Tandem Pairing in Heavy Fermion Superconductors

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We examine the internal structure of the heavy fermion condensate, showing that it necessarily involves a d-wave pair of quasiparticles on neighboring lattice sites, condensed in tandem with a composite pair of electrons bound to a local moment, within a single unit cell. These two components draw upon the antiferromagnetic and Kondo interactions to cooperatively enhance the superconducting transition temperature. The tandem condensate is electrostatically active, with a small electric quadrupole moment coupling to strain that is predicted to lead to a superconducting shift in the NQR frequency.

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In many strongly interacting materials, quasiparticles are ill-formed at the superconducting transition, giving the Cooper pair a non-trivial internal structure. The 115 family of heavy fermion superconductors [1–4] provide an extreme example of this phenomenon, where quasiparticle formation, through the screening of local moments by electrons, coincides with the onset of superconductivity.

The 115 family has long attracted great interest for the remarkable rise of the superconducting transition temperature from $T_c = 0.2K$ in CeIn$_3$ under pressure [5] to 2.3K in CeCoIn$_5$ [13] and then up to 18.5K in PuCoGa$_5$ [4]. While the abundance of magnetism in the phase diagram has led to a consensus that spin fluctuations drive the superconductivity in the cerium compounds [5–9], the presence of unquenched local moments at $T_c$ is difficult to explain within this picture. In a typical spin-fluctuation mediated heavy fermion superconductor, the local moments quench to form a Pauli paramagnet ($\chi(T) \sim \chi_0$) well before the development of superconductivity. Yet NpPd$_5$Al$_2$ [10] and Ce(Co,Ir)In$_5$ [2, 11] exhibit a Curie-Weiss susceptibility, $\chi(T) \sim 1/(T + T_{CW})$ down to $T_c$. Moreover, the highest transition temperatures are found in the actinide 115s, which show no signs of magnetism.

These observations led us to recently propose [12] that the actinide 115s are composite pair superconductors [13], where the heavy Cooper pair forms by combining two electrons in two orthogonal Kondo channels with a spin flip to form a composite pair, $\Lambda_C = \langle \sum |c_{1\downarrow}^\dagger c_{2\uparrow}^\dagger S_+|^N + 2 \rangle$, where $c_{1,2}^\dagger$ create electrons in two orthogonal Kondo screening channels [12, 13]. However, composite pairing alone cannot account for the importance of magnetism in the Ce 115 phase diagram.

We are led by these conflicting observations to propose a model for the 115 materials where the composite and magnetic mechanisms work in tandem to drive superconductivity. Composite pairing originates from two channel Kondo impurities, while magnetic pairing emerges from antiferromagnetically coupled Kondo impurities. These two systems are equivalent at criticality in the dilute limit [13], and we argue that this connection persists to the lattice superconducting state that conceals a common quantum critical point (QCP) [10].

$$\Psi = PG \exp(\Lambda^\dagger)|0\rangle,$$

where $\Lambda^\dagger = \sum_k \Delta_k (a_k^\dagger a_{-k}^\dagger)$ creates a d-wave pair of quasiparticles and $P_G$ is the Gutzwiller projection operator restricting the number of f-electrons to one. Acting the Gutzwiller projector on the f-electron reveals its internal structure as a composite between a conduction electron and a spin flip at a given site $j$, $P_G f_j^\dagger \sim (c_{j\downarrow}^\dagger S_+) P_G$. The pairing field $\Lambda^\dagger$ contains three terms

$$\Lambda^\dagger = \sum_k \left( c_{k\uparrow}^\dagger : f_{k\uparrow}^\dagger \right) \left( \frac{\Delta_k^{\uparrow \downarrow}}{\Delta_k^\dagger} \frac{\Delta_k^\dagger}{\Delta_k} \right) \left( c_{-k\downarrow}^\dagger f_{-k\uparrow}^\dagger \right) = \Psi_C^\dagger + \Psi_M^\dagger + \Psi_M^\dagger,$$

FIG. 1: (Color online) A tandem pair contains a superposition of magnetic and composite pairing, both with d-wave symmetry. The magnetic pair (left) contains neighboring f-electrons, while the composite pair (right) combines a spin flip and two conduction electrons. The unit cell is denoted by dotted lines, with dots indicating the local moment sites.

