

only difference that the fifth component (9 percent of total intensity) is in a considerably greater distance from the fourth component, approximately equal to the distance of the third and fourth components (200–198). All *P* and *R* lines reveal a similar structure.

This work was undertaken in the hope to clarify certain minor features of the structure of the lines in the spectrum of the mercury hydride, and to bring about the first proof of the existence of hyperfine structure in band spectra. The author believes that the second aim was achieved in a satisfactory manner. However, the general relations have not been clarified by this in-

vestigation. Just on the contrary, attempts to find an explanation of the hyperfine structure and of the deviations from the normal rotational isotope effect are meeting serious difficulties. It seems that a clarification of the problems brought forward can be expected from a thorough theoretical study of hyperfine structure and nuclear isotope shift effects in diatomic molecules.

*Note added in proof.*—The availability of concentrated samples of the isotope  $\text{Hg}_{199}$  has been recently announced [C. P. Keim, *Phys. Rev.* **76**, 1270 (1949)]. A corresponding study of the hyperfine structure of its hydride spectrum is in preparation at this laboratory.

## Some Aspects of Paramagnetic Relaxation

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This paper concerns the effect of interactions inside the spin system in giving a finite line width to the energy absorption lines in an oscillating magnetic field. The principal calculations are of absorption coefficients at low frequencies for copper salts. These absorption coefficients refer in most cases to the aperiodic line near zero frequency and not to the Larmor line. The first step is a discussion of the general procedure for reconstructing a shape function  $f(\nu)$  from its moments. The special case in which the zeroth, second, and fourth moments are known arises in the absence of a constant magnetic field, and at the Larmor frequency in a constant magnetic field perpendicular to the oscillating field. These cases are discussed and compared with experiment in Section III; extensive calculations have already been made by Van Vleck in the second case. The magnitude of the exchange coupling is the decisive factor, as pointed out by Gorter and Van

Vleck; and various methods of calculating this magnitude from experimental data are given. Low frequency absorption in a perpendicular field is discussed on the basis of a Gaussian approximation in Section IV, and the agreement with the experiments of Volger, Vrijer, and Gorter is good. In Section V it is shown that quantitative calculations only emphasize the discrepancy, pointed out by Broer, between theory and experiment for low frequency absorption in a parallel constant field. An explanation of the discrepancy is given in terms of the difficulty in resolving out the different lines in this case, due to the exchange broadening of the Larmor line, in contrast to the exchange narrowing of the Larmor line in a perpendicular field. In Section VI a calculation of the isolated susceptibility of a spin system is given for strong fields; it is found to be 0.80 of the thermodynamic or adiabatic susceptibility of Casimir and du Pré, even in the absence of exchange.

### I. INTRODUCTION

THIS paper is a condensation of the doctoral thesis submitted by the author at Harvard University, June, 1949. Its purpose is to discuss quantitative calculations on energy absorption by a paramagnetic salt in a magnetic field; these calculations being restricted to absorption in which the line breadth is due to interactions inside the spin system. The calculations of this paper are similar to those of Van Vleck<sup>1</sup> on the Larmor line in a perpendicular field; in the following paragraphs line shapes will be calculated for other lines of interest.

There are three principal cases which concern us; those in which the energy levels of the salt between which the absorption takes place are those which exist

A. in the absence of a constant magnetic field ( $H=0$ ),

B. in the presence of a field  $H=H_D$  perpendicular to the relatively weak field  $H_0 \exp(2\pi i\nu t)$  from which energy is absorbed,

C. in the presence of a field  $H=H_c$  parallel to the oscillating field  $H_0 \exp(2\pi i\nu t)$ .

<sup>1</sup> J. H. Van Vleck, *Phys. Rev.* **74**, 1168 (1948).

These three cases have been studied experimentally at relatively low frequencies by Gorter, Broer, and others at Leiden.<sup>2,3</sup> Cases A, B, and C are treated in Sections III, IV, and V, respectively. Remarks concerning the applicability of these methods to absorption at the Larmor frequency in a perpendicular field are made at the conclusion of Section III. Energy absorption at the Larmor frequency and at double the Larmor frequency in a parallel field is approached from the more familiar standpoint of the so-called isolated susceptibility of the spin system in Section VI. Absorption at high multiples of the Larmor frequency has not been investigated experimentally. Figure 1 summarizes the investigations made here and elsewhere on paramagnetic relaxation phenomena.

Broer<sup>4</sup> has shown that energy absorption due to spin-spin interaction is characterized completely by the

<sup>2</sup> L. J. F. Broer and J. Kemperman, *Physica* **13**, 465 (1947).

Volger, de Vrijer, and Gorter, *Physica* **13**, 62 (1947).

<sup>4</sup> L. J. F. Broer, thesis, Amsterdam, 1945.

shape function  $f(\nu)$  defined by

$$f(\nu)\Delta\nu = \sum_{\nu-\Delta\nu/2}^{\nu+\Delta\nu/2} |M_{kl}|^2 \quad (1)$$

with  $M_{kl}$  being a matrix element of the total magnetic moment of the salt between two states  $k$  and  $l$  of the spin system. All matrix elements are included in the right-hand sum for which the frequency difference  $\nu_{kl} = (E_k - E_l)/k$  of the two states  $k$  and  $l$  falls in the range  $\nu - \Delta\nu/2 \leq \nu_{kl} < \nu + \Delta\nu/2$ . The increment  $\Delta\nu$  must be small from a macroscopic standpoint, yet large enough so that a good many pairs of discrete states  $k, l$  are included in the sum. Experimental results are expressed in terms of  $f(\nu)$ ; the following sections deal with methods of approximating to this shape function.

The Hamiltonian of the spin system, whose wave functions are those between which the matrix elements  $M_{k,l}$  in Eq. (1) are to be calculated, is taken to be

$$\begin{aligned} \mathcal{H} = & -g\beta H \sum_i S_{zi} + \sum_{i>j} g^2\beta^2 r_{ij}^{-3} [\mathbf{S}_i \cdot \mathbf{S}_j \\ & - 3(\mathbf{S}_i \cdot (\mathbf{r}/r)_{ij})(\mathbf{S}_j \cdot (\mathbf{r}/r)_{ij})] \\ & + \sum_{i>j} g^2\beta^2 r_{ij}^{-3} A_{ij} \mathbf{S}_i \cdot \mathbf{S}_j = \mathcal{H}_0 + \mathcal{H}_1 \quad (2) \end{aligned}$$

with  $\mathcal{H}_0$  and  $\mathcal{H}_1$  defined by

$$\begin{aligned} \mathcal{H}_0 = & -g\beta H \sum_i S_{zi} + \sum_{i>j} g^2\beta^2 r_{ij}^{-3} [B_{ij} S_{zi} S_{zj} \\ & + C_{ij} \mathbf{S}_i \cdot \mathbf{S}_j] + \sum_{i>j} g^2\beta^2 r_{ij}^{-3} A_{ij} \mathbf{S}_i \cdot \mathbf{S}_j, \quad (3) \end{aligned}$$

$$\begin{aligned} \mathcal{H}_1 = & \sum_{i>j} g^2\beta^2 r_{ij}^{-3} [D_{ij} S_{i+} S_{j+} + D_{ij}^* S_{i-} S_{j-} \\ & + E_{ij} (S_{i+} S_{zj} + S_{zj} S_{i+}) + E_{ij}^* (S_{i-} S_{zj} + S_{zj} S_{i-})]. \quad (4) \end{aligned}$$

The coefficients  $B_{ij}$ ,  $C_{ij}$ ,  $D_{ij}$ , and  $E_{ij}$  are defined by

$$\begin{aligned} B_{ij} = & -3(\frac{3}{2}\gamma_{ij}^2 - \frac{1}{2}); \quad C_{ij} = -\frac{1}{3}B_{ij}; \\ D_{ij} = & -\frac{3}{4}(\alpha_{ij}^2 - \beta_{ij}^2 - 2i\alpha_{ij}\beta_{ij}); \\ E_{ij} = & -\frac{3}{2}\gamma_{ij}(\alpha_{ij} - i\beta_{ij}), \quad (5) \end{aligned}$$

where  $\alpha_{ij}$ ,  $\beta_{ij}$ ,  $\gamma_{ij}$  are the direction cosines of  $(\mathbf{r}/r)_{ij}$  with respect to the  $x$ ,  $y$ , and  $z$  axes, respectively; these axes being chosen so that  $H$ , the constant magnetic field, is along the  $z$  axis. The first term in (2),  $-g\beta H \sum_i S_{zi}$ , is the Zeeman energy; the expression

$$\sum_{i>j} g^2\beta^2 r_{ij}^{-3} [\mathbf{S}_i \cdot \mathbf{S}_j - 3(\mathbf{S}_i \cdot (\mathbf{r}/r)_{ij})(\mathbf{S}_j \cdot (\mathbf{r}/r)_{ij})]$$

is the magnetic dipole interaction energy;

$$\sum_{i>j} K_{ij} \mathbf{S}_i \cdot \mathbf{S}_j = \sum_{i>j} A_{ij} g^2\beta^2 r_{ij}^{-3} \mathbf{S}_i \cdot \mathbf{S}_j$$

is the exchange energy. It is supposed, in using (2), that

A. The orbital contribution to the magnetic moment of a paramagnetic atom is quenched completely out by the interaction of the surrounding crystalline electric fields. A first-order correction to this approximation is made by using, not  $g=2$ , but  $g$  as derived from static susceptibility measurements. (The spin only sus-

ceptibility is given theoretically by

$$\chi_0 = C/T = (\frac{1}{3})N g^2\beta^2 S(S+1)/kT,$$

with  $\beta$  the Bohr magneton,  $k$  Boltzmann's constant, and  $N$  the number of paramagnetic atoms per cubic centimeter. The effective gyromagnetic ratio  $g$  as here defined is given by twice the square root of the ratio of the experimental to the theoretical susceptibility.

B. There is no crystalline potential term in the Hamiltonian. This is equivalent to assuming, as far as calculations of the line shape are concerned, that  $S=\frac{1}{2}$ , or else that for some reason the crystalline splitting is negligibly small. For  $S=\frac{1}{2}$ , according to Kramer's theorem,<sup>5</sup> the twofold degenerate level of an atom cannot be split by any electric field, no matter what its strength or asymmetry. Comparison with experiment will be limited in the following to copper salts for which  $S$  is indeed  $\frac{1}{2}$ . Calculations in Section VI are not concerned with line shape and hold for any  $S$ .

The unperturbed Hamiltonian is  $\mathcal{H}_0$ , the perturbing energy  $\mathcal{H}_1$  enters in the calculations of Sections IV and V. The four terms in  $\mathcal{H}_1$  as given in (4) will be called  $\mathcal{H}_1^{(1)}$ ,  $\mathcal{H}_1^{(2)}$ ,  $\mathcal{H}_1^{(3)}$ , and  $\mathcal{H}_1^{(4)}$ , respectively, and are conveniently separated by this breakup for use in the perturbation processes of Sections IV, V, and VI.

