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Approximate Method for the Free Energy

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We propose an upper bound and a lower bound of the Helmholtz free energy in the statistical physics. A new approximate expression of the free energy is obtained. This approximate value of the free energy is proved to be greater than the lower bound and less than the upper bound. A systematic method which can be extended to improve the approximation is studied. The upper bound and the lower bound of the approximate free energy converge to the true free energy as the successive approximation proceeds. The method is first explained with the Ising ferromagnet and then applied to the Heisenberg ferromagnet. In the simplest approximation the result agrees with the Bethe-Peierls approximation for the Ising model and the constant coupling approximation for the Heisenberg model. A more accurate approximation is studied for the Ising ferromagnet.

§ 1. Introduction

In the many-body theory there are two essentially different methods for obtaining the approximate Helmholtz free energy; (1) the perturbation method[1] and (2) the variational method.[2] When the perturbation becomes large, the perturbation method is an inconvenient procedure and then the variational method is more appropriate. Bogolyubov's variational principle[3] has been successfully applied to a wide range of problems in the theory of many-particle systems. If we adopt the one-particle model Hamiltonian that can be exactly solved in the Bogolyubov variational method, we get a self-consistent result such as the molecular field theory in the ferromagnet[4] and the Hartree-Fock approximation in many-body problems. Since the variational method yields a result which is always greater than the correct answer, the mathematical meaning for improving upon the approximation in the variational method is strictly defined by lowering the upper bound of the free energy. But these variational methods, the molecular field theory and the Hartree-Fock approximation, have the unhappy feature that the correlation effects cannot be evaluated.

On the other hand we can calculate the correlation effects in the many-body system by using other approximate methods. For example, the Bethe-Peierls-Weiss approximation in the ferromagnet[5] which treats somewhat more accurately the interaction of a given spin with its nearest neighbors than the molecular field theory, contains the correlation effects. A more accurate approximation from the physical point of view may be obtained by making the considered cluster larger and larger. But in a case of this kind the approximation does not show an order relation between the true free energy and the approximate free energy. Thus in contrast with the variational theory the mathematical meaning for improving on the approximation in this method is not clear. Thus we cannot show how the method can be extended to improve the approximation from the mathematical point of view. Such features appear in the perturbation theory and a cluster expansion method.

When the model Hamiltonian cannot be explicitly expressed, Sawada's variational method[6] which is based on the Bogolyubov variational principle and includes the correlation effects, sometimes gives internal inconsistency results.

In this paper we present the expression of an upper bound and a lower bound of the Helmholtz free energy in the statistical physics. Adopting the explicitly expressed model Hamiltonian, we propose a new approximate free energy form which includes the correlation effects and is proved to be less than the upper bound and greater than the lower bound. We will also show a method which can be extended to improve the approximation.

In § 2, we will present an expression of the upper bound and the lower bound of the free energy and an approximate method for the free energy by adopting a model Hamiltonian. In § 3, we will show an expression of the lower bound of the free energy and the ground state energy. In § 4, we will apply this method to the Ising model and the Heisenberg model.

§ 2. Formalism

We start from the following two inequalities:

(i) Any two positive semi-definite, trace-class operators A and B on a separable Hilbert space satisfy the inequality

$$\mathrm{Tr}(A \log A - A \log B) \geqq \mathrm{Tr}(A-B), \tag{1}$$

provided that the operator $A \log A - A \log B$ is of trace-class. The equal sign in Eq. (1) holds if and only if $A=B$.[3]

(ii) If real functions $f_i(x)$ $(i=1, 2, \cdots, n)$ defined on the domain D and the summation $\sum_{i=1}^n f_i(x)$ have the minimum values on the domain D, then one has the inequality

$$\sum_{i=1}^{n} \min f_i(x) \leqq \min \sum_{i=1}^{n} f_i(x), \tag{2}$$

where by $\min f(x)$ we mean the minimum value of the real function $f(x)$.

Normalizing $\mathrm{Tr}\,A=\mathrm{Tr}\,B=1$, putting $B=e^{-\beta H}/\mathrm{Tr}\,e^{-\beta H}$ and substituting these into Eq. (1), we get

$$F \equiv -\frac{1}{\beta} \log \mathrm{Tr}\, e^{-\beta H} \leqq \mathrm{Tr}\Big(AH + \frac{1}{\beta} A \log A\Big), \tag{3}$$

where H is the Hamiltonian of the system and $\beta=1/kT$.

