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Energy Characteristics of Nearly Spherical Metallic Nanoparticles

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In the model of infinite depth spherical potential well, using the method of boundary shape perturbation, the effect of cross-section geometry changing on the energy characteristics of 0D metal systems was investigated. By modifying the boundary conditions of the conduction electrons radial wave function, the Fermi energy oscillations of metal nanoparticles with small eccentricity were calculated. It is shown that an increase in the eccentricity value leads to a decrease in the Fermi energy values and a shift of the oscillation maxima towards low frequencies. Applying the obtained results of the dimensional dependence of the Fermi energy for 0D systems, the calculation of the diagonal component of the dielectric function was carried out using the expansion of the dielectric tensor by powers of r_0/λ. The influence of the change in the cross-section on the absolute value and frequency position of the oscillation peaks of the dielectric function real and imaginary parts, which are directly related to the size quantization effect, was established. Calculations of the Fermi energy dimensional oscillation and the diagonal component of the dielectric function were performed for Ag, Li, and Al nanoparticles. Differences in the obtained results for nanoparticles of different metals are explained by different values k_{nl} and the relaxation time of conduction electrons.

Keywords: Eccentricity, Fermi energy, Dielectric function, Metallic nanoparticle.

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1. INTRODUCTION

The creation of brand-new optical and electronic devices involves the use of metal 0D systems, therefore considerable attention is paid to their creation and research. The possible use of metal nanoparticles as sensors in biology and medicine is due to their unique optical and spectral characteristics [1, 2]. The absorption of electromagnetic radiation by the specified structures leads to the appearance of a resonance peak, which is a consequence of the increase in the energy absorption cross-section of metal nanoparticles when the frequency of incident light approaches the frequency of surface plasmon resonance. At the same time, the frequency position and intensity of the absorption peak depends on the size and shape of nanostructures [3-5]. That is why the study of the relationship between the energy spectrum of nanoscale objects and their geometric parameters is relevant.

Experimental data and numerical modeling indicate that as the particle size increases, so does the deviation from spherical shape [6]. From a physical point of view, the theoretical study of an ellipsoidal nanosystem energy spectrum is a complex task, as it involves the solution of the Schrödinger equation for an arbitrary volume, which is one of the most difficult mathematical problems of physics. However, for the cases of nearly spherical shape nanoparticles, the problem is solved taking into account the perturbation theory [7]. The calculation of the influence of a spherical nanoobject shape deformation on the particle quantum states, within the functional method of surface shape perturbation, is given in [8]. An increase in the degree of mixing of pure states and splitting of energy levels was established with increasing quantum numbers n and l. The work [9] presents an analytical model for calculating the Fermi energy in the context of the deformation of a single particle from a spherical shape. The influence of non-sphericity on the eigenvalues and eigenfunctions of an ellipsoidal quantum dot was studied in [10] for the case of a finite height potential barrier. In this work, considering the preservation of the volume of a nanoparticle, the effect of small values of eccentricity on its energy and optical characteristics is investigated. For this, an approach is used that consists in modifying the boundary conditions of the electron radial wave function for the case of a spherically symmetric infinite depth well.

2. STATEMENT OF THE PROBLEM

The relationship between the induction components D_μ and the electric field strength E_ν in the case of anisotropic systems is described by the expression [11]

$$D_\mu = \sum_\nu \epsilon_{\mu\nu}(\mathbf{q}, \omega) E_\nu, \tag{1}$$

where $\epsilon_{\mu\nu}$ is the dielectric tensor:

$$\epsilon_{\mu\nu} = \delta_{\mu\nu} - \frac{4\pi e^2}{m_e^2 \omega^2 \Omega} \times \sum_{i,j} \frac{f_i - f_j}{\varepsilon_{ij} - \hbar\omega} \left\{ \left\langle j \left| e^{-i\mathbf{q}\cdot\mathbf{r}} \hat{p}_\mu \right| i \right\rangle - \frac{1}{2}\hbar q_\mu \left\langle j \left| e^{-i\mathbf{q}\cdot\mathbf{r}} \right| i \right\rangle \right\} \times \left\{ \left\langle i \left| e^{i\mathbf{q}\cdot\mathbf{r}} \hat{p}_\nu \right| j \right\rangle + \frac{1}{2}\hbar q_\nu \left\langle i \left| e^{i\mathbf{q}\cdot\mathbf{r}} \right| j \right\rangle \right\}. \tag{2}$$

