Statistical Theory of Spin-Spin Interactions in Solids*†

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A statistical theory of spin interactions is presented which takes its starting point from pair transitions rather than single-particle transitions. The approach through straightforward perturbation theory applied to pairs, and the approach through the time development of the pair-transition operator $S_x(t)$ are shown to be equivalent. The averaging over possible pair configurations is performed by means of a weight function which allows inclusion of the details of the lattice structure and of departures from random spin distribution. Concentration dependence and temperature dependence appear naturally in the formalism. The formalism is not intrinsically restricted to a particular type of spin interaction. Magnetic dipole forces, exchange of any specified magnitude and any specified finite range, and cross-relaxation effects can be included. Several aspects of moment theory are clarified. The existence of asymmetry in certain line shapes is indicated. The theory is applied to magnetic dipole interaction and exchange. The Fourier transform of the magnetic resonance line shape is derived in an exact, explicit, and semiclosed form, in which the details of the system under consideration appear parametrically. A formula is given for all the moments of the line, but it is shown that moments bear a direct relationship to the observed half-width only in the limit of very dense spin concentration. The results for limiting cases agree with those derived by Anderson and by Kubo and Tomita. In particular it appears that the line is always Lorentzian in the center and Gaussian in the wings, and that it approaches a pure Lorentzian shape as either the spin concentration or the effective nearest-neighbor distance become vanishingly small.

I. INTRODUCTION

AGGREGATES of weakly interacting particles are characterized by an absorption (or emission) spectrum that is nearly identical to the spectrum of the individual uncoupled particles, but whose frequencies are broadened into bands. The problem of relating a microscopically given interaction to the details of a macroscopically observed spectral line shape is a general one and of long standing.

A statistical approach to the theory of line shapes was initiated by Margenau,[1,2] and applied by him to the spectra of gases. Similar principles were first applied to spin interactions in solids by Anderson.[3–6] This approach rests essentially on the calculation of the autocorrelation function of the transition operator, e.g., of $S_x(t)$. The formalisms of Kubo and Tomita[7,8] and of Caspers[9] likewise are statistical theories which aim at approximations to a relaxation function. The complexity of the required computations, however, has restricted application of these formalisms to the establishment of asymptotic results and to a study of low-order moments, which appear as the expansion coefficients of the relaxation function.

Most practical calculations of magnetic resonance line shapes are based on the moment method of Van Vleck[10] or of Pryce and Stevens.[11] This method has been applied with considerable success to magnetically concentrated systems,[12–20] with more questionable success to dilute systems.[21,22] The moment approach suffers from the difficulty that moments are not directly measured experimentally. One measures the imaginary part of the susceptibility, and this information must be interpreted in terms of a known line shape to be related to moments.

In the present work we calculate the resonance line shape exactly and in detail. Our physical reasoning is closely related to that of Margenau and Anderson. We make no appeal to moments or to physical plausibility arguments, and our results apply to systems of any degree of dilution. The effects of exchange interactions can be incorporated precisely, as can the details of the

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crystal lattice and the possibly nonrandom distribution of paramagnetic spins.

In Sec. II, we consider the relevant two-body problem. In Sec. III, we formulate a statistical scheme for summing all pair interactions throughout the crystal. Random distribution of spins is assumed over the long range, but we leave open the question of short-range clustering. In Sec. IV we apply our formulation to magnetic dipole interactions and solve the resulting integrals exactly.

II. THE TWO-BODY PROBLEM

The quantum-mechanical two-body problem is embodied in the two-body Hamiltonian. We consider a Hamiltonian

$$\mathcal{H}=g\beta\mathbf{H}\cdot(\mathbf{S}_1+\mathbf{S}_2)+[F(\mathbf{S}_1)+F(\mathbf{S}_2)]+J\mathbf{S}_1\cdot\mathbf{S}_2 +(g_1g_2\beta^2/r^3)[\mathbf{S}_1\cdot\mathbf{S}_2-(3/r^2)(\mathbf{r}\cdot\mathbf{S}_1)(\mathbf{r}\cdot\mathbf{S}_2)]. \quad (1)$$

The first term represents Zeeman energy; the second is a crystal field term, which is a polynomial in the spin coordinates having transformation properties appropriate to the crystal symmetry; third is the exchange term; the fourth term represents the dipole interaction.

To be able to treat this Hamiltonian by perturbation methods it is essential to pick appropriate basis functions. Their choice depends on the relative magnitude of the first three terms, since these cannot be diagonalized simultaneously. Of course, it is always possible to obtain the zeroth-order states by numerical diagonalization, but usually it is sufficient to consider limiting situations.

If J is large, the "coupled" representation, in which $\mathbf{S}_1\cdot\mathbf{S}_2$ is diagonal, is appropriate. The wave functions are

$$\psi_M{}^S=\sum_{m_1} C(S_1,S_2,S;\,m_1,m_2,M)\psi_{m_1}{}^{S_1}\psi_{m_2}{}^{S_2}, \quad (2a)$$

with

$$m_2=M-m_1, \quad (2b)$$

where $\psi_{m_1}{}^{S_1}$ and $\psi_{m_2}{}^{S_2}$ are single-particle functions, and C denotes the Clebsch-Gordan coefficients. The matrix elements are given in terms of single-particle matrix elements by

$$\langle\sigma,\mu|\mathcal{H}|S,M\rangle=\sum_{m_1\mu_1} C^*(S_1,S_2,\sigma;\,\mu_1,\mu_2,\mu) \times C(S_1,S_2,S;\,m_1,m_2,M) \times\langle S_1\mu_1,S_2\mu_2|\mathcal{H}|S_1m_1,S_2m_2\rangle. \quad (3)$$

The energy levels in this scheme do not in general bear any resemblance to the energy levels for the single particle.

If J is small, an uncoupled representation is appropriate. The choice of wave functions now further depends on whether the two spins are alike or not. If the spins are unlike (belong to different species or occupy inequivalent sites), the wave functions are simply the product functions

$$\psi_{mn}=\psi_m{}^{S_1}\psi_n{}^{S_2}. \quad (4)$$

If the spins are alike, the wave functions are

$$\psi_{mn}=(1/\sqrt{2})[\psi_m{}^{S_1}\psi_n{}^{S_2}\pm\psi_n{}^{S_1}\psi_m{}^{S_2}], \quad m\neq n \quad (5a)$$

$$=\psi_m{}^{S_1}\psi_n{}^{S_2}, \quad m=n. \quad (5b)$$

The matrix elements for $m\neq n$ are given by

$$\langle mn|\mathcal{H}|MN\rangle=\tfrac{1}{2}(\langle m_1n_2|\mathcal{H}|M_1N_2\rangle+\langle n_1m_2|\mathcal{H}|N_1M_2\rangle \pm\langle m_1n_2|\mathcal{H}|N_1M_2\rangle\pm\langle n_1m_2|\mathcal{H}|M_1N_2\rangle). \quad (6)$$

The functions defined in Eq. (5) make the particles indistinguishable. This indistinguishability has nothing to do with Fermi or Bose statistics, since we are dealing with localized particles. It reflects the fact that we can devise no experiment to distinguish which member of the pair has actually absorbed the radiation, and this in turn is a consequence of the symmetry of two-body interactions.

The energy levels in either uncoupled scheme are sums of the single-particle energies, and every transition in the pair manifold connected by the off-diagonal elements of the rf spin operator has an energy interval that corresponds to some energy interval in the single-particle manifold. In general there will be numerous pair transitions of the same frequency, even if the frequencies of the single-particle transitions are all different.

The choice of one or the other representations specified by Eqs. (4) or (5) automatically accounts for the differences in the interaction between like and unlike spins, which were first pointed out by Van Vleck.[10] In the representation of Eq. (5), operators like $S_+{}^1S_-{}^2$ are diagonal, while in the representation of Eq. (4) they are not.

