New Approach to the Theory of Itinerant Electron Ferromagnets with LocalMoment Characteristics

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Itinerant Ferromagnetism I

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New Approach to the Theory of Itinerant Electron Ferromagnets with Local-Moment Characteristics*

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The understanding of ferromagnets, like iron, which exhibit localized moment behavior above the Curie point yet show itinerancy has long stood as a major theoretical problem. An account will be given of recent progress on this problem which was achieved through functional integral methods. This technique transforms the interacting electron system into an average over a system of non-interacting electrons moving in a Gaussian-weighted external "magnetic" field which acts only on the electronic spins. For a single magnetic impurity in a free electron metal, a single approximation allows one to go from Pauli paramagnetism to localized moment behavior in a smooth manner as the atomic exchange interaction is increased. The two impurity problem leads to an effective exchange coupling as in the Heisenberg model, which is antiferromagnetic for the nondegenerate orbital case studied here. Application of the technique to homogeneous systems leads to damped spin waves in the ferromagnet in lowest approximation.

I. INTRODUCTION

There has been a long-standing debate whether the "*d* electrons" in Fe, Co, and Ni are better described in zero order by a localized (Heisenberg) model or by an itinerant (band) model. Some of the experimental evidence has been summarized by Herring.[1] While much of the experimental evidence originally quoted in support of one or the other limiting model is in fact well accounted for by *either* limit, the bulk of the relevant data, with a few notable exceptions, supports the itinerant theory. Evidence supporting the band limit includes the large electronic specific heat, nonintegral magneton numbers observed in saturation moments, the magnetoresistance, and Hall effect, etc. for the three elements. This evidence leads to the inescapable conclusion that the *d* electrons must exhibit at least *some* itinerant character.

To our knowledge only for Fe is there any evidence which unambiguously favors the localized model. Small additions of Cu, Zn, Al, etc. to Ni lower the saturation moment per atom by an amount proportional to the number of valence electrons per solute atom, while addition of these elements to Fe reduces the moment by roughly 2.2 μ_B (the saturation moment per atom in pure Fe) irrespective of valence.[2,3] This behavior suggests that a reasonably well-developed localized moment resides on each Fe atom, while the moment on Ni is strongly influenced by its environment, as one expects in a band scheme. Co appears to be closer to Ni in this respect. In addition, it appears that the ratio of the Curie constant $[C = (T-\theta)\chi]$ and the saturation moment observed for Fe is too small to be accounted for by any reasonable choice of parameters in a purely band theoretic model. On the other hand, the band model gives a rather better account of this ratio for Ni.[4] Thus, it appears that while Ni (and possibly Co)

can be treated in zero order by a band model with effective exchange interaction parameters, Fe should be viewed as an intermediate coupling case for which *neither* the band nor localized limits form good zero-order approximations. This is not to say that many properties of Fe cannot be well accounted for by a band model. Rather most observed properties of Fe are relatively insensitive to its intermediate coupling nature. A viable theory should be able to account for these features plus the apparent "localized moments" as seen in the alloy experiments and in the paramagnetic susceptibility.

Recently, the beginnings of a theory to handle this intermediate coupling (or schizophrenic electron) regime have been worked out by Wang, Evenson, and Schrieffer.[5] The theory is still in its formative stages yet the general features of the approach look quite promising. In essence, by using an identity of Stratonovich,[6] one can exactly transform the partition function for the interacting assembly of *d* electrons to a partition function for *noninteracting* electrons moving in a space- and time-varying externally applied "magnetic field," the field being averaged over with Gaussian weight. The method, when applied to the problem of a single impurity atom with intra-atomic exchange (the Anderson model)[7] gives in lowest approximation a continuous variation of the susceptibility from enhanced Pauli paramagnetism (for weak exchange) to an ideal Curie law (for strong exchange), all within an itinerant scheme. Thus, one has hope that a careful application of the technique to a system like pure Fe will adequately treat both its itinerant and localized aspects.

