Hybridization in correlated bands studied with the Gutzwiller method: Application to fluctuating valence and heavy fermions

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A model with two hybridized orbitals per site, one of which is correlated and the other is not, is considered. A variational wave function of the Gutzwiller form is used to calculate the mass enhancement. Unlike models with one orbital per site, there is no metal-insulator transition in the model because the occupation in the correlated orbital deviates from unity as the correlation energy increases. The binding energy and the effective mass as a function of the correlation energy and the hybridization energy is calculated. The relationship of the wave function used to wave functions explicitly showing the Kondo effect is discussed.

INTRODUCTION

We consider the two-band Hamiltonian

$$H=\sum_{i,\sigma}\epsilon_a n_{i\sigma}+t_a(a_{i\sigma}^{\dagger}a_{i+1,\sigma}+\text{H.c.})+U\sum_{i,\sigma}n_{i\sigma}n_{i,-\sigma}+\sum_{i,\sigma}t_b(b_{i\sigma}^{\dagger}b_{i+1,\sigma}+\text{H.c.})+V\sum_{i,\sigma}a_{i\sigma}^{\dagger}b_{i\sigma}+\text{H.c.}\,, \quad (1)$$

where $n_{i\sigma}=a_{i\sigma}^{\dagger}a_{i\sigma}$. This model describes two nondegenerate orbitals a and b per atom with correlations in the a orbitals but none in the b orbitals. The two orbitals are hybridized on the same site; hybridization at different sites introduces no new features in our treatment. For $t_b \gg t_a$, U comparable or larger than t_b, and $V \ll t_b$, this is a bare-bones model for the rare-earth solids. By variation of ϵ_a, with respect to the chemical potential, one passes from the magnetic-metal regime to the fluctuating-valence regime and the heavy-fermion (fluctuating-moment) regime.[1] Very little is understood about the latter. The model described by (1) is also relevant to transition metals and compounds where the correlations in the d orbitals are much stronger than in the sp orbitals. The problem of hybridization in such situations is interesting. For very large U, there is in the model of Eq. (1), at most one a-type electron of a given spin at every site. Only b electrons of the same spin hybridize with it. Hybridization therefore depends on the spin configurations—basis functions with different spin configurations in a orbitals must be considered and hybridized with the b orbitals. The optimum linear combination of such configurations is the many-body ground state. One way of doing this is by an extension of the Gutzwiller variational method.[2] A brief account of this work has already been given.[3] Recently Rice and Ueda have reported work using the same approach.[4]

GUTZWILLER VARIATIONAL FUNCTION

As a generalization of the Gutzwiller wave function[2] to the case of two orbitals per site but with only one of them correlated, we consider a variational wave function constructed in the following manner:

$$\Phi_{G_a,\Gamma_a,G_b,\Gamma_b}=\prod_{G_a}a_{g\uparrow}^{\dagger}\prod_{\Gamma_a}a_{\gamma\downarrow}^{\dagger}\prod_{G_b}b_{g\uparrow}^{\dagger}\prod_{\Gamma_b}b_{\gamma\downarrow}^{\dagger}|0\rangle\,, \quad (2)$$

is a basis function in which $G_a=(g_1,\ldots,g_{m_a})$ and $\Gamma_a=(\gamma_1,\ldots,\gamma_{\mu_a})$ are a set of sites occupied by $\uparrow$ and $\downarrow$ spin electrons, respectively, in the a orbital; G_b and Γ_b are the same quantities for b orbitals. The variational wave function chosen is

$$\psi=\sum_{G_a,G_b,\Gamma_a,\Gamma_b}A(G_a,G_b,\Gamma_a,\Gamma_b)\Phi\,, \quad (3)$$

with

$$A(G_a,G_b,\Gamma_a,\Gamma_b)=\eta^{\nu}T_{G_a}T_{G_b}T_{\Gamma_a}T_{\Gamma_b}\,. \quad (4)$$

The T's are the determinants which give the projection from site and orbital occupation to band states, and are given in Gutzwiller's notation by

$$T_{G_a}=\left|L^{-1/2}e^{-k_a g_a}R(k)\begin{vmatrix}k_1\alpha & k_1\beta & \cdots & k_{m_a}\beta\\ g_1 a & g_1 b & \cdots & g_{m_a}b\end{vmatrix}\right|\,, \quad (5)$$

