Number parity effects in the normal state of $SrTiO_3$

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We study the recently discovered even-odd effects in the normal state of single-electron devices manufactured at strontium titanium oxide/lanthanum aluminum oxide interfaces (STO/LAO). Within the framework of the number parity-projected formalism and a phenomenological fermion-boson model, we find that, in sharp contrast to conventional superconductors, the crossover temperature T^* for the onset of number parity effect is considerably larger than the superconducting transition temperature T_c due to the existence of a pairing gap above T_c. Furthermore, the finite lifetime of the preformed pairs reduces by several orders of magnitude the effective number of states $N_{\rm eff}$ available for the unpaired quasiparticle in the odd-parity state of the Coulomb blockaded STO/LAO island. Our findings are in qualitative agreement with the experimental results reported by Levy and coworkers for STO/LAO-based single electron devices.

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I. INTRODUCTION

Number parity effects in superconductors were expected as soon as the Bardeen-Cooper-Schrieffer (BCS) microscopic model was developed [1]. Indeed, the BCS ground state corresponds to a coherent superposition of *pair* states in which the number of particles has even parity and the total number N is not fixed. Under these circumstances, the charge displacement operator $\exp(i\phi)$ (canonically conjugate with the number operator $\hat{N}$) has a fixed expectation value, which leads to the common notion that a macroscopic BCS superconductor has a complex order parameter Δ with a rigid phase ϕ. As soon as the BCS state is projected [2] onto *fixed* N, it becomes clear that one has to differentiate between two cases: (a) if the total number $N = 2n$ is even, all particles can participate in pair states and the ground state resembles the usual grand canonical BCS ground state; (b) if $N = 2n + 1$ is odd, the ground state will inevitably contain not only pairs, but also an unpaired electron (more precisely, the ground state will contain a Bogoliubov quasiparticle).

Intuitively, one would expect that the N vs $N + 1$ (even/odd) difference in a superconductor or any kind of paired fermionic state must be experimentally observable only if N is relatively small. Indeed, inspired by the success of the BCS theory, Bohr, Mottelson, and Pines [3] were the first of many who studied pairing and even-odd effects in nuclear matter, with particle numbers around $N \sim 10^2$. It was therefore, even more surprising, when Mooij *et al.* [4], Tinkham and coworkers [5], as well as Devoret and his colleagues [6,7] showed experimentally measurable difference between Coulomb blockaded mesoscopic superconducting islands that contain a billion, and a billion plus one electrons. As it turns out, the magnitude of N was less important. Instead, the quality of the Coulomb blockade turned out to be crucial: The superconducting islands had to be isolated from their environment with ultrasmall tunnel junctions and highly resistive electromagnetic environment, in order to ensure that N is a fixed, good quantum number.

The pioneering experiments on number parity effects in conventional superconductors were performed on single-electron (SET) devices consisting of lithographically patterned aluminum islands [8]. Even-odd effects emerged below a crossover temperature T^* that was always much lower than the superconducting transition temperature: $T^* \ll T_c$. Rather than being directly correlated with T_c, T^* is set by the experimentally measurable even-odd free energy difference $\delta\mathcal{F}_{\rm e/o} \sim \Delta_0 - k_B T \log N_{\rm eff}$. Here Δ_0 is the low temperature energy gap, and $N_{\rm eff}$ is the effective number of states [5–7,9] available for the unpaired electron to explore in the odd-number-parity state of the superconducting island. Within this parity projected framework [5,9] T^* corresponds to the temperature at which $\delta\mathcal{F}_{\rm e/o}$ becomes negligibly small: $T^* \sim \Delta_0/(k_B \log N_{\rm eff})$. For typical device parameters in these early experiments, the crossover temperature was measured to be around $T^* \sim 10^2$ mK for aluminum island with $T_c \sim 1$ K. Consequently, the effective number of states was typically around $N_{\rm eff} \sim 10^4$.

The experiments by Levy and his coworkers [10] on SET devices constructed on STO/LAO provided experimental evidence for a spectacular departure from the conventional number parity effects described above. Levy and his colleagues detected $T^* \sim 900$ mK, much higher than the superconducting transition temperature $T_c \sim 300$ mK measured for these devices. Even-odd effects remained detectable well into the "normal" phase of the superconductor, and persisted in magnetic fields $B^* \sim 1 \sim 4$T, much higher than the upper critical field of the device. Furthermore, the extracted N_{eff} is also drastically different: $N_{\text{eff}} \sim 2-3$.

A possible and relatively straightforward interpretation of novel experimental developments suggest that preformed pairs [11–13] persist into the normal state of STO-LAO well above the superconducting transition temperature. Consequently, fundamental changes must be made to the theoretical description of the number parity effects in this novel preformed pair phase. This paper is devoted to the presentation of a phenomenological theoretical framework aimed at providing a description of number parity effects in the normal phase of STO/LAO devices. Given the fact that the details of the microscopic mechanism behind the superconducting and preformed pair state of STO/LAO are not yet established, we use a phenomenological fermion-boson model [14] that allows us to describe a normal phase where both pairs and unpaired particles are present. Furthermore, the model allows pairs to decay into unpaired particles, and particles to form pairs. This theoretical picture provides in a natural way a finite pair lifetime [10] in the preformed pair state. We find, after performing the number parity projection developed earlier by Ambegaokar, Smith, and one of us [9], that the finite pair lifetime has drastic effect on the magnitude of N_{eff}. In fact, as we will show in detail below, the theoretical framework we develop in this paper can reproduce not only $T^* \gg T_c$, but also $N_{\text{eff}} \sim \mathcal{O}(1)$.

