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Spin Absorption Spectra

Abstract: Spin systems exhibit a whole spectrum of absorption lines when in small constant external magnetic fields giving Zeeman energies comparable to internal interaction energies. With such small constant magnetic fields, power is absorbed from an alternating magnetic field at zero frequency, at the Larmor frequency, and at harmonics of the Larmor frequency, both for perpendicular- and parallel-field configurations. The calculation of this spectrum for spin systems in powdered materials is the main purpose of this paper. Both magnetic dipole-dipole and electric quadrupole internal interactions are considered and treated as second-order perturbations on the Zeeman interaction. The intensities of the two absorption lines that occur at the Larmor frequency and double the Larmor frequency are obtained for the parallel-field case. The intensity, frequency shift, and second moment of the Larmor line, and the intensities of the lines that occur at zero frequency and double the Larmor frequency, are obtained for the perpendicular-field case. The second-order calculation for powdered materials gives results which are identical within a constant factor for both dipole-dipole and quadrupole interactions.

1. Introduction

The phenomenon of magnetic resonance in spin systems characterized by the use of applied constant magnetic fields giving Zeeman energies which are very large in comparison with internal energies, and by absorption of energy from an alternating magnetic field at the Larmor frequency, has been extensively investigated. The situation in which the Zeeman energy is only slightly larger than the internal energy is considered in this paper. As a result of internal interactions in the spin system, such as the magnetic dipole-dipole interaction or the electric quadrupole interaction of the spin system with the crystalline lattice, the magnetic resonance absorption spectrum changes markedly as the constant magnetic field becomes small. At low constant magnetic fields a whole spectrum of absorption lines occurring at zero frequency and at the Larmor frequency and its harmonics can be observed, both when the alternating field is perpendicular to the constant field and when they are parallel.

It was shown some time ago by Waller[1] that a spin system in the absence of an external magnetic field should absorb energy from low-frequency alternating magnetic fields. Broer[2] then considered the problem for non-vanishing external fields and found that absorption should occur at all the various harmonics of the Larmor frequency with the increasingly higher frequency lines decreasing rapidly in intensity. His work, together with the later work of Wright,[3] yielded the intensity of the lines at zero frequency, at the Larmor frequency, and at double the Larmor frequency, for both perpendicular- and parallel-field configurations. The second and fourth moments of the high-field Larmor line have been calculated by Van Vleck.[4] Recently, the second moments of all the lines mentioned in the penultimate sentence were obtained by Cheng.[5] Only the magnetic dipole-dipole internal interaction was considered in these papers. It is the purpose of the present study to present a uniform account of all the results which are obtained in the second order of perturbation, including both the magnetic dipole-dipole interactions among the spins and their electric quadrupole interactions with the crystalline lattice in which they are fixed.

The general properties of the susceptibility tensor and the intimate relation of this quantity to experimental measurements are discussed in Section 2. The quantum-mechanical formulation of the susceptibility is given in Section 3, and it is related to a spin correlation function in a manner amenable to calculation. In Section 4 this correlation function is calculated for a spin system in a powdered material, taking into account the magnetic dipole-dipole interaction as a second-order perturbation on the Zeeman energy. In the parallel-field case this calculation yields the intensities

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of the two absorption lines that occur at the Larmor frequency and double the Larmor frequency. For the perpendicular-field case the calculation gives the intensity, frequency shift, and second moment of the Larmor line, and the intensities of the lines that occur at zero frequency and double the Larmor frequency. Spins with angular momentum greater than one-half can possess an electric quadrupole moment and thus interact with electric-field gradients. A noncubic crystalline lattice structure, imperfections, or impurities in a cubic lattice give rise to such electric-field gradients at spin sites. This quadrupole interaction, in addition to the dipole-dipole interaction, is considered in Section 5. The calculation is carried out in the fashion of the previous dipole-dipole case, treating the quadrupole interaction as a second-order perturbation. This requires that the quadrupole interaction be a weak perturbation in the sense that few spins are in such large field gradients that their contribution to the absorption is split far from the center of a line. The results of the second-order quadrupole calculation for powdered materials are identical with those of the preceding second-order dipole-dipole calculation, except for a change in an over-all constant factor. The two interactions do not interfere in second order so that the combination of quadrupole and dipole-dipole interactions gives the same results as the pure dipole-dipole interaction case, except for the change of an over-all constant factor.

2. General properties of the susceptibility

A brief review will be given in this section of some general properties of the susceptibility tensor which will be used in subsequent calculations. The assumption of a linear causal connection between the induced magnetization and an applied spatially uniform magnetic field is conveyed in

$$\mathbf{m}(t) = \int_{-\infty}^{t} dt' \chi(t, t') \cdot \mathbf{h}(t') . \tag{1}$$

We shall limit our discussion to time-independent systems so that the real tensor (or dyadic) susceptibility χ is invariant under time translations,

$$\chi(t, t') = \chi(t - t') . \tag{2}$$

For the case of a monochromatic magnetic field,

$$\mathbf{h}(t) = \mathbf{h}_\omega e^{-i\omega t} + \mathbf{h}_\omega{}^* e^{+i\omega t} , \tag{3}$$

the integral connection (1) becomes

$$\mathbf{m}(t) = \chi(\omega) \cdot \mathbf{h}_\omega e^{-i\omega t} + \chi(\omega)^* \cdot \mathbf{h}_\omega{}^* e^{i\omega t} , \tag{4}$$

where $\chi(\omega)$ is the Fourier transform of $\chi(t)$,

$$\chi(\omega) = \int_0^\infty dt e^{i\omega t} \chi(t) , \tag{5}$$

and

$$\chi(\omega)^* = \chi(-\omega) , \tag{6}$$

as $\chi(t)$ is real. The average energy density stored in the system, $\bar{E}_s$, is

$$\begin{aligned} \bar{E}_s &= (\omega/2\pi) \int_0^{2\pi/\omega} dt [\mathbf{h}(t) \cdot \mathbf{m}(t)]/2 \\ &= \mathbf{h}_\omega{}^* \cdot \chi_s(\omega) \cdot \mathbf{h}_\omega , \end{aligned} \tag{7}$$

where $\chi_s(\omega)$ is the Hermitian part of the susceptibility tensor $\chi(\omega)$,

$$\chi_s(\omega) = [\chi(\omega) + \chi(\omega)^\dagger]/2 . \tag{8}$$

The cyclic energy density gain of the system, ΔE, is

$$\begin{aligned} \Delta E &= \int_0^{2\pi/\omega} dt \mathbf{h}(t) \cdot d[\mathbf{m}(t)]/dt \\ &= 4\pi \mathbf{h}_\omega{}^* \cdot \chi_a(\omega) \cdot \mathbf{h}_\omega , \end{aligned} \tag{9}$$

where $i\chi_a(\omega)$ is the skew-Hermitian part of the susceptibility tensor,

$$\chi_a(\omega) = [\chi(\omega) - \chi(\omega)^\dagger]/2i . \tag{10}$$

A general symmetry property that we shall use in our calculations is obtained from the requirement of time reversal invariance. We must now state that we are considering systems in a time-independent, spatially uniform, external magnetic field $\mathbf{H}_0$, and indicate the dependence of the susceptibility on this field explicitly,

$$\chi(\omega) = \chi(\omega; \mathbf{H}_0) .$$

Upon time reversal the external magnetic field reverses direction, the frequency changes sign, the stored energy remains the same, and the cyclic energy gain changes sign,

$$T : \begin{cases} \omega \to -\omega , & \mathbf{H}_0 \to -\mathbf{H}_0 \\ \bar{E}_s \to \bar{E}_s , & \Delta E \to -\Delta E . \end{cases}$$

Inspection of the relations for the energy stored and gained by the system, (7), (9), shows that this invariance property requires

$$\chi(\omega; \mathbf{H}_0) = \chi(-\omega; -\mathbf{H}_0)^\dagger \tag{11}$$

and, according to the reality property (6),

$$\chi(\omega; \mathbf{H}_0) = \chi(\omega; -\mathbf{H}_0)^T . \tag{12}$$

Hence, reversing the direction of the external magnetic field $\mathbf{H}_0$ is equivalent to the mathematical operation of transposing the susceptibility tensor.