Here $\delta_{\mu\nu}$ is the Kronecker's symbol; $i = \sqrt{-1}$; e is the electron charge; $\Omega = 4\pi r_0^3/3$ is the particle volume; m_e is the electron mass; $f_i = \left[\exp\left((\varepsilon_i - \varepsilon_F)/k_B T\right) + 1\right]^{-1}$ is the filling factor of the state with energy ε_i; $|i\rangle \equiv |n,l,m\rangle$

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and $\langle j| \equiv \langle n', l', m'|$ are the initial and final state vectors; $\varepsilon_{ij} = \varepsilon_i - \varepsilon_j$; T is the temperature. Here in after, we will consider $T = 0$.

In the general case, the wave functions and energy spectrum of electrons in the spheroidal 0D metal system can be considered in the spheroidal coordinate system. However, for the case of an elliptical section with a small eccentricity ($\varepsilon = \sin(\arccos(b/a)) << 1$, a and b are the major and minor semi-axes of the ellipse), by analogy with the work [12], we will use the method of shape perturbing of the boundary. As the zero approximation, we will take the radial wave function of an electron in a metal nanoparticle for the case of a potential infinite depth well:

$$R_{nl}(r) = A_{nl} j_l(k_{nl} r), \tag{3}$$

$$A_{nl} = \left(\int_0^{r_0} j_l^2(k_{nl} r) r^2 dr \right)^{-1/2}, \tag{4}$$

where $r_0 = (a + b)/2$ is the effective radius, $k_{nl} = \chi_{nl} / r_0$, χ_{nl} are the positive zeros of the l-th order spherical Bessel function; $n = 1, 2\ldots$ number the roots of the l-th order Bessel function.

Expanding the radial wave function at the boundary in degrees of eccentricity and limiting ourselves to the first two terms of the expansion, the boundary condition for the case of a weakly deformed nanospheroid can be written as

$$j_l(k_{nl} r) + \varepsilon r_0 \frac{d j_l(k_{nl} r)}{dr}\bigg|_{r=r_0} = 0. \tag{5}$$

Using the recurrence relations for the derivatives of the whole order Bessel function, we have

$$(1 + \varepsilon l) j_l(k_{nl} r_0) - \varepsilon r_0 k_{nl} j_{l+1}(k_{nl} r_0) = 0. \tag{6}$$

Ratio (6) determines the electron spectrum of an ellipsoidal nanoparticle with a small eccentricity in the case of a potential infinite depth well. Assuming $\varepsilon = 0$, we obtain the equation for the spectrum of conduction electrons in a spherically symmetric potential well with volume Ω.

Since the attention in this work is focused on the consideration of optical transitions between subbands, which are formed as a result of the size quantization effect, we assume that the wave vector lies in the zx plane, and the z axis is directed along the direction of wave propagation ($q_x = q_y = 0$; $\mathbf{q} \cdot \mathbf{r} = q_z z << 1$). Therefore, we obtain for the diagonal component of the dielectric tensor

$$\epsilon_{\mu\mu} = 1 - \frac{8\pi e^2 \hbar^2}{m_e^2 \Omega} \sum_{i,j} \frac{f_i}{\varepsilon_{ij}\left(\varepsilon_{ij}^2 - \hbar^2 \omega^2\right)} \left| \langle j| \hat{p}_\mu |i\rangle \right|^2, \tag{7}$$

