THE FRANCK-CONDON PRINCIPLE AND THE BROADENING OF ISOLATED SPECTRAL LINES IN PLASMAS

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The role of the Franck-Condon principle in the description of the pressure broadening of isolated spectral lines is investigated on the basis of the Jabłoński theory. Expressions for the correlation function of this theory are derived both in the semiclassical approximation as well as in a general way. First it is shown that the quasi-static Margenau-Holtsmark theory of line broadening follows from that of Jabłoński in the asymptotic case of heavy perturbers when the classical form of the Franck-Condon principle can be applied. On the other hand, the results of quantum-mechanical impact theory of line broadening due to electrons are re-derived under assumptions analogous to those used in the theories of scattering processes. For the non-spherically symmetrical interactions a general expression for the line shape is given which is in a close analogy with that derived on the basis of the resolvent operator technique.

1. *Introduction*

The phenomenon of the broadening of spectral lines due to the interactions with foreign gas atoms has been theoretically investigated in many different ways. Frequently used in practical applications are the impact treatments initiated on the classical ground by Lorentz [1], Lenz [2], Weisskopf [3] and Lindholm [4] and then generalized with the help of quantum-mechanical methods by Anderson [5], Sobelman [6], Baranger [7], [8], Kolb and Griem [9] and others. Opposite to them are the so-called statistical or (more appropriately) quasi-static theories developed for the first time by Holtsmark [10] for the Stark Broadening caused by interactions with ions and by Kuhn [11] and Margenau [12] for the Van der Waals interactions. These theories are based on the earlier formulation of the Franck-Condon principle (FCP), first introduced to the explanation of the pressure effects on spectral lines by Jabłoński in 1931 [13]. The most general form of the quasi-static theory has been worked out by Margenau [14].

The first fully quantum-mechanical theory of pressure broadening of spectral lines was formulated by Jabłoński [15] ,[16], [17] in a close analogy with the treatment of electronic band spectra in diatomic molecules, *i. e.* by application of the quantum-mechanical version

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of the FCP to calculations of the intensity distribution in the broadened line. Some years ago Jabłoński [18], [19], [20] has modified his theory indicating that the above analogy is incomplete because in the case of line broadening the shortness of the lifetime of the quasi-molecule formed by the emitter with perturbers in the state of collision should be taken into account. An essential feature of this treatment is that an interaction sphere of the emitter with perturbers is introduced. The radius ϱ_0 of this sphere can be determined from the criterion proposed by Jabłoński [18], [20]. This criterion says that only collisions for which the interaction potential $V(r)$ fulfil the condition:

$$\left| \int_{-\infty}^{+\infty} V(r(t))\, dt \right| \geqslant \hbar$$

are considered as leading to the formation of a quasi-molecule. In this formula $r(t) = (\varrho^2 + v^2 t^2)^{1/2}$ is the distance of the perturber from the emitter as a function of time t, ϱ the impact parameter and v the relative velocity of colliding particles. This version of Jabłoński's theory has been recently used to numerical calculations of the shape of Hg-resonance line broadened by A and He for densities above 15 Amagat [21], [22]. Although the earlier form of the FCP was used in these calculations a good agreement between the computed and experimental intensity distribution was obtained. The radius ϱ_0 of the interaction sphere depends on the electronic state of the emitter and on the velocity v. In the case of such systems as Hg-A and Hg-He this radius is less than 10 Å. A somewhat different situation, however, arises in the case of line broadening due to charged perturbers in ionized gases (plasmas). When the emitter is an ion then the above criterion leads to infinite value of the radius ϱ_0, since the interaction potential contains the Coulomb term. For neutral emitters in a plasma this criterion gives formally the finite value of ϱ_0. It should be noted, however, that in plasmas the characteristic distance is the Debye length, which is a measure of mutual screening of ions and electrons. Thus, it seems to be convenient to assume generally the radius ϱ_0 to be equal to the radius R of the macroscopic spherical container (*cf.* [16]). The problem of line broadening in a plasma has been solved in two different ways. Namely, the broadening by ions is usually taken into account on the basis of the quasi-static theory given by Holtsmark [10]. For electrons, however, this approach cannot be applied because they are moving too fast to be treated in this way. The theory of line broadening due to electrons has been proposed by Sobelman [6], [23] and Baranger [7]. Their starting point is similar to that of Jabłoński [16] but they apply the impact approximation analogous to that used in calssical collision theories. Another form of impact theory based on the assumption that perturbing electrons are moving along classical path has been given by Kolb and Griem [9] and Baranger [8] especially for the cases of overlapping lines. Numerous computations have proves that for plasmas with the density number of electrons $N_e \leqslant 10^{17}$ cm^{-3} the quantum-mechanical impact theories lead to a very good agreement of the calculated line shapes with the measured ones (*cf.* [24], [25], [26] and papers quoted there). The connection between the Jabłoński theory and quantum-mechanical impact theories has not been sufficinetly established so far, although some proofs were made by Sobelman [23] and Baranger [7] (*cf.* also [27]). Few years ago Fano [28] proposed the pressure broadening theory based on the resolvent operator technique and showed that in the central part of the line his formalism leads to the same results as those given by impact theories. Fano's approach has been recently developed by Fiutak [29], [30], who has shown that in the wings of the line such a treatment leads to the results of Jabłoński's theory [31], [32].

