Electron-Pair Resonance in the Coulomb Blockade

Eran Sela, H.-S. Sim, Yuval Oreg, M. E. Raikh, and Felix von Oppen

1Department of Condensed Matter Physics, Weizmann Institute of Science, Rehovot, 76100, Israel
2Department of Physics, Korea Advanced Institute of Science and Technology, Daejeon 305-701, Korea
3Department of Physics, University of Utah, Salt Lake City, Utah 84112, USA
4Institut für Theoretische Physik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany

We study many-body corrections to the cotunneling current via a localized state with energy $\epsilon_d$ at large bias voltages $V$. We show that the transfer of electron pairs, enabled by the Coulomb repulsion in the localized level, results in ionization resonance peaks in the third derivative of the current with respect to $V$, centered at $eV = \pm 2\epsilon_d/3$. Our results predict the existence of previously unnoticed structure within Coulomb-blockade diamonds.

Introduction.—Current flow through a single localized state (LS) coupled to metallic leads is a paradigm of quantum transport through nanostructures, with applications to many systems such as impurities embedded in tunnel barriers, quantum dots, single-molecule junctions, or carbon nanotubes; see, e.g., Refs. [1–4]. Despite its simplicity, this system exhibits a wide range of transport behaviors, including resonant and sequential tunneling, cotunneling, and the Kondo effect.

All of these regimes are captured remarkably well by a simple extension of the Anderson impurity model

$$H = \sum_{\sigma} \epsilon_d d_{\sigma}^\dagger d_{\sigma} + U n_{\sigma} n_{\bar{\sigma}} + \sum_{k,\alpha} \epsilon_k c_{k,\alpha}^\dagger c_{k,\alpha}$$

$$+ \sum_{k,\alpha} \{ t_{\alpha} d_{\sigma}^\dagger c_{k,\sigma} + t_{\alpha}^* c_{k,\bar{\sigma}} d_{\sigma} \}.$$  \hspace{1cm} (1)

which describes tunneling of amplitude $t_{\alpha}$ between the spin-degenerate LS of energy $\epsilon_d$ (with creation operator $d_{\sigma}^\dagger$) and number operator $n_{\sigma} = d_{\sigma}^\dagger d_{\sigma}$) and two leads $\alpha = L, R$ (with dispersion $\epsilon_k$ and creation operator $c_{k,\alpha}^\dagger$). For large on-site Coulomb repulsion $U$, double occupation of the LS is suppressed and the nature of transport depends on both $\epsilon_d$ (tunable by a gate voltage $V_g$) and the bias voltage $V$. Within the shaded areas of the stability diagram in Fig. 1, the average occupation $n_d = n_{\uparrow} + n_{\downarrow}$ of the LS is close to integer and current flow is suppressed by the Coulomb blockade. In contrast, current can flow by sequential-tunneling processes outside the shaded areas, where the average occupation of the dot is no longer integer. This picture of the Coulomb blockade has been confirmed experimentally for various systems [1–4].

It is the main point of this Letter that even the minimal model of Eq. (1) predicts additional structure within the Coulomb-blockaded region, emerging from two-electron ionization of the LS at large biases. This ionization process is an effect of many-body correlations, enabled by the on-site Coulomb repulsion, which is much more robust than the Kondo correlations emerging in the Kondo valley $n_d = 1$ at low temperatures and small voltages. Indeed, the fine structure due to the two-electron ionization process exists in both Kondo and non-Kondo valleys, as illustrated in Fig. 1.

The two-electron ionization requires biases beyond a threshold voltage $V_c$ (see the thick lines in Fig. 1). Below the threshold voltage, correlated two-electron transfers between the two leads constitute a precursor effect to two-electron ionization. While the limit of the Coulomb-blockaded region is characterized by a resonance peak in the differential conductance $dI/dV$, we find that the onset of two-electron ionization at $V_c$ is accompanied by a peak in $d^3I/dV^3$ [5]. Interestingly, the difference between both resonance phenomena emerges solely from familiar Fermi-liquid phase space factors which appear in the two-electron ionization rate. One important implication of this analogy is that the onset of two-electron ionization is accompanied by anomalous temperature sensitivity, even when $eV_c > T$, as is familiar for the boundary of the Coulomb-blockaded region.

