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Effect of a dimer of nanoparticles on the linewidth of forbidden E2 transitions

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Abstract. **In the framework of classical electrodynamics we have obtained and investigated analytical expressions for the radiation linewidth of forbidden E2 transitions in an atom located near a dimer of spherical particles. It is shown that the material of particles, their location and size have a significant effect on the linewidth of the E2 transition in the atom. It is found that in the gap between metal spherical nanoparticles, the linewidth of E2 transitions in the atom can take on substantially larger values than in the case of an atom near a single metal nanoparticle.**

Keywords: *linewidth, forbidden E2 transition, dimer of spherical particles.*

1. Introduction

It is known that in the vicinity of material bodies the rate of spontaneous decay of atoms and molecules and correspondingly the linewidth of emitted radiation can both increase and decrease (Purcell effect) [1]. Changing the linewidth is usually caused by electric dipole transitions [2]. However, atoms and molecules can be a source of a magnetic dipole, electric quadrupole and other types of multipole radiations, and the probabilities of these transitions also significantly change in the presence of nanoparticles [3–9]. In general, the probability of spontaneous emission strongly decreases with increasing multipole order. For example, the ratio of intensities of quadrupole and dipole radiations in a vacuum is $(a_0/\lambda)^2 \sim 10^{-6}-10^{-8}$, where a_0 is the linear dimension of a radiating system of charges, and λ is the wavelength [10]. Because this relationship is a small quantity, a study of quadrupole transitions (forbidden E2 transitions) is very complicated [11–13]. Nevertheless, quadrupole transitions are an important tool in ultra-high resolution spectroscopy (see, e.g., [14]).

Moreover, if an atom is located close to a body that produces a large inhomogeneity of the electric field, the linewidth of the forbidden E2 transitions in the atom can be increased due to a large field gradient [15, 16]. Note that in laser beams it is possible to create conditions for the enhancement of the effects of interaction with a quadrupole [17–19]. On the basis of these effects, approaches are now being developed using nanostructured materials, which make it possible to significantly improve spectroscopy of quadrupole transitions [20, 21].

To date, a theoretical investigation has been performed of a change in the linewidth of forbidden E2 transitions in an atom located near a spherical particle of a dielectric (metal) [3–5, 9], near a perfectly conducting cylinder [6], near a flat interface between a vacuum and a dielectric (metal) and in a plane gap between two dielectric (metal) media [7], near a structure in the form of metal nanostrips on a dielectric substrate [22], and also near an infinite two-dimensional periodic lattice of metal nanospheres [23].

A dimer of nanoparticles has a more interesting geometry, because it serves as a nanoantenna, which can be used to control efficiently both the radiation and the detection of the field. For the first time, this geometry was considered in [24] for two nanorods of finite length and square cross section. For this geometry, there is no analytical solution, and therefore Kern and Martin [24] studied numerically only some particular cases. This, of course, does not allow one to establish the fundamental physical laws and their dependence on the parameters of the problem. To establish the fundamental physical laws it is extremely important to have an analytical solution for nanoantennas consisting of nanoparticles of simple shape.

The purpose of this paper is to construct an analytical description of the influence of a dimer of identical spherical particles on the radiation linewidth of forbidden E2 transitions in the atom in the framework of classical electrodynamics. All analytical results in the work will be obtained for arbitrary sizes of particles and arbitrary distances between them, as well as for an arbitrary composition of the particles and arbitrary quadrupole moments of the atom.

The paper is structured as follows. In Section 2 we consider an electromagnetic field of an electric quadrupole source (atom) in the presence of a dimer of spherical particles. In Section 3 we derive an expression for the linewidth of the forbidden E2 transitions in the atom located near the dimer. In Section 4 we present the obtained results in graphic form and their discussion, and in Section 5 (Conclusions) we report the main results of the work.

2. Electromagnetic field of an electric quadrupole source (atom) in the presence of a dimer of spherical particles

To calculate the linewidth of the forbidden E2 transition, we first need to find the radiation field, which arises due to this

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transition. To this end, the forbidden transition is simulated by an electric quadrupole source. To find the radiation field produced near a dimer of spherical particles, we use the T-matrix method. This method is often used to describe the scattering of electromagnetic waves by clusters of spherical particles. The method is accurate and based on Mie theory for each particle and the addition theorem for vector spherical harmonics [25–30]. The original method was developed by Waterman [31] and later was significantly improved in [32–36]. A bibliography on the T-matrix method is available in [37].

