

## Coherence and Two-Photon Absorption\*

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A kinetic theory of the two-photon absorption from a single mode of the radiation field is presented. It is found that, in general, the rate of two-photon absorption depends on certain correlation functions, and hence on the coherence properties, of the field. The results are applied to the case of a pure coherent state and the case of a chaotic field.

### 1. INTRODUCTION

THE purpose of this paper is to discuss the connection between two-photon absorption and the coherence properties of the light beam inducing the process. As is shown subsequently, the rate of two-photon absorption depends, not on the average number of photons, but on certain correlation functions. There are states of the light field for which these correlation functions reduce to the average number of photons. Such, for example, is the case of a pure coherent state (in the Glauber<sup>1</sup> sense) of a single mode of the radiation field. In other cases, however, more complicated functions may be involved.

It has been suggested,<sup>2</sup> and arguments in favor of the suggestion have been advanced,<sup>3</sup> that the state of the field of a well-stabilized laser oscillator operating in a single mode is, to a good approximation, a pure coherent state. Near threshold, however, a random amplitude modulation is present,<sup>4</sup> but the light is quite intense and monochromatic. If laser light near threshold can be used to induce two-photon absorption, the results of this paper show that the process will be affected by the amplitude modulation. Well above threshold, the pure coherent state is approached and the two-photon absorption then depends only on the average number of photons. In general, the two-photon absorption could conceivably be used to measure the pertinent correlation functions.

Looked at from the viewpoint of photon statistics, the present work hopefully sheds some light on the physical significance of photon correlation functions.<sup>2,5</sup> In fact, a very similar case in which the two photons are absorbed by two different atoms has been discussed by Glauber.<sup>6</sup>

### 2. RATE OF TWO-PHOTON ABSORPTION

For the purposes of this paper, it will suffice to consider a single atom interacting with a single mode of the radiation field. The nonrelativistic Hamiltonian of the system, neglecting the term  $\mathbf{A}^2$ , using the dipole approximation, and introducing the usual creation and annihilation operators, is

$$H = \hbar\omega_0(a^\dagger a + \frac{1}{2}) + H^S + D(a^\dagger + a), \quad (2.1)$$

where  $\omega_0$  is the frequency of the field mode,  $H^S$  is the Hamiltonian of the atom, and  $D$ , which is defined by

$$D \equiv - (e/m)(\hbar/2\omega_0)^{1/2}(\mathbf{p} \cdot \boldsymbol{\epsilon}), \quad (2.2)$$

is the projection of the dynamic electric-dipole-moment operator on the polarization vector  $\boldsymbol{\epsilon}$  of the mode. The symbols  $e$ ,  $m$ , and  $\mathbf{p}$  indicate, as usual, the charge, the mass, and the momentum operator, respectively. The term  $\mathbf{A}^2$  is neglected for the sake of simplicity of presentation, since it does not add any new features to the problem at hand, as far as the photon statistics is concerned. A very interesting discussion of the significance of this term from the viewpoint of atomic dynamics, is given in Ref. 7.

The quantity that one should compute in a two-photon absorption experiment is the rate at which the process takes place. Thus, if

$$\chi(t) \equiv \text{Tr}\{\alpha^\dagger \alpha \rho(t)\} \quad (2.3)$$

is the expected number of photons at time  $t$ , the time rate of change of  $\chi$  is given by

$$d\chi(t)/dt = \text{Tr}\{\alpha^\dagger \alpha [d\rho(t)/dt]\}. \quad (2.4)$$

The time evolution of  $\rho(t)$  is determined by the formula

$$\rho(t+\tau) = U(\tau)\rho(t)U^\dagger(\tau), \quad (2.5)$$

where

$$U(\tau) \equiv e^{-(i/\hbar)H\tau} \quad (2.6)$$

is the time-evolution operator of the system. Now,

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<sup>1</sup> R. Glauber, Phys. Rev. **131**, 2766 (1963).

<sup>2</sup> R. Glauber, Phys. Rev. Letters **10**, 84 (1963).

<sup>3</sup> R. H. Picard and C. R. Willis, Phys. Rev. **139**, A10 (1965).

<sup>4</sup> H. Haken, Phys. Rev. Letters **13**, 329a (1964).

