

Improved Molecular Field Theory for the Regular and Dilute Heisenberg Ferromagnets

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It is shown that the constant-coupling approximation enables us to compute various thermodynamic quantities of the isotropic Heisenberg ferromagnets with the general spin magnitude S . For the dilute case, the critical concentration for any S is derived.

Recently Oguchi and co-workers¹⁾ developed a heuristic method corresponding to the constant-coupling approximation²⁾ for the Heisenberg spin systems but only for the case of $S=1/2$. We extend the method to the case of general spin magnitude S , from which we obtain an improved molecular field theory for the regular and dilute isotropic Heisenberg ferromagnets with spin magnitude S on each magnetic lattice site.

Regular Ferromagnet: We attach a spin variable \mathbf{S}_i to each lattice site i . If only nearest neighbor spin-spin interactions are allowed, the crudest parital Hamiltonian and the improved one in the molecular field framework, respectively, are given by

$$H_I = -z_1 \lambda s_i^z, \quad (1)$$

$$H_{II} = -J \mathbf{S}_1 \cdot \mathbf{S}_2 - (z_1 - 1) \lambda (S_1^z + S_2^z), \quad (2)$$

where z_1 is the coordination number and λ is the parameter of the molecular field. According to the vector coupling formula of two spins \mathbf{S}_1 and \mathbf{S}_2 , the orthonormalized resultant state $|S_0 m\rangle$ is expressed in terms of one-spin states $|S_1 m_1\rangle$, $|S_2 m_2\rangle$ as follows:

$$|S_0 m\rangle = \sum_{m_1, m_2} \delta_{m, m_1 + m_2} c(m_1 m_2 | S_0 m) |S_1 m_1\rangle |S_2 m_2\rangle, \quad (3)$$

where S and m 's of labels denote the eigenvalues of the magnitude and z -component of each spin and $C(m_1 m_2 | S_0 m)$ is the Clebsch-Gordan (C-G) coefficient³⁾ given by

$$C(m_1 m_2 | S_0 m) = \left[\frac{d(S_0)(S_0!)^2(2S - S_0)!(S_0 + m)!(S_0 - m)!}{(S_0 + 2S + 1)!(S - m_1)!(S + m_1)!(S - m_2)!(S + m_2)!} \right]^{1/2} \sum_{\kappa = \kappa_1}^{\kappa_2} K(\kappa); \quad (4)$$

$$d(S_0) = 2S_0 + 1, \quad \kappa_1 = \text{Max}(0, m), \quad \kappa_2 = \text{Min}(S_0, S_0 + m),$$

$$K(\kappa) = \frac{(-1)^{\kappa+S+m_2}(S_0+S+m_1-\kappa)!(S-m_1+\kappa)!}{(S_0-\kappa)!(S_0+m-\kappa)!(\kappa-m)!\kappa!}.$$

The straightforward combination calculations give the following identities on the C-G coefficients:

$$C(m_1 m_2|S_0 m) = (-1)^{S_0} C(-m_1 -m_2|S_0 -m), \quad (5)$$

$$A_0(S_0) = B_0(S_0) = 1, \quad A_1(S_0) = B_1(S_0) = S[1 - f(S_0)/f(0)], \quad (6)$$

$$A_2(S_0) = B_2(S_0) + A_1(S_0), \quad A_3(S_0) = B_3(S_0) + 3A_2(S_0) - 2A_1(S_0), \dots$$

where

$$A_n(S_0) \equiv [(2S+1)/d(S_0)] \sum_{m_2=-S}^{S_0-S} (S+m_2)^n |C(S m_2|S_0 S+m_2)|^2,$$

$$B_n(S_0) \equiv [(S_0+n)!(2S+1)!]/[(S_0-n)!(2S+n+1)!]$$

and $f(S_0)$ is an eigenvalue of $\mathbf{S}_1 \cdot \mathbf{S}_2$ given by

$$\mathbf{S}_1 \cdot \mathbf{S}_2 |S_0 m\rangle = f(S_0) |S_0 m\rangle, \quad (7)$$

$$f(S_0) = S_0(S_0+1)/2 - S(S+1).$$

Now let us define the normalized density matrices for (1) and (2), respectively, as follows:

$$\rho_I \equiv Z_I^{-1} \sum_{m_1} \exp(\beta \lambda z_1 m_1) |S_1 m_1\rangle \langle S_1 m_1|, \quad (8)$$

$$\rho_{II} \equiv Z_{II}^{-1} \sum_{S_0} \sum_m \exp[\beta J f(S_0) + \beta \lambda (z_1 - 1)m] |S_0 m\rangle \langle S_0 m|, \quad (9)$$

where

$$Z_I = \text{Tr} \exp(-\beta H_I), \quad Z_{II} = \text{Tr} \exp(-\beta H_{II}) \quad \text{and} \quad \beta = 1/k_B T. \quad (10)$$