In the case of a dimer of spherical particles, the T-matrix method is reduced to the introduction of two local coordinate systems associated with each particle. For definiteness, we assume that the origins of the local Cartesian coordinate systems are located in the centres of the particles; the systems have parallel and equally directed axes and a common z axis (Fig. 1). The coordinates and all other quantities related to the sth (s = 1, 2) particle will be denoted by an additional index 1 or 2. Below, we consider a dimer of identical spherical particles of radius a, made of a material with a permittivity and permeability ε and μ, respectively. The dimer resides in a medium with unity values of permittivity and permeability. The case of a dimer of different spherical particles can be considered similarly.

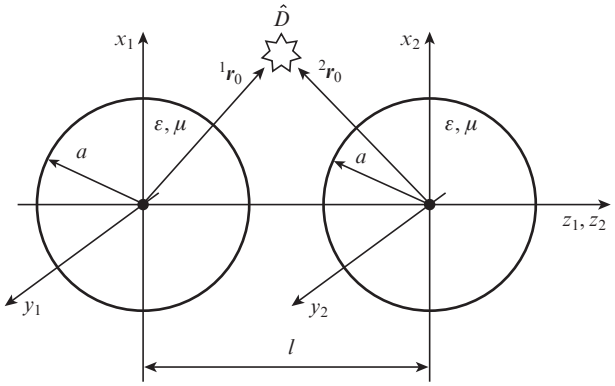

Figure 1. Geometry of the problem on an electric quadrupole source (atom) located near a dimer of identical spherical particles.

To solve the problem on emission of an electric quadrupole source near a dimer, it is necessary to write general expressions for the fields outside the particles with allowance for the quadrupole and general expressions for the fields inside the particles. Then, using boundary conditions on the surface of the particles, it is needed to find the unknown coefficients of expansions.

Using the representation of the field of a quadrupole source in spherical coordinates [9], for the intensities of the electric and magnetic fields of the source in local spherical coordinates associated with the sth particle, we write the expressions [the factor $\exp(-i\omega t)$, characterising the time dependence of the fields, is hereinafter omitted]:

$$ {}^s\boldsymbol{E}_0 = \begin{cases} \sum\limits_{n=1}^{\infty}\sum\limits_{m=-n}^{n}[\,{}^sA_{mn}^{(0)}\,{}^s\boldsymbol{N}\boldsymbol{\psi}_{mn} + {}^sB_{mn}^{(0)}\,{}^s\boldsymbol{M}\boldsymbol{\psi}_{mn}], & |\,{}^s\boldsymbol{r}\,| < |\,{}^s\boldsymbol{r}_0\,|, \\ \sum\limits_{n=1}^{\infty}\sum\limits_{m=-n}^{n}[\,{}^sC_{mn}^{(0)}\,{}^s\boldsymbol{N}\boldsymbol{\zeta}_{mn} + {}^sD_{mn}^{(0)}\,{}^s\boldsymbol{M}\boldsymbol{\zeta}_{mn}], & |\,{}^s\boldsymbol{r}\,| > |\,{}^s\boldsymbol{r}_0\,|, \end{cases} \quad (1) $$

$$ {}^s\boldsymbol{H}_0 = -\frac{\mathrm{i}}{k_0}\mathrm{rot}\,{}^s\boldsymbol{E}_0, $$

where ${}^s\boldsymbol{N}\boldsymbol{\psi}_{mn}$, ${}^s\boldsymbol{M}\boldsymbol{\psi}_{mn}$, ${}^s\boldsymbol{N}\boldsymbol{\zeta}_{mn}$, ${}^s\boldsymbol{M}\boldsymbol{\zeta}_{mn}$ and ${}^sA_{mn}^{(0)}$, ${}^sB_{mn}^{(0)}$, ${}^sC_{mn}^{(0)}$, ${}^sD_{mn}^{(0)}$ are the vector spherical harmonics and expansion coefficients [9], respectively, written in the sth local coordinate system; ${}^s\boldsymbol{r}$ and ${}^s\boldsymbol{r}_0$ are the radius vectors of the observation points and locations of the quadrupole, respectively; $k_0 = \omega/c$ is the wave number; ω is the frequency; and c is the speed of light (in vacuum). Expressions for the coefficients for (1) can be written as follows [9]:

$$ \begin{Bmatrix} {}^sA_{mn}^{(0)} \\ {}^sC_{mn}^{(0)} \end{Bmatrix} = \mathrm{i}k_0^2\frac{2n+1}{6n(n+1)} \times \sum_{\alpha,\beta=x,y,z} D_{\alpha\beta}(3\nabla'_\alpha - {}^s\hat{K}'_\alpha)\,\nabla'_\beta \begin{Bmatrix} b_{mn}^{<}({}^sr', {}^s\theta', {}^s\varphi') \\ b_{mn}^{>}({}^sr', {}^s\theta', {}^s\varphi') \end{Bmatrix}\Big|_{{}^s\boldsymbol{r}' = {}^s\boldsymbol{r}_0}, $$

