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## Parity effect in a mesoscopic superconducting ring

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**Abstract.** – We study a mesoscopic superconducting ring threaded by a magnetic flux when the single-particle level spacing is not negligible. It is shown that, for a superconducting ring with even parity, the behavior of persistent current is equivalent to what is expected in a bulk superconducting ring. On the other hand, we find that a ring with odd parity shows anomalous behavior such as fluxoid quantization at half-integral multiples of the flux quantum and paramagnetic response at low temperature. We also discuss how the parity effect in the persistent current disappears as the temperature is raised or the size of the ring increases.

What happens to superconductivity when the sample is made very small? Anderson [1] already addressed this fundamental question in 1959 and argued that as the size of a superconductor decreases and, accordingly, the average level spacing  $\delta$  becomes larger than the BCS gap  $\Delta$ , superconductivity is no longer possible. Recent experiments on ultrasmall “superconducting” nanoparticles [2] have led to reconsider this old, but fundamental question. In a series of experiments the authors of [2] studied transport through nanometer-scale Al grains and succeeded in getting the discrete eigenspectrum of a single superconducting grain. The results were found to depend on the parity, *i.e.* on the electron number in the grain being even or odd. These experiments initiated several theoretical investigations. von Delft *et al.* [3] used a model of uniform level spacing in a parity-projected mean-field theory [4] and found that the breakdown of superconductivity occurs at a value of  $\delta/\Delta \sim O(1)$  which is parity-dependent. This parity effect has been shown to increase when including the effects of level statistics [5]. Effects of quantum fluctuations [6], canonical description of BCS superconductivity [7], as well as transport theory for a nanoparticle coupled to superconducting leads [8] have also been subjects of the study along this line.

Another interesting example for studying the size effect on superconductivity is a mesoscopic superconducting ring threaded by a magnetic flux  $\Phi$ . It is well known that a conventional BCS superconducting ring exhibits fluxoid quantization at integer multiples of the flux quantum  $\Phi_0 = hc/2e$  and a diamagnetic response at  $\Phi = n\Phi_0$ , with  $n$  being an integer [9]. In this letter, we address the following question which is essentially the same as in a simply

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connected grain: What happens in a superconducting ring when the size of the ring becomes very small? For this purpose, we adopt the parity-projected mean-field theory [4] for an ideal mesoscopic ring. It is shown that the order parameter strongly depends on the parity when the size of the ring is small enough, as in the case of a grain. The most dramatic feature we show in our study is the behavior of the supercurrent (or persistent current) which strongly depends on the parity. For a ring with even parity, the behavior of the supercurrent is identical to that of a bulk superconducting ring. It exhibits fluxoid quantization at integer multiples of the flux quantum, and a diamagnetic response for small deviations of the flux from the integer multiples of the flux quantum. On the other hand, the characteristics are found to be very different for a small, odd parity ring. In a superconductor with odd parity, there is one unpaired quasiparticle. We find that at low temperature the existence of this quasiparticle drives the superconducting ring to a *half-integral* fluxoid quantization and a paramagnetic response at small values of the flux. We further show that the anomalous behavior in an odd-parity superconductor disappears at temperatures higher than the level spacing of single-electron spectra, where one recovers the behavior of a conventional superconducting ring. Finally, this parity-dependent behavior of supercurrent is shown to disappear in the thermodynamic limit.

The ideal superconducting ring can be described by the Hamiltonian

$$H = \sum_{j\sigma} \varepsilon_j^0 c_{j\sigma}^\dagger c_{j\sigma} - \lambda \delta \sum_{i,j} c_{i\uparrow}^\dagger c_{i\downarrow}^\dagger c_{j\downarrow} c_{j\uparrow}. \quad (1)$$

The single-particle energy is given by  $\varepsilon_j^0 = \frac{\hbar^2}{2mR^2}(j - f/2)^2$ , where  $R$  is the radius of the ring,  $f = \Phi/\Phi_0$  is the external flux divided by the flux quantum  $\Phi_0 = hc/2e$ , and  $j$  is an integer which corresponds to an angular momentum quantum number. This is obtained by solving the Schrödinger equation in a 1D noninteracting ring. Note that  $\bar{j} = -j$ .  $\lambda$  is the dimensionless BCS coupling constant.  $\delta = \hbar^2 N/8mR^2$  is the level spacing at the Fermi energy, where  $N$  is the number of electrons in the ring. We do not take into account the Zeeman splitting, namely  $h$ , because it is negligible unless the radius of the ring is very small. For  $\Phi \sim \Phi_0$  with a uniform magnetic field, the ratio of the level spacing  $\delta$  to the Zeeman splitting is proportional to  $R$  which is estimated as  $\delta/h \sim 10^{20} r_s R/m^2$ , where  $r_s$  is the average distance between electrons. For example, in a typical superconductor such as Al with  $R \sim 1 \mu\text{m}$ ,  $\delta/h \sim 10^4$ .

