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Numerical modelling of emission of a two-level atom near a metal nanoparticle with account for tunnelling of an electron from an atom into a particle

S.V. Fedorovich, I.E. Protsenko

Abstract. **We report the results of numerical modelling of emission of a two-level atom near a metal nanoparticle under resonant interaction of light with plasmon modes of the particle. Calculations have been performed for different polarisations of light by a dipole approximation method and a complex multipole method. Depending on the distance between a particle and an atom, the contribution of the nonradiative process of electron tunnelling from a two-level atom into a particle, which is calculated using the quasi-classical approximation, has been taken into account and assessed. We have studied spherical gold and silver particles of different diameters (10–100 nm). The rates of electron tunnelling and of spontaneous decay of the excited atomic state are found. The results can be used to develop nanoscale plasmonic emitters, lasers and photodetectors.**

Keywords: *plasmonics, dipole approximation, method of complex multipoles, emission near a particle, metal nanoparticles.*

1. Introduction

Experimental studies of silicon-based solar cells (SCs) have shown that metal nanoparticles deposited onto a SC surface over a dielectric (spacer) layer enhance the silicon fluorescence and, consequently, generation of photoelectrons. In particular, Uskov et al. [1] observed a maximal increase in fluorescence at a spacer thickness $d = 20–30$ nm; at $d = 10–15$ nm fluorescence decreased significantly, while at a smaller d it reduced to zero. On the other hand, it is known that the fluorescence quenching due to interaction of emitters near the surface of a nanoparticle with its higher multipole modes occurs at a distance of less than 5 nm from the source to the nanoparticle surface [2]. Therefore, we have hypothesised that a reduction in fluorescence in [1] may be caused by, inter alia, the tunnelling of electrons from a semiconductor SC substrate into nanoparticles at a given spacer thickness. In the present study, to determine how the electron tunnelling from the excited state of the emitter into a nanoparticle can affect fluorescence, we have considered a simple case of a single emitter near a nanoparticle (Fig. 1).

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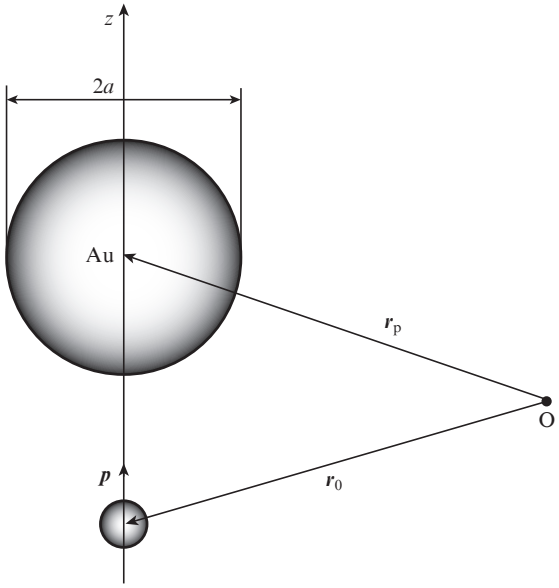

Figure 1. System under study.

A spherical metal (gold or silver) nanoparticle of radius a having a dielectric constant ε resided in a vacuum at a point whose radius vector $\boldsymbol{r}_p$ was at a certain distance from the emitter along the z axis, for example located at point $\boldsymbol{r}_0$ of the atom with a dipole moment $\boldsymbol{p}$ directed perpendicular or parallel to the z axis. As an emission characteristic of a nanoparticle–atom system we used the quantum yield of emission

$$q = \frac{\Gamma_r}{\Gamma}, \tag{1}$$

where Γ and Γ_r are, respectively, the rates of total and radiative decay of an excited state of an atom near a nanoparticle. To determine q, we used two numerical methods: dipole approximation method [3] and complex multipole method [4] with allowance for corrections for the tunnelling of an electron from the excited state of an atom into a nanoparticle and for the corresponding nonradiative energy loss. We should also add that the positive charge of the atom that occurs immediately after the tunnelling is then compensated by reverse tunnelling of an electron from a nanoparticle to the ground state of the atom.

