Cooper pair shape and odd-frequency pairing in superconductor junctions

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Abstract.
Cooper pair shape is not so simple in inhomogeneous superconducting systems. It is shown that pairing function in a normal metal is surprisingly anisotropic because of quasiparticle interference. We calculate angle resolved quasiparticle local density of states in NS bilayers which reflects such anisotropic shape of the pairing function. This unusual feature can be detected by a magneto-tunneling spectroscopy experiment.

1. Introduction
It is known that Cooper pairs consisting of two electrons are characterized by electric charge $2e$, macroscopic phase, internal spin, and by time and orbital structures [1]. The charge $2e$ manifests itself in various experiments, like Shapiro steps, flux quantization and excess current. The macroscopic phase generates the Josephson current [1]. The internal spin structure is classified into spin-triplet and spin-singlet states. Further, based on a symmetry with respect to the internal time, superconducting state can belong to the even-frequency or the odd-frequency symmetry class [2]. The orbital degree of freedom is described by an angular momentum quantum number $l$ [3, 4]. In $s$-wave superconductors with $l = 0$, the Cooper pair wave function is spherically symmetric on the Fermi surface, i.e. an angular structure of a Cooper pair is isotropic in momentum space. The shape of Cooper pairs in $p$-wave ($l = 1$) and $d$-wave ($l = 2$) superconductors is characterized by two-fold and four-fold symmetries, respectively [3]. The well established properties listed above hold in bulk superconductors. The presence of perturbations like spin-flip or interface scattering may change the symmetry of Cooper pairs. For instance, odd-frequency property of Cooper pairs in proximity structures was predicted in recent works [5, 6]. The shape of Cooper pair wave function in non-uniform systems like superconducting junctions is not necessarily the same as that in the bulk state. Despite the extensive study of the proximity effect during several past decades [1, 7], rather little attention has been paid to the problem of...
Cooper pair shape in non-uniform superconducting systems [8, 9]. This issue is quite important in view of current interest to the physics of superconducting nanostructures.

The aim of the present paper is to clarify the consequences of breakdown of translational symmetry in superconductors on the Cooper pair shape. For this purpose, we study the proximity effect in quasi-two-dimensional normal metal / superconductor (N/S) junctions by solving the Eilenberger equation. We analyze the pairing function and the local density of states (LDOS) in N/S junctions with spin-singlet s-wave and $d_{x^2-y^2}$-wave superconductors. The shape of the Cooper pair deviates seriously from that of the bulk with the generation of the odd-frequency component of the pairing function due to the formation of the Andreev–Saint-James bound states[10]. To detect the complex Cooper pair shape, we propose to use scanning tunneling spectroscopy in rotating magnetic field. We show that the calculated tunneling conductance exhibits complex patterns even in the s-wave case.

2. Model and Formulation

Let us consider a quasi-two-dimensional N/S junction, where the S region is semi-infinite and the normal metal has finite length $L$. A normal metal ($-L < x < 0$) is attached to a superconductor ($0 < x < \infty$).

We consider a perfect N/S interface with perfect transmissivity, while it can be shown that characteristic behavior of Cooper pairs remains qualitatively unchanged even in the presence of a potential barrier at the N/S interface.

The quasiclassical Green’s functions [11] in a normal metal (N) and a superconductor (S) are parameterized as

$$g_\pm^{(i)} = f_1^{(i)}\hat{r}_1 + f_2^{(i)}\hat{r}_2 + g_3^{(i)}, \quad (\hat{g}_\pm^{(i)})^2 = \hat{1}, \quad (1)$$

where a superscript $i (= N, S)$ are the Pauli matrices, and $\hat{1}$ is a unit matrix. The subscript $+$ (-) denotes a moving direction of a quasiparticle in the $x$ direction [11], and $\Delta_\pm(x)$ ($\Delta_\mp(x)$) is the pair potential for a left (right) going quasiparticle. In a normal metal, $\Delta_\pm(x)$ is set to zero because the pairing interaction is absent there. The Green’s functions can be expressed in terms of the Ricatti parameters [12],

$$f_1^{(i)} = \pm \nu_i[\Gamma_\pm^{(i)}(x) + \zeta_\pm^{(i)}(x)]/[1 + \Gamma_\pm^{(i)}(x)\zeta_\pm^{(i)}(x)], \quad (2)$$

$$f_2^{(i)} = \pm \nu_i[\Gamma_\pm^{(i)}(x) - \zeta_\pm^{(i)}(x)]/[1 + \Gamma_\pm^{(i)}(x)\zeta_\pm^{(i)}(x)], \quad (3)$$

$$g_3^{(i)} = [1 - \Gamma_\pm^{(i)}(x)\zeta_\pm^{(i)}(x)]/[1 + \Gamma_\pm^{(i)}(x)\zeta_\pm^{(i)}(x)], \quad (4)$$

