On the current gap of single-electron transistors

Valentin V. Pogosov*, Eugene V. Vasyutin

Department of Microelectronics and Semiconductor Devices,
Zaporozhye National Technical University, Zhukovsky Str. 63, Zaporozhye 69064, Ukraine

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Effects of the single-electron tunneling and the Coulomb blockade in a cluster structure (the molecular transistor) are investigated theoretically. In the framework of the particle-in-a-box model for the spherical and disk-shaped gold clusters, the electron spectrum, the temperature dependence of the chemical potential and the residual charge are calculated. We show that the residual charge is equal to the non-integer value of elementary charge $e$ and depends on the cluster’s shape. The equations for the analysis of the current-voltage characteristic are used under conservation condition for the total energy of the structure taking into account the contact potential difference. Restrictions associated with the Coulomb instability of a cluster are introduced into the theory in a simple way. It is shown that the critical charge of the cluster in the open electron system is close to the residual charge. For single-electron transistors based on small gold clusters the current gap and its voltage asymmetry are computed. We demonstrate that the current gap exhibits non-monotonic size dependences, which are related to the quantization of the electron spectrum and the Coulomb blockade.

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I. INTRODUCTION

Metal granules, which are weakly coupled via tunnel barriers to electron reservoirs, are of considerable interest in physics of low-dimensional systems (see reviews [1, 2] and references therein).

The tunneling current flowing through two massive electrodes can be controlled, if a cluster is placed between them. At first sight, the probability of electron tunneling (and consequently a value of the current) should be much greater in the presence of a granule between the reservoirs, than in the case of its absence. However, an opposite behavior was observed in experiments for the spherical-like [3, 4, 5, 6] and disk–shaped [7, 8] clusters. Measured $I−V$ characteristics have a plateau of the zero current (a current gap).

In Refs. [3, 4, 5] the structure with two tunnel junctions (Fig. 1) was represented by a thick Au (111) film covered by the $d_c \sim 10 \text{ Å}$ thick dielectric layer (with the dielectric constant $\epsilon \approx 3$), on which the small spherical-like gold clusters were organized. The tungsten tip (with small curvature of surface) of STM microscope was covered by a gold film with $10^{3}$ A thickness. Therefore we can consider all the three electrodes (two of them with a flat surface) as being gold. Using the circuit approach of Ref. [9], the capacitances, tunnel resistances and a “residual” (fractional) charge $Q_0$ of granules were extracted as fitting parameters from the measured dependence $I(V)$.

Earlier, a similar STM (Pt/Ir-tip) measurement for such a structure ($d_c \sim 1.4 \text{ nm}, \epsilon \sim 2.7$) based on a gold islands with monatomic height $H \approx 0.25 \text{ nm}$ (disk-shaped clusters) was carried out in the works [4, 5].

The experiments demonstrated the following features of the $I(V)$ behavior:

1. The gap width of the zero conductance is approximately proportional to the inverse radius of the disks (Fig. 4 in Ref. [4]) and spheres (Figs. 1(c) and 2(a) in Ref. [4]). This does not allow one to establish unequivocally classical or quantum origin of the gap. On the other hand, out of the current gap, the steps of the staircase are clearly visible (Fig. 3 in Ref. [5] and Fig. 1(b) in Ref. [5]).

2. For a disk, the gap width varies non-monotonically

* Corresponding author: vpogosov@zntu.edu.ua
with alteration of the collector–cluster distance under the fixed emitter–cluster one (Fig. 3 in Ref. 8).

The possibility of a fractional charge at tunneling structures was discussed in the Refs. 1, 10. In the percolation systems it is supposed that the charge \( q_0 \) at the each granule has a soliton origin. The value of this charge was calculated numerically in Refs. 11, 12.

However, not much attention was paid to this problem, as well as the current gap origin on the \( I - V \) curves and its asymmetry. Perhaps, this problem is related to the fractional quantization (or fractional statistics), when the decoupling of the spin and the electron quantum numbers of a charge is important.

The aim of this work is the computation of the current-voltage characteristic of the three-electrode structure, whose central electrode is a metal cluster with different sizes and shapes.

The outline of this paper is as follows. In Sec. II we formulate the problem of the influence of the well-separated energy levels and charging energy on the resonant tunneling through a metal cluster, which is weakly coupled to two massive electrodes. Our main assumption is that the thermal energy exceeds the width of transmission resonance. The present approach describes the case of strong inelastic scattering of electrons in the clusters that corresponds to the full thermalization regime. We calculate electron spectrum for the wells of various shape, chemical electron potential and residual charge. This charge is a result of equilibrium with electron sea. We use the density-functional approach for determination of the total energy of metal cluster in an external electric field. Next, we estimate the critical surplus charge of the spheroidal cluster, which leads to the Coulomb instability for a nonzero applied voltage. In Sec. III, we consider electron transport through a metallic quantum dot that can be described by a means of master equation. The contact potential difference is taken into account. In Sec. IV we perform the numerical analysis of the \( I - V \) curves for various set of parameters. The current jumps are investigated in details for the tunneling structures based on the magic and non-magic clusters. The model allows one to determine the size of current gap and its asymmetry on a voltage.

II. PRELIMINARY ANALYSIS AND FORMULATION OF THE PROBLEM

We consider spherical gold clusters whose radii vary in the range \( R \approx 7 - 14 \, \text{Å} \), \( R = N_0^{1/3} r_s \Rightarrow N_0 = 100 - 600 \) (\( r_s = 3.01 \, a_0 \) is the electron density parameter, \( a_0 \) is the Bohr radius). Similarly for disks of monatomic thickness: \( R \approx 5 - 42.5 \, \text{Å} \Rightarrow N_0 \approx 14 - 10^3 \). We introduce the characteristic charging energy \( \varepsilon_C = e^2 / C \), where \( C \) is a cluster capacitance. For spheres and disks we obtain \( \varepsilon_C \approx 1.82 - 1.06 \) and \( 3.2 - 0.42 \, \text{eV} \), respectively. Temperatures of structures are \( T < 30 \, \text{K} \).