$$ \begin{Bmatrix} {}^sB_{mn}^{(0)} \\ {}^sD_{mn}^{(0)} \end{Bmatrix} = k_0^3\frac{2n+1}{6n(n+1)} \times \sum_{\alpha,\beta=x,y,z} D_{\alpha\beta}\,{}^s\hat{L}'_\alpha\,\nabla'_\beta \begin{Bmatrix} b_{mn}^{<}({}^sr', {}^s\theta', {}^s\varphi') \\ b_{mn}^{>}({}^sr', {}^s\theta', {}^s\varphi') \end{Bmatrix}\Big|_{{}^s\boldsymbol{r}' = {}^s\boldsymbol{r}_0}, \quad (2) $$

where

$$ \begin{Bmatrix} b_{mn}^{<}({}^sr', {}^s\theta', {}^s\varphi') \\ b_{mn}^{>}({}^sr', {}^s\theta', {}^s\varphi') \end{Bmatrix} = \frac{(n-m)!}{(n+m)!}\frac{1}{k_0\,{}^sr'} \times \begin{Bmatrix} \zeta_n(k_0\,{}^sr') \\ \psi_n(k_0\,{}^sr') \end{Bmatrix} P_n^m(\cos{}^s\theta')\exp(-\mathrm{i}m\,{}^s\varphi'); \quad (3) $$

$D_{\alpha\beta}$ are the components of the matrix element of the quadrupole moment in the E2 transition; ∇'_α is the Cartesian component of the gradient operator ∇' over the coordinates of the point defined by the radius vector ${}^s\boldsymbol{r}'$; ${}^s\hat{L}'_\alpha$ and ${}^s\hat{K}'_\alpha$ are the Cartesian components of the operator ${}^s\hat{L}' = -\mathrm{i}({}^s\boldsymbol{r}' \times \nabla')$ and ${}^s\hat{K}' = -\mathrm{i}({}^s\hat{L}' \times \nabla')$, respectively; $0 \leqslant {}^sr' < \infty$, $0 \leqslant {}^s\theta' \leqslant \pi$ and $0 \leqslant {}^s\varphi' < 2\pi$ are the spherical coordinates of the point defined by the radius vector ${}^s\boldsymbol{r}'$; $P_n^m(x)$ is the associated Legendre function [38]; and $\psi_n(x)$ and $\zeta_n(x)$ are the Riccati–Bessel functions [38] related to the Bessel and Hankel functions by the expressions $\psi_n(x) = (\pi x/2)^{1/2}J_{n+1/2}(x)$ and $\zeta_n(x) = (\pi x/2)^{1/2}H_{n+1/2}^{(1)}(x)$. Note that in writing (2), as well as hereinafter we take into account the fact that the components of the electric quadrupole moment tensor and the components of the gradient operator do not change in the transition from one local Cartesian coordinate system to the other, because the axes of the considered local systems are parallel and equally directed (Fig. 1). Details of deriving expression (2) are given in [9].

The electric and magnetic field strengths induced outside of a dimer, i.e. strengths of the reflected fields, can be represented as the sum of the partial field strengths reflected from each of the particles, and written in the local coordinates [39]:

$$ \boldsymbol{E}_1 = \sum_{s=1}^{2}{}^s\boldsymbol{E}_1, \qquad \boldsymbol{H}_1 = \sum_{s=1}^{2}{}^s\boldsymbol{H}_1, \quad (4) $$

where

$$ {}^s\boldsymbol{E}_1 = \sum_{n=1}^{\infty}\sum_{m=-n}^{n}[\,{}^sC_{mn}^{(1)}\,{}^s\boldsymbol{N}\boldsymbol{\zeta}_{mn} + {}^sD_{mn}^{(1)}\,{}^s\boldsymbol{M}\boldsymbol{\zeta}_{mn}]; $$

$$ {}^s\boldsymbol{H}_1 = -\frac{\mathrm{i}}{k_0}\mathrm{rot}\,{}^s\boldsymbol{E}_1; \quad (5) $$

and the coefficients ${}^sC_{mn}^{(1)}$ and ${}^sD_{mn}^{(1)}$ are found with the help of boundary conditions. The strengths of the total field outside

of the particles are thus determined by the sum of expressions (1) and (4).

