Field-Correlation Effects in Two-Photon Processes

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The rate of two-photon absorption from an arbitrary state of the radiation field, and its dependence on the statistical properties of the field, are studied. It is found that when the density operator of the field factors into a product of single-mode density operators (in which case the modes are statistically independent), the rate depends on the spectral composition of the field. When the density operator is nonfactorable, the process depends on a photon doublet density. Therefore, the information obtained from two-photon experiments in the first case can, in principle, also be obtained from single-photon counting, while in the second case it would require coincidence counting.

1. INTRODUCTION

THE last two years have seen several[1–8] discussions of the connection between radiation field statistics and two-photon processes. The models employed by various authors are not always identical, and often it is difficult to see the relation between the different treatments. Of course, there are good reasons for this disparity. To mention a few: The state of the radiation field in a pulsed laser is not known; the atomic processes involved are not always well understood; and unfortunately, the meaning that different authors attach to the same term—such as coherence—is not always exactly the same.

One result about which all authors are in agreement[1–8] is that in the case of two-photon absorption from a single mode of the radiation field, the rate of the process for light in a chaotic state is twice the rate for light in a pure coherent (in the Glauber[9] sense) state. There is no doubt that in view of the conditions under which two-photon experiments are performed at the present time, the assumption of a single-mode excitation is rather unrealistic. Perhaps this assumption is unrealistic under most circumstances.

Thus it might be worthwhile to consider the general case of multimode excitation of the radiation field, and this has been done to a certain extent in some of the above-mentioned references, especially Refs. 7 and 8. These efforts have concentrated on assuming a model for the state of the field in a pulsed laser, and then comparing the results to the case of thermal light. There is one question, however, that does not seem to have received attention: Given an arbitrary state of the radiation field, how does a two-photon process depend on the state One may then ask under what conditions the results obtained in the literature can also be obtained (as special cases) from this general approach. Furthermore, one would like to know what information about the field a two-photon experiment would give.

It is to these questions that we wish to address ourselves in this paper. To fix matters, we consider the case of two-photon absorption. It has already been shown[5] that similar considerations—with minor modifications—apply to two-photon stimulated emission. We have also chosen a specific atomic system, namely a hydrogenlike atom. We shall be concerned with two-photon transitions from the ground ($1s$) to the $2s$ level which is truly metastable and where the two-photon transition is the lowest order allowed process.[10] The reason for making this choice is threefold. First, the theory of hydrogenlike atoms is well understood so that we can minimize the number of arbitrary assumptions in dealing with the problem. Second, this is a true two-photon transition without real intermediate states, provided that the incident radiation does not contain photons of energy $(E_{2p(1/2)}-E_{1s})$ (see also the discussion in Sec. 3). Third, it is quite likely that the hydrogen atom will be one of the candidates for experimental study of the aspects discussed herein, especially in view of recent advances in ultraviolet laser technology.

In Sec. 2 we derive an expression for the rate of two-photon absorption. We have considered only contributions due to the term $\mathbf{p}\cdot\mathbf{A}$. In the problem treated here this contribution is by far the most dominant. The possibility of contributions due to the term $\mathbf{A}^2$ has been discussed in the literature.[11–14] Its presence does not change the field-statistics aspects of the problem. Broadening of the atomic levels is taken into consideration. The derivation reveals that the rate of two-photon

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transitions depends on a correlation function of the field.

Section 3 is devoted to the study of this correlation function. Previous results are obtained as special cases. Then it is shown that when the density operator of the field is factorable in a product of single-mode density operators, the rate depends on the spectral composition of the field. Since the spectrum can be determined by single-photon counting, it follows that in that case the two-photon process does not give any information that can not be obtained from single-photon counting. When, however, the density operator is not factorable, the process gives information about a photon doublet density, and this information can otherwise be obtained from coincidence-counting experiments. Lastly, in Sec. 4, the results are discussed and compared to the results obtained by other authors.

It has been our intention to keep the essential parts of this analysis free of any assumptions about the state of the output of a pulsed laser. The spirit of this work is not to calculate the rate of two-photon absorption from a laser beam but rather to find what information such experiments can give about the properties of the radiation field.

The radiation field is described in terms of plane waves inside a cubic box. By letting the dimensions of the box become infinite we have plane waves with a continuous distribution of frequencies. Almost any state of the radiation field could be described by an appropriate superposition of such plane waves. It is these plane waves (Fourier components) that we mean whenever we refer to modes in the text. This is to be contrasted to laser-cavity modes. For example, in a well stabilized laser operating in a single-cavity mode, the output is described by a superposition of plane waves because there will always be some broadening and angular divergence.

