and the expressions (MT 3.10), (MT 5.14) for $\ln\Xi$ can be put into the form (6) by algebraic manipulations which need not be reproduced here.

The expressions (MT 3.7), (MT 5.12) for the entropy can be derived from (6) using the standard thermodynamic formulas, and are found to be related to the quasiparticle distribution function $\rho(k)$ by the ideal Fermi and Bose gas formulas. Although this result is implicit in past work,[2–7] the explicit recognition of the resultant connection with Landau's Fermi-liquid theory[11] is due to Morita and Tanaka.

[11] L. D. Landau, Zh. Eksperim. i Teor. Fiz. **30**, 1058 (1956) [English transl.: Soviet Phys.—JETP **3**, 920 (1957)]. See in particular Eqs. (3), (4).

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Theory of Wing Broadening of the Hydrogen Lyman-α Line by Electrons and Ions in a Plasma*

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The frequency distribution of the absorption and emission coefficients on the wings of the hydrogen Lyman-α line broadened by local fields of both electrons and (quasistatic) ions in a plasma is calculated in the classical path approximation for regions well outside the half-intensity points. Depending on velocities and frequency separations from the line center, electron collisions are treated by an impact theory, which accounts both for Debye shielding and for the finite duration of the collisions, or by the quasistatic theory. Quadrupole interactions are considered in addition to the usual dipole interactions, and the (dominant) contribution of dipole interactions to the impact broadening is calculated to higher orders in the iterated solution of the time-dependent Schrödinger equation. Asymmetries introduced by quadratic Stark effect, by quadrupole interactions, by field-strength dependence of the oscillator strengths, and by the ion broadening of the central component through quadratic-Stark-effect and quadrupole interactions are evaluated. Also considered are asymmetries from the variation of factors usually assumed to be constant (frequencies and Boltzmann factors), and from the transformation from frequency to wavelength increments. Remaining theoretical uncertainties in the absolute values of absorption or emission coefficients for typical plasma conditions are estimated to be less than 10% over ranges in which these coefficients vary by three orders of magnitude.

1. INTRODUCTION

In dense plasmas the shapes (profiles) of absorption and emission coefficients near atomic lines are considerably influenced by interactions between the absorbing or emitting species and ions and electrons. This is especially pronounced for hydrogen lines, because of their large (linear) Stark effect. For this reason, and because hydrogen is so abundant in stellar atmospheres, theoretical and experimental interest have been concentrated largely on the Stark broadening of hydrogen lines. For the central regions of the profiles it is often permissible to use the two extreme approximations to the general theory of pressure broadening, namely impact and quasistatic approximations for electrons and ions, respectively. With this simplification, and only considering dipole interactions, detailed profiles have been calculated for lines of the Lyman and Balmer series.[1] Agreement with experiments, especially for the Hβ line, for which the most precise calculations have been made,[2] is usually within the estimated theoretical uncertainties of about 10%.[3]

This very satisfactory agreement seems to obtain as long as the absorption coefficient is not more than two orders of magnitude below its peak value, and also only if asymmetries in the measured profiles are ignored. Further away from the line center agreement with various asymptotic formulas[1,4] is not as good for the Hβ line[5] and also not for higher members of the Balmer

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series.[6,7] While this is of no serious consequence for most laboratory applications of line-broadening theory, the actual behavior on the distant wings is most important for the analysis of stellar atmospheres where the central portions are obscured because of the large optical depths involved and are, moreover, normally dominated by Doppler effects.

Optical depths near the centers of the first members of the Lyman series tend to be large in laboratory plasmas as well. Therefore, experiments on Lyman lines[8–10] have been concerned with the distant line wings. Because of their great strengths, it has been possible to extend the measurements to smaller values of the normalized line-shape function than in most studies of Balmer lines without serious overlap with lines of different principal quantum numbers. This fact, and the possibility of examining the various corrections to the theory in much greater detail, makes further study of the Lyman-α line especially attractive, even though experimental problems in the vacuum ultraviolet region of the spectrum are rather severe. The hope is that certain conclusions drawn from comparison between Lyman-α measurements and theory can be generalized to explain some of the discrepancies found for the wings of other hydrogen lines, especially the excess intensities over twice the Holtsmark prediction found in one of the experiments.[5]

The present paper is organized as follows: Section 2 contains a discussion of the principal assumptions made in the subsequent calculations and an exposition of the asymptotic wing formula for lines subject to both quasistatic broadening through linear Stark effect and to impact broadening. (Corrections to this formula are derived in Appendix A.) In Sec. 3 the impact broadening is calculated to arbitrary order in the iterated solution of the time-dependent Schrödinger equation, using the dipole interaction. Corrections due to quadrupole interactions are evaluated in the following section, which also gives a discussion of the errors incurred in the impact broadening calculations. The results of these calculations are averaged over electron velocities in Sec. 5, where also the various cutoff parameters are chosen. The actual wing formula for Lyman-α is derived in Sec. 6, including the asymmetry between red and blue wings. (Details of the calculation of asymmetries introduced by higher order perturbations are given in Appendix B.) In Sec. 7 the results are summarized (including estimates of theoretical errors) and compared with measurements.

2. GENERAL THEORY

As in the earlier calculations,[1,2] the classical path approximation will be made throughout. Also, depending on velocities and frequency separations the broadening electrons will either be described by the impact or by the quasistatic approximation. (The latter is always used for ions.) By showing that the final results depend only weakly on the parameter which determines the transition between the validity regimes of impact and quasistatic approximations, this procedure can be justified. Furthermore, the cutoff at large impact parameters is not critical either, as it essentially only enters the "weak-collision" term through a logarithmic factor. When Debye shielding is the relevant mechanism, the equivalent cutoff has been shown to come at 1.123 times the Debye radius[11] rather than precisely at this radius. The error in the logarithm is thus 0.12 if this difference is ignored in view of the difficulties in accounting for the finite duration of collisions[12] with comparable exactitude. However, by varying the corresponding parameter, one finds that final results are not at all critically affected by the uncertainty in this cutoff parameter. The cutoff at small impact parameters necessitated in preceding calculations[1,2,11] by the breakdown of second-order perturbation theory is no longer required because the effects of dipole interactions are now calculated to higher orders and the then equally important quadrupole interactions are also included. This allows one to move the lower cutoff to the de Broglie wavelength divided by 2π as suggested by quantum-mechanical considerations,[13] e.g., for Lyman-α to a radius smaller by a factor about 3 than the former strong collision impact parameter. The uncertainty in the cross section due to applying the classical path approximation should thus be only about 10% of this strong-collision contribution which in turn gives usually only a small fraction of the total broadening.

The point of departure for the actual calculations of the line profile $L(\omega)$, where ω is the angular frequency separation from the unperturbed line, is again [see Eq. (56) of Ref. 1, Eq. (6) of Ref. 2, or Eqs. (4)–(35) of Ref. 3]

$$L(\omega)=\frac{1}{\pi}\int dFW(F)\,\mathrm{Re}\sum_{\alpha,\beta,\alpha',\beta'}\mathbf{d}_{\alpha\beta}\langle\langle\alpha\beta|[i\omega-(i/\hbar)[H_a(F)-H_b(F)]-\Phi_{ab}]^{-1}|\alpha'\beta'\rangle\rangle\mathbf{d}_{\alpha'\beta'}{}^{*}. \quad (1)$$

Here F denotes the strength of the quasistatic fields (mostly due to ions), $W(F)$ the corresponding distribution function, $\mathbf{d}_{\alpha\beta}$ the dipole vector matrix elements between sublevels α of the upper level (a) and sublevels β of the lower level (b) for the line. The sum over double indices α,β and α',β' (designating states in "line space") selects the line. Also, $H_a(F)$ and $H_b(F)$ are the Hamil-

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tonians describing the various sublevels (relative to the unperturbed levels) as functions of the quasistatic field strength, and Φ_{ab} is the impact broadening operator to be discussed in the next section. To a very good approximation, the lower level of Lyman-α is unperturbed and $H_b(F)$ thus almost vanishes, and Φ_{ab} essentially only operates in a space.

Furthermore, for large frequency separations, only two regions of F values contribute. In the first region (small F) the multiplicative factor of $W(F)$ in Eq. (1) is nearly independent of F and the term $H_a(F)-H_b(F)$ can thus be ignored. Also, this factor can be expanded in terms of $(-\Phi/\omega)$ and the remaining integral is simply $\int_0^\infty W(F)dF=1$. In the second region (large F) $W(F)$ is nearly constant while the above factor then has a sharp maximum for F values fulfilling

$$H_a(F)-H_b(F)\approx e(z_a-z_b)F=\hbar\omega. \quad (2)$$

Here the dipole approximation was employed and F was assumed to be in the z direction. Replacing $W(F)$ by its value for F from Eq. (2) the integration can again be performed, using

$$\int_{-\infty}^{+\infty} dx/(ix+1)=\pi.$$

It is consistent with these approximations to use for $W(F)$ the asymptotic Holtsmark distribution (for large F) which can be obtained from the probability of finding the nearest perturber in r, $r+dr$, i.e., $W(r)dr\approx 4\pi N_s r^2 dr$, through $W(F)=W(r)|dr/dF|$. With $F=e/r^2$ this results in

$$W(F)\sim 2\pi e^{3/2}N_s F^{-5/2}, \quad (3)$$

N_s being the density of (singly charged) ions and (quasistatic) electrons.

The indicated operations finally lead to

$$L(\omega)\sim\frac{2\pi}{|\omega|^{5/2}}\left(\frac{\hbar}{m}\right)^{3/2} N_s \sum_{\alpha,\beta}{}' \mathbf{d}_{\alpha\beta}\langle\langle\alpha\beta|(Z_a-Z_b)^{3/2}|\alpha\beta\rangle\rangle\mathbf{d}_{\alpha\beta}{}^* + \frac{1}{\pi\omega^2}\sum_{\alpha,\beta,\alpha',\beta'}\mathbf{d}_{\alpha\beta}\langle\langle\alpha\beta|(-\Phi_{ab})|\alpha'\beta'\rangle\rangle\mathbf{d}_{\alpha'\beta'}{}^*, \quad (4)$$

which is essentially Eq. (61) of Ref. 1. The first term is the usual asymptotic Holtsmark[14] result. (Here the sum is only over half the Stark components, and it was assumed that parabolic wave functions are employed. Also, Z_a and Z_b are now in atomic units.) The second term describes the impact broadening contribution.

