Shifts of hydrogen and ionized-helium lines from $\Delta n = 0$ interactions with electrons in dense plasmas

Hans R. Griem

Laboratory for Plasma and Fusion Energy Studies, University of Maryland, College Park, Maryland 20742

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Shifts from electron collisions associated with dipole interactions between degenerate levels of a given principal quantum number *n* are evaluated following D. B. Boercker and C. A. Iglesias [Phys. Rev. A 30, 2771 (1984)]. They are then used to recalculate the plasma shifts of hydrogen and ionized-helium lines from electron collisions, inhomogeneities in the ion-produced quasistatic fields, and some higher-order effects. Because of the partial cancellation of electron collisional shifts by the other effects, inclusion of the $\Delta n = 0$ collisional shifts leads to an increase of calculated line shifts by a factor \sim 1.5, which for Balmer lines of hydrogen and Paschen lines of ionized helium leads to markedly improved agreement with most measurements. Estimates for higher-Z members $(Z \ge 4)$ of the one-electron isoelectronic sequence yield $\Delta n = 0$, dipole contributions to the electroncollisional shifts which are much smaller than the effects of $\Lambda=0$, penetrating monopole interactions.

I. INTRODUCTION

In most calculations' of the Stark broadening of hydrogen lines by electrons and ions in a plasma, shifts and profile asymmetries are neglected. However, in experi m ents²⁻¹⁰ with good wavelength calibrations, the relatively broad lines of the hydrogen Balmer series, and also the Lyman- β line,¹¹ are seen to be shifted toward longer wavelengths by $\leq 5\%$ of their full widths. They also exhibit some profile asymmetries. (For Lyman- α , a recent experiment¹² yields a red shift which is only \sim 1.5% of the width.) This is in contrast to the probably much less accurate measurements $^{13-16}$ on the often very opticall thick lines of the ionized-helium Lyman series which indicate shifts toward shorter wavelengths, but in reasonable accord with measurements of ionized-helium Bal-'mer¹⁷ and Paschen^{17,18} series lines, which again show red shifts.

Initial observations (see Ref. 19) of small shifts for resonance lines of other one-electron ions (Be IV-C VI) were later found¹⁹ to be questionable because of difficulties with the wavelength calibrations due to differences in the streaming velocities in the various layers of laserproduced plasmas. However, a recent observation²⁰ of the Nex reso'nance lines in a laser-compressed plasma shows a red shift in accord with quantum-mechanical calculations²¹ of the effects of electron collisions, which in turn give results close to those of self-consistent (static) 'field calculations.^{21,}

Calculations of electron collision-induced shifts involving $\Delta n \neq 0$ interactions, where *n* is the principal quantum number of the initial or final state of the radiative transition, for ionized helium²³ and hydrogen,²⁴ gave red shifts which were in reasonable agreement with the observed red shifts, especially after blue shifts corresponding to the ion-radiator quadrupole interactions,²⁵ which actually cause small profile asymmetries, were also accounted for. However, the calculated shift of the HeII Balmer- α line

was smaller than measured¹⁸ (8 mÅ versus 25 mÅ at an electron density of $N_e = 10^{17}$ cm⁻³), not to mention the discrepancies with the observed blue shifts of He II Lyman-series lines.

The purpose of the present paper is to evaluate the electron-produced shifts from $\Delta n = 0$ interactions following Boercker and Iglesias, 26 and to discuss how these additional contributions affect the agreement or disagreement between measurements and calculations. The physics of the $\Delta n = 0$ contributions will be discussed in Sec. II, to be followed by estimates of the magnitudes and the relative importance for hydrogen lines in Sec. III and for ionized-helium lines in Sec. IV. The concluding section is an attempt at a synthesis of experiment-theory comparisons.

II. SHIFTS FROM INTERACTIONS INVOLVING ONLY STATES OF THE SAME PRINCIPAL QUANTUM NUMBER

In the kinetic-theory approach of Boercker and Iglesias, 2^6 $\Delta n = 0$, dipole-approximation, second-order contributions to the hydrogen line shift arise from two physical effects. First, although there is—because of the cancellation of electron and ion charges —no first-order effect associated with the mean value of the atomelectron interaction V , this interaction does introduce some anisotropy in the electron distribution function f , which is of order V . Reevaluation of the static shift associated with the mean interaction using this corrected distribution function thus gives a second-order shift to lower energies, as one would expect from such Boltzmannfactor —type of argument.

Second, there is a dynamical shift from field fluctuations which for small shifts, e.g., frequencies near the unperturbed line center, can be evaluated using the impact approximation. ' The corresponding width parameter involves $S(k, \omega)$, the spectral density of electron density or

field fluctuations (see, e.g., p. 143 of Ref. 1), and according to the Kramers-Kronig-relations, the associated shift is therefore determined by

$$
P\int_{-\infty}^{+\infty} S(\mathbf{k},\omega')d\omega'/2\pi(\omega-\omega') ,
$$

which for $\omega \rightarrow 0$, i.e., in the impact approximation, is normally assumed to vanish because of the symmetry of $S(k, \omega')$ in the classical limit. However, Boercker and Iglesias²⁶ realized that the quantum-statistical symmetry relation

$$
S(\mathbf{k}, -\omega) = \exp(\hbar \omega / k_B T) S(\mathbf{k}, \omega) ,
$$

on expansion of the exponential, gives

$$
(\frac{1}{2}k_B T)\int_{-\infty}^{+\infty} S(\mathbf{k},\omega')d\omega
$$

for the above principal-value integral, $(N_e/2k_B T)S(\mathbf{k})$, where $S(\mathbf{k})$ is the static form factor

$$
S(\mathbf{k}) = \frac{k^2}{k^2 + k_D^2} \tag{1}
$$

for the classical electron gas with

$$
k_D^2 = 4\pi N_e e^2 / k_B T \t{,} \t(2)
$$

and N_e is the free-electron density.

