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Stark-Effect Broadening of Hydrogen Lines

II. Observable Profiles

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The hydrogen-line profiles previously derived for the case of single encounters are integrated over all encounters to yield the observable profiles. The encounters are assumed to be uniformly distributed over different distances of closest approach, and the ions are assumed to have a Maxwellian velocity distribution. Approximation functions allow the integration to be carried through with rigor in the two limiting cases of very fast and very slow encounters, and with a probable error not exceeding ten percent in the more general case. The resultant profiles illustrate quantitatively Margenau's effect—the transition from impact to statistical broadening with increasing line width. The effect of fast electron encounters is shown to be negligible, in general, in comparison with the effect produced by an equal density of slowly moving ions. An evaluation is made of the error produced by the neglect of the inhomogeneity of the ionic field. The final formulas have a probable error of less than 12 percent for most cases of astrophysical interest.

THE perturbations which a passing ion produces on a hydrogen atom have recently been investigated by the author.[1] The profile of a line emitted by an atom so perturbed has been derived on the assumptions that the field of the ion is homogeneous and that the motion of the ion is uniform and rectilinear. The results of I may be conveniently summarized as follows. Let $J(x)$ be the intensity of emitted radiation as a function of x, where x equals $2\pi(\nu-\nu_0)$, and is simply the distance in angular frequency units from the line center ν_0. Let Γ be the radiative damping constant for the transition in question, and let $\pi\delta$ be the total phase shift produced by the encounter. When x is much greater than Γ, formula (20-I) is valid, provided that $f_\sigma(\xi)$ is substituted for $f_\delta(\xi)$ in accordance with Sections 2 and 3 of I; thus we have

$$J(x)=\frac{\Gamma}{2\pi x^2}\left\{1+\frac{\Omega(\delta,\,\xi)}{\Gamma}\delta^2 f_\sigma{}^2(\xi)\right\}, \tag{1}$$

where

$$\delta=q/\hbar vR, \tag{2}$$

$$\sigma^2=1+\delta^2,\quad \xi=xR/v, \tag{3}$$

and $\Omega(\delta,\xi)$ is the number of collisions per second for a particular δ and ξ; v is the velocity of the ion relative to the hydrogen atom, and R is the distance of closest approach between the ion and the atom. The function $f_\sigma(\xi)$ is defined by (21-I), and is represented graphically by Fig. 1 in I. It is evident from this figure that if σ is much greater than unity, $f_\sigma(\xi)$ is given by the statistical formula (30-I) derived for infinitely slow encounters. When δ is less than unity, σ is substantially unity and $f_\sigma(\xi)$ approaches the known limiting curve $f_1(\xi)$ given in (28a-I).

Strictly speaking, we have proved (1) only for the two limiting cases of δ large and δ small. The discussion of the lowest Lyman line given in Section 2 of I validates the functional form of (1), however, and it seems reasonable to expect that this formula is substantially correct for intermediate values of δ in other cases as well.

The above formulation assumes that all encounters are characterized by the same values of δ and ξ. In the more general case we must integrate (1) over all possible collisions to find the profile of a line emitted by a hydrogen atom in an assembly of ions. The actually observed line contour will be the same as this theoretical "observable profile" only when the emission takes place from a thin film and self-absorption is therefore negligible. This integration is carried out in Section 1 below. In Section 2 the results are qualitatively discussed and their range of validity is investigated.

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The integration of (1) over all possible values of δ and ξ may be regarded as an integration over R and v. If we let $\Omega_m'(R,v)dRdv$ be the

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[1] L. Spitzer, Jr., Phys. Rev. 55, 699 (1939), hereafter referred to as I.

number of times per second that a single hydrogen atom encounters an ion of mass M_m, of charge $Z_m e$, with a relative velocity between v and $v+dv$, and with a distance of closest approach between R and $R+dR$, then (1) becomes

$$J(x)=\frac{\Gamma}{2\pi x^2}\left\{1+\frac{1}{\Gamma}\sum_m\int_0^\infty dv\int_0^s \times\Omega_m'(R,v)\delta^2 f_\sigma^2(\xi)dR\right\}, \quad (4)$$

summed over all types of ion. The upper limit of integration over R in (4) is the average distance of the nearest ion of any type and is defined by

$$4\pi s^3/3=1/N, \quad (5)$$

where N is the total number of ions per cm^3. This is perhaps an arbitrary cut-off but represents roughly the fact that encounters such that R is greater than s will in general be completely screened. Fortunately the relevant results depend only logarithmically on this upper limit of integration s. In this way a consideration of successive, isolated, single encounters can be made to provide an adequate approximation to the actual situation.

The lower limit of integration over R has been set equal to zero in (4), although the theory in I breaks down for sufficiently small R, owing to the inhomogeneity of the ionic field, exchange forces, and other phenomena. It seems a better procedure, however, to include an admittedly inaccurate value for the contribution from these close encounters rather than to neglect them entirely. The error introduced from this source is discussed more fully in Section 2 below.

To obtain an explicit formula for $\Omega_m'(R, v)$ in (4) one may assume a Maxwellian velocity distribution for the relative motions of ions and hydrogen atoms. As before, the effect of the perturbation on the ionic motion may be neglected, and the simple geometrical cross section may be used in determining the frequency of collisions. With these two assumptions, $\Omega_m'(R, v)$ becomes

$$\Omega_m'(R,v)=2\pi RvN_m\cdot 4l_m^{\frac{3}{2}}\pi^{-\frac{1}{2}}v^2\exp -l_m v^2, \quad (6)$$

where

$$l_m=\frac{1}{2kT}\frac{M_m m_\mathrm{H}}{M_m+m_\mathrm{H}}; \quad (7)$$

m_H is the mass of the hydrogen atom, and N_m is the number of mth ions per cm^3.

