PLASMON RESONANCES IN NANOCOMPOSITES WITH DEGENERATED ELECTRON GAS OF METAL COMPONENTS AND THEIR DEMONSTRATION IN PHOTONICS OF MOLECULAR HYBRID SYSTEMS

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The paper shows that the spectra of plasmon resonances of metal nanoparticles substantially depend on the degeneracy level of the metal electron gas. Based on the linearized equation of Thomas-Fermi, the author has obtained expressions for dipole dynamic polarizabilities of two-component spherical particles with a degenerated electron gas. The investigator separately has considered case of a two-particle cluster, which polarizability is represented by the tensor of the second rank. Frequency dependencies of main characteristics of composite particles in a quasi-static approximation have been calculated. The author shows some ways to generalize the model to account for retardation effects. The paper reports in what way will change radiation characteristics of molecules located near the nanocomposites of this type, including the case of development of processes of non-radiative energy transfer from electronically excited centers to quenching centers.

Keywords: polarizability of spherical nanoparticles, two-particle cluster, degenerated electron gas, Thomas-Fermi screening, plasmons, spontaneous emission

Introduction

A number of papers [1-11] reported that the effect of conductive nanobodies on radiation and non-radiative transitions in molecules was rather strong. In metal optics, light scattering by spherical particles [1] often found an explanation in the assumption that the electron gas of a conductor was a gas of classical particles.

In the spirit of modern ideas, quantum properties of the electron gas (Fermi gas) are typical for metals up to their melting temperatures and for semiconductors it is true at a high doping level and under high temperatures [12-13]. In equilibrium, the electron energy distribution function for such degenerated gas is that of Fermi-Dirac. And the electron density distribution \( n(r) \) in heterogeneous systems such as metal clusters can be found from the solution of the Thomas-Fermi equation for the potential \( \phi(r) \) of the electric field [12]. In this regard, it is of interest to determine the impact of the degeneracy of the electron gas of nanoparticles on the transformation of electronic excitation energy of the molecules near metal nanoparticles, including the case when these particles function as quenchers of excited states. In this case, it is definitely important to establish plasmon resonances of nanoglobule dipole polarizability with regard to dissipative processes in the metal.

Problem Statement

For a neutral spherical conductive cluster with radius \( R \), with the number of atoms \( N \gg 1 \), on the right of the Thomas-Fermi equation for the potential \( \phi(r) \) in the "jellium model", there is a term, which represents a uniform density of positive metal ions, and for spherically symmetric case when \( r < R \), this equation can be written as [12]

\[
\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d\phi}{dr} \right) = 4e \left[ \frac{2me\phi(r)}{3\pi h^3} \right]^{\frac{3}{2}} - \frac{3eN}{R}.
\]
In most part of the ion sphere, the potential is constant \( \varphi = \varphi_0 \) and is determined by the number of ions \( N \) and the cluster radius \( R \) [13]

\[
\varphi_0 = \frac{(9\pi N)^{2/3}}{2^{7/3} \epsilon m R^2}.
\] (2)

The linearization of the Thomas-Fermi equation (1) carried out for a small monochromatic perturbation \( \delta \varphi(r, t) \) of the electrostatic potential \( \varphi \rightarrow \varphi_0 + \delta \varphi \), \( \delta \varphi \ll \varphi_0 \) leads to the following result using atomic units (\( m_e = e = h = 1 \)) when \( r < R \) [13]

\[
\nabla^2 \delta \varphi = \frac{4}{\pi \epsilon} \sqrt{2 \varphi_0 \delta \varphi}, \quad \varphi_0 = \frac{(9\pi N)^{2/3}}{2^{7/3} R^2}.
\] (3)

The equation (3) is known in mathematical physics as the Helmholtz equation, and it is the basic structure in the theory of electromagnetic scattering, but the constant \( k^2 = -\frac{4}{\pi \epsilon} \sqrt{2 \varphi_0} > 0 \), appearing in (3) is a parameter of electron gas degeneracy, rather than a squared wave number, as in the classical Helmholtz equation.

