

## Polarization of the spin- $S$ exchange-interaction model

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The spin- $S$  exchange interaction model of ferromagnetism is studied by the mean-field approximation. This model has  $4S(S+1)$  order parameters, and has infinitely many ground-state configurations. We define a single polarization parameter to describe the ordering of the system. Thermal variation of the polarization  $q(T)$  is determined for various spins. The phase transition is first order (except for  $S = \frac{1}{2}$ ) with phase transition temperature  $kT_c/Jz = (2S-1)/(4S \ln 2S)$ , where  $z$  is the coordination number, and the discontinuity of  $q$  at  $T_c$  is  $q_c = (2S-1)/2S$ .

### I. INTRODUCTION

The exchange operator was studied by Schrödinger 50 years ago.<sup>1</sup> The exchange operator  $P_{ij}$  has the property that it permutes the spin coordinates of  $\mathbf{S}_i$  and  $\mathbf{S}_j$ , which have the same spin multiplicity. That is,

$$P_{ij}|\alpha\rangle_i|\beta\rangle_j = |\beta\rangle_i|\alpha\rangle_j, \quad (1)$$

where  $|\alpha\rangle_i$  and  $|\beta\rangle_j$  are eigenstates of  $S_{iz}$  and  $S_{jz}$ , with eigenvalues  $\alpha$  and  $\beta$ , respectively. Schrödinger showed that  $P_{ij}$  can be expressed as a polynomial of degree  $2S$  in  $(\mathbf{S}_i \cdot \mathbf{S}_j)$ ,

$$P_{ij} = (-1)^{2S} \left[ 1 + \sum_{n=1}^{2S} \frac{(-1)^n}{(n!)^2} \prod_{m=1}^n [2\mathbf{S}_i \cdot \mathbf{S}_j + 2S(S+1) - m(m-1)] \right] \\ = \sum_{n=0}^{2S} A_n(S) (\mathbf{S}_i \cdot \mathbf{S}_j)^n, \quad (2)$$

where the coefficients  $A_n(S)$  can be obtained by expanding the products and rearranging terms. The exchange operator had been used to construct a spin model, called the exchange interaction model (EI model),<sup>2,3</sup> two decades ago to study the effect of nonlinear terms  $(\mathbf{S}_i \cdot \mathbf{S}_j)^n$  on the critical properties of spin systems. The EI model is of theoretical interest and has received attention recently.<sup>4-9</sup> The Hamiltonian of the EI model is given by

$$\mathcal{H} = -J \sum_{\langle ij \rangle} P_{ij} \quad (3a)$$

or, in the traceless form,

$$\mathcal{H} = -J \sum_{\langle ij \rangle} [P_{ij} - (2S+1)^{-1}], \quad (3b)$$

where  $J$  is the coupling constant and the summation is over all nearest-neighbor pairs of sites.

For a system of  $N$  spins, the exchange operators  $P_{ij}$  form elements of the symmetry group of degree  $N$ . By using permutation properties of  $P_{ij}$ , the EI model for general values of spin has been studied by several ap-

proaches, such as the high-temperature series expansions,<sup>3</sup> quantum Monte Carlo simulations,<sup>8</sup> and real-space renormalization-group methods.<sup>7</sup> These studies, however, did not investigate thermal variations of order parameters of the EI model. For systems which contain the nonlinear interaction  $(\mathbf{S}_i \cdot \mathbf{S}_j)^n$ , there are higher-order moments besides the dipole moments  $S_x$ ,  $S_y$ , and  $S_z$ . To study thermal variations of various moments, it is more appropriate to express  $P_{ij}$  in terms of spin tensor operators rather than  $(\mathbf{S}_i \cdot \mathbf{S}_j)^n$ .

For spin  $S = \frac{1}{2}$ , the EI model is identical to the Heisenberg model. When  $S = 1$ , the traceless EI model has been expressed as<sup>9</sup>

$$\mathcal{H} = \frac{-J}{2} \sum_{\langle ij \rangle} \left[ \sum_{\alpha} S_{i\alpha} S_{j\alpha} + \sum_{\beta} Q_{i\beta} Q_{j\beta} \right], \quad (4)$$

where  $S_{\alpha}$  are the three dipole operators  $S_x$ ,  $S_y$ , and  $S_z$  and  $Q_{\beta}$  are the five quadrupole operators

$$Q_0 = \sqrt{3}[S_z^2 - S(S+1)/3], \\ Q_1 = S_x^2 - S_y^2, \\ Q_{xy} = S_x S_y + S_y S_x, \\ Q_{xz} = S_x S_z + S_z S_x, \\ Q_{yz} = S_y S_z + S_z S_y. \quad (5)$$

Thermal averages of the dipole operators  $\langle S_{\alpha} \rangle$  and the quadrupole operators  $\langle Q_{\beta} \rangle$  for the spin-1 EI model [Eq. (4)] have been investigated by the mean-field approximation,<sup>10</sup> Green's function theory,<sup>9</sup> and a constant-coupling method.<sup>6</sup>

