

Correlation Effect on the Nuclear Magnetic Resonance Linewidth in Magnetic Materials

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In a magnetic medium the nuclear spins are coupled by the indirect Suhl-Nakamura interaction. This interaction contributes to the nuclear magnetic resonance (NMR) linewidth and gives rise to a shift in the NMR frequency which is important in the helium-temperature range for materials with a large concentration of nuclear spins and a large interaction range, b . When this frequency pulling is appreciable, there exists a relative narrowing of the NMR line of the same order of magnitude as the relative frequency shift. This narrowing arises because the motions of the nuclear spins within the interaction range, b , are correlated.

I. INTRODUCTION

It has been shown by Suhl¹ and Nakamura² that for ordered magnetic materials with a high concentration of nuclear spins, an important source of linewidth for the nuclear magnetic resonance (NMR) signal is the indirect nuclear spin-spin interaction via the exchange of virtual spin waves. These authors have calculated the second moment of the NMR line under the conditions of (1) complete nuclear disorder, i.e., an infinite nuclear temperature, T_n , and (2) complete order in the electronic spin system, i.e., zero electronic spin temperature, T_s . In the helium-temperature range ($\sim 1^\circ\text{K}$) these assumptions are usually justified because (1) the nuclear polarization is only of the order of a few percent, and (2) the electronic magnetization (sublattice magnetization in an antiferromagnet) has deviated only slightly from its saturation value. However, it has recently been shown³ that, if (a) the concentration of nuclear spins is large, e.g., material with Co and Mn and (b) the electronic resonance frequencies are low, there will be an important depression of the NMR frequency at low temperatures arising from the indirect interaction. The relative frequency shift in a ferromagnet is given by

$$-\delta\omega/\omega = (\omega_n/\omega_e) \langle (I_z)/\langle S_z \rangle \rangle, \quad (\text{I.1})$$

where $\omega_n = \gamma_n H_n = A \langle S_z \rangle / \hbar$, ω_e is the electronic resonance frequency, γ_n is the nuclear gyromagnetic ratio, A is the isotropic hyperfine coupling energy, and $\langle \rangle$ denotes thermal average. Taking $\omega_n = 3 \times 10^9 \text{ sec}^{-1}$, $\omega_e = 2 \times 10^{10} \text{ sec}^{-1}$, $I = S = \frac{5}{2}$ (plausible values for Mn^{++}) this gives $\delta\omega/\omega \approx 3 \times 10^{-3}/T$. The corresponding result for an antiferromagnet is

$$-\delta\omega/\omega \approx (\omega_{\text{ex}}\omega_n/\omega_e^2) \langle (I_z)/\langle S_z \rangle \rangle, \quad (\text{I.2})$$

where ω_{ex} is the exchange frequency, usually of the order of 10^{13} sec^{-1} . For Mn^{++} , and at an electronic frequency

of 9.4 kMc/sec, this gives a relative shift of about 40%. Such a large frequency pulling has, in fact, been observed by Heeger, Portis, and Witt⁴ in the canted antiferromagnet KMnF_3 . A much smaller frequency shift in ferrimagnetic MnFe_2O_4 has more recently been identified.⁵ The frequency pulling may be considered as a collective nuclear spin effect where a given spin experiences an effective field arising from all the neighboring spins within the interaction range, b . When this effect is large, as in KMnF_3 , the motion of individual spins, with a distance b , may be strongly correlated and the assumption (1) of complete nuclear spin disorder must be more carefully investigated even at comparatively high temperatures ($\sim 1^\circ\text{K}$) where the nuclear polarization is small. In Sec. II, we consider the lowest order correlation effect by calculating the second moment of the power spectrum of the nuclear resonance mode. The result is that there is a relative reduction of the linewidth (for a Gaussian line where the second moment is a good measure of the width) of the same order of magnitude as the frequency shifts given by (I.1) and (I.2) for ferromagnets and antiferromagnets, respectively.

