General Theory of Cross Relaxation. II. Higher Order Processes*

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The theory of part I is extended to multiple spin processes. The lowest order two-spin process yields a cross-relaxation probability W_{CR} whose principal characteristics are the same as those of W_{CR} for single spin flips. Higher order two-spin processes occur with much lower probability and this probability is not sharply peaked at harmonic coincidence. Three-spin and higher multiple K-spin processes yield functions $W_{CR}(\omega)$ whose width becomes progressively larger and less dependent on the concentration, and whose magnitude depends on the concentration n as n^K. The effects of short-range forces (exchange) are easily embodied in the theory, but in the absence of such forces special attention must be paid to the dipole fields of near neighbors, which are then likely to dominate the cross-relaxation process.

I. INTRODUCTION

IN part I[1] we presented a general formalism to describe the effect of the dipolar interaction on the otherwise uncoupled spins in a lattice. We applied our considerations particularly to nonradiative single-spin transitions. In the extension of the theory to higher order processes, we presuppose the entire machinery of part I.

In generalizing the previous results to more complex processes, we follow these steps: (1) generalize the statistical procedure developed in part I, (2) discuss two-spin processes in detail, (3) consider triple and higher multiple processes, and (4) consider subsidiary problems arising from near-neighbor interactions and inhomogeneous broadening.

II. STATISTICAL PROCEDURE

The matrix element used for single-spin flips was $\sum_i M_{1i}^2$. This element corresponded to an interaction in which spin one interacts with all the other spins in such a manner that spin one flips and all the others stay put. The spin variables of M_{1i} have a form like $S_-^1 S_z^i$.

Now let us consider a double flip. By a double flip we mean a process in which spin one flips down and any one of the others flips up. What is the appropriate statistical procedure and what matrix element do we embed in this procedure?

The statistics breaks up into two parts. First, we consider the interaction between spin one and some fixed spin p. The matrix element has the form $M_{1p}(\mathbf{r}_{1p})$ with spin variables typically of the form $S_-^1 S_+^p$. With this one-p combination fixed, we count the possible configurations of all the remaining spins. Secondly, we sum M_{1p} over all possible interactions. When one and p interact in a double flip, their interaction with one another is evidently on a different footing from their interaction with all the other spins.

A closely related question concerns the indistinguishability of the spins. Two spins are distinguishable

if any of the following conditions obtain: (1) They belong to a different species; (2) they occupy different Zeeman states; (3) they occupy different positions in the lattice. Conditions (1) and (2) are obvious. The implication of condition (3) is that we do not get a new configuration if we interchange spin q for spin p, but we do get a new configuration if we move spin p (or spin q) to a different lattice site.

Suppose that the distinguishability conditions (1) and (2) give N_1 spins of kind 1, N_2 of kind 2, and so forth, with a total of N spins. Suppose we fix the positions of A spins: A_1 of kind 1, A_2 of kind 2, and so forth. We now distribute the remaining $N-A$ spins randomly into the remaining $M-A$ lattice sites. The number of configurations is clearly

$$C(A) = \frac{(M-A)!}{(N_1-A_1)!(N_2-A_2)!\cdots(M-N)!}. \quad (1)$$

By Stirling's approximation, this becomes

$$C(A) = \frac{(M-A)^{M-A}e^{-N+A}}{(N_1-A_1)!(N_2-A_2)!(M-N)^{M-N}}. \quad (2)$$

Now

$$\lim_{M\to\infty}(M-A)^{M-A} = \lim_{M\to\infty} M^{M-A} \times (1-(A/M))^{M-A} = M^{M-A}e^{-A}, \quad (3)$$

so that (putting $n=N/M$)

$$C(A) = [M^{N-A}/(N_1-A_1)!(N_2-A_2)!\cdots] \times [e^{-N}/(1-n)^{M-N}]. \quad (4)$$

We notice that the second bracket of Eq. (4) is independent of A and will always cancel out when we compute a fractional number of configurations. For a two-spin process involving spin 1 and spin p, we have $A_1=A_2=1$, $A=2$, and the fractional number of configurations is

$$f = \frac{C(2)}{C(0)} = \frac{N_1 N_2 v^2}{V^N} \int dr_2 dr_3 \cdots dr_{p-1} dr_{p+1} \cdots dr_N, \quad (5)$$

where

$$v = V/M \quad (6)$$

and V has been replaced by $\int d\mathbf{r}$ in the numerator.

To obtain the transition probability, we need to introduce the transition operator and the appropriate energy constraint. The transition operator, as we have seen, is $M_{1p}^2(\mathbf{r}_{1p})$ summed over all $\mathbf{r}_{1p}$. The energy constraint is discussed in the next section. The transition probability may be symbolically written

$$W = \frac{2\pi}{\hbar} \frac{N_1 N_2 v^2}{V^N} \cdot \frac{1}{v}$$

$$\times \int M_{1p}^2 d\mathbf{r}_{1p} d\mathbf{r}_{12} \cdots d\mathbf{r}_{1,\,p-1} d\mathbf{r}_{1,\,p+1} \cdots d\mathbf{r}_{1N}$$

$$\times \text{energy constraint.} \quad (7)$$

We have introduced a factor $1/v$ to keep the units and dimensionality consistent in passing from the lattice sum for M_{1p}^2 to an integral. Also, the reference spin 1 has been chosen as origin of coordinates.

For a single-spin process, $C(1)/C(0)$ will have one N in front, and one more volume integral, so that W reduces to the expression 22 of part I.

The extension of this counting scheme to processes involving an arbitrary number of spins is obvious, and some examples will be given below.

III. TWO-SPIN PROCESSES

First, we formulate the energy constraint for the two-spin process. Second, we dicusss the first-order two-spin process. Third, we discuss a second-order two-spin process. Fourth, we consider the long-range process.

