1) We use here and below extensively a matrix notation, e.g., $\Delta Bq = \Delta\mu B^{\mu\nu} q_\nu$.

2) Without loss of generality, we can change over to a system in which $p^2=0$. The operator transformations used in Sec. 3 of Ref. 1 are useful in this case.

3) Formal transition from a right- to a left-hand polarized wave is possible by making the substitution $\omega \to -\omega$.

[1] V. N. Baĭer and A. I. Milstein, J. Phys. A 11, 297 (1978).
[2] V. N. Baĭer, V. M. Katkov, and V. M. Strakhovenko, Zh. Eksp. Teor. Fiz. 67, 453 (1974) [Sov. Phys. JETP 40, 225 (1975)].
[3] V. N. Baĭer, V. M. Katkov, A. I. Mil'shteĭn, and V. M. Strakhovenko, Zh. Eksp. Teor. Fiz. 69, 783 (1975) [Sov. Phys. JETP 42, 400 (1975)].
[4] V. N. Baĭer and A. I. Mil'shteĭn, Dokl. Akad. Nauk SSSR 231, 1100 (1976) [Sov. Phys. Dokl. 21, 734 (1976)].
[5] P. Redmond, J. Math. Phys. 6, 1163 (1965).
[6] K. Milton, W. Tsai, L. De Raad, and N. Dass, Phys. Rev. D 10, 1299 (1974).
[7] V. N. Baĭer, V. M. Katkov, and V. S. Fadin, Izluchenie relyativistskikh élektronov (Radiation of Relativistic Electrons), Atomizdat, 1973.

Translated by J. G. Adashko

Kinetics of saturation of a two-level system broadened inhomogeneously by the Doppler effect

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(Submitted 19 December 1977)
Zh. Eksp. Teor. 75, 402–407 (August 1978)

Kinetics of saturation of a Doppler spectrum by a monochromatic field is determined. It is shown that the kinetics is exponential and the rate of saturation is found. At high incident-wave intensities, the rate of saturation of a Doppler profile is proportional to the collision frequency. The distribution of the population difference between the velocities is determined. It is demonstrated that the power absorbed per unit time is proportional to the rate of saturation of a Doppler spectrum.

PACS numbers: 31.30.Jv, 32.80.–t

Investigations of the nature of elastic collisions by nonlinear spectroscopy methods are now popular.[1-5] These methods are particularly interesting because the nature of the velocity-changing elastic collisions has practically no effect on the luminescence spectra.[6]

We shall consider the kinetics of saturation, by a monochromatic field, of a two-level system broadened inhomogeneously by the Doppler effect, and we shall also deal with the steady-state absorption of the field by such a system. Since in most nonlinear spectroscopic investigations of gases and in studies of gas lasers the experimental results are interpreted using the model of relaxation constants, which ignores the changes in the atomic velocities as a result of collisions, we shall allow for the influence of collisions on the kinetics of absorption or saturation of a two-level system, and also on the steady-state nonlinear absorption. Following Kol'chenko *et al.*[1] and Burshteĭn,[5] we shall use the model of weak collisions to show that the kinetics of saturation of a Doppler spectrum is exponential when the frequency of the incident field corresponds to the wings of the Doppler profile, and we shall find the rate of saturation of this profile. Moreover, we shall determine the steady-state power absorption. The rate of saturation of a Doppler profile carries information on the type of collisions and it is proportional to the effective collision frequency.

The saturation method is used widely in investigations of migration in magnetic resonance spectra[7] and in solid-state laser materials.[8] We shall also analyze the effects of diffusion in the velocity space. We shall show that if $\nu \gg 1/T$, where ν is the effective frequency of the velocity-changing in collisions and T is the longitudinal relaxation time, the distribution of the population difference between the velocities v has a dip, which is different from the well-known Lamb and Bennett dips, and is of diffusion origin. Kol'chenko *et al.*[1] also observed a dip of diffusion nature but it corresponds to the criterion $\nu \ll 1/T$ and is associated with the transient stage of diffusion, whereas the dip found in our investigation is associated with the quasisteady stage of diffusion.

