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Comments on Superconductors with Magnetic Impurities

Akio SAKURAI

Institute for Solid State Physics
University of Tokyo, Roppongi, Tokyo

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A low lying excited state in a superconductor with a classical magnetic spin is studied in connection with the ground state problem. The occurrence of a level crossing between them is pointed out.

Low lying excited states in BCS superconductors with magnetic impurities are recently investigated by several authors. Soda, Matsuura and Nagaoka[1] were the first who found such a state within the gap in the superconducting state of an *s-d* exchange interaction system. Their approach was along a perturbational one corresponding to Yosida's approach[2] in a normal *s-d* system. Fowler and Maki[3] and Zittartz and Müller-Hartmann[4] examined the system in terms of the dispersion relations and of the two-time Green functions respectively. Although a satisfactory theory for the *s-d* system in superconducting state has not yet been obtained, all their results support the existence of low lying excited states.

On the other hand a *classical* spin in a superconductor was studied by Shiba,[5] who exactly showed the existence of a low lying excited state and pointed out that it remains in a quantal *s-d* system. In this exactly soluble model, as well as in a quantal system treated approximately, the level in the gap moves towards the Fermi level and crosses over it as the interaction strength is increased (for antiferromagnetic interaction in the *s-d* system and for both ferro- and antiferromagnetic interactions in the classical system). However, the physical interpretation of this behavior seems not to have been discussed by these authors.

This short note is aimed to clarify the features of the low lying excited state with special emphasis on a problem how the ground state changes with the interaction strength. As a soluble example we take an *s-d* system containing a classical impurity spin, where the essential formalism has been given by Shiba.[5]

Let us consider a BCS superconductor with a classical spin S orientated to the z-axis at the origin:

$$H=\sum_{k,\sigma}\varepsilon_k a_{k\sigma}^* a_{k\sigma}-\Delta\sum_k(a_{k\uparrow}^* a_{-k\downarrow}^*+a_{-k\downarrow}a_{k\uparrow})-\frac{JS}{2N}\sum_{k,k'}(a_{k\uparrow}^* a_{k'\uparrow}-a_{k\downarrow}^* a_{k'\downarrow}), \tag{1}$$

where Δ is the order parameter considered as given in this paper, though, in principle, it should be determined from $\langle a^*a^*\rangle$ self-consistently. In the ac-

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tual system the summation over k of the second term is to be confined by the phonon frequency cutoff, but it makes no essential change in the following discussion. We also neglect the spatial variation of the order parameter. The interaction strength J is taken as $JS=\text{const}$, while $S\to\infty$ in a classical limit of the s-d model.

For later convenience we use a method of equation of motion which is in principle equivalent to the Green function approach. Then the Hamiltonian (1) is easily diagonalized by taking

$$\beta_n=\sum_k (f_{nk}a_{k\uparrow}+g_{nk}a^*_{-k\downarrow})$$

as

$$H=\sum_n \omega_n\beta_n{}^*\beta_n+JS/2\,. \tag{1'}$$

All of the eigenmodes are classified into two types: $F_n=\pm G_n$, where $F_n\equiv\sum_k f_{nk}$ and $G_n\equiv\sum_k g_{nk}$. The coefficients are determined by

$$f_{nk}=\frac{\omega_n+\varepsilon_k\mp\Delta}{\omega_n{}^2-\varepsilon_k{}^2-\Delta^2}cF_n\,,\qquad g_{nk}=\frac{\omega_n-\varepsilon_k\mp\Delta}{\omega_n{}^2-\varepsilon_k{}^2-\Delta^2}cG_n\,,$$

where $c=-JS/2N$. The eigenfrequencies ω_n are obtained from a secular equation

$$A^\pm(\omega)=0\,, \tag{2}$$

where

$$A^\pm(\omega)\equiv 1-c(\omega\mp\Delta)\sum_k\frac{1}{\omega^2-E_k{}^2}\,, \tag{3}$$

$$E_k=\sqrt{\varepsilon_k{}^2+\Delta^2}\,.$$

Here we assumed a symmetrical conduction electron band, which is later treated as a square type with a band width $2D$. It is enough to examine the system for $c>0$ (antiferromagnetic coupling). Then there exists one mode β_0 within the gap with the energy

$$\omega_0=-\frac{1-\zeta^2}{1+\zeta^2}\Delta\,,\qquad \zeta=-\frac{JS\pi\rho}{2N}\,. \tag{4}$$

The origin of the one-particle energy is chosen so as to be the chemical potential of the system; there is a degeneracy with respect to the particle number.

