Parity Effect in Ground State Energies of Ultrasmall Superconducting Grains

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We study the superconductivity in small grains in the regime when the quantum level spacing $\delta\varepsilon$ is comparable to the gap Δ. As $\delta\varepsilon$ is increased, the system crosses over from superconducting to normal state. This crossover is studied by calculating the dependence of the ground state energy of a grain on the parity of the number of electrons. The states with odd numbers of particles carry an additional energy Δ_P, which shows nonmonotonic dependence on $\delta\varepsilon$. Our predictions can be tested experimentally by studying the parity-induced alternation of Coulomb blockade peak spacings in grains of different sizes. [S0031-9007(97)03091-3]

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The standard BCS theory [1] gives a good description of the phenomenon of superconductivity in large samples. However, it was noticed by Anderson [2] in 1959 that as the size of a superconductor becomes smaller, and the quantum level spacing in the sample $\delta\varepsilon$ approaches the superconducting gap Δ, the BCS theory fails. The interest in superconductivity in such *ultrasmall* grains was renewed by recent experiments by Ralph, Black, and Tinkham [3,4], who fabricated and studied nanometer-scale aluminum grains. In qualitative agreement with the prediction [2], they demonstrated [4] the existence of the superconducting gap in relatively large grains, with estimated level spacings $\delta\varepsilon \approx 0.02$ and 0.08 meV smaller than the superconducting gap $\Delta \approx 0.31$ meV, whereas no signs of superconductivity were observed [3] in smaller grains, $\delta\varepsilon \approx 0.7$ meV. These experiments raise a theoretical question about the nature of the crossover from superconducting to normal state in ultrasmall particles with level spacings $\delta\varepsilon \sim \Delta$.

This problem was addressed in two recent theoretical papers. von Delft *et al.* [5] explored the BCS gap equation in a finite-size system with equidistant discrete energy levels and found that, as the level spacing is increased, the superconducting gap of the grain vanishes at a certain critical value of $\delta\varepsilon$, which is of order Δ and depends on the parity of the total number of electrons in the grain. Smith and Ambegaokar [6] extended the treatment of Ref. [5] to take into account Wigner-Dyson fluctuations of the energy levels in the grain.

It is worth noting that the theories [5,6] treat the superconductivity in small grains within the self-consistent mean-field approximation for the superconducting order parameter. Although this approximation works well for large systems, one should expect the quantum fluctuations of the order parameter to grow when the level spacing $\delta\varepsilon$ reaches Δ. In this paper we present a theory of superconductivity in ultrasmall grains which includes the effects of quantum fluctuations of the order parameter. We show that the corrections to the mean-field results which are small in large grains, $\delta\varepsilon \ll \Delta$, become important in the opposite limit, $\delta\varepsilon \gg \Delta$.

The superconducting gap Δ studied in Refs. [5,6] is not well defined in the presence of quantum fluctuations. Therefore, we must first identify an *observable* physical quantity which characterizes the superconducting properties of small grains. The most convenient such quantity for our purposes is the ground state energy of the grain E_N as a function of the number of electrons N. More precisely, we study the so-called *parity effect* in ultrasmall grains, which is described quantitatively by parameter

$$\Delta_P = E_{2l+1} - \tfrac{1}{2}(E_{2l} + E_{2l+2}). \qquad (1)$$

In the ground state of a large superconducting grain with an odd number of electrons, one electron is unpaired and carries an additional energy $\Delta_P = \Delta$. This result is well known in nuclear physics and was recently discussed in connection with superconducting grains in Refs. [7,8]. The parity effect was demonstrated experimentally in Refs. [9,10], where the Coulomb blockade phenomenon [11] in a superconducting grain was studied. In such an experiment the intervals between Coulomb blockade peaks in which the grain charge is odd shrink by an amount proportional to Δ_P.

We describe the grain by the following Hamiltonian:

$$\hat{H} = \sum_{k\sigma} \varepsilon_k a_{k\sigma}^\dagger a_{k\sigma} - g \sum_{kk'} a_{k\uparrow}^\dagger a_{k\downarrow}^\dagger a_{k'\downarrow} a_{k'\uparrow}. \qquad (2)$$

Here k is an integer numbering the single-particle energy levels ε_k, the average level spacing $\langle \varepsilon_{k+1} - \varepsilon_k \rangle = \delta\varepsilon$, operator $a_{k\sigma}$ annihilates an electron in state k with spin σ, and g is the interaction constant. In Eq. (2) we assume zero magnetic field, so that the electron states can be chosen to be invariant under the time reversal transformation [2]. We include in Eq. (2) only the matrix elements of the interaction Hamiltonian responsible for the superconductivity; the contributions of the other terms are negligible in the weak coupling regime, $g/\delta\varepsilon \ll 1$, we consider. Finally, we did not include in Eq. (2) the charging energy responsible for the Coulomb blockade, as its contribution to the ground state energy is trivial.