Let’s determine the electron spectrum in spherical and cylindrical wells (see Appendix A). For the above mentioned sizes, calculation in both cases gives the close values of the spectrum discreteness, \( \Delta \varepsilon_p \approx 1.2 - 0.3 \, \text{eV} \), nearby to highest occupied level \( \varepsilon_{\text{HO}} \) at \( T = 0 \). Thus, for the whole range of \( R \) in experiments 4, 5, 6, 7, 8 we have to deal with a set of open 0D systems (quantum dots). The resulting inequality,

\[ \bar{E}_C \approx \Delta \varepsilon_p \gg k_B T, \]

(1)

corresponds, apparently, to two coexisting structures at \( I - V \) curves: effects of the spectrum quantization and the Coulomb blockade. The current-voltage characteristic should represent a superposition quantum staircase with a step \( \sim \Delta \varepsilon_p / e \) and the classical Coulomb one of the electrostatic nature with a step \( \sim \bar{E}_C / e \) along a voltage. However, detailed measurements 4, 5, 6, 7 performed to date do not yield an unequivocal conclusion about the effect of electron quantization levels upon the \( I(V) \).

In our opinion, the discreteness of the spectrum actually determines the zero conductance gap of the \( I - V \) curves observed in 4, 5, 6, 7, 8. Let’s consider the problem step by step.

A. Structure in the absence of voltage

The left and right electrodes (emitter and collector) represent the electron reservoirs. Each reservoir is taken to be in thermal equilibrium. A continuum of states is assumed in reservoirs, occupied according to the Fermi-Dirac distribution

\[ f(\varepsilon_{e,c} + W_{e,c}) = \left\{ 1 + \exp\left[\left(\frac{\varepsilon_{e,c} + W_{e,c}}{k_B T}\right)^{-1}\right] \right\}^{-1}, \]

(2)

where \( W_0 > 0 \) is the work function for a semi-infinite metal. In all cases energy \( U_0 < \varepsilon < 0 \) is counted off from the vacuum level, \( U_0 < 0 \) is the position of conductivity band of a semi-infinite metal.

The electron chemical potential \( \mu \) of a cluster in a quantum case can be defined by the normalization condition

\[ \sum_{p=1}^{\infty} f(\varepsilon_p - \mu) = N, \]

(3)

where sum runs over all one-electron states, \( N \) is the total number of thermalized conduction electrons in a cluster (taking into consideration the surplus and lacking electrons), and

\[ f(\varepsilon_p - \mu) = \left\{ 1 + \exp\left[\left(\frac{\varepsilon_p - \mu}{k_B T}\right)^{-1}\right] \right\}^{-1}. \]

(4)

If the electron spectrum is known, from Eq. 3 it is possible to calculate \( \mu \) of \( \text{Au}_{N_0} \), where \( N_0 \) is the number of the conduction electrons of neutral clusters. The Fermi level of non-magic clusters coincides with a real level in a cluster. For the magic ones it lies between the energy terms. Figure 2 depicts the chemical potential
of some spherical clusters as a function of temperature. Predictably, the dependence is slack and is completely determined by the level hierarchy in dots, and also by the number of electrons. Calculations show, that the temperature gradient of chemical potential can be both the positive and the negative, and at some temperatures it can change a sign. Similar behavior $\mu(N, T)$ for magic clusters $Na_N$ have been reported in Ref. [15].

A contact potential difference appears between a cluster and electrodes (Fig. 1)

$$\delta \phi = (W_0 + \mu)/e.$$  \hfill (5)

An equilibrium is reached by the noticeable charging of a cluster since it capacitance is finite. If $|\mu| < W_0$, a cluster is charged positively by a charge $Q_0 = -e(N' - N_0) > 0$, where $N'$ is determined by the solution of the Eq. \ref{eq:charge} with replacement $\mu \rightarrow -W_0$ for a spectrum $\{\varepsilon_p\}$ shifted on $-e\delta \phi$, according to the Koopmans' theorem \cite{12}. In similar theories, the presence of a contact potential difference were neglected.

Thus, we have

$$Q_0 = C\delta \phi.$$ \hfill (6)

This expression differs from the definition of $Q_0$ in the orthodox theory (Eq. (29 b) in Ref. \cite{10}).

A quasi-classical approximation, $W_0 + \mu(R) = \mu_1/R$, $\mu_1 = 1.9 \text{ eV} \times a_0$ \cite{13}, gives $Q_0 \approx +0.07 e$. In a quantum case, it is necessary to make a replacement $\mu \rightarrow \varepsilon^{\text{HO}}$. Otherwise, when $|\mu| > W_0$ the cluster is charged negatively ($\mu \rightarrow \varepsilon^{\text{LU}}$).

The non-integer value of $Q_0$ (in terms of the elementary charge) is due to the fact that the electron wave functions are not well localized. Therefore, electrons cannot be interpreted as classical particles, and a fraction of an electron (and its charge) can be found in the other electrode \cite{1, 10}.

Value $Q_0 \approx +0.5 e$ better than the others corresponds to the Kuzmin’s and Likharev’s experiment (Fig. 2(b) in Ref. \cite{3}) in which the $I - V$ was measured for the structure of two electrodes (alloy Pb/Au) and granule In of radius $R \approx 100 \text{ nm}$ separated by the oxide films. It is interesting to estimate $Q_0$ by Eq. \ref{eq:charge}. As the work function of the alloy is unknown, using accordingly 4 and 3.8 eV for Pb and In, we obtain considerably distinguished quantity $Q_0 \approx +13.6 e$. However, assuming the exact quantity $Q_0 \approx +0.5 e$, it is possible to solve the inverse problem and to find a work function of the alloy: 3.8012 eV (instead of 4 eV for Pb).