Most of our predictions for the single LS extend to a metallic dot with essentially zero level spacing where the stability diagram exhibits a sequence of Coulomb diamonds, reflecting the stepwise population of the dot with

---

PACS numbers: 73.23.Hk, 73.63.Kv

DOI: 10.1103/PhysRevLett.100.056809

FIG. 1 (color online). Schematic stability diagram of a single-level quantum dot. The thick lines within the shaded Coulomb-blockaded region are characterized by a resonance peak in $d^3I/dV^3$ due to opening of two-electron ionization. For $eV$ below the threshold voltage $eV_c = 2\epsilon_d/3$, tunneling of electron pairs is a precursor effect to two-electron ionization.
increasing gate voltage. It is easy to see that for the metallic dot, the boundaries of two-electron ionization translate into a sequence of inner diamonds. This is depicted in Fig. 2, where we include the effects of asymmetric capacitances between dot and electrodes.

In the remainder of the Letter, we quantify the behavior of the current near the two-particle threshold.

**Two-electron ionization.**—Ionization by means of single-particle tunneling becomes energetically allowed when the source chemical potential $eV/2$ is aligned with the LS, i.e., at $eV = \pm 2\epsilon_d$. In contrast, the two-particle ionization process, responsible for the predicted boundaries in the stability diagram, is depicted in Fig. 3(a). At finite bias, an electron tunneling between the leads can suffer an energy loss up to $eV$. Because of the on-site Coulomb repulsion, this energy loss can be transferred to a second electron from the source electrode, exciting it to energies up to $3eV/2$. Specifically, the second electron can populate (and thus ionize) the LS once its maximal energy exceeds $\epsilon_d$, i.e., for biases exceeding the threshold voltage

$$eV_c = 2\epsilon_d/3.$$  

The predicted lines in the stability diagram originating from the onset of two-electron ionization occur for $V = \pm V_c$. Thus, they are located within the Coulomb-blockaded region which extends up to $eV = \pm 2\epsilon_d$.

Microscopically, the two-electron ionization process proceeds as follows, cf. Fig. 3(a): (i) An electron with energy $\epsilon_1$ from the source electrode ($L$) enters the LS and (ii) tunnels into the state $E_1$ of the drain ($R$). In the same process, (iii) a second electron with opposite spin and energy $\epsilon_2$ tunnels from the source into the LS. The amplitudes of steps (i) and (iii) are proportional to $t_{L}^\star$, while that of step (ii) is proportional to $t_{R}^\star$. Thus, the ionization amplitude is given by

$$A_{\epsilon_1, \epsilon_2} = \frac{t_{L}^\star t_{R}^\star}{(\epsilon_d - \epsilon_1)(E_1 - \epsilon_1)}.$$  

Following standard perturbation theory, the energy denominators are given by the difference between the intermediate and initial energies. In Eq. (3), we assumed a large on-site Coulomb repulsion $U$ so that there is no contribution from virtual states with double occupation of the LS. If these states were included, the corresponding terms would exactly cancel the amplitude in Eq. (3) in the limit of vanishing $U$. This shows that two-electron ionization is enabled by the on-site interaction.

Based on Eq. (3) and energy conservation, the two-electron ionization rate per spin, at $T = 0$, is

$$\Gamma_{\text{ion}} = \frac{9\pi^2 \Gamma_R}{32\pi^2 e^2 V_c^4} \theta(V - V_c)$$  

of the two-electron ionization rate $\Gamma_{\text{ion}}$.

