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RENORMALIZATION OF THE COULOMB LAW IN ANOMALOUS ELECTRON TRANSPORT WITH GIANT CURRENT DENSITY AT ROOM TEMPERATURE

V. SERGENTU¹, I. TIGINYANU², V. URSAKI¹

¹Institute of Applied Physics of the Academy of Sciences of Moldova, Academy str. 5, MD-2028
Chisinau, Moldova, E-mail: vsergentu@yahoo.com

²Institute of Electronic Engineering and Nanotechnology of the Academy of Sciences of Moldova,
Academy str. 3/3, MD-2028 Chisinau, Moldova, E-mail: tiginyanu@asm.md

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Abstract. We propose an explanation of anomalous electron transport with giant current density at room temperature as a manifestation of high-temperature superconductivity in artificial periodic lattices of metallic nanospheres. The superconductivity is caused by emergence of strongly bound electron pairs for the electron states inside these spheres. This phenomenon is a consequence of the renormalization effect of the Coulomb law in a system of nanoobjects.

Key words: nanogranular materials, Coulomb law, Bose condensation, giant current density.

1. INTRODUCTION

The technical exploitation of nanogranular materials (NGM) allows many ground breaking applications for miniaturized and macroscopic structures and systems [1]. One of the fascinating phenomena in NGM is the anomalous electron transport with giant current density at room temperature. Among the most important properties of this phenomenon one can mention the following: (i) the NGM represents a spatially periodic or quasi-periodic system of metallic nanospheres with the diameter from 2 nm to 4 nm; (ii) current densities as high as 2 MA/cm² to 100 MA/cm² have been observed at room temperature; (iii) the phonon oscillations can not basically cause the emergence of Cooper pairs. We suggest that the phenomenon of giant current densities in NGM can be understood as a manifestation of the high temperature superconductivity [2, 3]. The superconductivity is basically superfluidity [4] of charged bosons in external fields [5, 6]. Representing charge carriers *e.g.* in metals, conduction electrons can form stable pairs in certain conditions. These pairs are in fact bosons from which a

boson condensate is formed which determines the property of superfluidity. Note that the phenomenon of superfluidity/superconductivity is realized even with a small part of the substance being in the condensate state. The Coulomb interaction prevents the formation of pairs, but it is strongly attenuated by the Debye screening. The electron-phonon interaction in ordinary metals with a high specific resistivity can be a reason for the formation of bound pair consisting of electrons with opposite spins (Cooper pair) [7]. Since the electron-phonon interaction in normal metals is weak, the binding energy of Cooper pairs is low and superconductivity manifests itself only at very low temperatures. However, the direct Coulomb interaction between charge carriers can lead in certain conditions to the formation of bound electron pairs. The excitons can produce a superfluid Bose-Einstein condensate at very high excitation levels by a strong electromagnetic field [8, 9]. At the same time, the excitons are neutral particles and do not manifest the property of superconductivity. It is known that in conventional superconductors even a low current creates a critical magnetic field which destroys the electron pairs and the phenomenon of superconductivity disappears. By using composite materials from conventional superconductors and normal conductors one can significantly increase the critical magnetic field [10].

The electron-electron Coulomb interaction in usual bulk materials can be a reason of the Mott metal-insulator transition [11]. A correlation between such transitions and the superconductivity has been revealed in granular high-temperature superconductors [12]. The existence of charge density wave in combination with Mott metal-insulator transition can be a reason of high-temperature superconductivity in bulk materials [13].