In the transition region between line core and line wing the asymptotic expansion must be carried further. This is done in Appendix A, following Kolb.[15] Also examined there are corrections due to Debye shielding of the ion fields and ion-ion interactions.

3. DIPOLE CONTRIBUTION TO IMPACT BROADENING

In this section the impact broadening operator Φ_{ab} is calculated to arbitrary order in the iterated solution of the Schrödinger equation for the time-development operator $U(t,t')$ in the interaction representation,

$$i\hbar dU(t,t')/dt=e^{iHt/\hbar}V(t)e^{-iHt/\hbar}U(t,t'). \quad (5)$$

However, the classical (straight) path and the dipole approximations for the interaction $V(t)$ are retained as in Refs. 1–4 and 11, i.e., for single collisions

$$V(t)=e^2\frac{\boldsymbol{\rho}+\mathbf{v}(t-t_0)}{|\boldsymbol{\rho}+\mathbf{v}(t-t_0)|^3}\cdot\mathbf{r}. \quad (6)$$

Here $\boldsymbol{\rho}$ is the position vector of the perturbing electron at the time t_0 of its closest approach, $\mathbf{v}$ its velocity, and $\mathbf{r}$ the coordinate vector operator of the atomic electron. As further approximations, the impact broadening of the ground-state (b) will again be neglected and also the differences in the matrix elements of the "unperturbed" Hamiltonian H, i.e., the differences in the energy levels of principal quantum number 2 due to quasistatic fields. A final assumption is that all collisions may either be considered completed in the relevant time interval or not contributing at all (see Refs. 11 and 12). Then the impact broadening operator becomes

$$\Phi=2\pi N\int vf(v)dv\int\rho d\rho\{U(\infty,-\infty)-1\}_{\rm av}$$
$$=2\pi N\int vf(v)dv\int\rho d\rho\left\{\sum_{n=1}^{\infty}\left(\frac{1}{i\hbar}\right)^n\int_{-\infty}^{+\infty}dt_n V(t_n)\times\int_{-\infty}^{t_n}dt_{n-1}V(t_{n-1})\cdots\int_{-\infty}^{t_2}dt_1 V(t_1)\right\}_{\rm av}, \quad (7)$$

where N is the density of impact broadening particles and $f(v)$ their velocity distribution function. The $\{\cdots\}_{\rm av}$ denotes the average over angles associated with $\boldsymbol{\rho}$ and $\mathbf{v}$. (The subscript av will be omitted from here on.)

All $V(t_n)$ may be assumed to describe the same perturbation by a single charged particle. (Mixed terms involving different perturbers average out for $n=1, 2, 3$ and are negligible for terms $n\geq 4$ since these contribute only for small impact parameters where simultaneous interactions are quite unlikely.) The multiple integrals thus reduce to powers of single integrals,

$$U(\infty,-\infty)-1=\sum_{n=1}^{\infty}\frac{1}{n!}\left(\frac{1}{i\hbar}\int_{-\infty}^{+\infty}V(t)dt\right)^n=\sum_{n=1}^{\infty}\frac{1}{n!}\left(\frac{2\hbar\mathbf{u}\cdot\mathbf{R}}{im\rho v}\right)^n, \quad (8)$$

[14] J. Holtsmark, Ann. Physik **58**, 577 (1919).
[15] A. C. Kolb, dissertation, University of Michigan, 1947 (unpublished); University of Michigan Engineering Research Institute, ASTIA Document No. AD 155040 (unpublished).

using Eq. (6) and introducing $\mathbf{u}=\boldsymbol{\rho}/\rho$, $\mathbf{R}=\mathbf{r}/a_0=me^2\mathbf{r}/\hbar^2$. This result will now be used to calculate the $\langle 2,1,\pm1|\Phi|2,1,\pm1\rangle$ matrix element, which controls the impact broadening of the unshifted component. (As explained at the beginning of Sec. 6, it is sufficient to consider only one of the Φ-matrix elements.) The nonzero $\mathbf{R}$-matrix elements are then

$$\langle p_{\pm1}|R_x|s_0\rangle=\frac{3}{\sqrt{2}},\quad \langle p_{\pm1}|R_y|s_0\rangle=\pm i\frac{3}{\sqrt{2}},$$
$$\langle p_0|R_z|s_0\rangle=3. \tag{9}$$

Here $|p_{\pm1}\rangle$ stands for $|nlm\rangle=|2,1,\pm1\rangle$, $|p_0\rangle$ for $|210\rangle$, and $|s_0\rangle$ for $|200\rangle$. Figure 1 demonstrates which matrix elements contribute to $\langle p_{\pm1}|(\mathbf{u}\cdot\mathbf{R})^n|p_{\pm1}\rangle$. The single lines designate the R_z matrix elements, i.e., contribute a factor $9u_z^2$ between vertexes i and $i+1$. The double lines correspond to R_x and R_y matrix elements which contribute $(\frac{9}{2})(u_x^2+u_y^2)$ for each of the two paths between subsequent vertexes. The end links of the chain result in the same factor, and summing the diagram thus yields for even $n=2l$ (for odd n the matrix element vanishes)

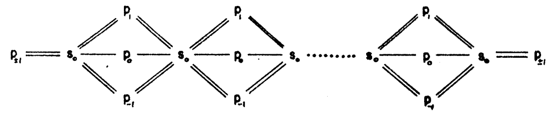

FIG. 1. Diagram of the matrix elements of $(\mathbf{u}\cdot\mathbf{R})^n$ which occur in the nth iteration of the time-dependent Schrödinger equation with the dipole interaction.

$$\langle p_{\pm1}|(\mathbf{u}\cdot\mathbf{R})^n|p_{\pm1}\rangle=2^{l-1}[\tfrac{9}{2}(u_x^2+u_y^2)]^l+2^{l-2}[\tfrac{9}{2}(u_x^2+u_y^2)]^{l-1}\frac{l-1}{1!}(3u_z)^2$$
$$+2^{l-3}[\tfrac{9}{2}(u_x^2+u_y^2)]^{l-2}\frac{(l-1)(l-2)}{2!}(3u_z)^4+\cdots+[\tfrac{9}{2}(u_x^2+u_y^2)](3u_z)^{2(l-1)}. \tag{10}$$

The first term is for all of the 2^{l-1} paths involving only R_x and R_y matrix elements. In the second term the paths contain one $s_0-p_0-s_0$ link, of which there are $l-1$, etc. (If several such links are involved, one must divide by the appropriate factorial to avoid counting a given sequence of intermediate states twice.) To perform the directional average, the factors $(u_x^2+u_y^2)^{l-i}$ are expanded by means of the binominal theorem,

$$\{\langle p_{\pm1}|(\mathbf{u}\cdot\mathbf{R})^n|p_{\pm1}\rangle\}=\tfrac{1}{2}3^{2l}\sum_{i=0}^{l-1}\frac{(l-1)!}{i!(l-1-i)!}\{(u_x^2+u_y^2)^{l-i}u_z^{2i}\}$$
$$=\tfrac{1}{2}3^{2l}\sum_{i=0}^{l-1}\frac{(l-1)!}{i!(l-1-i)!}\sum_{j=0}^{l-i}\frac{(l-i)!}{j!(l-i-j)!}\{u_x^{2(l-i-j)}u_y^{2j}u_z^{2i}\}$$
$$=\frac{(l-1)!}{2}3^{2l}\sum_{i=0}^{l-1}\frac{(l-i)}{i!(2i+1)}\sum_{j=0}^{l-i}\frac{1}{j!(l-i-j)!(2l-2i-2j+1)(2j+1)}, \tag{11}$$

using, e.g., $\{u_z^{2i}\}=1/(2i+1)$.

Substitution of Eqs. (8) and (11) into Eq. (7) and integration over ρ finally yields

$$\langle p_{\pm1}|\Phi|p_{\pm1}\rangle=-12\pi N\left(\frac{\hbar}{m}\right)^2\int\frac{dv}{v}f(v)\left[\ln\rho+\tfrac{3}{2}\sum_{l=2}^{\infty}\frac{(l-2)!(-1)^l}{(2l)!}\left(\frac{6\hbar}{m\rho v}\right)^{2(l-1)}\right.$$
$$\left.\times\sum_{i=0}^{l-1}\frac{(l-i)}{i!(2i+1)}\sum_{j=0}^{l-i}\frac{1}{j!(l-i-j)!(2l-2i-2j+1)(2j+1)}\right]_{\rho_{\min}}^{\rho_{\max}}. \tag{12}$$

A natural choice of $\rho_{\min}$ is suggested by quantum-mechanical considerations,[13,16] namely

$$\rho_{\min}=\hbar/mv=\lambda\!\!\!^{-}, \tag{13}$$

i.e., the impact parameter for which the relative angular momentum quantum number is 1. Summing the (first 10) terms corresponding to the lower limit and neglecting terms of higher order than $(\rho_{\min}/\rho_{\max})^2$ from the upper limit one then obtains

$$\langle p_{\pm1}|\Phi|p_{\pm1}\rangle=-12\pi N\left(\frac{\hbar}{m}\right)^2\int\frac{dv}{v}f(v)$$
$$\times\left[\ln\left(\frac{\rho_{\max}}{\rho_{\min}}\right)-0.967+1.90\left(\frac{\rho_{\min}}{\rho_{\max}}\right)^2\right]. \tag{14}$$

[16] H. R. Griem and K. Y. Shen, Phys. Rev. **122**, 1490 (1961).

(If the lower cutoff were made at $\lambda\!\!\!^{-}/\sqrt{2}$ or $\lambda\!\!\!^{-}\sqrt{2}$ the value of the bracket would increase or decrease by 0.05 or 0.03, respectively.) In the earlier calculations[1,2,11] the minimum impact parameter was chosen to correspond to $|\{\langle\alpha|U(\infty,-\infty)-1|\alpha\rangle\}|\approx 1$, yielding $\rho_w=4\sqrt{(\frac{2}{3})}\hbar/mv$ for Lyman-α, according to Eq. (19) of Ref. 1. Also, the so-called strong collision term in the expression for Φ was neglected. Comparison with Eq. (14) shows that this term can be accounted for by adding $\ln(4\sqrt{\frac{2}{3}})-0.967=0.215$ to $\ln(\rho_{\max}/\rho_w)$. Such a constant term is usually negligible when $\rho_{\max}$ is of the order of the Debye radius. For asymptotic wing formulas, however, $\rho_{\max}$ is often smaller than the Debye radius because only collisions within $\rho\approx v/\omega$ can be completed in times contributing to the Fourier integral representing the line shape.[12] A strong collision term was therefore reintroduced[4] and its value estimated by requiring a smooth transition from quasistatic to impact approximation regimes. For Lyman-α this interpolation procedure is now superseded by actual calculation. (Note here that the assumption of completed collisions is well justified in the calculation of higher order terms because these are only important at small impact parameters.)

