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Theory of collective magnetic excitations in strong crystal fields. I. Dynamics of the angular momentum tensor operators

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The collective motion of ionic spins in a crystal field of magnitude comparable with the exchange interaction is examined. A systematic scheme based upon angular momentum spherical tensor operators is developed to describe the dynamics of collective excitations in the system. The Green's-function equations of motion are linearized by suitably modified forms of conventional decoupling approximations, in particular the random-phase approximation. When the order parameters of the system are calculated, care is taken to eliminate correlation functions prohibited by kinematic restraints. Consequently, the order parameters are obtained uniquely by reducing a redundant set of Green's functions. Furthermore excitations out of different molecular-field levels are distinguished and the excitation out of the ground state is identified as the spin wave. The theory is applied to the spin-1 ($S = 1$) axial ferromagnet with some numerical results.

I. INTRODUCTION

The magnetic excitations in ferromagnets with strong crystal fields are being studied extensively, particularly for the rare-earth and actinide compounds.[1–3] The fundamental difficulty in this problem is that the crystal-field Hamiltonian and the interionic spin interaction Hamiltonian, typically the isotropic Heisenberg exchange Hamiltonian, do not commute and do not have compatible eigenstates. Attempts to devise a theory of collective excitations in such a system have therefore started from one of the two limiting cases: the strong-exchange-limit–spin-wave approximation, and the strong-crystal-field-limit–crystal-field exciton approximation. If the exchange interaction dominates, the crystal field may be treated as a perturbation and expanded in spin-wave coordinates.[4] In this approximation the crystal field is the origin of the anisotropy energy and contributes to the spin-wave energy gap; the common origin of the anisotropy energy and the spin-wave gap is a crucial assumption in conventional macroscopic resonance theory.[5] The energy gap displays a strong temperature dependence that may be attributed to spin-wave interactions due to the crystal field.[5–7] When the crystal field dominates the exchange interaction a different unperturbed Hamiltonian is used. The exchange Hamiltonian is replaced by a molecular field so that collective behavior is initially omitted. The operators that generate interstate transitions for this simplified Hamiltonian are adopted as the basis operators to describe the spin dynamics of the system. The full Hamiltonian is then recovered by adding the difference between the exchange Hamiltonian and the molecular-field Hamiltonian to the zeroth-order Hamiltonian, thus introducing the propagation of the crystal-field exciton and its dispersion. In most cases, however, the basis operators are replaced by quasiboson[8–13] or pseudospin operators[14–17] rather than expressed in terms of physical spin operators. Only for small spin systems an attempt has been made to describe the spin dynamics by means of physical spin operators.[18,19] When boson or pseudospin operators are used in place of physical spin operators, interactions between the excitations (dynamic and kinematic interactions) are not correctly accounted for. Therefore, the temperature renormalization will be inaccurate.

The purpose of this paper is to present a general method to study the spin dynamics of a magnetic system with a strong crystal field via the thermodynamic Green's functions of a complete set of the physical-spin (tensor) operators, leading to a unifying view of all the cases, from strong-crystal-field to strong-exchange limits. The use of physical-spin-tensor-operator Green's functions makes it possible, in principle, to describe correctly the renormalization of the excitation energy due to the interactions among the excitations. In practice, however, three operator Green's functions have to be decoupled[20] to make the calculation feasible. Here we make use of and generalize existing decoupling techniques: the random-phase approximation (RPA),[20] the Hartree-Fock approximation (HFA),[7] and the Callen decoupling method (CA),[21] which interpolates between RPA and HFA. The origins of the present method are in the theories of Murao and Matsubara[18] and Haley and Erdös.[19] The difficulties associated (a) with redundant sets of equations from which correlation functions are calculated, and (b) the imposition of kinematic restraints, are discussed in detail and an alternative and unique choice is presented within a systematic framework.

The organization of this paper is as follows: in Sec. II the angular momentum tensor operators are introduced and their commutation relations discussed. Important properties are that their components are linearly independent and that they are closed under commutation. In Sec. III the dynamical theory is outlined. The equations of motion are linearized by the three decoupling schemes mentioned above. The excitation energies and spin correlation functions are calculated via double-time thermal Green's functions.[20,22] Section IV is devoted to a study of the axial ferromagnet ($S=1$) with a degenerate ground state. A set of Green's functions that avoids any redundancy in the calculation of self-correlation functions is chosen. Correlation functions are computed in such a manner that it is not necessary to impose external kinematic restrictions. The theory is compared with those of Murao and Matsubara and Haley and Erdős, and the new results are interpreted physically and expressed quantitatively.