Expressions for the electric and magnetic field strengths induced inside the sth particle of the dimer, i.e. for the strengths of the transmitted fields, can be written in the form

$$
\begin{aligned}
{}^{s}\boldsymbol{E}_2 &= \sum_{n=1}^{\infty}\sum_{m=-n}^{n}[{}^{s}A_{mn}^{(2)}\,{}^{s}\boldsymbol{N}\boldsymbol{\psi}_{mn}^{\mathrm{p}} + {}^{s}B_{mn}^{(2)}\,{}^{s}\boldsymbol{M}\boldsymbol{\psi}_{mn}^{\mathrm{p}}],\\
{}^{s}\boldsymbol{H}_2 &= -\frac{\mathrm{i}}{kZ}\mathrm{rot}\,{}^{s}\boldsymbol{E}_2,
\end{aligned}
\tag{6}
$$

where $k = k_0\sqrt{\varepsilon\mu}$; $Z = \sqrt{\mu/\varepsilon}$ is the impedance; ${}^{s}\boldsymbol{M}\boldsymbol{\psi}_{mn}^{\mathrm{p}}$ and ${}^{s}\boldsymbol{N}\boldsymbol{\psi}_{mn}^{\mathrm{p}}$ are the vector spherical harmonics [9] written in the sth local coordinate system; and ${}^{s}A_{mn}^{(2)}$ and ${}^{s}B_{mn}^{(2)}$ can be found using the boundary conditions.

In order to determine the unknown coefficients in expansions (5) and (6), it is necessary to use the boundary conditions of continuity of the tangential components of the electric and magnetic field strengths on the surface of a sphere [40]. In this case, one should employ the addition theorem of the vector spherical harmonics (see., e.g., [41]), which allows the vector harmonics describing the field outside of a dimer and written in some local coordinates (for example, for $s = 2$) to be represented in the form of expansions in harmonics written in other local coordinates ($s = 1$). Substituting the data of the expansion in (5), we obtain expressions for the strengths ${}^{2}\boldsymbol{E}_1$ and ${}^{2}\boldsymbol{H}_1$ ($s = 2$) in the form of series over the vector spherical harmonics in the coordinates of the first sphere ($s = 1$). The thus found expressions are added to the expressions for the strengths ${}^{1}\boldsymbol{E}_1$ and ${}^{1}\boldsymbol{H}_1$ ($s = 1$) [see (4)] and can already be used to match the fields on the surface of the first particle. Similar actions are performed by using the boundary conditions on the surface of the second particle.

Since the atom in question resides outside of the spherical particles, we will not need explicit expressions for the coefficients entering into the equations for the fields inside the sphere to find the radiation linewidth, which is expressed in terms of the energy flux at infinity. For the coefficients ${}^{s}C_{mn}^{(1)}$ and ${}^{s}D_{mn}^{(1)}$, which describe the reflected field, we can obtain the equations:

$$
\begin{aligned}
&{}^{1}C_{mn}^{(1)} + \alpha_n\sum_{q=|m|}^{\infty}V_{mnq}\,{}^{2}C_{mq}^{(1)} + \alpha_n\sum_{q=|m|}^{\infty}W_{mnq}\,{}^{2}D_{mq}^{(1)} = -\alpha_n\,{}^{1}A_{mn}^{(0)},\\
&{}^{1}D_{mn}^{(1)} + \beta_n\sum_{q=|m|}^{\infty}V_{mnq}\,{}^{2}D_{mq}^{(1)} + \beta_n\sum_{q=|m|}^{\infty}W_{mnq}\,{}^{2}C_{mq}^{(1)} = -\beta_n\,{}^{1}B_{mn}^{(0)},\\
&{}^{2}C_{mn}^{(1)} + \alpha_n\sum_{q=|m|}^{\infty}(-1)^{q+n}V_{mnq}\,{}^{1}C_{mq}^{(1)}\\
&\quad - \alpha_n\sum_{q=|m|}^{\infty}(-1)^{q+n}W_{mnq}\,{}^{1}D_{mq}^{(1)} = -\alpha_n\,{}^{2}A_{mn}^{(0)},\\
&{}^{2}D_{mn}^{(1)} + \beta_n\sum_{q=|m|}^{\infty}(-1)^{q+n}V_{mnq}\,{}^{1}D_{mq}^{(1)}\\
&\quad - \beta_n\sum_{q=|m|}^{\infty}(-1)^{q+n}W_{mnq}\,{}^{1}C_{mq}^{(1)} = -\beta_n\,{}^{2}B_{mn}^{(0)},
\end{aligned}
\tag{7}
$$

where the lower limit of the summation over q should be assumed equal to 1 if $m = 0$, and equal to $|m|$ if $m \neq 0$; functions V_{mnq} and W_{mnq} are given in [41]; the scattering coefficients α_n и β_n have the form