B. Structure under voltage $V$

Between the emitter ($V = 0$) and the collector the positive voltage $V$ is applied. We consider a central electrode–granule in an external electric field. In a weak electric field approach we assume, that the ionic subsystem of a granule is not deformed, and the electronic “cloud”, generated by the own valence electrons, is deformed only.

The total energy of a granule is the functional of non-homogeneous electron concentration, $\mathcal{E}[n(r)]$. The functional contains a contribution responsible for the interaction of electrons and ions with an external field,

$$e \int [n(r) - n_i(r)](\mathbf{E} \cdot \mathbf{r}) \, d^3 r.$$ \hfill (7)

For simplicity, we suppose that the ion distribution $n_i(r)$ is spherically symmetric.

Let’s write down an electron distribution of a granule as

$$n(r) = n_0(r) + \delta n_1(r) + \delta n_2(r).$$ \hfill (8)

Here, $n_0(r)$ is the electron density of neutral cluster in the absence of the external field,

$$\int n_0(r) \, d^3 r = N_0,$$

$\delta n_1$ is the perturbation arising from the charging of granule, and $\delta n_2(r)$ is the next perturbation arising from the external field which responses for the polarization of a neutral granule,

$$\int \delta n_1(r) \, d^3 r = \Delta N, \quad \int \delta n_2(r) \, d^3 r = 0,$$ \hfill (9)

where $\Delta N > 0$ and $\Delta N < 0$ correspond to negatively and positively charged granule, respectively. We assume, that functions $n_0(r)$ and $n_1(r)$ are spherically symmetrical, and $n_2(r)$ is axially symmetrical. Then one can expand the $\mathcal{E}[n(r)]$ in the functional Taylor series down to the
second order of smallness with respect to $\delta n_1$ and $\delta n_2$,
\[ \hat{E}[n(r)] = \hat{E}[n_0(r)] + \sum_j \int \frac{\delta \hat{E}}{\delta n_j} \delta n_j \; d^3 r + \]
\[ \frac{1}{4} \sum_{j,k} \int \delta^2 \hat{E} \; \delta n_j(r) \delta n_k(r') \; d^3 r \; d^3 r' + \ldots \]
(10)

Here the functional derivatives are taken at $n(r) = n_0(r)$, and indexes $j$ and $k$ runs 1 and 2 according to the definition $\delta$. The zeroth-order expression $\hat{E}[n_0(r)] = \hat{E}_0$ is a total energy of a cluster before the charging ($\Delta N = 0$) and in the absence of the external field ($\hat{E} = 0$). The functional derivative
\[ \frac{\delta \hat{E}}{\delta n(r)} = \mu + e(E \cdot r), \]
(11)
where the constant $\mu$ is the chemical potential of electrons of a granule. For large clusters, $-\mu = W$ in the absence of charging and the external field.

Finally, in the semiclassical approximation, we get
\[ \hat{E} = \hat{E}_0 + \mu \Delta N - e\Delta N \eta V + (\Delta N)^2 \hat{E}_C / 2 - \alpha E^2 / 2 \]
(12)
(see Appendix B).

Solving separately the electrostatic problem for the same structure with fraction of the voltage $V > 0$ (Fig. 4), we obtain
\[ \eta = \frac{\epsilon_2 \epsilon_3 (d_c + \epsilon_1 L / 2 \epsilon_2)}{\epsilon_1 \epsilon_2 d_c + \epsilon_1 \epsilon_3 L + \epsilon_2 \epsilon_3 d_e} = \eta^+. \]
(13)

Here, $L \equiv 2R$, $H$ for a sphere of radius $R$ and a disk of thickness $H$, respectively, $\epsilon_1 \equiv \epsilon$, $\epsilon_2 = \epsilon_3 = 1$. Under Eq. 4 one can find the values $\eta^+ \lesssim 0.65$ and $\eta^+ \lesssim 0.55$ in experiments [3, 4, 5, 6, 7, 8] for the spherical-like and disk-shaped clusters, accordingly.

Now we examine the problem of critical surplus charges of a cluster in the presence of an external voltage. For convenience, further we use a contraction $n \equiv \Delta N$.

C. Coulomb instability of a cluster in electric field

It is necessary to note, that even the vanishing external electric field leads to the instability of a cluster because of the possibility of tunnelling of electrons. We assume, that a cluster relaxed in a metastable state over a period of time which is much smaller, than that between acts of tunnelling. As a result of the charging, the intrinsic mechanical “stress” leads to the “Coulomb explosion”. This problem was described in Ref. 13 for a single spherical cluster in absence of the field. Extending these results, one can write the following expression
\[ \mp \{ -\mu_{c,i} + |e\eta V| \} R / e + e / 2 \]
(14)
for the critical electronic or ionic charge in quasi-classical approximation. For the range $V = (0, 2V)$ we have:

i) $\eta \ll 1$. Transitions of electrons between the emitter and the cluster occur more often, than between the cluster and the collector, therefore the electrons are accumulated on the cluster. In this case their maximal number is
\[ n_{\max} \sim W_e R/e^2 + 1/2, \]
where $W_e = W_{e0} - \mu_{c1}/R$ and $n_{\max} \sim +2.5 - +6.5$.

ii) $\eta \approx 1$. Transitions of electrons between the cluster and the collector occur more often, than between the cluster and the emitter, therefore on the cluster the deficiency of electrons is observed. Using the ion work function, this number determines as
\[ n_{\min} = - (W_i + |e\eta V|) R / e^2 - 1/2, \]
where $W_i = W_{i0} - \mu_{c1}/R$ and $n_{\min} \approx -4 - -11$. Similarly, for $V = (-2, 0V)$ we have:

\begin{enumerate}
\item $n_{\min} \approx - W_i R / e^2 - 1/2 = -3.8 - -10.6.$
\item $n_{\max} = (W_e + |e\eta V|) R / e^2 + 1/2 \approx +3 - +8$.
\end{enumerate}

Below, the whole numbers $[n_{\max}]$ and $[n_{\min}]$ bound the summation in (14). The effect of spectrum quantization can change these numbers no more than in $\pm 1$ according to the first inequality in (14) (see Ref. 12).

