### Quantum theory of Rayleigh scattering

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**Abstract:** We suggest a quantum description of Rayleigh light scattering on atoms. We show that an entangled state of the excited atom and the incident photon is formed during the scattering. Due to entanglement, a photon is never completely absorbed by the atom. The formation of the scattering spectrum is considered as a relaxation of incident photons to the reservoir of free space modes that are in thermal equilibrium. Additional excitations of the reservoir modes occurring during scattering are treated as scattered light. We show that even if the frequency of incident photons is incommensurate with an atomic transition frequency, the scattered light spectrum has a maximum at the frequency of incident photons. In addition, the linewidth of the scattered light is much smaller than that of the spontaneous emission of a single atom. Therefore, the process can be considered as elastic.

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#### 1. Introduction

The internal structure of various materials is probed with a beam of particles (electrons, neutrons, ions, and photons). Photons are most commonly used to determine the structure of atoms and molecules.

The history of this method dates back to 1869 when Tyndall [1] observed light scattered by very small particles. The theory for Tyndall's observations was developed by Rayleigh [2], who treated the problem of elastic scattering of an electromagnetic (EM) wave by a subwavelength particle as forced oscillations of the polarization of the subwavelength particle. The theory predicted symmetry in forward and backward scattering of light from a single particle, the polarization of the scattered light, and successfully explained the blue color of the sky.

However, experimental data on the observation of bright lines in the solar spectrum [3,4] could not explained by this theory. Such lines indicated that the phenomenon is of resonant nature. Since the atoms are of subwavelength sizes, classical Rayleigh's theory predicted no resonant phenomena. The nature of these lines was only understood with the development of quantum mechanics [4], in which the lines were associated with the resonant transitions between the eigenstates of the electronic subsystems of atoms or molecules accompanied by emission of photons. The quantum-mechanical study of the eigenstates of atoms and transitions between them resulted in the development of optical spectroscopy. In contrast to Rayleigh's theory, the optical spectroscopy deals with resonance phenomena.

The adaptation of the theory of optical spectroscopy, which deals with resonances, to the nonresonant scattering problem inevitably requires phenomenological assumptions. Indeed, the scattering problem implies that the initial atomic state coincides with its final state; therefore, according to Fermi's golden rule, in the first order of the perturbation theory over the photon-atom interaction, the probability of a transition between identical initial and final states is zero. This is why to calculate the scattering cross section, the pioneering Placzek's theory [5] employs the

second order of the perturbation theory, in the form of the Kramers-Heisenberg formula [6] (see also [7] and [8]). The formula can be interpreted as a sequence of photon absorption and emission [9,10]. In particular, Placzek's theory implies that during the scattering process, the incident photon and a multilevel atom are in a superposition state, at which the excited atomic levels are populated with some probability amplitude. There is a finite probability that the incident photon is completely absorbed. Then, the dipole moment of the atom is nonzero, and the atom radiates without delay. However, due to transitions between different superposition states, the radiation line would be broad, which does not correspond to elastic scattering. To use this model for elastic scattering, one has to *postulate* (see [5]) that the emitted photon has the same frequency as the absorbed one. To avoid such an assumption and to apply the Kramers-Heisenberg formula, an existence of the resonant condition between incident photon and some level is assumed [5,9].

The reduction of the multilevel Placzek's model of an atom to a two-level system (TLS) makes Placzek's conclusions less obvious. Indeed, Placzek's theory implies that absorption/emission of photons is resonant. It is described by the resonant term of the Kramers-Heisenberg formula. On the other hand, Rayleigh scattering assumes that the photon frequency is incommensurate with atomic excitation frequencies. To reconcile this, one has to introduce the hypothesis of a virtual state – an intermediate state that is excited by an incident photon. However, since the linewidth of Rayleigh scattering coincides with the linewidth of the incident light, and the absorption-emission process includes spontaneous emission from the virtual state, the latter must have a very narrow linewidth or a very long lifetime. Experiments, on the contrary, show that the lifetime of the process is very short. To resolve this, it is often assumed that the virtual state is never populated. Consequently, there should be neither spontaneous decay, no broadening of the line of incident light. The virtual state approach is still used for describing Rayleigh scattering [11-14]. However, mainly, instead of the Kramers-Heisenberg formula, one uses either Lindblad or Heisenberg-Langevin equations [15-17]. Thanks to the clarity of the picture of the phenomenon created by the virtual state hypothesis, it is often used to explain the mechanisms of some phenomena in quantum optics, in particular, in the theory of the Raman effect (e.g., see [18-20]).

Recently, the problem of resonant scattering of photons on a quantum scatter placed in a waveguide has attracted considerable attention [15-17,21-29]. This problem is important in the context of quantum information and quantum communications systems. In [15-17,21-29], the main attention is devoted to calculation of probabilities of occupation of the final state. However, the formation of coherence of Rayleigh scattering has not been discussed.

The progress in the theory of Rayleigh scattering was mainly based on the following works. First, Rabi [4] considered the precession of a magnetic dipole moment in a magnetic field and showed that the probability of changing the spin direction of an atom to the opposite oscillates. Thus, for a quantum system, there appears an alternative for the evolution under the influence of an external force: not only can it transition between the eigenstates but also be driven by an external force.

Second, Jaynes and Cummings (JC) [30] considered the interaction of an atom with a single mode of an EM field found eigenstates of this system, referred to as dressed atom states. JC showed that not the transitions between the atomic eigenstates, but the transitions of the whole system between the found eigenstates were responsible for radiation.

In this paper, we develop a quantum theory of Rayleigh scattering of light by an atom. Our approach is based on the JC-Hamiltonian [12] that describes an atom interacting with incident photons from a mode of the EM field of free space. We call this mode *selected*. In the JC-eigenstates, the atomic state and state of the incident photon are entangled but the photon is never completely absorbed by the atom. During the scattering, an atomic level is excited nonresonantly. We show that the probability amplitudes of the excited atomic state oscillate with the frequency of the incident photon. Dealing with JC-eigenstates requires introduction

of an external force that can cause the transitions between them. As such an external force, we consider the interaction of the exited atom with the reservoir of free space modes. The excitations arising in the reservoir due to this interaction are treated as scattered photons. The spectrum of these photons has a maximum at the frequency of the selected mode, and the linewidth of the maximum is much narrower than the linewidth of the spontaneous emission from a single atom. We apply our results to the problems with various initial conditions for photons.

## Rayleigh scattering as relaxation of the Jaynes-Cummings system into free space modes

In further consideration, we assume that the frequency of the incident photon is incommensurable with any frequency of inter-level atomic transitions. This allows us to represent an atom as a TLS. This assumption is correct if the difference between the photon frequency and the frequency of the nearest eigenstate of the atom is greater than the linewidth of the eigenstate (see Appendix A for details).

Consider an atom placed in free space. Following the traditional scheme of quantization of the EM field, we assume that the volume V of the space in which quantization occurs is large but finite. We represent the atom by a TLS with the ground state  $|g\rangle$ , the excited state  $|e\rangle$ , and the transition frequency  $\omega_{\text{TLS}}$ . We assume that the EM modes of this volume are in thermal equilibrium with a given temperature T. The eigenstates of the modes are described by Fock states  $|n\rangle$  with a given number of photons in the mode.

The object of our investigation is a quantum atom interacting with a selected free space mode, to which  $n_0$  incident photons belong at the initial moment of time. The rest of the free space modes are considered as a reservoir. The number of photons  $n_0$  in this *selected mode* determines the energy of the incident wave as  $\hbar\omega_{SM}n_0$ . Other EM field modes are assumed to be empty. The scattering process is considered as the relaxation of photons in the selected mode into the reservoir. Additional excitations of the reservoir modes, which appear during the relaxation, are treated as scattered light.

We solve the scattering problem in two steps. First, we focus on the subsystem consisting of the atom and a selected mode with the wave vector  $\mathbf{k}_{\text{SM}}$ , the polarization  $\lambda_{\text{SM}}$ , and the frequency  $\omega_{\text{SM}} = c |\mathbf{k}_{\text{SM}}|$ . Suppose that this selected mode is excited, and there are  $n_0$  photons in it. Eigenfrequencies of this mode,  $\omega_{\text{SM}}(n + 1/2)$ , n = 0, 1, 2, ..., form an equidistant spectrum. Thus, initially, the selected mode is not in thermal equilibrium with the other free space modes. This mode plays the role of incident radiation. At this stage, we neglect the interaction of the atom with empty modes.

In the absence of the interaction between the modes and the atom, the system eigenstates are direct products of the eigenstates of the modes and the atom,  $|n, e\rangle$  and  $|n, g\rangle$ . When the interaction is taken into account, the atom and photon states are entangled. Following JC, we refer to them as  $|+, n\rangle$  and  $|-, n\rangle$  (see for detail [30]).

We suppose that the atom size is much smaller than the wavelength of the selected mode such that the interaction between the atom and the mode is considered in the dipole approximation. Then, the Hamiltonian of this subsystem in the rotating wave approximations has the form of the Jaynes-Cummings (JC)-Hamiltonian [31,32]:

$$\hat{H}_{\rm S} = \hbar\omega_{\rm TLS}\hat{\sigma}^{\dagger}\hat{\sigma} + \hbar\omega_{\rm SM}\hat{a}^{\dagger}\hat{a} + \hbar\Omega_{\rm R}(\hat{a}^{\dagger}\hat{\sigma} + \hat{\sigma}^{\dagger}\hat{a}), \tag{1}$$

where  $\Omega_{\mathbf{R}} = -\mathbf{E}_0 \cdot \mathbf{d}/\hbar = -\sqrt{2\pi\hbar\omega_{\mathrm{SM}}/V}\mathbf{e}_{\mathbf{k}_0,\lambda_0} \cdot \mathbf{d}/\hbar$  is the interaction constant (the Rabi frequency),  $\mathbf{e}_{\mathbf{k}_0,\lambda_0}$  is the unit polarization vector of the selected mode, **d** is the matrix element of the dipole transition of the TLS,  $\sigma = |g\rangle \langle e|$  and  $\sigma^{\dagger} = |e\rangle \langle g|$  are lowering and raising operators for the TLS, respectively, and  $\hat{a}$  and  $\hat{a}^{\dagger}$  are photon annihilation and creation operators, respectively.

The eigenstates of the Hamiltonian (1) are well-known [30] (see also [32,33]), this is basis of eigenstate of JC-model. Among them, there is the ground state that does not contain photons

 $(n = \left\langle \hat{a}^{\dagger} \hat{a} \right\rangle = 0)$ 

$$|g,0\rangle.$$
 (2)

We assume that the energy of this state is zero. Excited eigenstates can be combined in pairs:

$$|+,n\rangle = \cos\varphi_n |e,n-1\rangle + \sin\varphi_n |g,n\rangle, |-,n\rangle = -\sin\varphi_n |e,n-1\rangle + \cos\varphi_n |g,n\rangle, \quad n = 1, 2, \dots;$$
(3)

where  $\varphi_n = \tan^{-1} \left( 2\Omega_R \sqrt{n} / |\Delta| \right) / 2$ . The eigenfrequencies of these states are

$$\omega_{\pm,n} = (n-1)\omega_{\rm SM} + (\omega_{\rm SM} + \omega_{\rm TLS})/2 \pm \sqrt{\Omega_R^2 n + (\Delta/2)^2}, \ n = 1, 2, \dots,$$
(4)

where  $\Delta = \omega_{\text{SM}} - \omega_{\text{TLS}}$  is the frequency detuning. The value  $2\sqrt{\Omega_R^2 n + (\Delta/2)^2}$  is the frequency difference between the states  $|+, n\rangle$  and  $|-, n\rangle$ .

