

Magnetic impurities in d -wave superconductors

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We solve the problem of a magnetic impurity in a $d_{x^2-y^2}$ -wave superconductor by a variational method. A moment is found to exist in the superconducting state only if the Kondo temperature in the normal state is larger than the maximum in the superconducting gap function. If a moment exists in the superconducting state, and provided spin-orbit coupling is nonzero, it induces a time-reversal breaking superconducting state locally around the impurity which is a linear combination of the $d_{x^2-y^2}$ and d_{xy} states. The current pattern around the impurity in this state is evaluated. [S0163-1829(99)06137-8]

INTRODUCTION

Since magnetic impurities break time-reversal invariance, they tend to destroy superconductivity.¹ In superconducting ground states paired in a finite angular momentum (or its appropriate generalization in a lattice), nonmagnetic impurities are also pair-breaking since their potential, in general, does not transform in the same way as the order parameter.^{2,3}

Recently a new phenomenon associated with magnetic impurities in a $d_{x^2-y^2}$ condensate was proposed. It was argued that the interaction between the magnetic impurity spin and the orbital moment of the condensate can help to stabilize a new time-reversal violating phase $\alpha d_{x^2-y^2} + i\beta d_{xy}$.⁴ The physical point is that such a state has a finite orbital moment around the impurity. Provided the spin-orbit coupling is finite, such a state interacts linearly with the magnetic moment. Therefore it is necessarily induced with the ratio β/α of order $E_{so}/\delta E_c$ where E_{so} is the spin-orbit coupling energy and δE_c is the difference in condensation energy of the $d_{x^2-y^2}$ and the d_{xy} states.

In this paper we examine this idea through a variational method introduced for the Kondo (and mixed-valence) problem in normal metals.⁵ The variational method foreshadowed the development of the noncrossing approximation,⁶ the $1/N$ method⁷ and the slave-boson approach.⁸ For the ground state properties these methods produce the same results as the variational approach. First we ask the question: Under what condition can a moment exist in the superconducting state. This is the question of the disappearance of the Kondo-effect in a d -wave superconductor. This problem also has been examined.^{9,10} We hope, our simple approach, with results equivalent to those derived earlier, makes the physical issues clearer. Because the density of states of quasiparticles goes to zero linearly in energy, the logarithmic Kondo singularity in the scattering matrix of the moment with conduction electrons is absent but, with a finite exchange coupling, the Kondo effect and the disappearance of the magnetic moment is still possible. The condition for the moment to exist in the superconducting state is found to be $T_K/\Delta \leq 1$, where T_K is the Kondo temperature in the normal state and Δ is the maximum in the superconducting gap function. (This is a more stringent condition than in s -wave superconductors.^{11,12}) Second, we find the necessary condition for inducing the locally

time-reversal breaking state. In agreement with earlier conclusions, a finite spin-orbit coupling is found essential. With the variational wave-function, we also calculate the current distribution induced around the impurity. We also briefly discuss the problem of several impurities to conclude that a global time-reversal breaking phase is unlikely to result from this mechanism.

THE MODEL

We consider the usual BCS Hamiltonian (H_{BCS}) and the Anderson Hamiltonian (H_I) to describe the superconductor and the impurity respectively:

$$H_{BCS} = \sum_{\mathbf{k}\sigma} \lambda_{\mathbf{k}} \gamma_{\mathbf{k}\sigma}^\dagger \gamma_{\mathbf{k}\sigma} + E_G \quad (1)$$

with $\lambda_{\mathbf{k}} = \sqrt{\epsilon_{\mathbf{k}}^2 + \Delta_{\mathbf{k}}^2}$, where $\epsilon_{\mathbf{k}}$ are the energy of conduction electrons with respect to the chemical potential $\Delta_{\mathbf{k}} = \sum_{\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'}^{BCS} \langle c_{-\mathbf{k}\downarrow} c_{\mathbf{k}\uparrow} \rangle$ is the superconducting order parameter, $V_{\mathbf{k}\mathbf{k}'}^{BCS}$ is the BCS attractive interaction, and $c_{\mathbf{k}\uparrow}^\dagger$ creates an electron with momentum \mathbf{k} and spin \uparrow :

$$\gamma_{\mathbf{k}\uparrow} = u_{\mathbf{k}} c_{\mathbf{k}\uparrow} - v_{\mathbf{k}} c_{-\mathbf{k}\downarrow}^\dagger, \quad \gamma_{-\mathbf{k}\downarrow} = v_{\mathbf{k}} c_{\mathbf{k}\uparrow}^\dagger + u_{\mathbf{k}} c_{-\mathbf{k}\downarrow} \quad (2)$$

annihilate and create the quasiparticles in the superconducting state and

$$u_{\mathbf{k}} = \sqrt{\frac{1}{2} \left(1 + \frac{\epsilon_{\mathbf{k}}}{\lambda_{\mathbf{k}}} \right)}, \quad v_{\mathbf{k}} = \sqrt{\frac{1}{2} \left(1 - \frac{\epsilon_{\mathbf{k}}}{\lambda_{\mathbf{k}}} \right)} \frac{\Delta_{\mathbf{k}}}{|\Delta_{\mathbf{k}}|}. \quad (3)$$

The ground state is given by $|G\rangle = \prod_{\mathbf{k}} (u_{\mathbf{k}} + v_{\mathbf{k}} c_{\mathbf{k}\uparrow}^\dagger c_{-\mathbf{k}\downarrow}^\dagger) |0\rangle$ with an energy E_G .

