Spectral Properties of a Quantum Impurity in d-Wave Superconductors

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The variational approach of Gunnarsson and Schönhammer to the Anderson impurity model is generalized to study d-wave superconductors in the presence of dilute spin-1/2 impurities. We show that the local moment is screened when the hybridization exceeds a nonzero critical value at which the ground state changes from a spin doublet to a spin singlet. The electron spectral functions are calculated in both phases. We find that while a Kondo resonance develops above the Fermi level in the singlet phase, the spectral function exhibits a low-energy spectral peak below the Fermi level in the spin doublet phase. The origin of such a “virtual Kondo resonance” is the existence of low-lying collective excitations in the spin-singlet sector. We discuss our results in connection to recent spectroscopic experiments in Zn doped high-Tc superconductors.

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The physics of quantum impurities in high-Tc superconductors has generated an increasing amount of experimental and theoretical interests. NMR measurements in YBCO showed that replacing the Cu-atom in the CuO₂ plane by a nonmagnetic Zn or Li atom induces a spin-1/2 magnetic moment on the Cu ions in the vicinity of the impurity. Atomic resolution scanning tunneling microscope (STM) experiments on BSCCO found that the local density of states (DOS) near the Zn impurity exhibits a sharp resonance peak just below the Fermi energy. The origin of the resonance peak has been attributed to potential scattering, local moment formation, and magnetic Kondo scattering where it is identified with the Kondo resonance arising from the screening of the local moment by the electrons in d-wave superconductors (dSC). While it remains controversial as to which of the above is the dominant mechanism responsible for the low-energy conductance peak, and how the findings of NMR are reconciled with those of STM, it has become important to acquire basic understandings of the spectral properties of quantum impurities in dSC.

The ground state and the impurity spectral function in the non-superconducting phase with a vanishing density of states (DOS), i.e. the pseudogap phase, have been studied in detail following the work of Withoff and Fradkin. In this paper, we study these properties associated with the Kondo physics in the d-wave superconducting phase. In addition to the ground state properties, we determine the momentum dependent, conduction electron spectral function A(k, ω) in dSC. This is an important quantity since it is directly measured by angle-resolved photoemission spectroscopy (ARPES). To this end, we describe the localized impurity by the infinite-U Anderson model and generalize the variational large-N approach of Gunnarsson and Schönhammer for rare earth and actinide heavy fermion materials to the case of dSC. This is a reliable, physically transparent many body approach that allows an essentially analytical calculation of A(k, ω). Specifically, starting from the singlet BCS state with the impurity site empty (singlet) or singly occupied (doublet), we construct the variational wave functions of states in both the spin singlet and doublet sectors from a basis of states generated by the hybridization between the impurity and the conduction electrons to next to leading order in 1/N. We find that there exists a critical value for the hybridization that separates a spin doublet ground state from a singlet ground state where the local moment is fully screened. Using the variational wave functions, we calculate the T-matrix, the self-energy, and the spectral function of the conduction electrons in both the singlet phase and the local moment phase. We find that while a Kondo resonance naturally develops above the Fermi level in the singlet phase, A(k, ω) exhibits a spectral peak of similar strength below the Fermi energy in the local moment phase. The origin of this “virtual Kondo resonance” can be traced to the existence of low-lying collective spin singlet excitations above the doublet ground state in the local moment phase. The qualitatively different behaviors of the spectral function make it possible to distinguish between the two ground states by STM and ARPES.

The single impurity Anderson model in a dSC can be written as $H = H_c + H_d + H_v$,

$$H_c = \sum_{k\sigma} \epsilon_k c^\dagger_{k\sigma} c_{k\sigma} + \sum_k \Delta_k (c^\dagger_{k\uparrow} c^\dagger_{-k\downarrow} + h.c.),$$

$$H_d = \epsilon_d \sum_{\sigma} d^\dagger_{\sigma} d_{\sigma} + U d^\dagger_{\uparrow} d_{\downarrow} d^\dagger_{\downarrow} d_{\uparrow}$$

$$H_v = V \sum_{k\sigma} (c^\dagger_{k\sigma} d_{\sigma} + h.c.).$$

Here $c^\dagger_{k\sigma}$ creates an electron with a dispersion $\epsilon_k = -2t(\cos k_x + \cos k_y) - \mu$ in a dSC described by the gap function $\Delta_k = \frac{1}{2} \Delta_0 (\cos k_x - \cos k_y)$; $d^\dagger_{\sigma}$ creates a localized electron with energy $\epsilon_d$ at the impurity site, and $U$ is the on-site Coulomb repulsion. We take the infinite-U limit such that the impurity site is either empty or singly occupied. The hybridization between the impurity and the conduction electrons is described by the hybridization constant $V$ in $H_v$. For simplicity, only the case of $N = 2$...
is written explicitly in Eq. (1-3). The generalization to the case of $N$ orbital degeneracy with $NV^2 = O(1)$ is straightforward.12-14

