Quantum charge fluctuations in a superconducting grain

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We consider charge quantization in a small superconducting grain that is contacted by a normal-metal electrode and is controlled by a capacitively coupled gate. At zero temperature and zero conductance G between the grain and the electrode, the charge Q as a function of the gate voltage V_g changes in steps. The step height is e if $\Delta < E_c$, where Δ and E_c are, respectively, the superconducting gap and the charging energy of the grain. Quantum charge fluctuations at finite conductance remove the discontinuity in the dependence of Q on V_g and lead to a finite step width $\propto G^2\Delta$. The resulting shape of the Coulomb blockade staircase is of a novel type. The grain charge is a continuous function of V_g while the differential capacitance, dQ/dV_g, has discontinuities at certain values of the gate voltage. We determine analytically the shape of the Coulomb blockade staircase also at nonzero temperatures.

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I. INTRODUCTION

In the conditions of Coulomb blockade, the charge of a grain is well defined and discrete. It can be varied by means of the external parameter, gate voltage V_g. Periodically in V_g, the ground state of the system approaches a point of degeneracy, in which two consecutive allowed values of charge yield the same energy of the ground state. In the limit of no tunneling between the grain and particle reservoirs (leads), the degeneracy between the ground states is indeed reached at the corresponding special values of V_g. However, electron tunneling between the grain and leads may remove the degeneracy. The nature of the resulting many-body ground state is sensitive to the spectrum of excitations in the grain and in the leads. Except for the case of ultrasmall grains,[1] the level spacing between the single-particle excitations δ in metallic grains is usually negligible. Under this condition, there are the following three known types of evolution of the ground state with the variation of the external parameter V_g.

If the grain and leads are normal metals (N-I-N junction), the system at the charge degeneracy point can be mapped on the multichannel Kondo problem.[2] In this mapping, two subsequent values of charge and the gate voltage play the role of the pseudospin and magnetic field, respectively. (Normal grain charging was experimentally studied in Ref. 3.) Similar mapping is also possible[4] for a system consisting of a normal lead and a superconducting grain (S-I-N junction) in the case of relatively small charging energy $E_c < \Delta$ (Δ is the superconducting gap in the spectrum of excitations); tunneling then lifts the degeneracy between two states with charges differing by $2e$. The corresponding $2e$ steps in the grain charge were observed experimentally,[5,6] but there was no detailed study of the charge dependence on V_g near the degeneracy point.

In the opposite case of a fully superconducting system (S-I-S junction) with $E_c < \Delta$, the degeneracy removal is equivalent to the formation of an avoided crossing in a two-level system. Charge degeneracy for such junctions was studied experimentally.[7]

The third and the last of the studied classes of junctions is represented by a system consisting of a normal grain and a superconducting lead (N-I-S junction), in which case the degeneracy is not removed by tunneling. Indeed, the ground state is degenerate with respect to changing the number of electrons in the grain by one, whereas the particle reservoir may supply only pairs of electrons.[8]

We demonstrate here the existence of a different class of behavior of the ground state. It occurs in an S-I-N junction having a normal lead made of a metal and characterized by charging energy $E_c > \Delta$. An adequate model for such a junction has a large number of channels. We show that in the limit of an infinite number of channels, the dependence of charge Q on V_g has no discontinuities, but the corresponding differential capacitance, $C_{\mathrm{diff}} = dQ/dV_g$, remains singular, exhibiting a jump at some value of V_g. We find the full dependence $Q(V_g)$ at a finite (but small, $G \ll 4\pi e^2/\hbar$) conductance. The smearing of the steps in $Q(V_g)$ due to quantum fluctuations may be observed in experiments of the type performed in Refs. 5 and 6 at higher values of the junction conductance or by using the sensitive charge measuring techniques of Ref. 3. We also find the evolution of the $Q(V_g)$ dependence with temperature and find conditions at which thermal fluctuations do not mask the quantum effects.

It may seem that within the framework of the constant interaction model employed here and in the limit of small mean level spacing in the grain the shape of the Coulomb blockade staircase in the S-I-N case should not differ from that for the N-I-S system studied in Ref. 8. Indeed, the charging energy of the system, see Eq. (2) below, can be re-expressed in a similar form in terms of the number of electrons in the lead. Upon this procedure, the Hamiltonian of the S-I-N system is formally identical to that of an N-I-S system. The physical difference between these cases is that, despite the small mean level spacing in the grain, for the S-I-N system, it is possible in the experiments to reach the low-temperature regime, $T < T^* = \Delta/\ln(\sqrt{8\pi}\Delta/\delta)$, at which no thermal quasiparticles are present in the superconductor.[9]

For the N-I-S system with a macroscopic superconducting lead, such a regime is beyond experimental reach because the mean level spacing in the lead δ_l is many orders of magnitude smaller than that in the grain.

The paper is organized as follows. We present a simplified derivation of our main results in Sec. II. In Sec. III, we present a rigorous analysis of the problem, justify our main approximations, and evaluate corrections to them. In Sec. IV, we present a derivation of our finite-temperature results. In Sec. V, we summarize and discuss our main results.

II. QUALITATIVE CONSIDERATIONS AND MAIN RESULTS

In the absence of tunneling between a superconducting grain and a normal lead, the system is described by a Hamiltonian

$$H = H_c + H_s + H_l, \tag{1}$$

where H_c, H_s, and H_l describe, respectively, the charging energy of the grain, including the dependence on the gate voltage, the BCS state in the grain, and the lead,

$$H_c = E_c(\hat{N} - \mathcal{N})^2, \quad H_s = \sum_{k\sigma} \epsilon_k \gamma_{k\sigma}^\dagger \gamma_{k\sigma},$$

$$H_l = \sum_{p\sigma} \xi_p c_{p\sigma}^\dagger c_{p\sigma}. \tag{2}$$

Here $c_{p\sigma}^\dagger$ and $c_{p\sigma}$ are the creation and annihilation operators for electrons in the lead, $\gamma_{k\sigma}^\dagger$ and $\gamma_{k\sigma}$ are the corresponding operators for the Bogolubov quasiparticles in the superconducting grain; indices p and k denote orbital states in the lead and grain, respectively, and the spin indices take values $\sigma = \pm$. We assume that the electron spectrum ξ_p has a constant density of states near the Fermi level (which is a reasonable assumption for a metallic lead), while the Bogolubov quasiparticles have a gap Δ in their spectrum, $\epsilon_k = \sqrt{\zeta_k^2 + \Delta^2}$, where ζ_k is the electron spectrum (with the constant density of states, too) in the absence of superconductivity. The electron-number operator in the grain is denoted by $\hat{N}$. The electrostatic energy of the grain is of the order of $E_c = e^2/(2C)$ and depends on the gate voltage V_g via the term $\mathcal{N} = C_g V_g / e$ in Hamiltonian H_c, where C and C_g are the total and gate capacitances, respectively.

A. Position of the step

In the limit of vanishingly small single-particle mean level spacing in the grain, $\delta \to 0$, the ground-state energy of the system is periodic in gate voltage $\mathcal{N}$ with period 2. It is also a symmetric function of $\mathcal{N} - 2l$ with l being an integer. Therefore, when describing the shape of the Coulomb blockade steps, it suffices to study the steps between the charge plateaus with $2l$ and $2l+1$ electrons in the grain. The shape and position of the $2l-1 \to 2l$ steps is then readily obtained using the aforementioned symmetry properties.

Without tunneling, the charge of the grain $\hat{Q} = e\hat{N}$ commutes with the Hamiltonian (1) and thus is a conserved quantity. Minimizing the system energy with respect to the discrete number of electrons N, we find the positions of the steps in charge. The transition between the "even" and "odd" plateaus with $2l$ and $2l+1$ electrons in the grain, respectively, occurs at

$$\mathcal{N}_0 = 2l + \frac{E_c + \Delta}{2E_c}. \tag{3}$$

In the case of a normal grain ($\Delta = 0$), the steps are located at equally spaced half-integer values of $\mathcal{N}$. At a finite $\Delta < E_c$, the odd plateaus of the Coulomb staircase become narrower, the positions of the steps being shifted[10] by $\pm\Delta/(2E_c)$.

Tunneling between the lead and the grain results in a correction to the ground state of the system. The excitation spectra of the superconducting grain and normal lead differ from each other, leading to the difference in this "vacuum correction" between the even and odd states of the system. To evaluate the correction, we introduce the tunneling Hamiltonian H_t,

$$H_t = \sum_{kp\sigma} t_{kp} a_{k\sigma}^\dagger c_{p\sigma} + \text{H.c.} \tag{4}$$

The electron annihilation operators in the grain are related to the Bogolubov quasiparticle operators by $\gamma_{k\sigma} = u_k a_{k\sigma} - \sigma v_k a_{-k-\sigma}^\dagger$, where $-k$ labels the time-reversed state of k, and $u_k, v_k = (1/\sqrt{2})(1 \pm \zeta_k/\epsilon_k)^{1/2}$. The tunnel matrix elements t_{kp} are related to the conductance of the junction,

$$G = \frac{e^2}{2\pi\hbar} g, \quad g = 8\pi^2 \sum_{kp} |t_{kp}|^2 \delta(\zeta_k)\delta(\xi_p). \tag{5}$$

We are interested in the corrections to the ground-state energy introduced by H_t near a degeneracy point. Such vacuum corrections appear in the second order of the perturbation in H_t and result from the formation of virtual electron-hole pairs across the junction. Due to the charging energy, lower-energy excitations have $2l$ and $2l+1$ electrons on the grain near the degeneracy point defined by Eq. (3). Excitations with a different number of electrons on the grain cost extra energy $2E_c$. Therefore, in the even state, the prevailing type of excited electron-hole pairs has a hole in the normal lead (Fig. 1, left panel); while in the odd state, holes are predominantly created in the grain (right panel). In the latter state, the creation of a pair involves taking out an electron from the condensate, which costs extra energy 2Δ.

