

Localised plasmons in sphere-like fullerenes and nanoparticles with conducting shells: Classical electrodynamic approach

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Abstract. Based on the classical electrodynamic approach, we consider localised plasmons in fullerenes and small particles with metal layers and shells. At low energies of the radiation quantum, models of fullerenes as conducting shells are used taking into account the contribution of only π electrons, and at high energies, of both π and σ electrons. The obtained maxima of the scattering cross sections correspond to the values of 20 and 27 eV that were determined experimentally and in quantum models for the maxima of the photoionisation cross sections of fullerenes C_{60} and C_{28} , respectively. Approximate analytical results are presented for resonant frequencies, Q factors, radiation patterns, scattering and absorption cross sections for sphere-like particles and fullerenes, as well as integral equations and functionals for dielectric particles with a conducting shell of arbitrary shape. Analysis relies on the use of effective surface conductivity.

Keywords: localised plasmons, surface conductivity, fullerenes, graphene, scattering cross section, radiation pattern.

1. Introduction

In recent decades, there has been considerable interest in the study of plasmons – a phenomenon that has been known for a long time, but has found widespread use only a short time ago (see, for example, [1–6]). Plasmon polaritons can be bulk, surface, and localised. They can be described as waves and as electromagnetic oscillations induced by electronic or exciton excitations in a conducting structure. Localised plasmon polaritons (LPPs) considered in this work are oscillations in a certain conducting particle, for example, a metal particle; therefore, there arise problems to solve specific to them, involving determination of local fields, far-zone fields, complex resonant frequencies (frequencies and Q factors of resonances) of free oscillations and frequency properties of plane-wave scattering parameters [1–16].

Many papers are devoted to LPPs in different particles and to methods of their analysis. Their analysis is based both on classical electrodynamic approaches [1–24] in strict and various approximate statements and on quantum approaches that consider a particle as a quantum dot (quantum box) using approximate methods of strong coupling, density functional theory (DFT) [24–27] and similar methods, for example, the Thomas–Fermi hydrodynamic model [28, 29]. In an

azimuthally symmetric structure, LPPs can be approximately considered as resonances of surface plasmons travelling on the surface of a material. LPPs allow the local field to be enhanced and controlled and therefore they are widely used in various fields of physics, biology and medicine [1–6]. When excited by a plane wave, of interest are the problems of determining the differential and total cross sections [scattering, absorption (photoionisation) and extinction], as well as constructing radiation patterns of scattering. Since the dipole scattering cross section has a maximum near the resonant frequency [30], the calculation of resonant frequencies of dipole modes is important for describing the behaviour of particles in an exciting wave. To design nonlinear and tunable devices, particles with semiconductor shells and nuclei, the resonant frequencies of which can be tuned, are of interest [21]. Plasmon resonance frequencies in well-conducting semiconductor films such as InSb films and others can be reduced in the THz region and tuned by doping.

Most LPP studies considered spherical conducting (metal) or dielectric particles, since the Mie solution of the excitation problem [10–15] and the solution for free oscillations [7] obtained by the matching method are known for them. The matching method is also applicable to particles in the form of a triaxial ellipsoid [14]. Recently, layered spherical particles [17–20] and particles of arbitrary shape [1, 2, 12–15] have been studied, for some of which approximate results have been obtained [1–5, 31]. It is convenient to study resonances in multilayer spherical particles by the method of 4×4 transfer matrices for spherical layers [32], which allows one to consider an arbitrary number of layers. In the limit, this approach allows one to describe particles with a radially inhomogeneous permittivity profile. Particles with metal cores and dielectric shells, as well as with dielectric cores and conducting shells, are also of interest.

Classical approaches are usually based on expansion in wave spherical harmonics [17–19], on the Rayleigh approximation using the variable separation method for the scalar potential decomposed in the spherical harmonics of the Laplace equation [20], on the two-fluid model [23] and on other approaches. Although classical methods for multilayer structures are well known, including matching and integral equation (IE) methods, combined surface-volume IEs for particles with two-dimensional conducting shells have not been used, as well as characteristic equations based on matching. The aim of the present work is to obtain such equations and to study LPPs for particles with two-dimensional shells. For nanoshells of finite thickness, significantly shorter than the wavelength and the depth of wave penetration into them, the shells can be considered two-dimensional, which reduces the dimensionality of the problem and simplifies the calcula-

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tion. The second criterion is the mean free path λ_0 in comparison with the shell thickness. Small thickness means the impossibility of using parameters for bulk samples and the need for a quantum calculation of electron transport [33–36] or an approximation that takes into account dimensional effects [37, 38].

Fullerenes, i.e. nanoclusters or carbon molecules discovered in 1985, are able to support LPPs. The band structure of C_{20} , C_{60} and other fullerenes has a gap 1.7–2.0 eV wide, but when the fullerenes are doped with X_3C_{60} alkali metals, they acquire metallic properties and can even become superconducting at low temperatures (19 K for K_3C_{60} and 33 K for $RbCs_2C_{60}$). In fullerenes, as well as in graphene, π electrons participate in electron transport in the IR and optical ranges, which, due to the large localisation of the wave function near the surface, can be described by effective surface conductivity. A large number of publications stimulated experimental work on the detection of giant resonances in the energy range of 20–30 eV for C_{60} [39, 40], C_{28} and C_{20} [23–29]. In the hard UV and near X-ray ranges, the energy of quanta is greater than the energy of σ bonds, and all four valence electrons of the carbon atom are involved in the transport. They can be considered free and use can be made of the plasma approximation [22, 23]. To estimate the above frequencies, we note that for graphene, the overlap energy of neighbouring atoms (σ -bond energy) is $\lambda_0 = 3.033$ eV, and the overlap integral of σ electrons is $s_0 = 0.129$ eV [41]. The binding energy in fullerenes does not differ much from the above value; therefore, in the IR and optical ranges, the shell conductivity can be considered equal to the optical conductivity of graphene [34–36], and the plasma layer model is a good approximation in the UV and X-ray ranges.

The authors of Refs [23–27] considered photoionisation and obtained inelastic scattering cross sections for fullerenes C_{20} and C_{60} in the region of high quantum energies. A quantum mechanical model of a metal cluster and fullerene was used in the approximation of the simplified Hamiltonian (helium model), in the approximation of local density and random phases of the density functional theory. The authors of Ref. [22] considered LPPs in fullerene C_{60} based on the hydrodynamic approximation and the fullerene model in the form of a plasma spherical layer of given thickness. The study of the properties of C_{60} began a long time ago [23], and publications, of course, are not limited to those mentioned above.

In this paper, we consider free and forced oscillations (during scattering of a plane wave) in LPPs with two-dimensional shells, obtain the characteristic equations of free oscillations of spherical dielectric particles in the presence of a conducting shell, derive generalising equations [7] and present IEs and integro-differential equations (IDEs) for particles with a shell of arbitrary shape. Based on them, we consider low-frequency LPPs in sphere-like fullerenes and in a small dielectric cube with a shell. Full scattering cross sections and radiation patterns for fullerenes excited by a plane wave are presented.

2. Diffraction and free oscillations for particles with a conducting shell

Let us consider a nanoparticle classically interacting with an electromagnetic wave [time dependence $\exp(i\omega t)$] in the form of a volume V occupied by a dielectric with a permittivity $\epsilon(\mathbf{r})$ and surrounded by a conducting layer (shell) of thickness δ with a permittivity $\epsilon_m(\mathbf{r})$. Let $\epsilon_m(\mathbf{r})$ correspond to a metal and

be described by the Drude–Lorentz formula $\epsilon_m(\omega) = \epsilon_L(\omega) - \omega_p^2/(\omega^2 - i\omega\omega_c)$. Here ω_p and ω_c are the plasma frequency and the collision frequency. We consider the frequency to be low, and the Lorentz term ϵ_L to be independent and positive, which is true up to the optical range. The boundary of the volume is a closed surface S . Since the shell has the same thickness, its volume ΔV is inside the surfaces S and S' , where the surface S' is congruent to S and its points closest to S are at a distance equal to δ . For a shell, we introduce the volume density of the polarisation current $\mathbf{J} = \partial_t \mathbf{P}(\mathbf{r})$ and the volume conductivity $\gamma(\mathbf{r}) = i\omega\epsilon_0[\epsilon_m(\mathbf{r}) - 1]$:

$$\mathbf{J}(\omega, \mathbf{r}) = \gamma(\omega, \mathbf{r})\mathbf{E}(\omega, \mathbf{r}). \quad (1)$$

Relation (1) is suitable for any shell, not necessarily metallic, and for thin shells it is determined from the quantum approach to electron transport [33–36]. The criterion for shell thinness is the comparability (or smallness) of the shell thickness with the mean free path. If δ is of the order of the mean free path or less, the conductivity σ is determined by calculating the number of conduction modes depending on δ [33].