Having defined a suitable representation, the quantities of interest are the off-diagonal elements of the rf spin operator, which cause radiative transitions between pair states, and the diagonal elements of the dipole operator, which perturb the energy interval between pair states. The problem of summing these dipole perturbations of the pair transition frequencies and calculating the distribution of such sums is our principal task.

III. BASIC FORMALISM

We can approach the problem of summing the pair interactions throughout the crystal by taking our starting point either in the frequency domain or in the time domain. The first method begins by applying stationary perturbation theory to the pair Hamiltonian; the second method begins by considering the time development of $S_x(t)$. Both approaches yield insight into the physics involved, and we shall show that the same result can be derived from both.

A. Approach Through Stationary Perturbation Theory

We consider an atom whose zeroth-order energy structure contains a pair of levels with separation $\Delta E_0=\hbar\omega_0$.

For notational convenience we work with a shifted spectrum so that $\omega_0=0$, and the net perturbation caused by all the other atoms is ω. From the last term in (1) it is clear that ω is a function of the position coordinates $\mathbf{r}$ and of the quantum states q of all the other atoms relative to the one we are considering:

$$\omega=\omega(\mathbf{r}_1,\mathbf{r}_2,\cdots,\mathbf{r}_N,q_1,q_2,\cdots,q_N). \tag{7}$$

Each possible configuration of perturbers in this $4N$-dimensional space gives some value of ω. Our problem is somewhat similar to the microcanonical ensemble: Out of the total accessible $\mathbf{r}-q$ space we wish to find that portion corresponding to a given value of ω. We do not, however, assume equal *a priori* probabilities. Indeed, the detailed exigencies of the physical situation are embodied in a weight function

$$W_i=W(\mathbf{r}_i,q_i). \tag{8}$$

We define the following auxiliary quantities:

$$U=\int_{r=0} W d\mathbf{r}dq, \tag{9}$$

$$V=\int_{r=0} d\mathbf{r}. \tag{10}$$

The upper limit of the r integrals remains unspecified for the moment. We now impose the following implicit restriction on our weight function:

$$\lim_{V\to\infty}(U/V)=\lambda, \tag{11}$$

where λ is a constant. We shall construct a weight function appropriate to our problem shortly. We may now write for the intensity, at some particular value of ω,

$$I(\omega)=\frac{1}{U^N}\int W_1 d\mathbf{r}_1 dq_1\cdots W_N d\mathbf{r}_N dq_N \times\delta[\omega-\omega(\mathbf{r}_1\cdots\mathbf{r}_N,q_1\cdots q_N)], \tag{12}$$

where δ is the delta function. Replacing the δ by its Fourier transform, we obtain

$$I(\omega)=\frac{1}{U^N}\int W_1 d\mathbf{r}_1 dq_1\cdots W_N d\mathbf{r}_n dq_N \times\frac{1}{2\pi}\int_{-\infty}^{\infty}\exp\{-i\rho[\omega-\omega(\mathbf{r}_1\cdots\mathbf{r}_N,q_1\cdots q_N)]\}d\rho. \tag{13}$$

We now make the approximation, deferring its discussion for the moment, that the two-body perturbations are additive:

$$\omega(\mathbf{r}_1\cdots\mathbf{r}_N,q_1\cdots q_N)=\textstyle\sum_i\omega(\mathbf{r}_i,q_i). \tag{14}$$

This makes the integrals in (13) separable, and we have

$$I(\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty}e^{-i\rho\omega}\left[\frac{1}{U}\int W d\mathbf{r}dq\exp[i\rho\omega(\mathbf{r},q)]\right]^N d\rho. \tag{15}$$

The bracketed expression in (15), which assumes the form ∞/∞ as $N\to\infty$, can be handled by the following trick of Margenau[1]:

$$\frac{1}{U}\int\exp(i\rho\omega(\mathbf{r},q))W d\mathbf{r}dq =\frac{1}{U}\left\{\int W d\mathbf{r}dq-\int[1-\exp(i\rho\omega(\mathbf{r},q))]W d\mathbf{r}dq\right\} =[1-(U'/U)], \tag{16}$$

where

$$U'=\int[1-\exp(i\rho\omega(\mathbf{r},q))]W d\mathbf{r}dq. \tag{17}$$

We now let the number of particles N and the volume V go to ∞, while the number of particles per unit volume n' remains constant. Then $U\to\lambda V$, by (11). This, of course, is the motivation for imposing the condition (11) in the first place. Using $V=N/n'$, we now obtain from (16)

$$\lim_{N\to\infty}\left[\frac{1}{U}\int\exp(i\rho\omega(\mathbf{r},q))W d\mathbf{r}dq\right]^N =\lim_{N\to\infty}\left(1-\frac{n'U'}{\lambda N}\right)^N=e^{-n'U'/\lambda}. \tag{18}$$

Inserting this result into (15), we obtain

$$I(\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty}e^{-i\rho\omega}\,e^{-(n'U'/\lambda)}d\rho. \tag{19}$$

If we can construct a suitable function W, and do the necessary integrals, our problem is solved.

We proceed to construct a typical function W. To illustrate the flexibility available through the use of the weight function, we incorporate the following requirements:

(1) Exchange is large within a radius r_1, so that the coupled scheme is appropriate for $r<r_1$, the uncoupled for $r>r_1$.

(2) Furthermore we assume that the lattice departs from spherical symmetry to an extent that makes it necessary to consider discrete sites exactly, within a radius r_0, and we take $r_0>r_1$. For $r>r_0$ a continuous distribution of magnetic dipoles is assumed. It can be shown[23] that this assumption leads to negligible error for reasonable values of r_0. The use of such a hybrid coordinate space is ultimately motivated by the following consideration: The lattice sums for moments depend heavily on the near lying sites. On the other hand, if the energy falls off as $1/r^3$, while the number of particles per dr increases as r^2, one would at first sight expect a logarithmically *divergent* perturbation sum. This paradox alone leads one to suspect that moments do

[23] W. J. C. Grant, Ph.D. thesis, Department of Physics, MIT, Cambridge, Massachusetts, 1962 (unpublished).

not give a faithful representation of the line shape, and demands an investigation of the behavior of the perturbation sum at infinity. We wish to build into our weight function a formal device for handling simultaneously the initial terms of the perturbation sum and its asymptotic behavior as well.

(3) Finally we allow the possibility of a nonrandom distribution of spins. We do this by assigning to each lattice site $\mathbf{r}_i$ a number p_i, which is defined as the ratio of the actual probability of occupation to the probability of occupation if the distribution were random.

The q space [Eq. (7)] is obviously limited to points q_s with relative weights g_s, where the q_s are the first-order dipole perturbations and the g_s are the corresponding transition probabilities, for that portion of the pair manifold for which $\Delta E_0=\hbar\omega_0$. Our weight function therefore will contain the expression

$$\sum_s g_s\delta(q-q_s), \tag{20}$$

where δ is the Dirac delta function. The requirement of working with two representations can be expressed in terms of the Dirichlet factor,

$$D(x_1,x_2)=1, \quad x_1<x<x_2 \tag{21a}$$

$$=0, \quad \text{otherwise} \tag{21b}$$

so that expression (20) becomes

$$D(0,r_1)\sum_c g_c\delta(q-q_c)+D(r_1,\infty)\sum_u g_u\delta(q-q_u), \tag{22}$$

where c and u refer to the coupled and uncoupled energy schemes.