2. RATE OF TWO-PHOTON ABSORPTION

The nonrelativistic Hamiltonian of a single atom interacting with the radiation field can be written as

$$H=H^A+H^R+V, \tag{2.1}$$

where H^A is the Hamiltonian of the free atom, H^R the Hamiltonian of the radiation field, and V the interaction between the two. All Hamiltonians are assumed to have been divided by $\hbar$ throughout this paper. H^A is here understood as a hydrogen-atom Hamiltonian and its eigenstates will be denoted by $|a\rangle$, $|b\rangle$, $|c\rangle$, $\cdots$ with energies ω_a, ω_b, ω_c, $\cdots$, respectively. In terms of a plane-wave expansion inside a cubic box of linear dimension L, the radiation Hamiltonian reads

$$H^R=\sum_{\mathbf{k}\lambda}\omega_k a_{\mathbf{k}\lambda}{}^\dagger a_{\mathbf{k}\lambda}, \tag{2.2}$$

where $a_{\mathbf{k}\lambda}{}^\dagger$ and $a_{\mathbf{k}\lambda}$ are the usual dimensionless creation and annihilation operators for the $\mathbf{k}\lambda$ mode. The vector $\mathbf{k}$ represents the photon wave vector and λ is the polarization index assuming the values 1 and 2. The energy ω_k is given by kc, where c is thes peed of light. It will also be convenient to measure the energies of the atomic states in wave numbers defined by

$$k_a\equiv\omega_a/c. \tag{2.3}$$

The eigenstates of H^R are $|\cdots n(\mathbf{k}\lambda)\cdots\rangle$, where $n(\mathbf{k}\lambda)$ specifies the number of photons in the $\mathbf{k}\lambda$ mode. We shall also use the notation $|\{n(\mathbf{k}\lambda)\}\rangle$, or simply $|n\rangle$ for short.

Confining ourselves to dipole contributions to two-photon absorption, we can write V as

$$V=-\frac{(2\pi\alpha)^{1/2}}{m}L^{-3/2}\sum_{\mathbf{k}\lambda}\frac{\mathbf{p}\cdot\boldsymbol{\varepsilon}_{\mathbf{k}\lambda}}{\sqrt{k}}(a_{\mathbf{k}\lambda}{}^\dagger+a_{\mathbf{k}\lambda}), \tag{2.4}$$

where α is the fine structure constant, $\mathbf{p}$ is the momentum operator of the electron in the hydrogenlike atom, $\boldsymbol{\varepsilon}_{\mathbf{k}\lambda}$ is the polarization vector of the $\mathbf{k}\lambda$ mode, and m is the electronic mass.

Let now $\rho(t)$ be the density operator of the system "atom plus field," at time $t>0$. The operator $\rho(t)$ is related to the operator $\rho(0)$ through the equation

$$\rho(t)=U(t)\rho(0)U^\dagger(t), \tag{2.5}$$

where

$$U(t)=e^{-iHt} \tag{2.6}$$

is the time-evolution operator. At time $t=0$ atom and field are uncoupled, and therefore the density operator can be written as $\rho^A(0)\rho^R(0)$, the first factor being the density operator of the atom and the second the density operator of the field. Since the atom is initially assumed to be in its ground state which we shall denote hereafter by $|\alpha\rangle$, we may write

$$\rho_{cc}{}^A(0)=\delta_{ca} \tag{2.7}$$

where δ_{ca} is the Kronecker δ. All off-diagonal matrix elements obviously vanish. The density operator of the radiation field will be left completely arbitrary. What we wish to calculate is the rate at which the atom makes transitions from the ground state to the $2s$ state via two-photon absorption. We shall first carry out the calculation under the assumption that the levels of H^A are sharply defined, i.e., we shall neglect all broadening effects. Then we shall modify the results so as to include such effects.

Let us reserve the symbol $|b\rangle$ for the $2s$ state hereafter. In order to calculate the rate of the transitions $|a\rangle\rightarrow|b\rangle$ we first calculate the probability for the atom to be in state $|b\rangle$ at time $t>0$.

Clearly this probability is given by

$$\rho_{bb}{}^A(t)\equiv\sum_n\rho_{bn,bn}(t), \tag{2.8}$$

which is the appropriate matrix element of the reduced density operator obtained by taking the trace of the total operator with respect to radiation states. Using

Eq. (2.5) and the initial conditions we obtain

$$\rho_{bb}{}^{A}(t)=\sum_{n,m,m'} U_{bn,am}(t)\rho_{mm'}{}^{R}(0)U_{am',bn}{}^{\dagger}(t). \quad (2.9)$$

Terms corresponding to $m\neq m'$ depend on the phases of the modes in the initial state of the radiation field.