II. THE FUNCTIONAL INTEGRAL FORMULATION OF THE HUBBARD MODEL

The model we choose to consider for the ferromagnetic system is the multiorbital Hubbard model,[8] but

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for simplicity to begin with we will neglect the degeneracy of the d band and look at the nondegenerate-orbital Hubbard model. (In practice Hund's rule coupling due to orbital degeneracy is an important effect, needed to produce ferromagnetic rather than antiferromagnetic coupling between atoms. However, the essential localized-moment features of our problem are already contained in the simple case from which we start.) The Hamiltonian is

$$H = H_0 + H_1, \tag{2.1a}$$

with

$$H_0 = \sum_{ij\sigma} T_{ij}{}^{\sigma} c_{i\sigma}{}^+ c_{j\sigma} \tag{2.1b}$$

and

$$H_1 = \sum_i U_i n_{i\uparrow} n_{i\downarrow}, \tag{2.1c}$$

where U_i is the Coulomb interaction, assumed to act only when electrons are on the same atom (i.e., Wannier state). $U_i = U$ for the pure metal; the impurity problem corresponds to U_i varying over the lattice. The $c_{i\sigma}{}^+$, $c_{i\sigma}$ are creation and annihilation operators for electrons in Wannier state i with z component of spin $\sigma/2 = \pm\frac{1}{2}$. The $T_{ij}{}^{\sigma}$ include the usual transfer interaction, i.e., hopping integrals, and Zeeman energy for an externally applied field. We measure all energies relative to the chemical potential, μ.

If all the U_i were zero, H would be a one-body operator which could be exactly diagonalized in terms of the correct scattering states (or Bloch functions) which properly mix the Wannier states for the many sites. This would give an energy band picture for the resulting metallic system with the usual nearly temperature-independent Pauli susceptibility. On the other hand, if the hopping were zero, and there were one electron per site, one would have an insulating system. Then the susceptibility would be a spin-$\frac{1}{2}$ Curie law, $\chi \sim \beta$. These are the two important limiting cases: no localized moments or perfectly localized moments, depending on the size of the ratio T/U, where T is the nearest-neighbor hopping. As discussed above, for a system like iron one is dealing basically with an intermediate situation in which the magnetic effects appear to be close to the localized (insulator) limit, while transport properties are those of a metal. Unfortunately, it is just in this interesting case that it becomes very difficult to solve this problem. Perturbation theory in the appropriate small parameter, T/U or U/T, will not treat the regime where $T/U \sim 1$, and moreover, perturbation theory will not take us through the Mott transition where the system goes metallic from the small T/U insulator. We have hopes that the functional integral formulation of the problem will allow in a natural way those approximations which are useful in the regime $T/U \sim 1$.

To study the magnetic behavior of this system, it is convenient to calculate the grand partition function,

Z, for the Hamiltonian in the presence of an external field. Then we get the susceptibility, χ, for example, by differentiation of $\log Z$ with field h, where $Z = \mathrm{Tr}\, \exp[-\beta(H - \mu N)]$.

Stratonvich,[6] then Hubbard[9] and Mühlschlegel,[10] developed a functional integral method for calculating Z which begins with the identity (valid for any bounded operator a)

$$\exp(\pi a^2) = \int_{-\infty}^{\infty} d\chi \, \exp(-\pi\chi^2 + 2\pi a\chi), \tag{2.2}$$

as seen by completing the square in the exponent. To use this identity we can rewrite H_1 in any of several ways, e.g.,

$$U_i n_{i\uparrow} n_{i\downarrow} = -\tfrac{1}{2} U_i (n_{i\uparrow} - n_{i\downarrow})^2 + \tfrac{1}{2} U_i (n_{i\uparrow} + n_{i\downarrow}), \tag{2.3}$$

since $n_{i\sigma}{}^2 = n_{i\sigma}$ for fermion occupation number operators. Alternatively, we could write, as Hamann[11] did recently,

$$U_i n_{i\uparrow} n_{i\downarrow} = \tfrac{1}{4} U_i (n_{i\uparrow} + n_{i\downarrow})^2 - \tfrac{1}{4} U_i (n_{i\uparrow} - n_{i\downarrow})^2, \tag{2.4}$$

or by writing the fermion operators in terms of spin operators

$$U_i n_{i\uparrow} n_{i\downarrow} = \tfrac{1}{2} U_i (n_{i\uparrow} + n_{i\downarrow}) - \tfrac{2}{3} U_i \mathbf{S}_i \cdot \mathbf{S}_i \tag{2.5a}$$

$$= \tfrac{1}{4} U_i (n_{i\uparrow} + n_{i\downarrow})^2 - \tfrac{1}{3} U_i \mathbf{S}_i \cdot \mathbf{S}_i. \tag{2.5b}$$

