Effective Magnetic Moments of Heavy Fermions and the Wilson Ratio for Kondo Lattices

Z. Zou and P. W. Anderson

Joseph Henry Laboratories of Physics, Princeton University, Princeton, New Jersey 08544

(Received 12 May 1986)

The formation of heavy-fermion bands is discussed on the basis of the relativistic Korringa-Kohn-Rostoker equation. It is shown that only one specific linear combination of six local f states can hybridize with a conduction state of given **k** and spin. It follows that the magnetic moments of the heavy fermions are sharply quenched. The Wilson ratios calculated from these effective magnetic moments fit experimental data much better than without this correction.

PACS numbers: 75.20.En, 75.20.Hr

It has been commonly accepted[1] that some of the heavy-fermion compounds can be described as "Kondo lattices." In these compounds the magnetism of the f-shell ion is quenched by the Kondo effect, leaving behind a heavy Fermi liquid, and therefore a kind of Landau Fermi-liquid theory is applicable. Among these compounds, $CeCu_2Si_2$, UBe_{13}, and UPt_3 undergo exotic superconducting transitions between 0.1 and 1 K. In earlier papers Anderson and others[1,2] have pointed out the analogy between liquid ^{3}He and the heavy-fermion systems, i.e., that the heavy-fermion systems can be viewed as almost-localized Fermi liquids (Brinkman-Rice theory[3]). In this theory the enhancement of spin susceptibility and that of electronic specific heat at low temperature are related by

$$\frac{\chi}{\chi_0}=\frac{m^*}{m}\frac{1}{1+F_0^a}, \tag{1}$$

where χ and m^* are dressed spin susceptibility and mass, respectively, and m and χ_0 are the corresponding bare quantities. F_0^a is the usual Landau Fermi-liquid parameter. The Fermi-liquid theories for heavy fermions all agree in the weakness of the charge fluctuations and the importance of the spin fluctuations. The basic point is that the Stoner factor in (1) takes on a constant value in the localized spin-fluctuation theory. To distinguish the enhancement of χ due to spin fluctuations from that due to mass enhancement, the so-called Wilson ratio

$$R=\lim_{T\to 0}\frac{\chi/\chi_0}{m^*/m}=\frac{1}{1+F_0^a} \tag{2}$$

turns out to be quite useful. For an isolated Kondo atom $R=2$ while for the Brinkman-Rice-Gutzwiller liquid $R=4$. The enhancement factors for both the Kondo atom and the Gutzwiller liquid are due to a very similar mechanism: Namely, the local spin fluctuations are enhanced relative to the noninteracting Fermi liquid.

Anderson[2] has suggested that the most likely source of the attractive interaction responsible for the exotic superconductivity in the heavy-fermion superconductors is the electron-electron interaction due to the local spin fluctuations which determines the Stoner enhancement. However, one problem remains unsolved in this spin-fluctuation picture, i.e., the discrepancy between the predicted Wilson ratio and the experimentally measured one. Various authors[1] in the Fermi-liquid theory have different approaches to the spin fluctuation and give different R. But all values obtained from the spin-fluctuation models exceed unity ($R>1$). On the other hand, if the bare magnetic moments of the U ion or Ce ion are used in χ_0, the measured Wilson ratios range from 0.17 to 0.66.[4] The discrepancy is too big to ignore. Some authors[5] have taken this discrepancy as evidence that the spin-fluctuation theory does not apply to the low-temperature properties for heavy fermions, at least for $CeCu_2Si_2$. To reconcile this discrepancy, Brown, Bedell, and Quader[6] argued that the magnetic moments of the f electrons can be lowered by hybridization as well as by the exchange Coulomb interaction. But they ignored the effect of hybridization on the magnetic moments of the Bloch electrons. Thus, their mechanism is quite different from the one proposed here. Theirs is essentially a two-band model, which, we have argued elsewhere,[7] is a fundamentally incorrect picture. The present work is intended to settle the important issue of the Wilson ratios.

