

Review

# Beyond the Linear Stark Effect: A Retrospective

Alexander V. Demura 

Kurchatov Complex of Thermonuclear Energetics and Plasma Technologies,  
National Research Center “Kurchatov Institute”, Moscow 123182, Russia; demura45@gmail.com

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**Abstract:** A review of studies of the electric-field influence on spectral lines is presented, beginning from the discovery of the Stark effect, and in particular focused on phenomena related to the effects of the plasma microfield non-uniformity.

**Keywords:** Stark effect; microfield nonuniformity; asymmetry and shift of lineshapes

*In memory of—Gennadij Vasil’evich Sholin ( 26 August 1934–25 October 2014)—outstanding theorist in AMOP, plasma spectroscopy and plasma physics, amusingly understanding experiment and fantastically talented to work with experimentalists, keen and wise supervisor, giving rise to many original fruitful ideas at Kurchatov Institute of Atomic Energy, eminent erudite of human knowledge, great connoisseur of wildlife, bees and honey, berries, mushrooms, plants, and famous pleasant interlocuter of charming temper, well-known expert in French language, editor of translations of Hans Griem books into Russian and many more...*



*“Interactions are phenomena that need some dissymmetry for their existence.  
If there is no this dissymmetry then phenomenon is impossible”  
– Pierre Curie<sup>1</sup>*

<sup>1</sup> Translation of “Les effets, ce sont les phénomènes qui nécessitent toujours, pour se produire, une certaine dissymétrie. Si cette dissymétrie n’existe pas, le phénomène est impossible”, 8–10th lines from section VII—Curie P., Sur la symétrie dans les phénomènes physiques, symétrie d’un champ électrique et d’un champ magnétique, *J. Phys. Theor. Appl.* **3**, 393 (1894).

## 1. Research of Electric Field Action on Spectral Lines Using Canal Rays

The Stark [1] discovery and Lo Surdo observations [2] in 1913 of the spectral lines splitting in electric fields triggered innumerable further studies of various appearances of this phenomenon [3–186]. The originally observed splittings for hydrogen spectral lines seemed to be proportional to the first power of the electric field value [3,4].

Three years later, using the basic assumptions of the Bohr-Sommerfeld-Wilson theory of spectral lines [5–9], Shwartzschild [10] and Epshtein [11] independently calculated splittings of hydrogen spectral lines proportional to the first and second power of electric field value which are now known as the linear and quadratic Stark effects [10,11]. It is interesting to note that Sommerfeld provided to Epshtein his rule of quantization before it was published by himself [9]. After additional 3 years Kramers published results on calculations of the linear Stark effect components' intensities [12].

The various experimentalists measured, for example, the precise behavior of line splitting and intensity of resulting components versus the value of electric fields of atomic or molecular spectral lines of different elements and compounds [3,4,13–20]. It is important that at those times the effect was observed using canal rays [3,4,13–23]. In addition, the *dissymmetry of the splitting pattern with respect to the position of the unperturbed line wavelength recorded as a function of the direction of canal rays velocity with respect to the direction of the electric field in the condenser* [3,4,23]. Even up to now these results are not explained theoretically, although, for example, Nobel laureate, Russian academician Vitaly L. Ginzburg confessed in attempts to solve this problem.

In 1919 Holtsmark showed [24], that the spectral line could be broadened due to the Stark effect in the random in value and direction total electric field of perturbers, surrounding the radiating particle in a gas. In one of the first reviews, devoted to achievements of the quantum mechanics applications, Pauli pointed out on the necessity to take into account the spatial variations and time dependence of those fields in the Holtsmark's theory [25]. However, only after about 30 years did studies of these phenomena start with the works of Margenau and Meyerott [76] and Kogan [149,150].

In 1927–1929 Trautenberg and Gebauer experimentally discovered asymmetry (in original text dissymmetry) of intensities of red and blue Stark components and that their shift has parts varying as  $c_1 F^2 + c_2 F^3$  [17]. Increasing the values of the applied electric fields Trautenberg and Gebauer [18,19] and independently Kiuti [20] (using the Lo Surdo method) [2] observed the asymmetric patterns of Stark components' disappearance for several hydrogen Balmer lines, demonstrating that the blue components start to disappear at larger field values than the red ones. Lanczos in series of his papers [26–28] proposed the first consistent treatment of the above mentioned features.

From the 1930s to the 1950s, Gebauer continued with a more detailed study of asymmetric behavior of Stark effect patterns of hydrogen (mentioned in the third passage above and first discovered by J. Stark himself [4]) versus positions of observation points along the route of canal rays across the condenser with high electric field values, reviewed by his disciple and coauthor Jäger [21,22]. However, it seems that the published set of interesting and astonishing experimental data (see [21] and literature therein) is still insufficient for their clear theoretical treatment.

So, in the spirit of the Pierre Curie sayings above it is worth noting that asymmetries, and in particular the asymmetrical features of Stark patterns under discussion here are of interest to fundamental science.

## 2. Plasma of Gas Discharge

On the other hand Finkelburg in 1931 found the asymmetry of Balmer  $H_\beta$  line profile emitted from the arc discharge [29]. In fact, this and later observations of Stark broadened line asymmetries in plasmas [29–68] started to be a riddle for generations of researchers. The high precision measurements of asymmetric Stark profiles or shifts of hydrogen or hydrogen-like helium were performed by Kitaeva et al. [31,32], Wiese et al. [33,35–37], Boldt and Cooper [34], Preston [40,41], Grützmaier and Wende [43,44,61], Kelleher et al. [45,47,48], Helbig and Nick [49], Helbig et al. [60], Uhlenbusch et al. [52,57], Djurovic et al. [49,51,55,59], Parigger et al. [67,68] for  $Ly_\alpha$ ,  $Ly_\beta$ ,  $H_\alpha$ ,  $H_\beta$ ,  $P_\alpha$ ,

$P_\beta$  using wall stabilized capillary arcs, shock tubes, gas-liner pinch, z-pinch, glow and hollow cathode gas discharges, microwave discharges, laser plasmas etc. The most stable and reproducible light sources were wall stabilized capillary arcs and gas-puff pinches, which were considered as the etalon light sources. The asymmetry in the wings was reported by Boldt and Cooper [34], Fussmann [38], Preston [40]. The conditions of the measurements of all experiments [29–68] were rather limited by the range of parameters, where plasma sources were stationary and stable or reproducible. This specifics of various types of gas discharge operation prevented a systematic study of asymmetry as a function of density and temperature.

The first attempt to theoretically explain the asymmetry of the  $H_\beta$  line, observed by Finkelburg, was due to Griem in 1954 in his Ph.D. thesis [69], performed in Kiel in the beginning of the fifties, invoking the quadratic Stark effect (Q2S) [70]. He took into account Q2S corrections to energies, using data of Epstein, and intensities, using data of Gustavson [71] and Ryde [72], as well as the so called trivial asymmetry due to the transformation from the circular frequency scale to the wavelength one. His data fitted the profile [29] quite well, judging from the comparison presented in [69]. He considered electrons in what would today be called “impact approximation” [73–75], while the ion broadening was described using the Holtsmark distribution function [24]. The total profile was determined by the convolution of the Lorentz profile, formed due to the collisions of radiator with plasma electrons at the fixed value of ionic microfield, over the ionic microfield values using the Holtsmark microfield distribution function as a weight [73–75]. This construction for a long time served as the basis of the now so called Standard Theory (ST) of line broadening in plasmas [73–75].

In 1953, Sobelman and Vainstein [76] studied and evaluated the shifts and splitting of spectral lines of non-hydrogenic emitters with one valence electron caused by the nonuniformity of stationary electric field, in particular due to the binary interaction with charged particles in a gas.

In 1955, Margenau and Meyerott were the first to evaluate the shift of  $Ly_\alpha$  Stark components induced by the quadrupole interaction with the nearest neighbor ionic perturber [77], using a multipole expansion of interaction potential. They showed that the central component, which is not perturbed by the linear Stark effect is shifted due to the quadrupole interaction.

In a year the Lorentz form of distribution of the space derivatives of the Coulomb field of ensemble of plasma ions was obtained by Miliyanchuk [78] and nine years later seemingly independently by Müller [79]. These results in fact naturally correspond to obtained much earlier by Chandrasekhar and von Neumann in [80] and much later in Monte-Carlo simulations by Gilles [81]. Indeed, the problem of the nonuniformity of the Coulomb field was treated by Chandrasekhar and von Neumann [82] in the case when one must consider the vector total field of many perturber particles, interacting with the test one. Unfortunately these results did not become well known and part of them was derived over again [78,79]. Partly it was due to the calculation in [82] of the finite differences of the microfields in two points, separated from each other by the finite distance, determined through the radius-vector  $\delta\vec{r}$ . As it could be possible to classify later these results are valid when the number of particles in the Weiskopff sphere [73] of the quadrupole interaction is much more than unity. Moreover, the author of [78] also considered negative charges to be quasistatic from the beginning. Thus in their initial formulation results of these works may be applied only for a very rare unique conditions.

The next important step in the evaluation of the quadrupole interaction’s influence on the Stark profiles was done by Kudrin and Sholin [83]. They considered the binary case for the plasma ions, neglecting the influence of electrons, and by the correct construction of perturbation series found the analytical correction terms to the Stark components energies and wave functions linear in the perturbation parameter  $\varepsilon = n^2 a_0 / R_0 \ll 1$  due to the quadrupole interaction ( $n$ -the principal level quantum number,  $a_0$ - Bohr radius,  $R_0$ - is the mean interparticle distance). The parabolic wave functions were used, quantized along the electric field direction. The calculations were done for  $H_\beta$  and  $H_\delta$ . This allowed the determination of the peak shifts with respect to the line center, their intensities and hence their asymmetry. It was pointed out that results described the experimental data of Kitaeva and Sobolev [24,25] qualitatively well. Also as the quadratic Stark effect turned out to be of the next second

order in the small parameter  $\epsilon$  with respect to the quadrupole interaction the authors were critical of Griem's results [69].

