
SINGLE-ELECTRON OPTICAL PROPERTIES OF METAL NANOSHELLS WITH A NONCONCENTRIC CORE. ACCOUNT OF ELECTRON SPECTRUM QUANTIZATION

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Single-electron optical properties of a spherical nanoparticle composed of a dielectric core and a thin metallic shell and characterized by a slight shift of the core center with respect to the geometric center of a nanoparticle have been studied in the frequency range far from the plasmon resonance, where the contribution of the single-electron component is considerable. A model that allows the wave functions and the wavenumber spectrum for an electron in the shell of a composite nanoparticle of this type to be obtained is proposed. The model is used to obtain the matrix elements of optical transitions and the single-electron optical conductivity of a nanoparticle both with and without (semiclassical conductivity) quantization of the electron energy spectrum in the shell. It is shown that the aforementioned quantization effects result in the appearance of the oscillatory dependence of the optical conductivity of a nanoparticle on the light frequency. It is demonstrated that the influences of the center shift and the spectrum quantization on the optical conductivity of a nanoparticle can be considered independently in the first approximation.

1. Introduction

The development of nanotechnologies in the last decades enabled nanoparticles possessing various configurations and, respectively, various properties to be used in technical and engineering. In particular, metal nanoparticles are widely used in technical applications, and their efficiency is based, first of all, on their unique optical properties. For instance, these particles effectively absorb light with a given wavelength. Composite nanoparticles of this type, which were obtained during the last years – the so-called nanoshells [1–4], – allow those technologies to be developed further, by extending the working range of wavelengths in comparison with that for traditional

solid metallic nanoparticles. The nanoshell is a composite nanoparticle consisting of a dielectric core and a thin metallic shell. Note also that the optical properties of nanoshells can be controlled more flexibly than it is possible in traditional systems. Such a flexibility is associated with the fact that the internal and external radii of the metallic shell (its optical response is crucial to the whole particle) can be changed independently. It makes nanoshells especially promising for technical applications.

After nanoshells had been obtained, they have been actively studied for the last years both theoretically [5–11] (within the classical and quantum-mechanical approaches) and experimentally [3, 5, 12, 13]. However, their optical properties were studied mainly in a vicinity of the plasmon resonance frequency. At the same time, in the frequency range far from it, the contribution made to light absorption by individual transitions becomes dominating. In the works, where the contribution of individual transitions to the light absorption was studied, either of two opposite limiting cases was usually analyzed. The first case corresponds to a situation, when the distances between electron quantum levels are very small in comparison with the light quantum energy; then the summation over the discrete levels can be replaced by the integration. The second limiting case corresponds to a situation where the distances between the energy levels are of the same order as the light quantum energy; as a rule, a few (two or three) levels are taken into account in this case. However, there are many more electron levels in a typical shell. On the other hand, as is shown in this work, the quantum-mechanical effects, arising owing to the quantization of the electron energy

in a shell, cannot be neglected. The reason for all that consists in that the energy levels in a thin shell reveal the quasi-one-dimensional character, and the distance between them grows.

We show below that taking such dimensional quantum-mechanical effects into account results in the emergence of oscillatory dependences of the optical properties of a nanoshell on the metal coating thickness. The oscillatory dependences of both optical and electric properties of a metal nanowire on its thickness, similar to those obtained in this work, were experimentally observed in work [14]. Such a shape of the dependence for a solid metal nanowire, the thickness of which is relatively large, means that similar quantum-mechanical effects for thin shells are much stronger.

Note that, while studying the light absorption in small metal particles (in particular, in metallic nanoshells), both absorption components – electric, i.e. coupled with the electric vector of an electromagnetic wave, and magnetic ones – must be examined. This follows from the fact that either magnetic or electric absorption can dominate in such particles, depending on the particle's shape and dimension, as well as on the electromagnetic wave frequency [15]. However, it was magnetic absorption that was usually studied in the previous works dealing with the light absorption in such shells [16–18]. This makes a research of the electric absorption in metallic shells of various types challenging.

One of the unique properties of nanoparticles is known to be the dependence of particle's optical properties on the particle's shape and dimension (see, e.g., work [15]). Therefore, the optical properties are usually studied separately for nanoparticles with a specific shape; the particle can be either solid or composite, the latter case representing even a wider range of configurations.

