LINE BROADENING AS LIGHT EMISSION DURING A COLLISION PROCESS*

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A number of optical-collisional processes are analyzed in the light of two ideas developed by A. Jabłoński: 1) the relationship between the broadening process and the emission of a compound system consisting of an atom and broadening particle; 2) application of the Franck–Condon principle for determining the line profile of an atom interacting with the many-particle system. The line profile $I(\omega)$ is expressed in terms of a photon radiation cross section, $d\sigma/d\omega$ similar to the bremsstrahlung cross section. Both the interference between the two processes and the generalization of the results to the case of degenerated hydrogen-like states are discussed. Nonlinear effects of laser-light absorption in the line wings are considered. The Franck–Condon principle is used for determining the line profile of laser light absorption by an atom interacting with the many-particle system. For the case of hydrogen line broadening in a plasma this profile contains information on the ion field lifetime T_F.

1. We are indebted to Aleksander Jabłoński for two fundamental ideas concerning the interaction between radiation and matter, formulated in his well-known work General Theory of Pressure Broadening of Spectral Lines [1].

The first idea assumes that line broadening should be related to the emission, not of an individual atom, but of a unified radiating system involving the atom and the broadening particle. The second idea, closely related to the first one, assumes that an atom in the medium is a gigantic quasi-molecule which embodies the nuclei both of the radiator and all particles in the medium interacting with it. In this case the change in frequency of a radiated photon $\hbar\Delta\omega$ is due to the energy redistribution in the quasi-molecule and can be determined by using the Franck–Condon principle allowing this frequency change to relate with a certain (static) nuclear configuration within the molecule. Both ideas have great heuristic strength and, as discussed below, give rise to new interesting trends in the field recently called the Physics of Optical-Collisional Processes.

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* Dedicated to Professor Aleksander Jabłoński on the occasion of his 80th birthday.

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2. The idea of a quantum radiated by the compound system: an atom + a perturber, used by Jabłoński [1] allows us to consider the broadening effects from a more general point of view such as the emission (or absorption) of light during atomic particle collisions. It is clearly understood that these phenomena involve the ordinary bremsstrahlung as well. It is, therefore, quite natural to expect that both the line profile $I(\omega)$ and bremsstrahlung intensity may be expressed in terms of the differential cross section $d\sigma/d\omega$ of the photon emission during the collision. For this purpose the well-known expression for the transition probability of the "atom + perturber" system from the initial state "a" to the final state "b" with the emission of a quantum of frequency ω and momentum k may by rewritten as

$$W = \frac{2\pi}{\hbar} |\langle a|\hat{V}|b\rangle|^2 \delta(\varepsilon_a - \varepsilon_b) \frac{d^3 q_b}{(2\pi)^3} \frac{d^3 K}{(2\pi)^3}, \tag{1}$$

where $\hat{V}$ is the atom-radiation field interaction, $\langle a|$ and $|b\rangle$ the wave functions representing the product of the atomic wave functions φ_a, φ_b and wave functions $\psi^{\pm}_{q_{a,b}}$ of the scattered particle having momentum $q_{a,b}$ in the potentials U_a and U_b, corresponding to the initial and final states of the atom; ε_a, ε_b — the energy of the system in these states,

$$\varepsilon_a - \varepsilon_b = \frac{\hbar^2}{2M}(q_b^2 - q_a^2) - \hbar\Delta\omega, \qquad |a\rangle = \varphi_a \sqrt{\frac{M}{\hbar q_a}}\, \psi^{+}_{q_a}, \qquad |b\rangle = \varphi_b \psi^{-}_{q_b}. \tag{2}$$

In Eq. (2) the quantity $\hbar\Delta\omega = \hbar(\omega - \omega_0)$ determines the difference between the radiating photon frequency and the unperturbed transition frequency ω_0 in the atom. The wave function $|a\rangle$ in Eq. (2) as well as in the theory of bremsstrahlung (see [2] § 3.4) was taken normalized with respect to the unity flux density of the broadening particles. Therefore, after averaging Eq. (2) over the initial states and sum over the final states we obtain a photon radiation cross section $d\sigma/d\omega$ within the frequency range $d\omega$. There exists, however, an essential difference from the bremsstrahlung. The dipole moment of the scattering particle D is included in the interaction $\hat{V}$ with an electromagnetic field in the bremsstrahlung case, while in the case of broadening, the dipole moment of the atom d is included.

