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KINETIC EQUATION FOR A GAS OF EXCITED ATOMS

A. P. KAZANTSEV

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

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A generalized Boltzmann equation for the density matrix-describing polarization and the state distribution of atoms is derived by taking into account resonance exchange of excitations in slow atomic collisions. The atomic polarization and the velocity distribution of various density matrix components are assumed to be arbitrary. Exact values for the relaxation coefficients are obtained by numerical integration in the two-state approximation (s and p states). The equations deduced are used to determine the absorption-line shape for long electromagnetic waves.

1. INTRODUCTION

A process playing a very important part in a number of optical phenomena in gases is the resonant exchange of excitations when like atoms collide. The cross section of this process, as shown by Vlasov and Fursov,[1] is inversely proportional to the collision velocity and greatly exceeds the gas-kinetic cross section in a wide velocity interval. In collisions of this type, a change takes place in the polarization of the atom, the phase of the atomic oscillator collapses, and a redistribution of the population over the sublevels takes place. All these processes occur at approximately equal rates. It is of interest to take these effects into account in the kinetic equation for the density matrix that describes the polarization of the atom and the distribution over the levels.

This problem was considered earlier by Byron and Foley,[2] D'yakonov and Perel',[3] and Omont,[4] who obtained a kinetic equation for the averaged (over the atom velocities) density matrix describing the distribution over the sublevels. They assumed that the individual components of the density matrix have Maxwellian velocity distributions. A similar analysis was made also by Ali and Griem,[5] who obtained the scattering matrix by using perturbation theory which, strictly speaking, is not applicable in this case.

The purpose of the present paper is to obtain for arbitrary polarization of the atoms, a generalized Boltzmann equation for a density matrix whose elements have arbitrary velocity distributions. Although the distribution of the atom velocities can usually be regarded as Maxwellian, the same cannot be said in general of the density matrix. A deviation from the Maxwellian distribution occurs, for example, in an external field, and, more importantly in principle, as a direct result of the collisions in which excitation is transferred (the latter pertains also to the nondiagonal elements of the density matrix). This question will be discussed in greater detail at the end of the paper.

In addition, the off-diagonal elements of the density matrix are not assumed a priori to be small compared with the diagonal ones. The collision-integral terms that are nonlinear in the diagonal elements can obviously be important in the presence of a strong electromagnetic field, as in a gas laser.[1)]

The density of the interacting atoms is assumed to be sufficiently small, so that we can confine ourselves to pair collisions. The kinetic equation is in general nonlinear and integral. If degeneracy of the atomic states is taken into account, then the collision integral takes on a very cumbersome form, although its structure is relatively simple.

In the second section of the paper we discuss a general method for obtaining the kinetic equation with account taken of resonant excitation transfer, while in the third section we derive an equation for the density matrix of an atom with two states (s and p states). We note that the excitation-transfer cross section and the scattering matrix were obtained for this case by Vaĭnshteĭn and Galitskiĭ.[7]

[1)] We note that in a gas laser the parameter $N\bar{\lambda}^3$ (see formula (23)).is of the order of unity, so that the collisions under consideration can determine to a considerable degree the characteristic relaxation time. In particular, they can make a contribution to pressure effects[6].

Finally, in the last section of the paper we consider, by way of an example illustrating the application of the derived equations, the question of the shape of the absorption line of long electromagnetic waves. It turns out that the absorption line shape differs somewhat in this case from a Lorentz shape and is asymmetric.

2. KINETIC EQUATION

We consider first the general scheme for obtaining a kinetic equation for the density matrix $\rho_{mn}(\mathbf{v})$. Leaving out for the time being, for the sake of brevity, the indices that number the Zeeman sublevels, and using the energy representation, we can express the collision integral for $\rho_{mn}(\mathbf{v})$ in the usual form

$$\frac{\partial \rho_{mn}(\mathbf{v})}{\partial t} = \mathrm{St}_{mn}^{+}(\mathbf{v}) - \mathrm{St}_{mn}^{-}(\mathbf{v}). \tag{1}$$

The departure of the particles from the phase volume is determined by the number of collisions of the atoms per unit time, so that the departure term has the standard form

$$\mathrm{St}_{mn}^{-}(\mathbf{v}_1) = \rho_{mn}(\mathbf{v}_1) \int d\mathbf{a}\, d\mathbf{v}_2\, vF(\mathbf{v}_2), \tag{2}$$

where $d\mathbf{a} = a\,da\,d\varphi$ is an area element perpendicular to the relative velocity $\mathbf{v} = \mathbf{v}_2 - \mathbf{v}_1$, and $F(\mathbf{v})$ is the atomic-velocity distribution function

$$F(\mathbf{v}) = \sum_m \rho_{mm}(\mathbf{v}). \tag{3}$$

To obtain the emission term in (1) it is necessary to consider first the problem of collision of two atoms.

