Hund's Rule Theory for Heavy Fermion Superconductors

M. R. Norman

Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439

(Received 13 May 1993; revised manuscript received 20 July 1993)

In this paper, a multiorbital generalization of standard spin fluctuation theory is considered within an on-site approximation. For f electrons, this theory leads to an instability for a superconducting pair state which obeys Hund's rules, with $L=5$, $S=1$, and $J=4$. The degeneracy of this state is broken by crystalline effects, and realistic calculations for UPt_3 find a pair state with Γ_6^- (E_{2u}) symmetry, consistent with current experimental constraints.

PACS numbers: 74.20.Mn, 74.70.Tx

From the beginning of theoretical work on heavy fermion superconductors, it has been realized that there are strong connections between these metals and superfluid ^{3}He [1]. This has led many theorists to apply standard spin fluctuation theories which were developed for ^{3}He to the heavy fermion problem. So far, the results have been mixed. On the plus side, such theories give non-s-wave pairing states, and the evidence in most cases is that the heavy fermion superconductors are non-s-wave. On the minus side, the actual group representation these theories predict for UPt_3, the best studied of the heavy fermion superconductors, has so far not matched what the experimental data seem to indicate. Available data point to the pair state having Γ_6^- (E_{2u}) symmetry [2]. This state is an odd parity two-dimensional group representation with line and point nodes, and invariably is suppressed in the spin fluctuation calculations [3]. There are further qualitative problems with these theories. First, six of the seven known heavy fermion superconductors are uranium alloys. Second, all of the superconductors either have two formula units per cell [4], or have a magnetic-structural phase transition at a temperature above T_c so that there are two formula units per cell. Third, the magnetic susceptibilities of the two heavy fermion superconductors UPt_3 and UPd_2Al_3 look almost identical to that of $PrNi_5$, a localized f^2 system. Moreover, the magnetic susceptibility observed in URu_2Si_2 can be easily explained by an f^2 configuration [5]. The above facts suggest that some on-site interaction is playing a fundamental role in heavy fermion superconductivity, since such an interaction could (1) differentiate between Ce and U ions, (2) depend on having two formula units per cell due to having in phase or out of phase relations between the order parameters on the two sites [4], and (3) prefer an f^2 configuration. Standard antiferromagnetic spin fluctuation models, based as they are on having an attractive interaction between near neighbor sites, do not directly address these points.

An on-site model can be motivated by looking at the problem at the bare interaction level. The potential of two f electrons on a uranium site looks very similar to the bare interaction potential for ^{3}He. In particular, the potential is strongly repulsive at short distances due to the direct Coulomb interaction of the two f electrons, is attractive at intermediate distances (of order 3 a.u.) due to the Coulomb interaction of the f electrons with the uranium ion core, and decays to zero at large distances due to the exponential decay of the f electron wave function. The ground state of this potential is well known to have a symmetry of $^3H_4$ ($S=1$, $L=5$, $J=4$) as this state minimizes the Coulomb repulsion. This represents a qualitative difference from ^{3}He, since although a pair of ^{3}He atoms has $S=1$ also, there is no orbital dependence on the bare interaction and L is determined by the Landau parameters which are difficult to calculate. In the f^2 case, though, the orbital dependence of the interaction fixes L, with J being fixed by the strong spin-orbit coupling.

