An Orbitally Degenerate Spin

Fluctuation Model for Heavy Fermion Superconductivity

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In this paper, a generalization of standard spin fluctuation theory is considered by replacing the simple Hubbard interaction by the screened Hartree-Fock interaction for f electrons. This model is then used in both an LS and a JJ coupling scheme to construct the particle-particle scattering vertex in an on-site approximation. This vertex is shown to lead 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 anisotropy of the quasiparticle wavefunctions. Detailed calculations are presented for the case of $UPt_3$.

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After over a decade’s worth of theoretical work, there is no overall agreement on a microscopic theory for heavy fermion superconductivity. The overall prejudice, though, is that the underlying pairing mechanism is similar to that operative in superfluid $^3\text{He}$. Most attempts at a theory based on this approach have been to make the simplest possible modifications to the standard single orbital Hubbard interaction used in the $^3\text{He}$ problem. These attempts have had mixed success. The philosophy of this paper will be to actually do for heavy fermions what was done for $^3\text{He}$, that is to use the Hartree-Fock interaction between $f$ electrons including full orbital and spin-orbital effects and construct the effective particle-particle vertex by the appropriate diagrammatic summation. In principle, this theory contains all relevant physics within a spin fluctuation based approach. Even at the simplest level, new physics emerges which is not present when using a simple Hubbard interaction. In particular, the maximum instability in the particle-particle vertex occurs for a pair state which obeys Hund’s rules. For $f$ electrons, this corresponds to a state which has $L=5$, $S=1$, and $J=4$. The degeneracy of this multiplet is broken in real metals by crystalline anisotropy effects in the normal state. This is reflected by (1) the orbital and momentum dependence of the bare susceptibility bubble which forms the internal lines of the vertex and (2) the orbital and momentum dependence of the quasiparticle wavefunctions which form the external lines. In this paper, (1) is treated in a simple manner and (2) is treated within a band theoretic approximation. The frequency dependence of (1) and (2), which acts to set the overall scale for $T_c$, is also treated in a simple fashion. The theory has the advantage that it can be systematically improved by removing these approximations. The above ideas are illustrated by calculations for $\text{UPt}_3$.

In the first section, a motivation of this theory is given by looking at some systematics of heavy fermion superconductors and by comparing the heavy fermion problem to that of $^3\text{He}$. In the second section, the general formalism is described. The single orbital version of this theory is shown to yield the paramagnon model for $^3\text{He}$. The standard spin
fluctuation models worked on previously are then shown to be a lattice generalization of the single orbital model. In the third section, the formalism for the f electron problem is derived, with the particle-particle vertex equations solved for various approximations for the susceptibility bubble in both an LS and a JJ coupling scheme. General properties of the vertex are described based on group theory. In the fourth section, the pair vertex is projected onto the Fermi surface. Calculations are then described for the case of $UPt_3$ utilizing information from a relativistic band structure calculation. In the last section, future directions, including the question of inter-site pairing effects, will be discussed. A shorter version of this work has appeared earlier.$^1$

I. Introduction

Sufficient evidence has accumulated over the past eleven years to demonstrate that the superconductivity seen in a number of f electron metals with large effective mass is unconventional in nature, that is, the group representation describing the order parameter is almost certainly not the identity representation ($I_1^+$). This, along with a variety of other facts, casts doubt on a traditional electron-phonon mechanism as mediating the pairing. The first theoretical work in this area ten years ago showed a close connection of these metals with superfluid $^3He$. In particular, they are near both a magnetic and a localization instability. A classic example is $UPt_3$. Doping with $Pd$, for instance, causes this metal to become strongly antiferromagnetic. Further doping causes the f electrons to become localized.$^3$ Anderson$^2$ also emphasized that the on-site part of the interaction must be playing a major role given the large ratio ($\sim 0.1$) of the superconducting transition temperature to the Fermi energy. This important observation has been largely forgotten. Anderson$^4$ was also the first to point out that heavy fermion superconductors have two f atoms per unit cell. For on-site pairing, one can have an odd parity ground state in this case (with one atom per cell, the pair state would have to be even for on-site pairing).
This unusual observation has also been largely forgotten, except in a later paper by Appel and Hertel\textsuperscript{5} where a formalism for describing localized pairs for $UPt_3$ was developed in great detail. The reason the above points were largely forgotten was the observation of antiferromagnetic spin fluctuations in several heavy fermion superconductors by neutron scattering.\textsuperscript{6} Such fluctuations occur because of exchange interactions between near neighbor sites. This led to a picture of near neighbor pairing based on these fluctuations by a number of authors.\textsuperscript{7,8} Subsequent work largely concentrated on generalizing these simple theories to handle the non-symmorphic (HCP) lattice structure of $UPt_3$.\textsuperscript{9,10} These theories have had mixed success. In particular, available data on $UPt_3$ point to a pair state from a two dimensional group representation with both line and point nodes and probably of odd parity.$^{11,12}$ This state would have $\Gamma_6^{-}$ ($E_{2u}$) symmetry. Although non-trivial group representations occur in these calculations, this particular state has never emerged as the ground state. The last work done in this area by the author\textsuperscript{13} indicated that the anisotropy of the quasiparticle wavefunctions plays a fundamental role because this problem cannot be reduced to an effective one-band form given the two f atoms per unit cell. Therefore, simple theories as pursued above will simply be inadequate for describing real heavy fermion metals and any results generated by them questionable.

This paper is an attempt to break this theoretical deadlock. This work was motivated by several additional issues than those listed above. A number of alternate theories have been proposed recently, in particular by Cox\textsuperscript{14} and by Coleman et al,\textsuperscript{15} which emphasize an on-site pairing viewpoint. Cox’s work is important in that he emphasized the important role that orbital effects play in this problem. Another key motivation was an experiment by Osborn et al\textsuperscript{16} which detected excitations between Coulomb multiplets with high energy neutron scattering, not only in localized f metals like $Pr$ and $UPd_3$, but also in $UPt_3$ itself. This indicates that multiplet correlations present in atoms survives even in a metal with itinerant f quasiparticles. In Table 1, a list of the seven known heavy fermion
superconductors are listed. There are two striking things about this table. First, six of
the seven known heavy fermion superconductors are uranium alloys. Moreover, there is
strong experimental evidence that the uranium atoms are close to an \( f^2 \) configuration.
The magnetic susceptibilities of \( \text{UPt}_3 \) and \( \text{UPd}_2\text{Al}_3 \) look almost identical to that of
the local \( f^2 \) metal \( \text{PrNi}_3 \). The susceptibility of \( \text{URu}_2\text{Si}_2 \) has been most successfully
explained based on an \( f^2 \) ground state. Cox’s quadrupolar model for \( \text{UBe}_{13} \) is also
based on an \( f^2 \) configuration. It should also be noted that \( \text{UPt}_3 \) is very similar to \( \text{UPd}_3 \)
(similar crystal structures, almost identical f atom separations) yet the latter is clearly a
local \( f^2 \) metal. In the high energy neutron data, the Coulomb excitation seen in these
two metals looks very similar. This would be hard to accept if \( \text{UPt}_3 \) was not close to being
\( f^2 \). As for \( \text{CeCu}_2\text{Si}_2 \), it may not be like the rest, although it has been pointed out that
an \( f^2 \) admixture is needed to explain its properties with the Anderson impurity model.
The importance of these facts is that since the f atom has two bare f electrons per site,
this leads to a strong motivation that the superconducting pairs have two f quasiparticles
per site from a trial wavefunction point of view. The second striking point of Table 1 is
that all of these metals either have two f atoms per unit cell, or undergo some sort of
magnetic transition at temperatures above the superconducting transition which gives a
new unit cell with two f atoms. As discussed above, this fact has little relevance to a near
neighbor pairing model (since an atom in any crystal structure has near neighbors), but
plays a crucial role for on-site pairing (since one can have even parity or odd parity pairing
depending on the phase of the order parameter on the two sites).

