REVIEWS OF

MODERN PHYSICS

VOLUME 31, NUMBER 3 JULY, 1959

Structure of Spectral Lines from Plasmas*

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* Work supported by the Air Force Office of Scientific Research.

I. INTRODUCTION

RESEARCH on line broadening, though often regarded as pedestrian and unlikely to lead to new fundamental insights, is nonetheless inspired by a vision. One dreams that in a distant star or in some other inaccessible region filled with matter a few atoms, perhaps hydrogen atoms, emit lines whose structure can be analyzed in terrestrial laboratories. These lines carry in many cases information we have already learned to understand: red shifts revealing masses, Doppler shifts revealing motions, and sometimes Doppler widths revealing temperatures. It is clear that in principle all physical properties of the medium containing the radiating atoms are somehow reflected in the line structure, since they affect the forces between the radiating atom and its neighbors, the distances over which these forces are exerted, and the times during which they act. One hopes, therefore, that when the language of the spectral lines has been fully learned, a radiating atom in a distant material environment can serve as a noninterfering probe conveying significant data regarding pressure, temperature, or, more generally, the distribution of molecular speeds, and states of ionization in the surrounding medium. Such hope is now far from fulfillment, and this article attempts but a modest contribution to its realization.

This survey is limited to a small part of the line-width problem, a problem whose scope and complexity is not widely appreciated and which has suffered perhaps from an excessive optimism of authors who, on proposing a partially successful simple model yielding to mathematical treatment, have served enthusiastic notices that the whole problem is solved. When, as often happens, experimental observations fit the special model, the matter is easily regarded as closed despite logical difficulties, and it sometimes takes severely critical appraisals to set the problem on the path of progress again.

The part treated here is plasma broadening, a group of effects peculiar to lines emitted in a medium that is strongly ionized but has no net charge. Hence we do not consider the results of impacts between neutral molecules, nor any of the theories suitable principally for their description. Other review[1] articles fill this need. In a plasma, the heavy positive charges and the light electrons often require different treatment, as the following discussion shows. Attention is restricted to emission because in ionized media absorption is not often directly observable and the problems connected with phenomena of reabsorption necessitate considerations unrelated to the broadening agencies here reviewed. Nor are microwaves specifically included in our work; optical lines are our chief concern.

Applications of the theory are found in four widely separated fields of investigation: in astrophysics, gas discharges, strong shocks, and flames or explosions. Some practical urgency attaches to line-width studies because of the importance which all of these researches currently enjoy.

This introductory section surveys two very general methods that have found application to plasma line-broadening problems. One is called statistical theory; the other is variously called impact theory, velocity broadening or phase-shift broadening theory. They refer to different models that cannot easily be compared. Because of the intuitive difference of the models the effects they generate are sometimes regarded as separate or even additive, and oversimplifications have appeared as a result of this seductive fallacy. Statistical and impact theories are certain limiting instances of a more general theory, each having its own range of application, and each losing its validity in a large domain of physical conditions of interest to the experimenter. There are also situations in which both theories apply and give identical answers. But it happens that in plasma broadening the integrity of the two methods is rather better preserved than under almost any other circumstances, the reason being that the heavy ions exert long-range and slowly varying forces which satisfy the statistical theory, whereas the light and swift electrons are very often tractable by impact methods.

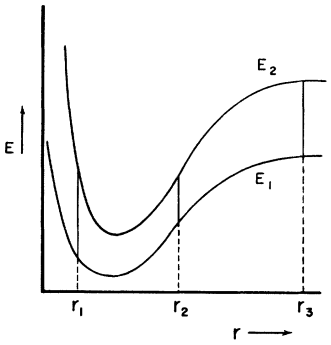

FIG. 1. Dependence of energies on interparticle distance.

A. Statistical Theory[2-4]

A spectral line arising from a transition between an upper level of energy E_2 and a lower of energy E_1, has its normal (radian) frequency $(E_2-E_1)/\hbar$. But E_2 and E_1 are not constants; they vary as a result of perturbations caused by other molecules, the "perturbers." In the presence of only one perturber the dependence of E_2 and E_1 on the distance, r, between the centers of the radiating and perturbing particle is given by the well-known potential energy curves, of which a typical set is drawn in Fig. 1. A transition occurring at a large distance r_3 has a normal ω, at r_2, ω is smaller and at r_1 larger than normal. Thus to every r there corresponds an $\omega(r)\equiv(E_2(r)-E_1(r))/\hbar$ and some ω's are more likely than others. In a statistical sense, the probability $P(\omega)$ equals the fraction of configuration space in which $E_2-E_1=\hbar\omega$ or, more precisely, that fraction times the Boltzmann factor, $\exp\{-[E_2(r)-E_2(\infty)]/kT\}$. It has been customary to neglect the Boltzmann factor on the supposition that it is practically 1 where $P(\omega)$ is large. This may sometimes lead to serious errors; yet we assume it here.