To understand this problem further, we review the energy levels of an f^2 ion. These energies are best expressed in an LS coupling scheme. Every configuration has an energy E_0, equivalent to the Coulomb repulsion U (E_0 is equal to the $L=0$ Coulomb multipole integral F^0 plus a combination of F^2, F^4, and F^6 terms). The splitting between singlet and triplet spin states is determined by the energy E_1 (a combination of F^2, F^4, and F^6 terms), with the three triplets having a coefficient of 0 and three of the four singlets having a coefficient of 2 (the singlet $^1S_0$ is the highest energy state with a coefficient of 9). This is similar to the paramagnon model for ^{3}He where these coefficients are the same (0 for triplet, 2 for singlet), but with the important difference that the splitting in the f electron case is not determined by the F^0 (charge fluctuation) term as in the single orbital Hubbard model used for ^{3}He but by the $L>0$ (shape fluctuation) terms (in phenomenological paramagnon models [6] this interaction is denoted as I). Moreover, the degeneracy of the three triplets is lifted by an orbital splitting term, E_3, which is another combination of $L>0$ terms. The lowest energy state is ^3H with an energy E_0-9E_3 with the next highest state being ^{3}F with an energy E_0. The energy E_0 determines the normal state Fermi energy for uranium systems since two f electrons are occupied per site (the effect of E_3 cannot be represented at the single particle level and is assumed to not enter into determining the quasiparticle Fermi energy, although this assumption could be debated). Since superconductivity is an instability of the Fermi surface, E_0 is

the zero of energy, analogous to the ^{3}He problem, where the energy of the triplet is the zero of energy. Unlike the ^{3}He paramagnon problem, the ^3H state has an energy lower than the energy zero; i.e., the interaction is already attractive at the bare interaction level. This is only true for a uranium (f^2) ion; for a cerium ion, the zero of energy is set by the Fermi energy of the f^1 configuration, and thus the bare interaction includes E_0 (the energy of f^2 above f^1) and is repulsive for all f^2 states. Despite the bare attraction for the uranium case (which might be an artifact of the assumed energy zero), one would not necessarily expect this to give a proper description of the physics. Use of the direct interaction potential for ^{3}He gave an incorrect pair state ($L=2$) (at the bare level of the paramagnon model, no attraction at all). It was necessary in that case to derive an induced interaction by summing bubble and ladder diagrams to obtain the proper physics. This leads to the vertex equation

$$\Gamma^{abcd}=\Gamma_0^{abcd}-\Gamma_0^{aecf}\chi_0^{ef}\Gamma^{fbed}, \quad (1)$$

where Γ_0 is the antisymmetrized Coulomb interaction (linear combination of the E_i terms) and the indices label orbitals. For the purposes of this paper, the susceptibility bubble, χ_0^{ef}, is treated as a number, χ_0 [7]. Solving this equation for the s electron case leads to the standard paramagnon results [8]. The f electron case is more complicated due to the presence of four interaction parameters (E_0,E_1,E_2,E_3) and fourteen orbitals. If only the E_0 term is kept, the equation can be analytically solved. The result is $E_0/(1-E_0\chi_0)(1+13E_0\chi_0)+E_0^2\chi_0/(1-E_0\chi_0)$. This has some important implications, in that the effective repulsion is reduced compared to the bare E_0 as long as χ_0 is not too close to being equal to $1/E_0$ (the divergence for $\chi_0=1/E_0$ is a localization instability). If only the E_1 term is kept, the equation can also be solved. For the triplet states, one obtains $-11E_1^2\chi_0/(1-81E_1^2\chi_0^2)(1-4E_1^2\chi_0^2)+2E_1^2\chi_0/(1-4E_1^2\chi_0^2)$, which has similarities to the single orbital case in that there is an induced attraction for the triplet states. There is a divergence for $9E_1\chi_0=1$ (a magnetic instability equivalent to $I\chi_0=1$ in the simple paramagnon model). For the ^1I state, the induced interaction is $(4E_1+13E_1^2\chi_0-126E_1^3\chi_0^2-162E_1^4\chi_0^3)/(1-81E_1^2\chi_0^2)(1-4E_1^2\chi_0^2)-2E_1$, which is again similar to the single orbital case in that there is an enhanced repulsion for singlet states. An analytic expression for the general case has not been obtained due to the complicated orbital sums. Instead, one can reduce the vertex equation to a series of matrix equations which can be diagonalized on a computer. This has been done for the ^3H, ^3F, ^3P, and ^1I states [9].