It was demonstrated that in a system of nano-objects (nanocylinders) pure electric modes can emerge in the limit of zero frequency which were called ultrashort modes [14, 15]. These modes do not exist in individual nano-objects, and they are in fact photonic crystal modes. The existence of ultrashort electric-type modes is indicative of a significant restructuring of that part of electrical interaction between the charges in a nanocylinder system which is usually associated with longitudinal fields [16]. It is known that the Coulomb law, *i.e.* the attraction of charges of opposite sign and the repulsion of charges of the same sign, is the main phenomenon of the theory of charge interaction in the limit of low frequencies. Each charged particle participates in the creation of the electric field potential

$$\Phi(\vec{r}) = \int \Pi(\vec{r}, \vec{r}') \Omega(\vec{r}') d\vec{r}' , \quad (1)$$

which creates a force field acting on the charges [$\Omega(\vec{r})$ is the charge density].

The function $\Pi^{(\text{Coulomb})} \sim |\vec{r} - \vec{r}'|^{-1} > 0$, *i.e.* it is positive. Due to this fact, the spatial periodically variable distribution of charges in the medium will tend to return to a uniform stable distribution, to which a wave vector $h \equiv 0$ corresponds. However, the existence of ultrashort modes $h \neq 0$ indicates that the spatial periodically

variable distribution of charges will be quite stable inside the nano-object system. This circumstance can be understood assuming that the law of charge interaction is significantly changed. We believe that under certain conditions the function $\Pi(r, r')$ changes its shape so that the charges of the same sign could attract to each other, while the charges of opposite sign could repulse each other for some distributions of charges $\Omega(r)$ containing $\hbar \neq 0$. Therefore, a significant modification or renormalization of the Coulomb law can occur.

The combination of nanomedia characterized by periodically variable parameters in the space with media containing free charge carriers opens possibilities for the creation of fundamentally new materials and devices. In this paper, we demonstrate this statement on the instance of a system of metallic nanospheres. We show that the modified Coulomb law can be a reason of the formation of stable electronic pairs, which are characteristic for the high-temperature superconductivity.

2. MATHEMATICAL MODEL

We will consider a system of metallic nanospheres immersed in vacuum and arranged in an infinite cubic lattice with the lattice constant a , it being interacting with the electromagnetic field in the limit of very low frequencies $\omega \ll (2\pi c/a)$. It follows from the Maxwell equations [17] that this case for a non-magnetic metal is described by the following equation:

$$\hat{\mathfrak{R}}\Phi(\vec{r}) = -\Omega(\vec{r})/\varepsilon_0, \quad (2)$$

for the potential and electric field $\vec{E}(\vec{r}) = -\nabla\Phi(\vec{r})$ ($\vec{H}(\vec{r}) \equiv 0$). Let us use the following notations:

$$\hat{\mathfrak{R}} = \hat{\mathfrak{S}} + \hat{\mathfrak{T}}, \quad (3)$$

$$\hat{\mathfrak{S}}\Phi(\vec{r}) = -\text{div}(\text{grad}(\Phi(\vec{r}))) + \Phi(\vec{r})/L_{sc}^2, \quad (4)$$

$$\hat{\mathfrak{T}}\Phi(\vec{r}) = -\Phi(\vec{r})(1 - \mathfrak{G}(\vec{r}))/L_{sc}^2. \quad (5)$$

The electrostatic screening length of the metal L_{sc} can be estimated according to the formula [18]

$$L_{sc} \propto \sqrt{\varepsilon_0 E_{sc} / e^2 n_0}, \quad (6)$$

where e is the electron charge, n_0 is the free electron concentration, E_{sc} is a parameter with dimensions of energy. This parameter equals to Fermi energy E_F in the case of a pure Fermi distribution of electrons. In the case of a non-Fermi (Maxwell or Bose) distribution, it will be equal to $k_B T$, where T is the temperature

and k_B is the Boltzmann constant. Since we assume the occurrence of the Bose condensation in the system, E_{sc} can take even lower values [19].