Generally speaking, the materials for making the single-electron devices can be separated into three categories (see Fig. 1): metals, BCS, and unconventional superconductors. Their density of states are shown, respectively, in panels (a), (b) and (c) of Fig. 1. While the single electron transistors with *ultra*small islands and discrete energy spectrum have also been investigated extensively [15,16], we will not discuss this regime here. According to our calculations, the density of states at the Fermi level should be vanishingly small in order to obtain a finite even/odd free energy difference. As a result, the single electron transistors made from BCS superconductors and unconventional superconductors [as shown in panels (b) and (c)] are expected to show even-odd effects, and a superconducting gap above T_c is necessary to cause $T^* \gg T_c$. The effective excitation number for the unpaired electrons in the odd-parity states is highly dependent on the density of states at $E = \Delta$, since the smallest excitation energy is assumed to be Δ [5–7]. In BCS superconductors [see panel (b)], the density of states at $E = \Delta$ is known to have a van Hove singularity, and this results in a large $N_{\text{eff}} \sim 10^4$. In unconventional superconductors [see panel (c)], the van Hove singularity is broadened by the presence of low energy quasiparticles, which results in a small $N_{\text{eff}} \sim \mathcal{O}(1)$.

Several possible microscopic superconducting mechanisms of the electron system at the STO/LAO interface have been proposed recently by different groups. Ruhman and Lee [17] suggested on the plasmon-induced superconducting mechanism. A nonperturbative approach within the plasmon model is being developed by Edelman and Littlewood [18]. Kedem *et al.* [19,20] related the mechanism to the ferroelectric mode. Arce-Gamboa and Guzmán-Verri [21] discovered the influence of strain on the ferroelectric mode and obtained the dependence of superconducting transition temperature on

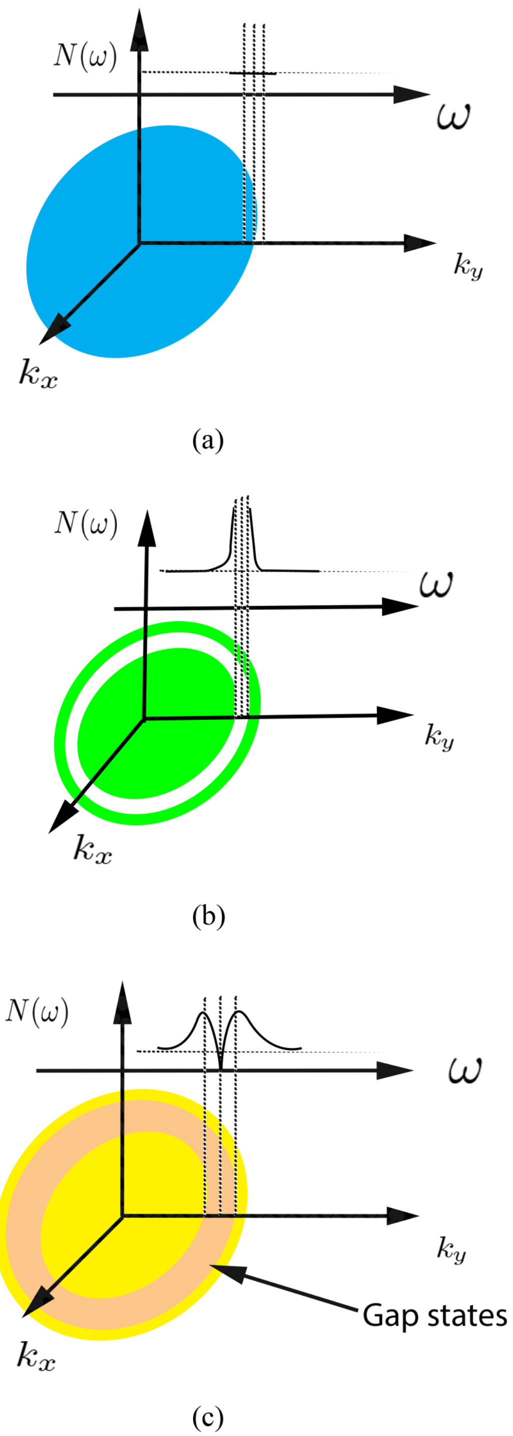

FIG. 1. Qualitative sketch of the momentum space and density of states for (a) the density of states in the metallic normal state; (b) a conventional superconductor with a superconducting gap, and (c) an unconventional superconductor with a zero-width gap at Fermi level. For the cases (b) and (c), even-odd effect can be expected because of the presence of the superconducting gaps.

cation doping. On the contrary, Wölfle and Balastsky [22] proposed the transverse optical phonons may be the glue for electron pairing. While these theories in STO/LAO may be able to explain the origin of superconducting phase self-consistently, some important experimental facts in remain unexplained. First of all, the pairing gap should persist above T_c. This is very important for the even-odd effects above T_c in the single electron transistors [23]. Next, the van Hove singularity in the density of states should be broadened out. This will lead to a small $N_{\rm eff}$ consistent with the experiments of Levy *et al.* [10]. The detailed discussion of these results will be presented in the sections below.

This paper is organized as follows. In Sec. II, two important physical quantities, the even/odd free energy difference and the effective excitation number for the unpaired electron in the odd-parity state, are related to the density of states within the phenomenological Dynes formula. In Sec. III, the boson-fermion model is introduced, and the analytic form of its electron Green's function is provided. The density of states and the physical quantities of the even-odd effect predicted by the model are calculated in Sec. IV. Finally, we present our conclusions in Sec. V.

II. EVEN/ODD FREE ENERGY DIFFERENCE AND EFFECTIVE EXCITATION NUMBER FOR THE UNPAIRED ELECTRON

A. Even/odd free energy difference

The electron system of the quantum dot at the STO/LAO interface is described by a general Hamiltonian $\hat{H}$. Within the number parity projection formalism [9], the canonical partition function with even/odd number parity is:

$$Z_{e/o} = \mathrm{Tr}\left\{\frac{1 \pm (-1)^{\hat{N}}}{2} e^{-\beta(\hat{H}-\mu\hat{N})}\right\} \tag{1}$$

where the symbol e/o corresponds to the even/odd parity, $\hat{N}$ is the electron number operator, while $\beta = \frac{1}{k_B T}$ where k_B is Boltzmann constant and T is the temperature.

