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Two-photon absorption of light emitted in a two-photon process

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Two-photon absorption of light emitted in two-photon spontaneous emission in the decay of metastable levels of atoms or ions is considered. It is shown by a quantum-mechanical calculation that the simultaneity of the emission of the two photons in such spontaneous emission leads to a sharp increase of the probability of two-photon absorption as compared with the case of light from ordinary sources. The probability of two-photon absorption is determined by the large instantaneous intensity of the two-photon spontaneous emission and does not depend on the mean intensity of the light beam.

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1. INTRODUCTION

As is well known, two-photon absorption of light is a nonlinear process and depends essentially on the fluctuations of the intensity of the light. In the present paper it is shown that two-photon spontaneous emission from metastable atoms or ions is a source of light whose fluctuations change the character of the two-photon absorption as compared with that of light from ordinary sources.

According to existing ideas, the photons emitted in a single act of spontaneous emission come out almost simultaneously, in a time interval of the order of the optical period; this interval can be estimated by applying the uncertainty principle to the intermediate state of the radiating system. Experimental studies[1–5] of two-photon spontaneous emission from atoms and ions by means of photon-coincidences confirm the simultaneity of the emissions to within the limits of experimental error. A quantum-mechanical calculation made in the present paper shows that owing to the grouping of the photons in time in two-photon simultaneous emission, such radiation is perceived by a two-photon absorber as radiation of large instantaneous intensity. This instantaneous intensity determines the effectiveness of two-photon absorption.

The probability of two-photon excitation of an absorbing atom, calculated per two-photon decay in the source, is independent of the mean luminous flux.

In order to increase the probability of two-photon absorption it is necessary to eliminate the divergence in space of the simultaneously emitted photons, say by focusing the spontaneous radiation with a concave mirror. In this case the coefficient of two-photon absorption of the light emitted in two-photon processes [see Eq. (4) of the present paper] is mainly governed by the same physical factors as the coefficient of ordinary one-photon absorption—the concentration n_0 of absorbing atoms and the ratio of the radiation width Γ of the metastable level to the Doppler width ω_d of the absorbing transition.

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2. THE PROBABILITY OF TWO-PHOTON ABSORPTION OF LIGHT EMITTED IN A TWO-PHOTON PROCESS

Let us consider two identical atoms a and b at a distance R ($\mathbf{R}=\mathbf{R}_b-\mathbf{R}_a$) from each other; a is the source and b the absorber in a case of two-photon spontaneous emission. We denote by $|0\rangle$ and $|l\rangle$ the ground and metastable state of each atom, and by $|l\rangle$ and $|n\rangle$ higher-energy states of each atom ($|l\rangle$ in atom a and $|n\rangle$ in atom b). Here $l=\{\alpha_1, I_1, M_1\}$ is a complete set of quantum numbers, I_1 being the quantum number for the total electronic angular momentum and M_1 the corresponding magnetic quantum number.

In each atom the direct transition $l\to 0$ is forbidden, but the transition $l\to 0$ and $l\to 1$ are allowed (the interaction of the atoms with the electromagnetic field is here considered in the dipole approximation).

As the result of the two-photon emission, atom a goes from the metastable state 1 to the ground state 0. The two-photon absorption takes atom b from the ground state 0 to state 1. The initial and final states of the electromagnetic field are vacuum states. We determine the quantum-mechanical amplitude for the transition $|1^a, 0^b\rangle\to|0^a, 1^b\rangle$ by calculating the effective matrix element V_{eff} of the radiative interaction between the atoms, taken between the states $|1^a, 0^b\rangle$ and $|0^a, 1^b\rangle$.

Because of the motion of the atoms in the absorbing gas the absorption two-quantum transition is subject to a broadening (Doppler broadening, or transit-time broadening if the incident light is focused). We describe this broadening by introducing the distribution $\rho(\omega)$ of the frequency ω_{10} of the absorbing atoms ($\hbar\omega_{10}=E_1-E_0$). The probability per unit time W of the transition $|1^a, 0^b\rangle\to|0^a, 1^b\rangle$ is then given by

$$W=\frac{2\pi}{\hbar^2}|V_{eff}|^2\rho(\omega), \tag{1}$$

where ω is the value of ω_{10} for the emitting atom. The conditional probability for excitation of the absorbing atom, referred to one act of two-photon emission in the source, is W/Γ.