Later Sholin [84] gave a detailed description of the correct perturbation series for energies and eigenfunctions, considering again the binary interaction of the hydrogen atom with an ion and using the multipolar expansion. He showed, that quadrupole corrections linear in the perturbation parameter  $n^2 a_0 / R_0$  induce the asymmetry of hydrogen Stark profiles. The analytical formulas for diagonal and off-diagonal matrix elements of atomic quadrupole moment and diagonal matrix elements for octupole moment, as well as for the second order correction to energy due to quadrupole interaction were presented for parabolic wave functions. The choice of parabolic wave functions in a reference frame with the quantization axis along the electric field direction was one of the most important physical ideas of this work. The asymmetry due to the quadrupole interaction in the line wings along with the assumption that electrons did not reach the regime of quasistatic broadening was also analyzed. The instructive figures for the deviation of Stark splitting patterns under the influence of the quadrupole interaction with nearest ion neighbor located at the fixed distance from the atom were presented, together with tables, containing all necessary constants for the calculation of quadrupole asymmetry characteristics, for lines Lyman- $\alpha, \beta, \gamma, \delta, \epsilon$ , Balmer- $\alpha, \beta$  and Paschen- $\alpha$ . As the latter tables were used in many further works some minor typos were detected there. The quadrupole asymmetry in the first order of perturbation parameter was evaluated in [84] also in the wings of Ly $_{\alpha}$  and compared with the Boldt and Cooper data [34]. This had shown quite reasonable agreement without the contribution of electrons. These experimental measurements of asymmetry in the wings of Ly $_{\alpha}$  [34] were also analyzed earlier in the paper of Nguyen-Hoe et al. [85], following the work of Kudrin and Sholin [83]. However, as pointed out in [84] the linear versus  $\epsilon$  corrections to intensity were missed, while the corrections proportional to  $\epsilon^2$  were not taken into account completely, although the method, used for a comparison of various asymmetry sources was quite detailed and instructive.

On the other hand, Sobelman [76] and independently later Griem [86] pointed out on a cancelation of the contributions due to the quadrupole terms from ions and electrons in the Stark profile. This was based on attempts to consider the radiator-perturber interaction for both perturber charge signs on an equal footing specifically in the frames of the quasistatic or the impact approximations [76,86]. However, later Sholin expressed an opposite view [83,84], based on taking into consideration the difference of the masses and thus in the characteristic time scales of the ionic and electronic electric fields, that led to the existence of the wide region of detunings from the line center, where there was no direct cancelation of these contributions. Beginning with Griem [69], Margenau with Meyerott [77] and Kudrin with Sholin [83] it was thought, that in this region ions are almost quasistatic, while electrons are impact [73–75]. The theoretical works in this field, in the words of Margenau and Lewis [87] “*were inspired by a vision*” of not so relatively large but quite distinct asymmetry features of hydrogen lines Stark profiles, observed in series of bright experiments with very high precision. Experiments indicate, that as a rule near the line center in one-photon emission profiles the blue side of the line is more intense. As the detuning increases the difference increases, reaches an extremum and then decreases, then changes sign and increases again (see, for example, [44]), as one goes towards the wings. Therefore, as a rule for sufficiently high density, where the fine structure splitting is much less than the Stark effect, hydrogen lines have a more intense red wing of the line than a blue one. This fact has put to rest objections against the transition of electrons to the quasistatic regime of line broadening in the far wings [81], that is intrinsically connected with the understanding of the cancelation mechanisms of quadrupole terms from ions and electrons. It should be noted that in [88] the asymmetry was calculated with respect to the purely quasistatic profile and the results could be strongly changed if one uses the more realistic profile with the electron contribution, as it was done in later papers like [89,92]. In the very far wings one can again expect the change of the asymmetry due to the decreasing of the intensity of the red wing with respect to the blue one, caused by the ionization of the atom in the microfield [26–28], and its relative increasing coming from Boltzmann factors [86], which definitely appear in the quantum approach [73]. Although there is no clear understanding what

is really happening, because the ionized electron may be more probably recaptured by the bare nearest perturber, providing the electric field in the far wing is created by the nearest neighbor. Moreover, the bumps in the far wings are known and observed, and were attributed to the extrema of the quantum energy terms of  $H_2^+$  [40]. Thus it may be stated that as the quadrupole effects from ions and electrons in the quasistatic (and thus semi-classical) approximation are thought to cancel each other, perhaps, one should apply the quantum theory for the correct treatment of the line asymmetry in the far wings, considering the energy terms of  $H_2^+$ .

There are also additional direct consequences of the line asymmetry—line shifts, a question that needs much caution in the experiment [35,39,43,48,50,51,55,56,58–60] and the theory [60,73–76, 92,99,102,105,113,123,132,143–145,147,148,151–186]. The short sketch of latter aspects is given in the Appendix A to avoid interruption of the main thread of review.

The binary approach outlined and constructed by Sholin for Coulomb perturbers [84], was completely realized for Ly- $\alpha$  by Bacon [89], who calculated explicitly all terms of the perturbation series including up to the second order in the perturbation parameter  $\varepsilon$ , i.e., besides quadratic Stark effect—second order quadrupole, octupole terms and corresponding second order terms for the intensity corrections. He also took into account the electron impact contribution to the total profile that immediately decreased the calculated asymmetry (compare with [92]) in comparison with the results of Boldt and Cooper [34]. In a later work [90] he performed calculations simultaneously for Ly- $\alpha$  and Ly- $\beta$  slightly improving the account of the contribution of the quadratic Stark effect, again following Sholin's binary approach and prescriptions [84]. Also in the center of the profiles the Hooper microfield distribution function [91] was used, and only in the wings—the Holtsmark one. The evaluation of the electron broadening was given with account of time ordering and using frequency dependent cut-offs [89,90], that in principle could influence asymmetry. It was noticed in [89,90] that the second order quadrupole contribution had only a minor effect. The tables for the profiles of Ly- $\alpha$  and Ly- $\beta$  were presented for  $T_e = 20,000$  K, and  $N_e = 10^{16}$ – $10^{18}$  cm $^{-3}$ . The behavior of the wings and asymmetry of both lines were presented and compared with the Fussmann experiment [38], later acknowledged to be in error.

In the case of ideal plasmas, the many-body problem of the nonuniform electric microfield interaction with the hydrogen atom was solved by Demura and Sholin [92] in the framework of the perturbation theory to the line shape. In fact, it was performed in the general settings of finding corrections to the Holtsmark profile as was first done by Griem [69] and Kogan [149,150]. Demura and Sholin introduced universal functions, connected with the constraint moments of the nonuniformity microfield tensor at the fixed vectorial values of the electric microfield strength vector in the frame of the generalized many-body quantum perturbation approach [92]. The consideration was based on the assumption that ions are quasistatic, while electrons are impact. This enabled the development of the formalism of the instant joint distribution functions of the electric microfield strength vector (of the total ion electric field) and the independent components of the nonuniformity microfield tensor (the number of which is equal to five in the pure Coulomb case). In this work for the first time the fundamental importance of the constraint moments of the nonuniformity microfield tensor as the characteristics of the spatial and temporal microfield fluctuations was understood. In [92] the two universal functions were introduced, defining asymmetry corrections to the Stark Holtsmark profile due to quadrupole shifts of frequencies  $\chi(\beta)$  and due to quadrupole corrections of intensity of Stark components  $\Lambda(\beta)$ , where  $\beta = F/F_0$  is the reduced microfield value,  $F_0$  is the value of normal Holtsmark field [24]. The most detailed at that time table of the Holtsmark function  $H(\beta)$  values, and ones of the other introduced universal functions were presented, together with the instructive figure for  $\chi(\beta)$  and  $\Lambda(\beta)$  functions. Namely this table of  $H(\beta)$  was included later in the book [147]. These numerical and graphical data were compared with the functions  $B_N(\beta)$ ,  $\Lambda_D(\beta)$  and  $\chi_N(\beta)$ , based on the nearest neighbor distribution  $W_N(\beta)$ , designated by subscript  $N$  and presented in the table and the figure too. It was shown that the obtained universal function  $B(\beta)$ , which determined the behavior of the tensor of non-uniformity constraint moments, coincided with the one introduced by Chandrasekhar—von



Neumann function [82], corresponding there to the mean difference of the microfield in two points, separated by the finite radius vector. That is why we intentionally preserved the designation of [82]. Also in [92] the formula for the shift of the line gravity center was first discussed and the expression for the asymmetry in the line wings was rederived with account of the impact electrons. In fact, the results obtained and the methods developed in this work now have been applied and widely used in many works of other authors on this and related subjects. In [92] the inclusion of electron contribution, and hence the relative increase of the unperturbed profile led to the reduction of Sholin's result of asymmetry [84] for the experiment of Boldt and Cooper [34]. After this correction the theoretical results of [92] for asymmetry in the wings became noticeably lower than the experimental ones [34] compared to [84]. This is because in [84] the Stark profile was calculated without account of the contribution of the electron impact broadening, as was mentioned above.

In the next year, 1976, Demura showed in his thesis [93] how to solve this problem for plasma with a finite coupling, applying the Baranger-Mozzer cluster expansion [94] for the construction of a joint distribution function of microfield and its non-uniformity tensor and hence their first moments, that allowed the generalization of the solution from [92] in the case of weakly coupled plasmas.