We will not discuss the relative merits of these ways of writing H_1, but in our present discussion we will use the first expression. We take the second term in (2.3) into H_0 so that

$$\bar{H}_0 = \sum_{ij\sigma} \bar{T}_{ij}{}^{\sigma} c_{i\sigma}{}^+ c_{j\sigma}, \qquad \bar{T}_{ij}{}^{\sigma} \equiv T_{ij}{}^{\sigma} + \tfrac{1}{2} U_i \delta_{ij}, \tag{2.6a}$$

$$\bar{H}_1 = -\sum_i \tfrac{1}{2} U_i (n_{i\uparrow} - n_{i\downarrow})^2. \tag{2.6b}$$

Now if $\bar{H}_0$ and $\bar{H}_1$ commuted, one could write $\exp(-\beta H)$ as $\exp(-\beta \bar{H}_0) \exp(-\beta \bar{H}_1)$. One could then use the Stratonovich identity to write

$$\exp[\beta \tfrac{1}{2} U_i (n_{i\uparrow} - n_{i\downarrow})^2]$$

$$= \int_{-\infty}^{\infty} d\xi_i \, \exp[-\pi\xi_i^2 + (2\pi\beta U_i)^{1/2}(n_{i\uparrow} - n_{i\downarrow})\xi_i]. \tag{2.7}$$

Unfortunately $\bar{H}_0$ and $\bar{H}_1$ do not commute, so before we can linearize the exponential we need to use the Feynman time-ordering trick:

$$e^{A+B} = T \exp\left(\int_0^1 d\tau (A_\tau + B_\tau)\right), \tag{2.8}$$

where τ is a fictitious "time;" T is the chronological ordering operator, which orders products like $A_\tau B_{\tau'} A_{\tau''}$ chronologically with larger "times" to the left. The A_τ and $B_{\tau'}$ can be treated as *commuting* operators so long as they are acted on by the T operator in the end. Using

this time-ordering trick then, the $\int d\xi_i$ becomes a functional integral over all possible functions $\xi_i(\tau)$, and

$$\exp(-\beta H) = T \int \prod_i \mathfrak{D}\xi_i(\tau) \, \exp\left(-\int_0^1 d\tau'\{\beta\bar{H}_{0\tau'}\right.$$

$$\left. + \sum_i \left[\pi\xi_i{}^2(\tau') - c_i\xi_i(\tau')(n_{i\uparrow\tau'} - n_{i\downarrow\tau'})\right]\}\right) \quad (2.9a)$$

with

$$c_i \equiv (2\pi\beta U_i)^{1/2}. \quad (2.9b)$$

The significant point here is that one has reduced the density matrix $\exp(-\beta H)$ for a system with the two-body Coulomb interaction to the average over the density matrix for a system with only one-body terms but in a random "magnetic" field $\xi_i(\tau)$ in the z direction. [Notice $\xi_i(\tau)$ enters $H(\xi_i)$ with S_z to contribute a Zeeman-like energy, where $\xi_i(\tau)$ looks like a magnetic field.] Thus we replace the exchange field one electron exerts on another by a fictitious external field which varies in time and from site to site, but which is so arranged as to reproduce *exactly* the effect of the actual interaction.

The $\mathrm{Tr}T$ in Z is applied only to the quantum-mechanical operators, $\bar{H}_0$ and $n_{i\sigma}$, and is not affected by the variable $\xi_i(\tau)$. Therefore we can interchange the order of doing the functional integral and the $\mathrm{Tr}T$ to obtain Z as a Gaussian functional average

$$Z = \int \prod_i \mathfrak{D}\xi_i(\tau) \, \exp\left(-\int_0^1 d\tau' \sum_i \pi\xi_i{}^2(\tau')\right)$$

$$\times Z(\xi_1, \xi_2, \cdots, \xi_N) \quad (2.10)$$

of a partition functional

$$Z(\xi_1, \xi_2, \cdots, \xi_N) \equiv \mathrm{Tr}T$$

$$\times \exp\left(-\int_0^1 d\tau'[\beta\bar{H}_{0\tau'} - \sum_{i\sigma} \sigma c_i\xi_i(\tau')n_{i\sigma\tau'}]\right). \quad (2.11)$$

This is an exact expression for Z. There are now two major pieces in the problem of evaluating Z from this expression: (1) evaluate $Z(\xi_1, \xi_2, \cdots, \xi_N)$ for arbitrary fields $\xi_i(\tau)$, $0 < \tau < 1$, and (2) carry out the functional average of $Z(\xi_1, \xi_2, \cdots, \xi_N)$. Notice that the functional integral is normalized so that if $Z(\xi_1, \xi_2, \cdots, \xi_N)$ is independent of the ξ_i, say it $= Z_0$, then $Z = Z_0$. This is the case, for example, if all $U_i = 0$.