In fourth-order perturbation theory of the interaction between the atoms and the quantized electromagnetic field the quantity V_{eff} is given by the processes of photon emission and absorption shown in Fig. 1. In these diagrams for the quantum-mechanical amplitude the upper horizontal line describes the state of atom a and the lower line, that of atom b. The dotted lines correspond to photons, and a summation is made over their wave vectors $\mathbf{k}'$, $\mathbf{k}''$ and polarization λ', λ''. It is also necessary to sum over the intermediate states l, n of the atoms.

The calculation of the effective matrix element is given in the Appendix. We shall now assume that the distance R is much larger than the wavelength λ_{10}. Confining ourselves for simplicity to the case in which the angular momenta of states 0 and 1 are both zero, $I_1=I_0=0$, we sum Eq. (12) of the Appendix over the magnetic quantum numbers M_1, M_n of the intermediate states and get

$$-\frac{i}{\hbar}V_{eff}=\frac{1}{9\pi}\frac{1}{\hbar^2c}\frac{\exp(ik_{10}R)}{R^2}\sum_{l,n}(1\|d\|n)(n\|d\|0)(0\|d\|l)(l\|d\|1)$$
$$\times\int_0^{k_{10}}dk\,k^2(k_{10}-k)^2\left\{\frac{1}{k+k_n}\frac{1}{k_{10}-k}+\frac{1}{k+k_{l1}}\frac{1}{k+k_{n1}}\right\}. \tag{2}$$

Here $l=\{\alpha_1, I_1\}$, $k_{ij}=(\hbar c)^{-1}(E_i-E_j)$, and we have used the usual notation for the reduced matrix element of the atomic dipole moment operator $\mathbf{d}$. Equations (1) and (2) make the probability W proportional to R^{-4}. The physical meaning of this dependence is clear; for each emitted photon there is a spatial divergence factor of $(4\pi R^2)^{-1}$. To increase the probability of two-photon absorption, it is necessary to focus the radiation from atom a into the smallest possible region containing the absorbing atom. If a concave mirror is used for the focusing, taking in a solid angle Ω of the radiation and concentrating it on an area S, then in the formula for W we must replace $(4\pi R^2)^{-2}$ with $S^{-2}(\Omega/4\pi)^2$.

We note that when the light is focused into a small region of space (comparable in extent with the wavelength λ_{10}), the frequency distribution $\rho(\omega)$ used in Eq. (1) for the absorbing atoms is determined by the time of passage through the region of focusing. This passage-time effect, which is a uniform broadening, can be estimated in terms of the Doppler width ω_d by setting $\rho(\omega)\to\omega_d^{-1}$.

The probability W/Γ for two-photon absorption depends on the ratio of the quantities $-iV_{eff}/\hbar$ and Γ. The constant Γ for two-photon decay of a metastable level has been considered in many papers (see, for example, [6,7]). The general formula for Γ can readily be reduced, for $I_0=I_1=0$, to the following form:

$$\Gamma=\frac{8}{27\pi}\frac{1}{\hbar^2c}\sum_{l,n}(1\|d\|n)(n\|d\|0)(0\|d\|l)(l\|d\|1)$$
$$\times\int_0^{k_{10}}dk\,k^3(k_{10}-k)^3\left\{\frac{1}{k+k_{n1}}\frac{1}{k_{10}-k}+\frac{1}{k+k_{l1}}\frac{1}{k+k_{n1}}\right\}. \tag{3}$$

Comparing Eq. (2) and (3), we see that the integrands in the expressions for $-iV_{eff}/\hbar$ and Γ differ by the factor $k(k_{10}-k)$. We take this factor in Eq. (3) out from under the integral sign, using for it the constant value $k_{10}^2/4$ (its value at the point $k=k_{10}/2$, where the product of the photon weight functions is a maximum).