As we have discussed in a previous paper,[1] these terms make a negligible contribution. This is due to the fact that, as a practical matter, the initial phases of the modes at optical frequencies are uncontrollable and hence individually random. With this understanding, therefore, we shall neglect these terms thus obtaining

$$\rho_{bb}{}^{A}(t)=\sum_{n,m}\rho_{mm}{}^{R}(0)\,|\,U_{bn,am}(t)\,|^{2}. \quad (2.10)$$

We wish to emphasize that no other assumption, except for the randomness of the initial phases, is made. The density operator can be otherwise completely arbitrary, but in calculating the rate of the two-photon absorption it is only the diagonal matrix elements that contribute. (See, also, the steps in going from Eq. (22) to Eq. (23) in Ref. 7.)

Now we observe that Eq. (2.10) contains all possible contributions to the transition $a\rightarrow b$. In order to single out the contribution due to two-photon absorption, one uses perturbation theory to calculate the appropriate contribution to the matrix element $U_{bn,am}(t)$. The initial state is $|a\rangle|\{m(\mathbf{k}\lambda)\}\rangle$. The final atomic state is $|b\rangle$, while the final field state is the initial one but with two photons, say $\mathbf{k}_1\lambda_1$ and $\mathbf{k}_2\lambda_2$, removed. Since similar calculations have appeared in the literature repeatedly,[1,5,7,8,15] we refrain from reproducing the steps here and we only give the final result which is

$$\rho_{bb}{}^{A}(t)=\sum_{m}\sum_{\mathbf{k}_1\lambda_1}\sum_{\mathbf{k}_2\lambda_2}2\frac{1-\cos(k_b-k_a-k_1-k_2)t}{(k_b-k_a-k_1-k_2)^2}\rho_{mm}{}^{R}(0)$$
$$\times L^{-6}(2\pi)^2\alpha^2(k_1k_2)^{-1}\eta(\mathbf{k}_1\lambda_1;\mathbf{k}_2\lambda_2)$$
$$\times\{m(\mathbf{k}_1\lambda_1)m(\mathbf{k}_2\lambda_2)-m(\mathbf{k}_1\lambda_1)\delta_{\mathbf{k}_1\mathbf{k}_2}\delta_{\lambda_1\lambda_2}\}, \quad (2.11)$$

where η is defined by

$$\eta(\mathbf{k}_1\lambda_1;\mathbf{k}_2\lambda_2)\equiv\frac{1}{cm^4}\left|\sum_{c}\left\{\frac{(\mathbf{p}_{bc}\cdot\boldsymbol{\varepsilon}_{\mathbf{k}_2\lambda_2})(\mathbf{p}_{ca}\cdot\boldsymbol{\varepsilon}_{\mathbf{k}_1\lambda_1})}{\omega_{bc}-\omega_{k_2}}\right.\right.$$
$$\left.\left.+\frac{(\mathbf{p}_{bc}\cdot\boldsymbol{\varepsilon}_{\mathbf{k}_1\lambda_1})(\mathbf{p}_{ca}\cdot\boldsymbol{\varepsilon}_{\mathbf{k}_2\lambda_2})}{\omega_{bc}-\omega_{k_1}}\right\}\right|^{2}. \quad (2.12)$$

The summation over c extends over all atomic states. The term linear in $m(\mathbf{k}\lambda)$ in Eq. (2.11) contributes only when both photons are absorbed from the same mode.

Now to obtain the rate of transitions $a\rightarrow b$, we calculate the quantity

$$h_{ab}\equiv\lim_{t\rightarrow\infty}\frac{1}{t}\rho_{bb}{}^{A}(t), \quad (2.13)$$

where, as we have discussed in an earlier paper,[1] the limit $t\rightarrow\infty$ means that this time interval is large comparted to the interaction time, that is, the time it takes for the two photons to be absorbed. For optical frequencies this time is of the order of 10^{-15} sec. Noting that

$$\lim_{t\rightarrow\infty}\frac{1-\cos xt}{x^2t}=\pi\delta(x), \quad (2.14)$$

we obtain

$$h_{ab}=\sum_{m}\sum_{\mathbf{k}_1\lambda_1}\sum_{\mathbf{k}_2\lambda_2}(2\pi)^3\alpha^2L^{-6}\delta(k_{ba}-k_1-k_2)(k_1k_2)^{-1}$$
$$\times\rho_{mm}{}^{R}(0)\eta(\mathbf{k}_1\lambda_1;\mathbf{k}_2\lambda_2)\{m(\mathbf{k}_1\lambda_1)m(\mathbf{k}_2\lambda_2)$$
$$-m(\mathbf{k}_1\lambda_1)\delta_{\mathbf{k}_1\mathbf{k}_2}\delta_{\lambda_1\lambda_2}\}. \quad (2.15)$$