The resulting vacuum corrections, ΔE_e and ΔE_o, at the even and odd sides of the step, respectively, are different from each other. This can be easily seen in the second-order perturbation theory in H_t,

$$\Delta E_o - \Delta E_e = \sum_{kp\sigma} |t_{kp}|^2 \left\{ \frac{u_k^2 \theta(-\xi_p)}{E_{kp}^-} + \frac{v_k^2 \theta(\xi_p)}{E_{kp}^+ + 2E_c} - \frac{u_k^2 \theta(-\xi_p)}{E_{kp}^- + 2E_c} - \frac{v_k^2 \theta(\xi_p)}{E_{kp}^+} \right\}, \tag{6}$$

where $E_{kp}^\pm = \epsilon_k \pm \xi_p \pm \Delta$. Here, the first and last terms account for the virtual excitations with $2l+1$ and $2l$ electrons on the grain, respectively, corresponding to the low-energy pro-

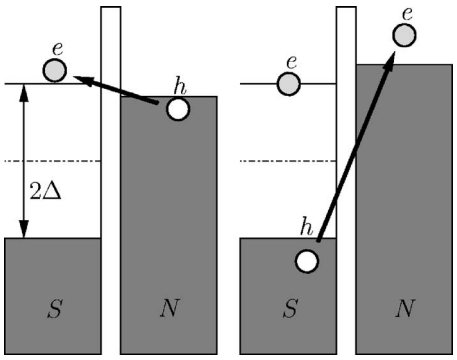

FIG. 1. Picture of the virtual electron-hole pairs contributing to the vacuum correction of the ground-state energy in a superconducting grain near the charge degeneracy point. On the even side of the charge degeneracy points (left panel), without coupling, all electrons in the grain are accommodated in the condensate. In the presence of the coupling, the virtual states consist of a hole created in the lead and an electron in the grain. On the odd side (right panel), one quasiparticle is inevitably present above the gap and the prevailing virtual states consist in creating a hole in the grain and an electron in the lead, with energy cost of at least 2Δ. In comparison, the virtual states which result from annihilation of a quasiparticle already present in the grain and creating an electron in the lead do not have such energy cost. However, by construction the number of such virtual states is much smaller than the number of states with the energy gap 2Δ. Therefore, the former do not contribute significantly to the vacuum correction.

cesses illustrated in Fig. 1. The second and third terms account for the excitations with $2l-1$ and $2l+2$ electrons on the grain, respectively. With these four processes, the sum (6) is converging at large energies. In order to evaluate Eq. (6), we introduce the energy-dependent conductance

$$g(\zeta,\xi) = 8\pi^2 \sum_{kp} |t_{kp}|^2 \delta(\zeta-\zeta_k)\delta(\xi-\xi_p). \tag{7}$$

In practice, $g(\zeta,\xi)\approx g$ for ζ and ξ is much smaller than the Fermi energy. We will show this on a specific model later [see Eq. (44)]. By inserting the identity $\int d\xi d\zeta \delta(\zeta-\zeta_k)\delta(\xi-\xi_p)=1$ into Eq. (6) and making use of Eq. (7), we obtain

$$\Delta E_o - \Delta E_e = \frac{g}{4\pi^2}\int_0^\infty d\xi \int_\Delta^\infty d\epsilon \frac{\epsilon}{\sqrt{\epsilon^2-\Delta^2}} \times\left(\frac{1}{E_-}+\frac{1}{E_+ + 2E_c}-\frac{1}{E_+}-\frac{1}{E_- + 2E_c}\right), \tag{8}$$

where $E_\pm = \epsilon+\xi\pm\Delta$. The corrected step position $\mathcal{N}^*$ to the first order in g is defined by the following equation:

$$2E_c(\mathcal{N}^*-\mathcal{N}_0) = \Delta E_o - \Delta E_e. \tag{9}$$

In the limit $\Delta \ll E_c$, the result of evaluation of Eq. (8) yields

$$\mathcal{N}^* = \mathcal{N}_0 + \frac{g}{4\pi^2}\frac{\Delta}{E_c}\left[1+\ln\frac{4E_c}{\Delta}\right] > \mathcal{N}_0. \tag{10}$$

At $(E_c-\Delta)\ll E_c$, the factor $[1+\ln(4E_c/\Delta)]$ in Eq. (10) should be replaced by $\sqrt{2}\ln[1/(3-2\sqrt{2})]\simeq 2.49$. Equation (10) should be viewed as the first two terms of the perturbative expansion for the $\mathcal{N}^*(g)$ function.

When the conductance of the contact increases, the odd plateaus become shorter, as is shown by Eq. (10). At the same time, the plateaus acquire a finite slope which can also be calculated in the second-order perturbation theory in H_t and is of the order of g/π^2 at integer values of $\mathcal{N}$. The slope must be small for the plateaus to be well defined. When $E_c-\Delta \ll E_c$, odd plateaus are completely suppressed at g exceeding $7.9(1-\Delta/E_c)$. Depending on the ratio Δ/E_c, this condition can be realized while the even plateaus still remain flat.

In the following, we neglect the *small* correction to the average grain charge Q related to the finite slope of the plateaus and determine the *large* (of the order of 1) variation of Q, which gives the shape of the step separating the even and odd plateaus in the Q vs V_g dependence.

B. Shape of the step at zero temperature

The shape of the step is described by the dependence of the average grain charge, $Q=e\langle\hat{N}\rangle$, on the gate voltage. At zero temperature, it can be found[10] by differentiating the ground-state energy of the system,

$$\langle\hat{N}\rangle_0 = \mathcal{N} - \frac{1}{2E_c}\frac{\partial E_g}{\partial \mathcal{N}}. \tag{11}$$

The shift of the step position evaluated above comes from the grain charge fluctuations with a typical energy of the order of Δ. On the other hand, the shape of the step is determined by the low-energy excitations. The band width for these excitations is controlled by the closeness to the (shifted) charge degeneracy point. This separation of energy scales allows us to derive an effective low-energy Hamiltonian H_0 in which the renormalization of the step position is already accounted for. The new Hamiltonian H_0 acts in a narrow energy band of width $D\ll\Delta$ and is designed to describe the low-energy physics of the system near the charge degeneracy point,

$$2E_c|\mathcal{N}-\mathcal{N}^*| \lesssim D. \tag{12}$$

The bandwidth is defined with the energy reference in Hamiltonian H_0 set as the energy of the odd state obtained from Hamiltonian $H+H_t$ in second-order perturbation theory. That is, energy $E_c(2l+1-\mathcal{N})^2+\Delta+\Delta E_o$ is subtracted from the initial Hamiltonian. All the states whose number of electrons on the grain differs from $2l$ or $2l+1$ have energy higher than $2E_c$. Thus, they are excluded from the low-energy subspace. Moreover, as a consequence of $D\ll\Delta$, the even states cannot accommodate any excitation in the grain (it would cost at least the energy 2Δ), while the odd states accommodate exactly *one* excitation. Starting from Eqs. (1) and (4) and using the Schrieffer-Wolff transformation, we are able to derive the low-energy Hamiltonian, see Sec. III. Here we present only the relevant terms for the discussion of that Hamiltonian

$$H_0 = \epsilon_0|0\rangle\langle 0| + \sum_{k\sigma} \frac{\xi_k^2}{2\Delta}|k\sigma\rangle\langle k\sigma| + \sum_{p\sigma} \xi_p c_{p\sigma}^\dagger c_{p\sigma} + \sum_{kp\sigma} [\tilde{t}_{kp}|k\sigma\rangle\langle 0|c_{p\sigma} + \tilde{t}_{kp}^* c_{p\sigma}^\dagger|0\rangle\langle k\sigma|]. \quad (13)$$

Here ϵ_0 is the energy of the grain in the even state $|0\rangle$; it accounts for the renormalization of the step position by virtual electron-hole pairs with energy exceeding D. Up to small terms of the order of $g\sqrt{\Delta D}$, this energy is $\epsilon_0 = 2E_c(\mathcal{N}-\mathcal{N}^*)$, cf. Eq. (10). The energies of allowed states for the Hamiltonian Eq. (13) are within the band of width $\sim 2D$. States $|k\sigma\rangle$ have an excitation in state $(k\sigma)$ of the grain with energy $\epsilon_k - \Delta \approx \xi_k^2/(2\Delta)$. The tunnel matrix elements $\tilde{t}_{kp} = u_k t_{kp} \approx (1/\sqrt{2})t_{kp}$ account for the coherence factors values at small energies. Note, that the Hamiltonian (13) allows only for zero or one additional electron in the grain.

With the change of energy reference, Eq. (11) defining the average grain charge must be replaced by

$$\langle \hat{N} \rangle_0 = 2l + 1 - \frac{1}{2E_c}\frac{\partial E_0}{\partial \mathcal{N}}, \quad (14)$$

where E_0 is the ground-state energy of the Hamiltonian (13).