III. FORMAL EXPRESSION FOR $Z(\xi_1, \xi_2, \cdots, \xi_N)$

To evaluate $Z(\xi_1, \cdots, \xi_N)$ we introduce a coupling constant λ multiplying the c_i. Then the density matrix $\rho_\lambda(\xi_1, \xi_2, \cdots, \xi_N)$ is just

$$\exp-\left(\int_0^1 d\tau\beta H_{\lambda\tau}\right).$$

Differentiation of $\log Z_\lambda$ with respect to λ yields

$$\frac{\partial \log Z_\lambda}{\partial\lambda} = \mathrm{Tr}T\left(\int_0^1 d\tau \sum_{i\sigma} \sigma c_i\xi_i(\tau)n_{i\sigma\tau}\rho_\lambda\right)\Big/ \mathrm{Tr}T\rho_\lambda$$

$$\equiv \sum_{i\sigma}\int_0^1 d\tau\sigma c_i\xi_i(\tau)\langle n_{i\sigma\tau}\rangle_\lambda, \quad (3.1)$$

where the identity on the right-hand side defines $\langle \ \rangle_\lambda$. Since $Z(\xi_1, \cdots, \xi_N) = Z_{\lambda=1}$, we would like to integrate (3.1) using the fact that $Z_{\lambda=0}$ is easy to find since it corresponds to $U_i = 0$. At this point one introduces Green functions to determine $\langle n_{i\sigma\tau}\rangle_\lambda$. We define

$$G_{ii}{}^{\lambda\sigma}(\tau, \tau') \equiv -\mathrm{Tr}T(c_{i\sigma\tau}c_{i\sigma\tau'}{}^+\rho_\lambda)/\mathrm{Tr}T\rho_\lambda, \quad (3.2)$$

so that

$$\langle n_{i\sigma\tau}\rangle_\lambda = G_{ii}{}^{\lambda\sigma}(\tau, \tau^+). \quad (3.3)$$

To find G^λ we write its equation of motion. By Fourier transforming all quantities, it is possible to formally solve for G^λ. The λ integral can then be done exactly so that we finally obtain a simple formal expression for $Z(\xi_1, \xi_2, \cdots, \xi_N)$:

$$Z(\xi_1, \xi_2, \cdots, \xi_N) = Z_0 \exp[\mathrm{Sp}\log(1-K)], \quad (3.4)$$

where Z_0 is the partition function for all $c_i = 0$. [Z_0 just leads to the Pauli susceptibity for the metal with the $U_i/2$ shift in level position, so $\exp[\mathrm{Sp}\log(1-K)]$ contains the interesting physics of local moments if they occur.] K is a known matrix defined by

$$K_{in,jn'}{}^{\sigma,\sigma'} = -\sigma c_i\xi_{i,n-n'}g_{ij}{}^\sigma(n')\delta_{\sigma\sigma'}, \quad (3.5)$$

where

$$\xi_i(\tau) = \sum_{\nu=-\infty}^{\infty} \xi_{i\nu}\exp(-2\pi i\nu\tau),$$

and $g_{ij}{}^\sigma(n)$ is the zero-order one-electron Green function Sp means trace in σ, i, and n variables.

We will find later in considering which approximations are necessary to evaluate Z that it is useful to treat the zero-frequency part of the effective potential, $-\sigma c_i\xi_{i0}$, separately (and exactly) in zero order. To do this, let $K \equiv Vg = (V_0 + V')g$, where

$$V_{0in,jn'}{}^{\sigma,\sigma'} = -\sigma c_i\xi_{i0}\delta_{ij}\delta_{\sigma\sigma'}\delta_{nn'}; \quad (3.6)$$

thus

$$\mathrm{Sp}\log(1-K) = \mathrm{Sp}\log(1-V_0g)$$

$$+ \mathrm{Sp}\log[1 - V'g(1-V_0g)^{-1}]. \quad (3.7)$$

Now define a new zero-order Green function by the Dyson-like equation

$$\bar{g} \equiv g(1-V_0g)^{-1}, \quad (3.8)$$

and let $K_0 \equiv V_0g$, $K' \equiv V'\bar{g}$; then

$$\mathrm{Sp}\log(1+K) = \mathrm{Sp}\log(1-K_0) + \mathrm{Sp}\log(1-K'). \quad (3.9)$$