Energy Constraint

In a two-spin process, spin one flips from state A to state B, while another spin flips from state C to state D. The labels A, B, C, D designate the quantum numbers of the unperturbed single-particle states. The corresponding unperturbed energies are $E_A{}^0, E_B{}^0, E_C{}^0, E_D{}^0$. These energies are perturbed by the dipole interaction, and in first order we write

$$E^{\text{tot}} = E^0 + E^{\text{dip}}. \quad (8)$$

E^{tot} and E^0 are numbers, but E^{dip} depends both on the specific configuration of all dipoles which the spin sees, and on the quantum state in which the spin finds itself. For a transition to be possible, we require zero change of over-all energy. The net change in Zeeman energy must be balanced by the net change in dipole energy:

$$(E_A{}^{\text{tot}} - E_B{}^{\text{tot}}) + (E_C{}^{\text{tot}} - E_D{}^{\text{tot}}) = 0, \quad (9)$$

Equation (9) replaces the analogous condition $E_A{}^{\text{tot}} - E_B{}^{\text{tot}} = 0$, which was appropriate for single flips.

To formulate the analogous energy constraint, we specify that: (1) spin 1 have energy $E_A{}^{\text{tot}}$ when in state A; (2) spin 1 have energy $E_B{}^{\text{tot}}$ when in state B; (3) spin p have energy $E_C{}^{\text{tot}}$ when in state C; (4) spin p have energy $E_D{}^{\text{tot}}$ when in state D; and (5) the constraint expressed in Eq. (9) holds. The total number of configurations for which Eq. (9) holds is obtained by integrating over all values of $E_A{}^{\text{tot}}, E_B{}^{\text{tot}}, E_C{}^{\text{tot}}, E_D{}^{\text{tot}}$. The energy constraint is then expressed as the operator

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

$$\times \delta[E_C{}^{\text{tot}} - (E_C{}^0 + E_C{}^{\text{dip}})] \delta[E_D{}^{\text{tot}} - (E_D{}^0 + E_D{}^{\text{dip}})]$$

$$\times \delta[E_A{}^{\text{tot}} - E_B{}^{\text{tot}} + E_C{}^{\text{tot}} - E_D{}^{\text{tot}}]$$

$$\times dE_A{}^{\text{tot}} dE_B{}^{\text{tot}} dE_C{}^{\text{tot}} dE_D{}^{\text{tot}}. \quad (10)$$

Performing the integrations reduces expression (10) to

$$\delta[(E_A{}^0 - E_B{}^0 + E_C{}^0 - E_D{}^0) - (E_B{}^{\text{dip}} - E_A{}^{\text{dip}} + E_D{}^{\text{dip}} - E_C{}^{\text{dip}})]. \quad (11)$$

The first parenthesis in expression (11) is the total change in unperturbed energy and we denote it by $\hbar\omega$. The second parenthesis is the negative of the change in dipole energy. We put

$$\hbar\Delta\omega_{AB} = E_B{}^{\text{dip}} - E_A{}^{\text{dip}}, \quad (12a)$$

$$\hbar\Delta\omega_{CD} = E_D{}^{\text{dip}} - E_C{}^{\text{dip}}. \quad (12b)$$

We again assume that the contributions of all spins to $\Delta\omega$ are additive:

$$\Delta\omega_{AB} = \sum_{k \neq 1} \Delta\omega_{AB}(\mathbf{r}_{1k}), \quad (13a)$$

$$\Delta\omega_{CD} = \sum_{k \neq p} \Delta\omega_{CD}(\mathbf{r}_{pk}). \quad (13b)$$

Expression (11) now becomes

$$\delta\left(\omega - \left[\sum_{k \neq 1} \Delta\omega_{AB}(\mathbf{r}_{1k}) + \sum_{k \neq p} \Delta\omega_{CD}(\mathbf{r}_{pk})\right]\right). \quad (14)$$

Finally, replacing the δ function by its Fourier transform, we have for the energy constraint:

$$\frac{1}{2\pi} \int_{-\infty}^{\infty} \exp\left\{-i\rho\left[\omega - \sum_{k \neq 1} \Delta\omega_{AB}(\mathbf{r}_{1k}) - \sum_{k \neq p} \Delta\omega_{CD}(\mathbf{r}_{pk})\right]\right\} d\rho$$

$$\equiv \frac{1}{2\pi} \int_{-\infty}^{\infty} (\exp\{i\rho[\Delta\omega_{AB}(\mathbf{r}_{1p}) + \Delta\omega_{CD}(\mathbf{r}_{p1})]\}$$

$$\times \prod_{k \neq 1,p} \exp\{i\rho[\Delta\omega_{AB}(\mathbf{r}_{1k}) + \Delta\omega_{CD}(\mathbf{r}_{pk})]\}) e^{-i\rho\omega} d\rho. \quad (15)$$

First-Order Process

We may now write the transition probability in the form of Eq. (7) using the energy constraint we have

just derived. We put $N_i/V = n_i/v$. We then have

$$W(\omega) = \frac{2\pi}{\hbar} \int_{-\infty}^{\infty} \frac{1}{2\pi} \left[n_1 n_2 \cdot \frac{1}{v} \int M_{1p}^2 \exp\{i\rho[\Delta\omega_{AB}(\mathbf{r}_{1p}) \right.$$

$$+\Delta\omega_{CD}(\mathbf{r}_{p1})]\} d\mathbf{r}_{1p} \left(\frac{1}{V} \int \exp\{i\rho[\Delta\omega_{AB}(\mathbf{r}_{1k}) \right.$$

$$\left. \left. +\Delta\omega_{CD}(\mathbf{r}_{pk})]\} d\mathbf{r}_{1k} \right)^{N-2} \right] e^{-i\omega\rho} d\rho. \quad (16)$$

This expression is very similar to Eq. (24) of part I, with the integral containing M_{1p}^2 corresponding to χ and the round bracket raised to the $(N-2)$ power corresponding to Φ. The difference is that χ and Φ cannot now be evaluated separately. They are coupled through the dependence of Φ on $\mathbf{r}_{1p}$. This becomes more apparent if we write $\mathbf{r}_{pk} = \mathbf{r}_{1k} - \mathbf{r}_{1p}$. As we integrate over $\mathbf{r}_{1p}$ to evaluate χ, we should simultaneously have to integrate out the $\mathbf{r}_{1p}$ dependence in Φ. This calculation would be impossible.