For two-dimensional structures such as graphene, the conductivity σ has a natural nature. For low frequencies, the main contribution is made by π electrons only. We will also model fullerenes with the conductivity σ , which is determined by the transport of π electrons or π and σ electrons. Then, the conductivity can be used in the classical approach. For a massive metal sample in the low-frequency limit, we obtain the Drude conductivity $\gamma(0) = \omega_p^2\epsilon_0/\omega_c$. If the shell thickness is small compared to the penetration depth and transverse currents can be neglected, we can introduce surface conductivity $\sigma = \gamma\delta$. If v is the coordinate along the external normal measured from the surface S , then the relation between the surface $[\mathbf{j}(\mathbf{r})]$ and volume $[\mathbf{J}(\mathbf{r})]$ current densities has the form $\mathbf{J}(\mathbf{r}) = \mathbf{j}(\mathbf{r})\delta(v)$. Volume and surface charge densities are similarly related: $\rho(\mathbf{r}) = \zeta(\mathbf{r})\delta(v)$. When integrated with the delta function, the volume integral degenerates into the surface integral. In a certain sense, for small δ (in comparison with the wavelength λ), relation (1) can be replaced by the relation $\mathbf{j}(\mathbf{r}) = \sigma\mathbf{E}_\tau(\mathbf{r})$, where $\mathbf{E}(\mathbf{r}) = \mathbf{v}(\mathbf{r}) \times \mathbf{E}(\mathbf{r}) \times \mathbf{v}(\mathbf{r}) = \mathbf{E}(\mathbf{r}) - \mathbf{E}_v(\mathbf{r})$ is the projection of the electric field vector onto the surface.

For an arbitrary particle, the problem can be formulated on the basis of IEs or IDEs. Of interest are both the problem of excitation by a given field, for example, by the plane-wave field $\mathbf{E}_{in}(\mathbf{r}) = \mathbf{E}_0 \exp(-i\mathbf{k}\mathbf{r})$ [the $\exp(i\omega t)$ dependence is omitted hereinafter] and the problems of eigenoscillations. In the general case, we have a representation of the vector potential of the scattered field

$$\mathbf{A}(\mathbf{r}) = \int_{V+\delta V} G(\mathbf{r} - \mathbf{r}', k_0)\mathbf{J}(\mathbf{r}')d^3r' \quad (2)$$

and representations of the fields

$$\mathbf{E}(\mathbf{r}) = \mathbf{E}_{in}(\mathbf{r}) + (ik_0)^{-1}Z_0(k_0^2 + \hat{L})\mathbf{A}(\mathbf{r}),$$

$$\mathbf{H}(\mathbf{r}) = \mathbf{H}_{in}(\mathbf{r}) + \nabla \times \mathbf{A}(\mathbf{r}).$$

In (2), d^3r' is the volume element; $G(\mathbf{r} - \mathbf{r}', k_0) = (4\pi R)^{-1} \times \exp(-ik_0 R)$ is the scalar Green's function; $R = |\mathbf{r} - \mathbf{r}'|$; $k_0 = \omega/c$; $Z_0 = \sqrt{\mu_0/\epsilon_0}$; $\mathbf{J}(\mathbf{r}) = i\omega\epsilon_0[\epsilon(\mathbf{r}) - 1]\mathbf{E}(\mathbf{r})$ is the polarisation current density; V is the volume; $\delta V = S$ is its boundary; and $\hat{L} = \nabla \otimes \nabla = \text{grad} \cdot \text{div}$ is an operator. The fields $\mathbf{E}_{in}(\mathbf{r})$ and $\mathbf{H}_{in}(\mathbf{r})$ correspond to an incident plane wave.

Representation (2) allows us to formulate several types of IEs and IDEs, including surface-volume ones (see [9]). They arise due to the superimposition of the boundary conditions $\mathbf{j} = \sigma \mathbf{E}_\tau$ on the surface and the continuity of the field \mathbf{E} in the volume. The advantages of IEs and IDEs are that they are solved only in the region of the particle, and the solutions are represented in the entire space, i.e. it is convenient to obtain sufficiently accurate analytical solutions using physical assumptions about the field and the surface current density. We write (2) as $\mathbf{A} = \hat{G}(\mathbf{J})_{V+\delta V}$, where \hat{G} is an integral operator. Introducing the integro-differential operators $\hat{L}\hat{G}(\mathbf{J})_{V+\delta V}$ and $\nabla \times \hat{G}(\mathbf{J})_{V+\delta V}$ and using vector integral theorems (on the gradient, on divergence and on the rotor), we can obtain a number of other IDE forms [8, 9].

In this paper, we will use a surface-volume IE of the form

$$[2 + \varepsilon(\mathbf{r})]\mathbf{E}(\mathbf{r})/3 = \mathbf{E}_{\text{in}}(\mathbf{r}) + [\hat{L}\hat{G}'(\mathbf{F})_V + k_0^2 \hat{G}(\mathbf{F})_V] - iZ_0(k_0^2 + \hat{L})\hat{G}(\mathbf{j})_S/k_0 \quad (3)$$

and an IDE of the form

$$\mathbf{j}(\mathbf{r}) = \sigma \mathbf{E}_\tau(\mathbf{r}) = -i\sigma Z_0 \oint_S [k_0 G(\mathbf{r} - \mathbf{r}', k_0) \mathbf{j}(\mathbf{r}')] - ic \nabla G(\mathbf{r} - \mathbf{r}', k_0) \zeta(\mathbf{r}') d^2 r'. \quad (4)$$

In (3) we introduced a vector proportional to the field, $\mathbf{F}(\mathbf{r}) = [\varepsilon(\mathbf{r}) - 1]\mathbf{E}(\mathbf{r})$, and in (4) we introduced the surface charge density $\zeta = i\nabla \mathbf{j} / \omega$. The physical meaning of these equations is very simple. Equation (3) means the continuity of the total electric field inside and outside the particle with the fulfilment of the radiation condition, while on the surface it is necessary to fulfil the boundary condition $\mathbf{E}_\tau(\mathbf{r}) = \sigma^{-1} \mathbf{j}$. This allows us to find both \mathbf{E} in the volume and \mathbf{j} on the surface. The equation is obtained by puncturing an infinitesimal spherical neighbourhood near the source point with calculating the integral over it based on Ostrogradsky's theorem; therefore, the integral operators should be understood in the sense of the main value according to Cauchy (denoted by a prime). As a result, a term arises outside the integral, and quadrature formulas can be used to calculate the integrals. In the absence of a shell, equation (3) becomes a volume IE of the type of a Fredholm equation of the second kind. Formula (4) corresponds only to oscillations of the conductive shell and is defined on it. By virtue of the equality $\mathbf{j} = \sigma \mathbf{E}_\tau$, it determines the tangential electric field produced by the distributions of the surface current and charge and corresponds to its expression in terms of the vector and scalar potentials: $\mathbf{E} = -ik_0 Z_0 \mathbf{A} - \nabla \varphi$, where $\varphi = iZ_0 \nabla \mathbf{A} / k_0$ [42]. The dimensionless (normalised) surface conductivity $\xi = \sigma Z_0$ is convenient.

The above, as well as other IEs and IDEs are usually used in the case of bodies of large electric size, when it is necessary to obtain a numerical solution using projection and variational algorithms of large dimension, for example, for dielectric resonators [8]. For nanoparticles, the use of the dipole approximation usually allows one to evaluate the influence of the shape on the resonant frequencies, cross sections and radiation pattern. To obtain the functional for determining the resonant frequency, we multiply (4) by $\mathbf{j}^*(\mathbf{r})$ and integrate over the surface, designating the result as $\|\mathbf{j}(\mathbf{r})\|^2 = (\mathbf{j}(\mathbf{r}), \mathbf{j}(\mathbf{r}))_S$. We denote the projection of the vector operator ∇ onto the surface as $\nabla_\tau = \nabla - \mathbf{v} \partial_\nu$ and consider the quantity $\mathbf{j}^*(\mathbf{r}) \nabla \eta(\mathbf{r}) = \nabla(\eta(\mathbf{r}) \mathbf{j}^*(\mathbf{r})) - \eta(\mathbf{r}) \nabla \mathbf{j}^*(\mathbf{r})$, where $\eta(\mathbf{r})$ is an arbitrary function.

Since the current density is the surface one, $\nabla \mathbf{j}^*(\mathbf{r}) = \nabla_\tau \mathbf{j}^*(\mathbf{r}) = i\omega \zeta^*(\mathbf{r})$.

