that produced from ionization by Kr radiation at 116.5 nm, which provided electrons with up to 1.3-eV energy. NO^- was not observed in either case, and the NO_2^- currents were equal within the experimental precision of 10%, which strongly indicates that the reaction producing NO_2^- is not of marginal energetics. This finding is consistent with the production of NO_2^- through reaction (18); however, it does not support the production of NO_2^- through reaction (16″) and, as a consequence, the relative absence of NO^- remains at this time to be satisfactorily explained. In pursuit of the solution to this dilemma other possible explanations are being investigated and will be reported as appropriate.

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Saturation Effects in Resonant Two-Photon Processes

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Resonant two-photon absorption is discussed for the case in which the exciting field may be intense enough and near enough to resonance to cause appreciable saturation. A single pair of levels in an otherwise quite general atom is assumed to satisfy the appropriate resonance condition, and equations are derived governing the time evolution of the associated 2×2 submatrix of the full atomic density matrix. Atomic relaxation is treated explicitly. The analysis, which treats both inversion-symmetric and inversion-nonsymmetric cases within the same general formalism, is developed systematically, the necessary approximations receiving careful discussion. The results are analogous to those for the corresponding one-photon process, but with a shift in the resonance frequency proportional to the intensity of the exciting field. This frequency shift is not identical to the one calculated by time-independent (second-order) perturbation theory, and becomes large when the energy of an intermediate state of the atom approaches the mean of the energies of the active states.

In this paper we shall treat the process of two-photon absorption[1-3] in the case in which saturation effects may be appreciable. We shall treat the incident field classically, and assume it to oscillate harmonically at a frequency very nearly equal to $\hbar^{-1}$ times one-half of the energy separation of a single pair of atomic states. Intermediate states, i.e., states which are coupled to both of the active states (the active states themselves, it should be noted, may behave in effect like "intermediate states" in inversion-nonsymmetric cases[4]) are treated in full generality. The only restriction placed on them is that their energies are required to lie far enough from resonance to exclude appreciable one- and two-photon field-induced transitions from the active states. The time-dependent atomic density operator is developed as a suitable linear combination of harmonics of the field frequency, and atomic relaxation is treated explicitly. We show that the elements of the 2×2 submatrix referring to the pair of active states obey equations formally analogous to those which arise in the more familiar one-photon process,[5,6,6a] but with a field-intensity-dependent shift in the resonance frequency.

This effective shift in the energy separation of the levels in question emerges directly from the solution of the time-dependent problem, and differs significantly from the shift predicted by time-independent second-order perturbation theory.

Let us consider an atom with energy eigenstates $|j\rangle$ and corresponding eigenvalues E_j, where $j = 0, 1, 2, \ldots$. The atom is assumed to be coupled to an incident electric field, in the dipole approximation, by the interaction Hamiltonian

$$H_I(t) = -\vec{\mu} \cdot \vec{E}(t) , \tag{1}$$

where the dipole moment operator $\vec{\mu}$ is allowed, in order to allow the possibility of inversion-nonsymmetric cases,[4] to have nonvanishing diagonal as well as off-diagonal matrix elements.[7] The electric field $\vec{E}(t)$ is assumed to oscillate at a fixed frequency ω and to be polarized in the direction specified by the unit vector $\hat{e}_0$:

$$\vec{E}(t) = (1/\sqrt{2})\,\hat{e}_0[\mathcal{E}(t) + \mathcal{E}^*(t)] , \tag{2a}$$

$$\mathcal{E}(t) = \mathcal{E}_0 e^{-i\omega t} . \tag{2b}$$

For simplicity, we shall assume that the atomic relaxation process is specified by the strong-collision model[5] (other relaxation processes may be treated in an entirely straightforward manner). The matrix elements of the time-dependent atomic density operator are then governed by the equations

$$\left(\frac{d}{dt} + i\omega_{jk} + \kappa\right)\rho_{jk}(t) - \kappa\,\delta_{jk}\bar{n}_j^{(0)} = i[\mathcal{E}(t) + \mathcal{E}^*(t)]\sum_{m=0}^{\infty}[\lambda_{jm}\rho_{mk}(t) - \rho_{jm}(t)\lambda_{mk}] , \tag{3}$$

