

Superradiance of several atoms near a metal nanosphere

I.E. Protsenko, A.V. Uskov

Abstract. Assuming that the number of emitters (atoms) near a spherical metal nanoparticle is large (more than a few hundred), so that their interaction with each other is strong and sufficient for the emergence of their collective states (Dicke states), it is shown that the nanoparticle accelerates the superradiance of the emitters in a similar way as it accelerates the spontaneous emission of a single emitter. In this case, part of the energy stored by the emitters is absorbed by a nanoparticle, and the rest of the energy is radiated as a superradiance pulse. For the parameters selected in this paper, the energy absorbed by the nanoparticle is approximately equal to the emitted energy. We have found the collective states of the emitters and nanoparticle and have derived expressions for the time dependence of the superradiance pulse power, pulse duration and time delay with respect to the moment of excitation of the emitters.

Keywords: metal nanosphere, localised plasmon resonance, collective spontaneous emission.

1. Introduction

It is known that the rate of spontaneous emission of a resonant emitter – an atom, molecule or quantum dot – can significantly increase near a metal nanoparticle [1]. Known also is the effect of collective spontaneous emission or superradiance [2, 3], when spontaneous emission of dipole–dipole interacting emitters located in a volume whose size is less than or on the order of the wavelength of their resonance emission appears in the form of a short pulse with some delay relative to the moment of excitation of the emitters. There arises a question whether the rate of collective spontaneous emission of emitters near a metal nanoparticle can increase as the rate of spontaneous emission of a single emitter? It is known from the theory of Dicke superradiance for resonant emitters in the absence of a nanoparticle that superradiance occurs when symmetric collective states (Dicke states) of the emitters are

formed: a permutation of emitters does not change these states. Can Dicke states or states close to them be formed for emitters near a nanoparticle? It can be assumed that for such conditions to appear, it is necessary that the interaction between the emitters be stronger than the interaction of each emitter and a nanoparticle.

Systems of emitters near metal nanoparticles in a volume that is less than or on the order of the wavelength were studied in a number of experiments on the generation of coherent radiation. For example, Noginov et al. [4] used the experimental conditions that are similar to those needed to observe superradiance: in paper [4] several thousand emitters, resonantly emitting in the visible spectral range, are located in a small volume – the shell of a spherical metal nanoparticles at a distance on the order of ten nanometres from its surface; the resonant frequency of the emitters and the localised plasmon resonance (LPR) frequency of the nanoparticle coincide, the emitters are rapidly (compared with the time of radiation) excited by an external field pulse, their density in the nanoparticle's shell is high and they interact strongly with one another. The experiments were used to measure the pulse characteristics (centre frequency, duration and energy) of the response field of the emitters on their incoherent excitation by an external field pulse with a frequency different from the LPR frequency.

In [5] we formulated a theory of superradiance for a single emitter near a metal nanoparticles on the basis of papers [6, 7], taking into account the delay in the interaction of the emitter and the nanoparticle, as well as the absorption of radiation in the nanoparticle and the interaction of the emitter with higher multipole modes of oscillations of its polarisation. Investigation of superradiance near metal nanoparticles is closely connected with the research on plasmonic nanolasers [8] – the only generators of the coherent electromagnetic field, the maximum size of which (several tens of nanometres) is much smaller than the wavelength of visible or near-IR light. Such nanolasers help solve an important problem of creating nanoscale optoelectronic interfaces that are compatible with microelectronic chips [9]. Phased arrays of nanolasers, studied theoretically [10] and experimentally [11], can be used to generate high-power and focused (single-mode) coherent radiation.

Superradiance near metal nanoparticles in connection with the development of nanoscale lasers is being successfully studied (see, for example, [12] and references therein). However, the authors of a number of papers, for example Pustovit and Shahbazyan [13], predicted on the basis of numerical calculations that although a superradiance pulse of the emitters near a metal nanoparticle is possible, it contains very little energy that does not exceed the energies of three

I.E. Protsenko P.N. Lebedev Physis Institute, Russian Academy of Sciences, Leninsky prosp. 53, 119991 Moscow, Russia; *Advanced Energy Technologies' LTD, Technopark Skolkovo, Novaya ul. 100, 143025 Skolkovo, Moscow region, Russia; National Research Nuclear University 'MEPhI', Kashirskoe sh. 31, 115409, Moscow, Russia; e-mail: protsenk@gmail.com;

A.V. Uskov P.N. Lebedev Physis Institute, Russian Academy of Sciences, Leninsky prosp. 53, 119991 Moscow, Russia; *Advanced Energy Technologies' LTD, Technopark Skolkovo, Novaya ul. 100, 143025 Skolkovo, Moscow region, Russia; e-mail: alexusk@lebedev.ru

Received 27 March 2014; revision received 27 November 2014
Kvantovaya Elektronika 45 (6) 561–572 (2015)
Translated by I.A. Ulitkin

excited emitters, regardless of their total number near the nanoparticle. This result is of interest, because it means very effective absorption of the emitters' radiation by the nanoparticle, which may be particularly useful for increasing the efficiency of photoemission from metal nanoparticles [14] in such applications as plasmon photovoltaics [15]. On the other hand, based on the results of [13], we can conclude that the superradiance energy of a large number of emitters is almost always completely absorbed by the metal nanoparticle, and it is bad for the applications of superradiance effects in plasmonic nanolasers. One of the goals of this paper is to show that under certain conditions the superradiance pulse near a metal nanoparticle can have the energy much greater than the energy of only three excited emitters, the pulse duration being much smaller than in the case of the same system of emitters without a nanoparticle.

A detailed numerical analysis of superradiance near a metal nanoparticle can be, in principle, performed by using the equations given in [5] or [13]. Technically, it is possible, probably, for no more than several tens of emitters, which was done in [13]. However, as will be shown below, to observe a superradiance pulse with the energy on the order of that stored in the emitters, the number of the latter should exceed 500–1000 (which was the case in the experiment [4]). For such a large number of emitters it is difficult to solve the problem numerically, which is why using the Dicke model we justify and use an approximate analytic approach to the analysis of superradiance near a metal nanoparticle. For simplicity, we consider the case of a spherical nanoparticle and assume that the emitters are located sufficiently close (but not too close, see below) to it – at a distance from 10 nm to several tens of nanometres from its surface, so that in describing their interaction with a nanoparticle one can use the quasi-static approximation.

Known is the expression for the superradiance pulse power of N identical atoms in a volume whose size is much smaller than the radiation wavelength [3]. Below we obtain a similar expression for the superradiance pulse power of atoms (emitters) in the vicinity of a metal nanoparticle. First, in Section 2 we reproduce known results: we describe collective spontaneous emission of two and then N atoms. Although this approach to the description of superradiance is well known (for example, it was given in [7]), it seems appropriate to present it again – firstly, as a reference material for the reader's convenience, and secondly, for the discussion of the approximations and some interesting issues concerning superradiance, in particular, the emergence of nonlinearity and the role of quantum fluctuations. Besides, the notations and results for superradiance of an ensemble of atoms will be used in Section 3 for one and then for N atoms (emitters) near a spherical metal nanoparticle, as well as for derivation of an expression for the time dependence of the superradiance pulse power. For typical parameters of the emitters and nanoparticle in Section 4 we estimate the power and energy of the superradiance pulse. In conclusion, we discuss the results.

2. Superradiance of several atoms (Dicke model)

2.1. Collective spontaneous emission of two atoms

Suppose that there are two identical atoms, each having a single valence electron and a frequency ω of this electron transition from the first excited state to the ground state. At the

initial time instant $t = 0$, the valence electrons of the atoms quickly – in a time much shorter than the time of radiation of the atoms – are excited by, for example, the external field pulse with a certain polarisation into the states with a transition dipole moment (hereinafter, the dipole moment), which is perpendicular to the straight line connecting the atoms (Fig. 1). After excitation there occurs spontaneous emission of the atoms, and they interact with each other by exchanging photons. For reasons of symmetry, it is obvious that the directions of the dipole moments of the atoms remain the same even in the case of spontaneous emission of atoms after their excitation; therefore, the other two modes of polarisation of the atoms, whose directions of the dipole moments are shown by dashed arrows in Fig. 1a, will not be excited and are neglected in this study. Let us determine the rate of spontaneous emission of such atoms (Fig. 1). The interaction between the atoms through the exchange of the photons becomes possible after one of them emits a photon (Fig. 2a). An atom, which remains excited, emits a photon and the unexcited atom can absorb it (Fig. 2b). After some time, the atoms emit a second photon in free space, and then they will be in the ground state. The interaction between the atoms through the exchange of the photons is a dipole–dipole interaction [16, 17]. If the atoms are close enough to each other – at a distance r , which is smaller than the wavelength λ of the emitted photons or equal to it, then the rate (the probability per unit time) Ω of their dipole–dipole interaction is large: it exceeds the rate of spontaneous emission γ_r of a single isolated atom, and thus at $r \leq \lambda$ the atomic interaction significantly affects their emission. If $r \gg \lambda$, then $\Omega \ll \gamma_r$, the interaction between the atoms can be neglected (because of its delay) and every atom emits independently.

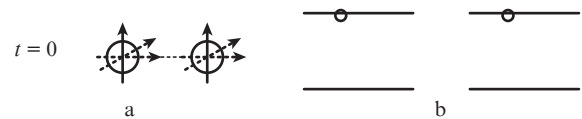


Figure 1. (a) Formulation of the problem for two emitters and (b) their excited states. Solid arrows show the directions of the transition dipole moments of the emitters during their excitation and spontaneous emission. Dashed arrows show the directions of the dipole moments of the transitions that are not excited.