This impasse can be overcome through the following consideration: Let us consider the limiting situations, $\mathbf{r}_{1p} \to 0$ and $\mathbf{r}_{1p} \to \infty$. In the first case, the $\mathbf{r}_{1p}$ dependence of Φ is eliminated and Φ has exactly the form we discussed in part I. It will essentially describe a quasiresonance line whose parameters are the algebraic sum of the parameters for the resonance lines $A \leftrightarrow B$ and $C \leftrightarrow D$. In the second case, we note that $\Delta\omega(\mathbf{r})$ depends on r as r^{-3}. Within any arbitrarily large neighborhood of spin 1, $\mathbf{r}_{pk}$ will be infinite, $\Delta\omega(\mathbf{r}_{pk})$ will be zero, and $\exp[i\rho\Delta\omega(\mathbf{r}_{pk})]$ will equal one. The converse is true within any arbitrarily large neighborhood of spin p. Consequently, each of the $(N-2)$ integrals in Φ breaks up into the sum of two integrals.

$$\lim \Phi_{r_{1p} \to \infty} = \left(\frac{1}{V} \int \{\exp[i\rho\Delta\omega_{AB}(\mathbf{r})] \right.$$

$$\left. +\exp[i\rho\Delta\omega_{CD}(\mathbf{r})]\} d\mathbf{r} \right)^{N-2}. \quad (17)$$

It is easily shown that Φ now corresponds to the convolution of the two resonance lines $A \leftrightarrow B$ and $C \leftrightarrow D$.

In either limit, Φ is functionally identical to an absorption line and has a width roughly twice of an absorption line. For most practical applications, this is sufficient information. If more detail is necessary one must split the calculation into two parts corresponding to $\mathbf{r}_{1p}$ very small and $\mathbf{r}_{1p}$ very large. For $\mathbf{r}_{1p}$ small it is always possible to calculate exactly the diagonal dipole elements which determine $\Delta\omega$. For $\mathbf{r}_{1p}$ large it is always possible to convolute known absorption lines.

What is the physical meaning of the preceding arguments? In the first place it is no longer exactly true that χ and Φ represent, respectively, the rf power spectrum of the dipole interaction and the level broadening. Such a

separation was possible for the single-spin theory of part I because of our assumption that the interactions of spin 1 were independent. Now, however, the interactions of spin 1 are not completely independent; they are correlated with the interactions of spin p. From our present point of view, we still assign to χ a meaning as power spectrum, and take care of the correlations in Φ. In line shape language, $\Phi(\rho)$ is the coherence relaxation function and its width corresponds to T_2. When two spins are very near one another, they are very strongly correlated. With respect to the rest of the system, they behave as a coupled unit with a coherence time equal to that of a single spin. When two spins are very far apart, on the other hand, they are uncorrelated, and their joint coherence time is given by

$$1/T_2(1,2) = [1/T_2(1)] + [1/T_2(2)] ,$$

or, if $T_2(1) = T_2(2)$,

$$T_2(1,2) = \tfrac{1}{2}T_2(1) = \tfrac{1}{2}T_2(2) .$$

The dependence of Φ on r_{1p} is thus interpretable as the dependence of the *pair* coherence time on the spin separation.

We may then write for the double-flip probability

$$W(\omega) = \frac{2\pi}{\hbar} \frac{n_1 n_2}{v} \int_{-\infty}^{\infty} \chi(\rho) \Phi(\rho) e^{-i\rho\omega} d\rho, \quad (18)$$

where

$$\chi(\rho) = \frac{1}{2\pi} \int M_{1p}^2 e^{i\rho\Delta\omega_\chi(\mathbf{r})} d\mathbf{r}, \quad (19)$$

$$\Delta\omega_\chi(\mathbf{r}) = \Delta\omega_{AB}(\mathbf{r}_{1p}) + \Delta\omega_{CD}(\mathbf{r}_{p1}) . \quad (20)$$

We now discuss briefly the more precise functional form of M_{1p} and $\Delta\omega$ appearing in Eqs. (18) to (20). The matrix element M_{1p} is, of course,

$$\langle A(1)C(p) | \mathcal{3C}^{\text{dip}} | B(1)D(p) \rangle .$$

In the absence of a crystal field, we would have

$$M_{1p} = g(3\cos^2\theta_{1p} - 1)/r_{1p}^3, \quad \Delta m_{\text{tot}} = 0, \quad (21a)$$

$$M_{1p} = g\sin^2\theta_{1p}/r_{1p}^3, \quad \Delta m_{\text{tot}} = \pm 2. \quad (21b)$$

The quantity g is the value of the appropriate spin matrix element. Like the matrix element for single flips, M_{1p} can be expressed even in the most general case as the product of an angular function and r^{-3}.

$$M_{1p} = m(\theta_{1p})/r_{1p}^3. \quad (22)$$

The $\Delta\omega$'s have the same form as in the single-spin process. In the absence of a crystal field

$$\Delta\omega_{AB}(\mathbf{r}_{1k}) = q_{AB}(3\cos^2\theta_{1k} - 1)/r_{1k}^3, \quad (23)$$

with an analogous expression for $\Delta\omega_{CD}$. The q_{AB} is the difference of the values assumed by the spin variables in the matrix elements $\mathcal{3C}_{AA}^{\text{dip}}$ and $\mathcal{3C}_{BB}^{\text{dip}}$. In the

general case, $\Delta\omega$ too can still be expressed as the product of an angular function and r^{-3}:

$$\Delta\omega(\mathbf{r}_{1k}) = f(\theta_{1k})/r_{1k}^{-3}. \qquad (24)$$

We see then that the χ of Eqs. (18) and (19) is identical in form to the single-spin χ of Eqs. (25) and (38) in part I. The functions $m(\theta)$ and $f(\theta)$ are still sums of Legendre polynomials of order two.