When we put this form back into the functional integral (2.10) to get Z, it is convenient to express the

functional integral in the $\xi_{i\nu}$ variables as we have done for $Z(\xi_1, \xi_2, \cdots, \xi_N)$. Then

$$Z = \int_{-\infty}^{\infty} \prod_i d\xi_{i0} \int \left(\prod_{\nu=1,i}^{\infty} 2d^2\xi_{i\nu} \right) \exp\left(- \sum_{\nu=-\infty,}^{\infty} \pi \mid \xi_{i\nu} \mid^2 \right)$$

$$\times Z(\xi_1, \cdots, \xi_N), \quad (3.10)$$

where $\xi_{i\nu}{}^* = \xi_{i,-\nu}$ and $d^2\xi_{i\nu}$ denotes an integral over the complex $\xi_{i\nu}$ plane. We now have an exact formal expression for Z which consists of an integral which is infinite-dimensional in Fourier space and N-dimensional in coordinate space ($N =$ number of atoms in solid). At this point we must introduce approximations.

In considering the full N-center problem, there are three somewhat distinct physical effects. The first is the formation of a quasi-localized moment; the second is the form of the interaction between these moments; and the third is the cooperative behavior of the total system. We discuss each of these effects below: the first question is considered in some detail in Sec. IV, while brief discussion of the other two is given in Secs. V and VI.

IV. THE ONE-CENTER PROBLEM

A. The Anderson Model

We begin our study of ferromagnets with local-moment behavior above T_c by considering temperatures $T_c \ll T \ll T_F$. (For iron $T_c \sim 1043°$K, and $T_F \sim 20\,000°$K.) At these high temperatures there is little short-range order in the spin system, so we can to lowest order consider the problem of the ferromagnet to be a collection of one-center problems, i.e., our chosen center thinks it is all alone in some "effective energy band" made up of all the spin-orientation averaged electronic orbitals of the system. We will see that the results are relatively insensitive to the precise nature of this effective band. Then our model has $U_i = 0$ except at the particular site we focus on where $U_i = U$ and in fact reduces to the usual Anderson model with

$$\bar{H}_0 = \sum_{k\sigma} \epsilon_{k\sigma} n_{k\sigma} + \sum_{\sigma} \bar{\epsilon}_{d\sigma} n_{d\sigma} + \sum_{k\sigma} [V_{kd}c_{k\sigma}^+ c_{d\sigma} + V_{kd}{}^* c_{d\sigma}^+ c_{k\sigma}],$$

$$(4.1)$$

$$\bar{\epsilon}_{d\sigma} \equiv \epsilon_{d\sigma} + U/2,$$

$$\bar{H}_1 = -\tfrac{1}{2} U (n_{d\uparrow} - n_{d\downarrow})^2,$$

where V_{kd} is the hopping potential from d to k, reflecting the fact that an electron initially on the d state in a localized orbital will decay into the band. The $\epsilon_{k\sigma}$ is the effective band mentioned above. The $T_{ij}{}^{\sigma}$ of the Hubbard model can be thought of as Fourier components of the $\epsilon_{k\sigma}$ expanded in the complete set of Wannier functions for a single band.

For a band density of states $N(\epsilon)$, the width of the "virtual level" on the d state, i.e., the inverse lifetime of the state with a single electron on the "impurity," is

given by

$$\Gamma \cong \pi N(\epsilon_d) \mid V_{kd} \mid^2_{\text{Av}}. \quad (4.2)$$

Here the interesting number which takes us from the local moment to the completely delocalized state is $U/\pi\Gamma$. (*Note*: One is not obliged to go over to the Anderson model language, but we could stick with the Hubbard form while taking only one of the $U_i \neq 0$. The advantage of the Anderson model in this case is its familiarity and the ready physical interpretation of the terms. The results are identical if one makes a careful correspondence of the various terms in the two representations of the model.)