We start from the Nozières[8] Fermi-liquid description for the single Kondo-impurity problem and treat the Kondo-lattice problem within the Korringa-Kohn-Rostoker (KKR) scheme. On the basis of a relativistic KKR equation which takes spin-orbit coupling into account, the hybridized heavy fermion bands are derived and the quasiparticle wave functions are obtained. It is found that only one specific linear combination of localized f states can hybridize with a conduction state for a given **k** and spin, and the quasiparticle band remains twofold degenerate as is required by the Kramers theorem. We will also work out the magnetic moment (i.e., g factor) of the quasiparticle as a function of $\hat{k}$. By averaging over the Fermi surface we will explicitly show how the magnetic moments of the heavy fermions are severely quenched. The modified Wilson ratio using the effective magnetic moment is

compared with experimental data, and fairly good agreement is achieved. It is important to recognize that theories based on the Nozières picture are one-band theories, in which one should think of the heavy electrons as renormalized free electrons, not f electrons. This point is obscured in Ref. 1.

Suppose we have solved the single Kondo-impurity problem in the sense of the Nozières Fermi-liquid picture: Well below T_K the impurity spin is frozen into a singlet. The effect of the spin on the conduction-electron state is characterized by phase shifts $\delta_\sigma(\epsilon)$. Because of virtual hopping to and from the impurity site, an indirect local interaction between quasiparticles appears (reminiscent of the local spin-fluctuation theory). Nozières[8] shows that near the Fermi surface, the phase shift for a spin-$\frac{1}{2}$ impurity can be written as

$$\delta_\sigma(\epsilon)=\tfrac{1}{2}\pi+\alpha(\epsilon-\epsilon_F)+\sigma m\phi^a, \tag{3}$$

where $\alpha=1/T_K$. (We will make the obvious generalization to larger J shortly.) The last term is the "molecular field" term due to the local spin fluctuations. We can ignore it when we concentrate on the single-particle properties such as the formation of the quasiparticle bands. It is responsible for the deviation of the Wilson ratio from 1 in the simple theories. Now we simply take over what is known about the impurity problem and put impurities together into a lattice. The electrons can then coherently scatter off of the periodic impurity array and form coherent Bloch states. Since the impurity atoms are far apart from each other, we expect that a "muffin-tin" approximation is fairly accurate. The simplest picture one can imagine is that the scattering potential at each impurity site is nonzero only within a muffin-tin radius ρ, which is taken much smaller than the lattice spacing, and that the electrons propagate freely outside the muffin-tin sphere. The phase shift $\delta(\epsilon)$ contains all the information about the potential scattering on the f-shell atoms. This simple picture enables us to do a formal band calculation using the KKR method. This approach is well known for transition metals, and was used by Razafimandimby, Fulde, and Keller[9] to treat the Kondo-lattice problem. They ignored the spin-orbit coupling, however, which is very important for heavy fermions. We think in terms of $CeCu_2Si_2$ or UBe_{13} where the pseudopotentials of the majority of the atoms are very weak and only the f-shell atom makes the compound differ severely from a nearly free-electron metal.

Under the muffin-tin approximation, the reciprocal lattice representation of the KKR equation is the most convenient for our purpose. This version of the KKR equation was first developed by Ziman[10] for nonrelativistic band calculations. We generalize it to the fully relativistic situation. The resulting equation is

$$\det\left\|\left(\epsilon-\frac{k_n^2}{2m}\right)\delta_{nn'}\delta_{ss'}+\sum_K\frac{B_K(ns)B_K(n's')}{2m\kappa\cot(\eta_K)}\right\|=0, \tag{4}$$

where $\mathbf{k}_n=\mathbf{k}+\mathbf{G}_n$, the $\mathbf{G}_n$ being reciprocal lattice vectors,

$$B_K(ns)=\sum_L\langle lm\tfrac{1}{2}s|\tfrac{5}{2}M\rangle\frac{4\pi}{\sqrt{\Omega}}\frac{j_l(k_n\rho)}{j_l(\kappa\rho)}Y_{lm}^*(\mathbf{k}_n), \tag{5}$$

η_K is the modified phase shift given by $\cot\eta_K=\cot\delta_K-n_l(\kappa\rho)/j_l(\kappa\rho)$, $\kappa=\sqrt{\epsilon}$, and ϵ is the energy measured from muffin-tin zero. $\langle lm\frac{1}{2}s|\frac{5}{2}M\rangle$ is the Clebsch-Gordan coefficient for spin-orbit–coupled states $J=\frac{5}{2}$, $L=(l,m)$, $K=(l,M)$. As discussed above, the phase shift $\delta_3(\epsilon)$ behaves like $\cot\delta_3=(\epsilon_F-\epsilon)/\Gamma$, $\Gamma=T_K$. The modified phase shift η_K is not quite the same as δ_K, but we assume that it behaves somewhat similarly to δ_3 with a displaced resonance position $\epsilon_0=\epsilon_F=\Gamma n_3(\kappa\rho)/j_3(\kappa\rho)$: $\cot\eta_K=(\epsilon_0-\epsilon)/\Gamma$. Other partial waves are expected to be nonresonant, i.e., to have a very weak pseudopotential which we have set equal to zero. Substituting the modified phase shift into the pseudopotential term in (4), we get

