SOVIET PHYSICS JETP VOLUME 32, NUMBER 3 MARCH, 1971

QUANTUM THEORY OF RESONANCE PARAMETRIC FLUORESCENCE

R. I. SOKOLOVSKIĬ

Institute of Semiconductor Physics, Siberian Division, Academy of Sciences, U.S.S.R.

Submitted August 29, 1969; resubmitted May 12, 1970

Zh. Eksp. Teor. Fiz. 59, 799–804 (September, 1970)

A theory of spontaneous parametric fluorescence induced by a powerful light wave propagating in a gaseous medium is considered. The frequency of the incident radiation is assumed to be close to that of an atomic transition. The fluorescence spectrum shape is calculated by perturbation theory. It is shown that spontaneous fluorescence produces broadening of the spectrum of radiation traveling through a resonant medium.

THE parametric amplification of radiation in a saturated resonant nonlinear medium has been investigated both theoretically and experimentally.[1-4] The investigated material is situated in an electromagnetic field whose frequency spectrum includes both a strong pump component ω_0 that saturates the resonant absorber and at least one weak field (signal) component of frequency ω_1 close to ω_0. The applied fields cause beats, having the difference frequency $\nu = \omega_0 - \omega_1$, in the populations of the combining levels. These beats modulate the dipole moment, with the result that harmonics with the frequencies $\omega_0 \pm \nu$ appear in the nonlinear polarization. If the saturation parameter κ for pumping exceeds unity ($\kappa > 1$) the phase relations between the nonlinear polarization and the signal lead to amplification of the weak field.[1-4] When $\kappa < 1$ absorption occurs.

In addition to the discussed induced process in the nonlinear medium the pump quanta can decay spontaneously to weak field quanta; this process is called spontaneous parametric fluorescence.[5] A strong monochromatic wave traveling through the resonant medium will then amplify the zero-point oscillations of the electromagnetic field, playing the role of a "signal," and the medium will begin to fluoresce. The theoretical task of determining the frequency distribution of the fluorescent energy and its angular properties was not investigated in[1-4] and is our present subject.

When the mean free path l of a gas molecule greatly exceeds the wavelength λ of a strong field ($l \gg \lambda$) independent scattering occurs on each molecule.[6] In this case a qualitative picture of the four-photon scattering spectrum can be derived from the following intuitive considerations. The largest population-beat amplitude of the combining levels will correspond to the frequency ν that accompanies the resonance $\omega_1 = \omega_{ms}$ (where ω_{ms} is the transition frequency). Therefore the continuous spectrum emitted by the atomic system possesses maximal intensity at the frequencies $\omega_0 \pm \nu$, where $\nu = \omega_0 - \omega_{ms}$. A quantitative description of the shape of the spontaneous fluorescence spectrum necessitates the quantization of the radiation field[7] and a solution of the Schrödinger equation for the closed atom-plus-field system:

$$i\frac{\partial}{\partial t}\Phi = \{H_a + V(t)\}\Phi, \tag{1}$$

where H_a is the Hamiltonian of the atom, $V = -\mathbf{D}\cdot\mathbf{E}(t)$, $\mathbf{D}$ is the atomic dipole moment, and $\mathbf{E}(t)$ is the electric field operator in the interaction representation. We have used a resonance approximation, assuming that the incident wavelength greatly exceeds atomic size.

In the study of scattering processes, including spontaneous parametric fluorescence, it is convenient to start with the integral form of the Schrödinger equation (1):

$$G(t, t_0) = G_a(t - t_0) - \frac{i}{\hbar}\int_{-\infty}^{+\infty} dt'\, G_a(t - t')\, V(t')\, G(t', t_0), \tag{2}$$

where $G(t, t_0)$ is the Green operator of the atom+field system and $G_a(t - t_0)$ is the Green operator of an atomic electron. The solution of (2) in the form of a perturbation series is well known.[8] The n-th order term is a functional of the product of the field strengths and can be expanded in normal products by means of Wick's theorem.[9] After expanding each term of the series in this way we obtain a solution of (2) as a functional of the normal products of the electromagnetic field operators. The term not containing field operators will obviously coincide with the electronic Green's function after radiation corrections. We furthermore assume the existence of different frequencies for all the atomic transitions. In this case the radiation corrections of the electronic Green's function in the resonance approximation are taken into account by summing a chain of diagrams that consist of the simplest self-energy diagram.[9] We thus obtain the following equation giving the Fourier transform of the Green's function for an atomic electron with self-energy corrections taken into account:

$$\bar{G}_a(\omega) = -\frac{1}{2\pi i}\sum_n |n\rangle \frac{1}{\omega - \omega_n + i\gamma_n/2}\langle n|. \tag{3}$$

Here $|n\rangle$ represents the set of stationary states of an undisturbed atom, ω_n is the unperturbed energy of one of these states (in units of $\hbar$) plus the radiative level shift, and γ_n is the sum of the Einstein coefficients for transitions from level n to lower-lying levels.