The calculations in subsequent sections deal for the most part with powdered materials. In the case of powdered materials, the only distinguished direction in space is that of the external magnetic field $\mathbf{H}_0$. On choosing this direction to be along the z axis, the susceptibility χ is invariant under the symmetry operations of arbitrary rotations about the z axis and a rotation of π about the x or y axis coupled with the reversal of the direction of $\mathbf{H}_0$. These symmetries require that the susceptibility tensor possess only three independent components and be of the form

$$\chi = \begin{bmatrix} \chi^{xx} & \chi^{xy} & 0 \\ -\chi^{xy} & \chi^{xx} & 0 \\ 0 & 0 & \chi^{zz} \end{bmatrix} \tag{13}$$

for powdered materials, and that the time reversal invariance statement (12) be satisfied.

This form of the susceptibility tensor can be diagonalized by the introduction of a complex "angular momentum" coordinate system corresponding to a change of emphasis from linear to circular polarization. The rotation operator J has the $j = 1$ representation in Cartesian coordinates

$$(J_\gamma)^{\alpha\beta} = i\varepsilon^{\alpha(\gamma)\beta}\,, \tag{14}$$

where $\varepsilon^{\alpha\beta\gamma}$ is the completely antisymmetric pseudotensor of rank three with $\varepsilon^{xyz} = +1$. The properties of this tensor allow the powder form of the susceptibility to be written as

$$\chi = \chi^{zz}\mathbf{1} + i\chi^{xy}\mathbf{J}_z + (\chi^{zz} - \chi^{xx})\mathbf{J}_z{}^2\,. \tag{15}$$

This demonstrates that in the coordinate system in which $\mathbf{J}^z$ is diagonal χ is also diagonal, with elements

$$\begin{aligned} \chi^+ &= \chi^{xx} + i\chi^{xy}\,, \\ \chi^0 &= \chi^{zz}\,, \\ \chi^- &= \chi^{xx} - i\chi^{xy}\,. \end{aligned} \tag{16}$$

In this coordinate system the time reversal symmetry (12) states that

$$\begin{aligned} \chi^{\pm}(\omega; \mathbf{H}_0) &= \chi^{\mp}(\omega; -\mathbf{H}_0), \\ \chi^0(\omega; \mathbf{H}_0) &= \chi^0(\omega; -\mathbf{H}_0)\,. \end{aligned} \tag{17}$$

3. Quantum-mechanical formulation of the susceptibility

The quantum-mechanical expression for the susceptibility is obtained by calculating the expectation value of the magnetization, treating the time-dependent magnetic field $\mathbf{h}(t)$ as a linear perturbation.

Before the application of the magnetic field $\mathbf{h}(t)$ the system is described by a time-independent Hamiltonian $\mathscr{H}$ and a statistical distribution ρ_n of the eigenstates of the Hamiltonian $|n\rangle$. A density operator ρ, which commutes with the Hamiltonian $\mathscr{H}$, can be defined by

$$\rho = \sum_n |n\rangle\rho_n\langle n|\,. \tag{1}$$

The density operator is normalized to the reciprocal volume of the system

$$Tr\rho = \sum_n \rho_n = 1/V\,. \tag{2}$$

The application of a time-dependent magnetic field $\mathbf{h}(t)$ which vanishes in the remote past gives rise to a magnetization

$$\mathbf{m}(t) = \sum_n \rho_n\langle n, t; h|\mathbf{M}|n, t; h\rangle\,, \tag{3}$$

where $|n, t; h\rangle$ moves under the action of the complete Hamiltonian,

$$i(d/dt)|n, t; h\rangle = [\mathscr{H} - \mathbf{h}(t)\cdot\mathbf{M}]|n, t; h\rangle\,, \tag{4}$$

and approaches the eigenstate $|n, t\rangle$ in the remote past. Here $\mathbf{M}$ is the magnetic-moment operator of the system, and we use natural units in which $\hbar = 1$. The dependence of $|n, t; h\rangle$ on $\mathbf{h}(t)$ is displayed by the introduction of an interaction representation state $|n, t; i\rangle$ which is defined by

$$|n, t; i\rangle = e^{i\mathscr{H}t}|n, t; h\rangle \tag{5}$$

and satisfies

$$i(d/dt)|n, t; i\rangle = -\mathbf{M}(t)\cdot\mathbf{h}(t)|n, t; i\rangle\,, \tag{6}$$

$$t \to -\infty: \quad |n, t; i\rangle \to |n\rangle\,, \tag{7}$$

where

$$\mathbf{M}(t) = e^{i\mathscr{H}t}\mathbf{M}e^{-i\mathscr{H}t}\,. \tag{8}$$

This differential equation, with its accompanying boundary condition, is equivalent to the integral equation

$$|n, t; i\rangle = |n\rangle + i\int_{-\infty}^{t} dt'\mathbf{M}(t') \cdot \mathbf{h}(t')|n, t'; i\rangle\,. \tag{9}$$

Performing a single iteration of the integral equation, inserting the resulting expression for the state vector $|n, t; h\rangle$ in the formula for the magnetization (3), and identifying the dynamic susceptibility with the linear dependence of the magnetization on the time-dependent field $\mathbf{h}(t)$ gives

$$\chi^{\alpha\beta}(t, t') = iTr\rho[M^\alpha(t), M^\beta(t')]\theta(t - t')\,. \tag{10a}$$

Here the step function $\theta(t)$ has been included to indicate explicitly the retarded, casual, nature of $\chi(t, t')$,

$$\theta(t) = \begin{cases} 0\,, & t < 0 \\ 1\,, & t > 0\,. \end{cases} \tag{11}$$

The time independence of the system, and the invariance of the trace under cyclic permutations of the operators it contains, give the alternate form

$$\chi^{\alpha\beta}(t - t') = iTr[\rho, M^\alpha(t)]M^\beta(t')\theta(t - t')\,. \tag{10b}$$

The general expression for the susceptibility will now be applied to a spin system consisting of N identical spins $\mathbf{s}_i$ with gyromagnetic ratio γ and spin I. The magnetic-moment operator is now given explicitly by

$$\mathbf{M} = \gamma\mathbf{S}\,, \tag{12}$$

where $\mathbf{S}$ is the total spin operator of the system,

$$\mathbf{S} = \sum_{i=1}^{N} \mathbf{s}_i, \qquad \mathbf{s}_i{}^2 = I(I + 1)\,. \tag{13}$$

The spin system will be assumed to be initially in thermal equilibrium with a large temperature T so that the statistical distribution operator

$$\rho = Ae^{-\mathscr{H}/kT} \tag{14}$$

can be approximated by

$$\rho = A[1 - (\mathscr{H}/kT)]\,. \tag{15}$$

The Hamiltonian $\mathscr{H}$ has a vanishing trace for the systems to be considered. Accordingly, to first order in $1/kT$, the normalization constant is given by

$$A = (VTr1)^{-1} = [V(2I+1)^N]^{-1}\,. \tag{16}$$

In the high-temperature limit the expression for the susceptibility (10b) reduces to

$$\begin{aligned} \chi^{\alpha\beta}(t-t') &= -iA(\gamma^2/kT)Tr[\mathscr{H}, S^\alpha(t)]S^\beta(t')\theta(t-t') \\ &= A(\gamma^2/kT)\{TrS^\alpha S^\beta\delta(t-t') \\ &\quad -[d/dt][TrS^\alpha(t)S^\beta(t')\theta(t-t')]\}\,. \end{aligned} \tag{17}$$

Now

$$TrS^\alpha S^\beta = NTr1(tr1)^{-1}trs^\alpha s^\beta\,, \tag{18}$$

where tr denotes the trace in the space of a single-spin operator. Using a result of Appendix A, Eq. (A.2), the previous equation becomes

$$TrS^\alpha S^\beta = (1/3)NI(I+1)(2I+1)^N\delta^{\alpha\beta}\,. \tag{19}$$

Introducing the spin-correlation function[6]

$$G^{\alpha\beta}(t-t') = [Tr(S^\nu)^2]^{-1}TrS^\alpha(t)S^\beta(t')\theta(t-t')\,, \tag{20}$$

we obtain an expression for the susceptibility in a form suitable for calculation,[7]

$$\chi^{\alpha\beta}(t-t') = \chi_0\{\delta^{\alpha\beta}\delta(t-t') - [d/dt][G^{\alpha\beta}(t-t')]\}\,, \tag{21}$$

where

$$\chi_0 = \gamma^2 NI(I+1)/3kTV \tag{22}$$

is the static susceptibility of the spin system.