From Eq. (1), the difference between the free energy of a system with an odd and even number of particles is

$$F_o - F_e = \frac{1}{\beta} \ln\left[\frac{1+\langle(-1)^{\hat{N}}\rangle}{1-\langle(-1)^{\hat{N}}\rangle}\right], \tag{2}$$

where $\langle\ldots\rangle \equiv \mathrm{Tr}\{e^{-\beta(\hat{H}-\mu\hat{N})}\ldots\}/Z$ and $Z = \mathrm{Tr}\{e^{-\beta(\hat{H}-\mu\hat{N})}\}$. ln is the natural logarithm with base e. The expectation value $\langle(-1)^{\hat{N}}\rangle$ is the parameter that signals the presence or absence of even-odd effects. When $\langle(-1)^{\hat{N}}\rangle = 0$, even-odd effects will not be observable. Let us assume that the Hamiltonian can be expressed in a more compact form $\hat{H} = \sum_{\mathbf{k},\sigma} e_{\mathbf{k}} \hat{c}^{\dagger}_{\mathbf{k},\sigma}\hat{c}_{\mathbf{k},\sigma}$. Using the relation $(-1)^{\hat{N}} = e^{(i\pi\hat{N})}$ and the above equations,

$$\begin{aligned}
\langle(-1)^{\hat{N}}\rangle &= \frac{\mathrm{Tr}\{e^{(i\pi\hat{N})}e^{-\beta(\hat{H}-\mu\hat{N})}\}}{\mathrm{Tr}\{e^{-\beta(\hat{H}-\mu\hat{N})}]\}} \\
&= \frac{\mathrm{Tr}\{e^{-\beta(\hat{H}-\mu\hat{N})+i\pi\hat{N}}\}}{\mathrm{Tr}\{e^{-\beta(\hat{H}-\mu\hat{N})}]\}} \\
&= \frac{\mathrm{Tr}\{\prod_{\mathbf{k}\sigma} e^{-\beta(e_{\mathbf{k}}\hat{n}_{\mathbf{k}\sigma}-\mu\hat{n}_{\mathbf{k}\sigma})+i\pi\hat{n}_{\mathbf{k}\sigma}}\}}{\mathrm{Tr}\{\prod_{\mathbf{k}'\sigma'} e^{-\beta(e_{\mathbf{k}'}\hat{n}_{\mathbf{k}'\sigma'}-\mu\hat{n}_{\mathbf{k}'\sigma'})}]\}} \\
&= \frac{\prod_{\mathbf{k}\sigma}\mathrm{Tr}\{e^{-\beta(e_{\mathbf{k}}\hat{n}_{\mathbf{k}\sigma}-\mu\hat{n}_{\mathbf{k}\sigma})+i\pi\hat{n}_{\mathbf{k}\sigma}}\}}{\prod_{\mathbf{k}'\sigma'}\mathrm{Tr}\{e^{-\beta(e_{\mathbf{k}'}\hat{n}_{\mathbf{k}'\sigma'}-\mu\hat{n}_{\mathbf{k}'\sigma'})}]\}} \\
&= \prod_{\mathbf{k}} \frac{(1-e^{-\beta(e_{\mathbf{k}}-\mu)})^2}{(1+e^{-\beta(e_{\mathbf{k}}-\mu)})^2} \\
&= \prod_{\mathbf{k}} \tanh^2\left(\frac{\beta(e_{\mathbf{k}}-\mu)}{2}\right).
\end{aligned} \tag{3}$$

The Baker-Campbell-Hausdorff formula and the relation that $[\hat{H},\hat{N}] = 0$ and $[\hat{n}_{\mathbf{k}\sigma},\hat{n}_{\mathbf{k}'\sigma'}] = 0$ are used in deriving the second and third equality. In the fifth equality, it is assumed that the momentum $\mathbf{k}$ and $\mathbf{k}'$ have the same range. The trace is calculated in the particle number representation, in which the particle number $\hat{n}_{\mathbf{k}\sigma}$ has two possible values, 0 and 1. It is also assumed that the spin σ has two possible values due to the fermionic nature of the particles, which produces the two squares in the fifth equality. If A is defined as $e^A \equiv \langle(-1)^{\hat{N}}\rangle$, then

$$A = 2\sum_{\mathbf{k}} \ln\left|\tanh\frac{\beta e_{\mathbf{k}}}{2}\right| = 2\int_{-\infty}^{+\infty} D(E)\ln\left|\tanh\frac{\beta E}{2}\right| dE, \tag{4}$$

where $D(E)$ is the density of states. Notice that the factor $\ln|\tanh\frac{\beta E}{2}|$ in the integrand is divergent when $E = 0$. This suggests that an energy gap is necessary for a system to show even-odd effects. In the absence of a pairing gap A is a large negative number and $e^A \approx 0$. The value of $\delta F_{e/o}$ will be approximately zero if the gap closes. This can be used to define the critical temperature of the onset of the even-odd effect, T^*. At the interface of STO/LAO, the even-odd effects appear above the superconducting transition temperature T_c. This implies the existence of a pairing gap above T_c. Scanning tunneling spectroscopy experiments also show that an energy gap persists above T_c [23]. This is one of the requirements for a system showing number-parity effects. Moreover, the factor $\ln|\tanh\frac{\beta E}{2}|$ turns to be zero when $E \gg E_F$. This suggests the part with the high energy does not contribute to the integral A. On the other hand, the density of states near Fermi level (gap states) can increase the value of $|A|$ greatly, and the even-odd effect parameter $\langle(-1)^{\hat{N}}\rangle = e^A = e^{-|A|} \ll 1$ is reduced accordingly. In this sense, the emergence of the gap states can weaken even-odd effects.