A simple way of describing a mesoscopic superconductor with fixed number parity  $P$  (denoted by e for even, and o for odd parity) is to adopt the parity-projected grand-canonical partition function [4]

$$Z_P(\mu) = \text{Tr} \frac{1}{2} [1 \pm (-1)^N] e^{-\beta(H - \mu N)}. \quad (2)$$

We evaluate  $Z_P$  using the BCS-type mean-field approximation, which consists in neglecting quadratic terms of the fluctuations:

$$\begin{aligned} c_{i\uparrow}^\dagger c_{i\downarrow}^\dagger c_{j\downarrow} c_{j\uparrow} &\simeq \langle c_{i\uparrow}^\dagger c_{i\downarrow}^\dagger \rangle c_{j\downarrow} c_{j\uparrow} + c_{i\uparrow}^\dagger c_{i\downarrow}^\dagger \langle c_{j\downarrow} c_{j\uparrow} \rangle - \langle c_{i\uparrow}^\dagger c_{i\downarrow}^\dagger \rangle \langle c_{j\downarrow} c_{j\uparrow} \rangle + \\ &+ \delta_{ij} \left( \langle c_{i\uparrow}^\dagger c_{i\uparrow} \rangle \langle c_{i\downarrow}^\dagger c_{i\downarrow} \rangle + \langle c_{i\uparrow}^\dagger c_{i\uparrow} \rangle c_{i\downarrow}^\dagger c_{i\downarrow} - \langle c_{i\uparrow}^\dagger c_{i\uparrow} \rangle \langle c_{i\downarrow}^\dagger c_{i\downarrow} \rangle \right). \end{aligned} \quad (3)$$

The ensemble average  $\langle \dots \rangle$  should be evaluated in a given parity  $P = \text{e}$  or  $P = \text{o}$ . The first three terms on the r.h.s of eq. (3) correspond to the mean-field approximation for the superconducting pairing. The last three terms are usually not considered since they give no contribution in the thermodynamic limit. However, those terms cannot be ignored in mesoscopic systems, though they were neglected in the previous mean-field description for ultrasmall superconducting grains [3]. Note that the validity of our mean-field treatment is

limited to the  $\delta < \Delta$  limit where the usual BCS approximation can be applied. As a result, we get the following expression for the mean-field Hamiltonian:

$$H = C_P + \sum_{j\sigma} \tilde{E}_j \gamma_{j\sigma}^\dagger \gamma_{j\sigma} + \mu N, \quad (4)$$

where  $\gamma_{j\sigma}$  ( $\gamma_{j\sigma}^\dagger$ ) destroys (creates) a quasiparticle;  $\gamma_{j\sigma} = u_j c_{j\sigma} - \sigma v_j c_{j\bar{\sigma}}^\dagger$ , and the constant  $C_P$  and the quasiparticle energy  $\tilde{E}_j$  are given by

$$C_P = \sum_j \left[ \frac{1}{2}(\varepsilon_j + \varepsilon_{\bar{j}}) - E_j \right] + \Delta_P^2 / \lambda \delta + \lambda \delta \sum_j \left[ u_j^2 f_{j\bar{\sigma}} + v_j^2 (1 - f_{j\sigma}) \right] \left[ u_j^2 f_{j\sigma} + v_j^2 (1 - f_{j\bar{\sigma}}) \right], \quad (5)$$

and

$$\tilde{E}_j = \frac{1}{2}(\varepsilon_j - \varepsilon_{\bar{j}}) + E_j, \quad (6)$$

respectively. Here  $\Delta_P = \lambda \delta \sum_j \langle c_{j\downarrow} c_{j\uparrow} \rangle$  is the parity-dependent order parameter which has to be calculated self-consistently.  $\varepsilon_j$  and  $E_j$  are defined as  $\varepsilon_j = \varepsilon_j^0 - \mu - \lambda \delta [u_j^2 f_{j\bar{\sigma}} + v_j^2 (1 - f_{j\sigma})]$  and  $E_j = \sqrt{\Delta_P^2 + (\varepsilon_j + \varepsilon_{\bar{j}})^2 / 4}$ , respectively. For simplicity we neglect the last term of  $\varepsilon_j$ . It does not change the qualitative feature of our results since its role is only to increase somewhat the effective level spacing near the Fermi level for large  $\delta$ .  $f_{j\sigma} = \langle \gamma_{j\sigma}^\dagger \gamma_{j\sigma} \rangle$  is the average occupation number of a state  $j$  with spin  $\sigma$ . It is parity-dependent and given by