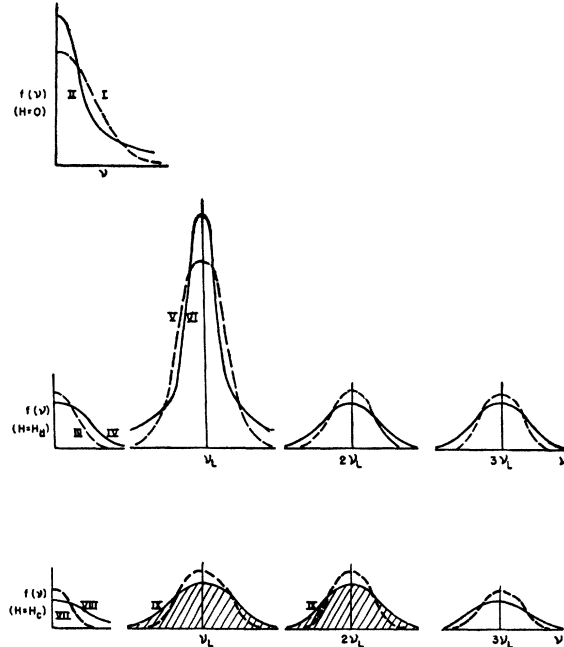


FIG. 1. The function  $f(\nu)$  for no constant magnetic field ( $H=0$ ); for a constant magnetic field perpendicular to the oscillating field ( $H=H_D$ ), and for a constant magnetic field parallel to the oscillating field ( $H=H_e$ ). The dotted lines are for negligible exchange; the solid lines show the effect of exchange. The various lines are discussed in the following places: Curve I; Broer, references 4, 7. Curve II; Section III of this paper. Curves III, IV; Section IV of this paper. Curves V, VI; Van Vleck, reference 1; see also end of Section II. Curves VII, VIII; Section V of this paper. Shaded Area IX; Section VI of this paper.

<sup>5</sup> H. A. Kramers, Proc. Phys. Soc., Amsterdam 33, 959 (1930).

In the so-called strong field limit, in which  $H$  is supposed very much larger than fields characterizing the dipolar and exchange energies, the unperturbed energy levels of  $\mathcal{H}_0$  are just

$$E_{M'} = -g\beta HM' \quad (6)$$

with  $M'$  the  $z$  component of the magnetic moment and a true quantum number for this system. Here the absorption, according to the simple Larmor precession picture, is at the Larmor frequency in a perpendicular field (or at zero frequency in no field). The usefulness of the form (4) for the perturbing energy results from the fact that in the strong field limit non-vanishing matrix elements for a given term of (4) are obtained only between wave functions differing in their associated energy values by one specific multiple of  $h\nu_L$ ,  $\nu_L$  being the Larmor frequency  $g\beta H/h$ . Thus, in the strong field limit the perturbing energy introduces additional absorption only at other multiples of the Larmor frequency; absorption bands appear near frequencies 0,  $2\nu_L$ ,  $3\nu_L$ , and in high order perturbation processes at still higher multiples of the Larmor frequency.

## II. THE METHOD OF MOMENTS\*

Because of the large number of energy levels of the spin system it is not feasible to compute wave functions, matrix elements  $M_{kl}$ , and thus  $f(\nu)$  from (2), (3), and (4) in a straightforward way. The only method of procedure that has proved useful up to the present time is the method of moments in which the following quantities are calculated:

$$\begin{aligned} \int_0^\infty f(\nu) d\nu &= \sum_{k \neq l} |M_{kl}|^2 = \text{Spur} |M^2|, \\ \int_0^\infty \nu^2 f(\nu) d\nu &= \sum_{k, l} \nu_k l^2 |M_{kl}|^2 \\ &= -h^{-2} \text{Spur} \psi_1^2; \psi_1 = (M\bar{U} - \bar{U}M), \\ \int_0^\infty \nu^4 f(\nu) d\nu &= \sum_{k, l} \nu_k l^4 |M_{kl}|^2 \\ &= h^{-4} \text{Spur} \psi_2^2; \psi_2 = M\psi_1 - \psi_1 M. \end{aligned} \quad (7a)$$

The quantities on the left in Eqs. (7a) are the moments of  $f(\nu)$ , by definition. In the following paragraphs average symbols for these moments will be used, as given in Eqs. (7b):

$$\int_0^\infty f(\nu) d\nu = \langle \nu^0 \rangle_{Av}; \left( \int_0^\infty \nu^k f(\nu) d\nu \right) / \langle \nu^0 \rangle_{Av} = \langle \nu^k \rangle_{Av}. \quad (7b)$$

The equivalence of the moments in this case to the right-hand members of Eqs. (7a) has been shown by Waller<sup>6</sup> and Broer<sup>7</sup> according to the general laws of

\* E. T. Whittaker and G. Robinson, *The Calculus of Observations* (Blackie & Son, Ltd., London, 1937), Chapter 8.

<sup>6</sup> I. Waller, *Zeits. f. Physik* **79**, 370 (1932).

<sup>7</sup> L. J. F. Broer, *Physica* **10**, 801 (1943).

matrix multiplication. For a single absorption band the relevant matrix elements  $M_{k, l}$  (where  $k$  and  $l$  are such that  $(E_k - E_l)/h$  is approximately the energy difference corresponding to the particular band under consideration) may be either those of the operator  $g\beta \sum_i S_{zi}$ , or  $g\beta \sum_i S_{xi}$ , in a zeroth approximation, or those obtained from these operators by perturbation calculations with the perturbing energies (4). The energy  $\bar{U}$  consists of all the Hamiltonian with eigenvalues small compared to the Larmor energy  $h\nu_L$ . If  $H=0$ ,  $\bar{U}$  consists of the complete Hamiltonian (2); if  $H \neq 0$ ,  $\bar{U}$  is just  $\mathcal{H}_0$ .

It is simpler to consider the problem of calculating  $f(\nu)$  from its moments for a single absorption band, rather than for all such bands at once. Once these moments (7) are known, the function  $f(\nu)$  can in principle be reconstructed in the following way. Suppose  $f_2(\nu)$  is defined by

$$f_2(\nu) = \langle \nu^0 \rangle_{Av} (2/\pi \langle \nu^2 \rangle_{Av})^\dagger \exp(-\nu^2 (2 \langle \nu^2 \rangle_{Av})) \quad (8)$$

with  $\langle \nu^0 \rangle_{Av} = \int_0^\infty f(\nu) d\nu$ . Then  $f_2(\nu)$  fits the zeroth and second moments. Let  $f_k(\nu)$  be a function fitting the moments  $\langle \nu^0 \rangle_{Av}$ ,  $\langle \nu^2 \rangle_{Av}$ ,  $\dots$ ,  $\langle \nu^k \rangle_{Av}$ . Then a function  $f_{k+2}(\nu)$  fitting the moments  $\langle \nu^0 \rangle_{Av}$ ,  $\dots$ ,  $\langle \nu^k \rangle_{Av}$  and also  $\langle \nu^{k+2} \rangle_{Av}$  is

$$\begin{aligned} f_{k+2}(\nu) &= f_k(\nu) + \left\{ \left[ \langle \nu^{k+2} \rangle_{Av} \right. \right. \\ &\quad \left. \left. - \int_0^\infty \nu^{k+2} f_k(\nu) d\nu \right] / (k+2)! \right\} (d/d\nu)^{k+2} f_2(\nu), \end{aligned} \quad (9)$$

since if the second term of (9) is multiplied by any power of  $\nu$  up to and including  $\nu^k$ , and integrated from 0 to  $\infty$ , the result is zero; however, for  $\nu^{k+2}$  the result is

$$\langle \nu^{k+2} \rangle_{Av} - \int_0^\infty \nu^{k+2} f_k(\nu) d\nu.$$

From this fact it follows that

$$\int_0^\infty \nu^j f_{k+2}(\nu) d\nu = \int_0^\infty \nu^j f_k(\nu) d\nu = \langle \nu^j \rangle_{Av}, \quad (j=0, \dots, k)$$

and

$$\int_0^\infty \nu^{k+2} f_{k+2}(\nu) d\nu = \langle \nu^{k+2} \rangle_{Av}.$$

The properties of the second term can be seen by integrating by parts;  $j$  of the  $k+2$  derivatives of (9) can be used to get rid of  $\nu^j$ , one of the remaining derivatives can be used to integrate, and the result is proportional to  $(d/d\nu)^{2m+1} f_2(\nu)$ . But the operator  $(d/d\nu)^{2m+1}$  just multiplies  $f_2(\nu)$  by a polynomial of odd order, which vanishes at the origin, and  $f_2(\nu)$  vanishes at  $\infty$ . If  $j$  is  $k+2$ , however, all  $k+2$  of the derivatives must be used to act on  $\nu^{k+2}$  and replace it simply by a factorial  $(k+2)!$  This  $(k+2)!$  just cancels the  $(k+2)!$  in the denominator of (9);  $\int_0^\infty f_2(\nu) d\nu$  remains, and this integral

is one. Thus,  $f_{k+2}(\nu)$  fits all moments up to and including  $\langle \nu^{k+2} \rangle_{\mathcal{N}}$ . By means of the formula (9) a sequence of functions can thus be constructed, on the basis of known moments, converging to  $f(\nu)$ .

### III. ABSORPTION WITH NO CONSTANT MAGNETIC FIELD PRESENT

The present section is concerned with calculating the moments (7), for  $H=0$ , substituting these moments into the appropriate formula (9), and comparing the approximate shape function thus obtained with the experimental results. There is only one absorption band to be considered here centered about zero frequency. The relevant magnetic moment is

$$M_z = g\beta \sum_i S_{zi}. \quad (10)$$

The relevant energy is the complete Hamiltonian (2); the operator expressions to be calculated and averaged are the right-hand sides of (7);  $\text{Spur} M_z^2$ ,  $-h^{-2} \text{Spur} (\mathcal{H} M_z - M_z \mathcal{H})^2$  etc.

