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EXCITATION OF ATOMS BY ELECTRONS AND BROADENING OF SPECTRAL LINES

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We discuss the connection between the theory of broadening of spectral lines in a plasma and the theory of atomic collisions. We formulate the conditions under which the broadening of spectral lines can yield information on inelastic scattering of slow electrons by excited atoms. By way of an example we consider the broadening of a series of lines, from which we estimate the cross sections for inelastic scattering of electrons by the He atom and by the Al^{++} ion at energies of the order of 3 eV. The obtained cross sections turn out to be in good agreement with those calculated in the Born approximation.

IT was shown by the author [1-3] and by Baranger [4-6] that the theory of impact broadening of spectral lines can be formulated in terms of the general theory of atomic collisions. In particular, the distribution of the intensity in the $n \to n'$ line, broadened as a result of collisions between the atom and electrons, is determined by the dispersion formula[1)]

$$I(\omega)\,d\omega = \frac{\gamma}{2\pi}\frac{d\omega}{(\omega-\omega_0-\Delta)^2+(\gamma/2)^2},$$

$$\gamma = 2N\langle v\sigma'\rangle, \qquad \Delta = N\langle v\sigma''\rangle, \tag{1}$$

where N and v are the concentration and velocity of the electrons, and σ' and σ'' the effective cross sections for the width and for the shift. The latter can be expressed in terms of the same S-matrix elements which determine the effective cross sections for elastic scattering σ_e and inelastic scattering σ_r from an atom in states n and n':

$$\sigma' = \mathrm{Re}\,\frac{\pi}{k^2}\sum_l (2l+1)\{1-\langle n|S_l|n\rangle^*\langle n'|S_l|n'\rangle\}, \tag{2}$$

$$\sigma'' = -\,\mathrm{Im}\,\frac{\pi}{k^2}\sum_l (2l+1)\{1-\langle n|S_l|n\rangle^*\langle n'|S_l|n'\rangle\}. \tag{3}$$

The effective cross sections σ_e and σ_r, and the total cross section $\sigma_t = \sigma_e + \sigma_r$, of the atom in the state n, are, as is well known (see, for example, [7])

$$\sigma_e = \frac{\pi}{k^2}\sum_l (2l+1)\,|1-\langle n|S_l|n\rangle|^2, \tag{4}$$

$$\sigma_r = \frac{\pi}{k^2}\sum_l (2l+1)\{1-|\langle n|S_l|n\rangle|^2\}, \tag{5}$$

$$\sigma_t = \mathrm{Re}\,\frac{2\pi}{k^2}\sum_l (2l+1)\{1-\langle n|S_l|n\rangle\}. \tag{6}$$

Although in the general case it is impossible to express σ' and σ'' in terms of σ_e and σ_r, it is possible to find an approximate relation connecting σ' with σ_e and σ_r. This connection can be used to obtain information on the scattering of electrons from an excited atom. It is convenient for what follows to write $\langle n | S_l | n \rangle$ and $\langle n' | S_l | n' \rangle$ in the form

$$\langle n|S_l|n\rangle = \exp(-\Gamma_l + i\eta_l),$$

$$\langle n'|S_l|n'\rangle = \exp(-\Gamma_l' + i\eta_l'). \tag{7}$$

Without appreciably reducing the accuracy of the calculation, we can assume that in the $n \to n'$ transition of an optical electron the state of the atomic residue does not change, and we can neglect the effect of distortion of the incident and scattered waves. It is then easy to show that, accurate to second-order terms in the perturbation, the interaction between the incoming electron and the atomic residue will make equal contributions to the phases η_l and η'_l, and will not affect the values of Γ_l and Γ'_l. Therefore the quantities $\Gamma_l + \Gamma'_l$ and $\eta_l - \eta'_l$ are completely determined by the interaction with the optical electron.