<sup>5</sup> L. Mandel, Phys. Rev. **136**, B1221 (1964).

<sup>6</sup> R. Glauber, in *Quantum Optics and Electronics*, edited by C. DeWitt (Gordon and Breach Science Publishers, Inc., New York, 1965).

<sup>7</sup> R. Guccione and J. Van Kranendonk, Phys. Rev. Letters **14**, 583 (1965).

approximating (see Appendix A)

$$\frac{d\rho(t)}{dt} \cong \frac{\Delta\rho(t)}{\Delta t} = \frac{\rho(t+\tau) - \rho(t)}{\tau}, \quad (2.7)$$

and combining Eqs. (2.4), (2.5), and (2.7) one obtains

$$\frac{dx(t)}{dt} = \text{Tr} \left\{ a^\dagger a \frac{U(\tau)\rho(t)U^\dagger(\tau) - \rho(t)}{\tau} \right\}. \quad (2.8)$$

Let  $|n\rangle$  and  $|s\rangle$  be the representations<sup>8</sup> diagonalizing  $a^\dagger a$  and  $H^S$ , respectively; i.e.,

$$a^\dagger a |n\rangle = n |n\rangle, \quad (2.9a)$$

and

$$H^S |s\rangle = E_s |s\rangle. \quad (2.9b)$$

Also, let  $t$  be the time at which the interaction occurs. Prior to that moment, atom and field are uncoupled and consequently one can assume that

$$\rho(t) = \rho^R(t)\rho^S(t), \quad (2.10)$$

where  $\rho^R(t)$  is the density operator of the field mode and

$\rho^S(t)$  the density operator of the atom before interaction. In almost all practical cases the atom will initially be in a definite energy eigenstate, presumably the ground state. But let us simply assume for the moment that  $\rho^S(t)$  is diagonal in the  $s$  representation. Then, Eq. (2.8) yields

$$\frac{dx(t)}{dt} = \sum_{\substack{nn'n'' \\ ss'}} n(1/\tau) \langle ns | U(\tau) | n's' \rangle \rho_{n'n''} \rho_{s's'}^R \times \langle n's' | U^\dagger(\tau) | ns \rangle - \sum_{n's'} n'(1/\tau) \rho_{n'n''} \rho_{s's'}^S. \quad (2.11)$$

Substituting the identity

$$\sum_{ns} \langle ns | U(\tau) | n's' \rangle \langle n's' | U^\dagger(\tau) | ns \rangle = 1, \quad (2.12)$$

into the second term of Eq. (2.11); separating the first term into two parts: one containing the diagonal matrix elements of  $\rho^R$  and a second containing the off-diagonal matrix elements; and combining the term containing the diagonal matrix elements with the second term of Eq. (2.11) one obtains

$$\frac{dx(t)}{dt} = \sum_{nn'} (n - n') \rho_{n'n''}^R \sum_{ss'} \rho_{s's'}^S \frac{|\langle ns | U(\tau) | n's' \rangle|^2}{\tau} + \sum_{\substack{nn'n'' \\ (n' \neq n'')}} n \rho_{n'n''}^R \sum_{ss'} \rho_{s's'}^S \frac{\langle ns | U(\tau) | n's' \rangle \langle n's' | U^\dagger(\tau) | ns \rangle}{\tau}. \quad (2.13)$$

The time interval  $\tau$  is assumed to be macroscopically small, but large compared to characteristic times of atomic transitions (see Appendix A). This concept of temporal coarse-graining is frequently used in quantum transport theory (see, for example, Ref. 9).

At this point, we make the assumption that the atom is initially in its ground state which will be denoted by  $|s_0\rangle$ . Then  $\rho_{s's'}^S = \delta_{s's_0}$  (Kronecker delta). In addition, let us replace  $n$  by  $n' + j$  and then rename  $n'$  by  $n$  and  $n''$  by  $m$ . The resulting equation is

$$\frac{dx(t)}{dt} = \sum_{n=0}^{\infty} \sum_{j=-\infty}^{\infty} j \rho_{nn}^R \sum_s \frac{|\langle (n+j)s | U(\tau) | ns_0 \rangle|^2}{\tau} + \sum_{\substack{nm=0 \\ (n \neq m)}}^{\infty} \sum_{j=-\infty}^{\infty} (n+j) \rho_{nm}^R \sum_s \frac{\langle (n+j)s | U(\tau) | ns_0 \rangle \langle ms_0 | U^\dagger(\tau) | (n+j)s \rangle}{\tau}. \quad (2.14)$$