The substitution of (6) into (4) and the use of (2) for δ yields an explicit integral formula for $J(x)$. This may be simplified by substituting u for $l_m v^2$ and by reintroducing ξ for Rx/v. This gives

$$J(x)=\frac{\Gamma}{2\pi x^2}\left\{1+\frac{4\pi^{\frac{1}{2}}}{\Gamma x^{\frac{1}{2}}}\sum_m\frac{N_m q_m^{\frac{3}{2}}}{\hbar^{\frac{3}{2}}}\gamma_1^{\frac{1}{2}}H_m(x)\right\}, \quad (8)$$

where

$$H_m(x)=\int_0^\infty e^{-u}du\int_0^{\gamma_1/\gamma_2 u^{\frac{1}{2}}} f_\sigma^2(\xi)d\xi/\xi, \quad (9)$$

and from (2) and (3),

$$\sigma^2=1+\gamma_1^2/u^2\xi^2, \quad (10)$$

while by definition we have

$$\gamma_1=q_m l_m x/\hbar, \quad \gamma_2=q_m l_m^{\frac{1}{2}}/\hbar s. \quad (11)$$

The quantity q_m/h is the Stark-effect shift in frequency units which a stationary charge $Z_m e$, placed at unit distance from the hydrogen atom, will produce in the particular component under consideration.

The dimensionless quantities γ_1 and γ_2, from which a subscript m is omitted, have each an important physical significance. For an ion with the most probable relative velocity $l_m^{-\frac{1}{2}}$, γ_1 equals the product $\delta^2 x/x_\mathrm{max}$, where

$$x_\mathrm{max}=q_m/\hbar R^2; \quad (12)$$

x_max is simply the maximum value of x for a given R in the limiting statistical case. Hence if γ_1 is small, δ for most collisions will be greater than unity only if x/x_max is very small. For sufficiently small values of x, $f_\sigma(\xi)$ equals $2\sin(\pi\sigma/2)/\sigma$, as is evident from (21-I), while for larger x δ will be small, if γ_1 is still small, and $f_\sigma(\xi)$ becomes substantially $f_1(\xi)$. If, on the other hand, γ_1 is large, δ will be so great that $f_\sigma^2(\xi)$ is given by the limiting form (30-I) until x/x_max is so large that $f_\sigma(\xi)$ vanishes in any case. Thus for large γ_1 we may expect the usual statistical formula to apply.

It follows from (2) that γ_2 in (11) is the value of δ for an encounter with an ion of velocity $l_m^{-\frac{1}{2}}$ and closest distance of approach s. If this is greater than unity all relevant encounters produce phase shifts greater than unity, since from (2) δ increases as R decreases. We have seen that when σ is much greater than unity, $f_\sigma(\xi)$ approaches the limiting statistical curve $f_\infty(\xi)$. The full statistical theory may therefore be used when γ_2 is large, and the analysis of Holtsmark[2] and Margenau[3] may be applied.

The ratio γ_1/γ_2^2 equals $xs^2\hbar/q$ and is simply the ratio $x/x_{\max}$ when R is equal to s. If all ions have the same charge Ze, this is practically equal to Holtsmark's[2] ratio β, or F/F_n, where F is the electrical intensity whose probability distribution at a point is under consideration, and F_n is a certain normal or average intensity defined by

$$F_n=\{8\pi(2\pi)^{\frac{1}{2}}/15\}^{\frac{2}{3}}ZeN^{\frac{2}{3}}. \tag{13a}$$

If we substitute for N from (5), this gives

$$F_n=\{2(2\pi)^{\frac{1}{2}}/5\}^{\frac{2}{3}}Ze/s^2=1.0018Ze/s^2. \tag{13b}$$

Thus F_n is essentially the field produced by a charge Ze at a distance s; $q/s^2\hbar$ will be the value of x produced by such a stationary charge—see (12)—and hence it follows that β equals $x/x_{\max}$ when R is equal to s. In other words, β is simply the ratio of the line shift x to the shift produced by a stationary ion at the average interionic distance s. This quantity β is of importance below in a comparison of the results of the statistical analysis with those of the more general treatment.

The evaluation of the double integral in (9) to obtain $H_m(x)$ is the central problem of the present analysis and gives directly the observable profile $J(x)$. The indicated integration can apparently not be carried out exactly in terms of known functions, particularly since $f_\sigma(\xi)$ is determined in I only for integral values of σ, and for other values must be found by interpolation. An approximate treatment may be adopted. It is evident from the graph of $\delta f_\delta^2(\xi)$ against $x/x_{\max}$ in I that while this function changes continuously from δ equal to one to δ equal to infinity, the difference between the curve for δ equal to four and that for δ equal to infinity is not very great. On the other hand, for $x/x_{\max}$ small, $f_\sigma(\xi)$ is given more accurately by $f_\sigma(0)$. We may approximate to $f_\sigma(\xi)$, then, in the following manner: when $x/x_{\max}$ is less than $\frac{1}{16}$ we assume

$$f_\sigma(\xi)=f_\sigma(0); \tag{14}$$

when $x/x_{\max}$ is greater than $\frac{1}{16}$, however, we set

$$f_\sigma(\xi)=\begin{cases} f_1(\xi) & 1<\sigma<1.5, \\ f_2(\xi) & 1.5<\sigma<3, \\ f_4(\xi) & 3<\sigma<5, \\ f_\infty(\xi) & 5<\sigma. \end{cases} \tag{15}$$