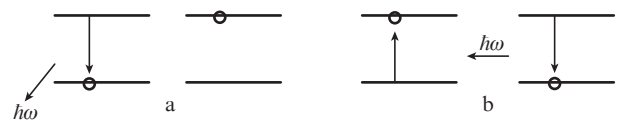


Figure 2. Scheme of the process in question: (a) one of the emitters in Fig. 1 emits a photon and (b) the emitters begin to interact, emitting and absorbing photons.

Following [2], we describe spontaneous emission of atoms with allowance for their interactions, for which purpose we consider the states of the atoms. We assume that the interaction between the atoms is strong enough: $\Omega \gg \gamma_r$, and hence in determining their states we can neglect spontaneous emission. We denote the states of the excited and unexcited atoms by 1 and 0, respectively. Then, the state of the two atoms in Fig. 1b will be $|11\rangle$, in Fig. 2a – $|01\rangle$ and in Fig. 2b – $|10\rangle$, whereas the state $|00\rangle$ corresponds to both atoms in the

ground state. The states of the two non-interacting atoms are shown in Fig. 3a. Due to the dipole–dipole interaction, instead of states $|01\rangle$ и $|10\rangle$ there appear their superpositions. If the atoms are at a small ($r \ll \lambda$) distance from each other, then these superpositions,

$$|\pm\rangle = (1/\sqrt{2})(|10\rangle \pm |01\rangle), \quad (1)$$

will have the energy $\hbar(\omega \pm \delta)$. If the atoms are at a distance $r \geq \lambda$, then they have other states with different statistical weights included in the superposition of the terms. To obtain such states, it is necessary to take into account the delay in the interaction of the atoms [17, 7]. The value of the shift $\hbar\delta$ of the energy levels of the atoms in Fig. 3b with respect to the levels used in Fig. 3a depends on the interaction energy, which increases with decreasing distance between the atoms. We assume that the atoms are close enough to each other so that their state is described by superposition (1), but not too close, so that the condition

$$\delta \ll \omega \quad (2)$$

is fulfilled. It can be shown [7] that there is a range of distances between the atoms for which expressions (1) and (2) are valid. When condition (2) is fulfilled, in calculating the rate of emission of two atoms we can neglect the change in the energy of the states $|\pm\rangle$ relative to the energies of the states $|01\rangle$ and $|10\rangle$ of the non-interacting atoms.

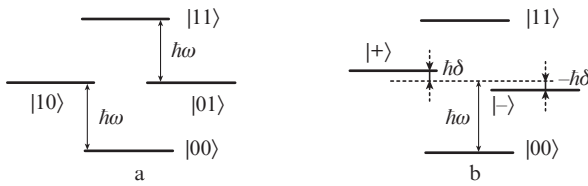


Figure 3. Energy states of two emitters: (a) without the interaction with each other and (b) with the interaction with each other through the exchange of a photon.

The sign of the symmetric state $|+\rangle$ is not changed by rearranging the atoms. The components of the operators of the dipole moments of the transitions of the left and right atoms in Figs 1–3 are denoted by \hat{d}_1 and \hat{d}_2 , respectively, and the corresponding matrix elements are denoted by $\langle \hat{d}_i \rangle = \langle \hat{d}_2 \rangle \equiv d$. Since the directions of the dipole moments in the emission of the photons by the atoms do not change, we consider only the components \hat{d}_1 and \hat{d}_2 of the vector operators of the dipole moments. The dipole moment operator of a system of two atoms is $\hat{d}^{(2)} = \hat{d}_1 + \hat{d}_2$, and the rate of spontaneous emission of atoms is $\gamma_{\alpha,\beta}^{(2)} \propto \langle \langle \alpha | \hat{d}^{(2)} | \beta \rangle \rangle^2$, where $\langle \alpha | \dots | \beta \rangle$ means averaging for the transition from the state $|\beta\rangle$ to the state $\langle \alpha |$, and α, β denote 10, 01, +, -, etc. The matrix elements have the form

$$\begin{aligned} \langle + | \hat{d}^{(2)} | 11 \rangle &= \langle 00 | \hat{d}^{(2)} | + \rangle = \sqrt{2} d, \\ \langle - | \hat{d}^{(2)} | 11 \rangle &= \langle 00 | \hat{d}^{(2)} | - \rangle = 0, \end{aligned} \quad (3)$$

i.e. in spontaneous emission of two closely spaced (when the delay in the interaction is negligible) atoms from the state $|11\rangle$, only their symmetric state is excited. The nonsymmetric state $|-\rangle$ is not excited and hence does not radiate: it is ‘dark’.

Note that some delay in the interaction is always present; therefore, the state $|-\rangle$ is never completely dark, and it is excited and emits with some probability. The rates of spontaneous transitions are expressed as

$$\gamma_{11+}^{(2)} = \gamma_{+00}^{(2)} = 2\gamma_r. \quad (4)$$

Thus, the spontaneous emission of two closely spaced atoms takes place according to the scheme in Fig. 4, where W_{11} and W_+ are the populations of the corresponding states of the atoms. This figure corresponds to the system of balance equations for W_{11} and W_+ :

$$\dot{W}_{11} = -2\gamma_r W_{11}, \quad \dot{W}_+ = 2\gamma_r W_{11} - 2\gamma_r W_+,$$

the solution of which under the initial conditions $W_{11}(0) = 1$, $W_+(0) = 0$ has the form

$$W_{11}(t) = \exp(-2\gamma_r t), \quad W_+(t) = 2\gamma_r t \exp(-2\gamma_r t). \quad (5)$$

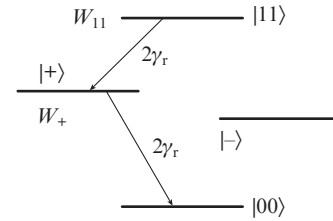


Figure 4. Transitions in the spontaneous emission of two closely spaced emitters.

The rate P_2 of emission of two atoms is equal to the negative sum of the rates of spontaneous emission from each state in Fig. 4:

$$P_2 \equiv 2\gamma_r W_{11} + 2\gamma_r W_+ = 2\gamma_r \exp(-2\gamma_r t)(1 + 2\gamma_r t). \quad (6)$$

If the atoms are far from each other and their interaction is negligible, then the rate of their emission

$$P_{20} = 2\gamma_r \exp(-\gamma_r t) \quad (7)$$

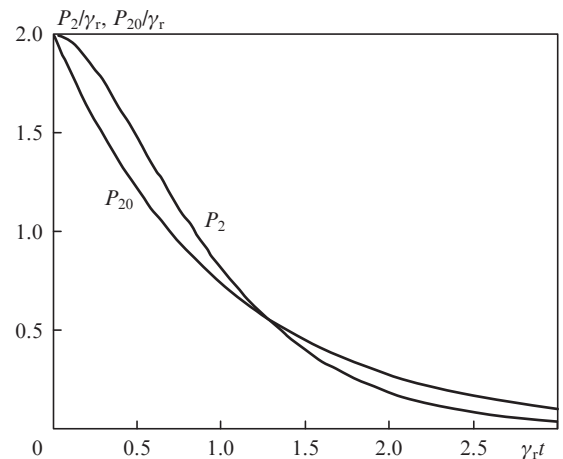


Figure 5. Rates of spontaneous emission of two interacting (P_2) and two non-interacting (P_{20}) emitters.

is the doubled rate of emission of a single atom. Note that expression (7) cannot be obtained directly from (6). For the transition from (6) to (7) we should take into account a delay in the interaction of atoms and make use of atomic states when condition (2) is not met [7, 17].

The dependences $P_2(t)$ and $P_{20}(t)$ are shown in Fig. 5. The dependence $P_2(t)$ has a maximum $2\gamma_r$ at $t = 0$, coinciding with the maximum $P_{20}(t)$; however, spontaneous emission of two interacting atoms at the initial stage is slightly faster than that of the non-interacting atoms.