$$\det\left\|\left(\frac{k_n^2}{2m}-\epsilon\right)\delta_{nn'}\delta_{ss'}-\sum_M\frac{V_{ns}^*(M)V_{n's'}(M)}{\epsilon_0-\epsilon}\right\|=0 \tag{6}$$

with $V_{ns}(M)=(\Gamma/2m\kappa)^{1/2}B_{3M,ns}$, $M=\frac{5}{2},\ldots,-\frac{5}{2}$. The pseudopotential term in (6) is highly energy dependent near ϵ_0. Following Heine,[11] we can transform Eq. (6) into a hybridization model:

$$\det\begin{vmatrix} k^2/2m-\epsilon & 0 & \boldsymbol{\alpha} \\ 0 & k^2/2m-\epsilon & \boldsymbol{\beta} \\ \boldsymbol{\alpha}^\dagger & \boldsymbol{\beta}^\dagger & \mathbf{1}(\epsilon_0-\epsilon)\end{vmatrix}=0, \tag{7}$$

where

$$\begin{aligned}\boldsymbol{\alpha}\equiv\mathbf{V}_\uparrow(M)&=-\alpha_0[(\tfrac{1}{7})^{1/2}Y_{32}(\mathbf{k}),(\tfrac{2}{7})^{1/2}Y_{31}(\mathbf{k}),\ldots,(\tfrac{6}{7})^{1/2}Y_{3-3}(\mathbf{k})],\\ \boldsymbol{\beta}\equiv\mathbf{V}_\downarrow(M)&=\alpha_0[(\tfrac{6}{7})^{1/2}Y_{33}(\mathbf{k}),(\tfrac{5}{7})^{1/2}Y_{32}(\mathbf{k}),\ldots,(\tfrac{1}{7})^{1/2}Y_{3-2}(\mathbf{k})],\end{aligned} \tag{8}$$

and $\mathbf{1}$ is a 6×6 unit matrix.

In (7) we have decoupled the $n=0$ plane wave from the higher plane waves at the expense of renormalizing the mixing matrix elements $\boldsymbol{\alpha}$, $\boldsymbol{\beta}$ as well as the local resonance.[11] However, the corrections to $\boldsymbol{\alpha}$, $\boldsymbol{\beta}$, and the local resonance are of order V^2, which is very small in the weak hybridization limit. Thus we can keep only the terms linear

in V in the secular equation (7). One can easily show that $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$ satisfy the symmetry relations

$$\boldsymbol{\alpha}\cdot\boldsymbol{\beta}^*=0$$

and

$$|\boldsymbol{\alpha}|^2=|\boldsymbol{\beta}|^2=\frac{3}{4\pi}\alpha_0^2, \tag{9}$$

where α_0 is proportional to $\sqrt{T_K}$. With the help of (9), Eq. (7) is readily diagonalized, giving rise to a set of hybridized quasiparticle bands. In general, we would get complicated bands because of the energy dependence of α_0. Fortunately, we are only interested in the band structure near the Fermi surface. So we are allowed to ignore the energy dependence of α_0 in determining the quasiparticle wave functions and we obtain the following hybridized bands:

$$\epsilon_{\pm}(\mathbf{k})=\tfrac{1}{2}\{\epsilon_k+\epsilon_0\pm[(\epsilon_0-\epsilon_k)^2+4\alpha^2]^{1/2}\}. \tag{10}$$

