Two-Photon Absorption and Coherence*

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We study the probabilities for two-photon absorption processes induced by both coherent and thermal light when acting on an atomic system. Calculations are performed with quantum electrodynamics, and we find results similar to those obtained with semiclassical methods; that is, the two-photon absorption probability depends on the statistical properties of the light used. This probability assumes its maximum value for coherent light.

I. INTRODUCTION

THE purpose of this work is to analyze whether and how the two-photon transition probability induced by a packet of light acting on an atomic system depends on the statistical properties of this packet, and to calculate its value (a) for a coherent beam and (b) for thermal light. In previous work Iannuzzi and Polacco[1] had predicted that the two-photon absorption probability, which can be observed when an atomic system is made to interact with a laser beam, would depend strongly on the structure of the beam; more exactly, that the probability obtainable with a normal laser would be n times smaller than the one which can be obtained with a Q-switched laser at the same energy, where n is the number of spikes present in the beam.

The results of those calculations, which were obtained in a semiclassical way, have been subsequently criticized by Guccione and Van Kranendonk[2] who claim that the two-photon transition probability does not depend on the statistical properties of the light employed. Later Lambropoulos, Kikuchi, and Osborn[3] came to the conclusion that the transition probability for coherent light depends on the phase of the light employed and that the result, which may be obtained by averaging over the different phases, is a factor of 2 smaller than the transition probability obtainable with thermal light. We think it worth noting that both authors[2,3] employ only monochromatic light in their considerations, whereas up to now experiments have been carried out only with packets of very short duration; moreover, the dependence of the two-photon transition probability on the phase of the incident coherent radiation, as deduced by Lambropoulos *et al.*,[3] appears to have no direct physical application. If we introduce[4] the concept of polychromatic light into our considerations, it appears that the phase relation among the different Fourier components of the packet, and not the absolute phase, plays an important role. It is also clear that only in a coherent packet will such phase relations cause single components of the packet to enhance the two-photon transition probability, and therefore make the coherent-light probability remarkably greater than the incoherent-light probability. As has already been mentioned, we shall evaluate in the present work the two-photon absorption probability both for a laser beam and for thermal light, and we shall carry out the calculations within the framework of quantum electrodynamics.

For the characterization of a coherent packet we shall make use of a pure coherent polychromatic state and we shall establish the phase relations among the single Fourier components. For this packet we have $\tau_l\Delta\nu\approx 1$, where τ_l is its duration. In order to analyze the transition probability caused by thermal light we shall use blackbody radiation in thermal equilibrium, which can be represented by a density-operator diagonal in the occupation numbers, appropriately filtered through a linear filter,[5] to obtain the same spectrum as that of our coherent packet. With this kind of light an atomic system will be illuminated for an interval τ with $\tau>\tau_c$, where τ_c is the coherence time defined[6] by $\tau_c\Delta\nu\approx 1$. As a consequence of this hypothesis we find that the transition probability for thermal light is proportional, in the ratio τ_c/τ, to the probability which is obtained with coherent light of the same energy. We can understand our result for the dependence of the transition probability for thermal light on radiation time, by the following intuitive argument. Let us consider two packets with the same total energy, the same frequency spectrum, and the same cross section, but let us suppose that the duration of the first packet is τ_1, and that the duration of the second is τ_2, with $\tau_2=\tau_1/2$. It is clear that under such a hypothesis, if $\mathcal{E}_1$ and $\mathcal{E}_2$ are the amplitudes of electric fields for the two packets, then $\langle\mathcal{E}_1^2\rangle=\frac{1}{2}\langle\mathcal{E}_2^2\rangle$ and therefore the two-photon absorption probability per unit time induced by the former packet will be a quarter of the probability induced by the latter (since this quantity is proportional to the square of radiation intensity). Therefore if we consider the different durations, it follows that the total transition probabilities $\mathcal{P}_1$ and $\mathcal{P}_2$ are such that $\mathcal{P}_2=2\mathcal{P}_1$. This argument does not apply to a coherent packet because establishing

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[1] M. Iannuzzi and E. Polacco, Phys. Rev. **138**, A806 (1965); Phys. Rev. Letters **13**, 371 (1964).

[2] R. Guccione and J. Van Kranendonk, Phys. Rev. Letters **14**, 583 (1965).

[3] P. Lambropoulos, C. Kikuchi, and R. K. Osborn, Phys. Rev. **144**, 1081 (1966).

[4] G. Fornaca, M. Iannuzzi, and E. Polacco, Nuovo Cimento **36**, 1230 (1965).

[5] A linear filter is a filter that changes the spectral response but not the statistical properties of radiation.

[6] L. Mandel and E. Wolf, Rev. Mod. Phys. **37**, 231 (1965).

the radiation width is equivalent to establishing its duration.