We now adopt the model Hamiltonian H_0 which is solved exactly and is close to the Hamiltonian H and we introduce the positive operator Y which satisfies

$$[H_0, Y]=0\,. \tag{4}$$

Putting

$$A=e^{-\beta H_0}Y/\mathrm{Tr}\,e^{-\beta H_0} \tag{5}$$

and inserting this into Eq. (3), we get

$$F\leqq -\frac{1}{\beta}\log \mathrm{Tr}\,e^{-\beta H_0}+\left\langle YV+\frac{1}{\beta}Y\log Y\right\rangle=F_0+J(Y), \tag{6}$$

where

$$\langle A\rangle=\mathrm{Tr}\,e^{-\beta H_0}A/\mathrm{Tr}\,e^{-\beta H_0}\,,\quad V=H-H_0$$

and

$$J(Y)=\left\langle YV+\frac{1}{\beta}Y\log Y\right\rangle. \tag{7}$$

Since $\mathrm{Tr}A=1$, the positive operator Y satisfies $\langle Y\rangle=1$. The equal sign in Eq. (6) holds if and only if $H=H_0$ and $Y=1$.

(A) *The case* $[H_0, V]=0$

First for simplicity we consider the case $[H_0, V]=0$. The minimum value for $J(Y)$ occurs where $\delta J(Y)=0$, so that noting $\langle Y\rangle=1$, we get

$$\min J(Y)=J(e^{-\beta V}/\langle e^{-\beta V}\rangle). \tag{8}$$

Inserting this value of Y into J, we obtain

$$\begin{aligned} F&=-\frac{1}{\beta}\log \mathrm{Tr}\,e^{-\beta H}=-\frac{1}{\beta}\log \mathrm{Tr}\,e^{-\beta H_0}-\frac{1}{\beta}\log\langle e^{-\beta V}\rangle \\ &=F_0+\min J(Y) \\ &\leqq F_0+J(Y). \end{aligned} \tag{9}$$

If we put $Y=1$ in this last form, we get the Bogolyubov variational principle as follows:

$$F\leqq F_0+J(1)=-\frac{1}{\beta}\log \mathrm{Tr}\,e^{-\beta H_0}+\langle V\rangle. \tag{10}$$

Now, we assume that V can be decomposed into a sum of terms:

$$V=\sum_{i=1}^{q}V_i\,, \tag{11}$$

where q is the number of the division of V. We have several methods to make this division of V, such as the method of cluster division or the decomposition of

V into one-body part and many-body parts.

It is convenient to introduce two new functions $g_1(\gamma)$ and $g_2(\gamma;q)$ defined by

$$g_1(\gamma)\equiv-\frac{1}{\gamma}\log\langle e^{-\gamma V}\rangle=\min\left\langle YV+\frac{1}{\gamma}Y\log Y\right\rangle, \tag{12}$$

and

$$g_2(\gamma;q)\equiv-\frac{1}{\gamma}\sum_{i=1}^{q}\log\langle e^{-\gamma V_i}\rangle=\sum_{i=1}^{q}\min\left\langle YV_i+\frac{1}{\gamma}Y\log Y\right\rangle \quad \text{for} \quad \langle Y\rangle=1\,. \tag{13}$$

Then, the following theorem holds:

Theorem 1. *If we put*

$$F_l(q\beta;q)\equiv F_0+g_2(q\beta;q),\ F_u(\beta/q)\equiv F_0+g_1(\beta/q) \ \textit{and}\ F_B\equiv F_0+\langle V\rangle;$$

then we have

$$F_l(q\beta;q)\leqq F\leqq F_u(\beta/q)<F_B \tag{14}$$

and

$$F_l(q\beta;q)\leqq F_{\text{mod}}\leqq F_u(\beta/q)<F_B\,, \tag{15}$$

where

$$F_{\text{mod}}\equiv F_0+g_2(\beta;q)=-\frac{1}{\beta}\log\operatorname{Tr}e^{-\beta H_0}-\frac{1}{\beta}\sum_{i=1}^{q}\log\langle e^{-\beta V_i}\rangle. \tag{16}$$