B. The Static Approximation

For general ξ_ν we do not know how to calculate $\mathrm{Sp} \log(1-K)$ in an exact way, even in this simpler problem. Also, we still need to do the functional integral. Mühlschlegal[10] showed that if one considers only ξ_0, neglecting all ξ_ν for finite ν in $Z(\xi)$, then Z is exact for $U/\pi\Gamma = 0$ and for $\pi\Gamma/U = 0$. This approximation has been termed the "static approximation" for obvious reasons. It also gives a smooth interpolation for Z between the two exact limits.

When we set $\xi_{\nu \neq 0} = 0$, $V \to V_0$ which is automatically diagonal in the σ and n variables; then

$$\mathrm{Sp} \log(1-K) \to \mathrm{Sp} \log(1-K_0) = \sum_{\sigma,n} \log(1 + \sigma c\xi_0 g_n{}^\sigma).$$

$$(4.3)$$

If we take $h = 0$, $\beta\Gamma$ large, and assume the so-called symmetric case where $\epsilon_d = -U/2$, we obtain

$$\log \frac{Z(\xi_0)}{Z_0} = \frac{2c\xi_0}{\pi} \tan^{-1} \frac{c\xi_0}{\beta\Gamma} - \frac{\beta\Gamma}{\pi} \log \left[1 + \left(\frac{c\xi_0}{\beta\Gamma} \right)^2 \right]. \quad (4.4)$$

[For general values of $\beta\Gamma$, ϵ_d, and h, $Z(\xi_0)$ can be expressed in terms of digamma functions.]

In the static approximation, then,

$$Z = \int_{-\infty}^{\infty} d\xi_0 \exp(-\pi\xi_0^2) Z(\xi_0)$$

$$= \int_{-\infty}^{\infty} d\xi_0 \exp[-\beta F_{st}(\xi_0)], \quad (4.5)$$

and the integral must be done numerically. $\beta F_{st}(\xi_0) = -\log Z(\xi_0) + \pi\xi_0^2$ is plotted in Fig. 1 for $U/\pi\Gamma = 0.2, 0.5, 1.0,$ and 5.0. For $U/\pi\Gamma \ll 1$, only small fluctuations of ξ_0 about the origin enter with appreciable weight, corresponding to weakly exchange-enhanced Pauli paramagnetism. For $U/\pi\Gamma \gtrsim 0.5$, minima develop symmetrically about the origin and a wide range of ξ_0 values enters with appreciable weight, corresponding to large amplitude localized spin fluctuations. $U/\pi\Gamma \gg 1$ is the strongly localized-moment regime, the two minima corresponding to the up and down spin states.[12] Unfortunately, the static approximation, while having many features which are correct (e.g., smooth transition

from Pauli to Curie law susceptibility), does not give proper leading order corrections in the two extreme cases.

C. The "RPA Prime"

We can improve on the static approximation by enlarging the class of functions $\xi(\tau)$ which we consider. In particular, we can include for *each* value of ξ_0 all Gaussian fluctuations of $\xi(\tau)$ about that average value. We then get proper leading corrections for $U/\pi\Gamma \ll 1$ and the leading corrections in the other limit are brought closer to the exact ones. By analogy to the random phase approximation (RPA), we call this scheme the "RPA'."

The RPA corresponds to retaining only the K^2 terms in the Sp $\log(1-K)$ occurring in (3.4). This gives a free energy arising entirely from Gaussian fluctuations in the "time-varying magnetic field." While this approximation is valid for small U, as $U/\pi\Gamma$ approaches unity, the free energy functional becomes strongly anharmonic as shown in Fig. 1 for ξ_0. It is in fact this anharmonic nature of F which ultimately leads to the Curie law for $U/\pi\Gamma \gg 1$.

To evaluate the RPA' we retain the Sp $\log(1-K')$ term in (3.9) to second order in K', while keeping the Sp $\log(1-K_0)$ exactly. The $\xi_{\nu\neq0}$ integrals, being Gaussian, can be performed, and one finds

$$\beta F_{RPA'}(\xi_0) = \beta F_{st}(\xi_0) + \sum_{\nu>0} \log[1-(c^2/\pi)\phi_\nu(\xi_0)], \quad (4.6)$$

where $\phi_\nu(\xi_0)$ is the "polarization bubble"

$$\phi_\nu(\xi_0) \equiv -\tfrac{1}{2} \sum_{\sigma,n} g_n{}^\sigma g_{n+\nu}{}^\sigma. \quad (4.7)$$

