

PACS numbers: 42.50.–p, 32.80.–t, 51.70.+f
DOI: 10.1070/QE2011v041n11ABEH014679

Collision frequencies in density-matrix kinetic equations describing nonlinear effects in the wings of spectral lines

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Abstract. **Using the eikonal approximation, we have calculated effective collision frequencies in density-matrix kinetic equations describing nonlinear effects in the wings of spectral lines. We have established the relation between the probabilities of absorption and stimulated emission and the characteristics of the radiation and elementary scattering event. The example of the power interaction potential shows that quantum mechanical calculation of the collision frequencies in the eikonal approximation and previously known spectral line wing theory give similar results for the probability of radiation absorption.**

Keywords: *density matrix, kinetic equations, collisions, spectral line wing, Einstein coefficients, population inversion, lasing.*

1. Introduction

Until recently, because of equal probabilities of absorption and stimulated emission, cw laser radiation was thought to be only capable of equalising the populations of levels in a two-level system and not producing population inversion. However, as it turned out, under certain conditions this ingrained idea is not true. Papers [1–10] show that in the presence of frequent collisions with buffer particles (thermostat), the probabilities of absorption and stimulated emission are not equal to each other in the wing of the absorption line of active gas particles. It was found that spectral densities of the Einstein coefficients for absorption [$b_{12}(\Omega)$] and stimulated emission [$b_{21}(\Omega)$] are related by expression [7, 8]

$$b_{21}(\Omega) = b_{12}(\Omega)\exp[-h\Omega/(k_{\rm B}T)], \qquad (1)$$

where $\Omega = \omega - \omega_{21}$ is the detuning of the radiation frequency ω from the frequency ω_{21} of transition between the levels $|2\rangle$ and $|1\rangle$; h is Planck's constant; $k_{\rm B}$ is the Boltzmann constant; T is the temperature. Equation (1) remains valid at any sign of Ω. When $h|\Omega| \ll k_{\rm B}T$, canonical equality for the probabilities of absorption and stimulated emission follows from (1).

In accordance with (1), it is possible to establish the population inversion in a two-level system with nonresonant absorption of cw radiation and, as a result, to obtain lasing at the resonant frequency. In [6, 8–10], this effect was registered experimentally – lasing was observed in the regime of superradiance (per single pass of the active medium) at the resonance transition of sodium atoms when pump radiation is absorbed in the 'blue' wing of the line. Lasing occurs only in the presence of a buffer gas at a high enough pressure (above 200 Torr).

The observed effect cannot be extensively described by the presently used quantum kinetic equations for the density matrix (see, for example, [11, 12]). These equations yield neither relation (1) nor suggest the possibility of population inversion in a two-level system under nonresonant optical excitation. In our recent paper [13] we have derived quantum kinetic equations for the density matrix of two-level particles with collision integrals describing nonlinear effects in the wings of spectral lines. From these equations it transpires that spectral densities of the Einstein coefficients are not equal for absorption and stimulated emission of radiation by a two-level quantum system in the far wing of the spectral line under conditions of frequent collisions. We have also established the relation between the collision frequencies entering into these equations and the characteristics of the radiation and elementary scattering event. In this case, the problem of calculation is reduced to the standard problem of calculation of collision frequencies at a known interaction potential of colliding particles. In [13], calculation of collision frequencies was beyond the scope of the analysis undertaken and not performed. This paper fills this gap and is devoted to calculation of collision frequencies in density-matrix kinetic equations obtained in [13] and describing nonlinear effects in the wings of spectral lines.

2. Formulation of the problem

Kinetic equations for the density matrix, defined in the basis of unperturbed atomic states, were obtained in [13] in the following formulation of the problem. We considered the gas absorbing radiation of two-level particles (with the ground level $|1\rangle$ and excited level $|2\rangle$), being mixed with the buffer gas. Collisions between the absorbing particles were neglected because the concentration of the buffer gas, $N_{\rm b}$, was assumed much higher than the concentration of the absorbing gas, N. We believed that in collisions the internal states of two-level particles do not change (elastic collisions). Absorbing particles are affected by a monochromatic field $\mathcal{E} = {\rm Re}\boldsymbol{E}\exp(-i\omega t)$ with the frequency ω, close to the frequency ω_{21} of the transition $2\rangle - |1\rangle$ between levels (here, $\boldsymbol{E}$ is the electric field strength). We considered the case of homogeneous broadening of the absorption line when the Doppler width is small compared with the impact width (the case of a sufficiently high buffer gas pressure). We assumed that detuning $\Omega = \omega - \omega_{21}$ of the

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Received 26 June 2011; revision received 30 August 2011
Kvantovaya Elektronika **41** (11) 1016–1022 (2011)
Translated by I.A. Ulitkin

emission frequency from resonance is small compared with the transition frequency, $|\Omega| \ll \omega_{21}$ (resonance approximation, or rotating-wave approximation), but at the same time is large compared with the impact half-width of the absorption line Γ,

$$|\Omega| \gg \Gamma. \tag{2}$$

In deriving kinetic equations for the density matrix [13], our main task was to find collision integrals, describing the change in density matrix elements due to elastic collisions with buffer gas particles in the region of radiation frequency detunings, strongly exceeding the impact half-width of the absorption lines [see condition (2)] when the radiative transitions occur in the collision event, and not on the free path (the so-called optical collisions [14–16]). The collision problem was solved using representations about 'interacting atom + field' compound systems (an atom 'dressed' by the field) [16, 17] as an independent physical object, which can be treated in the same way as an ordinary particle. This approach naturally takes into account the role of the radiation field in the events of collisions of a 'dressed' atom with buffer particles.

