

## Theory of the Proximity Effect in Junctions with Unconventional Superconductors

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We present a general theory of the proximity effect in junctions between diffusive normal metals (DN) and superconductors. Various possible symmetry classes in a superconductor are considered: even-frequency spin-singlet even-parity (ESE) state, even-frequency spin-triplet odd-parity state, odd-frequency spin-triplet even-parity (OTE) state and odd-frequency spin-singlet odd-parity state. It is shown that the pair amplitude in a DN belongs, respectively, to an ESE, OTE, OTE, and ESE pairing state since only the even-parity  $s$ -wave pairing is possible due to the impurity scattering.

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It is well established that superconductivity is realized due to the formation of Cooper pairs consisting of two electrons. In accordance with the Pauli principle, it is customary to distinguish spin-singlet even-parity and spin-triplet odd-parity pairing states in superconductors, where odd (even) refer to the orbital part of the pair wave function. For example,  $s$ -wave and  $d$ -wave pairing states belong to the former case while  $p$ -wave state belongs to the latter one [1]. In both cases, the pair amplitude is an even function of energy. However, the so-called odd-frequency pairing states when the pair amplitude is an odd function of energy can also exist. Then, the spin-singlet odd-parity and the spin-triplet even-parity pairing states are possible.

The possibility of realizing the odd-frequency pairing state was first proposed by Berezinskii in the context of <sup>3</sup>He, where the odd-frequency spin-triplet hypothetical pairing was discussed [2]. The possibility of the odd-frequency superconductivity was then discussed in the context of various mechanisms of superconductivity involving strong correlations [3,4]. There are several experimental evidences [5] which are consistent with the realization of the odd-frequency bulk superconducting state in Ce compounds [4,5]. In more accessible systems (ferromagnet/superconductor heterostructures with inhomogeneous magnetization) the odd-frequency pairing state was first proposed in Ref. [6] and then various aspects of this state were intensively studied [7]. At the same time, the very important issue of the manifestation of the odd-frequency pairing in proximity systems without magnetic ordering received no attention yet. This question is addressed in the present Letter.

Coherent charge transport in structures involving diffusive normal metals (DN) and superconductors ( $S$ ) was extensively studied during the past decade both experimentally and theoretically. However, almost all previous work was restricted to junctions based on conventional  $s$ -wave superconductors [8]. Recently, a new theoretical approach to study charge transport in junctions based on  $p$ -wave and  $d$ -wave superconductors was developed and applied to the

even-frequency pairing state [9,10]. It is known that in the anisotropic pairing state, due to the sign change of the pair potential on the Fermi surface, a so-called midgap Andreev resonant state (MARS) is formed at the interface [11,12]. As was found in [9,10], MARS competes with the proximity effect in contacts with spin-singlet superconductors, while it coexists with the proximity effect in junctions with spin-triplet superconductors. In the latter case, it was predicted that the induced pair amplitude in the DN has a peculiar energy dependence and the resulting local density of states (LDOS) has a zero energy peak (ZEP) [10]. However, the relation of this unusual proximity effect to the formation of the odd-frequency pairing state was not yet clarified. Furthermore, there was no study of the proximity effect in junctions with odd-frequency superconductors. The aim of the present Letter is to formulate a general theory of the proximity effect in the DN/ $S$  junctions applicable to any type of symmetry state in a superconductor forming the junction in the absence of spin-dependent electronic scattering at the DN/ $S$  interface. It will be shown that for spin-triplet [spin-singlet] superconductor junctions, odd-frequency spin-triplet even-parity (OTE) pairing state [even-frequency spin-singlet even-parity (ESE) pairing state] is generated in DN independent of the parity of the superconductor.

Before proceeding with formal discussion, let us present qualitative arguments illustrating the main conclusions of the Letter. Two constraints should be satisfied in the considered system: (1) only the  $s$ -wave even-parity state is possible in the DN due to isotropization by impurity scattering [1], (2) the spin structure of induced Cooper pairs in the DN is the same as in an attached superconductor. Then the Pauli principle provides the unique relations between the pairing symmetry in a superconductor and the resulting symmetry of the induced pairing state in the DN. Namely, for even-parity superconductors, ESE and OTE states, the pairing symmetry in the DN should remain ESE and OTE. On the other hand, for odd-parity superconductors, even-frequency spin-triplet odd-parity (ETO) and odd-frequency

spin-singlet odd-parity (OSO) states, the pairing symmetry in the DN should be OTE and ESE, respectively. The above results are based on general properties and independent of the details of the geometry and the spin structure of the spin-triplet superconductors.