Assuming that $n_0S^{3/2}$ atoms take part in the absorption of two simultaneously emitted photons, where n_0 is the concentration of atoms in the absorbing gas and $S^{1/2}$ is a linear dimension of the focusing region, we find for the total probability of two-photon absorption of the emitted photons the following estimate[1)]:

$$P=n_0S^{3/2}W/\Gamma=n_0S^{3/2}\frac{2\pi}{\hbar^2}\left|\frac{V_{eff}}{\Gamma}\right|^2\Gamma\rho(\omega)\approx\frac{9}{32\pi^3}n_0\frac{\Gamma}{\omega_d}\frac{\Omega^2\lambda_{10}^4}{S^{3/2}}. \tag{4}$$

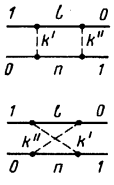

FIG. 1. Processes of radiative interaction of two atoms.

If the mirror collects radiation over a fairly large solid angle, $\Omega \gtrsim 1$, and the focusing is into a region with linear dimensions of the order of a wavelength, $S^{1/2} \sim \lambda_{10}$, we get in principle a value $P \sim n_0 \lambda^3 \Gamma / \omega_d$ for the probability of two-photon absorption.

A point of fundamental interest is the difference between this result and the relations which hold for two-photon excitation of an atom in the field of a monochromatic running or standing wave.[8,9] Two-photon excitation of an atom in the field of a monochromatic wave is a nonlinear process whose probability per unit time increases quadratically with the intensity of the light. The dependence of the rate of two-photon absorption on the mean intensity will also be nonlinear for any radiation with a fixed level of relative fluctuations in the intensity. On the other hand, as has been shown here, the dependence of two-photon absorption on the mean intensity is not nonlinear if the radiation comes from a source as the result of two-photon spontaneous transitions.

The reason for this is found in the following temporal properties of two-photon spontaneous emission. In such emission the emission of the first photon leads to a state of the complete system with an energy which differs from the initial energy by an amount of the order of the distance Δ between levels. According to the uncertainty relation, the emitting atom cannot remain in the intermediate state much longer than a time $\tau \sim \Delta^{-1}$; that is, the emission of the second photon follows after a time interval of the order of an optical period. The emission from a given atom is a "pulse" with total energy $\hbar\omega_{10}$ and a large instantaneous intensity, which is determined by the structure of the energy levels of the atom and does not depend on the mean value of the light flux. It is precisely this instantaneous intensity which determines the probability of two-photon absorption, and therefore the value of P depends only on the energy-level pattern of the atoms and on the experimental geometry.

What has been said is confirmed by the following rough calculation. Let us consider two-photon absorption in the field of a running wave with frequency $\omega_L = \omega_{10}/2$ and find the intensity of this wave for which the probability P_L of absorption of light quanta from the wave in a layer of matter of thickness $\sim \lambda_L$ (i.e., in the same distance as the size of the focusing region) is equal to the probability P of Eq. (4). For the probability per unit time for two-photon excitation of an atom in the field of a running wave (see Refs.[8,9]) we have the following estimate: $W_L \sim d^4 \Delta^4 I^2 / \hbar^2 c^6 \omega_d$, where d is the matrix element of the dipole moment, Δ is the frequency of the transition (which we take to be of the order of magnitude of the resonance defect for the intermediate state), and I is the flux per second of photons through an area λ_L^2. Noting that $\Gamma \sim d^4 \Delta^5 / \hbar^2 c^6$, we get for the probability $P_L = n_0 \lambda_L^3 W_I / I$ the value $P_L \sim n_0 \lambda_L^3 \Gamma I / \omega_d \Delta$, from which it follows that $P_L \sim PI/\Delta$. Accordingly, the nonlinear coefficient for two-photon absorption of a laser wave in a layer $\sim \lambda_L$ is comparable with the coefficient of two-photon absorption of (focused) two-photon spontaneous emission if the wave intensity is such that a photon of the laser light passes through an area λ_L^2 during one optical period. We note that for $\omega_{10} \sim 1.5 \cdot 10^{16}$ sec^{-1}, $\lambda_{10} \sim 1200$ Å (the two-photon transition $2S \to 1S$ in hydrogen) the corresponding intensity of the light beam is 10^8 W/cm^2.