We denote by C_{mn} the amplitude of the probability that the first atom is in state m and the second in state n. Recognizing that in the case of slow collisions the transitions in a quasimolecule consisting of two atoms occur only between states with identical energy, we can express the result of the collision in the form

$$C_{mn}(+\infty) = P_{mn}C_{mn}(-\infty) + iQ_{mn}C_{nm}(-\infty),$$

$$P_{mn} = P_{nm}, \quad Q_{mn} = Q_{nm}. \tag{4}$$

The amplitudes of the probability that the atoms remain in the initial state (P_{mn}) and that they go over into the state of the incoming atom (Q_{mn}) depend on the impact parameter and on the collision velocity.

We note that the probability amplitudes of the quasimolecule states determine a two-particle density matrix $R(\mathbf{v}_1, \mathbf{v}_2)$, viz., $R_{mm'nn'} = \overline{C_{mn}C^{*}_{m'n'}}$, where the superior bar denotes averaging over the ensemble of the atoms. We assume further, by analogy with an ordinary rarefied gas, that $R(\mathbf{v}_1, \mathbf{v}_2)$ breaks up approximately into products of single-particle density matrices:

$$R(\mathbf{v}_1, \mathbf{v}_2) = \rho(\mathbf{v}_1) \times \rho(\mathbf{v}_2). \tag{5}$$

We assume here that a direct product of the single-particle density matrices is sufficient, since the quantum effects connected with overlap of the electron shell can be neglected. Recognizing that the arrival term is given by

$$\int d\mathbf{a}\, d\mathbf{v}_2 v\, \mathrm{Sp}_2 \{SR(\mathbf{v}_1, \mathbf{v}_2)S^{+}\},$$

where S is the transition matrix defined in (4) and Sp_2 denotes summation over the indices of the incoming particles, and using (5), we can obtain for St^{+}_{mn} the following expression:

$$\begin{aligned}\mathrm{St}_{mn}^{+}(\mathbf{v}_1) = \int d\mathbf{a}\, d\mathbf{v}_2 v \sum_l \{&P_{ml}P_{nl}^{*}\rho_{mn}(\mathbf{v}_1)\rho_{ll}(\mathbf{v}_2) \\ &+ Q_{ml}Q_{nl}^{*}\rho_{mn}(\mathbf{v}_2)\rho_{ll}(\mathbf{v}_1) + iQ_{ml}P_{nl}^{*}\rho_{ln}(\mathbf{v}_1)\rho_{lm}(\mathbf{v}_2) \\ &- iP_{ml}Q_{nl}^{*}\rho_{ml}(\mathbf{v}_1)\rho_{nl}(\mathbf{v}_2)\}.\end{aligned} \tag{6}$$

We took account here of the fact that the main contribution to the exchange of excitations is made by collisions at large distances (on the order of $a_0\sqrt{v_0/v} \gg a_0$, where a_0 is the dimension of the atom and v_0 the characteristic velocity of the electron in the atom). Therefore the change in the velocity of the atom upon collision can be disregarded.

The individual terms in the right side of formula (6) have simple physical meaning: the term with P^2 describes the arrival of atoms in the state prior to the collision, the term with Q_2 the arrival of atoms that go over into the state of the incoming atoms, and the term with PQ the arrival of the atoms in mixed states.

We note that by virtue of the unitarity of the transformation (4), the equilibrium distribution

$$\rho_{mn}{}^{0} \sim \delta_{mn} \exp\{-(E_m + M\mathbf{v}^2/2)/kT\}$$

causes the total collision integral to vanish.

If we take the trace of (1), we get in our approximation, in lieu of the ordinary Boltzmann equation,

$$\partial F(\mathbf{v}) / \partial t = 0, \tag{7}$$

which obviously means that exchange of excitations does not change the atomic velocity distribution function.

3. THE TWO-LEVEL APPROXIMATION

We now consider in greater detail the effects connected with the degeneracy of the atomic levels.

We confine ourselves here only to transitions between states with momenta zero and 1. In this case the index m takes on the values 0 and 1i (i = 1, 2, 3).