A further motivation of the importance of on-site pairing can be obtained by comparing
the case of \( ^3\text{He} \) to uranium alloys. In Figure 1, a plot is shown of the interaction potential
of two He atoms. This is amazingly similar to what one would expect of two f electrons on
a uranium site. In particular, there is strong repulsion at small interparticle separation due
to the Coulomb repulsion between the two f electrons, there is attraction at intermediate
distances (or order 3 a.u.) since the ion core attraction exceeds this repulsion in this range (which leads to an \( f^2 \) ground state), and then the potential weakens at large separation due to the exponential decay of the \( f \) electron radial function. The direct interaction potential for \( ^3He \), though, has been shown to be inadequate for describing the pairing of He atoms in the superfluid state (it predicts \( L=2 \) pairing).\(^{24} \) The reason for this is the major role that collective effects play due to polarization of the medium.\(^{25,26,27,28,29} \) This led to the development of a paramagnon model for \( ^3He \). In this model, a much simpler direct interaction potential is used, a repulsive contact interaction between atoms of opposite spin. But this potential in turn is used to sum a diagrammatic series to all orders, thus including the important collective effects. This gives a good description of the superfluid state of \( ^3He \).\(^{27,30} \) In the next section, a generalization of this model is considered which includes orbital interaction effects necessary in dealing with \( f \) electrons. It is then shown that the paramagnon model for \( ^3He \), as well as previous spin fluctuation models for heavy fermions, are subsets of this more general theory.

II. General Formalism

The particle-particle vertex is defined by

\[
\Gamma^{abcd} = \Gamma_0^{abcd} - \sum_{e,f} \Gamma_0^{aecf} \chi_0^{ef} \Gamma^{fbed} \tag{1}
\]

where \( \Gamma_0 \) is the bare vertex, \( \chi_0 \) is the bare susceptibility bubble, the indices label orbitals, and the minus sign is due to the closed Fermion loop defining the bubble (in \( \Gamma \), the first two indices label incoming lines, the last two outgoing lines). \( \Gamma_0 \) is taken to be the antisymmetrized Coulomb interaction \((V^{abcd} - V^{abdc})\)

\[
\Gamma_0^{abcd} = \sum_k c_k^{abcd} F_k \tag{2}
\]

where \( c_k \) are combinations of 3j symbols and \( F_k \) are Coulomb multipole (Slater) integrals defined on page 217 of Condon and Odabasi.\(^{31} \) (A simpler expression of this type has been
used in earlier spin fluctuation work.\textsuperscript{32}) For s electrons, Eq. 2 reduces to

\[
\Gamma_0^{abcd} = \delta_{ac}\delta_{bd} - \delta_{ad}\delta_{bc} \equiv \frac{1}{2}(\delta_{ac}\delta_{bd} - \vec{\sigma}_{ac} \cdot \vec{\sigma}_{bd})
\]

where the last term is a scalar product of Pauli spin matrices and the indices now label just spins (1 for up, 2 for down). Eq. 1 is easily solved, giving\textsuperscript{27,28}

\[
\Gamma^{1111} = -F_0^2\chi_0/(1 - F_0^2\chi_0^2)
\]

\[
\Gamma^{1212} = F_0 + F_0^3\chi_0^2/(1 - F_0^2\chi_0^2)
\]

Eq. 4 (5) is a sum of odd (even) number of longitudinal (e=f) bubbles. The triplet (S=1) vertex is just Eq. 4, the singlet (S=0) vertex is \(2\Gamma^{1212} - \Gamma^{1111}\) (since \(\Gamma^{1212}\) is half the sum of the singlet and triplet vertex\textsuperscript{27}). Alternately, the singlet vertex is \(\Gamma^{1212} - \Gamma^{1221}\) (i.e., antisymmetrizing Eq. 5) where the latter term is a sum of transverse (e\(\neq f\)) bubbles (i.e., ladder diagrams). These expressions are equivalent of course. Eqs. 4 and 5 form the basis of the standard paramagnon model (where \(F_0\) is generally denoted as I).

The first thing to note from the above is that the triplet vertex is negative (attractive) and the singlet one positive (repulsive). Thus, the vertex exhibits Hunds first rule (maximal S). In the \(^3He\) problem, the L of the pair state is determined by projecting Eq. 4 onto the Fermi surface. Since it is isotropic, and L must be odd (since S=1), it is necessary to include the momentum dependence of \(\chi_0\) to obtain a non-zero projection. As expected, L=1 is found since this function has the largest projection on a spherical Fermi surface for odd L harmonics. Note that the momentum dependence is not critical, it is only neccessary to give a non-zero projection. In fact, very different models of the momentum dependence of the vertex give identical pairing coupling constants.\textsuperscript{33} A physical picture of the pairing in these models based on mutual interaction of the two particles via their polarization clouds has been given by Leggett.\textsuperscript{29}

This picture can be contrasted with that given for the heavy fermions and high \(T_c\) cuprates based on singlet (L=2) pairing.\textsuperscript{7} This “violation” of Hunds rules is obtained
by considering pairing of electrons on near neighbor atoms in a nearly antiferromagnetic metal. In such a case, $\chi(\vec{Q}) > \chi(0)$ where $\vec{Q}$ is the ordering wavevector (assumed to be commensurate with the lattice corresponding in real space to anti-alignment of near neighbor spins) and $\chi$ is the dressed bubble. This means in real space that $\chi(R, R')$ is negative ($R, R'$ are site indices, with $R'$ a near neighbor of $R$). This can be achieved by having momentum dependence in either $\chi_0$ or in $\Gamma_0$ ($\chi$ being defined by an equation similar to Eq. 1). The latter is preferable, in that commensurate $Q$ are rarely obtained for $\chi_0$ except in special circumstances, and has been used for fitting neutron scattering data both in heavy fermions and in high $T_c$ cuprates. Now, the same thing which gives a negative $\chi(R, R')$ also gives a sign for $\Gamma(R, R', R, R')$ opposite to that of $\Gamma(R, R, R, R)$. Therefore, if the order parameter is such that $\Delta(R, R)$ is zero and $\Delta(R, R')$ is non-zero (such as found for certain d-wave states), then one can have $S=0$ pairing. Note the complete difference in physics than that discussed above for the $^3He$ problem. In particular, the momentum dependence is crucial for this argument. From the lattice point of view, $^3He$ is actually more closely related to on-site pairing models than to near neighbor pairing models.

III. f Electrons

The formalism of the previous section is now applied to the problem of f electrons. At the bare interaction level, we are already faced with the problem that the uranium ion is in the intermediate coupling regime (i.e., midway between LS and JJ coupling). On the other hand, the spin-orbit interaction is large enough that in electronic structure calculations, no $j=7/2$ quasiparticles are occupied. Because of this, the susceptibility bubble $\chi_0$ will be almost pure $j=5/2$ in character. Therefore, even if the bare interaction is in the intermediate coupling regime, the effective interaction for quasiparticles which comes out of Eq. 1 will be in the JJ coupling limit. Despite this, we will start out by deriving results in the LS coupling limit to make connections to the $^3He$ problem discussed
in the last section. Then, we will turn to the JJ scheme.

