$=0.9\theta_{ic}$, and $E_i/k_B < 13.6K$. The cross section rises from the low-energy cutoff (which is quite sensitive to the form of the ripplon spectrum), and then bends over. The bending is a consequence of the fact that taking $\theta_i = 0.9\theta_{ic}$ makes θ_i a function of E_i. Were θ_i to be held constant, the cross section would rise monotonically with E_i. Finally, in Fig. 3, we plot the cross section for fixed $E_i/k_B = 4K$, $\theta_i = 0.9\theta_{ic}$, and $\frac{3}{8}\pi \leq \theta_f \leq \frac{5}{8}\pi$.

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Quantum Theory of Nonlinear Optical Processes with Time-Dependent Pump Amplitude and Phase: Frequency Conversion*

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The behavior of a simple theoretical model of a quantum-frequency converter with a time-dependent pump amplitude and phase is analyzed quantum mechanically. A sufficient condition ensuring periodic frequency conversion between the modes is found and exact solutions are given in these cases. The complete time-dependent density matrices which give the most complete statistical description of the system are presented for a variety of initial states of the system. In the general case where the sufficient condition is not satisfied, time-dependent-perturbation-theory results give corrections to the amplitude and the period of the energy exchange between the modes. Comparisons are made between these results and those of other authors.

I. INTRODUCTION

It is well known that nonlinear optical effects arise as a result of the nonlinear response of a medium to intense light fields obtainable in laser beams.[1] An important class of these phenomena involve nonlinear coupling between electromagnetic waves, usually referred to as parametric interactions.[2,3] The fundamental physical process underlying nonlinear parametric interactions has come to play a central role in several physical phenomena of interest. These include Raman and Brillouin effects, Stokes and anti-Stokes generations, etc. All these effects involve nonlinear coupling between various types of boson excitations such as phonons, spin waves, plasmons, rotons, polaritons, etc., as well as electromagnetic waves.[4]

In the optical regime two of the most important nonlinear parametric interactions are frequency conversion and parametric amplification where three electromagnetic modes are coupled. A quantum-mechanical model suitable for discussions of these effects was proposed some time ago by Louisell, Yariv, and Siegman.[5] The proposed model is macroscopic in that one introduces a phenomenological coupling for the three boson waves and does not deal with the microscopic origin of the coupling. It has been shown by Graham and Haken and by Graham[6] that the model of Ref. 5 may be looked upon as the effective Hamiltonian for the nonlinear interaction provided that the microscopic atomic transitions are virtual. Recently, a refinement of the model has been proposed by Crosignani, DiPorto, Ganiel, Solimeno, and Yariv[7,8] in which the finite coherence time of the c.w. laser pump is taken into account by allowing the pump amplitude and phase to be arbitrary time-dependent functions rather than constants. We shall adopt the latter model as the basis of this analysis of nonlinear optical processes.

The present paper is the first in a series of three which are devoted to a detailed study of the quantum theory of nonlinear optical processes with time-dependent pump amplitude and phase. In this first paper, the case of frequency conversion is investigated. We find a sufficient condition for the periodic continuous energy exchange between the two modes to take place with time-dependent pump amplitude and phase. The experimentally important case of nonzero detuning of the pump-field frequency satisfies this sufficient condition. In general we find that the period becomes a nonlinear function of time. If the sufficient condition is fulfilled, the model is exactly soluble and we obtain the complete form of the time-dependent density matrices of the two modes for a variety of initial states of the system. We shall find that the quantum frequency converter not only causes energy exchange between the two modes, but the coherence and statistical properties of the two modes are exchanged as well.

If the sufficient condition is not satisfied, the model is not exactly soluble. Instead we employ time-dependent perturbation theory assuming the deviation from the sufficient condition to be small. Explicit calculations are carried out to the lowest nontrivial order of perturbation. We find corrections to the amplitude and period of energy exchange between the modes.

The organization of the present paper is as follows. In Sec. II we describe the theoretical model and show that it belongs to a class satisfying the conditions of Glauber's theorem.[9] Exact conservation laws and algebraic properties of the model are pointed out. In Sec. III we obtain the sufficient condition and derive the rate of energy exchange between the modes as well as the time dependence of the field variables. In Sec. IV–VI the complete form of the density matrix of the two modes are obtained for a variety of initial states of the system. In Sec. VII we outline a time-dependent-perturbation-theory treatment of the model when the sufficient condition is not satisfied. In Sec. VIII a summary and discussions are presented and the present results are compared with those of other authors.

II. MODEL

The Hamiltonian proposed by the authors of Refs. 7 and 8 to describe a quantum frequency converter with time-dependent pump amplitude and phase is given by

$$H=\hbar\omega_1 a^\dagger a+\hbar\omega_2 b^\dagger b+\hbar\kappa(t)[a^\dagger b e^{-i(\omega_1-\omega_2)t+i\phi(t)}+ab^\dagger e^{i(\omega_1-\omega_2)t-i\phi(t)}], \quad (2.1)$$

where $\omega_{1,2}$ are the frequencies of the two modes a and b, respectively, and $\kappa(t)$ and $\phi(t)$ are the time-dependent pump amplitude and phase. Without loss of generality, the initial phase of the pump $\phi(0)$ may be chosen to vanish.