In this work, we study a class of composite nanoparticles, which drew attention of researchers not too long ago: the so-called nanoeggs [19–21]. These are usual (i.e. close to spherical) nanoshells with a symmetry violation. To be more specific, these are nanoshells, the core center of which is shifted with respect to the center of the whole nanoparticle. Besides the external dimension and the ratio between the dielectric core and shell dimensions, the optical properties of the nanoparticle are also governed by the relative shift between the core and nanoparticle centers. Hence, such composite nanoparticles propose a wider range of application, and their optical properties can be changed even more flexibly than the properties of symmetric composite nanoparticles. This work aimed at a theoretical study of the optical properties of a nanoparticle, in which the shift of its dielectric core center with

respect to the nanoparticle geometric center is small, i.e. in the case of weak symmetry violation. Namely, we determined the optical conductivity in the aforementioned shells taking the electric absorption into account in the single-electron approximation and for frequencies far from the plasmon resonance. When calculating the optical conductivity, the discreteness of electron energy levels was considered, which makes the results obtained applicable even to very thin shells.

2. Formulation of the Problem. A Working Model

Consider a nanoparticle consisting of a dielectric core and a thin metallic shell. Let the nanoparticle have a shape close to spherical—both the external boundary of the nanoparticle and the boundary of its dielectric core. Let the quantities a and b stand for the internal and external radii of the shell, respectively. We consider the case of a thin shell, so that the inequality $\frac{b-a}{b} \ll 1$ is satisfied.

In this work, we consider a nanoparticle, the internal and external centers of which, i.e. the geometric centers of the dielectric core and the external shell boundary, respectively, are shifted with respect to each other by a small distance Δl , so that the inequalities $\frac{\Delta l}{a} \ll 1$, $\frac{\Delta l}{b-a} \ll 1$, and, consequently, $\frac{\Delta l}{b} \ll 1$ are satisfied. To take such a small shift into account, let us first apply the well-known model of a symmetric spherical nanoshell [22] to determine a small correction to the optical conductivity of the shell stemming from the relative shift of the shell centers. According to work [22], we model the spherical metallic shell (the dielectric core does not give a substantial contribution to the particle conductivity) by an infinitely deep potential well for electrons (the validity of this model follows from the ratio between the Fermi energy and the work function for typical metals) and apply the single-electron model.

Let an electromagnetic wave, the length of which is much longer than the external shell size, fall on the nanoparticle described above. Then, the field created by the wave can be considered uniform inside the shell. Let the Oz axis be directed in the wave propagation direction, and let us consider the case where this direction coincides with the direction of a center shift in the shell. Then, passing to the corresponding spherical coordinate system (r, θ, ϕ) from the Cartesian one by the formulas

$$\left. \begin{aligned} x &= r \cos \varphi \sin \theta \\ y &= r \sin \varphi \sin \theta \\ z &= r \cos \theta \end{aligned} \right\}, \quad (1)$$

the small center shift Δl can be described, by making the substitution

$$b \rightarrow b(1 \pm \alpha \cos \theta), \quad \alpha = \frac{\Delta l}{b} \ll 1, \quad (2)$$

where the signs “+” and “-” correspond to the cases where the center of the external sphere is shifted with respect to the internal center in the wave propagation direction or oppositely to it, respectively.

From the condition $\frac{\Delta l}{b-a} \ll 1$, it follows that the shell thickness changes slowly and by a small value. Since the problem of finding the wave functions, energy spectrum, and wave numbers of an electron in the thin shell is reduced to a quasi-one-dimensional problem (i.e. an electron in a one-dimensional potential well), then, provided that the variation of the shell thickness is small and slow, we can use a relevant expression for a spherical shell, when considering every direction (θ, ϕ) . Hence, while finding a correction to the optical conductivity associated with a small shift between the centers, we can use the wave functions and the spectrum of wave numbers obtained for a spherical nanoshell in a weakly deformed potential well (with respect to the spherical one: $a = b = r$), the boundaries of which in the spherical coordinates are given by the equations $r = a$ and $r = b(1 \pm \alpha \cos \theta)$. The obtained wave functions and spectrum should be substituted into the matrix element of an optical transition.

Hence, our task consists in finding the optical conductivity of the nanoparticle described above, when an electromagnetic wave with a large (in comparison with the nanoparticle size) wavelength falls on it.

