The Quantum Kinetic Equation Method for Atoms and Molecules and its Application to the Calculation of Optical Characteristics of Gases

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An equation for the density matrix of an atom is derived in which allowance is made for the simultaneous effect of collisions with foreign particles on the internal and external degrees of freedom of the atom. Both elastic and inelastic scattering are taken into account, as well as the structure of the perturbing particles; the collision term in the equation is expressed in terms of the exact scattering amplitudes. As an example of the application of this equation to the calculation of the optical characteristics of gases, the spontaneous emission spectrum of the atoms is considered. It is shown that a correct description of collisions leads to a number of new qualitative effects. It is found, in particular, that light and heavy perturbing particles lead to essentially different types of broadening and to a different form for the statistical dependence of the Doppler and impact mechanisms of broadening.

THE development of quantum electronics and of many of its physical applications has attracted attention to a number of new problems in the theory of spectral line broadening and of other optical characteristics of a medium, including characteristics that are nonlinear in the electromagnetic field. The most convenient and general method for describing the different optical phenomena in gases is the method based on the equation for the density matrix. This method, however, is usually used in an extremely limited form—the density matrix is used to describe only the motion of the atomic electrons, while the interactions of the atoms and molecules are taken into account by the introduction of relaxation times. For this reason, difficulties arise in the treatment of a whole class of problems (stabilization of a laser frequency, laser spectroscopy, etc.), in which the fine effects of the interaction of the atoms and molecules of the medium are of considerable importance. The point is that, in the general case, collisions of an atom with the surrounding particles perturb both the electronic wavefunctions and the motion of the atom as a whole. Related to this, for example, is the well-known effect of the influence of collisions on Doppler broadening, and also the effect of the statistical dependence of Doppler and impact broadenings (cf., e.g.,[1-3]). Because of this, the need arises for an equation for the density matrix that takes into account the simultaneous effect of collisions on both the internal and external degrees of freedom of the atom.

In the present paper, we obtain an equation for the density matrix of an atom in a neutral gas, without any simplifying assumptions about the motion of the atom as a whole. We make the single physical assumption that the perturbation experienced by the atom due to the surrounding particles reduces to collisions separated in time. Such a gas-kinetic approach makes it possible to describe the perturbation by a collision term expressed in terms of the exact scattering amplitudes, with allowance for both elastic and inelastic channels. The equation takes into account the degeneracy of the atomic levels and also of the levels of the perturbing particles.

As an example of the application of the equations obtained, the problem of calculating the spontaneous emission spectrum of an atom is considered. Using this example, it is shown that the correct description of the collisions leads to a number of new qualitative effects. In particular, it is found that light and heavy perturbing particles lead to essentially different types of broadening.

A theory of spectral line broadening that takes into account the effect of collisions on the external and internal degrees of freedom of the atom was developed earlier in the framework of different approximations (cf.[3,4]). The nature of these approximations and their effect on the results will be discussed below.

1. EQUATION FOR THE DENSITY MATRIX

In this section we shall obtain an equation for the density matrix ρ of an atom without any simplifying assumptions about the motion of the atom as a whole. The interaction of the atoms is treated in the framework of the gas-kinetic approach, which makes it possible to describe the perturbation by a collision term $(d\rho/dt)_{col}$. Throughout below, we shall consider perturbation by foreign particles. Therefore, the collision term $(d\rho/dt)_{col}$ is linear in ρ and our required equation for the density matrix has the form

$$\frac{d\rho}{dt}=\frac{i}{\hbar}[H\rho]+\left(\frac{d\rho}{dt}\right)_{col},\quad \left(\frac{d\rho}{dt}\right)_{col}=\hat{G}\rho, \tag{1}$$

where $H = H_0 + V$, H_0 is the Hamiltonian of the unperturbed atom, V is the interaction of the atom with the electromagnetic field and $\hat{G}$ is a linear integral operator.

We turn now to the calculation of $\hat{G}$. We shall consider a system consisting of the atom and one perturbing particle, enclosed in a finite but sufficiently large volume V. So as not to overload the derivation with minor details, we first consider scattering of the atom by a structureless perturbing particle at rest.

Let the system at the initial moment be described by the wave function

$$\Phi_{ik}=\varphi_j(\mathbf{r})\,e^{i\mathbf{k}\mathbf{R}_a}/\sqrt{V}, \tag{2}$$

where $\varphi_j(\mathbf{r})$ is the electron wavefunction, $\mathbf{k}$ is the wave

vector of the motion of the atom as a whole, and $\mathbf{R}_a$ is the coordinate of the center of inertia of the atom. By time t, the system will be described by the wavefunctions

$$\Psi_{jk}(t) = \sum_{j'\varkappa} S_{jk,\,j'\varkappa}\Phi_{j'\varkappa}\exp\left\{-\frac{i}{\hbar}E_{j'\varkappa}t\right\}, \tag{3}$$

where $E_{j\kappa} = E_j + E_\kappa$, E_j is the energy of the stationary state j, $E_\kappa = \hbar^2\kappa^2/2m_a$, m_a is the atomic mass, and $S_{jk,\,j'\kappa}(0, t; \mathbf{R}_p)$ is the scattering matrix for the time interval (0, t), which depends on the coordinate $\mathbf{R}_p$ of the perturbing particle as a parameter. In accordance with (3), the increment $\Delta\rho(0, t)$ in the density matrix is

$$\Delta\rho(0, t) = S^+\rho S - \rho = T^+\rho T + T^+\rho + \rho T, \tag{4}$$

where $T = S - 1$. Since $e^{i\mathbf{k}\cdot\mathbf{R}} = e^{i\mathbf{k}\cdot(\mathbf{R}-\mathbf{R}_p)+i\mathbf{k}\cdot\mathbf{R}_p}$, for the matrix elements of T, averaged over $\mathbf{R}_p$, we have

$$\overline{T_{j\lambda,\,j'\lambda'}} \propto \delta_{\lambda,\,\lambda'} \qquad \overline{T^+_{j\lambda,\,j'\lambda'}T_{l\varkappa,\,l'\varkappa'}} \propto \delta_{\varkappa,\,\lambda'-\lambda+\varkappa'}.$$