When  $S > 1$ , there are higher-rank multipoles (spin tensor operators) besides  $S_{\alpha}$  and  $Q_{\beta}$ . The expression of  $P_{ij}$  in terms of products of spin tensor operators [similar to Eq. (4)] has not been given before. Studies of thermal variations of order parameters of the EI model for general spins are not yet available even in the simplest mean-field approximation. The spin- $S$  EI model has  $4S(S+1)$  order parameters (we can eliminate three of them by choosing the coordinates). It is difficult to study the thermal behavior of all order parameters for  $S \geq \frac{3}{2}$ . The purpose of this paper is to present a mean-field

theory of the EI model for general spins. In Sec. II we describe some properties of the Hermitian tensor operators  $Q_m^{(l)}$ . The exchange operator is expressed in terms of products of these operators. In Sec. III we briefly discuss the mean-field approximation and present some general properties of the EI model. Because of the symmetry of the exchange operator, we assume that all order parameters  $\langle Q_m^{(l)} \rangle$  have the same temperature dependence and define a single polarization parameter  $q(T)$ . Thermal variations of  $q(T)$  and the phase-transition temperatures are determined for various spins. In Sec. IV we discuss the physical meaning of the assumption that all order parameters have the same thermal behavior and show some numerical verifications of this assumption. A summary and discussion of our results are also given in this section.

## II. SPIN TENSOR OPERATORS

The unnormalized tensor operators  $O_m^{(l)}(S_z, S^\pm)$  are defined by the generating function<sup>11</sup>

$$\sum_{m=-l}^m t^m O_m^{(l)}(S_z, S^\pm) = (-tS^+ + 2S_z + S^-t^{-1})^l. \quad (6)$$

The normalization is chosen so that, in the classical limit [ $S_z = S \cos\theta$ ,  $S^\pm = S \sin\theta e^{\pm i\phi}$ , and  $S(S+1) \approx S^2 \gg 1$ ],

$$O_m^{(l)}(S_z, S^\pm) = S^l \sqrt{4\pi/(2l+1)} Y_{l,m}(\theta, \phi), \quad (7)$$

where  $Y_{l,m}$  are the spherical harmonics. The explicit form of  $O_m^{(l)}$  for  $l \leq 6$  have been given by Smith and Thornley.<sup>12</sup> The operators  $O_m^{(l)}$  are traceless for  $l \neq 0$  and are orthogonal in the sense that

$$\text{Tr} O_m^{(l)} O_{-m'}^{(l')} = (-1)^m \delta_{l,l'} \delta_{m,m'} / A(S, l), \quad (8)$$

where  $\delta_{l,l'}$  and  $\delta_{m,m'}$  are Kronecker delta functions and the constants  $A(S, l)$  are

$$A(S, l) = 2^{2l} (2l+1) (2S-l)! / (2S+l+1)!. \quad (9)$$

The operators  $O_m^{(l)}$  are non-Hermitian for  $m \neq 0$ . Expectation values (or thermal averages) of these operators are complex numbers in general. We define the Hermitian operators  $Q_{\pm m}^{(l)}$  as linear combinations of  $O_{\pm m}^{(l)}$ :

$$\begin{aligned} Q_m^{(l)} &= \frac{1}{\sqrt{2}} [(-1)^m O_m^{(l)} + O_{-m}^{(l)}], \\ Q_{-m}^{(l)} &= \frac{-i}{\sqrt{2}} [(-1)^m O_m^{(l)} - O_{-m}^{(l)}], \end{aligned} \quad (10)$$

for  $m > 0$ , and

$$Q_0^{(l)} = O_0^{(l)}.$$

It is straightforward to show that the Hermitian tensor operators  $Q_m^{(l)}$  are also traceless ( $l \neq 0$ ) and orthogonal. That is,

$$\text{Tr} Q_m^{(l)} = (2S+1) \delta_{l,0}, \quad (11)$$

$$\text{Tr} Q_m^{(l)} Q_{m'}^{(l')} = \delta_{l,l'} \delta_{m,m'} / A(S, l). \quad (12)$$

The first few Hermitian tensor operators are  $Q_0^{(0)} = 1$ ,  $Q_0^{(1)} = S_z$ ,  $Q_1^{(1)} = S_x$ , and  $Q_{-1}^{(1)} = S_y$  and, in terms of  $Q_{\beta}^{(2)}$  [Eq. (5)],  $Q_0^{(2)} = \sqrt{3} Q_0 / 2$ ,  $Q_1^{(2)} = \sqrt{3} Q_{xz} / 2$ ,  $Q_{-1}^{(2)}$

$= \sqrt{3} Q_{yz} / 2$ ,  $Q_2^{(2)} = \sqrt{3} Q_1 / 2$ , and  $Q_{-2}^{(2)} = \sqrt{3} Q_{xy} / 2$ .