The Fourier transform of the susceptibility is the quantity that is usually of experimental interest because it describes directly the energy stored and gained by a spin system in a monochromatic field $\mathbf{h}(t)$,

$$\chi^{\alpha\beta}(\omega) = \int_0^\infty dte^{i\omega t}\chi^{\alpha\beta}(t) = \chi_0[\delta^{\alpha\beta} + i\omega G^{\alpha\beta}(\omega)]\,. \tag{23}$$

The absorptive part of the susceptibility is

$$\chi_a{}^{\alpha\beta}(\omega) = \omega\chi_0 G_a{}^{\alpha\beta}(\omega)\,, \tag{24}$$

where

$$G_a{}^{\alpha\beta}(\omega) = (1/2)[G^{\alpha\beta}(\omega) + G^{\beta\alpha}(\omega)^*]\,. \tag{25}$$

According to the time translational invariance of the trace and its invariance under cyclic permutations,

$$TrS^\beta(t)S^\alpha(0) = TrS^\alpha(-t)S^\beta(0)\,, \tag{26}$$

and the absorptive part of the spin-correlation function may be written

$$\begin{aligned} G_a{}^{\alpha\beta}(\omega) &= (1/2)[Tr(S^\nu)^2]^{-1}\int_0^\infty dt[e^{i\omega t}TrS^\alpha(t)S^\beta(0) \\ &\qquad + e^{-i\omega t}TrS^\beta(t)S^\alpha(0)] \\ &= (1/2)[Tr(S^\nu)^2]^{-1}\int_{-\infty}^\infty dte^{i\omega t}TrS^\alpha(t)S^\beta(0)\,. \end{aligned} \tag{27}$$

Although an exact calculation of the spin-correlation function is in general impossible, the complete moments $\langle\omega^n\rangle$ of its absorptive part can be obtained by the following manipulation:

$$\begin{aligned} \langle\omega^n\rangle^{\alpha\beta} &= (1/\pi)\int_{-\infty}^\infty d\omega\omega^n G_a{}^{\alpha\beta}(\omega) \\ &= (1/2\pi)[Tr(S^\nu)^2]^{-1} \\ &\quad \times \int_{-\infty}^\infty d\omega\int_{-\infty}^\infty dt\{[(1/i)(d/dt)]^n e^{i\omega t}\} \\ &\quad \times TrS^\alpha(t)S^\beta(0) \\ &= (1/2\pi)[Tr(S^\nu)^2]^{-1} \\ &\quad \times \int_{-\infty}^\infty dt\left[\int_{-\infty}^\infty d\omega e^{i\omega t}\right][i(d/dt)]^n \\ &\quad \times TrS^\alpha(t)S^\beta(0) \\ &= [Tr(S^\nu)^2]^{-1}[i(d/dt)]^n TrS^\alpha(t)S^\beta(0)\big|_{t=0}, \end{aligned} \tag{28}$$

and the repeated use of the Heisenberg equation of motion,

$$i(d/dt)S^\alpha(t) = [S^\alpha(t), \mathscr{H}]\,. \tag{29}$$

Examination of Eq. (27) verifies that the diagonal elements of $G_a(\omega)$ are real, even functions of ω. Accordingly, the odd diagonal moments $\langle\omega^{2n+1}\rangle^{\alpha\alpha}$ vanish, while

$$\langle\omega^{2n}\rangle^{\alpha\alpha} = (2/\pi)\int_0^\infty d\omega\omega^{2n}G_a{}^{\alpha\alpha}(\omega)\,. \tag{30}$$

The simplest moment, the zero'th moment or normalization, can be obtained directly from Eq. (28)

$$\langle\omega^0\rangle^{\alpha\beta} = \int_{-\infty}^\infty (d\omega/\pi)G_a{}^{\alpha\beta}(\omega) = \delta^{\alpha\beta}\,. \tag{31}$$

This section will be concluded with the calculation of the "unperturbed" correlation function $\mathbf{G}_0$ for a spin system interacting with an external constant magnetic field $\mathbf{H}_0$ but with no internal interactions. Taking $\mathbf{H}_0$ along the z direction, the Zeeman Hamiltonian

$$\mathscr{H}_0 = -\gamma H_0\hat{z}\cdot\mathbf{S} = -\omega_0\hat{z}\cdot\mathbf{S} \tag{32}$$

yields the equation of motion

$$(d/dt)\mathbf{S}(t) = -i\omega_0[\hat{z}\cdot\mathbf{S}, \mathbf{S}(t)] = -\omega_0\hat{z}\times\mathbf{S}(t)\,. \tag{33}$$

Recalling that,

$$(d/dt)\theta(t-t') = \delta(t-t')\,, \tag{34}$$

the "unperturbed" correlation function

$$\mathbf{G}_0(t-t') = [Tr(S^{\nu})^2]^{-1} Tr\mathbf{S}(t)\mathbf{S}(t')\theta(t-t') \tag{20}$$

is seen to satisfy

$$[(d/dt) + \omega_0\hat{z}\times]\mathbf{G}_0(t-t') = \delta(t-t')\mathbf{1}\,. \tag{35a}$$

On introducing the rotation operator $\mathbf{J}_z$,

$$\mathbf{J}_z = i\hat{z}\times\,, \tag{36}$$

the previous equation becomes

$$[(d/dt) - i\omega_0\mathbf{J}_z\cdot]\mathbf{G}_0(t-t') = \delta(t-t')\mathbf{1}\,. \tag{35b}$$

This equation has the obvious solution, in the "angular momentum" coordinate system which diagonalizes $\mathbf{J}_z$,

$$G_0{}^{mm'}(t-t') = \delta^{mm'}e^{im\omega_0(t-t')}\theta(t-t')\,. \tag{37}$$

The Fourier transform of this solution is

$$\begin{aligned} G_0{}^{mm'}(\omega) &= \delta^{mm'}\int_0^{\infty} dt e^{im\omega_0 t}e^{-\varepsilon t} \\ &= \delta^{mm'}(i/(\omega + i\varepsilon + m\omega_0))\,, \end{aligned} \tag{38}$$

where a convergence factor $e^{-\varepsilon t}$ has been inserted in the integrand, and the limit $\varepsilon \to +0$ is implied. Explicitly, Eq. (38) is to be used in integrals in the following fashion

$$1/(\omega + i\varepsilon + a) = P/(\omega + a) - \pi i\delta(\omega + a)\,, \tag{39}$$

where P indicates that the principal part of the integral is to be taken. Thus the absorptive part of the unperturbed correlation function is given by

$$G_{oa}{}^{mm'}(\omega) = \delta^{mm'}\pi\delta(\omega + m\omega_0)\,. \tag{40}$$

This result expresses, in the language of spin correlation functions, the well-known fact that a spin system with no internal interactions in an external field $\mathbf{H}_0$ absorbs energy only from those circularly polarized magnetic fields

$$\mathbf{h}_{\pm}(t) = h(\hat{x}\cos\omega_0 t \pm \hat{y}\sin\omega_0 t) \tag{41}$$

that diagonalize the rotation operator $\mathbf{J}_z$ and are of the resonance frequency $\omega_o = \gamma H_0$.

4. Spin systems with dipole-dipole interactions

In this section a homogeneous spin system with internal magnetic dipole-dipole interactions in addition to an interaction with an external field $\mathbf{H}_0$ will be considered. The dipole-dipole interaction

$$\mathscr{H}_D = (1/2)\gamma \sum_{ij}{}' r_{ij}{}^{-3}(\mathbf{s}_i\cdot\mathbf{s}_j - 3\hat{r}_{ij}\cdot\mathbf{s}_i\hat{r}_{ij}\cdot\mathbf{s}_j) \tag{1}$$

will be treated as a perturbation on an unperturbed system which has only the Zeeman interaction

$$\mathscr{H}_0 = -\gamma H_0\hat{z}\cdot\mathbf{S} = -\omega_0\hat{z}\cdot\mathbf{S}\,, \tag{2}$$

and the correlation function $\mathbf{G}$ will be calculated to second order in $\mathscr{H}_D$ for powdered materials.