Substituting (3) into (9) and taking the trace over all possible states of S_2 , we may demand that

$$\text{Tr}_{(S_2)} \rho_{II} = \rho_I. \quad (11)$$

Because of the linear independence of projection operators $\{|S_1 m_1\rangle \langle S_1 m_1|\}$ in (11) we have $2S+1$ identities for their coefficients, which are not independent of each other. If we pick up those for $m_1 = \pm S$, that is,

$$Z_{II}/Z_I = \sum_{S_0} \sum_{m_2=-S}^{S_0-S} |C(S m_2|S_0 S+m_2)|^2 \exp[\beta J f(S_0) + \beta \lambda \zeta(m_2)], \quad (12)$$

$$Z_{II}/Z_I = \sum_{S_0} \sum_{m_2=-S}^{S_0-S} |C(S - m_2 | S_0 - S - m_2)|^2 \exp [\beta J f(S_0) - \beta \lambda \zeta(m_2)];$$

$$\zeta(m_2) = (z_1 - 1)(S + m_2) - z_1 S, \quad (13)$$

then, using (5), we obtain

$$\sum_{S_0} \exp [\beta J f(S_0)] \sum_{m_2=-S}^{S_0-S} |C(S m_2 | S_0 S + m_2)|^2 \sinh [\beta \lambda \zeta(m_2)] = 0. \quad (14)$$

Inclusion of the external field $H^z = h/g\mu_B$ into the foregoing formulations is straightforwardly made by the following replacement in (1) and (2), respectively;

$$\lambda z_1 \longrightarrow \lambda_h z_1 + h, \quad \lambda(z_1 - 1) \longrightarrow \lambda_h(z_1 - 1) + h; \quad (15)$$

$$\lambda_h = \lambda + \delta\lambda(h) \quad (\text{small field case}),$$

where $\delta\lambda(h)$ is the increment of λ induced by h . When the lattice is immersed in the very small external field, from (14) we have

$$\frac{\delta\lambda(h)}{h} = - \frac{\sum_{S_0} e^{\beta J f(S_0)} \sum_{m_2=-S}^{S_0-S} |C(S m_2 | S_0 S + m_2)|^2 m_2 \cosh [\beta \lambda \zeta(m_2)]}{\sum_{S_0} e^{\beta J f(S_0)} \sum_{m_2=-S}^{S_0-S} |C(S m_2 | S_0 S + m_2)|^2 \zeta(m_2) \cosh [\beta \lambda \zeta(m_2)]}. \quad (16)$$

The result (14) allows us to determine $\lambda_h(\beta)$ for any S and use of the density matrices (8) and (9) provides the means to compute various thermodynamic quantities of the system such as the critical temperature, susceptibility, internal energy, specific heat and spin correlation function. It is convenient to let \bar{X} denote $\text{Tr} [X \rho_{II}]$ only if X is such a diagonal operator as satisfies $X |S_0 m\rangle = X(S_0) |S_0 m\rangle$ with the eigenvalue $X(S_0)$. Then \bar{X} and the value at T_c and $h=0$, \bar{X}_c are calculated by

$$\bar{X} = \frac{\sum_{S_0} \sum_m X(S_0) \exp [\beta J f(S_0) + \beta \lambda_h(z_1 - 1)m + \beta h m]}{\sum_{S_0} \sum_m \exp [\beta J f(S_0) + \beta \lambda_h(z_1 - 1)m + \beta h m]}, \quad (17)$$

$$\bar{X}_c = \frac{\sum_{S_0} d(S_0) X(S_0) \exp [\beta_c J f(S_0)]}{\sum_{S_0} d(S_0) \exp [\beta_c J f(S_0)]}. \quad (18)$$

Letting λ and h tend to 0 in (14) with use of (6) and (18), the equation for determining the critical temperature T_c is derived as follows:

$$(z_1 - 1)\bar{A}_{1c} - z_1 S = 0 \quad \text{or} \quad \bar{f}_c = S(S+1)/(z_1 - 1). \quad (19)$$

The formula (19) is a generalization of the well-known result for $S=1/2$ and $z_1 > 4$, $\beta_c J = \ln [z_1 / (z_1 - 4)]^{1,2}$. It concludes that isotropic Heisenberg spin systems with

