# Two-Photon Absorption and Field Correlation Functions*

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(Received 18 July 1968)

The probability of an atom undergoing a transition to a given final state by means of two-photon absorption is expressed for arbitrary field states in terms of the second-order normally-ordered field correlation function, evaluated at the position of the atom. In the case of stationary fields, an expression for the absorption rate is found which reduces to a particularly simple form for narrow-bandwidth fields near resonance. The effect of field statistics is illustrated by comparing the absorption rate $w_2^{(ch)}$ for chaotic or Gaussian light to the rate $w_2^{(l)}$ for laser light. The rate for laser light is calculated within the context of a particular model based on the assumption of fixed field amplitude and random frequency modulation, and the chaotic light to which it is compared is assumed to have the same (Lorentzian) power spectrum. When the width $\kappa_f$ of the final atomic level is much greater than the bandwidth $b$ of the field, we obtain the previously derived result $w_2^{(ch)}/w_2^{(l)}=2$. When $\kappa_f \ll b$, on the other hand, the ratio between the two rates depends on the (mean) frequency of the field, and assumes the (maximum) value 4 when the field is exactly on resonance.

## I. INTRODUCTION

A NUMBER of discussions[1–6] have recently appeared of the problem of the simultaneous absorption of two photons by atomic systems. Particular attention has been paid to the dependence of the rates for such processes on the statistics of the exciting fields. Previous discussions have been based almost exclusively, however, on a modal expansion of the field throughout the region of space under consideration. The simplest analyses assume that only one mode of the field is excited, and thus are unable adequately to take into account the effects of time-dependent field correlations and field bandwidth. A more general analysis[6] of this kind, on the other hand, requires for its applicability a rather detailed knowledge of the density operator for all of the excited field modes, which may be difficult to obtain in practice. In this paper, the rate $w_2$ for two-photon absorption by an atom undergoing a transition from its ground state to a given excited state is expressed in terms of the second-order (normally-ordered) field correlation function $G^{(2)}(t_1',t_2';t_1,t_2)$ evaluated at the position of the atom. The two-photon absorption rate is thus expressed in terms of a function which plays a central role in the theory of counting statistics for one-photon absorption.[7,8]

The absorption rate for stationary fields is expressed in terms of a double integral of a certain atomic response function times the second-order spectral correlation function $F^{(2)}(\omega_1',\omega_2';\omega_1,\omega_2)$, in which the positive- and negative-frequency arguments both sum to the frequency of the final atomic state. In the case of narrow-bandwidth fields near resonance, the expression for $w_2$ is reduced to a single Fourier integral of the function $G^{(2)}(-t,-t;t,t)$. The analysis, which is based on second-order perturbation theory, is suitably generalized to take into account the effects of (natural) linewidth, both of the intermediate and of the final atomic states.

Two special cases—that of chaotic (frequency-filtered) radiation, and that of amplitude-stabilized laser light—are considered in detail. A model of laser light developed by previous authors is adopted, and used to calculate the second-order field correlation function. The two-photon absorption rate $w_2^{(l)}$ for laser light is then calculated, and compared to the rate $w_2^{(ch)}$ for chaotic light with the same power spectrum. It is found that if the mean frequency of the field is exactly on resonance (i.e., if it is equal to one-half the frequency of the final state), then the two rates are related by the formula

$$w_2^{(ch)}=4w_2^{(l)}$$

for transitions to an infinitely sharp final atomic level. This result remains valid as long as the width $\kappa_f$ of the final state is much smaller than the bandwidth $b$ of the field. If $\kappa_f \gg b$, on the other hand, we obtain the previously derived[1–3,5] result $w_2^{(ch)}=2w_2^{(l)}$. This relation follows directly from a formula expressing $w_2$ for arbitrary fields as a simple factor times $G^{(2)}(0,0;0,0)$, a formula which is shown to be valid if the width of the final state is much greater than the bandwidth of the field, and also if the final levels which can be excited by means of two-photon absorption occupy a broad band of energies.

## II. TWO-PHOTON ABSORPTION PROBABILITIES FOR ARBITRARY FIELDS

In evaluating the coupling between the field and the (hydrogenlike) atom under consideration, we shall work in the dipole approximation, and ignore the effects of

* Research supported in part by the U. S. Air Force Cambridge Research Laboratories, Office of Aerospace Research, under Contract No. F19628-68-C-0062.

[1] P. Lambropoulos, C. Kikuchi, and R. K. Osborn, Phys. Rev. **144**, 1081 (1966).
[2] M. C. Teich and G. J. Wolga, Phys. Rev. Letters **16**, 625 (1966).
[3] Y. R. Shen, Phys. Rev. **155**, 921 (1967).
[4] S. Carusotto, G. Fornaca, and E. Polacco, Phys. Rev. **157**, 1207 (1967).
[5] R. Guccione-Gush, H. P. Gush, and J. Van Kranendonk, Can. J. Phys. **45**, 2513 (1967).
[6] P. Lambropoulos, Phys. Rev. **168**, 1418 (1968).
[7] R. J. Glauber, in *Quantum Optics and Electronics*, edited by C. DeWitt, A. Blandin, and C. Cohen-Tannoudji (Gordon and Breach Science Publishers, Inc., New York, 1965).
[8] L. Mandel and E. Wolf, Rev. Mod. Phys. **37**, 231 (1965).

the term quadratic in the vector potential of the field.[9] The Hamiltonian for the system of atom and field is then

$$H_I(t)=\frac{e}{mc}p(t)A(t), \tag{2.1}$$

where $p(t)$ is the momentum operator of the valence electron, and $A(t)$ is the (freely-propagating) vector potential of the field, evaluated at the position ($r=0$) of the atom. It may be decomposed into positive- and negative-frequency parts,

$$A(t)=\mathcal{A}(t)+\mathcal{A}^\dagger(t), \tag{2.2}$$

in which the annihilation operator $\mathcal{A}(t)$ has the usual modal expansion in a region of volume $V$,

$$\mathcal{A}(t)=(\hbar c^2/2V)^{1/2}\sum_k \omega_k^{-1/2}\hat{e}_k a_k e^{-i\omega_k t}. \tag{2.3}$$

In this expression, $a_k$, $\omega_k$, and $\hat{e}_k$ are the annihilation operator, frequency, and polarization vector, respectively, for the mode specified by the index $k$.