As in the BCS theory, $H_c$ can be diagonalized by a Bogoliubov transformation: $c_{k\uparrow} = u_k \alpha_{k\uparrow} - v_k \alpha_{-k\downarrow}$, and $c_{-k\downarrow} = u_k \alpha_{-k\downarrow} + v_k \alpha_{k\uparrow}$, where $u_k^2 = (1 + \epsilon_k / E_k) / 2$ with $E_k = \sqrt{\epsilon_k^2 + \Sigma_k^2}$. $H_c$ and $H_v$ can be expressed in terms of the quasiparticles, $H_e = \sum_{k\sigma} E_k \alpha_{k\sigma}^\dagger \alpha_{k\sigma}$, and

$$H_v = V \sum_k \left[ (u_k \epsilon_{k\uparrow} - v_k \epsilon_{-k\downarrow}) \alpha_{k\uparrow} \right. 
\left. + (u_k \epsilon_{-k\downarrow} + v_k \epsilon_{k\uparrow}) \alpha_{-k\downarrow} \right] + h.c.] , \quad (4)$$

\[\begin{array}{cccc}
\epsilon_k & u_k & v_k & -u_k \\
\prod & \prod & \prod & \prod \\
\end{array}\]

FIG. 1. Schematics of the variational states. Singlet (first row) and doublet (second row) states to leading (a,b, and c) and next to leading order (d,e,f, and g) in $1/N$.

We now generalize the variational method of Gunnarson and Schönhammer to the case of superconductors.15 Since the BCS ground state $|\text{BCS}\rangle$ with the impurity level empty is a singlet (Fig. 1a), we can construct other states in the singlet sector by acting on $|\text{BCS}\rangle$ with the Hamiltonian $H$. Operating once with the hybridization term generates the type of states $|\epsilon_d \sigma \bar{E}_k \sigma \rangle$ shown in Fig. 1b in which a quasiparticle excitation with spin $\sigma$ is created from the dSC condensate and the impurity level is singly occupied by an electron with the opposite spin $\bar{\sigma}$. Taking the linear combination of all such states gives the trial wavefunction for the singlet state:

$$|S\rangle = A^s |\text{BCS}\rangle + \frac{1}{\sqrt{N}} \sum_{k\sigma} B_{k\sigma}^s |\epsilon_d \bar{\sigma} E_k \sigma \rangle$$

$$+ \sum_{k_1k_2\sigma} \frac{1}{\sqrt{N}} C_{k_1k_2}^s |E_{k_1} \bar{\sigma} E_{k_2} \sigma \rangle$$

$$+ \sum_{k_1k_2\sigma\sigma^\prime} \frac{1}{\sqrt{N}} D_{k_1k_2k_3k_4}^s |\epsilon_d \bar{\sigma}^\prime E_{k_1} \bar{\sigma} E_{k_2} \sigma E_{k_3} \sigma^\prime \rangle . \quad (5)$$

The last two terms in Eq. (5) contain singlet states generated to the next to leading order in the $1/N$ expansion shown in Figs. 1c and 1d. They correspond to states with two quasiparticle excitations and an unoccupied impurity level and three quasiparticles plus a singly occupied impurity level respectively. The parameters $A^s$ to $D^s$ are determined by minimizing the energy $E_s = \langle S|H|S\rangle / \langle S|S\rangle$. We find

$$B_{k\sigma}^s = \sqrt{NV} \epsilon_k \left[ E_{\sigma} - \epsilon_d - E_k - \Sigma_1(E_{\sigma} - E_k) \right]^{-1} ,$$

$$C_{k_1k_2}^s = V u_{k_1} B_{k_2}^s \left[ E_{\sigma} - E_{k_2} - \Sigma_0(E_\sigma - E_{k_2} - \epsilon_d) \right]^{-1} ,$$