Another attempt to incorporate in this approach the finiteness of plasma coupling parameter was done later in 1987 by Joyce, Woltz and Hooper [95], who considered multiply charged hydrogenic ions as radiators. The ion perturbers were considered static and Debye-screened by plasma electrons [96] as in [94] too. Electron broadening was described within the relaxation theory [97]. In [95] the APEX microfield distribution function [98] was used, which was designed for strongly coupled plasmas, but did not allow the systematic construction of the joint distribution functions of microfield and its non-uniformity tensor. That is why instead of the moments of joint distribution function in [95] the authors constructed an *ad hoc* non-uniformity tensor, which was not inherently related to the microfield in the APEX distribution function. The calculations included the quadratic Stark effect and the fine structure for the Argon<sup>17+</sup> Ly $\beta$  line for the electron temperature  $T_e = 800$  eV and the density interval  $N_e = 10^{23} - 3 \cdot 10^{24} \text{ cm}^{-3}$ . The asymmetry of profile maxima was analyzed as a function of density. It turned out that at large densities the influence of fine structure became negligible, which was expected, while the combined effect of the quadrupole and the quadratic Stark contributions increased. It was noticed that at  $N_e = 10^{23} \text{ cm}^{-3}$  the combined effect was nearly zero. The calculations were performed in both the spherical and the parabolic bases.

The same year, a team, led by Nguyen-Hoe, published calculations [53] of the profiles of Ly- $\beta$ , Ly- $\delta$  and Ly- $\gamma$  of hydrogenic fluorine ion in laser plasma with account of the electron collisional shifts [99], quadrupole interaction, quadratic Stark effect and dissolution of Stark components at large fields [100]. In [53] the authors used the low-frequency Hooper distribution function for ionic fields [94], while evaluating the contribution of the quadrupole interaction approximately by a binary expression, assuming the perturbation is caused exclusively by the nearest neighbor at the distance  $R = (eZ_p/F_0 \cdot \beta)^{1/2}$ . The authors of [53] proposed diagnostics based on a comparison of experimental data with the entire computed Lyman series [53]. The authors discussed taking account of high order corrections of the interaction potential, including the quadrupole and octupole corrections to the energy, but apparently omitted the second order quadrupole as well as first and second order wave functions corrections, since these are not mentioned at all. So, again the complete set of terms of claimed order was not included. This made the results of this complex work questionable. The presented curves for asymmetrical profiles were not smooth enough and give the impression of a low calculation accuracy.

Influenced by trends similar to the last two articles, a 1988 Kurchatov preprint by the author [102] described in detail the construction of joint distribution functions of electric microfield strength vector and its spatial and time derivatives for plasma with finite coupling and complex ionization composition on the basis of the Baranger-Mozzer cluster expansion [94]. The interest in complex plasma composition was triggered by liner compression experiments which produce plasma with many different ionization stages. This work generalizes results of [93], which were determined from a cluster expansion, on an arbitrary radiator charge  $Z_r$  and an arbitrary set of ion perturbers  $\{Z_p\}$ .

The analytical expressions were given for all universal functions, required by the cluster expansion. These universal functions, called  $B(\beta)$ ,  $\Lambda(\beta)$  and  $\chi(\beta)$  in [92], which determine the asymmetry for the Coulomb case were generalized for the case of a plasma with the electron Debye screening of ions and the ion-ion correlations and labeled as  $B_D(\beta)$ ,  $\Lambda_D(\beta)$  and  $\chi_D(\beta)$ , with  $D$  denoting the Debye radius [96]. For all functions involved, the analytical asymptotic was given for small  $\beta \ll 1$  and large  $\beta \gg 1$  reduced fields values. However, the numerical tables or graphs for the generalized universal functions were not presented. These general results, taking account of Debye screening of ion perturbers and ion-ion correlations were reported in 1988 in the ICSLS-IXth in Toruń, Poland [103].

In 1990, Halenka published an article [104], devoted to the asymmetry of hydrogen spectral lines, induced by quadrupole interactions in plasma with finite coupling, which in its general methods and results practically coincided with [95] for the particular case of hydrogen emitter and ion perturbers with unit charge. *The title of the article [104] force to wonder what is it “Mozzer-Baranger limit”, that does not correlates with the physical sense, that could be noted?* The article [104] did not include aspects of [102], addressing the construction and derivation of the joint distribution functions for the microfield strength and its time derivatives. However, Halenka performed detailed tabulation of the universal functions  $B_D(\beta)$ ,  $\Lambda_D(\beta)$ ,  $\chi_D(\beta)$  and the Baranger-Mozzer [87] microfield distribution function  $W_\rho(\beta)$ , changing the subscript “D” on “ $\rho$ ” for the isothermal plasma for several  $\rho$  values, conventionally expressed as a ratio of the mean particle distance  $R_0$  to the Debye radius  $D$ ,  $\rho = R_0/D$ . The results obtained were used in calculations of  $H_\beta$  Stark profiles and their asymmetry, following the general scheme from [92]. It was concluded that taking into account a finite plasma coupling led to a better agreement with experimental data, than in pure Coulomb case, but this did not remove all discrepancies between the calculations and the experiment. Due to a posteriori analysis presented by Halenka in [104] numerical and graphical data were quite accurate for the case considered.

The same year, 1990 Gavrilenko and Ispolatov [105] considered the broadening of multiply-charged helium-like ions in dense plasmas with account of quadrupole interaction terms taking account of the polarization term arising due to application of the Debye screening model for the field ions like in [102]. The data on the levels energy were provided by L.A.Vainstein [106]. The wave functions of the unperturbed Hamiltonian were constructed using the Vainstein’s mixing coefficients for  $LS$  coupling functions [106], taking account of spin-orbit and spin-spin interactions. The influence of levels with  $n' = n \pm 1$  due to dipole interaction in the second order was included also. Additionally, the Nguyen-Hoe group “polarization” shifts [99] were used. The approximate microfield distribution function of the Debye screened independent field particles was used neglecting the ion-ion correlations [94], but taking account of the repulsion between the perturber and radiator ions via the Boltzmann factor. This function was known from the works of Ecker and Müller [107] and Margenau and Lewis [87], but instead another article was cited [95]. The states of the upper radiating level were assumed equally populated, and one of the He-like ion electron had been assumed to always occupy the ground level. The expression for the first moment of the non-uniformity tensor after correction of its coefficient was the same as could be obtained from [102], whereas the authors cited their paper [108]. In [108] this expression was never used but instead another expression, derived in [92] for a pure Coulomb field, was employed. The main result of work under discussion was drastically large shifts of lines due to the polarization term, proportional to the microfield divergence. However, this result seemed to be spurious due to the omitted delta-function summand in this expression, which would led to a nullification of this shift, along with the condition of plasma quasineutrality [109].

In 1991 a Kurchatov preprint by Demura, Pleshakov and Sholin [110] appeared with the results of systematic calculations of asymmetrical hydrogen profiles within ST for the first four lines ( $\alpha, \beta, \gamma, \delta$ ) of the Lyman series and the first three lines ( $\alpha, \beta, \gamma$ ) of the Balmer series. The ions were considered quasistatic with the Holtsmark or nearest neighbor distribution function, and the electrons to be in the impact regime. The dipole and quadrupole interactions were included in the spirit of [85]. The paper contained the Fortran listing of the program, used in calculations and written by (at that time Ph.D. student) V.V.Pleshakov from Kourrov Astronomical Observatory of Ural Federal University. The impact

widths were calculated along with formulas, derived in [111] in terms of parabolic quantum numbers, using the (constant for all degenerate states) logarithmic factor, which was corrected relative to the one in [73]. For the asymmetry analysis the spectral difference of intensity between blue and red parts of the profiles was considered, and the analogous differences of integral intensities, for which the explicit analytical formulas were obtained. These characteristics were sensitive to the electron impact widths of Stark components. The asymmetry parameter  $A(\Delta\omega)$  was chosen as

$$A(\Delta\omega) = \frac{I_{blue}(\Delta\omega) - I_{red}(\Delta\omega)}{I_{blue}(\Delta\omega) + I_{red}(\Delta\omega)} \quad (1)$$

In [110] the letter  $\delta$  was used in (1) instead of conventional  $A$ . The  $A(\Delta\omega)$  definition given in (1) in fact diminishes the value of asymmetry parameter twice, since it would be more consistent to refer the asymmetry to  $[I_{blue}(\Delta\omega) + I_{red}(\Delta\omega)]/2$ . Besides that the asymmetry was calculated at detunings equal to HWHM,  $HW(HM/2)$ ,  $HW(HM/8)$  as was done in the pioneering work of Wiese et al. [36]. The analysis of results had shown that the values of asymmetry were systematically lower than what could be extracted from the experimental data. Therefore, it was pointed out that the electronic impact shifts could be an additional source of asymmetry, if they had a non-uniform distribution over the line profile. This could also result from an overestimation of the impact widths in the parabolic basis, known from the comparison with the results of calculations in the spherical one [111].

In 1993 Kilcrease, Mancini and Hooper [112] returned to the formalism of the work of Hooper et al. [95] from 1987. However, the relative progress concerned mostly attempts to better justify the application of the APEX approximation for the calculation of the mean constraint of the non-uniformity tensor. To our mind the theoretical methods and derivations in the work were mathematically too artificial, and not fully convincing. The authors also reported on the effect of the use of the extended basis of wave functions, including the contribution of levels with the different principal quantum numbers.

In 1994 two papers of Günter and Könies [113,114], devoted to the asymmetry calculations and based on the further development and application of the two-particle Green function technique [115], were published. In the first paper [113] the frequency-dependent electronic shift was computed in the dipole approximation. This shift changed its sign as a function of  $\Delta\omega$ . It was positive for  $\Delta\omega > 0$  and negative for  $\Delta\omega < 0$ . Specifically at large  $\Delta\omega$  this shift approached a constant value. In the second paper [114] the authors took into account the quadrupole interaction. The parabolic basis was used. The quadrupole contribution was approximated by the mean value of the microfield gradient, expressed versus  $B(\beta)$ , determined outside the Green function framework in [104]. The quadratic Stark shifts were used as well [70] in the nonquenching approximation, while the  $\Delta\omega$  dependence of their electronic impact shift was neglected. The authors claimed that they took into account also the factors of trivial asymmetry in the circular frequency scale, namely  $\omega^4$  and Boltzmann factors, first discussed to our knowledge by Griem [86]. The full asymmetrical profiles of  $Ly_\alpha$  and  $Ly_\beta$  for the conditions of the Grützmacher and Wende experiments [43,44] together with the asymmetry parameter were calculated. The comparison of obtained and experimental data demonstrated a reasonable agreement. The evident drawback, as was noticed in many papers, was omitting other terms proportional to the second order of the perturbation parameter already itemized above (the octupole, second order quadrupole, second order corrections to wave functions, etc.).