II. COMMUTATION RELATIONS AMONG THE ANGULAR MOMENTUM TENSOR OPERATORS

The study of crystal-field effect upon ions, via the use of angular momentum operator equivalents, was first developed by Stevens.[23] The operators are the components of irreducible tensor operators in a spherical symmetry, and conveniently describe the interaction of the angular momentum with a crystalline environment. Our normalization of these operators is chosen to agree with Buckmaster.[24]

The angular momentum (spin) operator equivalent of spherical harmonics $\tilde{O}_l^m$ may be obtained from the generating function[25,26]

$$\exp\{\tfrac{1}{2}w[2S_z - tS_+ + (1/t)S_-]\} = \sum_{l=0}^{\infty}\sum_{m=-l}^{l} \frac{\tilde{O}_l^m}{[(l+m)!(l-m)!]^{1/2}} w^l t^m \tag{2.1}$$

by equating coefficients of $w^l t^m$. Explicit expressions for the $\tilde{O}_l^m$ are not quoted here, but are tabulated by several authors.[24,27]

The components of the angular momentum (spin) tensor operator defined above are orthogonal to each other. Furthermore, for a system with spin S there are $2S+1$ molecular-field states for each spin, therefore $(2S+1)^2$ linearly independent operators are required for each spin in order to span the spin space of the system. The tensor operator $\{\tilde{O}_l^m\}$ ($l=0, 1, 2, \ldots, 2S$; $m=-l, -l+1, \ldots, l$) meets this requirement, since it contains $(2S+1)^2$ components as a whole. Thus, the entire components of the tensor operator form a complete orthogonal set of base operators in terms of which the dynamics of any spin system may be described, and any operator of the system may be expanded.

The dynamics of the system is studied via the equation of motion of the tensor operator. We note that the commutator between two components of the tensor operator, hence the equation of motion, can be conveniently given by[28-30]

$$[\tilde{O}_{l_1}^{m_1}, \tilde{O}_{l_2}^{m_2}] = \sum_L (-1)^{L+m_1+m_2}[(-1)^{l_1+l_2+L} - 1] \times (2L+1)^{1/2}\begin{pmatrix} l_1 & l_2 & L \\ m_1 & m_2 & -(m_1+m_2)\end{pmatrix} \times \alpha(l_1, l_2, L)\tilde{O}_L^{m_1+m_2} , \tag{2.2}$$

where $(\cdots)$ is the $3j$ symbol, and the coefficient $\alpha(l_1, l_2, L)$ is given by

$$\alpha(l_1, l_2, L) = (-1)^{2S+L}(2L+1)^{1/2}\begin{Bmatrix} l_1 & l_2 & L \\ S & S & S\end{Bmatrix} \times \frac{\langle S\|\tilde{O}_{l_1}\|S\rangle\langle S\|\tilde{O}_{l_2}\|S\rangle}{\langle S\|\tilde{O}_L\|S\rangle} , \tag{2.3}$$

where $\{\cdots\}$ is the $6j$ symbol and

$$\langle S\|\tilde{O}_l\|S\rangle = (2S+1)^{-1}\sum_{mm'}(-1)^{S+l_1+m} \times \begin{pmatrix} S & l_1 & S \\ m-m' & m' & -m\end{pmatrix}\langle S, m|\tilde{O}_{l_1}^{m'}|S, m-m'\rangle = 2^{-l}\left(\frac{(2S+l+1)!}{(2S-l)!}\right)^{1/2} \tag{2.4}$$

is the reduced matrix element.

Thus the commutator between the two components of the tensor operator is itself a linear combination of the components of the tensor operators, which are therefore closed under commutation.

III. SPIN DYNAMICS

A. Linearization of the equation of motion

The contraction and the commutation formulas presented in Sec. II make it possible to obtain the equation of motion of the entire tensor operator. If the Hamiltonian consists of only the single-ion tensor operators, the equation of motion is closed:

$$[\tilde{O}_{l_1}^{m_1}, \mathcal{H}] = \sum_{m_2, l_2} K_{l_1 l_2}^{m_1 m_2}\tilde{O}_{l_2}^{m_2} \tag{3.1}$$

or in tensor notation

$$[\underline{\tilde{O}}, \mathcal{H}] = \underline{K}\cdot\underline{\tilde{O}} , \tag{3.2}$$

where $\underline{K}$ is the dynamical tensor. The excitation energies are obtained by the diagonalization of the dynamical tensor. If the Hamiltonian contains any interionic interaction (e.g., Heisenberg exchange), the equation of motion becomes nonlinear:

$$[\underline{\tilde{O}}(\vec{n}_1), \mathcal{H}] = \underline{K}_1 \cdot \underline{\tilde{O}}(\vec{n}_1) + \sum_{\vec{n}_2} \underline{K}_2(\vec{n}_1, \vec{n}_2) \cdot \underline{\tilde{O}}(\vec{n}_1) \cdot \underline{\tilde{O}}(\vec{n}_2) , \qquad (3.3)$$

where $\vec{n}_1$ and $\vec{n}_2$ label lattice points. For the first-order tensor operator (spin-wave operators), however, it is well known that the linearization of (3.3) by a systematic decoupling scheme produces a satisfactory result. Guided by this knowledge, we will proceed to decouple (3.3) so that the second term takes the form

$$\sum_{\vec{n}_2} \underline{K}_2(\vec{n}_1, \vec{n}_2) \cdot \underline{\tilde{O}}(\vec{n}_1) \cdot \underline{\tilde{O}}(\vec{n}_2) \rightarrow \underline{K}_2^0 \cdot \underline{\tilde{O}}(\vec{n}_1) + \sum_{\vec{n}_2} \underline{K}_2^1(\vec{n}_1 - \vec{n}_2) \cdot \underline{\tilde{O}}(\vec{n}_2) . \qquad (3.4)$$