**FIG. 2** (color online). Stability diagram of a metallic quantum dot with vanishing level spacing. The threshold lines for two-electron ionization can be determined by examining the electrostatic energy of the circuit. Graphically they are obtained (e.g., for the central diamond) by rescaling the diagonal $\Delta D$ by a factor 3, so that $\Delta B = 3\Delta C = 3\Delta D$. Inset: Equivalent electric circuit for a metallic island.
It is crucial that energy exchange between electrons in the leads does not require direct interaction between them. Instead, this process is enabled by the finite Coulomb repulsion in the LS alone. In this regard, the underlying physics of two-particle ionization is similar to that of energy exchange between electrons in a bulk metal, facilitated by a magnetic impurity [6]. Indeed, it is the nonzero on-site Coulomb repulsion \( U \) that ultimately generates the magnetic impurity [7]. Curiously, similar processes can also be enabled by the pairing interaction in devices of two Josephson junctions in series, where they lead to subgap structure in the current [8].

After entering the empty LS with rate \( \Gamma_{\text{ion}} \) by two-electron ionization, the electron rapidly escapes into source or drain electrode by single-electron tunneling, with rates \( \Gamma_L \) and \( \Gamma_R \), respectively. Then, the average occupation of the LS is governed by the rate equation

\[
\frac{d}{dt} \langle n \rangle = \Gamma_{\text{ion}} (1 - \langle n \rangle) - \Gamma_L \langle n \rangle - \Gamma_R \langle n \rangle, \\
\text{which yields} \ \langle n \rangle = \frac{\Gamma_{\text{ion}}}{\Gamma_L + \Gamma_R}. 
\]

Since the net charge transfer is \( e \langle n \rangle \), the ionization current, the electron rapidly escapes into source or drain electrode by single-electron tunneling, with rates \( \Gamma_L \) and \( \Gamma_R \). Thus, it is an important question how the threshold anomaly Eq. (7) can be distinguished from the backgound cotunneling current. Equation (7) predicts that two-electron ionization induces a jump in \( dI/dV \) located at \( V = V_c \). We now turn to a more careful analysis of this jump, focusing first on the two-electron current below threshold, before deriving a general interpolation formula.

**Two-electron current below threshold.**—For voltages below the threshold, \( V < V_c \), ionization of the LS is no longer possible by two-electron processes. But two-electron processes can still excite electrons in the leads to just below the energy of the LS. We will now show that this constitutes a precursor effect to two-electron ionization which contributes a logarithmically singular threshold dependence to the differential conductance.

For large on-site Coulomb repulsion \( U \), the two-electron process below threshold proceeds microscopically as follows, cf. Fig. 3(b): (i) A spin-up electron from lead \( \alpha_1 \) with energy \( \varepsilon_1 \) enters the LS; (ii) the electron tunnels out to state \( E_1 \) in lead \( \alpha'_1 \); (iii) a spin-down electron from lead \( \alpha_2 \) with energy \( \varepsilon_2 \) enters the LS, and (iv) leaves into state \( E_2 \) in lead \( \alpha'_2 \). The corresponding amplitude is

\[
A_{\varepsilon_1 \to E_1} = \frac{\Gamma_{\alpha_1 \to \alpha'_1} \Gamma_{\alpha_2 \to \alpha'_2}}{(\varepsilon_d - \varepsilon_1)(E_1 - \varepsilon_1)(E_2 - \varepsilon_2)} + (1 \leftrightarrow 2),
\]

where the second term accounts for the four-step process described above with the exchanged order (iii) \( \leftrightarrow \) (iv) \( \leftrightarrow \) (ii). This results in a scattering rate

\[
\Gamma_{\alpha_1 \to \alpha_1'}^{(e)} = 2\pi \nu^4 \int \prod_{i=1}^{3} [d\varepsilon_i dE_i f(\varepsilon_i - \mu_{\alpha_i}) \\
\times \{1 - f(E_i - \mu_{\alpha_i})\}] |A_{\varepsilon_1 \to E_1}|^2 \\
\times \delta(\varepsilon_1 + \varepsilon_2 - E_1 - E_2).
\]