with $\nu_i = 1$ for $i = S$ and $\nu_i = -1$ for $i = N$. The parameters $\Gamma_\pm^{(i)}(x)$ and $\zeta_\pm^{(i)}(x)$ obey the Eilenberger equation of the Ricatti type [12],

$$iv_{Fx}\partial_x\Gamma_\pm^{(i)}(x) = -\Delta_\pm(x)[1 + (\Gamma_\pm^{(i)}(x))^2] + 2\varepsilon\nu_i\Gamma_\pm^{(i)}(x),$$

$$iv_{Fx}\partial_x\zeta_\pm^{(i)}(x) = -\Delta_\pm(x)[1 + (\zeta_\pm^{(i)}(x))^2] - 2\varepsilon\nu_i\zeta_\pm^{(i)}(x),$$

with $\varepsilon = \varepsilon + i\delta_0$ where $\varepsilon$ is the energy of a quasiparticle measured from the Fermi level and $\delta_0$ is the level broadening due to impurity scattering. $v_{Fx}$ is the x-component of Fermi velocity. In the clean limit, we consider $\delta_0 \ll \Delta_0$. Boundary condition at $x = -L$ is given by

$\zeta_\pm^{(N)}(-L) = -\Gamma_\pm^{(N)}(-L)$. Boundary condition at the N/S interface becomes

$\zeta_\pm^{(S)}(0) = -\Gamma_\pm^{(S)}(0)$ and $\zeta_\pm^{(N)}(0) = -\Gamma_\pm^{(N)}(0)$. The pair potential $\Delta_\pm(x)$ is expressed by $\Delta_\pm(x) = \Delta(x)\Phi_\pm(\theta) \Theta(x)$, where a form factor $\Phi_\pm(\theta)$ is given by $\Phi_\pm(\theta) = 1$ for s-wave symmetry and $\pm \sin 2\theta$ for $d_{x^2-y^2}$-wave one with $\theta$ being an incident angle of a quasiparticle measured from the $x$ direction. Bulk pair potential is $\Delta(\infty) = \Delta_0$, and we determine the spatial dependence $\Delta(x)$ in a self-consistent way.
For $x \gg L_0$, the angular structure of $f_{2\pm}^{(S)}$ follows that of the pair potential, whereas $f_{1\pm}^{(S)}$ is zero with $L_0 = \nu_F/T_C$ being a coherence length in N and $T_C$ being the transition temperature. The pairing function $f_{1\pm}^{(i)}$ is generated by inhomogeneity in a system and thus has a finite value only near the interface and in a normal metal. Recent study [6] have shown that $f_{1\pm}^{(i)}$ has an odd-frequency symmetry since functions $f_{1\pm}^{(i)}$ and $f_{2\pm}^{(i)}$ have opposite parities. The induced odd-frequency component has the odd (even) parity, respectively. Pairing function $f_1$ is defined in the angular domain of $-\pi/2 \leq \theta < 3\pi/2$. We denote $f_1(\theta)$ by $f_{\pm}^{(i)}(\theta)$ in the angle range $-\pi/2 \leq \theta < \pi/2$ and $f_1(\theta) = f_{\pm}^{(i)}(\pi - \theta)$ for $\pi/2 \leq \theta < 3\pi/2$. The angular structure of functions $f_2$ and $g$ is defined in the same manner. LDOS is given by the relation $\rho_L(\theta) = \text{Real}[g(\theta)]$. In the following, we calculate $f_1$, $f_2$, and $\rho_L$. After that we calculate the spectral properties of pair amplitudes and LDOS. In what follows, we fix temperature $T = 0.05T_C$, the length of the normal region $L = 5L_0$, and $\delta_0 = 0.01\Delta_0$.

### 3. Calculated Results

In Figs. 1 and 2 we show polar plots of $f_1$, $f_2$, and $\rho_L$ in s-wave and $d_{xy}$-wave junctions for various choices of $\varepsilon$ and $x$. Dashed, solid and dotted lines represent, respectively, the results for $x = \infty$ (superconductor), $x = 0$ (interface), and $x = -L/2$ (normal metal). The odd-frequency component is always absent for $x = \infty$. Since $\rho_L$ is independent of $x$ in N, the resulting value of $\rho_L$ at $x = 0$ is equal to that at $x = -L/2$. We fix $\varepsilon = 0.1\Delta_0$ in Figs. 1 and 2.

