Stark-Effect Broadening of Hydrogen Lines

I. Single Encounters

Lyman Spitzer, Jr.*

Harvard College Observatory, Cambridge, Massachusetts

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The profile of a hydrogen emission line is investigated on the assumption that the hydrogen atom is perturbed by passing ions. Provided that the ions do not approach to within ten times the average atomic radius the electric field of the ion may be assumed homogeneous and the matrix elements calculated for the usual Stark effect may be used. For a collision at low velocity or with close approach, the adiabatic approximation is valid, and the profile depends solely on the total phase shift produced by the collision. The Fourier analysis of the wave train may be carried through exactly for certain values of this phase shift. Nonadiabatic transitions are examined for the lowest lines, and an exact solution given for this case also. For higher lines a modified Born approximation is used. The Weisskopf collision broadening formula is shown to hold only in certain cases, and the dispersion curve smearing function for impact broadening is shown to lead in some instances to incorrect results.

THE theory of pressure broadening has led to rigorous solutions only for very slow encounters. In this limiting case the distribution over frequency of the intensity of an emission line, known as the profile of the line, is given simply by the statistical distribution of the perturbing potential produced by the passing ions. The analysis has been carried through by Holtsmark[1] and by Margenau[2] for various potential laws.

While this "statistical broadening," following Margenau's nomenclature, is on a rigorous theoretical basis, the corresponding "impact broadening" for fast particles has been less thoroughly treated. Investigations have usually followed one of two methods. The Weisskopf[3] method on the one hand assumes that two wave trains separated by a phase shift greater than unity[4] are incoherent, and that twice the mean time between such encounters may be taken as the effective damping constant. As will be shown below, this assumption is formally incorrect for frequencies sufficiently far removed from the line center; in addition it neglects the effect of the more distant

encounters which, in the case of ionic collisions with hydrogen atoms, may be numerically more important. The second method involves smearing the statistical distribution over some kind of impact distribution. This process is legitimate provided the impact distribution can be correctly chosen, but the dispersion curve sometimes used may lead to quite erroneous results. The approximations made by Lenz[5] restrict the validity of his solution to the core of the line.

For the case of a hydrogen atom perturbed by ions it is possible to give a solution for the line profile more nearly exact than any of the previous impact theories. In what follows three assumptions will be made throughout: (1) The matrix elements of the interaction potential between states of different total quantum number may be neglected, and values for the other matrix elements may be computed on the assumption that the atom is in a homogeneous field of strength Ze/r^2, where r is the distance from the nucleus of the atom to the ion. (2) Each collision, or encounter, may be assumed isolated from all the others. (3) The mass of the colliding particle may be taken infinitely large.

The first of these is the only really serious restriction. This corresponds to the assumption of a linear Stark effect, and neglects all exchange forces, quadratic terms in the Stark effect, forces

* National Reseach Fellow.

[1] J. Holtsmark, Ann. d. Physik **58**, 577 (1919).

[2] H. Margenau, Phys. Rev. **43**, 129 (1933); **44**, 931 (1933); H. Margenau and W. W. Watson, Rev. Mod. Phys. **8**, 22 (1936).

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

[4] See, however, H. Kallmann and F. London, Zeits. f. physik. Chemie **B2**, 207 (1929), where $\pi/2$ is taken as the critical phase shift.

[5] W. Lenz, Zeits. f. Physik **80**, 423 (1933).

caused by polarization and the like. More seriously, it neglects the inhomogeneity of the Coulomb field produced by the ion. Even if R, the distance of closest approach between the ion and the atom, is ten times $\bar{r}_e$, the average distance of the electron from the nucleus, the perturbing electric force may deviate from its average value by as much as 20 percent. The assumption of a uniform field is scarcely valid, then, for R less than 10 $\bar{r}_e$; since $\bar{r}_e$ equals at most $3n^2a/2$, where a is the radius of the first Bohr orbit, we may take

$$R > 8.0 \times 10^{-8} n^2,$$

where n is the total quantum number.

At such distances the exchange integrals will be very small and the exchange forces negligible. The quadratic Stark effect is also small at such distances. If the electric field is e/R^2, the ratio of the linear shift $\Delta\nu_1$ to the quadratic shift $\Delta\nu_2$ is given by

$$\frac{\Delta\nu_1}{\Delta\nu_2} = \frac{24n(k_2-k_1)R^2}{n^4[17n^2-3(k_1-k_2)^2-9m^2+19]a^2}$$

if k_2-k_1 is replaced by $n/2$ and m and 19 are neglected,

$$\frac{\Delta\nu_1}{\Delta\nu_2} \approx \frac{3R^2}{4a^2n^4} = \frac{27}{16}\left(\frac{R}{\bar{r}_e}\right)^2 > 150$$

if R is greater than 10 $\bar{r}_e$.

The second assumption simplifies the analysis and is actually not restrictive, as will appear in a second paper to be published shortly. The third assumption neglects both the effect of the perturbation on the motion of the ion relative to the atom and the actual uncertainty of the simultaneous position and motion of the ion. If the ion is an electron, this is, of course, appreciable. The effect of the perturbation is clearly negligible when the Stark shift is only a few angstroms. For the closest encounters, however, for which R equals $8 \times 10^{-8} n^2$, the maximum interaction energy equals the kinetic energy of a particle at a temperature of 1380° $(n-1)/n^3$; but these close encounters are not frequent and do not contribute appreciably to the observed profiles. As to the uncertainty principle, the results of the analysis depend not on v and R separately but on their product $(l+\frac{1}{2})\hbar/m$, where l is the

quantum number for total angular momentum. Since l is a definite constant for each collision the uncertainty principle does not affect the results.

In Section I below the adiabatic wave functions are used in an analysis of the profile of a single component of a hydrogen line when the hydrogen atom is perturbed by a passing ion. Deviations from the adiabatic approximation occur for rapid encounters; these are considered in Section II for the case of the first Lyman lines. In Section III the unperturbed wave functions are used in another determination of the line profile; this corresponds to the Born approximation and, unlike the nonadiabatic analysis in Section II, is applicable to transitions between any two perturbed levels. Integration of the effect of different collisions over all distances and velocities to yield the observable profiles will be the subject of a second paper.