Effective collision frequency of excited electrons in a cluster is defined as $\eta$.
\[ \tau_e^{-1} = \tau^{-1} + \nu_F R^{-1}, \quad \nu_F = (h/mr_e)(9\pi/4)^{1/3}, \]
(15)

where $\tau$ is a relaxation time in the bulk of the metal, caused by electron-electron collisions ($\tau \times 10^{14} = 6.23$ s for Au at $T = 75$ K [14]), and $\nu_F$ is the electron velocity at the Fermi surface in the bulk. The estimation performed in Ref. 24 gives a preferred electron collision on walls of a dot, therefore $\tau_e \approx R / \nu_F$. It leads to $\tau_e \Delta \varepsilon \approx (0.52 - 0.17) \eta$, i.e. to a broadening of levels.

During the resonant tunneling, the discreteness of the spectrum can be revealed only at low temperature (second of inequalities (14)).

The electron thermalization occurs much faster than acts of tunnelling. “New ” electrons fill up a number of own electrons, changing their distribution and, accordingly, the chemical potential. This state of the cluster will be a starting state for the next act of tunneling.

III. BASIC ENERGY AND KINETIC RELATIONS

We assume, that the total energy of all three electrodes $\hat{E}$ does not change during the tunneling. In the case of transition of $\Delta N$ electrons from the emitter to the granule (containing $n$ “surplus” electrons), we have from (12)
\[ \delta \hat{E} = - \delta N \varepsilon^2 + \delta N \varepsilon_p \]
\[ + \frac{(-e)^2}{2C} \left[(n + \delta N)^2 - n^2\right] - e\delta N \eta^+ V = 0. \]
(16)
In this equation we take into account that the electron ionizes from the level $\varepsilon_p$ on the emitter (whose capacitance is equal to zero) and then sticks to the level $\varepsilon_p$ in a granule with capacitance $C$.

By analogy with Ref. 21, using Eqs. 10 and 12 for $\delta N = 1$, and than taking into account a contact potential difference 5, for emitter–granule transition we have

$$\varepsilon_+ = \epsilon_p + \tilde{E}_C(n+1/2) - \epsilon_\eta^+ V,$$

where $\epsilon_p \equiv \varepsilon_p - e\delta \phi$. The arrow on the top indicates the energies which are determined by transfers according to Fig. 1. We suppose, that $n = n(V)$ and $n = 0$ at $V = 0$. However, the granule is charged by a $Q_0$ before voltage applied. Therefore, we assume that $n$ is the result of the applied voltage only.

For granule–emitter transition we have

$$\varepsilon_- = \epsilon_p + \tilde{E}_C(n-1/2) - \epsilon_\eta^+ V.$$  

Similarly, for the granule–collector and collector–granule transitions we have

$$\varepsilon_- = \epsilon_p + \tilde{E}_C(n+1/2) + e(1-\eta^+) V.$$  

Here the upper/under arrows at the left correspond to the following signs on the right. Independently of $n$ the relation

$$\varepsilon_+ - \varepsilon_- = \tilde{E}_C = \varepsilon_+ - \varepsilon_-$$

takes place. It agrees with well-known quasiclassical relation for clusters, IP – EA = $\tilde{E}_C$ (see, e.g. Ref. 13). Eqs. 17 – 19 represent a “gold rule” for transitions.

The tunneling of a single electron through barriers is determined by the tunnel rates $\Gamma_0$ which depend on the junction geometry and the voltage fraction $\eta$. In general, their evaluation is far from a trivial problem 2, 10. We assume that they are small and the temperature is not too low, i.e.

$$k_B T > h(\Gamma_0 + \Gamma_e) \ll \min\{\Delta \varepsilon_p, \tilde{E}_C\}.$$

By analogy with the theory of Ref. 12, we introduce the partial tunneling rates from electrodes to a granule

$$w_n^0 = 2 \sum_p \Gamma(\varepsilon^2) f(\varepsilon^2 + W_0^c) [1 - f(\varepsilon^2 - \mu_C^c)],$$

and from a granule to the electrodes

$$w_n^e = 2 \sum_p \Gamma(\varepsilon_-) f(\varepsilon_- + W_0^-) [1 - f(\varepsilon_- - \mu_C^-)].$$

where the factor 2 takes into account the spin degeneration of levels in electrodes. In view of the applied voltage (and charging for a granule) the spectrums (see Eqs. (17) – (19)) and the chemical potentials are shifted in distributions 2 and 41

$$W_0^- = W_0^c = \mu - e\delta \phi + \tilde{E}_C(n+1/2) - \epsilon_\eta^+ V,$$

$$\mu_C^- = \mu - e\delta \phi + \tilde{E}_C(n\pm1/2) + e(1-\eta^+) V, \quad W_0^c = W_0^c + eV.$$

