RADIATIVE DECAY ENGINEERING BY TRIAXIAL NANOELLIPSOIDS

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Abstract

Radiative decay rates of an atom placed near triaxial nanoellipsoid are investigated in long wavelength approximation. Analytical results are obtained in general case. It is shown that triaxial ellipsoid can be used for efficient control of decay rate of an atom, molecule or quantum dot. For example decay rate near silver ellipsoid can be enhanced by 5 orders of magnitude. It is also shown, that triaxial nanoellipsoid can be used for simultaneous efficient control of absorption and emission rates of fluorophores.
Because of development of nanotechnology, investigation of interaction of single atoms, molecules and quantum dots with optical fields in presence of nanobody becomes more and more topical. Special attention must be given here on spontaneous decay of atoms placed near nanobodies. Spontaneous emission is, above all, a source of light and its efficient control allows increase efficacy of light sources [1]. Spontaneous emission of single molecule can be used as a source of nanolocalized light [2], with help of such kind of sources, it is possible to examine nanometer-sized objects. On the other hand, decay rate is directly measured magnitude at fluorescent detection and identification of single molecules by scanning microscopes [3]. Influence of nanoparticles on fluorescence of single molecule can be used for detection and identification of small amount of molecules and for sequencing of DNA structure, without using additional fluorescent markers [4]. It is highly important to say, that if it is be possible to match fluorescent properties of nanoparticle with properties of detected molecule, then it will be possible to provide high selectivity of detection. On the other hand, nanotechnologies allow creating complex nanosystems, consisted of radiating nanoparticle (finite nanocylinder of semiconductor) and of nanoresonator (gold nanosphere) [5]. Besides this, the system of nanobody + nanoradiator (QD) can be used as amplifier of surface plasmons by stimulated emission of radiation (SPASER) [6]. And of course, it is obvious, that radiative decay rate is an important parameter, which influence on atoms' motion in optical fields of nanometer scale [7]. In all these cases, the main task is correct description of process of spontaneous decays near the nanoparticles of different shapes.

The aim of this work is an investigation of processes of spontaneous decay of excited atom (molecule or quantum dot) in the presence of ellipsoid-shaped nanobody with arbitrary ratio of principal semiaxes. The geometry of the considered system is presented on Fig. 1. Such general shape of the nanobody has not only academic interest, but also a practical one, because of possibility of control three dimensional parameters (or two dimensionless ones) allows describe nanoparticles of different shapes (nanospheres, nanoneedles, nanodisks, nanowires, and others) and it leads to wide possibilities in controlling of spontaneous emission decay rates of an atom, placed near of such nanobody, and in construction on this base of efficient nanosensors. Besides this, optical properties of nanoellipsoid and related local fields will suffer substantial change at different variations of nanoellipsoid’s shape.

In case of nanoparticles, relative radiative decay rate of an atom is defined by its dipole
momentum only (see, for example, \[8\])

\[
\left( \frac{\gamma}{\gamma_0} \right)^{\text{radiative}} = \frac{|d_{total}|^2}{|d_0|^2},
\]

(1)

where \(d_{total}\) is total dipole momentum of the atom + nanobody system; \(d_0\) is dipole momentum of an atom’s transition. Therefore, in this case, our task is to find total dipole momentum of the considered system in quasistatic approach.

To find the total dipole momentum, we need to solve a quasistatic problem with dipole source

\[
\text{rot}\mathbf{E} = 0, \quad \text{div}\mathbf{D} = 4\pi \rho,
\]

(2)

where density of the charge is defined by the standard expression:

\[
\rho = e^{-i\omega t} (d_0 \cdot \nabla') \delta^{(3)} (r - r').
\]

(3)

Here \(\delta^{(3)}\) is the spatial Dirac’s delta-function; \(r'\) is vector of coordinate of the atom; \(\nabla'\) means gradient over the atom’s coordinates. Hereafter we will omit the time dependence of the field. It is convenient to rewrite system (2) in the form of integral equation:

\[
\mathbf{E}(r) = \mathbf{E}_0(r) - \frac{1}{4\pi} \int_V d'r' (\mathbf{E}(r') \cdot \nabla') \frac{1}{|r - r'|}.
\]

(4)

Here \(\mathbf{E}_0(r)\) is dipole field in the absence of nanobody; and integration is taking over the nanobody’s (the ellipsoid) volume \(V\). Permittivity of the ellipsoid is denoted by \(\epsilon\); and permittivity of the surrounding medium we put equal to unit.