where κ is the collision frequency, $\bar{n}_j^{(0)}$ is the (thermal) probability of finding the atom in the state $|j\rangle$ immediately after a collision, and the quantities ω_{jk} and λ_{jk} are defined as

$$\omega_{jk} \equiv (E_j - E_k)/\hbar , \tag{4}$$

$$\lambda_{jk} \equiv (\vec{\mu}_{jk} \cdot \hat{e}_0)/\hbar\sqrt{2} . \tag{5}$$

In the resonant two-photon excitation process we wish to consider, the exciting field induces appreciable off-diagonal elements of the density operator which oscillate at frequencies in the neighborhood of the frequencies $\pm 2\omega$, as well as inducing appreciable changes in the slowly varying diagonal components $\bar{n}_j(t)$. In addition, small nonresonant terms are induced at frequencies which differ by $\pm\omega$ from the resonant components, i.e., at frequencies near $\pm\omega$ and $\pm 3\omega$. We define $\alpha_{jk}(t)$ as the term in $\rho_{jk}(t)$ with Fourier components in the neighborhood of the frequency $+2\omega$, and $\beta_{jk}^{(-)}(t)$ and $\beta_{jk}^{(+)}(t)$ as the terms with components near $+\omega$ and $+3\omega$, respectively, so that we may write

$$\alpha_{jk}(t) = e^{-2i\omega t}\,\bar{\alpha}_{jk}(t) , \tag{6a}$$

$$\beta_{jk}^{(-)}(t) = e^{-i\omega t}\,\bar{\beta}_{jk}^{(-)}(t) , \tag{6b}$$

$$\beta_{jk}^{(+)}(t) = e^{-3i\omega t}\,\bar{\beta}_{jk}^{(+)}(t) , \tag{6c}$$

where $\bar{\alpha}_{jk}(t)$ and $\bar{\beta}_{jk}^{(\pm)}(t)$ are slowly varying functions of time. The Hermiticity of $\rho(t)$ then implies that its matrix elements are given by the relation

$$\rho_{jk}(t) = \delta_{jk}\bar{n}_j(t) + [\alpha_{jk}(t) + \alpha_{kj}^*(t)] + [\beta_{jk}^{(-)}(t) + \beta_{kj}^{(-)*}(t)] + [\beta_{jk}^{(+)}(t) + \beta_{kj}^{(+)*}(t)] . \tag{7}$$

Let us substitute this expression for $\rho_{jk}(t)$ into Eq. (3) and then make the appropriate resonant approximation, i.e., equate separately to each term on the left-hand side only those terms on the right-hand side which oscillate at nearly the same frequency. We find in this way that the functions $\bar{n}_j(t)$, $\alpha_{jk}(t)$, and $\beta_{jk}^{(\pm)}(t)$ are governed by the differential equations

$$\left(\frac{d}{dt} + \kappa\right)(\bar{n}_j(t) - \bar{n}_j^{(0)}) = i\mathcal{E}^*(t)\sum_{m=0}^{\infty}[\lambda_{jm}\beta_{mj}^{(-)}(t) - \beta_{jm}^{(-)}(t)\lambda_{mj}] + \text{c. c.} , \tag{8a}$$

$$\left(\frac{d}{dt} + i\omega_{jk} + \kappa\right)\alpha_{jk}(t) = i\sum_{m=0}^{\infty}\{\lambda_{jm}[\mathcal{E}(t)\beta_{mk}^{(-)}(t) + \mathcal{E}^*(t)\beta_{mk}^{(+)}(t)] - [\mathcal{E}(t)\beta_{jm}^{(-)}(t) + \mathcal{E}^*(t)\beta_{jm}^{(+)}(t)]\lambda_{mk}\} , \tag{8b}$$

