General Theory of Cross Relaxation. I. Fundamental Considerations*

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A statistical analysis is made of spin transitions induced by dipole interactions which change the total magnetization while exactly conserving energy. The first-order effect of the dipole operator can be described by a function $\Phi(\omega)$, which is related to the level broadening observed in resonance lines. The second-order effect leads to a function $\chi(\omega)$ which represents the power spectrum of the dipole operator. The cross-relaxation probability $W_{CR}(\omega)$ is given by the convolution of these two functions. W_{CR} is calculated explicitly in various approximations, without appeal to moments. For single-spin flips in magnetically dilute systems, the magnitude of W_{CR} depends linearly on the concentration n. There is a very sharp peak at $\omega=0$ with a width proportional to the geometric mean of the resonance width and of the nearest-neighbor dipole energy.

I. INTRODUCTION

SINCE cross relaxation was first proposed[1] as an explanation of intermediate relaxation times,[2] much theoretical and experimental work has amplified and confirmed the occurrence of such a relaxation process. As a starting point, we summarize the present state of the theory. One considers a Hamiltonian

$$\mathcal{3C}=\mathcal{3C}_0+\mathcal{3C}_{\text{dip}}, \tag{1}$$

where $\mathcal{3C}_0$ includes Zeeman and crystal energies, and $\mathcal{3C}_{\text{dip}}$ is the dipole interaction energy. The cross-relaxation transition probability is given by

$$W(\omega)=(2\pi/\hbar)M^2 g(\omega), \tag{2}$$

where M is the transition matrix element arising from $\mathcal{3C}_{\text{dip}}$, $g(\omega)$ is a probability function peaked at $\omega=0$, and $\hbar\omega$ is the energy that is exchanged between $\mathcal{3C}_0$ and $\mathcal{3C}_{\text{dip}}$. In terms of a representation in which $\mathcal{3C}_0$ is diagonal, the $g(\omega)$ embodies the effect of the diagonal and semidiagonal parts of $\mathcal{3C}_{\text{dip}}$, which rearrange the entire dipole lattice in such a manner as to conserve over-all energy.

Two prescriptions have been used to calculate $g(\omega)$. The "exact" method evaluates moments of $g(\omega)$ by means of the usual trace formulas.[1,3] The "approximate" method considers $g(\omega)$ as the convolution of the resonance lines between which cross relaxation occurs. For instance, let $g_1(\omega)$ describe the line shape for absorption between states A and B, and let $g_2(\omega)$ describe the absorption line shape involving states C and D; then the $g(\omega)$, for a process in which one spin flips from A to B while another flips from D to C would be given by

$$g(\omega)=\int_{-\infty}^{\infty} g_1(\omega')g_2(\omega-\omega')d\omega', \tag{3}$$

where ω corresponds to the "leftover" energy, ΔE_{AB}

$-\Delta E_{CD}$. Since g_1 and g_2 are quite sharply peaked around $\omega=0$, g will also be peaked at $\omega=0$ in agreement with experiment.[4-8]

A number of difficulties have arisen, however, with the more detailed quantitative development of the theory. Among these we may mention the following:

(1) The "exact" moment calculations of Kopvillem,[9] Kiel,[10] and Hirono[11,12] indicate that the shape function which seems consistent with these calculations does not resemble the shape function which emerges from the "approximate" method. For 1- and 2-spin processes, Kopvillem predicts a square shape with a width of the same order as the resonant frequency, and essentially independent of concentration. Similarly, for a 3-spin process, Kiel and Hirono obtain leading terms for $g(\omega)$ which are in first-order concentration and frequency-independent. Equation (3), on the other hand, predicts a sharply peaked resonance function with a width and a concentration dependence similar to the absorption signal.

(2) The relationship of experimentally observed features to the predictions of either method seem somewhat unclear. For a concentrated system like LiF,[4] the convolution scheme provides a satisfactory interpretation for much, but not all, of the data. For dilute systems like ruby, the effects are also sharply resonant[6] and, at least for two-spin processes, appear to have a concentration-dependent width. On the other hand, this width seems to exceed considerably the absorption width expected from the convolution scheme. Furthermore, the intensity of the effect shows a concentration dependence unaccounted for by any calculation.

(3) There are also two conceptual difficulties. One

[1] N. Bloembergen, S. Shapiro, P. S. Pershan, J. O. Artman, Phys. Rev. 114, 445 (1958).
[2] J. A. Giordmaine, L. E. Alsop, F. R. Nash, and C. H. Townes, Phys. Rev. 109, 302 (1958).
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[7] R. W. Roberts, J. H. Burgess, and H. D. Tenney, Phys. Rev. 121, 997 (1961).
[8] A. A. Manenkov and A. M. Prokhorov, Zh. Experim. i Teor. Fiz. 42, 75 (1962) [English transl.: Soviet Phys.—JETP 15, 54 (1962)].
[9] U. K. Kopvillem, Fiz. Tverd. Tela. 2, 1829 (1960) [English transl.: Soviet Phys.—Solid State 2, 1653 (1960)].
[10] A. Kiel, Phys. Rev. 120, 137 (1960).
[11] M. Hirono, J. Phys. Soc. Japan 16, 766 (1961).
[12] M. Hirono, J. Radio Res. Labs. Japan 9, 73 (1961).

involves the sometimes ambiguous relationship of a function to its moments (to be more fully discussed in a future publication); the other concerns the precise origin and meaning of the shape function $g(\omega)$. Clarification of this latter question is one of the main objectives of the present work.

We shall re-examine the physical premises of the theory, construct a new mathematical formalism, and derive closed analytic expressions for the transition probability. While our theory is applicable to general cross-relaxation processes, we begin with the simplest possible process, in which a single spin flips.

II. ELEMENTARY PHYSICAL CONSIDERATIONS

We consider the Hamiltonian of Eq. (1).

$$\mathcal{3C} = \mathcal{3C}_0 + \mathcal{3C}_{\text{dip}}.$$

Without the interaction $\mathcal{3C}_{\text{dip}}$, each particle is independent, and its energy has eigenvalues E_A^0, E_B^0, etc. The eigenvalues of $\mathcal{3C}$ are then simply sums of the single-particle eigenvalues. Because the particles are coupled by $\mathcal{3C}_{\text{dip}}$, their individual energy is no longer a constant of the motion. Nevertheless, as long as $\mathcal{3C}_{\text{dip}}$ is small, it is still convenient to choose the eigenstates of $\mathcal{3C}_0$ as the zeroth-order eigenstates of $\mathcal{3C}$. The diagonal and off-diagonal elements of $\mathcal{3C}_{\text{dip}}$ are then defined with respect to a representation in which $\mathcal{3C}_0$ is diagonal. In first order, the diagonal elements of $\mathcal{3C}_{\text{dip}}$ can be thought of as shifting the energy of each particle, by an amount E^{dip}, from its unperturbed value E^0. The energy shift will be different for each ion, because each ion sees a different local field. The energies of all the particles in a given Zeeman state will form a distribution centered on the Zeeman energy. In this sense, one speaks of the dipole interaction as "smearing" the Zeeman levels. The energy shift of an individual ion will depend not only on the specific environment in which the ion finds itself, but also on the Zeeman state in which it happens to be, since the diagonal elements of $\mathcal{3C}_{\text{dip}}$ are not all equal.

In higher order, transitions between states can be considered as induced by the "rotating" off-diagonal dipole matrix elements. Just as each ion sees a different diagonal perturbation, so it sees a different transition operator. Both are effects of the same local field.