The entire discussion χ developed in part I applies without essential change to the two-spin case. Thus, we may write

$$\chi(\omega) = \frac{8\pi\langle m^2\rangle}{3r_0^3} \frac{1}{2L\epsilon} \ln|L\epsilon/\omega|, \quad |\omega| < L\epsilon \qquad (25)$$

$$= 0, \qquad\qquad\qquad |\omega| > L\epsilon.$$

Here, $\langle m^2\rangle$ is the average value of $m^2(\theta)$ over the sphere, L is the maximum value of $f(\theta)$, and $\epsilon = r_0^{-3}$. Unlike the single flip, the double flip is not characterized by the occurrence of $\Delta\omega$ and $-\Delta\omega$ in pairs. The resulting χ is asymmetric and this asymmetry is well approximated by the addition of an additive constant

on one side of the origin. As mentioned in part I, such asymmetry manifests itself primarily in the wings.

The discussion of $W(\omega)$ developed in part I also applies, with two changes: (1) There is now a coefficient of n^2 instead of n, so that the transition probability depends on the square of the concentration. (2) When calculating the central peak of W, we must use a Φ that is wider than its counterpart in the single-spin transition. The theory developed in part I regarding the shape of $W(\omega)$ and the concentration dependence of this shape applies to the double flip without further modification.

Second-Order Process

So far, we have treated the two-spin process in terms of first-order theory. It may happen, however, that the "resonant" condition is met, i.e., $\Delta E_{AB}^0 + \Delta E_{CD}^0 = 0$, or $\omega = 0$, but at the same time the matrix element M_{1p} vanishes. Such is the case for ruby at a number of magnetic field values when the field is parallel to the c axis. To see what effect is expected under these circumstances, we must go to second-order theory.

The second-order matrix element is given by

$$M_{1p}' = \sum_{X\neq B} \sum_{Y\neq D} \frac{\langle A(1)C(p)|\mathfrak{IC}^{\mathrm{dip}}|X(1)Y(p)\rangle\langle X(1)Y(p)|\mathfrak{IC}^{\mathrm{dip}}|B(1)D(p)\rangle}{E_{XY}-E_{BD}}, \qquad (26)$$

where X and Y are the intermediate states for spins 1 and p. Each of the first-order elements connecting the intermediate states to either the initial or final state is of the form of M_{1p} given in Eqs. (21) and (22). Equation (26) may be abbreviated in the notation of Eq. (22),

$$M_{1p}' = \sum_{XY} \frac{[m_1(\theta_{1p})m_2(\theta_{1p})/r_{1p}^6]}{\Delta E_{XY}}. \qquad (27)$$

In other words, M_{1p}' breaks up into products of an angular function, r^{-6}, and an energy denominator. The energy denominator is

$$1/\Delta E = 1/(\Delta E^0 + \Delta E^{\mathrm{dip}}) = (1/\Delta E^0)$$
$$\times[1-(\Delta E^{\mathrm{dip}}/\Delta E^0)+(\Delta E^{\mathrm{dip}}/\Delta E_0)^2\cdots]. \qquad (28)$$

Since, for the bulk of the transitions, ΔE^{dip} is small compared to ΔE^0, we approximate the energy denominator by $1/\Delta E^0$.

The number of terms in the XY sum is generally small. The reason for this is that the vanishing of the first-order matrix element is generally due to some symmetry condition which causes many of the other matrix elements to vanish as well. For instance, in the case of ruby at $0°$ orientation, for $g\beta H = 4D$, the transition $(\frac{3}{2}, -\frac{3}{2}) \leftrightarrow (-\frac{1}{2}, -\frac{1}{2})$ is linked by two intermediate states. Both terms in the sum over intermediate states are proportional to $P_{20}P_{21}r^{-6}$. The coefficients of the coordinate functions are 0.4 and -2.4 so that their sum is -2. We cite this example to illus-

trate that the order of magnitude of the sum is the same as the order of magnitude of each term.

We now proceed exactly as in the first-order theory. The integral for χ' is now

$$\chi'(\rho) = \frac{1}{2\pi} \cdot \frac{1}{(\Delta E)^2} \int_{r_0}^{\infty} \frac{m_1^2(\theta)m_2^2(\theta)}{r^{12}} e^{i\rho f(\theta)/r^3} d\mathbf{r}. \qquad (29)$$

We identify this integral with the integral $I(\rho,4)$ of Eq. (38) in part I. Then, according to Eq. (43) of part I, the integration over r (and φ) yields

$$\chi'(\rho) = \left(\frac{1}{\Delta E}\right)^2 \cdot \int_{-1}^{1} d(\cos\theta)\left(\frac{m_1^2(\theta)m_2^2(\theta)}{3r_0^9}\right)$$
$$\times \frac{\gamma[3, -i\rho\epsilon f(\theta)]}{[-i\rho\epsilon f(\theta)]^3}, \qquad (30)$$

where γ represents the incomplete γ function. We approximate $f(\theta)$, as before, by a function which assumes values $-L < f < L$ as $\cos\theta$ assumes values $-1 < \cos\theta < 1$, and we replace $m_1^2(\theta)m_2^2(\theta)$ by $\langle m_1^2 m_2^2\rangle$. With $\epsilon = r_0^{-3}$, we then have

$$\chi'(\rho) = \frac{1}{\epsilon} \cdot \left(\frac{1}{\Delta E}\right)^2 \frac{\langle m_1^2 m_2^2\rangle\epsilon^4}{3L} \int_{-L}^{L} df \frac{\gamma(3, -i\rho\epsilon f)}{(-i\rho\epsilon f)^3}. \qquad (31)$$

Through the relation[2]

$$\int \frac{\gamma(a,x)}{x^a} dx = -\frac{\gamma(a-1, x)}{x^{a-1}},\qquad (32)$$

we obtain

$$\chi'(\rho) = \frac{1}{\epsilon} \cdot \left(\frac{1}{\Delta E}\right)^2 \cdot \frac{\langle m_1{}^2 m_2{}^2\rangle \epsilon^4}{3} \cdot \left[\frac{\gamma(2, -x) - \gamma(2,x)}{x^3}\right], \quad (33)$$

where $x = -i\rho\epsilon L$. By means of the recursion formula[2]

$$\gamma(a+1, x) = a\gamma(a,x) - x^a e^{-x} \qquad (34)$$

and the relation

$$\gamma(1,x) = 1 - e^{-x}, \qquad (35)$$

Eq. (33) may be reduced to

$$\chi'(\rho) = \frac{1}{\epsilon}\left(\frac{1}{\Delta E}\right)^2 \frac{\langle m_1{}^2 m_2{}^2\rangle \epsilon^4}{3}$$

$$\times \left[e^{-x}\left(\frac{1}{x^3} + \frac{1}{x^2}\right) - e^x\left(\frac{1}{x^3} - \frac{1}{x^2}\right)\right]. \quad (36)$$

We have now explicitly evaluated $\chi'(\rho)$.