I

A change in potential will be adiabatic and will leave unchanged the quantum state of a system if the change occurs sufficiently slowly. In this case the equation for the line profile may readily be found from the usual Dirac radiation equations as used by Weisskopf and Wigner.[6] We may consider a two-state atom with an upper state A and a lower state B, with energies $E_A(t)$ and $E_B(t)$, respectively. If $H(t)$ is the Hamiltonian operator, $E_A(t)$ and $E_B(t)$ are given by the solutions of the equation

$$H(t)\psi_r(t) = E_r(t)\psi_r(t), \qquad (1)$$

where t is simply a parameter. For the case of a hydrogen atom perturbed by a passing ion, the eigenstates of (1) will be the usual hydrogenic states in parabolic coordinates, rotating so that the z axis is always pointing towards the ion.

Let $a(t)$ denote the probability amplitude of the state in which the electron is in A and there are no photons present. Similarly let $b_\rho(t)$ denote the corresponding amplitude of the state in which the electron is in B and a quantum of frequency ν_ρ has been emitted. If the interaction energy between the photon and the atom is

[6] V. Weisskopf and E. Wigner, Zeits. f. Physik **63**, 54 (1930).

taken as a perturbation, the usual equations for $a(t)$ and $b_\rho(t)$ become

$$i\hbar\, da/dt = E_A(t)a(t) + \sum_\rho j_{AB}{}^{\rho *}b_\rho(t), \qquad (2a)$$

$$i\hbar\, db_\rho/dt = \{E_B(t) + h\nu_\rho\}b_\rho(t) + j_{AB}{}^\rho a(t), \qquad (2b)$$

where $j_{AB}{}^\rho$ is the nondiagonal matrix element of the interaction energy between the light quantum and the atom.

A solution for $a(t)$ may be assumed of the form

$$a(t) = e^{-\frac{1}{2}\Gamma t}\exp\left\{\frac{-i}{\hbar}\int_0^t E_A(\tau)d\tau\right\}, \qquad (3)$$

which is equivalent to the assumption that the sum in (2a) equals $-\frac{1}{2}i\hbar\Gamma a(t)$. Thus $a(0)$ equals unity and $b_\rho(0)$ must vanish. The Γ used here is twice the usual quantity, but is the only reasonable definition in accordance with the usual concept of a damping constant, since the probability that the electron is in A will be given by $|a(t)|^2$, or $\exp -\Gamma t$, from (3). Integrating (2b) for $b_\rho(t)$, and substituting from (3) for $a(t)$, we find

$$b_\rho(t) = -ij_{AB}{}^\rho/\hbar\,\exp\left\{-2\pi i\nu_\rho t - \frac{i}{\hbar}\int_0^t E_B(\tau)d\tau\right\}$$

$$\times\int_0^t e^{-\frac{1}{2}\Gamma T}dT\,\exp\left\{2\pi i\nu_\rho T \qquad (4)\right.$$

$$\left.+\frac{i}{\hbar}\int_0^T (E_B(\tau) - E_A(\tau))d\tau\right\}.$$

The assumption of (3) may be verified by the use of (4) in computing the sum in (2a). The sum becomes essentially a double Fourier integral of $a(t)$ and hence is proportional to $a(t)$.

The line profile $J'(\nu)$ is simply $|b_{\rho(\nu)}(\infty)|^2$, which gives the distribution of emitted light quanta. It is evident from (4) that one obtains $J'(\nu)$ by squaring the absolute value of the Fourier integral of the damped wave train whose instantaneous frequency is $\{E_A(t) - E_B(t)\}/h$. This is the same result as obtained on the classical theory. If $E_B(t)$ is set equal to zero, $J'(\nu)$ is the absolute value squared of the Fourier transform of $a(t)$.

The result may be put in a more convenient notation. Let the unperturbed energies of A and B be E_{A0} and E_{B0}, respectively, and let the unperturbed frequency be $\nu_{AB} = (E_{A0} - E_{B0})/h$. Then let

$$\Delta_A(t) = \{E_A(t) - E_{A0}\}/\hbar, \qquad (5a)$$

$$\Delta_B(t) = \{E_B(t) - E_{B0}\}/\hbar, \qquad (5b)$$

$$x = 2\pi(\nu - \nu_{AB}). \qquad (6)$$

Here x represents the distance in angular frequency units from the unperturbed line center, while Δ_A and Δ_B represent the perturbations to the energy levels, again in angular frequency units. We set $J'(\nu(x))$ equal to $J(x)$ and the square of $|b_\rho(\infty)|$ in (4) becomes in this notation,

$$J(x) = \frac{\Gamma}{2\pi}\left|\int_0^\infty e^{i(x+\frac{1}{2}i\Gamma)T}dT\right.$$

$$\left.\times\exp\left\{-i\int_0^T (\Delta_A(\tau) - \Delta_B(\tau))d\tau\right\}\right|^2, \qquad (7)$$

where the integral over all x of $J(x)dx$ has been normalized to unity.

When states A and B are hydrogenic, we have the formula for the linear Stark effect

$$\Delta_A(t) = 3\hbar n_A(k_{2A} - k_{1A})F/2me, \qquad (8)$$

where n_A is the total quantum number of the Ath state and k_{2A} and k_{1A} are the quantum numbers for the η and ξ coordinates, respectively; F is the electric intensity. If F is produced by an ion of charge Ze at a distance $r(t)$, and if the velocity of the ion is v, its path is a straight line, and its distance of closest approach R is reached at a time t_0, then

$$F = Ze/r^2(t), \qquad (9)$$

$$r^2(t) = R^2 + v^2(t - t_0)^2, \qquad (10)$$

$$\Delta_A(t) - \Delta_B(t) = \frac{q/\hbar}{R^2 + v^2(t - t_0)^2}, \qquad (11)$$

where

$$q/\hbar = 3\hbar gZ/2m = 1.73gZ, \qquad (12)$$

$$g = n_A(k_{2A} - k_{1A}) - n_B(k_{2B} - k_{1B}). \qquad (13)$$

Also we find from (11), on integrating,

$$\int_{t_0}^T \{\Delta_A(\tau) - \Delta_B(\tau)\}d\tau = \frac{q}{\hbar Rv}\tan^{-1}\frac{v(T - t_0)}{R}. \qquad (14)$$