II. PROPERTIES OF LASER AND THERMAL RADIATION

The vector potential $\mathbf{A}=\mathbf{A}^{(+)}+\mathbf{A}^{(-)}$ may be expressed in terms of the annihilation and creation operators $a_{k,s}$ and $a_{k,s}^\dagger$ for photons of momentum $\hbar\mathbf{k}$ and polarization s ($s=1, 2$) in the form

$$\mathbf{A}^{(+)}=\left(\frac{2\pi\hbar c}{L_1L_2L_3}\right)^{1/2}\sum_{k,s} k^{-1/2}\boldsymbol{\varepsilon}_{k,s}a_{k,s}\exp[i(\mathbf{k}\cdot\mathbf{r}-ckt)],$$

$$\mathbf{A}^{(-)}=\left(\frac{2\pi\hbar c}{L_1L_2L_3}\right)^{1/2}\sum_{k,s} k^{-1/2}\boldsymbol{\varepsilon}_{k,s}^*a_{k,s}^\dagger\exp[-i(\mathbf{k}\cdot\mathbf{r}-ckt)],$$

where L_1, L_2, and L_3 give the dimensions of the quantization volume in the x, y, and z directions of a space-fixed coordinate system. The $a_{k,s}$ and $a_{k,s}^\dagger$ obey the commutation relations

$$[a_{k,s};\, a_{k',s'}]=[a_{k,s}^\dagger;\, a_{k',s'}^\dagger]=0,\qquad [a_{k,s};\, a_{k',s'}^\dagger]=\delta_{k,k'}\delta_{s,s'},$$

and the $\boldsymbol{\varepsilon}_{k,s}$ form a set of complex orthogonal unit vectors with

$$\boldsymbol{\varepsilon}_{k,s}^*\cdot\boldsymbol{\varepsilon}_{k,s'}=\delta_{s,s'},\quad \mathbf{k}\cdot\boldsymbol{\varepsilon}_{k,s}=0;$$

we consider only the transverse components of the field because the transverse part is the only part leading to observable effects.

A. Laser Radiation

In the Glauber P representation,[7] the density operator ρ of a field may be written

$$\rho=\int P(\{\alpha_{k,s}\})|\{\alpha_{k,s}\}\rangle\langle\{\alpha_{k,s}\}|d^2\{\alpha_{k,s}\},$$

where $|\{\alpha_{k,s}\}\rangle=\prod_{k,s}|\alpha_{k,s}\rangle$, $d^2\alpha=d(\mathrm{Re}\alpha)d(\mathrm{Im}\alpha)$, and $|\alpha_{k,s}\rangle$ is a pure coherent state defined by

$$a_{k,s}|\alpha_{k,s}\rangle=\alpha_{k,s}|\alpha_{k,s}\rangle.$$

For the matrix density of a laser beam we write

$$P(\{\alpha_{k,s}\})=\frac{1}{2\pi}\int_0^{2\pi}\prod_{k,s}P_{k,s}(\alpha_{k,s})d\bar\theta,\tag{1}$$

where

$$P_{k,s}(\alpha_{k,s})=\delta^{(2)}\{v_{k,s}\exp(i\bar\theta)-\alpha_{k,s}\},\tag{1'}$$

and

$$\delta^{(2)}(\alpha)=\delta(\mathrm{Re}\alpha)\delta(\mathrm{Im}\alpha).$$

Without loss of generality we can let $v_{k,s}$ be real. The $\bar\theta$ integration in Eq. (1) is necessary in view of our complete ignorance of the phase of the high-frequency field.[7] We recall that the square of $v_{k,s}$ represents the average photon number $\langle n_{k,s}\rangle$ of the $\mathbf{k}$ mode and s polarization. Thus the density matrix of a laser beam is

$$\rho_l=\frac{1}{2\pi}\int_0^{2\pi}d\bar\theta|\{v_{k,s}\exp(i\bar\theta)\}\rangle\langle\{v_{k,s}\exp(i\bar\theta)\}|,\tag{2}$$

and if we introduce Fock states[8] it has the form

$$\rho_l=\frac{1}{2\pi}\sum_{\{n\},\{m\}}\int_0^{2\pi}d\bar\theta\times\prod_{k,s}\exp(-v_{k,s}^2)v_{k,s}^{n_{k,s}+m_{k,s}}(n_{k,s}!m_{k,s}!)^{-1/2}\times\exp[i(n_{k,s}-m_{k,s})\bar\theta]|\{n_{k,s}\}\rangle\langle\{m_{k,s}\}|.\tag{3}$$

The Poynting vector[9] operator at $P(\mathbf{r})$ and t is

$$\mathbf{S}(\mathbf{r},t)=-\frac{1}{2}\frac{\hbar c^2}{L_1L_2L_3}\sum_{k_1,s_1}\sum_{k_2,s_2}\mathbf{k}_2\left(\frac{\omega_1}{\omega_2}\right)^{1/2}\boldsymbol{\varepsilon}_{k_1,k_1}^*\cdot\boldsymbol{\varepsilon}_{k_2,s_2}\times\{a_{k_1,s_1}\exp[i(\mathbf{k}_1\cdot\mathbf{r}-ck_1t)]-a_{k_1,s_1}^\dagger\exp[-i(\mathbf{k}_1\cdot\mathbf{r}_1-ck_1t)]\}\times\{a_{k_2,s_2}\exp[i(\mathbf{k}_2\cdot\mathbf{r}-ck_2t)]-a_{k_2,s_2}^\dagger\exp[-i(\mathbf{k}_2\cdot\mathbf{r}-ck_2t)]\},\tag{4}$$

and so the mean value of this operator for the coherent beam represented by Eq. (2) is

$$\langle\mathbf{S}(\mathbf{r},t)\rangle=\mathrm{Tr}\{\rho_l\mathbf{S}(\mathbf{r},t)\}=\frac{\hbar c^2}{L_1L_2L_3}\sum_{k_1,s_1}\sum_{k_2,s_2}\mathbf{k}_2\times(\omega_1/\omega_2)^{1/2}\boldsymbol{\varepsilon}_{k_1,s_1}^*\cdot\boldsymbol{\varepsilon}_{k_2,s_2}\langle n_{k_1,s_1}\rangle^{1/2}\langle n_{k_2,s_2}\rangle^{1/2}\times\cos[(\mathbf{k}_1-\mathbf{k}_2)\cdot\mathbf{r}-c(k_1-k_2)t].\tag{5}$$

We suppose now that the field is only formed by plane waves which propagate in the z direction and which are linearly polarized along the x axis with unit vector $\boldsymbol{\varepsilon}$.

