ON THE CONTRIBUTION OF THE ORIENTATION AND VELOCITY RELAXATION TO THE ATOMIC LINE SHAPE. I. MODERATE PRESSURE REGION*

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A formula has been derived describing the intensity distribution at the centre of an atomic line, when the perturbers are rare gas atoms. The formalism given previously by Bielicz and others has been generalized for the case of an anisotropic potential. The sudden approximation and the influence of the induced multipole momenta of the radiating atoms are also discussed.

1. Introduction

It is well-known that, in the low pressure range, the intensity distribution function of a spectral line depends both on Doppler and pressure effects. If one treats these two effects independently, the line shape is well described by a Voight profile. On the other hand, it is known that collisions of a radiating atom with perturbers change its velocity. Therefore, some correlation exists between the Doppler effect and pressure broadening. The correlation leads to an asymmetry of the line profile. This was pointed out theoretically by [1]—[5] and observed experimentally by [6]. The asymmetry depends strongly on the mass of the perturbers, namely, it increases with an increase in the perturber mass. The theoretical considerations [1]—[5] based on the simplified assumption that the interaction potential between atoms possesses spherical symmetry. In other words, such an assumption leads to the neglection of the reorientation and dealignment effects. Moreover, the collisional relaxation of the orientation and alignment as well as the higher multipole momenta of the radiating atom modify the line profile appreciably. These effects change both the width and the shift of the line and may also give rise to entirely new effects, e.g. the radiative transitions for some forbidden lines (see Kielhopf and Granier, Granier, Schuller [7]). This leads to the appearance of some satellite bands on the far wings of the

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line. So far many authors [8]—[10] have taken into account the influence of the relaxation of multipole momenta on the intensity distribution of the spectral line shape but neglected the velocity change of the radiating atom. In the present paper both effects are treated together.

We shall deal with the moderate pressure region, where the pressure broadening is larger than the Doppler effect, but the binary collision approximation is still valid. However, the very low pressure region, where the Doppler effect dominates the pressure broadening, will be considered in a forthcoming paper.

Section 2 contains, the formalism described in [3]—[5] but generalized for an anisotropic potential. In Section 3 we consider the relaxation of multipole momenta in a Liouville space. On the basis of the classical path approximation, a set of differential equations has been derived. These equations describe the time evolution of the multipole momenta. It permits us to calculate the mean value of the relaxation operator which allows one to describe the intensity distribution of a spectral line.

In Section 4 we consider the $1/2 \rightarrow 1/2$ transition in the alkali atoms perturbed by the rare gas atoms when reorientation effects do not occur. The simplest example of transitions when the reorientation effect takes place, is the $1 \rightarrow 0$ transition. For this transition we calculate the mean value of the relaxation operator in the sudden approximation. This is the subject of Section 5. In Section 6 the mean value of this operator is calculated also by numerically solving the obtained set of differential equations. The comparison between the results obtained by both methods is given in Table I. In Section 7 we study the influence of the induced quadrupole momenta on the intensity distribution of the dipole transition $3/2 \rightarrow 1/2$. The obtained results in Table II show that this contribution to the line shape is negligible.

2. The collisional relaxation of atoms

A comprehensive description of the atomic relaxation, as well as any other relaxation phenomena, is usually reduced to the investigation of the autocorrelation function $U(t)$, which is given by

$$U(t) = \mathrm{Tr}\,\{\varrho e^{-i\boldsymbol{\kappa}\cdot\boldsymbol{r}_0}\chi^{\dagger}e^{iHt}\chi e^{-iHt}e^{i\boldsymbol{\kappa}\cdot\boldsymbol{r}_0}\}, \tag{1}$$

where ϱ is the density matrix of the whole gas, H stands for its Hamiltonian, $\boldsymbol{r}_0$ is the position vector of the radiating atom, $\boldsymbol{\kappa}$ is the wave vector of light, χ is the operator of the respective multipole moment of the radiating atom. The trace is over the states of the gas, i.e. the radiating atom and the perturber. In our consideration we will assume that the total angular momentum of the perturbers is zero and that they do not have any internal degrees of freedom. An autocorrelation function of this type is sufficient to describe the emission or absorption spectra and the longitudinal relaxation of the atomic multipole momenta, provided that the medium is isotropic. In the higher order radiation processes, particularly concerning the scattering of light, the description of a spectroscopic experiment is often reduced to calculating these functions.

The intensity distribution function $I_{if}(\omega)$, which is related to the Fourier transform of the autocorrelation function $U(t)$ in the following way

$$I_{if}(\omega) = \mathrm{Re} \int_0^\infty dt\, e^{i\omega t} U(t), \tag{2}$$

is given by the imaginary part of the mean value of the resolvent operator $\overline{R_{if}}(\omega)$. Since we assume that the spectral lines are well resolved, we consider only the transition from the initial level i, labelled by a quantum number $\alpha_i j_i$, to the final level f, labelled by $\alpha_f j_f$. We neglect the nuclear spin of a radiating atom, and here j_a denotes the total orbital and electronic momentum, while α_a stands for the principal quantum number. The intensity distribution function of the multipole light with a given J is proportional to

$$I_{if}^{JM}(x) = -\frac{1}{\pi} \mathrm{Im}\, \overline{R_{if}^{JM}}(x), \tag{3}$$

where $x = \omega - \omega_{if}$ and J, M satisfy the following conditions

$$J = |j_i - j_f|, \ldots, |j_i + j_f|, \qquad M = 0, \pm 1, \pm 2, \ldots \pm J. \tag{4}$$

In the case of an isotropic medium the mean value of the resolvent operator $\overline{R_{if}^{JM}}(x)$ does not depend on M. Therefore, we will calculate $\overline{R_{if}^{J0}}(x)$ only.

When the density of the gas is low enough, the basis assumptions of the so-called impact theory are satisfied. Then coupling between the thermal bath and radiating atom is not too strong and the density matrix can be factorized as follows

$$\varrho \simeq \varrho_s \cdot \varrho_p, \tag{5}$$

where ϱ_s, ϱ_p are the density matrices of the radiating and thermal atom respectively. In this case, as was shown in the papers [3]—[5], the mean value of the resolvent operator for the emission spectra is given by the following formula

$$\overline{R_{if}^{JM}}(x) = \int d_3\boldsymbol{k}_0 \varrho^{1/2}(k_0^2/2m_0) \int d_3\boldsymbol{k}_0' \varrho^{1/2}(k_0'^2/2m_0) \left(e_{k_0'\kappa JM}, \frac{1}{x - \hat{h}_0^{(s)} - n\hat{v}_{if}(\infty)}\, e_{k_0\kappa JM} \right), \tag{6}$$

