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OSCILLATIONS IN A SYSTEM COMPRISING TWO-LEVEL MOLECULES AND A RADIATION FIELD

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The state of a system comprising one, two, or three two-level molecules and a radiation field is investigated in the interaction representation. It is shown that the interaction of molecules via the radiation field is decisive in the case of a self-consistent field and vanishes in a strong field. In the presence of a strong field, the oscillation spectrum consisting of integer harmonics is obtained for an arbitrary number of molecules.

ALEKSEEV, Vdovin, and Galitskiĭ[1] have demonstrated the existence of a collective effect in the radiation of a system of two-level molecules. It was also shown[2] that the effect can be described by introducing basis functions of the unperturbed Hamiltonian H_0 of the system comprising two-level molecules and a radiation field, with subsequent application of the perturbation-theory series for the evolution operator S(t). It turned out that many-photon radiative transitions arise in the system, with a maximum order (without "reabsorption" of the photons) determined by the density of the excited molecules (or of molecules in the ground state). The probabilities of the many-photon transitions increase with their order in accordance with a power law, so that the characteristic times of the collective processes turn out to be much shorter than the time of spontaneous emission of individual molecules. Taking this into account, we shall henceforth neglect the effect of the spontaneous emission on the dynamics of the system.

It was indicated in papers by the author[2] and by Dicke[3] that the probability of coherent emission does not depend on the wavelength. The same result is confirmed below. We confine ourselves in the exposition to an analysis of the interaction between the molecular system and only one type of photon. It is known that, as a rule, gas lasers and masers operating in the radio band operate in a single mode. The line width of gas lasers is exceedingly small and can lie in a region $\lesssim 1-2$ cps.

Recent communications report single-mode operation also in ruby lasers in the transient mode. We shall assume below that the width of the emission line (of both the self-consistent and strong field) is much smaller than the distance between the natural frequencies of the cavity, which can fluctuate as a function of the geometry in the range $\Delta \sim 10^{11}-10^{9}\ \mathrm{sec}^{-1}$ at a transition frequency $\omega_0 \sim 10^{15}\ \mathrm{sec}^{-1}$.

Starting out with the same premises as in the already mentioned papers, let us consider a system of molecules and a radiation field contained in a volume V. We shall investigate the case of a self-consistent field, when at the initial instant of time the system of molecules was excited and there were no photons, as well as the case of a strong external field, when the contribution made to it by the molecular subsystem can be neglected. The behavior of the system will be different under these limiting conditions. Neglecting, as before, the translational motion of the molecules and introducing the basis functions of the unperturbed Hamiltonian introduced by the author,[2] we obtain in the interaction representation a system of equations of motion for the amplitudes of the states of the unperturbed system ($\hbar = 1$):

$$i\frac{\partial C_n(t)}{\partial t} = \sum_{n'} \langle n|H^{int}|n'\rangle C_{n'}(t), \tag{1}$$

where n denotes the aggregate of the quantum numbers which determine the state of the system of molecules and of the radiation field.

In the case when the volume V contains one molecule which is excited at the initial instant of time and N photons, solution (1) takes the form

$$W_{2,N}(t) = 1 - W_{1,N+1}(t), \tag{2}$$

$$W_{1,N+1}(t) = \frac{2|a|^2(N+1)}{\varepsilon^2 + 4|a|^2(N+1)} \times \left\{1 - \cos\left[2\left(\frac{1}{4}\varepsilon^2 + |a|^2(N+1)\right)^{1/2} t\right]\right\};$$

$$\varepsilon = \omega - \omega_0, \quad a = \left(\frac{2\pi}{\omega_0 V}\right)^{1/2} \frac{e}{m}(\xi\mathbf{e}),$$

where ξ is the matrix element and e the polarization vector.