$$D_{k_1k_2k_3k_4}^s = \sqrt{NV} \epsilon_{k_3} C_{k_4}^s \left[ E_{\sigma} - \epsilon_d - E_{k_4} \right]^{-1} ,$$

where $E_{k_1} = E_{k_1} + E_{k_2}$, $E_{k_2} = E_{k_1} + E_{k_2} + E_{k_3}$, and

$$E_s = \sum_{k} \frac{NV^2 \epsilon_k^2}{E_{\sigma} - \epsilon_d - E_k - \Sigma_1(E_{\sigma} - E_k)} ,$$

$$\Sigma_0(\omega) = NV^2 \sum_{k} \frac{\epsilon_k^2 (\omega - E_k)^{-1} ,}$$

$$\Sigma_1(\omega) = V^2 \sum_{k} \frac{\epsilon_k (\omega - E_k - \Sigma_0(\omega - \epsilon_d - E_k))^{-1} .}$$

\[\begin{array}{cccc}
\epsilon_d & \epsilon_d & \epsilon_d & \epsilon_d \\
\prod & \prod & \prod & \prod \\
\end{array}\]

FIG. 2. Phase diagram of the infinite-U Anderson model in a dSC to leading (dashed line) and next to leading order (solid line) in $1/N$.

The variational state in the spin doublet sector can be constructed starting from the BCS state plus a singly occupied impurity level (Fig. 1e) in the large-$N$ limit. To next to leading order in $1/N$, two types of states are generated: one corresponds to a quasiparticle excitation and an empty impurity level (Fig. 1f) and the other to two quasiparticles out of the condensate and a singly occupied impurity level shown in Fig. 1g. Denoting the net moment in the doublet state by $\tau$, we have

$$|D\tau\rangle = A^d |\text{BCS}\epsilon_d \tau\rangle + \sum_{k} B_{k\tau}^d |E_k \tau\rangle$$

$$+ \frac{1}{\sqrt{N}} \sum_{k_1k_2\tau} C_{k_1k_2}^d |\epsilon_d \bar{\sigma} E_{k_1} \tau E_{k_2} \tau \rangle . \quad (10)$$

As in the singlet case, the variational parameters $A^d, B^d, C^d$, and the total energy are determined by minimizing $E_d = \langle D\tau|H|D\tau\rangle / \langle D\tau|D\tau\rangle$ in the doublet state:

$$B_{k\tau}^d = V u_k \left[ E_{\sigma} - E_k - \Sigma_0(E_\sigma - E_{k_1} - \epsilon_d) \right]^{-1} ,$$

$$C_{k_1k_2}^d = \sqrt{NV} \epsilon_{k_2} B_{k_1}^d \left[ E_{\sigma} - E_{k_1} - E_{k_2} - \epsilon_d \right]^{-1} ,$$

$$E_d = \epsilon_d + \sum_{k} \frac{V^2 \epsilon_k^2}{E_{\sigma} - E_k - \Sigma_0(E_\sigma - E_{k_1} - \epsilon_d)} . \quad (11)$$
The ground state and the phase diagram are obtained by comparing $E_s$ and $E_d$ derived in Eqs. (7) and (11) as a function of the impurity level $\epsilon_d$ and the hybridization $V$. We use the d-wave gap $\Delta_0$ as the energy unit, set $t$ to $\Delta_0$, and integrate over $k$ in the continuum limit. We find that, due to the linearly vanishing DOS in the dSC, the impurity spin can be fully screened by the Bogoliubov quasiparticles only if the hybridization $V$ is greater than a nonzero value. Similar to the pseudogap Kondo impurity model, both the spin singlet and the doublet local moment phases exist for an Anderson impurity in a dSC and are separated by a line of phase transitions in the phase diagram shown in Fig. 2.

