THE IMPACT AND DOPPLER BROADENING OF ATOMIC LINES

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The interrelation between the Doppler and impact broadening, which results from the change of the velocity of the radiating atom in an effect of collisions, is investigated. In particular, we analyze the effect of the collisional narrowing of the line and the applicability of the Voigt profiles to the description of the joined Doppler and collision broadening of the line. On the basis of the proposed general theory we have developed some approximate methods, which enable us to perform the numerical computations. Our results differ from the previous impact theory calculations even for those pressures, for which the Doppler effect is negligible. In particular, we have found that the asymmetry of the line contour is rather a rule than an exception.

1. Introduction

The aim of the present paper is to complete the analysis of the foreign gas broadening of the atomic lines, which has been commenced in the paper [1] and continued in the paper [2], to be referred here as the papers I and II, respectively. Generally, the present status of the theory and experiment enables us to secure a fairly good agreement of the results of theoretical computations with experimental data on the foreign gas broadening of the atomic lines. With the aid of computers, the accuracy of the theoretical calculations has been remarkably improved due to the use of some more realistic potentials (see Hindmarsh and others [3], also I and II) and by appropriate averaging, performed in the paper II, of the line shape parameters over the velocity distribution of the perturbers. Moreover, we have extended, in the second paper, the binary collision approximation so that it describes some nonlinearities in the dependence of the line shape parameters on pressure, which have been found experimentally by Ch'en and his coworkers [4] for the intermediate pressures ranging from about one to somewhere around ten atmospheres. What remains to be done, within the binary collision approximation, is to take into account the motion of the radiating atom, which is of vital importance for low pressures, where the Doppler broadening becomes comparable with the collisional contribution to the half-width of the line. Formerly, it has been generally accepted that in this case the shape of the line is

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given by the Voigt profile, while in the recent years some of the theorists, particularly Wittke and Dicke [5], Podgoreckii and Stepanov [6], Galatry [7], Rautian and Sobelman [8] and Chapell [9], have suggested a strong interrelation between the Doppler and collision broadening. The general outline of the first three of the quoted papers is based on the simple observation of Dicke [5] that the mean velocity of the radiating atom diminishes in consequence of its collisions with the walls of the gas container and with other atoms. Consequently, we may expect the collisional narrowing of spectral lines, provided that the collisions do not contribute remarkably to their half-widths. As we shall see, however, the full description of the real processes involved here is more complex. What is overlooked in this, rather oversimplified, picture is that the velocity is changed appreciably in effect of the strong collisions, *i.e.*, those collisions, which disturb drastically the radiation process. Moreover, the contribution of the Doppler width to the total line width diminishes with the increasing pressure even when we accept the Voigt profiles, *i.e.*, when we consider the Doppler and the collision effect to be statistically independent. The semiquantitative description of these complex problems has been developed in the paper of Rautian and Sobelman [8], while in the present paper we propose some more definite calculations. Our approach is in some aspects close to that of Ross [10] in spite of formal dissimilarities. However, our final results do not agree with those of this paper as far as the broadening by the heavy foreign gas is concerned.

We begin our analysis in Section 2 by a short recapitulation of the Liouville space concept, which plays a very important role in this paper. With this tool we have derived the general expression for the line shape function in the impact approximation, which holds in the low pressures region. In Section 3 we will show how to reckon the line shape in the eikonal approximation. Our numerical results reveal a fairly good agreement with the experimental data of Ch'en and others [4]. Moreover, we have found a strong asymmetry of the line contour, for the heavy foreign gas broadening, even in the range of low pressures. However, the experimental evidence is not yet, as far as we know, sufficiently definite at this point. The possibility of this asymmetry has been already suggested by Rautian and Sobelman [8].

2. *Translational and collisional contributions to the line shape*

The model of the system, *i. e.*, the radiating atom and the perturbing gas, which has been adopted and defined in the previous papers will be sustained here with the exception that we will take into account the motion of the radiating atom. Thus the Fourier transform of the intensity distribution function is given by the following formula

$$U_{if} = \mathrm{Tr}\,\{\varrho e^{-\kappa r_0} e^{iH_f t} e^{i\kappa r_0} e^{-iH_i t}\}, \tag{1}$$

where $\boldsymbol{\kappa}$ is the wave vector of light, while $\boldsymbol{r}_0$ is the position vector of the radiating atom. The Hamiltonians H_i and H_f consist of the kinetic energy H_0 of the perturbers and the radiating atom and the interaction potentials V_i or V_f of the perturbers with the radiating atom in its initial or final state, respectively.

The elucidation of our method requires the knowledge of the Liouville space formalism. As it has been stressed recently by one of us (J. F. [11]), this description is unambiguous only after the introduction of the metrics. Specifically, some operators, say A and B, acting in the Hilbert space of states of a given physical system, call it $\mathfrak{H}$-space, are in turn elements of another Hilbert space, call it Liouville space $\mathfrak{L}$, with the scalar product defined by

$$(A, B) = \mathrm{Tr}\,\{A^+B\}, \tag{2}$$

where the cross stands for the Hermitean conjugate and the trace is over the states of the $\mathfrak{H}$-space. It is clear that the scalar product (2) is well defined provided that traces Tr (A^+A) and Tr (B^+B) exist, *i. e.*, the elements of the $\mathfrak{L}$-space have to be Hilbert-Schmidt operators with respect to the $\mathfrak{H}$-space. In the following we shall distinguish the subspaces of the states of the radiating subsystem (the radiating atom) and the perturbing subsystem (the perturbers) by indices s and p, respectively. Thus, we will denote by $\mathfrak{H}^{(s)}$ the Hilbert space of states of the radiating atom and by $\mathfrak{L}^{(s)}$ the corresponding Liouville space, while the Hilbert space of states of the perturbers will be denoted by $\mathfrak{H}^{(p)}$.