Before considering the specific case of the dipole-dipole interaction, a general method of calculating $\mathbf{G}$ to second order in an arbitrary perturbation $\mathscr{H}_1$ on the Zeeman interaction $\mathscr{H}_0$ will be given. With this division of the Hamiltonian,

$$\mathscr{H} = \mathscr{H}_0 + \mathscr{H}_1\,,$$

the equation of motion of the spin operator becomes

$$(d/dt)\mathbf{S}(t) = -\omega_0\hat{z}\times\mathbf{S}(t) + i[\mathscr{H}_1(t), \mathbf{S}(t)]\,, \tag{3}$$

giving

$$\begin{aligned} &[(d/dt) + \omega_0\hat{z}\times]\mathbf{G}(t-t') = \delta(t-t')\mathbf{1} \\ &+ [Tr(S^{\nu})^2]^{-1} Tri[\mathscr{H}_1(t), \mathbf{S}(t)]\mathbf{S}(t')\theta(t-t')\,. \end{aligned} \tag{4}$$

Performing the same operations on $\mathbf{S}(t')$, and observing that in the applications that follow

$$Tr[\mathscr{H}_1, \mathbf{S}]\mathbf{S} = 0 \tag{5}$$

so that the linear perturbation term vanishes, yields

$$\begin{aligned} &[(d/dt + \omega_0\hat{z}\times)\mathbf{G}(t-t') - \delta(t-t')\mathbf{1}] \\ &\qquad\cdot(d^T/dt' - \times\hat{z}\omega_0) = \mathbf{I}(t-t')\,, \end{aligned} \tag{6}$$

where

$$\begin{aligned} \mathbf{I}(t-t') &= [Tr(S^{\nu})^2]^{-1} Tri[\mathscr{H}_1(t), \mathbf{S}(t)] \\ &\qquad\cdot i[\mathscr{H}_1(t'), \mathbf{S}(t')]\theta(t-t')\,. \end{aligned} \tag{7}$$

In Eq. (6), d^T/dt' signifies a derivative operating to the left on the variable t'. Since $\mathbf{G}$ depends only upon the time difference $t - t'$, the interaction function $\mathbf{I}$ must also depend only on this difference. Using the unperturbed correlation function $\mathbf{G}_0$ introduced in Section 3, the differential operations in Eq. (6) can be inverted. One obtains

$$\begin{aligned} \mathbf{G}(t-t') &= \mathbf{G}_0(t-t') + \int_{-\infty}^{\infty} dt_1 dt_2 \mathbf{G}_0(t-t_1) \\ &\qquad\cdot\mathbf{I}(t_1-t_2)\cdot\mathbf{G}_0(t_2-t')\,, \end{aligned} \tag{8}$$

as the application of the differential operators occurring in Eq. (6) to this result, and the use of the Eq. (3.35a) for $\mathbf{G}_0$ and its transpose, demonstrates. In Fourier space this equation becomes the simple algebraic relation

$$\mathbf{G}(\omega) = \mathbf{G}_0(\omega) + \mathbf{G}_0(\omega)\cdot\mathbf{I}(\omega)\cdot\mathbf{G}_0(\omega)\,. \tag{9}$$

The calculation of the interaction function $\mathbf{I}$ with the spin operators moving only under the application of the Zeeman interaction $\mathscr{H}_0$ yields the correlation function $\mathbf{G}$ to second order in the perturbation $\mathscr{H}_1$.

The preceding development will now be applied to the calculation of the correlation function for a spin system with dipole-dipole interactions. The commutator required for the evaluation of the interaction function $\mathbf{I}_D$ is

$$i[\mathscr{H}_D, \mathbf{S}] = 3\gamma^2 \sum_{ij}{}' r_{ij}{}^{-3}\hat{r}_{ij}\times\mathbf{s}_i\hat{r}_{ij}\cdot\mathbf{s}_j\,. \tag{10}$$

It can now be verified that the linear perturbation term (5) vanishes, for this entails

$$Tr[\mathscr{H}_D, \mathbf{S}]\mathbf{S} \sim Tr\mathbf{s}_i\mathbf{s}_j\mathbf{s}_k, = 0\,, \qquad i \neq j\,.$$

On inserting the commutator (10) in the definition (7) of the interaction function **I**, and introducing the now familiar and useful operator expression for the cross product,

$$(J^\beta)_{\alpha\gamma} = i\varepsilon^{\alpha(\beta)\gamma}\,, \tag{2.14}$$

we obtain

$$\begin{aligned} I_D^{\alpha\beta}(t-t') = -9\gamma^4 {\sum_{ij}}' {\sum_{kl}}' r_{ij}^{-3} r_{kl}^{-3} [Tr(S^\nu)^2]^{-1} \\ \cdot\, \theta(t-t') Tr \hat{r}_{ij} \cdot \mathbf{s}_i(t) \hat{r}_{ij} \cdot \mathbf{J}^\alpha \cdot \mathbf{s}_j(t) \hat{r}_{kl} \\ \cdot\, \mathbf{s}_k(t') \hat{r}_{ij} \cdot \mathbf{J}^\beta \cdot \mathbf{s}_l(t')\,. \end{aligned} \tag{11}$$

Now, with the neglect of the dipole-dipole interaction,

$$[tr(s^\nu)^2]^{-1} tr\mathbf{s}(t)\mathbf{s}(t')\theta(t-t') = \mathbf{G}_0(t-t')\,. \tag{12}$$

Accordingly, the trace occurring in (11) can be evaluated in zero'th order

$$i \neq j,\ k \neq l:$$

$$\begin{aligned} &[Tr(S^\nu)^2]^{-1} Tr s_i^\alpha(t) s_j^\beta(t) s_k^\gamma(t') s_l^\delta(t') \theta(t-t') \\ &= [I(I+1)/3N][\delta_{ik}\delta_{jl} G_0^{\alpha\gamma}(t-t') G_0^{\beta\delta}(t-t') \\ &\quad + \delta_{il}\delta_{jk} G_0^{\alpha\delta}(t-t') G_0^{\beta\gamma}(t-t')]\,, \end{aligned} \tag{13}$$

yielding the desired second-order expression

$$\begin{aligned} I_D^{\alpha\beta}(t) = 3\gamma^4 I(I+1) N^{-1} {\sum}' r_{ij}^{-6} \\ \times\, t\rho \mathbf{G}_0^T(t) \mathbf{J}^\alpha (\hat{r}_{ij}\hat{r}_{ij}) \mathbf{G}_0(t) [(\hat{r}_{ij}\hat{r}_{ij}), \mathbf{J}^\beta]\,. \end{aligned} \tag{14}$$

A compact and useful notation has been achieved here with the introduction of the symbol $t\rho$ which denotes the diagonal sum of tensor indices.

We shall now specialize the calculation to the case of powdered materials since this considerably reduces the number of algebraic manipulations and gives the results of most experimental interest. The interaction function **I** for a powdered material is obtained by averaging (14) over all crystal orientations. This averaging, according to Appendix B, gives

$$\langle \hat{r}^\alpha \hat{r}^\beta \hat{r}^\gamma \hat{r}^\delta \rangle_{\text{av}} = (1/15)(\delta^{\alpha\beta}\delta^{\gamma\delta} + \delta^{\alpha\gamma}\delta^{\beta\delta} + \delta^{\alpha\delta}\delta^{\beta\gamma})\,. \tag{B.3}$$

Thus, keeping in mind the antisymmetrical nature of the operator **J**, one obtains

$$\begin{aligned} \bar{I}_D^{\alpha\beta}(t) = (1/5)\gamma^4 I(I+1) N^{-1} {\sum_{ij}}' r_{ij}^{-6} \\ \times \{ t\rho \mathbf{G}_0(t) t\rho \mathbf{J}^\alpha \mathbf{G}_0(t) \mathbf{J}^\beta + t\rho \mathbf{J}^\alpha \mathbf{G}_0(t) t\rho \mathbf{J}^\beta \mathbf{G}_0(t) \\ + t\rho \mathbf{J}^\alpha \mathbf{G}_0(t) [\mathbf{J}^\beta \mathbf{G}_0(t) + \mathbf{G}_0(t) \mathbf{J}^\beta] \}\,. \end{aligned} \tag{15}$$

