Effect of Time Reversal Symmetry Breaking on the Density of States in Small Superconducting Grains

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We show that in ultra-small superconducting grains any concentration of magnetic impurities or infinitely small orbital effect of magnetic field leads to destruction of the hard gap in the tunneling density of states. Instead, though exponentially suppressed at low energies, the tunneling density of states exhibits the “soft gap” behavior, vanishing linearly with excitation energy, as the energy approaches zero.

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The gap in the tunneling density of states (DoS) is one of the most fundamental manifestations of microscopic mechanism\textsuperscript{4} of superconductivity\textsuperscript{5}. The existence of this gap is closely related to the time-reversal symmetry in the superconductor. As a result, non-magnetic impurities at low densities do not affect the gap, $\Delta$, in conventional superconductors (the Anderson theorem\textsuperscript{6}). It is magnetic impurities that violate the symmetry of the superconducting state and act as pair breakers. Therefore bound states below the gap are created and the gap is suppressed\textsuperscript{7}. This effect of the suppression of the gap has been observed experimentally and it is now a textbook example\textsuperscript{8}. It is magnetic impurities that violate the symmetry in the superconductor. As a result, non-magnetic impurities (at low densities) do not affect the gap, $\Delta$, of this superconducting state and act as pair breakers. Moreover, the magnetic impurities suppress the DoS. This suppression is forbidden at all. Even at much smaller density, the magnetic impurities suppress the DoS. This suppression of the hard gap manifests itself in the appearance of $\Delta$, smaller than the mean field gap $|\epsilon| < \Delta$,\textsuperscript{9}. However, at $n_m < 0.9 n_c$, the self-consistent Born approximation (SCBA) of Ref.\textsuperscript{10} predicts the DoS still vanishing at energies smaller than a certain value, which is referred to as the non-normalized gap $\epsilon^*$, (see dashed line in Fig. 1.)

In the region $0.9 n_c < n_m < n_c$, the so-called regime of gapless superconductivity occurs, where the gap in DoS vanishes even though the superfluid density still remains finite.

The prediction of SCBA about the existence of the finite gap in the density of states even at the already broken time reversal symmetry is intriguing since there is no longer a symmetry reason for vanishing of the DoS. The situation in some sense reminds the problem of exponentially small tails in the DoS at small energies in normal materials\textsuperscript{12}. The appearance of such tails is non-perturbative. It means, that any approach which consists of selecting some class of diagrams based on expansion in disorder strength will result in zero DoS under the gap. Rather, in order to find the shape of such tails one has to perform the instanton analysis (also known as the “optimal fluctuation method"\textsuperscript{13,14}). In this Letter, we perform such analysis for the effect of magnetic impurities or small magnetic field on the DoS of superconducting grains\textsuperscript{15}. We will demonstrate that the DoS at $|\epsilon| = 0$ becomes finite, though exponentially small, no matter how small the magnetic field or the concentration of magnetic impurities is. At $|\epsilon| \rightarrow 0$, the DoS is shown to exhibit the “soft gap” behavior vanishing linearly with excitation energy.

The Bogolyubov equations\textsuperscript{10} for quasiparticle spectrum in s-wave superconductors are

$$\epsilon \hat{\psi} = \hat{H} \hat{\psi},$$

where $\hat{\psi}$ is the Gor’kov-Nambu spinor\textsuperscript{11}

$$\hat{\psi} = \begin{pmatrix} u_{\alpha}(n) \\ v_{\alpha}(n) \end{pmatrix}, \quad \alpha = 1, 2.$$

Unless stated otherwise, Latin (Greek) indices label the orbital (spin) states. The mean field Hamiltonian is

$$\hat{H} = \begin{pmatrix} \hat{H} & \frac{\Delta}{\Delta - \hat{T}\hat{T}} \\ \frac{\Delta}{\Delta - \hat{T}\hat{T}} & \hat{H} \end{pmatrix}, \quad \hat{H} = \hat{H}^\dagger.$$

where the one-particle Hamiltonian $\hat{H}$ may act both on the orbital and spin coordinates of the electron, and $\hat{T}$ is the time inversion operator, $\hat{T} u_\alpha(n) = \sigma^y u_\beta(n)$, where $\sigma^y$ is the Pauli matrix, $\hat{T}^2 = 1$.