In the presence of N perturbers, the frequency distribution $I(\omega)$ is still given by $P(\omega)$, but configuration space now has $3N$ dimensions, and

$$I(\omega)d\omega=P(\omega)d(\omega)$$

$$=(4\pi/V)^N\int\cdots\int r_1^2r_2^2\cdots r_N^2dr_1\cdots dr_N. \quad (1.1)$$

The integration extends over the restricted domain in which

$$\omega-d\omega\leqslant\omega(r_1,r_2\cdots r_N)\leqslant\omega+d\omega.$$

[1] (a) V. Weisskopf, Physik. Z. **34**, 1 (1933); (b) H. Margenau and W. W. Watson, Revs. Modern Phys. **8**, 22 (1936); (c) A. Unsöld, Vierteljahresschr. astron. Ges. **78**, 213 (1943); (d) S. Ch'en and M. Takeo, Revs. Modern Phys. **29**, 20 (1957); (e) R. G. Breene, Revs. Modern Phys. **29**, 94, 1957; (f) I. I. Sobel'man, Progr. Phys. Sci. (U.S.S.R.) **54**, 551 (1954). (This paper contains useful comments on the interplay between the Doppler effect and interaction broadening, a problem not considered here.)

[2] (a) H. Margenau, Phys. Rev. **40**, 387 (1932); (b) **43**, 129 (1933); (c) **44**, 931 (1933); (d) **48**, 755 (1935); (e) **82**, 156 (1951).

[3] M. Kulp, Z. Physik **79**, 495 (1932); **87**, 245 (1933).

[4] (a) H. Kuhn, Phil. Mag. **18**, 987 (1934); (b) H. Kuhn and F. London, Phil. Mag. **18**, 983 (1934).

Usually, in application of statistical theory, additivity is assumed for the contributions to ω:

$$\omega(r_1 \cdots r_N) = \sum_i \omega(r_i).$$

This is often true for large r, but never for small r, where the main contribution to the interaction comes from the exchange forces. In a plasma, $\hbar\omega(r)$ for large r is the difference in atomic energy resulting from the Coulomb forces which are exerted by the passing ions and electrons. Mathematical techniques for evaluating the integrals in (1.1) involve the use of δ functions (Dirichlet's method) now so common as not to require review (see Margenau[2e] and Chandrasekhar[5]).

B. Impact Theory

An infinitely sharp line implies a radiating process of infinite duration. Natural line width arises from the fact that the upper state of the atom has a finite life time, and can be obtained by carrying out a Fourier analysis of the sinusoidal vibration for a finite time. According to the reasoning of Lorentz,[6] impacts of perturbers shorten the lifetime below the natural duration and thereby increase the width of the emitted line. Mathematical representation of this process is very simple: Suppose an atom is allowed to emit radiation of frequency ω' between times 0 and T. Then the distribution of Fourier amplitudes is given by

$$J(\omega,T) \propto \int_0^T e^{i(\omega-\omega')t} dt = \frac{e^{i(\omega-\omega')T}-1}{i(\omega-\omega')}.$$

If this were the only radiative act observed, the frequency distribution would be $|J(\omega,T)|^2$. The observed line, however, is a composite of radiations from many atoms radiating for different lengths of time, but with a mean time equal to τ, the reciprocal of the collision frequency ν_c. The probability that a given atom radiate for T seconds is $\tau^{-1}e^{-T/\tau}$. Hence the intensity at ω is

$$I(\omega) = \tau^{-1}\int_0^\infty |J(\omega,T)|^2 e^{-T/\tau} dT \propto \frac{1}{(\omega-\omega')^2+\nu_c^2}. \quad (1.2)$$

This is the famous Lorentz "dispersion" curve whose full width at half-maximum is $2\nu_c$ on the radian frequency scale. In this article the "half-width" $\omega_{\frac{1}{2}}$ is defined as full width of the line at a height equal to $\frac{1}{2}$ its maximum intensity. Formula (1.2), despite its simplicity, meets with singular success in predicting that a "pressure-broadened" line has a width proportional to the collision frequency, and since

$$\nu_c = nqv \quad (1.3)$$

in terms of the number density of perturbers n, the collision cross section q, and their velocity v, this width turns out to be proportional to the pressure at a constant temperature. Hence the name, pressure broadening.

The meaning of an impact is clear only if the molecules are rigid spheres, an hypothesis of the worst sort for ions. Even for neutral structures, Eq. (1.2) is not wholly satisfactory, for if used in conjunction with (1.3) q must take on values quite different from gas-kinetic cross sections, usually larger values. To hide the difficulty a new phrase was coined; theorists began to speak of *optical* cross sections, to the delight of experimenters who now had a brand new quantity to measure. The unpleasant fact is, however, that Lorentz' theory in its simple form breaks down when the perturbers are surrounded by force fields, i.e., when impacts are "soft".

Qualitatively speaking, collisions affect the radiative process in two ways:

(1) Some actually terminate it, quenching the upper state by transferring the energy of excitation prematurely to another place. Precisely under what conditions an impact will quench is not easy to say because this process requires a delicate balance of energies within perturber and radiator. But it is known that quenching occurs, because it manifests itself in an added line width *and* a reduction in the total line intensity.

(2) The other collision effect is a phase change in the emitted radiation accompanying the detuning of its frequency by a passing particle. If the phase change connected with a collision is large enough the passage will effectively divide the wave train into two incoherent ones, and this is tantamount to termination so far as line width is concerned. In this case no change in intensity accompanies this interruption because the atom goes on radiating a similar line during each successive free period. Lorentz did not distinguish between quenching and phase-altering impacts.