This equation gives the rate of two-photon transitions between two atomic levels with sharply defined energies. In actuality the levels will be broadened because of radiation damping, collisions, and perhaps other causes. One could have calculated the transition rate in a more sophisticated way so as to include these effects (see, for example, Refs. 16–18). The result, which we give here without proof, is that the δ function is replaced by the line-shape function $g(k_1,k_2)$ which is a nonsingular function of k_1 and k_2, peaked at $k_1+k_2=k_{ba}$. Thus, the rate of transitions between two broadened levels is

$$h=(2\pi)^3\alpha^2L^{-6}\sum_{\mathbf{k}_1\lambda_1}\sum_{\mathbf{k}_2\lambda_2}(k_1k_2)^{-1}g(k_1,k_2)\eta(\mathbf{k}_1\lambda_1;\mathbf{k}_2\lambda_2)$$
$$\times\sum_{m}\rho_{mm}{}^{R}(0)\{m(\mathbf{k}_1\lambda_1)m(\mathbf{k}_2\lambda_2)$$
$$-m(\mathbf{k}_1\lambda_1)\delta_{\mathbf{k}_1\mathbf{k}_2}\delta_{\lambda_1\lambda_2}\}. \quad (2.16)$$

Note that in this equation we have rearranged the summations somewhat. This is possible because the summation over m is actually an average over states of the radiation field, and therefore all factors except $m(\mathbf{k}_1\lambda_1)$ and $m(\mathbf{k}_2\lambda_2)$ can be taken out of the summation. In fact, as we shall see subsequently, it is through this summation that correlation effects enter in the process. To compress notation, we introduce the symbol

$$G(\mathbf{k}_1\lambda_1;\mathbf{k}_2\lambda_2)\equiv\sum_{m}\rho_{mm}{}^{R}(0)\{m(\mathbf{k}_1\lambda_1)m(\mathbf{k}_2\lambda_2)$$
$$-m(\mathbf{k}_1\lambda_1)\delta_{\mathbf{k}_1\mathbf{k}_2}\delta_{\lambda_1\lambda_2}\}, \quad (2.17)$$

in terms of which the transition rate reads

$$h=(2\pi)^3\alpha^2L^{-6}\sum_{\mathbf{k}_1\lambda_1}\sum_{\mathbf{k}_2\lambda_2}(k_1k_2)^{-1}g(k_1,k_2)$$
$$\times\eta(\mathbf{k}_1\lambda_1;\mathbf{k}_2\lambda_2)G(\mathbf{k}_1\lambda_1;\mathbf{k}_2\lambda_2). \quad (2.18)$$

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Clearly, G is a correlation function of the radiation field and we now turn to the study of this function.

3. CORRELATION EFFECTS

As pointed out earlier, it is the correlation function G that determines the dependence of the process on the field properties. This function depends on the density operator of the field at time $t=0$ which has been denoted by $\rho^R(0)$. Recalling that a state of the field is of the form $|\{m(\mathbf{k}\lambda)\}\rangle$, we shall hereafter denote this operator by $R=R(\{m(\mathbf{k}\lambda)\})$ in order to exhibit explicitly the fact that it depends on all modes. It is now obvious that G can also be written as

$$G=\mathrm{Tr}\{R(a_{\mathbf{k}_1\lambda_1}{}^{\dagger}a_{\mathbf{k}_1\lambda_1}a_{\mathbf{k}_2\lambda_2}{}^{\dagger}a_{\mathbf{k}_2\lambda_2} - a_{\mathbf{k}_1\lambda_1}{}^{\dagger}a_{\mathbf{k}_1\lambda_1}\delta_{\mathbf{k}_1\mathbf{k}_2}\delta_{\lambda_1\lambda_2})\}. \quad (3.1)$$

Using the commutation relations between creation and annihilation operators, G can also be written in the form

$$G(\mathbf{k}_1\lambda_1;\mathbf{k}_2\lambda_2)=\mathrm{Tr}\{Ra_{\mathbf{k}_1\lambda_1}{}^{\dagger}a_{\mathbf{k}_2\lambda_2}{}^{\dagger}a_{\mathbf{k}_1\lambda_1}a_{\mathbf{k}_2\lambda_2}\}, \quad (3.2)$$

which is sometimes more convenient, especially when one uses a representation in terms of coherent states.[8,9]