The time evolution of the state of the system of atom and field in the interaction picture is governed by the unitary time-development operator $U'(t)$, which is given, to second order, by the relation

$$U'(t)=1+\frac{1}{i\hbar}\int_0^t dt' H_I(t') -\frac{1}{\hbar^2}\int_0^t\int dt_1 dt_2\,\theta(t_1-t_2)H_I(t_1)H_I(t_2), \tag{2.4}$$

where $\theta(\tau)$ is the step function

$$\theta(\tau)\equiv 1 \quad \text{for} \quad \tau\geq 0$$
$$\equiv 0 \quad \text{for} \quad \tau<0. \tag{2.5}$$

Let us now assume that the atom is initially in its ground state $|0\rangle$ and that the field is initially in an arbitrary pure state $|\psi\rangle_F$. The probability that the atom has been excited to a given final state $|f\rangle$ at time $t$ is

$$P(t)=\sum_\varphi |{}_F\langle\varphi|\langle f|U'(t)|0\rangle|\psi\rangle_F|^2, \tag{2.6}$$

where the summation extends over all field states $|\varphi\rangle_F$. The probability $P(t)$ is given, in the general case, as the sum of terms corresponding to the absorption and emission of arbitrary numbers of photons. Two-photon absorption may be expected to contribute predominantly when: (a) one-photon absorption is excluded, either by the vanishing of the matrix element $\langle f|p(t)|0\rangle$ or by the absence of field components oscillating at the frequency $\omega_f$ of the final state; and (b) when the second-order processes which correspond to the successive absorption and emission of a photon are excluded by the impossibility of satisfying the condition $\omega_1-\omega_2=\omega_f$ with any two frequencies $\omega_1$ and $\omega_2$ within the bandwidth of the field. We may note that conditions (a) and (b) are both satisfied by a hydrogen atom, if the final state is taken to be the $2s$ state, and if the field power spectrum does not contain frequencies as high as that of first excited level.

The probability that the transition to the final state $|f\rangle$ has taken place through the absorption of two photons could be evaluated by expanding the initial-state vector $|\psi\rangle_F$ of the field in terms of photon number states, and then appropriately restricting the summation over field states $|\varphi\rangle_F$ in Eq. (2.6), for each term in the initial expansion. An equivalent and more useful procedure is to continue to allow the summation to extend over all field states, but (to second order) to retain only that term in the expansion (2.4) of $U'(t)$ which contains a product of two photon-annihilation operators. To simplify the resulting expression, we introduce the (second-rank tensor) function

$$\mathcal{L}(t_1,t_2)\equiv\theta(t_1-t_2)(e/\hbar mc)^2\langle f|p(t_1)p(t_2)|0\rangle \tag{2.7a}$$
$$=\theta(t_1-t_2)(e/\hbar mc)^2\sum_j p_{fj}p_{j0}e^{-i(\omega_j-\omega_f)t_1+i\omega_j t_2}. \tag{2.7b}$$

Then the probability of two-photon absorption may be written as

$$P_2(t)=\sum_\varphi\left|\left(\int_0^t\int dt_1 dt_2\,{}_F\langle\varphi|\mathcal{A}(t_1)\mathcal{A}(t_2)|\psi\rangle_F\mathcal{L}(t_1,t_2)\right)\right|^2$$
$$=\int_0^t\int\int\int dt_1' dt_2' dt_1 dt_2$$
$$\times\mathcal{L}^*(t_1',t_2')\,{}_F\langle\psi|\mathcal{A}^\dagger(t_1')\mathcal{A}^\dagger(t_2')\mathcal{A}(t_1)\mathcal{A}(t_2)|\psi\rangle_F$$
$$\times\mathcal{L}(t_1,t_2) \tag{2.8}$$

in which the vector indices are summed in an obvious manner.

The generalization of this relation to mixed initial states of the field is

$$P_2(t)=\int_0^t\int\int\int dt_1' dt_2' dt_1 dt_2$$
$$\times\mathcal{L}^*(t_1',t_2')G^{(2)}(t_1',t_2';t_1,t_2)\mathcal{L}(t_1,t_2) \tag{2.9}$$

in which the second-order *field correlation function*[7,8] $G^{(2)}$ is defined in terms of the initial density operator

[9] The contribution of this term is negligibly small in many cases of interest. For a discussion of its effect see R. Guccione and J. Van Kranendonk, Phys. Rev. Letters **14**, 583 (1965); R. Wallace, *ibid.* **17**, 397 (1966).

$\rho_F$ of the field as

$$G^{(2)}(t_1',t_2';t_1,t_2) \equiv \mathrm{tr}_F(\rho_F \mathcal{A}^\dagger(t_1')\mathcal{A}^\dagger(t_2')\mathcal{A}(t_1)\mathcal{A}(t_2)). \quad (2.10)$$

Equations (2.7), (2.9), and (2.10) thus specify the two-photon absorption probability for arbitrary initial states of the field in terms of functions defined separately in terms of the noninteracting systems of field and atom.

We may remark that our result is formally identical to that which we would obtain semiclassically, if we identified the two-photon absorption probability as that part of the atomic transition probability which is induced by the term in $U'(t)$ quadratic in the positive-frequency part of the (classical) field. The statistical average involved in the definition of $G^{(2)}$ would then represent the possibility of an ensemble of classical driving fields. This similarity to semiclassical theory is not surprising, inasmuch as two-photon absorption is inherently a stimulated process, the mathematical description of which does not involve the noncommutativity of $\mathcal{A}(t)$ and $\mathcal{A}^\dagger(t)$. On the other hand, it should be emphasized that many states of the quantum-mechanical field are characterized by correlation functions which have no classical counterparts. In a state containing exactly one photon, for example, the function $G^{(2)}$ is identically zero, a relation which can never be satisfied classically unless the field itself vanishes identically.

To express $P_2(t)$ in terms of the Fourier components of the field, we begin by making use of the Fourier expansion of the step function

$$\theta(\tau)=\frac{i}{2\pi}\int_{-\infty}^{\infty} d\omega \frac{e^{-i\omega\tau}}{\omega+i\epsilon} \quad (2.11)$$

in Eq. (2.7b). By then changing the variable of integration from $\omega$ to $\omega+\omega_j$, we find that the function $\mathcal{L}(t_1,t_2)$ may be expressed in the form

$$\mathcal{L}(t_1,t_2)=\frac{i}{2\pi}\int d\omega\, g(\omega) e^{i(\omega_f-\omega)t_1+i\omega t_2} \quad (2.12)$$

in which the function $g(\omega)$ is defined as

$$g(\omega)\equiv\left(\frac{e}{\hbar mc}\right)^2 \sum_j p_{fj}p_{j0}\frac{1}{\omega-\omega_j+i\epsilon}. \quad (2.13)$$

By substituting Eq. (2.12) for $\mathcal{L}(t_1,t_2)$ into Eq. (2.9), we find

$$P_2(t)=\int\int d\omega' d\omega\, g^*(\omega')\left\{(2\pi)^{-2}\int_0^t\int\int\int dt_1'dt_2'dt_1dt_2 \times e^{-i(\omega_f-\omega')t_1'-i\omega' t_2'+i(\omega_f-\omega)t_1+i\omega t_2} \times G^{(2)}(t_1',t_2';t_1,t_2)\right\} g(\omega). \quad (2.14)$$