4. CORRECTIONS TO IMPACT BROADENING

Of the various approximations leading to Eq. (14), the replacement of the complete interaction by the dipole term according to Eq. (6) is most critical. Therefore a quadrupole term should be added, i.e.,

$$V(t)\approx V_d(t)+V_q(t)=\frac{\hbar^2}{m}|\boldsymbol{\varrho}+\mathbf{v}(t-t_0)|^{-3}\bigg([\boldsymbol{\varrho}+\mathbf{v}(t-t_0)]\cdot\mathbf{R}+\tfrac{3}{2}a_0\bigg[\frac{\{[\boldsymbol{\varrho}+\mathbf{v}(t-t_0)]\cdot\mathbf{R}\}^2}{|\boldsymbol{\varrho}+\mathbf{v}(t-t_0)|^2}-\tfrac{1}{3}\mathbf{R}\cdot\mathbf{R}\bigg]\bigg). \quad (15)$$

On integration, this becomes

$$\int_{-\infty}^{+\infty}V(t)dt=\frac{\hbar^2}{m\rho v}\bigg(2\Big(\frac{\mathbf{R}\cdot\boldsymbol{\varrho}}{\rho}\Big)+\frac{a_0}{\rho}\bigg[2\Big(\frac{\mathbf{R}\cdot\boldsymbol{\varrho}}{\rho}\Big)^2+\Big(\frac{\mathbf{R}\cdot\mathbf{v}}{v}\Big)^2-\mathbf{R}\cdot\mathbf{R}\bigg]\bigg). \quad (16)$$

Averaged over angles associated with $\boldsymbol{\varrho}$ and $\mathbf{v}$ the integral clearly vanishes. Also, the quadrupole term therefore only contributes to second and higher order in $V(t)$. With Eqs. (8) and (11) follows now

$$\{\langle p_{\pm1}|U(\infty,-\infty)-1|p_{\pm1}\rangle\}=-6\Big(\frac{\hbar}{m\rho v}\Big)^2\bigg[1+28\Big(\frac{a_0}{\rho}\Big)^2-\frac{19}{5}\Big(\frac{\hbar}{m\rho v}\Big)^2+\cdots\bigg], \quad (17)$$

using $\{\rho_x^4\}=\{v_x^4\}=\frac{1}{5}$, $\{\rho_x^2\rho_y^2\}=\{\rho_x^2v_y^2\}=\{v_x^2v_y^2\}=\frac{1}{9}$, etc., and taking matrix elements. The two additional terms in the bracket represent second-order quadrupole and fourth-order dipole corrections, respectively, to the leading term from the second-order dipole interaction, namely, $-6(\hbar/m\rho v)^2$.

According to Eq. (7) the Φ-matrix element becomes, truncating the ρ integral at ρ_w,

$$\langle p_{\pm1}|\Phi|p_{\pm1}\rangle\approx-12\pi N\Big(\frac{\hbar}{m}\Big)^2\int\frac{dv}{v}f(v)\bigg[\frac{1}{12}\Big(\frac{mv\rho_w}{\hbar}\Big)^2+\ln\Big(\frac{\rho_{\max}}{\rho_w}\Big)+\Big(14a_0^2-\frac{19}{10}\frac{\hbar^2}{(mv)^2}\Big)\Big(\frac{1}{\rho_w^2}-\frac{1}{\rho_{\max}^2}\Big)\bigg]. \quad (18)$$

To account for $\rho<\rho_w$ here a strong-collision term $-Nv\pi\rho_w^2$ was added to the integral with ρ_w defined by $|\{\langle p_{\pm1}|U(\infty,-\infty)-1|p_{\pm1}\rangle\}|\approx 1$, i.e.,

$$\rho_w=\frac{\hbar\sqrt{6}}{mv}\bigg[1+28\Big(\frac{a_0}{\rho_w}\Big)^2-\frac{19}{5}\Big(\frac{\hbar}{m\rho_w v}\Big)^2+\cdots\bigg]^{1/2}\approx\frac{\hbar\sqrt{6}}{mv}\bigg[1+\frac{14}{3}\Big(\frac{mva_0}{\hbar}\Big)^2-\frac{19}{30}\bigg]^{1/2}, \quad (19)$$

when the second-order dipole result $\rho_w\approx\hbar(\sqrt{6})/mv=(\sqrt{6})\rho_{\min}$ is employed under the square root. This procedure yields

$$\langle p_{\pm1}|\Phi|p_{\pm1}\rangle\approx-12\pi N\Big(\frac{\hbar}{m}\Big)^2\int\frac{dv}{v}f(v)\bigg[\ln\Big(\frac{\rho_{\max}}{\rho_{\min}}\Big)-\Big(\ln\sqrt{6}+\frac{19}{30}-\frac{1}{2}\Big)+\frac{14}{3}\Big(\frac{mva_0}{\hbar}\Big)^2-14\Big(\frac{a_0}{\rho_{\max}}\Big)^2+\frac{19}{10}\Big(\frac{\hbar}{mv\rho_{\max}}\Big)^2\bigg], \quad (20)$$

using $\rho_w=(\sqrt{6})\rho_{\min}$ under the logarithm and in the quadrupole and fourth-order correction terms. The constant term in the bracket is now 1.03 as compared to 0.967 in Eq. (14), which may be considered an indication for the accuracy with which higher order terms (e.g., sixth-order dipole terms) are accounted for by this modified cutoff procedure.

In the calculations below, this constant will be replaced by 1, and the associated error be estimated as ± 0.05. The error due to neglecting higher multipole interactions will be assessed from the ratio of quadrupole and dipole contributions, assuming the error to be of the order of the quadrupole term multiplied with this ratio. Furthermore, the uncertainties stemming from the classical path approximation, which necessitated the $\rho_{\min}$ cutoff, should be of the order of the contribution caused by classical charged particle impacts within $\rho_{\min}$, i.e., of the order $Nv\pi\rho_{\min}^2$, corresponding to an uncertainty of 0.08 in the above constant. [This estimate is probably too high, judged by varying the lower cutoff impact parameter as discussed below Eq. (14).] Errors due to deviations from straight paths ought to be still smaller because the $p_{\pm 1}$ states possess no permanent dipole moments so that typical interaction energies are estimated by the quadrupole interaction as $V\approx 10a_0^2e^2/\rho^3 \approx a_0^2e^2(mv/\hbar)^3 = mv^2(\hbar v/e^2)$. The ratio of interaction and thermal energies is thus of the order $\hbar v/e^2$ or typically about 0.1. As the results are quite insensitive to perturber energy (temperature), and because the effects from curvatures in perturber paths tend to be cancelled by changes in the duration of the collisions,[16] no significant uncertainties are expected from this source. Also so-called back reactions[17] should be negligible (except, perhaps for the asymmetry), because perturber energies are considerably larger than changes in photon energies.

Another approximation was the neglect of the exponentials in Eq. (5), i.e., of the quasistatic splitting, which is of the order $\Delta\omega\approx 15ea_0F_0/\hbar\approx 40(\hbar/m)N^{2/3}$. This is to be compared with $v/\rho_w\approx mv^2/\hbar\sqrt{6}$ so that the parameter $z_w=\Delta\omega\rho_w/v$ is typically $z_w\approx 100(\hbar/mv)^2N^{2/3}$, which is usually about 0.01. Since even for z_w values as large as 0.4 corrections[3,11] due to the splitting between interacting levels stay below 4%, the quasistatic splitting should be negligible for most distant (weak) collisions as well.[17a] In principle, one should in addition correct for interactions with states of different principal quantum number, mainly $n=3$. Here the parameter z_w is estimated by $z_w\approx E_H(1/2^2-1/3^2)(\sqrt{6})/mv^2\approx 3E_H/mv^2$ which is normally much larger than 10. (E_H is the ionization energy of hydrogen.) Under such conditions, the contribution to the width is completely negligible,[11] as it then decreases exponentially with z_w. Also shifts caused by this interaction would not be significant. For similar reasons impact broadening of the lower (ground) state may safely be neglected.

Except for uncertainties from higher multipole (than quadrupole) interactions and the difficulties connected with the choice of $\rho_{\max}$, the matrix element of the impact broadening operator as calculated above should therefore have an accuracy corresponding to about 10% variation in the constant accompanying the logarithm in Eq. (20). Since the value of the bracketed term in this equation is almost always twice the magnitude of this constant, and since impact broadening contributes never much more than half the total wing intensity, the final error from this uncertainty in the impact broadening calculations is probably less than 3% in almost all cases. (See also Sec. 7.)

5. FINAL CALCULATION OF THE IMPACT BROADENING

To calculate the impact broadening from Eqs. (4) and (20), the velocity integration must be performed and the maximum impact parameter be determined. The value of the latter is only critical in the logarithm, i.e., in the second-order dipole interaction contribution. When Debye shielding is the dominant mechanism for reducing the effects of distant collisions, and when the shielding is as for slowly moving charges, then $\rho_{\max}$ can be shown[11] to be 1.123 times the Debye radius obtained for shielding by electrons only. However, as already pointed out in Sec. 2, at large separations from the line center the use of unshielded Coulomb fields in the interaction energies given by Eqs. (6) or (15) is not as critical as the assumption of completed collisions, which led to Eq. (7) and all subsequent expressions for the impact broadening operator. Actually, only collisions completed in times of the order $(\omega)^{-1}$ can contribute in the Fourier integral representing the line shape. Now the effective duration of a collision is about ρ/v, and ρ must accordingly stay below v/ω, as was first demonstrated by Lewis.[12] Appropriate conditions for $\rho_{\max}$ are therefore

$$\rho_{\max}\approx\min|v/\omega|\,,\quad \rho_D'=(kT/4\pi Ne^2)^{1/2}. \tag{21}$$

At a given frequency separation, the Lewis cutoff is thus to be used for small velocities and the Debye cutoff for large velocities.