The inner product of the  $l$ th-rank spin operators at sites  $i$  and  $j$  is defined as<sup>13</sup>

$$C_l(\mathbf{S}_i \cdot \mathbf{S}_j) = \sum_{m=-l}^l (-1)^m O_m^{(l)}(S_{iz}, S_i^\pm) O_{-m}^{(l)}(S_{jz}, S_j^\pm). \quad (13)$$

In terms of the Hermitian operators  $Q_m^{(l)}$ ,  $C_l(\mathbf{S}_i \cdot \mathbf{S}_j)$  is given by

$$C_l(\mathbf{S}_i \cdot \mathbf{S}_j) = \sum_{m=-l}^l Q_m^{(l)}(S_{iz}, S_i^\pm) Q_m^{(l)}(S_{jz}, S_j^\pm). \quad (14)$$

As  $Q_m^{(l)}$  are traceless, orthogonal, and Hermitian, if a Hamiltonian contains a term  $\sum_{\langle ij \rangle} C_l(\mathbf{S}_i \cdot \mathbf{S}_j)$ , the thermal averages of  $Q_m^{(l)}$  are the order parameters of the system.

The nonlinear term  $(\mathbf{S}_i \cdot \mathbf{S}_j)^n$  can be expressed as a linear combination of  $C_l(\mathbf{S}_i \cdot \mathbf{S}_j)$  for  $l \leq n$ . Therefore the exchange operator  $P_{ij}$  can be expressed as linear combination of  $C_l(\mathbf{S}_i \cdot \mathbf{S}_j)$  for  $l \leq 2S$ . It can be shown that<sup>14</sup>

$$P_{ij} = \sum_{l=0}^{2S} A(S, l) C_l(\mathbf{S}_i \cdot \mathbf{S}_j), \quad (15)$$

where  $A(S, l)$  are given by Eq. (9) and  $C_l(\mathbf{S}_i \cdot \mathbf{S}_j)$  by Eq. (14). From Eqs. (14) and (15), we see that there are

$$3 + 5 + 7 + \cdots + (4S+1) = 4S(S+1)$$

order parameters  $\langle Q_m^{(l)} \rangle$  for the spin- $S$  EI model.

Some expressions of  $P_{ij}$  are

$$\begin{aligned} P_{ij} &= 2C_1 + \frac{1}{2} \quad \text{for } S = \frac{1}{2}, \\ P_{ij} &= \frac{2}{3}C_2 + \frac{1}{2}C_1 + \frac{1}{3} \quad \text{for } S = 1, \\ P_{ij} &= \frac{4}{45}C_3 + \frac{1}{9}C_2 + \frac{1}{5}C_1 + \frac{1}{4} \quad \text{for } S = \frac{3}{2}, \\ P_{ij} &= \frac{2}{315}C_4 + \frac{1}{90}C_3 + \frac{2}{63}C_2 + \frac{1}{10}C_1 + \frac{1}{5} \quad \text{for } S = 2, \end{aligned} \quad (16)$$

where  $C_l$  are shorthand notations of  $C_l(\mathbf{S}_i \cdot \mathbf{S}_j)$ . The equation for  $S = \frac{1}{2}$  is well known. For  $S = 1$ , this result is the same as Eq. (4), but with different normalization of  $Q_m^{(2)}$ .

## III. MEAN-FIELD APPROXIMATION

For a lattice of coordination number  $z$ , the mean-field Hamiltonian<sup>10</sup> per spin  $\mathcal{H}_M$  of the traceless EI model is

$$\begin{aligned} \mathcal{H}_M &= -Jz \sum_{l=1}^{2S} \sum_{m=-l}^l A(S, l) \langle Q_m^{(l)} \rangle Q_m^{(l)} \\ &\quad + \frac{Jz}{2} \sum_{l=1}^{2S} \sum_{m=-l}^l A(S, l) \langle Q_m^{(l)} \rangle^2 \end{aligned} \quad (17)$$

and the Gibbs free energy per spin  $F$  is

$$-F/Jz = \frac{1}{K} \ln \text{Tr} \exp(-\mathcal{H}_M / kT), \quad (18)$$

where  $K = Jz / kT$  is the inverse temperature. The second term in Eq. (17) is a constant operator, which may be neglected if one is not interested in calculating the energy of the system. It is necessary to include this term to ob-

tain the correct energy, free energy, and specific heat.

The order parameters  $\langle Q_m^{(l)} \rangle$  are determined by the conditions that  $\partial F / \partial \langle Q_m^{(l)} \rangle = 0$ , which give the well-known equations

$$\langle Q_m^{(l)} \rangle = \frac{\text{Tr} Q_m^{(l)} \exp(-\mathcal{H}_M/kT)}{\text{Tr} \exp(-\mathcal{H}_M/kT)} \quad \text{for all } l \text{ and } m. \quad (19)$$

The above self-consistent equations may have many different sets of solutions  $\{\langle Q_m^{(l)} \rangle\}$ , and the one which has the lowest Gibbs free energy [Eq. (18)] describes the equilibrium state of the system.