Now let us remember that if an operator A fortunately satisfies the relation $[A,H]=\omega A$, then, A corresponding to $\omega>0$ (or <0) is an annihilation (or creation) operator for the excitation of the system. The ground state Φ is naturally determined by $A\Phi=0$ for all A of $\omega>0$.

Since this is indeed the case for our system, the ground state Ψ or Ψ' is determined by

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$$0<\zeta<1\,, \qquad \beta_0{}^*, \beta_i{}^*, \cdots, \beta_j\,, \cdots \Psi=0$$

or

$$1<\zeta\,, \qquad \beta_0, \beta_i{}^*, \cdots, \beta_j, \cdots \Psi'=0\,.$$

$\beta_i, \cdots$ and $\beta_j, \cdots$ are the operators corresponding to $\omega_i, \cdots <0$ and $\omega_j, \cdots >0$, respectively. We can recognize $\Psi'=\beta_0\Psi$. Notice that the ground state abruptly changes to Ψ' from Ψ at $\zeta=1$, when the level β_0 crosses the Fermi level. $|\omega_0|$ denotes the lowest excited energy of the system in any case.

The total energy change of the system consists of the contributions from continuum and the bound state. Together with the second term of the Hamiltonian (1′), we can obtain the energy change for Ψ,

$$\Delta E(\Psi)=\frac{1}{\pi}\sum_{S=\pm}\int_{-\sqrt{D^2+\Delta^2}}^{-\Delta} d\omega\,\tan^{-1}\frac{\mathrm{Im}\,A^S(\omega)}{\mathrm{Re}\,A^S(\omega)}+(\omega_0+\Delta)+\frac{JS}{2}\,, \tag{5}$$

where

$$-\tan^{-1}\frac{\mathrm{Im}\,A^\pm(\omega)}{\mathrm{Re}\,A^\pm(\omega)}$$
$$=-\tan^{-1}\frac{\pi\rho c\sqrt{(\omega\mp\Delta)/(\omega\pm\Delta)}}{1+\rho c\sqrt{(\omega\mp\Delta)/(\omega\pm\Delta)}\log|(D+\sqrt{\omega^2-\Delta^2})/(D-\sqrt{\omega^2-\Delta^2})|} \tag{6}$$

is the phase shift of the continuum mode of the type $F=\pm G$. For Ψ', we have $\Delta E(\Psi')=\Delta E(\Psi)-\omega_0$. $\Delta E(\Psi)$ and $\Delta E(\Psi')$ are numerically calculated and plotted by Fig. 1. As seen there, Ψ and Ψ' are perturbationally not connected at the critical value $\zeta=1$.

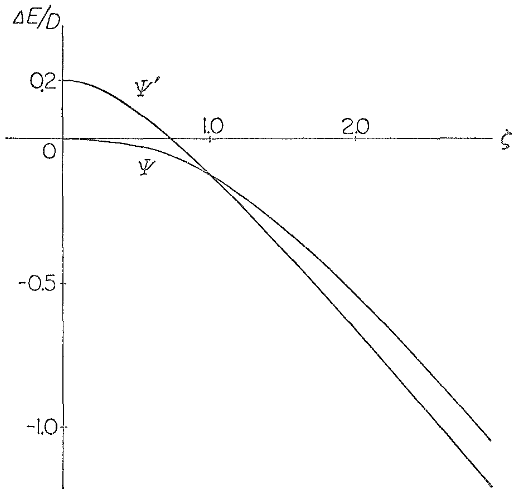

Fig. 1. Total energy changes with the interaction strength ζ in the states Ψ and Ψ' for $\Delta/D=0.2$.