We wish to calculate the probability that a particle will make a nonradiative transition from Zeeman state A, with unperturbed energy E_A^0, to Zeeman state B, with unperturbed energy E_B^0. Such a transition is possible only for a spin which happens to see a dipolar configuration such that, by flipping, it automatically changes the dipolar energy by the right amount to compensate for the change in Zeeman energy. Energy conserving transitions between separated Zeeman states A and B are possible because (1) the actual energy of a spin in state A or B will, in general, deviate from E_A^0 or E_B^0; (2) the magnitude of this perturbation
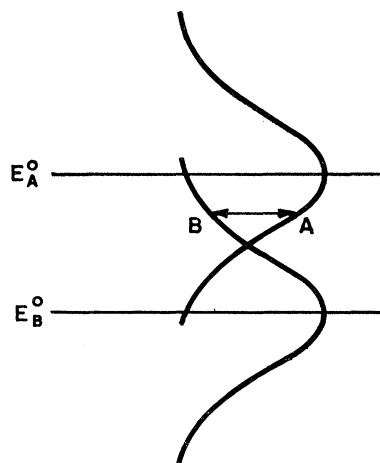

FIG. 1. Energy conserving transitions between different Zeeman states.

will be different when the spin finds itself in state A and when in state B.

Figure 1 shows a distribution of states around Zeeman energies E_A^0 and E_B^0. We are interested in transitions between points like A and B. Such transitions are nonradiative, since they fulfill the requirement

$$E_A^{\text{total}} = E_B^{\text{total}}, \tag{4}$$

where

$$E^{\text{total}} = E_0 + E^{\text{dip}}. \tag{5}$$

At the same time, such transitions change the relative populations of levels A and B, as well as the total magnetization of the system.

We do not require that each spin flip be accompanied by a dynamic rearrangement of the entire lattice to conserve energy, and in this respect our picture seems somewhat simpler than the one suggested by Bloembergen.

Stated in the present terms, the crux of the problem is to pick out those dipole configurations which meet the rather stringent requirement of Eq. (4). For each such configuration, we calculate the transition probability and then sum the result. The probability of finding a suitable dipole configuration can be considered as a density function. The total transition probability can then be interpreted as the average of the transition operator over this density function.

III. GENERAL EXPRESSION FOR CROSS-RELATION PROBABILITY

We now derive in integral form a general expression for the probability of a dipole-induced single-spin flip. For clarity's sake, we somewhat arbitrarily divide the discussion into three steps. First, we set up a formalism to project the suitable dipole configurations. Then we calculate the transition probability, summed over these configurations. Finally, we discuss the significance of the resulting formula from some alternate viewpoints.

The Density Function

We first calculate the total number of configurations that can result from putting N spins randomly into M lattice sites. If the average volume per lattice site is v, then M is simply the total volume in units of v. We define the spin concentration

$$n = N/M \equiv vN/V. \tag{6}$$

The total number of configurations is then

$$C = M!/N!(M-N)!. \tag{7}$$

By use of Stirling's approximation

$$x! = x^x e^{-x}, \tag{8}$$

and after some elementary computations, we obtain, for small n,

$$C = (1/N!)[M(1-n)]^N. \tag{9}$$

The factor $(1-n)$ accounts for the fact that we allow only one spin per lattice site rather than an arbitrary number. Stated in terms of the volume V

$$C = \frac{1}{N!}\left(\frac{1-n}{v}\right)^N V^N \equiv \frac{1}{N!}\left(\frac{1-n}{v}\right)^N \int d\mathbf{r}_1 \cdots d\mathbf{r}_N. \tag{10}$$

Let us consider the simple question: What is the probability that a spin in state A will have some specified energy $E_A{}^{\text{total}}$? Now

$$E_A{}^{\text{total}} = E_A{}^0 + E^{\text{dip}}. \tag{5}$$

$E_A{}^{\text{total}}$ and $E_A{}^0$ are numbers, but $E_A{}^{\text{dip}}$ is a function of the coordinates of every spin in the system. When we count the number of configurations, $C(E_A{}^{\text{total}})$, which fulfills the requirement (5), we proceed as before, except that we need to introduce the constraint [$\delta(x-x_0)$ is the Dirac delta function]

$$\delta[E_A{}^{\text{total}} - (E_A{}^0 + E_A{}^{\text{dip}})]$$

into the volume integrals of Eq. (10):

$$C(E_A{}^{\text{total}}) = \frac{1}{N!}\left(\frac{1-n}{v}\right)^N \int d\mathbf{r}_1 \cdots d\mathbf{r}_N$$
$$\times \delta[E_A{}^{\text{total}} - (E_A{}^0 + E_A{}^{\text{dip}})]. \tag{11}$$

The fractional number of configurations that meet this constraint is evidently

$$f(E_A{}^{\text{total}}) = C(E_A{}^{\text{total}})/C = \frac{1}{V^N}\int d\mathbf{r}_1 \cdots d\mathbf{r}_N$$
$$\times \delta[E_A{}^{\text{total}} - (E_A{}^0 + E_A{}^{\text{dip}})]. \tag{12}$$

In similar fashion, the condition that a particle in state B has an energy $E_B{}^{\text{total}}$ is expressed by the constraint

$$\delta[E_B{}^{\text{total}} - (E_B{}^0 + E_B{}^{\text{dip}})].$$

The condition, $E_A{}^{\text{total}} = E_B{}^{\text{total}}$, is expressed by the constraint

$$\delta[E_A{}^{\text{total}} - E_B{}^{\text{total}}].$$

Finally, to find the total number of "overlapping" states, one must integrate over-all values of $E_A{}^{\text{total}}$ and $E_B{}^{\text{total}}$. Thus, the fraction of configurations that satisfy our requirements is given by

$$f = \frac{1}{V^N}\int d\mathbf{r}_1 \cdots d\mathbf{r}_N \delta[E_A{}^{\text{total}} - (E_A{}^0 + E_A{}^{\text{dip}})]$$
$$\times \delta[E_B{}^{\text{total}} - (E_B{}^0 + E_B{}^{\text{dip}})]$$
$$\times \delta[E_A{}^{\text{total}} - E_B{}^{\text{total}}]dE_A{}^{\text{total}}dE_B{}^{\text{total}}. \tag{13}$$

Using the elementary properties of δ functions,[13] and the notation

$$\hbar\omega = E_A{}^0 - E_B{}^0, \tag{14}$$
$$\hbar\Delta\omega = E_B{}^{\text{dip}} - E_A{}^{\text{dip}}, \tag{15}$$

the expression (13) can be written more simply

$$f(\omega) = \frac{1}{V^N}\int d\mathbf{r}_1 \cdots d\mathbf{r}_N \delta[\omega - \Delta\omega]. \tag{16}$$

Replacing the δ function by its Fourier transform, we have

$$f(\omega) = \frac{1}{V^N}\int d\mathbf{r}_1 \cdots d\mathbf{r}_N \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-i\rho(\omega-\Delta\omega)}d\rho. \tag{17}$$

The $\Delta\omega$ in Eq. (17) is a function of all the $\mathbf{r}$'s. We assume that the contributions of all the particles to the energy shift $\Delta\omega$ are additive:

$$\Delta\omega = \sum_i \Delta\omega(\mathbf{r}_i) \tag{18}$$
$$\equiv \frac{1}{\hbar}\sum_i \mathcal{3C}_{BB}{}^{\text{dip}}(\mathbf{r}_i) - \mathcal{3C}_{AA}{}^{\text{dip}}(\mathbf{r}_i). \tag{19}$$

The approximation of additivity Eq. (18) involves an error of the order of the ratio of the dipolar energy to the Zeeman energy, which is small except for very low magnetic fields. With Eq. (18), the $\mathbf{r}$ integrals implied in Eq. (17) are now separable, and we may write

$$f(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \Phi(\rho)e^{-i\rho\omega}d\rho \tag{20}$$

with

$$\Phi(\rho) = \lim_{N\to\infty}\left[\frac{1}{V}\int d\mathbf{r}\, e^{i\rho\Delta\omega(\mathbf{r})}\right]^N. \tag{21}$$

The function $\Phi(\rho)$ and its Fourier transform $f(\omega)$ have been discussed by many authors.[14-17]

[13] H. Heitler, *Quantum Theory of Radiation* (Oxford University Press, New York, 1957), 3rd ed., p. 66 ff.
[14] H. Margenau and J. Watson, Rev. Mod. Phys. 8, 22 (1936).
[15] H. Margenau, Phys. Rev. 48, 755 (1935).
[16] P. W. Anderson, Phys. Rev. 76, 647 (1949).
[17] P. W. Anderson, Phys. Rev. 82, 342 (1951).

