Optical properties of a plasmonic nano-antenna: an analytical approach

Dmitry V Guzatov\textsuperscript{1,3} and Vasily V Klimov\textsuperscript{2,3}

\textsuperscript{1} Yanka Kupala Grodno State University, Ozheshko Street 22, 230023 Grodno, Belarus
\textsuperscript{2} P N Lebedev Physical Institute, Russian Academy of Sciences, Leninsky pr. 53, 119991 Moscow, Russia
E-mail: guzatov@gmail.com and vklim@sci.lebedev.ru

\textit{New Journal of Physics} 13 (2011) 053034 (26pp)
Received 17 January 2011
Published 19 May 2011
Online at http://www.njp.org/
doi:10.1088/1367-2630/13/5/053034

\textbf{Abstract.} The optical properties of a plasmonic nano-antenna made of two metallic nanospheroids (prolate or oblate) were investigated analytically in quasi-static approximation. It is shown that in clusters of two nanospheroids, three types of plasmonic modes can be present. Two of them can be effectively excited by a plane electromagnetic wave, while the third one can be effectively excited only by a nanolocalized light source (an atom, a molecule or a quantum dot) placed in the gap between the nanoparticles. Analytical expressions for the absorption cross-section, the enhancement of local fields and the radiative decay rate of an excited atom placed near such a nano-antenna are presented and analyzed.
1. Introduction

Very recently, quite a number of works have been devoted to the study of the optical properties of single nanoparticles and their clusters. Special attention is paid to metal nanoparticles with the help of which it is possible to enhance electric fields at frequencies of localized plasmon resonances [1–3]. On the basis of this effect, a variety of possible applications were considered. The most developed is the use of large local fields near a rough surface to increase surface-enhanced Raman scattering (SERS) [4]. Modification of fluorescence by means of nanoparticles of different shapes is the basis for the creation of nanobiosensors [5–9], nano-antennas [10–14], devices for the decoding of DNA structure [15], etc.

At present, the optical properties of single metallic nanospheres and their clusters [16–30], single nanospheroids [31–33], nanoellipsoids [34–37] and some other nanobodies [2, 3, 38] have been studied well enough from an analytical point of view. Many other nanoparticles’ shapes and nanoparticle clusters have been investigated only numerically. Unfortunately, numerical simulations often do not allow us to gain an understanding of the physical nature of interesting and complicated phenomena in the area. That is why analytical solutions are of principal importance.

In this paper, we present the results of an analytical study of the optical properties of clusters of two metallic prolate or oblate spheroidal nanoparticles. Such clusters are investigated both experimentally and numerically and form the basis for various possible applications, including nanosensors, nano-antennas and plasmon waveguides [39–46]. In principle, the optical properties of such two-spheroid clusters can be investigated analytically by full analogy to two-sphere clusters [19], [47–49]. However, as far as we know, there is only one analytical investigation of the optical properties of two-nanospheroid clusters carried out with the help of a plasmon hybridization method [50]. In this paper, the interaction between unperturbed plasmonic modes of prolate spheroids was calculated by numerical integration. Here, we continue the investigation of this system with the help of a new translational addition theorem [51]. It allows us to find an analytical description of the interaction between

New Journal of Physics 13 (2011) 053034 (http://www.njp.org/)
unperturbed plasmonic modes and to derive the solution for the cluster of two spheroidal nanoparticles, placed in an arbitrary external field. The geometry of the considered problem is shown in figure 1. For simplicity, we will consider that the cluster consists of two equal nanospheroids made of a material with dielectric constant $\varepsilon$ and placed in a vacuum.

Significant attention will be paid to the case of nearly touching and strongly interacting spheroids since this is the case that seems to be most interesting for applications, because a substantial enhancement of electric fields occurs there. The opposite case of weakly interacting spheroids can be easily treated with the approximation of spheroids by point dipoles with corresponding polarizabilities $\alpha$.

For an illustration of the analytical results obtained, we will consider the case of two identical (prolate or oblate) nanospheroids made of silver $\sigma$. We suppose that the largest size of the nanospheroid is equal to 30 nm and the aspect ratio of the spheroid is taken to be equal to 0.6.

The rest of this paper is organized as follows. In section 2, free plasmon oscillations of a two-nanospheroid cluster are investigated. The results of this section reveal the underlying physics and are necessary for interpreting the results of other sections. In section 3, we will consider the optical properties of a two-nanospheroid cluster placed in the field of a plane electromagnetic wave. Here, we find out the absorption cross-section and the factor of local field enhancement. In section 4, the objects of examination are the optical properties of a two-nanospheroid cluster placed in the field of a radiating atom or a molecule, whose decay rates are calculated here.

2. Plasmon oscillations in a cluster of two nanospheroids

It is well known that all optical properties of nanoparticles can be derived from their plasmonic spectra, i.e. from the related plasmon eigenvalues $\varepsilon_\nu$ and eigenfunctions $\mathbf{e}_\nu$ and $\mathbf{h}_\nu$, which are
solutions of the sourceless Maxwell equations \[53\],

\[
\begin{align*}
\text{rot } \mathbf{h}_\nu + i \left( \frac{\omega}{v_c} \right) \tilde{\varepsilon} \mathbf{e}_\nu &= 0, \\
\text{rot } \mathbf{e}_\nu - i \left( \frac{\omega}{v_c} \right) \mathbf{h}_\nu &= 0,
\end{align*}
\]

(1)

where \(\tilde{\varepsilon} = \varepsilon\) inside the nanoparticle and \(\tilde{\varepsilon} = 1\) outside it, \(\omega\) is the frequency of electromagnetic oscillations and \(v_c\) is the speed of light in vacuum. As a result, the electric field in the presence of any nanoparticle can be presented in the following form \[53\],

\[
\mathbf{E}(\mathbf{r}) = \mathbf{E}_0(\mathbf{r}) + \sum_\nu \mathbf{e}_\nu(\mathbf{r}) \left( \frac{\varepsilon(\omega) - 1}{\varepsilon - \varepsilon(\omega)} \right) \int_V (\mathbf{e}_\nu(\mathbf{r}) \mathbf{E}_0(\mathbf{r})) dV,
\]

(2)

where \(\varepsilon(\omega)\) describes the dependence of dielectric permittivity of the nanoparticle’s specific material on frequency \(\omega\), \(\mathbf{E}_0\) is the excitation field and \(\nu\) is a vector index that defines the specific plasmonic mode. From (2), it is possible to find the optical properties of a nanoparticle or a cluster of nanoparticles. So, to understand very complicated optical properties of a two-nanospheroid cluster, we should first investigate the plasmonic spectrum of this system.

To study the plasmon oscillations and other optical properties of clusters of two nanospheroids, it is enough to solve the quasi-static equations,

\[
\begin{align*}
\text{div}(\tilde{\varepsilon} \mathbf{e}_\nu) &= 0, \\
\text{rot } \mathbf{e}_\nu &= 0,
\end{align*}
\]

(3)

which can be reduced to solutions of the Laplace equations by substituting \(\mathbf{e}_\nu = -\nabla \varphi_\nu\),

\[
\begin{align*}
\Delta \varphi_\nu^{\text{in}} &= 0, \quad \text{inside the nanoparticle,} \\
\Delta \varphi_\nu^{\text{out}} &= 0, \quad \text{outside the nanoparticle,} \\
\varphi_\nu^{\text{in}} \big|_S &= \varphi_\nu^{\text{in}} \big|_S, \\
\varepsilon_\nu \frac{\partial \varphi_\nu^{\text{in}}}{\partial n} \big|_S &= \frac{\partial \varphi_\nu^{\text{out}}}{\partial n} \big|_S, \\
\end{align*}
\]

(4)

In (4), \(\varphi_\nu^{\text{in}}\) and \(\varphi_\nu^{\text{out}}\) are the potentials of plasmonic eigenfunctions inside and outside the nanoparticle correspondingly, and \(\frac{\partial \varphi_\nu}{\partial n} \big|_S\) denotes the normal derivative at the nanoparticles’ surface \(S\). The last equation in (4) provides continuity of the normal components of electrical induction. Note that in this case there is no need to find magnetic fields for the description of plasmonic oscillations.

The systems of equations obtained in such a way have nontrivial solutions only for some negative values of permittivity \(\varepsilon\) defining the frequency of plasmon oscillations \[2, 3\]. In the case of the Drude theory, \(\varepsilon(\omega) = 1 - \omega_{\text{pl}}^2/\omega^2\), the frequency of plasmon oscillations can be found from the expression

\[
\omega_\nu = \frac{\omega_{\text{pl}}}{\sqrt{1 - \tilde{\varepsilon}}} < \omega_{\text{pl}},
\]

(5)

where \(\omega_{\text{pl}}\) is the bulk plasmon frequency of a metal from which the nanoparticles are made. Our approach allows us to investigate arbitrary spheroids, but for simplicity in the present...
section we examine the equations for the plasmon oscillations in a cluster of two identical metal nanospheroids.