The present paper is devoted to the detailed investigation of special cases of the Jabłoński theory in its full quantum-mechanical form; in particular the connections between this theory and other theories developed from standpoints differing from that of Jabłoński are discussed. Only the cases of isolated lines will be considered here although the effects of overlapping lines can be also, in principle, included to the Jabłoński sheme. The main attention is devoted to the application of the Jabłoński quasi-molecular treatment to the broadening of spectral lines in plasmas so that all discussion is carried out assuming the radius of the interaction sphere to be equal to the macroscopic radius of the container. The procedure applied here is based on the correlation formulation of Jabłoński's theory given in a previous paper [34]. It seems that this procedure illustrates well the role of the Franck-Condon principle in the theoretical description of line broadening phenomena. Most of the considerations concern the spherically symmetrical interactions and are based on the WKB semiclassical approximation. This approximation is fruitful in many cases and has been recently succesfully adopted by Mies [35] to the explanation of the oscillatory structure of wings of vacuum-ultraviolet emission lines.

2. *The semiclassical correlation function*

In a recent paper [34] it was shown that in the case of macroscopic interaction sphere the Jabłoński basic formula for the intensity distribution $I(\omega)$ in a broadened line can be written in the form

$$I(\omega) = \frac{1}{2\pi}\int\limits_{-\infty}^{+\infty} ds\, e^{-i(\omega-\omega_0)s}\Phi(s), \tag{1}$$

where ω_0 denotes the unperturbed frequency of the line emitted (or absorbed) due to the transitions from the initial level with energy E_i^0 to the final level with energy E_f^0, *i.e.* $\omega_0 \equiv \omega_{if}^0 = \frac{E_i^0 - E_f^0}{\hbar}$. The correlation function $\Phi(s)$ is given by

$$\Phi(s) = e^{-NV_0[1-M(s)]} \tag{2}$$

(*cf.* Eq. (26) of paper [34]). Here N denotes the number of perturbers per unit volume and V_0 the total volume of a gas (container). $M(s)$ is defined as follows:

$$M(s) = \int\limits_{-\infty}^{+\infty} d\xi e^{i\xi s} I_1^c(\xi), \tag{3}$$

where $I_1^c(\xi)$ is the intensity distribution resulting from the interaction with a single perturber. If the quantum-mechanical version of the FCP is applied, then according to [16] for the case of spherically symmetrical interactions the $I_1^c(\xi)$ distribution can be generally presented in the from

$$I_1^c(\xi) = \sum_{l=0}^{l_{\max}} Q(l) A^2_{vi,vf,l}(\xi) \frac{dv_f}{dE_{vf}}, \tag{4}$$

where

$$A_{vi,vf,l}(\xi) = \langle \psi_{vi,l} | \psi_{vf,l} \rangle \equiv \int_0^R \psi_{vi,l}(r) \psi_{vf,l}(r) dr \tag{5}$$

is the overlap integral, $\psi_{vi,l}(r)$ and $\psi_{vf,l}(r)$ are the radial wave functions of the relative motion for the initial (i) and final (f) state of the emitter, respectively. $Q(l)$ denotes the probability of occurence of a certain value l of the quantum number of the angular momentum of the relative motion and $\frac{dv_f}{dE_{vf}}$ the density of final translational levels with energies E_{v_f}. In this procedure the continuous levels of the energy of motion of perturbers are treated as the discrete ones by introducing of the boundary condition $\psi_{v,l}(r) = 0$ for $r = R$, R being the radius of a container. According to [16] the probability distribution function $Q(l)$ and the density of levels $\frac{dv}{dE_v}$ can be presented in the form

$$Q(l) = \frac{3\hbar^2(2l+1)}{2R^2 p_v(\infty)} \tag{6}$$

$$\frac{dv}{dE_v} = \frac{\mu R}{\pi p_v(\infty)}, \tag{7}$$

where $p_v(\infty) = \sqrt{2\mu E_v}$ is the value of the radial component of the relative momentum for $r \to \infty$ and μ is the reduced mass. Substituting Eqs (6) and (7) into Eq. (3) one obtains

$$M(s) = a \sum_{l=0}^{l_{\max}} (2l+1) \int_{-\infty}^{+\infty} d\xi e^{i\xi s} A_l^2(\xi), \tag{8}$$

where

$$a = \frac{3}{4} \frac{\hbar^2}{\pi E_v p_v(\infty) R}. \tag{9}$$

and

$$A_l(\xi) \equiv A_{vi,vf,l}(\xi); \quad \hbar\xi = E_{vi} - E_{vf}. \tag{10}$$

Eqs (1) and (2) together with (8) represent a general solution of the line shape problem for the case of macroscopic interaction sphere. In general case the exact calculation of overlap integrals $A_1(\xi)$ is very difficult and can be carried out only by numerical methods. In many cases however good results can be obtained by using the WKB approximation. In this approximation the wave function $\psi_{v_i,l}(r)$ can be written as

$$\psi_{vi,l}(r) = \left(\frac{2p_{vi}(\infty)}{Rp_{vi}(r)}\right)^{1/2} \frac{1}{2i} \left\{\exp\left(i\left[\frac{1}{\hbar}\int\limits_{r_0}^{r} p_{vi}(r)\,dr + \delta_i(l)\right]\right) - \right.$$

$$\left. - \exp\left(-i\left[\frac{1}{\hbar}\int\limits_{r_0}^{r} p_{vi}(r)\,dr + \delta_i(l)\right]\right)\right\}, \tag{11}$$

where $\delta_i(l)$ is the phase and

$$p_{vi}(r) = \left[2\mu\,(E_{vi} - V_i(r)) - \frac{\hbar^2 l(l+1)}{r^2}\right]^{1/2} \tag{12}$$

is the radial component of relative momentum. $V_i(r)$ is the interaction energy as a function of the distance r of the perturber from the emitter in the state $|i\rangle$ and r_0 the classical turning point for which $p_{vi}(r_0) = 0$. For the final state of the emitter the function $\psi_{vf,l}(r)$ is given by the same expression as Eq. (10) with the replacing of subscript i replaced by f. This approximation breaks down in the neighbourhood of r_0. All effects originated in this region are neglected here. In order to include such effects it is necessary to use either the numerical solution of the Schrödinger equation or to apply the Kramers method [36] expressing the wave functions by means of Airy's integrals. These questions are not discussed here.