The spatial distribution of $\mathfrak{G}(\vec{r})$ in the vicinity of the coordinate origin is given by the value of

$$\mathfrak{G}(\vec{r}) = \theta(R - r), \quad (7)$$

where θ is the step function, R is the nanosphere radius. Our goal is to determine the Green's function for (2)

$$\Pi(\vec{r}, \vec{r}') = \int \Phi_{\vec{k}}^*(\vec{r}') \Phi_{\vec{k}}(\vec{r}) / \mathfrak{R}(\vec{k}) d^3k, \quad (8)$$

(in fact this is a modified Coulomb law for the potential), where $\mathfrak{R}(\vec{k})$ and $\Phi_{\vec{k}}(\vec{r})$ are the eigenvalues and eigenfunctions of the operator $\hat{\mathfrak{R}}$, satisfying the usual orthogonality relation $\int \Phi_{\vec{k}}^* \Phi_{\vec{k}'} d^3r = \delta(\vec{k} - \vec{k}')$. Because (8) can not be found in a general case, we will use the perturbation theory, assuming that the operator $\hat{\mathfrak{R}}$ is divided into the main term $\hat{\mathfrak{S}}$ and the perturbation $\hat{\mathfrak{T}}$.

The eigenfunctions and eigenvalues of the operator $\hat{\mathfrak{S}}$ are well known:

$$\begin{aligned} \Phi_{\vec{k}}^{(0)}(\vec{r}) &= \exp(i\vec{k}\vec{r}) / (2\pi)^{3/2}, \\ \mathfrak{S}(\vec{k}) &= k^2 + 1/L_{sc}^2. \end{aligned} \quad (9)$$

Then, the general Green's function is presented in the form of a series in the small parameter $\hat{\mathfrak{T}}$ in the perturbation theory of Green's function of Schrödinger-Poisson system [20]

$$\Pi = \Pi^{(0)} + \Pi^{(1)} + \Pi^{(2)} + \dots, \quad (10)$$

from which we will use only the first two terms for simplicity. The choice of $\hat{\mathfrak{S}}$ in the form of (5) means that we are first of all interested in the regions inside the nanospheres where the electrons are located. Then, the screened Coulomb interaction inside the metal (4) is taken as a basic approximation of the Coulomb law, while the action of the vacuum regions is considered as a perturbation $\hat{\mathfrak{T}}$ in the form of (5), because electrons are practically absent in these regions.

The main term $\hat{\mathfrak{S}}$ is chosen so that the Green's function is easily found by means of (2, 9), and the Green's function corresponds to the usual screened Coulomb law.

$$\Pi^{(0)}(\vec{r} - \vec{r}') = \exp[-|\vec{r} - \vec{r}'|/L_{sc}] / 4\pi|\vec{r} - \vec{r}'|. \quad (11)$$

The second term in (1) is given by the following formula [20]

$$\begin{aligned}\Pi^{(1)}(\vec{r}, \vec{r}') &= -\int d^3r'' \Pi^{(0)}(\vec{r} - \vec{r}'') \tilde{\mathfrak{S}}(\vec{r}'') \Pi^{(0)}(\vec{r}'' - \vec{r}') = \\ &= -\int \left[\Phi_{\vec{k}'}^{(0)*}(\vec{r}') \tilde{\mathfrak{S}}(\vec{k}, \vec{k}') \Phi_{\vec{k}}^{(0)}(\vec{r}) / (\mathfrak{N}(\vec{k}) \mathfrak{N}(\vec{k}')) \right] d^3k d^3k',\end{aligned}\quad (12)$$

where

$$\tilde{\mathfrak{S}}(\vec{k}, \vec{k}') = \int \Phi_{\vec{k}'}^{(0)*} \tilde{\mathfrak{S}} \Phi_{\vec{k}}^{(0)} d^3r. \quad (13)$$