After these preliminary explanations we give the function $\overline{U}_{if}(t)$ the form of the mean value of an operator $\hat{U}_{if}(t)$ in a state $\Phi_{\kappa}^{(s)}$, namely

$$\overline{U}_{if}(t) = (\Phi_{\kappa}^{(s)}, \hat{U}_{if}(t)\Phi_{\kappa}^{(s)}) \tag{3}$$

with the $\Phi_{\kappa}^{(s)}$-state defined by

$$\Phi_{\kappa}^{(s)} = \exp\,[i\kappa r_0]\,[Q(h_0^{(s)})]^{-\frac{1}{2}}\exp\,[-\tfrac{1}{2}\beta h_0^{(s)}] \tag{4}$$

provided that the system is in thermal equilibrium at the temperature $T = 1/k\beta$ so that the density matrix ϱ in (1) is given by the familiar canonical distribution of the states of the Hamiltonian H_i. The statistical sum $Q(h_0^{(s)})$ corresponds to the kinetic energy operator $h_0^{(s)}$ of the radiating atom. In general, we will denote by $Q(H)$ the statistical sum given in the following way:

$$Q(H) = \mathrm{Tr}\,\{\exp\,[-\beta H]\}, \tag{5}$$

where the trace is taken over the states of the corresponding Hamiltonian H.

As it follows from (1), the $\mathfrak{L}$ operator $\hat{U}_{if}(t)$ is defined in action on an operator A_0 in the following way

$$\begin{aligned} U_{if}(t)A_0 = Q(H_0)/Q(H_i)\,\mathrm{Tr}_p\Big\{&\Pi\Phi^{(p)}U_f^+(t, 0)\times \\ &\times \exp\,[iH_0t]A_0\exp\,[-iH_0t]\Pi\Phi^{(p)}\times \\ &\times U_i\left(t-\frac{i\beta}{2}, \frac{i\beta}{2}\right)\Big\}, \end{aligned} \tag{6}$$

where we have used the time development operators U_i and U_f, which are given by the common expression

$$U_{if}(z, z_0) = \mathrm{P}\exp\,[-i\int_{z_0}^{z} V_{i(f)}(z)dz], \tag{7}$$

with the operator P ordering the product of all the z-dependent operators along the path, in the complex plane, connecting z_0 and z. The trace in (5) is taken over the states of $\mathfrak{H}^{(p)}$, as indicated by index p, while Π means that the product has to be taken of all one-perturber operators $\Phi^{(p)}$, which are defined as follows

$$\Phi^{(p)} = [Q(h_0^{(p)})]^{-\frac{1}{2}} \exp\left\{-\frac{\beta}{2} h_0^{(p)}\right\}, \tag{8}$$

where $h_0^{(p)}$ denotes the kinetic energy of one of the perturbers.

The translational contribution to the line shape is essential only for dilute gases, since for the normal and high pressures the collisional contribution dominates very distinctly. Thus we may evaluate the operator $\hat{U}_{if}(t)$ in the impact approximation, which leads to the following differential equation

$$i\frac{\partial}{\partial t}\hat{U}_{if}(t) = U_{if}(t)\,(nv_{if}(\infty)+h_0^{(s)}), \tag{9}$$

where the $\mathfrak{L}^{(s)}$ operator $\hat{v}_{if}(\infty)$ is given as follows

$$\hat{V}_{if}(\infty)A_0 = \Omega \lim_{t\to\infty} Q(h_0^{(p)})/Q(h_i)\,\mathrm{Tr}_p\,\{\Phi^{(p)}e^{-ih_0t}e^{ih_ft}\times$$
$$\times[A_0 e^{\frac{\beta}{2}h_0}\Phi^{(p)}v_i - v_f A_0 e^{\frac{\beta}{2}h_0}\Phi^{(p)}]\times$$
$$\times e^{-\beta h_i}e^{-ih_it}e^{ih_0t}\}, \tag{10}$$

while the density of the perturbers, denoted by n, is defined as the ratio of the total number of the perturbers to the volume Ω. The operator $\hat{h}_0^{(s)}$ is the $\mathfrak{L}^{(s)}$ kinetic energy operator, *i. e.*,

$$\hat{h}_0^{(s)}A_0 = A_0h_0^{(s)} - h_0^{(s)}A_0. \tag{11}$$

The introduction of the operator $\hat{v}_{if}(\infty)$ reduces the problem to a binary collision calculation, since the expression (10) contains only quantities related to the radiating atom and one of the perturbing atoms. Particularly, the trace in taken over the states of the one-perturber space, while the operators h_i and h_f are essentially the Hamiltonians of the system radiating atom-one perturber, *i. e.*,

$$h_{i(f)} = h_0 + v_{i(f)}, \tag{12}$$

where v_i or v_f are the potentials of the interaction of a perturber with the radiating atom in its initial or final states, respectively, and h_0 is the kinetic energy of their relative motion.

Eventually, we arrive at the relatively simple form of the operator $\hat{U}_{if}(t)$, namely

$$\hat{U}_{if}(t) = \exp\{-[n\hat{v}_{if}(\infty)+\hat{h}_0^{(s)}]t\}, \tag{13}$$

which is distinctive for the impact approximation.

The next step of our analysis consists in understanding that the conservation of the total momentum of the gas results in the conservation of the $\mathfrak{L}$ momentum operator $\hat{k}_s$, which is related as follows

$$\hat{k}_s A_0 = k_s A_0 - A_0 k_s \tag{14}$$

to the momentum operator k_s of the radiating atom. In fact, on the right-hand side of (10) we average some expressions commuting with the total momentum over the momentum distribution of the perturbers. Therefore, the resulting $\mathfrak{L}^{(s)}$ operator commutes with $\hat{k}$. Since this last commutes also with the $\mathfrak{L}^{(s)}$ kinetic energy operator $\hat{h}_0^{(s)}$, we may conclude that it commutes with the operator $\hat{U}_{if}(t)$, which gives the time evolution of our system (the radiating atom) under the influence of the thermal bath of the perturbers. Moreover, the $\mathfrak{L}^{(s)}$ state $\Phi_{\kappa}^{(s)}$, defined by (4), is an eigenstate of $\hat{k}$ with the eigenvalue $\boldsymbol{\kappa}$ equal to the momentum of the absorbed photon. Thus we are really operating within the subspace of $\mathfrak{L}^{(s)}$, call it $\mathfrak{L}_{\kappa}^{(s)}$, of all those eigenstates of $\hat{k}$, which pertain to the eigenvalue κ. In the subspace $\mathfrak{L}_{\kappa}^{(s)}$ we will introduce a complete set of states, which we denote by $e_{k_0\kappa}$ and define by the following equations

$$k_s e_{k_0\kappa} = (k_0 + \kappa) e_{k_0\kappa}$$

$$e_{k_0\kappa} k_s = k_0 e_{k_0\kappa}. \tag{15}$$

These states will be normalized to the Dirac δ-function, that is

$$(e_{k\kappa}, e_{k'\kappa}) = \delta_3(k-k'). \tag{16}$$

We will consider all the $\mathfrak{L}$ operators introduced above to be some operators in the subspace $\mathfrak{L}_{\kappa}^{(s)}$. Particularly, the operator $\hat{v}_{if}(\infty)$ is given in $\mathfrak{L}_{\kappa}^{(s)}$, in the limit of the infinite volume, as follows