As it is known, induced dipole momentum of a body is defined by following formula

\[
\delta\mathbf{d} = \frac{\epsilon - 1}{4\pi} \int_V d\mathbf{r}\mathbf{E}(r),
\]

(5)

and we need only to calculate integral over the nanobody’s volume. To calculate it, we can use expression (4), and to write

\[
\int_V d\mathbf{r}\mathbf{E}(r) = \int_V d\mathbf{r}\mathbf{E}_0(r) - \frac{1}{4\pi} \int_V d'r' (\mathbf{E}(r') \cdot \nabla') \nabla' \int_V d'r \frac{1}{|r - r'|}.
\]

(6)
Some amazing property of ellipsoid is that the last integral in (6) depends on position of point \( r' \) inside the ellipsoid in quadratic manner, and in that way we will come to algebraic system of equation for induced dipole momentum

\[
\delta \mathbf{d} + \frac{\epsilon - 1}{4\pi} (\delta \mathbf{d} \cdot \nabla') \nabla' \int_V \frac{d\mathbf{r}}{|\mathbf{r} - \mathbf{r}'|} = \frac{\epsilon - 1}{4\pi} \int_V d\mathbf{r} \mathbf{E}_0(\mathbf{r}),
\]

which has the next solution

\[
\delta \mathbf{d} = \tilde{\alpha} \cdot \frac{1}{V} \int_V d\mathbf{r} \mathbf{E}_0(\mathbf{r}),
\]

where \( V = \frac{4}{3} \pi abc \) is ellipsoid’s volume; and \( \tilde{\alpha} \) is the tensor of ellipsoid’s polarizability

\[
\tilde{\alpha} = \frac{\epsilon - 1}{4\pi} V \left( I + \frac{\epsilon - 1}{4\pi} \nabla' \nabla' \int_V \frac{d\mathbf{r}}{|\mathbf{r} - \mathbf{r}'|} \right)^{-1}.
\]

If the coordinate axes coincide with the principal axes, the polarizability has well known form

\[
\tilde{\alpha} = \begin{pmatrix}
\alpha_{xx} & 0 & 0 \\
0 & \alpha_{yy} & 0 \\
0 & 0 & \alpha_{zz}
\end{pmatrix},
\]

where

\[
\alpha_{xx} = \frac{1}{4\pi} \left( 1 - \epsilon_{xx} \right) \left( \frac{\epsilon - 1}{\epsilon - \epsilon_{xx}} \right), \quad \epsilon_{xx} = 1 - \left( \frac{1}{2} abc I_a \right)^{-1}, \quad I_a = \int_0^\infty \frac{du}{(a^2 + u) R(u)}, \quad R(u) = \left[ (a^2 + u) (b^2 + u) (c^2 + u) \right]^{1/2}.
\]

Other components of tensor can be obtained by cyclic permutation of all parameters and indexes.

One should note, that expressions can be expressed through complete and incomplete elliptical integrals in general case. It can be expressed through Legendre’s functions of first and second type or through elementary functions in case of degeneration of triaxial ellipsoid into spheroid or sphere \[10\]-\[11\].
In this way, presented above expression for the induced dipole momentum in an arbitrary external field can be expressed by the next formula

$$\delta \mathbf{d} = \hat{\alpha} \cdot \langle \mathbf{E}_0 \rangle,$$  \hspace{1cm} (13)

where $\langle \mathbf{E}_0 \rangle$ is the field of external source averaged over ellipsoid’s volume. This expression is a key mark one, because of possibility of solving of the considered problem just by averaging over the nanobody’s volume. Expression (13) can be also used as an estimate one for dipole momentum of nanoparticle of other geometry (like nanocube, finite nanocylinder, and others). Of course, we can use it in that case only, when polarizability of nanoparticle is known.

