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Quadrupolar exchange effects on the dynamics of high-temperature paramagnets

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The spin dynamics of paramagnets with both isotropic dipolar and isotropic quadrupolar exchange terms in the spin-spin interaction Hamiltonian is investigated in the high-temperature limit. In particular, lowest-order integral equations for the dynamical two point correlation functions, which are measurable in magnetic resonance and ultrasonic magnetic resonance experiments are derived by the use of a previously developed diagrammatic technique. These equations are valid for all values of the dipolar to quadrupolar exchange energy ratio and for all values of the spin quantum number S. A systematic study of the numerical solutions to these equations is then made for $1 \leq S \leq 7/2$ and for various combinations of dipolar and quadrupolar exchange energies. The results of these calculations for the case of $S = 7/2$ are used in the following paper to help explain the observed nuclear acoustic resonance spectra in Ta^{181}.

I. INTRODUCTION

The concept of spin-spin interactions in a magnetic system is most often thought of in terms of the mutual interaction of the spins via their dipole ($l=1$) moments. In principle, however, the spins in such a system may also interact via their higher-order ($l>1$) multipole moments. It is the purpose of the present paper to investigate the effects on the high-temperature spin dynamics of the presence of a coupling between the quadrupole ($l=2$) moments of such spins.

First, however, it is useful to give a brief discussion of the usual interactions which take place between the dipole moments of the spins in a magnetic system. The simplest such interaction is described by the isotropic Heisenberg spin-exchange Hamiltonian,[1,2] which can be written

$$H_{\mathrm{ex}} = -\frac{1}{2} \sum_{i \neq j} J_0(i,j)\, \vec{S}(i) \cdot \vec{S}(j) , \tag{1}$$

where $\vec{S}(i)$ is the vector spin operator at the lattice site i and $J_0(i,j)$ is the exchange energy associated with a pair of spins at sites i and j. The interaction described by Eq. (1) is often the dominant spin-spin coupling in electronic spin systems and the exchange energy $J_0(i,j)$, whose range usually extends only over the first few neighbor shells,[1,2] is well understood to come physically from direct exchange in metallic magnetic systems and from indirect or superexchange in magnetic insulating systems.[1]

Although the Heisenberg exchange interaction is also often present in nuclear spin systems,[3-5] the dominant spin-spin interaction in these systems is usually the dipolar interaction,[6] which has the form

$$H_d = -\frac{1}{2} \sum_{i \neq j} \sum_{a,b} J_{ab}(i,j) S_a(i) S_b(j) , \tag{2}$$

where a and b run over the Cartesian indices x, y, and z and $J_{ab}(i,j) \sim 1/|\vec{R}_i - \vec{R}_j|^3$, where $\vec{R}_i$ and $\vec{R}_j$ are the position vectors of the lattice sites i and j; this interaction is thus a long-range anisotropic interaction. The dipole interaction is also often present in electron-spin systems, but it is usually much weaker than the Heisenberg interaction in such systems. It should also be noted that the spin-spin interaction in systems of spins with anisotropic exchange may also be written in the general form of Eq. (2) with $J_{ab}(i,j)$ being a short-range interaction in that case.

In principle, the coupling between a pair of spins in a magnetic system need not be limited to an interaction which takes place via their dipole moments and thus need not be representable as a coupling between the dipolar spin operators S_a. As is discussed in the literature,[7-9] a complete dynamical description of a single spin of magnitude S requires $(2S+1)^2$ independent operators.[7,8] At temperatures such that kT is large compared to any spin-spin interaction energy, the most convenient complete set of dynamical spin operators in the set of irreducible tensor multipole operators[7-9] $A_{lm}(i)$, where l and m are integers such that $|m| \leq l$ and $0 \leq l \leq 2S$. By using these operators, one may write the most general bilinear spin-spin interaction between pairs of spins (or between pairs of any physical quantities which are representable in terms of spin or angular momentum operators) as

$$H = -\frac{1}{2} \sum_{i \neq j} \sum_{l,m,m'} J_{l,m,m'}(i,j) A_{lm}(i) (A_{lm'}(j))^{\dagger} , \tag{3a}$$

where $J_{l,m,m'}(i,j)$ is a generalized potential which couples the spins at the sites i and j. For convenience, we rewrite Eq. (3a) as

$$H=\sum_{l=1}^{2S} H_l\,, \tag{3b}$$

where

$$H_l=-\frac{1}{2}\sum_{i\neq j}\sum_{l,m,m'} J_{l,m,m'}(i,j)A_{lm}(i)(A_{lm'}(j))^\dagger\,. \tag{3c}$$

The physical origins of the decomposition, Eq. (3b), should be quite clear. Since the A_{lm} with $l=1$ and $m=\pm1,0$ are proportional to the dipolar spin operators $S_\pm$, S_z, respectively, H_1 describes the general interaction between pairs of spins via their dipole ($l=1$) moments. In the general anisotropic case, H_1 is proportional to the dipolar or anisotropic exchange interaction, while if the potential $J_{l,m,m'}$ is isotropic (independent of m,m'), H_1 is proportional to the isotropic exchange interaction. Likewise, the $l=2$ term in Eq. (3) describes the general interaction between a pair of spins via their quadrupole ($l=2$) moments. The terms with $l>2$ in Eq. (3) are similarly interpreted.

Examples of systems where the interaction H_2 is known to be important are the molecular crystals solid H_2, D_2, HD,[10,11] and N_2.[12] In these systems, the anisotropic interaction energy $J_{2,m,m'}(i,j)$ has its physical origins in the electric quadrupole-quadrupole interaction between molecules[10,11] and thus varies as $1/|\vec{R}_i-\vec{R}_j|^5$. The $A_{2m}(i)$ in these systems represent the irreducible tensor operators of the rotational angular momenta of the molecules. In particular, in solid molecular hydrogen and deuterium, H_2 is the dominant orientationally dependent interaction between molecules. In addition to molecular crystal systems, the anisotropic quadrupolar interaction described by H_2 has been shown to be important in some rare-earth magnetic systems.[13-15]

For simplicity, throughout the rest of the paper we consider only isotropic interactions and keep only the $l=1$ and $l=2$ terms in the summation in Eq. (3b). Thus the Hamiltonian to be considered has the form

$$H=H_1+H_2\,, \tag{4a}$$

where

$$H_1=-\frac{1}{2}\sum_{i\neq j} J_1(i,j)\sum_{m=-1}^{1} A_{lm}(i)(A_{lm}(j))^\dagger\,, \tag{4b}$$

and

$$H_2=-\frac{1}{2}\sum_{i\neq j} J_2(i,j)\sum_{m=-2}^{2} A_{2m}(i)(A_{2m}(j))^\dagger\,. \tag{4c}$$

As is stated above, H_1 given by Eq. (4b) is clearly proportional to the usual isotropic dipolar exchange Hamiltonian given by Eq. (1). In the rest of this paper we shall extend this terminology to the isotropic quadrupolar interaction. Thus in Eq. (4c), H_1 and H_2 will be referred to, respectively, as the dipolar and quadrupolar exchange interactions. It should be noted that in adopting this terminology, we have at this point made no assumptions regarding the range of the "exchange" potentials $J_1(i,j)$ and $J_2(i,j)$.

There has recently been speculation[16,17] that the dominant spin-spin interaction between the nuclear spins in Ta is the quadrupolar exchange Hamiltonian H_2 rather than the usual dipolar exchange interaction H_1. The physical origin of the coupling between the quadrupole moments of the nulcear spins in this system is probably an indirect coupling via the conduction electrons,[16,17] and since ^{181}Ta has a large quadrupole moment, this interaction could be the dominant one between the nuclear spins.