In the absence of interactions, $g = 0$, the parity parameter Δ_P can be easily calculated. Indeed, the ground state energy E_N is found by summing up N lowest single-particle energy levels. This results in $E_{2l+1} = E_{2l} + \varepsilon_{l+1}$ and $E_{2l+2} = E_{2l} + 2\varepsilon_{l+1}$. Substituting this into Eq. (1), we find that, without the interactions, $\Delta_P = 0$.

For weak interactions, one can start with the first-order perturbation theory in g. In this approximation an electron in state k interacts only with an electron with the opposite spin in the same orbital state k. Thus when the "odd" $(2l + 1)$st electron is added to the grain, it is the only electron in the state $l + 1$ and does not contribute to the interaction energy, $\delta E_{2l+1} = \delta E_{2l}$. The next, $(2l + 2)$nd electron goes to the same orbital state and interacts with it: $\delta E_{2l+2} = \delta E_{2l+1} - g$. From Eq. (1) we now find

$$\Delta_P = \tfrac{g}{2}, \quad \text{at } g \to 0. \tag{3}$$

One should note that the result (3) is not quite satisfactory even in the weak coupling case $g/\delta\varepsilon \ll 1$. Indeed, the low-energy properties of a superconductor are usually completely described by the gap Δ. The interaction constant g is related to the gap Δ in a way which depends on a particular microscopic model, so the result (3) cannot be directly compared with experiments.

This problem can be resolved by considering corrections of higher orders in g, which are known [12] to give rise to logarithmic renormalizations of g. In the leading-logarithm approximation the renormalized interaction constant is found [12] as

$$\tilde{g} = \frac{g}{1 - \frac{g}{\delta\varepsilon} \ln \frac{D_0}{D}}. \tag{4}$$

Here D_0 is the high-energy cutoff of our model, which has the physical meaning of Debye frequency, and $D \ll D_0$ is the low-energy cutoff. At zero temperature, $D \sim \delta\varepsilon$. Taking into account the relation between the gap in a large grain Δ and microscopic interaction constant $\Delta \sim D_0 e^{-\delta\varepsilon/g}$, we find with logarithmic accuracy $\tilde{g} = \delta\varepsilon/\ln(\delta\varepsilon/\Delta)$. Finally, substituting the renormalized interaction constant into Eq. (3), we get

$$\Delta_P = \frac{\delta\varepsilon}{2\ln\frac{\delta\varepsilon}{\Delta}}, \qquad \Delta \ll \delta\varepsilon. \tag{5}$$

Unlike the first-order result (3), Δ_P is now expressed in terms of experimentally observable parameters Δ and $\delta\varepsilon$ rather than the model-dependent interaction constant g.

It is instructive to compare Eq. (5) with the results of Refs. [5,6]. In a very small grain with $\delta\varepsilon \gg \Delta$, the mean-field gap studied in Refs. [5,6] vanishes, and no parity effect is expected. However, our result (5) predicts that in small grains the parity effect is *stronger* than in the large ones. This behavior is due to the strong quantum fluctuations of the order parameter which persist even when its mean-field value studied in Refs. [5,6] vanishes. The physics of the fluctuations of the order parameter is hidden in the renormalization procedure leading to Eq. (4). Below, we present a different technique, which explicitly shows the role of the fluctuations. It will allow us to rigorously derive Eq. (5) and to study the fluctuation corrections in the case of large grains, $\delta\varepsilon \ll \Delta$.

A convenient way to treat the fluctuations of the order parameter is by using a path integral technique [13]. This approach gives an exact expression for the grand partition function of a superconductor:

$$Z(\mu, T) = \operatorname{Tr} \exp\left(-\frac{\hat{H} - \mu\hat{N}}{T}\right), \qquad \hat{N} = \sum_{k\sigma} a_{k\sigma}^{\dagger} a_{k\sigma}. \tag{6}$$

Here μ is the chemical potential, T is the temperature, and $\hat{N}$ is the operator of the number of electrons in the grain. At $T \to 0$ the dominating term in $Z(\mu, T)$ corresponds to the ground state of the grain with a certain number of electrons:

$$Z(\mu, T \to 0) = e^{-\Omega(\mu)/T}, \qquad \Omega(\mu) = \min_N\{E_N - \mu N\}. \tag{7}$$

Thus we can find the ground state energy E_N by studying the grand partition function (6).