where m_0 is the mass of the radiative atom, n is the perturber density and $\varrho(k_0^2/2m_0) = Q(k_0^2/2m_0) \exp(-\beta k_0^2/2m_0)$ is the canonical distribution matrix. The Liouville space momentum eigenvectors $e_{k_0\kappa JM}$ are defined analogically as in papers [3] and [4] by the relations

$$\boldsymbol{k}_s e_{k_0\kappa JM} = (\boldsymbol{k}_0 + \boldsymbol{\kappa}) e_{k_0\kappa JM}, \qquad e_{k_0\kappa JM} \boldsymbol{k}_s = \boldsymbol{k}_0 e_{k_0\kappa JM}, \tag{7}$$

and

$$(e_{k_0\kappa JM}, e_{k_0'\kappa J'M'}) = \delta_{JJ'}\delta_{MM'}\delta(\boldsymbol{k}_0 - \boldsymbol{k}_0'), \tag{8}$$

where $\boldsymbol{k}_s$ is the momentum operator of the radiating atom $\boldsymbol{k}_0$ being the corresponding eigenvalue. Hence, $e_{k_0\kappa JM}$ is the eigenvector of the kinetic operator in Liouville space with the following eigenvalue

$$\hat{h}_0^{(s)} e_{k_0\kappa JM} = -(\boldsymbol{k}_0\boldsymbol{\kappa}/m_0 + \kappa^2/2m_0) e_{k_0\kappa JM}. \tag{9}$$

The collisional relaxation operator $\hat{v}_{if}(\infty)$ is given here by the following formula

$$\hat{v}_{if}(\infty)e_{k_0\kappa JM} = (2\pi)^{-3}\int d_3\boldsymbol{k}_1\varrho(k_1^2/2m_1)\,[T_{kk}(\alpha_i j_i)-T_{kk}(\alpha_f j_f)]e_{k_0\kappa JM}$$
$$+i(2\pi)^{-3}\int d_3\boldsymbol{k}_1\varrho^{1/2}(k_1^2/2m_1)\int d_3\boldsymbol{k}_1'\varrho^{1/2}(k_1'^2/2m_1)\int d_3\boldsymbol{k}_0'\varrho^{1/2}(k_0'^2/2m_0)$$
$$\times\delta(\boldsymbol{k}_1-\boldsymbol{k}_0-\boldsymbol{k}_1'+\boldsymbol{k}_0')\delta(\varepsilon_k-\varepsilon_{k'})\sum_{m_i,m_f}\sum_{m_i',m_f'}(-1)^{2(j_i-m_i)}C(j_f j_i J;\, m_f-m_i M)$$
$$\times C(j_f j_i J',\, m_f'-m_i' M')\,\langle m_i|T_{kk'}^{(i)}|m_i'\rangle\,\langle m_f'|T_{k'k}^{\dagger(f)}|m_f\rangle e_{k_0'\kappa J'M'}, \tag{10}$$

where $\boldsymbol{k}_1$ is the momentum and m_1 is the mass of the perturber atom, $\boldsymbol{k}$, ε_k are, respectively, the momentum and kinetic energy of relative motion. All the elements of the transition amplitude T_{kk} diagonal in m_i or m_f are equal for the given atomic level and we denote them by

$$\langle m_i|T_{kk'}^{(i)}|m_i\rangle = T_{kk'}(\alpha_i j_i), \quad \langle m_f|T_{kk'}^{(f)}|m_f\rangle = T_{kk'}(\alpha_f, j_f). \tag{11}$$

It has been shown in papers [3] and [4] that the basic formula (6) can be simplified by means of two distinct approximations which are valid in different pressure regions. In the region where the collisional effects dominate over Dopller broadening, the approximation used in the paper of Bielicz and others [3] is applicable and we have

$$\overline{R_{if}^{J0}}(x) = \tfrac{1}{2}\,[X_{if}+(\overline{\hat{Y}_{if}^2})^{1/2}]^{-1}+\tfrac{1}{2}\,[X_{if}-(\overline{\hat{Y}_{if}^2})^{1/2}]^{-1}, \tag{12}$$

where

$$X_{if} = x-n\overline{v_{if}}(\infty)-\kappa^2/2m_0, \tag{13}$$

and

$$\overline{\hat{Y}_{if}^2} = n^2[\overline{v_{if}}(\infty)]_\beta\{[\overline{v_{if}}(\infty)]_\beta-[\overline{v_{if}}(\infty)]_{\beta'}\}+\kappa^2/\beta m_0. \tag{14}$$

In the last relation the subscripts β and β' indicate that two different temperatures are used to calculate $\overline{v_{if}}(\infty)$, namely, the actual temperature of gas T and $T' = (1+2m_1/m_0)T$. The relations (12)—(14) will not change essentially, if we incorporate the reorientation effects. However, the form of the relaxation operator $\hat{v}_{if}(\infty)$ and also its average value $\overline{v_{if}}(\infty)$ will change, according to the formula (10). The respective computing procedure is described in the next section of this paper.

3. The reorientation effect

In Section 2 we showed that in the pressure region where the collisional effects dominate, the problem of finding the line shape reduces to the calculation of the mean value of the collisional relaxation operator $\overline{v_{if}}(\infty)$. In order to calculate $\overline{v_{if}}(\infty)$ we have to determine the time evolution of the multipole operator $\chi(t)$.

Therefore, let us consider two colliding atoms in the space-fixed system(sfs). The centre of sfs is the mass centre of the atoms and the x-axis is taken along the direction of

the relative motion (Fig. 1). As many others, we assume that the atoms follow a straight-line classical path, thus we have

$$r = [v^2(t-t_0)^2+b^2]^{1/2}, \quad \sin\beta(t) = v(t-t_0)/r, \tag{15}$$

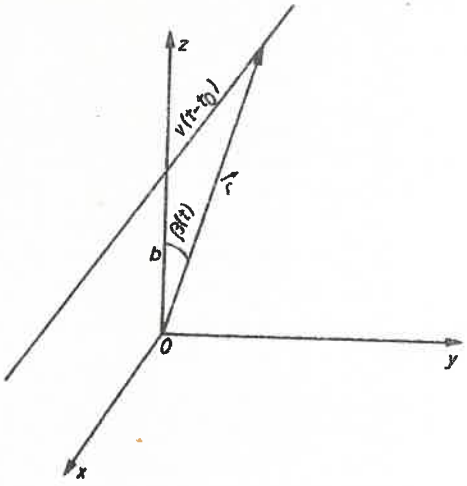

Fig. 1. The space-fixed system sfs

where b is the impact parameter, v stands for the relative velocity, t_0 being the time of collision. By rotating the sfs around the y-axis through an angle $\beta(t)$, we obtain another body-fixed system (bfs). Note that the interaction potential is invariant under rotation about the z'-axis and reflections in the $x'y$ plane.