$$\begin{aligned} \hat{v}_{if}(\infty) e_{k_0\kappa} = (2\pi)^3 \int d_3 k_0' \int d_3 k_1' \times \\ \times \varrho(\varepsilon_{k'}) \exp\{\tfrac{1}{2}\beta[\varepsilon(k'+\lambda\kappa')+\varepsilon(k)-\varepsilon^{(p)}(k_1)-\varepsilon^{(p)}(k_1')]\} \times \\ \times [(\psi^{+}_{k'+\lambda\kappa}, \chi_{k+\lambda\kappa})(\chi_k, v_i \varphi^{+}_{k'}) - \\ -(\psi_{k'+\lambda\kappa}, v_f \chi_{k+\lambda\kappa})(\chi_k, \varphi^{+}_{k'})] e_{k'_0\kappa} \end{aligned} \tag{17}$$

with $\lambda = m_p/m_s + m_p$ and k_1 given by the total momentum conservation

$$k_1 = k_0' + k_1' - k_0. \tag{17a}$$

In these relations we have denoted by $\varepsilon(k)$ and k the kinetic energy and the momentum of the relative motion, while $\varepsilon^{(p)}(k_1)$ and k_1 are the corresponding quantities for the perturber alone and $\varrho(\varepsilon_k)$ is an eigenvalue of the density matrix $\varrho(h_i)$. As in the previous papers we have denoted by χ_k the plane wave, while the wave functions φ_k^{+} and $\psi_{k'}^{+}$ are the outgoing waves corresponding to the Hamiltonians h_i and h_f, respectively. Expression (17) may be, furthermore, simplified by neglecting the momentum $\boldsymbol{\kappa}$ of the photon as compared to the momentum transferred in the collision. Introducing the transition amplitudes $\mathcal{T}^{(i)}_{kk'}$ and $\mathcal{T}^{(f)}_{kk'}$ by relations

$$\mathcal{T}^{(i)}_{kk'} = (\chi_k, v_f \psi^+_{k'}) \tag{18a}$$

and

$$\mathcal{T}^{(f)}_{kk'} = (\chi_k, v_i \varphi^+_{k'}) \tag{18b}$$

we thus arrive at the following formula

$$\begin{aligned}
\bar{v}_{if}(\infty) e_{k_0\kappa} \approx (2\pi)^3 \int d_3 \boldsymbol{k}'_0 \int d_3 \boldsymbol{k}'_1 \varrho(\varepsilon_{k'}) \times \\
\times \exp \{\tfrac{1}{2}\beta[\varepsilon(\boldsymbol{k}') + \varepsilon(\boldsymbol{k}) - \varepsilon^{(p)}(\boldsymbol{k}_1) - \varepsilon^{(p)}(\boldsymbol{k}'_1)]\} \times \\
\times [\delta_3(\boldsymbol{k}_0 - \boldsymbol{k}'_0)(\mathcal{T}^{(i)}_{kk} - \mathcal{T}^{(f)}_{kk})^* - \\
-2\pi\delta(\varepsilon_k - \varepsilon_{k'})(\mathcal{T}^{(f)}_{kk'})^* \mathcal{T}^{(i)}_{kk'}] e_{k'_0\kappa}.
\end{aligned} \tag{19}$$

We have thus achieved the stage where standard methods of quantum damping theory may be used. To this end let us introduce the mean value $\bar{O}$ of an $\mathfrak{L}^{(s)}_\kappa$ operator $\hat{O}$ in the state $\Phi^{(s)}_\kappa$ in the usual way

$$\bar{O} = (\Phi^{(s)}_\kappa, \hat{O}\Phi^{(s)}_\kappa), \tag{20}$$

where the state $\Phi^{(s)}_\kappa$ is, as it results from (4), given as the superposition of the states $e_{k_0\kappa}$ in the following terms

$$\Phi^{(s)}_\kappa = [Q(h^{(s)}_0)]^{-\frac{1}{2}} \int d_3 \boldsymbol{k}_0 \exp\left\{-\frac{\beta}{2}\varepsilon^{(s)}(\boldsymbol{k}_0)\right\} e_{k_0\kappa}. \tag{21}$$

The line shape function $J_{if}(x)$ is now related to the mean value of the resolvent operator $\hat{R}_{if}(x)$ in the following way

$$J_{if}(x) = \frac{1}{\pi}\bar{R}_{if}(x), \tag{22}$$

whereas the resolvent operator itself is given by the formula

$$\hat{R}_{if}(x) = (x + n\hat{v}_{if}(\infty) + \hat{h}^{(s)}_0)^{-1}. \tag{23}$$

The formal solution of our problem will be easy to find after we introduce suitable projection operators, namely $\hat{P}_{||}$ defined by

$$\hat{P}_{||} A_0 = (\Phi^{(s)}_\kappa, A_0)\Phi^{(s)}_\kappa \tag{24}$$

and $\hat{P}_\perp$ given as the orthogonal supplement of the previous one

$$\hat{P}_\perp = \hat{1} - \hat{P}_{||}, \tag{25}$$

where $\hat{1}$ stands for the unit operator in $\mathfrak{L}^{(s)}_\kappa$.

The mean value of the resolvent operator is to be presented now (compare [11]) in the following terms

$$R_{if}(x) = (x+n\bar{v}_{if}(\infty)+\bar{h}_0^{(s)}+\mathfrak{M}_{if})^{-1} \tag{26}$$

with the function $\mathfrak{M}_{if}$ defined by the following set of relations

$$\mathfrak{M}_{if} = -\left(\Phi_{\kappa}^{(s)}, \hat{Y}_{if}\hat{P}_{\perp}\frac{1}{X_{if}+\hat{P}_{\perp}\hat{Y}_{if}\hat{P}_{\perp}}\hat{P}_{\perp}\hat{Y}_{if}\Phi_{\kappa}^{(s)}\right), \tag{27}$$

where the operator $\hat{Y}_{if}$ is given by

$$\hat{Y}_{if} = n\hat{v}_{if}(\infty)+\hat{h}_0^{(s)}-n\bar{v}_{if}(\infty)-\bar{h}_0^{(s)} \tag{28}$$

and X_{if} is a shorthand notation for the following function

$$X_{if} = x+n\bar{v}_{if}(\infty)+\bar{h}_0^{(s)}. \tag{29}$$

These relations, combined with the formula (19), form the basis of our method and the numerical upshots, which will be presented in the next section.