We first consider the ground-state property of  $\mathcal{H}_M$ . At the zero temperature  $T=0$ , the system is in a ground state. The wave functions of a spin- $S$  particle have the general form

$$|\phi_i\rangle = \sum_{\alpha=-S}^S a_{i\alpha} |\alpha\rangle, \quad (20)$$

where  $|\alpha\rangle$  are eigenstates of  $S_z$  with eigenvalues  $\alpha$  and  $a_{i\alpha}$  are constants subject to the normalization that

$$\langle \phi_i | \phi_i \rangle = \sum_{\alpha=-S}^S a_{i\alpha}^* a_{i\alpha} = 1. \quad (21)$$

The ground state of the EI model is the wave function  $|\phi_k\rangle$ , which minimizes the energy

$$\langle \mathcal{H}_M \rangle = \frac{-Jz}{2} \sum_{l=1}^{2S} \sum_{m=-l}^l A(S, l) \langle \phi_k | Q_m^{(l)} | \phi_k \rangle^2, \quad (22)$$

where  $\langle \phi_k | Q_m^{(l)} | \phi_k \rangle$  are the expectation values of  $Q_m^{(l)}$  in the state  $|\phi_k\rangle$ .

For different  $|\phi_k\rangle$ ,  $\langle \phi_k | Q_m^{(l)} | \phi_k \rangle$  are different. But we show in the Appendix that, for any state  $|\phi_k\rangle$ ,

$$\langle Q_m^{(l)} \rangle = (\text{Tr} \mathbf{1})^{-1} \left[ \text{Tr} Q_m^{(l)} \left( 1 + K \sum_{l'=1}^{2S} \sum_{m'=-l'}^{l'} A(S, l') \langle Q_{m'}^{(l')} \rangle Q_{m'}^{(l')} + \dots \right) \right]. \quad (26)$$

From the orthogonality relation Eq. (12), we have

$$\langle Q_m^{(l)} \rangle = \frac{K}{2S+1} \langle Q_m^{(l)} \rangle + \dots \quad \text{for all } l (\neq 0) \text{ and } m. \quad (27)$$

Equation (27) means that all nonzero order parameters  $\langle Q_m^{(l)} \rangle$  occur simultaneously at the temperature  $kT_0/Jz = (2S+1)^{-1}$ , if the phase transition is second order. We have calculated the free energies numerically for some solutions near  $T_0$ . Our results, however, show that the phase transitions are first order except for  $S = \frac{1}{2}$ .

To study thermal variations of the order parameters  $\langle Q_m^{(l)} \rangle$  associated with a given ground state  $|\phi_k\rangle$ , we write

$$\langle Q_m^{(l)} \rangle = q_m^{(l)}(T) \langle \phi_k | Q_m^{(l)} | \phi_k \rangle \quad \text{for all } l (\neq 0) \text{ and } m, \quad (28)$$

with  $q_m^{(l)}(0) = 1$ . In general, different values of  $l$  and  $m$

$$\sum_{l=0}^{2S} \sum_{m=-l}^l A(S, l) \langle \phi_k | Q_m^{(l)} | \phi_k \rangle^2 = 1. \quad (23)$$

Therefore any pure state  $|\phi_k\rangle$  has the same ground-state energy

$$\langle \mathcal{H}_M \rangle = \frac{-Jz}{2} \frac{2S}{2S+1}. \quad (24)$$

The EI model has infinitely many ground-state configurations. (Some of them are equivalent so that they can be transformed into one another by rotations of coordinate axes.)

At finite temperatures, the system is no longer in a pure state. There exists a set of  $2S+1$  orthogonal wave functions  $|\phi_0\rangle, |\phi_1\rangle, \dots, |\phi_i\rangle, \dots, |\phi_{2S}\rangle$ . (There are infinitely many different ways to select the set of  $2S+1$  wave functions. But different sets of wave functions are transformed into one another by unitary transformations.) The system has the probability  $p_i$  to be in the state  $|\phi_i\rangle$  ( $p_i$  are proportional to the Boltzmann factors), and the thermal averages are

$$\langle Q_m^{(l)} \rangle = \sum_{i=0}^{2S} p_i \langle \phi_i | Q_m^{(l)} | \phi_i \rangle. \quad (25)$$

Equation (25) is the same as Eq. (19). In general, the set of  $4S(S+1)$  coupled equations has infinitely many sets of solutions (similar to the case  $T=0$ ). It is impractical and not meaningful to study all the solutions. We will only investigate their common properties.

If there is a second-order phase transition at the temperature  $T_0$ , near this temperature,  $\langle Q_m^{(l)} \rangle \ll 1$ . By expanding  $\exp(-\mathcal{H}_M/kT)$  in power series of  $\langle Q_m^{(l)} \rangle$ , Eq. (19) becomes

will lead to different functions  $q_m^{(l)}(T)$ . Moreover, the solutions  $q_m^{(l)}(T)$  may be different for different pure states  $|\phi_k\rangle$ . For the spin-1 EI model, it has been shown that  $q_m^{(l)}(T)$  are the same for all values of  $l$  and  $m$ , and for all different ground-state solutions.<sup>10</sup> It has also been proved by the high-temperature series-expansion method that thermal fluctuations of the  $2S$  independent multipoles have the same temperature dependence for all spins and for all lattices.<sup>15</sup> It is reasonable to make the assumption that

$$q_m^{(l)}(T) = q(T) \quad \text{for all } l (\neq 0) \text{ and } m. \quad (29)$$

Physical meanings and some numerical verifications of Eq. (29) will be discussed in Sec. IV.