This equation gives the time rate of change of the number of photons due to all processes. Here, we are specifically interested in that part of the time rate of change which is due to the simultaneous absorption of two photons. Let us denote this part by  $(d\chi/dt)_{(-2)}$ . It is evident that, from the first term in the right side of Eq. (2.14), the subterm corresponding to  $j = -2$  gives such a contribution. We shall denote this contribution

by  $(d\chi/dt)_{(-2)'}'$ ; that is

$$\left(\frac{dx}{dt}\right)'_{(-2)} = -2 \sum_{n=0}^{\infty} \rho_{nn}^R \sum_s \frac{|\langle (n+2)s | U(\tau) | ns_0 \rangle|^2}{\tau}. \quad (2.15)$$

Presumably, there will be also a contribution from the second term in the right side of Eq. (2.14). It is not *a priori* obvious that this contribution also comes from the subterm  $j = -2$ . In fact, as is shown subsequently, there is a contribution from  $j = 0$  as well. Thus, we denote by  $(d\chi/dt)_{(-2)''}$  the contribution from the second term. We now have

$$\left(\frac{dx}{dt}\right)_{(-2)} = \left(\frac{dx}{dt}\right)'_{(-2)} + \left(\frac{dx}{dt}\right)''_{(-2)}. \quad (2.16)$$

<sup>8</sup> Since we are not interested in stationary fields only, it might be considered disadvantageous to describe the field in terms of the  $n$  representation. This is probably true, but one also has to calculate the matrix elements of  $U(\tau)$  and it is extremely inconvenient to do so in any other representation. Of course, the representation chosen should not have any essential consequence on the final results, as long as nothing important is neglected.

<sup>9</sup> R. K. Osborn and E. Klevans, *Ann. Phys. (N. Y.)* **15**, 105 (1961).

The remaining calculation is a matter of computing the matrix elements of  $U(\tau)$ . For the sake of simplicity, we ignore all questions of line shape and use conventional perturbation theory based on the expansion<sup>10</sup>

$$U(\tau) = U^{(0)}(\tau) \left[ 1 - i\hbar^{-1} \int_0^\tau dt U^{(0)\dagger}(t) V U^{(0)}(t) - \hbar^{-2} \int_0^\tau dt \int_0^t dt' U^{(0)\dagger}(t) V U^{(0)}(t-t') V U^{(0)}(t) + \dots \right], \quad (2.17)$$

where

$$U^{(0)}(t) \equiv e^{-(i/\hbar)H^0 t}, \quad (2.18a)$$

$$H^0 \equiv \hbar\omega_0(\alpha^\dagger\alpha + \frac{1}{2}) + H^S, \quad (2.18b)$$

and

$$V \equiv D(\alpha^\dagger + \alpha). \quad (2.18c)$$

A straightforward, but somewhat lengthy calculation, in which only terms conserving energy are retained, yields

$$\left(\frac{dx}{dt}\right)_{(-2)}' = - \sum_{n=0}^{\infty} 2n(n-1)\rho_{nn}^R \times \left\{ \sum_{ss'} (2\pi/\hbar^4) |D_{ss'}|^2 |D_{s's_0}|^2 (\omega_0 - \omega_{s's_0})^{-2} \times [\delta(\omega_0 - \omega_{ss'}) + \delta(2\omega_0 - \omega_{ss_0})] \right\}, \quad (2.19a)$$

where

$$\omega_{ss_0} = (E_s - E_{s_0})/\hbar. \quad (2.19b)$$

The appearance of the delta functions is due to the assumption that the levels of the atom are sharply defined. When the broadening of the levels is taken into consideration, the delta functions are replaced by appropriate line-shape functions. The factor  $(\omega_0 - \omega_{s's_0})^{-2}$  and the term  $\delta(\omega_0 - \omega_{ss'})$  indicate that the process is enhanced if there exist intermediate states lying approximately half-way between the initial and the final state.

