Resonances in superconductors

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In the case of superconductors with BCS singlet pairing the presence of resonant impurities necessarily gives rise to localized states within the gap irrespective of the gap between the energy of resonance and the Fermi energy.

1. It is known that magnetic impurities in a superconductor with the *s* pairing give rise to a zero-gap superconducting state. This is because a single magnetic impurity (in contrast to a potential impurity) gives rise to a bound state inside the superconductor gap.[2]

We show that there is a more general mechanism of the formation of bound states inside the gap: this is the resonant scattering mechanism. It is found that in the case of a single resonant center the existence of bound states is independent of the position of the resonant level ε_0 relative to the Fermi energy μ and is also independent of the strength of the intracenter Hubbard repulsion U. The resonant scattering mechanism of the formation of bound states discussed here is, in a limited sense, similar to the magnetic mechanism only if $\varepsilon_0 < \mu < \varepsilon_0 + U$, when only one electron is present in a center.

2. The model Hamiltonian of this problem is

$$\hat{H} = \sum_{\mathbf{k},\sigma} (\varepsilon_\mathbf{k} - \mu) c_{\sigma\mathbf{k}}^+ c_{\sigma\mathbf{k}} + \varepsilon_0 \sum_\sigma d_\sigma^+ d_\sigma + U \hat{n}_\sigma \hat{n}_{-\sigma}$$

$$+ \frac{1}{N^{1/2}} \sum_{\mathbf{k},\sigma} (V_\mathbf{k} c_{\mathbf{k}\sigma}^+ d_\sigma + \text{H.c.}) + \sum_\mathbf{k} (\Delta c_{\sigma\mathbf{k}}^+ c_{-\sigma\mathbf{k}}^+ + \text{H.c.}). \quad (1)$$

Here, $\varepsilon_\mathbf{k}$ is the dispersion law of the band electrons; $V_\mathbf{k}$ represents hybridization of the band and impurity states; $\mathbf{k}$ and σ represent the quasimomentum and the spin of the investigated state; $c_{\sigma\mathbf{k}}$ and d_σ are the Fermi annihilation operators; $\hat{n}_\sigma$ is the electron number operator for a resonant center with a spin σ; and N is the total number of the band states.

We consider the following cases: purely resonant scattering ($U = 0$), infinitely strong repulsion ($U \to +\infty$), and the case of intermediate values of U.

3. In the case of the Hamiltonian (1) with $U = 0$, we consider the Green's functions

$$G_{\mathbf{k}d} = -i\langle T c_{\sigma\mathbf{k}} d_\sigma^+ \rangle, \quad F_{\mathbf{k}d} = -i\langle T c_{-\sigma\mathbf{k}}^+ d_\sigma^+ \rangle,$$

$$G_{dd} = -i\langle T d_\sigma d_\sigma^+ \rangle, \quad F_{dd} = -i\langle T d_{-\sigma}^+ d_\sigma^+ \rangle$$

and readily find the following system of equations for these functions:

$$(\omega - \varepsilon_0) G_{dd} = 1 + \frac{1}{N^{1/2}} \sum_\mathbf{k} V_\mathbf{k} G_{\mathbf{k}d},$$

$$(\omega - \varepsilon_\mathbf{k}) G_{\mathbf{k}d} = \frac{1}{N^{1/2}} V_\mathbf{k} G_{dd} + \Delta F_{\mathbf{k}d},$$

$$-(\omega + \varepsilon_\mathbf{k}) F_{\mathbf{k}d} = \frac{1}{N^{1/2}} V_\mathbf{k} F_{dd} - \Delta G_{\mathbf{k}d}, \quad (2)$$

$$-(\omega + \varepsilon_0) F_{dd} = \frac{1}{N^{1/2}} \sum_\mathbf{k} V_\mathbf{k} F_{\mathbf{k}d}.$$

In these equations and in what follows, all the energies are measured from the Fermi level μ.