In the zeroth order in $\tilde{t}_{kp}$, the wave function of an even state is a direct product of $|0\rangle$ for the grain and some state $|f\rangle$ of the Fermi sea in the lead; the ground state is $|0\rangle \otimes |f_0\rangle$. Tunneling terms in Eq. (13) modify the eigenfunctions. In the lowest order of perturbation theory, the wave function acquires the form

$$|\Psi\rangle = \left(A|0\rangle + \sum_{kq\sigma} \beta_{kq\sigma} c_{p\sigma}|k\sigma\rangle\right) \otimes |f\rangle. \quad (15)$$

The second term in parentheses in Eq. (15) describes the amplitude of a quasiparticle-hole pair state created due to the tunneling; this amplitude is small within the perturbation theory. In higher orders of the perturbation theory, additional electron-hole pairs may be created in the normal lead. However, as we show in Sec. II C, these additional terms are small if the number N_{ch} of quantum channels in the junction is large. In the simplest case, the number of channels is of the order of the junction area measured in units of the Fermi wavelength in the metallic electrodes (see Sec. III for details), and the condition $N_{\mathrm{ch}} \gg 1$ is not restrictive. If it is satisfied, the wave function Eq. (15) is valid beyond the perturbation theory. Having this in mind, for now we may use it as a trial function for an eigenstate originating from the state $|f\rangle$ in the absence of tunneling. Then the ground-state energy E_0 is the lowest value of E which solves the equation

$$E = \epsilon_0 + \sum_{kp\sigma} \frac{|\tilde{t}_{kp}|^2 \theta(-\xi_p)}{E - \xi_k^2/(2\Delta) + \xi_p}. \quad (16)$$

To determine E_0, we first consider the case $\mathcal{N} > \mathcal{N}^*$. Then, Eq. (16) is solved with $E_0 \lesssim 0$ on the scale of the mean level spacing, so that the first negative term with vanishing denominator in the sum compensates $\epsilon_0 > 0$. Now, at $\mathcal{N} < \mathcal{N}^*$, we look for a solution $E_0 < 0$. By introducing the identity $\int d\xi d\zeta \delta(\zeta - \zeta_k)\delta(\xi - \xi_p) = 1$ into Eq. (16) and making use of $g(\zeta, \xi) \approx g$, see Eq. (7), we transform this equation into

$$E = \epsilon_0 - \frac{g}{8\pi^2}\int d\zeta d\xi \frac{\theta(\xi)}{\frac{\zeta^2}{2\Delta} + \xi - E}. \quad (17)$$

The integral in Eq. (17) is well defined at $E < 0$, it is converging at small energies ξ and ζ, and the contribution of large energies restricted by the bandwidth D is of the same order $g\sqrt{\Delta D}$ as the terms neglected in ϵ_0 (in Sec. III, we'll show that such terms compensate exactly). Therefore, Eq. (17) yields the equation $E_0 = \epsilon_0 - (g/4\pi)\sqrt{-2\Delta E_0}$, which can easily be solved after restriction $E_0 < 0$. The resulting lowest-energy solution of Eq. (16) is

$$E_0(\mathcal{N}) = -2E_c\delta\mathcal{N}\left(\sqrt{1 + \frac{\mathcal{N}^* - \mathcal{N}}{\delta\mathcal{N}}} - 1\right)^2 \theta(\mathcal{N}^* - \mathcal{N}),$$

$$\delta\mathcal{N} = \left(\frac{g}{8\pi}\right)^2 \frac{\Delta}{E_c}. \quad (18)$$

It is separated at $\mathcal{N} < \mathcal{N}^*$ from the continuum of states $E > 0$ allowed by Eq. (16) and can be associated with a bound state. This state is formed by the quasiparticle (virtually) populating the grain and the corresponding hole in the lead. Upon approaching the threshold value $\mathcal{N} = \mathcal{N}^*$, the binding energy of this state vanishes, $E_0(\mathcal{N}) \propto (\mathcal{N} - \mathcal{N}^*)^2$. At $\mathcal{N} \geqslant \mathcal{N}^*$, the hole is not localized near the junction any more; the formerly discrete energy level merges with the edge of the continuum spectrum. The described qualitative change of the spectrum at the even-odd transition is identical to the one in a well-known problem of *single-particle* quantum mechanics. Indeed, the same transformation occurs with the spectrum of a particle attracted to a three-dimensional well upon the gradual reduction of the well depth; the particle becomes delocalized at a certain strength of the potential,[12] and the discrete energy level ceases to exist.

The number of electrons in the grain at zero temperature is obtained from Eqs. (14) and (18)

$$\langle \hat{N} \rangle_0 = 2l + 1 - \theta(\mathcal{N}^* - \mathcal{N}) f\left(\frac{\mathcal{N}^* - \mathcal{N}}{\delta\mathcal{N}}\right),$$

$$f(x) = 1 - \frac{1}{\sqrt{1+x}}. \quad (19)$$

Eq. (19) describes the transition between the even plateau with $2l$ electrons in the grain and the odd plateau with $2l+1$ electrons. The dependence of $\langle \hat{N} \rangle_0$ on $\mathcal{N}$ is shown in Fig. 2.

At the degeneracy point $(\mathcal{N} = \mathcal{N}^*)$, the charge is a continuous function of $\mathcal{N}$, but there is a jump in the differential capacitance, $C_{\mathrm{diff}} = C_g d\langle \hat{N} \rangle_0 / d\mathcal{N}$. We can define the step position by equation $\langle \hat{N} \rangle_0 = 2l + \frac{1}{2}$ and characterize the step width by the value of $W_0 = (d\langle \hat{N} \rangle_0 / d\mathcal{N})^{-1}$ at the step position. The smearing of the steps of the Coulomb staircase occurs in the second-order in g, with a typical width $W_0 = 16\delta\mathcal{N}$.

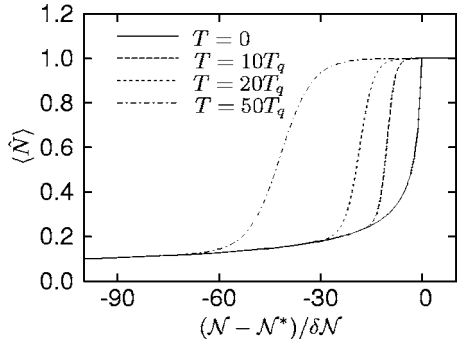

FIG. 2. Coulomb staircase at different temperatures $T=0$ (thick line) and $T=10,\ 20,\ 50T_q$. $\langle \hat{N} \rangle$ is the average number of electrons in the grain, V_g is the gate voltage. The plots correspond to the following values of parameters: $g=2$, $\Delta/E_c=0.7$, $\sqrt{8\pi}\Delta/\delta=10^4$. With these parameters, $T^* \approx 0.1\Delta$, $T_q \approx 0.001\Delta$, and $\mathcal{N}^* \approx 2l+0.8$. The correction due to the finite slope of the steps at integer values of $C_g V_g/e$ is not accounted for in the plots.

C. Shape of the step at finite temperature

We turn now to the effect of a finite temperature T on the average grain charge $\langle \hat{N} \rangle$. Equation (14) can still be used, except that E_0 should be replaced with the free energy $F=-T \ln Z$, where

$$Z = \mathrm{Tr} \exp(-\beta H_0) \tag{20}$$

is the partition function of the system[10] described by the Hamiltonian (13).

To compute Z, we must determine the energies of the excited states. For that we once again will be using Eq. (15) as a trial wave function. The corresponding eigenenergy can be represented in the form $E=\mathcal{E}_f+\mathcal{E}$. Here $\mathcal{E}_f$ is the energy of the "bare" state $|f\rangle$. In the limit of a thermodynamically large lead, $\mathcal{E}$ is a solution of the already used Eq. (16), where the step function $\theta(\xi)$ should be replaced by the Fermi distribution function. Similarly to the zero temperature case, there are two classes of solutions at $\mathcal{N}<\mathcal{N}^*$. In the first class there is just one discrete solution whose energy at low temperatures is $\mathcal{E}=E_0$ [see discussion in the paragraph below Eq. (22)]. The second class is represented by continuum spectrum $\mathcal{E}=\xi_k^2/(2\Delta)-\xi_p$. The full energy for a state in the second class can be written in the form $E=\bar{\mathcal{E}}_f+\zeta^2/(2\Delta)$, where $\bar{\mathcal{E}}_f$ is the energy of the state that differs from $|f\rangle$ by the presence of one hole in state p. Since the partition function involves summation over all states, the difference between $\bar{\mathcal{E}}_f$ and $\mathcal{E}_f$ drops out and we have,

$$Z = \sum_f e^{-\beta(\mathcal{E}_f+E_0)} + \sum_{f,k\sigma} e^{-\beta[\mathcal{E}_f+\zeta_k^2/(2\Delta)]}. \tag{21}$$

Factorizing the $\mathcal{N}$-independent partition function of the lead, $Z_{\mathrm{lead}}=\Sigma_f e^{-\beta\mathcal{E}_f}$, and integrating the second term over k, we get

$$Z = Z_{\mathrm{lead}}[e^{-\beta E_0} + N_{\mathrm{eff}}(T)], \quad N_{\mathrm{eff}}(T) = \sqrt{\frac{8\pi\Delta T}{\delta^2}}, \tag{22}$$

where δ is the one-electron level spacing in the grain. A rigorous derivation of the finite-temperature partition function is detailed in Sec. IV.

We would like to note that the replacement of $\theta(\xi)$ by the Fermi function in Eq. (16) leads to a small difference between the energy of the discrete state and E_0. This finite-temperature correction is small in T/E_0. For the purpose of evaluating the partition function this correction can be ignored at all temperatures because at $T/E_0 \gtrsim 1/\ln N_{\mathrm{eff}}(T)$ [see Eq. (22)], the partition function is already dominated by the contribution from the states of the continuum, while T/E_0 is still small.

