Ground-state properties of a spin-1 Heisenberg ferromagnet with an arbitrary crystal-field potential

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The ground-state properties of a spin-1 Heisenberg ferromagnet with an arbitrary crystal-field potential are studied using the linked-cluster series expansion. In the linked-cluster expansion method quantum and spin-fluctuation correlations have been systematically included. We have obtained the magnetization and susceptibility series at zero temperature for a general lattice. The quantum fluctuations play an essential role in determining the magnetic ordering at $T=0$. The dependence of magnetic ordering on the crystal-field potentials and the critical values of the crystal-field potential for which magnetic ordering exists are discussed. The observed values of magnetization from the linked-cluster series expansion are appreciably depressed from its mean-field approximation values due to the quantum fluctuations.

Crystal-field effects in magnetic systems have long been recognized.[1] In real magnetic materials with localized moments, the crystal-field anisotropy plays a major role in determining the magnetic behavior of the system. The influence of crystal field on the thermodynamical properties of spin systems has been an important theoretical problem for many magnetic materials. Many models have been proposed for study. In this paper, we investigate the ground-state properties of the spin-1 quantum Heisenberg model with arbitrary crystal-field potential using the linked-cluster expansion method. The model has been proposed to study the magnetic properties of ferromagnetic Ni(2+) compounds with axial and rhombic crystal fields.[2]

This spin system has a phase transition at zero temperature. The mean-field approximation is generally used to study the thermodynamic quantities because of the complexities caused by the single-ion anisotropy term. However, in the mean-field approximation both quantum and spin-fluctuation correlations have been neglected. The works beyond the molecular-field approximation are a study of thermodynamic properties in the random phase approximation[3] and a more accurate study of the thermodynamic quantities using the linked-cluster expansion.[4] The linked-cluster expansion method has been the most efficient theoretical method for the study of realistic models of magnetic materials. The method can solve the many-body quantum spin systems with crystal-field single-ion anisotropies treated exactly and provides the most accurate results for the thermodynamic quantities of the systems.[5,6]

We obtain the first five coefficients of magnetization and susceptibility series for a general lattice and for an arbitrary range of exchange interaction. We, however, present only the series for the fcc lattice.

The Hamiltonian of the spin-1 ferromagnet with arbitrary crystal-field potential is given by

$$H=-D\sum_i (S_i^z)^2+E\sum_i [(S_i^x)^2-(S_i^y)^2] - \sum_{(i,j)} J_{ij}\mathbf{S}_i\cdot\mathbf{S}_j - g\mu_B h\sum_i S_i^z \ , \tag{1}$$

where D and E are positive parameters and measure the strength of the uniaxial and biaxial anisotropy. The E term describes fluctuation along the x axis and forces the spins to lie in the y-z plane. A Zeeman energy term is included in the Hamiltonian to find the magnetization and susceptibility. We restrict to an ordering along the z axis.

The Hamiltonian is divided into an unperturbed Hamiltonian H_0 and a perturbation part as H_1,

$$H=H_0+H_1 \ . \tag{2}$$

H_0 includes all single-ion potentials and a self-consistent field term extracted from the two-ion interaction potential. The self-consistent field is characterized by a parameter ($\langle S^z\rangle$) which minimizes the free energy of the system,

$$H_0=-D\sum_i (S_i^z)^2+E\sum_i [(S_i^x)^2-(S_i^y)^2] - h_{\rm eff}\sum_i S_i^z+NJz\langle S^z\rangle^2 \ . \tag{3}$$

H_1 includes the effects of correlations of the fluctuations,

$$H_1=-\sum_{(i,j)} J_{ij}[(S_i^z-\langle S^z\rangle)(S_j^z-\langle S^z\rangle)+S_i^+S_j^-] \ , \tag{4}$$

where z is the number of nearest neighbors and $h_{\rm eff}=g\mu_B h+2Jz\langle S^z\rangle$.

