

Microscopic View of Exchange Narrowing*

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In this paper two methods are presented for calculating the spin-pair correlation functions for an exchange-narrowed system of spins. These methods are applied to an isotropic Heisenberg paramagnet with a relatively small anisotropic interaction. The first method consists of a microscopic derivation of the spin correlation function itself. By neglecting successively higher correlation functions, a usable equation is obtained. In the second method, sum-rule moment expansions are used to determine the frequency-dependent linewidth rather than the spin correlation function itself. Electron-paramagnetic-resonance line shapes are evaluated using these techniques and are compared with experimental data and with other theoretical work.

I. INTRODUCTION

Although the fundamental physics of exchange narrowing has been understood for some time,¹⁻³ to our knowledge there has been no truly microscopic derivation of equations describing the process. Calculations of exchange-narrowed linewidths are usually made by fitting a profile $I(\omega)$ to various moments of I . Since the line shape is determined only if $I(\omega)$ is fitted to all moments, it is customary to assume a line shape whose parameters are characterized by the moments available.⁴ It turns out that one must assume the "right" form for $I(\omega)$ in order to obtain an answer that agrees well with experiments. Of course, in practice one uses the additional input that the experimentally observed line is essentially Lorentzian in character. It is the purpose of this paper to derive equations describing exchange narrowing from microscopic equations of motion without assuming a functional form and to study a sum-rule moment fit for the spin correlation functions which is somewhat different than the method usually employed.

In the remainder of this section the model and some properties of the spin correlation functions used are discussed. The equations used to describe exchange narrowing are derived in Sec. II. In the first method microscopic equations of motion for the spin operators are used to construct an expression for the frequency-dependent linewidth and thus the spin correlation function. The basic approximation used is a factorization of a four-spin correlation function. The second method employs an exact spectral representation of the spin correlation function to generate approximations to the linewidth in terms of a moment sum-rule method. The methods are compared with other methods and with experiments in Sec. III.

The full model used in this paper is an anisotropic Heisenberg paramagnet in a uniform external field. The Hamiltonian is

$$H = - \sum_{\alpha} \hbar h_0 S_z(\alpha, t) - \frac{1}{2} \sum_{i,j,\alpha,\alpha'} S_i(\alpha, t) J_{ij}(\alpha, \alpha') S_j(\alpha', t), \quad (1)$$

where $S(\alpha, t)$ is the spin operator at the site α which evolves in time t according to the Heisenberg representation. Latin subscripts refer to Cartesian directions and $h_0 = \gamma_e H_0$, where H_0 is a uniform applied magnetic field which defines the z direction. The energy $J_{ij}(\alpha, \alpha')$ describes the interaction between spins at different sites α and α' . It is convenient to break J_{ij} into an isotropic and nonisotropic part:

$$\begin{aligned} J_{ij}(\alpha, \alpha') &= J_{ij}(\alpha', \alpha) = J_{ji}(\alpha', \alpha) \\ &= J_0(\alpha, \alpha') \delta_{ij} + I_{ij}(\alpha, \alpha'), \\ J_0(\alpha, \alpha') &= \frac{1}{3} \sum_i J_{ii}(\alpha, \alpha'), \quad J_{ii}(\alpha, \alpha) = 0 \end{aligned} \quad (2)$$

where I_{ij} (an example of which might be the dipolar interaction) is assumed to be much smaller than J_0 .

The properties of the system described by the above Hamiltonian are conveniently discussed in terms of the dynamic response functions which express the linear response of the system to an additional weak field.⁵ To first order

$$\delta \langle S_i(\alpha, t) \rangle = \sum_{\alpha', j} \int_{-\infty}^{\infty} dt' \chi_{ij}(\alpha t; \alpha', t') \delta H_j(\alpha' t'), \quad (3)$$

$$\chi_{ij}(\alpha t; \alpha' t') = (i/\hbar) \eta(t-t') \langle [S_i(\alpha, t), S_j(\alpha', t')] \rangle,$$

where $\eta(t)$ is the step function and the angular brackets $\langle X \rangle$ denote the average value of X in the canonical ensemble. The quantity $\delta \langle S \rangle$ is the spin induced by the additional weak field δH . Since the system is translationally invariant in time and has the invariance of the crystal lattice under translations through a lattice vector, χ can be transformed in space and time according to the prescription