3. Expression for Optical Conductivity in Terms of a Sum Over the Electron States

In order to calculate the optical conductivity of the nanoparticle described in the previous section, let us apply the method presented in work [22]. First, let us write down components of the conductivity of the nanoshell in terms of optical transition matrix elements for an electron. The optical conductivity in the wave propagation direction (the Oz axis) looks like

$$\sigma = \frac{\pi e^2 \omega}{V_s} \sum_{i,f} |\langle i|z|f \rangle|^2 f(E_i)(1 - f(E_f)) \times \delta(E_f - E_i - \hbar\omega), \quad (3)$$

where V_s is the nanoshell volume; ω is the wave frequency; the indices i and f denote the initial and final

electron states, respectively; E_i and E_f are the energies of an electron in the initial and final states, respectively; and $f(E)$ is the distribution function of electrons over the energy states.

To find the matrix elements, let us apply a technique used in work [22]. First, we find the wave functions and the spectrum of wave numbers for an electron in the metallic shell. Then, using them, we calculate the matrix elements of the z -coordinate operator. At last, summing up over the initial and final states of the electron, we obtain the conductivity.

Consider firstly a spherically symmetric shell. The wave functions and the spectrum of wave numbers for it can be obtained after separating – in spherical coordinates (1) – the variables in the Schrödinger equation for the electron in an infinitely deep potential well. According to work [22], after solving the Schrödinger equation, satisfying the boundary conditions, and taking into account that the shell is thin ($\frac{b-a}{b} \ll 1$), the wave function ψ and the spectrum of wave numbers k in the case of a spherical shell look like

$$\begin{aligned} \psi(r, \theta, \varphi) &\approx \\ &\approx \left(\frac{2}{b-a}\right)^{1/2} \frac{1}{r} \sin\left(kr - (l+1)\frac{\pi}{2} + \alpha\right) Y_{lm}(\theta, \varphi), \quad (4) \\ k &= \frac{\pi n}{b-a}, \quad (5) \end{aligned}$$

where Y_{lm} are the Legendre polynomials, and a and b are the internal and external, respectively, radii of the potential well, which correspond to the internal and external, respectively, radii of the metallic shell.

Substitution (2) changes the matrix element of the optical transition in the wave propagation direction. The matrix element for a spherical nanoshell looks like

$$\begin{aligned} \langle i|z|f \rangle &= \int_0^{2\pi} d\varphi \int_0^\pi \sin\theta d\theta \int_a^b r^2 dr Y_{lm}(\theta, \varphi) Y_{l'm'}^*(\theta, \varphi) \times \\ &\times \frac{2}{b-a} \frac{1}{r^2} \sin\left(kr - (l+1)\frac{\pi}{2} + \alpha\right) \times \\ &\times \sin\left(k'r - (l'+1)\frac{\pi}{2} + \alpha'\right) r \cos\theta. \quad (6) \end{aligned}$$

Notice that this expression includes the reciprocal of the difference $b - a$. The integral over the radial variable

$$\int_a^b r \sin\left(kr - (l+1)\frac{\pi}{2} + \alpha\right) \times$$

$$\begin{aligned} & \times \sin \left(k'r - (l' + 1) \frac{\pi}{2} + \alpha' \right) dr = \\ & = \frac{1 - (-1)^{n+n'}}{2} \frac{2k'2k}{\left((k')^2 - k^2 \right)^2} \end{aligned} \quad (7)$$

includes the square of this difference, because, according to Eq. (5), $\frac{kk'}{\left((k')^2 - k^2 \right)^2} \sim (b-a)^2$. Ultimately, after substitution (2) into the matrix element (6), the integral over the radial variables changes proportionally to the quantity

$$(b-a)^2 (b-a)^{-1} = b-a \rightarrow (b-a) \left(1 \pm \frac{\alpha b}{b-a} \cos \theta \right).$$

This means that, for the integral over the radial variable, which enters into the matrix element (6), we obtain

$$\begin{aligned} & \int_0^{2\pi} d\varphi \int_0^{\pi} d\theta Y_{lm}^*(\theta, \varphi) \cos \theta Y_{l'm'}(\theta, \varphi) \sin \theta \rightarrow \int_0^{2\pi} d\varphi \times \\ & \times \int_0^{\pi} d\theta Y_{lm}^*(\theta, \varphi) \cos \theta Y_{l'm'}(\theta, \varphi) \times \\ & \times \sin \theta \left(1 \pm \frac{\alpha b}{b-a} \cos \theta \right). \end{aligned} \quad (8)$$