2.2. Superradiance of N atoms

In the framework of the Dicke model, the symmetric states originating in the approximation of an instantaneous interaction between the atoms will result in spontaneous emission of an arbitrary number of interacting atoms. Nonsymmetric states are not excited in this case and are not considered below. Let us denote the symmetric states of N atoms, from which we have $n \leq N$ excited ones (let us call them ‘states with n excitations’), by $|N, n\rangle$. To determine the rate of emission, we find the square of the matrix element of the dipole moment of the transition between symmetric states $|N, n\rangle$ and $|N, n - 1\rangle$. The state $|N, n\rangle$ is the sum of C_N^n terms, each of which corresponds to the non-interacting atoms: n excitations are distributed over $N \geq n$ atoms. For example, the state $|3, 2\rangle = (1/\sqrt{3})(|110\rangle + |101\rangle + |011\rangle)$. The states from the superposition $|N, n\rangle$ undergo a transition, in the spontaneous radiative decay, into lower-energy states from the superposition $|N, n - 1\rangle$. For example, the term $|110\rangle$ of the state $|3, 2\rangle$ changes into the term $|100\rangle$ or $|010\rangle$ of the state $|3, 1\rangle = (1/\sqrt{3})(|100\rangle + |010\rangle + |001\rangle)$. Thus, if $\hat{d}^{(N)} = \sum_{i=1}^N \hat{d}_i$ is the operator of the dipole moment of N atoms with the matrix elements $\langle \hat{d}_i \rangle = d$, then the matrix elements are

$$\langle N, n - 1 | \hat{d}^{(N)} | N, n \rangle = \frac{1}{\sqrt{C_N^n}} \frac{1}{\sqrt{C_N^{n-1}}} n C_N^n d, \tag{8}$$

$$\langle \hat{d}^{(N)} \rangle^2 = \frac{C_N^n}{C_N^{n-1}} n^2 d^2 = (N - n + 1) n d^2.$$

Accordingly, the rate of spontaneous emission in the transition from the state $|N, n\rangle$ into $|N, n - 1\rangle$ is

$$\gamma_n^{(N)} = (N - n + 1) m \gamma_r. \tag{9}$$

To determine the rate $P_N(t)$ of spontaneous emission of a system of N interacting atoms, it is necessary to solve a system of rate equations for the populations $W_n^{(N)}$ of the states $|N, n\rangle$ ($n = N, \dots, 1$):

$$\begin{aligned} \dot{W}_N^{(N)} &= -\gamma_N^{(N)} W_N^{(N)}, \\ &\dots\dots\dots \\ \dot{W}_n^{(N)} &= \gamma_{n+1}^{(N)} W_{n+1}^{(N)} - \gamma_n^{(N)} W_n^{(N)}, \\ &\dots\dots\dots \\ \dot{W}_1^{(N)} &= \gamma_2^{(N)} W_2^{(N)} - \gamma_1^{(N)} W_1^{(N)}, \end{aligned} \tag{10}$$

and then the found $W_n^{(N)}$ are substituted into the expression

$$P_N = \sum_{n=1}^N \gamma_n^{(N)} W_n^{(N)} = \gamma_r \sum_{n=1}^N (N - n + 1) n W_n^{(N)}. \tag{11}$$

System (10) can in principle be solved analytically: the solution is found sequentially for the first, second, and other equations. However, at $N, n \gg 1$, the approximate expression for P_N can be obtained without solving system (10). Indeed, the rate P_N of spontaneous emission is the velocity of change in the average number of the excited atoms $\langle n \rangle \equiv \sum_{n=1}^N n W_n^{(N)}$: $P_N = d\langle n \rangle / dt$. This can be seen directly from the simple example of three atoms. Thus,

$$\frac{d\langle n \rangle}{dt} = \gamma_r \sum_{n=1}^N (N - n + 1) n W_n^{(N)} \equiv \gamma_r [(N + 1)\langle n \rangle - \langle n^2 \rangle], \tag{12}$$

where $\langle n^2 \rangle \equiv \sum_{n=1}^N n^2 W_n^{(N)}$. In the general case, equation (12) cannot be solved without preliminary solving system (10); however, at $N, n \gg 1$ we can use in (12) the approximation $\langle n^2 \rangle \approx \langle n \rangle^2$, and then, instead of (12) and (10) we derive one, though nonlinear, equation for $\langle n \rangle$:

$$\frac{d\langle n \rangle}{dt} = \gamma_r [(N + 1)\langle n \rangle - \langle n \rangle^2]. \tag{13}$$

The approximation $\langle n^2 \rangle \approx \langle n \rangle^2$ neglects the quantum fluctuations of the number of the excited atoms. The passage from expression (12) to (13) or, equivalently, by a system of linear equations (10) to a single, but nonlinear equation (13) is an interesting example of how by neglecting the fluctuations in the linear quantum system there appears nonlinearity and the number of dynamic variables describing the system is significantly reduced.

Known is the analytical solution of (13) with initial conditions $\langle n \rangle(0) = N$ (when all the atoms at $t = 0$ are excited):

$$\langle n \rangle(t) = \frac{1}{2} \left[1 - (N + 1) \tanh \left(\frac{N + 1}{2} \gamma_r t - \frac{\ln N}{2} \right) \right].$$

Differentiating this solution with respect to time, we obtain the superradiance rate in the Dicke model

$$P_N(t) = \gamma_r \left(\frac{N + 1}{2} \right)^2 \operatorname{sech}^2 \left[\frac{N + 1}{2} \left(\gamma_r t - \frac{\ln N}{N + 1} \right) \right]. \tag{14}$$

Equation (14) determines the superradiance pulse duration $2/[\gamma_r(N + 1)]$ and time $(N + 1)/(\gamma_r \ln N)$ of its delay relative to the moment of excitation of the atoms. The approximation $\langle n^2 \rangle \approx \langle n \rangle^2$ does not violate the law of conservation of energy

$$\int_0^\infty P_N(t) dt = N, \tag{15}$$

i.e., the number N of emitted photons corresponds to the number of excited atoms.

Let us formulate again the simplifying assumptions used in the Dicke model:

1. The identity of the interaction of each atom with all others. The denial of this assumption leads to the fact that ‘bright’ symmetric states of the atoms will become nonsymmetric. In varying degrees, ‘dark’, nonsymmetric states of the atoms will also be excited and radiate.
2. The absence of the influence of spontaneous emission on the state of the system, with the states, which correspond

to condition (2), or similar states of many atoms being obtained by neglecting their emission. This is a good approximation provided that the interaction between the atoms is strong enough: the spontaneous emission rate of an isolated atom with respect to the rate of the interaction of this atom with the others is small.

3. Neglect of the delay in the interaction between the atoms.

4. The frequencies of the transitions between the states of the interacting atoms are assumed to be the same, but in fact they are different from the transition frequencies of the non-interacting atoms by $\sim \delta E_{\text{int}}/\hbar$, where δE_{int} is the fluctuation of the interaction energy between the atoms. This difference will lead to an inhomogeneous broadening of the transitions in an ensemble of atoms [16] and should be taken into account in a more detailed analysis, especially at high densities of atoms.

3. Superradiance of several atoms near a spherical metal nanoparticle

Let us assume now that several atoms reside near a spherical metal nanoparticle, and the frequency ω of the transitions of the atoms in free space and the localised plasmon resonance (LPR) frequency of the nanoparticles coincide. We consider the nanoparticle as a quantum harmonic oscillator with the states $|n_p\rangle$ ($n_p = 0, 1, \dots$ is the number of vibrational quanta) and the matrix element of the dipole moment transition operator \hat{d}_p between the neighbouring states $\langle n_p | \hat{d}_p | n_p + 1 \rangle = d_p \sqrt{n_p + 1}$. We consider that the delay in the interaction between the atoms and a nanoparticle can be ignored, which corresponds to the quasi-static approximation. Unlike superradiance of atoms without a nanoparticle the case under consideration has the following features:

- the harmonic oscillator takes part in the interaction, which can be excited, in principle, to any high state;
- the dipole moment d_p of the oscillator differs from the dipole moment d of the atom;
- the nanoparticle-oscillator has nonradiative losses; and
- the atom (emitter) also exhibits nonradiative losses due to its interaction with a weakly emitting multipole modes of the nanoparticle, whose entire energy of fluctuations is virtually absorbed by the nanoparticle.

We denote the basic states of the system without taking into account the interaction of the atoms and nanoparticle as $|N, n - n_p\rangle |n_p\rangle$, where $|N, n - n_p\rangle$ is the state of N atoms, among which there are $n - n_p$ excited atoms, the total number of the excitations in this system state being equal to n . Let us consider first the case of a single atom near a nanoparticle, and then the case of several atoms.

3.1. Radiance of a single atom near a spherical nanoparticle

Let us assume that no more than one plasmon – a quantum of LPR oscillations of the electron density of the nanoparticles – can exist in the system: the latter is thus considered as a two-level system. This approximation is justified, because the plasmon exhibits greater losses and is more difficult to excite than even several atoms near the nanoparticle.

For simplicity we assume that at the initial moment the atom (emitter), located near the spherical nanoparticle at a distance r from its centre, is transferred to the excited state by the pulse of the external field, whose polarisation is either parallel to the straight line connecting the emitter and the

nanoparticle centre, or perpendicular to it. In this case, the directions of the dipole moments of the nanoparticle and the emitter during emission remain parallel to each other: the same spatial polarisation mode of the nanoparticles and the emitter, which was excited, emits. Other polarisation modes are not excited, and we do not consider them.