The results are summarized in Fig. 1, where the various effective interactions are plotted versus χ_0. The values of E_i were obtained from Goldschmidt [10] (these values give an F^0 of 1.83 eV, consistent with spectroscopic data in heavy fermion uranium compounds). As one can see, the triplets become increasingly attractive and the singlet increasingly repulsive as χ_0 increases with a divergence for $(E_0+9E_1)\chi_0=1$. χ_0 is difficult to estimate since spin-orbit and anisotropy effects play a major role [7]. For illustrative purposes, we assume a "Stoner" renormalization of 4 as seen in ^{3}He. For this value of χ_0 (0.137), the ^3H energy is -2.3 eV relative to the f^2 zero of energy.

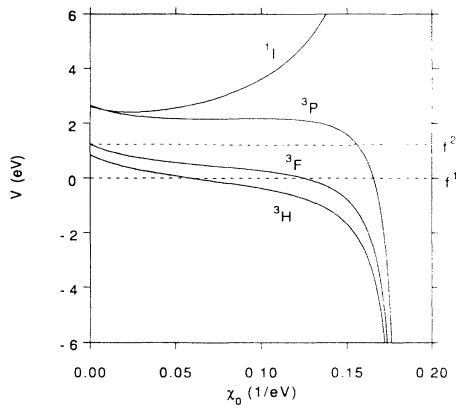

FIG. 1. Effective interaction (eV) for ^3H, ^3F, ^3P, and ^1I versus χ_0 for parameters appropriate to a U ion [10] ($E_0=1225$ meV, $E_1=470.3$ meV, $E_2=1.923$ meV, $E_3=43.28$ meV). The zeros of energy for the f^1 and f^2 cases are marked by the dashed lines.

One can estimate the effective pairing matrix element by realizing that the quasiparticle renormalization in the heavy fermion case is mostly frequency dependent in nature [11]. This would renormalize the induced interaction discussed above by a factor of Z^2 since each of the four external lines in the vertex is renormalized by $Z^{1/2}$ (only Z of the bare f electron is in the quasiparticle pole). Z^{-1} is equal to the mass renormalization factor, known from de Haas-van Alphen measurements to be about 16 in UPt_3 [12]. This renormalizes the ^3H matrix element of 2.3 eV to about 100 K. This value will be further reduced when projecting onto pair states at the Fermi energy which have the symmetry of a particular group representation. Below, this projection factor is shown to be about $\frac{1}{8}$, so the final value is 12.5 K. Since the renormalized (quasiparticle) Fermi energy, E_F, is about 60 K in UPt_3 (specific heat γ, neutron scattering linewidth), the pairing coupling constant, NV_4Z^2, is about 0.21 (where N is the renormalized density of states and V_4 is the interaction potential in the $^3H_4$ channel). With a cutoff of order E_F, this gives a BCS estimate for T_c of 0.6 K. The agreement with experiment is somewhat fortuitous, of course, but the point is that the effective coupling constant is at least of the right order of magnitude.

One might wonder why such a large interaction of order eV would not lead to a high T_c for more itinerant systems with Z closer to 1. The reason is that the effective interaction parameters used here are only appropriate for nearly localized f^2 systems. The E_i parameters have been extracted from fits to spectroscopy data on the

TABLE I. Hexagonal basis functions for $J=4$. The forms listed in this table should be (a) antisymmetrized ($|\mu\rangle|\nu\rangle - |\nu\rangle|\mu\rangle$) and (b) symmetrized (+ representation) or antisymmetrized (− representation) with respect to site before use. For Γ_5, α and β are variational coefficients such that the sum of their squares is equal to 1, and this representation occurs twice (α, β and β, $-\alpha$). Note that Γ_5 and Γ_6 are doublets obtained by replacing $|\mu\rangle$ by $|-\mu\rangle$.