In 1995 Demura and Stehle [116] published an expanded and updated version of the general results of Demura from [102] on the application of the Baranger-Mozer (BM) cluster expansion [94] to the problem of simultaneous account of dipole and quadrupole interactions of hydrogenic radiators in plasma with an arbitrary ionization composition. It was an invited lecture of Demura at ICSLS-12th in Toronto in 1994. The calculations of the aforementioned universal functions were performed within B-M by Stehle and within Monte-Carlo by Gilles in the charged and neutral points and corresponding graphs were presented. The application of the Monte-Carlo approach allowed extending the regime of interest to the strongly coupled plasmas. The paper contained also a general analysis in terms of the



characteristic parameters  $h_{i,e}$  for ions—subscript  $i$  and electrons—subscript  $e$ , determining the number of particles in the Weisskopf sphere and discussion of a specific role of the central component. It was pointed out that estimates showed, that parameter  $h$  for the quadrupole interaction with ions  $h_i^Q \ll 1$ , corresponded to binary and even to impact regime of broadening, while parameter  $h$  for the leading dipole interaction  $h_i^D \geq 1$  corresponded to many-body and dynamic broadening regime. Thus the usage of these criteria became questionable for the complex type of potential, containing as in this case two potentials of different power. The behavior and significance of polarization terms due to the electrons pile-up around a quasi-free ion, related to application of the model of Debye screened field particles was analyzed as well.

In the same year, an article of Demura, Gilles and Stehle [117] was published, aimed on a research of the nonuniform microfield statistics. It is started with compact formula for the first constraint moment of the microfield nonuniformity tensor, obtained by the first author. Its structure was the same as the first moment of the first time derivative of microfield in [82]. The general results of application of the Baranger-Mozer cluster expansion were again presented with some minor modifications in comparison with previous works. The short description of the general results of Kilcrease, Mancini and Hooper of the APEX utilization was presented [112] to retrieve the key differences from the Markoff joint distribution function formalism [80,82,127]. The universal functions  $W(\beta)$ ,  $B_D(\beta)$  and  $B_{D0}(\beta)$ , related to the polarization terms, were calculated for the different values of the conventional parameter  $a = R_0/D$  in the neutral and charged points by the B-M and Monte-Carlo (MC) methods, and showed good agreement even for rather small Debye values corresponding to  $a \sim 1$ . The comparison with the results of nearest neighbor was also given. The calculations using the APEX program [118,119], provided to the French co-authors, allowed a comparison of the APEX, MC and B-M microfield distribution functions  $W(\beta)$  as a function of density for a fixed temperature of argon plasmas, in order to get an idea on the applicability of B-M results. Additionally, the results for the pair correlation functions were presented in the Hypernetted Chain approximation (HNC), utilized in APEX, and MC results in Debye-Hückel approximation. The net result was that the B-M approach suffered due to the implementation of an oversimplified pair distribution function. The article contained also a unique presentation of the joint distribution function of the microfield magnitude and magnitude of its gradient, obtained within MC by D.Gilles.

In 1997, Günter and Könies published the results of calculations of the asymmetrical profiles of  $H_\beta$  and  $H_\gamma$  [120] by the same Green function technique, as was used for  $Ly_\alpha$  and  $Ly_\beta$  in 1994 [114]. The consideration of the quadrupole and the quadratic Stark effects was performed in the same approximations as before [114]. However, in this case they also approximately constructed the evolution operator in order to account the influence of ion dynamics within the model microfield method (MMM) [121,122]. A comparison with experimental data and other theoretical works was given. The center of gravity shift (CGS) and the estimated line shift (ELS) (introduced by Wiese) were evaluated for both lines. The peak asymmetry was analyzed for  $H_\beta$ . The authors discussed and compared values of contributions of various mechanisms in formation of studied characteristics and claimed a good agreement with experimental measurements [36,42,46,49,56,60]. As was noted by the authors, the inclusion of ion dynamics with the help of MMM decreased the absolute values of the profile asymmetry. Nevertheless, the results of this and previous works of this team seems to be not quite reproducible. Indeed, there were no other authors who could either before or after include contribution to asymmetry from the  $\omega^4$  and Boltzmann factors. It was obvious that the first factor should produce the strong blue asymmetry, while the second factor likely would produce the red one. Since the exponential function is stronger than any power law, the net effect of these factors should result in a red asymmetry contribution. However, within the conventional definition of line profile the red part of profile  $-\infty < \Delta\omega < 0$  would lead to the exponential divergence due the Boltzmann factor  $\exp[-(\omega_0 + \Delta\omega)/T]$ , where  $\omega_0$  is the unperturbed frequency of the transition and  $\Delta\omega$  is the detuning from the line center. Moreover, in this paper all terms of asymmetry corrections of the same second order (as quadratic Stark effect) were not included.

The next year, 1998, Stobbe, Könies, Günter and Halenka published another paper related to the shifts and widths of He II lines [123]. They used again the Green function approach with the same approximate treatment of the ion quadrupole interaction and quadratic Stark effect, but additionally included the effects of fine structure and ion dynamics using the MMM method, as in the previous paper [120]. Comparison with published experimental data for  $H_\alpha$  showed that Griem's calculations almost coincided with them, while results of [123] were significantly lower. At the same time, comparison with unpublished data for  $P_\alpha$  of Grützmacher and Johannsen from 1994 demonstrated an almost perfect agreement, while Griem's results were much larger. These authors also presented the experimental results of Glenzer and Kunze, but gave no reference to them.

In 1997, Kilcrease, Murillo and Collins again considered the problems of incorporating quadrupole effects within APEX formalism [124,125]. In particular the ratio of the APEX screening parameter to Debye-Hückel length was calculated versus electron density. The constraint field gradients versus field value were calculated using APEX, molecular dynamics (MD) and Monte-Carlo simulations, and nearest neighbor distribution. A larger sensitivity to the number of particles simulated was noted for the gradients than for the microfield distribution. It was concluded that the APEX formalism provides a rather reliable description of gradients and that the model of Debye-Hückel potential was not realistic enough. This was achieved by the comparison of model calculations with the originally obtained to this problem results of Molecular Dynamics (MD). The study of the APEX application to the account of quadrupole interaction was continued in the further work of Kilcrease and Murillo [126] where some kind of the constraint distribution functions of the field gradients was constructed, again by a rather artificial and not convincing way that was characteristic for all quasi-APEX derivations (compare with [127]). In fact, it was a Gauss type approximation that at last did not match too well to MD results.

In 2000, Günter and Sorge published a paper [128], where managed to join the two particle Green function formalism with the computer simulation (CS) of ion microfield. The trivial asymmetry in the circular frequency scale and Doppler effect also were included. The first two lines of Lyman series were calculated to compare with results of experiments [43,44]. The quadrupole interaction was calculated by substituting in the Hamiltonian the first moment of the non-uniformity tensor taken at the particular point of microfield histories  $\vec{E}(t)$  along with [104]. The wave functions were taken in the reference frame rotating with the microfield, which enabled to use the simple formula for the quadratic Stark effect at the cost of calculations of rotation operations. The authors besides Stark profiles and their asymmetries, simulated the microfield covariance and noted that fluctuation in this case was much larger than in calculations of the correlation functions. The results of simulation were compared with the analytical ones for static ions, simulated static ions and MMM implementation. In these calculations the dependencies of electron impact shifts and widths on  $\Delta\omega$  were omitted. A better agreement with experiment was noted.

Also in 2000, the paper [129] of Stehle, Gilles and the author appeared, devoted to study of quadrupole effects with account of ion dynamics within the MMM [130]. It was confirmed that the ion dynamics essentially decreases the size of asymmetry, as was expected on the basis of general consideration. Special attention was paid to study of the electron polarization term, proportional to the divergence of microfield in the model of Debye screened independent field particles. From the general consideration of ion and electronic fields on the same footing it was shown that the evaluation of this term alone was a drawback of the Debye screened free particle model of field ions. To remove this difficulty one had to account for *ion* polarization term as well, that in the simplest case accounts for the positive ion background that compensated the extra negative charge in a pile-up of electrons around the plasma ion. The ion compensating background decreased the asymmetry as well. Thus in reality the very large shifts appeared due to the electron polarization term alone in [105] turned out to be erroneous. It should be noted that in [129] the consideration was given to the range of parameters, where the idea of microfield was valid, that neglects the penetrating configurations of perturbing particles. The calculations were performed in the circular frequency scale

and none of trivial asymmetry effects were accounted for. The asymmetrical features of  $\text{He}^+ \text{Ly}_\alpha$  were calculated using the Baranger-Moser cluster expansion universal functions  $W(\beta)$ ,  $B(\beta)$ ,  $(B_{D0}(\beta) - B_G)$  for  $N_e = 10^{18} \text{ cm}^{-3}$  and  $T_e = 2 \cdot 10^4 \text{ K}$ , while for  $\text{Ar}^{17+} \text{Ly}_\alpha$  MC simulations for  $N_e = 10^{24}, 10^{25} \text{ cm}^{-3}$  and  $T_e = 800 \text{ eV}$ . To characterize the asymmetry, two types of its features were calculated—the asymmetry parameter  $A(\Delta\omega)$  from (1), where  $I_{blue}(\Delta\omega) = I(\Delta\omega)$  and  $I_{red}(\Delta\omega) = I(-\Delta\omega)$ , and the bisector values depending on relative intensity. Also several ways of the definition of  $\Delta\omega$  were tested with respect to the line maximum and with respect to the unperturbed frequency.