The conditions imposed on the $\mathbf{r}$ space can similarly be embodied in an expression of the form

$$D(0,r_0)\sum_i vp_i\delta(\mathbf{r}-\mathbf{r}_i)+D(r_0,\infty). \tag{23}$$

The quantity v is the volume per lattice site and is needed to keep the dimensionality consistent.

The total weight function is the product of expressions (22) and (23), which we write in expanded form:

$$\begin{aligned}W(\mathbf{r},q)=&D(0,r_1)v\sum_i p_i\delta(\mathbf{r}-\mathbf{r}_i)\sum_c g_c\delta(q-q_c)\\&+D(r_1,r_0)v\sum_i p_i\delta(\mathbf{r}-\mathbf{r}_i)\sum_u g_u\delta(q-q_u)\\&+D(r_0,\infty)\sum_u q_u\delta(q-q_u).\end{aligned} \tag{24}$$

The complicated appearance of such a weight function reflects the complications we have set ourselves to handle.

We can now readily calculate U from Eq. (9). Inserting (24) into (9) we obtain:

$$U=v\sum_c\sum_{i=1}^{A}p_ig_c+v\sum_u\sum_{i=A+1}^{B}p_ig_u+\sum_u g_u\int_{r_0}d\mathbf{r}. \tag{25}$$

We have labeled the atom situated at $\mathbf{r}_1$ as atom A, and the atom situated at $\mathbf{r}_0$ as atom B. If we define

$$X=v\sum_c\sum_{i=1}^{A}p_ig_c+v\sum_u\sum_{i=A+1}^{B}p_ig_u-\sum_u g_u\int_0^{r_0}d\mathbf{r}, \tag{26}$$

then

$$U=X+\sum_u g_u\int_0 d\mathbf{r} \tag{27}$$

and

$$\lim_{V\to\infty}\frac{U}{V}=\sum_u g_u. \tag{28}$$

Thus W fulfills the condition (11), with $\lambda=\sum_u g_u$.

We calculate U' in the same way as U. We first make a slight change in notation. Referring to (18) and (19), we define the molar concentration $n=n'v$, and a corresponding $V'=U'/v\sum_u g_u$, so that $n'U'/\sum_u g_u=nV'$. Inserting (24) into (17) we now have

$$\begin{aligned}V'=&\frac{1}{\sum_u g_u}\sum_c\sum_{i=1}^{V}p_ig_c[1-\exp(i\rho\omega(\mathbf{r}_i,q_c))]\\&+\sum_u\sum_{i=A+1}^{B}p_ig_u[1-\exp(i\rho\omega(\mathbf{r}_i,q_u))]\\&+\frac{1}{v}\sum_u g_u\int_{r_0}^{\infty}[1-\exp(i\rho\omega(\mathbf{r},q_u))]d\mathbf{r}\end{aligned} \tag{29}$$

and

$$I(\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty}e^{-i\rho\omega}\exp(-nV')d\rho. \tag{30}$$

B. Approach Through Time Development of $S_x(t)$

We now rederive our result, using an alternative approach through the time domain. This approach has been discussed by Lowe and Norberg[24] for the case of the completely filled lattice. Our aim here is to show how the time domain theory applies to the randomly populated lattice and what meaning can be given within this framework to the weight function W.

We begin with, the theorem that the energy density spectrum of a signal is the Fourier transform of its autocorrelation function. The autocorrelation of a time function $\varphi(t)$ is defined as

$$F(\rho)=\langle\varphi(t+\rho)\varphi(t)\rangle/\langle|\varphi(t)|^2\rangle, \tag{31}$$

where the $\langle\ \rangle$ denote a suitable time average. We are concerned with the time signal $S_x(t)$, where S_x refers to the entire N-body system. The Hamiltonian of this system is $\mathcal{H}_0+\mathcal{H}'$, where $\mathcal{H}'$ is the dipole energy. As with the single pair system, we assume a representation in which $\mathcal{H}_0$ is diagonal, with eigenvalues E_{0m}, E_{0n}, $\cdots$, and with $\omega_{0mn}=(E_{0m}-E_{0n})/\hbar$. If the ω_0 for allowed transitions are not all equal we construct a suitable projection of the operator S_x, so as to connect only

[24] J. J. Lowe and R. E. Norberg, Phys. Rev. **107**, 46 (1957).

states differing in unperturbed energy by the same amount.

As before, we must average over all allowed coordinate configurations of the N-body system. The conventional device for averaging over states is the density matrix W_{ij}.[25] In general, the ensemble average of an operator O is given by

$$\langle O\rangle=\sum_{ij} W_{ij}O_{ji}=\mathrm{Tr}(WO), \tag{32}$$

where W is normalized so that

$$\mathrm{Tr}(W)=1. \tag{33}$$

The indices represent symbolically all the indices needed to specify the state.

To clarify our use of the density matrix W, we make two remarks:

(a) The states whose distribution we define by W are coordinate configurations of the N-body system. For each such state, there are a vast number of magnetic substates. Thus our states are essentially described by two quantum numbers, a coordinate label and a magnetic label. Since we consider a fixed lattice, there are no transitions between coordinate states. Transitions between magnetic states are governed by the operator S_x. Consequently, there is no time dependence in W; the time dependence is contained entirely in S_x.

We shall use Greek indices to specify the coordinate configuration, Latin indices to specify the magnetic state within the coordinate configuration.

(b) We do *not* define

$$W_{\nu\mu}=\exp(-\mathfrak{IC}_{\nu\mu}/kT)/\mathrm{Tr}[\exp(-\mathfrak{IC}/kT)].$$

This definition is appropriate for a description of temperature equilibrium in the canonical ensemble, which is not the problem we are trying to describe here by means of the density matrix. The notion of temperature equilibrium is meaningless when one thinks of all the possible distributions of impurities in a fixed lattice. We define $W_{\mu\mu}$ simply as the probability of finding the system in the state (μ). The applicable constraints are, for the present, left completely at our disposal.

We now wish to calculate the function

$$F(\rho)=\mathrm{Tr}[W\langle S_x(t+\rho)S_x^*(t)\rangle/\langle S_x^2(t)\rangle]. \tag{34}$$

We let w and s_x represent the single pair matrices corresponding to the N-pair matrices W and S_x. Then

$$F(\rho)=\mathrm{Tr}[w\langle s_x(t+\rho)s_x^*(t)\rangle/\langle s_x^2(t)\rangle]^N. \tag{35}$$

We eliminate the explicit ρ dependence of s_x by going into the Heisenberg representation:

$$s_x(t+\rho)=\exp(i\mathfrak{IC}\rho/\hbar)s_x(t)\exp(-i\mathfrak{IC}\rho/\hbar) \tag{36}$$

and

$$\langle\mu,k|s_x(t+\rho)|\nu,j\rangle=\exp(i\omega_0\rho)\times\langle\mu,k|\exp(i\mathfrak{IC}'\rho/\hbar)s_x(t)\exp(-i\mathfrak{IC}'\rho/\hbar)|\nu,j\rangle. \tag{37}$$

[25] R. C. Tolman, *Principles of Statistical Mechanics* (Oxford University Press, London, 1938), Chap. 9.

The t dependence now cancels out in (35). This is as it should be, since the initial time is arbirtary and can have no effect on the final result. We write the numerator in (35) explicitly, using the summation convention for repeated indices:

$$\exp(i\omega_0\rho)\langle\nu|w|\mu\rangle\langle\mu,k|\exp(i\mathfrak{IC}'\rho/\hbar)|\alpha,a\rangle\times\langle\alpha,a|s_x|\beta,b\rangle\langle\beta,b|\exp(-i\mathfrak{IC}'\rho/\hbar)|\gamma,j\rangle\times\langle\gamma,j|s_x^*|\nu,k\rangle. \tag{38}$$

Since our particles are stationary in the lattice, there can be no matrix elements between different coordinate configurations. Consequently, $\nu=\gamma=\beta=\alpha=\mu$.