[7] R. Glauber, Phys. Rev. 131, 2766 (1963).

[8] The pure coherent state of the field may be written

$$|\alpha_{k,s}\rangle=\exp(-\tfrac{1}{2}|\alpha_{k,s}|^2)\sum_n\frac{\alpha_{k,s}^n}{(n!)^{1/2}}|n_{k,s}\rangle,$$

where the $|n_{k,s}\rangle$ are Fock states.

[9] A. I. Akhiezer and V. B. Berestetskii, *Quantum Electrodynamics* (Interscience Publishers, Inc., New York, 1965), p. 161.

Hence Eq. (5) becomes

$$\langle S(\mathbf{r},t)\rangle=\frac{\hbar c^2}{L_1L_2L_3}\sum_{k_1,k_2}(k_1k_2)^{1/2}\langle n_{k_1}\rangle^{1/2}\langle n_{k_2}\rangle^{1/2}\times\cos[(k_1-k_2)(z-ct)]. \quad (5a)$$

We now replace the summation over k by an integral, according to the usual rule,[10]

$$\frac{1}{L_3}\sum_k\to\frac{1}{2\pi}\int dk\,,\qquad \langle n_k\rangle\to(2\pi/L_3)N(k). \quad (6)$$

In order to have a quasimonochromatic wave with central frequency ck_0, we choose[10]

$$N(k)=\pi^{-1/2}ln\exp[-l^2(k-k_0)^2], \quad (7)$$

with l much larger than $1/k_0$, where n is the average number of photons which are present in the laser beam. It follows from Eqs. (5a), (6), and (7) that

$$\langle S(\mathbf{r},t)\rangle_l=\frac{\hbar c^2}{2L_1L_2}\pi^{-3/2}ln\int dk_1\int dk_2\,(k_1k_2)^{1/2}\times\exp\{-\tfrac{1}{2}l^2[(k_1-k_0)^2+(k_2-k_0)^2]\}\times\cos[(k_1-k_2)(z-ct)], \quad (8)$$

and after the integration we obtain to a very good approximation

$$\langle S(\mathbf{r},t)\rangle_l=\frac{\hbar c^2}{L_1L_2}\pi^{-1/2}nl^{-1}k_0\exp\left[-\frac{1}{l^2}(z-ct)^2\right].$$

We see that the quantity l therefore corresponds to the spatial extension of the packet in the z direction.

The total energy I_{Tl} of the laser light per unit area is expressed by

$$I_{Tl}=\int_{-\infty}^{+\infty}\langle S(\mathbf{r},t)\rangle_l dt=\hbar c\pi^{-1/2}n_0l\times\int k\exp[-l^2(k-k_0)^2]dk=\hbar cn_0k_0\,, \quad (9)$$

where $n_0=n/L_1L_2$ represents the average photon number per unit area. Thus we deduce that the total energy of the laser light per unit area and wave number k is

$$I_l(k)=\hbar c\pi^{-1/2}n_0lk\exp[-l^2(k-k_0)^2]. \quad (10)$$

B. Thermal Radiation

The density operator ρ_t for thermal light in the Fock representation is diagonal and has the following form[6]:

$$\rho_t=\sum_{\{n\}}f(\{n_{k,s}\})|\{n_{k,s}\}\rangle\langle\{n_{k,s}\}|\,, \quad (11)$$

where

$$f(\{n_{k,s}\})=\prod_{k,s}[(1+\langle n_{k,s}\rangle)(1+1/\langle n_{k,s}\rangle)^{n_{k,s}}]^{-1}, \quad (12)$$

and $\langle n_{k,s}\rangle$ is the average number of photons in the $\mathbf{k},s$ mode. The expectation value of the Poynting vector [see Eq. (4)] for the thermal field represented by Eq. (11) is

$$\langle\mathbf{S}(\mathbf{r},t)\rangle_t=\mathrm{Tr}\{\rho_t\mathbf{S}(\mathbf{r},t)\}=\frac{\hbar c^2}{L_1L_2L_3}\sum_{k,s}\mathbf{k}\langle n_{k,s}\rangle.$$

We suppose that the thermal radiation passes a linear filter and that the out-field has a central frequency ck_0, is polarized along the x axis, and that it is propagating in the positive z direction. If the thermal radiation after the linear filter has the same frequency spectrum as that of our laser beam, we can use Eqs. (6) and (7), and we have

$$\langle S(t)\rangle_t=\pi^{-1/2}\hbar c^2ln_1\int k\exp[-l^2(k-k_0)^2]dk\approx\hbar c^2n_1k_0\,, \quad (13)$$

where

$$n_1=n/L_1L_2L_3$$

represents the volumetric density of the average photon number. Thus we may define the spectral intensity of radiation (i.e., the energy per unit area, time, and wave number) as in Eq. (10) in the following manner:

$$I_t(k)=\pi^{-1/2}\hbar c^2ln_1k\exp[-l^2(k-k_0)^2]. \quad (14)$$

III. U-MATRIX CALCULATION

A system of particles in the presence of a radiation field may be described by a Hamiltonian

$$H=H_p+H_r+H_{\mathrm{int}}=H_0+H_{\mathrm{int}}\,,$$

where H_p refers to the particles, H_r refers to the radiation field, H_{int} represents the interaction between the particles and the field, and $H_p+H_r=H_0$. The nonrelativistic interaction Hamiltonian of a charged particle with an electromagnetic field is

$$H_{\mathrm{int}}=-(e/mc)\mathbf{A}\cdot\mathbf{p}+(e^2/2mc^2)\mathbf{A}^2, \quad (15)$$

where the symbols in this equation have the usual meaning.

