# A MASTER EQUATION APPROACH
# TO
# NONLINEAR OPTICS AND CHEMICAL REACTIONS

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of Waikato in fulfilment of the
requirements for the degree of
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# ABSTRACT

Part 1 of this thesis consists of a theoretical quantum statistical analysis of several nonlinear optical processes. As an introduction a master equation describing the time behaviour of the field in a general irreversible nonlinear interaction between an optical photon field and a number of two level atoms is given. This master equation is then used to calculate the exact time dependent statistical properties of the light fields in certain special processes: two photon emission by atoms, two photon absorption by atoms and Raman scattering of photons by atoms. The steady states of the emission-absorption processes are examined, and found to have interesting statistical properties not found in the field states normally met with. Part 1 is concluded with a brief examination of approximate methods of solutions for the nonlinear processes studied.

Part 2 is a brief study of the nature of concentration fluctuations and correlations in chemically reacting systems, using the stochastic master equation approach. The time dependent fluctuations and spatial correlations are discussed for a space dependent model of a linear chemically reacting system. These results are compared with those obtained when correlations are ignored. The steady state behaviour of a particular nonlinear chemical system is then examined. Deterministic and non space-dependent stochastic analysis show that when certain system parameters are varied, the system's behaviour is very similar to that of a thermodynamic system which undergoes a second order phase transition. A space-dependent analysis is then given, and this makes the analogy very close indeed.

# CONTENTS

## PART 1

## PART 2

## CHAPTER 1 INTRODUCTION TO PART ONE

In recent years there has been much theoretical and experimental interest in the various non-linear effects which can occur when light fields interact with certain types of matter. As is now well-known, such non-linear effects arise because of the non-linear response of the material medium to strong pumping fields. These effects may be described classically by the non-linear dependence of the medium's polarization $\underset{\sim}{P}$ on the electric field $\underset{\sim}{E}$ ( Armstrong et al. 1962), or quantum mechanically by multi-photon emission and absorption ( Lambropoulos et al. 1966, Shen 1967, Walls 1971a).

In one class of non-linear optical processes we take the nature of any pumping fields into account explicitly, and consider the direct coupling of this pump field to two or more other modes of the light field. The interaction with the atoms of the medium is taken into account implicitly in the expression for the susceptibility of the medium. Examples of such processes are parametric amplification and frequency conversion. Thorough analyses (both classical and quantum mechanical) of such processes have already been presented in the literature (see, eg., Louisell et al. 1961, Armstrong et al. 1962, McLean 1963 (unpublished lecture notes), Walls and Tindle 1972, Raiford 1974, Wonneberger and Lempert 1973). In part one of this thesis we shall consider a different class of non-linear optical processes. In this class we take the atomic nature of the interaction with the light fields into account explicitly. The presence of any pumping fields is taken into account implicitly in the thermal populations of the atomic levels.

Effects which fall into this class are multi-photon emission and absorption by atoms, and the Raman effect. The actual idea of multiphoton emission and absorption by atoms is not a new one; the theoretical possibility of such processes was first given by Goppert-Mayer (1931). Theoretical analyses of problems of this type have already been given by Lambropoulis et al. (1966), Lambropoulis (1967), Shen (1967 and 1969) and Agarwal (1970), and more recently by McNeil and Walls (1974), Tornau and Bach (1974), Loudon and Simaan (1975 a and b) and Simaan (1975).

In step with the theoretical studies there has been an ever-increasing interest in experimental investigations of these non-linear interactions. The Raman effect has of course been the subject of thorough investigation, and now finds many applications in modern experimental technology, especially spectroscopy. Of particular interest at present is the study of multiphoton emission and absorption. With the advent of higher powered laser pumping sources it has become possible to produce scattered light of sufficient intensity for detection, so that stimulated multiphoton experiments are now common. Further, direct observation of spontaneous two photon emission has been reported ( Lipeles et al. 1965 and O'Conell et al. 1975, where further references are also given). The two photon interaction is obviously the easiest multiphoton process to study experimentally, although higher order processes have been observed. The theoretical paper on two photon emission by Lambropoulis (1967) indicated a strong dependence of the two photon production or absorption rate on the statistics of the light, and this has initiated a number of photon statistics experiments to confirm this prediction. The most recent confirmation has been reported by Krasinski et al. (1974). Their paper contains further references to other work of a similar nature. Two photon absorption has become of particular importance recently because of its applications in spectroscopy. If the atomic transition is induced by pairs of photons from beams travelling in opposite directions there is no Doppler shift. This lack of Doppler line broadening means that a high resolution of spectral lines is possible. This was predicted by Vasilenko et al. (1970) and confirmed experimentally by Biraben et al. (1974), Levenson and Bloembergen (1974), Hansch et al. (1974) and Dritchard et al.(1974). Other advantages of two photon spectroscopy include the possibility of direct transitions between atomic ground state and higher levels for which parity considerations preclude a one photon transition. Further discussion is given in the above papers, and in the theoretical paper by Salomaa and Stenholm (1975).

There has even been discussion on the possibility of a laser oscillator in which the lasing transition is a multiphoton one. A quantum mechanical analysis of such lasing action has been given by McNeil and Walls (1975 b and c). A useful survey of multiphoton work up to the late 1960's is given by Gold (1969). In our work we shall be interested in processes which occur at frequencies in the optical range. At such frequencies individual photons may be detected. Further, production of photons by spontaneous emission of atoms may now be no longer insignificant, especially at low field intensities. Thus to adequately explain these processes we require a quantum mechanical analysis.

Since de-excitation of atoms occurs randomly, there will occur fluctuations in the measured field variables. The processes creating the fields are non-linear, so that we may expect the fluctuations to play a strong role. Hence a statistical analysis of the problems is important. The approach we take will thus be a quantum statistical one; i.e. we will investigate the behaviour of the density operator describing the behaviour of the interacting light fields. From this operator we may calculate the mean values of any functions of the field variables. Of particular physical interest are the mean field intensities, intensity fluctuations and intensity correlations.

The formalism required for our analysis is introduced in chapter two. The quantum mechanical hamiltonian for the atom-light field interaction is given and discussed. Following Shen (1967 and 1969) we give a master equation which governs the time behaviour of the density operator of the atom-light field system. By tracing out the atomic variables we obtain an operator equation for the density operator of the light fields alone. This equation completely describes the statistical behaviour of the light fields.

In chapter three we use the theory of chapter two to examine the behaviour of some specifie non-linear processes, and we present time dependent solutions for the diagonal (in the Fock, or number state, representation) elements of the density operators for the light fields in these processes. The solutions for two photon emission by atoms have already been studied in some detail by other workers ( Lambropoulis et al. 1966, Lambropoulis 1967 and Shen 1967 and 1969) and we merely present their results for completeness. We then consider two photon absorption by atoms, examining two cases: in the first case both photons involved in a transition come from the same mode of the light field, in the second case the two photons come from different modes. The one mode problem has been studied earlier by Agarwal (1970) and here we extend his theoretical analysis. The properties of the solutions for the two photon absorption problem have since been studied in more detail by Tornau and Bach (1974) who consider the one mode case, and by Loudon and Simaan (1975 a and b) who consider both the one mode and two mode cases.

The final process we consider here is the Raman scattering of light by atoms. Some analysis of the photon statistics of the scattered light (Stokes' radiation) has been given by other workers (Walls 1970 and 1971b, Chandra and Prakash 1971). A master equation approach has already been given by Walls (1973), who uses phonon modes instead of atoms. In his work the incident light is assumed to satisfy the parametric approximation. That is, it is assumed to be so intense that its depletion and statistical properties can be ignored. In our analysis we are able to obtain solutions without making this approximation; we retain the correlation between the incident and scattered light. The solutions for Raman scattering have since been examined in more detail by Simaan (1975).

For each of the above problems we present graphically the time evolution of physical quantities such as mean intensities and correlation functions, for various initial conditions.

Because of certain conserved quantities, the steady states in these non-linear problems depend on the initial conditions as well as on the external pumping parameters (in this case the thermal populations of the atomic levels). This is of interest because it allows the possibility of obtaining states of the electromagnetic field which have different statistical properties to the states normally found. In chapter four we examine the steady states of some of the processes studied in chapter three, and calculate their second order correlation functions which provide some measure of their statistical properties.

Chapter five concludes part one with a brief look at some approximate solutions for the processes we have been studying. Such approximate solutions provide a more transparent view of the processes, and also enable us to make some connection with the classical theory of non-linear optics.

Parts of chapters three and five have already appeared in print in the article "A Master Equation Approach to Non-Linear Optics", Journal of Physics 7A 617(1974), and parts of chapter four have appeared in "Possibility of Observing Enhanced Photon Bunching from Two Photon Emission", Physics Letters 51A 233(1975).

# CHAPTER 2 QUANTUM FORMULATION

## 2.1 Hamiltonian for the Atom-Field System

We shall describe the atom-field interaction which occurs in the non-linear interaction of light with matter by an ensemble of N independent two level atoms interacting with an optical electromagnetic field inside a resonant cavity. Transitions between the two atomic levels are n-photon processes in which m-photons are emitted and n - m photons are absorbed.

We may write the total hamiltonian for such a system as:

$$H = H_F + H_A + H_{AF} \qquad (2.1)$$

where $H_F$ and $H_A$ are respectively the hamiltonians for the unperturbed electromagnetic field and the atoms, and $H_{AF}$ is the hamiltonian describing the interaction between the atoms and the light field. $H_{AF}$ for a single "one electron" atom may be written as (Dirac 1967):

$$H_{AF} = \frac{e}{2m}(\underset{\sim}{p}\cdot\underset{\sim}{A}) + \underset{\sim}{A}\cdot p) + \frac{e^2}{2m}\underset{\sim}{A} \qquad (2.2)$$

where $\underset{\sim}{p}$ is the electron's momentum, and $\underset{\sim}{A}$ is the electromagnetic vector potential at the electron's position. We shall assume the electromagnetic radiation is of wavelength much larger than atomic dimensions. This means $\underset{\sim}{A}$ is essentially constant over the volume of an atom, so we may take for $\underset{\sim}{A}$ its value at the (fixed) position of the atom's nucleus.

We now introduce quantization of the electric field and second quantization of the atom. The electric field is described by the vector potential field $\underset{\sim}{A}$ already mentioned, and the atom's electron is described by the electron wave function field $\psi(\underset{\sim}{r})$. We make these fields quantum mechanical operators by replacing by operators the c- number coefficients in the Fourier expansions of $\underset{\sim}{A}(\underset{\sim}{r},t)$ and $\psi(\underset{\sim}{r})$ (see, e.g. Dirac 1967, Haken 1970):

$$\underset{\sim}{A}(\underset{\sim}{r},t) = \sum_{\underset{\sim}{k}} \sqrt{\frac{\hbar}{2\omega_{\underset{\sim}{k}}\varepsilon_0}} \left[ a_{\underset{\sim}{k}}^{\dagger}\, \underset{\sim}{u}_{\underset{\sim}{k}}(\underset{\sim}{r}) + a_{\underset{\sim}{k}}\, \underset{\sim}{u}_{\underset{\sim}{k}}^{*}(\underset{\sim}{r}) \right] \qquad (2.3)$$

$$\psi(\underset{\sim}{r}) = \sum_{j} \left[ c_j\, \phi_j(\underset{\sim}{r}) + c_j^{\dagger}\, \phi_j^{*}(\underset{\sim}{r}) \right] \qquad (2.4)$$

The $\underset{\sim}{u}_{\underset{\sim}{k}}(\underset{\sim}{r})$ and $\phi_j(\underset{\sim}{r})$ are appropriate normalized orthogonal mode eigenfunctions. $V$ is the volume of the cavity. In (2.4) the index "$j$" indicates the levels of the atom.

The electric field "creation" and "destruction" operators $a_{\underset{\sim}{k}}^{\dagger}$, $a_{\underset{\sim}{k}}$ obey the boson commutation rules:

$$[a_k^{\dagger}, a_{k'}] = \delta_{kk'} \qquad (2.5)$$

and have associated with them the Fock (number) states $|n_k\rangle$:

$$\begin{aligned} a_k^{\dagger}|n_k\rangle &= \sqrt{n_k+1}\,|n_k+1\rangle \\ a_k|n_k\rangle &= \begin{cases} \sqrt{n_k}\,|n_k-1\rangle, & n_k > 0 \\ 0, & n_k = 0 \end{cases} \end{aligned} \qquad (2.6)$$

The atomic "raising" and "lowering" operators $c_j^{\dagger}$, $c_j$ obey the fermion anticommutation rules:

$$[c_j^\dagger, c_k]_+ = \delta_{jk} \tag{2.7}$$

and have associated with them the atomic level states $|j\rangle$ :

$$\begin{aligned} c_1^\dagger |1\rangle &= |2\rangle \quad , \quad c_1 |1\rangle = 0 \\ c_2^\dagger |2\rangle &= 0 \quad , \quad c_2 |2\rangle = |1\rangle \end{aligned} \tag{2.8}$$

If the $N$ atoms are independent, their electronic wavefunctions will not overlap, so that $N$ atoms may be taken into account simply by adding the single atom terms together. To the $C_i$ we add a further index "$\lambda$" which indicates the particular atom a $C_i$ is describing. When the above quantization procedures are carried out, the hamiltonians $H_F$ and $H_A$ become:

$$H_F = \sum_k \hbar \omega_k a_k^\dagger a_k \tag{2.9}$$

$$H_A = \frac{1}{2}\hbar\omega_{12} \sum_{\lambda=1}^{N} ( c_{2\lambda}^\dagger c_{2\lambda} - c_{1\lambda}^\dagger c_{1\lambda} ) \tag{2.10}$$

where $\hbar\omega_{12} = \Delta E_{12}$ is the energy difference between the two atomic levels.

In a multiphoton process the transitions are between states such as $|1; n_1, n_2\rangle$ and $|2; n_1-1, n_2-1\rangle$, or more generally, between states for which the transition involves the emission of m photons and the absorption of n - m photons. Thus when using expansion methods to calculate physical quantities like transition probabilities or the rate of change of a density operator, it is necessary to go to nth order terms in $H_{AF}$ to obtain the first non-zero contribution (Lambropoulos 1967, Agarwal 1970). This is equivalent to using first order theory with the following effective hamiltonian (Shen 1967, Agarwal 1970, Walls 1971a);which we shall use:

$$H_{AF} = \hbar \varepsilon^{(n,n-m)} \left[ \sum_{\lambda} c_{2\lambda}^{+} c_{1\lambda} \prod_{j=1}^{m} a_j^{+} \prod_{k=m+1}^{n} a_k + h.c. \right] \qquad (2.11)$$

where $\varepsilon^{(m,n-m)}$ is proportional to the atomic matrix element for the n-photon transition.

In the steps leading to the hamiltonian (2.11) we neglect certain terms. The first term neglected is the $\underset{\sim}{A}^2$ term in (2.2) which is very much smaller than the $\underset{\sim}{p}.\underset{\sim}{A} + \underset{\sim}{A}.\underset{\sim}{p}$ terms. The other terms ignored represent either n photon processes which we are not interested in, or processes which are highly energy non-conserving. Neglecting the last mentioned type of terms is commonly called the rotating wave approximation. The effect of such terms is negligible for times larger than the inverse frequency of the atomic transition (see, e.g. Haken 1970, where further references are given. See also Carmichael 1972).

The n-photon processes we are not interested in may be physically excluded by appropriate choice of experimental conditions. If the experiment takes place in a resonant cavity, the cavity may be tuned to allow only the frequencies of those field modes which take part in the particular process of interest. If the experiment is to be carried out in a crystal, the unwanted processes may be excluded if a birefringent crystal is used. In such crystals the speed of light c is a function of wave polarization and direction as well as of frequency $\omega$ . By appropriate choice of polarizations and directions of the interacting field waves, we may obtain matching of wave numbers $\underset{\sim}{K}$ ("index matching") which enhances the process of interest and excludes other processes (see Yariv 1967 for further details). The second method is more applicable in travelling wave situations, in which one mode is an explicit pumping field. A quantum mechanical analysis of such travelling wave situations is lengthy (Tucker and Walls 1969), and we shall be taking the fields in the analyses following to be standing wave modes; we will not be investigating propagation aspects.

## 2.2 Master Equation Describing the Field

We shall now obtain an equation governing the time behaviour of the quantum statistical properties of the light field as it interacts with the atoms. The quantum statistical properties of the total atom-field system may be described by the density matrix (Dirac 1967):

$$\rho_T = \sum_{\psi} p_{\psi} |\psi\rangle\langle\psi| \tag{2.12}$$

where the $|\psi\rangle$ are normalized states of the system, obeying the Schrodinger equation $i\hbar\frac{\partial|\psi\rangle}{\partial t} = H|\psi\rangle$. The time behaviour of $\rho_T$ in the interaction picture (Dirac 1967) is then given by:

$$i\hbar\frac{\partial\rho_T}{\partial t} = [H_{AF}, \rho_T] \tag{2.13}$$

with the operators $\rho_T$ and $H_{AF}$ now in the interaction picture. Since we are interested in the statistical properties of the light field, not of the atoms, we trace out over the atoms to consider the density operator for the field alone:

$$\rho(t) = \mathrm{Tr}_A\{\rho_T(t)\} \tag{2.14}$$

In order to evaluate the trace we assume the atoms are initially in thermal equilibrium, and that this remains essentially unperturbed by the interaction. Thus

$$\rho_T(t) \simeq \rho(t) \otimes \rho_A(0) \tag{2.15}$$

where

$$\rho_A(0) = \prod_{\lambda=1}^{N} \rho_\lambda(0) \tag{2.16}$$

The irreversible equation of motion (known as the master equation) for $\rho(t)$ may then be derived from equation (2.13) by standard techniques. (For a comprehensive discussion of the derivation of quantum mechanical master equations in the context of quantum optics, see the excellent review articles of Haken 1970 and Agarwal 1973). Under the Born and Markov approximations, the master equation obtained is:

$$\begin{aligned}\frac{\partial\rho}{\partial t} &= K^{(m,n-m)} N_1\{[O\rho, O^\dagger] + [O, \rho O^\dagger]\} \\ &\quad + K^{(m,n-m)} N_2\{[O, O^\dagger\rho] + [\rho O, O^\dagger]\}\end{aligned} \tag{2.17}$$

where

$$K^{(m,n-m)} \propto g(\omega_{12})\,|\varepsilon^{(m,n-m)}|^2 \int_V d^3\underline{r}\; N(\underline{r}) \prod_{j=1}^{n} |u_j(\underline{r})|^2$$

and

$$O = \prod_{j=1}^{m} a_j^\dagger \prod_{k=m+1}^{n} a_k$$

$g(\omega)$ is the atomic lineshape function, $N_1$ and $N_2$ are the occupation numbers of the atomic levels $|1\rangle$ and $|2\rangle$, and $N(\underset{\sim}{r})$ is the atomic density in the matter. We have assumed the transition is resonant, ie:

$$\omega_{12} = \left| \sum_{i=1}^{m} \omega_i - \sum_{k=m+1}^{n} \omega_k \right| \tag{2.18}$$

Equation (2.17) completely describes the statistical behaviour of the light as it interacts with the matter. Note that no mechanism for losses has been included.

Methods for solving equations like (2.17) in operator form are few. To obtain any form of solution we must usually convert such operator equations to c-number equations by introducing some representation. Usually we either introduce the "P-representation" (Glauber 1963) for $\rho$ , or take the equations matrix elements in the Fock representation. In the case of (2.17) the nonlinearity means the equation in the Fock representation is easier to handle.

We call a matrix element of $\rho$ or any other field operator a diagonal element when the matrix element is taken between equal states, and off-diagonal when it is taken between unequal states. If the off-diagonal elements are all zero, the operator is said to be diagonal in the particular representation used to calculate the matrix elements. For a complete statistical description of the field we must know $\rho$ completely, i.e. we must know all of its matrix elements. However, to evaluate the expectation values $\mathrm{Tr}\{\hat{F}\rho\}$ of diagonal field operators (such as field intensity $\langle a_k^\dagger a_k\rangle$, intensity fluctuations $\langle\{a_k^\dagger a_k - \langle a_k^\dagger a_k\rangle\}^2\rangle$ , and intensity correlations $\langle\{a_k^\dagger a_k - \langle a_k^\dagger a_k\rangle\}\{a_j^\dagger a_j - \langle a_j^\dagger a_j\rangle\}\rangle$ we require only the diagonal elements of $\rho$ , and we shall restrict our attention to the diagonal part of equation (2.17). The off-diagonal part is in general difficult to solve. It should be noted that equation (2.17) implies that off-diagonal elements are connected only to other off-diagonal elements. Hence if all off-diagonal elements are initially zero, they will remain so. In this case the solution for the diagonal elements of $\rho$ gives a complete description of the fields. The expectation value of any non-diagonal field operator (such as field amplitude $a_k$ ) will remain zero for all times.

# CHAPTER 3 TIME DEPENDENT SOLUTIONS FOR PARTICULAR NONLINEAR PROCESSES

## 3.1 Two Photon Emission by Atoms.

The first process we shall consider is multiphoton emission from excited atoms, with the emission of two photons in each atomic de-excitation. We maintain an inverted atomic population by some external pumping mechanism (for example, keeping the atoms at a high temperature), so that in (2.17) we may set $N_1 = 0$ and $N_2 = N$, the total number of atoms.

There are two cases to consider, depending on which modes the cavity is tuned to select. One is the case where the two photons emitted in an atomic de-excitation are emitted into two distinct fixed modes with $\omega_1 + \omega_2 = \omega_{12}$. The other is the degenerate case where the two photons are emitted into a single fixed mode with $2\omega = \omega_{12}$. We shall consider the second case first, since it is less cumbersome mathematically.

### 3.1.1 Emission into a Single Mode.

When the two photon modes degenerate into a single mode, the operator $O$ in (2.17) becomes $aa$. With $N_1 = 0$, equation (2.17) thus gives:

$$\frac{\partial \rho}{\partial t} = -K^{(0,2)}\{[aa, a^+a^+\rho] + [\rho aa, a^+a^+]\} \tag{3.1}$$

where $N_2 = N$ is absorbed in $K^{(0,2)}$.

The equation for the diagonal elements of $\rho$ in the Fock representation is then:

$$\frac{\partial \rho_n(\tau)}{\partial \tau} = n(n-1)\,\rho_{n-2}(\tau) - (n+2)(n+1)\,\rho_n(\tau) \qquad (3.2)$$

where $\tau = 2K^{(0,2)}t$ and $\rho_n(\tau) = \langle n|\rho(\tau)|n\rangle$.

The solution to (3.2) has been given by Lambropoulos (1967), and we include it here for completeness. The equation may be solved using a Laplace transform method, giving

$$\rho_n(\tau) = n! \sum_{\lambda=0 \text{ or } 1}^{n} \frac{\rho_\lambda(0)}{\lambda!} \sum_{\mu=\lambda}^{n} A_{n,\lambda}(\mu) \exp[-(\mu+1)(\mu+2)\tau] \qquad (3.3)$$

where

$$A_{n,\lambda}(\mu) = \Big[\prod_{\substack{q=\lambda \\ q\neq\mu}}^{n} (q-\mu)(q+\mu+3)\Big]^{-1}$$

The summation and product variables $\lambda, \mu, q$ range over even values when $n$ is even, and over odd values when $n$ is odd.

Any initial distribution of the photon field may be taken into account by inserting the appropriate initial distribution $\rho_\lambda(0)$ directly into equation (3.3). Typical initial states met with in experimental situations are the chaotic state which has the distribution $\rho_\lambda = \frac{1}{M+1}\left(\frac{M}{M+1}\right)^\lambda$ and the coherent state which has the distribution $\rho_\lambda = e^{-M}\frac{M^\lambda}{\lambda!}$ . $M$ is the mean number of photons in the state. A coherent state of the electric field is a special state for which the field correlations $g^{(n)} = \langle E^{(-)}(\underline{r}_1,t_1)\ldots E^{(-)}(\underline{r}_n,t_n)E^{(+)}(\underline{r}_{n+1},t_{n+1})\ldots E^{(+)}(\underline{r}_{2n},t_{2n})\rangle$ factorize for all $n$ (Glauber 1963, 1967). $E^{(-)}$ and $E^{(+)}$ are respectively the $-$ve and $+$ve frequency parts of the electric field. The factorization property implies a lack of spatial and temporal correlations, hence the name "coherent" state. The stabilized output of a laser oscillator is a close approximation to such a state, thus a laser is a suitable source for initially coherent radiation. A chaotic state of the field is that state for which the entropy $Tr(\rho \ln \rho)$ of the photon field is a maximum for a specified mean photon number (Glauber 1963, 1967). In this sense it is a state of maximum disorder, hence the name "chaotic". An appropriate source for an initial chaotic state is a thermal light source, such as a heated mercury discharge lamp, whose random emission of photons generates such a state. Further discussion of the correlation properties of the coherent and chaotic states is given in chapter 4.

From the distribution (3.3) we may calculate the time behaviour of the mean number of photons, the photon number fluctuation and the expectation values of other diagonal field operators. For example, the mean number is

$$\langle n(\tau)\rangle = Tr(a^{+}a\rho) = \sum_{n=0}^{\infty} n\rho_{n}(\tau) \qquad (3.4)$$

The time behaviours of the mean and the second order correlation function for an initial vacuum state ( $\rho_{\lambda}(0) = \delta_{\lambda,0}$ ) is shown in figures 1 and 2 respectively. The second correlation function $g^{(2)}$ is the normalized form of the non-local version of $G^{(2)}$ defined above, $g^{(2)} \propto \langle a^{+}a^{+}aa\rangle$ , and is given by

$$g^{(2)} = \frac{\langle n(n-1)\rangle}{\langle n\rangle^{2}} \qquad (3.5)$$

Discussion of these figures follows section (3.1.2).

The initial condition $\rho_\lambda(0) = \delta_{\lambda,0}$ corresponds to experiments observing spontaneous two photon emission. Direct observation of such spontaneous emission has been reported by Lipeles et al. (1965), and more recently by O'Conell et al. (1975) where further references are given. Initially, two photon emission experiments involved stimulated emission, using high powered laser pumping sources, in order to produce output light of intensity sufficient for detection. To describe this situation we would use a coherent state initial distribution $\rho_\lambda(0)$ in (3.3).