The function  $q(T)$  describes the degree of polarization of the system. In general,  $q(T)$  may depend on the state  $|\phi_k\rangle$ . We will see immediately that all  $|\phi_k\rangle$  have the same  $q(T)$ . From Eq. (23),

$$\sum_{l=1}^{2S} \sum_{m=-l}^l A(S, l) \langle \phi_k | Q_m^{(l)} | \phi_k \rangle^2 = \frac{2S}{2S+1}. \quad (30)$$

Substituting Eqs. (28)–(30) into Eq. (17), we obtain

$$-\mathcal{H}_M/kT = Kq(T)\rho_k - \frac{Kq(T)}{2S+1} [1 + Sq(T)], \quad (31)$$

where

$$\rho_k = \sum_{l=0}^{2S} \sum_{m=-l}^l A(S, l) \langle \phi_k | Q_m^{(l)} | \phi_k \rangle Q_m^{(l)}. \quad (32)$$

As shown in the Appendix,  $\rho_k$  is the density matrix of the pure state  $|\phi_k\rangle$ . The density matrix  $\rho_k$  has  $2S+1$  eigenvalues; one of them is 1 and the others are 0. Therefore

$$\text{Tr exp}[Kq(T)\rho_k] = e^{Kq+2S} \quad (33)$$

and

$$F/Jz = -\frac{1}{K} \ln(e^{Kq+2S}) + \frac{q(1+Sq)}{2S+1}. \quad (34)$$

We see that  $F/Jz$  is the same for all states  $|\phi_k\rangle$  and so is the polarization  $q(T)$ , which is determined by  $\partial F/\partial q = 0$ . That is,

$$q = \frac{e^{Kq}-1}{e^{Kq+2S}}. \quad (35)$$

Consider the spin- $\frac{3}{2}$  system for illustration. Figure 1 plots the free energy [Eq. (34)] for  $S = \frac{3}{2}$  and for several temperatures  $K^{-1}$ . The values of  $q$  which have the zero slope are the solutions of Eq. (35). When  $K^{-1} < K_0^{-1} = (2S+1)^{-1}$ , the free energy has only one minimum at  $q > 0$ . This solution corresponds to a point on the line  $AB$  in Fig. 2. For  $K^{-1} > K_m^{-1} = 0.310680$ , a minimum of  $F$  occurs only at  $q = 0$ . When  $K_0^{-1} < K^{-1} < K_m^{-1}$ , a free-energy curve has two minima

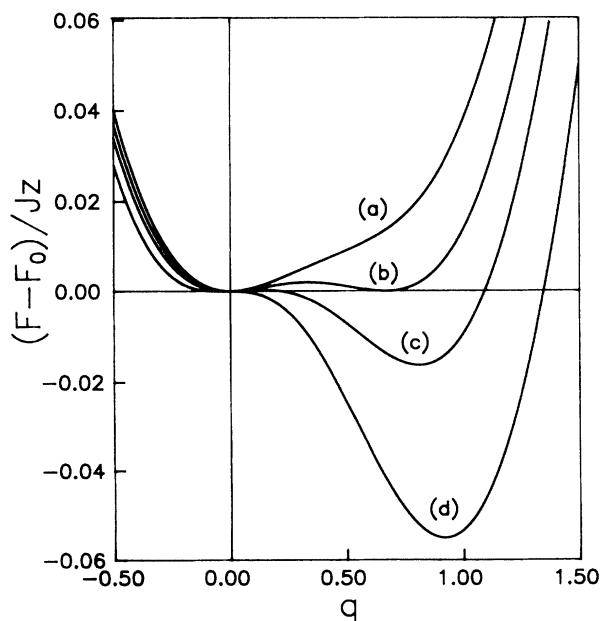


FIG. 1. Gibbs free energies as functions of  $q$  for  $S = \frac{3}{2}$  and for temperatures (a)  $K^{-1} = 0.33$ , (b)  $K_c^{-1} = 0.303413$ , (c)  $K^{-1} = 0.28$ , and (d)  $K^{-1} = 0.24$ . A constant  $F_0/Jz = -K^{-1} \ln(2S+1)$  is subtracted from Eq. (34).