We start by reviewing the multiplet structure of the $f^2$ uranium ion, shown in Figure 2. There are 3 spin triplets (L=1,3,5, each spin-orbit split into 3 orbital multiplets) and 4 spin singlets (L=0,2,4,6). This level structure can be fit by the following scheme. At the Hartree-Fock level, only Slater integrals of even rank appear. Fits of the spectra can be achieved by reducing these integrals on average by 38%. This effect is due to screening caused by Coulomb correlations (i.e., the particles try to avoid one another, thus reducing their effective interaction) which can be approximately calculated within a configurational interaction (CI) scheme. In addition, CI causes effective operators of odd rank to appear not present at the Hartree-Fock level (known as Trees parameters). These terms are rather small, though, and we ignore them. To discuss the level scheme, it is useful to find linear combinations of the $c_k$ coefficients of Eq. 2 which more clearly reflect the group theoretical structure of the f electrons, which are labeled $e_k$. This has been achieved by Racah and is equivalent to replacing the Slater integrals $F_k$ (k=0,2,4,6) by linear combinations $E_k$ (k=0,1,2,3). $E_0$ is defined such that all $f^2$ terms have this energy ($e_0=1$). It is equal to $F_0$ plus a linear combination of the other $F_k$ terms and is equivalent to the Hubbard U parameter (the other $E_k$ parameters do not contain $F_0$). $E_1$ is defined so as to distinguish spin singlets from spin triplets, with $e_1=0$ for triplets and $e_1=2$ for all singlets but L=0. Note that these coefficients are identical to the s-electron problem of the previous section. Thus, $E_1$ plays the same role in the f electron problem as the paramagnon I ($F_0$) plays in the $^3$He problem. This is quite interesting, since $E_1$ is a shape fluctuation term instead of a charge fluctuation term (i.e., it does not involve $F_0$). This means that the inclusion of orbital degeneracy qualitatively changes the physics relative to single orbital models. As for the L=0 singlet, it has $e_1=9$. This is another consequence of orbital degeneracy, basically L=0 has a different group structure than L=2,4,6 since it already appears at the $f^0$ level (i.e., it has a different "quasi-spin" or "seniority"). We summarize by writing
down the expression for $e_1$

$$e_1 = <LS|q_{12} + \frac{1}{2} - 2\vec{s}_1 \cdot \vec{s}_2|LS> = 2 - S(S + 1) + 7\delta_{L0}$$ (6)

where 1,2 label the two electrons, $q$ is the seniority operator, and $\vec{s}$ is the spin operator. Note the similarity to the last expression of Eq. 3. As for $e_2$, it is isomorphic to $L=2,4,6$ and thus acts to split these three multiplets apart (it is zero for all other $L$ states). The expression for this term is quite complicated and will not be written down. The most interesting parameter is $E_3$. It acts to split apart the three spin triplets, with $e_3 = -9,0,33$ for $L=5,3,1$ respectively (it is non-zero for all terms but $L=0$). This can be written as

$$e_3 = \left[ \frac{1}{2} - S(S + 1) \right][L(L + 1) - 24g(U)]$$ (7)

where $g(U)$ is the Casimir operator of the group $G_2$ with $U$ labeling the representation of $G_2$ appropriate for a particular LS state (note that $L(L+1)$ is the Casimir operator for the group $SO_3$). The interest is that this has similarities to the case of $p$ electrons, where VanVleck$^{39}$ showed long ago that the interaction between two $p$ electrons can be written as

$$w_{12} = F_0 + (-5 - 3\vec{l}_1 \cdot \vec{l}_2 - 12\vec{s}_1 \cdot \vec{s}_2)F_2$$ (8)

with $\vec{l}$ the orbital angular momentum operator. This looks like an orbital generalization of the last expression in Eq. 3. A summary of the $e_k$ coefficients for the $f^2$ states is given in Table 2.

We now turn to a solution of Eq. 1. At this time, we will assume that $\chi_0^{ef} = \chi_0$ (i.e., no orbital dependence to the bubble). This approximation will be discussed below. States of definite LS have antisymmetrized wavefunctions. So, the vertex for the state $L=5, M_L=5$ ($S=1, M_S=1$) will be

$$\Gamma_{5,5} = \Gamma^{3232} - \Gamma^{3223} - \Gamma_0^{3232}$$ (9)

where indices label $m_l$ (with all spins up). The first term involves longitudinal bubbles, the second transverse bubbles, and the last compensates for double counting (since the
bare vertex is antisymmetric by definition). Vertices for other LS states can be obtained by either using the appropriate antisymmetric combination of the $\Gamma$ or by employing Slater’s diagonal sum rule.\(^{31}\) This is equivalent to the two forms of the singlet vertex in the paramagnon model discussed after Eq. 5.

In certain cases, analytic results can be derived by expanding Eq. 1 into a bubble summation, just as was done in the previous section for \(^3He\). In particular, let us start with just including the $E_0$ term. The result for all states of definite LS is

$$\Gamma = E_0/[(1 - E_0\chi_0)(1 + 13E_0\chi_0)] + E_0^2\chi_0/(1 - E_0\chi_0)$$  \hspace{1cm} (10)$$

The first term comes from longitudinal bubbles, the second from transverse bubbles and double counting. Note that 13 is the orbital degeneracy (14) minus 1. This expression, plotted in Figure 3, is always repulsive. The behavior of this term is that as $\chi_0$ increases from zero, the repulsion is reduced compared to $E_0$ then begins to increase again and diverges at $E_0\chi_0=1$. This corresponds to a localization instability.

Now assume that only $E_1$ is non-zero. Analytic results can also be obtained. For the spin triplet states, Eq. 1 is now

$$\Gamma = -11E_1^2\chi_0/[(1 - 81E_1^2\chi_0^2)(1 - 4E_1^2\chi_0^2)] + 2E_1^2\chi_0/(1 - 4E_1^2\chi_0^2)$$  \hspace{1cm} (11)$$

where the first term comes from longitudinal bubbles, the second from transverse bubbles. This expression, plotted in Figure 4, is zero for $\chi_0=0$ and then has a negative divergence as $9E_1\chi_0$ approaches 1, corresponding to a magnetic instability. This behavior is analogous to the triplet vertex in \(^3He\). Eq. 1 can also be solved for the L=6 singlet

$$\Gamma = (4E_1 + 13E_1^2\chi_0 - 126E_1^3\chi_0^2 - 162E_1^4\chi_0^3)/[(1 - 81E_1^2\chi_0^2)(1 - 4E_1^2\chi_0^2)] - 2E_1$$  \hspace{1cm} (12)$$

where the first term comes from longitudinal bubbles, the second from transverse bubbles, and the third from double counting. Just as for the singlet vertex in \(^3He\), this interaction,
plotted in Figure 4, is repulsive for $\chi_0=0$ (equal to $2E_1$) and has a positive divergence at $9E_1\chi_0=1$. This expression should also be valid for the $L=2$ and $L=4$ singlets. The vertex for the $L=0$ state would be more repulsive.

The general solution to Eq. 1 is difficult to construct analytically due to the complicated nature of the bare vertex when all $E_k$ terms are included. Solving numerically would also appear to be difficult since there are four orbital indices involved. Progress can be made, though, by defining

$$\tilde{\Gamma}^{be} = \Gamma^{b+n,e,b+e+n}$$

(13)

with this definition, Eq. 1 reduces to

$$\tilde{\Gamma}^{be} = \tilde{\Gamma}^{be}_0 - \sum_f \tilde{\Gamma}^{bf}_0 \chi_0^{f+n} \tilde{\Gamma}^{fe}$$

(14)

Thus, an $N^4$ matrix equation has been reduced to an $N^2$ matrix equation for each value of $n$ ($n=0$ are the longitudinal bubbles, the rest are transverse bubbles). This is easily solved on the computer given input values for the $E_k$ and $\chi_0$.

The $E_k$ parameters were taken from Goldschmidt. They have been fit to uranium ion data (the level scheme for $\chi_0=0$ in Figure 5 differs in some quantitative details from the experimental level scheme of Figure 2 since spin-orbit has not been included at this point). These parameters are on average 62% of their Hartree-Fock values due to screening. By comparing to the high energy neutron scattering data of Osborn et al on $UPt_3$, these parameters should be reduced by another 28% when going into the solid. The latter effect is only of quantitative significance and is based on one transition which is seen (assumed to be from $^3H_4$ to $^3F_2$), so is ignored in order to use the well established values of $E_k$ listed in Goldschmidt’s article. Hopefully, detailed solid state values of these parameters will become available with further experimental work. An additional note is that the fitted $E_0$ is referenced to some arbitrary value of the energy zero, so has no intrinsic meaning. The value listed in the Goldschmidt article, though, gives an $F_0$ of 1.83 eV which is
fortuitously close to estimates of the screened Coulomb U for uranium,\(^{40}\) so we retain it without adjustment.