H_0 can be diagonalized exactly to obtain the eigen-

states

$$|\epsilon_1\rangle=|0\rangle\ , \tag{5}$$

$$|\epsilon_2\rangle=\sin\theta|1\rangle+\cos\theta|-1\rangle\ , \tag{6}$$

$$|\epsilon_3\rangle=\cos\theta|1\rangle-\sin\theta|-1\rangle\ , \tag{7}$$

and eigenenergies

$$\epsilon_1=Jz\langle S^z\rangle^2\ , \tag{8}$$

$$\epsilon_2=Jz\langle S^z\rangle^2-D+(E^2+h_{\rm eff}^2)^{1/2}\ , \tag{9}$$

$$\epsilon_3=Jz\langle S^z\rangle^2-D-(E^2+h_{\rm eff}^2)^{1/2}\ . \tag{10}$$

In Eqs. (5)–(7), $|m\rangle$ $(m=\pm1,0)$ denotes an eigenstate of the S^z operator with eigenvalue m. The mixing angle θ is given by

$$\tan\theta=\frac{E}{h_{\rm eff}+(E^2+h_{\rm eff}^2)^{1/2}}\ . \tag{11}$$

In the mean-field approximation, the zero-field ground-state susceptibility per site in the paramagnetic phase is

$$\chi_0^0=\frac{g^2\mu_B^2}{E-2Jz} \tag{12}$$

and the zero-field ground-state magnetization per site in the ordered phase is

$$M_0^0=g\mu_B\left[1-\left[\frac{E}{E_c}\right]^2\right]^{1/2}\ ,\quad E<E_c=2Jz$$
$$=0\ ,\quad \text{otherwise}\ . \tag{13}$$

Thus there exists a critical value E_c above which long-range ordering disappears. This behavior of the system is due to the quantum-mechanical nature of spin and does not occur if one considers the ground state in the classical spin systems. Since the mean-field approximation has ignored entirely the correlations of quantum and spin fluctuations which play an important role in the determination of E_c, the mean-field prediction for the critical E_c is independent of the uniaxial crystal-field potential D.

To improve the theory, terms describing the interactions of spin fluctuations, H_1 of Eq. (4), should be incorporated in the calculation. The brief outline of the linked-cluster expansion follows. The free energy F can be written as

$$F=F_0+\Delta F\ , \tag{14}$$

where F_0 is the free-energy term corresponding to the mean-field Hamiltonian H_0. ΔF, the corrections of free energy to F_0 due to the quantum and thermal fluctuation correlations, is expressed as[7]

$$\Delta F=-\frac{1}{\beta}\sum_{n=1}^{\infty}\frac{(-1)^n}{n!}\int_0^\beta d\tau_1\int_0^\beta d\tau_2\cdots\int_0^\beta d\tau_n\langle T_\tau[H_1(\tau_1)H_1(\tau_2)\cdots H_1(\tau_n)]\rangle_c\ , \tag{15}$$

where $\beta=(k_BT)^{-1}$ and T_τ is the τ-ordering operator which orders operators in the product with τ labels decreasing from left to right. The subscript c denotes the cumulant part of the τ-ordered product, or, in the diagram analysis, the contribution of the connected diagrams.

The τ dependence of $S^\alpha(\tau)$ is complicated. To facilitate the calculation, we use the standard basis operators:

$$L_{mn}\equiv|\varepsilon_m\rangle\langle\varepsilon_n|\ ,\quad m,n=1,2,3\ , \tag{16}$$

where $|\varepsilon_m\rangle$, $|\varepsilon_n\rangle$ are eigenstates of mean-field Hamiltonian H_0.

These operators satisfy the multiplication rule and the commutation relation:

$$L^i_{\alpha\beta}L^i_{\gamma\eta}=\delta_{\beta\gamma}L^i_{\alpha\eta}\ , \tag{17}$$

$$[L^i_{\alpha\beta},L^j_{\gamma\eta}]=\delta_{ij}(\delta_{\beta\gamma}L^i_{\alpha\eta}-\delta_{\eta\alpha}L^i_{\gamma\beta})\ . \tag{18}$$

The standard basis operators in the interaction picture have the simple τ dependence,

$$L_{mn}(\tau)=e^{(\varepsilon_m-\varepsilon_n)\tau}L_{mn}(0)\ . \tag{19}$$

Spin operators can be written as a linear combination of the standard basis operators,

$$S^\alpha=\sum_{m,n}|\varepsilon_m\rangle\langle\varepsilon_m|S^\alpha|\varepsilon_n\rangle\langle\varepsilon_n|$$
$$=\sum_{m,n}\langle\varepsilon_m|S^\alpha|\varepsilon_n\rangle L_{mn}\ . \tag{20}$$

It is convenient to represent the terms in the series expansion by diagrams. Diagrams involving up to four interaction lines are shown in Table I, where a line denotes a longitudinal interaction $(S_i^z-\langle S^z\rangle)(S_j^z-\langle S^z\rangle)$. Similarly, a solid line with an arrow denotes a transverse interaction $S_i^+S_j^-$.

The contribution of an nth-order graph to the free energy is given by the following rules.