The choice of $\frac{1}{16}$ as the critical value of $x/x_{\max}$ is somewhat arbitrary. As was shown above, the value of δ at this point will be $4\gamma_1^{\frac{1}{2}}$ for an ion with the relative velocity $l_m^{-\frac{1}{2}}$. If this value of δ is greater than three, the contribution of (14) to (9) will be not greater than four percent of the total, and thus quite negligible. For small γ_1, on the other hand, the transition at $x/x_{\max}$ equal to $\frac{1}{16}$ will take place directly between $f_\sigma^2(0)$ and $f_1^2(\xi)$, and both will be very nearly equal to four, as may be seen from the form of these functions as given in (20) below. The transition in this case is therefore continuous and independent of the particular transitional value of $x/x_{\max}$ chosen.

When β is less than $\frac{1}{16}$, $x/x_{\max}$ is always less than $\frac{1}{16}$ and $f_\sigma(0)$ replaces $f_\sigma(\xi)$ for all u and ξ. In this case the integrals in (9) are independent of x. We shall assume throughout that β is greater than $\frac{1}{16}$ and deduce the results for this other case by taking the limit as β decreases to $\frac{1}{16}$. It is apparently necessary to assume also that γ_2 is considerably less than unity, say less than 0.2. When γ_2 is very small, simultaneous encounters are not very important, and deviations from the statistical assumptions may be considered. When γ_2 is only slightly less than unity, and γ_1 is also less than unity, both effects are important and the present theory breaks down.

With these simplifications the integration in (9) becomes straightforward. We may define

$$L(x, u)=\int_0^\infty f_\sigma^2(\xi)d\xi/\xi; \tag{16}$$

then we find from (9), omitting the subscript m when there is no ambiguity

$$H(x)=H^1(x)-H^2(x), \tag{17}$$

$$H^1(x)=\int_0^\infty e^{-u}L(x, u)du, \tag{18}$$

$$H^2(x)=\int_0^\infty e^{-u}du\int_{\gamma_1/\gamma_2u^{\frac{1}{2}}}^\infty f_\sigma^2(\xi)d\xi/\xi. \tag{19}$$

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[2] J. Holtsmark, Ann. d. Physik **58**, 576 (1919).

[3] H. Margenau, Phys. Rev. **43**, 129 (1933); H. Margenau and W. W. Watson, Rev. Mod. Phys. **8**, 22 (1936).

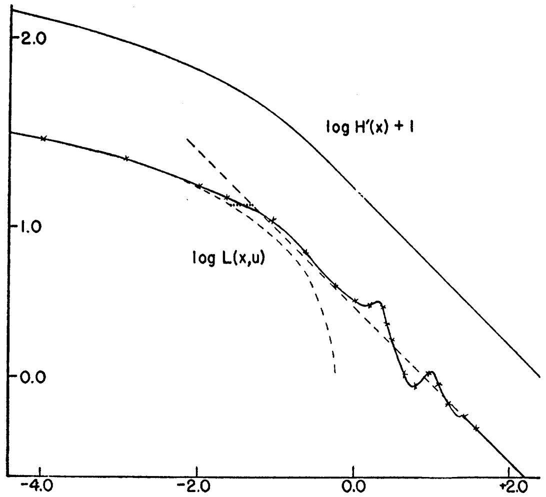

FIG. 1. The lower solid-line curve shows log $L(x, u)$ as a function of log γ_1/u. The two asymptotic forms are shown by the dashed-line curves. The upper curve gives log $H^1(x)+1.00$ as a function of log γ_1. Both ordinates and abscissae are common logarithms.

The functions in (14), (15) and (16) may be obtained from (27-I), (28a-I) and (30-I); we find

$$f_\sigma^2(0)d\xi/\xi=\frac{4\sin^2\pi\sigma/2}{\sigma(\sigma^2-1)}d\sigma, \qquad (20a)$$

$$f_1^2(\xi)d\xi/\xi=4\xi\{K_1^2(\xi)+K_0^2(\xi)\}d\xi, \qquad (20b)$$

$$f_2^2(\xi)d\xi/\xi=2\pi^2\xi e^{-2\xi}d\xi, \qquad (20c)$$

$$f_4^2(\xi)d\xi/\xi=2\pi^2\xi(1-\xi)^2e^{-2\xi}d\xi, \qquad (20d)$$

$$f_\infty^2(\xi)d\xi/\xi=\begin{cases}\dfrac{\pi u^{\frac{1}{2}}}{2\gamma_1^{\frac{1}{2}}}\dfrac{d(x/x_{\max})}{(1-x/x_{\max})^{\frac{1}{2}}} & x/x_{\max}<1,\\ 0 & x/x_{\max}>1.\end{cases} \qquad (20e)$$

These functions have been averaged over positive and negative values of ξ. The resultant profiles must accordingly be summed over all states, independently of the sign of q_m.

