THE SECOND MOMENT OF A PARAMAGNETIC ABSORPTION LINE, INCLUDING THE EFFECT OF FINE AND HYPERFINE STRUCTURE

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A formula has been obtained for calculating the reduced second moment of a paramagnetic resonance line and the low-frequency paramagnetic absorption, taking into account the electric field within the crystal. A formula is given for calculating the fine structure constants of nuclear and electronic paramagnetic absorption from the experimental value of the second moment of the absorption curve. A study is made of the way in which the spin-spin paramagnetic relaxation time depends on the interaction of the electron magnetic moments with the internal electric field and the nuclear magnetic moments. As an example, the order of magnitude of the spin-spin relaxation time has been estimated for diamagnetic crystals containing Mn^{++} ions as an impurity.

1. INTRODUCTION

THE well-known formulas of Van Vleck (reference 1, Eq. 11) and Broer (reference 2, Eq. 12) for evaluating the reduced second moment $<(\Delta\nu)^2>$ of a paramagnetic resonance line $f(\nu)$, and the reduced second moment $<\nu^2>$ of a low-frequency paramagnetic absorption line $\varphi(\nu)$, do not take into account the fine and hyperfine structure of the absorption line, and cannot be used to study the internal interactions in many paramagnetic crystals and liquids. After the appearance of Van Vleck's paper,[1] a number of authors derived formulas for calculating $<(\Delta\nu)^2>$, taking into account the internal electric field E, but limiting themselves to particular cases. They considered ions[3] with electron spins of S = 1, the central line $f(\nu)$ for ions[4] with half-integral spins S, and ions[5] with anisotropic g-factors and with $S = \frac{1}{2}$. As for the $\varphi(\nu)$ lines, Kopvillem[6] in calculating $<\nu^2>$ considered the anisotropy of the g-factor and the exchange interaction, and also the interaction $\mathcal{H}_{hfs}$ between the nucleus inside the ion and the magnetic field created at the location of the nucleus by the uncompensated electrons in the ion.

In the present paper a formula is obtained for calculating the reduced second moment of an absorption line for a quantum of constant radio-frequency, for paramagnetic centers which are magnetically equivalent and have an arbitrary spin S, in the following two cases:

a) The field E splits the energy spectrum of the spin system of the paramagnetic material into a series of discrete quasi-continuous bands whose widths depend on the magnetic dipole interaction $\mathcal{H}_d$ and on the exchange interactions $\mathcal{H}_{ex}$ among the paramagnetic centers. In this case the $f(\nu)$ line splits up into a series of fine-structure components $f_{M,M-1}(\nu)$ corresponding to the magnetic dipole transitions $|S, M> \longleftrightarrow |S, M-1>$ between the states $|S, M>$ and $|S, M-1>$ of the paramagnetic centers. (M is the magnetic quantum number.) It should be noted that it is possible to classify the components of the line $f(\nu)$ according to the number M if the static magnetic field H_0 is considerably stronger than the field E, or if the field H_0 is directed along an axis of symmetry of the field E. We shall evaluate the reduced second moment $<(\Delta\nu)^2>_{M,M-1}$ for every component $f_{M,M-1}(\nu)$.

b) The energy spectrum of the spin system consists of a single quasi-continuous band whose width depends on the interactions $\mathcal{H}_d$, $\mathcal{H}_{ex}$, $\mathcal{H}_{hfs}$, and the interaction $\mathcal{H}_E$ of the paramagnetic centers with the field E. The condition that the spectrum of the spin system be quasi-continuous is frequently fulfilled in materials such as dielectric crystals and solutions containing ions of the iron group or the rare earths, with electronic configurations corresponding to $3d^5\,^6S$ or $4f^7\,^8S$. There will be a $\varphi(\nu)$ line under the condition[2] that the frequency ν of the alternating magnetic field H_t is of the order of magnitude of the reciprocal of the paramagnetic spin-spin relaxation time τ_{ss}, and its shape will portray the distribution function for the transition frequencies of the paramagnetic

centers between the levels of the quasi-continuous spectrum of the spin system, arising under the influence of $\mathcal{H}_d$, $\mathcal{H}_{ex}$, $\mathcal{H}_{hfs}$, and $\mathcal{H}_E$. We shall calculate $\langle \nu^2 \rangle$ for a $\varphi(\nu)$ line, taking into account all of the interactions enumerated above.

