

General Theory of Cross Relaxation. IV. Moments*

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The moment method for calculating C-R shape functions is discussed in the light of our previous calculation of the C-R probability W_{CR} . The principal result is that the moments calculated by Bloembergen's formalism are the moments of the power spectrum of the dipole operator, i.e., of our function χ . The question of the uniqueness of the function generated from moments and the question of the concentration dependence of the moments are also discussed.

WE have previously presented a general calculation of the cross-relaxation probability in spin systems.¹ The calculation was based on essentially statistical arguments and yielded the C-R probability W_{CR} in explicit functional form. In particular, it appeared that, if ω denotes the energy imbalance in the C-R process, $W_{CR}(\omega)$ is given by the convolution of two functions: $\chi(\omega)$, which corresponds to the power spectrum of the dipole transition operator, and $\Phi(\omega)$, which is related to the level broadening such as is observed in resonance lines. Since previous calculations²⁻⁶ have been based primarily on the moment method, it is of some interest to investigate the relationship between such moments and the directly calculated functions obtained in G .

By the n th moment of a function $F(\omega)$ we mean

$$\langle \omega^n \rangle = \int_{-\infty}^{\infty} \omega^n F(\omega) d\omega. \quad (1)$$

If we consider the Fourier transform of $F(\omega)$,

$$G(\rho) = \int_{-\infty}^{\infty} F(\omega) e^{i\omega\rho} d\omega, \quad (2)$$

then an equivalent definition of $\langle \omega^n \rangle$ is

$$\langle \omega^n \rangle = i^{-n} (dG^n(\rho)/d\rho^n)_{\rho=0}. \quad (3)$$

It is generally true that a complete set of moments completely determines a function. There also exist algorithms for constructing a function which will fit an arbitrary number of sequential even moments.⁷

Van Vleck⁸ has given a general prescription for calculating the moments of a quantum-mechanical operator Q . His method can be summarized as follows: Define an operator U_{2n} by the recursion relation

$$U_{2n} = [\mathcal{H}, U_{2n-2}] \quad (4a)$$

$$G(\rho) = \frac{\text{Tr}\{[Q_0 + Q_1(i\rho) + \frac{1}{2}Q_2(i\rho)^2 + \dots + (1/n!)Q_n(i\rho)^n + \dots]Q_0^*\}}{\text{Tr}(Q_0Q_0^*)}$$

$$U_0 = Q. \quad (4b)$$

Then

$$\hbar^{2n} \langle \omega^{2n} \rangle = (-)^n \text{Tr} U_{2n}^2 / \text{Tr} U_0^2. \quad (5)$$

For instance, for $n=1$, we obtain the familiar second moment formula

$$\hbar^2 \langle \omega^2 \rangle = -\text{Tr}[\mathcal{H}, Q]^2 / \text{Tr} Q^2. \quad (6)$$

In applying this formula to cross-relaxation, one identifies \mathcal{H} with the diagonal and "semidiagonal" parts of \mathcal{H}_{dip} , and Q with the off-diagonal parts of \mathcal{H}_{dip} . The resulting moments are then used to estimate the shape function $g(\omega)$ in Ref. 2.

We shall show that (1) the moments calculated by the above method refer to the power spectrum $\chi(\omega)$; (2) ratios between low-order moments cannot always distinguish even widely different functions, such as the logarithmic χ and a Gaussian; (3) no concentration dependence should be associated with the moments of Ref. 2; (4) in the limit of vanishing concentrations, $W_{CR}(\omega)$ does not possess any moments.

I. RELATION OF VAN VLECK MOMENTS TO THE POWER SPECTRUM

The moments defined by Eqs. (4) and (5) are the moments of the power spectrum of the operator Q . To see this, we recall the theorem that the power spectrum of $Q(t)$ is the Fourier transform of the autocorrelation of $Q(t)$. The autocorrelation, $G(\rho)$, is defined

$$G(\rho) = \frac{\text{Tr}\langle Q(t+\rho)Q^*(t) \rangle_{\text{time-average}}}{\text{Tr}\langle Q^2(t) \rangle_{\text{time-average}}}. \quad (7)$$

Using the shorthand

$$Q_n = \partial^n Q / \partial (i\rho)^n \quad (8)$$

we expand $G(\rho)$ in powers of $i\rho$:

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¹ W. J. C. Grant, Phys. Rev. **134**, A1554 (1964); *ibid.* **134**, A1564 (1964); *ibid.* **134**, A1574 (1964). These papers will be collectively referred to as G.