Lenz and Weisskopf[7] incorporated the idea of phase changes in the impact theory and achieved thereby a measure of success in giving meaning to an optical cross section, or an "optical impact radius." In the absence of perturbations, Weisskopf reasoned, ω=constant=ω' and the phase is a linear function of t, $\omega' t$. This corresponds to a sharp line. If an appreciable change $\Delta\varphi$ is added to this linear trend during a perturbation, that perturbation acts like Lorentz's impact. Now

$$\Delta\varphi = \int(\omega-\omega')dt = \hbar^{-1}\int(\Delta E_2 - \Delta E_1)dt, \quad (1.4)$$

where $\Delta E(r)$ is the departure of the E curves in Fig. 1 from their final values. Writing $\epsilon(r)$ for the second difference $\Delta(E_2-E_1)$ and assuming ΔE_2 to be so small

[5] S. Chandrasekhar, Revs. Modern Phys. **15**, 1 (1943).
[6] H. Lorentz, Proc. Amsterdam Acad. Sci. **8**, 591 (1906).
[7] (a) W. Lenz, Z. Physik **25**, 299 (1924); (b) V. Weisskopf, Z. Physik **75**, 287 (1932).

that the perturber is deflected but very little from its straight-line path, then, if it flies by at a closest distance ρ from the radiator and has a speed v,

$$\Delta\varphi=\hbar^{-1}\int\epsilon(\rho^2+v^2t^2)^{\frac{1}{2}}dt=\Delta\varphi(\rho,v). \tag{1.5}$$

The added phase depends on ρ and v. An *effective* impact, i.e., one which kills coherence, is an impact for which $\Delta\varphi\gtrsim\varphi_0$, a quantity presumably of order of magnitude 1. Thus the relation $\Delta\varphi=\varphi_0$ divides all impacts into two ideal classes, those which broaden and those which do not. Since a smaller ρ leads in general to a larger $\Delta\varphi$, the relation $\Delta\varphi=\varphi_0$ defines a $\rho_c(v)$ *below* which all impacts broaden the line. Therefore $\pi\rho_c^2(v)$ plays the role of Lorentz' q and may be introduced in (1.3) and (1.2). Here then is a qualitative reason why optical cross sections may differ from gas kinetic ones, and why they depend on v.

We shall often encounter the equation $\Delta\varphi=\varphi_0$ as a limiting condition separating the ranges in which different kinds of treatment are necessary. The precise value of φ_0 never matters, but we assume it to be of order magnitude 1 (or $\pi/2$, or even π) and call it the *critical phase*. If $\Delta\varphi$ arises from single impacts, the critical phase defines an *optical radius* or *critical impact distance* ρ_c, which depends on v and on the form of ϵ, i.e., the law of interaction. Likewise, there results an *optical cross section* $\pi\rho_c^2$.

Numerous refinements of this theory have been proposed.[4b,8] One of them is treated later in some detail because of its success in applications even under circumstances in which its *a priori* validity is not evident (see Sec. IV).

C. Relation Between Statistical and Impact Theories

The two physical pictures underlying the treatments in parts A and B of this section are so completely unrelated that a decision as to their domains of validity cannot be made on simple intuitive grounds. Attempts to combine the results in phenomenological ways, by merely saying that both are present independently and thus "folding" one distribution into the other[2d,4b] have had some success,† but lack fundamental justification. It is necessary to fall back upon a mathematical formalism more general than either treatment A or B, and to see under what conditions it reduces to these species of description.

Such a formalism is available in the Fourier integral for the line width, suitably generalized.[9,10] A classical observable Q, which is a function of momenta and coordinates of some physical system, is represented in quantum mechanics by a matrix with elements Q_{ij}. The classical intensity distribution within a line,

$$I(\omega)=\frac{2\omega^4}{3\pi c^3}\left|\int_{-\infty}^{\infty}\mu(t)e^{-i\omega t}dt\right|^2, \tag{1.6}$$

is such an observable involving momenta and velocities of the radiating atom through the varying dipole moment μ and the atomic frequency ω. The observed value of Q for the state of the system which is represented by the statistical matrix $\mathbf{S}$ is

$$\bar{Q}=\text{trace}(SQ).$$

Thus the quantum mechanical intensity distribution (we omit the bar) is, because of (1.6),

$$I(\omega)\propto\text{trace}\left\{S\int dt\mu(t)e^{-i\omega t}\int dt'\mu(t')e^{i\omega t'}\right\}, \tag{1.7}$$

where S, $\mu(t)$, and $\mu(t')$ are matrices, the latter two in the so-called moving system or in "the Heisenberg form" (see the following). From (1.7), statistical and impact theories can both be derived as certain limiting cases.[8d,11]

The Hamiltonian H for the emitting atom is a function of t because of the perturbations that broaden the line. Introducing a time-development matrix U which satisfies the Schrödinger equation,

$$i\hbar\dot{U}=HU, \tag{1.8}$$

then

$$\mu(t)=U^\dagger\mu U,$$

μ being the time-constant (Schrödinger) matrix $\mu_{ij}^0=\int\psi_i^*(\sum_n er_n)\psi_j d\tau$. Now suppose the perturbers are fixed in space. Then H does not depend on t and (1.8) has the solutions $U_{lm}=\exp[(-i/\hbar)E_l t]\delta_{lm}$, where E_l is a stationary eigenvalue of H. This approximation is too drastic and yields no line width; however, almost as simple and quite significant is the answer obtained by making the *adiabatic hypothesis*.‡

The adiabatic hypothesis in its quantum mechanical form says that, under conditions specified forthwith, Eq. (1.8) has a solution of the form

$$U_{lm}=\exp\left[-\frac{i}{\hbar}\int_0^t E_l(t')dt'\right], \tag{1.9}$$

[8] (a) W. Lenz, Z. Physik **80**, 423 (1933); (b) C. Reinsberg, Z. Physik **111**, 95 (1938); (c) E. Lindholm, Arkiv Mat. Astron. Fysik **28B**, No. 3 (1941); (d) H. M. Foley, Phys. Rev. **69**, 616 (1946).