We are thus able to calculate, in terms of known functions, the fraction of configurations for which an *energy conserving* transition between two Zeeman states is possible. This fraction is a function of the energy separation $\hbar\omega$ of the Zeeman states. We have referred to it as a density function because it gives the density of available configurations as a function of ω.

The Transition Operator

The introduction of the transition operator is straightforward. This operator is $(\sum M_i)^2$, where M_i is the off-diagonal dipole matrix element connecting Zeeman states A and B, and involving the ith spin and the reference spin we are considering. The M_i are functions of the coordinate variables. Consequently, the transition matrix element is different for each allowed configuration of spins. This means that in the process of picking out suitable configurations from the ensemble, we weight each configuration separately with its own transition operator. In other words, the transition matrix element goes inside the coordinate integrals of Eq. (13). Analogous to Eq. (16), we now obtain for the actual transition probability

$$W(\omega) = \frac{2\pi}{\hbar}\frac{1}{V^N}\int dr_1\cdots dr_N[\sum_i M^2(r_i)]\delta(\omega-\Delta\omega). \quad (22)$$

We note that

$$(\sum M_i)^2 = \sum M_i^2. \quad (23)$$

The cross terms vanish in the understood integration over time because of the different time dependence of each M_i.

Each term in the sum over i gives an identical integral, so that

$$W(\omega) = \frac{2\pi}{\hbar}\frac{n}{v}\int_{-\infty}^{\infty}\chi(\rho)\Phi(\rho)e^{-i\rho\omega}d\rho, \quad (24)$$

where

$$\chi(\rho) = \frac{1}{2\pi}\int dr M^2(r)e^{i\rho\Delta\omega(r)}, \quad (25)$$

and $\Phi(\rho)$ is defined in Eq. (21). Actually, the N in Eq. (21) is here replaced by $N-1$, but this makes no difference whatsoever since

$$\lim_{V\to\infty}\left[\frac{1}{V}\int dr e^{i\rho\Delta\omega(r)}\right] = 1. \quad (26)$$

We remark parenthetically that our discussion is applicable rather more simply to resonance lines. The differences are the following: Our constraint $\Delta E^{\text{total}}=0$ is replaced by the constraint $\Delta E^{\text{total}}=\Delta E^{\text{Zeeman}}$, which merely shifts the center frequency. The transition operator is changed to S_x^2, without any coordinate dependence, which eliminates $\chi(\rho)$ in Eq. (24). In particular, $\Phi(\rho)$ remains the same. Thus, $\Phi(\rho)$ is

essentially the Fourier transform of the resonance line shape. The function $\Phi(\rho)$ is therefore accessible to us through experiment, even if we were not able to calculate it.

Equation (24) is our general formula for the single-spin cross-relaxation probability, as a function of the Zeeman level separation, $\hbar\omega$.

Alternate Interpretations

Equation (24) can be given a variety of physical interpretations. First of all, the function $\chi(\rho)$ is closely related to the autocorrelation function of the transition operator, summed over the lattice. The autocorrelation of a function $F(t)$ is defined as

$$C(\rho) = \langle F(t+\rho)F^*(t)\rangle_{\text{time average}}. \quad (27)$$

If F is an operator, then in the Heisenberg representation

$$F(t+\rho) = \exp(i\mathcal{H}\rho/\hbar)F(t)\exp(-i\mathcal{H}\rho/\hbar). \quad (28)$$

When F and $\mathcal{H}$ refer to the off-diagonal and diagonal parts of $\mathcal{H}^{\text{dip}}$, we obtain

$$M(t+\rho) = e^{i\rho\Delta\omega}M(t) \quad (29)$$

and

$$C(\rho) = \langle |M(t)|^2\rangle_{\text{time average}}e^{i\rho\Delta\omega}. \quad (30)$$

Summing $C(\rho)$ over the lattice yields our $\chi(\rho)$. We have defined, in Eq. (27), an unnormalized autocorrelation function, which is not usual. In point of fact, our $\chi(\rho)$ is unnormalized. It accounts for the magnitude of the transition matrix element as well. Indeed

$$\int_{-\infty}^{\infty}W(\omega)d\omega = \frac{2\pi}{\hbar}\frac{n}{v}\int dr M^2. \quad (31)$$

This can be seen immediately by evaluating the Fourier transform of $W(\omega)$, that is, $\chi(\rho)\Phi(\rho)$, at $\rho=0$.

If $\chi(\rho)$ is the autocorrelation function of the transition operator, then its Fourier transform is the power spectrum of this operator. The Fourier transform of the function Φ, as we have seen, is essentially the resonance line shape. The transition probability is thus given by the scaled power spectrum of the transition operator convoluted with the spectrum of the broadened levels. If the transition operator were a δ function in ω space, then we would surely expect that energy could not be conserved in a single-spin flip unless the Zeeman level separation were of the order of the dipolar broadening. This assumption is implicit in the calculation of the cross-relaxation probability according to the scheme represented in Eq. (3). Conversely, if the levels were sharp, they would see a resonant component of the interaction mechanism only when the level separation fell within the Fourier spectrum of this mechanism. This latter consideration, in fact, provided the basis for the calculation of spin-lattice relaxation in Bloembergen, Purcell, and Pound's classic

nuclear relaxation paper.[18] In our case, the levels as well as the transition operator have a spectrum, and the resulting width is obtained by convolution.

Alternatively, one can interpret Eq. (24) simply as an application of the "Golden Rule":

$$W = (2\pi/\hbar)|\mathfrak{IC}_{\text{transition}}|^2 \rho(E). \tag{32}$$

We must be somewhat careful in our interpretation of this formula. Any particular single spin, in flipping from Zeeman level A to level B, does not have available a continuum of states, but exactly one well-defined, albeit perturbed state. This state is either degenerate with the initial state or it is not; accordingly, $\rho(E)$ is either 1 or 0. We must then sum these Kronecker-δ probabilities over the discrete manifold of N spin states. If we replace the discrete manifold by a continuum of levels, and the Kronecker δ by a Dirac δ, we are immediately led to the equations that we have already derived.

In a third interpretation, we could regard $\rho(E)$ in Eq. (32) as referring to the lattice as a whole. It would then be a true density function. Given two Zeeman states separated in unperturbed energy by ΔE^0, and broadened into a continuous set of states by the dipole interaction, then ρ would represent the average occupancy of that subset of states for which $\Delta E^{\text{total}} = 0$. Thus, $\rho(E)$ would correspond to our $f(\omega)$ in Eq. (21). When averaging the transition matrix element over the distribution ρ, one must evidently integrate over all the random variables involved. In the present case these include the space coordinates. This is precisely what we have done. This interpretation is implicit in the spin-spin line shape formula first given by Waller,[19] and quoted in Ref. 18. We note that in Ref. 1, however, the spatial average of the matrix element and the level density function are calculated separately.