where index $\mu = \{x, y, z\}$, and the calculation of the square of the matrix element of the projection of the momentum operator takes the form

$$\left| \langle j| \hat{p}_\mu |i\rangle \right|^2 = \frac{\hbar^2}{3} \left\{ l \mathscr{G}_{(-)}^2 \delta_{l-1,l'} + (l+1) \mathscr{G}_{(+)}^2 \delta_{l+1,l'} \right\}, \tag{8}$$

$$\mathscr{G}_{(\pm)} = k_{nl} A_{nl} A_{n',l\pm1} \int_0^{r_0} j_{l\pm1}(k_{n',l\pm1} r)\, j_{l\pm1}(k_{nl} r) r^2 dr.$$

Absorption in (7) is taken into account by replacing $\omega \to \omega + i/\tau$, where τ is the relaxation time. To locally conserve the number of electrons, we use the complex dielectric function $\bar{\epsilon}(\omega, \tau)$ associated with $\epsilon(\omega, \tau)$ by the following relations:

$$\mathrm{Re}\,\bar{\epsilon}(\omega, \tau) = \mathrm{Re}\,\epsilon(\omega + i/\tau) - \frac{1}{\omega\tau} \mathrm{Im}\,\epsilon(\omega + i/\tau), \tag{9}$$

$$\mathrm{Im}\,\bar{\epsilon}(\omega, \tau) = \mathrm{Im}\,\epsilon(\omega + i/\tau) + \frac{1}{\omega\tau} \left[\mathrm{Re}\,\epsilon(\omega + i/\tau) - 1 \right]. \tag{10}$$

Substituting (7) into (9)-(10) and summing over n', n, l and m, we obtain

$$\mathrm{Re}\,\bar{\epsilon}_{\mu\mu}(k_\omega, k_\tau) = 1 - \frac{4k_p^4}{\hbar^2 N} \Phi_{(-)}, \tag{11}$$

$$\mathrm{Im}\,\bar{\epsilon}_{\mu\mu}(k_\omega, k_\tau) = -\frac{4k_p^4}{\hbar^2 N} \frac{k_\tau^2}{k_\omega^2} \Phi_{(+)}, \tag{12}$$

where

$$\Phi_{(\pm)} = \sum_{n,l,m,n'} \frac{f_{nlm} \left| \langle j| \hat{p}_\mu |i\rangle \right|^2}{k_{nl}^2 - k_{n'l'}^2} \frac{\left(k_{nl}^2 - k_{n'l'}^2\right)^2 \pm k_\omega^4 \pm k_\tau^4}{\left[\left(k_{nl}^2 - k_{n'l'}^2\right)^2 - k_\omega^4 + k_\tau^4 \right]^2 + 4k_\omega^4 k_\tau^4},$$

$k_p^2 = 2m_e\omega_p/\hbar$, $k_\omega^2 = 2m_e\omega/\hbar$, $k_\tau^2 = 2m_e/\hbar\tau$, $\omega_p^2 = 4\pi e^2 \bar{n}/m_e$ and a step function was used as an approximation of the filling factor $f_{nlm} = \Theta(\varepsilon_F - \varepsilon_{nlm})$.

To carry out calculations according to formulas (11) and (12), it is necessary to take into account the following transcendental relation, which determines the Fermi level ε_F in the 0D system [13]:

$$\bar{n}\Omega = \sum_{\kappa=1,3,\ldots} \frac{8}{\pi\kappa} \sum_{n,l} \sin \frac{\pi\kappa\varepsilon_{nl}}{\varepsilon_F}, \tag{13}$$

where $\bar{n}$ is the concentration of conduction electrons. Ratio (13) together with equation (6) describes the dependence of the Fermi level position in a spheroidal nanoparticle with small eccentricity depending on its size.