B. Effective excitation number for the unpaired electron

With the assumption that the smallest excitation energy for electrons is Δ, we can calculate the effective excitation number for the unpaired electron as follows [5–7]:

$$N_{\rm eff} = \int_{\Delta_0}^{\infty} D(E)\exp\left(-\beta(E-\Delta)\right)dE. \tag{5}$$

In Eq. (5), the density of states at $E = \Delta$ contributes most to the effective excitation number for the unpaired electron in the odd-parity states. If it is assumed that the van Hove singularity in $D(E)$ exists, it can easily produce a large $N_{\rm eff} \sim 10^4$ or more in BCS superconductors. However, the experiments [10] at the interface of STO/LAO discover a very small

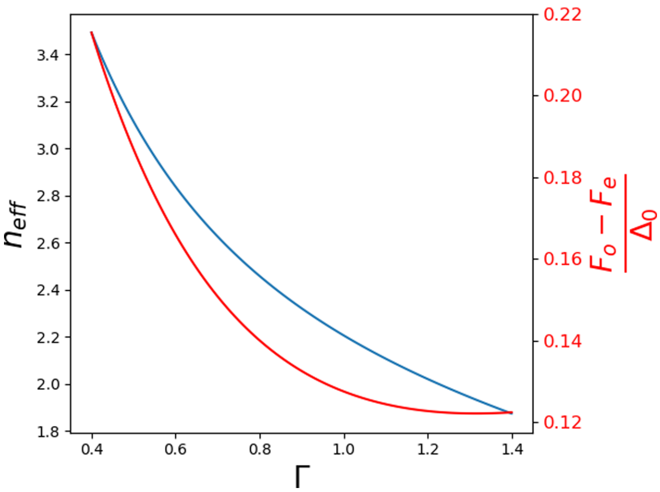

FIG. 2. Γ vs the even/odd free energy difference $\delta F_{e/o}$ and the number of the effective excitation states for the unpaired quasiparticles N_{eff}.

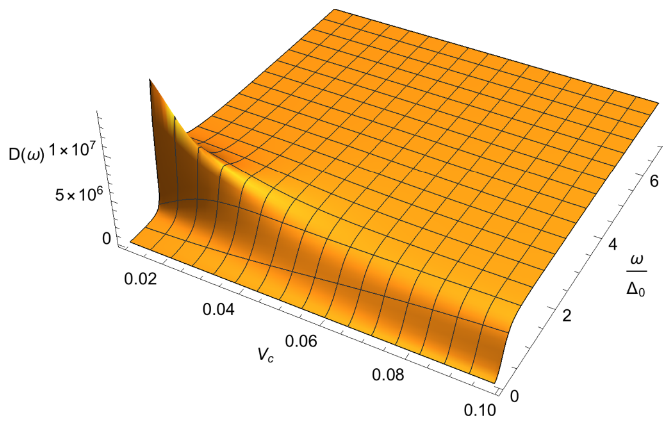

FIG. 3. The density of states $D(\omega)$ is plotted along with the variation of V_c. $D(\omega)$ and V_c are plotted in atomic units at the temperature $\sim$ 63 mK.

$N_{\mathrm{eff}} \sim 1$. This indicates that the van Hove singularity was broadened out in the density of states.

C. Even-odd effect phenomenology with the Dynes formula

As we can see in the above discussion, the even-odd effects are related to the density of states of the small island in the single electron transistors. In order to reproduce the experimental results, the van Hove singularity should, at least, be broadened. This can be provided by the lifetime effects of electron pairs. Here we adopt the phenomenological Dynes formula and calculate the even/odd free energy difference $\delta F_{e/o}$ and the effective excitation number for the unpaired electron N_{eff}

To be explicit, we will use the following form for the density of states [24]

$$D_d(E) = D_n(0)\mathrm{Re}\frac{|E - i\Gamma|}{\sqrt{(E - i\Gamma)^2 - \Delta^2}} \tag{6}$$

where $D_n(0)$ is the density of states in the normal state, Γ is the phenomenological imaginary part of the single-particle self-energy, and Δ is the superconducting energy gap. With Eqs. (2)–(5), the even/odd free energy difference $\delta F_{e/o}$ and the effective excitation state number for the unpaired electron N_{eff} are calculated and plotted in Fig. 2. As we can see, with increasing Γ, N_{eff} reduces to ∼1. The even/odd free energy difference is finite provided that the superconducting gap Δ does not close. This result is independent of any microscopic model of the superconducting state. In order for the pairing-induced even-odd effect to be experimentally observable, the density of states at the Fermi level must vanish, and broadening Γ has to be small compared to the gap Δ_0.

III. THE BOSON-FERMION MODEL

As mentioned in Sec. I, there is no consensus yet on the microscopic theory of superconductivity in STO. In order to reproduce a Dynes-like density of states, we turn to the phenomenological boson-fermion model. For a single-band model, electrons are assumed to have a Bogoliubov quasiparticle dispersion $E_{\mathbf{k}} = \sqrt{\epsilon_{\mathbf{k}}^2 + \Delta^2}$, where $\epsilon_{\mathbf{k}} = \frac{\hbar^2 k^2}{2m^*} - \mu_F$. Other factors including external gate voltage, doping, temperature dependence, etc. can change the values of electrons' effective mass m^*, which are in the range of $0.9\, m_e - 1.4\, m_e$ where m_e is the free electron mass in vacuum [25]. In our analysis, for the convenience of the calculations, we assumed that the effective mass of the quasiparticle is m_e. Since the carrier density can be tuned over a very large regime, the value of Fermi energy can vary from 0.1 meV to 20 meV, from which the corresponding Fermi velocity is approximately from 10^3 m/s to 10^5 m/s [26,27]. In the present paper, the Fermi velocity is assumed to be approximately 10^4 m/s. Although these parameters indeed have a wide experimental range, reasonable values can generate the fermion density of states shown in Fig. 3. The Hamiltonian of the electrons can be written as:

$$\hat{H}_{0e} = \sum_{\mathbf{k},\sigma} E_{\mathbf{k}} \hat{c}^\dagger_{\mathbf{k},\sigma} \hat{c}_{\mathbf{k},\sigma}. \tag{7}$$