The total phase shift produced in the collision is

thus $\pi q/\hbar R v$. If we set

$$\delta = q/\hbar R v, \qquad (15)$$

and substitute (14) into (7), we find, after integrating by parts, using (11), and assuming that the integral (14) taken from 0 to t_0 is essentially equal to $\frac{1}{2}\pi\delta$,

$$J(x) = \frac{\Gamma}{2\pi} \frac{1}{x^2 + (\frac{1}{2}\Gamma)^2} \left| i - \frac{\delta v}{R} e^{-\frac{1}{2}i\pi\delta} \right.$$ (16)

$$\times \int_0^\infty \frac{e^{i(x+\frac{1}{2}i\Gamma)T} dT \exp\{-i\delta\tan^{-1}v(T-t_0)/R\}}{1+v^2(T-t_0)^2/R^2} \left. \right|^2.$$

The quantity δ is of fundamental importance in the theory and reappears throughout the analysis. It is equal to $1/\pi$ times the total phase shift produced by the encounter. Since v/R is in general much greater than $\frac{1}{2}\Gamma$, a factor $\exp i(x+\frac{1}{2}i\Gamma)t_0$ may be taken outside the integral in (16). Also, unless x is comparable with Γ, the process of averaging over t_0 will remove the cross product when the square of the absolute value is taken in (16). If, furthermore, T is set equal to $\tau+t_0$ and the lower limit of integration is extended from $-t_0$ to $-\infty$, we have

$$J(x) = (\Gamma/2\pi x^2) \left\{ 1 + e^{-\Gamma t_0}\delta^2 v^2/R^2 \right.$$

$$\times \left| \int_{-\infty}^{+\infty} \frac{e^{ix\tau}\exp\{-i\delta\tan^{-1}v\tau/R\}}{1+v^2\tau^2/R^2} d\tau \right|^2 \left. \right\}. \quad (17)$$

The $(\frac{1}{2}\Gamma)^2$ in the denominator of (16) has been neglected in (17) since this latter formula is valid only for x greater than $\frac{1}{2}\Gamma$ in any case. Introducing the new variables

$$u = v\tau/R, \quad \xi = xR/v, \qquad (18), (19)$$

and integrating (17) over t_0, assuming $\Omega(\delta, \xi)$ collisions per second, we have, finally, for a particular δ and ξ,

$$J(x) = \frac{\Gamma}{2\pi x^2} \left\{ 1 + \frac{\Omega(\delta, \xi)}{\Gamma}\delta^2 f_\delta^2(\xi) \right\}, \qquad (20)$$

$$f_\delta(\xi) = \int_{-\infty}^{+\infty} \frac{e^{i(\xi u - \delta\tan^{-1}u)}}{1+u^2} du. \qquad (21)$$

There are several inferences to be drawn from (20) and (21). In the first place $f_\delta(\xi)$ clearly goes to zero with increasing ξ and for sufficiently large
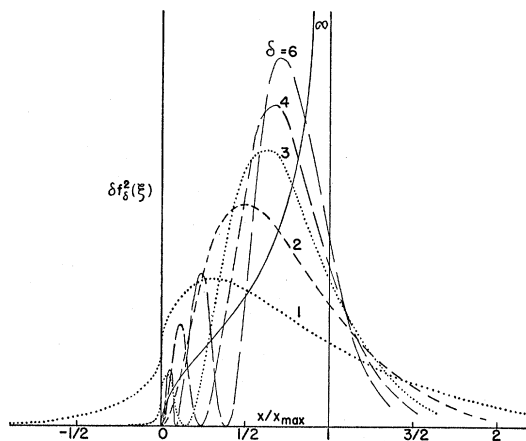

FIG. 1. Line profiles for single encounters. The curves represent $f_\delta^2(\xi)$ for various values of the phase shift $\pi\delta$. Those with odd δ are shown by dotted lines, those with even δ by dashed ones; the solid line represents the statistical distribution; i.e., the limiting case of infinite δ. The abscissae are in units of x/x_{max}, where x is $2\pi(\nu-\nu_{AB})$ and x_{max} is the maximum value of x in the limiting statistical case. The ordinates are proportional to $\{x^2+(\frac{1}{2}\Gamma)^2\}J(x)$, where $J(x)$ is the line profile; the constant of proportionality is adjusted to give equal areas under all the curves.

x the line profile is quite unaffected by the collisions. This is contrary to statements that the effect of collisions with δ greater than some critical value is simply to split the line into noninterfering parts, each with a much greater damping constant. In the second place $\delta f_\delta(0)$ equals 2 sin $(\pi\delta/2)$, as is evident from (21) with the substitution $\tan^{-1}u = \theta$; or, if we average over δ, $\delta^2 f_\delta^2(0)$ equals two. Thus for sufficiently small ξ, Γ is replaced by $2\Omega(\delta, \xi)$, summed over all δ sufficiently large. If $\Omega_{1/\pi}$ is the total number of collisions for which δ is greater than $1/\pi$, or the phase shift is greater than unity, this gives

$$J(x) = \Omega_{1/\pi}/\pi x^2, \qquad (22)$$

which is Weisskopf's[7] result.

For integral values of δ, (21) may be integrated exactly. Using the formula

$$\exp(-i\tan^{-1}u) = (1-iu)/(1+u^2)^{\frac{1}{2}}, \quad (23)$$

and expanding $(1-iu)^\delta$, one finds

$$f_\delta(\xi) = \int_{-\infty}^{+\infty} \frac{e^{iu\xi}du}{(1+u^2)^{1+\frac{1}{2}\delta}}$$

$$\times\left(1-i\delta u+\frac{\delta(\delta-1)(-iu)^2}{2!}\cdots+(-iu)^\delta\right). \quad (24)$$

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[7] V. Weisskopf, reference 3. Compare also reference 4.