We now make the approximation, deferring its discussion for the moment, of ignoring the off-diagonal elements of $\mathfrak{IC}'$:

$$\mathfrak{IC}_{mn}'=\mathfrak{IC}_m'\delta_{mn}. \tag{39}$$

The sum (38) now collapses into

$$e^{i\omega_0\rho}\sum_\mu w_\mu\sum_{kj}\exp(i\omega'_{\mu,kj})s_x^2{}_{kj}. \tag{40}$$

The $\omega'_{\mu,kj}$ are the perturbations of all the single pair transitions corresponding to an unperturbed frequency ω_0 and to the coordinate configuration μ. The $s_x^2{}_{kj}$ are the associated transition probabilities and are independent of μ. We take $\omega_0=0$, as before, insert (40) into (35), and take the Fourier transform:

$$I(\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty}e^{-i\rho\omega}\times\Big[\sum_\mu w_\mu\sum_{kj}\exp(i\omega'_{\mu,kj})s_x^2{}_{kj}/\sum_{kj}s_x^2{}_{kj}\Big]^N d\rho. \tag{41}$$

This result is identical to that expressed in (15). We point out the correspondence between the density matrix and the *normalized* weight function, and the appearance of the $\sum s_x^2$, which corresponds, of course, to the $\sum g$ in our weight function.

C. Approximations and Limitations

(1) First and obviously we assume that the dipole interaction is small compared to the Zeeman energy. This is the justification for the first-order approximations (14) and (39). To be more specific, we consider the physical meaning of taking pair interactions to be additive [Eq. (4)]. We are considering atom Z, and considering the effect upon it of, say, atom Y. What we ignore is the fact that atom Y is itself perturbed by all the other atoms, X, W, etc. The error we commit is of order $\Delta\mathfrak{y}/\mu$, where $\mathfrak{y}$ is the magnetic moment and $\Delta\mathfrak{y}$ is the perturbation in the moment. If we dot both numerator and denominator into $\mathbf{H}$, we have the ratio of the perturbation energy to the transition energy, or, in experimental terms, the ratio of the linewidth to the center frequency. In practice, for electron transitions at magnetic fields of the order of kilogauss, the error will be of the order of 1%.

The first-order approximation becomes poor under two circumstances: (a) At low magnetic fields, the off-diagonal dipole elements can be expected to give a frequency-dependent line shape. (b) In certain cases the interaction between nearest neighbors may be strong enough for the off-diagonal dipole terms to induce non-negligible correlations. This effect may occur when a nuclear moment in a filled paramagnetic lattice finds itself much closer to its nearest neighbor (or neighbors) than to the next successive neighbor shells.

(2) We require that the signal be small. This condition is required for the assumption that the magnetic distribution of the perturbing spins is a random one, or equivalently that it can be characterized by a temperature. We exclude from the present consideration situations characterized by large departures from equilibrium or by the existence of large externally imposed correlations within the spin system.

(3) The expression for $I(\omega)$ in terms of the configuration integrals of Eq. (12) implies a random spatial distribution of spins. This concept is clearly appropriate for a dilute system. In a filled lattice, however, the distribution is ordered, not random, so that the appropriateness of the formalism is no longer obvious. In particular, while the configuration counting is equivalent to considering the number of ways in which N spins can be put into M boxes, one to a box, the passage to a continuous integral representation fails to exhibit this constraint in any explicit way. Colossal errors in configuration counting are prevented by proper normalization, but a precise quantitative description is not expected for filled lattices.

Anderson[26] has proposed a time domain function

$$F(t)=\prod_j [1-n(1-\cos\omega_j\rho)], \tag{42}$$

where j runs over sites and the perturbations with q and $-q$ occur in pairs. From Eq. (19) it is clear that our time function can similarly be written

$$F(t)=\prod_j \exp[n(1-\cos\omega_j\rho)]. \tag{43}$$

The two expressions are equivalent when $n(1-\cos\omega_j\rho)$ is small. This will be true (a) for all values of ρ when n is small, (b) for all values of n when $\frac{1}{2}\omega^2\rho^2$ is small, that is as long as we are within the central hump.

Since we are primarily concerned with randomly populated lattices, we have not attempted to formulate a systematic correction scheme which would allow a more rigorous treatment of the filled lattice.

We now discuss several points related to our present calculation.

D. Moment Theory

As a by-product of our calculation, we can clarify several points regarding moment theory. We shall discuss the following: (1) general expressions for all the moments, (2) the implications regarding the line shape in the limit of vanishing concentrations, (3) the implications regarding the validity of the moment approach to the line shape problem, (4) the existence of odd moments.

(1) To obtain general expressions for all the moments, we use the well-known theorem[6,7] that, if

$$I(\omega)=\int_{-\infty}^{\infty} e^{-i\omega\rho}F(\rho)d\rho \tag{44}$$

then

$$\langle\omega^n\rangle=\partial^n F/\partial(i\rho)^n. \tag{45}$$

In our case

$$F=e^{-nV'(\rho)}. \tag{46}$$

From (17), $V'(0)=0$ and $F(0)=1$. Taking the derivatives is trivial. We list the first few moments, indicating successive derivatives of V' by subscripts to facilitate notation. The derivatives are to be understood with respect to $i\rho$ and evaluated at $\rho=0$.

$$\langle\omega^1\rangle=-nV_1', \tag{47a}$$

$$\langle\omega^2\rangle=-nV_2'+n^2(V_1)^2, \tag{47b}$$

$$\langle\omega^3\rangle=-nV_3'+3n^2V_1'V_2'+n^3(V_1')^3, \tag{47c}$$

$$\langle\omega^4\rangle=-nV_4'+n^2[3(V_2')^2+4V_1'V_3'] -6n^3(V_1')^2V_2'+n^4(V_1')^4. \tag{47d}$$

If we write V' in a notationally simplified form, using s as an over-all index, then

$$V'=\sum_s g_s(1-e^{i\omega_s\rho}) \tag{48}$$

and the derivatives of V', again evaluated at $\rho=0$, are

$$V_0'=0, \tag{49a}$$

$$V_1'=-\sum g_s\omega_s, \tag{49b}$$

$$V_2'=-\sum g_s\omega_s^2, \tag{49c}$$

$$V_n'=-\sum g_s\omega_s^n. \tag{49d}$$

Unlike the moments obtained elsewhere[10,21,24,27] our moments contain terms depending on odd derivatives of the time function, since we do not exclude asymmetric line shapes. On the other hand, some of the three and higher multiparticle terms are missing from our moments. In the language of Bersohn and Das, we sum all 2-particle diagrams but we sum n-particle diagrams only if they can be represented as linked 2-particle diagrams, linked by the same particle.

By making our transition probabilities g temperature-dependent, we arrive substantially at the temperature-dependent moments discussed by McMillan and Opechowski.[20] We write V' from (29) in the schematic form

$$V'=\sum_{\mu\gamma}\sum_{ij} g_{ij}V_{\mu\nu ij}/\sum_{\mu\gamma}\sum_{ij} g_{\mu\nu ij}, \tag{50}$$

[26] P. W. Anderson, Bull. Am. Phys. Soc. **2**, 345 (1957).

[27] R. Bersohn and T. P. Das, Phys. Rev. **130**, 98 (1963).

where the Greek indices represent the summation over lattice points, the Latin indices the summation over pair transitions. The derivatives of the $V_{\mu\nu ij}$ are similar to the ones given in (49), but without the summation that appears there. The g's are, explicitly,

$$g_{\mu\nu ij}=|\langle\mu k|s_x|\nu j\rangle|^2(e^{-E_{\mu k}/kT}-e^{-E_{\nu j}/kT}). \quad (51)$$

If we insert these expressions into the moment formulas (47), then the first term of each formula corresponds exactly to the formulas given by McMillan and Opechowski. The reason these authors obtain only the first term is that they implicitly define concentration-independent moments at the outset.