$$
\begin{aligned}
\alpha_n &= \frac{\psi_n(ka)\psi_n'(k_0a) - Z\psi_n'(ka)\psi_n(k_0a)}{\psi_n(ka)\zeta_n'(k_0a) - Z\psi_n'(ka)\zeta_n(k_0a)};\\
\beta_n &= \frac{Z\psi_n(ka)\psi_n'(k_0a) - \psi_n'(ka)\psi_n(k_0a)}{Z\psi_n(ka)\zeta_n'(k_0a) - \psi_n'(ka)\zeta_n(k_0a)};
\end{aligned}
\tag{8}
$$

and the prime in the function denotes its derivative. If the particles of the dimer are located at a large distance from one another, we can be put $V_{mnq} \approx 0$ and $W_{mnq} \approx 0$ in (7) [41], which leads to the relations

$${}^{s}C_{mn}^{(1)} = -\alpha_n\,{}^{s}A_{mn}^{(0)}, \qquad {}^{s}D_{mn}^{(1)} = -\beta_n\,{}^{s}B_{mn}^{(0)}, \tag{9}$$

which express the solution for the field scattered by the sth spherical particle [9] and written in the sth local coordinate system. This confirms the correctness of equations (7).

As is clear from (7), the structure of the resulting equations is such that the subscript n in them is changed, while the subscript m can be fixed. To solve numerically expression (7), we use truncated equations with $n \leqslant n_{\max}$. The greater the $n_{\max}$, the more accurate the results for the coefficients ${}^{s}C_{mn}^{(1)}$ and ${}^{s}D_{mn}^{(1)}$, which is due to their tendency to zero at $n \to \infty$ [42]. We should also take into account the mutual configuration of spherical particles: the closer they are to each other, the greater $n_{\max}$ is required to achieve a given accuracy [42].

3. Linewidth of E2 transitions in the atom located near a dimer of spherical particles

The relative radiation linewidth of forbidden E2 transitions in the atom located near a dimer of spherical particles can be calculated in the framework of classical electrodynamics as the ratio of the total radiation power P_{r} of the system consisting of a quadrupole source and a dimer to the radiation power P_0 of a source in the absence of a dimer. The power P_0 is found from the known expression [43]:

$$P_0 = \frac{ck_0^6}{360}\sum_{\alpha,\beta=x,y,z}|D_{\alpha\beta}|^2. \tag{10}$$

To find P_{r}, we will use the formula [40]

$$P_{\mathrm{r}} = \frac{c}{8\pi}\int_S \mathrm{d}S\,\mathrm{Re}\{[(\boldsymbol{E}_0 + \boldsymbol{E}_1),(\boldsymbol{H}_0^* + \boldsymbol{H}_1^*)]\boldsymbol{n}\}, \tag{11}$$

where the integration is performed over a closed surface S, covering the atom and the dimer; $\boldsymbol{n}$ is the external normal to this surface; and the asterisk in (110 denotes complex conjugation. As the surface S it is convenient to take a sphere of infinite radius with a centre at any of the local coordinate systems. For example, performing calculations in the local coordinates of the first particle ($s = 1$) and normalising to the radiation power in free space, we find the expression:

$$
\begin{aligned}
\frac{\gamma_{\mathrm{r}}}{\gamma_0} = \frac{P_{\mathrm{r}}}{P_0} &= \frac{c}{2k_0^2P_0}\sum_{n=1}^{\infty}\sum_{m=-n}^{n}\frac{n(n+1)}{2n+1}\frac{(n+m)!}{(n-m)!}\\
&\times\left[\left|{}^{1}C_{mn}^{(0)} + {}^{1}\tilde{C}_{mn}^{(1)}\right|^2 + \left|{}^{1}D_{mn}^{(0)} + {}^{1}\tilde{D}_{mn}^{(1)}\right|^2\right],
\end{aligned}
\tag{12}
$$

for the relative linewidth $\gamma_{\mathrm{r}}/\gamma_0$ of the E2 transition in the atom, where $\gamma_0 = 4P_0/(\hbar\omega)$ is the linewidth of the E2 transition in the atom in the absence of a dimer [7];

$$
\begin{aligned}
{}^1\tilde{C}^{(1)}_{mn} &= {}^1C^{(1)}_{mn} + \sum_{q=|m|}^{\infty}[\tilde{V}_{mnq}\,{}^2C^{(1)}_{mq} + \tilde{W}_{mnq}\,{}^2D^{(1)}_{mq}];\\
{}^1\tilde{D}^{(1)}_{mn} &= {}^1D^{(1)}_{mn} + \sum_{q=|m|}^{\infty}[\tilde{V}_{mnq}\,{}^2D^{(1)}_{mq} + \tilde{W}_{mnq}\,{}^2C^{(1)}_{mq}];
\end{aligned}
\qquad (13)
$$

the lower limit of the summation over q should be assumed equal to 1 if $m = 0$, and equal to $|m|$ if $m \neq 0$; and functions $\tilde{V}_{mnq}$ and $\tilde{W}_{mnq}$ are given in [40].