If the integral of the first term in (24) is called $g_\delta(\xi)$, then this auxiliary function can be integrated[8] and

$$g_\delta(\xi) = \frac{2^{\frac{1}{2}(1-\delta)}\pi^{\frac{1}{2}}}{\Gamma(1+\frac{1}{2}\delta)}\xi^{\frac{1}{2}(1+\delta)}K_{\frac{1}{2}(1+\delta)}(\xi), \quad (25)$$

where $K_\nu(\xi)$ is the usual Bessel function of the second kind for imaginary argument. In terms of $g_\delta(\xi)$, $f_\delta(\xi)$ becomes

$$f_\delta(\xi) = g_\delta(\xi) \mp \delta\frac{d}{d\xi}g_\delta(\xi) + \frac{\delta(\delta-1)}{2!}\frac{d^2}{d\xi^2}g_\delta(\xi)\cdots, \quad (26)$$

where the minus signs on alternate terms go with positive ξ and vice versa.

When δ is an even positive integer 2α, (26) reduces to

$$f_{2\alpha}(\xi) = 2\pi(-1)^{\alpha-1}\xi e^{-\xi}\,{}_1F_1(1-\alpha, 2, 2\xi) \quad (27)$$

when ξ is positive, and vanishes when ξ is negative. ${}_1F_1(a, b, x)$ is the confluent hypergeometric series. When δ is equal to one and three, respectively, $f_\delta(\xi)$ becomes

$$f_1(\xi) = 2\xi\{K_1(\xi) \pm K_0(\xi)\}, \quad (28a)$$

$$f_3(\xi) = \tfrac{2}{3}\xi\{K_1(\xi)(-1\pm4\xi) + K_0(\xi)(\mp3+4\xi)\}, \quad (28b)$$

where again the upper signs go with positive ξ and vice versa. It is evident from (21) that $f_{-\delta}(\xi)$ equals $f_\delta(-\xi)$.

It is readily shown that the integral of $f_\delta^2(\xi)$ over ξ is independent of δ. From the defining formula (21) and from standard theorems on Fourier transforms it follows that

$$\int_{-\infty}^{+\infty} f_\delta^2(\xi)d\xi = 2\pi\int_{-\infty}^{+\infty}\frac{du}{(1+u^2)^2} = \pi^2. \quad (29)$$

In Fig. 1 $f_\delta^2(\xi)$ is shown for δ equal to 1, 2, 3, 4 and 6, together with the limiting case of infinite δ. The abscissae represent ξ/δ, a quantity which equals $x/x_{\max}$, where $x_{\max}$ is $q/\hbar R^2$; thus $x/x_{\max}$ is the ratio of the observed frequency shift $\nu-\nu_{AB}$ to the maximum frequency shift in the limit $\delta\to\infty$. To preserve equal areas under each curve, the ordinates are taken to represent $\delta f_\delta^2(\xi)$. Except possibly for $f_1^2(\xi)$, none of these curves deviate markedly from the limiting curve $\delta f_\delta^2(\xi)$ as δ approaches infinity. This limit may be derived directly from (21) or more simply from the usual formula for statistical broadening. In this case $J(x)\cdot dx$ is proportional to the time during which the perturbing potential $\Delta_A-\Delta_B$ lies between x and $x+dx$, in angular frequency units; hence $J(x)$ is proportional to dt/dx, where x equals $q/\hbar r^2(t)$, from (11). Therefore we have, using (10),

$$\frac{dx}{dt} = -\frac{2q}{\hbar r^3}\frac{v^2(t-t_0)}{r}.$$

Since furthermore,

$$v^2(t-t_0)^2 = r^2 - R^2 = R^2(x_{\max}/x - 1),$$

we have, taking out an x^{-2}, see (20), and normalizing to π^2 in accordance with (29),

$$\lim_{\delta\to\infty}\delta f_\delta^2(\xi) = 2\pi(x_{\max}/x - 1)^{-\frac{1}{2}}. \quad (30)$$

It will be noted that the curves for $f_\delta^2(\xi)$ all fall off as $\xi^\alpha\exp-2\xi$. Thus if values of $f_\delta^2(\xi)$ are to be obtained from $f_\infty^2(\xi)$, the limit in which the statistical theory is valid, by use of a smearing function of one sort or another, one must use a function that falls off at least as fast as $\xi^\alpha\exp-2\xi$ if the result is to be asymptotically correct. The dispersion curve sometimes used does not satisfy this requirement, since this falls off only as ξ^{-2}. The "block" and triangle functions used by Margenau are better approximations from this standpoint.

It is also possible to determine $J(x)$ from a consideration of the perturbed wave functions for the ion.[9] If the perturbing potentials are proportional to $1/r^2$, the perturbed wave functions are Bessel functions and the problem can be handled exactly, without neglecting the effect of the potential on the motion of the ion. In general the method leads to the little-investigated hypergeometric functions of the second kind and is thus of little use. When $\delta/2$ is an integer α, however, the formulae simplify. If M and l are the mass and orbital quantum number, respectively, of the incident ion, and the perturbing potential is q/r^2 for the upper state, and zero for

[8] G. N. Watson, Theory of Bessel Functions (Cambridge University Press, 1922), Section 6.16, p. 172.

[9] See W. V. Houston, Phys. Rev. 54, 884 (1938). This corresponds to his method 3 as opposed to method 2 used above.

the lower state, $J(x)$ is given by (20); if q is positive (corresponding to δ positive and the perturbing force repulsive) $f_\delta(\xi)$ is given by

$$f_{2\alpha}(\xi) = 2\pi(-1)^{\alpha-1}\left(1 - \frac{2\xi}{l+\frac{1}{2}}\right)^{\frac{1}{2}(l+\frac{1}{2})}$$

$$\times {}_2F_1(1-\alpha, l+\tfrac{3}{2}+\alpha; 2; 2\xi/l+\tfrac{1}{2}), \quad (31)$$

where ${}_2F_1(a, b; c; x)$ is the ordinary hypergeometric series, in this case a terminating polynomial, and where

$$\xi = x\hbar(l+\tfrac{1}{2})/2E_0, \quad (32)$$

and E_0 is the initial or final energy of the ion for an emission or absorption line, respectively; δ is defined in (15). When ξ is negative, $f_{2\alpha}(\xi)$ vanishes. For l large (31) goes over into (27). A similar formula holds when α is negative. If close encounters were sufficiently important it would be possible to investigate by means of these formulas the effect of interaction energies large comparable with the original ionic energy E_0.