The evolution of the multipole operator $\chi(t)$ in the sfs (in the Heisenberg picture) is given by the following equation in Liouville space

$$i\dot{\chi}(t) = \hat{V}'(t)\chi(t), \tag{16}$$

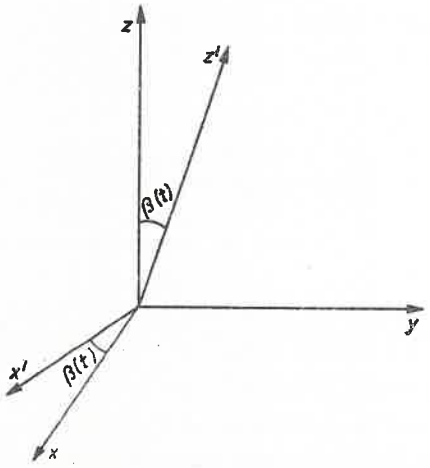

Fig. 2. The body-fixed system bfs

where $\hat{V}'(t)$ is the interaction operator in Liouville space. $\hat{V}'(t)$ in sfs is connected with $\hat{V}(t)$ in bfs by the following transformation

$$\hat{V}'(t) = e^{-i\beta(t)\hat{L}_y}\hat{V}(t)e^{i\beta(t)\hat{L}_y}, \tag{17}$$

so we obtain

$$i\dot{\chi}(t) = e^{-i\beta(t)\hat{L}_y}\hat{V}(t)e^{i\beta(t)\hat{L}_y}\chi(t). \tag{18}$$

A convenient way of introducing the basis is to write it down in terms of Liouville space angular momentum eigenvectors

$$e_{JM} = \sum_{m_i,m_f} (-1)^{(j_i-m_i)}C(j_f j_i J;\, m_f - m_i M)\, |\alpha_f j_f m_f\rangle \langle \alpha_i j_i m_i|, \tag{19}$$

where we limit ourselves to the Liouville subspace connected with the given atomic transition $|\alpha_i j_i m_i\rangle \to |\alpha_f j_f m_f\rangle$. Expanding $\chi(t)$ in this basis

$$\chi(t) = \sum_{J,M} \chi_{JM}(t) e_{JM}, \tag{20}$$

and inserting it into equation (18), we obtain the following final equations

$$i\dot{\chi}_{JM}(t) = \sum_{J',M',M''} d^J_{MM''}(\beta) d^{J'}_{M'M''}(\beta) V^{|M|}_{JJ'} \chi_{J'M'}(t). \tag{21}$$

We have used here the well-known formulas

$$(e_{JM}, e^{-i\beta(t)\hat{L}_y} e_{J'M'}) = \delta_{JJ'} d^J_{tMM'}(\beta), \qquad (e_{JM}, e^{i\beta(t)\hat{L}_y} e_{J'M'}) = \delta_{JJ'} d^J_{M'M}(\beta),$$

and

$$(e_{JM}, \hat{V}(t) e_{J'M'}) = \delta_{MM'} V^{|M|}_{JJ'}.$$

In order to calculate the matrix elements of $\hat{V}(t)$ we make use of the Liouville space definition for a scalar product and we get

$$V^{|M|}_{JJ'} = \sum_{m_i,m_f} (-1)^{2(j_i-m_i)} C(j_f j_i J;\, m_f - m_i M) C(j_f j_i J';\, m_f - m_i M)$$

$$[V^{|m_i|}(\alpha_i j_i) - V^{|m_f|}(\alpha_f j_f)], \tag{22}$$

where $V^{|m_i|}(\alpha_i, j_i)$ and $V^{|m_f|}(\alpha_f, j_f)$ stand for matrix elements of the interaction operator in the usual Hilbert space

$$V^{|m_i|}(\alpha_i j_i) = \langle \alpha_i j_i m_i | V(t) |\alpha_i j_i m_i\rangle, \qquad V^{|m_f|}(\alpha_f j_f) = \langle \alpha_f j_f m_f | V(t) |\alpha_f j_f m_f\rangle. \tag{23}$$

One should notice that the differential equations (21) contain also elements non-diagonal in the quantum number J. The appearance of these elements is caused by the fact that higher multipole momenta can be induced during a collision. To evaluate their influence on the line shape, in Section 7 we give the respective numerical calculations.

4. The transition $1/2 \to 1/2$

In the case of the transition $\alpha_i j_i \to \alpha_f j_f$ when $j_i = j_f = 1/2$, the potential is isotropic in both states and reorientation effects do not appear. As it has been shown in the paper of Bielicz and others [3], the mean value of the resolvent operator in the impact approximation is then given by

$$\overline{v_{if}}(\infty) = \pi\bar{v}(R_m)^2[-\overline{d(\zeta)} - i\overline{w(\zeta)}], \tag{24}$$

where $\zeta = \varepsilon_m R_m/\bar{v}$, $\bar{v}$ is the mean value of the relative velocity, R_m, ε_m describe the interacting potential

$$V^{1/2}(\alpha_i 1/2) - V^{1/2}(\alpha_f 1/2) = -\varepsilon_m u(b/R_m, vt/R_m), \tag{25}$$

namely the position and depth of its extremum. The functions $d(z)$ and $w(z)$ are given by

$$d(z) = 2\int_0^\infty d\varrho\varrho \sin\left[z\int_0^\infty ds u(\varrho, s)\right], \qquad w(z) = 2\int_0^\infty d\varrho\varrho\{1-\cos\left[z\int_0^\infty ds u(\varrho, s)\right]\}, \tag{26}$$

and bars signify that they are averaged over the velocity in the following way

$$\overline{d(\zeta)} = (54/\pi)^{1/2}\int_0^\infty dz \exp\left[-\tfrac{3}{2}\left(\frac{\zeta}{z}\right)^2\right] z^{-5} d(z),$$

$$\overline{w(\zeta)} = (54/\pi)^{1/2}\int_0^\infty dz \exp\left[-\tfrac{3}{2}\left(\frac{\zeta}{z}\right)^2\right] z^{-5} w(z). \tag{27}$$

The functions $d(z)$ and $w(z)$ have been computed and tabulated by Czuchaj and Fiutak [12] for the Lennard–Jones potentials (6–8), (6–10), (6–12) and for a certain modification of the Buckingham potential. As it has been shown in the Fig. 3 [12] for the Lennard–Jones potential (6–12), the functions $d(z)$ and $w(z)$ do not suffer too strong changes when averaged velocity as defined by (27). Therefore, the functions $d(\zeta)$ and $w(\zeta)$ are sometimes used instead of $\overline{d(\zeta)}$ and $\overline{w(\zeta)}$. The numerical values for $\overline{d(\zeta)}$ and $\overline{w(\zeta)}$ for the Lennard–Jones potential (6–8) are given in the paper of Bielicz and others [3].