A final comment concerns the energy zero of the problem. Superconductivity involves an instability of the Fermi surface. For a uranium ion, two f electrons are occupied. Even in band structure calculations for \(UPt_3\), the number of occupied \(j=5/2\) f electrons is just above two. Thus, the term \(E_0\) (the Coulomb repulsion between the two f electrons) is already included in the definition of Fermi energy and represents the zero of energy for the uranium problem (for the cerium case, where only one f electron is occupied, \(E_0\) is not included in the energy zero, since it represents the energy of \(f^2\) above \(f^1\)). But, the energy term for the \(L=5\) ground state of an \(f^2\) ion is \(E_0 - 9E_3\). What about the term \(E_3\)? Since this term cannot be reduced to an effective single particle form, it would not seem to enter into the definition of the quasiparticle Fermi energy. This gives the rather bizarre result that the \(L=5\) vertex is already attractive at the bare interaction level. Of course, one could imagine a scenario where one considered an \(f^2-f^3\) Anderson lattice model, with the effects of \(E_3\) built into the ground states. The effective quasiparticle operators in this case might implicitly contain the effects of \(E_3\). Since a detailed theory of this has not been worked out yet, we cannot make any definitive conclusions one way or the other. Since the effective interaction, though, strongly departs from the bare value as \(\chi_0\) increases from zero, this question is of minor significance. For purposes of this paper, we assume that the energy zero is at \(E_0\) for the \(f^2\) case and 0 for the \(f^1\) case.

In Figure 5, \(\Gamma\) is plotted for the triplet states \(L=5\), \(L=3\), and \(L=1\) and for the singlet \(L=6\). The other singlets will have similar behavior. Just as found for the \(^3He\) problem, the triplet interactions are attractive and the singlet ones repulsive, with an instability in both cases at \((E_0 + 9E_1)\chi_0=1\). Note this criteria is a combination of the two analytic results discussed above, thus the instability has both a localization and a magnetic component. This observation indicates that the debate concerning both \(^3He\) and heavy fermions about
whether the physics is nearly localized or nearly magnetic is merely semantics, as both
effects are intertwined. A significant difference from the $^3\text{He}$ case is the effect of orbital
interactions in the current problem. In $^3\text{He}$, the orbital degeneracy of the pair state is
lifted by Fermi surface projection of the vertex; in the f electron case, this degeneracy is
already lifted by the interaction itself. Note that the largest attractive instability is for
$L=5$, $S=1$ (in such a state, the Coulomb repulsion is minimized). Thus, the pair state is
predicted to satisfy both Hunds first and second rules, and is a generalization of the results
obtained for $^3\text{He}$.

We now turn to a discussion of the problem at the JJ coupling level, which as argued
above, is more physically relevant at the quasiparticle level than the LS scheme (or even
the intermediate coupling scheme). The bare interaction vertex can be gotten by replacing
the orbital-spin indices of Eq. 2 by the indices $\mu$ which range from $-5/2$ to $5/2$ (we assume
only $j=5/2$ quasiparticles are involved). By taking into account the mixed spinor nature of
the relativistic orbitals, the formulas for $c_k$ can be calculated in a manner similar to that
used on p. 217 of Condon and Odabasi.\textsuperscript{31} Note that only $k=2$ and 4 are involved ($k=6$
comes in when considering $j=7/2$ states). The resulting expressions were checked against
tabulated results on page 560 of de-Shalit and Talmi.\textsuperscript{41} As in the LS case, the $F_k$ are not
useful in exploiting the group properties of the f electrons, so one rotates to another basis
$E_k$. It should be noted that these $E_k$ are not the same $E_k$ as in the LS case. They have
been discussed in the context of nuclear physics, where JJ coupling has been traditionally
of more use,\textsuperscript{42} and the analogous $e_k$ coefficients are listed in Table 3. In this case, there
are only 3 terms, $J=4,2,0$ (corresponding to $L=5,3,1$ in the LS case). As in the LS case, $e_0$
is 1 for all states. $e_1$ is 3 for $J=0$, 0 otherwise which has analogies to $e_1$ in the LS case. In
particular, $J=0$ appears at the $f^0$ level and thus has a different quasi-spin (i.e., seniority)
than $J=2,4$. The term $e_2$ splits the latter two states apart (similar to $e_3$ in the LS case).
In this notation, the ground state $J=4$ term is $E_0 - 5E_2$. This is lower than the $E_0$ energy
zero just as found for the L=5 LS case. By fitting these values for states of definite J, we can infer an interaction vertex analogous to VanVleck’s\(^{39}\) of Eq. 8 for the p electron LS case

\[
w_{12} = E_0 + \frac{q_{12}}{2} E_1 + [-2\vec{j}_1 \cdot \vec{j}_2 - \frac{5}{2}(1 + q_{12})]E_2 \tag{15}
\]

where \(q_{12}\) is a seniority operator \(< J|q_{12}|J > = 6\delta_{J0}\) and \(\vec{j}\) is the total angular momentum operator.

Analogous analytic series can also be constructed. In particular, keeping just \(E_0\) gives an expression like Eq. 10 with 13 replaced by 5 since the orbital degeneracy is now 6 instead of 14.

We now solve Eq. 1 exactly as done for the LS case. The interaction parameters are again obtained from Goldschmidt.\(^{35}\) The results are plotted in Figure 6. An attractive instability is found for J=4, a repulsive instability for J=2,0. The instability occurs at a value \((E_0 + E_1 + 12E_2)\chi_0=1\). This result is important in that it makes a very definite prediction, if a paramagnon like picture analogous to \(^3He\) applies to heavy fermion superconductors, a pair state of relative J=4 should be realized.

How does this change if we replace uranium by cerium? First, the energy zero does not contain \(E_0\) so that the bare interaction is more repulsive. Second, \(E_0\) is about 3 times larger since U is around 6 eV for cerium ions.\(^{43}\) Although this means that the instability occurs for a smaller value of \(\chi_0\), we expect the interaction to be more repulsive since \(E_0\) is larger. This is illustrated in Figure 7 which is analogous to Figure 6 except parameters tabulated by Goldschmidt for the cerium ion are used\(^{44}\) (with an \(E_0\) of 6.0 eV). As can be seen, the interaction in all channels is repulsive except very close to the instability for J=4. On the other hand, in strong coupling calculations for the paramagnon model in \(^3He\), the calculated superfluid transition temperature actually turns off as the instability is approached since the energy scale of the paramagnon (proportional to \(1-I\chi_0\)) is going to
zero (that is, the $T_c$ maximum is near but not at the instability). Because of this, pairing is possible for cerium alloys but much less likely than the uranium case where one finds a larger range of $\chi_0$ where there is attraction. An alternate view is that a pair wavefunction with two f quasiparticles has much less overlap with the bare f ion wavefunction in the cerium case since the $f^2$ component in cerium is much smaller than in uranium. This is in accord with experimental observations discussed in the first section.

We now discuss the issue of orbital and momentum dependence of the susceptibility bubble. In heavy fermion uranium alloys, there is not much evidence for crystal field effects. This indicates that all the $j=5/2$ f orbitals are strongly mixed, as predicted by band theory (as discussed for Kondo lattice models by Zwicknagl, if the Kondo temperature is larger than the crystal field splittings, then all f orbital energies get renormalized to the Fermi energy and are intermixed; this appears to be the case in $UPt_3$). Because of this, one would expect the orbital and momentum dependence of $\chi_0$ to be rather weak. There are inter-site interactions, though, which give the full susceptibility, $\chi$, momentum dependence. An argument against the importance of this effect for the pairing has been given by Anderson where he emphasizes the dominance of the on-site interaction given the large ratio of $T_c$ to $E_F$. The issue of intersite pairing will be discussed in the last section. On the other hand, the susceptibility in metals like $UPt_3$ is strongly dependent on field direction. Whether this is a consequence of crystal field effects or simply due to inter-site correlations is an unresolved matter although neutron scattering data in $UPt_3$ point to the latter. If this is a crystal field effect, it can be represented by $\chi_0$. If $\chi$ is maximal for fields along the c axis (like in $URu_2Si_2$), this indicates that the longitudinal bubbles are dominant. If one redoes Figure 6 with just longitudinal bubbles, then the J multiplets are split into various $M_J$ terms (actually, those $M_J$ combinations which have the appropriate crystal symmetry) with the maximum $M_J$ configuration having the most attractive instability. On the other hand, if $\chi$ is maximal for fields in the basal plane (like in $UPt_3$) then transverse bubbles
with n=1 are dominant (n as defined in Eq. 13 and 14). This in turn leads to the minimum \( M_J \) configuration being preferred. Higher values of n would indicate the importance of quadrupolar (n=2) effects, etc. These terms play an important role in certain theories.\(^{14,20}\)

These observations are summarized in Table 4 (where it should be noted that a J=4 state is always preferred). In this paper, these effects will be further ignored although they are relatively easy to incorporate if they can be accurately determined (and if they are indeed due to \( \chi_0 \) itself). An argument that these effects cannot be too strong is that an \( M_J=0 \) pair state is not consistent with experimental data in \( UPt_3 \) since it is a single dimensional group representation, although similar anisotropic spin fluctuation work in a spin-only approximation gave an analogous \( M_S=0 \) pair state,\(^{10}\) which is consistent with observations of anisotropy in the upper critical field.\(^{47}\) These issues will be discussed further in the next section. As will be discussed in the next section, projection of the vertex on the Fermi surface will also lead to lifting of the degeneracy of the J manifold (analogous to the lifting of L degeneracy in \( ^3He \)). It is that effect we concentrate on in this paper.