$$\left(\frac{d}{dt} + i\omega_{jk} + \kappa\right)\beta_{jk}^{(-)}(t) = i\mathcal{E}(t)\lambda_{jk}[\bar{n}_k(t) - \bar{n}_j(t)] + i\mathcal{E}^*(t)\sum_{m=0}^{\infty}[\lambda_{jm}\alpha_{mk}(t) - \alpha_{jm}(t)\lambda_{mk}] , \tag{9a}$$

$$\left(\frac{d}{dt} + i\omega_{jk} + \kappa\right)\beta_{jk}^{(+)}(t) = i\mathcal{E}(t)\sum_{m=0}^{\infty}[\lambda_{jm}\alpha_{mk}(t) - \alpha_{jm}(t)\lambda_{mk}] . \tag{9b}$$

At this point we shall make the assumption that the two-photon process under consideration induces appreciable transitions only between a single pair of states, which we shall call $|0\rangle$ and $|1\rangle$ (without, however, implying any ordering in energy between either one of these states and any other state $|j\rangle$ for which $j \geq 2$). The energy separation between the states $|0\rangle$ and $|1\rangle$ is thus taken to be approximately equal to twice the energy $\hbar\omega$ of one field quantum, so that we have

$$\omega_{10} \equiv (E_1 - E_0)/\hbar \approx 2\omega , \tag{10}$$

a relation which we assume to be well satisfied for the pair of states in question, but not for any other pair of states in the atom. It is apparent then from Eqs. (6a) and (8b) that the only appreciable (positive) double-frequency component in the density

matrix is the one for which $j=1$ and $k=0$. Calling this component simply $\alpha(t)[\equiv \alpha_{10}(t)]$ we may make the approximation

$$\alpha_{jk}(t) = \delta_{j1}\delta_{0k}\alpha(t) \tag{11}$$

in Eqs. (9). We find then that the functions $\beta_{jk}^{(\pm)}(t)$ obey the equations

$$\left(\frac{d}{dt} + i\omega_{jk} + \kappa\right)\beta_{jk}^{(-)}(t) = i\mathcal{E}(t)\lambda_{jk}(\bar{n}_k(t) - \bar{n}_j(t)) + i\mathcal{E}^*(t)(\lambda_{j1}\delta_{0k} - \delta_{j1}\lambda_{0k})\alpha(t) , \tag{12a}$$

$$\left(\frac{d}{dt} + i\omega_{jk} + \kappa\right)\beta_{jk}^{(+)}(t) = i\mathcal{E}(t)(\lambda_{j1}\delta_{0k} - \delta_{j1}\lambda_{0k})\alpha(t) . \tag{12b}$$

The 2×2 submatrix of the full density matrix which refers to the states $|0\rangle$ and $|1\rangle$ has, in addition (possibly) to small nonresonant components proportional to $e^{\pm i\omega t} \approx e^{\pm i\omega_{10}t/2}$ and $e^{\pm 3i\omega t} \approx e^{\pm 3i\omega_{10}t/2}$, the appreciable resonant components $\bar{n}_1(t) \approx \rho_{11}(t)$, $\bar{n}_0(t) \approx \rho_{00}(t)$, $\alpha(t) \approx \rho_{10}(t)$, and $\alpha^*(t) \approx \rho_{01}(t)$. The resonant components obey, according to Eqs. (8), the differential equations

$$\left(\frac{d}{dt} + \kappa\right)(\bar{n}_1(t) - \bar{n}_1^{(0)}) = i\mathcal{E}^*(t)\sum_{j=0}^{\infty}[\lambda_{1j}\beta_{j1}^{(-)}(t) - \beta_{1j}^{(-)}(t)\lambda_{j1}] + \text{c. c.} , \tag{13a}$$

$$\left(\frac{d}{dt} + \kappa\right)(\bar{n}_0(t) - \bar{n}_0^{(0)}) = i\mathcal{E}^*(t)\sum_{j=0}^{\infty}[\lambda_{0j}\beta_{j0}^{(-)}(t) - \beta_{0j}^{(-)}(t)\lambda_{j0}] + \text{c. c.} , \tag{13b}$$

$$\left(\frac{d}{dt} + i\omega_{10} + \kappa\right)\alpha(t) = i\sum_{j=0}^{\infty}\{\lambda_{1j}[\mathcal{E}(t)\beta_{j0}^{(-)}(t) + \mathcal{E}^*(t)\beta_{j0}^{(+)}(t)] - [\mathcal{E}(t)\beta_{1j}^{(-)}(t) + \mathcal{E}^*(t)\beta_{1j}^{(+)}(t)]\lambda_{j0}\} . \tag{13c}$$