For the velocity integration a new variable is introduced, namely,

$$y=\tfrac{1}{2}(mv^2/kT)\,, \tag{22}$$

in terms of which the switch between the two expressions for $\rho_{\max}$ must come at

$$y_{\max}=\frac{m\omega^2}{8\pi Ne^2}=\frac{1}{32\pi a_0^3N}\left(\frac{\hbar\omega}{E_H}\right)^2\approx\frac{9}{512\pi a_0^3N}\left(\frac{\Delta\lambda}{\lambda}\right)^2. \tag{23}$$

The impact approximation will of course only be applicable if the velocity exceeds some minimum value below which the quasistatic approximation should be used. The transition must be made when the characteristic frequency v/ρ of a given collision is of the order of the quasistatic splitting $|\Delta\omega|=3\hbar/m\rho^2$ for one of the shifted components of Lyman-α. The corresponding minimum

[17] M. Baranger, *Atomic and Molecular Processes*, edited by D. R. Bates (Academic Press Inc., New York, 1962), Chap. 13.

[17a] *Note added in proof.* Calculations of electron impact broadening of hydrogen lines[1,4] recently have been criticized [H. Van Regemorter, Compt. Rend. **259**, 3979 (1964)] because the splitting $\Delta\omega$ of the levels by quasistatic ion fields was neglected. Inclusion of this effect results in another maximum impact parameter,[11] e.g., for Eq. (14), at $\rho_{\max}\approx v/\Delta\omega$, which could be effective if it were smaller than the Lewis cutoff[12] at $\rho_{\max}\approx v/\omega$. However, on the line wings the frequency separation ω from the line center is of necessity much larger than the linewidth. Since the latter is of the order of the average quasistatic splitting, one has $\omega\gg\Delta\omega$, and the Lewis cutoff impact parameter is considerably smaller (and thus relevant) than the maximum impact parameter proposed by Van Regemorter. This fact invalidates his explanation of the discrepancies between theory[4] and experiment which were observed[6,7] on the wings of Balmer lines from levels with large principal quantum numbers.

value of y is thus estimated to be

$$y_{\min}=\frac{3\hbar|\omega|}{2kT}\approx\frac{9}{8}\frac{E_H}{kT}\left|\frac{\Delta\lambda}{\lambda}\right|, \quad (24)$$

when ρ is expressed in terms of $\Delta\omega\approx\omega$.

Assuming a Maxwell distribution of velocities and using $f(y)=f(v)dv/dy$, the normalized y-distribution function is

$$f(y)=\left(\frac{2m}{\pi kT}\right)^{1/2}ve^{-y}=\frac{2}{\sqrt{\pi}}y^{1/2}e^{-y}. \quad (25)$$

The fraction of electrons contributing to the quasistatic broadening of the shifted Stark components is therefore

$$\Delta R_s(y_{\min})=\int_0^{y_{\min}}f(y)dy =\frac{4}{3\sqrt{\pi}}y_{\min}^{3/2}\left(1-3\sum_{n=1}^{\infty}\frac{y_{\min}^n}{(2n+3)n!}\right). \quad (26)$$

These slow electrons might also give rise to some impact broadening of the unshifted component, even though the situation is complicated through the presence of the quasistatic effects which separate the interacting levels and thus reduce the contribution from dipole interactions.

For a model calculation, assume that the splitting corresponds to the quasistatic value at closest approach, $|\Delta\omega|=3\hbar/m\rho^2$, and that the quadrupole interaction dominates the impact broadening under these conditions. According to Eq. (17), the strong-collision (Weisskopf) impact parameter would then obey

$$\rho_w'=(168)^{1/4}(\hbar a_0/mv)^{1/2}, \quad (27)$$

and the parameter $z_w'=\Delta\omega\rho_w'/v\approx 3\hbar/m\rho_w'v$

$$z_w'\approx\frac{3}{(168)^{1/4}}\left(\frac{\hbar}{ma_0v}\right)^{1/2}\gtrsim\left(\frac{\lambda}{\Delta\lambda}\right)^{1/4}, \quad (28)$$

using Eq. (24). Compared to the zero-splitting results the dipole term in Eq. (17) is reduced[3,11] by a factor $\pi z e^{-2z}$ which is below 0.05 for all practical cases ($\Delta\lambda<30$ Å), making the dipole contribution completely negligible indeed. This justifies using the quadrupole term in Eq. (27), and with Eq. (7) the Φ-matrix element now becomes

$$\langle p_{\pm1}|\Phi'|p_{\pm1}\rangle\approx-2\pi N\int_0^{y_{\min}}v\rho_w'^2f(y)dy =-2\pi(168)^{1/2}\frac{\hbar a_0}{m}N\Delta R_s(y_{\min}), \quad (29)$$

where a strong-collision term was added. The impact broadening from $y>y_{\min}$ follows from Eqs. (14) and (25) as approximately

$$\langle p_{\pm1}|\Phi|p_{\pm1}\rangle\approx-24\pi\left(\frac{2m}{\pi kT}\right)^{1/2}\left(\frac{\hbar}{m}\right)^2N, \quad (30)$$

using $\{[\cdots]\}\approx2$. The ratio of these contributions is therefore with $\Delta R_s\approx4y_{\min}^{3/2}/3\sqrt{\pi}\approx(E_H\Delta\lambda/kT\lambda)^{3/2}$

$$\frac{\langle p_{\pm1}|\Phi'|p_{\pm1}\rangle}{\langle p_{\pm1}|\Phi|p_{\pm1}\rangle}\approx\frac{E_H}{kT}\left(\frac{\Delta\lambda}{\lambda}\right)^{3/2}. \quad (31)$$

For the two past experiments[8–10] and under all foreseeable future conditions, this ratio stays well below 0.1 and the impact broadening of the unshifted components by slow electrons may thus be neglected.

With Eqs. (20)–(25) the desired Φ-matrix element finally becomes

$$\langle p_{\pm1}|\Phi|p_{\pm1}\rangle=-12\pi\left(\frac{2m}{\pi kT}\right)^{1/2}\left(\frac{\hbar}{m}\right)^2N\Bigg[\int_{y_{\min}}^{\infty}\frac{e^{-y}}{y}dy-\frac{1}{2}\int_{y_{\max}}^{\infty}\frac{e^{-y}}{y}dy+(\ln3-1)e^{-y_{\min}} +\frac{14}{3}\frac{kT}{E_H}(1+y_{\min})e^{-y_{\min}}-\frac{7}{4}y_{\min}\frac{\Delta\lambda}{\lambda}e^{-y_{\min}}+\frac{19}{90}\left(y_{\min}e^{-y_{\min}}-y_{\min}^2\int_{y_{\min}}^{\infty}\frac{e^{-y}}{y}dy\right)\Bigg], \quad (32a)$$

using $\ln\sqrt{6}+19/30-\frac{1}{2}\approx1$. Also, for the last two terms in Eq. (20), $\rho_{\max}\approx v/\omega$ was employed throughout because only small velocities are important here. These terms stem from the upper cutoffs in the quadrupole and fourth-order dipole interaction terms, respectively. The magnitude of the (negative) quadrupole term is below 10^{-2} for $\Delta\lambda<30$ Å and may thus be neglected for the following. Futhermore, the last term is, when at all important, a very slowly increasing function of $y_{\min}$ and then combines with $(\ln3-1)e^{-y_{\min}}$ to a nearly constant term of about 0.1. For actual calculations it therefore suffices to use the simpler formula

$$\langle p_{\pm1}|\Phi|p_{\pm1}\rangle=-12\pi\left(\frac{2m}{\pi kT}\right)^{1/2}\left(\frac{\hbar}{m}\right)^2N\left[\int_{y_{\min}}^{\infty}\frac{e^{-y}}{y}dy-\frac{1}{2}\int_{y_{\max}}^{\infty}\frac{e^{-y}}{y}dy+\frac{14}{3}\frac{kT}{E_H}(1+y_{\min})e^{-y_{\min}}+\frac{1}{10}\right], \quad (32b)$$

without incurring additional errors any larger than the uncertainty of ±0.1 in the value of the square bracket due to the various causes discussed in the preceding section.

6. ASYMPTOTIC WING FORMULAS AND ASYMMETRIES

The calculation of the impact broadening of the $l=1$, $m=\pm 1$ levels is sufficient for the present purpose, because in the asymptotic formula Eq. (4) impact and quasistatic broadening are completely separated so that the *nlm* representation can be used for the impact broadening. Accordingly, here only $2p_{\pm 1}$ and $2p_0$ need be considered as upper states. Since these states are distinguished from each other simply by a rotation, their diagonal Φ-matrix elements must be the same for isotropic distributions in perturber phase space. (All off-diagonal matrix elements vanish in this representation.) The impact broadening term is thus obtained by substituting Eq. (32b) into Eq. (4), normalizing $\sum \mathbf{d}_{\alpha\beta}\cdot\mathbf{d}_{\alpha\beta}^*$ to 1. For the quasistatic term, parabolic wave functions are required, and it must be remembered that only $\frac{1}{6}$ of the total intensity is in a given shifted component whose z-matrix element is $\pm 3a_0$. The asymptotic line shape becomes in the indicated manner

$$L(\omega)\sim\frac{\sqrt{3}\pi}{|\omega|^{5/2}}\left(\frac{\hbar}{m}\right)^{3/2}N(1+\Delta R_s)+\frac{24}{\sqrt{\pi}|\omega|^2}\frac{\hbar a_0}{m}\left(\frac{E_H}{kT}\right)^{1/2}N[\cdots]$$
$$=\frac{\sqrt{3}\pi}{|\omega|^{5/2}}\left(\frac{\hbar}{m}\right)^{3/2}N\left(1+\Delta R_s+\frac{8\sqrt{3}}{\pi^{3/2}}a_0\times\left|\frac{mE_H}{\hbar kT}\omega\right|^{1/2}[\cdots]\right)\equiv L_H R, \quad (33)$$

with ΔR_s as given by Eq. (26). Here L_H is the asymptotic Holtsmark result for Lyman-α and R therefore the ratio of actual asymptotic wing intensity to the asymptotic Holtsmark formula for ion broadening. To facilitate comparison with experiment, R is best expressed in terms of the relative wavelength separation $\Delta\lambda/\lambda$ from the center of the line, namely

$$R=1+\frac{9}{4\sqrt{2}\pi}\left(\frac{E_H}{kT}\right)^{3/2}\left|\frac{\Delta\lambda}{\lambda}\right|^{3/2}\left(1-\frac{3}{5}y_{\min}+\frac{3}{14}y_{\min}^2\right)+\frac{6\sqrt{2}}{\pi^{3/2}}\left(\frac{E_H}{kT}\right)^{1/2}\left|\frac{\Delta\lambda}{\lambda}\right|^{1/2}$$
$$\times\left[\int_{y_{\min}}^{\infty}\frac{e^{-y}}{y}dy-\frac{1}{2}\int_{y_{\max}}^{\infty}\frac{e^{-y}}{y}dy+\frac{14}{3}\frac{kT}{E_H}(1-\tfrac{1}{2}y_{\min}^2+\tfrac{1}{3}y_{\min}^3)+\tfrac{1}{10}\right]\equiv 1+\Delta R_s+\Delta R_i, \quad (34)$$

using expansions for $\Delta R_s(y_{\min})$ and the quadrupole term in the impact contribution which are sufficiently accurate for $y_{\min}<0.5$.