Using the fluctuation-dissipation theorem, also the static shift can be expressed in terms of $S(k)$; and the primary result of Boercker and Iglesias for the $\Delta n = 0$, second-order dipole approximation shift was, in Eq. (2.25) of Ref. 26,

$$
\hbar d = -\frac{N_e}{k_B T} \int d\mathbf{k} \frac{1}{(2\pi)^3} D_{\mu\mu'}(\mathbf{k}) [S(\mathbf{k}) - \frac{1}{2} S(\mathbf{k})], \quad (3)
$$

where $D_{uu'} \sim k^{-2}$ involves the spatial Fourier transforms of the products of interaction energy matrix elements between upper states of the line. For a given plasma wave number, the dynamical shift is therefore one-half of the static shift and in the opposite direction. That the dynamical shift is a blue shift can be understood in terms of the plasmon picture: while induced emission and absorption of plasmons cancel each other, spontaneous emission of plasmons does add, on the average, some energy to the emitted photons if the entire process is viewed as a two-quantum process. However, before accepting Eq. (3} for shift calculations, it is necessary to discuss its validity range in k space.

In both cases an upper limit of the integral over k (at least for hydrogen lines) is necessitated by the unitarity restriction to be imposed on the second-order perturbation theory. With the identification $k_{\text{max}} = \rho_{\text{min}}^{-1}$ this results, according to Ref. 24, in a maximum k value,

$$
k_m = \left(\frac{3}{2}\right)^{1/2} \frac{mv}{\hbar} \left[\sum_{l'} \frac{l}{2l+1} \left[nl'\left|\frac{r}{a_0}\right|nl\right]^2\right]^{-1/2}
$$

$$
\approx \frac{mv}{\hbar n^2}, \qquad (4)
$$

where n is the principal quantum number of the upper level and *l* its orbital quantum number. Only $\Delta n = 0$, $l = l \pm 1$ interactions with strengths measured by the corresponding radial matrix elements are considered, and the second version is not to be used for quantitative calculations. According to Eq. (1) and because of $D_{\mu\mu'} \sim k^{-2}$, the integrals in Eq. (3) are then

$$
I = \int_0^{k_m} d\mathbf{k} \, k^{-2} S(k) = 4\pi \int_0^{k_m} \frac{k^2}{k^2 + k_D^2} dk
$$

= $4\pi k_m - 4\pi k_D \tan^{-1}(k_m / k_D)$. (5)

Since the actual values of k_m in the various hydrogen experiments fulfill $k_m > 10k_D$, the integrals are well approximated by

or
$$
I \approx 4\pi k_m \left[1 - \frac{\pi}{2} \frac{k_D}{k_m} \right]
$$
. (6)

III. SHIFTS OF HYDROGEN LINES FROM $\Delta n = 0$ DIPOLE INTERACTIONS WITH ELECTRONS

The net shift from perturber atom correlations and the quantum-mechanical asymmetry of the spectral density $S(k, \omega)$ in the dynamical contribution is from Eqs. (3) and (6), and using the Fourier-transformed dipole interaction matrix elements

$$
V_{\mu}(k) = e^2 \int d\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} \frac{\mathbf{r}_{\mu}\cdot\mathbf{r}}{r^3} = 4\pi e^2 \frac{\mathbf{k}\cdot\mathbf{r}_{\mu}}{k^2} i
$$
 (7)

in

$$
D_{\mu\mu'} = V_{\mu}(\mathbf{k})V_{\mu'}(-\mathbf{k}) ,
$$
 (8)

$$
d = -\frac{4}{3} \frac{N_e \hbar k_m}{k_B T} \left[\frac{\hbar}{m} \right]^2 \frac{\mathbf{r}_{\mu} \cdot \mathbf{r}_{\mu'}}{a_0^2} \left[1 - \frac{\pi}{2} \frac{k_D}{k_m} \right]. \tag{9}
$$

In this expression, the r_{μ} and $r_{\mu'}$ are the atomic dipole operators, whose matrix elements are according to Eq. (467) of Ref. ¹

$$
\sum_{l'} \langle nl | \mathbf{r}_{\mu} | nl' \rangle \cdot \langle nl' | \mathbf{r}_{\mu'} | nl \rangle
$$

= $\frac{9}{4}n^2(n^2 - l^2 - l - 1)a_0^2 \delta_{\mu\mu'}$. (10)

The factor $\frac{1}{3}$ in Eq. (9) arises from the average over relative orientations of the vectors r_{μ} and **k**.

Expression (10) is essentially equal to the squarebracketed expression in Eq. (4) for k_m , because of ectors \mathbf{r}_{μ} and **k**.

ssentially equal to the square

Eq. (4) for k_m , because of
 $\frac{3}{2}n(n^2-l_{\geq}^2)^{1/2}$,

$$
(nl|(r/a_0)|nl') = \frac{3}{2}n(n^2 - l^2) ^{1/2}
$$

so that our estimate for the $\Delta n = 0$ shift from weak collisions becomes on the average over perturber velocities

$$
d_w = -4 \left[\frac{3m}{\pi k_B T} \right]^{1/2} \left[\frac{\hbar}{m} \right]^2 n (n^2 - l^2 - l - 1)^{1/2}
$$

$$
\times N_e \left[1 - \frac{\pi}{2} \left[\frac{k_D}{k_m} \right] \right].
$$
 (11)

Here we must use the linear average of v in the correction term, which should of course be small, i.e., fulfil

$$
\frac{\pi}{2} \frac{k_D}{k_m} \approx \frac{\pi^2}{\sqrt{3}} \frac{E_H}{k_B T} (N_e a_0^3)^{1/2} n (n^2 - l^2 - l - 1)^{1/2}
$$

 $\lesssim 0.25$ (12)

for the approximation (6) for I to be within $\sim 10\%$ of the exact value in Eq. (5). This condition is at least marginally fulfilled under the various experimental conditions.²⁻¹² In any event, the approximation tan⁻¹(k_m / k_D) $\approx \pi /2$ used here underestimates the $\Delta n = 0$ shift.