5. The transition $1 \to 0$

Now we consider the transition $\alpha_i j_i \to \alpha_f j_f$ with $j_i = 1$, $j_f = 0$. The only value for J is $J = 1$. From (21) we obtain the following set of equations:

$$i\dot{\chi}_{11}(t) = V_{11}^1\chi_{11}(t) - \tfrac{1}{2}(V_{11}^1 - V_{11}^0)\sin^2\beta(t)[\chi_{11}(t) - \chi_{1-1}(t)]$$

$$+ \frac{1}{\sqrt{2}}(V_{11}^1 - V_{11}^0)\sin\beta(t)\cos\beta(t)\chi_{10}(t),$$

$$i\dot{\chi}_{1-1}(t) = V_{11}^1\chi_{1-1}(t)+\tfrac{1}{2}(V_{11}^1-V_{11}^0)\sin^2\beta(t)\,[\chi_{11}(t)-\chi_{1-1}(t)]$$

$$-\frac{1}{\sqrt{2}}(V_{11}^1-V_{11}^0)\sin\beta(t)\cos\beta(t)\chi_{10}(t),$$

$$i\dot{\chi}_{10}(t) = [V_{11}^1\sin^2\beta(t)+V_{11}^0\cos^2\beta(t)]\chi_{10}(t)$$

$$+\frac{1}{\sqrt{2}}(V_{11}^1-V_{11}^0)\sin\beta(t)\cos\beta(t)\,[\chi_{11}(t)-\chi_{1-1}(t)]. \tag{28}$$

Introducing cartesian coordinates

$$\chi_x(t) = \frac{1}{\sqrt{2}}[\chi_{11}(t)-\chi_{1-1}(t)], \quad \chi_y(t) = \frac{1}{\sqrt{2}}[\chi_{11}(t)+\chi_{1-1}(t)], \quad \chi_z(t) = \chi_{10}(t) \tag{29}$$

we separate (28) into two independent sets of equations

$$i\dot{\chi}_y(t) = V_{11}^1\chi_y(t), \tag{30a}$$

and

$$i\dot{\chi}_x(t) = [V_{11}^1\cos^2\beta(t)+V_{11}^0\sin^2\beta(t)]\chi_x(t)+(V_{11}^1-V_{11}^0)\sin\beta(t)\cos\beta(t)\chi_z(t),$$

$$i\dot{\chi}_z(t) = [V_{11}^1\sin^2\beta(t)+V_{11}^0\cos^2\beta(t)]\chi_z(t)+(V_{11}^1-V_{11}^0)\sin\beta(t)\cos\beta(t)\chi_x(t). \tag{30b}$$

The solution of the coupled system of differential equations (30b) is obtainable through numerical computation only. However, it is generally believed that the result can be reasonably estimated by means of the so-called sudden approximation, known also as the scalar approximation which has been introduced by Byron and Foley [11] in the calculation of the shape of the double-resonance signal. This approximation has been extensively used in the calculation of the line shape [9].

The sudden approximation is based on the assumption that we may disentangle the time evolution of the system by neglecting the time ordering of the formal solution the set (30). Thus, the sudden approximation leads to the following time evolution

$$\chi(t) = \exp\left[-i\int_{-\infty}^{t}\hat{V}'(t')dt'\right]\chi(-\infty), \tag{31}$$

instead of the formal solution

$$\chi(t) = \hat{P}\exp\left[-i\int_{-\infty}^{t}\hat{V}'(t')dt'\right]\chi(-\infty), \tag{32}$$

which is exact.

There exists some doubt, however, whether the validity of the sudden approximation is well established in all cases of interest. Therefore, we shall compare the results obtained through direct computation with those given by the sudden approximation to prove the applicability of the latter for our purposes.

In the case of the transition $1 \to 0$, which is considered above, we have the following simple solution at infinity in the sudden approximation

$$\begin{pmatrix} \chi_y(+\infty) \\ \chi_x(+\infty) \\ \chi_z(+\infty) \end{pmatrix} = \exp\left[+i \begin{pmatrix} D_1 & 0 & 0 \\ 0 & D_2 & 0 \\ 0 & 0 & D_3 \end{pmatrix} \right] \begin{pmatrix} \chi_y(-\infty) \\ \chi_x(-\infty) \\ \chi_z(-\infty) \end{pmatrix}, \tag{33}$$

with the coefficients D_i given by

$$D_1 = \int_{-\infty}^{\infty} V_{11}^1 dt, \quad D_2 = \int_{-\infty}^{\infty} [V_{11}^1 \cos^2 \beta(t) + V_{11}^0 \sin^2 \beta(t)] dt,$$

$$D_3 = \int_{-\infty}^{\infty} [V_{11}^1 \sin^2 \beta(t) + V_{11}^0 \cos^2 \beta(t)] dt. \tag{34}$$

Using the formulas (29) and (33) we can average $\chi_{10}^{\dagger}(-\infty)\chi_{10}(+\infty)$ over all orientations of colliding atoms with the assumption that the gas is isotropic and

$$\langle \chi_{10}^{\dagger}(-\infty)\chi_{10}(-\infty)\rangle_{\text{orientation}} = 1. \tag{35}$$

Thus, the mean value of the collisional relaxation operator $\overline{v_{if}}(\infty)$ in the sudden approximation takes the form

$$\overline{v_{if}}(\infty)^{\text{sudd}} = \tfrac{2}{3}\pi\bar{v}\langle \int_0^{\infty} dbb(3 - e^{+iD_1} - e^{+iD_2} - e^{+iD_3})\rangle_v, \tag{36}$$

where $\langle \ldots \rangle_v$ denotes the velocity average.

From the formulas (22) and (23) we obtain

$$V_{11}^1 = V^1(\alpha_i 1) - V^0(\alpha_f 0) = -\varepsilon_m^{(1)} u(b/R_m^{(1)}, vt/R_m^{(1)}),$$

$$V_{11}^0 = V^1(\alpha_i 0) - V^0(\alpha_f 0) = -\varepsilon_m^{(0)} u(b/R_m^{(0)}, vt/R_m^{(0)}), \tag{37}$$

where we introduce a notation analogous to that used for the transition $1/2 \to 1/2$, namely the parameters describing the extremum of potentials (37), where $R_m^{(1)}$, $R_m^{(0)}$ are their positions, $\varepsilon_m^{(1)}$, $\varepsilon_m^{(0)}$ are their depths. Therefore $\overline{v_{if}}(\infty)^{\text{sudd}}$ is related to the dimensionless functions by

$$\overline{v_{if}}(\infty)^{\text{sudd}} = \pi\bar{v}(R_m^{(0)})^2[-\overline{d(\zeta, a_l, a_k, \ldots; 1 \to 0)^{\text{sudd}}} - i\overline{w(\zeta, a_l, a_k, \ldots; 1 \to 0)^{\text{sudd}}}, \tag{38}$$

where

$$\zeta = \varepsilon_m^{(0)} R_m^{(0)}/\bar{v} \tag{39}$$

and $a_l, a_k, \ldots$ are the parameters describing the anisotropy of the potential V_{11}^M.