Rep	Basis function
Γ_5	$\alpha\|\frac{5}{2}\rangle\|\frac{3}{2}\rangle+\beta(0.8018\|\frac{5}{2}\rangle\|-\frac{1}{2}\rangle+0.5976\|\frac{3}{2}\rangle\|\frac{1}{2}\rangle)$
Γ_3	$0.7071\|\frac{5}{2}\rangle\|\frac{1}{2}\rangle+0.7071\|-\frac{5}{2}\rangle\|-\frac{1}{2}\rangle$
Γ_4	$0.7071\|\frac{5}{2}\rangle\|\frac{1}{2}\rangle-0.7071\|-\frac{5}{2}\rangle\|-\frac{1}{2}\rangle$
Γ_6	$0.5345\|\frac{5}{2}\rangle\|-\frac{3}{2}\rangle+0.8452\|\frac{3}{2}\rangle\|-\frac{1}{2}\rangle$
Γ_1	$0.2673(\|\frac{5}{2}\rangle\|-\frac{5}{2}\rangle+3\|\frac{3}{2}\rangle\|-\frac{3}{2}\rangle+2\|\frac{1}{2}\rangle\|-\frac{1}{2}\rangle)$

uranium atom. On average, they are 62% of their Hartree-Fock values due to configuration interaction effects. In UPt_3, the excitation from the $^3H_4$ ground state to the $^3F_2$ state has been seen by high energy neutron scattering [13] and has an energy of 0.373 eV. This is 72% of the atomic value indicating a further reduction of the E_i due to solid state screening effects. In normal transition metals, these parameters are much more strongly screened and lead to a low estimate of T_c for triplet superconductivity in palladium [14]. As for cerium alloys, the interaction is repulsive at the bare interaction level due to the Coulomb repulsion (E_0) of f^2 relative to f^1 (the value of which is about 3 times larger than in uranium). At the induced interaction level, the instability happens at a smaller value of χ_0 due to the larger E_0 term, yet the large E_0 causes the interaction to remain repulsive until very close to the instability. It is well known that strong coupling effects act to turn off the superconductivity before the instability is reached since the energy scale of the paramagnon is going to zero [15]. For this reason, although pairing is possible in the cerium case, it is less likely.

The actual symmetry of the gap is found by constructing the quasiparticle pair state $|k,-k\rangle$ using relativistic band structure wave functions and projecting this onto $J=4$. The degeneracy of the $J=4$ state is broken due to lattice effects which should be well described by the momentum dependence of the band structure wave functions (although these wave functions fail to describe the frequency dependence of the quasiparticle states, they give a Fermi surface shape in good agreement with experimental data, indicating that their momentum dependence is reliable). For hexagonal UPt_3, the 18-fold degeneracy of $J=4$ in the isotropic case ($2J+1$ times the number of f sites in the unit cell, which is two) will be broken into three singlets (Γ_1, Γ_3, and Γ_4) and three doublets (two Γ_5, one Γ_6), with each occurring twice [+ (even parity) representations have the order parameter in phase on both sites, and − (odd) have it out of phase]. In Table I, these states are given in terms of pairs of single particle $j=\frac{5}{2}$ f states. The group transformation properties of these states are listed by Appel and Hertel [16].

For each k point, there are four degenerate states available to construct $|k,-k\rangle$ from [17]. The singlet (even parity) combination is $(|k,Tk\rangle-|PTk,Pk\rangle)/2$ (denoted d_0) and the triplet (odd parity) combinations are $|k,Pk\rangle$ $(-d_x+id_y)$, $|PTk,Tk\rangle$ (d_x+id_y), and $(|k,Tk\rangle+|PTk,Pk\rangle)/2$ (d_z), where P is the parity operator and T the time reversal one. The odd parity combinations define a "d" vector which lives in a pseudospin space.

