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Contribution to the statistics of an ensemble of nonlinear quantum oscillators excited by an external periodic force

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The level population of an ensemble of oscillators is considered in the case when the resonant quantum number n_r determined from the condition $E_{n_r+1} - E_{n_r} \approx \hbar\omega_l$ is satisfied (ω_l is the frequency of the external force). It is shown that on levels with $n \geq n_r$ there can appear an excess population that can be relatively large even if the relaxation time is much shorter than the time of excitation by the external force. It is noted that laser radiation can exert an appreciable stimulating action on chemical reactions with large activation energy, whereas reactions with low activation energy are not subject to this influence.

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1. Experiments[1-5] have shown that even relatively weak laser radiation acting continuously on a dense gas mixture[1-4] or on a solid[5] is capable of exciting the above-thermal impurity resonant molecules contained in the medium, and consequently stimulate chemical reactions in which these molecules participate. A theoretical interpretation of these experiments calls for the study of the statistics of an ensemble of particles excited by an external force (i. e., by a laser radiation) and located in a thermostat (i. e., in an ambient of nonresonant molecules).

Similar problems were considered recently in a number of studies.[6-9] The present note deals with an ensemble of nonlinear one-dimensional oscillators. After simplifying the initial equations by the averaging method (sec. 2), we obtain their solution in the case of oscillators with rapidly relaxing phase (Sec. 3). The last model admits of a simple analytic solution and at the same time contains enough physical substance for numerical estimates (Sec. 4) and some qualitative conclusions (Sec. 5).

2. The initial equation for the density matrix ρ of a linear oscillator can be assumed in the form[10,11]

$$i\hbar\dot{\rho}-[H-F(t)x,\rho]=\frac{\hbar\nu}{2}((1+N)(2a\rho a^+-a^+a\rho-\rho a^+a) +N(2a^+\rho a-aa^+\rho-\rho aa^+)), \quad (1)$$

where H is the Hamiltonian, with $H|n\rangle=E_n|n\rangle$ and

$$E_n=\hbar\omega_v(n+1/2), \quad (2)$$

ω_v is the natural frequency, $F(t)$ is the external force,

$$x=(\hbar/2m\omega_v)^{1/2}(a+a^+), \quad (3)$$

$$\langle n|a^+|n-1\rangle=\langle n-1|a|n\rangle=n^{1/2}, \quad (4)$$

$$N=[\exp(\hbar\omega_v/T)-1]^{-1} \quad (5)$$

is the thermal quantum number, T is the temperature of the thermostat, and ν^{-1} is the characteristic relaxation time of the oscillator in the thermostat. Equation (1) admits under conditions (2)–(5) of an exact solution.[11]

Proceeding to consideration of a nonlinear oscillator, we confine ourselves to a harmonic external force $F(t)=F\cos\omega_l t$ and to the resonant case

$$|E_n-\hbar\omega_l(n+1/2)|\ll E_n. \quad (6)$$

Expressions (1) and (3)–(5) can then be left unchanged, apart from the substitution $\omega_v\to\omega_l$ in (3) and in (5). Thus, the nonlinearity of the oscillator manifests itself only in that its energy spectrum E_n differs from (2). That this approximation is admissible was proved in Ref. 12.

We introduce the matrix β:

$$\rho_{mn}=\beta_{mn}\exp[-i\omega_l(m-n)t].$$

The matrix β varies little over the period of the external force; now, discarding the rapidly oscillating terms, we get from (1)

$$\dot{\beta}_{mn}+i\beta_{mn}[(E_m-E_n)/\hbar-\omega_l(m-n)]+1/2i(\beta_{m\,n-1}n^{1/2}f^*-\beta_{m-1\,n}m^{1/2}f +\beta_{m\,n+1}(n+1)^{1/2}f-\beta_{m+1\,n}(m+1)^{1/2}f^*) =\nu N(mn)^{1/2}\beta_{m-1\,n-1}+\nu(1+N)[(m+1)(n+1)]^{1/2}\beta_{m+1\,n+1} -\nu[(m+n)(N+1/2)+N]\beta_{mn}, \quad (7)$$

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where $f=Fx_{01}/\hbar$. The quantity $|f|$ has the meaning of the field broadening. In the steady state, the matrix β, unlike the matrix ρ, does not depend on the time. We consider henceforth only the steady state.

3. When there is no external force, the matrices ρ and β are diagonal, with

$$\rho_{nn}=\beta_{nn}=\frac{N^n}{(1+N)^{n+1}}=\left(1-\exp\left(-\frac{\hbar\omega_l}{T}\right)\right)\exp\left(-\frac{\hbar\omega_l n}{T}\right).$$

We introduce the factor l_n by which the population on the level n differs from the equilibrium population:

$$\beta_{nn}=l_nN^n/(1+N)^{n+1}.$$

If the external force is weak and (or) if the oscillator relaxation is fast enough, the off-diagonal elements of the matrix β are small.