The generation of the OTE state in the DN attached to the ETO  $p$ -wave superconductor is of particular interest. A similar OTE state can be generated in superconducting junctions with diffusive ferromagnets [6,7] but due to different physical mechanism. Although the symmetry properties can be derived from the basic arguments given above, the quantitative model has to be considered to prove the existence of nontrivial solutions for the pair amplitude in the DN in each of the above cases.

Let us start with the general symmetry properties of the quasiclassical Green's functions in the considered system. The elements of retarded and advanced Nambu matrices  $\hat{g}^{R,A}$

$$\hat{g}^{R,A} = \begin{pmatrix} g_{\alpha,\beta}^{R,A} & f_{\alpha,\beta}^{R,A} \\ \bar{f}_{\alpha,\beta}^{R,A} & \bar{g}_{\alpha,\beta}^{R,A} \end{pmatrix} \quad (1)$$

are composed of the normal  $g_{\alpha,\beta}^R(\mathbf{r}, \varepsilon, \mathbf{p})$  and anomalous  $f_{\alpha,\beta}^R(\mathbf{r}, \varepsilon, \mathbf{p})$  components with spin indices  $\alpha$  and  $\beta$ . Here  $\mathbf{p} = \mathbf{p}_F / |\mathbf{p}_F|$ ,  $\mathbf{p}_F$  is the Fermi momentum,  $\mathbf{r}$  and  $\varepsilon$  denote coordinate and energy of a quasiparticle measured from the Fermi level.

The function  $f^R$  and the conjugated function  $\bar{f}^R$  satisfy the following relation [13,14]:

$$\bar{f}_{\alpha,\beta}^R(\mathbf{r}, \varepsilon, \mathbf{p}) = -[f_{\alpha,\beta}^R(\mathbf{r}, -\varepsilon, -\mathbf{p})]^* \quad (2)$$

The Pauli principle is formulated in terms of the retarded and the advanced Green's functions in the following way [13]:

$$f_{\alpha,\beta}^A(\mathbf{r}, \varepsilon, \mathbf{p}) = -f_{\beta,\alpha}^R(\mathbf{r}, -\varepsilon, -\mathbf{p}). \quad (3)$$

By combining the two above equations, we obtain  $\bar{f}_{\beta,\alpha}^R(\mathbf{r}, \varepsilon, \mathbf{p}) = [f_{\alpha,\beta}^A(\mathbf{r}, \varepsilon, \mathbf{p})]^*$ . Further, the definitions of the even-frequency and the odd-frequency pairing are  $f_{\alpha,\beta}^A(\mathbf{r}, \varepsilon, \mathbf{p}) = f_{\alpha,\beta}^R(\mathbf{r}, -\varepsilon, \mathbf{p})$  and  $f_{\alpha,\beta}^A(\mathbf{r}, \varepsilon, \mathbf{p}) = -f_{\alpha,\beta}^R(\mathbf{r}, -\varepsilon, \mathbf{p})$ , respectively. Finally we get

$$\bar{f}_{\beta,\alpha}^R(\mathbf{r}, \varepsilon, \mathbf{p}) = [f_{\alpha,\beta}^R(\mathbf{r}, -\varepsilon, \mathbf{p})]^* \quad (4)$$

for the even-frequency pairing and

$$\bar{f}_{\beta,\alpha}^R(\mathbf{r}, \varepsilon, \mathbf{p}) = -[f_{\alpha,\beta}^R(\mathbf{r}, -\varepsilon, \mathbf{p})]^* \quad (5)$$

for the odd-frequency pairing. In the following, we will focus on Cooper pairs with  $S_z = 0$  for the simplicity, remove the external phase of the pair potential in the superconductor and concentrate on the retarded part of the Green's function. In the case of pairing with  $S_z = 1$  our final results will not be changed. We consider a junction consisting of a normal ( $N$ ) reservoir and a superconducting reservoir connected by a quasi-one-dimensional diffusive conductor (DN) with a length  $L$  much larger than the mean free path. The interface between the DN