II. MOMENT CALCULATION

Following Ref. 3, we define the nuclear spin waves and their power spectrum $P_q(\Omega)$ by

$$A_{q^+} = \sum_i e^{iq \cdot r_i} I_i^+ \quad (\text{II.1})$$

and

$$P_q(\Omega) = \int dt \langle A_{q^-}(0) A_{q^+}(t) \rangle e^{i\Omega t}. \quad (\text{II.2})$$

The moments of $P_q(\Omega)$ will be determined for the Hamiltonian $H = H_0 + H_1$, where the first-order Hamiltonian H_0 is given by

$$H_0 = -A \langle S_z \rangle \sum_i I_i^z \quad (\text{II.3})$$

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¹ H. Suhl, Phys. Rev. **109**, 606 (1958).

² T. Nakamura, Progr. Theoret. Phys. (Kyoto) **20**, 542 (1958).

³ P. G. de Gennes, F. Hartmann-Boutron, and P. A. Pincus, Compt. Rend., **254**, 1264 (1962); P. G. de Gennes, P. A. Pincus, F. Hartmann-Boutron, and J. M. Winter, Phys. Rev. **129**, 1105 (1963).

⁴ A. J. Heeger, A. Portis, and G. Witt, in Proceedings of the International Conference on Magnetic and Electric Resonance and Relaxation, Eindhoven, 1962 (unpublished).

⁵ A. J. Heeger and T. Houston, Bull. Am. Phys. Soc. **8**, 213 (1963).

and the second-order term H_1 is^{1,2}

$$H_1 = -\sum_{i \neq j} U_{ij} I_i^+ I_j^-, \quad (\text{II.4})$$

with

$$U_{ij} = \left(\frac{A^2 S}{2N} \right) \sum_{\mathbf{q}} \frac{e^{i\mathbf{q} \cdot (\mathbf{R}_i - \mathbf{R}_j)}}{\hbar \omega_e(\mathbf{q})}. \quad (\text{II.5})$$

The first moment of $P_{\mathbf{q}}(\Omega)$ gives the nuclear spin-wave spectrum,³ i.e.,

$$\langle \Omega_{\mathbf{q}} \rangle = \int P_{\mathbf{q}}(\Omega) \Omega d\Omega / \int P_{\mathbf{q}}(\Omega) d\Omega, \quad (\text{II.6})$$

where the frequency pulling arises from H_1 . The linewidth $\Delta\Omega$ of the uniform nuclear resonance mode ($\mathbf{q}=0$) is related to the second moment of the power spectrum,

$$\langle \Omega^2 \rangle = \int P(\Omega) \Omega^2 d\Omega / \int P(\Omega) d\Omega, \quad (\text{II.7})$$

by

$$(\Delta\Omega)^2 = \langle \Omega^2 \rangle - \langle \Omega \rangle^2. \quad (\text{II.8})$$

Using (II.2), the first and second moments are given, respectively, by

$$\langle \Omega \rangle = +i \langle A^- dA^+ / dt \rangle / \langle A^- A^+ \rangle, \quad (\text{II.9})$$

and

$$\langle \Omega^2 \rangle = -\langle A^- d^2 A^+ / dt^2 \rangle / \langle A^- A^+ \rangle, \quad (\text{II.10})$$

where $i\hbar(dA^+/dt) = [A^+, H]$. The resonance frequency is then determined from (II.3), (II.4), and (II.9) to be

$$\langle \Omega \rangle = A \langle S_z \rangle - 2 \sum_{i \neq j, l} U_{ij} \langle I_i^- I_i^+ I_j^2 \rangle / \sum_{ij} \langle I_i^- I_j^+ \rangle. \quad (\text{II.11})$$