3. ANALYSIS OF CALCULATION RESULTS

The calculations were performed for slightly deformed spheroidal nanoparticles Ag ($Z = 1$), Li ($Z = 1$) and Al ($Z = 3$), where the electron concentration $\bar{n} = \left(4\pi r_s^3/3\right)^{-1}$ with the corresponding values of the average distance between electrons $r_s = 3.02a_0$, $3.28a_0$ and $2.07a_0$, Z is the valence of the metal.

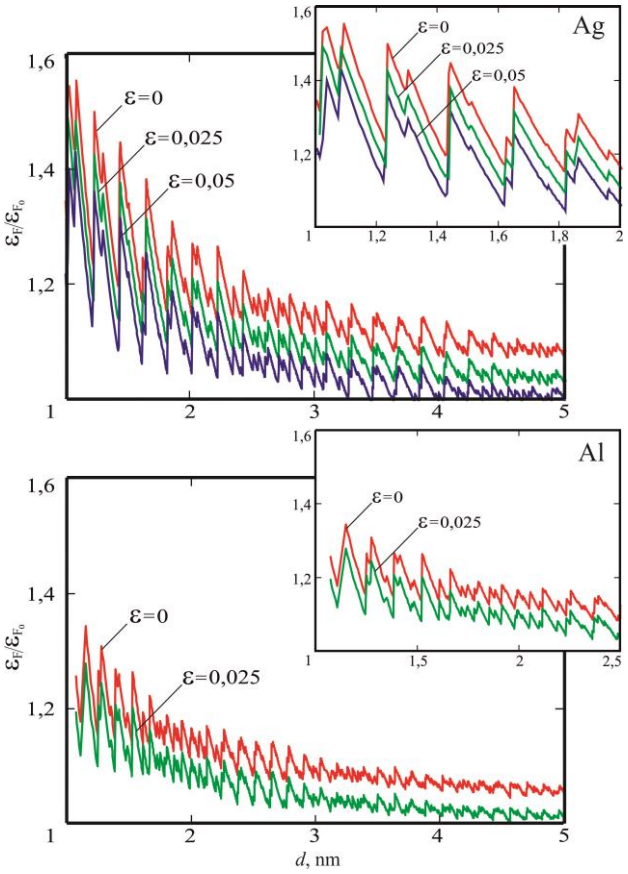

Fig. 1 – Size dependence of the Fermi energy of Ag and Al nanoparticles at different values of eccentricity ε

Fig. 1 shows the dimensional dependence of the Fermi energy of Ag and Al nanoparticles at different eccentricity values. The dependences for a spherical nanoparticle ($\varepsilon = 0$) and a weakly deformed spheroid ($\varepsilon = 0.025$; 0.05) are similar and have a "stochastic" character due to the presence of a pair of quantum numbers n and l. The period and amplitude of the oscillations approach the Fermi energy values in a 3D metal ε_{F_0} with an increase in the diameter $d = 2r_0$ of the nanoparticle. Filling a higher energy level leads to a "jump-like" growth of ε_F. The appearance of each individual peak is due to the fulfillment of the following condition for each individual pair of numbers (n', l'):

$$\chi_{n'l'} = k_F r_0.$$

An increase in the eccentricity value leads to a decrease in the amplitude of oscillations and their slight shift to the area of lower frequencies. The decrease in the values of the Fermi energy dimensional dependence is caused by the lowering of the energy levels and the decrease in the distance between them.

The difference in the Fermi energy dimensional dependence of Ag and Al nanoparticles is due to different values of k_{nl}. Thus, in the case of Al nanoparticle, the root distribution density χ_{nl} is greater and, as a result, the scale of oscillations is smaller.