$$\begin{aligned} \chi_{ij}(\alpha t; \alpha' t') &= \frac{1}{N} \sum_{\mathbf{q}} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} e^{i\mathbf{q} \cdot (\alpha - \alpha') - i\omega(t-t')} \\ &\times \chi_{ij}(\mathbf{q}, \omega), \end{aligned} \quad (4)$$

where the summation is carried out over all wave vectors \vec{q} in the first Brillouin zone. In addition, $\chi_{ij}(\vec{q}, \omega)$ obeys the Kramers-Kronig relation

$$\chi_{ij}(\vec{q}, \omega) = \int_{-\infty}^{\infty} \frac{d\omega'}{\pi} \frac{\chi_{ij}'(\vec{q}, \omega')}{\omega - \omega' - i\epsilon}, \quad (5)$$

where ϵ is infinitesimal and positive. The spectral weight function $\chi_{ij}'(\vec{q}, \omega)$, the imaginary part of $\chi_{ij}(\vec{q}, \omega)$, gives the absorptive response and, in the limit $q \rightarrow 0$, is the quantity often measured in electron-paramagnetic-resonance (EPR) experiments.

It is convenient to introduce a spectral representation for $\chi_{ij}(\vec{q}, \omega)$ which is useful in discussing linewidths and line shapes. In the following, let the subscript ξ denote the combinations of subscripts zz , $+-$, and $-+$ where $S_{\pm} = S_x \pm iS_y$. Further, let h_{ξ} be 0, h_0 , and $-h_0$ when ξ is zz , $+-$, and $-+$, respectively. Now note that χ may be written in the following form^{5,6}:

$$z \left[1 - \frac{\chi_{\xi}(\vec{q}, 0)}{\chi_{\xi}(\vec{q}, z)} \right]^{-1} = h_{\xi} - \int_{-\infty}^{\infty} \frac{d\omega}{\pi} \frac{\Gamma_{\xi}(\vec{q}, \omega)}{\omega - z}, \quad (6)$$

since the left-hand side is an analytic function of complex z except possibly on the real axis. After a little algebra this can be put into the form

$$\begin{aligned} [\chi_{\xi}(\vec{q}, z)/\chi_{\xi}(\vec{q}, 0)] - 1 &= -z/[z - h_{\xi} - \Delta_{\xi}(\vec{q}, z)], \\ \Delta_{\xi}(\vec{q}, z) &= \int_{-\infty}^{\infty} \frac{d\omega}{\pi} \frac{\Gamma_{\xi}(\vec{q}, \omega)}{z - \omega}. \end{aligned} \quad (7)$$

To evaluate $\chi(z)$ for real ω the analytic continuation $z \rightarrow \omega + i\epsilon$ is used to obtain

$$\frac{\chi_{\xi}'(\vec{q}, \omega)}{\chi_{\xi}(\vec{q}, 0)} = \frac{\omega \Gamma_{\xi}(\vec{q}, \omega)}{[\omega - h_{\xi} - \Delta_{\xi}(\vec{q}, \omega)] + \Gamma_{\xi}^2(\vec{q}, \omega)}. \quad (8)$$

In this form it is easily seen that $\Gamma_{\xi}(\vec{q}, \omega)$ is a frequency- and wave-vector-dependent linewidth and that $\Delta_{\xi}(\vec{q}, \omega)$, its Kramers-Kronig partner, is a frequency shift or the dispersion.

II. FORMULATION

A. Microscopic Formulation

Since it is assumed that the nonisotropic part of J_{ij} is much smaller than the isotropic part, the spatially uniform ($q=0$) decay rate or linewidth may be calculated using perturbation theory where H_p , the part of the Hamiltonian containing $I_{ij}(\alpha, \alpha')$, is the perturbation. The isotropic part of the Hamiltonian does not contribute to this decay rate. The frequency-dependent transition probability from state a to state b is

$$W_{ab}(\omega) = (2\pi/\hbar) |\langle a | H_p | b \rangle|^2 \delta(E_a - E_b + \hbar\omega) \quad (9)$$

to lowest order in H_p . For reasons which will become clear later, however, the decay rate for all \vec{q} , not just $\vec{q}=0$, is also calculated, and thus H_p is replaced by H in Eq. (9).