For the calculation of line rather than level shifts, two additional steps are required. Some allowance must be made for the shifts of the lower levels of the Balmer lines, and the shifts must be averaged over orbital quantum numbers. Although the authors of Ref. 26(a) explicitly neglected the shifts of lower levels, we will now assume Eq. (9) to hold also for the shift of the lower level. [See Ref. 26(b) for a justification of this assumption.] The line shift should then be given by the difference of these level shifts, since the underlying "plasmon"-atom collisions are inelastic and thus not subject to the upper —lower-level interference effect' occurring in elastic electron-atom scattering. (There is, of course, no such question for the static shift.) However, there is cancellation in the electron collision broadening of the line due to this interference term, i.e., the square root of the square-bracket term in Eq. (4) must be replaced by the difference of the corresponding square roots for upper and lower levels, if broadening from inelastic collisions and any other subtle $effects^{27,28} were indeed negligible.$

So, if the upper-level shift is written as L_u^2/L_u , the line shift becomes $(L_u^2 - L_l^2)/(L_u - L_l) = L_u + L_l^2$, i.e., equal to the sum of the level shifts calculated according to Eq. (11), at least to the extent that the last factor can be replaced by 1. If this is not the case, and since the second term in Eq. (9) does not really depend on k_m , it is obvious that for line rather than level shifts the difference of these second terms should be used. A plausible formula for the $\Delta n = 0$, weak collision, line shift is therefore

$$
d_{12} = -4 \left[\frac{3m}{\pi k_B T} \right]^{1/2} \left[\frac{\hbar}{m} \right]^2 N_e \left[n_1 (n_1^2 - l_1^2 - l_1 - 1)^{1/2} \left[1 - \frac{\pi}{2} \left[\frac{k_D}{k_{m1}} \right] \right] + n_2 (n_2^2 - l_2^2 - l_2 - l)^{1/2} \left[1 + \frac{\pi}{2} \left[\frac{k_D}{k_{m2}} \right] \right] \right],
$$
\n(13)

I

with subscripts 1 and 2 labeling quantum numbers of upper and lower states and k_{m1} and k_{m2} given by relations corresponding to Eq. (4).

In view of the strong (linear) dependence of the dominant terms in Eqs. (11) and (13) on the momentum cutoffs, these formulas should be considered provisional, especially in view of the possible role of inelastic collisions in the determination of k_m . To obtain some measure of the corresponding theoretical errors, Balmer line shifts due to the $\Delta n = 0$ dipole interactions were calculated using both Eqs. (13) and (11) . As to the *l* average, $(2l_2+1)f_{21}$ was used as weight factor, f_{21} being the $l_2 \rightarrow l_1$ absorption oscillator strengths. It was found that shifts from Eq. (13) are larger than those from Eq. (11) by factors \sim 1.5, 1.2, 1.15, and 1.1, respectively, for the α , β , γ , and δ lines of the Balmer series. However, since effects of inelastic collisions were neglected in the derivation of Eq. (13), applying these factors would most likely result in overestimates of the $\Delta n = 0$ weak collision shifts. This can be seen by adding $\Delta n \neq 0$ terms to the quantity $L_u - L_l$ used in deriving Eq. (13). They (mostly) involve the characteristic B functions of the semiclassical theory¹ of impact broadening, with typical values²⁴ of $B \approx 0.5$. Using approximate dipole matrix elements corresponding to Eq. (467) of Ref. 1, one then obtains reduction factors of 1.5, 1.1, 1.06, and 1.04, respectively. In other words, after applying these factors, the remaining differences from Eq. (11) are $\leq 10\%$, i.e., insignificant. In Table I, $\Delta n = 0$ shifts are therefore given only according to Eq. (11) , but multiplied by a factor 1.2 to allow for strong collisions corresponding to $k > k_m$. As discussed in Refs. 24, 29, and 30, such a factor has some theoretical justification for $\Delta n \neq 0$ shifts, but it certainly needs support from future higher-order calculations.

Calculations for the Lyman lines, which are also presented in Table I, were done again using Eq. (11), also multiplied by 1.2, for $l = 1$. Because of the mixing of l levels by the ion microfield, this simple procedure is not exact either; e.g., in the case of Lyman- α , the $l = 1$ and 0 levels contribute with relative weights $\frac{2}{5}$ and $\frac{1}{6}$. Accord ing to Eq. (11) the ion-field-averaged $\Delta n = 0$ shift is therefore about 12% larger than the $(l = 1)$ -level shift. Corresponding errors for higher members of the series should be somewhat smaller, because the l dependence becomes weaker for larger principal quantum numbers n_1 .

For comparison, the electron-collisional shifts from $\Delta n \neq 0$ interactions calculated earlier²⁴ are also listed in Table I, as are the total electron-collisional shifts given by the sum of the $\Delta n \neq 0$ contributions and the $\Delta n = 0$ contributions calculated here. It is seen that for Lyman- α the total electron-collisional shifts are larger than the previous result by factors 1.7, 1.5, or 1.4, depending on the temperature. For Lyman- β , there are increases by about 25-15%, with increases of $\leq 10\%$ for the other Lyman lines. In the case of the Balmer series, the increases are by factors of 1.46, 1.35, and 1.26 for H_{α} , depending on the temperature. The electron-collisional shift of H_β is increased by about 35%, 28%, and 21%, respectively, for H_{γ} by about 22%, 19%, or 15%. The increases for H_{δ} are about 10% or less, i.e., not significant.

All these comparisons were for an electron density of 10^{17} cm⁻³. Since the $\Delta n = 0$ contribution is slightly nonlinear in density, the increases are relatively larger at lower densities and smaller at higher densities. For H_{α} ,

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calculations are therefore also presented in Table I for $N_e = 10^{18}$ cm⁻³ (in parentheses). The increases in the electron-collisional shifts are by factors 1.38, 1.31, and 1.24, depending on the temperature.

