Possible effect of emission collapse in an ensemble of interacting molecules

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The possible effect of collapse of spontaneous and stimulated emission in an ensemble of interacting molecules is predicted. It is supposed that this emission is caused by transitions between rotational levels of molecules. A molecule is modeled by a rotor nonlinearly interacting with the environment, and the dynamics of its state is theoretically investigated. For this purpose the nonlinear Schrödinger equation is solved. We have obtained that under certain conditions rotor's states must change in a jump. Also, at a temperature below some limit, the Bose condensation of rotor's states can take place, so spontaneous and stimulated emission attributed to rotation of molecules can disappear in molecules at the temperature below the critical value.

A quantum rotor is a well-known object. In particular, model representation of diatomic molecules as a rigid rotor is widely used for analysis of their rotational states. However, despite that the behavior of an isolated rotor has been studied quite thoroughly, some features inherent in an ensemble of rotors are not understood, for example, collapse of their rotation at a temperature below some threshold. This effect was observed experimentally in molecular gases. As the gas temperature drops below some limit, its thermal capacity no longer depends on the rotational degrees of freedom of the molecules. This behavior of thermal capacity is believed[1] to be caused by the insufficient molecular translational energy for efficient excitation of the rotational states. This explanation has a purely qualitative character and, seemingly, is not comprehensive. In particular, it fails to explain the stepwise change of the thermal capacity. This stepwise change is indicative of some collective phenomena in the ensemble of molecules, because some Bose condensation of the rotor's states is observed. This condensation must affect the optical properties of the ensemble of molecules.

In this paper, we consider one of the possible mechanisms of this condensation and its effect on the emission of molecules at low temperatures.

The theoretical model of Bose condensation is constructed for an ensemble of rotors based on the method developed in Ref. 2.

The initial assumption in this method is that no isolated quantum systems exist in nature. Any quantum system interacts with its environment. Therefore, if we separate some quantum subsystem as some isolated formation, then its states should be described by a nonlinear equation, because any change in this subsystem automatically affects the quantum states of neighboring particles, which, in their turn, affect the subsystem.

In Ref. 3 it has been shown that the following equation

$$\Phi(\psi) = \lambda\hat{A}\langle\psi|\hat{B}|\psi\rangle, \qquad (1)$$

is a rather versatile operator accounting for the self-effect of a separated quantum subsystem through its environment. In Eq. (1) λ is the parameter describing the feedback strength; $\hat{A}$ and $\hat{B}$ are the operators, whose explicit form is determined by the model describing the interaction of the subsystem with the environment; ψ is the wave function of the subsystem.

When considering the interaction of the separated subsystem (molecule) with the environment, we should necessarily keep in mind that any quantum fluctuations of the environment cause a response from the subsystem. The environment is formed by other molecules. Any change in the states of these molecules is connected with some change of electric fields in them. At quantum transitions, these changes occur in a jump, and because the Coulomb interaction is a long-range one, the external perturbations of an isolated subsystem must predominantly be stochastic. From here on, assuming the ensemble of rotors to be rather rare, strong collisions, which, by the way, can be described by a time-regular (in the mathematical sense) operator, are believed improbable.

The behavior of systems experiencing stochastic perturbation is usually analyzed[4] using the formalism of density matrix. A peculiarity of this approach is in simultaneous consideration of the dynamics of solutions of n^2 equations, where n is the number of states of the quantum subsystem that are taken into account. Since in the case of a nonlinear system all states are interrelated and the transition between states can be stepwise, the use of this approach in theoretical consideration of even few states is difficult. Therefore, in analysis of the states of interacting rotors, we use the formalism of effective wave functions,[5] which allows us to decrease the

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number of equations to be analyzed. These effective wave functions are constructed so that the mean values of physical quantities calculated with them are close to those calculated using the density matrix. They satisfy the nonlinear Schrödinger equation:

$$i\hbar\frac{\partial\psi}{\partial t}=\frac{1}{1+i\alpha}\left(\hat{T}+\chi\right)\psi+U\psi+\frac{i\alpha}{1+\alpha^2}\langle\psi|\hat{T}+\chi|\psi\rangle\psi, \quad (2)$$

where

$$\chi = kT/2. \quad (3)$$

In Eqs. (2) and (3) $\hat{T}$ is the ordinary operator of kinetic energy; U is the operator of potential energy; k is the Boltzmann constant; T is the ambient temperature; α is the positive parameter, whose value is related to the thermostat density.