As the first approximation of the perturbation theory 12, for small $V$, $\mu$ is determined not only by the formal shift of the well depth, but also by the number of conduction electrons in the state ($N = N_0 + n_q, n_q = n + [Q_0/e]$). The use of the chemical potentials is correct in a quasi-equilibrium state, i.e. when the intervals between acts of tunneling are much longer than the relaxation time of a granule. It is also supposed, that the external field and the Coulomb blockade do not remove degeneration of levels. In this case, at $T = 0$, probabilities 21 – 24 will be nonzero for the intervals:

$$\mu_C^- \leq \varepsilon_- \leq -W_0^- \leq \varepsilon_+ \leq \mu_C^-;$$

$$\mu_C^- \leq \varepsilon_- \leq -W_0^- \leq \varepsilon_+ \leq \mu_C^-.$$

Let’s denote the total electron transition rates to a granule and back on electrodes, as

$$w_n^e = w_n^e + w_n^-,$$  

and from a granule to the electrodes

$$w_n^- = w_n^- + w_n^-.$$

In the limit of weak tunneling, the probability $P_n$ of the finding of $n$ for the above mentioned electrons at central electrode is defined by the master equation 10

$$\tilde{P}_n = w_n^{out} P_{n+1} + w_n^{in} P_{n-1} - (w_n^{in} + w_n^{out}) P_n.$$  

The requirement of the stationarity, $\dot{P}_n = 0$, gives the recurrent relation

$$P_{n+1} = P_n w_n^{in} / w_n^{out}.$$  

The dc current flowing through a quantum granule (with restriction on its instability 14), is determined as

$$I = -e \sum_{n_{\min} < 0} P_n (w_n^e - w_n^-) = -e \sum_{n_{\max} > 0} P_n (w_n^e - w_n^-).$$  

Let’s consider an exotic case of the “strong quantization” for electron spectrum 14:

$$\Delta \varepsilon_p \gg \tilde{E}_C.$$  

This regime is hypothetically reached by a significant increase of the cluster capacitance (the cluster shape must be changed to the needle-like or disk-like one under the
condition that its volume is fixed (see, e.g. Ref. 13, experiments with disks and nanowires). Thus the residual charge \( Q_0 \) in (9), which provides a contact potential difference, is proportional to the capacitance and can have large magnitude. When the voltage is applied, the charge, which is caused by the transferring surplus electrons, is much less than \( Q_0 \). Therefore it insignificantly influences the cluster energetics. In reality, the inequality \( \Delta \varepsilon_p \gg \tilde{E}_C \) is not possible for the atomic chain. Nevertheless, this case is useful from the methodical point of view to analyze the current gap of \( I - V \) characteristics.

As an assumption, we use the fixed tunnel rates at the Fermi level in the emitter. It is correct for the small voltages, \( eV \ll W \). Neglecting in (17) and (18) terms \( \sim \tilde{E}_C \), it is easy to obtain the result, similar to Ref. 16:

\[
I = I_0 \sum_p \left[ f(\varepsilon^c + W_p^c) - f(\varepsilon^c + W_p^\tilde{c}) \right],
\]

where \( I_0 = 2e\Gamma^e\Gamma^c/(\Gamma^e + \Gamma^c) \). At \( T \rightarrow 0 \), it is convenient to write Eq. (28) as a "combination" of the staircase functions:

\[
I/I_0 \rightarrow \sum_p \left[ \theta(\varepsilon_p + W_0) - \theta(\varepsilon_p + W_0^\tilde{c}) \right],
\]

where for shifted spectrums in the emitter and the collector the following notations are introduced: \( \varepsilon_p \equiv \varepsilon_p - e\eta^+V \) and \( \varepsilon_p^\tilde{c} = \varepsilon_p + e(1 - \eta^-)V \).

Let’s remind, that the expressions in this section are written down for \( V > 0 \). In the case \( V < 0 \), the \( I(V) \) can be received, if we set \( V = 0 \) on a collector and \( V > 0 \) on the emitter. Now for Eqs. (19), (17), (19) we have

\[
\eta^- = \frac{\varepsilon_2\varepsilon_3(\varepsilon_1d_e/\epsilon_3 + \varepsilon_1L/2\varepsilon_2)}{\varepsilon_1\varepsilon_2d_e + \varepsilon_1\varepsilon_3L + \varepsilon_2\varepsilon_3d_e},
\]

\[
\varepsilon^c = \varepsilon_p + \tilde{E}_C(n \pm 1/2) - e(1 - \eta^-)V,
\]

\[
\varepsilon\tilde{c} = \varepsilon_p + \tilde{E}_C(n \mp 1/2) + e\eta^-V.
\]

Also using

\[
W_p^\tilde{c} \equiv W_0^\tilde{c}, \quad \tilde{\mu}_C = \mu - e\delta\phi + \tilde{E}_C(n \pm 1/2) - e(1 - \eta^-)V,
\]

\[
\tilde{\mu}_C = \mu - e\delta\phi + \tilde{E}_C(n \mp 1/2) + e\eta^-V, \quad \tilde{W}_p = W_0^c + eV
\]

and \( I \rightarrow -I \), for derived dependence \( I(V) \) at \( V > 0 \) it is necessary to make mirror reflection relative to \( V = 0 \) on area \( V < 0 \). In such a case, for example, value of the \( I_0 \) in Eq. (29) on \( V > 0 \) differs from \( I_0 \) on \( V < 0 \) since the tunnel rates are different.

In the general case, for calculation of \( I - V \) (27) it is necessary to know probabilities \( P_n \). Their statistical determination is a complicated problem 22. In the experiments, the size of the cluster and its location are known only approximately, therefore detailed calculations of \( P_n \) are not suitable. Using the recurrent relations we can find the ratios \( P_{n \neq 0}/P_0 \).