The limits implied in (14) and (15) may be expressed in terms of σ and ξ if we use (10) and the formula

$$x/x_{\max}=u\xi^2/\gamma_1, \qquad (21)$$

which may be derived from (3), (11) and (12). If the denominator of (20a) is resolved into partial fractions, the integral can then be evaluated in terms of logarithms and the cosine integral $Ci(x)$, which is tabulated in Jahnke and Emde.[4] The second function integrates directly to $4\xi K_1(\xi)K_0(\xi)$, as may be seen by differentiation and application of the recurrence formulas for Bessel functions. The other integrations are elementary.

The resultant curve for $L(x, u)$ is shown by the lower solid curve in Fig. 1. The two dashed lines are the asymptotic curves,

$$L(x, u)=\pi u^{\frac{1}{2}}/\gamma_1^{\frac{1}{2}} \qquad (22a)$$

for large u, which follows directly from (20e), and the series expansion for small u,

$$L(x, u)=4\ln u/\gamma_1-0.69, \qquad (22b)$$

where ln u/γ_1 denotes the logarithm of u/γ_1 to the base e.

Consideration of the defining integral (16) indicates that the oscillations of $L(x, u)$ shown in Fig. 1 are probably not real, since $f_\sigma^2(\xi)/\xi$ is a function which oscillates from zero through positive values with an amplitude that increases slowly with ξ until finally σ approaches unity and the function decreases monotonically. An increase in γ_1/u will shift any particular zero or maximum of the function to greater ξ but should not produce any rapid oscillations in the integral. The oscillations shown in Fig. 1 can in any case be traced to defects in the approximations (14) and (15) and are produced by the joining of two of the functions used in such a way that both functions have maxima, or both have minima, in their respective ranges.

If, then, we draw a smooth curve through the oscillations of $L(x, u)$ in Fig. 1, we see that the resultant curve follows closely either one or the other of the two asymptotic curves. The two dashed lines, connected by the dotted horizontal line, form an approximation curve whose vertical distance from the curve for $L(x, u)$ never exceeds 0.05 on the logarithmic scale, and which therefore represents $L(x, u)$ with an accuracy of about 12 percent for the short transition region and is of course correct at the two limits.

The connecting horizontal line is defined by

$$L(x, u)=13.80, \quad 0.0520>\gamma_1/u>0.0266. \qquad (23)$$

If this and the two asymptotic curves are

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[4] E. Jahnke and F. Emde, *Tables of Functions* (B. G. Teubner, 1933), p. 78.

integrated over their respective ranges in (18), $H^1(x)$ becomes

$$H^1(x)=\pi^{\frac{3}{2}}\,\mathrm{erf}\,(4.39\gamma_1^{\frac{1}{2}})/2\gamma_1^{\frac{1}{2}}+4Ei(37.4\gamma_1), \qquad (24)$$

where
$$\mathrm{erf}\,(x)=\frac{2}{\pi^{\frac{1}{2}}}\int_0^x \exp\,(-t^2)dt, \qquad (25a)$$

$$Ei(x)=\int_x^\infty \exp\,(-t)dt/t. \qquad (25b)$$

These functions are also tabulated in Jahnke-Emde. When γ_1 is greater than 0.10 or less than 0.03, (24) becomes, respectively,

$$H^1(x)=\pi^{\frac{3}{2}}/2\gamma_1^{\frac{1}{2}}, \qquad (26a)$$

$$H^1(x)=4\ \ln\ 1/\gamma_1-3.02+61\gamma_1, \qquad (26b)$$

with an accuracy better than five percent. This function is shown by the upper curve of Fig. 1 and its values are given in Table I.

To determine $H(x)$ and hence $J(x)$ we must also calculate the correction term $H^2(x)$ given by (19). At the lower limit of integration over ξ in (19), $x/x_{\max}$ and σ are equal to β and to $(1+\gamma_2^2/u)^{\frac{1}{2}}$, respectively, as is evident from (21) and (10). From (14) and (15) it follows that if we take β greater than $\frac{1}{16}$ and γ_2 less than 0.2—the restrictions assumed above—$f_\sigma(\xi)$ will be replaced by $f_1(\xi)$ if u is greater than 0.032. The contribution to (19) from values of u less than 0.032 will be quite negligible, and we may therefore replace $f_\sigma^2(\xi)$ by $f_1^2(\xi)$ for all values of u and ξ in (19).

The indefinite integral over ξ in (19) thus equals $4\xi K_1(\xi)K_0(\xi)$, as we have already seen. This is not a convenient function to integrate over u. If we make the approximation

$$\xi K_1(\xi)K_0(\xi)\approx Ei(\tfrac{1}{2}e^{\frac{1}{2}\pi}\xi)+\tfrac{1}{2}\pi e^{-2\xi}, \qquad (27)$$

where $Ei(x)$ is given in (25b), the functions are equal for large ξ and for small ξ, and differ nowhere by more than six percent. With this approximation, then, we have for (19), integrating the first term by parts,