Equation (3) can be used to allow for the self-energy corrections in the formulas for the transition probabilities. For this purpose we must exclude terms containing self-energy insertions into the electron line and then describe the latter by means of (3). It is also easily verified that in the resonance approximation we have

$$G(t,t_0)=\bar{G}_\mathrm{a}(t-t_0)+\sum_{n=1}^{\infty}\left(\frac{i}{\hbar}\right)^n\int_{-\infty}^{+\infty}dt_1\ldots\int_{-\infty}^{+\infty}dt_n\bar{G}_\mathrm{a}(t-t_1)D_{i_1}$$

$$\times\bar{G}(t_1-t_2)D_{i_2}\ldots D_{i_n}\bar{G}_\mathrm{a}(t_n-t_0)N\{E_{i_1}(t_1)E_{i_2}(t_2)\ldots E_{i_n}(t_n)\},\qquad(4)$$

where in calculating the N-products we must drop nonresonance terms making contributions that are of the order of the ratio of the line width to the transition frequency. Duplication of indices will here and hereafter denote summation. The operator $\bar{G}_a(t-t_0)$ is related to the operator (3) by the Fourier transform

$$\bar{G}_\mathrm{a}(t-t_0)=\int_{-\infty}^{+\infty}e^{-i\omega(t-t_0)}\bar{G}_\mathrm{a}(\omega)\,d\omega,$$

and $E(t_j)$ is the electromagnetic field operator in the interaction representation:

$$\mathbf{E}(t)=\int d\mathbf{k}\{\mathbf{E}^+(\mathbf{k})e^{-i\omega_k t}+\mathbf{E}^-(\mathbf{k})e^{i\omega_k t}\}.\qquad(5)$$

For transitions in the case where an atom is in its ground state at both the beginning and end of the process, the operator describing the field change (the S matrix) is obtained from (4) by averaging over the ground state $\varphi_S(x)$ of the system. We can also select the phase factor of the wave function[8] so that

$$S=1+\sum_{n=2}^{\infty}\left(\frac{i}{\hbar}\right)^n\int_{-\infty}^{+\infty}dt_1\ldots\int_{-\infty}^{+\infty}dt_n\,\langle\varphi_s(x,t_1)|D_{i_1}G_\mathrm{a}(t_1-t_2)$$

$$\times D_{i_2}\ldots G_\mathrm{a}(t_{n-1}-t_n)D_{i_n}|\varphi_s(x,t_n)\rangle N\{E_{i_1}(t_1)E_{i_2}(t_2)\ldots E_{i_n}(t_n)\}.\qquad(6)$$

The energy in the frequency interval $\Delta\omega$ that is scattered by the atomic system into a solid angle element Δ_0 oriented in the direction of the wave vector **k** can be obtained from the equation

$$\Delta\mathscr{E}=(\hbar\omega)^2\left(\delta_{ij}-\frac{k_ik_j}{k^2}\right)$$

$$\times\left\langle\frac{\delta R^+}{\delta E_i^+(\mathbf{k})}\frac{\delta R}{\delta E_j^-(\mathbf{k})}\right\rangle k^2\,dk\,do.\qquad(7)$$

Here averaging is performed over the initial state, and the R matrix and S matrix are related by $S = 1 - 2\pi R$.

The calculations are considerably simplified by using Eq. (5) and a Fourier expansion of the electron Green's function (3). The expression for the S matrix can then be written explicitly as a functional of the operator functions $E_i^-(\mathbf{k})$ and $E_j^+(\mathbf{k})$. The coefficient functions of this functional can be associated with Feynman diagrams.[8-10] The factor $(2\pi i/\hbar)D_j^{lk}$(D^{lk} is the dipole matrix element moment between the l and k states) will correspond to a vertex, and a solid line segment will correspond to the Green's function (3). Energy is conserved at each vertex, and integration is performed over all intermediate frequencies.