$R(k)$ is the 2×2 orthonormal matrix which transforms the orbital space (a,b) to the band space denoted by (α,β). For the uncorrelated problem $R(k)$ is specified by an angle $\theta_{\text{unco}}(k)$, given by

$$\theta_{\text{unco}}(k)=\tan^{-1}\{[\epsilon_\alpha(k)-\epsilon_a(k)]/V\}\,, \quad (6)$$

where $\epsilon_{\alpha,\beta}(k)$ are the two bands obtained from diagonalizing the Hamiltonian (1) with $U=0$,

$$\epsilon_{\alpha,\beta}(k)=\tfrac{1}{2}[\epsilon_a(k)+\epsilon_b(k)]\pm\tfrac{1}{2}\{[\epsilon_a(k)-\epsilon_b(k)]^2+4V^2\}^{1/2}\,, \quad (7)$$

and $\epsilon_{a,b}(k)$ are the nonhybridized and uncorrelated bands ($V=0$, $U=0$). For the correlated problem $R(k)$ may in general be determined variationally. Our choice is specified below.

In Eq. (4) ν is the number of sites with double occupation in the a orbial, and η is a variational parameter. The ground-state energy is given by

$$\langle H\rangle=\nu U+\textstyle\sum_k\epsilon_a(k)\langle C_{ka}^{\dagger}C_{ka}\rangle+\epsilon_b(k)\langle C_{kb}^{\dagger}C_{kb}\rangle+V\sum_k(\langle C_{ka}^{\dagger}C_{kb}\rangle+\langle C_{kb}^{\dagger}C_{ka}\rangle)\,. \quad (8)$$

The density matrices $\langle C_{ka}^{\dagger}C_{ka}\rangle$, $\langle C_{ka}^{\dagger}C_{kb}\rangle$, etc., are evaluated by use of Eq. (3).

They are given as

$$\langle C_{ka}^{\dagger} C_{ka} \rangle = \begin{cases} q_{aa} + (1-q_{aa}) m_a, & k < k_a \ , \\ q_{aa} \sin^2\theta(k) + (1-q_{aa}) m_a, & k_a < k < k_a \ , \\ (1-q_{aa}) m_a, & k_b < k < k_{ZB} \ , \end{cases} \quad (9a)$$

$$\langle C_{ka}^{\dagger} C_{kb} \rangle = \begin{cases} 0, & k < k_a \ , \\ q_{ab} |\tfrac{1}{2} \sin[2\theta(k)]|, & k_a < k < k_b \ , \\ 0, & k_b < k < k_{ZB} \ , \end{cases} \quad (9b)$$

$$\langle C_{kb}^{\dagger} C_{kb} \rangle = \begin{cases} 1, & k < k_a \ , \\ \cos^2[\theta(k)], & k_a < k < k_b \ , \\ 0, & k_b < k < k_{ZB} \ , \end{cases} \quad (9c)$$

where k_{ZB} is the zone-boundary wave vector. In Eq. (9b) m_a is the average occupation per site of the a orbital per spin for the nonmagnetic case. In (9a) and (9b), $\theta(k)$ specifies the orthonormal 2×2 matrix $R(k)$. q_{aa} is identical to Gutzwiller's q [his Eq. (B6)],

$$q_{aa} = \frac{(m_a - \nu)(L - m_a - \mu_a + \nu)}{m_a (L - m_a)} \left[1 + \frac{\mu_a - \nu}{L - m_a - \mu_a + \nu} \eta \right]^2 , \quad (10)$$

with the variational parameter η given as

$$\eta^2 = \frac{\nu (L - m_a - \mu_a + \nu)}{(m_a - \nu)(\mu_a - \nu)} \ . \quad (11)$$

For the case $V = 0$, the density matrix $\langle C_{ka}^{\dagger} C_{ka} \rangle$ of the correlated orbital has a discontinuity with magnitude q_{aa} at the Fermi wave vector k_a, while the density matrix $\langle C_{kb}^{\dagger} C_{kb} \rangle$ is the usual Fermi distribution with a discontinuity $q_{bb} = 1$ at k_b. Realizing that q_{aa} and q_{bb} are appropriate quasiparticle renormalization factors for the appropriate Green's functions, one may guess that

$$q_{ab} = (q_{aa} q_{bb})^{1/2} \ . \quad (12)$$

This has also been found combinatorially.