![FIG. 3: The calculated size dependence of the residual charge \( Q_0 \) for the structure based on the clusters of various shape: sphere (dotted line) and disk (solid line). For illustration, \( Q_0 \) of magic sphere Au_{439} is marked as ×.](image

### IV. APPLICATION AND DISCUSSION

The cluster is charged positively before the application of voltage. The size dependence of a charge \( Q_0(N_0) \) for referred gold clusters is demonstrated on Fig. 4. For the above mentioned sizes of spherical clusters, \( Q_0 < e \). However, \( Q_0 \) can accept a values larger then \( e \) for the disks of monatomic thickness. Additional charging of the cluster can lead to the Coulomb instability, because the quantity \( Q_0 \) is close to a critical charge 13.

Moreover, cluster’s anomalous electrostriction is possible as a result of the charging 24.

Setting the collector–granule distance \( d_c \), parameter \( \beta = \Gamma^e/\Gamma^c \) and using the recurrent relation (20) for Eq. (27), it is possible to calculate the reduced dc current \( I \equiv I/(eP_0\Gamma^e) \). We do not evaluate separately the threshold voltages, in our scheme it appears automatically.

The results of calculations of the \( I - V \) characteristics for the structures Au/Au_{439}/Au, based on spherical clusters, are presented in Fig. 4. For completeness of analysis, the voltage behavior of the reduced probabilities \( P_n(V) \equiv P_n/P_0 \) and the stream \( \Delta\omega_n = \tilde{\omega}_n^c - \tilde{\omega}_n^\tilde{c} \) are given also.

The current jumps are stipulated by the jumps of \( \tilde{P}_{-1}(V) \) and \( \Delta\omega_0(V) \), because the current is formed by their product. Making use of the equality \( \tilde{I} \equiv \sum_n \tilde{I}_n(V) \) in accordance with Eq. (27) one can fix also the “threshold” values \( n \).

As one can surmise, the jump of probability \( \tilde{P}_{-1}(V) \) causes the current jump in the threshold voltage \( V_{0+} \). Note that the jumps of the stream \( \Delta\omega_0 \) at \( V = V_{0+} \) and \( V_{0-} \) are determined by jumps of \( \tilde{P}_{-1}(V) \) or \( \Delta\omega_0 \), respectively.
FIG. 4: The current–voltage curves (solid lines) and its components, calculated from Eq. (27) \((\beta = 1, \eta^+ = 0.1, T = 30 \text{ K})\). \(\Delta \omega_n(V)\) is given in \(\Gamma^e\) units.

As is seen from Fig. 4, the role of partial current components (with \(|n| > 1\)) grow with increasing \(N_0\). The charging leads to energy shift of spectrum according to Eqs. (17) – (19). Thus the different parts of a spectrum are involved during tunneling. The electron chemical potential of magic cluster \(\text{Au}_{40}\) does not coincide with a energy level at a zero voltage.

The current gap width \(\Delta V_g = V_{0+} + |V_{0-}|\) in all cases is determined by values \(n = 0, -1\), and the boundaries can be defined by the position of lowest unoccupied level as

\[
|V_{0\pm}| = \frac{\tilde{E}_C/2 + \Delta \varepsilon}{(2 - \eta^\pm)},
\]

where \(\Delta \varepsilon = \{\mu_p - \varepsilon^{L_U}\text{ and } 0\}\) for the magic and non-magic clusters, accordingly. The probability \(P_{-1}\) prevails over \(P_{+1}\), because the “granule–collector” stream is more than a “emitter–granule” one and the granule is charged positively (i.e. \(n < 0\)).

Within the applied voltage the \(I – V\) characteristics versus \(\eta^+\) are shifted to the right and the gap width decreases a little. The calculated \(I – V\) curves of the structure \(\text{Au/Au}_{600}/\text{Au}\) for fixed \(\eta^+\) and different \(\beta\) are shown in Fig. 5. In this model, the current gap is practically independent on \(\beta\), however, the current jumps are strongly dependent on the value of \(\beta\), which, in its turn, has no influence on threshold voltages.

In order to illustrate our results, in Fig. 6 we compare the size dependences \(\Delta V_g(N_0)\) calculated from Eqs. (27) and (28) for spheres and disks. The largest quantities \(\Delta V_g\) correspond to the magic granules, for which \(\Delta \varepsilon \neq 0\). For the case of “strong quantization” the size of a current gap for non-magic clusters is equal to zero explicitly, because the emitter Fermi level is in line to the closed levels in cluster. Calculations demonstrate the non-monotonic dependence \(\Delta V_g(\eta^+)\). These results shows also, that a charging leads to the growth of a gap.

The actual forms of current gap for the structure based on magic disk \(\text{Au}_{178}\) \((R \approx 3.5 \text{ nm})\) are plotted in Fig. 7. Our calculations show that the dependence \(\Delta V_g(\eta^+)\) is slightly non-monotonic. However, in experiments the gap varied as \(0.8 \rightarrow 0.4 \rightarrow 0.7 \text{ V}\) for the cyclic variation of \(d_c \approx 1 \rightarrow 2 \rightarrow 1 \text{ Å}\). The reasons of such considerable difference, apparently consist in the following effects: broadenings of levels, amplifications nonlinearities in the strong electric field, and in energy dependence of tunneling rates. At high rates the capacitance ceases to be classical and can strongly grow \((\tilde{E}_C \rightarrow 0)\) showing non-monotonic dependence from \(\Gamma^e\). It means, that in a reality we deal with the intermediate cases (between limiting estimations from Eqs. (27) and (28) in Fig. 7). Only in these situations the observed behavior of gap width is more or less clear.

Let’s discuss other features of the tunnel construction. In spite of the fact that the emitter and a collector are made of one material, the chemical potentials of electrons

FIG. 5: Calculated \(I – V\) curves at \(T = 30 \text{ K}\) for structure based on spherical clusters. For presentation the curves are shifted slightly on a vertical.
are not equal to each other: the emitter is represented by a thick film of Au (111), and a collector is a polycrystal of Au. Their work functions are different [27]. We assume also that $W < W_0$ for low-dimensional systems [13]. Except for it the emitter is covered with a dielectric film, that also influences a electron work function. We can estimate this contribution.