Let us calculate this integral. For convenience, we introduce the notation $\frac{\alpha b}{b-a} = \beta$. From the well-known formulas for Legendre polynomials,

$$\begin{cases} Y_{lm}(\theta, \varphi) \equiv \sqrt{\frac{2l+1}{4\pi} \frac{(l-m)!}{(l+m)!}} P_l^m(\cos \theta) e^{im\varphi}, \\ x P_l^m(x) = \frac{l-m+1}{2l+1} P_{l+1}^m + \frac{l+m}{2l+1} P_{l-1}^m \end{cases} \quad (9)$$

the following recurrent relation can be derived:

$$\begin{aligned} Y_{lm}(\theta, \varphi) \cos \theta &= \sqrt{\frac{2l+1}{4\pi} \frac{(l-m)!}{(l+m)!}} P_l^m(\cos \theta) e^{im\varphi} \cos \theta = \\ &= \sqrt{\frac{2l+1}{4\pi} \frac{(l-m)!}{(l+m)!}} e^{im\varphi} \left(\frac{l-m+1}{2l+1} P_{l+1}^m + \frac{l+m}{2l+1} P_{l-1}^m \right) = \\ &= \sqrt{\frac{(l+m+1)(l-m+1)}{(2l+1)(2l+3)}} Y_{l+1}^m + \end{aligned}$$

$$+ \sqrt{\frac{(l+m)(l-m)}{(2l+1)(2l-1)}} Y_{l-1}^m. \quad (10)$$

Using this property of Legendre polynomials and their orthogonality, we obtain

$$\begin{aligned} & \int_0^{2\pi} d\varphi \int_0^{\pi} d\theta Y_{lm}^*(\theta, \varphi) \cos \theta Y_{l'm'}(\theta, \varphi) \sin \theta (1 \pm \beta \cos \theta) = \\ &= \int_0^{2\pi} d\varphi \int_0^{\pi} d\theta (\gamma(l+1, m) Y_{l+1, m}^* + \gamma(l, m) Y_{l-1, m}^* \pm \\ & \pm \beta (\gamma(l+1, m) \gamma(l+2, m) Y_{l+2, m}^* + (\gamma^2(l+1, m) + \gamma^2 \times \\ & \times (l, m)) Y_{l, m}^* + \gamma(l, m) \gamma(l-1, m) Y_{l-2, m}^*)) Y_{l'm'}(\theta, \varphi) \sin \theta = \\ &= \delta_{m, m'} (\gamma(l', m') \delta_{l, l'-1} + \gamma(l, m) \delta_{l, l'+1} \pm \\ & \pm \beta (\gamma(l', m') \gamma(l'-1, m') \delta_{l, l'-2} + \\ & + (\gamma^2(l+1, m) + \gamma^2(l, m)) \delta_{l, l'+1} \\ & + \gamma(l, m) \gamma(l-1, m) \delta_{l, l'-2})). \end{aligned} \quad (11)$$

Here, we introduced the function

$$\gamma(l, m) \equiv \sqrt{\frac{(l+m)(l-m)}{(2l+1)(2l-1)}} \quad (12)$$

of two integer arguments. After the integration over the angular and radial variables, we substitute the obtained value of the matrix element $\langle i|z|f \rangle$ into expression (3) for the conductivity. Owing to the mutual orthogonality of delta indices, we obtain

$$\begin{aligned} \sigma &= \frac{2\pi e^2 \hbar^4}{V_s m_e^4 \omega^3} \frac{1}{(b-a)^2} \sum_{n, l, m, n', l', m'} (1 - (-1)^{n+n'}) k^2 (k')^2 \times \\ & \times f(E_i) (1 - f(E_f)) \delta(E_f - E_i - \hbar\omega) \delta_{m, m'} (\gamma^2(l', m') \delta_{l, l'-1} + \\ & + \gamma^2(l, m) \delta_{l, l'+1} \pm \beta^2 (\gamma^2(l', m') \gamma^2(l'-1, m') \delta_{l, l'-2} + \end{aligned}$$

$$+(\gamma^2(l+1, m) + \gamma^2(l, m))^2 \delta_{l, l'} + \gamma^2(l, m) \gamma^2(l-1, m) \delta_{l, l'-2}). \tag{13}$$