Using Eq. (14), we obtain the average grain charge at finite temperature

$$\langle \hat{N} \rangle = 2l + 1 - \frac{\theta(\mathcal{N}^*-\mathcal{N})}{1+N_{\mathrm{eff}}(T)e^{\beta E_0(\mathcal{N})}} f\left(\frac{\mathcal{N}^*-\mathcal{N}}{\delta\mathcal{N}}\right), \tag{23}$$

where $E_0(\mathcal{N})$ and $f(x)$ are defined in Eqs. (18) and (19), respectively.

The temperature dependence of the Coulomb staircase is shown in Fig. 2. At $T \to 0$ Eq. (23) reproduces the average charge $\langle \hat{N} \rangle_0$ given by Eq. (19). At finite temperature, the odd plateaus become broader. The position of the step, defined by equation $\langle \hat{N} \rangle = 2l + \frac{1}{2}$, results from the competition between the energy of the grain in an even state E_0 and the entropy of the large number of odd states given by $N_{\mathrm{eff}}(T)$ in Eq. (22). The step is shifted from $\mathcal{N}=\mathcal{N}^*$ to $\mathcal{N}=\mathcal{N}^*(T)$,

$$\mathcal{N}^*(T) = \mathcal{N}^* - \frac{T}{2E_c} \ln N_{\mathrm{eff}}(T) \tag{24}$$

when

$$T \gtrsim T_q = \left(\frac{g}{8\pi}\right)^2 \frac{\Delta}{\ln \dfrac{g\Delta}{\delta\sqrt{8\pi}}}, \tag{25}$$

that is when the shift exceeds the zero-temperature width of the step, $W_0=16\delta\mathcal{N}$. Note that the thermal width $W_T=T/E_c$ of the charge step at $T \gtrsim T_q$ is smaller than that at zero temperature, $W_{T_q} \lesssim W_0$. We thus expect a strong nonmonotonic temperature dependence of the step width with the minimum width occurring at $T \sim T_q$. The temperature dependence of the step position and width are shown in Fig. 3.

The junction conductance g does not affect the charge steps at $T \gg T_q$. At even larger temperature, $T \sim T^* = \Delta/\ln(\sqrt{8\pi}\Delta/\delta)$, the odd plateaus were shown to reach the same size as the even ones.[10]

In the rest of the paper, we aim at giving a rigorous derivation of the main results, Eqs. (18), (19), and (23). We'll show that they hold for the experimentally relevant case of a wide multichannel junction between the grain and the lead. In Sec. III, we derive the low-energy effective Hamiltonian (13); we demonstrate there that the corrections in the number

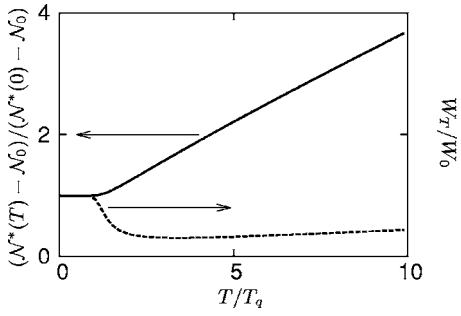

FIG. 3. Temperature dependence of the step position, $\mathcal{N}^*(T)$, and width W_T. The same values of parameters as in Fig. 2 are used.

of channels to the ground-state energy are small. In Sec. IV, we derive the partition function for our system.

III. EFFECTIVE HAMILTONIAN AND THE GRAIN CHARGE AT ZERO TEMPERATURE

In this section, we derive the effective low-energy Hamiltonian (13) which is used to describe the shape of the step of the Coulomb staircase between the even state of the grain with a charge $Q=(2l)e$ and the odd state with a charge $Q=(2l+1)e$. We show that it gives the same physics as the Hamiltonian of the system, $H+H_t$, given by Eqs. (1) and (4), for a wide multichannel contact between the grain and the lead.

The effective Hamiltonian H_0 is acting in a narrow bandwidth D, on a limited set of states which was characterized in Sec. II: only low-energy electrons (or holes) may be excited in the lead, and the states of the grain are only those with zero or one low-energy excitation,

$$|\xi_k|, E_c(\mathcal{N}^* - \mathcal{N}) + \zeta^2/2\Delta \lesssim D.$$

The states outside the bandwidth D are accounted in H_0 perturbatively. For the present problem, it is enough to calculate such a contribution in the second order in H_t. Therefore, the appropriate Schrieffer-Wolff transformation of the initial Hamiltonian is[11]

$$H_0 \approx M(H+H_t)M - MH_t(1-M)\frac{1}{H}H_tM. \tag{26}$$

Here, M is the projector operator on the unperturbed states whose energy lies within the band D. We obtain

$$H_0 = H' + V,$$

$$H' = \epsilon_0 P_e + \sum_{k\sigma} \frac{\zeta_k^2}{2\Delta} P_o \gamma_{k\sigma}^\dagger \gamma_{k\sigma} P_o + \sum_{p\sigma} \xi_p c_{p\sigma}^\dagger c_{p\sigma}$$

$$V = \sum_{kp\sigma} [\tilde{t}_{kp} P_o \gamma_{k\sigma}^\dagger c_{p\sigma} P_e + \tilde{t}_{kp}^* P_e c_{p\sigma}^\dagger \gamma_{k\sigma} P_o] + \sum_{p\neq p'\sigma} \sum_{i=e,o} w_{pp'}^i c_{p\sigma}^\dagger c_{p'\sigma} P_i + \sum_{k\neq k'\sigma} w_{kk'} P_o \gamma_{k\sigma}^\dagger \gamma_{k'\sigma} P_o. \tag{27}$$

Here, P_e and P_o are projection operators on the even and odd states with $2l$ or $2l+1$ electrons in the grain, respectively, $\tilde{t}_{kp}=u_k t_{kp}$, and

$$\epsilon_0 = 2E_c(\mathcal{N}_0 - \mathcal{N}^*) + \sum_{kp\sigma}{}' \frac{|\tilde{t}_{kp}|^2 \theta(-\xi_p)}{\frac{\zeta_k^2}{2\Delta} - \xi_p}. \tag{28}$$

The prime here means that only excited states in the bandwidth D (i.e., such as $|\zeta_k^2/(2\Delta) - \xi_p| < D$) are included. Introducing the identity $\int d\zeta d\xi \delta(\zeta-\zeta_k)\delta(\xi-\xi_p)$ into Eq. (28) and making use of $g(\zeta,\xi)\approx g$, see Eq. (7), we obtain

$$\epsilon_0 = 2E_c(\mathcal{N} - \mathcal{N}^*) + \frac{g}{8\pi^2}\int d\zeta d\xi \frac{\theta(\xi)\theta\left(D - \frac{\zeta^2}{2\Delta} - \xi\right)}{\frac{\zeta^2}{2\Delta} + \xi}. \tag{29}$$

The integral in Eq. (29) is converging. It yields

$$\epsilon_0 = 2E_c\left(\mathcal{N} - \mathcal{N}^* + \frac{g}{2\pi^2}\frac{\sqrt{2\Delta D}}{2E_c}\right). \tag{30}$$

The degeneracy point $\mathcal{N}$ defined by condition $\epsilon_0=0$ would slightly differ from $\mathcal{N}^*$. This difference comes from the virtual states with energies within the band D; such states were accounted for in the evaluation of $\mathcal{N}^*$, but do not contribute to ϵ_0. This difference is small at small ($D \ll \Delta$) bandwidth. Note, that by construction of the Hamiltonian H_0, we need energy ϵ_0 at $\mathcal{N}=\mathcal{N}^*$ to be within the band D. This sets a condition $D \gtrsim (g^2/2\pi^4)\Delta$, which does not contradict our initial assumption $D \ll \Delta$.

Perturbation V in Eq. (27) has terms describing electron-hole pair fluctuations across the junction and terms describing scattering off the junction within the grain or lead. The latter terms correspond to second-order processes in H_t generated by the Schrieffer-Wolf transformation (26). For instance, the term corresponding to scattering off the lead when the grain is in the even state has probability amplitude

$$w_{pp'}^e = -\sum_k{}'' t_{kp'} t_{kp}^* \left(\frac{u_k^2}{\epsilon_k - \Delta} - \frac{v_k^2}{2E_c + \epsilon_k + \Delta}\right). \tag{31}$$

Here, the first and second term in parentheses correspond to virtual excitations with charge $(2l+1)e$ and $(2l-1)e$ in the grain, respectively; the double prime means that only virtual states with excitation energy outside the bandwidth are included in the sum, it reduces to condition $\epsilon_k - \Delta > D$ for the first term (we also used property $t_{kp}^* = t_{-k-p}$ valid for the tunneling Hamiltonian preserving the time-reversal symmetry). The amplitudes $w_{pp'}^o$ and $w_{kk'}$ have expressions similar to Eq. (31). We will put terms proportional to $w_{pp'}^i$ and $w_{kk'}$ in V aside for a while and return to the discussion of their effect at the end of the section.