The first two moments have been calculated by Broer.<sup>4,7</sup> His results are, in brief,

$$\int_0^\infty f(\nu) d\nu = \frac{1}{3} N g^2 \beta^2 S(S+1) = kT\chi_0, \quad (11)$$

$$\int_0^\infty \nu^2 f(\nu) d\nu = -h^{-2} \text{Spur} \psi_1^2 = kT\chi_0 \langle \nu^2 \rangle_{\mathcal{N}}, \quad (12)$$

$$\psi_1 = \left[ U + V, g\beta \sum_i S_{zi} \right] = -3ig^2\beta^3 \sum_{k \neq l} \times \{ r_{kl}^{-3} (\mathbf{S}_k \times (\mathbf{r}/r)_{kl})_z (\mathbf{S}_l \cdot (\mathbf{r}/r)_{kl}) \}, \quad (13)$$

$$\langle \nu^2 \rangle_{\mathcal{N}} = \int_0^\infty \nu^2 f(\nu) d\nu / \int_0^\infty f(\nu) d\nu = g^2 \beta^2 H_i^2 / h^2, \quad (14)$$

$$H_i^2 = 2g^2 \beta^2 S(S+1) \sum_P r_{Pq}^{-6}. \quad (15)$$

The appropriate approximation (9) is  $k+2=2$ ,  $k=0$ ; (9) becomes

$$f_2(\nu) = (2/\pi \langle \nu^2 \rangle_{\mathcal{N}})^{1/2} \langle \nu^0 \rangle_{\mathcal{N}} \exp(-\nu^2/2 \langle \nu^2 \rangle_{\mathcal{N}}). \quad (16)$$

An important point to notice is that  $\langle \nu^2 \rangle_{\mathcal{N}}$  is independent of the exchange constant  $A$ . The mathematical reason for this is that the exchange energy  $\sum_{i>j} K_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$  commutes with  $g\beta \sum_i S_{zi}$ ; thus the operator  $\psi_1$  of (13) is independent of  $A$ . This point will be discussed more fully later, in Section IV.

The experimental results which we will discuss are usually limited because of technical difficulties to such low frequencies that only  $f(0)$  can be determined; they are expressed in terms of a quantity  $\rho'(0)$  defined by

$$\rho'(0) = \pi f(0) / 2kT\chi_0. \quad (17)$$

According to (16) and (17) the theoretical formula

for  $\rho'(0)$  is

$$\rho'(0) = (\pi/2 \langle \nu^2 \rangle_{\mathcal{N}})^{1/2} = (\pi/2)^{1/2} (h/g\beta H_i). \quad (18)$$

Table I summarizes (18) *versus* experimental values for certain copper salts. The quantity  $\bar{C}$ , given in the last column of Table I, is the empirical correction factor to the theory based on the zeroth and second moments only. The following paragraphs attempt to estimate  $\bar{C}$  as it differs from unity.

In order to take into account the effects of exchange which are responsible<sup>8,1</sup> for the discrepancies indicated in Table I, it is necessary at least to calculate the fourth moment, as this is the first moment to depend on  $A$ , the exchange constant. The appropriate formula is

$$\langle \nu^4 \rangle_{\mathcal{N}} = \int_0^\infty \nu^4 f(\nu) d\nu / \int_0^\infty f(\nu) d\nu \quad (19)$$

$$\int_0^\infty \nu^4 f(\nu) d\nu = h^{-2} \text{Spur} \psi_2^2 \quad (20)$$

$$\psi_2 = [U + V, \psi_1]; \quad \psi_1 \text{ given in (13)}. \quad (21)$$

Direct commutation results in

$$\psi_2 = -9g^5\beta^5 \sum'_{k,l} [A_{kl}^{(1)} + (1 + A_{kl}) A_{kl}^{(2)}] r_{kl}^{-6} - 3g^5\beta^5 \sum'_{k,l,u} [(1 + A_{kl}) B_{klu} + D_{klu}] r_{kl}^{-3} r_{ku}^{-3} \quad (22)$$

with

$$A_{kl}^{(1)} = (\mathbf{S}_i \cdot (\mathbf{r}/r)_{kl})^2 [(\mathbf{r}/r)_{kl} \times ((\mathbf{r}/r)_{kl} \times \mathbf{S}_k)]_z \quad (23)$$

$$2A_{kl}^{(2)} = \{ [(\mathbf{S}_k \times (\mathbf{r}/r)_{kl}) \times \mathbf{S}_l]_z, (\mathbf{S}_l \cdot (\mathbf{r}/r)_{kl}) \}_+ + \{ \mathbf{S}_l \cdot \mathbf{S}_k \times (\mathbf{r}/r)_{kl}, (\mathbf{S}_k \times (\mathbf{r}/r)_{kl})_z \}_+ \quad (24)$$

$$B_{klu} = [(\mathbf{S}_k \times \mathbf{S}_l) \times (\mathbf{r}/r)_{kl}] (\mathbf{S}_u \cdot (\mathbf{r}/r)_{kl}) + (\mathbf{S}_k \times \mathbf{S}_l \cdot (\mathbf{r}/r)_{kl}) (\mathbf{S}_u \times (\mathbf{r}/r)_{kl})_z \quad (25)$$

$$-\frac{1}{3} D_{klu} = [(\mathbf{S}_k \times (\mathbf{r}/r)_{kl}) \times (\mathbf{r}/r)_{kl}]_z (\mathbf{S}_l \cdot (\mathbf{r}/r)_{kl}) \times (\mathbf{S}_u \cdot (\mathbf{r}/r)_{kl}) + (\mathbf{S}_k \times (\mathbf{r}/r)_{kl})_{kl} r_{ku} \times (\mathbf{S}_l \cdot (\mathbf{r}/r)_{kl}) (\mathbf{S}_u \cdot (\mathbf{r}/r)_{kl})_z. \quad (26)$$

The symbol  $\{A, B\}_+$  or  $[A, B]_+$  is taken to mean  $AB + BA$ ; and the symbol  $\{A, B\}$  or  $[A, B]$  means  $AB - BA$ .

For a spin of  $\frac{1}{2}$  it is easy to show that

$$A_{kl}^{(2)} + A_{lk}^{(2)} = 0, \quad (27)$$

and since the  $A_{kl}^{(2)}$  terms occur symmetrically in (22), the relation (27) causes the  $A^2$  terms to drop out of (22). Since the crystalline potential terms were omitted originally, this theory will be applied only to substances with a spin of  $\frac{1}{2}$ ; therefore we shall, for the sake of simplicity, omit the  $A_{kl}^{(2)}$  term from now on. This term will presumably be only a small correction for not too large  $S$ .

<sup>8</sup> C. J. Gorter and J. H. Van Vleck, Phys. Rev. 72, 1128 (1947).

The next problem is to square the expression (22) with the  $A_{kl}^{(2)}$  term omitted. Omission of terms whose average is zero results in

$$\psi_2^2 = K_1 + K_2 + K_3 \quad (28)$$

with

$$K_1 = 81g^{10}\beta^{10} \sum'_{k,l} A_{kl}^{(1)} r_{kl}^{-12}, \quad (29)$$

$$K_2 = 81g^{10}\beta^{10} \sum'_{k,l,l'} A_{kl}^{(1)} A_{kl'}^{(1)} r_{kl}^{-6} r_{kl'}^{-6} \quad (30)$$

$$K_3 = 9g^{10}\beta^{10} \sum_{i=0}^5 L_i \quad (31)$$

$$L_0 = \sum'_{k,l,l'} A_{kl} B_{kll'} r_{kl}^{-3} r_{kl'}^{-3} \times [P_{kll'}^6 A_{kl} B_{kll'} r_{kl}^{-3} r_{kl'}^{-3}] \quad (32)$$

$$L_1 = 2 \sum'_{kll'} A_{kl} B_{kll'} r_{kl}^{-3} r_{kl'}^{-3} \times [P_{kll'}^6 B_{kll'} r_{kl}^{-3} r_{kl'}^{-3}] \quad (33)$$

$$L_2 = 2 \sum'_{kll'} D_{kll'} r_{kl}^{-3} r_{kl'}^{-3} \times [P_{kll'}^6 A_{kl} B_{kll'} r_{kl}^{-3} r_{kl'}^{-3}] \quad (34)$$

$$L_3 = \sum'_{kll'} B_{kll'} r_{kl}^{-3} r_{kl'}^{-3} [P_{kll'}^6 B_{kll'} r_{kl}^{-3} r_{kl'}^{-3}] \quad (35)$$

$$L_4 = 2 \sum'_{kll'} D_{kll'} r_{kl}^{-3} r_{kl'}^{-3} [P_{kll'}^6 B_{kll'} r_{kl}^{-3} r_{kl'}^{-3}] \quad (36)$$

$$L_5 = \sum'_{kll'} D_{kll'} r_{kl}^{-3} r_{kl'}^{-3} [P_{kll'}^6 D_{kll'} r_{kl}^{-3} r_{kl'}^{-3}]. \quad (37)$$

The  $L_0$  term will, when evaluated, be proportional to  $A^2$ ; it is the only "pure" exchange term in  $\psi_2^2$ . The two terms  $L_1$  and  $L_2$  will be proportional to  $A$ ; they are terms coupling dipole and exchange interactions. The terms  $L_3$ ,  $L_4$ , and  $L_5$  are pure dipole terms, along with  $K_1$  and  $K_2$ . In evaluating numerically the various terms of (28), two assumptions will be made: first, that exchange acts only between nearest neighbors, and thus  $A_{ij} = 0$  unless  $i, j$  are nearest neighbors; and second, that the paramagnetic atoms are arranged on a simple cubic lattice, so that the number of nearest neighbors is  $z = 6$ .

There are two factors affecting the relative difficulty of numerically evaluating the  $L_i$ 's. One of these results from the fact that  $D_{kll'}$  is a far more complicated expression than  $B_{kll'}$ . Thus in  $L_i$  terms in which  $D_{kll'}$  enters, approximation methods will be used. Secondly it is far simpler to evaluate sums involving exchange interactions, since the pairs of atoms involved do not have to be summed over all possible pairs of neighbors. Involved algebraic manipulation and numerical calcu-

lation finally results in<sup>9</sup>

$$9g^{10}\beta^{10} \text{Spur} L_0 = 40.7g^{10}\beta^{10} S^3 (S+1)^3 A^2 d^{-12}, \quad (\text{error small}), \quad (38)$$

$$9g^{10}\beta^{10} \text{Spur} L_1 = 89g^{10}\beta^{10} N A S^3 (S+1)^3 d^{-12}, \quad (\text{error small}), \quad (39)$$

$$9g^{10}\beta^{10} \text{Spur} L_2 = -80g^{10}\beta^{10} N A S^3 (S+1)^3 d^{-12}, \quad (\text{estimated error negative and less than } -12 \text{ percent}), \quad (40)$$

$$9g^{10}\beta^{10} \text{Spur} L_3 = 75g^{10}\beta^{10} N S^3 (S+1)^3 d^{-12}, \quad (\text{estimated error positive and less than } 25 \text{ percent}), \quad (41)$$

$$9g^{10}\beta^{10} \text{Spur} L_4 = -110g^{10}\beta^{10} N S^3 (S+1)^3 d^{-12} \quad (\text{estimated error negative and less than } 25 \text{ percent}), \quad (42)$$

$$9g^{10}\beta^{10} \text{Spur} L_5 = 1.7 \cdot 10^2 g^{10}\beta^{10} N S^3 (S+1)^3 d^{-12}, \quad (\text{estimated error positive and less than } 25 \text{ percent}), \quad (43)$$

$$\text{Spur} K_2 = 83g^{10}\beta^{10} N S^3 (S+1)^3 d^{-12}, \quad (\text{error small}), \quad (44)$$

$$\text{Spur} K_3 = [22 - 7S^{-1}(S+1)^{-1}] g^{10}\beta^{10} N S^3 \times (S+1)^3 d^{-12}, \quad (\text{error small}). \quad (45)$$