For the decay rate $\Gamma_{\alpha\alpha}(\vec{q}, \omega)$, appropriate to $\chi_{\alpha\alpha}(\vec{q}, \omega)$, only that part of H which does not commute with $S_z(\vec{q})$ is used. The total decay rate or linewidth is obtained by averaging W over initial states, summing over final states, and dividing by 2. After expressing the δ function as a time integral and using the time development of the operators in the Heisenberg representation, it is easily seen that

$$\Gamma_{\alpha\alpha}(\vec{q}, \omega) = \frac{1}{2\hbar^2} \int_{-\infty}^{\infty} dt e^{i\omega t} \frac{\langle [S_{\alpha}(\vec{q}, t), H] [S_{\alpha}(\vec{q}, 0), H] \rangle}{\langle S_{\alpha}^2(\vec{q}) \rangle}, \quad (10)$$

where

$$S_{\alpha}(\vec{q}, t) = \sum_{\alpha} S_{\alpha}(\alpha, t) e^{-i\vec{q} \cdot \alpha}. \quad (11)$$

The thermal average is over states of H (a Brillouin-Wigner-type perturbation theory) and

$$\begin{aligned} [S_{\alpha}(\vec{q}, t), H] &= \frac{1}{2} \sum_{\alpha, \alpha', l} [J_{+l}(\alpha, \alpha') S_{-}(\alpha, t) S_l(\alpha'; t) \\ &\quad - J_{-l}(\alpha, \alpha') S_{+}(\alpha, t) S_l(\alpha'; t)] e^{-i\vec{q} \cdot \alpha}. \end{aligned} \quad (12)$$

In this equation, the spherical vector components of A ($A_{\pm}, A_{\pm} = A_x \pm iA_y$) are used but the sum over l refers to Cartesian components.

In order to get Eq. (10) into a useful form, some further approximations must be made. The approximation made here is to factor the four-spin correlation function into products of two-spin correlation functions. Since only correlation functions that depend on a time difference will contribute, the approximation becomes

$$\begin{aligned} \langle S_i(\alpha_1, t) S_j(\alpha_2, t) S_k(\alpha_3, 0) S_l(\alpha_4, 0) \rangle \\ = \langle S_i(\alpha_1, t) S_k(\alpha_3, 0) \rangle \langle S_j(\alpha_2, t) S_l(\alpha_4, 0) \rangle \\ + \langle S_i(\alpha_1, t) S_l(\alpha_4, 0) \rangle \langle S_j(\alpha_2, t) S_k(\alpha_3, 0) \rangle. \end{aligned} \quad (13)$$

Except for terms of order $(\beta\hbar h_0)^2$ compared to 1, this decomposition becomes exact in the limit $J \rightarrow 0$ (where $\beta = 1/kT$, the inverse temperature in energy units). These last terms are insignificant in the regime considered in this paper. Further, since it is assumed that the isotropic part of J_{ij} dominates the anisotropic part, only those correlation functions which conserve spin are appreciable, i.e., $\langle S_{+}S_{-} \rangle$, $\langle S_{-}S_{+} \rangle$, and $\langle S_z S_z \rangle$, while those which do not are negligible, i.e., $\langle S_{+}S_{+} \rangle$, $\langle S_{-}S_{-} \rangle$, and $\langle S_{+}S_z \rangle$.

The fluctuation-dissipation theorem⁵ can be used to relate the above spin correlation functions to the $\chi_{ij}(\alpha, \alpha', \omega)$ discussed in Sec. I. The prescription⁵ is

$$\begin{aligned} f_{ij}(\alpha, \alpha'; t - t') &= \frac{1}{2} \langle S_i(\alpha, t) S_j(\alpha', t') \rangle, \\ \chi_{ij}''(\alpha, \alpha', \omega) &= (1 - e^{-\beta\hbar\omega}) f_{ij}(\alpha, \alpha'; \omega) \\ &= (e^{\beta\hbar\omega} - 1) f_{ji}(\alpha', \alpha; -\omega), \end{aligned} \quad (14)$$

where f is transformed according to Eq. (4). After a considerable amount of algebra, the following equation is obtained:

$$\Gamma_{xx}(\tilde{q}, \omega) = \frac{1}{4\hbar^2 \chi_{xx}(\tilde{q}, 0) \beta N} \sum_{\tilde{q}'} \int_{-\infty}^{\infty} \frac{d\omega'}{\pi} \left\{ \frac{1}{4} [J_{xx}(\tilde{q}') + J_{yy}(\tilde{q}') - J_{xx}(\tilde{q}' - \tilde{q}) - J_{yy}(\tilde{q}' - \tilde{q})]^2 g_{+-}(\tilde{q}', \omega') g_{+-}(\tilde{q}' - \tilde{q}, \omega' - \omega) \right. \\ \left. + [J_{xx}^2(\tilde{q}') + J_{yy}^2(\tilde{q}')] g_{xx}(\tilde{q}' \omega') [g_{+-}(\tilde{q}' - \tilde{q}, \omega' - \omega) + g_{+-}(\tilde{q}' - \tilde{q}, \omega' + \omega)] + \frac{1}{4} ([J_{xx}(\tilde{q}') - J_{yy}(\tilde{q}')] \right. \\ \left. \times [J_{xx}(\tilde{q}') + J_{xx}(\tilde{q}' - \tilde{q}) - J_{yy}(\tilde{q}') - J_{yy}(\tilde{q}' - \tilde{q})] + 4J_{xy}(\tilde{q}') [J_{xy}(\tilde{q}') + J_{xy}(\tilde{q}' - \tilde{q})]] g_{+-}(\tilde{q}' \omega') \right. \\ \left. \times [g_{+-}(\tilde{q}' - \tilde{q}, -\omega - \omega') + g_{+-}(\tilde{q}' - \tilde{q}, \omega - \omega')] \right\}, \quad (15)$$

where

$$g_{ij}(\tilde{q}\omega) = \chi_{ij}'(\tilde{q}, \omega) / \omega. \quad (16)$$

The high-temperature limit, $\beta\hbar\omega \ll 1$ for all relevant frequencies, has been assumed. The exchange functions $J_{ij}(\alpha, \alpha')$ have been Fourier transformed in the same way that the spatial part of $\chi_{ij}(\alpha, \alpha'; t - t')$ was and N is the number of atoms in the crystal.

In a similar fashion, the linewidth function for $\chi_{+-}(\tilde{q}, \omega)$ is seen to be

$$\Gamma_{+-}(\tilde{q}, \omega) = \frac{1}{\hbar^2 \chi_{+-}(\tilde{q}, 0) \beta N} \sum_{\tilde{q}'} \int_{-\infty}^{\infty} \frac{d\omega'}{\pi} \left\{ [\frac{1}{2} J_{xx}(\tilde{q}') + \frac{1}{2} J_{yy}(\tilde{q}') - J_{xx}(\tilde{q}' - \tilde{q})]^2 g_{+-}(\tilde{q}' \omega') g_{xx}(\tilde{q}' - \tilde{q}, \omega - \omega') \right. \\ \left. + (J_{xx}(\tilde{q}') [J_{xx}(\tilde{q}') + J_{xx}(\tilde{q}' - \tilde{q})] + J_{yy}(\tilde{q}') [J_{yy}(\tilde{q}' - \tilde{q}) + J_{yy}(\tilde{q}' - \tilde{q})]) g_{xx}(\tilde{q}' \omega') g_{xx}(\tilde{q}' - \tilde{q}, \omega - \omega') \right. \\ \left. + \frac{1}{4} g_{+-}(\tilde{q}' \omega') g_{+-}(\tilde{q}' - \tilde{q}, \omega - \omega') + \frac{1}{4} [J_{xx}^2(\tilde{q}') + J_{yy}^2(\tilde{q}')] g_{+-}(\tilde{q}' \omega') g_{+-}(\tilde{q}' - \tilde{q}, \omega + \omega') \right. \\ \left. + \frac{1}{4} ([J_{xx}(\tilde{q}') - J_{yy}(\tilde{q}')]^2 + 4J_{xx}^2(\tilde{q}')) g_{+-}(\tilde{q}' \omega') g_{xx}(\tilde{q}' - \tilde{q}, \omega + \omega') \right\}. \quad (17)$$

Note that if $q=0$, only the anisotropic part of J_{ij} contributes to the Γ 's as indicated in the discussion preceding Eq. (9).

Since $\Delta(\tilde{q}\omega)$ can be obtained from $\Gamma(\tilde{q}, \omega)$ and $\chi''(\tilde{q}\omega)$ can be obtained from Δ and Γ , Eqs. (8), (15), and (17) form a set of coupled nonlinear integral equations for $\chi_{+-}'(\tilde{q}\omega)$ and $\chi_{xx}'(\tilde{q}\omega)$. Before relating these equations to other work and discussing their validity, another method of evaluating Γ will be examined.