Next we compute the matrix elements

$$\langle (n+j)s | U(\tau) | ns_0 \rangle \quad \text{and} \quad \langle ms_0 | U^\dagger(\tau) | (n+j)s \rangle.$$

The results of the calculation are presented in Appendix B. When the two matrix elements are multiplied, one finds that there are only two terms which are of the same order as the terms in Eq. (2.19a), conserve energy, and satisfy the requirement  $n \neq m$ . Consequently, the contribution from the second term of the right side of Eq. (2.14) is

$$\left(\frac{dx}{dt}\right)_{(-2)}'' = - \left\{ \sum_{n=0}^{\infty} \rho_{n(n-2)}^R (n-2)(n-1)[n(n-1)]^{1/2} + \sum_{n=0}^{\infty} \rho_{n(n+2)}^R n(n+1)[(n+1)(n+2)]^{1/2} \right\} \times \left\{ \sum_{ss'} (2\pi/\hbar^4) |D_{ss'}|^2 |D_{s's_0}|^2 (\omega_0^2 - \omega_{s's_0}^2)^{-1} \times \delta(\omega_0 - \omega_{ss'}) \right\}. \quad (2.20)$$

<sup>10</sup> A. Messiah, *Quantum Mechanics* (John Wiley & Sons, Inc., New York, 1962), Vol. II, p. 724.

It will greatly facilitate the subsequent discussion if we introduce the symbols:

$$\sigma_1 \equiv \sum_{ss'} (2\pi/\hbar^4) |D_{ss'}|^2 |D_{s's_0}|^2 (\omega_0 - \omega_{s's_0})^{-2} \times \delta(\omega_0 - \omega_{ss'}), \quad (2.21a)$$

$$\sigma_2 \equiv \sum_{ss'} (2\pi/\hbar^4) |D_{ss'}|^2 |D_{s's_0}|^2 (\omega_0^2 - \omega_{s's_0}^2)^{-1} \times \delta(\omega_0 - \omega_{ss'}), \quad (2.21b)$$

$$\sigma_3 \equiv \sum_{ss'} (2\pi/\hbar^4) |D_{ss'}|^2 |D_{s's_0}|^2 (\omega_0 - \omega_{s's_0})^{-2} \times \delta(2\omega_0 - \omega_{ss_0}), \quad (2.21c)$$

and

$$G_1 = \sum_{n=0}^{\infty} \rho_{nn}^R 2n(n-1), \quad (2.22a)$$

$$G_2 = \sum_{n=0}^{\infty} \rho_{n(n-2)}^R (n-2)(n-1)[n(n-1)]^{1/2}, \quad (2.22b)$$

$$G_3 = \sum_{n=0}^{\infty} \rho_{n(n+2)}^R n(n+1)[(n+1)(n+2)]^{1/2}. \quad (2.22c)$$

Then, the rate of two-photon absorption is

$$(d\chi/dt)_{(-2)} = -G_1\sigma_1 - G_1\sigma_3 - G_2\sigma_2 - G_3\sigma_2 \quad (2.23)$$

The dependence of the process on the dynamics of the atom is contained in the  $\sigma$ 's while the dependence on the field is contained in the  $G$ 's. The last two terms come from the off-diagonal matrix elements of the density operator of the field mode in the  $n$  representation.

Note that  $\sigma_2$  can become negative as well as positive, in contrast to  $\sigma_1$  and  $\sigma_3$  which are never negative. This implies that the presence of the off-diagonal matrix elements of  $\rho^R$  can either enhance or diminish the rate. An order of magnitude comparison between  $\sigma_1$  and  $\sigma_2$  shows that  $\sigma_2/\sigma_1$  is of the order of  $(\omega_0 - \omega_{s's_0})/(\omega_0 + \omega_{s's_0})$ . If there exists, therefore, an intermediate level half-way between the initial and the final state, then  $\sigma_2$  is negligible as compared to  $\sigma_1$ . If  $\omega_0$  is much different than any  $\omega_{s's_0}$  the two quantities are comparable. In the latter case, however, probably both  $\sigma_1$  and  $\sigma_2$  are negligible as compared to  $\sigma_3$  (it is assumed that there exists a level  $s$  such that  $2\omega_0 \simeq \omega_{ss_0}$ ). Of course, the above discussion is meaningful only if one understands the delta functions as replaced by nonsingular line-shape functions.