Assume that the states $|1, 0\rangle |1\rangle$ and $|1, 1\rangle |0\rangle$ of the nanoparticle and atom, without allowance for their interaction, have the same energy $\hbar\omega$. If the atom and nanoparticle are close to each other, then it is necessary to take into account their resonant interaction via an electromagnetic field, due to which the system will be in a superposition of the states $|1, 0\rangle |1\rangle$ and $|1, 1\rangle |0\rangle$:

$$A_0^{(1,1)} |1, 1\rangle |0\rangle + A_1^{(1,1)} |1, 0\rangle |1\rangle. \quad (16)$$

The coefficients $A_{n_p}^{(1,n)}$ vary slowly compared with the factor $\exp(-i\omega t)$, omitted in (16), and are determined from the system of equations

$$\begin{aligned} \dot{A}_0^{(1,1)} &= -(\gamma/2)A_0^{(1,1)} - i\Omega_{\text{dd}}^{(1)}A_1^{(1,1)}, \\ \dot{A}_1^{(1,1)} &= -(\Gamma/2)A_1^{(1,1)} - i\Omega_{\text{dd}}^{(1)}A_0^{(1,1)}, \end{aligned} \quad (17)$$

which follow from the Schrödinger equation that describes the interaction of the nanoparticle with the atoms in view of the relaxation of their excited states [14]. The terms $-(\gamma/2)A_0^{(1,1)}$ and $-(\Gamma/2)A_1^{(1,1)}$ correspond to the relaxation processes in (17), where $\Gamma = \Gamma_r + \Gamma_{\text{nr}}$ is the relaxation rate (line width) of the LPR, taking into account the contributions of the radiative (Γ_r) and nonradiative (Γ_{nr}) relaxations; and $\hbar\Omega_{\text{dd}}^{(1)}$ is the matrix element of the energy operator of the dipole–dipole interaction of the nanoparticle and atom. Under conditions of the quasi-static approximation

$$\hbar\Omega_{\text{dd}}^{(1)} = -\frac{\xi n_0}{2r^3} dd_p, \quad (18)$$

where d and d_p are the matrix elements of the dipole moments of the atom and nanoparticle, which are assumed real; n_0 is the refractive index of a transparent medium, into which the atom and nanoparticle are placed; and the factor $\xi = 2$, if the directions of the transition dipole moments are parallel to the straight line connecting the centres of the nanoparticle and atom, and $\xi = -1$, if the directions are perpendicular to this straight line. Expression (18) was obtained in the Appendix. In the first of equations (17), $\gamma = \gamma_r + \gamma_{\text{nr}}$, where γ_{nr} is the emission rate of the emitter into all the higher multipole modes, an explicit expression for which is found in [18]. Higher multipole modes of the nanoparticle virtually do not emit, so that all their energy heats the nanoparticle, and therefore γ_{nr} is the rate of nonradiative losses of the emitter near the nanoparticle.

Introducing the dimensionless time $\tau = (\Gamma/2)t$ we rewrite (17) in the form

$$\begin{aligned} \dot{A}_0^{(1,1)} &= -(\gamma/\Gamma)A_0^{(1,1)} - i\Omega_{11}A_1^{(1,1)}, \\ \dot{A}_1^{(1,1)} &= -A_1^{(1,1)} - i\Omega_{11}A_0^{(1,1)}, \end{aligned} \quad (19)$$

where $\Omega_{11} = 2\Omega_{\text{dd}}^{(1)}/\Gamma$.

Having solved system (19), we can find the wave functions of the system states with a single excitation. However, if for two atoms without a nanoparticle the interaction leads to the

emergence of new, $|\pm\rangle$, mutually orthogonal, $\langle + | - \rangle = 0$, basic states of both atoms, similar mutually orthogonal states of the atom and nanoparticle are, strictly speaking, impossible to construct, since there is dissipation in the system: nonradiative and radiative energy losses of the atom and nanoparticle. Recall that in determining the states of the interacting atoms in the Dicke model the energy dissipation due to the spontaneous emission was neglected, because the rate of the interaction between the atoms was assumed much greater than the rate of spontaneous emission of a single atom. In the case of a nanoparticle the rate Γ is high: $\Gamma \gg \gamma$. Indeed, in our case $\Gamma \sim \Gamma_r$ and is about a few terahertz (see estimates in Section 3.2), while for optical transitions in atoms $\gamma \sim \gamma_r \approx 0.1$ GHz. Thus, the loss in the nanoparticle greatly affects its interaction with the atoms and must be taken into account when determining the collective states. For symmetry and convenience in the first of equations (19) we leave the term describing the radiative and nonradiative losses of the atom, although it is small compared with the second one.

In the general case, instead of (19) one should use the system of equations for the density matrix elements – binary combinations of the coefficients $A_i^{(1,1)}$ ($i = 0, 1$), i.e., populations $|A_i^{(1,1)}|^2$ of the states $|1, 0\rangle|1\rangle$ and $|1, 1\rangle|0\rangle$, and for the off-diagonal elements – products $A_0^{(1,1)}A_1^{(1,1)*}$. However, we consider the case of a weak interaction of the atom and nanoparticle when $\Omega_{11} \ll 1$. For the ordinary parameters of the emitter and the nanoparticle the last relation holds if the emitter is at a distance greater than 15–20 nm from the centre of the nanoparticle; this distance is used in calculations below. Indeed, according to (18) and the well-known formula for the rate of spontaneous emission of a dipole in free space [3]

$$\Omega_{11} = 2\Omega_{\text{dd}}^{(1)}/\Gamma \sim 2\sqrt{\gamma_r \Gamma_r} / [\Gamma(kr)^3] \sim (kr)^{-3} \sqrt{\gamma_r / \Gamma_r},$$

where $k = 2\pi n_0 / \lambda_{\text{LPR}}$, and λ_{LPR} is the LPR wavelength in vacuum. Assuming that $\gamma_r \sim 10^8$ Hz, $\Gamma_r \sim 10^{12}$ Hz, such that $\sqrt{\gamma_r / \Gamma_r} \ll 1$, as well as $\lambda_{\text{LPR}} = 520$ nm and $n_0 = 1.5$ (for a gold nanoparticle in a polymeric shell), we obtain $2\Omega_{\text{dd}}^{(1)}/\Gamma < 0.3 \ll 1$ at $r > 18$ nm. In the general case, energy (18) of the interaction of the nanoparticle and the emitter includes a term proportional to $(kr)^{-3}$ and corresponding to the quasi-static approximation, as well as the terms proportional to $(kr)^{-2}$ and $(kr)^{-1}$. The term corresponding to the quasi-static approximation is at least three times larger than the other terms if $(kr)^3 < 0.1 \ll 1$, which is satisfied for $r < 26$ nm. Thus, the assumptions of the weak interaction and the quasi-static approximation are met in a not very large but finite interval $18 < r < 26$ nm, which is sufficient for the estimates in the first approximation, although for more accurate estimates and a wider interval of r , we should abandon the quasi-static approximation.

Under the conditions $\Omega_{11} \ll 1$ и $\gamma/\Gamma \sim \gamma_r/\Gamma_r \ll 1$ in (19) we can eliminate adiabatically $A_1^{(1,1)}$, by setting $\dot{A}_1^{(1,1)} = 0$. Then, $A_1^{(1,1)} = -i\Omega_{11}A_0^{(1,1)}$, and this expression is substituted into the first equation (19), after which it is reduced to the relation $\dot{A}_0^{(1,1)} = -(\gamma/\Gamma + \Omega_{11}^2)A_0^{(1,1)}$. Thus, it turns out that the state of the system with a single excitation (either the atoms or the nanoparticle is excited) is the only one and can be approximately, up to terms proportional to Ω_{11}^2 , described by the wave function

$$|\Psi_{11}\rangle = a_0^{(1,1)}(|1, 1\rangle|0\rangle - i\Omega_{11}|1, 0\rangle|1\rangle), \quad (20)$$

where $a_0^{(1,1)} = 1/\sqrt{1 + \Omega_{11}^2} \approx 1$ is determined from the normalisation condition $\langle \Psi_{11} | \Psi_{11} \rangle = 1$. Since the state with this energy is the only one, the issue of its orthogonality to any other state does not arise. The population W_{11} of state (20) decreases exponentially due to the radiative and nonradiative transitions to the state $|1, 0\rangle|0\rangle$ with the rate $\gamma + \Gamma\Omega_{11}^2$ and increases because the same transitions with the rate Γ from the state $|1, 1\rangle|1\rangle$. Note that for the weak interaction ($\Omega_{11} \ll 1$), the increment of the attenuation of state (20) is purely real, i.e., a change in the radiation frequency of the emitter and nanoparticle, compared to the radiation frequency of the emitter in free space, can be neglected up to terms proportional to Ω_{11}^2 .

We can write the system of equations of the population balance:

$$\begin{aligned} \dot{W}_{12} &= -\Gamma W_{12}, \\ \dot{W}_{11} &= \Gamma W_{12} - (\gamma + \Gamma\Omega_{11}^2) W_{11}, \\ \dot{W}_{10} &= (\gamma + \Gamma\Omega_{11}^2) W_{11}, \end{aligned} \quad (21)$$

where W_{12} and W_{10} are the populations of the states $|1, 1\rangle|1\rangle$ and $|1, 0\rangle|0\rangle$, respectively; and the time is the dimensional value.

To determine the rate of emission of the atom–nanoparticle system, it is necessary in (21) to divide the rates of radiative and nonradiative relaxations. It is obvious that for the transition $|1, 1\rangle|1\rangle \rightarrow |\Psi_{11}\rangle$, for which $\Gamma = \Gamma_r + \Gamma_{\text{nr}}$, the term proportional to Γ_r is the rate of the radiative relaxation, and proportional to Γ_{nr} is that of the nonradiative relaxation. To find out which part of the relaxation rate (proportional to $\gamma + \Gamma\Omega_{11}^2$) of the state $|\Psi_{11}\rangle$ corresponds to the radiative relaxation, and which – to the nonradiative one, we calculate the matrix elements of the dipole moment operator $\hat{d} + \hat{d}_p$ of the atom and the nanoparticle for the transition $|\Psi_{11}\rangle \rightarrow |1, 0\rangle|0\rangle$. The rate of the radiative relaxation is determined by the square of the matrix element $\hat{d} + \hat{d}_p$. With accuracy up to small corrections, proportional to Ω_{11}^2 , and using the condition $d_p \gg d$, which follows from the relations $\Gamma_r/\gamma_r = d_p^2/d^2$ and $\Gamma_r/\gamma_r \gg 1$, we find

$$\begin{aligned} &\langle 1, 0 | \langle 0 | \hat{d} + \hat{d}_p | \Psi_{11} \rangle \\ &= \langle 1, 0 | \langle 0 | (\hat{d} + \hat{d}_p) (|1, 1\rangle|0\rangle - i\Omega_{11}|1, 0\rangle|1\rangle) = d - i\Omega_{11}d_p. \end{aligned}$$

The rate of the radiative relaxation for the transition $|\Psi_{11}\rangle \rightarrow |1, 0\rangle|0\rangle$ is proportional to $|d - i\Omega_{11}d_p|^2$; therefore it is equal to $\gamma_r + \Gamma_r\Omega_{11}^2$. Accordingly, the rate of the nonradiative relaxation of this transition $\gamma + \Gamma\Omega_{11}^2 - (\gamma_r + \Gamma_r\Omega_{11}^2) = \gamma_{\text{nr}} + \Gamma_{\text{nr}}\Omega_{11}^2$.