B. Sum-Rule Moment Expansions

In this subsection a sum-rule moment expansion for the spectral function will be explored. Since the spin-spin lifetime is relatively independent of H_0 and crystal orientation for many substances, only the special case of $H_0=0$ and a cubic lattice with interspin spacing a is considered in this subsection. Under these assumptions, $\chi_{+-} = 2\chi_{xx}$ and $\Gamma_{+-} = \Gamma_{xx}$, and we write $\chi \equiv \chi_{xx}$. Since EPR experiments are performed with essentially spatially uniform external fields, all equations are in the $\tilde{q}=0$ limit and the \tilde{q} dependence of all quantities will also be suppressed.

The absorptive susceptibility or spectral function $\chi''(\omega)$ is totally determined by the collection of all of its moments M_n , where

$$M_n = \int_{-\infty}^{\infty} \frac{d\omega}{\pi} \omega^{n-1} \frac{\chi''(\omega)}{\chi(0)}. \quad (18)$$

This definition is chosen to conform⁴ with that conventionally used: (i) Only even moments are non-zero, (ii) $M_0=1$, and (iii) $\chi''(\omega)/\chi(0)\omega$ is the spec-

tral profile $I(\omega)$.

The usual procedure is to assume an m -parameter functional form for $I(\omega)$ and to fit the functional form to the first $2m$ moments. The procedure⁷ used here is to use the spectral representation given by Eq. (6) and to fit an assumed form for $\Gamma(\omega)$ to its moments. By performing a high-frequency expansion in powers of z^{-2} on the representation given by Eq. (7) and equating coefficients, the moments of $\Gamma(\omega)$ can be related to the moments of $\chi''(\omega)$. The first three moments L_n , where

$$L_n = \int_{-\infty}^{\infty} \frac{d\omega}{\pi} \omega^n \Gamma(\omega), \quad (19)$$

are related to the M_n by the equations

$$L_0 = M_2, \quad L_2 = M_4 - M_2^2, \quad L_4 = M_6 - 2M_4M_2 + M_2^3. \quad (20)$$

The moment sum-rule expansion described in this subsection has the advantage of being easy to compare with the results of the microscopic equations in Sec. II A. It is also in some respects more satisfying than the conventional method for the following reasons. Since all moments of both $\Gamma(\omega)$ and $I(\omega)$ are finite, both functions must decrease exponentially as $|\omega| \rightarrow \infty$. As is shown in Sec. III, when virtually any simple function [such as $A \exp(-|\gamma\omega|^p)$] is used for $\Gamma(\omega)$, results are obtained from the first few moments which agree reasonably well with experiments. In addition, both line shapes which are Gaussian-like and line shapes which are Lorentzian-like can be described by the use of a single-function form for $\Gamma(\omega)$. For

the example given $\chi''(\omega)$ is Lorentzian in character if $|\gamma\omega| \ll 1$ and is exponentially decreasing in character if $|\gamma\omega| \gg 1$. The above method is preferable if $\Gamma(\omega)$ is expected to exhibit less structure than $\chi''(\omega)$. This is the case for exchange-narrowed systems where $\chi''(\omega)$ is Lorentzian for small ω but must be exponentially decreasing for sufficiently large ω .

C. Discussion

Consider now the validity of the approximations which led to Eqs. (15) and (17). The use of second-order time-dependent perturbation theory is valid if the relevant matrix elements are much less than typical energy differences. If $\tilde{q}=0$, the matrix elements are of order I_{ik} . When $qa \ll 1$ (where a is a lattice spacing), there are additional terms of order $J_0(qa)^2$, and when qa is not small, the matrix elements are of order J_0 . Since most energy differences are of order J_0 , this approximation is good when $qa \ll 1$ and $|I_{ij}| \ll J_0$. In fact a moment sum-rule expansion shows that this gives all moments M_n correctly except for terms of order $(I_{ij}/J_0)^2$ and $(qa)^2$ compared to 1. This paper deals primarily with the limit $qa \rightarrow 0$, so that these terms cause no trouble. On the other hand, approximating the four-spin correlation function by products of two-spin correlation functions is more serious. It might be expected that this gives reasonable results only in the high-frequency limit $\hbar\omega \gg J_0(qa)^2$. However, if H_p is zero, the phenomenology⁵ of spin diffusion says that $\hbar\Gamma(q, \omega)$ is independent of the ratio $\hbar\omega/J_0(qa)^2$ for small q and ω ($qa \ll 1$, $\hbar\omega \ll J_0$). It is expected that this behavior will persist even with the addition of H_p and thus $\hbar\Gamma(\tilde{q}, \omega)$ will contain terms of order I^2/J_0 and $J_0(qa)^2$ for small \tilde{q} and ω , again independent of the ratio $\hbar\omega/J_0(qa)^2$.