We divide the closed surface into two parts by the contour C , which will become the boundary of each of them, and consider the integral $(\mathbf{j}(\mathbf{r}) \nabla \eta(\mathbf{r}))_S$. The integral of the first term is zero. Indeed, $\nabla(\eta(\mathbf{r}) \mathbf{j}^*(\mathbf{r})) = \nabla_\tau(\eta(\mathbf{r}) \mathbf{j}^*(\mathbf{r}))$. Applying the Gauss theorem to two-dimensional divergence on both surfaces, we obtain two integrals over the contour of $\eta(\mathbf{r}) \mathbf{j}^*(\mathbf{r}) \mathbf{n}(\mathbf{r})$, where the normal to the contour lies in the plane tangent to the surface and is taken for two parts of the surface with different signs. To eliminate doubts about the applicability of the two-dimensional Gauss theorem to a non-planar surface, we divide it into a large number of adjacent surfaces ΔS_m so that each of them can be considered plane. Passing to the limit $m \rightarrow \infty$, we obtain the desired result.

Thus, $(\mathbf{j}(\mathbf{r}) \nabla \eta(\mathbf{r}))_S = -i\omega(\zeta(\mathbf{r}) \eta(\mathbf{r}))_S$. Choosing the second integral in (4) as $\eta(\mathbf{r})$, we obtain the functional

$$\Psi(\mathbf{j}) = (\mathbf{j}(\mathbf{r}), \mathbf{j}(\mathbf{r}))_S + ik_0 \sigma Z_0 \oint_S \oint_S [\mathbf{j}^*(\mathbf{r}) G(\mathbf{r} - \mathbf{r}', k_0) \mathbf{j}(\mathbf{r}')] + c^2 \zeta^*(\mathbf{r}) G(\mathbf{r} - \mathbf{r}', k_0) \zeta(\mathbf{r}') d^2 r' d^2 r. \quad (5)$$

It has a zero stationary value, from which, approximately setting $\mathbf{j}(\mathbf{r})$, it is possible to approximately determine the complex resonant frequency $\omega = \omega' + i\omega''$. A strict characteristic equation should be constructed by expanding $\mathbf{j}(\mathbf{r})$ into basic functions and varying (5) with respect to expansion coefficients. This will lead to a homogeneous system of linear algebraic equations, the zero value of the determinant of which will give the characteristic equation. Thus, approximately setting $\mathbf{j}(\mathbf{r})$ for physical reasons, it is possible to iteratively solve (5), obtaining the resonant frequency and Q factor.

We write the quasi-static equation for a dielectric body in the form $\mathbf{E}(\mathbf{r}) = -\nabla \varphi(\mathbf{r})$, neglecting in (4) the first term under the integral containing k_0 . It determines the jump in the normal component of the electric field upon crossing the boundary. Indeed, $\nabla \varphi(\mathbf{r})$ is the potential of the double layer, having a jump ζ/ε_0 when passing through the surface. Therefore, for a jump in the normal component of the field, we have

$$\varepsilon_0 E_\nu(\mathbf{r} + 0) = -\oint_S \mathbf{v}(\mathbf{r}) \nabla G(\mathbf{r} + 0 - \mathbf{r}', k_0) \zeta(\mathbf{r}') d^2 r' + \zeta(\mathbf{r})/2,$$

$$\varepsilon_0 E_\nu(\mathbf{r} - 0) = -\oint_S \mathbf{v}(\mathbf{r}) \nabla G(\mathbf{r} - \mathbf{r}', k_0) \zeta(\mathbf{r}') d^2 r' - \zeta(\mathbf{r})/2$$

and we obtain the expression for ζ through the indicated jump. The relation $E_\nu(\mathbf{r} + 0) = \varepsilon E_\nu(\mathbf{r} - 0)$ yields a quasi-static IE for the surface charge density

$$\zeta(\mathbf{r}) = 2\varepsilon_0 \frac{1 - \varepsilon}{1 + \varepsilon} \oint_S \mathbf{v}(\mathbf{r}) \nabla G(\mathbf{r} - \mathbf{r}', k_0) \zeta(\mathbf{r}') d^2 r'. \quad (6)$$

Equation (6) yields a quasi-stationary distribution of the plasmon surface charge [1]. Its frequency dependence is also determined by the dependence $\varepsilon(\omega)$. The condition $\varepsilon \approx -1$ is characteristic of plasmonics, and then for a nonzero charge distribution to exist, the integral should be close to zero.

To scatter a plane wave with an electric field amplitude E_0 on a particle, it is necessary to solve the above inhomogeneous equations and determine the densities \mathbf{j} and $\mathbf{J}_p = i\omega \varepsilon_0 \times (\varepsilon - 1)\mathbf{E}$ proportional to E_0 , and then, as usual, use them in

the relations determining the Poynting vector flux $\mathcal{S} = r\Phi(\theta, \varphi)/r^3$ in the far zone through the surface of a large radius R [42–45]. Here $\Phi(\theta, \varphi)$ is the radiation power diagram ([43], p. 320). Then the total scattering cross section Σ can be defined as the integral of $R^2\Phi(\theta, \varphi)$ over the entire solid angle divided by $E_0^2/(2Z_0)$.

3. Free and forced oscillations in spherical particles

In the case of a spherical surface, the problem has an analytical solution. For the problem of excitation of a ball by a plane wave, this is the Mie solution [10–15, 46]. The characteristic equations of free oscillations for the E and H modes are presented in [7, 46] and have the form

$$D^e(\omega) = \frac{n}{kr_0}(\varepsilon - 1) + \frac{J_{n-1/2}(kr_0)}{J_{n+1/2}(kr_0)} - \varepsilon^{1/2} \frac{H_{n-1/2}^{(2)}(k_0r_0)}{H_{n+1/2}^{(2)}(k_0r_0)} = 0, \quad (7)$$

$$D^m(\omega) = \frac{\varepsilon^{1/2} J_{n-1/2}(kr_0)}{J_{n-1/2}(kr_0)} - \frac{H_{n-1/2}^{(2)}(k_0r_0)}{H_{n+1/2}^{(2)}(k_0r_0)} = 0. \quad (8)$$

Here $k = k_0\sqrt{\varepsilon}$. Using the Debye potentials [42, 44] and sewing the fields with allowance for the presence of a conducting shell on the particle, it is easy to obtain the equations for the E and H modes:

$$\xi\sqrt{\varepsilon}\partial_x\psi_n^-(x_0) = i[f_n\psi_n^+(x_0) - \varepsilon\psi_n^-(x_0)], \quad (9)$$

$$\xi\psi_n^-(x_0) = i[g_n\partial_y\psi_n^+(x_0) - \sqrt{\varepsilon}\partial_x\psi_n^-(x_0)]. \quad (10)$$

Here $\xi = \sigma Z_0$; $x_0 = kr_0$; $\chi_0 = k_0r_0$; r_0 is the particle radius; $\psi_n^-(x_0) = \sqrt{\pi x_0/2} J_{n+1/2}(x_0)$ and $\psi_n^+(x_0) = \sqrt{\pi \chi_0/2} H_{n+1/2}^{(2)}(\chi_0)$ are the Riccati–Bessel and Riccati–Hankel functions, respectively; and

$$f_n = \frac{\partial_r\psi_n^-(x_0)}{\partial_r\psi_n^+(x_0)} = \varepsilon^{1/4} \frac{x_0 J_{n-1/2}(x_0) - n J_{n+1/2}(x_0)}{\chi_0 H_{n-1/2}^{(2)}(\chi_0) - n H_{n+1/2}^{(2)}(\chi_0)}, \quad (11)$$

$$g_n = \frac{\psi_n^-(x_0)}{\psi_n^+(x_0)} = \varepsilon^{1/4} \frac{J_{n+1/2}(x_0)}{H_{n+1/2}^{(2)}(\chi_0)} \quad (12)$$

are the coefficients. Equations (7) and (8) follow from (9) and (10) for $\xi = 0$. For fullerenes, we need to set $\varepsilon = 1$, $x_0 = \chi_0$. For a ball, the classical strict solution for Mie scattering is given by the formula [46]

$$\Sigma = \frac{2\pi}{k_0^2} \sum_{n=1}^{\infty} (2n+1)(|a_n|^2 + |b_n|^2),$$

where

$$a_n = \frac{\sqrt{\varepsilon}\psi_n^-(\chi_0)\psi_n^-(x_0) - \psi_n^-(x_0)\psi_n^-(\chi_0)}{\sqrt{\varepsilon}\psi_n^-(\chi_0)\psi_n^+(x_0) - \psi_n^+(x_0)\psi_n^-(\chi_0)},$$

$$b_n = \frac{\psi_n^-(\chi_0)\psi_n^-(x_0) - \sqrt{\varepsilon}\psi_n^-(x_0)\psi_n^-(\chi_0)}{\psi_n^-(\chi_0)\psi_n^+(x_0) - \sqrt{\varepsilon}\psi_n^+(x_0)\psi_n^-(\chi_0)}.$$