The Heisenberg equations of motion which follow from the Hamiltonian (2.1) are

$$i\frac{d}{dt}a(t)=\omega_1 a(t)+\kappa(t)b(t)e^{-i(\omega_1-\omega_2)t+i\phi(t)}, \quad (2.2)$$

$$i\frac{d}{dt}b(t)=\omega_2 b(t)+\kappa(t)a(t)e^{i(\omega_1-\omega_2)t-i\phi(t)}. \quad (2.3)$$

Thus the Heisenberg equations of motion for the field operators $a(t)$ and $b(t)$ express their time derivatives in terms of the operators themselves, but not their adjoints $a^\dagger(t)$ and $b^\dagger(t)$. Thus the Hamiltonian in Eq. (2.1) satisfies the required condition for Glauber's theorem[9] to be valid and we conclude that if the modes are initially coherent, they remain coherent at all times. Then the Schrödinger state vector at time t is given by

$$|t\rangle=U(t)\,|t=0\rangle=U(t)\,|\alpha_0,\beta_0\rangle=|\alpha(t),\beta(t)\rangle, \quad (2.4)$$

where $U(t)$ is the unitary time-development operator generated by the Hamiltonian (2.1) and $|\alpha_0,\beta_0\rangle$ denote coherent states[10] which are right eigenstates of the annihilation operators a and b with eigenvalues α_0 and β_0, respectively. In fact the time-dependent eigenvalues $\alpha(t)$ and $\beta(t)$ obey the same differential equations as the operators $a(t)$ and $b(t)$,

$$i\frac{d}{dt}\alpha(t)=\omega_1\alpha(t)+\kappa(t)\beta(t)e^{-i(\omega_1-\omega_2)t+i\phi(t)}, \quad (2.5)$$

$$i\frac{d}{dt}\beta(t)=\omega_2\beta(t)+\kappa(t)\alpha(t)e^{i(\omega_1-\omega_2)t-i\phi(t)}, \quad (2.6)$$

Unfortunately for arbitrary functions $\kappa(t)$ and $\phi(t)$, the coupled differential equations (2.5) and (2.6) are not in general exactly soluble.[8] Without exactly solving the equations we can nevertheless deduce an exact conservation law of the system.

The exact conservation law is due to the invariance properties of the Hamiltonian (2.1) under the transformation generated by the unitary operator

$$T(\theta) \equiv e^{i\theta[a^\dagger(t)a(t)+b^\dagger(t)b(t)]}, \tag{2.7}$$

where the parameter θ is a real constant. Thus the infinitesimal generator of $T(\theta)$, $a^\dagger(t)a(t) + b^\dagger(t)b(t)$, must be a constant of motion,

$$[a^\dagger(t)a(t) + b^\dagger(t)b(t), H] = 0 \tag{2.8}$$

or

$$N_a(t) + N_b(t) = N_a(0) + N_b(0) \equiv 2I. \tag{2.9}$$

Thus the time dependence of the number operators in the two modes are completely determined if we know the time dependence of their difference $N_a(t) - N_b(t)$, which is the quantity of interest in a quantum frequency converter. We also note that if we define

$$J_3 \equiv \tfrac{1}{2}[N_a(t) - N_b(t)], \tag{2.10}$$

$$J_+ \equiv a^\dagger(t)b(t), \tag{2.11}$$

$$J_- \equiv a(t)b^\dagger(t), \tag{2.12}$$

the J_i operators obey angular momentum commutation relations,

$$[J_\pm, J_3] = \mp J_\pm, \tag{2.13}$$

$$[J_+, J_-] = 2J_3, \tag{2.14}$$

and together with the constant of motion I, they form the generators of the algebra $U(2)$. In fact the Hamiltonian (2.1) itself may be expressed in terms of the generators of the $U(2)$ algebra,

$$\begin{aligned} H = {} & \hbar\omega_1(I + J_3) + \hbar\omega_2(I - J_3) \\ & + \hbar\kappa(t)(J_+ e^{-i(\omega_1-\omega_2)t+i\phi(t)} + \text{H.c.}). \end{aligned} \tag{2.15}$$

We shall see that these algebraic properties will play an important role in obtaining solutions to the model.

III. A SUFFICIENT CONDITION FOR PERIODIC ENERGY EXCHANGE

As we remarked earlier, for arbitrary time-dependent pump amplitude and phase the model is not exactly soluble. However, a large class of exact solutions can be obtained by imposing the condition[11] that the pump amplitude and phase vary in such a way that $\dot{\phi}(t)/\kappa(t) = C$, where C is an arbitrary real constant. To see how this comes about, let us first transform into a "rotated" frame generated by the unitary operator

$$\begin{aligned} R(t) = \exp\{ & -i(I + J_3)[\omega_1 t - \phi(t)/2] \\ & - i(I - J_3)[\omega_2 t + \phi(t)/2]\}. \end{aligned} \tag{3.1}$$

The Schrödinger state vector in the rotated frame $|t\rangle_R$ given by

$$|t\rangle_R = R(t)\,|t\rangle \tag{3.2}$$

then obeys the following Schrödinger's equation:

$$\begin{aligned} i\frac{\partial}{\partial t}\,|t\rangle_R &= \{\kappa(t)[J_+ + J_-] + \dot{\phi}(t)J_3\}\,|t\rangle_R \\ &\equiv H_R(t)\,|t\rangle_R. \end{aligned} \tag{3.3}$$

Because of the noncommutativity of the Hamiltonian in the rotated frame at two different times,

$$[H_R(t), H_R(t')] \neq 0, \tag{3.4}$$

the differential equation (3.3) cannot be directly integrated. The most general integrability condition is given by

$$\dot{\phi}(t)/\kappa(t) = C, \tag{3.5}$$

which is the most general condition for the vanishing of the commutator in Eq. (3.4).