Below, we determine the distance at which the tunnelling introduces significant changes in the value of the quantum yield of emission, obtained by two calculation methods.

2. Description of emission of an atom near a nanoparticle by the dipole approximation method

To describe the electric field of a metal particle with a dipole moment $\boldsymbol{p}$, we have introduced the Green's function $G(\boldsymbol{r},\boldsymbol{r}')$ [3], which is a tensor, and relates an electric dipole with a dipole moment $\boldsymbol{p}$, located at point $\boldsymbol{r}'$, and its field $\boldsymbol{E}$ at point $\boldsymbol{r}$:

$$\boldsymbol{E}(\boldsymbol{r}) = G(\boldsymbol{r},\boldsymbol{r}')\boldsymbol{p}(\boldsymbol{r}'), \tag{2}$$

where

$$G(\boldsymbol{r},\boldsymbol{r}') = G^0(\boldsymbol{r},\boldsymbol{r}') + G^0(\boldsymbol{r},\boldsymbol{r}_\mathrm{p})\alpha(\omega)\varepsilon_0 G^0(\boldsymbol{r}_\mathrm{p},\boldsymbol{r}'); \tag{3}$$

ε_0 is the dielectric constant of vacuum; $G^0(\boldsymbol{r},\boldsymbol{r}')$ is the Green's function in free space (in the absence of a particle) [5, 6],

$$G^0_{ij}(\boldsymbol{r},\boldsymbol{r}') = \left(k^2\boldsymbol{e}_i\boldsymbol{e}_j\delta_{ij} + \delta_{ij}\frac{\partial}{\partial x_i}\frac{\partial}{\partial x_j}\right)\frac{\exp(\mathrm{i}kR)}{4\pi\varepsilon_0 R}; \tag{4}$$

$k = \omega/c$ is the emission wavenumber; R is the distance between the particle centre and the atom; x_i and x_j are the ith and the jth coordinates in the selected coordinate system; $\boldsymbol{e}_i$ and $\boldsymbol{e}_j$ are the unit vectors that are codirectional with the coordinate axes; $i, j = 1, 2, 3$; c is the velocity of light in vacuum;

$$\alpha(\omega) = \frac{\alpha_0(\omega)}{1 - \mathrm{i}(k^3/6\pi)\alpha_0(\omega)} \tag{5}$$

is the polarisability of a particle;

$$\alpha_0(\omega) = 4\pi a^3\frac{\varepsilon(\omega) - 1}{\varepsilon(\omega) + 2} \tag{6}$$

is the quasi-static polarisability of a nanoparticle; and $\varepsilon(\omega)$ is the dielectric constant of the nanoparticle material.

Expressions for the ratios of the rates Γ (without the electron tunnelling) and Γ_r of losses of an atom near a nanoparticle to the rate Γ^0 of its radiative losses in free space have the form [7, 8]

$$\frac{\Gamma}{\Gamma^0} = 1 + \frac{6\pi\varepsilon_0}{k^3}\mathrm{Im}[\boldsymbol{\mu}G^0(\boldsymbol{r}_0,\boldsymbol{r}_\mathrm{p})\alpha(\omega)\varepsilon_0 G^0(\boldsymbol{r}_\mathrm{p},\boldsymbol{r}_0)\boldsymbol{\mu}], \tag{7}$$

$$\frac{\Gamma_\mathrm{r}}{\Gamma^0} = \frac{\Gamma}{\Gamma^0} - \frac{\Gamma_\mathrm{nr}}{\Gamma^0} = \frac{\Gamma}{\Gamma^0} - \frac{\omega\varepsilon_0}{2}\left[\mathrm{Im}\,\alpha(\omega) - \frac{k^3}{6\pi}|\alpha(\omega)|^2\right] \times |G^0(\boldsymbol{r}_\mathrm{p},\boldsymbol{r}_0)\boldsymbol{p}|^2, \tag{8}$$

where $\boldsymbol{\mu}$ is the unit vector that is codirectional with the vector $\boldsymbol{p}$; and Γ_nr is the rate of nonradiative losses.

