Theory of Itinerant Ferromagnets with Localized-Moment Characteristics: Two-Center Coupling in the Functional-Integral Scheme*

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The coupling between two magnetic centers in a band is discussed within the framework of the functional-integral scheme. The model used is the single-orbital Hubbard model with Coulomb repulsion only on the two magnetic sites. In lowest approximation, antiferromagnetic Ising coupling is obtained when the moments are nearest neighbors. When the moments are far apart, Ruderman-Kittel-Kasuya-Yosida coupling is the most important of several terms.

A functional-integral technique has recently been applied[1,2] to the theory of ferromagnetism in systems like iron which exhibit localized-moment behavior above the Curie point yet show itinerancy. This recent work considered the general formulation of the problem and the details of the one-center problem (i.e., the ferromagnet at temperatures sufficiently high to eliminate short-range order). In this paper we study the two-center problem in detail to gain insight into the coupling of moments in this system.

Considerable previous work has been done on the two-center problem in a two-impurity Anderson model.[3] All of that work was done within the framework of Hartree-Fock approximation. Alexander and Anderson, Moriya, and Liu studied the case of two close impurities, while Kim and Nagaoka, and Caroli studied mainly the case where the two impurities are widely separated. These authors were primarily interested in the coupling energy in the localized-moment regime, where the Coulomb repulsion U is the dominant energy in the problem. Unfortunately, it is in this case that Hartree-Fock is least reliable. The differences in approach and in choice of model have made it difficult to compare the present results in detail with the previous work; however, many qualitative features are the same.

The model we have considered is the nondegenerate orbital Hubbard model[4] with Coulomb repulsion on the two magnetic centers of the system, i.e., a two-impurity Wolff model. (In practice, Hund's rule coupling due to orbital degeneracy is an important effect. However, the introduction of degenerate orbitals involves considerable mathematical complication, so we have restricted our attention to the simpler nondegenerate case for the time being.) The Hamiltonian is, then, $H = H_0 + H_1$, where if $\sigma = \pm 1$,

$$H_0 = \sum_{ij\sigma} T_{ij}^{\sigma} c_{i\sigma}^{\dagger} c_{j\sigma} , \tag{1a}$$

and

$$H_1 = U(n_{a\uparrow} n_{a\downarrow} + n_{b\uparrow} n_{b\downarrow}) . \tag{1b}$$

The T_{ij}^{σ} contain any one-center potential, including Zeeman energy, as well as the hopping matrix elements or Fourier components of $\epsilon(\vec{k})$ expanded in the complete set of Wannier functions for one band. Following the procedure discussed in detail in Ref. 2, we obtain the two-center "static approximation" by keeping only the zero-frequency components of the random fields $\xi_a(\tau)$ and $\xi_b(\tau)$. Then we obtain

$$Z_{\text{static}} = \int_{-\infty}^{\infty} d\xi_{a0} \int_{-\infty}^{\infty} d\xi_{b0}\, e^{-\pi(\xi_{a0}^2 + \xi_{b0}^2)} Z_{\text{st}}(\xi_{a0}, \xi_{b0}) , \tag{2a}$$

where

$$Z_{\text{st}}(\xi_{a0}, \xi_{b0}) = Z_0 e^{\text{Sp ln}(1-K_0)} . \tag{2b}$$

Z_0 is the partition function for $c = (2\pi\beta U)^{1/2} \to 0$ as before, and the spur (trace) is

$$\text{Sp ln}(1-K_0) = \sum_{n\sigma} \ln\{[1 + \sigma c \xi_{a0} G_{aa}^{\sigma 0}(n)][1 + \sigma c \xi_{b0} G_{bb}^{\sigma 0}(n)] - c^2 \xi_{a0}\xi_{b0} G_{ab}^{\sigma 0}(n) G_{ba}^{\sigma 0}(n)\} , \tag{3a}$$

where for $i, j = a$ or b

$$G_{ij}^{\sigma 0}(n) = \frac{1}{n} \sum_{\vec{k}} \frac{e^{i\vec{k}\cdot(\vec{R}_i - \vec{R}_j)}}{i\omega_n - \beta\epsilon_{\vec{k}}} . \tag{3b}$$