III. COMPARISON

In this section the results of Sec. II are evaluated and compared to experimental results on the cubic antiferromagnet RbMnF₃. Only the high-temperature limit is considered, and thus

$$\chi_{zz}(\tilde{q}, 0) = \frac{1}{2} \chi_{+-}(\tilde{q}, 0) = \frac{1}{3} \beta S(S+1)$$

independent of \tilde{q} . The magnetic Mn ions in RbMnF₃ have spin $\frac{5}{2}$ and form a simple cubic lattice with spacing $a = 4.24$ Å. $J_0(\alpha, \alpha')/k$ is 6.8 °K for nearest neighbors and essentially zero for further neighbors.⁸ The anisotropic part of the Hamiltonian is believed to be almost entirely due to the dipolar interaction

$$I_{ij}(\alpha, \alpha') = \frac{(\gamma_e \hbar)^2 (\delta_{ij} - 3r_i r_j / r^2)}{r^3}, \quad (21)$$

where r is the vector from α to α' whose Cartesian components are r_i . The line shape observed⁹ in

this substance is Lorentzian with a linewidth of 58 G or 1.0×10^9 sec⁻¹.

A. Microscopic Equations

First consider an estimate of the frequency-dependent transverse linewidth $\Gamma_{+-}(\omega) = \Gamma_{+-}(0, \omega)$ from Eq. (17). This expression involves a sum and an integral over the $\chi''(\tilde{q}, \omega)$. Since no good solution exists for these quantities even in the absence of the dipolar interaction, the phenomenological form¹⁰

$$\chi_t(\tilde{q}, \omega) = \chi_t(\tilde{q}, 0) D q^2 / [(\omega - h_t)^2 + D^2 q^4] \quad (22)$$

is used, where D is the diffusion constant. This form is phenomenologically correct for small \tilde{q} and ω except for corrections due to I_{ij} , which are important only over a negligibly small volume of phase space. The products of I_{ij} 's in Eq. (17) are replaced by their averages over the Brillouin zone. In view of the crudity of Eq. (22) and the fact that the $I_{ij}(\tilde{q})$ are slowly varying, this additional simplification is well justified. Finally, the sum over \tilde{q} is replaced by a spherical integral. Using these simplifications, the following equation is obtained:

$$\Gamma_{+-}(\omega) = A [f(\omega - 2h_0) + \frac{3}{2}f(\omega - h_0) + \frac{3}{2}f(\omega) + f(\omega + h_0)], \quad (23)$$

where

$$f(\omega) = \int_0^{(6\pi^2)^{1/3}} \frac{2x^4 \bar{D}}{\omega^2 + 4\bar{D}^2 x^4} \frac{dx}{2\pi^2}, \quad \bar{D} = D a^2 \quad (24)$$

$$A = \frac{2}{3} \gamma_e^4 \hbar^2 S(S+1) \sum r_i^{-6},$$

where the sum over r_i includes all neighbors of a given magnetic ion.

The $\frac{10}{3}$ rule can easily be seen from these equations. If $\bar{D} \gg h_0$, $\Gamma_{+-}(h_0)$ is $\frac{10}{3}$ times as large as when $\bar{D} \ll h_0$. In the limit of extreme exchange narrowing, $\bar{D} \gg h_0$,

$$\Gamma_{+-}(h_0) \simeq \Gamma_{+-}(0) = \gamma = \frac{(5A/\bar{D})(6\pi^2)^{1/3}}{4\pi^2}.$$

The diffusion constant D can be expressed in terms of J_0 and a as $D = (Ja^2/\hbar^2)[S(S+1)]^{1/2} \alpha$, where estimates¹¹ of α range from about 0.2 to 0.4. For RbMnF₃, this gives γ ranging from about 0.25×10^9 sec⁻¹ (14 G) to 0.5×10^9 sec⁻¹ (29 G), which is $\frac{1}{4}$ to $\frac{1}{2}$ of the experimental value. This discrepancy is not surprising because the phenomenological form of $\chi''(\tilde{q}, \omega)$ used in Eq. (17) is valid only for small \tilde{q} and ω . More realistic forms for $\chi''(\tilde{q}, \omega)$ at higher values of \tilde{q} will increase the value for γ by a factor of 2 or more.