The crucial characteristic of the system is the symmetry of $\hat{H}$ with respect to the time inversion,

$$\hat{H} = \hat{H}^* + \hat{H}^a; \quad \hat{T} \hat{H}^a \hat{T} = \hat{H}^a; \quad \hat{T} \hat{H}^* \hat{T} = -\hat{H}^a.$$

If the time inversion symmetry is preserved, $\hat{H}^a = 0$, both diagonal entrees of the Hamiltonian $\hat{H}$ can be diagonalized simultaneously,

$$\hat{H}^s = \hat{\xi} = \text{diag}(\xi_1, \xi_2, \ldots),$$

and one obtains the eigenvalues of Hamiltonian $\hat{H}^s$
\[ \epsilon_i = \pm \sqrt{\xi_i^2 + \Delta^2}, \]  

so that the hard gap in the one-particle excitation spectrum exists independently of further model assumptions on $H^a$. However, if the time inversion symmetry is broken, the answer is not universal and we need to further specify the model. We adopt $H^a$ to be independent $M \times M$, $(M \to \infty)$ Random Matrices. \(^2\)

\[ \langle |H_{ij}|^2 \rangle = M \left( \frac{\delta_{ij}}{\pi} \right)^2, \quad \langle |H_{ij}|^2 \rangle = \frac{1}{\gamma} = \frac{1}{2\pi} \frac{\delta_{ij}}{2\pi}, \]  

satisfying the constraint \(^3\). (We will omit the spin indices where it does not cause any confusion.) Here $\delta_\mathcal{I} = \langle \xi_{i+1} - \xi_i \rangle \ll \Delta$ is the mean level spacing, the parameter $\tau_H^{-1} \lesssim \Delta$ characterizes the strength of pairing-breaking potential (see below), and $\langle \ldots \rangle$ stands for the ensemble averaging. Therefore, $H^a$ belongs to either orthogonal or symplectic ensembles and $H^a$ describes the crossover to the unitary ensemble. In what follows, we choose the basis of the eigenstates of the Hamiltonian $\hat{H}^a$, so that $H^a$ has the form \(^4\) while $H^a$ in this basis is a random matrix with the correlation function \(^5\).

The DoS in the system is expressed in terms of the disorder averaged Green function

\[ \langle \nu(\epsilon) \rangle = -\frac{1}{2\pi} \text{ImTr}(G^R(\epsilon), \quad G^R(\epsilon) = \frac{1}{\epsilon - \mathcal{H} + i0}. \]  

If the time reversal symmetry is preserved, $\tau_H \to \infty$, the DoS is given by the usual BCS expression

\[ \langle \nu(\epsilon) \rangle = \frac{\delta_1}{|\epsilon|} \frac{\epsilon}{\sqrt{\epsilon^2 - \Delta^2}}. \]

Before we proceed, let us discuss the physical situations for which the random matrix description (RMT) \(^6\) is applicable. It is well known \(^7\) that RMT description of the spectrum requires all the relevant energy scales to be much smaller than the Thouless energy $E_T$. It translates to the condition that the size of the grains $R$ to be much smaller than the coherence length $\xi$, see Ref. \(^8\) for recent experiments on such grains. The parameter $\tau_H^{-1}$, can be related to the physical characteristics of such grains. If magnetic field is applied it penetrates through the small grain without screening and

\[ \tau_H^{-1} = E_T \left( \Phi/\Phi_0 \right)^2, \]  

where $\Phi$ is the magnetic flux penetrating through the grain and $\Phi_0 = h\epsilon/2e$ is the flux quantum. In the case of the doping by magnetic impurities the time $\tau_H$ is given by the spin-spin scattering time

\[ \tau_H^{-1} = \tau_S^{-1} = \pi n_v N_s V_s^2 S(S + 1), \]  

where $n_v$ is the concentration of magnetic impurities, $S$ is the impurity spin, $V_s$ is the scattering matrix element and $\nu_0$ is the thermodynamic density of states. Finally, the possibility to neglect the non-Gaussian correlations of the Hamiltonian $H^a$ is guarded by the requirement that no matrix element of $H^a$ exceeds the Thouless energy. As we shall see below, the characteristic value of the matrix elements contributing to the low energy tail of the DoS is of the order of $\Delta \ll E_T$, so that the Gaussian approximation is justified. (All of these assumptions definitely break down in bulk systems $R \gg \xi$.)

The exponentially small tails in the DoS were considered in Refs. \(^9\). The idea is to look for the fluctuations of the random potential $\hat{H}^a$ which form a low energy bound state, thus leading to non-zero DoS at such energy. The probability to form such a bound state is determined by the distribution of the matrix elements $H^a_{ij}$ and, while exponentially small, should be maximized by choosing the “optimal” fluctuation of the potential. The resulting DoS is then proportional to this probability.