Therefore, the matrix element $\Delta\rho_{\mathbf{mk},\,\mathbf{nk}'}$ can be written in the form

$$\Delta\rho_{m\mathbf{k},n\mathbf{k}'} = \Delta\rho^{(1)}_{m\mathbf{k},n\mathbf{k}'} + \Delta\rho^{(2)}_{m\mathbf{k},n\mathbf{k}'}, \tag{5}$$

$$\Delta\rho^{(1)}_{m\mathbf{k},n\mathbf{k}'} = \sum_j T^+_{m\mathbf{k},j\mathbf{k}}\rho_{j\mathbf{k},n\mathbf{k}'} + \sum_j T_{j\mathbf{k}',n\mathbf{k}'}\rho_{m\mathbf{k},j\mathbf{k}'}, \tag{6}$$

$$\Delta\rho^{(2)}_{m\mathbf{k},n\mathbf{k}'} = \sum_{jj'\varkappa} T^+_{m\mathbf{k},\,j\varkappa}T_{j'\varkappa-\mathbf{k}+\mathbf{k}',\,n\mathbf{k}'}\rho_{j\varkappa,\,j'\varkappa-\mathbf{k}+\mathbf{k}'}, \tag{7}$$

where the matrix elements of T are now already determined in the system of coordinates centered on the perturbing particle. As is well-known, they can be expressed in terms of the scattering amplitudes $f_{jj'}(\lambda\lambda')$ of stationary scattering theory (cf., e.g.,[5])

$$T_{j\lambda,\,j'\lambda'} = i\frac{2\pi\hbar}{m_a}f_{jj'}(\lambda, \lambda')\frac{1}{V}\int_0^t\exp\left\{\frac{i}{\hbar}(E_{j\lambda} - E_{j'\lambda'})x\right\}dx. \tag{8}$$

It is obvious from physical considerations that we are interested only in that part of (6) and (7) which, after separation of the time factor $\exp[i(E_{mk} - E_{nk'})t/\hbar]$, increases linearly with t, since, by describing the perturbation in Eq. (1) by the collision term $(d\rho/dt)_{col}$, we are assuming such a dependence a priori. The situation here is analogous to that which arises, for example, in the determination of the transition probability per unit time from a dimensionless transition probability in the interval (0, t).

It is not difficult to see that the necessary dependence on t arises in (6) if the summation over j in the first sum in (6) is confined to states m', and in the second sum, to states n', where the states m' and n' belong respectively to the same energy levels as m and n ($E_{m'} = E_m$, $E_{n'} = E_n$). The sum over j and j' in the expression (7) can conveniently be decomposed into two parts:

$$\text{I} - j = m', \quad j' = n'; \qquad \text{II} - j \neq m', \quad j' \neq n'.$$

It can be shown that if we are not interested in the special case of overlapping spectral lines (when the frequencies ω_{mn}, $\omega_{jj'}$ of several different atomic transitions fall in the same spectral region $\Delta\omega \sim 1/\tau$, where $1/\tau$ are the characteristic frequencies of collisions for the problem considered), then for the off-diagonal matrix elements $(\hat{G}\rho)_{\mathbf{mk},\,\mathbf{nk}'}$ ($E_m \neq E_n$), the sum II can be omitted. For matrix elements of the type $(\hat{G}\rho)_{\mathbf{mk},\,\mathbf{m'k'}}$, and $(\hat{G}\rho)_{\mathbf{nk}',\,\mathbf{n'k'}}$, including those diagonal in the electron quantum numbers, we have a different situation. We shall come back to this question below[1)].

Since $\rho_{j\lambda,\,j\lambda'} \propto \exp[i(E_{j\lambda} - E_{j'\lambda'})t/\hbar]$, each term of the sum I contains the time factor

$$\exp\left[\frac{i}{\hbar}(E_{mk} - E_{nk'})t\right]\left\{\exp\left[\frac{i}{\hbar}(E_{m'\varkappa} - E_{n'|\varkappa-\mathbf{k}+\mathbf{k}'|} - E_{mk} + E_{nk'})t\right]\right.$$
$$\left.\times\int_0^t\exp\left[\frac{i}{\hbar}(E_{mk} - E_{m'\varkappa})x\right]dx\int_0^t\exp\left[\frac{i}{\hbar}(E_{n'|\varkappa-\mathbf{k}+\mathbf{k}'|} - E_{nk'})x'\right]dx'\right\}.$$

The expression in curly brackets oscillates rapidly in all cases with the exception of the case when $E_\kappa - E_k = E_{|\kappa-\mathbf{k}+\mathbf{k}'|} - E_{k'}$. In this case, for the product of the time integrals, we have

$$\left|\int_0^t\exp\left[\frac{i}{\hbar}(E_{mk} - E_{m\varkappa})x\right]dx\right|^2 \to 2\pi\hbar\delta(E_k - E_\varkappa)t = 2\pi\frac{m_a}{\hbar k}\delta(\varkappa - k)t. \tag{9}$$

By defining $(d\rho/dt)_{col}$ as the proportionality coefficient in the relation $\Delta\rho(0, t) \propto t$, we obtain an expression proportional to $1/V$, which is natural, since there is only one perturbing particle in the volume V. In the framework of the gas-kinetic approach, the passage to the general case is effected by multiplying this expression by NV, where N is the concentration of the perturbing particles. After this, we can pass to the limit $V \to \infty$, replacing the summation over κ by an integration:

$$\sum_\varkappa \to \int\frac{V\,d\varkappa}{(2\pi)^3}.$$

As a result, we obtain

$$(\hat{G}\rho)_{mk,\,nk'} = iN\frac{2\pi\hbar}{m_a}\sum_{m'n'}[\delta_{mm'}f_{n'n}(\mathbf{k}, \mathbf{k}) - \delta_{nn'}f^*_{m'm}(\mathbf{k}', \mathbf{k}')]\,\rho_{m'n'}(\mathbf{k}, \mathbf{k}')$$
$$+ N\frac{\hbar k}{m_a}\sum_{m'n'}\int dO_\varkappa f^*_{m'm}(\varkappa, \mathbf{k})\,f_{n'n}(\varkappa - \mathbf{k} + \mathbf{k}', \mathbf{k}')\,\rho_{m'n'}(\varkappa, \varkappa - \mathbf{k} + \mathbf{k}'). \tag{10}$$

Here, we have changed the notation $\rho_{j\lambda,\,j'\lambda'}$ to $\rho_{jj'}(\lambda, \lambda')$ for convenience.