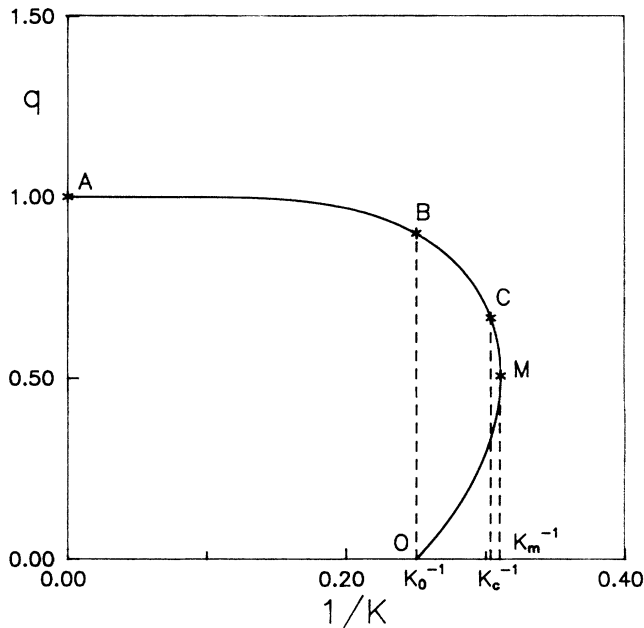


FIG. 2. Polarization parameter  $q(T)$  for  $S = \frac{3}{2}$ . The corresponding temperatures at points  $O(B)$ ,  $M$ , and  $C$  are  $K_0^{-1} = \frac{1}{4}$ ,  $K_m^{-1} = 0.310680$ , and  $K_c^{-1} = 0.303413$ , respectively.

and one maximum. The maximum, which gives an unstable solution, corresponds to a point on the line  $MO$  in Fig. 2. One of the minima occurs at  $q > 0$  (a point on the line section  $BM$ ); and the other at  $q = 0$ . For  $K^{-1} < K_c^{-1} = 0.303413$ , the  $q > 0$  solution has the lowest free energy, while  $q = 0$  has the lowest free energy when  $K^{-1} > K_c^{-1}$  ( $q > 0$  is metastable). The system exhibits a first-order phase transition at the temperature  $kT_c/Jz = 0.303413$ .

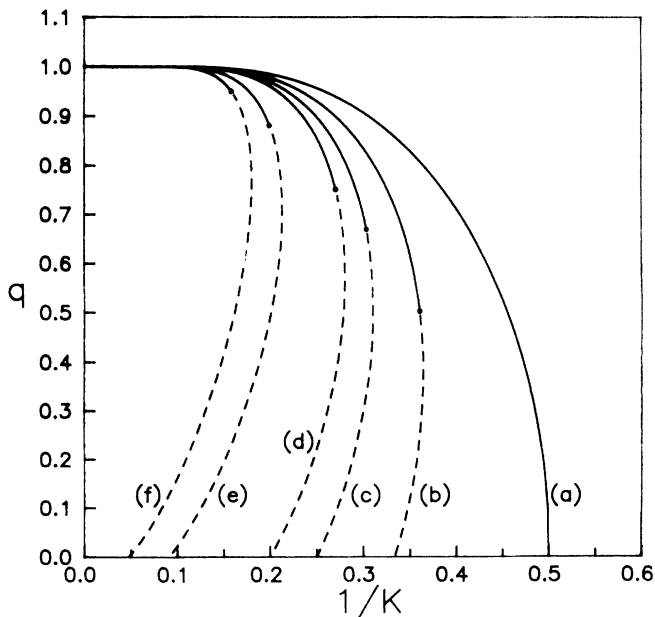


FIG. 3. Polarization parameters  $q(T)$  for various spins: (a)  $S = \frac{1}{2}$ , (b)  $S = 1$ , (c)  $S = \frac{3}{2}$ , (d)  $S = 2$ , (e)  $S = 5$ , and (f)  $S = 10$ . The dashed lines are metastable or unstable solutions.

For general spins the polarization parameters  $q$  as functions of  $K^{-1}$  [Eq. (35)] are shown in Fig. 3. We see that  $dq/dT > 0$  for  $q \ll 1$  and for  $S \neq \frac{1}{2}$ . This indicates that the EI model undergoes a first-order phase transition for  $S \geq 1$ . The first-order transition temperature  $K_c^{-1}$  can be obtained from the condition that the free energy of the order phase [Eq. (34)] is equal to that of the disorder phase,  $F_0/Jz = -K^{-1} \ln(2S+1)$ . Let  $\delta F$  be the difference between Eq. (34) and the disorder free energy; the temperature  $K_c^{-1}$  and discontinuity of  $q$  at  $K_c^{-1}$ , denoted  $q_c$ , are determined by Eq. (35) together with  $\delta F = 0$ . They can be solved analytically. For general  $S$  we obtain  $q_c = (2S-1)/2S$  and  $K_c^{-1} = (2S-1)/(4S \ln 2S)$ . The solutions of  $q(T)$  which are metastable or unstable are indicated by dashed lines in Fig. 3. From  $q(T)$ , the internal energy  $E = -JzSq^2/(2S+1) = -E_0q^2$  and the specific heat  $C = dE/dT = kE_0K^2(dq^2/dK)$  can be determined easily.

#### IV. SUMMARY AND DISCUSSIONS

We have studied the EI model in the mean-field approximation for general spins. We first expressed the exchange operator in term of Hermitian tensor operators  $Q_m^{(l)}$  [Eq. (15)]. Thermal averages of these operators,  $\langle Q_m^{(l)} \rangle$ , are order parameters of the system. In general, there are  $4S(S+1)$  order parameters (some of them can be eliminated by proper choice of the coordinate axes). Any pure state  $|\phi_k\rangle$  [Eq. (20)] has the same lowest free energy [Eq. (24)]. The EI model has infinitely many ground-state configurations. As the temperature increases, the order parameters (absolute values) decrease. From an exact series-expansion result that all multipolar phase transitions of the EI model are exactly degenerated with the dipolar transition<sup>15</sup> (thermal fluctuations of all multipoles have the same temperature dependence), we assume that

$$\langle Q_m^{(l)} \rangle = q(T) \langle \phi_k | Q_m^{(l)} | \phi_k \rangle \quad (36)$$

for all values of  $l (\neq 0)$  and  $m$ , and for any pure state  $|\phi_k\rangle$ .