IV. SHIFTS OF IONIZED HELIUM AND HIGHER-Z ONE-ELECTRON LINES FROM $\Delta n = 0$ DIPOLE INTERACTIONS WITH ELECTRONS

Before applying estimates for the effects of $\Delta n = 0$ interactions analogous to those for hydrogen by scaling the dipole matrix elements with $1/z = \frac{1}{2}$, it is necessary to question the underlying assumption of straight classical paths. With this assumption, the scaled values of k_m become, according to Eq. (4),

$$
k_m(z) \approx \left(\frac{2}{3}\right)^{1/2} \frac{m v z}{\hslash n \left(n^2 - l^2\right)^{1/2}} \approx \frac{m v z}{\hslash n^2} \ . \tag{14a}
$$

Curvature in the long-range Coulomb field generated by the point charge $z - 1$, on the other hand, would be important for $k > \rho_c^{-1} \approx mv^2/(z - 1)e^2$, where ρ_c corresponds to a 90' deflection. The quantity

$$
\rho_c k_{\text{max}} \approx (z-1)(e^2/\hbar v)z/n^2
$$

is of order $4(z-1)/n^2$, using

$$
(e^2/\hbar v) = (2E_{\rm H}/mv^2)^{1/2} \approx (E_{\rm H}/k_B T)^{1/2} \approx 4/z.
$$

For $z = 2$, such long-range Coulomb effects will therefore be important only for $n = 2$.

The classical path approximation as such also remains valid, because k_m is smaller than the inverse of the de Broglie wavelength by a factor z/n^2 . However, there is the possibility that the dipole approximation used in Ref. 26 and in Sec. III becomes invalid. This would happen for $k > z/n^2 a_0$, i.e., for impact parameters smaller than the nth Bohr orbit. Using Eq. (14a) one estimates $n^2 a_0 k_{\text{max}} / z \approx \hbar v / e^2 \approx z / 4$ so that also this complication is not important for $z = 2$.

As an aside, we remark, that for $z > 4$, using

$$
k_m(z) \approx \left(\frac{2}{3}\right)^{1/2} \frac{z/a_0}{n \left(n^2 - l^2\right)^{1/2}} \approx \frac{z}{n^2 a_0} \tag{14b}
$$

instead of Eq. (14a) would be a better choice. This momentum cutoff is below the de Broglie and Coulomb cutoffs by factors $(z/n^2)(e^2/\hbar v)\approx 4/n^2$ and $(z-1)(z/n^2)(e^2/\hbar v)^2 \approx 16/n^2$. While the classical path assumption per se is therefore reasonably valid for most lines, Coulomb effects are likely to be important for $n \leq 4$. There is then considerable cancellation in the orbit integrals of the dipole interaction so that $k_m(z) \approx \rho_c^$ should be the effective cutoff, i.e.,

$$
k_m(z) \approx \frac{mv^2}{(z-1)e^2} \tag{14c}
$$

Using the smaller of Eqs. (14b) and (14c) in Eq. (9), one finds that $\Delta n = 0$ dipole contributions to the electron-
collisional shifts of lines from one-electron ions with $z \gtrsim 4$

 $+$

are generally $\leq 10\%$ of the shifts calculated in Ref. 21, which are mostly due to the $\Lambda = 0$ (penetrating monopole) term in the multipole expansion of the electron-ion interaction. Such relatively small $\Delta n = 0$ contributions are certainly insignificant, both theoretically and experimentally.

Returning therefore to ionized helium lines, i.e., to the straight classical path, unitarity, cutoff in Eq. (14a) and to Eq. (11), the appropriate estimate for $\Delta n = 0$ contributions to the electron-collisional shifts of ionized helium lines becomes

$$
d_w = -2 \left[\frac{3m}{\pi k_B T} \right]^{1/2} \left[\frac{\hbar}{m} \right]^2 n (n^2 - l^2 - l - 1)^{1/2} N_e,
$$
\n(15)

if the dipole matrix element is divided by $z = 2$ and the square bracket is replaced by 1. The latter simplification is appropriate, because the quantity k_D/k_m in Eq. (11) scales as z^{-3} at fixed density but assuming $T\sim z^2$, whereas the density scaling is only according to $N_e^{1/2}$.

Shifts calculated from Eq. (15), again multiplied with 1.2 to allow for strong collisions, are listed in Table II, together with the $\Delta n \neq 0$ shifts obtained earlier²³ and with the corresponding total electron-collisional shifts. The increases over the $\Delta n \neq 0$ shifts for the first lines in the three spectral series are by factors of about 1.4, 1.3, and 1.2 for the He II lines corresponding to the Lyman- α , H_{α}, and Paschen- α lines of hydrogen at temperatures near 4×10^4 K, with somewhat smaller increases for higher series members.

The shifts should be very close to linear up to densities of 10^{18} cm⁻³, judging by the analogy to the two H_a calculations presented in Table I and the scaling of the ratio of k_D / k_m discussed above. However, the fine-structure splitting neglected here and in Refs. 23 and 26 could be very important, e.g., for the lines analogous to Lyman- α and Lyman- β , and also for HeII H_a, even at densities well in excess of 10^{17} cm⁻³. Such fine-structure effects, together with some other possible shift contributions, will be discussed when comparing measured and calculated shifts in Sec. V. However, one possibly large contribution must already be mentioned here, namely, the firstorder static contribution caused by the excess negative charge in the vicinity of an ion (plasma polarization), if one includes the long-range Coulomb interaction in the perturber Hamiltonian.¹ The corresponding zeroth-order electron distribution function is spherically symmetric. Therefore the first-order static shift according to Eq. (2.12) of Ref. 26 would arise only from the $\Lambda = 0$ (penetrating) monopole term in the multipole expansion of the interaction Hamiltonian. This term could be quite large by itself, giving an additional red shift, but should not be used without the penetrating monopole contributions to the dynamical shift. As discussed above, for $He⁺$ these contributions come from very close collisions and therefore require (future) calculations to all orders which, more likely than not, will show that shifts from such collisions and higher-order static shifts nearly cancel the first-order static shift. However, any net contribution may well be large enough to affect the correction factor

1.2 which would probably be relatively large for small principal quantum numbers and low temperatures.