We conclude this section with a discussion of the general vertex. In \( ^3He \), the full vertex can be written in a form analogous to the bare expression in Eq. 3, that is a density piece proportional to the delta functions and a spin piece proportional to the scalar product of spin operators.\(^{27}\) Given the similarity of Eq. 3 to that of, say, Eq. 15, this should also be possible in the f electron case (as long as one restricts to states of definite LS or J). In particular, there will be a density piece, a quasi-spin (seniority) piece, and an orbital piece proportional to the scalar product of total angular momentum operators. This justifies some of the phenomenological interactions used in previous work.\(^{13}\) Further exploitation of these ideas should give us a more fundamental insight into the properties of the full vertex for f electrons. We should note that the screened Slater integrals \( F_k \) can be considered as analogues of the Landau F functions of Fermi liquid theory.
IV. Application to $UPt_3$

We now wish to employ the formalism in the previous section to a real heavy fermion superconductor. We choose for this purpose $UPt_3$. There are two good reasons for this. First, a variety of experimental data exist on this metal which gives us a fairly good idea about what the order parameter is. Second, extensive deHaas-vanAlphen data on $UPt_3$\textsuperscript{48} give a Fermi surface in fairly good agreement with LDA band structure calculations.\textsuperscript{49} This indicates that the momentum dependence of the LDA wavefunctions is fairly trustworthy. The frequency dependence is not, of course, since the effective mass in the measurements is about 16 times the LDA band mass. This is due to the fact that in heavy fermions, the self energy has a large frequency derivative leading to a large mass enhancement. Investigation of transport properties indicates the momentum derivative of the self-energy must be rather weak so that the self-energy ”rides” with the Fermi energy.\textsuperscript{50} That is why the shape of the LDA Fermi surface is about correct even though the mass is off by a large factor. These issues are of importance since we want to convert the formalism of the previous section to apply to quasiparticle states. We can do this approximately by taking the four bare external lines of the vertex in Eq. 1 and multiplying each of them by the wavefunction renormalization factor $Z^{1/2}$, where as indicated above $1/Z \sim 16$. This represents the effect that only $Z$ of the bare electron is in the quasiparticle pole.

To proceed further, note that

$$<J, \alpha | \Gamma | J', \alpha'> = \delta_{JJ'} \delta_{\alpha,\alpha'} \Gamma_{J,\alpha}$$ (16)$$

where $\alpha$ is a basis function of $J$ which has the appropriate crystal symmetry. For axial symmetry, this would just be $M$. For hexagonal symmetry, they are listed in Table 5.\textsuperscript{5} The dependence of $\Gamma$ on $\alpha$ occurs if anisotropy is put into $\chi_0$ as discussed in the last section. Also, for a multi-dimensional group representation, $\Gamma$ will be the same for each $\alpha$ in the representation, unless the symmetry is lowered by some external perturbation.
This has relevance for Ginzburg-Landau models of the phase diagram for \( UPt_3 \) and will be discussed later. For now, though, we assume only a \( J \) dependence for \( \Gamma \). These are plotted in Figure 6. Given this, we can now calculate the paring interaction on the Fermi surface. We do this by constructing the product \(|\vec{k}, -\vec{k}\rangle\) and expanding this in terms of \(|J, \alpha\rangle\). The first thing to note is that there are two degenerate states for each \( \vec{k} \) (\( \vec{k}, PT\vec{k} \) where \( P \) is the parity operator and \( T \) the time reversal one) and two for \(-\vec{k}\) (\( P\vec{k}, T\vec{k} \)).

The combination \( \frac{1}{2}(|\vec{k}, T\vec{k}\rangle - |PT\vec{k}, P\vec{k}\rangle) \) defines a pseudo-spin singlet, \( d_0 \). The three combinations \( \frac{1}{2}(|PT\vec{k}, T\vec{k}\rangle - |\vec{k}, P\vec{k}\rangle) = d_x \), \( -\frac{i}{2}(|PT\vec{k}, T\vec{k}\rangle + |\vec{k}, P\vec{k}\rangle) = d_y \), and \( \frac{1}{2}(|\vec{k}, T\vec{k}\rangle + |PT\vec{k}, P\vec{k}\rangle) = d_z \) define a pseudo-spin triplet, known as the \( d \) vector.

In the current theory, only the part of \(|\vec{k}, -\vec{k}\rangle\) on the same site is involved in Eq. 16. (Note that although the pair interaction is only attractive for particles on the same site, the pairs are correlated out to a distance of the coherence length, much like the problem of bound states of a potential well where the particles spend most of their time outside the well.) Now, the part of \(|\vec{k}\rangle\) involving \( j=5/2 \) states is

\[
|\vec{k}\rangle = \sum_{\mu i} a_{\mu i}^{n\vec{k}} |\mu\rangle_i
\]

where \( \mu \) runs from \(-5/2\) to \( 5/2 \), \( i \) is the \( f \) atom site index (1,2 for \( UPt_3 \)), and \( n \) is the band index (five bands are predicted to cross the Fermi energy in \( UPt_3 \)). Thus, the coefficient of \(|\vec{k}, -\vec{k}\rangle\) involving \( j=5/2 \) states on the same site with the correct group representation structure for a particular total \( J \) (\( J=0,2,4 \)) is

\[
A_{k}^{Jj\alpha} = \tilde{P}_{J\alpha} \sum_{\mu i} a_{\mu i}^{n\vec{k}} a_{\nu i}^{n-\vec{k}}
\]

where \( j \) represents the pseudo-spin combination (0 for singlet, \( x,y,z \) for triplet) and \( \tilde{P} \) is a projection operator which takes that part of the sum which has the form of one of the basis functions (Table 5) with the appropriate pseudo-spin combination discussed above. Because of antisymmetry, \( A \) changes sign from one site to the other site in the unit cell for
pseudo-spin triplets, and does not for pseudo-spin singlets (for one f atom per cell, only pseudo-spin singlets exist\(^{53}\)). Summarizing, the particle-particle vertex is

\[
< \vec{k}', -\vec{k}'| \Gamma | \vec{k}, -\vec{k} > = Z^2 \sum_{J\alpha jj'} \Gamma_J A^J_{\vec{k}, \alpha j}^* A^J_{\vec{k}'} \tag{19}
\]

Since Eq. 19 is separable in \(\vec{k}\) and \(\vec{k}'\), this allows us to write down the BCS coupling constant

\[
\lambda_{J\alpha} = N \Gamma_J Z^2 \sum_j < |A^J_{\vec{k}, \alpha j}|^2 > \tag{20}
\]

where \(N\) is the density of states, \(< >\) is an average over a narrow energy shell about the Fermi energy, and \(j\) runs over \(0\) for even parity, \(x,y,z\) for odd parity. For \(UPt_3\), this average was done on a regular grid of 561 \(\vec{k}\) points in the irreducible wedge (1/24) of the Brillouin zone, keeping those \(n\vec{k}\) states within 1 mRy of the Fermi energy (182 states total). Those points that are in symmetry planes of the zone are plotted in Figure 8. The number 1 mRy was chosen so as to have enough points to give a good representation of the Fermi surface with this size grid. Note that in this model

\[
\Delta_{J\alpha j}(\vec{k}) \propto A^J_{\vec{k}, \alpha j} \tag{21}
\]

where \(\Delta\) is the order parameter.