In RPA one decouples (3.3) symmetrically

$$\underline{\tilde{O}}(\vec{n}_1) \cdot \underline{\tilde{O}}(\vec{n}_2) \rightarrow \langle \underline{\tilde{O}}(\vec{n}_1) \rangle \underline{\tilde{O}}(\vec{n}_2) + \langle \underline{\tilde{O}}(\vec{n}_2) \rangle \underline{\tilde{O}}(\vec{n}_1) . \qquad (3.5)$$

If the inverse of the operator identity

$$\tilde{O}_{l_1}^{m_1} \tilde{O}_{l_2}^{m_2} = \sum_L (-1)^{l_1+l_2+m_1+m_2} (2L+1)^{1/2} \times \begin{pmatrix} l_1 & l_2 & L \\ m_1 & m_2 & -(m_1+m_2) \end{pmatrix} \alpha(l_1, l_2, L)\, \tilde{O}_L^{m_1+m_2} \qquad (3.6)$$

is used to express one spin tensor in terms of the product of two—thus enabling one to rewrite the second tensor of (3.3) as the product of three tensor operators—HFA will result from symmetrical decoupling of the three operator terms. The inverse of (3.6), however, is not unique, and a scheme proposed later will be applied here to select the appropriate expression.

The Callen approximation is constructed from a linear combination of RPA and HFA:

$$\underline{K}^{\mathrm{CA}} = (1-\alpha)\underline{K}^{\mathrm{RPA}} + \alpha \underline{K}^{\mathrm{HFA}} , \qquad (3.7)$$

where

$$\alpha = |\langle \tilde{O}_1^0 \rangle| / S . \qquad (3.8)$$

(3.4) may now be diagonalized by Fourier transformation to yield

$$[\underline{\tilde{O}}(q), \mathcal{H}] = \underline{K}(q) \tilde{O}(q) , \qquad (3.9)$$

where

$$\underline{\tilde{O}}(q) = \frac{1}{\sqrt{N}} \sum_{\vec{n}} e^{i\vec{q}\cdot\vec{n}} \underline{\tilde{O}}(\vec{n}) \qquad (3.10)$$

$$\underline{K}(q) = \underline{K}_1 + \underline{K}_2^0 + \sum_{\vec{n}} e^{i\vec{q}\cdot\vec{n}} \underline{K}_2^1(\vec{n}) . \qquad (3.11)$$

B. Angular momentum tensor-operator Green's functions

We define the angular momentum spherical tensor-operator Green's functions

$$G_{q_1,q_2}^{l_1,m_1;l_2,m_2}(t) = \langle\langle \tilde{O}_{l_1}^{m_1}(q_1, t);\ \tilde{O}_{l_2}^{m_2}(q_2, 0) \rangle\rangle . \qquad (3.12)$$

The properties of the double-time thermodynamic Green's function $\langle\langle A(t); B(0) \rangle\rangle$ are discussed by Zubarev.[22]

The Fourier transform of (3.11)

$$G_{q_1,q_2(E)}^{l_1,m_1;l_2,m_2} = \langle\langle \tilde{O}_{l_1}^{m_1}(q_1);\ \tilde{O}_{l_2}^{m_2}(q_2) \rangle\rangle_E = \int_{-\infty}^{\infty} e^{iEt/\hbar} \langle\langle \tilde{O}_{l_1}^{m_1}(q_1, t);\ \tilde{O}_{l_2}^{m_2}(q_2, 0) \rangle\rangle\, dt \qquad (3.13)$$

satisfies the equation of motion

$$\omega \langle\langle \tilde{O}_{l_1}^{m_1}(q_1);\ \tilde{O}_{l_2}^{m_2}(q_2) \rangle\rangle_\omega = \langle [\tilde{O}_{l_1}^{m_1}(q_1),\ \tilde{O}_{l_2}^{m_2}(q_2)] \rangle + \langle\langle [\tilde{O}_{l_1}^{m_1}(q_1), \mathcal{H}];\ \tilde{O}_{l_2}^{m_2}(q_2) \rangle\rangle_\omega . \qquad (3.14)$$