The superconducting gap of the 2D electron system at the interface of STO/LAO, Δ vanishes at $T_s \sim 300$ mK, and it turns into superconducting state at $T_c \sim 190$ mK [23]. This suggests that between T_c and T_s the superconducting phase is destroyed, but the superconducting gap is preserved. This regime corresponds to the preformed pair state. The present model is devoted to studying the preformed pair state and superconducting state. Notice that the coherence length of pairs is ∼70–100 nm in (001)-STO/LAO and 40−75 nm for (011)-STO/LAO [28]. In order to give an approximate description of small-sized preformed pairs, we introduce a bosonic field $\hat{b}_{\mathbf{q}}$ with elementary charge unit $-2e$. For a small momentum $\mathbf{q}$, the dispersion of the pairs is approximated [2] as $\xi_{\mathbf{q}} = \xi_0 + \hbar v|q| - \mu_b$. The bosonic velocity v represents the speed of the electron pairs, and it has not been measured in the current experiments. The choice of the values of v, ξ_0 and μ_b is discussed in the Appendix A. The Hamiltonian for the bare bosonic field is:

$$\hat{H}_{0p} = \sum_{\mathbf{q}} \xi_{\mathbf{q}} \hat{b}^\dagger_{\mathbf{q}} \hat{b}_{\mathbf{q}} \tag{8}$$

where $\hat{b}_{\mathbf{q}}^{\dagger}$ and $\hat{b}_{\mathbf{q}}$ are defined to commute with $\hat{c}_{\mathbf{k},\sigma}^{\dagger}$ and $\hat{c}_{\mathbf{k},\sigma}$. The interaction Hamiltonian between the fermions and bosons is assumed to be

$$\hat{H}_1 = \sum_{\mathbf{k},\mathbf{q}} \frac{V_1(\mathbf{q})}{\sqrt{n_0}} \hat{b}_{\mathbf{q}}^{\dagger} \hat{c}_{-\mathbf{k}+\frac{\mathbf{q}}{2}\downarrow} \hat{c}_{\mathbf{k}+\frac{\mathbf{q}}{2}\uparrow} + \text{H.c.} \tag{9}$$

From the above, the total Hamiltonian is

$$\hat{H} = \hat{H}_0 + \hat{H}_1 \tag{10}$$

where

$$\hat{H}_0 = \hat{H}_{0e} + \hat{H}_{0p}. \tag{11}$$

The total particle number is defined as $\hat{N} = \sum_{\mathbf{k},\sigma} \hat{c}_{\mathbf{k},\sigma}^{\dagger} \hat{c}_{\mathbf{k},\sigma} + 2\sum_{\mathbf{q}} \hat{b}_{\mathbf{q}}^{\dagger} \hat{b}_{\mathbf{q}}$, and it can be proven that $[\hat{N}, \hat{H}] = 0$. The first-order approximation of the self-energy is

$$\Sigma(\mathbf{k}, \omega) = \frac{L}{2\pi\hbar^2} \int \frac{|V_1(\mathbf{q})|^2 d\mathbf{q}}{n_0} \frac{1}{\omega - \frac{(\xi_{\mathbf{q}} - E_{\mathbf{q}-\mathbf{k}})}{\hbar} + i\eta} \times \left(\frac{1}{e^{\beta\xi_{\mathbf{q}}} - 1} + \frac{1}{e^{\beta E_{\mathbf{q}-\mathbf{k}}} + 1} \right) \tag{12}$$

where L is the length of the quantum dot in the middle of the single electron transistor, and n_0 is the total number of quasiparticles in the quantum dot. $n_0 \sim 500$ [10]. Notice that the superconductivity of the STO/LAO system is considered to be one-dimensional [10], which makes our proposed theory to be one-dimensional as well. Let us now introduce a momentum dependent interaction kernel $V_1(q)$ as an example interaction that reproduces a Dynes-like density of states:

$$V_1 = V_c \sqrt{\frac{(\xi_{\mathbf{q}} - E_{\mathbf{q}-\mathbf{k}})^2}{(\xi_{\mathbf{q}} - E_{\mathbf{q}-\mathbf{k}})^2 + \Delta_0^2}} \tag{13}$$

where V_c is the strength of the coupling. Notice that the factor $\xi_{\mathbf{q}} - E_{\mathbf{q}-\mathbf{k}}$ in fact is equivalent to the frequency of the electron in Green's function ω. The calculation of the self-energy is presented in Appendix A.

IV. EVEN-ODD EFFECT WITHIN THE BOSON-FERMION MODEL

With Eqs. (A2) and (A3), the one-particle Green's function can be written as:

$$G(\mathbf{k}, \omega) = \frac{1}{\omega - \epsilon_{\mathbf{k}} - \Sigma' - i\Gamma} \tag{14}$$

where $\epsilon_{\mathbf{k}} = \sqrt{\Delta^2 + \left(\frac{\hbar^2(k^2-k_F^2)}{2m^*}\right)^2} \approx \sqrt{\Delta^2 + \left(\hbar v_F^*(k - k_F)\right)^2}$, $v_F^* \equiv \frac{\hbar k_F}{m^*}$, $\Sigma' = \Sigma_{\mathbf{k}}'(\omega)|_{k=k_F}$, $\Gamma = \Gamma_{\mathbf{k}}(\omega)|_{k=k_F}$. Numerical calculations show that $\Sigma' \ll \Delta$ at low temperature and consequently Σ' is negligible.

The density of states is given by

$$D(\omega) = L \int_{-\infty}^{\infty} A(\mathbf{k}, w) d\mathbf{k} \tag{15}$$

where $A(\mathbf{k}, \omega) = -\frac{1}{\pi}\text{Im}(G(\mathbf{k}, \omega))$ and $L \approx 500$ nm is the length of the small island in the middle of the single electron transistor. Notice that only $\epsilon_{\mathbf{k}}$ is dependent on the momentum $\mathbf{k}$ in the spectral weight function $A(\mathbf{k}, \omega)$. This allows us to deduce an exact result in the mathematical expression of $D(\omega)$ with the residue theorem (see Appendix B).