Absorption and extinction cross sections are also expressed through the above coefficients. The expansion in the small parameter $\chi_0 \ll 1$ with only the dipole term $n = 1$ taken into

account leads to the well-known formula for the scattering cross section [see (92.4) in [16]], which for a small particle in the form of a thin spherical dielectric shell of thickness δ in the low-frequency limit yields $\Sigma = 3|(\varepsilon - 1)/(\varepsilon + 2)|^2 \times (\omega r_0/c)^4 \delta^2$. For fullerenes, we take

$$\Sigma = 3|\xi|^2(kr_0)^4/[3 + \xi''/(k_0\delta)]^2 + \xi'^2(k_0\delta)^{-2},$$

where $\xi = \xi' + i\xi''$ is the normalised conductivity; and δ is the thickness characterising the spread of the electron density $\rho(r)$ obtained, for example, by the DFT method. For C_{60} , the calculations yield $\delta \sim 1$ at. units [25]. With increasing frequency, multipole resonances can appear; however, after the dipole resonance, the frequencies are high, and a quantum approach should be used for fullerenes, which gives high-frequency asymptotics for model potentials [27].

In the dipole approximation for a wave polarised along the z axis, the density of the induced volume current on the conducting shell can be taken in the form $J_\theta(r, \varphi, \theta) = -\sigma E_0 \sin\theta \delta(r - r_0)$. Using formulas (2.94) for the vector potential and (2.28) for the Green's function from [42], we calculate the components A_θ , H_φ and the flux of the Poynting vector P_Σ of the scattered field in the far zone $k_0r \gg 1$:

$$A_\theta = \frac{\sigma E_0 r_0}{ik_0 r} \sum_{n=0}^{\infty} I_n(\cos\theta) (2n+1) \psi_n^+(k_0 r) \psi_n^-(k_0 r_0), \quad (13)$$

$$H_\varphi(r, \theta) = r^{-1} \partial_r (r A_\theta) = -i\sigma E_0 r_0 r^{-1} \times \sum_{n=0}^{\infty} I_n(\cos\theta) (2n+1) [\psi_n^+(k_0 r) \psi_n^-(k_0 r_0)], \quad (14)$$

$$P_\Sigma = \pi Z_0 \int_0^\pi |H_\varphi(r, \theta)|^2 r^2 \sin\theta d\theta = \frac{|\xi|^2 E_0^2 \pi r_0^2 I(k_0 r_0)}{Z_0}, \quad (15)$$

where

$$\Sigma = 2P_\Sigma Z_0 / E_0^2 = 2|\xi|^2 \pi r_0^2 I(k_0 r_0); \quad (16)$$

$$I_n(\cos\theta) = \int_{-1}^1 P_n(x \cos\theta) \sqrt{1-x^2} dx; \quad (17)$$

$$I(k_0 r_0) = \int_0^\pi \sin\theta \left[\sum_{n=0}^{\infty} I_n(\cos\theta) (2n+1) \psi_n^-(k_0 r_0) \right]^2 d\theta = \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} I_{nm} (2n+1)(2m+1) \psi_n^-(k_0 r_0) \psi_m^-(k_0 r_0); \quad (18)$$

$$I_{nm} = \int_{-1}^1 \int_{-1}^1 P_n(xx') P_m(xx') \sqrt{1-x^2} dx' dx. \quad (19)$$

In obtaining (16), we used the property $\psi_n^\pm(x) = \psi_{n-1}^\pm(x) - n\psi_n^\pm(x)/x$ and the asymptotic behaviour $\psi_n^+(x) \approx \exp[-ix - i(n-1/2)\pi/2 - i\pi/4]$ with a large argument. The scattering cross section (16) is proportional to the squared modulus of dimensionless conductivity. Integrals (17) are calculated through a generalised hypergeometric function (formulas (2.17.2) from [47]), and the first few integrals can be easily calculated. The obtained relations correspond to the low-frequency limit. To take into account the resonances, one should consider the variation of the incident field $E_z = E_0 \exp(-ik_0 x)$ and the surface current density

$$\mathbf{j}_\theta(\theta) = \sum_{n=1}^N j_n \partial_\theta P_n(\cos\theta). \quad (20)$$

Relation (20) for $n = 1, 2, \dots$ corresponds to the dipole, quadrupole and higher multipole moments [42]. For nonspherical azimuthally symmetric particles with the shape defined by the equation $r = f(\theta)$, one should search for the density j_θ in used in (5) in the form of expansion (20). By determining the component of the scattered field E_θ and the incident field $E_{\text{in}\theta} = -E_0 \exp(-ik_0 r_0 \sin\theta) \sin\theta$ on the surface of the sphere, we impose the impedance condition $E_{\text{in}\theta} + E_\theta = j_\theta(\theta)$. Using the orthogonality relations for the derivatives of Legendre polynomials [42]

$$\int_0^\pi \partial_\theta P_n(\cos\theta) \partial_\theta P_m(\cos\theta) \sin\theta d\theta = \delta_{nm} \frac{2n(n+1)}{2n+1}, \quad (21)$$

we find the expansion coefficients in (20) and all radiation parameters. In fact, this is nothing but the solution of the IE. Note that for the polynomials themselves and the associated Legendre functions, orthogonality relations hold [42]. The solution is conveniently found by using relations (2.107), (2.109), and (2.113) from [42]. As a result, we obtain

$$E_\theta = -r^{-1} r_0 Z_0 \sum_{n=1}^N j_n \partial_\theta P_n(\cos\theta) \psi_n^+(k_0 r) \psi_n^-(k_0 r_0), \quad (22)$$

$$H_\varphi = ir^{-1} r_0 \sum_{n=1}^N j_n \partial_\theta P_n(\cos\theta) \psi_n^+(k_0 r) \psi_n^-(k_0 r_0). \quad (23)$$

Assuming now that $r = r_0$ and $B(\chi_0) = 1 + \xi \psi_n^+(\chi_0) \psi_n^-(\chi_0)$, and also using (21), we find

$$j_n = \frac{-\sigma E_0 (2n+1) \tilde{I}_n(\chi_0)}{2n(n+1) B(\chi_0)}, \quad (24)$$

where

$$\tilde{I}_n(\chi_0) = \int_0^\pi \exp(-i\chi_0 \sin\theta) \partial_\theta P_n(\cos\theta) \sin^2\theta d\theta. \quad (25)$$

Assuming $\xi = 0$ and $k_0 r_0 \rightarrow 0$, we have $j_1 = -\sigma E_0$, which justifies the above approximation $J_\theta(r, \varphi, \theta) = -\sigma E_0 \sin\theta \delta(r - r_0)$, in which the term J_θ in expression (22) is omitted. Denoting the amplitude by $A_n(\chi_0) = \psi_n^-(\chi_0)$, formula (16) according to (23) can be written in the form that does not contain integrals:

$$\Sigma_1 = \frac{8|\xi|^2 \pi r_0^2 A_1^2(\chi_0)}{3}, \quad (26)$$

where the subscript 1 denotes the dipole approximation. The strict formula, taking into account N multipole expansions and the field response to the current, has the form:

$$\Sigma = \pi r_0^2 |\xi|^2 \sum_{n=1}^N \frac{(2n+1) |\tilde{I}_n(\chi_0)|^2 A_n^2(\chi_0)}{n(n+1) |B(\chi_0)|^2}. \quad (27)$$

It should calculate the integral (25), which, taking into account the two terms of the expansion of the exponential for small $k_0 r_0$, assumes a simple form

$$\tilde{I}_n(\chi_0) \approx -4\delta_{n1}/3 - i\chi_0 \int_0^\pi \partial_\theta P_n(\cos\theta) \sin^3\theta d\theta. \quad (28)$$

Here $|\tilde{I}_n(\chi_0)|^2 \approx 16\delta_{n1}/3 + \chi_0^2 I_n^2$; and I_n is the integral. In the general case, expression (15) is calculated by expanding the exponent in the form of a series, each member of which is calculated through a generalised hypergeometric function. Instead of such a complex process, it is easier to use the direct calculation of the first several integrals. In particular, $I_1 = -3\pi/8$, $I_2 = -3/5$, and $\Sigma = \Sigma_1 + \chi_0^2 \Delta\Sigma_1$. In this formula, the refined result for (26) has the form

$$\Sigma_1 = \frac{4\pi^2 r_0^2 |\xi|^2 A_1^2(\chi_0)/3}{|1 + i\xi A_1(\chi_0) \exp(-i\chi_0) (1 - i\chi_0^{-1} - \chi_0^{-3})|^2}, \quad (29)$$

where $A_1(\chi_0) = \sin\chi_0 + \cos\chi_0/\chi_0 - \sin\chi_0/\chi_0^2$, and the additional correction $\Delta\Sigma_1$ is given by formula (27), into which the integrals I_n should be substituted. For $k_0 r_0 \ll 1$ we have $A_1(\chi_0) \approx \chi_0/3$, and expression (29) implies the expression corresponding to Rayleigh scattering: $\Sigma_1 = 4\pi(k_0 r_0)^4 \pi r_0^2/3$. The amplitude maximum $|\xi|A(\chi_0)$ approximately determines the dipole resonance, but for fullerenes it occurs at very high frequencies lying in the X-ray range, when $\lambda \approx 4r_0$, which corresponds to a have-wave dipole.