Using equations (3)–(8), we can obtain expressions for the total and radiative losses in different directions of the dipole moment of the atom – parallel (subscript ∥) and perpendicular (subscript ⊥) to the z axis of the coordinate system:

$$\frac{\Gamma_\perp}{\Gamma^0} = 1 + \frac{3k^3}{2\pi}\mathrm{Im}\left\{\alpha(\omega)\exp(2\mathrm{i}kz)\left[\frac{1}{(kz)^6} + \frac{1}{\mathrm{i}(kz)^5} + \frac{-1}{(kz)^4}\right]\right\}, \tag{9}$$

$$\frac{\Gamma_\parallel}{\Gamma^0} = 1 + \frac{3k^3}{8\pi}\mathrm{Im}\left\{\alpha(\omega)\exp(2\mathrm{i}kz)\left[\frac{1}{(kz)^2} + \frac{1}{\mathrm{i}(kz)^3} + \frac{1}{(kz)^6} + \frac{1}{\mathrm{i}(kz)^5} + \frac{-1}{(kz)^4}\right]\right\}, \tag{10}$$

$$\frac{\Gamma_{\mathrm{r}\perp}}{\Gamma^0} = 1 + \frac{k^6}{4\pi^2}|\alpha(\omega)|^2\left[\frac{1}{(kz)^6} + \frac{1}{(kz)^4}\right] + \frac{k^3}{\pi}\mathrm{Re}\,\alpha(\omega)\frac{1}{(kz)^3}, \tag{11}$$

$$\frac{\Gamma_{\mathrm{r}\parallel}}{\Gamma^0} = 1 + \frac{k^6}{16\pi^2}|\alpha(\omega)|^2\left[\frac{1}{(kz)^6} - \frac{1}{(kz)^4}\right] - \frac{k^3}{2\pi}\mathrm{Re}\,\alpha(\omega)\frac{1}{(kz)^3}. \tag{12}$$

3. Description of emission of an atom near a nanoparticle by the multipole method

This method takes into account not only the dipole, but also all higher multipole moments of oscillations of the electron density of a nanoparticle. Its essence is that the entire space is divided into regions (domains) in which the dielectric function is assumed constant. The total field at any point is a superposition of fields from the domains surrounding the given point [9].

The field in each region of space is determined by solving the scalar Helmholtz equations for the components of the electric and magnetic fields:

$$(\nabla^2 + k^2)\boldsymbol{E}(\boldsymbol{r}) = 0, \qquad (\nabla^2 + k^2)\boldsymbol{H}(\boldsymbol{r}) = 0. \tag{13}$$

The components $\boldsymbol{E}$ and $\boldsymbol{H}$ are given in the form of products

$$f_{nm}(\boldsymbol{r}) = b_n(kR)\,Y_n^m(\vartheta,\varphi), \tag{14}$$

where $\boldsymbol{r} = \{R, \vartheta, \varphi\}$ is a set of three coordinates of the spherical coordinate system. The vectors of the electric and magnetic fields $\boldsymbol{E}$ and $\boldsymbol{H}$ are defined as a sum over all domains – $\sum_j a_j \boldsymbol{f}_j$. The parameters a_j are found from the boundary conditions on the boundaries of the domains:

$$\begin{aligned}
&\boldsymbol{n}(\boldsymbol{r}_k)\times[\boldsymbol{E}_i(\boldsymbol{r}_k) - \boldsymbol{E}_j(\boldsymbol{r}_k)] = 0,\\
&\boldsymbol{n}(\boldsymbol{r}_k)\times[\boldsymbol{H}_i(\boldsymbol{r}_k) - \boldsymbol{H}_j(\boldsymbol{r}_k)] = 0,\\
&\boldsymbol{n}(\boldsymbol{r}_k)\times[\varepsilon_i(\boldsymbol{r}_k)\boldsymbol{E}_i(\boldsymbol{r}_k) - \varepsilon_j(\boldsymbol{r}_k)\boldsymbol{E}_j(\boldsymbol{r}_k)] = 0,\\
&\boldsymbol{n}(\boldsymbol{r}_k)\times[\varepsilon_i(\boldsymbol{r}_k)\boldsymbol{H}_i(\boldsymbol{r}_k) - \varepsilon_j(\boldsymbol{r}_k)\boldsymbol{H}_j(\boldsymbol{r}_k)] = 0,
\end{aligned} \tag{15}$$

where $\boldsymbol{n}(\boldsymbol{r}_k)$ is the unit vector of the normal to the interface between the domains at point $\boldsymbol{r}_k$; $\boldsymbol{E}_i$ and $\boldsymbol{H}_i$ are the vectors of the electric and magnetic fields of the ith domain; and ε_i is the dielectric function in the ith domain.

4. Tunnelling contribution

The rate Γ_t of electron tunnelling from the excited state of an atom into a nanoparticle can be defined as a frequency v of spatial oscillations of the electron in a certain energy state, multiplied by the electron tunnelling probability W:

$$\Gamma_\mathrm{t} = vW. \tag{16}$$

The energy level diagram of an atom and nanoparticle is shown in Fig. 2. The atom is given in the form of a two-layered quantum well having energies E_0 and E_1, width h, height V and barrier width l between the nanoparticle and the atom; E_F is the Fermi level of a metal particle. The oscillation frequency of the electron in the well is found from [10] the expression

$$v = \frac{\sqrt{m}\,h}{\sqrt{2E_e}}, \tag{17}$$

where m is the mass of the electron, and E_e is its energy.

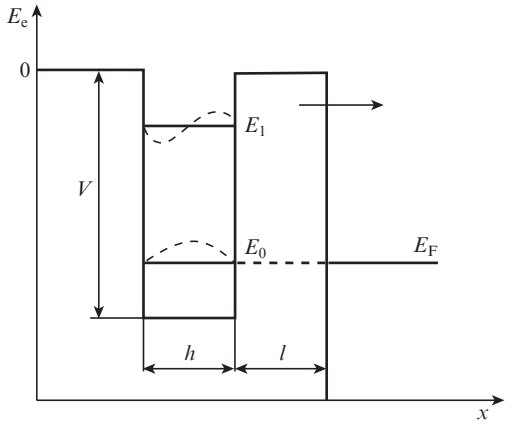

Figure 2. Energy level diagram of an atom (left) and a nanoparticle (right).

The transmission coefficient of an electron through a potential barrier between the atom and the nanoparticle is [9]

$$D = \exp\left\{-\frac{2}{\hbar}\int_{x_1}^{x_2}\sqrt{2m[-E_e + U(x)]}\,dx\right\}, \tag{18}$$

where $U(x)$ is the height of the potential barrier in the presence of a particle. If we take into account the image force, then

$$U(x) = V - \frac{e^2}{4|l-x|}, \tag{19}$$

where V is the barrier height shown in Fig. 2; x is the coordinate of the electron; and e is its charge. If we move the reference point to the origin of the potential barrier, the lower limit of integration is $x_1 = 0$, and the upper limit is determined by the expression

$$E_e = V - \frac{e^2}{4|l-x_2|}. \tag{20}$$

As a result of calculations taking (19) and (20) into account, the exponent in (18) is

$$-\frac{2}{\hbar}\int_0^{x_2}\sqrt{2m\left(-E_e + V - \frac{e^2}{4|l-x|}\right)}\,dx = \frac{1}{\hbar}\sqrt{2m}\sqrt{V-E_e}\left[\sqrt{\frac{1}{2}}\frac{\beta}{V-E_e} - \sqrt{\frac{l}{4}}\sqrt{l+\frac{\beta}{V-E_e}} + \frac{\beta}{2(V-E_e)}\ln\left(\frac{\beta}{V-E_e} + \sqrt{\frac{2\beta}{V-E_e}}\right) - \frac{\beta}{2(V-E_e)} \times \ln\left(1+\sqrt{l+\frac{\beta}{V-E_e}}\right)\right], \tag{21}$$