One problem with this method of calculating E_N is that, because of the parity effect (1) with $\Delta_P > 0$, the odd charge states do not contribute to $Z(\mu, T \to 0)$. To find E_{2l+1} let us consider the effect of interactions on the unperturbed ground state of $2l + 1$ electrons. Since the state $l + 1$ is filled with one electron, the interaction term in the Hamiltonian (2) can neither create nor destroy a pair in this state. Thus E_{2l+1} can be found as

$$E_{2l+1} = \varepsilon_{l+1} + \tilde{E}_{2l}, \tag{8}$$

where $\tilde{E}_{2l}$ is the ground state energy of a grain with $2l$ electrons for the system (2) with state $k = l + 1$ excluded.

The idea of the path integral approach [13] is to replace the formulation (2) of the problem in terms of electronic operators $a_{k\sigma}$ by an equivalent formulation in terms of the superconducting order parameter $\Delta(\tau)$. The latter is introduced as an auxiliary field for a Hubbard-Stratonovich transformation splitting the quartic interaction term in Eq. (2) into quadratic pair creation and annihilation operators. Then the trace over the fermionic variables can be calculated, and one finds

$$Z(\mu, T) = \int D^2\Delta(\tau) e^{-S[\Delta]}, \tag{9}$$

where the action $S[\Delta]$ is defined as

$$S[\Delta] = -\sum_k \left[\operatorname{Tr} \ln \hat{G}_k^{-1} - \frac{\xi_k}{T}\right] + \frac{1}{g}\int_0^{1/T} |\Delta(\tau)|^2 d\tau. \tag{10}$$

Here $\xi_k = \varepsilon_k - \mu$, and the inverse Green's function

$$\hat{G}_k^{-1}(\tau,\tau') = \left[-\frac{d}{d\tau} - \xi_k \sigma^z - \Delta(\tau)\sigma^+ - \Delta^*(\tau)\sigma^- \right] \times \delta(\tau - \tau'), \quad (11)$$

where $\sigma^\pm = \sigma^x \pm i\sigma^y$, and $\sigma^{x,y,z}$ are the standard Pauli matrices. $\hat{G}^{-1}$ satisfies antiperiodic boundary conditions: $\hat{G}_k^{-1}(\tau + T^{-1}) = -\hat{G}_k^{-1}(\tau)$.

Unlike in the case of large superconductors [13], the order parameter Δ in Eqs. (9)–(11) does not depend on the coordinates, and thus the contributions of different states k in the action (10) decouple. This results from the simplified form of the interaction term in the Hamiltonian (2). The space fluctuations of Δ are negligible for grains smaller than the coherence length of the superconductor; this condition is well satisfied in ultrasmall grains. On the other hand, the time fluctuations of Δ accounted for in Eqs. (9)–(11) lead to the corrections to the mean-field BCS theory and are studied below.

First, we consider the regime of weak interactions, $\Delta \ll \delta\varepsilon$. In this case, the Δ-dependent terms can be considered to be a small perturbation $\hat{V} = \Delta\sigma^+ + \Delta^*\sigma^-$, and one can formally expand the action (10) in power series in $\hat{V}$ using

$$\operatorname{Tr}\ln(\hat{G}_0^{-1} - \hat{V}) = \operatorname{Tr}\ln\hat{G}_0^{-1} - \sum_{j=1}^{\infty} \frac{1}{j} \operatorname{Tr}(\hat{G}_0\hat{V})^j. \quad (12)$$

The first-order term vanishes because matrix $\hat{V}$ is off diagonal, so we study the quadratic in the Δ contribution to the action. The calculations are more convenient to perform in terms of the Fourier components Δ_m of the order parameter, defined in the usual way:

$$\Delta(\tau) = T\sum_m \Delta_m e^{-i\omega_m\tau}, \qquad \omega_m = 2\pi T m. \quad (13)$$

The calculation of the second-order contribution to the action (10) is straightforward and gives

$$\delta S = T\sum_m \frac{1 - \alpha(i\omega_m)}{g} |\Delta_m|^2, \qquad \alpha(E) = g\sum_k \frac{\operatorname{sgn}\xi_k}{2\xi_k - E}. \quad (14)$$