The impurity Hamiltonian is

$$H_I = \epsilon_0 \sum_{\sigma} d_{0\sigma}^\dagger d_{0\sigma} + U_0 n_{0\uparrow} n_{0\downarrow} + \sum_{\mathbf{k}\sigma} V_{\mathbf{k}} d_{0\sigma}^\dagger c_{\mathbf{k}\sigma} + \text{H.c.} \quad (4)$$

$d_{0\sigma}^\dagger$ creates an electron with spin σ in the impurity orbital and $n_{0\uparrow} = d_{0\uparrow}^\dagger d_{0\uparrow}$. We take the limit $U_0 \rightarrow \infty$.

With the Bogoliubov transformation, Eq. (2), the hybridization term [third term in Eq. (4)] is

$$H_{d,c} = \sum_{\mathbf{k}\sigma} V_{\mathbf{k}} [d_{0\uparrow}^\dagger (u_{\mathbf{k}}^* \gamma_{\mathbf{k}\uparrow} + v_{\mathbf{k}} \gamma_{-\mathbf{k}\downarrow}^\dagger) + d_{0\downarrow}^\dagger (-v_{\mathbf{k}} \gamma_{\mathbf{k}\uparrow}^\dagger + u_{\mathbf{k}}^* \gamma_{-\mathbf{k}\downarrow})] + \text{H.c.}, \quad (5)$$

where we have assumed $V_{\mathbf{k}} = V_{-\mathbf{k}}$.

We also include the spin-orbit interaction between the spin of the impurity (\mathbf{s}) and the angular momentum of the conduction electrons (\mathbf{L}):

$$H_{s-o} = g \int dr^2 \frac{\mathbf{s}(0) \cdot \mathbf{L}(r)}{|\mathbf{r}|^3} \quad (6)$$

with $\mathbf{s} = d_{0\alpha}^\dagger \sigma_{\alpha\beta} d_{0\beta}$ (σ are the usual Pauli matrices) and $\mathbf{L}(\mathbf{r}) = c_{r\sigma}^\dagger \mathbf{L} c_{r\sigma}$. L^+ and L^- mix states which are even with odd under reflection about the x - y plane. As odd states have zero amplitude in the x - y plane L^+ and L^- are irrelevant in two dimensions, which is the case we consider with copper-oxide metals in mind. L_z scatters a \mathbf{k} state to a \mathbf{k}' states with $|\mathbf{k}| = |\mathbf{k}'|$.

The spin-orbit interaction can therefore be rewritten as

$$\begin{aligned} H_{s-o} &= g s_z \sum_{\mathbf{k}, \mathbf{k}' \sigma} L_z^{\mathbf{k}\mathbf{k}'} c_{\mathbf{k}\sigma}^\dagger c_{\mathbf{k}'\sigma} \\ &= g s_z \sum_{\mathbf{k}, \mathbf{k}' \sigma} L_z^{\mathbf{k}\mathbf{k}'} c_{\mathbf{k}\sigma}^\dagger c_{\mathbf{k}'\sigma} \\ &= g s_z \sum_{\mathbf{k}, \mathbf{k}' \sigma} L_z^{\mathbf{k}\mathbf{k}'} [(\gamma_{\mathbf{k}\uparrow}^\dagger \gamma_{\mathbf{k}'\uparrow} - \gamma_{-\mathbf{k}\downarrow}^\dagger \gamma_{-\mathbf{k}'\downarrow}) (u_{\mathbf{k}} u_{\mathbf{k}'}^* + v_{\mathbf{k}} v_{\mathbf{k}'}^*) \\ &\quad + \gamma_{\mathbf{k}\uparrow}^\dagger \gamma_{-\mathbf{k}'\downarrow}^\dagger (u_{\mathbf{k}} v_{\mathbf{k}'} - v_{\mathbf{k}} u_{\mathbf{k}'}) + \text{H.c.}]. \end{aligned}$$

L_z anticommutes with the time-reversal operator (T). Therefore $L_z^{\mathbf{k}\mathbf{k}'} = -L_z^{\mathbf{k}'\mathbf{k}} = (L_z^{\mathbf{k}'\mathbf{k}})^* = i \text{Im}(L_z^{\mathbf{k}'\mathbf{k}})$. For plane waves $L_z^{(k, \varphi)(k', \varphi')} = i \hbar k_r^2 / R \sin(\varphi - \varphi')$, where R is the radius of the sample. We absorb the coefficient in L_z defining a coupling g' . L_z is invariant under rotations around \hat{z} and changes sign under reflection over planes which contains the \hat{z} . If the problem has square symmetry in the x - y plane then we have a C_{4v} group symmetry and L_z transforms as the one dimensional representation A_{2g} . The other possible representation of the same group are the one dimensional $A_{1g}(s)$, $B_{1g}(d_{x^2-y^2})$, and $B_{2g}(d_{xy})$, and the double representation $E(p_x, p_y)$.