At large distances, only the dipole-dipole interaction of the atoms is significant

$$V(\mathbf{r}) = \frac{(\mathbf{d}_1\mathbf{d}_2)}{r^3} - 3\frac{(\mathbf{d}_1\mathbf{r})(\mathbf{d}_2\mathbf{r})}{r^5}. \qquad (8)$$

In the dipole approximation, the amplitudes of the states of the quasimolecule, in which both atoms are in 0 or 1 states, are not changed by the collision:

$$C_{0,0}(+\infty) = C_{0,0}(-\infty), \quad C_{1i,1j}(+\infty) = C_{1i,1j}(-\infty). \qquad (9)$$

The amplitudes of the remaining states of the quasimolecules change in accordance with the following equation (repeated indices will henceforth signify summation from 1 to 3):

$$C_{0,1i}(+\infty) = P_{ij}C_{0,\mathrm{i}_{1j}}(+\infty) + iQ_{ij}C_{1j,0}(-\infty), \qquad (10)$$

the matrices P and Q being real (see (19)) and satisfying, by virtue of unitarity, the relation

$$P_{ik}P_{il} + Q_{ik}Q_{il} = \delta_{kl}, \quad Q_{ik}P_{il} = Q_{il}P_{ik}. \qquad (11)$$

It is convenient to introduce a special notation for the density matrix:

$$n = \overline{C_0C_0^*}, \quad n_i = \overline{C_{1i}C_0^*}, \quad n_{ij} \equiv n_{ji}^* = \overline{C_{1i}C_{1j}^*}. \qquad (12)$$

We note that the atomic velocity distribution function is, in the case of two states, obviously $f(\mathbf{v}) = n(\mathbf{v}) + n_{ii}(\mathbf{v})$. We shall normalize $f(\mathbf{v})$ to unity.

We now write down the collision integral for the individual components of the density matrix. Splitting the two-particle density matrix in accord with (5) and using (9) and (10), we get

$$\frac{\partial n(\mathbf{v}_1)}{\partial t} = N\int d\mathbf{a}\, d\mathbf{v}_2\, v\, \{(P_{ik}P_{il} - \delta_{kl})n_{kl}(\mathbf{v}_2)n(\mathbf{v}_1) + Q_{ik}Q_{il}n_{kl}(\mathbf{v}_1)n(\mathbf{v}_2) + iQ_{ik}P_{il}n_k(\mathbf{v}_1)n_l(\mathbf{v}_2) - iQ_{ik}P_{il}n_k^*(\mathbf{v}_1)n_l(\mathbf{v}_2)\}. \qquad (13)$$

$$\frac{\partial n_i(\mathbf{v}_1)}{\partial t} = N\int d\mathbf{a}\, d\mathbf{v}_2\, v\{(P_{ik} - \delta_{ik})n_k(\mathbf{v}_1)n(\mathbf{v}_2) + n_i(\mathbf{v}_1)(P_{kl} - \delta_{kl})n_{kl}(\mathbf{v}_2) + iQ_{ik}n_k(\mathbf{v}_2)n(\mathbf{v}_1) - iQ_{kl}n_{il}(\mathbf{v}_1)n_k(\mathbf{v}_2)\}, \qquad (14)$$

$$\frac{\partial n_{ij}(\mathbf{v}_1)}{\partial t} = N\int d\mathbf{a}\, d\mathbf{v}_2 v\, \{(P_{ik}P_{jl} - \delta_{ik}\delta_{jl})n_{kl}(\mathbf{v}_1)n(\mathbf{v}_2) + Q_{ik}Q_{jl}n_{kl}(\mathbf{v}_2)n(\mathbf{v}_1) + iQ_{ik}P_{jl}n_k(\mathbf{v}_2)n_l^*(\mathbf{v}_1) - iQ_{jk}P_{il}n_k^*(\mathbf{v}_2)n_l(\mathbf{v}_1)\}. \qquad (15)$$

Here N—density of the atoms.

With the aid of (11) it is easy to establish that not only the distribution function $f(\mathbf{v})$, but also the total number of particles in each state is conserved

$$\int d\mathbf{v}\frac{\partial n(\mathbf{v})}{\partial t} = \int d\mathbf{v}\frac{\partial n_{ii}(\mathbf{v})}{\partial t} = 0. \qquad (16)$$