Motivated by this speculation, we have investigated the high-temperature spin dynamics of a system where the interaction between spins contains both dipolar and quadrupolar exchange terms. In particular, for the system described by the Hamiltonian of Eq. (4), we have calculated the two-point dynamical spin-correlation functions which are measurable in electromagnetic and ultrasonic magnetic resonance experiments. These correlation functions are also characterized by a quantum number l. The $l=1$ or dipolar correlation function is measurable in an ordinary magnetic resonance experiment,[9,18] while the $l=2$ or quadrupolar correlation function is measurable in an ultrasonic magnetic resonance experiment.[9,18] The $l=1$ and $l=2$ correlation functions are in general very different from each other.[9] Here we are primarily interested in how these correlation functions (or line-shape functions) depend on the type of exchange Hamiltonian and on the spin quantum number S. We have thus calculated both the $l=1$ and the $l=2$ correlation functions for various combinations of dipolar and quadrupolar exchange and for a number of values of the spin quantum number S. The approximation used is the infinite-temperature "bubble approximation" or mode-mode coupling approximation which has previously yielded good results when applied to a variety of other spin problems[9,19-23] and is the lowest-order approximation in a systematic diagrammatic expansion of the spin self-energy in a Brillouin-Wigner kind of perturbation theory in the spin-spin interaction.[9] In the following paper,[24] we use some of the results obtained here for the $l=1$ and $l=2$ correlation functions to explain the observed nuclear acoustic resonance (NAR) line shapes obtained for ^{181}Ta.

Isotropic spin-spin interactions which take place via dipolar and quadrupolar exchange are often referred to in the literature as Heisenberg and biquadratic exchange interactions.[25-33] The Hamiltonian between pairs of spins in the presence of these interactions may be written

$$H' = -\frac{1}{2}\sum_{i\neq j} J_0(i,j)\vec{S}(i)\cdot\vec{S}(j) - \frac{1}{2}\sum_{i\neq j} j(i,j)(\vec{S}(i)\cdot\vec{S}(j))^2 , \tag{5}$$

where the term proportional to $j(i,j)$ is referred to as the biquadratic exchange term. The physical and mathematical differences between the Hamiltonian of Eqs. (4) and (5) are worth noting. As is shown in Appendix A, they are identical if J_1 and J_2 are chosen to be the appropriate functions of J_0 and j and if multipolar interactions with $l > 2$ are neglected. However, the relationship between the quantities J_1, J_2 and J_0, j is not a trivial one in that J_1 depends on J_0, j, and S. Further, Eq. (5) may be viewed as the first two terms in a power series expansion in powers of $(\vec{S}(i)\cdot\vec{S}(j))$ while Eq. (4) is an expansion in terms of the multipole components of the spins. By means of methods like those used in Appendix A, equations relating the coefficients in the two series could be derived.

We feel that the multipole expansion is the more general and physically more intructive way to express the interaction. Furthermore, at least at high temperatures, it is also superior from a computational point of view. In Eq. (4) the contribution to the spin-spin interaction from each spin multipole component occurs in a separate term. Thus the contributions from the dipole $(l=1)$ and quadrupole $(l=2)$ moments are distinct and the interaction energies J_1 and J_2 represent the true dipolar and quadrupolar exchange energies in the sense that they are the total energies which characterize these multipolar interactions. Therefore, the physical meaning of the terms in the multipolar expansion can be clearly understood because they can be associated with the usual multipole moments of atoms or nuclei in the theory of electromagnetism. The terms in the expansion can thus be related to well known quantities with which every physicist is familiar.

On the other hand, in the series expansion in powers of $(\vec{S}(i)\cdot\vec{S}(j))$, the individual terms have no such simple physical interpretation; a term proportional to $(\vec{S}(i)\cdot\vec{S}(j))^n$ contains in general contributions from all multipoles with $l \leq n$. A precise physical meaning for such a term is therefore difficult to obtain. The total dipolar energy obtained from a generalization of Eq. (5) to nth order would, for example, be a series containing n terms, with each term in the series being identifiable with the part of the corresponding term in the generalized Hamiltonian which is proportional to the dipole-dipole interaction.

For these reasons, we will take the Hamiltonian given by Eq. (4) as the fundamental interaction for spin systems where coupling between the quadrupole moments of the spins is present. However, in order to make contact with a large body of literature[25-33] which uses Eq. (5) as the fundamental interaction, in Appendix A we show the relationship between the quantities J_0, j and J_1, J_2 if multipolar interactions with $l > 2$ are neglected.

In addition to the ^{181}Ta nuclear-spin system, there are a number of electron-spin systems where isotropic quadrupolar or biquadratic exchange effects are believed to be important. For example, such effects have been observed in magnetic compounds such as MnAs, UO_2, UP, TbSb, MnO, α-MnS, EuSe, and $PrAlO_3$,[34] in rare-earth vanadates, arsenates, phosphates, and pnictides, and in certain spinels (such as $MnCr_2S_4$ and $Li_{0.5}Fe_{1.7}Al_{1.8}O_4$).[34] In addition, the existence of such interactions has been shown to be important for the explanation of the EPR spectra in the system MgO:Mn^{2+}.[25,26] In such systems, the quadrupolar exchange energy $J_2(i,j)$ has its physical origin in a variety of different effects, each of which could be present in a given system separately or in the presence of any or all of the others. Among the effects which are believed to be responsible for this interaction energy are cooperative Jahn-Teller distortions,[15] orbital contributions to superexchange,[1,35] multielectron exchange,[36,37] magnetostriction,[25] virtual-phonon coupling,[15] indirect exchange via conduction electrons,[38] crystal field effects,[13] and electric quadrupole-quadrupole interactions.[13,35] In some cases, these quadrupolar couplings between spins can exceed the usual dipolar coupling; this is especially true if the magnetic ions are of the Jahn-Teller type.[15] Unfortunately, despite the importance of such quadrupolar effects in the systems mentioned above and despite the fact that current experimental techniques would probably make such experiments feasible in at least some of these systems, there appears at present to be no experiments in any such systems which have measured the high-temperature correlation functions that we calculate.

Because of the importance of quadrupolar spin-spin interactions in the compounds listed above, as well as the interest in the Hamiltonians in Eqs. (4) and (5) as interesting model systems in themselves, there have been numerous calculations in the literature of the dynamical and thermodynamical properties of magnetic systems described by these interactions. Usually, these calculations have dealt with the properties of such a model systems at either very low temperatures or at temperatures near the dipolar or quadrupolar transition temperature.[25-33] To our knowledge, there are no calculations which refer to the high-temperature correlation functions which we calculate; our calculation is valid only in the extreme high-temperature limit where kT is much greater than any dipolar or quadrupolar ordering temperature.

The remainder of this paper is organized as follows. Section II contains a brief discussion of the formalism used to calculate the dynamical $l=1$ and $l=2$ correlation functions. In particular, the spin self-energy method[9] is applied to the spin system whose interaction is described by the Hamiltonian of Eq. (4) and the lowest order or "bubble" equations for the self-energy, which result in nonlinear integral equations for the correlation functions, are derived for this system for all values of the spin quantum number S. In Sec. III, the method of solution of these equations is discussed and they are solved numerically for $1 \leq S \leq \frac{7}{2}$ and for various ratios of dipolar to quadrupolar exchange energies. Because the methods used in Secs. II and III for the derivation and solution of the nonlinear integral equations for the spin-correlation functions are so similar to previous calculations,[9,19-23] the discussion in these sections will be as brief as possible, with only those details which are unique to the current problem discussed at any great length. Finally, Sec. IV contains a brief summary and conclusions.

II. FORMALISM

Following Ref. 9, the two-point correlation functions which we will consider here are defined in the high-temperature limit as

$$G_{\alpha\beta}(i,j;t-t') = \langle A_\alpha(i,t) A_\beta^\dagger(j,t')\rangle \theta(t-t') , \qquad (6)$$

where the angular brackets denote a thermal average, $\theta(t)$ is a step function, and $\alpha=(l,m)$. The quantities A_α are the irreducible tensor operators mentioned in Sec. I. The correlation functions $G_{\alpha\beta}$ may be Fourier transformed in time and space in the standard manner[9]

$$G_{\alpha\beta}(i-j,t-t') = \frac{1}{N} \sum_{\vec{q}} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} G_{\alpha\beta}(\vec{q},\omega) e^{i\vec{q}\cdot(\vec{r}_i-\vec{r}_j)} \times e^{-i\omega(t-t')} , \qquad (7)$$

where N is the number of lattice sites and the summation is over all wave vectors $\vec{q}$ in the first Brillouin zone. The Fourier-transformed function $G_{\alpha\beta}(\vec{q},\omega)$ is the quantity of primary interest in the

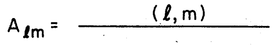

FIG. 1. Graphical representation for the operator A_{lm}.

calculations to follow.