and the superconductor ( $S$ ) at  $x = L$  has a resistance  $R_b$  and the  $N$ /DN interface at  $x = 0$  has a resistance  $R_{b'}$ . For  $R_{b'} = \infty$ , the present model is reduced to the DN/ $S$  bilayer with vacuum at the DN free surface. The Green's function in the superconductor can be parametrized as  $g_{\pm}(\varepsilon)\hat{\tau}_3 + f_{\pm}(\varepsilon)\hat{\tau}_2$  using Pauli matrices, where the suffix  $+$  ( $-$ ) denotes the right (left) going quasiparticles.  $g_{\pm}(\varepsilon)$  and  $f_{\pm}(\varepsilon)$  are given by  $g_{+}(\varepsilon) = g_{\alpha,\beta}^R(\mathbf{r}, \varepsilon, \mathbf{p})$ ,  $g_{-}(\varepsilon) = g_{\alpha,\beta}^R(\mathbf{r}, \varepsilon, \bar{\mathbf{p}})$ ,  $f_{+}(\varepsilon) = f_{\alpha,\beta}^R(\mathbf{r}, \varepsilon, \mathbf{p})$ , and  $f_{-}(\varepsilon) = f_{\alpha,\beta}^R(\mathbf{r}, \varepsilon, \bar{\mathbf{p}})$ , respectively, with  $\bar{\mathbf{p}} = \bar{\mathbf{p}}_F / |\mathbf{p}_F|$  and  $\bar{\mathbf{p}}_F = (-p_{Fx}, p_{Fy})$ . Using the relations (4) and (5), we obtain that  $f_{\pm}(\varepsilon) = [f_{\pm}(-\varepsilon)]^*$  for the even-frequency pairing and  $f_{\pm}(\varepsilon) = -[f_{\pm}(-\varepsilon)]^*$  for the odd-frequency pairing, respectively, while  $g_{\pm}(\varepsilon) = [g_{\pm}(-\varepsilon)]^*$  in both cases.

In the DN region only the  $s$ -wave even-parity pairing state is allowed due to isotropization by impurity scattering [1]. The resulting Green's function in the DN can be parametrized by  $\cos\theta\hat{\tau}_3 + \sin\theta\hat{\tau}_2$  in a junction with an even-parity superconductor and by  $\cos\theta\hat{\tau}_3 + \sin\theta\hat{\tau}_1$  in a junction with an odd-parity superconductor. The function  $\theta$  satisfies the Usadel equation [15]

$$D \frac{\partial^2 \theta}{\partial x^2} + 2i\varepsilon \sin\theta = 0 \quad (6)$$

with the boundary condition at the DN/ $S$  interface [9]

$$\frac{L}{R_d} \left( \frac{\partial \theta}{\partial x} \right) \Big|_{x=L} = \frac{\langle F_1 \rangle}{R_b}, \quad (7)$$

$$F_1 = \frac{2T_1(f_S \cos\theta_L - g_S \sin\theta_L)}{2 - T_1 + T_1(\cos\theta_L g_S + \sin\theta_L f_S)}, \quad (8)$$

and at the  $N$ /DN interface

$$\frac{L}{R_d} \left( \frac{\partial \theta}{\partial x} \right) \Big|_{x=0} = \frac{\langle F_2 \rangle}{R_{b'}}, \quad F_2 = \frac{2T_2 \sin\theta_0}{2 - T_2 + T_2 \cos\theta_0}, \quad (9)$$

respectively, with  $\theta_L = \theta|_{x=L}$  and  $\theta_0 = \theta|_{x=0}$ . Here,  $R_d$  and  $D$  are the resistance and the diffusion constant in the DN, respectively. The brackets  $\langle \dots \rangle$  denote averaging over the injection angle  $\phi$

$$\langle F_{1(2)}(\phi) \rangle = \frac{\int_{-\pi/2}^{\pi/2} d\phi \cos\phi F_{1(2)}(\phi)}{\int_{-\pi/2}^{\pi/2} d\phi T_{1(2)} \cos\phi}, \quad (10)$$