To obtain $\chi'(\omega)$ we need

$$\chi'(\omega) = \int_{-\infty}^{\infty} \chi'(\rho) e^{-i\omega\rho} d\rho. \qquad (37)$$

This Fourier transform is obtained almost trivially from expression (36) by taking successive integrals of δ functions located at $\omega = \pm\epsilon L$. The Fourier transform of expression (36) is

$$\chi'(\omega) = \frac{2\pi\langle m_1{}^2 m_2{}^2\rangle\epsilon^2}{9r_0{}^3(\Delta E)^2} \frac{3}{4L\epsilon}\left[1 - \left(\frac{\omega}{L\epsilon}\right)^2\right], \quad |\omega| < L\epsilon$$

$$= 0, \qquad\qquad\qquad\qquad\qquad\qquad |\omega| > L\epsilon. \qquad (38)$$

$\chi'(\omega)$ turns out to be a parabola. It has a half-width of $0.7L\epsilon$. For $L = 2q$, as is appropriate for ruby at $0°$ orientation, this half-width corresponds to 1.4 times the effective nearest-neighbor dipole energy. This width is much larger than the width of any reasonable $\Phi(\omega)$ at low concentrations. It follows that $W'(\omega)$, obtained by convoluting Φ and χ', will have essentially the same shape as $\chi'(\omega)$.

The coefficient in front of the second-order W' is down from that of the first-order W by $\frac{1}{6}$ $(\bar{m}\epsilon/\Delta E_0)^2$. Since $\bar{m}\epsilon$ is approximately the dipole energy and ΔE_0 is approximately the Zeeman energy, this factor is typically of order 10^{-2}. This is not all, however. The second-order $W'(\omega)$ shows no sharp resonance. If we consider a $\Phi(\omega)$ of width one-tenth the nearest-neighbor dipole energy, the sharp resonance of the first-order W decreases the ratio of $W'(0)/W(0)$ by almost another order of magnitude. Far away from the resonant condition, however, W' eventually may become comparable to W.

In summary, the second-order process gives rise to an effect which is relatively small, as expected, and which is quite spread out in its frequency dependence. One would not expect this process to be directly observable, but it does contribute, to some extent, to "general" cross-relaxation, i.e., to relaxation which appears more or less independent of any resonance condition between levels.

Long-Range Process

Finally, we consider still a third type of two-spin process. In this process, spin 1 and spin p both flip, but independently of one another. It represents, in a sense, the joint probability of two single spin flips. Because the two spins operate independently, their separation becomes irrelevant. Our theory gives a reasonable account of the nonexistence of such a process.

The matrix element governing this process is

$$M_{1p}'' = \sum_{XY}\left\{\frac{\langle A(1)X(i)|\mathcal{3C}^{\mathrm{dip}}|B(1)X(i)\rangle\langle C(p)Y(j)|\mathcal{3C}^{\mathrm{dip}}|D(p)Y(j)\rangle}{E_C - E_D}\right.$$

$$\left. + \frac{\langle C(p)Y(j)|\mathcal{3C}^{\mathrm{dip}}|D(p)Y(j)\rangle\langle A(1)X(i)|\mathcal{3C}^{\mathrm{dip}}|B(1)X(i)\rangle}{E_A - E_B}\right\}. \qquad (39)$$

The two portions of this matrix element correspond to the two possibilities of either spin 1 or spin p flipping first, thus giving rise to different intermediate states. Since our method always envisions *exact* conservation of energy in any one process, one energy denominator is the *exact* negative of the other. By abbreviating the notation in an obvious manner, we have

$$M_{1p}'' = \frac{1}{\Delta E}\sum_{XY}(M_{1i}M_{pj} - M_{pj}M_{1i}). \qquad (40)$$

If $i \neq j$, the spins referred to in M_{1i} and M_{pj} are all different, M_{1i} and M_{pj} commute, and M_{1p}'' vanishes identically. If $i = j$, M_{1p}'' does not vanish. However, the extra index "uses up" one more volume integral in our configuration counting [see Eqs. (7) and (16)], and as a result, there is an extra factor of $1/V$ left over. This leads to a transition probability which is down by a factor of N, where N is the number of spins in the crystal. Physically, spin 1 and spin p cannot interact at all without any interaction mechanism. They can interact via some common third spin i, but since they act independently, the chances of their "picking" out

[2] A. Erdely, F. Oberhettinger, W. Magnus, and F. G. Tricomi, *Higher Transcendental Functions* (McGraw-Hill Book Company, Inc., New York, 1948), Vol. 2.

the same spin i from the N available spins are down by a factor of N.

This completes our treatment of the two-spin process.

IV. HIGHER ORDER PROCESSES

Triple and higher multiple spin flips are handled in a fashion quite analogous to double flips. The principal difference is that dipole operators can never connect more than two spins at a time; for this reason, multiple-spin processes must be treated in higher order perturbation theory.