We could indeed have written down Eqs. (24) and (25) almost immediately by invoking any of these three considerations. Our more pedestrian presentation, while perhaps less elegant, has been aimed at giving as clear a justification as possible for the mathematical expression of the theory.

Finally, we remark that the concentration dependence of the shape of $W(\omega)$ resides entirely in Φ, not in χ. The level broadening described by Φ depends linearly on the concentration for low concentrations and is proportional to the square root of the concentration for high concentrations, if the broadening is due to the dipole field. This, of course, is well known. The power spectrum of the transition operator, described by χ depends only upon the spatial integrals of the relevant coordinate functions. The *relative* occupation probabilities of the lattice sites are clearly not affected by the concentration; hence, the functional form of these

integrals is not affected. Of course, the concentration enters also as a scale factor in Eq. (24) governing the absolute magnitude of $W(\omega)$.

IV. EVALUATION OF THE INTEGRALS

Our next task is to evaluate the function χ and its Fourier transform. The transition probability itself will be proportional to the convolution of this transform with the transform of Φ.

Definition of $\Delta\omega$ and M

As a preliminary, we must define the functions represented by $\Delta\omega(\mathbf{r})$ and $M(\mathbf{r})$ in Eqs. (24) and (25). In Bloembergen's tabulation of dipole matrix elements,[1] his A and B functions correspond to our $\Delta\omega(\mathbf{r})$ and his C, D, E, and F functions correspond to our $M(\mathbf{r})$. Abbreviating his notation, we write

$$\Delta\omega(\mathbf{r}) = q(3\cos^2\theta - 1)/r^3, \tag{33}$$

$$M(\mathbf{r}) = g(\sin\theta\cos\theta)/r^3, \quad \text{if} \quad \Delta m = \pm 1, \tag{34}$$

$$M(\mathbf{r}) = g(\sin^2\theta)/r^3, \quad \text{if} \quad \Delta m = \pm 2. \tag{35}$$

Here q and g contain appropriate diagonal and off-diagonal spin-matrix elements. These expressions are valid only for two special cases: (1) There is no crystal field, or, (2) if there is a crystal field, the magnetic axis coincides with the crystal axis. In the more general case, when the magnetic field makes an arbitrary angle with the crystal axis, the expressions are generalized as follows:

$$\Delta\omega(\mathbf{r}) = \sum_{k=0}^{2} q_k P_{2k} \equiv \frac{1}{r^3} f(\theta), \tag{36}$$

$$M(\mathbf{r}) = \frac{1}{r^3} \sum_{k=0}^{2} g_k P_{2k} \equiv \frac{1}{r^3} m(\theta). \tag{37}$$

Here P_{2k} are the Legendre polynomials P_{20}, P_{21}, P_{22}, and the q_k and g_k now represent exceedingly complicated functions of the spin-matrix elements, the magnetic field, and the crystal field parameters. But even in the most general case, $\Delta\omega$ and M resolve into a product of an angular function and r^{-3}.

Evaluation of χ

Instead of evaluating $\chi(\rho)$ directly, we consider first a slightly more general integral than the one in Eq. (25):

$$I(\rho,n) = \int_{-1}^{1} d\cos\theta \int_{r_0}^{\infty} r^2 dr \frac{m^2(\theta)}{r^{3n}} e^{[i\rho f(\theta)/r^3]}, \tag{38}$$

so that

$$\chi(\rho) = I(\rho,2). \tag{39}$$

The lower limit of the r integral is the nearest-neighbor distance r_0. This distance can never be zero since two particles cannot occupy the same spot.

[18] N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. **73**, 679 (1947).

[19] I. Waller, Z. Physik **79**, 370 (1932).

To perform the integration over r, we put

$$a = \rho f(\theta), \tag{40}$$

$$t = -ia/r^3. \tag{41}$$

We obtain

$$I(\rho,n) = \int_{-1}^{1} d\cos\theta \frac{m^2(\theta)}{3(-ia)^{n-1}} \int_{0}^{-ia/r_0^3} e^{-t} t^{n-2} dt. \tag{42}$$

The t integral will be recognized as defining the incomplete γ function[20] so that

$$I(\rho,n) = \int_{-1}^{1} d\cos\theta \left(\frac{m^2(\theta)}{3r_0^{3(n-1)}}\right) \frac{\gamma(n-1, -ia/r_0^3)}{(-ia/r_0^3)^{n-1}}, \tag{43}$$

$$\chi(\rho) = \int_{-1}^{1} d\cos\theta \left(\frac{m^2(\theta)}{3r_0^3}\right) \frac{\gamma(1, -ia/r_0^3)}{-ia/r_0^3}. \tag{44}$$

After a slight manipulation of the expansion[20]

$$\gamma(a,x) = \sum_{n=2}^{\infty} \frac{(-)^n x^{a+n}}{n!(a+n)}, \tag{45}$$

the result of Eq. (44) may be written

$$\chi(\rho) = \int_{-1}^{1} d\cos\theta \left(\frac{m^2(\theta)}{3r_0^3}\right) \left(\frac{1-e^{i\rho f(\theta)/r_0^3}}{-i\rho f(\theta)/r_0^3}\right). \tag{46}$$

The result (46) could, of course, be obtained directly from (38), but we shall need the general expression (43) later on.

We must still do the angular integral and then take the Fourier transform. These operations cannot be performed analytically for the most general angular functions $m(\theta)$ and $f(\theta)$ defined in Eqs. (36) and (37). We shall, therefore, consider a number of special cases, amenable to calculation, from which the significant features of the result will become apparent.

Let us assume, as is invariably the case for a transition probability $W(\omega)$ that is symmetric in ω, that the diagonal perturbations $\Delta\omega$ and $-\Delta\omega$ occur in pairs, the perturbation of either sign being associated with the same off-diagonal M. Under this assumption, we shall make, in turn, a sequence of approximations:

Case a. We replace both angular functions in Eq. (46) by some constant average value, $\langle m^2 \rangle$ and $\langle f \rangle$.

Case b. We replace $m^2(\theta)$ by some average value; replace $f(\theta)$ by a function defined only by the property that, as $\cos\theta$ goes from -1 to $+1$, the function assumes with equal likelihood all values from $-L$ to L.

Case c. We replace $m(\theta)$ by $g(\sin\theta \cos\theta)$ and $f(\theta)$ by $q(3\cos^2\theta-1)$. These functions can be considered as specializations of Eqs. (36) and (37) by setting $q_1 = q_2$

[20] A. Erdely, F. Oberhettinger, W. Magnus, and F. G. Tricomi, *Higher Transcendental Functions* (McGraw-Hill Book Company, Inc., New York, 1954), Chap. 6.

$= g_0 = g_2 = 0$. They are the physically correct functions when the magnetic field is parallel to the c axis.

Case d. Finally, we consider the possibility that $\Delta\omega$ does not occur in pairs, so that $W(\omega)$ will not be symmetric. We shall evaluate the integrals with the physically exact functions $m(\theta) = g(\sin\theta \cos\theta)$ and $f(\theta) = q(3\cos^2\theta-1)$.

The actual computations are quite involved. They are outlined in the Appendix. Here we only present and discuss the results.

It is convenient to define the quantity

$$\epsilon = 1/r_0^3. \tag{47}$$

Then expressions like $q\epsilon$, $L\epsilon$, $\langle f \rangle\epsilon$ all represent, at least to order of magnitude, the effective nearest-neighbor dipole energy.