If the linearization procedure discussed in Sec. III A (3.1) is applied, the equation of motion of the Green's tensor $\underline{G}_{q_1,q_2}(\omega)$ takes the form

$$[\underline{K}(q_1) - \omega \underline{I}]\, \underline{G}_{q_1,q_2}(\omega) = -\underline{N}_{q_1,q_2} , \qquad (3.15)$$

where $\underline{N}_{q_1,q_2}$ is the commutator tensor

$$N_{q_1,q_2}^{l_1 m_1;l_2,m_1} = \langle [\tilde{O}_{l_1}^{m_1}(q_1),\ \tilde{O}_{l_2}^{m_2}(q_2)] \rangle . \qquad (3.16)$$

The Green's tensor and the correlation functions of the system are obtained from (3.12). As has been noted by other authors, it is possible to calculate one correlation function from several different sets of Green's functions. We will develop a unique expansion of the self-correlation functions that excludes terms containing kinematically forbidden transitions. This expansion, together with a systematic theory based solely upon dipole transition operators removes the redundant equations satisfactorily.

IV. APPLICATION TO SIMPLE FERROMAGNETS WITH $S=1$

A. Molecular-field approximation (MFA) and kinematic considerations

We consider a Heisenberg ferromagnet with two-fold crystal field, in an applied field H, described by the Hamiltonian

$$\mathcal{H} = -\sum_{\vec{n}_1 \vec{n}_2} J(\vec{n}_1 - \vec{n}_2) [\tilde{O}_1^0(\vec{n}_1) \tilde{O}_1^0(\vec{n}_2) - 2\tilde{O}_1^1(\vec{n}_1) \tilde{O}_1^{-1}(\vec{n}_2)] + B_2^0 \sum_{\vec{n}} \tilde{O}_2^0(\vec{n}) + \gamma H \sum_{\vec{n}} \tilde{O}_1^0(\vec{n}) , \qquad (4.1)$$

where $\tilde{B}_2^0$ is negative, $\gamma = g|\mu_B|$, and g is the Landé g factor. The exchange interaction removes the ground-state (doublet) degeneracy. In the ferromagnetic phase we take the $S^z = -1$ state to be the ground state.

In the MFA the exchange interaction is replaced by a molecular field ϕ which formally adds to the applied field H; the dynamical tensor is given exactly by

$$\underline{K} = \begin{bmatrix} \phi & -D & 0 \\ -D & \phi & 0 \\ 0 & 0 & 2\phi \end{bmatrix} , \quad D = -\tfrac{3}{2}B_2^0 , \qquad (4.2)$$

with eigenvalues

$$\omega_{1,2} = \phi \mp D ; \quad \omega_3 = 2\phi . \qquad (4.3)$$

The generators of excitations are obtained from (3.12):

$$S_-^1 = \frac{1}{\sqrt{2}}\left(\tilde{O}_1^{-1} - \frac{2}{\sqrt{3}}\tilde{O}_2^{-1}\right) = 2\begin{bmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} ,$$

$$S_-^2 = \frac{1}{\sqrt{2}}\left(\tilde{O}_1^{-1} + \frac{2}{\sqrt{3}}\tilde{O}_2^{-1}\right) = 2\begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 1 & 0 \end{bmatrix} , \qquad (4.4)$$

$$S_-^3 = \sqrt{\tfrac{2}{3}}\;\tilde{O}_2^{-2} = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{bmatrix} ,$$

where, on the right-hand side, the generators are written in a matrix representation, with $\tilde{O}_n^0$ diagonal. It becomes clear that the $S_\pm^\alpha$ are (apart from multiplicative factors) the standard basis operators of Haley and Erdös.[19] A diagram of the levels and excitation energies is shown in Fig. 1.

We now consider the kinematics of the components of tensor operators. For a system with N molecular-field levels there are $\frac{1}{2}N(N-1)$ operators $\tilde{O}_n^m$ $(m > 0)$, whereas there are $(N-1)$ order parameters $\langle \tilde{O}_n^0 \rangle$. The order parameters may always be expanded in terms of diagonal single-site correlation functions composed of products of the $\tilde{O}_n^m$. For example, in the system under discussion the relevant operator indentities are (deferring until later discussion of the quadrupole or $\tilde{O}_2^2$ operators)

$$\begin{aligned} \tilde{O}_1^1\tilde{O}_1^{-1} &= \tfrac{4}{3}\tilde{O}_2^1\tilde{O}_2^{-1} = -\tfrac{2}{3} - \tfrac{1}{2}\tilde{O}_1^0 + \tfrac{1}{3}\tilde{O}_2^0 , \\ \tilde{O}_1^1\tilde{O}_2^{-1} &= \tilde{O}_2^1\tilde{O}_1^{-1} = -\tfrac{1}{4}\sqrt{3}\,(\tilde{O}_1^0 + 2\tilde{O}_2^0) . \end{aligned} \qquad (4.5)$$

However, the inverse relationships obtained by solving (4.5) for the $\tilde{O}_n^0$ are not unique, i.e., the $\tilde{O}_n^0$ may be expressed in terms of the different products (and linear combinations of them) shown on the left-hand side.