Equations (10)–(12) also specify how the Fermi-surface discontinuities and the effective hybridization energy depend on the average magnetization. In our calculation, however, only the nonmagnetic case $m_a = \mu_a$ is considered.

We determine $R(k)$ variationally in terms of a function $\theta(k)$ which is of the same form as $\theta_{unco}(k)$, but with $(\epsilon_a^0 - \epsilon_b^0)$ [where ϵ_a^0 and ϵ_b^0 are the centers of the bands $\epsilon_a(k), \epsilon_b(k)$ specified in Eq. (7)] replaced by a variational function $(\epsilon_a^0 - \epsilon_b^0)_v(k)$ and with V replaced by a variational function $V_v(k)$. As may be seen by inspecting Eqs. (9a)–(9c), this is of consequence only in the region $k_a < k < k_b$, where we take them to be constants which we determine variationally. $\theta(k)$ governs the distortion of the quasiparticle bands as U/t_a increases and is a very important function. Beside these two quantities, ν and k_a/k_b are also determined variationally. For $U/t_a \gg 1$, the occupation of the correlated orbital is 0 or 1 and $\nu \approx 0$. k_a/k_b is found to be given essentially by its correlated value; we do not know any basic reason why this should be so. V_v is found to be simply $q^{1/2}V$ and $(\epsilon_a^0 - \epsilon_b^0)_v$ is such as to pin the effective correlated orbital to the chemical potential both in the fluctuating-valence and the fluctuating-moment (heavy-Fermi-liquid) regimes.

RESULTS—FLUCTUATING VALENCE

For simplicity, a one-dimensional model is chosen with $\epsilon_a(k) = \epsilon_a^0 + t_a(k - 0.5)$, $\epsilon_b(k) = t_b(k - 0.5)$, and $0 < k < 1$. We assumed the case of half-filled bands; i.e., $m_a + m_b = 1$. This leads to $k_a + k_b = 1$. As a consequence, the Fermi energy is always pinned in the range of the correlated band. In addition, we studied only the case $\epsilon_a^0 = 0$. In the calculations we always put $t_b = 10$ and investigated various cases $t_a/t_b \ll 1$ and $V/t_b \ll 1$, with $0 \leq U < \infty$. The condition $4V^2 < t_a t_b$ leads to a metallic situation, while $4V^2 > t_a b_b$ results in a band gap. We could have averted the semiconducting situation for $t_a \approx 0$ by considering the total occupation $\neq 2$. No essential difference in the physics is involved.

In Fig. 1, the values of the renormalization parameter q_{aa} and of m_a, the charge per atom in the correlated orbital, are plotted as a function of U/t_a. In all cases, q_{aa} drops more or less rapidly and reaches saturation for $U \approx t_b$. A similar behavior is found for m_a. In the large-U limit, ν becomes very small and the results in Fig. 1 follow

$$q_{aa} \approx (1 - 2m_a)/(1 - m_a) \left[1 + 2 \left(\frac{\nu}{1 - 2m_a} \right)^{1/2} \right] \quad (13)$$

very well, as also seen from Eqs. (10) and (11). Only in the case $t_a \gg V$, q_{aa} shows its largest drop near $U \approx 8\langle \epsilon_a \rangle$, where a metal-insulator transition occurs in the one-band case.[5]

Figure 2 presents the binding energy and the effective-mass enhancement q_{aa}^{-1} as a function of V/t_a for an asymptotically large value of U. For insignificant V/t_a the energy