The foregoing considerations refer to the dependence of the process on the properties of the atom alone. Consider now the functions  $G$ . One can easily show that

$$G_1 = 2 \text{Tr}\{\rho^R \alpha^\dagger \alpha \alpha^\dagger \alpha\}, \quad (2.24a)$$

$$G_2 = \text{Tr}\{\rho^R \alpha^\dagger \alpha \alpha \alpha^\dagger \alpha\}, \quad (2.24b)$$

and

$$G_3 = \text{Tr}\{\rho^R \alpha^\dagger \alpha^\dagger \alpha \alpha^\dagger \alpha\}. \quad (2.24c)$$

Thus the dependence of the process on the field comes through these correlation functions. Note that  $G_3 = G_2^*$  so that  $G_2 + G_3$  is real, as it should since  $d\chi/dt$  is ob-

servable. In the event that  $G_2$  and  $G_3$  can be ignored [either because  $(G_2+G_3)\sigma_2$  is small or  $\rho^R$  is diagonal in the  $n$  representation, in which case  $G_2=G_3=0$ ], Eq. (2.24a) shows that the two-photon absorption measures the second-order normal-ordered correlation function of the field mode. Subsequently we examine the cases of two particular states of the field mode.

### 3. PURE COHERENT STATE

In this Section, we assume that the field mode is initially in a pure coherent state  $|\beta\rangle$  which is defined by

$$\alpha|\beta\rangle = \beta|\beta\rangle. \quad (3.1)$$

Then, in Glauber's  $P$  representation<sup>1</sup>  $\rho^R$  reads

$$\rho^R = \int \delta^{(2)}(\alpha-\beta) |\alpha\rangle\langle\alpha| d^2\alpha. \quad (3.2)$$

The traces in Eqs. (2.24) are conveniently calculated by using Eq. (3.2) and Eqs. (4.2) and (7.21) of Ref. 1. In the case of  $G_2$  and  $G_3$ , one first writes them as a linear combination of normal-ordered products of third and second order. The result of the calculation is

$$G_1 = 2|\beta|^4 = 2\langle n \rangle^2, \quad (3.3)$$

and

$$G_2+G_3 = 2|\beta|^2(2+|\beta|^2)[(\text{Re}\beta)^2 - (\text{Im}\beta)^2], \quad (3.4)$$

where  $\langle n \rangle \equiv |\beta|^2$  is the average number of photons.

It is therefore concluded that, if the contribution of  $G_2+G_3$  can be ignored, the process is proportional to the square of the average number of photons. Presumably, in most practical cases the contribution of  $G_2+G_3$  can be neglected because of the smallness of  $\sigma_2$ .

Let us now look at  $G_2+G_3$  independently of the magnitude of  $\sigma_2$ . As Eq. (3.4) shows,  $G_2+G_3$  depends on the absolute phase of the laser beam, assuming that such a beam is in a pure coherent state. If one were to perform the experiment many times, the initial phase of the laser beam would, as a practical matter, be uncontrollably random. This situation would correspond to a mixture of coherent states with uniformly distributed phases. Then, the effect of  $G_2+G_3$  averaged over many measurements vanishes. This is to be expected since such a density operator is stationary and hence its off-diagonal matrix elements vanish (see Ref. 1, p. 2784). Thus, it appears that in almost all practical cases the effect of  $G_2+G_3$  vanishes. To perform an experiment in which this effect would not be vanishingly small, one would need a light source of fairly controllable phase.