The above analysis (particularly figure 1) shows clearly that amplification occurs in the two photon emission process, and there has been speculation whether such amplification can be controlled to produce self-sustained oscillations (Lambropoulos 1967). That is, is it possible to obtain lasing action when the transition in the lasing atoms is a two-photon transition? It appears that the very large fluctuations in the emission process (figure 2) precludes the possibility of formation of coherent behaviour. However, the theoretical work of McNeil and Walls (1975 a and b) shows that when losses and the nonlinear action with the lasing atoms are taken into account, lasing action is possible (see also Yuen, 1975). Although the two photon transition is relatively weak, once this weakness is overcome, high light intensities may be achieved. For this reason there is strong experimental interest in developing such lasers (Carmen et al. 1974, R. Byer, Stanford private communication, P. Sorokin, I.B.M. private communication).

It should be noted that should we be interested in the off-diagonal elements of $\rho$ we may solve the equation for these elements in a fairly straightforward manner, using the same method as used to solve equation (3.2).

### 3.1.2 Emission into Two Modes.

When the atoms emit pairs of photons into different modes, the operator $O$ in (2.17) is $a_1 a_2$ where "1" and "2" are the mode labels. With $N_1 = 0$, the master equation (2.17) is

$$\frac{\partial \rho}{\partial t} = -NK^{(0,2)}\{[a_1 a_2, a_1^+ a_2^+ \rho] + [\rho a_1 a_2, a_1^+ a_2^+]\} \qquad (3.6)$$

The equation for the diagonal elements of $\rho$ is then:

$$\frac{\partial \rho_{n_1,n_2}}{\partial \tau} = n_1 n_2\, \rho_{n_1-1,n_2-1}(\tau) - (n_1+1)(n_2+1)\, \rho_{n_1,n_2}(\tau) \qquad (3.7)$$

where $\tau = NK^{(2,0)}t$ and $\rho_{n_1,n_2} = \langle n_1, n_2 | \rho | n_1, n_2 \rangle$.

We now observe that $[H, a_2^+ a_2 - a_1^+ a_1] = 0$, so that $n_2 - n_1$, or more generally, any function of $n_2 - n_1$ is a constant of the motion. In our statistical analysis, this corresponds to the fact that, according to (3.7), the $\rho_{n_1,n_2}$ are connected only along lines $n_2 - n = \lambda$ where $\lambda$ is any integer, and hence that the expectation value of any function of $n_2 - n_1$ is a constant of the motion. The simplest constant of the motion is given by the Manley-Rowe type of conservation equation $\langle n_2(\tau)\rangle - \langle n_1(\tau)\rangle =$ constant.

We may thus solve equation (3.7) in a one dimensional manner by solving the equation along the lines $n_2 - n_1 = \lambda$, $\lambda \geq 0$:

$$\frac{\partial \rho_{n,n+\lambda}}{\partial \tau} = n(n+\lambda)\, \rho_{n-1,n-1+\lambda}(\tau) - (n+1)(n+1+\lambda)\, \rho_{n,n+\lambda}(\tau) \quad (3.8)$$

where $\lambda$ is a parameter, and $n = n_1$, is the difference variable. The Laplace transform of equation (3.8) yields

$$\bar{\rho}_{n,n+\lambda}(s) - \frac{n(\lambda+n)}{[s+(n+1)(n+\lambda+1)]}\,\bar{\rho}_{n-1,n-1+\lambda}(s) = \frac{\rho_{n,n+\lambda}(0)}{[s+(n+1)(n+\lambda+1)]} \qquad (3.9)$$

where $\bar{\rho}_{n,n+\lambda}(s) = \int_0^\infty e^{-s\tau}\rho_{n,n+\lambda}(\tau)\,d\tau$.

Equation (3.9) is readily solved and inverted. If $\lambda < 0$, we let $\lambda' = -\lambda$, and interchange the roles of $n_1$ and $n_2$ in (3.8) and now consider $\rho_{n+\lambda',n}(\tau)$. This quantity also obeys the Laplace transform equation (3.9), so that the general solution for $\rho_{n_1,n_2}(\tau)$ is:

$$\rho_{n_1,n_2}(\tau) = n_1!\,n_2!\sum_{k=m}^{n_1}\frac{\rho_{k,k+\lambda}(0)}{k!\,(k+\lambda)!}\sum_{j=k}^{n_1}A_{n_1,\lambda}(k,j)\,\exp[-(j+1)(j+\lambda+1)\tau] \qquad (3.10)$$

where $A_{n_1,\lambda}(k,j) = \Big[\prod_{\substack{i=k\\ i\neq j}}^{n_1}(i-j)(i+j+\lambda+2)\Big]^{-1}$, $\lambda = n_2 - n_1$, $m = \max(0,-\lambda)$

Any initial two mode photon distribution may be taken into account by inserting the appropriate distribution function in the form $\rho_{k,k+\lambda}(0)$ into (3.10).

The solution (3.10) is the full coupled distribution for both modes, and from this we may calculate correlations between the modes (e.g. $\langle n_1 n_2\rangle - \langle n_1\rangle\langle n_2\rangle$) as well as the means and variances of the separate modes. To obtain the distribution function for a single mode, $\rho_{n_1}(\tau)$, say, we simply sum $\rho_{n_1,n_2}(\tau)$ of equation (3.10) over the other mode variable $n_2$.

In figures 1 and 2 we show the time evolution of the mean and second order correlation function of one of the modes when both modes are initially in the vacuum state $\rho_{n_1,n_2}(0) = \delta_{n_1,0}\,\delta_{n_2,0}$.

This corresponds to experiments involving two photon spontaneous emission. In this case $\rho_{n_1,n_2}(\tau) = \rho_{n_1}(\tau)\,\delta_{n_1,n_2}$, so the behaviour is symmetric in the two modes.

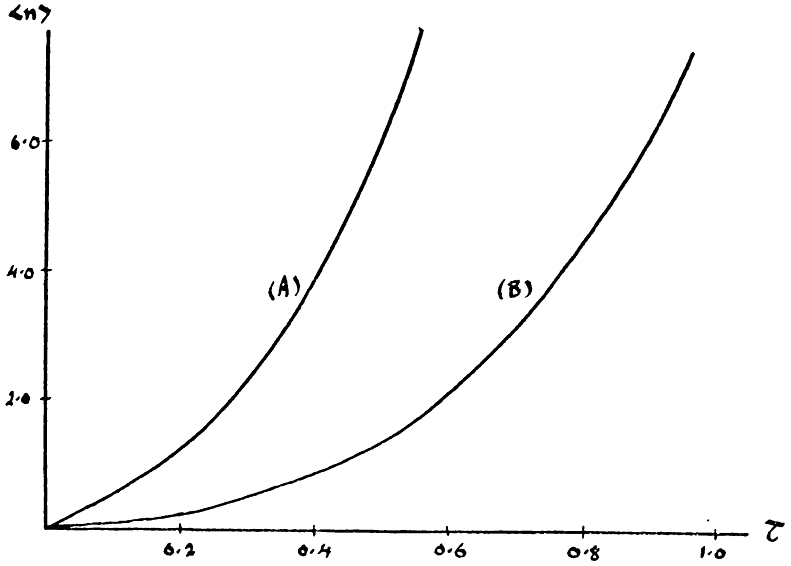

Fig.1 Two-photon emission, all modes initially vacuum. Mode mean photon number.

(A) Single mode (B) Two mode

Figure 1 shows that even when the emission is spontaneous, the intensity grows very rapidly with $\tau$, much more rapidly than the $e^{\tau}$ behaviour of one photon spontaneous emission. This is because the two photon emission rate $\sim$ (intensity)$^2$ rather than just intensity, so that once the vacuum fluctuations are amplified, growth is rapid. The growth is faster in the one mode case because the spontaneous emission rate goes as $4N_2$ rather than just $N_2$ as in the two mode case (see equations (5.1) and (5.18)).

In the case of stimulated emission, where there is a finite number of photons present initially, the growth rate will be even larger, as equations (5.1) and (5.18) show. The growth rate depends on the stimulation term $N_2\langle n\rangle$ and the additional terms ( $N_2\langle n(n-1)\rangle$ in the one mode case, $N_2\langle n_1 n_2\rangle$ in the two mode case) which depend on the statistics. These additional terms reflect the underlying nature of the processes. In the one mode case the emission process requires the coincidences of pairs of photons from the same mode, and $\langle n(n-1)\rangle$ is a measure of the rate of such coincidences (see chapter 4). In the two mode case the process requires coincidences of pairs of photons from different modes, and $\langle n_1 n_2\rangle$ is a measure of this. Thus in the one mode case the emission rate will depend strongly on the initial statistics through the quantity $\langle n(n-1)\rangle$ , so that the growth will be larger for an initially chaotic state ($\langle n(n-1)\rangle_0 = 2\langle n(0)\rangle^2$ ) than for an initially coherent state ($\langle n(n-1)\rangle_0 = \langle n(0)\rangle^2$ ) of the same mean; however the dependence on the initial mode statistics will be less strong, the dependence occurring only via the dependence of $\langle n_1 n_2\rangle$ on the mode statistics (equation (5.20)).

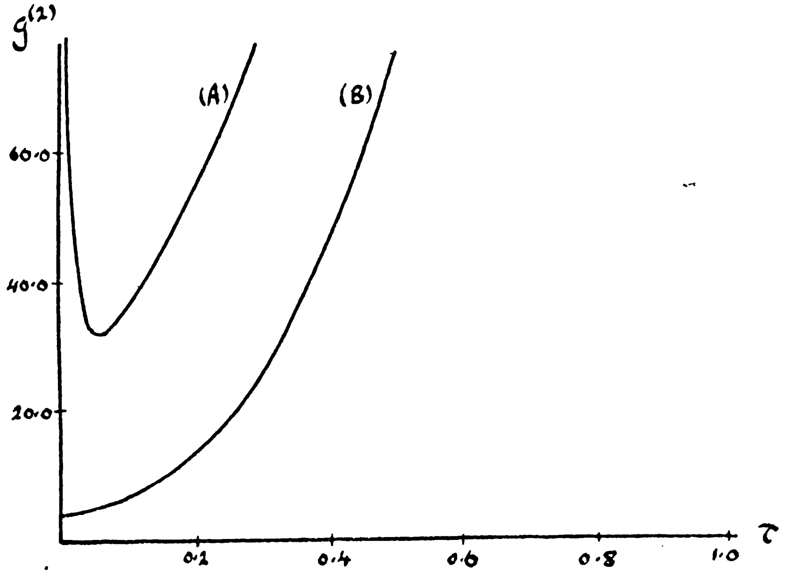

Fig.2 Two-photon emission, all modes initially vacuum. Second order correlation functions $g^{(2)}$.

(A) Single mode (B) Two mode

Figure 2 shows that $g^{(2)}$ also increases rapidly with time, with the growth more rapid in the one mode case (the divergence of $g^{(2)}$ at $\tau=0$ corresponds to the initial vacuum state). The nonlinear emission process is very "noisy" , or "chaotic", amplifying the fluctuations very rapidly. $g^{(2)}$ for one photon emission is constant at the value 2 corresponding to a chaotic state. The two photon $g^{(2)}$ functions exceed the value 2, that the fields become in some sense more chaotic than a normal chaotic state. Further discussion on this is given in chapter 4.

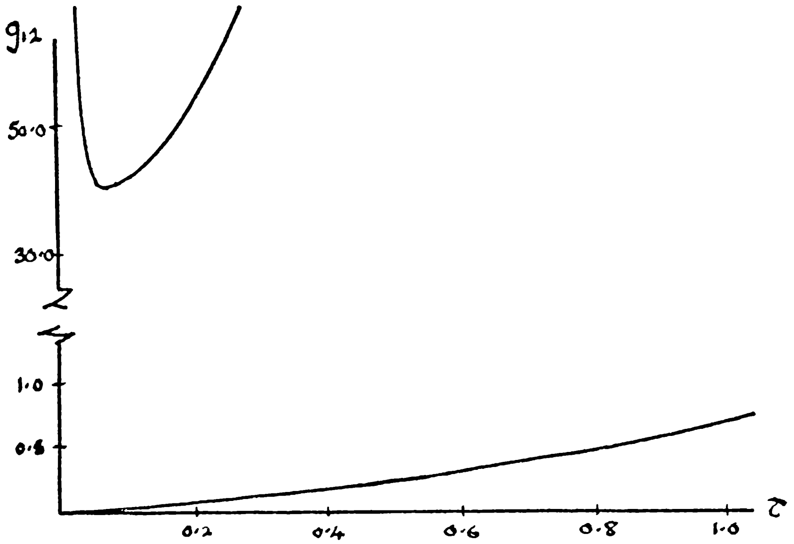

Fig. 3 Two mode correlation function $g_{12}$.

(A) Emission into initially vacuum modes.
(B) Absorption from initial number states, $\langle n(0)\rangle = 10$.

The growth of the normalized correlation function $g_{12}$ for the same initial conditions as in figures 1 and 2 is shown in figure 3. Note that, since the distribution function has the form $\varrho_{n_1}(\tau)\,\delta_{n_1,n_2}$ in this case, $g_{12}$ will be equal to the normalized fluctuation $[\langle n^2\rangle - \langle n\rangle^2]/\langle n\rangle^2$ of each mode.

It should be noted that the equation for the off-diagonal elements $\langle n_1', n_2' | \rho | n_1, n_2 \rangle$ may be solved in a manner similar to that used in this section (Shen 1969).

## 3.2. Two Photon Absorption by Atoms.

We shall now consider multiphoton absorption by atoms, with two photons being absorbed in each atomic excitation. We maintain practically all the atoms in their lower state by external means, such as keeping the atoms at a low temperature. Thus in (2.17) we may set $N_1 \simeq N$ and $N_2 \approx 0$ . Again we have two cases possible, depending on the modes allowed by the cavity tuning. In one case, each of the pair of photons absorbed in an atomic transition come from different modes, with $\omega_1 + \omega_2 = \omega_{12}$ , and in the other case the two photons come from the same mode with $2\omega = \omega_{12}$ . We shall consider the degenerate case $2\omega = \omega_{12}$ first.

### 3.2.1 Absorption From a Single Mode.

In this degenerate case, the operator $O$ in the master equation (2.17) is $aa$ . With $N_1 = N$ and $N_2 = 0$ , (2.17) is then

$$\frac{\partial \rho}{\partial t} = K\{[aa\rho, a^+a^+] + [aa, \rho a^+a^+]\} \tag{3.11}$$

where $K = NK^{(0,2)}$

The equation for the diagonal matrix elements of $\rho$ is then:

$$\frac{\partial \rho_n(\tau)}{\partial \tau} = (n+2)(n+1)\rho_{n+2}(\tau) - n(n-1)\rho_n(\tau) \tag{3.12}$$

where $\tau = 2Kt$ and $\rho_n(\tau) = \langle n | \rho | n \rangle$.

Equation (3.12) is most easily solved by introducing a generating function $F(x,\tau)$ defined by

$$F(x,\tau) = \sum_{n=0}^{\infty} \rho_n(\tau)x^n \quad , \quad |x| \leq 1 \qquad (3.13)$$

To convert equation (3.12) to an equation in $F(x,\tau)$ we multiply each side of (3.12) by $x^n$ and sum over $n$ . Using the definition (3.13) we may write the resulting equation as:

$$\frac{\partial F}{\partial \tau} = (1-x^2)\frac{\partial^2 F}{\partial x^2} \qquad (3.14)$$

The general solution to this equation may be readily found by using a separation of variables technique (McQuarrie 1967), and is:

$$F(x,\tau) = \sum_{n=0}^{\infty} A_n C_n^{-\frac{1}{2}}(x) . \exp[-n(n-1)\tau] \qquad (3.15)$$

The $C_n^{-\frac{1}{2}}(x)$ are Gegenbauer polynomials and the $A_n$ are coefficients to be determined. Such a series solution was also obtained by Agarwal (1970). We proceed here to further this work by explicitly calculating these coefficients. Equation (3.15) has the form of a Fourier series, except that the $C_n^{-\frac{1}{2}}(x)$ are not orthogonal polynomials. However, we observe that (see, e.g. Abramowitz and Stegun 1965)

$$\frac{dC_n^{-\frac{1}{2}}(x)}{dx} = -C_{n-1}^{\frac{1}{2}}(x) = -P_{n-1}(x) \qquad (3.16)$$

where the $P_n(x)$ are Legendre polynomials, orthogonal on $[-1,1]$ . Thus differentiation of equation (3.15) w.r.t. $x$ yields a Fourier series in Legendre polynomials for $\frac{\partial F}{\partial x}$ , and the $A_n (n=1,2,\ldots)$

may be evaluated from the initial condition

$$\frac{\partial F(x,\tau=0)}{\partial x} = \sum_{n=1}^{\infty} n\,\rho_n(0)\,x^n \tag{3.17}$$

using the orthogonality of the $P_n(x)$ and the integrals given in the appendix. This yields all the $A_n$ apart from $A_0$. Although $A_0$ is not required in order to calculate the distribution moments, it may be found by observing that, according to equation (3.15):

$$F(x,\tau=\infty) = A_0 - A_1 x \tag{3.18}$$

Further, because (3.12) implies that the $\rho_{2m}(\tau)$ and $\rho_{2m+1}(\tau)$ are uncoupled, $\sum_{m=0}^{\infty} \rho_{2m}(\tau)$ and $\sum_{m=0}^{\infty} \rho_{2m+1}(\tau)$ are constants of motion. It follows that

$$A_0 = \sum_{m=0}^{\infty} \rho_{2m}(\tau=\infty) = \sum_{m=0}^{\infty} \rho_{2m}(0) \tag{3.19a}$$

$$A_1 = -\sum_{m=0}^{\infty} \rho_{2m+1}(\tau=\infty) = -\sum_{m=0}^{\infty} \rho_{2m+1}(0) \tag{3.19b}$$

We may now write the $A_n$ expressions as:

$$A_m = -\sqrt{\pi}\,(2m-1) \sum_{l=m}^{\infty} \frac{l!}{2^l \left(\frac{l-m}{2}\right)!\,\Gamma\!\left(\frac{m+l+1}{2}\right)}\,\rho_l(0) \tag{3.20}$$

where the summation variable $l$ takes even values only when $m$ is even, and odd values only when $m$ is odd.

The result (3.20) means that $F(x,\tau)$ is now completely determined in terms of the arbitary initial distribution. This in turn means that the $\rho_n(\tau)$ are completely determined: by the definition (3.13) of $F(x,\tau)$ we see that for a given $n$, $\rho_n(\tau)$ is the coefficient of $x^n$ in the power series expansion of $F(x,\tau)$. Using the explicit power series expansions for the $C_n^{-\frac{1}{2}}(x)$ (or alternatively $P_n(x)$ in the $\frac{\partial F(x,\tau)}{\partial x}$ series) (see, e.g. Abramowitz and Stegun 1965) we obtain

$$\rho_n(\tau) = \frac{-1}{2^{n-1}\, n!} \sum_{l=0}^{\infty} A_{n+2l} \frac{(-1)^l (2n+2l-2)!}{2^{2l}\, l!\, (n+l-1)!} \exp[-(n+2l)(n+2l-1)\tau] \quad (3.21)$$

We may now calculate expressions for $\langle n\rangle$, $g^{(2)}$ and other moments using $\rho_n(\tau)$. However, these may be obtained more directly from the generating function $F(x,\tau)$, since by definition of $F(x,\tau)$,

$$\langle n\rangle = \sum_{n=0}^{\infty} n\rho_n(\tau) = \left[\frac{\partial F}{\partial x}\right]_{x=1} \quad (3.22\ a)$$

$$\langle n(n-1)\rangle = \sum_{n=0}^{\infty} n(n-1)\,\rho_n(\tau) = \left[\frac{\partial^2 F}{\partial x^2}\right]_{x=1} \quad (3.22\ b)$$

More generally, the mth factorial moment is given by

$$\langle n(n-1)(n-2)\cdots(n-m)\rangle = \left[\frac{\partial^{m+1} F}{\partial x^{m+1}}\right]_{x=1}. \quad (3.22\ c)$$

Utilizing various properties of the $C_n^{-\frac{1}{2}}(x)$, or alternatively $P_n(x)$, (see, e.g. Abramowitz and Stegun 1965) we obtain

$$\langle n(\tau)\rangle = -\sum_{n=1}^{\infty} A_n \exp[-n(n-1)\tau] \quad (3.23)$$

$$\langle n(n-1)\rangle = -\frac{1}{2}\sum_{n=2}^{\infty} A_n\, n(n-1) \exp[-n(n-1)\tau] \quad (3.24)$$

The time behaviours of the mean $\langle n\rangle$ and the second order correlation function $g^{(2)}$ for an initial chaotic light beam and for an initial coherent light beam of the same mean number are shown in figures 4 and 5. The initial chaotic state corresponds to absorption of light from a thermal source, the initial coherent state corresponds to absorption of light from a laser beam.

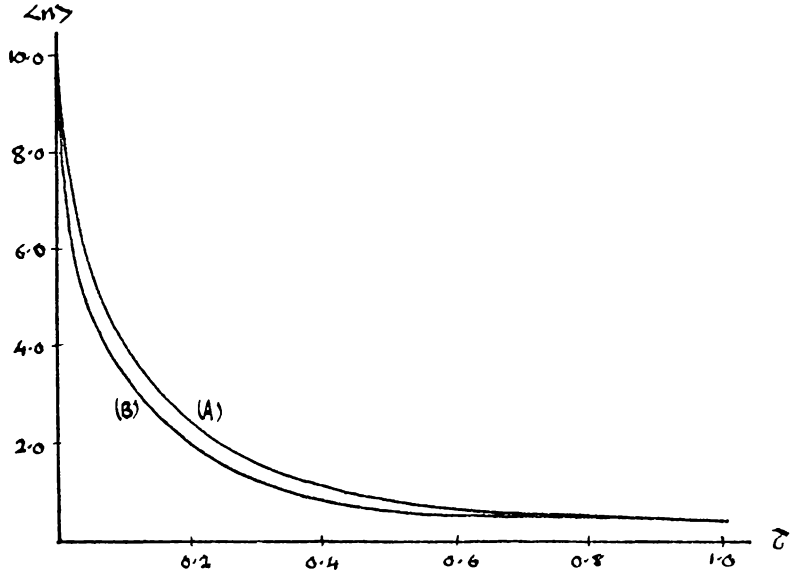

Fig.4 Two-photon absorption from a single mode, $\langle n(0)\rangle = 10$.
Mean photon number.
(A) Mode initially coherent. (B) Initially chaotic.

Figure 4 shows the expected decay of photon intensity with time for both initial states. The decay is faster if the field is initially chaotic, because the decay rate (equation (5.18) with $N_2 = 0$ ) is $\langle n(n-1)\rangle$ , or $g^{(2)}\langle n\rangle^2$, and $g^{(2)}_{chaotic} = 2.g^{(2)}_{coherent}$. Thus, initially at least, the absorption rate from a chaotic beam is twice that from a coherent beam. Physically, the $g^{(2)}$ function is a measure of photon pair coincidences (see chapter 4), and photon pair coincidences are exactly what is required for two-photon absorption to occur (see Teich and Wolga 1966).

Note that in neither case does the mean intensity tend to zero exactly (the vacuum state). Rather, the field tends to the state given by equations (3.18) and (3.19), so that $\langle n(\tau=\infty)\rangle = \sum_{m=0}^{\infty} \rho_{2m+1}(0)$ which is $\langle n(0)\rangle/[2\langle n(0)\rangle + 1]$ for an initial chaotic state, and $\frac{1}{2}[1 - e^{-2\langle n(0)\rangle}]$ for an initial coherent state. If $\langle n(0)\rangle \gg 1$, both these expressions yield $\langle n(\infty)\rangle \doteq 0.5$ which is negligable compared with $\langle n(0)\rangle$, and is of no practical interest.

The two photon absorption versus $K\tau$ is much faster than the simple $\langle n(0)\rangle e^{-K\tau}$ behaviour of the intensity in one photon absorption, because of the dependence of the absorption rate on $\langle n(n-1)\rangle$ rather than simply $\langle n\rangle$. However, in general, $K_{2\text{photon}} \ll K_{1\text{photon}}$.

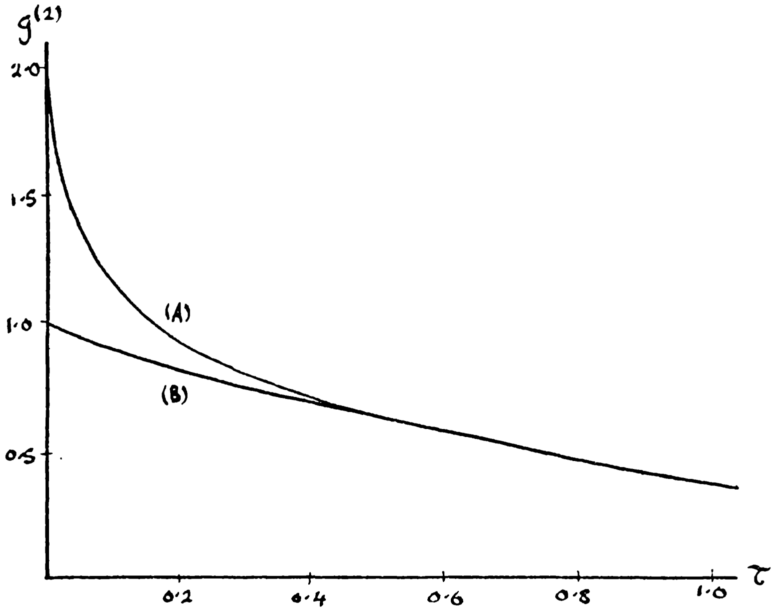

Fig.5 Two-photon absorption from a single mode, $\langle n(0)\rangle = 10$. Second order correlation function $g^{(2)}$.
(A) Mode initially coherent. (B) Initially chaotic.

Figure 5 shows that for both the initially chaotic and the initially coherent states $g^{(2)}$ decays with time - the absorption process is a "smoothing out" process. As equations (3.18) and (3.19) show, $\langle n(n-1)\rangle$ decays to zero, so that since $\langle n\rangle$ tends to a nonzero value, $g^{(2)}$ tends to zero. For comparison $g^{(2)}$ for an initial number state with the same initial mean of 10 is shown. Because $\sum_{m=0}^{\infty}\rho_{2m+1}(0)$ is zero, $\langle n\rangle$ tends to zero exactly in this case. In fact $\langle n\rangle^2$ tends to zero faster than $\langle n(n-1)\rangle$ does, so that $g^{(2)}$ for this case diverges as $\tau$ increases. In the case of an initial number state with odd mean, $\langle n(\tau)\rangle$ tends to a non-zero value, so that $g^{(2)}$ will tend to zero.