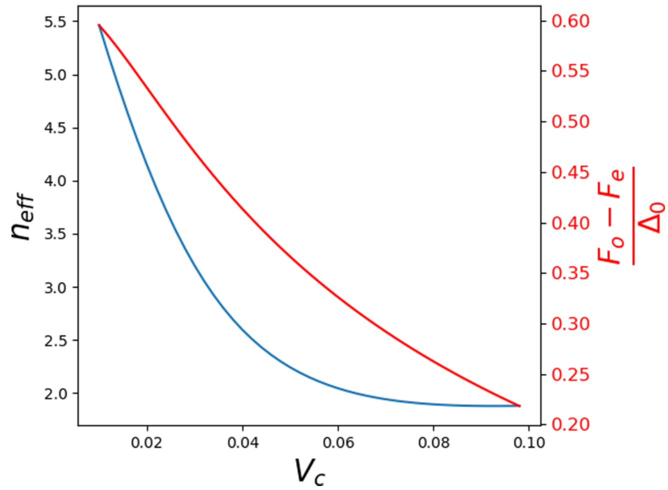

FIG. 4. The even-odd free energy difference and the effective excitation number for the unpaired electron versus V_c. It is plotted in atomic units also at the temperature ~ 63 mK. $m^* = m_e$, $n_0 = 500$, $L = 530$ nm, $v_F^* = 8.8\times10^3$ m/s and $v = 0.073c$, where c is the speed of light in vacuum.

As shown in Fig. 3, the decay and formation of the electron pairs produces many gap states and broadens the van Hove singularity in the density of states. The effects can reduce the even/odd free energy difference $\delta\mathcal{F}_{\text{e/o}}$, and the effective excitation number for the unpaired electron in the odd-parity state N_{eff}, and this can be measured in experiments. In addition, a zero superconducting gap makes a finite spectral function at the Fermi level, and in that case, the density of states, $D(\omega)$, is finite at ϵ_F. This can destroy the even-odd effects. As shown in Fig. 4, the results on the even-odd effects calculated by the boson-fermion model is very similar to those we obtained from Dynes' model density of states. This indicates that the shape of the density of states is particularly important in our deductions. However, it is only determined by three parameters, the Fermi velocity of electrons, the length of the quantum dot and the decay rate of electron pairs. In contrast, the other microscopic parameters are less important.

Note that the even-odd free energy difference is positive definite as it compares the free energies of an electronic system with $2N + 1$ and $2N$ particles, respectively. In the low-temperature limit, keeping only the leading terms, we get $\delta F \sim \Delta - k_B T \ln N_{\text{eff}}$. This limit is useful to estimate the temperature scale $T_{\text{even/odd}}$ where the energy difference Δ becomes comparable to the entropic contribution $k_B T \ln N_{\text{eff}}$. In this temperature range, higher-order terms in the expansion of δF become significant. However, around this temperature, as shown in the early experiments [5–7] the even-odd free energy difference becomes immeasurably small.

It would of course be desirable to provide a theoretical explanation for the experimentally observed temperature dependence of the even-odd effects. In the absence of a self-consistent microscopic theory of the superconducting and the preformed pair state of STO/LAO, a fully theoretical analysis of the temperature dependence is not yet possible. In contrast, there is plenty of experimental data on the temperature dependence of single particle spectral properties, the spectral gap in particular. Indeed, Richter [23], suggested that the temperature dependence of the spectral gap can be modeled phenomenologically by a simple expression that depends only on the low temperature value Δ of the gap and the temperature T^* when the gap closes. In Appendix C we present a phenomenological calculation of temperature dependence of the density of states, the broadening, and the even-odd free energy by using the temperature dependence of the pairing gap extracted by Richter [23].

V. CONCLUSIONS

In the present paper, we argue that the even-odd effects seen in the normal state of STO originate from superconducting preformed pairing. This in turn imposes severe constraints on the density of states and consequently any microscopic model aimed at explaining the superconducting and normal state of STO/LAO. First, the density of states at Fermi level should be zero below and above T_c. Next, the gap states are necessary to reduce the even/odd free energy difference and weaken the even-odd effects. Finally, the van Hove singularity needs to be broadened out in order to obtain a small N_{eff}. These constraints for the density of states are not immediately satisfied by most current microscopic theories.

The broadening of the van Hove singularity in the density of states may be a fingerprint of the lifetime effects of electron pairs. Single-electron transistor experiments are very sensitive in detecting lifetime effects, as well as the existence of the superconducting gap, the gap states and the broadening of the van Hove singularity. Moreover, compared to the difficult experimental conditions to perform reliable scanning tunneling spectroscopy, single electron devices can be relatively easy to operate in some strongly interacting electron systems. Furthermore, the decay and formation of electron pairs may widely exist in many different types of superconductors, including BCS superconductors. The application of the single-electron transistor devices to study novel superconductors is therefore very promising.

Although the microscopic mechanism of the superconductivity in STO is still under development, the BCS-BEC crossover theory is remarkably helpful. Throughout the crossover from the BCS to BEC limit, a mean field like transition to the superfluid can indeed be defined. In the weak coupling BCS regime, as shown by Patton [29], the spectroscopic changes in the single particle density of states are restricted to the so-called critical regime, where fluctuations in the superconducting order parameter are significant. We found, however, that in the intermediate coupling regime, the gradual loss of spectral weight in the single particle density of states around the Fermi level occurs at considerably higher temperature scales (which we interpreted as the emergence of a pseudogap due to resonant pair scattering [30]).

Within the BCS-BEC framework, it seems that STO/LAO is in the intermediate coupling regime [31]. In Levy's experiments [10], the electron pairing is observed above the superconducting transition temperature. The gradually increasing density of states around the Fermi level is another evidence STO stays between BCS and BEC limits [32].