In Table 6, coupling constants\(^{54}\) for \(UPt_3\) are shown modulo \(N \Gamma_J Z^2\) with the largest occurring for \(J=0, \Gamma_1^+\). This is just the BW state with spin-orbit,\(^{55}\) with a coupling constant proportional to the square of the ratio of the \(j=5/2\) f density of states to the total density of states. From Figure 6, though, the \(\lambda_{2\alpha}\) and \(\lambda_{0\alpha}\) coupling constants are repulsive and so do not play a role. For the attractive \(J=4\) case, the largest coupling constants are for odd parity states. This is because three pseudo-spin triplet terms contribute to Eq. 20 in this case as opposed to one pseudo-spin singlet for even parity states. The importance of this is that pseudo-spin triplets only exist because of the two f atoms per unit cell, which as illustrated in Table 1, all heavy fermion superconductors have. This is a property
of an on-site pairing theory, and has no relevance in near neighbor pairing models. The largest coupling constant occurs for $\Gamma_6^-$ ($E_{2u}$) symmetry, although several other states have comparable sized coupling constants ($\Gamma_1^-, \Gamma_4^-$). Note that this is an odd parity two dimensional group representation.

Let us discuss this state. For the odd parity case, the order parameter is a vector. At a general $\vec{k}$, all three components are involved because of the relativistic nature of the wavefunction coefficients. For two dimensional group representations, this means that the state will be non-unitary ($\vec{d} \times \vec{d}^* \neq 0$). A discussion of the case of non-unitary d vectors can be found in Sigrist and Ueda\textsuperscript{56} which play a major role in a recent phenomenological theory of $UPT_3$.\textsuperscript{57} In the non-unitary case, there are two gaps for each $\vec{k}$

$$\Delta_{\sigma}(\vec{k})^2 = |\vec{d}(\vec{k})|^2 + \sigma |\vec{d}(\vec{k}) \times \vec{d}^*(\vec{k})|^2$$

(22)

where $\sigma$ is $+/-$. Plots of this for the $\Gamma_6^-$ state are shown in Figures 9 and 10 with the total density of states shown in Figure 11. No attempt has been made to fit these gaps to simple functions\textsuperscript{58} because the complex momentum dependence of the wavefunctions would prohibit this. Instead, some general properties can be inferred. For instance, the $d_z$ component vanishes for $k_z=0$ as expected from earlier work.\textsuperscript{59} A surprise, though, is that all three d vector components vanish on the zone face $k_z=\pi/c$. Thus, this state has a line node gap function, and provides a counterargument to earlier statements that line node gap functions are not possible for odd parity states.\textsuperscript{59} Moreover, all d vector components vanish along the axis $k_x=0, k_y=0$ which gives rise to point nodes. A gap function of this sort (line nodes perpendicular to the c axis, point nodes along the c axis) is consistent with a variety of experimental data in $UPT_3$, including specific heat,\textsuperscript{60} transverse ultrasound,\textsuperscript{61} penetration depth,\textsuperscript{62} thermal conductivity,\textsuperscript{63} NMR,\textsuperscript{64} and tunneling\textsuperscript{65} data. Note that despite the small value of the second gap in Figure 10, no "normal" component is seen in the density of states of Figure 11. Thus, this non-unitary state differs from the one considered by Machida et al\textsuperscript{57} where one of the gap components vanishes identically for
all \( \vec{k} \) so that there is a normal component with half the value of the normal state (in the theory of Coleman et al.\textsuperscript{15} a similar normal component occurs). It should be remarked that although earlier specific heat data\textsuperscript{60} indicated a sizable normal component, this is probably due to impurity effects since newer data do not show this component.\textsuperscript{66} As for the two dimensional nature of the group representation, our current understanding of the field-temperature-pressure phase diagram of \( UPt_3 \) is in strong support of such a state.\textsuperscript{12,67,68} In particular, weak magnetism is present which lowers the symmetry to orthorhombic. This acts to split the superconducting transition into two transitions. Pressure acts to eliminate both the magnetism and the splitting,\textsuperscript{69} thus giving strong support for a two dimensional group representation, as opposed to two nearly degenerate single dimensional group representations. The main problem with this scenario is the presence of a term in the gradient part of the free energy which tends to mix the two components of the representation except for certain field directions. This is in contradiction to experiment which shows a fairly isotropic phase diagram with respect to field direction (this was the main motivation for the nearly degenerate model\textsuperscript{70,71}). Sauls, though, has shown that for an axially symmetric Fermi surface and axially symmetric basis functions, this mixing term is zero for the \( E_2 \) representation.\textsuperscript{12} In the general case, it is not, but its mixing term is smaller than that of the \( E_1 \) representation. This work will be discussed in another paper,\textsuperscript{72} but it suffices to say here that for the current theory, the mixing term for our \( \Gamma_{6}^{-} (E_{2u}) \) state is small enough so as to be promising in regards to explaining the phase diagram. Alternate theories based on two nearly degenerate representations\textsuperscript{70,71,73} are also consistent with the current theory given the closeness of the coupling constants for \( \Gamma_{6}^{-} \), \( \Gamma_{1}^{-} \), and \( \Gamma_{4}^{-} \) (the latter state having the same line node structure as \( \Gamma_{6}^{-} \)).

A final issue concerns the question of parity. No change below \( T_c \) for \( UPt_3 \) has been seen in the Knight shift\textsuperscript{74} or induced moment form factor,\textsuperscript{75} indicating no change in the magnetic susceptibility below \( T_c \). This is in support of an odd parity state, although
one could argue that in the heavy fermions, the quasiparticle (intraband) part of the susceptibility is small compared to the VanVleck (interband) part, so this conclusion is not definitive. Choi and Sauls have also shown that the observed low temperature directional anisotropy of the upper critical field is most easily explained with an odd parity pair state with \( M_S = 0 \) (note, the quantization axis is assumed to be along c). Such a state came out of earlier non-relativistic spin fluctuation calculations which took into account the directional anisotropy of the susceptibility. In the current case, though, spin and orbital components are mixed and so a pure \( M_S = 0 \) state is not possible. On the other hand, the state found here, \( |M_J| = 1 \), has the largest projection of J on the basal plane of any two dimensional group representation (\( M_J = 0 \) has the largest projection, but is a singlet), so is promising in that regard. To test this quantitatively would require a detailed calculation of the upper critical field with both spin and orbital degrees of freedom taken into account. Certainly, if the current predicted state is correct, the \( H_{c2} \) anisotropy cannot just be a spin effect as envisioned by Choi and Sauls. This can be seen as follows.

A direct translation of their idea to the current state would be to have a state of pure \( d_z \) character in pseudo-spin space. This can be tested by rotating in pseudo-spin space at each \( \vec{k} \) so that the state \( |\vec{k}\rangle \) has maximal \( J_z \) along the chosen quantization axis. This was done for quantization axes along the a, b, and c axes of the hexagonal crystal (for the a and b case, this lowers the system to orthorhombic symmetry). In all cases, the averages \( < |d_i|^2 >_{\vec{k}} \) were within 20% to 30% of each other, i.e. there is no dominant \( d_z \) component. This is consistent with the highly non-unitary nature of this state seen in Figures 9 and 10. As indicated above, then, orbital effects in the upper critical field must be playing an important role. This would require a theory for calculating \( H_{c2} \) for a non-unitary multi-component d vector in the strong spin-orbit coupling limit.