In the case when $N \gg 1.4|a|^2 N \gg \epsilon^2$, Eq. (2) goes over into the well-known expression (see[4], page 173):

$$W_{2,N}(t) = 1 - W_{1,N}(t),$$
$$W_{1,N}(t) = {}^1/_2\{1 - \cos[2(|a|^2 N)^{1/2} t]\}. \tag{2'}$$

Assume now that there are in the volume two molecules which are excited at the initial instant. We have altogether four state amplitudes, $C_{22,N}$, $C_{21,N+1}$, $C_{12,N+1}$, and $C_{11,N+2}$; the first figure stands here for the state of the first molecule, the second for the state of the second molecule, and the last index represents the number of photons. We have for the amplitudes the following system of equations of motion:

$$i\frac{\partial C_{22,N}}{\partial t} = a\sqrt{N+1}\, e^{i\mathbf{kR}_2 + i\varepsilon t} C_{21,N+1}$$
$$+ a\sqrt{N+1}\, e^{i\mathbf{kR}_1 + i\varepsilon t} C_{12,N+1},$$

$$i\frac{\partial C_{21,N+1}}{\partial t} = a^*\sqrt{N+1}\, e^{-i\mathbf{kR}_2 - i\varepsilon t} C_{22,N}$$
$$+ a\sqrt{N+2}\, e^{i\mathbf{kR}_1 + i\varepsilon t} C_{11,N+2},$$

$$i\frac{\partial C_{12,N+1}}{\partial t} = a^*\sqrt{N+1}\, e^{-i\mathbf{kR}_1 - i\varepsilon t} C_{22,N}$$
$$+ a\sqrt{N+2}\, e^{i\mathbf{kR}_2 + i\varepsilon t} C_{11,N+2},$$

$$i\frac{\partial C_{11,N+2}}{\partial t} = a^*\sqrt{N+2}\, e^{-i\mathbf{kR}_1 - i\varepsilon t} C_{21,N+1}$$
$$+ a^*\sqrt{N+2}\, e^{-i\mathbf{kR}_2 - i\varepsilon t} C_{12,N+1}, \tag{3}$$

with the amplitudes satisfying the initial conditions

$$C_{22,N}(0) = 1,$$
$$C_{12,N+1}(0) = C_{21,N+1}(0) = C_{11,N+2}(0) = 0. \tag{4}$$

Making a substitution which is universal and feasible for an arbitrary number of molecules:

$$C_{22,N} = C'_{22,N}, \qquad C_{11,N+2} = e^{-i\mathbf{kR}_1 - i\mathbf{kR}_2 - 2i\varepsilon t} C'_{11,N+2},$$
$$C_{21,N+1} = e^{-i\mathbf{kR}_2 - i\varepsilon t} C'_{21,N+1}, \quad C_{12,N+1} = e^{-i\mathbf{kR}_2 - i\varepsilon t} C'_{12,N+1}, \tag{5}$$

(**R** is the coordinate of the center of gravity of the molecule), we arrive, taking into account the fact that by virtue of (4) $C_{21,N+1}(t) = C_{12,N+1}(t)$, at the system

$$i\frac{\partial C'_{22,N}}{\partial t} = 2a\sqrt{N+1}\, C'_{21,N+1},$$
$$i\left(\frac{\partial}{\partial t} - i\varepsilon\right) C'_{21,N+1} = a^*\sqrt{N+1}\, C'_{22,N} + a\sqrt{N+2}\, C'_{11,N+2},$$
$$i\left(\frac{\partial}{\partial t} - 2i\varepsilon\right) C'_{11,N+2} = 2a^*\sqrt{N+2}\, C'_{21,N+1}. \tag{6}$$

We note that by virtue of (5) the final results do not depend on the wavelength. The corresponding determinant yields in the general case three different irrational real roots, so that in a system of two molecules, generally speaking, there are oscillations of the state probabilities with three noncommensurate frequencies

$$|\Omega_1 - \Omega_2|, \quad |\Omega_1 - \Omega_3|, \quad |\Omega_2 - \Omega_3|.$$

Thus, even in such a simple system, the motion is nonperiodic and the initial state does not repeat.