3. *Line shape calculations in the eikonal approximation*

In the previous papers, namely I and II, we have not taken into account the translational motion of the radiating atom, which results in the appearance of the terms $\bar{h}_0^{(s)}$ and $\mathfrak{M}_{if}$ in (26). The term $n\bar{v}_{if}$ represents the purely collisional effect and has been already calculated in II for the Lennard-Jones (12–6) potential. These calculations have been extended, in the present paper, for the Lennard-Jones (8–6) potential which is given by

$$V[R] = -\varepsilon_m\left[3\left(\frac{R_m}{R}\right)^8-4\left(\frac{R_m}{R}\right)^6\right]. \tag{30}$$

The complex line shift parameter $\bar{v}_{if}(\infty)$ is then related, as it has been shown in II, to the dimensionless functions $\bar{d}(\zeta)$ and $\bar{w}(\zeta)$ by

$$\bar{v}_{if}(\infty) = \pi n\bar{v}R_m^2(\bar{d}(\zeta)-i\bar{w}(\zeta)), \tag{31}$$

where $\bar{v}$ denotes the mean velocity of the relative motion and the parameter ζ is given by

$$\zeta = \varepsilon_m R_m/\bar{v}h. \tag{32}$$

The functions $\bar{d}(\zeta)$ and $\bar{w}(\zeta)$ play a leading role in the line shape calculations for the low pressure foreign gas broadening. Therefore, we have tabulated them in Table I for the L.-J. (8–6) potential, which seems to be more appropriate than other Lennard-Jones potentials as far as the description of the pressure broadening is concerned. These data have been also presented graphically on Fig. 1.

The major task now is the calculation of the function $\mathfrak{M}_{if}$. The simplest way seems to be the use of the following expansion

$$\mathfrak{M}_{if} = -\frac{\overline{\hat{Y}_{if}^2}}{X_{if}}+\frac{\overline{\hat{Y}_{if}^3}}{X_{if}^2}-\frac{\overline{\hat{Y}_{if}^2\hat{P}_{\perp}\hat{Y}_{if}^2}}{X_{if}^3}+\ldots. \tag{33}$$

TABLE I

Computed values of the functions $\overline{d(\zeta)}$ and $\overline{w(\zeta)}$ with the Lennard-Jones (8–6) potential

ζ	$\overline{d(\zeta)}$	$\overline{w(\zeta)}$	$\frac{\overline{d(\zeta)}}{\overline{w(\zeta)}}$	ζ	$\overline{d(\zeta)}$	$\overline{w(\zeta)}$	$\frac{\overline{d(\zeta)}}{\overline{w(\zeta)}}$
0.001	−0.015	0.225	−0.066	0.7	1.416	1.153	1.228
0.003	−0.040	0.245	−0.163	0.8	1.550	1.290	1.201
0.005	−0.053	0.265	−0.199	0.9	1.666	1.428	1.166
0.008	−0.065	0.285	−0.229	1.0	1.763	1.564	1.127
0.010	−0.071	0.297	−0.240	1.1	1.851	1.700	1.089
0.012	−0.074	0.310	−0.239	1.2	1.921	1.827	1.051
0.015	−0.071	0.325	−0.219	1.3	1.970	1.948	1.011
0.020	−0.056	0.347	−0.162	1.4	2.017	2.061	0.978
0.025	−0.040	0.365	−0.110	1.5	2.067	2.167	0.953
0.030	−0.026	0.382	−0.067	1.6	2.091	2.266	0.923
0.035	−0.012	0.396	−0.030	1.7	2.117	2.358	0.898
0.040	+0.001	0.410	+0.004	1.8	2.146	2.442	0.878
0.045	0.015	0.419	0.035	1.9	2.165	2.519	0.859
0.050	0.028	0.428	0.065	2.0	2.183	2.595	0.825
0.06	0.054	0.443	0.123	2.2	2.213	2.715	0.815
0.07	0.082	0.458	0.179	2.4	2.243	2.820	0.795
0.08	0.109	0.467	0.233	2.6	2.274	2.909	0.781
0.09	0.136	0.478	0.285	2.8	2.309	2.987	0.772
0.10	0.163	0.487	0.335	3.0	2.337	3.056	0.764
0.2	0.423	0.574	0.736	3.2	2.384	3.118	0.764
0.3	0.668	0.667	1.002	3.4	2.443	3.179	0.768
0.4	0.884	0.774	1.142	3.6	2.494	3.250	0.766
0.5	1.082	0.892	1.212	3.8	2.551	3.305	0.772
0.6	1.259	1.016	1.239	4.0	2.631	3.360	0.783

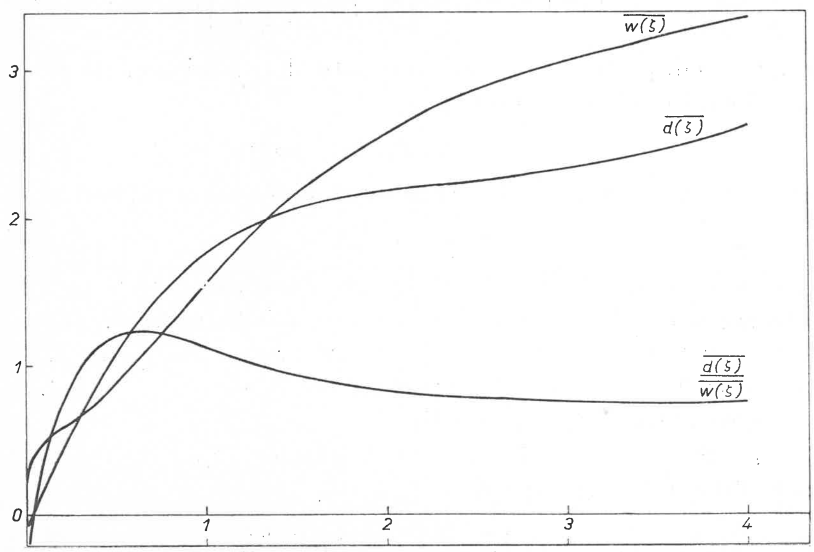

Fig. 1. Dependence of $\overline{d(\zeta)}$ and $\overline{w(\zeta)}$ and their ratio on ζ