Case a

$$\chi(\omega) = \frac{4\pi\langle m^2 \rangle}{3r_0^3 \epsilon \langle f \rangle} \left[u_1\left(\frac{\omega}{\epsilon\langle f \rangle}+1\right) - u_1\left(\frac{\omega}{\epsilon\langle f \rangle}-1\right) \right], \tag{48}$$

$$\begin{aligned} u_1(x) &= 0, \quad x < 0 \\ &= 1, \quad x > 0. \end{aligned} \tag{49}$$

Equation (48) represents a square shape of range $-\epsilon\langle f \rangle < \omega < \langle f \rangle\epsilon$, and magnitude $4\pi\langle m^2 \rangle/3r_0^3 \epsilon\langle f \rangle$. The area is $8\pi\langle m^2 \rangle/3r_0^3$. In ruby, the nearest-neighbor dipole energy in the absence of exchange would be about 2.3 kMc/sec, so that this result is rather reminiscent of Kopvillem's.[8]

What happens to this disconcerting square shape, once we assume almost any kind of nonconstant angular function $f(\theta)$, is intuitively apparent. As we integrate over θ we shall be summing different square waves corresponding to different values of f. These rectangles are all centered at the origin and their height is inversely proportional to their extent along the ω axis. The result must inevitably be a function with a maximum at the origin and a falling monotonically to zero in the wings. If the range of $f(\theta)$ includes the value zero, which it does in all practical cases, the resulting function must approach infinity at the origin. The area of $\chi(\omega)$ is always equal to $\chi(\rho)_{\rho=0}$, and inspection of Eq. (46) shows that this area still remains $8\pi m^2/3r_0^3$, regardless of any assumption about m and f. Consequently, the convolution of this singular function with the bell-shaped transform of $\Phi(\rho)$ will always give a finite, more or less bell-shaped result. We already know, then, from these very general considerations, that the cross-relaxation probability $W(\omega)$ must have a resonant shape.

Case b

$$\begin{aligned} \chi(\omega) &= \frac{8\pi\langle m^2 \rangle}{3r_0^3} \frac{1}{2L\epsilon} \ln\frac{L\epsilon}{\omega}, \quad |\omega| < L\epsilon \\ &= 0, \quad |\omega| > L\epsilon. \end{aligned} \tag{50}$$
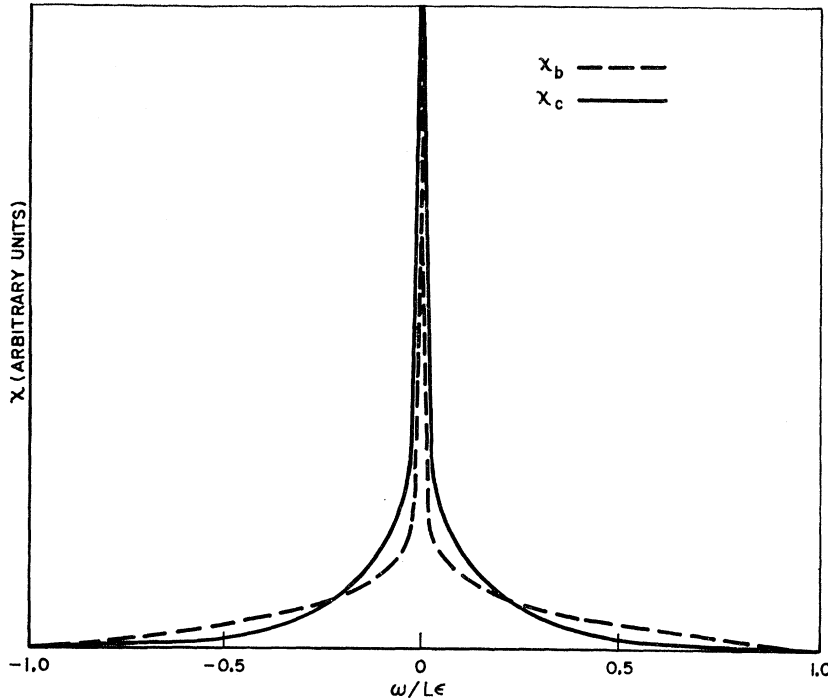
FIG. 2. χ_b [Eq. (50)] and χ_c [Eq. (53)].

This function has a logarithmic singularity at the origin and an area of $8\pi\langle m^2\rangle/3r_0^3$, as expected. The "half-power" width is, of course, undefined. If we define a half-width $\omega_{1/2}$ by the relation

$$\int_0^{\omega_{1/2}} \chi(\omega)d\omega = \tfrac{1}{2}\int_0^{\infty} \chi(\omega)d\omega, \tag{51}$$

then $\omega_{1/2}$ turns out to be

$$\omega_{1/2}= L\epsilon/5.4 \cong L\epsilon/2e. \tag{52}$$

Case c

If $|\omega|<q\epsilon$,

$$\chi(\omega)=\frac{4\pi g^2}{27\sqrt{3}r_0^3q\epsilon}\left\{\sqrt{3}+\ln\frac{\sqrt{3}-1}{\sqrt{3}+1}\right.$$

$$-\tfrac{1}{3}\left[\left(1-\frac{\omega}{q\epsilon}\right)^{1/2}\left(5+\frac{\omega}{q\epsilon}\right)+\left(1+\frac{\omega}{q\epsilon}\right)^{1/2}\left(5-\frac{\omega}{q\epsilon}\right)\right]$$

$$\left.+\ln\left|\frac{[1-(\omega/q\epsilon)]^{1/2}+1}{[1-(\omega/q\epsilon)]^{1/2}-1}\right|+\ln\left|\frac{[1+(\omega/q\epsilon)]^{1/2}+1}{[1+(\omega/q\epsilon)]^{1/2}-1}\right|\right\}. \tag{53a}$$

If $q\epsilon< |\omega| <2q\epsilon$,

$$\chi(\omega)=\frac{4\pi g^2}{27\sqrt{3}r_0^3q\epsilon}\left\{\sqrt{3}+\ln\frac{\sqrt{3}-1}{\sqrt{3}+1}-\frac{1}{3}\left(1+\frac{|\omega|}{q\epsilon}\right)^{1/2}\right.$$

$$\left.\times\left(5-\frac{|\omega|}{q\epsilon}\right)+\ln\left|\frac{[1+(|\omega|/q\epsilon)]^{1/2}+1}{[1-(|\omega|/q\epsilon)]^{1/2}-1}\right|\right\}. \tag{53b}$$

If $|\omega| >2q\epsilon$,

$$\chi(\omega)=0. \tag{53c}$$

In Fig. 2 we display this function, together with the simple logarithmic function of Eq. (50). In Eq. (50) we have chosen $L=2$ and $\langle m^2\rangle=\langle\sin^2\theta \cos^2\theta\rangle=2/15$, and in Eq. (53) we have put $g=q=1$, so that the parameters match in both expressions. With this choice of numbers, the logarithmic function behaves like $\ln|\omega|^{-0.0444/\epsilon}$ near the origin, whereas the more complicated function behaves like $\ln|\omega|^{-0.0856/\epsilon}$. The exact function has the sharper singularity. The areas, as well as all qualitative features are the same.