In the case of a two-nanospheroid cluster, we will look for a solution as follows. The total potential outside the spheroids will be the sum of their partial potentials (we will omit the mode index \( \nu \) further) [20, 54],

\[
\phi^{\text{out}} = \phi^{\text{out}}_1 + \phi^{\text{out}}_2,
\]

while the potentials inside each nanospheroid will be denoted by \( \phi^{\text{in}}_j \) (\( j = 1, 2 \)). To find \( \phi^{\text{out}} \) and \( \phi^{\text{in}}_1, \phi^{\text{in}}_2 \), it is natural to use spheroidal coordinates. In the case of a prolate nanospheroid, the relation between the Cartesian and the spheroidal coordinates (1 \( \leq \xi < \infty \), \(-1 \leq \eta \leq 1\), \(0 \leq \phi \leq 2\pi\)) is [55]

\[
x = f \sqrt{(\xi^2 - 1)(1 - \eta^2)} \cos \phi, \quad y = f \sqrt{(\xi^2 - 1)(1 - \eta^2)} \sin \phi, \quad z = f \xi \eta,
\]

where \( f = \sqrt{c^2 - a^2} \) is half of the focal distance in a prolate spheroid (\( a < c \)) whose surface is set by the equation \((x^2 + y^2)/a^2 + z^2/c^2 = 1\).

In the case of an oblate spheroid (\( a > c \)), the relation between the Cartesian and the spheroidal coordinates (0 \( \leq \xi < \infty \), \(-1 \leq \eta \leq 1\), \(0 \leq \phi \leq 2\pi\)) has the following form [55],

\[
x = f \sqrt{(\xi^2 + 1)(1 - \eta^2)} \cos \phi, \quad y = f \sqrt{(\xi^2 + 1)(1 - \eta^2)} \sin \phi, \quad z = f \xi \eta,
\]

where \( f = \sqrt{a^2 - c^2} \) is half of the focal distance in the oblate spheroid. Let us note that this expression can be obtained from (7) by the substitutions \( \xi \to i\xi \) and \( f \to -if \). Further, we will use this formal replacement since it is fundamental and allows us to find a solution for oblate spheroids if the solution for prolate spheroid geometry is known [54–57].

### 2.1. Plasmon oscillations in a cluster of two identical prolate nanospheroids

To find plasmonic spectra of a two-nanospheroid cluster, it is natural to use two local systems of spheroidal coordinates \( (\xi_j, \eta_j, \phi_j, j = 1, 2) \), the origins \( o_j \) of which are placed at the centers of corresponding nanospheroids and separated from each other by the distance \( l \) (see figure 1(a)). The coordinates (and all other values) related to the first or second nanospheroid will be denoted by the index ‘1’ or ‘2’, respectively. The potential inside the \( j \)th nanospheroid can be presented in the following form [58] \((j = 1, 2)\),

\[
\phi^{\text{in}}_j = \sum_{n=0}^{\infty} \sum_{m=0}^{n} P_n^{m}(\xi_j) P_n^{m}(\eta_j) (A^{(j)}_{mn} \cos(m\phi_j) + B^{(j)}_{mn} \sin(m\phi_j)),
\]

where \( P_n^{m}(\eta) \) is an associated Legendre function [59] defined in the region \(-1 \leq \eta \leq 1\) and \( P_n^{m}(\xi) \) is an associated Legendre function [59] defined in a complex plane with the branch cut from \(-\infty\) to \(+1\). The partial potential outside the \( j \)th nanospheroid can be presented [58] as \((j = 1, 2)\)

\[
\phi^{\text{out}}_j = \sum_{n=0}^{\infty} \sum_{m=0}^{n} Q_n^{m}(\xi_j) P_n^{m}(\eta_j) (C^{(j)}_{mn} \cos(m\phi_j) + D^{(j)}_{mn} \sin(m\phi_j)),
\]
where \( Q_n^m(\xi) \) is an associated Legendre function of the second kind \([59]\) defined in a complex plane with the branch cut from \(-\infty \) to \(+1\).

By construction, the potentials (9) and (10) are solutions of the Laplace equation \([58]\). So, to find a solution of (4), one should use only the boundary conditions

\[
\varphi_1^{in}|_{\xi_1=\xi_0} = \varphi_1^{out}|_{\xi_1=\xi_0}, \\
\varepsilon \frac{\partial \varphi_1^{in}}{\partial \xi_1}|_{\xi_1=\xi_0} = \frac{\partial \varphi_1^{out}}{\partial \xi_1}|_{\xi_1=\xi_0},
\]

\[
\varphi_2^{in}|_{\xi_2=\xi_0} = \varphi_2^{out}|_{\xi_2=\xi_0}, \\
\varepsilon \frac{\partial \varphi_2^{in}}{\partial \xi_2}|_{\xi_2=\xi_0} = \frac{\partial \varphi_2^{out}}{\partial \xi_2}|_{\xi_2=\xi_0},
\]

(11)

where \( \xi_0 = c/\sqrt{\varepsilon^2 - \alpha^2} = c/f \) are local radial coordinates defining the surfaces of the nanospheroids and \( \varepsilon \) is the permittivity of materials from which the nanoparticles are made. To reduce the boundary conditions (11) to a system of linear equations, we apply the translational addition theorem to the wave functions of the prolate nanospheroid \([51]\). In the case of two identical coaxial nanospheroids, this theorem gives \((j, s = 1, 2, j \neq s, \phi_1 = \phi_2)\)

\[
Q_n^m(\xi_j) P_n^m(\eta_j) = \sum_{q=m}^{\infty} S_{mqmn}^{(1)} P_q^m(\xi_j) P_q^m(\eta_j),
\]

(12)

where

\[
S_{mqmn}^{(1)} = \frac{(-1)^q (2q + 1) (q-m)! (n+m)!}{(q+m)! (n-m)!} \times \sum_{r=0}^{\infty} \sum_{k=0}^{\infty} \frac{(q+n+2r+2k)!}{(2q+2r+1)!! (2n+2k+1)!! (2r)!! (2k)!!} \left( \frac{f}{l} \right)^{2r+2k+q+n+1},
\]

\[
S_{mqmn}^{(2)} = (-1)^{q+n} S_{mqmn}^{(1)}.
\]

(13)

Applying the boundary conditions (11) and the theorem (12), one can obtain the following system of equations \((n = 0, 1, 2, \ldots; m = 0, 1, 2, \ldots, n),\)

\[
\left( \frac{d P_n^m(\xi_0)}{d\xi_0} Q_n^m(\xi_0) - P_n^m(\xi_0) \frac{d Q_n^m(\xi_0)}{d\xi_0} \right) C_{mn}^{(1)} + (\varepsilon - 1) P_n^m(\xi_0) \frac{d P_n^m(\xi_0)}{d\xi_0} \sum_{q=m}^{\infty} S_{mnmq}^{(0)} (-1)^{m+q} C_{mq}^{(2)} = 0,
\]

\[
\left( \frac{d P_n^m(\xi_0)}{d\xi_0} Q_n^m(\xi_0) - P_n^m(\xi_0) \frac{d Q_n^m(\xi_0)}{d\xi_0} \right) (-1)^{m+n} C_{mn}^{(2)} + (\varepsilon - 1) P_n^m(\xi_0) \frac{d P_n^m(\xi_0)}{d\xi_0} \sum_{q=m}^{\infty} S_{mnmq}^{(0)} C_{mq}^{(1)} = 0.
\]

(14)

When deriving (14), we made use of the fact that, for identical nanospheroids, \( S_{mnmq}^{(2)} = (-1)^{m+q} S_{mnmq}^{(1)} \) (see (13)) and take \( S_{mnmq}^{(0)} = (-1)^{m+n} S_{mnmq}^{(1)} \). The system of equations for \( D_{mn}^{ij} \) is identical to (14) and gives no additional information for plasmonic spectra of coaxial spheres. So, we will not consider it further.

As it results from the symmetry of the considered cluster and the system (14), there are two independent types of solutions (plasmonic modes) with opposite parity. To select these modes,
one should choose $C_{mn}^{(1)} = \pm (-1)^{m+n} C_{mn}^{(2)}$ in (14). As a result, we shall obtain the following system of equations for the modes with definite parity,

$$
\left( \varepsilon \frac{d P_n^m(\xi_0)}{d\xi_0} Q_n^m(\xi_0) - P_n^m(\xi_0) \frac{d Q_n^m(\xi_0)}{d\xi_0} \right) C_{mn}^{(1)} \pm (\varepsilon - 1) P_n^m(\xi_0) \frac{d P_n^m(\xi_0)}{d\xi_0} \sum_{q=0}^{\infty} S_{mnq}^0 C_{mq}^{(1)} = 0,
$$

(15)

where ‘+’ and ‘−’ signs correspond to modes that are symmetric (+) or antisymmetric (−) relative to $z \to -z$ transformation. It is important to note that separation of the spectra into symmetric and antisymmetric plasmon modes is possible only in the case when there is a plane of symmetry. When $m$ is even, antisymmetric modes have nonzero dipole moment and they are ‘bright’ modes. In contrast, symmetric modes have zero dipole moment and are ‘dark’ modes when $m$ is even. In the case of odd $m$, the ‘bright’ and ‘dark’ modes correspond to the symmetric and antisymmetric modes, respectively. One can expect that the antisymmetric mode $m = 0$ will have the largest polarizability and thus will be the ‘brightest’ one for the excitation of our cluster with a longitudinally (along the $z$-axis) polarized plane wave.