Proof. Using the inequality (2), we get

$$\begin{aligned}
g_2(q\beta;q)&=\sum_{i=1}^{q}\min\left\langle YV_i+\frac{1}{q\beta}Y\log Y\right\rangle\\
&=\sum_{i=1}^{q}\min\left\langle YV_i+\frac{1}{q\beta}Y\log Y\right\rangle+\sum_{i=1}^{q}\min\frac{q-1}{q\beta}\langle Y\log Y\rangle\\
&\leqq\sum_{i=1}^{q}\min\left\langle YV_i+\frac{1}{\beta}Y\log Y\right\rangle=g_2(\beta;q)\\
&\leqq\min\left\langle Y\sum_{i=1}^{q}V_i+\frac{q}{\beta}Y\log Y\right\rangle=g_1(\beta/q)<(g_1)_{Y=1}=\langle V\rangle
\end{aligned}$$

and

$$\begin{aligned}
g_2(q\beta;q)&=\sum_{i=1}^{q}\min\left\langle YV_i+\frac{1}{q\beta}Y\log Y\right\rangle\\
&\leqq\min\left\langle YV+\frac{1}{\beta}Y\log Y\right\rangle=g_1(\beta)\\
&=\min\left\langle YV+\frac{1}{\beta}Y\log Y\right\rangle+\min\frac{q-1}{\beta}\langle Y\log Y\rangle\\
&\leqq\min\left\langle YV+\frac{q}{\beta}Y\log Y\right\rangle=g_1(\beta/q)<(g_1)_{Y=1}=\langle V\rangle.
\end{aligned}$$

Thus we have the following inequalities:

$$g_2(q\beta; q) \leqq g_2(\beta; q) \leqq g_1(\beta/q) < \langle V \rangle \tag{17}$$

and

$$g_2(q\beta; q) \leqq g_1(\beta) \leqq g_1(\beta/q) < \langle V \rangle. \tag{18}$$

These prove Eqs. (14) and (15). Here we have used $q>1$ and the inequality

$$\langle Y \log Y \rangle \geqq 0 = \min \langle Y \log Y \rangle \tag{19}$$

which is proved by using Jensen's inequality $\langle F(x) \rangle \geqq F(\langle x \rangle)$ for a convex function $F(x)$. Equation (19) is obtained by taking $F(Y) = Y \log Y$ and using $\langle Y \rangle = 1$.

Equation (14) shows that an upper bound of the free energy is $F_B = F_0 + \langle V \rangle$, which can be easily calculated and a more accurate upper bound is given by $F_u(\beta/q) = F_0 + g_1(\beta/q)$, which unfortunately cannot be calculated in general. Equation (14) also shows that a lower bound of the free energy is $F_l(q\beta; q) = F_0 + g_2(q\beta; q)$. We find from Eq. (15) that $F_{\rm mod}$ has the same upper and the same lower bound of the true free energy. It therefore follows from Eqs. (14) and (15) that we can adopt the function $F_{\rm mod}$ which can be easily calculated as an approximation of the free energy.

Next we consider two kinds of division of V named by Q_1 and Q_2. The numbers of the division in the case of Q_1 and Q_2 are q_1 and q_2 respectively, where we assume $q_1 > q_2$. We now make each division of Q_2 include q_1/q_2 divisions of Q_1 as follows:

$$V = \sum_{i=1}^{q_1} V_i = \sum_{l=1}^{q_2} V_l\,, \tag{20}$$

where

$$V_l = \sum_{i=l(1)}^{l(q_1/q_2)} V_i\,. \tag{21}$$

Then we obtain the following theorem:

Theorem 2. *If V is decomposed into two kinds of sum of terms defined by Eqs. (20) and (21), then we have*

$$F_l(q_1\beta; q_1) \leqq F_l(q_2\beta; q_2) \leqq F_{\rm mod},\ F \leqq F_u(\beta/q_2) \leqq F_u(\beta/q_1) < F_B\,. \tag{22}$$

Proof. Using Eqs. (2) and (19), we obtain

$$\left\langle YV + \frac{1}{\beta} Y \log Y \right\rangle \leqq \sum_{l=1}^{q_2} \left\langle YV_l + \frac{1}{\beta} Y \log Y \right\rangle = \left\langle YV + \frac{q_2}{\beta} Y \log Y \right\rangle$$
$$\leqq \left\langle YV + \frac{q_1}{\beta} Y \log Y \right\rangle.$$