To expose the interplay between magnetic and composite pairing, we examine the internal structure of a heavy fermion pair. In a Kondo lattice, the heavy quasiparticles are a linear combination $c_{1\uparrow} = u_k c_{k\uparrow}^\dagger + v_k f_{k\uparrow}^\dagger$, where $c$ and $f$ create conduction and localized electrons, respectively [17]. The wavefunction is...
The diagonal terms, with $\Delta \epsilon_k^c = u_k^c \Delta_k$ and $\Delta \epsilon_k^+ = v_k^+ \Delta_k$, create f- and conduction electron pairs. A d-wave pair of f-electrons is an inter-site operator, taking the form
\[
\Psi_M^\dagger = \sum_{i,j} \Delta M(R_{ij}) \left( (c^i_{\uparrow \downarrow} S_{ij})(c^j_{\uparrow \downarrow} S_{ij+}) \right)
\] (3)
outside the Gutzwiller projection. However, if we expand the off-diagonal terms in real space,
\[
\Psi_C^\dagger = \sum_{i,j} \Delta C(R_{ij}) \left[ c^i_{\uparrow \downarrow} c^j_{\uparrow \downarrow} S_{ij} \right]
\] (4)
where $\Delta C(R) = \sum_k (u_k^c v_k \Delta_k) e^{i k R}$, we find a composite pair formed between a triplet pair of conduction electrons and a spin flip[12–14]. Unlike its diagonal counterparts, which are necessarily inter-site, composite pairs are compact objects formed from pairs of orthogonal Wannier states surrounding a single local moment (Fig. 1).

Magnetic interactions favor the inter-site component of the pairing, while the two-channel Kondo effect favors the composite intra-site component. However, both components will always be present in the superconducting Kondo lattice. If the product of the Kondo screening channels has a d-wave symmetry, the composite and magnetic order parameters necessarily couple linearly to one another, a process that enhances the transition temperature over a large region of the phase diagram, providing a natural explanation for both the actinide and Ce 115s.

To treat these two pairing mechanisms simultaneously, we introduce the two channel Kondo-Heisenberg model,
\[
H = H_c + H_{K1} + H_{K2} + H_M
\] (5)
and solve it in the symplectic-N limit[12], where
\[
H_c = \sum_k \epsilon_k c^\dagger_k c_k, \quad H_M = J_H \sum_{\langle ij \rangle} \vec{S}_i \cdot \vec{S}_j
\] (6)
\[
H_{KT} = J_T \sum_j \psi^\dagger_{j\uparrow \downarrow} \sigma_{ab} \psi_{j\uparrow \downarrow} \cdot \vec{S}_j
\] (7)
where $\vec{S}_j$ is the local moment on site $j$, and $\psi_{j\uparrow \downarrow}$ is the Wannier state representing a conduction electron on site $j$ with symmetry $\Gamma$, $\psi_{j\uparrow \downarrow} = \sum_k \Phi_{j\uparrow \downarrow} \epsilon_k c_{k\sigma} e^{i k R_j}$.

where the form factor $\Phi_{j\uparrow \downarrow}$ is only diagonal in the spin indices in the absence of spin-orbit. Microscopically, the two orthogonal Kondo channels, $J_T$ arise from virtual fluctuations from the ground state doublet to excited singlets, where the two channels correspond to adding and removing an electron, respectively. The Ce 4f$^1$ state is split by tetragonal symmetry into three Kramer’s doublets, where $\Gamma_T^\uparrow$ is the ground state doublet[18, 19], so we may summarize the virtual valence fluctuations with:
\[
4 \Gamma_T^\uparrow \rightarrow 4 f^1 (\Gamma_T^\uparrow) \rightarrow 4 f^2 (\Gamma_T^\uparrow \otimes \Gamma_6)
\] (9)

Requiring the composite pairing to resonate with the d-wave magnetic pairing[20] uniquely selects $\Gamma_T^\uparrow \otimes \Gamma_6$ as the lowest doubly occupied state, as this combination leads to d-wave composite pairing[12]. A simplified two dimensional model is sufficient to illustrate the basic physics, where the d-wave composite pair now comes from the combination of s-wave hybridization in channel one and d-wave hybridization in channel two[21, 22]. The magnetism is included as an explicit RKKY interaction, $J_H$ between neighboring local moments $(ij)$, generated by integrating out electron in bands far from the Fermi surface. Treating the magnetism as a Heisenberg term leads to a two band version of resonating valence bond (RVB) superconductivity[23], where the local moments form valence bonds which “escape” into the conduction sea through the Kondo hybridization to form charged, mobile Cooper pairs[24].