We consider a triple flip in which spin 1 goes from state A to state B, spin p from C to D, spin q from E to F. If the selection rule $\Delta m = \pm 1$ holds for each spin, the possible processes are that either spin 1 or spin 2 or spin 3 flips first with the remaining two spins flipping second, or the converses of these three possibilities. There are thus six intermediate states, with a given process and its converse having energy denominators that are exact negatives of one another. These processes have been discussed in their detailed application to LiF by Pershan.[3] In the more general case, when m is not a good quantum number, there is no selection rule. The number of processes can become very large and the matrix elements very complicated. Nevertheless, a typical term, together with its converse, can be represented by

$$M_{1pq} = (M_{1p}M_{1q} - M_{1q}M_{1p})/\Delta E . \tag{41}$$

M_{1pq} does not vanish since M_{1p} and M_{1q} do not commute. The coordinate dependence of M_{1p} and M_{1q} is defined in Eqs. (21) and (22). We therefore have

$$M_{1pq} = \frac{1}{\Delta E} \frac{m_1(\theta_{1p})m_2(\theta_{1q})}{r_{1p}{}^3 r_{1q}{}^3} . \tag{42}$$

When following our previous reasoning, the operator for a triple flip becomes

$$M^2 = \left(\frac{1}{v\Delta E}\right)^2 \int \frac{m_1{}^2(\theta_{1p})m_2{}^2(\theta_{1q})}{r_{1p}{}^6 r_{1q}{}^6} d\mathbf{r}_{1p} d\mathbf{r}_{1q} . \tag{43}$$

In our configuration counting, we must include the fact that we have already assigned three spins to three "boxes" and thus, the analog of Eq. (5) is

$$f = \frac{C(3)}{C(0)} = \frac{N_1 N_2 N_3 v^3}{V^N} \int d\mathbf{r}_{12} \cdots d\mathbf{r}_{1, p-1}$$

$$\times d\mathbf{r}_{1, p+1} \cdots d\mathbf{r}_{1, q-1} d\mathbf{r}_{1, q+1} \cdots d\mathbf{r}_{1N} . \tag{44}$$

In setting up the energy constraint, we require that $\Delta E^0 + \Delta E^{\mathrm{dip}} = 0$ when all three spins are considered. In analogy to expression (15), this constraint turns out to

³ P. S. Pershan, Phys. Rev. **117**, 109 (1960).

be

$$\frac{1}{2\pi} \int_{-\infty}^{\infty} \exp\{i\rho[\Delta\omega_{AB}(\mathbf{r}_{1p}) + \Delta\omega_{AB}(\mathbf{r}_{1q}) + \Delta\omega_{CD}(\mathbf{r}_{p1})$$

$$+ \Delta\omega_{CD}(\mathbf{r}_{pq}) + \Delta\omega_{FG}(\mathbf{r}_{q1}) + \Delta\omega_{FG}(\mathbf{r}_{qp})]\}$$

$$\times \prod_{k \neq 1,\, p,\, q} \exp\{i\rho[\Delta\omega_{AB}(\mathbf{r}_{1k}) + \Delta\omega_{CD}(\mathbf{r}_{pk})$$

$$+ \Delta\omega_{FG}(\mathbf{r}_{qk})]\}e^{-i\rho\omega}d\rho . \tag{45}$$

Finally, defining $\Delta\omega_x$ in analogous fashion as in Eq. (20) we have

$$W(\omega) = \frac{2\pi}{\hbar} \frac{n_1 n_2 n_3}{v^2} \int_{-\infty}^{\infty} \chi(\rho)\Phi(\rho)e^{-i\rho\omega}d\rho , \tag{46a}$$

$$\chi(\rho) = \frac{1}{2\pi} \cdot \left(\frac{1}{\Delta E}\right)^2 \int \left[\frac{m_1{}^2}{r_{1p}{}^6}e^{i\rho\Delta\omega_x(\mathbf{r}_{1p})}\right]$$

$$\times \left[\frac{m_2{}^2}{r_{1p}{}^6}e^{i\rho\Delta\omega_x(\mathbf{r}_{1q})}\right]e^{i\rho\Delta\omega_x(\mathbf{r}_{pq})}d\mathbf{r}_{1p}d\mathbf{r}_{1q} , \tag{46b}$$

$$\Phi(\rho) = \left(\frac{1}{V} \int \exp\{i\rho[\Delta\omega_{AB}(\mathbf{r}_{1k}) + \Delta\omega_{CD}(\mathbf{r}_{pk})\right.$$

$$\left. + \Delta\omega_{FG}(\mathbf{r}_{qk})]\}d\mathbf{r}_{1k}\right)^{N-3} . \tag{46c}$$

Once again, χ and Φ are not really separable, but our previous discussion of this point applies without change.

A new difficulty arises, however, because χ itself is now given by two integrals which are not separable. They are not separable because of the appearance of $\mathbf{r}_{pq}$ in the third exponential. To test the effect of this coupling term, we have computed $\chi(\omega)$ numerically, both with and without the coupling term. We used P_{21} for $m(\theta)$ and P_{20} for $\Delta\omega_x$. We find that the two χ's generated in this way have virtually the same shape, except that the χ without the coupling term is narrower by about a factor of 1.5. It appears to be still practicable, therefore, to calculate χ on the basis of separable integrals with the proviso that one expects the correct function to be qualitatively the same but somewhat broader.

Each of the separate integrals gives the power spectrum of the projection of the dipole operator governing the interaction between spin 1 and spin p and between spin 1 and spin q, respectively. If these two interactions were completely independent, there would be no coupling term, and the joint power spectrum would simply be the convolution of the individual power spectra. But the transitions do not occur independently; hence, a coupling term. In picturesque language, the relative squiggles of spins 1 and p are modulated by the squiggles of spin q, and the spectrum is broadened.
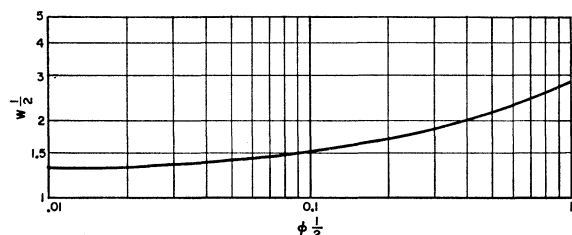
FIG. 1. Three-spin functions: W half-width versus Φ half-width in units of χ half-width.

The calculation of the triple flip $W(\omega)$ again resolves itself into the convolution of the χ and Φ functions of part I. Only now we need two χ's with their associated Φ's instead of one. We note that $W(\omega)$ will have a factor proportional to the cube of the concentration and to the square of the ratio of the dipole energy to the Zeeman energy.