Approximation (26) does not yield a resonance at low frequencies $\chi_0 \ll 1$, while in the refined formula (29) it takes place. Indeed, we represent the normalised conductivity in the form $\xi = \xi_0/(1 + i\omega/\omega_c)$ or $\xi = \xi_0/(1 + i\chi/\chi_c)$. Here $\chi_c = \omega_p r_0/c$. We have $|\xi|^2 = \xi_0^2 \chi_c^2 / (\chi_0^2 + \chi_c^2)$, $\xi' = \xi_0^2 \chi_c^2 / (\chi_0^2 + \chi_c^2)$, $\xi'' = \xi_0 \chi_0^2 \chi_c / (\chi_0^2 + \chi_c^2)$. The value of ξ_0 is constant for quantum energies less than 3 eV when it is determined by the transport of π electrons only. In the UV range, four valence electrons of each carbon atom participate in the transport, and the value of ξ_0 is greater, and at energies above 80 eV, all six electrons participate in the transport. Assuming $\chi_c \ll \chi_0 \ll 1$, we obtain

$$\Sigma_1 = \frac{4\pi^2 r_0^2}{27} \times \frac{\xi_0^2 \chi_c^2 \chi_0^2 (\chi_0^2 + \chi_c^2)}{[(\chi_0^2 + \chi_c^2 - \xi_0 \chi_c (1 - \chi_c)/3)]^2 + (\xi_0 \chi_c)^2 (\chi_c/\chi_0 + \chi_0)^2/9}.$$

The maximum value of this expression approximately lies in the region where the expression in square brackets in the denominator vanishes: $\chi_0 = \sqrt{\xi_0 \chi_c (1 - \chi_c)/3} - \chi_c^2 \approx \sqrt{\xi_0 \chi_c/3}$. At the point of maximum

$$\Sigma_1 = \frac{4\pi^2 r_0^2}{3} \frac{\chi_c (\xi_0/3 + \chi_c)}{(1 + 3/\xi_0)^2} \approx \frac{4\pi^2 r_0^2 \xi_0 \chi_c}{9}.$$

Applying the approximations $|kr_0| \ll 1$, $|kr_0|_0 \ll 1$ for free oscillations of a metal particle to equation (7), we obtain their characteristic equation

$$n\varepsilon_m + n + 1 = \frac{(kr_0)^2}{2n-1}, \quad (30)$$

from which, neglecting the right-hand side, we have the zeroth approximation $\varepsilon_n^{(0)} = -1 - 1/n$ and the resonant frequency $\omega_n' = \omega_p/\sqrt{(1 + \varepsilon_L) + 1/n}$. Substituting the approximation $\varepsilon_m = \varepsilon_n^{(0)} = -1 - 1/n$ in the right-hand side of (30), we obtain

$$\varepsilon_n^{(1)} = -1 - 1/n - (k_p r_0)^2 \frac{1 + 1/n}{n(2n-1)(\varepsilon_L + 1 + 1/n)}. \quad (31)$$

This expression implies that the resonant frequency in the first approximation is $\omega_n' = \omega_p/\sqrt{\varepsilon_L - \varepsilon_n^{(1)}}$; moreover, $\varepsilon_1^{(1)} = -2 -$

$(k_p r_0)^2 \times [3(\varepsilon_L + 2)]^{-1}$. For a silver particle of size $r_0 = 10$ nm, $k_p r_0 = 0.6$ and $\varepsilon_1^{(1)} = -2.01$ ($\varepsilon_L = 22.5$). To assess the Q factor, it is necessary to calculate the complex permittivity $\varepsilon_n = -|\varepsilon_n'| - i\varepsilon_n''$ at this frequency and substitute it into equation (30). It will take the form

$$\omega_n' + i\omega_n'' = (c/r_0)\sqrt{(2n-1)[n-(n+1)]/(\varepsilon_n' + i\varepsilon_n'')}.$$

Assuming the imaginary part to be small, we obtain

$$\omega_n' + i\omega_n'' = \frac{c}{r_0}\sqrt{(2n+1)\left[n - \frac{(n+1)}{|\varepsilon_n'|}\right]} \times \left\{1 + \frac{i\varepsilon_n''(n+1)/|\varepsilon_n'|^2}{2[n-(n+1)/|\varepsilon_n'|]}\right\}. \quad (32)$$

The inequality $|\varepsilon_n'| > 1 + 1/n$ must be fulfilled, but since it is close to equality, the Q factor of oscillations cannot be high even at low dissipation. Taking $\varepsilon_1' = -2.01$, $\varepsilon_1'' = 0.1$ and $r_0 = 3$ nm, we obtain $\omega_1' + i\omega_1'' = 1.04 \times 10^{15}(1 + i0.476)$ Hz and $Q_1 = 1.05$. The above formulas give only qualitative estimates, but one should really use the iterative solution [9] of the strict characteristic equation (7) (see Fig. 1 below).

We also consider the case of a thin (of the order of several nanometres) metal shell on a dielectric ball with permittivity ε . For a film of thickness δ , we can introduce surface conductivity in the form $\sigma = i\omega\varepsilon_0\delta[\varepsilon_m(\omega) - 1] = iZ_0^{-1}k_0\delta(\varepsilon - 1)$. Due to the small thickness and condition $\varepsilon_m \sim -1$ in the plasmonic region, the dimensionless conductivity $\xi = \sigma Z_0 = ik_0\delta(\varepsilon_m - 1)$ is small: $\xi \ll 1$. However, for fullerenes in the plasma approximation $\xi = -i(k_0 r_0)(\delta/r_0)\omega_p^2/\omega^2$ at a frequency at which $k_0 r_0 = 0.03$, we have $\omega_p^2/\omega^2 \approx 5$, and for $\delta/r_0 = 0.3$ we obtain $|\xi| = 0.045$; at lower frequencies this value is even higher. With a small value of $|\xi|$, the approximation $k_0 r_0 \ll 1$ for high- Q oscillations can be performed only for the E modes. We rewrite relation (9) in the form:

$$\chi_0 = k_0 r_0 = \frac{i\xi n}{[1 - \chi_0^2/(2n^2 - n)]^{-1} + \varepsilon(1 + 1/n)^{-1}},$$

or

$$\chi_0 \approx \frac{i\xi n}{1 + \chi_0^2/(2n^2 - n) + \varepsilon(1 + 1/n)^{-1}}, \quad (33)$$

where the zeroth approximation $\chi_0^{(0)} = in\xi(1 + 1/n)/(\varepsilon + 1 + 1/n)$. For the dipole mode, $n = 1$, we have $k_0^{(0)} r_0 = 2i\xi/(\varepsilon + 2)$. The first approximation takes the form:

$$\chi_0^{(1)} = \frac{i\xi n(1 + 1/n)}{1 - n^2\xi^2(1 + 1/n)^3/[(\varepsilon + 1 + 1/n)^2(2n^2 - n)] + \varepsilon}. \quad (34)$$

Here $\xi = \xi' + \xi''$, and we assume $\xi' \ll |\xi''|$. Oscillations will have a Q factor if the conductivity is highly reactive: $|\xi''|/|\xi'| \gg 1$. For a metal shell, the conductivity is inductive: $\xi'' < 0$. The second approximation is obtained by substituting $\chi_0^{(1)}$ in (33). The obtained relations (33) and (34) require the conditions $|\xi| \ll 1$, $\chi_0 \ll 1$ to be satisfied; otherwise, the complex roots of the characteristic equation (9) should be sought for.