Let us sum up firstly over the quantum numbers l, l', m , and m' . The number m is known to vary within the limits $-l \leq m \leq l$, and the number l from 0 to $2n$. The presence of the delta indices $\delta_{m, m'}$ and $\delta_{l, l'+1}$ affects the summation procedure. Actually, the numbers l and l' vary from 0 to $2 \times \min(n, n') \pm 1$, and the number m from $-\min(l, l')$ to $\min(l, l')$. If the absorption takes place, as it is in our case, n is smaller than n' ; therefore, $0 \leq (l, l') \leq 2n$. Here, we neglect 1 in comparison with $2n$, because the summation is carried out over a narrow region of thermal smearing near the Fermi energy, for which $n \gg 1$. It also follows that the terms with small l, l', m , and m' cannot give a substantial contribution to the final sum, so that we can consider those quantum numbers to be much larger than 1 and, in particular, that $\gamma^2(l, m) \approx \frac{l^2 - m^2}{4l^2}$. After taking all those facts into account, the summation over the quantum numbers l, l', m , and m' can be carried out as follows:

$$\begin{aligned} & \sum_{l, m, l', m'} \delta_{m, m'} (\gamma^2(l', m') \delta_{l, l'-1} + \gamma^2(l, m) \delta_{l, l'+1} \pm \\ & \pm \beta^2 (\gamma^2(l', m') \gamma^2(l'-1, m') \delta_{l, l'-2} + (\gamma^2(l+1, m) + \\ & + \gamma^2(l, m))^2 \delta_{l, l'} + \gamma^2(l, m) \gamma^2(l-1, m) \delta_{l, l'-2})) \approx \\ & \approx \sum_{l, m, l', m'} \delta_{m, m'} \delta_{l, l'} (2\gamma^2(l, m) \pm 6\beta\gamma^4(l, m)) = \\ & = \sum_{m=-\tilde{l}}^{\tilde{l}} (2\gamma^2(\tilde{l}, m) \pm 6\beta\gamma^4(l, m)) \approx \\ & \approx \frac{2\tilde{l}}{3} \pm 6\beta \frac{\tilde{l}}{5} = \frac{2\tilde{l}}{3} \left(1 \pm \frac{3}{5} \beta^2 \right). \end{aligned} \tag{14}$$

Here, $\tilde{l} = \min(l, l')$.

We see that taking the shift of centers in a deformed ellipsoid into account results in the appearance of the constant factor $1 \pm \frac{3}{5} \beta^2$ in the expression for the conductivity already at this stage. Summing up further over \tilde{l} ,

$$\sum_{\tilde{l}=0}^{2n} \tilde{l} = \frac{2n(2n-1)}{2} \approx \frac{(2n)^2}{2} = 2 \left(\frac{b-a}{\pi} k \right)^2, \tag{15}$$

and substituting the result obtained into expression ([13]), we arrive at the expression for the optical conductivity in terms of the sum over n and n' ,

$$\begin{aligned} \sigma &= \frac{8e^2 \hbar^4}{3\pi V_s m_e^4 \omega^3} \left(1 \pm \frac{3}{5} \left(\frac{\Delta l}{b-a} \right)^2 \right) \times \\ & \times \sum_{n, n'} \left(1 - (-1)^{n+n'} \right) k^4 (k')^2 f(E) \times \\ & \times (1 - f(E')) \delta(E' - E - \hbar\omega). \end{aligned} \tag{16}$$

The core shift has no effect on the total shell volume, and the volume V_s in this formula remains therefore unchanged.

4. Calculation of the Optical Conductivity

We calculate sum (16), which was obtained for the optical conductivity, in two stages. At first, we replace the sum over the electron states by the integral, neglecting the effects connected with the energy quantization of the electron spectrum. Calculating the obtained integral similarly to how it was done in work [22], we write down the optical conductivity σ_0 in this approximation in the form

$$\sigma_0 = \frac{32e^2 (b-a)^2}{3\pi^3 \hbar^4 \omega^3 V_s} \left(1 \pm \frac{3}{5} \left(\frac{\Delta l}{b-a} \right)^2 \right) E_F^3 g_{\text{sph}}(\nu), \tag{17}$$

where E_F is the Fermi energy, $\nu = \hbar\omega/E_F$, and

$$\begin{aligned} g_{\text{sph}}(\nu) &= \int_{1-\nu}^1 q^{3/2} \sqrt{q+\nu} dq = \left(\frac{(q(q+\nu))^{3/2}}{3} - \right. \\ & \left. - \frac{\nu(2q+\nu)\sqrt{q(q+\nu)}}{8} + \frac{\nu^3}{8} \ln(\sqrt{q} + \sqrt{q+\nu}) \right) \Big|_{1-\nu}^1. \end{aligned} \tag{18}$$

The expression obtained does not take into account quantum-mechanical effects associated with the discreteness of the electron spectrum (information about the quantization becomes lost at the stage of changing from summation to integration). However, it makes allowance for the Pauli principle.