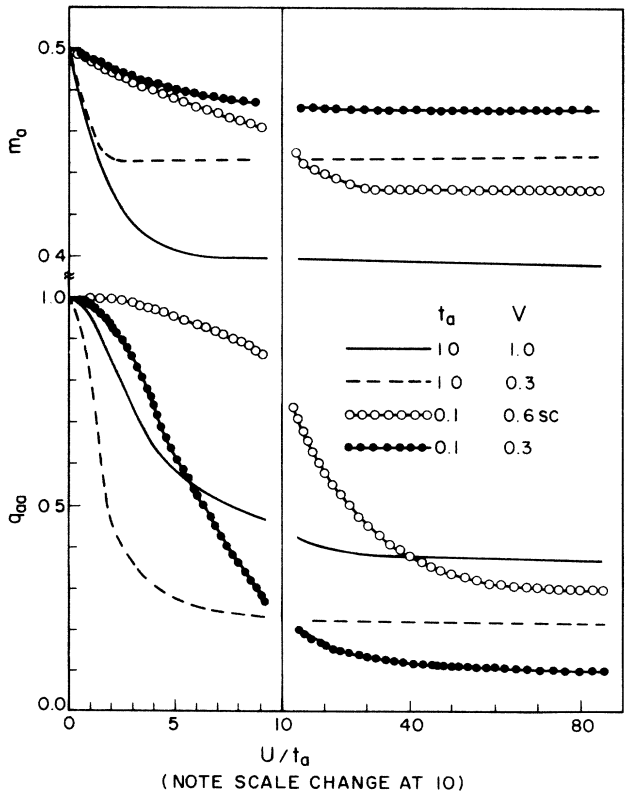

FIG. 1. The quasiparticle amplitude q_{aa} and the average occupation in the correlated orbital per spin m_a as a function of U/t_a, for various values of V/t_a.

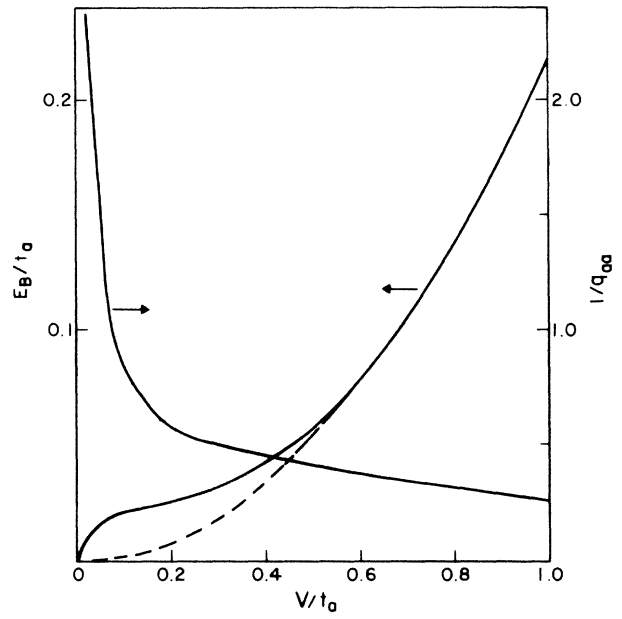

FIG. 2. The binding energy E_B in units of t_a and the effective-mass enhancement $\approx q_{aa}^{-1}$ as a function of V/t_a for an asymptotically large value of U/t_a.

increases quadratically as expected for this model and the effective mass has a weak dependence. The model has a phase transition at $V=0^+$; for $V=0$ the correlated orbitals are totally localized. This is reflected in the apparent non-analytic behavior of the energy as $V/t_a \to 0$, and the rapid growth in the effective mass.

Figure 3 contrasts the hybridization angle $\theta(k)$ in the $U=0$ and the $U \to \infty$ limit as well as presents various components of the density matrix. For large U, charge is transferred from the correlated to the uncorrelated orbital paying a prize in kinetic energy. Compared to the case in which $\theta_{\text{unco}}(k)$ is used, there is extra transfer at small k and smaller transfer at large k. Note that $\langle C_{ka}^{\dagger} C_{ka} \rangle$ has discontinuities both at k_a and k_b, but is otherwise nearly flat reflecting the almost localized state of electrons in this orbital. Note also the sharp decreases in the effective hybridization-induced density matrix $\langle C_{ka}^{\dagger} C_{ka} \rangle$ from its value for $U=0$.

There is an enhancement of the effective mass by a factor $1/q$ in this model just as in the one-band model.[5] This may also be seen easily through Eq. (8) which for $U \to \infty$ ($\nu U = 0$) *describes* the energy of two noninteracting bands hybridized with a matrix element $q^{1/2}V$. This is qualitatively similar to the naive Hubbard-type decoupling schemes[6] which renormalize the hybridization matrix element by $(1-2m_a)^{1/2}$ for $m_a = \mu_a$. The physics is trivial: Hybridization conserves spin and therefore in a mean-field approximation is reduced by the average occupation of the *other* spin.

HEAVY-FERMION (FLUCTUATING-MOMENT) REGIME

In this regime,

$$(\epsilon_b^0 - \epsilon_a^0) > V^2/t_b \ , \tag{14}$$

but this difference must also be bounded on the other side.