Substituting the wave functions (2) into (1) we see that the matrix elements of the operator $\boldsymbol{d}$ split into the products of the atomic matrix elements $\boldsymbol{d}_{ab}$ over the states φ_{ab} and overlap integral of the wave functions $\psi^{\pm}_{q_{a,b}}$. Then, expanding ([2] § 3.4) into orbital momentum as in the case of bremsstrahlung, we obtain

$$\frac{d\sigma}{d\omega} = \frac{4}{3} \frac{\omega^3 |d_{ab}|^2}{c^3} \frac{\pi^2}{v_a E_a q_b} \sum_l (2l+1)\, |A_l|^2, \tag{3}$$

where A_l is the overlap integral of the radial wave functions of the scattering particle having the momentum l,

$$A_l = \int_0^\infty dr r^2 R_{q_a l}(r) R_{q_b l}(r). \tag{4}$$

The radiation power per unit volume $Q(\omega)$ takes the form

$$Q(\omega) = N_A N \hbar\omega \int v_a f(v_a) \frac{d\sigma}{d\omega} dv_a = N_A N \langle d\sigma/d\omega \rangle_{v_a}, \tag{5}$$

where N_A, N are the concentrations of atoms and broadening particles, $\langle \ldots \rangle_v$ — the averaging over velocity. Dividing Eq. (5) by the total atomic radiation intensity we obtain an expression for the line profile,

$$I(\omega) = N \frac{\pi^2 \hbar}{E_a q_b} \sum_l (2l+1) |A_l|^2. \tag{6}$$

Eq. (6) was first derived by Jabłoński [1] in a somewhat different way, using the particle wave function in a finite normalized volume. The same approach was followed by Szudy [3], and Szudy and Baylis [4], who analyzed various limiting cases of Eq. (6). It should be noted that the relation between the line profile parameters and scattering cross section, following from Eq. (6) in the impact limiting case was determined by Sobelman [5]. The analogy between bremsstrahlung and spectral line broadening, resulting from Eqs. (3)–(6) indicates the possibility of their interference in electronic broadening. This effect is more easily taken into account if we substitute the total dipole moment $\langle a|\boldsymbol{d}+\boldsymbol{D}|b\rangle$ of the "atom + electron" system into Eq. (1). The interference of both processes in the electron-ion scattering was calculated by Burgess [6].

The above conclusion, assuming both the scattering and emission to be a single elementary event, indicates also that there exists interference between the scattering and radiation amplitudes. Such an interference was first considered by Persival and Seaton [7] when calculating the polarization of atomic radiation excited by an electron beam.

3. For the case of hydrogen line broadening in a plasma Eq. (6) needs to be generalized by taking into account the "accidental" degeneration of the levels with respect to the atomic electron orbital momentum l_A. The atom-broadening particle dipole interaction potential $V_d = -e\boldsymbol{r}\boldsymbol{R} \cdot R^{-3}$ is, on one hand, non-central and, on the other, it decreases with R, following the same law as the centrifugal potential $V_{cf} = \hat{l}^2 R^{-2}$. The first circumstance only leads to the conservation of the total angular momentum $\boldsymbol{L} = \boldsymbol{l}+\boldsymbol{l}_A$ and the latter leads to the appearance of an additional integral of motion [8, 9].

$$\hat{\Lambda} = \hat{l}^2 - 2Mr_A(\boldsymbol{n}\boldsymbol{n}_A), \quad \hat{\Lambda}\psi = \lambda\psi, \tag{7}$$

where $\hat{l}$, M are the orbital moment and mass of the ion, $\boldsymbol{n} = \boldsymbol{R}/R$ — the unity vector along $\boldsymbol{R}$.

The use of the wave functions $\psi^{\lambda L}$ corresponding to the particular values of the operators L and $\hat{\Lambda}$ is convenient because the solutions of the radial Schrödinger equation are expressed in terms of the Bessel functions $I_\nu(qr)$ as well as for the case of free motion [10]. In this case the information on the dipole interaction is contained only in the index $\nu = \sqrt{\lambda+1/4}$ of these functions. As the results, overlap integrals such as those in Eq. (4)

are expressed analytically (in terms of the hypergeometrical function). The function $\psi^{\lambda L}$ used in the general formula (1) leads to a simple expression for Lyman line profiles [11],

$$I(\omega) = \frac{\pi^2 \hbar N}{3E_a q_b} \sum_{\lambda,L} (2L+1)\left[(a^{\lambda L}_{1L-1}A^{L-1}_{\lambda L})^2 + (a^{\lambda L}_{1L+1}A^{L+1}_{\lambda L})^2\right], \tag{8}$$

where the algebraic coefficients $a^{\lambda L}_{l\lambda l}$ determine the transition to the representation of quantum numbers λ, L[1]; $A_{\nu\nu'}$ — the overlap integrals of the radial (Bessel) functions. A comparison of Eqs. (8) and (6) shows that the transitions accompanied by a change in the angular momentum of the broadening ion by ± 1 as well as all the scattering channels λ make a contribution to the hydrogen line profile. Note that in the limiting case $L \gg \sqrt{n^2 M}$ the results of an accurate classical calculation [13] follow from Eq. (8).