The frequency pulling arises when the thermal averages in the second term of (II.11) are evaluated using the Hamiltonian, H :

$$\langle O \rangle = \text{Tr}[O e^{-\beta H}] / \text{Tr}[e^{-\beta H}].$$

If we let σ denote the normalization factor, i.e.,

$$\sigma = \sum_{ij} \langle I_i^- I_j^+ \rangle, \quad (\text{II.12})$$

the linewidth becomes

$$\begin{aligned} (\Delta\Omega)^2 \cong & (2/\hbar^2 \sigma) \left[2 \sum_{i \neq j, l \neq j} U_{ij} U_{lj} \langle I_m^- I_i^+ I_j^2 I_i^2 \rangle \right. \\ & \left. + \sum_{i \neq j, l \neq j} U_{ij} U_{li} \langle (I_m^- I_j^+ I_i^+ I_l^-) - \langle I_m^- I_j^+ I_i^+ I_l^- \rangle \right]. \end{aligned} \quad (\text{II.13})$$

The thermal averages are calculated by expanding the Boltzmann factors in powers of β , i.e., $(kT)^{-1}$. In the limit of infinite nuclear spin temperature, i.e., the zeroth

power of β in the expansion, only the second term of (II.13) is nonvanishing and the linewidth becomes

$$\begin{aligned} (\Delta\Omega)_{\infty}^2 &= 2\hbar^{-2} \sum_{i \neq j} U_{ij}^2 \langle I_i^- I_i^+ \rangle \langle I_j^- I_j^+ \rangle / N \sum_i \langle I_i^- I_i^+ \rangle \\ &= \frac{4}{3} I(I+1) \sum_i U_{ij}^2, \end{aligned} \quad (\text{II.14})$$

where we have used the fact that $\text{Tr}(I^- I^+) = \frac{2}{3} I(I+1)$. The sum over lattice sites in (II.14) is easily^{1,2} performed and gives

$$(\Delta\Omega)_{\infty}^2 = \frac{\pi I(I+1)}{6S^2} \frac{\omega_n^4}{\omega_{\text{ex}}^{3/2} \omega_e^{1/2}}. \quad (\text{II.15})$$

This gives a width of several Mc/sec for Mn^{2+} for $\omega_e \approx 10$ kMc/sec. This is probably the most important T_2 mechanism in materials with Mn^{55} or Co^{59} .

We now evaluate $(\Delta\Omega)^2$ from (II.13) keeping terms to first order in β in order to find any polarization or correlation effects. The lowest order temperature corrections to (II.14) are, thus, obtained in a straightforward way as

$$\begin{aligned} (\Delta\Omega)_{T^2} &= \beta \{ 2[2I(I+1)/3]^2 \\ &\quad \times [\sum_{ijl} \langle U_{ij} U_{li} U_{ij} \rangle - \sum_{ij} \langle U_{ij}^2 \rangle \langle \sum_l U_{lm} \rangle] \\ &\quad + [(10/3)I(I+1) + \frac{2}{3}] \sum_{ij} \langle U_{ij}^3 \rangle \}. \end{aligned} \quad (\text{II.16})$$

We shall see shortly that the negative term in (II.16) is the largest, and neglecting the others for the moment the total width becomes

$$\begin{aligned} (\Delta\Omega)^2 &= (4I(I+1)/3) \sum_{ij} \langle U_{ij}^2 \rangle \\ &\quad \times [1 - (2I(I+1)/3) \langle \sum_i U_{ij} \rangle \beta]. \end{aligned} \quad (\text{II.17})$$

The second term in the brackets is precisely the resonance frequency shift given in (II.11). Thus, neglecting the positive term in (II.16), we find a relative reduction of the second moment precisely equal to the relative frequency pulling. The first positive term in (II.16) may easily be shown to be related to the negative term by

$$\sum_{ijl} \langle U_{ij} U_{li} U_{ij} \rangle = \frac{1}{4} \langle \sum_{ij} \langle U_{ij}^2 \rangle \rangle \langle \sum_l \langle U_{lm} \rangle \rangle. \quad (\text{II.18})$$

The third term is much smaller than those and is quite negligible. The final result is, then, that there is a reduction of the second moment given by

$$\frac{\delta(\Delta\Omega)}{\Delta\Omega_{\infty}} \cong \frac{3\delta\Omega}{8\Omega}. \quad (\text{II.19})$$

For cases such as KMnF_3 at liquid-helium temperatures where $\delta\Omega/\Omega \approx 40\%$, we might expect approximately a 20% narrowing of the nuclear resonance at low power levels. Of course, this reduction of the second moment would get larger at even lower temperatures.