† This process is not the same as adding the half-widths.

[9] P. W. Anderson, Phys. Rev. **76**, 647 (1949).

[10] S. Bloom and H. Margenau, Phys. Rev. **90**, 791 (1953).

[11] (a) The procedure here follows H. Margenau and R. Meyerott, Astrophys. J. **121**, 194 (1955). See also: (b) H. Margenau, Z. Physik **86**, 523 (1933); (c) T. Holstein, Phys. Rev. **79**, 744 (1950); (d) M. Mizushima, Phys. Rev. **83**, 94 (1951); **84**, 363 (1951); (e) P. W. Anderson, Phys. Rev. **86**, 809 (1952).

‡ The word "adiabatic" has come to be almost meaningless through unprincipled use in modern physics. This becomes evident in Sec. IIB, where various specific senses of "adiabatic" and its opposite, "diabatic" (or its atrocious, pleonastic synonym, non-adiabatic), are discussed. In the present context, the meaning should be clear from the discussion.

where the $E_l(t)$ are solutions of

$$H\psi_l(t)=E_l(t)\psi_l(t), \tag{1.10}$$

an equation sometimes called the adiabatic Schrödinger equation. The hypothesis is valid if, during the perturbation interval t, and for all states m,

$$\left|\int_0^t \frac{(dH/dt')_{lm}}{E_l(t')-E_m(t')}\left\{\exp\frac{i}{\hbar}\int_0^{t'}[E_l(t'')-E_m(t'')]dt''\right\}dt'\right|\ll 1. \tag{1.11}$$

Here l is the atomic state initially present, m some other state. With (1.9) and (1.10) $\mu(t)$ takes a simple form:

$$\left.\begin{aligned}\mu_{lm}&=\mu_{lm}{}^0\exp[i\varphi_{lm}(t)]\\ \varphi_{lm}&=\hbar^{-1}\int_0^t[E_l(t')-E_m(t')]dt'\end{aligned}\right\}. \tag{1.12}$$

We now introduce this into (1.7) and assume that S is diagonal, a form which can always be brought about by proper choice of state functions. Then, after a few steps (among them the replacement of the variables $t'-t$ by τ) there results

$$I(\omega)\propto\int d\tau e^{i\omega\tau}C(\tau), \tag{1.13a}$$

$$C(\tau)=\sum_{if}S_i|\mu_{if}{}^0|^2\int_{-\infty}^{\infty}\exp\{-i[\varphi_{if}(t+\tau)-\varphi_{if}(t)]\}dt. \tag{1.13b}$$

The function $C(\tau)$, whose Fourier transform is the intensity distribution, is called the correlation function; its general features form the substance of an elegant mathematical discipline called the statistics of time series; hence, this manner of writing $I(\omega)$ is finding increasing favor with theorists. Qualitatively, the meaning of C is clear: $\varphi_{if}(t+\tau)$ and $\varphi_{if}(t)$ are certainly equal when $\tau=0$; hence, $C(0)$ is large. If φ has a short "memory" so that it quickly loses correlation with its previous values, $C(\tau)$ will fall off rapidly with τ. It is then something like a δ function and $I(\omega)$ is broad. If, on the other hand, $\varphi(t)$ remains correlated with itself (in the absence of interaction there is a linear correlation for all time: $\varphi=\text{const}\cdot t$) during an appreciable period, $C(\tau)$ will differ from 0 for that period, and $I(\omega)$ will be correspondingly narrow. One may indeed show that the half-width of $I(\omega)$ is approximately the reciprocal of the half-width of $C(\tau)$.

In arriving at (1.13), which is suggestive of the starting point of the Lorentz theory, we have used only the adiabatic hypothesis. Its correctness is tied to inequality (1.11).

An analysis of the conditions under which that inequality is true is given in the next section. We observe here primarily that (1.11) contains both the nondiagonal element $(dH/dt)_{lm}$ and the energy difference $E_l(t)-E_m(t)$; its validity depends on the relation between them. The remainder of this section takes (1.11) for granted and concerns itself with the manner in which E_l-E_m changes in time, for the applicability of statistical and impact theories depends on the behavior of that difference alone.

The statistical theory results if the difference changes slowly. The quantity φ may then be expanded in a Taylor series

$$\varphi(t+\tau)=\varphi(t)+\varphi'(t)\cdot\tau+\cdots,$$

and all terms in higher powers of τ may be neglected. The convergence here is generally good if only $\varphi''(t)(\tau^2/2)\ll 1$ for all values of t and those values of τ which matter in the integration of (1.13a), i.e., for which $C(\tau)\neq 0$. In (1.13b) we assume for simplicity that only one atomic state $i=1$ was initially present ($S_i=\delta_{i1}$) and that only one $\mu_{1f}{}^0$, namely $\mu_{12}{}^0$, is of appreciable magnitude. Then

$$C(\tau)\propto\int e^{i\varphi'_{12}(t)\tau}dt=\int\exp\{-i[E_2(t)-E_1(t)]\tau/\hbar\}dt;$$

hence,

$$I(\omega)\propto\int d\tau e^{i\omega\tau}\int\exp\{-i[(E_2-E_1)/\hbar]\tau\}dt.$$

The integral over τ now leads to a δ function which is different from zero only at those times t when ω, the line frequency under consideration, equals $[E_2(t)-E_1(t)]/\hbar$, our former $\omega(r_1\cdots r_N)$. By the rules of statistical mechanics (ergodic theorem) these times have probabilities equal to the fractional volume of configuration space in which $\omega(r_1\cdots r_N)=\omega$. The exact formal analysis here involves ranges $d\omega$, near equalities and probability densities, which we suppress, placing thereby a heavy burden of infinities and zeros upon the proportionality signs. With a little care the reader can supply these purely mathematical details. In sum

$$I(\omega)\propto\int\cdots\int\delta[\omega,\omega(r_1\cdots r_N)]d\mathbf{r}_1\cdots d\mathbf{r}_N, \tag{1.14}$$

and this is the $P(\omega)$ of Eq. (1.1).