If we retain only the first term of this expansion, we get for the mean value of the resolvent a relatively simple expression, namely

$$\bar{R}_{if}(x) = \tfrac{1}{2}[(X_{if} - \sqrt{\overline{\hat{Y}^2_{if}}})^{-1} + (X_{if} + \sqrt{\overline{\hat{Y}^2_{if}}})^{-1}], \tag{34}$$

where $\overline{\hat{Y}^2_{if}}$ is given as follows

$$\overline{\hat{Y}^2_{if}} = n^2[\overline{(\hat{v}_{if}(\infty))^2} - (\bar{v}_{if}(\infty))^2 + \overline{(\hat{h}_0^{(s)})^2} - (\bar{h}_0^{(s)})^2]. \tag{35}$$

As we shall see in the Appendix, the following formula holds

$$\overline{(v_{if}(\infty))^2} = [\bar{v}_{if}(\infty)]_\beta [\bar{v}_{if}(\infty)]_{\beta'}, \tag{36}$$

where the subscripts β and β' indicate that we shall use in the calculation of $\bar{v}_{if}(\infty)$ different temperatures, namely, the actual temperature of the gas for the first factor and $T' = \left(1 + 2\dfrac{m_p}{m_s}\right) T$ for the second one. Thus the first factor on the right-hand side of (36) shall be calculated directly from the formula (31), while for the second we shall take the functions $\bar{d}$ and $\bar{w}$ at the point $\zeta' = \sqrt{1 + 2\dfrac{m_p}{m_s}}\,\zeta$ instead of ζ. Since the mean square deviation of the operator $h_0^{(s)}$ is given by

$$\overline{(\hat{h}_0^{(s)})^2} - (\bar{h}_0^{(s)})^2 = \frac{\kappa^2}{\beta m_0} \tag{37}$$

provided that we assume the initial distribution of the velocity to be Maxwellian, we may conclude that the knowledge of the functions $\bar{d}$ and $\bar{w}$ suffices, in our approximation, to establish the line shape if the potential constants ε_m and R_m are fixed. More specifically, the line profile is givem by the following formula

$$J_{if}(x) = \frac{1}{2\pi} \times$$

$$\times \frac{-\operatorname{Im} n\bar{v}_{if}(\infty) + \operatorname{Im}\sqrt{\overline{\hat{Y}^2_{if}}}}{[x + \operatorname{Re} n\bar{v}_{if}(\infty) - \operatorname{Re}\sqrt{\overline{\hat{Y}^2_{if}}}]^2 + [-\operatorname{Im} n\bar{v}_{if}(\infty) + \operatorname{Im}\sqrt{\overline{\hat{Y}^2_{if}}}]^2} +$$

$$+ \frac{-\operatorname{Im} n\bar{v}_{if}(\infty) - \operatorname{Im}\sqrt{\overline{\hat{Y}^2_{if}}}}{[x + \operatorname{Re} n\bar{v}_{if}(\infty) + \operatorname{Re}\sqrt{\overline{\hat{Y}^2_{if}}}]^2 + [-\operatorname{Im} n\bar{v}_{if}(\infty) - \operatorname{Im}\sqrt{\overline{\hat{Y}^2_{if}}}]^2} \tag{38}$$

as the superposition of two Lorentzian profiles, provided that the corrections due to the translational motion are small as compared against the "pure" collisional half-width, *i. e.*

$$|\overline{\hat{Y}^2_{if}}| \ll |\operatorname{Im} n\bar{v}_{if}(\infty)|^2. \tag{39}$$

Thus our approximation certainly fails when the Doppler broadening becomes comparable with the collisional contribution. However, according to our estimates, we hope that for sufficiently big Doppler contribution the Voigt profile describes the line shape correctly. This situation is illustrated in two diagrams, on which we compare the Voigt profiles with those calculated by us. The first one, namely Fig. 2, gives the corresponding profiles with the Doppler width nearly equal to the collisional contribution. In this case the Voigt profile may be even better suited for the description of the actual line shape than

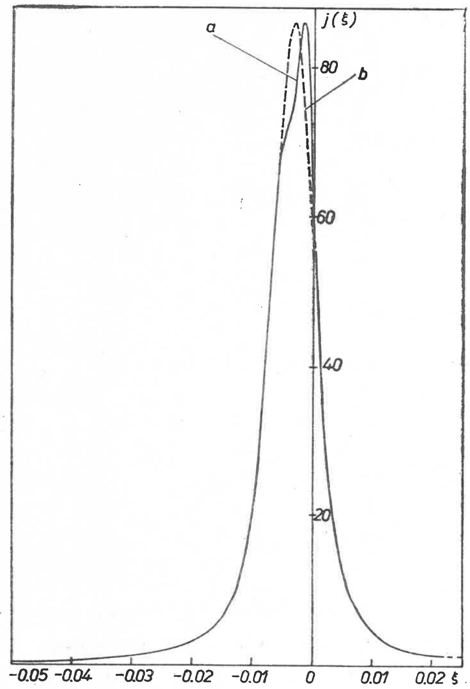

Fig. 2. Profile (*a*) resulting from formula (38) and the corresponding Voigt profile (*b*). Both computed for the $Cs(1)^2P_{1/2}$ line broadening by krypton at r. d. = 0.05 and T = 305°K

that calculated in our approximation. On the other hand, in Fig. 3 the collisional contribution is twice as large as that in the Fig. 2, so we expect that our profile is more appropriate than the Voigt one. These diagrams show that the transition from our to Voigt profiles with decreasing density is smooth except for the top of the line contour, where our formulas lead to a distinct asymmetry. This asymmetry is presumably excessive, due to the breaking down of our approximation, in the case shown in Fig. 2, but may reflect a real situation in the case of Fig. 3. In any case, the differences between those two profiles are not likely to be the object of an experimental check, since the actual lines corresponding to the contours shown on both figures are very narrow. In addition, let us point out that we may consider the profile resulting from (38) as an approximation of the Voigt profile, provided that we do not take into account the collisional, *i. e.* proportional to the perturbers density, contribution to the function $\overline{\hat{Y}_{if}^2}$. In Fig. 3 we have demonstrated that in this way we get a fairly good approximation of the Voigt profile. Therefore, we may conclude that we have every good reason to suppose that our method gives the right description of the line profile as long as the condition (39) is satisfied.