Substituting Eq. (10) into Eq. (5) and neglecting the terms which are the very rapidly oscillating functions of r the overlap integral $A_l(\xi)$ can be written in the form (*cf.* Eq. (33) of [16])

$$A_l(\xi) = \frac{[p_{vi}(\infty)p_{vf}(\infty)]^{1/2}}{2R} \int\limits_0^R \frac{dr}{[p_{vi}(r)\,p_{vf}(r)]^{1/2}} \left\{\exp\left(\frac{i}{\hbar}\int\limits_{r_0}^{r} [p_{vi}(r) - p_{vf}(r)]\,dr + \right.\right.$$

$$\left.\left. + i[\delta_i(l) - \delta_f(l)]\right) + \exp\left(-\frac{i}{\hbar}\int\limits_{r_0}^{r} [p_{vi}(r) - p_{vf}(r)]\,dr - i[\delta_i(l) - \delta_f(l)]\right)\right\}. \tag{13}$$

The overlap integral in this form is still very complicated and cannot be further simplified without additional assumptions. There are, however, two extremaly different physical conditions for which Eq. (12) leads to the intensity distribution expressed in a clossed form. It is shown below that these limiting cases of the Jabłoński theory can be identified with two kinds of pressure broadening theories known as the quasi-static and impact theories.

3. *Quasi-static case*

Let us suppose that the average distance between particles is sufficiently small so that the emitter permanently and strongly interacts with a perturber. Jabłoński [16] has pointed out that the largest contribution to the value of the overlap integral given by Eq. (13) comes from the region of r in the neighbourhood of $r = r_c$ for which $p_{vi}(r_c) = p_{vf}(r_c)$, because just in this region the oscillation of the integrand of Eq. (13) becomes slowest. It follows from the condition $p_{vi}(r_c) = p_{vf}(r_c)$ that r_c is that distance at which, according to the earlier version of FCP, the transition $v_i \rightarrow v_f$ takes place leading to the shift of frequency equal to

$$\xi = \omega - \omega_0 = \frac{1}{\hbar}\,(V_i(r) - V_f(r)). \tag{14}$$

As the next step Jabłoński has expanded the integrand of Eq. (13) in series in the neighbourhood of r_c and neglected all but the first two nonvanishing terms. Substitution of Eq. (13) into Eq. (4) and some further simplifications (allowed in the case of sufficiently heavy perturbers) lead to

$$I_1^c(\xi)_{vi} = \frac{3r_c^2}{R^3}\left[1 - \frac{V_i(r_c)}{E_{vi}}\right]^{1/2} \frac{dr_c}{d\xi}. \tag{15}$$

$I_1^c(\xi)_{vi}$ should be averaged over all energies E_{vi} occurring in the gas under consideration although in many cases the substitution $E_{vi} = \frac{3}{2}kT$, as was done by Jabłoński [16], appears to be a sufficient approximation. This averaging, however, can be easily performed assuming the Maxwell-Boltzmann distribution function $f(E)$ for energy of perturbers given by

$$f(E) = \frac{2}{\sqrt{\pi}}\,\frac{\sqrt{E}}{(kT)^{3/2}}\,e^{-\frac{E}{kT}} \tag{16}$$

(k is the Boltzmann constant and T the temperature).

The resulting averaged distribution is:

$$\begin{aligned} I_1^c(\xi) &= \int_{V_i(r_c)}^{\infty} I_1^c(\xi)_{vi} f(E_{vi})\, dE_{vi} \\ &= \frac{6r_c^2}{\sqrt{\pi}\,R^3(kT)^{3/2}}\,\frac{dr_c}{d\xi}\int_{V_i(r_c)}^{\infty} [E_{vi} - V_i(r_c)]^{1/2}\, e^{-\frac{E_{vi}}{kT}}\, dE_{vi}, \end{aligned} \tag{17}$$

where the lower limit of integration is $V_i(r_c)$ because Eq. (15) is valid only for $E_{vi} \geqslant V_i(r_c)$. The integration in Eq. (17) can be performed analytically:

$$\int_{V_i(r_c)}^{\infty} [E_{vi} - V_i(r_c)]^{1/2} e^{-\frac{E_{vi}}{kT}}\, dE_{vi} = (kT)^{3/2}\Gamma(\tfrac{3}{2})e^{-\frac{V_i(r_c)}{kT}}, \tag{18}$$

and thus, since $\Gamma(\frac{3}{2}) = \frac{\sqrt{\pi}}{2}$,

$$I_1^c(\xi) = \frac{3r_c^2}{R^3}\,e^{-\frac{V_i(r_c)}{kT}}\,\frac{dr_c}{d\xi}. \tag{19}$$

Substituting this formula into Eq. (3) $M(s)$ can be written as

$$M(s) = \frac{3}{R^3}\int_{-\infty}^{+\infty} r_c^2\,\frac{dr_c}{d\xi}\,e^{-\frac{V_i(r_c)}{kT}}\,e^{i\xi s}\,d\xi. \tag{20}$$

If, according to Eq. (14), ξ is expressed as a function of r_c (hereafter denoted by r): $\xi = \Delta\omega(r)$ then $M(s)$ can be rewritten as the integral over r:

$$M(s) = \frac{3}{R^3} \int_0^R r^2 e^{i\Delta\omega(r)s} e^{-\frac{V_i(r)}{kT}} dr. \tag{21}$$

With this $M(s)$ the correlation function (Eq. (2)) becomes

$$\Phi(s) = e^{-4\pi N\beta(s)}, \tag{22}$$

where

$$\beta(s) = \int_0^R [1 - e^{i\Delta\omega(r)s - \frac{V_i(r)}{kT}}] r^2 dr. \tag{23}$$

Hence the intensity distribution in the broadened line (Eq. (1)) is

$$I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} ds e^{-i(\omega-\omega_0)s - 4\pi N\beta(s)} \tag{24}$$

For $V_i(r) \ll kT$ Eq. (23) becomes approximately

$$\beta(s) = \int_0^R [1 - e^{i\Delta\omega(r)s}] r^2 dr. \tag{25}$$

Eq. (24) with $\beta(s)$ given by Eq. (25) is identical with the most general formula for the line shape of the quasi-static theory of pressure broadening proposed by Margenau in 1951 [14].