The functional integral (9) is now easily evaluated by integrating over the real and imaginary parts of each Δ_m. We normalize the result for the partition function Z by its value Z_0 for a noninteracting system, which corresponds to $\alpha = 0$ in Eq. (14),

$$\frac{Z(\mu,T)}{Z_0(\mu,T)} = \prod_m \frac{1}{1 - \alpha(i\omega_m)} = \prod_m \prod_k \frac{2\xi_k - i\omega_m}{2\tilde{\xi}_k - i\omega_m} = \prod_k \frac{\sinh(\xi_k/T)}{\sinh(\tilde{\xi}_k/T)}. \quad (15)$$

Here $\tilde{\xi}_k$ are defined by $1 - \alpha(2\tilde{\xi}_k) = 0$. Assuming weak interactions, $\Delta \ll \delta\varepsilon$, we find $\tilde{\xi}_k = \xi_k + \delta\xi_k$, where

$$\delta\xi_k = -\frac{g}{2} \frac{\operatorname{sgn}\xi_k}{1 - \frac{g}{2}\sum_{k'\neq k} \frac{\operatorname{sgn}\xi_{k'}}{\xi_{k'} - \xi_k}}. \quad (16)$$

We can now compare the result (15) with the definition (7) of $\Omega(\mu)$ and find

$$\delta\Omega(\mu) = \sum_k \delta\xi_k \operatorname{sgn}\xi_k. \quad (17)$$

One can easily see that for $\varepsilon_l < \mu < \varepsilon_{l+1}$ this correction does not depend on μ. According to (7) such $\delta\Omega$ should be interpreted as the correction δE_{2l} to the ground state energy of $2l$ electrons present in the grain in this range of μ. We then use the rule (8) to find δE_{2l+1}. To do this we exclude the state $k = l + 1$ from the sums in Eqs. (16) and (17), and calculate $\delta E'_{2l}$. The result for Δ_P coincides with Eq. (5).

We now turn to the case of stronger interactions, $\Delta \gg \delta\varepsilon$. A good starting point in this regime is the standard BCS theory [1], which corresponds to a mean-field approximation for the order parameter in the path integral approach [13]. Substituting a time-independent Δ into the action (10), one finds

$$\Omega(\mu) = \sum_k (\xi_k - \epsilon_k) + \frac{1}{g}|\Delta|^2. \quad (18)$$

Here $\epsilon_k = (\xi_k^2 + |\Delta|^2)^{1/2}$, and the value of $|\Delta|$ must be chosen in a way which minimizes Ω. This means that $|\Delta|$ is determined from the usual BCS equation:

$$\sum_k \frac{1}{2\epsilon_k} = \frac{1}{g}. \quad (19)$$

In the continuous limit $\delta\varepsilon/\Delta \to 0$, one can apply the rule (8) and find that the exclusion of one state from the sum over k in Eq. (18) results in the energies of odd charge states exceeding those of the even ones by $\Delta_P = \Delta$.

To find the corrections to Δ_P due to the finite $\delta\varepsilon$ a more careful treatment of the mean-field approximation is required. One can easily see that not only a time-independent $\Delta_0(\tau) = |\Delta|$, but also any path $\Delta_M(\tau) = |\Delta|e^{i2\pi MT\tau}$ with integer M is a minimum of the action (10) which must be taken into account. It is convenient to treat the path $\Delta_M(\tau)$ in Eq. (11) by performing a gauge transformation $\hat{U} = \exp(i\pi MT\tau\sigma^z)$, which eliminates the time dependence of $\Delta_M(\tau)$ and shifts the chemical potential $\mu \to \mu - i\pi MT$ [14]. Thus, instead of $Z = e^{-\Omega/T}$, the partition function at $T \to 0$ is now

$$Z(\mu,T) = \sum_M e^{-\Omega(\mu - i\pi MT)/T} = e^{-\Omega(\mu)/T}\sum_M e^{i\pi\Omega'(\mu)M},$$

where $\Omega(\mu)$ is given by Eq. (18). We have expanded $\Omega(\mu - i\pi MT)$ in Taylor series in $i\pi MT$, and neglected the terms vanishing at $T \to 0$. It is now obvious that

$Z(\mu, T) = 0$ unless the derivative of Ω is an even integer:

$$\Omega'(\mu_{2l}) = -2l\,. \tag{20}$$

Thus the mean-field approximation can be applied only for discrete values of chemical potential μ_{2l} corresponding to solutions with $2l$ electrons. For the odd number of electrons, μ_{2l+1} is found as μ_{2l} in a system with one state $k = l + 1$ at the Fermi level excluded. At $\Delta \gg \delta\varepsilon$, one always gets $\mu_{N+1} - \mu_N = \delta\varepsilon/2$.