It should be noted that expression (12) corresponds to the case of a two-level atom. In this case, $D_{\alpha\beta} = (D_{\alpha\beta})_{\rm fi}$ should be considered as an electric quadrupole moment of the i → f transition with frequency $\omega_{\rm fi} \approx \omega$ [7]. To take into account the possibility of transition into several states, it is necessary to sum the corresponding partial linewidths over the final states.

It should also be noted that the use of the classical and quantum theories to calculate the rates of the spontaneous decay of the electric quadrupole source near a material body leads, strictly speaking, to different results. Klimov and Ducloy [7] have shown the equivalence of the classical and quantum approaches only in the description of the total rate of the spontaneous decay of the quadrupole near the material body in the case of weak interaction, when the spontaneous decay can be described by the decay rate and a single transition frequency. If the interaction between the atom and the body is strong, there arise complex effects, for the description of which it is needed to make use of quantum electrodynamics [44, 45]. In addition, there is no exact equivalence of the quantum and classical approaches in calculating the radiative rate of the spontaneous decay of an atom near an absorbing body. The situation is further complicated by the fact that in the framework of the quantum theory one should use a nonstandard quantization scheme [46–49].

In this paper we consider only the radiative rate of the spontaneous decay (i.e. the radiation linewidth), because this value is measured in the experiments. The nonradiative channel of the spontaneous decay, i.e. the channel associated with the Joule loss in the material of the spheres, will be discussed in a separate publication.

4. Analysis of the results and graphic illustrations

The linewidth of the E2 transition in the atom near a dimer of spherical particles depends on many parameters and its overall description is very complex. Below, we will present, for clarity, a graphic illustration of some specific regimes of interaction of the atom with dimers of different composition. In the present paper we restrict ourselves to only the most interesting case of the atom in the gap between the particles on a common z axis passing through the centres of the particles (Fig. 1), because in this case, the local fields are maximal. In this geometry, the expression for the coefficients ${}^sA^{(0)}_{mn}$, ${}^sB^{(0)}_{mn}$, ${}^sC^{(0)}_{mn}$ and ${}^sD^{(0)}_{mn}$ are greatly simplified [9], and so different from zero are only the coefficients ${}^sC^{(1)}_{mn}$ and ${}^sD^{(1)}_{mn}$ with $m = 0, \pm1, \pm2$.

Next, let us consider some special cases of the atom with a given quadrupole moment. It should be noted that in the experiment it is difficult to contemplate a situation with a strictly predetermined orientation of the quadrupole moment. However, consideration of the atoms with the average orientation of the quadrupole moment leads to a drastic weakening of all the effects. Therefore, below we consider atoms with a fixed orientation of the moments. Here we confine ourselves to the cases of the atom with a radially oriented quadrupole moment with $D_{xx} = D_{yy}$ and $D_{xy} = D_{xz} = D_{yz} = 0$, located on the z axis [4], as well as the atom with a tangentially oriented quadrupole moment with $D_{xx} = D_{zz}$ (or $D_{yy} = D_{zz}$) and $D_{xy} = D_{xz} = D_{yz} = 0$ [4]. Other cases with different values of the quadrupole moments, including averaged ones, can be considered using the general expressions found in this work.

Figure 2 shows the relative linewidth of the forbidden E2 transition in the atom located in the gap of the dimer of the dielectric spheres near the surface of the first sphere and near the surface of a dielectric sphere as a function of k_0a.

One can see from Fig. 2 that at $k_0a \to 0$ the linewidth of the E2 transition in the atom increases. The asymptotic expression for the linewidth in the case of an atom located on the surface of a dielectric nanosphere ($k_0a \ll 1$) can be found and has, for radially (rad) and tangentially (tan) oriented quadrupole moments of the atom, the form [4]:

$$
\left(\frac{\gamma_{\rm r}}{\gamma_0}\right)_{\rm rad} \approx \frac{180}{(k_0a)^2}\left(\frac{\varepsilon-1}{\varepsilon+2}\right)^2, \quad \left(\frac{\gamma_{\rm r}}{\gamma_0}\right)_{\rm tan} \approx \frac{45}{(k_0a)^2}\left(\frac{\varepsilon-1}{\varepsilon+2}\right)^2. \qquad (14)
$$