We have found that because of the interaction of the atom with the nanoparticle, the rate of its emission in free space increases by $\Gamma_r\Omega_{11}^2$ with respect to the rate γ_r of spontaneous emission of the atom without a nanoparticle. When the atom interacts with the nanoparticle, apart from emission there also arises nonradiative relaxation of its excited state due to the absorption of part of radiation of the atom by the nanoparticle, including the excitation of virtually nonradiative multipole modes of vibrations of its electron density. The nonradiative relaxation of the atom occurs at a rate $\gamma_{\text{nr}} + \Gamma_{\text{nr}}\Omega_{11}^2$. Assume that the emitter is not too close to the surface of the nanoparticle (i.e., at a distance of greater than 5 nm

* Basic mutually orthogonal states must include in the general case the states of the thermostat – electromagnetic field modes, where radiation is emitted and through which the emitters and nanoparticle interact.

[18]), so that $\gamma_{nr} \leq \gamma_r$. Because $\Gamma_r, \Gamma_{nr} \gg \gamma_r, \gamma_{nr}$, then $\Gamma_r \Omega_{11}^2 \gg \gamma_r$ and $\Gamma_{nr} \Omega_{11}^2 \gg \gamma_{nr}$ even for $\Omega_{11}^2 \ll 1$ (weak interaction of the atom and nanoparticle).

3.2. Superradiance of N atoms near a spherical nanoparticle

Consider a spherical nanoparticle in a dielectric shell of radius r , the surface of which contains a large number ($N \gg 1$) of atoms (emitters). At the initial instant of time, due to the action of the coherent pulse of the external field they undergo a transition into the excited state, the dipole moments of the transitions from which to the ground state have the same direction. For the reasons of symmetry, for $N \gg 1$ one can assume that the dipole moment of the nanoparticle, excited during the exchange of photons between the nanoparticle and the emitters after their excitation, will have the same direction. Let us make certain of it. Note that in the quasi-static approximation a point dipole-emitter near a spherical nanoparticle interacts with it as if the dipole moment of the nanoparticle were concentrated in its centre. The polarisation direction of an emitter near a nanoparticle generally does not coincide with the direction of the dipole moment of the nanoparticle because the electric dipole radiation of the emitter has both a component parallel to its dipole moment and a component directed along the straight line connecting the centres of the nanoparticle and the emitter (see Fig. 6a). However, if the number N of the emitters in the nanoparticle shell is sufficiently large ($N \gg 1$) and at the initial instant of time they are equally polarised with the excitation pulse, then

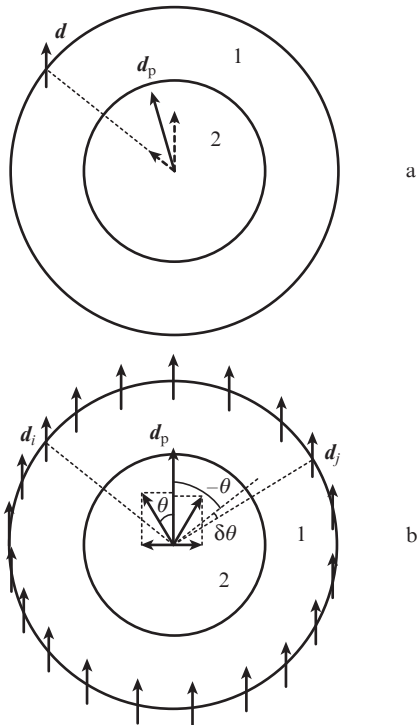


Figure 6. Formulation of the problem (a) with a single emitter on shell 1 of a spherical metal nanoparticle 2 (the direction of the dipole moment of the nanoparticle induced by radiation of the emitter does not coincide in the general case with the direction of the dipole moment of the emitter) and (b) with $N \gg 1$ emitters residing on the shell of a spherical metal nanoparticle and having the same direction of the dipole moments.

the system has a symmetry axis – the direction of the initial polarisation of the emitters. We assume that the emitters are on the surface of the nanoparticle shell, i.e., at the same distance from its centre. Then, the field components of the emitters, parallel to the symmetry axis, are coherently (in phase) summed in the centre of the nanoparticle. The field components of the emitters, perpendicular to the symmetry axis, are mutually eliminated with good accuracy: for each dipole \mathbf{d} , the direction to which from the nanoparticle centre makes an angle θ with the vertical – the direction of the vector \mathbf{d} , we can find another almost axially symmetric dipole the direction to which makes an angle with the vertical close to $-\theta$ (Fig. 6b). Of course, the arrangement of the dipoles lacks the total axial symmetry because the distribution of the emitters on the shell is random. However, if the dipole on the shell is shifted with respect to its middle, axially symmetric position, then this shift is on the order of $2r(\pi/N)^{1/2}$, which is the characteristic size of part of the shell surface per dipole. Accordingly, for $N \gg 1$ the fluctuations $\delta\theta$ with respect to the angle corresponding to the middle, axially symmetric positions of the emitters are small: $\delta\theta \sim \sqrt{\pi/N} \ll 1$. With the same accuracy the field components of the emitters, perpendicular to the symmetry axis, are mutually eliminated and we can assume that the direction of the dipole moment of the nanoparticle coincides with the direction of the dipole moments of the emitters.

We estimate when the energy of the dipole–dipole interaction of the atom with the nanoparticle is small compared to the average energy of the interaction between this atom and other $N - 1 \approx N$ atoms on the surface of the shell of the particle:

$$\frac{n_0 d d_p}{r^3} \ll N n_0 d^2 \left\langle \frac{1}{r^3} \right\rangle, \quad (22)$$

where $\langle 1/r^3 \rangle$ denotes averaging over all the atoms. One can estimate that the $\langle 1/r^3 \rangle \leq 1/r^3$. Taking into account the last inequality and expressing condition (22) through the rates $\Gamma_r \propto d_p^2$ and $\gamma_r \propto$ of spontaneous emission of the emitter and the nanoparticle, we obtain that (22) is satisfied if

$$\Gamma_r / \gamma_r \ll N^2. \quad (23)$$

For a spherical nanoparticle of radius a we can obtain an expression [5]

$$\Gamma_r = \frac{2n_0^3 a^3 \omega^4}{(1 + 2n_0^2)^2 c^3},$$

where ω is the LPR frequency, and c is speed of light in vacuum. For $a = 10$ nm the rate $\Gamma_r = 7$ THz for gold or silver nanoparticles. Assuming $\gamma_r \approx 0.1$ GHz for the dipole allowed transitions of the emitter, we obtain that condition (23) is met for $N \gg 260$, i.e., the surface of the nanoparticle shell should contain at least 500–1000 emitting atoms.

We assume that the number of emitters is large enough and condition (23) holds. Then, we can assume that the collective states (Dike states) of the emitters are formed and these states will interact with the nanoparticle. The operator of the dipole–dipole interaction of the nanoparticle and collective states of the emitters

$$\hat{V}_{dd} = -(n_0/2) \left[\hat{d}_p \sum_{i=1}^N \hat{d}_i^+ (-1 + 3 \cos^2 \theta_i) / r_i^3 + \text{c. c.} \right],$$

where θ_i is the angle between the direction of the dipole moment of the i th atom and the segment of length r_i , connecting the centres of the i th nanoparticle and atom (Fig. 6b). Due to the fact that the quantity $(-1 + 3\cos^2\theta_i)/r_i^3$ varies from atom to atom, the matrix elements \hat{V}_{dd} will be different from zero not only for the transitions between symmetric states of the emitters, which is quite important, if the number of the emitters is on the order of about 1. However, for a large number of emitters such transitions can be neglected. Indeed, in describing the nanoparticle we use its ‘macroscopic’ field, which is proportional to the total dipole moment \hat{d}_p , associated with oscillations of a large number of conduction electrons, rather than its ‘microscopic’ field, which is the sum of fields from each electron separately. Similarly, we can use a macroscopic field of the shell containing a large number of emitters, which is proportional to the total dipole moment of the shell, $\sum_{i=1}^N \hat{d}_i$. Therefore, the expression for the operator \hat{V}_{dd} of the dipole–dipole interaction between the nanoparticle and collective states of a large number of emitters can be written with high accuracy in the form