The resulting pairing matrix element for this model is then

$$\langle k',-k'|H_{\text{eff}}|k,-k\rangle_P=(V_4Z^2)A_{k'}^{*\Gamma\nu j'}A_k^{\Gamma\nu j}, \tag{2}$$

where P represents the projection with $A_k^{\Gamma\nu j}$ being the coefficient of the expansion of $|k,-k\rangle$ which has $J=4$ with the symmetry of the group representation Γ and basis ν (for a two-dimensional representation), and j is the index of the d vector (0 for even, x,y,z for odd). Since the matrix element is separable in k and k', it is trivial to write down the appropriate BCS coupling constant

$$\lambda=NV_4Z^2\sum_j\langle|A_k^{\Gamma\nu j}|^2\rangle_k, \tag{3}$$

where N is the density of states, $\langle\,\rangle_k$ is an average over a narrow energy shell about the Fermi energy, and j runs over 0 for the even parity case and x,y,z for the odd parity case.

The $j=\frac{5}{2}$ part of the band structure wave functions can be written as $|k\rangle=\sum a_{\mu i}^{nk}|\mu\rangle_i$ where μ runs from $-\frac{5}{2}$ to $\frac{5}{2}$, i is the site index (1,2), and n is the band index (band calculations predict that five f bands contribute to the Fermi surface of UPt_3; such a surface is in good agreement with de Haas-van Alphen data [12]). Thus, the A coefficients can be written as $\sum a_{\mu i}^{nk}a_{\nu i}^{n-k}$ with k denoting either k or PTk and $-k$ denoting Pk or Tk, with the appropriate linear combinations being those which match the basis states in Table I and have the correct parity form (d_0 for even and d_x,d_y,d_z for odd). The average in Eq. (2) was done by constructing a regular grid of 561 k points in the irreducible wedge (1/24) of the Brillouin zone and keeping those nk states which are within 1 mRy of the Fermi energy (182 nk points for UPt_3).

In Table II, the results of this calculation are given. The odd parity states have larger coupling constants since there are three terms contributing instead of the one term for the even parity case. This is of interest since the odd parity states only exist because of the presence of two f atoms in the primitive cell, which, as mentioned in the introduction, all heavy fermion superconductors have. The largest coupling constant occurs for a state of Γ_6^- symmetry. This state is an odd parity two-dimensional group representation. It has point nodes along the c axis and a line of nodes in the $k_z=\pi/c$ zone face. It is interesting to note that although only the d_z component of the gap

TABLE II. Coupling constants for $J=4$ for UPt_3. These are normalized to the coupling constant for the $J=0$, Γ_1^+ state and should be multiplied by this quantity (0.495, which is the square of the ratio of the $j=\frac{5}{2}f$ to the total density of states) and the quantity NV_4Z^2 to convert to real coupling constants.

Rep	Even (+)	Odd (−)
Γ_5	0.139	0.148
Γ_5	0.059	0.203
Γ_3	0.048	0.129
Γ_4	0.027	0.242
Γ_6	0.036	0.253
Γ_1	0.153	0.229

function vanishes on the $k_z=0$ zone face as expected based on group theory arguments [18], all three d vector components vanish on the $k_z=\pi/c$ zone face, proving a counterexample to the argument in those papers that a line node gap function is not possible for odd parity states. Although the actual form of the gap function in the current case is extremely complicated since the $a_{\mu i}^{nk}$ are strong functions of momentum, this state (1) is from a two-dimensional group representation and can thus explain the unusual phase diagram seen for UPt_3, (2) has the correct nodal structure to explain various thermodynamic data of UPt_3, and (3) is an odd parity state with the largest possible moment projection onto the basal plane for a two-dimensional group representation ($M_J=\pm 1$), which is necessary to explain the observed directional anisotropy of the upper critical field [19]. It should be remarked, though, that the states Γ_1^- and Γ_4^- have coupling constants close to that of Γ_6^- and the ordering of the coupling constants will thus be sensitive to the cutoff of the energy shell used in the averaging in Eq. (2). The values tabulated in Table II should be multiplied by the quantity NV_4Z^2 to convert to an actual coupling constant, and, as discussed above, the resulting coupling constant for Γ_6^- is of the right order to explain the observed value of T_c. Similar calculations have also been done for $J=2$ (^3F) and $J=0$ (^3P). For $J=2$, the largest coupling constant also has Γ_6^- symmetry (its value modulo V_2 is 0.85 of the $J=4$ one). For $J=0$, the largest coupling constant has Γ_1^+ symmetry. Its value modulo V_0 is a factor of 4 larger than $J=4$, so it is reassuring to find a repulsive V_0 over a wide range of Fig. 1 (in the JJ coupling scheme, V_2 and V_0 are repulsive [9]).