Collisional relaxation considered in [13] allowed us to reduce the problem to an effective two-level model of 'dressed' atoms (with two levels $|\varphi_1(n)\rangle$ and $|\varphi_2(n)\rangle$, Fig. 1). These levels are characterised by wave functions [16, 17]

$$\begin{aligned} |\varphi_1(n)\rangle &= b_1|1\rangle|n\rangle + b_2|2\rangle|n-1\rangle, \\ |\varphi_2(n)\rangle &= b_2^*|1\rangle|n\rangle - b_1|2\rangle|n-1\rangle, \end{aligned} \tag{3}$$

where b_1, b_2 are the expansion coefficients of the compound-system functions in wave functions of an atom (states $|1\rangle$, $|2\rangle$) and a field (states $|n\rangle$, n is the number of photons in a laser field) that do not interact:

$$b_1 = \frac{1}{\sqrt{2}}\sqrt{1-\frac{\Omega}{\Omega_R}}; \quad b_2 = \frac{G}{|G|}\frac{1}{\sqrt{2}}\sqrt{1+\frac{\Omega}{\Omega_R}};$$

$$\Omega_R = \sqrt{4|G|^2+\Omega^2}; \quad G = \frac{d_{21}E}{2\hbar}; \tag{4}$$

d_{21} is the matrix element of the dipole moment of transition $|2\rangle - |1\rangle$. Strictly speaking, the coefficients b_1 and b_2 depend on n. However, we neglected their variation as a function of n, assuming that in the quantum-mechanical state of the laser field, the uncertainty of the number of photons Δn is much smaller than the average number of photons $\bar{n}$, which is considered large:

$$\Delta n \ll \bar{n}, \quad \bar{n} \gg 1. \tag{5}$$

Energies $E_i(n)$ ($i = 1, 2$) related by the expression

$$E_2(n) = E_1(n) + \hbar\Omega_R \tag{6}$$

correspond to states $|\varphi_i(n)\rangle$ of a 'dressed' atom. According to (6), the state $|\varphi_2(n)\rangle$ of a 'dressed' atom is located above the state $|\varphi_1(n)\rangle$ by the value of generalised Rabi frequency Ω_R (in the frequency scale) (Fig. 1). Between levels $|\varphi_1(n)\rangle$ and $|\varphi_2(n)\rangle$ there occur collisional transitions at frequencies ν_{12} and ν_{21} (these transitions are shown in Fig. 1 by curved arrows), and the relaxation of low-frequency coherence between states $|\varphi_2(n)\rangle$ and $|\varphi_1(n)\rangle$ is characterised by the frequency ν. Change in frequencies with variation in n, taking condition (5) into account, can be neglected. It is the collision frequencies (ν_{12}, ν_{21}, and ν) that enter into final density-matrix kinetic equations describing nonlinear effects in the wings of spectral lines [13].

For an effective two-level model of 'dressed' atoms (Fig. 1), use can be made of known expressions for the collision integrals [12, 18], obtained under the impact approximation (this approximation means that the time of collisions is much smaller than the time of the free path). Assuming that the active and buffer particles have an equilibrium (Maxwellian) velocity distribution for the collision frequencies ν_{12}, ν_{21}, we obtain, from the formulas given in [12, 18], the expressions describing them in terms of characteristics of the elementary scattering event (through the scattering amplitudes) [13]:

$$\begin{aligned} \nu_{12} &= \frac{2N_b}{(\sqrt{\pi}\,\bar{u})^3}\int d\boldsymbol{u}\, d\boldsymbol{u}_1 \exp\left(-\frac{\boldsymbol{u}^2}{\bar{u}^2}\right)|f_{21}(\boldsymbol{u}_1|\boldsymbol{u})|^2 \\ &\quad\times\delta\left(\boldsymbol{u}_1^2 - \boldsymbol{u}^2 + \frac{2\hbar\Omega_R}{\mu}\right), \\ \nu_{21} &= \frac{2N_b}{(\sqrt{\pi}\,\bar{u})^3}\int d\boldsymbol{u}\, d\boldsymbol{u}_1 \exp\left(-\frac{\boldsymbol{u}^2}{\bar{u}^2}\right)|f_{12}(\boldsymbol{u}_1|\boldsymbol{u})|^2 \\ &\quad\times\delta\left(\boldsymbol{u}_1^2 - \boldsymbol{u}^2 - \frac{2\hbar\Omega_R}{\mu}\right), \quad \bar{u} = \sqrt{\frac{2k_B T}{\mu}}, \end{aligned} \tag{7}$$

where $\boldsymbol{u}$ and $\boldsymbol{u}_1$ are the relative velocities of the colliding particles before and after collision; μ is the reduced mass of the colliding particles; $\delta(x)$ is the delta function; $f_{ji}(\boldsymbol{u}_1|\boldsymbol{u})$ is the amplitudes of scattering of a 'dressed' atom from a structureless buffer particle; subscripts i and j ($i, j = 1, 2$) denote, respectively, the set of quantum numbers of initial and final states of a 'dressed' atom [1 corresponds to the state $|\varphi_1(n)\rangle$ with energy $E_1(n)$, and 2 – to the state $|\varphi_2(n)\rangle$ with energy $E_2(n)$, see Fig. 1].

To calculate scattering amplitudes in formula (7), we need to know the matrix elements W_{ij} of the interaction operator of colliding particles $\hat{U}$ in the basis of 'dressed' states:

$$W_{ij} = \langle\varphi_i(n)|\hat{U}|\varphi_j(n)\rangle, \quad i, j = 1, 2. \tag{8}$$

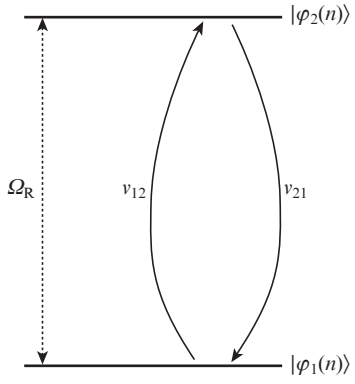

Figure 1. Effective two-level model of 'dressed' atoms for a collisional problem. Collisional transitions with frequencies ν_{12} and ν_{21} occur between the levels $|\varphi_1(n)\rangle$ and $|\varphi_2(n)\rangle$.