(1) Associate a τ label with each arrow or line and a site label with each vertex.

(2) Associate a J_{ij} with each arrow or line.

(3) Associate a spin operator product with each vertex. An arrow pointing into a vertex contributes S_i^+ and an arrow pointing out of the vertex contributes S_i^-. A vertex for a line contributes $(S_i^z-\langle S^z\rangle)$. Assign the τ label of each arrow or line to the corresponding operators. Form the cumulant of the τ-ordered product associated with each vertex.

(4) Form the product of cumulant and J_{ij} associated with the graph.

(5) Integrate over $d\tau$ variable from 0 to β.

(6) Sum the lattice labels over all lattice sites.

(7) Multiply the contribution by the weight of the

graph.

(8) Multiply the result by $(-1)^n/n!$.

Summation over the lattice sites is obtained by taking the appropriate free multiplicity as the lattice constant[8] and multiplying the term by J^n. The free multiplicity can be expressed in terms of weak embedded lattice constants used in the conventional high-temperature series expansion.[9] The weight factors of the graphs and the lattice constants (weak embedded lattice constant) of the graphs are shown in Table I.

Each diagram represents a term in the expansion of $-\beta\Delta F$. The first step in the calculation of the τ integrals implied by each graph is to express the cumulants or the semi-invariants in terms of moments or thermal averages. Next the spin operators in each product are replaced by standard basis operators. Finally, the integrals containing a product of standard basis operators are calculated by using the multiple-site Wick reduction theorem.

TABLE I. List of free-energy connected graphs (cumulants).

graph	weight	lattice constant
	1	z
	1	z
	2	z
	6	z
	6	z
	4	z
	2	$6p_3$
	6	$6p_3$
	8	$6p_3$
	24	z
	24	z
	3	z
	4	z
	1	z
	8	z

graph	weight	lattice constant
	48	z^2
	24	z^2
	24	z^2
	12	z^2
	6	z^2
	12	z^2
	12	z^2
	3	z^2
	3	z^2
	48	z^2
	48	$6p_3$

graph	weight	lattice constant
	48	$6p_3$
	48	$6p_3$
	48	$6p_3$
	48	$6p_3$
	48	$6p_3$
	96	$6p_3$
	24	$8p_4+2z^2-z$
	6	$8p_4+2z^2-z$
	12	$8p_4+2z^2-z$
	6	$8p_4+2z^2-z$
	48	$8p_4+2z^2-z$

The replacement of the product of spin operators by standard basis operators in the thermal average expression is done using a symbolic manipulation program. All nonzero contributions are found and regrouped with terms of the same τ by the program. The multiple-integrals containing τ-ordered products of standard basis operators are calculated by using the multiple-site Wick reduction theorem.[6] A computer can be used to handle the integration procedure,

$$\int_0^\beta d\tau_1 \cdots \int_0^\beta d\tau_k \cdots \int_0^\beta d\tau_n \langle T_\tau[O_1(\tau_1)\cdots O_k(\tau_k)\cdots O_n(\tau_n)]\rangle_0$$
$$= \frac{1}{\epsilon_k}\int_0^\beta d\tau_1 \cdots \int_0^\beta d\tau_n [\langle T_\tau\{[O_1,O_k]_{\tau_1}\cdots O_n(\tau_n)\}\rangle_0$$
$$+\langle T_\tau\{O_1(\tau_1)[O_2,O_k]_{\tau_2}\cdots O_n(\tau_n)\}\rangle_0 + \cdots \langle T_\tau\{O_1(\tau_1)\cdots[O_n,O_k]_{\tau_n}\}\rangle_0] \,. \quad (21)$$

We have obtained the first five coefficients in the susceptibility series and the magnetization series. The series obtained have been checked in (i) the $E=0$ limit and (ii) the $D=0$ and $E=0$ limit. In the $E=0$ limit, the result of the current calculation agrees completely with Wentworth and Wang.[6] In the $D=0$ and $E=0$ limit, the series reduced to the well-known result found for the isotropic Heisenberg system.[10] Furthermore we calculate the free energy and susceptibility by the two point cluster method. The results of this calculation of the free energy and susceptibility series agree with the series calculated by the linked-cluster expansion by taking $z=1$ and $p_4=0$.