$$f_{j\sigma} = \frac{f_+(\tilde{E}_j)Z_+ \mp f_-(\tilde{E}_j)Z_-}{Z_+ \pm Z_-}, \quad (7)$$

for  $P = e$  (upper sign) and  $P = o$  (lower sign), where  $f_\pm(E) = 1/(e^{\beta E} \pm 1)$  and  $Z_\pm = \prod_{j\sigma} (1 \pm e^{-\beta \tilde{E}_j})$ .  $u_j, v_j$  are BCS coherence factors:

$$u_j^2 = 1 - v_j^2 = \frac{1}{2} \left( 1 + \frac{\varepsilon_j + \varepsilon_{\bar{j}}}{2E_j} \right). \quad (8)$$

The parity-dependent chemical potential  $\mu_P$  is determined by the relation

$$\langle N \rangle = \frac{1}{\beta} \frac{\partial}{\partial \mu} \log Z_P(\mu) |_{\mu=\mu_P}, \quad (9)$$

that holds provided that  $\mu_P$  lies halfway between the last filled and first empty level if  $P = e$ , and on the singly occupied level if  $P = o$  [3].

The mean-field self-consistency condition  $\Delta_P = \lambda \delta \sum_j \langle c_{j\downarrow} c_{j\uparrow} \rangle$  leads to the relation

$$1 = \lambda \delta \sum_{j=-j_c}^{j_c} \frac{1}{2E_j} (1 - f_{j\downarrow} - f_{j\uparrow}), \quad (10)$$

where  $j_c$  is the cutoff value of  $j$  in the summation. At  $T = 0$  with  $\Phi = 0$  the occupation of quasiparticles reduces to  $f_{j\sigma} = \frac{1}{4}$  if the level lies on the chemical potential, namely  $j = \pm j_F$ , for  $P = o$ , and zero otherwise. The factor  $1/4$  is due to the orbital degeneracy of the ring,  $\varepsilon_j^0 = \varepsilon_{\bar{j}}^0$ ,

as well as the spin degeneracy. For nonzero external flux, the orbital degeneracy is lifted and  $f_{j_F\sigma} = 1/2$  (but  $f_{j_F\sigma} = 0$ ) for odd parity. This nonzero value of quasiparticle occupation gives rise to the so called “blocking effect”. That is, the odd-parity superconductor has one unpaired electron, which prevents pair scattering of other pairs into/out of the singly occupied state and reduces the order parameter as compared to that of an even-parity superconductor [10].

In the framework of the parity-projected grand-canonical description, three different cases appear in solving the “gap” equation: i) even parity with fully occupied highest level ( $N = 4j_F + 2$ ), ii) even parity with partially occupied highest level ( $N = 4j_F$ ), and iii) odd parity ( $N = 4j_F \pm 1$ ). It is important to note that the self-consistent equation (10) does not depend on the flux if  $\langle N \rangle$  is kept unchanged under variation of the flux. The condition of constant  $\langle N \rangle$  leads to the flux-dependent chemical potential

$$\mu_P(f) = \mu_P(0) + \frac{\hbar^2}{8mR^2} f^2. \quad (11)$$

$E_j$  is independent of  $f$  with this condition, and accordingly eq. (10) is also flux-independent at low temperature,  $k_B T < \delta, \Delta_P$ .

Figure 1 shows the pairing parameter as a function of  $\delta$  keeping the electron density constant. In solving the equation we chose  $\lambda = 0.2$ , close to that of Al [11], and  $j_c = 2j_F$ . The pairing parameter which is obtained by solving eq. (10) depends strongly on the parity as in the grain superconductor. In the odd-parity superconductor the order parameter is suppressed compared to the one for even parity. However, the behavior of the pairing parameter as a function of the level spacing is somewhat different from the grain superconductor with equal level spacing [3] or with randomly distributed levels [5]. It is due to the existence of orbital degeneracy in the ideal ring geometry. If the highest occupied level is fully filled (case i)), the chemical potential lies halfway between the last filled and the first empty level. In this case there exists a critical level spacing  $\delta_c/\Delta_0 \sim O(1)$ , where  $\Delta_e$  goes to zero as in the mean-field solution for the grain superconductivity. If the highest occupied level is partially filled (both for even and odd parity) the chemical potential lies on that level. Pair scattering of electrons between these orbitally degenerate levels makes it impossible to have a solution with  $\Delta_P = 0$ . On the other hand, the presence of any weak disorder will lift the orbital degeneracy and give a solution with  $\Delta_P = 0$ . Note that, in a very small grain with  $\delta \gg \Delta_0$ , quantum fluctuations are important and the mean-field treatment becomes invalid [6].