To solve this model, we use a fermionic spin representation, $\vec{S}_j = f^\dagger_j \vec{\sigma}_N f_j$; symplectic-N maintains the time-reversal properties of SU(2) in the large N limit by using the symplectic generalization of the Pauli matrices $\vec{\sigma}_N$ to construct the spin Hamiltonians[12],
\[
H_{KT}(j) = \frac{J_T}{N} \left[ (\psi_{j\uparrow \downarrow} \tau_3 f_j)(\psi_{j\uparrow \downarrow} e^\dagger f_j) + (\psi_{j\uparrow \downarrow} \epsilon^\dagger f_j)(\psi_{j\uparrow \downarrow} f_j) \right]
\]
\[
H_M(ij) = -\frac{J_H}{N} \left[ (f^\dagger_j f_j)(f^\dagger_k f_i) + (f^\dagger_j f_j)(f_i f_k) \right]
\] (10)
where $\epsilon$ is the large N generalization of $i \sigma_2$. Each quartic term can be decoupled by a Hubbard-Stratonovich field, leading to normal, $V_T$ and anomalous, $\Delta_T$ hybridization in each Kondo channel and particle-hole, $h_{ij}$ and pairing, $\Delta^\dagger_{ij}$ terms for the spin liquid. The SU(2) gauge symmetry of the Hamiltonian, $f \rightarrow uf +ve^\dagger f^\dagger$ is used to eliminate $\Delta_1$. The lowest energy solutions contain only pairing fields in the magnetic and second Kondo channels, giving rise to three Hubbard-Stratonovich fields, $V_1$, $\Delta_2$ and $\Delta_H$, where $\Delta_H$ is d-wave in the plane, so that $\Delta_H^\dagger = \Delta_H(\cos k_x - \cos k_y)$. Using the Nambu notation, $c^\dagger_k = (c^\dagger_k, \epsilon^\dagger c_{-k})$, $\tilde{f}^\dagger_k = (f^\dagger_k, \epsilon^\dagger f_{-k})$, and defining $\nu_k = V_{ij} \Phi_{1jk} + \Delta_2 \Phi_{2k}$, the mean field Hamiltonian can be concisely written as
\[
H = \sum_k \left( c^\dagger_k \tilde{f}^\dagger_k \nu_k \frac{\epsilon_k}{\nu_k} \lambda \tau_3 + \Delta_H^\dagger \tau_1 \tilde{f}^\dagger_k \right) + N \left( V_{ij}^\dagger V_{ij} + \frac{\Delta_2^\dagger}{J_2} + \frac{4 \Delta_H^\dagger}{J_H} \right),
\] (11)
where $\lambda$ is the Lagrange multiplier enforcing the constraint $n_f = 1$. The mean field Hamiltonian can be diagonalized analytically. Upon minimizing the free energy, we obtain four equations for $\lambda, V_{ij}, \Delta_2$, and $\Delta_H$. Solving these numerically, and searching the full parameter space of $J_2/J_1, J_H/J_1$ and $T$ to find both first and second order phase transitions, we find four distinct phases: a light Fermi liquid with free local moments when all parameters are zero, at high temperatures; a heavy Fermi
liquid when either $V_1$ or $\Delta_2$ are finite, with symmetry $\Gamma$, below $T_{K1}$: a spin liquid state decoupled from a light Fermi liquid when $\Delta_H$ is finite, below $T_{SL}$; and a tandem superconducting ground state with $V_1$, $\Delta_2$ and $\Delta_H$ all finite, below $T_c$, as shown in Fig. 2. There is no long range magnetic order due to our fermionic spin representation.

Experimentally, CeMnIn$_5$ can be continuously tuned from $M = $ Co to Rh to Ir[3]. While CeRhIn$_5$ is a canonical example of a magnetically paired superconductor, where moderate pressure reveals a superconducting dome as the Néel temperature vanishes[1], further pressure[25] or Ir doping on the Rh site[3] leads to a second dome, where spin fluctuations are weaker[26]. We assume that the changing chemical pressure varies the relative strengths of the Kondo and RKKY couplings, so that doping traces out a path through the phase diagram in dot-dashed white) are plotted for comparison. Temperatures are scaled by $T_{K1}$, which may itself vary as one moves around the phase diagram[27]. While we always find a superconducting ground state, due to our choice of a fermionic spin representation, real materials will have an antiferromagnetic ground state for $T_{SL}/T_{K1}$ sufficiently large.

A qualitative understanding of this tandem pairing can be obtained within a simple Landau expansion. For $T \sim T_c \ll T_{K1}$, $\Phi \equiv \Delta_2$ and $\Psi \equiv \Delta_H$ will be small, and the free energy can be expressed as

$$F = \alpha_1(T_c - T)\Psi^2 + \alpha_2(T_c - T)\Phi^2 + 2\gamma\Psi\Phi + \beta_1\Psi^4/4 + \beta_3\Phi^4 + 2\beta_2(\Psi^2\Phi^2)$$

(12)

$\alpha_1, \beta_{1,2,3}$, and $\gamma$ are all functions of $\lambda$ and $V_1$ and can be calculated exactly in the mean field limit. The linear coupling of the two order parameters, $\gamma = \partial F/\partial \Delta_2 \partial \Delta_H$ is always nonzero in the heavy Fermi liquid, leading to an enhancement of the transition temperature,

$$T_c = \frac{T_{c1} + T_{c2}}{2} + \sqrt{\frac{(T_{c1} - T_{c2})^2}{2} + \frac{\gamma^2}{\alpha_1 \alpha_2}}$$

(13)

For $\beta_1 \beta_2 > \beta_1^2$, the two order parameters are only weakly repulsive, leading to smooth crossovers from magnetic to composite pairing under the superconducting dome[28].