If we impose the condition (3.5) on the time dependence of the pump amplitude and phase, one can directly integrate Eq. (3.3) to yield

$$|t\rangle_R = \exp\Big[-i\int_0^t dt'\, H_R(t')\Big]\,|t = |0\rangle_R, \tag{3.6}$$

where $U_R(t)$ is the unitary time-development operator in the rotated frame.

The unitary time-development operator $U(t)$ generated by the Hamiltonian Eq. (2.1) with the condition Eq. (3.5) can now be written down:

$$U(t) = R(t)U_R(t). \tag{3.7}$$

To find the time dependence of the field operators and the number operators it only remains to explicitly evaluate the unitary transformation generated by $U(t)$ in Eq. (3.7). We find the following results:

$$\begin{aligned} N_a(t) - N_b(t) = {} & [N_a(0) - N_b(0)]\cos\omega(t) \\ & - [a^\dagger(0)b(0) + a(0)b^\dagger(0)]\cos\gamma(t)\sin\omega(t) \\ & - i[a^\dagger(0)b(0) - a(0)b^\dagger(0)]\sin\gamma(t)\sin\omega(t), \end{aligned} \tag{3.8}$$

$$\begin{aligned} a(t) = e^{-(\omega_1 t - \phi(t)/2} i[& a(0)\cos\tfrac{1}{2}\omega(t)\, e^{-i\gamma(t)} \\ & - b(0)\sin\tfrac{1}{2}\omega(t)], \end{aligned} \tag{3.9}$$

$$\begin{aligned} b(t) = e^{-i(\omega_2 t + \phi(t)/2)} i[& b(0)\cos\tfrac{1}{2}\omega(t)\, e^{i\gamma(t)} \\ & + a(0)\sin\tfrac{1}{2}\omega(t)], \end{aligned} \tag{3.10}$$

where the periods $\omega(t)$ and $\gamma(t)$ are determined from

$$\sin\tfrac{1}{2}\omega(t) = \frac{2}{(C^2+4)^{1/2}} \sin\frac{(C^2+4)^{1/2}}{2} \int_0^t dt'\, \kappa(t'), \tag{3.11}$$

$$\tan[\gamma(t)-\pi/2]=\frac{C}{(C^2+4)^{1/2}}\tan\frac{(C^2+4)^{1/2}}{2}\int_0^t dt'\,\kappa(t').\tag{3.12}$$

The crucial step in the evaluation of the unitary transformation is the observation that because of the algebraic properties discussed at the end of Sec. II, $U_R(t)$ represents a finite rotation and can be decomposed into three Euler rotations with $\omega(t)$ and $\gamma(t)$ the time-dependent Euler angles. We shall have further occasions later on to make use of these observations.

From Eq. (3.8) we conclude that provided the stated condition Eq. (3.5) is satisfied, there is continuous periodic energy exchange between the two modes with the periods being nonlinear functions of time and determined by Eqs. (3.11) and (3.12). It is interesting to note that the condition Eq. (3.4) does not place any restriction on how rapidly the pump phase and amplitude can vary with time. In the case of nonzero detuning of the pump-field frequency and constant pump amplitude we have $\dot{\phi}=\Delta t$ and $C=\Delta/\kappa$, where Δ is the detuning. We see that the detuning affects both the amplitude and the period of energy exchange between the modes.

IV. SOLUTIONS FOR DENSITY OPERATOR WITH INITIAL STATE POSSESSING P REPRESENTATION

In Sec. III we obtained solutions to the equations of motion of the field operators and the number operators. These solutions can be used to find various time-dependent expectation values and moments of field strengths. However, the density matrix provides the most complete statistical description available for the system and accordingly we shall devote the present and the next two sections to finding and representing the density matrix for a variety of initial states of the system. In this section we consider initial states of the system possessing a well-behaved diagonal coherent-state representation.[10] We begin by assuming that both modes are initially coherent,

$$\rho(0)=|\alpha_0,\beta_0\rangle\langle\alpha_0,\beta_0|,\tag{4.1}$$

The density matrix at time t is then easily found by using Glauber's theorem, Eq. (2.4):

$$\begin{aligned}\rho(t)&=U(t)\,|\alpha_0,\beta_0\rangle\langle\alpha_0,\beta_0|\,U^\dagger(t)\\&=|\alpha(t),\beta(t)\rangle\langle\alpha(t),\beta(t)|,\end{aligned}\tag{4.2}$$

where $\alpha(t)$ and $\beta(t)$ have the same time dependence as the field operators $a(t)$ and $b(t)$, namely,

$$\alpha(t)=i[\alpha_0\cos\tfrac{1}{2}\omega(t)e^{-i\gamma(t)}-\beta_0\sin\tfrac{1}{2}\omega(t)]e^{-i[\omega_1 t-i\phi(t)/2]},\tag{4.3}$$

$$\beta(t)=i[\beta_0\cos\tfrac{1}{2}\omega(t)e^{i\gamma(t)}+\alpha_0\sin\tfrac{1}{2}\omega(t)]e^{-i[\omega_2 t+i\phi(t)/2]}.\tag{4.4}$$