For the purpose of this paper it will suffice to consider a single atom interacting with the field and to consider only electric-dipole contributions to a transition, and so we neglect the term $\mathbf{A}^2$ of the interaction Hamiltonian. We must now compute the rate at which the two-photon absorption takes place. For this we introduce the time-evolution operator of the system $U(t_2,t_1)$ and the S operator, which in the Dirac picture[11] is related to the

[10] O. Von Roos, Phys. Rev. **135**, A43 (1964).

[11] S. Schweber, *Relativistic Quantum Field Theory* (Harper & Brothers, New York, 1964), Secs. 11.C and 11.E.

time translation $U(t_2,t_1)$ by the formal expression

$$S=U(+\infty,-\infty).$$

We recall that the total density matrix ρ_{Ti}, which describes the field and the atomic system before interaction, is related to the matrix after interaction by

$$\rho_{Tf}=U\rho_{Ti}U^{\dagger}. \tag{16}$$

Making use of the definition

$$\mathcal{H}_{\rm int}=\exp(iH_0t/\hbar)H_{\rm int}\exp(-iH_0t/\hbar),$$

where $H_{\rm int}$ is the Schrödinger operator, we may write the operator as follows[11]:

$$U=1+U_1+U_2\cdots,$$

with

$$U_1=\left(-\frac{i}{\hbar}\right)\int_{t_1}^{t_2}d\tau_1\,\mathcal{H}_{\rm int}(\tau_1),$$

$$U_2=\left(-\frac{i}{\hbar}\right)^2\int_{t_1}^{t_2}d\tau_1\int_{t_1}^{\tau_1}d\tau_2\,\mathcal{H}_{\rm int}(\tau_1)\mathcal{H}_{\rm int}(\tau_2).$$

Thus it is evident that the terms U_1 and U_2 give contributions to the one-photon and two-photon transitions, respectively. In order to evaluate the absorption of the photons by an atomic system we need to introduce in Eq. (15) only the annihilation operator $\mathbf{A}^{(+)}$ evaluated at $\mathbf{r}_0$, the spatial position of the atomic system. Hence we have

$$U_1(t_2,t_1)=\left(\frac{i}{\hbar}\right)\frac{e}{mc}\left(\frac{2\pi\hbar c}{L_1L_2L_3}\right)^{1/2}\sum_{k,s}k^{-1/2}\times\int_{t_1}^{t_2}d\tau\,\exp(iH_0\tau/\hbar)a_{k,s}\times\exp(i\mathbf{k}\cdot\mathbf{r}_0)\boldsymbol{\varepsilon}_{k,s}\cdot\mathbf{p}\exp(-iH_0\tau/\hbar), \tag{17}$$

and

$$U_2(t_2,t_1)=-\frac{e^2}{\hbar^2c^2m^2}\left(\frac{2\pi\hbar c}{L_1L_2L_3}\right)\sum_{k_1,s_1}\sum_{k_2,s_2}(k_1k_2)^{-1/2}\times\int_{t_1}^{t_2}d\tau_1\int_{t_1}^{t_1}d\tau_2\,\exp(iH_0\tau_1/\hbar)a_{k_1,s_1}\times\exp(i\mathbf{k}_1\cdot\mathbf{r}_0)\boldsymbol{\varepsilon}_{k_1,s_1}\cdot\mathbf{p}\exp[iH_0(\tau_2-\tau_1)/\hbar]a_{k_2,s_2}\times\exp(i\mathbf{k}_2\cdot\mathbf{r}_0)\boldsymbol{\varepsilon}_{k_2,s_2}\cdot\mathbf{p}\exp(-iH_0\tau_2/\hbar). \tag{18}$$

For sake of simplicity, without lack of generality, we can suppose the atomic system to be at the origin of our coordinate system, i.e., $\mathbf{r}_0=0$.

IV. ONE- AND TWO-PHOTON ABSORPTION WITH A LASER PACKET

Let $|i\rangle$ and $|f\rangle$ be two stationary states of the atomic system having the energies E_{pi} and E_{pf}. Before the interaction, the atom and field are uncoupled and consequently one can assume that

$$\rho_{Ti}=\rho_{pi}\rho_{li}, \tag{19a}$$

where $\rho_{pi}=|i\rangle\langle i|$ is the density operator of the atom in the initial stationary state $|i\rangle$, and ρ_{li} is the density operator of the field which we suppose to be the laser light described by Eq. (3). So we have

$$\rho_{Ti}=\sum_{\{n\},\{m\}}g(\{n\},\{m\})|i,\{n\}\rangle\langle i,\{m\}|,$$

where

$$g(\{n\},\{m\})=\frac{1}{2\pi}\int_0^{2\pi}d\bar{\theta}\times\prod_{k,s}\exp(-v_{k,s}^2)\frac{v_{k,s}^{\,n_{k,s}+m_{k,s}}}{(n_{k,s}!m_{k,s}!)^{1/2}}\exp[i(n_{k,s}-m_{k,s})\bar{\theta}].$$