Equation (2) has been derived by the method of Feynman path integrals. This method rather naturally accounts for the stochastic perturbation. To do this, all stochastic perturbations are formally included in the list of causes affecting the realization of possible paths between the initial and final states of a quantum system. Then, in constructing the integral equation for the propagator (this equation is equivalent to the Schrödinger equation), in place of summing the contributions of all possible trajectories to the probability amplitude, we can simply average this propagator over the probabilities of realization of possible trajectories. Note that, for the time intervals sufficient for considering the statistical properties of the quantum subsystem's environment, the effect from the stochastic operator in the Feynman propagator tends to zero. Nevertheless, this stochastic perturbation is taken into account integrally in the averaged propagator with the aid of the parameters α and χ (in derivation of Eq. (2), these parameters were assumed varying adiabatically). The last term in Eq. (2) is a particular form of the functional $\Phi(\psi)$.

The explicit form of the functional $\Phi(\psi)$ is determined from the following reasoning.[5] First, the operators $\hat{A}$ and $\hat{B}$ are believed not to disturb the group properties of the Feynman propagator. Second, it is assumed that, despite the rotors undergo impact perturbation, their decay is improbable, that is, the effective wave functions keep time normalization. Then, accurate to the terms vanishing at the unitary transformation, the following equation results

$$\Phi(\psi)=\frac{i\alpha}{1+\alpha^2}\langle\psi|\hat{T}+\chi|\psi\rangle, \quad (4)$$

i.e., just that used in Eq. (2).

The wave functions satisfying Eq. (2) can be presented as

$$\psi = \tilde{\psi}/\langle\tilde{\psi}|\tilde{\psi}\rangle^{1/2}, \quad (5)$$

where $\tilde{\psi}$ is the solution of the following equation

$$i\hbar\frac{\partial\psi}{\partial t}=\frac{1}{1+i\alpha}\left(\hat{T}+\chi\right)\psi+U\psi. \quad (6)$$

Similarly to Eq. (2), Eq. (6) was derived by the method of path integrals, but neglecting the feedback. The Neumann equation

$$i\hbar\frac{\partial\rho}{\partial t}=[\hat{H}_0,\rho]-i\alpha\{\hat{T},\rho\}-i2\alpha\chi\rho \quad (7)$$

for the statistical operator

$$\rho = |\tilde{\psi}\rangle\langle\tilde{\psi}|, \quad (8)$$

derived from Eq. (6) coincides, accurate to designations, with that from Ref. 6 derived by the Lax method[7] (in this method the feedback is neglected) upon reduction of the density matrix of the large system to the statistical operator of the separated subsystem. In Eq. (7) the square brackets denote the commutator, and the braces denote the anticommutator. The operator $\hat{H}_0$ is the Hamiltonian of the isolated quantum subsystem.

Equation (5) shows one of the ways to find the solution of the Schrödinger equation (2). However, because of the nonlinearity, this equation permits other solutions as well. Considering them, we make use of the well-known postulate following from the experimental data: the principle of superposition is valid for the wave functions describing the state of some steady-state quantum subsystem.

With this postulate in mind and taking Eq. (5) into account, we can write any solution of Eq. (2) in the form

$$\psi(\mathbf{r},t)=\sum_n C_n(t)\psi_n(\mathbf{r}). \quad (9)$$

Here $\psi_n(\mathbf{r})$ are the eigenfunctions of the stationary Schrödinger equation

$$\frac{1}{1+i\alpha}\hat{T}\psi_n+U\psi_n=E_n\psi_n, \quad (10)$$

where

$$E_n=\tilde{E}_n-\frac{1}{1+i\alpha}\chi. \quad (11)$$

In Eq. (11) $\tilde{E}_n$ is the separation constant arising in passing from Eq. (6) to the stationary Schrödinger equation.

As known,[8] the operator of potential energy of a rigid rotor can be set equal to zero. Therefore, the eigenfunctions of Eq. (10) in the case at hand coincide with the eigenfunctions of the equation

$$\hat{T}\psi_{lm}=E_l\psi_{lm}, \quad (12)$$

whose solution is well-known:

$$\psi_{lm}=Y_l^m(\vartheta,\varphi)=$$

$$=a_m\sqrt{\frac{(2l+1)(l-|m|)!}{4\pi(l+|m|)!}}P_l^{|m|}(\cos\vartheta)\exp(im\varphi). \quad (13)$$

In Eq. (13) a_m is the constant:

$$a_m = \begin{cases} 1, & (m \geq 0) \\ -1, & (m < 0); \end{cases} \qquad (14)$$

$l = 0, 1, 2, 3, \ldots$ is the orbital quantum number; $m = 0, \pm 1, \pm 2, \ldots, \pm l$ is the magnetic quantum number; ϑ and φ are spherical angles; $P_l^m(x)$ is the associated Legendre polynomial.