The difference between the atomic populations $n(v,t) = \rho_{11}(v,t) - \rho_{22}(v,t)$, traveling at a velocity v, is described in the rate approximation by an equation which has the following form in the weak collision model[6]

$$\frac{\partial n(v,t)}{\partial t} = -2W(v,\omega-\omega_0)\,n(v,t) + \nu\left[1 + v\frac{\partial}{\partial v} + d\frac{\partial^2}{\partial v^2}\right] n(v,t) - \frac{1}{T}\left[n(v,t) - n_0\varphi(v)\right] \tag{1}$$

with the initial condition

$$n(v,0) = n_0\varphi(v) = \frac{n_0}{(2\pi d)^{1/2}}\exp\left(-\frac{v^2}{2d}\right). \tag{2}$$

Here, n_0 is the equilibrium difference between the populations if level 1 is the ground state, whereas if both levels are excited, then n_0/T represents pumping of level 1; T is the relaxation time of the population difference; ν is the frequency of the velocity-changing collisions. The probability of a transition $W(v, \omega-\omega_0)$ is described by

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$$W(v,\omega-\omega_0)=\frac{2V^2\Gamma}{(\omega-\omega_0-kv)^2+\Gamma^2} \tag{3}$$

where Γ is the homogeneous width of the transition; ω_0 is the frequency of the transition; k is the wave number; $k=\omega/c$; ω is the frequency of the incident wave; c is the velocity of light; $V=|d_{12}|E_0$; d_{12} is the matrix element of the dipole moment; E_0 is the amplitude of the incident field.

Following Burshteĭn and Kofman,[5] we shall introduce a function $m(v,t)$, which satisfies the equation

$$\frac{\partial m(v,t)}{\partial t}=-2W(v,\omega-\omega_0)m(v,t)+\nu\left[1+v\frac{\partial}{\partial v}+d\frac{\partial^2}{\partial v^2}\right]m(v,t) \tag{4}$$

subject to the initial condition

$$m(v,0)=\varphi(v)=(2\pi d)^{-1/2}\exp(-v^2/2d). \tag{5}$$

Then, $n(v,t)$ can be expressed in terms of $m(v,t)$ as follows:

$$n(v,t)=n_0 m(v,t)e^{-t/T}+\frac{n_0}{T}\int_0^t m(v,t')e^{-t'/T}dt'. \tag{6}$$

In contrast to Burshteĭn and Kofman,[5] we shall not assume that the frequency of the incident field is equal to the transition frequency ω_0.

We shall now apply the Laplace transformation to Eq. (4). We then obtain

$$pm(p,v)-\nu\left[1+v\frac{\partial}{\partial v}+d\frac{\partial^2}{\partial v^2}\right]m(p,v)=-2W(v,\omega-\omega_0)m(p,v)+\varphi(v). \tag{7}$$

Using a Green function $G(p,v,v')$, we can rewrite Eq. (7) in the equivalent integral form:

$$m(p,v)=-2\int G(p,v,v')W(v',\omega-\omega_0)m(p,v')dv'+\frac{\varphi(v)}{p}, \tag{8}$$

where the Green function $G(p,v,v')$ satisfies

$$pG(p,v,v')-\nu\left[1+v\frac{\partial}{\partial v}+d\frac{\partial^2}{\partial v^2}\right]G(p,v,v')=\delta(v-v'). \tag{9}$$

Equation (8) is obtained utilizing

$$\int G(p,v,v')\varphi(v')dv'=\varphi(v)/p, \tag{10}$$

which follows from the fact that $\varphi(v)$ is stationary in relation to Eq. (9).

We shall consider the most interesting case of a narrow homogeneous line, which corresponds to the condition $\Gamma\ll dk^2/(\omega-\omega_0)$. In this case, since the function $W(v,\omega-\omega_0)$ has a sharp maximum at $v=v_0=(\omega-\omega_0)/k$, it can be replaced by $\alpha\delta(v-v_0)$, where

$$\alpha=2\pi V^2/k. \tag{11}$$

This replacement allows us to solve easily Eq. (8); the solution is

$$m(p,v)=-\alpha G(p,v,v_0)m(p,v_0)+\varphi(v)/p, \tag{12}$$

where

$$m(p,v_0)=\varphi(v_0)/p[1+\alpha G(p,v_0,v_0)]. \tag{13}$$

The Green function $G(p,v,v')$ for Eq. (9) is the Laplace transform of the nominal probability function[9]

$$\varphi(v',v,\tau)=\frac{1}{\{2\pi d(1-\exp(-2\nu\tau))\}^{1/2}}\times\exp\left\{-\frac{[v-v'\exp(-\nu\tau)]^2}{2d[1-\exp(-2\nu\tau)]}\right\}. \tag{14}$$