Proceeding from indirect experimental measurements [28], the work function decreases with growth dielectric constant $\epsilon$ of coating. The calculations of the electron work function $W_d$ for cylindrical nanowires in a dielectric confinement are done in Ref. [29]: $W_d$ decreases approximately on 20% at magnitude as $\epsilon$ rise from 1 to 4. The basic contribution thus can be related to the change of electrostatic dipole barrier which contribution to a work function of system gold–vacuum makes up to 30% [27]. Hence, this contribution also makes a upper limit of the change of $W_d$ for metal–dielectric–vacuum system. Owing to $W_d < W_0$ the inequality $W > W_d$ is possible, that leads to negative charging of the cluster before the application of voltage. The film–cluster contact also will change the cluster energetics. At last, the metal-nonmetal transition for gold cluster can appears

FIG. 6: The current gap calculated from Eq. (27) ($d_c = 2\text{Å}$ and $\beta = 10$). Solid lines show the gaps calculated from Eq. (28) for the case of “strong quantization”.

V. SUMMARY

In this paper, we presented an approach for the calculation for the $I − V$ characteristics of SET based on the metal clusters.

In the framework of the particle-in-a-box model for the spherical and disk-shaped gold clusters, the electron spectrum was calculated. In this model, the work function of clusters is smaller that of semi-infinite metal electrodes. It resulted in the appearance of a contact potential difference between a cluster and electrodes. Residual charge is equal to non-integer elementary charge $e$, which corresponds to the charge of cluster in chemisorption regime. For the small spherical clusters, positive charge is less than $e$. However, this charge can accept a values larger than $e$ for the disks of monoatomic thickness. Additional charging of the clusters can lead to the Coulomb instability, because it is close to a critical charge. The charging results in the energy shift of the spectrum.

The current-voltage characteristics were analyzed taking into account the contact potential difference. The approach was applied to calculate the trapped offset charges that determine the transport behavior of molecular-like structures. For single-electron transistors based on the small gold clusters the current gap and its voltage asymmetry were computed. The largest quantities gap correspond to the magic granules. For the case of “strong quantization”, the size of a current gap for non-magic clusters is equal to zero explicitly, because the emitter Fermi level is in line to the closed levels in cluster. The results shows, that a charging leads to the growth of a gap. The evaluations demonstrated a slightly non-monotonic dependence (in comparison with the experiments) of the gap size from cluster – collector distance. At high tunneling rates the capacitance ceases to be classical and must
strongly change.

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APPENDIX A: ELECTRON SPECTRUM IN CYLINDRICAL-LIKE CLUSTERS

As an approximation, the profile of the one-electron effective potential in the cluster can be represented as a potential well the depth $U_0 < 0$. The three-dimensional Schrödinger equation for a quantum box can be separated to the one-dimensional equations. The spectrum of wave numbers in a spherical and cylindrical potential wells are determined from the continuity condition of a logarithmic derivative of the wave function on the boundaries.

For a disk of radius $R$ and thickness $H$ it is necessary to solve the equation:

$$k_{nm} I'_m(k_{nm}R) = \tau_{nm} K'_m(\tau_{nm}R)$$

where $I_m$ is the Bessel function, $K_m$ is the McDonald function, the stroke denotes a derivative over an argument, $k_{nm} = \sqrt{k_0^2 - \tau_{nm}^2}$, $\tau_{nm} = \sqrt{2m_e U_0}/c$, and $m_e$ is the electron mass. The $n = 1, 2, 3...$ number the roots of the Eq. for the fixed $m = 0, \pm1, \pm2...$

Using the perturbation theory, the finite well problem can be reduced to the infinite well one:

$$k_{nm} = k_{nm}^{(0)} + k_{nm}^{(1)} + ..., \quad |k_{nm}^{(1)}/k_{nm}^{(0)}| \ll 1,$$

where $k_{nm}^{(0)}$ defines the spectrum of infinitely depth well. Numbers $k_{nm}^{(0)}$ are determined by solutions of the equation

$$I_m(k_{nm}^{(0)}R) = 0.$$

In the first approximation we have

$$k_{nm}^{(1)} = \frac{k_{nm}^{(0)} K_m(\tau_{nm}^{(0)}R)}{R \tau_{nm}^{(0)} K'_m(\tau_{nm}^{(0)}R)}.$$

The estimation gives $k_{nm}^{(1)} < 0.07 k_{nm}^{(0)}$, confirming sufficient accuracy of the theory.

Quantization of the wave vector $k_s$ along the cylinder axis is determined by the solution of the equation:

$$k_s H = s \pi - 2 \arcsin(k_s/k_0),$$

where $s$ is the integer number. Neglecting the area near cylinder edges, the energy spectrum is calculated by a simple way as follows

$$\varepsilon_{nms} = U_0 + \frac{\hbar^2}{2m_e} (k_{nm}^2 + k_s^2).$$

In addition to the spin degeneration, there is a double degeneration with respect to the sign of index $m$, since $k_{n,m} = k_{n,-m}$. Further, the spectrum of cluster is denoted as $\varepsilon_{np}, p = 1, 2, 3...$ is the number of an one-electron state. All levels are numbered in order to increase energies.

APPENDIX B: ENERGY OF CLUSTER IN EXTERNAL ELECTRICAL FIELD

Using spherical coordinates, we remove the center point $z = 0$ in a center of a granule, and we direct a $z$ axis from a collector to the emitter under the conservation the potential difference between them. Then an electric field $E = E\hat{z}$, where $\hat{z}$ is a unit vector along an $z$ axis.