Under the assumption that the interaction is of the Lennard–Jones (6–k) type, the functions $\overline{d(\zeta, a_6, a_k; 1 \to 0)^{\text{sudd}}}$, $\overline{w(\zeta, a_6, a_k; 1 \to 0)^{\text{sudd}}}$ can be expressed by the functions $\overline{d(\zeta)}$ and $\overline{w(\zeta)}$ (Eq. (27)) in the following way

$$\overline{d(\zeta, a_6, a_k: 1 \to 0)^{\text{sudd}}} = \tfrac{1}{3}[\eta'\overline{d(\zeta')} + \eta''\overline{d(\zeta'')} + \eta'''\overline{d(\zeta''')}],$$

$$\overline{w(\zeta, a_6, a_k; 1 \to 0)^{\text{sudd}}} = \tfrac{1}{3}[\eta'\overline{w(\zeta')} + \eta''\overline{w(\zeta'')} + \eta'''\overline{w(\zeta''')}], \tag{40}$$

where the parameters η', η'', η''' depend only on a_6, a_k. Thus, when k is equal to 8 or 12, $\overline{d(\ldots; 1 \to 0)^{\text{sudd}}}$, $\overline{w(\ldots; 1 \to 0)^{\text{sudd}}}$ do not require additional numerical calculations for we can use here Table I of Bielicz and others [3] or Fig. 3 of Czuchaj and Fiutak [12]. For example, in the case $k = 12$, if we assume the following form for anisotropy parameters

$$a_6 = (\varepsilon_m^{(1)}/\varepsilon_m^{(0)})\,(R_m^{(1)}/R_m^{(0)})^6, \qquad a_{12} = a_6(R_m^{(1)}/R_m^{(0)})^6, \tag{41}$$

we have

$$\eta' = (a_{12}/a_6)^{1/3}, \quad \eta'' = [(1+11a_{12})/2(1+5a_6)]^{1/3}, \quad \eta''' = [(11+a_{12})/2(5+a_6)]^{1/3},$$
$$\zeta' = a_6(a_6/a_{12})^{5/6}\zeta, \quad \zeta'' = [(1+5a_6)\,(\eta'')^{-5/2}/6]\zeta,$$
$$\zeta''' = [(5+a_6)\,(\eta''')^{-5/2}/6]\zeta. \tag{42}$$

Furthermore, there exist analogous relations between $d(r, a_6, a_{12}; 1 \to 0)^{\text{sudd}}$, $w(r, a_6, a_{12}; 1 \to 0)^{\text{sudd}}$ and the functions $d(r)$, $w(r)$ as (40)—(42), where $r = \varepsilon_m^{(0)} R_m^{(0)}/v$. In Table I the results of calculations for $d(r, a_6, a_{12}; 1 \to 0)^{\text{sudd}}$ and $w(r, a_6, a_{12}; 1 \to 0)^{\text{sudd}}$

TABLE I

The comparison between the values of $d(\ldots)$ and $w(\ldots)$ obtained in a sudden approximation and with the help of the numerical method

r	a_{12}	a_6	d^{num}	d^{sudd}	Δd	$\Delta d\%$	w^{num}	w^{sudd}	Δw	$\Delta w\%$
1	0.2	0.3	0.946	0.873	−0.073	7.5%	0.925	0.876	−0.049	5%
1	0.2	0.9	1.253	1.187	−0.066	5%	1.594	1.329	−0.265	16.5%
1	0.9	0.2	0.519	0.681	0.162	31%	0.961	1.049	0.088	9%
1	0.5	0.7	1.347	1.249	−0.098	7%	1.217	1.149	−0.068	5.5%
2	0.5	0.7	1.748	1.460	−0.288	16%	2.223	1.751	−0.472	21%
3	0.5	0.7	1.604	1.632	0.028	1.5%	2.576	2.642	0.066	2.5%
10	0.5	0.7	2.888	2.813	−0.075	2.5%	3.990	3.804	−0.185	4.5%

made for a chosen sets of parameters in the sudden approximation are given and a comparison is made between them and the corresponding results obtained with the help of the numerical method presented in the subsequent section.

6. *The numerical solutions*

The set of equations (30) has to be rearranged in order to simplify the numerical calculations. While the solution of the equation (30a) is simply given by

$$\chi_\nu(t) = \exp\left[-i \int_{-\infty}^{t} V_{11}^1(t')dt'\right]\chi_\nu(-\infty), \tag{43}$$

the two remaining equations couple two complex functions $\chi_x(t)$, $\chi_z(t)$. However, it is easy to show that they form in xz-plane the vector of constant moduli i.e.

$$\chi_x^*(t)\chi_x(t)+\chi_z^*(t)\chi_z(t) = c^2. \tag{44}$$

Therefore, we can express these functions in the following form

$$\chi_x(t) = c \sin\gamma(t)e^{i\alpha_x(t)}, \quad \chi_z(t) = c\cos\gamma(t)e^{i\alpha_z(t)}. \tag{45}$$

Inserting this solution into (30b) we get the following set of equations

$$\dot{u}(t) = -2(V_{11}^1-V_{11}^0)\sin\beta(t)\cos\beta(t)\operatorname{ctg}[2\gamma(t)]\sin u(t)+(V_{11}^1-V_{11}^0)[2\sin^2\beta(t)-1],$$
$$\dot{\gamma}(t) = (V_{11}^1-V_{11}^0)\sin\beta(t)\cos\beta(t)\cos u(t), \tag{46}$$

which couple two real functions $\gamma(t)$ and $u(t)$, where the function $u(t)$ is defined by

$$u(t) = \int_{-\infty}^{t}(V_{11}^1-V_{11}^0)\sin\beta(t')\cos\beta(t')dt'-\alpha_z(t)+\alpha_x(t)+\pi/2. \tag{47}$$

Using formulae (43), (45)—(47) and averaging $\chi_z^*(-\infty)\chi_z(+\infty)$ over all orientations of colliding atoms we have

$$\overline{v_{if}(\infty)}^{\text{num}} = (\pi\cdot\bar{v}2/3)\langle\int_0^\infty dbb[3-e^{iD_1}-2Qe^{iD}]\rangle_v, \tag{48}$$

where

$$D_1 = \int_{-\infty}^{\infty}V_{11}^1dt, \quad D = \tfrac{1}{2}\int_{-\infty}^{\infty}(V_{11}^1+V_{11}^0)dt,$$

$$Q = \tfrac{1}{2}\{\cos\gamma(+\infty)\cos[u(+\infty)/2-J(+\infty)]-\sin\gamma(+\infty)\cos[u(+\infty)/2+J(+\infty)]\},$$

$$J(+\infty) = \int_{-\infty}^{\infty}(V_{11}^1-V_{11}^0)\frac{\sin u(t)}{\sin[2\gamma(t)]}dt. \tag{49}$$