² N. Bloembergen, S. Shapiro, P. S. Pershan, and J. O. Artman, Phys. Rev. **114**, 445 (1958).

³ U. K. Kopvillem, Fiz. Tverd. Tela **2**, 1829 (1960) [English transl.: Soviet Phys.—Solid State **2**, 1653 (1960)].

⁴ A. Kiel, Phys. Rev. **120**, 137 (1960).

⁵ M. Hirono, J. Phys. Soc. Japan **16**, 766 (1961).

⁶ M. Hirono, J. Radio Res. Lab. (Japan) **9**, 73 (1961).

⁷ A. Wright, Phys. Rev. **76**, 1826 (1949).

⁸ J. H. Van Vleck, Phys. Rev. **74**, 1168 (1948).

It follows from Eq. (3) and the above expression that the $(2n)$ th moment of the power spectrum of Q is given by

$$\langle \omega^{2n} \rangle = \text{Tr}(Q_{2n}Q_0^*) / \text{Tr}(Q_0Q_0^*). \quad (9)$$

The Van Vleck formula [Eq. (5)] can be written in terms of derivatives of Q by means of the general relation

$$\dot{F} = (\hbar/i)[\mathcal{H}, F]. \quad (10)$$

Equation (5) then becomes

$$\langle \omega^{2n} \rangle = \text{Tr}(Q_n Q_n^*) / \text{Tr}(Q_0 Q_0^*). \quad (11)$$

To identify Van Vleck-type moments with those of the power spectrum, we therefore need to prove that

$$\text{Tr}(Q_{2n}Q_0^*) = \text{Tr}(Q_n Q_n^*). \quad (12)$$

We prove Eq. (12) in several steps. First we shall need the following properties of the binomial coefficients $C(n, m)$:

$$C(n, m) = n! / m!(n-m)!, \quad 0 \leq m \leq n \quad (13a)$$

$$C(n, m) = 0, \quad m < 0, \quad m > n, \quad (13b)$$

$$C(n+1, m) = C(n, m) + C(n, m-1), \quad (14)$$

$$C(n, m) = C(n, n-m), \quad (15)$$

$$C(n+x, m) = \sum_{j=0}^x C(x, j)C(n, m-j), \quad (16)$$

$$C(2n, m) = \sum_{j=0}^n C(n, j)C(n, m-j). \quad (17)$$

Equations (13) to (15) are well known. Equation (17) follows from Eq. (16) by setting $x=n$. We prove Eq. (16) by induction: The equation holds for arbitrary x and m , and $n=0$ —since $C(0, m-j)=0$ unless $j=m$, in which case it equals 1. We now show that if Eq. (16)

holds for n , then it holds for $n+1$. By Eq. (14)

$$C(n+x+1, m) = C(n+x, m) + C(n+x, m-1). \quad (18)$$

Then, by assumption that Eq. (16) holds for n ,

$$C(n+x+1, m) = \sum_{j=0}^x C(x, j)C(n, m-j) + \sum_{j=0}^x C(x, j)C(n, m-j-1). \quad (19)$$

By combining the sums, and again invoking Eq. (14),

$$C(n+x+1, m) = \sum_{j=0}^x C(x, j)C(n+1, m-j). \quad (20)$$

This proves the theorem (16).