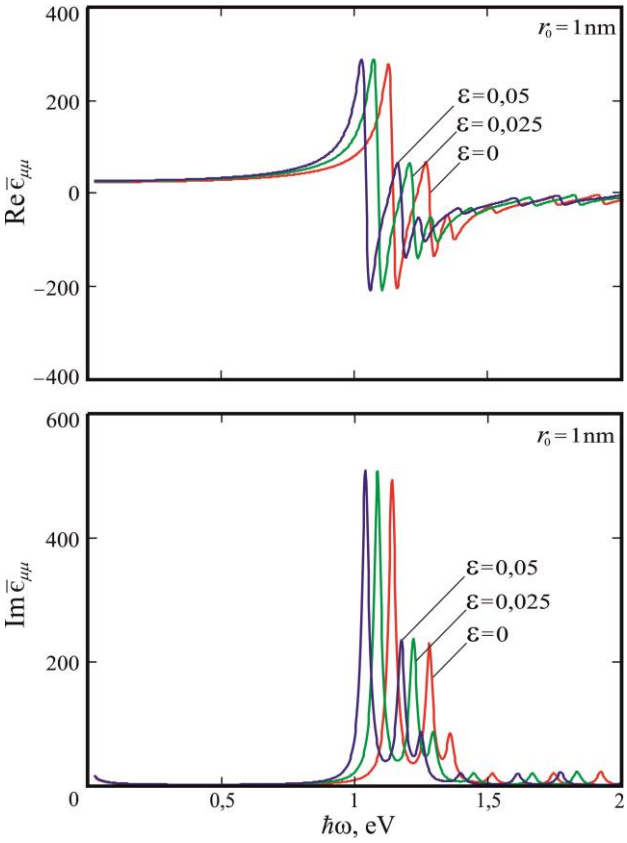

Fig. 2 – Frequency dependences of $\mathrm{Re}\,\bar{\epsilon}_{\mu\mu}$ and $\mathrm{Im}\,\bar{\epsilon}_{\mu\mu}$ with radius $r_0 = 1$ nm at different values of eccentricity ε

Fig. 2 and Fig. 3 show the frequency dependences of the real $\mathrm{Re}\,\bar{\epsilon}_{\mu\mu}$ and imaginary $\mathrm{Im}\,\bar{\epsilon}_{\mu\mu}$ dielectric function parts of Ag nanoparticle with radius $r_0 = 1$ and 2 nm, taking into account different eccentricity values. A characteristic feature of the given dependences is the presence of resonance peaks formed as a result of the size quantization effect. The frequency position, number, and absolute value of resonance peaks are directly related to optical transitions between subbands.

A change in the geometry of a nanoparticle affects the position and magnitude of size quantization peaks. Thus, an increase in the eccentricity ε leads to a slight fluctuation in the amplitude of oscillations and their shift towards low frequencies, which is associated with a decrease in energy levels. Assuming that $n = n'$, the position of peaks can be estimated using the formula $\hbar\omega = \hbar^2\left(k_{nl}^2 - k_{n'l'}^2\right)/2m_e$. A decrease in the distance between subbands causes the appearance of optical peaks at lower frequencies.

An increase in the radius of a nanoparticle (Fig. 3) shifts oscillations towards low frequencies, the distance between them decreases, and the oscillations begin to merge with each other. New peaks appear in the entire frequency range due to the increase in the number of subbands. At the same time, the influence of eccentricity on the frequency position of resonant peaks decreases since the difference between the distances of subbands decreases as the radius increases.