Functions $\gamma(t)$, $u(t)$ form the solution of the differential set (46) with the following initial conditions

$$u(-\infty) = 0, \quad \gamma(-\infty) = -\pi/4. \tag{50}$$

So, we find that functions $\overline{d(\zeta, a_k, a_l, \ldots; 1\to 0)}^{\text{num}}$ and $\overline{w(\zeta, a_k, a_l, \ldots; 1\to 0)}^{\text{num}}$ can be treated as a result of velocity averaging as understood in formula (27) over the expressions

$$d(r, a_k, a_l, \ldots; 1\to 0)^{\text{num}} = \tfrac{1}{3}\eta' d(r')+\tfrac{4}{3}\int_0^\infty d\varrho\cdot\varrho Q\sin D,$$

$$w(r, a_k, a_l, \ldots; 1\to 0)^{\text{num}} = \tfrac{1}{2}\eta' w(r')+\tfrac{4}{3}\int_0^\infty d\varrho\cdot\varrho[1-Q\cos D], \tag{51}$$

where

$$r = \varepsilon_m^{(0)}R_m^{(0)}/v, \quad \varrho = b/R_m^{(0)}. \tag{52}$$

The parameters $a_k, a_l, \ldots$ describe, similarly as in the previous chapter, the anisotropy of the potential $V_{11}^{|M|}$ and in the case of the Lennard–Jones potential (6–12), a_6, a_{12}, η' have the same form as in the equations (41), (42) and $r = a_6(a_6/a_{12})^{5/6} \cdot r$. In Table I the values of $d(r, a_6, a_{12}; 1 \to 0)$ and $w(r, a_6\, a_{12}; 1 \to 0)$ obtained alternatively by direct computation and calculated in the frame of the sudden approximation are listed, and also the following differences $\Delta d = d(\ldots)^{\text{sudd}} - d(\ldots)^{\text{num}}$, $\Delta w = w(\ldots)^{\text{sudd}} - w(\ldots)^{\text{num}}$, and relative differences $\Delta d\% = [\Delta d/d(\ldots)^{\text{num}}] \cdot 100\%$, $\Delta w\% = [\Delta w/w(\ldots)^{\text{num}}] \cdot 100\%$, are given. These differences, in general, do not exceed 20 percent, in one special case, however, we found $\Delta d\% = 31\%$. It shows that the sudden approximation, despite its being very useful and effective in most cases, can nevertheless sometimes lead to serious divergences. No dependence of $\Delta d\%$ and $\Delta w\%$ on r or on parameters characterizing the anisotropy of the potential was found. In such a situation, on the grounds of the calculations performed, it is hard to say when the sudden approximation leads to reasonable results.

7. The reorientation effect in the 3/2 → 1/2 transition

Up to now there was no need to consider the non-diagonal elements $V_{JJ'}^{|M|}$. In equation (10), since for the $1 \to 0$ transition there exists only one value of J. Also in the $1/2 \to 1/2$ transition these elements do not play any role since this is the case of an isotropic system. The simplest case for which these non-diagonal elements become is the $3/2 \to 1/2$ transition, for which J is equal to 1 or 2. The physical picture involved here is the transformation of the dipole momentum into the quadrupole momentum during the collision and vice versa. In other words, we want to take into account the alignment and dealignment in the effect of a collision. For this purpose we will solve equation (10) in the scalar approximation. Although the discussion of the previous chapter shows that the scalar approximation breaks down in some cases, still we hope that, in most cases of interest, it will not distort the results drastically.

As in the case of the $1 \to 0$ transition, we introduce the following set multipole components

$$\chi_{JM}^{(\pm)}(t) = [\chi_{JM}(t) \pm \chi_{J-M}(t)]/\sqrt{2}. \tag{53}$$

In terms of these variables, the solution of (10) in the sudden approximation is reduced to the following form

$$\chi_{22}^{(-)}(+\infty) = \exp(iD_3)\chi_{22}^{(-)}(-\infty), \qquad \begin{pmatrix}\chi_{11}^{(+)}(\infty)\\ \chi_{21}^{(+)}(\infty)\end{pmatrix} = \exp\left[i\begin{pmatrix}D_1 & N_1\\ N_1 & D_2\end{pmatrix}\right]\begin{pmatrix}\chi_{11}^{(+)}(-\infty)\\ \chi_{21}^{(+)}(-\infty)\end{pmatrix},$$

$$\begin{pmatrix}\chi_{11}^{(-)}(\infty)\\ \chi_{21}^{(-)}(\infty)\end{pmatrix} = \exp\left[i\begin{pmatrix}D_4 & N_2\\ N_2 & D_5\end{pmatrix}\right]\begin{pmatrix}\chi_{11}^{(-)}(-\infty)\\ \chi_{21}^{(-)}(-\infty)\end{pmatrix},$$

$$\begin{pmatrix}\chi_{10}(\infty)\\ \chi_{20}(\infty)\\ \chi_{22}^{(+)}(\infty)\end{pmatrix} = \exp\left[i\begin{pmatrix}D_6 & N_3 & N_4\\ N_3 & D_7 & N_5\\ N_4 & N_5 & D_8\end{pmatrix}\right]\begin{pmatrix}\chi_{10}(-\infty)\\ \chi_{20}(-\infty)\\ \chi_{22}^{(+)}(-\infty)\end{pmatrix}, \tag{54}$$

where the elements D_i, N_i are given by the following integrals

$$D_1 = -\int_{-\infty}^{\infty} V_{11}^1 dt, \quad D_2 = -\int_{-\infty}^{\infty} [V_{22}^2 \sin^2\beta(t) + V_{22}^1 \cos^2\beta(t)]dt,$$

$$D_3 = D_8 = -\int_{-\infty}^{\infty} \{\tfrac{1}{4} V_{22}^2[1+\cos^2\beta(t)]^2 + V_{22}^1 \sin^2\beta(t)\cos^2\beta(t) + \tfrac{3}{4} V_{21}^0 \sin^4\beta(t)\}dt,$$

$$D_4 = -\int_{-\infty}^{\infty} [V_{11}^1 \cos^2\beta(t) + V_{11}^0 \sin^2\beta(t)]dt,$$

$$D_5 = -\int_{-\infty}^{\infty} \{V_{22}^2 \cos^2\beta(t)\sin^2\beta(t) + V_{22}^1[1-4\sin^2\beta(t)\cos^2\beta(t)]$$