It is clear from this relation that the probability of two-photon absorption involves products of two positive-frequency and two negative-frequency field components, whose frequencies sum to (approximately) $\omega_f$ and $-\omega_f$, respectively.[9a] If the field consists of a pulse of finite extent, then the probability of two-photon absorption after the pulse has passed the atom may be expressed in terms of the second-order spectral correlation function

$$\tilde{G}^{(2)}(\omega_1',\omega_2';\omega_1,\omega_2) \equiv \int_{-\infty}^{\infty}\int\int\int dt_1'dt_2'dt_1dt_2 e^{-i\omega_1' t_1'-i\omega_2' t_2'+i\omega_1 t_1+i\omega_2 t_2} \times G^{(2)}(t_1',t_2';t_1,t_2) \quad (2.15)$$

as

$$P_2=\int\int d\omega' d\omega\, g^*(\omega') \times \tilde{G}^{(2)}(\omega_f-\omega',\omega';\omega_f-\omega,\omega)g(\omega). \quad (2.16)$$

## III. TWO-PHOTON ABSORPTION RATES FOR STATIONARY FIELDS

In many cases of interest, the fields we deal with do not consist of a pulse of finite duration, but may be considered to continue indefinitely for all times. A *stationary field* is defined as one whose statistical properties are independent of the choice of the origin of time. The second-order field correlation function, for example, obeys the identity

$$G^{(2)}(t_1',t_2';t_1,t_2)=G^{(2)}(t_1'+\tau,t_2'+\tau;t_1+\tau,t_2+\tau) \quad (3.1)$$

for all times $\tau$. It should be emphasized that this relation and the corresponding relations for all of the other field correlation functions are all that is necessary to specify stationarity. In particular, the presence of off-diagonal matrix elements in the $n$-quantum expansion of the density operator is not excluded, as it would be, for example, if we also required that the modes of oscillation of the field be statistically independent of one another.

The condition (3.1) on $G^{(2)}$ implies that the spectral correlation function $\tilde{G}^{(2)}$ defined by Eq. (2.15) has the form

$$\tilde{G}^{(2)}(\omega_1',\omega_2';\omega_1,\omega_2)=\delta(\omega_1'+\omega_2'-\omega_1-\omega_2) \times F^{(2)}(\omega_1',\omega_2';\omega_1,\omega_2). \quad (3.2)$$

The function $F^{(2)}$, which we shall call the reduced second-order spectral correlation function, is defined only for arguments satisfying the $\delta$-function condition $\omega_1'+\omega_2'=\omega_1+\omega_2$. One way of evaluating it is to use Eq. (3.1) to express $G^{(2)}(t_1',t_2';t_1,t_2)$ in terms of its value for $t_2=0$, and then to translate the three remain-

[9a] *Note added in proof.* This relation has been derived in a semiclassical context by G. Fornaca, M. Iannuzzi, and E. Polacco, Nuovo Cimento 36, 1230 (1965).

ing variables of integration in Eq. (2.15) by the amount $-t_2$. We find

$$F^{(2)}(\omega_1',\omega_2';\omega_1,\omega_2) = (2\pi)^{-1}\int_{-\infty}^{\infty}\int\int dt_1'dt_2'dt_1 e^{-i\omega_1' t_1'-i\omega_2' t_2'+i\omega_1 t_1} \times G^{(2)}(t_1',t_2';t_1,0). \quad (3.3)$$

The probability of two-photon absorption between the initial time and the time $t$ may be found by similarly evaluating the expression in curly brackets in Eq. (2.14). We have then

$$P_2(t)=(2\pi)^{-2}\int\int d\omega' d\omega \times g^*(\omega')\left\{\int_0^t dt_2\int_{-t_2}^{(t-t_2)}\int\int dt_1'dt_2'dt_1 \times e^{-i(\omega_f-\omega')t_1'-i\omega' t_2'+i(\omega_f-\omega)t_1} \times G^{(2)}(t_1',t_2';t_1,0)\right\} g(\omega). \quad (3.4)$$

If the time $t$ is much greater than the inverse bandwidth of the field,

$$t \gg (1/\Delta\omega), \quad (3.5)$$

then we may approximate the limits on the integrals over $t_1$, $t_1'$, and $t_2'$ by $\pm\infty$. The probability $P_2(t)$ is then proportional to time

$$P_2(t)=w_2(\omega_f)t, \quad (3.6)$$

where we have, by virtue of Eq. (3.3),

$$w_2(\omega_f)=(2\pi)^{-1}\int\int d\omega' d\omega \times g^*(\omega')F^{(2)}(\omega_f-\omega',\omega';\omega_f-\omega,\omega)g(\omega). \quad (3.7)$$

This is our fundamental result for the two-photon absorption rate for stationary fields.

Our calculation has so far not included the effects of (natural) linewidth, either of the intermediate or of the final atomic states. Such effects are most simply taken into account by introducing damping terms into the basic equations for the amplitudes of the atomic states. One finds in this way that the effect of linewidth in the intermediate states is represented by replacing the function $g(\omega)$ given by Eq. (2.13) by the function

$$g(\omega)=\left(\frac{e}{\hbar mc}\right)^2\sum_j p_{fj}p_{j0}\frac{1}{\omega-\omega_j+\frac{1}{2}i\kappa_j}, \quad (3.8)$$

in which $\kappa_j$ is the decay rate by spontaneous emission from (and hence the natural linewidth of) the state $|j\rangle$. The width of the final state, on the other hand, is represented by averaging the result for a given final-state energy over a Lorentzian line-shape function[10] of width $\kappa_f$, so that we have

$$w_2=\frac{\kappa_f}{2\pi}\int d\nu[(\omega_f+\nu)^2+\tfrac{1}{4}\kappa_f^2]^{-1}w_2(\omega_f+\nu), \quad (3.9)$$

where $\hbar\omega_f$ is the mean energy of the final state, and $w_2(\omega_f+\nu)$ is given by Eqs. (3.7) and (3.8), with $\omega_f\rightarrow\omega_f+\nu$.