In order to obtain self-consistent equations for the $G_{\alpha\beta}(\vec{q},\omega)$ in the presence of both dipolar and quadrupolar exchange, the diagrammatic method developed in Refs. 9 and 39 will be used and applied to the Hamiltonian given in Eq. (4). Since it is basically the same method as was employed for several previous calculations,[9,19-23] the following derivation will be as brief as possible with the main emphasis being on the features which are unique to the problem at hand. The starting point for the derivation is the expression of the correlation function in terms of a mass operator or self-energy $\Sigma_{\alpha\beta}(\vec{q},\omega)$.[9,39] In the high-temperature limit, this function is defined by the equation[9,39]

$$\omega G_{\alpha\beta}(\vec{q},\omega) - \Sigma_{\alpha\gamma}(\vec{q},\omega) G_{\gamma\beta}(\vec{q},\omega) = i\delta_{\alpha\beta} , \qquad (8)$$

where γ is summed over. This definition of Σ is only practical, however, if the self-energy can be expressed in terms of the correlation function G. A diagrammatic method for doing precisely that was developed in Refs. 9 and 39 and will now be applied to the Hamiltonian of Eq. (4).

The graphical representation of the operators A_{lm} which we will use will be a single line with the label (l,m) as is illustrated in Fig. 1. The Reiter-type[7,9] vertices for the interaction, Eq.

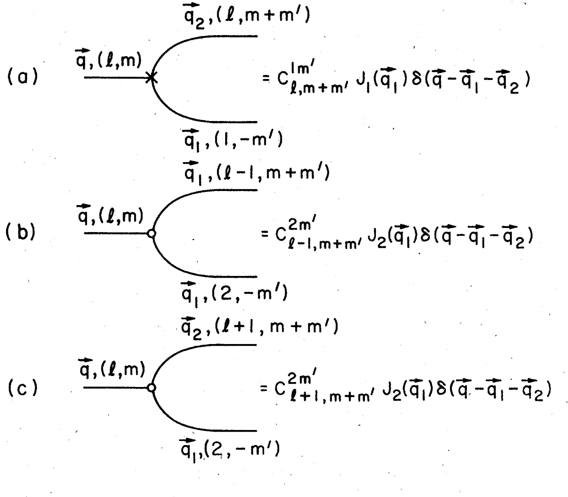

FIG. 2. Basic vertices for the Hamiltonian of Eq. (4). (a) Basic vertex for the dipolar exchange term; (b) and (c) basic vertices for the quadrupolar exchange term.

(4), are formed exactly as in previous calculations[9, 19-23] and are shown with their analytic expressions in Fig. 2, where a cross at the vertex corresponds to J_1, while an open circle corresponds to J_2. Only the vertices shown in Fig. 2 will be considered here since they give all of the moments exactly to order $1/z$, where z is the number of spins in the range of the interaction.[9, 39] In that figure, the quantities $C^{lm'}_{l,m+m'}$ and $C^{2m'}_{l\pm1,m+m'}$ are coefficients related to the commutators of the A_{lm} in the following manner:

$$[A_{1m'},A_{lm}]=C^{1m'}_{l,m+m'}A_{l,m+m'}\ , \tag{9a}$$

and

$$[A_{2m'},A_{lm}]=C^{2m'}_{l-1,m+m'}A_{l-1,m+m'}+C^{2m'}_{l+1,m+m'}A_{l+1,m+m'}\ . \tag{9b}$$

The explicit forms for these coefficients as functions of l, m, and S are derived in Appendix B.

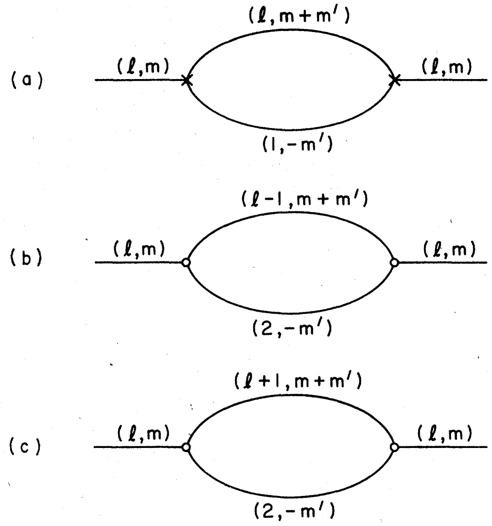

FIG. 3. Basic "bubble" diagrams. (a) Contribution of dipolar exchange; (b) and (c) contributions of quadrupolar exchange.

For the infinite temperature limit under consideration here, only the diagonal correlation functions $G_{\alpha\alpha}$ and diagonal self-energies $\Sigma_{\alpha\alpha}$ are nonzero. Furthermore, because the interaction is isotropic, all of these functions are independent of m. Therefore, in the following discussion, the abbreviations $G_{\alpha\alpha}=G_\alpha=G_{lm}=G_l$ and $\Sigma_{\alpha\alpha}=\Sigma_\alpha=\Sigma_{lm}=\Sigma_l$ will be used. The vertices shown in Fig. 2 can be used to construct diagrams for Σ_l which are valid to any order in the interaction. Here, however, only the lowest-order or "bubble" approximation[9, 39] will be considered and the remainder of this paper will be concerned only with this lowest-order approximation. These "bubble" diagrams are formed by connecting two of the vertices of Fig. 2. The basic bubble diagrams are shown in Fig. 3. In this lowest-order approximation, it was found that the "cross term" between the J_1 and J_2 vertices which appears to be present for $l=2$ vanishes. Evaluation of these diagrams by the rules discussed in Refs. 9 and 39 gives the following expression for $\Sigma_l(\vec{q},t)$:

$$\begin{aligned}\Sigma_l(\vec{q},t)=&\frac{i3l(l+1)}{S(S+1)N}\sum_{\vec{q}_1}[(J_1(\vec{q}_1))^2-J_1(\vec{q}_1)J_1(\vec{q}-\vec{q}_1)\delta_{l1}]G_1(\vec{q}_1,t)G_l(\vec{q}-\vec{q}_1,t)\\&+\frac{i}{N}\sum_{\vec{q}_1}G_2(\vec{q}_1,t)\{[(J_2(\vec{q}_1))^2-J_2(\vec{q}_1)J_2(\vec{q}-\vec{q}_1)\delta_{l3}]F_-(l,S)G_{l-1}(\vec{q}-\vec{q}_1,t)\\&\qquad+[(J_2(\vec{q}_1))^2-J_2(\vec{q}_1)J_2(\vec{q}-\vec{q}_1)\delta_{l1}]F_+(l,S)G_{l+1}(\vec{q}-\vec{q}_1,t)\}\ ,\end{aligned} \tag{10}$$

where $J_1(\vec{q})$ and $J_2(\vec{q})$ are the Fourier transforms of $J_1(i,j)$ and $J_2(i,j)$, the coefficient $3l(l+1)/S(S+1)$ comes from the evaluation of $\sum_{m'}(C^{lm'}_{l,m+m'})^2$ using the explicit expressions shown in Appendix B, and the functions $F_\pm(l,S)$ are derived and defined in that Appendix. It should be noted from the expressions in Appendix B that $F_-(1,S)=F_+(2S,S)=0$ as they should (this means that Σ_l is not coupled to G_{2S+1} or G_0). Equations (8) and (10) form a set of self-consistent integral equations for the G_l and Σ_l. For a given S there are $2S$ coupled equations.

III. SOLUTION OF THE EQUATIONS AND NUMERICAL RESULTS

In this section, the solutions to nonlinear integral equations derived in Sec. II will be described for the cases $1\leq S\leq\frac{7}{2}$ and for several combinations of dipolar and quadrupolar exchange. The method of solution is a procedure which is similar to that used in previous calculations[9,19-23]; this method will therefore be only briefly discussed here.