The result is the same as those derived by the Gutzwiller method or functional-integral method.[12] The point we want to make is that out of the six localized f states only one specific linear combination can mix with a conduction state at a given $\mathbf{k}$ and spin. To make it clear, we work out two degenerate wave functions corresponding to energy $\epsilon_-(\mathbf{k})$:

$$\psi_\mu^{(-)}=A\left[|\mathbf{k}\uparrow\rangle+\frac{1}{\epsilon_- -\epsilon_0}\sum_{M=5/2}^{M=-5/2}\alpha_M^*(\mathbf{k})|\tfrac{5}{2},M\rangle\right], \tag{11a}$$

$$\psi_\nu^{(-)}=A\left[|\mathbf{k}\downarrow\rangle+\frac{1}{\epsilon_- -\epsilon_0}\sum_{M=5/2}^{M=-5/2}\beta_M^*(\mathbf{k})|\tfrac{5}{2},M\rangle\right], \tag{11b}$$

where μ and ν are pseudospin indices. A is a normalization constant given by $A=[1+\alpha^2/(\epsilon_- -\epsilon_0)^2]^{-1/2}$. The degenerate wave functions $\psi_\mu^{(-)}$ and $\psi_\nu^{(-)}$ are obviously orthogonal to each other because of Eq. (9), as a consequence of the Kramers theorem. As a matter of a fact, we could have gotten the same result from the periodic Anderson model including spin-orbit coupling, in which the mixing matrix element is of the form, $V_{M\sigma}(\mathbf{k})\sim Y_{3M-\sigma}(\mathbf{k})\langle 3lM-\sigma,\tfrac{1}{2}\sigma|\tfrac{5}{2}M\rangle$. In the spirit of the Gutzwiller approach,[11] one can get rid of the large U term in the periodic Anderson model, which amounts to a renormalization of V and the local resonance energy. Upon replacing V and the local resonant energy by their renormalized values, one gets an effective Hamiltonian of the form

$$H_{\rm eff}=\sum_{\mathbf{k}\sigma}\epsilon(\mathbf{k})C_{\mathbf{k}\sigma}^\dagger C_{\mathbf{k}\sigma}+\epsilon_0\sum_{iM}f_{iM}^\dagger f_{iM}+\sum_{i\mathbf{k}M\sigma}[\tilde V_{M\sigma}(\mathbf{k})f_{iM}^\dagger C_{\mathbf{k}\sigma}+\text{H.c.}]. \tag{12}$$

Equation (12) is a single-particle Hamiltonian. Diagonalization of Eq. (12) yields the hybridized bands (10) and the wave functions (11a) and (11b).

Now we want to show the suppression of the magnetic moments of the heavy fermions using the wave functions (11a) and (11b). If we assume that we have a very weak magnetic field along the z axis which provides us with a quantization direction, the z component of the magnetic moment is then $\hat\mu_z=\hat l_z+2\hat S_z$. Let the diagonal parts of $\hat\mu_z$, within the bases (11a) and (11b), be μ_0 and $-\mu_0$, the off-diagonal pieces λ and λ^*. A straightforward calculation gives

$$\mu_0(\mathbf{k})=A^2\left[1+\frac{1}{(\epsilon_- -\epsilon_0)^2}\frac{6}{7}\sum_M|\alpha_M(\mathbf{k})|^2M\right], \tag{13a}$$

$$\lambda(\mathbf{k})=\frac{A^2}{(\epsilon_- -\epsilon_0)^2}\frac{6}{7}\sum_M\alpha_M(\mathbf{k})\beta_M^*(\mathbf{k})M. \tag{13b}$$

Actually one has to consider the Van Vleck–type terms in general and calculate the interband matrix elements. But in our case they are relatively negligible because of the small phase space or large energy denominators. The eigenvalues of $\hat\mu_z$, μ are easily obtained as functions of wave vector $\hat k$, $\mu(\mathbf{k})=\pm(\mu_0^2+|\lambda|^2)^{1/2}$. Although in our model the Fermi surface is isotropic, the magnetic moments of the quasiparticles on the Fermi surface have a strong anisotropy. In order to get an effective magnetic moment, one has to make an average over the Fermi surface. Let us calculate the Pauli spin susceptibility: $\chi=N^*(\epsilon_F)\mu_{\rm eff}^2$, where $N^*(\epsilon_F)$ is the renormalized heavy-fermion density of states, and $\mu_{\rm eff}$ is defined as the effective magnetic moment of the heavy fermions by

$$\mu_{\rm eff}^2=(4\pi)^{-1}\int d\Omega\,[\mu_0^2(\mathbf{k})+|\lambda(\mathbf{k})|^2]. \tag{14}$$