In 2002, Demura, Helbig and Nikolić published a paper on the interdependence of asymmetry and shift characteristics [131]. By comparison of the experimentally measured profiles of  $\text{H}_\beta$  it was shown that the asymmetry is a very sensitive function of the reference point. Then the asymmetry of  $\text{H}_\beta$  was calculated within the general approach of Demura-Sholin [92] sequentially adding various asymmetry factors and comparing the obtained results on each step with the experimental data. The following asymmetry factors and their combinations were tested: the transformation from the circular frequency scale to the wavelength one; the quadrupole effects; the quadratic Stark effect corrections to shift; the quadratic Stark effect corrections to intensity; the octupole shifts. These factors were calculated with both Holtsmark and Nearest neighbor distribution function. It followed from the obtained results that: 1. Quadrupole effects alone could not describe observations; 2. The agreement of the calculated data with experiment became worse with increasing  $\Delta\omega$ , which is due to the drastic decrease of experimental accuracy in the wings; 3. The account of asymmetry due to  $\omega^4$  and Boltzmann factors in the calculations led to the large disagreement with the experimental data. As an option it was proposed to include the latter factors in the spectra background. All numerical calculations in this paper were done by D.Nikolić.

In 2002, Olchawa published a paper [132], devoted to computer simulations of Stark profiles of  $\text{H}_\alpha$  with the simultaneous account of the interactions with plasma electrons and ions. The specific construction of the extended basis of wave functions was employed [132]. The field of electrons were considered Coulomb and the ion fields Debye shielded. The interactions between perturbors were neglected. The author claimed taking account of the quadrupole interaction or field gradients (FG), the quadratic Stark effect (Q2S) with account of the interaction with adjacent levels and the fine structure (FS). The shift of calculated  $\text{H}_\alpha$  profile was reported in the density range  $N_e = 6 \cdot 10^{17} \div 10^{19} \text{ cm}^{-3}$  and compared with results of the other works. The calculated shift reached the value of  $40 \text{ \AA}$  at a density a bit lower than  $N_e = 10^{19} \text{ cm}^{-3}$ . At the same time, the analysis of the associated with this shift asymmetry was not performed. It is interesting, that without the inclusion of FS the value of shift was larger in this region. The experimental points were lower than predicted by calculations, while their accuracy reported to be around  $20 \text{ \AA}$  at those densities. It is worth noting that a rather complicated way of construction of the extended basis was used (see [132]).

In 2005, Djurović, Nikolić, Savić, Sorge and Demura published a paper focused on asymmetry analysis of new experimental measurements of  $\text{H}_\beta$  profiles in T-tube plasmas [62]. To achieve a more complete description of asymmetry and to reveal the hidden mechanisms of this phenomenon, the conventional as well as new parameters of asymmetry were analyzed. It was decided to perform comparison with the results of standard theory (ST) approach with addition of only the quadrupole interaction [92] and collisional electron shifts [113]. The electron collisional shifts were calculated within the theoretical framework of S.Günter [113]. The non-diagonal elements of the electron impact broadening operator were neglected (in the parabolic basis). The HWHM of the calculated profiles were a bit larger than Griem results [74,75]. The Debye screening, electron polarization term and ion-ion correlations were neglected in this work, so all universal functions were Holtsmark-based. The comparison with experimental data showed that this simple theoretical model qualitatively correctly presented the sign of asymmetry and the detuning from the line center, where it changes its sign, but the magnitude of asymmetry was noticeably less than experiment for all defined asymmetry parameters. This could be partly due to an overestimation of electron impact widths [111] and partly to neglecting the plasma coupling [102,104,116,117], which evidently would increase the magnitude

of the universal functions [92]. The considered asymmetry parameters were similar to those used in [36]. Also the authors again discussed the inclusion of the  $\omega^4$  and Boltzmann factors. At the time the idea of adding these factors in the definition of spectra background was severely criticized and rejected by the co-authors—experimentalists. Indeed, the estimates of inclusion of those factors into the trivial asymmetry led to a blue asymmetry at all frequency detunings, that contradicted the experimental data. Therefore, the authors concluded that these factors still represented a problem for the consistent treatment.

In 2006, González and Gigoso published results of study the asymmetry of Balmer lines ( $\alpha, \beta, \gamma, \delta$ ) by computer simulations in the  $\mu$  model [133]. The interactions of the plasma perturbers with the emitter in [133] were considered in the dipole approximation. The electric fields of plasma perturbers were assumed to be Debye shielded with  $R_D$ , determined by the electron temperature and density. The basis set of wave functions (WF) included all states from  $n = 1$  to  $n = 5$  in the case of  $H_\beta$  line, thus effectively that meant a complete inclusion of Q2S corrections within chosen basis. The data obtained for the conditions of experiment for  $H_\beta$  [62] showed a very good agreement for the total profile and for all three asymmetry parameters (see [62]).

In 2007, Halenka and Olchawa published their derivation of quadrupole and octupole tensor of the Debye shielded ion microfield at a neutral point [134] and claimed, that they implemented a Mayer-Mayer cluster expansion [135]. Two years later in 2009 Halenka published the same type of calculations [136] for the octupole tensor at a charged point and this time attributed it to the implementation of Baranger-Mozier cluster expansion scheme [94]. From a comparison of the both derivations it follows that only the second allegation was correct. The derivations and even the designations in the implementation of Baranger-Mozier cluster expansion scheme in [134,136] are similar to the one in [102]. However, both works [134,136] contained the results of calculations of universal functions, introduced in [102], for quadrupole and octupole microfield tensors at a neutral point and for the latter one at a charged point too. The analysis showed that these numerical and graphical data were quite accurate and could be recommended for further studies.

In 2008, Demura, Demchenko and Nikolić published detailed calculations [137] of asymmetry parameters for all individual  $H_\beta$  Stark components. The sensitivity of asymmetry patterns was studied by the sequential addition of the various terms of trivial asymmetry (here only transformation from circular frequency scale to wavelength one), quadrupole corrections to frequency, quadrupole corrections to intensity, Q2S corrections to frequency, Q2S corrections to intensity, electronic collision shifts and widths of particular Stark components. The ions were considered quasistatic, while electrons-impact. The electronic collision shifts were calculated for us by S. Sorge, using the program of S. Günter within the two particle Green function approach [138]. The basis of WF contained only those with the same principal quantum number  $n$ . The Holtsmark and nearest neighbor distribution functions were used. It was noted that in such settings it was not possible to use the expansion of the resolvent by perturbation parameter due to the appearance of divergences under the integration over microfield values. That is why the only way was to substitute the constraint moments over the gradients directly into the resolvent, as was originally proposed by Joyce, Woltz and Hooper in [95]. The numerical calculations were done by G. V. Demchenko and D. Nikolić, using two different codes. The results revealed that Q2S shifts produced extrema in the dependencies of asymmetry parameter versus detuning from the line center in the wavelength scale  $\Delta\lambda$ . The asymmetry parameter was also sensitive to the value of the electron impact widths. It decreased with increasing electron widths. It was noted that in many papers, the inclusion of Q2S was performed inconsistently. Namely the Q2S corrections to intensity were neglected. Taking these corrections into account showed that the asymmetry parameters were negative for practically all Stark components of  $H_\beta$  in the entire range of  $\Delta\lambda$ . Since in some other works Q2S corrections, considered in the extended basis, led to a positive asymmetry parameter, one could conclude that the WF extended basis implementation for Q2S was crucial here.



The work again investigated the influence of the  $\omega^4$  and Boltzmann exponential factors. The first point was to limit the frequency to  $\omega = 0$ , i.e.,  $\Delta\omega = -\omega_0$ , where  $\omega_0$  is the unperturbed circular frequency. This is because negative frequencies are not defined, and this is a potential source of asymmetry. This in principle changes the profile definition and normalization. Normalization was enforced on that interval i.e.,  $\Delta\omega = (-\omega_0, \infty)$ . We recalculated the asymmetry parameter for  $H_\beta$  with those factors and compared it with experimental data [139], obtained in V.Helbig's lab. It turned out that its sign was negative if the Boltzmann temperature  $T_a$ , describing the relative level population of the emitter, was equal to the electronic temperature  $T_e$ . A positive sign was obtained for  $T_a = T_e/3.5$ . This is physically plausible due to the construction of a wall stabilized arc with enforced cooling. It was additionally assumed that the electron impact widths were overestimated and some reduction coefficient of 1.4 was introduced. This also in principle was plausible since the non-diagonal matrix elements of impact operator were neglected. Indeed, it was noticed that the parabolic electron impact widths were larger than those, obtained with the spherical basis functions and using a matrix inversion of the resolvent, i.e., without the diagonal approximation. After this correction, agreement with experiment was almost perfect. Meanwhile also one must keep in mind that experimental accuracy in line wings was not high, thus error bars were large. However, Helbig opposed the assumption of deviation of the temperature, corresponding to population of atomic levels, from the electron one due to the conventional opinion about LTE in the arc discharge.

In 2009, Djurović, Ćirišan, Demura, Demchenko, Nikolić, Gigosos and González presented measured asymmetrical experimental Stark profiles of  $H_\beta$  and their interpretation in terms of Standard Theory (ST) and Computer Simulations (CS) [66]. The measurements were performed on three different installations in order to extend the range of available plasma parameters like the electron density and temperature and concerned mainly the central part of the line. The ST and CS approaches did not include the disputable asymmetry  $\omega^4$  and Boltzmann exponential factors. ST asymmetry calculations were performed in the same settings as in the paper described above [137]. However, here the ST calculations were compared primarily with peak asymmetry versus the plasma electron density (see Figure 5 in [66]). The ST data were presented adding the effect of various asymmetry factors to assess their importance. The best fit was achieved with a non-perturbative approach with the reduced electron impact widths by a factor of 1.4 and the electron impact shifts included, calculated by Omar and Sorge [140], using the program of S.Günter. In this figure from [66] the agreement was better at high densities, since for lower densities the assumptions of ST became clearly invalid. The CS were performed practically in the same settings, as it was done earlier [133], but for a much wider range of plasma parameters and only for one  $H_\beta$  line. The interactions between electrons and ions were disregarded in CS. On the other hand the WF basis for CS was much larger than for ST. As was concluded above from comparison of contributions of various mechanisms of asymmetry, performed in different papers, the usage of extended basis, i.e., quenching collisions, is a crucial ingredient of CS-experiment agreement. CS demonstrated a very good accuracy in description of the total experimental profile as well as spectral behavior of the conventional asymmetry parameter. Also the dependencies of peak asymmetry versus plasma density obtained in CS and ST were compared with the enlarged set of experimental data, obtained in different papers (see [66] for details). The same were performed for the relative dip, the separation of the peaks and the ratio of peak separation to FWHM. In all these figures CS data better corresponded to the experimental trends and values, since clearly CS were more powerful and flexible in the description of real perturber dynamics and interactions and thus better suited to regimes and values of Stark broadening on an equal footing by plasma ions and electrons. Agreement of CS with experiment indicates that factors not included in CS (which use classical trajectories), such as dynamic screening or a dielectric formalism, were not that important as far as shifts and asymmetries are concerned in this case.