$$T_1 = \frac{4\cos^2\phi}{Z^2 + 4\cos^2\phi}, \quad T_2 = \frac{4\cos^2\phi}{Z'^2 + 4\cos^2\phi}, \quad (11)$$

where  $T_{1,2}$  are the transmission probabilities,  $Z$  and  $Z'$  are the barrier parameters for two interfaces. Here  $g_s$  is given by  $g_s = (g_+ + g_-)/(1 + g_+g_- + f_+f_-)$  and  $f_s = (f_+ + f_-)/(1 + g_+g_- + f_+f_-)$  for the even-parity pairing and  $f_s = i(f_+g_- - f_-g_+)/(1 + g_+g_- + f_+f_-)$  for the odd-parity pairing, respectively, with  $g_{\pm} = \varepsilon/\sqrt{\varepsilon^2 - \Delta_{\pm}^2}$  and  $f_{\pm} = \Delta_{\pm}/\sqrt{\Delta_{\pm}^2 - \varepsilon^2}$ .  $\Delta_{\pm} = \Delta\Psi(\phi_{\pm})$  for even-frequency pairing and  $\Delta_{\pm} = \Delta_{\text{odd}}(\varepsilon)\Psi(\phi_{\pm})$  for odd-frequency pairing,  $\Psi(\phi_{\pm})$  is the form factor with

$\phi_+ = \phi$  and  $\phi_- = \pi - \phi$ .  $\Delta$  is the maximum value of the pair potential for even-frequency pairing.

In the following, we will consider four possible symmetry classes of superconductor forming the junction and consistent with the Pauli principle: ESE, ETO, OTE, and OSO pairing states. We will use the fact that only the even-parity  $s$ -wave pairing is possible in the DN due to the impurity scattering and that the spin structure of pair amplitude in the DN is the same as in an attached superconductor.

1. *Junction with ESE superconductor.*—In this case,  $f_{\pm}(\varepsilon) = f_{\pm}^*(-\varepsilon)$  and  $g_{\pm}(\varepsilon) = g_{\pm}^*(-\varepsilon)$  are satisfied. Then,  $f_S(-\varepsilon) = f_S^*(\varepsilon) = f_S^*$  and  $g_S(-\varepsilon) = g_S^*(\varepsilon) = g_S^*$  and we obtain for  $F_1^*(-\varepsilon)$

$$F_1^*(-\varepsilon) = \frac{2T_1[f_S \cos\theta_L^*(-\varepsilon) - g_S \sin\theta_L^*(-\varepsilon)]}{2 - T_1 + T_1[\cos\theta_L^*(-\varepsilon)g_S + \sin\theta_L^*(-\varepsilon)f_S]}.$$

It follows from Eqs. (6)–(9) that  $\sin\theta^*(-\varepsilon) = \sin\theta(\varepsilon)$  and  $\cos\theta^*(-\varepsilon) = \cos\theta(\varepsilon)$ . Thus the ESE state is formed in the DN, in accordance with the Pauli principle.

2. *Junction with ETO superconductor.*—Now we have  $f_{\pm}(\varepsilon) = f_{\pm}^*(-\varepsilon)$  and  $g_{\pm}(\varepsilon) = g_{\pm}^*(-\varepsilon)$ . Then,  $f_S(-\varepsilon) = -f_S^*(\varepsilon) = -f_S^*$  and  $g_S(-\varepsilon) = g_S^*(\varepsilon) = g_S^*$ . As a result,  $F_1^*(-\varepsilon)$  is given by

$$F_1^*(-\varepsilon) = -\frac{2T_1[f_S \cos\theta_L^*(-\varepsilon) + g_S \sin\theta_L^*(-\varepsilon)]}{2 - T_1 + T_1[\cos\theta_L^*(-\varepsilon)g_S - \sin\theta_L^*(-\varepsilon)f_S]}.$$

It follows from Eqs. (6) and (9) that  $\sin\theta^*(-\varepsilon) = -\sin\theta(\varepsilon)$  and  $\cos\theta^*(-\varepsilon) = \cos\theta(\varepsilon)$ . Thus the OTE state is formed in the DN. Remarkably, the appearance of the OTE state is the only possibility to satisfy the Pauli principle, as we argued above. Interestingly, the OTE pairing state can be also realized in superconductor/ferromagnet junctions [6,7], but the physical mechanism differs from the one considered here.