The solution of this system of equations yields the following expressions for G_{dd} and F_{dd}:

$$G_{dd} = \frac{\omega + \omega\alpha(\omega) + \tilde{\varepsilon}_0}{[\omega + \omega\alpha(\omega) - \tilde{\varepsilon}_0][\omega + \omega\alpha(\omega) + \tilde{\varepsilon}_0] - \Delta^2\alpha^2(\omega)},$$

$$F_{dd} = \frac{\Delta\alpha(\omega)}{[\omega + \omega\alpha(\omega) - \tilde{\varepsilon}_0][\omega + \omega\alpha(\omega) + \tilde{\varepsilon}_0] - \Delta^2\alpha^2(\omega)}, \quad (3)$$

where

$$\alpha(\omega) = -\frac{1}{N} \sum_\mathbf{k} \frac{|V_\mathbf{k}|^2}{\omega^2 - \varepsilon_\mathbf{k}^2 - \Delta^2},$$

$$\tilde{\varepsilon}_0 = \varepsilon_0 + \frac{1}{N} \sum_\mathbf{k} \frac{|V_\mathbf{k}|^2 \varepsilon_\mathbf{k}}{\omega^2 - \varepsilon_\mathbf{k}^2 - \Delta^2}. \quad (4)$$

If the density of the band electron states $\varepsilon_\mathbf{k}$ near the Fermi energy can be assumed to the constant and equal to $N(O)$, it follows from Eq. (4) that (for $V_\mathbf{k} = V = \text{const}$):

$$\alpha(\omega) = \frac{\Gamma}{(\Delta^2 - \omega^2)^{1/2}}, \quad \tilde{\varepsilon}_0 = \varepsilon_0, \quad \Gamma = \pi V^2 N(0). \quad (5)$$

Under these conditions the equation for the determination of the energy of bound states inside the gap is

$$\omega^2 (1 + 2\alpha) = \varepsilon_0^2 + \Gamma^2. \quad (6)$$

This equation has two solutions $\omega_\pm$ inside the gap ($\omega_\pm^2 < \Delta^2$) for all the values of Δ, ε_0, and Γ.

In two limiting cases the roots of Eq. (6) and the residues of the delayed (electron) part of the Green's function $\pi^{-1} \operatorname{Im} G_{dd}^R$ can readily be found analytically. For $\Delta^2 \gg \varepsilon_0^2 + \Gamma^2$,

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$$\omega_\pm \approx \pm(\varepsilon_0^2+\Gamma^2)^{1/2},$$
$$\frac{1}{\pi}\operatorname{Im} G_{dd}^R \approx \frac{1}{2}\left[1 \pm \frac{\varepsilon_0}{(\varepsilon_0^2+\Gamma^2)^{1/2}}\right]. \tag{7}$$

If $\Delta^2 \ll \varepsilon_0^2 + \Gamma^2$, then

$$\omega_\pm \approx \pm\Delta\left[1 - \frac{2\Gamma^2\Delta^2}{(\varepsilon_0^2+\Gamma^2)^2}\right],$$
$$\frac{1}{\pi}\operatorname{Im} G_{dd}^R \approx 2\frac{\Gamma^2\Delta^2}{(\varepsilon_0^2+\Gamma^2)^2}\left(1 \pm \frac{2\Delta\varepsilon_0}{\varepsilon_0^2+\Gamma^2}\right). \tag{8}$$

In the former case ($\Delta^2 \gg \Gamma^2 + \varepsilon_0^2$) the resonance is weakly coupled to the band electrons and its energy lies near the Fermi level μ. This resonance creates two strongly localized states inside the gap 2Δ. Such a situation may occur in the case of the tunnel junction when a resonant center is separated spatially from the bulk of a superconductor.

The second case ($\Delta^2 \ll \Gamma^2 + \varepsilon_0^2$) describes how resonant impurities in the bulk of a semiconductor influence its spectrum. In this case the bound states are weakly localized [their radius is $\sim \hbar v_F(\Delta - |\omega_\pm|)^{-1}$, where v_F is the Fermi velocity] and they are split from the gap edge by an amount proportional to Δ^3. Therefore, in practice they cannot be observed in small-gap superconductors.