II

It is of importance to investigate the limits within which the change of potential is adiabatic and (20) is a valid approximation. Nonadiabatic processes have been investigated by Güttinger[10] and more rigorously by Schwinger[11] for the case of a rotating magnetic field. For a passing ion the analysis is somewhat similar. The perturbations produced by the radiation field will be neglected, since it is evident from (20) that the value of Γ does not affect the shape of the line provided that x is greater than $\frac{1}{2}\Gamma$ but not so great that the collision term $f_\delta^2(\xi)$ in (20) is negligible. Let $a_r(t)$ be the probability amplitude of the rth state, where as before $\psi_r(t)$ satisfies Eq. (1). In the general equation

$$i\hbar\partial\Psi/\partial t = H(t)\Psi, \quad (33)$$

we let

$$\Psi = \Sigma_r a_r(t)\psi_r(t), \quad (34)$$

and find, multiplying through by $\psi_s^*(t)$ and integrating over space,

$$-\frac{da_s}{dt} = i\frac{E_s(t)}{\hbar}a_s(t) + \sum_r k_{sr}a_r(t), \quad (35)$$

[10] P. Güttinger, Zeits. f. Physik 73, 169 (1931).
[11] J. Schwinger, Phys. Rev. 51, 648 (1937).

where

$$k_{sr}(t) = \int \psi_s^*(t)\frac{\partial\psi_r}{\partial t}(t)d\tau; \quad (36)$$

$d\tau$ is an element of volume.

A more convenient expression is available for $k_{sr}(t)$. Differentiation of (1) yields, after rearrangement,

$$\left(\frac{\partial H}{\partial t} - \frac{dE_r}{dt}\right)\psi_r = (E_r(t) - H(t))\frac{\partial\psi_r}{\partial t}. \quad (37)$$

Multiplying by $\psi_s^*(t)$, integrating, and making use of the fact that $H(t)$ is an Hermitian operator and that ψ_s is orthogonal to ψ_r we find, for $s \neq r$,

$$\left(\frac{\partial H}{\partial t}\right)_{sr} = (E_r(t) - E_s(t))k_{sr}. \quad (38)$$

If we neglect states of different total quantum number, k_{ss} vanishes, since ψ_s is not a function of the scalar electric intensity and for any rotation such that the coordinate system does not rotate about its instantaneous z_e axis, where subscripts e refer to electronic coordinates in the perturbed atom, ψ_s will be orthogonal to its rate of change $\partial\psi_s/\partial t$.[12] Eq. (38) thus suffices to determine all relevant k_{sr}.

If the field intensity is again given by (9) and (10), and the ion is assumed to be moving in the $z_e y_e$ plane, where $y_e = (r_e^2 - z_e^2)^{\frac{1}{2}}\cos\varphi_e$, that part of H which varies with time will be $-z_e Ze^2/r^2(t)$, and a simple calculation shows that $\partial H/\partial t$ is given by

$$\frac{\partial H}{\partial t} = \frac{Ze^2 v}{r^4(t)}\{2z_e v(t-t_0) - y_e R\}. \quad (39)$$

Since the matrix of z_e is diagonal for states of the same total quantum number, only the term in y_e need be considered. Combining the formula for $E_s(t)$,

$$E_s(t) = -\frac{Ze^2 z_{ss}}{r^2(t)}, \quad (40)$$

[12] This may be proved as follows: To preserve the normalization of ψ_s independently of t, k_{ss} must be purely imaginary; i.e., $k_{ss}^* = -k_{ss}$. If we take the plane $\varphi_e = 0$ to be the plane in which the ion is moving, this plane will be stationary, and $\partial\psi_s/\partial t$ will have the same symmetry properties with respect to reflection in this plane as ψ_s. Since ψ_s^* is the reflection of ψ_s in this plane, the same relation will hold between $\partial\psi_s/\partial t$ and $\partial\psi_s^*/\partial t$. Hence k_{ss} is unchanged when its complex conjugate is taken, and is purely real. Therefore k_{ss} must vanish.

with (38) and (39) above, we find

$$k_{sr} = \frac{vR}{r^2(t)} \frac{y_{sr}}{z_{rr} - z_{ss}}, \qquad (41)$$

where y_{sr} and z_{ss} are the matrix elements of y_e and z_e, respectively. In formula (40) E_{A0} has been set equal to zero.

If now the variable w is introduced, where

$$\{v^2(t-t_0)^2 + R^2\} dw = vRdt, \qquad (42a)$$

$$w = \tan^{-1} v(t-t_0)/R, \qquad (42b)$$

and if $r^2(t)$ is expressed in terms of $E_s(t)$, from (40), then (35) takes the form

$$\frac{da_s}{dw} + i\delta_{ss}a_s + \sum_{r \neq s} \frac{y_{sr}}{z_{rr} - z_{ss}} a_r = 0, \qquad (43)$$

where δ_{ss} is defined by

$$\delta_{ss} = -Ze^2 z_{ss}/\hbar vR. \qquad (44)$$

Note that for the Lyman lines and for all lines with unperturbed lower states, this is the same quantity as the δ defined in (15).

The set of simultaneous first-order equations in (43) have constant coefficients and may be solved in any finite case. In practice y_{sr} vanishes except between states whose magnetic quantum number m differs by plus or minus one. For the first excited state of hydrogen the solution is not complicated. If the eigenfunctions are denoted by $\psi_{k_1, k_2, m}$, let the states $\psi_{100}, \psi_{001}, \psi_{00-1}$ and ψ_{010} be enumerated as ψ_1, ψ_2, ψ_3 and ψ_4, respectively. Then it follows from the eigenfunctions involved[13] that

$$z_{11} = -z_{44}; \quad z_{22} = z_{33} = 0;$$

$$y_{12} = y_{21} = y_{13} = \cdots = y_{34} = -\tfrac{1}{2}z_{11}. \qquad (45)$$

If δ_{ss} is set equal to δ, (43) becomes

$$da_1/dw + i\delta a_1 + \tfrac{1}{2}(a_2 + a_3) = 0, \qquad (46a)$$

$$da_2/dw - \tfrac{1}{2}(a_1 - a_4) = 0, \qquad (46b)$$

and similarly for a_3 and a_4. If a solution is assumed of the form $\exp i\sigma w$, the determinant of the coefficients of the a_s in (46) must vanish and σ is given by

$$\sigma = 0, \quad \pm(1 + \delta^2)^{\frac{1}{2}}. \qquad (47)$$

[13] H. Bethe, *Handbuch der Physik*, Vol. 24/1, p. 297.