First, we focus on the s-wave case (Fig. 1). As shown in Fig. 1(a), at $x = \infty$ the even-frequency component $f_2$ has a circular shape reflecting the s-wave symmetry. However, at $x = 0$, the shape (solid line) slightly deviates from the circular shape, while the shape in N ($x = -L/2$) drastically changes. The shape of $f_1$ at $x = 0$ and $x = -L/2$ exhibits the butterfly-like pattern (Fig. 1(b)). Such anisotropic property of $f_1$ and $f_2$ affects the LDOS as shown in Fig.1(c). In particular, LDOS at the interface strongly deviates from the circular shape. At the interface, the shape of $\rho_L$ in Fig.1(c) is quite similar to that of $f_1$ shown in Fig.1(b).

These profiles can be qualitatively understood as follows. At $x = 0$, the relations $f_{1\pm}^{(N)} = \pm\Gamma(1 - \alpha^2)/\Xi$, and $g_{\pm}^{(N)} = (1 + \alpha^2\Gamma^2)/\Xi$ are satisfied with $\Xi = 1 - \Gamma^2\alpha^2$, $\Gamma = \Gamma_{\mp}^{(S)}(0)$ and $\alpha = \exp[2i\varepsilon L/(\nu_F \cos \theta)]$. For $\varepsilon \ll \Delta_0$, the relations $\Gamma \sim 1/i$ and $f_{1\pm} = i\Delta_0$ are satisfied. Thus shape of function $f_1$ is similar to that of $\rho_L$. This argument is valid even for $\varepsilon = 0.1\Delta_0$ as shown in Fig.1. The directions of the spin projections in LDOS are characterized by small value of $\Xi$, which has close relation to the formation of the Andreev–Saint-James bound states [10, 13].
Next, we discuss the results for \( d_{xy} \)-wave junctions shown in Fig. 2 where mid-gap Andreev resonant state \([14]\) are formed at the interface. In a superconductor \((x = \infty)\), functions \(f_2\) and \(g\) are given by \(\Delta_0 \sin 2\theta / \sqrt{\varepsilon^2 - \Delta_0^2 \sin^2 2\theta}\) and \(\varepsilon / \sqrt{\varepsilon^2 - \Delta_0^2 \sin^2 2\theta}\), respectively. As shown by dashed lines in Fig. 2, the amplitudes of \(f_2\) and \(g\) become large along the directions \(\theta = [\sin^{-1}(\varepsilon/\Delta_0)]/2\). The shapes of \(f_1\) and \(\rho_L\) at the N/S interface are similar to those in \(s\)-wave superconductor junctions [solid lines in Fig. 2(b), (c)].

Here, we propose an experimental setup to measure complex Cooper pair shape, based on magneto-tunneling spectroscopy, \textit{i.e.}, scanning tunneling spectroscopy (STS) in the presence of magnetic field. Let us consider a situation where magnetic field is applied parallel to the N/S plane. Tunneling current at a fixed bias voltage is measured as a function of the angle \(\phi\) between the \(x\) axis and the direction of magnetic field. The vector potential in this configuration is given by \((A_x, A_y) = -\lambda H \exp(-z/\lambda)(\sin \phi, \cos \phi)\) [15]. We assume that thickness of a quasi-two-dimensional superconductor is sufficiently small compared to a magnetic field penetration depth \(\lambda\). Magnetic field shifts the quasiparticle energy \(\varepsilon\) to \(\varepsilon - H \Delta_0 \sin(\phi - \theta)/B_0\) where \(B_0 = \hbar/(2\varepsilon \pi^2 \lambda)\) and \(\xi = \hbar v_F/\pi \Delta_0\). Here, to evaluate the order of magnitude of \(B_0\), we explicitly write the Plank constant. For typical values of \(\xi \sim \lambda \sim 100\text{nm}\), the magnitude of \(B_0\) is of the order of 0.02 Tesla. Local density of states measured in the considered magneto-tunneling STS configuration is given by [16], \(\rho_S(\phi) = f^{3\pi/2} \rho_L(\theta, \phi) d\theta\). At sufficiently low temperatures the applied bias voltage \(V\) satisfies the relation \(eV = \varepsilon\). \(\rho_S(\phi)\) is a periodic function of \(\phi\) and we denote its maximum value as \(\rho_M\). In the following, we focus on the normalized value \(\rho(\phi)\) defined by \(\rho(\phi) = \rho_S(\phi)/\rho_M\).

In Fig. 3, \(\rho = \rho(\phi)\) is plotted as a function of \(\phi\). In the \(s\)-wave case, \(\rho(\phi)\) in bulk is always unity due to the isotropic nature of the \(s\)-wave pairing as shown by curve B. On the other hand, \(\rho\) at the N/S interface has an oscillatory dependence due to the deviation of the Cooper pair shape from the circular one. It is remarkable that the line shape of curve A changes drastically with the increase of \(\varepsilon\) as seen from Figs. 3(a) (b) and (c). This sensitivity to \(\varepsilon\) variation reflects the complex shape of \(\rho_L\) shown in Fig. 1.