The asymptotic Holtsmark result in terms of $\Delta\lambda$ follows from $S(\Delta\lambda)=L(\omega)|d\omega/d\Delta\lambda|$ as

$$S_H(\Delta\lambda)\sim L_H(|\omega|)\left|\frac{d\omega}{d\Delta\lambda}\right|$$
$$\approx\left[L_H\left(\frac{2\pi c|\Delta\lambda|}{\lambda_2}\right)-\frac{dL_H}{d\omega}|\omega|\frac{\Delta\lambda}{\lambda}\right]\frac{2\pi c}{\lambda^2}\left(1-2\frac{\Delta\lambda}{\lambda}\right)$$
$$\approx\frac{16\sqrt{2}\pi}{3\lambda}\left|\frac{\lambda}{\Delta\lambda}\right|^{5/2}a_0^3N\left(1+\frac{1}{2}\frac{\Delta\lambda}{\lambda}+\cdots\right), \quad (35)$$

using

$$\omega=2\pi c[(\lambda+\Delta\lambda)^{-1}-\lambda^{-1}]=-(2\pi c\Delta\lambda/\lambda^2)(1-\Delta\lambda/\lambda+\cdots)$$

and assuming that $L(-\omega)=L(+\omega)$. (The term involving $dL_H/d\omega$ was first introduced by Boldt and Cooper.[10] In case of impact broadening it just cancels the term from $d\omega/d\Delta\lambda$.) Besides the asymmetry coming in through this transformation, there are many other causes of asymmetry. To assess them, higher order interactions must be considered also in the quasistatic theory. This is done in Appendix B whose principal result is contained in Eq. (B9). According to it, quadrupole interactions lead to an increase of the red component as do the usually more important quadratic Stark effect and changes in the dipole matrix elements. The quasistatic broadening of the unshifted component acts in the same sense and is also estimated in Appendix B.

Further factors influencing the asymmetry are the slowly varying functions of the frequency which were ignored in the definition[3,17] of the line shape, namely the fourth power of the actual frequency $\omega_0+\omega$ and the Boltzmann factors (for emission) or just the actual frequency (for absorption). These factors probably affect the impact broadening as well (which still remains to be shown) so that Eq. (33) should in case of emission be multiplied by

$$A_e=\left(\frac{\omega_0+\omega}{\omega_0}\right)^4\exp\left(-\frac{\hbar\omega}{kT}\right)\approx 1+4\frac{\omega}{\omega_0}-\frac{\hbar\omega}{kT}, \quad (36a)$$

or in case of absorption by

$$A_a=\frac{\omega_0+\omega}{\omega_0}=1+\frac{\omega}{\omega_0}. \quad (36b)$$

According to Eq. (35) transformation to wavelength units introduces another asymmetry into the quasistatic terms, and together with the correction terms from

Eq. (B9) follows finally

$$S(\Delta\lambda)\sim\frac{16\sqrt{2}\pi}{3\lambda}\left|\frac{\lambda}{\Delta\lambda}\right|^{5/2}a_0^3N\left[1+\Delta R_s+\Delta R_i+\Delta R_u+\frac{\Delta\lambda}{|\Delta\lambda|}\left|\frac{\Delta\lambda}{2\lambda}\right|^{1/2}(1-\Delta R_s)+\frac{37}{4}\frac{\Delta\lambda}{\lambda}(1+\Delta R_s)\right]\times\left\{\begin{matrix}1-\frac{3}{4}(\Delta\lambda/\lambda)(16/3-E_H/kT)\\ 1-\Delta\lambda/\lambda\end{matrix}\right\},\quad(37)$$

where the upper expression in braces is for emission, and the lower for absorption. The quantities ΔR_s and ΔR_i can be obtained from Eqs. (26) and (34), while ΔR_u is estimated in Appendix B from the quasistatic shift of the unshifted component due to quadrupole interactions and quadratic Stark effect. Numerical results of these calculations are presented in Fig. 2 and suggest to replace ΔR_u by

$$\Delta R_u=\tfrac{9}{2}(\Delta\lambda/\lambda),\quad \text{for}\quad \Delta\lambda>0 \quad(38a)$$

$$\Delta R_u=0,\quad \text{for}\quad \Delta\lambda<0. \quad(38b)$$

7. DISCUSSION AND COMPARISON WITH EXPERIMENT

Before applying Eq. (37), which summarizes the results of the present calculations, to the line wings of Lyman-α the validity of this asymptotic formula must be verified along the lines of Appendix A. If necessary a correction factor $1+(\Delta S/S)$ must be applied to Eq. (37), using Eq. (A10) with R from Eq. (34). This correction is only important for relatively small separations from the line center, where ΔR_i, i.e., the impact broadening term, is much larger than ΔR_s, ΔR_u and the other terms responsible for the asymmetry. This justifies the principal assumption made in Appendix A to calculate this correction, namely that the broadening was only due to quasistatic interactions with ions through the linear Stark effect and to electron impacts. Another assumption is always made implicitly, namely that broadening mechanisms not involving singly charged particles as perturbers and also Doppler effects are negligible.

The correction terms in Eq. (37) which describe asymmetries through quadrupole interactions, quadratic Stark effects and changes in the dipole moments contribute usually less than 10% to the first bracket in this equation. Since they all stem from the quasistatic part, higher order terms not accounted for in these calculations should not affect the profile significantly. To estimate remaining theoretical errors it is therefore sufficient to estimate errors from uncertainties in the electron impact contribution ΔR_i, or, rather, those from the sum of ΔR_i and ΔR_s, because errors originating in the somewhat arbitrary choice of the parameter $y_{\min}$ in Eq. (24) compensate each other partially. Accounting for uncertainties in the parameters $y_{\min}$, $y_{\max}$, the ± 0.1 uncertainty in the constant accompanying the exponential integrals in Eq. (34) as discussed in Sec. 4, and assuming that higher multipole interactions would add a certain fraction of the quadrupole term which is of the order of the ratio of quadrupole and dipole contributions, the error in R is estimated as

$$\Delta R\approx\frac{6\sqrt{2}}{\pi^{3/2}}\left(\frac{E_H}{kT}\right)^{1/2}\left|\frac{\Delta\lambda}{\lambda}\right|^{1/2}\left(\left[\frac{2}{\sqrt{\pi}}y_{\min}^{3/2}(1-y_{\min}+\tfrac{1}{2}y_{\min}^2)-e^{-y_{\min}}\right]\frac{\Delta y_{\min}}{y_{\min}}+\tfrac{1}{2}e^{-y_{\max}}\frac{\Delta y_{\max}}{y_{\max}}\pm\frac{1}{10}+\left[\frac{14kT}{3E_H}(1-\tfrac{1}{2}y_{\min}^2+\tfrac{1}{3}y_{\min}^3)\right]^2\left[\int_{y_{\min}}^{\infty}\frac{e^{-y}}{y}dy-\frac{1}{2}\int_{y_{\max}}^{\infty}\frac{e^{-y}}{y}dy\right]^{-1}\right),\quad(39)$$

using Eq. (34). The relative error in the wing intensity is then given by $\Delta R/R$, a reasonable choice of the relative uncertainties in the cutoff parameters being $\pm\frac{1}{2}$. (Note also that higher multipole interactions will always increase the broadening.)

Two experiments are available for comparison with the calculated wing profiles. In one experiment[10] the absorption coefficient was measured absolutely in a stablized arc on both wings of the line. Because of the observed asymmetry of the wing intensities, averages were taken and the data then presented in terms of the asymptotic Holtsmark result. The measured quantity therefore corresponds according to Eq. (37) to

$$\bar{R}=1+\Delta R_s+\Delta R_i+\langle\Delta R_u\rangle_{\text{av}},\quad(40)$$

corrected for deviations from the asymptotic formula using Eq. (A10), if necessary. This $\bar{R}$ is compared in Fig. 3 with the experimental data. To illustrate the relative importance of electron impact broadening (ΔR_i), this contribution is also given separately. Quite clearly, it is the most important correction, implying that completely quasistatic calculations cannot be trusted. The other corrections, ΔR_s and $\langle\Delta R_u\rangle_{\text{av}}$ are too small to be shown on this graph. The total, $\bar{R}$ (corrected for deviations from the asymptotic formula), does not at all agree with the measurements, unless one assumes a systematic experimental error of about a factor 1.25. (This exceeds the estimated experimental error of 10% which was obtained assuming individual systematic errors to be completely independent. However, if all systematic errors should be in the same direction, a 25% reduction of the measured values would be consistent with the individual errors given in Ref. 10.) With a corresponding upward correction applied to the measurements, agreement is obtained at intermediate wavelengths, when theoretical errors are estimated as indicated earlier in this section, remaining experimental errors as about $\pm 5\%$ and errors in the correction from Eq. (A10) as $\pm 20\%$.

However, at small wavelength separations measured points still lie considerably lower than expected and at large distances the measured wing absorption coefficient is definitely larger than predicted theoretically. Alternatively, if the 1.25 correction factor were not applied to the measurements, these would be much too low near the line center. In any event, the decay of the experimental profile is significantly slower than is calculated. A possible explanation is that van der Waals broadening by argon atoms (which are the main constituents of the arc plasma) is no longer negligible on the far wings. It would give a contribution proportional to $\Delta\lambda^{-3/2}$ and might therefore be important for large $\Delta\lambda$. Following standard procedures, this correction is estimated to amount to no more than 5% in the symmetrized profile. However, interatomic distances corresponding to $\Delta\lambda \gtrsim 10$ Å are such that the sum of perturbed and perturbing atom radii is comparable or even smaller. This fact invalidates these estimates but suggests that effects due to atom-atom interactions might actually be larger.