To estimate the parameters of plasmons in fullerenes, one needs to know their effective surface conductivity. Let us estimate the resonances for low frequencies, assuming that the conductivity of fullerenes is equal to the conductivity of graphene. The surface conductivity of graphene in the framework of the Kubo – Greenwood approaches and nonequilib-

rium Green's functions was obtained in a number of works (see, for example, [34–36]) both with and without spatial dispersion. It consists of intraband and interband conductivities: $\sigma(\omega) = \sigma_{\text{intra}}(\omega) + \sigma_{\text{inter}}(\omega)$. Taking into account spatial dispersion and the tensor character of the conductivity $\hat{\sigma}$ is important for surface plasmons. For LPPs, the scalar conductivity of graphene σ obtained by calculating the corresponding integral in the momentum space in the vicinity of two Dirac points of the Brillouin zone with linear isotropic dispersion, – the dependence of the π electron energy on the momentum – can be used approximately as the effective conductivity. For low thermal energies (at $k_B T \ll |\mu_c|$), the temperature dependence of the interband conductivity can be neglected, and then [34–36]

$$\sigma_{\text{inter}}(\omega, \mu, \omega_c, 0) = \frac{-ie^2}{4\pi\hbar} \ln \left[\frac{2|\mu_c| - (\omega - i\omega_c)\hbar}{2|\mu_c| + (\omega - i\omega_c)\hbar} \right]. \quad (35)$$

At low quantum energies compared with the chemical potential ($\omega\hbar \ll |\mu_c|$), this conductivity is small and corresponds to a capacitive type conductivity: $\sigma_{\text{inter}} \approx e^2(i\omega + \omega_c)/(4\mu|\mu_c|)$. At high quantum energies, it is close to the quantum conductivity $e^2/(4\hbar)$: $\sigma_{\text{inter}} \approx e^2/(4\hbar) + i|\mu_c|/[(\omega - i\omega_c)\pi\hbar^2]$. An energy gap arises in curved graphene; therefore, in the model of fullerene–low-energy quantum interaction, the interband conductivity is neglected. We take the intraband conductivity in the form [34–36]

$$\sigma = \sigma_{\text{intra}}(\omega, \mu, \omega_c, T) = \frac{\sigma_{0\text{intra}}}{1 + i\omega/\omega_c}, \quad (36)$$

$$\sigma_{0\text{intra}} = \frac{e^2 k_B T}{\pi\hbar^2 \omega_c} \ln \left\{ 2 \left[1 + \cosh \left(\frac{\mu_c}{k_B T} \right) \right] \right\}, \quad (37)$$

where T is the temperature. Inductive type conductivity (36) has a frequency dependence similar to the Drude formula. Using it in (33), in the zeroth approximation we obtain

$$\omega_n = \omega_n' + i\omega_n'' = \sqrt{\frac{n\xi_0 c \omega_c (1 + 1/n)}{(1 + \varepsilon + 1/n)r_0}} \left(1 + \frac{i\omega_c}{2\omega_n'} \right). \quad (38)$$

Here $\xi_0 = \sigma_{0\text{intra}} Z_0$. In this approximation, the Q factor is $Q_n = \omega_n'/\omega_n''$. For the dipole mode $\omega_1' = \sqrt{(2/3)c\omega_c\xi_0}$. Let us estimate this frequency for fullerenes. At $\mu_c = 0.1$ eV, $T = 300$ K and $\omega_c = 10^{12}$ Hz, we obtain $\xi_0 = 5.16$, and for fullerene C_{60} ($r_0 = 0.346$ nm) according to the estimate $\omega_1' = 1.05 \times 10^{16}$ and $Q_1 \approx 10^4$. At this frequency $|\xi| = 5.16 \times 10^{-4}$, i.e., the expansion is applicable, but approximation (36) of the Kubo–Greenwood model taking into account the contribution of only π electrons does not work. Even for fullerene C_{540} ($r_0 = 1.01$ nm), formula (38) corresponds to a quantum with an energy of 3.8 eV, which is already higher than the energy γ_0 . In reality, formula (38) can be used only for giant fullerenes whose radius is greater than 1.6 nm, or for dielectric particles with a metal shell in the case of frequencies not exceeding the frequency of quantum transitions. To obtain accurate results, one should numerically search for complex roots (9).

The scattered and radiated fields can be represented as an expansion in spherical harmonics [7, 44]:

$$E_\theta^\pm = r^{-1} \left\{ \begin{aligned} & [\tilde{A}^\pm \partial_r \partial_\theta - ik_0 m Z_0 \tilde{B}^\pm / \sin \theta] \cos(m\varphi) \\ & [\tilde{A}^\pm \partial_r \partial_\theta + ik_0 m Z_0 \tilde{B}^\pm / \sin \theta] \sin(m\varphi) \end{aligned} \right\} \times \psi_n^\pm(k^\pm r) P_n^m(\cos \theta),$$

$$E_\varphi^\pm = r^{-1} \left\{ \begin{aligned} &[-m\tilde{A}^\pm \partial_r / \sin\theta + ik_0 Z_0 \tilde{B}^\pm \partial_\theta] \sin(m\varphi) \\ &[m\tilde{A}^\pm \partial_r / \sin\theta + ik_0 Z_0 \tilde{B}^\pm \partial_\theta] \cos(m\varphi) \end{aligned} \right\} \\ \times \psi_n^\pm(k^\pm r) P_n^m(\cos\theta).$$

Here, the sign ‘+’ corresponds to the region $r > r_0$, and the sign ‘-’ corresponds to the region $r < r_0$; $k^+ = k_0$; $k^- = k_0 \sqrt{\varepsilon}$; $\varepsilon^- = \varepsilon$ and $\varepsilon^+ = 1$. For fullerene, $\varepsilon = 1$, and for a metal particle $\varepsilon = \varepsilon_m$. The tangential magnetic field is $\mathbf{H}_\tau^\pm = \mathbf{r} \times \mathbf{E}_\tau (\varepsilon^\pm)^{1/2} / (Z_0 r)$. We note a significant difference between these representations for the field scattered and emitted by free oscillations. In the first case, the real frequency is given by the incident wave, and in the region $r > r_0$ the functions $\psi_n^\pm(kr_0)$ determine the correct behaviour in the form of a diverging spherical wave. In the second case, the frequency is complex, and the functions $\psi_n^\pm(kr_0) \sim \exp(-i\omega r/c)$ determine the field growing at infinity. In monograph [45], this fact is considered to be a consequence of the law of conservation of energy and is explained by the endless consideration of the process in time (which is impossible in reality): The exponentially large oscillations that took place in the particle in the distant past make a contribution to the field in a more distant region. Real finite decaying oscillations that began at some moment have a complex spatial distribution of the field. In this regard, we note an error in [7], where instead of an increasing Hankel function of the second kind, a Bessel function of the first kind was used, which, however, did not lead to an error in determining the resonant frequencies.

4. Introduction of the surface conductivity of a nanocluster

Consider the method of introducing classical effective surface conductivity for fullerene. We assume that the problem of quantum mechanics about the charge distribution density $\rho(r, \omega)$ in fullerene exposed to an external electromagnetic field $\mathbf{E} = \mathbf{E}_0 \exp(i\omega t)$ is solved. Due to the smallness of the particles, the delay is neglected. The above problem can be solved by various methods, for example, using the density functional theory or the molecular dynamics method. In particular, the classical model of polarisation of fullerenes by a point charge was considered in [48]. It is shown that it is in good agreement with the results obtained by the DFT method. We define the polarisation $\mathbf{p} = \alpha \mathbf{E}_0$ (dipole moment) of fullerene as $\mathbf{p} = \int \rho(r) \mathbf{r} d^3 r$. On the other hand, defining \mathbf{p} through the surface current density $\mathbf{j} = \sigma \mathbf{E}_\tau$, surface conductivity and surface charge density $\zeta = i \nabla_\tau \mathbf{j} / \omega = i \sigma \nabla_\tau \mathbf{E}_\tau / \omega$ in the form

$$\mathbf{p} = \int_S \zeta(r) \mathbf{r} d^2 r,$$

we can obtain σ . We direct \mathbf{E}_0 along the z axis. For the sphere $\mathbf{E}_\tau = -E_0 \sin\theta$. In this case, there is only one component on the sphere, $\mathbf{E}_\theta = -E_0 \sin\theta$, therefore $\nabla_\tau \mathbf{E}_\tau = -(r_0 \sin\theta)^{-1} \times \partial_\theta (\sin\theta E_\theta) = -2E_0 (r_0 \sin\theta)^{-1} \cos\theta$. Then

$$p_z = \alpha E_0 = \int \rho(r) z d^3 r = \frac{2\pi^2 i \sigma r_0^2 E_0}{\omega}, \quad (39)$$

from which it follows that $\sigma = -i\alpha\omega / (2\pi^2 r_0^2)$. The result depends on the method for determining $\rho(r)$ and α . For high-

energy photons, formula (36) is not applicable; therefore, it is desirable to estimate the conductivity taking into account all four π and σ electrons. Based on various approximate approaches, such as the DFT method, hydrodynamic approximation for a Fermi plasma and classical methods, the authors of a number of works (see, for example, [22–29]) obtained the photoionisation cross sections of C_{20} , C_{28} and C_{60} with maxima in the hard UV range, caused by the collective excitation of oscillations of all the electrons in the cluster. From the classical point of view, it is not difficult to understand why these frequencies lie in this region. For high frequencies, π and σ electrons can be assumed free and fullerene can be considered as a plasma. Assuming C_{60} to be ball, we obtain the number of electrons per unit volume, $N = 1.38 \times 10^{30}$, and the plasma frequency of 6.98×10^{16} Hz, i.e., approximately four times higher than that of copper. For such a ball, we have $\omega'_p = \omega_p / \sqrt{3} = 4.03 \times 10^{16}$ Hz, or 26 eV. If we consider fullerene as a plasma layer with $\delta = r_0/3$, the volume concentration and ω_p will be approximately the same. In reality, $\rho(r)$ has a narrow peak in the region $r = r_0$ [25]. The distance Δr from the surface at which $\rho(r)$ practically drops to zero is about 1 at. units of length.