Note that the first term in (3.1) is equal to

$$\langle m(\mathbf{k}_1\lambda_1)m(\mathbf{k}_2\lambda_2)\rangle,$$

which is the expected value of a doublet photon density. The second term is equal to $\langle m(\mathbf{k}_1\lambda_1)\rangle$, which is the expected value of a singlet-photon density. For $\mathbf{k}_1=\mathbf{k}_2$ and $\lambda_1=\lambda_2$ the doublet density becomes $\langle m^2(\mathbf{k}_1\lambda_1)\rangle$, which is the second moment of the photon distribution in the $\mathbf{k}_1\lambda_1$ mode. It should be emphasized that the above averages are not simple quantum expectation values but quantum statistical averages. In this notation, the correlation function reads

$$G(\mathbf{k}_1\lambda_1;\mathbf{k}_2\lambda_2) = \langle m(\mathbf{k}_1\lambda_1)m(\mathbf{k}_2\lambda_2)\rangle-\langle m(\mathbf{k}_1\lambda_1)\rangle\delta_{\mathbf{k}_1\mathbf{k}_2}\delta_{\lambda_1\lambda_2}. \quad (3.3)$$

It is well known that two-photon processes are observable only when the average number of photons in the light beam is much larger than one. In that case, the linear term can be neglected as compared to the quadratic term $\langle m^2(\mathbf{k}_1\lambda_1)\rangle$, which is of the order of $\langle m(\mathbf{k}_1\lambda_1)\rangle^2$. For those modes for which $\langle m\rangle$ is not larger than one, this approximation is not valid but their contribution to the two-photon process is negligible anyway. In calculating the rate of two-photon absorption, therefore, we can neglect the linear term. This approximation is not really necessary but it simplifies writing and it is a sound one. We then take the transition rate to be

$$h=(2\pi)^3\alpha^2L^{-6}\sum_{\mathbf{k}_1\lambda_1}\sum_{\mathbf{k}_2\lambda_2}(k_1k_2)^{-1}g(k_1,k_2) \times\eta(\mathbf{k}_1\lambda_1;\mathbf{k}_2\lambda_2)\langle m(\mathbf{k}_1\lambda_1)m(\mathbf{k}_2\lambda_2)\rangle. \quad (3.4)$$

A. Factorable Density Operator

The form of the boublet density as a function of $\mathbf{k}_1\lambda_1$ and $\mathbf{k}_2\lambda_2$ depends on the density operator. Let us consider first the case in which the density operator factors in a product as follows:

$$R(\{m(\mathbf{k}\lambda)\})=\prod_{\mathbf{k}\lambda}R_{\mathbf{k}\lambda}(m(\mathbf{k}\lambda)), \quad (3.5)$$

where $R_{\mathbf{k}\lambda}(m(\mathbf{k}\lambda))$ is the density operator of the $\mathbf{k}\lambda$ mode. When this is the case the various modes are statistically independent, as in thermal light sources for example. Then, for $\mathbf{k}_1\neq\mathbf{k}_2$ and/or $\lambda_1\neq\lambda_2$, we shall have

$$\langle m(\mathbf{k}_1\lambda_1)m(\mathbf{k}_2\lambda_2)\rangle=\langle m(\mathbf{k}_1\lambda_1)\rangle\langle m(\mathbf{k}_2\lambda_2)\rangle, \quad (3.6)$$

where

$$\langle m(\mathbf{k})\rangle\equiv\sum_{m=0}^{\infty}(R_{\mathbf{k}\lambda})_{mm}m. \quad (3.7)$$

For $\mathbf{k}_1\lambda_1=\mathbf{k}_2\lambda_2$ the doublet density reduces to the second moment of the photon distribution in the mode. Separating these terms in Eq. (3.4) it becomes

$$h=(2\pi)^3\alpha^2L^{-6}\sum_{\mathbf{k}_1\lambda_1}\sum_{\mathbf{k}_2\lambda_2\neq\mathbf{k}_1\lambda_1}(k_1k_2)^{-1}g(k_1,k_2)\eta(\mathbf{k}_1\lambda_1;\mathbf{k}_2\lambda_2) \times\langle m(\mathbf{k}_1\lambda_1)\rangle\langle m(\mathbf{k}_2\lambda_2)\rangle+(2\pi)^3\alpha^2L^{-6}\sum_{\mathbf{k}_1\lambda_1}k_1^{-2}g(k_1,k_1) \times\eta(\mathbf{k}_1\lambda_1;\mathbf{k}_1\lambda_1)\langle m^2(\mathbf{k}_1\lambda_1)\rangle. \quad (3.8)$$