We next prove the following:

$$Q_n = \hbar^n \sum_{m=0}^n (-)^m C(n, m) \mathcal{H} C^{n-m} Q_0 \mathcal{H} C^m. \quad (21)$$

Again we proceed by induction. Equation (21) holds trivially for $n=0$. Using Eq. (21) and (10),

$$Q_{n+1} = \hbar^{n+1} \sum_{m=0}^n (-)^m C(n, m) \mathcal{H} C^{n+1-m} Q_0 \mathcal{H} C^m - \hbar^{n+1} \sum_{m=0}^n (-)^m C(n, m) \mathcal{H} C^{n-m} Q_0 \mathcal{H} C^{m+1}. \quad (22)$$

In the second sum, set $m' = m+1$:

$$+ \hbar^{n+1} \sum_{m'=1}^{n+1} (-)^{m'} C(n, m'-1) \mathcal{H} C^{n+1-m'} Q_0 \mathcal{H} C^{m'}.$$

The lower limit of this sum can formally be extended to 0, since $C(n, -1)$ is zero by Eq. (13b). Similarly the upper limit of the first sum in Eq. (22) can be extended to $n+1$, since $C(n, n+1)=0$. We then have, changing the dummy index back to m ,

$$Q_{n+1} = \hbar^{n+1} \sum_{m=0}^{n+1} (-)^m [C(n, m) + C(n, m-1)] \mathcal{H} C^{n+1-m} Q_0 \mathcal{H} C^m. \quad (23)$$

Since the bracketed expression equals $C(n+1, m)$ [by Eq. (14)], we have completed the proof of Eq. (21).

From Eq. (21), we have, since \mathcal{H} is Hermitian,

$$Q_n^* = \hbar^n \sum_{k=0}^n (-)^k C(n, k) \mathcal{H} C^k Q_0^* \mathcal{H} C^{n-k} \quad (24)$$

$$Q_n Q_n^* = \hbar^{2n} \sum_{m, k=0}^n (-)^{m+k} C(n, m) C(n, k) \mathcal{H} C^{n-m} Q_0 \mathcal{H} C^{m+k} Q_0^* \mathcal{H} C^{n-k}. \quad (25)$$

Since the trace of a product is invariant under cyclic permutation of the factors,

$$\text{Tr} Q_n Q_n^* = \hbar^{2n} \text{Tr} \sum_{m, k=0}^n (-)^{m+k} C(n, m) C(n, k) \mathcal{H} C^{2n-(m+k)} Q_0 \mathcal{H} C^{m+k} Q_0^*. \quad (26)$$

We now set $p = m + k$. We observe that as p runs from 0 to n , m runs from 0 to p ; as p runs from $n+1$ to $2n$, m runs from $p-n$ to n . Now Eq. (26) becomes

$$\begin{aligned} \text{Tr} Q_n Q_n^* = \hbar^{2n} \text{Tr} \left[\sum_{p=0}^n (-)^p \mathcal{J} \mathcal{C}^{2n-p} Q_0 \mathcal{J} \mathcal{C}^p Q_0^* \sum_{m=0}^p C(n, m) C(n, p-m) \right. \\ \left. + \sum_{p=n+1}^{2n} (-)^p \mathcal{J} \mathcal{C}^{2n-p} Q_0 \mathcal{J} \mathcal{C}^p Q_0^* \sum_{m=p-n}^n C(n, m) C(n, p-m) \right]. \quad (27) \end{aligned}$$

The first m sum in Eq. (27) can formally be extended up to n , and the second m sum down to 0, since the additional terms all vanish by Eq. (13b). Each m sum may therefore be replaced by $C(2n, p)$, in view of Eq. (17). The p sums now coalesce.

$$\text{Tr} Q_n Q_n^* = \hbar^{2n} \text{Tr} \sum_{p=0}^{2n} (-)^p C(2n, p) \mathcal{J} \mathcal{C}^{2n-p} Q_0 \mathcal{J} \mathcal{C}^p Q_0^*. \quad (28)$$

But from Eq. (21), we see that this is precisely the expansion for $\text{Tr} Q_{2n} Q_0^*$.

This completes the proof of Eq. (12). This means we have shown that the moments generated by the trace formulas (4) to (6) apply to the power spectrum of the off-diagonal elements of $\mathcal{J} \mathcal{C}_{\text{dip}}$. This power spectrum is essentially given by the function $\chi(\omega)$ discussed by G.