When it does not, which is primarily the case when the Doppler broadening becomes comparable, or exceeds, the collisional contribution, we expect that the Voigt profile is adequate and the transition from ours to the Voigt profile goes rather smoothly. Particularly, our results indicate that the dependence of the half-width on pressure is close to that

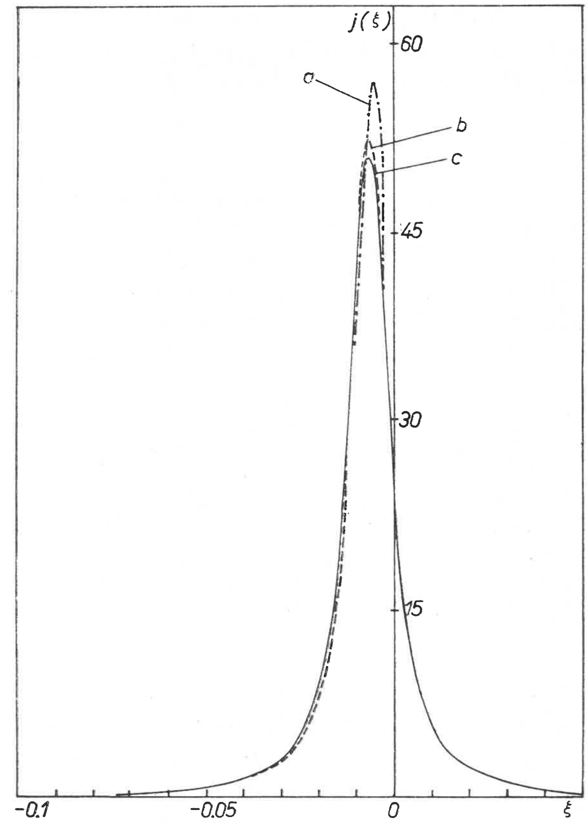

Fig. 3. Profile (*a*) resulting from (38), the corresponding Voight profile (*b*) and profile (*c*) following from (38) without translational effects in $\overline{Y}^2_{if}$ (approximation of the Voigt profile). All these profiles computed for the $Cs(1)^2P_{1/2}$ line broadening by krypton at r. d. = 0.1 and $T = 305°K$

following from the Voigt profile as given, *e. g.*, in the recent paper of Armstrong [12]. This dependence is rather weak at low pressures and becomes nearly linear for higher pressures as long as the impact theory holds. Similarly, the results of our test calculations do not indicate any appreciable deviation from the linearity in the dependence of the line shift on the density of the perturbers in the low pressure range, *i. e.* up to one atmosphere. However, we have found in some cases a strong asymmetry of the line profile.

Our test calculations have been adjusted to the experimental results of Ch'en and others [4] on cesium lines broadening by inert gases. In these calculations we have accepted the recently calculated by Mahan [13] potential constants C_6 of the long-range part of the potential. There is not much doubt left that the evaluation performed by Mahan is correct, for its results agree within a few percent with the earlier results of Dalgarno [14] as well as with those of ours [15]. The remaining relation for the two potential constants, ε_m and R_m, we have obtained by adjusting the value of ζ so that the quotient of the function $\bar{d}$ to $\bar{w}$ has approached, as closely as possible, the experimentally found ratio of the line shift to half-width. The values of the line shift and half-width, which we obtained, in turn, from the formula (38), are in fairly good agreement with the experimental data, as shown in Table II, except for the broadening by helium gas. In the case of the helium broadening of the cesium resonance $P_{1/2}$ line it was not even possible to obtain a reasonably good

TABLE II

Comparison of experimental values of line shift and half-width of the cesium resonance line broadening by inert gases at 1 r. d., with results of theoretical calculations

Foreign gas	Cesium line	Theoretical half-width in cm^{-1}	Experimental half-width in cm^{-1}	Theoretical line shift in cm^{-1}	Experimental lines shift in cm^{-1}	The adequate value of ζ
He	$^2P_{3/2}$	0.27 (82°C)	0.38 (82°C)	+0.009 (82°C)	+0.015 (82°C)	0.029
	$^2P_{3/2}$	0.26 (27°C)		+0.005 (27°C)		
Ne	$^2P_{1/2}$	0.14 (53°C)	0.15−0.2	−0.029 (53°C)	−0.035 (53°C)	0.102
	$^2P_{1/2}$	0.15 (97°C)	(47°C)	−0.029 (97°C)		
Ne	$^2P_{3/2}$	0.14 (47°C)	0.15−0.2	−0.070 (47°C)	−0.08 (53°C)	0.34
	$^2P_{3/2}$	0.14 (97°C)	(47°C)	−0.075 (97°C)		
Ar	$^2P_{1/2}$	0.25 (32°C)	0.30 (31°C)	−0.138 (32°C)	−0.238 (31°C)	0.62
Kr	$^2P_{1/2}$	0.22 (32°C)	0.28 (32°C)	−0.13 (32°C)	−0.20 (32°C)	0.62

agreement with experiment. On the other hand, in the case of argon and krypton broadening the agreement might be even better if we tried to find the optimal value of ζ. However, the procedure of adjusting of ζ is rather laborious, while the experimental evidence does not seem yet to be quite definite as long as the absolute magnitude of the line shape parameters is concerned.

Having the potential $V[R]$ fixed, we have analyzed the line shapes in the region of the densities from 0.1 to 1 r. d. (the relative density units, or shortly r. d., have been introduced by Ch'en as the ratio of the actual density of the foreign gas to its density at one atmosphere and 0°C). We have found that the collisional contribution to $\overline{\hat{Y}_{if}^2}$ is substantial in the case of krypton and argon broadening, less so for the neon broadening and is quite negligible in the case of helium. In consequence, our results indicate a strong asymmetry of the line profiles in the case of argon and krypton, but only slight deviation from symmetry in the case of neon and helium. Particularly, the ratio of the red semi-half-width to the violet one oscillates, in the case of argon broadening, from 1.2 at 1 r. d. and 0.5 r. d. up to the value of 1.4 at 0.1 r. d., while in the krypton case the value of this ratio varies from 1.2 at 0.2 r. d. up to 1.5 at 0.1 r. d. and 1.37 at 1 r. d. and 0.4 r. d. The experimental evidence is not sufficiently definite at this point. Let us note also that our results imply an unusually strong dependence on the temperature of the helium line shift, but rather moderate influence of the temperature on the line shape in the remaining cases. This temperature dependence is, for the most part, due to the change of $n\bar{v}_{if}(\infty)$. Particularly, as it follows from (31) and (32), the purely collisional contribution to the line shift and half-width is proportional to the ratio of $\bar{d}$ to ζ and $\bar{w}$ to ζ, respectively, while the temperature is