The density of states of the impurity d electrons $\pi^{-1}\operatorname{Im} G_{dd}^R$ [in addition to the δ-like singularities of Eqs. (7) and (8) inside the gap] in general has three additional peaks. One of them is close to ε_0 (it is retained also in the nonsuperconducting state) and the other two are at the edges of the gap. The density of states per center corresponding to the last two peaks, $N_d(\omega)$, can be described by the following expression if we have $|\omega| \gg \Delta$ and $\varepsilon_0^2 \gg \Delta^2$:

$$N_d(\omega) \approx \frac{\varepsilon_0^2\Gamma(\omega)}{\varepsilon_0^4+4\omega^2\Gamma^2(\omega)}, \quad \Gamma(\omega)=\Gamma\frac{|\omega|}{(\omega^2-\Delta^2)^{1/2}}. \tag{9}$$

Equation (9) describes a fairly sharp peak of $N_d(\omega)$ with the maximum amplitude $N_d \approx \Delta^{-1}$ at $\omega^2 - \Delta^2 \approx \Delta^4\Gamma^2/\varepsilon_0^4$.

It should be pointed out that, according to Eqs. (7) and (8), the maximum splitting of the levels 2Δ from the edges of the gap corresponds to $\varepsilon_0 = 0$. If the energy of the most strongly split-off levels $|\omega_\pm|$ is denoted by ω_m, it then follows from Eqs. (7) and (8) that at low values of ε_0^2 the energy of the impurity levels $\omega_\pm$ obeys $\omega_\pm^2 - \omega_m^2 \sim \varepsilon_0^2$. This means that in the presence of some nonzero distribution $\rho(\varepsilon_0)$ of the resonance centers in the energy ε_0 the density of the impurity levels $N_d(\omega)$ within the gap 2Δ has the following square root singularity if $\varepsilon_0^2 \to 0$:

$$N_d^{-1}(\omega) \propto (\omega^2-\omega_m^2)^{1/2}$$

at energies $\omega = \pm\omega_m$. This singularity of the density of the impurity states may simulate a singularity of the density of the band states at the edges of the main BCS gap.

4. We now have to consider how the above pattern of behavior changes if we allow for the Hubbard repulsion U of the electrons at a resonant center. This can be done in the limit $U \to |+\infty$, using the following reasoning. Assume that at the initial moment t_0 the hybridization of V makes the density of electrons n_σ with a spin σ at a center nonzero. This density is governed by the corresponding imaginary part of the Green's function $G_{d\sigma,d\sigma}$. Then, electrons with the opposite spin at the center experience the repulsive potential $U_\sigma = Un_\sigma$. Via a Hartree diagram this potential occurs in the fourth equation of the system (2) if we replace $(\omega + \varepsilon_0)$ with $(\omega + \varepsilon_0 + U_\sigma)$. Then, the solution of this equation for the function $F_{-\sigma d,\sigma d}$ in the limit $U \to \infty$ gives

$$F_{-\sigma d,\sigma d} \propto U_\sigma^{-1} \to 0.$$

In this limit the first three solutions of Eq. (2) form a closed system whose solution for the function $G_{\sigma d,\sigma d}$ is

$$G_{\sigma d,\sigma d} = \frac{1}{\omega+\omega\alpha(\omega)-\varepsilon_0}. \tag{10}$$

In contrast to the case $U = 0$, we find that if $U \to +\infty$, then inside the superconducting gap the function (10) has only one pole:

$$\omega = \begin{cases} \varepsilon_0\left(1 - \dfrac{\Gamma}{\Delta}\right), & \Delta^2 \gg \varepsilon_0^2+\Gamma^2, \\ \Delta\dfrac{\varepsilon_0}{(\Gamma^2+\varepsilon_0^2)^{1/2}}, & \Delta^2 \ll \varepsilon_0^2+\Gamma^2. \end{cases} \tag{11}$$