We assume that the selected mode initially contains  $n_0$  photons, and the atom is in the ground state so that the system initial state is  $|n_0, g\rangle$ . This state is not the JC-eigenstate. Therefore, as we show below (Sec. 3.1), the Rabi oscillations of the atom population begin. After damping of these oscillations, the system is in-JC eigenstate. It should be emphasized that the mean value of the atomic dipole moment between JC-eigenstates is non-zero. As a consequence, the dipole transition occurs even in the first order of the perturbation over the interaction between the atom and the free-space mode reservoir (see also Appendix B).

In the second step, we consider the scattering process. In the formalism described above, this process is reduced to the evolution of the JC- system, which interacts with other free space modes. We emphasize that the relaxation of the system occurs due to the interaction of the atom with the free space modes, while the selected mode does not interact directly with the other free space modes. The excitation of free space modes is treated as scattering.

The Hamiltonian of the free space modes has the form [9,32]:

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$$\hat{H}_{\mathbf{R}} = \sum_{\mathbf{k},\lambda} \hbar \omega_{\mathbf{k},\lambda} \hat{a}^{\dagger}_{\mathbf{k},\lambda} \hat{a}_{\mathbf{k},\lambda}, \tag{5}$$

where  $\omega_{\mathbf{k},\lambda}$  is the frequency of the free space mode with the wave vector  $\mathbf{k}$  and the polarization  $\lambda$ ,  $\hat{a}_{\mathbf{k},\lambda}$  and  $\hat{a}_{\mathbf{k},\lambda}^{\dagger}$  are annihilation and creation operators, respectively. The atomic dipole moment interacts with these modes. The corresponding interaction Hamiltonian has the form

$$\hat{H}_{\rm SR} = \sum_{\mathbf{k},\lambda} \hbar \gamma_{\mathbf{k},\lambda} (\hat{a}^{\dagger}_{\mathbf{k},\lambda} \hat{\sigma} + \hat{\sigma}^{\dagger} \hat{a}_{\mathbf{k},\lambda}), \tag{6}$$

where  $\gamma_{\mathbf{k},\lambda} = -|\mathbf{d}| \sqrt{2\pi \hbar \omega_{\mathbf{k},\lambda}/V} / \hbar$  is the interaction constant of the atomic dipole moment with the electric field of the free space mode. The form of Hamiltonian (6) indicates that the interactions of an atom with each mode are independent. Further, it is convenient to rewrite the operator of the interaction of the system with reservoir (6) in the basis of the eigenstates of the JC- system, i.e. in basis (2)-(3). One can show that in this basis, the Hamiltonian  $\hat{H}_{SR}$  of the interaction of the system with the reservoir can be written as

$$\hat{H}_{SR} = \sum_{\mathbf{k},\lambda} \hbar \gamma_{\mathbf{k},\lambda} a_{\mathbf{k},\lambda}^{\dagger} (\cos \varphi_1 \hat{S}_{(g,0)(+,1)} - \sin \varphi_1 \hat{S}_{(g,0)(-,1)} + \sum_{n=1}^{\infty} (\cos \varphi_n \sin \varphi_{n-1} \hat{S}_{(+,n-1)(+,n)} - \sin \varphi_n \sin \varphi_{n-1} \hat{S}_{(+,n-1)(-,n)} + \cos \varphi_n \cos \varphi_{n-1} \hat{S}_{(-,n-1)(+,n)} - \sin \varphi_n \cos \varphi_{n-1} \hat{S}_{(-,n-1)(-,n)})) + \text{h.c.}$$
(7)

where we introduce the notations for the operators of possible transitions between the JCeigenstates:

$$\hat{S}_{(+,n-1)(+,n)} = |+, n-1\rangle \langle +, n|, \qquad \hat{S}_{(+,n-1)(-,n)} = |+, n-1\rangle \langle -, n|, 
\hat{S}_{(-,n-1)(+,n)} = |-, n-1\rangle \langle +, n|, \qquad \hat{S}_{(-,n-1)(-,n)} = |-, n-1\rangle \langle -, n|, 
\hat{S}_{(g,0)(-,1)} = |g, 0\rangle \langle -, 1|$$
(8)

Following our two-step procedure, first, we find the dynamics of the JC-system supposing that the state of the free-space mode reservoir is not changed. At this step we obtain the master equation and find its quasi-stationary solution.

Knowing the JC-eigenstates we exclude the free space mode variables with the exception of the selected mode. For this, we have to assume that the reservoir of free space modes is in a state of thermal equilibrium at a given temperature. Neglecting relativistic effects, we can assume that the frequencies are limited to the optical range. Further, we assume that T = 0, i.e., the free space modes are empty. Following the standard procedure, we obtain the density matrix in basis (3), which obeys the master equation of the Lindblad form (the explicit form the Lindblad supperoperator is given in Appendix C) [32,34,35]:

$$\frac{\partial \hat{\rho}}{\partial t} = \frac{i}{\hbar} [\hat{\rho}, \hat{H}_{\rm S}] + \sum_{n} \frac{\gamma_n}{2} (2\hat{S}_n \hat{\rho} \hat{S}_n^{\dagger} - \hat{S}_n^{\dagger} \hat{S}_n \hat{\rho} - \hat{\rho} \hat{S}_n^{\dagger} \hat{S}_n). \tag{9}$$

Here  $S_n$  is the transition operators between the JC-eigenstates determined by Eq. (8);  $\gamma_n$  is the characteristic rate of the transition between eigenstates obtained by averaging over the free space modes (for a detailed derivation, see [32,34–36]).

Each term in Eq. (9) having  $2\hat{S}\hat{\rho}\hat{S}^{\dagger} - \hat{S}^{\dagger}\hat{S}\hat{\rho} - \hat{\rho}\hat{S}^{\dagger}\hat{S}$  as a factor describes the transitions of the system between the JC-eigenstates { $|g, 0\rangle$ ,  $|+, n\rangle$ ,  $|-, n\rangle$ }, n = 1, 2, ... We emphasize that it is the interaction of the JC- system with the reservoir of free space modes that leads to a transition between the eigenstates of this subsystem.

Rayleigh scattering is non-resonant; therefore, for simplicity, we consider the limiting case of a large detuning,  $|\Delta| \gg \Omega_R \sqrt{n}$ , and a large volume of the resonator,  $V \to \infty$ . To be specific, we assume  $\omega_{\text{SM}} < \omega_{\text{TLS}}$ . Then, using  $\varphi_n = \tan^{-1} \left( 2\Omega_R \sqrt{n} / |\Delta| \right) / 2 \simeq \Omega_R \sqrt{n} / |\Delta|$ ,  $\sin \varphi_n \simeq \varphi_n \simeq \Omega_R \sqrt{n} / |\Delta|$ , and  $\cos \varphi_n \simeq 1$ , the expression for eigenfrequencies (4) and states (3) can be expanded in a small parameter  $\Omega_R \sqrt{n} / \Delta$ :

$$\omega_{n,-} \approx n\omega_{\rm SM} - \Omega_R^2 n / |\Delta|, \qquad |-,n\rangle \approx -\frac{\Omega_{\rm R} n}{|\Delta|} |e,n-1\rangle + |g,n\rangle, \tag{10}$$

$$\omega_{n,+} \approx (n-1)\omega_{\rm SM} + \omega_{\rm TLS} + \Omega_R^2 n / |\Delta|, \qquad |+,n\rangle \approx |e,n-1\rangle + \frac{\Omega_{\rm R}\sqrt{n}}{|\Delta|}|g,n\rangle. \tag{11}$$

One can see that in the limit  $\Delta \gg \Omega_R \sqrt{n}$ , the eigenfrequencies  $\omega_{n,-}$ , Eq. (10), for the eigenstates  $|n, -\rangle$  coincide with the eigenfrequencies  $n\omega_{SM}$  of the selected mode with the accuracy  $\Omega_R^2 n/|\Delta| \ll 1$ , and the difference between the frequencies of the levels  $|n, -\rangle$  with different *n* is equal to  $\omega_{CM} - \Omega_R^2/|\Delta|$ , i.e., with the accuracy  $\Omega_R^2/|\Delta|$  it coincides with the frequency of the selected mode  $\omega_{SM}$ . Thus, we can expect that a photon with a frequency  $\omega_{SM}$  is emitted during the transition between eigenstates  $|n, -\rangle$ . Note that in this consideration, states with the transition frequency  $\omega_{SM}$  arise naturally, and we do not have to introduce an additional virtual level.

Further, we expand the density matrix over eigenstates (2)-(3). In Appendix C, we show that in the limit  $\Delta \gg \Omega_R \sqrt{n}$  and for the initial condition  $\hat{\rho}(0) = |g, n_0\rangle \langle g, n_0|$ , only the states  $|-, n\rangle$  are mainly occupied. Let us denote  $p_n(t) = \langle -, n | \hat{\rho}(t) | -, n \rangle$ ,  $\gamma_0 \Omega_R^2 n / |\Delta| \equiv \gamma_n$ , and  $\omega_{n,-} = \omega_n$ . The quantity  $p_n(t)$  has the meaning of the probability of the occupation of the entangled state of the selected mode and the atom  $|-, n\rangle = -\sin \varphi_n |e, n - 1\rangle + \cos \varphi_n |g, n\rangle$ , while  $\gamma_n$  has the meaning

of the transition rate form the state  $|-, n\rangle$  to the state  $|-, n - 1\rangle$ . Equations for  $p_n(t)$  take the form (see Appendix C):

$$\dot{p}_{n_0}(t) = -\gamma_{n_0} p_{n_0}, \dot{p}_n(t) = -\gamma_n p_n(t) + \gamma_{n+1} p_{n+1}(t), \qquad 1 \le n < n_0,$$

$$\dot{p}_0(t) = \gamma_1 p_1(t),$$
(12)

with the initial condition

$$p_{n_0}(0) = 1, p_n(0) = 0, \ 0 \le n < n_0,$$
 (13)

In terms of the solution of system (12) with initial conditions (13), the one-time average of the atom population can be written as

$$\left\langle \hat{\sigma}^{\dagger}(t)\hat{\sigma}(t)\right\rangle \simeq \sum_{k=n_0}^{1} \sin^2 \varphi_k p_k(t) \simeq \sum_{k=n_0}^{1} (\Omega_R^2 k/|\Delta|^2) p_k(t),$$
 (14)

At the second step, we find the radiation spectrum. To do this, we first write the Heisenberg equation for the operator  $\hat{a}_{\mathbf{k},\lambda}(t)$ :

$$\dot{\hat{a}}_{\mathbf{k},\lambda}(t) = \frac{i}{\hbar} [\hat{H}_{\mathrm{S}} + \hat{H}_{\mathrm{SR}} + \hat{H}_{\mathrm{R}}, \hat{a}_{\mathbf{k},\lambda}] = -i\omega_{\mathbf{k},\lambda} \hat{a}_{\mathbf{k},\lambda}(t) - i\sqrt{\frac{2\pi\omega_{\mathbf{k},\lambda}}{V\hbar}} \mathbf{e}_{\mathbf{k},\lambda} \cdot \mathbf{d}\hat{\sigma}(t)$$
(15)

Integration of Eq. (15) gives

$$\hat{a}_{\mathbf{k},\lambda}(t) = \hat{a}_{\mathbf{k},\lambda}(0)\exp(-i\omega_{\mathbf{k},\lambda}t) - i\sqrt{\frac{2\pi\omega_{\mathbf{k}}}{V\hbar}}\mathbf{e}_{\mathbf{k},\lambda} \cdot \mathbf{d}\int_{0}^{t} d\tau \hat{\sigma}(\tau)\exp(-i\omega_{\mathbf{k},\lambda}(t-\tau))$$
(16)

The mean value of the photon number in each mode is (see also [34]):

$$\left\langle \hat{a}_{\mathbf{k},\lambda}^{\dagger}(t)\hat{a}_{\mathbf{k},\lambda}(t) \right\rangle \equiv n_{\mathbf{k},\lambda}(t)$$

$$\simeq \left| \sqrt{\frac{2\pi\omega_{\mathbf{k}}}{V\hbar}} \mathbf{e}_{\mathbf{k},\lambda} \cdot \mathbf{d}_{eg} \right|^{2} t\pi \int_{0}^{\infty} d\tau \left\langle \hat{\sigma}^{\dagger}(t+\tau)\hat{\sigma}(t) \right\rangle \exp(-i\omega_{\mathbf{k},\lambda}\tau)$$

$$(17)$$

Note, that to calculate the radiation spectrum by using Eq. (17), we should suppose that  $t>t_{st}$  so that the system reaches its stationary state determined by the master Eq. (9).