$g^{(2)}_{chaotic}$ falls rapidly initially, becoming closely equal to $g^{(2)}_{coherent}$ after $K\tau \simeq 0.4$ ; then the decay is slower. Note that the nonclassical effect of photon antibunching ( $g^{(2)} < 1$ , see chapter 4) sets in early (immediately if the initial state is coherent). However, this is only noticeable for $\tau \gtrsim 0.4$, where $\langle n(\tau)\rangle$ has already dropped to only 0.1 of its initial value. Thus in general the effect will be hard to observe experimentally because of the low photon intensities. In the one photon absorption situation $g^{(2)}$ remains constant at $g^{(2)}(\tau=0)$ , independently of the initial state; the distribution retains its initial form as the mean decreases.

### 3.2.2 Absorption From Two Modes.

When the atoms absorb pairs of photons from different modes, the operator $O$ in the master equation (2.17) is $a_1a_2$ where "1" and "2" are the mode labels. With $N_2=0$ , (2.17) is then

$$\frac{\partial\rho}{\partial t} = K\{[a_1a_2\rho, a_1^{+}a_2^{+}] + [a_1a_2, \rho a_1^{+}a_2^{+}]\} \qquad (3.25)$$

where $K = NK^{(0,2)}$.

The equation for the diagonal matrix elements of $\rho$ is thus

$$\frac{\partial \rho_{n_1,n_2}}{\partial t} = (n_1+1)(n_2+1)\,\rho_{n_1+1,n_2+1}(\tau) - n_1 n_2\,\rho_{n_1,n_2}(\tau) \qquad (3.26)$$

where $\tau = 2Kt$ and $\rho_{n_1,n_2} = \langle n_1,n_2|\rho|n_1,n_2\rangle$.

As in the case of emission into two modes, the $\rho_{n_1,n_2}$ are coupled only along the lines $n_2-n_1=\lambda$ , a constant integer, so that we may solve (3.26) as aone dimensional problem along these lines:

$$\frac{\partial \rho_{n,n+\lambda}}{\partial \tau} = (n+1)(n+1+\lambda)\,\rho_{n+1,n+1+\lambda} - n(n+\lambda)\,\rho_{n,n+\lambda} \qquad (3.27)$$

where $n$ is the difference variable and $\lambda$ is a parameter.

We again make use of a generating function technique to solve (3.27):

$$F_\lambda^{(+)}(x,\tau) = \sum_{n=0}^{\infty} \rho_{n,n+\lambda}(\tau).\,x^n \quad , |x|\leq 1 \qquad (3.28)$$

Multiplying equation (3.27) by $x^n$ and summing over $n$ yields the following equation for $F_\lambda^{(+)}(x,\tau)$ :

$$\frac{\partial F_\lambda^{(+)}(x,\tau)}{\partial \tau} = x(x-1)\frac{\partial^2 F_\lambda^{(+)}}{\partial x^2} + (\lambda+1)(1-x)\frac{\partial F_\lambda^{(+)}}{\partial x} \qquad (3.29)$$

The general solution of this equation may be obtained using a separation of variables method (McQuarrie 1967):

$$F_\lambda^{(+)}(x,\tau) = \sum_{n=0}^{\infty} A_n^{(+)}(\lambda)\,\mathcal{G}_n(\lambda,\lambda+1;x)\exp[-n(n+\lambda)\tau] \qquad (3.30)$$

where the $\mathcal{G}_n$ are Jacobi polynomials and the $A_n^{(+)}(\lambda)$ are coefficients to be determined. Equation (3.30) has the form of a Fourier series except that the $\mathcal{G}_n(\lambda,\lambda+1;x)$ are not orthogonal.

However we use the property (Abramowitz and Stegun 1965):

$$\frac{d}{dx} G_n(p,q,x) = n\, G_{n-1}(p+2,q+1,x) \tag{3.31}$$

which for $p=\lambda$, $q=\lambda+1$ yields polynomials orthogonal on $[0,1]$. Thus differentiation of (3.30) yields a Fourier series for $\frac{\partial F_\lambda(x,\tau)}{\partial \tau}$ in terms of Jacobi polynomials. The $A_n^{(+)}(\lambda)$, $n=1,2,\ldots$ may then be evaluated from the initial condition of the type (3.17) using the orthogonality of the $G_n(p,q,x)$ and the integrals given in the appendix. $A_0^{(+)}(\lambda)$ may be found by observing that equation (3.30) implies

$$F_\lambda^{(+)}(x,\tau=\infty) = A_0^{(+)}(\lambda) \tag{3.32}$$

and that since (3.26) couples the $\rho_{n_1,n_2}(\tau)$ only along the lines $n_2-n_1 = \text{constant}$, $\sum_{n=0}^{\infty} \rho_{n,n+\lambda}(\tau)$ is a constant of the motion for any non negative $\lambda$. Thus:

$$A_0^{(+)}(\lambda) = \sum_{n=0}^{\infty} \rho_{n,n+\lambda}(\infty) = \sum_{n=0}^{\infty} \rho_{n,n+\lambda}(0) \tag{3.33}$$

If $\lambda<0$, we let $\lambda' = -\lambda$ and interchange the roles of $n_1$ and $n_2$ in (3.26) and now consider $\rho_{n+\lambda',n}(\tau)$. We define a further generating function $F_\lambda^{(-)}(x,\tau)$:

$$F_\lambda^{(-)}(x,\tau) = \sum_{n=0}^{\infty} \rho_{n+\lambda,n}(\tau)\, x^n \tag{3.34}$$

which obeys the same equation (3.29) as $F_\lambda^{(+)}(x,\tau)$, and so takes a similar form to $F_\lambda^{(+)}(x,\tau)$. We may write $F_\lambda^{(\pm)}(x,\tau)$ as

$$F_\lambda^{(\pm)}(x,\tau) = \sum_{n=0}^{\infty} A_n^{(\pm)}(\lambda)\, G_n(\lambda,\lambda+1,x) \exp[-n(n+\lambda)\tau] \tag{3.35}$$

where

$$A_n^{(+)}(\lambda) = \frac{(2n+\lambda)!}{n!(n+\lambda)!}\sum_{k=n}^{\infty}\frac{k!(k+\lambda)!}{(k-n)!(k+\lambda+n)!}\rho_{k,k+\lambda}(0) \tag{3.36a}$$

$$A_n^{(-)}(\lambda) = \frac{(2n+\lambda)!}{n!(n+\lambda)!}\sum_{k=n}^{\infty}\frac{k!(k+\lambda)!}{(k-n)!(k+\lambda+n)!}\rho_{k+\lambda,k}(0) \tag{3.36b}$$

Equations (3.35) and (3.36) now completely determine all the $\rho_{n_1,n_2}(\tau)$ in terms of the arbitary initial distribution $\rho_{n_1,n_2}(0)$. A typical two-photon absorbtion experiment would use a laser beam at fixed frequency for one mode, and a tunable thermal source as the other mode. In this case $\rho_{n_1,n_2}(0) = P_1(n_1)\,P_2(n_2)$ where $P_1(n_1)$ is the poisson distribution of a coherent state, and $P_2(n_2)$ is the geometric distribution of a chaotic state.

From the definitions of $F_\lambda^{(\pm)}(x,\tau)$ we see that when $n_2-n_1 \geq 0$, $\rho_{n_1,n_2}(\tau)$ is the coefficient of $x^{n_1}$ in $F_{n_2-n_1}^{(+)}(x,\tau)$ and when $n_2-n_1 \leq 0$, $\rho_{n_1,n_2}(\tau)$ is the coefficient of $x^{n_2}$ in $F_{n_1-n_2}^{(-)}(x,\tau)$. Thus:

$$\rho_{n_1,n_2}(\tau) = \frac{1}{n_1!\,n_2!}\sum_{l=0}^{\infty} c_l(n_1,n_2)\exp[-(n_1+l)(n_2+l)\tau] \tag{3.37}$$

where

$$c_l(n_1,n_2) = \frac{(-1)^l}{l!}(n_1+n_2+2l)(n_1+n_2+l)!\sum_{k=n_1+l}^{\infty}\frac{k!(k+n_2-n_1)!}{(k-n_1-l)!(k+n_2+l)!}\rho_{k,k+n_2-n_1}(0)$$

From the $\rho_{n_1,n_2}(\tau)$ we may calculate the expectation values of any diagonal field operator, such as $\langle n_1\rangle$, $\langle n_1(n_1-1)\rangle$, $\langle n_1 n_2\rangle$. However, as pointed out in section (3.2.1) it is more convenient to obtain these directly from the generating function, which is

$$F(x_1,x_2,\tau) = \sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\rho_{n_1,n_2}(\tau)\,x_1^{n_1}x_2^{n_2} \tag{3.38}$$

$$= \sum_{\lambda=0}^{\infty} x_2^{\lambda}F_\lambda^{(+)}(x_1x_2,\tau) + \sum_{\lambda=1}^{\infty}F_\lambda^{(-)}(x_1x_2,\tau)$$

The moments are given by

$$\langle n_1(n_1-1)\cdots(n_1-\ell_1)\,n_2(n_2-1)\cdots(n_2-\ell_2)\rangle = \left[\frac{\partial^{\ell_1+\ell_2+2}F}{\partial^{\ell_1+1}x_1\,\partial^{\ell_2+1}x_2}\right]_{x_1=1,\,x_2=1} \qquad (3.39)$$

Using the properties of the Jacobi polynomials we obtain the following expressions for the modes' mean numbers, first factorial moments andnumber correlation:

$$\langle n_{\substack{1\\2}}(\tau)\rangle = \sum_{\lambda=0}^{\infty}\sum_{n=1}^{\infty}(n+\lambda)!\,B_n(\lambda)\exp[-n(n+\lambda)\tau] + \sum_{\lambda=1}^{\infty}\lambda A_0^{(\mp)}(\lambda) \qquad (3.40)$$

$$\begin{aligned}\langle n_{\substack{1\\2}}(n_{\substack{1\\2}}-1)\rangle = {} & \sum_{\lambda=0}^{\infty}\sum_{n}(n+\lambda+1)!\;B_n(\lambda)\exp[-n(n+\lambda)\tau] \\ & + 2\sum_{\lambda=0}^{\infty}\sum_{n=1}^{\infty}\frac{(n-1)!\,(n+\lambda)!}{\Gamma(2n+\lambda)}\,A_n^{(\pm)}(\lambda)\exp[-n(n+\lambda)\tau] \\ & + \sum_{\lambda=2}^{\infty}\lambda(\lambda-1)\;A_0^{(\mp)}(\lambda).\end{aligned} \qquad (3.41)$$

$$\begin{aligned}\langle n_1 n_2\rangle = {} & \sum_{\lambda=0}^{\infty}\sum_{n=2}^{\infty}(n+\lambda+1)!\;B_n(\lambda)\exp[-n(n+\lambda)\tau] \\ & + \sum_{\lambda=1}^{\infty}\sum_{n=1}^{\infty}(\lambda+1)\,(n+\lambda)!\;B_n(\lambda)\exp[-n(n+\lambda)\tau]\end{aligned} \qquad (3.42)$$

where

$$B_n(\lambda) = \frac{(n-1)!}{\Gamma(2n+\lambda)}\left\{A_n^{(+)}(\lambda) + A_n^{(-)}(\lambda)\right\}$$

The time behaviours of the means and $g^{(2)}$ functions when both modes are initially in identical number states is shown in figures 6 and 7 in comparison with the single mode case. The correlation function $[\langle n_1 n_2\rangle - \langle n_1\rangle\langle n_2\rangle]/\langle n_1\rangle\langle n_2\rangle$ for the same initial condition is given in figure 3 in comparison with the two mode emission correlation function. Note that for this initial state the distribution function has the form $\rho_{n_1,n_2}(\tau) = P_1(n_1)\,\delta_{n_1,n_2}$, so that the behaviour is symmetric in the two modes, and the correlation function is also equal to the normalized fluctuation $[\langle n^2\rangle - \langle n\rangle^2]/\langle n\rangle^2$ of each mode.

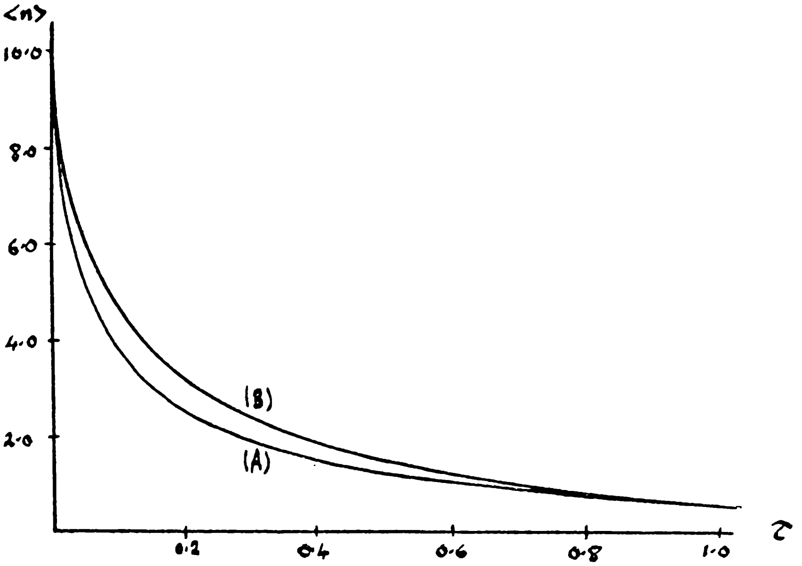

Fig.6 Two-photon absorption from initial number states, $\langle n(0) \rangle = 10$. Mode mean photon number.

(A) Single mode. (B) Two mode.

Figure 6 shows that for the special initial condition of all modes initially in equal number states, the absorption is initially more rapid in the two mode case, but quickly becomes more rapid for the one mode absorption. The initial rates are $N\langle n(n-1)\rangle_0$ for single mode absorption (equation (5.1)) and $N\langle n_1 n_2\rangle_0$ for two mode absorption (equation (5.18)), and for the given initial conditions $\langle n(n-1)\rangle = \langle n(0)\rangle[\langle n(0)\rangle - 1] < \langle n_1 n_2\rangle_0 = \langle n(0)\rangle^2$. However, as equations (5.2) and (5.20) show, the rate of change of $\langle n(n-1)\rangle$ is more negative than the rate of change of $\langle n_1 n_2\rangle$, so that the single mode absorption becomes more rapid.

For more realistic initial conditions (i.e. initially coherent or chaotic modes) the single mode absorption rate is always higher than the two mode absorption rate (for equal $\langle n(0)\rangle$ in all modes). This is because $\langle n(n-1)\rangle_0 \geqslant \langle n(0)\rangle^2$, $\langle n(n-1)(n-2)\rangle_0 \geqslant \langle n(0)\rangle^3$ and so on, for such initial conditions. Thus in experimental observations of multiphoton absorption, a single mode light source will yield more efficient absorption than a multimode source.

In the one mode case we saw that because of the $\langle n(n-1)\rangle$ dependence, the sbsorption rate is increased if the mode is initially chaotic. A similar effect occurs in the two mode case, where the rate depends on the statistics via $\langle n_1 n_2\rangle$, which is governed by equation (5.20). The rate is increased if one mode is initially chaotic, and increased even more if both modes are initially chaotic. If one of the modes is initially a number state this conclusion is not necessarily true (Simaan and Loudon 1975b), but such an initial state is a non-realistic one in practice.

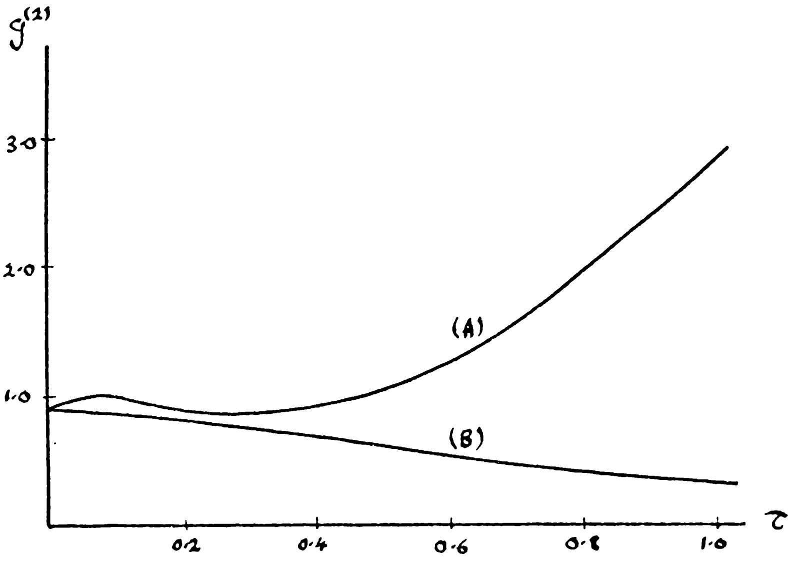

Fig.7 Two-photon absorption from initial number states, $\langle n(0)\rangle = 10$. Second order correlation functions $g^{(2)}$.

(A) Single mode. (B) Two mode.

Figure 7 compares the one mode and two mode absorption $g^{(2)}$ function for all modes initially in equal number states. The behaviour of the single mode $g^{(1)}$ has been explained already. In contrast, the $g^{(2)}$ function for each mode in the two mode case, is a decreasing function of time: the removal of fluctuations is smoother in the two mode case, so that $\langle n_{\substack{1\\2}}(n_{\substack{1\\2}}-1)\rangle$ tends to zero more rapidly than $\langle n_{\substack{1\\2}}\rangle^{2}$ does.

As figure 3 shows, $g_{12}$ for two mode absorption with the modes initially in equal number states is an increasing function of time which means $\langle n_1\rangle\langle n_2\rangle$ tends to zero faster than $\langle n_1 n_2\rangle$ does. For other, more realistic initial states, $g_{12}$ decreases from 0 to $-1$, corresponding to $\langle n_1 n_2\rangle/\langle n_1\rangle\langle n_2\rangle$ decreasing from 1 to 0. (see Simaan and Loudon 1975b).

## A Note on the Case $N_1$, $N_2$ Both Nonzero.

The general case with atomic populations $N_1$ and $N_2$ both nonzero, where both emission and absorption can occur, seems to be intractible to solution at present. Even the distributions' moment equations cannot in general be solved exactly (some approximate solutions are presented in chapter 5). However, there is one special situation, that in which the atomic level populations are equal: $N_1 = N_2 = N/2$. Here, even though the master equations for the $\rho_n$ or $\rho_{n_1,n_2}$ still cannot be solved exactly, the equations for the moments can be solved exactly. The results for this special case are given in chapter 5, in sections (5.1.1) and (5.1.2).

Several authors have since presented extended analyses of the above work on two-photon absorption, in which they investigate the properties of the solutions for the generating functions and the probability distributions in some detail. The one mode case has been examined by Tornau and Bach (1974), and Loudon and Simaan (1975a), and the two mode case by Loudon and Simaan (1975b).

## 3.3 The Raman Effect.

The general master equation (2.17) may also describe the Raman scattering of photons by atoms. In the Raman effect, incident (pumping) light at frequency $\omega_p$ is scattered by atoms, undergoing a change in frequency corresponding to the atomic transition frequency $\omega_{12}$. If a pump photon induces an atomic excitation, the re-emitted photon has frequency $\omega_S = \omega_p - \omega_{12}$ (figure 8), and is called a Stokes photon. If a pump photon scatters off an already excited atom and de-excitation is induced, the re-emitted photon has frequency $\omega_{AS} = \omega_p + \omega_{12}$ (figure 9), and is called an anti-Stokes photon. Progressively higher order effects may also occur when Stokes or anti-Stokes photons themselves interact with the atoms.

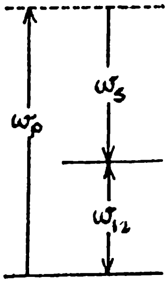

Fig.8 Stokes scattering.

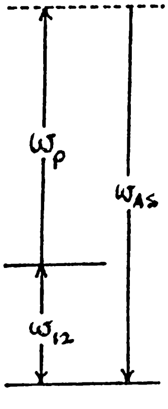

Fig.9 Antistokes scattering.

Walls (1973) has already presented a similar master equation, describing Raman scattering by photons. In his work he is able to solve this equation completely for the $P$ representation of (Glauber 1963) for the Stokes field alone, and for the coupled Stokes and anti-Stokes fields. However, this is done at the expense of having to make the parametric approximation in which the pump field is assumed to be sufficiently intense that it remains unchanged in the interaction, so that no pump depletion is allowed for. Here we shall present a solution for at least the diagonal part of (2.17) without making this parametric approximation.

We shall assume that because of external effects we can take $N_1 \simeq N$ , $N_2 \simeq 0$ . In this case Stokes scattering will dominate, so we may ignore anti-Stokes scattering. We further assume that the cavity tuning discourages anti-Stokes scattering, and any higher order Stokes and anti-Stokes generation. The scattered field we are describing is thus the Stokes field. The master equation describing this scattered field and the pumping field follows from equation (2.17) with $O = a_p a_s^+$ where the suffices "p" and "s" indicate "pump" mode and "Stokes" mode respectively. The master equation with $N_2 = 0$ is thus:

$$\frac{\partial \rho(t)}{\partial t} = NK^{(1,1)}\left\{[a_p a_s^+ \rho, a_p^+ a_s] + [a_p a_s^+, \rho a_p^+ a_s]\right\} \qquad (3.43)$$

The equation for the diagonal elements of $\rho$ in the Fock representation is then

$$\frac{\partial \rho_{n_s,n_p}(\tau)}{\partial \tau} = n_s(n_p+1)\,\rho_{n_s-1,n_p+1}(\tau) - (n_s+1)\,n_p\,\rho_{n_s,n_p}(\tau) \qquad (3.44)$$

where $\tau = 2NK^{(1,1)}t$ and $\rho_{n_s,n_p} = \langle n_s, n_p|\rho|n_s, n_p\rangle$

As in the case of two mode emission and absorption the $\rho_{n_s,n_p}$ are coupled only along certain straight lines in $n_s, n_p$ space, in this case the lines are $n_s + n_p = \lambda$ , a positive constant. Hence we solve the equation along such lines:

$$\frac{\partial \rho_{n,\lambda-n}}{\partial \tau} = n(\lambda-n+1)\rho_{n-1,\lambda-n+1}(\tau) - (n+1)(\lambda-n)\rho_{n,\lambda-n}(\tau) \qquad (3.45)$$

where $n = n_s$ is the difference variable and $\lambda = n_s + n_p \geqslant 0$ is a parameter. The Laplace transform of equation (3.45) yields:

$$\bar{\rho}_{n,\lambda-n}(s) - \frac{n(\lambda-n+1)}{[s+(n+1)(\lambda-n)]}\bar{\rho}_{n-1,\lambda-n+1}(s) = \frac{\rho_{n,\lambda-n}(0)}{[s+(n+1)(\lambda-n)]} \qquad (3.46)$$

where $\bar{\rho}_{n,\lambda-n}(s) = \int_0^\infty e^{-s\tau}\rho_{n,\lambda-n}(\tau)\,d\tau$

We thus obtain for the Laplace transform of $\rho_{n_s,n_p}(\tau)$ :

$$\bar{\rho}_{n_s,n_p}(s) = \frac{n_s!}{n_p!}\sum_{m=0}^{n_s}\frac{(n_s+n_p-m)!}{m!\prod_{j=m}^{n_s}[s+p_j(\lambda)]}\rho_{m,\lambda-m}(0) \qquad (3.47)$$

where $p_j(\lambda) = (j+1)(\lambda-j)$ and $\lambda = n_s+n_p$

Inversion of (3.47) then yields the full solution of $\rho_{n_s,n_p}(\tau)$ in terms of the arbitary initial distribution $\rho_{n_s,n_p}(0)$ . Care must be taken when inverting (3.47) since when $[\lambda]/2 \in [m, n_s]$ the denominator $\prod_{j=m}^{n_s}[s+p_j(\lambda)]$ will contain repeated factors, and the inverse will not be the simple $\sum_n A_n e^{-\mu_n\tau}$ behaviour. The full inversion is given in the appendix. From this expression we may calculate the time dependent behaviour of the expectation value of any diagonal field quantity.

The normal situation in Raman scattering experiments is the observation of Stokes emission into a vacuum state under the action of a pump source. The initial distribution for such a situation takes the form $\rho_{n_s,n_p}(0) = \delta_{n_s,0}P_n(n_p)$ where $P_p(n_p)$ is the initial distribution for the pump mode. If the pump is a thermal source of mean intensity $\langle n_p(0)\rangle$, $P_p(n_p) = [1+\langle n_p(0)\rangle]^{-1}.[\langle n_p(0)\rangle/1+\langle n_p(0)\rangle]^{n_p}$; if the pump is a stabilized laser beam, to a good approximation $P_p(n_p) = e^{-\langle n_p(0)\rangle} \langle n_p(0)\rangle^{n_p}/n_p!$. In figure 10 we give the time behaviour of the Stokes mean number for Stokes emission into an initial vacuum for an initially coherent pump mode and for an initially chaotic pump mode. For comparison the solution of Walls (1973) under the parametric approximation on the pump mode, and the approximate solution (5.41) are also shown. Figure 11 gives the behaviour of the $g^{(2)}$ functions for the fields, and figure 12 the behaviour of $g_{12} = [\langle n_s n_p\rangle - \langle n_s\rangle\langle n_p\rangle]/\langle n_s\rangle\langle n_p\rangle$, for the same initial conditions as for figure 10.

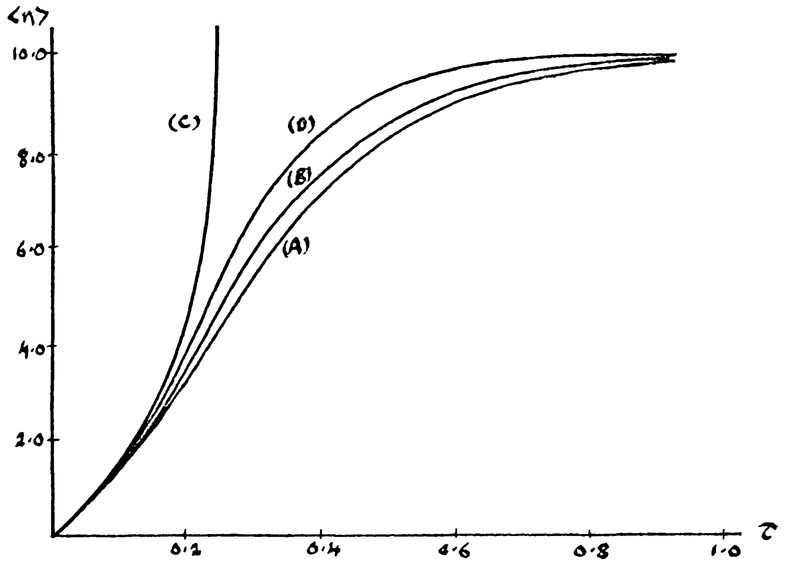

Fig.10 Raman scattering, $\langle n_s(0)\rangle = 0$, $\langle n_p(0)\rangle = 10$.
Stokes mode mean photon number.