One first suspects that these interactions would enhance the red wing relative to the blue wing. This is not necessarily true, though, because at small distances interactions would be repulsive and therefore result in contributions on the blue wing. Directly measured (instead of such asymmetries in intensities at points $\pm|\Delta\lambda|$ from the line center) were the mean wavelengths $\Delta\lambda_2$ (measured from the "unperturbed" line) of points of equal intensities on the two wings as function of their distance $2\Delta\lambda_1$ from each other. The quantity $\Delta\lambda_2$ is accordingly defined by

$$S(|\Delta\lambda_1+\Delta\lambda_2|)\equiv S(-|\Delta\lambda_1-\Delta\lambda_2|). \quad (41)$$

From Eqs. (37) and (38) it follows then for the case of absorption

$$\Delta\lambda_2 \approx \Delta\lambda_1\left[\left(\frac{1-\Delta R_s}{R}\right)\left(\frac{\Delta\lambda_1}{2\lambda}\right)^{1/2} + \left(\frac{46}{4R}+\frac{37\Delta R_s}{4R}-1\right)\frac{\Delta\lambda_1}{\lambda}\right]\left|\frac{\Delta\lambda dS}{Sd\Delta\lambda}\right|^{-1}. \quad (42)$$

The first term in the square bracket stems from quad-

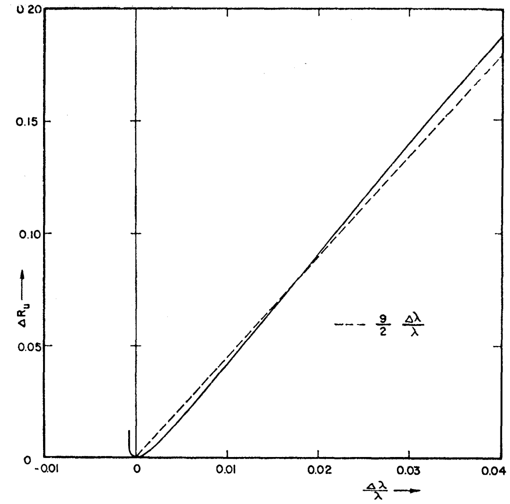

FIG. 2. Correction ΔR_u to the asymptotic Holtsmark result from quasistatic ion broadening of the unshifted component and the approximation $\Delta R_u \approx \frac{9}{2}\Delta\lambda/\lambda$.

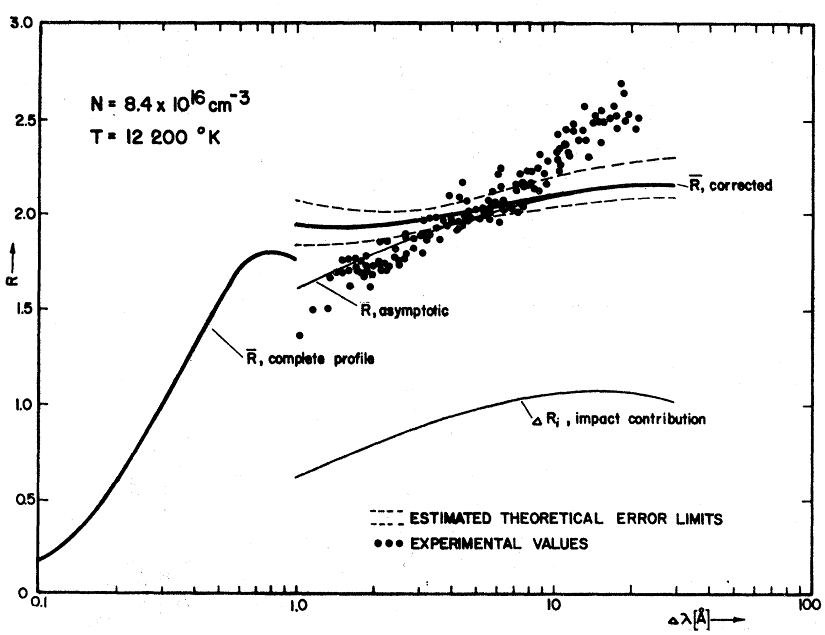

FIG. 3. Comparison of measured (Ref. 10) (multiplied by 1.25) and calculated profiles, both relative to the asymptotic Holtsmark result, at $N=8.4\times10^{16}$ cm^{-3} and $T=12\,200$°K. Also shown are the results of complete profile calculations (Ref. 1) (recalculated with the new Φ-matrix elements and using the distribution functions of Ref. 22), the profile not corrected for deviations from asymptotic formulas, the impact broadening contribution, and the theoretical error estimates.

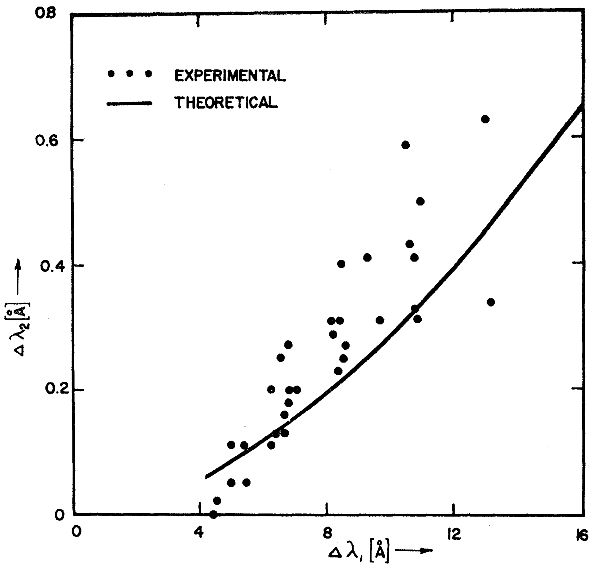

FIG. 4. Comparison of measured asymmetry (Ref. 10) (shift $\Delta\lambda_2$ in mean wavelength of points of equal intensity on both wings of the line from unperturbed line center as function of their mean separation $\Delta\lambda_1$ from the line center), and the present calculations.

rupole interactions and is usually the smaller of the two terms at wavelengths where the asymmetry is noticeable. In the second term, quadratic Stark effect, changes of the dipole moments, ion broadening of the unshifted component and transformation to wavelength increments contribute $(7/4)(1+\Delta R_s)/R$, $7(1+\Delta R_s)/R$, $9/4R$ and $\frac{1}{2}(1+\Delta R_s)$ to the coefficient of $\Delta\lambda_1/\lambda$, with -1 coming from the wavelength factor in the absorption coefficient.

As seen from Fig. 4, agreement between measured and calculated asymmetries is almost satisfactory in view of the scatter of the measured points and the uncertainties associated with the calculations. However, measured (red) asymmetries are mostly above the calculated values, which might be due to some additional broadening mechanism favoring the red wing. As likely there is a small systematic error in the wavelength measurements. These were referred to the center of the absorption line which may well be shifted to the blue by quadrupole effects on the unshifted component. A blue shift of only 0.05 Å, resulting in the same upward shift of all measured points on Fig. 4, would account for much of the disagreement.

A previous analysis[18] of the asymmetry achieved only qualitative agreement, not only because the corrections to the dipole moments used[19] differed from those deduced here but also because a λ^4 dependence was assumed rather than the λ dependence appropriate for absorption. Moreover, the transformation to wavelengths, the contribution from the unshifted component and the fact that only about half of the wing intensity can be calculated with the quasistatic approximation, were ignored. For these reasons and because the variation of the Boltzmann factors was not included, this analysis is not applicable for emission either.

The other experiment[8,9] was performed with a high-pressure electric shock tube, using helium as the carrier gas. Because of difficulties with impurity lines on the blue wing and the limited number of shots for a given tube, only the red wing was measured. Also, the experimentally obtained line profile was presented on a relative intensity scale, since measurements of the emissivity[8] yielded absolute emission coefficients limited in accuracy to about a factor of 2 (due chiefly to uncertainties in the measured temperature). These absolute measurements were therefore reported[9] only as results consistent with theory.[4]

As in the arc experiment, an intensity range of 3 orders of magnitude was covered, even though in terms of $\Delta\lambda/F_0$ measurements were performed nearer to the line center. To compare with theory, the asymptotic formula Eq. (40) must therefore be corrected according to Eq. (A10) out to the farthest point. For $|\Delta\lambda|\lesssim 3$ Å this correction becomes too large in this case ($\gtrsim 15\%$) to be reliable. Here comparison must be made with complete profile calculations.[1] In principle, asymmetry corrections should be included as well, following Eq. (37) (for emission). This correction amounts to $+13\%$ for the outermost point measured ($\Delta\lambda\approx 15$ Å), but is probably mostly canceled by the reduction in the photoelectric yield[20] of the gold cathode used in the detecting system.[21] Neglecting, therefore, theoretical and experimental asymmetry corrections, experiment and theory are compared in Fig. 5, again using Eq. (39) for a theoretical error estimate, assuming a $\pm 20\%$ error in Eq. (A10), and applying a suitable normalization factor to the measured values.

Though the scatter is large, the shapes of calculated and an appropriately smoothed (hypothetical) measured curve would agree quite closely. This also holds for points near the ends of the measured range, in contrast to the situation in the arc experiment. If any significant disagreement should exist, it is rather in the opposite sense now, that is the experimental profile seems to decay somewhat faster. Because of the scatter in the experimental points, such conclusions are rather tentative and should be supported by additional experiments, preferably on an absolute scale or, equivalently, over a sufficiently large part of the profile that it can be normalized directly. The best carrier gas would be helium with its small van der Waal's constant and atomic radius.