### 4. CHAOTIC FIELD

Now, let us consider a field described by a Gaussian density operator. This corresponds to the Planck distribution and Glauber<sup>1</sup> has introduced the term "chaotic"

for such a field. The density operator is given by<sup>1</sup>

$$\begin{aligned} \rho^{\text{RG}} &= \frac{1}{\pi\langle n \rangle} \int e^{-|\alpha|^2/\langle n \rangle} |\alpha\rangle\langle\alpha| d^2\alpha \\ &= \frac{1}{1+\langle n \rangle} \sum_{n=0}^{\infty} \left( \frac{\langle n \rangle}{1+\langle n \rangle} \right)^n |n\rangle\langle n|, \end{aligned} \quad (4.1)$$

where again  $\langle n \rangle$  is the average number of photons. This density operator is diagonal in the  $n$  representation and there is no contribution arising from off-diagonal matrix elements. Computing  $G_1$  as indicated in the preceding section, one finds

$$G_1 = 4\langle n \rangle^2. \quad (4.2)$$

Thus, for the same average number of photons (or average energy), the effect of a Gaussian density operator appears to be larger than that of a pure coherent state by a factor of 2, provided that in the latter case the contribution of  $G_2+G_3$  can be ignored. It is not *a priori* obvious that states of the field mode for which the difference is larger do not exist.

Incidentally, the last two sections provide an illustration of the usefulness of Glauber's coherent states. It would have been very difficult to calculate the correlation functions  $G$  without using the  $P$  representation of the density operator.

### 5. DISCUSSION

It has been shown that the rate of two-photon absorption from a single mode of the radiation field depends on the stochastic properties of the field mode and the pertinent correlation functions have been found. The calculations in Secs. 3 and 4 show that there exist states of the field for which the process simply depends on the average energy. This dependence, however, is not the same for all such states, as the two specific examples illustrate. Moreover, states of the mode exist for which the process does not depend on the average energy only, but also on higher order correlation functions.

At the present time, experimental observation of the process is achievable only by using strongly coherent light sources, i.e., lasers. In interpreting such experiments, it is customary to consider the appropriate matrix element of the atomic transition involved, square its absolute value and multiply it by the square of the average energy. This procedure is in agreement with the results of Sec. 3, as long as the laser beam can be assumed to be in a pure coherent state. Recently, however, the statement has been made<sup>7</sup> that this dependence on the average energy is the same for both coherent and incoherent light. It is felt that the results of this paper contradict the above statement. Moreover, the actual laser light may not be in a pure coherent state. For example, it might be describable by a density operator for which  $P(\alpha)$  is not a delta function but a peaked function of  $\alpha$ .

It is evident that the formula usually quoted in the literature (see, for example, Ref. 7) disregards the off-diagonal matrix elements of  $\rho^R$ . This is to be expected since the average energy does not depend on the off-diagonal elements of  $\rho^R$  in the  $n$  representation, simply because  $\langle n \rangle = \sum_0^\infty n \rho_{nn}^R$ . The foregoing analysis has shown that in some cases this is justified rigorously or approximately. It is justified rigorously for a density operator diagonal in the  $n$ -representation or for a pure coherent state  $|\beta\rangle$  for which  $\text{Re}\beta = \text{Im}\beta$  [see Eq. (3.3)]. It is justified approximately if this neglect is based on the order of magnitude of  $\sigma_2$ . In other cases it might not be justified at all. We wish to stress that we are not referring to the importance of the off-diagonal matrix elements of  $\rho^R$  in describing the state of the field mode. Our remarks concern the contribution of these matrix elements to the particular atomic process under consideration.

It is perhaps worth noting that if one considers the term corresponding to  $j = -1$  in Eq. (2.14), the contribution to  $d\chi/dt$  arising from single-photon absorption is obtained. Then, proceeding along the same lines, one finds that the process will always depend on the average number of photons, independently of the state of the field. Moreover, the off-diagonal matrix elements of  $\rho^R$  do not contribute in this case. This is easily verified by multiplying the two matrix elements given in Appendix B and examining the appropriate terms. The two-photon absorption, on the other hand, is essentially a coincidence experiment and it should be expected to depend on the statistics (or the coherence or the fluctuations, whichever term is deemed to be more appropriate) of the field. Thus one might expect fluctuations in two-photon absorption experiments which are due to changes in the statistics of the beam even if the power remains unchanged. The present analysis brings these effects out because it is based on the study of the kinetics of the process and not on the relevant matrix elements alone.

#### APPENDIX A

In this Appendix we discuss the motivation for formulating the problem in terms of the rate of change of the average number of photons, as well as the time coarse-graining procedure.