We shall invoke kinematics to select the correct combinations of products. We note, following Haley and Erdös[19] that it is possible to construct unphysical self-correlation functions from the standard basis operators $S_\mp^\alpha$. For example $\langle S_-^1 S_+^2 \rangle$ is the expectation value of a process in which there is a transition from $S^z = -1$ level to $S^z = 0$, simultaneously accompanied by a transition from $S^z = 1$ to $S^z = 0$ (Fig. 1). Such a process is physically forbidden and Halley and Erdös invoke the "monotopic restriction" (or kinematic restraint) by setting such self-correlation functions—occurring in the evaluation of the order parameters from coupled equations for the Green's functions—to zero. However, if the diagonal operators are decomposed such that all equivalent expressions on the left-hand side of (4.5) have equal weight, the inverse of (4.5) is

$$\begin{aligned} \tilde{O}_1^0 &= -1 - \tfrac{3}{4}\tilde{O}_1^1\tilde{O}_1^{-1} - \tilde{O}_2^1\tilde{O}_2^{-1} \\ &\quad - \tfrac{1}{6}\sqrt{3}\,(\tilde{O}_1^1\tilde{O}_2^{-1} + \tilde{O}_2^1\tilde{O}_1^{-1}) , \\ \tilde{O}_2^0 &= \tfrac{1}{2} + \tfrac{3}{8}\tilde{O}_1^1\tilde{O}_1^{-1} + \tfrac{1}{2}\tilde{O}_2^1\tilde{O}_2^{-1} \\ &\quad - \tfrac{1}{4}\sqrt{3}\,(\tilde{O}_1^1\tilde{O}_2^{-1} + \tilde{O}_2^1\tilde{O}_1^{-1}) . \end{aligned} \qquad (4.6)$$

It may readily be deduced, by considering the inverse of the relationships (4.4) substituted into the right-hand side of (4.6), that all unphysical processes $\langle S_\mp^\alpha S_\pm^\beta \rangle$ $(\alpha \neq \beta)$ are excluded by cancellation in the equal weight decomposition. This decomposition, therefore, uniquely expresses the order parameters in terms of self-correlation functions in a manner that removes the necessity to impose kinematic restraints externally. We shall utilize Eqs. (4.6) in both the calculation of the order parameters[31] (Sec. IV B) and the Hartree-Foch expansion [cf. remarks following Eq. (3.5)].

An additional problem arises if the quadrupole operators $\tilde{O}_2^{\pm 2}$ (rather than the dipole operators $\tilde{O}_1^{\pm 1}$, $\tilde{O}_2^{\pm 1}$) are used to calculate the order parameters $\langle \tilde{O}_n^0 \rangle$. Although in MFA no inconsistency arises, the quadrupole mode will be shown (Sec. IV B) to display no dispersion in RPA, and a dif-

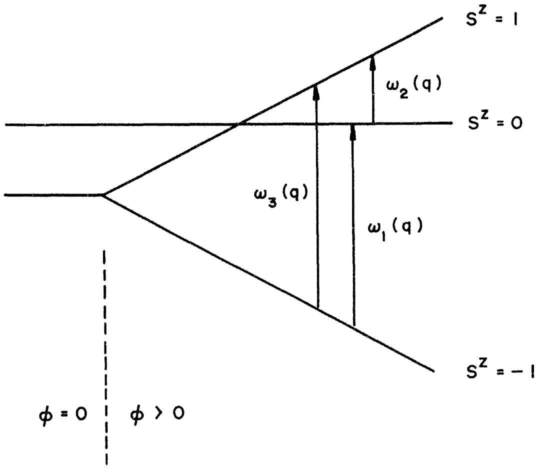

FIG. 1. Schematic diagram of the molecular-field states as a function of the molecular field ϕ and the excitation among the states.

ferent result is obtained when dynamics are described in terms of it. However, the set of $(N-1)$ operators $\tilde{O}_n^1$ is sufficient to specify the spin dynamics in MFA and will describe satisfactorily collective motion when only dipole transitions are prompted by the exchange interaction. The quadrupole mode may be identified with the dispersionless two-magnon single-ion bound state.[32] A consistent collective excitation theory including all three types of excitation must treat both single and two-excition bands, in which case the $\tilde{O}_2^2$ mode would show dispersion. Such a theory is of greater importance when there are terms in the Hamiltonian promoting quadrupole transitions (such as biquadratic exchange) rather than the present case, which we will describe in terms of dipole transitions.