Let us calculate the ground-state energy of H_0. At $\mathcal{N} < \mathcal{N}^*$, the unperturbed ground state on the even side, $|e\rangle = |0\rangle \otimes |f_0\rangle$, is the direct product of the BCS ground state with $2l$ electrons in the grain, $|0\rangle$, times Fermi sea ground state in the lead, $|f_0\rangle$. Its bare energy is ϵ_0. In the presence of V, we

determine its renormalized energy E_0 with Brillouin-Wigner perturbation theory.[11] It is the solution of the infinite order equation

$$E_0 = \epsilon_0 + \langle e|V|e\rangle + \sum_{n\neq 0} \frac{\langle e|V|n\rangle\langle n|V|e\rangle}{E_0 - \epsilon_n} + \sum_{n_1,\cdots,n_j\neq 0} \frac{\langle e|V|n_1\rangle\langle n_1|V|n_2\rangle\cdots\langle n_j|V|e\rangle}{(E_0-\epsilon_{n_1})\cdots(E_0-\epsilon_{n_j})} + \cdots, \tag{32}$$

where $|n\rangle$ are eigenstates of H', with energy ϵ_n. Anticipating that, for typical S-I-N systems with multichannel contacts, the series in the Eq. (32) can be truncated at the term of the second order in V, we obtain

$$E_0 = \epsilon_0 + \sum_{kp\sigma}{}' \frac{|\tilde{t}_{kp}|^2\theta(-\xi_p)}{E_0 - \frac{\zeta_k^2}{2\Delta} + \xi_p}. \tag{33}$$

Here again, the prime means that only excited states in the bandwidth D are included. This equation is identical to Eq. (16). As a result of the summation in Eq. (33), the bandwidth D disappears from the equation for the ground-state energy and we arrive at Eq. (18).

The above result holds when a higher order in V terms can be neglected in Eq. (33). This is the case for a generic tunnel junction between a lead and metallic grain. Indeed, typically, the area of junction S exceeds significantly the square of the Fermi wavelength in a metal. The effective number of quantum channels in the junction, $N_{\rm ch}\sim Sk_F^2 \gg 1$ provides us with a parameter allowing the truncation of series Eq. (33) in the ballistic regime. In a realistic setup, electrons are backscattered to the junction from the impurities and the boundaries in the grain and in the lead. In a typical situation of a small junction to a macroscopic lead, the backscattering of electrons from the lead to the junction may be neglected. Therefore, we concentrate on the effects of electron returns from the grain to the junction. Due to the finite grain size such returns are bound to occur. Quantum interference between returning electron trajectories in the grain may lead to a reduction of $N_{\rm ch}$.[13] However, we shall see that the corresponding contribution to Eq. (19) remains small in the parameter $1/N_{\rm ch}^{\rm eff} = \delta/g\Delta \ll 1$.

We start with the analysis of higher-order perturbation theory terms which involve matrix elements $\tilde{t}_{kp}$ only. Let us first consider the even side of the transition, at $\mathcal{N}<\mathcal{N}^*$. The first term in Eq. (32) that we neglect is

$$J = \sum_{kk'pp'\sigma}{}' \frac{\theta(-\xi_p)\theta(\xi_{p'})\tilde{t}_{kp}\tilde{t}^*_{kp'}\tilde{t}_{k'p'}\tilde{t}^*_{k'p}}{[E_0-\epsilon_{kp}][E_0-\epsilon_{pp'}][E_0-\epsilon_{k'p}]}, \tag{34}$$

where $\epsilon_{kp}=\zeta_k^2/(2\Delta)-\xi_p$ and $\epsilon_{p'p}=\epsilon_0+\xi_{p'}-\xi_p$, and the prime means that $|\epsilon_{kp}|,|\epsilon_{k'p}|,|\epsilon_{p'p}|<D$. We define the correlation function

$$K(\xi,\xi';\zeta,\zeta') = \sum_{kk'pp'} t_{kp}t^*_{kp'}t_{k'p'}t^*_{k'p}\delta(\xi-\xi_p)\delta(\xi'-\xi_{p'}) \times \delta(\zeta-\zeta_k)\delta(\zeta'-\zeta_{k'}), \tag{35}$$

which simplifies Eq. (34) to

$$J = -\int' d\xi d\xi' d\zeta d\zeta' \frac{\theta(-\xi)\theta(\xi')K(\xi,\xi';\zeta,\zeta')}{[\epsilon_{\zeta\xi}-E_0][\epsilon_{\xi'\xi}-E_0][\epsilon_{\zeta'\xi}-E_0]}, \tag{36}$$

with $\epsilon_{\zeta\xi}=\zeta^2/(2\Delta)-\xi$ and $\epsilon_{\xi'\xi}=\epsilon_0+\xi'-\xi$; the prime means $|\epsilon_{\zeta\xi}|,|\epsilon_{\xi'\xi}|,|\epsilon_{\zeta'\xi}|<D$.

The value of J depends on a concrete model of the junction. We consider here a thin homogeneous insulating layer separating the grain from lead; the appropriate barrier potential is $U(\mathbf{r})=U_0\delta(z)$, where z is the distance from the interface. The transmission coefficient $\mathcal{T}$ for such a barrier depends on the angle of incidence for the incoming electron characterized by the normal component k_z of its momentum $\mathbf{k}$; in the limit of low-barrier transparency $\mathcal{T}(k_z)=(k_z/mU_0)^2 \ll 1$. The dimensionless conductance of the junction is $g=\mathcal{T}Sk_F^2/4\pi$, where k_F is the Fermi wave vector and S is the area of the junction and $\mathcal{T}=\mathcal{T}(k_F)$. We can introduce the number of channels in the junction by expressing the conductance $g=\bar{\mathcal{T}}N_{\rm ch}$ in terms of the angle-averaged transmission coefficient, $\bar{\mathcal{T}}=\mathcal{T}/3$. This definition of $N_{\rm ch}$ yields $N_{\rm ch}=3Sk_F^2/4\pi$. In terms of the matrix elements in the tunneling Hamiltonian, the above model of the barrier corresponds to

$$t_{\mathbf{kp}} = \frac{\sqrt{\mathcal{T}}}{\nu\sqrt{V_l V}} k_z p_z \delta^2(\mathbf{k}_\parallel - \mathbf{p}_\parallel), \tag{37}$$

with $\nu=(mk_F/2\pi^2)$, V, and V_l being the density of states, volume of the grain and volume of the lead, respectively; m is the effective electron mass. For a derivation of Eq. (37), see, for instance, Ref. 14. Equation (37) accounts for the conservation of the component $\mathbf{k}_\parallel$ of the electron momentum parallel to the barrier. Inserting now Eq. (37) into (35), we obtain the correlation function in the ballistic regime

$$K_{\rm b}(\xi,\xi';\zeta,\zeta') = \frac{3g^2}{8\pi^4 N_{\rm ch}}. \tag{38}$$

We can now evaluate Eq. (36). It yields the dominant contribution in $|E_0|$

$$J_{\rm b} = -\frac{g^2}{8\pi^2 N_{\rm ch}}\Delta \ln\frac{D}{-E_0}\ln\frac{D}{\epsilon_0}. \tag{39}$$

In the vicinity of the degeneracy point, at $\mathcal{N}^*-\mathcal{N}\lesssim\delta\mathcal{N}$, the energy E_0 is much smaller than $\epsilon_0\propto g(\Delta D)^{1/2}$, as the bandwidth D satisfies the conditions $(g^2/2\pi^2)\Delta \ll D \ll \Delta$. Therefore, the logarithmic term $\ln(D/\epsilon_0)$ in Eq. (39) is approximately constant and of the order of $\ln(1/g)$. As the result, for a grain in the "ballistic" regime, the contribution (39) yields a correction to the grain charge

$$\delta Q \sim e\frac{\ln(1/g)}{N_{\rm ch}}\frac{\delta\mathcal{N}}{\mathcal{N}^*-\mathcal{N}}. \tag{40}$$

Note, at $\mathcal{N}^*-\mathcal{N}\sim\delta\mathcal{N}$, this correction is parametrically small, provided that $N_{\rm ch}\gg 1$.

The form of Eq. (40) of the correction to the charge and the ballistic-regime estimate Eq. (39) hold as long as the virtual excitation in the grain travels a distance shorter than the grain size L and the electron mean free path ℓ; for definiteness, we assume $L\lesssim\ell$. The length of the path of the excitation depends on its typical energy given by $|E_0|$. Indeed, the velocity of excitation is $v\sim v_F\zeta/\Delta$, and the time of travel is limited by $1/|E_0|$; here v_F is the Fermi velocity. The limitation on the excitation path length sets the condition for the applicability of the ballistic approximation, $\Delta|E_0|\gtrsim v_F^2/L^2$. The condition is violated sufficiently close to the charge degeneracy point,

$$\mathcal{N}^*-\mathcal{N}\sim\frac{gv_F}{E_cL}. \tag{41}$$

Closer to the degeneracy point, the estimate Eq. (40) is replaced by

$$\delta Q\sim e\frac{\ln(1/g)}{N_{\rm ch}^{\rm eff}}\left(\frac{\delta\mathcal{N}}{\mathcal{N}^*-\mathcal{N}}\right)^2,\quad \frac{1}{N_{\rm ch}^{\rm eff}}=\frac{\delta}{g\Delta}. \tag{42}$$

We turn now to the estimate of the fourth-order term (34) in the presence of multiple returns of the virtual excitation to the junction and to the derivation of Eq. (42).