Equations (10) and (13)–(15) have been written out in an arbitrary system of coordinates. Yet the transition matrices P and Q are best calculated in a coordinate system fixed in the collision plane, where we shall denote them by P^0 and Q^0. It is clear that P and Q are connected with P^0 and Q^0 by the orthogonal rotation

$$P_{ij} = D_{ii'}D_{jj'}P^0{}_{i'j'}, \quad Q_{ij} = D_{ii'}D_{jj'}Q^0{}_{i'j'}, \qquad (17)$$

where $D_{ii'} = (\mathbf{e}_i \cdot \overset{0}{\mathbf{e}}_{i'})$ and $\mathbf{e}_i$ and $\overset{0}{\mathbf{e}}_{i'}$ are unit vectors of an arbitrary coordinate system and of the coordinate system fixed in the (**a**, **v**) plane. As shown by Vaĭnshteĭn and Galitskiĭ,[7] the transition matrices P^0 and Q^0 are of the form

$$P_{ij}{}^0 = \delta_{ij}P_i + \varepsilon_{2ij}P, \quad Q_{ij}{}^0 = \delta_{ij}Q_i + \varepsilon_{2ij}Q, \qquad (18)$$

$$P_1 + iQ_1 = \cos\chi\, e^{i(2\alpha/3-\psi)}, \quad P_2 + iQ_2 = e^{-4i\alpha/3},$$

$$P_3 + iQ_3 = \cos\chi\, e^{i(2\alpha/3+\psi)}, \quad P + iQ = \sin\chi\, e^{2i\alpha/3}. \qquad (19)$$

It is assumed here that the vectors **a** and **v** lie in the plane (1, 3), with **v** directed along $\overset{0}{\mathbf{e}}_3$. The tensor ϵ_{ijk} is a completely antisymmetrical unit tensor. The real functions χ and ψ depend on the parameter

$$\alpha = \frac{3}{2}\frac{|\langle 0|\mathbf{d}|1i\rangle|^2}{\hbar v a^2} \qquad (20)$$

and are determined from the solution of the system of equations

$$i\frac{du_1}{dx} = \alpha\{(1 - 2x^2)u_1 + 2x\sqrt{1 + x^2}u_2\},$$

$$i\frac{du_2}{dx} = \alpha\{2x\sqrt{1 - x^2}u_1 - (1 - 2x^2)u_2\}, \qquad (21)$$

$$x = \frac{vt}{\sqrt{a^2 + v^2t^2}}$$

with boundary conditions

$$u_1(-1) = 1, \quad u_1(+1) = \cos\chi\, e^{i\psi},$$

$$u_2(-1) = 0, \quad u_2(+1) = \sin\chi. \qquad (22)$$

In all the collision integrals it will be advantageous to separate the characteristic relaxation frequency γ:

$$\gamma = N\lambda\!\!\!^{-3}\gamma_0, \quad \gamma_0 = \frac{4}{3}(\hbar\lambda\!\!\!^{-3})^{-1}|\langle 0|\mathbf{d}|1i\rangle|^2, \tag{23}$$

where γ_0 is the reciprocal lifetime relative to the spontaneous transitions, and $2\pi\lambda\!\!\!^{-}$ is the wavelength corresponding to emission at the transition frequency.

Integration with respect to a in (13)–(15) can be replaced by integration with respect to the dimensionless parameter α:

$$2\pi N\int_0^\infty da\, avA(a) = \frac{9\pi\gamma}{8}\int_0^\infty \frac{d\alpha}{\alpha^2}A(\alpha) \equiv \gamma\langle A\rangle. \tag{24}$$

Let us expand $n_{ij}(\mathbf{v})$ and $\operatorname{Im}[n_i(\mathbf{v}_1)n_j^*(\mathbf{v}_2)]$ in terms of irreducible tensors:

$$n_{ij}(\mathbf{v}) = {}^1/_3\delta_{ij}\eta(\mathbf{v}) + i\varepsilon_{ijk}\eta_k(\mathbf{v}) + \eta_{ij}(\mathbf{v}),$$

$$\eta_{ij} = \eta_{ji}, \qquad \eta_{ii} = 0, \tag{25}$$

$$2\operatorname{Im}[n_i(\mathbf{v}_1)n_j^*(\mathbf{v}_2)] = {}^1/_3\delta_{ij}\nu(\mathbf{v}_1, \mathbf{v}_2) + \nu_{ij}(\mathbf{v}_1, \mathbf{v}_2), \tag{26}$$

where all η and ν are real.