Next we discuss the parity-dependent behavior of the persistent current in the “superconducting” state. Because we deal with an isolated ring, the current should be calculated in the canonical description, while we use the parity-projected grand-canonical partition function. However, the number fluctuation in the grand-canonical treatment is very small at low temperature and the free energy with a fixed number  $N$ , namely  $F_N$ , can be written as

$$F_N \simeq -\frac{1}{\beta} \log Z_P + \mu_P N. \quad (12)$$

Note that this relation is exact at  $T = 0$ . The persistent current is given by

$$I = -c \frac{\partial F_N}{\partial \Phi}, \quad (13)$$

which gives the following expression by using the mean-field Hamiltonian (4):

$$I = I_{\text{dia}} + I_{\text{para}}, \quad (14)$$

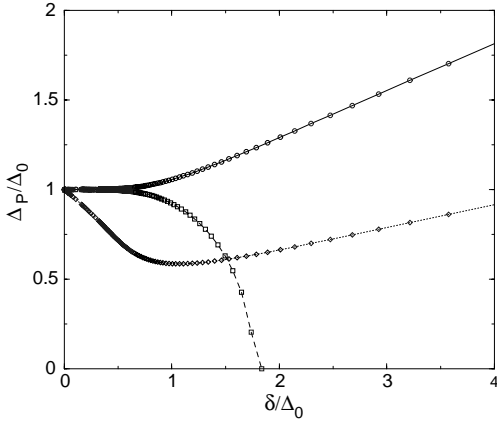


Fig. 1

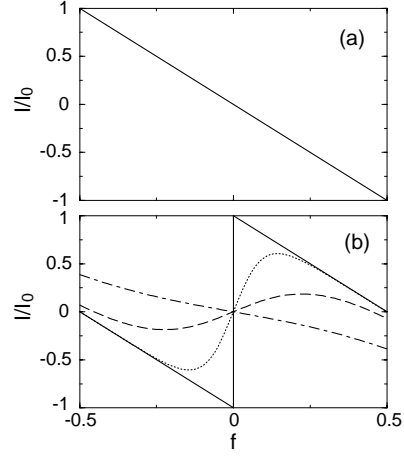


Fig. 2

Fig. 1 – The pairing parameters as a function of the single-particle level spacing for  $\lambda = 0.2$  with  $j_c = 2j_F$ . Lines with symbols show the results for three different cases,  $P = e$  with  $N = 4j_F$  (solid line with circles),  $P = o$  with  $N = 4j_F \pm 1$  (dotted line with diamonds), and  $P = e$  with  $N = 4j_F + 2$  (dashed line with squares).  $\Delta_0$  denotes the bulk gap.

Fig. 2 – The persistent current as a function of the dimensionless Aharonov-Bohm flux  $f = \Phi/\Phi_0$  with  $\Phi_0 = hc/2e$  (a) for even parity, and (b) for odd parity at  $t = 0$  (solid line),  $t = 0.1$  (dotted line),  $t = 0.3$  (dashed line), and  $t = 0.7$  (dot-dashed line).

where  $I_{\text{dia}}$  and  $I_{\text{para}}$  are the diamagnetic and the paramagnetic contribution to the current, respectively,

$$I_{\text{dia}} = -c \frac{\partial \mu_P}{\partial \Phi} N, \quad (15)$$

$$I_{\text{para}} = -c \sum_{j\sigma} \frac{\partial \tilde{E}_j}{\partial \Phi} f_{j\sigma}. \quad (16)$$

Note that at low temperature ( $k_B T < \delta, \Delta_P$ ) the constant term  $C_P$  in the Hamiltonian (4) does not contribute to the current since it is independent of the flux.

For even parity, the paramagnetic contribution to the persistent current is absent at  $k_B T \ll \Delta_e$  since  $f_{j\sigma} = 0$  for  $P = e$ . Thus, the persistent current for  $P = e$ ,  $I^e$ , is equal to  $I_{\text{dia}}$  and obtained from eqs. (11) and (15):

$$I^e = -2I_0 f, \quad (17)$$

where  $I_0 = ev_F/(2\pi R)$ , with  $v_F = \frac{\hbar}{m} \frac{j_F}{R}$  being the Fermi velocity and  $f = \Phi/\Phi_0$  (see fig. 2(a)). The behavior of  $I^e$  is essentially equivalent to what is expected in the bulk superconducting ring.