It should be emphasized that this narrowing effect arises because the nuclear spins within a Suhl range $(H_{\text{ex}}/H_A)^{1/2}a$ have motions which are no longer

completely random but are correlated by the indirect interaction itself.

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Perturbation-Moment Method: Application to Band Structure of Impure Semiconductors

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A contour integral method of calculating spectral moments from the perturbation expansion of a characteristic function is described. The moments are used to provide a sort of "analytic continuation" of the perturbation expansion for the density of states into a Legendre polynomial expansion valid for low energies. The method is tested on the one-dimensional impurity band structure problem. The results are less accurate than Klauder's best diagram-summing approximation. The inaccuracy of the results is attributed to poor convergence of the perturbation expansion for the moments. We apply the method to the three-dimensional impurity problem where the impurities are represented by randomly located screened Coulomb potentials. At intermediate densities the perturbation expansion for the moments converges much faster than in one dimension, hence, the results should be more accurate. Although the Thomas-Fermi method should not be accurate at intermediate densities, it agrees remarkably well with the perturbation-moment results.

INTRODUCTION

IN an earlier paper¹ the author suggested that it might prove useful to compute the spectral moments by perturbation theory and then invert the moments to find the density of states, rather than to compute the density of states directly from the perturbation expansion. In the present paper a more elegant scheme for obtaining the spectral moments from perturbation theory by using contour integration is described (Sec. III). The method is tested on the one-dimensional impurity band structure problem (Sec. V) and is applied to the three-dimensional impurity band structure problem (Sec. VI).

We use a characteristic function closely related to Van Hove's² resolvent operator. The characteristic function is expanded as a power series in the perturbation operator following Van Hove and Hugenholtz.³ The expansion is shown to be nonconvergent for the impurity problem so that the expansion is at best asymptotic. Convergence is best at high energy. The moment method would be a technique for analytically continuing the perturbation expansion to low energy if the perturbation expansion were truly convergent.

The moment approach is a different *type* of approach from the diagram summation techniques used in field theory. Both methods begin with the same type of perturbation expansion but the diagram summation methods select special subsets of terms which can be summed to infinite order. The partially resummed function is then assumed to apply, at least approximately, to a greater range of energies than the original perturbation expansion. In the moment method, as we have used it, no diagrams are summed to infinite order. All diagrams are included through fourth order and the spectral moments are used to analytically continue the perturbation expansion valid at high energy into a Legendre polynomial expansion valid at low energies.⁴

A great many variations on the use of spectral moments are possible. They could be used together with summations to infinite order and they could be inverted using functions other than Legendre polynomials. We have not explored these possibilities, however.

The problem of the band structure of impure semiconductors has been most extensively studied in one dimension.⁵⁻⁷ Quantitative three-dimensional calculations

⁴ The problem of moment inversion by Legendre polynomial expansion has been discussed by A. A. Maradudin, P. Mazur, E. W. Montroll, and G. H. Weiss, *Rev. Mod. Phys.* **30**, 175 (1958); E. W. Montroll, *J. Chem. Phys.* **10**, 218 (1942); **11**, 481 (1943).

⁵ M. Lax and J. C. Phillips, *Phys. Rev.* **110**, 41 (1958).

⁶ H. Frisch and S. Lloyd, *Phys. Rev.* **120**, 1175 (1960).

⁷ J. R. Klauder, *Ann. Phys. (N. Y.)* **14**, 43 (1961).

¹ E. O. Kane, *Phys. Rev.* **125**, 1094 (1962).

² The resolvent operator is discussed in Ref. 3.

³ N. M. Hugenholtz in *The Many Body Problem*, edited by C. DeWitt (John Wiley & Sons, Inc., New York, 1958), p. 1.