where $\beta = e^2/4$. Substituting (21) into (18), we obtain that

$$W = \left[\frac{\beta/(V-E_e) + \sqrt{2\beta/(V-E_e)}}{1+\sqrt{l+\beta/(V-E_e)}}\right]^{(1/\hbar)\sqrt{2m\beta}/\sqrt{4(V-E_e)}} \times \exp\left\{\frac{1}{\hbar}\sqrt{2m}\left[\frac{\beta}{\sqrt{2(V-E_e)}} - \sqrt{\frac{l}{4}}\sqrt{l(V-E_e)+\beta}\right]\right\}. \tag{22}$$

For the probability of tunnelling from a level with E_1, instead of E_e we should substitute E_1, calculated on the assumption $E_0 = E_F$, into (22).

The rate of spontaneous emission of an atom in the absence of a particle [11] has the form

$$\Gamma^0 = \frac{4}{3}\frac{\omega^3 p_0^2}{4\pi\varepsilon_0\hbar c^3}, \tag{23}$$

where

$$\boldsymbol{p}_0 = \int \psi_1^*(\boldsymbol{r})\,e\boldsymbol{r}\,\psi_0(\boldsymbol{r})\,d^3\boldsymbol{r} \tag{24}$$

is the dipole moment of the transition of an atom from a level with E_1 to a level with E_0; and ψ_0 and ψ_1 are the wave functions of the electron in the quantum well at levels with E_0 and E_1, respectively [10].

Figure 3 shows the dependences of the ratio of the tunnelling rate Γ_t to the rate of spontaneous emission Γ^0 on the distance between the nanoparticle and the atom. From expressions (7) and (8) we can determine the rate Γ_{nr} of nonradiative losses of the atom without the tunnelling effect. With the tunnelling contribution taken into account, Γ_{nr} is replaced by

$$\Gamma_{nr}^1 = \Gamma_{nr} + \Gamma_t, \tag{25}$$

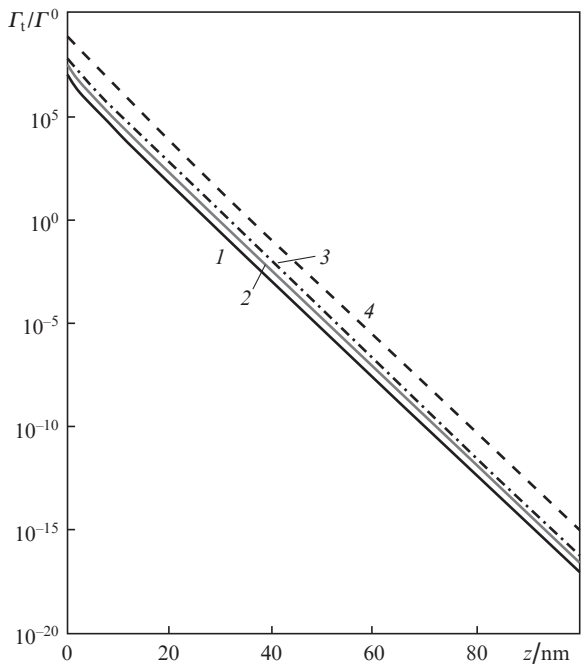

Figure 3. Calculated dependences of the ratio of the tunnelling rate to the rate of spontaneous emission of an atom in the absence of a nanoparticle on the distance between the nanoparticles and the atom at $U = 6.25\times10^{-19}$ J, $E_F = 3.43\times10^{-19}$ J, $h = 10^{-9}$ m, $\omega = (1)\ 3.7\times10^{15}$, $(2)\ 2.5\times10^{15}$, $(3)\ 1.9\times10^{15}$ and $(4)\ 0.75\times10^{15}$ s^{-1}.