To gain some intuition about the form of the optimal fluctuations, let us consider the simplest possible realization of the random potential $\hat{H}^a$ where it couples only two eigenstates $i_0$, $j_0$ of the Hamiltonian $\hat{H}^a$:

\[ \hat{H}^a_{ij} = \begin{cases} iV; & i = i_0, j = j_0; \\
-iV; & i = j_0, j = i_0; \\
0; & \text{otherwise}. \end{cases} \]  

All states with $i \neq i_0, j_0$ decouple, and the relevant Hamiltonian reduces to $4 \times 4$ matrix:

\[ \hat{H}(0) = \begin{pmatrix} \hat{H}_{i_0 i_0} & \hat{H}_{i_0 j_0} \\
\hat{H}_{j_0 i_0} & \hat{H}_{j_0 j_0} \end{pmatrix}, \quad \hat{H}_{i_0 i_0} = iV \hat{I}_N, \quad \hat{H}_{i_0 j_0} = \hat{H}_{j_0 i_0}^{*}, \quad \hat{H}_{j_0 j_0} = \hat{H}_{i_0 i_0}^{*}, \]  

where $\hat{I}_N$ is the $2 \times 2$ unit matrix in Gor’kov-Nambu space, and $\hat{\sigma}_z$ are the Pauli matrices in this space. The eigenvalues of the matrix $\hat{H}^{(0)}$ are

\[ \epsilon_{1,2} = \pm \left[ (\Delta - |V| + \frac{\xi_0^2}{2\Delta})^2 + \xi_0^2 \right]^{1/2}, \]  

\[ \epsilon_{3,4} = \pm \left[ (\Delta + |V| + \mathcal{O}(\xi_0^2)) \right], \quad \xi_{\pm} = \frac{\xi_{i_0} \pm \xi_{j_0}}{2}. \]

Two of these eigenvalues, $\epsilon_{1,2}$, lie above the gap, and are not interesting for our purposes. The other two, $\epsilon_{3,4}$, correspond to the bound states under the gap. Clearly, by suitable choice of $V$ (and $\xi$s), we can tune $\epsilon_{1,2}$ to the desired energy $\epsilon$. The averaged DoS is proportional to the probability $P(V)$ to find such value of the matrix element. According to Eqs. \(^9\) and \(^10\), we have

\[ P(V) \propto \exp \left( -\frac{\gamma}{2} V^2 \right) \]

The minimal value of $V$, providing the level \(^11\) to have energy $\epsilon$, is $|V| = \Delta - |\epsilon|$, and we obtain

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\[ \langle \nu(\epsilon) \rangle \propto \exp \left[ -\frac{\gamma}{2} (|\epsilon| - \Delta)^2 \right] \tag{12} \]

where we omit all pre-exponential factors (to be calculated below).

Equation (12) is the main physical result of this Letter. We have shown that the DoS in the ultra small superconducting grain possesses the exponentially small tail at low energies even below the renormalized value of the gap obtained using the self-consistent Born approximation.

To make our derivation rigorous we have (i) to prove that the ansatz (11) is indeed a saddle point in the ensemble averaging; (ii) to calculate the pre-exponential factor by summing over all saddle points \((i_0, j_0)\) and integrating over the fluctuations around the saddle point.

**Saddle point** — To find the saddle point one has to minimize the exponent of the Gaussian probability (11)

\[ \mathcal{E} = \frac{\gamma}{2} \sum_{i \neq j} |H_{ij}^a|^{2} \tag{13} \]

with respect to all the matrix elements \(H_{ij}^a\), subjected to constraint (11) and the condition

\[ \epsilon = \epsilon_0\{H^a\} \tag{14} \]

where \(\epsilon_0\{H^a\}\) is the smallest eigenvalue of the Hamiltonian (11). This involves finding a solution of the equations

\[ \frac{\partial}{\partial H_{ij}^a} \left[ \mathcal{E} + \sum_{i' \neq j'} \Lambda_{i'j'} (H_{i'j'}^a + H_{j'i'}^a) + \lambda \epsilon_0\{H^a\} \right] = 0 \tag{15} \]

for all \(1 \leq i < j \leq M\). Here \(\Lambda_{i'j'}\) and \(\lambda\) are the Lagrange multipliers to be found from the conditions (11) and (14). Excluding \(\Lambda_{ij}\), we find from Eq. (15)

\[ H_{ij}^a = \frac{\lambda}{2\gamma} \left[ \frac{\partial \epsilon_0}{\partial H_{ij}^a} - \frac{\partial \epsilon_0}{\partial H_{ji}^a} \right], \tag{16} \]

where

\[ \frac{\partial \epsilon_0}{\partial H_{ij}^a} = \tilde{u}^*(i)\tilde{v}(j) + \tilde{v}^*(i)\tilde{u}(j). \]