As follows from (14), at $k_0a \to 0$ the linewidths for atoms with radially and tangentially oriented quadrupole moments increase indefinitely. The asymptotic expressions for atoms

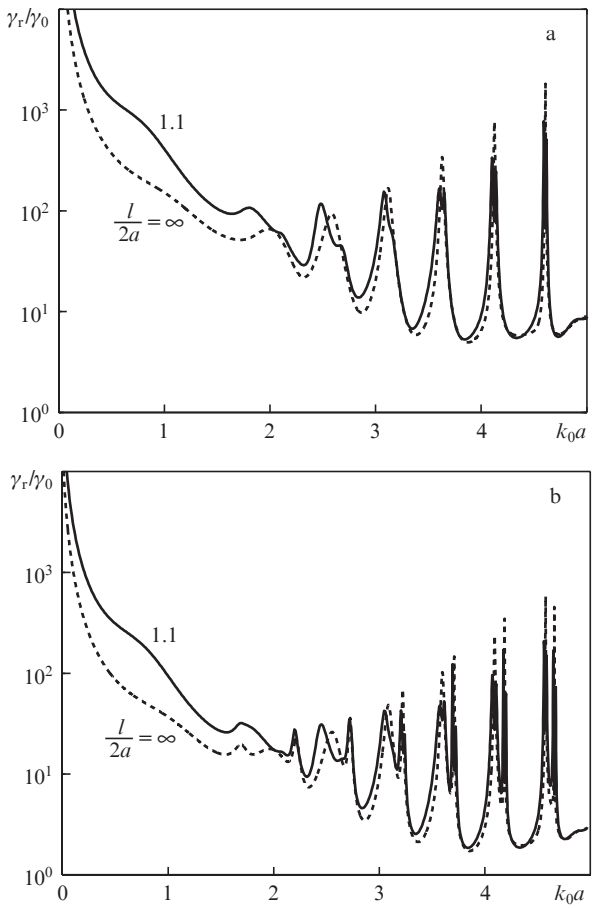

Figure 2. Relative radiation linewidth of the forbidden E2 transition in an atom having (a) radial and (b) tangential orientations of the electric quadrupole moment and located near the first sphere of the dimer (${}^1r_0 = a$ and ${}^2r_0 = l - a$) on the z axis as a function of k_0a for a given $l/(2a)$. Permittivity and permeability of the dimer particles are $\varepsilon = 6$ and $\mu = 1$. The case of a single sphere corresponds to $l/(2a) = \infty$.

with other orientations of the quadrupole moment are given in [9]. One can see from Fig. 2 that when the spheres of the dimer are closely located, relationship (14) is changed: at $k_0a \to 0$ the rate of an increase in γ_r/γ_0 in the case of an atom in the gap between two nanospheres increases as compared with the case of an atom near a nanosphere.

With increasing k_0a, the dependence of the relative linewidth of the forbidden E2 transition in the atom located in the gap of the dimer of dielectric spheres becomes more complex. One can see from Fig. 2 that there appears an oscillatory dependence of the linewidth on k_0a at a large number of peaks corresponding to one or another of the whispering gallery modes, which are excited by the atom in the dimer. In this case, the proximity of the second sphere leads to a shift and splitting of the peaks, corresponding to one particle, due to an excitation of a large number of modes in the dimer.

It follows from Fig. 2 that a significant difference in the linewidths of forbidden E2 transitions in the atom near one sphere and in the gap of a dimer of two spheres is observed in the case of nanospheres ($k_0a \ll 1$). This difference is even more enhanced for metal nanospheres ($\varepsilon < 0, \mu > 0$), because in the gap between closely located metal nanoparticles the local field increases.

Figure 3 shows the relative linewidth of the forbidden E2 transition in the atom with a radially oriented electric quadrupole moment, which is located in the gap of a dimer of two metal nanospheres and near the surface of a metal nanosphere, as a function of the permittivity.

One can see from Fig. 3a that the linewidths for a nanodimer and a nanosphere are different. The relative radiation linewidth of the E2 transition in the atom located in the gap between the nanospheres can take substantially higher values than in the atom near a nanosphere. In the case of the dimer, the dependence of the relative linewidth on the permittivity has many peaks due to a large number of plasmon modes excited in a nanodimer than those excited in a nanoparticle. With decreasing distance between the nanospheres the number of excited modes increases. For an atom with a radially oriented quadrupole moment, which is located in the gap of a dimer near the surface of one of the nanospheres (Fig. 3a), L- and M-modes are excited [50, 51], and for the atom located in the centre of the gap (Fig. 3b), T- and M-modes are excited [50, 51].