Now, let us insert corrections to expression (17) by considering the discrete behavior of the wavenumber spectrum. For this purpose, instead of replacing the sum

over n and n' , which enters into formula (16), by the integral, let us use the exact summation formula, namely, the Poisson formula

$$\sum_{n=1}^{\infty} y_1(n) = \int_0^{\infty} dn \left(y_1(n) + 2 \sum_{s=1}^{\infty} y_1(n) \cos(2\pi sn) \right), \quad (19)$$

where y_1 is an arbitrary function of the positive integer argument n . To calculate the sum in Eq. (16), the Poisson formula must be applied twice: while summing up over n and n' . When summing up over n' , the Poisson formula has to be applied to the expression that contains the delta function of discrete indices, namely, the function

$$G(E(n) + \hbar\omega) \equiv \sum_{n'=1}^{\infty} \left(1 - (-1)^{n-n'} \right) \times \delta(E(n') - E(n) - \hbar\omega). \quad (20)$$

For this operation to be correct, it should be noted that, as the delta function, we mean the limiting case for the family of classical functions (e.g., belonging to the class C^∞). At the passage to the limit, the area under the classical function remains equal to 1, when the characteristic width of a figure confined by the curve tends to zero, and its height grows infinitely. For our purposes, it is convenient to use the family of classical functions, which look like

$$\delta^*(x) = \begin{cases} 0, & x < -\frac{\Delta E}{2}, \\ \frac{1}{\Delta E}, & -\frac{\Delta E}{2} < x < \frac{\Delta E}{2}, \\ 0, & x > \frac{\Delta E}{2} \end{cases}, \quad (21)$$

at $\Delta E \rightarrow 0$. The Poisson formula is applied to the expression that contains δ^* . Then the passage to the limit $\Delta E \rightarrow 0$ is made. In addition, the multiplier $(1 - (-1)^{n'-n})$ in expression (20) can be replaced by its average value – it is unity – not only when changing from summation to integration (this replacement is evident in this case), but also when using the Poisson formula for the summation. The correctness of this approximation can be proved rigorously by separately considering the variants of even or odd n' in expression (20). The application of the Poisson formula to both cases produces identical expressions.

Bearing in mind those remarks, we replace the discrete function $(1 - (-1)^{n-n'})$ in Eq. (20) by its average value, which equals 1, and the delta function by δ^* . Then, we

apply the Poisson formula to the obtained sum, similarly to how it was done in work [22]. Having applied the Poisson formula twice (for summations over n and n') and taking into account that $E \approx E_F$ and $E_F \gg \theta$, where θ is the temperature in terms of energy units, we obtain the sought optical conductivity in the form

$$\begin{aligned} \sigma(\omega) &= \sigma_0(\omega) + \Delta\sigma = \sigma_0(\omega) \times \\ &\times \left(1 + \frac{2\pi\theta \left(1 - e^{-\frac{\hbar\omega}{\theta}} \right)^{-1} (\Phi(E_F) - \Phi(E_F - \hbar\omega))}{E_F^3 \tilde{g}_{\text{sph}}(\nu)} \right) = \\ &= \frac{8e^2}{\pi^4 \hbar} \frac{(b-a)^2}{b^3 - a^3} \left(1 \pm \frac{3}{5} \left(\frac{\Delta l}{b-a} \right)^2 \right) g_{\text{sph}}(\nu) \times \\ &\times \left(1 + \frac{2\pi\theta \left(1 - e^{-\frac{\hbar\omega}{\theta}} \right)^{-1} (\Phi(E_F) - \Phi(E_F - \hbar\omega))}{E_F^3 \nu^3 g_{\text{sph}}(\nu)} \right), \end{aligned} \quad (22)$$

where

$$\Phi(E_F) = E_F^{3/2} (E_F + \hbar\omega)^{1/2} \sum_{s=1}^{\infty} \frac{\sin \varphi_s(E_F)}{\text{sh}(\pi\theta\varphi'_s(E_F))}, \quad (23)$$