We then obtained the zero temperature susceptibility series and the zero temperature magnetization series by calculating the finite temperature series in the limit that temperature T approaches zero or β approaches infinity,

$$M^0 = \lim_{\beta\to\infty} -\frac{\partial F}{\partial h} = g\mu_B \sum_{n=0}^{\infty} m_n^0(D,E,h_{\text{eff}})\{2Jz/E\}^n \quad (22)$$

and

$$\chi^0 = \lim_{\beta\to\infty} -\frac{\partial^2 F}{\partial h^2} = \frac{g^2\mu_B^2}{E}\sum_{n=0}^{\infty} a_n^0(D,E,h_{\text{eff}})\{2Jz/E\}^n \,, \quad (23)$$

where $h_{\text{eff}} = g\mu_B h + 2JzM^0/g\mu_B$. In the Appendix we list the polynomials of a_n^0 for $\chi^0(h=0)$ for the fcc lattice. The coefficients m_n^{10} are too long to be presented here. The coefficients are available upon request.

The standard ratio test method[10] is employed to analyze the series. At $T=0$, the critical value of $E/2Jz$ is estimated (in the disordered phase) by the extrapolation:

$$\frac{E_c}{2Jz} = \frac{1}{n-m}[n\nu_n^0(D,E_c) - m\nu_m^0(D,E_c)] \,, \quad (24)$$

where $\nu_n^0 = a_n^0/a_{n-1}^0$. With the values of $D/2Jz$ fixed, $E_c/2Jz$ is found by solving Eq. (24) self-consistently. The values of $E_c/2Jz$ as a function of $D/2Jz$ found with $n=4$ and $m=3$ for a fcc lattice are shown in Fig. 1. The mean-field result is also plotted (dashed line) for comparison. The easy-axis anisotropy $D/2Jz$ favors the magnet-

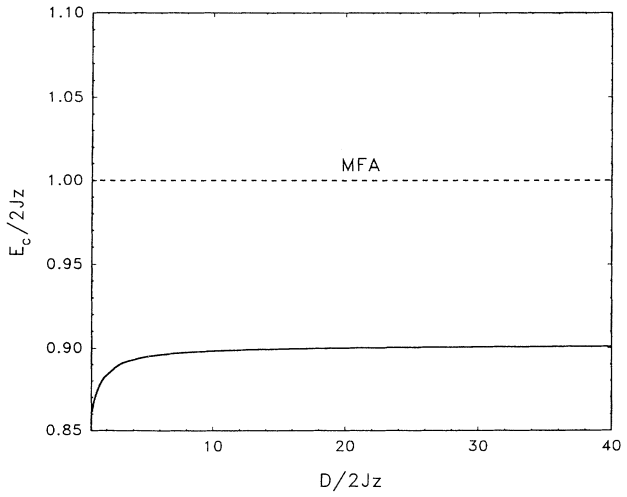

FIG. 1. The critical point for the magnetic ordering at zero temperature $E_c/2Jz$ as a function of $D/2Jz$. The solid line gives results of the linked-cluster series expansion for a fcc lattice. The dashed line gives mean-field approximation.

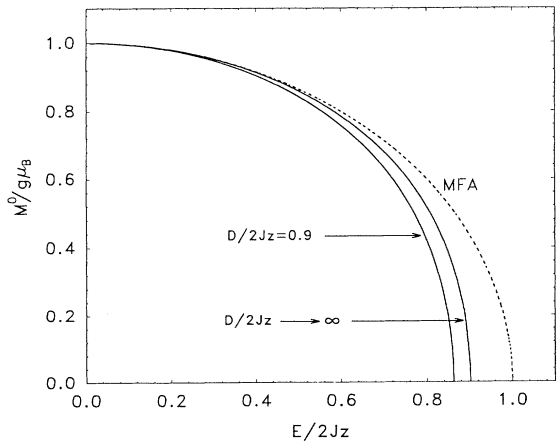

FIG. 2. Magnetization at zero temperature as a function $E/2Jz$ for $D/2Jz=0.9$ and $D/2Jz=\infty$ at zero external field. The solid line gives results of the linked-cluster expansion for a fcc lattice. The dashed line gives mean-field approximation.

TABLE II. Coefficients for Eq. (A1).