TABLE I. *$H^1(x)$ as a function of γ_1—formula (24).*

γ_1	$H^1(x)$	γ_1	$H^1(x)$	γ_1	$H^1(x)$
1.00	2.78	0.060	10.0	0.004	19.3
0.75	3.22	.050	10.6	.002	22.1
.50	3.94	.040	11.3	.001	24.7
.25	5.57	.030	12.3	.00075	25.8
.10	8.39	.020	13.6	.00050	27.4
.090	8.7	.010	15.9	.00025	30.2
.080	9.1	.008	16.7	.00010	33.8
.070	9.5	.006	17.8	.00001	43.0

$$H^2(x)=2\{F(1.447\gamma_3)-\pi\gamma_3F'(\gamma_3)\}, \qquad (28)$$

where by definition

$$\gamma_3=4\gamma_1^2/\gamma_2^2, \qquad (29)$$

$$F(z)=\int_0^\infty \exp\,(-zu-u^{-\frac{1}{2}})du/u, \qquad (30)$$

$$-F'(z)=\int_0^\infty \exp\,(-zu-u^{-\frac{1}{2}})du. \qquad (31)$$

Values of $F(\gamma_3)$, $\gamma_3F'(\gamma_3)$, and $H^2(x(\gamma_3))$ are given in Table II. They are calculated from series expansions for small γ_3 and from asymptotic formulas for large γ_3. Intermediate values, for which γ_3 is greater than 0.10, are somewhat uncertain; those for $F(\gamma_3)$ were found by numerical integration in a few cases; those for $\gamma_3F'(\gamma_3)$ were found from the first two differences of $F(\gamma_3)$.

When γ_3 is less than 0.04, we have to within five percent,

$$H^2(x)=4\ \ln\ \gamma_2/\gamma_1-0.688-6.7\gamma_1/\gamma_2. \qquad (32)$$

Combining (17), (26b), and (32) we have, if γ_1 is less than $\gamma_2/10$ and γ_2 is less than 0.2,

$$H(x)=4\ \ln\ 1/\gamma_2-2.33+61\gamma_1+6.7\gamma_1/\gamma_2, \qquad (33)$$

which is accurate to within 10 percent; thus $H(x)$ approaches asymptotically a value independent of γ_1. This asymptotic result holds also for β less than $\frac{1}{16}$, as we have seen above. When γ_1 is large, on the other hand, γ_3 will be even larger, since γ_2 is assumed to be small. For such values, $H^2(x)$ vanishes exponentially and $H(x)$ equals $H^1(x)$, which in this case is given by (26a).

These formulas give the profiles of a single component of a hydrogen line. For comparison with the corresponding result in the statistical case, we change from $J(x)$ to $W(\beta)$, defined by

$$W(\beta)d\beta=J(x)dx. \qquad (34)$$

As we have seen—formula (13b)—β is the ratio of x to the static line shift produced by a stationary ion at a distance s; hence we have

$$\beta=xs^2\hbar/q=\gamma_1/\gamma_2^2, \qquad (35)$$

where we assume for convenience that q is not a function of m; i.e., that all ions have the same charge. From (5), (8), (11), (34) and (35) we find

$$\beta^2 W(\beta)=2J(x)\times x^2 s^2 \hbar/q, \tag{36a}$$

$$=3\pi^{-\frac{3}{2}}\textstyle\sum_m \gamma_2 H_m(x) N_m/N, \tag{36b}$$

where the first term in (8) has been assumed negligible. The right-hand side of (36) has been multiplied by two to make the result comparable with that of the usual statistical treatment, in which $J(x)$ is summed over only half the possible components of a spectral line, since each component will on the statistical theory be displaced wholly to the violet or wholly to the red, in general, depending on the sign of q.

In Fig. 2 is shown the function $\beta^2 W(\beta)$, computed from (36b) for various values of γ_2 on the assumption that only one type of perturbing ion is present. The solid line given for comparison is the statistical curve calculated from Holtsmark's[2] analysis by Verweij.[5] The dashed horizontal lines are the values derived from the Weisskopf[6] formula (22-I),

$$J(x)=\Omega_{1/\pi}/\pi x^2, \tag{37}$$

where $\Omega_{1/\pi}$ is the total number of collisions per second for which δ is less than $\delta_0(R')$, or in this case $1/\pi$. If we integrate $\Omega'(R, v)$ in (6) from zero to R', and determine R' from (2), then we find for (37), after we have integrated over v,

$$J(x)=\frac{2}{\pi^{\frac{1}{2}}}\sum_m \frac{\pi^2 q^2 l_m^{\frac{1}{2}} N_m}{\hbar^2 x^2}, \tag{38}$$

and therefore, from (36a),

$$\beta^2 W(\beta)=3\pi^{\frac{1}{2}}\textstyle\sum_m \gamma_2 N_m/N. \tag{39}$$

This result is simply (36b) with $H_m(x)$ set equal to π^2, a result which may be derived directly from (9), replacing $f_\sigma{}^2(\xi)$ by $2/\delta^2$ and integrating from $\delta=1/\pi$ to $\delta=\infty$. Hence the true asymptotic value of $\beta^2 W(\beta)$ for small β differs from the Weisskopf value as π^2 differs from $4\cdot\ln 1/\gamma_2 - 2.33$, as is evident from (33). This difference vanishes for $\gamma_2=0.047$. The excess of the Weisskopf formula for larger γ_2 is attributable to its neglect of the necessary substitution of $f_\sigma(\xi)$ for $f_\delta(\xi)$ in (1), while the opposite error for smaller γ_2 arises from the neglect, in the Weisskopf analysis, of the more distant collisions. These errors are in opposite directions; and for values of γ_2 between 0.3 and 0.017, the Weisskopf formula gives results for small β that are accurate to within 40 percent.