If we are interested only in the spectral composition of four-photon scattering that occurs in the field of a monochromatic wave of frequency ω_0 close to the transition frequency ω_{ms} between the ground (s) state and excited (m) state, it is sufficient to consider only the contribution to the R matrix from the diagram in Fig. 1. Equation (7) then represents the scattered energy only for frequencies $\omega \neq \omega_0$. A standard calculation[10] then gives

$$\Delta\mathscr{E}=\frac{\omega^4D^2\sin^2\psi}{c^3[(\omega-\omega_{ms})^2+\gamma_m^2/4]^2}\frac{\gamma_{ms}}{\gamma_m}F_2\left(\frac{\omega}{\omega_0}\right)$$

$$\times\frac{1}{\pi}\int_{-\infty}^{+\infty}dt[\mathbf{DE}(t)/2\hbar]^4\,d\omega\,do,\qquad(8)$$

where γ_{ms} is the Einstein coefficient of the m-s transition, ψ is the angle between the wave vector **k** and the dipole moment **D**, and $F_2(\omega/\omega_0)$ is given by

$$F_2\left(\frac{\omega}{\omega_0}\right)=\frac{\gamma_m}{4\pi}\left|\frac{1}{\omega-\omega_{ms}+i\gamma_m/2}+\frac{1}{2\omega_0-\omega-\omega_{ms}+i\gamma_m/2}\right|^2.$$

When $\Omega\equiv\omega_{ms}-\omega_0=0$ the intensity distribution of spontaneous fluorescence is determined by the square of a Lorentzian profile with the width $\gamma_m/2$. As the ratio Ω/γ_m increases the spectrum is deformed in such a way that for $\Omega/\gamma_m \gg 1$ it consists, in accordance with the foregoing discussion, of two Lorentzian lines each having the width $\gamma_m/2$, and with their maxima at $\omega = \omega_{ms}$ and $\omega = 2\omega_0 - \omega_{ms}$. The integral intensity of scattered energy is proportional to the incident radiation flux multiplied by the resonance scattering cross section and the saturation factor.

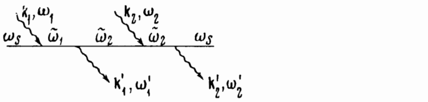

FIG. 1. A diagram describing the two-photon scattering. $\mathbf{k}_j$, ω_j, $\mathbf{k}_j'$, ω_j' (j = 1, 2) are the wave vectors and frequencies of the absorbed and emitted quanta; $\tilde{\omega}_j$ (j = 1, 2, 3) represents the energies of intermediate states.

In the other limiting case $l \ll \lambda$ there is interference between the radiation from different dipoles, and light scattering can be observed only in directions obeying the "synchronism" condition $2\mathbf{k}_0 = \mathbf{k}_1 + \mathbf{k}_2$.[11] This condition together with energy conservation ($2\omega_0 = \omega_1 + \omega_2$) determines the dependence of the scattered light frequency on the observation direction or the tuning characteristic $\vartheta(\omega)$,[5] where ϑ is the angle between the observation direction **n** and the wave vector $\mathbf{k}_0$ of the strong field. The tuning-characteristic distribution of the radiation intensity can be derived from the radiation emitted by an ensemble of dipoles occupying a finite volume V.[11] Light absorption near the resonance frequency is taken into account by introducing the dielectric constant $\epsilon(\omega) = \epsilon'(\omega) - i\epsilon''(\omega)$ into the Heisenberg equation of motion for the field operators. We must also know the mean value of the field commutator in a dispersive medium; this can be obtained from the relation with a retarded Green's function[12]:

$$\langle[E_i^+(\mathbf{k},\omega),E_j^-(\mathbf{k}',\omega')]\rangle=\frac{\hbar}{2\pi}\frac{2}{\varepsilon''}\left(\delta_{ij}-\frac{k_ik_j}{k^2}\right)$$

$$\times\delta(\mathbf{k}-\mathbf{k}')\delta(\omega-\omega')\frac{1}{\pi}\frac{1}{1+(k-\omega c^{-1}\sqrt{\varepsilon'})^2/\alpha^2(k)}$$

$$\alpha(k)=k\varepsilon''/2\varepsilon'.$$

We now easily obtain an expression for the power emitted by a volume V into a unit of solid angle oriented in the direction **n**, per unit frequency

$$w(\mathbf{n},\omega)=V\frac{\hbar\omega^4|\chi|^2\mathscr{E}^4\sin^2\beta}{2\pi\varepsilon''(\omega')}\frac{1}{1+(k'-\omega'c^{-1}\sqrt{\varepsilon'(\omega')})^2/\alpha^2(k')}.\qquad(9)$$