$$+3V_{22}^0 \sin^2\beta(t)\cos^2\beta(t)\}dt, \quad D_6 = -\int_{-\infty}^{\infty} [V_{11}^1 \sin^2\beta(t) + V_{11}^0 \cos^2\beta(t)]dt,$$

$$D_7 = -\int_{-\infty}^{\infty} \{\tfrac{3}{4} V_{22}^2 \sin^4\beta(t) + 3V_{22}^1 \sin^2\beta(t)\cos^2\beta(t) + \tfrac{1}{4} V_{22}^0[3\cos^2\beta(t)-1]^2\}dt,$$

$$N_1 = -\int_{-\infty}^{\infty} V_{21}^1 \cos\beta(t)dt, \quad N_2 = -\int_{-\infty}^{\infty} \{V_{21}^1 \cos\beta(t)[\cos^2\beta(t)-\sin^2\beta(t)]$$

$$+\sqrt{3}\, 3V_{21}^0 \sin^2\beta(t)\cos^2\beta(t)\}dt,$$

$$N_3 = -\int_{-\infty}^{\infty} \{\sqrt{3}\, V_{21}^1 \sin^2\beta(t)\cos\beta(t) + \tfrac{1}{2} V_{21}^0[3\cos^2\beta(t)-1]\}dt,$$

$$N_4 = -N_3/\sqrt{3},$$

$$N_5 = -\int_{-\infty}^{\infty} \left\{\frac{\sqrt{3}}{4} V_{22}^2 \sin^2\beta(t)[1+\cos^2\beta(t)] - \sqrt{3}\, V_{22}^1 \sin^2\beta(t)\cos^2\beta(t)\right.$$

$$\left. + \frac{\sqrt{3}}{4} V_{22}^0 \sin^2\beta(t)[3\cos^2\beta(t)-1]\right\} dt. \tag{55}$$

Using formula (22) we can express all elements of the potential $V_{JJ}^{|M|}$, by the following differences

$$V^{3/2}(\alpha_i 3/2) - V^{1/2}(\alpha_f 1/2) = V_{3/2}^{3/2}, \quad V^{1/2}(\alpha_i 3/2) - V^{1/2}(\alpha_f 1/2) = V_{3/2}^{1/2}. \tag{56}$$

Substituting them into integrals D_i, N_i we have that $D_6 = D_7$. If we assume that the gas is isotropic in the case of a dipole transition we have the following expression in the

sudden approximation

$$\langle \chi_z^{\dagger}(-\infty)\chi_z(+\infty)\rangle_{\text{orientation}} = \tfrac{1}{3}\left\{(1\quad 0)\times\exp\left[i\begin{pmatrix} D_1 & N_1 \\ N_1 & D_2\end{pmatrix}\right]\times\begin{pmatrix}1\\0\end{pmatrix}\right.$$

$$+(1\quad 0)\times\exp\left[i\begin{pmatrix} D_4 & N_2 \\ N_2 & D_5\end{pmatrix}\right]\times\begin{pmatrix}1\\0\end{pmatrix}+(1\quad 0\quad 0)\times\exp\left[i\begin{pmatrix} D_6 & N_3 & -N_3/\sqrt{3} \\ N_3 & D_6 & N_5 \\ -N_3/\sqrt{3} & N_5 & D_8\end{pmatrix}\right]$$

$$\left.\times\begin{pmatrix}1\\0\\0\end{pmatrix}\right\}. \tag{57}$$

First two terms can be transformed with the help of the well known identity

$$\exp\left[i\begin{pmatrix} a & b \\ b & -a\end{pmatrix}\right] = \begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}\cos\Gamma + \frac{i}{\Gamma}\begin{pmatrix} a & b \\ b & -a\end{pmatrix}\sin\Gamma, \tag{58}$$

where $\Gamma = (a^2+b^2)^{1/2}$. In order to transform the remaining term we use the fact that the matrix

$$\hat{W} = \begin{pmatrix} 0 & N_3 & -N_3/\sqrt{3} \\ N_3 & 0 & N_5 \\ -N_3/\sqrt{3} & N_5 & D_8-D_6\end{pmatrix}, \tag{59}$$

is hermitian. Therefore, there exists a unitary transformation $\hat{T}$, which leads $\hat{W}$ to the diagonal form

$$\hat{T}^{-1}\hat{W}\hat{T} = \begin{pmatrix}\lambda_1 & 0 & 0\\ 0 & \lambda_2 & 0\\ 0 & 0 & \lambda_3\end{pmatrix}. \tag{60}$$

Introducing the following coefficients

$$q = -\tfrac{1}{27}(D_8-D_6)^3 - \tfrac{1}{6}(D_8-D_6)(N_5^2-\tfrac{5}{3}N_3^2) + \frac{1}{\sqrt{3}}N_3^2N_5,$$

$$p = \tfrac{1}{9}(D_8-D_6)^2 + \tfrac{4}{9}N_3^2 + \tfrac{1}{3}N_5^2, \tag{61}$$

and

$$\cos\varphi = |q|/p^{3/2}, \tag{62}$$

we have that

$$\lambda_1 = -2 \operatorname{sign}(q)\sqrt{p}\cos(\varphi/3)+(D_8-D_6)/3,$$
$$\lambda_2 = \operatorname{sign}(q)\sqrt{p}\,[\cos(\varphi/3)+\sqrt{3}\sin(\varphi/3)]+(D_8-D_6)/3,$$
$$\lambda_3 = \operatorname{sign}(q)\sqrt{p}\,[\cos(\varphi/3)-\sqrt{3}\sin(\varphi/3)]+(D_8-D_6)/3. \tag{63}$$

Using the above relations we can express $\overline{v_{if}}(\infty)^{\text{sudd}}$ by the functions

$$d(r, a_l, a_k, \ldots; 3/2 \to 1/2)^{\text{sudd}} = \tfrac{2}{3}\int_0^\infty d\varrho\,\varrho\Big[\cos\Gamma_1 \sin\tfrac{1}{2}(D_1+D_2)+\cos\Gamma_2\sin\tfrac{1}{2}(D_4+D_5)$$
$$+\frac{(D_1-D_2)}{2\Gamma_1}\sin\Gamma_1\cos\tfrac{1}{2}(D_1+D_2)+\frac{(D_4-D_5)}{2\Gamma_2}\sin\Gamma_2\cos\tfrac{1}{2}(D_4+D_5)$$
$$+(T_{11})^2\sin(D_6+\lambda_1)+(T_{12})^2\sin(D_6+\lambda_2)+(T_{13})^2\sin(D_6+\lambda_3)\Big],$$