The expressions for determining the kinetics are given by the inverse Laplace transformation in going from Eq. (12) to Eq. (13):

$$m(v,t)=-\alpha\int_0^t m(v_0,t-\tau)\varphi(v_0,v,\tau)d\tau+\varphi(v), \tag{15}$$

$$m(v_0,\tau)=\frac{1}{2\pi i}\int_{a-i\infty}^{a+i\infty}m(p,v_0)e^{p\tau}dp. \tag{16}$$

We shall now analyze Eqs. (13) and (16) in the limiting case of a detuning $\omega-\omega_0$ far from the center of a Doppler profile, $v_0\gg\sqrt{d}$, and for times $t\gg\nu^{-1}$. In this case the denominator of Eq. (13) is dominated by values in the range $p\ll\nu$. Therefore, we shall expand this denominator as a series in p retaining only the terms of the first order of smallness. Then, Eq. (13) becomes

$$m(p,v_0)=\varphi(v_0)\Big/\left[1+\frac{\alpha}{\nu v_0}\right]\left[p+\frac{\alpha\varphi(v_0)}{1+\alpha/\nu v_0}\right]. \tag{17}$$

It is clear from the above expression that $m(p,v_0)$ has a pole at

$$-p=p_0=\frac{\alpha\varphi(v_0)}{1+\alpha/\nu v_0}. \tag{18}$$

Therefore, it follows from Eq. (16) that the kinetics of population saturation at a point v_0 is given by

$$m(v_0,\tau)=\frac{\varphi(v_0)}{1+\alpha/\nu v_0}\exp(-p_0\tau). \tag{19}$$

Applying Eq. (19), we can transform the kinetics equation (15) into

$$m(v,t)=\varphi(v)\exp(-p_0t)-p_0\exp(-p_0t)\int_0^t[\varphi(v_0,v,\tau)-\varphi(v)]d\tau. \tag{20}$$

We have used here the circumstance that the integrand in Eq. (20) converges in a time much shorter than p_0^{-1}.

The integral (20) is easily calculated. We can expand τ subject to $\nu\tau\ll1$ in the argument of the exponential function and in the radicand of Eq. (14); this gives

$$\varphi(v_0,v,\tau)=\frac{1}{2(\pi d\nu\tau)^{1/2}}\times\exp\left\{-\frac{v^2-v_0^2}{4d}-\frac{vv_0\nu\tau}{4d}-\frac{(v-v_0)^2}{4d\nu\tau}\right\}. \tag{21}$$

The integral (20) is then calculated easily with the aid of Eq. (21) and if $|v-v_0|\ll v_0$, we obtain the following expression for the kinetics of change of $m(v,t)$:

$$m(v,t)=m_0(v)\exp(-p_0t), \tag{22}$$

where

$$m_0(v)=\varphi(v)\left[1-\frac{\alpha/\nu v_0}{1+\alpha/\nu v_0}\exp\left(-\frac{v_0|v-v_0|}{d}\right)\right]. \quad (23)$$

Substituting Eq. (22) into Eq. (6), we obtain the equation for the kinetics of saturation of a Doppler profile:

$$n(v,t)=\frac{n_0m_0(v)p_0T}{p_0T+1}\exp\left(-p_0t-\frac{t}{T}\right)+\frac{n_0m_0(v)}{p_0T+1}. \quad (24)$$

The integrated population difference $n(t)$ is obtained directly from Eq. (20) by integration with respect to v:

$$n(t)=\frac{n_0p_0T}{p_0T+1}\exp\left(-p_0t-\frac{t}{T}\right)+\frac{n_0}{p_0T+1}. \quad (25)$$

It is clear from Eq. (24) that the shape of a Doppler profile is hardly affected, with the exception of a narrow region $|v-v_0|\sim d/v_0$ in the vicinity of the point v_0, where a dip forms in a time of the order of ν^{-1}. The profile as a whole saturates at a rate p_0+T^{-1} reaching a steady-state value

$$n_s(v)=\frac{n_0m_0(v)}{p_0T+1}. \quad (26)$$

We shall now analyze Eq. (18) describing the rate of saturation p_0 of a Doppler profile. At low intensities of incident electromagnetic waves such that $\alpha \ll \nu v_0$, the rate p_0 is proportional to the intensity of the incident field:

$$p_0=\alpha\varphi(v_0)=\left(\frac{2\pi}{d}\right)^{1/2}\frac{V^2}{k}\exp\left[-\frac{(\omega-\omega_0)^2}{2k^2d}\right]. \quad (27)$$