To study plasmon oscillations in clusters of two prolate spheroidal nanoparticles, we have solved the eigenvalue problems (15) numerically. In figure 2, the normalized plasmon frequency $\omega/\omega_{pl}$ of a cluster of two prolate nanospheroids (see figure 1(a) for the geometry), corresponding to the first four plasmon modes, is shown as a function of normalized distances $l/2c$ between the nanospheroids' centers. Eigenvalues $\varepsilon$ have been obtained as a nontrivial solution of the equation system (15) in the case of an axis-symmetric problem ($m = 0$). Then, the obtained solutions have been substituted into (5) to obtain the plasmon oscillation frequency.

In figure 2, one can observe that plasmon frequencies of a cluster of two prolate nanospheroids tend to plasmon frequencies of a single nanospheroid (see figure 2(c)) if the distances between the nanospheroids are large enough. When the width of the gap between the nanospheroids tends to zero, the solutions of the equations (15) behave very differently. For symmetric modes (figure 2(a)), there are two branches: T-modes and M-modes. Modes of ‘T’ type can be obtained by the method of hybridization of plasmon modes of a single prolate nanospheroid [50]. When the width of the gap between the nanoparticles is decreasing to zero, normalized plasmonic frequencies of T-modes tend to various values in the range from $0$ to $1/\sqrt{2}$, in analogy to a two-sphere cluster [21, 60]. T-modes with higher indices (not shown for clarity) will concentrate near $\omega/\omega_{pl} = 1/\sqrt{2}$. In figure 2(a), one can also see that at very short distances between the nanospheroids ($l/2c < 1.1$), a new type of plasmonic modes (M-modes) appears. M-modes are characterized by strong spatial localization in the gap between the nanoparticles. As a result, they can be effectively excited only by a strongly nonuniform electric field of the molecule or the quantum dot. Values of plasmonic frequencies of these modes lie in the range $\omega_{pl}/\sqrt{2} < \omega < \omega_{pl}$. As the gap width decreases to zero, the plasmon frequency of M-modes tends to the bulk plasmon frequency $\omega_{pl}$.

In figure 2(b), nontrivial solutions of the equation system (15) for the antisymmetric potential in an axial-symmetric case ($m = 0$) are shown. In analogy to a two-sphere cluster, we will call these modes L-modes (longitudinal) because they are ‘bright’ only for longitudinal excitation. These modes can be described by the hybridization method of plasmon oscillations of single nanospheroids forming the considered cluster [50]. As the width of the gap between
Figure 2. Normalized frequencies of the first few plasmonic oscillations in a cluster of two identical prolate spheroidal nanoparticles as a function of the distance between the nanospheroids’ centers. The axis-symmetrical case ($m = 0$) is considered, and the aspect ratio of a single spheroid is $a/c = 0.6$ ($\xi_0 = 1/\sqrt{1 - (a/c)^2}$). (a) Symmetrical modes (the eigenvalues of (15) with ‘+’ sign), (b) antisymmetric modes (the eigenvalues of (15) with ‘−’ sign). Dashed lines show plasmon frequencies of a single prolate nanospheroid $\omega_{pl} = \sqrt{P_m(\xi_0)/Q_m(\xi_0)}$. Panel (c) shows plasmon frequencies of the single prolate nanospheroid as a function of the inverse aspect ratio $c/a$. The vertical line corresponds to $a/c = 0.6$ and allows us to select asymptotic values for panels (a) and (b).

Prolate nanospheroids decreases to zero, normalized plasmon frequencies of these modes tend to zero as it also takes place in the case of spherical nanoparticles [21, 60]. Plasmonic frequencies of L-modes of higher orders (not shown) tend to $\omega_{pl}/\sqrt{2}$, and concentration of an infinite number of L-modes occurs near this value.

In figure 3, the distribution of a surface charge of plasmonic modes of the lowest order in clusters of two identical prolate nanospheroids is shown. It is seen in this figure that the T- and M-modes have symmetric distribution of the surface charge in contrast to the antisymmetric $L = 1$ mode. This behavior, of course, is in agreement with the symmetry of the equations (15). Another interesting feature is that the surface charge of T-modes is distributed over the surface of all of the nanoparticles for any distances between them, while for M- and L-modes it is...
Figure 3. Distribution of a surface charge (a.u.) of the lowest plasmon mode in a cluster of two identical prolate spheroidal nanoparticles according to the solution of the equations (15). The axial-symmetrical case \((m = 0)\) is considered, and the aspect ratio of a single spheroid is \(a/c = 0.6\). The distance between the nanospheroids’ centers is \(l/2c = 1.03\) (a), \(l/2c = 1.2\) (b). The distribution of a surface charge in a single spheroid is shown in panel (c). Red corresponds to the positive charge and blue to the negative one.

concentrated near the gap between the nanospheroids if the distance between them is sufficiently small. It is interesting to note also that the surface charge of M-modes is more concentrated in comparison with that of L-modes. Indeed, due to an electroneutrality requirement, the total surface charge on each nanospheroid should be equal to zero. Here, both positive and negative charges of the M-modes are localized near the gap between the nanoparticles so that in the rest of the nanoparticles the charge is almost equal to zero, as is clearly seen in figure 3(a). At the same time, in the case of L-modes for each of the nanospheroids, near the gap a charge of only one sign is concentrated, and a charge of the opposite sign is distributed with small magnitude over the remaining surface of the nanoparticles. Therefore, strictly speaking, the surface charge in an L-mode is distributed over the entire surface of the cluster of nanoparticles although it is not clearly seen at small distances between the nanoparticles (see figure 3(a)). As the distance increases, the charge distribution changes in the cluster: it spreads over the nanoparticles’ surface, tending in the limit to a distribution corresponding to single prolate nanospheroids (see figure 3(c)).

2.2. Plasmon oscillations in a cluster of two identical oblate nanospheroids

In this geometry, one should also use local systems of coordinates \((\xi_j, \eta_j, \phi_j, j = 1, 2)\) that are connected to each nanospheroid, have origins \(o_j\) in their centers and are separated from each other by the distance \(l\) (see figure 1(b)). Now, the electric potential inside the \(j\)th nanospheroid
can be presented in the form \((j = 1, 2)\)

\[
\varphi_j^{in} = \sum_{n=0}^{\infty} \sum_{m=0}^{n} P_n^m(i\xi_j) P_n^m(\eta_j) (A_{mn}^{(j)} \cos(m\phi_j) + B_{mn}^{(j)} \sin(m\phi_j)),
\]

and the partial potential outside the \(j\)th oblate nanospheroid will look like \((j = 1, 2)\)

\[
\varphi_j^{out} = \sum_{n=0}^{\infty} \sum_{m=0}^{n} Q_n^m(i\xi_j) P_n^m(\eta_j) (C_{mn}^{(j)} \cos(m\phi_j) + D_{mn}^{(j)} \sin(m\phi_j)).
\]

The total potential outside the nanospheroids will be expressed by \((6)\). As boundary conditions for the potential, \((11)\), where \(\xi_0 = c/\sqrt{a^2 - c^2} = c/f\), is used. In the case of oblate nanospheroids, the addition translation theorem has the following form \([51]\) \((j, s = 1, 2, j \neq s)\),

\[
Q_n^m(i\xi_j) P_n^m(\eta_j) \left\{ \begin{array}{l}
\cos(m\phi_j) \\
\sin(m\phi_j)
\end{array} \right\} = \sum_{q=0}^{\infty} \sum_{p=0}^{q} P_q^p(i\xi_j) P_q^p(\eta_j) \left\{ \begin{array}{l}
M_{pqmn}^{(j)} \cos(p\phi_j), \\
N_{pqmn}^{(j)} \sin(p\phi_j),
\end{array} \right\}
\]

where

\[
M_{pqmn}^{(1)} = (-1)^{p+m}(L_{pqmn} + T_{pqmn}), \quad M_{pqmn}^{(2)} = (-1)^{p+m}M_{pqmn}^{(1)},
\]

\[
N_{pqmn}^{(1)} = (-1)^{p+m}(L_{pqmn} - T_{pqmn}), \quad N_{pqmn}^{(2)} = (-1)^{p+m}N_{pqmn}^{(1)},
\]

in which

\[
L_{pqmn} = \frac{(-1)^q(2 - \delta_{0p})(2q + 1)(q - p)!(n + m)!}{2(q + p)!(n - m)!} R_{pqmn}, \\
T_{pqmn} = \frac{(-1)^m R_{pq,-m,n}}{2(q + p + 1)!} \sum_{r=0}^{\infty} \sum_{k=0}^{\infty} \frac{(q + n + 2r + 2k - p + m)!}{(2q + 2r + 1)!!(2n + 2k + 2r)!!(2r)!!(2k)!!} \left( \frac{-i}{f} \right)^{2r+2k+q+n+1} P_{q+n+2r+2k}^{p-m} (0),
\]

and \(\delta_{0p}\) is a Kronecker delta symbol. Now, substituting \((16)\) and \((17)\) into \((11)\) and making use of the translational addition theorem \((18)\), we obtain the following system of equations \((n = 0, 1, 2, \ldots; m = 0, 1, 2, \ldots, n)\),

\[
\left( \frac{\epsilon \frac{dP_n^m(i\xi_0)}{d\xi_0}}{Q_n^m(i\xi_0)} - P_n^m(i\xi_0) \frac{dQ_n^m(i\xi_0)}{d\xi_0} \right) C_{mn}^{(1)}
\]

\[
+ (\epsilon - 1) P_n^m(i\xi_0) \frac{dQ_n^m(i\xi_0)}{d\xi_0} \sum_{q=0}^{\infty} \sum_{p=0}^{q} M_{mnpq}^{(0)} (-1)^p C_{pq}^{(2)} = 0,
\]

\[
\left( \frac{\epsilon \frac{dP_n^m(i\xi_0)}{d\xi_0}}{Q_n^m(i\xi_0)} - P_n^m(i\xi_0) \frac{dQ_n^m(i\xi_0)}{d\xi_0} \right) (-1)^m C_{mn}^{(2)}
\]

\[
+ (\epsilon - 1) P_n^m(i\xi_0) \frac{dQ_n^m(i\xi_0)}{d\xi_0} \sum_{q=0}^{\infty} \sum_{p=0}^{q} M_{mnpq}^{(0)} C_{pq}^{(1)} = 0.
\]