An interesting simplification of these results occurs for narrow-bandwidth fields near resonance. Let us introduce the function $\mathcal{G}^{(2)}(t_1',t_2';t_1,t_2)$ by means of the definition

$$G^{(2)}(t_1',t_2';t_1,t_2)\equiv e^{i\omega_0(t_1'+t_2'-t_1-t_2)}\mathcal{G}^{(2)}(t_1',t_2';t_1,t_2), \quad (3.10)$$

where $\omega_0$ is the mean frequency of the field. We note that $\mathcal{G}^{(2)}$ is approximately constant when the difference between any two of its arguments is much less then the reciprocal bandwidth $1/\Delta\omega$. We now assume that $\Delta\omega$ is small enough so that the function $g(\omega)$ varies by small relative amounts over the range $\Delta\omega$,

$$g(\omega\pm\Delta\omega)\approx g(\omega), \quad (3.11)$$

and that the mean frequency $\omega_0$ of the field is near enough to the resonant frequency $\frac{1}{2}\omega_f$ so that the relation

$$g(\omega\pm(\omega_0-\tfrac{1}{2}\omega_f))\approx g(\omega) \quad (3.12)$$

is satisfied. Then, since the function $F^{(2)}$ is nonvanishing only when all of its arguments are within the range $\Delta\omega$ of $\omega_0$, it is clear that we may replace the function $g(\omega)$ in Eq. (3.7) by its value for $\omega=\omega_0$. We then have

$$w_2(\omega_f)=(2\pi)^{-1}g^*(\omega_0)\times\left[\int\int d\omega' d\omega\, F^{(2)}(\omega_f-\omega',\omega';\omega_f-\omega,\omega)\right]g(\omega_0) = (2\pi)^{-1}g^*(\omega_0)\left[\int\int\int\int d\omega_1' d\omega_2' d\omega_1 d\omega_2 \times\delta(\omega_1'+\omega_2'-\omega_f)\delta(\omega_1+\omega_2-\omega_f) \times F^{(2)}(\omega_1',\omega_2';\omega_1,\omega_2)\right]g(\omega_0). \quad (3.13)$$

Let us now substitute the identity

$$\delta(\omega_1'+\omega_2'-\omega_f)\delta(\omega_1+\omega_2-\omega_f) = 2\delta(\omega_1'+\omega_2'+\omega_1+\omega_2-2\omega_f)\delta(\omega_1'+\omega_2'-\omega_1-\omega_2) = \pi^{-1}\int_{-\infty}^{\infty} dt\, e^{-i(\omega_1'+\omega_2'+\omega_1+\omega_2-2\omega_f)t} \times\delta(\omega_1'+\omega_2'-\omega_1-\omega_2) \quad (3.14)$$

[10] When collisional processes contribute to line-broadening, the Lorentzian function must be replaced by a more general line-shape function. See, for example, M. L. Goldberger and K. M. Watson, *Collision Theory* (John Wiley & Sons, Inc., New York, 1964), Chap. 8.

into the right-hand side of Eq. (3.13) and then make use of the definition (3.2) and the Fourier inversion of Eq. (2.15). In this way we find

$$w_2(\omega_f)=2g^*(\omega_0)\Big[\int_{-\infty}^{\infty} dt\, e^{2i\omega_f t} \times G^{(2)}(-t,-t;t,t)\Big]g(\omega_0) \quad (3.15a)$$

$$=2g^*(\omega_0)\Big[\int_{-\infty}^{\infty} dt\, e^{i(2\omega_f-4\omega_0)t} \times \mathcal{G}^{(2)}(-t,-t;t,t)\Big]g(\omega_0), \quad (3.15b)$$

where the last relation follows from Eq. (3.10). Thus the two-photon absorption rate for narrow-bandwidth stationary fields is given in terms of a simple Fourier integral of the second-order field correlation function, with both positive-frequency components equal to $t$ and both negative-frequency components equal to $-t$.

The relations (3.15) were derived for the case of a final state with fixed energy $\hbar\omega_f$, and are valid only if the width of the final state is small compared to the bandwidth of the field,

$$\kappa_f \ll \Delta\omega, \quad (3.16)$$

or, equivalently, only if the lifetime of the final state is large compared to the coherence time of the field. In the general case, the two-photon absorption rate may be obtained by substituting either of the Eqs. (3.15) into Eq. (3.9) and performing the indicated integration. We find

$$w_2=2g^*(\omega_0)\Big[\int_{-\infty}^{\infty} dt\, e^{2i\omega_f t-\kappa_f|t|} \times G^{(2)}(-t,-t;t,t)\Big]g(\omega_0) \quad (3.17a)$$

$$=2g^*(\omega_0)\Big[\int_{-\infty}^{\infty} dt\, e^{i(2\omega_f-4\omega_0)t-\kappa_f|t|} \times \mathcal{G}^{(2)}(-t,-t;t,t)\Big]g(\omega_0). \quad (3.17b)$$

If the width of the final state is large compared to the bandwidth of the field,

$$\kappa_f \gg \Delta\omega, \quad (3.18)$$

then the function $\mathcal{G}^{(2)}(-t,-t;t,t)$ in Eq. (3.17b) may be replaced by its value for $t=0$,

$$G^{(2)}(0)\equiv G^{(2)}(0,0;0,0)=\langle[\mathcal{A}^\dagger(0)]^2[\mathcal{A}(0)]^2\rangle, \quad (3.19)$$

and hence we have

$$w_2=g^*(\omega_0)G^{(2)}(0)g(\omega_0)\Big[\frac{\kappa_f}{\frac{1}{4}\kappa_f^2+(2\omega_0-\omega_f)^2}\Big]. \quad (3.20)$$

The two-photon absorption rate in this limit is thus proportional to the second-order field correlation function with vanishing arguments,[1–3,5,11] and a Lorentzian function of width $\kappa_f$, centered at $\omega_0=\frac{1}{2}\omega_f$.

We may remark that the proportionality of $w_2$ to $G^{(2)}(0)$ is a feature of all two-photon absorption processes in which a broad band of final atomic states is accessible. We may extend our results to include photoionization, for example, simply by integrating the rate given by Eq. (3.15b) over the density of final atomic states $n(\omega_f)$. If the function $n(\omega_f)$ varies slowly within the frequency bandwidth of the field, we find

$$w_2=2\pi g^*(\omega_0)G^{(2)}(0)g(\omega_0)n(2\omega_0). \quad (3.21)$$

## IV. CHAOTIC FIELDS: MODE INDEPENDENCE

A chaotic field may be defined as one for which the field density operator factors into density operators for each mode

$$\rho_F=\prod_k \rho_k, \quad (4.1)$$

where each of the single-mode density operators $\rho_k$ is stationary (diagonal in the $n$-quantum representation) and is characterized by a geometric law for the quantum-number probabilities:

$$\rho_k=\frac{1}{1+\bar{n}_k}\sum_{n_k}\Big(\frac{\bar{n}_k}{1+\bar{n}_k}\Big)^{n_k}|n_k\rangle_k\,{}_k\langle n_k|. \quad (4.2)$$

No restriction is made on the mean quantum numbers

$$\bar{n}_k\equiv\langle a_k^\dagger a_k\rangle, \quad (4.3)$$

as there would be, for example, in the case of thermal radiation.