If we write the density operator ρ_{Tf} after the interaction as

$$\rho_{Tf}=\rho_{lf}\rho_{pf}, \tag{19b}$$

where ρ_{lf} is the density operator of the field and ρ_{pf} the density operator of the atomic system, then the transition probability of the atom to state $|f\rangle$ is given by $\mathrm{Tr}\{\rho_{Tf}|f\rangle\langle f|\}$. The Eq. (19b) allows us to affirm that[12]

$$\mathrm{Tr}\{\rho_{Tf}|f\rangle\langle f|\}=\mathrm{Tr}\{\rho_{pf}|f\rangle\langle f|\}\mathrm{Tr}\{\rho_{lf}\}. \tag{20}$$

Recalling our assumptions with regard to the field, we need consider only $\mathbf{k}$, s modes with k_x and k_y null, and polarization vector $\boldsymbol{\varepsilon}_s$ equal to $\boldsymbol{\varepsilon}$ in all following calculations. We introduce the following equalities which may be readily derived:

$$|h_1\rangle=\langle f|S_1|\{n_\kappa\},i\rangle=\frac{ie}{\hbar mc}\left(\frac{2\pi\hbar c}{L_1L_2L_3}\right)^{1/2}\times\sum_k k^{-1/2}n_k^{+1/2}\langle f|\boldsymbol{\varepsilon}\cdot\mathbf{p}|i\rangle\int_{-\infty}^{+\infty}dt\times\exp[i(E_{pf}-E_{pi}-\hbar ck)t/\hbar]|\{n_\kappa-\delta_{\kappa k}\}\rangle, \tag{21a}$$

and

$$|h_2\rangle=\langle f|S_2|\{n_\kappa\},i\rangle=-\frac{e^2}{\hbar^2c^2m^2}\left(\frac{2\pi\hbar c}{L_1L_2L_3}\right)\sum_{k_1,k_2}(k_1k_2)^{-1/2}\times n_{k_1}^{1/2}n_{k_2}^{1/2}\langle f|(\boldsymbol{\varepsilon}\cdot\mathbf{p})R(k_1)(\boldsymbol{\varepsilon}\cdot\mathbf{p})|i\rangle\int_{-\infty}^{+\infty}dt\times\exp\{i[E_{pf}-E_{pi}-\hbar c(k_1+k_2)]t/\hbar\}\times|\{n_\kappa-\delta_{\kappa k_1}-\delta_{\kappa k_2}\}\rangle, \tag{21b}$$

where

$$R(k)=(H_p-E_{pi}-\hbar ck)^{-1}.$$

[12] A. Messiah, *Mecanique Quantique* (Dunod Cie., Paris, 1962), Vol. I, pp. 235 and 281.

In order to study the rate at which one-photon absorption takes place we must introduce in Eq. (16) the S_1 corresponding to Eq. (17). So with the help of Eqs. (20) and (21a) we obtain

$$\mathrm{Tr}\{\rho_{Tf}|f\rangle\langle f|\}=\frac{e^2}{\hbar^2m^2c^2}\left(\frac{2\pi\hbar c}{L_1L_2L_3}\right)\sum_{k_1}\sum_{k_2}\sum_{\{n\},\{m\}}g(\{n\},\{m\})(k_1k_2)^{-1/2}(n_{k_1}m_{k_2})^{1/2}$$
$$\times\int_{-\infty}^{+\infty}dt_1\int_{-\infty}^{+\infty}dt_2\exp[i(E_{pf}-E_{pi}-\hbar ck_1)t_1/\hbar-i(E_{pf}-E_{pi}-\hbar ck_2)t_2/\hbar]$$
$$\times|\langle f|\boldsymbol{\varepsilon}\cdot\mathbf{p}|i\rangle|^2\langle\{m_\kappa-\delta_{\kappa k_2}\}|\{n_\kappa-\delta_{\kappa k_1}\}\rangle.\quad(22)$$

If we approximate[13] the preceding expression as follows:

$$\langle\{m_\kappa-\delta_{\kappa k_2}\}|\{n_\kappa-\delta_{\kappa k_1}\}\rangle\approx\langle\{m_\kappa\}|\{n_\kappa\}\rangle,$$

we find that

$$\sum_{\{n\},\{m\}}g(\{n\},\{m\})n_{k_1}{}^{1/2}m_{k_2}{}^{1/2}\langle\{m_\kappa\}|\{n_\kappa\}\rangle=\langle n_{k_1}\rangle^{1/2}\langle n_{k_2}\rangle^{1/2}.$$