An extension of the reasoning here outlined permits proof of two propositions of interest in the use of the statistical method.[1f,8a,11]

1. Far in the wings of a line, i.e., as $|\omega-\omega'|\to\infty$, ($\omega'$ is again the normal frequency) the statistical theory is always applicable. The value of $|\omega-\omega'|$ beyond which this is true depends on the form of the interaction and cannot be generally specified.

Later we have occasion to return to this proposition (which we call for short the *wing theorem*) and therefore give its more detailed proof, which closely follows

Sobel'man. Substituting Eq. (1.13b) into (1.13a) and dropping the subscripts and the sum we have

$$I(\omega) \propto \int d\tau e^{i\omega\tau} \int e^{-i[\varphi(t+\tau)-\varphi(\tau)]} dt,$$

with the understanding, however, that this quantity must be averaged over different collisions.

Let us *redefine* φ *(without bothering to change notation) to mean only the variable part of the phase which is contributed by the perturbation.* We then have for the second integral

$$\int e^{-i[\omega'\tau+\varphi(t+\tau)-\varphi(t)]} dt.$$

On interchanging the order of integrations, we have

$$I(\omega) \propto \int e^{i\varphi(t)} dt \int d\tau e^{i[\Delta\omega\tau-\varphi(t+\tau)]},$$

where $\Delta\omega=\omega-\omega'$. We now set $t+\tau=s$ in the second integral and obtain

$$I(\omega) \propto \int e^{i(\varphi-\Delta\omega t)} dt \int e^{-i[\varphi(s)-\Delta\omega s]} ds.$$

In the wings of the line, i.e., for sufficiently large $\Delta\omega$ the contributions to

$$\int e^{i(\varphi-\Delta\omega t)} dt$$

come from intervals Δt_k around the points t_k, defined by $\varphi'(t_k)=\Delta\omega$ since in other regions the rapid oscillations of the integrand tend to cancel. We can then write

$$\int e^{i(\varphi-\Delta\omega t)} dt \doteq \sum_k \int_{\Delta t_k} e^{i[\varphi-\Delta\omega t]} dt.$$

We next expand the exponent in a Taylor series about t_k obtaining

$$\sum_k e^{i[\varphi(t_k)-\Delta\omega t_k]} \int_{\Delta t_k} \exp i\left[\frac{\varphi''(t_k)}{2!}(t-t_k)^2 + \frac{\varphi'''(t_k)}{3!}(t-t_k)^3+\cdots\right] dt.$$

The important range of the integration, Δt_k, is of the order

$$\sqrt{2}[\varphi''(t_k)]^{-\frac{1}{2}}.$$

If, in this range, the term proportional to $(t-t_k)^3$ is small, the integration can be extended to infinity. This condition is

$$\varphi'''(t_k)[\varphi''(t_k)]^{-\frac{3}{2}} \ll 1. \tag{1.15}$$

We then obtain for the integral,

$$\sum_k e^{i[\varphi(t_k)-\Delta\omega t_k]}[\varphi''(t_k)]^{-\frac{1}{2}},$$

and, for $I(\omega)$,

$$I(\omega) \propto \sum_{kl} e^{i[\varphi(t_k)-\varphi(t_l)-\Delta\omega(t_k-t_l)]}[\varphi''(t_k)\varphi''(t_l)]^{-\frac{1}{2}}.$$

The average over all collisions causes the terms for which $k \neq l$ to cancel, and we find

$$I(\omega) \propto \sum_k [\varphi''(t_k)]^{-1}.$$

The sum here can be interpreted as proportional to the length of time during which

$$\Delta\omega = \varphi'(t_k)$$

or

$$\omega = \omega' + \varphi' \equiv \hbar^{-1}[E_i(t_k) - E_f(t_k)].$$

Thus $I(\omega)$ is proportional to the time that the atom spends in the perturbed condition with the energy separation between levels given by $\hbar\omega$. This leads again to Eq. (1.14) by arguments already presented; hence the wing theorem.

2. If a spectral line is broadened by *single impacts* of perturbers (low density) and Δt is the time during which the passing particle moves a distance equal to the impact parameter ρ, the statistical theory is applicable provided

$$\omega_{\frac{1}{2}} \cdot \Delta t \gg 1. \tag{1.16}$$

Here $\omega_{\frac{1}{2}}$ is the actual, measured half-width. Proof of theorem 2 rests upon the assumption that for an individual impact the perturbation can be written in the form

$$E_2 - E_1 = \text{const} r^{-\sigma},$$

where r is the distance between radiator and perturber and σ a small positive integer, so that $\varphi(t)$ can be constructed for any impact, If one then employs inequality (1.15) noticing that, by virtue of (1.13a), the half-width of $C(\tau)$ is the reciprocal of the half-width of $I(\omega)$, a little algebra leads to formula (1.16).