The driving functions $\beta(t)$ and $\beta^*(t)$ in these relations play a role which is in fact very similar to the role played by the amplitudes of the intermediate states in second-order perturbation-theory calculations of two-photon absorption. It is necessary, in order to reduce the problem to one referring only to the states $|0\rangle$ and $|1\rangle$, to make a further assumption, essentially equivalent to the assumption that the intermediate states are virtual rather than real: We must assume that no appreciable one-photon field-induced transitions take place from either one of the states $|0\rangle$ or $|1\rangle$ to any other state of the atom.[8] This is simply the condition that the quantities $|E_j - E_0|$ and $|E_j - E_1|$ are not too close to the energy $\hbar\omega$ of a field quantum, and it guarantees that the intermediate amplitudes $\beta(t)$ in Eq. (13) will be small. We must assume, in particular, that the relations

$$|\omega_{jk} - \omega| \gg \kappa , \tag{14a}$$

$$|\omega_{jk} - \omega| \gg |\tfrac{1}{2}\omega_{10} - \omega| \tag{14b}$$

are satisfied for all ω_{jk} for which either j or k is 0 or 1. If we also assume that the frequency bandwidths of the functions $\bar{n}(t)$ and $\alpha(t)$ in Eqs. (12) are small compared to $|\omega_{jk} - \omega|$ (the condition required to justify this assumption is discussed later), then we may easily show that Eqs. (12) can be solved for $\beta_{jk}^{(\pm)}(t)$ simply by making the approximations

$$\frac{d}{dt}\beta_{jk}^{(-)}(t) \approx -i\omega\beta_{jk}^{(-)}(t) \approx -\tfrac{1}{2}i\omega_{10}\beta_{jk}^{(-)}(t) ,$$

$$\frac{d}{dt}\beta_{jk}^{(+)}(t) \approx -3i\omega\beta_{jk}^{(+)}(t) \approx -\tfrac{3}{2}i\omega_{10}\beta_{jk}^{(+)}(t) .$$

The functions $\beta_{jk}^{(\pm)}(t)$ are thus given at any time by the relations

$$\beta_{jk}^{(-)}(t) = \left(\frac{1}{\omega_{jk} - \frac{1}{2}\omega_{10}}\right)\{\mathcal{E}(t)\lambda_{jk}[\bar{n}_k(t) - \bar{n}_j(t)] + \mathcal{E}^*(t)(\lambda_{j1}\delta_{0k} - \delta_{j1}\lambda_{0k})\alpha(t)\} , \tag{15a}$$

$$\beta_{jk}^{(+)}(t) = \left(\frac{1}{\omega_{jk} - \frac{3}{2}\omega_{10}}\right)\mathcal{E}(t)(\lambda_{j1}\delta_{0k} - \delta_{j1}\lambda_{0k})\alpha(t) , \tag{15b}$$

for all pairs of indices j and k satisfying the off-resonant conditions described above. Since these conditions are by hypothesis valid for all of the functions on the right-hand sides of Eqs. (13), the functions $\beta(t)$ may be eliminated entirely from the problem, thus reducing the Eqs. (13) to a form in which only $\alpha(t)$ and the occupation numbers $\bar{n}_j(t)$ appear explicitly.