In exactly the same way, we can also calculate $(d\rho/dt)_{col}$ in the case when the perturbing particle is moving. Let $\mathbf{R}_a$ and $\mathbf{R}_p$ be the coordinates of the atom and the perturbing particle, $\mathbf{R} = \mu_a\mathbf{R}_a + \mu_p\mathbf{R}_p$ be the coordinate of the center of inertia, $\mathbf{r} = \mathbf{R}_a - \mathbf{R}_p$ be the relative distance, and m_p be the mass of the perturbing particle:

$$\mu_a = \frac{m_a}{m_a + m_p}, \quad \mu_p = \frac{m_p}{m_a + m_p}, \quad \mu = \frac{m_a m_p}{m_a + m_p}. \tag{11}$$

We write the wavefunction of the system, without allowance for the interaction, in two representations—in terms of $\mathbf{R}_a$ and $\mathbf{R}_p$, and in terms of $\mathbf{R}$ and $\mathbf{r}$:

$$\Phi_{j\mathbf{k}_a\mathbf{k}_p} = \varphi_j\frac{\exp(i\mathbf{k}_a\mathbf{R}_a)}{\sqrt{V}}\frac{\exp(i\mathbf{k}_p\mathbf{R}_p)}{\sqrt{V}}$$
$$= \varphi_j\frac{\exp[i(\mathbf{k}_a + \mathbf{k}_p)\mathbf{R}]}{\sqrt{V}}\frac{\exp[i(\mu_p\mathbf{k}_a - \mu_a\mathbf{k}_p)\mathbf{r}]}{\sqrt{V}}. \tag{12}$$

[1)]In solving problems that are linear in the electromagnetic field, such as the calculation of an emission or absorption spectrum, it is sufficient to know the matrix elements of the type $(\hat{G}\rho)_{\mathbf{mk},\mathbf{nk}'}$ (cf. Sec. 3). The need for matrix elements of the type $(\hat{G}\rho)_{\mathbf{mk},\,\mathbf{m'k'}}$ arises in solving nonlinear problems. Therefore, we shall consider these matrix elements in Sec. 2, where we shall give the approximate expressions for $(\hat{G}\rho)$ that are most convenient for deriving concrete solutions.

All the subsequent calculations are repeated without substantial changes. The matrix elements of ρ, obviously, must be determined by means of the wavefunctions in the laboratory system of coordinates (we recall that the operator ρ acts only on the atomic wavefunctions). To calculate the matrix T, we must use the representation of Φ in terms of **R** and **r**. In this case, the averaging over $\mathbf{R}_p$ is replaced by integration over **R**. It is necessary to average the expression for $(d\rho/dt)_{col}$ thus obtained over the distribution $W_p(\mathbf{k}_p)$ of wave vectors of the perturbing particle. We give the final expression:

$$(\hat{G\rho})_{m\mathbf{k},n\mathbf{k}'} = iN\frac{2\pi\hbar}{\mu}\sum_{m'n'}\int d\mathbf{q}\, W_p\left(\frac{\mu_p\mathbf{k}-\mathbf{q}}{\mu_a}\right)[\delta_{mm'}f_{nn'}(\mathbf{q},\mathbf{q})$$

$$-\delta_{nn'}f^*_{m'm}(\mathbf{q}-\mathbf{k}+\mathbf{k}',\mathbf{q}-\mathbf{k}+\mathbf{k}')]\rho_{m'n'}(\mathbf{k},\mathbf{k}')$$

$$+N\frac{\hbar}{\mu}\sum_{m'n'}\int d\boldsymbol{\varkappa}\, d\mathbf{q}\, W_p\left(\frac{\mathbf{k}-\mu_a\boldsymbol{\varkappa}-\mathbf{q}}{\mu_a}\right)\delta(|\boldsymbol{\varkappa}-\mathbf{k}+\mathbf{k}'|-q) \quad (13)$$

$$\times\frac{1}{q^2}|\boldsymbol{\varkappa}-\mathbf{k}+\mathbf{q}|f^*_{m'm}(\boldsymbol{\varkappa}-\mathbf{k}+\mathbf{q},\mathbf{q})$$

$$\times f_{n'n}(\boldsymbol{\varkappa}-\mathbf{k}+\mathbf{q}+\mu_p(\mathbf{k}'-\mathbf{k}),\mathbf{q}+\mu_p(\mathbf{k}'-\mathbf{k}))\rho_{m'n'}(\boldsymbol{\varkappa},\boldsymbol{\varkappa}+\mathbf{k}'-\mathbf{k}).$$

As can be checked easily, in the case of a particle at rest ($m_a/m_p \to 0$, $\mu_p \to 1$, $\mu_a \to 0$), (13) goes over to (10). The apparently greater complexity of (13) compared with (10) is associated only with the fact that the matrix ρ is defined in the laboratory coordinate system, while the matrix T and scattering amplitudes f are calculated in the center-of-mass system.

It is not difficult to generalize expression (13) to the case when the perturbing particle has internal structure characterized by the quantum numbers α. For this, it is sufficient to make the replacement

$$f_{n'n}\to\sum_\alpha W_\alpha f^{\alpha\alpha}_{n'n}, \quad f^*_{m'm}\to\sum_\alpha W_\alpha f^{\alpha\alpha^*}_{m'm}$$

in the first term of the right-hand side of (13), and the replacement

$$f^*_{m'm}f_{n'n}\to\sum_{\alpha\alpha'}W_\alpha f^{\alpha'\alpha^*}_{m'm}f^{\alpha'\alpha}_{n'n},$$

in the second term, where W_α is the population of the state α.

In deriving the expression (13) in the framework of the gas-kinetic approach, we have made practically no supplementary simplifying assumptions—the motion of the atom as a whole is treated quantum-mechanically, the interaction is described by exact scattering amplitudes, the degeneracy of the levels is considered, and so on.

The following treatment will be performed for the simplest case of non-degenerate atomic levels and a structureless perturbing particle, when the summation over m′ and n′ does not appear, with $f_{m'm} = f_m$ and $f_{n'n} = f_n$.