V. COMPARISON WITH MEASURED SHIFTS

The question naturally arises whether inclusion of the $\Delta n = 0$ contribution to the electron-collisional shifts improves the agreement between measured shifts of optically thin lines with theory, relative to the comparisons made in Refs. 23 and 24 and including recent measurements. To within the accuracy of all the experiments in which shifts were measured as a function of electron density and certainly also of the various calculations in the present and preceding papers, these shifts are linear in density and will therefore be scaled to a nominal density of 10^{17} cm⁻³. (Only for H_a, some comparisons will be made at $N_e = 10^{18}$ cm⁻³.) However, for hydrogen the temperature dependence of the electron-collisional shifts will be allowed for by interpolation or extrapolation of the calculated values listed in Table I. For ionized helium, $T=4\times 10^4$ K will be assumed, both because the total electron-collisional shifts according to Table II are only very weakly dependent on temperature and because the temperatures in the experiments may be less accurate than those in the hydrogen experiments.

The comparison for hydrogen lines is presented in Table III. Except for Lyman- α and Lyman- β , one notes that calculated shifts are consistent with the experiment. (For Lyman- α and H_{α}, fine-structure splittings are \sim 0.005 and 0.14 Å, respectively, i.e., not at all negligible.) In case of Lyman- β , the estimated experimental¹¹

error is $\pm 50\%$, and after the calculated value $\Delta\lambda_{\text{theor}}$ is corrected for asymmetries from quadratic Stark effects and other sources³¹ (see Appendix) the upper limit of the measurement of \sim 8 mÅ still falls short of the calculated value of 13 mA.

For the Balmer series, more experiments are available, especially for H_{α} . Also in this case, the measured shifts tend to be smaller than calculated, as for Lyman- β . However, the various measurements do deviate from each other by as much as a factor of 2, which can probably not be explained in terms of temperature or residual density dependencies. Compared to these deviations, the additional asymmetry corrections are negligible. The average of the ratio of (corrected) calculated and measured shifts is \sim 1.17 (or 1.06 if the measurement¹⁰ giving the largest deviation is omitted). For the H_{α} line, inclusion of the $\Delta n = 0$ electron-collisional shift therefore seems to improve the agreement that would be obtained without this contribution. (The average factors would be ~ 0.87 or 0.78 in this case.) However, any firm conclusion would be premature, not only in view of experimental errors but also because of theoretical errors associated with the unitarized perturbation theory. For example, if one had not used the factor 1.2 to allow for shifts caused by strong collisions, the average factors would be 0.92, or 0.84 without Ref. 10. The ion-quadrupole shifts and other asymmetry corrections are relatively small for H_{α} , so that the latter comparison could indeed suggest that omission of the factor 1.2 might be better.

For the H_{β} and H_{ν} lines, ion-quadrupole shifts and other asymmetry effects are much more important than

TABLE III. Comparison of measured and calculated wavelength shifts of hydrogen lines at ^a nominal electron density of 10' cm⁻³, $\Delta \lambda_{exp}$ and $\Delta \lambda_{there} = \Delta \lambda_{el} + \Delta \lambda_{QP}$, with $\Delta \lambda_{el}$ being the total shift caused by electrons, $\Delta \lambda_{QP}$ the ion quadrupole shift. A calculate value corrected also for quadratic Stark effects $\Delta\lambda_{OS}$ and other profile asymmetries $\Delta\lambda_{TR}$ is given in parentheses (see text).

$\Delta\lambda$ (Å)											
Expt. ^a	Line	$T(10^4 \text{ K})$	$\Delta\lambda_{\rm expt}$	$\Delta \lambda_{\rm theor}$	$\Delta\lambda_{\rm el}$	$\Delta\lambda_{\rm OP}$	$\Delta\lambda_{\rm OS}$	$\Delta\lambda_{\text{TR}}$			
12	Lyman- α	1.5	0.003	0.006(0.006)	0.007	-0.001	-1.5×10^{-5}	1×10^{-6}			
11	Lyman- β	1.6	0.005	0.013(0.013)	0.016	-0.003	-5×10^{-4}	5×10^{-4}			
5	H_{α}	1.3	0.57								
6	H_{α}	1.3	0.43	0.54(0.52)	0.645^{b}	-0.107	-0.012	-0.008			
8	H_{α}	1.2	0.52								
10	H_{α}	1.9	0.31	0.57(0.53)	0.675 ^c						
9	H_{α}	2.5	0.43	0.59(0.55)	0.694 ^d	-0.107	-0.026°	-0.014°			
	H_{α}	>4.0	0.64	0.63(0.59)	0.734 ^f						
	H_{β}	1.3	0.70		1.025^{b}	-0.239	-0.063	-0.192			
17 ^b	H_{β}	1.3	0.82	0.79(0.54)							
5	H_{ν}	1.3	0.85		1.77 ^b	-0.69	-0.16	-0.29			
17 ^b	H_{ν}	1.3	0.68	1.08(0.63)							

^aThe experiments are numbered according to the references.

 b Using the mean of the values for 10 500 and 15 800 K.

^cUsing 0.103 times the value calculated for 15 800 K, 10^{18} cm⁻³.

Using a factor 0.106 to extrapolate from Table I.

^eUsing 0.1 times the value calculated for $N_e = 10^{18}$ cm⁻³.