We can proceed beyond the static approximation by the RPA′[2] or by the more sophisticated methods that have recently been applied to the one-center problem.[5] In both the one- and two-center problems, we find that the static approximation is exact for $T_{ij} \equiv 0$ or for $U = 0$. The RPA′ gives the right leading corrections from the latter limit, while the methods of Ref. 5 also fix up the leading corrections in the former limit. One obtains a smooth interpolation through the $U/\Delta \sim 1$ region (Δ being the bandwidth) by either the static approximation or the approximations of Ref. 5.

We have considered two cases in the two-center problem: (i) when atoms a and b are nearest neighbors, and (ii) when atoms a and b are far apart so that $\vec{R}_{ab} = \vec{R}_a - \vec{R}_b$ is much larger than a lattice spac-

ing. In both these cases the ln term in (3a) can be expanded into a noninteracting term plus coupling terms with the first coupling term dominating the interaction energy when one looks at either U/Δ or Δ/U small. This is true because in the expansion for coupling energy, the ratio of successive terms is the small parameter U/Δ or Δ/U. This fact is obvious when a and b are far apart so $G_{ab}^{\sigma 0}(n)$ must be small compared to $G_{aa}^{\sigma 0}(n)$. The noninteracting term is, of course, simply the one-center term which was discussed in Refs. 1 and 2. The coupling part in general, without expansion of the ln in (3a), leads to extremely complicated integrals, so we will report here on only the leading coupling term.

$G_{aa}^{\sigma 0}(n)$ is given by (3b), but to proceed we must evaluate the $\vec{k}$ sum. In Ref. 1 this is done using a Lorentzian state density. However, now that we are looking at coupling terms, the long tails on the Lorentzian lead to unphysical effects in case (i) (a, b near neighbors) when the hopping is very small; in particular, $G_{ab}^{\sigma 0}$ remains finite as $T_{ij} \to 0$ for that case. For this reason, we have used a Lorentzian-squared state density [i.e., $N(\epsilon) = 2\Delta^3/\pi(\Delta^2 + \epsilon^2)^2$] to evaluate $G_{aa}^{\sigma 0}$ in case (i). When a and b are nearest neighbors, $G_{ab}^{\sigma 0}$ is found from the equation of motion for $G_{aa}^{\sigma 0}$ to be

$$G_{ab}^{\sigma 0}(n) = [i\omega_n G_{aa}^{\sigma 0}(n) - 1]/z\beta T ,$$

where a tight-binding band is assumed, so that $T_{ij} = T$ if i, j are nearest neighbors, and $T_{ij} = 0$ otherwise (except for the one-center potentials on a and b), and z is the number of nearest neighbors. If the width Δ of the normalized Lorentzian-squared state density used in case (i) is chosen to be $z^{1/2}T$, then the leading terms in $G_{ab}^{\sigma 0}$ and $G_{aa}^{\sigma 0}$ as $\omega \to 0$, ∞, and $T \to 0$, ∞, all agree with those obtained from inserting the tight-binding assumption into (3b). In case (ii), we have used a simple Lorentzian state density to evaluate $G_{aa}^{\sigma 0}$; $G_{ab}^{\sigma 0}$ is left in the form (3b) when a and b are widely separated. Since we have assumed a tight-binding form for T_{ij}, the width of the Lorentzian, Δ, in case (ii) must also be proportional to T. For additional simplification we have taken $T_{aa} = T_{bb} = -\frac{1}{2}U$.

We have called the dominant coupling term in the cases studied $-\beta C(\xi_a, \xi_b)$ so that C is the coupling free energy for fields ξ_a, ξ_b. We will discuss its form when $U/\Delta \gg$ or $\ll 1$.

