the last term in the parenthesized expression, which yields to a fourth-degree equation for  $H$ , is insignificant. If this term is discarded, the resonant fields become

$$H^\pm = \frac{g_m}{g_1 g_2} \frac{h\nu}{\beta} \left\{ 1 - \frac{|p| z J}{h\nu} \mp \left[ \frac{\overline{\Delta g^2}}{4} - \frac{\overline{\Delta g^2}}{2} \frac{|p| z J}{h\nu} + \frac{p^2 z^2 J^2}{(h\nu)^2} - \frac{g_1 g_2 (1-p^2) z J^2}{g_m^2 (h\nu)^2} \right]^{1/2} \right\}, \quad (26)$$

where  $\overline{\Delta g} = \Delta g / g_m$ .

The presence of two resonant fields can be described in another way by introducing the effective value  $g^{\text{eff}}$  by the formula

$$H^\pm = \frac{h\nu}{g_{2,1}^{\text{eff}} \beta}.$$

Comparison of Eq. (26) with Eq. (5) of Ref. 6 shows that Eq. (26), first, allows for  $|p| \neq 1$  in the terms present in Ref. 5 and second, contains a term that is proportional to  $(1-p)^2$  and describes the exchange-merging of MR lines, with the role of this effect growing as the spin polarization decreases. Merging is not reflected in the theoretical results of Ref. 6, since it cannot be obtained by the molecular field method. We believe, however, that high-temperature merging was observed by Kuroda, Motokawa, and Date<sup>6</sup> not only in combination with line repulsion but also in pure form. (See Fig. 8 of Ref. 6, which illustrates the tendency of the experimental points  $g^{\text{eff}}$  to merge at room temperature ( $p \approx 0$ ), in comparison with the narrow theoretical lines constructed according to the formulas

$$g_1^2 = g_{\parallel}^2 \sin^2(45^\circ - \theta) + g_{\perp}^2 \cos^2(45^\circ - \theta), \\ g_2^2 = g_{\parallel}^2 \cos^2(45^\circ - \theta) + g_{\perp}^2 \sin^2(45^\circ - \theta).$$

The values of  $J$  that we found by comparing the difference between the resonant fields given by Eq. (26) and Fig. 6 of Ref. 6 turned out to be approximately 0.19 K ( $J/h \approx 4.03$  GHz) and  $-0.2$  K ( $J/h \approx -4.17$  GHz). These were then substituted into the formula for the intensity ratio:

TABLE I.

	$\theta$	$(\chi''_{LF}\chi''_{HF})_{\text{theor}}$	$(\chi''_{LF}\chi''_{HF})_{\text{expt}}$
$T=4.2$ K, $ p =1$	$15^\circ$	0.12	0.20
	$45^\circ$	0.35	0.33
$T=77$ K, $ p =0.27$	$15^\circ$	0.54	0.51
	$22.5^\circ$	0.7	0.61
	$45^\circ$	0.86	0.83

$$\frac{\chi''_{LF}}{\chi''_{HF}} = \left(\frac{g_2}{g_1}\right)^2 \frac{(1 - \eta_{LF})^2}{(1 + \eta_{HF})^2}, \quad (27)$$

where  $\chi''_{LF}$  and  $\chi''_{HF}$  denote the low- and high-field susceptibilities. The corresponding values of  $\eta$  are given by Eqs. (22) and (23) with

$$\begin{aligned} (\tilde{\omega}_a^0 - \tilde{\omega}_b^0)_{LF} &= \frac{\Delta g \beta H^+}{\hbar} - \frac{2(1-p^2)zJ^2}{\hbar \Delta g \beta H^+}, \\ (\tilde{\omega}_a^0 - \tilde{\omega}_b^0)_{HF} &= \frac{\Delta g \beta H^-}{\hbar} - \frac{2(1-p^2)zJ^2}{\hbar \Delta g \beta H^-}. \end{aligned} \quad (28)$$

Table I lists the theoretical values of the line intensity ratio calculated with Eq. (27), with allowance for Eqs. (28), together with the experimental data of Kuroda, Motokawa, and Date<sup>6</sup> for chlorine salt.

## 5. CONCLUSION

To summarize, we have derived a simplified system of equations for the first Green's functions of exchange-coupled inequivalent spins in a strong constant magnetic field. We have found the spectrum of such a spin system to be valid up to values of  $J^2$  of the order of the square of the difference of the spin partial frequencies. We have derived expressions for the imaginary part of the complex magnetic susceptibility.

Comparison of the results with the qualitative and quantitative experimental data of Refs. 3–6 in the merging–splitting and suppression–enhancement of MR lines of highly polarized spins shows good agreement.

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