We describe the shell as a plasma with permittivity $\varepsilon_p(r) = 1 - \varepsilon\rho(r)/(\varepsilon_0 m\omega^2)$ and conductivity $\gamma = i\omega\varepsilon_0(\varepsilon_p - 1)$. Due to the narrowness of the peak, it corresponds to inductive surface conductivity $\sigma = -i\omega_p^2 \delta / (\omega c)$, or

$$\sigma = \int_{r_0 - \Delta r}^{r_0 + \Delta r} \gamma(r) dr = -\frac{i\varepsilon}{m\omega} \int_{r_0 - \Delta r}^{r_0 + \Delta r} \rho(r) dr = -\frac{i\varepsilon\zeta}{m\omega}. \quad (40)$$

Here $\rho(r) = \zeta \delta(r - r_0)$; $\delta = 2\Delta r$. For C_{60} , the law of conservation of charge is expressed as

$$q = 240e = 4\pi \int_{r_0 - \Delta r}^{r_0 + \Delta r} \rho(r) r^2 dr = 4\pi r_0^2 \zeta, \quad (41)$$

from which it follows that $\sigma = -60ie^2 / (\pi r_0^2 m\omega) = \omega_p^2 \varepsilon_0 \delta / \omega$. Choosing for $\rho(r)$ an approximation in the form of an equilateral triangle in the region $r_0 - \Delta r < r < r_0 + \Delta r$ with a maximum $\rho(r_0)$ and zeros at $r = r_0 \pm \Delta r$, from (40) we find $\sigma = -2ie\rho(r_0)\Delta r / (m\omega)$. From (41) with the same approximation, assuming $\Delta r/r_0 \ll 1$, we obtain $\rho(r_0) = 108e / (\pi\Delta r r_0^2)$, whence $\sigma = -216ie^2 / (\pi r_0^2 m\omega)$. Thus, the triangular approximation yields a more than three times higher value of surface conductivity than the approximation in the form of the delta function. The quantity $\zeta = 60e / (\pi r_0^2)$ can be interpreted as the surface charge density. Using $\xi = -i\omega_p^2 \delta / (c\omega)$, at $\omega = 10^{16}$ Hz (~ 6.56 eV) we obtain $|\xi| = 0.16$, i.e., at a frequency exceeding 10^{16} Hz, expansions in small parameters are applicable. To take into account dissipation, as usual, a substitution $\omega^2 \rightarrow \omega^2 - i\omega\omega_c$ should be made. In the considered range, we take $\omega_c = 10^{13}$ Hz, which gives $\xi_0 = 173.7$. Using the zeroth approximation (38), we obtain $\omega'_p = 3.144 \times 10^{16}$ Hz (20.6 eV), which is in good agreement with experiments and modelling using quantum methods [24–26]. According to the estimate, the frequency corresponding to the maximum of the scattering and absorption cross sections $\omega \approx \sqrt{\xi_0} \omega_c c / 3r_0 = 2.24 \times 10^{16}$ Hz. It should be noted that this is a very rough estimate. Numerical analysis implies a value of 18.15 eV. Thus, the results presented correspond to the known maximum photoionisation cross section. In the considered approximation, the result depends on the form of $\rho(r)$. In particular, the triangular approximation leads to an overestimated value of ξ .

5. Numerical results

Obtaining accurate numerical results for free LPPs in continuous spherical particles and for LPPs in spherical shells requires a rigorous iterative solution of equation (7) or (8) and (9) or (10), respectively. For particles with nonspherical shells, it is necessary to solve equation (5) and equations similar to it. This equation defines hybrid modes and can also be used for spherical shells. For these modes, in the first approximation, it is sufficient to take one component j_θ in the form (20), but subsequent approximations require taking into account many modes. For the dipole mode, $j_\theta = -j_0 \sin\theta$ and $\zeta = -2ij_0 \cos\theta / (\omega r_0)$. The radiation pattern of the multipole mode has the form [42] $\Phi(\theta) = [\partial_\theta P_n(\cos\theta)]^2$, but, in the general case (20), taking into account (24), it is given by the expression

$$\Phi(\theta) = \sum_{n=1}^N \sum_{m=1}^N j_n j_m^* A_n A_m \partial_\theta P_n(\cos\theta) \partial_\theta P_m(\cos\theta).$$

The impedance condition is satisfied when many current modes (20) are taken into account; therefore, the radiation pattern $\Phi(\theta)$ and the cross section (27) are complex.

Figure 1 shows the results of an iterative solution of equation (9) for a spherical metal particle with permittivity according to the Drude–Lorentz model in the form of the dependences of the resonant frequency and Q factor on the radius. For radii of metal nuclei and shell thicknesses of the order of tens of nanometres, the Drude–Lorentz approximation in the

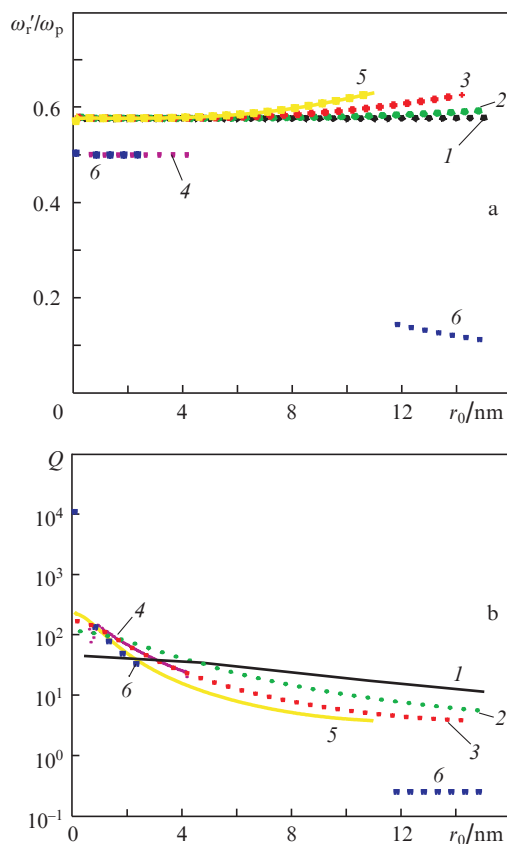


Figure 1. Dependences of (a) the normalised resonant frequency and (b) Q factor of the main mode ($n = 1$) on the particle radius at $\epsilon_L = (1-4)$ 1 and $(5-6)$ $2-10.002$ and plasma frequencies of (1) 10^{16} , (2) 2×10^{16} , (3) 3×10^{16} , (4, 5) 4×10^{16} and (6) 6×10^{16} ; $\omega_c = 10^{14}$ Hz.

optical range still works. The results are represented by points that are obtained as a converging iterative process with a residual of an equation no worse than 10^{-8} . It can be seen that the frequencies are weakly dependent on the radius.