The model Hamiltonian considered in this paper is

$$H = H_{\text{BCS}} + H_I + H_{s-o}. \quad (7)$$

VARIATIONAL CALCULATIONS

We consider a variational wavefunction which is a spin-doublet, reflecting a moment in the ground state, as well as a variational wave function which does not have a moment in the ground state. For the doublet we choose the wave function

$$|D \uparrow\rangle = \left(d_{0\uparrow}^\dagger + \sum_{\mathbf{k}} \alpha_{\mathbf{k}} \gamma_{\mathbf{k}\uparrow}^\dagger + d_{0\uparrow}^\dagger \sum_{\mathbf{k}\mathbf{k}'} a_{\mathbf{k}\mathbf{k}'} \gamma_{\mathbf{k}\uparrow}^\dagger \gamma_{-\mathbf{k}'\downarrow}^\dagger \right) |G\rangle. \quad (8)$$

The first two terms are mixed by the hybridization, while the last term, which is a singlet pair of quasiparticles coupled to the local moment is mixed with the first term by the spin-orbit coupling under certain conditions. The $U = \infty$ constraint is obeyed.

The variational functions $\alpha_{\mathbf{k}}$, $a_{\mathbf{k}\mathbf{k}'}$ are determined by the condition $\delta(\langle D|H|D\rangle - E_D \langle D|D\rangle) = 0$, where the doublet energy (E_D) is referred to the energy of the BCS state. We get

$$E_D = \epsilon_0 - \sum_{\mathbf{k}} \alpha_{\mathbf{k}} V_{\mathbf{k}} u_{\mathbf{k}}^* - \frac{g}{2} \sum_{\mathbf{k}\mathbf{k}'} L_z^{\mathbf{k}\mathbf{k}'} (u_{\mathbf{k}}^* v_{\mathbf{k}'}^* - v_{\mathbf{k}}^* u_{\mathbf{k}'}) a_{\mathbf{k}\mathbf{k}'}. \quad (9)$$

One should notice that $\alpha_{\mathbf{k}}$ and $a_{\mathbf{k}\mathbf{k}'}$ have the symmetry of $V_{\mathbf{k}}$ and $L_z \cdot v_{\mathbf{k}}$, respectively. In a pure $d_{x^2-y^2}$ superconductor $a_{\mathbf{k}\mathbf{k}'}$ has d_{xy} symmetry (as $\Gamma_{A_{2g}} \otimes \Gamma_{B_{1g}} = \Gamma_{B_{2g}}$). In the symmetric s wave $a_{\mathbf{k}\mathbf{k}'} = 0$ because the form factor $F_f = u_{\mathbf{k}} v_{\mathbf{k}'} - v_{\mathbf{k}} u_{\mathbf{k}'}$ vanish for $|\mathbf{k}| = |\mathbf{k}'|$. It is also worth noting that momenta k, k' with different signs of the coherence factor $v_{\mathbf{k}}$ give the largest contributions. The complete expression of $\alpha_{\mathbf{k}}$ and $a_{\mathbf{k}\mathbf{k}'}$ and E_D are given in the Appendix.

Consider next the state without a moment in the ground state. H_{BCS} and H_I commutes with total spin (S_T , impurity + conduction electron spins) while H_{s-o} does not. Then the eigenstates of H cannot be classified by the total spin S_T . As a consequence the usual singlet solution ($S_T = 0$) is replaced by a state with total spin projection z , $S_z = 0$, we will continue calling this state the singlet for simplicity.

The simplest *singlet* variational wave-function has the form

$$\begin{aligned} |S\rangle &= \left(1 + \sum_{\mathbf{k}} \beta_{\mathbf{k}} S_{\mathbf{k}}^\dagger + \sum_{\mathbf{k}\mathbf{k}'} M_{\mathbf{k}\mathbf{k}'} \gamma_{\mathbf{k}\uparrow}^\dagger \gamma_{-\mathbf{k}'\downarrow}^\dagger \right. \\ &\quad \left. + \sum_{\mathbf{k}\mathbf{k}''} \frac{b_{\mathbf{k}\mathbf{k}''}}{2} T_{\mathbf{k}}^\dagger \gamma_{\mathbf{k}\uparrow}^\dagger \gamma_{-\mathbf{k}''\downarrow}^\dagger \right) |G\rangle, \quad (10) \\ S_{\mathbf{k}}^\dagger &= d_{0\uparrow}^\dagger \gamma_{-\mathbf{k}\downarrow}^\dagger - d_{0\downarrow}^\dagger \gamma_{\mathbf{k}\uparrow}^\dagger, \\ T_{\mathbf{k}}^\dagger &= d_{0\uparrow}^\dagger \gamma_{-\mathbf{k}\downarrow}^\dagger + d_{0\downarrow}^\dagger \gamma_{\mathbf{k}\uparrow}^\dagger. \end{aligned}$$

Again the last term can be nonzero only due to spin-orbit scattering. The first three terms naturally arise in a model with hybridization and $U = \infty$.¹¹ The complete expression of the coefficients of Eq. (10) as well as the expression for the ground state energy E_S are given in Appendix B.