We will first consider $C(\xi_a, \xi_b)$ when a and b are nearest neighbors and $U/\Delta \gg 1$. From the noninteracting term in $Z(\xi_a, \xi_b)$ we see that the effective free energy has sharp minima when ξ_{a0}, $\xi_{b0} = \pm c/2\pi$, i.e., $c\xi_{a0}$, $c\xi_{b0} = \pm\beta U$. Then we can expand the general result for $\beta C(\xi_{a0}, \xi_{b0})$ to obtain in the static approximation

$$C(\xi_{a0}, \xi_{b0}) \cong -\frac{\Delta}{\pi z} + \frac{\beta c^2 \xi_{a0}\xi_{b0} T^2}{c(\xi_{a0} - \xi_{b0})}\left(\frac{\mathrm{sgn}\,\xi_{a0}}{c^2\xi_{a0}^2} - \frac{\mathrm{sgn}\,\xi_{b0}}{c^2\xi_{b0}^2}\right). \quad (4)$$

If $c\xi_{a0} = c\xi_{b0} = \beta U$, i.e., the two moments are $\uparrow\uparrow$,

$$C_{\uparrow\uparrow} \cong -\Delta/\pi z + 2T^2/U , \quad (5a)$$

and if $c\xi_{a0} = -c\xi_{b0} = \beta U$, i.e., the two moments are $\uparrow\downarrow$,

$$C_{\uparrow\downarrow} \cong -\Delta/\pi z + T^2/U . \quad (5b)$$

We see that the antiparallel arrangement is favored, being lower in energy than the parallel arrangement by T^2/U. In perturbation theory, however, one finds the energy difference to be $2T^2/U$. Our particular form of the functional-integral formulation of this problem puts $2U$ for U in the static approximation, and the techniques of Ref. 5 are needed to renormalize $2U$ back to U. So this is the expected static approximation result, and higher approximations should make a quantitative, but not qualitative, difference. Doing RPA′, for example, one obtains a result which favors antiparallel alignment more strongly than static approximation, as expected from the perturbation-theory result. This system is more like an Ising model than a Heisenberg model because the energy is a function of total S_z rather than total S. To go over to a Heisenberg model in this formalism one needs to include high-frequency parts of $\xi_a(\tau)$ and $\xi_b(\tau)$ with $\xi_a(\tau)$ and $\xi_b(\tau)$ phase coupled to give the proper mixing of $\uparrow\uparrow$ and $\downarrow\downarrow$ into triplet and singlet $S_z = 0$ states. An alternative possibility is to use a vector random field as mentioned in Ref. 2. Other difficulties then arise, however.

Again in case (i) if $U/\Delta \ll 1$, the effective free energy has a minimum for ξ_{a0}, ξ_{b0} near zero. Then the static approximation gives

$$C(\xi_{a0}, \xi_{b0}) \cong 4U\xi_{a0}\xi_{b0}/3z\beta\Delta . \quad (6)$$

This again favors antiparallel alignment of the extremely fuzzy moments distinguishable in this limit. The RPA′ calculation gives a factor favoring the parallel configuration which is of comparable order but smaller in magnitude.

In case (ii) with $U/\Delta \gg 1$, we obtain for the coupling energy in the static approximation near $c\xi_{a0}$, $c\xi_{b0} = \pm\beta U$,

$$C(\xi_{a0}, \xi_{b0}) \cong \frac{4}{N^2}\sum_{\vec{k},\vec{k}'} \frac{e^{i(\vec{k}-\vec{k}')\cdot\vec{R}_{ab}}}{\epsilon_{\vec{k}'} - \epsilon_{\vec{k}}}\left[-f_{\vec{k}}\Delta^2\left(1 - \frac{\Delta^2}{\eta^2}\right)\right.$$
$$+ f_{\vec{k}}\epsilon_{\vec{k}}^2\left(1 - \frac{6\Delta^2}{\eta^2}\right) + f_{\vec{k}}\frac{\epsilon_{\vec{k}}^4}{\eta^2}$$
$$\left. - 2\frac{\Delta}{\pi}\epsilon_{\vec{k}}\left(1 - 2\frac{\Delta^2}{\eta^2} + 2\frac{\epsilon_{\vec{k}}^2}{\eta^2}\right)\ln|\beta\epsilon_{\vec{k}}|\right], \quad (7a)$$