According to the Wiener-Khinchin theorem [31,37,38], the scattering spectrum can be expressed in terms of the Fourier transform of the two-time correlation function  $\langle \hat{\sigma}^{\dagger}(t_1)\hat{\sigma}(t_2) \rangle$ ,  $t_1 > t_2$ [32,34]. According to the general theory [31,32,34], to find  $\langle \hat{\sigma}^{\dagger}(t_1)\hat{\sigma}(t_2) \rangle$ ,  $t_1 > t_2$ , one needs to solve master Eq. (9) two times with two different initial conditions. First, we need to solve Eq. (9), and find  $\hat{\rho}(t_2)$ . Then, it is necessary to solve master Eq. (9) for  $t \le t_1$  with the initial condition  $\hat{\rho}(0) = \hat{\sigma}\hat{\rho}(t_2)$ . The obtained value we denote as  $\hat{\rho}(t_1 - t_2)$ . According to the quantum regression theorem [31,32,34],  $\langle \hat{\sigma}^{\dagger}(t_1)\hat{\sigma}(t_2) \rangle$  is equal to  $\text{Tr}(\hat{\sigma}^{\dagger}\hat{\rho}(t_1 - t_2))$ . With the aid of master Eq. (9), one can obtain

$$\left\langle \hat{\sigma}^{\dagger}(t+\tau)\hat{\sigma}(t)\right\rangle \simeq \sum_{k=n_0}^{1} \left(\Omega_R^2 k/|\Delta|\right)^2 p_k(t) \exp((i\omega_{\rm CM} - (\gamma_k + \gamma_{k-1})/2)\tau).$$
(18)

A specific calculation of the radiation depends on the initial value of the number of photons  $n_0$  in the selected mode, and how we obtain the limit  $V \rightarrow \infty$ . Different limits give the answers obtained within the approaches of Placzek [5], Berestetskii-Lifshitz-Pitaevskii [9], and the

coherent initial state [39] suggested by Glauber. The latter case, in our opinion, corresponds most closely to the formulation of the problem in which the field is considered as classical.

Thus, we develop a theory in which scattering is considered as a relaxation of an interacting atom and a photon from the selected mode to the reservoir of the other free space modes. We obtain the master equation for the system dynamics, Eq. (9), and simplify this equation in the case of large detuning between the frequency of selected mode and atomic transition frequency, Eqs. (12). Note that all the levels in the system considered, Eq. (4), are real, and there is no necessity to introduce a virtual level. Below, we show that the model developed reproduces the elasticity of the Rayleigh scattering, and in the case of a coherent initial state of a photon from the selected mode, it yields the same results as a theory in which an incident photon is described as a classical field.

#### 3. Different cases of photon scattering on an atom

To illustrate an application of our theory, we consider four specific cases of the scattering problem distinguishing by initial conditions,

First, we consider the initial condition with one photon in the selected mode. This case corresponds to the Berestetskii-Lifshitz-Pitaevskii [9] approach. We demonstrate that even in this case, there is no absorption of a photon but only Rabi oscillations arise. This case is difficult to realize in experiment, and it is considered only to clarify the physics of the phenomenon.

Second, we consider more realistic case with  $n_0$  incident photons and the transition to the state with  $n_0 - 1$  photons in the selected mode. This case corresponds to Placzek's formulation of the problem. We show that in this case, a narrow spectral line arises. However, to solve the problem of scattering of  $n_0$  photons, it is necessary to solve system of equations (12), which takes into account the transitions between all eigenstates (10).

In the third example, we consider scattering of  $n_0$  photons taking into account a cascade of transitions between the JC-states. We show that this case reproduces almost all experimental features of Rayleigh scattering, namely, narrow spectral line and quasistationary occupancy of the atom states. However, the dipole moment of the atom is zero.

Finally, to reproduce a coherent response of the atom with a non-zero dipole moment, we consider the case of a coherent initial state of the selected mode. In such case, we obtain both a narrow spectral line and a non-zero quasistationary dipole moment of the atom.

#### 3.1. Berestetskii-Lifshitz-Pitaevskii approach of a single incident photon

First, we assume that initially in the selected mode, only one photon is present, i.e., the initial condition is  $n_0 = 1$ . Such a formulation was considered in [9].

As mentioned above, without interaction with the reservoir, in the system consisting of the atom and photon, the atom's probability of being excited,  $\langle \hat{\sigma}^{\dagger}(t)\hat{\sigma}(t)\rangle \equiv p_e(t)$ , and the mean number of photons,  $\langle \hat{a}^{\dagger}(t)\hat{a}(t)\rangle \equiv n_{\rm ph}(t)$ , should exhibit Rabi oscillations. The interaction of the system with the free space mode reservoir leads to vanishing with the rate  $\gamma_1$  from the Eq. (12) of both  $p_e(t)$  and  $n_{\rm ph}(t)$  against the background of damping of the Rabi oscillations. Indeed, numerical simulation of Eq. (9) demonstrates such behavior (see Fig. 1). From this numerical simulation, we conclude that there are two characteristic times in the system dynamics,  $\gamma_0^{-1}$  and  $(\gamma_0 \Omega_R^2 / |\Delta|^2)^{-1}$ .

We can see that at the initial time,  $t \le \gamma_0^{-1}$ , both  $p_e(t)$  and  $n_{ph}(t)$  oscillate with the Rabi frequency  $2\sqrt{\Omega_R^2 + (\Delta/2)^2}$ . The Rabi oscillations of both quantities dissipate with the characteristic rate  $\sim \gamma_0$ . The presence of the Rabi oscillations means that the photon from the selected mode does not absorb.

After the dissipation of Rabi oscillations, the probability of the atom to be in the excited state reaches the value  $(\Omega_R^2/|\Delta|^2)$ . At the time  $t \gg \gamma_0^{-1}$ , the system dynamics obeys Eq. (12), which

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**Fig. 1.** Time dependence of (a) the probability of the atom to be in the excited state and (b) the number of photons in the selected mode.

solution has the form

$$p_1(t) = \exp(-\gamma_0 (\Omega_R^2 / |\Delta|^2) t).$$
 (19)

The solution for the atom population, Eq. (14), is

$$\left\langle \hat{\sigma}^{\dagger}(t)\hat{\sigma}(t)\right\rangle \equiv p_{e}(t) \simeq (\Omega_{R}^{2}/|\Delta|^{2})\exp(-\gamma_{0}(\Omega_{R}^{2}/|\Delta|^{2})t).$$
(20)

Eq. (20) shows that the atom radiates with the rate  $\gamma_0(\Omega_R^2/|\Delta|^2)$ . At the initial time, the excitation energy is  $\Omega_R^2/|\Delta|^2$ . Usually, in problems about an atom in free space, the infinite volume limit is considered. In this limit, the coupling constant approaches zero as  $\Omega_R \sim 1/\sqrt{V} \rightarrow 0$  and the radiation rate is infinitely small. In this formulation, two-time correlation function (18) has the form

$$\left\langle \hat{\sigma}^{\dagger}(t+\tau)\hat{\sigma}(t)\right\rangle \simeq \exp(i\omega_{\rm SM}\tau)\Omega_R^2/|\Delta|^2 \exp(-\gamma_0(\Omega_R^2/|\Delta|^2)t)\exp(-\gamma_0(\Omega_R^2/2|\Delta|^2)\tau).$$
(21)

Note that if we fix the time and find the spectrum as the Fourier transform of the two-time correlation function with respect to  $\tau$ , then we obtain a Lorentz line centered at the frequency  $\omega_{\text{SM}}$  of the selected mode with the width  $\sim \gamma_0(\Omega_R^2/2|\Delta|^2) \ll \gamma_0$ . Thus, in this formulation, a narrow emission line is reproduced. However, this narrow line corresponds to extremely slow radiation. Further, the total detectable energy emitted by the atom is  $\sim \Omega_R^2/|\Delta|^2$ , i.e., in the limit considered, it is also extremely small.

One can calculate the scattering cross section by dividing the total radiated energy by the energy flux that the selected mode creates at the atom location. Since the energy flux  $\sim \Omega_R^2$  [31,40], small quantities are canceled out, and the cross section becomes finite (it is given in [5] and [9]). However, the finite value of the scattering cross section is obtained due to the division of two infinitely small quantities: incident and radiated energies. Such problem formulation does not correspond to an experiment in which the finite field energy flows over a finite time, and the final radiation energy is detected.

The smallness of the radiation energy can be avoided if we consider the limit at which the average field value at the atom location is finite. For this, we put  $\Omega_{\rm R} \sim 1/\sqrt{V} \rightarrow 0$  and  $n_0 \sim V \rightarrow \infty$ , then  $\Omega_{\rm R}\sqrt{n_0} \rightarrow \text{const}$ , i.e., we consider a large initial value of the number of photons in the selected mode so that for any volume, the electric field of the selected mode is finite. We continue to assume that the detuning is so large that  $\Omega_{\rm R}\sqrt{n_0}/\Delta \ll 1$ .

#### 3.2. Placzek's approach: the scattering of one photon from the $n_0$ ensemble of photons

In the approach developed by Placzek [5], one considers a single transition process, in which the number of photons is changed by unity. To reproduce the result of this approach, it is necessary,

in system (12), to retain only one equation that describes the dynamics of the initial state  $|n_0, -\rangle$ . We assume that the initial state of the system is  $p_{n_0}(0) = 1$ . Other states are supposed to be empty all the time, i.e.  $p_n(0) = p_n(t) = 0$ ,  $1 \le n < n_0$ . After such simplification, the system of Eqs. (12) reduces to

$$\dot{p}_{n_0}(t) = -\gamma_{n_0} p_{n_0} \tag{22}$$

Solving this equation for the population of the excited state of the atom, we obtain

$$\left\langle \hat{\sigma}^{\dagger}(t)\hat{\sigma}(t)\right\rangle \simeq (\Omega_R^2 n_0/|\Delta|^2)\exp(-\gamma_0(\Omega_R^2 n_0/|\Delta|^2)t).$$
 (23)

For the two-time correlation function, we have

$$\left\langle \hat{\sigma}^{\dagger}(t+\tau)\hat{\sigma}(t)\right\rangle \simeq \exp(i\omega_{\rm SM}\tau)\Omega_R^2 n_0/|\Delta|^2 \exp\left(-\gamma_0 \left(\frac{\Omega_R^2 n_0}{|\Delta|^2}\right)t\right) \exp(-\gamma_0 (\Omega_R^2 n_0/2|\Delta|^2)\tau).$$
(24)

If we fix time and make the Fourier transform of Eq. (24), we obtain the Lorentzian line with the width  $\gamma_0(\Omega_R^2 n_0/2|\Delta|^2) \ll \gamma_0$ . In this case, the total radiated energy is finite and equal  $\Omega_R^2 n_0/|\Delta|^2$ . Thus, in the limit  $\Omega_R \sim 1/\sqrt{V} \rightarrow 0$ ,  $n_0 \sim V \rightarrow \infty$ , and  $\Omega_R \sqrt{n_0} \rightarrow \text{const}$ , the result is close to experiment: the spectrum is centered on the frequency of the selected mode  $\omega_{\text{SM}}$  and has a narrow line  $\gamma_0(\Omega_R^2 n_0/2|\Delta|^2) \ll \gamma_0$ .