The matrix elements W_{11} and W_{22} of the interaction operator $\hat{U}$ characterise the collisional shifts of levels $|\varphi_1(n)\rangle$ and $|\varphi_2(n)\rangle$ of the compound system and the matrix elements W_{12} and W_{21} characterise the collisional transitions between levels $|\varphi_1(n)\rangle$ and $|\varphi_2(n)\rangle$ of the system.

Taking into account relations (3), we obtain for the matrix elements W_{ij} the expressions describing them in terms of matrix elements U_{ii} of the interaction operator in the basis of the unperturbed states of the atom (we assume that there are no collisional transitions between the levels of active particle and so $U_{12} = U_{21} = 0$) [6, 14, 16]:

$$W_{11} = \frac{U_{11} + U_{22}}{2} - \frac{\Omega}{2\Omega_{\mathrm{R}}}(U_{11} - U_{22}),$$

$$W_{22} = \frac{U_{11} + U_{22}}{2} + \frac{\Omega}{2\Omega_{\mathrm{R}}}(U_{11} - U_{22}), \tag{9}$$

$$W_{12} = \frac{G^*}{\Omega_{\mathrm{R}}}(U_{11} - U_{22}),\ W_{21} = W_{12}^*,\ U_{ii} = \langle\, i|\hat{U}|\, i\,\rangle,\ i = 1, 2.$$

The matrix elements U_{ii} characterise the shifts of levels $|i\rangle$ of the active particles due to collisions. Note that the matrix elements W_{ij} contain both the parameters of the initial interaction potential of the colliding particles and the parameters of radiation. This means that radiation quantum participates in the collision event. In the basis of the unperturbed states of the atom, collisions do not lead to transitions between states $|1\rangle$ and $|2\rangle$ ($U_{12} = 0$) and, in this sense, they are 'elastic'. The nonzero intensity ($G \neq 0$) gives rise to collisional transitions between levels $|\varphi_1(n)\rangle$ and $|\varphi_2(n)\rangle$ of a 'dressed' atom ($W_{12} \neq 0$), i.e., the collisions are accompanied by the emergence of an inelastic channel with energy gap $\hbar\Omega_{\mathrm{R}}$. There also occurs a change in the elastic scattering channel.

For the collisional transition frequencies v_{12} and v_{21}, using the reciprocity theorem for the amplitudes of the forward and reverse processes [12, 19] we easily obtain from expressions (7) the relation

$$\frac{v_{12}}{v_{21}} = \exp\left(-\frac{\hbar\Omega_{\mathrm{R}}}{k_{\mathrm{B}}T}\right), \tag{10}$$

reflecting the principle of detailed equilibrium (see, for example, [20]).

The resulting kinetic equations for the density matrix in the unperturbed atomic basis, which describe nonlinear effects in the wings of the spectral lines, are rather complicated [13] and we do not present them here. For a not-too-high intensity, such that

$$|G| \ll |\Omega|, \tag{11}$$

kinetic equations for the density matrix are simplified and reduced to the balance equations for level populations [13]:

$$\left(\frac{\mathrm{d}}{\mathrm{d}t} + A\right)\rho_{22} = \begin{cases} v_{21}\rho_{11} - v_{12}\rho_{22}, & \Omega > 0, \\ v_{12}\rho_{11} - v_{21}\rho_{22}, & \Omega < 0. \end{cases} \tag{12}$$

Here, ρ_{ii} is the population of level $|i\rangle$ ($i = 1, 2$); A is the rate of spontaneous decay of excited level $|2\rangle$. Populations of the levels are related with the concentration N of absorbing particles by the expression (normalisation condition)

$$\rho_{11} + \rho_{22} = N. \tag{13}$$

When the intensity (11) is not too high, for the collision frequencies v_{12} and v_{21} we can set

$$\Omega_{\mathrm{R}} = |\Omega| \tag{14}$$

in relation (10). Then, balanced equation (12) takes the form

$$\left(\frac{\mathrm{d}}{\mathrm{d}t} + A\right)\rho_{22} = \begin{cases} v_{21}\{\rho_{11} - \rho_{22}\exp[-\hbar\,|\Omega|/(k_{\mathrm{B}}T)]\}, & \Omega > 0, \\ v_{21}\{\rho_{11}\exp[-\hbar\,|\Omega|/(k_{\mathrm{B}}T)] - \rho_{22}\}, & \Omega < 0. \end{cases} \tag{15}$$

In this equation the unknown quantity is the collision frequency v_{21}.The remaining quantities are either well known (rate A of spontaneous decay of the excited level), or given by experimental conditions (frequency detuning Ω, temperature T). We will calculate below the collision frequency v_{21} entering into equation (15).

3. Calculation of the collision frequency v_{21} in the eikonal approximation

Calculation of the collision frequency v_{21} by (7) is actually reduced to calculation of scattering amplitude $f_{12}(\boldsymbol{u}_1|\boldsymbol{u})$. Its calculation is in general a complicated problem and time consuming computations require the use of various approximate methods. In the case of scattering of fast particles, the eikonal approximation is applicable [12, 19]. In this approximation, the expression [12, 18]

$$f_{12}(\boldsymbol{u}_1|\,\boldsymbol{u}) = -\mathrm{i}\frac{\mu u_1}{2\pi\hbar}\int S_{12}(\boldsymbol{\rho})\exp\left[\mathrm{i}\frac{\mu u_1}{\hbar}(\hat{\boldsymbol{u}} - \hat{\boldsymbol{u}}_1)\boldsymbol{\rho}\right]\mathrm{d}\boldsymbol{\rho},$$

$$\hat{\boldsymbol{u}} \equiv \frac{\boldsymbol{u}}{u}, \quad \hat{\boldsymbol{u}}_1 \equiv \frac{\boldsymbol{u}_1}{u_1}, \quad u_1^2 = u^2 + \frac{2\hbar\Omega_{\mathrm{R}}}{\mu} \tag{16}$$