By adding and subtracting the quantity $\langle m(\mathbf{k}_1\lambda_1)\rangle^2$, we can also write (3.8) as

$$h=(2\pi)^3\alpha^2L^{-6}\sum_{\mathbf{k}_1\lambda_1}\sum_{\mathbf{k}_2\lambda_2}(k_1k_2)^{-1}g(k_1k_2)\eta(\mathbf{k}_1\lambda_1;\mathbf{k}_2\lambda_2) \times\langle m(\mathbf{k}_1\lambda_1)\rangle\langle m(\mathbf{k}_2\lambda_2)\rangle+(2\pi)^3\alpha^2L^{-6}\sum_{\mathbf{k}_1\lambda_1}k_1^{-2}g(k_1,k_2) \times\eta(\mathbf{k}_1\lambda_1;\mathbf{k}_1\lambda_1)(\langle m^2(\mathbf{k}_1\lambda_1)\rangle-\langle m(\mathbf{k}_1\lambda_1)\rangle^2), \quad (3.9)$$

where the restriction on the summation in the first term has now been removed.

The single-mode case can be obtained from either Eq. (3.8) or (3.9) by taking $\langle m(\mathbf{k}_1\lambda_1)\rangle\langle m(\mathbf{k}_2\lambda_2)\rangle=0$ for $\mathbf{k}_1\neq\mathbf{k}_2$ and/or $\lambda_1\neq\lambda_2$. It turns out then that the rate is proportional to $\langle m^2(\mathbf{k}\lambda)\rangle$ as has already been discussed in the literature,[1,5,7,8] and we shall not elaborate on this any further.

Continuing with the multimode case, we now pass to the continuum by replacing the summations by integrations according to the well-known formula[16]

$$\sum_{\mathbf{k}\lambda}\rightarrow\sum_{\lambda}\frac{L^3}{(2\pi)^3}\int k^2dkd\Omega, \quad (3.10)$$

where $d\Omega=\sin\vartheta d\vartheta d\varphi$ is the differential of the solid angle in a system of spherical polar coordinates. Now, $\langle m(\mathbf{k}\lambda)\rangle$ represents the number of photons of polariza-

tion λ in d^3k about $\mathbf{k}$ in $\mathbf{k}$ space. Thus we have

$$h=\frac{\alpha^2}{(2\pi)^3}\sum_{\lambda_1,\lambda_2}\int_0^\infty\int_0^\infty dk_1dk_2(k_1k_2)g(k_1,k_2)\int\int d\Omega_1d\Omega_2$$
$$\times\eta(\mathbf{k}_1\lambda_1;\mathbf{k}_2\lambda_2)\langle m(\mathbf{k}_1\lambda_1)\rangle\langle m(\mathbf{k}_2\lambda_2)\rangle$$
$$+\alpha^2L^{-3}\sum_{\lambda_1}\int_0^\infty dk_1g(k_1,k_1)\int d\Omega_1\eta(\mathbf{k}_1\lambda_1;\mathbf{k}_1\lambda_1)$$
$$\times(\langle m^2(\mathbf{k}_1\lambda_1)\rangle-\langle m(\mathbf{k}_1\lambda_1)\rangle^2). \quad (3.11)$$

The second term is of the order of L^{-3} as compared to the first and we may neglect it in the case of multimode excitation. This is a consequence of the fact that as $L\to\infty$, the density of modes increases and the probability for two photons of the same mode to be absorbed simultaneously decreases. It is worth noting at this point that when the light beam consists of a superposition of pure coherent states, i.e., when each mode is in a pure coherent state, then the probability distribution $(R_{\mathbf{k}\lambda})_{mm}$ is a Poisson distribution.[9] In that case, $\langle m^2\rangle-\langle m\rangle^2=\langle m\rangle$ and, since terms linear in $\langle m(\mathbf{k}\lambda)\rangle$ can be neglected as discussed earlier, the second term in (3.11) is negligible even if only a few modes are excited.