3. *Junction with OTE superconductor.*—In this case  $f_{\pm}(\varepsilon) = -f_{\pm}^*(-\varepsilon)$  and  $g_{\pm}(\varepsilon) = g_{\pm}^*(-\varepsilon)$ . Then  $f_S(-\varepsilon) = -f_S^*(\varepsilon)$  and  $g_S(-\varepsilon) = g_S^*(\varepsilon)$  and one can show that  $F_1^*(-\varepsilon)$  has the same form as in the case of ETO superconductor junctions. Then, we obtain  $\sin\theta^*(-\varepsilon) = -\sin\theta(\varepsilon)$  and  $\cos\theta^*(-\varepsilon) = \cos\theta(\varepsilon)$ . These relations mean that the OTE pairing state is induced in the DN.

4. *Junction with OSO superconductor.*—We have  $f_{\pm}(\varepsilon) = -f_{\pm}^*(-\varepsilon)$ ,  $g_{\pm}(\varepsilon) = g_{\pm}^*(-\varepsilon)$  and  $f_S(-\varepsilon) = f_S^*(\varepsilon)$ ,  $g_S(-\varepsilon) = g_S^*(\varepsilon)$ . One can show that  $F_1^*(-\varepsilon)$  takes the same form as in the case of ESE superconductor junctions. Then, we obtain that  $\sin\theta^*(-\varepsilon) = \sin\theta(\varepsilon)$  and  $\cos\theta^*(-\varepsilon) = \cos\theta(\varepsilon)$ . Following the same lines as in case 1, we conclude that the ESE pairing state is induced in the DN.

We can now summarize the central conclusions as follows:

	Symmetry of the pairing in superconductors	Symmetry of the pairing in the DN
1	Even-frequency spin-singlet even-parity (ESE)	ESE
2	Even-frequency spin-triplet odd-parity (ETO)	OTE
3	Odd-frequency spin-triplet even-parity (OTE)	OTE
4	Odd-frequency spin-singlet odd-parity (OSO)	ESE

Note that for even-parity superconductors the resulting symmetry of the induced pairing state in the DN is the same as that of a superconductor (cases 1 and 3). On the other hand, for odd-parity superconductors, the induced pairing state in the DN has symmetry different from that of a superconductor (cases 2 and 4).

To illustrate the main features of the proximity effect in all the above cases, we calculate the LDOS  $\rho(\varepsilon) = \text{real}[\cos\theta(\varepsilon)]$  and the pair amplitude  $f(\varepsilon) = \sin\theta(\varepsilon)$  in the middle of the DN layer at  $x = L/2$ . We fix  $Z = 1$ ,  $Z' = 1$ ,  $R_d/R_b = 1$ ,  $R_d/R_{b'} = 0.01$  and  $E_{\text{Th}} = D/L^2 = 0.25\Delta$ .

We start from junctions with ESE superconductors and choose the  $s$ -wave pair potential with  $\Psi_{\pm} = 1$  (Fig. 1). The LDOS has a gap and the real (imaginary) part of  $f(\varepsilon)$  is an even (odd) function of  $\varepsilon$  consistent with the formation of the even-frequency pairing. In junctions with ETO superconductors, we choose  $p_x$ -wave pair potential with  $\Psi_+ = -\Psi_- = \cos\phi$  as a typical example. In this case, a unusual proximity effect is induced where the resulting LDOS has a zero energy peak (ZEP) [10]. The resulting LDOS has a ZEP [10] since  $g^2(\varepsilon) + f^2(\varepsilon) = 1$  and  $f(\varepsilon = 0)$  becomes a purely imaginary number. This is consistent with  $f(\varepsilon) = -f^*(-\varepsilon)$  and the formation of the OTE pairing in the DN. To discuss junctions with an odd-frequency superconductor we choose  $\Delta^{\text{odd}}(\varepsilon) = \bar{C}\varepsilon/[1 + (\varepsilon/\Delta)^2]$  as the simplest example of the  $\varepsilon$  dependence of an odd-frequency superconductor pair potential. At  $\varepsilon = \Delta$ , the magnitude of  $\Delta^{\text{odd}}(\varepsilon)$  becomes maximum. Here we choose  $\bar{C} < 1$  when LDOS of bulk superconductor does not have a gap around  $\varepsilon = 0$ . Let us first consider junctions with OTE superconductors and choose an  $s$ -wave pair potential as an example. The resulting LDOS has a ZEP, in contrast to junctions with ESE superconductors where the resulting LDOS has no ZEP. The formation of the ZEP is due to the similar reason in the ETO superconductor junctions, where  $f(\varepsilon = 0)$  is a pure imaginary number. Finally, let us discuss junctions with OSO superconductors and choose an  $p_x$ -wave pair as an example. In this case, the ESE pairing is induced in the DN and  $f(\varepsilon) = f^*(-\varepsilon)$  is satisfied. The