Tran Minch et al. [14] obtained more general formulae for $I(\omega)$ which are not related to the dipole approximation. Their structure is substantially more complicated than Eq. (8). However, it may be reduced to Eq. (8), using the dipole approximation, see [11]. These results are discussed in Ref. [15].

4. In the Jabłoński theory [1], the relation between the wing shape and Franck-Condon's principle is established by calculating the overlap integrals (4) with the help of quasiclassical wave functions. The result for the transition probability $W(\omega)$ is

$$W(\omega) = 4\pi|V_0|^2 \left[\hbar v_R \left|\frac{d(U_a - U_b)}{dR}\right|\right]^{-1}\Bigg|_{R=R_0}, \qquad U_a - U_b\big|_{R=R_0} = \hbar\Delta\omega, \tag{9}$$

where $V_0 = \boldsymbol{d}_{ab}\varepsilon_0$ — the interaction of the atom and the radiation of the monochromatic field $\varepsilon_0 \cos \omega t$, the derivations of the potentials and radial velocity v_R are taken at the points of stationary phase.

The structure of Eq. (9) resembles the well-known Landau-Zener formula ([10] § 90). It determines the transition probability between two crossing terms. Therefore, the point of this transition R_0 may by regarded as a certain crossing point of the terms, in which, however, the "term" itself also includes the quantum of energy $\hbar\omega$ as is seen in Eq. (9). Thus we are talking about the crossing of the terms in the compound (composite) system "quasimolecule + electromagnetic field".

Let us write down the Schrödinger equation for transitions in a two-level system in the presence of an electromagnetic field,

$$\left.\begin{aligned} i\hbar\dot{a} &= U_a(t)a + V_0 e^{i\Delta\omega t} b \\ i\hbar\dot{b} &= U_b(t)b + V_0 e^{-i\Delta\omega t} a \end{aligned}\right\} \qquad \begin{aligned} a(-\infty) &= 1 \\ b(-\infty) &= 0 \end{aligned} \tag{10}$$

If the potentials $U_{a,b}(t)$ vary sufficiently slowly, points R_0 satisfying Eq. (9) will make substantial contribution to the transition probability $W = |b(+\infty)|^2$. If the value V_0 is assumed to be small, then Jabłoński's result (9) should be immediately obtained for W.

[1] Their explicit form for level $n = 2$ was obtained by Seaton [12].

Suppose, however, that V_0 is not necessarily small (for example, due to the large strength of the laser field ε_0). Then, the absorption probability W may be derived using the Zener formula ([10] § 90)

$$W = 2e^{-p}(1-e^{-p}), \quad p = 2\pi|\boldsymbol{d}_{ab}\boldsymbol{\varepsilon}_0|^2 \left[\hbar v_R \left| \frac{d(U_a - U_b)}{dR} \right|\right]^{-1}\Bigg|_{R=R_0}. \tag{11}$$

It is seen from (11) that for $p \geqslant 1$ the absorption decreases sharply due to the repulsion of the quasimolecular terms by the laser field.

According to (11), the corresponding critical value $\varepsilon_0 \equiv \varepsilon_0^*$ depends on the velocity v_R and the potentials U_a, U_b of the interatomic (broadening) interaction. Both these quantities are small in atomic units, thus the quantity ε_0^* is also small. The estimations [16–18] show that under ordinary gas-kinetic conditions, the value ε_0^* is of the order of 10^4–10^6 V/cm, and this value is easily attainable for modern lasers. It is clear that these effects open up new possibilities in studying absorption in the line wings, associated with the possibility of the active influence of the applying laser light upon the collision broadening processes. In connection with this it is of interest to recall the recent experiments by Bounch-Bruevich et al. [19], who observed non-linear effects in the line wings of alkali elements (Na, Rb, Cs).