(2) We notice that in the limit of vanishing concentrations the quantities $\langle\omega^m\rangle$ are all linear in the concentration. This means that the quantities $\langle\omega^m\rangle^{1/m}$ have the property that, for $N>M$, the ratio $\langle\omega^N\rangle^{1/N}/\langle\omega^M\rangle^{1/M}$ always tends to infinity as the concentration tends to zero. This means that all moments, beginning with the second, diverge. This immediately precludes the possibility of a finite cutoff for the line shape as well as the possibility of any sort of exponential falloff in the wings, at vanishing concentrations. We observe that this result is completely independent of the specific interaction mechanism or of the specific physical details of the system.

(3) We also notice that moments are essentially the Maclaurin coefficients of the Fourier transform of the line shape. It is in this sense that a knowledge of the moments implies a knowledge of the line shape. To obtain the line shape at the origin, we need to know the behavior of the transform to infinity. This information is not in general accessible through a Maclaurin series, which is an expansion about zero.

Some very plausible and physically common line shapes have Fourier transforms which do not possess convergent expansions about the origin or whose Maclaurin series does not exist at all. For example, the transform of a Lorentz line has a cusp at the origin—the Maclaurin coefficients of F (and the moments of I) all diverge. More generally, if $I=1/P$, where P is a polynomial of degree N, then the moments of I and the Maclaurin coefficients of F will diverge, beginning with the Nth. From our remarks in (2) above, at low concentrations F tends to a singular function with a discontinuous first derivative at the origin. In the limit of vanishing concentrations, a moment expansion does not exist.

(4) We observe that the vanishing of the odd moments is not a necessary consequence of the general theory. Equation (49) shows that the odd moments vanish if for every ω_s there exists a partner of the same magnitude but of opposite sign, and associated with the same transition probability g_s. Consider a pure, unperturbed Zeeman multiplet; the states are symmetrical in m and all the transition frequencies are equal. We now consider the first-order effect of a perturbation. If the perturbation is described by an even-order tensor, it will shift the positive and negative states of the same $|m|$ the same way, and consequently will displace the transitions symmetrically. The condition for the vanishing of odd moments is then fulfilled, if we look at the entire spectrum. This does not mean, however, that it is fulfilled for each component line in the spectrum separately. For the individual lines of a multiplet with "zero-field" splitting, odd moments are in general to be expected.

E. Cross Relaxation

With slight revision of our present method, we can formulate a cross-relaxation theory. In other words, we could take into account the fact that the off-diagonal perturbations actually couple transitions of different ω_0. Following Bloembergen *et al.*[28] we could treat the off-diagonal elements as time-dependent perturbations. The off-diagonal elements would appear in place of $S_x(t)$ in our development. The expression (40) would then become

$$\sum_\mu w_\mu \sum_{NM} e^{i\omega_{NM}\rho} \sum_{kj} e^{i\omega'_{\mu,NM,kj}} |\mathcal{K}_{\mu,NM,kj}|^2. \quad (52)$$

Here, NM labels the manifold of states with $E_{0N}-E_{0M}=\hbar\omega_{NM}$, and kj, as before, labels the individual states within such a manifold. $\mathcal{K}_{NM,kj}$ is the complete off-diagonal element connecting $\mathcal{K}_{MM,jj}$ and $\mathcal{K}_{NN,kk}$. For dipole interaction, $|\mathcal{K}_{NM,kj}|^2$ will now contain terms depending on coordinates, such as $\sin^2\theta\cos^2\theta/r^6$ and $\sin^4\theta/r^6$. The cross-relaxation formalism developed by Grant[29] is essentially based on this approach.

F. Exchange

The short range of exchange is handled in moment calculations[14] by terminating the J sum at the nearest neighbor. For the purpose of defining the r dependence of J, it obviously makes no difference whether one puts a Dirichlet factor into a weight function or into J itself. When J is large compared to the transition frequency, however, it is unrealistic to assume that the zeroth-order energy levels and transition probabilities are still given by the uncoupled representation. Only when all transitions are degenerate, and if one desires only the second moment, is the representation immaterial,[10] but when one is not dealing with a pure Zeeman multiplet, the appropriate projection of operators and truncation of the Hamiltonian will be profoundly affected. This is especially true of moments, which depend heavily on near neighbors.

The effect of exchange on the zeroeth-order energy structure also raises similar misgivings about statistical two-parameters theories,[5,6] in which the dipole "width" and the exchange "width" are described by independent

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

[29] W. J. C. Grant, Phys. Rev. **134**, A1554 (1964); **134**, A1565 (1964); **134**, A1574 (1964).

and unique numbers, the dipole width usually being derived from a second moment. The second moment depends on J because of the altered energy structure, and the averaged effect of exchange is difficult to relate directly to the J appearing in the Hamiltonian, since the magnitude of the interaction, its range, and all possible variations of its effect on different transitions, are necessarily lumped into one parameter. Our use of the appropriate representation, over the appropriate range, for the pair Hamiltonian, obviates these difficulties.

IV. MAGNETIC DIPOLE INTERACTION

Our next task is to evaluate the integral for $I(\omega)$, given in Eq. (30), and consequently also the integral for V' contained in (29). We shall first discuss some approximations; next we derive an explicit solution for the V' integral; finally we point out some results obtainable from this solution without detailed numerical calculation.

A. Approximations

(1) Perhaps the nearest lying prescription for obtaining the line shape would be to use its moments, which we have already formally obtained. One of our chief aims, however, is to extricate ourselves from questions of convergence and uniqueness which beset moment expansions. Besides, from a practical point of view, the numerical calculation of higher moments involves computationally unmanageable lattice sums.

(2) We consider the expansion of V' in powers of $i\rho$. We might hope in this way to Fourier transform each factor separately and then convolute. The first few factors are as follows:

$$e^{-nV'}=e^{a_0}e^{a_1 i\rho}e^{-a_2\rho^2}e^{-a_3 i\rho^3}e^{a_4\rho^4}, \tag{53}$$

where the a's are $-V_n'/n!$, with V_n' the nth derivative of V' evaluated at $\rho=0$. We notice from (49), that $a_0=0$, and the even a's are all positive. The first factor gives $\delta(0)$, and can be interpreted as determining an amplitude scale factor. The next gives $\delta(\omega-a_1)$, or the position of the center frequency. The next gives a Gaussian of deviation $(2a_2)^{1/2}$, which invites interpretation as a half-width. The next term gives a Bessel function:

$$\begin{aligned} B&=\pi\alpha^{-2/3}x^{1/3}[J_{1/3}(x)+J_{-1/3}(x)], && \omega>0\\ &=\sqrt{3}\alpha^{-2/3}x^{1/3}K_{1/3}(x), && \omega<0 \end{aligned} \tag{54}$$

where $J_{\pm 1/3}$ and $K_{1/3}$ are Bessel functions (see Jahnke and Emde[30]), $\alpha=(6.75a_3)^{1/2}$ and $x=|\omega^{3/2}|/\alpha$. The asymptotic forms for these functions are

$$B\approx\left(\frac{6\pi}{\alpha}\right)^{1/2}\omega^{-1/4}\cos\left(\frac{\omega^{3/2}}{\alpha}-\frac{\pi}{4}\right), \qquad \omega\gg\alpha \tag{55a}$$

$$B\approx(3\pi/2\alpha)^{1/2}\omega^{-1/4}\exp(-|\omega^{3/2}|/\alpha), \quad \omega\ll-\alpha. \tag{55b}$$

These expressions can be interpreted as containing information about the asymmetry of the line. To extract anything more quantitative would require very detailed analysis, as we are pitting an extremely rapid wiggle on one side against a rapidly decaying exponential on the other, and it is by no means obvious which one will kill the convolution integral faster.