It is equally true, although it is not apparent from the foregoing discussion, that the contributions from the occupation numbers $\bar{n}_j(t)$ for $j \geq 2$ vanish identically when Eqs. (15) are substituted into Eqs. (13). Equations (13a) and (13b), for example, when the functions $\beta^{(-)}(t)$ in them are obtained from Eq. (15a), take the simple form

$$\left(\frac{d}{dt} + \kappa\right)(\bar{n}_1(t) - \bar{n}_1^{(0)}) = -ig_2^*\mathcal{E}^{*2}(t)\alpha(t) + ig_2\mathcal{E}^2(t)\alpha^*(t) , \tag{16a}$$

$$\left(\frac{d}{dt} + \kappa\right)(\bar{n}_0(t) - \bar{n}_0^{(0)}) = ig_2^*\mathcal{E}^{*2}(t)\alpha(t) - ig_2\mathcal{E}^2(t)\alpha^*(t) , \tag{16b}$$

where the complex parameter g_2 is defined as

$$g_2 = \sum_{j=0}^{\infty}\frac{\lambda_{1j}\lambda_{j0}}{\omega_{j0} - \frac{1}{2}\omega_{10}} \tag{17a}$$

$$= \sum_{j=2}^{\infty}\frac{\lambda_{1j}\lambda_{j0}}{\omega_{j0} - \frac{1}{2}\omega_{10}} + \frac{(\lambda_{11} - \lambda_{00})\lambda_{10}}{\frac{1}{2}\omega_{10}} . \tag{17b}$$

Equations (16) for the occupation numbers $\bar{n}_1(t)$ and $\bar{n}_0(t)$ have the same form as the ones which arise in the analogous one-photon process, but with the positive-frequency part of the driving field $\mathcal{E}(t)$ replaced by $\mathcal{E}^2(t)$, and with the dipole matrix element connecting the two states in question replaced by g_2, the effective "two-photon matrix element" that appears in perturbation-theory treatments of two-photon absorption.[1,2]

That essentially the same analogy holds for the equation governing the time dependence of $\alpha(t)$ can be verified by substituting for the functions $\beta(t)$ in Eq. (13c) the values given by Eqs. (15). Again we find that the contributions from the terms proportional to $\bar{n}_j(t)$ for $j \geq 2$ cancel out, and the equation for $\alpha(t)$ is found to be, in direct analogy to the one-photon case,

$$\left(\frac{d}{dt} + i(\omega_{10} + \delta\omega_{10}) + \kappa\right)\alpha(t) = -ig_2\mathcal{E}^2(t)\,[\bar{n}_1(t) - \bar{n}_0(t)]\,, \tag{18}$$

where g_2 is the parameter defined by Eqs. (17), and the field-intensity-dependent frequency shift $\delta\omega_{10}$ is given by the relation

$$\delta\omega_{10} = -2|\mathcal{E}_0|^2 \sum_{j=0}^{\infty}\left(\frac{|\lambda_{j1}|^2\omega_{j1}}{\omega_{j1}^2 - \frac{1}{4}\omega_{10}^2} - \frac{|\lambda_{j0}|^2\omega_{j0}}{\omega_{j0}^2 - \frac{1}{4}\omega_{10}^2}\right)\,. \tag{19}$$

This expression for the shift in resonance frequency resembles the result one would obtain by calculating the energy shifts for the states $|0\rangle$ and $|1\rangle$ by means of time-independent second-order perturbation theory, replacing the driving field by its rms value. The result given by Eq. (19) is significantly different from the time-independent result,[8a] however, in the presence of the term $\frac{1}{4}\omega_{10}^2 \approx \omega^2$ in the denominators. This difference is especially important if the energy of an intermediate state $|j\rangle$ lies near the mean of the energies E_0 and E_1 [while not, of course, violating the conditions (14)], the value for $\delta\omega_{10}$ given by Eq. (19) becoming singular in the limit $E_j \to \frac{1}{2}(E_1 + E_0)$. Singularities also exist, it should be noted, both for $E_j \to E_1 + \frac{1}{2}\hbar\omega_{10}$ and for $E_j \to E_0 - \frac{1}{2}\hbar\omega_{10}$.