In the case of the scattering of electrons by a non-hydrogenlike atom (such a case will be considered below), this interaction increases very rapidly with increasing principal quantum number. Therefore, as a rule, the only contribution made to (7) is the perturbation of the upper level. This

1)It is assumed here for simplicity that the levels n and n' are nondegenerate.

allows us to put

$$\langle n|S_l|n\rangle^* \langle n'|S_l|n'\rangle \approx \langle n|S_l|n\rangle^* = \exp(-\Gamma_l - i\tilde{\eta}_l), \quad (8)$$

where $\tilde{\eta}_l$ is that part of the scattering phase shift for which the multiple interaction with the optical electron (dipole, quadrupole, etc.) is responsible.

Usually the principal role is played by the dipole interaction. In this case $\tilde{\eta}_l$ is determined by scattering by the polarization potential of the optical electron. In a similar approximation

$$\sigma' = {}^1/_2(\tilde{\sigma}_e + \sigma_r), \quad (9)$$

where $\tilde{\sigma}_e$ is determined by formula (4) with

$$\langle n|S_l|n\rangle = \exp(-\Gamma_l + i\tilde{\eta}_l).$$

Inasmuch as

$$1 - |\langle n|S_l|n\rangle|^2 = \sum_m{}' |\langle n|S_l|m\rangle|^2,$$

we have in the general case

$$\sigma_r = \sum_m{}' \sigma(n, m),$$

$$\sigma(n, m) = \frac{\pi}{k^2} \sum_l (2l+1) |\langle n|S_l|m\rangle|^2, \quad (10)$$

where $\sigma(n, m)$ is the cross section for the transition from the level n to the level m. Frequently, however, only one transition makes the main contribution to the sum over m in (10). As a rule, this is the transition to the closest level, allowed by the selection rule for electric dipole radiation with relatively large oscillator strength f. The same level also makes the main contribution to the polarization potential responsible for the term $\tilde{\sigma}_e$ in (9). For example, in the broadening of the λ4713 Å (2^3P-4^3S), λ4121 Å (2^3P-5^3S), and λ5048 Å (2^1P-4^1S) HeI lines the main role is played by the levels 4^3P, 5^3P, and 4^1P respectively [3]. For lines of this type

$$2\sigma' \approx \tilde{\sigma}_e + \sigma(n, m). \quad (11)$$

As is well known, the presence of an inelastic scattering channel n → m leads of necessity to the presence of elastic scattering, that is, when $\Gamma_l \neq 0$ we have $\tilde{\sigma}_e \neq 0$ even if $\tilde{\eta}_l = 0$ [7]. It can be shown [3] that if the following inequality is satisfied

$$\beta = \left(f \frac{\mathrm{Ry}}{|\Delta E|}\right)^{1/2} \frac{|\Delta E|}{m\langle v^2\rangle} = \left(f \frac{\mathrm{Ry}}{|\Delta E|}\right)^{1/2} \frac{\pi|\Delta E|}{8kT} < 0.6, \quad (12)$$

where f is the oscillator strength of the n → m transition, $|\Delta E| = |E_n - E_m|$, and v is the electron velocity, then $\tilde{\sigma}_e$ depends very little on η_l, and is determined almost completely by the value of Γ_l. We can therefore put $\langle n|S_l|n\rangle \approx \exp(-\Gamma_l)$. Inasmuch as in this case

$$1 - |\langle n|S_l|n\rangle|^2 = \sum_{m'}{}' |\langle n|S_l|m'\rangle|^2 \approx |\langle n|S_l|m\rangle|^2$$

and $\Gamma_l > 0$, we get

$$|1 - \langle n|S_l|n\rangle|^2 = (1 - e^{-\Gamma_l})^2 < 1 - e^{-2\Gamma_l} = |\langle n|S_l|m\rangle|^2.$$

Consequently $\tilde{\sigma}_e < \sigma(n, m)$.

Thus, if the conditions listed above are satisfied, the electronic part γ_{el} of the line width satisfies the inequality

$$N\langle v\sigma(n, m)\rangle < \gamma_{el} < 2N\langle v\sigma(n, m)\rangle. \quad (13)$$

In a strongly ionized plasma, at a sufficiently high charged-particle concentration (for example, under the conditions of a spark discharge), only ions make an appreciable contribution to the broadening, other than that of the electrons. The contribution of the ions to the broadening can be estimated quite reliably, for owing to the low velocities it is possible to apply to the broadening by the ions the adiabatic approximation, which in turn is determined by the constant of the quadratic Stark effect for the line in question. In addition, in the overwhelming majority of cases, namely when $\beta > 0.01$, the value of γ_{el} is at least double γ_{ion} [3].