We note that the relations (4.1) and (4.2) are equivalent to the moment relations

$$\langle a_{k_1'}^\dagger\cdots a_{k_n'}^\dagger a_{k_1}\cdots a_{k_m}\rangle = \delta_{nm}\bar{n}_{k_1}\cdots\bar{n}_{k_n}\sum_p \delta_{k_1'k_{p(1)}}\cdots\delta_{k_n'k_{p(n)}}, \quad (4.4)$$

where the summation is taken over all permutations $p$ on $n$ integers. The mean value of the product of two creation operators and two annihilation operators is thus

$$\langle a_{k_1'}^\dagger a_{k_2'}^\dagger a_{k_1}a_{k_2}\rangle=\bar{n}_{k_1}\bar{n}_{k_2}[\delta_{k_1'k_1}\delta_{k_2'k_2}+\delta_{k_1'k_2}\delta_{k_2'k_1}], \quad (4.5)$$

and the second factorial quantum-number moment for a given mode is

$$\langle a_k^{\dagger 2}a_k^2\rangle=\langle a_k^\dagger a_k(a_k^\dagger a_k-1)\rangle=2\bar{n}_k^2. \quad (4.6)$$

The field correlation functions are easily evaluated with the aid of these relations and the modal expansion (2.3) of the field. Restricting our attention to the values of these functions when the spatial arguments are set equal to zero, we find that the first-order field correla-

[11] The necessity of assuming a relatively broad final level to justify this result has also been noted by R. H. Lehmberg, thesis, Brandeis University, 1967 (unpublished).

tion function is given by

$$G^{(1)}(t',t)\equiv\langle\mathcal{E}^{\dagger}(t')\mathcal{E}(t)\rangle \tag{4.7}$$

$$=\Gamma(t-t'), \tag{4.8}$$

where

$$\Gamma(t)=(\hbar c^2/2V)\sum_k \hat{e}_k\hat{e}_k(\bar{n}_k/\omega_k)e^{-i\omega_k t}. \tag{4.9}$$

The product of an arbitrary number of creation operators and annihilation operators may be expressed in terms of the first-order correlation function as[12]

$$\langle\mathcal{E}^{\dagger}(t_1')\cdots\mathcal{E}^{\dagger}(t_n')\mathcal{E}(t_1)\cdots\mathcal{E}(t_m)\rangle$$
$$=\delta_{nm}G^{(n)}(t_1'\cdots t_n';t_1\cdots t_n)$$
$$=\delta_{nm}\sum_p G^{(1)}(t_1',t_{p(1)})\cdots G^{(1)}(t_n',t_{p(n)}). \tag{4.10}$$

These relations, generalized in an obvious manner to different spatial as well as temporal points, provide a characterization of chaotic fields fully equivalent to that given by Eqs. (4.1) and (4.2) for the density operator. It is important to realize, however, that the relations (4.10) for the field correlation functions may be satisfied to a very high degree of approximation even when the individual density operators $\rho_k$ for the field modes have forms very different from that given by Eq. (4.2). Indeed, as we shall now show, the relations (4.10) are valid in the limit $V\to\infty$, in an asymptotic sense presently to be defined, for any field in which the modes of oscillation are stationary and statistically independent of one another, irrespective of the statistics of the individual modes. This theorem, which is a generalization of the central limit theorem for a single random variable, may be illustrated by evaluating the second-order field correlation function, which, according to Eqs. (4.10) and (4.8), is given for chaotic fields by

$$G^{(2)}(t_1',t_2';t_1,t_2)=\Gamma(t_1-t_1')\Gamma(t_2-t_2')$$
$$+\Gamma(t_1-t_2')\Gamma(t_2-t_1'). \tag{4.11}$$

To evaluate this function for any density operator satisfying Eq. (4.1), we first introduce the parameters

$$J_k\equiv\langle a_k{}^{\dagger 2}a_k{}^2\rangle, \tag{4.12}$$

which would be equal to $2\bar{n}_k{}^2$ if $\rho_k$ were given by Eq. (4.3). In the general case, since the field modes are assumed to be stationary and statistically independent, it is clear that the expression on the left-hand side of Eq. (4.5) can be nonvanishing only if: (a) $k_1=k_1'$, $k_2=k_2'$, but $k_1\neq k_2$; (b) $k_1=k_2'$, $k_2=k_1'$, but $k_1\neq k_2$; or, (c) $k_1=k_2=k_1'=k_2'$. In cases (a) and (b), the quantity on the left-hand side of Eq. (4.5) is just $\langle a_{k_1}{}^{\dagger}a_{k_1}\rangle\langle a_{k_2}{}^{\dagger}a_{k_2}\rangle \equiv\bar{n}_{k_1}\bar{n}_{k_2}$, while in case (c) it is $J_{k_1}$. These relations are equivalent to the formula

$$\langle a_{k_1'}{}^{\dagger}a_{k_2'}{}^{\dagger}a_{k_1}a_{k_2}\rangle=\bar{n}_{k_1}\bar{n}_{k_2}(\delta_{k_1'k_1}\delta_{k_2'k_2}+\delta_{k_1'k_2}\delta_{k_2'k_1})$$
$$+(J_{k_1}-2\bar{n}_{k_1})\delta_{k_1k_2}\delta_{k_2k_1'}\delta_{k_1'k_2'}. \tag{4.13}$$

[12] R. J. Glauber, Phys. Rev. **131**, 2766 (1963).

If we make use of this relation and the modal expansion (2.3) to evaluate $G^{(2)}$, we find

$$G^{(2)}(t_1',t_2';t_1,t_2)$$
$$=\Gamma(t_1-t_1')\Gamma(t_2-t_2')+\Gamma(t_1-t_2')\Gamma(t_2-t_1')$$
$$+(1/V)\mathcal{J}(t_1+t_2-t_1'-t_2'), \tag{4.14}$$

where the function $\mathcal{J}$ is defined as

$$\mathcal{J}(t)\equiv\frac{\hbar^2c^4}{4V}\sum_k \hat{e}_k\hat{e}_k\hat{e}_k\hat{e}_k(J_k-2\bar{n}_k)\omega_k{}^{-2}e^{-i\omega_k t}. \tag{4.15}$$

In the limit of infinite quantization volume, the summation over discrete modes is replaced by $V$ times an integration over $k$ space (along with a sum over polarization vectors). It follows therefore, that if we keep the mode expectation values $\bar{n}_k$ and $J_k$ fixed as functions of $k$ (as we must do, for example, to guarantee that $G^{(1)}(t',t)$ remain fixed), we shall find that the function $\mathcal{J}(t)$ approaches a constant. It is clear, then, that in this limit the third term on the right-hand side of Eq. (4.14) approaches zero, and therefore that the second-order field correlation function approaches the value (4.11) for chaotic fields. Similar relations are easily derived for all of the higher-order correlation functions, and it follows that the field itself is chaotic, in the limit $V\to\infty$, for any density operator of the form (4.1), provided that each of the single-mode density operators $\rho_k$ is stationary.