If we substitute this last equation in Eq. (22) and take the limiting case of the continuum, following Eq. (6), we get

$$\mathrm{Tr}\{\rho_{Tf}|f\rangle\langle f|\}=\frac{e^2}{\hbar m^2c^3}\frac{(2\pi)^2}{L_1L_2}\int dk_1\int dk_2$$
$$\times(k_1k_2)^{-1/2}N^{1/2}(k_1)N^{1/2}(k_2)\delta(k_{fi}-k_1)$$
$$\times\delta(k_{fi}-k_2)|\langle f|\boldsymbol{\varepsilon}\cdot\mathbf{p}|i\rangle|^2,$$

where $ck_{fi}=\omega_{fi}=(E_{pf}-E_{pi})\hbar^{-1}$. Introducing the properties of the laser light expressed by Eq. (7), and with the approximations used previously, the probability of the one-photon absorption $P_{i\to f}{}^{(1)}$ is expressed by

$$P_{i\to f}{}^{(1)}=\mathrm{Tr}\{\rho_{Tf}|f\rangle\langle f|\}=(2\pi)^2\frac{e^2}{\hbar^2m^2c^4}\frac{1}{k_{fi}{}^2}$$
$$\times I_l(k_{fi})|\langle f|\boldsymbol{\varepsilon}\cdot\mathbf{p}|i\rangle|^2,\quad(23)$$

where $I_l(k_{fi})$ is given by Eq. (10). This result is identical to that obtained with a semiclassical treatment.[14]

For the two-photon absorption, substituting the value of S_2 resulting from Eq. (18) into Eq. (16) and recalling the relations (20) and (21b), we have

$$\mathrm{Tr}\{\rho_{Tf}|f\rangle\langle f|\}=\left(\frac{e^2}{\hbar m^2c^2}\right)^2\left(\frac{2\pi\hbar c}{L_1L_2L_3}\right)^2\sum_{k_1,k_2,k_3,k_4}\sum_{\{n\},\{m\}}g(\{n\},\{m\})(k_1k_2k_3k_4)^{-1/2}(n_{k_1}n_{k_2}m_{k_3}m_{k_4})^{1/2}$$
$$\times\langle f|T(k_1)|i\rangle\langle i|T^\dagger(k_3)|f\rangle\int_{-\infty}^{+\infty}dt_1\int_{-\infty}^{+\infty}dt_2\exp\{i[E_{pf}-E_{pi}-\hbar c(k_1+k_2)]t_1/\hbar-i[E_{pf}-E_{pi}-\hbar c(k_3+k_4)]t_2/\hbar\}$$
$$\times\langle\{m_\kappa-\delta_{\kappa k_3}-\delta_{\kappa k_4}\}|\{n_\kappa-\delta_{\kappa k_1}-\delta_{\kappa k_2}\}\rangle,\quad(24)$$

where

$$T(k)=(\boldsymbol{\varepsilon}\cdot\mathbf{p})R(k)(\boldsymbol{\varepsilon}\cdot\mathbf{p}).$$

Making the following approximation

$$\langle\{m_\kappa-\delta_{\kappa k_3}-\delta_{\kappa k_4}\}|\{n_\kappa-\delta_{\kappa k_1}-\delta_{\kappa k_2}\}\rangle\approx\langle\{m_\kappa\}|\{n_\kappa\}\rangle,$$

we then have[13]

$$\sum_{\{n\},\{m\}}g(\{n\},\{m\})(n_{k_1}n_{k_2}m_{k_3}m_{k_4})^{1/2}\langle\{m_k\}|\{n_k\}\rangle=\langle n_{k_1}\rangle^{1/2}\langle n_{k_2}\rangle^{1/2}\langle n_{k_3}\rangle^{1/2}\langle n_{k_4}\rangle^{1/2}.$$

If we introduce this result into Eq. (24) and take into account Eqs. (6) and (7), we obtain that the probability of two-photon absorption $P_{i\to f}{}^{(2)}$ is given by

$$P_{i\to f}{}^{(2)}=\mathrm{Tr}\{\rho_{Tf}|f\rangle\langle f|\}=\frac{(2\pi)^2e^4}{m^4c^4}\left(\frac{1}{L_1L_2}\right)^2\int dk_1\int dk_2$$
$$\times\int dk_3\int dk_4\,(k_1k_2k_3k_4)^{-1/2}N^{1/2}(k_1)N^{1/2}(k_2)$$
$$\times N^{1/2}(k_3)N^{1/2}(k_4)\delta(k_{fi}-k_1-k_2)\delta(k_{fi}-k_3-k_4)$$
$$\times\langle f|T(k_1)|i\rangle\langle i|T^\dagger(k_3)|f\rangle.$$

Thus if we integrate, remembering that l is very large,

[13] With lengthy calculations it is possible to prove that this approximation is unnecessary.

[14] E. Corinaldesi and F. Strocchi, *Relativistic Wave Mechanics* (North-Holland Publishing Company, Amsterdam, 1963), p. 271.

we get, to a good approximation,

$$P_{i\to f}{}^{(2)}=\frac{16\pi^2e^4}{\hbar^2m^4c^6}\left(\frac{1}{k_{fi}k_0}\right)^2 I_{Tl}{}^2 \exp[-2l^2(k_0-k_{fi}/2)^2] \times|\langle f|T(k_{fi}/2)|i\rangle|^2, \quad (25)$$

where I_{Tl} is expressed by Eq. (9).