Here we have used $q_1 \langle Y \log Y \rangle \geqq q_2 \langle Y \log Y \rangle$ for the last inequality. Thus we get

$$g_1(\beta) \leqq g_1(\beta/q_2) \leqq g_1(\beta/q_1)\,. \tag{23}$$

Similarly we have

$$\min\left\langle YV_l+\frac{1}{\beta q_2}Y\log Y\right\rangle=\min\left\langle Y\sum_{i=l(1)}^{l(q_1/q_2)}V_i+\frac{1}{\beta q_2}Y\log Y\right\rangle$$

$$=\min\sum_{i=l(1)}^{l(q_1/q_2)}\left\langle YV_i+\frac{1}{\beta q_1}Y\log Y\right\rangle\geqq\sum_{i=l(1)}^{l(q_1/q_2)}\min\left\langle YV_i+\frac{1}{\beta q_1}Y\log Y\right\rangle.$$

Summing over the index l in this inequality, we get

$$g_2(q_2\beta;q_2)\geqq g_2(q_1\beta;q_1). \tag{24}$$

From Eqs. (17), (18), (23) and (24), we obtain

$$g_2(q_1\beta;q_1)\leqq g_2(q_2\beta;q_2)\leqq g_2(\beta;q_2),\quad g_1(\beta)\leqq g_1(\beta/q_2)\leqq g_1(\beta/q_1)<\langle V\rangle.$$

This proves Eq. (22). Therefore it follows from Eq. (22) that we get the systematic method which can be extended to improve the approximation. In order to obtain a closer approximation of the free energy, we must make the division of V larger and each division includes several previous divisions of V like Eq. (21). Equation (22) shows that the new approximate energy $F_{\mathrm{mod}}=F_0+g_2(\beta;q_2)$, has a less upper bound and a greater lower bound than those of previous approximate free energy $F_{\mathrm{mod}}=F_0+g_2(\beta;q_1)$.

(B) *The case* $[H_0, V]\neq 0$

We start from the following inequality:

$$F\leqq-\frac{1}{\beta}\log\mathrm{Tr}\,e^{-\beta H_0}+\left\langle YV+\frac{1}{\beta}Y\log Y\right\rangle. \tag{25}$$

By using the assumption of Eq. (4), we can write

$$\langle YV\rangle=\langle YV_D\rangle, \tag{26}$$

where V_D is a diagonal element defined by

$$V_D=\sum_n|n\rangle\langle n|V|n\rangle\langle n| \tag{27}$$

and $|n\rangle$ is the eigenstate of the model Hamiltonian H_0.

Then we arrive at the following result:

Theorem 3. *If we put*

$$F_u'\equiv-\frac{1}{\beta}\log\mathrm{Tr}\,e^{-\beta H_0}-\frac{1}{\beta}\log\langle e^{-\beta V_D}\rangle,$$

then we have

$$F\leqq F_u'\leqq F_B. \tag{28}$$

Proof. From Eqs. (25) and (26), we have

$$F\leqq\min\left(-\frac{1}{\beta}\log\mathrm{Tr}\,e^{-\beta H_0}+\left\langle YV_D+\frac{1}{\beta}Y\log Y\right\rangle\right)$$

$$= -\frac{1}{\beta} \log \mathrm{Tr}\, e^{-\beta H_0} - \frac{1}{\beta} \log \langle e^{-\beta V_D} \rangle = F_u'$$

$$\leqq F_0 + \langle V_D \rangle = F_0 + \langle V \rangle = F_B\,.$$

We can apply the results of case (A) to the upper bound F_u' of the free energy.

§ 3. The lower bound of the free energy and the ground state energy

In the case $[H_0, V]=0$, Eq. (14) shows the lower bound of the free energy as $F_l(q\beta; q) = F_0 + g_2(\beta q; q)$. In this chapter, however, we consider the general case.

From Eq. (3) we have

$$F = \min\left\{\mathrm{Tr}\left(AH + \frac{1}{\beta} A \log A\right)\right\} \quad \text{for} \quad \mathrm{Tr}\, A = 1\,. \tag{29}$$

Then the following theorem holds:

Theorem 4. *If the Hamiltonian is decomposed into a sum of terms*

$$H = \sum_{i=1}^{q} H_i\,, \tag{30}$$

then we have

$$F_q \equiv -\frac{1}{\beta q} \sum_{i=1}^{q} \log \mathrm{Tr}\, e^{-\beta H_i} \leqq F \tag{31}$$

and

$$E_g \geqq \sum_{i=1}^{q} (\text{the lowest energy of } H_i) \equiv E_q\,, \tag{32}$$

where E_g is the ground state energy of H.