In the case of broadening by ions the frequency shifts, $\Delta\omega$ are caused by the electric fields $\boldsymbol{E}$ produced by particular ions situated at different distances from the emitter. As was shown by Traving [37] [38] the Hotsmark expression for the intensity distribution in the line broadened by ions can be formally derived from Eqs (24) and (25) by replacing of scalar magnitudes $\Delta\omega$ and s by vectors $\boldsymbol{E}$ and $\boldsymbol{\sigma}$ ($|\boldsymbol{\sigma}| = s$), respetively.

It should be noted that for neutral gases and in the case of a Van der Waals potential ($\Delta\omega(r) = C_6 \cdot r^{-6}$) the integration in Eq. (24) with $\beta(s)$ given by Eq. (25) can be carried out analytically and this leads to the well known Margenau's distribution (*cf.* [14] and [12]) with both half-width and shift of the line proportional to the square of perturbers concentration. Bergeon *et al.* [39] [40] have applied the Lennard-Jones potential to calculations of $\beta(s)$ (Eq. (25)) and have shown that in certain cases the inversion of the direction of the line shift, as observed for Rb-lines perturbed by heavier atoms at very high pressures, follows from Eq. (24). Recently, Hindmarsh and Farr [41], [42] (*cf.* also [43]) have shown that for low pressures of perturbing gases Eqs (24) and (25) with the Lennard-Jones potential do give rise to the occurrence of additional maxima on the long wavelength side of the line (red satellite bands). The calculated positions of these maxima appeared to be in satisfactory agreement with the measured positions of the maxima of red satellites produced by Kr on the potassium line λ 4047 Å [44].

4. *Scattering case*

(*Theory of line broadening by electrons*)

Now the second asymptotic case of Jabłoński's theory, entirely different from that discussed above, will be considered. Let us calculate namely the overlap integral given by Eq. (13) assuming that all the perturbers are at the distances r so large that their motion can be treated practically as a free motion. First of all let us remark that with the WKB wave functions the overlap integral $A_l(\xi)$ in Eq. (13) can be generally rewritten in the form

$$A_l(\xi) = \frac{[p_{vi}(\infty)p_{vf}(\infty)]^{1/2}}{2R} \int\limits_0^R \frac{dr}{[p_{vi}(r)p_{vf}(r)]^{1/2}} \times$$

$$\times \left\{\exp\left[\frac{2i\mu}{\hbar}\int\limits_{r_0}^{r} \frac{E_{vi}-E_{vf}+V_i(r)-V_f(r)}{p_{vi}(r)+p_{vf}(r)}\, dr + i(\delta_i(l)-\delta_f(l))\right] + \right.$$

$$\left. + \exp\left[-\frac{2i\mu}{\hbar}\int\limits_{r_0}^{r} \frac{E_{vi}-E_{vf}+V_i(r)-V_f(r)}{p_{vi}(r)+p_{vf}(r)}\, dr - i(\delta_i(l)-\delta_f(l))\right]\right\}, \tag{26}$$

where the substitution

$$p_{vi}(r)-p_{vf}(r) = \frac{2\mu}{p_{vi}(r)+p_{vf}(r)}\,[E_{vi}-E_{vf}+V_i(r)-V_f(r)] \tag{27}$$

resulting from Eq. (11) was introduced.

Taking into account only the region of very large r's so that the perturbers motion can be practically treated as the free one we assume that: $V_i(r) \approx 0$, $V_f(r) \approx 0$ and $p_v(r) \approx \approx p_v(\infty)$. Moreover for real physical situations it can be assumed that

$$p_{vi}(r)+p_{vf}(r) \approx 2p_{vi}(r) \approx 2p_{vi}(\infty),$$
$$p_{vi}(r)p_{vf}(r) \approx [p_{vi}(r)]^2 \approx [p_{vi}(\infty)]^2. \tag{28}$$

The above assumptions are analogous to those applied in the quantum description of scattering processes. It is obvious that they can be valid only for sufficiently low densities of perturbing particles. Under these assumptions and for $r_0 = 0$ Eq. (26) becomes

$$A_l(\xi) = \frac{1}{2R}\int\limits_0^R dr \left\{e^{i\left(\frac{\mu\xi}{p_v(\infty)}r+\delta_i(l)-\delta_f(l)\right)} + e^{-i\left(\frac{\mu\xi}{p_v(\infty)}r+\delta_i(l)-\delta_f(l)\right)}\right\}, \tag{29}$$

where $\xi = \frac{1}{\hbar}(E_{vi}-E_{vf})$ and $p_{vi}(\infty)$ is denoted simply by $p_v(\infty)$.