'Using a factor 0.112 for the extrapolation to higher temperatures.

for H_{α} . Their accuracy must therefore also be questioned, especially at densities below 10^{17} cm⁻³ and nearthe line centers, where some errors are known to arise from the quasistatic approximation used to calculate $\Delta\lambda_{\text{OP}}$ in Ref. 24 and $\Delta\lambda_{\text{OS}}$ and $\Delta\lambda_{\text{TR}}$ in the Appendix of the present paper. A future calculation of ion-produced shifts allowing for ion dynamics will probably result in smaller asymmetry corrections, say, halfway between the two $\Delta\lambda_{\text{theor}}$ values in Table III. In that event, it would appear that measured shifts of H_β are larger than calculated values, but probably only by a factor of \sim 1.2, after ion dynamics is allowed for, while H_{γ} may turn out to have a correspondingly smaller shift than suggested by the mean of the two calculated values, ~ 0.86 Å. (There are, of course, also ion dynamical effects for H_{α} , not to mention the Lyman lines.) Omitting the $\Delta n = 0$ electron-collisional shift would cause up to factor \sim 2 discrepancies for H_{β} and H_{γ} .

Summing up, it seems that the present calculations are usually well within a factor \sim 1.5 of measured shifts of hydrogen Balmer lines and that the electron-produced shifts may be within $\sim 20\%$ of their true values, in spite of the use of perturbation theory and the linear dependence on the cutoff momentum or strong collision impact parameter. However, more accurate measurements and calculations are required to confirm these conclusions and to reach an accuracy of $\sim 10\%$. Still, on the average, over all Balmer lines, and using the theoretical values corrected for all asymmetries, the ratios of measured and calculated shifts are 1.11 or 1.06 without Ref. 10. Without the $\Delta n = 0$ contributions, these ratios are 1.7 or 1.6, respectively.

For ionized helium experimental data obtained at the National Bureau of Standards are listed in Table IV, together with the present calculations and the various asymmetry corrections. For the Paschen lines, the agreement is within quoted experimental errors, except for the more recent measurement of Paschen- α , where the measured value^{17(a)} is a factor \sim 1.8 below the calculations, strikingly similar to the situation with respect to the more recent measurement¹⁰ of the H_a line of hydrogen. Such a low measured value has now also been reported³² at significantly larger temperatures by factors ²—3. (See Ref. 32 for a summary of previous measurements of this line.) Calculated shifts are expected to be smaller at these higher temperatures, but not by more than \sim 20%, which would leave a factor \sim 1.4 disagreement. Some of this may be due to experimental errors which appear to be as large as $\pm 50\%$, judging by the differences between various measurements. At least some of the experiments may also have suffered from unresolved impurity lines on the blue side of the line profiles, 33 which would then give the appearance of a small blue shift.

If one takes the mean value of the Paschen- α shifts in Table IV, the agreement with experiment is again distinctly improved by including the $\Delta n = 0$ electroncollisional shifts, from an average experiment-theory factor of about 1.4 to 1.0. Whether or not this improvement is significant depends on the resolution of the discrepancy between the Paschen- α measurements and on a verification of our assumptions regarding the first-order static shift and the higher-order penetrating monopole contributions. Should these assumptions be sustained, one could conclude that the electron-shift calculations, including the $\Delta n = 0$ term and the factor 1.2 for the effects of strong collisions, have $\sim 20\%$ accuracy also for these ionized helium lines. ects of strong collisions, have \sim 20% accuracy also for
ese ionized helium lines.
For the H_a line of He II, the measured shift^{17(a)} is

larger than the calculated shift by a factor \sim 2.5, or \sim 2 if comparison is made with an earlier measurement which gave a 17-mÅ red shift instead of the 24-mÅ one which gave a 17-mA red shift instead of the 24-mA one
from the probably more accurate measurement of Pitt-
man and Fleurier.^{17(a)} However, these disagreements man and Fleurier.^{17(a)} However, these disagreements may be mostly due to the large fine-structure splitting of \sim 140 mÅ, which was neglected in the calculations. Especially for the lower level of the line, fine-structure splitting and Stark shifts in typical electric microfields are spiriting and stark similar typical electric interollents are
actually of the same order. According to Lüders, 35 the major effect for so-called unshifted components appears to be a somewhat diminished fine structure, i.e., increas in $2p_{1/2}$ level energies by about $\frac{1}{3}$ of the field-free fine structure (see Fig. ¹ of Ref. 35). Only detailed calculations could show whether the corresponding red shift of \sim 50 mÅ would not be reduced by too much of a factor to let this explanation stand. There will have to be dynamical calculations also for ions because of the relatively small width of this line near $N_e = 10^{17}$ cm⁻³. Equally desirable are measurements at sufficiently high densities, such that both fine-structure and ion-dynamical effects would become small.

A recent z-pinch experiment³⁶ has extended the density range to -2×10^{18} cm⁻³, giving shifts equivalent to 5 to 20 mÅ at $N_e = 10^{17}$ cm⁻³ for the H_a line of He II, against \sim 10 mÅ from the present calculations. However, the shift reported for H_β is equivalent to \sim 35 mÅ at $N_e = 10^{17}$ cm⁻³, and therefore larger than the calculate electron-collisional shift, which is about 20 mA (see Table II), from which ¹ or 2 mA should still be subtracted to allow for ion quadrupole effects.

VI. CONCLUSIONS

The overall conclusion of this work is that measured and calculated shifts of hydrogen and ionized helium lines generally agree to within a factor \sim 1.5 with each other, provided the densities are high enough that finestructure and ion-dynamical effects can indeed be neglected. It is possible that, as more accurate experiments become available, the factor of agreement would become \sim 1.2, which would then indicate that second-order perturbation theory is better than one might expect from the strong dependence on the corresponding cutoff momentum.

The inclusion of $\Delta n = 0$ electron-collisional shifts gave greatly improved agreement between measurements and calculations for both hydrogen and ionized helium lines. However, important questions remain regarding strong collision effects in both cases, and on the first-order static shift for ionized helium lines.