It is seen that  $L_1$  and  $L_2$  cancel, within the accuracy of the evaluation of the lattice sums. Omission of these two terms then yields for  $h^{-4} \text{Sp}\psi_2^2$ :

$$h^{-4} \text{Sp}\psi_2^2 = g^{10}\beta^{10} N d^{-12} h^{-4} S^3 (S+1)^3 [40.7A^2 + 2.4 \cdot 10^2 - 7S^{-1}(S+1)^{-1}]. \quad (46)$$

Division by  $\langle \nu^0 \rangle_{Av}$  from (11), and use of (14) then results in

$$\langle \nu^4 \rangle_{Av} = h^{-4} \text{Sp}\psi_2^2 / \langle \nu^0 \rangle_{Av} = (\langle \nu^2 \rangle_{Av})^2 [0.43A^2 + 2.6 - 0.1S^{-1}(S+1)^{-1}] \quad (47)$$

for the fourth moment. Possibly a term proportional to  $A$ , of magnitude probably positive and less than 0.1A, may be present. The coefficient 2.6 is accurate to around 25 percent. Thus the value  $[2.6 - 0.1/S(S+1)]$  implies that, to within the accuracy of our calculations, if  $A$  is negligible, the mean fourth frequency is just what one would get by integrating the function (16) times  $\nu^4$  from zero to infinity. If there is no appreciable exchange, the function (16) is therefore a good approximation to the actual function describing the shape of the line. This fact has been demonstrated by Van Vleck<sup>1</sup> in connection with the Larmor line in a perpendicular field; Pake and Purcell<sup>10</sup> have tested this theoretical prediction for the substance  $\text{CaF}_2$  and found it to be very well confirmed experimentally.

The formula for  $f_4(\nu)$  is

$$f_4(\nu) = kT \chi_0 (2/\pi \langle \nu^2 \rangle_{Av})^{\frac{1}{2}} \{ 1 + (\langle \nu^4 \rangle_{Av} / 3 \langle \nu^2 \rangle_{Av}^2) / 4! \} (d/d\nu)^4 \exp(-\nu^2 / 2 \langle \nu^2 \rangle_{Av}). \quad (48)$$

<sup>9</sup> A. Wright, thesis, Harvard, 1949.

<sup>10</sup> G. E. Pake and E. M. Purcell, Phys. Rev. **74**, 1184 (1948).

TABLE I. Gaussian approximation to  $f(\nu)$ : theory versus experiment for  $\rho'(0)$ .

Substance	$H_i$	Form (18) for $\rho'(0)$	Exp. $\bar{C} = \frac{\text{Exp. } \rho'(0)}{\text{Form (18)}}$	
$\text{Cu}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	200	2.0	5.7	2.8
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	370	1.1	4.2	3.8
$\text{Cu}(\text{BrO}_3)_2 \cdot 6\text{H}_2\text{O}$	250	1.6	7.1	4.4
$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	590	0.69	6.0	8.7

Formulas (48) and (17) result in

$$\rho'(0) = (\pi/2\langle\nu^2\rangle_{Av})^{1/2} [1 + \frac{1}{8}(\langle\nu^4\rangle_{Av}/\langle\nu^2\rangle_{Av}^2 - 3)]. \quad (49)$$

A comparison of (18) and (49) shows that a theoretical calculation, say  $\bar{C}'$ , of the coefficient  $\bar{C}$  of Table I, in this approximation, is just

$$\bar{C}' = \{1 + \frac{1}{8}[\langle\nu^4\rangle_{Av}/\langle\nu^2\rangle_{Av}^2 - 3]\} = 1 + (\frac{1}{8})0.43A^2. \quad (50)$$

In a purely formal way, without considering whether or not the function (48) is a good enough approximation to the actual shape function, the  $A$  which is necessary according to the experimental values for  $\bar{C}$ , given in Table I, can be calculated from formula (50). These values of  $A$  are called  $A_1$  and are listed in column 3 of Table II.

Now let us investigate the convergence of the sequence (9) near the origin  $\nu=0$ , as it depends on the magnitude of  $A$ . The next approximation,  $f_6(\nu)$ , will differ from  $f_4(\nu)$  by

$$f_6(\nu) - f_4(\nu) = \left[ \langle\nu^6\rangle_{Av} - \int_0^\infty \nu^6 f_4(\nu) d\nu \right] / 6! \\ \times (d/d\nu)^6 \exp(-\nu^2/2\langle\nu^2\rangle_{Av}). \quad (51)$$

At the origin this becomes

$$-15[\langle\nu^6\rangle_{Av} - 15\langle\nu^2\rangle_{Av}\langle\nu^4\rangle_{Av} + 30(\langle\nu^2\rangle_{Av})^3] / [6!(\langle\nu^2\rangle_{Av})^3]. \quad (52)$$

The condition that the expression (49) for  $\rho'(0)$  be a good approximation is therefore that

$$|15[\langle\nu^6\rangle_{Av} - 15\langle\nu^2\rangle_{Av}\langle\nu^4\rangle_{Av} + 30(\langle\nu^2\rangle_{Av})^3] / [6!(\langle\nu^2\rangle_{Av})^3]| \\ \ll [\langle\nu^4\rangle_{Av}/(\langle\nu^2\rangle_{Av})^2 - 3] / 8. \quad (53)$$

The moment  $\langle\nu^6\rangle_{Av}$  is not known; however it is reasonable to expect that

$$\langle\nu^6\rangle_{Av} \cong [C_1 A^4 + C_2 A^2 + C_3](\langle\nu^2\rangle_{Av})^3 \quad (54)$$

with  $C_1 \cong 0.1$ ,  $C_2 \cong 3$ , and  $C_3 \cong 15$ .<sup>9</sup> The expression (53), written, using (54), in terms of  $A$ , becomes

$$|0.1A^4 - 3A^2| \ll 2.5A^2 \quad \text{or} \\ A \ll [(1/0.1)(2.5+3)]^{1/2} = 7. \quad (55)$$

Thus, for  $A \ll 7$  formula (49) will be an adequate approximation. When  $A$  is of the order of 7 or larger however, the convergence of the sequence (9) will be very slow and another approach is indicated. We will return briefly to this question after we have considered other methods of estimating  $A$  accurately.

There are two further methods of estimating  $A$  which we will consider. The first of these is based on the formula (56) below for the ratio of the specific heat constant  $b$  to Curie's constant  $C$ , in terms of  $A$  and  $H_i$  of (15):

$$(b/C) = (b_{\text{mag.}} + b_{\text{exch.}}) / C = (H_i^2/2)[1 + 0.36A^2]. \quad (56)$$

This formula is due to Van Vleck;<sup>11</sup> the experimental determination of  $(b/C)$  has been made from spin-lattice relaxation data by Broer and Kemperman,<sup>2</sup> and by Volger, Vrijer, and Gorter,<sup>3</sup> for Cu salts. Column 4 of Table II gives  $(b/C)$  as derived from their data; column 5 gives  $A_2$  as obtained from these values of  $(b/C)$  and formula (56).

The second method is based on formula (57), due to Opechowski,<sup>12</sup> for the temperature constant  $\Theta$  occurring in the Curie-Weiss formula for the static susceptibility  $\chi = C/(T - \Theta)$ , in terms of  $b$ , the gas constant  $R$ , and the number of nearest neighbors  $b - b_{\text{mag.}}$  of a paramagnetic atom:

$$(b - b_{\text{mag.}}) / R = b_{\text{exch.}} / R = 3\Theta^2 / 2z. \quad (57)$$

Formula (56) in turn relates  $b$  to  $A$  and  $H_i$ . The number of nearest neighbors  $z$  is usually 6;  $R$  is  $8.315 \cdot 10^7$ . Column 6 of Table II gives values for several salts; column 7 gives values for  $A_3$ , as derived from formulas (57), with (56) and these values for  $\Theta$ .

The first point to be noticed in Table II is that  $A_2$  and  $A_3$  agree well for all substances for which both methods are available. The agreement is well within experimental error. Thus we may regard  $A$  as known from  $A_2$  and  $A_3$ .

For  $\text{CuNH}_4(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  the actual  $A$  is thus about 4.5. The inequality (55) is satisfied to a first order of magnitude, but not accurately. This is reflected in the fact that  $A_1$  is 6; thus  $A_1$  and  $A_2$  certainly agree to order of magnitude, but not accurately. The disagreement is moreover in the proper direction. For  $A = 4.5$  the left-hand side of (53) is negative; therefore, as can be seen from (52), the next contribution to  $\rho'(0)$  is positive. Thus the actual  $A$  should be, and is, smaller than  $A_1$ . Unfortunately, no data on  $\rho'(0)$  are available for  $\text{CuK}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ ; thus no  $A_1$  can be calculated. The agreement would presumably be a little better for this substance.

The remaining substances do not have exchange coupling of such a magnitude, as indicated by  $A_2$  and  $A_3$ , that the inequality (55) is satisfied. Thus the parentheses in the  $A_1$  column indicate that (48) and (49) are not good approximations and agreement with  $A_2$  and  $A_3$  should not be expected. All the  $A_1$  in parentheses are less than  $A_2$  and  $A_3$ , as would be expected, since the next contribution (52) to  $\rho'(0)$  is negative in these cases. Thus the values for  $A_2$  and  $A_3$  are at least adequate to account for the observed values of  $\rho'(0)$ .

Thus we may say that the above theory agrees with experiment as far as it goes. For the substances with very large values of the exchange constant, another mathematical method of approach to the problem other than that based on (8) and (9) is indicated. The same mathematical situation exists at the Larmor frequency in a perpendicular field; calculations on this

<sup>11</sup> J. H. Van Vleck, J. Chem. Phys. 5, 320 (1937).

<sup>12</sup> W. Opechowski, Physica 4, 181 (1937).

TABLE II. Magnitude of the exchange coupling by various methods.

Substance	$H_i$	$A_1$ (b/C) · 10 <sup>-6</sup>	$A_2$	$\Theta$	$A_3$
Cu(NH <sub>4</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> · 6H <sub>2</sub> O	200	6	0.18	4.5	—
CuK <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> · 6H <sub>2</sub> O	220	—	0.12	3.3	0.052
CuSO <sub>4</sub> · 5H <sub>2</sub> O	370	(7)	10–20	25	–0.70
Cu(C <sub>2</sub> H <sub>5</sub> N)(NO <sub>3</sub> ) <sub>2</sub>	140	—	0.25	8.3	—
CuCl <sub>2</sub> · 2H <sub>2</sub> O	590	(12)	—	—	–5
Cu(BrO <sub>3</sub> ) <sub>2</sub> · 6H <sub>2</sub> O	250	(8)	—	—	1.5

subject have been made by Van Vleck.<sup>1</sup> However, the available data for this case also applies to substances for which the exchange coupling is very large, such as CuSO<sub>4</sub> · 5H<sub>2</sub>O and CuCl<sub>2</sub> · 2H<sub>2</sub>O. The approximation method (9) is not adequate for these cases either. It is uncertain as to what alternate procedure could be used.