Equation (25) gives us the transition probability when the absorption linewidth $\delta\omega$ is much less than the width $\Delta\omega=c/l$ of the incident radiation. On the other hand, if the upper level belongs to a band we have $\Delta\omega\ll\delta\omega$ and we must introduce the line-shape function $g(\omega-\omega_c)$ which we suppose normalized so that

$$\int_0^\infty g(\omega-\omega_c)d\omega=1.$$

So, if $\Delta\omega\ll\delta\omega$, we get for the probability of two-photon absorption

$$\bar{P}_{i\to f}{}^{(2)}=\frac{4\pi^2e^4}{\hbar^2m^4c^6}(2\pi)^{1/2}\frac{1}{k_0{}^4}\Delta\omega g(2\omega_0-\omega_c)I_{Tl}{}^2 \times|\langle f|T(k_0)|i\rangle|^2. \quad (26)$$

V. ONE- AND TWO-PHOTON ABSORPTION WITH THERMAL LIGHT

If we consider the radiation field as consisting of thermal radiation then the density operator ρ_{Ti} of the atom and the field before interaction is diagonal and its expression is given by

$$\rho_{Ti}=\rho_t|i\rangle\langle i|=\textstyle\sum_{\{n\}} f(\{n_k\})|i,\{n_k\}\rangle\langle i,\{n_k\}|,$$

where $f(\{n_k\})$ is defined in Eq. (12). We suppose that the atom interacts with the field in the time interval $(0-\tau)$ which is large compared to characteristic times of atomic transitions and to the coherence time of radiation. According to this assumption, Eqs. (22) and (24) will still be valid, provided that we replace $\sum_{\{n\},\{m\}}\times g(\{n\},\{m\})$ by $\sum_{\{n\}} f(\{n_\kappa\})\delta_{\{n\},\{m\}}$. This substitution is due to the different structure of the density operator of the field.

Moreover, we must modify the limits of integration accordingly in order to take into account that the evolution of the density operator resulting from the interaction can be obtained by applying the time-translation operator instead of the S operator. Therefore, following Eq. (22), the one-photon transition probability is given by the expression

$$\mathrm{Tr}\{\rho_{Tf}|f\rangle\langle f|\}=\frac{2\pi\hbar c}{L_1L_2L_3}\frac{e^2}{\hbar^2c^2m^2}\sum_{k_1,k_2}\sum_{\{n\}} f(\{n_k\})(k_1k_2)^{-1/2} \times(n_{k_1}n_{k_2})^{1/2}|\langle f|\boldsymbol{\varepsilon}\cdot\mathbf{p}|i\rangle|^2\int_0^\tau dt_1\int_0^\tau dt_2 \times\exp[i(E_{pf}-E_{pi}-\hbar ck_1)t_1/\hbar-i(E_{pf}-E_{pi}-\hbar ck_2)t_2/\hbar] \times\langle\{n_\kappa-\delta_{\kappa k_2}\}|\{n_\kappa-\delta_{\kappa k_1}\}\rangle. \quad (27)$$

We recall the equality

$$\textstyle\sum_{\{n\}} f(\{n_\kappa\})(n_{k_1}n_{k_2})^{1/2}\langle\{n_\kappa-\delta_{\kappa k_2}\}|\{n_\kappa-\delta_{\kappa k_1}\}\rangle =\langle n_{k_1}\rangle\delta_{k_1k_2}.$$

If we go into the continuum as in Eq. (6), we can write Eq. (27) in the following form:

$$\mathrm{Tr}\{\rho_{Tf}|f\rangle\langle f|\}=\frac{2\pi\hbar c}{L_1L_2L_3}\frac{e^2}{\hbar^2m^2c^2}\int k^{-1}N(k) \times\left|\int_0^\tau dt\exp[i(E_{pf}-E_{pi}-\hbar ck)t/\hbar]\right|^2 \times|\langle f|\boldsymbol{\varepsilon}\cdot\mathbf{p}|i\rangle|^2dk.$$

If we now introduce the radiation structure expressed by Eq. (7), we obtain that the probability of one-photon absorption for thermal light $P_{i\to f}{}^{(1)}$ is given by

$$P_{i\to f}{}^{(1)}=(2\pi)^2\frac{e^2}{\hbar^2m^2c^4}\frac{1}{k_{fi}{}^2}I_{\tau t}(k_{fi})|\langle f|\boldsymbol{\varepsilon}\cdot\mathbf{p}|i\rangle|^2, \quad (28)$$

where

$$I_{\tau t}(k)=\int_0^\tau I_t(k)dt$$

is the energy irradiated in time τ, which can be readily calculated from Eq. (14).

In Eq. (28) we have made use of the approximation generally employed in perturbation problems,[15] that

$$\left|\int_0^\tau dt\exp[i(E_{pf}-E_{pi}-\hbar ck)t/\hbar]\right|^2\approx\frac{2\pi\tau}{c}\delta(k_{fi}-k).$$

By analogy with Eq. (24) the two-photon transition probability may be written

$$\mathrm{Tr}\{\rho_{Tf}|f\rangle\langle f|\}=\left(\frac{e^2}{\hbar m^2c^2}\right)^2\left(\frac{2\pi\hbar c}{L_1L_2L_3}\right)^2\sum_{k_1,k_2,k_3,k_4}\sum_{\{n\}} f(\{n_k\})(k_1k_2k_3k_4)^{-1/2}(n_{k_1}n_{k_2}n_{k_3}n_{k_4})^{1/2} \times\langle f|T(k_1)|i\rangle\langle i|T^\dagger(k_3)|f\rangle\int_0^\tau dt_1\int_0^\tau dt_2\exp\{i[E_{pf}-E_{pi}-\hbar c(k_1+k_2)]t_1/\hbar-i[E_{pf}-E_{pi}-\hbar c(k_3+k_4)]t_2/\hbar\} \times\langle\{n_\kappa-\delta_{\kappa k_3}-\delta_{\kappa k_4}\}|\{n_\kappa-\delta_{\kappa k_1}-\delta_{\kappa k_2}\}\rangle. \quad (29)$$

[15] A. Messiah, *Mecanique Quantique* (Dunod Cie., Paris, 1964), Vol. II, pp. 627 and 628.