Four-spin and higher order processes require no new physical or computational considerations. We note that a matrix element of the form $M_{1p}M_{qr}$ gives zero contribution. The two factors commute and the element will be identically cancelled by its converse. This is important since there is no implicit requirement in such a matrix element that spins 1 and p be near spins q and r.

When K spins flip, we will therefore require $(K-1)$ 'th-order perturbation theory, and the matrix element will be a sum of terms each of which contains $(K-1)$ products. Our counting scheme will generate a concentration dependence of order n^K, and the $(K-1)$ products of dipole operators will generate a factor of (dipole energy/Zeeman energy)$^{2(K-2)}$. The functional form can be estimated by convoluting $(K-1)$ χ functions and their associated Φ's. Owing to this increasing number of convolutions, it is clear that higher order processes will show a less and less marked resonance effect, and that their $W(\omega)$ will become more and more smeared over ω space. When this consideration is coupled with the step n dependence of these processes, we have at least a partial explanation of why the "general" cross-relaxation increases so markedly at higher concentrations.

The concentration dependence of the *shape* of $W(\omega)$ enters exclusively through the Φ functions, as we have seen in part I. We showed that $W(\omega)$ for a one-spin process has a width which varies as the square root of the Φ width. If the resonance line is homogeneous, the width of this $W(\omega)$ will vary as $n^{1/2}$. The same argument applies without change to the two-spin process. For higher multiple processes, however, the concentration dependence of the width of $W(\omega)$ is much weaker. In Fig. 1, we show the half-width of W as a function of the half-width of Φ, for a three-spin process. The curve is virtually flat until the Φ width is about one-tenth the χ width. The slope of the curve then increases gradually

and reaches the value $\frac{1}{2}$ only when Φ and χ have equal widths. The concentration dependence of the width of $W(\omega)$ rapidly disappears as the number of spins involved increases. The reason for this is that the successive convolutions rapidly smear out the sharp central peak which alone depends critically on the width of Φ.

V. EXCHANGE

We have so far ignored certain considerations which do not alter the general structure of our calculation, but which nonetheless may have a pronounced effect on actual results.

An exchange interaction of the form $J(\mathbf{S}_1 \cdot \mathbf{S}_2)$ frequently occurs between neighboring transition metal ions. If such an interaction is present, we distinguish two cases: (1) When the exchange energy is of the same order as the dipole energy, we treat these two interactions in parallel fashion. We still consider the unperturbed energy of the ion as an eigenvalue of a single-ion state. We consider the diagonal elements of $J(\mathbf{S}_1 \cdot \mathbf{S}_2)$ as contributing to $\Delta\omega$ and we consider the off-diagonal elements as contributing to the transition matrix elements. The integral defining χ [Eq. (25), part I] will, of course, be split into two parts. The first part sums over those sites that are exchange coupled, the second over the rest of space. (2) When the exchange energy becomes comparable to the Zeeman or crystal field energy, the unperturbed states can no longer be considered as single-ion states. If J is large enough, E^0 is given by the diagonal elements in a representation in which $J(\mathbf{S}_1 \cdot \mathbf{S}_2)$ is diagonal. In any case, since the energy separations between pair states are now, in general, quite different from the energy separations between single-particle states, such exchange coupled pairs do not, in general, contribute to the resonant cross-relaxation process. In terms of computational procedure, this means that the integral defining χ starts at a radius where exchange is no longer large.

This prescription is somewhat oversimplified for two reasons. First, it may happen accidentally that the separation between some of the pair levels does, in fact, coincide closely with the separation between some of the single-particle levels. Secondly, as we have seen, the frequency width of higher order processes becomes large. At the same time, the number of pair levels is $(2S+1)$ times the number of single-particle levels. As the requirement of harmonic coincidence is made less and less stringent, it becomes more and more probable that some of the level separations in the larger pair manifold will meet an approximate harmonic condition. One expects that exchange coupled pairs would, in general, enhance the probability of higher order processes, particularly under conditions where the single-particle levels alone do not exactly meet the harmonic condition. Such participation of exchange-coupled pairs in the

cross-relaxation process has been discussed by Bloembergen and Pershan[4] and by Gill and Elliott.[5]

VI. THE NEAR-NEIGHBOR SPECTRUM

From the very beginning, we have replaced lattice sums by volume integrals, using the volume per lattice site v to keep the dimensionality consistent. Clearly, such a substitution is valid when the density of lattice sites per unit solid angle is large. For the calculation of Φ this procedure will introduce a negligible error, except possibly in certain concentrated systems. The principal reason for this is that the dominant contribution to Φ comes from distant lattice sites. For the calculation of χ, the equivalence of the discrete and "continuous" lattice is of much more restricted validity, because the

FIG. 2. $W(\omega)$ for simple cubic lattice, [001] direction, $M = \sin\theta \cos\theta$ (arbitrary units).

[4] N. Bloembergen and P. S. Pershan, in *Advances in Quantum Electronics*, edited by J. R. Singer (Columbia University Press, New York, 1961), p. 373.

[5] J. C. Gill and R. J. Elliott, in *Advances in Quantum Electronics*, edited by J. R. Singer (Columbia University Press, New York, 1961), p. 399.

dominant contribution comes from close-lying sites. It is valid when a substantial number of neighbor shells are strongly exchange coupled. In this case, as we saw in the preceding section, there is no contribution to χ until the sites fall outside the exchange radius. An example is ruby, where exchange is large over at least the first seven neighbor shells. The equivalence is not valid when the nearest neighbors participate in the cross-relaxation process. The contribution of these neighbors will dominate over the contribution of the rest of the lattice because of the r^{-6} dependence of the transition operator. The integral for χ is then replaced by a sum.

$$\chi(\rho) = \frac{1}{2\pi} \sum_j \frac{m_j{}^2(\theta_j)}{r_j{}^6} e^{i\Delta\omega_j\rho}, \qquad (47)$$

where the sum need extend only as far as the first few, sometimes only the first, neighbor shells. Then $\chi(\omega)$ will be given by a series of δ functions

$$\chi(\omega) = \sum_j \frac{m_j{}^2(\theta_j)}{r_j{}^6} \delta(\omega - \Delta\omega_j) . \qquad (48)$$