The next term gives a divergent result. This implies no physical divergence, of course, but only that we are pushing the technique too far. We have, after all, not proven whether and under what circumstances the expansion of the exponential and convolution of the results is a convergent process. The failure of the technique as $\rho\to\infty$ clearly indicates its failure for $\omega\approx 0$. A finite cutoff for ρ, or in other words, the behavior of the ρ integral near the origin, still gives a legitimate approximation to the behavior of $I(\omega)$ in the far wings.

(3) The V' integral in Eq. (29) has been solved explicitly by making certain limiting assumptions. We consider the integral

$$V_j(\rho)=\int_{r_0}^{\infty}\{1-\exp[i\rho\omega(\mathbf{r},q_j)]\}d\mathbf{r}. \tag{56}$$

For dipole interaction, $\omega(\mathbf{r},q_j)$ typically has the form

$$\omega(\mathbf{r},q_j)=q_j\frac{g^2\beta^2}{\hbar}\frac{(3\cos^2\theta-1)}{r^3}. \tag{57}$$

Anderson has calculated this integral,[4,31] using the following assumptions: (1) The unperturbed system is a Kramers doublet. (2) The perturbations with q and $-q$ occur with equal probability. (3) $r_0=0$. The first assumption involves no essential limitation. The second one is, of course, the condition for the vanishing of odd moments, or for the symmetry of the line, which we discussed in the previous section. It is not applicable in systems where the transitions are not all equal. Its effect is to eliminate the imaginary part of V', with very great calculational simplification. The third assumption disregards not only the discreteness of the lattice, but the existence of a limiting nearest-neighbor distance. The effect will be to exaggerate the wings of the line somewhat. Anderson's result is a Lorentzian with half-width

$$\omega_{1/2}=\frac{n}{v}\frac{8\pi^2}{9\sqrt{3}}\frac{qg^2\beta^2}{\hbar}. \tag{58}$$

When assumption (3) is removed, but the angular dependence of the dipole interaction is disregarded instead, Anderson derives an expression for the center intensity only, in the limit of vanishing concentration:

$$\lim_{n\to 0} I(0)=I_0[1+(n/v)]. \tag{59}$$

We shall make none of these approximations, but we shall use Anderson's results as a check on the asymptotic behavior of our own results.

[30] E. Jahnke and F. Emde, *Tables of Functions* (Dover Publications Inc., New York, 1945), reprint, Chap. 8.

[31] P. W. Anderson (private communication).

B. Exact Solution

The exact evaluation of $V_j(\rho)$, as defined in Eqs. (56) and (57), is sketched in the Appendix. A more detailed calculation may be found in Ref. 23. For both analytical and computational purposes it is convenient to represent $V_j(\rho)$ in ascending series and asymptotic series. The mathematical steps reducing Eq. (A20) of the Appendix to such expansions are again to be found in Ref. 23. We use the notation

$$x_0=1/r_0^3, \tag{60}$$

$$c=(q_j x_0 g^2\beta^2/\hbar)\rho. \tag{61}$$

Then the results are:

Ascending series

$$\mathrm{Re}V_j=\frac{8\pi}{9x_0}[\tfrac{1}{2}\cos 2c-\tfrac{3}{2}+\cos c\sum_{\substack{m=0\\ m\text{ even}}}^{\infty}a_m c^m+\sin c\sum_{\substack{m=1\\ m\text{ odd}}}^{\infty}a_m c^m], \tag{62a}$$

$$\mathrm{Im}V_j=\frac{8\pi}{9x_0}[c+\tfrac{1}{2}\sin 2c+\cos c\sum_{\substack{m=1\\ m\text{ odd}}}^{\infty}a_m c^m-\sin c\sum_{\substack{m=0\\ m\text{ even}}}^{\infty}a_m c^m]. \tag{62b}$$

$$a_m=\frac{1}{m!}\left(3^m-m\sum_{p=0}^{m}\frac{3^p}{p+\frac{1}{2}}\right); \tag{62c}$$

Asymptotic series

$$\mathrm{Re}V_j=\frac{8\pi}{9x_0}\left\{\frac{\pi k}{\sqrt{3}}-\tfrac{3}{2}-\left(\frac{\pi}{3}\right)^{1/2}k^{1/2}+\left[\cos\left(k+\frac{\pi}{4}\right)\sum_{\substack{m=2\\ m\text{ even}}}^{\infty}b_m k^{-m}+\sin\left(k+\frac{\pi}{4}\right)\sum_{\substack{m=3\\ m\text{ odd}}}^{\infty}b_m k^{-m}\right]\right.$$

$$\left.+\cos 2k\sum_{\substack{m=2\\ m\text{ even}}}^{\infty}\beta_m(3k)^{-m}-\sin 2k\sum_{\substack{m=3\\ m\text{ odd}}}^{\infty}\beta_m(3k)^{-m}\right\}, \tag{63a}$$

$$\mathrm{Im}V_j=\pm\frac{8\pi}{9x_0}\left\{-\left(\frac{\pi}{3}\right)^{1/2}k^{1/2}\left[\cos\left(k+\frac{\pi}{4}\right)\sum_{\substack{m=3\\ m\text{ odd}}}^{\infty}b_m k^{-m}-\sin\left(k+\frac{\pi}{4}\right)\sum_{\substack{m=2\\ m\text{ even}}}^{\infty}b_m k^{-m}\right\}\right.$$

$$\left.+\cos 2k\sum_{\substack{m=3\\ m\text{ odd}}}^{\infty}\beta_m(3k)^{-m}+\sin 2k\sum_{\substack{m=2\\ m\text{ even}}}^{\infty}\beta_m(3k)^{-m}+\left(1+\frac{1}{\sqrt{3}}\ln\frac{\sqrt{3}-1}{\sqrt{3}+1}\right)k\right\}. \tag{63b}$$

Here, the upper sign is for $c>0$, the lower sign for $c<0$,

$$b_m=(\tfrac{1}{2})_m \tag{63c}$$

$$\beta_m=\tfrac{1}{2}(\tfrac{1}{2})_{m-1}-\sum_{p=0}^{\infty}3^{-p-1}(p+\tfrac{1}{2})_m. \tag{63d}$$

In (63c) and (63d) the notation $(a)_n$ means $(a)_n=a(a+1)(a+2)\cdots(a+n-1)$, with $(a)_0=1$, and in (63a) and (63b), $k=|c|$.

By further expanding the trigonometric functions in Eqs. (62), and forming Cauchy products, we obtain a pure Maclaurin series for V_j:

$$V_j=\frac{8\pi}{9x_0}\sum_{m=2}^{\infty}\left[\frac{2^{m-1}}{m!}+\frac{1}{m!}\sum_{n=0}^{m}(-)^{m-n}\binom{m}{n}\times\left(3^n-n\sum_{p=0}^{n}\frac{3^p}{p+\frac{1}{2}}\right)\right](ic)^m, \tag{64}$$

where $\binom{m}{n}$ are binomial coefficients.

We recall that V' defined in (29) is essentially

$$V'=\text{lattice sum}+(\sum_j g_j V_j/v\sum_j g_j) \tag{65}$$

and $I(\omega)$ is the Fourier transform of $e^{-nV'}$. Further steps in the detailed calculation of the dipolar line shape require detailed knowledge of the q's and g's for particular systems and the numerical inversion of a one-dimensional Fourier transform.