5. By applying Jabłonski's theory [1] the absorption of electromagnetic radiation by an atom interacting with a large number of broadening particles, will now be considered. In this case the potentials in Eq. (10) are produced by the many particle system. Therefore, their variation with time is of a random character. We deal, essentially, with the stochastic differential equations.

The system of Eqs. (10) in the case under consideration may be solved by assuming a sufficiently slow (adiabatic) time variation of the perturbation. Following Jabłoński's theory [1], this enables us to apply the Franck-Condon principle, according to which the main contribution to the absorption is made by the points of the configurational space $R_1 \ldots R_N$ satisfying the condition

$$\kappa(\boldsymbol{R}_1, \cdots, \boldsymbol{R}_N) = U_a(\boldsymbol{R}_1, \cdots, \boldsymbol{R}_N) - U_b(\boldsymbol{R}_1, \cdots, \boldsymbol{R}_N) = \hbar\Delta\omega. \tag{12}$$

Moreover, if expression $V_0 = \boldsymbol{d}_{ab}\boldsymbol{\varepsilon}_0$ in Eq. (10) is small this approach should yield the same result as the static approach of the broadening theory [2]: $I(\omega) \sim |\boldsymbol{d}_{ab}\boldsymbol{\varepsilon}_0|^2 W(\omega)$ i. e. the line profile is proportional to the distribution function $W(\kappa)$ of the static frequency shifts.

Note that the line displacement as a function of the molecular static configuration on the broadening of highly ecited atomic lines in the Fermi problem [20] for a dense gas has been obtained by Firsov [21]. When the hydrogen lines broaden in a plasma then $\kappa = CF$ (where C is the Stark constant, F — the ion field), and the function $W(\kappa)$ coincides with the well-known Holtsmark distribution function $H(F)$ [22, 23]. Kogan [24] has derived the static distribution $I(\omega)$ from a general time scheme taking into account the ion field dynamics, and obtained the corrections for the thermal motion of the ions.

When V_0 is sufficiently large the absorption should decrease exponentially [25] as in the case of (11),

$$I(\omega) \sim W(\Delta\omega)\left\langle |\boldsymbol{d}_{ab}\boldsymbol{\varepsilon}_0|^2 \exp\left[-\frac{2\pi}{\hbar}|\boldsymbol{d}_{ab}\boldsymbol{\varepsilon}_0|^2\left/\left|\frac{d\kappa}{dt}\right|\right]\right\rangle_{\kappa=\hbar\Delta\omega}, \tag{13}$$

where $\langle\ldots\rangle_{\kappa=\hbar\Delta\omega}$ denotes averaging over all values of the derivative $d\kappa/dt$ for fixed $\kappa = \hbar\Delta\omega$ as well as with respect to the angle $\theta_{d\varepsilon_0}$ between the vectors $\boldsymbol{\varepsilon}_0$ and $\boldsymbol{d}_{ab}$.

Eq. (13) may be considered as the generalization of the Franc-Condon principle for the case of a strong interaction with an electromagnetic field causing the transition.

If the result (13) is applied to the Holtsmark broadening of the hydrogen lines in plasma, then the derivative $\langle|d\kappa/dt|\rangle_F$ is equal to $\langle|d\kappa/dt|\rangle_F \sim C\langle|\dot{F}|\rangle_F \sim CF/T_F$ to within an order of magnitude, where T_F is the ion field lifetime [23]. Using this estimate $\langle|d\kappa/dt|\rangle_F$ in (13) and averaging with respect to the angle $\theta_{d\varepsilon_0}$ we obtain [25]

$$I(\omega) \sim V_0^2 H(\Delta\omega/CN^{2/3})\,(\Delta\omega/V_0^2T_F)^{3/2}|_{CF=\Delta\omega}. \tag{14}$$

It follows from (14) that the absorption decreases in a strong electromagnetic field, causing distortion in the Holtsmark profile. The particular calculations [25–27] show that for the H_β line in the plasma with $N \sim 10^{15}$ cm^{-3} and $T \sim 1$ eV this effect becomes appreciable event at fields of $\varepsilon_0 — 10^4$ V/cm.

In this case, as is seen from Eq. (14), the observation of the profiles in a strong laser field makes the direct experimental determination of the many-particle ion field lifetime T_F possible.

6. The problems considered above are associated with new trends in the theory of broadening are based on the pioneer ideas suggested by Jabłoński more than 30 years ego, which is far from being complete. Jabłoński's approach enables one to obtain an elegant solution of a number of optical-collisional problems as well as points out the important theoretical problems. Among them is primarily the problem of consistent quantum description of line broadening by a many-particle system.

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