If the initial states are given by a superposition of coherent states in the form

$$\rho(0)=\int d^2\alpha\,d^2\beta\,P(\alpha)P(\beta)\,|\alpha,\beta\rangle\langle\alpha\beta|,\tag{4.5}$$

then the density matrix at time t is given by

$$\rho(t)=\int d^2\alpha\,d^2\beta\,P(\alpha)P(\beta)\,|\alpha(t),\beta(t)\rangle\langle\alpha(t),\beta(t)|.\tag{4.6}$$

We are particularly interested in the case where one of the modes are initially chaotic in the sense of possessing Gaussian P representation. If we let

$$P(\alpha)=\delta^2(\alpha-\alpha_0),\tag{4.7}$$

$$P(\beta)=\frac{1}{\pi\langle m\rangle}e^{-|\beta-\beta_0|^2/\langle m\rangle},\tag{4.8}$$

and substitute, Eqs. (4.7) and (4.8) into Eq. (4.6), we obtain

$$\begin{aligned}\rho(t)=\int&\frac{d^2\alpha\,d^2\beta}{\pi\langle m\rangle}\delta^2(\alpha-\alpha_0)e^{-|\beta-\beta_0|^2/\langle m\rangle}\\&\times|\alpha(t),\beta(t)\rangle\langle\alpha(t),\beta(t)|.\end{aligned}\tag{4.9}$$

It is more convenient at this point to consider the reduced density matrix for mode A or mode B only defined by

$$\rho_A(t)\equiv\mathrm{Tr}_B\,\rho(t),\tag{4.10}$$

$$\rho_B(t)\equiv\mathrm{Tr}_A\,\rho(t).\tag{4.11}$$

Taking the indicated trace and performing the integration we obtain

$$\rho_A(t)=\int\frac{d^2\gamma}{\pi\langle m\rangle S^2(t)}\exp\left[\frac{-|\gamma-\alpha(t)|^2}{\langle m\rangle S^2(t)}\right]|\gamma\rangle\langle\gamma|,\tag{4.12}$$

$$\rho_B(t)=\int\frac{d^2\gamma}{\pi\langle m\rangle C^2(t)}\exp\left[\frac{-|\gamma-\beta(t)|^2}{\langle m\rangle C^2(t)}\right]|\gamma\rangle\langle\gamma|,\tag{4.13}$$

where

$$S(t)\equiv\sin\tfrac{1}{2}\omega(t),\tag{4.14}$$

$$C(t)\equiv\cos\tfrac{1}{2}\omega(t).\tag{4.15}$$

Equations (4.12) and (4.13) show that as the energy is oscillating between the two modes, the coherence and photon statistical proterties are exchanged as well. It is as though the photons remember their initial coherence and statistical properties and carry these properties with them as they oscillate between the modes.

For later purposes we shall record here also the case where both modes are initially chaotic, i.e., $P(\alpha)$ also takes the form

$$P(\alpha)=\frac{1}{\pi\langle n\rangle}\,e^{-|\alpha-\alpha_0|^2/\langle n\rangle} \tag{4.16}$$

and $P(\beta)$ is given by Eq. (4.8). Then the reduced density matrices at time t are given by

$$\rho_A(t)=\int\frac{d^2\gamma}{\pi[\langle n\rangle C^2(t)+\langle m\rangle S^2(t)]}\times\exp\left[\frac{-|\gamma-\alpha(t)|^2}{\langle n\rangle C^2(t)+\langle m\rangle S^2(t)}\right]|\gamma\rangle\langle\gamma|\,, \tag{4.17}$$

$$\rho_B(t)=\int\frac{d^2\gamma}{\pi[\langle n\rangle S^2(t)+\langle m\rangle C^2(t)]}\times\exp\left[\frac{-|\gamma-\beta(t)|^2}{\langle n\rangle S^2(t)+\langle m\rangle C^2(t)}\right]|\gamma\rangle\langle\gamma|\,. \tag{4.18}$$

The advantage of describing the system in terms of density matrices such as Eqs. (4.2), (4.12), (4.13), (4.17), and (4.18) is that the mean value of the normally ordered product of an arbitrary number of field operators can be calculated as moments of the P representation. In the case of Gaussian P representation they can be shown to be proportional to associated Laguerre polynomials. The required moments have been worked our by Mollow and Glauber[12] and will not be repeated here. We simply write down the result for the case of $\rho_A(t)$, $\rho_B(t)$ given by Eqs. (4.17) and (4.18), since the other cases that we have considered may be obtained as special cases by taking the limits $\langle n\rangle\to 0$ or $\langle m\rangle\to 0$ or both:

$$\mathrm{Tr}\rho_A(t)(a^\dagger)^n(a)^m=n\,![\langle n\rangle C^2(t)+\langle m\rangle S^2(t)]^n[\alpha(t)]^{m-n}\times L_n^{(m-n)}\left(\frac{-|\alpha(t)|^2}{\langle n\rangle C^2(t)+\langle m\rangle S^2(t)}\right), \tag{4.19}$$

$$\mathrm{Tr}\rho_B(t)(b^\dagger)^n(b)^m=n\,![\langle m\rangle C^2(t)+\langle n\rangle S^2(t)]^n[\beta(t)]^{m-n}\times L_n^{(m-n)}\left(\frac{-|\beta(t)|^2}{\langle m\rangle C^2(t)+\langle n\rangle C^2(t)}\right). \tag{4.20}$$