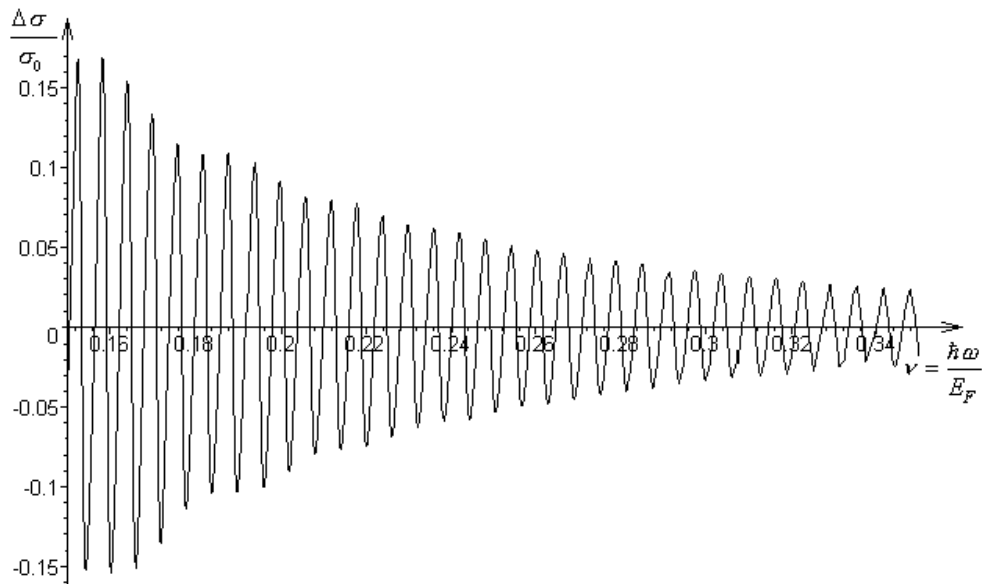
$$\varphi_s(E) \equiv s \frac{2(b-a)}{\hbar} \sqrt{2m_e} \left(\sqrt{E + \hbar\omega} - \sqrt{E} \right), \quad (24)$$

and

$$\begin{aligned} \Delta\sigma &= \sigma_0 \frac{2\pi\theta \left(1 - e^{-\frac{\hbar\omega}{\theta}} \right)^{-1} (\Phi(E_F) - \Phi(E_F - \hbar\omega))}{E_F^3 \tilde{g}_{\text{sph}}(\nu)} = \\ &= \frac{8e^2}{\pi^4 \hbar} \frac{(b-a)^2}{b^3 - a^3} g_{\text{sph}}(\nu) \left(1 \pm \frac{3}{5} \left(\frac{\Delta l}{b-a} \right)^2 \right) \times \\ &\times \frac{2\pi\theta \left(1 - e^{-\frac{\hbar\omega}{\theta}} \right)^{-1} (\Phi(E_F) - \Phi(E_F - \hbar\omega))}{E_F^3 \tilde{g}_{\text{sph}}(\nu)} \end{aligned} \quad (25)$$

is a correction to the conductivity associated with the spectrum quantization.

The obtained expression (22) for the conductivity consists of two components. These are the semiclassical conductivity (formula (17)), which does not make allowance



Dependence of the relative quantum-mechanical correction $\frac{\Delta\sigma}{\sigma_0}$ on the light frequency for a nanoparticle with $E_F = 5.53$ eV (the Fermi energy for gold), the dielectric core radius $a = 40$ nm, and the average shell thickness $b - a = 100$ nm

for the discreteness of the wavenumber spectrum of an electron in the shell, and the small correction (formula (25)), which takes those effects into consideration. One can see that the initial sum for the optical conductivity (16) differs from the corresponding sum for a symmetric spherical nanoshell [22] by the multiplier $1 \pm \frac{3}{5} \left(\frac{\Delta l}{b-a}\right)^2$ before the sum. This multiplier is independent of n . Hence, the optical conductivity of a nanoparticle differs from that of the corresponding spherical nanoshell by the same multiplier $1 \pm \frac{3}{5} \left(\frac{\Delta l}{b-a}\right)^2$.

A graphic representation of the relative quantum-mechanical correction $\frac{\Delta\sigma}{\sigma_0}$ as a function of the parameter ν for a spherical nanoparticle with $E_F = 5.53$ eV (it is the Fermi energy for gold), the dielectric core radius $a = 40$ nm, and the average shell thickness $b - a = 100$ nm is shown in Figure (as is seen from Eq. (22), this correction does not depend on Δl , the distance between the centers). The figure, as well as the results of numerical calculations, testifies that the quantum-mechanical corrections cannot be neglected. For thinner shells, the contribution of that correction is even more considerable. Hence, the account of the electron energy quantization leads to the appearance of an oscillatory dependence of optical conductivity components on the frequency of light that falls on the shell. The corresponding analysis shows that the frequency of oscillations depends on the shell thickness. As was already mentioned in Introduc-

tion, the dependence of such kind was observed even for rather thick nanowires [14].