It would be possible to obtain explicit expressions for the transition probabilities, but there is no need to pursue the analysis further. It is shown above and in the work of Houston[9] and Weisskopf[3] that when the upper state of a radiative transition is perturbed in any way, the line profile is given by the absolute value squared of the Fourier transform of the state function. From the nature of the solution above it is evident that there will be three components of the lowest hydrogen line: one an unshifted line with σ equal to zero; the second arises from the state function

$$a(t) = a(t_0) \exp \{i(1+\delta^2)^{\frac{1}{2}} \tan^{-1} v(t-t_0)/R\}, \qquad (48)$$

and the third is the complex conjugate of the second. Comparing these results with the integral in (16) we see that the breakdown of the adiabatic hypothesis affects the form of the line profile in only one way: $f_\delta(\xi)$ in (20) is replaced by $f_\sigma(\xi)$, where the functional form of $f_\sigma(\xi)$ is still defined by (21) and where σ is taken equal to $(1+\delta^2)^{\frac{1}{2}}$—the trivial value zero in (47) may be neglected. The relative intensities of the shifted and the unshifted components are investigated in Section III below, where the approximation is made that δ is small, but where the analysis takes into account the effect of transitions among the various lower states and eliminates the quantities y_{sr}.

III

When the potential changes rapidly with the time it becomes convenient to assume as a first approximation that the change in the atomic wave functions in the course of the collision may be neglected. This corresponds to the Bohr approximation for fast collisions, except that the emphasis here is on the radiation emitted rather than on the electrons scattered. As in the case of the nonadiabatic transitions discussed above, one cannot use directly the integral in (7) for the line profile, but must start afresh from the Dirac radiation equations.

If only the upper states of a radiative transition are perturbed by collisions, the analysis is not involved.[9] The inclusion of perturbation terms in the equations for the lower states, however, introduces complications. Let there be two states A_1 and A_2 with the same unperturbed

energy E_{A0}; let there be two lower states B_1 and B_2 with unperturbed energy E_{B0}. Let the diagonal matrix elements of the perturbing ionic field be $\hbar\Delta_{A1}(t)$, $\hbar\Delta_{A2}(t)$, $\hbar\Delta_{B1}(t)$, and $\hbar\Delta_{B2}(t)$; let the non-diagonal terms be $\hbar K_A(t)$ and $\hbar K_B(t)$. Let the probability coefficient of a radiative transition from A_1 to B_1 per unit time be Γ. As usual $a_1(t)$ and $a_2(t)$ will represent the probability amplitudes of states A_1 and A_2, while $b_{1\rho}(t)$ and $b_{2\rho}(t)$ will represent the corresponding amplitudes for the states in which the electron is in B_1 and B_2, respectively, and a photon of frequency ν_ρ has been emitted. Then if x is again defined by (6), the equations for the derivatives with time of the probability amplitudes become[6]

$$da_1/dt = -i\Delta_{A1}(t)a_1 - iK_A(t)a_2 - \tfrac{1}{2}\Gamma a_1, \quad (49a)$$

$$db_{1\rho}/dt = -i(x + \Delta_{B1}(t))b_{1\rho}$$
$$\qquad\qquad - iK_B(t)b_{2\rho} - ij_{AB}{}^\rho a_1(t), \quad (49b)$$

$$db_{2\rho}/dt = -i(x + \Delta_{B2}(t))b_{2\rho} - iK_B{}^*(t)b_{1\rho}, \quad (49c)$$

where $j_{AB}{}^\rho$ is the matrix element for the radiative transition; its value does not concern us. The equation for $a_2(t)$ is not needed. Except for the terms in K_A and K_B these equations (49) are identical with (2), provided that the notational changes of (5) and (6) are made. If the integral over time of $K_B(t)$ is small, these equations may be solved for $b_{1\rho}$ and $b_{2\rho}$ by successive approximations.

First we have for $a_1(t)$

$$a_1(t) = e^{-\frac{1}{2}\Gamma t}h_1(t), \quad (50)$$

$$h_1(t) = \exp\left(-i\int_0^t \Delta_{A1}(\tau)d\tau\right)$$

$$\times \left\{ h_1(0) - i\int_0^t K_A(T)a_2(T) \right.$$

$$\left. \times \exp\left(i\int_0^T \Delta_{A1}(\tau)d\tau + \tfrac{1}{2}\Gamma T\right)dT \right\}. \quad (51)$$

This satisfies the boundary condition $a_1(0)$ equal to $h_1(0)$. For $b_{1\rho}(t)$ and $b_{2\rho}(t)$ one obtains the integral formulas

$$b_{1\rho}(t) = -ip_1{}^*(t)\int_0^t p_1(T)dT$$

$$\times \{j_{AB}{}^\rho e^{-\frac{1}{2}\Gamma T}h_1(T) + K_B(T)b_{2\rho}(T)\}, \quad (52a)$$

$$b_{2\rho}(t) = -ip_2{}^*(t)\int_0^t p_2(T)dT \cdot K_B{}^*(T)b_{1\rho}(T), \quad (52b)$$

where

$$p_1(t) = \exp\left\{ixt + i\int_0^t \Delta_{B1}(\tau)d\tau\right\}, \quad (53)$$

and similarly for $p_2(t)$.