The shift of the one-electron state energy due to the direct Coulomb interaction between the $\Psi(\vec{r})$ states, which differ only in spin, in the zero order approximation with respect to the small parameter $\tilde{\mathfrak{S}}$ is equal to [11]

$$E^{(0)} = e^2 / \varepsilon_0 \int |\Psi(\vec{r})|^2 \Pi^{(0)}(\vec{r}, \vec{r}') |\Psi(\vec{r}')|^2 d^3r d^3r' = \int \left[|\mathbf{I}(\vec{k})|^2 / \mathfrak{N}(\vec{k}) \right] d^3k, \quad (14)$$

where

$$\mathbf{I}(\vec{k}) = \int \Phi_{\vec{k}}^{(0)}(\vec{r}) |\Psi(\vec{r})|^2 d^3r. \quad (15)$$

The shift of energy due to the direct Coulomb interaction for the same one electron state, but in the first order approximation with respect to the parameter $\tilde{\mathfrak{S}}$ is equal to

$$E^{(1)} = -e^2 / \varepsilon_0 \int \left[\mathbf{I}^*(\vec{k}') \mathbf{I}(\vec{k}) \tilde{\mathfrak{S}}(\vec{k}, \vec{k}') / (\mathfrak{N}(\vec{k}') \mathfrak{N}(\vec{k})) \right] d^3k d^3k', \quad (16)$$

where

$$\tilde{\mathfrak{S}}(\vec{k}, \vec{k}') = -\frac{1}{L_D^2} \left(\frac{R}{a} \right)^3 \sum_{\vec{q}_n} \tilde{\mathfrak{G}}(|q_n| R) \delta(\vec{k} - \vec{k}' - \vec{q}_n), \quad (17)$$

\vec{q}_n is the wave-vector of the reciprocal three-dimensional square lattice, $\tilde{\mathfrak{G}}(x) = 4\pi [\sin(x) - x \cos(x)] / x^3$.

In contrast to Ref. [11], we will use a simplest model of free electrons in an infinite spherical potential well [21] for the description of one-electron states inside a metallic nanosphere. Then, the one-electron state is defined by three quantum numbers: m (the energy levels are degenerate with respect to this quantum number), l and $k_{n,l}$ (or n). The one-electron eigenvalues and eigenfunctions are

$$\begin{aligned}E_{l,n}^{(sphere)} &= (\hbar k_{n,l})^2 / 2\mu, \\ \Psi(\vec{r}) &= Y_{lm}(\vec{n}) \Psi_l(\vec{r})\end{aligned}\quad (18)$$

where μ is electron effective mass, $C_{n,l} = \sqrt{2k_{n,l} / \left[R^2 (J_{L+0.5}(k_{n,l}R)^2 - J_{L-0.5}(k_{n,l}R) J_{L+1.5}(k_{n,l}R)) \right]}$ is a normalizing

constant [22] for the function $\Psi_l(\vec{r}) = C_{n,l} J_{L+0.5}(k_{n,l}r) / \sqrt{k_{n,l}r}$ (where $\int |\Psi|^2 = 1$, $Y_{lm}(\cdot)$ and $J_{l+0.5}(\cdot)$ are spherical Bessel functions). Note that the units of $C_{n,l}$ are $1/\text{nm}^{3/2}$. Figure 1 presents the dependence of the Fermi energy of the electron subsystem of a nanosphere upon its radius at an electron gas concentration of $n_0 = 10^2 \text{ nm}^{-3}$.

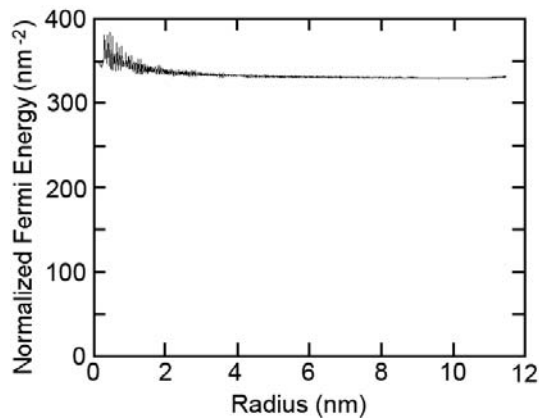


Fig. 1 – Dependence of the normalized Fermi energy $2\mu E_F / \hbar^2$ (nm^{-2}) of the electron subsystem of a nanosphere upon its radius R .