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APPENDIX A: CALCULATIONS OF THE SELF-ENERGY

The decay rate of quasiparticles is defined to be $\Gamma = \text{Im}(\Sigma(\mathbf{k},\omega))$. In order to facilitate the calculations, it is assumed that $\Sigma(\mathbf{k},\omega) = \Sigma(\mathbf{k},\omega)|_{|\mathbf{k}|=k_F}$. From Eq. (A3) and with the above approximations, the decay rate of electron pairs is

$$\Gamma(\omega) = \frac{1}{\hbar^2}\int \frac{L|V_1(\mathbf{q})|^2 d\mathbf{q}}{2n_0}\delta\left(\omega - \frac{(\xi_{\mathbf{q}} - E_{\mathbf{q}})}{\hbar}\right) \times \left(\frac{1}{e^{\beta\xi_{\mathbf{q}}}-1} + \frac{1}{e^{\beta E_{\mathbf{q}}}+1}\right). \tag{A1}$$

When q is very small and $\hbar v_F^* q \ll \Delta$, the equation $\omega - (\xi_{\mathbf{q}} - E_{\mathbf{q}}) = 0$ becomes $\omega - (\xi_0 + v|q| - \mu_b) + \Delta \approx 0$ where $\hbar$ is assumed to be unity. This leads to the solution that $\omega \approx v|q|$. The frequency of the electrons ω is in the order of $\sim \Delta$. This self-consistently proves that q is very small and $v_F^* q \ll \Delta$. With the results, we obtain

$$\Gamma(\omega) \approx \frac{L\left|V_1\left(\frac{\omega}{v}\right)\right|^2}{vn_0}\left(\frac{1}{e^{\beta(\Delta+\omega)}-1} + \frac{1}{e^{\beta\Delta}+1}\right). \tag{A2}$$

The inequation $v_F^* q \ll \Delta$ indicates that the temperature is below 800 mK, and this indicates the theory will fail above 800 mK. The Ginzburg number of the 2D electron system $Gi \sim 0.02$, which suggests that the mean field approach will fail in the temperature regime above 800 mK. Our theory does not violate the Ginzburg criterion. Since the bosonic speed v can be absorbed into the electron-boson matrix element V_c in the calculations of decay rates of electrons [see Eq. (A2)], the value of v is not important. We will be using V_c as the only parameter to reduce the number of parameters present in the paper. The estimated values of ξ_0 and μ_b are from the conservation of energy $\hbar\omega = \xi_q - E_q$ during the formation and decay of electron pairs. If $\xi_0 - \mu_b$ is larger than Δ, the δ function in Eq. (A1) will be zero, which results in that the density of states in the regime $0 < \hbar\omega < \xi_0 - \mu_b - \Delta$ is zero. This contradicts with the density of states measured in scanning tunneling spectroscopy experiments [23]. For convenience, the value of $\xi_0 - \mu_b$ is set to the Δ, while the evaluation has no influence on the conclusions. Moreover, with the particle-hole parity symmetry and Kramers-Krönig relation, the real part of the self-energy is

$$\Sigma'(\omega) = \text{Re}(\Sigma(k = k_F,\omega)) = \frac{2\omega}{\pi}P\int_0^\infty \frac{\Gamma(\omega')}{\omega'^2 - \omega^2}d\omega' \tag{A3}$$

Numerical calculations show that the real part of the self-energy has a negligible effect in generating the predicted density of states.

APPENDIX B: CALCULATIONS OF THE DENSITY OF STATES

The denominator of the spectral weight function is $(w - \sqrt{\Delta^2 + (\hbar v_F^*(k - k_F))^2} - \Sigma')^2 + \Gamma^2$. If the denominator equals to zero, there are four solutions of the momentum k that two solutions are in upper half-plane of the complex plane of k and two solutions are in the lower half. Furthermore, there are four different cases. If we set $a = (\omega - \Sigma')^2 - \Gamma^2 - \Delta^2$, $b = 2\Gamma(\omega - \Sigma')$

$a > 0, b > 0$...................I

$a > 0, b < 0$...................II

$a < 0, b > 0$...................III

$a < 0, b < 0$...................IV.

For case I, four solutions of the momentum k in the upper half-plane are

$$k_1 = k_F - \frac{1}{v_F^*}\sqrt{R}e^{\frac{-\theta i}{2}} \tag{B1}$$

$$k_2 = k_F + \frac{1}{v_F^*}\sqrt{R}e^{\frac{\theta i}{2}} \tag{B2}$$

where $\theta = \arctan\frac{b}{a}$, $R = \sqrt{a^2 + b^2}$. For case II,

$$k_1 = k_F + \frac{1}{v_F^*}\sqrt{R}e^{\frac{-\theta i}{2}} \tag{B3}$$

$$k_2 = k_F - \frac{1}{v_F^*}\sqrt{R}e^{\frac{\theta i}{2}}. \tag{B4}$$

For case III,

$$k_1 = k_F - \frac{1}{v_F^*}\sqrt{R}e^{\frac{-(\theta+\pi)i}{2}} \tag{B5}$$

$$k_2 = k_F + \frac{1}{v_F^*}\sqrt{R}e^{\frac{(\theta+\pi)i}{2}}. \tag{B6}$$

For case IV,

$$k_1 = k_F - \frac{1}{v_F^*}\sqrt{R}e^{\frac{(\theta-\pi)i}{2}} \tag{B7}$$

$$k_2 = k_F + \frac{1}{v_F^*}\sqrt{R}e^{\frac{(-\theta+\pi)i}{2}}. \tag{B8}$$

After applying Jordan's lemma and the residue theorem, we obtain the density of states, for case I,

$$D(\omega) = \frac{2L}{v_F^*}\left[\frac{\omega - \Sigma'}{\sqrt{R}}\cos\left(\frac{\theta}{2}\right) + \frac{\Gamma}{\sqrt{R}}\sin\left(\frac{\theta}{2}\right)\right]. \tag{B9}$$