Separating from the measured width γ the electronic part γ_{el}, we can obtain (accurate up to ~50%) the value of $\langle v\sigma(n, m)\rangle$. This uncovers a new possibility of experimentally investigating inelastic scattering of electrons by excited atoms. As is well known, the experimental data on inelastic scattering cross sections are very skimpy, and all pertain to transitions from the ground state. The measurement of the cross sections of the transitions between the excited states entails very great difficulties. On the other hand, measurement of the widths of the spectral lines is a much simpler problem.

It is of interest first to determine the degree to which the Born approximation is applicable to the calculation of the cross sections for the excitation of an atom by slow electrons (kT ~ 1–5 eV). It would be more accurate to speak of a normalized Born approximation. The point is that within the framework of the Born method the normalization can become violated—the partial Born cross sections σ^B exceed at small values of l the theoretical limit $\pi(2l+1)/k^2$. Elimination of this shortcoming with the aid of any method of cutting off σ_l^B leads to appreciable improvement of the results (for example, for the excitation of the resonance levels of alkali-element atoms). One such method is based on the use of the R-matrix (see [8]).

It is precisely for transitions between excited

λ, Å	Transitions	γ_{theor}, Å	γ_{meas}, Å	ΔE, eV
4713	$(2\,^3P - 4\,^3S)$	3	3	0.113
4121	$(2\,^3P - 5\,^3S)$	6.2	6.2	0.056
5048	$(2\,^1P - 4\,^1S)$	4.6	4.2	0.069

levels, when ΔE is small, that this effect can play an appreciable role. The Born approximation is certainly applicable if $e^2/\hbar v \ll 1$ or $E \gg me^4/2\hbar^2 \approx 13.6$ eV (E = electron energy). This general condition does not contain any concrete characteristics of the transition in question and in principle can be sufficient but not necessary. For transitions from the ground state, the excitation energy ΔE amounts to several eV, and the condition $e^2/\hbar v \ll 1$ is equivalent to the condition $E/\Delta E \gg 1$. For the transition between excited states, the latter condition is frequently satisfied also when $e^2/\hbar v \sim 1$ and even $e^2/\hbar v > 1$. The question arises: is it possible in this case to count on the applicability of the Born method (with or without account of normalization).

Experimental data on the broadening of spectral lines in a plasma are quite abundant. The broadening of more than 100 lines of HeI, NeII, ArII, KrII, AlIII, SnIV, SiIII, and SiIV was studied [9-13] under conditions when the broadening by charged particles exceeded all other types of broadening. A large number of reliable experimental data is discussed also in the review of Baranger [14]. An analysis of all this material shows that the theory of broadening of spectral lines, even in the simplest approximation based on the simplified variant of the Born method (with allowance for normalization) gives very good agreement with experiment[2]. The discrepancy between the measured width and those calculated does not exceed 30% in an overwhelming majority of cases (see [3,14]). For example, in the case of the above-mentioned HeI lines, calculation and experiment give for the line width γ at $N = 0.25 \times 10^{17}$ and $T = 30{,}000°$ K ($kT \approx 3$ eV)[3] the values listed in the table.

For each of these lines, the main contribution to γ is made by the interaction with electrons, and relation (13) is satisfied—the electronic broadening is determined almost completely by the transitions 4^3S-4^3P, 5^3S-5^3P, and 4^1S-4^1P, respectively. We can cite many such examples demonstrating the applicability of the normalized Born approximation in those cases when the electron energy amounts to only several eV, but $E/\Delta E \gg 1$. At the present time we do not know of a single example contradicting this statement.