Figure 2 illustrates the dependence of the nanosphere radius upon the quantum numbers $k_{n,L}$ and L for states on the Fermi level so that all the electron states lower than this energy are totally filled, while the states higher than this energy are empty.

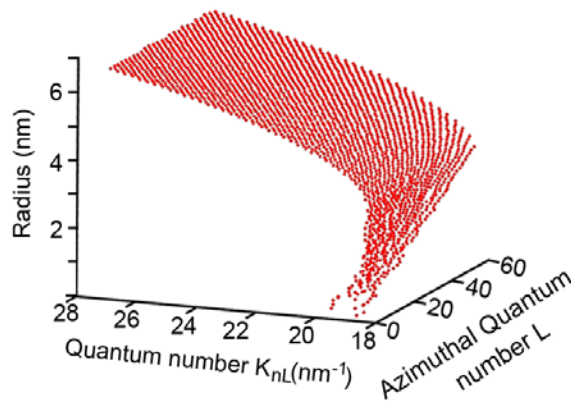


Fig. 2 – Dependence of the nanosphere radius R upon the quantum numbers $k_{n,L}$ and L for the states on the Fermi level.

We see from this graphs that some peculiarities are observed for $R < 3$ nm, which can be associated with quantum size effect. Further, by using the known one-electron wave functions (18), one can obtain the general shift of energy in the form of a series

$$E_{l,n}^{(\uparrow\downarrow)} = E_{l,n}^{(0)} + (a/L_{sc})^2 \left[\Delta E_{l,n}^{(1)} - \sum_{\bar{q}_n} E_{l,n}^{(1)}(\bar{q}_n) \right], \quad (19)$$

where

$$E_{l,n}^{(0)} = \frac{e^2}{\epsilon_0} \int_0^R r_1^{3/2} r_2^{3/2} \Xi_l^{(0)}(r_1, r_2) |\Psi_l(\vec{r}_1)|^2 |\Psi_l(\vec{r}_2)|^2 dr_1 dr_2, \quad (20)$$

$$\Xi_l^{(0)}(r_1, r_2) = I_{l+0.5}(r_1/L_{sc}) K_{l+0.5}(r_2/L_{sc}), \quad (21)$$

$$\Delta E_{l,n}^{(1)} = \frac{1}{(2\pi)^3} \frac{e^2}{a^2 \epsilon_0} \int_0^R r_1^{3/2} r_2^{3/2} \Xi_l^{(1)}(r_1, r_2, 0) |\Psi_l(\vec{r}_1)|^2 |\Psi_l(\vec{r}_2)|^2 dr_1 dr_2, \quad (22)$$

$$E_{l,n}^{(1)}(\bar{q}_n) = \frac{e^2}{a^2 \epsilon_0} \left(\frac{R}{a} \right)^2 \tilde{\mathfrak{G}}(l, q_n | R), \quad (23)$$

$$\cdot \int_0^R r_1^{3/2} r_2^{3/2} \Xi_l^{(1)}(r_1, r_2, \bar{q}_n) |\Psi_l(\vec{r}_1)|^2 |\Psi_l(\vec{r}_2)|^2 dr_1 dr_2$$

$$\Xi_l^{(1)}(r_1, r_2, \bar{q}_n) = \int Y_{l0}^*(\vec{n}_{\bar{k}+\bar{q}_n/2}) Y_{l0}(\vec{n}_{\bar{k}-\bar{q}_n/2}) \cdot \frac{J_{l+0.5}(|\vec{k}+\bar{q}_n/2|r_1) J_{l+0.5}(|\vec{k}-\bar{q}_n/2|r_2)}{k [(\vec{k}+\bar{q}_n/2)^2 + 1/L_{sh}^2] [(\vec{k}-\bar{q}_n/2)^2 + 1/L_{sh}^2]} d^3k, \quad (24)$$