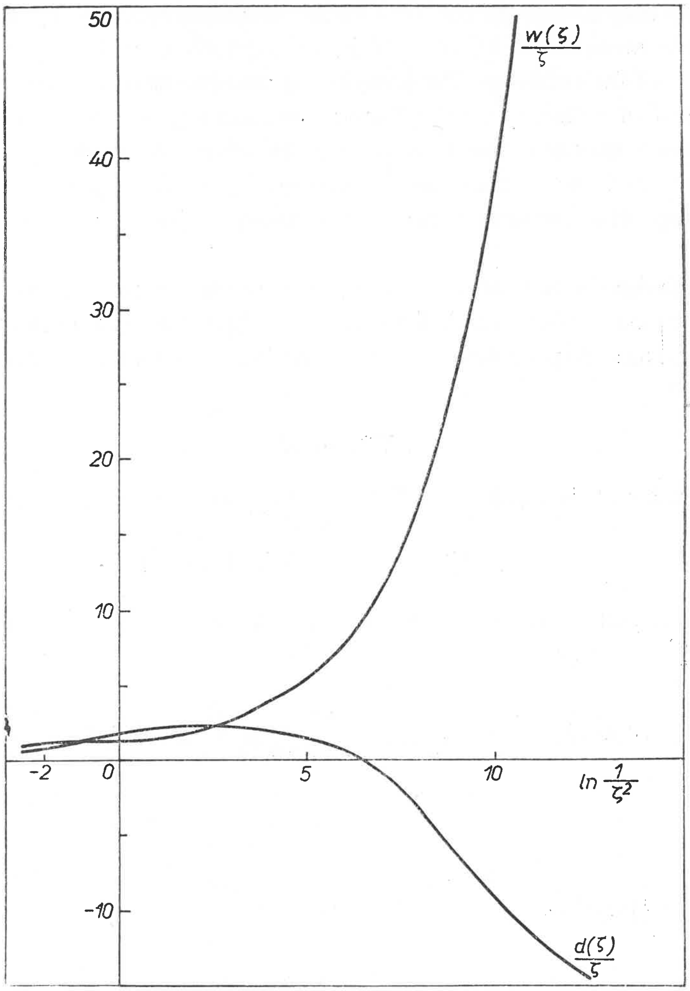

Fig. 4. Dependence of line shift and half-width on temperature. The line shift and half-width are proportional to $\overline{d(\zeta)}/\zeta$ and $\overline{w(\zeta)}/\zeta$ respectively, while $\ln 1/\zeta^2 = \ln 3kh^2/\varepsilon_m^2 R_m^2 \mu + \ln T$, where k — Boltzmann's constant

proportional to the inverse square of ζ. Thus, as it is demonstrated in Fig. 4, knowing the dependence of $\bar{d}$ and $\bar{w}$ on ζ we may deduce the temperature dependence of the main, purely collisional, part of the complex line shift.

Ending our investigation let us summarize the main points. We have shown that it is possible, within the eikonal approximation, to work out the algorithm for establishing the line shape for the densities of the foreign gas ranging from 0.1 up to 1 r. d. Below this range we expect the Voigt profile to be valid, while above, but only up to about 10 r. d., the extension of the impact theory, worked out in II, should be used. In the case of heavy foreign gas we have found the translational effects to be important even at high pressures. This is due not only to the dependence of the line shape on the velocity of the radiating atom, which has been accounted for, in a rather simplified manner, by Mizushima [16], but also to some more subtle effects, which are generally caused by the change of this velocity in effect of the collisions. Particularly, we presume that we have fully taken into account the effect of collisions on the Doppler broadening, which has been analyzed in some of the papers quoted in the Introduction. However, our model is well suited only for the description of the atomic lines broadening by foreign gases. In the other cases we may only hope that our investigation may supply a new insight on some unsolved problems.

We acknowledge the help of our colleagues from the computing centre of our University. Special thanks are due to dr A. Schurmann and Mrs E. Niedźwiedzka for the elaboration of the computational programmes, which have been of vital importance for our work.

APPENDIX

The mean value of the square of the operator $\hat{v}_{if}(\infty)$ is, by definition, given as follows

$$\overline{[\hat{v}_{if}(\infty)]^2} = (\Phi_{\kappa}^{(s)}, \hat{v}_{if}(\infty)\hat{v}_{if}(\infty)\Phi_{\kappa}^{(s)}). \tag{A1}$$

Using the explicit form (10) of the $\mathfrak{L}_{\kappa}^{(s)}$ operator $\hat{v}_{if}(\infty)$ and the representation (4) of the state $\Phi_{\kappa}^{(s)}$ we obtain

$$\overline{[\hat{v}_{if}(\infty)]^2} = \lim_{t\to\infty} \frac{1}{Q(h_0^{(s)})Q(h_0^{(p)})Q(h_0^{(p)})} \int d_3\boldsymbol{k}_0 \int d_3\boldsymbol{k}_1 \times$$
$$\times \langle \boldsymbol{k}_0|\langle \boldsymbol{k}_1| e^{-\frac{\beta}{2}h_{0}(s)} e^{-i\kappa r_0} e^{-\frac{\beta}{2}h_{0}(p)} e^{-ih_0t} e^{ih_ft} \times$$
$$\times \{\textstyle\int d_3\boldsymbol{k}'_1 \langle \boldsymbol{k}'_1| e^{-\frac{\beta}{2}h_{0}(p)} e^{-ih_0t} e^{ih_ft} [e^{i\kappa r_0} e^{-\frac{\beta}{2}h_{0}(s)} e^{-\frac{\beta}{2}h_{0}(p)} e^{\frac{\beta}{2}h_0} v_i -$$
$$- v_f e^{i\kappa r_0} e^{-\frac{\beta}{2}h_{0}(s)} e^{-\frac{\beta}{2}h_{0}(p)} e^{\frac{\beta}{2}h_0}] e^{-\beta h_i} e^{-ih_it} e^{ih_0t} e^{\frac{\beta}{2}h_0} |\boldsymbol{k}'_1\rangle \times$$
$$\times e^{-\frac{\beta}{2}h_{0}(p)} e^{\frac{\beta}{2}h_0} v_i - v_f \textstyle\int d_3\boldsymbol{k}'_1 \langle \boldsymbol{k}'_1| e^{-\frac{\beta}{2}h_{0}(p)} e^{-ih_0t} e^{ih_ft} \times$$
$$\times [e^{i\kappa r_0} e^{-\frac{\beta}{2}h_{0}(s)} e^{-\frac{\beta}{2}h_{0}(p)} e^{\frac{\beta}{2}h_0} v_i - v_f e^{i\kappa r_0} e^{-\frac{\beta}{2}h_{0}(s)} e^{-\frac{\beta}{2}h_{0}(p)} e^{\frac{\beta}{2}h_0}] \times$$
$$\times e^{-\beta h_i} e^{-ih_it} e^{ih_0t} e^{\frac{\beta}{2}h_0} |\boldsymbol{k}'_1\rangle e^{-\frac{\beta}{2}h_{0}(p)} e^{\frac{\beta}{2}h_0} \} \times$$
$$\times e^{-\beta h_i} e^{-ih_it} e^{ih_0t} e^{\frac{\beta}{2}h_0} |\boldsymbol{k}_1\rangle |\boldsymbol{k}_0\rangle. \tag{A2}$$