Here \(\tilde{u}(n), \tilde{v}(n)\) are the components of the Nambu spinor \(\tilde{\psi}_j\) [see Eq. (8)], corresponding to the eigenstate \(\epsilon_0\). Substituting Eqs. (14) and (15) into Eqs. (11), (13), we obtain

\[ \epsilon \tilde{\psi}_j = \left( \xi_j \tilde{x} + \Delta \tilde{x} + \hat{A} \right) \tilde{\psi}_j - \hat{B} \tilde{\psi}_j^*, \]

\[ \hat{A} = \frac{\lambda}{2\gamma} \sum_n \tilde{\psi}_n^i \otimes \tilde{\psi}_n, \quad \hat{B} = \frac{\lambda}{2\gamma} \sum_n \tilde{\psi}_n^f \otimes \tilde{\psi}_n, \tag{17} \]

which, together with the normalization condition,

\[ \sum_j |\tilde{\psi}_j^i \tilde{\psi}_j| = 1 \]

constitute the matrix analogue of the non-linear Schrödinger equation of Ref. (8).

The essential simplicity of the random matrix model (14) stems from the independence of the non-linear terms \(\hat{A}, \hat{B}\) of the state index \(j\). Namely, that Eq. (17) can be considered as a linear equation for a state \(j\), while the coefficients \(\hat{A}, \hat{B}\) have to be found self-consistently. With non-linear terms \(\hat{A}, \hat{B}\) fixed, the non-trivial solution to Eq. (17) for a given eigenvalue \(\epsilon\) exists only for two values of \(\xi_j\) [similar to Eq. (8)]. It means, that at most only two states can be mixed. According to Eq. (10), it indicates that ansatz (11) we adopted from the very beginning is the only possible form of the saddle point.

**Pre-exponential factor** — Having convinced ourselves, that we have found the optimal fluctuation and, thus, the exponent (12) correctly, we turn to the calculation of the pre-exponential factor in this expression. Our starting point is once again the optimal fluctuation (11), however, we wish to take into account all the other matrix elements \(H_{mj}^a\) which couple the states \(m = i_0, j_0\) with all other states \((j \neq i_0, j_0)\). Since the exponential tail comes from the two levels \(i_0, j_0\), coupled by the large matrix element \(V \gg 1/\sqrt{\gamma}\), the elements \(H_{mj}^a\) may take only its typical value \(\approx 1/\sqrt{\gamma} \ll \Delta\). Therefore, all of them can be treated in perturbation theory. To the second order in \(H_{mj}^a\) the effective Hamiltonian acting in the reduced Hilbert space of the two states \(i_0, j_0\) acquires the form (10) with the entrees changed due to the mixture of all the other levels (indices \(m, n = i_0, j_0\)):

\[ \hat{H}_{mn}^{eff} = \hat{H}_{mn}^{(0)} + \sum_{j \neq i_0, j_0} H_{mj}^a \epsilon I_N + \xi_j \delta_{jn}^{(N)} + \Delta \delta_{jn}^{(N)} H_{jn}^a. \tag{18} \]

Substituting Eq. (18) into Eq. (9) we obtain the contribution of two lowest levels into the (non-averaged) DoS:

\[ \nu(\epsilon) = |\epsilon|(1 - Z) \left[ \epsilon^2(1 - Z)^2 - W^2 \right]; \tag{19} \]

\[ W^2 = \left( 1 + Z \right) \Delta + \frac{\xi^2}{2\Delta} - \left| H_{i_0j_0}^a \right|^2 + \xi^2 + Y^2, \]

where \(\xi_{\pm}\) are given by Eq. (11), and we introduced

\[ Z = \sum_{j \neq i_0, j_0} \left| H_{i_0j}^a \right|^2 + \left| H_{j_0j}^a \right|^2 \]

\[ Y = \sum_{j \neq i_0, j_0} \frac{\xi_j H_{i_0j}^a H_{j_0j}^a}{\epsilon^2 - \xi_j^2 - \Delta^2}. \]

For the optimal fluctuation (11), the argument of the \(\delta\)-function reproduces the spectrum (11).