Finally, estimates of $\Delta n = 0$ electron-collisional shifts for higher $(z \ge 4)$ members of the one-electron isoelectronic sequence suggest that they are negligible compared with the then dominant $\Lambda=0$ penetrating monopole interaction effects.

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APPENDIX

Although quadrupole interactions with ions cause profile asymmetries of order $1/r³$, where r is the separation of the nearest perturbing ion from the radiator, quadratic Stark effects, i.e., terms of order $1/r⁴$, are not necessarily negligible. Corresponding corrections, $\Delta\lambda_{OS}$, to the calculated line shifts will be estimated here together with shifts $\Delta\lambda_{TR}$ associated with actual variations of factors in the line profile expression which are assumed constant in most calculations.

Quadratic Stark effects, together with the usual linear Stark effect, yield frequency displacements

$$
\omega = CF - QF^2
$$
 (A1)

for a given (static) fieldstrength F . The coefficients C and Q are constants for a given component, and any subtle effects on their magnitudes associated with the field gradients (quadrupole interactions) will be neglected. The quasistatic line shape is then

$$
L(\omega) = W(F) | dF / d\omega |
$$
 (A2)

and its first moment

$$
\overline{\omega}(\omega') = \int_{-\omega'}^{\omega'} L(\omega) d\omega = \int \omega W(F) |dF/d\omega| d\omega , \qquad (A3)
$$

with the fieldstrength distribution function $W(F)$. On the average over positive and negative values of C , the integral turns out to be proportional to Q , but before evaluating it, changes in relative intensities due to $\Delta n \neq 0$ interactions should also be considered, because these contribute to the same order as the terms proportional to Q.

These intensity changes arise from the first-order wave-function corrections, i.e., from

$$
| n \rangle \rightarrow | n \rangle + \sum_{n'} | n' \rangle \frac{\langle n' | z | n \rangle}{E_n - E_{n'}} eF , \qquad (A4)
$$

where n and n' designate all three quantum numbers and E_n and $E_{n'}$ the unperturbed energies. Also, F is as usual assumed to be in the z direction. Including a corresponding correction, the quasistatic line shape and its first frequency moment become

$$
L(\omega) = W(F)(1 + AF) |dF/d\omega|
$$
 (A2')

and

$$
\overline{\omega}(\omega') = \int_{-\omega'}^{\omega'} \omega(1 + AF)W(F) | dF/d\omega | d\omega , \quad (A3')
$$

with the asymmetry coefficient

$$
A = 2e \sum_{n'} \frac{r_{\ln'}}{r_{\ln}} \frac{\langle n' | z | n \rangle}{E_n - E_{n'}} , \qquad (A5)
$$

if perturbations of the lower level l of the line are neglected and AF is assumed to be small. The quantities r_{ln} and $r_{\rm in}$ correspond to radial matrix elements between unperturbed wave functions, and the factor 2 arises because intensities are quadratic in these matrix elements.

The frequency interval in Eq. (A3) should remain approximately symmetrical in order to simulate experimental shift definitions. Instead of upper limits for the fieldstrength integral, i.e.,

$$
F' = \left(\omega'/C\right) \,,\tag{A6}
$$

one should therefore use $F' + \Delta F'$ defined by

$$
C(F' + \Delta F') - Q(F')^2 = CF'
$$
 (A7)

in the leading term of Eq. (A3'), which does not contain Q or A. Averaging then the results for the two Stark components of given $|C|$ and only keeping first-order terms in Q and A , the first frequency moment becomes

$$
\overline{\omega} = -(Q - CA) \int_0^F F^2 \omega(F) dF + Q(F')^3 W(F') . \quad (A3'')
$$

Had we used instead of a symmetrical frequency interval nearly equal wing intensities to define the interval, the last term would have to be multiplied by $\frac{4}{5}$.

It would not be very meaningful to evaluate this expression exactly, because octupole terms and also lower multipole terms evaluated in second-order perturbation theory actually contribute to the same order in an expansion in inverse powers of the radiator-perturber separation $r³⁷$ It seems unlikely that these omissions would cause large errors in the $1/r⁴$ terms estimated here, but they certainly suggest further simplifications of the coefficients, notably of

$$
Q - CA = \frac{e^2}{\hbar} \sum \frac{1}{E_{n'} - E_n} \left[\langle n' | z | n \rangle^2 + 2 \frac{r_{\text{ln}'}}{r_{\text{ln}}} \langle n' | z | n \rangle \right]
$$

$$
\times \langle n | z | n \rangle \right]. \quad (A8)
$$

As far as the magnitude of the second term is concerned, it should typically be about half as large as the first term, see, e.g., Eqs. (65) and (66) of Ref. 1. However, its sign is negative, because $n' = n + 1$ dominates, so that compare to the nth radial wave function there is an additional node, causing $\langle n+1 | z | n \rangle \langle n | z | n \rangle$ to be negative.³⁸ Using such an estimate we obtain

$$
\overline{\omega} \approx -\frac{1}{2} Q \int_0^{F'} F^2 W(F) dF + Q(F')^3 W(F') , \qquad (A3''')
$$

with³⁹

$$
Q \approx \frac{n^6}{\hbar z^4} a_0^3 \tag{A9}
$$

where z is the nuclear charge.

Using for simplicity Holtsmark distribution functions for $F = \beta F_0$ with an upper limit $\beta' = 2.5$ to model shift

TABLE IV. Comparison of measured and calculated wavelength shifts of ionized-helium lines at a nominal electron density of 10^{17} cm⁻³. The notation is as in Table III.