In the case of a self-consistent field ($N = 0$) and exact resonance ($\epsilon = 0$), we have

$$\Omega_1 = 0, \quad \Omega_{2,3} = \pm\sqrt{6}|a|^2. \tag{7}$$

If the radiation field is assumed strong, so that in the case of exact resonance ($\epsilon = 0$) we have $N \gg 1$, or else $N \gg 1$ and $|a|N^{1/2} \gg 2\epsilon$ ($\epsilon \neq 0$), the frequencies are

$$\Omega_1 = 0, \quad \Omega_{2,3} = \pm 2(N|a|^2)^{1/2}. \tag{7'}$$

Since there are only two different frequencies, one of which is equal to zero, the motion is under the conditions indicated above periodic. The probabilities of the states of the molecules and of the self-consistent radiation field are given by the expressions

$$W_{22,0} = {}^1/_9[2 + \cos\Omega t]^2, \qquad W_{21,1} = {}^1/_6 \sin^2\Omega t,$$
$$W_{11,2} = {}^2/_9[1 - \cos\Omega t]^2 \qquad (\Omega = |\Omega_{2,3}|), \tag{8}$$

and the time-averaged probabilities are

$$\overline{W}_{22,0} = {}^1/_2, \quad \overline{W}_{21,1} = {}^1/_{12}, \quad \overline{W}_{11,2} = {}^1/_3. \tag{8'}$$

Thus, the system "stays" longest in the initial state. Inasmuch as the amplitudes C_{12} and C_{21} do not interfere, the normalization is of the form

$$W_{22,0} + 2W_{21,1} + W_{11,2} = 1. \tag{9}$$

When a sufficiently strong radiation field falls on the molecular system from the outside, so that $N \gg 1$ and in addition $(N|a|^2)^{1/2} \gg 2\epsilon$, if $\epsilon \neq 0$, the contribution made to it by the molecules can be neglected, and we arrive at the following state probabilities:

$$W_{22,N} = {}^1/_4[1 + \cos\Omega t]^2, \qquad W_{21,N} = {}^1/_4 \sin^2\Omega t,$$
$$W_{11,N} = {}^1/_4[1 - \cos\Omega t]^2, \qquad \Omega = 2|a|N^{1/2}. \tag{10}$$

Comparing (10) with (2′), we see that the following relations are satisfied

$$W_{22,N} = W_{2,N}^2, \qquad W_{21,N} = W_{2,N} W_{1,N}, \qquad W_{11,N} = W_{1,N}^2, \tag{10'}$$

i.e., the probabilities of the collective states are equal to the product of the probabilities of the states of the isolated molecules but, as we shall show below, with allowance for the initial conditions. Indeed, Eqs. (10) correspond to the case when both molecules were at the upper level at the initial instant; (10′) contains the "single-molecule" state probabilities, when each molecule is at the initial instant of time at the upper level.

We now change the initial conditions. Assume that at the instant t = 0 only the first molecule is in the upper level, i.e., the initial conditions are of the form

$$C_{21,N}(\tilde{0}) = 1, \quad C_{22,N-1} = C_{12,N} = C_{11,N+1} = 0. \qquad (11)$$

By virtue of the different initial conditions, the amplitudes C_{21} and C_{12} are now different, and the corresponding system of equations of motion is obtained from (8) by replacing N with N − 1. Making a well-known substitution, in the case when $\epsilon = 0$ and N = 0 (self-consistent field and exact resonance), we arrive at a solution of the form

$$C_{21,0}(t) = {}^1/_2[1 + \cos\Omega t],$$
$$C_{12,0}(t) = {}^1/_2[1 - \cos\Omega t],$$
$$C_{11,1}(t) = -i(\Omega/2a)\sin\Omega t, \qquad \Omega = 2^{1/2}|a|. \qquad (12)$$

In this case, as before, we have the frequencies

$$\Omega_1 = 0, \qquad \Omega_{2,3} = \pm\Omega,$$

so that we see that the change in initial conditions in the case of a self-consistent field changes the frequency spectrum, and furthermore in a definite direction. Namely, the frequencies observed in a self-consistent system should decrease with decreasing "quantity of excitation," as is indeed the case.

Squaring the modulus of the amplitudes (12), we obtain the probabilities of the states

$$W_{12,0}(t) = {}^1/_4[1 - \cos\Omega t]^2, \quad W_{21,0}(t) = {}^1/_4[1 + \cos\Omega t]^2,$$
$$W_{11,1}(t) = {}^1/_2\sin^2\Omega t. \qquad (13)$$

It is interesting to note that a phase shift equal to π, the same as in the initial conditions (11), is conserved in the probabilities, so that the molecules oscillate, interchanging places in the level occupation-number space. Averaging (13) over the time we get

$$\overline{W}_{21,0} = {}^3/_8, \qquad \overline{W}_{12,0} = {}^3/_8, \qquad \overline{W}_{11,1} = {}^1/_4.$$