To evaluate the second-order spectral correlation function defined by Eq. (2.15), we begin by introducing the first-order spectral function

$$\gamma(\omega)\equiv\int_{-\infty}^{\infty}dt\,e^{i\omega t}\Gamma(t). \tag{4.16}$$

We find then by substituting Eq. (4.11) into Eq. (2.15)

$$\tilde{G}^{(2)}{}_{\lambda_1'\lambda_2'\lambda_1\lambda_2}(\omega_1',\omega_2';\omega_1,\omega_2)$$
$$=\delta(\omega_1'-\omega_1)\delta(\omega_2'-\omega_2)\gamma_{\lambda_1'\lambda_1}(\omega_1)\gamma_{\lambda_2'\lambda_2}(\omega_2)$$
$$+\delta(\omega_1'-\omega_2)\delta(\omega_2'-\omega_1)\gamma_{\lambda_2'\lambda_1}(\omega_1)\gamma_{\lambda_1'\lambda_2}(\omega_2), \tag{4.17}$$

where we have written the vector indices explicitly to facilitate later work. The reduced second-order spectral-field correlation function is therefore

$$F^{(2)}{}_{\lambda_1'\lambda_2'\lambda_1\lambda_2}(\omega_1',\omega_2';\omega_1,\omega_2)=\delta(\omega_1'-\omega_1)\gamma_{\lambda_1'\lambda_1}(\omega_1)\gamma_{\lambda_2'\lambda_2}(\omega_2)$$
$$+\delta(\omega_2'-\omega_1)\gamma_{\lambda_2'\lambda_1}(\omega_1)\gamma_{\lambda_1'\lambda_2}(\omega_2). \tag{4.18}$$

To simplify the expression which results from substituting this relation into Eq. (3.7), we first note that, by virtue of the definitions (2.10), (2.15), and (3.2) and the commutativity of $\mathcal{E}(t_1)$ and $\mathcal{E}(t_2)$, the function $F^{(2)}$ is invariant under either of the interchanges $(\omega_1,\lambda_1)\leftrightarrow(\omega_2,\lambda_2)$ or $(\omega_1',\lambda_1')\leftrightarrow(\omega_2',\lambda_2')$, for arbitrary fields. To make use of these symmetry properties, we introduce the function

$$\bar{g}_{\lambda_1\lambda_2}(\omega)\equiv\tfrac{1}{2}[g_{\lambda_1\lambda_2}(\omega)+g_{\lambda_2\lambda_1}(\omega_f-\omega)] \tag{4.19a}$$

$$=\bar{g}_{\lambda_2\lambda_1}(\omega_f-\omega), \tag{4.19b}$$

which may be expressed in dyadic notation as

$$\bar{g}(\omega)=\frac{1}{2}\left(\frac{e}{\hbar mc}\right)^2 \times\sum_j\left[\frac{p_{fj}p_{j0}}{\omega-\omega_j+\frac{1}{2}i\kappa_j}+\frac{p_{j0}p_{fj}}{-\omega+\omega_f-\omega_j+\frac{1}{2}i\kappa_j}\right]. \quad (4.20)$$

It is clear then that we may replace the function $g(\omega)$ in Eq. (3.7) by the function $\bar{g}(\omega)$, so that we have, for arbitrary (stationary) fields

$$w_2(\omega_f)=(2\pi)^{-1}\int\int d\omega' d\omega \times\bar{g}^*(\omega')F^{(2)}(\omega_f-\omega',\omega';\omega_f-\omega,\omega)\bar{g}(\omega). \quad (4.21)$$

If we now make use of Eq. (4.18) in Eq. (4.21), we find that each term on the right-hand side of Eq. (4.18) contributes equally, and we obtain

$$w_2(\omega_f)=\pi^{-1}\int d\omega \times\mathrm{tr}[\bar{g}^*(\omega)\gamma(\omega_f-\omega)\bar{g}(\omega_f-\omega)\gamma(\omega)], \quad (4.22)$$

in which tr indicates summation over vector indices. Equation (4.22) thus expresses the two-photon absorption rate for chaotic fields in terms of the spectral first-order field correlation function $\gamma(\omega)$.

Let us now consider the case of narrow-bandwidth fields near resonance, i.e., fields with bandwidth $\Delta\omega$ and mean frequency $\omega_0$ satisfying the conditions (3.11) and (3.12). We also specialize to the case of plane-polarized fields, and evaluate $g(\omega)$, $G^{(2)}$, and $\Gamma$ with all vector indices in the direction of field polarization. We find then from Eqs. (3.17a) and (4.11) that the two-photon absorption rate to a final state of width $\kappa_f$ is

$$w_2=2|g(\omega_0)|^2\int_{-\infty}^{\infty}dt\, e^{i\omega_f t-\frac{1}{2}\kappa_f|t|}[\Gamma(t)]^2. \quad (4.23)$$

## V. ABSORPTION FROM LASER LIGHT

A number of authors[13] have devised a model of laser light based on the assumption of a fixed field amplitude, with a small randomly varying frequency, leading to phase diffusion. This model, which has been expressed in terms of the complex amplitude of a single field mode within the laser cavity, is easily modified so as to describe the field at a fixed point outside the cavity. In this section we shall review the model briefly, and calculate the second-order field correlation function, which we shall then use to evaluate the two-photon absorption rate.

[13] See, for example, Ref. 7, Lecture XV; J. R. Klauder and E. C. G. Sudarshan, *Fundamentals of Quantum Optics* (W. A. Benjamin, Inc., New York, 1968), Chap. 9.