In both of the cases (a) and (b) we shall consider only electron paramagnetic absorption lines. Nevertheless, all the results we obtain may be applied unchanged to the case of nuclear magnetic resonance. For this purpose the operator $\mathcal{H}_E$ would describe the quadrupole and higher-order interactions between atomic nuclei with spins $I > \frac{1}{2}$ and the gradient of the internal electric field E. We shall assume throughout that the spin-lattice interaction is very much smaller than the interaction $\mathcal{H}_1$ within the spin system, and that these spin-spin interactions are the only ones which determine the shape of the paramagnetic absorption line.

2. REDUCED SECOND MOMENT FOR THE FINE-STRUCTURE COMPONENTS OF A PARAMAGNETIC RESONANCE LINE

Let a static magnetic field H_0 be directed along the z axis, which coincides with one of the principal axes of the g-tensor of the paramagnetic ions, and let H_t be parallel to x. We write the Hamiltonian of the spin system in the form

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1, \quad \mathcal{H}_0 = \mathcal{H}_z + \mathcal{H}_E, \quad \mathcal{H}_1 = \sum_{i>j}\sum_{\alpha,\gamma} P_{\alpha\gamma}^{ij} S^i_\alpha S^j_\gamma, \quad (1)$$

where $\mathcal{H}_1$ is the perturbation, $\mathcal{H}_z$ is the Zeeman energy operator of the paramagnetic ions in the field H_0, $\mathcal{H}_E$ is the Stark energy operator of the ions in the field E, $P_{\alpha\gamma}^{ij}$ is a second order tensor describing the internal interactions in the paramagnetic material, i and j are indices distinguishing the ions, and α and γ are indices denoting the coordinate axes. In our case

$$\mathcal{H}_1 = \mathcal{H}_d + \mathcal{H}_{ex}, \quad P_{\alpha\gamma}^{ij} = g_\alpha g_\gamma \beta^2 (r_{ij}^{-3} - 3r_{ij}^{-5}\alpha^{ij}\gamma^{ij}) - n_{\alpha\gamma}^{ij} J^{ij}, \quad (2)$$

where β is the Bohr magneton, g_α is the spectroscopic splitting factor along the axis α, r_{ij} is the radius vector connecting the i-th and j-th ions, α^{ij} is the projection of the vector r_{ij} on the α axis, J^{ij} is the exchange integral[1] for the ions i and j, and $n_{\alpha\gamma}^{ij}$ is a coefficient characterizing the anisotropy of the exchange interaction, due to the influence of the field E.

To calculate $\langle (\Delta\nu)^2 \rangle$ we shall use the formula[1]

$$\langle (\Delta\nu)^2 \rangle = -h^{-2} \mathrm{Sp}\{[\overline{\mathcal{H}_1}, \mathcal{H}_t]^2\}\{\mathrm{Sp}(\mathcal{H}_t^2)\}^{-1}, \quad \mathcal{H}_t = \sum_{i=1}^N \overset{+}{S}^i_x, \quad (3)$$

where h is Planck's constant, N is the number of paramagnetic ions in the sample, $\overline{\mathcal{H}}_1$ is the portion of the operator $\mathcal{H}_1$ which commutes with $\mathcal{H}_0$, and the notation [,] denotes the formation of the commutator. The operator $\mathcal{H}_t$ describes the effect of the field H_t on the spin system of the paramagnetic material, and its component operators $\overset{+}{S}^i_x$ are obtained from S^i_x by removing all matrix elements which do not correspond to the frequency of the field H_t. In our case the field H_t causes transitions between the $|S, M\rangle$ and $|S, M-1\rangle$ states only, and consequently the only non-null matrix elements of the operator S^i_x are of the form $\langle S, M | S^i_x | S, M-1\rangle$ and $\langle S, M-1 | S^i_x | S, M\rangle$. Using (1) to (3), we obtain