Hence, a small shift Δl between the shell and core centers along the wave propagation direction gives rise to the appearance of the term $\frac{3}{5} \left(\frac{\Delta l}{b-a}\right)^2$ of the second order of smallness in the expression for the corresponding conductivity component. One can see that the effects associated with the discreteness of the electron spectrum in the shell and the effects associated with a shift of the centers affect the optical conductivity independently. Therefore, the core center shift in a nanoparticle with a very thin shell (i.e. when the account of electron spectrum quantization is needed) can be taken into account by introducing the same multiplier $1 \pm \frac{3}{5} \left(\frac{\Delta l}{b-a}\right)^2$ into the conductivity formulas; this concerns both the general expression for the conductivity in terms of a sum over electron states (formula (16) and the semiclassical one (formula (17)).

5. Conclusion

The optical properties of a metallic nanoparticle, the shape of which is close to spherical, have been studied in the case of a small shift between the dielectric core center and the external shell center. In particular, we obtained an expression for the single-electron optical conductivity of such a nanoparticle. The shell was considered thin

in comparison with nanoparticle dimensions, the condition being satisfied for typical nanoeggs. The final expression (22) takes into account the effects associated with the discrete electron energy spectrum (they manifest themselves as oscillations in the dependence of the optical conductivity on the incident light frequency) and demonstrates the following:

– The small relative shift between the centers of the dielectric core and the external boundary of a nanoparticle Δl results in a variation of the nanoparticle conductivity by a small relative value $\frac{3}{5} \left(\frac{\Delta l}{b-a} \right)^2$ as compared with the conductivity of corresponding spherically symmetric nanoshell. The optical conductivity increases, if the external shell center is shifted with respect to the core center in the wave propagation direction, and decreases, if the shift is in the opposite direction;

– The account of quantum-mechanical effects associated with the discreteness in the spectrum of wave numbers of an electron (and, accordingly, in its energy spectrum) results in the appearance of an oscillatory dependence of the nanoparticle optical conductivity on the incident light frequency. The frequency and the relative amplitude of oscillations increase, if the thickness of the metallic shell decreases. The oscillatory dependence is similar to that obtained in work [22];

– The electron spectrum discreteness and the relative shift between the nanoparticle centers, when calculated to the first order of smallness, gives rise to independent corrections to the optical properties of the nanoparticle.

As one can see, the relative change of the conductivity $\frac{3}{5} \left(\frac{\Delta l}{b-a} \right)^2$ connected with the shift between the nanoparticle centers is proportional to the squared shift and reciprocal to the squared shell thickness. Since this correction is of the second order of smallness, this means that the optical properties of a metallic nanoshell are stable with respect to small relative shifts between the core and shell centers, and their dependence on this shift is weak.

A further development of this topic may include the study of spherical nanoeggs making no assumptions concerning the smallness of the relative shift between the centers of the dielectric core and the external shell boundary.

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ОДНОЕЛЕКТРОННІ ОПТИЧНІ
ВЛАСТИВОСТІ МЕТАЛЕВИХ НАНООБОЛОНОК
З НЕКОНЦЕНТРИЧНИМ ЯДРОМ. ВРАХУВАННЯ
КВАНТУВАННЯ ЕЛЕКТРОННОГО СПЕКТРА

V.V. Kulish

Р е з ю м е

Роботу присвячено дослідженню одноелектронних оптичних властивостей (внесок одноелектронної компоненти є суттєвим

у областях частот, далеких від плазмонного резонансу) сферичної наночастинки, що складається з діелектричного ядра та тонкої металевої оболонки, зі слабким зміщенням центра ядра відносно геометричного центра всієї наночастинки. Запропоновано модель, що дозволяє записати хвильові функції та спектр хвильових чисел для електрона у оболонці композитної наночастинки такого типу. За допомогою цієї моделі отримано матричні елементи оптичних переходів та одноелектронну оптичну провідність наночастинки як без урахування (напівкласична провідність), так і з урахуванням квантування хвильових чисел електрона у оболонці. Показано, що врахування вищезазваних ефектів квантування приводить до появи осцилюючої залежності оптичної провідності наночастинки від частоти світла. Показано, що вплив зміщення центрів та квантування спектра на оптичну провідність наночастинки у першому наближенні можна враховувати незалежно.