However, the important difference from experiment and from the formulation of the problem with the classical field remains. This is the choice of the time *t*, after which one starts measuring the spectrum. In experiment and in the formulation of the problem with a classical field, the population of the excited state of an atom reaches a stationary state, and the time *t* can formally be set to infinity. The system reaches dynamic equilibrium: at each moment of time, some energy is radiated and some enters from the external field. However, in the above solution, if *t* tends to infinity, the factor  $\exp(-\gamma_0(\Omega_R^2 n_0/|\Delta|^2)t)$  results in zero probability of an atom to be in the excited state, Eq. (24). This corresponds to the fact that the system from the state with  $n_0$  photons passes to a state with  $n_0 - 1$  photons - one photon is emitted then the process stops. However, as indicated above, it is necessary to consider subsequent processes of transitions between eigenstates and photon radiation. This is done in the next subsection.

## 3.3. Many photons in the mode, multiple transitions between the eigenstates of the JC system: achieving dynamic equilibrium

Consider the same limit as in the previous case,  $\Omega_{\rm R} \sim 1/\sqrt{V} \rightarrow 0$ ,  $n_0 \sim V \rightarrow \infty$ , and  $\Omega_{\rm R}\sqrt{n_0} \rightarrow \text{const.}$  In the previous section, we take into account only the transition between the states  $|-, n_0\rangle$  and  $|-, n_0 - 1\rangle$ , and only solve equations for  $p_{n_0}$  and  $p_{n_0-1}$  from system (12). Now we solve full system of equations (12). In the case  $n_0 \gg 1$ , the rate of transitions between states for which  $|n - n_0| \ll n_0$  are approximately the same:  $\gamma_n = \gamma_0(\Omega_R^2 n/|\Delta|^2) \approx \gamma_0(\Omega_R^2 n_0/|\Delta|^2) \equiv \gamma_{\rm eff.}$  System (12), in which all transition rates are the same, corresponds to the Markov-Poisson process, which solution is well known [41]:

$$p_{n_0}(t) = \exp(-\gamma_{\text{eff}}t),$$

$$p_{n_0-1}(t) = (\gamma_{\text{eff}}t/1!)^1 \exp(-\gamma_{\text{eff}}t),$$

$$p_{n_0-k}(t) = (\gamma_{\text{eff}}t/k!)^k \exp(-\gamma_{\text{eff}}t).$$
(25)

Using solution (25) we find the average population of the excited state of the atom

$$\left\langle \hat{\sigma}^{\dagger}(t)\hat{\sigma}(t)\right\rangle \simeq (\Omega_R^2 n_0/|\Delta|^2) \exp(-\gamma_{\text{eff}} t) \sum_{k=n_0}^1 \frac{(\gamma_{\text{eff}} t)^{n_0-k}}{k!} \underset{n_0 \to \infty}{\longrightarrow} (\Omega_R^2 n_0/|\Delta|^2).$$
(26)

One can see that in the limit of a large initial number of photons in the selected mode, the population of the upper state of the atom reaches the constant value of  $(\Omega_R^2 n_0 / |\Delta|^2)$ . Note that

this value is proportional to the square of the dipole moment,  $\Omega_R^2 \sim \omega_{CM} d^2 / \hbar V$  which is obtained in the problem with the classical field [34].

For a two-time correlation function, we obtain

$$\left\langle \hat{\sigma}^{\dagger}(t+\tau)\hat{\sigma}(t)\right\rangle \approx \exp(i\omega_{\mathrm{SM}}\tau)\exp(-\gamma_0(\Omega_R^2 n_0/|\Delta|^2)\tau)\Omega_R^2 n_0/|\Delta|^2\exp(-\gamma_0(\Omega_R^2 n_0/|\Delta|^2)t)\sum_{k=n_0}^1 \frac{(\gamma_{\mathrm{eff}}t)^{n_0-k}}{k!}.$$
(27)

In the limit  $n_0 \sim V \rightarrow \infty$ ,  $t \rightarrow \infty$ , and  $\gamma_{\text{eff}} t/n_0 \rightarrow 0$ , we have

$$\left\langle \hat{\sigma}^{\dagger}(t_{\rm st}+\tau)\hat{\sigma}(t_{\rm st})\right\rangle \simeq \frac{\Omega_{\rm R}^2 n_0}{\Delta^2} \exp\left(\left(i\omega_{\rm CM}-\gamma_0 \frac{\Omega_{\rm R}^2 n_0}{\Delta^2}\right)\tau\right).$$
 (28)

The limit  $\gamma_{\text{eff}} t/n_0 \rightarrow 0$  reflects that during the system evolution, the time is such that the initial number of photons in the selected mode does not deviate significantly from  $n_0$ .

The two-time correlation function corresponds to the spectrum that is centered on the frequency of the selected mode and has the width  $\gamma_0(\Omega_R^2 n_0/\Delta^2) \ll \gamma_0$ . We also note that the two-time correlation function is calculated after the time  $t_{st}$  for which the population of the excited state reaches the stationary value ( $\Omega_R^2 n_0/\Delta^2$ ). This corresponds to the spectrum that is measured in a system that has reached dynamic equilibrium.

For the radiation spectrum, from Eq. (17) we obtain (see also [34])

$$\left\langle \hat{a}_{\mathbf{k},\lambda}^{\dagger}(t)\hat{a}_{\mathbf{k},\lambda}(t)\right\rangle \simeq \frac{\left|\sqrt{\frac{2\pi\omega_{\mathbf{k}}}{V\hbar}}\mathbf{e}_{\alpha,\mathbf{k}}\cdot\mathbf{d}_{eg}\right|^{2}t(\gamma_{0}\Omega_{\mathrm{R}}^{2}n_{0}/\Delta^{2})^{2}}{\left(\omega_{\mathbf{k},\lambda}-\omega_{\mathrm{SM}}\right)^{2}+\left(\gamma_{0}\Omega_{\mathrm{R}}^{2}n_{0}/\Delta^{2}\right)^{2}}.$$
(29)

Thus, we obtain the Lorentzian distribution of photons in frequencies, centered on the frequency of the selected mode and having the width  $\gamma_0 \Omega_R^2 n_0 / \Delta^2 \ll \gamma_0$ . The number of photons increases with time. This reflects that the system has reached dynamic equilibrium and continuously emits photons.

Let us compare the dynamics of the process considered here with the dynamics in Placzek's theory. In the latter, it was assumed the system transitions from the initial state to a given final state. Subsequent transitions were not considered. In the approach developed here, the system make a cascade of transitions between the entangled states  $|-, n\rangle$ , until the system reaches its ground state  $|g, 0\rangle$ .

#### 3.4. Coherent state of the mode formation of the atomic dipole moment: coherent Rayleigh scattering

In the previous sections, we show that when all possible transitions between the eigenstates are taken into account, the population inversion of the atom reaches a quasistationary value that does not change until a large number of photons remains in the selected mode. However, there is still a discrepancy with the classical formulation of the problem. The average value of the atomic dipole moment is also zero,

$$\langle \hat{\sigma}(t) \rangle = \cos \varphi_1 \rho_{(g,0)(+,1)} - \sin \varphi_1 \rho_{(g,0)(-,1)} + \sum_{n=2}^{\infty} (\cos \varphi_n \sin \varphi_{n-1} \rho_{(+,n-1)(+,n)})$$
  
-  $\sin \varphi_n \sin \varphi_{n-1} \rho_{(+,n-1)(-,n)} + \cos \varphi_n \cos \varphi_{n-1} \rho_{(-,n-1)(+,n)} - \sin \varphi_n \cos \varphi_{n-1} \rho_{(-,n-1)(-,n)}) = 0.$ (30)

since the corresponding off-diagonal elements of the density matrix are equal to zero (see Eqs. (49) in Appendix C), this equation differs significantly from the classical case. When the

field is described classically, the dipole moment is nonzero, and it oscillates with the frequency of the external field. Thus, Eq. (30) corresponds to incoherent light. An experimentally realized situation can be described adequately by a theory in which light is described classically. Therefore, for the field, one has to choose the initial condition in which a nonzero dipole moment is excited.

For this, the coherent state of the field,  $|\alpha\rangle = \exp(-|\alpha|^2/2) \sum_{n=0}^{\infty} \left(\alpha^n/\sqrt{n!}\right) |n\rangle$ , should be considered as the initial condition, i.e., instead of  $\hat{\rho}(0) = |g, n_0\rangle \langle g, n_0|$ , we use  $\hat{\rho}(0) = |g, \alpha\rangle \langle g, \alpha|$ . The coherent state has a nonzero average value of electric and magnetic fields:  $\langle \alpha | \hat{E}(\mathbf{r}) | \alpha \rangle = \sqrt{2\pi\hbar\omega_{\rm SM}/V}Re\alpha\exp(i\mathbf{kr})$  [32].

In the limit of a large detuning,  $\Omega_{\rm R}^2 |\alpha|^2 / \Delta^2 \ll 1$ , a large amplitude of the exciting field,  $|\alpha|^2 \gg 1$ , on the time-scale  $t \gg \gamma_0^{-1}$ , for the mean value of atomic dipole moment, we obtain (see Appendix D):

$$\langle \hat{\sigma}(t) \rangle \simeq \frac{e^{-i\omega_{\rm SM}t}\Omega_R|\alpha|}{|\Delta|} \exp\left(-\frac{|\alpha|^2\gamma_0\Omega_R^2}{|\Delta|^2}t\right).$$
 (31)

Equation (31) describes quasistationary oscillations of a dipole with the frequency of the selected mode. The spectrum of the signal described by Eq. (31) represents the Lorentz line centered on the frequency of the incident field  $\omega_{SM}$  and has the width  $\Omega_R^2 \gamma_0 |\alpha|^2 / \Delta^2 \ll \gamma_0$ . This width is much smaller than the linewidth of the spontaneous emission of the atom. Therefore, at times  $\gamma_0^{-1} \ll t \ll (\Omega_R^2 \gamma_0 |\alpha|^2 / \Delta^2)^{-1}$ , we have harmonic oscillations of the dipole moment with the frequency  $\omega_{SM}$  of the selected mode with the amplitude  $\Omega_R |\alpha| / |\Delta|$  that is exactly equal to the amplitude of the oscillations of the dipole moment of the atom in the problem in which the field is considered classically.

#### 4. Conclusion

In this paper, we treat the scattering process as a process of relaxation of the system consisting of an atom and an incident field into free space modes. We model the incident field as a mode selected from the set of free space modes of the EM field and the set of the initial number of photons in this selected mode. The eigenstates of the system are a superposition of the excited states of the atom and the mode. As an initial condition, we consider the state, which is realized in experiment. In this state, the atom is in the ground state, but the selected mode is excited. Since the initial state is not a system eigenstates. Then, from this superposition state, the system passes to another superposition state, emitting a photon. In contrast to Placzek's theory, photon emission from the superposition state occurs already in the first order of perturbation over the atom-free-space EM interaction (details see in Appendix B). This process continues until no photons remain in the selected mode. Due to the oscillations of the system between its eigenstates, the consideration of the scattering process as a two-photon process is not adequate because there is no state in which the initial photon is completely absorbed.