$$\langle (\Delta\nu)^2 \rangle_{M,M-1} = \{h^2(2S+1)\}^{-1} \sum_{i(\neq j)} | Q_1 (P_{xx}^{ij} + P_{yy}^{ij})^2$$
$$+ Q_2 P_{zz}^{ij2} + Q_3 P_{zz}^{ij}(P_{xx}^{ij} + P_{yy}^{ij}) + Q_1(P_{xy}^{ij} - P_{yx}^{ij})^2 |,$$

$$Q_1 = \frac{1}{16}\{2(S+M)^2(S-M+1)^2 + (S+M+1)^2(S-M)^2$$
$$+ (S+M-1)^2(S-M+2)^2\},$$

$$Q_2 = \frac{2S+1}{12}\{(2S+1)^2 - 1\},$$

$$Q_3 = -\frac{1}{2}(S+M)(S-M+1). \quad (4)$$

If the spin system of the paramagnetic material contains ions i and k which are not equivalent, and paramagnetic resonance occurs in ions of the type k having a spin S', then the corresponding reduced second moment $\langle (\Delta\nu)^2 \rangle_{S'}$ can be calculated with the aid of a formula obtained from (4) by setting $Q_1 = Q_2 = 0$ and substituting S'^k for S^j and k for j. If the paramagnetic centers all have the same spin, but are acted on by different intra-crystalline electric fields E, then the corresponding reduced second moment $\langle (\Delta\nu)^2 \rangle_0$ for the fine structure component $f_{1/2,-1/2}(\nu)$ is calculated from formula (14) of reference 4. It should be noted that the quantities $\langle (\Delta\nu)^2 \rangle_{M,M-1}$, $\langle (\Delta\nu)^2 \rangle_S$, and $\langle (\Delta\nu)^2 \rangle_0$ are additive.

3. REDUCED SECOND MOMENT FOR LOW-FREQUENCY PARAMAGNETIC ABSORPTION LINES

The Hamiltonian of the spin system is of the form

$$\mathcal{H} = \mathcal{H}_1,$$
$$\mathcal{H}_1 = \sum_{i>j}\sum_{\alpha,\gamma} P_{\alpha\gamma}^{ij} S^i_\alpha S^j_\gamma + \sum_{i=1}^N\sum_\alpha (D^i_\alpha S^{i2}_\alpha + E^i_\alpha S^{i4}_\alpha + A^i_\alpha S^i I^i_\alpha), \quad (5)$$

where (D_α, E_α) and A_α are the elements of tensors characterizing the interactions $\mathcal{H}_E$ and $\mathcal{H}_{hfs}$ respectively (see reference 7). In the present

case $S_x^i = \overset{+}{S}_x^i$, and the operator $\mathcal{H}_t$ has the form

$$\mathcal{H}_t = \beta \sum_{i,\alpha} g_{t\alpha}^i S_\alpha^i, \quad g_{t\alpha}^i = g_\alpha \cos(\alpha, t), \tag{6}$$

where (α, t) is the angle between the direction of the field H_t and the α axis. Using (3) and the expressions (5) and (6) we obtain

$$\langle \nu^2 \rangle = \{hg\}^{-2}(\langle \nu^2 \rangle_{d+ex} + \langle \nu^2 \rangle_E + \langle \nu^2 \rangle_{hfs}), \tag{7}$$

where subscripts are added in order to distinguish the brackets of the corresponding interactions. The values of the second moments on the right hand side of (7) are given by the following expressions:

$$\langle \nu^2 \rangle_{d+ex} = L \sum_{i(\neq j)} \sum (e_{\theta\psi\pi} e_{\gamma\epsilon\pi} g_{t\epsilon}^i g_{t\psi}^i P_{\gamma\delta}^{ij} P_{\theta\delta}^{ij} + e_{\gamma\epsilon\nu} e_{\theta\psi\delta} g_{t\epsilon}^i g_{t\psi}^i P_{\gamma\delta}^{ij} P_{\nu\theta}^{ij}), \tag{8}$$

$$\langle \nu^2 \rangle_{hfs} = R \sum e_{\gamma\lambda\nu} e_{\delta\psi\nu} g_{t\lambda}^i g_{t\psi}^i A_{\gamma\theta} A_{\delta\theta}, \tag{9}$$

$$\langle \nu^2 \rangle_E = \sum g_{t\beta}^{i2} \{ e_{\alpha\beta\gamma}^2 (v_1 D_\alpha^{i2} + v_2 E_\alpha^{i2} + v_3 D_\alpha^i E_\alpha^i)$$