We finally turn to a discussion of \( T_c \). We should note that the density of states already contains the renormalization factor \( 1/Z \) (i.e., \( N = N_0/Z \) where \( N_0 \) is the bare density
of states). This means that the prefactor $N \Gamma_J Z^2$ in Eq. 20 is analogous to the form $\lambda_\Delta/(1 + \lambda_Z)$ found in strong coupling theories\textsuperscript{45} since $N_0 \Gamma_J$ would be the pairing coupling constant, $\lambda_\Delta$, and $1/Z - 1$ would be the mass coupling constant, $\lambda_Z$. This is consistent with the fact that renormalization of the external lines of the vertex is a strong coupling effect. On the other hand, the frequency dependence of the bubble has not been kept, so one has to simulate this by providing an energy cut-off of order the renormalized Fermi energy. We note that the size of the specific heat coefficient\textsuperscript{3} and the neutron scattering linewidth\textsuperscript{6} are consistent with a renormalized energy scale for $U Pt_3$ of order 5 meV. This is also consistent with estimating a band structure Fermi energy and multiplying this by $Z$. The last thing to be determined is $\Gamma_J$. This is made difficult by the fact that $\chi_0$ is being treated as a number in this paper, whereas in reality it is a highly complicated function of momentum, frequency, and band and orbital indices. Given the strong dependence of $\Gamma_J$ on $\chi_0$ (and also the question of the energy zero), the exponential dependence of $T_c$ on coupling constant, and the uncertainties mentioned in the above approximations, the most illustrative approach is just to see what value of $\chi_0$ is needed to obtain the observed $T_c$. With a $T_c$ of 0.5 K and a cut-off of 5 meV, this gives a value for $\lambda$ of 0.205. Since $\lambda = N \Gamma_4 Z^2 c$ where $c$ from Table 6 for $J=4$, $\Gamma_6^-$ is 0.125, this gives a $\Gamma_4$ of -2.1 eV relative to the energy zero. From Figure 6, this gives a $\chi_0$ of 0.335, which is 0.92 of the divergence value, giving a Stoner renormalization of 12, comparable to the mass renormalization value of 16 assumed from the beginning. Since spin fluctuation models based on the observed heavy fermion dynamic susceptibility have a mass renormalization which goes like the Stoner factor, as opposed to the log of the Stoner factor which one gets for a Lindhard function\textsuperscript{8}, then there is a overall consistency in these numbers. This can be further demonstrated by estimating $\chi$, obtained by multiplying $\chi_0$ by the Stoner renormalization (12) then by the square of the orbital degeneracy (36). This gives a value of about 150 states/eV, comparable to the 180 states/eV given by the specific heat $\gamma$ of
Moreover, converting $\chi$ to proper units (with $g=6/7$ and $j=5/2$) gives 0.0075 emu/mol, comparable to data from susceptibility measurements. To obtain a more reliable estimate of these parameters would require doing a full strong coupling calculation retaining the frequency dependence of the bubble.

The large estimated size of $\Gamma J$ of order 2 eV which must be renormalized downwards by $Z^2$ might seem somewhat worrisome. After all, wouldn’t one expect high $T_c$ in transition metals where $Z$ is closer to one? The question of renormalizing the interaction downwards has been discussed by Anderson and reviewed by Lee et al. The main point to emphasize here is that the interaction parameters of this paper are only appropriate for a system close to an $f^2$ configuration, and the same thing that is causing the large value of $\Gamma J$ is also causing a small value for $Z$. In transition metals, the $E_k$ parameters are largely screened out and play no role. Instead, one collapses back to a standard spin fluctuation model with a Stoner interaction parameter $I$. Estimates based on this $I$ give extremely low estimates of $T_c$, even in palladium which has a large Stoner renormalization.

V. Future Directions

An advantage of the current approach is that the theory is systematically improvable by removing various approximations made in this paper. The most severe of these is treating $\chi_0$ as a number. A proper strong coupling calculation would include the frequency dependence of this object. This is not too difficult if the simple relaxational form is used

$$\chi_0(\omega) = \frac{\chi_0 \Gamma}{\Gamma - i\omega}$$

where $\Gamma$ is the neutron scattering linewidth. Work of this sort has been done in earlier spin fluctuation models. Of more interest is the momentum and orbital dependence of this object. The philosophy of this paper is similar to that espoused early on by Anderson, that is the size of the effective interaction is large enough (large ratio of $T_c$ to $E_F$) that the on-site interaction must play the central role. This is also consistent with the observation that
one of the defining properties of the heavy fermion metals is their large atom separation\textsuperscript{79} giving weak inter-site interaction effects. Even neutron scattering data indicate that that part of the susceptibility where the bulk of the fluctuating moment is has a relatively mild momentum dependence.\textsuperscript{6} On the other hand, these effects played a crucial role in earlier spin fluctuation models, so it is of interest to see how they would enter the current formalism. In the real space approach taken here, these effects would be simulated by adding a term $\chi_0(R, R')$ in addition to the term $\chi_0(R, R)$ where $R, R'$ are site indices with $R'$ a near neighbor of $R$. Near neighbor effects would show up in Eq. 1 at first order in this bubble. At second order in this bubble, there would be terms which would also affect on-site pairing ($\chi_0(R, R')\chi_0(R', R)$). Assuming Eq. 1 can be solved, one is left with a vertex which contains on-site terms, near neighbor terms, etc. The general properties of this vertex along with the functional forms of the near neighbor and next near neighbor pairs are discussed in Appel and Hertel.\textsuperscript{5} One simply has to combine this work with that one to get a complete solution. It is complicated, but doable. A simple argument, though, can be used against near neighbor pairing in that the same sign difference between on-site and near neighbor interactions in the antiferromagnetic case which gives rise to $S=0$ pairing in the single orbital case (end of Section II) should give $J=0$ pairing in the orbitally degenerate case, since from Figure 6, $J=0$ has maximal repulsion for the on-site case. Such a state is a singlet, and is completely inconsistent with the data we have discussed on $UPt_3$.

The other issue concerns orbital dependence of the bubble. Calculations of this sort exist in the literature for $UPt_3$\textsuperscript{80} and are rather tedious, as they involve calculating matrix elements of relativistic wavefunctions over a fine enough grid in k space to get reliable values of $\chi_0$. As discussed in Section III, one might get around this difficulty by simulating these effects with some effective crystal field model. The most probable picture based on the temperature dependence of the neutron scattering data, though, is that this effect enters
most prominently in the $\chi_0(R, R')$ term.\textsuperscript{6}

The next issue concerns feedback effects which are important in the physics of superfluid $^3$He. In that case, all L=1 states are degenerate at $T_c$. Therefore, one would expect the isotropic state, the BW state, to have the lowest free energy. On the other hand, the susceptibility changes below $T_c$ which affects the pair interaction and favors states with maximal anisotropy, giving rise to the ABM state.\textsuperscript{27,29} In the current problem, though, (1) this degeneracy is already broken in the normal state due to the crystal lattice and (2) there is no experimental evidence for a change in the susceptibility below $T_c$ (based on Knight shift\textsuperscript{74} and induced moment form factor\textsuperscript{75} measurements), although it should be noted that the interband, or VanVleck, component most likely dominates the susceptibility.\textsuperscript{80} (Neutron scattering experiments which access the low momentum, low frequency part of the dynamic susceptibility would be helpful in extracting out the quasiparticle part of the susceptibility and seeing how it changes below $T_c$.) Because of this, feedback effects probably do not play an important role in the heavy fermion problem (the large ratio of $T_c$ to $E_F$ would argue against this, though). A related effect is whether the interaction changes as a function of field (this could be connected to the $H_{c2}$ anisotropy discussed in the previous section). Magnetization data look very linear in field for all field directions for the field range of interest\textsuperscript{3} which would argue against this. On the other hand, as $T_c$ depends exponentially on coupling constant, small changes in the quasiparticle wavefunctions in an applied field could lead to noticeable effects, especially given the low effective Fermi energy. This could be simulated in the current theory by rediagonalizing the band structure wavefunctions in the presence of the appropriate field and see how the coupling constants listed in Table 6 change.

A related effect is the observed splitting of $T_c$ in $UPt_3$ that was discussed in the previous section. This has been treated in the past by a phenomenological symmetry breaking field thought to be due to the orthorhombic distortion associated with the weak
antiferromagnetism. This could also be simulated in the current model by applying a weak staggered field (the new orthorhombic cell would contain four uranium atoms) and rediagonalizing the band structure wavefunctions, from which the splitting of the coupling constants could be determined.