The first term in (4.6) is just the free energy due to the mean value of the fluctuating field, while the second term represents the free energy of the fluctuations about this mean. Clearly, this approximation is reasonable if
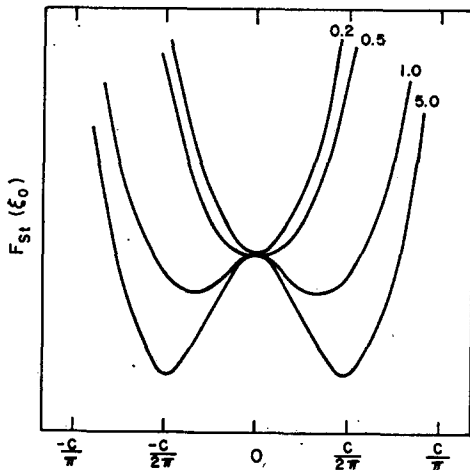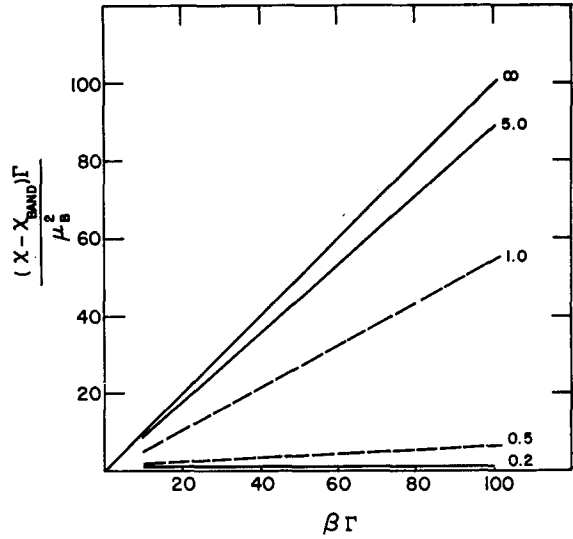

FIG. 2. Plots of the dimensionless quantities $(\chi-\chi_{band})\Gamma/\mu_B{}^2$ versus $\beta\Gamma$. The full lines are calculated directly from (4.9a) and (4.9b) within RPA'; the dashed lines are calculated by the static approximation. The asymptote for large $U/\pi\Gamma$ is the correct Curie law for a free spin $\frac{1}{2}$. For small $U/\pi\Gamma$, the correct exchange-enhanced Pauli susceptibility is obtained.

the fluctuations are sufficiently small, as is the case when $U/\pi\Gamma \ll 1$. As $U/\pi\Gamma$ increases toward unity, the fluctuations become large, and hence non-Gaussian. Then the Gaussian terms included in RPA' are not even sufficient to make the ξ_0-integral converge. However, when $U/\pi\Gamma$ becomes very large, the free energy functional develops sharp minima. For reasonable temperatures, the only important contributions to the ξ_0 integral must come from the neighborhood of these minima, so the integral can be restricted to that neighborhood. Then RPA' again gives well-behaved results.

D. The Magnetic Susceptibility

$$\chi = \beta^{-1}(\partial^2 \log Z/\partial h^2)|_{h=0}.$$

The applied field, h, will clearly enter $Z_h(\xi)/Z_{0h}$ additively with the fictitious field ξ_0. Hence,

$$\frac{Z_h(\xi_0, \xi_{\nu\neq0})}{Z_{0h}} = \frac{Z_{h=0}(\xi_0+\beta\mu_B h/c, \xi_{\nu\neq0})}{Z_{0h}}.$$

Therefore, we put $\xi_0' = \xi_0 + \beta\mu_B h/c$, and

$$\frac{Z_h}{Z_{0h}} = \int_{-\infty}^{\infty} d\xi_0' \int \left(\prod_{\nu>0} 2d^2\xi_\nu\right)$$

$$\times \exp[-\pi(\xi_0'-\beta\mu_B h/c)^2] \exp[Sp \log(1-K)], \quad (4.8)$$

the only h dependence being displayed explicitly in the Gaussian weight factor. Then

$$\chi = (\mu_B{}^2/U)(2\pi\langle\xi_0{}^2\rangle - 1) + \chi_{band}, \quad (4.9a)$$