We carry out a comparative analysis of the various initial conditions, which are commonly used in the literature. We demonstrate that if only one photon is initially in the selected mode (the Berestetskii-Lifshitz-Pitaevskii approach [9]), then the radiation spectrum has an extremely narrow line. However, the system radiation is extremely slow, and the total radiated energy is also small. Note that this approach describes the experimental situation when only one photon interacts with the atom. It can be achieved if the external beam is extremely attenuated.

In Placzek's approach [5], the initial number of photons is large so that the field at the atom's location is measurable. The analysis of this approach shows that a cascade of transitions between the eigenstates of the JC-system leads to dynamic equilibrium of the atom with a constant population of the excited level. An atom in this state continuously emits photons that form a spectrum centered on the frequency of the selected mode with a linewidth that is much smaller

than the width of the line of the spontaneous relaxation of the atom. However, radiated light is incoherent. This approach describes the experimental situation when an external beam is incoherent, e.g., the beam from a mercury-vapor lamp.

To obtain a coherent response, one needs to have a coherent initial state of the mode with a large number of photons. The latter actually means that the field can be considered to be classical. This approach describes a common experimental situation in which coherent laser light is used.

To conclude, we develop a microscopic theory of Rayleigh scattering of light by atoms that describes the main features observed in experiment. This includes the elasticity of the scattering and coherence of the scattered light. The theory does not use any phenomenological assumptions, such as an additional virtual level that has been widely used in previous theoretical approaches.

#### Appendix A: role of high-lying levels

To confirm the validity of our TLS-approach, we consider a three-level atom with the ground state  $|g\rangle$  and two excited states  $|e_1\rangle$  and  $|e_2\rangle$ . The Hamiltonian of such a system has the form

$$\hat{H}_{\rm S} = \hbar \omega_{\rm TLS}^{(1)} \hat{\sigma}_1^{\dagger} \hat{\sigma}_1 + \hbar \omega_{\rm TLS}^{(2)} \hat{\sigma}_2^{\dagger} \hat{\sigma}_2 + \hbar \omega_{\rm SM} \hat{a}^{\dagger} \hat{a} + \hbar \Omega_{\rm R}^{(1)} (\hat{a}^{\dagger} \hat{\sigma}_1 + \hat{\sigma}_1^{\dagger} \hat{a}) + \hbar \Omega_{\rm R}^{(2)} (\hat{a}^{\dagger} \hat{\sigma}_2 + \hat{\sigma}_2^{\dagger} \hat{a}), \quad (32)$$

where  $\hat{\sigma}_1 = |g\rangle \langle e_1|$  and  $\hat{\sigma}_2 = |g\rangle \langle e_2|$  are the dipole transition operators from the excited states to the ground state. We cannot diagonalize  $\hat{H}_{S}$  exactly. However, because the interaction constants are much smaller than the transition frequencies of the atom and the selected mode,  $\Omega_R^{(1,2)} \ll$  $\omega_{\text{TLS}}^{(1,2)}$ ,  $\omega_{\text{SM}}$ , we use the perturbation theory. The unperturbed eigenstates are  $|g,n\rangle$ ,  $|e_1,n\rangle$ , and  $|e_2,n\rangle$  with eigenfrequencies  $n\omega_{\rm SM}$ ,  $(n-1)\omega_{\rm SM} + \omega_{\rm TLS}^{(1)}$ , and  $(n-1)\omega_{\rm SM} + \omega_{\rm TLS}^{(2)}$ , respectively. For a perturbation that does not depend on time, we can find corrections to the unperturbed eigenfrequencies and eigenstates:

$$\omega_{n,-} \approx n\omega_{\rm SM} - (\Omega_{\rm R}^{(1)})^2 n / |\Delta_1| - (\Omega_{\rm R}^{(2)})^2 n / |\Delta_2|,$$
  
$$|-,n\rangle \approx -\frac{\Omega_{\rm R}^{(1)} \sqrt{n}}{|\Delta_1|} |e_1, n-1\rangle - \frac{\Omega_{\rm R}^{(2)} \sqrt{n}}{|\Delta_2|} |e_2, n-1\rangle + |g, n\rangle.$$
 (33)

One can see that in the limit  $\Delta_i \gg \Omega_R \sqrt{n}$  (i = 1,2), for the eigenstates  $|-, n\rangle$ , the eigenfrequencies  $\omega_{n,-}$ , Eq. (10), coincide with the eigenfrequencies  $n\omega_{\rm SM}$  of the selected mode with the accuracy  $(\Omega_{\rm R}^{(1)})^2 n/|\Delta_1| + (\Omega_{\rm R}^{(2)})^2 n/|\Delta_2| \ll 1$ ; and the difference between the frequencies of the levels  $|-,n\rangle$  with different *n* is equal to  $\omega_{\rm CM} - (\Omega_{\rm R}^{(1)})^2/|\Delta_1| - (\Omega_{\rm R}^{(2)})^2/|\Delta_2|$ , i.e., with the accuracy  $(\Omega_R^{(1)})^2/|\Delta_1| + (\Omega_R^{(2)})^2/|\Delta_2|$  it coincides with the frequency of the selected mode  $\omega_{SM}$ . Thus, the main conclusion that there is the level, which frequency is close to the frequency of the selected mode, remains valid.

Further, let us discuss the effect of the other excited levels on the system dynamics. Under the influence of the system interaction with the radiative reservoir, the system transitions from the state  $|-,n\rangle$  to the state  $|-,n-1\rangle$ , and so on. The transition rates are found as matrix elements of the interaction Hamiltonian of the system with the reservoir of free space modes between these states. Each excited level has the contribution to the eigenstate proportional to  $\Omega_{\mathbf{R}}^{(i)} n / |\Delta_i|$ . Thus, all formulas for TLS remain valid for the case of several excited levels of the atom with the replacement  $\Omega_R \sqrt{n}/|\Delta| \rightarrow \Omega_R^{(1)} \sqrt{n}/|\Delta_1| + \Omega_R^{(2)} \sqrt{n}/|\Delta_2|$ . Finally, the contribution from each excited level is of the first order. However, these contributions

decrease with an increase in the detuning from the frequency of the selected mode.

#### Appendix B: why does Placzek's theory require the second order of the perturbation theory?

As pointed in the Introduction, Placzek's theory that considers scattering as a two-step process of absorption and emission has internal contradictions and phenomenological assumptions. Many

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works for quantitative evaluation do not use the concept of the virtual level. The concept is rather used for a qualitative explanation of the mechanism of the phenomenon. In this approach, photon emission arises in the second order of perturbation over the interaction of an atom with the free-space EM. In this Appendix, we show that photon emission arises in the first order of the perturbation theory.

Usually, the photon absorption-emission theory of scattering is considered as a special case of the spectroscopic theory of absorption and emission of photons during the transitions of an atom between its own states. This theory assumes that the transitions are caused by the incident field. In the first order of the perturbation theory, according to Fermi's golden rule, the probability of the transition between initial and final states, which is caused by the dipole interaction  $\hat{V} = -\mathbf{d} \cdot \mathbf{E}$ , is proportional to  $|\langle i|\hat{V}|f\rangle|^2$  [5]. Since in the case of elastic scattering, the matrix elements of the dipole moment between the same atomic states are zero,  $|\langle i| \hat{V} | f \rangle|^2 = 0$ , the second order of perturbation theory is usually used. The resulted formula interprets the elastic scattering of light as of two-steps process. In the first step, the atom absorbs an incident photon and transitions from the ground to an excited state. The latter is a superposition of excited atomic states. In the second step, the excited atom emits a photon and relaxes to the ground state.

We show that there is no need using the second order of perturbation theory. The correct results can be obtained in first order.

According to the theory of open quantum systems [35,42-44], for calculating the transition probability per unit time, Fermi's golden rule can only be applied to transitions between eigenstates of the system, which are caused by interactions with a reservoir. The application of Fermi's golden rule to states that are not eigenstates of the system can lead to incorrect results.

For Rayleigh scattering, the eigenstates of an atom interacting with the mode of the scattered field are JC states, and the reservoir is free space modes. Note that the initial state  $|i\rangle = |g,1\rangle$ , at which the atom is in the ground state and the scattered photon is in the Fock state, is not a system eigenstate. Thus, the quantity  $|\langle i|\hat{V}|f\rangle|^2 = |\langle g,1|\hat{V}|g,0\rangle|^2$  is not the transition probability and it cannot be used in the perturbation theory based on Fermi's golden rule. This shows that a description of Rayleigh scattering as a two-step absorption/emission process of a photon is not justified. When true system eigenstates are used, Rayleigh scattering can be described in the first order of the perturbation theory.

Only the values  $|\langle +, n | V | g, 0 \rangle|^2$  and  $|\langle -, n | V | g, 0 \rangle|^2$  have the meaning of the transition probabilities. Recall that  $\{|g,0\rangle, |-,n\rangle, |+,n\rangle$   $n = 1, 2, ... \}$  are the JC-eigenstates with n photons, while V describes the interaction of the atom with the electric field of free space modes. One can see that for n = 1, the transition probabilities are not zero. The substitution of the expansion of  $V|g, 0\rangle$  over the full system of the JC-eigenfunctions into expression for  $\langle +, n | V|g, 0\rangle$ gives  $\langle +, 1 | V | g, 0 \rangle = b_{00} \langle +, 1 | g, 0 \rangle + \sum_{n} (b_{0,-n} \langle +, 1 | -, n \rangle + b_{0,+n} \langle +, 1 | +, n \rangle) = b_{0,+1}$ . In a general case, this quantity is not zero. Therefore, we have to consider the Rayleigh scattering as a first order process.

#### Appendix C: master equation for the Fock initial state of the selected mode

Here, we present the explicit form of the master equation in the JC-eigenstate basis. The operator  $\hat{\sigma}$  in this basis has the form:

$$\hat{\sigma} = \cos \varphi_1 \hat{S}_{(g,0)(+,1)} - \sin \varphi_1 \hat{S}_{(g,0)(-,1)} + \sum_{n=1}^{\infty} (\cos \varphi_n \sin \varphi_{n-1} \hat{S}_{(+,n-1)(+,n)} - \sin \varphi_n \sin \varphi_{n-1} \hat{S}_{(+,n-1)(-,n)} + \cos \varphi_n \cos \varphi_{n-1} \hat{S}_{(-,n-1)(+,n)} - \sin \varphi_n \cos \varphi_{n-1} \hat{S}_{(-,n-1)(-,n)},$$
(34)