New Journal of Physics 13 (2011) 053034 (http://www.njp.org/)
By deriving (21), we take into account the fact that $M^{(2)}_{mnpq} = (-1)^m p M^{(1)}_{mnpq}$ (see (19)) and denote $M^{(0)}_{mnpq} = (-1)^m M^{(1)}_{mnpq}$. The system of equations for $D^{(l)}_{mn}$ is analogous to (21), and we will not analyze it here.

Owing to the symmetry of a cluster of two identical oblate nanospheroids, there are two types of plasmon oscillations: symmetric and antisymmetric, relative to the symmetry plane. To select these modes, we take $C^{(1)}_{mn} = \pm (-1)^m C^{(2)}_{mn}$. As a result, we shall obtain the following system of equations,

$$
\varepsilon \frac{dP^m_n(i\xi_0)}{d\xi_0} Q^m_n(i\xi_0) - P^m_n(i\xi_0) \frac{dQ^m_n(i\xi_0)}{d\xi_0} C^{(1)}_{mn} \pm (\varepsilon - 1) P^m_n(i\xi_0) \frac{dP^m_n(i\xi_0)}{d\xi_0} \sum_{q=0}^{\infty} \sum_{p=0}^{q} M^{(0)}_{mnpq} C^{(1)}_{pq} = 0,
$$

where the ‘+’ and ‘−’ signs correspond to modes that are symmetric (+) or antisymmetric (−) relative to the $x \rightarrow -x$ transformation.

In figure 4, the dependence of normalized plasmon frequencies $\omega/\omega_{pl} = 1/\sqrt{1 - \varepsilon}$ of a cluster of two identical oblate nanospheroids on normalized distances $l/2a$ between the nanoparticles’ centers is shown for the first four plasmon modes. Eigenvalues $\varepsilon$ were obtained as a solution of the equations systems (22).

One can see in figure 4 that in clusters of two oblate nanospheroids, modes of ‘T’, ‘M’ and ‘L’ types, which are analogous to T-, M- and L-modes of a cluster made of two prolate spheroids (see figure 2), can exist. The T- and M-modes are the solutions of the system (22) with ‘+’ sign, whereas the L-modes are the solutions of the system (22) with ‘−’ sign. T- and L-modes can be derived by the method of hybridization of plasmonic modes of two oblate nanospheroids and their plasmonic frequencies are lying in the range $0 < \omega < \omega_{pl}/\sqrt{2}$. An infinite number of plasmonic frequencies of higher L- and T-modes lie near $\omega_{pl}/\sqrt{2}$. When the width of the gap decreases to 0, the ratio $\omega/\omega_{pl}$ for T-modes tends to various values in the range from 0 to $1/\sqrt{2}$, whereas plasmonic frequencies of L-modes approach zero in analogy to L-modes in a cluster of two spherical nanoparticles [21, 60]. Plasmonic frequencies of strongly localized M-modes (figure 4(a)) lie in the range $\omega_{pl}/\sqrt{2} < \omega < \omega_{pl}$, as it happens in a cluster of two spherical nanoparticles [21, 60]. As the width of the gap between oblate nanospheroids decreases to zero, plasmon frequencies of M-modes tend to bulk plasmon frequency $\omega_{pl}$, analogous to the case of a two-sphere cluster [21, 60]. For large distances between the spheroids, M-modes disappear, and the plasmon frequencies of L- and T-modes of a cluster of two oblate nanospheroids tend to plasmonic frequencies of a single spheroid (see figure 4(c)) and can be found by means of a self-consistent model with approximation of spheroids by anisotropic point dipoles.

In figure 5, the distribution of a surface charge of plasmon modes of lower order in a cluster of two identical oblate nanospheroids is shown. One can see in this figure that the charge distribution is symmetric in T- and M-modes, while in L-mode it is antisymmetric, in agreement with the definition of these modes. For small distances between nanospheroids, charges in M- and L-modes are strongly localized near the gap. In contrast, when the distance between the spheroids increases, the charge distribution tends to a symmetric or antisymmetric combination of a surface charge in a single oblate nanospheroid (see figure 5(c)).
Figure 4. Normalized plasmon frequencies of the first few modes in a cluster of two identical oblate nanospheroids as a function of the distance between their centers. (a) Symmetrical modes (the eigenvalues of $\mathbf{2}$ with ‘+’ sign) and (b) antisymmetric modes (the eigenvalues of $\mathbf{2}$ with ‘−’ sign). By dashed lines, the plasmon frequencies of a single oblate nanospheroid $\omega_{pl} = \frac{1}{2} \left\{ \frac{dP_m(i\xi_0)}{d\xi_0} Q_n^m(i\xi_0) - \frac{dQ_m^m(i\xi_0)}{d\xi_0} \right\}$ are shown. The aspect ratio of a single oblate nanospheroid is $c/a = \frac{1}{\sqrt{(a/c)^2 - 1}}$. Panel (c) shows plasmon frequencies of a single oblate nanospheroid as a function of the inverse aspect ratio $a/c$. The vertical line corresponds to $c/a = 0.6$ and allows us to select asymptotic values for panels (a) and (b).

Thus, in a cluster of two oblate or prolate spheroidal nanoparticles, fundamental symmetric and antisymmetric plasmon modes of ‘T’, ‘M’ and ‘L’ types can be excited, and it is these modes that define all the optical properties of a two-nanospheroid cluster.

3. A cluster of two metal nanospheroids in the field of a plane electromagnetic wave

In this section, we will consider a two-spheroid cluster in a uniform electric field with the potential

$$\varphi_0 = -E_{0x}x - E_{0y}y - E_{0z}z,$$

where the time factor $e^{-i\omega t}$ is omitted. This case corresponds to a plane wave incidence and is important for the transformation of far fields into near fields, the enhancement of electric fields
Figure 5. Distribution of a surface charge (a.u.) of the lowest plasmon modes in a cluster of two identical oblate spheroidal nanoparticles according to the solution of the equations (22). The aspect ratio is $c/a = 0.6$. The distance between the nanospheroids’ centers is $l/2a = 1.05$ (a) and $l/2a = 1.4$ (b). The distribution of a surface charge in a single spheroid is shown in panel (c). Red corresponds to the positive charge and blue to the negative one.

and the effective excitation of atoms and molecules. Here again, we restrict ourselves to two special cases of nanospheroids’ shape and position that are most interesting for applications (figures 1(a) and (b)).

3.1. A cluster of two prolate nanospheroids

Here, we will also use local systems of spheroidal coordinates, the origins of which are placed in the nanospheroids’ centers (see figure 1(a)). The potential inside the $j$th nanospheroid again can be presented as a series in spheroidal harmonics (9), while the potential outside the nanospheroids should now be presented in the form

$$
\phi_{\text{out}} = \phi_{\text{out}}^{1} + \phi_{\text{out}}^{2} + \phi_{0},
$$

(24)

where $\phi_{\text{out}}^{1}$ and $\phi_{\text{out}}^{2}$ are contributions from the first and second nanospheroids (see (10)), and $\phi_{0}$ is the potential of the external electric field (23).