The equilibrium solution to Eqs. (16) and (18) for the occupation numbers $\bar{n}_1$ and $\bar{n}_0$ is

$$\bar{n}_1 - \bar{n}_1^{(0)} = \frac{\frac{1}{2}\Omega_2^2}{\kappa^2 + (\omega_{10} + \delta\omega_{10} - 2\omega)^2 + \Omega_2^2}\,(\bar{n}_0^{(0)} - \bar{n}_1^{(0)})\,, \tag{20a}$$

$$\bar{n}_0 - \bar{n}_0^{(0)} = -(\bar{n}_1 - \bar{n}_1^{(0)})\,, \tag{20b}$$

where Ω_2 is the two-photon transition rate

$$\Omega_2 = 2g_2|\mathcal{E}_0|^2\,. \tag{21}$$

It is worth noting that just as in the case of resonant one-photon transitions, the exciting field in the two-photon case does not alter the trace of the submatrix referring to the pair of active levels, i.e., $\bar{n}_1 + \bar{n}_0 = \bar{n}_1^{(0)} + \bar{n}_0^{(0)}$. This relation is a simple consequence of our assumption that no resonant one-photon transitions take place from either of the states $|0\rangle$ and $|1\rangle$ to any other state. In fact, if we extend this assumption so as to apply to any pair of states, i.e., if we assume that Eqs. (14) hold for all pairs of indices j and k, then Eqs. (15) also hold quite generally, and we find by substituting Eq. (15a) into Eq. (8a) that for $j \geq 2$,

$$\left(\frac{d}{dt} + \kappa\right)[\bar{n}_j(t) - \bar{n}_j^{(0)}] = 0\,, \tag{22}$$

and hence that in equilibrium $\bar{n}_j = \bar{n}_j^{(0)}$. The atomic populations for states other than $|0\rangle$ and $|1\rangle$ are thus unaltered by the driving field in the approximation we are considering.[9]

That this approximation requires that an additional condition be placed either on the energies of the intermediate states or on the intensity of the driving field can be seen by considering the exact equilibrium solution to Eq. (12a), without making use of the conditions (14). In place of the factor $[\omega_{jk} - \frac{1}{2}\omega_{10}]^{-1}$ in Eq. (15a), we then have the factor $(\omega_{jk} - \omega - i\kappa)^{-1}$, leading to a correction term in $\beta_{jk}^{(-)}(t)$ approximately equal to $(\omega - \frac{1}{2}\omega_{10} + i\kappa)/(\omega_{jk} - \omega)^2$ times the expression in curly brackets in Eq. (15a). When this correction is included in the relation (8a), we find that the correction to the occupation numbers $\bar{n}_j$ (in equilibrium) is of order $\mathcal{E}^2\lambda^2/(\omega_{jk} - \omega)^2$. We must therefore impose, in addition to the conditions (14), the further condition

$$|\omega_{jk} - \omega| \gg |\lambda\mathcal{E}_0|\,, \tag{23}$$

which may easily be satisfied even when the values of the relevant parameters lead to an appreciable degree of saturation. It is worth noting that this same condition (23) also implies that the parameter Ω_2, which is essentially the frequency bandwidth of the functions $\bar{n}(t)$ and $\alpha(t)$, is small compared with $|\omega_{jk} - \omega|$, and hence is necessary to justify the adiabatic approximations of Eqs. (15) in the time-dependent case.

As a check on the consistency of our approximations, it is interesting, finally, to calculate the rate at which the driving field does work. This quantity is, by virtue of Eqs. (1), (2), and (5)–(7),

$$\frac{dW}{dt} = -\frac{\partial\vec{E}(t)}{\partial t}\cdot \mathrm{tr}[\rho(t)\vec{\mu}]$$

$$= -i\hbar\omega\mathcal{E}^*(t)\sum_{j,k=0}^{\infty}\lambda_{kj}\,\beta_{jk}^{(-)}(t) + \text{c.c.}\,, \tag{24}$$

the latter expression representing an average over many periods of oscillation of the field. By substituting Eq. (15a) for $\beta_{jk}^{(-)}(t)$ into Eq. (24) and making use of Eq. (10), we find the relation

$$\frac{dW}{dt} = \hbar\omega_{10}[-ig_2^*\mathcal{E}^{*2}(t)\,\alpha(t) + ig_2\mathcal{E}^2(t)\alpha^*(t)]\,, \tag{25}$$

which corresponds exactly to the analogous relation in the case of resonant one-photon excitation, and expresses, via Eqs. (16), dW/dt as the rate of change of internal energy $(E_1 dn_1/dt + E_0 dn_0/dt)$ of the atom plus a term representing energy loss due to collisions.