V. SOLUTIONS FOR DENSITY OPERATOR WITH INITIAL NUMBER EIGENSTATES

In principle, since the coherent states form a complete (in fact an overcomplete) set, we may first expand an arbitrary initial state in terms of the coherent-state basis and apply the results of Secs. II and IV to obtain the density matrix at time t. Such an approach, although possible in principle, is inconvenient in practice. In particular, if the initial states are eigenstates of the number operator, the expansion in terms of a diagonal coherent-state representation is extremely singular.[13] We shall find that it is in fact simpler and more concise to work in the number-state basis. This comes about because of the observations we made at the end of Sec. II on the algebraic properties of the model, namely, the operators in the Hamiltonian form a $SU(2)$ or $U(2)$ algebra. Consequently, the unitary operator $U_R(t)$ may be looked upon as the operator for finite rotation. In addition, J^2 may be written as

$$\begin{aligned}J^2&=\tfrac{1}{2}(J_+J_-+J_-J_+)+J_3^2\\&=\tfrac{1}{4}(N_a+N_b)(N_a+N_b+2)\\&=I(I+1)\,,\end{aligned} \tag{5.1}$$

where I is the constant of motion defined in Eq. (2.9). Consequently, eigenstates of the number operators $|n_a,n_b\rangle$ are also eigenstates of the angular momentum operators and may be labeled in terms of the eigenvalues j, m of J^2 and J_3, respectively. From Eqs. (2.10) and (5.1) we have

$$j=\tfrac{1}{2}(N_a+N_b)\,, \tag{5.2}$$

$$m=\tfrac{1}{2}(N_a-N_b)\,. \tag{5.3}$$

We note that according to Eqs. (5.1) and (2.8) j is a constant of motion.

The action of $U_R(t)$ on an eigenstate of the number operator may now simply be obtained:

$$\begin{aligned}U_R(t)|n_a,n_b\rangle&=U_R(t)|j,m\rangle\\&=\textstyle\sum_{m'}D^j_{m'm}(\gamma(t)-\pi,\omega(t),\gamma(t))|j,m'\rangle\,,\end{aligned} \tag{5.4}$$

where $D^j_{m'm}$ are the standard rotation matrices[14] and $\omega(t)$ and $\gamma(t)$ are the Euler angles determined from Eqs. (3.11) and (3.12). From standard formulas for the rotation matrices we obtain

$$D^j_{m'm}(\gamma(t)-\pi,\omega(t),\gamma(t))=e^{-i(m+m')\gamma(t)}(-1)^{j+m'-m}\left[\frac{(j+m')!}{(j-m')!(j+m)!(j-m)!}\right]^{1/2}\times[\sin\tfrac{1}{2}\omega(t)]^{-m'+m}[\cos\tfrac{1}{2}\omega(t)]^{-m-m'}\frac{d}{d\cos^2\frac{1}{2}\theta}[(\cos^2\tfrac{1}{2}\theta)^{j+m}(1-\cos^2\tfrac{1}{2}\theta)^{j-m}]\,. \tag{5.5}$$

The density matrix at time t is then given by

$$\begin{aligned}\rho(t)&=U(t)\rho(0)U^\dagger(t)=U(t)\,|n_a,n_b\rangle\langle n_a,n_b|\,U^\dagger(t)=U(t)\,|j,m\rangle\langle j,m|\,U^\dagger(t)\\&=\sum_{m'm''}D^j_{m'm}(\gamma(t)-\pi,\omega(t),\gamma(t))D^{j*}_{mm''}(\gamma(t)-\pi,\omega(t),\gamma(t))\,|jm'\rangle\langle jm''|\\&\quad\times\exp\{i(m''-m')[\omega_1t+\phi(t)/2]-i(m''-m')[\omega_2t-\phi(t)/2]\}\,.\end{aligned}\tag{5.6}$$

As an example consider the probability of finding n_a' photons in the A mode and n_b' photons in the B mode at time t. It is given by

$$\begin{aligned}\langle n_a',n_b'|\rho(t)|n_a',n_b'\rangle&=\sum_{m'm''}D^j_{m'm}(\gamma(t)-\pi,\omega(t),\gamma(t))D^{j*}_{mm''}(\gamma(t)-\pi,\omega(t),\gamma(t))\\&\quad\times\langle n_a',n_b'|jm'\rangle\langle jm''|n_a',n_b'\rangle\exp\{i(m''-m')[(\omega_1-\omega_2)t+\phi(t)]\}\\&=\sum_{m'm''}D^j_{m'm}(\gamma(t)-\pi,\omega(t),\gamma(t))D^{j*}_{mm''}(\gamma(t)-\pi,\omega(t),\gamma(t))\\&\quad\times\delta_{j,(n_a'+n_b')/2}\,\delta_{(n_a'-n_b')/2,m'}\,\delta_{(n_a'-n_b')/2,m''}\exp\{i(m''-m')[(\omega_1-\omega_2)t+\phi(t)]\}\\&=|D^{j=(n_a'+n_b')/2}_{(n_a'-n_b')/2,(n_a-n_b)/2}(\gamma(t)-\pi,\omega(t),\gamma(t))|^2\,.\end{aligned}\tag{5.7}$$

The expectation value of the product of an arbitrary number of field operators may also be easily evaluated. We first observe that the density matrix is diagonal in j for all time; hence the expectation values of any product with unequal number of field operators and their adjoints must vanish, i.e.,

$$\mathrm{Tr}\rho(t)(a^\dagger)^{l_1}(b^\dagger)^{l_2}(a)^{l_3}(b)^{l_4}=0\quad\text{unless }l_1+l_2=l_3+l_4\,.\tag{5.8}$$