As the surplus charge is effectively distributed over a surface, it is quite reasonable to use

$$\delta n_1(r) = A \delta_D(r - R),$$

where $\delta_D(r - R)$ is the Dirac delta—function. In spite of the fact that the form $\delta_D$ corresponds to the total screening of a surplus charge inside a granule, this form is rather convenient for the calculations. Then, we use the linear response approach (see, e.g. Ref. [17])

$$\delta n_2(r, \theta) = Y(r) E \cos \theta.$$

The constant $A$ in Eq. and spherically symmetric function $Y(r)$ in are determined from the normalization condition and a global minimum of the functional, $\delta \tilde{E} [n(r)] \rightarrow 0$.

One of the terms, interesting for us, is

$$-e \int \delta n_1(r) \varphi(z) \, d^3r,$$

where $\varphi$ is an external electrostatic potential. In the case of $V > 0$ and vacuum collector-emitter space $\varphi(z) = V(z - d_e - L/2)/d$, where $d = d_e + L + d_c$.

After the integration in spherical coordinates, the term, which is proportional to $z$, vanishes, and, as a result, we have $-e \Delta V \eta V$, $\eta$ is a fraction of a voltage. Other three terms

$$\int \frac{\delta n_1(r) \delta n_2(r') + \delta n_1(r) \delta n_1(r') + \delta n_2(r) \delta n_2(r')}{|r - r'|} \, d^3r \, d^3r'$$

give a basic contribution to the second order of expansion. The first integral in Eq. vanishes after the integration on corners, second and the third ones were calculated earlier at the definition of the ionization potential (see, e.g. Ref. [12]) and polarizabilities of a cluster $\alpha = -(4\pi/3) \int_0^\infty Y(r) r^3 dr \equiv R_{\rm eff}^3$. Finally we obtain Eq. [12].
[1] K. K. Likharev, Proc. IEEE 87 606 (1999).
[2] J. von Delft and D. C. Ralph, Phys. Rep. 345 61 (2001).
[3] L. S. Kuzmin and K. K. Likharev, JETP Lett. 45, 495 (1987).
[4] T. Ohgi, H.-Y. Sheng, Z.-C. Dong, H. Nejoh and D. Fujita, Appl. Phys. Lett. 79 2453 (2001).
[5] T. Ohgi and D. Fujita, Phys. Rev. B 66 115410 (2002); Physica E 18 349 (2003).
[6] T. Ohgi, Y. Sakotsubo, Y. Ootuka and D. Fujita, Appl. Phys. Lett. 84 604 (2004).
[7] B. Wang, X. Xiao, X. Huang, P. Sheng and J.G. Hou, Appl. Phys. Lett. 77 1179 (2000).
[8] J. G. Hou, B. Wang, J. Yang, X. R. Wang, H. Q. Wang, Q. Zhu and X. Xiao, Phys. Rev. Lett. 86 5321; 87 049903 (2001).
[9] A. N. Korotkov and Yu. V. Nazarov, Physica B 173 217 (1991).
[10] M. Ya. Azbel’, Phys. Rev. B 59 8049 (1999).
[11] D. M. Kaplan, V. A. Sverdlov and K. K. Likharev, Phys. Rev. B 68 045321 (2003).
[12] R. Parthasarathy, X.-M. Lin, K. Elteto, T. Rosenbaum and H.M. Jaeger, Phys. Rev. Lett. 92 076801 (2004).
[13] V. V. Pogosov, V. P. Kurbatsky and Vasyutin E. V., Phys. Rev. B 71 195410 (2005).
[14] S. P. Gubin, Yu. V. Gulayev, G. B. Khomutov, V. V. Kislov, V. V. Kolesov, E. S. Soldatov, K. S. Sulaimankulov and A. S. Trifonov, Nanotechnol. 13 185 (2002).
[15] L. I. Kurkina and O. V. Farberovich, Sol. St. Commun. 98 469 (1996).
[16] D. V. Averin, A. N. Korotkov and K. K. Likharev, Phys. Rev. B 44 6199 (1991).
[17] D. R. Snider and R. S. Sorbello, Phys. Rev. B 28 5702 (1983).
[18] D. M. Wood and N. W. Ashcroft, Phys. Rev. B 25 6255 (1982).
[19] A. V. Sokolov, Optical Properties of Metals. Moscow, Nauka (1961).
[20] V. P. Kurbatsky and V.V. Pogosov, JTP Lett. 26 84 (2000).
[21] C. W. J. Beenakker, Phys. Rev. B 44 1646 (1991).
[22] O. Millo, D. Katz, D. Steiner, E. Rothenberg, T. Mokari, M. Kazes and U. Banin, Nanotechnol. 15, R1 (2004).
[23] M. Brack, O. Genzken and K. Hansen, Z. Phys. D 21 65 (1991).
[24] V.V. Pogosov, Solid State Commun. 81 129 (1992).
[25] J. Wang, H. Guo, J.−L. Mozos, C. C. Wan, G. Taraschi and Q. Zheng, Phys. Rev. Lett. 80 4277 (1998).
[26] J. König and H. Schoeller, Phys. Rev. Lett., 80 4277 (1998).
[27] V.V. Pogosov and O. M. Shstepea, Ukr. Phys. J. 47 1065 (2002); [cond-mat/0310176].
[28] A. Modinos, Field. Thermionic and Secondary Electron Emission Spectroscopy, Plenum Press 1984.
[29] A. N. Smogunov, L. I. Kurkina, S. I. Kurganskii and O. V. Farberovich, Surf. Sci. 391 245 (1997).
[30] H.-G. Boyen, A. Ethirajan, G. Kastle, F. Weigl, P. Ziemann, G. Schmid, M. G. Garnier, M. Buttner and P. Oelhafen, Phys. Rev. Lett. 94 016804 (2005).