If an excitation bounces off the grain walls many times, it is reasonable to expect chaotization of its motion. We concentrate on the realistic case of wide-area junctions, for which the sample-specific variations of the observables are small compared to the corresponding ensemble-averaged quantities.[15] Below we dispense with the variations and consider the average value of δQ. This prompts one to consider ensemble-averaged observables, rather than their specific values for a given grain. To this end, we need to express J of Eq. (34) in terms of the correlation functions of the electron states in the grain. We start with representing[14] the matrix elements t_{kp} in terms of the true electron eigenstates ϕ_k^* and χ_p,

$$t_{kp}=\frac{\sqrt{\mathcal{T}}}{8\pi^2\nu}\int_S d^2\mathbf{x}\,\partial_z\phi_k^*(\mathbf{r})\,\partial_z\chi_p(\mathbf{r})\big|_{z=0}. \tag{43}$$

Here, $\mathbf{x}$ is the longitudinal with respect to the barrier component of coordinate $\mathbf{r}=(\mathbf{x},z)$. Inserting Eq. (43) into (7) and averaging independently over the states in the grain and in the lead, we can relate the energy-dependent conductance to the impurity-averaged electron Green's functions,

$$g(\zeta,\xi)=\frac{\mathcal{T}}{8\pi^2\nu^2}\int_S d^2\mathbf{x}d^2\mathbf{x}'X_\zeta(\mathbf{x},\mathbf{x}')X_\xi(\mathbf{x}',\mathbf{x}). \tag{44}$$

Here subscripts ζ and ξ refer to the grain and lead, respectively,

$$X_\zeta(\mathbf{x},\mathbf{x}')=\partial_z\partial_{z'}K_\zeta(\mathbf{r},\mathbf{r}')\big|_{z,z'=0}, \tag{45}$$

and $K_\zeta(\mathbf{r},\mathbf{r}')$ is expressed in terms of the averaged ($\langle\ldots\rangle$) retarded (R) and advanced (A) Green's functions,

$$K_\zeta(\mathbf{r},\mathbf{r}')\equiv-\frac{1}{2\pi i}\langle G_\zeta^R(\mathbf{r},\mathbf{r}')-G_\zeta^A(\mathbf{r},\mathbf{r}')\rangle = \left\langle\sum_k\phi_k(\mathbf{r})\phi_k^*(\mathbf{r}')\,\delta(\zeta-\zeta_k)\right\rangle, \tag{46}$$

the function $X_\xi(\mathbf{x},\mathbf{x}')$ is defined in a similar way. In the bulk one finds[16]

$$K_\zeta^\infty(\mathbf{r}-\mathbf{r}')=-\nu\frac{\sin k_FR}{k_FR}e^{-R/2\ell},\quad R=|\mathbf{r}-\mathbf{r}'|, \tag{47}$$

hardly dependent on ζ at excitation energy much smaller than the Fermi energy. As the conductance is determined by tunneling events taking place on the spatial range $1/k_F$ close to the junction, it is enough to take the Green's functions for half-infinite spaces with the appropriate boundary condition that they vanish at the interface. For instance, the Green's function in the grain (in the half space $z>0$) is

$$K_\zeta(\mathbf{r},\mathbf{r}')=K_\zeta^\infty(\mathbf{x}-\mathbf{x}',z-z')-K_\zeta^\infty(\mathbf{x}-\mathbf{x}',z+z'). \tag{48}$$

Inserting Eqs. (47) and (48) into (44), we find that $g(\zeta,\xi)$ weakly depends on ζ and ξ at excitation energies much smaller than the Fermi energy. Therefore, we can set $\zeta\approx\xi\approx 0$ in Eq. (44) and obtain $g(\zeta,\xi)\approx g$. After evaluation of the integral in Eq. (44), we recover the result $g=\bar{\mathcal{T}}N_{\rm ch}$ of the ballistic regime. At the same time, the correlation function (35) is strongly affected by the disorder.[13] Using Eqs. (43) and (35), we find

$$K_{\rm d}(\xi,\xi';\zeta,\zeta')=\frac{\mathcal{T}^2}{(8\pi^2\nu)^2}\int_S d^2\mathbf{x}_1\ldots d^2\mathbf{x}_4X_\xi(\mathbf{x}_1,\mathbf{x}_4) \times X_{\xi'}(\mathbf{x}_3,\mathbf{x}_2)[X_\zeta(\mathbf{x}_2,\mathbf{x}_1)X_{\zeta'}(\mathbf{x}_4,\mathbf{x}_3) + \mathcal{D}(\mathbf{x}_2,\mathbf{x}_1;\mathbf{x}_4,\mathbf{x}_3)].$$

Here, we neglected the electron returns to the junction in the lead and, therefore, averaged independently from each of the other two Green's functions for a particle in the lead. The first term in the brackets represents a similar procedure for the excitation in the grain; it leads eventually to Eqs. (38)–(40) above. The last term in the brackets is the irreducible part of the average product of two Green's functions; it accounts for the multiple returns of the excitation to the junction. Unlike the first term, the decay of $\mathcal{D}$ as a function of distance between $\mathbf{x}_2,\mathbf{x}_1$ and $\mathbf{x}_4,\mathbf{x}_3$ is slow on the scale $1/k_F$. The corresponding contribution to $K_{\rm d}$ was evaluated, e.g., in the context of theory of Andreev reflection in the presence of disorder[13] and reads

$$K_{\rm d}^{\rm irr}(\xi,\xi';\zeta,\zeta')=\frac{g^2}{128\pi^5\nu}\int\frac{d^2\mathbf{x}d^2\mathbf{x}'}{S^2}[P_{\zeta'-\zeta}(\mathbf{r}',\mathbf{r}) + P_{\zeta-\zeta'}(\mathbf{r},\mathbf{r}')]_{z=z'=0}.$$

Here $P_\omega(\mathbf{r},\mathbf{r}')$ describes the evolution of the probability density to find an electron at a given point $\mathbf{r}$. For diffusive mo-

tion (under the condition $\ell \ll L$), the diffuson $P_\omega(\mathbf{r},\mathbf{r}')$ obeys the diffusion equation,

$$(i\omega - D\nabla_{\mathbf{r}}^2)P_\omega(\mathbf{r},\mathbf{r}') = \delta^3(\mathbf{r}-\mathbf{r}'), \tag{49}$$

and $D=(v_F\ell)/3$ is the diffusion constant in the grain. At frequencies ω smaller than the Thouless energy D/L^2, the solution of Eq. (49) reaches the universal (zero-mode) limit where

$$P_\omega(\mathbf{r},\mathbf{r}') + P_{-\omega}(\mathbf{r}',\mathbf{r}) \approx \frac{2\pi}{V}\delta(\omega) \tag{50}$$

is independent of the coordinates in the grain. In the case of a smaller grain, $L \lesssim \ell$, Eq. (49) does not hold, but the universal limit for $P_\omega(\mathbf{r},\mathbf{r}')$ is the same[15] and is reached at $\omega \lesssim v_F/L$. At small $|E_0|$, the contribution of $K_{\mathrm{d}}^{\mathrm{irr}}$ may dominate the value of J [see Eq. (36)]. With the help of Eq. (50), we may now evaluate Eq. (36) to find

$$J_{\mathrm{d}} \approx -\frac{g^2\ln(1/g)}{64\pi^3}\delta\sqrt{\frac{2\Delta}{-E_0}}. \tag{51}$$

Here $\delta=1/\nu V$ is the electron level spacing in the grain. Equation (51) yields (in the region $\mathcal{N}^*-\mathcal{N} \ll \delta\mathcal{N}$) a correction to the charge presented in Eq. (42) above.

Comparing Eqs. (40) and (42), we see that if the linear sizes of grain and junction coincide, the ballistic and diffusive results match each other at the gate voltage given by Eq. (41). The correction Eq. (42) remains small everywhere except a very narrow region around the charge degeneracy point, $\mathcal{N}^*-\mathcal{N} \lesssim \delta\mathcal{N}/(N_{\mathrm{ch}}^{\mathrm{eff}})^{1/2}$.

On the odd side of the charge degeneracy point, at $\mathcal{N} > \mathcal{N}^*$, the unperturbed ground state is $P_o\gamma_{k\sigma}^\dagger|e\rangle$, where k is the closest to the Fermi level state. In the zeroth in $1/N_{\mathrm{ch}}^{\mathrm{eff}}$ limit, the ground-state energy is zero. The correction induced in E_0 by the perturbation V in the Hamiltonian H_0 is found from this equation

$$E_0 = \sum_p{}' \frac{|\tilde{t}_{kp}|^2\theta(\xi_p)}{E_0-\epsilon_0-\xi_p}. \tag{52}$$

As the tunneling matrix element involves a single state k, its solution should exhibit strong mesoscopic fluctuations. The typical value, however, is easy to find

$$E_0 \sim -\frac{1}{2\pi^2}g\delta\ln(1/g). \tag{53}$$

Therefore, the coupling to the lead induces a small shift of $\mathcal{N}^*$, which scales proportionally to the one-level spacing in the grain and is of the order of $g\delta/E_c$. Beyond this small shift, the ground-state energy at $\mathcal{N}>\mathcal{N}^*$ is not modified by perturbation V.

Now we return briefly to the effect of the terms proportional to $w_{kk'}$ and $w_{pp'}^i$ in V. Indeed, they do also contribute to the Brillouin-Wigner expansion (32) and give correction to the ground-state energy (18). In particular, at $\mathcal{N}<\mathcal{N}^*$, the fourth-order-in-$H_t$ corrections to E_0 formed with such terms are given by integrals similar to Eq. (36). They only differ by the energy ranges of integration which account for the virtual states outside the bandwidth involved in the evaluation of $w_{kk'}$ and $w_{pp'}^i$. The resulting correction is of the same order as, and not more singular at $\mathcal{N}\to\mathcal{N}^*$ than the contributions we have already evaluated [see Eqs. (39) and (51)].