Proof. Using Eqs. (2), (29) and (30), we get

$$F = \min\left\{\mathrm{Tr}\left(A \sum_{i=1}^{q} H_i + \frac{1}{\beta} A \log A\right)\right\} \geqq \sum_{i=1}^{q} \min\, \mathrm{Tr}\left(AH_i + \frac{1}{\beta q} A \log A\right)$$

$$= -\frac{1}{\beta q} \sum_{i=1}^{q} \log \mathrm{Tr}\, e^{-\beta H_i}\,,$$

which proves Eq. (31). In the limit $T=0$ in Eq. (31) we get Eq. (32).

Next we consider two kinds of division of H named by Q_1 and Q_2. The number of the division of Q_1 and Q_2 are q_1 and q_2 respectively. Applying a technique similar to that for theorem 2 to this case, we arrive at the following result:

Theorem 5. *If $q_1 > q_2$ and each division of Q_2 includes q_1/q_2 divisions of Q_1, then we have*

$$F \geqq F_{q_2} \geqq F_{q_1} \tag{33}$$

and

$$E_q \geqq E_{q_2} \geqq E_{q_1} . \tag{34}$$

This theorem shows that we can get a more accurate lower bound of the ground state energy by making the division of the Hamiltonian large.

§ 4. Applications

(A) *Ising model*

First as an example of Eqs. (15) and (16), we consider the Ising model. The Hamiltonian of the Ising model is given by

$$H = -\frac{J}{2} \sum_{\langle ij \rangle} \sigma_i \sigma_j - h \sum_{i=1}^{N} \sigma_i , \tag{35}$$

where σ_i is the z-component of the Pauli spin operator at the i-th atom, N is the total number of atoms and the summation is taken over all nearest neighbor spins and h is the external field. Here we have put $g\mu_B = 1$ in Eq. (35).

In the present problem we take our model Hamiltonian H_0 as follows:

$$H_0 = -I_0 \sum_{i=1}^{N} \sigma_i , \tag{36}$$

where I_0 is a variational parameter. The meaning of this variation is as follows:

From Eqs. (15) and (16) we have

$$F_{\text{mod}} = -\frac{1}{\beta} \log \operatorname{Tr} e^{-\beta H_0} - \frac{1}{\beta} \sum_{i=1}^{q} \log \langle e^{-\beta V_i} \rangle \leqq F_u = F_0 + g_1(\beta/q) .$$

We consider the minimum value of F_{mod}. This equation shows that the minimum value of F_{mod} is always less than the upper bound F_u of the free energy. And so the minimum value of F_{mod} may be fairly good approximation of the free energy. As we are making the division of the Hamiltonian large, F_u is tending to the free energy. Therefore the minimum of F_{mod} is also tending to the exact free energy.

(i) We now consider the simplest case that the division of V is given by

$$V = \sum_{\langle ij \rangle}^{zN/2} V_{ij} = \sum_{\langle ij \rangle}^{zN/2} \left\{ -\frac{J}{2} \sigma_i \sigma_j - \frac{1}{z} (h - I_0)(\sigma_i + \sigma_j) \right\}, \tag{37}$$

where z is the number of the nearest neighbors.

From Eq. (36), we have

$$\langle \sigma \rangle = \tanh \beta I_0 . \tag{38}$$

Using Eqs. (16) and (37), we get

$$\frac{F_{\text{mod}}}{N} = -\frac{1}{N\beta} \log \operatorname{Tr} e^{-\beta H_0} - \frac{z}{2\beta} \log \langle e^{-\beta V_{ij}} \rangle$$

$$= -\frac{1}{\beta}\left(1-\frac{z}{2}\right)\log 2 - \frac{1}{\beta}(1-z)\log\cosh\beta I_0 - \frac{zK}{2\beta}$$

$$-\frac{z}{2\beta}\log\left[\cosh\left(\frac{2\beta h}{z}+\frac{2(z-1)}{z}\beta I_0\right)+e^{-2K}\right], \tag{39}$$