B. Green's functions in RPA

The Fourier transforms of the equations of motion for $\tilde{O}_1^{-1}(\vec{n})$, $\tilde{O}_2^{-1}(\vec{n})$, and $\tilde{O}_2^{-2}(\vec{n})$ are, in RPA,

$$\begin{aligned}
&[\tilde{O}_1^{-1}(q),\mathcal{H}]=A_1(q)\tilde{O}_1^{-1}(q)+(2/\sqrt{3})B_1(q)\tilde{O}_2^{-1}(q)\ ,\\
&[\tilde{O}_2^{-1}(q),\mathcal{H}]=A_2(q)\tilde{O}_2^{-1}(q)+\tfrac{1}{2}\sqrt{3}\,B_2(q)\tilde{O}_1^{-1}(q)\ , \qquad (4.7)\\
&[\tilde{O}_2^{-2}(q),\mathcal{H}]=A_3(q)\tilde{O}_2^{-2}(q)\ ,
\end{aligned}$$

where

$$\begin{aligned}
A_1(q)&=-2\langle\tilde{O}_1^0\rangle[J(0)-J(q)]\ ,\\
B_1(q)&=\tfrac{3}{2}B_2^0=-D\ ,\\
A_2(q)&=-2\langle\tilde{O}_1^0\rangle J(0)\ , \qquad (4.8)\\
B_2(q)&=4\langle\tilde{O}_2^0\rangle J(q)-D\ ,\\
A_3(q)&=-4\langle\tilde{O}_1^0\rangle J(0)\ .
\end{aligned}$$

Thus we obtain the set of Green's functions:

$$\langle\langle\tilde{O}_1^{-1}(q);\ \tilde{O}_1^1(-q)\rangle\rangle$$

$$=\frac{\langle\tilde{O}_1^0\rangle[\omega-A_2(q)]+2\langle\tilde{O}_2^0\rangle B_1(q)}{[\omega-\omega_1(q)][\omega-\omega_2(q)]}\ , \qquad (4.9a)$$

$$\frac{2}{\sqrt{3}}\langle\langle\tilde{O}_2^{-1}(q);\ \tilde{O}_1^1(-q)\rangle\rangle$$

$$=\frac{2\langle\tilde{O}_2^0\rangle[\omega-A_1(q)]+\langle\tilde{O}_1^0\rangle B_2(q)}{[\omega-\omega_1(q)][\omega-\omega_2(q)]}\ , \qquad (4.9b)$$

$$\tfrac{4}{3}\langle\langle\tilde{O}_2^{-1}(q);\ \tilde{O}_2^1(-q)\rangle\rangle$$

$$=\frac{\langle\tilde{O}_1^0\rangle[\omega-A_1(q)]+2\langle\tilde{O}_2^0\rangle B_2(q)}{[\omega-\omega_1(q)][\omega-\omega_2(q)]}\ , \qquad (4.9c)$$

$$\frac{2}{\sqrt{3}}\langle\langle\tilde{O}_1^{-1}(q);\ \tilde{O}_2^1(-1)\rangle\rangle$$

$$=\frac{2\langle\tilde{O}_2^0\rangle[\omega-A_2(q)]+\langle\tilde{O}_1^0\rangle B_1(q)}{[\omega-\omega_1(q)][\omega-\omega_2(q)]}\ , \qquad (4.9d)$$

$$\langle\langle\tilde{O}_2^{-2}(q);\ \tilde{O}_2^2(-q)\rangle\rangle=-\frac{\frac{3}{2}\langle\tilde{O}_1^0\rangle}{\omega-\omega_3(q)}\ , \qquad (4.9e)$$

where

$$\begin{aligned}
\omega_{1,2}(q)&=\tfrac{1}{2}[A_1(q)+A_2(q)]\mp\Gamma(q)\ ,\\
\Gamma(q)&=\{\tfrac{1}{4}[A_1(q)-A_2(q)]^2+B_1(q)B_2(q)\}^{1/2}\ , \qquad (4.10)\\
\omega_3(q)&=A_3(q)\ .
\end{aligned}$$

As predicted in Sec. III, the set of Green's functions (4.9) is redundant, since there are only two order parameters, $\langle\tilde{O}_1^0\rangle$ and $\langle\tilde{O}_2^0\rangle$. Our interpretation of Murao and Matsubara's theory is that they used (4.9c) and (4.9d) to calculate the order parameters. Again we interpret that Haley and Erdös[19] chose (4.9a) and (4.9b) as a consequence of the manner in which the kinematic restraint was imposed externally. In the scheme described in Sec. IV A all four Green's functions (4.9) are used to obtain the order parameters via the expansions (4.6). After some algebra, we find

$$\begin{aligned}
\langle\tilde{O}_1^0\rangle&=-\frac{1+2\Phi_1}{1+3\Phi_1+3\Phi_1^2-\Phi_2-3\Phi_2^2}\ ,\\
2\langle\tilde{O}_2^0\rangle&=-\langle\tilde{O}_1^0\rangle\frac{1+2\Phi_2}{1+2\Phi_1}\ ,
\end{aligned} \qquad (4.11)$$

where

$$\begin{aligned}
\Phi_1&=\frac{1}{2N}\sum_q[f_1(q)+f_2(q)]\ ,\\
\Phi_2&=-\frac{1}{2N}\sum_q\frac{B_1(q)+B_2(q)}{2\Gamma(q)}[f_1(q)-f_2(q)]\ , \qquad (4.12)\\
f_{1,2}(q)&=\frac{1}{e^{\omega_{1,2}(q)/kT}-1}\ .
\end{aligned}$$