We neglect all the elements β_{mn} if $|m-n|\geq 2$; the elements $\beta_{n-1\,n}$ closest to the diagonal are expressed in the form

$$\beta_{n-1\,n}=\lambda_nN^n/(1+N)^{n+1}.$$

In Refs. 10 and 11, and correspondingly in Eqs. (1) and (7), only one relaxation time $\tau=\nu^{-1}$ is involved. Yet it is known from experiment that in most two-level and multilevel quantum systems the relaxation time of the off-diagonal elements or the phase relaxation time T_2 is much shorter than the population relaxation time T_1. We introduce accordingly the frequencies

$$\nu_1=T_1^{-1},\ \nu_2=T_2^{-1}.$$

Putting $\dot\beta_{nn}=0$, we get from (7)

$$\begin{aligned}&{}^1/_2in^{1/2}(1+N)(\lambda_nf-\lambda_n^*f^*)+{}^1/_2i(n+1)^{1/2}N(\lambda_{n+1}^*f^*-\lambda_{n+1}f)\\&=\nu_1[2n(N+{}^1/_2)+N]Nl_n-\nu_1nN(1+N)l_{n-1}-\nu_1(1+n)N^2l_{n+1}.\end{aligned}\tag{8}$$

Assuming $\dot\beta_{n-1\,n}=0$, we obtain from (7)

$$\begin{aligned}&i\frac{n^{1/2}N}{2(1+N)}[Nl_n-(1+N)l_{n-1}]f^*\\&-i\lambda_nN\delta\omega_n=\nu_2[(2n-1)(N+{}^1/_2)\\&\quad+N]N\lambda_n-\nu_2N(1+N)\cdot\\&\quad\cdot[n(n-1)]^{1/2}\lambda_{n-1}\\&\quad-\nu_2N^2[n(n+1)]^{1/2}\lambda_{n+1},\end{aligned}\tag{9}$$

where the frequency detuning is

$$\delta\omega_n=\omega_l-(E_n-E_{n-1})/\hbar.$$

In the case of a nonlinear oscillator, $\delta\omega_n$ depends on n. We emphasize that the condition (6) does not prevent $\delta\omega_n$ from changing greatly with changing n; for example, $\delta\omega_n$ can reverse sign or vanish.

Let $\hbar\omega_l>T$, then $N<1$; in addition, we assume that the factor l_n and the quantity λ_n change little when n is changed by unity. As will be made clear later on, these conditions are not contradictory. We confine ourourselves to the values $n\gg 1$ and regard l_n and λ_n as continuous functions of n; we then obtain from (9) and (8)

$$\lambda_n=-i\frac{n^{1/2}f^*}{\nu_2/4n+2i\delta\omega_n}l_n,\tag{10}$$

$$\frac{dl_n}{dn}=i\frac{\lambda_nf-\lambda_n^*f^*}{2N\nu_1n^{1/2}}=\frac{\nu_2|f|^2}{N\nu_1(\nu_2^2/4n+16\delta\omega_n^2n)}l_n.\tag{11}$$

Equation (11) determines the factor l_n of interest to us.

We note that l_n always increases with increasing n. This increase is particularly rapid when $\delta\omega_n=0$, i. e., when the frequency of the external force is close to the frequency of the transitions:

$$E_{n+1}-E_n=\hbar\omega_l.\tag{12}$$

The solid line on the figure shows schematically plots of $\delta\omega_n$, l_n and ρ_{nn}, as well as the value of n_r at which the condition (12) is satisfied.

4. If the nonlinear oscillator simulates a resonant vibrational mode of a polyatomic molecule, the frequency detuning $\delta\omega_n$ can be assumed in the form

$$\delta\omega_n=\begin{cases}\delta\omega_0 & n<n_{qc}\\ 0 & n>n_{qc}\end{cases}\tag{13}$$

(see the dashed curves in the figure).

The choice of $\delta\omega_n$ in the form (13) is justified by the fact that for polyatomic molecules the level density in the upper part of the energy spectrum becomes very large, i. e., a quasicontinuum appears and starting with a certain $n=n_{qc}$ resonant pairs of levels are obtained for any laser frequency.