Figure 2 shows the results of calculating the normalised frequency dependences of the scattering cross section for C_{60} using formulas (26) and (29) as functions of the normalised frequency $\tilde{f} = k_0 r_0 / 2\pi = r_0 / \lambda$. We used the normalisation $\tilde{\Sigma} = \Sigma / (\xi_0^2 \chi_c^2 \Sigma_0)$, where $\Sigma_0 = \pi r_0^2$ is the geometric section. The curves in Fig. 2 for different fullerenes hardly differ if $\tilde{f} > 0.01$, but their absolute maxima are proportional to $r_0^2 \Sigma_0$, i.e. to the fourth degree radius, and the absolute frequencies are inversely proportional to the radius. It can be seen that the frequencies of the maxima correlate well with the resonant frequencies of free oscillations in the same way as for scattering by a dipole. The absolute values of the cross section depend on the collision frequency, which can be a function of frequency; therefore, their experimental determination allows us to find ω_c , which can also be determined from the absorption cross section:

$$\begin{aligned} \Sigma_a &= 2\pi r_0^2 E_0^{-2} Z_0 \text{Re} \int_0^\pi (jE_\theta^*) \sin\theta d\theta \\ &= 4\pi r_0^2 E_0^{-2} Z_0 \text{Re}(\sigma)^{-1} \sum_{n=1}^N \frac{n(n+1)}{2n+1} |j_n|^2. \end{aligned}$$

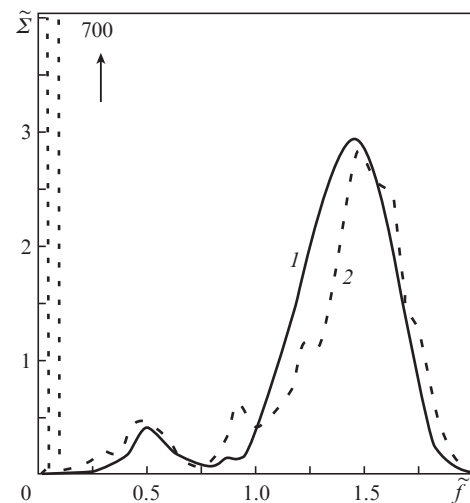


Figure 2. Dependences of the normalised scattering cross section $\tilde{\Sigma} = \Sigma / (\xi_0^2 \chi_c^2 \pi r_0^2)$ on the normalised frequency $\tilde{f} = 2r_0/\lambda$: (1) calculation by formula (26), and (2) calculation by formula (29). The arrow shows the peak value of dependence (2): $\tilde{\Sigma} \sim 700$.

In the first approximation, taking into account one harmonic, we obtain

$$\Sigma_a \approx \pi r_0^2 \frac{3\xi' |\tilde{I}_1(\chi_0)|^2}{4|1 + \xi\psi_{1'}^+(\chi_0)\psi_{1'}^-(\chi_0)|^2}.$$

The approximation was obtained for spheroidal fullerenes: $\chi_0 \ll 1$. In this approximation, $\tilde{I}_1(\chi_0) = 4/3$. In the low-frequency region, the maximum cross section Σ_a is approximately the same as Σ_1 :

$$\Sigma_{\text{amax}} \approx \pi r_0^2 \frac{4\xi'/3}{\{\text{Re}[\xi\psi_{1'}^+(\chi_0)\psi_{1'}^-(\chi_0)]\}^2}.$$

Table 1. Free oscillations and the frequency of the maximum scattering cross section for the dipole mode of fullerenes.

Fullerenes	Frequencies and Q factors of free oscillations				Frequencies of the first maximum	
	$\hbar\omega/\text{eV}$ by formula (5)	$\hbar\omega/\text{eV}$ by formula (9)	Q (10^{-3}) by formula (5)	Q (10^{-3}) by formula (9)	$\hbar\omega/\text{eV}$ by formula (29)	$\hbar\omega/\text{eV}$ by formula (26)
C ₂₀	34.01	34.67	3.2	5.3	25.89	1478.3
C ₂₈	28.12	28.55	3.1	4.4	23.95	1249.3
C ₃₂	27.20	27.46	2.8	4.2	21.11	1168.1
C ₆₀	20.55	20.78	2.7	3.2	19.15	853.5
C ₇₀	18.90	19.24	2.6	2.9	18.41	790.2
C ₁₄₀	13.22	13.60	1.9	2.1	15.94	558.7
C ₂₄₀	10.04	10.39	1.4	1.6	13.54	426.4
C ₂₆₀	9.66	9.98	1.2	1.5	13.27	409.7
C ₅₄₀	6.56	6.93	0.9	1.1	11.06	284.3
C ₉₆₀	4.98	5.19	0.7	0.8	9.57	213.2
C ₁₅₀₀	4.01	4.15	0.5	0.6	8.56	170.6

Table 1 shows the results of calculating the resonance frequencies and Q factors of the dipole mode ($n = 1$) obtained using formulas (5) and (9). The frequencies of the dipole scattering maxima calculated by formulas (26) and (29) are also presented. The high-frequency resonances in Table 1 are determined by the correspondence of the cluster perimeter to the wavelength. Their frequencies are large due to the small radius. It is interesting that such Schumann resonances with extremely low frequencies (the lowest frequency of 7.8 Hz) are due to the propagation of a Zenneck surface plasmon along the Earth's surface.

Figure 3 shows the results of calculating the radiation pattern for the power $\Phi(\theta, \varphi)$ of the scattered field for a cubic dielectric particle of size $a = 60$ nm with permittivity $\varepsilon = 3$ covered with a metal shell 10 nm thick at a wavelength of $\lambda = 500$ nm. The total particle size was 80 nm. The results are based on an iterative solution of volume IDE (3) using quadrature formulas to calculate matrix elements. The metal shell is considered as a bulk structure with a complex metal permittivity $\varepsilon_m = -2 - 0.2i$. The plane wave field was $\mathbf{E}_{\text{in}} = \mathbf{z}_0 \exp(-ik_0 x)$, and the dimension of the problem, taking into account symmetry, was 256. Symmetry made it possible to solve the IE in only one octant and only for two field compo-

nents, E_x and E_z , using cubic piecewise constant finite elements.

6. Conclusions

Based on the classical approach, we have obtained characteristic equations for free LPPs in shelled spherical particles and sphere-like fullerenes. We have presented general IEs and IDEs for diffraction problems and problems of free oscillations in dielectric particles of arbitrary shape in the presence of a conducting shell described by surface conductivity, as well as a functional for determining resonant frequencies. In the low-frequency and dipole approximations, we have obtained scattering cross sections for a spherical shell. The results are given for resonant frequencies and scattering cross sections for metal nanoparticles in the form of a sphere and fullerenes, as well as radiation patterns for dielectric cubic particles coated with a metal shell. In the latter case, the solution of the volume IE is used.

For spheroidal fullerenes with the number of atoms less than 240, the resonant frequencies of the dipole mode fall in the hard UV range, and they coincide well with the frequencies obtained by other methods. For giant fullerenes with icosahedral symmetry, they move to the far UV range, but the accuracy of these results is worse due to violation of sphericity. So, for C₂₈ and C₆₀ we have frequencies of 28.55 and 28.78 eV, and for C₉₆₀ and C₁₅₀₀ we have frequencies of 5.19 and 4.16 eV, respectively. The obtained relations can easily be generalised to composite double-layer and even multilayer concentric shells, for which the matrix matching method proposed in [32] is convenient. For composite fullerenes, however, the position of the internal particle corresponds to the minimum binding energy and may be asymmetric. For elongated closed and open nanotubes, a general approach is needed based on the solution of an IDE, the result of which strongly depends on their orientation with respect to the field. Depending on the length of the nanotubes, longitudinal dipole resonances can lie in the optical and IR ranges. As in graphene [36], optically pumped fullerenes in the THz range can become active and have a negative real part of conductivity. This can be used by producing active layers containing such fullerenes. For modelling, mixing formulas are more convenient. More rigorous approaches require solving quantum problems for quantum dots (quantum boxes) consisting of a large number of atoms. It is important to calculate the number of plasmon excitation modes. The applicability of the

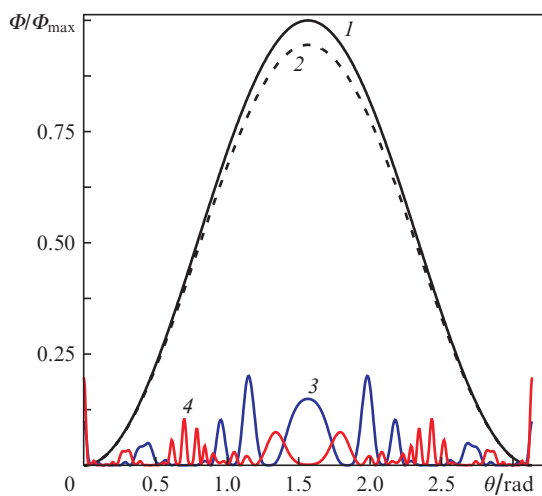


Figure 3. Normalised radiation patterns of power at azimuthal angles $\varphi = (1) 0, (2) \pi, (3) \pi/4$ and $(4) \pi/2$.

above classical results follows from the correspondence of the obtained frequencies to quantum calculations.

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