The electric potential of the incident plane wave (23) in local coordinates of the $j$th ($j = 1, 2$) prolate nanospheroid looks like

$$
\phi_{0}^{(j)} = f (E_{0x} \cos(\phi_{j}) + E_{0y} \sin(\phi_{j})) P_{1}^{1}(\xi_{j}) P_{1}^{1}(\eta_{j}) - f E_{0z} P_{1}(\xi_{j}) P_{1}(\eta_{j}) + (-1)^{j+1} E_{0z} \frac{l}{2},
$$

(25)

Making use of the boundary conditions (11) and the translational addition theorem (12), one can obtain the following system of equations for the coefficients $C_{mn}^{(1)}$ and $C_{mn}^{(2)}$ that define...
the outside field (see (10) and (24)) \( (n = 0, 1, 2, \ldots; m = 0, 1, 2, \ldots, n) \),

\[
\left( \varepsilon \frac{dP_n^m(\xi_0)}{d\xi_0} - Q_n^m(\xi_0) - P_n^m(\xi_0) \frac{dQ_n^m(\xi_0)}{d\xi_0} \right) C_{mn}^{(1)} + (\varepsilon - 1) P_n^m(\xi_0) \frac{dP_n^m(\xi_0)}{d\xi_0} \sum_{q=m}^{\infty} S_{nmq}^{(2)} C_{mq}^{(2)}
\]

\[= a_{mn}^{(1)} (\varepsilon - 1) P_n^m(\xi_0) \frac{dP_n^m(\xi_0)}{d\xi_0}, \]

\[
\left( \varepsilon \frac{dP_n^m(\xi_0)}{d\xi_0} - Q_n^m(\xi_0) - P_n^m(\xi_0) \frac{dQ_n^m(\xi_0)}{d\xi_0} \right) C_{mn}^{(2)} + (\varepsilon - 1) P_n^m(\xi_0) \frac{dP_n^m(\xi_0)}{d\xi_0} \sum_{q=m}^{\infty} S_{nmq}^{(1)} C_{mq}^{(1)}
\]

\[= a_{mn}^{(2)} (\varepsilon - 1) P_n^m(\xi_0) \frac{dP_n^m(\xi_0)}{d\xi_0}, \quad (26)\]

where \( (j = 1, 2) \)

\[a_{mn}^{(j)} = -\delta_{n1} \frac{f}{E_{0z}} (\delta_{m1} E_{0x} - \delta_{m0} E_{0z}) + (-1)^j \delta_{m0} \delta_{m0} E_{0z} \frac{l}{2}. \quad (27)\]

The equation system for coefficients \( D_{mn}^{(1)} \) and \( D_{mn}^{(2)} \) \( (n, m = 1, 2, 3, \ldots) \) can be obtained from (26) by substituting \( b_{mn}^{(1)} = b_{mn}^{(2)} = -\delta_{n1} \frac{f}{E_{0z}} \) instead of \( a_{mn}^{(j)} \).

It should be noted here that due to axial symmetry of the considered cluster, the system of equations (26) allow one to find the coefficients \( C_{mn}^{(j)} \) and \( D_{mn}^{(j)} \) for given order \( m \), while degree \( n \) runs over \( n = m, m+1, m+2, \ldots, m+N \), where \( N \) is a large number that defines the accuracy of the solution.

The induced dipole moment of a cluster of two prolate nanospheroids, placed in the field of a plane electromagnetic wave, can be calculated in analogy to a single prolate nanospheroid [32], that is, by finding far-field asymptotes of the potential (24). As a result, for the dipole moment induced in the \( j \)th nanospheroid \( (j = 1, 2) \), we have

\[d_x^{(j)} = \frac{2f^2}{3} C_{11}^{(j)}, \quad d_y^{(j)} = \frac{2f^2}{3} D_{11}^{(j)}, \quad d_z^{(j)} = \frac{f^2}{3} C_{01}^{(j)}, \quad (28)\]

and the total dipole moment of the cluster will be the sum of the momenta (28). An absorption cross-section can be easily found if the dipole momenta (28) are known [61],

\[\sigma_{\text{abs}} = 4\pi \left( \frac{\omega}{v_c} \right) \frac{\text{Im}(dE_{0z}^*)}{|E_0|^2}, \quad (29)\]

where \( d = d^{(1)} + d^{(2)} \) denotes the dipole momentum of the whole system, and the asterisk denotes the operation of complex conjugation.

In figure 6, the absorption cross-section of a cluster of two identical prolate nanospheroids made from silver is shown as a function of wavelength. For longitudinal \( (z) \) polarization, the cross-section has two peaks that correspond to longitudinal plasmonic oscillations with \( L = 1, 2 \) (see figure 2(b)). It is very important that both of the peaks are split substantially relative to the case of a single spheroid (the ‘\( z' \) dashed curve) due to a strong interaction between the nanospheroids.
Figure 6. Absorption cross-section of a cluster of two identical prolate nanospheroids made from silver as a function of wavelength. The large semi-axes of the nanospheroids are \( c = 15 \) nm, the aspect ratios are \( a/c = 0.6 \) and the distance between the nanospheroids’ centers is \( l/2c = 1.05 \). The labels \( y \) and \( z \) correspond to polarization of an incident wave along the \( y \) and \( z \) axes. The circles correspond to finite element simulations with Comsol Multiphysics® software. The doubled absorption cross-section of a single nanospheroid is shown by the dashed curve.

In contrast, for transversal (\( x \) or \( y \)) polarization one can see only one peak due to the excitation of the symmetrical \( T = 1 \) mode, and this peak is shifted just slightly relative to the single spheroid resonance (the ‘\( y \)’ dashed curve). This means that transversal (\( x \) or \( y \) polarization) excitation of a two-spheroid cluster induces only a weak interaction between the nanospheroids (see the dispersion curves for T-modes in figure 2(a)). Owing to this weak interaction, the absorption cross-section is approximately equal to double of a single spheroid.

It should be noted that in figure 6 the maxima of absorption, corresponding to plasmon oscillations of M-type that should lie in the interval \( \omega_{pl}/\sqrt{2} < \omega < \omega_{pl} \), which corresponds to \( 326 < \lambda < 337 \) nm for silver [52], are not visible. This is related to the fact that M-modes interact with a homogeneous electric field weakly and can be effectively excited only by a source of radiation that is nonuniform in comparison with the size of the gap between nanoparticles [60] (see figure 3).

To control the correctness and accuracy of our analytical calculations, we have also carried out finite element simulation of this system with Comsol Multiphysics® software. The results of this simulation are shown by circles in figure 6. One can see that there is fine agreement between the analytical and pure numerical calculations. This fact confirms the correctness and accuracy of both of the approaches.

3.2. A cluster of two oblate nanospheroids

The case of two oblate nanospheroids is in many aspects similar to the case of two prolate nanospheroids considered above. So let us again choose local systems of coordinates that are connected to each of the nanospheroids and have origins in their centers (see figure 1(b)). The
potential inside the \( j \)th nanospheroid can be presented again as a series in spheroidal harmonics (16), whereas the potential outside the oblate spheroids can be presented in the form

\[
\varphi^{\text{out}} = \varphi_1^{\text{out}} + \varphi_2^{\text{out}} + \varphi_0,
\]

where \( \varphi_1^{\text{out}} \) and \( \varphi_2^{\text{out}} \) are contributions from the first and second nanospheroids (see (17)) and \( \varphi_0 \) is the potential of the external electric field (23). In the local coordinates of the \( j \)th \((j = 1, 2)\) oblate nanospheroid, it looks like

\[
\varphi_0^{(j)} = -i f (E_{0x} \cos(\phi_j) + E_{0y} \sin(\phi_j)) P_j^1(i\xi_j) P_1^1(\eta_j) + i f E_{0z} P_1(i\xi_j) P_1(\eta_j) + (-1)^j E_{0z} \frac{l}{2}. \tag{31}
\]

Making use of the boundary conditions (11) with \( \xi_0 = c/\sqrt{a^2 - c^2} = c/f \), and the translational addition theorem (18), we shall obtain the following systems of equations \((n = 0, 1, 2, \ldots; m = 0, 1, 2, \ldots, n)\),

\[
\left( \varepsilon \frac{dP_n^m(\xi_0)}{d\xi_0} - \frac{dQ_n^m(\xi_0)}{d\xi_0} \right) C_{mn}^{(1)} + (\varepsilon - 1) P_n^m(\xi_0) \frac{dP_n^m(\xi_0)}{d\xi_0} \sum_{q=0}^{\infty} \sum_{p=0}^{\infty} M_{nmpq}^{(2)} C_{pq}^{(2)} = a_n^{(1)} (\varepsilon - 1) P_n^m(\xi_0) \frac{dP_n^m(\xi_0)}{d\xi_0},
\]

\[
\left( \varepsilon \frac{dP_n^m(\xi_0)}{d\xi_0} - \frac{dQ_n^m(\xi_0)}{d\xi_0} \right) C_{mn}^{(2)} + (\varepsilon - 1) P_n^m(\xi_0) \frac{dP_n^m(\xi_0)}{d\xi_0} \sum_{q=0}^{\infty} \sum_{p=0}^{\infty} M_{nmpq}^{(1)} C_{pq}^{(1)} = a_n^{(2)} (\varepsilon - 1) P_n^m(\xi_0) \frac{dP_n^m(\xi_0)}{d\xi_0}, \tag{32}
\]

where \((j = 1, 2)\)

\[
a_{mn}^{(j)} = i \delta_{n1} f (\delta_{m1} E_{0x} - \delta_{m0} E_{0y}) + (-1)^{j+1} \delta_{m0} \delta_{n1} E_{0x} \frac{l}{2}. \tag{33}
\]

The equation system for coefficients \( D_{mn}^{(1)} \) and \( D_{mn}^{(2)} \((n, m = 1, 2, 3, \ldots)\) can be obtained from (32) by substituting \( b_{mn}^{(1)} = b_{mn}^{(2)} = i \delta_{n1} f E_{0y} \) instead of \( a_{mn}^{(j)} \), and \( N_{mn}^{(j)} \) instead of \( M_{mn}^{(j)} \).

Apparently, the equations (32) have a more complicated structure than (26) because now, due to the lack of axial symmetry, one cannot split the system of equations into systems with fixed order \( m \) of the Legendre function.