$c^2_{i,j,k,l,m}$	d^2	i	j	k	l	m
91	24	0	0	3	0	0
−6	24	0	0	1	2	0
−4	24	0	−1	2	2	0

$c^3_{i,j,k,l,m}$	d^3	i	j	k	l	m
−88	288	0	−1	1	4	0
−28	288	0	−2	2	4	0
−6	288	2	0	2	0	0
+2036	288	0	0	4	0	0
−60	288	0	0	0	4	0
+5	288	2	−1	3	0	0
−187	288	0	−1	3	2	0
−8	288	2	−2	2	2	0
−282	288	0	0	2	2	0
+12	288	2	0	0	2	0

$c^4_{i,j,k,l,m}$	d^4	i	j	k	l	m
+2880	41472	0	2	1	0	2
+7200	41472	0	−1	0	4	2
−5760	41472	0	1	0	2	2
+1440	41472	0	1	2	0	2
+2880	41472	0	0	−1	4	2
−8640	41472	0	0	1	2	2
−2880	41472	0	−1	2	2	2
+5760	41472	0	−2	1	4	2
+1440	41472	0	−3	2	4	2

$c^4_{i,j,k,l,m}$	d^4	i	j	k	l	m
+168	41472	4	−1	0	2	0
+94	41472	4	0	1	0	0
+74	41472	4	−2	3	0	0
−168	41472	4	−1	2	0	0
−188	41472	4	0	−1	2	0
+148	41472	4	−2	1	2	0
−128	41472	4	−3	2	2	0
−35280	41472	0	−1	0	6	0
−14904	41472	0	0	−1	6	0
−5472	41472	0	−3	2	6	0
−25848	41472	0	−2	1	6	0
+542173	41472	0	0	5	0	0
−698	41472	0	2	3	0	0
+2112	41472	2	−1	0	4	0
+1512	41472	0	1	4	0	0
−117507	41472	0	0	3	2	0
−3786	41472	2	0	3	0	0
−13473	41472	0	−2	3	4	0
−22	41472	0	2	1	2	0
−77472	41472	0	−1	4	2	0
−45182	41472	0	−1	2	4	0
+592	41472	0	1	2	2	0
+3168	41472	2	−1	4	0	0
+6426	41472	2	0	1	2	0
+2480	41472	2	0	−1	4	0
−4302	41472	2	−2	3	2	0
−1744	41472	2	−2	1	4	0
−1376	41472	2	−3	2	4	0
−348	41472	0	1	0	4	0
−32057	41472	0	0	1	4	0

ic ordering. When $D/2Jz$ is small comparable to quantum fluctuation from $E/2Jz$, the effects of zero point fluctuation are important. Consequently, the value of $E_c/2Jz$ is small in order to destroy the magnetic ordering. As $D/2Jz$ increases, the effect of correlation of spin fluctuation is suppressed. Therefore, the value of $E_c/2Jz$ must be large enough to destroy the magnetic ordering. Since the model being studied is the quantum spin system, the critical value for the magnetic ordering in $D/2Jz \to \infty$ limit (Ising limit) is different from the mean-field approximation.

Similarly, at $T=0$, we obtain the magnetization as a function of $E/2Jz$ by using the ratio method. If the self-consistently determined value of $M^0/g\mu_B$ has been chosen then the equation

$$\bar{M}^0/g\mu_B = \frac{\sum_{n=0}^{\infty} m_n^0(D,E,h_{\text{eff}})\{2Jz/E\}^n}{M^0/g\mu_B - \sum_{n=0}^{\infty} m_n^0(D,E,h_{\text{eff}})\{2Jz/E\}^n} \tag{25}$$

should diverge as the order of the series $M^0/g\mu_B$ goes to infinity. The magnetization as a function of crystal-field potential $E/2Jz$ for a fcc lattice is shown in Fig. 2 for a certain value of $D/2Jz$. The corresponding mean-field result is plotted (dashed line) for comparison. It is clear that the quantum spin fluctuations have substantially reduced the critical value of E from the mean field value $2Jz$.

In summary, we have studied the ground-state properties of a spin-1 ferromagnet with arbitrary crystal-field potentials using the linked-cluster expansion. We have shown that the quantum fluctuations play a major role in determining the magnetic ordering of the quantum spin systems at $T=0$. Higher-order terms are desirable for an in-depth study of this system.

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APPENDIX

The coefficients of the susceptibility series in the paramagnetic phase are polynomials in the variables x, z, p, q, and u as

$$a_n^0=\frac{d^n}{E}\sum_{i,j,k,l,m} c_{i,j,k,l,m}^n q^i x^j z^k p^l u^m \; ; \quad n\geq 2 \; ,$$
$$a_0^0=1/E \; ; \quad a_1^0=2/E \; , \tag{A1}$$

where $q=1/(E-D)$, $x=1/D$, $z=1/E$, $p=1/(E+D)$, and $u=1/(2E+D)$. d^n is a common denominator for nth-order series. The coefficients in Eq. (A1) are listed in Table II for the fcc lattice.

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