Eq. (29) can be easily transformed to the following form

$$A_l(\xi) = \frac{1}{2R}\left\{\int\limits_{-R}^{0} dr e^{-i\frac{\mu\xi}{p_v(\infty)}r+i(\delta_i(l)-\delta_f(l))} + \int\limits_0^R dr e^{-i\frac{\mu\xi}{p_v(\infty)}r-i(\delta_i(l)-\delta_f(l))}\right\} \tag{30}$$

Introducing the Heaviside step function $f_l(r)$ defined by

$$f_l(r) = \begin{cases} +(\delta_i(l)-\delta_f(l)) & \text{for} \quad r \geqslant 0, \\ -(\delta_i(l)-\delta_f(l)) & \text{for} \quad r < 0, \end{cases} \tag{31}$$

one obtains

$$A_l(\xi) = \frac{1}{2R} \int_{-R}^{R} d\, r e^{-i \frac{\mu\xi}{p_v(\infty)} r - i f_l(r)} \tag{32}$$

Hence, the square of the overlap integral $A_l^2(\xi) = A_l(\xi) \cdot A_l^*(\xi)$ is given by

$$A_l^2(\xi) = \frac{1}{4R^2} \int_{-R}^{R} \int_{-R}^{R} dr_1 dr_2\, e^{-i \frac{\mu\xi}{p_v(\infty)} (r_1-r_2) - i[f_l(r_1)-f_l(r_2)]}. \tag{33}$$

Substitution of this expression into Eq. (8) leads in this case to

$$M(s) = \frac{a}{4R^2} \sum_{l=0}^{l_{\max}} (2l+1) \int_{-R}^{R} \int_{-R}^{R} dr_1 dr_2 e^{-i[f_l(r_1)-f_l(r_2)]} \times$$

$$\times \int_{-\infty}^{+\infty} d\xi\, e^{i\xi \left(s - \frac{r_1-r_2}{p_v(\infty)} \mu\right)}. \tag{34}$$

Since

$$\int_{-\infty}^{+\infty} d\xi\, e^{i\xi \left(s - \frac{r_1-r_2}{p_v(\infty)} \mu\right)} = \frac{2\, \pi p_v(\infty)}{\mu}\, \delta \left(\frac{(p_v(\infty)}{\mu}\, s + r_2 - r_1 \right), \tag{35}$$

where δ denotes the Dirac function, Eq. (34) becomes

$$M(s) = \frac{\pi a p_v(\infty)}{2R^2 \mu} \sum_{l=0}^{l_{\max}} (2l+1) \int_{-R}^{R} dr_2\, e^{i f_l(r_2)} \int_{-R}^{R} dr_1\, e^{-i f_l(r_1)}\, \delta \left(\frac{p_v(\infty)}{\mu}\, s + r_2 - r_1 \right). \tag{36}$$

However,

$$\int_{-R}^{R} dr_1 e^{-i f_l(r_1)}\, \delta \left(\frac{p_v(\infty)}{\mu}\, s + r_2 - r_1 \right) = e^{-i f_l \left(\frac{p_v(\infty)}{\mu} s + r_2 \right)}, \tag{37}$$

so that Eq. (36) yields

$$M(s) = \frac{\pi a p_v(\infty)}{2R^2 \mu} \sum_{l=0}^{l_{\max}} (2l+1) \int_{-R}^{R} dr_2\, e^{i f_l(r_2) + i f_l \left(\frac{p_v(\infty)}{\mu} s + r_2 \right)}, \tag{38}$$

where the function $f_l\left(\frac{p_v(\infty)}{\mu}s+r_2\right)$ is defined in the same manner as the function $f_l(r)$ in Eq. (31). Using this definition it is easy to show that Eq. (38) can be transformed to the form

$$M(s)=\frac{3}{4}\frac{\hbar^2}{p_v^2(\infty)R^3}\sum_{l=0}^{l_{\max}}(2l+1)\left\{2R-s\frac{p_v(\infty)}{\mu}\left[1-e^{-2i(\delta_i(l)-\delta_f(l))}\right]\right\}. \tag{39}$$

The factor before the sum results from Eq. (9) if the equality

$$\frac{\pi a p_v(\infty)}{2R^2\mu}=\frac{3}{4}\frac{\hbar^2}{p_v^2(\infty)R^3} \tag{40}$$

is taken into account.

Let us remark that according to Eq. (6)

$$\frac{3}{4}\frac{\hbar^2}{p_v^2(\infty)R^3}\sum_{l=0}^{l_{\max}}(2l+1)2R\equiv\sum_{l=0}^{l_{\max}}Q(l)=1, \tag{41}$$

where the value $l_{\max}$ must be chosen so as to fulfil this condition. Thus Eq. (39) becomes

$$M(s)=1-\frac{3\hbar^2 vs}{4R^3p_v^2(\infty)}\sum_{l=0}^{l_{\max}}(2l+1)\left[1-e^{-2i(\delta_i(l)-\delta_f(l))}\right], \tag{42}$$

where the substitution $p_v(\infty)=\mu v$, v being the relative velocity, was introduced. Let us also substitute $p_v(\infty)=\hbar k$ and denote

$$\sigma=\frac{\pi}{k^2}\sum_{l=0}^{l_{\max}}(2l+1)\left[1-e^{2i(\delta_f(l)-\delta_i(l))}\right], \tag{43}$$

then Eq. (42) yields

$$M(s)=1-\frac{v\sigma}{V_0}s, \tag{44}$$

where $V_0=\frac{4}{3}\pi R^3$ is the total volume of the container. According to Eq. (2) the correlation function $\Phi(s)$ is now given by

$$\Phi(s)=e^{-Nv\sigma s}. \tag{45}$$

With this $\Phi(s)$ Eq. (1) leads to the Lorentzian intensity distribution

$$I(\omega)=\frac{\gamma}{2\pi}\frac{1}{(\omega-\omega_0-\Delta)^2+\left(\frac{\gamma}{2}\right)^2}, \tag{46}$$

where the shift Δ and half-width γ of the line can be written as

$$\gamma = 2Nv \operatorname{Re} \sigma = 2Nv \frac{\pi}{k^2} \sum_{l=0}^{l_{\max}} (2l+1)[1-\cos 2(\delta_f(l)-\delta_i(l))], \tag{47}$$

$$\Delta = -Nv \operatorname{Im} \sigma = Nv \frac{\pi}{k^2} \sum_{l=0}^{l_{\max}} (2l+1) \sin 2 (\delta_f(l)-\delta_i(l)). \tag{48}$$

Eqs (47) and (48) are the basic formulae of the quantum-mechanical impact theory of the pressure broadening of isolated spectral lines. They were first derived by Sobelman [6], [23] for interactions having spherical symmetry. Baranger [7] used the modern methods of the quantum scattering theory and showed generally that both the half-width and shift of the line can be expressed in terms of the elements of the S-matrix. For the case of the spherically symmetrical interactions he obtained Eqs (47) and (48). The analogy between the scattering of atoms (or electrons on atoms) and this asymptotic case of the pressure broadening of spectral lines exists in Eqs (47)–(48) because both these phenomena are described by the same phases [45].