In 2016, Gomez, Nagayama, Kilcrease, Montgomery and Winget published a study on higher order multipole moments in formation of Stark profiles [141], attempting to equally describe interactions with plasma electrons and ions. The  $H_\beta$  line shape was again the aim of the paper as in many



previous works. The noninteracting Debye screened particles with straight trajectories were used for simulations of neutral radiator broadening with the same electron Debye screening for electrons and ions. The authors aimed to reconsider simulations done in the previous work [66], including the electron and ion quadrupole interactions and using an extended basis like for Q2S for all cases. This allowed an improved description of asymmetry in the range of densities larger than  $3 \cdot 10^{17} \text{ cm}^{-3}$ , where accounting for only the dipole interaction of ions and electrons overestimated profile asymmetry in the extended basis [66]. The authors thought that the relative importance of higher order terms was not sensitive to temperature variation. It was shown, that adding only the ion quadrupole interaction to dipole of ions and electrons, led to worse agreement with experiment, than adding quadrupole interaction from ions and electron together. The calculations performed with the sedecapole contribution from particles of both signs did not noticeably enhance the accuracy. A posteriori one could infer, that the decrease of peaks asymmetry magnitude after addition of the electron quadrupole contribution could be due to the increased magnitude of electron broadening. Indeed near the line center, where peaks are located the broadening by electrons is likely nonimpact. However, to our knowledge at the moment the results of [141] are not confirmed in the independent CS, performed by the other groups.

### 3. Influence of Quadrupole Interaction with Ions and Electrons on Line Wings

During the preparation of this paper it was understood that an explicit proof of statements on disappearance of asymmetry in the far wings of Stark broadened spectral lines due to the total quadrupole interaction of plasma ions and electrons was not given. In fact, it was widely spread opinion, the origin of which is difficult to point out exactly. For example, in the monograph ([73], see §39.4) for the case of non-hydrogen spectra it is said that *total quadrupole shift for equal density of electrons and ions is zero*. Meanwhile there were doubts that according to CS setting the mentioned cancelation seemingly would not occur. So, below we consider the sufficiently large  $\Delta\omega$  from the line center, where the ion and electron interaction with the neutral radiator are static. Then the wings of the Stark profile can be accurately represented using the nearest neighbor distribution function [127]. Keeping in mind the additivity of the electron  $I_e(\Delta\omega)$  and the ion  $I_i(\Delta\omega)$  contributions and the dependence of nearest neighbor distribution only on the total particle density  $N = N_i + N_e$  we can write in atomic units, denoting the intensity of the “ $k$ ”-th Stark component with  $I_k$ , conventionally assembling the blue  $k > 0$  and red  $k < 0$  lateral Stark components together

$$I(\Delta\omega) = \frac{1}{\sum_k I_k} \sum_k I_k [I_i(\Delta\omega) + I_e(\Delta\omega)], \quad (2)$$

In Equation (2), the sum in the denominator  $\sum_k I_k$  means the total intensity of the line, so that  $k$  runs over  $k > 0$  and  $k < 0$  both, together with all central components  $I_{oc}$  if they exist for the given line, while in the numerator the sum runs only over positive  $k$  and all central components.

The functions  $I_{i,e}(\Delta\omega)$  involve an integration over the nearest neighbor distances. We would make no distinction between electron or ion  $R$  in  $I_e(\Delta\omega)$  and  $I_i(\Delta\omega)$  since this specifics of charge sign is contained already in the expressions for quasistatic profiles for the fixed  $R$  position of the perturber in  $L_{il}(\Delta\omega) + L_{ic}(\Delta\omega)$  and  $L_{el}(\Delta\omega) + L_{ec}(\Delta\omega)$ . Here the subscripts “il”, “el” designate ionic and electronic contributions due to the lateral Stark components, while the subscripts “ic”, “ec” designate the ionic and electronic contribution from central Stark components. As one could see the probability to encounter electron or ion in the location of the nearest neighbor is defined simply by the ratio of the density of the chosen species to the total density

$$I_i(\Delta\omega) + I_e(\Delta\omega) = \int_0^\infty dR 4\pi R^2 (N_i + N_e) \exp \left[ -\frac{4\pi R^3 (N_i + N_e)}{3} \right] \left( \frac{N_i}{N_i + N_e} [L_{il}(\Delta\omega) + L_{ic}(\Delta\omega)] + \frac{N_e}{N_i + N_e} [L_{el}(\Delta\omega) + L_{ec}(\Delta\omega)] \right) \quad (3)$$

As one could check the expression for  $L_{el,ec}(\Delta\omega)$  could be obtained from  $L_{il,ic}(\Delta\omega)$  by changing the sign in constants  $D_k, \varepsilon_k, Q_k$ . The properties of this constants with respect to this operation are specified below

$$L_{il}(\Delta\omega) = \left[ \left(1 + \frac{\varepsilon_{kl}}{R}\right) \delta\left(\Delta\omega - \frac{D_{kl}}{R^2} - \frac{Q_{kl}}{R^3}\right) + \left(1 - \frac{\varepsilon_{kl}}{R}\right) \delta\left(\Delta\omega + \frac{D_{kl}}{R^2} - \frac{Q_{kl}}{R^3}\right) \right], \quad (4)$$

$$L_{el}(\Delta\omega) = \left[ \left(1 + \frac{\varepsilon_{kl}}{R}\right) \delta\left(\Delta\omega + \frac{D_{kl}}{R^2} + \frac{Q_{kl}}{R^3}\right) + \left(1 - \frac{\varepsilon_{kl}}{R}\right) \delta\left(\Delta\omega - \frac{D_{kl}}{R^2} + \frac{Q_{kl}}{R^3}\right) \right] \quad (5)$$

$$L_{ic}(\Delta\omega) = \delta\left(\Delta\omega - \frac{Q_{kc}}{R^3}\right), \quad L_{ec}(\Delta\omega) = \delta\left(\Delta\omega + \frac{Q_{kc}}{R^3}\right) \quad (6)$$

In Equations (4)–(6) and below  $\delta(x)$  designates Dirac delta function. In the above equations the  $\varepsilon_{kl}$  is the correction to intensity of the  $k$ -th lateral Stark component due to quadrupole interaction,  $D_{kl}$  is the linear Stark effect constant for  $k$ -th lateral Stark component, and  $Q_{kl,kc}$  is the constant of the  $k$ -th lateral  $l$  or central  $c$  Stark components shift due to quadrupole interaction. Also in the presentation of (2)–(6) we used the properties of these characteristics with respect to the change of sign of perturbing particles. The constant of linear Stark effect obviously changes its sign under the change of the perturber sign, so  $D_{kl}^{(e)} = -D_{kl}^{(i)}$ ; however it does not change the linear Stark effect pattern of splitting, since it is symmetric. The  $\varepsilon_{kl}$  for lateral Stark components is formed by the matrix elements of the same charge, which enter in the quadrupole interaction in the numerator, and dipole interaction in the denominator. Thus it is the even function with respect to change of the charge sign  $\varepsilon_k^{(e)} = \varepsilon_k^{(i)}$ . Contrary to this the quadrupole shift  $Q_k$  changes its sign due to the change of the charge sign  $Q_k^{(e)} = -Q_k^{(i)}$ . Additionally, from the beginning the following relations between constants corresponding to the blue (larger circular frequency,  $k > 0$ ) and red (smaller circular frequency,  $k < 0$ ) lateral Stark components are fulfilled:  $\varepsilon_{kl} = -\varepsilon_{-kl}$ ,  $D_{kl} = -D_{-kl}$ ,  $Q_{kl} = Q_{-kl}$  [76,85]. For the central Stark components  $\varepsilon_{kc} = 0$  for any hydrogenlike emitter [84,92]. The Equations (4)–(6) above are presented using these properties and we expressed constants, related to electrons, via constants for ions. As could be easily verified the profile defined in (2)–(6) is normalized to unity.

Since the quadrupole term is smaller than the dipole one the  $\delta$ -functions in (4) and (5) could be expanded for the lateral Stark components

$$\delta\left(\Delta\omega - \frac{D_{kl}}{R^2} - \frac{Q_{kl}}{R^3}\right) \approx \delta\left(\Delta\omega - \frac{D_{kl}}{R^2}\right) - \frac{Q_{kl}}{R^3} \delta'\left(\Delta\omega - \frac{D_{kl}}{R^2}\right) \quad (7)$$

$$\delta\left(\Delta\omega - \frac{D_{kl}}{R^2} + \frac{Q_{kl}}{R^3}\right) \approx \delta\left(\Delta\omega - \frac{D_{kl}}{R^2}\right) + \frac{Q_{kl}}{R^3} \delta'\left(\Delta\omega - \frac{D_{kl}}{R^2}\right) \quad (8)$$

and keep only the terms of the zero and first order in the perturbation parameter  $\varepsilon \ll 1$ , mentioned above.