is valid for the scattering amplitude $f_{12}(\boldsymbol{u}_1|\boldsymbol{u})$ where the function $S_{12}(\boldsymbol{\rho})$ (the vector $\boldsymbol{\rho}$ is the projection of the radius vector $\boldsymbol{r}$, connecting the colliding particles, onto the plane that is perpendicular to the velocity $\boldsymbol{u}$; $\boldsymbol{\rho}$ is usually interpreted as the vector of the impact parameter) is determined from the system of equations

$$\left(\hat{u}\nabla + \mathrm{i}\frac{W_{11}}{\hbar u_1}\right)S_{12} = -\frac{\mathrm{i}}{\hbar u_1}W_{12}S_{22}\exp\left[\mathrm{i}\frac{\mu}{\hbar}(u - u_1)\boldsymbol{r}\hat{\boldsymbol{u}}\right],$$

$$\left(\hat{u}\nabla + \mathrm{i}\frac{W_{22}}{\hbar u}\right)S_{22} = -\frac{\mathrm{i}}{\hbar u}W_{21}S_{12}\exp\left[\mathrm{i}\frac{\mu}{\hbar}(u_1 - u)\boldsymbol{r}\hat{\boldsymbol{u}}\right]. \tag{17}$$

As noted above, the eikonal approximation [formulas (16), (17)] is applicable in the case of scattering of fast particles when the de Broglie wavelength of the colliding particles is much shorter than the characteristic radius of interaction ρ_W and the matrix elements of the interaction operator W_{ij} are considerably smaller than the kinetic energies of the colliding particles [12, 19]:

$$\frac{\hbar}{\mu u} \ll \rho_W, \quad |\,W_{ij}| \ll \frac{\mu u^2}{2}. \tag{18}$$

In addition, the energy transmitted in collisions should be relatively small [19], which means the fulfilment of the condition

$$\hbar\Omega_{\mathrm{R}} \ll \frac{\mu u^2}{2}. \tag{19}$$

For further calculations, equations (17) can be conveniently considered in the coordinate system with the axis z, which coincides with the direction of free motion (along the vector $\hat{\boldsymbol{u}}$); in this case, the vector $\boldsymbol{\rho}$ lies in the xy plane and the vector $\boldsymbol{r}$ is represented as two components: $\boldsymbol{r} = \boldsymbol{\rho} + \hat{\boldsymbol{u}}z$. Interaction between the particles is assumed central, and the matrix elements W_{ij} in this case depend only on the distance $r = (\rho^2 + z^2)^{1/2}$ between the colliding particles. In this coordinate system, equations (17) take the form:

$$\begin{aligned}
&\Big(\frac{\mathrm{d}}{\mathrm{d}z} + \mathrm{i}\frac{W_{11}}{\hbar u_1}\Big)S_{12} = -\frac{\mathrm{i}}{\hbar u_1} W_{12}S_{22}\exp\Big[\mathrm{i}\frac{\mu}{\hbar}(u-u_1)z\Big],\\
&\Big(\frac{\mathrm{d}}{\mathrm{d}z} + \mathrm{i}\frac{W_{22}}{\hbar u}\Big)S_{22} = -\frac{\mathrm{i}}{\hbar u} W_{21}S_{12}\exp\Big[\mathrm{i}\frac{\mu}{\hbar}(u_1-u)z\Big].
\end{aligned} \tag{20}$$

One can see from expressions (9) that for a not-too-high intensity (11), we can set

$$W_{11} = \begin{cases} U_{22}, & \Omega > 0,\\ U_{11}, & \Omega < 0,\end{cases} \qquad W_{22} = \begin{cases} U_{11}, & \Omega > 0,\\ U_{22}, & \Omega < 0,\end{cases} \tag{21}$$

so that the condition

$$|W_{12}|, |W_{21}| \ll |W_{11}|, |W_{22}| \tag{22}$$

is fulfilled.

This allows one to search for the solution of equations (20) in the form

$$S_{ij} = S_{ij}^{(0)} + S_{ij}^{(1)}, \tag{23}$$

where $S_{ij}^{(0)}$ is the solution of equations (20) at $W_{12} = W_{21} = 0$, and the small corrections $S_{ij}^{(1)}$ are caused by the matrix elements W_{12} and W_{21}. Due to the fact that $W_{12} = 0$, collisional transitions between levels of a 'dressed' atom are absent, we should assume $S_{12}^{(0)} = 0$. Therefore, $S_{12} = S_{12}^{(1)}$. From (20) with (22) and (23) taken into account, for the quantity $S_{12}^{(1)}$ we have the equation

$$\begin{aligned}
&\Big(\frac{\mathrm{d}}{\mathrm{d}z} + \mathrm{i}\frac{W_{11}}{\hbar u_1}\Big)S_{12}^{(1)} = -\frac{\mathrm{i}}{\hbar u_1} W_{12}S_{22}^{(0)}\exp\Big[\mathrm{i}\frac{\mu}{\hbar}(u-u_1)z\Big],\\
&S_{22}^{(0)} = \exp\Big(-\frac{\mathrm{i}}{\hbar u}\int_{-\infty}^{z} W_{22}\mathrm{d}z\Big).
\end{aligned} \tag{24}$$

Solving this linear inhomogeneous differential equation, for $S_{12} = S_{12}^{(1)}$ we obtain the expression:

$$S_{12}(\rho) = -\frac{\mathrm{i}}{\hbar u_1}\int_{-\infty}^{\infty} W_{12}(\rho,z)\exp[\mathrm{i}g(\rho,z)]\mathrm{d}z, \tag{25}$$

where

$$\begin{aligned}
g(\rho,z) = &-\int_{-\infty}^{z}\frac{W_{22}(\rho,z')}{\hbar u}\mathrm{d}z'\\
&-\int_{z}^{\infty}\frac{W_{11}(\rho,z')}{\hbar u_1}\mathrm{d}z' + \frac{\mu}{\hbar}(u-u_1)z.
\end{aligned} \tag{26}$$