Let us consider a quantum system represented by the Hamiltonian  $H^0$  and subject to the perturbation  $V$ . The density operator  $\rho$  of the system obeys the equation [see Eq. (2.5)]

$$\rho(t+\tau) = U(\tau)\rho(t)U^\dagger(\tau), \quad (\text{A1})$$

which yields

$$\rho_{MM}(t+\tau) = \sum_{M'M''} U_{MM'}(\tau)\rho_{M'M''}(t)U_{M''M}^\dagger(\tau), \quad (\text{A2})$$

where  $|M\rangle$  are the eigenstates of  $H^0$ . This equation can

also be written in the form

$$\begin{aligned} \rho_{MM}(t+\tau) &= \sum_{M'} |U_{MM'}(\tau)|^2 \rho_{M'M'}(t) \\ &+ \sum_{\substack{M'M'' \\ (M' \neq M'')}} U_{MM'}(\tau)\rho_{M'M''}(t)U_{M''M}^\dagger(\tau). \end{aligned} \quad (\text{A3})$$

Without any approximation, Eq. (A3) can be written as

$$\begin{aligned} \rho_{MM}(t+\tau) &= \rho_{MM}(t) + \sum_{M'} |U_{MM'}(\tau)|^2 (\rho_{M'M'}(t) - \rho_{MM}(t)) \\ &+ \sum_{\substack{M'M'' \\ (M' \neq M'')}} U_{MM'}(\tau)\rho_{M'M''}(t)U_{M''M}^\dagger(\tau). \end{aligned} \quad (\text{A4})$$

Note that Eqs. (A1) to (A4) are valid for all times  $t$  and time intervals  $\tau$ .

Suppose now that the system is prepared in state  $|M_0\rangle$  at time  $t$ . Then

$$\rho_{M'M'}(t) = \delta_{M'M_0} \quad (\text{A5a})$$

and

$$\rho_{M'M''}(t) = 0 \quad \text{for } M' \neq M''. \quad (\text{A5b})$$

The probability that the system be in state  $|M\rangle$  after time  $\tau$  then is

$$\rho_{MM}(t+\tau) = |U_{MM_0}(\tau)|^2, \quad (\text{A6})$$

for  $M \neq M_0$ . This shows that  $|U_{MM_0}(\tau)|^2$  represents the transition probability  $M_0 \rightarrow M$  quite exactly. It is also clear that to measure this transition probability one must satisfy at least two requirements: First, prepare the system in state  $|M_0\rangle$  and second, choose the appropriate measurement (experiment) that will indeed measure the occupation probabilities  $\rho_{MM}$ . In the experiment envisaged in this paper,  $|M\rangle$  would have the form  $|m\rangle|s\rangle$ . Preparing the system in a state such that Eqs. (A5) are satisfied would automatically exclude laser light since such light is not in a pure number state. Instead, one has to average over all transition probabilities which usually involve the same atomic matrix element but an average over an infinite number of field matrix elements. For this reason, it was considered preferable to study the rate of change of the average number of photons and identify the contributions due to two-photon absorption. Moreover it is felt that the method is rather general and can be used to study other nonlinear (as well as linear) optical processes from a quantum-mechanical standpoint.

Up to this point, no restriction has been imposed upon the time interval  $\tau$ . Now one wishes to obtain an estimate for the rate at which the process takes place. From the operational standpoint it is desirable that the time  $\tau$  be sufficiently long compared to the interaction time so that enough events take place. On the other hand,  $\tau$  must be short enough for the perturbation calculation—and hence the time-independent transition probability per unit time—to be meaningful. In general, this can be

expressed by the relation  $W_{M_0 \rightarrow M} \tau \lesssim 1$ , where  $W_{M_0 \rightarrow M}$  is the transition probability per unit time. These restrictions on  $\tau$  are not different than the restrictions met in conventional time-dependent perturbation theory (e.g., see Ref. 9, Chap. XVII, Sec. 4). Here, we simply recognize at the outset that the limit  $\tau \rightarrow 0$  cannot be taken [as Eq. (B4) shows] and we incorporate this restriction into the starting Eq. (2.7). The approxima-

tion is valid to the extent that perturbation theory is valid.