Thereafter assuming plasma quasineutrality and for concreteness setting  $\Delta\omega > 0$  and using the expansion (7) and (8), one could be convinced even without taking the integrals using the properties of delta-functions and its derivatives that terms linear in the perturbation parameter, namely proportional to  $\varepsilon_k$  or  $Q_k$ , cancel each other for the lateral Stark components. Taking then  $\Delta\omega < 0$  one would find the same.

For the central Stark components  $D_{kc} = 0$  and the delta-function could not be expanded. Assuming some definite sign of  $Q_{kc} > 0$  it is seen that only ions contribute to a blue shift of the central component for  $\Delta\omega > 0$ . In addition, otherwise for  $\Delta\omega < 0$  only electrons contribute to a red shift of the central component. Thus one could see that taking into account simultaneously the ion and electron quadrupole contributions no cancellation takes place for the central Stark components, but instead the symmetrization occurs. For  $N_i = N_e$  the total intensity of all components shifted to the blue and red doubles.

So, indeed the first order quadrupole asymmetry sources cancel in the wings only for lateral Stark components as was predicted by Sobel'man, Griem and Sholin. As for the central Stark components their contribution appears due to electrons also in the opposite wing of the line with respect to ions, and one gets splitting in two symmetrical components with the same intensity. This provides no asymmetry. Thus the hydrogen line asymmetry due to the first order quadrupole interaction disappears in line wings, where the Stark broadening by ions and electron could be considered as static.

At this stage one encounters another problem—how far is this wing, where are the formulas written above valid? The conventional theory of spectral line broadening gives the answer, when one considers only one power potential—dipole one [73,116] for our case, while nothings is known when the potential has two power terms “dipole+quadrupole”.

Therefore, considering the lateral Stark components under the action of plasma ions when the detuning from the line center is larger than the ion dipole Weisskopf frequency  $\Delta\omega \gg \Omega_W^{(Di)}$  [73] the above presented formulas are valid for sure. For electrons it necessary to satisfy similar inequality  $\Delta\omega \gg \Omega_W^{(De)}$ . Thus the condition  $\Delta\omega \gg \max\{\Omega_W^{(Di)}, \Omega_W^{(De)}\}$  is necessary for achieving the asymptotic behavior for lateral components. As the dipole interaction is zero for the central components than its asymptotic form appear under the similar condition with the quadrupole Weisskopf frequencies  $\Delta\omega \gg \max\{\Omega_W^{(Qi)}, \Omega_W^{(Qe)}\}$ . Summing all that up we come to condition

$$\Delta\omega \gg \max\{\Omega_W^{(Di)}, \Omega_W^{(De)}, \Omega_W^{(Qi)}, \Omega_W^{(Qe)}\} \quad (9)$$

It is instructive to present estimates of Weisskopf frequencies according to general expressions in [73], corresponding to dipole interaction of ions and electrons

$$\Omega_W^{(Di)} \sim \left(\frac{\hbar v_i}{e^2}\right)^2 \frac{Z_r}{n^2 Z_p}, \quad \Omega_W^{(De)} \sim \left(\frac{\hbar v_e}{e^2}\right)^2 \frac{Z_r}{n^2}, \quad (\Omega_W^{(Di)} / \Omega_W^{(De)}) \sim \left(\frac{v_i}{v_e}\right)^2 \frac{1}{Z_p} \quad (10)$$

and quadrupole one

$$\Omega_W^{(Qi)} \sim \left(\frac{\hbar v_i}{e^2}\right)^{3/2} \frac{Z_r}{n^2 Z_p^{1/2}}, \quad \Omega_W^{(Qe)} \sim \left(\frac{\hbar v_e}{e^2}\right)^{3/2} \frac{Z_r}{n^2}, \quad (\Omega_W^{(Qi)} / \Omega_W^{(Qe)}) \sim \left(\frac{v_i}{v_e}\right)^{3/2} \frac{1}{Z_p^{1/2}}, \quad (11)$$

where  $Z_r$  is the hydrogenic radiator nucleus charge and  $Z_p$  is the ion perturber charge,  $e$  is the value of electron charge,  $\hbar$  is the Planck constant,  $v_i, v_e$  are ion and electron velocities. It is seen that ion dipole and quadrupole Weisskopf frequencies are smaller than corresponding ones for electrons.

On the other hand, the ratios of the dipole to quadrupole Weisskopf frequencies for the same perturber shows, that for ions and electrons they are likely less than unity till the values of their velocities are smaller than the (velocity) atomic unit

$$(\Omega_W^{(Di)} / \Omega_W^{(Qi)}) \sim \left(\frac{\hbar v_i}{e^2 Z_p}\right)^{1/2}, \quad (\Omega_W^{(De)} / \Omega_W^{(Qe)}) \sim \left(\frac{\hbar v_e}{e^2}\right)^{1/2} \quad (12)$$

Having in mind some realistic parameters of experiments one could conclude, that the quasistatic regime normally switched on earlier for the dipole interaction for ions than for the quadrupole interaction. For electrons the ratio of corresponding Weisskopf frequencies could be less and more than unity depending on plasma parameters.

Returning to the cancelation of contributions it could occur only when both the ion and electron profiles of lateral components reach the same asymptotic. So, in the gaps when the electron profile did not reach the same dipole asymptotic there is no cancelation of ion asymmetry. The similar reasoning refers to the central components, and as long as the electron quadrupole profile does not reach the ion quadrupole asymptote, there would be ion quadrupole asymmetry of the central component.

As the definition of the central components itself depends on the dipole interaction one could not consider them under the action of only quadrupole interaction. However, within the conventional consideration of the line broadening theory the resolution of this dilemma is unclear [73]. Moreover, the existing and used criteria in fact had originated from the adiabatic theory of broadening [73] and thus are not exact in the general case. In this context the CS seems to be the only tool, that could clarify this problem and the study of *dynamic* quadrupole contribution of the central components in such settings gains a principal importance [142].

#### 4. Discussion

The presented analysis of published experimental and theoretical data on the asymmetry of Stark profiles has first shown that up to now it was not possible to complete calculations of asymmetry in the ST setting, according to the Sholin's prescriptions of taking all terms of the second order over perturbation parameter  $\varepsilon$  within the non-quenching approximation, because even the second order moment of quadrupole interaction is still unknown. On the other hand the application of the perturbative theoretical approach [84] with the incomplete set of the second order corrections did not provide the satisfactory agreement with experimental data [63,66,131,137].

Meanwhile the several publications appeared, where CS were used to obtain the asymmetrical hydrogen profiles with the incomplete [66,133] and seemingly numerically complete sets of the second order terms [134] within the Kudrin-Sholin approach [83,84]. The ion and electron interactions with the radiator were treated on an equal footing, and the obtained results quite well described the known experimental data. In these works the calculations were performed in the extended basis [56,132,133,141].

As could be concluded from above by the comparison of the contributions of various mechanisms of asymmetry, performed in different papers, the usage of extended basis play a crucial role in achieving within CS the satisfactory reproductions of the experimental data trends. Indeed, the implementation of the extended basis means in fact the application of “close coupling” approach from the theory of electron-atom collisions [73,147] to the description of the Stark broadening phenomenon. It is well known that the theory of collisions has the inherent links with the theory of Stark broadening [143–147]. In the “close coupling” approach, depending on the given set of aims, not only the itemized terms of multipole potential expansion could be taken into account, but also the monopole and the polarization terms as well and the penetrating configurations, where the notion of microfield obviously is inapplicable [147]. In fact, it is a way of enriching the broadening consideration by taking into account the other atomic radiative-collisional processes.

Thus it was quite unexpected that the conventional perturbative approach, adopted for the line broadening within the initial setting [148], failed to give the satisfactory treatment of the observed Stark profiles asymmetry, and only the correctly performed CS simulations in the *extended basis* with the simultaneous account of dynamics of the ionic and the electronic plasma microfields provided reasonable description of the total Stark profiles and their asymmetry properties [66,133,141] in a wide range of plasma parameters deviation.

Additionally, reminding about the unsolved task of  $\omega^4$  and Boltzmann factors contributions to the asymmetry description, we have to conclude that the problem under study is not closed and many questions have to be understood and explained yet.

The performed research revealed that the asymmetry of hydrogen lines is much more complicated and physically rich phenomenon, than it was thought earlier. It could not be treated only within microfield inhomogeneity, but is influenced by many physical factors, where the simultaneous dynamics of ionic and electron microfields play a significant role. It is also became clear that originally suggested to its description the perturbative approach with non-quenching approximation are not adequate enough. Also it was understood that even the deviations from LTE could noticeably affect its behavior.

This review does not pretend on encircling of all research in this field and the choice of material is subjective along with the knowledge and vision of the author.

As an epilogue it is worthy to remember one of G.V. Sholin sayings, that scientists (and people at large) get so familiar with long “established” results that no one thinks of questioning them. For example, why only transitions between levels with *even* principal quantum numbers do not have unshifted central Stark components? Why  $\varepsilon_k$  and  $Q_k$  possess the asymmetry properties of their sign with respect to symmetrical lateral Stark components? At the moment we have no general proof or explanation for that...

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## Appendix A. On Theoretical Shifts of Hydrogenlike Emitters

In spite of a huge number of papers, devoted to the theory of the spectral line shifts of hydrogen and hydrogenlike ions in plasmas, it is quite difficult to get a clear understanding of their sources and mechanisms, and compare the results of calculations, obtained within different approaches. This could be concluded even from the titles of the rather short list of references [60,73–76,92,99,102,105,113,123,132,142–144,147,148,151–186]. Moreover, it is necessary to underline from the beginning that the results in this field are very complicated and often controversial [60,73–76,92,99,102,105,113,123,132,142–144,147,148,151–186]. As in the case of asymmetry of hydrogen spectral lines the way of definition of the shift is very important [113,129,131]. Presently the theoretical and experimental errors for the shifts in distinction to the widths could reach more than 100% [132]! Moreover, to the best of the author’s knowledge, there is not a single comprehensive review that is devoted to the analysis of the theoretical results in this field in the literature. So, to our mind the time for a thorough coverage of this field has not come yet. That is why we restrict ourselves in this situation to a short sketch of our vision.