To find Δ_P we substitute in Eq. (1) the ground state energy as $E_N = \Omega(\mu_N) + \mu_N N$. The contribution of the second term to Δ_P is $-\delta\varepsilon/2$. In evaluating the contribution of $\Omega(\mu_N)$ one has to take into account the dependence of μ_N on N and the suppression [7,8] of the self-consistent gap in Eq. (18) $\Delta_{\mathrm{odd}} = \Delta - \delta\varepsilon/2$ for odd N due to the exclusion of one state k from the gap equation (19). Combining all the contributions, we get the following mean-field result:

$$\Delta_P = \Delta - \frac{\delta\varepsilon}{2}, \qquad \delta\varepsilon \ll \Delta\,. \tag{21}$$

It is interesting that a similar quantity $\tilde{\Delta}_P = -E_{2l} + (E_{2l-1} + E_{2l+1})/2$ is unaffected by finite-level spacing up to the terms linear in $\delta\varepsilon$, i.e., $\tilde{\Delta}_P = \Delta$. Thus, at $\delta\varepsilon \ll \Delta$, we have $\Delta_P = \Delta_{\mathrm{odd}}$ and $\tilde{\Delta}_P = \Delta_{\mathrm{even}}$.

Although the result $\Delta_P = \Delta$ can be obtained from the mean-field theory, an evaluation of corrections to it due to the level spacing requires taking into account the effects of the fluctuations of the order parameter. One can find the contribution of the fluctuations by expanding the action near $\Delta(\tau) = |\Delta|$ using Eq. (12). The second-order correction to the action is [15,16]

$$\delta S = T \sum_m |\delta_m^R \gamma_m^{1/2} + i\delta_m^I \gamma_m^{-1/2}|^2 \times \sum_k \frac{\omega_m}{2\epsilon_k(\omega_m\gamma_m - 2i\xi_k)}\,,$$

where $\delta_m^{R,I}$ are the Fourier components of the real and imaginary parts of the fluctuation $\Delta(\tau) - |\Delta|$, and $\gamma_m = (1 + 4|\Delta|^2/\omega_m^2)^{1/2}$. Now we evaluate the path integral (9) by integrating over all $\delta_m^{R,I}$ and find the contribution of the fluctuations to $\Omega(\mu)$,

$$\delta\Omega(\mu) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \times \ln \left| \sum_k \frac{g|\omega|}{2\epsilon_k(\sqrt{\omega^2 + 4|\Delta|^2} - 2i\xi_k)} \right|\,.$$

A comparison of the expressions for $\delta\Omega$ in the cases of even and odd numbers of electrons shows that they coincide up to the terms of order $\delta\varepsilon$. Thus the fluctuations of the order parameter do not affect the result (21).

Finally, we discuss the mesoscopic fluctuations of Δ_P given by our results (5) and (21). It is clear from Eq. (16) that, unlike $\delta\varepsilon$ in the numerator of Eq. (5), the one in the argument of the logarithm is sensitive to the Wigner-Dyson fluctuations of ξ_k. Thus the relative mesoscopic fluctuation of the result (5) is small, $\delta\Delta_P/\Delta_P \sim 1/\ln(\delta\varepsilon/\Delta)$. It is also interesting to compare the mesoscopic fluctuation of the gap Δ originating from the level fluctuations in Eq. (19) with the small corrections in Eq. (21). One can easily express [15] the correction to Δ in terms of the correction to the density of states $\nu(\xi)$ in Eq. (19). Then the mean-square fluctuation of the gap is found using the well-known results for the correlator $\langle\nu(\xi)\nu(\xi')\rangle$, and we get $\sqrt{\langle(\delta\Delta)^2\rangle} = \delta\varepsilon/\pi\sqrt{2}$.

In conclusion, we have studied the parity effect (1) in the ground state energies of an ultrasmall superconducting grain. Although the quantum fluctuations of the order parameter can be neglected for large grains, Eq. (21), they play a crucial role in small grains, Eq. (5). As the size of the grain decreases, the parity effect first weakens, Eq. (21), but then starts increasing, Eq. (5). Thus we expect a minimum of Δ_P at a certain size of the grain such that $\delta\varepsilon \sim \Delta$.

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