$z_1 \leq 4$ have no solution for the critical temperature and for the ferromagnetic phase in the case of $S=1/2$. The total energy is given by

$$E_{\text{tot}} = -(Nz_1/2)J\bar{f} - Nh \text{Tr} [S\bar{f}_1\rho_1]; \quad (20)$$

$$\begin{aligned} \text{Tr} [S\bar{f}_1\rho_1] &= S B_S[\beta(\lambda_{hz_1} + h)S] \\ &= S B_S[\beta\lambda_{z_1}S] + S^2(z_1\delta\lambda + h)B'_S[\beta\lambda_{z_1}S] \quad (\text{small field case}), \end{aligned} \quad (21)$$

where $B_S[\dots]$ and $B'_S[\dots]$ are the Brillouin function and its derivative, respectively. From (14), (16) and (21), we get the parallel susceptibility χ_{\parallel} and the magnetization M in the vicinity of the critical temperature T_c as follows:

$$\chi_{\parallel}(T > T_c) = \frac{S(S+1)z_1 N(g\mu_B)^2 [\bar{A}_{1c} - S]}{3J[(z_1-1)(\bar{A}_{1f})_c - z_1 S\bar{f}_c](T - T_c)/T_c}, \quad \chi_{\parallel}(T \gtrsim T_c) = 2\chi_{\parallel}(T \lesssim T_c), \quad (22)$$

$$\begin{aligned} M/(Ng\mu_B) &= \frac{S(S+1)z_1}{3} \left[\frac{6\beta_c J[z_1 S\bar{f}_c - (z_1-1)(\bar{A}_{1f})_c](T_c - T)/T_c}{(z_1-1)^3 \bar{A}_{3c} - 3z_1(z_1-1)^2 S\bar{A}_{2c} + 2z_1^3 S^3} \right]^{1/2} (T \lesssim T_c), \end{aligned} \quad (23)$$

For $S=1/2$, (22) gives

$$\chi_{\parallel}(T \gtrsim T_c) = N(g\mu_B)^2 / [J(z_1 - 4)(T - T_c)/T_c]. \quad (24)$$

Dilute Ferromagnet: We suppose that two nearest neighboring sites 1, 2 in the dilute ferromagnet happen to be occupied by S_1, S_2 , respectively. Owing to the randomly distributed magnetical vacancies on the sites surrounding the $\langle 12 \rangle$ pair, the parameter of the molecular field associated with these surrounding sites should be diluted with the concentrations of magnetic ions p . Then we have the partial Hamiltonians

$$H_I = -z'_1 \lambda S_1^z, \quad H_{II} = -JS_1 \cdot S_2 - (z'_1 - 1)\lambda(S_1^z + S_2^z); \quad (25)$$

$$z'_1 \equiv 1 + p(z_1 - 1).$$

It is concluded from (25) that the formulations for the dilute case are deduced formally from those for the regular case by merely replacing the coordination number:

$$z_1 \longrightarrow z'_1. \quad (26)$$

Then as a matter of course, any thermodynamic variable such as T has to be substituted by that of the dilute system. From (19) and (26), the relation between the concentration p and the critical temperature T_c is given by

$$P = \frac{S(S+1) \sum_{S_0} d(S_0) \exp[\beta_c J f(S_0)]}{(z_1 - 1) \sum_{S_0} d(S_0) f(S_0) \exp[\beta_c J f(S_0)]}. \quad (27)$$

Letting T_c tend to 0 in (27), we obtain the value of the critical concentration as follows:

$$p_c = (S+1)/[S(z_1-1)], \quad (28)$$

which is the generalization of $p_c = 3/(z_1-1)^{1/2}$ for $S=1/2$. The numerical results of p_c for the cubic lattices are shown in Table I. The internal energy is given by

$$E_{\text{int}} = -(Nz_1/2)p^2 J \bar{f}_d, \quad (29)$$

where \bar{f}_d stands for the \bar{f} of the dilute system.

Table I. The calculated critical concentration p_c for the cubic lattices.

S	z_1		
	6 (s.c.)	8 (b.c.c.)	12 (f.c.c.)
1/2	0.600	0.429	0.273
1	0.400	0.286	0.182
3/2	0.333	0.238	0.152
2	0.300	0.214	0.136
5/2	0.280	0.200	0.127

Finally we note that the present method can be generalized for the anisotropic case including the XY model and Ising model with a general spin S . A full note will be published elsewhere.

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References

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