This formula has been proved for individual impacts only, and $\omega_{\frac{1}{2}}$ is the actual half-width of the line; in the wing theorem, the value of ω beyond which the statistical theory holds bears no general relation to the half-width and differs in different situations.

Next, we demonstrate that (1.13) leads to the impact results when the phase changes $\Delta\varphi$ occur suddenly and are therefore separated in time. We use (1.13) later on to obtain impact formulas more refined than those of Lorentz or Weisskopf, following the work of Foley, Lindholm, and others. At present we retrace the step that led to (1.13) and write

$$I(\omega) \propto \left| \int \mu_{12}{}^0 e^{-i[\omega t-\varphi_{12}(t)]} dt \right|^2, \tag{1.17}$$

assuming again that the atom has only two levels. If sudden impacts occur at times $t=T_i$, and if these impacts add amounts $\hbar a_i$ to the phase of the atom,

$$E_2-E_1=\hbar[\omega'+\sum_i a_i\delta(t,T_i)]$$

so that

$$\varphi_{12}\equiv\varphi(t)=\omega' t+A_j \quad \text{for } T_j\leqslant t<T_{j+1},$$

where $T_1<T_2<T_3\cdots$ and

$$A_j=\sum_{i=1}^{j} a_i.$$

Then the integral in (1.17) is

$$\mu_{12}^0\sum_j e^{iA_j}\int_{T_j}^{T_{j+1}} e^{-i(\omega-\omega')t}dt.$$

When the square of the absolute value of the sum is taken, there will appear the terms

$$|\mu_{12}^0|^2\sum_j\left|\int_{T_j}^{T_{j+1}} e^{-i(\omega-\omega')t}dt\right|^2 \tag{1.18}$$

and, in addition, cross terms with factors $e^{i(A_k-A_j)}$. If the a_i are unrelated, the sum of these will effectively banish. The remaining summation in (1.16) extends over different free times $T_{j+1}-T_j=T$ and is equivalent to the integration over T in Eq. (1.2). Under these assumptions the Lorentz formula is therefore established.

The wings of a line rarely follow the Lorentz formula, whereas the central core often conforms to it. The reason for this is not hard to see.

We spoke of sudden phase changes $\Delta\varphi$. In quantitative terms, "sudden" means that the change in $\varphi(t)$ occurring in the integrand of Eq. (1.17) as the result of a collision is limited to a time interval Δt small compared to the period of the other exponential factor of the integrand, i.e.,

$$\Delta t\ll 2\pi/\omega. \tag{1.19}$$

Unless the collisions overlap completely (long-range forces, high density of perturbers) this inequality is satisfied for sufficiently *small* ω, that is to say, near the center of the line. This result might be called the "core theorem" in contradistinction to the wing theorem. The former says that the core of a line "results from impacts," while the latter *claims that the wings* "are statistical."

These considerations allow these qualitative inferences: impact theories describe lines at high temperatures and for sudden perturbations, i.e., at low densities; statistical theories meet success at low temperatures and for heavy perturbers, especially at high densities where many interactions coincide and produce small net fluctuations of energy at the radiating atom.

To account for the contour of a given spectral line when neither impact nor statistical theory can be fully trusted, the center of the line can usually be interpreted as resulting from impacts, the wings as statistically broadened. More is said about this in Sec. IV.

We should comment on the consequences of Eq. (1.7) when the adiabatic hypothesis cannot be made, that is, when condition (1.11) is violated. This contingency is most likely to arise when the spacings, E_l-E_k, are small, hence in the microwave region, and under other more special circumstances. The story is then somewhat involved: the best account of it is to be found in Anderson's article.[9]

In the plasma situation the statistical theory promises a satisfactory description of the ion effects, and it would seem that impact theories might be suited to treat the swift electrons. But in this latter task, unfortunately, a fundamentally new problem arises. All theories here surveyed require the use of a potential energy of interaction ϵ, which is a function of the perturber position. Basically, then, they assume that the perturber has a classical path. This is not true in general for electrons, whose position is quite diffuse when the speed is definite because of the uncertainty principle. To operate with an $\epsilon(r)$ may therefore be meaningless, and a new approach is needed. In the next section, we offer qualitative arguments designed to permit some discrimination of conditions under which classical path theories are useful, and related considerations.

II. CLASSICAL-PATH HYPOTHESIS AND CRITERIA FOR ADIABATICITY

A. Classical Path

Essential to the foregoing analysis of spectral line broadening are two assumptions: first, that the perturber has a classical path, i.e., is a point particle with spatial coordinates that are functions of the time; and, secondly, that adiabaticity prevails, so that the perturber disturbs (without mixing) only the two states between which the system is radiating. The lack of a completely general workable approach to the broadening problem confers a good deal of importance upon a knowledge of the conditions under which such assumptions hold. As instances of treatments where these assumptions are not invoked we note the quantum theories of Jablonski[12] and of Kivel, Bloom, and Margenau[13]; another example is the theory of dielectric relaxation of Debye,[14] which treats the broadening induced by reorientation transitions in the radiator during collisions. The broadening mechanisms pertaining to these latter theories are quite different from those discussed in Sec. I. The two classes of results arise from opposite extremes in the physical model for the

[12] A. Jablonski, Phys. Rev. **68**, 78 (1945).

[13] Kivel, Bloom, and Margenau, Phys. Rev. **98**, 495 (1955).