Van Vleck<sup>1</sup> has indicated an interesting analogy between the relaxation theory of Bloembergen, Purcell, and Pound,<sup>13</sup> relating to phenomena in substances with molecular rotation, and the theory in terms of moments. He points out that this analogy would predict a value for the line breadth for very large exchange coupling of the order of magnitude  $h\langle\Delta\nu^2\rangle_N/\tilde{A}$ . The quantity  $\tilde{A}$  relates to Van Vleck's notation; changing over the notation to that in terms of  $A$ , and using the value which Van Vleck has obtained for the mean square frequency of the Larmor line, we have that the line width should be of the order of magnitude of  $2\langle\langle\Delta\nu^2\rangle_N\rangle^{1/2}/A$ .

Half-widths of the Larmor line have been obtained for two Cu salts, CuSO<sub>4</sub> · 5H<sub>2</sub>O and CuCl<sub>2</sub> · 2H<sub>2</sub>O. (Van Vleck has pointed out that, in an effort to reduce the broadening in cupric salts due to anisotropy in the  $g$ -factor,<sup>14</sup> it is advisable to use relatively small constant fields, inasmuch as this broadening is proportional to the applied field. Thus the half-breadths which we will use are those furnished by the measurements of Zavoisky,<sup>15</sup> at relatively low resonant frequencies.) We have obtained an  $A$  value for each of these two substances: 25 and 120, respectively. The half-widths according to the formula in the preceding paragraph would then be for the two substances, respectively,  $\sim 16$  gauss and  $\sim 5.5$  gauss. The observed values are 175 and 125 gauss. One would not expect the difference between observed and predicted values to be off by more than a factor of about two or three because of proportionality factors which could not be obtained through the analogy. However, the conclusive point is that the predicted *ratio* of the two line breadths, which should be independent of any proportionality factors, is  $\sim 3$ . The observed ratio is 1.4. Thus the approach of Bloembergen, Purcell, and Pound does not seem applicable in this case. It is uncertain as to just what the mathematical approach should be.

<sup>13</sup> Bloembergen, Purcell, and Pound, Phys. Rev. **73**, 679 (1948).

<sup>14</sup> M. H. L. Pryce, Nature **162**, 538 (1948).

<sup>15</sup> E. Zavoisky, J. Phys. U.S.S.R. **10**, 170, 197 (1945).

#### IV. ABSORPTION IN THE APERIODIC LINE IN A PERPENDICULAR MAGNETIC FIELD

In the presence of a perpendicular magnetic field the single absorption band centered about zero frequency shifts to an absorption band centered about the Larmor frequency  $g\beta H/h = \nu_L$ . In addition, because of the presence of the spin-spin interaction which spoils any selection rule, absorption bands of weaker intensity are present at frequencies of approximately 0,  $2\nu_L$ , and  $3\nu_L$  (and in higher order perturbation processes at still higher multiples of the Larmor frequency). A direct calculation of  $\sum_k \nu_k |M_{k,l}|^2$ ,  $\sum_k \nu_k^2 |M_{k,l}|^2$ ,  $\dots$  including all pairs of states  $k, l$  as was done in Section III in connection with absorption for no magnetic field present would be completely inappropriate. The sum  $\sum_k \nu_k |M_{k,l}|^2$  would give the area under the function  $f(\nu)$  including all the absorption lines: in the remaining moments the higher frequency bands would actually contribute more due to the weighting factors of  $\nu_k^2$ ,  $\nu_k^4$ ,  $\dots$ . No information at all could be obtained in this way about the low frequency band.

It is necessary to limit the states  $k, l$  appearing in the various series in some way to states with energy differences which are  $\ll g\beta H$ . The problem is to construct, by means of perturbation formulas, an operator expression from  $g\beta \sum_i S_{x_i}$  which gives the correct matrix elements  $(M_x)_{k,l}$  between levels with small energy differences (small compared to  $g\beta H$ ) and no matrix elements for other pairs of states. If we designate this expression by  $(M_x)_{l.f.}$ , (l.f. meaning low frequency), then the moments to be calculated are

$$\text{Sp}(M_x)_{l.f.}^2; \quad -h^{-2} \text{Sp}[\mathcal{I}C_0(M_x)_{l.f.} - (M_x)_{l.f.}\mathcal{I}C_0]; \quad \dots \quad (58)$$

A first-order perturbation theory is sufficient to give non-vanishing matrix elements of  $g\beta \sum_i S_{x_i}$  between states for which  $\nu_{kl} \ll \nu_L$ . The perturbed low frequency elements for  $g\beta \sum_i (S_{x_i} - iS_{y_i})$  and for  $g\beta \sum_i (S_{x_i} + iS_{y_i})$  will first be calculated, and then an average taken to obtain the low frequency elements of  $g\beta \sum_i S_{x_i}$ . This procedure will be simpler and less ambiguous because the selection rules  $\Delta M = -1$  and  $\Delta M = +1$  for  $\sum_i (S_{x_i} - iS_{y_i})$  and  $\sum_i (S_{x_i} + iS_{y_i})$ , respectively, are sharper than the selection rule  $\Delta M = \pm 1$  for  $\sum_i S_{x_i}$ ; thus the energy terms of (4) involved in the respective calculations will be more sharply separated from one another.

According to first-order perturbation theory the new wave functions are

$$\psi^{(1)M'P'} = \psi^{(0)M'P'} + \sum_{M''' = M' \pm 2, \pm 1} \times \psi^{(0)M'''P'''} (\mathcal{I}C_1)_{M'''P'''; M'P'} / (M''' - M') g\beta H, \quad (59)$$

the factor  $(M''' - M') g\beta H$  in the denominator representing a difference of unperturbed energy levels according to (6). Use of the Hermitian properties of the perturbing energy and of the formula

$$F_{M'P'; M''P''} = \int \psi^{*M'P'} F \psi^{M''P''} d\tau \quad (60)$$

for the matrix elements of an operator results in the following expression for the first-order perturbed wave functions of an operator  $F$ :

$$(F^{(1)})_{M'P';M''P''} = (F^{(0)})_{M'P';M''P''} + \sum_{M''(\neq M'')P'''} (F^0)_{M'P';M''P'''} \times (\mathcal{H}C_1)_{M''P''';M''P''} / (M'' - M') g\beta H + \sum_{M''(\neq M'')P'''} (\mathcal{H}C_1)_{M'P';M''P'''} \times (F^0)_{M''P''';M''P''} / (M'' - M') g\beta H. \quad (61)$$

Let the operator  $F$  now be  $g\beta \sum_i (S_{xi} - iS_{yi})$ . The zeroth-order elements  $(F^{(0)})_{M'P';M''P''}$  are then

$$(F^{(0)})_{M'P';M''P''} = \delta^{M'M'-1} (F^{(0)})_{M'P';M'+1P''}. \quad (62)$$

Substitution of (62) into (61), together with  $M' = M''$  in order to get low frequency elements, results in

$$(F^{(1)})_{M'P';M'P''} = [F^0 \mathcal{H}C_1^{\Delta M=1} - \mathcal{H}C_1^{\Delta M=1} F^0]_{M'P';M'P''} / g\beta H_D. \quad (63)$$

That part of  $\mathcal{H}C_1$  with matrix elements of the type

$$(\mathcal{H}C_1)_{M'+1,P''';M'P''} \text{ or } (\mathcal{H}C_1)_{M'P';M'-1,P'''} \text{ is } \mathcal{H}C_1^{(3)}; \quad (64)$$

therefore (64) becomes

$$[g\beta \sum_i (S_{xi} - iS_{yi})]_{l.f.} = (1/H_D) [\sum_i (S_{xi} - iS_{yi}) \mathcal{H}C_1^{(3)}]. \quad (65)$$

A similar expression holds for the matrix elements

$$[g\beta \sum_i (S_{xi} + iS_{yi})]_{l.f.} = (1/H_D) [\sum_i (S_{xi} + iS_{yi}) \mathcal{H}C_1^{(4)}], \quad (66)$$

the appropriate part of  $\mathcal{H}C_1$  being  $\mathcal{H}C_1^{(4)}$ . Direct commutation results in

$$[g\beta \sum_i (S_{xi} + iS_{yi})]_{l.f.} = (g^2 \beta^2 / H_D) \sum' F_{ij}^* \gamma_{ij}^3 \times [2S_{zi} S_{zj} - S_{xi} S_{xj} - S_{yi} S_{yj}] \quad (67)$$

$$[g\beta \sum_i (S_{xi} - iS_{yi})]_{l.f.} = -(g^2 \beta^2 / H_D) \sum' F_{ij} \gamma_{ij}^{-3} \times [-2S_{zi} S_{zj} + S_{xi} S_{xj} + S_{yi} S_{yj}]. \quad (68)$$

An average of (67) and (68) then results in

$$[g\beta \sum_i S_{xi}]_{l.f.} = (g^2 \beta^2 / H_D) \sum' (-\frac{3}{2} \gamma_{ij} \alpha_{ij}) \gamma_{ij}^{-3} \times [2S_{zi} S_{zj} - S_{xi} S_{xj} - S_{yi} S_{yj}]. \quad (69)$$

It must be remembered that the direction cosines in (69), and in the commutator of (69) with  $\mathcal{H}C_0$ , refer to axes such that the magnetic field is along the  $z$  axis. In order to make use of the usual lattice sums in any

equations the transformation formulas

$$\gamma_{ij} = \lambda_1 \alpha_{ij}' + \lambda_2 \beta_{ij}' + \lambda_3 \gamma_{ij}'; \quad \alpha_{ij} = \nu_1 \alpha_{ij}' + \nu_2 \beta_{ij}' + \nu_3 \gamma_{ij}' \quad (70)$$

must be used. The expression which will be obtained for the zeroth and second moments of  $f(\nu)$  will be functions of the cosines  $\lambda_1, \lambda_2, \lambda_3$  of the field  $H_0$  with respect to the crystalline axes; and also of the direction cosines  $\nu_1, \nu_2, \nu_3$  of the oscillating field  $H_0 \exp(2\pi i \nu_3)$  with respect to these axes. These expressions will then be averaged over all directions of  $\lambda_1, \lambda_2, \lambda_3, \nu_1, \nu_2, \nu_3$ . The two resultant moments will refer to a powder, and will be those of interest since the physical measurements have been made only on powders.