with

$$\frac{1}{\beta^2\eta^2} \equiv \frac{1}{c^2\xi_{a0}^2} + \frac{1}{c^2\xi_{a0}\xi_{b0}} + \frac{1}{c^2\xi_{b0}^2} , \quad (7b)$$

and $f_{\vec{k}}$ is the Fermi distribution function for $\epsilon_{\vec{k}}$. If $c\xi_{a0} = c\xi_{b0} = \beta U$, then $\eta^2 = \frac{1}{3}U^2$, and if $c\xi_{a0} = -c\xi_{b0} = \beta U$, then $\eta^2 = U^2$.

The first term in the brackets of (7a) is a part independent of relative spin orientation plus the Ruderman-Kittel-Kasuya-Yosida[6] (RKKY) coupling term with exchange integral, J, given by $2\Delta^2/U \sim T^2/U$. In the Schrieffer-Wolff transformation[7] J is given by $8T^2/U$ when $\epsilon_d = -\frac{1}{2}U$; however, the proportionality constant between J and T^2/U here depends on the relation between the bandwidth of our effective Lorentzian band Δ and the hopping integral T. One should do a calculation which is consistent in the sense of using the tight-binding band throughout the calculation in order to get the correct J to compare to the Schrieffer-Wolff transformation.

The next two terms in brackets in (7a) give contributions to $C(\xi_{a0}, \xi_{b0})$ which fall off much faster with increasing separation distance than does the contribution from the first term if one considers energy bands proportional to k^2. In that case, the RKKY term goes as $1/R^3$ while the other terms go as $1/R^7$ or faster. One would, therefore, not expect these terms to be important except for very unusual energy bands.

The last term in brackets in (7a) contains $\ln|\beta\epsilon_{\vec{k}}|$ and so looks reminiscent of the Kondo effect, but appears in order J^2 rather than J^3 as one obtains in Kondo effect. As was mentioned previously,[1,2] the static approximation does not properly include the Kondo effect in the one-center problem. For essentially the same reasons as in the one-center problem, we do not expect the static approximation to treat $\ln T$ terms correctly, so this last term should be canceled off in a better solution of the problem.

When $U/\Delta \ll 1$ in case (ii), the coupling energy for ξ_{a0}, ξ_{b0} near zero in the static approximation is given by

$$C(\xi_{a0}, \xi_{b0}) \cong -\frac{8\pi U \xi_{a0}\xi_{b0}}{\beta N^2} \sum_{\vec{k}\vec{k}'} \frac{e^{i(\vec{k}-\vec{k}')\cdot\vec{R}_{ab}}}{\epsilon_{\vec{k}'} - \epsilon_{\vec{k}}} f_{\vec{k}}. \quad (8)$$

We expect the improved approximations for case (ii) to give quantitative corrections to the static approximation similar to those observed in case (i); however, an explicit calculation is possible only if we specify a consistent band structure since the $\vec{k}$ sums will appear in denominators of the RPA′ or higher approximation terms. At this stage specialization to a detailed energy band structure does not seem to be sufficiently enlightening to be worthwhile.

The regime $U/\Delta \sim 1$ demands more accurate treatment of $\xi_i(\tau)$ than has been done heretofore. We expect the static approximation to be qualitatively correct in this region (except for the Kondo-like term mentioned above), but further work is necessary to improve the calculations there.

We also expect the introduction of orbital degeneracy to produce a ferromagnetic ground state under proper conditions. Work is proceeding on these effects.

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