In our case, external field is the electric field from dipole situated at point $r'$

$$\mathbf{E}_0 (r) = \nabla (\mathbf{d}_0 \cdot \nabla) \frac{1}{|r - r'|}.$$  \hspace{1cm} (14)

An average over the ellipsoid’s volume given by (14) can be expressed through one-dimensional integrals [12]. As a result we have

$$\langle \mathbf{E}_0 \rangle = \nabla (\mathbf{d}_0 \cdot \nabla) J,$$  \hspace{1cm} (15)

where

$$J = \frac{3}{4} \left\{ I (\zeta) - x^2 I_a (\zeta) - y^2 I_b (\zeta) - z^2 I_c (\zeta) \right\},$$  \hspace{1cm} (16)

$$I (\zeta) = \int_\zeta^\infty \frac{du}{R (u)}, \hspace{1cm} I_a (\zeta) = \int_\zeta^\infty \frac{du}{(a^2 + u) R (u)},$$

$$I_b (\zeta) = \int_\zeta^\infty \frac{du}{(b^2 + u) R (u)}, \hspace{1cm} I_c (\zeta) = \int_\zeta^\infty \frac{du}{(c^2 + u) R (u)},$$  \hspace{1cm} (17)

and where function $R (u)$ is defined by formula (12). Hereafter we will omit primes subscript in atom’s coordinates.

In case of atom, located outside the ellipsoid, the point $\zeta$ is a positive root of the cubic equation: $\frac{x^2}{a^2 + \zeta} + \frac{y^2}{b^2 + \zeta} + \frac{z^2}{c^2 + \zeta} = 1$; and it follows in this case, that $\zeta$ is the function of coordinates of atom’s position. In the case, when atom is situated inside the ellipsoid, we
must put $\zeta = 0$ and it means that spontaneous emission decay rate does not depend on atom’s position.

Thus, spontaneous emission decay rate of an single atom located near triaxial nanoellipsoid, and when atom has arbitrary oriented dipole momentum, has the following form

$$
\left( \frac{\gamma}{\gamma_0} \right)^{\text{radiative}} = \frac{|\mathbf{d}_{\text{total}}|^2}{|\mathbf{d}_0|^2}, \quad \delta \mathbf{d} = \hat{\alpha} \cdot \nabla (\mathbf{d}_0 \cdot \nabla) J, \quad (18)
$$

where $J$ is defined by formula (16).

Expression (18) is a fundamental result, and we can use it to obtain well known expressions for spontaneous emission decay rate of an atom placed near nanospheroid [10]-[11] and near nanocylinder [8].

In some particular cases, expression for relative decay rate (18) can be substantially simplified. For example, when atomic dipole is situated on $z$-axis of the Cartesian system at point $z$ and it oriented along $x$-axis we have

$$
\left( \frac{\gamma}{\gamma_0} \right)^{\text{radiative}} = \left| 1 - \frac{1}{2} abc (1 - \epsilon_{xx}) \left( \frac{\epsilon - 1}{\epsilon - \epsilon_{xx}} \right) I_a \left( z^2 - c^2 \right) \right|^2. \quad (19)
$$

In that case when atom is situated on $z$-axis at point $z$ and its dipole momentum is oriented along $z$-axis also we have

$$
\left( \frac{\gamma}{\gamma_0} \right)^{\text{radiative}} = \left| 1 + \frac{1}{2} abc (1 - \epsilon_{zz}) \left( \frac{\epsilon - 1}{\epsilon - \epsilon_{zz}} \right) \times \right.
\left. \times \left\{ \frac{2}{\sqrt{(z^2 + a^2 - c^2)(z^2 + b^2 - c^2)}} - I_b \left( z^2 - c^2 \right) \right\} \right|^2. \quad (20)
$$

It is important to note, that founded expressions do not have sense (became infinite large) at some (negative) values of permittivity. This phenomenon corresponds to cases of plasmon resonance excitation. If we take into account higher terms of expansion over inverse wavelength (radiative corrections) than this divergence disappears [13], but plasmon resonance remains.

Highly important moment is that for arbitrary value of $\epsilon (\lambda)$, i.e. for arbitrary material at arbitrary frequency, it is possible to find a whole series of ellipsoids of different shapes having plasmon resonances. This variety is a base for different effects.

On the other hand, slightly changing of the ellipsoid’s shape with settled value of permittivity is a reason of radical changing in spontaneous emission decay rate.
On Figures 2 and 3 dependences of spontaneous emission decay rate of an atom placed near silver ($\epsilon = -15.37 + i0.231$ ($\lambda = 632.8$ nm)) nanoellipsoid on atom position are presented. From Fig. 2(a) ($b/c = 0.6$, $a/c = 0.105$) it is well seen substantial decrease of the radiative decay rate inside of ellipsoid (where decay rate is constant) and four regions of substantial enhancement of radiative decay exist near ellipsoid’s surface. Slightly changing of the ellipsoids shape ($b/c = 0.6$, $a/c = 0.046$) we have another plasmon excitation, as it presented on Fig. 2(b). In this case, in contrary to spontaneous emission process presented by Fig. 2(a), there is substantial acceleration of the radiative decay rate of an atom placed inside the ellipsoid.