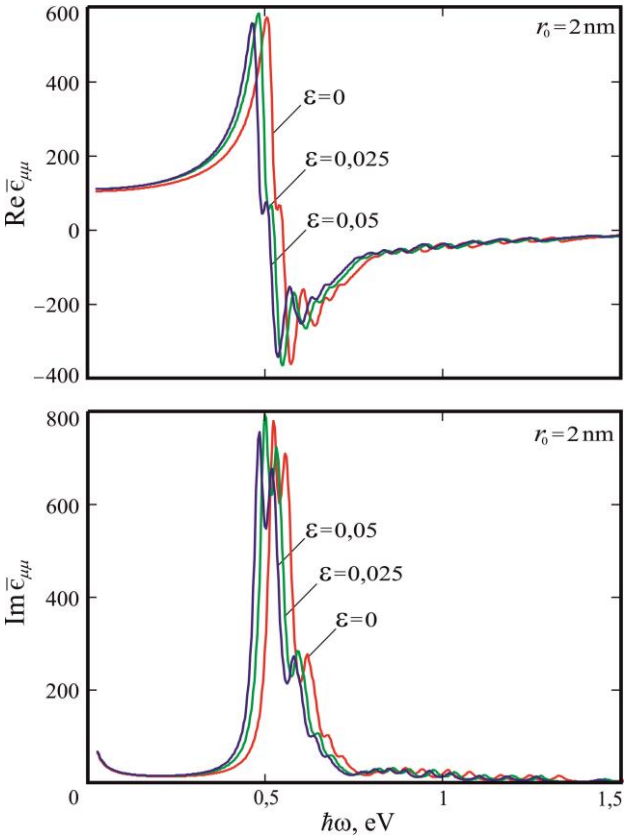

Fig. 3 – Frequency dependences of $\mathrm{Re}\,\bar{\epsilon}_{\mu\mu}$ and $\mathrm{Im}\,\bar{\epsilon}_{\mu\mu}$ with radius r_0 = 2 nm at different values of eccentricity ε

Functions $\mathrm{Re}\,\bar{\epsilon}_{\mu\mu}$ and $\mathrm{Im}\,\bar{\epsilon}_{\mu\mu}$ in the low frequency range behave differently. That is true that $\mathrm{Re}\,\bar{\epsilon}_{\mu\mu}$ is sign variable, while $\mathrm{Im}\,\bar{\epsilon}_{\mu\mu}$ remains positive over the entire frequency range.

Differences in the optical characteristics of nanoparticles of the same radius (r_0 = 1.5 nm) and eccentricity (ε = 0.05), but made of different metals, are primarily explained by different values of k_{nl}. As a result, the maximum of $\mathrm{Im}\,\bar{\epsilon}_{\mu\mu}$ for Al is shifted to the right, in contrast to Ag and Li nanoparticles (Fig. 4). The smoothness of the curves of Al and Li nanoparticles is due to the small value of the parameter τ. A characteristic feature of these dependences is a monotonic increase in $\mathrm{Im}\,\bar{\epsilon}_{\mu\mu}$, which reaches its maximum value at a frequency $\hbar\omega \approx 0.6$ eV for Li and $\hbar\omega \approx 1$ eV for Al, and a subsequent smooth decrease as $\hbar\omega \to \infty$.

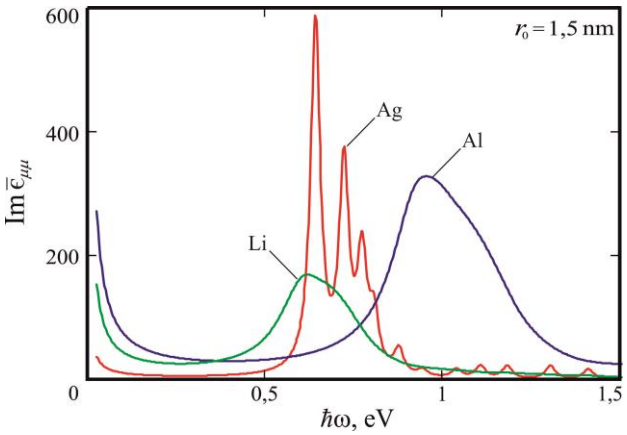

Fig. 4 – Frequency dependences of $\mathrm{Im}\,\bar{\epsilon}_{\mu\mu}$ for nanoparticles of various metals at eccentricity value ε = 0.05