**The spectrum of natural plasmon oscillations in a nanoparticle**

When the ion density in a globule is fixed, the potential \( \varphi_0 \) does not depend on a cluster radius [13]. Without an external field, the dielectric permittivity \( \varepsilon(\Omega) \) due to free electrons in the cluster is determined on the frequency \( \Omega \) of natural oscillations of the electron density in a nanoglobule as a real function of \( \Omega \) argument.

\[
\varepsilon(\Omega) = 1 - \left( \omega_p / \omega \right)^2 < 0.
\] (4)

Here \( \omega_p = \sqrt{4\pi \epsilon^2 n_e / m} \) is the plasma frequency; \( n_e \) is the concentration of electrons. Let us introduce the notation

\[
k^2 = -\frac{4}{\pi \epsilon} \sqrt{2 \varphi_0} = -\frac{4}{\pi \epsilon l^2} > 0, \quad \text{or} \quad k^2 = -\frac{4m_e^{3/2} \epsilon^{5/2}}{\pi h^3} \sqrt{2 \varphi_0} > 0,
\] (5)

where \( l = (2\varphi_0)^{-1/4} \) is the length of the Thomas-Fermi screening. Then the equation (3) in spherical coordinates when \( r < R \) takes the form

\[
\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \delta \varphi \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \delta \varphi \right) = -k^2 \delta \varphi.
\] (6)

The solution of the equation (6) for the internal area \( r < R \), regular at the origin, is in the form of natural dipole oscillations

\[
\delta \varphi(r, t) = A j_l(kr) P_l(\cos \theta) \cos \Omega t.
\] (7)
Here $P_l(\cos \theta)$ is the Legendre polynomial of $l$ degree, and $j_l(z)$ is a spherical Bessel function, in particular for the oscillation of dipole type $l=1$. The constant $A$ in (7) determines the natural oscillations amplitude of the degenerated electron gas density.

Regular at infinity solution of the Laplace equation for the perturbing additive $\delta \varphi(r,t)$ of the potential out of $r > R$ ionic sphere can be written as

$$
\delta \varphi(r,t) = \frac{B}{r^2} P_l(\cos \theta) \cos \Omega t.
$$

The constant $B$ in (8) is the amplitude of the oscillating dipole moment $\varphi(t)$ of the nanocluster. According to the conditions of potential continuity $\delta \varphi(r,t)$ at the boundary of the ionic sphere $r = R$, as well as of the continuity of the normal projection of the electrostatic induction vector on the base of (7) and (8) we find an implicit expression for the natural frequency $\Omega$ of the dipole oscillations of the cluster electron cloud in the Thomas-Fermi approximation [13-14]

$$
\Omega = \frac{\omega}{P} \sqrt{1 + \frac{2(kR \cot kR - 1)}{(kR)^2}}.
$$

As a matter of fact, taking into account (4) and (5), the expression (9) is a transcendental equation with respect to $\Omega$. Gadomsky and Shalin [15] reported on a set of roots (9) located at a certain radius $R$ of a nanocluster in the visible spectral region. It turned out that the natural frequency spectrum $\Omega$ is sensitive to changes in the radius $R$ both in relation to the area of localization of discrete levels, and in respect of their relative positions. Within the limit of a very small cluster $kR \ll 1$ in (9) $\Omega_m = \omega / \sqrt{3}$ follows, that is, from the entire spectrum there remains the only well-known frequency Mie of surface dipole oscillations of a small sphere.

Fig.1 shows calculated on the basis of (9) dependencies of the natural frequencies $\Omega$ of different branches of the nanosphere plasmon oscillations on its radius $R$, expressed in terms of lengths of the Thomas-Fermi screening $l = (2\varphi_0)^{-1/4}$.

![Fig.1. Dependencies of the squares of the natural frequencies $\Omega$ of various branches of the plasmon oscillations of a metal nanosphere on its radius $R$, expressed in lengths of Thomas-Fermi screening $l = (2\varphi_0)^{-1/4}$](image-url)
We conveniently named the lower branch "Mie frequency branch". When $kR \to 0$, the value $\Omega_{M} = \omega_{p} / \sqrt{3}$ is typical for it. Branches of higher frequency only appear for greater values $R/l$. Fig. 1 shows two of them. For natural frequencies $\Omega$ of all branches, monotonic decrease in their values with increasing parameter $R/l$ is characteristic. The transition to a non-degenerated electron gas takes place when $l \to \infty$, then the lower branch degenerates into a straight line $(\Omega_{M} / \omega_{p})^{2} \to 1/3$, and the upper branches disappear.

It follows from (12) and Fig. 1 that with the growth of the cluster radius $R$ the frequency $\Omega$ of the lower branch decreases, as compared to a constant frequency Mie $\Omega_{M} = \omega_{p} / \sqrt{3}$. For gold, the electron concentration is $n_{e} = 5.9 \times 10^{22}$ cm$^{-3}$ [15], the plasma frequency is $\omega_{p} = 13.7 \times 10^{13}$ rad/sec, $k^2 = -3.17 \times 10^{16} \varepsilon^{-1}$ cm$^{-2}$. Then the inequality $kR \gg 1$ holds for optical frequencies and for nanocluster with the radius of $R \geq 1$ nm; and apparent dependence of frequency $\Omega$ on the cluster radius $R$ in (9) is essential.