where $I_{l+0.5}(\cdot)$, $K_{l+0.5}(\cdot)$ are modified Bessel functions [22], $\Xi_l^{(\bullet)}(r_1, r_2) \equiv \Xi_l^{(\bullet)}(r_2, r_1)$. One can neglect the value of $\Delta E_{l,n}^{(1)}$ for $R/a > 0.04$. Since the functions

$E_{l,n}^{(1)}(\bar{q}_n) \Big|_{\bar{q}_n \neq 0}$ tend to zero when $q_n \rightarrow \infty$ as $(1/q_n)^5$, we will estimate hereinafter

only $E_{l,n}^{(1)}(\bar{q}_n) \Big|_{\bar{q}_n = 0}$. The following estimation is used of the modulus of one-

electron wave functions (18):

$$\begin{aligned} |\Psi(\vec{r})|^2 \Big|_{l \gg 1} &= \frac{C^2}{p_{n,l} r} |J_{l+0.5}(p_{n,l} r)|^2 \sum_{M=0;L} C_{lm,l-m}^{LM} Y_{LM}(\vec{n}) \Big|_{L \approx l \gg 1} \approx \\ &\approx \frac{C^2}{p_{n,l} r} |J_{l+0.5}(p_{n,l} r)|^2 Y_{l0}(\vec{n}), \end{aligned} \quad (25)$$

where $C_{lm,l-m}^{LM}$ are the Clebsch-Gordan coefficients [23] which exhibit a rather sharp maximum as a function of L at $l \gg 1$.

3. RESULTS AND DISCUSSIONS

The estimation of possibilities for the formation of bound electron pairs by means of formula (19) among a multitude of possible electron states at different nanosphere radii is a complicated task. Therefore, we will take into account first of all the electron states with maximum values of the normalization constant $C_{n,l}$ among all the states situated nearby the Fermi level. We assume that the occurrence of the quantum size effects involves a change of one-electron density of states inside the nanosphere similar to that taking place in the electronic band structure near the Fermi level [24, 25]. At high values of $C_{n,l}$, the one-electron density of states is less spatially uniform and more “concentrated” in separate regions of the space inside the nanosphere. We suggest that such states are most sensitive to any modifications of the Coulomb law. Figure 3 presents the dependence of the effective length $L_{\text{eff}} = C_{n,l}^{-2/3}$ upon the quantum numbers $k_{n,l}$ and l for the states on the Fermi level at a concentration of the electron gas of $n_0 = 10^2 \text{ nm}^{-3}$. This graph suggests that the most significant effect will come from electron states with small values of $k_{n,l}$ and with values of l up to 30. According to Fig. 2, this corresponds to nanosphere radii $R < 3 \text{ nm}$.

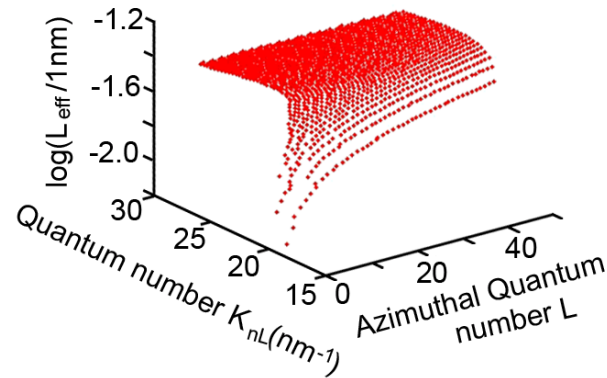


Fig. 3 – Dependence of the effective length $L_{\text{eff}} = C_{n,l}^{-2/3}$ upon the quantum numbers $k_{n,L}$ and L for states on the Fermi level which separates the filled and empty one-electron states.