Passing now to the centre-of-mass system with $\boldsymbol{P}$ and $\boldsymbol{k}$ denoting the total and relative momentum, respectively, we arrive at

$$[v_{if}(\infty)]^2 = \lim_{t\to\infty} \frac{1}{Q(K)Q(h_0)Q(h_0^{(p)})} \int d_3\boldsymbol{k} e^{-\beta\frac{k^2}{2\mu}} \langle \boldsymbol{k}| e^{ih_f t} \int d_3\boldsymbol{P} e^{-\beta\frac{P^2}{2M}} \times$$

$$\times \langle \boldsymbol{P}|[\int d_3\boldsymbol{k}_1' e^{-\beta\varepsilon(k_1')} \langle \boldsymbol{k}_1'| e^{-ih_0 t} e^{ih_f t}(v_i - v_f) e^{-ih_i t} e^{ih_0 t} |\boldsymbol{k}_1'\rangle v_i -$$

$$- v_f \int d_3\boldsymbol{k}_1' e^{-\beta\varepsilon(k'_1)} \langle \boldsymbol{k}_1'| e^{-ih_0 t} e^{ih_f t}(v_i - v_f) e^{-ih_i t} e^{ih_0 t} |\boldsymbol{k}_1'\rangle \times$$

$$\times e^{-ih_i t}|\boldsymbol{P}\rangle|\boldsymbol{k}\rangle, \tag{A3}$$

where $M = m_s + m_p$, μ is the reduced mass $\left(\mu = \dfrac{m_s m_p}{m_s + m_p}\right)$ and K denotes the kinetic energy of centre-of-mass.

The integral over $\boldsymbol{P}$ is easily evaluated after we transform the integral over the momentum $\boldsymbol{k}_1'$ of the perturber on the integral over the corresponding relative momentum $\boldsymbol{k}'$, *i. e.*

$$\int d_3\boldsymbol{P} e^{-\beta\frac{P^2}{2M}} \langle \boldsymbol{P}|[\int d_3\boldsymbol{k}_1' e^{-\beta\varepsilon(k'_1)} \langle \boldsymbol{k}_1'| e^{-ih_0 t} e^{ih_f t}(v_i - v_f) \times$$

$$\times e^{-ih_i t} e^{ih_0 t}|\boldsymbol{k}_1'\rangle|\boldsymbol{P}\rangle = \int d_3\boldsymbol{P} e^{-\beta\frac{P^2}{2M}} \int d_3\boldsymbol{k}' e^{-\frac{\beta}{2m_p}\left(k' + \frac{m_p}{M}P\right)^2} \times$$

$$\times \langle \boldsymbol{k}'| e^{-ih_0 t} e^{ih_f t}(v_i - v_f) e^{-ih_i t} e^{ih_0 t} |\boldsymbol{k}'\rangle \tag{A4}$$

where

$$\boldsymbol{k}_1 = \boldsymbol{k} + \frac{m_p}{M}\boldsymbol{P}.$$

The exponential, temperature-dependent, factors in the last relation may be rearranged as follows

$$e^{-\beta\frac{P^2}{2M}} e^{-\beta\frac{1}{2m_p}\left[k'^2 + 2\frac{m_p}{M}(k'P) + \frac{m_p^2}{M^2}P^2\right]} =$$

$$= e^{-\beta'\frac{k'^2}{2\mu}} e^{-\beta''\frac{(P+\alpha k')^2}{2M}} \tag{A5}$$

with

$$\beta' = \frac{m_s}{M + m_p}\beta, \quad \beta'' = \left(1 + \frac{m_p}{M}\right)\beta$$

and

$$\alpha = \frac{M}{M + m_p}.$$

Since we may shift the total momentum $\boldsymbol{P}$ by the value of $\alpha\boldsymbol{k}'$ without any change in (A4), we arrive, eventually, at the following result

$$\overline{[\hat{v}_{if}(\infty)]^2} = \sqrt{\frac{\beta^3}{(2\pi M)^3}}\sqrt{\frac{\beta^3}{(2\pi\mu)^3}}\sqrt{\frac{\beta^3}{(2\pi m_p)^3}}\sqrt{\frac{(2\pi M)^3}{\beta''^3}} \times$$

$$\times \lim_{t\to\infty} \int d_3\boldsymbol{k} e^{-\beta\frac{k^2}{2\mu}} \langle \boldsymbol{k}| e^{ih_f t}(v_i - v_f)e^{-ih_i t}|\boldsymbol{k}\rangle \times$$

$$\times \int d_3\boldsymbol{k}' e^{-\beta'\frac{k'^2}{2\mu}} \langle \boldsymbol{k}'| e^{ih_f t}(v_i - v_f)e^{-ih_i t}|\boldsymbol{k}'\rangle =$$

$$= \lim_{t\to\infty} \int d_3\boldsymbol{k} e^{-\beta\frac{k^2}{2\mu}} \langle \boldsymbol{k}| e^{ih_f t}(v_i - v_f)e^{-ih_i t}|\boldsymbol{k}\rangle \times$$

$$\times \int d_3\boldsymbol{k}' e^{-\beta'\frac{k'^2}{2\mu}} \langle \boldsymbol{k}'| e^{ih_f t}(v_i - v_f)e^{-ih_i t}|\boldsymbol{k}'\rangle \quad \text{(A6)}$$

from which the formula (36) follows immediately.

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