In conclusion the writer thanks E. B. Aleksandrov, who suggested this problem to him, for his interest in the work and valuable discussions.

APPENDIX

We calculate the effective matrix element V_{eff}. The quantity $-iV_{\text{eff}}/\hbar$ is given by the Laplace transform of the sum of the perturbation-theory terms represented by Fig. 2, taken at $s = 0$ (s is the Laplace variable).[2)]

We can put the result of the summation over the direction of the wave vector and over the polarization of the photon in each photon line in the form

$$\sum_{\lambda} \int \frac{d\Omega_{\mathbf{k}}}{4\pi} (\mathbf{d}_{nm}\mathbf{e}_{\mathbf{k}\lambda})(\mathbf{e}_{\mathbf{k}\lambda}\mathbf{d}_{lp}) \exp(\pm i\mathbf{kR}) = \frac{\exp(ikR)}{ikR} N_{lp}^{nm}(k, \mathbf{R}) - \frac{\exp(-ikR)}{ikR} N_{lp}^{nm}(-k, \mathbf{R}), \tag{5}$$

where

$$\sum_{\mathbf{k},\lambda} \to \frac{L^3}{(2\pi)^3} \sum_{\lambda} \int \frac{d\Omega_{\mathbf{k}}}{4\pi} \int_0^{\infty} k^2\, dk,$$

$$N_{lp}^{nm}(k, \mathbf{R}) = 2\pi \left\{ (\mathbf{d}_{nm}\mathbf{d}_{lp}) \left(1 + \frac{i}{kR} - \frac{1}{(kR)^2}\right) + (\mathbf{d}_{nm}\hat{\mathbf{R}})(\hat{\mathbf{R}}\mathbf{d}_{lp}) \left(-1 - \frac{3i}{kR} + \frac{3}{(kR)^2}\right) \right\}. \tag{6}$$

Here $\mathbf{d}_{nm}$ is the matrix element of the operator for the dipole moment of the atom, $d\Omega_k$ is an element of solid angle, $\hat{\mathbf{R}}$ is the unit vector in the direction of $\mathbf{R}$, and L^3 is the quantization volume. We start here from the operator for the interaction of the atom with the quantized electromagnetic field, given by $-(\mathbf{d} \cdot \mathbf{E})$. As has been shown,[10] in the dipole approximation the term $-(\mathbf{d} \cdot \mathbf{E})$ is equivalent to the complete interaction, i.e., it includes also the interaction of the atoms via the longitudinal electromagnetic field (concerning the choice of the interaction operator for the treatment of two-photon processes see also Ref.[11]).

We note that the factor appearing in the photon line from the product of the matrix elements and the density of photon states is an odd function of k [the result of the averaging in Eq. (5) is an even function, and the factor k^3 from the density of photon states and the matrix elements is odd]. We also make use of the fact that the

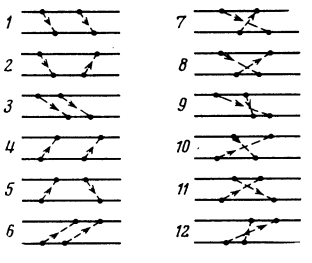

FIG. 2. Contributions to the quantity $-iV_{\text{eff}}/\hbar$ (the instants at which the photons are emitted and absorbed are time-ordered).

dependence on one of the photon momenta can be represented in the form

$$\int_0^\infty dk\left(\frac{F(k)}{k+\Delta}+\frac{F(k)}{k-\Delta}\right)=\int_{-\infty}^{\infty} dk\frac{F(k)}{k+\Delta}, \tag{7}$$

where $F(k)=-F(-k)$, and the integration can be done by means of Cauchy's theorem. For the sum of the contributions 1–6 in Fig. 2 this is accomplished by reducing the expression constructed, for particular quantum numbers n, 1, from the energy denominators to the form