In a normal metal, due to the Kondo-effect, the singlet always has lower energy. In the limit $\epsilon_0 \ll -|V|$,

$$\epsilon_0 \sim -2V^2 \rho_0 \ln \left(\frac{W}{E_D - E_S} \right), \quad (11)$$

where ρ_0 is the density of states at the Fermi level and W is the half-width band. We obtain the usual Kondo temperature

$$T_K = E_D - E_S = W \exp \left(\frac{-1}{2\rho_0 J} \right) \quad (12)$$

with $J = V^2 / |\epsilon_0|$.

For an s -wave superconductor ($\Delta_{\mathbf{k}} = \Delta_0$) in the same limit, $E_S \rightarrow \epsilon_0 + \Delta_0$ while $E_D \rightarrow \epsilon_0$. As a consequence the low

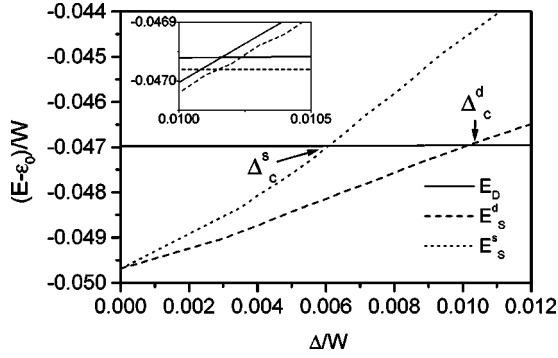


FIG. 1. Doublet energy $E_D^s = E_D^d$ (full line), and singlet energies E_S^s (dotted line) and E_S^d (dashed line) as a function of Δ_0 , for s -wave and $d_{x^2-y^2}$ superconductors. Δ_c^s and Δ_c^d denote the values of the superconducting order parameter where the levels crosses. Other parameters are $\epsilon_0/W = -0.4$, $V/W = 0.28\Delta_c$. The inset shows E_D^d and E_S^d with the inclusion of an spin-orbit interaction, with a constant coupling $g'/W = 0.1$ (dashed lines) compared with the $g' = 0$ case (full lines), near the crossing Δ_c^d .

energy state evolves from a singlet to the doublet when $-\epsilon_0/|V|$ grows.^{11,12} In both cases the contribution of spin-orbit term is 0.

The low energy limit of the density of states of a superconductor with nodes (points in 2D, lines in 3D) at the Fermi level is $\rho(\omega) = \rho_0\omega/\Delta_0$. The logarithmic singularity leading to the Kondo effect is replaced by a term proportional to $\omega \ln(\omega)$ in the superconductor. An approximate analytic expression of binding energy obtained from Eqs. (B1),(B2) is

$$\epsilon_0 \sim -2V^2\rho_0 \left[\frac{E_D^d - E_S^d}{\Delta_0} \ln \left(\frac{|E_D^d - E_S^d|}{E_D^d - E_S^d + \omega_c} \right) + \frac{\omega_c}{\Delta_0} + \ln \left(\frac{W}{\omega_c + (E_D^d - E_S^d)} \right) \right], \quad (13)$$

where we have assumed a superconducting density of states linear in energy up to $\omega_c \sim \Delta_0$, and constant from there to W , and we have approximated the self-energy terms in Eq. (B2), $-\Gamma_1(\lambda_{\mathbf{k}} - E_S) - \Gamma_2(\lambda_{\mathbf{k}} - E_S)$, by $E_D^d - \epsilon_0$. Using Eq. (12), it is possible to re-express Eq. (13) as

$$\frac{E_D^d - E_S^d}{\Delta_0} \ln \left(\frac{|E_D^d - E_S^d|}{\Delta_0} \right) \sim \ln \left(\frac{\Delta_0}{T_K} \right). \quad (14)$$

We conclude from Eq. (14) that the doublet has lower energy if $\Delta_0 > T_K$.

In Fig. 1 we show E_D and E_S as a function of Δ_0 for a $d_{x^2-y^2}$ order parameter $\Delta_{\mathbf{k}} = \Delta_0 \cos(2\varphi)$, where φ is the polar angle, and an s -wave superconductor, $\Delta_{\mathbf{k}} = \Delta_0$. We assume a constant noninteracting density of states $\rho_0 = 1/2W$, with W the half-band width. Other parameters are $\epsilon_0/W = -0.4$, $V/W = 0.28$. It can be seen that while E_D remain almost constant and equivalent for s and d , E_S grows as Δ increases. This reflects the displacement of the low-energy excited states to higher energies and is faster for the gapped s wave (E_S^s). As a consequence there is a crossing of levels at a given Δ_c . In the inset the effect of the spin-orbit coupling is shown. Both E_D^d and E_S^d takes advantage of this term gaining a similar amount of energy and leaving Δ_c^d unaffected.