In conclusion, an orbital degenerate generalization of the ^{3}He paramagnon model has been applied to f electrons and yields a superconducting pair state which satisfies Hund's rules ($L=5$, $S=1$, $J=4$). The degeneracy of this state is lifted by crystalline effects. Realistic calculations for the case of UPt_3 give a pair state with Γ_6^- symmetry which is consistent with experimental data with a reasonable estimate for T_c. The theory also explains the preference for heavy fermion superconductors to be uranium alloys, and also the role that the crystal structure (two formula units per unit cell) plays in the pairing.

This work was supported by U.S. Department of Energy, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38. The author would like to acknowledge the hospitality of the Physics Department, Uppsala University, where some of this work was completed, and to thank Kathyrn Levin for many helpful discussions.

[1] P. W. Anderson, Phys. Rev. B **30**, 1549 (1984).
[2] M. R. Norman, Physica (Amsterdam) **194C**, 203 (1992), and references therein.
[3] M. R. Norman, Phys. Rev. B **48**, 6315 (1993); **43**, 6121 (1991); **41**, 170 (1990).
[4] P. W. Anderson, Phys. Rev. B **32**, 499 (1985).
[5] G. J. Nieuwenhuys, Phys. Rev. B **35**, 5260 (1987).
[6] A simpler Hund's rule interaction has been proposed earlier for palladium metal, S. Doniach, Phys. Rev. Lett. **18**, 554 (1967).
[7] The philosophy of this paper is that, for heavy fermions, the momentum and orbital dependence of the bubble are not critical for the physics, and is ignored at this stage (consistent with fits to neutron scattering data). Orbital dependence of the bubble will not change the ordering of the multiplets in Fig. 1, but can influence how the degeneracy of the multiplet is broken. Momentum dependence of the bubble will add intersite pairing effects, which in the context of this paper are assumed not to be important. These issues will be considered further in a longer paper.
[8] P. W. Anderson and W. F. Brinkman, in *The Physics of Liquid and Solid Helium*, edited by K. H. Bennemann and J. B. Ketterson (Wiley, New York, 1978), Pt. II, p. 177.
[9] An LS scheme was employed to better relate to ^{3}He. A more realistic JJ coupling scheme will be presented in a longer paper, where attraction is only found for $J=4$.
[10] Z. B. Goldschmidt, Phys. Rev. A **27**, 740 (1983).
[11] C. M. Varma, Phys. Rev. Lett. **55**, 2723 (1985).
[12] M. R. Norman, R. C. Albers, A. M. Boring, and N. E. Christensen, Solid State Commun. **68**, 245 (1988).
[13] R. Osborn, K. A. McEwen, E. A. Goremychkin, and A. D. Taylor, Physica (Amsterdam) **163B**, 37 (1990).
[14] D. Fay and J. Appel, Phys. Rev. B **16**, 2325 (1977).
[15] K. Levin and O. T. Valls, Phys. Rev. B **17**, 191 (1978).
[16] J. Appel and P. Hertel, Phys. Rev. B **35**, 155 (1987).
[17] P. W. Anderson, Phys. Rev. B **30**, 4000 (1984); K. Ueda and T. M. Rice, Phys. Rev. B **31**, 7114 (1985).
[18] G. E. Volovik and L. P. Gor'kov, Sov. Phys. JETP **61**, 843 (1985); E. I. Blount, Phys. Rev. B **32**, 2935 (1985).
[19] C. H. Choi and J. A. Sauls, Phys. Rev. Lett. **66**, 484 (1991).