4. CONCLUSIONS

Formulas for the dielectric function real and imaginary parts of weakly deformed metal nanoparticles, the radius of which is equal to the Fermi wavelength of electrons, have been obtained considering the diagonal response approximation. Taking into account the eccentricity, the dependence of the Fermi level position and the number of filled or partially filled subbands has been calculated. The effect of changing the geometry of the cross-section is taken into account by modifying the boundary conditions for the radial part of the electron wave function for the case of an infinite depth potential well. The dependence of the optical characteristics of the nanoparticle with increasing eccentricity has been shown. In particular, the oscillatory peaks, which are associated with size quantization effects, are shifted towards low frequencies due to the lowering of energy levels and ф decrease in the distance between optical transitions. The influence of the material on the frequency dependence of the dielectric tensor has been demonstrated on the example of Ag, Li, and Al nanoparticles.

REFERENCES

1. C. Forestiere, G. Miano, S. Boriskina, L. Negro, *Opt. Exp.* **17**, 9648 (2009).
2. Erik C. Dreaden, Megan A. Mackey, Xiaohua Huang, Bin Kangy, Mostafa A. El-Sayed, *Chem. Soc. Rev.* **40**, 3391 (2011).
3. S. Sucu, A. I. Mese, S. E. Okan, *Physica E* **40**, 2698 (2008).
4. Al. L. Efros, A.V. Rodina, *Phys. Rev. B.* **47**, 10005 (1993).
5. K.-H. Kim, A. Hisakou, J. Herrmann, *Optics* **18**, 7488 (2010).
6. D. Tobia, E. De Biasi, M. Granada, H. E. Troiani, G. Zampieri, E. Winkler, R. D. Zysler, *J. Appl. Phys.* **108**, 104303 (2010).
7. K.G. Dvoyan, E.M. Kazaryan, L.S. Petrosyan, *Physica E* **28**, 333 (2005).
8. V.P. Dzyuba, Yu.N. Kulchin, V.A. Milichko, *Phys. Solid State* **56**, 359 (2014).
9. K. Warda, *J. Nanosci. Nanotechnol.* **12**, No1, 284 (2012).
10. A. Bagga, S. Ghosh, P.K. Chattopadhyay, *Nanotechnol.* **16**, 2726 (2005).
11. V.P. Kurbatsky, V.V. Pogosov, *Phys. Rev. B* **81**, 155404 (2010).
12. A.V. Korotun, A.O. Koval, *J. Nano- Electron. Phys.* **7** No 4, 04067 (2015).
13. A.O. Koval, *J. Nano- Electron. Phys.* **14** No 2, 02013 (2022).

Енергетичні характеристики майже сферичних металевих наночастинок

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У моделі сферичної потенційної ями нескінченної глибини з використанням методу збурення форми межі досліджено вплив зміни геометрії поперечного перерізу на енергетичні характеристики 0D-металевих систем. Шляхом модифікації граничних умов радіальної хвильової функції електронів провідності розраховано осциляції енергії Фермі металевих наночастинок з малим ексцентриситетом. Показано, що збільшення значення ексцентриситету призводить до зменшення значення енергії Фермі та зсуву максимумів осциляцій у бік низьких частот. Застосовуючи отримані результати розмірної залежності енергії Фермі для 0D-систем, проведено обчислення діагональної компоненти діелектричної функції з використанням розкладання діелектричного тензора за ступенями r_0/λ. Встановлено вплив зміни поперечного перерізу на абсолютну величину та частотне положення осциляційних піків реальної та уявної частин діелектричної функції, які безпосередньо пов'язані з ефектом розмірного квантування. Розрахунки розмірної осциляції енергії Фермі та діагональної компоненти діелектричної функції виконані для наночастинок Ag, Li та Al. Відмінності одержаних результатів для наночастинок різних металів пояснюються різними значеннями k_{nl} та часом релаксації електронів провідності.

Ключові слова: Ексцентриситет, Енергія Фермі, Діелектрична функція, Металева наночастинка.