The quantity $\langle m(\mathbf{k}\lambda)\rangle$ is the frequency and angular spectrum of the incident radiation. To put Eq. (3.11) in a form that is closer to actual experimental situations, let us consider a beam confined in a narrow solid angle and linearly polarized. This means that the propagation vectors of essentially all photons lie within a small angle around a central unit vector k_0. If, in addition, the beam is linearly polarized, we can replace $\boldsymbol{\varepsilon}_{\mathbf{k}_1\lambda_1}$ and $\boldsymbol{\varepsilon}_{\mathbf{k}_2\lambda_2}$ by $\boldsymbol{\varepsilon}_0$ in $\eta(\mathbf{k}_1\lambda_1;\mathbf{k}_2\lambda_2)$, where $\boldsymbol{\varepsilon}_0$ is the polarization vector of the beam. Then η ceases to depend on the angle and can be taken out of the integrals with respect to Ω_1, and Ω_2. We shall denote this angle-independent quantity by $\eta_0(k_1;k_2)$ because it still depends on k_1 and k_2. The angle integrations now reduce to $\int\langle m(\mathbf{k}\lambda)\rangle d\Omega$, which is essentially the frequency spectrum of the incident radiation. We introduce the symbol

$$S(k)\equiv\int\langle m(\mathbf{k}\lambda)\rangle d\Omega \quad (3.12)$$

for this quantity. The number of photons per unit wave number is given by $k^2S(k)$, and this is what one might properly call the spectrum. Substituting now in Eq. (3.11) and neglecting the second term, we obtain

$$h=\frac{\alpha^2}{(2\pi)^3}\int_0^\infty\int_0^\infty dk_1dk_2(k_1k_2)g(k_1,k_2)$$
$$\times\eta_0(k_1;k_2)S(k_1)S(k_2), \quad (3.13)$$

where the summations over λ_1 and λ_2 do not appear any longer since the beam is assumed to be linearly polarized.

This equation shows that in the case of a narrow, linearly polarized beam, the transition rate depends on a generalized autocorrelation function (in $\mathbf{k}$ space) of the spectral density of the incident radiation. The autocorrelation function of the spectral density is

$$\int_0^\infty(k-k')^2S(k-k')k'^2S(k')dk'.$$

In (3.13) we have a generalized form of this because of the presence of the functions $g(k_1,k_2)$ and $\eta_0(k_1;k_2)$, and the factors k_1 and k_2, which weigh each value of the integrand differently. In the limiting case of narrow spectrum $S(k)$ and slowly varying function $g(k_1,k_2)$ and $\eta_0(k_1;k_2)$, one would have the usual autocorrelation function.

The functions $S(k)$ and $g(k_1,k_2)$ will generally be more or less peaked but nonsingular functions, for most practical cases. The function $\eta_0(k_1;k_2)$ requires closer examination. From Eq. (2.12) we see that we have the resonance denominators $k_b-k_c-k_2$ and $k_b-k_c-k_1$, where k_b is the energy of the $2s$ level and k_c stands for energies of all virtual intermediate levels. For all such intermediate levels in a hydrogenlike atom [except the $2p(\frac{1}{2})$ level] we shall have $k_b<k_c$, and therefore no singularities will occur over the range of integration in (3.13). For the level $2p(\frac{1}{2})$ we have $k_b>k_c$, and η_0 is singular for k_1 or $k_2=k_b-k_c$. Note, however, that because of energy conservation between initial and final state, the appreciable contribution to the integral in (3.13) comes from pairs of k_1 and k_2 such that $k_1+k_2\cong k_{ba}\pm$linewidth. And the linewidth is usually much smaller than k_{ba}. This implies that only if the product $S(k_1)S(k_{ba}-k_1)$ goes to zero slower than $(k_1-k_{bc})^{-2}$ goes to infinity (as $k_1\to k_{bc}$) shall we have a difficulty from the singularity. This, of course, depends on the spectrum of the incident radiation. For this to happen, the incident radiation must contain an appreciable number of photons having energy equal to $k_{2p(1/2)}-k_{1s}$. In that case we shall have transitions from $1s$ to $2s$ via the real intermediate level $2p(\frac{1}{2})$. This is not a true two-photon absorption but two successive single-photon absorptions. Of course, when the lifetime of the real intermediate state is shorter than the coherence time the incident radiation, the distinction between the two processes is essentially lost.[19] Nevertheless, the second process is basically different and its mathematical description should be formulated somewhat differently. If the spectrum of the incident radiation falls off rapidly enough as $k\to k_{2p(1/2)}-k_{1s}$, we shall have no singularities in (3.13). This would, for example, be the case with light sources such as lasers which have extremely narrow spectra.