In order to calculate the zeroth moment of  $f(\nu)$ , (69) must be squared and averaged over the spin functions, then the transformation formulas (70) must be applied, and appropriate lattice sums substituted. For a calculation of the second moment, the commutator of (69) with  $\mathcal{H}C_0$  is the expression to be squared and evaluated. The results of these two calculations are

$$\langle \nu^0 \rangle_{\text{av}} = 0.72 g^4 \beta^4 N S^2 (S+1)^2 H_D^{-2} d^{-6} \times [1 + 6.8(\lambda_1^2 \nu_1^2 + \lambda_2^2 \nu_2^2 + \lambda_3^2 \nu_3^2)] \quad (71)$$

$$\langle \nu^2 \rangle_{\text{av}} = g^4 \beta^4 \hbar^{-2} d^{-6} [1 + 6.8(\lambda_1^2 \nu_1^2 + \lambda_2^2 \nu_2^2 + \lambda_3^2 \nu_3^2)]^{-1} \{ S(S+1) [-50(\lambda_1^6 \nu_1^2 + \lambda_2^6 \nu_2^2 + \lambda_3^6 \nu_3^2) + 100(\lambda_1^2 \lambda_2^2 \nu_3^2 + \lambda_1^2 \lambda_3^2 \nu_1^2 + \lambda_2^2 \lambda_3^2 \nu_1^2) - 100\lambda_1^2 \lambda_2^2 \lambda_3^2 + (43 + 49A^2)(\lambda_1^2 \nu_1^2 + \lambda_2^2 \nu_2^2 + \lambda_3^2 \nu_3^2) + 32(\lambda_1^4 + \lambda_2^4 + \lambda_3^4) + (-26 + 3A^2)] - 7A^2(\lambda_1^2 \nu_1^2 + \lambda_2^2 \nu_2^2 + \lambda_3^2 \nu_3^2) \}. \quad (72)$$

In calculating  $\langle \nu^2 \rangle_{\text{av}}$  the terms involving a single power of  $A$  have been calculated to be zero or have been estimated to be small. Thus in view of difficulties involved in calculating them they have been omitted. Because of an accidental cancellation it was possible to calculate the pure dipole terms in (72) accurately without too great difficulty, also the pure exchange terms are accurate. The expression for  $\langle \nu^0 \rangle_{\text{av}}$ , (71), is also accurate. The appropriate expressions for a powder have been calculated by averaging (71) and (72) over  $\lambda_1, \lambda_2, \lambda_3, \nu_1, \nu_2, \nu_3$  as

$$\langle \nu^0 \rangle_{\text{av}} = 1.7 g^4 \beta^4 N S^2 (S+1)^2 H_D^{-2} d^{-6}, \quad (73)$$

$$\langle \nu^2 \rangle_{\text{av}} = g^4 \beta^4 \hbar^{-2} d^{-6} [S(S+1)(5.0 + 5.0A^2) - 0.6A^2]. \quad (74)$$

The approximation to  $f(\nu)$  if two moments are known is just  $f_2(\nu)$ , a Gaussian shape function:

$$f_2(\nu) = (2/\pi \langle \nu^2 \rangle_{\text{av}})^{\frac{1}{2}} \exp(-\nu^2 / 2 \langle \nu^2 \rangle_{\text{av}}), \quad (75)$$

$\langle \nu^0 \rangle_{\text{av}}$ , and  $\langle \nu^2 \rangle_{\text{av}}$  being given by (73) and (74), respectively. Such a Gaussian is presumably a good approximation to the shape function, since exchange enters into the mean square frequency (74) in contrast



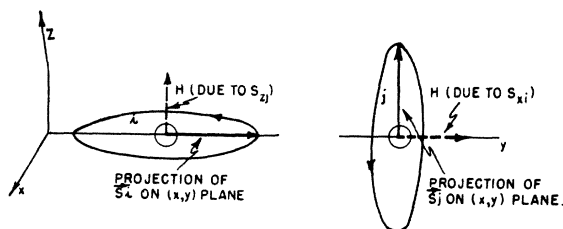


FIG. 2. Explanation of exchange broadening in terms of Larmor precessions; the quantity  $S_{xi} + S_{xj}$  remain constant (zero) at all points of the cycle, thus no energy can be absorbed in the  $x$  direction.

to the situation for the line with no field present or for the Larmor line in a perpendicular field. Therefore, there is no such phenomenon as exchange narrowing present to any great degree in the case that we are discussing, but rather an exchange broadening. The situation here is not critically dependent upon the higher moments to any large extent, since (74) with (75) takes both dipole and exchange forces into account. The fourth moment calculated mathematically will be of the order  $A^4$ ; also the fourth moment calculated from (75) is of order  $A^4$ . Similarly, all higher moments are given correctly as regards order of magnitude by integrating (75).

It is perhaps interesting to consider the difference between exchange narrowing and exchange broadening on the basis of a Larmor precession model. The first point to be noticed is that dipolar broadening is always present. One can in the usual way,<sup>13</sup> regard a dipolar term of the type  $\sum_{i>j} g^2 \beta^2 r_{ij}^{-3} B_{ij} S_{zi} S_{zj}$  as analogous to a sort of Zeeman energy, with  $\sum_j g \beta r_{ij}^{-3} B_{ij} S_{zj}$  representing a mean dipolar field due to atoms  $j$  acting on the magnetic moment  $g\beta S_{zi}$  of atom  $i$ . This field will vary as atom  $i$  varies; thus the resonance frequency will shift slightly over the crystal and the absorption line will be spread out. A measure of the magnitude of the dipolar field is  $H_i$ ; thus we expect, and always find, a term in the root-mean-square frequency proportional to  $H_i$ .

The question arises as to why the exchange interaction cannot always be treated in a similar way, and why there is not always a term in the root-mean-square frequency proportional to  $AH_i$ . Figure 2 illustrates an explanation in terms of Larmor precessions for the case of absorption in the absence of a magnetic field. The mathematical explanation is, of course, that  $g\beta \sum_i S_{xi}$ , the relevant component of the magnetic moment, commutes with the exchange energy, as pointed out in Section III. The exchange interaction, as far as just two atoms are concerned, is proportional to  $S_{xi} S_{xi} + S_{yi} S_{yj} + S_{zi} S_{zj}$ . Figure 2 interprets the term  $S_{xi} S_{xj}$  as a field in the  $z$  direction,  $S_{zj}$ , due to atom  $j$ , acting on atom  $i$ ; and the term  $S_{yi} S_{yj}$  is similarly interpreted as a field in the  $y$  direction due to atom  $j$  acting on atom  $i$ . Figure 2 is drawn for an instant of time such that  $S_{yi} > 0$ ,  $S_{zj} > 0$ . The moments  $S_{xi}$ ,  $S_{xj}$  at

this particular instant of time are zero, and the directions of precession, as shown in the figure, are such that the sum  $S_{xi} + S_{xj}$  remains zero at all later points of the cycle. Thus any absorption due to the precessional motion of one of the atoms is canceled by an equal and opposite effect due to the other atom, and no net absorption at a frequency other than zero can occur as a result of the effects of exchange.

We thus see that there will be no exchange broadening in this case. Not only will the exchange precessions cause no spreading of the absorption however, but they will tend to disrupt the precessional effects of the dipole terms which do contribute to the broadening. Thus there will finally be a certain narrowing effect of the exchange interaction.

The cancellation shown in Fig. 2 depends on the equality of the magnitudes of the magnetic moments under consideration for the two atoms  $i$  and  $j$ . If the magnetic moments are to be calculated by means of a perturbation calculation, then the magnitude of this moment for an atom will vary over the crystal as the mean field acting on the atom varies. The magnitudes in Fig. 2 for atoms  $i$  and  $j$  will not be the same and cannot cancel at all instants of time. In this case the exchange effects can be pictured as fluctuating fields, and exchange broadening is present.

Experiments<sup>3</sup> have determined the variation of the absorption coefficient  $\rho'(0)$  as a function of the magnetic field  $H_D$ . According to the definition (17), for a shape function (75),  $\rho'(0)$  in large fields is given by

$$\rho'(0) = 0.61 [0.30(1 + 0.9A^2)]^{-1/2} (H_i^2 / 2H_D^2) \times [\pi^{1/2} h / (2^{1/2} g \beta H_i)]. \quad (76)$$

We know, moreover, what  $\rho'(0)$  is for  $H_D = 0$ ; the expression (18) times  $\bar{C}$ , with  $\bar{C}$  determined experimentally (see Table I). A reasonable method of combining  $\rho'(0)$  for no field and (76) into one formula is on the basis of a Debye curve

$$\rho'(H_D, \nu=0) = \rho'(0,0) (H_i^2 / 2) / [(H_i^2 / 2) + p H_D^2] \quad (77)$$

with  $p$  as calculated on this basis given by

$$p = 0.9 \bar{C} [1 + 0.9A^2]^{1/2}. \quad (78)$$

The experiments of Volger, Vrijer, and Gorter determine  $(\rho'(H_D) / \rho'(H_D = 0))$  as a function of  $H_D$  for several Cu salts. Consequently, a direct comparison of (77), (78) with experiment is possible. Figure 3 shows this comparison for Cu salts, for which  $\bar{C}$  has also been measured. Curve A in Fig. 3 shows (77) for  $p = 0.9 \bar{C} [1 + 0.9A^2]^{1/2}$ , as given in (78); curve B shows (77) for  $p = 0.9 [1 + 0.9A^2]^{1/2}$ . Both these cases are important for two reasons. In the first place, this correction in formula (78) is in a sense a phenomenological one. The value of  $\bar{C}$  as it differs from unity is due to higher order corrections to the theory for an  $A$  of zero; these corrections are very difficult to evaluate. In the second place, there will be higher order corrections to the function (75), which could be taken into account by

introducing an analogous constant  $\bar{K}$  into (75) and (76). Then (78) would be

$$p = 0.9(\bar{C}/\bar{K})(1 + 0.9A^2)^{\frac{1}{2}}. \quad (79)$$

It is believed that these corrections will be of a lower order of magnitude than in the case with no field present, since the mean square frequency includes the first-order effect of exchange as well as of the dipole forces. Thus  $\bar{K}$  will never exceed  $\bar{C}$ . However, for a substance such as  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ , in which  $A$  is very large, it is possible that these corrections might be appreciable. Thus, the experimental curve in large fields should lie somewhere between (77) with  $p = 0.9\bar{C}(1 + 0.9A^2)^{\frac{1}{2}}$  and with  $p = 0.9(1 + 0.9A^2)^{\frac{1}{2}}$ . A glance at Fig. 3 shows that for  $\text{Cu}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , the substance for which we might expect the best agreement, the curves agree at large  $H_D$  pretty well with the experimental curves. It is gratifying that the curve with the observed value of  $\bar{C}$  in  $p$  agrees a little better as far as numerical values go with the experimental curve. It is also to be noted that the curve with  $\bar{C} = 1$  in  $p$  lies above the experimental curve at large  $H_D$ , thus the correction to (75) is small and  $\bar{K}$  is less than  $\bar{C}$ .