(A) Pump initially coherent. (B) Pump initially chaotic.
(C) Parametric approximation on pump. (D) Approximate solution.

Figure 10 shows that there is a rapid initial increase of Stokes photons (with initial slope equal to $\langle n_p(0)\rangle$, by equation (5.36)), then a slower approach to the state, where, as expected, all the pump photons have been converted to Stokes photons. Note that the difference between the initially chaotic and initially coherent states for the mean is small, and becomes smaller as $\langle n_p(0)\rangle$ is made larger. The approximate solution follows the exact solution fairly closely, with particularly good agreement at small and large $\tau$ where the decorrelation approximation $\langle n_s n_p\rangle \simeq \langle n_s\rangle\langle n_p\rangle$ is good. The effect of correlations on is most noticeable in the range $\tau \geqslant 0{\cdot}2$, where the correlation $\langle n_s n_p\rangle - \langle n_s\rangle\langle n_p\rangle$ is significantly different from zero (see figure 12). As expected, the solution under the parametric approximation is close to the exact solutions only for small $\tau$, where pump depletion is small.

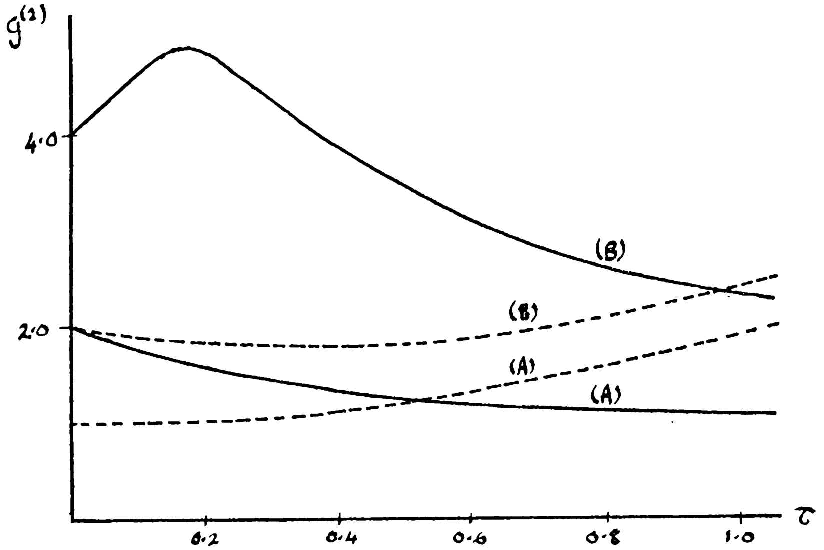

Fig.11 Raman scattering, $\langle n_s(0)\rangle = 0, \langle n_p(0)\rangle = 10$.
Second order correlation functions $g^{(2)}$.

— Stokes. - - Antistokes.
(A) Pump initially coherent. (B) Pump initially chaotic.

From figure 11 we see that the gross behaviour of the $g^{(2)}$ functions is that $g_p^{(2)}$ increases with time and $g_s^{(2)}$ decays from the initial value of $2g_p^{(2)}(0)$ (see chapter 5, equation (5.45)) to the value of $g_p^{(2)}(0)$ . This behaviour of $g_s^{(2)}$ corresponds to the fact that when the initial distribution is $\rho_{n_s,n_p}(0) = \delta_{n_s,0} P_p(n_p)$ , the steady state distribution "swaps" the two modes, giving $\rho_{n_s,n_p}(\infty) = P_p(n_s)\,\delta_{n_p,0}$ (Simaan 1975). $g_p^{(2)}(0)$ is an increasing function of time because as the vacuum steady state $\delta_{n_p,0}$ is approached, $\langle n_p(n_p-1)\rangle$ tends to zero less rapidly than $\langle n_p\rangle^2$ does. Note that, in agreement with the short time solution (5.43), $g_p^{(2)}(0)$ is unaltered for short times for either of the initial pump distributions i.e. its slope at is zero for both initial conditions. One feature of $g_s^{(2)}$ is the initial growth when the pump is initially chaotic. This behaviour is demonstrated in the short time solution equation (5.47).

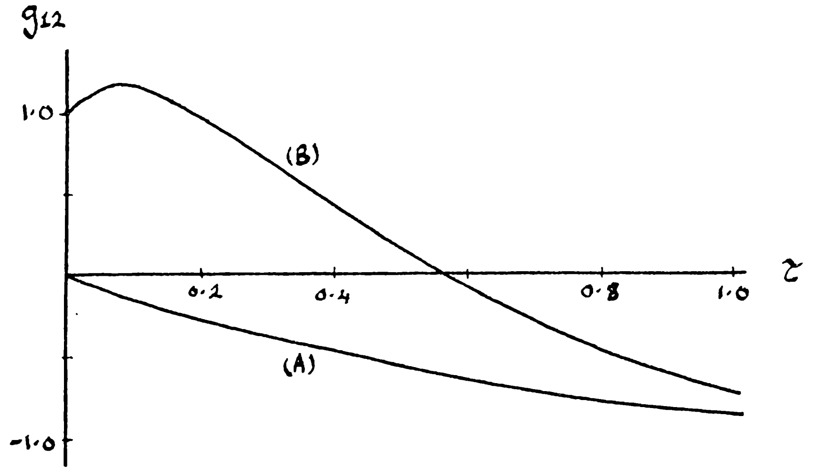

Fig.12 Raman scattering, $\langle n_s(0)\rangle = 0$, $\langle n_p(0)\rangle = 10$.
Correlation function $g_{12}$ .
(A) Pump initially coherent. (B) Pump initially chaotic.

From figure 12 we see that the gross feature of $g_{12}$ for the pump initially chaotic or coherent is a decay from the initial values $g_p^{(2)}(0) - 1$ (see chapter 5, (5.48)) to the steady state value −1. This corresponds to $\langle n_s n_p\rangle / \langle n_s\rangle\langle n_p\rangle$ decaying from $g_p^{(1)}(0)$ to 0. Thus even though $\langle n_p\rangle$ tends to zero, $\langle n_s n_p\rangle$ tends to zero more rapidly. Note that when the pump mode is initially chaotic, $g_{12}$ is an increasing function for short times ($\tau \lesssim 0{\cdot}1$), as pointed out in chapter 5 (equation (5.50)).

## The Off-diagonal Elements of $\rho$

If the off-diagonal elements of $\rho$ are required, the equation for these elements may be solved using the techniques used in this section. However, the procedure becomes quite complicated.

## The Anti-Stokes Field.

If the external pumping is arranged to give $N_1 \simeq 0$, $N_2 \simeq N$, then antistokes scattering will predominate. The master equation (2.17) also describes this situation: we set $N_1 = 0$, $N_2 = N$ and $O = a_p a_{AS}^{\dagger}$. The procedure for solution is then very similar to that outlined above, and we obtain a solution for $\bar{\rho}_{n_{AS}, n_p}(s)$ of the same form as equation (3.47), with $p_j(\lambda) = (j+1)(\lambda-j)$, $\lambda = n_p + n_{AS}$. However, in most cases of physical interest the Stokes process is the dominant one.

## Atomic Level Populations $N_1$ and $N_2$ Both Nonzero.

As in the emission and absorption problem, exact solutions when the atomic level populations are both nonzero appear to be difficult to obtain. However, in the case $N_1 = N_2 = N/2$, exact solutions for the moment equations may again be obtained. These results are presented in chapter 5, section (5.2).

It should be noted that an extended analysis of the above work has since been given by Simaan (1975), who investigates in some detail the properties of the photon distribution corresponding to equation (3.47) and the associated moments of that equation.

## CHAPTER 4 STEADY STATES: PHOTON BUNCHING AND ANTIBUNCHING

It is of some interest to investigate the steady states of the two-photon processes studied in chapter 3. As we saw in that chapter, the master equations decouple the $\rho_{n_1,n_2}(\tau)$ or $\rho_n(\tau)$ somewhat, with the $\rho_{n_1,n_2}(\tau)$ or $\rho_n(\tau)$ being coupled only for those $n_1$ and $n_2$ or $n$ lying in certain subsets. This means there exist constants of the motion of the form $\sum\rho_{n_1,n_2}$ and $\sum\rho_n(\tau)$, where the sums are taken over certain subsets only in $n_1, n_2$ or $n$ space. Because these quantities are constant they persist for all times; thus the steady states of the processes will depend on the initial conditions as well as on the external parameters ( the atomic level populations $N_1$ and $N_2$ in this case ). This should be contrasted with the corresponding one photon processes, for which the steady state has a thermal-like distribution which depends only on the external parameters. This dependence on the initial conditions means that by imposing certain initial conditions we can obtain states of the electric field which differ markedly in their statistical properties from those states normally found.

One useful measure of the statistics of a field mode is the second order correlation function $g^{(2)} = \langle n(n-1)\rangle/\langle n\rangle^2$ for that mode (see Glauber 1963, 1970). This quantity in effect gives a measure of the correlations or coincidences between photons arriving at any given point. Interest in this quantity was first stimulated by the Hanbury-Brown Twiss (H.B.T) experiment (Hanbury-Brown and Twiss 1956) which essentially measured $g^{(2)}$ for a chaotic light field. In this case it was found that $g^{(2)} = 2$ , which indicated some correlation between photons. When the same experiment is repeated using a stabilized laser beam instead, it is found that $g^{(2)} = 1$ , characteristic of a coherent state, which laser light closely approximates. In this case there is no correlation between photons in that mode. When $g^{(2)} > 1$, this is called the bunching effect, since it indicates that photons are not arriving "equally spaced" in time. For some photon distributions, $g^{(2)} < 1$ , and this is referred to as the "anti-bunching" effect. Stoler (1974) has suggested an experimental method to observe such an effect using the parametric subharmonic generation process. More recently Carmicheal and Walls (1976a,b) have shown that such an effect will be observed when using photon correlation techniques to measure the resonant stark effect in atoms. We shall be investigating the behaviour of $g^{(2)}$ for the steady state distributions of some of the nonlinear processes of chapter 3.

The steady state behaviour in the special cases in chapter 3 is not particularly interesting, because assuming that either $N_1 = 0$ or $N_2 = 0$ means that the modes either "blow up" or are depleted to fairly trivial steady state distributions. We shall take $N_1$ and $N_2$ both nonzero so that the combination of pumping and depletion due to the atoms leads to nontrivial steady states. We shall consider two photon emission and absorption, both single mode and two mode.

## 4.1 Single Mode Emission and Absorption.

When $N_1$ and $N_2$ are both nonzero, the master equation (2.17) with $O = aa$ yields the following equation for $\rho_n(\tau) = \langle n|\rho(\tau)|n\rangle$:

$$\frac{\partial \rho_n(t)}{\partial t} = 2K^{(0,2)} N_1\{(n+1)(n+2)\rho_{n+2}(t) - (n-1)n\,\rho_n(t)\} + 2K^{(0,2)} N_2\{(n-1)n\,\rho_{n-2}(t) - (n+1)(n+2)\rho_n(t)\} \tag{4.1}$$

This equation is in fact the combination of equations (3.2) and (3.11). In the steady state $\frac{\partial \rho_n(t)}{\partial t} = 0$, so that the R.H.S. of (4.1) is zero. Because of the way the $\rho_n(t)$ are coupled in (4.1) detailed balance must hold (see, e.g. Graham 1973), thus the single equation splits into two equivalent equations:

$$\begin{aligned} N_1\rho_{n+2}(\infty) - N_2\rho_n(\infty) &= 0 \\ -N_1\rho_n(\infty) + N_2\rho_{n-2}(\infty) &= 0 \end{aligned} \tag{4.2}$$

These have the solution

$$\left.\begin{aligned} \rho_{2n}(\infty) &= \rho_0(\infty)\,(N_2/N_1)^n \\ \rho_{2n+1}(\infty) &= \rho_1(\infty)\,(N_2/N_1)^n \end{aligned}\right\}, \quad n = 0, 1, 2, \ldots \tag{4.3}$$

The terms $\rho_0(\infty)$ and $\rho_1(\infty)$ are determined by using the fact that

$$\begin{aligned} c_1 &= \sum_m \rho_{2m}(t) = \sum_m \rho_{2m}(0) \\ c_2 &= \sum_m \rho_{2m+1}(t) = \sum_m \rho_{2m+1}(0) \end{aligned} \tag{4.4}$$

are constants of motion (see chapter 3, section 3.2.1). Summing (4.3) over $n$ will then yield expressions for $\rho_0(\infty)$ and $\rho_1(\infty)$ in terms of $c_1$ and $c_2$. Thus:

$$\begin{aligned} \rho_{2n}(\infty) &= c_1(1-N_2/N_1)(N_2/N_1)^n \\ \rho_{2n+1}(\infty) &= c_2(1-N_2/N_1)(N_2/N_1)^n \end{aligned} \tag{4.5}$$

This shows explicitly how the distribution depends on the initial distribution through $c_1$ and $c_2$. Note that we require $N_2/N_1 < 1$ in order that $\rho_n(\infty)$ be normalizable. If $N_2 \geqslant N_1$, there is no steady state. The distribution (4.5) is similar in form to the one-photon thermal distribution $\rho_n = (1-N_2/N_1)(N_2/N_1)^n$ The mean and first factorial moment of (4.5) are:

$$\langle n \rangle = c_2 + 2(N_2/N_1)/(1-N_2/N_1) \tag{4.6}$$

$$\langle n(n-1) \rangle = \frac{2(N_2/N_1)}{(1-N_2/N_1)^2}\left[1+3(N_2/N_1)+2c_2(1-N_2/N_1)\right] \tag{4.7}$$

The $g^{(2)}$ function is thus:

$$g^{(2)} = 2 + \frac{(\bar{n}-c_2)(2-c_2)-4\bar{n}c_2}{2\bar{n}^2} \tag{4.8}$$

where $\bar{n}$ is the $\langle n \rangle$ if equation (4.6). We see that the behaviour of $g^{(2)}$ depends on the external parameters $N_2/N_1$, and on the initial conditions (through $c_2$).

We shall first consider two photon spontaneous emission into a vacuum. In this case $\rho_n(0) = \delta_{n,0}$, so that $c_2 = 0$, and:

$$g^{(2)} = 2 + 1/\bar{n} \tag{4.9}$$

where

$$\bar{n} = 2(N_2/N_1)/(1-N_2/N_1) \tag{4.10}$$

Here $g^{(2)}$ is always greater than 2, and may in fact be considerably greater than 2, when the atomic inversion is small (i.e. when $N_1 \simeq N_2$ ). We thus have enhanced photon bunching in this situation. We will obtain the $g^{(2)}$ (4.9) for any initial distribution with the $\rho_{2m+1}(0)$ all zero. However, in general, such distributions (apart from $\rho_n(0) = \delta_{n,0}$ ) will be very difficult to set up, so that, experimentally, spontaneous two photon emission into a vacuum will be the best way of observing enhanced photon bunching.

The above result is changed if there is a photon field of finite intensity present initially: If the initial distribution is chaotic, with $\rho_n(0) = \frac{1}{(1+\bar{n}_0)} \cdot \left(\frac{\bar{n}_0}{1+\bar{n}_0}\right)^n$ , then

$$C_2 = \bar{n}_0 / 2(\bar{n}_0 + 1) \tag{4.11}$$

If the initial distribution is coherent, with

then:

$$C_2 = \frac{1}{2} \cdot \left[ 1 - e^{-2\bar{n}_0} \right] \tag{4.12}$$

If the initial means $\bar{n}_0$ are sufficiently large ( $\bar{n}_0 >> 1$ ) then both (4.11) and (4.12) reduce to $C_2 \approx \frac{1}{2}$ , and:

$$g^{(2)} = 2 - 1/2\bar{n}^2 \tag{4.13}$$

where
$$\bar{n} = 1/2 + \frac{2(N_2/N_1)}{(1-N_2/N_1)} \tag{4.14}$$

In this case $g^{(2)}$ ranges from 0 to 2 as $N_2/N_1$ goes from 0 to its maximum of 1. Since $g^{(2)} \leqslant 2$ , no enhanced bunching effect is possible. However, since $g^{(2)}$ may be less than 1, antibunching is possible. (Simaan and Loudon 1975a). However, $g^{(2)} < 1$ requires, by (4.13), $\bar{n} < 0{\cdot}7$. Such small intensities would make this anticorrelation effect very difficult to observe experimentally.

## 4.2 Two Mode Emission and Absorption

With $N_1$ and $N_2$ both nonzero and $O = a_1 a_2$, the master equation (2.17) yields the following equation for $\rho_{n_1,n_2}(t) = \langle n_1,n_2|\rho|n_1,n_2\rangle$ :

$$\frac{\partial\rho_{n_1,n_2}(t)}{\partial t} = 2K^{(0,2)} N_1 \{(n_1+1)(n_2+1)\rho_{n_1+1,n_2+1} - n_1 n_2 \rho_{n_1,n_2}\} \qquad (4.15)$$

$$+ 2K^{(0,2)} N_2 \{n_1 n_2 \rho_{n_1-1,n_2-1} - (n_1+1)(n_2+1)\rho_{n_1,n_2}\}$$

This is the combination of equations (3.7) and (3.26). Because detailed balance holds in the steady state we obtain the following pair of equivalent equations when $\frac{\partial\rho_{n_1,n_2}}{\partial t} = 0$ :

$$N_1 \rho_{n_1+1,n_2+1}(\infty) - N_2 \rho_{n_1,n_2}(\infty) = 0 \qquad (4.16)$$

$$-N_1 \rho_{n_1,n_2}(\infty) + N_2 \rho_{n_1-1,n_2-1}(\infty) = 0$$

These have the solution

$$\rho_{n,n+\lambda}(\infty) = \rho_{0,\lambda}(\infty)(N_2/N_1)^n \qquad (4.17)$$

$$n = 0,1,2,\ldots,\ \lambda = 0,1,2,\ldots$$

$$\rho_{n+\lambda,n}(\infty) = \rho_{\lambda,0}(\infty)(N_2/N_1)^n$$

The terms $\rho_{0,\lambda}(\infty)$ and $\rho_{\lambda,0}(\infty)$ are determined by using the constants of motion (see chapter 3, section 3.2.2)

$$C_\lambda^{(+)} = \sum_n \rho_{n,n+\lambda}(t) = \sum_n \rho_{n,n+\lambda}(0) \qquad (4.18)$$

$$C_\lambda^{(-)} = \sum_n \rho_{n+\lambda,n}(t) = \sum_n \rho_{n+\lambda,n}(0).$$

Summing (4.17) over $n$ will yield expressions for the $\rho_{0,\lambda}(\infty)$ and $\rho_{\lambda,0}(\infty)$ in terms of the $C_\lambda^{(\pm)}$. Thus:

$$\rho_{n_1,n_2}(\infty) = \begin{cases} C^{(+)}_{n_2-n_1}\cdot(1-N_2/N_1)(N_2/N_1)^{n_1} & , \; n_2 \geq n_1 \\ C^{(-)}_{n_1-n_2}\cdot(1-N_2/N_1)(N_2/N_1)^{n_2} & , \; n_2 \leq n_1 \end{cases} \tag{4.19}$$

Thus again the steady state distribution depends explicitly on the initial distribution, through the $C_\lambda^{(\pm)}$. The distribution is similar to a geometric distribution. In order that $\rho_{n_1,n_2}(\infty)$ be normalizable, $N_2/N_1 < 1$ is required. If $N_2 \geq N_1$, the distribution "blows up" and there is no steady state.

The means and first factorial moments of the distribution (4.19) are:

$$\langle n_{\substack{1\\2}} \rangle = \frac{(N_2/N_1)}{(1-N_2/N_1)} + \sum_{\lambda=1}^{\infty} \lambda C_\lambda^{(\mp)} \tag{4.20}$$

$$\langle n_{\substack{1\\2}}(n_{\substack{1\\2}}-1) \rangle = \frac{2(N_2/N_1)^2}{(1-N_2/N_1)^2} + \frac{2(N_2/N_1)}{(1-N_2/N_1)} \sum_{\lambda=1}^{\infty} \lambda C_\lambda^{(\mp)} + \sum_{\lambda=2}^{\infty} \lambda(\lambda-1)\, C_\lambda^{(\mp)} \tag{4.21}$$

The correlation $\langle n_1 n_2 \rangle$ is :

$$\langle n_1 n_2 \rangle = \frac{(N_2/N_1)(N_2/N_1+1)}{(1-N_2/N_1)^2} + \frac{(N_2/N_1)}{(1-N_2/N_1)} \sum_{\lambda=1}^{\infty} \lambda \left\{ C_\lambda^{(+)} + C_\lambda^{(-)} \right\} \tag{4.22}$$

We shall first consider the steady state achieved when in one of the modes (say mode 1) there is emission into an initial vacuum. In this case $\rho_{n_1,n_2}(0) = \delta_{n_1,0}\, P_2(n_2)$ where $P_2(n_2)$ is the initial distribution for mode 2, so that $C_\lambda^{(+)} = P_2(\lambda)$ and

$c_\lambda^{(-)} = 0$ . The distribution (4.19) is thus:

$$\rho_{n_1,n_2}(\infty) = \theta(n_2-n_1)\,P_2(n_2-n_1)(1-N_2/N_1)(N_2/N_1)^{n_1} \tag{4.23}$$

The reduced distribution for mode 1 alone is thus an ordinary geometric thermal distribution, independent of the initial distribution in mode 2:

$$\rho_{n_1}(\infty) = (1-N_2/N_1)(N_2/N_1)^{n_1} \tag{4.24}$$

The reduced distribution for mode 2 depends on the form of the initial distribution of mode 2. For example, for an initially vacuum state, the distribution (4.23) is

$$\rho_{n_1,n_2}(\infty) = \delta_{n_1,n_2}(1-N_2/N_1)(N_2/N_1)^{n_1} \tag{4.25}$$

Thus in the case of emission into an initial vacuum in both modes, the steady state distributions in each mode are identical ordinary geometric distributions as in (4.24).

If mode 2 is initially chaotic, with mean $\overline{n_2(0)}$ , then carrying out the summations in equations (4.20) and (4.21) yields for mode 2's $g^{(2)}$ :

$$g_2^{(2)} = 2 - \frac{2\,\bar{n}_1\,\overline{n_2(0)}}{[\bar{n}_1 + \overline{n_2(0)}]^2} \tag{4.26}$$

where $\bar{n}_1 = (N_2/N_1)/(1-N_2/N_1)$ is the mean in mode 1 with the distribution (4.24). If mode 2 is initially coherent,

$$g_2^{(2)} = 2 - \frac{\overline{n_2(0)}\,[2\bar{n}_1 + \overline{n_2(0)}]}{[\bar{n}_1 + \overline{n_2(0)}]^2} \tag{4.27}$$

In both (4.26) and (4.27) we see that always $1 \leq g_2^{(2)} \leq 2$ , so that neither antibunching nor enhanced bunching $(g^{(2)} > 2)$ will occur.

For more general conditions the situation becomes more complicated. For example, if both modes are initially chaotic with means $\overline{n_1(0)}$ and $\overline{n_2(0)}$ , the mode 1 $g^{(2)}$ is:

$$g_1^{(2)} = 2 - 2 \cdot \frac{\overline{n_1(0)}\,[\overline{n_1(0)} + 1]\,[\bar{n}_1 - \overline{n_1(0)}]}{\overline{n_2(0)} \cdot (\bar{n}_1)} \qquad (4.28)$$

where $\bar{n}_1$ is the $\langle n_1 \rangle$ of equation (4.20):

$$\langle n_1 \rangle = \frac{(N_2/N_1)}{(1 - N_2/N_1)} + \frac{\overline{n_2(0)}}{[\overline{n_1(0)} + \overline{n_2(0)} + 1]} \qquad (4.29)$$

Enhanced bunching will occur when $\bar{n}_1 < \overline{n_1(0)}$ . $g_1^{(2)}$ is always greater than 1, so no antibunching effect can be observed. Similar conclusions may be made about mode 2.

We have seen that in both the single mode and single mode cases of two photon emission and absorption it is possible, by suitable choices of atomic inversions and/or initial conditions, to produce steady state light fields which have $g^{(2)}$ values greater than 2. The light fields from such sources will thus exhibit an enhanced H.B.T. effect.

Production of steady state light fields which will give an antibunching effect appears to be fairly difficult, with apparently only the single mode source producing such light. In this case, however, the intensity is so low that experimental observation would be very difficult.

## CHAPTER 5 APPROXIMATE SOLUTIONS

The work of chapter 3 provides exact solutions for the diagonal part of the density operator for each process, and from these solutions we may calculate exact expressions for mean intensities, variances, correlations, etc. However, in general, such expressions are fairly complicated, and do not give an immediate idea of the behaviour of the light fields. It is thus useful to investigate approximate solutions for the mean numbers and so on, in order to provide a more transparent view of the behaviour of the light. Such approximate solutions also allow us to make some connection with the classical theory of nonlinear optics, where statistics (and quantum effects) are not taken into account.

The crudest approximation ignores statistics completely, giving equations for the field intensities, and ignoring fluctuations and correlations. The next best approximation allows the inclusion of some higher moments, and thus takes some fluctuation and correlation into account. In certain situations approximations may also be made on the exact statistical expressions of chapter 3.

There are other approximations which may be made. One is to make linearizing approximations on the master equations and solve the approximate equations which result. Another method involves expanding themoments in power series in time, and calculating the expansion coefficients perturbatively from the moment equations. This method is obviously most useful for obtaining short-time approximate solutions.