For the calculation of the absorption cross-section of a cluster in the field of a plane electromagnetic wave, one can again use (29), where dipole momenta of each spheroid can be expressed by the next way \((j = 1, 2)\),

\[
d_x^{(j)} = -\frac{2 f^2}{3} C_{11}^{(j)}, \quad d_y^{(j)} = -\frac{2 f^2}{3} D_{11}^{(j)}, \quad d_z^{(j)} = -\frac{f^2}{3} C_{01}^{(j)}. \tag{34}
\]

In figure 7, the absorption cross-section of a cluster of two identical oblate nanospheroids made from silver is shown as a function of wavelength. For longitudinal \((x)\) polarization, the cross-section has two peaks, which correspond to antisymmetric plasmonic oscillations with \( L = 1, 2 \) (see figure 4(b)). It is very important that now only one peak \((L = 1)\) is shifted substantially.
Figure 7. The absorption cross-section of a cluster of two identical oblate nanospheroids made from silver as a function of the wavelength. The large semi-axes of the nanospheroids are $a = 15$ nm, the aspect ratios are $c/a = 0.6$ and the distance between the nanospheroids’ centers is $l/2a = 1.05$. The labels $x$ and $y$ correspond to polarization of an incident wave along the $x$ and $y$ axes. The circles correspond to finite element simulations with Comsol Multiphysics® software. The doubled absorption cross-section of a single nanospheroid is shown by the dashed curve.

relative to the case of a single spheroid (the ‘$x$, $y$’ dashed curves) owing to a strong interaction between the nanospheroids. The $L = 2$ mode suffers only a small shift, in agreement with figure 4(b).

For transversal ($y$) polarization, one can see only one peak owing to the excitation of the symmetrical $T = 1$ mode, and this peak is only slightly shifted relative to the single spheroid resonance (the dashed curve). This means that transversal ($y$ polarization) excitation of a two-spheroid cluster results in only a weak interaction between the nanospheroids (see the dispersion curves for the $T$-modes in figure 4(a)). Due to this weak interaction, the absorption cross-section for this polarization is approximately equal to the doubled cross-section of a single spheroid. It is also interesting that the plasmonic frequency of the $L = 2$ mode is very close to the plasmonic frequency of the $T = 1$ mode. This fact can be easily understood from the analysis of figure 4. Indeed, when the width of the gap tends to zero, the plasmonic frequency of $L = 2$ modes also decreases to zero, while the plasmonic frequency of the $T = 1$ mode increases slightly. So, at some point these modes will intersect and have the same frequency, and we observe this situation in figure 7.

It should be noted that in figure 7 the maxima of absorption corresponding to plasmon oscillations of M-type are again not visible. It is related to the fact that M-modes interact with a homogeneous electric field weakly and can be effectively excited only by a source of radiation that is nonuniform in comparison with the size of the gap between nanoparticles [60] (see figure 3).

To control the correctness and accuracy of our analytical calculations for a cluster of two oblate spheroids, we have also carried out finite element simulation of this system with Comsol Multiphysics® software. The results of this simulation are shown by circles in figure 7. One can
see that there is fine agreement between the analytical and pure numerical calculations. This fact confirms the correctness and accuracy of both the approaches again.

3.3. Enhancement of local fields

The most important characteristic of nanoparticle clusters is the incident field enhancement factor in the gap between nanoparticles. This is the characteristic that allows us to determine the excitation rate of molecules near nanoparticles or the intensity of SERS [4]. Moreover, achieving high values of this factor is the main goal of optical nano-antenna development.

The distribution of squared electric field for the \( L = 1 \) resonance in a cluster of two prolate spheroids is shown in figure 8, which shows that, indeed, maximal field enhancement takes place in the gap between the nanoparticles on their surfaces. The field maxima are also present in the outer side of the cluster; however, field amplitude is essentially less there. According to general theorems for harmonic functions, the field maximum can be reached only on the region boundaries. In our case, the field maxima are reached in those points of the spheroids’ surface where the distance between the spheroids is minimal.

Using (10) and (17), one can find explicit expressions for the field enhancement factor \( G \). For clusters of two identical prolate spheroids in the considered configuration (figure 1(a)), one can obtain the following expression for the field maximum in the case of an incident field polarized along the \( z \)-axis,

\[
G = \frac{|E|^2}{|E_{0z}|^2} = 1 - \frac{1}{E_{0z}} \sum_{n=1}^{\infty} C_{0n} \left( \frac{dQ_n(\xi_1)}{d\xi_1} + \frac{dQ_n(\xi_2)}{d\xi_2} \right)^2,
\]

(35)
Figure 9. Enhancement of $|E|^2$ in the gap between two identical silver nanospheroids as a function of the wavelength. P and O labels correspond to prolate and oblate spheroids correspondingly. The large semi-axes of the nanospheroids are 15 nm, the aspect ratios are 0.6, $l/2c = 1.05$ for a cluster of prolate spheroids and $l/2a = 1.05$ for a cluster of oblate spheroids. Enhancements for single nanospheroids are shown by the dashed curve.

where $\xi_1 = c/f$ and $\xi_2 = (l - c)/f$, while $C_{0n} = C_{0n}^{(1)} = -(-1)^nC_{0n}^{(2)}$. In the most interesting case of a small gap and strongly prolate spheroids, $\xi_1, \xi_2 \approx 1$, and one may use the asymptotic form $\frac{dQ_{m}(i\xi_1)}{d\xi_1} \approx -\frac{i}{2(\xi-1)}$. As a result, the field enhancement factor takes the form

$$G = \left| \frac{|E|^2}{|E_0|^2} \right|^2 \approx \left| \frac{1}{2E_0f} \left( \frac{1}{\xi_1 - 1} + \frac{1}{\xi_2 - 1} \right) \sum_{n=1}^{\infty} C_{0n} \right|^2. \quad (36)$$

In the case of clusters of two identical oblate spheroids (figure 1(b)) and incident field polarized along the x-axis, we obtain

$$G = \left| \frac{|E|^2}{|E_0|^2} \right|^2 = \left| \frac{1}{E_0f} \sum_{n=1}^{\infty} \sum_{m=0}^{n} C_{mn} \frac{dP_{m}(\eta)}{d\eta} \right|_{\eta=0} \left( \frac{1}{\xi_1} Q_{n}^m(i\xi_1) - \frac{1}{\xi_2} Q_{n}^m(i\xi_2) \right) \right|^2 \right|_{\eta=0} \left( \frac{1}{\xi_1} Q_{n}^m(i\xi_1) - \frac{1}{\xi_2} Q_{n}^m(i\xi_2) \right) \right|^2,$$

$$= \left| 1 - \frac{1}{E_0f} \sum_{n=1}^{\infty} \sum_{m=0}^{n} C_{mn} P_{n}^m(0) \right| \left( \frac{1}{\xi_1} dQ_{n}^m(i\xi_1) + \frac{1}{\xi_2} dQ_{n}^m(i\xi_2) \right) \right|^2,$$

$$= \left( \frac{1}{\xi_1^2} + \frac{1}{\xi_2^2} \right)^2 \left( \frac{1}{\xi_1} dQ_{n}^m(i\xi_1) + \frac{1}{\xi_2} dQ_{n}^m(i\xi_2) \right) \right|^2 \right|,$$

where $\xi_1 = \sqrt{a^2/f^2 - 1}$ and $\xi_2 = \sqrt{(l - a)^2/f^2 - 1}; C_{mn} = -(-1)^mC_{mn}^{(1)} = C_{mn}^{(2)}$.

In figure 9, the dependence of squared electric field enhancement (35) and (37) for clusters of two identical silver nanospheroids on the wavelength is shown. Comparing peak positions with the dispersion curves in figures 2 and 4, one can come to a conclusion that only ‘L’ type
plasmon modes are excited in the clusters for the considered configurations of nanospheroids and incident electromagnetic wave polarizations (along the line joining the nanoparticles’ centers). In particular, the excitation of the \( L = 1 \) and \( L = 2 \) modes is noticeable. At that, the position of squared field enhancement peaks agrees with the maxima of absorption cross-section shown in figures 6 and 7 by the solid lines \( z \) and \( x \) correspondingly. It should be mentioned that the value of squared field enhancement near a cluster of two nanospheroids can reach values of up to \( 10^6 \). In the case of single nanoparticles, this value is almost two orders lower than that of clusters (cf solid and dashed curves in figure 9). This fact determines the greater attractiveness of metal nanoparticle clusters in comparison to single nanoparticles for the investigation of SERS and SEF. Note that the obtained great values of the field enhancement factor can be slightly lower in practice, since for small particles and for small gaps between them, nonlocal and other effects not considered in this research become essential.

4. A cluster of two nanospheroids in the field of a radiating atom

In the previous section, we considered the case of a nano-antenna placed in the field of a plane wave. However, highly nonuniform optical fields occur very often in the nano-environment. For example, such fields arise when a plasmonic nano-antenna is excited by an atom or a molecule or any other nanolocalized source of light. So, in this section, we will consider the important case of a two-nanospheroid cluster in the field of electric dipole sources. The excitation of the cluster by magnetic dipole and electric quadrupole sources can be analyzed analogously.