Finally, integrating in (13)–(15) with respect to φ, we obtain ultimately after straightforward but cumbersome calculations

$$\begin{aligned}\frac{\partial\eta(\mathbf{v}_1)}{\partial t} &= \gamma\int d\mathbf{v}_2\{A_{pp}\eta(\mathbf{v}_1)n(\mathbf{v}_2)\\ &+ A_{qq}\eta(\mathbf{v}_2)n(\mathbf{v}_1) + A_{pq}\nu(\mathbf{v}_1, \mathbf{v}_2)\\ &+ \Delta_{ij}[B_{pp}\eta_{ij}(\mathbf{v}_1)n(\mathbf{v}_2) + B_{qq}\eta_{ij}(\mathbf{v}_2)n(\mathbf{v}_1)\\ &+ B_{pq}\nu_{ij}(\mathbf{v}_1, \mathbf{v}_2)]\},\end{aligned} \tag{27}$$

$$\begin{aligned}\frac{\partial\eta_i(\mathbf{v}_1)}{\partial t} &= \gamma\int d\mathbf{v}_2\{(a_{pp}\delta_{ij} + b_{pp}\Delta_{ij})\eta_j(\mathbf{v}_1)n(\mathbf{v}_2)\\ &+ (a_{qq}\delta_{ij} + b_{qq}\Delta_{ij})\eta_j(\mathbf{v}_2)n(\mathbf{v}_1) + [a_{pq}\varepsilon_{ilj}\Delta_{jk} - a_{qp}\varepsilon_{ikj}\Delta_{jl}\\ &- ((a_{pq} + a_{qp})/2 + b_{pq})\Delta_{ij}\varepsilon_{jkl}]\operatorname{Re}[n_k(\mathbf{v}_1)n_l^*(\mathbf{v}_2)]\},\end{aligned} \tag{28}$$

$$\begin{aligned}\frac{\partial\eta_{ij}(\mathbf{v}_1)}{\partial t} &= \gamma\int d\mathbf{v}_2\{S_{ij;\,kl}(pp)\eta_{kl}(\mathbf{v}_1)n(\mathbf{v}_2)\\ &+ S_{ij;\,kl}(qq)\eta_{kl}(\mathbf{v}_2)n(\mathbf{v}_1)\\ &+ S_{ij;\,kl}(pq)\nu_{kl}(\mathbf{v}_1, \mathbf{v}_2) + {}^1/_3(\Delta_{ij} - {}^1/_3\delta_{ij})[B_{pp}\eta(\mathbf{v}_1)n(\mathbf{v}_2)\\ &+ B_{qq}\eta(\mathbf{v}_2)n(\mathbf{v}_1) + B_{pq}\nu(\mathbf{v}_1, \mathbf{v}_2)]\},\end{aligned} \tag{29}$$

$$\begin{aligned}\frac{\partial n_i(\mathbf{v}_1)}{\partial t} &= \gamma\int d\mathbf{v}_2\{[a_p\delta_{ij}f(\mathbf{v}_2) + b_p(\Delta_{ij}n(\mathbf{v}_2)\\ &+ \delta_{ij}\Delta_{kl}n_{kl}(\mathbf{v}_2))]n_j(\mathbf{v}_1)\\ &+ b_q(\Delta_{ij}n(\mathbf{v}_1) - n_{il}(\mathbf{v}_1)\Delta_{lj})]n_j(\mathbf{v}_2)\}.\end{aligned} \tag{30}$$

We used here the notation

$$\begin{aligned}S_{ij;\,kl}(pq) &= {}^1/_2[C_{pq}(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) + {}^2/_3(D_{pq} + D_{qp})\delta_{ij}\Delta_{kl}\\ &- D_{pq}(\Delta_{ik}\delta_{jl} + \Delta_{jk}\delta_{il}) - D_{qp}(\Delta_{il}\delta_{jk}\\ &+ \Delta_{jl}\delta_{ik}) + 2E_{pq}(\Delta_{ij} - {}^1/_3\delta_{ij})\Delta_{kl}]\\ &\times\Delta_{ij}(\mathbf{v}) \equiv \Delta_{ij} = v_iv_j/v^2.\end{aligned} \tag{31}$$

The remaining matrices S(pp) and S(qq) are obtained from (31) by replacing q and p with p and q, respectively. The equation for $n(\mathbf{v})$ can be omitted, so that the distribution function $f(\mathbf{v})$ is conserved.

Since the collision cross section is inversely proportional to v, the kernels in the collision integrals are either constants or depend only on the angle functions Δ_{ij}. The terms with index pp correspond to departure of the atoms without a change in polarization (the integral kernel δ_{ij}), and with change of polarization (kernel Δ_{ij}), and similarly the terms with index qq describe the arrival of atoms. The terms with indices pq and qp, which are quadratic in n_i, describe apparently effects of the saturation type.