To summarize this section, we have demonstrated that in the case of a wide junction ($N_{\mathrm{ch}} \gg 1$) corrections to the ground-state energy Eq. (18) are parametrically small. The smearing of the nonanalytical $\mathcal{N}$-dependence of the grain charge [see Eq. (19)] vanishes in the limit of zero-level spacing δ in the grain. Identifying $|0\rangle$ and $|k\sigma\rangle$ with $P_e|\Phi\rangle$ and $P_o\gamma_{k\sigma}^\dagger|\Phi\rangle$, respectively, where $|\Phi\rangle$ is the BCS ground state in the grain in the grand-canonical ensemble, and discarding the terms proportional to $w_{kk'}$ and $w_{pp'}^i$ in V, we can put the Hamiltonian (27) in the form of (13).

We note finally that in the opposite limit of a point contact, $N_{\mathrm{ch}}=1$, instead of the jump in C_{diff} we would find a smooth crossover[17] of width $\delta\mathcal{N}$ in the region of even-odd transition.

IV. CHARGE STEPS AT FINITE TEMPERATURE

In this section, starting from the effective Hamiltonian (13) for a wide, multichannel contact between the superconducting grain and a normal lead, we derive rigorously Eq. (22), which gives the partition function of the system near the charge degeneracy point $\mathcal{N}^*$.

A. Density of states

To compute Z, we must determine the excited states.

Without coupling, the many-body even eigenstates of the system without excitation in the grain are denoted $|0,f\rangle \equiv |0\rangle\otimes|f\rangle$. We recall that $|0\rangle$ is the wave function for the grain in the even state, while $|f\rangle$ is the wave function of the lead corresponding to a particular set $f\equiv\{n_{p\sigma}\}$ of electron occupation numbers for each state $(p\sigma)$. The energy of the state $|0,f\rangle$ is $\mathcal{E}_f+\epsilon_0$, where

$$\mathcal{E}_f = \sum_{p\sigma}\xi_p[n_{p\sigma}-\theta(\xi_p)] \tag{54}$$

is the excitation energy for the lead in state $|f\rangle$. The many-body odd states with one excitation in state $(k\sigma)$ in the grain are $|k\sigma,f\rangle\equiv|k\sigma\rangle\otimes|f\rangle$, their energy is $\mathcal{E}_f+\xi_k^2/(2\Delta)$.

At finite coupling, the even and odd states hybridize. In order to find the eigenenergies, we can still use Brillouin-Wigner perturbation theory like we did for determining the ground-state energy in Sec. III. Starting from an unperturbed eigenstate $|0,f\rangle$, we can write the Brillouin-Wigner equation for its energy in the presence of the coupling by replacing $\{|e\rangle,\epsilon_0,E_0\}$ with $\{|0,f\rangle,\mathcal{E}_f+\epsilon_0,E\}$ in Eq. (32). The solutions of this equation are the exact eigenenergies. For a wide junction (in the limits $\delta\to0$ and $N_{\mathrm{ch}}\to\infty$), such an equation can still be truncated up to second-order terms in the perturbation V, like in Sec. III. However, the Brillouin-Wigner equation generalizing Eq. (33)

$$E = \epsilon_0+\mathcal{E}_f+\sum_{kq\sigma}{}'\frac{|\tilde{t}_{kq}|^2 n_{q\sigma}}{E-\mathcal{E}_f+\xi_q-\xi_k^2/(2\Delta)}, \tag{55}$$

now defines a large number of excited states and is impractical to solve for each of them. The prime in the sum means

that only unperturbed eigenstates in the bandwidth D are included in the sum. Here, let us note that Eq. (33) is obtained from (55) for the particular set $f_0=\{n_{p\sigma}\}$ determined by the Fermi function at zero temperature, $n_{p\sigma}=\theta(-\xi_p)$, and with the property $\mathcal{E}_{f_0}=0$. At zero temperature, we were only looking for the solution with lower energy, corresponding to the ground state.

The partition function (20), which is the sum over the full set of eigenstates E_λ, can be expressed in terms of the exact density of states, $\nu(E)$

$$Z=\int_{-\infty}^{\infty} dE\nu(E)e^{-\beta E}, \tag{56}$$

where $\nu(E)=\Sigma_\lambda \delta(E-E_\lambda)$. The density of state is related to the exact Green's function $G_E=(E-H_0)^{-1}$ at energy E

$$\nu(E)=-\frac{1}{\pi}\,\mathrm{Im\,Tr}\,G_{E_+}, \quad E_+=E+i0^+. \tag{57}$$

We evaluate Tr G in the basis of the unperturbed eigenstates $|0,f\rangle$ and $|k\sigma,f\rangle$. Thus, we can write the density of states

$$\nu(E)=-\frac{1}{\pi}\,\mathrm{Im}\left[\sum_f G_{E_+}(0,f)+\sum_{k\sigma,f} G_{E_+}(k\sigma,f)\right] \tag{58}$$

in terms of the diagonal elements of G_E in this basis,

$$G_E(0,f)=\langle 0,f|(E-H_0)^{-1}|0,f\rangle, \tag{59a}$$

$$G_E(k\sigma,f)=\langle k\sigma,f|(E-H_0)^{-1}|k\sigma,f\rangle. \tag{59b}$$

In order to evaluate $G_E(0,f)$, we need to introduce the additional matrix elements of G_E,

$$G_E(0,f;0,f')=\langle 0,f|(E-H_0)^{-1}|0,f'\rangle, \tag{60a}$$

$$G_E(k\sigma,f;0,f')=\langle k\sigma,f|(E-H_0)^{-1}|0,f'\rangle. \tag{60b}$$

They solve the closed set of equations

$$\delta_{ff'}=(E-\mathcal{E}_f-\epsilon_0)G_E(0,f;0,f')-\sum_{kq\sigma}{}' \tilde{t}_{kq}n_{q\sigma}G_E(k\sigma,f_{q\sigma};0,f'), \tag{61a}$$

$$0=[E-\mathcal{E}_f-\zeta_k^2/(2\Delta)]G_E(k\sigma,f;0,f')-\sum_q{}' \tilde{t}_{kq}^*(1-n_{q\sigma})G_E(0,f^{q\sigma};0,f'). \tag{61b}$$

Here we defined $\delta_{ff'}=1$ if all the electron occupation numbers in the sets f and f' coincide, otherwise $\delta_{ff'}=0$. Moreover, the set $f_{q\sigma}$ (respectively $f^{q\sigma}$) coincides with f, except for the occupation number in state $(q\sigma)$ which is set to $n_{q\sigma}=0$ (respectively $n_{q\sigma}=1$). Inserting (61b) into (61a) and defining the self-energy

$$\tilde{\Sigma}_E(0,f)=\sum_{kq\sigma}{}' \frac{|\tilde{t}_{kq}|^2 n_{q\sigma}}{E-\mathcal{E}_f+\xi_q-\zeta_k^2/(2\Delta)}, \tag{62}$$

we get the equation

$$\delta_{ff'}=[E-\mathcal{E}_f-\epsilon_0-\tilde{\Sigma}_E(0,f)]G_E(0,f;0,f')-\sum_{k,p\neq q,\sigma}{}' \frac{\tilde{t}_{kq}\tilde{t}_{kp}^* n_{q\sigma}(1-n_{p\sigma})}{E-\mathcal{E}_f+\xi_q-\zeta_k^2/(2\Delta)}G_E(0,[f_{q\sigma}]^{p\sigma};0,f'). \tag{63}$$

The second term in the right-hand side (rhs) of this equation gives a negligible contribution in the limit $N_{\mathrm{ch}}\to\infty$. (This can be shown along the same lines as in Sec. III.) As a result, we find

$$G_E(0,f)\equiv G_E(0,f;0,f)=[E-\mathcal{E}_f-\epsilon_0-\tilde{\Sigma}_E(0,f)]^{-1}. \tag{64}$$

The last term in Eq. (28) defining ϵ_0 depends on bandwidth D. By subtracting this term from ϵ_0 and adding it to $\tilde{\Sigma}_E(0,S)$, we write the Green's function (64) equivalently,

$$G_E(0,f)=[E-\mathcal{E}_f-\omega_0-\Sigma_E(0,f)]^{-1}, \tag{65}$$

where $\omega_0=2E_c(\mathcal{N}-\mathcal{N}^*)$, and

$$\Sigma_E(0,f)=\tilde{\Sigma}_E(0,f)+\epsilon_0-\omega_0. \tag{66}$$

Inserting Eqs. (28) and (62) into (66), we obtain

$$\Sigma_E(0,f)=\sum_{kq\sigma}\left\{\frac{|\tilde{t}_{kq}|^2 n_{q\sigma}}{E-\mathcal{E}_f+\xi_q-\zeta_k^2/(2\Delta)}-\frac{|\tilde{t}_{kq}|^2\theta(-\xi_q)}{\xi_q-\zeta_k^2/(2\Delta)}\right\}. \tag{67}$$

At high energies $|\xi_p|$, the electron occupation numbers asymptotically behave as the zero-temperature Fermi function. Therefore, the sum in Eq. (67) is convergent and we do not need to specify anymore that only the states in the low-energy subspace are included in it.