As will be seen from the following, in applications we shall be interested in the matrix elements $\rho_{mn}(\mathbf{k},\mathbf{k}')$ for which the difference $\mathbf{k}-\mathbf{k}'$ is equal to the wave vector **p** of a photon. Therefore, the small difference $\mathbf{k}-\mathbf{k}'$ can be omitted from the arguments of the scattering amplitudes. Further, we shall transform the first of the integrals in the right-hand side of (13), adding and subtracting the term

$$q\int dO_\lambda f^*_m(\mathbf{q},\boldsymbol{\lambda})f_n(\mathbf{q},\boldsymbol{\lambda}).$$

in the square brackets. We shall expand the scattering amplitudes in a series in partial waves (cf., e.g.,[6]):

$$f(\mathbf{q},\boldsymbol{\lambda}) = \frac{1}{2iq}\sum_l(2l+1)[S^l-1]P_l(\cos\theta_{\mathbf{q}\boldsymbol{\lambda}}), \quad S^l = e^{2i\delta_l}; \quad (14)$$

here, l is the angular momentum of the relative motion, and $\delta_l = \eta_l + i\beta_l$ are the complex phase shifts. Substituting (14) into (13) and using the orthogonality properties of the Legendre polynomials, we obtain (we recall that we are now considering non-degenerate levels m, n and a structureless perturbing particle)

$$(\hat{G\rho})_{m\mathbf{k},n\mathbf{k}'} = -[{}^1\!/_2\tilde{\Gamma}(k)+i\tilde{\Delta}(k)]\rho_{mn}(\mathbf{k},\mathbf{k}')-\tilde{\nu}(k)\rho_{mn}(\mathbf{k},\mathbf{k}')$$

$$+N\frac{\hbar}{\mu}\int d\boldsymbol{\varkappa}d\mathbf{q}\, W_p\left(\frac{\mathbf{k}-\mu_a\boldsymbol{\varkappa}-\mathbf{q}}{\mu_a}\right)\delta(|\boldsymbol{\varkappa}-\mathbf{k}+\mathbf{q}|-q)\frac{1}{q^2}|\boldsymbol{\varkappa}-\mathbf{k}+\mathbf{q}|$$

$$\times f_m^*(\boldsymbol{\varkappa}-\mathbf{k}+\mathbf{q},\mathbf{q})f_n(\boldsymbol{\varkappa}-\mathbf{k}+\mathbf{q},\mathbf{q})\rho_{mn}(\boldsymbol{\varkappa},\boldsymbol{\varkappa}+\mathbf{k}'-\mathbf{k}), \quad (15)$$

where

$$\frac{1}{2}\tilde{\Gamma}(k)+i\tilde{\Delta}(k) = N\int d\mathbf{q}\frac{\hbar q}{\mu}W_p\left(\frac{\mu_p\mathbf{k}-\mathbf{q}}{\mu_a}\right)[\sigma'(q)+i\sigma''(q)], \quad (16)$$

$$\tilde{\nu}(k) = N\int d\mathbf{q}\frac{\hbar q}{\mu}W_p\left(\frac{\mu_p\mathbf{k}-\mathbf{q}}{\mu_a}\right)\sigma_y^{mn}(q), \quad (17)$$

$$\sigma'(q)+i\sigma''(q) = \frac{\pi}{q^2}\sum_l(2l+1)[1-S_n^lS_m^{l*}], \quad (18)$$

$$\sigma_y^{mn}(q) = \int dO_\lambda f_m^*(\mathbf{q},\boldsymbol{\lambda})f_n(\mathbf{q},\boldsymbol{\lambda}) = \frac{\pi}{q^2}\sum_l(2l+1)[S_n^l-1][S_m^l-1]^*. \quad (19)$$

The quantities σ' and σ'' are the effective cross-sections for the width and shift in the quantum theory of impact broadening[7]. Moreover, the quantities $\tilde{\Gamma}$ and $\tilde{\Delta}$ differ from the usual expressions for the width Γ and the shift Δ of impact theory, since they depend on k. Only in the limiting case of very light perturbing particles ($\mu_p \to 0$, $\mu_a \to 1$) does the dependence on k disappear and $\tilde{\Gamma}(k) \to \Gamma$, $\tilde{\Delta}(k) \to \Delta$. The parameter $\tilde{\nu}(k)$ in (15) plays the role of the gas-kinetic collision frequency, depending on k. However, the effective cross section σ_e^{mn}, unlike the elastic scattering cross section σ_e, is expressed not in terms of the square of the modulus of the scattering amplitude $|f|^2$, but in terms of the product $f_m^*f_n$. For this reason, the quantities σ_e^{mn} and $\tilde{\nu}$ are complex in the general case. If one of the scattering amplitudes, f_m or f_n, is equal to zero, then σ_e^{mn} and $\tilde{\nu} = 0$. At the same time, the integral over $\boldsymbol{\kappa}$ and **q** in (13) goes to zero, and the form taken by the collision term (15) is as if the motion of the atom as a whole experienced no perturbations at all. If the scattering is purely elastic ($\beta_l = 0$, $|S^l| = 1$) and, moreover, the same for both states ($f_m = f_n$), then $\tilde{\Gamma} = \tilde{\Delta} = 0$.

2. THE LIMITING CASES OF HEAVY AND LIGHT PERTURBING PARTICLES

In the limiting case of scattering of a light atom by heavy perturbing particles

$$\mu_a\to 0, \quad \mu_p\to 1, \quad \mu\to m_a, \quad W_p((\mu_p\mathbf{k}-\mathbf{q})/\mu_a)\to\delta(\mathbf{k}-\mathbf{q})$$

the expression (15) takes the form

$$(\hat{G\rho})_{m\mathbf{k},n\mathbf{k}'} = -N\frac{\hbar k}{m_a}[\sigma'(k)+i\sigma''(k)+\sigma_y^{mn}(k)]\rho_{mn}(\mathbf{k},\mathbf{k}')$$

$$+N\frac{\hbar k}{m_a}\int dO_{\boldsymbol{\varkappa}}f_m^*(\boldsymbol{\varkappa},\mathbf{k})f_n(\boldsymbol{\varkappa},\mathbf{k})\rho_{mn}(\boldsymbol{\varkappa},\boldsymbol{\varkappa}-\mathbf{k}+\mathbf{k}'). \quad (20)$$

If the scattering is almost isotropic, then, taking the product $f_m^* f_n$ outside the integral, we obtain

$$(\hat{G}\rho)_{mk,nk'} = -N\frac{\hbar k}{m_a}[\sigma'(k)+i\sigma''(k)+\sigma_y^{mn}(k)]\rho_{mn}(\mathbf{k},\mathbf{k}') + N\frac{\hbar k}{m_a}\sigma_y^{mn}(k)\int\frac{dO_\varkappa}{4\pi}\rho_{mn}(\varkappa,\varkappa-\mathbf{k}+\mathbf{k}'), \quad (21)$$

where $|\boldsymbol{\varkappa}| = k$.