TABLE II. *$H^2(x)$ as a function of γ_3—formulas* (28) *to* (31)

γ_3	$F(\gamma_3)$	$-\gamma_3 F'(\gamma_3)$	$H^2(x)$
10^{-5}	9.88	0.995	25.1
10^{-4}	7.51	.982	20.5
0.001	5.28	.945	15.8
.010	3.18	.852	11.1
.020	2.62	.802	9.70
.040	2.08	.734	8.24
.060	1.80	.687	7.42
.080	1.61	.649	6.80
.10	1.45	.618	6.38
.20	1.20	.53	5.0
.40	0.71	.44	3.9
.60	.54	.38	3.2
.80	.44	.33	2.7
1.00	.37	.29	2.4
1.20	.31	.26	2.1
1.40	.27	.23	1.8
1.60	.24	.21	1.7
1.80	.22	.20	1.6
2.00	.198	.188	1.46
2.50	.160	.153	1.19
3.00	.136	.137	1.05
4.00	.102	.110	0.82
5.00	.076	.090	.66
6.00	.059	.076	.55
7.00	.048	.064	.46
8.00	.039	.055	.39
9.00	.033	.048	.33
10.0	.027	.042	.29
15.0	.014	.025	.172
20.0	.0084	.0158	.108
40.0	$2.1\cdot 10^{-4}$	.0047	.030
80.0	$3.1\cdot 10^{-5}$	.0010	.006

The profiles of Fig. 2 must now be summed over all components of a given hydrogen line. Let the subscript j denote a particular component. To evaluate the observable profile $J(x)$, or the atomic line absorption coefficient α_ν, one must form the weighted average of $J_j(x)$ over all the components. Combining (8) and (17), we find for $J(x)$, again normalized to unity,

$$J(x)=\frac{1}{2\pi x^2}\left\{\sum_j \Gamma_j \varphi_j + 4\frac{\pi^{\frac{1}{2}}}{x^{\frac{1}{2}}\hbar^{\frac{3}{2}}}\right.$$

$$\left.\times\sum_j \varphi_j \sum_m N_m q_{mj}{}^{\frac{3}{2}} \gamma_1{}^{\frac{1}{2}} (H_{mj}{}^1(x) - H_{mj}{}^2(x))\right\}, \tag{40}$$

where the φ_j are normalized oscillator strengths given by

$$\varphi_j = f_j/\textstyle\sum_j f_j, \tag{41}$$

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[5] S. Verweij, Publ. of the Astron. Inst. of the Univ. of Amst., No. 5 (1936).

[6] V. Weisskopf, Physik. Zeits. **34**, 1 (1933).

and where $H_{mj}^1(x)$ as a function of γ_1, and $H_{mj}^2(x)$ as a function of γ_3 (defined in (29)), are given in (24) and (28), and in Tables I and II, respectively. When γ_1 is less than one, it is convenient to make the substitution in (40)

$$\frac{q_{mj}^{\frac{3}{2}}\gamma_1^{\frac{1}{2}}}{x^{\frac{1}{2}}\hbar^{\frac{3}{2}}}=\frac{q_{mj}^2 l_m^{\frac{1}{2}}}{\hbar^2}, \tag{42}$$

which follows from (11).

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Apart from the physical assumptions made at the beginning of I, formula (40) should have an accuracy considerably greater than that provided by any previous impact theory. Three sets of approximation functions have been used: (14) and (15) for $f_\sigma(\xi)$ in the calculation of $L(x, u)$; (22a), (22b) and (23) for $L(x, u)$ in the calculation of $H^1(x)$; and finally (27) in the computation of $H^2(x)$. The first of these should produce an error in the smoothed $L(x, u)$ of less than 15 percent. The second and third are accurate, as we have already seen, to within 12 percent and 6 percent, respectively. Hence the total mathematical error cannot exceed 33 percent. If we take half the maximum error in each case as the probable error introduced from each source, the total probable error introduced by the mathematical approximations will be equal to or less than 9.7 percent. When γ_1 and γ_3 are both very different from unity, (40) should be accurate to within one or two percent.

The calculated profiles in Fig. 2 show two characteristics. Since a horizontal line represents a dispersion curve profile c/x^2, where c is some constant, the curves of Fig. 2 show in the first place that, as x increases, $J(x)$ changes from c/x^2 to the statistical profile, which in this case is $c'/x^{5/2}$. This transition from impact to statistical broadening was first pointed out on theoretical grounds by Margenau,[7] and has been observed in the laboratory as a transition in the rate of line growth which takes place with increasing pressure. Experimental difficulties have of course prevented a laboratory observation of this effect for the hydrogenic case analyzed here.

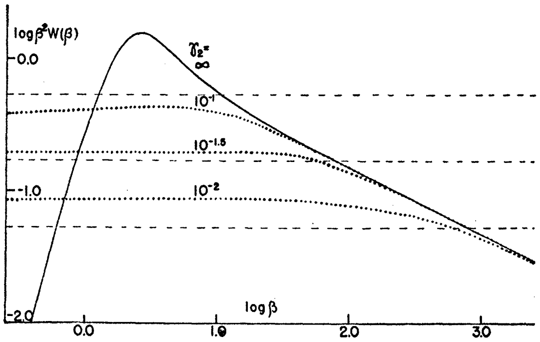

FIG. 2. Profile of a single component of a hydrogen line. Abscissae represent log β, where β is the ratio of $\nu-\nu_0$ to the displacement produced by a stationary ion at the average interionic distance s. Ordinates represent log $\beta^2 W(\beta)$, where $W(\beta)d\beta$ is the probability of finding β in the range $d\beta$. The solid line is the Holtsmark statistical curve, while the dotted lines are calculated from (36b) for various values of γ_2, a quantity which varies inversely with the average ionic velocity. The horizontal dashed lines give the corresponding values of log $\beta^2 W(\beta)$ derived from the Weisskopf impact formula.