For convenience, G_l and Σ_l are first expressed in terms of their spectral representations as

$$G_l(\vec{q},\omega)=i\int_{-\infty}^{\infty}\frac{d\omega'}{\pi}\,\frac{g_l(\vec{q},\omega')}{\omega-\omega'+i\epsilon}\,, \tag{11a}$$

and

$$\Sigma_l(\vec{q},\omega)=\int_{-\infty}^{\infty}\frac{d\omega'}{\pi}\,\frac{\Gamma_l(\vec{q},\omega')}{\omega-\omega'-i\epsilon}\,,$$

$$\equiv \Pi_l(\vec{q},\omega)-i\Gamma_l(\vec{q},\omega)\,, \tag{11b}$$

where ϵ is a positive infinitesimal quantity. The quantity $g_l(\vec{q},\omega)$ is the line-shape function measured in magnetic resonance ($l=1$) and ultrasonic magnetic resonance ($l=2$) experiments. This function is related to the functions $\Pi_l(\vec{q},\omega)$ and $\Gamma_l(\vec{q},\omega)$ by the equation

$$g_l(\vec{q},\omega)=\frac{\Gamma_l(\vec{q},\omega)}{[\omega-\Pi_l(\vec{q},\omega)]^2+[\Gamma_l(\vec{q},\omega)]^2}\,, \tag{12}$$

as may be seen by combining Eqs. (8) and (11). If the above spectral function representations are used and Eq. (10) is Fourier transformed, the result is

$$\begin{aligned}\Gamma_l(\vec{q},\omega)=\frac{3l(l+1)}{S(S+1)N}\sum_{\vec{q}_1}\,[(J_1(\vec{q}_1))^2-J_1(\vec{q}_1)\,J(\vec{q}-\vec{q}_1)\delta_{l1}]\int_{-\infty}^{\infty}\frac{d\omega_1}{\pi}\,g_1(\vec{q}_1,\omega_1)g_l(\vec{q}-\vec{q}_1,\omega-\omega_1)\\ +\frac{1}{N}\sum_{\vec{q}_1}\int_{-\infty}^{\infty}\frac{d\omega_1}{\pi}\,g_2(\vec{q}_1,\omega_1)\{[(J_2(\vec{q}_1))^2-J_2(\vec{q}_1)\,J_2(\vec{q}-\vec{q}_1)\delta_{l3}]\,F_-(l,S)g_{l-1}(\vec{q}-\vec{q}_1,\omega-\omega_1)\\ +[(J_2(\vec{q}\;))^2-J_2(\vec{q}_1)\,J_2(\vec{q}-\vec{q}_1)\delta_{l1}]\,F_+(l,S)\,g_{l+1}(\vec{q}-\vec{q}_1,\omega-\omega_1)\}\,,\end{aligned} \tag{13}$$

Equations (12) and (13) are the sets of nonlinear integral equations that we will solve in this section. Solving these equations could be very difficult in the general case. Thus, as in previous calculations,[9,19-23] only the "local" versions of these equations will be solved. This "local" approximation may be mathematically expressed in real space by the equation $G_\alpha(i,j,t)\simeq\delta\vec{r}_i,\vec{r}_j\,G_\alpha(t)$, which amounts to treating the $G_\alpha(\vec{q},t)$ as $\vec{q}$ independent functions. The philosophy behind making such a "local" or $\vec{q}$-independent approximation has been thoroughly discussed before.[9,19-23] Essentially, by making such an approximation to Eq. (13) and obtaining the solution to that approximate equation one makes errors of the order of $1/z$. But since Eq. (13) is itself only valid to that order, making such an approximation cannot cause too great an error. It should be emphasized that such an approximation is not a necessary one to solve Eq. (13) but is is a convenient one which has proven useful and accurate in the past[9,19-23] and which makes the solution of Eq. (13) much simpler numerically. It should also be emphasized that although the "local" or $\vec{q}$-independent functions which result from solving the local system of equations are not necessarily good approximations to the corresponding $\vec{q}$-dependent functions, they can be used to generate a first approximation to the latter functions. This can be accomplished by substitution of the "local" solutions into the "nonlocal" or $\vec{q}$-dependent equations. Furthermore, it has been shown previously[9,39] that in some cases the functions $g_\alpha(\vec{q},\omega)$ are independent of $\vec{q}$ to a first approximation. Finally, many magnetic resonance and ultrasonic magnetic resonance properties depend only on either the $\vec{q}$-independent functions or the $\vec{q}$-dependent functions at small $\vec{q}$. This fact has been domonstrated in previous calculations[9,19-23] and will be utilized again in the following paper.[24]

In what follows, it is convenient to use dimensionless variables so that frequencies are measured relative to V, which is defined as

$$V^2=\frac{6}{S(S+1)}\,(V_1^2+5V_2^2)\,, \tag{14a}$$

where

$$V_l^2 \equiv \frac{1}{N}\sum_{\vec{q}_1} (J_l(\vec{q}_1))^2, \quad l=1,2\,. \tag{14b}$$

When frequencies are measured in these units, the second moment of the "local" linewidth function $\Gamma_1(\omega)$[9] is unity; the quantity V^2 is the second moment of this function. In terms of such dimensionless variables, the "local" version of Eq. (13) takes the form

$$\begin{aligned}\tilde{\Gamma}_l(y) = {} & \frac{3l(l+1)}{S(S+1)}\frac{V_1^2}{V^2}\int_{-\infty}^{\infty}\frac{dy_1}{\pi}\,\tilde{g}_1(y_1)\tilde{g}_l(y-y_1)\\ & +\frac{V_2^2}{V^2}\int_{-\infty}^{\infty}\frac{dy_1}{\pi}\,\tilde{g}_2(y_1)[F_-(l,S)\tilde{g}_{l-1}(y-y_1)\\ & +F_+(l,S)\tilde{g}_{l+1}(y-y_1)]\,,\end{aligned} \tag{15}$$

where $y=\omega/V$ is a dimensionless frequency and the tilde on the function $\tilde{\Gamma}_l(y)$ and $\tilde{g}_l(y)$ denotes that they are dimensionless. Similarly, the dimensionless "local" forms of Eqs. (11) and (12) are

$$\tilde{g}_l(y)=\tilde{\Gamma}_l(y)/\{[y-\tilde{\Pi}_l(y)]^2+[\tilde{\Gamma}_l(y)]^2\}\,, \tag{16}$$

and

$$\tilde{\Pi}_l(y)=\mathrm{P}\int_{-\infty}^{\infty}\frac{dy_1}{\pi}\,\frac{\tilde{\Gamma}_l(y_1)}{y-y_1}\,, \tag{17}$$

where P denotes the principle part integral. Equations (15)–(17) are the "local" equations which will now be solved.

These equations have been solved numerically for all values of S in the range $1 \leqslant S \leqslant \frac{7}{2}$ for a variety of ratios of V_1 to V_2. Some representative results for the "local" dipolar and quadrupolar spectral functions $\tilde{g}_1(y)$ and $\tilde{g}_2(y)$ are shown in Figs. 4–8. The $\tilde{g}_l(y)$ for $l>2$ were also obtained, of course, but since they appear to be inaccessible experimentally, they will only briefly be described at the end of this section. In the figures, the particular cases $V_2=0$, $V_1=0$, and $V_1=V_2$, corresponding to pure dipolar exchange, pure quadrupolar exchange, and equal dipolar and quadrupolar exchange, respectively, are shown; the first case is shown for arbitrary S, the second for both $S=1$ and $S=\frac{7}{2}$, and the third for both $S=\frac{3}{2}$ and $S=\frac{7}{2}$.

The case of pure dipolar exchange ($V_2=0$) is illustrated in Fig. 4. It is clear from Eq. (15) that in this case the local functions are independent of S; the curves for $\tilde{g}_1(y)$ and $\tilde{g}_2(y)$ shown in that figure are therefore valid for all S. Furthermore, the results presented in that figure are identical to the results for those functions which we obtained in Ref. 9, as they should be. It can be seen from Fig. 4 that both functions are monotonically decreasing functions of y and that both fall off exponentially at large values of y. In fact, $\tilde{g}_1(y)$ looks quite similar to a true Gaussian function. However, it is slightly flatter around $y=0$ than a true Gaussian. On the other hand, $\tilde{g}_2(y)$ is decidedly non-Gaussian in that is is much flatter near $y=0$ and falls off much more steeply with increasing y.

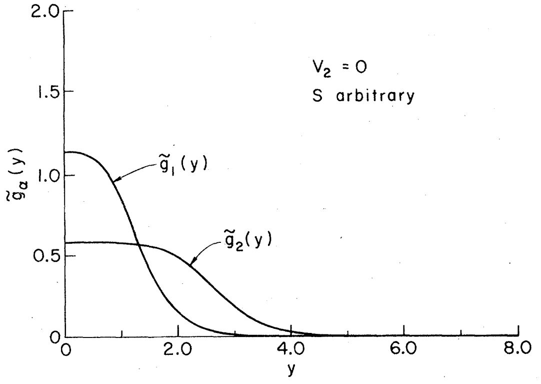

FIG. 4. Dipolar and quadrupolar spectral functions $\tilde{g}_1(y)$ and $\tilde{g}_2(y)$ for $V_2=0$ and S arbitrary.