Here \( f(\varepsilon) = \left[ e^{\varepsilon/T} + 1 \right]^{-1} \) and \( \mu_{\text{LS}} = \mp eV/2 \). The resulting two-electron tunneling current is

\[
I = \int \prod_{i=1}^{3} [d\varepsilon_i dE_i f(\varepsilon_i - \mu_{\alpha_i}) \\
\times \{1 - f(E_i - \mu_{\alpha_i})\}] |A_{\varepsilon_1 \to E_1}|^2 \\
\times \delta(\varepsilon_1 + \varepsilon_2 - E_1 - E_2).
\]

For large on-site Coulomb repulsion \( U \), the two-electron process below threshold proceeds microscopically as follows, cf. Fig. 3(b): (i) A spin-up electron from lead \( \alpha_1 \) with energy \( \varepsilon_1 \) enters the LS; (ii) the electron tunnels out to state \( E_1 \) in lead \( \alpha'_1 \); (iii) a spin-down electron from lead \( \alpha_2 \) with energy \( \varepsilon_2 \) enters the LS, and (iv) leaves into state \( E_2 \) in lead \( \alpha'_2 \). The corresponding amplitude is

\[
A_{\varepsilon_1 \to E_1} = \frac{\Gamma_{\alpha_1 \to \alpha'_1} \Gamma_{\alpha_2 \to \alpha'_2}}{(\varepsilon_d - \varepsilon_1)(E_1 - \varepsilon_1)(E_2 - \varepsilon_2)} + (1 \leftrightarrow 2),
\]

where the second term accounts for the four-step process described above with the exchanged order (iii) \( \leftrightarrow \) (iv) \( \leftrightarrow \) (ii). This results in a scattering rate

\[
\Gamma_{\alpha_1 \to \alpha_1'}^{(e)} = 2\pi \nu^4 \int \prod_{i=1}^{3} [d\varepsilon_i dE_i f(\varepsilon_i - \mu_{\alpha_i}) \\
\times \{1 - f(E_i - \mu_{\alpha_i})\}] |A_{\varepsilon_1 \to E_1}|^2 \\
\times \delta(\varepsilon_1 + \varepsilon_2 - E_1 - E_2).
\]

Here \( f(\varepsilon) = \left[ e^{\varepsilon/T} + 1 \right]^{-1} \) and \( \mu_{\text{LS}} = \mp eV/2 \). The resulting two-electron tunneling current is

\[
I = \int \prod_{i=1}^{3} [d\varepsilon_i dE_i f(\varepsilon_i - \mu_{\alpha_i}) \\
\times \{1 - f(E_i - \mu_{\alpha_i})\}] |A_{\varepsilon_1 \to E_1}|^2 \\
\times \delta(\varepsilon_1 + \varepsilon_2 - E_1 - E_2).
\]

Since both \( E_1 \) and \( E_2 \) in the denominator of Eq. (10) are close to \( eV/2 \), the remaining integration yields the singular contribution

\[
\frac{dI}{dV} = \frac{2e^2}{h} \frac{3\Gamma_{L}^2 \Gamma_{R} + \frac{3}{2} \Gamma_{L}}{(2\pi)^2(eV)^2} \ln \left[ \frac{eV_c - eV}{eV - T} \right]
\]

The appearance of \( T \) dependence in Eq. (11) at \( eV_c \gg T \) resembles the behavior of the conductance near the onset of sequential tunneling at \( eV = \pm 2\varepsilon_d \), cf. Fig. 1. In fact, we find that the analogy between the onset of sequential tunneling at \( eV = \pm 2\varepsilon_d \) and the onset of two-electron ionization at \( V = \pm V_c \) goes much further. The lines \( eV = \pm 2\varepsilon_d \) in the stability diagram separate transport regimes with real occupation (sequential tunneling) and virtual occupation (cotunneling) of the LS. Similarly, the lines \( V = \pm V_c \) separate regimes with real occupation (two-electron ionization) and virtual occupation (pair tunneling) of the LS. We now explore this analogy on a quantitative level.