$$+ e_{\alpha\beta\gamma} e_{\gamma\beta\alpha} (v_1 D_\alpha^i D_\gamma^i + v_4 E_\alpha^i E_\gamma^i + v_3 D_\alpha^i E_\gamma^i) \},$$

$$L = \tfrac{1}{3} S(S+1), \quad R = \tfrac{1}{3} I(I+1), \quad g^2 = \sum g_{t\alpha}^2, \tag{10}$$

where $e_{\alpha\beta\gamma}$ is the unit antisymmetric tensor (with e_{xyz} taken to be unity), and all the indices $\alpha, \beta, \gamma, \theta, \ldots$ are to be summed over the range x, y, z. In formula (9) the index θ is introduced to denote the principal axes of the tensor A. The coefficients v_γ are calculated from the formulas

$$v_1 = b \, \text{Sp} \{[S_\alpha, S_\gamma]_+^2\} = \tfrac{4}{5} S(S+1) - \tfrac{3}{5},$$

$$v_2 = b \, \text{Sp} \{[S_\alpha^2, [S_\alpha, S_\gamma]_+]_+^2\} = \tfrac{16}{21} S^3(S+1)^3$$

$$- \tfrac{268}{105} S^2(S+1)^2 + \tfrac{112}{35} S(S+1) - \tfrac{9}{7},$$

$$v_3 = b \text{Sp} \{[S_\alpha, S_\gamma]_+ [S_\alpha^2, [S_\alpha, S_\gamma]_+]_+\}$$

$$= \tfrac{24}{35} S^2(S+1)^2 - \tfrac{38}{35} S(S+1) + \tfrac{6}{7},$$

$$v_4 = b \, \text{Sp} \{[S_\alpha^2, [S_\alpha, S_\gamma]_+]_+ [S_\gamma^2, [S_\alpha, S_\gamma]_+]_+\} = \tfrac{16}{35} S^3(S+1)^3$$

$$- \tfrac{4}{7} S^2(S+1)^2 - \tfrac{2}{5} S(S+1) + \tfrac{3}{7},$$

$$b = \{\tfrac{1}{3} S(S+1)(2S+1)\}^{-1}, \tag{11}$$

where $\alpha \neq \gamma$; $\alpha, \gamma = x, y, z$; and the symbol $[,]_+$ denotes the formation of the anticommutator. In Eqs. (8) to (10) it is assumed that the mean values derived for the coefficients of the Hamiltonian (5) are determined by the formula

$$\langle A_\alpha^i A_\beta^k \rangle = A_\alpha A_\beta, \tag{12}$$

If the coefficients A_α^i have an arbitrary distribution $\psi(i)$, then

$$\langle A_\alpha^i A_\beta^k \rangle = (N_\alpha N_\beta)^{-1} \sum_{i,k} \psi(i)\psi(k) A_\alpha^i A_\beta^k. \tag{13}$$

In the case (13), the fine and hyperfine structure of the $\varphi(\nu)$ line cannot be resolved by magnetic dilution of the sample, and the coefficients of the Hamiltonian (5) can be found only by comparing the experimental and theoretical moments of the $\varphi(\nu)$ line. It should be mentioned that the coefficients of the Hamiltonian (5) can have different values for magnetically dilute and magnetically concentrated samples. The formulas (8) to (10) which we have obtained can be used to study this question.

In the case of paramagnetic solutions or powders, where the field H_t occurs at arbitrary angles to the x, y, z axes fixed to the molecules or microcrystals, the coefficients $g_{t\alpha} g_{t\beta}$ in expressions (8) to (10) should be replaced by their mean values, found from the formula

$$\langle g_{t\alpha} g_{t\beta} \rangle = \tfrac{1}{3} g_\alpha g_\beta \delta_{\alpha\beta}, \quad \langle g^2 \rangle = \tfrac{1}{3} \sum g_\alpha^2, \tag{14}$$

where $\delta_{\alpha\beta}$ is the Kronecker symbol.