II. INDETERMINACY OF FUNCTIONS RESULTING FROM A FIT TO MOMENTS

The ratio of the fourth to the second moment has been used to show that the moment calculation predicts a Gaussian shape. The calculated ratios are indeed quite close to those obtained from a Gaussian function, in a variety of physical circumstances.^{5,6,9} How is this possible, if, as we claim, these moments actually refer to $\chi(\omega)$, which does not in the least resemble a Gaussian? Furthermore, for a three-spin process, the relevant functions are presumably replaced essentially by their convolutions with themselves. Under this operation, a Gaussian goes into a Gaussian, but χ goes into a function of a different form. The appearance of very similar moment ratios for both two and three-spin calculations would seem to be further evidence for the Gaussian shape.

We have calculated the moments of our function χ , as defined in part I of G, Eq. (50). We have also calculated the moments of $\chi * \chi$, the convolution of χ with itself. In Table I, we tabulate these moment ratios with

TABLE I.^a Moment ratios of χ , $\chi * \chi$, and a Gaussian.

	$\langle \omega^4 \rangle^{1/4} / \langle \omega^2 \rangle^{1/2}$	$\langle \omega^6 \rangle^{1/6} / \langle \omega^4 \rangle^{1/4}$	$\langle \omega^8 \rangle^{1/8} / \langle \omega^6 \rangle^{1/6}$
Gaussian	1.32	1.19	1.14
χ	1.34	1.17	1.11
$\chi * \chi$	1.33	1.39	

^a χ is defined in part I, Eq. (50). $\chi * \chi$ is the convolution of χ with itself.

those obtained from a Gaussian. If we use the χ as defined by Eq. (53) in part I of G, the moment ratios are slightly higher, namely, 1.47, 1.24, and 1.15, respectively.

It is apparent that low-order moments do not give a sufficiently unique description of the shape of a function. In particular, a Gaussian, χ , and $\chi * \chi$ are not distinguishable from one another by this method.

This result is less startling than appears at first sight. If two functions, $F_1(\omega)$ and $F_2(\omega)$, have similar moment ratios, it is not F_1 and F_2 but their Fourier transforms $G_1(\rho)$ and $G_2(\rho)$, that will behave similarly in the neighborhood of the origin. No conclusion can in general be drawn about F_1 and F_2 themselves. F depends on the shape of G not only near $\rho = 0$, but over the entire range $-\infty < \rho < \infty$. Thus, the first few terms of the Maclaurin expansions of $\exp(-\rho^2)$, $1/(1+\rho^2)$, and $\text{Si}(\rho)/\rho$ may have quite similar ratios, but it would be wrong to conclude that their Fourier transforms, $\exp(-\omega^2)$, $\exp(-|\omega|)$, and $\ln(1/|\omega|)$, bear a striking resemblance to one another.

III. CONCENTRATION DEPENDENCE OF THE MOMENTS OF THE POWER SPECTRUM

In G it was shown that the concentration dependence of the shape of $W_{\text{CR}}(\omega)$ resides entirely in the level broadening, which enters through the function Φ , and not in the power-spectrum χ . Since we have shown that the moments calculated according to Ref. 2 refer to χ , these moments ought not to exhibit any concentration dependence. This seems in contradiction to several other calculations.³⁻⁶

The method by which the spin concentration n is introduced into moment calculations was first proposed by Kittel and Abrahams¹⁰ in their calculation of resonance line shapes of dilute systems. They showed that in the calculation of lattice sums a factor n^k is associated with terms referring to k sites (not counting the reference spin). But the analogy between resonance lines and cross-relaxation functions is surely not self-evident. We propose that the manner in which sums over spin interactions enter the calculation of the absorption resonance is in fact quite different from the manner in which such sums enter the calculation of the rf dipolar spectrum.

The absorption is given by the diagonal dipole matrix

⁹ P. S. Pershan, Phys. Rev. **117**, 109 (1960).