Hereinafter we will use an empiric parameter of Plasmon Length [26], which value can be considered as an upper limit of L_{sc} . The dependence of the energy shift $E_{l,n}^{(\uparrow\downarrow)}$ upon the radius of metallic nanospheres for different one-electron

states (18) is described by (19) and consists of two different terms. As a result, from Fig. 4 one can observe that the formation of a stable electron pair is impossible at low values of the radius $R < 1$ nm, as $E_{n,l}^{(0)} > 0$ reaches higher positive values. This indicates on the possibility of a metal-insulator transition. At the same time, by a comparison of each term of (19) in Fig. 4 and Fig. 5 one can conclude that stable electron pairs are possible even for a pure Fermi screening $L_{sc} = 10^2$ nm and $3 \text{ nm} > R > 1 \text{ nm}$ for a part of electron states with high values of l . Then, the shift of energy $E_{l,n}^{(\uparrow\downarrow)} < 0$ and the formation of a bound electron pair are energetically quite possible at least for a part of electron states. In this case, one should take into account that in fact there are even lower values of the parameter L_{sc} , for which the first term decreases and the second one increases, as Bose particles and Bose condensate emerge in the system.

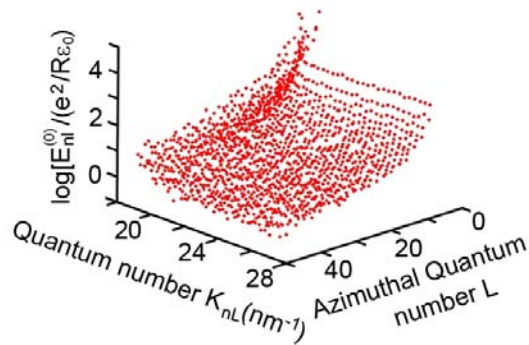


Fig. 4 – Dependence of the dimensionless energy $E_{n,l}^{(0)} / (e^2 / R \epsilon_0)$ upon the quantum numbers $k_{n,L}$ and L for states at the Fermi level.

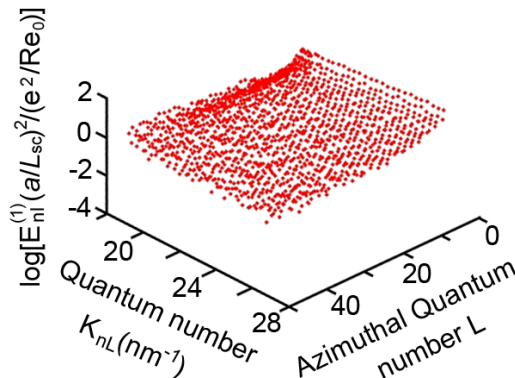


Fig. 5 – Dependence of the dimensionless energy $E_{n,l}^{(1)} (a/L_{sc})^2 / (e^2 / R \epsilon_0)$ upon the quantum numbers $k_{n,L}$ and L for states at the Fermi level.

In our calculations we have taken into account the discrete character of the energetic spectrum and the fact that only a part of electrons participates in the screening process. We used the relationship $L_{sc} \rightarrow L_{sc} \cdot \exp(\Delta/2k_B T)$, where Δ is the mean value of the energy gap between the neighboring levels of electron energy inside the nanosphere. The value of $\Delta \sim E_F/N$, where $N = 4\pi R^3/3n_0$, is the number of levels below the Fermi energy.

Generally, one can conclude that the formation of bound quasi-Cooper pairs with a large binding energy is quite possible.

4. CONCLUSION

The results of our analytical consideration show that the renormalized Coulomb law, the quantum size effect on the density of one-electron functions, and the existence of a strong positive feedback between the phenomena of electron pair formation and Bose condensation can be the reason for the emergence of an anomalous electron transport with giant current density at room temperature.

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