Note that the surface charge in the case of L- and M-modes is concentrated near the gap between the nanoparticles [50, 52], and so these modes are effectively excited by a local source (atom). It follows from Fig. 3a that with the approach of the nanospheres, the relative linewidth of the E2 transition in the atom for the L- and M-modes increases. With the separation of the nanospheres, M-modes disappear faster than L-modes, because they occur only at $l/(2a) < 1.2$ [50, 51]. Note that in their properties M-modes are 'dark' modes.

The third type of modes in a dimer is T-modes. They have a charge distribution mainly outside of the gap between the nanoparticles [50, 52] and are therefore most effectively excited by a plane electromagnetic wave. One can see from Fig. 3b that with the approach of the nanospheres, the relative linewidth for the T-mode decreases.

Therefore, the electric quadrupole source can excite all types of plasmon modes arising in a dimer of metal nanoparticles. A large number of plasmon modes allow one to control the spontaneous decay of an atom located in the gap of a dimer if we change the distance between the nanoparticles.

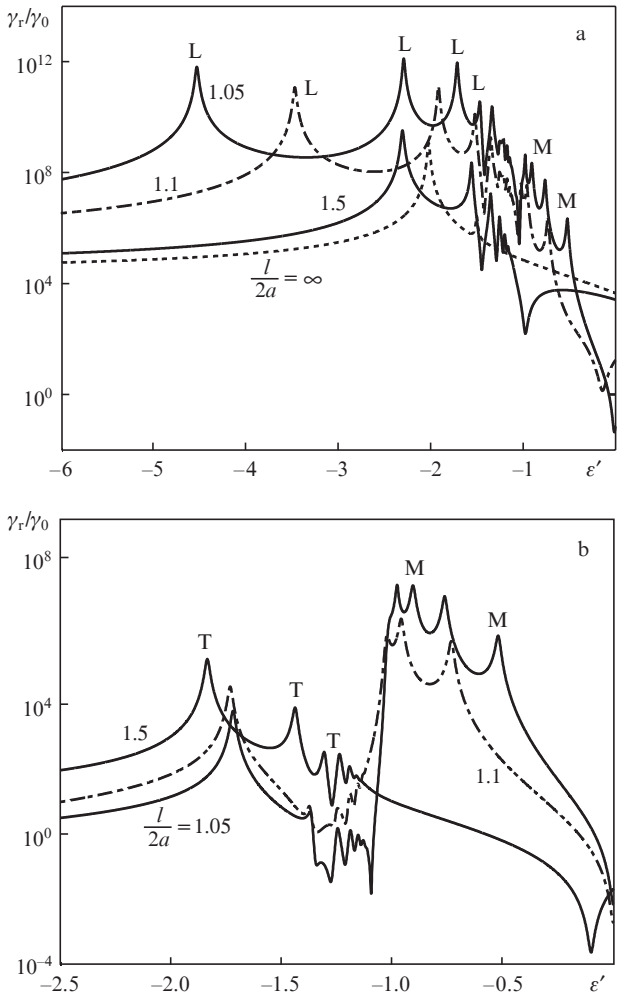

Figure 3. Relative radiation linewidth of the forbidden E2 transition in an atom having a radially oriented electric quadrupole moment and located on the z axis (a) in a gap of the dimer near the first nanosphere (${}^1r_0 = a$ and ${}^2r_0 = l - a$) and (b) in the centre of the gap between the nanospheres (${}^1r_0 = {}^2r_0 = l/2$) as a function of the real part of the permittivity of the nanospheres $\varepsilon = \varepsilon' + i0.01$ for $\mu = 1$, $k_0a = 0.1$ and a given $l/(2a)$. The case of a single nanosphere with an atom located near the surface corresponds to $l/(2a) = \infty$. The letters L, T and M denote the peaks corresponding to the excitation of L-, T- and M-modes in the dimer of the nanospheres [50, 51].

5. Conclusions

Thus, within the framework of classical electrodynamics we have obtained and studied analytical expressions for the radiation linewidth of the forbidden E2 transitions in the atom, which is located near a dimer of identical spherical particles of arbitrary material, size and mutual position. We have studied the features of the emission of atoms with different values of the quadrupole moment for the dielectric and metal dimer.

It is shown that in case of an atom in the gap of a dimer of spherical metal nanoparticles, the radiation linewidth of the forbidden E2 transitions can take values that are substantially greater than in the case of a quadrupole source near a single metal nanoparticle. We have also shown that such an atom can excite all types of plasmon modes that exist in the dimer of metal nanoparticles.

The results obtained can be used to calculate the linewidth of the forbidden E2 transitions in atoms located near a dimer of spherical particles and to interpret the experimental data on the interaction of nanoparticles with atoms and molecules, including the design of nanolasers and spasers.

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