The DoS (11) should be averaged over the fluctuations of the matrix elements and summed over states \(i_0, j_0\)

\[ \langle \nu(\epsilon) \rangle = \sum_{i_0, j_0} \prod_{i < j} \int _{\sqrt{2\pi\gamma}} \left( \frac{d (\text{Im} H_{ij}^a)}{2\pi\gamma} \right) \exp \left( -\frac{\gamma}{2} |H_{ij}^a|^2 \right) \nu(\epsilon). \tag{20} \]
At energies $\epsilon \gg \delta_1$, we can neglect the level repulsion and replace the sum over $i_0, j_0$ by the integral
\[
\sum_{i_0,j_0} \rightarrow \frac{1}{2\delta_1^2} \int d\xi_{i_0} d\xi_{j_0},
\]
where factor of $1/2$ excludes double counting the same configurations $(i_0,j_0)$ and $(j_0,i_0)$. Then straightforward integration in Eq. (24) utilizing the condition $|\epsilon| \gg \delta_1/(\Delta \tau_H)$ yields the averaged DoS:
\[
\langle \nu(\epsilon) \rangle = \frac{1}{\delta_1} F_1(\epsilon) \exp \left[ -\pi F_2(\epsilon) \right] 
\]
(21)
\[
F_1(\epsilon) = \frac{2|\epsilon|}{\sqrt{\delta_1 (\Delta + 4|\epsilon| \tau_H \sqrt{\Delta^2 - \epsilon^2})}} \left( \frac{\Delta + |\epsilon|}{\Delta - |\epsilon|} \right)^{\frac{1}{2}};
\]
\[
F_2(\epsilon) = \tau_H \frac{(\Delta - |\epsilon|)^2}{\delta_1} - \frac{5}{4} \frac{\sqrt{\Delta^2 - \epsilon^2}}{\delta_1^2}.
\]

Equation (21) is the main quantitative result of this Letter. It gives the parametrically exact description of the exponential tail in the DoS. It is valid as long as the exponent $F_2$ is larger than unity. At low energies $\epsilon \ll \Delta$ we can neglect the second term in $F_2(\epsilon)$, reproducing the qualitative result Eq. (12).

At larger energies, when $\epsilon$ approaches $\Delta$, the validity of our considerations and of Eq. (23) breaks down at the point $\epsilon^*$ where the two terms in the exponent $F_2(\epsilon)$ become of the same order. Remarkably, that the point $\Delta - |\epsilon^*| \simeq \delta_1/(\Delta \tau_H)^{2/3}$ is parametrically the same as the “renormalized gap”, $\epsilon^*$, predicted by SCBA [4]. Combining these results, we can describe the DoS in the grain by the continuous function depicted on Fig. 1.

At small energies $\epsilon \to 0$ result [21] vanishes linearly due to the pre-exponential factor $F_1(\epsilon)$. The appearance of this linear suppression is easy to reveal already on the level of qualitative analysis. Indeed, one can see from Eq. (12) that the levels near the $\epsilon = 0$ repel each other due to the difference in energies of the one electron state $\xi$. It means that the contributions of the levels is always limited by $|\xi_i - \xi_j| < |\epsilon|$ which gives the corresponding smallness in the integration domain. Finally, $|\epsilon| \lesssim \delta_1$, the level repulsion [12] between those orbits should be taken into account which results in the additional suppression by a factor $(\epsilon/\delta_1)^{\beta}$, where $\beta = 1/4$ in the absence (presence) of the spin-orbit coupling.

To conclude, we have shown that in a small superconducting grain breaking the time reversal symmetry leads to the appearance of the exponentially small tail in the DoS at energies smaller than the BCS gap. The DoS is non zero for all energies $|\epsilon| < \Delta$ except for the point $\epsilon = 0$, where the DoS vanishes linearly in energy. Thus the grain no longer exhibits the hard gap in the excitation spectrum as predicted by Ref. [4]. Our results are non perturbative as they were obtained by considering the optimal fluctuation of the random potential.

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\[\text{FIG. 1. DoS for a superconducting grain with broken time reversal symmetry. The thick solid line is the tail of the DoS [21]. The dashed line represents the result of the self-consistent Born approximation Ref. [4]. The inset shows the behavior of the tail at $\epsilon \to 0$. The curves are plotted for $\Delta = 3.5\delta_1$ and $\tau_H = 1.5\delta_1^{-1}$.}\]

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