$$\begin{aligned}M_{1n}^{(1)}=&\frac{1}{k_{l1}+k_{n0}}\left\{\frac{1}{k''+k_{n1}}\left(\frac{1}{k'+k''-k_{10}-is}+\frac{1}{k'-k''+k_{10}+is}\right)\right.\\&+\frac{1}{k'+k_{l1}}\left(\frac{1}{k''+k'-k_{10}-is}+\frac{1}{k''-k'+k_{10}+is}\right)\\&+\frac{1}{k''+k_{10}}\left(\frac{1}{k'+k''+k_{10}+is}+\frac{1}{k'-k''-k_{10}-is}\right)\\&\left.+\frac{1}{k'+k_{n0}}\left(\frac{1}{k''+k'+k_{10}+is}+\frac{1}{k''-k'-k_{10}-is}\right)\right\},\end{aligned} \tag{8}$$

and that for the sum of contributions 7–12 in Fig. 2 to the form

$$\begin{aligned}M_{1n}^{(2)}=&\frac{1}{k'+k_{l1}}\frac{1}{k'+k_{n1}}\left(\frac{1}{k''+k'-k_{10}-is}+\frac{1}{k''-k'+k_{10}+is}\right)\\&+\frac{1}{k''+k_{n0}}\frac{1}{k''+k_{10}}\left(\frac{1}{k'+k''+k_{10}+is}+\frac{1}{k'-k''-k_{10}-is}\right).\end{aligned} \tag{9}$$

For the effective matrix element we find

$$\begin{aligned}-\frac{i}{\hbar}V_{eff}=&\frac{1}{i(2\pi)^4\hbar^2c}\frac{1}{R^2}\sum_{l,n}\int_0^\infty k'^2\,dk'\int_0^\infty k''^2\,dk''\\&\times\{M_{1n}^{(1)}[\exp(ik'R)N_{n0}^{tl}(k',\mathbf{R})-(k'\leftrightarrow -k')]\\&\times[\exp(ik''R)N_{1n}^{t0}(k'',\mathbf{R})-(k''\leftrightarrow -k'')]\\&+M_{1n}^{(2)}[\exp(ik'R)N_{1n}^{tl}(k',\mathbf{R})-(k'\leftrightarrow -k')]\\&\times[\exp(ik''R)N_{n0}^{t0}(k'',\mathbf{R})-(k''\leftrightarrow -k'')]\}.\end{aligned} \tag{10}$$

In each term of this expression one integration (over k' or over k'') can be done as we have indicated. Some of the terms so obtained contain an oscillating function $\exp(\pm 2ikR)$ in the integrand for the remaining integration. We drop these terms, since in the case with which we are concerned, when the distance between the atoms is much larger than the wavelength ($k_{10}R\gg 1$), their contribution is negligibly small. In the other terms, with $k_{10}R\gg 1$, we set

$$N_{lp}^{nm}(k,\mathbf{R})\to N_{lp}^{nm}(\hat{\mathbf{R}})=2\pi[(\mathbf{d}_{nm}\mathbf{d}_{lp})-(\mathbf{d}_{nm}\hat{\mathbf{R}})(\hat{\mathbf{R}}\mathbf{d}_{lp})]. \tag{11}$$

After some manipulations we finally obtain the following expression for the effective matrix element:

$$\begin{aligned}-\frac{i}{\hbar}V_{eff}=&\frac{1}{(2\pi)^3}\frac{1}{\hbar^2c}\frac{\exp(ik_{10}R)}{R^2}\sum_{l,n}\int_0^{k_{10}}dk\,k^2(k_{10}-k)^2\\&\times\left\{\frac{1}{k+k_{n1}}\frac{1}{k_{10}-k}N_{1n}^{t0}(\hat{\mathbf{R}})N_{n0}^{tl}(\hat{\mathbf{R}})+\frac{1}{k+k_{n1}}\frac{1}{k+k_{l1}}N_{1n}^{tl}(\hat{\mathbf{R}})N_{n0}^{t0}(\hat{\mathbf{R}})\right\}.\end{aligned} \tag{12}$$

[1)] Since we do not take into account the attenuation of the light intensity within the extent of the absorbing volume, we must restrict ourselves to the case $P\ll 1$.

[2)] It is easy to see that we are here neglecting the retardation time of the light over the distance R. A sufficient condition for this approach to the calculation of the probability is that the retardation time be small compared with the characteristic times of the system associated with radiative, collision, and inhomogeneous broadening.

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