4. REDUCED SECOND MOMENT OF THE $\varphi(\nu)$ LINE FOR Zn(HCOO)$_2 \cdot$2H$_2$O WITH Mn^{++} IMPURITY

As an example of the use of formulas (9) and (10) let us take the case of low-frequency paramagnetic absorption occurring at a Mn^{++} ion in a crystal of Zn(HCOO)$_2 \cdot$2H$_2$O. From the experiments of Hadders et al.[8] it is known that for Mn^{++} ions the width $\Delta\nu_{1/2}$ of the $\varphi(\nu)$ line at half-amplitude is determined by the interactions within the spin system. For small concentrations of Mn^{++} ions the order of magnitude of $\langle \nu^2 \rangle$ is determined by the interactions $\mathcal{H}_E$ and $\mathcal{H}_{hfs}$. From (7), (9), and (10) we obtain

$$\langle \nu^2 \rangle = (hg)^{-2}(\langle \nu^2 \rangle_E + \langle \nu^2 \rangle_{hfs}) = (hg)^{-2}\{g_{tx}^2[v_1(D_y - D_z)^2$$

$$+ v_2(E_y^2 + E_z^2) + v_3(D_y E_y + D_z E_z - D_y E_z - D_z E_y)$$

$$+ v_4(-2E_y E_z)$$

$$+ R(A_{ya_1}^2 + A_{ya_2}^2 + A_{ya_3}^2 + A_{za_1}^2 + A_{za_2}^2 + A_{za_3}^2)]$$

$$+ g_{tx} g_{ty}[-R(A_{xa_1} A_{ya_1} + A_{xa_2} A_{ya_2} + A_{xa_3} A_{ya_3})] + Q\}, \tag{15}$$

where Q contains terms of the type g_{ty}^2, g_{tz}^2, $g_{tz} g_{tx}$, etc., obtained by permutations of the subscript indices given above.

The tensor elements occurring in (15) can be found by comparing the Hamiltonian (5) with the spin Hamiltonian $\mathcal{H}_S$ for an isolated Mn^{++} ion, as given by Bowers and Owen:[7]

$$\mathcal{H}_S = g\beta(H_z S_z + H_x S_x + H_y S_y) + \tfrac{a}{6}(S_z^4 + S_x^4 + S_y^4)$$

$$+ D\left(S_z^2 - \tfrac{35}{12}\right) + E(S_x^2 - S_y^2) + A(S_z I_z + S_x I_x + S_y I_y). \tag{16}$$

From (5) and (16) it follows that $E_x = E_y = E_z$ $= a/6$; $D_z = D$, $D_x = E$, $D_y = -E$; $A_{xx} = A_{yy}$ $= A_{zz} = A$; and $g_x = g_y = g_z = g$.

Making these substitutions, we obtain

$$\langle \nu^2 \rangle = h^{-2} \left\{ \frac{1}{18} a^2 (v_2 - v_4) + 2A^2 R + v_1 [\cos^2(t, x)(E + D)^2 \right.$$
$$\left. + \cos^2(t, y)(E - D)^2 + \cos^2(t, z)(E + D)^2] \right\}. \quad (17)$$

Substituting into (17) the numerical values D $= 0.0485$ cm^{-1}; $g = 1.999$; $E = 0.011$ cm^{-1}; a $= 0.0009$ cm^{-1}; $A = 0.0091$ cm^{-1}; $v_1 = 6.4$, v_2 $= 341.7$, $v_4 = 259.4$, and $R = 2.917$, we obtain

$$\langle \nu^2 \rangle = \{43.72 + 2035 [\cos^2(t, x)$$
$$+ \cos^2(t, z)] + 808.2 \cos^2(t, y)\} \cdot 10^{16} \text{ sec}^{-2} \quad (18)$$

Using Broer's formula,[2] $\tau_{ss} = (\pi/2 \langle \nu^2 \rangle)^{1/2}$, we find from (18) that $\tau_{ssx} = \tau_{ssz} = 2.8 \times 10^{-10}$sec and $\tau_{ssy} = 4.3 \times 10^{-10}$ sec, where the subscripts x, y, and z are introduced to denote the direction of the field H_t which perturbs the spin system.