4.1. A cluster of two prolate nanospheroids

The case of two prolate nano-spheroids in the field of a dipole source of radiation can be considered in perfect analogy to the case of the same cluster in a uniform field. One should again look for solutions in the form (39) and then apply the boundary conditions (11). The only difference is that now the external potential is the potential \( \varphi_0 \) of the dipole that has the following form in the \( j \)th local system of coordinates of a prolate spheroid [58] \((j = 1, 2)\),

\[
\varphi_0^{(j)} = \left( \mathbf{d}_0 \nabla_j \right) \frac{1}{|\mathbf{r} - \mathbf{r}'|} = \sum_{n=0}^{\infty} \sum_{m=0}^{n} \left\{ P_n^m(\xi_j) P_n^m(\eta_j) \left[ (\mathbf{d}_0 \nabla_j) \alpha_{mn}^{(j)} \cos(m\phi_j) + (\mathbf{d}_0 \nabla_j) \beta_{mn}^{(j)} \sin(m\phi_j) \right], \xi_j < \xi_j', \right. \\
\left. Q_n^m(\xi_j) Q_n^m(\eta_j) \left[ (\mathbf{d}_0 \nabla_j) \gamma_{mn}^{(j)} \cos(m\phi_j) + (\mathbf{d}_0 \nabla_j) \sigma_{mn}^{(j)} \sin(m\phi_j) \right], \xi_j > \xi_j'. \right. \quad (38)
\]

In (38), \( \mathbf{d}_0 \) denotes the dipole momentum of a source placed at \( \mathbf{r}' \), \( \nabla_j \) is a gradient over \( \mathbf{r}' \) in local coordinates and

\[
\alpha_{mn}^{(j)} = \frac{1}{f} (2 - \delta_{m0}) (-1)^m (2n + 1) \left[ \frac{(n - m)!}{(n + m)!} \right]^2 Q_n^m(\xi_j) Q_n^m(\eta_j) \begin{cases} \cos(m\phi_j) \\ \sin(m\phi_j) \end{cases}, \\
\beta_{mn}^{(j)} = \frac{1}{f} (2 - \delta_{m0}) (-1)^m (2n + 1) \left[ \frac{(n - m)!}{(n + m)!} \right]^2 P_n^m(\xi_j) P_n^m(\eta_j) \begin{cases} \cos(m\phi_j) \\ \sin(m\phi_j) \end{cases}, \\
\gamma_{mn}^{(j)} = \frac{1}{f} (2 - \delta_{m0}) (-1)^m (2n + 1) \left[ \frac{(n - m)!}{(n + m)!} \right]^2 P_n^m(\xi_j) P_n^m(\eta_j) \begin{cases} \cos(m\phi_j) \\ \sin(m\phi_j) \end{cases}, \\
\sigma_{mn}^{(j)} = \frac{1}{f} (2 - \delta_{m0}) (-1)^m (2n + 1) \left[ \frac{(n - m)!}{(n + m)!} \right]^2 Q_n^m(\xi_j) Q_n^m(\eta_j) \begin{cases} \cos(m\phi_j) \\ \sin(m\phi_j) \end{cases}. \quad (39)
\]
are expansion coefficients of the unit charge potential in local coordinates of a prolate spheroid.

As a result of applying the boundary conditions, one can obtain a system of equations for the unknown coefficients \( C_{mn}^{(j)} \), \( D_{mn}^{(j)} \) in (10). The new system can be easily derived from (26) if one makes the following replacement for the coefficients \( a_{mn}^{(j)} \) and \( b_{mn}^{(j)} \),

\[
\begin{align*}
a_{mn}^{(1)} &= - (d_0 \nabla') \alpha_{mn}^{(1)}, & a_{mn}^{(2)} &= - (d_0 \nabla') \alpha_{mn}^{(2)}, \\
b_{mn}^{(1)} &= - (d_0 \nabla') \beta_{mn}^{(1)}, & b_{mn}^{(2)} &= - (d_0 \nabla') \beta_{mn}^{(2)},
\end{align*}
\]

where \( \alpha_{mn}^{(j)} \) and \( \beta_{mn}^{(j)} \) are defined by (39).

After the systems for coefficients \( C_{mn}^{(j)} \) and \( D_{mn}^{(j)} \) have been solved with taking into account (40), one can find the total induced dipole moment of both the prolate nanospheroids,

\[
d_x = \frac{2 f^2}{3} (C_{11}^{(1)} + C_{11}^{(2)}), \quad d_y = \frac{2 f^2}{3} (D_{11}^{(1)} + D_{11}^{(2)}), \quad d_z = \frac{f^2}{3} (C_{01}^{(1)} + C_{01}^{(2)}).
\]

Knowing the dipole momenta (41), it is easy to find (see e.g. [62]) the radiative decay rate of an excited atom placed near the cluster of two prolate nanospheroids,

\[
g = \frac{P_{\text{rad}}}{\hbar \omega} = \frac{\omega_3}{3 \hbar \nu_c^2} |d_0 + d|^2,
\]

where \( P_{\text{rad}} \) is the radiation power at frequency \( \omega \) and \( \hbar \omega \) is the emitted photon energy.

The radiative decay rate is a very important characteristic in applications such as SERS, SEF, nanolasers and so on. To characterize the radiative decay rate, it is natural to normalize it to the radiative decay rate of a dipole in free space, \( g_0 = \frac{P_{\text{rad}}}{\hbar \omega} = \frac{\omega_3}{3 \hbar \nu_c} |d_0|^2 \).

In figure 10, the normalized radiative decay rate of a dipole source placed at the middle point of the gap is shown. As is clearly seen in figure 10(a), if the distance between the prolate nanospheroids is small (figure 10(a), curves \( \alpha \) and \( \delta \)), the dipole source with a moment oriented perpendicular to the cluster’s axis of rotation can excite both symmetrical T- and M-modes. This fact contrasts with the case of the excitation of the same cluster with a plane wave, when M-modes with peaks located in the region of \( \lambda < 337 \text{ nm} \) (see figure 2(a)) are not excited. When the distance between the nanospheroids increases (see figure 10(a)), the peak corresponding to M-modes shifts to \( \lambda \approx 337 \text{ nm} \) (\( \omega \approx \omega_{\text{pl}}/\sqrt{2} \)) and then disappears. After that point, only the peaks corresponding to plasmonic T-modes can be observed. Of course, this picture is in agreement with the behavior of the plasmonic M-modes shown in figure 2(a). We also note that for large enough distances between the nanospheroids (see figure 10(a), curve \( \gamma \)), the self-consistent model [3, 22], in which nanoparticles are replaced by point dipoles with corresponding polarizabilities [3, 35], can be effectively used for the calculation of the radiative decay rate (dashed curve).

When the dipole moment of a source is oriented along the axis of symmetry (figure 10(b)), only antisymmetric L-modes can be excited owing to symmetry reasons. From figure 10(b), one can also see that for small enough distances between the spheroids there are two plasmonic modes (\( L = 1, 2 \)) that interact with the dipole source. When the distance between the spheroids diminishes, right peaks of radiation power shift towards long wavelengths. At large distances between the nanospheroids, there is only one maximum corresponding to the \( L = 1 \) plasmonic mode (see figure 10(b), curve \( \gamma \)). In this case, the radiative decay rate of a dipole placed near a
Figure 10. Normalized radiative decay rate of a dipole placed at the middle point between two identical prolate nanospheroids made from silver as a function of the wavelength. The dipole source moment is oriented along the $x$ or $y$ axes (a) and along the $z$ axis (b). The large semi-axes of the nanospheroids are $c = 15 \text{ nm}$, the aspect ratios are $a/c = 0.6$. The curves $\alpha$, $\beta$, $\gamma$ and $\delta$ correspond to $l/2c = 1.05$, $1.1$, $1.3$ and $1.03$, respectively. The asymptotic expression obtained by approximation of the spheroids by point dipoles ($l/2c = 1.3$) is shown by the dashed curve.

Cluster of two prolate nanospheroids can be calculated also by making use of the self-consistent analytical model in which the spheroids are approximated by point dipoles (see the dashed curve in figure 10(b)).

4.2. A cluster of two oblate nanospheroids

The case of two oblate nanospheroids in the field of a dipole source of radiation can be considered in perfect analogy to a case of the same cluster in a uniform field. One should again look for solutions in the forms (16) and (17) and then apply the boundary conditions (11) with $\xi_0 = c/\sqrt{a^2 - c^2} = c/f$. The only difference is that now the external potential is the potential $\varphi_0$ of the dipole that has the following form in the $j$th local system of coordinates of an oblate spheroid [58] ($j = 1, 2$),

$$
\varphi_0^{(j)} = \frac{(d_0 \nabla_j)}{|r - r'|}
\left\{\begin{array}{l}
P_m^{m}(i \xi_j) P_n^{m}(\eta_j) \left[ (d_0 \nabla_j) \alpha_{mn}^{(j)} \cos(m \phi_j) + (d_0 \nabla_j) \beta_{mn}^{(j)} \sin(m \phi_j) \right], \xi_j < \xi_j' \\
Q_n^{m}(i \xi_j) P_n^{m}(\eta_j) \left[ (d_0 \nabla_j) \gamma_{mn}^{(j)} \cos(m \phi_j) + (d_0 \nabla_j) \sigma_{mn}^{(j)} \sin(m \phi_j) \right], \xi_j > \xi_j'
\end{array}\right.
$$

(43)
In (43), $d_0$ denotes the dipole momentum of a source placed at $r'$, $\nabla'_j$ is the gradient over $r'$ in local coordinates, and

$$
\alpha_{mn}^{(j)} = \frac{i}{f} (2 - \delta_{m0}) (-1)^m (2n + 1) \left[ \frac{(n-m)!}{(n+m)!} \right]^2 Q_m^n(i\xi'_j) P_m^n(\eta'_j) \left\{ \begin{array}{c} \cos(m\phi'_j), \\
\sin(m\phi'_j), \end{array} \right.
$$

$$
\beta_{mn}^{(j)} = -i(d_0\nabla'_j)\alpha_{mn}^{(j)}, \quad a_{mn}^{(2)} = -i(d_0\nabla'_j)\alpha_{mn}^{(2)},
$$

$$
\gamma_{mn}^{(j)} = \frac{i}{f} (2 - \delta_{m0}) (-1)^m (2n + 1) \left[ \frac{(n-m)!}{(n+m)!} \right]^2 P_m^n(i\xi'_j) P_m^n(\eta'_j) \left\{ \begin{array}{c} \cos(m\phi'_j), \\
\sin(m\phi'_j), \end{array} \right.
$$

are the expansion coefficients of the unit charge potential in local coordinates of an oblate spheroid.