If we go into the continuum after taking account of the following relation

$$\sum_{\{n\}} f(\{n_\kappa\})(n_{k_1}n_{k_2}n_{k_3}n_{k_4})^{1/2} \times\langle\{n_\kappa-\delta_{\kappa k_3}-\delta_{\kappa k_4}\}|\{n_\kappa-\delta_{\kappa k_1}-\delta_{\kappa k_2}\}\rangle = \langle n_{k_1}\rangle\langle n_{k_2}\rangle(\delta_{k_1,k_3}\delta_{k_2,k_4}+\delta_{k_1,k_4}\delta_{k_2,k_3}), \quad (30)$$

then Eq. (29) becomes

$$\mathrm{Tr}\{\rho_{Tf}|f\rangle\langle f|\} = \frac{\pi\tau}{c}\left(\frac{e^2}{hm^2c^2}\right)^2\left(\frac{2\pi hc}{L_1L_2L_3}\right)^2\int dk_1\int dk_2 \times(k_1k_2)^{-1}N(k_1)N(k_2)\delta(k_{fi}-k_1-k_2) \times|\langle f|T(k_1)+T(k_2)|i\rangle|^2.$$

If now we introduce Eq. (7) for the radiation, we have for the two-photon absorption probability with thermal light $P_{i\to f}^{(2)}$

$$P_{i\to f}^{(2)} = 4\left(\frac{\pi}{2}\right)^{1/2}\frac{1}{l}\frac{1}{c\tau}\,\frac{16\pi^2e^4}{h^2m^4c^6}\left(\frac{1}{k_{fi}k_0}\right)^2 I_{\tau t}^2 \times\exp[-2l^2(k_0-k_{fi}/2)^2]|\langle f|T(k_{fi}/2)|i\rangle|^2, \quad (31)$$

where

$$I_{\tau t}=\int_0^\tau I_t dt.$$

Equation (31) gives us the transition probability when $\delta\omega\ll\Delta\omega$, i.e., when the absorption linewidth is much smaller than the width of the incident radiation. On the other hand, if $\Delta\omega\ll\delta\omega$, we can easily perform calculations as in the preceding paragraph.

VI. DISCUSSION AND CONCLUSION

An examination of Eqs. (23) and (28) shows that the one-photon absorption does not depend on the statistical properties of the light employed. In fact, such formulas, which give the transition probability for thermal light and the transition probability for a coherent beam, respectively, are the same. If we compare Eq. (25) with Eq. (31), we notice that they differ from each other by the factor

$$B=4\left(\frac{\pi}{2}\right)^{1/2} l\frac{1}{c\tau}.$$

Introducing the coherence time, this factor may be written in another form

$$B\approx\left(\frac{2}{\pi}\right)^{1/2}\frac{\tau_c}{\tau}. \quad (32)$$

Such an expression shows clearly that the transition probability for two-photon absorption really depends on the statistical properties of the light employed, which is expressed, in this case, by τ_c.

It is easy to see that these considerations are still valid in the two-photon transition $E1E2$ and $E1M1$[2] and so on. So for a laser beam formed by n spikes we have $\tau_c/\tau\approx 1/n$. The dependence of the transition probability, for these interactions, on the statistical properties of light can be made more evident by introducing the second-order correlation function, defined as follows[7]:

$$G^{(1,1)}(\mathbf{r}_1,t_1;\,\mathbf{r}_2,t_2)=\mathrm{Tr}\{\rho\mathbf{A}^{(-)}(\mathbf{r}_1,t_1)\mathbf{A}^{(+)}(\mathbf{r}_2,t_2)\},$$

where ρ is the density operator of the field. From Eq. (12) and with the help of our assumptions on the field we have

$$G^{(1,1)}(\mathbf{r},t_1;\,\mathbf{r},t_2)=\left(\frac{2\pi hc}{L_1L_2L_3}\right)\sum_k k^{-1}\langle n_k\rangle\exp[ick(t_2-t_1)].$$

We observe that in our case the function $G^{(1,1)}$ is independent of $\mathbf{r}$.

Introducing this result into Eq. (29), after considering Eq. (30), and supposing that $|\langle f|T(k)|i\rangle|^2$ is nearly constant for the modes in which the occupation number is evaluated, we may write

$$P_{i\to f}^{(2)}\approx\frac{2}{h^2}\left(\frac{e^2}{m^2c^2}\right)^2|\langle f|T(k_{fi}/2)|i\rangle|^2\int_0^\tau dt_1\int_0^\tau dt_2 \times\exp[ick_{fi}(t_1-t_2)]|G^{(1,1)}(t_1,t_2)|^2.$$

Once more the relation between $P_{i\to f}^{(2)}$ and the correlation function $G^{(1,1)}(t_1,t_2)$ shows the validity of our affirmations. We notice that if in Eq. (32) $\tau_c\approx\tau$ we have $B\approx 1$, and therefore we obtain again the results of Eq. (25).

We have supposed in all our calculations that the $f(\{n_\kappa\})$ represent a set of statistically independent Bose-Einstein distributions. This concept seems to play no role in the transition probability, since it is appears only in Eq. (30). On the contrary, the statistical independence of the photons or of the photon groups is automatically taken care of in the transition probability by supposing that the operator density is diagonal in the Fock states and that $\tau_c<\tau$.