To obtain information on the excitation cross sections, particular interest attaches in the case

$$\Delta E \gtrsim kT/4, \tag{14}$$

where the main contribution to the quantity $\langle v\sigma(n, m)\rangle$ is made by the region of the maximum cross section. Condition (14) is completely compatible with (12). For example, when $kT \sim 2$ eV and $\Delta E \sim 0.5$ eV, the values of β_e in the interval $0.01 < \beta_e < 0.6$ correspond to an oscillator strength $f \sim 3 \times 10^{-4} - 0.75$. An example of such a type can be found among the AlIII lines investigated in [13]. The electronic parts of the widths of the lines λ3703 Å and 3713 Å ($5S^2S_{1/2}-4p^2P_{1/2,3/2}$) are determined almost completely (> 90%) by the transitions $5s^2S_{1/2} \rightarrow 5p^2P_{1/2,3/2}$, and for these transitions $\Delta E/kT \approx 0.32$. Consequently, the near-threshold region $E \sim (1-4)\Delta E$ encompasses the maximum of the Maxwellian distribution. Inasmuch as Mazing et al.[13] did not make an independent determination of the electron concentration N_e, we can determine N_e only from the broadening of other lines, particularly the lines λ4512 Å, 4529 Å, 5697 Å, and 5722 Å. the scatter of the values of N_e obtained in this manner is quite small (less than 6%). The average value is $N_e = 1.51 \times 10^{17}$.

For this value of N_e, the calculated and measured γ are respectively

λ, Å	γ_{calc}, Å	γ_{meas}, Å
3703	1.09	1.14
3713	1.19	1.29

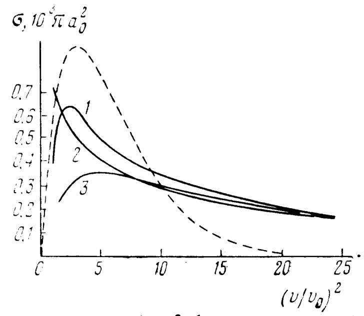
The discrepancy between calculation and experiment does not exceed 15%. Thus the effective cross section for the transition $5s^2S_{1/2}-5p^2P_{1/2,3/2}$ of Al^{++} also is given by the normalized Born approximation [including the region $E \sim (1-3)\Delta E$], with a very small error.

Under the experimental conditions, the main contribution to γ_{ion} is given by the ions N^{++}. Separating γ_{ion}, and also the term $\langle v\tilde{\sigma}_e\rangle N_e$, we can obtain

$$0.8\cdot 10^3\pi a_0^2 \geqslant \frac{\langle v\sigma(5s\,^2S - 5p\,^2P)\rangle}{\langle v\rangle} \geqslant 0.4\cdot 10^3\pi a_0^2. \tag{15}$$

The figure shows the results of the calculation of the cross section $\sigma(5s^2S-5p^2P)$ in the Born approximation with and without allowance of normalization, and in the Born-Coulomb approximation. The latter differs from the Born method in that account is taken of the distortion of the

[2] Usually the so-called Bethe approximation is used in the calculation[3].



Effective cross section of the transition: 1 – Born approximation, 2 – Born-Coulomb approximation, 3 – normalized Born approximation, dashed curve – Maxwellian distribution for electrons at T = 30,000°K, v_0 – velocity corresponding to the excitation threshold.

incident and scattered waves by the Coulomb field of the ionic residue. The normalization was calculated by the R-matrix method, and it is assumed that only the matrix element connecting the levels $5s^2S$ and $5p^2P$ differs from zero. We see that the Born-Coulomb approximation practically does not change the value of $\langle v\sigma \rangle$ compared with the Born approximation, and allowance for normalization reduces $\langle v\sigma \rangle$ somewhat. It can be expected that a simultaneous allowance for both effects (such calculations were not carried out) will yield for $\langle v\sigma \rangle$ values which do not differ much from the Born approximation. The averaging of the Born cross section over the velocity distribution yields

$$\langle v\sigma\rangle / \langle v\rangle = 0.435 \cdot 10^3 \pi a_0^2, \qquad (16)$$

which is in good agreement with (15).

It appears that an investigation of the broadening of other spectral lines, which make it possible to obtain information on the effective cross sections of inelastic scattering by excited atoms, is a very interesting problem.

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