For case II,

$$D(\omega) = -\frac{2L}{v_F^*}\left[\frac{\omega - \Sigma'}{\sqrt{R}}\cos\left(\frac{\theta}{2}\right) + \frac{\Gamma}{\sqrt{R}}\sin\left(\frac{\theta}{2}\right)\right]. \tag{B10}$$

For case III,

$$D(\omega) = \frac{2L}{v_F^*}\left[\frac{\omega - \Sigma'}{\sqrt{R}}\cos\left(\frac{\theta + \pi}{2}\right) + \frac{\Gamma}{\sqrt{R}}\sin\left(\frac{\theta + \pi}{2}\right)\right]. \tag{B11}$$

For case IV,

$$D(\omega) = -\frac{2L}{v_F^*}\left[\frac{\omega - \Sigma'}{\sqrt{R}}\cos\left(\frac{\theta - \pi}{2}\right) + \frac{\Gamma}{\sqrt{R}}\sin\left(\frac{\theta - \pi}{2}\right)\right]. \tag{B12}$$

APPENDIX C: TEMPERATURE DEPENDENCE OF THE BOSON-FERMION MODEL

The empirical temperature dependence of the pairing gap at the STO/LAO interface was extracted by Richter [23,32]:

$$\Delta(T) = \delta\frac{k_B T^*}{e}\tanh\frac{\pi}{\delta}\sqrt{c\left(\frac{T^*}{T} - 1\right)} \tag{C1}$$

with $\delta = 1.61$, $T^* = 1$ K, $c = 0.61$ as the best fit parameters. Richter attributes the phase transition around the temperature T_c where the sheet resistance becomes zero to the Kosterlitz Thouless transition [23,32]. Furthermore, Levy *et al.* demonstrated that electron pairs exist between T_c and T^* [10]. It is noteworthy that the gap closes at approximately 900 mK as in Levy's experiments [10], and 300 mK in Richter's experiments [23,32]. The value of T^* may vary from sample to sample, but we argue the gap closes as in Eq. (C1) as long as the value 300 mK of T^* is replaced with 900 mK. The relation between the gap and temperature is plotted as Fig. 5.

With these relations, we can proceed to calculate the density of states and the even-odd free energy difference. First, the density of states is generated and plotted in Fig. 6 with the same parameters in the above section.

The experimental fact that $N_{\text{eff}} \sim \mathcal{O}(1)$ can be reproduced by calculating the slope of the function $\delta\mathcal{F}_{e/o}$, which is shown in Fig. 7.

More importantly, the parameters are set in the specific regime mentioned from the above sections. This leads to a reasonable explanation of the experimental data. Outside of the chosen parameter regime, the calculated value of the even-odd free energy difference will be problematic. This, on the other hand, is another evidence that the model is not forced to fit the experimental data.

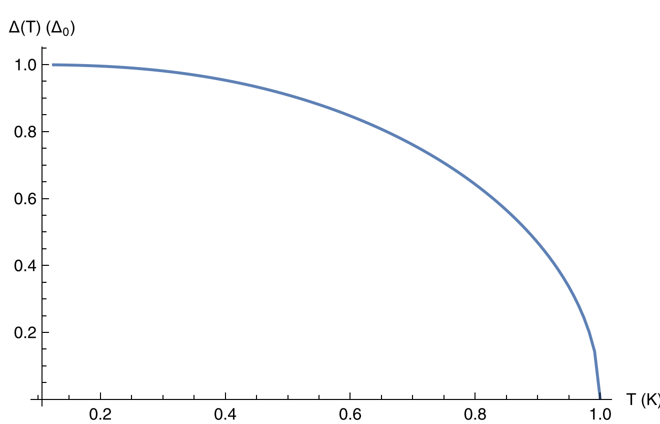

FIG. 5. Relation between the pairing gap Δ and the temperature T.

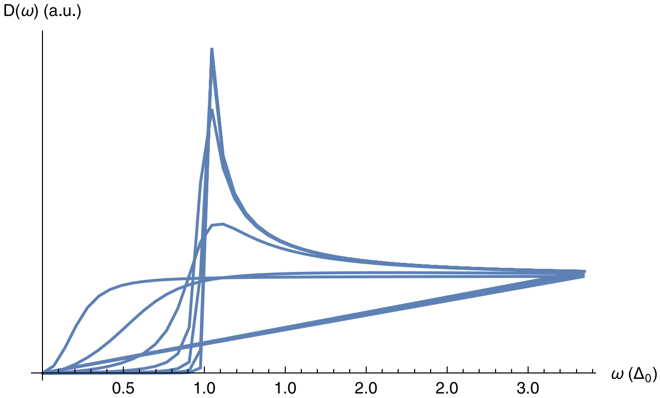

FIG. 6. Relation between the density of states and the electron energy when Δ is set to be different values. The case with von Hove singularity corresponds to the situation in low temperatures.

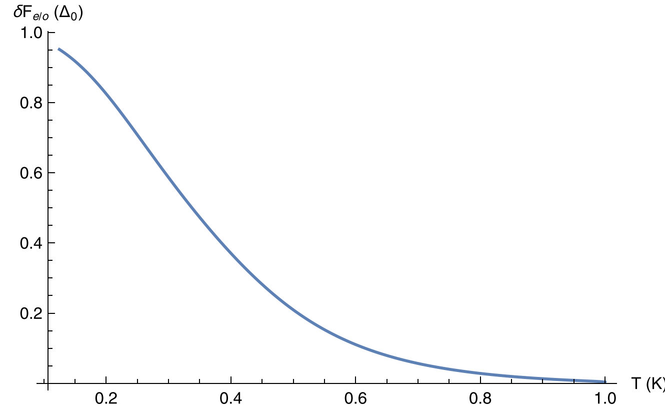

FIG. 7. The relation between the free energy difference $\delta\mathcal{F}_{e/o}$ and temperature T.

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