Case d

If $\omega<-q\epsilon$,

$$\chi(\omega)=0. \tag{54a}$$

If $-q\epsilon<\omega<0$,

$$\chi(\omega)=\frac{4\pi g^2}{27\sqrt{3}r_0^3q\epsilon}\left\{-\frac{1}{3}\left(\frac{\omega}{q\epsilon}+1\right)^{1/2}\left(\frac{\omega}{q\epsilon}-5\right)\right.$$

$$\left.+\ln\left|\frac{[1+(\omega/q\epsilon)]^{1/2}+1}{[1+(\omega/q\epsilon)]^{1/2}-1}\right|\right\}. \tag{54b}$$

If $0<\omega<2q\epsilon$,

$$\chi(\omega)=\frac{4\pi g^2}{27\sqrt{3}r_0^3q\epsilon}\left\{\sqrt{3}+\ln\frac{\sqrt{3}-1}{\sqrt{3}+1}-\frac{1}{3}\left(\frac{\omega}{q\epsilon}+1\right)^{1/2}\right.$$

$$\left.\times\left(\frac{\omega}{q\epsilon}-5\right)+\ln\left|\frac{[1+(\omega/q\epsilon)]^{1/2}+1}{[1+(\omega/q\epsilon)]^{1/2}-1}\right|\right\}. \tag{54c}$$

If $\omega > 2q\epsilon$,

$$\chi(\omega) = 0. \tag{54d}$$

We remark that this function is not symmetric in ω. The asymmetry is important primarily in the wings. $\chi(\omega)$ and $\chi(-\omega)$ assume identical form as ω approaches zero. The associated function $\Phi(\omega)$ behaves similarly. It seems likely, therefore, that any asymmetry arising from the present considerations would be accessible only to measurements made under conditions where large amounts of energy are transferred to or from the dipole system.

Qualitatively there is little difference between the symmetric case c and the nonsymmetric case d, just as little difference results from using the approximate f and m of case b instead of the f and m of case c, which represent the dipole interaction exactly provided the Zeeman and crystal field operators commute. In all cases there is a logarithmic singularity at the origin, and an over-all width determined by the effective nearest neighbor dipole energy. It is clear that these characteristics of χ can be expected to hold even when the most general form of f and m allowed by Eqs. (36) and (37) is physically appropriate.

Convolution

As indicated by Eq. (24), the function we seek, $W(\omega)$, is proportional to the convolution of $\Phi(\omega)$ and $\chi(\omega)$.

The widths of two convoluted functions, generally speaking, add in some fashion. Two Lorentz curves add width algebraically, two Gaussians add width rms wise. In particular, in the limit that the width of one function goes to zero, the resultant width approaches the width of the other function. A δ function simply leaves its partner intact. Our function $\chi(\omega)$ is an exception to this rule. Its peculiar properties under convolution are of considerable importance in determining the shape of $W(\omega)$.

As far as the effect on the resultant width is concerned, the exact shape of Φ does not make much difference, particularly when Φ is either very much broader or very much narrower than χ. If we use the simplified form of $\chi(\omega)$ given in Eq. (50), and simplify $\Phi(\omega)$ by a square shape of unit area and half-length a, we can do the convolution analytically.

If $a > L\epsilon$, it turns out that the resulting half-width is always identically a. Thus, when Φ is broader than χ, χ adds no width at all, but merely smooths out the discontinuity of the square shape. In this case χ is practically equivalent to a δ function. The more interesting case is when $a < L\epsilon$. Then the convolution gives:

If $0 < |\omega| < (L\epsilon - a)$,

$$W(\omega) = \frac{C}{4}\left[\frac{2}{L\epsilon} + \frac{1}{L\epsilon}\left(\frac{\omega}{a} + 1\right)\ln\left|\frac{L\epsilon}{\omega + a}\right| + \frac{1}{L\epsilon}\left(1 - \frac{\omega}{a}\right)\ln\left|\frac{L\epsilon}{a - \omega}\right|\right]. \tag{55a}$$

If $(L\epsilon - a) < |\omega| < (L\epsilon + a)$,

$$W(\omega) = \frac{C}{4}\left[\frac{1}{a} + \frac{1}{L\epsilon}\left(1 - \frac{|\omega|}{a}\right)\left(\ln\left|\frac{L\epsilon}{a - |\omega|}\right| + 1\right)\right]. \tag{55b}$$

If $|\omega| > (L\epsilon + a)$,

$$W(\omega) = 0. \tag{55c}$$

$$C = \frac{2\pi}{\hbar}\frac{n}{v}\frac{8\pi\langle m^2\rangle}{3r_0{}^3}. \tag{55d}$$

From Eq. (55a), the quantity $\omega_{1/2}$, the half-width of the resultant $W(\omega)$, can easily be calculated. We define

$$N = \omega_{1/2}/a. \tag{56}$$

Then Eq. (55a) can be written

$$W(0) = \frac{C}{2L\epsilon}\left[1 + \ln\frac{L\epsilon}{a}\right], \tag{57}$$

$$W(Na) = \frac{C}{2L\epsilon}\left[1 + \frac{(N+1)}{2}\ln\frac{L\epsilon}{(N+1)a} - \frac{(N-1)}{2}\ln\frac{L\epsilon}{(N-1)a}\right]. \tag{58}$$

If the χ width $L\epsilon/2e$ is much larger than a, $\omega_{1/2}$ will be likewise much larger than a, and N will be large. If we expand the logarithms to first power in $1/N$, Eq. (58) can be reduced to

$$W(Na) = \ln(L\epsilon/Na). \tag{59}$$

If we now solve $W(Na) = \frac{1}{2}W(0)$, we obtain

$$Na = \omega_{1/2} = [2a(L\epsilon/2e)]^{1/2}. \tag{60}$$

This is a remarkable result. As the Φ width a goes to zero, $\omega_{1/2}$ of W does not approach $\omega_{1/2}$ of χ, $L\epsilon/2e$, as one would intuitively expect, but rather it approaches zero. This strange property of multiplying widths rather than adding them turns out to be very nearly true even when Φ and χ have comparable widths, as can be seen from Fig. 3. We have done the convolution of the physically real χ of Case c, using square waves, Gaussians, and Lorentzians for Φ. The convolutions were done numerically on the IBM 7090, and the behavior of the half-widths is illustrated in Fig. 3.

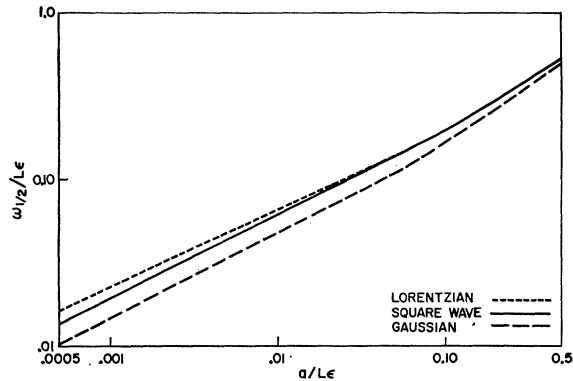The shape of the resulting function is also noteworthy. When Φ and χ have comparable widths, the

FIG. 3. Half-width ($\omega_{1/2}$) of convolution of Φ with χ_c, versus half-width (a) of Φ. For $\Phi=$square wave, $\omega_{1/2}\sim a^{0.50}$; $\Phi=$Gaussian, $\omega_{1/2}\sim a^{0.50}$, $\Phi=$Lorentzian, $\omega_{1/2}\sim a^{0.48}$.

shape is nearly that of Φ. As Φ becomes narrower than χ, the shape of their convolution somewhat resembles an upside-down funnel. These changes in the shape of $W(\omega)$ are illustrated in Fig. 4. [The extreme changes in shape have necessitated drawing Fig. 4(a) on a different scale than Figs. 4(b) and 4(c), as indicated.]

The significance of the present result is that it is the key to the concentration dependence of the width of $W(\omega)$. As we have already remarked, this dependence is contained entirely in Φ. Our χ has a width of the order of the effective nearest-neighbor interaction. In general, one would expect χ to be considerably broader than Φ. If χ added width, in convolution, like normal functions, one would predict a concentration-dependent width only for very high concentrations. The unusual behavior of χ in this regard predicts a dependence proportional to the square root of the concentration, even at vanishing concentrations. Furthermore, χ introduces the multiplicative factor $(L\epsilon/e)^{1/2}$, which makes the widths substantially larger than the resonance width a. This convolution property of χ thus enables us to meet all the experimentally given

requirements: to have $W(\omega)$ much narrower than either the resonant frequency or the maximum dipole energy, but much broader than the absorption width, *and* at the same time concentration-dependent.