therefore, the quantum yield of emission is

$$q = \frac{\Gamma_r}{\Gamma + \Gamma_t}. \qquad (26)$$

Figures 4 and 5 show dependences of the quantum yield on the distance between the nanoparticle and the atom, obtained by two numerical methods taking into account tunnelling at different polarisations of the emitting atom for a gold or silver nanoparticle. One can see that the allowance for a set of multipole modes greatly affects the quantum yield and gives a more accurate result than in the case when only the dipole mode is taken into account. Thus, both methods do not account for the tunnelling effect, which makes a significant contribution at short distances between the atom and the

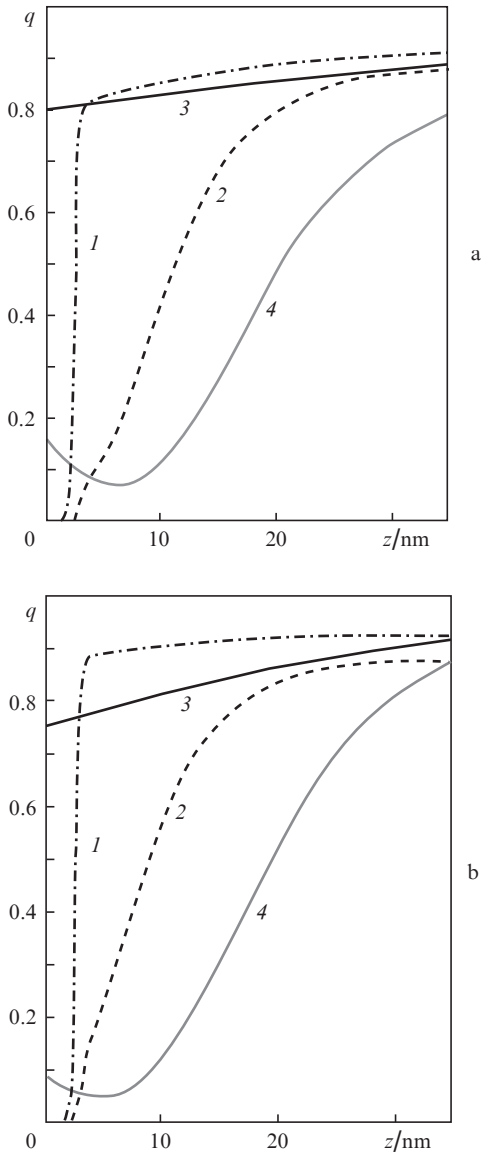

Figure 4. Quantum yield of emission of an atom as a function of the distance z from (a) a gold (λ = 650 nm, ε = –12.99 + i1.09, a = 40 nm) nanoparticle and (b) a silver (λ = 354 nm, ε = –2.03 + i0.6, a = 40 nm) nanoparticle. Use is made of the dipole approximation method taking into account (*1*, *2*) and neglecting (*3*, *4*) the contribution of tunnelling at polarisation directions of the atom (*1*, *3*) along and (*2*, *4*) perpendicular to the z axis.