[1]See W. Heitler, in *The Quantum Theory of Radiation*, 3rd ed. (Oxford U. P., London, 1957), Chap. 4, for an outline of the basic (perturbation) theory of multiphoton processes.

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[3]A comprehensive review of the experimental and theoretical literature on multiphoton processes is given by A. M. Bonch-Bruevich and V. A. Khodovoi, Usp. Fiz. Nauk 85, 3 (1965) [Soviet Phys. Usp. 8, 1 (1965)].

[4]A. Gold and J. P. Hernandez [Phys. Rev. 139, A2002 (1965)] have discussed the possibility of observing both one- and two-photon transitions between the same pair of levels, due to phonon-assisted parity mixing.

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[6a]T. Oka and T. Shimizu [Phys. Rev. A 2 , 587 (1970)] have observed strong two-photon excitations in the microwave region. Their discussion of the process, which is based on pure states, leads for the simple models they consider to results similar to ours.

The analysis presented here applies equally well, with minor changes in notation, to the case of rf-induced transitions between Zeeman sublevels in a strong magnetic field (Ref. 3). In that case diagonal matrix elements in the interaction Hamiltonian will be present whenever the rf field has nonvanishing components in the direction of the constant applied field.

[8]In effect what we are requiring is that the process under consideration be a bona fide two-photon process, and not simply a succession of one-photon processes.

[8a]Time-independent perturbation theory does, on the other hand, lead to Eq. (19) for the frequency shift if the incident field is treated *quantum-mechanically*, and is represented by a single highly excited mode of oscillation.

[9]It should be noted, however, that for atomic relaxation mechanisms other than the particularly simple one under consideration here, the field may *indirectly* affect the atomic populations $\bar{n}_j$ for $j \geq 2$ (as well as the quantity $\bar{n}_1 + \bar{n}_0$), since altering the ratio $\bar{n}_1/\bar{n}_0$ would in general have the effect of producing a net decay rate to (or from) the other states of the atom.

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Ground-State Energy of a Many-Particle Boson System

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The ground state of a many-particle boson system is studied for two closely related limits: the uniform limit and the weak coupling limit. The former is defined by $\alpha = 1 - g(0) \ll 1$ and the latter by $\beta = (N - N_0)/N \ll 1$, where $g(r)$ is the radial distribution function and N_0 is the mean occupation number of the zero-momentum state. In the uniform limit the variation-perturbation approach based on (a) the method of correlated basis functions and (b) the series expansion in powers of α is found to be equivalent to the field-theoretic treatment given by Brueckner (for the charged-boson gas) in the weak coupling limit. In particular, it is shown that the variation-perturbation energy obtained for the uniform limit in the momentum representation is identical through second order to the ground-state energy evaluated for $\beta \ll 1$ by summing one- and two-ring diagrams in the Bogoliubov occupation-number representation. The charged-boson gas and the one-dimensional boson system with a δ-function interaction are considered to examine some of the interesting features of the uniform-limit procedure.

I. INTRODUCTION

In recent years, the ground state of a many-body boson system has been studied with a great variety of approximation methods. In particular, the field-theoretic techniques in conjunction with the Bogoliubov canonical transformation[1] have been widely employed in the development of exact theories for many-body boson systems—such as the hard-sphere boson gas at low density[2,3] and the charged-boson gas at high density.[4,5] These procedures are based on the Bogoliubov weak coupling limit[1] defined by the condition that the major fraction of the particles are in the zero-momentum state (i.e., nearly complete Bose-Einstein condensation into the state $k = 0$). Under this special limiting condition the Bogoliubov canonical transformation enables one to carry out the exact and complete summation of one-