If the condition $V(r) \ll kT$ is fulfilled, the phase $\delta(l)$ can be expressed as [45]

$$\delta_i(l) = -\int_{\frac{\hbar l}{p_v(\infty)}}^{\infty} \frac{\mu V_i(r)}{\hbar^2 \left\{\frac{p_v^2(\infty)}{\hbar^2} - \frac{(l+\frac{1}{2})^2}{r^2}\right\}} dr \tag{49}$$

In the classical limit, *i.e.* for large l, $\hbar\sqrt{l(l+1)} \approx \hbar l = p_v(\infty)\varrho$ (ϱ being the impact parameter) so that $\delta_i(l)$ can be expressed as a function of ϱ: $\delta_i(l) = \delta_i(\varrho)$ and $\delta_f(l) = \delta_f(\varrho)$. Assuming that the perturbers are moving along straight lines, the distance $r(t)$ of the perturber from the emitter as a function of time t is equal to $r(t) = (\varrho^2+v^2t^2)^{1/2}$. Under these assumptions it is easy to show that

$$\delta(\varrho) = -\frac{1}{2\hbar} \int_{-\infty}^{+\infty} V((\varrho^2+v^2t^2)^{1/2}) dt, \tag{50}$$

where $V(r(t)) = V(\varrho^2+v^2t^2)^{1/2})$ is the interaction potential expressed as a function of time. Hence

$$2(\delta_f(l)-\delta_i(l)) = \frac{1}{\hbar} \int_{-\infty}^{+\infty} \Delta V(r(t)) dt = \int_{-\infty}^{+\infty} \Delta\omega(r(t))\, dt \equiv \eta(\varrho), \tag{51}$$

$\eta(\varrho)$ is the phase shift of the classical oscillator resulting from the collision with a perturber for the value ϱ of the impact parameter. Moreover, in classical case the summation over l

in Eqs (47)–(48) can be replaced by the integration over ϱ using the following condition

$$\frac{\pi h^2}{p_v^2(\infty)}(2l+1) = 2\pi\varrho d\varrho \tag{52}$$

resulting from the comparison of the quantum probability distribution $Q(l)$ (Eq. (6)) with a classical distribution $Q(\varrho)$ for impact parameters ϱ (*cf.* [16]). Then Eqs (47)–(48) can be transformed to the form

$$\gamma = 2Nv\int_0^\infty [1-\cos\eta(\varrho)]\, 2\pi\varrho d\varrho, \tag{53}$$

$$\Delta = Nv\int_0^\infty \sin\eta(\varrho)\cdot 2\pi\varrho d\varrho. \tag{54}$$

These expressions are the Lindholm-Foley formulae for the half-width and shift of the line ([4], [27]). Let us further mention that the inelastic collisions can be taken into account by introducing of the complex phases $\delta(l)$ instead of real ones ($\delta(l)\to\delta(l)+i\Gamma(l)$). Then, in this case Eqs (47)–(48) should be replaced by the following formulae (*cf.* [23]):

$$\gamma = 2Nv\frac{\pi}{k^2}\sum_{l=0}^{l_{\max}}(2l+1)[1-e^{-2(\Gamma_i(l)+\Gamma_f(l))}\cos 2(\delta_f(l)-\delta_i(l))], \tag{55}$$

$$\Delta = Nv\frac{\pi}{k^2}\sum_{l=0}^{l_{\max}}(2l+1)e^{-2(\Gamma_i(l)+\Gamma_f(l))}\sin 2\,(\delta_f(l)-\delta_i(l)). \tag{56}$$

According to Vainshtein and Sobelman [46] $\Gamma_i(l)$ and $\Gamma_f(l)$ can be expressed by means of the total probabilities of transitions from levels i and f, respectively, to other levels of the emitter induced by the collisions with the perturbing electron (non-adiabatic collisions) (*cf.* also [23]).

5. *General remarks*

All the considerations given above concern the case of spherically symmetrical fields and the formalism used there was the same as that applied by Jabłoński [16], *i.e.* the continuous levels of the translational energy were treated as the discrete levels. After multiplying of the squares of the overlap integrals by the density levels factor and averaging over all l with the weights $Q(l)$ this procedure leads to Eq. (4) for the distribution $I_l^c(\xi)$. However, for the problems of line broadening due to non-spherically symmetrical internactions it is convenient to rewrite Eq. (4) in a more general fashion starting from the general quantum-mechanical formula for the transition probability between continuous states.