On the other hand, the paramagnetic contribution is important for  $P = o$  because of an unpaired quasiparticle.  $I_{\text{dia}}$  is identical for  $P = o$  and  $e$ . At low temperature ( $k_B T < \delta$ )  $I_{\text{para}}$  can be written as follows:

$$I_{\text{para}} \simeq 2I_0 (f_{j_F \sigma} - f_{j_F \sigma}), \quad (18)$$

where

$$f_{\pm j_F \sigma} \simeq \frac{1}{2} \frac{e^{\pm f/t}}{(e^{f/t} + e^{-f/t})}. \quad (19)$$

$t$  is the dimensionless temperature  $t = k_B T / \delta$ . At zero temperature  $I_{\text{para}}$  reduces to  $\text{sgn}[f] I_0$  and the total current for  $P = 0$ ,  $I^0$ , is given by

$$I^0 = I_0 (\text{sgn}[f] - 2f). \quad (20)$$

As shown in the solid line of fig. 2(b), the current vanishes at half-flux quantum,  $f = \pm 1/2$ , while it has maximum value of  $|I^0|$  at  $f = 0$ . This implies that the possible values of fluxoid in a ring with odd parity are half-integers,  $\pm \Phi_0/2$ ,  $\pm 3\Phi_0/2$ , etc., in contrast to the conventional fluxoid quantization at integer multiples of  $\Phi_0$ . Note that the fluxoid  $\Phi'$  is defined in a conventional way [9]:

$$\Phi' = \Phi + \frac{(2m)c}{2e} \oint v_s \cdot dl, \quad (21)$$

where  $v_s$  is the supercurrent velocity.

The parity-dependent behavior of the persistent current found above should be distinguished from that of a normal ring of noninteracting electrons with spin 1/2 considered by Loss and Goldbart [12]. In a normal ring with spin 1/2, the persistent current depends on the number of particles with modulo 4. Periodicity and oscillation amplitude depend on the number, and the current response is diamagnetic only for  $N = 4j_F + 2$  (the case of fully occupied top level). On the other hand, a mesoscopic superconducting ring shows only the parity dependence that originates from the electron pairing. The periodicity and amplitude of oscillation remain unchanged as  $\Phi_0 (= hc/2e)$  and  $I_0$ , respectively.

The effect of temperature on the persistent current is shown in fig. 2(b).  $I_{\text{para}}$  is reduced as the temperature is raised. It is clear that the effect of the unpaired quasiparticle disappears with increasing  $T$ ; the persistent current will show a behavior as in fig. 2(a), at temperature higher than  $t \sim 1$ . Actually there is a crossover temperature  $t^* = 0.5$  where the current response at small flux changes from paramagnetic to diamagnetic. (That is  $\frac{dI^0}{d\Phi}|_{\Phi=0}(t = t^*) = 0$ .)

Let us, finally, discuss the condition under which the parity effect can be observed in the persistent current. As noted above, the condition for the existence of the paramagnetic contribution to the persistent current is  $T < T^*$ , with  $k_B T^* / \delta = 0.5$ . Thus, the crossover temperature is given by

$$k_B T^* = 2.5(\text{eV}) \frac{r_s}{R}, \quad (22)$$

where  $r_s$  is the average distance between electrons. For Al  $r_s = 1.10 \text{ \AA} = 2.07 a_0$ , with  $a_0$  being the Bohr radius. For a ring with  $R \sim 5 \times 10^4 r_s \sim 5 \mu\text{m}$ ,  $T^* \sim 1 \text{ K}$  is comparable to the transition temperature of bulk Al. If the ring is not strictly 1D, the level spacing is reduced and, accordingly, the crossover temperature  $T^*$  is lowered as compared to the ideal 1D ring with the same radius. Furthermore,  $T^* \rightarrow 0$  if  $R \rightarrow \infty$ . In other words, the parity effect disappears in the thermodynamic limit, and our treatment coincides with the conventional BCS description.

In conclusion, we have investigated the parity-dependent properties of a mesoscopic superconducting ring threaded by a magnetic flux. The properties in the persistent current of an even-parity ring are similar to those of a bulk superconductor. On the other hand, a ring with odd parity shows unconventional behavior: the fluxoid quantization at half-integer multiples of the flux quantum. Moreover, there exists a paramagnetic response at temperatures below

a characteristic temperature of the order of the level spacing. We have also shown that this parity effect of the persistent current disappears as the temperature is raised or as the size of the ring increases.

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