where

$$K=\beta J/2\,. \tag{40}$$

We differentiate Eq. (39) with respect to I_0, and place $\partial F_{\mathrm{mod}}/\partial I_0$ equal to zero in accordance with the requirement of obtaining the minimum value of F_{mod}. Thus we get

$$\tanh\beta I_0 = \frac{\sinh(2\beta h/z+(2(z-1)/z)\beta I_0)}{\cosh(2\beta h/z+(2(z-1)/z)\beta I_0)+e^{-2K}}, \tag{41}$$

namely,

$$e^{-2K}\sinh\beta I_0 = \sinh(2\beta h/z+(z-2)\beta I_0/z)\,. \tag{42}$$

By the differentiation of the free energy with respect to the magnetic field h, and by the use of Eq. (42), the magnetization is given by

$$\langle\sigma\rangle = -\frac{1}{N}\frac{\partial F_{\mathrm{mod}}}{\partial h} = \frac{\sinh(2\beta h/z+(2(z-1)/z)\beta I_0)}{\cosh(2\beta h/z+(2(z-1)/z)\beta I_0)+e^{-2K}}\,. \tag{43}$$

This is consistent with the result obtained by using Eqs. (38) and (41). In the case $z=2$, Eq. (43) agrees with the exact result.

From Eq. (42), the Curie temperature is given by

$$\frac{kT_c}{J} = \frac{1}{\log(z/(z-2))}\,. \tag{44}$$

This result is in agreement with that of the Bethe-Peierls approximation.[5)]

(ii) We next consider a larger division of V than that provided by Eq. (37). We only treat the plane square lattice ($z=4$) and the simple cubic lattice ($z=6$). We take the division of V as shown in Fig. 1(A) for the square lattice and in Fig. 1(B) for the simple cubic.

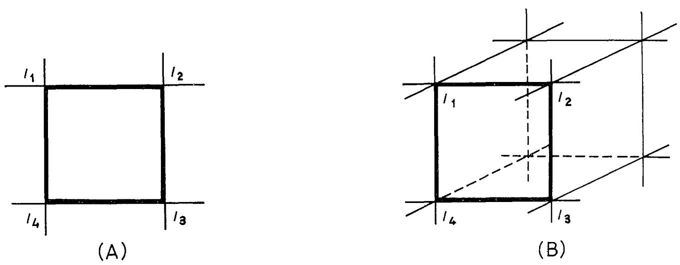

Fig. 1.

Thus we can write

$$V=\sum_{i=1}^{zN/8} V_i, \tag{45}$$

where

$$V_i=-\frac{J}{2}(\sigma_{i_1}\sigma_{i_2}+\sigma_{i_2}\sigma_{i_3}+\sigma_{i_3}\sigma_{i_4}+\sigma_{i_4}\sigma_{i_1})-\frac{2}{z}(h-I_0)(\sigma_{i_1}+\sigma_{i_2}+\sigma_{i_3}+\sigma_{i_4}). \tag{46}$$

Using Eqs. (16) and (46), we get

$$\frac{F_{\rm mod}}{N}=-\frac{1}{\beta N}\log {\rm Tr} e^{-\beta H_0}-\frac{z}{8\beta}\log\langle e^{-\beta V_i}\rangle$$
$$=\frac{3z-8}{8\beta}\log 2+\frac{z-2}{2\beta}\log\cosh\beta I_0-\frac{z}{8\beta}\log X, \tag{47}$$

where

$$X=e^{4K}\cosh\left\{\frac{8\beta h}{z}+\left(4-\frac{8}{z}\right)\beta I_0\right\}+4\cosh\left\{\frac{4\beta h}{z}+\left(2-\frac{4}{z}\right)\beta I_0\right\}+2+e^{-4K}. \tag{48}$$

Again I_0 is determined by setting $\partial F_{\rm mod}/\partial I_0=0$. This gives the following expression for I_0:

$$\tanh\beta I_0=\frac{1}{X}\left[e^{4K}\sinh\left\{\frac{8\beta h}{z}-\left(4-\frac{8}{z}\right)\beta I_0\right\}+2\sinh\left\{\frac{4\beta h}{z}+\left(2-\frac{4}{z}\right)\beta I_0\right\}\right]. \tag{49}$$

The magnetization is given by

$$\langle\sigma\rangle=-\frac{1}{N}\frac{\partial F_{\rm mod}}{\partial h}=\frac{1}{X}\left[e^{4K}\sinh\left\{\frac{8\beta h}{z}+\left(4-\frac{8}{z}\right)\beta I_0\right\}+2\sinh\left\{\frac{4\beta h}{z}+\left(2-\frac{4}{z}\right)\beta I_0\right\}\right]. \tag{50}$$

Here we have used Eq. (49). This result is also consistent with Eqs. (38) and (49).