The theoretical error estimates [see Figs. 3 and 5 and the discussion preceding Eq. (39)] suggest that absolute

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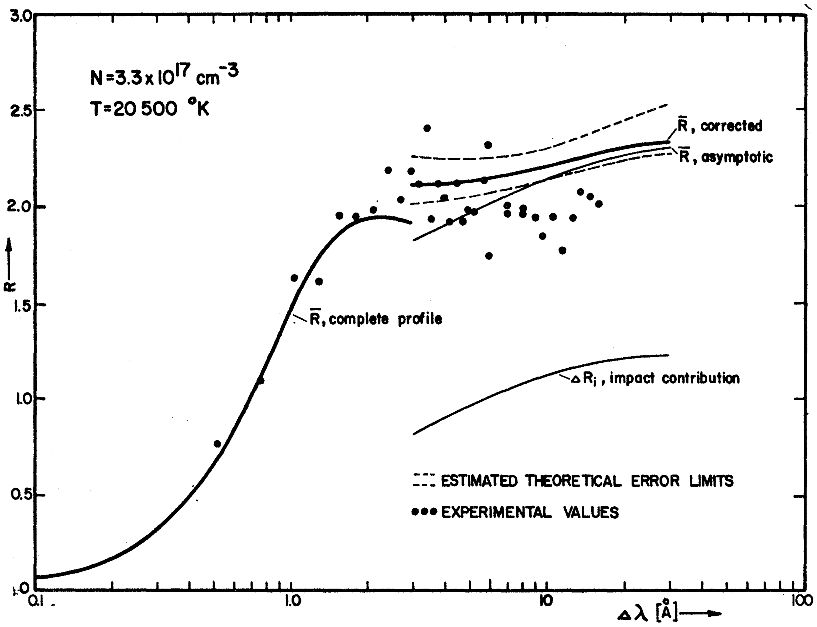

FIG. 5. Comparison of measured (Refs. 8, 9) and calculated profiles, both relative to the asymptotic Holtsmark result, at $N=3.3\times10^{17}$ cm^{-3} and $T=20\,500$°K. Also shown are the results of complete profile calculations (Ref. 1) (recalculated with the new Φ-matrix elements and using the distribution functions of Ref. 22), the profile not corrected for deviations from asymptotic formulas, the impact broadening contribution, and the theoretical error estimates.

absorption or emission coefficients of Lyman-α can be calculated to $\pm10\%$ over at least three orders of magnitude in intensity and including the asymmetry of the two wings, as long as only charged particles are responsible for the broadening. Extension of similar calculations to other hydrogen lines, mainly to those of the Balmer series, would certainly be very desirable but also constitute a rather formidable task. For the time being it must therefore suffice to conjecture from the $\pm10\%$ agreement between previously proposed wing formulas[4] and the present calculations (for the conditions of the two experiments[8–10]) that these earlier wing formulas should be quite reliable for other hydrogen lines as well. Large errors ($>20\%$) are expected only when the Lewis cutoff[12] is ignored, when asymptotic formulas are invalid as such, when Debye shielding is important, or when there is serious overlap with lines of different principal quantum number.

Figures 3 and 5 also show that calculated intensities exceed twice the Holtsmark value by about 10% on the far wings. This excess is mainly due to electron impact broadening through quadrupole interactions. A similar effect may well occur for all other hydrogen lines. The magnitude of the electron impact broadening contribution as indicated on these figures exemplifies further how premature it is to conclude from experiments giving the electron contribution as about equal to the quasistatic ion broadening that also the electrons are acting quasistaticly. More refined experimental techniques would be needed to test such a contention, e.g., precision measurements of the asymmetry which is different in the impact or quasistatic approximations. On the theoretical side, it would be of some interest to improve the accuracy and range of the complete profile calculations to study the transition region to the validity regime of asymptotic wing formulas. (At present it appears possible that some of the discontinuity between the curves in Figs. 3 and 5 is due to integration errors for the outmost points of the complete profiles.)

APPENDIX A

To estimate higher order terms in the asymptotic expansion of Eq. (1) which lead to Eq. (4) and all subsequent wing formulas, consider the (imaginary) case of a line with only two (symmetrically broadened and shifted) Stark components. According to Eq. (1) and assuming Φ_{ab} has only diagonal matrix elements, its normalized line shape is

$$L(\omega)=\frac{w}{2\pi}\left(\int_0^\infty \frac{W(F)dF}{(\omega-CF)^2+w^2}+\int_0^\infty \frac{W(F)dF}{(\omega+CF)^2+w^2}\right), \quad \text{(A1)}$$

with

$$w=-\mathrm{Re}\langle\langle\alpha\beta|\Phi_{ab}|\alpha\beta\rangle\rangle$$

and

$$C=|(e/\hbar)\langle\langle\alpha\beta|z_a-z_b|\alpha\beta\rangle\rangle|$$

from Eq. (2). For statistically independent charges, $W(F)$ is according to Holtsmark[14]

$$W(F)=\frac{2\beta}{\pi F_0}\int_0^\infty \sin(\beta\eta)\exp(-\eta^{3/2})\eta d\eta\,, \quad \text{(A2)}$$

where F_0 is the normal field strength, $F_0\approx(4\pi/3)^{2/3}eN_s^{2/3}$, and β the relative field strength, $\beta=F/F_0$. Introducing

$\gamma=w/F_0$, $\delta=\omega/F_0$, and $l(\delta)=F_0L(\omega)$ this reduced profile becomes with $\sin(\beta\eta)=-i\,\mathrm{Im}\exp(i\beta\eta)$

$$l(\delta)=\frac{\gamma}{i\pi^2}\,\mathrm{Im}\int_{-\infty}^{+\infty}\frac{\beta d\beta}{(\delta-C\beta)^2+\gamma^2}\times\int_0^{\infty}\exp(i\beta\eta-\eta^{3/2})\eta d\eta\,, \quad \text{(A3)}$$

after F in the second term of Eq. (A1) is replaced by $-F$ and use is made of $W(-F)=W(F)$. The integral over β can be done by contour integration, closing the path in the upper β plane,

$$l(\delta)=\frac{1}{i\pi C^2}\,\mathrm{Im}(\delta+i\gamma)\times\int_0^{\infty}\exp\left[i(\delta+i\gamma)\frac{\eta}{C}-\eta^{3/2}\right]\eta d\eta\,. \quad \text{(A4)}$$

If $\exp(-\eta^{3/2})$ is expanded, the remaining integration can be performed term by term, using

$$\int_0^{\infty}\exp(-wt)t^z dt=z!w^{-(z+1)}\,,$$

$$l(\delta)=\frac{1}{\pi C}\sum_0^{\infty}\frac{(-1)^n}{n!}\left(\frac{3n+2}{2}\right)!\,\mathrm{Re}\left(\frac{C}{\gamma-i\delta}\right)^{(3n+2)/2}. \quad \text{(A5)}$$

This is equivalent to a result first found by Kolb.[15]

Further expansion in terms of γ/δ gives

$$l(\delta)=\frac{\gamma}{\pi\delta^2}\left[1-\left(\frac{\gamma}{\delta}\right)^2+\cdots\right]+\frac{15|C|^{3/2}}{8\sqrt{2\pi}|\delta|^{5/2}}\times\left[1+\frac{5}{2}\left|\frac{\gamma}{\delta}\right|-\frac{35}{8}\left(\frac{\gamma}{\delta}\right)^2+\cdots\right]+\frac{12|C|^3}{\pi\delta^4}\left[1-10\left(\frac{\gamma}{\delta}\right)^2+\cdots\right]+\cdots. \quad \text{(A6)}$$

The square brackets approach 1 on the line wings, and the first term ($n=0$) therefore corresponds to the impact broadening term in Eq. (4). In the same limit, $(\gamma/\delta)\rightarrow 0$, the second term ($n=1$) evidently corresponds to the quasistatic term in Eq. (4). The third term ($n=2$) is then a first-order correction to the asymptotic form of the quasistatic theory. Calling the quasistatic and impact broadening terms l_s and l_i, respectively, and neglecting corrections of order $(\gamma/\delta)^2$ and terms $n\geq 3$, the profile can be written as

$$l(\delta)\approx(l_s+l_i)\left(1+\left[\frac{32}{5}\left(\frac{2}{\pi}\right)^{1/2}\left|\frac{C}{\delta}\right|^{3/2}+\frac{5}{2}\left|\frac{\gamma}{\delta}\right|\right]\left(1+\frac{l_i}{l_s}\right)^{-1}\right). \quad \text{(A7)}$$

Besides this correction to the asymptotic formula corrections in the quasistatic contribution due to Debye shielding by electrons and ion-ion correlations must be considered. The field strength from the nearest ion is now

$$F\approx(e/r^2)[1+(r/\rho_D)]\exp(-r/\rho_D)\approx(e/r^2)[1-(1/2)(r/\rho_D)^2+\cdots],$$

where ρ_D is the Debye radius accounting for shielding by both ions and electrons of densities $N_i=N_e=N$. (Detailed calculations of field strength distribution functions[22] suggest that this choice of ρ_D actually results in a slight over-correction.) With $\omega=CF$ follows

$$\omega\approx(Ce/r^2)[1-(1/2)(r/\rho_D)^2+\cdots]\approx(Ce/r^2)[1-(Ce/2\omega\rho_D^2)],$$

when the first approximation is used in the correction term. The quasistatic relation $L_s(\omega)=W(r)|dr/d\omega|\sim 4\pi r^2N_s|dr/d\omega|$ then yields

$$L_s(\omega)\sim 2\pi N_s\frac{|Ce|^{3/2}}{|\omega|^{5/2}}\left(1-\frac{5Ce}{4\omega\rho_D^2}\right). \quad \text{(A8)}$$

From Eqs. (A7) and (A8) the relative correction to the asymptotic wing formula, i.e., to Eq. (4), is finally estimated to be

$$\frac{\Delta L(\omega)}{L(\omega)}\approx\frac{1}{R}\left[\frac{32}{5}\left(\frac{2}{\pi}\right)^{1/2}\left|\frac{C}{\delta}\right|^{3/2}+\frac{5}{2}\left|\frac{\gamma}{\delta}\right|-\frac{5Ce}{4\delta F_0\rho_D^2}\right], \quad \text{(A9)}$$

with $R=1+l_i/l_s$ being the correction factor to the usual asymptotic Holtsmark result, which is given by Eq. (34) and accounts mainly for the electron impact broadening. (The quantity ΔR_s tends to be negligible when $\Delta L/L$ is important.)