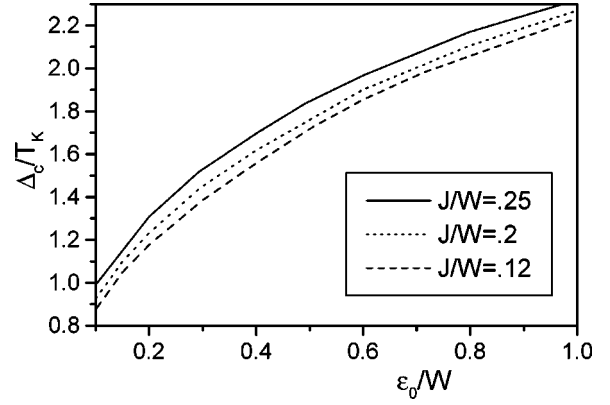


FIG. 2. Critical values $\Delta_c^d/T_K(J)$ as a function of $|\epsilon_0|/W$ for different values of J .

Figure 2 shows Δ_c^d as a function of $|\epsilon_0|/W$ for different values of J . It can be seen that Δ_c^d approximately scales with $T_K = W \exp(-W/J)$. The quotient Δ_c^d/T_K lies in the range 0.8–2.4 while T_K and Δ_0 vary by several orders of magnitude.

Changes in the macroscopic superconducting density of states $\rho(\omega \sim 0)$ will change the above results. A finite concentration of impurities in a d superconductor induces a finite $\rho(\omega = 0)^2$ and helps to stabilize the singlet, while a complex macroscopic phase such as $d_{x^2-y^2} + id_{xy}$ has the opposite effect.

We can see how the doublet modifies the superconducting condensate

$$\frac{\langle D\sigma | c_{-\mathbf{k}\downarrow} c_{\mathbf{k}\uparrow} | D\sigma \rangle}{\langle D\sigma | D\sigma \rangle} = u_{\mathbf{k}} v_{\mathbf{k}} \left(1 - \frac{\alpha_{\mathbf{k}}^2 + \sum_{\mathbf{k}'} a_{\mathbf{k}\mathbf{k}'}^2}{1 + \sum_{\mathbf{k}} \alpha_{\mathbf{k}}^2 + \sum_{\mathbf{k}\mathbf{k}'} a_{\mathbf{k}\mathbf{k}'}^2} \right). \quad (15)$$

It can be seen that the presence of the impurity diminishes the $(\mathbf{k}\uparrow, -\mathbf{k}\downarrow)$ pairing; this reduction is of the order $1/N$ (N is the number of sites), for one impurity but is measurable for a finite concentration of impurities. For $V_{\mathbf{k}} = V$, the largest values of $\alpha_{\mathbf{k}}^2$ occur at the nodes of $\Delta_{\mathbf{k}}$. Therefore these states lose a greater relative weight. This tendency agrees with the extended gapless region located in the gap function centered around the nodes, found in a momentum-dependent scattering for nonmagnetic impurities in unconventional superconductors.² The singlet has a similar effect on the correlation function $\langle c_{-\mathbf{k}\downarrow} c_{\mathbf{k}\uparrow} \rangle$ [$\alpha_{\mathbf{k}}^2 + \sum_{\mathbf{k}'} a_{\mathbf{k}\mathbf{k}'}^2$, should be replaced by $2\beta_{\mathbf{k}}^2 + \sum_{\mathbf{k}\mathbf{k}'} M_{\mathbf{k}\mathbf{k}'}^2 + \sum_{\mathbf{k}'\mathbf{k}''} b_{\mathbf{k}\mathbf{k}'\mathbf{k}''}^2$ in Eq. (13)]. In this case a bigger distortion is expected (in general $\beta_{\mathbf{k}}$ is greater than $\alpha_{\mathbf{k}}$).

The spin-orbit interaction introduces a new correlation

$$\langle D\sigma | D\sigma \rangle F_{\mathbf{k}\mathbf{k}'}^D = \langle D\sigma | c_{-\mathbf{k}\downarrow} c_{\mathbf{k}\uparrow} | D\sigma \rangle = \frac{ig\sigma \text{Im}(L_z^{\mathbf{k}\mathbf{k}'}) (u_{\mathbf{k}'} v_{\mathbf{k}} - v_{\mathbf{k}'} u_{\mathbf{k}})}{(\lambda_{\mathbf{k}} + \lambda_{\mathbf{k}'} + \delta_D)}. \quad (16)$$

If the symmetry of the pure superconductor is $d_{x^2-y^2}$, $F_{\mathbf{k}\mathbf{k}'}^D \sim id_{xy}$. We can calculate the induced order parameter in real space:

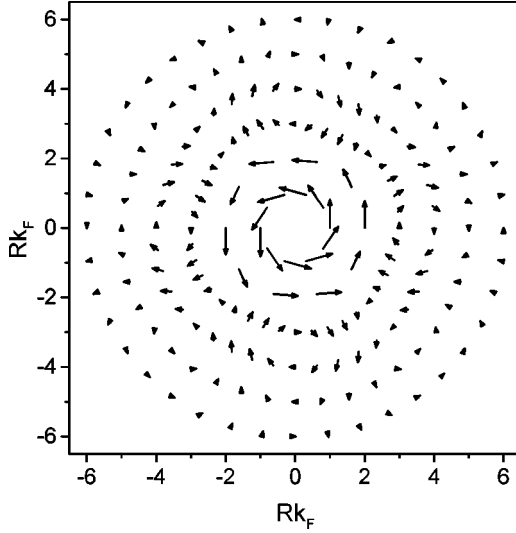


FIG. 3. Current density $\mathbf{j}(\mathbf{R})$ around the impurity. The magnitude and direction of the arrows represent the current at that point. The sense of the currents depends on the impurity spin projection s_z .