If $l_1+l_2=l_3+l_4$, the product of field operators can always be expressed in terms of the angular momentum operators J_i's and I. Hence it is sufficient to consider the expectation values of the product of normal ordered $U(\alpha)$ generators.

$$\begin{aligned}\mathrm{Tr}\rho(t)(J_+)^P(I)^q(J_3)^r(J_-)^S&=\sum_{m'm''}D^j_{m'm}(\gamma(t)-\pi,\omega(t),\gamma(t))D^{j*}_{mm''}(\gamma(t)-\pi,\omega(t),\gamma(t))\\&\quad\times\exp\{i(m''-m')[(\omega_1-\omega_2)t+\phi(t)]\}\langle jm''|J_+^PI^qJ_3^rJ_-^S|jm'\rangle\\&=\sum_{m'm''}D^j_{m'm}(\gamma(t)-\pi,\omega(t),\gamma(t))D^{j*}_{mm''}(\gamma(t)-\pi,\omega(t),\gamma(t))\\&\quad\times\exp\{i(m''-m')[(\omega_1-\omega_2)t+\phi(t)]\}\delta_{m'-s,m''-p}\\&\quad\times(m'-S)^qj^q\left[\frac{(j+m')!(j-m'+s)!(j+m'')!(j-m''+p)!}{(j+m'-s)!(j-m')!(j+m''-p)!(j-m'')!}\right]^{1/2}\,.\end{aligned}\tag{5.9}$$

VI. SOLUTIONS FOR DENSITY MATRIX WITH MIXED INITIAL STATES

In this section we shall consider the case where the initial states of one mode possess a well-behaved P representation while the other is an eigenstate of the number operator. The initial density matrix for this case may be written in the number representation and its time development solved by the method of Sec. V. This approach, although in principle feasible, is too cumbersome to be useful. We shall show in this section that for the case of one mode initially eigenstates of the number operator, the other initially possessing Gaussian P representation centered at the origin, a closed form for the density matrix at time t can be obtained. We shall closely follow here the method of Mollow and Glauber.[12]

We start with the solutions (4.17) and (4.18) for the case where both modes initially possess Gaussian P representation with $\alpha_0=\beta_0=\alpha(t)=\beta(t)=0$. In the number representation the initial state of the A mode may be written as

$$\begin{aligned}\rho_A(0)&=\frac{1}{1+\langle n\rangle}\sum_{n=0}^{\infty}\left[\frac{\langle n\rangle}{1+\langle n\rangle}\right]^n|n\rangle_{A\,A}\langle n|\\&=(1-x)\sum_{n=0}^{\infty}x^n|n\rangle_{A\,A}\langle n|\,,\end{aligned}\tag{6.1}$$

where

$$x=\langle n\rangle/(1+\langle n\rangle)\,.$$

On the other hand we may also expand $\rho_A(t)$ given in Eq. (4.17) into a polynomial in x if we make the substitution

$$\langle n\rangle=x/(1-x)\tag{6.2}$$

into Eq. (4.17). The result is

$$\begin{aligned}\rho_A(t)&=(1-x)\sum_{n=0}^{\infty}x^n\int d^2\gamma\,|\gamma\rangle\langle\gamma|\,[\pi\langle m\rangle S^2(t)]^{-1}\\&\quad\times e^{-|\gamma|^2/\langle m\rangle S^2(t)}x[\mu(t)]^nL_n(y(\gamma,t))\,,\end{aligned}\tag{6.3}$$

where

$$\mu(t)=\frac{(1+\langle m\rangle S^2(t)-1}{\langle m\rangle S^2(t)}\,, \tag{6.4}$$

$$y(\gamma(t))=\frac{-|\gamma|^2C^2(t)}{\langle m\rangle S^2(t)[S^2(t)(1+\langle m\rangle)-1]}\,, \tag{6.5}$$

and we have made use of the expansion formula

$$e^{-abx/(1-bx)}=(1-x)\sum_n x^n b^n L_n(a)\,. \tag{6.6}$$

Since Eqs. (6.1) and (6.3) are related by a linear transformation

$$\rho_A(t)=\mathrm{Tr}_B U(t)\rho(0)U^\dagger(t)=\mathrm{Tr}_B U(t)\rho_A(0)\rho_B(0)U^\dagger(t)\,, \tag{6.7}$$

we may substitute Eqs. (6.1) and (6.3) into (6.7) and equate coefficients of x^n to obtain

$$\begin{aligned}\rho_A^n(t)&=\int\frac{d^2\gamma}{\pi\langle m\rangle S^2(t)}\,e^{-|\gamma|^2/<m>S^2(t)}\\&\quad\times[\mu(t)]^n L_n(y(\gamma,t))|\gamma\rangle\langle\gamma|\\&=\mathrm{Tr}_B U(t)\rho_A^n(0)\rho_B(0)U^\dagger(t)\,,\end{aligned} \tag{6.8}$$

where

$$\rho_A^n(0)\equiv|n\rangle_{A\,A}\langle n|\,.$$

Thus the reduced density matrix for the A mode at time t possess a P representation in the form

$$\begin{aligned}P(\gamma,t)&=[\pi\langle m\rangle S^2(t)]^{-1}e^{-|\gamma|^2/<m>S^2(t)}\\&\quad\times[\mu(t)]^n L_n(y(\gamma,t))\,.\end{aligned} \tag{6.9}$$

The expression for $P(\gamma,t)$ has a number of interesting features. For $t=t_n$ such that $S^2(t_n)=1$, it is a pure Gaussian and is exactly equal to the initial Gaussian P representation for the B mode. For $t=t_m$ such that $S^2(t_m)=0$, it is extremely singular at the origin and vanishes everywhere else and gives rise to a pure n quantum state. Thus we see again that the coherence and statistical properties of the photons are exchanged between the two modes as energies are transferred between the modes.