To facilitate application to experiments, it is best to express the above result in terms of the wavelength separation $\Delta\lambda\approx\omega\lambda^2/2\pi c$ from the center of the line. For Lyman-α

$$[C=3\hbar/me\,,\ w=\gamma F_0\approx 48\pi^{1/2}a_0(\hbar/m)\times(E_H/kT)^{1/2}N\ln(\rho_D'/\rho_{\min}')]$$

the correction now becomes

$$\frac{\Delta S(\Delta\lambda)}{S(\Delta\lambda)}\approx\left(\frac{485}{R}a_0^3N\left|\frac{\lambda}{\Delta\lambda}\right|^{3/2}\right)\times\left(1+\left[1.18\ln\frac{kT}{18E_H}(a_0^3N)^{-1/2}-1.04\left(\frac{E_H}{kT}\right)^{1/2}\right]\left(\frac{E_H}{kT}\right)^{1/2}\left|\frac{\Delta\lambda}{\lambda}\right|^{1/2}\right), \quad \text{(A10)}$$

where E_H is again the ionization energy of hydrogen and

[22] B. Mozer and M. Baranger, Phys. Rev. 118, 626 (1960).

a_0 the Bohr radius. The impact width was estimated from Eqs. (28)–(30) of Ref. 1, using the value $\langle\alpha|\mathbf{r}_a\cdot\mathbf{r}_a|\alpha\rangle = 18a_0^2$ which is appropriate for the shifted components. The use of these relations is justified in this connection, because deviations from the asymptotic formula are only important at relatively small separations from the line center where the upper limit for the relevant values of impact parameters is indeed well estimated by the Debye radius ρ_D' accounting for electron shielding only (see Sec. 5) and where collisions within $\rho_{\min}'\approx 4\hbar/mv$ are negligible. Neglecting off-diagonal matrix elements of the electron impact broadening operator Φ_{ab} should also not cause significant errors, as these terms are only important if the quasistatic splitting for a given ion field is not much larger than the Φ_{ab} matrix elements, which for Lyman-α only happens very near to the line center.

Equation (A10) can be used to estimate corrections necessitated by the only approximate validity of the asymptotic wing formula Eq. (4), provided these corrections are small. Usually it turns out that corrections connected with the impact term (containing the logarithm) and the Debye shielding (the negative term) of the quasistatic fields are about equally important, and that they are both of the same order as the correction to the original asymptotic Holtsmark formula as given by the first factor in Eq. (A10).

APPENDIX B

To estimate asymmetries of quasistaticly broadened lines ordinarily subject to linear Stark effect, the perturbation theory must be carried to second order in the dipole interaction, and in addition quadrupole interactions must be considered to first order. Therefore the strengths of the shifted components are now affected by the perturbation, and there is also a contribution from the unshifted component to the quasistatic broadening.

The appropriate interaction Hamiltonian is from Eq. (15), choosing the line connecting atom and perturber as z axis,

$$V(r)\approx\pm\frac{\hbar}{mr^2}\left[R_z+\frac{3}{2}\frac{a_0}{r}(R_z^2-\tfrac{1}{3}R^2)\right], \qquad \text{(B1)}$$

where the plus or minus signs apply to electrons and ions as perturbers, respectively. Standard perturbation theory yields for the quasistatic shift

$$\Delta\omega(r)=\pm\frac{\hbar}{2mr^2}\langle 2s_0\pm 2p_0|R_z+\frac{3}{2}\frac{a_0}{r}(R_z^2-\tfrac{1}{3}R^2)$$
$$\pm\frac{\hbar^2}{mr^2}\sum_{n,l}{}'\frac{R_z|nl\rangle\langle nl|R_z}{E_2-E_n}|2s_0\pm 2p_0\rangle \qquad \text{(B2)}$$

to second order in the dipole interaction and first order in the quadrupole interaction. ($|2p_0\rangle$ and $|2s_0\rangle$ designate the wave functions $|210\rangle$ and $|200\rangle$.) Upon taking matrix elements and summation over intermediate states ($n\neq 2$, $l=0, 1, 2$), including the continuum, this results in

$$\Delta\omega_+(r)=\frac{3\hbar}{mr^2}\left[1\pm 2\frac{a_0}{r}-28\left(\frac{a_0}{r}\right)^2\right], \qquad \text{(B3a)}$$

$$\Delta\omega_-(r)=-\frac{3\hbar}{mr^2}\left[1\mp 2\frac{a_0}{r}+28\left(\frac{a_0}{r}\right)^2\right], \qquad \text{(B3b)}$$

for "blue" and "red" components. (The quadratic-Stark-effect coefficient, i.e., the second-order dipole term, was first evaluated by Wentzel[23] and Waller.[24])

In a consistent perturbation theory, the changes in the absolute values squared of the dipole moments entering the quasistatic term in Eq. (4) must also be considered, i.e.,

$$|\mathbf{d}_{\alpha\beta}|^2\sim\left|\left\langle(2s_0\pm 2p_0)\right.\right.$$
$$\left.-\frac{\hbar^2}{mr^2}\sum_n{}'\frac{\langle 2s_0|R_z|np_0\rangle\langle np_0}{E_2-E_n}|R_z|1s_0\right\rangle$$
$$\left.-\frac{\hbar^2}{mr^2}\sum_{n'}{}'\frac{n'p_0\rangle\langle n'p_0|R_z|1s_0\rangle}{E_1-E_{n'}}\right|^2, \qquad \text{(B4)}$$

if only the dipole interaction with ions is included. Using $E_n=-e^2/2a_0n^2$ and treating the terms involving sums over intermediate states as small quantities this can be written as

$$|\mathbf{d}_{\alpha\beta}|^2\sim|\langle 2p_0|R_z|1s_0\rangle|^2$$
$$\times\left[1\pm\frac{4}{\sqrt{3}}\left(\frac{a_0}{r}\right)^2\left(\sum_n{}'\frac{\langle 2s|R|np\rangle\langle np|R|1s\rangle}{(1/2^2-1/n^2)\langle 2p|R|1s\rangle}\right.\right.$$
$$\left.\left.+\sum_{n'}{}'\frac{\langle 2s|R|n'p\rangle\langle n'p|R|1s\rangle}{(1-1/n'^2)\langle 2p|R|1s\rangle}\right)\right], \qquad \text{(B5)}$$

where R_z matrix elements have been replaced by those for R taken between radial wave functions. These radial matrix elements were calculated by Gordon,[25,26] and

[23] G. Wentzel, Z. Physik **38**, 518 (1926).
[24] J. Waller, Z. Physik **38**, 635 (1926).
[25] W. Gordon, Ann. Physik **2**, 1031 (1929).
[26] See also Eq. (63–4) in H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Systems* (Academic Press Inc., New York, 1957).

with them Eq. (B5) becomes

$$|\mathbf{d}_{\alpha\beta}|^2\sim|\langle 2p_0|R_z|1s_0\rangle|^2\left[1\pm16\left(\frac{a_0}{r}\right)^2\left(1+2^{10}(\sqrt{10})\sum_{n=3}^{\infty}\left(\frac{n^2-3n+2}{n^2+3n+2}\right)^n n^9\left(n^2-\frac{8}{5}\right)(n^2-1)^{-3}(n^2-4)^{-4}\right.\right.$$
$$\left.\left.+2^9(\sqrt{10})\int_0^{\infty}\frac{\exp[-2x^{-1/2}(\tan^{-1}\sqrt{x}+\tan^{-1}2\sqrt{x})]}{(1+x)^3(1+4x)^4(1+8x/5)^{-1}}dx\right)\right]. \quad \text{(B6)}$$

(To extend the summation over intermediate states lying in the continuum, the sum over n can be written as an integral involving the variable $x=-1/n^2$ between the limits $x=0$ and $x\rightarrow\infty$.) Summing and integrating numerically follows

$$|\mathbf{d}_{\alpha\beta}|^2\sim\langle 2p_0|R_z|1s_0\rangle|^2[1\pm56(a_0/r)^2], \quad \text{(B7)}$$

where according to Eq. (B2), e.g., the plus sign is associated with the red component. The contributions to the correction term from bound states $n\geq3$ and continuum states are 58 and 13%, respectively, with 29% from $n=2$. (This result differs considerably from a recently published value[19] even if the λ^4 factor variation included in Ref. 19 were accounted for. With the present result, the correction for this combined quantity is only half as large and of opposite sign.)

Using Eqs. (B3) and (B7) the quasistatic broadening of the shifted components can now be computed beyond the usual first-order dipole approximation from $L(\omega)\sim|d_{\alpha\beta}(r)|^2 4\pi Nr^2|dr/d\omega|$. Inverting the various power series, normalizing and adding a correction ΔR_u for the quasistatic ion broadening of the unshifted component through quadrupole and quadratic Stark effects one then obtains for broadening by ions

$$L(\omega)\sim\frac{\sqrt{3}\pi}{|\omega|^{5/2}}\left(\frac{\hbar}{m}\right)^{3/2}N\left[1+\Delta R_u\mp2\left|\frac{\hbar\omega}{6E_H}\right|^{1/2}\mp(70\pm\tfrac{1}{2})\left|\frac{\hbar\omega}{6E_H}\right|\right], \quad \text{(B8)}$$

the upper and lower signs applying to blue and red wings, respectively. For electrons the term $2|\hbar\omega/6E_H|^{1/2}$ has the opposite sign, as it stems from the first-order quadrupole interaction. From Eqs. (33) and (B8) the total wing profile is thus approximately

$$L(\omega)\sim L_H(\omega)\left[R+\Delta R_u\mp2\left|\frac{\hbar\omega}{6E_H}\right|^{1/2}(1-\Delta R_s)\mp70\left|\frac{\hbar\omega}{6E_H}\right|(1+\Delta R_s)\right], \quad \text{(B9)}$$

with ΔR_s from Eq. (26) and neglecting $\pm\frac{1}{2}$ against 70.

It remains to calculate the contribution ΔR_u from the unshifted component. The quasistatic shift of this component through first-order quadrupole interactions and quadratic Stark effect is

$$\Delta\omega(r)=\left[12\left(\frac{a_0}{r}\right)^3-156\left(\frac{a_0}{r}\right)^4\right]\frac{E_H}{\hbar}\approx-\frac{3}{4}\left(\frac{\Delta\lambda}{\lambda}\right)\frac{E_H}{\hbar}. \quad \text{(B10)}$$

With $S_u(\Delta\lambda)\approx\frac{2}{3}4\pi Nr^2|dr/d\Delta\lambda|$ and dividing by the Holtsmark result from Eq. (37) this yields

$$\Delta R_u(\Delta\lambda)\approx\frac{1}{2^{3/2}}\left(\frac{r}{a_0}\right)^2\left|48\left(\frac{a_0}{r}\right)^4-832\left(\frac{a_0}{r}\right)^5\right|^{-1}\left|\frac{\Delta\lambda}{\lambda}\right|^{5/2}, \quad \text{(B11)}$$

where r is still to be determined from Eq. (B10). This must be done numerically.