Finally, it is clear from Figs. 2 and 3 that all the essential features of our results hold whether we use the χ of Eq. (50) or the more complicated one of Eq. (53). Thus, it is unnecessary to evaluate χ explicitly for general $\Delta\omega$ and M [Eqs. (36) and (37)]. The relevant parameters are the average of M^2, the range of f, which we have called L, and the value of r_0. These parameters can, in principle, be readily calculated for any physical situation, and they will define χ in terms of Eq. (50).

V. SUMMARY

We have laid a physical foundation for a general theory of cross relaxation, and we have applied our considerations particularly to single-spin transitions. Our formulation makes it unnecessary to appeal to moments or to plausibility arguments; rather, it yields the relevant functions exactly, within the limits of the physical assumptions. We review the principal steps of the argument.

(1) For each spin, the dipole interaction causes both diagonal, "static," energy shifts, and transitions between Zeeman levels.

(2) Due to the energy shifts, transitions between Zeeman states are possible which strictly conserve energy.

(3) The transition probability depends on the density of degenerate states. This density is obtained by counting the number of dipole configurations which meet the relevant energy constraint. The transition probability is given by integrating over this distribution the square of the off-diagonal dipole elements. We note a certain analogy to the method of the micro-canonical ensemble, where the trick also is to calculate
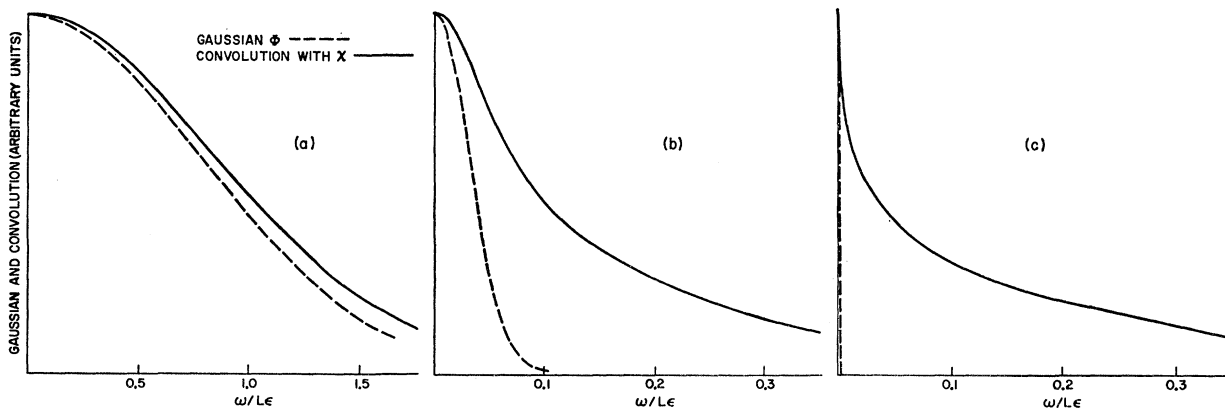

FIG. 4. Convolution of χ_c and Gaussian Φ, for various values of $\omega_{1/2}$ (Gaussian)$/\omega_{1/2}(\chi_c)$.
(a) $\omega_{1/2}(G)/\omega_{1/2}(\chi_c)=5$. (b) $\omega_{1/2}(G)/\omega_{1/2}(\chi_c)=0.2$. (c) $\omega_{1/2}(G)/\omega_{1/2}(\chi_c)=0.008$.

the phase volume (number of configurations) corresponding to a given energy.

(4) We showed that the equations derived in this manner can also be derived from the Fourier analysis of the dipole operator and from any of several interpretations of first-order time-dependent perturbation theory.

(5) For single flips, the transition probability $W(\omega)$ was given by the convolution of two functions, $\chi(\omega)$ and $\Phi(\omega)$. χ is essentially the power spectrum of the off-diagonal elements of $\mathcal{3C}^{\mathrm{dip}}$. To an excellent approximation, it depends on ω as $\ln|1/\omega|$. Φ describes essentially the level broadening due to the diagonal elements of $\mathcal{3C}^{\mathrm{dip}}$. It is equivalent to the absorption line shape. The convolution of Φ and χ, which yields $W(\omega)$, has a sharp peak whose width is proportional to the geometric mean of the χ width and the Φ width. This sharp peak is superposed on a broad spectrum whose width is of the same order as the nearest-neighbor dipole energy. The transition probability per spin is linear in the concentration n, and for low concentrations its width in ω space is proportional to the square root of the concentration.

We have considered only single-spin flips explicitly, while experimental measurements are made on double, triple, or higher multiple processes. Nevertheless, the frequency and concentration dependence of our cross-relaxation probability satisfies a number of experimental features which have not been accounted for previously in terms of a single unified calculation.

The explicit extension of the theory to multiple-spin processes is the principal subject of the succeeding paper (part II); detailed quantitative application of the entire theory to typical experiments is made in part III.

APPENDIX: EVALUATION OF χ UNDER VARIOUS APPROXIMATIONS

We refer to Eq. (46). If we assume that the diagonal perturbations $\Delta\omega$ and $-\Delta\omega$ come in pairs, then Eq. (46) becomes

$$\chi(\rho) = \int_{-1}^{1} d\cos\theta \left(\frac{m^2(\theta)}{3r_0{}^3}\right)\left(\frac{e^{-i\rho f(\theta)\epsilon} - e^{i\rho f(\theta)\epsilon}}{-i\rho f(\theta)\epsilon}\right) \quad \text{(A1a)}$$

$$\equiv \int_{-1}^{1} d\cos\theta \left(\frac{2m^2(\theta)}{3r_0{}^3}\right)\frac{\sin[\rho f(\theta)\epsilon]}{\rho f(\theta)\epsilon}, \quad \text{(A1b)}$$

where ϵ is defined in Eq. (47).

Case a. If we set $m^2(\theta) = \langle m^2\rangle$ and $f(\theta) = \langle f\rangle$, then Eq. (A1b) reduces to

$$\chi(\rho) = (4m^2/3r_0{}^3)\sin\epsilon\langle f\rangle\rho/\epsilon\langle f\rangle\rho). \quad \text{(A2)}$$

The Fourier transform of $(\sin x)/x$ is well known.[21] It

is a square wave of amplitude π extending from -1 to 1. Hence, we arrive at the Eq. (48) for $\chi(\omega)$, given in the text.

Case b. If we replace f by a function which goes from $-L$ to L as $\cos\theta$ goes from -1 to 1, Eq. (A1) becomes

$$\chi(\rho) = \int_{-L}^{L} df \left(\frac{2\langle m^2\rangle}{3Lr_0{}^3}\right)\frac{\sin\epsilon f\rho}{\epsilon f\rho}. \quad \text{(A3)}$$

The integral will be recognized as essentially the sine-integral function (Ref. 20, p. 145), and so

$$\chi(\rho) = \frac{4\langle m^2\rangle}{3r_0{}^3}\frac{\mathrm{Si}(L\epsilon\rho)}{L\epsilon\rho}. \quad \text{(A4)}$$

The Fourier transform of $\mathrm{Si}(x)/x$ is also well known,[21] and so we arrive at Eq. (50) in the text.