The above assumption can also be considered in the following way. Since any pure state is a ground state, the Hamiltonian is isotropic in the  $(2S+1)$ -dimensional vector space. If any pure state is selected, a particular direction is singled out, but the other  $2S$ -dimensional subspace remains isotropic. Therefore, if the system is in a state  $|\phi_k\rangle$  at  $T=0$ , we can select  $2S$  other states such that the set of  $2S+1$  states are orthonormal (they form a basis set of the space). At a finite temperature  $T$ , the system will have an equal probability  $p(T)$  to be in any of the  $2S$  states. Then the probability that the system remains in state  $|\phi_k\rangle$  is  $1-2Sp(T)$ . Equation (25) gives

$$\begin{aligned} \langle Q_m^{(l)} \rangle &= [1-2Sp(T)] \langle \phi_k | Q_m^{(l)} | \phi_k \rangle \\ &+ \sum_{i \neq k} p(T) \langle \phi_i | Q_m^{(l)} | \phi_i \rangle \\ &= [1-(2S+1)p(T)] \langle \phi_k | Q_m^{(l)} | \phi_k \rangle. \end{aligned} \quad (37)$$

Here we have used the traceless property of  $Q_m^{(l)}$  that

$$\sum_{i=0}^{2S} \langle \phi_i | Q_m^{(l)} | \phi_i \rangle = 0 \quad \text{for all } l \neq 0 \text{ and } m, \quad (38)$$

where the summation is taken over any set of  $(2S+1)$  orthonormal states. Equation (37) is the same as Eq. (36) with  $q = 1 - (2S+1)p$ .

Equation (29) is obvious for  $S = \frac{1}{2}$ , and it has been shown numerically for  $S=1$ .<sup>10</sup> We have also considered some pure states and verified this property numerically for  $S = \frac{3}{2}$ . Consider the pure state  $|\phi\rangle = (|\frac{3}{2}\rangle + |-\frac{3}{2}\rangle)/\sqrt{2}$ , for example. There are only two nonvanishing moments  $\langle \phi | Q_3^{(3)} | \phi \rangle = (\frac{45}{8})^{1/2}$  and  $\langle \phi | Q_0^{(2)} | \phi \rangle = \frac{3}{2}$ . If we allow these moments to have different thermal behaviors, Eqs. (18), (19), and (28) give the coupled equations

$$\begin{aligned} q_0^{(2)} &= 1 - 2\Delta^{-1} \exp(-Kq_0^{(2)}/2), \\ q_3^{(3)} &= \Delta^{-1} \sinh(Kq_3^{(3)}/2), \end{aligned} \quad (39)$$

with

$$\Delta = \exp(-Kq_0^{(2)}/2) + \cosh(Kq_3^{(3)}/2).$$

Numerically, we find that the only non-negative solution of Eq. (39) is  $q_0^{(2)} = q_3^{(3)} = q(T)$  [ $q(T)$  is the solution of Eq. (35) for  $S = \frac{3}{2}$ ]. For the pure state  $|\phi\rangle = |\frac{3}{2}\rangle$ , the nonvanishing moments are  $\langle \phi | Q_0^{(3)} | \phi \rangle = \frac{3}{4}$ ,  $\langle \phi | Q_0^{(2)} | \phi \rangle = \frac{3}{2}$ , and  $\langle \phi | Q_0^{(1)} | \phi \rangle = \frac{3}{2}$ . Numerical calculations also show that the only set of non-negative solution is  $q_0^{(3)} = q_0^{(2)} = q_0^{(1)} = q(T)$ . The above calculations only give numerical checks of the validity of Eq. (36). A rigorous proof of this property is desired.

For a system with a set of order parameters  $\{\langle Q_m^{(l)} \rangle\}$ , the polarization  $q(T)$  can be calculated from Eqs. (30) and (36):

$$q(T) = \left[ \frac{2S+1}{2S} \sum_{l=1}^{2S} \sum_{m=-l}^l A(S,l) \langle Q_m^{(l)} \rangle^2 \right]^{1/2}. \quad (40)$$

Thermal variations of  $q(T)$  for the spin- $S$  EI model have been calculated in the mean-field approximation. We find that the phase transition is first order with  $kT_c/Jz = (2S-1)/(4S \ln 2S)$  and the discontinuity of  $q$  at  $T_c$  is  $q_c = (2S-1)/2S$ . Although the mean-field approximation is not expected to give accurate estimates of  $T_c$ , mean-field results are usually qualitatively correct for three-dimensional lattices. The result that the phase transition is first order is very important because some of the previous studies (such as the extrapolation of  $T_c$  from high-temperature susceptibility series<sup>2,3</sup>) based on the assumption that the phase transition is second order. More sophisticated approaches to determine whether the phase transition of the EI model is first or second order are desired.