It was shown that the resonances of the dipole dynamic polarizability of the nanocluster corresponded to all the natural frequencies $\Omega$ of the local plasmon oscillations; and occurrence of new branches with greater parameter values $kR \gg 1$ made the polarizability spectrum more complicated, unlike the case of small values $kR \ll 1$, when the electron gas was practically non-degenerated and there remained only one frequency $\Omega_{M} = \omega_{p} / \sqrt{3}$ that was Mie frequency in the spectrum.

**The dipole dynamic polarizability**

The dipole dynamic polarizability $\alpha(\omega)$, determining both the scattering and dissipation of the field energy is a key feature of the interaction of nanosystem with monochromatic electromagnetic field $E(\omega)$ of the frequency $\omega$ [1, 5, 14]. The expression for the dipole polarizability $\alpha(\omega)$ of a bimetallic layered spherical nanocomposite (Fig. 2) was obtained in [16]

$$\alpha(\omega) = \frac{\varepsilon(\omega)k \left[ j'_{i}(kR_{2}) - \beta y'_{i}(kR_{2}) \right] - \varepsilon_{m}(1/R_{2}) \left[ j_{i}(kR_{2}) - \beta y_{i}(kR_{2}) \right]}{\varepsilon(\omega)k \left[ j'_{i}(kR_{2}) - \beta y'_{i}(kR_{2}) \right] + 2\varepsilon_{m}(1/R_{2}) \left[ j_{i}(kR_{2}) - \beta y_{i}(kR_{2}) \right]} R_{3}^{3}. \quad (10)$$

![Fig. 2](image-url) The frequency dependence (in units of plasma frequency $\omega_{p}$) of the real (1) and imaginary (2) parts of the polarizability $\alpha(\omega)$ of the bimetallic layered spherical nanocomposite with the radii of $R_{1} = 2$ and $R_{2} = 8$ nm, as well as and its module $|\alpha(\omega)|$ (3) in nm$^{3}$. $\omega_{p} = 1$, $\omega_{p'} = 1.1$, $\gamma = 0.03$, $\gamma' = 0.02$, $\varepsilon_{m} = 1.2$, $l = 0.7$, $l' = 0.12$ nm.
Here, the function $\beta = \beta(\omega, k, k, R)$ depends on the dielectric permittivity of the metal shell $\varepsilon_{\text{shell}}(\omega) = \varepsilon_z(\omega) = \varepsilon(\omega)$, on the dielectric permittivity of the spherical core $\varepsilon_r(\omega) = \varepsilon_1(\omega)$ and its radius $R_1$.

$$\beta(\omega, k, k, R_1) = \frac{\varepsilon(\omega)k_j^\prime(kR_1) - \varepsilon_r(\omega)j_j^\prime(kR_1)}{\varepsilon(\omega)k_x^\prime(kR_1) - \varepsilon_r(\omega)j_x^\prime(kR_1)}/j_j(kR_1).$$  (11)

When $R_1 \to 0$ (a solid metal ball 1) in (14) results in $\beta(\omega, kR_1) \to 0$ and for the polarizability $\alpha(\omega)$ we obtain from (10)-(11) the known result [13-14].

$$\alpha(\omega) = R^3\left[1 + \frac{3\varepsilon_m(\omega)k(\omega)R\cot(\omega)R - 1}{2(\varepsilon(\omega) - \varepsilon_m)(\omega)(\omega)R\cot(\omega)R - 1} + \varepsilon(\omega)(\omega)R^2\right].$$  (12)

In clusters, in contrast to individual nanoparticles, there are additional dimensional parameters defining the structure and configuration of the compound system. Moreover, when associates are formed, it is possible to be included in a complex group of particles consisting of a variety of materials: metals, semiconductors and dielectrics. It is obvious that effective electrodynamic characteristics of such composites are significantly different from those of the individual particles.