[14] (a) P. Debye, *Polar Molecules* (Chemical Catalog Company, Inc., New York, 1929), Chap. V; (b) J. H. Van Vleck and V. Weisskopf, Revs. Modern Phys. **17**, 227 (1945).

interaction. We now formulate some simple criteria for the validity of the description of Sec. I. Special consideration is given to the interaction of a radiating hydrogen atom with electrons and protons.

Quantum mechanics yields an accurate account of atomic phenomena, and, through the uncertainty principle, also defines the limits of classical mechanics. This principle focuses attention on our inability to describe certain details of an event, such as the collision between two systems, without introducing finite disturbances in the parameters necessary for such description. When these disturbances compete in magnitude with the events one wishes to investigate, the event imagined cannot be observed in the degree of detail demanded, for then a classical picturization is without basis, and we must use quantum mechanics.

Classical-path theories assume that the distance of separation r between the perturber and the radiator is expressible as

$$r(t)=(\rho^2+v^2t^2)^{\frac{1}{2}}, \tag{2.1}$$

which requires exact specification of both its position and velocity at each instant of time. For this is to be meaningful the uncertainties in these quantities, as derived from quantum considerations, must be small in comparison with their actual magnitudes.

Numerous authors base their use of (2.1) on the magnitude of the angular momentum involved in a collision,[1c,8d,15] relying on the correspondence principle to validate classical analysis for large orbits. If $\mathbf{L}$ is the angular momentum of the perturber with respect to a radiator at rest, then, $L\approx l\hbar$. For large values of the integer l we may identify $\mathbf{L}$ with $m\mathbf{r}\times\mathbf{v}$, which during the collision may be taken to be $\approx mrv$.

The relation above in the form

$$mrv\approx l\hbar$$

and the uncertainty principle,

$$m\Delta r\Delta v=\hbar,$$

yield on division

$$(\Delta r/r)\cdot(\Delta v/v)=1/l, \tag{2.2}$$

and this is much smaller than 1 if l is large.

Equation (2.2) implies that for sufficiently large l any specified relative accuracy in r and v can be accomplished without violating the uncertainty principle, i.e., without need for abandoning the assumption of a classical path. For example, if $l\approx 100$ we may choose the orbit of the perturber such that $\Delta r/r\approx\Delta v/v\approx 1/10$, which ratios represent an acceptable percentage accuracy in the specification of these parameters.[9]

The preceding argument leaves many detailed questions unanswered. Let us consider the problem with a measure of skepticism which, fortunately, will later prove excessive. For the process of collision broadening to be tractable by means of a classical path we must require that the inequality

$$(\Delta r/r)\cdot(\Delta v/v)\ll 1 \tag{2.3}$$

holds throughout the time of any collision and for all impact radii of importance. When the classical path is derived properly as the limiting form of a quantum mechanical description these requirements lead to relations more specific than (2.3), relations which depend upon the mass of the perturbers, the density and temperature of the gas, and the type of interaction which pertains to the problem.

Collisions with large angular momenta, as shown by Eq. (2.2), can be described classically; this means that the perturbing particles correspond to wave packets, well localized both in coordinates and momentum, the limits of this localization being Δr and Δv. We now imagine a wave packet with a mean spatial extension a and a mean momentum mv, this latter quantity being equal to the actual momentum of the classical particle. In addition, we let r be the distance between the radiator and the center of the packet; it therefore corresponds to the collision distance previously denoted by the same symbol. For the validity of the classical description we demand that

$$a\lesssim r, \tag{2.4}$$

the ultimate limit of the classical description being $a\approx r$.

In all applications of the theory the interaction is taken to be vanishingly small outside of a finite region of space, the linear dimension of which is designated by d. Physically, this distance represents the extent of penetration of the field of the radiator into its surroundings. For the case of a neutral plasma this distance is the Debye length[16]

$$d=6.90(T/n)^{\frac{1}{2}}, \tag{2.5}$$

where d is given in centimeters, T in degree absolute, and n in cm^{-3}.

We consider the interaction region to be a cube of dimensions d, oriented for convenience with an axis parallel to the perturber's path. The time during which the perturbation is in effect, τ_p, is then of the order of d/v, a constant for all values of r up to approximately d, beyond which distance it vanishes.

In a classical description of the passage of the perturber through the interaction region, the collision time must be shorter than the time during which the perturber diffuses quantum mechanically through the distance r. This diffusion results from the initial localization of the packet and proceeds with a velocity of the order of $\hbar/ma$. It is therefore necessary that

$$r/(\hbar/ma)\gg d/v. \tag{2.6}$$

Because of (2.4) this inequality must hold for, $a\approx r$;

[15] (a) L. Spitzer, Phys. Rev. **55**, 699 (1939); (b) E. Lindholm, Arkiv Mat. Astron. Fysik **32A**, No. 17 (1945).

[16] L. Spitzer, *The Physics of Fully Ionized Gases* (Interscience Publishers, Inc., New York, 1956).

hence, we get from (2.6)

$$a \gg (d\lambda)^{\frac{1}{2}}, \tag{2.7}$$

where λ is the mean de Broglie wavlength of the perturber, $\hbar/mv$.

Applying this basic inequality to the most distant collisions with least momentum uncertainty for which $r \approx d \approx a$, we obtain $a \gg \lambda$, which (since $a \approx r$) is nothing more than the condition that $l \gg 1$. Thus, the criterion (2.7) reduces to the conditions that the angular momentum be large when applied to the most distant collisions; in general, (2.7) is more restrictive than $l \gg 1$.