## 5.1 Two Photon Emission and Absorption Approximate Solutions

### 5.1.1 Emission Into a Single Mode

To obtain equations of motion for the mean value of a field operator A, we multiply the master equation by the operator and take the trace of this equation. If the operator is diagonal in the number state (Fock) representation, this is equivalent to multiplying the equation for the diagonal elements of $\rho$ by the matrix element $\langle n|A|n\rangle$ of A and summing over $n$. Thus for the first moment, or mean number $\langle n\rangle = \langle a^\dagger a\rangle$ and first factorial moment $\langle n(n-1)\rangle$ with $N_1$ and $N_2$ both non zero,

$$\frac{d\langle n\rangle}{d\tau} = 2(N_2-N_1)\langle n(n-1)\rangle + 8N_2 + 4N_2 \qquad (5.1)$$

$$\frac{d\langle n(n-1)\rangle}{d\tau} = 4(N_2-N_1)\langle n(n-1)(n-2)\rangle + 2(13N_2-N_1)\langle n(n-1)\rangle \qquad (5.2)$$
$$+ 32N_2\langle n\rangle + 4N_2$$

where $\tau = 2K^{(0,2)}t$ .

In general, each moment is coupled to the next highest moment, which is to be expected for a nonlinear process. The moment equations thus form a non-closed hierachy, and must be truncated in order to obtain any closed solution.

The crudest approximation we can make is to ignore statistics, and set $\langle n^2\rangle \simeq \langle n\rangle^2$. This is equivalent to setting the variance zero, or ignoring fluctuations. Under this approximation we may solve equation (5.1) to obtain:

$$\langle n(\tau)\rangle \simeq \frac{[\langle n(0)\rangle + a + b](a-b) + [\langle n(0)\rangle + b - a](a+b)\exp[4(N_2-N_1)a\tau]}{[\langle n(0)\rangle + a + b] - [\langle n(0)\rangle + b - a]\exp[4(N_2-N_1)a\tau]} \qquad (5.3)$$

where $a = \frac{[12N_1N_2 + (N_1+N_2)^2]^{\frac{1}{2}}}{2(N_2 - N_1)}$ , $b = \frac{2N_2 + (N_1+N_2)}{2(N_2 - N_1)}$

In the case of pure emission, $N_1 = 0$ and $N_2 = N$ , and (5.3) becomes

$$\langle n(\tau)\rangle = \frac{2[\langle n(0)\rangle + 1]e^{2N\tau} - [\langle n(0)\rangle + 2]}{[\langle n(0)\rangle + 2] - [\langle n(0)\rangle + 1]e^{2N\tau}} \qquad (5.4)$$

The expression (5.4) exhibits the correct qualitative behaviour, with the intensity of emitted light increasing with time. This expression is valid only if $\sigma^2 \approx 0$ , i.e. only if the distribution is sharply peaked. The results of chapter 3 show that, in fact, the distribution spreads out quite rapidly, so that (5.4) is valid only for short times, and for sharply peaked initial distributions. Note that the approximate mean (5.4) becomes infinite at the finite time $\tau = \frac{1}{2}\ln\{[\langle n(0)\rangle + 2]/[\langle n(0)\rangle + 1]\}$, whereas the exact mean becomes infinite only at infinite time. Note also that this expression for $\langle n(\tau)\rangle$ differs from that which would be obtained from a completely classical calculation in that it contains the purely quantum mechanical effect of spontaneous emission. Thus as well as including amplification of the initial intensity $\langle n(0)\rangle$ , (5.4) (and indeed (5.3)) allows the growth of $\langle n\rangle$ by the amplification of spontaneous emission into the vacuum state.

In the case of pure absorption, $N_1 = N$ and $N_2 = 0$ , and (5.3) reduces to

$$\langle n(\tau)\rangle \simeq \frac{\langle n(0)\rangle}{\langle n(0)\rangle + [1 - \langle n(0)\rangle]e^{2N\tau}} \qquad (5.5)$$

This is the same result as one obtains in a classical analysis which should be expected, since spontaneous emission plays no part in the absorption process.

We may improve the approximation to allow for other initial distributions by assuming that for small times the distributions are not perturbed too much from their initial form. This enables us to replace $\langle n(n-1)\rangle$ in equation (5.1) by a term appropriate to the particular initial distribution. (The replacement $\langle n^2\rangle \simeq \langle n\rangle^2$ above corresponds to an initial number state.)

For an initially chaotic state, $\langle n(n-1)\rangle = 2\langle n\rangle^2$ , and

$$\langle n(\tau)\rangle \simeq \frac{[\langle n(0)\rangle + 1](1+4N\tau) - 1}{1 - 4[\langle n(0)\rangle + 1]N\tau} \qquad (N_1 = 0) \qquad (5.6)$$

$$\langle n(\tau)\rangle \simeq \frac{\langle n(0)\rangle}{1 + 4\langle n(0)\rangle N\tau} \qquad (N_2 = 0) \qquad (5.7)$$

For an initially coherent state, $\langle n(n-1)\rangle = \langle n\rangle^2$ , and

$$\langle n(\tau)\rangle \simeq \frac{[\langle n(0)\rangle + 2 - \sqrt{2}](2+\sqrt{2})e^{\sqrt{2}N\tau} - [\langle n(0)\rangle + 2 + \sqrt{2}](2-\sqrt{2})}{[\langle n(0)\rangle + 2 + \sqrt{2}] - [\langle n(0)\rangle + 2 - \sqrt{2}]e^{\sqrt{2}N\tau}} \qquad (N_1 = 0) \qquad (5.8)$$

$$\langle n(\tau)\rangle \simeq \frac{\langle n(0)\rangle}{1 + 2\langle n(0)\rangle N\tau} \qquad (N_2 = 0) \qquad (5.9)$$

Note that these solutions all contain the correct qualitative short-time behaviour of $\langle n\rangle$ , and in the case of emission include spontaneous emission.

An alternative method for obtaining short-time solutions for the moments is to expand them in power series in $\tau$ (c.f. Simaan and Loudon 1975a):

$$\langle f(n)\rangle = \langle f(n)\rangle_0 + \langle f(n)\rangle_1 \tau + \langle f(n)\rangle_2 \tau^2 + \cdots \qquad (5.10)$$

Upon inserting the appropriate expansions into the moment equations and equating coefficients of like powers of $\tau$, we obtain soluble equations for the coefficients $\langle f(n)\rangle_k$. Thus the coefficients of the $\tau$ term in the expansions for $\langle n\rangle$ and $\langle n(n-1)\rangle$ are simply the R.H S. of respectively equations (5.1) and (5.2) evaluated at $\tau = 0$. The short-time approximate solution (to first order in $\tau$) for the second order correlation function is then

$$g^{(2)} \simeq g^{(2)}(0) + \frac{1}{\langle n(0)\rangle^2}\left[\langle n(n-1)\rangle_1 - \frac{2\langle n(n-1)\rangle_0}{\langle n(0)\rangle}\langle n\rangle_1\right]\tau \qquad (5.11)$$

The accuracy of the expressions may be extended indefinitely by adding the successive terms in powers of $\tau$. However, to obtain these coefficients we must go to successively higher moment equations.

For an initially chaotic state, $\langle n(n-1)\rangle_0 = 2\langle n(0)\rangle^2$ and $\langle n(n-1)(n-2)\rangle_0 = 6\langle n(0)\rangle^3$, so that

$$g^{(2)}_{chaotic} \simeq 2 + \frac{4}{\langle n(0)\rangle^2}\left[4(N_2 - N_1)\langle n(0)\rangle^3 + (5N_2 - N_1)\langle n(0)\rangle^2 + 4N_2\langle n(0)\rangle + N_2\right]\tau \qquad (5.12)$$

For an initially coherent state, $\langle n(n-1)\rangle_0 = \langle n(0)\rangle^2$ and $\langle n(n-1)(n-2)\rangle_0 = \langle n(0)\rangle^3$, so that

$$g^{(2)}_{coherent} \simeq 1 + \frac{2}{\langle n(0)\rangle^2}\left[(5N_2 - N_1)\langle n(0)\rangle^2 + 12N_2\langle n(0)\rangle + 2N_2\right]\tau \qquad (5.13)$$

The corresponding short-time forms for the production rate are:

$$\frac{d\langle n\rangle}{d\tau}_{\text{coherent}} = 4\left[(N_2-N_1)\langle n(0)\rangle^2 + 2N_2\langle n(0)\rangle + N_2\right] + 4\left\{3(N_2-N_1)^2\langle n(0)\rangle^3 \right. \\ +(17N_2-N_1)(N_2-N_1)\langle n(0)\rangle^2 + 16N_2(2N_2-N_1)\langle n(0)\rangle \\ \left. + 2N_2(5N_2-N_1)\right\}\tau \tag{5.14}$$

$$\frac{d\langle n\rangle}{d\tau}_{\text{chaotic}} = \frac{d\langle n\rangle}{d\tau}_{\text{coherent}} + 4\left[5(N_2-N_1)^2\langle n(0)\rangle^3 + (17N_2-N_1)(N_2-N_1)\langle n(0)\rangle^2\right]\tau \tag{5.15}$$

Note that in the situation of (5.12) enhanced bunching ($g^{(2)}>2$) may occur for certain ranges of $N_1$, $N_2$ and $\langle n(0)\rangle$, and in the situation of (5.13) antibunching ($g^{(2)}<1$) is possible.

Further discussion of the short time behaviour is given by Simaan and Loudon (1975a) and Chandra and Prakash (1970).

### Exact Solutions for the Case $N_1 = N_2$

One important special case occurs when the atomic level populations are equal, i.e. when $N_1 = N_2 = N/2$. In this case, in each of the moment equations the term involving the next higher moment vanishes, and the equations may be solved exactly (Lambropoulis 1967). Thus for the mean number:

$$\langle n(\tau)\rangle = \langle n(0)\rangle e^{2N\tau} + \frac{1}{2}(e^{2N\tau}-1) \tag{5.16}$$

The first term represents the contribution from amplification of the photons initially present, the second represents the contribution from amplification of spontaneous emission. There is no steady state, in agreement with the results of chapter 4.

The first factorial moment is:

$$\langle n(n-1)\rangle = \langle n(n-1)\rangle_0 e^{11N\tau} + \frac{16}{9}\left[\langle n(0)\rangle + \tfrac{1}{2}\right]\left(e^{11N\tau} - e^{2N\tau}\right) + \frac{1}{11}\left(e^{11N\tau} - 1\right) \qquad (5.17)$$

In this case we see explicitly that $g^{(2)}$ and the normalized fluctuation $\sigma^2/\langle n\rangle^2$ are increasing functions of time.

Various other approximate methods exist. These include judicious truncation of the moment equations to form a closed set of equations (see, e.g. Lambropoulis 1967, McQuarrie 1967), and linearization of the master equation for $\rho_n(\tau)$ (see, e.g. Degiorgio and Ghielmetti 1971, Weiss 1972).

### 5.1.2 Emission Into Two Modes

Equations for the various moments may be obtained in the manner outlined in the previous section. Thus, for the moments up to the second:

$$\frac{d\langle n_1\rangle}{d\tau} = \frac{d\langle n_2\rangle}{d\tau} = (N_2 - N_1)\langle n_1 n_2\rangle + N_2\langle n_1\rangle + N_2\langle n_2\rangle + N_2 \qquad (5.18)$$

$$\begin{aligned}\frac{d\langle n_1(n_1-1)\rangle}{d\tau} &= 2(N_2 - N_1)\langle n_1(n_1-1)n_2\rangle + 4N_2\langle n_1 n_2\rangle \\ &\quad + 2N_2\langle n_1(n_1-1)\rangle + 4N_2\langle n_1\rangle\end{aligned} \qquad (5.19a)$$

$$\begin{aligned}\frac{d\langle n_2(n_2-1)\rangle}{d\tau} &= 2(N_2 - N_1)\langle n_1 n_2(n_2-1)\rangle + 4N_2\langle n_1 n_2\rangle \\ &\quad + 2N_2\langle n_2(n_2-1)\rangle + 4N_2\langle n_2\rangle\end{aligned} \qquad (5.19b)$$

$$\frac{d\langle n_1 n_2\rangle}{d\tau} = (N_2-N_1)\langle n_1(n_1-1)n_2\rangle + (N_2-N_1)\langle n_1 n_2(n_2-1)\rangle$$
$$+(5N_2-N_1)\langle n_1 n_2\rangle + N_2\langle n_1(n_1-1)\rangle + N_2\langle n_2(n_2-1)\rangle$$
$$+ 3N_2\langle n_1\rangle + 3N_2\langle n_2\rangle + N_2 \qquad (5.20)$$

Again, the moment equations form a non-closed hierarchy. The crudest approximation we may make is that the two modes are uncorrelated, i.e. $\langle n_1 n_2\rangle \simeq \langle n_1\rangle\langle n_2\rangle$ . This yields the following approximate solution of equation (5.19) for $N_1 \neq N_2$ :

$$\langle n_1(\tau)\rangle \simeq \frac{[\langle n_1(0)\rangle + a + b](a-b) + [\langle n_1(0)\rangle + b - a](a+b)\exp[2(N_2-N_1)a\tau]}{[\langle n_1(0)\rangle + a + b] - [\langle n_1(0)\rangle + b - a]\exp[2(N_2-N_1)a\tau]} \qquad (5.21)$$

where $a = \left[\frac{D^2}{4} + \frac{N_1N_2}{(N_2-N_1)^2}\right]^{\frac{1}{2}}$ , $b = \frac{D}{2} + \frac{N_2}{(N_2-N_1)}$ , $D = \langle n_2(0)\rangle - \langle n_1(0)\rangle$
$\langle n_2(\tau)\rangle$ is given by $\langle n_2(\tau)\rangle = \langle n_1(\tau)\rangle + D$ .

In the case of pure emission, $N_1 = 0$ and $N_2 = N$ , so that (5.21) becomes:

$$\langle n_1(\tau)\rangle \simeq \begin{cases} \dfrac{(D+1)[\langle n_1(0)\rangle + 1]e^{DN\tau} - [\langle n_2(0)\rangle + 1]}{[\langle n_2(0)\rangle + 1] - [\langle n_1(0)\rangle + 1]e^{DN\tau}} , & D \neq 0 \\[2ex] \dfrac{\langle n_1(0)\rangle + [\langle n_1(0)\rangle + 1]N\tau}{1 - [\langle n_1(0)\rangle + 1]N\tau} , & D = 0 \end{cases} \qquad (5.22)$$

These expressions give the correct qualitative behaviour of growth of the intensity in each mode, and include spontaneous emission (as does the original expression (5.21)). Since correlations do build up in time, the expression (5.22). are valid only for short times, and for initially uncorrelated modes. Note that again these approximate expressions become infinite at a finite time.

In the case of pure absorption, $N_1 = N$ and $N_2 = 0$ , and (5.21) becomes:

$$\langle n_1(\tau)\rangle \simeq \begin{cases} \dfrac{D\langle n_1(0)\rangle e^{-DN\tau}}{\langle n_2(0)\rangle - \langle n_1(0)\rangle e^{-DN\tau}} , & D \neq 0 \\[2ex] \dfrac{\langle n_1(0)\rangle}{\langle n_1(0)\rangle N\tau + 1} , & D = 0 \end{cases} \qquad (5.23)$$

with $\langle n_2(\tau)\rangle = \langle n_1(\tau)\rangle + D$ .

These results are exactly those obtained by a classical analysis (McLean 1963, see also Loudon 1973). These solutions are again valid for short times following an initially uncorrelated state.

The powers series expansion method may be used here (c.f. Simaan and Loudon 1975b). Again, the coefficients of the $\tau$ terms in the expansions for $\langle n_1(\tau)\rangle$ , $\langle n_1(n_1-1)\rangle$ , $\langle n_1 n_2\rangle$ and so on are the R.H.S. of the appropriate equations (5.18)-(5.20) evaluated at $\tau = 0$ . The first order approximations for the $g^{(2)}$ are given by equations of the type (5.11) with appropriate mode labelling. Since in most situations the modes will be initially uncorrelated, we obtain:

$$g_{1\,\mathrm{coherent}}^{(2)} \simeq 1 + 2N_2 \frac{[\langle n_2(0)\rangle + 1]}{\langle n_1(0)\rangle}\tau \qquad (5.24)$$

$$g_{1\,\mathrm{chaotic}}^{(2)} \simeq 2 \qquad (5.25)$$

Thus for short times an initially chaotic mode retains its chaotic nature, independently of $N_1$ and $N_2$ . In the case of pure

Erratum: Page 64: Equation (5.26) should read:

$$g_{12}(\tau) = g_{12}(0) + \frac{1}{\langle n_1(0)\rangle\langle n_2(0)\rangle}\left[\langle n_1 n_2\rangle_1 - \langle n_1 n_2\rangle_0\left(\frac{\langle n_1\rangle_1}{\langle n_1(0)\rangle} + \frac{\langle n_2\rangle_1}{\langle n_2(0)\rangle}\right)\right]\tau$$

absorption ( $N_2 = 0$ ) an initially coherent mode will retain its coherent nature for small times. This behaviour is to be expected from the nature of the process involved. Since the interaction takes photons from different modes, we expect the coupled mode properties (such as correlation) to change before the single mode properties. Thus for short times, each mode behaves as if it were in a one-photon process.

The first order approximation for the correlation function

$g_{12}(\tau) = [\langle n_1 n_2\rangle - \langle n_1\rangle\langle n_2\rangle] / \langle n_1\rangle\langle n_2\rangle$ is :

$$g_{12}(\tau) \simeq g_{12}(0) + \frac{1}{\langle n_1(0)\rangle\langle n_2(0)\rangle}\left[\langle n_1 n_2\rangle_1 - \left(\frac{\langle n_1\rangle_1}{\langle n_1(0)\rangle} + \frac{\langle n_2\rangle_1}{\langle n_2(0)\rangle}\right)\right]\tau \qquad (5.26)$$

Thus if both modes are initially independently coherent,

$$g_{12}(\tau) \simeq \frac{1}{\langle n_1(0)\rangle\langle n_2(0)\rangle}\Big[(2N_2 - N_1)\langle n_1(0)\rangle\langle n_2(0)\rangle + N_2\langle n_1(0)\rangle + N_2\langle n_2(0)\rangle + N_2\Big]\tau \qquad (5.27)$$

Hence, as predicted above, the correlation grows immediately, even in the pure absorption case $N_2 = 0$, where $g_{12} \simeq -N_1\tau$ , i.e.: the correlation grows in a negative sense.

If mode 1 is initially chaotic, and mode 2 initially independently coherent, $g_{12}(\tau)$ is the expression (5.27) with the following term added:

$$\frac{1}{\langle n_1(0)\rangle\langle n_2(0)\rangle}\left[(N_2 - N_1)\langle n_1(0)\rangle^2\langle n_2(0)\rangle + N_2\langle n_1(0)\rangle^2\right]\tau \qquad (5.28)$$

If both modes are initially independently chaotic we must add a further term of the form (5.28) with $\langle n_1(0)\rangle$ and $\langle n_2(0)\rangle$ interchanged. Further discussion is given by Simaan and Loudon (1975b).

## Pure Absorption With One Mode Initially Very Intense.

An situation often encountered in absorption experiments is that in which one of the modes is initially very much more intense than the other, say $\langle n_2(0)\rangle \gg \langle n_1(0)\rangle$. Since $\langle n_2(\tau)\rangle - \langle n_1(\tau)\rangle$ is a constant, $\langle n_2(\tau)\rangle \gg \langle n_1(0)\rangle$ for all times. In this case it is possible to derive approximate solutions for the moments from the exact expressions of section (3.2.2) (McNeil and Walls 1974, Simaan and Loudon 1975b).

The expression (3.40) for $\langle n_1(\tau)\rangle$ may be written

$$\langle n_1(\tau)\rangle = \sum_{n_1^0}\sum_{n_2^0} \langle n(n_1^0, n_2^0)\rangle\, P_1(n_1^0)\, P_2(n_2^0) \qquad (5.29)$$

where $P_1$ and $P_2$ are the initial uncorrelated mode distributions and $\langle n(n_1^0, n_2^0)\rangle$ is the mean given by (3.40) for the initial distribution $\rho_{n_1,n_2}(0) = \delta_{n_1,n_1^0}\,\delta_{n_2,n_2^0}$. It is clear that the main contribution to the sums in (5.29) occurs when $P_1$ and $P_2$ are near their maxima, i.e. when $n_1^0 \simeq \langle n_1(0)\rangle$ and $n_2^0 \simeq \langle n_2(0)\rangle$ (assuming $P_1$ and $P_2$ are reasonably peaked distributions). Since $\langle n_2(0)\rangle \gg \langle n_1(0)\rangle$ it is then sufficient to consider only the $n = 1$ term in the expressions for the $A_n^{(\pm)}(\lambda)$. We thus obtain the approximate expression:

$$\langle n_1(\tau)\rangle \simeq \sum_{n_1^0}\sum_{n_2^0} n_1^0 \,\frac{(n_2^0 - n_1^0 + 2)}{(n_2^0 + 1)}\, P_1(n_1^0)\, P_2(n_2^0)\, \exp\left[-(n_2^0+1)\tau\right] \qquad (5.30)$$

$$\simeq \langle n_1(0)\rangle \sum_{n_2^0} P_2(n_2^0) \exp(-n_2^0\tau)$$

We thus obtain an expression for the weak mode mean $\langle n_1(0)\rangle$

which depends on the initial statistics of the intense mode, but is independent of the initial statistics of the weak mode. The intense mode mean $\langle n_2(\tau)\rangle$ is given by $\langle n_2(\tau)\rangle = \langle n_1(\tau)\rangle + \langle n_2(0)\rangle - \langle n_1(0)\rangle$. The sum in (5.30) may be evaluated for the distributions $\rho_2$ usually encountered in practice. Thus if mode 2 is the light from an intense laser beam, $\rho_2(n_2)$ is poisson, and

$$\langle n_1(\tau)\rangle \simeq \langle n_1(0)\rangle \exp[\langle n_2(0)\rangle (e^{-\tau} - 1)] \tag{5.31}$$

If mode 2 has a very sharp initial distribution, so that $\rho_2(n_2) \simeq \delta_{n_2, \langle n_2(0)\rangle}$ , then:

$$\langle n_1(\tau)\rangle \simeq \langle n_1(0)\rangle \exp[-\langle n_2(0)\rangle \tau] \tag{5.32}$$

In this case we have one-photon absorption behaviour; the result is that obtained when the parametric approximation is made for the intense mode.

If mode 2 is light from an intense thermal source, $\rho_2(n_2)$ is geometric, and

$$\langle n_1(\tau)\rangle \simeq \frac{\langle n_1(0)\rangle}{[\langle n_2(0)\rangle(1-e^{-\tau}) + 1]} \tag{5.33}$$

In this case the approximation is expected to be less valid, since $\rho_2(n_2)$ is not peaked around its mean $\langle n_2(0)\rangle$ .

Similar approximate expressions may be obtained for the higher moments (McNeil and Walls 1974, Simaan and Loudon 1975b).

## Exact Solutions for the Case $N_1 = N_2$

As in the single mode case, we may solve the moment equations exactly in the case $N_1 = N_2 = N/2$ , because the coupling which makes the set of equations into an infinite hierarchy vanishes. Thus for the mean numbers:

$$\langle n_1(\tau)\rangle = \langle n_1(0)\rangle e^{N\tau} + \tfrac{1}{2}\left[\langle n_2(0)\rangle - \langle n_1(0)\rangle + 1\right]\left(e^{N\tau} - 1\right) \qquad (5.34a)$$

$$\langle n_2(\tau)\rangle = \langle n_2(0)\rangle e^{N\tau} + \tfrac{1}{2}\left[\langle n_1(0)\rangle - \langle n_2(0)\rangle + 1\right]\left(e^{N\tau} - 1\right) \qquad (5.34b)$$

Again, there is no steady state, in agreement with the results of chapter 4.

The solutions for the second moments are:

$$\begin{bmatrix} \langle n_1 n_2\rangle \\ \langle n_1(n_1-1)\rangle \\ \langle n_2(n_2-1)\rangle \end{bmatrix} = c_1\begin{bmatrix} 0 \\ 1 \\ -1 \end{bmatrix} + c_2\begin{bmatrix} 0 \\ 1 \\ 1 \end{bmatrix} e^{N\tau} + c_3\begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix} e^{3N\tau} + \frac{N\tau}{6}\begin{bmatrix} 1 \\ -2 \\ -2 \end{bmatrix} \qquad (5.35)$$

where

$$c_1 = \tfrac{1}{6}\left[2\langle n_1 n_2\rangle_0 + \langle n_1(n_1-1)\rangle_0 - \langle n_2(n_2-1)\rangle_0 + \langle n_1(0)\rangle + \langle n_2(0)\rangle + 1 - 4D\right]$$

$$c_2 = \tfrac{1}{2}\left[\langle n_1(n_1-1)\rangle_0 - \langle n_2(n_2-1)\rangle_0 - \langle n_1(0)\rangle - \langle n_2(0)\rangle - 1 + 2D\right]$$

$$c_3 = \tfrac{1}{6}\left[4\langle n_1 n_2\rangle_0 + \langle n_1(n_1-1)\rangle_0 + \langle n_2(n_2-1)\rangle_0 + 4\langle n_1(0)\rangle + \langle n_2(0)\rangle + 1\right]$$

$$D = \langle n_2(0)\rangle - \langle n_1(0)\rangle$$

We see explicitly that the $g^{(2)}$ , the normalized fluctuation $\sigma^2/\langle n\rangle^2$ and the correlation $g_{12}$ are all increasing functions of time.

## 5.2 The Raman Effect.

We may obtain moment equations from the master equation in the usual manner. Thus, for themoments up to the second, with $N_1$ and $N_2$ both non zero:

$$\frac{d\langle n_s\rangle}{d\tau} = -\frac{d\langle n_p\rangle}{d\tau} = (N_2-N_1)\langle n_s n_p\rangle + N_1\langle n_p\rangle - N_2\langle n_s\rangle \tag{5.36}$$

$$\frac{d\langle n_s(n_s-1)\rangle}{d\tau} = 2(N_2-N_1)\langle n_s(n_s-1)\langle n_p\rangle + 4N_1\langle n_s n_p\rangle - 2N_2\langle n_s(n_s-1)\rangle \tag{5.37}$$

$$\frac{d\langle n_p(n_p-1)\rangle}{d\tau} = 2(N_2-N_1)\langle n_s n_p(n_p-1)\rangle - 2N_1\langle n_p(n_p-1)\rangle + 4N_2\langle n_s n_p\rangle \tag{5.38}$$

$$\begin{aligned}\frac{d\langle n_s n_p\rangle}{d\tau} = {} & (N_2-N_1)\langle n_s(n_s-1)n_p\rangle + (N_1-N_2)\langle n_s n_p(n_p-1)\rangle \\ & -2N\langle n_s n_p\rangle + N_2\langle n_s(n_s-1)\rangle + N_1\langle n_p(n_p-1)\rangle\end{aligned} \tag{5.39}$$

where $\tau = 2K^{(1,1)}t$.