For \(d_{xy}\)-wave case, the line shape of \(\rho\) in the bulk has periodic oscillations with the period \(0.5\pi\). The amplitude of the oscillations is reduced with the increase of \(\varepsilon\) as shown by the curves B in Figs. 4(a), (b) and (c). On the other hand, the line shapes of the curves A change drastically with the increase of \(\varepsilon\). This sensitivity originates from the complex patterns of \(\rho_L\) shown in Fig. 2.

As seen from the above results, by changing the magnitude of the bias voltage \(V\) and the rotation angle \(\phi\), it is possible to clarify the remarkable deformation of Cooper pairs. Therefore,
magnetotunneling spectroscopy provides the way to detect bulk symmetry of the pair potential.

Next, we discuss that impurity scattering effects in N. We concentrate on the s-wave symmetry. To change the magnitude of impurity scattering in N, we choose $\bar{\varepsilon}$ in the equation of Ricatti parameters as $\bar{\varepsilon} = \varepsilon + i\delta$. The Riccati parameters in N satisfy following equations discussed in the revised version.

\[
iv_F x \partial_x \Gamma^{(N)}_\pm(x) = -2\varepsilon \Gamma^{(N)}_\pm(x),
\]

\[
iv_F x \partial_x \zeta^{(N)}_\pm(x) = 2\bar{\varepsilon} \zeta^{(N)}_\pm(x),
\]

with $\bar{\varepsilon} = \varepsilon + i\delta$ where $\varepsilon$ is the energy of a quasiparticle measured from the Fermi level. The mean free path in N is given by $h v_F / \delta$.

In order to clarify the influence of the impurity scattering effect in N on line shapes of curves in Figs. 3 and 4, we choose $\delta = 0.03\Delta_0$ and $\delta = 0.1\Delta_0$ with $L = 5L_0$ for the first. On the other hand, in the S region, we fix $\delta = \delta_0 = 0.01\Delta_0$ in the following. As shown in Figs. 5 and 6, $\rho = \rho(\phi)$ has an oscillatory dependence. This oscillatory dependence does not vanish even if we choose $\delta = 0.1\Delta_0$, where the mean free path in the normal metal is approximately the same.
as that of the width of the normal region. The line shape of $\rho(\phi)$ is sensitive to the change of $\varepsilon$ irrespective of the strength of the impurity scattering in the normal metal as far as the mean free path is longer than the width of the normal metal.

Next, we consider much more short normal metal case, with $L = 0.8L_0$. We choose $\delta = 0.01\Delta_0$, $\delta = 0.1\Delta_0$ and $\delta = 0.5\Delta_0$ in the following. In the present parameter choice, the length of the mean free path is larger than that of the width of the normal metal. On the other hand, in the S region, we fix $\delta = \delta_0 = 0.01\Delta_0$. As shown in Figs. 7 and 8, $\rho = \rho(\phi)$ has an oscillatory dependence. This oscillatory dependence does not vanish even if we choose $\delta = 0.5\Delta_0$, where the mean free path in the normal metal is approximately the same as the coherence length. The line shape of $\rho(\phi)$ is sensitive to the change of $\varepsilon$ irrespective of the strength of the impurity scattering and the width of the normal metal. We must emphasize that our obtained results in Figs. 3 and 4 are not to be smeared out for an experimentally accessible concentration of the impurities.

To summarize, the oscillatory behavior of $\rho$ can be detected if the following two conditions are fulfilled: $l > L$ and $l > L_0$, where $l$ is the mean free path in N. To satisfy these conditions, normal metals with high mobility are desirable. Superconducting junctions with 2D-electron gas realized in InAs [17] or Graphene[18] are possible candidates due to high electronic mobility in both types of materials. Furthermore, large magnitude of $T_C$ or $\Delta_0$ helps to satisfy the second condition. From this viewpoint, junctions with high $T_C$ cuprates extensively studied by now [19] are promising candidates. Surface roughness could also lead to a broadening of the oscillatory
behavior of $\rho$. This effect is controlled by an effective scattering length within the surface layer (see Refs. [20, 9]). Both bulk and surface scattering lead to mixing of quasiparticle trajectories at different angles, while the general angular shape of the Cooper pair does not change and can be determined at realistic experimental conditions.

4. Conclusion
In summary, we have studied the Cooper pair shape in normal-metal/superconductor (N/S) junctions by using the quasiclassical Green’s function formalism. The quasiparticle interference leads to striking deformations in the shape of a Cooper pair wave function in a normal metal. We also show that the anisotropic shape of Cooper pairs could be resolved by scanning tunneling spectroscopy experiments in magnetic field. The Cooper pair deformation is a common feature of non-uniform superconducting systems in the clean limit. This provides a key concept to explore novel quantum interference phenomena in superconducting nanostructures.

5. References
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