It is now convenient to work in the "angular momentum" coordinate system, for, as was shown in Section 2 for the susceptibility tensor, the only nonvanishing components of the spin correlation function of a powdered material are $\bar{G}^+$, $\bar{G}^0$, $\bar{G}^-$, with

$$\bar{G}^-(t-t'; \mathbf{H}_0) = \bar{G}^+(t-t'; -\mathbf{H}_0)\,. \tag{16}$$

Since the unperturbed correlation function $\mathbf{G}_0$ is diagonal in this coordinate system, the interaction function $\bar{\mathbf{I}}$ is also diagonal, and, according to (16), only the components $\bar{I}^+$, $\bar{I}^0$ need be calculated. Recalling the discussion that led to the diagonal form (2.13) of the susceptibility given in Section 2 and the transformation (2.16), one finds that these components are

$$\begin{aligned} \bar{I}_D^0(t) = (1/5)\gamma^4 I(I+1) N^{-1} {\sum_{ij}}' r_{ij}^{-6} \\ \times \{ t\rho \mathbf{G}_0(t) t\rho \mathbf{J}^z \mathbf{G}_0(t) \mathbf{J}^z + t\rho \mathbf{J}^z \mathbf{G}_0(t) t\rho \mathbf{J}^z \mathbf{G}_0(t) \\ + t\rho \mathbf{J}^z \mathbf{G}_0(t) [\mathbf{J}^z \mathbf{G}_0(t) + \mathbf{J}^z \mathbf{G}_0(t)] \}\,, \end{aligned} \tag{17}$$

and

$$\begin{aligned} \bar{I}_D^+(t) = (1/5)\gamma^4 I(I+1) N^{-1} {\sum_{ij}}' r_{ij}^{-6} \\ \times \{ t\rho \mathbf{G}_0(t) t\rho 2^{-1/2} \mathbf{J}^- \mathbf{G}_0(t) 2^{-1/2} \mathbf{J}^+ \\ + t\rho 2^{-1/2} \mathbf{J}^- \mathbf{G}_0(t) t\rho 2^{-1/2} \mathbf{J}^+ \mathbf{G}_0(t) \\ + t\rho 2^{-1/2} \mathbf{J}^- \mathbf{G}_0(t) \\ \cdot\, [2^{-1/2} \mathbf{J}^+ \mathbf{G}_0(t) + \mathbf{G}_0(t) 2^{-1/2} \mathbf{J}^+] \}\,, \end{aligned} \tag{18}$$

where

$$\mathbf{J}^\pm = \mathbf{J}^x \pm i\mathbf{J}^y\,. \tag{19}$$

Since the trace is invariant under unitary transformations, the terms appearing above can be evaluated in the "angular momentum" coordinate system. This greatly facilitates computation. With the use of the familiar properties of the rotation operator

$$\mathbf{J}^z |m\rangle = m|m\rangle\,,$$

$$2^{-1/2}\mathbf{J}^\pm |m\rangle = \begin{cases} |m \pm 1\rangle\,, & |m \pm 1| \leqq 1\,, \\ 0\,, & |m \pm 1| > 1\,, \end{cases} \tag{20}$$

the cyclic symmetry of the trace, and the result of Section 3

$$G_0^{mm'}(t) = \delta^{mm'} e^{im\omega_0 t}\theta(t)\,, \tag{3.37}$$

we secure

$$\begin{aligned} \bar{I}_D^0(t) = (1/3)\langle \Delta\omega^2 \rangle_D [4e^{2i\omega_0 t} + e^{i\omega_0 t} \\ + e^{-i\omega_0 t} + 4e^{-2i\omega_0 t}]\theta(t)\,, \end{aligned} \tag{21}$$

and

$$\begin{aligned} \bar{I}_D^+(t) = (1/3)\langle \Delta\omega^2 \rangle_D [2e^{2i\omega_0 t} + 3e^{i\omega_0 t} \\ + 3 + 2e^{-i\omega_0 t}]\theta(t)\,, \end{aligned} \tag{22}$$

where

$$\langle \Delta\omega^2 \rangle_D = (3/5)\gamma^4 I(I+1) N^{-1} \sum_{ij} r_{ij}^{-6}\,. \tag{23}$$

The Fourier transform of the "powder correlation function", $\bar{\mathbf{G}}(\omega)$, is obtained from the Fourier transform of **I**,

$$\bar{\mathbf{I}}_D(\omega) = \int_0^\infty dt e^{i\omega t} e^{-\varepsilon t} \bar{\mathbf{I}}_D(t) , \tag{24}$$

according to

$$\begin{aligned}\bar{G}_D{}^0(\omega) &= G_0{}^0(\omega) - G_0{}^0(\omega)\bar{I}_D{}^0(\omega)G_0{}^0(\omega) \\ &= \frac{i}{\omega + i\varepsilon} + \frac{i}{\omega + i\varepsilon}\Big\{(1/3)\langle\Delta\omega^2\rangle_D \\ &\quad \times \Big[\frac{4}{\omega + i\varepsilon + 2\omega_0} + \frac{1}{\omega + i\varepsilon + \omega_0} \\ &\quad + \frac{1}{\omega + i\varepsilon - \omega_0} + \frac{4}{\omega + i\varepsilon - 2\omega_0}\Big]\Big\} \frac{1}{\omega + i\varepsilon},\end{aligned} \tag{25}$$

and

$$\begin{aligned}\bar{G}_D{}^\pm(\omega) &= \frac{i}{\omega + i\varepsilon \pm \omega_0} + \frac{i}{\omega + i\varepsilon \pm \omega_0}\Big\{(1/3)\langle\Delta\omega^2\rangle_D \\ &\quad \times \Big[\frac{2}{\omega + i\varepsilon \pm 2\omega_0} + \frac{3}{\omega + i\varepsilon \pm \omega_0} + \frac{3}{\omega + i\varepsilon} \\ &\quad + \frac{2}{\omega + i\varepsilon \mp \omega_0}\Big]\Big\} \frac{1}{\omega + i\varepsilon \pm \omega_0} ,\end{aligned} \tag{26}$$

where the symmetry property (16) is indicated in the last equation.

The quantity of usual experimental interest is the cyclic energy gain of the system which is proportional to the absorptive part of the spin-correlation function. In the case of the diagonal form under consideration, this absorptive part is simply the real part of the correlation function,

$$\bar{G}_a{}^{mm'}(\omega) = Re\bar{G}^{mm'}(\omega) . \tag{27}$$

Upon making use of the symbolic relations which obtain validity in integrations

$$\begin{aligned}Im \frac{1}{(\omega + i\varepsilon - a)^n} &= -\frac{\pi}{(n-1)!}\left(-\frac{d}{d\omega}\right)^n \delta(\omega - a) \\ &= \frac{-\pi(-1)^n}{(n-1)!}\delta^{(n)}(\omega - a) ,\end{aligned} \tag{28}$$

and

$$\begin{aligned}\delta^{(1)}(\omega - a)f(\omega)g(\omega) &= -f^{(1)}(a)g(\omega)\delta(\omega - a) \\ &\quad + f(a)g(\omega)\delta^{(1)}(\omega + a) ,\end{aligned} \tag{29}$$

the absorptive part of the spin-correlation function is found to be given by

$$\begin{aligned}(1/\pi)\bar{G}_{aD}{}^0(\omega) &= \delta(\omega) + (1/3)\langle\Delta\omega^2\rangle_D\omega_0{}^{-2} \\ &\times \{\delta(\omega + 2\omega_0) + \delta(\omega + \omega_0) + \delta(\omega - \omega_0) \\ &+ \delta(\omega - 2\omega_0) - 4\delta(\omega)\} ,\end{aligned} \tag{30}$$

$$\begin{aligned}(1/\pi)\bar{G}_{aD}{}^+(\omega) &= \delta(\omega \pm \omega_0) + (1/3)\langle\Delta\omega^2\rangle_D\omega_0{}^{-2} \\ &\quad \times [2\delta(\omega \pm 2\omega_0) + 3\delta(\omega) \\ &\quad + (1/2)\delta(\omega \mp \omega_0) - (11/2)\delta(\omega \pm \omega_0) \\ &\quad \pm 2\omega_0\delta^{(1)}(\omega \mp \omega_0) \\ &\quad + (3/2)\omega_0{}^2\delta^{(2)}(\omega \pm \omega_0)] .\end{aligned} \tag{31}$$

The $\delta(\omega)$ terms of Eq. (30) which give an absorption line at zero frequency should be omitted. Detailed examination of these terms show that they arise entirely from diagonal matrix elements and do not correspond to actual transitions.