The case of pure quadrupolar exchange ($V_1=0$) is illustrated for $S=1$ and for $S=\frac{7}{2}$ in Figs. 5 and 6, respectively. As can be seen from those figures, the results for both the dipolar and the quadrupolar spectral functions in this case are very different from the results obtained for the case of pure dipolar exchange and the results obtained in this case for $S=1$ and for $S=\frac{7}{2}$ are also very different from each other. For $S=1$, il-

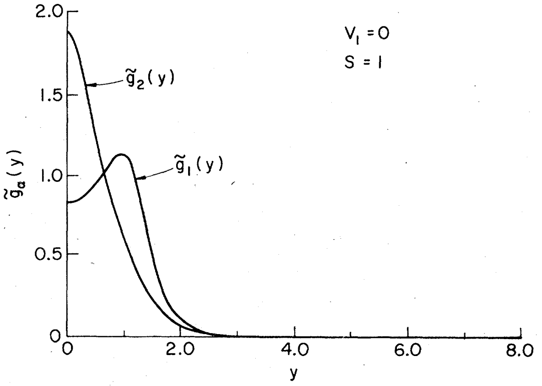

FIG. 5. Functions $\tilde{g}_1(y)$ and $\tilde{g}_2(y)$ for $V_1=0$ and $S=1$.

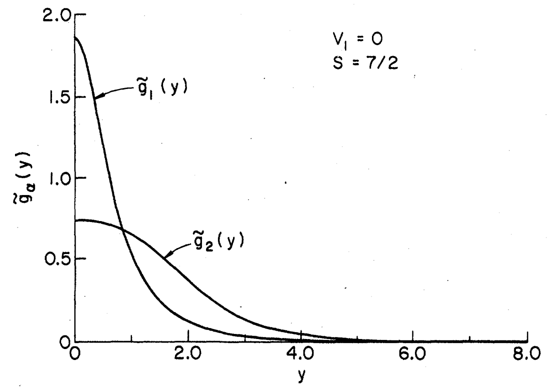

FIG. 6. Functions $\tilde g_1(y)$ and $\tilde g_2(y)$ for $V_1 = 0$ and $S = \frac{7}{2}$.

lustrated in Fig. 5, the dipolar spectral function $\tilde g_1(y)$ shows a dip as y goes to zero and peaks at a point away from $y = 0$. This is similar to the behavior found for this function using the "bubble" approximation in other systems.[29,30] On the other hand, the quadrupolar spectral function $\tilde g_2(y)$ for $S = 1$, also illustrated in Fig. 5, in an almost Lorentzian-like function for values of y up to 1.0 at which point it has fallen to $\frac{1}{4}$ to its value at $y = 0$. For larger values of y it begins to fall off exponentially fast. There is a marked contrast between the $S = 1$ results for pure quadrupolar exchange shown in Fig. 5 and the $S = \frac{7}{2}$ results for that case shown in Fig. 6. For $S = \frac{7}{2}$, as may be seen in that figure, the dipolar spectral function $\tilde g_1(y)$ is now sharply peaked and almost Lorentzian-like for values of y up to 1.0. In fact, the shape of $\tilde g_1(y)$ for $S = \frac{7}{2}$ closely resembles the shape of $\tilde g_2(y)$ for $S = 1$. On the other hand, the quadrupolar spectral function for the case of $S = \frac{7}{2}$ and pure quadrupolar exchange is very Gaussian-like throughout the entire frequency range. However, it is slightly flatter and falls off slightly steeper than a true Gaussian. It is clear from a comparison of Figs. 5 and 6 with Fig. 4 that for both $S = 1$ and $S = \frac{7}{2}$ both $\tilde g_1(y)$ and $\tilde g_2(y)$ in the pure quadrupolar exchange case are markedly different from the corresponding functions in the pure dipolar exchange case.

We have also calculated both $\tilde g_1(y)$ and $\tilde g_2(y)$ for the case of pure quadrupolar exchange ($V_1 = 0$) for values of S intermediate between $S = 1$ and $S = \frac{7}{2}$. We have found that the largest change as a function of S in this case occurs for those functions on changing from $S = 1$ to $S = \frac{3}{2}$, with the shapes of both functions for $S = \frac{3}{2}$ being more nearly like those for $S = \frac{7}{2}$ than for $S = 1$. The case $S = 1$ and $V_1 = 0$ thus seems to be somewhat of a special case. In fact, for $S = \frac{3}{2}$, the dipolar function $\tilde g_1(y)$ is already sharply peaked at the origin and almost twice the amplitude of the quadrupolar spectral function $\tilde g_2(y)$ and the latter function is already very Gaussian-like. This behavior is very dissimilar to the shapes of those functions for $S = 1$ and pure quadrupolar exchange. Furthermore, we have found that the changes in the functions $\tilde g_1(y)$ and $\tilde g_2(y)$ which occur as the spin quantum number increases beyond $S = \frac{3}{2}$ are very gradual, with the major changes being that $\tilde g_1(y)$ becomes more sharply peaked and $\tilde g_2(y)$ becomes rounder at $y = 0$ as S is increased. In addition, we have found that these changes in the $l = 1$ and $l = 2$ spectral functions with increasing S become smaller as the value of S becomes larger. In fact, the results for those functions for $S = \frac{5}{2}$ are almost identical to those for $S = \frac{7}{2}$, with the differences being imperceptible on the scale of Fig. 6.

Thus, one may say that, insofar as the dipolar and quadrupolar spectral functions in a system with only quadrupolar exchange are concerned, the classical ($S = \infty$) limit where these functions will be independent of S has been reached for all practical purposes at $S = \frac{5}{2}$. Physically, this means that the fact that the spins are quantized is, at least for the calculation of $\tilde g_1(y)$ and $\tilde g_2(y)$, no longer important for $S \geq \frac{5}{2}$. It should be noted, however, that is has been previously shown[23] for other systems that when the classical limit is reached for all practical purposes for a given physical quantity, it is not necessarily true that it has been reached for all physical quantities. Thus, the fact that the classical limit has been attained for $\tilde g_1(y)$ and $\tilde g_2(y)$ for a system with pure quadrupolar exchange does not necessarily imply that it has been attained for other quantities of interest (e.g., spin-diffusion coefficients, dipolar linewidths, etc.) or for systems described by other

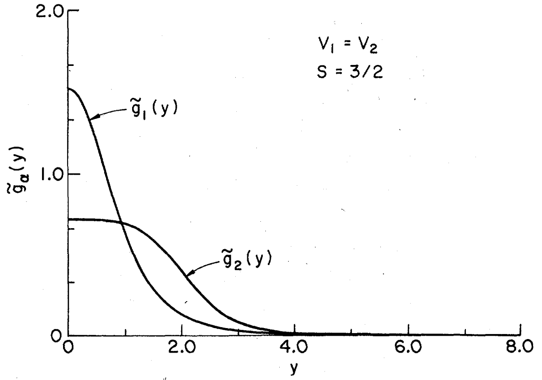

FIG. 7. Functions $\tilde g_1(y)$ and $\tilde g_2(y)$ for $V_1 = V_2$ and $S = \frac{3}{2}$.

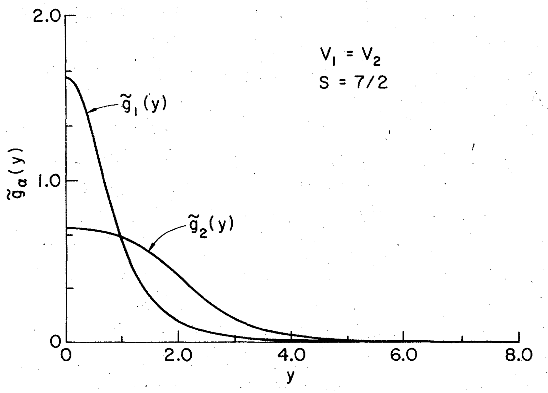

FIG. 8. Functions $\tilde{g}_1(y)$ and $\tilde{g}_2(y)$ for $V_1 = V_2$ and $S = \frac{7}{2}$.

Hamiltonians. Therefore, one should be cautious in assuming that the quantization of the spins will not be important for $S > \frac{5}{2}$. Furthermore, as has also been previously pointed out,[23] the "classical limit" as used in the above sense is not the true classical limit, which would be formally obtained by properly taking the $S = \infty$ limit of Eq. (15). It is not yet clear exactly how to do this.