The virtue of this method is that the $\frac{10}{3}$ factor and order of magnitude of γ can be clearly seen from a microscopic derivation. It appears to be useful for calculating γ more exactly only if the nonlinear integral equation can be solved or a better solution for $\chi''(\tilde{q}, \omega)$ can be obtained in the absence of I_{ij} .

B. Sum-Rule Moment Expansion

Now consider the sum-rule moment method for evaluating $\Gamma(\omega)$ which was described in Sec. II B. (Recall that only the case of a cubic lattice and $H_0=0$ was considered.) The first three moments for RbMnF_3 have been computed by others⁹ and the first three nonzero L_n are

$$L_0 = 2.68 \times 10^{21} \text{ sec}^{-2} (9.0 \times 10^6 \text{ G}^2),$$

$$L_2 = 10^{47} \text{ sec}^{-4} (1.1 \times 10^{18} \text{ G}^4),$$

$$L_4 = 3 \times 10^{73} \text{ sec}^{-6} (1.1 \times 10^{30} \text{ G}^6).$$

Without further knowledge of the details of the system, $\Gamma(\omega)$ is arbitrary except that it must be non-negative (stable system) and it must decrease exponentially as $|\omega|$ approaches infinity (all moments are finite). A possible simplest¹² function that satisfies these requirements is

$$\Gamma(\omega) = \gamma e^{-|\alpha\omega|^p}, \quad (25)$$

where $\gamma = \Gamma(0)$ has units of sec^{-1} , α has units of sec , and p is a positive number.

By fitting γ and α (with arbitrary p) to L_0 and L_2 , one finds that

$$\gamma = \frac{1}{2} \pi p \left(\frac{L_0^3 \Gamma(3/p)}{L_2 \Gamma^3(1/p)} \right)^{1/2}$$

$$= 0.69p \left(\frac{\Gamma(3/p)}{\Gamma^3(1/p)} \right)^{1/2} \times 10^9 \text{ sec}^{-1}. \quad (26)$$

If one wishes to make a two-parameter fit, claiming the freedom to choose p as the freedom of choice of functional form, results ranging from $\gamma = 0.4 \times 10^9 \text{ sec}^{-1}$ or 23 G (when $p \rightarrow \infty$) to $\gamma \rightarrow \infty$, i.e., infinitely large linewidth (when $p \rightarrow 0$), may be obtained. The somewhat appealing choice of $p=2$ yields $\gamma = 0.55 \times 10^9 \text{ sec}^{-1}$ (32 G), about one-half of the experimental value. If the third moment L_4 is used to determine p , the result is $p \approx 0.85$ and $\gamma \approx 1.2 \times 10^9 \text{ sec}^{-1}$ (70 G), in good agreement with the experimental value of $1.0 \times 10^9 \text{ sec}^{-1}$ (58 G).

The above analysis has been written in such a way as to point up the arbitrariness involved in choosing a functional form. The method used in the present paper is in some sense more pleasing in that much of this arbitrariness is removed. On the other hand, it is not clear how quickly the moment method converges and the result $\gamma = 1.2 \times 10^9 \text{ sec}^{-1}$ may only be fortuitously close to the experimental value. Unfortunately, one feels that higher and higher moments of $\Gamma(\omega)$ [or $I(\omega)$] have less to do with the values of these functions near $\omega = 0$.

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⁶This is essentially the spectral representation used by H. S. Bennett and P. C. Martin, *Phys. Rev.* **138**, A608 (1965).

⁷This treatment is very much like the analogous treatment for diffusion discussed in Ref. 6. Extensive work using sum-rule moment expansions for the isotropic Heisenberg model has been published. See, for example, Daniel G. McFadden and Raya A. Tahir-Kheli, *Phys.*

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¹⁰This is a generalization of the form considered in Ref. 6. By studying the integral equations derived in this paper when $I_{ij}=0$, it is reasonable to expect that $\Gamma(\vec{q}, \omega)$ goes as q^2 independent of ω for small \vec{q} and ω .

¹¹There are many references on this. See, for instance, M. Blume and J. Hubbard, *Phys. Rev. B* **1**, 3815 (1970), and references therein.

¹²Since the word "simplest" has no well-defined mathematical meaning, Eq. (25) is arbitrary to that extent.