The increase near the origin over the theoretical curves, present in all the substances investigated, is due to the absorption from the Larmor line, which is

not yet resolved out for these values of the magnetic field. The position of the Larmor line is  $\nu_L \propto H_D$ , and a field strength roughly the breadth of the Larmor line in Gauss is necessary to resolve out this line. Due to the exchange narrowing of the Larmor line in a perpendicular field this is accomplished for relatively weak fields in a perpendicular field; however in a parallel field the Larmor line is exchange broadened, and the resolution is difficult to obtain. This point will be referred to later (see the end of Section V).

#### V. ABSORPTION AT LOW FREQUENCIES IN A PARALLEL MAGNETIC FIELD

The relevant component of the magnetic moment whose shape function  $f(\nu)$  is to be investigated is in this case

$$M_z = g\beta \sum_i S_{zi}. \quad (80)$$

It has been pointed out by Broer<sup>4,7</sup> that low frequency matrix elements of this operator vanish, when these elements are calculated on the basis of a first-order perturbation treatment. Use of a second-order perturbation theory is necessary. As Broer observes, the moments of the shape function,  $\langle \nu^0 \rangle_{AV}$ ,  $\langle \nu^2 \rangle_{AV}$ ,  $\dots$  will be proportional to  $(H_i^4/H_c^4)$  in such a situation. Now, in describing the experimental results it is customary to

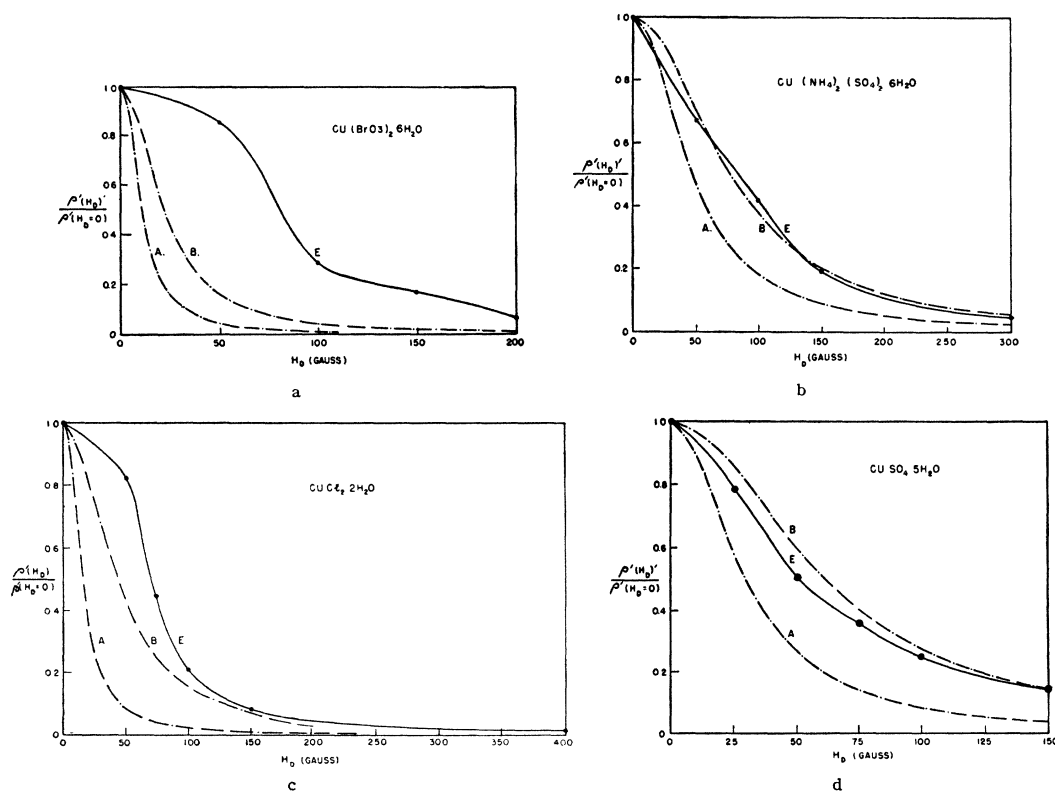


FIG. 3. The theoretical variation with field strength of the absorption coefficient at zero frequency,  $\rho'(H_D)$ . Curves E are the experimental curves. Curves A are theoretical curves of the type (77) with  $p$  given in (78); curves B are theoretical curves of the type (77) with  $p$  given by (78) without a  $\bar{C}$ . The reasons for these two theoretical curves are given in the text.

modify the definition (17) in the presence of a parallel magnetic field. The usual definition in the presence of a magnetic field  $H_c$  is

$$\rho'(0) = \pi [2kT\chi_{\text{adiabatic}}]^{-1} f(0);$$

$$\chi_{\text{adiabatic}} = b\chi_0 / (b + CH_c)^2. \quad (81)$$

Thus two powers of  $H_c$  are removed by the definition (81), therefore, according to the theory for the aperiodic line the quantity  $\rho'(0)$  as defined by (81) should be proportional to  $H_i^2/H_c^2$ .

Experiments have been carried out for magnetic fields several times the mean dipolar field  $H_i$  for a good many substances; in no case has a significant decrease been observed. Figure 4 summarizes the observed situation: the first number in parenthesis gives the mean dipolar field for the salt.

It was uncertain as to whether or not this effect was compatible with the theory, since no quantitative calculations had been made. Therefore, we have calculated the zeroth and second moments of  $f(\nu)$ ; and obtained an approximation to the absorption coefficient  $\rho'(0)$  by fitting the known  $\rho'(0)$  at zero field and the calculated value at large fields with a Debye curve.

The zeroth and second moments have been calculated to be

$$\langle \nu^0 \rangle_{\text{AV}} = 3.0g^6\beta^6NS^3(S+1)^3H_c^{-4}d^{-12}$$

$$= 0.13\chi_0kT(H_i^2/2H_c^2)^2 \quad (82)$$

$$\langle \nu^2 \rangle_{\text{AV}} = 2.4(1+1.8A^2)g^4\beta^4h^{-2}d^{-6}$$

$$= 0.19(1+1.8A^2)g^2\beta^2H_i^2/h^2. \quad (83)$$

Both formulas are calculated for a specific direction of the field  $H_c$ , corresponding to  $\lambda_1 = \lambda_2 = 0, \lambda_3 = 1$ . Also the expression (83), because of its complicated nature, has been calculated for a spin of  $\frac{1}{2}$ . The theoretical formula for  $\rho'(0)$ , according to (82) and (83), can be reasonably taken to be

$$\rho'(H_c, \nu=0) = \rho'(0,0) [(H_i^2/2)/(H_i^2/2 + p H_c^2)], \quad (84)$$

with

$$p = \bar{C} [3.0(1+1.8A^2)^{\frac{1}{2}}(1+0.36A^2)], \quad (85)$$

just as in the perpendicular field case. Formula (85) shows that the predicted decrease of  $\rho'(0)$ , proportional to  $1/H_c^2$ , should take place in fields the order of  $H_i/A^{\frac{1}{2}}$ ; thus quantitative calculations only emphasize the discrepancy between theory and experiment. For

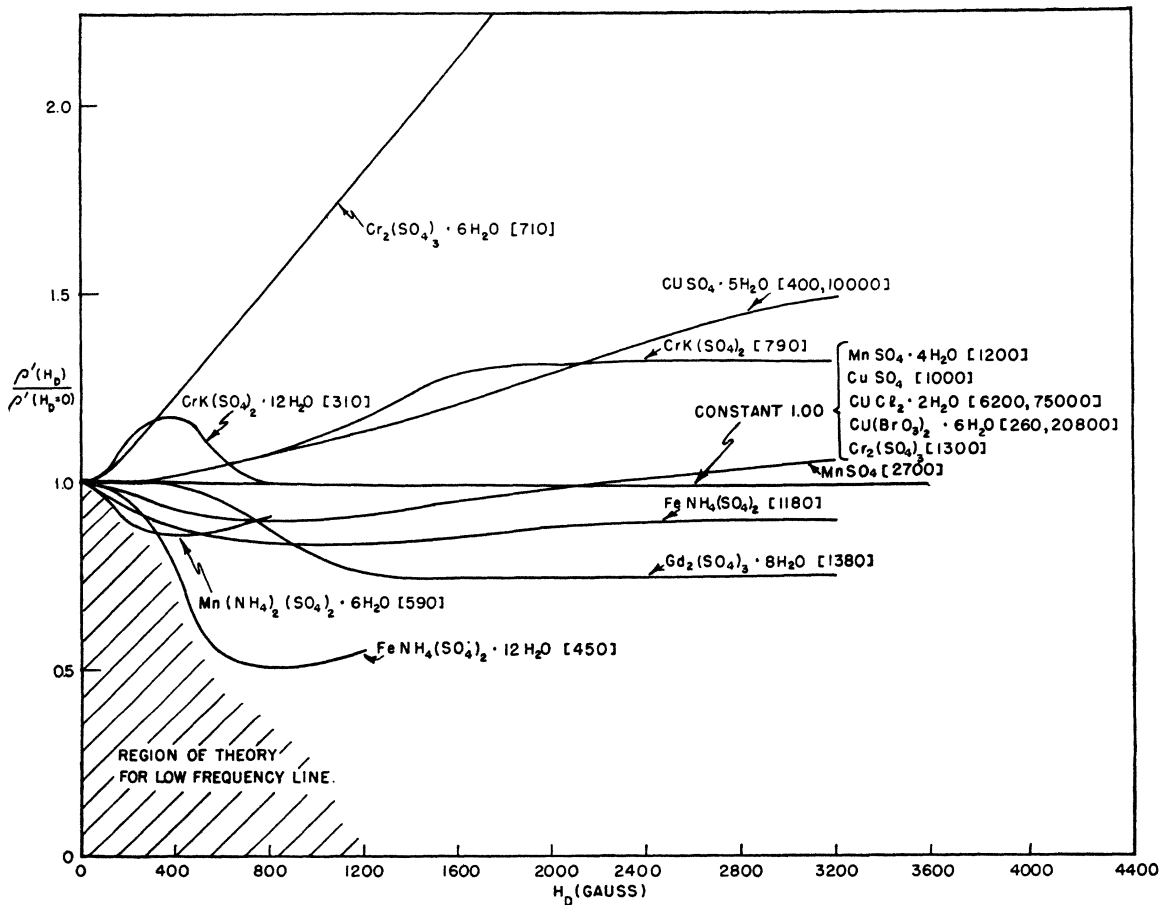


FIG. 4. Experimental variation of  $\rho'(H_c)$  as a function of  $H_c$ , the parallel constant magnetic field, for various salts. The first term in brackets in  $H_i$ , the second term (given when known) is  $AH_i$ . (Note: The subscripts to  $H$  which appear in the figure should be  $c$ , not  $d$ .)

this reason a sketch of the calculation of (82), (83), (84), and (85) shall not be given.<sup>9</sup> Instead, a proposed explanation of this discrepancy will be presented.