The variables separation constant in Eq. (10)

$$E_l = \hbar^2 l(l+1)/(2J) \qquad (15)$$

is the intrinsic energy of the rotor, where J is the moment of inertia of the rotor.

Taking Eqs. (12)–(15) into account, we can refine the Eq. (9) to a more specific form:

$$\psi = \sum_l \sum_{m=-l}^{l} C_{lm}(t)\psi_{lm}. \qquad (16)$$

In Eq. (16) the coefficients $C_{lm}(t)$ are, generally, irregular functions of time, and under certain conditions they can change in a jump.

Consider this in a more detail.

As the Schrödinger equation used here is nonlinear, not all its solutions are equiprobable.[2] Since we are mainly interested in population of energy levels, introduce the occupation numbers $P_{lm} = |C_{lm}(t)|^2$. Using Eq. (2), we can readily show that these occupation numbers satisfy the system of equations:

$$\frac{\partial P_{lm}}{\partial t} = \frac{2\alpha}{(1+\alpha^2)\hbar}\left[-(E_l + \chi) + \sum_{l_1}(E_{l_1} + \chi)\sum_{m_1=-l_1}^{m_1=l_1} P_{l_1 m_1}\right]P_{lm}$$

$$(l = 0, 1, 2, 3, \ldots;\ m = 0, \pm 1, \pm 2, \ldots, \pm l). \qquad (17)$$

The most probable states of the rotor can be found, if we put the derivatives in the left-hand side of Eq. (17) to zero. However, we cannot find all possible values of $P_{lm} = |C_{lm}(t)|^2$ from the system of equations

$$\left[-(E_l + \chi) + \sum_{l_1}(E_{l_1} + \chi)\sum_{m_1=-l_1}^{m_1=l_1} P_{l_1 m_1}\right]P_{lm} = 0$$

$$(l = 0, 1, 2, 3, \ldots;\ m = 0, \pm 1, \pm 2, \pm 3, \ldots, \pm l). \qquad (18)$$

Nevertheless, if we sum the right-hand and left-hand sides of Eqs. (17) over the magnetic quantum number, then such analysis can be performed at least for populations of the energy levels $P_l = \sum_{m=-l}^{l} P_{lm}$.

From the system of differential equations

$$\frac{\partial P_l}{\partial t} = \frac{2\alpha}{(1+\alpha^2)\hbar}\left[-(E_l + \chi) + \sum_{l_1}(E_{l_1} + \chi)P_{l_1}\right]P_l \qquad (19)$$

it follows that for the most probable P_l values the system of nonlinear algebraic equations

$$\left[-(E_l + \chi) + \sum_{l_1}(E_{l_1} + \chi)P_{l_1}\right]P_l = 0 \qquad (20)$$

is valid.

This system has a countable set of solutions: P_l can take the values of only unity and zero, and only one occupation number can be equal to unity. This means that the states with the fixed energy corresponding to the eigenvalues of the Hamiltonian are most probable for a rotor in the thermostat.

Since the initial equation is nonlinear, all the rotor's states are interrelated. Therefore, when analyzing the dynamics of an occupied level, it is necessary to monitor simultaneously all the unoccupied levels. To do this, note that near the equilibrium position for the unoccupied quantum states of the rotor in the one-dimensional approximation the constant $C_{lm}(t)$ satisfies the equation

$$\frac{\partial C_{lm}}{\partial t} = -\frac{i+\alpha}{(1+\alpha^2)\hbar}\left(\frac{\hbar^2 l(l+1)}{2J} + \chi\right)C_{lm} +$$

$$+\frac{\alpha}{(1+\alpha^2)\hbar}\left(\frac{\hbar^2 l(l+1)}{2J} + \chi\right)|C_{lm}|^2 C_{lm}. \qquad (21)$$