In the other limiting case of light perturbing particles, it is convenient to represent (15) in a different form, introducing in place of $\boldsymbol{\varkappa}$ the integration variable $\Delta\mathbf{k} = \boldsymbol{\varkappa} - \mathbf{k}$:

$$(\hat{G}\rho)_{mk,nk'} = -[{}^1/_2\tilde{\Gamma}(k)+i\tilde{\Delta}(k)]\rho_{mn}(\mathbf{k},\mathbf{k}') - \bar{\nu}(k)\rho_{mn}(\mathbf{k},\mathbf{k}') + N\int A(\mathbf{k}+\Delta\mathbf{k},\Delta\mathbf{k})\rho_{mn}(\mathbf{k}+\Delta\mathbf{k},\mathbf{k}'+\Delta\mathbf{k})d(\Delta\mathbf{k}), \quad (15a)$$

$$A(\lambda,\Delta\mathbf{k}) = \int d\mathbf{q}\, W_p\left(\frac{\lambda\mu_p-\mathbf{q}}{\mu_a}\right)\frac{\hbar}{\mu q}\delta(|\mathbf{q}+\Delta\mathbf{k}|-q) \times f_m^*(\mathbf{q}+\Delta\mathbf{k},\mathbf{q})f_n(\mathbf{q}+\Delta\mathbf{k},\mathbf{q}). \quad (22)$$

In the limit $\mu_a \to 1$, $\mu_p \to 0$, $\mu \to \mu_p$, the quantities $\tilde{\Gamma}(k)$ and $\tilde{\Delta}(k)$ no longer depend on k: $\tilde{\Gamma}(k) \to \Gamma$, $\tilde{\Delta}(k) \to \Delta$. Moreover, neglecting terms of order m_p/m_a, we can bring the integral term in (15a) to the form $\nu\rho_{mn}(\mathbf{k},\mathbf{k}')$. We finally obtain

$$(\hat{G}\rho)_{mk,nk'} = -[{}^1/_2\Gamma + i\Delta]\rho_{mn}(\mathbf{k},\mathbf{k}'). \quad (23)$$

In the next order in the ratio m_p/m_a, using the standard procedure for deriving the Fokker-Planck equation, we can obtain

$$(G\rho)_{mk,nk'} = -[{}^1/_2\Gamma + i\Delta]\rho_{mn}(\mathbf{k},\mathbf{k}') + \nu_d[\mathrm{div}_\lambda(\lambda\rho_{mn}(\lambda,\lambda+\mathbf{k}'-\mathbf{k}))_{\lambda=\mathbf{k}}] + \alpha[\Delta_\lambda\rho_{mn}(\lambda,\lambda+\mathbf{k}'-\mathbf{k})]_{\lambda=\mathbf{k}}, \quad (24)$$

$$\nu_d\mathbf{k} = \int d(\Delta\mathbf{k})\,\Delta\mathbf{k}A(\mathbf{k},\Delta\mathbf{k}), \quad (25)$$

$$\alpha\delta_{ij} = \int d(\Delta\mathbf{k})\Delta k_i\Delta k_j A(\mathbf{k},\Delta\mathbf{k}). \quad (26)$$

It is possible to show that Eq. (24) is also applicable for an arbitrary relation between the masses m_a and m_p, if the amplitudes f_m and f_n have a sharp maximum at small scattering angles.

The parameters ν_d and α are complex. If $f_m = f_n$, then ν_d and α become real and coincide with the corresponding coefficients of the Fokker-Planck equation describing diffusion of particles. In this case, $\alpha = \bar{v}^2\nu_d/2$ (cf., e.g.,[8]). In the case of a perturbing action by particles of different sorts μ

$$\left(\frac{d\rho}{dt}\right)_{col} = \sum_\mu\left(\frac{d\rho}{dt}\right)_{col}^{(\mu)}, \quad (27)$$

and therefore the approximate expressions (21), (23) and (24) for $(\hat{G}\rho)$ enable us to describe practically all the concrete situations of interest.

In the solution of problems that are not linear in the electromagnetic field, we also need the matrix elements of $(\hat{G}\rho)$ that are diagonal in the internal quantum numbers. We shall give these for the two limiting cases of heavy and light perturbing particles. In the first case, with m = n, it follows from (18) and (19) that $\sigma'' = 0$, $\sigma' = \sigma_i^m$, and $\sigma_e^{mn} = \sigma_e^m$, where σ_i^m is the total (summed over all transitions m → j) inelastic scattering cross-section, and σ_e^m is the elastic scattering cross-section for the state m. In addition, for m = n, we must take into account the terms j = j' = m in the sum over j and j' in (7). Repeating all the calculations, in the approximation (21) it is not difficult to obtain

$$(\hat{G}\rho)_{mk,mk'} = -N\frac{\hbar k}{m_a}[\sigma_i^m(k)+\sigma_e^m(k)]\rho_{mn}(\mathbf{k},\mathbf{k}') + N\frac{\hbar k}{m_a}\sigma_e^m(k)\int\frac{dO_\varkappa}{4\pi}\rho_{mm'}(\varkappa,\varkappa-\mathbf{k}+\mathbf{k}') + N\frac{\hbar}{m_a}\sum_j\varkappa_j\sigma_{jm}(\varkappa_j)\int\frac{dO_{\varkappa_j}}{4\pi}\rho_{jj}(\varkappa_j,\varkappa_j-\mathbf{k}+\mathbf{k}'), \quad (28)$$

where $E_j + \hbar^2\kappa_j^2/2m_a = E_m + \hbar^2k^2/2m_a$; the summation over j is extended over the levels $E_j \le E_m + \hbar^2k^2/2m_a$; σ_{jm} is the cross-section for the transition j → m.

In the case of light perturbing particles, we can confine ourselves to the approximation

$$(\hat{G}\rho)_{mk,mk'} = -\gamma_m\rho_{mm}(\mathbf{k},\mathbf{k}') + \sum_j\gamma_{jm}\rho_{mm}(\mathbf{k},\mathbf{k}'), \quad (29)$$

where γ_m is the total probability of a transition from level m and γ_{jm} are the transition probabilities for j → m.