The results for the local spectral functions $\tilde{g}_1(y)$ and $\tilde{g}_2(y)$ are illustrated for the case of equal dipolar and quadrupolar exchange energies ($V_1 = V_2$) in Figs. 7 and 8, which show these functions in this case for $S = \frac{3}{2}$ and $S = \frac{7}{2}$, respectively. Most of the remarks made above for the pure quadrupolar exchange case also apply to the results presented in these figures. The case of $S = 1$ is discussed below. For $S = \frac{3}{2}$, shown in Fig. 7, the dipolar spectral function $\tilde{g}_1(y)$ is much more sharply peaked at $y = 0$ than is the quadrupolar spectral function $\tilde{g}_2(y)$ and has an amplitude at the origin which is more than twice the amplitude of the latter function. Both functions are Gaussian-like in this case, but $\tilde{g}_1(y)$ is too sharp at $y = 0$ to be a true Gaussian, while $\tilde{g}_2(y)$ is too flat. The results for $S = \frac{7}{2}$, shown in Fig. 8, are not very different from the $S = \frac{3}{2}$ results. Here, the $l = 1$ spectral function is even more sharply peaked than it is for $S = \frac{3}{2}$, becoming almost Lorentzian-like for small y, while the $l = 2$ function is much rounder and even more Gaussian-like than it is for $S = \frac{3}{2}$. Again, we have also calculated $\tilde{g}_1(y)$ and $\tilde{g}_2(y)$ for all values of S in the range $1 \leq S \leq \frac{7}{2}$, but have only displayed the results for $S = \frac{3}{2}$ and $S = \frac{7}{2}$. As in the pure quadrupolar exchange case, the changes in these functions with increasing S between $S = \frac{3}{2}$ and $S = \frac{7}{2}$ are very gradual with the major changes being that $\tilde{g}_1(y)$ becomes more sharply peaked with increasing S while $\tilde{g}_2(y)$ becomes rounder near the origin. In this case also, the changes with increasing S diminish as S becomes larger until at $S = \frac{5}{2}$ no further appreciable change occurs if S is increased. Thus, the classical limit is again reached for all practical purposes at $S = \frac{5}{2}$, insofar as the shapes of the $l = 1$ and $l = 2$ spectral functions are concerned.

Not surprisingly, the shapes of the spectral functions for a given value of S in the case of equal dipolar and quadrupolar exchange energies ($V_1 = V_2$) are intermediate between their shapes for $V_2 = 0$ (Fig. 4) and their shapes for $V_1 = 0$ (Figs. 5 and 6). However, the results in this case for these functions at a given value of S are, with the exception of the special case of $S = 1$ discussed below, more nearly like the results for the case of only quadrupolar exchange than like those for pure dipolar exchange. This fact can be easily understood, by noting that, according to Eq. (14a), the quadrupolar exchange energy V_2 enters the second moment of the local linewidth function $\Gamma_1(\omega)$ with a weight which is five times the weight of the dipolar exchange energy V_1. A similar situation will also hold for the higher moments. Thus, even though $V_1 = V_2$, which implies that the dipolar and quadrupolar exchange interactions make equal contributions to the *Hamiltonian*, quadrupolar exchange will be dominant in the second and higher *moments* and thus in the shape of the spectral functions.

As was true for $S = 1$ and $V_1 = 0$, the case $S = 1$ and $V_1 = V_2$ is somewhat special in the sense that the results obtained for the spectral functions in this situation are very different from those obtained for other values of S. In this special case, the dipolar and quadrupolar spectral functions are equal. Furthermore, $\tilde{g}_1(y)$ is the same for this case as it is for the case of pure dipolar exchange ($V_2 = 0$, S arbitrary), which is illustrated in Fig. 4. Thus we have

$$\tilde{g}_1(y)\big|_{\substack{V_2=0\\ S\ \text{arbitrary}}} = \tilde{g}_1(y)\big|_{\substack{V_1=V_2\\ S=1}} = \tilde{g}_2(y)\big|_{\substack{V_1=V_2\\ S=1}} . \tag{18}$$

It can be shown analytically that Eq. (18) must be true; this is done explicitly in Appendix C. As may be seen by comparing Figs. 4 and 6 and using Eq. (18), the dipolar spectral function for $S = 1$ is markedly changed by the presence or absence of the dipolar exchange energy V_1, changing from a function which peaks at a frequency away from $y = 0$ in the case $V_1 = 0$ to a function which is Gaussian-like about $y = 0$ in the case $V_1 = V_2$.

As was mentioned above, in order to obtain self-consistent solutions for the spectral functions $\tilde{g}_1(y)$ and $\tilde{g}_2(y)$, it is also necessary to find all $\tilde{g}_l(y)$ for $2 < l \leq 2S$. Although these higher-order spectral functions are probably not accessible experimentally, it is nevertheless worthwhile to at least mention in passing some of the salient features of these functions. In general, these functions behave similarly to the functions $\tilde{g}_1(y)$ and $\tilde{g}_2(y)$. For the case of pure dipolar exchange ($V_2 = 0$ and S arbitrary) $\tilde{g}_l(y)$ for $l > 2$ is very similar in shape to $\tilde{g}_2(y)$ (Fig. 4) but weaker in amplitude at $y = 0$, becoming flatter and flatter near the origin and dropping to zero at larger values of y as l increases. For example, $\tilde{g}_7(y)$ is virtually a constant over the frequency range where $\tilde{g}_1(y)$ and $\tilde{g}_2(y)$ are nonzero. For both the case of pure quadrupolar exchange ($V_1 = 0$), and the case of equal dipolar and quadrupolar exchange ($V_1 = V_2$) the results obtained for the $\tilde{g}_l(y)$ for $l > 2$ follow a pattern as a function of increasing l which is similar to that just described for $V_2 = 0$; the larger the value of l, the flatter and broader the function and the smaller its amplitude, with the exception of the function $\tilde{g}_{2S-1}(y)$ for the case $V_1 = 0$, which will be discussed shortly. As a function of S for l fixed, the $\tilde{g}_l(y)$ in these cases behave similarly to the functions $\tilde{g}_1(y)$ and $\tilde{g}_2(y)$. In particular, as S is increased $\tilde{g}_l(y)$ becomes more sharply peaked about $y = 0$, with the $\tilde{g}_l(y)$ for $S = \frac{7}{2}$ being much more Lorentzian-like than the same function for $S = 1$; the major exception is again the function $\tilde{g}_{2S-1}(y)$ for the case $V_1 = 0$. The function $\tilde{g}_{2S-1}(y)$ for pure quadrupolar exchange was found to always have a shape similar to that found for $\tilde{g}_1(y)$ in the case $S = 1$ and $V_1 = 0$. In particular, in this case this function always has a dip at $y = 0$ and a peak at a frequency away from the origin. Finally, the classical limit for the functions $\tilde{g}_l(y)$ was in all cases found to occur for all practical purposes at a higher value of S than it occurred for the functions $\tilde{g}_1(y)$ and $\tilde{g}_2(y)$, with, for example, the function $\tilde{g}_5(y)$ for $S = 3$ and the same function for $S = \frac{7}{2}$ showing appreciable differences.

IV. SUMMARY AND CONCLUSIONS

In the preceding discussion, we have presented a general theory for the first principles calculation of dynamical two-point spin-correlation functions in a spin system described by a Hamiltonian, Eq. (4), containing both dipolar and quadrupolar exchange interactions. By the use of a previously developed diagrammatic technique[9,39] a set of integral equations, Eqs. (12) and (13), for these correlation functions was obtained. These equations are applicable at all ratios of the quadrupolar exchange energy to the dipolar exchange energy and for all values of the spin quantum number S and they are valid in the infinite-temperature limit, which is defined as the temperature range where kT is much larger than any spin-spin interaction energy. Furthermore, as discussed previously,[9] these equations form the lowest-order approximation in a hierarchy of self-consistent approximations which may be generated by carrying the diagrammatic technique to higher-order diagrams. The expected accuracy of these equations is of the order of $1/z$, where z is the number of nearest neighbors in the range of the interaction; they give the second moments of the correlation functions exactly while only giving the higher moments to order $1/z$.