This equation coincides in the form with the known equation describing the single-parameter family of vector fields on the plane:

$$\frac{\mathrm{d}z}{\mathrm{d}t} = z(i\omega + \varepsilon + kz\bar{z}), \qquad (22)$$

the peculiarities of whose solution are well studied.[9,10] In Eq. (22), z is the complex coordinate; ω and k are the real non-zero constants; ε is the real parameter. In the considered case

$$z = C_{lm};\ \ \omega = -\frac{1}{(1+\alpha^2)\hbar}\left(\frac{\hbar^2 l(l+1)}{2J} + \chi\right);$$

$$\varepsilon = -k = -\frac{\alpha}{(1+\alpha^2)\hbar}\left(\frac{\hbar^2 l(l+1)}{2J} + \chi\right). \qquad (23)$$

At all ε values the point $z = 0$ in Eq. (23) is the equilibrium position of the focal type. And at $\varepsilon < 0$ (which is true for the situation at hand) this focus is stable. Consequently, if the parameter α is significantly different from zero, then in the absence of strong, regular in time, perturbations the determined "zero" equilibrium states are stable and the rotor cannot transit into them from the "occupied" state. In other words, the rotor, because of the stochastic character of perturbation, must be in one of the unoccupied states with certain values of the orbital and magnetic quantum numbers.

In the case that the parameter α is close to zero, the unoccupied states lose stability (as known, at $k > 0$ and ε tending to zero, the focuses $z = 0$ in Eq. (22) become unstable) and the state of the rotor can vary even under a weak perturbation. This

circumstance allows us to study the regularities of transition from one equilibrium state into another.

Equation (22) has a fold singularity; therefore, as ε approaches zero from the negative side at some low, but nonzero value $|\varepsilon| = \delta$, the available peculiarities can disturb the system from the nearly equilibrium state.[9–11] In such a case, the system transits into either other far equilibrium position or some limit cycle, or other more complex attractor. A "catastrophe" occurs. This means that at the parameter α less than some critical value (at which the Schrödinger equation still remains nonlinear) quantum states can change in a jump. Consider variation of the population of energy levels in this case using the two-level approximation.

Supposing that the transition involves only two quantum states, write the system of equations determining the state of the rotor:

$$\frac{\partial P_{lm}}{\partial t} = \frac{2\alpha}{(1+\alpha^2)\hbar}\left[\left(\frac{\hbar^2 l(l+1)}{2J} + \frac{kT}{2}\right)(P_{lm} - 1) + \right.$$

$$\left. + \left(\frac{\hbar^2 l_1(l_1+1)}{2J} + \frac{kT}{2}\right)P_{l_1m_1}\right]P_{lm} = F(P_{lm}, P_{l_1m_1}),$$

$$\frac{\partial P_{l_1m_1}}{\partial t} = \frac{2\alpha}{(1+\alpha^2)\hbar}\left[\left(\frac{\hbar^2 l_1(l_1+1)}{2J} + \frac{kT}{2}\right)(P_{l_1m_1} - 1) + \right.$$

$$\left. + \left(\frac{\hbar^2 l(l+1)}{2J} + \frac{kT}{2}\right)P_{lm}\right]P_{l_1m_1} = \Phi(P_{lm}, P_{l_1m_1}). \qquad (24)$$

Assume that the rotor is in the equilibrium state corresponding to the energy level E_l. This means that the following is valid:

$$P_{l_1} = \begin{cases} 1, & l_1 = l; \\ 0, & l_1 \neq l. \end{cases} \qquad (25)$$

For the reasons mentioned above, we can expect that only one P_{lm} is nonzero.

Consider first the case of coinciding l and l_1, and $l \neq 0$.

Since the equality

$$P_{lm} + P_{lm_1} = 1 \qquad (26)$$

is valid in the considered approximation, it follows from Eq. (24)

$$\frac{\partial P_{lm}}{\partial t} = 0, \quad \frac{\partial P_{lm_1}}{\partial t} = 0. \qquad (27)$$

Taking into account the properties of the solution of Eq. (22), we can conclude that, at stochastic perturbation of the rotor, quantum transitions are possible only between the states having different energy.

In the case that $l \neq l_1$, the population of the quantum states, as in the previous case, is determined by the system of equations (24). The parameters giving the information about the character of stationary states of the rotor and their dynamics are the Jacobian of the system of equations (24)

$$\Delta = \begin{vmatrix} F'_{P_{lm}}(P_{lm}, P_{l_1m_1}) & F'_{P_{l_1m_1}}(P_{lm}, P_{l_1m_1}) \\ \Phi'_{P_{lm}}(P_{lm}, P_{l_1m_1}) & \Phi'_{P_{l_1m_1}}(P_{lm}, P_{l_1m_1}) \end{vmatrix} \qquad (28)$$

and the sum of diagonal elements of this Jacobian

$$\sigma = F'_{P_{lm}}(P_{lm}, P_{l_1m_1}) + \Phi'_{P_{l_1m_1}}(P_{lm}, P_{l_1m_1}), \qquad (29)$$

calculated at the equilibrium point (assuming that $P_{lm} = 1;\ P_{l_1m_1} = 0$) [Ref. 12].