FIG. 1. Effective free energy F_{st} for a τ—independent field ξ_0, as given by (4.4). The curves are labeled by $U/\pi\Gamma$. c is $(2\pi\beta U)^{1/2}$.

where

$$\langle \xi_0{}^2 \rangle \equiv Z^{-1} \int_{-\infty}^{\infty} d\xi_0 \int \left(\prod_{\nu>0} 2d^2\xi_\nu \right) \xi_0{}^2 \exp(-\pi\xi_0{}^2)$$

$$\times \exp[\text{Sp} \log(1-K)], \quad (4.9b)$$

and χ_{band} is the Pauli susceptibility for the band electrons. Numerical results for χ are shown in Fig. 2 for several values of $U/\pi\Gamma$.

To our knowledge, this approach achieves, for the first time, a Curie-like susceptibility at high temperatures in the interesting region without starting from a zero-order approximation which already contains a moment. Rather, this theory deduces a Curie law which does not rest on such assumptions. This was one of our original important objectives for this first stage of the problem, and it became clear that in order to obtain a Curie-like susceptibility for temperatures $T_c \ll T \ll U$, there would have to be some sort of "collective degrees of freedom" associated with the magnetization. The fluctuations in this collective mode (i.e., the localized spin fluctuations in the system) should occur on a time scale that is much slower than the time scale set by the band width (i.e., the level width of the virtual state in the one-center problem). At first sight the ξ_0 might be considered to be the only important collective degree of freedom, all other variables undergoing small fluctuations about the value of ξ_0 in question. The breakdown of RPA' for $U/\pi\Gamma \sim 1$ underlines the fact that in the intermediate coupling regime a number of variables undergo large non-Gaussian fluctuations. Presumably, the ξ_ν for a range of frequencies, ν, much smaller than $\beta\Gamma$ will enter on approximately the same footing, while the large ν terms will serve mainly to produce an increase in the effective level width. We are pursuing these questions as well as problems including orbital degeneracy in the model.

V. THE TWO-CENTER PROBLEM

To investigate a Heisenberg-like description of the system in which quasi-localized moments are coupled via a pairwise interaction, one can study the problem of two magnetic atoms imbedded in a nonmagnetic host; i.e., $U_a = U_b = U$, $U_i = 0$ if $i \neq a$ or b in (2.6). Within the static approximation, one again retains only ξ_{i0} ($i = a$ or b). Proceeding as in the one-center problem, when a and b are nearest neighbors, one finds an antiferromagnetic coupling. Presumably by including orbital degeneracy one would, under suitable circumstances, obtain ferromagnetic coupling.[13] Due to the fact that the scalar ξ field within the static approximation does not account for transverse fluctuations of the moments, the coupling is of the Ising form. For two widely spaced impurities the interaction is of the RKKY form, while for intermediate separations several terms of comparable order complicate the interaction.[14]

VI. THE N-CENTER PROBLEM

The treatment of cooperative effects is very natural within the functional integral representation.[15] In the ferromagnetic state, the presence of long-range magnetic order enters through the special importance of the time- and space-averaged $\xi_i(\tau)$, $\xi_{q=0,\nu=0}$, which plays the role of a molecular field. Collective excitations (damped spin waves) enter if one treats the remaining parts of the $\xi_i(\tau)$ field within a Gaussian approximation analogous to the RPA' discussed in Sec. IVC. Since the spin waves involve transverse fluctuations of the ordered moments, and since approximations do not necessarily preserve the rotational invariance of the system, it is important that one treat the problem in a manifestly rotationally invariant fashion to insure that the spin-wave energies properly go to zero for long wavelengths. This can be accomplished by writing the two-body interaction as in (2.5). The interaction is now linearized by a vector field, $\boldsymbol{\xi}_i(\tau)$. Treating $\boldsymbol{\xi}_{q=0,\nu=0}$ in zero order, the RPA' gives the free energy of the ferromagnetic state in terms of the $\boldsymbol{\xi}_{00}$ average of the usual RPA partition function in a molecular field, $\boldsymbol{\xi}_{00}$. This approximation does not include the localized-moment behavior, and one must combine the collective effects with those treated in the two preceding sections to obtain a more faithful picture of the intermediate-coupling ferromagnet.

While there are yet many difficulties to overcome in finally working out the detailed, quantitative theory of ferromagnetism in iron, we believe that this functional integral technique holds good promise in this and in other very difficult many-body problems where large fluctuations play a crucial role.

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