$$\begin{aligned} \Delta_i(\mathbf{R}, \mathbf{r}) &= \frac{\langle D\sigma | c_{\mathbf{R}-\mathbf{r}_\downarrow} c_{\mathbf{R}+\mathbf{r}_\uparrow} | D\sigma \rangle}{\langle D\sigma | D\sigma \rangle} \\ &= \frac{1}{N} \sum_{\mathbf{k}\mathbf{k}'} e^{i\mathbf{R}(\mathbf{k}-\mathbf{k}')} e^{i\mathbf{r}(\mathbf{k}+\mathbf{k}')} F_{\mathbf{k}\mathbf{k}'}^D. \end{aligned} \quad (17)$$

Note that as $\mathbf{k} \neq \mathbf{k}'$, Δ_i depends on \mathbf{R} . Taking the impurity site ($\mathbf{R}=0$) as the center of the symmetry this state has a d_{xy} symmetry. Centered at a different site \mathbf{R} , $\Delta_i(\mathbf{R}, \mathbf{r})$ does not have a definite symmetry in the relative coordinate \mathbf{r} . This state produces a complex pattern of spontaneous currents around the impurity which can be seen evaluating the current density operator

$$\begin{aligned} \mathbf{j}(\mathbf{R}) \langle D\sigma | D\sigma \rangle &= \langle D\sigma | \hat{\mathbf{j}}(\mathbf{R}) | D\sigma \rangle \\ &= \sigma c \sum_{\mathbf{k}\mathbf{k}'} e^{i\mathbf{R}(\mathbf{k}-\mathbf{k}')} (\mathbf{k} + \mathbf{k}') \\ &\quad \times (u_{\mathbf{k}} v_{\mathbf{k}'} - v_{\mathbf{k}} u_{\mathbf{k}'}) a_{\mathbf{k}\mathbf{k}'}^*, \end{aligned} \quad (18)$$

where the constant $c = e\hbar/m \text{Vol}$.

Expanding the form factor $(u_{\mathbf{k}} v_{\mathbf{k}'} - v_{\mathbf{k}} u_{\mathbf{k}'})^2$ of Eq. (18) in the first two spherical harmonics we can get an approximate analytical form for this current

$$\mathbf{j}(R, \varphi) \propto \frac{J_1^2(R)}{R} - \cos^2(\varphi) \left(\frac{J_1^2(R)}{R} - 8 \frac{J_1(R)J_2(R)}{R^2} \right) + \dots, \quad (19)$$

where $J_n(R)$ is the usual Bessel function of order n .

In Fig. 3 we show the current density $\mathbf{j}(\mathbf{R})$. The magnitude and direction of the arrows represent the current at that point. This pattern can be understood as the sum of a net current around the impurity and eight secondary currents. Four of them are around the points $\mathbf{R}\mathbf{k}_F = (\pm 4, 0)$ and $\mathbf{R}\mathbf{k}_F = (0, \pm 4)$, and have the same sense as the net current, and the other are around the points $\mathbf{R}\mathbf{k}_F = (\pm 4, \pm 4)$, with the oppos-

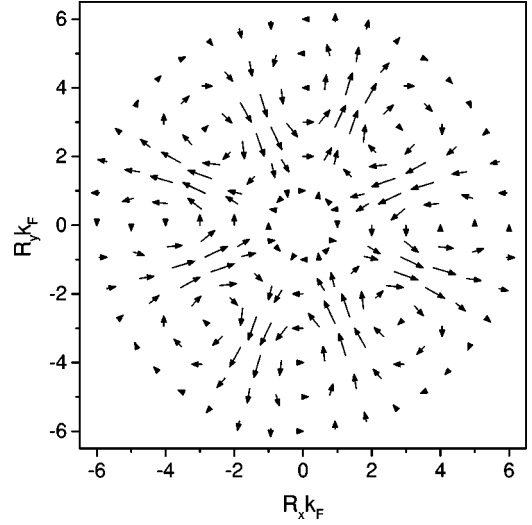


FIG. 4. Current density $\mathbf{j}(\mathbf{R})$ around the impurity after subtracting the net current (Fig. 5). The magnitude and direction of the arrows represent the current at that point.

site sense (see Fig. 4). The sense of the net current depends on the impurity spin projection s_z . Figure 5 shows the net current flowing [$J(R) = (1/2\pi)\mathbf{j}(\mathbf{R})\mathbf{d}\varphi$] as a function of the distance to the impurity. As before we can get the approximate analytical results

$$J(R) \propto \frac{J_1^2(R)}{2R} + 4 \frac{J_1(R)J_2(R)}{R^2} + \dots \quad (20)$$

The sign of the current varies with distance but the total current around the impurity is not zero. We have neglected any diamagnetic current produced by the magnetic field induced by the spontaneous current. For the singlet the two momenta correlation gives $F_{\mathbf{k}\mathbf{k}'}^S = M_{\mathbf{k}\mathbf{k}'}(u_{\mathbf{k}'}u_{\mathbf{k}} - v_{\mathbf{k}}v_{\mathbf{k}'})$, but for $v_{\mathbf{k}}$ real (real macroscopic superconducting state), this state preserves the time-reversal symmetry ($T|S\rangle = |S\rangle$) and does not have any spontaneous current.