It must be remembered, as was mentioned at the conclusion of Section IV, that a certain minimum field strength is necessary to resolve out the Larmor line and make measurements at low frequencies actually refer to the aperiodic line. Now, in a parallel field the Larmor line is exchange broadened; this means that the breadth of this line, which is of order of magnitude of the mean square frequency of the line, varies as

$$[1 + \text{const.} \cdot A^2] g\beta H_i / h. \quad (86)$$

Also it is to be noticed that the field strength necessary to resolve out this line is roughly (86), its line breadth, measured in Gauss. Thus exchange broadening of the Larmor line in a parallel field implies that field larger by factors of 10 or 100 than the mean dipolar field are necessary to effect this resolution. Such fields have not yet been used experimentally, as the second term in parentheses in Fig. 4 shows. This term is  $AH_i$ , and is given for those (copper) salts for which  $A$  is known. Thus the experimental data actually refers to the unresolved Larmor line, for which  $\rho'(0)$ , as defined by (81), should be roughly constant for fields so far used.

A number of effects will influence the variation of  $\rho'(0)$ . First, the shift of position of the Larmor line must be taken into account; second, its shape about this mean position is important; and third, the low frequency line will have a small effect. A combination of these variations causes the observed behavior shown in Fig. 4 and makes this behavior somewhat difficult to predict. Also an arbitrary factor has been removed in the definition (81), which probably is not quantitatively correct. If too large a factor has been removed,  $\rho'(0)$  increase with  $H_c$ , and vice versa. The important thing to notice is that the average behavior is around constancy.

## VI. THE ADIABATIC AND ISOLATED SUSCEPTIBILITIES

The situation with regards to the Larmor line in a parallel constant field is slightly different from that for the absorption lines corresponding to the various conditions discussed in the preceding sections. There are no measurements on the absorption line as regards its shape and intensity in this case; thus the mean square frequency is not of interest. However the sum of  $\langle \nu^0 \rangle_{Av} = \int_0^\infty f(\nu) d\nu$  for the Larmor line and for the line at double the Larmor frequency is just proportional to the isolated susceptibility for the spin system in large fields. This latter susceptibility is of a great deal of interest as far as its numerical agreement or disagreement with the adiabatic susceptibility of Casimir and du Pre<sup>16</sup> is concerned.

The experimental situation is as follows: in studies of spin-lattice relaxation usually the susceptibility  $\chi'_{\text{lattice}}$ <sup>16</sup> obeys a relation of the following sort within the accuracy of the experiments,

$$\chi'_{\text{lattice}} = \chi_\infty + (\chi_0 - \chi_\infty) / (1 + \rho^2 \nu^2), \quad (87)$$

with  $\rho$  a constant with respect to  $\nu$ . According to one point of view,  $\chi_\infty$  is the contribution to the susceptibility  $\chi = (\partial M / \partial H_c)_T$ , obtained upon differentiation of  $M = [\sum_i \langle -\partial W / \partial H_c \rangle \exp(-W_i / kT)] / [\sum_i \exp(-W_i / kT)]$ , keeping the factors  $\exp(-W_i / kT)$  constant, and differentiating only  $(-\partial W_i / \partial H_c)$  with respect to  $H_c$ . For sufficiently high frequency the spin system may be considered isolated; and since the distribution of systems in the various energy states, given by the factors  $\exp(-W_i / kT)$ , cannot change for an isolated substance, the quantity

$$\chi_{\text{iso}} = [\sum_i \langle -\partial^2 W_i / \partial H_c^2 \rangle \exp(-W_i / kT)] / [\sum_i \exp(-W_i / kT)]$$

thus obtained is the isolated susceptibility of the system according to statistical mechanics. On the other hand, according to the thermodynamic theory of Casimir and du Pre,<sup>16</sup>  $\chi_\infty$  is the adiabatic susceptibility

$$\chi_{\text{adiabatic}} = [b / (b + CH_c^2)] \chi_0. \quad (88)$$

It is not definite as to whether these quantities, the isolated and the adiabatic susceptibilities, are actually the same.\*\*

The adiabatic susceptibility is in large fields inversely proportional to  $H_c^2$ :

$$\chi_{\text{adiabatic}} \sim (b/C) \chi_0 / H_c^2; \quad (b/C) = (1 + 0.36A^2) H_c^2 / 2. \quad (89)$$

Matrix elements of the magnetic moment  $g\beta \sum_i S_{zi}$  which are, when squared and averaged, inversely proportional to  $H_c^2$ , can be obtained with the Hamiltonians (3) and (4) for the unperturbed and perturbing energies, by using a first-order perturbation theory. Division by  $kT$  will then result in the isolated susceptibility in large fields for a system with the Hamiltonian [(3) + (4)]. It is found that the appropriate matrix elements will be just the area under  $f(\nu)$  for the Larmor line plus this area for the line at double the Larmor frequency.

A perturbation formula similar to (63) is necessary. The usual commutation relations then result in the following expression for the isolated susceptibility in

\*\* Van Vleck (unpublished) has calculated an expression for the difference between the two susceptibilities. His results show that the difference between the two susceptibilities will vanish only if the energies  $W_i$  or the derivatives  $\partial W_i / \partial H_c$  coincide for all states  $i$  of the spin system, or if the energy depends on the fields  $H_c$  as  $W_i = W_i^{(0)} \varphi(H_c) + \psi(H_c)$  with  $\varphi, \psi$  the same for all  $i$ . The actual expression which he obtains for the difference  $\chi_{\text{ad}} - \chi_{\text{iso}}$  is

$$(1/kT) [ \langle (W^2)_{Av} - \bar{W}^2 \rangle \langle (W^2)_{Av} - \langle W' \rangle_{Av}^2 \rangle - \langle (W W')_{Av} - \bar{W} \langle W' \rangle_{Av} \rangle^2 ] / [ \langle W^2 \rangle_{Av} - \bar{W}^2 ],$$

$W'$  being  $(\partial W / \partial H_c)$ .

<sup>16</sup> H. B. G. Casimir and F. K. du Pre, *Physica* 5, 507 (1938).

large fields:

$$\chi_{\text{iso}} = [kTH_c^2]^{-1} \left[ \sum_{i=1}^4 \langle |\mathcal{H}_1^i|^2 \rangle_{\text{av}} \right]. \quad (90)$$

The energy terms can be easily squared and averaged; when this is done the following result is obtained:

$$\chi_{\text{iso}} = \frac{4}{9} g^4 \beta^6 S^2 (S+1)^2 (kTH_c^2)^{-1} \sum'_{i,j} r_{ij}^{-6} [ |F^{ij}|^2 + |D^{ij}|^2 ]. \quad (91)$$

It is necessary to make substitutions similar to (70) in (91), and then average over all directions of  $\lambda_1, \lambda_2, \lambda_3$ . The following values then result for the lattice sums:

$$\sum'_{i,j} |F^{ij}|^2 r_{ij}^{-6} = \sum'_{i,j} |D^{ij}|^2 r_{ij}^{-6} = 2.52. \quad (92)$$

Substitution into (91) then gives

$$\chi_{\text{iso}} = 2.24 g^4 \beta^4 S^2 (S+1)^2 / (kTH_c^2). \quad (93)$$

Use of  $\chi_0 = Ng^2 \beta^2 S(S+1)/3kT$  and (15) then results in

$$\chi_{\text{iso}} = 0.80 \chi_0 H_c^2 / 2H_c^2. \quad (94)$$

L. J. F. Broer has made an independent calculation of the ratio of the adiabatic and isolated susceptibilities for spins in a large field without exchange (private communication). He arrived at the factor of 0.80. This factor is the same as that of (94).

#### VII. ACKNOWLEDGMENTS

In conclusion, the writer should like to take this opportunity of expressing her deep appreciation to Professor J. H. Van Vleck for suggesting this subject as a research topic. She would like to acknowledge his invaluable counsel and helpful criticism. Also she would like to express her appreciation for the Atomic Energy Commission Predoctoral Fellowship which made this research possible.

### Precision Wave-Length Measurements of the 1.1- and 1.3-Mev Lines of $\text{Co}^{60}$ with the Two-Meter Focusing Curved-Crystal Spectrometer\*

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Recent improvements in the two-meter focusing curved-crystal gamma-ray spectrometer are described which have extended its quantum energy range well above 1 Mev and have also yielded much better luminosity and resolving power than were obtained initially. The improved components are (1) the crystal holder whose aperture and resolving power have been nearly doubled and (2) the collimator the new model of which can now discriminate between the reflected and transmitted beams when these differ in direction by only 8 minutes of arc, a threefold improvement over our first model. Our plans for further possible improve-

ments and the factors governing these are also discussed. Wave-lengths of two gamma-rays emitted following  $\beta$ -decay of  $\text{Co}^{60}$  have been measured with this new equipment using a source of about 50 mc strength and found to have values of  $(9.308 \pm 0.005) \times 10^{-11}$  cm and  $(10.580 \pm 0.005) \times 10^{-11}$  cm corresponding to quantum energies of  $1.3316 \pm 0.0010$  Mev and  $1.1715 \pm 0.0010$  Mev, respectively. The lines appear to have equal intensities. The integrated reflection coefficient of the (310) planes of the curved-quartz crystal still appears to follow a  $\lambda^2$ -dependence on wave-length down to 9 x.u. the shortest so far observed.

#### EXTENSION OF THE WAVE-LENGTH RANGE OF THE TWO-METER FOCUSING CURVED-CRYSTAL GAMMA-RAY SPECTROMETER

THE two-meter focusing curved-crystal gamma-ray spectrometer<sup>1-3</sup> has up to the date of the work here described, been applied only to the measurement of nuclear gamma-ray lines of quantum energy equal to or less than 640 kev.<sup>4-7</sup> Many natural and artificial radioactive sources of great interest exist however which have lines in the quantum energy range from 1 to 2 Mev and even far beyond this. Our present experience in measuring these ultra-short wave-lengths by direct

crystal diffraction has shown that the upper limit of quantum energy beyond which the precision of the method falls to a value comparable with the precision obtainable with the magnetic  $\beta$ -ray spectrometer is probably fixed by the characteristics of the crystal planes used for the diffraction. In the case of our present two-meter curved-crystal spectrometer utilizing the (310) planes of quartz this limiting precision for the measurement of wave-lengths seems to correspond to an uncertainty of about  $\pm 0.005$  x.u. This uncertainty is essentially constant independent of the wave-length measured. Thus, at a wave-length of 5 x.u. or about 2.5 Mev, a precision of the order of one part in a thousand in wave-length measurement can still be obtained. It has, therefore, seemed well worth while to try to extend the range of applicability of the instrument as far as possible above the 1 Mev value. Such an extension requires the following two improvements in the method.

\* Assisted by the Joint Program of the AEC and the ONR.

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<sup>5</sup> Watson, West, Lind, and DuMond, *Phys. Rev.* **75**, 505 (1949).

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