Case c. If we set $f = q(3\cos^2\theta - 1)$ and $m^2 = g^2\sin^2\theta \times \cos^2\theta$, Eq. (A1) becomes

$$\chi(\rho) = \frac{g^2}{3r_0{}^3\epsilon q} \int_{-1}^{1} d\cos\theta \left(\frac{\sin^2\theta \cos^2\theta}{3\cos^2\theta - 1}\right)\left(\frac{1}{-i\rho}\right)$$
$$\times \{\exp[-i\rho\epsilon q(3\cos^2\theta - 1)]$$
$$- \exp[i\rho\epsilon q(3\cos^2\theta - 1)]\}. \quad \text{(A5)}$$

The angular integrals in Eq. (A5) cannot be done analytically as they stand. Instead, we shall avail ourselves of the well-known[21] theorem that if

$$\int f(\rho)e^{-i\omega\rho}d\rho = F(\omega), \quad \text{(A6)}$$

then

$$\int \frac{f(\rho)}{-i\rho}e^{-i\omega\rho}d\rho = \int_{-\infty}^{\omega} F(\omega')d\omega'. \quad \text{(A7)}$$

We use the following ploy: First we take the Fourier transform of Eq. (A5) ignoring the $-i\rho$ in the denominator. Then we do the angular integral. Finally, we integrate with respect to ω' as indicated by Eqs. (A6) and (A7).

The first step immediately yields

$$\frac{4\pi g^2}{3r_0{}^3\epsilon q} \int_{0}^{1} d\cos\theta \left(\frac{\sin^2\theta \cos^2\theta}{3\cos^2\theta - 1}\right)$$
$$\times \{\delta[\omega' + \epsilon q(3\cos^2\theta - 1)]$$
$$- \delta[\omega' - \epsilon q(3\cos^2\theta - 1)]\}. \quad \text{(A8)}$$

Since the integrand is symmetric in $\cos\theta$, we have written the integral over half the interval and multiplied by 2.

We now perform the angular integral in Eq. (A8). Integrals of the form in Eq. (A8) are handled by the

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[21] A. Erdely, F. Oberhettinger, W. Magnus, and F. G. Tricomi, *Tables of Integral Transforms* (McGraw-Hill Book Company, Inc., New York, 1954), Vol. I, Chaps. 1 and 2.

following general procedure:

$$\int_a^b G(x)\delta[F(x)]dx = \int_{F(a)}^{F(b)} G(x)\,(dF/dx)^{-1}\delta(F)dF$$

$$= \frac{G}{(dF/dx)}\bigg|_{F(x)=0} \quad \text{if } F(x)=0 \text{ at some point in the interval } a\leqq x\leqq b$$

$$= 0, \quad \text{if } F(x)\neq 0 \text{ at every point in the interval } a\leqq x\leqq b. \tag{A9}$$

Using the first δ function in Eq. (A8), the correspondence with Eq. (A9) is

$$G(\cos\theta) = \frac{4\pi g^2}{3r_0^3\epsilon q}\frac{\sin^2\theta\,\cos^2\theta}{3\cos^2\theta-1}, \tag{A10}$$

$$F(\cos\theta) = \omega' + \epsilon q(3\cos^2\theta - 1), \tag{A11}$$

$$\frac{dF}{d\cos\theta} = 6\epsilon q\,\cos\theta. \tag{A12}$$

From Eq. (A11) we have $F=0 => \cos\theta = (\epsilon q - \omega'/3\epsilon q)^{1/2}$, and after some algebra,

$$\frac{G}{(dF/d\cos\theta)}\bigg|_{F=0} = -\frac{2\pi g^2}{27\sqrt{3}r_0^3\epsilon^2 q^2}\Big(1-\frac{\omega'}{\epsilon q}\Big)^{1/2}\Big(1+\frac{2\epsilon q}{\omega'}\Big). \tag{A13}$$

This result is valid if $[\omega' + \epsilon q(3\cos^2\theta-1)]=0$ at some point on the interval $0\leqq\cos\theta\leqq 1$, or in other words, if $-2\epsilon q<\omega'<\epsilon q$. If ω' lies outside these limits, the result is 0.

We have completed the angular integral. The expression (A13) corresponds to $F(\omega')$ in Eq. (A7). It remains to integrate over ω'. The main point is that the integral over ω', from $-\infty$ to ω, must be considered separately for three cases:

(1) $\omega<-2\epsilon q$: The integrand is always 0 and the integral vanishes.

(2) $-2\epsilon q<\omega<\epsilon q$: The integrand is given by Eq. (A13) and the limits are $-2\epsilon q$ to ω.

(3) $\omega>\epsilon q$: The integrand is given by Eq. (A13) and the limits are $-2\epsilon q$ to ϵq.

The integration is straightforward. We quote only the results

$\omega<-2\epsilon q$: \qquad\qquad 0; \hfill (A14a)

$-2\epsilon q<\omega<\epsilon q$:

$$\frac{4\pi g^2}{27r_0^3\epsilon q}\bigg[-\frac{1}{3}\Big(1-\frac{\omega}{\epsilon q}\Big)^{1/2}\Big(5+\frac{\omega}{\epsilon q}\Big)$$
$$-\ln\bigg|\frac{[1-(\omega/\epsilon q)]^{1/2}-1}{[1-(\omega/\epsilon q)]^{1/2}+1}\bigg|+\sqrt{3}+\ln\frac{\sqrt{3}-1}{\sqrt{3}+1}\bigg]; \tag{A14b}$$

$\omega>\epsilon q$:

$$\frac{4\pi g^2}{27r_0^3\epsilon q}\bigg[\sqrt{3}+\ln\frac{\sqrt{3}-1}{\sqrt{3}+1}\bigg]. \tag{A14c}$$

These are the results for the first δ function in Eq. (A8). The computation for the second δ function is carried out analogously. The result is

$\omega<-\epsilon q$: \qquad\qquad 0; \hfill (A15a)

$-\epsilon q<\omega<2\epsilon q$:

$$-\frac{4\pi g^2}{27\sqrt{3}r_0^3\epsilon q}\bigg[\frac{1}{3}\Big(1+\frac{\omega^{1/2}}{\epsilon q}\Big(5-\frac{\omega}{\epsilon q}\Big)$$
$$+\ln\bigg|\frac{[1+(\omega/\epsilon q)]^{1/2}-1}{[1+(\omega/\epsilon q)]^{1/2}+1}\bigg|\bigg]; \tag{A15b}$$

$\omega>2\epsilon q$:

$$-\frac{4\pi g^2}{27\sqrt{3}r_0^3\epsilon q}\bigg[\sqrt{3}+\ln\frac{\sqrt{3}-1}{\sqrt{3}+1}\bigg]. \tag{A15c}$$

Finally, combining the results of Eqs. (A14) and (A15), we arrive at the function given in Eq. (53) in the text.

Case d. If the $\Delta\omega$'s do not occur in pairs, we revert to Eq. (46) in the text rather than to Eq. (A1). We note that the only difference between Eq. (46) and Eq. (A1) is that in Eq. (46) there is a 1 in place of one of the exponentials in Eq. (A1). The computation is therefore essentially unaltered from *Case c*, the same basic arguments applying step for step. The result of the first step [Eq. (58)] will now have one of its δ functions replaced by $\delta(\omega')$. The angular integration for that portion of Eq. (A8) which now contains $\delta(\omega')$ offers no subtleties. The final integration over ω' merely replaces the $\delta(\omega')$ by a unit step at $\omega=0$. The result for this portion of the integral is

$\omega<0$: \qquad\qquad 0; \hfill (A16a)

$\omega>0$:

$$\frac{4\pi g^2}{27\sqrt{3}r_0^3\epsilon q}\bigg[\sqrt{3}+\ln\frac{\sqrt{3}-1}{\sqrt{3}+1}\bigg]. \tag{A16b}$$

By combining Eqs. (A15) and (A16), we arrive at the $\chi(\omega)$ given by Eq. (54) in the text.