The values of these constants near the equilibrium points depend on the orbital quantum number, moment of inertia, temperature, and the parameter α:

$$\Delta = \left(\frac{\alpha}{(1+\alpha^2)}\right)^2 \frac{1}{J}\left[\frac{\hbar^2 l(l+1)}{J} + kT\right]\left[l(l+1) - l_1(l_1+1)\right]; \qquad (30)$$

$$\sigma = \frac{\alpha}{\hbar(1+\alpha^2)}\left\{\frac{\hbar^2}{J}\left[2l(l+1) - l_1(l_1+1)\right] + kT\right\}. \qquad (31)$$

Since $\Delta \neq 0$, the equilibrium points are tough: there are no other equilibrium points near them. Therefore, if the rotor leaves the equilibrium position, then, unless some stable cycle arises, it either transits into other equilibrium state or returns into the initial one.

Consider possible versions of the rotor's behavior in a more detail.

Let $l > l_1$. In this case $\Delta > 0$. There is a knot.[12] Since $\sigma > 0$, this equilibrium point is unstable. Therefore, in the presence of prerequisites for a "catastrophe," the rotor can leave this state in a jump. There are no stable cycles here. Actually, if, after leaving the equilibrium state, the rotor finds itself in the state described by a superposition of wavefunctions of the upper and lower states, then finally it transits to the lower energy level. According to Eq. (5), this superposition has the form

$$\psi = \left[C_l \exp\left(-\frac{(i+\alpha)\hbar l(l+1)}{2J(1+\alpha^2)}t\right)\psi_l + C_{k_1} \times \right.$$

$$\left. \times \exp\left(-\frac{(i+\alpha)\hbar l_1(l_1+1)}{2J(1+\alpha^2)}t\right)\psi_{l_1}\right] \Big/ \left[|C_l|^2 \exp\left(-\frac{\alpha\hbar l(l+1)}{J(1+\alpha^2)}t\right) + \right.$$

$$\left. + |C_{l_1}|^2 \exp\left(-\frac{\alpha\hbar l_1(l_1+1)}{J(1+\alpha^2)}t\right)\right]^{\frac{1}{2}},$$

Consider one version more: $l < l_1$.

The equilibrium point in this case is a saddle and also unstable. This means that the population of the rotor's lower level, as in the case with $l > l_1$, can change in a jump. However, there is an important difference here. Such changes are not always possible.

Actually, if the rotor is disturbed from the equilibrium position so that its new state is described

by the superposition (32), then with time the rotor returns into the initial state. Generally, the rotor's trajectory from the equilibrium position is a loop tangent to the saddle separatrix.[12] The stability of this loop depends on the sign of σ [Ref. 12]. If this parameter is negative at the equilibrium point, then the loop is stable; otherwise it is unstable. Consequently, the jump like change of the rotor's equilibrium position is possible only if $\sigma > 0$. Otherwise, once the rotor leaves the equilibrium position, even with some prerequisites for the quantum jump, it returns into the initial state. This means that the upper state finally turns out unpopulated. From Eq. (31) it follows that the rotor cannot change the equilibrium position in a jump at

$$T < \frac{\hbar^2}{kJ}\left[l_1(l_1+1) - 2l(l+1)\right]. \qquad (33)$$

That is, at the temperature below the limit determined by Eq. (33), the rotor, falling into the lower equilibrium position, cannot transit to the upper level without a strong external action. Consequently, if we consider an ensemble of rotors, then at the temperature below the critical one

$$T < 2\hbar^2/kJ\,, \qquad (34)$$

because of the density fluctuations of the thermostat, only the lower energy state of the rotors is occupied. Thus, the Bose condensation of the rotor's states takes place. Seemingly, it is just this effect that manifests itself in the thermal capacity of gases. An important property of such states is that both spontaneous and stimulated emission must be absent in the ensemble of rotors. At a temperature below the limit determined by Eq. (34), any emission caused by rotation disappears: molecules become invisible.

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