The field broadening is equal to $f=E=Ed/\hbar$, where E is the laser-radiation electric field intensity and d is the characteristic dipole moment. To compare the theory with real experiments we must choose $\delta\omega_0=10\ \text{cm}^{-1}=3\times10^{11}\ \text{sec}^{-1}$, $n_{qc}=3$, $I=10\ \text{W/cm}^2$ ($E=87\ \text{V/cm}$), $d=0.1\ \text{db}=10^{-19}$ cgs units, and then $f=1.47\times10^{-4}\ \text{cm}^{-1}=4.41\times10^6\ \text{sec}^{-1}$, $\nu_1=10^7\ \text{sec}^{-1}$, $\nu_2=3\times10^9\ \text{sec}^{-1}$. Let the mixture temperature be $T=100$ K; if such a mixture is exposed to CO_2 laser radiation, then $\hbar\omega_l=1360$ K and $N=3.4\times10^{-2}$.

The condition that the off-diagonal elements be small

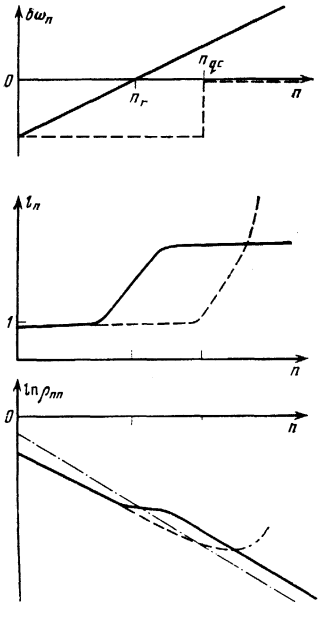

FIG. 1. Dependences of the frequency detuning $\delta\omega_n$, of the excess-population factor l_n and of the population ρ_{nn} on the quantum number n for two types of nonlinearity. The dash-dot line shows the equilibrium ρ_{nn} dependence.

is of the form $\lambda_n \lesssim l_n$; Eq. (8) can be written in differential form if $dl_n/dn \lesssim l_n$. In the region $n > n_{qc}$ these conditions are satisfied if

$$4|f|n^{3/2}/\nu_2 \lesssim 1, \tag{14a}$$

$$4|f|^2 n/N\nu_1\nu_2 \lesssim 1. \tag{14b}$$

We substitute now the numerical values; from (14a) we get $n \lesssim 30$, from (14b) we have $n \lesssim 13$. According to (11) we have $l_n \approx 1$ at $n < n_{qc}$. In the region $n > n_{qc}$ we have

$$l_n = \exp\left\{\frac{2|f|^2}{N\nu_1\nu_2}(n^2 - n_{qc}^2)\right\}. \tag{15}$$

The characteristic time f^{-1} of laser excitation is longer than the characteristic relaxation times ν_1^{-1} and ν_2^{-1}; therefore at first glance it would seem that the radiation cannot alter noticeably the equilibrium population. This statement, however, is valid only at relatively small n, inasmuch as Eq. (15) yields $l_5 = 1.8$; $l_{10} = 32$; $l_{13} = 440$. Thus, the factor l_n increases rapidly with increasing n in the quasicontinuum region (see dashed curves in the figure).

We note here that Eqs. (8) and (9) remain valid up to $n = 30$, but in the interval $13 < n < 30$ the differential approximation (11) cannot be used.

It is of interest to compare Eq. (15) with the expression obtained for l_n for a linear oscillator with one relaxation time ν^{-1}. Using the results of Ref. 11, we can show that

$$l_n = \exp\left\{-\frac{|f|^2}{(1+N)(\nu^2+4\delta\omega^2)}\right\} L_n\left\{-\frac{|f|^2}{N(1+N)(\nu^2+4\delta\omega^2)}\right\} \tag{16}$$

where L_n is a Laguerre polynomial. Putting $\delta\omega = 0$ and $\nu = 3 \times 10^7$ sec^{-1} we obtain $l_0 = 0.98$; $l_{10} = 21$; $l_{30} = 573$.

5. We note some qualitative features of the considered models.

1. An excess population (above the equilibrium value) is obtained under the influence of a periodic external force on the resonant levels determined from the condition (12) as well as on levels that lie above the resonant ones.

2. The magnitude of the excess population (the factor l_n) always increases with increasing quantum number and can become appreciable in the upper part of the energy spectrum, whereas $l_n = 1$ in the lower part. Lasar radiation can thus exert an appreciable stimulating on chemical reactions or other processes with large activation energy, whereas reactions with low activation energy are not subject to this influence.

3. In the upper part of the energy spectrum, the factor l_n increases with decreasing temperature.

4. The factor l_n can greatly exceed unity even in a strong collisional regime, when the characteristic relaxation time is much shorter than the laser-excitation time.

A more exact analysis of the statistics of the excited particles requires, above all, an investigation of the influence of high level density on the excitation and relaxation, as well as allowance for the nonmonochromaticity of the external force (see Refs. 13 and 14 in this connection). We assume that this analysis will confirm the qualitative conclusions presented above.

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