In the presence of a strong external radiation field ($N \gg 2$, $N^{1/2}|a| \gg 2\epsilon$) a solution of the equations of motion satisfying (11) is of the form ($\Omega = 2|a|N^{1/2}$)

$$C_{22,N} = -{}^1/_2\sin\Omega t, \qquad C_{11,N} = -{}^1/_2\sin\Omega t,$$
$$C_{21,N} = {}^1/_2[1 + \cos\Omega t], \quad C_{12,N} = -{}^1/_2[1 - \cos\Omega t]. \qquad (14)$$

The probabilities of the states will be described by the expressions

$$W_{22,N} = {}^1/_4\sin^2\Omega t, \qquad W_{11,N} = {}^1/_4\sin^2\Omega t,$$
$$W_{21,N} = {}^1/_4[1 + \cos\Omega t]^2, \quad W_{12,N} = {}^1/_4[1 - \cos\Omega t]^2. \qquad (15)$$

Comparing (15) with (2′), we see that (15) can be written in the form of a product of "single-molecule" probabilities with allowance for the initial conditions

$$\begin{aligned} W_{22,N} &= W^{\uparrow}_{2,N} W^{\downarrow}_{2,N}, & W_{21,N} &= W^{\uparrow}_{2,N} W^{\downarrow}_{1,N}, \\ W_{12,N} &= W^{\uparrow}_{1,N} W^{\downarrow}_{2,N}, & W_{11,N} &= W^{\uparrow}_{1,N} W^{\downarrow}_{1,N}. \end{aligned} \qquad (16)$$

Thus, the system "remembers" its initial state also in the case of a strong radiation field, and the molecules move in a connected fashion. It is clear, however, that in a situation wherein it is meaningless to speak of initial states of the amplitudes, for example when the times of all kinds of relaxation processes (interaction with phonons, with other levels, collisions between molecules) are of the same order of magnitude or smaller than the characteristic period of the oscillations of the molecules in the radiation field, the solutions obtained above are meaningless. In such a situation, the system in question should "fall apart," so that each molecule will oscillate in a strong field completely independently of the others.

When the molecular system is in a strong external radiation field, the frequency spectrum obviously should not change with the initial conditions. Indeed, it can be shown that the determinant which determines the frequencies in the case of an arbitrary number of molecules and a strong radiation field does not depend on the initial conditions. If we consider the interaction of three molecules with the radiation field, when at the initial instant of time all three molecules are at the upper level, then in the general case oscillations will take place with six frequencies:

$$|\Omega_1 - \Omega_2|; \qquad |\Omega_1 - \Omega_3|; \qquad |\Omega_2 - \Omega_3|;$$
$$|\Omega_1 - \Omega_4|; \qquad |\Omega_2 - \Omega_4|; \qquad |\Omega_3 - \Omega_4|,$$

since the solution of the corresponding equation for the frequencies yields four real irrational roots. We note that in general, for n molecules, one obtains n + 1 different frequencies (in the state amplitude), one of which is always zero when the number of molecules is even.

In the case of a self-consistent field and exact resonance, only two different frequencies remain

$$\Omega_1 = (10 + \sqrt{73})\,|a| \gtrsim 4|a|,$$
$$\Omega_2 = (10 - \sqrt{73})\,|a| \gtrsim |a|,$$

and the state probabilities will contain three frequencies:

$$\Omega_1, \quad \Omega_2, \quad \Omega_1 - \Omega_2,$$

which are noncommensurate, so that the motion is not periodic.

Since the probabilities themselves are represented by cumbersome and obscure expressions, we present here only the time-averaged probabilities of the collective states:

$$\overline{W}_{222,0} \gtrsim {}^1/_3, \quad 3\overline{W}_{221,1} \sim {}^1/_4,$$
$$3\overline{W}_{211,2} \sim {}^1/_{12}, \qquad \overline{W}_{111,3} \sim {}^1/_4. \tag{17}$$

We see that the system is for a rather long time in an excited state.