### APPENDIX B

Let  $F(x)$  be a function of the real variable  $x$  defined by

$$F(x) \equiv (e^{ix\tau} - 1)/x. \quad (\text{B1})$$

Then, one obtains

$$\begin{aligned} & \langle (n+j)s | U(\tau) | ns_0 \rangle \\ &= e^{-i[(n+j)\omega_0 + \omega_s]\tau} \left\{ \delta_{j0} \delta_{ss_0} - \delta_{j1} (n+1)^{1/2} \hbar^{-1} D_{ss_0} F(\omega_0 + \omega_{ss_0}) - \delta_{j(-1)} n^{1/2} \hbar^{-1} D_{ss_0} F(-\omega_0 + \omega_{ss_0}) \right. \\ &+ \delta_{j0} n \sum_{s'} \frac{D_{ss'} D_{s's_0}}{\hbar^2 (-\omega_0 + \omega_{s's_0})} [F(\omega_{ss_0}) - F(\omega_0 + \omega_{ss'})] + \delta_{j0} (n+1) \sum_{s'} \frac{D_{ss'} D_{s's_0}}{\hbar^2 (\omega_0 + \omega_{s's_0})} [F(\omega_{ss_0}) - F(-\omega_0 + \omega_{ss'})] \\ &+ \delta_{j2} [(n+1)(n+2)]^{1/2} \sum_{s'} \frac{D_{ss'} D_{s's_0}}{\hbar^2 (\omega_0 + \omega_{s's_0})} [F(2\omega_0 + \omega_{ss_0}) - F(\omega_0 + \omega_{ss'})] \\ &\left. + \delta_{j(-2)} [n(n-1)]^{1/2} \sum_{s'} \frac{D_{ss'} D_{s's_0}}{\hbar^2 (-\omega_0 + \omega_{s's_0})} [F(-2\omega_0 + \omega_{ss_0}) - F(-\omega_0 + \omega_{ss'})] \right\}, \quad (\text{B2}) \end{aligned}$$

and

$$\begin{aligned} & \langle ms_0 | U^\dagger(\tau) | (n+j)s \rangle \\ &= e^{i[(n+j)\omega_0 + \omega_s]\tau} \left\{ \delta_m(n+j) \delta_{ss_0} + \delta_m(n+j-1) (n+j)^{1/2} \hbar^{-1} D_{s_0s} F(\omega_0 + \omega_{ss_0}) - \delta_m(n+j+1) (n+j+1)^{1/2} \hbar^{-1} D_{s_0s} F^*(\omega_0 - \omega_{ss_0}) \right. \\ &+ \delta_m(n+j-2) [(n+j)(n+j-1)]^{1/2} \sum_{s'} \frac{D_{s's} D_{s_0s'}}{\hbar^2 (\omega_0 + \omega_{s's_0})} [F^*(2\omega_0 + \omega_{ss_0}) - F^*(\omega_0 + \omega_{ss'})] \\ &+ \delta_m(n+j+2) [(n+j+1)(n+j+2)]^{1/2} \sum_{s'} \frac{D_{s's} D_{s_0s'}}{\hbar^2 (-\omega_0 + \omega_{s's_0})} [F(\omega_0 - \omega_{ss'}) - F(2\omega_0 - \omega_{ss_0})] \\ &+ \delta_m(n+j) (n+j+1) \sum_{s'} \frac{D_{s's} D_{s_0s'}}{\hbar^2 (\omega_0 + \omega_{s's_0})} [F^*(\omega_{ss'}) + F(\omega_0 - \omega_{ss'})] \\ &\left. + \delta_m(n+j) (n+j) \sum_{s'} \frac{D_{s's} D_{s_0s'}}{\hbar^2 (-\omega_0 + \omega_{s's_0})} [F^*(\omega_{ss'}) - F^*(\omega_0 + \omega_{ss'})] \right\}, \quad (\text{B3}) \end{aligned}$$

where the asterisk indicates the complex conjugate. Note that  $F(x)$  has the property  $F(-x) = -F^*(x)$ . The delta functions arise from the approximation

$$\lim_{\tau \rightarrow \infty} |e^{ix\tau} - 1|^2 / x^2 \tau = 2\pi \delta(x). \quad (\text{B4})$$