CONCLUSIONS

In summary we have shown, in agreement with previous results, that a magnetic impurity in a $d_{x^2-y^2}$ superconductor has a transition from a Kondo singlet to an unscreened dou-

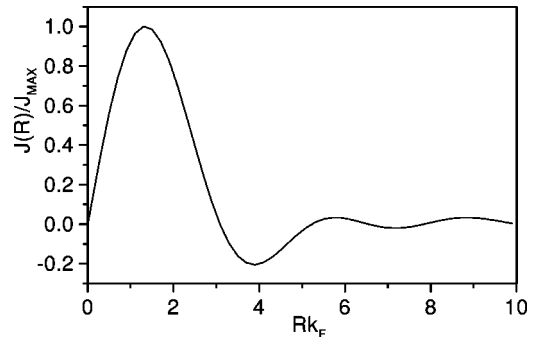


FIG. 5. Net current $J(R) = 1/2\pi\oint \mathbf{j}(\mathbf{R})\mathbf{d}\varphi$ as a function of the distance to the impurity.

blet as the superconductivity is turned on. The coupling between the spin of the impurity and the orbital momenta of the electrons induces a complex secondary component of the superconducting order parameter around the impurity in the doublet.

What are the observable consequences of the complex order parameter around the magnetic impurity for the case of dilute impurity concentrations? A complex order parameter by itself leads to a finite gap in the excitation spectra of the superconductor. But the potential scattering due to the impurity, not considered in this paper, if it is not sitting in a center of symmetry of the crystal, produces a finite density of states at low energies and spoils this effect. The principal effect of such a potential scattering in the current around the impurity is that the current decays in a length of the order of magnitude of the mean-free path, rather than as a power law obtained in this paper.

Global time reversal breaking due to the current around the magnetic impurities is possible only if they are aligned ferromagnetically. This is because the direction of the current depends on the direction of the magnetic moment. Ferromagnetic alignment is unlikely in general. A spin glass state, with an associated glassy pattern of currents, is much more likely. If a ferromagnetic alignment of the impurity spins is achieved, the nature of superconductivity is strongly affected and may be even destroyed. The physical properties in such a case have been discussed for *s*-wave superconductors.^{13,14}

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APPENDIX A

The coefficient of the doublet [Eq. (8)] are given by

$$a_{\mathbf{k}\mathbf{k}'} = -i \frac{g}{2l_{\mathbf{k}\mathbf{k}'}} \text{Im}(L_z^{\mathbf{k}\mathbf{k}'}) (u_{\mathbf{k}} v_{\mathbf{k}'} - v_{\mathbf{k}} u_{\mathbf{k}'}) + \frac{V_{\mathbf{k}} V_{\mathbf{k}'} V_{\mathbf{k}'}^*}{(\lambda_{\mathbf{k}} - E_D) l_{\mathbf{k}\mathbf{k}'}} + \frac{V_{\mathbf{k}} V_{\mathbf{k}'}^*}{(\lambda_{\mathbf{k}} - E_D) l_{\mathbf{k}\mathbf{k}'}} \sum_{\mathbf{k}''} V_{\mathbf{k}''} V_{\mathbf{k}''} a_{\mathbf{k}''\mathbf{k}}, \quad (\text{A1})$$

$$l_{\mathbf{k}\mathbf{k}'} = \epsilon_0 + \lambda_{\mathbf{k}} + \lambda_{\mathbf{k}'} - E_D,$$

$$\alpha_{\mathbf{k}} = \frac{-V_{\mathbf{k}} u_{\mathbf{k}}}{\lambda_{\mathbf{k}} - E_D - \Gamma_{a\mathbf{k}}} - i \frac{g}{2(\lambda_{\mathbf{k}} - E_D - \Gamma_{a\mathbf{k}})} \times \sum_{\mathbf{k}'} V_{\mathbf{k}'} V_{\mathbf{k}'}^* \text{Im}(L_z^{\mathbf{k}\mathbf{k}'}) \frac{(u_{\mathbf{k}} v_{\mathbf{k}'} - v_{\mathbf{k}} u_{\mathbf{k}'})}{l_{\mathbf{k}\mathbf{k}'}} \quad (\text{A2})$$

$$\Gamma_{a\mathbf{k}} = \sum_{\mathbf{k}'} \frac{V_{\mathbf{k}'}^2 V_{\mathbf{k}'}^2}{\epsilon_0 + \lambda_{\mathbf{k}} + \lambda_{\mathbf{k}'} - E_D}.$$

The second terms in Eqs. (A1) and (A2) ($\alpha_{\mathbf{k}}$ and $a_{\mathbf{k}\mathbf{k}'}$) only gives a contribution to the energy if $\Gamma_{V \otimes \Gamma_V} \otimes \Gamma_{L_z} = \Gamma_V$, where Γ_V , Γ_v , and Γ_{L_z} are the respective irreducible

representations. In a C_{4v} group this is only possible if $\Gamma_V = E(p_x, p_y)$. This means that the excited [second and third terms in Eq. (8)] connected with $d_{0\uparrow}^\dagger$ via H , are not connected to each other. The third term in Eqs. (A1) contributes if $\Gamma_{L_z} = \Gamma_V$.