3. THE SPONTANEOUS EMISSION SPECTRUM

As the simplest example of the use of the equations obtained above, we shall examine the problem of calculating the contour $I(\omega)$ of an isolated spectral line corresponding to the atomic transition m → n.

The function $I(\omega)$ can be calculated if the density matrix $\rho(t)$ of the system is known (cf., e.g.,[9]).

$$I(\omega) = \frac{1}{\pi}\mathrm{Re}\sum_{\alpha\beta\alpha'\beta'}W_\alpha\mathbf{P}_{\alpha'\beta}\mathbf{P}_{\beta\alpha}\rho_{\alpha'\beta'}^{(\alpha\beta)}(\omega), \quad (30)$$

$$\rho_{\alpha'\beta'}^{(\alpha\beta)}(\omega) = \int_0^\infty e^{-i\omega t}\rho_{\alpha'\beta'}^{(\alpha\beta)}(t)\,dt. \quad (31)$$

The subscripts α, α' and β, β' respectively label the states belonging to the initial and final levels of the systems, W_α is the population of the state α, $\mathbf{P}$ is the radiation transition operator, and $\rho_{\alpha'\beta'}^{(\alpha\beta)}(t)$ is the $\alpha'\beta'$ element of the density matrix $\rho(t)$, the superscripts $\alpha\beta$ denoting the initial condition $\rho_{\alpha'\beta'}^{(\alpha\beta)}(0) = \delta_{\alpha\alpha'}\delta_{\beta\beta'}$. In our case,

$$\alpha \to m\mathbf{k}_0,\quad \beta \to n\mathbf{k},\quad \alpha' \to m\boldsymbol{\varkappa}_0,\quad \beta' \to n\boldsymbol{\varkappa},\quad \mathbf{P} = \mathbf{d}e^{i\mathbf{p}\mathbf{R}_a},$$

where $\mathbf{d} = e\mathbf{r}$ is the electric dipole moment of the atom, and $\mathbf{p}$ is the photon wave vector.

Using the wavefunctions (2) and (12) and taking into account that

$$\langle m\mathbf{k}_0|\mathbf{P}|n\boldsymbol{\varkappa}_0\rangle = \frac{(2\pi)^3}{V}\mathbf{d}_{mn}\delta(\mathbf{k}_0-\mathbf{p}-\boldsymbol{\varkappa}_0),$$

$$\langle m\mathbf{k}|\mathbf{P}|n\boldsymbol{\varkappa}\rangle = \frac{(2\pi)^3}{V}\mathbf{d}_{mn}\delta(-\mathbf{k}+\mathbf{p}+\boldsymbol{\varkappa}),$$

it is not difficult to obtain, after passing to the limit $V \to \infty$,

$$I(\omega) = \frac{|\mathbf{d}_{mn}|^2}{\pi}\mathrm{Re}\int_0^\infty d\mathbf{k}_0 d\mathbf{k}\,W(\mathbf{k}_0)\rho_{mk,nk-p}^{(mk_0,nk_0-p)}(\omega) = \frac{1}{\pi}\mathrm{Re}\int_0^\infty d\mathbf{k}\,F_{mn}^\omega(\mathbf{k},\mathbf{k}-\mathbf{p}), \quad (32)$$

where the function $F_{mn}^\omega(\mathbf{k},\mathbf{k}-\mathbf{p})$ is defined as the corresponding element of the density matrix $\rho(\omega)$, averaged over $\mathbf{k}_0$.

Using Eq. (1), where $H = H_0$, it is not difficult to obtain the following equation for the function F:

$$-W(\mathbf{k})+i\left(\Delta\omega-\frac{\hbar}{m_a}\mathbf{kp}\right)F_{mn}^{e}(\mathbf{k},\mathbf{k}-\mathbf{p})=(\hat{G}F^{e})_{m\mathbf{k},n\mathbf{k}-\mathbf{p}}, \quad (33)$$

where $\Delta\omega = \omega - \omega_{mn}$. In Eq. (33), we have neglected the effect of the photon recoil, putting $\mathbf{k}^2 - (\mathbf{k}-\mathbf{p})^2 \approx 2\mathbf{k}\cdot\mathbf{p}$.

We start with the simplest case of perturbation of an atom by electrons. In accordance with (32), (33) and (22) we obtain[2)]

$$I(\omega)=\frac{1}{\pi}\mathrm{Re}\int\frac{W(\mathbf{k})\,d\mathbf{k}}{i(\Delta\omega+\Delta-\hbar\mathbf{kp}/m_a)+\Gamma/2}. \quad (34)$$

This expression is the usual convolution of Doppler and dispersion contours.

We shall now consider the case of isotropic scattering of an atom by heavy perturbing particles, which is comparatively simple for concrete calculations and conserves, moreover, all the basic qualitative features of the general case. For applications, an isotropic distribution of the velocities of the atoms is of greatest interest. Accordingly, putting

$$W(\mathbf{k})=\frac{1}{4\pi k^2}w(k),\quad \int_0^\infty w(k)\,dk=1, \quad (35)$$

integrating over the directions of $\mathbf{k}$ in the right- and left-hand sides of (33), and making use of (21), we find

$$\int\frac{dQ_{\mathbf{k}}}{4\pi}F_{mn}^{e}(\mathbf{k},\mathbf{k}-\mathbf{p})=\frac{w(k)}{4\pi k^2}g(k,\omega)\left[1-N\frac{\hbar}{m_a}k\sigma_e^{mn}g(k,\omega)\right]^{-1} \quad (36)$$

$$4\pi g(k,\omega)=\int dO_{\mathbf{k}}\left[i\left(\Delta\omega-\frac{\hbar}{m_a}\mathbf{kp}\right)+N\frac{\hbar}{m_a}k(\sigma'+i\sigma''+\sigma_e^{mn})\right]^{-1}$$

$$=i2\pi\frac{m_a}{\hbar kp}\ln\left\{\left[i\Delta\omega+N\frac{\hbar k}{m_a}(\sigma'+i\sigma''+\sigma_e^{mn})-i\frac{\hbar}{m_a}kp\right]\times\left[i\Delta\omega+N\frac{\hbar k}{m_a}(\sigma'+i\sigma''+\sigma_e^{mn})+i\frac{\hbar}{m_a}kp\right]^{-1}\right\}. \quad (37)$$

$$\times I(\omega)=\frac{1}{\pi}\mathrm{Re}\int_0^\infty dk\,w(k)\,g(k,\omega)\left[1-N\frac{\hbar k}{m_a}\sigma_e^{mn}g(k,\omega)\right]^{-1}. \quad (38)$$