The "local" versions of these equations were solved numerically and a study was made of their solutions for $1 \leq S \leq \frac{7}{2}$ and for the cases of pure dipolar exchange, pure quadrupolar exchange, and equal dipolar and quadrupolar exchange. In the numerical study, we placed particular emphasis on the dipolar and quadrupolar spectral functions, $\tilde{g}_1(y)$ and $\tilde{g}_2(y)$, which are measurable in magnetic resonance and ultrasonic magnetic resonance experiments. Among other interesting behavior, we found from these solutions that for $S = \frac{5}{2}$ the classical or $S = \infty$ limit has been reached insofar as the S dependence of the shapes of the functions $\tilde{g}_1(y)$ and $\tilde{g}_2(y)$ is concerned. In other words, for $S \geq \frac{5}{2}$ these functions are for all practical purposes independent of S for all values of the dipolar exchange energy to quadrupolar exchange energy ratio.

The two basic limitations of the present theory are its restriction to the lowest order or "bubble" approximation to the spin self-energy and its restriction to the infinite-temperature limit. It might be possible to overcome these restrictions by appropriate generalizations of the present theory. For example, for the case of dipolar exchange only, Fedders[40] has been able to take into account higher-order diagrams in the spin self-energy by performing a resummation of an infinite subset of these diagrams and an extension of his method to simultaneously include the effects of dipolar and quadrupolar exchange might be possible. Also, Reiter[7,41] has proposed an extension of the diagrammatic spin self-energy formalism which enables one to calculate dynamical two-point spin-correlation functions at all temperatures in the range $T_c \leq T < \infty$, where T_c is a magnetic ordering temperature. Again, he has made this generalization only for the case of dipolar exchange, but his formalism could perhaps be extended to include quadrupolar exchange effects. Either of these possible extensions of the present formalism would be a formidable task. Also, as is shown in the next paper,[24] the present formalism is adequate to help explain the magnetic and ultrasonic magnetic resonance data in ^{181}Ta, which was the original motivation for these calculations. Furthermore, experimental data which measures the correlation functions that we have calculated in other systems described by the Hamiltonian of Eq. (4) does not, to our knowledge, exist. Thus we feel that the above generalizations of the present formalism should await more experimental data.

APPENDIX A: RELATIONSHIP BETWEEN THE QUANTITIES J_0 AND j AND THE QUANTITIES J_1 AND J_2

If all multipolar interactions with $l>2$ are neglected, we can write the spin-spin interaction in the form of Eq. (4), repeated here for convenience:

$$H=H_1+H_2\,, \tag{A1}$$

where

$$H_1=-\frac{1}{2}\sum_{i\neq j}J_1(i,j)\sum_{m=-1}^{1}A_{1m}(i)(A_{1m}(j))^\dagger\,, \tag{A2}$$

and

$$H_2=-\frac{1}{2}\sum_{i\neq j}J_2(i,j)\sum_{m=-2}^{2}A_{2m}(i)(A_{2m}(j))^\dagger\,, \tag{A3}$$

where $J_1(i,j)$ and $J_2(i,j)$ are the dipolar and quadrupolar exchange energies, respectively. Traditionally, the spin Hamiltonian in the presence of both dipolar and quadrupolar spin-spin interactions has been written in the form of Eq. (5), also repeated here for convenience

$$\begin{aligned}H'=&-\frac{1}{2}\sum_{i\neq j}J_0(i,j)\vec{S}(i)\cdot\vec{S}(j)\\&-\frac{1}{2}\sum_{i\neq j}j(i,j)(\vec{S}(i)\cdot\vec{S}(j))^2,\end{aligned} \tag{A4}$$

where $J_0(i,j)$ and $j(i,j)$ are the Heisenberg and biquadratic exchange energies, respectively. The relationships between the spin operators and the operators A_{lm} for $l=1,2$ take the form[9]

$$A_{1,\pm1}=\mp S_\pm/[\tfrac{2}{3}S(S+1)]^{1/2}\,, \tag{A5}$$

$$A_{10}=S_z/[\tfrac{1}{3}S(S+1)]^{1/2}\,, \tag{A5$'$}$$

$$A_{2,\pm2}=S_\pm^2/[\tfrac{2}{15}S(S+1)(2S-1)(2S+3)]^{1/2}\,, \tag{A6}$$

$$A_{2,\pm1}=\mp\{S_\pm,S_z\}/[\tfrac{2}{15}S(2S-1)(2S+3)]^{1/2}\,, \tag{A6$'$}$$

and

$$A_{20}=[S_z^2-\tfrac{1}{3}S(S+1)]/[\tfrac{1}{45}S(S+1)(2S-1)(2S+3)]^{1/2}\,. \tag{A7}$$

These expressions may be used in Eq. (A4) to obtain expressions for the quantities $\vec{S}(i)\cdot\vec{S}(j)$ and $(\vec{S}(i)\cdot\vec{S}(j))^2$ in terms of the A_{lm}. After a considerable amount of algebra, we find

$$\vec{S}(i)\cdot\vec{S}(j)=\tfrac{1}{3}S(S+1)\sum_{m=-1}^{1}A_{1m}(i)(A_{1m}(j))^\dagger\,, \tag{A8}$$

and

$$\begin{aligned}(\vec{S}(i)\cdot\vec{S}(j))^2=&\frac{S(S+1)(2S-1)(2S+3)}{30}\\&\times\sum_{m=-2}^{2}A_{2m}(i)(A_{2m}(j))^\dagger\\&-\frac{S(S+1)}{6}\sum_{m=-1}^{1}A_{1m}(i)(A_{1m}(j))^\dagger\\&+\frac{S^2(S+1)^2}{3}\,.\end{aligned} \tag{A9}$$

If it is assumed that both the Hamiltonian of Eqs. (A1)–(A3) and that of (A4) describe the same set of spins, the two may be equated. Then, using Eqs. (A8) and (A9) in Eq. (A4), one may find a relationship between the interaction energies $J_1(i,j)$, $J_2(i,j)$ and $J_0(i,j)$, $j(i,j)$. If the unimportant constant term in Eq. (A9) is neglected, these relationships take the form

$$J_1(i,j)=\tfrac{1}{3}S(S+1)[J_0(i,j)-\tfrac{1}{2}j(i,j)]\,, \tag{A10}$$

and

$$J_2(i,j)=\tfrac{1}{30}S(S+1)(2S-1)(2S+3)j(i,j)\,. \tag{A11}$$

Thus, the true dipolar exchange energy for the system described by the Hamiltonian of Eq. (A4) is not $J_0(i,j)$, but a linear combination of $J_0(i,j)$ and $j(i,j)$, as was claimed in the text.

APPENDIX B: COMMUTATION PROPERTIES OF THE A_{lm}; EVALUATION OF THE QUANTITIES $C^{1m'}_{l,m+m'}$ AND $C^{2m'}_{l+1,m+m'}$ AND THE FUNCTIONS $F_\pm(l,S)$

From the tensor properties of the A_{lm}, it is easily shown that the commutators of Eq. (9) have the forms

$$[A_{1m'},A_{lm}]=C(1m';lm;l,\,m+m')A_{l,m+m'} \tag{B1}$$

and

$$\begin{aligned}[A_{2m'},A_{lm}]=&C(2m';lm';l-1,\,m+m')A_{l-1,m+m'}\\&+C(2m';lm';l+1,\,m+m')A_{l+1,m+m'}\,.\end{aligned} \tag{B2}$$