Linear polarization is used in a typical experimental setup. The intensities, width, and shift which the results above imply will now be given explicitly for this case.[8]

Equation (30) yields directly the two second-order results for the case of the time varying field $\mathbf{h}(t)$ parallel to the static field $\mathbf{H}_0$: intensity of the line[3] at ω_0

$$\int_{\sim\omega_0} d\omega(2/\pi)\bar{G}_{aD}{}^0(\omega) = (2/3)\langle\Delta\omega^2\rangle_D\omega_0{}^{-2} , \tag{32}$$

intensity of the line[3] at $2\omega_0$

$$\int_{\sim 2\omega_0} d\omega(2/\pi)\bar{G}_{aD}{}^0(\omega) = (2/3)\langle\Delta\omega^2\rangle_D\omega_0{}^{-2} . \tag{33}$$

The discussion of Eq. (3.28) given in Section 3 shows that the second-order perturbation calculation gives the *exact total* second moment; and according to (30) this is

$$\begin{aligned}\langle\omega^2\rangle^{zz} &= \int_0^\infty d\omega\omega^2(2/\pi)\bar{G}_{aD}{}^0(\omega) \\ &= (10/3)\langle\Delta\omega^2\rangle_D .\end{aligned} \tag{34}$$

The case of linear polarization with the time varying field $\mathbf{h}(t)$ perpendicular to the static field $\mathbf{H}_0$ requires the evaluation of G^{xx}. This is obtained by inverting the transformation (2.16),

$$G^{xx} = G^{yy} = (1/2)(G^+ + G^-) . \tag{35}$$

With the help of this transformation, (31) yields the following second-order perturbation results:

intensity of the Larmor line

$$\int_{\sim\omega_0} d\omega(2/\pi)\bar{G}_{aD}{}^{xx}(\omega) = 1 - (5/3)\langle\Delta\omega^2\rangle_D\omega_0{}^{-2} , \tag{36}$$

shift toward higher frequency of the Larmor line

$$\int_{\sim\omega_0} d\omega(\omega - \omega_0)(2/\pi)\bar{G}_{aD}{}^{xx}(\omega) = (2/3)\langle\Delta\omega^2\rangle_D\omega_0{}^{-1} \tag{37}$$

second moment of the Larmor line[4]

$$\int_{\sim\omega_0} d\omega(\omega-\omega_0)^2(2/\pi)\bar{G}_{aD}{}^{xx}(\omega)=\langle\Delta\omega^2\rangle_D\,, \tag{38}$$

intensity of the line at zero frequency[2]

$$\int_{\sim 0} d\omega(2/\pi)\bar{G}_{aD}{}^{xx}(\omega)=\langle\Delta\omega^2\rangle_D\omega_0{}^{-2}\,, \tag{39}$$

intensity of the line[2] at $2\omega_0$

$$\int_{\sim 2\omega_0} d\omega(2/\pi)\bar{G}_{aD}{}^{xx}(\omega)=(2/3)\langle\Delta\omega^2\rangle\omega_0{}^{-2}\,. \tag{40}$$

The absorptive part of the spin correlation function is normalized as

$$\int_0^\infty d\omega(2/\pi)\bar{G}_{aD}{}^{xx}(\omega)=1\,, \tag{41}$$

and gives the *exact total* second moment

$$\begin{aligned}\langle\omega^2\rangle^{xx}&=\int_0^\infty d\omega\omega^2(2/\pi)\bar{G}_{aD}{}^{xx}(\omega)\\&=\omega_0{}^2+(10/3)\langle\Delta\omega^2\rangle_D\,.\end{aligned} \tag{42}$$

Finally, we observe that with the inclusion of the neglected $\hbar$ and the replacement of γ by the more conventional $g\beta$, where β is the Bohr magneton,

$$\langle\Delta\omega^2\rangle_D=(3/5)g^4\beta^4\hbar^{-2}I(I+1)N^{-1}\sum_{ij}{}' r_{ij}{}^{-6}\,. \tag{43}$$

5. Spin systems with quadrupole interactions

In this section the electric quadrupole interaction of a spin system with electric-field gradients will be considered in addition to the magnetic dipole-dipole interaction worked out in the preceding section. The quadrupole interaction will be treated as a second-order perturbation in the formalism of the previous sections. This requires that it is a weak interaction in the sense that few spins are in such large field gradients that their contribution to an absorption line is split so far from the line as to be unobserved.[9] The calculation will be performed for powdered materials. If the electric potential at the position of the i'th spin is denoted by ϕ_i, the "irreducible part" of the gradient of the electric field strength at the i'th spin is

$$V_i^{\alpha\beta}=[\nabla^\alpha\nabla^\beta-(1/3)\delta^{\alpha\beta}\nabla^2]\phi_i=V_i^{\beta\alpha}\,. \tag{1}$$

The tensor $V_i^{\alpha\beta}$ is "irreducible" since it is symmetric and possesses a vanishing diagonal sum,

$$t\rho V_i=V_i^{\alpha\alpha}=0\,. \tag{2}$$

The electric quadrupole Hamiltonian is then[10]

$$\mathscr{H}_Q=\sum_{i=1}^N A_i^{\alpha\beta}s_i{}^\alpha s_i{}^\beta\,, \tag{3}$$

where

$$A_i^{\alpha\beta}=[eQ/2I(2I-1)]V_i^{\alpha\beta}\,. \tag{4}$$

The first step in the calculation of the correlation function, according to the development at the beginning of Section 4, is the evaluation of the commutator of $\mathscr{H}_Q$ and $\mathbf{S}$. After a short calculation, one finds

$$i[\mathscr{H}_Q,S^\alpha]=-\sum_i A_i^{\mu\nu}\varepsilon^{\nu\alpha\zeta}\{s_i{}^\mu,s_i^\zeta\}\,, \tag{5}$$

where the curly brackets denote the anticommutator,

$$\{s_i{}^\mu,s_i^\zeta\}=s_i{}^\mu s_i^\zeta+s_i^\zeta s_i{}^\mu\,. \tag{6}$$

It is shown in Appendix A that the trace of three spin operators is a completely antisymmetrical tensor. Hence, the linear quadrupole perturbation vanishes,

$$Tr[\mathscr{H}_Q,\mathbf{S}]\mathbf{S}\sim tr\{\mathbf{s},\mathbf{s}\}\mathbf{s}=0\,,$$

since it involves the trace of three spin operators of which two occur in a symmetrical form. Furthermore, there is no interference between the dipole-dipole interaction and the quadrupole interaction in second order. This interference would involve a function

$$\begin{aligned}I_{Q-D}{}^{\alpha\beta}(t-t')=[Tr(S^\nu)^2]^{-1}Tri[\mathscr{H}_Q,S^\alpha(t)]\\ \times i[\mathscr{H}_D,S^\beta(t')]\theta(t-t')\,,\end{aligned} \tag{7}$$

and a function $\mathbf{I}_{D-Q}$ of the same form but with $\mathscr{H}_Q$ and $\mathscr{H}_D$ interchanged. With the use of Eq. (5) for the first commutator appearing above and Eq. (4.10) for the second, it is seen that Eq. (7) contains only terms of the form

$$Tr\mathbf{s}_i(t)\mathbf{s}_i(t)\mathbf{s}_j(t')\mathbf{s}_k(t')\quad\text{with}\quad j\neq k$$

which vanish in lowest order.

Thus our task reduces to the evaluation of

$$\begin{aligned}I_Q{}^{\alpha\beta}(t-t')&=[Tr(S^\gamma)^2]^{-1}Tri[\mathscr{H}_Q,S^\alpha(t)]\\&\quad\times i[\mathscr{H}_Q,S^\beta(t')]\theta(t-t')\\&=[Tr(S^\gamma)^2]^{-1}\sum_{ij}A_i{}^{\mu\nu}A_j{}^{\lambda\kappa}\varepsilon^{\nu\alpha\zeta}\varepsilon^{\kappa\beta\eta}\\&\quad\times Tr\{s_i{}^\mu(t),s_i^\zeta(t)\}\\&\quad\times\{s_j{}^\lambda(t'),s_j{}^\eta(t')\}\theta(t-t')\,.\end{aligned} \tag{8}$$

The terms with $i\neq j$ in Eq. (8) vanish, for they are composed of two factors, each of the form

$$A_i^{\mu\nu}\varepsilon^{\nu\alpha\zeta}tr\{s^\mu,s^\zeta\}\sim A_i^{\mu\nu}\varepsilon^{\nu\alpha\mu}=0\,.$$

This simply states that the quadrupole interaction involves only a single spin. Accordingly,

$$\begin{aligned}I_Q{}^{\alpha\beta}(t-t')=[Tr(s^\gamma)^2]^{-1}\sum_i A_i^{\mu\nu}A_i^{\lambda\kappa}\varepsilon^{\nu\alpha\zeta}\varepsilon^{\kappa\beta\eta}(Tr1/tr1)\\ \times tr\{s^\mu(t),s^\zeta(t)\}\{s^\lambda(t'),s^\eta(t')\}\theta(t-t')\,.\end{aligned} \tag{9}$$