It is easy to see that at small densities the expression (38) goes over to the usual Doppler intensity distribution with width $\Delta\omega_D = \bar{v}p$, where $\bar{v}$ is the average speed $v = \hbar k/m_a$ of the atom. If we assume that the scattering in one of the states m and n can be neglected, when $\sigma_e^{mn} = 0$ (see (19)), then

$$I(\omega)=\frac{1}{\pi}\mathrm{Re}\int_0^\infty\frac{W(v)\,dv}{i(\Delta\omega-vp)+{}^1/_2\tilde{\Gamma}(v)+i\tilde{\Delta}(v)}. \quad (39)$$

This formula differs from (34) in that the parameters $\tilde{\Gamma}$ and $\tilde{\Delta}$ depend on v. Unlike (34), the contour (39) is asymmetric. If we omit the term $\mathbf{v}\cdot\mathbf{p}$, then in place of a single Lorentzian contour, as in (34), we obtain a superposition of Lorentzian contours, each of which is characterized by a width $Nv\sigma'(v)$, a shift $Nv\sigma''(v)$ and a weight w(v); the asymmetry of the distribution (39) is conserved. If $\sigma' = \sigma'' = 0$ (the scattering is purely elastic and $f_m = f_n$), and $\sigma_e^{mn} \neq 0$, then (38) describes the effect of narrowing of the Doppler contour by collisions. In fact, expanding (37) in a series in the parameter $p/N\sigma_e^{mn}$ up to terms of order $(p/N\sigma_e^{mn})^2$, we obtain for sufficiently large N

$$I(\omega)=\frac{1}{\pi}\mathrm{Re}\int_0^\infty dv\frac{w(v)}{i\Delta\omega+\tilde{D}p^2}$$

$$=\int_0^\infty dv\,w(v)\frac{\mathrm{Re}\,\tilde{D}p^2}{\pi}\frac{1}{(\Delta\omega+\mathrm{Im}\,\tilde{D}p^2)^2+(\mathrm{Re}\,\tilde{D}p^2)^2}, \quad (40)$$

where $\tilde{D} = {}^1/_3 v/N\sigma_e^{mn}(v)$. The intensity distribution (40) is a superposition of Lorentzian contours with widths $2\mathrm{Re}\,\tilde{D}p^2 \sim N^{-1}$, shifts $\mathrm{Im}\,\tilde{D}p^2\,N^{-1}$ and weight w(v). The resulting contour (40) is asymmetric. Thus, (40) gives a generalization of the well-known Dicke effect of diffusional narrowing of the Doppler contour[10]. We recall that Dicke's theory gives a single Lorentzian contour (symmetric) with width $2Dp^2$, where D is the diffusion coefficient, and zero shift.

If σ' and σ'' are less than σ_e^{mn} but are not equal to zero, then on increase of N there is first a narrowing of the Doppler contour to a width $\sim Nv\sigma'$, and then a broadening.

We turn now to examine another limiting case, describing the small-angle scattering. Substituting the collision term from (24) into Eq. (33) and solving the resulting equation by the method used in[3], in which equations with a similar structure were considered, we can obtain

$$I(\omega)=\frac{1}{\pi}\mathrm{Re}\int_0^\infty\exp\left\{i\left[-\Delta\omega+\frac{\hbar}{m_a}\mathbf{kp}-\frac{\Gamma}{2}-i\Delta\right]t\right\}\times\exp\left\{-\frac{1}{2}P(t)p^2\right\}dt, \quad (41)$$

$$P(t)=\frac{2\alpha}{\nu_d^3}[\nu_d t-1+e^{-\nu_d t}]-\frac{1}{\nu_d^2}\left(\frac{\bar{v}^2}{2}-\frac{\alpha}{\nu_d}\right)\times\left\{e^{-\nu_d t}-1-\frac{1}{2}(e^{-2\nu_d t}-1)\right\}. \quad (42)$$

As was noted above, the parameters ν_d and α are complex. If we assume that the scattering is the same in states m and n and $f_m = f_n$, then ν_d and α become real and coincide with the corresponding coefficients of the Fokker-Planck equation for the classical distribution function. In this case, $\alpha = \nu_d v^2/2$[8], the second term in expression (42) vanishes, and (cf.[3])

$$I(\omega)=\frac{1}{\pi}\mathrm{Re}\left[\frac{\Delta\omega_D^2}{2\nu_d}-i\left(\Delta\omega+\frac{\Gamma}{2}+i\Delta\right)\right]^{-1}\times\Phi\left(1.1+\frac{\Delta\omega_D^2}{2\nu_d^2}-i\frac{1}{\nu_d}\left(\Delta\omega+\frac{\Gamma}{2}+i\Delta\right),\frac{\Delta\omega_D^2}{2\nu_d}\right), \quad (43)$$

where $\Delta\omega_D = \bar{v}p$, and $\Phi(\beta,\gamma,z)$ is a confluent hypergeometric function. By considering the different limiting cases of expression (43) (cf.[3]), it can be shown that (43) describes the same effects as formula (38) does. The parameters Γ, Δ and ν_d, however, do not depend on k.

The chief difference from (43) in the general case $f_m \neq f_n$ consists in the fact that for complex parameters ν_d and α, the intensity distribution becomes asymmetric and an additional shift of the maximum appears compared with Δ.

4. DISCUSSION OF THE RESULTS

The results of the calculation of the spectrum $I(\omega)$ by means of the equations obtained above for the density matrix contain a number of new elements, the most interesting of which are the following. Even in the treatment of the most simple example—purely impact broadening, qualitative differences from the formulae usually used arise. Only in the case of broadening by light particles, such as electrons, does a single Lorentzian

[2)] Below we omit the factor $|d_{mn}|^2$ in expressions for the intensity $I(\omega)$ throughout.

contour arise, with width $\Gamma = N\langle v\sigma'(v)\rangle$ and shift $\Delta = N\langle v\sigma''(v)\rangle$, where v is the speed of the electrons and the angular brackets denote averaging over v. In the general case, after averaging over the velocities of the perturbing particles, the widths $\tilde{\Gamma}$ and $\tilde{\Delta}$ retain their dependence on the velocity v_a of the atom.