The constant coefficients in (27)–(31) are connected with the scattering-matrix components averaged in the sense of (24) in the following fashion:

$$\begin{aligned}A_{pq} &= {}^1/_3\langle P_1Q_1 + P_2Q_2 + P_3Q_3 + 2PQ\rangle,\\ B_{pq} &= {}^1/_2\langle 2P_3Q_3 + PQ - P_1Q_1 - P_2Q_2\rangle,\\ a_{pq} &= {}^1/_2\langle P_3(Q_1 + Q_2) + PQ\rangle,\\ a_{qp} &= {}^1/_2\langle Q_3(P_1 + P_2) + PQ\rangle,\\ b_{pq} &= {}^1/_2\langle P_1Q_2 + P_2Q_1\rangle - {}^1/_2(a_{pq} + a_{qp}),\\ C_{pq} &= {}^1/_4\langle(P_1 + P_2)(Q_1 + Q_2)\rangle,\\ D_{pq} &= C_{pq} - a_{pq} + \langle PQ\rangle,\\ D_{qp} &= C_{pq} - a_{qp} + \langle PQ\rangle,\\ 2E_{pq} &= \langle {}^3/\ (P_1Q_1 + P_2Q_2)\\ &+ {}^1/_4(P_1Q_2 + P_2Q_1)\\ &+ P_3(Q_3 - Q_1 - Q_2) + Q_3(P_3 - P_1 - P_2)\rangle,\\ a_p &= \langle {}^1/_2(P_1 + P_2) - 1\rangle, \quad a_q = {}^1/_2\langle Q_1 + Q_2\rangle,\\ b_p &= \left\langle P_3 - \frac{P_1 + P_2}{2}\right\rangle, \quad b_q = \left\langle Q_3 - \frac{Q_1 + Q_2}{2}\right\rangle.\end{aligned} \tag{32}$$

The remaining coefficients with indices pp and qq are obtained from (33) by making in the corresponding coefficient the substitutions $Q_i \to P_i$, $Q \to P$ or $P_i \to Q_i$, $P \to Q$. Exceptions are the "diagonal" coefficients A_{pp}, a_{pp}, and C_{pp}, which differ from this definition by a term -1, so that

$$A_{pp} = \langle {}^1\!/_3(P_1^2 + P_2^2 + P_3^2 + 2P^2) - 1 \rangle,$$

$$a_{pp} = \left\langle \frac{P_3(P_1 + P_2) + P^2}{2} - 1 \right\rangle,$$

$$C_{pp} = \langle {}^1\!/_4(P_1 + P_2)^2 - 1 \rangle. \qquad (33)$$

Using the explicit form of the scattering-matrix elements (formula (19)) we can readily show that the following relations hold:

$$A_{pp} + A_{qq} = 0, \qquad B_{pp} + B_{qq} = 0; \qquad (34)$$

$$a_p = a_{pp} - a_{qq}, \qquad a_q = -(a_{pq} + a_{qp}),$$

$$b_p = b_{pp} - b_{qq}, \qquad b_q = -2b_{pq}. \qquad (35)$$

The coefficient A_{qq} serves to express the cross section σ for resonant excitation exchange in the collision of two atoms, one of which is in the s state and the other in the p state and is unpolarized:

$$\sigma = \frac{\lambda\!\!\!^{-3}\gamma_0}{v} A_{qq}. \qquad (36)$$

The remaining coefficients take into account the correlation existing in scattering between the atom polarization and the collision velocity.

All the integrals (32) and (33) converge quite rapidly. Indeed, in the region of small α, i.e., at long impact distances, the elements of the scattering matrix behave as follows:

$$1 - P_i \sim \alpha^2, \quad P \sim \alpha^2, \quad Q \sim Q_3 \sim \alpha^3, \qquad (37)$$
$$Q_1 \cong -Q_2 \cong {}^4\!/_3\alpha.$$

Thus, the slowest to decrease are Q_1 and Q_2. However, at small values of α the quanties Q_1 and Q_2 are encountered only in the form the combinations $Q_1 + Q_2 \sim \alpha^3$ and $Q_1Q_2 \sim \alpha^2$, so that no logarithmic divergence occurs in (32).