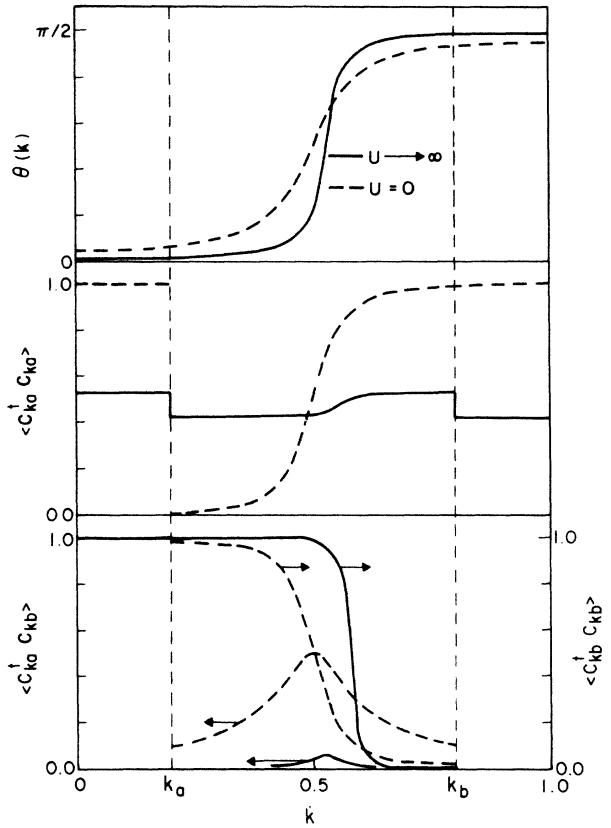

FIG. 3. The correlated hybridization angle $\theta(k)$ at asymptotically large values of U/t_a compared with that at $U=0$. Also shown are the strongly correlated limit and the uncorrelated limit of the various density matrices. All the results are for $V/t_a = 0.3$.

Otherwise the situation found in ordinary rare-earth metals and compounds results, with well-defined local magnetic moments and magnetic order at low temperatures. The only modificationn from the calculations described above are that $k_a = k_{ZB}$, so that there is only one Fermi vector, k_b. An average occupation of 2 per site leads to a semiconducting situation (except for the magnetic case discussed below). We did our calculations with an occupation of 2.5 per site.

The study of the density matrices, Fig. 4, as the parameters in (13) as well as U are varied is very revealing. As U is increased $\langle C_{ka}^{\dagger} C_{ka} \rangle$ decreases and $\langle C_{kb}^{\dagger} C_{kb} \rangle$ increases but with the discontinuity in occupation in both still at k_b (Luttinger's theorem). The sharpness with which $\theta(k)$ goes from near 0 to near 1 increases with U reflecting the effective decrease in hybridization $q^{1/2}V$. The additional charge in the b orbitals is accommodated above k_F with its shape governed by $\theta(k)$.

Figure 4 was calculated with $t_b = 10$, $V=1$, and $\epsilon_b^0 - \epsilon_a^0 = 1$. When we increased $\epsilon_b^0 - \epsilon_a^0$ to 2 with the other parameters held fixed, we found that for $U \gtrsim 8$, minimum energy obtains with $\langle C_{ka}^{\dagger} C_{ka} \rangle = \frac{1}{2}$ independent of k. There is now exactly one electron/atom in the correlated orbital. Therefore $q=0$. $\langle C_{kb}^{\dagger} C_{kb} \rangle$ now has a discontinuity at a new Fermi wave vector (which is nearly the point in Fig. 4 where the sharp but continuous dropoff occurs); it is 1 below and 0 above this point. Clearly a phase transition to the local-moment regime from the fluctuating-moment regime has occurred. Rice and Ueda[4] have investigated this