We can, however, directly obtain some information about the behavior of $I(\omega)$.

We can write explicit closed formulas for all the moments. The derivatives V_n' which appear in Eqs. (47) are very simply related to the coefficients of the Maclaurin series (64). We rewrite (64) in the following

form:

$$V_j=\frac{8\pi}{9x_0}\sum_m a_m\left(q_j\frac{g^2\beta^2x_0}{\hbar}\right)^m(i\rho)^m, \tag{66}$$

where a_m is the expression in square brackets in (64). Then by (65) or (29),

$$V_m'=\frac{8\pi}{9x_0v}m!a_m\left(\frac{g^2\beta^2x_0}{\hbar}\right)^m\sum_j g_jq_j{}^m/\sum_j g_j. \tag{67}$$

When these V_m' are inserted into expressions (47), any number of moments can be calculated readily. For instance, for $m=2$, we obtain $a_2=-3/5$ and

$$\langle\omega^2\rangle=n\frac{16\pi x_0}{15v}\frac{g^4\beta^4}{\hbar^2}\sum_j g_jq_j{}^2/\sum_j g_j. \tag{68}$$

We can also determine the behavior of $I(\omega)$ under various limiting conditions by examining the leading terms in our series expansions.

The leading term in the ascending series (64) is proportional to $-\rho^2$. So for small c, $F(\rho)$, the Fourier transform of $I(\omega)$, looks like a Gaussian. The leading term of the asymptotic series (63) is proportional to $-|\rho|$, so that for large c, $F(\rho)$ behaves like the Fourier transform of a Lorentzian. Since the asymptotic behavior of a function and the behavior of its Fourier transform near the origin mutually determine one another, $I(\omega)$ must be asymptotically Gaussian, but Lorentzian near the origin. This result is consonant with the work of Kubo and Tomita.[7,8]

The coefficient in front of the Maclaurin series is proportional to n/x_0. If n/x_0 is large, $\exp(-nV')$ will become small fast; in other words, most of the area of the transform comes from the region where it behaves to a first approximation like a Gaussian. Consequently, the shape will tend to Gaussian for large concentrations and small x_0. If the reverse conditions hold, the exponential falls off slowly, and most of the transform comes from the region where the asymptotic series is valid. We then obtain a predominantly Lorentzian shape.

For the Lorentzian limit, keeping only the leading terms in (63a), we write

$$I(\omega)=n\sum_j g_j\int_{-\infty}^{\infty}e^{-i\omega\rho}e^{-A|\rho|n}e^{Bn}$$
$$=2n\sum_j g_je^{Bn}An/[(An)^2+\omega^2], \tag{69}$$

where we have prefixed the factor $n\sum_j g_j$ because our machinery normalizes all lines to the same area, and where

$$A=\frac{1}{v}\frac{8\pi^2}{9\sqrt{3}}\frac{\sum g_jq_j}{\sum g_j}\frac{g^2\beta^2}{\hbar} \tag{70}$$

$$B=\frac{4\pi}{3x_0}\frac{1}{v}. \tag{71}$$

If we expand the exponential to first order in n, we obtain

$$I(0)\approx(2\sum_j g_j/A)(1+Bn). \tag{72}$$

In the limit of vanishing concentrations, we obtain a Lorentzian with a half-width An. If there is one pair of q's, as is assumed by Anderson, we are in exact agreement with his result (58). The expression (72) for the center intensity differs from Anderson's result (59) by the factor B. This discrepancy lies partly in the fact that Anderson omitted the angular dependence in his derivation, partly in his choosing x_0 so as to make B equal to unity. Thus, under the same limiting assumptions, our results check with Anderson's.

We notice that the half-width is independent of x_0 in this approximation.

In the Gaussian limit, valid for high concentration, $I(\omega)$ is characterized by its second moment, which we have explicitly calculated in (68). The width is proportional to the square-root of this moment, which implies a dependence on $n^{1/2}$ and on $r_0^{-3/2}$. The $n^{1/2}$ dependence is, of course, a familiar result in this limiting situation.

It is possible, in a rough and rather arbitrary sense, to define a concentration at which we cross over from the Gaussian to the Lorentzian shape. We demarcate the borderline between these two extreme approximations by the requirement that for $c=1$, the Fourier transform, $\exp(-nV')$, should have $1/e$ of its value for $c=0$. The value of the concentration so determined depends, of course, on the details of the lattice structure and of the transitions we are considering. As a typical example we might consider the Cr-Cr interactions in ruby. If we use $x_0=0.048988$ Å^{-3}, which corresponds to the nearest-neighbor distance, the crossover concentration is 24% for the $(\frac{1}{2},-\frac{1}{2})$ transition, 29% for the $(\frac{3}{2},\frac{1}{2})$ transition. If exchange is large as far as the 11th neighbor shell, then for the $(\frac{3}{2},\frac{1}{2})$ transition a value of x_0 one-tenth as large would not be unrealistic. The corresponding concentration would be 3%. Since commonly used concentrations range from 0.1% downwards, and concentrations much greater than 1% are not physically attainable, it is clear that, in this context, we are well in the Lorentzian region. On the other hand, if we consider interaction with aluminum nuclei, whose concentration is practically 100%, we are well in the Gaussian region.

It is interesting to test our formulation in the most unfavorable case, that of a filled lattice with a well-defined group of nearest neighbors. The fluorine resonance in CaF_2 is a classical example of such a situation. When the field is in the [100] direction, the dipole interaction is strongly dominated by the six nearest neighbors. The Lowe and Norberg[24] calculation yields a time function with a half-width of 12 μsec and whose tail shows a series of damped beats. The corresponding resonance line is a smoothed square shape with a cutoff at about 6 G. Our method yields a time function with a

half-width of 11 μsec. The function is nearly Gaussian, with insignificant modulation in the wings. The corresponding resonance line is a Gaussian with half-width 5 G. The details are wrong, but even in this case the general picture turns out to be correct.

SUMMARY

The statistical theory of spin-spin interactions which we have presented combines physical generality with mathematical simplicity. Its mathematical simplicity stems principally from three factors: (1) By working from the beginning with a pair concept instead of a single-particle concept, we bypass entirely the notational encumbrance of projection operators, clarify the definition of the relevant operators, and considerably facilitate the computation of their matrix elements. (2) We eliminate the time dependence at a very early stage; in fact we can bypass the time-dependent description altogether. (3) We avoid the machinery of expansion, approximation, and convolution by finding a direct solution to the basic integral. As a consequence of the mathematical tractability of the formalism, we can include explicitly the physical details of the problem by means of a suitable weight function, and still obtain a complete solution.

In a subsequent paper, we shall make detailed application of the present results to the paramagnetic resonances of Cr in ruby.

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APPENDIX: EVALUATION OF THE BASIC INTEGRAL

We sketch the steps in the evaluation of the integral

$$V_j(\rho)=2\pi\int_{-1}^{1}d\cos\theta\int_{r_0}^{\infty}drr^2 \times\left\{1-\exp\left[\frac{i\rho q_j g^2\beta^2}{\hbar}\frac{(3\cos^2\theta-1)}{r^3}\right]\right\}. \quad \text{(A1)}$$

We set

$$a=\rho(q_j g^2\beta^2/\hbar)(3\cos^2\theta-1), \quad \text{(A2)}$$

$$x=1/r^3, \quad \text{(A3)}$$

and perform a partial integration to obtain

$$V_j=\frac{2\pi}{3}\int_{-1}^{1}d\cos\theta\left[\frac{e^{iax_0}}{x_0}-\frac{1}{x_0}-ia-ia\int_0^{x_0}\frac{e^{iax}}{x}dx\right]. \quad \text{(A4)}$$

The first term in (A4), after some transformations, yields

$$\frac{2\pi}{3\sqrt{3}x_0}(-ic)^{-1/2}e^{-ic}\gamma(\tfrac{1}{2},-3ic), \quad \text{(A5)}$$

where $c=q_j x_0 g^2\beta^2\rho/\hbar$, and $x_0=r_0^{-3}$ [Eqs. (60) and (61)], and γ is the incomplete gamma function.[32] The second and third terms trivially yield $-4\pi/3x_0$ and 0. The x integral in the fourth term diverges at $x=0$. If we replace the lower limit by t, we obtain for this term

$$\frac{4\pi}{3}\int_0^1 d\cos\theta[a\mathrm{Si}(ax_0)-ia\mathrm{Ci}(ax_0)+ia\ln(ax_0) +ia(\beta-\ln x_0)+ia\ln t]. \quad \text{(A6)}$$

The functions Si and Ci are the sine and cosine integral functions[30,32] and β in Euler's constant.