Making the decoupling approximation $\langle n_s n_p\rangle \simeq \langle n_s\rangle\langle n_p\rangle$ enables us to obtain the following approximate solution of equation (5.36), valid for short times following an initially uncorrelated state:

$$\langle n_s(\tau)\rangle \simeq \frac{[\langle n_s(0)\rangle + a + b](a-b) + [\langle n_s(0)\rangle + b - a](a+b)\,e^{2(N_2-N_1)a\tau}}{[\langle n_s(0)\rangle + a + b] - [\langle n_s(0)\rangle + b - a]\,e^{2(N_2-N_1)a\tau}} \tag{5.40}$$

where $a = \dfrac{[(S+1)^2(N_1-N_2)^2 + 4N_1N_2]^{1/2}}{2(N_2-N_1)}$ , $b = \dfrac{(N_1-N_2)S - (N_1+N_2)}{2(N_2-N_1)}$

and $S = \langle n_s(0)\rangle + \langle n_p(0)\rangle$ .

Since $S = \langle n_s\rangle + \langle n_p\rangle$ is a constant of the motion, $\langle n_p(\tau)\rangle$ is given by $\langle n_p(\tau)\rangle = S - \langle n_s(\tau)\rangle$ .

In the case $N_2 = 0$ , the expression (5.40) reduces to

$$\langle n_s(\tau)\rangle \simeq \frac{S[\langle n_s(0)\rangle + 1]\, e^{(S+1)N\tau} - \langle n_p(0)\rangle}{[\langle n_s(0)\rangle + 1]\, e^{(S+1)N\tau} + \langle n_p(0)\rangle} \tag{5.41}$$

These expressions yield the correct qualitative behaviour of the intensities: the Stokes' intensity builds up from $\langle n_s(0)\rangle$ to $\langle n_s(0)\rangle + \langle n_p(0)\rangle$ as the pump intensity is depleted from $\langle n_p(0)\rangle$ to zero. These should be compared with results obtained using a classical analysis (McLean 1963, Bloembergen 1965, see also Loudon 1973). The result (5.41) allows the build up Stokes radiation directly from the vacuum by amplification of spontaneous emission. Equation (5.41) as a function of time is plotted in figure 10, for $\langle n_s(0)\rangle = 0$ and $\langle n_p(0)\rangle = 10$ .

The power series expansion method may again be used (c.f. Simaan 1975), with the coefficients of the $\tau$ terms being given by the R.H.S. of the appropriate equations (5.36)-(5.39) evaluated at $\tau = 0$ . The first order expressions for the $g^{(2)}$ and the correlation $g_{12} = [\langle n_s n_p\rangle - \langle n_s\rangle\langle n_p\rangle]/\langle n_s\rangle\langle n_p\rangle$ are then given by expressions of the type (5.11) and (5.26) with appropriate mode labelling. In the situation $N_1 = N$ , $N_2 = 0$ we find, for initially uncorrelated modes:

$$g_s^{(2)}(\tau) \simeq g_s^{(2)}(0) + \frac{2\langle n_p(0)\rangle}{\langle n_s(0)\rangle}\left[2 - \frac{\langle n_s(n_s-1)\rangle_0}{\langle n_s(0)\rangle^2}\right] N\tau \tag{5.42}$$

$$g_p^{(2)}(\tau) \simeq g_p^{(2)}(0) \tag{5.43}$$

$$g_{12}(\tau) \simeq \Big[\langle n_p(0)\rangle \Big(1 + \frac{1}{\langle n_s(0)\rangle}\Big)\Big(\frac{\langle n_p(n_p-1)\rangle_0}{\langle n_p(0)\rangle^2}\Big) - \langle n_s(0)\rangle\Big(\frac{\langle n_s(n_s-1)\rangle_0}{\langle n_s(0)\rangle^2} - 1\Big) - 1\Big] N\tau \tag{5.44}$$

Thus $g_p^{(2)}$ remains unaltered for short times independently of the initial state, and $g_s^{(2)}$ remains unaltered if the Stokes' mode is initially chaotic. This is to be expected, since for short times the modes will behave as if they were in the corresponding one-photon processes: the pump mode in one-photon absorption, and the Stokes' mode in one-photon emission. The correlation $g_{12}(\tau)$ grows immediately, independently of the initial states.

The above results are modified if the Stokes' photons are emitted into an initial vacuum, i.e. if $\langle n_s(0)\rangle = 0$. In order to obtain the terms linear in $\tau$ in the $g_s^{(2)}$ and $g_{12}$ power series we must go to higher order terms in the moments' power series. We find:

$$g_s^{(2)} \simeq 2g_p^{(2)}(0) + 2\Big\{\langle n_p(n_p-1)(n_p-2)\rangle_0 - \frac{\langle n_p(n_p-1)\rangle_0^2}{\langle n_p(0)\rangle} - \frac{1}{3}\langle n_p(n_p-1)\rangle_0\Big\} N\tau \tag{5.45}$$

Thus if the pump is initially coherent,

$$g_s^{(2)} \simeq 2 - \frac{2}{3}\langle n_p(0)\rangle^2 N\tau \tag{5.46}$$

and $g_s^{(2)}$ decays immediately. If the pump is initally chaotic,

$$g_s^{(2)} \simeq 4 + 4\langle n_p(0)\rangle^2\big[\langle n_p(0)\rangle - 1/3\big] N\tau \tag{5.47}$$

so that $g_s^{(2)}$ is initially increasing for $\langle n_p(0)\rangle > 1/3$, i.e.

for any practical situation.

$$g_{12}(\tau) \simeq g_p^{(2)}(0) - 1 + \frac{1}{2\langle n_p(0)\rangle^2}\Big[\langle n_p(n_p-1)(n_p-2)\rangle_0 - \frac{\langle n_p(n_p-1)\rangle_0^2}{\langle n_p\rangle_0^2} - \langle n_p(n_p-1)\rangle_0\Big]N\tau \tag{5.48}$$

If the pump is initially coherent,

$$g_{12}(\tau) \simeq -\frac{\langle n_p(0)\rangle}{2} N\tau \tag{5.49}$$

so that $g_{12}$ is initially zero and decays immediately. If the pump is initially chaotic,

$$g_{12}(\tau) \simeq 1 + [\langle n_p(0)\rangle - \tfrac{1}{2}]N\tau \tag{5.50}$$

and $g_{12}$ is initially increasing if $\langle n_p(0)\rangle > \tfrac{1}{2}$, which again will be the normal situation.

Further discussion of the short-time solutions is given by Simaan (1975), and also by Chandra and Prakash (1971).

When the pump mode is initially much more intense than the Stokes' mode (the usual experimental situation) it is possible to obtain from the exact solutions of section (3.3) approximate solutions rather like those for the corresponding situation in two mode two-photon absorption (see Simaan 1975).

## Exact Solutions for the Case $N_1 = N_2$

When $N_1 = N_2 = N/2$ each moment equation becomes uncoupled from the higher moments and it is possible to solve the equations exactly. Thus for the mean numbers:

$$\langle n_s(\tau)\rangle = \langle n_s(0)\rangle e^{-N\tau} + \tfrac{1}{2}[\langle n_s(0)\rangle + \langle n_p(0)\rangle](1-e^{-N\tau}) \qquad (5.51\,a)$$

$$\langle n_p(\tau)\rangle = \langle n_p(0)\rangle e^{-N\tau} + \tfrac{1}{2}[\langle n_s(0)\rangle + \langle n_p(0)\rangle](1-e^{-N\tau}) \qquad (5.51\,b)$$

In this case the balance of emission and absorption yields the steady state $\langle n_s(\infty)\rangle = \langle n_p(\infty)\rangle = \tfrac{1}{2}[\langle n_s(0)\rangle + \langle n_p(0)\rangle]$.

The second moments are:

$$\begin{bmatrix} \langle n_s(n_s-1)\rangle \\ \langle n_p(n_p-1)\rangle \\ \langle n_s n_p\rangle \end{bmatrix} = c_1 \begin{bmatrix} 2 \\ 2 \\ 1 \end{bmatrix} + c_2 \begin{bmatrix} 1 \\ -1 \\ 0 \end{bmatrix} e^{-N\tau} + c_3 \begin{bmatrix} 1 \\ 1 \\ -1 \end{bmatrix} e^{-3N\tau} \qquad (5.52)$$

where
$$c_1 = \tfrac{1}{6}[\langle n_s(n_s-1)\rangle_0 + \langle n_p(n_p-1)\rangle_0 + 2\langle n_s n_p\rangle_0],$$
$$c_2 = \tfrac{1}{2}[\langle n_s(n_s-1)\rangle_0 - \langle n_p(n_p-1)\rangle_0]$$
$$c_3 = \tfrac{1}{6}[\langle n_s(n_s-1)\rangle_0 + \langle n_p(n_p-1)\rangle_0 - 4\langle n_s n_p\rangle_0].$$

## CHAPTER 6 INTRODUCTION TO PART 2

There is currently considerable interest in the behaviour of systems far from thermodynamic equilibrium, particularly in the steady states of such non-equilibrium systems. In order that a system be maintained far from equilibrium it must be an open system. That is, the system is able to exchange matter or energy with its surroundings, so that it is driven irreversibly far from equilibrium (assuming the "sources" and "sinks" comprising the surroundings are not in equilibrium amongst themselves). Steady state is reached when the inflowing matter and energy balances the outflow. An obvious example of an open system in nature is the earth's atmosphere, with the sun and the earth's surface being the main components of its surroundings. An example of an open system in the laboratory is the electric field in a laser oscillator cavity. In this case the "surroundings" are the lasing atoms by which photons are created in the cavity, and the exterior of the cavity, to which photons are lost through the partially transmitting mirror at one end of the cavity. In the theoretical analysis of open systems, the system surroundings are generally idealized to be large reservoirs acting as sources and sinks of energy and matter, and there is a continual flow through the system from sources to sinks.

Of particular interest at present are open systems which are non-linear, that is, open systems whose behaviour governing equations are in some way non-linear. In the absence of any "pumping

Erratum: Page 74 line 22: "Progogine" should read "Prigogine".

forces" (i.e: source reservoirs), a system evolves under the dissipative effect of any sink reservoir present into a state of thermodynamic equilibrium with this reservoir. A pumping force will now amplify small fluctuations around this equilibrium and drive the system away from equilibrium. If the pump force is small, the now non-equilibrium behaviour of the system is simply a linear extension of the equilibrium behaviour, and the resulting steady states of the system are said to lie on the "thermodynamic branch" (Glansdorff and Prigogine 1971, Graham 1973). In the case of a linear system, the steady states remain on the thermodynamic branch for all strengths of the pumping force.

However, in the case of a non-linear system, it generally happens that there exists a critical pumping strength, above which the system develops multiple steady states. (Rashevsky 1960, Edelstein 1970, Glansdorff and Prigogine 1971, Nicolis 1971, Nitzan et al. 1974), and the steady states on the thermodynamic branch become unstable. Large fluctuations which result from the instability are amplified by the pumping force and the system is driven onto a new, non-thermodynamic branch (Glansdorff and Prigogine 1971, Graham 1973). This is accompanied by an abrupt change in the system's properties. This new type of order has been termed "order through fluctuations" (Glansdorff and Progogine 1971, Prigogine and Nicolis 1971), and the ordered structures appearing past the instability have been termed "dissipative structures" (ibid.). Such dissipative structures exhibit coherent space-time behaviour in contrast to the chaotic behaviour of the system near thermal equilibrium. Dissipative structures have been observed experimentally in chemically reacting systems (Zhabotinsky 1964, Busse 1969, Herschowitz-Kaufman 1970, Winfree 1974).

One feature of the behaviour of non-linear systems far from equilibrium which attracted great interest from physicists was the close analogy between thebehaviour of certain of these systems around their point of instability and the behaviour of certain well-known thermodynamic equilibrium systems undergoing phase transitions. An example of a non-equilibrium phase transition occurs in the laser oscillator, and this has been analysed in some detail (Graham and Haken 1970, DeGiorgio and Scully 1970, Grossman and Ritcher 1971, Dohm 1972). Further examples are the parametric oscillator (Graham 1973), the driven harmonic oscillator (Drosdziok 1973), and the tunnel diode (Landauer and Woo 1971).

Theoretical studies of chemically reacting systems also provide examples of far from equilibrium phase transition behaviour. A chemically reacting system may be made to exhibit far from equilibrium behaviour by taking the initial and final reactants to form respectively source and sink reservoirs. The behaviour of intermediate species under interaction with these reservoirs is then that of an open system. A number of theoretical studies have been made of reactions which behave like first or second order phase transitions. Deterministic analyses have been given by Glansdorff and Prigogine (1971), Schlögl (1972) and Nitzan et al. (1974). Stochastic analyses have been given by McNeil and Walls (1974), Turner (1974), Nitzan et al. (1974), Matheson et al.(1975), Prigogine et al. (1975), Gardiner et al. (1976).

As well as temporal evolution of an open system under the action of its surroundings there may also occur spatial variation within the system, due to diffusion of component species at a rate comparable to the rate of their reactions. This is important in the formation of dissipative structures with spatial variation. Various authors have presented deterministic analyses of chemically reacting systems including spatial dependence (Schlögl 1972, Ortoleva and Ross 1974, Nitzan et al.1974).

There has been much interest recently in extending stochastic analytic methods to allow for the spatial variation of components in a chemical system (Kitahara 1974, Nitzan et al. 1974, Nicolis et al. 1974a,b, Kuramoto 1974, Malek-Mansour and Nicolis 1975, Gardiner et al. 1975, 1976, Lemarchand and Nicolis 1976). A stochastic approach is especially useful because it allows the calculation of such statistical quantities as mean fluctuations, temporal correlations, and spatial correlations. From the last two mentioned we may obtain correlation times and correlation lengths which measure the extent of respectively temporal and spatial correlations in the system in question. Knowledge of these two quantities enable us to make a very close analogy indeed to phase transition-like behaviour.

A related problem in the study of spatial behaviour in chemically reacting systems is the nature of, and the difference between, local and global fluctuations in such systems. Whether or not global fluctuations should be poissonian had already been the subject of vigorous discussion (Nicolis and Babloyantz 1969, Nicolis and Prigogine 1971, Nicolis 1972, Kuramoto 1973, Nicolis et al. 1974a). Work on the nature of local fluctuations began with Nicolis et al. (1974a,b) who use a bivariate probability distribution describing the numbers of reactant molecules in some fixed but arbitrary small volume of the system and the number in the remainder of the system. By ignoring the correlations between the two, they obtain a non-linear master equation which yields fluctuations that are poissonian in nature in small volumes, and non-poisson globally. Similar conclusions have been found by other workers whose results are slightly modified because they retain spatial correlations in their analyses. (Kuramoto 1974, Gardiner et al. 1975, 1976, Van Kampen 1976, Lemarchand and Nicolis 1976).

In chapter seven of this thesis we examine a simple linear non-equilibrium chemical system, allowing for spatial dependence. Following Kitahara (1974), the possibility of spatial dependence is taken into account by dividing the system's volume into a number of small volume cells, and allowing diffusion to take place between the cells, as well as the reaction proceeding in each cell. We then consider the multi-variate probability distribution function which describes the number of reactant molecules in each cell. The master equation governing the behaviour of this distribution function is given, and exact time-dependent solutions for the mean number, fluctuations and correlations are presented, together with analysis of their behaviour.

In chapter eight we consider a non-linear non-equilibrium chemical reaction which has been shown by deterministic analyses to undergo behaviour analogous to that of a second order phase transition. In the first part of this chapter the system is analysed in a global sense, and an exact solution for the steady state distribution function is presented and its behaviour analysed. In the second part we make a local stochastic analysis of the system, obtaining approximate solutions for the mean and correlation functions (temporal and spatial). From the correlation functions we obtain the system's correlation length and correlation time. We then compare the behaviour of this system with the behaviour of a thermodynamic equilibrium system undergoing a second order phase transition.

Parts of chapter eight have already appeared in print (McNeil and Walls 1974, Gardiner et al. 1976).

# CHAPTER 7 CORRELATIONS AND LOCAL FLUCTUATIONS IN A LINEAR CHEMICAL SYSTEM

In this chapter we shall consider the development of correlations and local fluctuations in a simple linear chemically reacting system. By "linear" we mean that in any reaction occuring in the system, say $A+B+\cdots \rightleftharpoons X+Y+\cdots$ the reactant of interest appears only once on either side of this equation. An equivalent definition is given by Gardiner et al. (1976). We shall consider the following particular reaction:

$$A \xrightarrow{k_1} X \xrightarrow{k_2} B \qquad (7.1)$$

in which $A$ is converted to $B$ via the intermediate $X$. $k_1$ and $k_2$ are the rate constants which occur in the deterministic equations governing (7.1). We take the initial and final reactants $A$ and $B$ to form large, essentially unperturbed reservoirs which act respectively as source and sink for $X$, and we consider the behaviour of the intermediate $X$. It should be noted that this example can be regarded as a special case of the linear isomerization studied in section 2 of Gardiner et al. (1976).

The global stochastic analysis of (7.1) is well-known: we consider an ensemble of identical systems in which (7.1) takes place, and let the number of species $X$ be a random variable taking values $x$. In the global analysis, this is the number in the whole system. The master equation governing the time behaviour of the probability distribution $P(x,t)$ of $X$ is then (see, e.g., Mcquarrie 1967, Glansdorff and Prigogine 1971):

$$\frac{dP(x,t)}{dt} = k_1A[P(x-1,t) - P(x,t)] + k_2[(x+1)P(x+1,t) - xP(x,t)] \quad (7.2)$$

where $A$ is the number of species $A$ in the system. The solution for the generating function $F(s,t) = \sum_{x=0}^{\infty} s^x P(x,t)$ is:

$$F(s,t) = \exp\left[\frac{k_1A}{k_2}(1-e^{-k_2t})(s-1)\right] F_0\{e^{-k_2t}(s-1)+1\} \quad (7.3)$$

where $F_0(y)$ is the generating function at $t=0$. The steady state $F(s,t=\infty) = \exp\left[\frac{k_1A}{k_2}(s-1)\right]$ corresponds to the poisson distribution:

$$P(x,t=\infty) = \exp\left[-\frac{k_1A}{k_2}\right] \frac{(k_1A/k_2)^x}{x!} \quad (7.4)$$

(Glansdorff and Prigogine 1971). Thus global fluctuations in the steady state are poisonian:

$$\overline{\delta X^2} = \overline{X} = \frac{k_1A}{k_2} \quad (7.5)$$

We shall now make a local analysis of (7.1), following the method of Kitahara (1974):

The system's volume $V$ is divided into $N$ equal cells, with each cell large enough to allow a stochastic analysis (that is, it may contain up to an "infinite" number of $X$ ), but small enough that the concentration of $X$ across the cell is essentially uniform. The system is now described by the multivariate distribution function $P(x_1,x_2,\dots,x_N;t) = P(\underset{\sim}{x};t)$ where the random variable $X_i$ is the number of species $X$ in cell $i$ .

The number of $X$ in a cell (and hence the probability distribution $P(\underset{\sim}{x};t)$ ) is altered in two ways. The first is by chemical reaction. If the concentration across a cell is uniform, the contribution to $\frac{dP}{dt}$ from the reaction occurring in cell $i$ is simply the R.H.S. of equation (7.2) with $P(x), P(x\pm1)$, and $x$ replaced by $P(\underset{\sim}{x})$, $P(x_i\pm1,\hat{\underset{\sim}{x}})$ and $x_i$ respectively, and with $A$ now the number of species $A$ in one cell (for simplicity assumed to be the same for all cells - i.e. $A$ is homogeneous). Here $\hat{\underset{\sim}{x}}$ means all those $x_j$ not explicitly referred to are unchanged in value. The second way in which $X_i$ is altered is by the diffusion of from or to other cells. This is the tendency of the system to "smooth out" spatial inhomogeneities which may arise locally as the reactions proceed. If the cell $i$ to cell $j$ transition probability per unit time per $X$ molecule is $d_{ij}$ , the master equation governing $P(\underset{\sim}{x},t)$ including both diffusion and the chemical reactions is (c.f. Kitahara, 1974).

$$\frac{dP(\underset{\sim}{x},t)}{dt} = \sum_i\sum_j d_{ij}\left\{(x_i+1)P(x_i+1, x_j-1, \hat{\underset{\sim}{x}}) - x_i P(\underset{\sim}{x})\right\} + \sum_i \left\{k_1 A\left[P(x_i-1,\hat{\underset{\sim}{x}}) - P(\underset{\sim}{x})\right] + k_2\left[(x_i+1)P(x_i+1,\hat{\underset{\sim}{x}}) - x_i P(\underset{\sim}{x})\right]\right\} \tag{7.6}$$

We may define a multidimensional generating function in analogy to the one dimensional one:

$$F(s_1,s_2,\ldots,s_N;t) = \sum_{x_1=0}^{\infty}\sum_{x_2=0}^{\infty}\cdots\sum_{x_N=0}^{\infty}\left[\prod_{i=1}^{N} s_i^{x_i}\right] P(\underset{\sim}{x};t) \tag{7.7}$$

Since $P(\underset{\sim}{x};t)$ satisfies (7.6), $F(\underset{\sim}{s};t)$ will satisfy:

$$\frac{\partial F}{\partial t} = \sum_i\sum_j d_{ij}(s_i-s_j)\frac{\partial F}{\partial s_i} + \sum_{i=1}^{N}(1-s_i)\left(k_2\frac{\partial F}{\partial s_i} - k_1 A F\right) \tag{7.8}$$

Equation (7.8) may be solved in a manner similar to that used by Darvey and Staff (1966) to obtain:

$$F(\underset{\sim}{s};t) = \exp\left\{\sum_{i=1}^{N} \frac{k_1 A}{k_2}\left[s_i - 1 + \sum_{j=1}^{N} \lambda_{ij}^{-1} z_j\right]\right\} F_0(\underset{\sim}{\omega}) \qquad (7.9)$$

where $\omega_i = 1 + \sum_k \lambda_{ik}^{-1} z_k$ , $z_k = e^{-\mu_k t} \sum_{i=1}^{N} \lambda_{ki}(s_i - 1)$

$(\lambda_{ij})$ is the matrix of the $N$ eigenvectors of

$$\begin{pmatrix} -\sum_j d_{1j} - k_2 & d_{21} & d_{31} & \cdots & d_{N1} \\ \vdots & & & & \\ d_{1N} & d_{2N} & \cdots & \cdots & -\sum_j d_{Nj} - k_2 \end{pmatrix} \underset{\sim}{\lambda} = \mu \underset{\sim}{\lambda} \qquad (7.10)$$

and the $\mu_k$ are the associated $N$ eigenvalues. $F_0(\underset{\sim}{y})$ is the generating function at $t = 0$ .

## 7.1 The Steady State.

The steady state of (7.9) is particularly simple. In the limit $t \to \infty$, $F(\underset{\sim}{s};t)$ becomes

$$F(\underset{\sim}{s};t=\infty) = \prod_{i=1}^{N} \exp\left[\frac{k_1 A}{k_2}(s_i - 1)\right] \qquad (7.11)$$

Thus in the steady state there is no correlation between cells, and the distribution in each cell is poisson with mean $\overline{X_i} = \frac{k_1 A}{k_2} = \overline{\delta X^2}$

$$P(\underset{\sim}{x};t=\infty) = \prod_{i=1}^{N} \exp\left(-\frac{k_1 A}{k_2}\right) \frac{(k_1 A/k_2)^{x_i}}{x_i!} \qquad (7.12)$$

Thus in the steady state it is valid to ignore correlations between the cells (c.f. Kitahara 1974, Nicolis et al. 1974a,b), and fluctuations are poissonian. In the case of a nonlinear chemical reaction, this will no longer be true (see, e.g. Gardiner et al. 1976).

## 7.2 Transient Behaviour

We now consider correlations and fluctuations in the time dependent behaviour of the system. For correlations to be absent, the probability distribution must factorize: $P(\underset{\sim}{x};t) = \prod_{i=1}^{N} P_i(x_i,t)$ , or equivalently, the generating function must factorize: $F(\underset{\sim}{s},t) = \prod_{i=1}^{N} F_i(s_i,t)$ . As (7.9) shows, this is in general not true. Since the exponential terms in (7.9) factorize, the factorization properties of $F(\underset{\sim}{s};t)$ depend on the factorization properties of $f_0(\underset{\sim}{s})$ ; i.e. on the correlations in the initial distribution. Now it is not sufficient that the initial distribution simply have no correlations, because even though this will mean $f_0(\underset{\sim}{\omega})$ factorizes into $\prod_{i=1}^{N} f_{0_i}(\omega_i)$ , the arguments $\omega_k$ are still linear combinations of the $s_i$ . Thus in order that $f_0(\underset{\sim}{\omega})$ factorizes into separate $s_i$ terms, the $f_{0_i}(\omega_i)$ must also be exponential functions. Thus for non correlated transient behaviour, $f_0(\underset{\sim}{s})$ must be of the form:

$$f_0(\underset{\sim}{s}) = \prod_{i=1}^{N} \exp[\langle x_i(0)\rangle (s_i - 1)] \tag{7.13}$$

where the $\langle x_i(0)\rangle$ are arbitary initial cell means, and the normalization factors $e^{-\langle x_i(0)\rangle}$ have been included. Equation (7.13) is the generating function for uncorrelated poisson distributions with means $\langle x_i(0)\rangle$ . We thus have the result: the system (7.1) has noncorrelated transient behaviour if and only if the system has no correlations initially and each cell distribution is initially poisson. It is not sufficient that there simply be no initial correlations (c.f. Gardiner et al. 1976). With the initial distribution given by (7.13), the generating function is:

$$F(\underset{\sim}{s};t) = \prod_{i=1}^{N} \exp[\langle x_i(t)\rangle(s_i-1)] \qquad (7.14)$$

where the time dependent mean $\langle x_i(t)\rangle$ is given by $\left[\frac{\partial F}{\partial s_i}\right]_{\underset{\sim}{s}=\underset{\sim}{1}}$, i.e.

$$\langle \rho_i(t)\rangle = \frac{\langle x_i(t)\rangle}{V} = \frac{k_1[A]}{k_2}\Big(1-\sum_{\ell}\sum_{k}\lambda_{\ell k}\lambda_{ki}^{-1}e^{-\mu_k t}\Big) + \sum_{\ell}\sum_{k}\lambda_{\ell k}\lambda_{ki}^{-1}e^{-\mu_k t}\langle x_\ell(0)\rangle \qquad (7.15)$$

Thus as well as remaining uncorrelated, the system's cell distributions remain poisson.