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## APPENDIX

Any matrix of a spin- $S$  system can be expressed as a linear combination of the  $(2S+1)^2$  tensor operators  $Q_m^{(l)}$ . A density matrix  $\rho$  can be written as

$$\rho = \sum_{l=0}^{2S} \sum_{m=-l}^l C_{l,m} Q_m^{(l)}, \quad (\text{A1})$$

where  $C_{l,m}$  are constants. The ensemble average of  $Q_m^{(l)}$  is

$$\begin{aligned} \langle Q_m^{(l)} \rangle &= \text{Tr} Q_m^{(l)} \rho \\ &= \sum_{l'=0}^{2S} \sum_{m'=-l'}^{l'} C_{l',m'} \text{Tr} Q_m^{(l)} Q_{m'}^{(l')} \\ &= C_{l,m} / A(S, l). \end{aligned} \quad (\text{A2})$$

Here we have used Eq. (12). Substituting Eq. (A2) into Eq. (A1),

$$\rho = \sum_{l=0}^{2S} \sum_{m=-l}^l A(S, l) \langle Q_m^{(l)} \rangle Q_m^{(l)}. \quad (\text{A3})$$

For a pure state  $|\phi_i\rangle$ ,  $\langle Q_m^{(l)} \rangle = \langle \phi_i | Q_m^{(l)} | \phi_i \rangle$ , the corresponding density matrix is

$$\rho_i = \sum_{l=0}^{2S} \sum_{m=-l}^l A(S, l) \langle \phi_i | Q_m^{(l)} | \phi_i \rangle Q_m^{(l)}. \quad (\text{A4})$$

This is Eq. (32) in the text. From Eqs. (11) and (12),  $\rho_i$  has the properties

$$\text{Tr} \rho_i = 1, \quad (\text{A5})$$

$$\text{Tr} \rho_i^2 = \sum_{l=0}^{2S} \sum_{m=-l}^l A(S, l) \langle \phi_i | Q_m^{(l)} | \phi_i \rangle^2. \quad (\text{A6})$$

The density matrix of the pure state  $|\phi_i\rangle$  can also be expressed as  $\rho_i = |\phi_i\rangle \langle \phi_i|$ , which has the well-known feature

$$\rho_i^2 = \rho_i. \quad (\text{A7})$$

Equation (23) follows from Eqs. (A5)–(A7).

For a set of  $2S+1$  orthonormal states  $|\phi_0\rangle, |\phi_1\rangle, \dots, |\phi_j\rangle, \dots, |\phi_{2S}\rangle$ ,

$$\rho_i |\phi_j\rangle = |\phi_i\rangle \langle \phi_i | \phi_j \rangle = \delta_{ij} |\phi_j\rangle. \quad (\text{A8})$$

Therefore the density matrix  $\rho_i$  has one eigenvalues  $\lambda=1$  (with eigenvector  $|\phi_i\rangle$ ) and  $2S$  degenerate eigenvalues  $\lambda=0$  (with eigenvectors  $|\phi_j\rangle, i \neq j$ ).

<sup>1</sup>E. Schrödinger, Proc. R. Ir. Acad. A **47**, 39 (1941).

<sup>2</sup>G. A. T. Allan and D. D. Betts, Proc. Phys. Soc. London **91**, 341 (1967).

<sup>3</sup>H. H. Chen and R. I. Joseph, J. Math. Phys. **13**, 725 (1972).

<sup>4</sup>C. K. Lai, J. Math. Phys. **15**, 1675 (1974).

<sup>5</sup>B. Sutherland, Phys. Rev. B **12**, 3795 (1975).

<sup>6</sup>H. A. Brown, Phys. Rev. B **31**, 3118 (1985).

<sup>7</sup>H. H. Chen, Y. C. Chen, and F. Lee, Phys. Lett. A **125**, 2351 (1987); H. H. Chen and F. Lee, Phys. Rev. B **42**, 10 540 (1990).

<sup>8</sup>Y. C. Chen, H. H. Chen, and F. Lee, Phys. Lett. A **130**, 257

(1988).

<sup>9</sup>E. B. Brown, Phys. Rev. B **40**, 775 (1989).

<sup>10</sup>H. H. Chen and P. M. Levy, Phys. Rev. B **7**, 4267 (1973).

<sup>11</sup>L. R. Walker, in *Magnetism*, edited by G. T. Rado and H. Shul (Academic, New York, 1963), Vol. 1, pp. 307–308.

<sup>12</sup>D. Smith and J. H. M. Thornley, Proc. Phys. Soc. London **89**, 779 (1966).

<sup>13</sup>M. F. Thorpe, J. Appl. Phys. **42**, 1410 (1971).

<sup>14</sup>H. H. Chen (unpublished).

<sup>15</sup>H. H. Chen and R. I. Joseph, Phys. Rev. B **2**, 2706 (1970).