In the second place it is immediately evident from Fig. 2 that $J(x)$ decreases with γ_2 and hence decreases as the velocity increases. In an assembly containing equal numbers of electrons and positive ions, the latter are usually moving sufficiently slowly so that their value of γ_2 is greater than unity and their perturbations produce the statistical effect. The electrons may be moving sufficiently rapidly, however, so that their corresponding γ_2 is a very small quantity. Unless x is so large that the statistical formula holds for electrons as well as for positive ions, it follows that the contribution of the electrons to $J(x)$ will be negligible.

It may be noted that, subject again to the restrictions imposed in I, (40) includes all the relevant effects. "Collision broadening," regarded as producing transitions from one quantum level to another, is equivalent, not supplementary, to the above analysis.

The physical simplifications introduced in I may now be re-examined with the above analysis in mind. The assumption of single encounters is an adequate approximation when γ_2 is less than about a fifth. $J(x)$ in this case depends only logarithmically on γ_2, and because of this fact an arbitrary decrease in the effective s does not change the line profile appreciably, but increases γ_2 and eliminates the effect of distant multiple encounters. Multiple encounters at close distances have a negligible probability.

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[7] H. Margenau, reference 3.

A second limitation of the theory is that R must be greater than $10\bar{r}_e$, or $7.91\cdot 10^{-8}n_A^2$, where n_A is the total quantum number of the upper state of the transition in question, and $\bar{r}_e$ denotes the average value of r_e for the state $l=0$, $n=n_A$. This restriction is necessary primarily because of the inhomogeneity of the ionic field. One may find a first approximation to the error introduced by the neglect of this inhomogeneity. Let subscripts e denote electronic coordinates; R, the distance from the ion to the atomic nucleus; and ρ the distance from the electron to the ion; then

$$\rho^2=R^2+r_e^2-2z_eR, \tag{43}$$

where as usual the z_e axis is taken along R. If we let the nuclear charge be Ze, then the perturbing potential energy V is given by

$$V=-\frac{Ze^2}{\rho}=-\frac{Ze^2}{R}\left\{1+\frac{z_e}{R}+\frac{1}{2R^2}(3z_e^2-r_e^2)\cdots\right\}. \tag{44}$$

The term in z_e gives the usual Stark-effect displacement. To evaluate the next term we make use of the fact that it is the levels of large $\bar{z}_e$ that produce the observed line broadening; it is these levels, therefore, in which we are primarily interested. When z_e is large, the average value of r_e^2 is not much greater than the average value of z_e^2, which, in turn, is approximately given by $(\bar{z}_e)^2$. In such a case the perturbing potential (with neglect of the constant term) becomes roughly

$$\bar{V}=-\frac{Ze^2}{R^2}\bar{z}_e\left\{1+\frac{\bar{z}_e}{R}\right\}. \tag{45}$$

Since $\bar{z}_e$ is at most $\bar{r}_e$, the relative error in $\bar{V}$ produced in the most strongly shifted components by the inhomogeneity of the ionic field will be $\bar{r}_e/R$, to this approximation. This correction term will lead to an asymmetrical line, since it is independent of the sign of $\bar{z}_e$. This is reasonable physically, since a very close point charge will depress levels with positive $\bar{z}_e$ more than it will raise those of negative $\bar{z}_e$. When R is less than 3 or 4 times $\bar{r}_e$, this approximation may be expected to break down; higher terms in (44) and the higher order approximations of the perturbation theory will both become important.

To examine more closely the range of validity of the theory, and to clarify the meaning of the quantities used in Section 1, we derive several useful relationships. From (11-I) and (12-I) we see that the Stark-effect frequency shift $\Delta\nu_{AB}$ of a given component produced by a stationary charge Z_me at a distance R is given by

$$\Delta\nu_{AB}=\frac{q_m}{hR^2}=\frac{3\hbar Z_m}{4\pi m_e}\frac{g}{R^2}=\frac{0.275gZ}{R^2}, \tag{46}$$

$$g=n_A(k_{2A}-k_{1A})-n_B(k_{2B}-k_{1B}), \tag{47}$$

where k_1 and k_2 are the quantum numbers for the ξ and η coordinates, respectively. If Z_m is taken to be unity, R is taken as the distance of closest approach, and g is replaced by pn_A^2, where $|p|$ ranges from zero to approximately unity, one finds from (2), (46), (7) and (11) that

$$\delta=\frac{1.73pn_A^2}{vR}=\frac{2.19\cdot 10^8p}{v}\frac{\bar{r}_e}{R}, \tag{48}$$

$$\Delta\lambda_{AB}=1.22\cdot 10^3\left(\frac{\bar{r}_e}{R}\right)^2\frac{pn_B^4}{n_A^2[1-(n_B/n_A)^2]^2}A, \tag{49}$$

$$\gamma_1=2.18\cdot 10^8p\frac{w_m}{T}\frac{\Delta\lambda}{\lambda_0}\left\{\left(\frac{n_A}{n_B}\right)^2-1\right\}, \tag{50a}$$

$$\gamma_2^2=4.74\cdot 10^{-8}p^2\frac{w_m}{T}n_A^4N^{\frac{2}{3}}, \tag{50b}$$

where A denotes angstrom units, T the absolute temperature, and w_m is defined as $M_m/(M_m+m_\mathrm{H})$; for an electron, w_m is $5.4\cdot 10^{-4}$, for a proton it is $\frac{1}{2}$, and for other ions it is practically unity; $2\pi\Delta\nu_{AB}$ is simply $x_{\max}$, $\Delta\lambda_{AB}$ equals $C\Delta\nu_{AB}/\nu_0^2$, and $\Delta\lambda$ equal $cx/2\pi\nu_0^2$. It is clear from (48) that when R is as small as $10\bar{r}_e$, δ will be very large unless v is at least 10^6 cm/sec. This is an observable thermal velocity only in the case of electrons, and for heavy atoms such close encounters will accordingly be adiabatic.