While the development of conventional superconductivity does not change the underlying charge distribution, tandem pairing is electrostatically active, as composite pairing redistributes charge, leading to an electric quadrupole moment. The transition temperature of the 115 superconductors is known to increase linearly with the lattice $c/a$ ratio[29], conventionally attributed to decreasing dimensionality. Our theory suggests an alternative interpretation: in a condensate with a quadrupole moment, $Q_{zz} \propto \Psi^2$, which couples linearly to the tetragonal strain, $\Delta F \propto -Q_{zz}u_{tet}$, the second term in the Landau free energy becomes $\alpha_2[1 - (T/(T_c + \lambda u_{tet}))]\Psi^2/2$, naturally accounting for the linear increase in $T_c$. The development of a condensate quadrupole moment should be also detectable as a shift of the nuclear quadrupole resonance (NQR) frequency at the nuclei of the surrounding ions.
The link between f-electron valence and the Kondo effect is well established, but tandem pairing introduces a new element to this relationship. Changes in the charge distribution around the Kondo ion can be read off from its coupling to the changes in the chemical potential, \( \Delta \rho(x) = |e| \delta H / \delta \mu(x) \). The sensitivity of the Kondo couplings to \( \mu \) is obtained from a Schrieffer-Wolff transformation of a two-channel Anderson model, which gives \( J_{\uparrow \downarrow}^{-1} = \Delta E_{\uparrow \downarrow} / V_{\Gamma,0}^2 \). Here, \( V_{\Gamma,0} \) are the bare hybridizations and \( \Delta E_{\uparrow \downarrow} \) are the charge excitation energies. With a shift in \( \mu \to \mu + \delta \mu(x) \), \( \Delta J_{\uparrow \downarrow}^{-1} = \pm |\Phi_{\Gamma}(x)|^2 \delta \mu(x) / V_{\Gamma,0}^2 \). The sign is positive for \( J_1 \) and negative for \( J_2 \) because they involve fluctuations to the empty and doubly occupied states, respectively: \( f^0 \Gamma \equiv f^1 \Gamma \equiv f^2 \). Differentiating \( \rho(x) \) with respect to \( \delta \mu(x) \), the change in \( \rho(x) \) will be:

\[
\Delta \rho(x) = |e| \left[ \left( \frac{V_{\Gamma,1}}{V_{\Gamma,0}} \right)^2 |\Phi_{\Gamma}(x)|^2 - \left( \frac{V_{\Gamma,2}}{V_{\Gamma,0}} \right)^2 |\Phi_{\Gamma}(x)|^2 \right].
\]

(14)

For equal channel strengths, the total charge is constant, and the f-ion will develop equal hole densities in \( \Gamma_{\uparrow \downarrow} \) and electron densities in \( \Gamma_0 \), leading to a positive change in the electric field gradient, \( \partial E_z / \partial z \propto (T_c - T) > 0 \) at the in-plane In site that will appear as a shift in the NQR frequencies growing abruptly below \( T_c \) (see Figure 4).

FIG. 4: (Color online) Predicted NQR frequency shift, \( \Delta \nu_{NQR} \) in CeMnIn. The inset shows the relative locations of the indiums in-, In(1) and out-of-plane, In(2). \( \Delta \nu_{NQR} \) measures the change in the electric field gradient (EFG) due to the onset of superconductivity. For equal channel strengths, the total charge of the f-ion remains unity, but the increasing occupations of the empty and doubly occupied sites cause holes to build up with symmetry \( \Gamma_{\uparrow \downarrow} \) (orange) and electrons with symmetry \( \Gamma_0 \) (blue). The change in charge distribution and resulting electric fields are shown above in a slice along the [110] direction (dashed line in the inset). The positive EFG, \( \partial E_z / \partial z \) at the In(1) site will lead to a sharp positive shift in \( \nu_{NQR} \) starting at \( T_c \).

The f-electron valence should also contain a small superconducting shift, observable with core-level X-ray spectroscopy, obtained by integrating \( \Delta \sigma_f(T) \propto \Psi_c \propto \Delta_2 \) when \( J_1 > J_2 \). While the development of Kondo screening leads to a gradual valence decrease through \( T_K \), as it is a crossover scale, the development of superconductivity is a phase transition, leading to a sharp mean-field increase. Observation of sharp shifts at \( T_c \) in either the NQR frequency or the valence would constitute an unambiguous confirmation of the electrostatically active tandem condensate.

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