¹⁰ C. Kittel and E. Abrahams, Phys. Rev. **90**, 238 (1953).

elements. The dipole energy of any one spin is the algebraic sum of the potentials due to all the other spins. It is *one* number. If we calculate the distribution of such numbers assigned to different spins, we obtain the "level broadening," which leads directly to the resonance line shape. This problem is analogous to the random walk. The drunkard who staggers a certain number of steps of arbitrary direction and size will arrive at one definite spot. The positions of a large number of such drunkards form a distribution which we can in principle calculate. The width of the distribution is clearly dependent on the number and on the size of the steps. If we relate the number of steps to the number of spins, we obtain the "expanded lattice" picture. In this picture, each site contributes the full perturbation, but the distance between sites is scaled according to the concentration. If we relate the size of the steps to the concentration, we obtain the "random distribution" picture. On this picture, the perturbation from each site is scaled by the concentration, but the spacing between sites is left unaltered. Kittel and Abrahams showed that the "random distribution" picture is valid for the calculation of the moments of the resonance curve.

The power spectrum of the dipole operator, on the other hand, depends on both the off-diagonal and diagonal matrix elements of this operator. The spectrum which any one spin sees is again the sum of its interactions with all the other spins. But it is *not* an algebraic sum. It is *not* one number. It is already a distribution. The ordinates correspond to the squares of the off-diagonal elements, and the abscissas correspond to the associated diagonal elements. The averaging of such distributions has nothing in common with a random walk. Rather, it is analogous to the ergodic problem, if we relate space sampling to summing the spectra seen by different spins, and if we relate time sampling to summing the spectra seen by one spin as, in thought, we allow all possible configurations of its environment. (In fact the equivalence of these two averages is presupposed in the entire theory of G.) Clearly, as we denumerate all these configurations, each lattice site becomes occupied an equal number of times. Consequently the average spectrum can be calculated by considering a fully occupied lattice, regardless of the concentration. To the extent that the spins interact as independent pairs, the concentration affects only the intensity of the oscillating field; it does not affect its average spectral distribution.

The multiple sums over all *spins* which appear in the theoretical formulas are, from a practical point of view, purely symbolic. They could not conceivably ever be

calculated, and even if, per impossible, they could be calculated, they would be different for every individual crystal. The *lattice* sums which invariably replace them are the fruit of some statistical argument. We have indicated that the statistical argument which applies to the diagonal dipole perturbations is quite different from the one which applies to the spectral distribution of the off-diagonal elements. The basic reason for this is that in one case we are essentially doing a random-walk problem, in the other we are essentially taking a straightforward average. In particular, it is not at all clear that the manner in which concentration is introduced can be transferred from one case to the other.

Nevertheless, we note that one of the more startling conclusions of previous calculations was that the moments actually turned out to be dominated by a concentration independent term—a conclusion with which, needless to say, we are in hearty agreement.

IV. MOMENTS OF W_{CR} IN THE LIMIT OF LOW CONCENTRATIONS

We now show that the complete cross-relaxation function, $W_{CR}(\omega)$, does not possess moments in the limit of vanishing concentrations. From Eq. (3), we see that the n th moment of $F(\omega)$ corresponds (except for a factor $i^n/n!$) to the n th Maclaurin coefficient of $G(\rho)$. In this sense, the moments of a function determine the function. It is not true, however, that every determined function has a complete set of moments. A Lorentzian, for instance, has no moments of order 2 or greater. Its Fourier transform is $\exp(-a|\rho|)$, whose derivatives diverge at the origin. A moment expansion exists for $F(\omega)$ if and only if its Fourier transform $G(\rho)$ can be expanded in a Maclaurin series.

The cross-relaxation shape function has a Fourier transform which is the product of two functions:

$$g(\rho) = \chi(\rho)\Phi(\rho).$$

For low concentrations, such as are encountered in ruby, for instance, $\Phi(\rho)$ approaches the form $\exp(-a|\rho|)$, which is the transform of a Lorentzian. For this function, a Maclaurin expansion does not exist. It is easy to show in general that if any factor in a product has an n th derivative which diverges at the origin, then all derivatives of the product, starting with the n th, will diverge at the origin. It follows that $g(\rho)$ cannot be approximated by a Maclaurin expansion. More specifically, at vanishing concentrations, all the moments (except the zeroth) of the cross-relaxation function $W_{CR}(\omega)$ are undefined.