C. Small-*D* limit

When D is small compared to $J(0)$, (4.10) reduces to

$$\begin{aligned}
\omega_1(q)&=-2\langle\tilde{O}_1^0\rangle[J(0)-J(q)]-\frac{2\langle\tilde{O}_2^0\rangle}{\langle\tilde{O}_1^0\rangle}D+\cdots\ ,\\
\omega_2(q)&=-2\langle\tilde{O}_1^0\rangle J(0)+\frac{2\langle\tilde{O}_2^0\rangle}{\langle\tilde{O}_1^0\rangle}D+\cdots\ .
\end{aligned} \qquad (4.13)$$

$\omega_1(q)$ is clearly the spin-wave excitation energy, with the anisotropy term correctly renormalized,[6,7] obeying the Callen-Callen power law.[33] On the other hand, $\omega_2(q)$ appears to represent the molecular-field excitation energy without dispersion, at least in RPA; this is understandable since the spin precession in the $S^z=0$ state is perpendicular to the precession of the renormalized spin. In the spin-wave approximation,[32] $\omega_1(q)$ is set equal to $\omega_2(q)$. In the present theory $\omega_1(q)$ and $\omega_2(q)$ are distinguished. The difference, however, may be incorporated into the order parameters only through the proper equal weight decomposition (4.6). It is for this reason that the results of Murao and Matsubara,[18] and Haley and Erdős[19] were reduced to the MFA and the Tahir-Kheli and ter Haar[34] results, respectively.

The Curie temperature for nearest-neighbor interaction is obtained from (4.11), in the isotropic limit, as

$$\frac{kT_C}{J}=\frac{4}{3}\,\frac{zS(S+1)}{1+F(-1)}\quad (S=1)\,, \tag{4.14}$$

where z is the coordination number and

$$F(-1)=\frac{1}{N}\sum_q \frac{J(0)}{J(0)-J(q)}\,. \tag{4.15}$$

The Curie temperature given by (4.14) is somewhat higher than the values obtained by the high-temperature-series expansion,[35,36] but is very close to that evaluated by Callen,[21] probably by coincidence.

At low temperatures the expansion of the magnetization by T for isotropic case yields the spurious T^3 term.[37] The magnitude of the T^3 term is equal to the RPA spin-wave theory,[38] but opposite in sign.

Obviously these inaccuracies were introduced by the RPA decoupling (3.5), and could only be eliminated by improved decoupling schemes.[39,40]

D. Ising limit

When D is large compared with $J(0)$, (4.10) yields

$$\begin{aligned}\omega_1(q)&=-D+2\langle\tilde{O}_2^0\rangle J(q)\\&\quad-\langle\tilde{O}_1^0\rangle[2J(0)-J(q)]+\cdots\,,\\ \omega_2(q)&=D+2\langle\tilde{O}_2^0\rangle J(q)\\&\quad-\langle\tilde{O}_1^0\rangle[2J(0)-J(q)]+\cdots\,.\end{aligned} \tag{4.16}$$

The crystal-field splitting D is *not* renormalized, and the excitations are identified as the crystal-field excitons. The thermal behavior of the system, therefore, may be approximately described by MFA.

In extending the present theory to the case when $D/J(0)$ is much greater than unity, we encounter one minor difficulty. In paramagnetic state ($T > T_C$), $\langle\tilde{O}_2^0\rangle$ is given by

$$\langle\tilde{O}_2^0\rangle=\frac{2}{1-6\Phi_2}=\frac{1}{2+3(\Phi_{21}+\Phi_{22})}\,, \tag{4.17}$$

where

$$\begin{aligned}\Phi_{21}&=\frac{1}{N}\sum_q C(q)f_1(q)\,,\\ \Phi_{22}&=\frac{1}{2N}\sum_q [C(q)-1]\,,\\ C(q)&=-\frac{B_1(q)+B_2(q)}{2\Gamma(q)}\\ &=\frac{D-2\langle\tilde{O}_2^0\rangle J(q)}{D[1-4\langle\tilde{O}_2\rangle J(q)/D]^{1/2}}\,.\end{aligned} \tag{4.18}$$