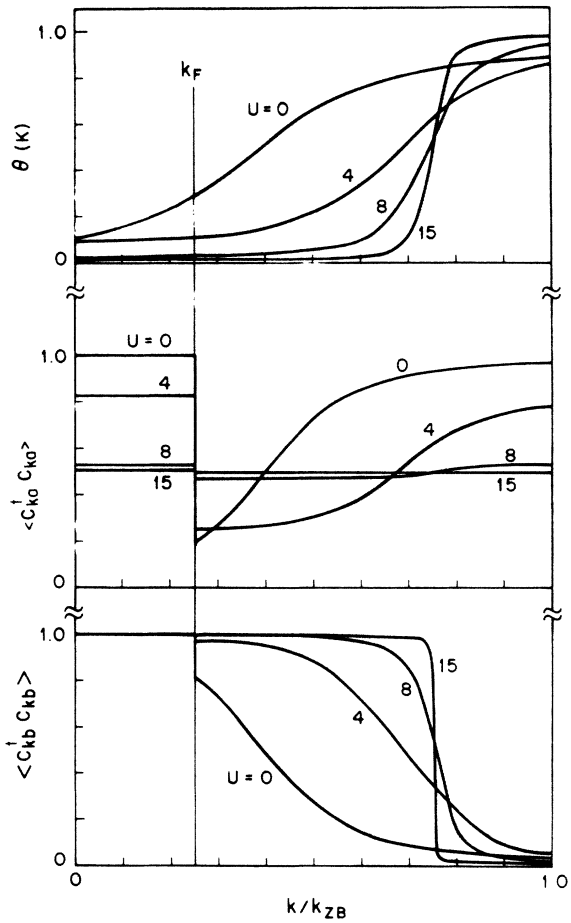

FIG. 4. Same as Fig. 3 for the heavy Fermion-liquid regime. The parameters used are $\epsilon_b^0 - \epsilon_a^0 = 1$, $t_b = 10$, $V = 1$. Note that in $\langle C^\dagger_{kb} C_{kb} \rangle$ all the curves shown have a discontinuity at k_F.

transition including orbital degeneracy N, which has only the effect of changing V^2 to NV^2 and $1-2m_a$ in Eq. (13) to $1-Nm_a$. They claim that the fluctuating-moment (heavy-fermion) regime occurs only at large N. We believe this not to be true. It is true though that the fluctuating moment regime occurs over a *larger* range of $(\epsilon_b^0 - \epsilon_a^0)$ *larger* the product NV^2.

From Eq. (8), one can again deduce that the effective mass in the heavy Fermi-liquid regime, for $\nu U = 0$, is proportional to $(qV^2)^{-1}$ for small t_a. q is again given by (13) and depends on the deviation of the occupation of the correlated orbital from unity. One can similarly deduce that the compressibility, $d\mu/dN$ or d^2E/dN^2, remains at the value specified by the light band, i.e., remains unrenormalized. This is unlike the one-component Fermi liquid and in accord with deductions made earlier.[6] This in turn means that the effective-mass enhancement is given by $(1+F_0^S)$ and not $(1+\frac{1}{3}F_1^S)$ where F_l^S is the lth partial wave of the spin-symmetric Landau parameter.

DISCUSSION

Several interesting things learned in the calculation have already been discussed. The question to ask is how well does the variational wave function describe the fluctuating valence or the Kondo-lattice situation. Only the single Kondo or fluctuating-valence impurity have been understood so far. The wave function (3) for only one site having an a orbital is the linear combination of $|\phi_{FS}\rangle$, the Fermi sea, with the a orbital unoccupied, $|\phi_{FS}\rangle$ with the a orbital singly occupied and $|\phi_{FS}\rangle$ with the a orbital doubly occupied. If we take U very large the last one has negligible weight. If we work with the total number of electrons constant the singlet part of the wave function then is

$$[\alpha_0 + \sum_{k,\sigma} \alpha(k) C^\dagger_{a\sigma} C_{k\sigma}] |\phi_{FS}\rangle \ , \tag{15}$$

where $|\phi_{FS}\rangle$ is the ground-state wave function of the free-electron Fermi sea. $\alpha(k)$ now serves the same purpose as $R(k)$. This is precisely of the form proposed by Varma and Yafet[7] for the ground state of a magnetic impurity in a metal, with $\alpha(k)$ as a variational function, and its generalization to the orbitally degenerate case is asymptotically exact for large degeneracy.[8] The one-site version of Eq. (3) contains together with (15) linear admixtures with doublet and triplet wave functions as well.

As mentioned earlier Eq. (15) describes well the ground state of a Kondo or fluctuating-valence impurity (especially when generalized for large orbital degeneracy). The low-temperature properties of that problem require consideration of the phase shift of the conduction electrons[9] by virtual fluctuation between the singlet ground state and the magnetic excited states. This effect is included in the single-site version of Eq. (3) through admixtures discussed in the last paragraph.