A simplest two-particle cluster can be formed by two nanoglobules of different composition and size, as well as of completely identical ones, providing a high symmetry of the dimer [1, 17]. In a typical case of sufficiently distant from each other cluster globulas (at a distance $R$, which is substantially greater than the radii $R_1, R_2$, of each of the particles $R >> R_1, R_2$), taking into account the mutual influence of the particles on one another, its polarizability can be determined in the approximation of interacting quasi-point dipoles (14). In this case, the effective polarizability $\tilde{\alpha}_c(\omega)$ of the nanocluster can be expressed in terms of the polarizabilities $\tilde{\alpha}_1(\omega), \tilde{\alpha}_2(\omega)$ of its components with regard to their anisotropic properties [17-18].

$$\tilde{\alpha}_c(\omega) = \left[\mathbf{I} - \tilde{\alpha}_1(\omega)\tilde{\alpha}_2(\omega)\mathbf{G}(\mathbf{R})\mathbf{G}(\mathbf{R})\right]^{-1}\tilde{\alpha}_1(\omega)\left[\mathbf{I} + \tilde{\alpha}_2(\omega)\mathbf{G}(\mathbf{R})\right] + \tilde{\alpha}_2(\omega)\left[\mathbf{I} + \tilde{\alpha}_1(\omega)\mathbf{G}(\mathbf{R})\right].$$  (13)

The double arrow above the values in (1) indicates their tensor mode. The sign $[\mathbf{T}]^{-1}$ is the tensor inverse to the tensor $\mathbf{T}: [\mathbf{T}]^{-1} \mathbf{T} = \mathbf{I}$. The particles may have spheroidal or ellipsoidal shapes, i.e. they possess anisotropic properties of polarizability due to the nonsphericity of their shapes [1]. In case of spherical particles, the anisotropy of their polarizability takes place when the spherical particles get into an external (magnetic) field. As noted in [1], the expression (1) is correct allowing for effects of retardation. In this case corresponding expressions for dyadic (tensor) Green's functions $\mathbf{G}(\mathbf{R})$ should be used [1]. For sufficiently large system extents, comparable to the wavelength $\lambda$, it necessary to take into account the finiteness of the electromagnetic signal propagation velocity. The allowance for this condition results in the following expression for the Green's tensor $\overline{\mathbf{G}}(\mathbf{R}, k)$ $(k = 2\pi / \lambda)$ as [1]

$$\overline{\mathbf{G}}(\mathbf{R}, k) = -\frac{\exp(ikR)}{R^3}\left[(1 - iR) - 3\mathbf{R} \otimes \mathbf{R} - k^2R^2\left(\mathbf{I} - \mathbf{R} \otimes \mathbf{R} / R^2\right)\right].$$  (14)
In the quasi-static case – without taking into account the effect of the retardation – the dyadic Green’s function (tensor) is written as $\tilde{G}(\mathbf{R}) = R^{-5} \left[ 3 \mathbf{R} \otimes \mathbf{R} - \mathbf{I} R^2 \right]$.

Fig. 3 shows the spectra of real parts of the polarizabilities of the nanocluster composed of nanoparticles of the same radius, but of different metals and those of a single spherical nanoparticle [18]. The graphs show that the two-component material composition of the cluster results in the broadening of the cluster spectrum as compared to the spectrum of a single particle.

![Graph showing the spectra of real parts of polarizabilities](image)

Fig. 3. Spectra of real parts of polarizabilities of the cluster (red, top) and a single spherical nanoparticle (black, bottom). $\varepsilon_m = 1.2$, $\gamma_1 = 1.42 \times 10^4$, $\gamma_2 = 1.45 \times 10^4 \text{c}^{-1}$, $l_1 = 0.2$, $l_2 = 0.3 \text{ nm}$, $\omega_{pl1} = 1.37 \times 10^6$, $\omega_{pl2} = 1.38 \times 10^6 \text{c}^{-1}$, $R_1 = R_2 = 5$, $r = 12 \text{ nm}$

Fig. 4 shows the spectra of real and imaginary parts of the polarizability of a cluster consisting of two spherical nanoparticles of the same radius, but different conductive materials, i.e., different values of length $l$ of Thomas-Fermi screening of the spheres plasma. The calculations showed [18] that even small changes in the parameter $l$ in the second significant digit result in significant qualitative changes in the spectra.

To explain the changes in the electron absorption spectra, as well as spontaneous and stimulated light emission of colored solutions with metallic nanoparticles observed during experiments, the authors have offered a simple model of transformation of forced and spontaneous electric dipole transitions in organic molecules, located in the vicinity of a single metal nanoparticle [10].