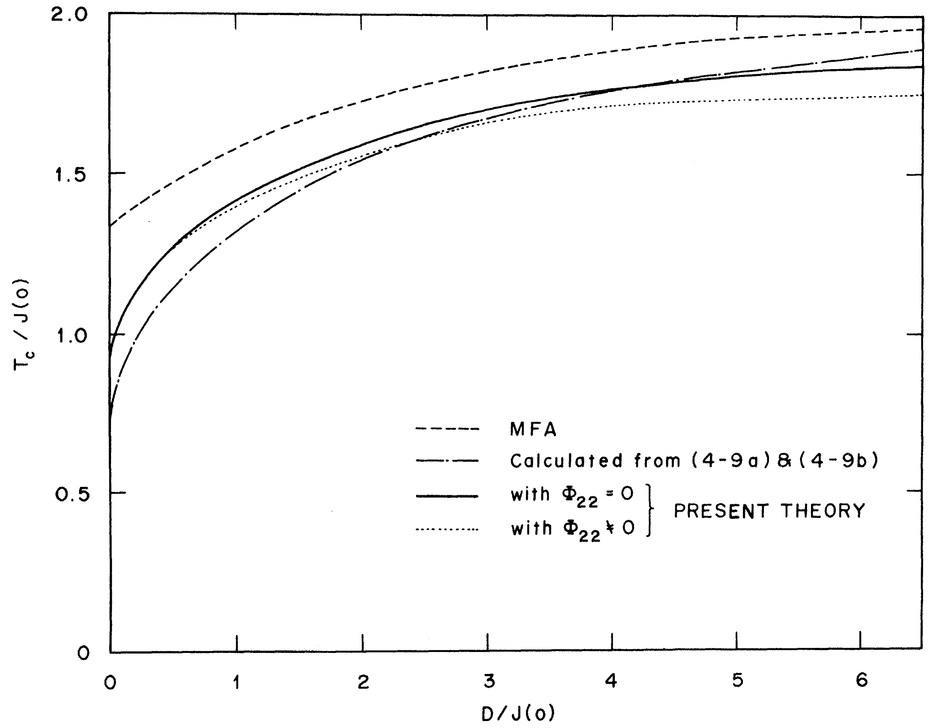

FIG. 2. Curie temperature $T_C/J(0)$ calculated by various methods as a function of $D/J(0)$. For details see text.

Φ_{21} represents thermal spin excitations, but Φ_{22} does not. Our interpretation is that Φ_{22} is a spurious "zero-point" spin excitation term which arose due to the inaccurate decoupling. Φ_{22} is usually very small, nevertheless, it leads to erronous results when $D/J(0)$ is large and Φ_{21} is small. In particular, it yields $\lim_{D/J(0)\to\infty}[T_C/J(0)]=0$, where as in MFA $\lim_{D/J(0)\to\infty}[T_C/J(0)]=2$. It must be pointed out that such inaccuracies are inherent in the decoupling theories, and that the earlier theories[18,19] are not free from them either. If we assume that $\Phi_{22}=0$, in the limit of $D/J(0)\to\infty$ (Ising limit) $T_C/J(0)$ yields

$$\lim_{D/J(0)\to\infty}[T_C/J(0)]=\frac{\sum_q[2J(0)-J(q)]e^{J(q)/kT_C}}{\sum_q e^{J(q)/kT_C}}\cdot \qquad (4.19)$$

A numerical work was undertaken to illustrate these results. No specific crystal structure was assumed since a cubic lattice is in contradiction to an axial crystal field and one has a large variety of choice for noncubic structures. Instead, a density of exchange interaction

$$\mathfrak{D}(J(q))\propto[1-|J(q)/J(0)|]^{1/2} \qquad (4.20)$$

was chosen so that the sum over q could be replaced by the integral over $J(q)$

$$d(J(q))\mathfrak{D}(J(q)) \;. \qquad (4.21)$$

The set of equations (4.10)-(4.12) was solved by iteration to obtain a self-consistent answer. With these assumptions, the transition temperature $T_C/J(0)$ was calculated as a function of $D/J(0)$. The results are compared with other results in Fig. 2. In the Ising limit, $T_C/J(0)$ is equal to 1.88 in the present case.

V. CONCLUSION

The angular momentum tensor-operator equivalents of spherical harmonics conveniently describe the collective motion of spins in a strong crystal field. The tensor properties of the operator equivalents have been utilized to show that their Green's functions are readily calculable when suitable decoupling techniques are employed. For the $S=1$ ferromagnet the Green's tensor of the present work is consistent with equivalent sets of Green's functions obtained by Murao and Matsubara[18] and Haley and Erdös.[19] Inspection of the spectroscopic density of the Green's functions shows that in the present method a different dispersion is assigned to each molecular-field transition, whereas in the spin-wave theory they are set equal. This difference is further established in the theory by a unique expansion of each order parameter—equal weight combination of self-correlation functions being chosen to exclude kinematically forbidden correlations. Although the results described here are not yet free of some minor inaccuracies produced mainly due to the random-phase approximation employed to decouple the Green's functions, the theory presents a unified and self-consistent view of the $S=1$ Heisenberg magnet in the crystalline field, together with the results described in the following paper.

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