In lowest order, with $t>t'$,

$$\mathbf{s}(t)=\mathbf{G}_0(t-t')\cdot\mathbf{s}(t')\,, \tag{10}$$

since both $\mathbf{s}(t)$ and $\mathbf{G}_0(t-t')$ satisfy the same equation of motion for $t>t'$ and

$$t \to t' + 0: \qquad \mathbf{G}_0(t - t') \to \mathbf{1} .$$

Equation (10) and the following result from Appendix A,

$$\begin{aligned} trs^\sigma s^\tau s^\lambda s^\eta = (1/15)tr1I(I+1)\{&\delta^{\sigma\tau}\delta^{\lambda\eta}[(1/2) + I(I+1)] \\ &\times \delta^{\sigma\lambda}\delta^{\tau\eta}[-2 + I(I+1)] \\ &+ \delta^{\sigma\eta}\delta^{\tau\lambda}[(1/2) + I(I+1)]\} , \end{aligned} \tag{A.4}$$

reduce Eq. (9), in lowest order, to

$$\begin{aligned} I_Q{}^{\alpha\beta}(t) = {}&(1/5)[4I(I+1) - 3] \\ &\times N^{-1} \sum_i t\rho \mathbf{G}_0 \mathbf{J}^\alpha \mathbf{A}_i \mathbf{G}_0(t)[\mathbf{A}_i, \mathbf{J}^\beta] . \end{aligned} \tag{11}$$

The correlation function will be evaluated only for the case of powdered materials. It will be found shortly that the averaged quadrupole function $\mathbf{I}_Q$ is directly proportional to the average dipole-dipole function $\mathbf{I}_D$ of Section 4. There we obtained

$$\begin{aligned} I_D{}^{\alpha\beta}(t) = {}&3\gamma^4 I(I+1)N^{-1} \sum_{ij}{}' r_{ij}{}^{-6} \\ &\times t\rho \mathbf{G}_0(t)\mathbf{J}^\alpha(\hat{r}_{ij}\hat{r}_{ij})\mathbf{G}_0(t)[(\hat{r}_{ij}\hat{r}_{ij}), \mathbf{J}^\beta] . \end{aligned} \tag{4.14}$$

Now, according to Appendix B,

$$\begin{aligned} \langle A_i{}^{\alpha\beta} A_i{}^{\gamma\delta}\rangle_{\text{av}} = {}&(1/10)t\rho\mathbf{A}_i{}^2 \\ &\times [\delta^{\alpha\gamma}\delta^{\beta\delta} + \delta^{\alpha\delta}\delta^{\beta\gamma} - (2/3)\delta^{\alpha\beta}\delta^{\gamma\delta}] \end{aligned} \tag{B.6}$$

while

$$\begin{aligned} \langle(\hat{r}_{ij}\hat{r}_{ij})^{\alpha\beta}(\hat{r}_{ij}\hat{r}_{ij})^{\gamma\delta}\rangle_{\text{av}} = {}&(1/15) \\ &\times [\delta^{\alpha\gamma}\delta^{\beta\delta} + \delta^{\alpha\delta}\delta^{\beta\gamma} + \delta^{\alpha\beta}\delta^{\gamma\delta}] . \end{aligned} \tag{B.3}$$

The last term in the square brackets in these equations does not contribute to the average of (11) or (4.14) since it gives rise to a term of the form

$$t\rho \cdots [\mathbf{1}, \mathbf{J}_\beta] = 0 .$$

Hence

$$\begin{aligned} \bar{I}_Q{}^{\alpha\beta}(t) = {}&(1/5)[4I(I+1) - 3]N^{-1} \sum_i (1/10)t\rho\mathbf{A}_i{}^2 \\ &\times [3\gamma^4 I(I+1)N^{-1} \sum_{ij}{}' r_{ij}{}^{-6}(1/15)]^{-1} \\ &\times \bar{I}_D{}^{\alpha\beta}(t) . \end{aligned} \tag{12}$$

Recalling that

$$\langle\Delta\omega^2\rangle_D = (3/5)\gamma^4 I(I+1)N^{-1} \sum_{ij}{}' r_{ij}{}^{-6} \tag{4.23}$$

and defining

$$\langle\Delta\omega^2\rangle_Q = (3/50)[4I(I+1) - 3]N^{-1} \sum_i t\rho\mathbf{A}_i{}^2 , \tag{13}$$

Eq. (12) can be written as

$$\bar{I}_Q{}^{\alpha\beta}(t) = \frac{\langle\Delta\omega^2\rangle_Q}{\langle\Delta\omega^2\rangle_D} \bar{I}_D{}^{\alpha\beta}(t) . \tag{14}$$

Thus we find that for powdered materials, the results in second order for the quadrupole interaction are identical with the corresponding second-order results for the dipole-dipole interaction provided only that $\langle\Delta\omega^2\rangle_D$ is replaced by $\langle\Delta\omega^2\rangle_Q$. Since to this order of perturbation there is no interference between the dipole-dipole and quadrupole interactions, the complete second-order results for a spin system with both dipole-dipole and quadrupole interactions are given at the end of Section 4 upon replacing $\langle\Delta\omega^2\rangle_D$ by $\langle\Delta\omega^2\rangle$, where

$$\langle\Delta\omega^2\rangle = \langle\Delta\omega^2\rangle_D + \langle\Delta\omega^2\rangle_Q . \tag{15}$$

In terms of the electric field gradient,

$$\langle\Delta\omega^2\rangle_Q = (3/200)\frac{e^2Q^2}{\hbar^2}\frac{4I(I+1) - 3}{I^2(2I-1)^2}(1/N)\sum_i t\rho\mathbf{V}_i^2 \tag{16}$$

where the neglected $\hbar$ has been restored, and, of course,

$$t\rho\mathbf{V}_i{}^2 = \sum_{\alpha\beta} V_i{}^{\alpha\beta}V_i{}^{\beta\alpha} = \sum_{\alpha\beta}(V_i^{\alpha\beta})^2 . \tag{17}$$

Acknowledgments

I should like to thank Dr. Arthur G. Anderson for suggesting the investigation of the subject matter treated here and Robert Norris for his patience in reading the manuscript.

Appendix A: Spin traces

The trace operation does not distinguish a direction in space. Hence the trace of the product of n spin operators is an invariant tensor of rank n. This simple property will be used to evaluate the spin traces below.

Since no invariant vector exists, the trace of a single spin vanishes,

$$trs^\alpha = 0 . \tag{1}$$

The δ symbol is the only invariant second-rank tensor. Accordingly, the trace of two spin operators is

$$\begin{aligned} trs^\alpha s^\beta &= \delta^{\alpha\beta}tr(s^\nu)^2 = \delta^{\alpha\beta}(1/3)tr\mathbf{s}^2 \\ &= (1/3)I(I+1)tr1\delta^{\alpha\beta} \\ &= (1/3)I(I+1)(2I+1)\delta^{\alpha\beta} . \end{aligned} \tag{2}$$

The trace of three spin operators, which individually transform as pseudo-vectors, is an invariant pseudo-tensor of rank three and hence is proportional to the only rank three invariant pseudo-tensor $\varepsilon^{\alpha\beta\gamma}$. Since $\varepsilon^{\alpha\beta\gamma}$ is completely antisymmetric, the spin commutation relations and the preceding result yield

$$\begin{aligned} trs^\alpha s^\beta s^\gamma &= (1/2)tr[s^\alpha, s^\beta]s^\gamma = (i/2)\varepsilon^{\alpha\beta\nu}trs^\nu s^\gamma \\ &= (i/6)I(I+1)tr1\varepsilon^{\alpha\beta\gamma} . \end{aligned} \tag{3}$$

The trace of four spin operators transforms as an invariant fourth-rank tensor and hence must be related to the fourth-rank tensors which can be formed by taking permutations of the indices of $\delta^{\alpha\beta}\delta^{\gamma\delta}$,

$$tr s^{\alpha}s^{\beta}s^{\gamma}s^{\delta} = a\delta^{\alpha\beta}\delta^{\gamma\delta} + b\delta^{\alpha\gamma}\delta^{\beta\delta} + c\delta^{\alpha\delta}\delta^{\beta\gamma} .$$

The cyclic trace property

$$tr s^{\delta}s^{\alpha}s^{\beta}s^{\gamma} = tr s^{\alpha}s^{\beta}s^{\gamma}s^{\delta}$$

shows that the coefficients a and c must be identical. The remaining coefficients a and b can be found by contracting various indices and using Eqs. (2), (3),

$$\begin{aligned} tr \mathbf{s}^2 s^{\gamma}s^{\delta} &= I(I+1) tr s^{\gamma}s^{\delta} \\ &= (1/3)I^2(I+1)^2 tr 1\delta^{\gamma\delta} = (3a+b+a)\delta^{\gamma\delta} , \end{aligned}$$

$$\begin{aligned} tr s^{\alpha}s^{\beta}s^{\alpha}s^{\delta} &= tr \mathbf{s}^2 s^{\beta}s^{\delta} + tr s^{\alpha}[s^{\beta}, s^{\alpha}]s^{\delta} \\ &= (1/3)I(I+1) tr 1[I(I+1) - 1]\delta^{\beta\delta} \\ &= [a + 3b + a]\delta^{\beta\delta} . \end{aligned}$$