The greatest difference arises in the case of scattering of a light atom by heavy (almost stationary) perturbing particles. Here, a single Lorentzian contour appears only for $N \to \infty$, when the function w(v) can be regarded as a δ-function; however

$$\Gamma = N\bar{v}_a\sigma'(\bar{v}_a), \quad \Delta = N\bar{v}_a\sigma''(\bar{v}_a),$$

where $\bar{v}_a$ is the average velocity of the atom. In the intermediate region of pressures, the line contour is asymmetric. The same differences in the operation of averaging over the velocities of the atoms and of the perturbing particles also appear in all the other results, e.g., in (40).

The perturbations due to perturbing particles of different sorts combine in completely different ways, depending on the masses of these particles. If the perturbing particles of type 1 and type 2 are heavy, then in formula (39), for example, the sum

$$\tilde{\Gamma}_1(v_a) + \tilde{\Gamma}_2(v_a) + i\tilde{\Delta}_1(v_a) + i\tilde{\Delta}_2(v_a).$$

appears. But if the perturbation is created by heavy particles and electrons, then

$$\tilde{\Gamma}_1 = N_1 v_a \sigma'(v_a), \quad \Gamma_2 = N_2\langle v_2\sigma'(v_2)\rangle,$$
$$\Delta_1 = N_1 v_a \sigma''(v_a), \quad \Delta_2 = N_2\langle v_2\sigma''(v_2)\rangle.$$

All this is a reflection of the statistical dependence of the Doppler and impact broadenings, which is expressed in the equations for the density matrix by the dependence of the parameters $\tilde{\Gamma}$, $\tilde{\Delta}$, $\tilde{\nu}$, $\tilde{\nu}_d$, and $\tilde{\alpha}$ on k.

The second characteristic feature of the equations obtained is the fact that the parameters σ_{mn}, ν, ν_d, and α responsible for the Doppler broadening compensation effect are complex. It is not difficult to show that in the examples treated, and also in the general case, asymmetry arises for two reasons—the dependence on k of the parameters of the equation, and the fact that σ_{mn}, ν, ν_d, and α are complex.

It is interesting to note that the difference between the cases of heavy and light perturbing particles remains also in the equation for the diagonal matrix elements

$$\rho_{mn}(\mathbf{k}, \mathbf{k}) = N_m(\mathbf{k}),$$

where $N_m(\mathbf{k})$ is the population of the state m**k**. Putting $\mathbf{k}' = \mathbf{k}$ in (28), assuming the distribution of atoms to be isotropic in **k** and integrating over the directions of **k**, it is easy to obtain an equation for the populations $N_m(k) = \int dO_{\mathbf{k}} N_m(\mathbf{k})$:

$$\frac{dN_m(k)}{dt} = -N\frac{\hbar k}{m_a}\sigma_1^{\,m}(k)N_m(k) + N\frac{\hbar}{m_a}\sum_j \varkappa_j\sigma_{jm}(\varkappa_j)N_j(\varkappa_j). \quad (44)$$

Because of the k-dependence of the coefficients of this equation, it is not possible to integrate this over k to obtain the usual equation for the populations N_m of the levels

$$\frac{dN_m}{dt} = -\gamma_m N_m + \sum_j \gamma_{jm} N_m, \quad (45)$$

which, for the case of light perturbing particles, follows from (29).

In conclusion, it is interesting to compare the results obtained with the results of [3,4].

In [3], the kinetics of the motion of the atom as a whole were described by means of the classical distribution function of the atoms in the coordinates and velocities f(**R**, v, t); therefore, the parameters of the type ν, ν_d, and α in the equations were determined by starting from model collision terms unconnected with the true scattering amplitudes. Therefore, to describe the effect of the statistical dependence of the Doppler and impact broadenings in [3], specific assumptions were made on the form of the collision term in the equation for f(**R**, v, t). The asymmetry of the spectral characteristics arose because of the fact that the parameters of the type ν, ν_d and α were complex.

In [4], an equation was obtained for the density matrix, describing the elastic scattering of an atom by stationary perturbing particles in the Born approximation. The equation for the density matrix obtained in [4] has the same structure as Eq. (20) (the k-dependence of the parameters of the equation, the complexity of the parameter ν, etc.), while the expression for $I(\omega)$ in the case of isotropic scattering coincides with (38), if in (38) we replace the exact scattering amplitudes f_m and f_n by the elastic scattering amplitudes in the Born approximation.

In the most recent work known to us [2], a detailed analysis of the deficiencies of the phenomenological approach is given. In this work, an approximation of the same type as that of [4] is used.

[1] S. G. Rautian and I. I. Sobel'man, IEEE J. Quantum Electron. **2**, 446 (1966).
[2] P. R. Berman and W. E. Lamb, Jr., Phys. Rev. A **2**, 2435 (1970).
[3] S. G. Rautian and I. I. Sobel'man, Usp. Fiz. Nauk **90**, 209 (1966) [Sov. Phys. Usp. **9**, 701 (1967)].
[4] T. L. Andreeva, Zh. Eksp. Teor. Fiz. **54**, 641 (1968) [Sov. Phys. JETP **27**, 342 (1968)].
[5] T.-Y. Wu and T. Ohmura, Quantum Theory of Scattering, Prentice-Hall, N.J., 1962 [Russ. Transl., Nauka, M., 1969].
[6] L. D. Landau and E. M. Lifshitz, Kvantovaya mekhanika (Quantum Mechanics), Fizmatgiz, M., 1963 [English translation published by Pergamon Press, Oxford, 1965].
[7] I. I. Sobel'man, Vvedenie v teoriyu atomnykh spektrov (Introduction to the Theory of Atomic Spectra), Fizmatgiz, M., 1963.
[8] S. Chandresekhar, Rev. Mod. Phys. **15**, 1 (1943) [Russ. Transl. IIL, M., 1947].
[9] V. A. Alekseev and I. I. Sobel'man, Zh. Eksp. Teor. Fiz. **55**, 1874 (1968) [Sov. Phys. JETP **28**, 991 (1969)].
[10] R. Dicke, Phys. Rev. **89**, 472 (1953).

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