Let E_i^0 and E_f^0 denote the energies of the isolated emitter in the initial and final states, respectively. In the Born-Oppenheimer approximation the total energies of the system are equal to $E_i = E_i^0 + \varepsilon_i$ and $E_f = E_f^0 + \varepsilon_f$, ε_i and ε_f being the energies of the relative motion of the perturber for the initial and final states of the emitter. Let us denote

$$\omega_{if} = \frac{1}{\hbar}(E_i - E_f) = \omega_0 + \frac{1}{\hbar}(\varepsilon_i - \varepsilon_f), \tag{57}$$

where $\omega_0 = \frac{1}{\hbar}(E_i^0 - E_f^0)$ is the unperturbed frequency of the line. Applying the Franck-Condon principle the $I_l^c(\xi)$ "Condon intensity distribution" can be now written generally as

$$I_1^c(\xi) = \sum_{i,f} \delta(\xi + \omega_0 - \omega_{if}) |\langle \psi_i | \psi_f \rangle|^2 \varrho_i, \tag{58}$$

where ψ_i and ψ_f are the wave functions of the relative motion of the perturber for the initial and final electronic state of the emitter, respectively; ϱ_i denotes the probability the occurence of a given initial state of the perturber motion (the single perturber density matrix). The functions ψ_i and ψ_f are the solutions of the Schrödinger equations:

$$H_i|\psi_i\rangle = \varepsilon_i|\psi_i|\rangle \quad \text{and} \quad H_f|\psi_f\rangle = \varepsilon_f|\psi_f\rangle, \tag{59}$$

where H_i and H_f are the hamiltonians of the relative motion of the perturber and can be expressed as

$$H_i = K + V_i \quad \text{and} \quad H = K + V_f \tag{60}$$

where K denotes the kinetic energy hamiltonian and V_i and V_f are the interaction energy operators for the initatial and final state of the emitter, respectively.

Substituting Eq. (58) into Eq. (3) the $M(s)$ function can be easily transformed to the following form

$$M(s) = \sum_{i,f} e^{i(\omega_{if} - \omega_0)s} |\langle \psi_i | \psi_f \rangle|^2 \varrho_i. \tag{61}$$

According to Eqs (57)–(58) this formula can be rewritten as

$$M(s) = \mathrm{Tr}\,[e^{-\frac{i}{\hbar}H_f s} e^{\frac{i}{\hbar}H_i s} \hat{\varrho}], \tag{62}$$

where the trace is to be taken over the states of the relative motion of the perturber, and $\hat{\varrho}$ is the perturber density matrix. Using the integral equation (*cf. e.g.* [7])

$$T(s) \equiv e^{-\frac{i}{\hbar}H_f s} e^{\frac{i}{\hbar}H_i s} = 1 - \frac{i}{\hbar} \int_0^s dt e^{-\frac{i}{\hbar}H_f t} (H_f - H_i) e^{\frac{i}{\hbar}H_i t}, \tag{63}$$

Eq. (62) yields

$$M(s) = 1 - G(s), \tag{64}$$

where

$$G(s) = \mathrm{Tr}\,[(1 - T(s))\hat{\varrho}], \tag{65}$$

or

$$G(s) = \frac{i}{\hbar} \int_0^s dt\, \mathrm{Tr}\, [e^{-\frac{i}{\hbar}H_f t}(H_f - H_i)e^{\frac{i}{\hbar}H_i t}\hat{\varrho}], \tag{66}$$

$T(s)$ being defined by Eq. (63)

According to Eq. (2) and (64) the correlation function is now given by

$$\Phi(s) = e^{-NV_0 G(s)} \tag{67}$$

This form of the correlation function is identical with that first derived by Baranger [7]. Substituting this $\Phi(s)$ into (Eq. 1) the intensity distribution $I(\omega)$ can be written in the form

$$I(\omega) = \frac{1}{\pi} \mathrm{Re} \int_0^\infty ds e^{-i(\omega-\omega_0)s} e^{-NV_0 G(s)}. \tag{68}$$

In the asymptotic case of large s this formula leads to the Lorentzian line shape with both half-width and shift proportional to the perturbers density. As was shown by Baranger [7] in this case the half-width and shift of the line can be expressed in terms of the scattering amplitudes of the perturber by the emitter in its initial and final state. For the spherically symmetrical interactions the Baranger formulae become identical with Eqs (47)–(48) resulting from the WKB approximation discussed in the previous sections. In general case, however, Eq. (68) cannot be further essentially simplified.

Let us remark that the $T(s)$ operator defined by Eq. (63) can be expressed in the following form

$$T(s) = e^{-\frac{i}{\hbar}Ks} U_f(s) e^{\frac{i}{\hbar}Ks} U_i^+(s), \tag{69}$$

where

$$U_i(s) = \mathscr{P} e^{-\frac{i}{\hbar}\int_0^s \tilde{V}_i(t)dt} \tag{70}$$

$\mathscr{P}$ being the Dyson chronological operator and $\tilde{V}_i(t)$ is

$$\tilde{V}_i(t = e^{\frac{i}{\hbar}Kt} V_i e^{-\frac{i}{\hbar}Kt} \tag{71}$$

For the final state of the emitter the $U_f(s)$ and $\tilde{V}_f(t)$ operators are defined by the same formulae the subscript i being replaced by f. The above form of the operator $T(s)$ appear to be useful for the investigation of the connections of the quantum-mechanical treatment with the so-called classical path approximation first introduced to the pressure broadening theory by Anderson [5]. The mathematical foundations of these connections have been recently studied in detail by Fiutak and Czuchaj [33].

Assuming that the motion of the perturber occurs along straight lines the distance $r(t)$ between perturber and emitter can be written as $r(t) = (\varrho^2 + (x_0 + vt)^2)^{1/2}$, where ϱ is the impact parameter, x_0 the position on the trajectory for the time $t = 0$ and v the relative velocity. The trace in Eq. (66) can be now replaced by an averaging over x_0, ϱ and v. In the classical case the operator $T(s)$ can be expressed as the following time-dependent function

$$T_{Cl}(s) = e^{-\frac{i}{\hbar}\int\limits_0^s \Delta V(r(t))dt}, \tag{72}$$

where $\Delta V(r(t)) = V_i(r(t)) - V_f(r(t))$, $V_i(r(t))$ and $V_f(r(t))$ are the classical interaction potentials for the initial and final state of the emitter. According to Eq. (66)–(67) the classical correlation function is then given by

$$\Phi_{Cl}(s) = e^{-Ng(s)}, \tag{73}$$

where

$$g(s) = 2\pi \int\limits_0^\infty \varrho d\varrho \int\limits_{-\infty}^{+\infty} dx_0 [1 - e^{-\frac{i}{\hbar}\int\limits_0^s \Delta V([\varrho^2+(x_0+vt)^2]^{1/2})\, dt}]. \tag{74}$$

This is the basic formula of the Anderson-Talman method [48] (*cf.* also [37]). In the asymptotic case in the limit $v \to 0$ and $N \to \infty$ Eq. (74) reduces to the quasi-static formula identical with Eq. (25), whereas for $v \to \infty$ and $N \to 0$ it gives the Lindholm-Foley expressions of the phase shift theory (Eqs (47)–(48)).