Analogous picture takes place in case of $z = 0$ cross section of spontaneous emission decay rate, as it presented on Fig. 3. In that case, on Fig. 3(a) ($b/c = 0.6$, $a/c = 0.105$) near the ellipsoid regions of substantial prohibition of radiative decay occurs (from the left and from the rights sides of ellipsoid’s surface). In case of decreasing of semi-axis $a$, in approximately down to two times ($b/c = 0.6$, $a/c = 0.046$), the situation is changes to opposite one, as it clearly presented on Fig. 3(b). And as it was mentioned above, instead of delay of spontaneous decays, now we have substantial acceleration.

Thus, spontaneous emission decay rate near triaxial ellipsoids of arbitrary shape depends on geometry of the ellipsoid and of spatial localization of an atom in highly nontrivial way. In some regions, there is substantial acceleration of transitions, but in other regions substantial inhibition can occur. Analogously, in the case of incidence of plain electromagnetic wave (i.e. dipole source situated at infinity), the field distribution near triaxial nanoellipsoid also has rather complicated structure, where regions of substantial enhancement and substantial inhibition exist. All above mentioned means, that triaxial ellipsoids can be used for effective control of local plasmon fields and therefore, it can replace more complicated constructions of simple nanoparticles [14].

Of course, in case of strong acceleration of spontaneous emission decay rates, the perturbation theory will be unusable for strong dipole transitions. In this case, Rabi’s oscillations can occur, but theory of such processes is also can be developed on the base of the method presented in our paper.

So far, we considered process of spontaneous emission, i.e. we have assumed that an atom is in some excited state. But the triaxial ellipsoid can be used for efficient excitation of the atoms and molecules having their absorption bandwidth in resonance with plasmon oscil-
lations of the ellipsoid. Moreover, triaxial ellipsoids (in contrast to spheroids and spheres) can be used for simultaneous amplification (or inhibition) of absorption and emission. It is due to the fact that for every kind of fluorophore, there such ellipsoid exists for which one of the resonant frequencies lies in absorption bandwidth and the other one lies in emission bandwidth. For example, if we consider ellipsoid made of silver with the next aspect ratios $a/c = 0.273$ and $b/c = 0.447$, then it has plasmon resonances at 355 nm and 465 nm and these two lines correspond to frequency domains of absorption and emission bandwidths of 
Hoechst 33342 fluorophore [15]. Analogously, silver ellipsoid with aspect ratios $a/c = 0.357$ and $b/c = 0.414$ has plasmon resonances at 346 nm and 445 nm and these two lines corresponds to absorption and emission bandwidth of Alexa 532 fluorophore [15]. In its turn, the simultaneous amplification of absorption and emission rates leads to substantial increase of fluorescent intensity and also leads to possibility of detection and observing of molecules with higher temporal resolution. Discovered effect allows investigate that fluorophores, which is uninteresting without using of the triaxial nanoellipsoid (or other nanoparticles of complicated shapes).

In conclusion, analytical expressions for spontaneous emission decay rate of a single atom placed near triaxial nanoellipsoid are founded. Obtained results show, that for metallic ellipsoids there is inhibition enhancement in several orders of magnitude of spontaneous decay are possible for an atom (or a molecule) and it is strongly depends on atom’s location near the ellipsoid. It was shown, that triaxial ellipsoids can be used for simultaneous control of absorption and emission processes of light by single molecule.

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Fig. 1: Geometry of the problem.
Fig. 2: Relative radiative decay rate of an atomic dipole with orientation of the moment along $y$-axis and placed near silver nanoellipsoid ($\epsilon = -15.37 + i0.231$ ($\lambda = 632.8$ nm)) as a function of atom’s position in $x = 0$ plane. Red arrow indicates orientation of dipole momentum. Colorbar is in logarithmic scale.
Fig. 3: Relative radiative decay rate of an atomic dipole with orientation of the moment along $y$-axis and placed near silver nanoellipsoid ($\epsilon = -15.37 + i0.231$ ($\lambda = 632.8$ nm)) as a function of atom’s position in $z = 0$ plane. Red arrow indicates orientation of dipole momentum. Colorbar is in logarithmic scale.