We calculate the integral in (25) by the method of stationary phase. Contribution into the integral is made by the vicinity of points at which the function $g(\rho,z)$ is stationary, i.e., where the derivative $\partial g/\partial z = 0$. Phase $g(\rho,z)$ is stationary at two points: $z_{1,2} = \pm\sqrt{r_0^2 - \rho^2}$ to which the distance r_0 between the colliding particles corresponds. The value of r_0 corresponds to the point of intersection of the compound-system terms and is determined from the equation

$$W_{11}(r_0) - W_{22}(r_0) = \hbar\Omega_{\mathrm{R}}, \tag{27}$$

which follows from the equation $\partial g/\partial z = 0$ under conditions (11), (18), (19) and an additional condition

$$\frac{\hbar\Omega_{\mathrm{R}}}{2\mu u^2} \ll \Big|\frac{U_{11} - U_{22}}{U_{11} + U_{22}}\Big|, \tag{28}$$

which denotes not very close coincidence between the interaction potentials of buffer particles and atoms in the ground and excited states. Calculation of the integral in (25) by the method of stationary phase gives

$$\begin{aligned}
S_{12}(\rho) = &\,\mathrm{i}G^*\,\mathrm{sgn}\Omega\sqrt{\frac{2\pi\hbar r_0}{uF}}\\
&\times\frac{\exp\{\mathrm{i}[\delta_1(\rho)+\alpha_1]\} + \exp\{\mathrm{i}[\delta_2(\rho)+\alpha_2]\}}{(r_0^2 - \rho^2)^{1/4}},
\end{aligned} \tag{29}$$

where the quantity

$$F = \Big|\frac{\mathrm{d}[U_{11}(r) - U_{22}(r)]}{\mathrm{d}r}\Big|_{r=r_0} \tag{30}$$

characterises the difference between the slopes of the compound-system terms at the point of intersection; functions $\delta_{1,2}(\rho)$ are determined by the expression [upper and lower signs refer to the $\delta_1(\rho)$ and $\delta_2(\rho)$, respectively]

$$\begin{aligned}
\delta_{1,2}(\rho) = &-\int_{\mp\sqrt{r_0^2-\rho^2}\,\mathrm{sng}\Omega}^{\infty}\frac{U_{11}(r)}{\hbar u}\mathrm{d}z\\
&-\int_{\pm\sqrt{r_0^2-\rho^2}\,\mathrm{sng}\Omega}^{\infty}\frac{U_{22}(r)}{\hbar u}\mathrm{d}z \mp \frac{|\Omega|}{u}\sqrt{r_0^2-\rho^2};
\end{aligned} \tag{31}$$

$\alpha_{1,2} = \pm\pi/4$ at $\partial^2 g(z_{1,2})/\partial z^2 \gtrless 0$. Hereafter, in calculations in view of conditions (11), (19), we set $u_1 = u$ and $\Omega_{\mathrm{R}} = |\Omega|$.

Consider now formula (16) for the scattering amplitude $f_{12}(\boldsymbol{u}_1|\boldsymbol{u})$. In the same coordinate system where equations (20) are written, it takes the form (we assume that the vector $\hat{\boldsymbol{u}}_1$ lies in the xz plane and $u_1 = u$):

$$\begin{aligned}
f_{12}(\boldsymbol{u}_1|\boldsymbol{u}) = &-\mathrm{i}\frac{\mu u}{2\pi\hbar}\int_0^{\infty}\rho S_{12}(\rho)\mathrm{d}\rho\\
&\times\int_0^{2\pi}\exp(-\mathrm{i}q\rho\cos\varphi)\mathrm{d}\varphi, \quad q = \frac{\mu u\sin\theta}{\hbar},
\end{aligned} \tag{32}$$

where θ is the scattering angle ($\cos\theta = \hat{\boldsymbol{u}}_1\hat{\boldsymbol{u}}$). Using the integral representation for the zero-order Bessel functions of the first kind $J_0(x)$ (see, for example, [21]), we find that in (32) the integral over φ is equal to $2\pi J_0(q\rho)$. In the case of scattering at angles corresponding to the laws of classical mechanics (with $\theta \gg \theta_{\mathrm{d}}$, where $\theta_{\mathrm{d}} \sim \hbar/(\mu u\rho_W)$ is the angle of quantum mechanical diffraction), we can assume $q\rho \gg 1$. This condition makes it possible to use the asymptotic expansion [21]

$$J_0(q\rho) \approx \frac{1}{\sqrt{2\pi q\rho}}\{\exp[\mathrm{i}(q\rho - \pi/4)] + \exp[-\mathrm{i}(q\rho - \pi/4)]\}. \tag{33}$$

In view of (29) and (33), formula (32) takes the form

$$f_{12}(\boldsymbol{u}_1|\boldsymbol{u}) = G^* \mathrm{sng}\Omega \sqrt{\frac{\mu r_0}{F\sin\theta}}[J_1^{(+)} + J_1^{(-)} + J_2^{(+)} + J_2^{(-)}],$$

$$J_k^{(\pm)} = \int_0^\infty \frac{\sqrt{\rho}\exp\left[\mathrm{i}\varphi_k^{(\pm)}(\rho)\right]}{(r_0^2-\rho^2)^{1/4}}\mathrm{d}\rho, \tag{34}$$

$$\varphi_k^{(\pm)}(\rho) = \delta_k(\rho) + \alpha_k \pm (q\rho - \pi/4), \quad k = 1,2.$$