If now we expand $b_{1\rho}t$ in a series of successive approximations,

$$b_{1\rho}(t) = b_{1\rho}{}^{(0)}(t) + b_{1\rho}{}^{(1)}(t) + b_{1\rho}{}^{(2)}(t)\cdots, \quad (54)$$

and similarly for $b_{2\rho}(t)$, we obtain $b_{1\rho}{}^{(0)}(t)$ from (52a), integrating by parts and neglecting $K_B(t)$. This leads to the formula

$$b_{1\rho}{}^{(0)}(t) = \frac{p_1{}^*(t)j_{AB}{}^\rho}{x + \frac{1}{2}i\Gamma}\left\{ h_1(0) - h_1(t)p_1(t)e^{-\frac{1}{2}\Gamma t} \right.$$

$$\left. + \int_0^t p_1(T)e^{-\frac{1}{2}\Gamma T}\left(\frac{dh_1}{dT} + i\Delta_{B1}h_1(T)\right)dT \right\}, \quad (55)$$

which satisfies the boundary condition $b_{1\rho}(0)$ equal to zero. Substitution of this into (52b) gives $b_{2\rho}{}^{(1)}(t)$. If we neglect all terms that, when squared, contain products or powers of the K's and the Δ's higher than the second, we have

$$b_{2\rho}{}^{(1)}(t) = \frac{-ip_2{}^*(t)j_{AB}{}^\rho}{x + \frac{1}{2}i\Gamma}\left\{ h_1(0)\int_0^t l^*(T)dT \right.$$

$$\left. - \int_0^t p_2(T)e^{-\frac{1}{2}\Gamma T}K_B{}^*(T)h_1(T)dT\cdots \right\}, \quad (56)$$

where by definition

$$l(t) = K_B(t)p_1(t)p_2{}^*(t). \quad (57)$$

Similarly,

$$b_{1\rho}{}^{(2)}(t) = \frac{-p_1{}^*(t)j_{AB}{}^\rho}{x + \frac{1}{2}i\Gamma}h_1(0)$$

$$\times \int_0^t l(\tau)d\tau\int_0^\tau l^*(T)dT + \cdots. \quad (58)$$

Other terms in $b_{1\rho}{}^{(2)}(t)$ are of effectively higher order since their cross products with $b_{1\rho}{}^{(0)}(t)$ vanish on the average. Since $b_{2\rho}{}^{(0)}$, $b_{1\rho}{}^{(1)}$ and $b_{2\rho}{}^{(2)}$ all vanish, we have to the second order of approximation,

$$|b_{1p}(\infty)|^2+|b_{2p}(\infty)|^2=|j_{AB}{}^p|^2/(x^2+(\tfrac{1}{2}\Gamma)^2)$$

$$\Big[\,|h_1(0)|^2\Big\{1+\Big|\int_0^\infty l(T)dT\Big|^2$$

$$-2\Re\int_0^\infty l(\tau)d\tau\int_0^\tau l^*(T)dT\Big\}$$

$$+\Big|\int_0^\infty p_1(T)e^{-\frac{1}{2}\Gamma T}dT\Big\{\frac{dh_1}{dT}+i\Delta_{B1}h_1\Big\}\Big|^2$$

$$+\Big|\int_0^\infty p_2(T)e^{-\frac{1}{2}\Gamma T}dTK_B\ h_1\Big|^2\Big],\quad(59)$$

since, as above, cross terms containing $p_1(T)$ or $p_2(T)$ cancel out when an average is taken over t_0,—the time of closest approach. The symbol $\Re$ denotes the real part of the double integral. If one takes real and imaginary parts of $l(t)$ in the double integral and integrates by parts, it will be seen that this term cancels the one immediately preceding. If we normalize to unity, take $\exp-\tfrac{1}{2}\Gamma T$ outside the integrals, substitute from (50) and (49a) for dh_1/dT, and finally make use of the fact that the change in h_1 and h_2 in the course of the collision may be neglected, taking both these quantities outside the integral and setting the mean square value of each equal to unity, we have for $J(x)$, when $x\gg\tfrac{1}{2}\Gamma$,

$$J(x)=\Gamma/2\pi x^2\Big[1+\exp(-\Gamma t_0)$$

$$\times\Big\{\Big|\int_0^\infty e^{+ixT}(\Delta_{A1}-\Delta_{B1})dT\Big|^2$$

$$+\Big|\int_0^\infty e^{ixT}K_AdT\Big|^2+\Big|\int_0^\infty e^{ixT}K_B{}^*dT\Big|^2\Big\}\Big].\quad(60)$$

The integrals of Δ_{B1} and Δ_{B2} in the exponents,—see (53) and (57)—have been dropped, as these would first appear in the fourth order. Ordinarily the mean-square value of h_1 or h_2 would be $\tfrac{1}{2}$, but to make the results comparable with those of the previous section, each state must be assumed to have unit population. In deriving (60) we have made use of the fact that the

phases of h_1 and h_2 will be random in general and that any terms involving cross products will vanish.

The functional form of the Δ's and the K's will depend on the choice of axes. If the z_e axis (again in parabolic coordinates) is taken parallel to the direction of motion of the ion, and the y_e axis is in the plane of motion, $\Delta_{A1}(T)-\Delta_{B1}(T)$ will equal $q\sin\theta/\hbar r^2$, where θ is the angle subtended at the atom by the distance from the ion to its point of closest approach. Since the matrix of z_e is diagonal, K_A and K_B will arise from the matrix of y_e alone and hence K_A will equal $\kappa_A\cos\theta/\hbar r^2$, where κ_A is some constant. A similar formula holds for K_B. Since

$$\sin\theta=v(T-t_0)/r,\quad\cos\theta=R/r,\quad(61)$$

we have, using (10) and (15),

$$\int_0^\infty e^{ixT}(\Delta_{A1}-\Delta_{B1})dT=\delta\int_{-\infty}^{+\infty}e^{i\xi u}\frac{udu}{(1+u^2)^{\frac{3}{2}}},\quad(62)$$

$$\int_0^\infty e^{ixT}K_AdT=\frac{\kappa_A}{\hbar Rv}\int_{-\infty}^{+\infty}e^{i\xi u}\frac{du}{(1+u^2)^{\frac{3}{2}}}.\quad(63)$$

These integrals have already appeared in I and equal $-idg_1(\xi)/d\xi$ and $g_1(\xi)$, respectively (see (25)). Hence (60) gives

$$J(x)=\frac{\Gamma}{2\pi x^2}\Big\{1+4\exp(-\Gamma t_0)\xi^2$$

$$\times\Big(\delta^2K_0{}^2(\xi)+\frac{\kappa_A{}^2+\kappa_B{}^2}{\hbar^2R^2v^2}K_1{}^2(\xi)\Big)\Big\}.\quad(64)$$

Suppose, however, that the z_e and y_e axes are interchanged. The roles of the Δ's and the K's will be precisely reversed, and in (64) $K_0{}^2$ and $K_1{}^2$ will become interchanged. When $J(x)$ is summed over all possible components of a particular hydrogen line n,—weighting $J(x)$ for each component by the oscillator strength of that component—the result must clearly be independent of the choice of axes. The weighted sum of all values of δ^2 must therefore equal the corresponding sum over all $\kappa_A{}^2$ and $\kappa_B{}^2$. If (64) is

going to be summed we may legitimately replace $(\kappa_A{}^2+\kappa_B{}^2)/\hbar^2R^2v^2$ by δ^2.