Considering the most relevant terms the doublet energy E_D is given by

$$E_D - \epsilon_0 = -\delta_D = -\Gamma_1(-E_D) - \Gamma_2(-E_D) \quad (\text{A3})$$

with

$$\Gamma_1(x) = \sum_{\mathbf{k}'} \frac{V_{\mathbf{k}'}^2 u_{\mathbf{k}'}^2}{\epsilon_0 + \lambda_{\mathbf{k}'} + x},$$

$$\Gamma_2(x) = \frac{g^2}{4} \sum_{\mathbf{k}\mathbf{k}'} \frac{|L_z(uv - vu)|_{\mathbf{k}\mathbf{k}'}^2}{\epsilon_0 + \lambda_{\mathbf{k}'} + \lambda_{\mathbf{k}} + x}.$$

APPENDIX B

For the singlet [Eq. (10)], the ground state energy is calculated to be

$$E_S = \epsilon_0 - \delta_S = 2 \sum_{\mathbf{k}} \beta_{\mathbf{k}} V_{\mathbf{k}} V_{\mathbf{k}}^*, \quad (\text{B1})$$

where

$$\beta_{\mathbf{k}} = \frac{-V_{\mathbf{k}} V_{\mathbf{k}}}{\lambda_{\mathbf{k}} + \epsilon_0 - E_S - \Gamma_1(\lambda_{\mathbf{k}} - E_S) - \Gamma_2(\lambda_{\mathbf{k}} - E_S)} + \beta_{\mathbf{k}}^{corr}. \quad (\text{B2})$$

The coefficients are given by

$$\beta_{\mathbf{k}}^{corr} = \frac{\sum_{\mathbf{k}'} \beta_{\mathbf{k}'} \{A_{\mathbf{k}\mathbf{k}'}^{(1)} - A_{\mathbf{k}\mathbf{k}'}^{(2)} + ig/2[L_z(uu^* + vv^*)]_{\mathbf{k}\mathbf{k}'}\}}{\lambda_{\mathbf{k}} + \epsilon_0 - E_S - \Gamma_1(\lambda_{\mathbf{k}} - E_S) - \Gamma_2(\lambda_{\mathbf{k}} - E_S)}, \quad (\text{B3})$$

$$A_{\mathbf{k}\mathbf{k}'}^{(1)} = \frac{V_{\mathbf{k}} u_{\mathbf{k}} V_{\mathbf{k}'} u_{\mathbf{k}'}}{\lambda_{\mathbf{k}} + \lambda_{\mathbf{k}'} - E_S}$$

$$A_{\mathbf{k}\mathbf{k}'}^{(2)} = \frac{g^2}{4} \sum_{\mathbf{k}''} \frac{L_z(uv - vu)_{\mathbf{k}'\mathbf{k}''} L_z(uv - vu)_{\mathbf{k}\mathbf{k}''}^*}{\lambda_{\mathbf{k}} + \lambda_{\mathbf{k}'} + \lambda_{\mathbf{k}''} + \epsilon_0 - E_S},$$

$$M_{\mathbf{k}\mathbf{k}'} = \frac{-(V_{\mathbf{k}} u_{\mathbf{k}} \beta_{\mathbf{k}'} + V_{\mathbf{k}'} u_{\mathbf{k}'} \beta_{\mathbf{k}})}{\lambda_{\mathbf{k}} + \lambda_{\mathbf{k}'} - E_S}, \quad (\text{B4})$$

$$b_{\mathbf{k}\mathbf{k}'\mathbf{k}''} = -i \frac{g}{2} \frac{\beta_{\mathbf{k}} \text{Im}(L_z)(uv - vu)_{\mathbf{k}'\mathbf{k}''}}{\lambda_{\mathbf{k}} + \lambda_{\mathbf{k}'} + \lambda_{\mathbf{k}''} + \epsilon_0 - E_S}. \quad (\text{B5})$$

$A_{\mathbf{k}\mathbf{k}'}^{(1)}$, $A_{\mathbf{k}\mathbf{k}'}^{(2)}$ and the last term in Eq. (B3) contribute only in very special cases [i.e., $A_{\mathbf{k}\mathbf{k}'}^{(1)}$ gives a contribution only if $\Gamma_V \otimes \Gamma_V = \Gamma_V$ ($\Gamma_V = \Gamma_v = A_{1g}(s)$ or $\Gamma_V = E(p_x, p_y)$)]. They do not contribute for the *d*-wave superconductor consider in the main text.

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