This level can occupy any position in the gap 2Δ if we vary ε_0. The density of the impurity states for $\omega^2 \gg \Delta^2$ and $\varepsilon_0^2 \gg \Delta^2$ is now somewhat different from that given by Eq. (9):

$$N_d(\omega) \approx \frac{\Gamma(\omega)}{\varepsilon_0^2+\Gamma^2(\omega)}. \tag{12}$$

A lower and wider peak with a maximum amplitude $N_d \sim \varepsilon_0^{-1}$ occurs at $\omega^2 - \Delta^2 = \Delta^2\Gamma^2/\varepsilon_0^2$. It is interesting that the results of this section agree with the conclusions reached in Ref. 2 if we replace the exchange integral I in the expression $H_{\text{int}} = \frac{1}{2}I(1 - 4\hat{\sigma}\hat{S})$ with V^2/ε_0.

5. Finally, we have to consider the situation which appears in the case of intermediate values of U. This can be done in the mean-field approximation by postulating an effective potential $U_\sigma = Un_\sigma$ exerted on a given electron by other electrons with the opposite spin. In this approximation the equations for the Green's functions are obtained from the system (2) by substitutions in the first and fourth equations:

$$\omega-\varepsilon_0 \to \omega-\tilde{\varepsilon}-U_-,$$
$$\omega+\varepsilon_0 \to \omega+\tilde{\varepsilon}-U_-, \tag{13}$$

where

$$U_- = {}^1/_2(U_\sigma-U_{-\sigma}), \quad \tilde{\varepsilon}=\varepsilon_0+{}^1/_2(U_\sigma+U_{-\sigma}).$$

Then, the positions of the impurity levels inside the gap are governed by the roots of the secular equation:

$$\omega^2(1+2\alpha)-\tilde{\varepsilon}^2-\Gamma^2+U_-^2-2U_-\omega(1+\alpha)=0, \tag{14}$$

where the effective Coulomb potential U_- is calculated self-consistently using the occupancy of the states with the opposite spins. It follows from Eq. (14) that for $U \neq 0$, the energies of two localized states of Eqs. (7) and (8) become spin-split. If $U_-^2 \gg 4\Delta^2$, two of them merge with the gap edges, whereas the other two form in the limit $U_-^2 \to \infty$ a spin-nondegenerate level of Eq. (11).

Note that for finite values of the repulsive potential U the energies of the levels given by Eq. (14) depend on the actual occupancy numbers of these levels at the beginning and end of the process. Therefore, the experimentally observed spectra of superconductors depend on the nature of the experiment, which is true also of tunneling across a Hubbard center.[3]

6. We conclude by considering an alternative interpretation of the results, which apparently is unrelated to the resonant scattering and the physical consequences of such a theory.

The results obtained above can be interpreted in the spirit of the one-band theory if we consider a resonant center located at some point in the crystal as the cause of the local change in the electron–electron coupling constant λ. This change in the coupling constant because of the one-dimensional nature of the density of state in the BCS scheme must cause a bound state to form. Therefore, it is natural to assume that the formation of these states inside the gap is not due to the magnetic interaction (because the Hubbard exchange $I = V^2/U$ disappears in the limit $U \to \infty$), but due to the local change in λ (which may depend on the spin). On the other hand, if we have $U = 0$, the appearance of two symmetric levels or states inside the main gap can be due to the induced superconductivity in the non-superconducting system (impurity level).

In a rigorous analysis of this problem it would be necessary to allow self-consistently for the change in the gap near a resonant center. This can change the results of the present paper quantitatively but should not affect the qualitative nature (in accordance with the variational Rayleigh–Ritz principle) of the very existence of bound states inside the gap.

From the experimental point of view it would be very important to find levels near (at a distance proportional to Δ^3) the gap edge. This would result in additional absorption of electromagnetic radiation at frequencies proportional to $|T - T_c|^{3/2}$ near the temperature of the transition to the superconducting state.

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