If, as before, there are $\Omega(\delta, \xi)$ collisions per second for some particular values of ξ and δ, $J(x)$ is given by (20) where now $f_0'(\xi)$ replaces $f_\delta(\xi)$, and

$$f_0'(\xi) = 2\xi(K_1{}^2(\xi)+K_0{}^2(\xi))^{\frac{1}{2}}, \qquad (65)$$

or in other words $f_0'^2(\xi)$ is simply the average over plus and minus values of $f_1{}^2(\xi)$. This is in accord with the conclusion reached in II that the shape of the line profile is given by the adiabatic approximation provided that δ is replaced by σ or $(1+\delta^2)^{\frac{1}{2}}$. The change in $f_\sigma(\xi)$ as δ goes from one to zero is hence very small. The observed profile will of course vary considerably over this range, since as δ goes to zero, ξ corresponds to larger and larger x (see (19)).

Also it is evident from (52b) that the probability of a transition from B_1 to B_2 is approximately given by the square of the time integral of $K_B(t)$. This is simply $1/2\pi$ times the total collision phase shift, or in this case $2\kappa_B/\hbar vR$. This is usually of the same order as δ (see formula (45)). Thus the change in the atomic wave functions becomes appreciable and the Born approximation becomes invalid in the same region as that in which the adiabatic approach becomes approximately valid; i.e., for δ between one-half and two.

Supplementary Identifications in the Spectra of K, Ca, Sc and Ti

L. W. PHILLIPS

Department of Physics, University of Illinois, Urbana, Illinois

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About 65 lines, belonging to the aluminum-like spectra of K and Ca, and the silicon-like spectra of Ca, Sc and Ti, are reported. All known term values for these ions are listed. Ionization potentials for Ca VII and Sc VIII are estimated as approximately 127 volts and 158 volts, respectively.

WHITFORD,[1] who used Ekefors'[2] list of K and Ca wave-lengths, has published the identifications of a number of lines, part of which belong to those spectra of potassium and calcium which are isoelectronic with Al I and Si I. A previous paper from this laboratory[3] reported

[1] A. E. Whitford, Phys. Rev. **46**, 793 (1934).
[2] E. Ekefors, Zeits. f. Physik **71**, 53 (1931).
[3] P. G. Kruger and L. W. Phillips, Phys. Rev. **52**, 97 (1937).

TABLE I. *Classified lines of* K VII, Ca VIII, Ca VII, Sc VIII *and* Ti IX.

INT.	λ(VAC)	v(CM⁻¹)	CLASSIFICATION	INT.	λ(VAC)	v(CM⁻¹)	CLASSIFICATION
		K VII				Ca VIII	
4	403.980	247,537	$s^2p\ {}^2P_{3/2}-\ s^2d\ {}^2D_{3/2}$	8*	357.983	279,343	$sp^2\ {}^4P_{5/2}-\ spd\ {}^4D_{3/2}$
10	403.783	247,658	${}^2P_{3/2}-\ {}^2D_{5/2}$	8	357.497	279,723	${}^4P_{5/2}-\ {}^4D_{5/2}$
0	402.267	248,591	$sp^2\ {}^4P_{5/2}-\ spd\ {}^4D_{3/2}$	12	357.347	279,840	${}^4P_{5/2}-\ {}^4D_{7/2}$
4	401.758	248,906	${}^4P_{5/2}-\ {}^4D_{5/2}$	5	355.692	281,142	${}^4P_{3/2}-\ {}^4D_{1/2}$
7	401.534	249,045	${}^4P_{5/2}-\ {}^4D_{7/2}$	8	354.985	281,702	${}^4P_{3/2}-\ {}^4D_{3/2}$
1	400.091	249,943	${}^4P_{3/2}-\ {}^4D_{1/2}$	9	354.508	282,081	${}^4P_{3/2}-\ {}^4D_{5/2}$
3	399.485	250,322	${}^4P_{3/2}-\ {}^4D_{3/2}$	4	353.699	282,726	${}^4P_{1/2}-\ {}^4D_{1/2}$
2	398.988	250,634	${}^4P_{3/2}-\ {}^4D_{5/2}$	2	353.004	283,283	${}^4P_{1/2}-\ {}^4D_{3/2}$
8	398.931	250,670	$s^2p\ {}^2P_{1/2}-\ s^2d\ {}^2D_{3/2}$	10	184.160	543,005	$s^2p\ {}^2P_{3/2}-\ s^24s\ {}^2S_{1/2}$
0	398.252	251,097	$sp^2\ {}^4P_{1/2}-\ spd\ {}^4D_{1/2}$	7	182.713	547,305	${}^2P_{1/2}-\ {}^2S_{1/2}$
1	397.674	251,462	${}^4P_{1/2}-\ {}^4D_{3/2}$	4	179.510	557,073	$sp^2\ {}^4P_{5/2}-\ sp4s\ {}^4P_{3/2}$
7	176.106	567,840	$s^2p\ {}^2P_{3/2}-\ s^24d\ {}^2D_{5/2}$	2	179.188	558,073	${}^4P_{3/2}-\ {}^4P_{1/2}$
5	175.189	570,812	${}^2P_{1/2}-\ {}^2D_{3/2}$	6	178.687	559,637	${}^4P_{1/2}-\ {}^4P_{1/2}$