The occupied β_0 level localizes a half up-spin electron and a half down-spin hole in the vicinity of the impurity. We can also show that the total electronic spin is 0 for Ψ, (in accord with the result of the zero paramagnetic susceptibility at $T=0$,[6]) but -1 for Ψ'.*) Then, the continuum is considered to *localize* -1 electronic spin because of the local property of the perturbation. That is, a down electronic spin is captured by the impurity in the state Ψ' (see Fig. 2). We should remark here that the phase shifts (6) at the top of the continuum band, $-\Delta$, below the Fermi level are $-\pi/2$ and 0 for $+$ and

*) The total number of the electrons is unchanged ($=N$) for both.

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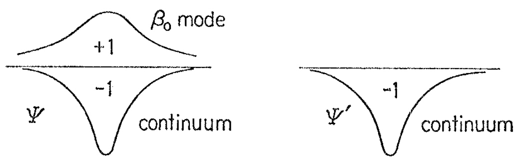

Fig. 2. Electronic spin localizations around the impurity in the states Ψ and Ψ'.

— types of the modes respectively. This fact is independent of the interaction strength $c(>0)$ or the gap parameter, and results from the divergent state density at $\omega \to -\Delta$.

To examine the localized mode β_0 we introduce the difference of the expectation value, $\langle A \rangle_0 \equiv \langle A \rangle_\Psi - \langle A \rangle_{\Psi'}$, which represents the contribution to A of β_0 only. For the bulk order parameter it is

$$2 \sum_k \langle a_{k\uparrow}^* a_{-k\downarrow}^* \rangle_0 = \frac{1-\zeta^2}{1+\zeta^2}.$$

Therefor, β_0 contributes to destroy the superconducting parameter by one in N in the ground state when $\zeta \to 1$. The ground state is always more superconducting than the lowest excited state.

For the total energy of the system, $\langle H \rangle_0 = \omega_0$. It comes from just the pairing energy of the superconductor; the kinetic energy term and the coupling term of spins have been cancelled by each other. The magnetic effect of the impurity to β_0 is indirect in this sence.

The order parameter or the spin density at the impurity site changes like $\propto \zeta/(1+\zeta^2)^2$ if only the β_0 mode is taken into account. The mode is most localized at the interaction strength $\zeta = 1/\sqrt{3}$. On the other hand the total contribution (including both β_0 and the continuum) to the number of the electron spin at the impurity site in the state Ψ decreases from 0 and approaches -1 when the interaction ζ increases, as plotted in Fig. 3. For large ζ, even in the state Ψ, the total electron spin is strongly localized mainly due to the continuum and gains the coupling energy.

As shown, the state Ψ' is the lowest excited one for weak interactions. However, it becomes the ground state for $\zeta > 1$ naturally. The situation would be the same in a quantal *s-d* system. Then, it would be quite reasonable that the wave function considered by Soda, Matsuura and Nagaoka behaves as representing an

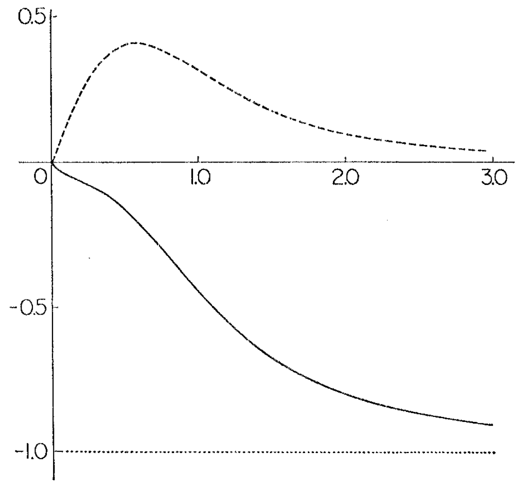

Fig. 3. Number of the electronic spin at the impurity site in the state Ψ. (Contribution only from β_0 mode is plotted by a dotted line.) $\Delta/D = 0.2$.

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excited state for weak interaction ($T_K < T_{c0}$) and the ground state for strong interaction.[1)]

If one treats the same problem in terms of Green functions in Nambu space, two symmetrical poles will appear in the gap. They correspond to β_0 and the conjugate, β_0^*, modes in our formalism and nothing else.[4)] The interchange $\Psi \to \Psi'$ for the ground state is automatically considered by means of the Green function formalism.

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