Equations (21) and the coefficients (32) and (33) were numerically integrated with an electronic computer. The results are listed in the table. The coefficients a_p, a_q and b_p, b_q were determined from (35). To compare the results of the calculations with the results obtained by others, let us integrate Eqs. (27)–(30) with respect to velocity, assuming formally that all the components of the density matrix have a Maxwellian velocity distribution. The results of the integration will be denoted by a superior bar:

$$\partial\bar{\eta} / \partial t = 0; \qquad (27')$$

$$\partial\bar{\boldsymbol{\eta}}_i / \partial t = \gamma_1 \bar{\boldsymbol{\eta}}_i \bar{n},$$

$$\gamma_1 = [a_{pp} + a_{qq} + {}^1\!/_3(b_{pp} + b_{qq})]\gamma = -8.6\gamma; \qquad (28')$$

$$\partial\eta_{ij} / \partial t = \gamma_2 \eta_{ij} \bar{n}, \quad \gamma_2 = [C_{pp} + C_{qq} - {}^2\!/_3(D_{pp} + D_{qq})$$
$$+ {}^2\!/_{15}(E_{pp} + E_{qq})]\gamma = -7\gamma;$$

$$\partial\bar{n}_i / \partial t = \gamma' \bar{n}_i + i\gamma''(\bar{n}\delta_{ij} - \bar{n}_{ij})\bar{n}_j, \qquad (29')$$

$$\gamma' = (a_p + b_p / 3)\gamma = -5{,}7\gamma,$$

$$\gamma'' = (a_q + b_q / 3)\gamma = -1{,}9\gamma. \qquad (30')$$

	pp	pq	qp	qq
A	−5.3	0,783		5,3
B	4,61	1,24		−4.61
a	−5,93	0,287	0,881	0.497
b	−3,65	1,08		−5.91
C	−8,51	0,81		0,534
D	−1,33	1,38	0.766	1,21
E	2,09	0,822		4.57

In the last equation we used the condition $\bar{f} = 1$. Relations (28′) and (29′) coincide with the equations obtained by D'yakonov and Perel'.[3]

In concluding this section we note that the condition under which we can confine ourselves only to pair collisions signifies, as is well known, smallness of the effective radius of the interaction compared with the distance between particles. In this case this condition is expressed by the inequality

$$\gamma\sqrt{\gamma_0} \ll (\Delta\omega)^{3/2}, \qquad (38)$$

where $\Delta\omega$ is the Doppler width.

4. ABSORPTION LINE SHAPE

In this section we use the derived equations to obtain the shape of the electromagnetic-radiation absorption line in a rarefied gas.

To calculate the dielectric constant of the gas it is necessary to consider the complete equations of motion for the density matrix:

$$\frac{\partial\rho}{\partial t} + \mathbf{v}\nabla\rho = \frac{1}{i\hbar}[H, \rho] + \mathrm{St}(\rho),$$

$$H = H_0 + H_i, \quad H_i = \mathbf{E}(t)\mathbf{d}, \quad \mathbf{E}(t) = \mathbf{E}e^{-i\omega t} + \text{c.c.} \qquad (39)$$

where $\mathbf{E}(t)$ is the electric field intensity.

The spatial dependence of the field will be disregarded, since we consider the case $\Delta\omega \ll \gamma$. With this, condition (38) may still remain in force, since usually $\gamma_0 \ll \Delta\omega$.

For small deviations from the equilibrium position it is sufficient to consider only the equation for $n_i(\mathbf{v})$. Separating the time dependence in the form $\exp(-i\omega t)$ and discarding $n_{ij}(\mathbf{v})$ compared with $n(\mathbf{v}) \cong f(\mathbf{v})$, we obtain

$$\Omega n_i(\mathbf{v}) = -\frac{E_i d}{\hbar} f(\mathbf{v}) + \gamma \int d\mathbf{u} \{ i a_q f(\mathbf{v}) n_i(\mathbf{u}) + \Delta_{ij}(\mathbf{v} - \mathbf{u})$$
$$\times [b_p f(\mathbf{u}) n_j(\mathbf{v}) + i b_q f(\mathbf{v}) n_j(\mathbf{u})]\},$$

$$\Omega = i(\omega_0 - \omega) - a_p\gamma, \qquad (40)$$

where ω_0 is the transition frequency. We shall assume that the atoms have a Maxwellian velocity distribution

$$f(\mathbf{v}) = (\sqrt{\pi}s)^{-3}e^{-v^2/s^2}. \tag{41}$$

It follows from (4) that the solution takes the form

$$n_i(\mathbf{v}) = (f_1(v)\delta_{ij} + f_2(v)\Delta_{ij})\frac{E_j d}{\hbar\Omega}, \tag{42}$$

and the functions $f_1(v)$ and $f_2(v)$ do not coincide with $f(v)$. The exact functions f_1 and f_2 can hardly be obtained, and therefore we confine ourselves to the approximate solution obtained in the form of an expansion in powers of the parameter γ/Ω. We note that at large values of $|\omega_0 - \omega|$ this parameter becomes small.