B. Nonfactorable Density Operator

The foregoing discussion has shown that when the density operator is factorable, it is the spectral com-

[19] J. Shapiro and G. Breit, Phys. Rev. **113**, 179 (1959).

position of the field that determines the rate of two-photon absorption. In general, the density operator is not factorable, and in that case we have

$$\langle m(\mathbf{k}_1\lambda_1)m(\mathbf{k}_2\lambda_2)\rangle \neq \langle m(\mathbf{k}_1\lambda_1)\rangle\langle m(\mathbf{k}_2\lambda_2)\rangle. \quad (3.14)$$

The left side contains more information than simply the spectral composition of the beam. It is a correlation function whose value depends on the degree to which the modes of the field are statistically correlated. The special case examined in Sec. 3 A corresponds to completely uncorrelated[20] (statistically independent) modes. The right side in (3.14) is a quantity that can be determined by simply measuring the energy (or power) of the field as a function of frequency, direction of propagation and polarization. The left side would require coincidence experiments as discussed further in the following section. It should be pointed out that the ratio

$$\langle m(\mathbf{k}_1\lambda_1)m(\mathbf{k}_2\lambda_2)\rangle / \langle m(\mathbf{k}_1\lambda_1)\rangle\langle m(\mathbf{k}_2\lambda_2)\rangle$$

can in principle have any value between 0 and ∞. Its value of course depends on the state of the field.

4. DISCUSSION AND CONCLUSIONS

The analysis in this paper has shown that whenever the modes of the field are statistically independent—in the sense that the density operator factors in a product of operators each describing one mode—the rate of two-photon absorption depends on the spectral composition of the energy of the field. No other statistical properties of the field enter into the picture then.

Suppose, for example, that we have two light sources; one consisting of a direct product of pure coherent states with random initial phases, and a second consisting of a direct product of chaotic states.[9] If the average number of photons per mode is the same in both sources, then the rate of two-photon absorption will be the same (see also Ref. 8 where factorable density operators are assumed and where the same conclusion is reached).

The authors of Ref. 7 have calculated the rate of two-photon absorption for the case of thermal light and for the case of a model for pulsed laser light. The latter is assumed to be a direct product of pure coherent states with random phases. In both cases the density operator is factorable and their results indicate that there is a difference between the two cases. In view of the results of the present paper, the above difference is due to the fact that the spectral composition of the two models is different. The different coherence (statistical) properties of the two models do not affect the process. In addition, when discussing the case of thermal light, the authors assume that the atom interacts with the field for a time longer than the coherence time of the radiation. However, the time of interaction (per two-photon process) is determined by the lifetime of the intermediate state. In our model, for example, this is of the order of 10^{-15} sec. Whether their assumption is valid or not will depend on the light source. And it would take a light source of an extremely large linewidth to justify the assumption. It appears, therefore, that it is questionable whether the quantity the authors calculate for the case of thermal light does actually represent a two-photon absorption rate (see also the discussion in Ref. 8). The point to be made is that two-photon absorption provides us with a coincidence counter of intrinsically small resolution time, and it is only when this time is smaller than the coherence time of the light that correlation effects appear.[21]

Such effects appear either when only a single mode is excited[1,5,6,8] or when many statistically correlated modes participate. Under present experimental possibilities it is the latter case that is more interesting. It suggests that two-photon processes may in principle be used to determine whether the modes of a light source are statistically independent or not.

Although we wish to keep this discussion free of any assumptions about the field of a high-power laser, it should be pointed out that it is not *a priori* obvious that the modes in such lasers are uncorrelated. In fact, Ducuing and Bloembergen[22] have presented evidence pointing to the opposite. Independently of what the state of the laser field is, however, Glauber[23] has emphasized that very unusual states of the field can exist and it is relevant to know how two-photon processes depend on, and what information they give about the field.

The general conclusion, therefore, is: When the density operator of the field is factorable, the information obtained from two-photon processes can also be obtained from single-photon counting experiments; when the density operator is not factorable, two-photon processes provide information that otherwise would require coincidence counting experiments.

Strictly speaking, in the first case, the process depends on a generalized autocorrelation function of the spectrum and the direct measurement of that function does require coincidence counting again. However, if the spectrum is known (and this can be measured by single-photon counting) the autocorrelation function can be calculated. It is in this sense that two-photon absorption and single-photon counting give equivalent information. In the second case, knowledge of the spectrum does not suffice to calculate the correlation function $G(\mathbf{k}_1\lambda_1;\mathbf{k}_2\lambda_2)$. More information about the state of the field is needed.

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[20] W. B. Davenport and W. L. Root, *An Introduction to the Theory of Random Signals and Noise* (McGraw-Hill Book Co., New York, 1958).

[21] See, for example, L. Mandel and E. Wolf, Rev. Mod. Phys. **31**, 231 (1965).

[22] J. Ducuing and N. Bloembergen, Phys. Rev. **133**, A1493 (1964).

[23] R. J. Glauber, in *Proceedings of the Physics of Quantum Electronic Conference, San Juan, Puerto Rico, 1965*, edited by by P. Kelley, B. Lax, and P. E. Tannenwald (McGraw-Hill Book Co., Inc., New York, 1966).