The calculation of the integral in Eq. (14) is lengthy but rather straightforward. The result[13] depends upon the parameter $x=\alpha_0^2/(\epsilon_- -\epsilon_0)^2$, which is to be determined. It turns out that x is approximately the enhancement of the density of states: $N^*(\epsilon_F)\approx N_0(\epsilon_F)\alpha^2/(\epsilon_- -\epsilon_0)^2$. For the compounds that we are discussing, $x>1000\gg 1$, the terms with x^2 in Eq. (14) dominate, and one has $\mu_{\rm eff}^2=1.16\mu_B^2$. The bare magnetic moment for the f^1 valence state is $\mu_0=2.54\mu_B$, and therefore $(\mu_{\rm eff}/\mu_0)^2=0.18$. This shows that the effective magnetic moments of the heavy fermions are severely quenched. The modified Wilson ratio is given by

$$R=\left(\frac{\mu_{\rm eff}}{\mu_0}\right)^2\frac{1}{1+F_0^a}=\frac{0.18}{1+F_0^a}. \tag{15}$$

Thus $1/(1+F_0^a)$, the interaction part of the Wilson ra-

tio, is

$$\frac{1}{1+F_0^a} = \frac{R}{(\mu_{\rm eff}/\mu_0)^2} = 5.56 R_{\rm obs} > 1. \quad (16)$$

In conclusion, we have discussed in this Letter the formation of heavy-fermion bands on the Kondo lattice based on the relativistic KKR equation. It is shown that, in the presence of spin-orbit coupling, only one selected linear combination of six local f states can hybridize with a conduction state of given $\mathbf{k}$ and spin. This is not a new or unexpected result in band theory but has been ignored in previous theories of this problem. One of the consequences following from this property is that the magnetic moments of the heavy-fermion quasiparticles are sharply reduced. As a consequence the observed susceptibility is much affected by Fermi-liquid interactions, implying a Wilson ratio >1 as expected. The fact that the moment comes out comparable to that of the f-electron spins in the Curie-law regime, while not unexpected, comes from the many-body interactions between the quasiparticles in the coherent regime near $T=0$, not from their intrinsic moments. We note also two other relevant consequences of our theory: (i) The form factor of the moment is almost purely f-like as observed, because $x \gg 1$, and (ii) the Fermi surface is almost free-electron-like, in spite of the large renormalization.

It is important to recognize that the model we use is oversimplified, specifically in not containing crystal-field splitting or realistic band structures for such substances as UPt_3. We believe that a large correction to R applies in all cases, but our calculations apply to the symmetric $J=\frac{5}{2}$ case only.

One of us (Z.Z.) wishes to thank Dr. G. Baskaran and Dr. A. Khurana for many useful discussions. This work was supported in part by the National Science Foundation, under Grant No. DMR 8020263.

[1]P. A. Lee, T. M. Rice, J. W. Serene, L. J. Sham, and J. W. Wilkins, Comments on Condens. Matter Phys. **12**, 99 (1986).

[2]P. W. Anderson, Phys. Rev. B **30**, 1549, 4000 (1984).

[3]P. W. Anderson and W. F. Brinkman, in *The Helium Liquids,* edited by J. G. M. Armitage and I. E. Farquhar (Academic, New York, 1975), pp. 315–416.

[4]G. R. Stewart, Rev. Mod. Phys. **56**, 755 (1984).

[5]W. Lieke, U. Rauchschwalbe, C. D. Bredl, F. Steglich, J. Arts, and F. R. deBoer, J. Appl. Phys. **53**, 2111 (1982).

[6]G. E. Brown, K. S. Bedell, and K. F. Quader, to be published.

[7]P. W. Anderson, in *Moment Formation in Solids,* edited by W. J. L. Buyers (Plenum, New York, 1984), pp. 313–326.

[8]P. Nozières, J. Low Temp. Phys. **17**, 31–42 (1974).

[9]H. Razafimandimby, P. Fulde, and J. Keller, Z. Phys. B **54**, 111–120 (1984).

[10]J. M. Ziman, Proc. Phys. Soc. **86**, 337 (1965).

[11]V. Heine, Phys. Rev. **153**, 673 (1967).

[12]T. M. Rice and K. Ueda, Phys. Rev. Lett. **55**, 995 (1985); N. Read, D. M. Newns, and S. Doniach, Phys. Rev. B **30**, 384 (1984).

[13]All numerical values of the Clebsch-Gordan coefficients are adopted from *Tables of the Clebsch-Gordan coefficients,* compiled by The Institute of Atomic Energy, Academia Sinica (Science Press, Peking, 1965).