It is interesting to compare with this the results obtained using the nonlinear master equation of Kitahara (1974) and Nicolis et al. (1974a,b) obtained by neglecting spatial correlations (and assuming spatial homogeneity). The equation for the generating function of a single cell is:

$$\frac{\partial F(s,t)}{\partial t} = D(1-s)\Big[\frac{\partial F}{\partial s} - \langle x\rangle F\Big] + (1-s)\Big[k_2\frac{\partial F}{\partial s} - k_1 A F\Big] \qquad (7.16)$$

where $D = \sum_j d_{ij}$ ( $j$ summation is over cells adjacent to $i$ ) is a measure of decay through diffusion (Kitahara 1974), and $\langle x\rangle = \left[\frac{\partial F}{\partial s}\right]_{s=1}$ is the time dependent mean (this term makes the equation (7.16) nonlinear). Equation (7.16) has the solution

$$F(\underset{\sim}{s};t) = \exp\Big[(s-1)\Big\{1 - \frac{D\langle x\rangle + k_1 A}{D+k_2}e^{-(D+k_2)t}\Big] \times \qquad (7.17)$$

$$\times F_0\big[1+(s-1)e^{-(D+k_2)t}\big]$$

where $F_0(y)$ is the generating function at $t=0$. Since $\langle x\rangle = \left[\frac{\partial F}{\partial s}\right]_{s=1}$ we may obtain $\langle x\rangle$ self consistently from (7.17). This result agrees with the above analysis only when correlations do not exist; i.e. only when the initial cell distributions are independently poisson. In this case (7.17) remains poisson, with mean

$$\langle\rho(t)\rangle = \frac{\langle x(t)\rangle}{V} = \langle\rho(0)\rangle e^{-k_2 t} + \frac{k_1[A]}{k_2}\left(1-e^{-k_2 t}\right) \qquad (7.18)$$

## 7.3 Arbitary Initial Conditions.

In the linear reaction, the cell means $\langle x_i(t)\rangle$ are independent of the initial statistics, so that the $\langle x_i(t)\rangle$ are given by equation (7.15) for any initial distribution.

The intercell correlation is given by $\langle x_i, x_j\rangle = \langle x_i x_j\rangle - \langle x_i\rangle\langle x_j\rangle$. We shall consider the associated function $\hat{g}_{ij} = \langle x_i, x_j\rangle - \delta_{ij}\langle x_i\rangle = \left[\frac{\partial^2 F}{\partial s_i \partial s_j}\right]_{\underline{s}=1} - \langle x_i\rangle\langle x_j\rangle$ From (7.9) this is:

$$\tilde{g}_{ij}(t) = \sum_m \sum_n \phi_{mi}(t)\,\phi_{nj}(t)\,\hat{g}_{mn}(0) \qquad (7.19)$$

where $\phi_{ij}(t) = \sum_k \lambda^{-1}_{ik}\lambda_{kj}e^{-\mu_k t}$.

The quantity $\tilde{g}_{ij}(t)$ is a measure of the deviation from uncorrelated poissonian behaviour; it is exactly zero for uncorrelated poissonian fluctuations.

It should be noted that when the system is of infinite volume ( $N\to\infty$), the equations for the mean, correlations and so on may be readily solved by Fourier series methods. The solutions are the Fourier series analogues of the solutions presented in the following section, which are obtained by Fourier transform methods.

## 7.4 The Continuum Approximation

It is instructive to examine the behaviour of the mean $\langle \varrho \rangle$ and correlation function $g/V^2$ in the limit when these become continuous variables in $\underset{\sim}{r}$ space. The equations for these quantities may be readily obtained from the generating function equation (7.8). The mean $\langle x_k \rangle$ is given by $\langle x_k \rangle = \left[\frac{\partial F}{\partial s_k}\right]_{\underset{\sim}{s}=\underset{\sim}{1}}$ and thus obeys

$$\frac{\partial \langle x_k \rangle}{\partial t} = \sum_i \sum_j d_{ij} \left[ \delta_{ik} \langle x_i \rangle - \delta_{jk} \langle x_k \rangle \right] - k_2 \langle x_k \rangle + k_1 A \qquad (7.20)$$

Dividing by $V$ , the cell volume and taking the limit $\ell$ (cell dimension) ⟶ mean free path between collisions yields the continuum limit equation for $\langle \varrho(\underset{\sim}{r}) \rangle = \langle x(\underset{\sim}{r}_k) \rangle / V$ :

$$\frac{\partial \langle \varrho \rangle}{\partial t} = D \nabla^2 \langle \varrho \rangle - k_2 \langle \varrho \rangle + k_1 [A] \qquad (7.21)$$

where $D = \lim_{\ell \to m.f.p.} d/\ell^2$ is Fick's diffusion constant, and $d$ is the value of $d_{ij}$ for $i$ and $j$ adjacent cells (we assume an isotropic medium). Equation (7.21) has the solution (for an infinite volume system):

$$\langle \varrho(\underset{\sim}{r}, t) \rangle = \frac{k_1 [A]}{k_2} (1 - e^{-k_2 t}) + \\ + e^{-k_2 t} \frac{1}{(4\pi D t)^{3/2}} \int d^3 \underset{\sim}{r}' \langle \varrho(\underset{\sim}{r}', t=0) \rangle . e^{-|\underset{\sim}{r} - \underset{\sim}{r}'|^2 / 4Dt} \qquad (7.22)$$

This consists of a purely chemical part, plus a diffusive part modified by the chemical decay term $e^{-k_2 t}$. If the system is initially homogeneous, $\langle \rho(\underline{r}', t=0)\rangle = \langle \rho \rangle_0$, and

$$\langle \rho(\underline{r},t)\rangle = \frac{k_1[A]}{k_2}(1-e^{-k_2 t}) + \langle \rho \rangle_0 e^{-k_2 t} \tag{7.23}$$

which agrees with the results of the previous sections.

Consider now the correlation function $g_{ij} = \langle x_i x_j\rangle - \delta_{ij}\langle x_i\rangle$ $= \left[\frac{\partial f}{\partial s_i \partial s_j}\right]_{\underline{s}=\underline{1}}$. In the continuum limit this quantity obeys the equation

$$\frac{\partial g(\underline{r},\underline{r}')}{\partial t} = D(\nabla_{\underline{r}}^2 + \nabla_{\underline{r}'}^2) g - 2k_2 g(\underline{r},\underline{r}') + k_1[A]\{\langle \rho(\underline{r})\rangle + \langle \rho(\underline{r}')\rangle\} \tag{7.24}$$

where $g(\underline{r},\underline{r}') = \lim\limits_{l \to m.f.p.} g_{ij}/V^2$.

If $\langle \rho(\underline{r})\rangle$ is initially homogeneous, it will remain homogeneous. In this case, (7.24) implies that $g(\underline{r},\underline{r}',t)$ will be a function of $\underline{r}-\underline{r}'$ and $t$ only, and the function $\hat{g}(\underline{r},t) = \langle \rho(\underline{r}), \rho(0)\rangle - \delta(\underline{r})\langle \rho(0)\rangle$ obeys the equation

$$\frac{\partial \hat{g}(\underline{r},t)}{\partial t} = 2D\nabla^2 \hat{g}(\underline{r},t) - 2k_2 \hat{g}(\underline{r},t) \tag{7.25}$$

This has the solution

$$\tilde{g}(\underline{r},t) = e^{-k_2 t} \frac{1}{(4\pi D t)^{3/2}} \int d^3\underline{r}'\, \hat{g}(\underline{r},t=0)\, e^{-|\underline{r}-\underline{r}'|^2/4Dt} \tag{7.26}$$

which is typical diffusion behaviour, modified by the chemical decay term. Equation (7.26) is the infinite system, continuum analogue of equation (7.19). It is easy to see how the correlations depend on the initial distribution. If the system is initially correlated then obviously there are time dependent correlations. If the system is initially uncorrelated, $\hat{g}(\underline{r},t=0) = \delta(\underline{r})[\sigma^2(\underline{r},t=0) - \langle\rho\rangle_0]$ where $\sigma^2$ is the single cell variance, and (7.26) yields

$$\hat{g}(\underline{r},t) = e^{-k_2 t} \quad \frac{\sigma_0^2 - \langle\rho\rangle_0}{(4\pi D t)^{3/2}} \; e^{-r^2/4Dt} \tag{7.27}$$

Thus correlations build up immediately, unless $\sigma_0^2 = \langle\rho\rangle_0$ , i.e. unless the initial single cell (or local) distribution are poissonian.

Further discussion, along with generalizations, is given in the work by Gardiner et al. (1976).

# CHAPTER 8 GLOBAL AND LOCAL ANALYSIS OF A NONEQUILIBRIUM SECOND-ORDER PHASE TRANSITION.

We shall consider the following nonlinear chemical reaction scheme, which consists of one reaction in which an intermediate $X$ is produced linearly, and one reaction in which $X$ is produced autocatalytically. Allowing the reverse reaction in this second reaction introduces nonlinearity to the system.

$$\begin{aligned} B + X &\underset{k_3}{\overset{k_1}{\rightleftharpoons}} C \\ A + X &\underset{k_4}{\overset{k_2}{\rightleftharpoons}} 2X \end{aligned} \qquad (8.1)$$

The $k_i$ are the normal deterministic rate constants, and the species $A$ , $B$ and $C$ are assumed to be in excess so that they form large, essentially unperturbed source and sink reservoirs. We shall be interested in the behaviour of the intermediate species $X$ .

A deterministic analysis of this reaction scheme has been given by Schögl (1972), and a similar scheme has also been treated deterministically by Nitzan et al. (1974). In the absence of spatial dependence, the deterministic equation for the concentration $[X]$ of $X$ is:

$$\frac{d[X]}{dt} = -\delta[X]^2 + (K_2 - K_1)[X] + \beta K_2 \qquad (8.2)$$

where

$$K_1 = k_1[B] \qquad K_2 = k_2[A]$$

$$\beta K_2 = k_3[C] \qquad \delta = k_4$$

In the steady state the R.H.S. of (8.2) is zero, and for

$\beta \neq 0$ there is only one physically meaningful solution for $[X]$, for all physical values of the parameters $K_1$, $K_2$, $\delta$. If, however, the back reaction $C \rightarrow X + B$ does not occur, so that $\beta = 0$, we find the following steady state behaviour:

$$[X]_{s.s.} = \begin{cases} 0 & , K_2 \leq K_1 \\ 0 \text{ or } \dfrac{K_2 - K_1}{\delta} & , K_2 > K_1 \end{cases} \tag{8.3}$$

i.e: as $K_2$ is increased from zero, there is a critical point $K_2 = K_1$, above which the steady state solution for the concentration of $X$ becomes multiple valued. This already begins to resemble the phase transition-like behaviour mentioned in chapter six. We may increase the analogy by considering the stability of the solutions (8.3). We make a small perturbation $\varepsilon$ to the state concentration $[X]_{s.s.}$, and examine the behaviour of this perturbation. Since $[X] = [X]_{s.s.} + \varepsilon$ obeys the equation (8.2) and it is assumed that $\varepsilon \ll [X]_{s.s.}$, we find

$$\varepsilon \propto e^{-t/\tau_R} \tag{8.4}$$

where the regression time $\tau_R$ is

$$\tau_R = -\left[(k_2 - k_1) - 2\delta [X]_{s.s.}\right]^{-1} \tag{8.5}$$

The regression time is a measure of the time to return or otherwise to the unperturbed steady state, so it is a measure of the stability of the unperturbed state. When $K_2 < K_1$, $[X]_{s.s.}$ is 0, so that $\tau_R = (k_1 - k_2)^{-1}$ which is positive, and the perturbation thus decays away. Thus for $K_2 < K_1$, the state $[X]_{s.s.} = 0$ is stable. When $K_2 = K_1$, $\tau_R = \infty$, so that the perturbation does not decay; the system is now only marginally stable. When $K_2 > K_1$, the solution $[X]_{s.s.} = 0$ yields $\tau_R = (K_1 - K_2)^{-1}$, which is now negative, so that the perturbation grows rather than decays. The system is obviously unstable in this case. On the other hand, $[X]_{s.s.} = \frac{K_2 - K_1}{\delta}$ yields $\tau_R = K_2 - K_1$, which is positive. This solution is thus stable, and will be the steady state adopted by the system when $K_2 > K_1$. In the terminology of chapter six, the system is driven onto a new branch past the point of instability $K_2 = K_1$. Because $K_2$ is a measure of the source which produces $X$, it is for this system the pumping parameter mentioned in chapter six. Note that although $\beta$ is also a measure of production of $X$, its production of $X$ is in a chaotic manner, rather than the coherent autocatalytic or stimulated production represented by $K_2$. In fact, as the above analysis shows, the chaotic production represented by $\beta$ must be removed in order that the stimulated production be allowed to induce the co-operative behaviour leading to the transition.

It should be noted that upon insertion of the stable solution into (8.5) we obtain for the regression time

$$\tau_R = |K_2 - K_1|^{-1} \tag{8.6}$$

Thus the regression time diverges as $|K_2 - K_1|^{-1}$ at the unstable, or critical point $K_2 = K_1$.

The behaviour of the concentration $[X]_{s.s.}$ and its regression time $\tau$ is closely analogous to the behaviour of the order parameter in a system which undergoes a classical equilibrium second-order phase transition (for example the magnetization in a feromagnetic system). In the present case, the situation is obviously a nonequilibrium one, since in general the two reactions in (8.1) will not be separately in equilibrium; there is a physical flow of $X$ through the system.

## 8.1 Non Space-Dependent Stochastic Analysis.

By applying a stochastic analysis to the system (8.1) we may introduce fluctuations of species number in a natural way. In this section we are interested in studying $P(x,t)$ the probability there are a total of $x$ molecules of species $X$ in the whole system at time $t$ ; we shall not consider spatial dependence. Non space-dependent stochastic analyses of systems similar to (8.1) have been given by McNeil and Walls (1974), who use a master equation method, and Nitzan et al. (1974) who use a Langevin equation approach. Here we shall use a master equation approach to examine the behaviour of the probability function $P(x,t)$.

Using standard techniques (see, e.g. McQuarrie 1967, Glansdorff and Prigogine 1971) we obtain the following Markovian master equation for $P(x,t)$ :

$$\begin{aligned}\frac{dP(x,t)}{dt} &= K_1[(x+1)P(x+1) - xP(x)] + \beta K_2 V[P(x-1) - P(x)] \\ &\quad + K_2[(x-1)P(x-1) - xP(x)] + \frac{\delta}{V}[x(x+1)P(x+1) - (x-1)xP(x)] \qquad (8.7)\end{aligned}$$

where $K_1, K_2, \beta, \delta$ are as defined following equation (8.2), and $V$ is the physical volume of the system.

We shall now consider the steady state, for which $\frac{dP(x,t)}{dt} = 0$ , so that the R.H.S. of (8.7) = 0. For this system detailed balancing holds in the steady state, so that setting the R.H.S. of equation (8.7) = 0 is equivalent to the two equations

$$[K_1(x+1) + \frac{\delta}{V}(x+1)x]\,P(x+1) = [K_2\beta V + K_2 x]\,P(x)$$

$$[K_1 x + \frac{\delta}{V}\,x(x-1)]\,P(x) = [K_2\beta V + K_2(x-1)]\,P(x-1) \qquad (8.8)$$

These yield for $P(x)$ :

$$P(x) = \frac{P(0)}{x!}\prod_{l=1}^{x}\frac{[K_2\beta V + K_2(l-1)]}{[K_1 + \frac{\delta}{V}(l-1)]} \qquad (8.9)$$

where $P(0) = [{}_1F_1(\beta V, \frac{K_1}{\delta}V; \frac{K_2}{\delta}V)]^{-1}$, and ${}_1F_1$ is the confluent hypergeometric function. Alternatively, the generating function $F(s) = \sum_{x=0}^{\infty} s^x P(x)$ is:

$$F(s) = \frac{{}_1F_1(\beta V, \frac{K_1}{\delta}V; \frac{K_2}{\delta}Vs)}{{}_1F_1(\beta V, \frac{K_1}{\delta}V; \frac{K_2}{\delta}V)} \qquad (8.10)$$

In order to obtain the phase transition-like behaviour found by Schlogl we must consider the limit $\beta \to 0$ . However, setting $\beta = 0$ in (8.9) yields the trivial steady state $P(x) = \delta_{x,0}$ for all values of $K_1$ , $K_2$ and $\delta$ , which is the state with no $X$ remaining. We must remember that the transition occurs in the macroscopic limit, which is the limit $V \to \infty$ , along with $A, B, C \to \infty$ so that $\frac{A}{V}$ , $\frac{B}{V}$ and $\frac{C}{V}$ remain finite. Hence we must first take the limit $V \to \infty$ (with $K_1$ , $K_2$ , $\beta$ remaining finite), then consider $\beta \to 0$ .

## 8.1.1 Modes of the Distribution.

It is of some interest to examine the mode(s) (maximum point(s)) of the distribution (8.9). In the macroscopic limit the mode(s) correspond to the macroscopic value(s) of $X$. The extreme points of the distribution occur at $x$ values for which $P(x) = P(x-1)$. For the distribution (8.9) this yields the points

$$\frac{x}{V} = \frac{(K_2-K_1+\delta/V) \pm \sqrt{(K_2-K_1+\delta/V)^2 - 4K_2\,\delta/V\,(1-\beta V)}}{2\delta} \qquad (8.11)$$

Thus for certain ranges of the parameters $K_1$, $K_2$, $\delta$ and $\beta$ it is possible that the distribution becomes bimodal, a situation which describes systems in which nucleation may occur, with first order phase transition-like behaviour (Matheson, Walls, Gardiner 1975). However, some care must be taken here, since this bimodal behaviour vanishes in themacroscopic limit. In fact, in the macroscopic limit, the points (8.11) tend to the deterministic values of $[X]$ given by the solution of equation (8.2). Thus taking the limit $\beta \to 0$ yields for the extreme points:

$$\frac{x}{V} = \begin{cases} 0 & , \quad K_2 \leq K_1. \\ 0 \text{ and } \dfrac{K_2-K_1}{\delta} & , \quad K_2 \geq K_1 \end{cases} \qquad (8.12)$$

For $K_2 \leq K_1$, the extreme occurs at $\frac{x}{V} = 0$, and is a maximum. For $K_2 \geq K_1$, there are two extreme points. $\frac{x}{V} = 0$ gives a minimum and $\frac{x}{V} = \frac{K_2-K_1}{\delta}$ gives a maximum. Thus $\frac{x}{V} = 0$ has a low probability of occurring, and so it is unstable. $\frac{x}{V} = \frac{K_2-K_1}{\delta}$ has a high probability and so is stable. This stochastic analysis is thus in agreement with the deterministic results.

### 8.1.2 Mean Number and Fluctuations.

We may calculate exact expressions for the various moments of the distribution (8.9); the mean, or first moment, is given by $\langle x\rangle = \left[\frac{\partial f}{\partial s}\right]_{s=1}$ and is:

$$\frac{\langle x\rangle}{V} = \frac{K_2}{\delta}\cdot\frac{\beta V}{\frac{K_1}{\delta}\cdot V}\;\frac{{}_1F_1\left(\beta V+1, \frac{K_1}{\delta}V+1; \frac{K_2}{\delta}V\right)}{{}_1F_1\left(\beta V, \frac{K_1}{\delta}V; \frac{K_2}{\delta}V\right)} \tag{8.13}$$

The first factorial moment $\langle x(x-1)\rangle = \left[\frac{\partial^2 f}{\partial s^2}\right]_{s=1}$ is:

$$\frac{\langle x(x-1)\rangle}{V^2} = \left(\frac{K_2}{\delta}\right)^2 \frac{\beta V(\beta V+1)}{\frac{K_1}{\delta}V\left(\frac{K_1}{\delta}V+1\right)}\;\frac{{}_1F_1\left(\beta V+2, \frac{K_1}{\delta}V+2; \frac{K_2}{\delta}V\right)}{{}_1F_1\left(\beta V, \frac{K_1}{\delta}V; \frac{K_2}{\delta}V\right)} \tag{8.14}$$

We may calculate the macroscopic limit of these expressions using the asymptotic form of the ${}_1F_1$ function given by Erdélyi (1953), which is:

$$\lim_{V\to\infty} {}_1F_1(aV+\alpha, bV+\beta; cV+\gamma) = \frac{\Gamma(bV+\beta)}{\Gamma(aV+\alpha)\,\Gamma\{(b-a)V+\beta-\alpha\}}\left(\frac{2\pi}{u_2}\right)^{1/2} \times$$
$$\times\, e^{-t_2(cV+\gamma)}\,(1+t_2)^{(b-a)V+\beta-\alpha}\,(-t_2)^{aV+\alpha} \tag{8.15}$$

where $t_2$ is the root of $ct(t+1) - a(t+1) - (b-a) = 0$ which lies between -1 and 0, and $u_2 = a(1+t_2)^2 + (b-a)t_2^2$.

We thus have for the mean concentration

$$\lim_{V\to\infty}\frac{\langle x\rangle}{V} = \frac{(K_1-K_2) \pm \sqrt{(K_1-K_2)+4\delta\beta}}{2\delta} \tag{8.16}$$

which is the deterministic result, and will yield the phase transition-like behaviour when $\beta \to 0$ .

For the first factorial moment, we have

$$\lim_{V\to\infty}\frac{\langle x(x-1)\rangle}{V^2} = \left\{\frac{\langle x\rangle}{V}\right\}^2 \tag{8.17}$$

From equn. (8.17) we see that the poissonian form of fluctuation, with $\langle x^2\rangle - \langle x\rangle^2 = \langle x\rangle$ , is regained in the infinite volume limit. For $K_2 < K_1$ the fluctuations are zero. For $K_2 > K_1$ we can consider the relative fluctuations $\frac{\langle x^2\rangle - \langle x\rangle^2}{\langle x\rangle^2}$ which for the poissonian situation are $\frac{1}{\langle x\rangle}$ , or $\frac{\delta}{K_2 - K_1}$ . Thus as the critical point is approached from $K_2$ above $K_1$ , the relative fluctuations diverge as $(K_2 - K_1)^{-1}$ , with the infinite relative fluctuation at $K_2 = K_1$ corresponding to the instability at this point. As $K_2$ increases above $K_1$ , the new branch becomes more stable, and the relative fluctuations decrease.

### 8.1.3 Two Time Correlation Function; Correlation Time.

From the deterministic analysis we obtain one time constant inherent in the system. This is the regression time which is a measure of the stability of the system since it is a measure of the time for a perturbation to decay or otherwise. The stochastic analysis yields a corresponding time constant for the system . This is the correlation time, a measure of the time for which the state of the system remains correlated to some initial state. This correlation time is found from consideration of the two-time average $\langle x(t)\, x(t')\rangle$ which is defined as

$$\langle x(t)x(t')\rangle = \sum_{x}\sum_{x'} x x' \, P(x,t;\, x',t') \qquad (8.18)$$

The joint probability $P(x,t;\, x',t')$ is related to the conditional probability $P(x,t\,|\,x',t')$ by Baye's law(see e.g. Feller 1968):

$$P(x,t;\, x',t') = P(x',t')\, P(x,t\,|\,x',t') \qquad (8.19)$$

and $P(x,t\,|\,x',t')$ is the solution of the master equation (8.7) subject to the initial condition $x'$ at $t'$ .

The equation for $\langle x(t)x(t')\rangle$ may thus be obtained from the master equation (8.7) or from the two-time generating function

$$F(s,s') = \sum_{x}\sum_{x'} s^{x} s'^{x'} P(x,t;x',t') \tag{8.20}$$

which obeys the same equation in $s$ & $t$ as $F(s)$. Since $\langle x(t)x(t')\rangle = \left[\frac{\partial^2 F}{\partial s\,\partial s'}\right]_{s=1=s'}$ we have

$$\frac{\partial}{\partial t}\langle x(t)x(t')\rangle = -\frac{\delta}{V}\langle x(t')x(x-1)(t)\rangle + (K_2-K_1)\langle x(t)x(t')\rangle + \beta K_2 V\langle x(t')\rangle \tag{8.21}$$

In order to close this equation, we need to find some approximation for $\langle x(t')x(x-1)(t)\rangle$ in terms of lower moments. We shall use the approximation used by Gardiner et al. (1976) which resembles the Gaussian approximation:

$$\begin{aligned}\langle x_i x_j x_k\rangle_f &= [\langle x_i x_j\rangle_f - \langle x_i\rangle\langle x_j\rangle]\langle x_k\rangle + [\langle x_j x_k\rangle - \langle x_j\rangle\langle x_k\rangle]\langle x_i\rangle \\ &\quad + [\langle x_k x_i\rangle_f - \langle x_k\rangle\langle x_i\rangle]\langle x_j\rangle + \langle x_i\rangle\langle x_j\rangle\langle x_k\rangle\end{aligned} \tag{8.22}$$

In the steady state $\langle x\rangle = \langle x(t')\rangle$ , and $\langle x(t)x(t')\rangle$ will become a function of $\tau = t-t'$ only. Using this, combined with the equation for the mean in the steady state, we obtain

$$\frac{\partial}{\partial \tau}\langle x(\tau)x\rangle = \left[(K_2-K_1) - 2\frac{\langle x\rangle}{V}\right]\langle x(\tau)x\rangle + 2\frac{\delta}{V}\langle x\rangle^3 \tag{8.23}$$

From equation (8.23) we see that the correlation time is obviously $\tau_c = \left[(K_2-K_1) - 2\delta\frac{\langle x\rangle}{V}\right]$ ,or, using the expression for $\frac{\langle x\rangle}{V}$ in the limit $V\to\infty$ , $\beta\to 0$ ,

$$\tau_c = |K_2-K_1|^{-1} \tag{8.24}$$

Thus, as might be expected, the correlation time is the same as the regression time.

## 8.2 Space-Dependent Stochastic Analysis.

A study of the fluctuations and correlations in a local sense for this chemical reaction is important, both for an understanding of the nature of these fluctuations for a non-linear system, and for reinforcing the analogy between the behaviour of the particular system (8.1) and second order phase transition behaviour. In order that local behaviour be investigated, we must introduce spatial dependence into the stochastic analysis. A space dependent stochastic analysis of a model similar to (8.1) has been made by Nitzan et al. (1974), who use a Langevin equation approach. Here, we again use a master equation approach . The two approaches are not necessarily equivalent.