When solving the corresponding system of equations of motion, again with inclusion of the initial conditions [$C_{222,0}(0) = 1$, all others equal to zero], we made use of the equality

$$C_{221,1} = C_{212,1} = C_{122,1}, \qquad C_{211,2} = C_{121,2} = C_{112,2}.$$

When there is a strong external field, the state probabilities of the three molecules are

$$W_{222,N} = {}^1/_{16}[\cos^2 \Omega_1 t + 6\cos \Omega_1 t \cos \Omega_2 t + 9\cos^2 \Omega_2 t],$$
$$W_{221,N} = {}^1/_{16}[\sin^2 \Omega_1 t + 2\sin \Omega_1 t \sin \Omega_2 t + \sin^2 \Omega_2 t],$$
$$W_{211,N} = {}^1/_{16}[\cos^2 \Omega_1 t - 2\cos \Omega_1 t \cos \Omega_2 t + \cos^2 \Omega_2 t],$$
$$W_{111,N} = {}^1/_{16}[\sin^2 \Omega_1 t - 6\sin \Omega_1 t \sin \Omega_2 t + 9\sin^2 \Omega_2 t],$$

where

$$\Omega_1 = 3|a|N^{1/2}, \qquad \Omega_2 = |a|N^{1/2}. \tag{18}$$

Comparing (18) and (2′), we can easily verify that (18) can be represented again in the form of a product of "single-molecule" probabilities (with allowance for the fact that all three molecules are at the initial instant at the upper level):

$$W_{222,N} = W^{\uparrow 3}_{2,N}, \quad W_{111,N} = W^{\uparrow 3}_{1,N},$$

$$W_{221,N} = W^{\uparrow 2}_{2,N} W^{\uparrow}_{1,N}, \quad W_{211,N} = W^{\uparrow}_{2,N} W^{\uparrow 2}_{1,N},$$

Finally, let us consider the case when there are n molecules in the volume. We assume that they are all at the initial instant of time either at the upper or at the lower level. When the radiation field is sufficiently strong, so that $N \gg n$ in the case when $\epsilon = 0$, or $N \gg n$ with $N^{1/2}|a| \gg N\epsilon$, when $\epsilon \neq 0$, the determinant giving the frequencies assumes the form

$$D_n(\Omega) = \begin{vmatrix} \Omega & naN^{1/2} & 0 & \cdots\cdots & 0 & 0 \\ a^*N^{1/2} & \Omega & (n-1)a^*N^{1/2} & \cdots\cdots & 0 & 0 \\ 0 & 2a^*N^{1/2} & \Omega & \cdots\cdots & 0 & 0 \\ \cdots & \cdots & \cdots\cdots & \cdots\cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots\cdots & \cdots\cdots & \cdots & \cdots \\ 0 & 0 & \cdots\cdots & (n-1)a^*N^{1/2} & \Omega & aN^{1/2} \\ 0 & 0 & \cdots\cdots & 0 & na^*N^{1/2} & \Omega \end{vmatrix} \tag{19}$$

The determinant contains only terms proportional to an integer power of $|a|$. Redefining D_n by introducing in it in place of a and a* the quantity $|a|$ and making the substitution $\Omega = \Omega'|a|N^{1/2}$, we arrive at the determinant $D_n(\Omega')$, the calculation of which is carried out with the aid of the recurrence formula

$$D_n(\Omega') = (\Omega' + n)D_{n-1}(\Omega' - 1).$$

Applying this formula successively n times, we obtain ultimately

$$D_n(\Omega') = \begin{cases} \prod\limits_{k=0}^{m} [\Omega'^2 - (2k)^2], & n = 2m, \\ \prod\limits_{k=0}^{m} [\Omega'^2 - (2k+1)^2], & n = 2m+1. \end{cases} \tag{20}$$

Thus, oscillations (of a collective character) arise in the system with multiple harmonics of the type

$$\Omega = \begin{cases} 0, \ \pm 2|a|N^{1/2}, \ \pm 4|a|N^{1/2}, \ \ldots \ \pm n|a|N^{1/2}, \\ \qquad\qquad n = 2m; \\ \pm|a|N^{1/2}, \ \pm 3|a|N^{1/2}, \ \ldots \ \pm n|a|N^{1/2}, \\ \qquad\qquad n = 2m+1. \end{cases} \tag{21}$$

The probability of the states contains in addition to Ω also difference frequencies, and in the case of an odd number of molecules the entire spectrum should be observed. As indicated above, the spectrum obtained is not sensitive to initial conditions.

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