**Correspondence of one-electron and two-electron ionization.**—We start by noting that Eqs. (7) and (11) yield
we find the relation pair resonance are reproduced by Eq. (12). For above and below-threshold limits, Eqs. (7) and (10), of the electron resonance which are the familiar voltage dependencies of the physical cutoff of the singularity in Eq. (11). Most importantly, at both virtual and real occupations of the LS, i.e., it describes the two-electron resonance. Indeed, it can be verified that the above and below-threshold limits, Eqs. (7) and (10), of the pair resonance are reproduced by Eq. (12). For \( V \approx V_c \), Eq. (12) constitutes an approximate interpolation formula, due to the attachment of an energy-independent width \( \Gamma \) to the two-particle resonance.

We compare Eq. (12) with a single-particle resonance

\[
J_{\text{PR}}^{1PR}[V, \epsilon_d] = \frac{2e}{\hbar} \Gamma_L \Gamma_R \int \frac{d\epsilon}{(2\pi)^2} \frac{f(\epsilon - \epsilon_d V) - f(\epsilon + \epsilon_d V)}{(\epsilon - \epsilon_d)^2 + (\Gamma/2)^2}
\]

The qualitative difference between the two expressions arises from the appearance of the Fermi-liquid phase space factor \([ ((\pi T)^2 + (\epsilon - eV^2)^2) \] in the two-particle resonance Eq. (12). This phase space factor can be removed by taking two derivatives with respect to voltage of Eq. (12). In this way, we find the relation

\[
d^3 I/dV^3 \approx \frac{\Gamma_L (2\Gamma_R + \Gamma_L)}{(2\pi)^2} \frac{d}{dV} J_{\text{PR}}^{1PR}[2V, \epsilon_d - eV/2].
\]

In view of the known properties of the single-particle resonance, this result constitutes our principal prediction. For \( T \ll \Gamma \), Eq. (13) predicts a Lorentzian peak in \( d^3 I/dV^3 \) inside the Coulomb-blockade diamond. Importantly, at \( V = V_c \), both \( d^3 I/dV^3 \) and \( d^3 I_{\text{PR}}^{1PR}/dV^3 \) have the same order of magnitude \( \sim \Gamma/2(\hbar v_f^2) \). These results are illustrated in Fig. 4. Note that, for \( T \gg \Gamma \), Eq. (13) also predicts temperature broadening of the peak in \( d^3 I/dV^3 \).

**Discussion and conclusion.** Previously it was believed that in the course of cotunneling through a LS, electrons from the source arrive at the drain one by one. Here we demonstrated that there exists a well-pronounced, although more delicate, transport regime where two-electron processes (of opposite spin) contribute to the current. We emphasize that this regime is captured by the standard Anderson Hamiltonian (1).

Intriguingly, our reasoning is easily extended to regimes associated with \( N \)-particle ionization of the LS \((N > 2)\). These induce additional boundaries in the stability diagram Fig. 1 at even lower voltages \( eV < eV_c(N) < 2\epsilon_d/(2N - 1) \).

A naive estimate of the corresponding near-threshold behavior of the current gives \( \sim \theta(V - V_c(N))\frac{\Gamma}{(2N - 1)(eV - eV_c(N))^{2/2}} \). However, destructive interference between different sequences of \( N \)-electron transitions might lead to further reduction of the current.

Throughout this Letter, we considered an empty LS at zero bias (non-Kondo valley \( \epsilon_d > 0 \)). The analysis of the ionization process of the occupied LS (Kondo valley \( \epsilon_d < 0 \)) is entirely analogous, and differs only by the order of virtual transitions.

This work was supported by the DFG (No. Sfb 658, No. Spp 1243; F.v.O.), DIP (F.v.O. and Y.O.), ISF and BSF (Y.O.), MOST (Israeli-Korean S&T Cooperation; H.S.S. and Y.O.), KRF (No. 2005-070-C00065, No. 2006-331-C00118; H.S.S.), and NSF (Grant No. DMR-0503172; M.E.R.). One of us (F.v.O.) acknowledges hospitality by the Weizmann Institute (EU program No. RITA-CT-2003-506095).