We may allow for spatial dependence in the stochastic analysis of this model by the procedure outlined in chapter seven: we subdivide the system into small cells, and consider the multi variate probability distribution $P(x_1,x_2,\dots,x_N,t) = P(\underset{\sim}{x},t)$ , where $x_K$ represents the number of molecules of species $X$ in cell $k$ . As in chapter seven we obtain a master equation for $P(\underset{\sim}{x},t)$ which describes the reaction proceeding in each cell, and also the diffusion of $X$ between cells:

$$\begin{aligned}\frac{dP(\underset{\sim}{x},t)}{dt} = {} & \sum_i\sum_j d_{ij}\left[(x_i+1)P(x_i+1,x_j-1,\underset{\sim}{x}') - x_i P(\underset{\sim}{x},t)\right] + \sum_i \Big\{ \\ & K_1\left[(x_i+1)P(x_i+1,\underset{\sim}{x}') - x_i P(\underset{\sim}{x})\right] + K_2\left[(x_i-1)P(x_i-1,\underset{\sim}{x}')\right. \\ & \left.- x_i P(\underset{\sim}{x})\right] + K_2\beta V\left[P(x_i-1,\underset{\sim}{x}') - P(\underset{\sim}{x})\right] \\ & + \frac{\delta}{V}\left[(x_i+1)x_i P(x_i+1,\underset{\sim}{x}') - x_i(x_i-1)P(\underset{\sim}{x})\right]\Big\}\end{aligned} \qquad (8.25)$$

Here we shall assume thesystem is isotropic, so as defined in chapter seven, $d_{ij} = \begin{cases} d, & \text{cells } i,j \text{ nearest neighbours} \\ 0, & \text{otherwise.} \end{cases}$

$V$ is the volume of a cell, and $k_1, k_2, \beta, \delta$ are as previously defined.

The equation for the generating function $F(\underset{\sim}{s},t) = \sum_{x_1}\cdots\sum_{x_N}\prod_i s_i^{x_i} P(\underset{\sim}{x},t)$ is then:

$$\frac{\partial F}{\partial t} = \sum_i\sum_j d_{ij}(s_i - s_j)\frac{\partial F}{\partial s_i} + \sum_i (1-s_i)\left[\frac{\delta}{V} s_i \frac{\partial^2 F}{\partial s_i^2} + k_1\frac{\partial F}{\partial s_i} - k_2 s_i \frac{\partial F}{\partial s_i} - \beta k_2 V F\right] \qquad (8.26)$$

## 8.2.1 Approximate Solutions for Mean and Correlations.

It is now straighforward to calculate the equations of motion for the various moments of $P(\underset{\sim}{x},t)$. The first moments are the mean numbers $\langle x_k\rangle$ in the cells, and are given by $\langle x_k\rangle = \left[\frac{\partial F}{\partial s_k}\right]_{\underset{\sim}{s}=\underset{\sim}{1}}$. Taking the continuum approximation, we obtain from (8.26) the following equation for $\langle\rho(\underset{\sim}{r})\rangle = \lim_{V\to 0}\frac{\langle x(\underset{\sim}{r}_k)\rangle}{V}$ :

$$\frac{\partial\langle\rho(\underset{\sim}{r})\rangle}{\partial t} = D\nabla^2\langle\rho(\underset{\sim}{r})\rangle + (k_2-k_1)\langle\rho(\underset{\sim}{r})\rangle + \beta k_2 - \delta\lim_{V\to 0}\frac{\langle x_k(x_k-1)\rangle}{V^2} \qquad (8.27)$$

Where, as defined in chapter seven, $D = \lim_{\ell\to m.f.p} d/\ell^2$, $\ell$ being the dimension of a cell.

We shall consider the second moments, or correlations, in the form $g_{ij} = \langle x_i x_j\rangle - \delta_{ij}\langle x_i\rangle = \left[\frac{\partial^2 F}{\partial s_i \partial s_j}\right]_{\underset{\sim}{s}=\underset{\sim}{1}}$. In the continuum approximation we obtain the following equation for $g(\underset{\sim}{r},\underset{\sim}{r}') =$

$$\lim_{l \to \text{m.f.p.}} \frac{g_{ij}}{V^2} = \langle \rho(\underline{r})\rho(\underline{r}')\rangle - \delta(\underline{r}-\underline{r}')\langle\rho(\underline{r})\rangle :$$

$$\frac{\partial}{\partial t} g(\underline{r},\underline{r}') = D[\nabla_{\underline{r}}^2 + \nabla_{\underline{r}'}^2]\, g(\underline{r},\underline{r}') + 2(K_2-K_1)\, g(\underline{r},\underline{r}') + K_2\beta[\langle\rho(\underline{r})\rangle + \langle\rho(\underline{r}')\rangle]$$
$$+ 2K_2\,\delta(\underline{r}-\underline{r}')\langle\rho(\underline{r})\rangle - 2\frac{\delta}{V}\,\delta(\underline{r}-\underline{r}') \lim_{l\to \text{m.f.p.}} \frac{\langle x_i(x_i-1)\rangle}{V^2} \qquad (8.28)$$
$$- \delta \lim_{l\to\text{m.f.p}} \frac{1}{V^3}\left[\frac{\partial^3 F}{\partial s_i \partial s_j^2} + \frac{\partial^3 F}{\partial s_i^2 \partial s_j}\right]_{\underline{s}=\underline{1}}$$

We see that the $\frac{\partial^3 F}{\partial s_i^3}$ term in the equation for $F(\underline{s},t)$ means that each moment is coupled to the next highest order moments, so that the moment equations form a non-closed hierarchy. In order to solve the two moment equations (8.27) and (8.28) we must close them using some approximation scheme. We shall use the Gaussian-like approximation scheme given in equation (8.22). To further simplify the solution, we shall also assume that the reduced distribution in each cell is poissonian, that is we put $\langle x(x-1)\rangle \simeq \langle x\rangle^2$ for each cell. Under these approximations the steady state forms of equns. (8.27) and (8.28) are:

$$(K_2-K_1)\langle\rho\rangle + \beta K_2 - \delta\langle\rho\rangle^2 = 0 \qquad (8.29)$$

$$D\nabla^2 g(\underline{r}) + [(K_2-K_1) - \delta\langle\rho\rangle]\, g(\underline{r}) + K_2\,\delta^{(3)}(\underline{r})\,[\langle\rho\rangle - \delta\langle\rho\rangle^2] \qquad (8.30)$$
$$+ \beta K_2\langle\rho\rangle + \delta\langle\rho\rangle^3 = 0$$

Here we have use the fact that the system will be homogeneous in the mean, so that $\langle\rho(\underline{r})\rangle = \langle\rho\rangle$, and that $g(\underline{r},\underline{r}')$ will be a function of $\underline{r}-\underline{r}'$ only, so that $\underline{r}$ in (8.30) now means $\underline{r}-\underline{r}'$.

Equation (8.29) is exactly the deterministic equation (8.2) for $\langle\rho\rangle$, and so yields the deterministic solution, which exhibits the transition-like behaviour in the limit $\beta \to 0$, i.e: equation (8.3). Solution of equation (8.30) by Fourier transform yields the following expression for the correlation function $\langle\rho(\underline{r}),\rho(\underline{r}')\rangle = \langle\rho(\underline{r})\rho(\underline{r}')\rangle - \langle\rho(\underline{r})\rangle\langle\rho(\underline{r}')\rangle = g(\underline{r},\underline{r}') +$ $\delta(\underline{r}-\underline{r}')\langle\rho(\underline{r})\rangle - \langle\rho(\underline{r})\rangle\langle\rho(\underline{r}')\rangle$ :

$$\langle\rho(\underline{r}),\rho(0)\rangle = \delta^3(\underline{r})\langle\rho\rangle + \frac{K_1\langle\rho\rangle - \beta K_2}{4\pi D r}\, e^{-r/\ell_c} \qquad (8.31)$$

where the correlation length $\ell_c = \left[\frac{D}{K_1 - K_2 + 2\delta\langle\rho\rangle}\right]^{1/2}$

In the limit $\beta\to 0$ , the correlation length becomes

$$\ell_c = \left[\frac{D}{|K_2 - K_1|}\right]^{1/2} \qquad (8.32)$$

This is symmetric about the transition point $K_2 = K_1$ , and at the transition point, where the $\langle\rho\rangle$ versus $K_2$ slope is discontinuous, be comes infinite. This behaviour is closely analogous to the behaviour of the correlation length of the order parameter in a second order phase transition (see, e.g. Stanley (1971 ) where further references are given). Thus even though the interaction is short range (nearest neighbour cells only), the coherent autocatalytic production of X induces a correlation such that each point is correlated to every other point in the system at the transition point. It should be noted that the critical exponent (classically the power of $\frac{1}{|T-T_c|}$ occuring in $\ell_c$ , or in this case the power of $\frac{1}{|K_2-K_1|}$) has the classical value of $\frac{1}{2}$. This should be compared with the work of Nitzan et al. (1974) who obtain similar behaviour using a linearized Langevin equation analysis of their system. Similar behaviour in the spatial correlations in liquids exhibiting the Benard instability has been found by Zaitsev and Schliomis (1971), Graham (1974), and Boon (1975).

A point to note is that when solving the equations (8.27) and

(8.28) for $\langle\rho(\underset{\sim}{r})\rangle$ and $g(\underset{\sim}{r},\underset{\sim}{r}')$ it is not essential to make the continuum approximation before the equations can be solved. However, after solving the equations it turns out that this assumption is true provided $\delta/Dl \ll 1$ where $l$ is the dimension of the cell at which the continuum approximation becomes valid. A detailed discussion of this point is given in the work by Gardiner et al. (1976).

### 8.2.2 Two Time Correlation Function; Correlation Time.

As in the non space dependent analysis, it is useful to study the two time correlation function in this space dependent analysis, in order to increase the analogy to second order phase transition behaviour. The two-time correlation function in the space dependent case is $g(\underset{\sim}{r},\underset{\sim}{r}';t,t') = \langle\rho(\underset{\sim}{r},t),\rho(\underset{\sim}{r}',t')\rangle$ , and its equation of motion is most easily obtained using the equation for the two-time generating function $F(\underset{\sim}{s},\underset{\sim}{s}';t,t') = \sum_{\underset{\sim}{x}}\sum_{\underset{\sim}{x}'}\prod_i s_i^{x_i}\prod_i s_i'^{x_i'}P(\underset{\sim}{x},t;\underset{\sim}{x}',t')$ . Since this generating function obeys the same equation as the one-time generating function in the unprimed variables, equn.(8.26), we obtain for $\langle\rho(\underset{\sim}{r},t)\rho(\underset{\sim}{r}',t')\rangle$ in the continuum approximation:-

$$\begin{aligned}\frac{\partial}{\partial t}\langle\rho(\underset{\sim}{r},t)\rho(\underset{\sim}{r}',t')\rangle &= D\nabla_{\underset{\sim}{r}}^2\langle\rho(\underset{\sim}{r},t)\rho(\underset{\sim}{r}',t')\rangle + \beta K_2\langle\rho(\underset{\sim}{r}',t')\rangle \\ &\quad - (K_1-K_2)\langle\rho(\underset{\sim}{r},t)\rho(\underset{\sim}{r}',t')\rangle - \delta\lim_{V\to 0}\frac{\langle x_r(x_r-1)x_{r'}(t')\rangle}{V^3}\end{aligned} \tag{8.33}$$

where $D$ has its usual definition.

Again, the nonlinearity means that the second moment $\langle xx'\rangle$ is coupled to the third moment $\langle x(x-1)x'\rangle$ , and we utilize the approximation (8.22) to close the equation (8.33).

We shall now consider the steady state, in which situation

$\langle\rho(\underline{r},t)\rho(\underline{r}',t')\rangle$ will be a function of $\underline{r}-\underline{r}'$ and $t-t'$ only. We obtain the following equation for $g(\underline{r},\underline{r}';t,t')$ :

$$\frac{\partial}{\partial\tau}g(\underline{r},\tau) = D\nabla^2 g(\underline{r},\tau) - \left[(k_1-k_2)+2\delta\langle\rho\rangle\right] g(\underline{r},\tau) \tag{8.34}$$

where $\underline{r}-\underline{r}'$ is replaced by $\underline{r}$ , and $\tau = t-t'$ .

The solution of (8.34) must satisfy the "initial" condition that $g(\underline{r},\tau=0)$ must be equal to $g(\underline{r})$ of equn. (8.31). We obtain (in the limit $\beta\to 0$ ):

$$g(\underline{r},\tau) = \frac{\langle\rho\rangle}{(4\pi D\tau)^{3/2}}\, e^{-r^2/4D\tau - D\tau/\ell_c^2} + \frac{k_1\langle\rho\rangle}{8\pi D r}\left[e^{-r/\ell_c}\,\mathrm{erfc}\left(\frac{\sqrt{D\tau}}{\ell_c}-\frac{r}{2\sqrt{D\tau}}\right) + e^{r/\ell_c}\,\mathrm{erfc}\left(\frac{\sqrt{D\tau}}{\ell_c}+\frac{r}{2\sqrt{D\tau}}\right)\right] \tag{8.35}$$

This consists of a standard diffusion term modified by the chemical term $e^{-D\tau/\ell_c^2} = e^{-|k_2-k_1|^{-1}\tau}$ along with a mixed diffusion and chemical term.

In the small $\tau$ and large $\tau$ limits we may replace the erfc functions by less cumbersome approximate expressions. Power series expansion of the erfc functions yields the following small form for $g(\underline{r},\tau)$ :

$$g(\underline{r},\tau) \simeq \langle\rho\rangle e^{-r^2/4D\tau}\left[\frac{1}{(4\pi D\tau)} - \frac{4k_1(D\tau)^{3/2}}{\sqrt{\pi}\, r^3}\right] + \frac{k_1\langle\rho\rangle}{4\pi D r}\, e^{-r/\ell_c^2} \tag{8.36}$$

Use of the asymptotic forms of the erfc functions yields the following large $\tau$ behaviour for $g(\underline{r},\tau)$ :

$$g(\underline{r},\tau) \simeq \left[\frac{e^{-r^2/4D\tau}}{(4\pi D\tau)^{3/2}} + \frac{k_1\ell_c}{4\pi r(\pi D^2\tau)^{1/2}}\right]\langle\rho\rangle\, e^{-D\tau/\ell_c^2} \tag{8.37}$$

If we consider the long time behaviour of $g(\underline{r},\tau)$ to give the measure of the correlation time, then it is clear from equation (8.37) that this time is given by

$$\tau_c = \ell_c^2/D = |k_2 - k_1|^{-1} \qquad (8.38)$$

The relation $\tau_c = \ell_c^2/D$ was found also by Graham (1974) in his work on the Benard instability. The result (8.38) for $\tau_c$ is, not unexpectedly, the same as that found for the system in the non space dependent analysis, equn.(8.24).

The result (8.38) may be obtained in a more transparent manner by directly integrating equn.(8.34) over a volume $V$ with dimensions much larger than the correlation length $\ell_c$ . In this case the surfaces terms created by $\nabla^2$ vanish, and we obtain

$$\langle X[V,\tau], X[V,0]\rangle = \sigma^2[V,0] \,.\, e^{-\tau/\tau_c} \qquad (8.39)$$

## 8.2.3 Fluctuations In Finite and Infinite Volumes.

We may consider fluctuations in finite volumes and correlations between finite volumes, rather than the point quantities, by direct integration of the point correlation function $\langle \rho(\underline{r},t), \rho(\underline{r}',t')\rangle$ over the volumes in question. We first consider the fluctuations in a subvolume $\Delta V$ of the system, which we take to be spherical, with radius $R$ . The two time correlation function is $\langle X[\Delta V,\tau], X[\Delta V,0]\rangle = \int_{\Delta V} d^3\underline{r} \int_{\Delta V} d^3\underline{r}' \langle \rho(\underline{r},\tau), \rho(\underline{r}',0)\rangle$ . In the limit $\tau \to 0$ , this becomes the variance $\sigma^2$ of $\Delta V$ , which is a measure of the fluctuations in the volume $\Delta V$ :

$$\sigma^2[\Delta V] = \langle X[\Delta V]\rangle \left\{ 1 + \frac{3k_1 \ell_c^5}{2DR^3} \left[ \left(1 - \frac{R^2}{\ell_c^2} + \frac{2}{3}\frac{R^3}{\ell_c^3}\right) - e^{-2R/\ell_c}\left(1 + \frac{R}{\ell_c}\right)^2 \right] \right\} \qquad (8.40)$$

If $R \ll l_c$, this becomes

$$\sigma^2[\Delta V] \simeq \langle X[\Delta V]\rangle\left[1 + \frac{2K_1R^2}{5D}\right] \qquad (8.41)$$

Thus in the limit $R \to 0$, the fluctuations become Poissonian in form, in agreement with the assumption made in deriving equations (8.29) and (8.30). This assumption is in effect the assumption that a local equilibrium exists in each small cell.

If $R \gg l_c$, (8.40) becomes

$$\sigma^2[\Delta V] \simeq \langle X[\Delta V]\rangle\left[\frac{K_1}{|K_1-K_2|} - \frac{3}{2}\frac{K_1}{|K_1-K_2|}\cdot\frac{l_c}{R}\right] \qquad (8.42)$$

In the limit $R \to \infty$, this does not tend to the exact result (8.17) of the non space dependent analysis because of the approximations which have been made in the space dependent analysis. The two agree only in the limit $K_2 \ll K_1$, i.e. well below the threshold $K_2 = K_1$.

It is of some interest to consider the correlation between a small volume $\Delta V$ of the system, and the rest of the system's volume $V-\Delta V$. This correlation is

$$\begin{aligned}\langle X[\Delta V], X[V-\Delta V]\rangle &= \int_{\Delta V} d^3\underline{r} \int_{V-\Delta V} d^3\underline{r}' \, \langle \rho(\underline{r}), \rho(\underline{r}')\rangle \\ &= \int_{\Delta V} d^3\underline{r} \int_{V} d^3\underline{r}' \langle \rho(\underline{r}), \rho(\underline{r}')\rangle - \int_{\Delta V} d^3\underline{r} \int_{\Delta V} d^3\underline{r}' \langle \rho(\underline{r}), \rho(\underline{r}')\rangle\end{aligned} \qquad (8.43)$$

The pioneering work in this topic by Nicolis et al. was concerned with the fluctuations in a small volume $\Delta V$ of the system and those in the large surrounding volume $V-\Delta V$. Their factorization ansatz essentially neglects the correlation (8.43) between these two volumes.

If we assume $V$ is large, so that its dimension $V^{1/3} \gg l_c$, the integration over $V$ in the first integral may be easily evaluated by integrating the correlation function equation (8.30) and ignoring the surface terms generated by $\nabla^2 g$. The integration over $\Delta V$ then yields simply the factor $\Delta V$. The second integral is precisely $\sigma^2[\Delta V]$ given by (8.40). If we define by writing (8.40) as

$$\sigma^2[\Delta V] = \langle X[\Delta V] \rangle \left( 1 + f(\Delta V) \right) \tag{8.44}$$

the normalized correlation coefficient $C[\Delta V, V-\Delta V] = \dfrac{\langle X[\Delta V], X[V-\Delta V] \rangle}{\sigma[\Delta V]\,\sigma[V-\Delta V]}$ is then, in thelimit $\Delta V \ll V$,

$$C[\Delta V, V-\Delta V] \simeq \frac{K_1 - 1 - f(\Delta V)}{\sqrt{|K_2 - K_1|}} \cdot \left[\frac{\Delta V}{V}\right]^{1/2} \tag{8.45}$$

The normalized correlation is thus not infinitesimal, and tends to zero as approximately $\left[\dfrac{\Delta V}{V}\right]^{1/2}$ only.

## CHAPTER 9 CONCLUDING REMARKS

In part 1 we presented exact solutions of the master equation describing various two-photon interactions with two level atoms. As expected for nonlinear processes we found that the behaviour of the light (even the first moments) depends on the statistics, with the dependence most strong at low intensities. Thus the current experiments examining the dependence of two photon absorption on the statistics of the ingoing light are of interest. Similar experiments on Raman scattering do not seem to have yet been carried out; such experiments would be of interest in the light of the work in this thesis.

The price paid for obtaining exact solutions is that the expressions are rather complicated, and there is a resultant loss of clarity. It is necessary to compute the expressions to provide a clear view of the time behaviour. In some cases the slow convergence of the moment series and the large arrays required give some computational problems.

Extension of the method of chapter 3 to higher order non linear emission processes is possible, although the solutions would become rather complicated. In the case of absorption, higher order nonlinearity gives higher order derivatives in the generating function equation, and it is difficult to see the orthogonal polynomials series method working in these cases. It is possible numerical solutions may be obtained.

The steady states examined in chapter 4 have rather interesting properties, however the low photon intensities involved mean that these properties are probably not of much pratical interest.

The work of chapter 5 shows that it is possible to obtain approximate solutions which can be reasonably accurate, and give a clearer view of the behaviour of the light fields. The other approximate methods mentioned have been used in other nonlinear problems such as superadiant emission of photons by atoms (Degiorgio and Ghielmetti 1972).

One interesting theoretical possibility worth further investigation is that the even and odd coherent functions already described in the literature (Dodonov, Malkin and Man'ko 1974) may provide representations of field states in a manner analogous to the "P" representation in terms of the normal coherent states.

The work of part 2 provides results for fluctuations and spatial correlations in chemically reacting systems which are amenable to experimental confirmation or otherwise, using, e.g. light scattering techniques (see,e.g. Cummins and Pike 1974) or fluorescence correlation spectroscopy (Elson and Magde, 1974, Magde, Elson and Welds, 1974).

A major short-coming in the theoretical work on phase transition models is the nature of the approximations necessary to truncate non-closed systems of moment equations. The closure approximation used in this present work is closely related to the gaussian approximation, and thus it fails at the critical point because the standard deviation becomes infinite there. Preliminary work on alternative closure schemes is already under way (D.F.Walls, private communication). Note that because of the approximations used here, the space dependent analysis yields nonpoissonian global fluctuations, while the exact global analysis yields poissonian fluctuations.

The question of boundary conditions has been avoided in this present work. In the analysis of the second order phase transition model we have assumed an infinite sized system, so that boundary conditions do not enter the problem. In the work in chapter 7 any boundary conditions in the $N$ cell problem will be taken into account either in the eigenvalues $\mu_k$ and eigenvectors $\underset{\sim}{\lambda}_k$ through the $d_{ij}$ , or by modifications to the master equation.

# APPENDIX

## 1. Orthogonality and Integral Relations Required in Chapter 3.

To evaluate the coefficients $A_n$ in the polynomial expansion of the generating function for the single mode two photon absorption process (section 3.2.1) we use the well-known orthogonality relation for Legendre polynomials:

$$\int_{-1}^{1} P_n(x) P_m(x)\,dx = \delta_{m,n} \frac{2}{2n+1} \qquad \text{(A1)}$$

along with the following integral relations:

$$\int_{-1}^{1} x^{\lambda} P_n(x)\,dx = 0 \qquad , \lambda < n \qquad \text{(A2)}$$

$$\int_{-1}^{1} x^{\lambda} P_n(x)\,dx = \frac{\sqrt{\pi}\,\Gamma(\lambda+1)}{2^{\lambda+1}\Gamma(1+\frac{\lambda-n}{2})\,\Gamma(\frac{\lambda+n+3}{2})} \quad , \quad \begin{array}{c} n \text{ even and } \lambda \text{ odd} \\ \text{or} \\ n \text{ odd and } \lambda \text{ even} \end{array} \qquad \text{(A3)}$$

To evaluate the coefficients $A_n(\lambda)$ in the polynomial expension of the generating function $F_\lambda(x,\tau)$ for the two mode two photon absorption process (section 3.2.2) we use the Jacobi polynomial orthogonality relation

$$\int_{-1}^{1} x^{q-1}(1-x)^{p-q} G_n(p,q,x)\, G_m(p,q,x)\,dx = \delta_{m,n} \frac{n!\,\Gamma(n+p-q+1)\Gamma(n+p)\,\Gamma(n+q)}{(2n+p)\,[\Gamma(2n+p)]^2} \qquad \text{(A4)}$$

and the integral

$$\int_{-1}^{1} x^{\lambda}(1-x)^{p-q} G_n(p,q,x)\,dx = \frac{n!\,\Gamma(n+p)\,\Gamma(\lambda+1)\,\Gamma(\lambda-q+2)\,\Gamma(p-q+n+1)}{\Gamma(2n+p)\,\Gamma(\lambda-n-q+2)\,\Gamma(p-q+n+\lambda+2)} \qquad \text{(A5)}$$

## 2. Inversion of Laplace Transform of the Raman Effect Distribution.

The inversion of $\bar{\rho}_{n_s,n_p}(s)$ (equation (3.47)), allowing for possible repeated factors in the denominator, yields for $\rho_{n_s,n_p}(\tau)$ :

$$\rho_{n_s,n_p}(\tau) = \frac{n_s!}{n_p!}\Big[\sum_{m=m^*}^{n_s} \frac{(\lambda-m)!}{m!} \sum_{j=m}^{n_s} A_j^{m,n_s}(\lambda)\exp\{-p_j(\lambda)\tau\} + \qquad (A6)$$

$$+ \Theta(n_s-M)\, f_{M,n_s}(\lambda;\tau)\Big]$$

where

$$M = \begin{cases} \lambda/2 & , \lambda \text{ even} \\ (\lambda-1)/2 & , \lambda \text{ odd} \end{cases} \qquad \text{and} \qquad m^* = M\,\Theta(n_s-M)$$

and

$$\Theta(x) = \begin{cases} 0 & , x<0 \\ 1 & , x \geq 0 \end{cases}$$

$$f_{M,n_s}(\lambda,\tau) = \sum_{m=0}^{M} \frac{(\lambda-m)!}{m!} \sum_{j=m}^{M-1} \sum_{i=M}^{n_s} A_j^{m,M-1}(\lambda)\, A_i^{M,n_s}(\lambda) \quad \times \qquad (A7)$$

$$\times \Big[\frac{\exp\{-p_j(\lambda)\tau\} - \exp\{-p_i(\lambda)\tau\}}{p_i(\lambda) - p_j(\lambda)} + \delta_{p_i(\lambda),p_j(\lambda)}\, \tau \exp\{-p_j(\lambda)\}\Big]$$

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