To develop our analysis in quantum-mechanical terms, we begin by introducing the *coherent states*[12] of the field, which are particularly useful when the physical quantities we are dealing with are expressible as expectation values of normally ordered products of field creation and annihilation operators. A coherent state with complex amplitudes $\{\alpha_k\}$ may be expressed in terms of the vacuum state $|0\rangle_F$ by means of the relation

$$|\{\alpha_k\}\rangle_F=\exp[\sum_k(a_k^\dagger\alpha_k-\alpha_k^* a_k)]|0\rangle_F, \quad (5.1)$$

and has the eigenvalue property

$$a_k|\{\alpha_k\}\rangle_F=\alpha_k|\{\alpha_k\}\rangle_F. \quad (5.2)$$

For a wide variety of field states, the density operator for the field may be written in the $P$ representation[12,14]

$$\rho_F=\int(\prod_k d^2\alpha_k)P(\{\alpha_k\})|\{\alpha_k\}\rangle_F\,{}_F\langle\{\alpha_k\}|, \quad (5.3)$$

where $P(\{\alpha_k\})$ is a relatively well-behaved function of the oscillator amplitudes $\alpha_k$. Normally ordered moments may be written in the $P$ representation in a form closely resembling the corresponding classical expressions. The $n$th-order field correlation function, for example, is given by

$$G^{(n)}(t_1'\cdots t_n';t_1\cdots t_n)=\int(\prod_k d^2\alpha_k)P(\{\alpha_k\}) \times\prod_{j=1}^{n}[\mathfrak{A}^*(\{\alpha_k\},t_j')\mathfrak{A}(\{\alpha_k\},t_j)], \quad (5.4)$$

where $P(\{\alpha_k\})$ is the weight function for the initial density operator for the field, and

$$\mathfrak{A}(\{\alpha_k\},t)\equiv(\hbar c^2/2V)^{1/2}\sum_k\omega_k^{-1/2}\alpha_k e^{-i\omega_k t}. \quad (5.5)$$

Here we have again restricted our discussion to the case of equal spatial points $r_j=0$, and to simplify our calculations we have assumed the field to be plane-polarized.

The classical form of Eq. (5.4) enables us to carry out discussions of quantum-field statistics in the language of classical probability theory. If the weight function $P(\{\alpha_k\})$ is non-negative definite (as we shall assume it to be), then we may speak of the expansion (5.3) of the density operator as representing an ensemble of $c$-number fields of the form (5.5). A light beam with fixed amplitude $I^{1/2}$, for example, is described by a weight function $P(\{\alpha_k\})$ which vanishes for all values of $\{\alpha_k\}$ except those for which

$$|\mathfrak{A}(\{\alpha_k\},t)|=I^{1/2}, \quad (5.6)$$

for all $t$. Such a beam may be thought of as a statistical

[14] E. C. G. Sudarshan, Phys. Rev. Letters **10**, 277 (1963).

ensemble of fields of the form

$$\mathfrak{A}(t)=I^{1/2}e^{-i\varphi(t)}, \tag{5.7}$$

where $\varphi(t)$ is a stochastic function of time.

Let us now assume that the field is generated by a source oscillating at the frequency $\omega(t)=\omega_0+\Delta\omega(t)$, where $\Delta\omega(t)$ is a small, slowly varying function of time, satisfying $\langle\Delta\omega(t)\rangle=0$. The phase of the field at time $t$ is thus

$$\varphi(t)=\varphi_0+\omega_0 t+\Delta\varphi(t), \tag{5.8a}$$

where

$$\Delta\varphi(t)=\int_0^t dt'\Delta\omega(t'). \tag{5.8b}$$

We assume the initial phase $\varphi_0$ to be uniformly distributed between 0 and $2\pi$, as we must to insure stationarity. The frequency modulation function $\Delta\omega(t)$ is assumed to be governed by a (real) *stationary joint Gaussian random process*: This means that the moments of $\Delta\omega(t)$ are given in terms of the second-moment function

$$\langle\Delta\omega(t)\Delta\omega(t')\rangle\equiv\mathfrak{F}(t-t') \tag{5.9}$$

by the formulas

$$\langle\Delta\omega(t_1)\cdots\Delta\omega(t_{2n+1})\rangle=0, \tag{5.10a}$$

$$\langle\Delta\omega(t_1)\cdots\Delta\omega(t_{2n})\rangle=(2^m m!)^{-1}\sum_p \mathfrak{F}(t_{p(1)}-t_{p(2)})\cdots \times\mathfrak{F}(t_{p(2n-1)}-t_{p(2n)}), \tag{5.10b}$$

where the sum extends over all permutations $p$ on $2n$ integers. An equivalent characterization of a joint Gaussian random process is in terms of the *characteristic functional*

$$\chi[f(\tau)]\equiv\left\langle\exp\left[i\int d\tau\,\Delta\omega(\tau)f(\tau)\right]\right\rangle, \tag{5.11}$$

which is given by[15]

$$\chi[f(\tau)]=\exp\left\{-\frac{1}{2}\left\langle\left[\int d\tau\,\Delta\omega(\tau)f(\tau)\right]^2\right\rangle\right\} \tag{5.12a}$$

$$=\exp\left\{-\frac{1}{2}\int\int d\tau d\tau' f(\tau)\mathfrak{F}(\tau-\tau')f(\tau')\right\} \tag{5.12b}$$

for arbitrary functions $f(\tau)$.

[15] The relation (5.12a) follows from the fact that the integral within the exponential function in Eq. (5.11) is itself a (real) Gaussian random variable.

The first-order field-correlation function is given by

$$G^{(1)}(t',t)\equiv\langle\mathfrak{A}^*(t')\mathfrak{A}(t)\rangle$$
$$=Ie^{-i\omega_0(t-t')}\left\langle\exp\left(i\int_t^{t'}d\tau\Delta\omega(\tau)\right)\right\rangle$$
$$=Ie^{-i\omega_0(t-t')}\exp\left(-\frac{1}{2}\int_0^{|t-t'|}\int d\tau d\tau'\mathfrak{F}(\tau-\tau')\right), \tag{5.13}$$

where the last step follows from Eqs. (5.11) and (5.12b) by putting $f(\tau)=1$ for $\tau$ between $t$ and $t'$, and $f(\tau)=0$ otherwise.

Let us now assume that the correlation time for the random frequency modulation is much smaller than any other time we need consider. We may then approximate the function $\mathfrak{F}(\tau)$ by

$$\mathfrak{F}(\tau)\sim 2b\delta(\tau), \tag{5.14}$$

where

$$b=\frac{1}{2}\int_{-\infty}^{\infty}d\tau\,\mathfrak{F}(\tau). \tag{5.15}$$

We find then from Eq. (5.13) that the function $\Gamma(t)$ defined by Eq. (4.8) is given in this limit by[13]

$$\Gamma(t)=Ie^{-i\omega_0 t-b|t|}. \tag{5.16}$$

The power spectrum of the field is thus the Lorentzian function

$$\gamma(\omega)=I\frac{2b}{(\omega-\omega_0)^2+b^2}. \tag{5.17}$$

The second-order field correlation function is given by

$$G^{(2)}(t_1',t_2';t_1,t_2)\equiv\langle\mathfrak{A}^*(t_1')\mathfrak{A}^*(t_2')\mathfrak{A}(t_1)\mathfrak{A}(t_2)\rangle, \tag{5.18}$$

and the function $\mathcal{G}^{(2)}$ defined by Eq. (3.10) is therefore given by

$$\mathcal{G}^{(2)}(t_1',t_2';t_1,t_2)$$
$$=I^2\langle\exp\{i[\Delta\varphi(t_1')+\Delta\varphi(t_2')-\Delta\varphi(t_1)-\Delta\varphi(t_2)]\}\rangle$$
$$=I^2\exp\{-\tfrac{1}{2}\langle[\Delta\varphi(t_1')+\Delta\varphi(t_2')-\Delta\varphi(t_1)-\Delta\varphi(t_2)]^2\rangle\}, \tag{5.19}$$

where the last step follows from Eq. (5.12a) and the definition (5.8b) of $\Delta\varphi(t)$ as an expression linear in the stochastic function $\Delta\omega(t)$.