$$\begin{aligned}\hat{V}_{dd} &= -\frac{n_0}{2r^3} \left(\hat{d}_p \sum_{i=1}^N \hat{d}_i^+ + \text{c. c.} \right) (-1 + 3\langle \cos^2\theta \rangle) \\ &= -\frac{n_0}{4r^3} \left(\hat{d}_p \sum_{i=1}^N \hat{d}_i^+ + \text{c. c.} \right),\end{aligned}\quad (24)$$

where the angle brackets denote averaging over all the atoms. The matrix element \hat{V}_{dd} , given by (24), is nonzero if the matrix element $\sum_{i=1}^N \hat{d}_i$ is different from zero, which only takes place for the transitions between the symmetric states of the atoms. The matrix elements of transition (24) between the states $|N, n_e - 1\rangle |n_p + 1\rangle$ and $|N, n_e\rangle |n_p\rangle$ with the same energy are

$$\begin{aligned}\langle n_p | \langle N, n_e | \hat{V}_{dd} | N, n_e - 1 \rangle | n_p + 1 \rangle \\ = \langle n_p + 1 | \langle N, n_e - 1 | \hat{V}_{dd} | N, n_e \rangle | n_p \rangle \\ = \hbar \Omega_{dd} [(N - n_e + 1) n_e (n_p + 1)]^{1/2},\end{aligned}$$

where $n_e = n - n_p$;

$$\hbar \Omega_{dd} = -\frac{n_0}{4r^3} d d_p. \quad (25)$$

We assume that the interaction of the emitters and the nanoparticle is weak; therefore, no more than one plasmon is excited in it, i.e., $n_p = 0, 1$, and the system has no more than $N + 1$ excitations. The system states with the same energy, similar to (16), are

$$A_0^{(N,n)} |N, n\rangle |0\rangle + A_1^{(N,n)} |N, n - 1\rangle |1\rangle, \quad n = 1, \dots, N; \quad (26)$$

the coefficients $A_0^{(N,n)}$, $A_1^{(N,n)}$ are determined from the equations

$$\begin{aligned}\dot{A}_0^{(N,n)} &= -(\gamma_n^{(N)}/\Gamma) A_0^{(N,n)} - i\Omega_{Nn} A_1^{(N,n)}, \\ \dot{A}_1^{(N,n)} &= -A_1^{(N,n)} - i\Omega_{Nn} A_0^{(N,n)},\end{aligned}\quad (27)$$

and $\dot{A}_1^{(N,N+1)} = -A_1^{(N,N+1)}$. In equations (27), $\gamma_n^{(N)}$ is the rate of emission of N atoms, some of which have n excited atoms, determined by (9);

$$\Omega_{Nn} = 2(\Omega_{dd}/\Gamma)[(N - n + 1)n]^{1/2}; \quad (28)$$

use is made of the dimensionless time $\tau = \Gamma t/2$. We assume that, as in the case of an atom and a nanoparticle, the interaction is weak ($\Omega_{Nn} \ll 1$) and the plasmon relaxation is rapid ($\gamma_n^{(N)}/\Gamma \ll 1$). Then, adiabatically excluding $A_1^{(N,n)}$ from (27) and assuming there $\dot{A}_1^{(N,n)} = 0$, we find

$$\begin{aligned}A_1^{(N,n)} &= -i\Omega_{Nn} A_0^{(N,n)}, \\ \dot{A}_0^{(N,n)} &= -(\gamma_n^{(N)}/\Gamma + \Omega_{Nn}^2) A_0^{(N,n)}\end{aligned}\quad (29)$$

and the wave function of the state of the ‘emitters – nanoparticle with n excitations’ system

$$|\Psi_{Nn}\rangle = (1 + \Omega_{Nn}^2)^{-1/2} (|N, n\rangle |0\rangle - i\Omega_{Nn} |N, n - 1\rangle |1\rangle). \quad (30)$$

Solving (29) and using (9) and (28) we obtain that the population $W_{Nn} = |A_0^{(N,n)}|^2$ the state with the wave function (30) decreases due to radiative and nonradiative relaxations with the rate

$$\Gamma_{Nn} = (N - n + 1)n[\gamma + 4(\Omega_{dd}^2/\Gamma)]. \quad (31)$$

The system thus relaxes into the state $|\Psi_{N, n-1}\rangle$, but the value W_{Nn} increases with the rate $\Gamma_{N, n+1}$ due to the transition $|\Psi_{N, n+1}\rangle \rightarrow |\Psi_{Nn}\rangle$. Calculating the matrix elements of the operator

$$\hat{d}_{\text{tot}} = \hat{d}_p + \sum_{i=1}^N \hat{d}_i$$

of the total dipole moment of the nanoparticle and atoms for the transition $|\Psi_{Nn}\rangle \rightarrow |\Psi_{N, n-1}\rangle$, we find an expression

$$\begin{aligned}\langle \langle N, n - 1 | \langle 0 | + i\Omega_{Nn} \langle N, n - 2 | \langle 1 | \\ \times \left(\hat{d}_p + \sum_{i=1}^N \hat{d}_i \right) (|N, n\rangle |0\rangle - i\Omega_{Nn} |N, n - 1\rangle |1\rangle) = \\ = \sum_{i=1}^N \langle \langle N, n - 1 | \hat{d}_i | N, n \rangle - i\Omega_{Nn} d_p\end{aligned}$$

with the accuracy up to terms of order of $\Omega_{Nn}^2 \ll 1$. Calculating the squares of the moduli of the matrix elements \hat{d}_{tot} , we determine the rates

$$\gamma_{Nn} = (N - n + 1)n[\gamma_r + 4\Gamma_r(\Omega_{dd}/\Gamma)^2]$$

of the radiative relaxation at the transitions $|\Psi_{Nn}\rangle \rightarrow |\Psi_{N, n-1}\rangle$. Neglecting the fast process – plasmon relaxation from the excited state, we obtain a system of rate equations for the populations W_{Nn} of the states $|\Psi_{Nn}\rangle$:

$$\begin{aligned}\dot{W}_{NN} &= -\Gamma_{NN} W_{NN}, \\ \dots\dots\dots \\ \dot{W}_{Nn} &= \Gamma_{N, n+1} W_{N, n+1} - \Gamma_{Nn} W_{Nn}, \\ \dots\dots\dots \\ \dot{W}_{N0} &= \Gamma_{N1} W_{N1}.\end{aligned}\quad (32)$$

Thus, under conditions of a strong interaction between the emitters when there exist their symmetric states, the nanoparticle changes the process of superradiance of atoms so that due to an increase in the rate of spontaneous emission of a single atom the rate of superradiance increases. Due to the absorption of radiation of atoms by a nanoparticle, there occurs a nonradiative relaxation of the populations of the excited states of atoms, which, as the rate of superradiance, increase because of the interaction of atoms.

4. Characteristics of superradiance near a metal nanoparticle

4.1. Time dependence of the superradiance pulse power

As for superradiance of several atoms, in this case, we can find the exact solution of the system of balance equations (32) by solving it from the first equation, and then determine the rate of superradiance. For the latter, we can obtain an analytic expression similar to (14) if we neglect the fluctuations in the number of excited atoms. The radiance power of N atoms near the nanoparticle is

$$P_N^p(t) = \frac{d\langle n \rangle}{dt} - [\gamma_{nr} + 4\Gamma_{nr}(\Omega_{dd}/\Gamma)^2]\langle (N - n + 1)n \rangle, \quad (33)$$

where the second term on the right-hand side is the average rate of nonradiative decay of populations of states of the atoms; and

$$\langle (N - n + 1)n \rangle = \sum_{n=1}^N W_{Nn} (N - n + 1)n. \quad (34)$$

The expression for $d\langle n \rangle/dt$ will be the same as expression (14) obtained in the Dicke model for atoms without a nanoparticle, but instead of γ_r one must substitute

$$\gamma_p = \gamma + 4\Omega_{dd}^2/\Gamma$$

i.e., the total rate of decay of the population of a single atom near the nanoparticle. Considering that at the initial instant of time all the atoms are excited and neglecting quantum fluctuations, i.e., making the substitution $\langle n^2 \rangle \approx \langle n \rangle^2$, by analogy with (14) we obtain

$$\begin{aligned} \frac{d\langle n \rangle}{dt} &\equiv \gamma_p \langle (N - n + 1)n \rangle \\ &= \gamma_p \left(\frac{N+1}{2} \right)^2 \operatorname{sech}^2 \left[\frac{N+1}{2} \left(\gamma_p t - \frac{\ln N}{N+1} \right) \right]. \end{aligned} \quad (35)$$

Form (33)–(35) we find the superradiance power of the atoms in the presence of a nanoparticle:

$$P_N^p(t) = \gamma_{pr} \left(\frac{N+1}{2} \right)^2 \operatorname{sech}^2 \left[\frac{N+1}{2} \left(\gamma_p t - \frac{\ln N}{N+1} \right) \right], \quad (36)$$

where $\gamma_{pr} = \gamma_r + 4\Gamma_r(\Omega_{dd}/\Gamma)^2$ is the rate of spontaneous emission of an atom near a nanoparticle, averaged over the positions of the atoms. Result (36) is quite understandable. In the case of weak interactions between atoms and a nanoparticle ($\Omega_{dd}/\Gamma \ll 1$), the latter accelerates the superradiance in the same degree as the radiation of a single atom. In this case, the

nanoparticle absorbs part of the energy that the atoms had at the initial instant time, the rate of energy absorption also increasing as the rate of emission of a single atom near the nanoparticle. Only part (γ_{pr}/γ_p) of the energy stored by the atoms at the initial instant of time is radiated with a delay $(N+1) \times (\gamma_p \ln N)^{-1}$ in the form of a superradiance pulse with a duration $\{[(N+1)/2]\gamma_p\}^{-1}$.