From Eqs. (48) and (50), the Curie temperature is given by

$$\frac{kT_c}{J}=\frac{2}{\log(z+4+2\sqrt{z^2-4}/(3z-8))}. \tag{51}$$

The Curie temperatures evaluated by Eq. (51) are listed in Table I.

Table I. Comparison of Curie temperatures k_BT_C/J

method	$z=4$	$z=6$
mean field	2	3
Bethe[a)]	1.443	2.466
Kirkwood[b)]	1.476	2.469
Kikuchi[c)]	1.213	2.382
exact	1.135	
present result	1.385	2.446

a) See Ref. 5). b) See Ref. 7). c) See Ref. 8).

(B) *Heisenberg ferromagnet*

We consider the Heisenberg ferromagnet. The Hamiltonian is given by

$$H=-2J\sum_{\langle ij\rangle}\boldsymbol{S}_i\cdot\boldsymbol{S}_j-h\sum_{i=1}^{N}S_i^z\,, \tag{52}$$

where $\boldsymbol{S}_i$ is the spin operator of the i-th spin.

We adopt the model Hamiltonian H_0 which is given by

$$H_0=-I_0\sum_{i=1}^{N}S_i^z\,. \tag{53}$$

Thus we get

$$V=H-H_0=\sum_{\langle ij\rangle}^{zN/2}V_{ij}\,, \tag{54}$$

where

$$V_{ij}=-2J\boldsymbol{S}_i\cdot\boldsymbol{S}_j-\frac{1}{z}(h-I_0)\,(S_i^z+S_j^z)\,. \tag{55}$$

From Eqs. (16) and (54), we obtain

$$\frac{F_{\mathrm{mod}}}{N}=-\frac{1}{\beta}\log 2\cosh\beta I_0-\frac{z}{2\beta}\log\langle e^{-\beta V_{ij}}\rangle\,. \tag{56}$$

This expression is in agreement with the two-spin cluster result of Stribe, Herbert and Callen[9] and is identical to the constant coupling approximation.

(C) *Antiferromagnet*

As an example of Eqs. (32) and (34), we consider the antiferromagnet. The Heisenberg antiferromagnet is expressed by

$$H=2|J|\sum_{\langle ij\rangle}\boldsymbol{S}_i\cdot\boldsymbol{S}_j=\sum_{\langle ij\rangle}H_{ij}\,, \tag{57}$$

where

$$H_{ij}=2|J|\boldsymbol{S}_i\cdot\boldsymbol{S}_j=|J|\{(\boldsymbol{S}_i+\boldsymbol{S}_j)^2-\boldsymbol{S}_i^2-\boldsymbol{S}_j^2\}. \tag{58}$$

The lowest energy of H_{ij} is

$$E_{ij}=-2|J|S^2\left(1+\frac{1}{S}\right). \tag{59}$$

Inserting Eq. (59) into Eq. (32), we have

$$E_g>-zN|J|S^2\left(1+\frac{1}{S}\right). \tag{60}$$

If we adopt a larger division of H which is composed of the cluster of nearest neighbor of a given spin

$$H=\sum_i H_i\,,$$

where

$$H_i = -2|J|\boldsymbol{S}_i \cdot \sum_{j=1}^{z} \boldsymbol{S}_j = |J|\{(\boldsymbol{S}_i + \sum_j \boldsymbol{S}_j)^2 - \boldsymbol{S}_i^2 - (\sum_j \boldsymbol{S}_j)^2\}, \qquad (61)$$

then the lowest energy of H_i is given by

$$E_i = -|J|S(zS+1). \qquad (62)$$

Substituting Eq. (62) into Eq. (32) and using Eqs. (34) and (60), we get

$$E_g > -zN|J|S^2\left(1+\frac{1}{zS}\right) > -zN|J|S^2\left(1+\frac{1}{S}\right). \qquad (63)$$

This result has already been obtained by Anderson.[10)]

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