The author would like to conclude by saying that the physics of heavy fermion superconductors is complicated enough (as this paper demonstrates) that the picture offered here may not be complete. On the other hand, he feels that the ultimate theory for these materials must look in some form like what is being proposed here, since the orbital dependence of the f electrons and the short range nature of the interactions should play a crucial role. It is promising that this model has certain qualitative features reflected in the data (preference for uranium with two f atoms per unit cell) which are hard to understand from earlier spin fluctuation theories. Also, the predicted pair state for \( UPt_3 \) has many promising aspects also missing in earlier theories. Moreover, there is a conceptual beauty to having a pair state which has maximal L and maximal S, as this is a direct generalization of the physics of \(^3He\) with which heavy fermions share many qualitative features. Hopefully, with increased experimental and theoretical effort, we can determine whether this is indeed the right approach to pursue for solving this problem.

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52. In the LMTO formalism employed here, there are radial functions and their energy derivatives involved in the variational wavefunctions. The latter terms are small in the current case and can be ignored in the coupling constant calculations.

53. The relativistic J=4 pair state is primarily L=5, S=1 in nature, but this has no relation to the pseudo-spin character of the pair state.

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Table 1. List of known heavy fermion superconductors with the number of f atoms per unit cell. In parenthesis is the nature of the low temperature distorted phase in the single f atom case (QP - quadrupolar, AF - antiferromagnetic, ? - not fully determined) and the resulting number of f atoms.

| Case          | f Atoms    |
|---------------|------------|
| $UPt_3$       | 2          |
| $UBe_{13}$    | 2          |
| $U_2PtC_2$    | 2          |
| $URu_2Si_2$   | 1 (QP/AF - 2) |
| $UPd_2Al_3$   | 1 (AF - 2) |
| $UNi_2Al_3$   | 1 (AF - 2) |
| $CeCu_2Si_2$  | 1 (? - 2 ?) |
Table 2. $f^2$ energies in the LS scheme.\textsuperscript{37}

| Term | Energy |
|------|--------|
| $^3H$ | $E_0 - 9E_3$ |
| $^3F$ | $E_0$ |
| $^3P$ | $E_0 + 33E_3$ |
| $^1I$ | $E_0 + 2E_1 + 70E_2 + 7E_3$ |
| $^1G$ | $E_0 + 2E_1 - 260E_2 - 4E_3$ |
| $^1D$ | $E_0 + 2E_1 + 286E_2 - 11E_3$ |
| $^1S$ | $E_0 + 9E_1$ |
Table 3. $f^2$ energies in the JJ scheme.\cite{42} Note that the $E_k$ parameters are different from those defined in the LS scheme.

| Term | Energy         |
|------|---------------|
| $J = 4$ | $E_0 - 5E_2$ |
| $J = 2$ | $E_0 + 9E_2$ |
| $J = 0$ | $E_0 + 3E_1$ |
Table 4. Summary of anisotropic $\Gamma$ for $J=4$ using parameters of Figure 6. $n$ is the type of bubble used (defined in Eq. 14), $\chi_0$ is the value ($eV^{-1}$) at which the divergence occurs, and $M$ signifies which $M_J$ state is the most attractive (with other attractive $M_J$ states listed in parenthesis). Note there is no attraction for $n=5$. For $J=2$, attraction is found for $M_J = 0$ in the $n=3,4$ cases, but weaker than $J=4$. For $J=0$, no attraction is found.

| $n$ | $\chi_0$ | $M$      |
|-----|----------|----------|
| 0   | 0.365    | 4 (3)    |
| 1   | 0.365    | 0 (1,2)  |
| 2   | 0.420    | 0 (2)    |
| 3   | 0.420    | 1        |
| 4   | 0.420    | 0        |
| 5   | 0.420    | -        |
Table 5. Hexagonal basis functions for J=4. The forms listed in this table should be (a) antisymmetrized ($|\mu > |\nu > -|\nu > |\mu >$) and (b) symmetrized (+ representation) or antisymmetrized (- representation) with respect to site before use. For $\Gamma_5$, $\alpha$ and $\beta$ are variational coefficients such that the sum of their squares is equal to one, and this representation occurs twice ($\alpha, \beta$ and $-\alpha, -\beta$). Note that $\Gamma_5$ and $\Gamma_6$ are doublets obtained by replacing $|\mu >$ by $|-\mu >$.

| Rep | Basis Function |
|-----|----------------|
| $\Gamma_5$ | $\alpha|5/2 > |3/2 > +\beta(0.8018|5/2 > | -1/2 > +0.5976|3/2 > |1/2 >)$ |
| $\Gamma_3$ | $0.7071|5/2 > |1/2 > +0.7071| -5/2 > | -1/2 >$ |
| $\Gamma_4$ | $0.7071|5/2 > |1/2 > -0.7071| -5/2 > | -1/2 >$ |
| $\Gamma_6$ | $0.5345|5/2 > | -3/2 > +0.8452|3/2 > | -1/2 >$ |
| $\Gamma_1$ | $0.2673(|5/2 > | -5/2 > +3|3/2 > | -3/2 > +2|1/2 > | -1/2 >$) |
Table 6. Coupling constants for $UPt_3$. These should be multiplied by the quantity $N\Gamma_4 Z^2$ to convert to real coupling constants.

| Rep | J=4 (+) | J=4 (-) | J=2 (+) | J=2 (-) | J=0 (+) | J=0 (-) |
|-----|---------|---------|---------|---------|---------|---------|
| $\Gamma_5$ | 0.069   | 0.073   |         |         |         |         |
| $\Gamma_5$ | 0.029   | 0.101   | 0.049   | 0.071   |         |         |
| $\Gamma_3$ | 0.024   | 0.064   |         |         |         |         |
| $\Gamma_4$ | 0.013   | 0.120   |         |         |         |         |
| $\Gamma_6$ | 0.018   | 0.125   | 0.035   | 0.106   |         |         |
| $\Gamma_1$ | 0.076   | 0.114   | 0.065   | 0.099   | 0.495   | 0.057   |
1. Interaction potential between two He atoms. The interaction potential of two f electrons of a uranium ion would look similar with appropriately scaled axes (with attraction in that case due to the ion core).

2. $f^2$ multiplet structure of a $U^{4+}$ ion. Energy is plotted versus $J$, with labels referring to $L$.

3. Effective interaction of Eq. 10 versus $\chi_0$.

4. Effective interaction of Eq. 11 (triplet, lower curve) and Eq. 12 (singlet, upper curve) versus $\chi_0$. This is very similar to the effective interaction in the $^3He$ problem.

5. Effective interaction (LS) in eV for $^3H$, $^3F$, $^3P$, and $^1I$ versus $\chi_0$ for parameters appropriate to a U ion ($E_0 = 1225$ 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.

6. Effective interaction (JJ) in eV for $J=4,2,0$ versus $\chi_0$ for a U ion. Same parameters and notation as in Figure 5.

7. Effective interaction (JJ) in eV for $J=4,2,0$ versus $\chi_0$ for parameters appropriate to a Ce ion ($E_0 = 6000$ meV, $E_1 = 484.5$ meV, $E_2 = 2.293$ meV, $E_3 = 47.67$ meV; note these are LS $E_k$). The zero of energy is the dashed line.

8. Plot of the k points used in the calculations on $UPt_3$ in symmetry planes of the Brillouin zone constructed from a uniform grid within an energy cutoff of 1 mRy of the Fermi energy. Lines represent the Fermi surface.
9. Plots of $|\Delta_{\sigma}(\vec{k})|$ with $\sigma = +$ for $\Gamma_6^-$ state on the grid of points of Figure 8. Size of the dots represent the magnitude of the gap. Where no dots appear, gap is zero or very small.

10. Same as Figure 9, but with $\sigma = -$.

11. Smoothed fit to the density of states (normalized to the normal state value) constructed from the gaps plotted in Figures 9 and 10. Energy units are normalized to the value of the largest gap.