We can determine $G_E(k\sigma,f)$ in a similar way. In the same limit $N_{\mathrm{ch}}\to\infty$, we obtain

$$G_E(k\sigma,f)=g_E(k\sigma,f)+g_E(k\sigma,f)^2\sum_p |\tilde{t}_{kp}|^2(1-n_{p\sigma})\times G_E(0;f^{p\sigma}). \tag{68}$$

The first term in the rhs of Eq. (68) coincides with the Green's function for the unperturbed state $|k\sigma,f\rangle$ with one excitation in the grain, $g_E(k\sigma,f)=[E-\mathcal{E}_f-\zeta_k^2/(2\Delta)]^{-1}$. The second term comes from its hybridization with the many-body states with no excitation in the grain.

Inserting Eqs. (65) and (68) into (58), we express the density of states as the sum of different contributions,

$$\nu(E)=\sum_f\left[\sum_{k\sigma}\delta\left(E-\mathcal{E}_f-\frac{\zeta_k^2}{2\Delta}\right)+\delta\nu_f(E)\right], \tag{69}$$

$$\delta\nu_f(E)=-\frac{1}{\pi}\,\mathrm{Im}\left[G_{E_+}(0,f)\left(1-\frac{d\Sigma_{E_+}(0,f)}{dE}\right)\right]. \tag{70}$$

In Eq. (69), the sum of δ functions comes from the first term in Eq. (68), while the terms $\delta\nu_f(E)$ come from Eq. (65) and the second term in Eq. (68).

In Sec. IV B, we use Eqs. (69) and (70) to evaluate the partition function. We show that the contribution of $\delta\nu_f(E)$, Eq. (70), to the partition function can be approximated by that of a single state with energy $E=E_0+\mathcal{E}_f$ and derive Eq. (22) for the partition function. Finally, we show that Eqs. (22) and (23) accurately account for the thermodynamic quantities of the grain in the entire temperature range $T<T^*$ and at any sign of $\mathcal{N}-\mathcal{N}^*$ as well.

B. Partition function

Inserting Eq. (69) into (56), we obtain the partition function

$$Z=\sum_f e^{-\beta\mathcal{E}_f}\left(\sum_{k\sigma} e^{-(\beta\zeta_k^2/2\Delta)}+\int_{-\infty}^{\infty} d\omega e^{-\beta\omega}\delta\nu_f(\omega+\mathcal{E}_f)\right). \tag{71}$$

Introducing the reduced partition function of the grain, $\tilde{Z}=Z/Z_{\text{lead}}$ and inserting Eqs. (65) and (66) into (70), we obtain

$$\tilde{Z}=N_{\text{eff}}(T)-\int_{-\infty}^{\infty} d\omega\frac{e^{-\beta\omega}}{\pi}\,\text{Im}\left\langle\frac{1-d\Sigma_f(\omega_+)/d\omega}{\omega_+-\omega_0-\Sigma_f(\omega_+)}\right\rangle_T. \tag{72}$$

Z_{lead} and $N_{\text{eff}}(T)$ were defined in Eq. (22). In the second term of Eq. (72), $\langle\ldots\rangle_T$ denotes thermal averaging over with the Hamiltonian of the isolated lead and we introduced the reduced self-energy

$$\Sigma_f(\omega)=\Sigma_{\omega+\mathcal{E}_f}(0,f). \tag{73}$$

The integrand in the second term in Eq. (72) is a regular function of the occupation numbers $n_{p\sigma}$. We can expand the integrand in series in the set of $n_{p\sigma}$. Then we replace them by their thermal average $f(\xi_p)=[1+\exp(\beta\xi_p)]^{-1}$. [Their fluctuations $\langle[n_{p\sigma}-f(\xi_p)]^2\rangle_T$ scale as the inverse number of electrons in the lead and can be safely ignored in the thermodynamic limit.] Finally, we resum the series and obtain

$$\tilde{Z}=N_{\text{eff}}(T)-\int_{-\infty}^{\infty} d\omega\frac{e^{-\beta\omega}}{\pi}\,\text{Im}\,\frac{1-d\Sigma(\omega_+)/d\omega}{\omega_+-\omega_0-\Sigma(\omega_+)}, \tag{74}$$

in terms of the thermally averaged self-energy

$$\Sigma(\omega)\equiv\langle\Sigma_f(\omega)\rangle_T=\sum_{kq\sigma}\left\{\frac{|\tilde{t}_{kq}|^2 f(\xi_q)}{\omega+\xi_q-\zeta_k^2/(2\Delta)}-\frac{|\tilde{t}_{kq}|^2\theta(-\xi_q)}{\xi_q-\zeta_k^2/(2\Delta)}\right\}. \tag{75}$$

In (75), we can replace the summations over k and p by integrals, then integrate over ζ_k, then take the integrals over ξ_p by parts. Finally, we get

$$\Sigma(\omega_+)\equiv\frac{g}{16\pi T}\int_{-\infty}^{\infty} d\xi\frac{\sqrt{2\Delta(-\omega_+-\xi)}}{\cosh^2(\xi/2T)}. \tag{76}$$

Equations (74) and (76) express the thermodynamic quantities of the system in terms of two definite integrals. They form the main results of this section. Below we show that the grain charge may be approximated by Eq. (23).

If the Boltzmann weight $e^{-\beta\omega}$ is removed from the integrand in the second term of Eq. (74) it integrates to unity. Indeed, at $g=0$, this term corresponds to the density of states of the single state of the grain without quasiparticle on it. Therefore, by the counting argument it must still correspond to a single state at finite coupling. It is easy to see that only the spectral weight of the Green's function residing at frequencies $\omega\lesssim-\omega_i\equiv-T\ln N_{\text{eff}}(T)$ results in the nonnegligible contribution to the partition function in comparison with that of the first *large* term. We can, therefore, restrict the integration over ω in the second term of Eq. (74) to $\omega<\omega_i$.

For $\omega<-\omega_i$, the integral in the last expression can be readily evaluated and yields

$$\Sigma(\omega_+)\approx\frac{g}{4\pi}\sqrt{2\Delta(-\omega)}\left[1+\mathcal{O}\left(\frac{T}{|\omega|}\right)\right]-i\frac{g}{4}\sqrt{\frac{\Delta T}{2\pi}}e^{\beta\omega}. \tag{77}$$

It is clear from Eq. (77) that the integral over ω in Eq. (74) converges at the lower limit. Its integrand has a pole precisely at $E_0<0$ when $\mathcal{N}<\mathcal{N}^*$ [see Eq. (18)]. If $E_0<-\omega_i$, the pole E_0 lies within the region of integration over ω and gives the dominant contribution to the integral which equals to $\exp(-\beta E_0)$. At higher temperatures, the integral in the second term in Eq. (74) may not be evaluated by taking the residue at the pole. However at these temperatures, the second term is negligible in comparison with the first one. This is also true at $\mathcal{N}>\mathcal{N}^*$ when $E_0=0$, and, thus, we obtain Eq. (22).

V. CONCLUSION

We studied charge quantization in a small superconducting grain with charging energy $E_c>\Delta$ contacted by a normal-metal electrode in the limit when the single-particle mean level spacing in the grain δ is small. At zero conductance g of the junction between the grain and the electrode, the steps in the charge vs gate voltage dependence $Q(\mathcal{N})$ are sharp and positioned in the dimensionless gate voltage $\mathcal{N}$ at $\mathcal{N}_0=2l\pm[1/2+\Delta/(2E_C)]$.

At a finite conductance and zero temperature, the steps are shifted by an amount $\propto g\Delta/E_C$, Eq. (10), making the odd charge plateaus even shorter. The charge steps become asymmetric and acquire a finite width $W_0\propto g^2\Delta/E_C$. We find the shape of the Coulomb blockade staircase $Q(\mathcal{N})$ for the experimentally relevant case of a wide junction with a large number of tunneling channels N_{ch}. In the $N_{\text{ch}}\to\infty$ limit the ground-state energy of the system can be determined analytically and is given by Eq. (18). The resulting grain charge in the ground state is given by Eq. (19). Although the charge steps are broadened at $g\neq0$ and the dependence $Q(\mathcal{N})$ becomes continuous, the differential capacitance remains singular, displaying discontinuities at certain values of the gate voltage.

At finite temperature $T<T^*=\Delta/\ln(\sqrt{8\pi}\Delta/\delta)$, we obtain analytic expressions for the partition function in terms of two definite integrals, Eqs. (74) and (76). The resulting grain charge can be approximated by Eq. (23). The shape of the charge step is plotted in Fig. 2 for several characteristic val-

ues of the system parameters. At temperatures exceeding the characteristic "quantum" temperature scale T_q, Eq. (25), the steps acquire an additional thermal shift described by Eq. (24). Finite tunneling also leads to a nonmonotonic temperature dependence of the steps width with the minimal width achieved at $T \sim T_q$. The temperature-dependent shift of the step and its width are plotted in Fig. 3.

The existing experiment on such systems[5,6] perhaps is not sensitive enough to see the quantum broadening evaluated in this paper. Indeed one may think that the saturation of the ratio between even and odd plateaus at low temperature observed in the experiment was due to the quantum fluctuations rather than due to an impurity creating a state within the gap, as suggested by the authors of Ref. 6. This explanation, however, calls for fairly large junction conductance of the order of $g=5$. This value exceeds the experimental estimate of 25 kΩ for the resistance of the junction[18] and also would have lead to a significant slope of the charge plateaus, contrary to the observations.[6] Nevertheless, the evaluated broadening for the N-I-S junction is easier to measure than the charge step width in a normal-grain device (there the width is exponentially small at small g). A recent experiment[3] mapped out a considerable portion of a charge step, broadened by quantum fluctuations, in a normal device. We expect that similar experiments with a hybrid device considered in this paper may resolve the structure of an entire step.

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