The solution of these equations yields

$$\begin{aligned} tr s^{\alpha}s^{\beta}s^{\gamma}s^{\delta} = (1/15)I(I+1) tr 1\{&\delta^{\alpha\beta}\delta^{\gamma\delta}[(1/2) + I(I+1)] \\ &+ \delta^{\alpha\gamma}\delta^{\beta\delta}[-2 + I(I+1)] \\ &+ \delta^{\alpha\delta}\delta^{\beta\gamma}[(1/2) + I(I+1)]\} . \end{aligned} \tag{4}$$

Appendix B: Tensor averages

Consider various arbitrary vectors $\mathbf{k}$, $\mathbf{l}$, $\cdots$ which are fixed in a rigid body. The average of the product of their components,

$$\langle k^{\alpha}l^{\beta}\cdots\rangle_{\text{av}} ,$$

is obtained when the rigid body in which the vectors are fixed is rotated over all possible orientations. The averaging process does not distinguish a direction in space. Thus the average of the product of n vectors is an invariant tensor of rank n. This simple property will be used to evaluate the averages below in a manner similar to that used in the preceding appendix to evaluate spin traces.

The average of the product of two vectors must be proportional to the invariant δ symbol,

$$\langle k^{\alpha}l^{\beta}\rangle_{\text{av}} = a\delta^{\alpha\beta} .$$

The constant a is determined by contracting $\alpha\beta$,

$$\langle \mathbf{k}\cdot\mathbf{l}\rangle_{\text{av}} = \mathbf{k}\cdot\mathbf{l} = 3a ,$$

and thus

$$\langle k^{\alpha}l^{\beta}\rangle_{\text{av}} = (1/3)\mathbf{k}\cdot\mathbf{l}\delta^{\alpha\beta} . \tag{1}$$

The average of the product of four vectors must be of the form

$$\langle k^{\alpha}l^{\beta}m^{\gamma}n^{\delta}\rangle_{\text{av}} = a\delta^{\alpha\beta}\delta^{\gamma\delta} + b\delta^{\alpha\gamma}\delta^{\beta\delta} + c\delta^{\alpha\delta}\delta^{\beta\gamma} .$$

The constants a, b, c are determined by forming various contractions and using Eq. (1),

$$\langle \mathbf{k}\cdot\mathbf{l}m^{\gamma}n^{\delta}\rangle_{\text{av}} = (3a + b + c)\delta^{\gamma\delta} = \mathbf{k}\cdot\mathbf{l}(1/3)\mathbf{m}\cdot\mathbf{n}\delta^{\gamma\delta} ,$$

$$\langle \mathbf{k}\cdot\mathbf{m}l^{\beta}n^{\delta}\rangle_{\text{av}} = (a + 3b + c)\delta^{\beta\delta} = \mathbf{k}\cdot\mathbf{m}(1/3)\mathbf{l}\cdot\mathbf{n}\delta^{\beta\delta} ,$$

$$\langle \mathbf{k}\cdot\mathbf{n}l^{\beta}m^{\gamma}\rangle_{\text{av}} = (a + b + 3c)\delta^{\beta\gamma} = \mathbf{k}\cdot\mathbf{n}(1/3)\mathbf{l}\cdot\mathbf{m}\delta^{\beta\gamma} .$$

These equations yield

$$\begin{aligned} \langle k^{\alpha}l^{\beta}m^{\gamma}n^{\delta}\rangle_{\text{av}} = (1/30)\{&(4\mathbf{k}\cdot\mathbf{l}\mathbf{m}\cdot\mathbf{n} - \mathbf{k}\cdot\mathbf{m}\mathbf{l}\cdot\mathbf{n} \\ &- \mathbf{k}\cdot\mathbf{n}\mathbf{l}\cdot\mathbf{m})\delta^{\alpha\beta}\delta^{\gamma\delta} \\ &+ (-\mathbf{k}\cdot\mathbf{l}\mathbf{m}\cdot\mathbf{n} + 4\mathbf{k}\cdot\mathbf{m}\mathbf{l}\cdot\mathbf{n} \\ &- \mathbf{k}\cdot\mathbf{n}\mathbf{l}\cdot\mathbf{m})\delta^{\alpha\gamma}\delta^{\beta\delta} + (-\mathbf{k}\cdot\mathbf{l}\mathbf{m}\cdot\mathbf{n} \\ &- \mathbf{k}\cdot\mathbf{m}\mathbf{l}\cdot\mathbf{n} . + 4\mathbf{k}\cdot\mathbf{n}\mathbf{l}\cdot\mathbf{m})\delta^{\alpha\gamma}\delta^{\beta\delta}\} . \end{aligned} \tag{2}$$

In Section 4 the average of four identical unit vectors is needed. It follows from the previous result that this average is

$$\langle \hat{r}^{\alpha}\hat{r}^{\beta}\hat{r}^{\gamma}\hat{r}^{\delta}\rangle_{\text{av}} = (1/15)(\delta^{\alpha\beta}\delta^{\gamma\delta} + \delta^{\alpha\gamma}\delta^{\beta\delta} + \delta^{\alpha\delta}\delta^{\beta\gamma}) . \tag{3}$$

The product of two second-rank tensors which are fixed in a rigid body transforms as the direct product $k^{\alpha}l^{\beta}m^{\gamma}n^{\delta}$. Thus Eq. (2) yields the average

$$\begin{aligned} \langle A^{\alpha\beta}B^{\gamma\delta}\rangle_{\text{av}} = (1/30)\{&4t\rho\mathbf{A}t\rho\mathbf{B} - t\rho\mathbf{A}^T\mathbf{B} - t\rho\mathbf{A}\mathbf{B})\delta^{\alpha\beta}\delta^{\gamma\delta} \\ &+ (-t\rho\mathbf{A}t\rho\mathbf{B} + 4t\rho\mathbf{A}^T\mathbf{B} - t\rho\mathbf{A}\mathbf{B})\delta^{\alpha\gamma}\delta^{\beta\delta} \\ &+ (-t\rho\mathbf{A}t\rho\mathbf{B} - t\rho\mathbf{A}^T\mathbf{B} + 4t\rho\mathbf{A}\mathbf{B})\delta^{\alpha\delta}\delta^{\beta\gamma}\} , \end{aligned} \tag{4}$$

where

$$t\rho\mathbf{A} = A^{\alpha\alpha}, \quad t\rho\mathbf{A}^T\mathbf{B} = A^{\beta\alpha}B^{\beta\alpha}, \quad \text{etc.} \tag{5}$$

This general result gives directly the average of the square of a symmetrical, traceless, second-rank tensor, such as that needed in Section 5,

$$\begin{aligned} \langle A^{\alpha\beta}A^{\gamma\delta}\rangle_{\text{av}} &= (1/15)t\rho\mathbf{A}^2 \\ &\times [(3/2)(\delta^{\alpha\gamma}\delta^{\beta\delta} + \delta^{\alpha\delta}\delta^{\beta\gamma}) - \delta^{\alpha\beta}\delta^{\gamma\delta}] . \end{aligned} \tag{6}$$

References and footnotes

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6. It should be noted that the spin correlation function (20) also describes directly the free induction decay of the spin system. See, for example, I. J. Lowe and R. E. Norberg, *Phys. Rev.* **107**, 46 (1957).
7. Similar results have been obtained by R. Kubo and K. Tomita, *J. Phys. Soc. Japan* **9**, 888 (1954).
8. An experimental verification of most of the following relations for the nuclear spin absorption of lithium nuclei in lithium metal has been obtained by A. G. Anderson, *Phys. Rev.* **125**, 1517 (1962). References to other experiments may be found in this paper.
9. That the quadrupole interaction be weak is also required for the maintenance of a uniform spin temperature throughout the spin system when an alternating magnetic field of long duration is applied. For it is an interaction not among the spins themselves but between the spin system and lattice.
10. See, for example, the article of M. H. Cohen and F. Reif in *Solid State Physics*, Academic Press, Inc., New York, 1957, Vol. 5, p. 331.

Received December 20, 1961