$\Delta\lambda$ (mÅ) _a												
Expt. ^a	Line	$\Delta\lambda_{\rm expt}$	$\Delta\lambda_{\rm theor}$	$\Delta\lambda_{\rm el}$	$\Delta\lambda_{\rm OP}$	$\Delta \lambda_{\rm OS}^{\rm b}$	$\Delta\lambda_{TR}^{\nu}$					
17 ^{a,b}	H_{α}	24	9.5(9.4)	11.2	-1.7	-0.05	-0.004					
17 ^a	Paschen- α	105		214	-23	-3	-1					
17 ^b 18	Paschen- α	170 ^c	191 (187)									
17 ^b 18	Paschen- β	240°	212 (190)	260	-48	-8	-14					
$17,^{\rm b}18$	Paschen- γ	250 ^c	262 (231)	371	-109	-15	-16^{d}					

'The experiments are numbered according to the references.

Using asymmetry corrections calculated between $\frac{1}{2}$ of maximum intensity points rather than betwee $\frac{1}{4}$ intensity points as in case of hydrogen lines.

^cAverage values with estimated experimental errors of \sim 30, 40, and 60 mÅ, for the α , β , and γ lines.

^dEstimated using the same width parameter as for the Paschen- β line.

definitions in the experiments, the quantities $\Delta\lambda_{\text{QS}}$ contained in Tables III and IV were thus, for shifted components, calculated from

$$
\Delta\lambda_{\text{QS}}^S = -10^{-8} \frac{\lambda^2}{2\pi c} \overline{\omega}
$$

= $10^{-8} \frac{\lambda^2}{2\pi c} \frac{n^6}{\hbar z^4} a_0^3 F_0^2$

$$
\times \left[\frac{1}{2} \int_0^\beta \beta^2 H(\beta) d\beta - (\beta')^3 H(\beta') \right], \quad (A10)
$$

where $H(\beta)$ is the Holtsmark distribution. The expression in large parentheses is not very sensitive to the upper limit of the integral. The value $(\cdots)=-1.5$ would be $(\cdots)=-1.75$ if we chose $\beta'=3.5$ instead of $\beta'=2.5$, corresponding to an additional factor-of-2 decrease in the relative line intensity. For the alternative interval definition, the values in large parentheses are -1.1 or -1.2 , respectively.

For unshifted components the above estimate cannot be used, because it was predicated on having the linear Stark effect as the leading term. Another difficulty is the breakdown of the quasistatic approximation in the central profile region, which cannot be ignored here. For most of the lines and conditions in Tables III and IV, a better point of departure is the ion-impact approximation [see, e.g., Eq. (263) of Ref. I], which yields in the notation of the present paper,

$$
\overline{\omega} = -11.3N(Qe^2)^{2/3} \left[\frac{k_B T}{M'} \right]^{1/6}, \tag{A11}
$$

M' being the reduced radiator-perturber mass. The corresponding wavelength shifts are so small that, except for Lyman- α , they do not contribute significantly to the $\Delta\lambda_{\rm OS}$ values in the tables, which are the weighted averages of shifts of shifted and unshifted components, using the corresponding oscillator strengths as weight factors. Any deviations from the impact approximation would increase the quadratic Stark shifts of the unshifted components, e.g., according to Fig. (12) of Ref. ¹ by as much as a factor 1.5 for the H_v line. Even this increased shift

would not change $\Delta\lambda_{\text{QS}}$ from the -0.16-Å value estimat ed here, using -1.2 for the term in large parentheses in Eq. (A10). In any case, the $\Delta\lambda_{OS}$ should only be viewed as, say, factor \sim 2 estimates. Fortunately, they are negligibly small for most lines, except for H_y, where $\Delta\lambda_{OS}$ is \sim 15% of the net calculated shift without the correction discussed here.

Corrections of the same order are to be expected from asymmetries due to a number of trivial causes.³¹ According to Eq. (4-96) of this reference, the profile correction factor to be applied to the conventional profile expression 1s

$$
C = 1 - \left| 6 - \frac{\hbar \omega_0}{k_B T} \right| \frac{\Delta \lambda}{\lambda} = 1 - a \frac{\Delta \lambda}{\lambda} , \qquad (A12)
$$

where $\hbar \omega_0$ is the unperturbed photon energy. The corresponding term accounts for the variation of the Boltzmann factor governing the relative populations of the upper levels of the line. Its use is appropriate only in the quasistatic approximation. We will therefore use only half this term, since corresponding electron effects were already included through the static-shift term in Sec. II. of the term $-6\Delta\lambda/\lambda$, two-thirds are due to the ω dependence of intensities, which is normally neglected. The remaining third comes from a more accurate transformation from frequency to wavelength intervals than the usual approximation d ($\Delta \lambda$) $\approx -(\lambda^2 / 2\pi c) d\omega$.

If the uncorrected profile is $I(\Delta\lambda)$, the mean wavelength shift corresponding to these asymmetries is

$$
\overline{\Delta\lambda} = -\frac{a}{\lambda} \int_{-\Delta\lambda'}^{\Delta\lambda'} \Delta\lambda^2 I(\Delta\lambda) d(\Delta\lambda)
$$

$$
\approx -\frac{2}{\pi} \frac{a}{\lambda} w^2 \left[\frac{\Delta\lambda'}{w} - \tan^{-1} \left(\frac{\Delta\lambda'}{w} \right) \right], \tag{A13}
$$

assuming, for simplicity, a Lorentzian profile $I(\Delta\lambda)$ with a half-width-at-half-maximum width w . Using $\Delta\lambda'/w = \sqrt{3}$ and 1, respectively, for the hydrogen and ionized helium lines and w values corresponding to Tables IIIa and IIIb in Ref. 1, the $\Delta\lambda_{TR}$ values in the last columns of Tables III and IV could then be estimated from Eqs. (A12) and (A13). They, as the $\Delta\lambda_{OS}$ values, scale with density faster than linear, e.g., as $N^{4/3}$ to the extent that w follows the Holtsmark scaling, $w \sim N^{2/3}$. This additional density dependence was allowed for in the comparisons with the H_{α} measurements of Refs. 7, 9, and 10, but could be safely ignored in the other cases. Finally, since the temperature-dependent term in Eq. (A12) is small, $T = 1.3 \times 10^4$ K was used for most hydrogen lines,

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