In terms of this model, if there is a conductive nanoparticle or a cluster with a degenerated electron gas, the rate of photon absorption is determined by the expression [11]

$$w(\omega) = \frac{2}{\hbar^2} \frac{\gamma}{(\omega - \omega_y)^2 + \gamma^2} \left| \mathbf{p} \left[ \tilde{\mathbf{I}} + \tilde{\mathbf{G}}(\mathbf{R}) \tilde{\alpha}(\omega) \right] \mathbf{E}(\omega) \right|^2,$$

where $\gamma$ is the breadth of Lorentz profile of a molecule absorption band; $\mathbf{p}$ is an electron dipole transition moment.
The spontaneous emission rate of the molecule located near a nanoparticle at the distance $R$ of it is defined by the similar expression. However, there is no $E(\omega)$ field in it [10]

$$w_{sp}(\omega) = \frac{4}{3} \frac{\omega^3}{\hbar c^3} \left[ I + \mathbf{G}(\mathbf{R})\tilde{\alpha}(\omega) \right] \mathbf{p}^2.$$  \hfill (16)

When calculating the emission spectra of molecules near metal nanobodies, it is necessary to take into account the possibility of nonradiative transfer of electron excitation energy of the molecule to a conducting particle or a metal nanocluster. The impact of a metal nanoparticle is not only limited by increased spontaneous transitions in the molecule. It is necessary to take into account the transfer of electron excitation energy of the molecule to the plasmon modes of the nanoparticle and further attenuation of these modes. The rate $U$ of such a process is proportional to the imaginary part of the scalar polarizability of the nanoparticle [14]

$$U(\omega, r, \theta) = \frac{1}{2\hbar} \text{Im} \alpha(\omega) \frac{P^2}{\varepsilon_m^2 r^6} (1 + 3\cos^2 \theta),$$  \hfill (17)

where $\varepsilon_m$ is the dielectric permittivity of the medium at the transition frequency $i \rightarrow f$, and $\text{Im} \alpha(\omega) > 0$.

The spontaneous emission and nonradiative energy transfer to the nanoparticle are competing processes of decay of the excited state of the molecule. To take into account both of them, it is necessary to define the proportion of molecules decayed by radiation (quantum yield of luminescence)

$$\eta(\omega, r, \theta) = \frac{w_{sp}(\omega, r, \theta)}{w_{sp}(\omega, r, \theta) + U(\omega, r, \theta) + K},$$  \hfill (18)

where $K$ is the rate of nonradiative decay of dye molecules without the nanoparticle.
In the more general case of an anisotropic nanoparticle [19] or a two-particle cluster with metal components with degenerated electron gas, the absorption of energy of electronic excitation of a molecule occurs with different efficiency depending on the direction of the vector \( \mathbf{p} \) about the tensor \( \bar{\alpha} (\omega) \) axes of the nanocluster polarizability. Thus, the probability of energy transfer to an anisotropic nanoparticle with polarizability \( \bar{\alpha} (\omega) \) and volume \( V \) per time unit (rate) \( U_a (\omega) \) now can be represented using characteristics of the molecule and the particle (nanocluster) as follows

\[
U_a (\omega) = \frac{1}{2 \hbar} V \text{Im} \left[ \mathbf{E}^\prime (\omega) \bar{\alpha} (\omega) \mathbf{E} (\omega) \right] = \frac{1}{2 \hbar} V \text{Im} \left[ \mathbf{p} \bar{G} (\mathbf{R}) \bar{\alpha} (\omega) \bar{G} (\mathbf{R}) \mathbf{p} \right].
\]

**Conclusion**

Thus, in the photonics of molecular metal nanocomposites it is necessary to take into account quantum properties of the metal electron gas. The spectrum of the dipole polarizability of a nanoantenna with degenerated electron gas of a metal contains a much larger number of resonance bands as compared with the spectrum of the non-degenerated conductor. The formation of the nearfield of a nanoparticle or a cluster makes for distinguishing spatial domains within which the molecule will emit photons more efficiently; and knowledge of detailed polarization characteristics of a plasmon reflector makes it possible to determine the optimum conditions of its impact on the radiative transitions in a molecule or a quantum dot. In this paper, in the model of a degenerated electron gas, the authors obtained frequency dependencies of real and imaginary parts of the dipole polarizability of a conducting spherical nanoparticle and that of a composite "a dielectric core—a shell" for a variety of particle radius values, the length of the Thomas-Fermi screening and a damping constant. An expression for the polarizability tensor of a two-particle cluster, composed of the conductive spherical particles or layered composites "a core—a shell" is presented. It is found that the spectra of dynamic polarizabilities and absorption cross-sections of the clusters have a complex multiresonance structure and a strong dependence on the configuration parameters of the cluster, the metal degeneracy level and the kinetic characteristics of its electron gas.

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