

Application of Thermodynamic Green's Function Formalism to Ferromagnetism

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We study the magnetic behavior of a lattice where there is a single localized orbital at each lattice site which is either vacant, singly, or doubly occupied. The principal interactions are nearest neighbor exchange and the Coulomb repulsion which tends to prevent doubly occupied sites. The description is in terms of one and two particle thermodynamic Green's functions. Three different treatments of the correlations are used in finding the two particle Green's functions. Writing G_2 as a product of one particle Green's functions G_1 reduces to the Heisenberg first approximation when there are no ionic states. A second approximation where $G_2 = \Omega G_1 G_1$, Ω being a correlation matrix, results in a theory to some extent similar to the constant coupling method. Results are given for Curie point for several different lattices. A third approximation capable of accurately describing the limit of very large Coulomb repulsion is briefly discussed.

The object of this paper is to report briefly on an application of the thermodynamic Green's function formalism¹⁾ to the description of a ferromagnet near the Curie temperature T_C . Usually one describes a ferromagnet by the exchange Hamiltonian

$$H_e = -2J \sum_{i>j} S_i \cdot S_j$$

where the exchange interaction J is between nearest neighbors only and H_e only applies to the model where the spin per lattice site is constant and electrons do not move from site to site. The Green's function approach provides the possibility of relaxing this restriction and also of giving an accurate description of the exchange coupling of the spins.

Since spin waves are the exact elementary excitations at low temperatures for H_e , it is convenient near 0°K to use Green's functions constructed from spin wave annihilation and creation operators. This has been carried out by Bogoliubov and Tiablikov.²⁾ For T near T_C , however, the excitations are not at all like spin waves and there is an advantage in using ordinary fermion creation and annihilation operators $a_{i\sigma}(t)$ and $a_{i\sigma}^+(t)$ at a site i

because of their simple anticommutation relations. This would of course only complicate the problem near 0°K .

The initial Hamiltonian in our method is taken to be

$$H = -(\epsilon_0 + \mu)(N_{\sigma_1} + N_{\sigma_1'}) - \mu_0 H_0 (N_{\sigma_1} - N_{\sigma_1'}) + \frac{1}{2} \iint \frac{\psi^+(rt)\psi^+(r't)\psi(r't)\psi(rt)}{|r-r'|} dr dr'. \quad (1)$$

H_0 is an applied magnetic field and spin σ_1 is opposite to σ_1' . Expanding $\psi(rt)$ as

$$\psi(rt) = \sum_{i,\sigma} a_{i\sigma}(t) u_{i\sigma}(r) \quad (2)$$

where the \sum_i is over all lattice sites and we limit ourselves to one type of orbital $u_{\sigma}(r - \mathbf{R}_i) = u_{i\sigma}(r)$ about each site. Also we require

$$\int u_{i\sigma}^*(r) u_{j\sigma'}(r) d\tau = \delta_{\sigma\sigma'} \delta_{ij}.$$

The general Hamiltonian (1) is now restricted in that we only keep for the present discussion nearest neighbor exchange and the Coulomb repulsion K_{ii} of two electrons on the same site i . Then (1) reduces to

$$\begin{aligned}
H = & - \sum_{i\sigma} (\varepsilon_0 + \mu) a_{i\sigma}^+ a_{i\sigma} \\
& - \mu_0 H_0 \sum_i [a_{i\sigma_1}^+ a_{i\sigma_1} - a_{i\sigma_1}^+ a_{i\sigma_1}] \\
& + \frac{1}{2} \sum_{\sigma\sigma'} a_{i\sigma}^+ a_{i\sigma}^+ a_{i\sigma} a_{i\sigma'} K_{ii} \\
& - \frac{1}{2} \sum_{ik\sigma\sigma'} a_{i\sigma}^+ a_{k\sigma}^+ a_{k\sigma'} a_{i\sigma'} J_{ik}. \quad (3)
\end{aligned}$$

Here ε_0 is the binding energy per electron to a site and henceforth we absorb ε_0 into μ the chemical potential which is determined so that on the average there is one electron per site.