5. DISCUSSION OF RESULTS

1. Formula (4) is the generalization of a number of known results. Let $\mathcal{H}_1 = \mathcal{H}_d + \mathcal{H}_{ex}$; then from (4), if (a) $S = \frac{1}{2}$ and the temperature $T = \infty$, we have formulas (2) to (4) from a paper[5] by the author; (b) adding the condition that the g-factor be isotropic, $g_{\alpha\alpha} = $ const, we get Eq. (11) of Van Vleck's paper[1] for $S = \frac{1}{2}$; (c) if $S = 1$ and $g_{\alpha\alpha} = $ constant for the fine structure components $f_{1/2,-1/2}(\nu)$, we obtain equation (8) of Kambe and Ollom.[4]

2. Note the following peculiarities of Eq. (4):

a) The quantity $\langle (\Delta\nu)^2 \rangle_S$, characterizing the local field at the position of the paramagnetic center i, depends on S and is uniform for all the fine-structure components.

b) In the presence of strong intracrystalline electric fields the exchange interaction makes a contribution to $\langle (\Delta\nu)^2 \rangle_{M,M-1}$ and, generally speaking, there are no paramagnetic resonance lines. This is due to the fact that the energy of the paramagnetic centers depends on the orientation of the magnetic moments of the centers with respect to the symmetry axes of the field E.

c) Fine-structure components due to the transitions $|S, M\rangle \longleftrightarrow |S, M-1\rangle$ or $|S, 1-M\rangle$ $\longleftrightarrow |S, -M\rangle$ have the same reduced second moment.

d) The quantity $4(Q_1 + Q_2 - Q_3)/9(2S + 1) = W$, corresponding to the factor $\frac{1}{3}S(S + 1)$ in Van Vleck's formula,[1] is greatest for the transition $|S, \frac{1}{2}\rangle \longleftrightarrow |S, -\frac{1}{2}\rangle$ and drops off monotonically as the quantity $|M|$ increases.

e) The ratio $\frac{10}{3} : 1 : \frac{4}{9}$, relating the reduced second moment $\langle (\Delta\nu)^2 \rangle_\Sigma$ which includes the contributions from all the satellite lines, to

$\langle (\Delta\nu)^2 \rangle_{M,M-1}$ and $\langle (\Delta\nu)^2 \rangle_S$ in the case $E = 0$ (see reference 9), is replaced in our case by the formula

$$\langle (\Delta\nu)^2 \rangle_\Sigma : \langle (\Delta\nu)^2 \rangle_{M, M-1} : \langle (\Delta\nu)^2 \rangle_S$$
$$= \frac{10}{9} S(S + 1) : W : [4Q_2/9(2S + 1)]$$

which depends on M as well as on S.

3. Let us now return to formulas (8) to (10). When $S = \frac{1}{2}$, (8) and (9) become identical with (10) and (11) of the author's work in reference 6. If $H_t \parallel x$ and $g_\alpha = $ constant, (8) is identical with Broer's formula (see reference 2). If all the coefficients in the Hamiltonian (5) are zero except E_z and D_z, then (10) agrees with Bersohn's formula (7) (reference 10).

4. The spin-spin paramagnetic relaxation time which we have calculated for a manganese ion agrees in order of magnitude with the results of experiments by Hadders et al.[8] As to the anisotropy of the time τ_{ss}, experimental data are almost entirely lacking. It should be noted that we previously predicted that the time τ_{ss} should depend on the interaction of the electron spins of the paramagnetic ions with the field E surrounding them and with the inner nucleus of the ion (see reference 6), whereas this dependence was first observed experimentally by Townes and his co-workers.[11]

5. Measurements of the quantity $\langle \nu^2 \rangle$ can be made at very low concentrations of paramagnetic centers, where a comparison of the experimental and theoretical results can be made without considering dipole-dipole and exchange interactions between centers. These conditions can be fulfilled conveniently in the case of liquids, where the term $\langle \nu^2 \rangle_{d+ex}$ must be averaged on the basis of some hypothetical assumption as to the nature of the intermolecular motions. A comparison of our results for the manganese ion with the corresponding data for the same ion in aqueous solutions (see reference 12) shows that when crystals containing Mn^{++} ions are dissolved, the field E around the Mn^{++} ion is altered. The coefficients in the Hamiltonian (5) which characterize the field E around a Mn^{++} ion in aqueous solution are several times smaller than the values which we have used in our calculations.

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