One of the advantages of the variational wave function approach is that it allows a reliable and transparent many-body calculation of the spectral function\textsuperscript{12}, $A(k, \omega) = (-1/2\pi)\text{Im}G_c(k, \omega)$, where $G_c(k, \omega)$ is the impurity averaged, retarded normal Green’s function for the conduction electrons. The local Green’s function $G_c(i, j, \tau, t) = -i\theta(t)|\phi_0\rangle\langle c_{i\sigma}(t), c_{j\sigma}^\dagger(0)|\phi_0\rangle$ where $|\phi_0\rangle = |S\rangle, |D\tau\rangle$ represent the fully interacting singlet and doublet (with polarization $\tau$) ground states. Both the local electron Green’s function at the impurity site and the impurity averaged conduction electron Green’s function in momentum space can be written in terms of the T-matrix, which can be obtained from the variational wave functions. Using the Nambu representation, the local Green’s function can be written as:

$$
\hat{G}_c(r, r', \omega) = \hat{G}_c^r(r - r', \omega) + \hat{G}_c^d(r, \omega) \hat{T}(\omega) \hat{G}_c^d(-r', \omega) \hat{T}(\omega) = |V|^2 \hat{G}_d(\omega),
$$

where $\hat{G}_d(\omega)$ is the local electron Green’s function at the impurity site. The impurity averaged Green’s function is given by

$$
\bar{G}_c(k, \omega) = \left[\omega - \epsilon_d \hat{\sigma}_z - \Delta_k \hat{\sigma}_x - \rho_{\text{imp}} \hat{T}(\omega)\right]^{-1},
$$

where $\rho_{\text{imp}}$ is the density of impurities. Using the variational wave functions, $G_d(\omega)$ can be derived in closed form to first order in $1/N$. For the singlet ground state we obtain,

$$
G_{dt}^S(\omega + i\delta) = \langle S|d_1^{\dagger} \frac{1}{\omega + i\delta - H + E_S} d_1^\dagger |S\rangle + \langle S|d_1^{\dagger} \frac{1}{\omega + i\delta + H - E_S} d_1^\dagger |S\rangle \approx
$$

$$
A^2 \left\frac{1}{\omega - \epsilon_d - \Sigma_d(\omega + i\delta + E_S) + E_S + i\delta} + \left(\frac{1}{\omega + \epsilon_d + \Sigma_d(-\omega - i\delta + E_S) - E_S + i\delta}\right) \sum_k \frac{1}{N} B_k \frac{u_k V}{\omega + E_k - E_S + i\delta} \right)^2 \times
$$

$$
\left(\left(\omega - \Sigma_0(\omega + i\delta - \epsilon_d + E_D) - E_D + i\delta\right) \sum_k \frac{1}{N} B_k^2 \frac{1}{\omega - \epsilon_d - E_k + E_D + i\delta} \right)
$$

where $\Sigma_d(\omega + i\delta) = \sum_k u_k^2 V^2/(\omega - E_k + i\delta)$. In the local moment phase, the spin SU(2) symmetry is broken and the STM measures the spin averaged tunneling density of states. Since the total Hamiltonian is invariant when the spin up and down electrons are interchanged, averaging over the conduction electron spin is equivalent to averaging over the polarization of the local moment ground state. We thus obtain

$$
G_{dt}^D(\omega + i\delta) = \frac{1}{2} G_{dt}^{D\uparrow}(\omega + i\delta) + \frac{1}{2} G_{dt}^{D\downarrow}(\omega + i\delta) = \sum_{\tau=\uparrow, \downarrow} \frac{1}{2} \left(\langle D\tau|d_1^{\dagger} \frac{1}{\omega + i\delta - H + E_D} d_1^\dagger |D\tau\rangle + \langle D\tau|d_1^{\dagger} \frac{1}{\omega + i\delta + H - E_D} d_1^\dagger |D\tau\rangle \right) \approx
$$

$$
A^2 \left\frac{1}{\omega + \Sigma_0(-\omega - i\delta - \epsilon_d + E_D) - E_D + i\delta} + \left(\frac{1}{\omega - \Sigma_0(\omega + i\delta - \epsilon_d + E_D) + E_D + i\delta}\right) \sum_k \frac{1}{N} B_k \frac{v_k}{\omega - \epsilon_d - E_k + E_D + i\delta} \right)^2 \times
$$

$$
\left(\left(\omega - \Sigma_0(\omega + i\delta - \epsilon_d + E_D) + E_D + i\delta\right) \sum_k \frac{2}{N} B_k^2 \frac{1}{\omega - \epsilon_d - E_k + E_D + i\delta} \right)
$$