Our development closely follows that of Martin and Schwinger³⁾ where many of the details involved in this work are explained. Accordingly, we define our n -particle Green's function G_n as

$$\begin{aligned}
G_n(i_1\sigma_1t_1 \cdots i_n\sigma_nt_n : i_1'\sigma_1't_1' \cdots i_n'\sigma_n't_n') \\
= -(i)^n \varepsilon < | (a_{i_1\sigma_1}(t_1) \cdots \\
\times a_{i_n\sigma_n}(t_n) a_{i_n'\sigma_n'}^+(t_n') \cdots a_{i_1'\sigma_1'}^+(t_1')) | >, \quad (4)
\end{aligned}$$

which is the time ordered product of the $a_{i\sigma}(t)$ operators as defined in eq. (3.4) of M. S. It is readily shown that the set of primed lattice sites of a G_n must be the same as the set of unprimed sites, and, furthermore, $G_1(i\sigma t : i'\sigma' t')$ is diagonal in spin as well as site for the Hamiltonian as in (3). The magnetization $\sigma(\beta, H_0)$ is give as

$$\begin{aligned}
\sigma(\beta, H_0) = & -i \sum_i [G_{i\sigma=\alpha}(t, t^+) - G_{i\sigma=\beta}(t, t^+)] \\
= & -\frac{i}{\tau} \sum_{i\nu} e^{-\frac{i\pi\nu}{\tau}(t-t^+)} \\
& \times \left[G_{i\sigma=\alpha}\left(\frac{\pi\nu}{\tau}\right) - G_{i\sigma=\beta}\left(\frac{\pi\nu}{\tau}\right) \right]. \quad (5)
\end{aligned}$$

Here $\beta=1/kT$ when not used to indicate a spin direction. The $G_{i\sigma}(\pi\nu/\tau)$ are the Fourier coefficients of the periodic time dependent functions $G_{i\sigma}(t-t')$ as explained in eq. (5.19) of M.S. The equation of motion for G_1 is

$$\begin{aligned}
[i\partial/\partial t + \mu] G_{i\sigma}(t-t') \\
= & -i \sum_i K_{ii} G_2(i\sigma't, i\sigma t : i\sigma't', i\sigma't^+) \\
& + i \sum_{k \neq i, \sigma'} \sum_{\sigma} J_{ki} G_2(k\sigma t, i\sigma't : i\sigma't', k\sigma't^+) \\
= & \delta(t-t'). \quad (6)
\end{aligned}$$

Because of the definition of the thermodynamic Green's functions as grand canonical averages, the K_{ii} interaction must be retained in (6). In the limit of large K_{ii} the problem reduces to that of the $J_{ij} S_i \cdot S_j$ model where there is always one spin at every site. The

entire character of the results depends on the particular approximation made for G_2 . It should be noted that the G_2 for two particles on the same site describes a highly correlated situation when K_{ii} becomes large and in that instance must be treated more accurately than the G_2 describing nearest neighbor exchange. We now discuss three separate approaches.

The first approximation is simply to write

$$\begin{aligned}
G_2(i\sigma_1t_1, j\sigma_2t_2 : k\sigma_1't_1', l\sigma_2't_2') \\
= G_1(i\sigma_1t_1, k\sigma_1't_1') \\
\times G_1(j\sigma_2t_2, l\sigma_2't_2') \delta_{\sigma_1\sigma_1'} \delta_{\sigma_2\sigma_2'} \delta_{ik} \delta_{jl} \\
- G_1(i\sigma_1t_1, l\sigma_2't_2') \\
\times G_1(j\sigma_2t_2, k\sigma_1't_1') \delta_{\sigma_1\sigma_2'} \delta_{\sigma_2\sigma_1'} \delta_{il} \delta_{jk}. \quad (7)
\end{aligned}$$

Since (7) neglects all dynamical correlation, it will be a very poor approximation if K_{ii} is allowed to become large. Inserting (7) in (6) and taking the Fourier transform, we obtain the analogue of (5.41) of M.S., i.e.,

$$G_{i\sigma_1}\left(\frac{\pi\nu}{\tau}\right) = \frac{1}{\frac{\pi\nu}{\tau} + \mu + \mu_0 H_0 + ZJN_{\sigma_1} - K_{ii}N_{\sigma_2}}. \quad (8)$$

Here the applied magnetic field H_0 favors the σ_1 spin orientation and N_{σ_2} is the thermal average of the number of electrons at a lattice site of spin σ_2 which is opposite to σ_1 . Z is the number of nearest neighbors. The condition that $N_{\sigma_1} + N_{\sigma_2} = 1$ requires that $\mu = (K_{ii} - ZJ)/2$. Thus the magnetization given in (5) is

$$\sigma = \tanh \frac{\beta}{2} \left[\mu_0 H + \left\{ \frac{ZJ + K_{ii}}{2} \right\} \sigma \right]. \quad (9)$$