4.2. Estimate of the superradiance power and energy

The superradiance power P_N^p can be expressed through the parameters of the nanoparticle. To this end, let us represent P_N^p in γ_r units and in the dependence on the dimensionless time $\tau = \gamma_r t$:

$$\gamma_r^{-1} P_N^p(\tau) = F_r \left(\frac{N+1}{2} \right)^2 \operatorname{sech}^2 \left[\frac{N+1}{2} \left(F_p \tau - \frac{\ln N}{N+1} \right) \right], \quad (37)$$

where $F_p = 1 + \gamma_{nr}/\gamma_r + 4\Omega_{dd}^2/(\gamma_r \Gamma)$ is the factor that describes an emitter-averaged increase, with respect to γ_r , in the rates of radiative and nonradiative relaxations, and $F_r = 1 + (\Gamma_r/\Gamma)4\Omega_{dd}^2/(\gamma_r \Gamma)$ is the factor that describes an increase in the radiative relaxation of the excited state of an atom near a nanoparticle. Guzatov and Klimov [18] derived expressions for γ_{nr} ,

$$\gamma_{nr}^{\parallel} = \frac{3\gamma_r \Gamma_{nr}}{2\Gamma_r} \frac{1}{(r/a - 1)^3}, \quad \gamma_{nr}^{\perp} = \frac{\gamma_{nr}^{\parallel}}{2},$$

for the cases, when the dipole moments of emitter transitions are directed, respectively, along and perpendicular to the axis connecting the centres of the nanoparticle and the emitter. However, under these conditions considered here the dipole moment of the emitter makes an angle θ to the mentioned axis (Fig. 6b). We can assume that the initial pulse excites the emitter to a state with a transition dipole moment that is parallel to the emitter axis – the centre of the nanoparticles, with a probability $\cos^2\theta$. Averaging over the emitters on the surface of a spherical shell gives an average probability of excitation in the direction parallel to the axis $\cos^2\theta = 1/2$ (and the same – in the perpendicular direction); therefore,

$$\frac{\gamma_{nr}}{\gamma_r} = \frac{1}{2\gamma_r} (\gamma_{nr}^{\parallel} + \gamma_{nr}^{\perp}) = \frac{9\Gamma_{nr}}{4\Gamma_r} \frac{1}{(r/a - 1)^3}. \quad (38)$$

Taking into account relation (25), the expression for the rate of spontaneous emission of an emitter is $\gamma_r = 4n_0\omega^3 d^2/(3hc^3)$. We can also derive the same expression for the Γ_r , but with the substitution of d by d_p and the relation for $\Gamma = \Gamma_r + \Gamma_{nr}$,

$$\frac{4\Omega_{dd}^2}{\gamma_r \Gamma} = \frac{9}{64(kr)^6} \frac{1}{1 + \Gamma_{nr}/\Gamma_r}, \quad (39)$$

where $k = \omega/c$ is the LPR wavenumber. Substituting (38) and (39) into the expressions for F_p and F_r , we find

$$\begin{aligned} F_p &= 1 + \frac{9\Gamma_{nr}}{4\Gamma_r} \frac{1}{(r/a - 1)^3} + \frac{9}{64(kr)^6} \frac{1}{1 + \Gamma_{nr}/\Gamma_r}, \\ F_r &= 1 + \frac{9}{64(kr)^6} \frac{1}{(1 + \Gamma_{nr}/\Gamma_r)^2}. \end{aligned} \quad (40)$$

For a spherical nanoparticle of radius a

$$\frac{\Gamma_{nr}}{\Gamma_r} = \frac{\varepsilon''(\omega)}{2(ka)^3 n_0^5}, \quad (41)$$

where $\varepsilon''(\omega)$ is the absolute value of the imaginary part of the dielectric constant of the nanoparticle at the LPR frequency. Relation (41) follows from the well-known dispersion equation for the dipole mode of the nanoparticle [19]. The expression for the polarisability α_p of a spherical nanoparticle of radius a has the form [20]

$$\alpha_p = a^3(\varepsilon - n_0^2)/(2n_0^2 + \varepsilon), \quad (42)$$

where $\varepsilon(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega)$ is the dielectric constant of the metal of the nanoparticle. The LPR frequency of the nanoparticle is determined from the condition for the vanishing real part of the denominator in (42):

$$\varepsilon'(\omega) = -2n_0^2. \quad (43)$$

The dielectric constant of the metal of the nanoparticle is described by the Drude formula

$$\varepsilon(\omega) = 1 - \omega_p^2/(\omega^2 + i\Gamma_{nr}\omega), \quad (44)$$

where ω_p is the plasma frequency. For silver, we use the same parameters as in [21]: $\hbar\Gamma_{nr} = 0.067$ eV, $\hbar\omega_p = 8.04$ eV. For gold, according to [22], $\hbar\Gamma_{nr} = 0.045$ eV, $\hbar\omega_p = 8.45$ eV. The emitters are arranged on the surface of the dielectric shell of the metal nanoparticle, the refractive index of the shell is $n_0 = 1.5$ and the particles themselves are in a transparent medium (e.g., water) with approximately the same refractive index. Using the above data and ignoring in (44) the term $\Gamma_{nr}\omega$ as compared with ω^2 , from (43) and (44) we determine the LPR frequency ω and $\varepsilon''(\omega)$ at this frequency:

$$\omega = \frac{\omega_p}{(2n_0^2 + 1)^{1/2}}, \quad \varepsilon''(\omega) = \frac{\omega_p^2 \Gamma_{nr}}{\omega^3}.$$

From these expression, for the LPR of a silver (gold) nanoparticle we obtain an estimate $\hbar\omega = 3.43$ (3.6) eV, which corresponds to the LPR wavenumber in vacuum $k = 0.017$ (0.018) nm⁻¹ and $\varepsilon''(\omega) = 0.107$ (0.069).

Figure 7 shows the time dependences of the superradiance pulse power for $N = 500$ atoms on the surface of a dielectric shell of radius 25 nm of a spherical silver or gold nanoparticle of radius 10 nm. Curves (1) and (2) were calculated accord-

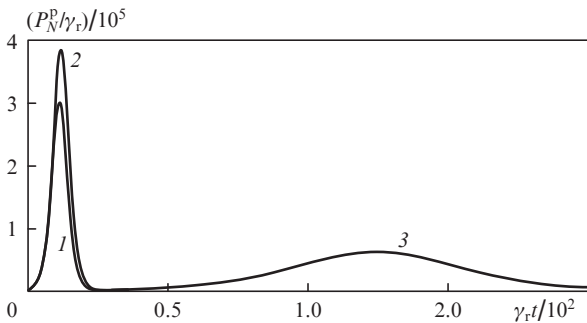


Figure 7. Superradiance pulse powers of 500 emitters on the surface of a spherical shell of radius 25 nm of (1) silver and (2) gold spherical nanoparticles of radius 10 nm and (3) on the surface of a dielectric spherical nanoparticle of radius 25 nm.

ing to formula (37). For comparison, Fig. 7 shows curve (3) – superradiance pulse of 500 atoms on the surface of a dielectric nanoparticle, obtained with the help of (14). Superradiance pulses (1) and (2) in the presence of a nanoparticle contain part (F_r/F_p) of the stored energy: pulse (1) – 44%, and pulse (2) – 59%. The superradiance pulse (3) in the absence of a nanoparticle contains all the initial energy of the atoms.

5. Conclusions

Assuming that the number of emitters near a metal nanoparticle is large (more than several hundred), so that the interaction between the emitters is much stronger than the interaction of each emitter and a nanoparticle, and that there exist symmetrical Dicke states of the emitters, the rate of superradiance near a nanoparticle increases, compared to the rate of superradiance of the emitters in the absence of a nanoparticle, in the same manner as the rate of spontaneous emission of an emitter near a nanoparticle. At the same time, due to the absorption by the nanoparticle, only part, F_r/F_p , of the energy stored by the emitters radiates, where F_r and F_p are given by (40). For a gold or silver nanoparticle of 10 nm in radius, the radiated energy, as follows from Fig. 7 and our estimates, is approximately 50% of the stored energy. We have derived an analytical expression for the time dependence of the superradiance pulse power in the Dicke model approximations, in particular by neglecting the quantum fluctuations in the number of the excited emitters and inhomogeneous broadening of the emitter transitions. The superradiance pulse near a metal nanoparticle proves sufficiently shorter, and its delay is much less than in the absence of the nanoparticle.

Sufficiently high superradiance energy is what differs our results from the numerical calculation [13], where the energy of no more than three emitters of the total number (several dozens) was transferred into the superradiance pulse. The reason for the difference consists in our assumption about the existence of symmetric states of the emitters near a nanoparticle. The substantiation for this assumption is as follows: at a sufficiently large number of the emitters in the shell of a nanoparticle, the interaction of the emitter with all the other emitters becomes stronger than its interaction with the nanoparticle. In this case, we can assume that the collective states (Dicke states) are formed in the system emitters and these states interact with the nanoparticle. Collective spontaneous emission of the emitters is accelerated by the nanoparticle, where part of radiation is absorbed therein.