Here $\mathcal{E}$ is the amplitude of the strong field with the frequency ω_0; $\mathbf{k}' = 2\mathbf{k}_0 - \mathbf{k}$, $\mathbf{k} = \omega c^{-1}\sqrt{\epsilon(\omega)}\,\mathbf{n}$; $\omega' = 2\omega_0 - \omega$; β is the angle between the vectors $\mathbf{k}'$ and χ, and χ is defined by

$$\chi_i = e_j e_k{}^0 e_l{}^0\,\overline{D_i D_j D_k D_l} \times \frac{n_0}{2\hbar^3}\left[\frac{1}{\omega_0 - \omega_{ms} + i\gamma_m/2}\right]^2 \times \left[\frac{1}{\omega - \omega_{ms} + i\gamma_m/2} + \frac{1}{2\omega_0 - \omega - \omega_{ms} + i\gamma_m/2}\right]^2,$$

where e is the polarization vector of the scattered radiation and e^0 is the polarization vector of the incident radiation; n_0 is the atomic density. The bar denotes averaging over the orientations of the dipole moment.

The last factor in (9) determines the tuning characteristic $\vartheta(\omega)$ and its width. It is reasonable to define this curve as the geometric locus of points in the (ϑ, ω) plane for which $k' = \omega' c^{-1}\sqrt{\epsilon'}$. If $\Delta(\omega) = \epsilon'(\omega) - 1 \ll 1$ we have approximately $\vartheta = \sqrt{(\Delta + \tilde{\Delta}')/2}$, where $\tilde{\Delta} = \Delta(2\omega - \omega_0)$. The intensity distribution along the curve is determined by the factor $F_2(\omega/\omega_0)/\epsilon''(\omega')$.

With increasing strength of the field impinging on the atomic system the saturation factor also increases, and processes come into play that are associated with the conversion of three strong-field quanta into spontaneous parametric fluorescence energy. The frequencies of the emitted quanta obey the energy conservation law: $3\omega_0 = \omega_1 + \omega_2 + \omega_3$. This is a sixth-order perturbation-theoretical process that is described by the diagram in Fig. 2. When $l \gg \lambda$ it is in principle impossible to distinguish spectroscopically between the contributions of the four-photon and six-photon processes to the fluorescence spectrum. Nevertheless, for large values of "detuning" ($\Omega/\gamma_m \gg 1$: Rayleigh scattering) the six-photon processes lead to spectral broadening of the radiation traveling through the medium. To calculate the "halo" appearing about the incident frequency ω_0 we can replace the R matrix in Eq. (7) with a term corresponding to the diagram in Fig. 2. By a standard calculation in which terms of the order γ_m/Ω are dropped we obtain the power scattered in a unit solid angle around the direction of the wave vector $\mathbf{k}$ within a frequency interval $\Delta\omega$:

$$w = \frac{\omega^4 D^2 \sin^2\psi}{c^3} \cdot \frac{1}{\pi}\left[\frac{(\mathbf{DE}/2\hbar)^2}{(\omega_0 - \omega_{ms})^2 + \gamma_m{}^2/4}\right]^3 \times 2\left(\frac{\gamma_{ms}}{\gamma_m}\right)^2 \frac{1}{\pi}\frac{\gamma_m}{(\omega - \omega_0)^2 + \gamma_m{}^2} \tag{10}$$

which is valid in the vicinity of the frequency ω_0. Thus the "halo" around the scattered line ($\Omega \gg \gamma_m$) is of Lorentzian form and of width γ_m.

In the opposite limiting case $\lambda \gg l$ there is interference between the radiation from different sources, and light can be scattered only in directions satisfying the synchronism condition $3\mathbf{k}_0 = \mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3$.[11] This equation in conjunction with energy conservation determines in the (ω, ϑ) plane a region $|3\mathbf{k}_0 - \mathbf{k}_1| \ll |\mathbf{k}_1| + |\mathbf{k}_2|$ of high scattered light intensity; this can be called the tuning region. For $\Delta(\omega) \ll 1$ the tuning curve lies inside the tuning region. Thus the six-photon processes appear as a background when four-photon fluorescence is observed.

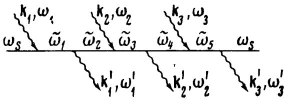

FIG. 2. A diagram describing the three-photon scattering. $\mathbf{k}_j$, ω_j; $\mathbf{k}_j'$, ω_j' (j = 1, 2, 3) are the wave vectors and frequencies of the absorbed and emitted quanta; $\tilde{\omega}_j$ (j = 1, 2, 3, 4, 5) represents the energies of intermediate states.

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Translated by I. Emin
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