Finally, $W(\omega)$ will be given by a sum of resonance curves, each displaced from the origin by $\Delta\omega_j$ and weighted by the corresponding transition operator:

$$W(\omega) \sim \sum_j \frac{m_j{}^2(\theta_j)}{r_j{}^6} \Phi(\omega - \Delta\omega_j) . \qquad (49)$$

In systems that are very dilute and have no inhomogeneous broadening, the various Φ's may be resolvable. To illustrate, we show, in Fig. 2, $W(\omega)$ for a simple cubic lattice with the magnetic field in the [001] direction and with $\Delta\omega_j = (3\cos^2\theta_j - 1)/r_j{}^3$, $m_j = \sin\theta_j \cos\theta_j$. The width of Φ has been taken as 1/50 the nearest-neighbor dipole energy. The peak at 18 is due to the (0,1,1) and equivalent sites. The six nearest neighbors are not effective because their m_j vanishes. If we take $m_j = (3\cos^2\theta - 1)$, then the neighbors at $(0, 0, \pm 1)$ will produce an effect 32 times greater than the (0,1,1) neighbors and 11 times as far away from the origin. The shape of W is quite sensitive to the angular functions involved. This means it is quite sensitive to the particular matrix element for a given process and to the direction of the magnetic field.

In more concentrated systems or in systems with substantial inhomogeneous broadening, Φ will be too broad to resolve subsidiary peaks such as shown in Fig. 2. Nevertheless, the shift of the peak away from $\omega = 0$, i.e., away from the exact resonance condition, will still occur.

The shift of the peak cross-relaxation probability away from the harmonic condition becomes intuitively obvious if one considers that the matching of level separations must include the diagonal dipole energy as well as the Zeeman energy. Thus, the peak in cross re-
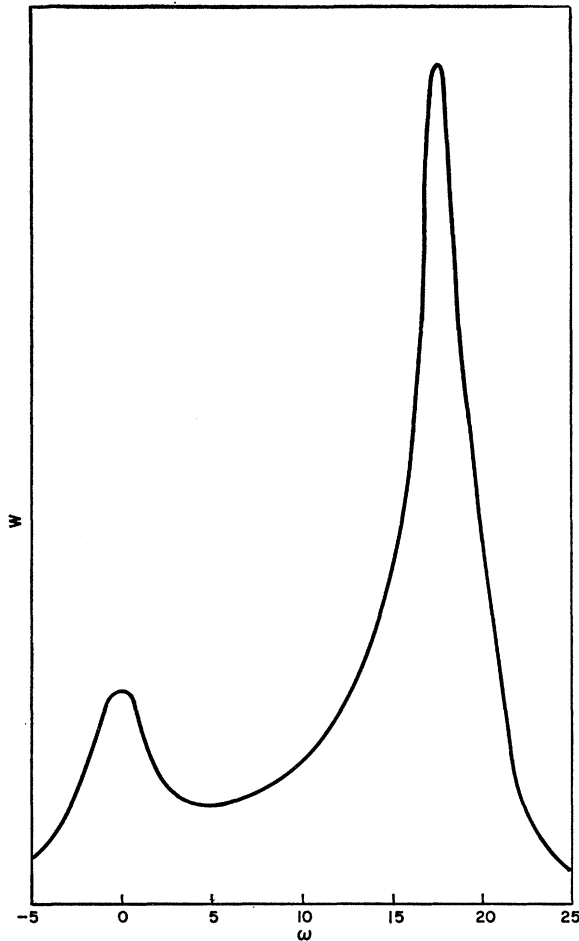
laxation still occurs where the total energies are exactly matched, but this point will be somewhat displaced from the point where the Zeeman energies alone are exactly matched. The amount of displacement depends rather critically on the specific operating conditions.

VII. INHOMOGENEOUS BROADENING

Inhomogeneous broadening affects the distribution of energy levels about their unperturbed value. In our formalism this distribution manifests itself in the function Φ. The question whether Φ should include the inhomogeneous broadening or not is isomorphic to the question whether the spin packets within an inhomogeneous line cross-relax together or separately. For limiting cases one can give an unequivocal answer. If the spin-diffusion time within the inhomogeneous line is much shorter than the cross-relaxation time for one packet, then the whole line relaxes together. If the spin-diffusion time is much longer than the cross-relaxation time, then the packets relax separately. To put this in terms of numbers, we take $T_2 = 10^{-8}$ sec and $T_{12} = 10^{-3}$ sec. For T_{diff} we use Bloembergen's rule of thumb[6]

$$T_{\text{diff}} = T_2 \times (T_2/T_2^*)^3 , \qquad (50)$$

where $1/T_2^*$ is the total width of the inhomogeneous line. We then obtain the condition that the homogeneous width of the line must be much greater than

[6] N. Bloembergen, S. Shapiro, P. S. Pershan, and J. O. Artman, Phys. Rev. 114, 445 (1959).

2% of the inhomogeneous width, if the entire line is to relax as a whole. If this condition is met, Φ should therefore include the inhomogeneous broadening. If this condition is not met, the situation becomes complicated. Relaxation takes place between all the spin packets in one inhomogeneously broadened level and all the spin packets in the other inhomogeneously broadened level. At the same time spin diffusion takes place within each of the levels.

VIII. SUMMARY

We have extended the basic cross-relaxation theory of part I to relaxation processes of all orders. Among other results we have derived the following: (1) For a K-spin process, the magnitude of the transition probability depends on concentration as n^K. (2) The frequency width of the transition probability is proportional to the square root of the Φ width for one- and two-spin processes. For three-spin processes, the width of W depends on the width of Φ only when Φ and χ have comparable widths, and even then the dependence is relatively feeble. For higher multiple processes, the dependence of the W width on the Φ width is negligible. Instead, the width of the K-spin W is roughly proportional to K. (3) In the absence of strong exchange interactions, the nearest neighbors dominate the cross-relaxation process. In this case, W is obtained from the convolution of Φ functions with a discrete near-neighbor spectrum, and its peak may be displaced from the harmonic point by an amount corresponding to the nearest-neighbor dipole energy.