For many purposes it seems worth while to transform the general line shape formula given by Eq. (68) to another equivalent form. Namely, let us denote

$$F(s) = e^{-i(\omega-\omega_0)s}\Phi(s) \tag{75}$$

and let us treat, for a moment, ω as a complex magnitude with $\mathrm{Im}\,\omega > 0$. Then Eq. (68) yields

$$I(\omega) = \frac{1}{\pi}\mathrm{Re}\int\limits_0^\infty F(s)ds. \tag{76}$$

According to Eqs (67) and (75) the differential equation to be fulfilled by $F(s)$ is

$$\frac{dF(s)}{ds} = -i(\omega-\omega_0)F(s) - NV_0 e^{-i(\omega-\omega_0)s}\frac{dG(s)}{ds}\Phi(s). \tag{77}$$

Integrating this equation over s and using Eq. (76) we obtain (in the limit $\mathrm{Im}\,\omega \to 0$)

$$I(\omega) = \frac{1}{i(\omega-\omega_0)+H(0)}\left\{1 + \int\limits_0^\infty ds e^{-i(\omega-\omega_0)s}\frac{dH(s)}{ds}\int\limits_0^\infty dt e^{-i(\omega-\omega_0)t}\Phi(t+s)\right\}, \tag{78}$$

where

$$H(s) = NV_0\frac{dG(s)}{ds}. \tag{79}$$

Let us remark that according to Eq. (67) we have

$$\Phi(s) = e^{-NV_0 G(s)} = \lim_{n\to\infty}\left[1-\frac{1}{V_0}G(s)\right]^n = \lim_{n\to\infty}[\mathrm{Tr}\,(T(s)\hat{\varrho})]^n, \tag{80}$$

where $n = NV_0$ is the total number of perturbers. Hence for the finite number n the correlation function $\Phi(s)$ can be accepted in the form

$$\Phi(s) = (\mathrm{Tr}[T(s)\hat{\varrho}])^n, \tag{81}$$

and similarly

$$\Phi(s+t) = (\mathrm{Tr}[T(s+t)\hat{\varrho}])^n. \tag{82}$$

In the region of low densities of perturbers the procedure of averaging the operator T for the time t and s can be made separately so that $\Phi(s+t)$ can be represented by the product

$$\Phi(s+t) \approx \Phi(s)\Phi(t). \tag{83}$$

Under this assumption Eq. (78) yields

$$I(\omega) = \frac{1}{\pi}\mathrm{Re}\,\frac{1}{i(\omega-\omega_0)+H(0)-L(\omega)}, \tag{84}$$

where

$$L(\omega) = \int\limits_0^\infty dt e^{-i(\omega-\omega_0)t}\Phi(t)\frac{dH(t)}{dt}, \tag{85}$$

and

$$H(0) = NV_0\frac{i}{\hbar}\mathrm{Tr}\,[(H_f-H_i)\hat{\varrho}], \tag{86}$$

or

$$I(\omega) = \frac{1}{\pi}\,\frac{\gamma(\omega)}{(\omega-\omega_0-\Delta(\omega))^2+(\gamma(\omega))^2}, \tag{87}$$

where

$$\gamma(\omega) = \mathrm{Re}\,L(\omega), \tag{88}$$

and

$$\Delta(\omega) = -\mathrm{Im}\,L(\omega)-iH(0). \tag{89}$$

These expressions are identical with those derived by Fiutak and Czuchaj [33] (*cf.* also [32]) from the theory based on the resolvent operator method [31], [28]. These expressions were used by them to the extensive discussion of the validity conditions of the classical path approximation. The more general classical path treatment, which includes the effects of overlapping lines and also, in principle, the non-additivity of interactions has been recently offered by Smith *et al.* [49] on the basis of the Zwanzig projection operator technique. In the case of isolated lines and additive interactions their line shape formula is in close analogy with Eq. (84).

6. *Concluding remarks*

As it was shown in the present paper the two different approaches, generally applied in the investigations of the broadening of spectral lines in plasmas follow directly from the Jabłoński theory as the two opposite asymptotic cases of this theory. This conclusion was reached entirely within the framework of Jabłoński's theory without any changes of the assumptions of this theory. The only modification made is the replacement of the original formulation of the theory by the correlation formulation. Depending on the assumptions introduced to the calculation of the Condon overlap integrals, the different final results for the intensity distribution, half-width and shift of the line, were obtained. It was shown, in particular, that in the case when only weak collisions are taken into account in overlap integrals, the results of the quantum-mechanical impact theory follow from that of Jabłoński. On the other hand, taking into account strong collisions only and, in addition, assuming the validity of the earlier version of FCP, the quasi-static theory is obtained. Numerous investigations have proved that the quantum-mechanical impact theory is usually valid for electrons and the quasi-static one for ions (*cf. e.g.* [25], [26], [38], [47]). Hence one can conclude on the general validity of the Franck-Condon principle as well as the Jabłoński treatment in the description of the broadening of isolated spectral lines in plasmas.

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