Calculating the integral $J_k^{(\pm)}$ in expression (34) by the method of stationary phase [expansion of phase $\varphi_k^{(\pm)}(\rho)$ to the quadratic term], we obtain

$$J_k^{(\pm)} = \sqrt{2\pi\rho_k^{(\pm)}\left|\frac{\mathrm{d}^2\delta_k(\rho_k^{(\pm)})}{\mathrm{d}\rho^2}\right|^{-1}}\frac{\exp\{\mathrm{i}[\varphi_k^{(\pm)}(\rho_k^{(\pm)}) + \beta_k]\}}{\left[r_0^2 - (\rho_k^{(\pm)})^2\right]^{1/4}}, \tag{35}$$

where $\beta_k = \pm\pi/4$ at $\mathrm{d}^2\delta_k(\rho_k^{(\pm)})/\mathrm{d}\rho^2 \gtrless 0$, and points $\rho_k^{(\pm)}$ of the stationary phase are found from the equation

$$\frac{\mathrm{d}\varphi_k^{(\pm)}(\rho_k^{(\pm)})}{\mathrm{d}\rho} = \frac{\mathrm{d}\delta_k(\rho_k^{(\pm)})}{\mathrm{d}\rho} \pm q = 0. \tag{36}$$

To calculate the collision frequency ν_{21} from (7), this expression should include the scattering amplitude (34) with the quantities $J_k^{(\pm)}$ from (35). At the same time, because of the phase difference of the quantities $J_k^{(\pm)}$ in the integrand for ν_{21}, we can neglect oscillating cross-terms appearing in the square of modulus of the sum of the quantities $J_k^{(\pm)}$. With this in mind, for the collision frequency ν_{21} we obtain the expression:

$$\nu_{21} = \frac{2|G|^2\mu r_0}{\sqrt{\pi}F}\frac{N_\mathrm{b}}{\bar{u}^3}\int_0^\infty u^3\exp\left(-\frac{u^2}{\bar{u}^2}\right)\mathrm{d}u$$

$$\times\int\frac{B_1^{(+)} + B_1^{(-)} + B_2^{(+)} + B_2^{(-)}}{\sin\theta}\mathrm{d}\hat{\boldsymbol{u}}\,\mathrm{d}\hat{\boldsymbol{u}}_1, \tag{37}$$

where

$$B_k^{(\pm)} = \rho_k^{(\pm)}\left|\frac{\mathrm{d}^2\delta_k(\rho_k^{(\pm)})}{\mathrm{d}\rho^2}\right|\sqrt{r_0^2 - (\rho_k^{(\pm)})^2}\Bigg]^{-1}, \quad k = 1,2. \tag{38}$$

Equation (37) allows a simplification and for the further calculations it is convenient to represent it in the form

$$\nu_{21} = QK_\mathrm{oc}, \tag{39}$$

where

$$K_\mathrm{oc} = \frac{8\pi^2|G|^2\hbar r_0^2 N_\mathrm{b}}{F} \tag{40}$$

has the dimension of the collision frequency, and Q is a dimensionless quantity defined by the expression

$$Q = \frac{2\mu}{\sqrt{\pi}\hbar r_0\bar{u}^3}\int_0^\infty u^3\exp\left(-\frac{u^2}{\bar{u}^2}\right)\mathrm{d}u$$

$$\times\int_0^\pi[B_1^{(+)} + B_1^{(-)} + B_2^{(+)} + B_2^{(-)}]\mathrm{d}\theta. \tag{41}$$

The value of K_oc was introduced in [16] (we preserve the notation used in [16]) and is defined as 'the number of optical collisional transitions per unit volume and time,' calculated in the quasi-classical approximation. In fact, it is analogous to the collision frequency ν_{21}, calculated in the quasi-classical approximation. Thus, the dimensionless parameter Q characterises the degree of coincidence of quantum mechanical (ν_{21}) and quasi-classical (K_oc) calculations of the frequency of optical collisions (calculations coincide at $Q = 1$).

For further calculations, it is necessary to set the specific form of matrix elements $U_{ii}(r)$. Below, we consider the case of the power potential of interaction of the colliding particles.

4. Power potential of interaction

In the case of a power potential of interaction, the matrix elements $U_{ii}(r)$ have the form

$$U_{ii}(r) = \frac{c_i}{r^l}, \quad i = 1,2. \tag{42}$$

We believe that for the atoms in the ground ($i = 1$) and excited ($i = 2$) states, the exponent l is the same, and the coupling constants c_1 and c_2 are different. For definiteness, we assume in calculations below that l is an even number, and $c_2 > c_1$.

Calculation of the dimensionless quantity Q by formula (41) with account for (42) leads to the expression:

$$Q = \frac{2\varepsilon_0}{\sqrt{\pi}la}[Q_1^{(+)} + Q_1^{(-)} + Q_2^{(+)} + Q_2^{(-)}], \tag{43}$$

$$Q_k^{(\pm)} = \int_0^\infty x^4\exp(-x^2)\mathrm{d}x\int_0^{\pi/2} g_k^{(\pm)}\mathrm{d}\theta,$$

$$g_k^{(\pm)} = 2(x_k^{(\pm)})^2\Big|(-1)^k\left[1 + (x_k^{(\pm)})^2\right]x_k^{(\pm)}$$

$$\pm\frac{\varepsilon_0 x^2\sin\theta}{a}\sqrt{1-(x_k^{(\pm)})^2}\Big|^{-1}, \quad \varepsilon_0 = \mu\bar{u}^2\left(\frac{c_1+c_2}{r_0^l}\right)^{-1},$$

$$a = \frac{c_2 - c_1}{c_1 + c_2}, \quad x = \frac{u}{\bar{u}}, \quad x_k^{(\pm)} = \frac{\rho_k^{(\pm)}}{r_0}, \quad k = 1,2.$$