Substitution of this equation into Hamiltonian (6) of the interaction of the system with the reservoir gives

$$\hat{H}_{SR} = \sum_{\mathbf{k},\lambda} \hbar \gamma_{\mathbf{k},\lambda} a_{\mathbf{k},\lambda}^{\dagger} \left( \cos \varphi_{1} | g, 0 \right) \left\langle +, 1 | - \sin \varphi_{1} | g, 0 \right\rangle \left\langle -, 1 | \right. \\ \left. + \sum_{n=1}^{\infty} \left( \cos \varphi_{n} \sin \varphi_{n-1} | +, n-1 \right) \left\langle +, n | - \sin \varphi_{n} \sin \varphi_{n-1} | +, n-1 \right\rangle \left\langle -, n | \right. \\ \left. + \cos \varphi_{n} \cos \varphi_{n-1} | -, n-1 \right\rangle \left\langle +, n | - \sin \varphi_{n} \cos \varphi_{n-1} | -, n-1 \right\rangle \left\langle -, n | \right. \right. \\ \left. + \sum_{n=1}^{\infty} \hbar \gamma_{\mathbf{k},\lambda} a_{\mathbf{k},\lambda}^{\dagger} \left( \cos \varphi_{1} \hat{S}_{(g,0)(+,1)} - \sin \varphi_{1} \hat{S}_{(g,0)(-,1)} \right) \\ \left. + \sum_{n=1}^{\infty} \left( \cos \varphi_{n} \sin \varphi_{n-1} \hat{S}_{(+,n-1)(+,n)} - \sin \varphi_{n} \sin \varphi_{n-1} \hat{S}_{(+,n-1)(-,n)} \right) \right. \\ \left. + \cos \varphi_{n} \cos \varphi_{n-1} \hat{S}_{(-,n-1)(+,n)} - \sin \varphi_{n} \cos \varphi_{n-1} \hat{S}_{(-,n-1)(-,n)} \right) \right) + \text{h.c.},$$

$$(35)$$

where we introduce the notations for the operators of possible transitions between the eigenstates of the subsystem:

$$\hat{S}_{(+,n-1)(+,n)} = |+, n-1\rangle \langle +, n|, \hat{S}_{(+,n-1)(-,n)} = |+, n-1\rangle \langle -, n|, 
\hat{S}_{(-,n-1)(+,n)} = |-, n-1\rangle \langle +, n|, \hat{S}_{(-,n-1)(-,n)} = |-, n-1\rangle \langle -, n|, 
\hat{S}_{(g,0)(-,1)} = |g, 0\rangle \langle -, 1|.$$
(36)

Knowing the eigenstates of the JC-system, it is possible to exclude free space mode variables with the exception of the selected mode. For this, it is necessary to assume that the reservoir of free space modes is in a state of thermal equilibrium at a given temperature. Neglecting relativistic effects, we can assume that the frequencies are limited to the optical range. Further, we assume that T = 0, i.e., the free space modes are empty. Following the standard procedure, we obtain the density matrix in basis (3), which obeys the master equation of the Lindblad form [32,34,35]:

$$\begin{split} \partial \hat{\rho} / \partial t &= \frac{i}{\hbar} [\hat{\rho}, \hat{H}_{\rm S}] + \\ &+ \frac{\gamma_0}{2} \cos^2 \varphi_1 (2 \hat{S}_{(g,0)(+,1)} \hat{\rho} \hat{S}^{\dagger}_{(g,0)(+,1)} - \hat{S}^{\dagger}_{(g,0)(+,1)} \hat{S}_{(g,0)(+,1)} \hat{\rho} - \hat{\rho} \hat{S}^{\dagger}_{(g,0)(+,1)} \hat{S}_{(g,0)(+,1)}) \\ &+ \frac{\gamma_0}{2} \sin^2 \varphi_1 (2 \hat{S}_{(g,0)(-,1)} \hat{\rho} \hat{S}^{\dagger}_{(g,0)(-,1)} - \hat{S}^{\dagger}_{(g,0)(-,1)} \hat{S}_{(g,0)(-,1)} \hat{\rho} - \hat{\rho} \hat{S}^{\dagger}_{(g,0)(-,1)} \hat{S}_{(g,0)(-,1)}) \\ &+ \frac{\gamma_0}{2} \sum_{n=1}^{\infty} (\cos^2 \varphi_n \sin^2 \varphi_{n-1}) \\ &\times (2 \hat{S}_{(+,n-1)(+,n)} \hat{\rho} \hat{S}^{\dagger}_{(+,n-1)(+,n)} - \hat{S}^{\dagger}_{(+,n-1)(+,n)} \hat{S}_{(+,n-1)(+,n)} \hat{\rho} - \hat{\rho} \hat{S}^{\dagger}_{(+,n-1)(+,n)} \hat{S}_{(+,n-1)(+,n)}) \\ &+ \sin^2 \varphi_n \sin^2 \varphi_{n-1} (2 \hat{S}_{(+,n-1)(-,n)} \hat{\rho} \hat{S}^{\dagger}_{(+,n-1)(-,n)} - \hat{S}^{\dagger}_{(+,n-1)(-,n)} \hat{S}_{(+,n-1)(+,n)} \hat{\rho} - \hat{\rho} \hat{S}^{\dagger}_{(-,n-1)(+,n)} \hat{S}_{(-,n-1)(+,n)}) \\ &+ \cos^2 \varphi_n \cos^2 \varphi_{n-1} (2 \hat{S}_{(-,n-1)(+,n)} \hat{\rho} \hat{S}^{\dagger}_{(-,n-1)(+,n)} - \hat{S}^{\dagger}_{(-,n-1)(+,n)} \hat{S}_{(-,n-1)(+,n)} \hat{\rho} - \hat{\rho} \hat{S}^{\dagger}_{(-,n-1)(+,n)} \hat{S}_{(-,n-1)(+,n)}) \\ &+ \sin^2 \varphi_n \cos^2 \varphi_{n-1} (2 \hat{S}_{(-,n-1)(-,n)} \hat{\rho} \hat{S}^{\dagger}_{(-,n-1)(-,n)} - \hat{S}^{\dagger}_{(-,n-1)(-,n)} \hat{S}_{(-,n-1)(-,n)} \hat{\rho} - \hat{\rho} \hat{S}^{\dagger}_{(-,n-1)(-,n)} \hat{S}_{(-,n-1)(+,n)}) \\ &+ \sin^2 \varphi_n \cos^2 \varphi_{n-1} (2 \hat{S}_{(-,n-1)(-,n)} \hat{\rho} \hat{S}^{\dagger}_{(-,n-1)(-,n)} - \hat{S}^{\dagger}_{(-,n-1)(-,n)} \hat{S}_{(-,n-1)(-,n)} \hat{\rho} - \hat{\rho} \hat{S}^{\dagger}_{(-,n-1)(-,n)} \hat{S}_{(-,n-1)(-,n)}) \\ &+ \sin^2 \varphi_n \cos^2 \varphi_{n-1} (2 \hat{S}_{(-,n-1)(-,n)} \hat{\rho} \hat{S}^{\dagger}_{(-,n-1)(-,n)} - \hat{S}^{\dagger}_{(-,n-1)(-,n)} \hat{S}_{(-,n-1)(-,n)} \hat{\rho} - \hat{\rho} \hat{S}^{\dagger}_{(-,n-1)(-,n)} \hat{S}_{(-,n-1)(-,n)}) ) \\ &+ \sin^2 \varphi_n \cos^2 \varphi_{n-1} (2 \hat{S}_{(-,n-1)(-,n)} \hat{\rho} \hat{S}^{\dagger}_{(-,n-1)(-,n)} - \hat{S}^{\dagger}_{(-,n-1)(-,n)} \hat{S}_{(-,n-1)(-,n)} \hat{\rho} - \hat{\rho} \hat{S}^{\dagger}_{(-,n-1)(-,n)} \hat{S}_{(-,n-1)(-,n)}) ) \\ &+ \sin^2 \varphi_n \cos^2 \varphi_{n-1} (2 \hat{S}_{(-,n-1)(-,n)} \hat{\rho} \hat{S}^{\dagger}_{(-,n-1)(-,n)} - \hat{S}^{\dagger}_{(-,n-1)(-,n)} \hat{S}_{(-,n-1)(-,n)} \hat{\rho} - \hat{\rho} \hat{S}^{\dagger}_{(-,n-1)(-,n)} \hat{S}_{(-,n-1)(-,n)}) ) \\ &+ \sin^2 \varphi_n \cos^2 \varphi_{n-1} \hat{S}_{(-,n-1)(-,n)} \hat{\rho} \hat{S}^{\dagger}_{(-,n-1)(-,n)} \hat{S}_{(-,n-1)(-,n)} \hat{S}_{(-,n-1)(-,n)} \hat{S}_{(-,n-1)(-,n)} \hat{S}_{(-,n-1)(-,n)} \hat{S}_{(-,n-1)(-,n)} \hat{S}_{(-,n-1)(-,$$

Here  $\gamma_0 = 4\omega_0^3 |\mathbf{d}_{eg}|^2 / 3\hbar c^3$  is the characteristic rate of the transition between eigenstates obtained by averaging over the free space modes (for a detailed derivation, see [32,34–36]). If we were to consider one atom in free space, then this quantity would be the rate of spontaneous emission.

Equation (37) is obtained after averaging the Hamiltonian of the interaction of the atom with modes of free space over degrees of freedom of modes of free-space. This is rather cumbersome but has a clear physical interpretation. Specifically, each term in Eq. (37)having  $2\hat{S}\hat{\rho}\hat{S}^{\dagger} - \hat{S}^{\dagger}\hat{S}\hat{\rho} - \hat{\rho}\hat{S}^{\dagger}\hat{S}$  as a factor describes the transitions of the system between the eigenstates

 $\{|g,0\rangle, |+,n\rangle, |-,n\rangle\}, n = 1, 2, ...$  The explicit form of the  $\hat{S}$ -operators is given by Eqs. (8). We emphasize again that it is the interaction of the JC-system with the reservoir of free space modes that leads to a transition between the eigenstates of this subsystem.

Further, we expand the density matrix over eigenstates (2)-(3):

$$\hat{\rho} = \rho_{(g,0)(g,0)}|g,0\rangle \langle g,0| + \sum_{n=1}^{\infty} \left(\rho_{(g,0)(+,n)}|g,0\rangle \langle +,n| + \rho_{(g,0)(-,n)}|g,0\rangle \langle -,n| + \rho_{(+,n)(g,0)}|+,n\rangle \langle g,0| + \rho_{(-,n)(g,0)}|-,n\rangle \langle g,0| \right) + \sum_{n_1,n_2=1}^{\infty} \left(\rho_{(+,n_1)(+,n_2)}|+,n_1\rangle \langle +,n_2| + \rho_{(+,n_1)(-,n_2)}|+,n_1\rangle \langle -,n_2| + \rho_{(-,n_1)(+,n_2)}|-,n_1\rangle \langle +,n_2| + \rho_{(-,n_1)(-,n_2)}|-,n_1\rangle \langle -,n_2| \right).$$
(38)

One of Eq. (37) features is that it defines the independent dynamics of the diagonal and off-diagonal terms of the density matrix [45]. Specifically, from Eq. (37) for diagonal elements, we obtain the following equations

$$\dot{\rho}_{(+,n)(+,n)} = -\gamma_0 \cos^2 \varphi_n \rho_{(+,n)(+,n)} + \gamma_0 \cos^2 \varphi_{n+1} \sin^2 \varphi_n \rho_{(+,n+1)(+,n+1)} + \gamma_0 \sin^2 \varphi_{n+1} \sin^2 \varphi_n \rho_{(-,n+1)(-,n+1)},$$
(39)

$$\dot{\rho}_{(-,n)(-,n)} = -\gamma_0 \sin^2 \varphi_n \rho_{(-,n)(-,n)} + \gamma_0 \cos^2 \varphi_{n+1} \cos^2 \varphi_n \rho_{(+,n+1)(+,n+1)} + \gamma_0 \sin^2 \varphi_{n+1} \cos^2 \varphi_n \rho_{(-,n+1)(-,n+1)},$$
(40)

$$\dot{\rho}_{(g,0)(g,0)} = \gamma_0 \cos^2 \varphi_1 \rho_{(+,1)(+,1)} + \gamma_0 \sin^2 \varphi_1 \rho_{(-,1)(-,1)}.$$
(41)

One can see that for the dynamics of the diagonal elements, only "down" transitions with a decrease in energy are possible. This is a consequence of our assumption that the free space mode reservoir is at zero temperature.