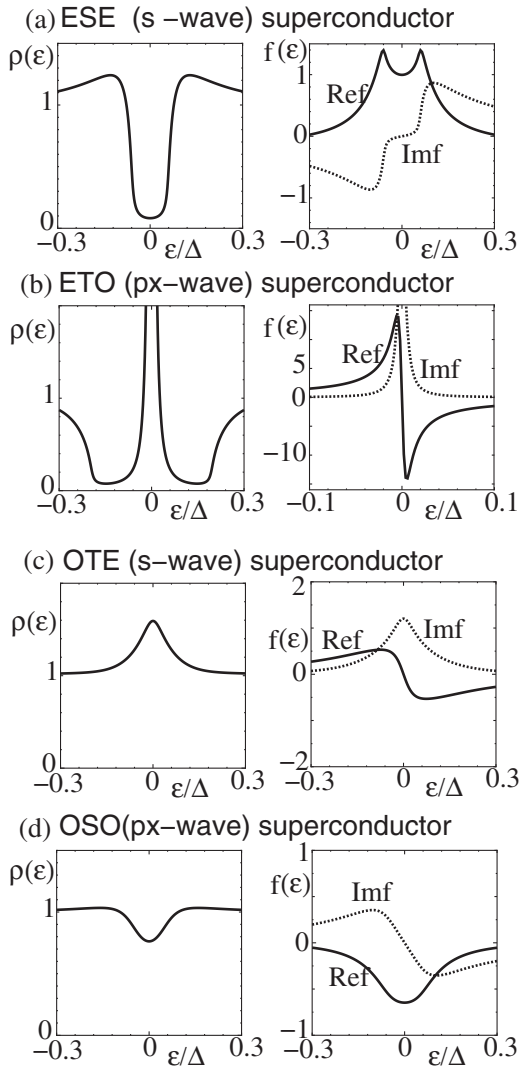


FIG. 1. Local density of states  $\rho(\epsilon)$  and pair amplitude  $f(\epsilon)$  at the center of the DN,  $x = L/2$  is plotted. Ref and Imf denote the real and imaginary part of  $f(\epsilon)$ . The pairing symmetry of the superconductor is (a) ESE, (b) ETO (c) OTE, and (d) OSO, respectively. For (c) and (d), we choose  $\bar{C} = 0.8$ . The resulting symmetry of  $f(\epsilon)$  is (a) ESE, (b) OTE (c) OTE and (d) ESE, respectively.

resulting LDOS has a gap since  $f(\epsilon = 0)$  becomes a real number, in contrast to junctions with OTE superconductors.

In summary, we have formulated a general theory of the proximity effect in superconductor/diffusive normal metal junctions. Four symmetry classes in a superconductor allowed by Pauli principle are considered: (1) even-frequency spin-singlet even-parity (ESE), (2) even-frequency spin-triplet odd-parity (ETO), (3) odd-frequency spin-triplet even-parity (OTE) and (4) odd-frequency spin-singlet odd-parity (OSO). We have found that the resulting symmetry of the induced pairing state in the DN is (1) ESE (2) OTE (3) OTE, and (4) ESE, respectively. The symmetry

in DN is established due to the isotropization of the pair wave function by the impurity scattering and spin conservation across the interface. This universal feature is very important to classify unconventional superconductors by using proximity effect junctions.

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