As was done in the text, throughout the rest of this Appendix the abbreviations

$$C^{1m'}_{l,m+m'}=C(1m';lm;l,\,m+m') \tag{B3}$$

and

$$C^{2m'}_{l\pm1,m+m'}=C(2m';lm;l\pm1,\,m+m') \tag{B4}$$

will be used. The quantity $C^{1m'}_{l,m+m'}$ is almost trivially calculated from the well known commutation relations

$$[S_z,A_{lm}]=mA_{lm} \tag{B5}$$

and

$$[S_\pm, A_{lm}] = [l(l+1) - m(m\pm 1)]^{1/2} A_{l,m\pm 1}, \tag{B6}$$

along with the relations between the A_{1m} and the operators S_z and $S_\pm$,[9] shown in Eqs. (A3) and (A4). Combining Eqs. (B5), (B6), (A3), and (A4) with Eq. (B1) yields

$$C^{1,\pm 1}_{l,m\pm 1} = \mp \left(\frac{3[l(l\pm 1) = m(m\pm 1)]}{2S(S+1)} \right)^{1/2} \tag{B7}$$

and

$$C^{10}_{lm} = [3/S(S+1)]^{1/2} m\,. \tag{B8}$$

The evaluation of the $C^{2m'}_{l\pm 1, m+m'}$ in closed form is also straightforward but requires a large amount of algebra. Curiously, although recursion relations between these quantities have been derived and utilized,[42] closed-form expressions for them have apparently only been derived for the case $m'=0$.[23] Here, a method similar to that discussed in Ref. 32 will be used to derive expressions for the $C^{2m'}_{l\pm 1, m+m'}$ which are valid for all l, m, m', and S. One can obtain the general expression for the commutator of two irreducible tensor spin operators by the use of their tensor properties.[43] For the tensor operators A_{lm} this commutator takes the form[23]

$$[A_{l_1 m_1}, A_{l_2 m_2}] = \sum_{m_3 = l_3}^{l_3} \sum_{l_3 = |l_1 - l_2|}^{|l_1 + l_2|} [(-1)^{l_1+l_2+l_3} - 1](2l_3+1) \begin{Bmatrix} l_1 & l_2 & l_3 \\ S & S & S \end{Bmatrix} \times \begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \times \frac{\langle S \| A_{l_1} \| S\rangle \langle S \| A_{l_2} \| S \rangle}{\langle S \| A_{l_3} \| S \rangle} A^\dagger_{l_3 m_3}, \tag{B9}$$

where

$$\begin{Bmatrix} l_1 & l_2 & l_3 \\ S & S & S \end{Bmatrix}$$

is a 6-j coefficient,

$$\begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$$

is a 3-j coefficient, $\langle S \| A_l \| S \rangle$ is the reduced matrix element of A_{lm}, and $A^\dagger_{l_3 m_3}$ is the Hermitian conjugate of $A_{l_3 m_3}$. Comparison of Eq. (B9) with Eq. (B2) for the case $l_1 = 2$, $m_1 = m'$, $l_2 = l$, $m_2 = m$ yields explicit expressions for the $C^{2m'}_{l\pm 1, m+m'}$, which have the form

$$C^{2m'}_{l-1, m+m'} = (-1)^{m+m'} [(-1)^{2l+1} - 1](2l-1) \begin{Bmatrix} 2 & l & l-1 \\ S & S & S \end{Bmatrix} \times \begin{pmatrix} 2 & l & l-1 \\ m' & m & -(m+m') \end{pmatrix} \frac{\langle S \| A_2 \| S \rangle \langle S \| A_l \| S \rangle}{\langle S \| A_{l-1} \| S \rangle} \tag{B10}$$

and

$$C^{2m'}_{l+1, m+m'} = (-1)^{m+m'} [(-1)^{2l+3} - 1](2l+3) \begin{Bmatrix} 2 & l & l+1 \\ S & S & S \end{Bmatrix} \times \begin{pmatrix} 2 & l & l+1 \\ m' & m & -(m+m') \end{pmatrix} \frac{\langle S \| A_2 \| S \rangle \langle S \| A_l \| S \rangle}{\langle S \| A_{l+1} \| S \rangle}\,. \tag{B11}$$

These expressions can be straightforwardly evaluated, but a considerable amount of algebra is required. The $\langle S \| A_l \| S \rangle$ and the 3-j and 6-j coefficients can be evaluated by methods which may be found in any standard quantum mechanics text.[44] The results of such an evaluation are

$$C^{2m'}_{l-1, m+m'} = \frac{\sqrt{45}}{2} (-1)^{2S} \left(\frac{4S(S+1) - (l-1)(l+1)}{(2l-1)(2l+1)S(S+1)(2S-1)(2S+3)} \right)^{1/2} g_-(l,m,m') \tag{B12}$$

and

$$C^{2m'}_{l+1, m+m'} = \frac{\sqrt{45}}{2} (-1)^{2S} \left(\frac{4S(S+1) - l(l+2)}{(2l+1)(2l+3)S(S+1)(2S-1)(2S+3)} \right)^{1/2} g_+(l,m,m'), \tag{B13}$$

where the $g_\pm(l,m,m')$ are defined as

$$g_-(l,m,\pm 2)=\pm\frac{\sqrt{6}}{3}[(l\mp m)(l\mp m-1)\times(l\mp m-2)(l\pm m+1)]^{1/2}, \tag{B14}$$

$$g_-(l,m,\pm 1)=\mp\frac{\sqrt{6}}{3}[l\pm 2m+1][(l\mp m)(l\mp m-1)]^{1/2}, \tag{B15}$$

$$g_-(l,m,0)=2m[(l+m)(l-m)]^{1/2}, \tag{B16}$$

$$g_+(l,m,\pm 2)=\pm\frac{\sqrt{6}}{3}[l\mp m)(l\pm m+3)\times(l\pm m+2)(l\pm m+1)]^{1/2}, \tag{B17}$$

$$g_+(l,m,\pm 1)=\pm\frac{\sqrt{6}}{3}[l\mp 2m][(l\pm m+2)(l\pm m+1)]^{1/2}, \tag{B18}$$

and

$$g_+(l,m,0)=-2m[(l+m+1)(l-m+1)]^{1/2}. \tag{B19}$$

The functions $F_\pm(l,S)$ which occur in Eq. (10) are defined as

$$F_\pm(l,S)=\sum_{m'}(C^{2m'}_{l\pm 1,m+m'})^2. \tag{B20}$$

By substitution of Eqs. (B12)-(B19) into Eq. (B20) and after a considerable amount of straightforward but tedious algebra, one can obtain the results

$$F_-(l,S)=\frac{15l(l-1)(l+1)}{2l+1}\times\left(\frac{4S(S+1)-(l-1)(l+1)}{S(S+1)(2S-1)(2S+3)}\right) \tag{B21}$$

and

$$F_+(l,S)=\frac{15l(l+1)(l+2)}{2l+1}\times\left(\frac{4S(S+1)-l(l+2)}{S(S+1)(2S-1)(2S+3)}\right). \tag{B22}$$

As can be seen, these functions are independent of the quantum number m, as they should be, and they have the properties that $F_-(1,S)=F_+(2S,S)=0$, as is claimed in the text.

APPENDIX C: PROOF OF EQUATION (18)

The relations, Eq. (18), may be shown analytically to be true. The proof is as follows. In the case $V_2=0$ and S arbitrary, Eq. (15) gives for $l=1$,

$$\tilde{\Gamma}_1(y)=\int_{-\infty}^{\infty}\frac{dy_1}{\pi}\tilde{g}_1(y_1)\tilde{g}_1(y-y_1) \qquad (V_2=0, S\text{ arbitrary}). \tag{C1}$$

Also, in the case $V_1=V_2$ and $S=1$, that equation yields the following expressions for $l=1$ and $l=2$:

$$\tilde{\Gamma}_1(y)=\frac{1}{6}\int_{-\infty}^{\infty}\frac{dy_1}{\pi}\tilde{g}_1(y_1)\tilde{g}_1(y-y_1)+\frac{5}{6}\int_{-\infty}^{\infty}\frac{dy_1}{\pi}\tilde{g}_2(y_1)\tilde{g}_2(y-y_1) \qquad (V_1=V_2,\ S=1) \tag{C2}$$

and

$$\tilde{\Gamma}_2(y)=\int_{-\infty}^{\infty}\frac{dy_1}{\pi}\tilde{g}_1(y_1)\tilde{g}_2(y-y_1) \quad (V_1=V_2,\ S=1), \tag{C3}$$

where use has been made of the expressions for the functions $F_\pm(l,S)$ which are derived in Appendix B. In Eqs. (C1)-(C3) $\tilde{\Gamma}_l(y)$ is, of course, related to $\tilde{g}_l(y)$ by Eqs. (16) and (17) of the text. It may now be easily seen that the relation $\tilde{g}_1(y)=\tilde{g}_2(y)$ is a solution to the system of equations given by Eqs. (C2) and (C3) and that furthermore, the expressions for $\tilde{\Gamma}_1(y)$ and $\tilde{\Gamma}_2(y)$ which result when this equality is taken into account are identical to that given in Eq. (C1). Thus

$$\tilde{g}_1(y)\Big|_{\substack{V_2=0\\ S\text{ arbitrary}}}=\tilde{g}_1(y)\Big|_{\substack{V_1=V_2\\ S=1}}=\tilde{g}_2(y)\Big|_{\substack{V_1=V_2\\ S=1}} \tag{C4}$$

as was claimed in the text.

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