Here, the dimensionless points of stationary phase $x_k^{(\pm)}$ are found from equation (36), which, for the power potential of interaction (42), takes the form

$$\frac{b(l)}{(x_k^{(\pm)})^l}\left[\frac{\pi}{2} \pm a\arctan\sqrt{\frac{1}{(x_k^{(\pm)})^2} - 1}\right] \pm a\sqrt{1-(x_k^{(\pm)})^2}$$

$$\times\sum_{m=1}^{l/2}\frac{b_m}{(x_k^{(\pm)})^{2m-1}} \pm \varepsilon_0 x^2\sin\theta = 0, \tag{44}$$

$$b(l) = \frac{l}{\sqrt{\pi}}\frac{\Gamma(\frac{1}{2}(l+1))}{\Gamma(\frac{1}{2}(l+2))},$$

$$b_m = \begin{cases} 1, & m = 1, \\ \dfrac{(l-1)(l-2)\ldots(l+3-2m)}{(l-2)(l-4)\ldots(l+2-2m)}, & m \geqslant 2, \end{cases}$$

where $\Gamma(x)$ is the gamma function. In this equation, signs '+' and '–' before the parameter a correspond to points $x_1^{(\pm)}$ and $x_2^{(\pm)}$, the sign '±' before the parameter ε_0 corresponds to the sign '±' in $x_1^{(\pm)}$ [$+a$, $\pm\varepsilon_0$ correspond to point $x_2^{(\pm)}$ and $-a$, $\pm\varepsilon_0$

– to point $x_2^{(\pm)}$]. It follows from the analysis of (44) that when $c_2 > c_1 > 0$, there are only two points of stationary phase – $x_1^{(-)}$ and $x_2^{(-)}$. In this case, formula (43) has only two integrals – $Q_1^{(-)}$ and $Q_2^{(-)}$, because the integrals $Q_1^{(+)}$ and $Q_2^{(+)}$ are absent.

The integral $Q_2^{(-)}$, when calculated by formula (43), diverges because the denominator of $g_2^{(-)}$ vanishes for some values of the scattering angle θ and the dimensionless velocity x. This feature is due the fact that in (35) for $J_2^{(-)}$ at these points, the value of $\mathrm{d}^2\delta_2(\rho_2^{(-)})/\mathrm{d}\rho^2$ vanishes. This means that the integral $J_2^{(-)}$) (34) at these points should be calculated using the equation that is different from (35). Namely, in calculating the integral $J_2^{(-)}$ by the method of stationary phase, the phase itself in the vicinity of a stationary point should be expanded in a Taylor series up to cubic term [as opposed to the quadratic term when formula (35) is derived). By calculating the integral $J_2^{(-)}$ in (34) by the method of stationary phase, expanding phase $\varphi_2^{(-)}(\rho)$ up to cubic term (the quadratic term in this expansion is neglected because of its smallness near the critical points), we obtain

$$J_2^{(-)} = \frac{(4/3)^{1/6}\Gamma(1/3)}{\left|\mathrm{d}^3\delta_2(\rho_2^{(-)})/\mathrm{d}\rho^3\right|^{1/3}} \frac{\sqrt{\rho_2^{(-)}}\exp[\mathrm{i}\varphi_2^{(-)}(\rho_2^{(-)})]}{\left[r_0^2 - (\rho_2^{(-)})^2\right]^{1/4}}, \qquad (45)$$

where the point $\rho_2^{(-)}$ of the stationary phase is still given by (36). Substitution of (35) by (45) means that at critical points θ, x, the function $g_2^{(-)}$ (43) should be replaced by the function $g_{2N}^{(-)}$, determined from the expression

$$g_{2N}^{(-)} = \frac{1}{\pi}\left(\frac{4}{3}\right)^{1/3}\Gamma^2\left(\frac{1}{3}\right)\left(\frac{lak_0}{\varepsilon_0 x}\right)^{1/3} \frac{(x_2^{(-)})^{5/3}\sqrt{1-(x_2^{(-)})^2}}{\left|H_2^{(-)}\right|^{2/3}}, \qquad (46)$$

$$k_0 = \frac{\mu\bar{u}r_0}{\hbar}, \quad H_2^{(-)} = 2(l+2)(x_2^{(-)})^6 - (2l+5)(x_2^{(-)})^4 + (l+3)(x_2^{(-)})^2 - l + \frac{(l+1)\varepsilon_0 x^2 \sin\theta}{a x_2^{(-)}}\left[1-(x_2^{(-)})^2\right]^{3/2}.$$

In the numerical calculation of the integral $Q_2^{(-)}$, we replace the function $g_2^{(-)}$ by the function $g_{2N}^{(-)}$only if the condition $g_2^{(-)} > g_{2N}^{(-)}$ is met.

Figure 2 shows the results of numerical calculations of $Q = v_{21}/K_{\mathrm{oc}}$ by (43) (44), (46), depending on the ratio of the coupling constants of interaction c_1/c_2 at different l for the power potential of interaction and at different ε_0, which is equal to the ratio of thermal energy of the colliding particles to the characteristic value of the interaction potential. Numerical analysis shows that the ratio v_{21}/K_{oc} is insensitive to the value of the parameter k_0, and, therefore, the calculations were performed for only one value $k_0 = 45$, characteristic of, for example, the Na + He system at $T = 580$ K and $r_0 = 5 \times 10^{-8}$ cm. The values of ε_0 were chosen big enough in order to satisfy the condition of applicability of the eikonal approximation $|U_{11}|, |U_{22}| \ll \mu u^2/2$ at velocities that are much lower than the thermal velocity [this condition is necessary for the correctness of the integrand in formula (43) for Q at $u \ll \bar{u}$]. One can see from Fig. 2 that the ratio v_{21}/K_{oc} is close to unity and increases slowly with increasing ratio c_1/c_2. For power potentials with $l = 6$, 12 and 18, the difference of the ratio v_{21}/K_{oc} from unity decreases with increasing parameter ε_0 and at $\varepsilon_0 = 2000$ is about 10%.

Thus, the quantum-mechanical (v_{21}) and quasi-classical (K_{oc}) calculations of the optical collision frequency give similar results: the ratio v_{21}/K_{oc} is close to unity when the condition of applicability of the eikonal approximation is met (for sufficiently large parameters of ε_0).