For the off-diagonal elements, we obtain [45]:

$$\dot{\rho}_{(+,n_1)(+,n_2)} = (-i(\omega_{+,n_2} - \omega_{+,n_1}) - \gamma_0(\cos^2\varphi_{n_2} + \cos^2\varphi_{n_1})/2)\rho_{(+,n_1)(+,n_2)}, \ n_1 \neq n_2.$$
(42)

$$\dot{\rho}_{(-,n_1)(+,n_2)} = (-i(\omega_{+,n_2} - \omega_{-,n_1}) - \gamma_0(\cos^2\varphi_{n_2} + \sin^2\varphi_{n_1})/2)\rho_{(-,n_1)(+,n_2)}, \ n_1 \neq n_2.$$
(43)

$$\dot{\rho}_{(+,n_1)(-,n_2)} = (-i(\omega_{-,n_2} - \omega_{+,n_1}) - \gamma_0(\sin^2\varphi_{n_2} + \cos^2\varphi_{n_1})/2)\rho_{(+,n_1)(-,n_2)}, \ n_1 \neq n_2.$$
(44)

$$\dot{\rho}_{(-,n_1)(-,n_2)} = (-i(\omega_{-,n_2} - \omega_{-,n_1}) - \gamma_0(\sin^2\varphi_{n_2} + \sin^2\varphi_{n_1})/2)\rho_{(-,n_1)(-,n_2)}, \ n_1 \neq n_2.$$
(45)

$$\dot{\rho}_{(0,g)(+,n)} = (-i\omega_{+,n} - \gamma_0 \cos^2 \varphi_n/2)\rho_{(0,g)(+,n)}.$$
(46)

$$\dot{\rho}_{(0,g)(-,n)} = (-i\omega_{-,n} - \gamma_0 \sin^2 \varphi_n/2)\rho_{(0,g)(-,n)}.$$
(47)

Each off-diagonal element of the density matrix oscillates and simultaneously decays exponentially and independently of other elements.

Suppose that at the initial moment, the whole system is in the state  $|g, 0\rangle$  with the density matrix  $\hat{\rho}(0) = |g, n_0\rangle \langle g, n_0|$ . This state is not an eigenstate, and the expansion over eigenstates (2)-(3) gives

$$\hat{\rho}(0) = |g, n_0\rangle \langle g, n_0| = \sin^2 \varphi_{n_0} |n, +\rangle \langle n, +| + \cos^2 \varphi_{n_0} |n, -\rangle \langle n, -|$$
  
+  $\sin \varphi_{n_0} \cos \varphi_{n_0} (|n_0, +\rangle \langle n_0, -| + |n_0, -\rangle \langle n_0, +|)$  (48)

Thus, the initial conditions for Eqs. (39)–(47) have the form:

$$\rho_{(n_0,+)(n_0,+)}(0) = \sin^2 \varphi_{n_0}, 
\rho_{(n_0,-)(n_0,-)}(0) = \cos^2 \varphi_{n_0}, 
\rho_{(n_0,-)(n_0,+)} = \rho_{(n_0,+)(n_0,-)}(0) = \sin \varphi_{n_0} \cos \varphi_{n_0},$$
(49)

with all other elements of the density matrix equal to zero.

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Let us consider how the initial condition  $\hat{\rho}(0) = |g, n_0\rangle \langle g, n_0|$  is expanded over the basis of eigenstates in the limit  $\Delta \gg \Omega_R \sqrt{n}$ . Using approximate equalities  $\sin \varphi_n \simeq \varphi_n \simeq \Omega_R \sqrt{n}/|\Delta|$  and  $\cos \varphi_n \simeq 1$ , we obtain:

$$\rho_{(-,n_0)(-,n_0)}(0) \simeq 1, \ \rho_{(+,n_0,)(+,n_0)}(0) = \Omega_R^2 n/|\Delta|^2 \ll 1, 
\rho_{(-,n_0)(+,n_0)}(0) = \rho_{(+,n_0)(-,n_0)}(0) = \Omega_R \sqrt{n}/|\Delta| \ll 1.$$
(50)

We, therefore, assume that  $\rho_{(n_0,-)(n_0,-)}(0) = 1$  and  $\rho_{(+,n_0)(+,n_0)}(0) = \rho_{(-,n_0)(+,n_0)}(0) = \rho_{(+,n_0)(-,n_0)}(0) = 0$ . As noted above, with a decrease in energy, only downward transitions are realized. Therefore, due to the initial condition  $\rho_{(\pm,n)(\pm,n)}(0) = 0$ ,  $n > n_0$ , the matrix element  $\rho_{(n_0,+)(n_0,+)}$  is equal to zero all the time.

Now, using the approximations obtained above, we consider the diagonal elements of the density matrix. We begin with  $\rho_{(n_0,-)(n_0,-)}(t)$ . From Eq. (40), using  $\sin \varphi_n \simeq \varphi_n \simeq \Omega_R \sqrt{n}/|\Delta|$  and  $\cos \varphi_n \simeq 1$ , we have:

$$\dot{\rho}_{(-,n_0)(-,n_0)}(t) = -\gamma_0 \frac{\Omega_R^2 n}{|\Delta|} \rho_{(-,n_0)(-,n_0)}(t).$$
(51)

Since  $\rho_{(+,n_0)(+,n_0)}(0) = 0$ , from Eq. (40) we obtain

$$\dot{\rho}_{(-,n_0-1)(-,n_0-1)}(t) = -\gamma_0 \frac{\Omega_R^2(n-1)}{|\Delta|} \rho_{(-,n_0-1)(-,n_0-1)}(t) + \gamma_0 \frac{\Omega_R^2 n}{|\Delta|} \rho_{(-,n_0)(-,n_0)}(t).$$
(52)

Next, we consider the equation for  $\rho_{(+,n_0-1)(+,n_0-1)}(t)$ . From Eq. (39), using  $\rho_{(+,n_0)(+,n_0)}(t) = 0$  we obtain

$$\dot{\rho}_{(+,n_0-1)(+,n_0-1)}(t) = -\gamma_0 \rho_{(+,n_0-1)(+,n_0-1)}(t) + \gamma_0 \frac{\Omega_R^4 n(n-1)}{|\Delta|^4} \rho_{(-,n_0)(-,n_0)}(t),$$

$$\rho_{(+,n_0-1)(+,n_0-1)}(0) = 0.$$
(53)

The factor  $\Omega_R^4 n(n-1)/|\Delta|^4$  is of the second order of smallness with respect to the parameter  $\Omega_R^2 n/|\Delta| \ll 1$ . Therefore, in Eq. (53), we neglect the term  $(\gamma_0 \Omega_R^4 n(n-1)/|\Delta|^4) \rho_{(-,n_0)(-,n_0)}$ . Then, solution (53) is  $\rho_{(+,n_0-1)(+,n_0-1)}(t) = 0$ .

Repeating the above arguments for the elements  $\rho_{(+,n)(+,n)}$ ,  $n < n_0 - 1$ , of the density matrix, we obtain that  $\rho_{(+,n)(+,n)}(t) = 0$ . At the same time, for  $\rho_{(-,n)(-,n)}(t)$ ,  $n < n_0 - 1$  we obtain the equation of the same form as Eq. (52). For brevity, let us denote  $\rho_{(n,-)(n,-)}(t) \equiv p_n(t)$ ,  $\gamma_0 \Omega_R^2 n / |\Delta| \equiv \gamma_n$ , and  $\omega_{n,-} = \omega_n$ . The quantity  $p_n(t)$  has the meaning of the probability of the occupation of the entangled state of the selected mode and the atom  $|-,n\rangle = -\sin \varphi_n |e, n-1\rangle + \cos \varphi_n |g, n\rangle$ , while  $\gamma_n$  has the meaning of the transition rate form the state  $|-,n\rangle$  to the state  $|-,n-1\rangle$ . From Eq. (51) we obtain equations for  $p_n(t)$ :

$$\dot{p}_{n_0}(t) = -\gamma_{n_0} p_{n_0}$$
  

$$\dot{p}_n(t) = -\gamma_n p_n(t) + \gamma_{n+1} p_{n+1}(t), \qquad 1 \le n < n_0$$

$$\dot{p}_0(t) = \gamma_1 p_1(t)$$
(54)

with the initial condition

$$p_{n_0}(0) = 1, p_n(0) = 0, \ 0 \le n < n_0.$$
(55)

This are Eqs. (25) of the main text.

#### Appendix D: master equation for the coherent initial state of the selected mode

In this Appendix, we obtain Eq. (31) that gives the mean value of atomic dipole moment. We consider the case of the coherent initial state,  $\hat{\rho}(0) = |g, \alpha\rangle \langle g, \alpha|$ , where  $|\alpha\rangle = \exp(-|\alpha|^2/2) \sum_{n=0}^{\infty} \left( \alpha^n / \sqrt{n!} \right) |n\rangle$ 

is the coherent state of the field. The expansion of such an initial state over eigenstates (3) has the form:

$$\begin{aligned} \hat{\rho}(0) &= \exp(-|\alpha|^{2}) \left[ |g, 0\rangle \langle g, 0 | + \right. \\ &+ \sum_{n_{1}=1}^{\infty} \left( \sin \varphi_{n_{1}} \frac{\alpha^{n_{1}}}{\sqrt{n_{1}!}} |+, n_{1}\rangle \langle g, 0 | + \cos \varphi_{n_{1}} \frac{\alpha^{n_{1}}}{\sqrt{n_{1}!}} |-, n_{1}\rangle \langle g, 0 | \right) \\ &+ \sum_{n_{2}=1}^{\infty} \left( \sin \varphi_{n_{2}} \frac{\alpha^{*n_{2}}}{\sqrt{n_{2}!}} |g, 0\rangle \langle +, n_{2} | + \cos \varphi_{n_{2}} \frac{\alpha^{*n_{2}}}{\sqrt{n_{2}!}} |g, 0\rangle \langle -, n_{2} | \right) \\ &+ \sum_{n_{1}, n_{2}=1}^{\infty} \left( \sin \varphi_{n_{1}} \sin \varphi_{n_{2}} \frac{\alpha^{n_{1}}}{\sqrt{n_{1}!}} \frac{\alpha^{*n_{2}}}{\sqrt{n_{2}!}} |+, n_{1}\rangle \langle +, n_{2} | + \sin \varphi_{n_{1}} \cos \varphi_{n_{2}} \frac{\alpha^{n_{1}}}{\sqrt{n_{1}!}} \frac{\alpha^{*n_{2}}}{\sqrt{n_{2}!}} |+, n_{1}\rangle \langle -, n_{2} | \\ &+ \cos \varphi_{n_{1}} \sin \varphi_{n_{2}} \frac{\alpha^{n_{1}}}{\sqrt{n_{1}!}} \frac{\alpha^{*n_{2}}}{\sqrt{n_{2}!}} |-, n_{1}\rangle \langle +, n_{2} | + \cos \varphi_{n_{1}} \cos \varphi_{n_{2}} \frac{\alpha^{n_{1}}}{\sqrt{n_{1}!}} \frac{\alpha^{*n_{2}}}{\sqrt{n_{2}!}} |-, n_{1}\rangle \langle -, n_{2} | \\ \end{aligned} \right] .$$
(56)