The polarization of the gas in an external field is determined by the vector $n_i(\mathbf{v})$ averaged over the velocities. From (40) we obtain, accurate to Ω^{-3},

$$\bar{n}_i = \frac{E_i d}{\hbar} g(\Omega), \quad g(\Omega) = \frac{1}{\Omega}\left[1 + \left(ia_q + \frac{b_p + ib_q}{3}\right)\frac{\gamma}{\Omega}\cdot\right.$$
$$\left. + \left[\left(ia_q + \frac{b_p + ib_q}{3}\right)^2 + \varepsilon(b_p + ib_q)^2\right]\left(\frac{\gamma}{\Omega}\right)^2 + \ldots\right], \tag{43}$$

$$\varepsilon = \frac{1}{3}\int d\mathbf{v}\, d\mathbf{u}\, d\mathbf{w}\, f(\mathbf{v}) f(\mathbf{u}) f(\mathbf{w}) \Delta_{ij}(\mathbf{v} - \mathbf{u}) \Delta_{ij}(\mathbf{v} - \mathbf{w}) - \frac{1}{9}. \tag{44}$$

The expression for the function $g(\Omega)$ obviously contains terms (corresponding to the Maxwellian part of the distribution function $n_i(\mathbf{v})$) which can be eliminated by making the substitution $\Omega \rightarrow \Omega_0 = i(\omega_0 - \gamma'' - \omega) - \gamma'$ (see formula (30′))

$$g(\Omega_0) = \frac{1}{\Omega_0}\left[1 + \varepsilon(b_p + ib_q)^2\left(\frac{\gamma}{\Omega_0}\right)^2 + \ldots\right]. \tag{45}$$

The term in the right side of (45), which is proportional to ϵ, is connected with the deviation of the distribution function $n_i(\mathbf{v})$ from Maxwellian. Indeed, if we neglect the correlation between the velocity of the atom and its polarization, i.e., make the substitution $\Delta_{ij} \rightarrow \frac{1}{3}\delta_{ij}$, then ϵ vanishes.

The absorption coefficient is determined as a function of the frequency by the expression

$$\operatorname{Re} g(\Omega_0) = \frac{\gamma'}{(\delta\omega)^2 + \gamma'^2}\left\{1 + \frac{\varepsilon\gamma'^2[3\gamma'^2 - (\delta\omega)^2]}{[\gamma'^2 + (\delta\omega)^2]^2}\cdot\right.$$
$$\left.\times(b_p^2 - b_q^2 + 2b_p b_q \delta\omega/\gamma') + \ldots\right\},$$
$$\delta\omega = \omega_0 - \gamma'' - \omega. \tag{46}$$

Thus, the absorption coefficient is not an even function with respect to $\delta\omega$. The origin of this symmetry can be explained qualitatively as follows. According to (42), the gas is a mixture of dipoles of two types: "non-inertial" dipoles oriented along the field (distribution function $f_1(\mathbf{v})$), and "inertial" dipoles which are polarized along the atom velocity (distribution function $f_2(\mathbf{v})$). The natural frequencies of dipoles 1 and 2 differ somewhat, owing to the interaction. For this reason, the absorption line contour, being a sum of two Lorentz contours, has an asymmetric form.

Collision integrals of the type given in the right side of (40) (without account of the tensor properties) were investigated by Rautian and Sobel'man,[8] who have shown that when $\gamma \sim \Delta\omega$ the absorption line contour becomes asymmetrical. The asymmetry vanishes when $\gamma \ll \Delta\omega$ and $\gamma \gg \Delta\omega$. In the case considered by us, owing to the polarization effects, the asymmetry remains also when $\gamma \gg \Delta\omega$, and is not connected with the corrections $\Delta\omega/\gamma$. However, numerically the deviation of the absorption line shape from Lorentzian is small. Calculation of the integral (44) leads to the value

$$\varepsilon = \pi/\sqrt{3} - 16/9 \sim 3\cdot 10^{-2}.$$

Using the numerical values for the coefficients a_p, a_q, and b_p, b_q, we can easily estimate that the function $g(\Omega_0)$ differs from $1/\Omega_0$ by not more than 1%.

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Note added in proof (November 2, 1966). The cross section for the transfer excitation during atomic collisions was also calculated by Watanabe [9]. Formula (36) coincides with the corresponding corrected expression of [9].

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