It is apparent in (9) that the Coulomb interaction has not been accurately treated because a net σ would be produced if J were zero through the K_{ii} part alone. In the limit that K_{ii} is so large that there is always one spin per site, (7) is a totally inadequate approximation. However, in that limit we know the exact ground state is one spin at each site all in the same direction, say σ_1 . We further more know that the energy required to remove an electron from the ground state is ZJ . This, then, implies that in the $\beta=\infty$ limit $G_{i\sigma_1}(\pi\nu/\tau)$ should have a single isolated pole at $\pi\nu/\tau = -ZJ$. Substituting $\mu = (K_{ii} - ZJ)/2$ into (8), we see that in this approximation $G_{i\sigma_1}(\pi\nu/\tau)$ has a pole at $\beta=\infty$ at

$$\frac{\pi\nu}{\tau} = -\frac{ZJ}{2} - \frac{K}{2}.$$

If we choose $K=ZJ$ so that this pole has the known exact value for the $JS_i \cdot S_j$ model, then (9) becomes

$$\sigma = \tanh \frac{\beta}{2} (\mu_0 H_0 + ZJ\sigma), \quad (10)$$

this being the familiar Heisenberg first approximation. This result leads us to make the following remarks. First, K_{ii} is likely to be of the order of J_{ij} and certainly not so large as to actually exclude from the statistical ensemble states where some sites are doubly occupied and others empty. The Green's function formulation is a natural means of taking such states into account. However, the only results that we can compare with are derived from the $JS_i \cdot S_j$ model. In order to reduce this theory to that model K_{ii} must be regarded as an adjustable parameter rather than a wholly physical quantity. (If the correlations were really described with sufficient accuracy, K_{ii} and the chemical potential would drop out of the problem.)

The second approach we discuss is the Ω approximation described in Section 5 of M.S. A detailed account of this theory as applied to the problem of nuclear matter has been given by Puff⁽⁴⁾.

Its essential feature is its short range character in that only correlations between directly interacting pairs of spins are retained. In the no correlation approximation (7) two spins interact as though one spin were the source of an effective magnetic field which acts on the other spin. There is no scattering in the sense that two electrons could flip their spins as a result of this exchange interaction. In this Ω approximation this spin flip or scattering process is included. One arrives at the Ω approximation as follows. The equation of motion for G_n involves G_{n+1} and G_{n-1} . This chain of coupled equations is broken by writing G_3 as a linear combination of products of G_2 's and G_1 's. One then obtains an integral equation for G_2 which if iterated generates the ladder diagrams so familiar in the theory of nuclear matter. In brief the two particle Green's function G_2 is written as $G_2 = \Omega G_1 G_1$ where Ω can be regarded as a correlation matrix. One finds that in place of (8)

$$G_{i\sigma_1} \left(\frac{\pi\nu}{\tau} \right) = \frac{1}{\frac{\pi\nu}{\tau} + \mu + \mu_0 H_0 - V_{i\sigma_1} \left(\frac{\pi\nu}{\tau} \right)} \quad (11)$$

where the temperature and frequency dependent potential V is

$$V_{i\sigma_1} = -\frac{1}{\tau} \sum_{j, \sigma_2, \nu'} [K_{ii} < \sigma_1 \sigma_2 | \Omega_{ii}(\nu + \nu') | \sigma_1 \sigma_2 > \delta_{ij} + J_{ij} < \sigma_1 \sigma_2 | \Omega_{ij}(\nu + \nu') | \sigma_1 \sigma_2 >] G_{j\sigma_2}(\nu'). \quad (12)$$

Inserting (12) into (11) one is led to an equation relating $G_{i\sigma_1}$ at different frequencies and involving $G_{i\sigma_2}$ as well. An approximate solution, whose details will be published elsewhere, has been obtained. One is led to a $G_{i\sigma_1}(\pi\nu/\tau)$ with a branch line on the real axis instead of a number of isolated poles. This branch line shrinks to a single point in the 0°K limit.

We expect this behavior from physical considerations since the singularities of $G_{i\sigma_1}(\pi\nu/\tau)$ occur at the energies changes involved in either adding an electron of spin σ_1 or removing one from the system. Thus in the ferromagnetic ground state let all the spins be up. Then $G_{i\sigma}$ for up spin will have a single pole at the energy required to remove such an electron. This energy will be unique because the Hamiltonian (3) does not allow motion of the hole in the excited state. At any non-zero temperature some of the systems of the ensemble will be in states above the ground state and $G_{i\sigma}(\pi\nu/\tau)$ should indeed have a branch line as the energy spectrum of the excited states is continuous for a large system. This is in marked contrast to the results of any cluster method such as the B.P.W. scheme or the constant coupling theory where the one particle Green's function always has a finite number of poles.