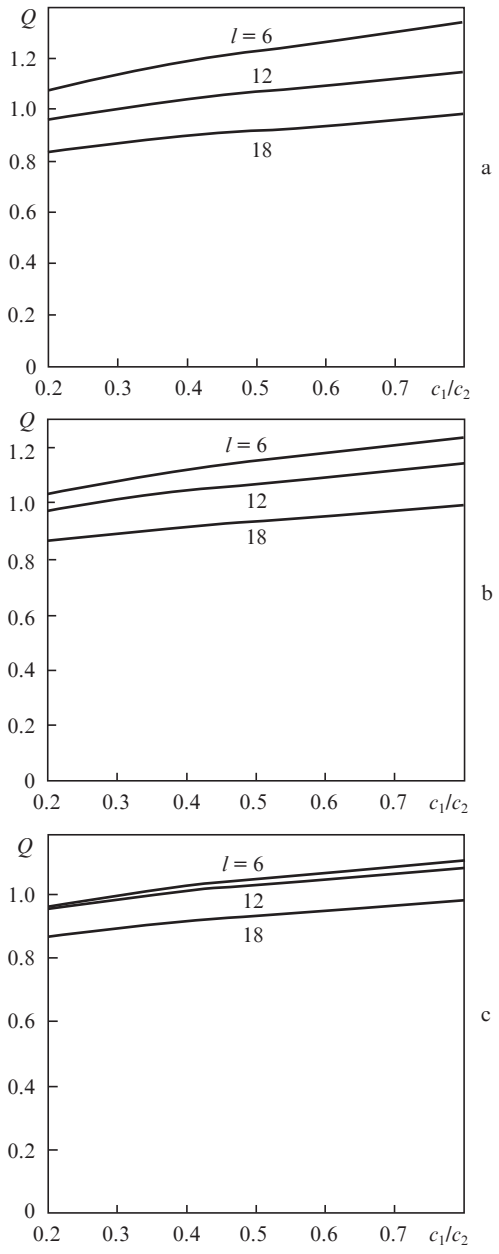

Figure 2. Dependence of $Q = v_{21}/K_{\mathrm{oc}}$ on the ratio of coupling constants c_1/c_2 at different l for the power potential of interaction and at $k_0 = 45$, $\varepsilon_0 = 500$ (a), 1000 (b) and 2000 (c).

5. Results and conclusions

Thus, we have performed the quantum-mechanical calculation of the collision frequency v_{21}, which is part of the density-matrix kinetic equation describing nonlinear effects in the wings of spectral lines. The collision frequency depends in a complex manner on the interaction potential of the colliding particles and on the radiation parameters (intensity and frequency detuning). Numerical analysis has shown that the quantum-mechanical calculation of the collision frequency in the eikonal approximation gives a result, similar to that which is already known from the quasi-classical theory of spectral

line wing [16]. Namely, the collision frequency ν_{21} is close to K_{oc} (introduced in [16]) and defined as 'the number of optical collisional transitions per unit volume and time' (Fig. 2c).

Our analysis suggests that under these conditions, for the collision frequency ν_{21} in the kinetic equations for the density matrix, obtained in [13] and describing nonlinear effects in the wings of spectral lines, we can set with a small error

$$\nu_{21} = K_{oc}. \tag{47}$$

This relationship allows us to write the collision frequency ν_{21} in the same form in which the frequency K_{oc} is represented in papers [14–16]:

$$\nu_{21} = \frac{2|G|^2}{\Omega^2}\Gamma_{oc}(\Omega). \tag{48}$$

The value of $\Gamma_{oc}(\Omega)$ enters into the modified Lorentz equation [15, 16], which describes the entire contour of the spectral lines, including the far wings. In general, $\Gamma_{oc}(\Omega)$ depends on the frequency detuning Ω and the radiation intensity (on the parameter $|G|$). In the case of a not-too-strong field (11), the dependence $\Gamma_{oc}(\Omega)$ on the radiation intensity disappears, and we deal only with the dependence on the detuning frequency [16]. For a small detuning of the radiation ($|\Omega| \ll \Omega_W$, where Ω_W is the Weisskopf frequency [16]), the value of $\Gamma_{oc}(\Omega)$ is equal to impact half-width of the absorption line Γ [16], and for a large detuning ($|\Omega| \gg \Omega_W$), it can be both much higher or much smaller than Γ [16]. The collision frequency ν_{21} decreases with increasing detuning modulus $|\Omega|$ [16].

Under stationary conditions, from (15) with account for (48) and normalisation condition (13) we obtain the known expression [10, 22] for the population difference of the excited ($|2\rangle$) and ground ($|1\rangle$) levels:

$$\rho_{22} - \rho_{11} = N\frac{\varkappa\{1 - \exp[-\hbar|\Omega|/(k_B T)]\}\mathrm{sgn}\Omega - 1}{1 + \varkappa\{1 + \exp[-\hbar|\Omega|/(k_B T)]\}}, \tag{49}$$

$$\varkappa = \frac{2|G|^2\Gamma_{oc}(\Omega)}{A\Omega^2}.$$

The value of $\varkappa$ has the meaning of the saturation parameter for the transition $|2\rangle - |1\rangle$ (at $|\Omega| \gg \Gamma$). It follows from (49) that at a sufficiently high intensity of the exciting radiation ($\varkappa > 1$) and at a positive detuning of the radiation ($\Omega > 0$) there is a population inversion at the transition $||2\rangle - |1\rangle$. As mentioned in Introduction, this effect is experimentally recorded in the form of generation of coherent radiation at the resonance transition of sodium atoms when pump radiation affects the 'blue' wing of the absorption line [6, 8–10].

Acknowledgements. This work was supported by the program of the Physical Sciences Division of the RAS 'Fundamental Optical Spectroscopy and its Applications' (Project No. 9.5) and the grant of the President of the Russian Federation for State Support of Leading Scientific Schools (Grant No. NSh-4339.2010.2).

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