As a result of applying the boundary conditions, one can obtain the system of equations for the unknown coefficients $C_{mn}^{(j)}$, $D_{mn}^{(j)}$ in (17). The system of equations for these coefficients can be easily derived from (32) if one makes the following replacement for the coefficients $a_{mn}^{(j)}$ and $b_{mn}^{(j)}$,

$$
a_{mn}^{(1)} = -i(d_0\nabla'_j)\alpha_{mn}^{(1)}, \quad a_{mn}^{(2)} = -i(d_0\nabla'_j)\alpha_{mn}^{(2)},
$$

$$
b_{mn}^{(1)} = -i(d_0\nabla'_j)\beta_{mn}^{(1)}, \quad b_{mn}^{(2)} = -i(d_0\nabla'_j)\beta_{mn}^{(2)},
$$

where $\alpha_{mn}^{(j)}$ and $\beta_{mn}^{(j)}$ are defined in (44).

The total induced dipole moment of a cluster of two oblate nanospheroids can be found by using the following expressions,

$$
d_x = -\frac{2f^2}{3}(C_{11}^{(1)} + C_{11}^{(2)}), \quad d_y = -\frac{2f^2}{3}(D_{11}^{(1)} + D_{11}^{(2)}), \quad d_z = -\frac{f^2}{3}(C_{01}^{(1)} + C_{01}^{(2)}).
$$

In figure 11, the normalized radiative decay rate of a dipole placed at the middle point between the oblate nanospheroids is shown. As one can see in figure 11(a), if the dipole moment of a source is oriented along the line connecting the oblate nanospheroids’ centers, only plasmonic L-modes are excited as it took place for the case of a cluster of two prolate nanospheroids (cf figure 10(b)). When the distance between the nanospheroids is large enough ($\gamma$ curve), the properties of radiative decay of a dipole source located near the cluster can be more and more precisely approximated by means of the self-consistent model where spheroids are modeled by point dipoles (see figure 11(a), dashed curve).

From figure 11(b) and (c), which correspond to the case of the dipole moment of a source oriented along the $y$ and $z$ axes, one can conclude that only symmetric T-modes are presented here. Nevertheless, at small enough distances between the nanospheroids, one can expect that M-modes are also excited but cannot be seen due to large losses (large imaginary part of dielectric permittivity) in the silver spheroids. If the imaginary part of permittivity of spheroidal nanoparticles’ material is small enough, for example, in the case of silicized carbon (SiC) [63], all fine features of the spectra and M-modes in particular will be clearly visible, as was demonstrated in [21, 22] with the example of a cluster of two spheres.
Figure 11. The normalized radiative decay rate of a dipole placed at the middle point between two identical oblate nanospheroids made from silver as a function of wavelength. The dipole source moment is oriented along the $x$ (a), $y$ (b) and $z$ (c) axes. The large semi-axes of the nanospheroid are $a = 15$ nm and the aspect ratio is $c/a = 0.6$. The curves $\alpha$, $\beta$ and $\gamma$ correspond to $l/2a = 1.05$, 1.1 and 1.3, respectively. The asymptotic expression obtained by approximation of the spheroids by point dipoles ($l/2a = 1.3$) is shown by the dashed curve.

5. Conclusion

Thus, in the present work, the optical properties of clusters made of two metal nanospheroids are considered theoretically, and analytical results are obtained. Plasmonic eigenoscillations were analyzed in detail, and it was found that in a cluster of two prolate or oblate nanospheroids there can be three types of plasmon modes. Two of them (low frequency, $0 < \omega < \omega_{pl}/\sqrt{2}$, L- and T-modes) can be effectively excited by a plane electromagnetic wave, while the third type (high frequency, $\omega_{pl}/\sqrt{2} < \omega < \omega_{pl}$, M-modes) can be excited only by a strongly nonuniform field of a nanolocalized source of light (a molecule, a quantum dot) located in the gap between two adjacent nanoparticles.

We have also investigated the excitation of a nano-antenna made from two silver nanospheroids by the fields of a plane wave and an electric dipole. The results of these investigations allow us to obtain the absorption cross-section of the nano-antenna as a function of wavelength for various polarizations of an incident plane electromagnetic wave and to attribute all of the observable peaks to the excitation of corresponding plasmonic modes. We also
analyzed the radiative decay rate (or local density of state) of an excited atom placed in the gap between nanospheroids and attributed all observable peaks to the excitation of corresponding plasmonic modes.

The obtained analytical results can be used in many applications based on plasmonic nanoantennas or the enhancement of local fields (SERS, SEF, nanolasers, nano-optical circuits and so on). In addition, our results are very important for controlling the accuracy of different computational software programs that have no a priori test of accuracy.

Acknowledgments

We thank the Russian Foundation for Basic Research (grants 11-02-92002, 11-02-01272 and 11-02-91065) for financial support. We also thank Ulrike Woggon for her helpful comments.

References

[1] Raether H 1998 Surface Plasmons on Rough and Smooth Surfaces and on Gratings (Berlin: Springer)
[2] Maier S A 2007 Plasmonics: Fundamentals and Applications (New York: Springer)
[3] Klimov V V 2009 Nanoplasmonics (Moscow: Fizmatlit) (in Russian)
[4] Kneipp K, Moskovits M and Kneipp H eds 2006 Surface-Enhanced Raman Scattering (Berlin: Springer)
[5] Liu Y, Bishop J, Williams L, Blair S and Herron J 2004 Nanotechnology 15 1368
[6] Haes A J, Zou S L, Schatz G C and Van Duyne R P 2004 J. Phys. Chem. B 108 6961
[7] Haes A J, Zou S L, Schatz G C and Van Duyne R P 2004 J. Phys. Chem. B 108 109
[8] Chah S, Hammond M R and Zare R N 2005 J. Chem. Phys. 121 227402
[9] Ruppin R 1982 J. Chem. Phys. 76 1681
[10] Novotny L 2007 Phys. Rev. Lett. 98 266802
[11] Taminiau T H, Stefani F D and Van Hulst N F 2008 Opt. Express 16 10858
[12] Fischer H and Martin O J F 2008 Opt. Express 16 9144
[13] Lakowicz J R, Malicka J, Gryczynski I, Gryczynski Z and Geddes C D 2002 J. Chem. Phys. D: Appl. Phys. 36 240
[14] Ruppin R 1982 J. Chem. Phys. 76 1681
[15] Ruppin R 1982 Phys. Rev. B 26 3440
[16] Claro F 1982 Phys. Rev. B 25 7875
[17] Schmeits M and Dambly L 1991 Phys. Rev. B 44 12706
[18] Gerardy J M and Ausloos M 1980 Phys. Rev. B 22 4950
[19] Klimov V V and Guzatov D V 2007 Phys. Rev. B 75 024303
[20] Klimov V V and Guzatov D V 2007 Quantum Electron. 37 209
[21] Chu P and Mills D L 2008 Phys. Rev. B 77 045416
[22] Li K, Stockman M I and Bergman D J 2003 Phys. Rev. Lett. 91 227402
[23] Genov D A, Sarychev A K, Shalaev V M and Wei A 2004 Nano Lett. 4 153
[24] Nordlander P, Oubre C, Prodan E, Li K and Stockman M I 2004 Nano Lett. 4 899
[25] Romero I, Aizpurua J, Bryant G W and Garcia de Abajo F J 2006 Opt. Express 14 9988
[26] Danckwerts M and Novotny L 2007 Phys. Rev. Lett. 98 026104
[27] Quinten M, Leitner A, Krenn J R and Aussenegg F R 1998 Opt. Lett. 23 1331
[28] Maier S A, Kik P G and Atwater H A 2002 Appl. Phys. Lett. 81 1714
[29] Wang D-S and Kerker M 1981 Phys. Rev. B 24 1777
[30] Klimov V V, Ducloy M and Letokhov V S 2002 Eur. Phys. J. D 20 133
[31] Trugler A and Hohenester U 2008 Phys. Rev. B 77 115403

New Journal of Physics 13 (2011) 053034 (http://www.njp.org/)