We next present results for the spectral function of the conduction electrons. The impurity level is fixed at $\epsilon_d = -1.4\Delta_0$. We choose $V = 1.6\Delta_0$ for the doublet local moment phase at a corresponding valence $\langle n_d \rangle = 0.93$, and $V = 1.8\Delta_0$ for the singlet state with $\langle n_d \rangle = 0.58$. We will show that along nodal directions of the d-wave gap, where SC coherence is absent ($u_k^2 = 1, v_k^2 = 0$ for $|k| < k_f$), the spectral function exhibits qualitatively different behaviors in the two different phases. In Figs. 3a and 3b, the solid lines depict the low-energy spectra along
the nodes at \(k_x = k_y = 0.63k_f\). In the singlet phase (Fig. 3b), a resonance peak appears above the Fermi level, which is the expected Kondo resonance. Physically, this can be understood by considering an intermediate state in the infinite-U limit with one less electron than the singlet ground state. An added electron at the resonance energy creates a quasiparticle excitation and forms a singlet state that has a large overlap with the Kondo singlet state. The intrinsic width of the Kondo resonance is captured by the present variational wave function approach. In contrast, the spectrum in the local moment phase (Fig. 3a) shows, remarkably, a resonance peak below the Fermi level. This peak does not have the usual meaning of a Kondo resonance. Instead, it can be understood as a virtual Kondo resonance. Although the ground state is a doublet and the local moment is unscreened, the collective singlet states of the type given by Eq. (5) exist as low energy excitations above the doublet ground state. When an electron is removed from the SC condensate, quasiparticle excitations with the opposite spin can be created to screen the local moment and occupy the virtual spin singlet state. Note that, in general, depending on the sign of the particle-hole asymmetry, the Kondo resonance in the singlet phase can be either above (the present case for the infinite-U Anderson model) or below the Fermi level. The virtual Kondo resonance in the local moment phase is located on the opposite side of the Fermi level compared to the Kondo resonance.

![Fig. 3. Momentum resolved spectral functions in the local moment (a) and the singlet (b) phases along the nodal (solid lines) and anti-nodal (dashed lines) directions.](image)

The behavior of the spectra along anti-nodal directions of the d-wave gap is shown in dashed lines in Figs. 3a and 3b at \(k_x = k_f\), \(k_y = 0\). Due to the strong SC coherence \((u_k^x, u_k^y \neq 0)\), the Kondo and the virtual Kondo resonances are reflected on the hole and the particle sides such that the resulting spectra show nearly symmetric resonance peaks. These results suggest that both ARPES and STM experiments STM can be used to distinguish between these two ground states.

Finally, we turn to the local density of states (LDOS) as measured by STM experiments,

\[
\rho(r, \tau, \omega) = -\frac{1}{\pi} \sum_{k, k', \sigma} \text{Im} G_{c}(k', \sigma, k, \tau, \omega) e^{-i(k-k')r}. 
\]

In Fig. 4, the LDOS at the impurity site is shown for both the singlet and the local moment phases. Due to the high symmetry of this tunneling point, the LDOS spectrum is dominated by the contribution from the low energy quasiparticle excitations along the nodal directions. As a result, the tunneling spectrum closely resembles that of \(A(k, \omega)\) along nodal directions: a single resonance peak above the Fermi level in the singlet phase and below the Fermi level in the local moment phase. The STM data interpreted this way would suggest that the Zn-doped BSCCO surface is in the local moment phase. The LDOS away from the impurity is shown in the insets of Fig. 4. The conductance spectra in both phases still exhibit a single peak along nodal directions, whereas along antinodal directions two peaks appear due to the SC coherence. The amplitude of the peaks is significantly reduced than at the impurity site.

![Fig. 4. The LDOS spectrum at the impurity site in the singlet (dashed line) and the local moment (solid line) phases. The insets show the LDOS away from the impurity along nodal (dashed lines) and anti-nodal (solid lines) directions in local moment (b) and singlet (a) phases.](image)

To conclude, we have studied the spectral properties of electrons in dSC coupled to localized Anderson impurities in both the singlet and the local moment phases using the variational wave function approach. Our results show that Kondo screening is not a prerequisite for the emergence of low energy resonance peaks in the spectral function. Even if the impurity spin is not screened, the virtual Kondo resonance due to collective spin singlet excitations would still lead to a sharp resonance peak, but located on the opposite side of the Fermi level compared to the Kondo resonance in the singlet phase. It is the evolution of the resonance peak positions that reveals the
screening properties of the local moment in the ground states, which can in principle be measured by ARPES and STM experiments.

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