It may be remarked that the correlation matrix satisfies the equation

$$\Omega_{12} = 1_{12} + iG_1^0 G_1 V_{12} \Omega_{12}. \quad (13)$$

In order that the correct symmetry for G_2 be recovered, it is customary to replace the G_1 in (13) by G_1^0 giving the result of M.S. equation (5.60).

$$\Omega_{12} = 1_{12} + iG_1^0 G_1^0 V_{12} \Omega_{12}.$$

This replacement of G_1 by the one particle Green's function for non interacting electrons G_1^0 leads to the result the spin system will not completely magnetize at 0°K. This was avoided by using $G_1^H G_1^H$ in the Ω equation where G_1^H is the G_1 obtained by taking $G_2 = G_1 G_1 \pm G_1 G_1$, i.e., the Hartree G_1 . Since this no correlation G_1 treats K_{ii} very poorly if K_{ii}

becomes large, we cannot expect meaningful results in the Ω approximation in the limit $K_{ii} \rightarrow \infty$. Thus the best procedure to reduce our approach to the one spin per site model seems to be to pick K_{ii} so that the exact 0°K pole of $G_{i\sigma_1}(\pi\nu/\tau)$ is obtained.

Carrying out the formal solution for $G_{i\sigma_1}(\pi\nu/\tau)$ one finds that it is given as a function of the magnetization σ , the chemical potential μ , and the temperature or β . Inserting the result for $G_{i\sigma_1}(\pi\nu/\tau)$ into the expression for the magnetization (5) leads to the following equation for σ

$$\frac{1+\sigma}{2} = \frac{2}{\pi} \times \int_{-1}^{+1} dy \frac{\sqrt{1-y^2}}{1 + \exp(-\beta J(Z\sigma + C) + 2\beta J y \sqrt{ZF})}. \quad (14)$$

Here F is a function of σ , β , Z , and J having the value $(Z+2)/4$ for $\beta=0$ and monotonically decreasing to zero as β approaches ∞ . If F and C are zero, this equation for σ becomes the Heisenberg first approximation. Equation (14) is solved for σ at fixed values of β , Z and J and the value of C determined so that $\langle n_{i\sigma_1} \rangle + \langle n_{i\sigma_2} \rangle = 1$. This was carried out on the I.B.M. 709 starting at sufficiently high temperatures so that $\sigma=0$. The temperature was lowered until σ as found from (14) suddenly increases thus determining the Curie point. We list the ratio $2kT_c/ZJ$ for our results and those of several other methods in the Table below.

Method	Simple Cubic	B.C.C.	F.C.C.
Mol. Field	1.000	1.000	1.000
Oguchi	0.950	0.970	—
Constant Coupling	0.607	0.721	0.822
B. P. W.	0.617	0.725	—
Spherical Model	0.660	0.718	0.740
Green's Func. $G_2 = \Omega G_1 G_1$	0.684	0.714	0.724

It is to be emphasized that for the purposes of comparison we have attempted to reduce the grand canonical ensemble to only those states where there is always one spin at every lattice site. This was done by using the K_{ii} appearing in the Ω approximation as

an adjustable parameter. Physically this limiting situation would be obtained by letting K_{ii} go to $+\infty$ but the Ω approximation is not accurate enough to properly describe such a large interaction. Of course K_{ii} is actually of order J and the statistical treatment of ferromagnetism should include ionic states. This will have a considerable effect on the Curie point and the inclusion of these states is accomplished in a very natural way by the Green's function approach.

Finally we briefly mention a third approach. It is of some interest to see if the $K_{ii} \rightarrow \infty$ limit cannot be treated more generally than the phenomenological procedure described above. In this limit it can be shown that the following equation holds exactly

$$G_2(i\sigma_2 t, i\sigma_1 t' : i\sigma_1 t', i\sigma_2 t') = -iG_{i\sigma_1}^>(t-t'), \quad (15)$$

where the symbol $>$ means that t is always later than t' . Therefore, the K_{ii} interaction in (6) can be taken over to the right hand side of that equation as an inhomogeneous term and the remaining G_2 for the exchange interaction described by the Ω approximation or any other appropriate scheme. One finds the equation for $G_{i\sigma_1}(\pi\nu/\tau)$ to be

$$G_{i\sigma_1}\left(\frac{\pi\nu}{\tau}\right) = \frac{1 + K_{ii}G^+\left(\frac{\pi\nu}{\tau}\right)}{\frac{\pi\nu}{\tau} + \mu + \mu_0 H_0 - V_{i\sigma_1}\left(\frac{\pi\nu}{\tau}\right)} \quad (16)$$

where $V_{i\sigma_1}(\pi\nu/\tau)$ is the same as (12) except with no K_{ii} term and $G_{i\sigma_1}^+(\pi\nu/\tau)$ is non-zero only for the real part of $\pi\nu/\tau$ positive. The potential V involves $G_{i\sigma_1}$ and (16) is really a complicated self-consistent equation for $G_{i\sigma_1}$. Due to lack of space we defer a discussion of this problem to a later publication.

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DISCUSSION

W. KOHN: Are you acquainted with the work of Des Cloiseaux in France who uses a very similar model allowing, as you do, more than one electron per site.

G. W. PRATT: No, I am not aware of this work.