For these adiabatic encounters the statistical theory is valid and the wings of a line will be produced only by very close encounters. In this case $J(x)$ is proportional to $R^2(x)dR/dx$; $4\pi R^2(x)dR$ is the volume of the shell from which a stationary ion produces a Stark-effect shift between x and $x+dx$ in angular frequency units. To a first approximation dR/dx is unchanged by the inhomogeneity, provided that x is held fixed, and hence the relative error in $J(x)$ is simply the relative error in $R^2(x)$ for a known x, or approximately the relative error in x for a given R, since x is approximately inversely proportional to R^2. If we assume that the broadening of the spectral line is produced largely in the upper state of the transition, then it follows from (45) that the correction factor for $J(x)$ in this case is approximately $1\mp\bar{r}_e/R$, where the minus sign goes with positive x and vice versa; this assumes that the wings of the line are produced by the most strongly shifted Stark-effect components.

When R is less than $3\bar{r}_e$ the theory is no longer valid; hence from (49) it is evident that the formulas for $J(x)$ do not apply if $\Delta\lambda_{AB}$ for the Balmer series ($n_B=2$) exceeds $2160/n_A{}^2$ angstroms. If n_A is greater than 7, this upper limit is greater than half the separation between successive lines, and is hence not a serious restriction. For the lower members of the series this limiting shift is greater than is usually observed in stellar spectra.

When electrons are involved, the case is somewhat different. At a temperature of 5000° the electronic velocity is $4\cdot 10^7$ cm/sec., and δ is only $\frac{1}{2}$ when R equals $10\bar{r}_e$. A substantial portion of $L(x, u)$ and of $H(x)$ arises from encounters for which δ is greater than this value; unlike the statistical case discussed above, the inhomogeneity of the ionic field at close distances will therefore affect $J(x)$ even when x is relatively small. A rigorous treatment would be difficult here, but it is not difficult to set an upper limit on the error involved provided that γ_1 is small.

In such a case $L(x, u)$ may be regarded as the sum of two parts—the first comprising all encounters for which δ is greater than some critical value δ_0, which we may take equal to 1, the second including the more distant encounters. The first part follows approximately the Weisskopf formula (37), where now unity replaces $1/\pi$ as the critical value of the phase shift. The second part, which is six times as great as the first provided γ_1 is less than $\frac{1}{3}$, and twenty times as great if γ_1 is less than $1/30$, arises from the more distant encounters, and will be largely unaffected by the inhomogeneity of the perturbing field. The relative error in δ will be $2\bar{r}_e/\pi R$, as we see from (45); the extra factor $2/\pi$ arises from the integration of $\vec{V}(t)$ over t, replacing R by $(v^2t^2+R^2)^{\frac{1}{2}}$ as in I. When R equals $3\bar{r}_e$, this gives a relative error of 21 percent in R, for a fixed δ, and, since the total number of relevant collisions is proportional to R^2, a relative error of 42 percent in the first part of $L(x, u)$. This gives a corresponding error of less than six percent in the sum of both parts, if γ_1 is less than $\frac{1}{3}$. If δ is less than unity when R equals $3\bar{r}_e$, and hence if the temperature exceeds 14,000°, this error must be increased slightly. The relative increase in the error will presumably be less than the relative increase in T, however, and hence if T is as much as 30,000°, the relative error should not exceed 13 percent. As γ_1 increases the error rises until it approaches the corresponding error in the statistical case, which according to (45) may be as much as 30 percent.

One may conclude, then, that (40), supplemented by the Holtsmark-Verweij statistical formula, gives values of $J(x)$ which, if one neglects the inhomogeneity of the ionic field, have a probable error of not more than ten percent and are asymptotically correct, except for the intractable case when γ_2 is approximately between 0.2 and 2 and γ_1 is at the same time less than unity. The inhomogeneity introduces a correction factor for the statistical case; for the impact case—when γ_1 is small—the additional error introduced is less than 13 percent, provided T does not exceed 30,000°. If, as before, we take half the upper limit on the error as the value of the probable error, this gives a total probable error for the impact case of less than 12 percent. When $\Delta\lambda_{AB}$ is greater than $135n_B{}^4/n_A{}^2$ angstroms, the theory breaks down.

One more restriction may be noted. The neglect of the cross-product terms in (16-I) and (1) is legitimate only if x is sufficiently far removed from the line center. It is of course physically obvious that if the line is very much widened by perturbations, the normalized intensity must decrease over a central region whose width may be many times greater than the value of the radiative damping constant Γ.

It is a very real pleasure to record here my indebtedness to the National Research Council for a grant which has made this work possible, and to Dr. Harlow Shapley, Dr. Donald Menzel, and the staff of the Harvard College Observatory for the opportunity to use the facilities of the Observatory and to profit by many informal and informative discussions.