The shift of a spectral line is formed in the first place due to a perturbation of the radiator (absorber) atomic structure by the plasma environment, that results in the distortion of the electronic density distribution inside the atom, and the boundary conditions at the atom-plasma interface, which in turn changes the initial distribution of the oscillator strengths over the components of a multiplet.

However, since in general the effective time of the profile formation is determined by the reciprocal of the detuning from the line center  $\Delta\omega$ , *pari passu* it relates to the main profiles characteristic as the line width and the shift [147,148,183,184] as well, which are integral by the definition too. Nevertheless, it could be imagined that these peculiarities could be described by the introduction of the  $\Delta\omega$ -dependent shift and width operators in the resolvent (see, for example, [162]). So, as the contributions of various mechanisms in the line width and the line shift operators depend on  $\Delta\omega^{-1}$ , it should result in the nonuniform distribution of the corresponding effective width and the shift values in the resolvent. In practice this kind of self-consistent consideration has not yet realized, because of its complexity.

When an emitter is immersed in plasma, it is perturbed by the ionic and electronic electric fields. Let us first for simplicity assume that we are working within the ST assumptions [73–75] and neglect a possible presence in the plasma composition of neutral species.

Thus the ionic fields are static, while electronic fields are impact [73–75]. The structure of the multiplet could be influenced first by a slow ionic microfield that could in principle induce the deviations of the positions of components of multiplets and thus a shift of the line at large, for example, due to the Q2S and the microfields gradients, that to some extent are described in the main text.



Another type of shifts in plasmas concerns the lines of *ions* and could be attributed to the stationary deviation of the electron density distribution inside the emitter, induced by the shielding of the nucleus of the emitter by plasma electrons, penetrating inside the ion or confining the emitter electronic shells from the outside. The first attempt to estimate this kind of shifts for HeII lines was undertaken in [151], where it was classified as a “plasma polarization shift” (PPS) [99,151,152]. The idea of PPS is ascribed to Griem. Since that [151,152] various models of its evaluation were proposed [99,153,154,156,170,172–174,176,182,185]. This type of shift is also attributed to different realizations of ion sphere model (ISM) [99,156,170,173,176,185].

The idea of PPS was elaborated, developed [99,153,154,156,170,172–174,176,182,185] and criticized [160,167,175] in a great number of papers, and it is impossible to point out all of them here. As it was noted in [160], the PPS results, classified in [160] as the *effect of initial electron correlations* [161–165,167], could substantially overestimate the observations, because of the unaccounted for frequency-dependent *dynamic* contribution to the ion line shift [160,167,177], related to the dynamic screening of the electron perturbors in plasma [162,167].

Nevertheless, the studies of the PPS idea are continued [185] in spite of expressed criticism [160,167,175].

Evidently, the rapid electric fields due to the collisions with electrons could also contribute to the line shift. The general form of the expression for this shift  $d_{if}$  of the transition  $i \rightarrow f$  was derived in the impact limit by Baranger [143–145] as

$$d_{if} = \left\langle -\frac{2\pi\hbar N_e}{m_e} \Re[f_i(0) - f_f(0)] + i\frac{v_e N_e}{2} \int d\Omega [f_f^*(\Omega)f_i(\Omega) - f_f(\Omega)f_i^*(\Omega)] \right\rangle_{Av},$$

where  $f_{i,f}(\Omega)$  is the electron scattering amplitude on the emitter in the upper  $i$  or lower level  $f$ ,  $\Omega$  is the solid angle. *The beauty of this result is that it is obtained for any interaction potential of perturbors with an emitter, using a general momentum representation of wave functions!*

According to the Baranger theory [143–145], the quantum calculations of the HeII Ly-alpha shifts in the impact approximation were performed by Yamamoto and Narumi [155]. The authors used the Hartree-Fock wave functions and the R-matrix technique for the scattering problem. The result was of the order of  $10^{-4}$  Å and red, while the earlier experimental measurements reported blue shifts more than two orders of magnitude larger (see [155]) and attributed to PPS.

It goes without saying that it is simpler to use an additional approximation, expanding the scattering amplitude and calculate the so called second-order shifts [157,158,160,164,169,171,177,182]. Griem calculated the second-order electron inelastic collision shifts due to the dipole interaction in the impact approximation with the account of transitions to the adjacent levels with  $n' = n \pm 1$  [157,158]. However, the estimations showed, that the shift magnitude was smaller than what would be needed to describe observations.

Just the next year Boercker and Iglesias [160] shown that additionally a nonzero contribution to the second-order collisional shifts due to the transitions between degenerate states, belonging to the same principal quantum number  $\Delta n = 0$ , exists. This became possible due to the implementation of the theory of charge-density fluctuations in plasma broadening, developed by Dufty, Boercker and Iglesias (DBI) [161–164]. Besides the “static” (resulted from the average of the initial correlations of radiator-electron interaction [164]) and the “dynamic” parts of this shift were distinguished in [160], that had different signs and partially compensate each other [160]. Although in both cases the same physical effect—the Debye electron screening—was put to grounds (the static and dynamic screening, of a moving charge in plasma), the results differ by a factor of 2 and have opposite signs. It is worth noting that this separation on the “static” and “dynamic” parts is rather artificial, because in fact it concerns the evaluation of the same improper integral in the singular point of one of the arguments  $\Delta\omega = 0$ , corresponding to the impact limit. From the mathematical point of view the integral under consideration [160] is equal to the sum of the two contributions in this limit  $\Delta\omega \rightarrow 0$ : the residue in the point of singularity plus the principal value integral. The first term is called “static” part, while the second—“dynamic” part [160], although both already do not depend on  $\Delta\omega$ , since it is put equal to

zero. So, the total shift separation in [160] is a sum of the “static” and the “dynamic” parts [160] was done only for the visualization.

The derivation in [160] is performed in assumption that  $\Delta\omega \ll \omega_{pe}$ , where  $\omega_{pe}$  is the electron plasma frequency. It is interesting to note that this “static” part in fact corresponds to the small  $\Delta\omega$  and has no relation to the quasistatic limit. The static part of shift also could be considered as a consequence of the assumption of LTE between the immersed emitter and plasma environment [164], that is not assumed in the other considerations [183,184] due to the existing criticism of the Debye plasma model itself. In [160] the eigenfunctions of the electron perturbers were used in the momentum representation, and in general the results could be applied for any type of the interaction potential.

The comparison of [160] with the two-particle Green function approach (TPGF) [168] showed that within the impact approximation and in the high temperature limit both theories [160,168] result in the expressions for the shift, which coincide even literally [168]. This could be expected due to the operation with the same physical notions of screening in the ionized gas and the implementation of momentum representation for the wave functions of the perturbers [160,168]. We note that within the TPGF formalism the many calculations of the line shifts (mainly induced by electron collisions) were performed and their results were compared with available experimental data, while there are only a few such calculations within the DBI approach [177]. So, a more thorough study of the comparison of these approaches in view of their correspondence to the experimental data is required.

At last the procedures of calculations of these shifts were adjusted in the papers of Griem, Boercker, Iglesias and Lee [165,166,169,171]. As follows from the consideration presented in [171], the main cause of the Boercker-Iglesias dipole shifts with  $\Delta n = 0$  [150] or equivalently from the TPGF technique [113,114,120,123,168] in the impact limit, the high temperature approximation and neglect of the electron correlations is the dropping of the approximation of the constant momentum of the electron perturber during collision with the target. In other words, this is but a correct account of the principle of detailed balance [147,168,171]. As it is noted in [171] in order to transfer the energy to the target the perturber should have it first.

So, in the case of ST settings for the *hydrogenic* emitters without effects, described in [160], there could be no electron collision shifts in the *no quenching* impact approximation as follows from the symmetry considerations (see P.Curie quote). Namely, the attempts of the justification of this point by the analytical and numerical means were considered correspondingly by Alexiou [178], Halenka [180] and Alexiou, Griem, Halenka and Olchawa [181]. Thus the effects, described in [160,168,171], seem to be presently the only cause of the electronic collisions dipole shift in no quenching approximation.

For the ion emitter the static and dynamical parts will have the additional contribution from the monopole term in [160].

In 2003 Alexiou published the study [179] of the total line shift formation of the hydrogenic ions performed within the nonperturbative semiclassical approach, analyzing the various contributions versus the values of impact parameters  $\rho$  and velocities  $v$  of plasma electrons with the account of the terms of the multipolar potential expansion beyond the dipole one. The study of the influence of the particular values of the particle velocities on the interaction dynamics and, hence, on the shift characteristics [179] demonstrated increased complexity of the total shift formation. The contributions from the various ranges of the  $\rho, v$  variables are subjected to the strong concurrence, leading to changes of the shift sign [179]. At the same time, the results are strongly dependent on the assumptions of the Debye model [179]. It is also noted the sensitivity of results for the shifts to the deviation from LTE assumption [179,182]. However, in spite of the exactness of performed study [179] it did not allow to claim the reliability of the total shift calculations.

Recently in 2018 Stollberg, Stambulchik, Duan, Gigosos, Herrero, Iglesias and Mossé published a paper with the new measurements of the width and shift of He II  $P_\alpha$  [186]. The comparison of obtained experimental data for the He II  $P_\alpha$  [186] with the previous ones has shown reasonable agreement. The several codes, described earlier elsewhere, were applied for the calculations of the shifts, related to the experimental plasma parameters: ST(Duan), MELS(Iglesias), SimU(Stambulchik) (see [186]).

The comparison of the calculated shifts for  $N_e = 10^{18} \text{ cm}^{-3}$  as a function of temperature does not show the same trends. The results of the SimU shifts calculations as a function of plasma density shows strong dependence on the rank of the extended basis. In spite of the obtained new results and the evident overall progress of this work the calculated shifts were found smaller than the observed ones.

Thus, the presented above consideration demonstrates the necessity of the further extensive studies of this complicated topic.

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