VII. TIME-DEPENDENT PERTURBATION THEORY

In the previous sections we have given an exhaustive theory of a quantum frequency converter in the case where the pump amplitude and phase satisfies $\dot\phi(t)/\kappa(t)=C$. In this section we shall briefly outline a time-dependent perturbation theory in the cases where the deviation from the exact soluble condition is small, namely,

$$\dot\phi(t)-C\kappa(t)=\lambda(t)\ll 1 \tag{7.1}$$

and C may be determined from the condition that $\int_0^t dt\,\lambda^2(t)$ is minimum. Referring back to Eq. (3.3), the Hamiltonian in the rotated frame may be written as

$$\begin{aligned}H_R(t)&=\kappa(t)[J_+ + J_- + (C/2)J_3]+\lambda(t)J_3\\&=H_R^0(t)+H'(t)\,.\end{aligned} \tag{7.2}$$

The time development of the system with $\lambda(t)=0$ has been completely solved and we use that as the starting point and treat $H'(t)$ perturbatively. It is more convenient to work in the interaction picture related to the rotated frame by

$$|t\rangle_1=U_R(t)\,|t\rangle_R\,, \tag{7.3}$$

where $U_R(t)=\exp[-i\int_0^t H_R^0(t')\,dt']$. The perturbation Hamiltonian $H'(t)$ in the interaction picture becomes

$$\begin{aligned}H_I'(t)&=U_R^\dagger(t)H'(t)U_R(t)\\&=\lambda(t)[J_3\cos\omega(t)-J_x\cos\gamma(t)\sin\omega(t)\\&\qquad+J_y\sin\gamma(t)\sin\omega(t)]\,.\end{aligned} \tag{7.4}$$

To lowest order in $\lambda(t)$, the effect of the perturbation Hamiltonian on the time development of the field operators and the number operators can be easily determined and the results are

$$N_a^{(1)}(t)-N_b^{(1)}(t)=N_a^0(t)-N_b^0(t)\,, \tag{7.5}$$

$$\begin{aligned}a^{(1)}(t)&=e^{-i[\omega_1 t-\phi(t)/2]}i(a(0)\\&\quad\times\{\cos\omega(t)\,e^{-i\gamma(t)}[1-iA(t)]-i\sin\omega(t)\\&\qquad\times[B(t)-C(t)]\}+b(0)\{\sin\omega(t)[1-iA(t)]\\&\qquad-i\cos\omega(t)e^{-i\gamma(t)}[B(t)+C(t)]\})\,.\end{aligned} \tag{7.6}$$

$$\begin{aligned}b^{(1)}(t)&=e^{-i[\omega_2 t+\phi(t)/2]}i(b(0)\{\cos\omega(t)\,e^{i\gamma(t)}[1-iA(t)]\\&\quad+i\sin\omega(t)[B(t)+C(t)]\}a(0)\{\sin\omega(t)[1-iA(t)]\\&\quad+i\cos\omega(t)\,e^{i\gamma(t)}[B(t)-C(t)]\})\,,\end{aligned} \tag{7.7}$$

where

$$A(t)=\tfrac{1}{2}\int_0^t\lambda(t')\cos\omega(t')\,dt'\,, \tag{7.8}$$

$$B(t)=\tfrac{1}{2}\int_0^t\lambda(t')\cos\gamma(t')\sin\omega(t')\,dt'\,, \tag{7.9}$$

$$C(t)=\tfrac{1}{2}\int_0^t\lambda(t')\sin\gamma(t')\sin\omega(t')\,dt'\,. \tag{7.10}$$

Thus to lowest order in $\lambda(t)$, the energy exchange between the modes is not affected. To second order in $\lambda(t)$, however, the effect of the perturbation Hamiltonian is to cause modifications to the amplitude and the period of energy exchange between the modes.[15]

VIII. DISCUSSIONS

In this paper the consequences of the deviation from ideal coherence of the driving pump field in the frequency converter have been examined by considering a model of quantum frequency converter with time-dependent pump amplitude and phase. We find that provided the condition $\dot{\phi}(t)/\kappa(t)=C$ is satisfied there is continuous periodic energy exchange between the modes with the periods being nonlinear functions of time. Also presented is the complete time-dependent density matrix for the system for a variety of initial states which provides the most complete statistical description available for the system. To the best of my knowledge this complete statistical description has not been given[16] before even in the case of ideal pump coherence, i.e., $\dot{\phi}(t)=\dot{\kappa}(t)=0$. The ideal case is of course contained in our results as a special case by taking the limit $C\rightarrow 0$ and $\kappa(t)\rightarrow\kappa$. For cases where the deviation $\lambda(t)=\dot{\phi}(t)-C\kappa(t)$ is small, we have outlined a time-dependent perturbation theory treatment and showed that corrections to amplitude and period of energy exchange between the modes are present only in second order of $\lambda(t)$.