Stevens,[10] Brandow,[11] and Fazekas[12] have proposed generalizations of (15) to the lattice of the form,

$$\prod [\alpha_0 + \sum_{i,\sigma} \alpha(k) e^{i\mathbf{k}\cdot\mathbf{R}_i} C^\dagger_{ia\sigma} C_{k\sigma}] |\phi_{FS}\rangle \ . \tag{16}$$

An expansion of the product and comparison with Eq. (3) is instructive:

$$\Phi \sim [1 + \sum_{i,\sigma} \alpha(k) e^{i\mathbf{k}\cdot\mathbf{R}_i} C^\dagger_{ia\sigma} C_{k\sigma} + \sum_{\substack{i,j,(i<j) \\ \sigma,\sigma'}} \beta(k,k') e^{i(\mathbf{k}\cdot\mathbf{R}_i + \mathbf{k}\cdot\mathbf{R}_j)} C^\dagger_{ia\sigma} C^\dagger_{ja\sigma'} C_{k\sigma} C_{k'\sigma} + \cdots] |\phi_{FS}\rangle \ . \tag{17}$$

The second term is more general than merely an expansion of (16), by which $\beta(k,k')$ would have been equal to $\alpha(k)\alpha(k')$. With the first two terms alone Eq. (17) is a generalization of the wave function used to consider[13] the interaction between two impurities. Such a wave function describes the single "impurity" renormalization as well as the pairwise interference between different "impurities." To leading approximation in the well-defined local-moment limit this interference is merely the Ruderman-Kittle-Kasuya-Yosida coupling. The Gutzwiller-type wave function, Eq. (3), as well as Eq. (16), has these effects built in but with special relationships between α's, β's, etc., so that the variational freedom to describe interaction effects is limited.

Some other limitations of this approach ought to be mentioned. As mentioned, the single-site version of Eq. (3) describes well the ground state of a Kondo or fluctuating-

valence impurity, and the quasiparticles described through it are also reasonable. There are limitations however in the approximations used in evaluating with Eq. (3) for the lattice problem. The Gutzwiller method is a mean field method and each site is considered to be in the average configuration. This can lead to serious flaws in the relative admixture of different configurations at a site and in the effective interaction between sites. Also this approach does not contain the many-body effects in the interaction among pairs of sites. The latter have been found recently[14] to have in perturbation theory as interesting singularities as in the Kondo problem but with different energy scale. They should lead to important renormalizations in the low-temperature properties. What the Gutzwiller approach does contain is a good single-site mean-field approximation consistent with the Luttinger theorem.

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[1]See, for example, C. M. Varma, Rev. Mod. Phys. **48**, 219 (1976); Comments Solid State Phys. **11**, 221 (1985).

[2]M. C. Gutzwiller, Phys. Rev. **137**, A1726 (1965).

[3]C. M. Varma, in *Moments Formation in Solids,* edited by W. J. L. Buyers (Plenum, New York, 1984).

[4]T. M. Rice and K Ueda, in *Proceedings of the Taniguchi Symposium, Japan, 1985* (Springer-Verlag, Berlin, in press).

[5]W. F. Brikman and T. M. Rice, Phys. Rev. B **2**, 4302 (1970).

[6]C. M. Varma, J. App. Phys. **57**, 3064 (1985); also in *Proceedings of the Taniguchi Symposium, Japan, 1985* (Springer-Verlag, Berlin, in press).

[7]C. M. Varma and Y. Yafet, Phys. Rev. B **13**, 295 (1975).

[8]O. Gunnarson and K. Schönhammer, Phys. Rev. Lett. **50**, 604 (1983).

[9]K. Wilson, Rev. Mod. Phys. **47**, 773 (1975); P. Nozières, J. Low Temp. Phys. **17**, 31 (1974).

[10]K. W. H. Stevens, J. Phys. C **11**, 985 (1976).

[11]B. H. Brandow, Int. J. Quantum Chem. Symp. **13**, 423 (1978).

[12]P. Fazekas, in *Valence Instabilities,* edited by P. Wachter and H. Boppart (North-Holland, Amsterdam 1982), and in Koln Conference Proceedings, edited by D. Wohleben (unpublished).

[13]C. M. Varma and M. Schlüter, in *Valence Fluctuations in Solids,* edited by L. Falicov, W. Hanke, and M. Maple (North-Holland, Amsterdam, 1981).

[14]E. Abrahams and C. M. Varma (unpublished), and C. M. Varma, in Ref. 4.