The frequency dependence of the rate of saturation is the Gaussian and it reproduces the velocity distribution of the absorbing atoms. In general, the dependence of p_0 on the intensity is nonlinear and at high intensities $\alpha \gg \nu v_0$ it is independent of the intensity:

$$p_0=\nu v_0\varphi(v_0)=\frac{\nu(\omega-\omega_0)}{(2\pi d)^{1/2}k}\exp\left[-\frac{(\omega-\omega_0)^2}{2k^2d}\right]. \quad (28)$$

In this case the dependence of the rate itself is proportional to frequency ν of the velocity-changing collisions.

The last result has a simple physical interpretation. At high intensities there is rapid and complete saturation at the point v_0 in the velocity space and, consequently, a dip is burnt in the population distribution $m(v,t)$, subsequent saturation being governed by the diffusion flux directed to the point v_0 in the velocity space, i.e., it is limited by the velocity-changing collisions. Since the rate of saturation is proportional to the collision frequency ν, measurements of p_0 should give ν and, consequently, the cross section of the velocity-changing collisions.

Equations (24) and (25) describe completely the kinetics of saturation of a Doppler profile. The population difference $n(v,t)$ can be measured by determining the absorption or luminescence at a neighboring transition.

In addition to the kinetics of saturation of a Doppler profile, it is interesting to consider the absorption of the incident field under steady-state conditions after the completion of relaxation processes. The power N absorbed per unit time is

$$N=\hbar\omega\int W(v,\omega-\omega_0)n_s(v)dv=\hbar\omega\frac{n_0p_0}{p_0T+1}. \quad (29)$$

For a very large detuning when $p_0T \ll 1$, Eq. (29) simplifies and we find that the absorbed power is proportional to the saturation rate p_0:

$$N=\hbar\omega n_0p_0. \quad (30)$$

As mentioned earlier in connection with Eq. (18), the rate p_0 is generally a nonlinear function of the intensity of the absorbed field and it becomes independent of the intensity when its value is high. It is clear from Eq. (30) that the absorbed power behaves in exactly the same way. The profile of the absorption line is then the same for high and low intensities and is basically Gaussian. Measurements of the absorbed power N can also be used to determine the collision frequency ν. The solution of this problem is restricted by the condition $V^2\Gamma/k^2d \ll 1$. If this condition is not obeyed, the field saturates the whole spectrum before collisions between atoms begin to affect the kinetics.

[1]A. P. Kol'chenko, A. A. Pukhov, S. G. Rautian, and A. M. Shalagin, Zh. Eksp. Teor. Fiz. **63**, 1173 (1972) [Sov. Phys. JETP **36**, 619 (1973)].

[2]V. A. Alekseev, T. L. Andreeva, and I. I. Sobel'man, Zh. Eksp. Teor. Fiz. **64**, 813 (1973) [Sov. Phys. JETP **37**, 413 (1973)].

[3]S. N. Bagaev, E. V. Baklanov, and V. P. Chebotaev, Preprint No. 22, Institute of Semiconductor Physics, Siberian Branch of the Academy of Sciences of the USSR, Novosibirsk, 1972.

[4]A. I. Burshteĭn and A. G. Kofman, Kvantovaya Elektron. (Moscow) **2**, 482 (1975) [Sov. J. Quantum Electron. **5**, 274 (1975)].

[5]A. I. Burshteĭn and A. G. Kofman, Pis'ma Zh. Eksp. Teor. Fiz. **25**, 251 (1977) [JETP Lett. **25**, 231 (1977)].

[6]S. G. Rautian and I. I. Sobel'man, Usp. Fiz. Nauk **90**, 209 (1966) [Sov. Phys. Usp. **9**, 701 (1967)].

[7]E. L. Wolf, Phys. Rev. **142**, 555 (1966).

[8]V. V. Grigor'yants, Author's Abstract of Doctoral Thesis, Institute of Radio Electronics, Academy of Sciences of the USSR, Moscow, 1972.

[9]A. I. Burshteĭn, Kvantovaya kinetika (Quantum Kinetics), Part 1, Novosibirsk State University, 1968.

Translated by A. Tybulewicz