The effects of pump coherence on frequency conversion have also been examined by the authors of Refs. 7 and 8. The case considered by them is that of constant amplitude and time-dependent phase, which does not satisfy the present condition. Thus their work and mine have very little overlap and, furthermore, they only solved the equations of motion approximately by the WKB method and did not give a density-matrix treatment. On the other hand, if the phase variation is slow, then $\lambda(t)$ which is essentially proportional to $\dot{\phi}(t)$ is also small and the present perturbation-theory treatment may be compared with their results. They also found that phase variation affects the rate and amplitude of energy exchange between the modes in agreement with the present result. However, they further stated that this degradation is exponential in $\lambda^2(t)$. To arrive at this conclusion, one must have a treatment of the model accurate to all order of $\lambda^2(t)$ or perform perturbation calculations to all orders of $\lambda(t)$. I do not believe that their approximation scheme has the required accuracy. In fact their approximation has exactly the same order of accuracy as my lowest-order perturbation-theory treatment, as can be seen from the fact that their solutions for the field variables violate canonical commutation realtions to second order in $\lambda(t)$. I also believe that their conclusion on equal partition of photons in the two modes in the asymptotic limit is also not warranted by their treatment. One further point of difference between their results and mine should be noted. They concluded that if the initial states of the system are coherent, asymptotically it will possess statistical properties intermediate between coherent and thermal light. This is in direct variance with Glauber's theorem, which guarantees that the system remains coherent for all time if initially coherent. The resolution of the difference lies in the realization that to arrive at their conclusion they have performed an average over a random-pump-phase ensemble. Thus their formalism describes an ensemble of experiments in which the pump phases are allowed to be completely random, whereas mine describes the results of a single experiment for which pump amplitude and phase are more or less determined functions of time or many repeated experiments with identically prepared sources. Therefore the correct conclusion is that the frequency-converted light is always coherent if initially coherent and the incoherence discussed by the authors of Refs. 7 and 8 is due to averaging over a random-pump-phase ensemble. Experimentally the present formalism would be appropriate to describe the output of a parametric frequency converter with a c.w. laser pump, whereas those of Refs. 7 and 8 would be appropriate to describe the ensemble-averaged output with a pulsed laser pump. This is an example of the well known fact that the results of an individual experiment can be quite unlike that of the ensemble average.

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Statistical Mechanics of Reacting Coulomb Gases*

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A quantum-statistical-mechanical formulation is developed for determining the equation of state of Coulomb gases. The procedure is to develop the activity expansion of the grand partition function into a true perturbation expansion in which the divergences present in the cluster expansion of the Coulomb gas have been eliminated. Ionization and dissociation appear quite naturally in this approach even though only the total number of nuclei and electrons in the system are specified. Considerable insight into the quantum-mechanical perturbation result is obtained from the classical perturbation theory. The form of the static screened Coulomb potential that replaces the classical Debye-Hückel potential is discussed. An application to the equation of state of gaseous hydrogen which takes account of all *e*-*e*, *p*-*p*, and *e*-*p* interactions is given. The formation of higher clusters such as H-*e*, H-*p*, H-H, etc., can also be systematically included. Owing to the extensive numerical calculations required, this has currently only been done in an approximate way. It is shown that the simple one-level Saha equation, including Debye-Hückel corrections for the free charges, is fairly accurate for $\rho < 10^{-3}$ g/cm^3. At greater densities the differences become significant.

I. INTRODUCTION

The literature dealing with the equation of state of multicomponent partially ionized gases is extensive.[1] However, no unambiguous general formulism for obtaining the equation of state at arbitrary gas densities has been given. The usual approach is to develop some criteria for cutting off the divergence of the atomic partition function[2] and to assume that the charged particles interact according to the Debye-Hückel theory. The free energy is then minimized subject to the stoichiometric constraints to obtain ionization equilibrium and thus the equation of state. Another approach that has been used is to assume that the bound states are also perturbed by the free charges in the system, according to the Debye-Hückel potential.[3] This gives a convergent partition function; however, it has the serious shortcoming that the thermal properties are not continuous functions of V and T; i.e., the partition function changes discontinuously at those V and T points at which bound states are perturbed into the continuum. In this paper we will approach the problem from the fundamental viewpoint of quantum-statistical mechanics and thus obtain a general formulism which is free of the difficulties associated with the above approaches.

II. QUANTUM-MECHANICAL ACTIVITY EXPANSION AND THE FORMATION OF BOUND PAIRS

Before dealing with the Coulomb gas it is instructive to first demonstrate that the activity expansion is the natural expansion to use for reacting gases. For simplicity we consider a one-component ordinary gas. The activity expansion of the pressure[4] is obtained by assuming

$$P/kT = b_1 z + b_2 z^2 + b_3 z^3 + \cdots , \tag{1}$$

where the b's are undetermined constants and

$$z = (2s+1)\lambda^{-3} e^{\mu/kT} \tag{2}$$

is called the activity (actually the standard definition of the activity is the ratio z/n, where n is the number density), μ is the chemical potential,

$$\lambda = (2\pi\hbar^2/mkT)^{1/2}$$

is the de Broglie wavelength, and s is the spin. If Eq. (1) is substituted in the grand partition function there results

$$\Xi = e^{pV/kT} = e^{V\sum_{j=1}^{\infty} b_j z^j} = 1 + \sum_{N\geq 1} \frac{Z_N V^N}{Z_1^N} z^N , \tag{3}$$

where Z_N is the canonical partition function for N particles in the volume V. If like coefficients are