To simplify the evaluation of the statistical average in Eq. (5.19), let us begin by choosing the (arbitrary) origin of time far enough in the past so that all four times $t_1'$, $t_2'$, $t_1$, and $t_2$ are positive. The value of a diagonal term such as $\langle[\Delta\varphi(t_1)]^2\rangle$ is then, by virtue of Eqs. (5.8b), (5.9), and (5.14),

$$\langle[\Delta\varphi(t_1)]^2\rangle=2bt_1. \tag{5.20}$$

A cross term, such as $2\langle\Delta\varphi(t_1)\Delta\varphi(t_2)\rangle$ in Eq. (5.19), may be similarly evaluated. Denoting by $t_<$ the smaller of the two terms $t_1$ and $t_2$, we find

$$2\langle\Delta\varphi(t_1)\Delta\varphi(t_2)\rangle=4bt_< \\ =4b[\tfrac{1}{2}(t_1+t_2)-\tfrac{1}{2}|t_1-t_2|]. \quad (5.21)$$

By using these relations and similar ones for the remaining terms in the statistical average in Eq. (5.19), we find that the second-order correlation function for a fixed-amplitude random frequency-modulated field is[15a]

$$\mathcal{G}^{(2)}(t_1',t_2';t_1,t_2)=I^2\exp[b(|t_1-t_2|+|t_1'-t_2'| \\ -|t_1-t_1'|-|t_2-t_2'|-|t_1-t_2'|-|t_2-t_1'|)], \quad (5.22)$$

which is explicitly independent of the origin of time, and thus valid for all (positive and negative) values of its arguments.

The statistical constancy of the field amplitude may be exhibited by evaluating Eq. (5.22) at $t_2'=t_2$, and then noting that the resulting expression is independent of $t_2$: if we make use of Eq. (5.16) and the definitions (4.8) and (3.10), we find

$$G^{(2)}(t_1',t_2;t_1,t_2)=IG^{(1)}(t_1',t_1). \quad (5.23)$$

When all four arguments of $G^{(2)}$ are equal, we have

$$G^{(2)}(0)=I^2=[G^{(1)}(0)]^2, \quad (5.24)$$

in contrast to the relation

$$G^{(2)}(0)=2[G^{(1)}(0)]^2, \quad (5.25)$$

which holds for Gaussian fields.

Let us now assume that the field bandwidth $\Delta\omega=b$ and mean frequency $\omega_0$ satisfy Eqs. (3.11) and (3.12). Then we may evaluate the two-photon absorption rate $w_2^{(l)}$ for our model of laser light by making use of Eq. (5.22) for $\mathcal{G}^{(2)}$ in Eq. (3.17b). We find then

$$w_2^{(l)}=I^2|g(\omega_0)|^2\frac{2(4b+\frac{1}{2}\kappa_f)}{(4b+\frac{1}{2}\kappa_f)^2+(2\omega_0-\omega_f)^2}. \quad (5.26)$$

It is instructive to compare this result to the two-photon absorption rate $w_2^{(\mathrm{ch})}$ for chaotic fields with the same power spectrum, and hence the same first-order correlation function. If we substitute Eq. (5.16) for $\Gamma(t)$ into Eq. (4.23), we find

$$w_2^{(\mathrm{ch})}=I^2|g(\omega_0)|^2\frac{4(2b+\frac{1}{2}\kappa_f)}{(2b+\frac{1}{2}\kappa_f)^2+(2\omega_0-\omega_f)^2}. \quad (5.27)$$

In the limit in which the width of the final state is much greater than the bandwidth of the field ($\kappa_f\gg b$), the rates given by Eqs. (5.26) and (5.27) approach the values given by Eq. (3.20), where $G^{(2)}(0)$ is equal to $I^2$ for coherent light and $2I^2$ for chaotic light. The ratio between the absorption rates is therefore[1-3,5]

$$w_2^{(\mathrm{ch})}/w_2^{(l)}=2 \quad \text{for} \quad \kappa_f\gg b, \quad (5.28)$$

a result which also is valid, according to Eq. (3.21), for photoionization by means of two-photon absorption.[16]

In the limit $\kappa_f\ll b$, however, which corresponds to transitions to an infinitely sharp line, the rates given by Eqs. (5.26) and (5.27) approach the asymptotic values

$$w_2^{(l)}=I^2|g(\omega_0)|^2\frac{2b}{4b^2+(\omega_0-\frac{1}{2}\omega_f)^2}, \quad (5.29)$$

$$w_2^{(\mathrm{ch})}=I^2|g(\omega_0)|^2\frac{2b}{b^2+(\omega_0-\frac{1}{2}\omega_f)^2}. \quad (5.30)$$

The ratio between these rates depends on the amount by which the mean frequency $\omega_0$ of the field differs from the resonant frequency $\frac{1}{2}\omega_f$. If the beam is exactly on resonance, the two-photon absorption rate for chaotic light is four times that for laser light,

$$w_2^{(\mathrm{ch})}=4w_2^{(l)} \quad \text{for} \quad \kappa_f\ll b \\ (\omega_0-\tfrac{1}{2}\omega_f)\ll b, \quad (5.31)$$

while if the beam is far off resonance [but with $(\omega_0-\frac{1}{2}\omega_f)$ still satisfying Eq. (3.12)], the two rates are equal,

$$w_2^{(\mathrm{ch})}=w_2^{(l)} \quad \text{for} \quad \kappa_f\ll b \\ (\omega_0-\tfrac{1}{2}\omega_f)\gg b. \quad (5.32)$$

These results for transitions to a very sharp level, unlike the relation (5.28) for a (relatively) broad level, depend upon the specific form (5.22) of the second-order field correlation function, and hence on the particular model we have adopted for laser light.

[15a] *Note added in proof.* B. Picinbono and E. Boileau [J. Opt. Soc. Am. **58**, 784 (1967)] have analyzed in detail the model of laser light that we have presented. They obtain formulas for the field correlation functions of all orders, and find the result (5.22) for the second-order correlation function.

[16] This result has been confirmed experimentally by F. Shiga and S. Imamura, Phys. Letters **25A**, 706 (1967).