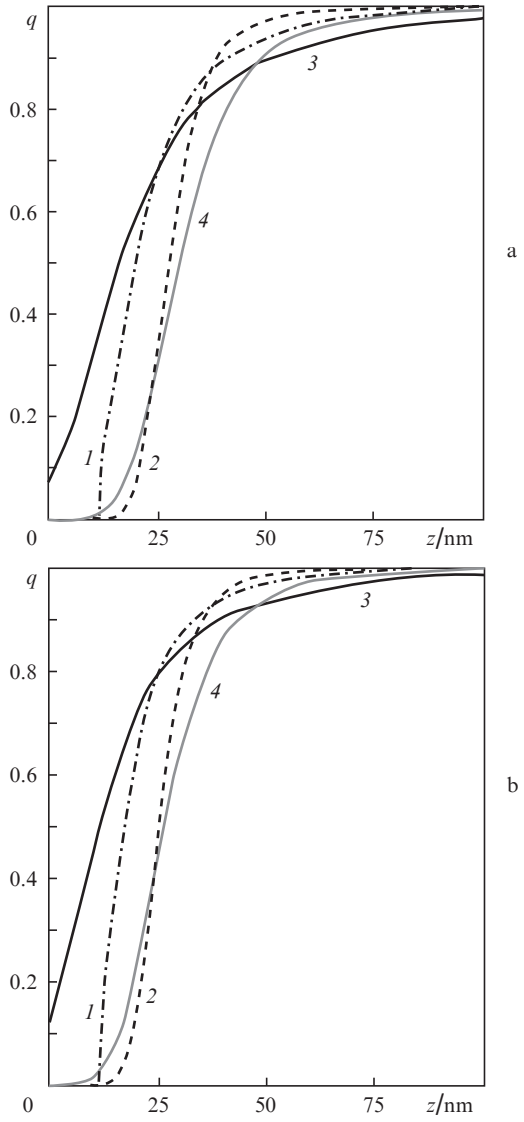

Figure 5. Same as in Fig. 4, using the multipole method.

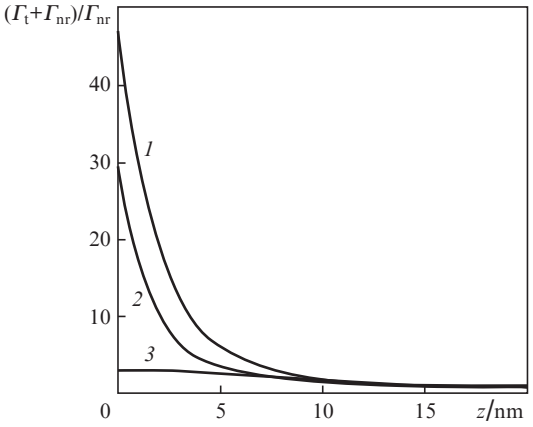

Figure 6. Ratio of the rate of nonradiative losses taking into account the tunnelling contribution to the rate of nonradiative losses without tunnelling as a function of distance z between the atom and the particle. In the calculations use is made of a gold particle (λ = 650 nm, ε = –12.99 + i1.09) with radii (*1*) 80, (*2*) 40 and (*3*) 10 nm. The rates of nonradiative losses are calculated by the dipole approximation method. The atom is polarised perpendicular to the z axis.

particle. This contribution can be found by constructing the dependence of the ratio of the rate of nonradiative losses, taking into account tunnelling $\Gamma_{nr} + \Gamma_t$ to the rate of nonradiative losses without tunnelling Γ_{nr} on the distance z between the atom and the particle (Fig. 6). One can see that the contribution of tunnelling becomes noticeable at distances of about 10–15 nm between the atom and the particle and depends on the particle radius.

5. Conclusions

Simulation of electromagnetic interaction between a nanoparticle and an emitting two-level atom by two methods shows that the allowance for higher multipoles qualitatively and quantitatively affects the quantum yield of emission of an atom. Neglect of the contribution of higher modes leads to inaccurate calculations. The effect of electron tunnelling from the excited state of an atom into a nanoparticle, followed by nonradiative relaxation of the electron energy, has a strong influence on the quantum yield of emission of an atom at small distances between particles. The above figures show that the tunnelling effect makes a more significant contribution when the calculation is based only on the dipole mode of oscillations of the electron density of the nanoparticle. In calculations taking into account the contribution of higher multipoles, the tunnelling effect is not noticeable. The rate of tunnelling begins to make a significant contribution at distances of less than 15 nm from the atom to the surface of the nanoparticle. In this case, the rate of tunnelling is independent of the particle size and polarisation of emission. This may explain the results of SC experiments when the fluorescence of a silicon SC with a coating comprising metal nanoparticles is considerably reduced if the thickness of the dielectric layer (spacer) between the SC layer and the layer of nanoparticles was less than 10–15 nm.

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