We observe that the logarithmic divergence, as $t\to 0$, is independent of θ. If the integration over θ were continuous, instead of being an approximation to a lattice sum, then $\int_{-1}^{1}d\cos\theta(3\cos^2\theta-1)\ln t$ would still remain zero even as we let t approach zero. Of course $t\to 0$, corresponds to $r\to\infty$. Analysis shows that the difference between the integral and the discrete sum is proportional to $t^4\ln t$, a quantity which vanishes as $t\to 0$. The sum over θ "becomes continuous" faster than $\ln t$ becomes infinite; that is, the summation over angles does in fact kill the radial divergence. Physically, an energy perturbation that falls off as r^{-3}, or slower, gives a diverging effect as r increases. We are spared a catastrophe, however, because the angular dependence of the perturbation produces sufficient cancellation.

The functions $\mathrm{Si}(z)$ and $[\ln z-\mathrm{Ci}(z)]$ are entire, so that there is no intrinsic ambiguity in (A6). To be able to continue, however, we must handle $\ln z$ and $\mathrm{Ci}(z)$ separately. Each function has a branch point at the origin, and care is needed to treat both singularities in an identical manner.

After a few more changes of variable, interspersed with partial integrations, (A6) is brought into the form

$$\frac{4\pi i}{9(3c)^{1/2}x_0}\left[e^{-ic}\int_0^{3c}\left(1-\frac{2c}{w-c}\right)w^{1/2}e^{iw}dw -\int_0^{3c}\left(1-\frac{2c}{w-c}\right)w^{1/2}dw\right], \quad \text{(A7)}$$

where $w=3c\cos^2\theta$. Each integral has a pole at $w=c$ and a branch point at $w=0$. To guarantee equal treatment of both integrals we evaluate

$$\int_0^{3c}\left(1-\frac{2c}{w-c}\right)w^{1/2}e^{ixw}dw \quad \text{(A8)}$$

and then specialize to $x=1$ and $x=0$. With $u=xw$ and $b=xc$, (A8) becomes

$$x^{-3/2}\int_0^{3b}\left(1-\frac{2b}{u-b}\right)u^{1/2}e^{iu}du. \quad \text{(A9)}$$

[32] *Higher Transcendental Functions* (Bateman Manuscript Project) edited by A. Erdely, F. Oberhettinger, W. Magnus, and F. G. Tricomi (McGraw-Hill Book Company, Inc., New York, 1954), Vol. 2.

After a little maneuvering, the first term in (A9) gives

$$(i/x)^{3/2}\gamma(\tfrac{3}{2}, -3ib). \tag{A10}$$

For $x=1$ we use the recursion relation for γ functions[32] to obtain

$$\tfrac{1}{2}i^{3/2}\gamma(\tfrac{1}{2}, -3ic)-i(3c)^{1/2}e^{3ic}. \tag{A11}$$

For $x=0$, the expansion

$$\gamma(a,x)=\sum_{n=0}^{\infty}\frac{(-)^n x^{a+n}}{n!(a+n)} \tag{A12}$$

reduces (A10) to

$$\tfrac{2}{3}(3c)^{3/2}. \tag{A13}$$

The second term in (A9) is handled by means of the following scheme:

$$\int_0^{3b}\frac{u^{1/2}}{u-b}e^{iu}du=\int_0^{\infty}\frac{u^{1/2}}{u-b}e^{iu}du-\int_{3b}^{\infty}\frac{u^{1/2}}{u-b}e^{iu}du. \tag{A14}$$

The integral from 0 to ∞ is evaluated as a contour integral in the complex plane, with real axis u and imaginary axis v. For $b>0$, we choose a counterclockwise path around the first quadrant, indenting the contour into the first quadrant at the origin and at b. The loop integral vanishes by Cauchy's integral theorem, and we obtain

$$\int_0^{\infty}\frac{u^{1/2}}{u-b}e^{iu}du=\pi ib^{1/2}e^{ib}+i^{1/2}\int_0^{\infty}\frac{v^{1/2}e^{-v}}{v+ib}dv. \tag{A15}$$

The v integral is a representation of the incomplete gamma function, and eventually one obtains

$$\int_0^{\infty}\frac{u^{1/2}}{u-b}e^{iu}du=\pi ib^{1/2}e^{ib}+(\pi i)^{1/2}-ie^{ib}(\pi b)^{1/2}\Gamma(\tfrac{1}{2},ib). \tag{A16}$$

The integral from $3b$ to ∞ in (A14) is evaluated by expanding $1/(u-b)$ in descending powers of u and substituting $t=(u/3b)-1$. The nth term of the series in t then becomes an integral representation of the confluent hypergeometric function,[32] $\psi(1, \frac{3}{2}-n, -3ib)$. This function, in turn, can be written as an incomplete gamma function, consistent with our previous notation. One finally obtains

$$\int_{3b}^{\infty}\frac{u^{1/2}e^{iu}}{u-b}du=\sum_{n=0}^{\infty}(-i)^{n-1/2}b^n\Gamma(-n+\tfrac{1}{2}, -3ib). \tag{A17}$$

Specializing to $x=1$ [see Eqs. (A8) and (A9)] merely involves replacing b by c in (A16) and (A17), and x by 1. Specializing to $x=0$ again involves series expansions for incomplete gamma functions. The second term in (A9) then becomes

$$\lim_{x\to 0}-\frac{2b}{x^{3/2}}\int_0^{3b}\frac{u^{1/2}e^{iu}}{u-b}du=2c^{3/2}\ln\frac{\sqrt{3}-1}{\sqrt{3}+1}+4\sqrt{3}c^{3/2}. \tag{A18}$$

In our contour integration, as well as in certain implied limiting procedures, we have considered $c>0$. The result for $c<0$ is the complex conjugate of the result for $c>0$. We set

$$k=|c|. \tag{A19}$$

If $c<0$, then $ik\to -ik$, but k remains unchanged.

Finally, we collect the integrated terms to obtain

$$\begin{aligned}V_j(\rho)=\frac{8\pi}{9\sqrt{3}x_0}\Big[&\pi k+\Big(\sqrt{3}+\ln\frac{\sqrt{3}-1}{\sqrt{3}+1}\Big)ic\\&-\pi^{1/2}k\Gamma(\tfrac{1}{2},ic)+(-i\pi c)^{1/2}e^{-ic}\\&+\tfrac{1}{2}e^{-ic}(-ic)^{-1/2}\gamma(\tfrac{1}{2}, -3ic)+(\sqrt{3}/2)(e^{2ic}-3)\\&-e^{-ic}\sum_{n=0}^{\infty}(-ic)^{n+1/2}\Gamma(-n+\tfrac{1}{2}, -3ic)\Big].\end{aligned} \tag{A20}$$