$$w(r, a_l, a_k, \ldots; 3/2 \to 1/2)^{\text{sudd}} = \tfrac{2}{3}\int_0^\infty d\varrho\,\varrho\Big[3-\cos\Gamma_1\cos\tfrac{1}{2}(D_1+D_2)$$
$$-\cos\Gamma_2\cos\tfrac{1}{2}(D_4+D_5)+\frac{(D_1-D_2)}{2\Gamma_1}\sin\Gamma_1\sin\tfrac{1}{2}(D_1+D_2)+\frac{(D_4-D_5)}{2\Gamma_2}$$
$$\times\sin\Gamma_2\sin\tfrac{1}{2}(D_4+D_5)-(T_{11})^2\cos(D_6+\lambda_1)-(T_{12})^2\cos(D_6+\lambda_2)$$
$$-(T_{13})^2\cos(D_6+\lambda_3)\Big], \tag{64}$$

averaged over the velocity (see formulas (27)), where T_{1i}, as elements of $\hat{T}$, are given by

$$T_{1i} = \left[1+\frac{(\lambda_i N_5 - N_3^2/\sqrt{3})^2+(\lambda_i^2-N_3^2)^2}{N_3^2(N_5-\lambda_i/\sqrt{3})^2}\right]^{-1/2}, \tag{65}$$

and

$$\Gamma_1 = \{\tfrac{1}{4}(D_1-D_2)^2+N_1^2\}^{1/2}, \quad \Gamma_2 = \{\tfrac{1}{4}(D_4-D_5)^2+N_2^2\}^{1/2}. \tag{66}$$

The parameters ϱ, r, which appear in formulas (64), are respectively

$$\varrho = b/R_m^{(3/2)}, \quad r = \varepsilon_m^{(3/2)}R_m^{(3/2)}/v, \tag{67}$$

where $R_m^{(3/2)}$ is the minimum position and $\varepsilon_m^{(3/2)}$ is the minimum depth of the potential $V_{3/2}^{3/2}$ (see equations (56)). The parameters a_l, a_k, ... describe the anisotropy of the potential $V_{JJ'}^M$.

Now we want to establish the influence of the induced momenta which appear during the collision, on the line shape. Therefore, we calculate the functions $d(r, a_k, a_l, \ldots; 3/2 \to 1/2)$ and $w(r, a_l, a_k, \ldots; 3/2 \to 1/2)$ neglecting these induced momenta. In other words we assume that all elements of the operator $\hat{V}$, nondiagonal in quantum numbers J,

are equal to zero. Thus, in the sudden approximation we have

$$d(r, a_l, a_k, \ldots; 3/2 \to 1/2)^{\text{sudd-(p)}} = \tfrac{2}{3} \int_0^\infty d\varrho\varrho(\sin D_1 + \sin D_4 + \sin D_6),$$

$$w(r, a_l, a_k, \ldots; 3/2 \to 1/2)^{\text{sudd-(p)}} = \tfrac{2}{3} \int_0^\infty d\varrho\varrho(3 - \cos D_1 - \cos D_4 - \cos D_6), \qquad (67)$$

where D_1, D_4, D_6 have the same form as in equations (55). In Table II a comparison is made between the values of $d(\ldots)$ and $w(\ldots)$ calculated for the Lennard–Jones potential (6–12), respectively, with and without the contribution of the induced momenta. Also

TABLE II

The contribution of induced quadrupole momenta in the dipole transition $3/2 \to 1/2$

r	a_{12}	a_6	$d(\ldots)$	$d(\ldots)^{(p)}$	Δd	$\Delta d\%$	$w(\ldots)$	$w(\ldots)^{(p)}$	Δw	$\Delta w\%$
1	20	5	2.216	2.304	−0.088	4.0%	2.267	2.196	+0.071	3.1%
1	20	3	1.612	1.479	+0.133	8.3%	1.532	1.485	+0.047	3.1%
1	10	3	1.913	1.893	+0.020	1.1%	1.755	1.673	+0.082	4.7%
1	5	3	1.896	1.975	−0.079	4.1%	2.124	1.907	+0.217	10.1%
1	5	2	1.702	1.679	+0.023	1.3%	1.533	1.502	+0.031	2.0%
2	5	2	2.249	2.305	−0.056	2.5%	2.790	2.739	+0.051	1.8%
0.5	5	2	0.919	0.997	−0.078	8.5%	0.991	0.887	+0.104	10.5%
0.1	5	2	0.097	0.086	+0.011	11.3%	0.709	0.721	−0.012	1.7%
0.05	5	2	−0.016	−0.023	+0.007	40%	0.648	0.659	−0.011	1.7%

the following differences $\Delta d = d(\ldots)^{\text{sudd}} - d(\ldots)^{\text{sudd-(p)}}$, $\Delta w = w(\ldots)^{\text{sudd}} - w(\ldots)^{\text{sudd-(p)}}$, and the relative differences $\Delta d\% = [\Delta d/d(\ldots)^{\text{sudd}}] \cdot 100\%$, $\Delta w\% = [\Delta w/w(\ldots)^{\text{sudd}}] \cdot 100\%$, are given there. The values of the relative differences are computed up to an accuracy of $\pm 0.2\%$, the only exception being $\Delta d\%$ for $r = 0.1$ computed to an accuracy of $\pm 2.5\%$ and $\Delta d\%$ for $r = 0.05$ established with a 10% accuracy. As it is clearly seen from this table, the relative differences lie in a range of a few percent which show that the influence of the induced momenta is negligible (these differences are generally smaller than those given in Table I which correspond to the divergences between values respectively computed and obtained from the sudden approximation). However, $\Delta d\%$ becomes significant for small r's and the induced momenta can contribute considerably here.

8. *Summary*

In Table I the value for $d(\ldots)$ and $w(\ldots)$ are given — calculated in the sudden approximation and obtained numerically in the frame of the classical path and impact theory approximations. In most cases the corresponding values differ by a few percent, however, there are individual incidences where the differences is greater than 10%. This argues that there are situations where the sudden approximation fails. In this paper only values for $r \geqslant 1$ were investigated, since for small r's the numerical method becomes too rough.

Computations were performed for the $1 \rightarrow 0$ transition but the conclusions made above can be easily generalized for other transitions.

The second problem we attempted to solve is the influence of induced multipole momenta on the spectral line shape whose appearance is signalized by non-diagonal elements arising in equation (21). However, as it is clearly seen from the calculations obtained for a $3/2 \rightarrow 1/2$ transition in Section 7, this contribution is negligible in most cases of interest. It should be emphasized that the calculations were performed in the sudden approximation and for $r \geqslant 1$ the differences $d(\ldots)$ and $w(\ldots)$ are smaller than the accuracy of the method itself. These differences grow significantly when r decreases but the lack of information concerning the validity of the sudden approximation method for small r's gives no possibility for establishing whether this behavior is caused by the influence of induced momenta or whether it is only a phantom produced by an inadequacy of the method.

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