In expansion (56) of the density matrix over eigenstates, in contrast to expansion (48), there are all kind of off-diagonal elements. Equation (30) shows that to calculate the average dipole moment, we need to know the dynamics of not all off-diagonal matrix elements, but only  $\rho_{(g,0)(+,1)}$ ,  $\rho_{(+,n-1)(+,n)}$ ,  $\rho_{(-,n-1)(+,n)}$ , and  $\rho_{(-,n-1)(-,n)}$ . According to Eqs. (42)–(47), these matrix elements obey the equations

$$\dot{\rho}_{(+,n-1)(+,n)} = \left(-i(\omega_{+,n} - \omega_{+,n-1}) - \frac{\gamma_0}{2}(\cos^2\varphi_n + \cos^2\varphi_{n-1})\right)\rho_{(+,n-1)(+,n)},\tag{57}$$

$$\dot{\rho}_{(-,n-1)(+,n)} = \left(-i(\omega_{+,n} - \omega_{-,n-1}) - \frac{\gamma_0}{2}(\cos^2\varphi_n + \sin^2\varphi_{n-1})\right)\rho_{(-,n-1)(+,n)},\tag{58}$$

$$\dot{\rho}_{(+,n-1)(-,n)} = \left(-i(\omega_{-,n} - \omega_{+,n-1}) - \frac{\gamma_0}{2}(\sin^2\varphi_n + \cos^2\varphi_{n-1})\right)\rho_{(+,n-1)(-,n)},\tag{59}$$

$$\dot{\rho}_{(-,n-1)(-,n)} = \left(-i(\omega_{-,n} - \omega_{-,n-1}) - \frac{\gamma_0}{2}(\sin^2\varphi_n + \sin^2\varphi_{n-1})\right)\rho_{(-,n-1)(-,n)},\tag{60}$$

$$\dot{\rho}_{(0,g)(+,1)} = (-i\omega_{+,1} - \gamma_0 \cos^2 \varphi_1/2)\rho_{(0,g)(+,1)},\tag{61}$$

$$\dot{\rho}_{(0,g)(-,1)} = (-i\omega_{-,1} - \gamma_0 \sin^2 \varphi_1/2)\rho_{(0,g)(-,1)},\tag{62}$$

and in accordance with Eq. (56), the initial conditions of these matrix elements have the form

$$\rho_{(+,n-1)(+,n)}(0) = \exp(-|\alpha|^2) \sin \varphi_n \sin \varphi_{n-1} \frac{\alpha^{n-1}}{\sqrt{(n-1)!}} \frac{\alpha^{*n}}{\sqrt{n!}},$$
(63)

$$\rho_{(-,n-1)(+,n)}(0) = \exp(-|\alpha|^2) \cos \varphi_n \sin \varphi_{n-1} \frac{\alpha^{n-1}}{\sqrt{(n-1)!}} \frac{\alpha^{*n}}{\sqrt{n!}},$$
(64)

$$\rho_{(+,n-1)(-,n)}(0) = \exp(-|\alpha|^2) \sin \varphi_n \cos \varphi_{n-1} \frac{\alpha^{n-1}}{\sqrt{(n-1)!}} \frac{\alpha^{*n}}{\sqrt{n!}},\tag{65}$$

$$\rho_{(-,n-1)(-,n)}(0) = \exp(-|\alpha|^2) \cos \varphi_n \cos \varphi_{n-1} \frac{\alpha^{n-1}}{\sqrt{(n-1)!}} \frac{\alpha^{*n}}{\sqrt{n!}},$$
(66)

$$\rho_{(0,g)(+,1)}(0) = \exp(-|\alpha|^2) \sin \varphi_1 \frac{\alpha^*}{\sqrt{1!}},\tag{67}$$

$$\rho_{(0,g)(-,1)}(0) = \exp(-|\alpha|^2) \cos \varphi_1 \frac{\alpha^*}{\sqrt{1!}}.$$
(68)

Solutions (57)-(62) with initial conditions (63)-(68) are

$$\rho_{(+,n-1)(+,n)}(t) = e^{-|\alpha|^2} \sin \varphi_n \sin \varphi_{n-1} \frac{\alpha^{n-1}}{\sqrt{(n-1)!}} \frac{\alpha^{*n}}{\sqrt{n!}} e^{\left(-i(\omega_{+,n}-\omega_{+,n-1})-\frac{\gamma_0}{2}(\cos^2\varphi_n+\cos^2\varphi_{n-1})\right)t}, \quad (69)$$

$$\rho_{(-,n-1)(+,n)}(t) = e^{-|\alpha|^2} \cos \varphi_n \sin \varphi_{n-1} \frac{\alpha^{n-1}}{\sqrt{(n-1)!}} \frac{\alpha^{*n}}{\sqrt{n!}} e^{\left(-i(\omega_{+,n}-\omega_{-,n-1})-\frac{\gamma_0}{2}(\cos^2\varphi_n+\sin^2\varphi_{n-1})\right)t}, \quad (70)$$

$$\rho_{(+,n-1)(-,n)}(t) = e^{-|\alpha|^2} \sin \varphi_n \cos \varphi_{n-1} \frac{\alpha^{n-1}}{\sqrt{(n-1)!}} \frac{\alpha^{*n}}{\sqrt{n!}} e^{\left(-i(\omega_{-,n}-\omega_{+,n-1})-\frac{\gamma_0}{2}(\sin^2\varphi_n+\cos^2\varphi_{n-1})\right)t}, \quad (71)$$

$$\rho_{(-,n-1)(-,n)}(t) = e^{-|\alpha|^2} \cos \varphi_n \cos \varphi_{n-1} \frac{\alpha^{n-1}}{\sqrt{(n-1)!}} \frac{\alpha^{*n}}{\sqrt{n!}} e^{\left(-i(\omega_{-,n}-\omega_{-,n-1})-\frac{\gamma_0}{2}(\sin^2\varphi_n+\sin^2\varphi_{n-1})\right)t}, \quad (72)$$

$$\rho_{(0,g)(+,1)}(t) = e^{-|\alpha|^2} \sin \varphi_1 \frac{\alpha^*}{\sqrt{1!}} e^{(-i\omega_{+,1} - \gamma_0 \cos^2 \varphi_1/2)t},\tag{73}$$

$$\rho_{(0,g)(-,1)}(t) = e^{-|\alpha|^2} \cos \varphi_1 \frac{\alpha^*}{\sqrt{1!}} e^{(-i\omega_{-,1} - \gamma_0 \sin^2 \varphi_1/2)t}.$$
(74)

Substituting Eqs. (69)–(74) into the expression for the dipole moment, Eq. (30), we obtain

$$\begin{aligned} \langle \hat{\sigma}(t) \rangle &= e^{-|\alpha|^2} \left( \cos \varphi_1 \sin \varphi_1 \frac{\alpha^*}{\sqrt{1!}} e^{(-i\omega_{+,1} - \gamma_0 \cos^2 \varphi_1/2)t} - \sin \varphi_1 \cos \varphi_1 \frac{\alpha^*}{\sqrt{1!}} e^{(-i\omega_{-,1} - \gamma_0 \sin^2 \varphi_1/2)t} \right. \\ &+ \sum_{n=2}^{\infty} \frac{\alpha^{n-1}}{\sqrt{(n-1)!}} \frac{\alpha^{*n}}{\sqrt{n!}} \left( \cos \varphi_n \sin^2 \varphi_{n-1} \sin \varphi_n e^{\left(-i(\omega_{+,n} - \omega_{+,n-1}) - \frac{\gamma_0}{2} (\cos^2 \varphi_n + \cos^2 \varphi_{n-1})\right)t} \right. \\ &- \sin^2 \varphi_n \sin \varphi_{n-1} \cos \varphi_{n-1} e^{\left(-i(\omega_{-,n} - \omega_{+,n-1}) - \frac{\gamma_0}{2} (\sin^2 \varphi_n + \cos^2 \varphi_{n-1})\right)t} \\ &+ \cos^2 \varphi_n \cos \varphi_{n-1} \sin \varphi_{n-1} e^{\left(-i(\omega_{+,n} - \omega_{-,n-1}) - \frac{\gamma_0}{2} (\cos^2 \varphi_n + \sin^2 \varphi_{n-1})\right)t} \\ &- \sin \varphi_n \cos^2 \varphi_{n-1} \cos \varphi_n e^{\left(-i(\omega_{-,n} - \omega_{-,n-1}) - \frac{\gamma_0}{2} (\sin^2 \varphi_n + \sin^2 \varphi_{n-1})\right)t} \end{aligned}$$

In the limit of large detuning,  $\Omega_R^2 |\alpha|^2 / \Delta^2 \ll 1$ , the quantities  $\Omega_R^2 |\alpha|^2 / \Delta^2$  and  $\sin \varphi_n \simeq \Omega_R \sqrt{n} / |\Delta|$  are small parameters, while  $\cos \varphi_n \simeq 1$ . Therefore, the main contribution to sum (75) is made by the first, second, fifth, and sixth terms, which are proportional to the first power of the small parameter. Further, the decay rate of the first and fifth terms are  $\gamma_0 \cos^2 \varphi_1 / 2 \simeq \gamma_0 / 2$  and  $\gamma_0 (\cos^2 \varphi_n + \sin^2 \varphi_{n-1}) / 2 \simeq \gamma_0 / 2$ , respectively. Thus, on the time-scale  $t \gg \gamma_0^{-1}$ , these terms are equal to zero. In turn, the decay rate of the second and six terms are  $\gamma_0 \sin^2 \varphi_1 / 2 \simeq \gamma_0 \Omega_R^2 n / 2 |\Delta|^2 \ll \gamma_0$  and  $\gamma_0 (\sin^2 \varphi_n + \sin^2 \varphi_{n-1}) / 2 \simeq \gamma_0 \Omega_R^2 n / |\Delta|^2 \ll \gamma_0$ , respectively. Thus, we conclude that on the time-scale  $t \gg \gamma_0^{-1}$ , the second and sixth terms give the main contribution to Eq. (75):

$$\langle \hat{\sigma}(t) \rangle = -\frac{e^{-i\omega_{\rm SM}t} \Omega_R}{|\Delta|} e^{-|\alpha|^2} \left( \frac{\alpha^*}{\sqrt{1!}} e^{-(\gamma_0 \Omega_R^2 n/2|\Delta|^2)t} + \sum_{n=2}^{\infty} \sqrt{n} \frac{\alpha^{n-1}}{\sqrt{(n-1)!}} \frac{\alpha^{*n}}{\sqrt{n!}} e^{-(\gamma_0 \Omega_R^2 n/|\Delta|^2)t} \right), \quad (76)$$

where expression (10) is used for eigenfrequencies.

Now, assuming that the condition for the non-resonant excitation  $\Omega_{\rm R}^2 |\alpha|^2 / \Delta^2 \ll 1$  remains true, we consider the limit of a large amplitude of the exciting field,  $|\alpha|^2 \gg 1$ . Since in this case, the main contribution to sum (76) is made by the terms for which  $n \simeq |\alpha|^2$ , we can calculate this

sum approximately. Assuming that inside the sum, the value  $\sqrt{n}$  is slowly changing and replacing it with the value  $\sqrt{n} \simeq |\alpha|$ , we obtain:

$$\langle \hat{\sigma}(t) \rangle \simeq -\frac{e^{-i\omega_{\mathrm{SM}}t}\Omega_R|\alpha|}{|\Delta|}e^{-|\alpha|^2} \sum_{n=0}^{\infty} \frac{|\alpha|^{2n}}{n!} e^{-(\gamma_0 \Omega_R^{2n}/|\Delta|^2)t} = e^{|\alpha|^2(e^{-(\gamma_0 \Omega_R^{2n}/|\Delta|^2)t}-1)} \frac{e^{-i\omega_{\mathrm{SM}}t}\Omega_R|\alpha|}{|\Delta|}.$$
 (77)

Next, we consider times at which the field amplitude in the selected mode remains almost unchanged, i.e., times  $t \ll (\gamma_0 \Omega_R^2 / |\Delta|^2)^{-1}$ . Then, expression (77) is simplified to give Eq. (31)

$$\langle \hat{\sigma}(t) \rangle \simeq \frac{e^{-i\omega_{\rm SM}t}\Omega_R|\alpha|}{|\Delta|} \exp\left(-\frac{|\alpha|^2\gamma_0\Omega_R^2}{|\Delta|^2}t\right).$$
 (78)

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