Note that the same large number of the emitters is required to observe the nonlinear effects in a dipole (plasma) nanolaser [23]: the generation threshold and narrowing of its line. It is possible that a large (at least several hundred) number of the emitters in low- Q plasmonic nanoscale systems are a common condition for observation of nonlinear effects in them, an example of which is the superradiance. If the number of the emitters is relatively small – a few dozen or less (with a radius of the nanoparticle and its shell of about tens of nanometres), the result of [13], or close to it, can be valid for superradiance. Pustovit and Shahbazyan [13] assumed that the emitters are incoherently excited: their excited states at the initial instant of time corresponded to arbitrary directions of the dipole moments of the transitions to the ground state. We considered a simpler case of coherent excitation of the emitters to the state with the same direc-

tion of the transition dipole moment. Obviously, the initial coherent excitation increases the efficiency of the interaction of the emitters with each other. This is another reason for the fact that in our case the energy of a superradiance pulse is much higher than in [13].

The assumption that, even in the absence of a nanoparticle, only collective, totally symmetric Dicke states are excited requires a more rigorous study and determination of the range of parameters for which it is well fulfilled. In similar systems without a metal nanoparticle, this assumption is no longer valid because of the difference in the interaction of each of the emitters with other emitters and the corresponding inhomogeneous broadening (self-broadening) [16]. As a result, during emission excited are not only bright, totally symmetric states of the emitters, but also dark, nonsymmetric states. If the dark states are excited quite effectively (in fact, cease to be dark), then there arises a superradiance pulse: partially dark state will, sooner or later, radiate, which will lead to the destruction of a superradiance pulse. In the case of a nanoparticle, as pointed out in [13], the dark states can also interact effectively with higher multipole modes of the nanoparticle, which may not only lead to the pulse broadening, but also to a further reduction of its energy. On the other hand, it follows from Fig. 7 that if there exist the Dicke states of the emitters, superradiance occurs very rapidly, during a time of ~ 10 ps. Efficient excitation of the dark modes of the emitters and higher multipole modes of the nanoparticle in such a short time may not be possible. Furthermore, if the emitters are arranged at a distance of more than 5–10 nm from the nanoparticle surface, their interaction with higher multipole modes of the nanoparticle is unlikely to significantly affect the superradiance, because the effective interaction of the emitter with these modes occurs when the distance from the emitter to the nanoparticle surface is less than 5 nm [18].

Self-broadening of the state of the emitters near a nanoparticle requires a separate study. It is determined by fluctuations of the energy of the interaction of the emitters with each other: the more uniformly the emitters are distributed in the shell, the less the fluctuations of their interaction energy and self-broadening. In addition, in the case of a metal nanoparticle the superradiance pulse is much shorter than without it, and self-broadening of the emitters' transitions is same in both cases. It gives hope for the observation of a superradiance pulse of the emitters near the metal nanoparticle, which may have occurred in [4]. It is likely that suitable will be elongated ellipsoid or cylindrical nanoparticles, or nanowires rather than spherical nanoparticles. Note that in experiments superradiance in the absence of a nanoparticle was observed in elongated, extended systems [16].

The above estimates show that under certain conditions it is possible to obtain a superradiance pulse in a system of emitters in the vicinity of a metal nanoparticle with the energy which forms a significant part (tens of percent) of the energy stored by the emitters. These results will be useful in developing a plasmon nanolaser based on superradiance, in analogy with 'superradiant' lasers experimentally investigated in [24]. Such nanolasers can be used to produce narrow optical beams in the same manner as phased antenna arrays are used in the radio frequency range. It is possible that the effect of acceleration of superradiance of the emitters near a metal nanoparticle will be useful for generation of short pulses.

Appendix. Energy of the dipole–dipole interaction of a nanoparticle and an atom

The operator of the dipole moment of the atom $\hat{d}\exp(-i\omega t) + \hat{d}^+\exp(i\omega t)$ has matrix elements $d\exp(-i\omega t)$ and $d^*\exp(i\omega t)$ of the transitions, respectively, from the excited to the ground state of the atom and vice versa. The matrix elements can be considered real: $d^* = d$. The electric field $[\hat{E}_p\exp(-i\omega t) + \hat{E}_p^+\exp(i\omega t)]/2$ from the nanoparticle at the place of the position of the atom is also the operator, because it depends on the amplitudes \hat{d}_p and \hat{d}_p^+ of the operator $\hat{d}_p\exp(-i\omega t) + \hat{d}_p^+\exp(i\omega t)$ of the dipole moment of the nanoparticle. For small distances r between the atom and the nanoparticle such that the $kr \ll 1$ ($k = 2\pi n_0 c/\omega$, n_0 is the refractive index of the transparent medium in which the atom and nanoparticle are placed), $\hat{E}_p = \xi n_0 d_p/r^3$, where $\xi = 2$ if the directions of the transition dipole moments are parallel to the straight line connecting the centres of the nanoparticle and the atom, and $\xi = -1$ if the directions are perpendicular to this line. Thus, the operator of the energy of the dipole–dipole interaction of the nanoparticle and the atom

$$\begin{aligned} & -\left[\hat{d}\exp(-i\omega t) + \hat{d}^+\exp(i\omega t)\right]\frac{1}{2}[\hat{E}_p\exp(-i\omega t) + \hat{E}_p^+\exp(i\omega t)] \\ & = -\frac{1}{2}(\hat{d}\hat{E}_p^+ + \hat{d}^+\hat{E}_p) = -\frac{\xi n_0}{2r^3}(\hat{d}\hat{d}_p^+ + \hat{d}^+\hat{d}_p), \end{aligned}$$

and its matrix element

$$\langle 1, 1 | \langle 0 | -\frac{\xi n_0}{2r^3}(\hat{d}\hat{d}_p^+ + \hat{d}^+\hat{d}_p) | 1, 0 \rangle | 1 \rangle = -\frac{\xi n_0}{2r^3} dd_p.$$

References

1. Rycenga M., Cogley C.M., Zeng J., Li W., Moran C.H., Zhang Q., Qin D., Xiaet Y. *Chem. Rev.*, **111**, 3669 (2011).
2. Dicke R.H. *Phys. Rev.*, **93**, 99 (1954).
3. Allen L., Eberly J.H. *Optical Resonance and Two-Level Atoms* (New York: Dover Publications, Inc., 1987; Moscow: Mir, 1978).
4. Noginov M.A., Zhu G., Belgrave A.M., Bakker R., Shalaev V.M., Narimanov E.E., Stout S., Herz E., Suteewong T., Wiesner U. *Nature*, **460**, 1110 (2009).
5. Protsenko I.E., Uskov A.V., Rudoi V.M. *Zh. Eksp. Teor. Fiz.*, **146**, 265 (2014).
6. Richter Th. *Ann. Phys.*, **491**, 266 (1979).
7. Protsenko I.E. *Zh. Eksp. Teor. Fiz.*, **130**, 195 (2006).
8. Protsenko I.E., Uskov A.V., Zaimidoroga O.A., Samoilov V.N., O'Reilly E.P. *Phys. Rev. A*, **71**, 063812 (2005).
9. Nezhad M.P., Simic A., Bondarenko O., Slutsky B.A., Mizrahi A., Fainman Y. *Proc. SPIE Int. Soc. Opt. Eng.*, **7942**, 79420A (2011).
10. Andrianov E.S., Pukhov A.A., Dorofeenko A.V., Vinogradov A.P., Lisyansky A.A. *Opt. Express*, **19**, 24849 (2011).
11. Zhou W., Dridi M., Suh J.Y., Kim C.H., Co D.T., Wasielewski M.R., Schatz G.C., Odom T.W. *Nat. Nanotechnol. Lett.*, **8**, 506 (2013).
12. Fleury R., Alu A. *Phys. Rev. B*, **87**, 201101(R) (2013).
13. Pustovt V.N., Shahbazyan T.V. *Phys. Rev. Lett.*, **102**, 077401 (2009).
14. Protsenko I.E., Uskov A.V. *Usp. Fiz. Nauk*, **185**, 543 (2012).
15. Ikhsanov R.Sh., Protsenko I.E., Uskov A.V. *Pis'ma Zh. Tekh. Fiz.*, **39**, 1 (2013).
16. Andreev A.V., Emel'yanov V.I., Il'inskii Yu.A. *Kooperativnyye yavleniya v optike* (Cooperative Phenomena in Optics) (Moscow: Nauka, 1988).

17. Milonni P.W., Knight P.L. *Phys. Rev. A*, **10**, 1096 (1974).
18. Guzatov D.V., Klimov V.V. *Chem. Phys. Lett.*, **412**, 341 (2005).
19. Klimov V.V. *Nanoplazmonika* (Nanoplasmonics) (Moscow: Fizmatlit, 2009) p. 120.
20. Landau L.D., Lifshitz E.M. *Electrodynamics of Continuous Media* (Oxford: Pergamon Press, 1984; Moscow: Fizmatlit, 2001).
21. Khurgin J.B., Sun G. *J. Opt. Soc. Am. B*, **26**, B83 (2009).
22. Olmon R.L., Slovick B., Johnson T.W., Shelton D., Oh S.-H., Boreman G.D., Raschke M.B. *Phys. Rev. B*, **86**, 235147 (2012).
23. Protsenko I.E. *J. Russ. Laser Res.*, **33**, 559 (2012).
24. Bohnet J.G., Chen Z., Weiner J.M., Meiser D., Holland M.J., James K., Thompson J.K. *Nature*, **484**, 78 (2012).