In addition to the condition that the passage of the perturber through the interaction region retain its meaning in view of the diffusion of wave packets, we might also require that the interaction itself be classical in terms of precise momentum exchanges.

The interaction energy between the perturber and the radiator is $V(r)$ in the classical description. This can usually be expressed in the form

$$V(r) = C_\sigma / r^\sigma,$$

C_σ being some constant. The momentum exchange for the collision is then

$$\Delta p = -\int \nabla V(t) dt.$$

Another quantity of interest in this connection is the phase change per collision

$$\Delta\varphi = \hbar^{-1} \int V(t) dt.$$

In both these integrals we replace dt by dx/v and $V(t)$ by $C_\sigma(\rho^2 + v^2 t^2)^{-\sigma/2}$. The integrations should then extend from $-d/2$ to $d/2$, but a sufficient approximation results when they are performed from $-\infty$ to $+\infty$. Curvature of the path is neglected in this procedure. Elementary calculation yields

$$\Delta p = \frac{\sigma C_\sigma}{v\rho^\sigma} \pi^{\frac{1}{2}} \frac{\Gamma[(\sigma+1)/2]}{\Gamma[(\sigma+2)/2]} \approx \frac{V(\rho)}{v}$$

and

$$\Delta\varphi = \frac{C_\sigma}{\hbar v \rho^{\sigma-1}} \pi^{\frac{1}{2}} \frac{\Gamma[(\sigma-1)/2]}{\Gamma(\sigma/2)}.$$

The critical impact distance ρ_c is that value of ρ for which $\Delta\varphi = 1$ (see the end of Sec. IB). Solving this equation for C_σ in terms of ρ_c and inserting in Δp, we find

$$\Delta p = (\rho_c/\rho)^{\sigma-1}(\sigma - 1/\rho)\hbar. \tag{2.8}$$

To regard the perturber wave as a classical particle is to neglect its momentum uncertainty $\hbar/a$. The same uncertainty is thus introduced also in the states of the radiator system during and after the collision. The validity of the classical interaction is certainly assured if we require that all momentum (and thereby all corresponding energy) exchanges between the perturber and the radiator exceed this neglected uncertainty. The classical picture therefore holds only when:

$$\Delta p \approx V(\rho)/v \gg \hbar/a. \tag{2.9a}$$

This places an *upper* limit on the magnitude of ρ for which the interaction may be treated classically.

When the opposite inequality

$$\Delta p \approx V(\rho)/v \ll \hbar/a \tag{2.9b}$$

holds, the momentum uncertainty in the system far exceeds the momentum exchanges of the classical description, and the spread in momenta must be incorporated into the description of the perturber (or, what is equivalent, the spatial spread of the packet must be taken into account). Then the classical picture of a collision breaks down.

From (2.9a) using the more accurate expression for Δp, from Eq. (2.8), we have

$$\rho \ll \alpha_\sigma \rho_c (a/\rho)^{1/(\sigma-1)}, \tag{2.10}$$

where $\alpha_\sigma = (\sigma-1)^{1/(\sigma-1)}$ is of the order of unity, as seen in the correlation of σ with α_σ below:

σ	2	3	4	6
α_σ	1.00	1.41	1.44	1.38

Since $a \leqslant r$ for all r during the collision, and r can take on the value ρ, (2.10) seems to imply

$$\rho \ll \alpha_\sigma \rho_c. \tag{2.11}$$

This is essentially the condition $\Delta\varphi \gg 1$. We conclude that only collisions within the optical radius are amenable to a classical-path treatment and all those which occur outside of ρ_c must be treated by means of quantum mechanics. We return to this somewhat surprising conclusion at the end of this section.

Letting $a \approx \rho$ as the least stringent condition for the classical path we obtain in place of (2.10)

$$a \ll \alpha_\sigma \rho_c. \tag{2.12}$$

The validity of the classical description for collisions within ρ_c is also contingent on the enforcement of (2.7). On combining (2.7) and (2.12), there results on eliminating,

$$(d\lambda)^{\frac{1}{2}} \ll \rho_c. \tag{2.13}$$

This condition for the validity of the classical path is effectively independent of the actual size of the wave packet describing the perturber. Margenau and Kivel[17] actually computed the dimension of a one-dimensional packet [see Eq. (2.23)] and required it to be less than the size of the radiator. In this way they found that the width of the Lyman-α line of hydrogen may be computed classically at $T \approx 6000°$K if the perturber mass $> 10^{-26}$ g, which is true for protons but not for

[17] H. Margenau and B. Kivel, Phys. Rev. **98**, 1822 (1955).

TABLE I. Broadening of H_α by first-order Stark effect. Temperatures for protons and electrons *below* which the classical-path treatment holds, for various values of the density.

n (cm^{-3})	(°K) (protons)	(°K) (electrons)
10^{12}	4×10^6	50
10^{14}	4×10^7	500
10^{16}	4×10^8	5000
10^{18}	4×10^9	50 000

TABLE II. Broadening by second-order Stark effect. Temperatures for protons and electrons below which the classical-path treatment holds, for various values of the electron (ion) density.

n (cm^{-3})	(°K) (protons)	(°K) (electrons)
10^{12}	10^7	0.1
10^{14}	10^{10}	100
10^{16}	10^{15}	10^5
10^{18}	10^{16}	10^8

electrons. All this is in keeping with the present result, which is derived in a more general way.

After substituting (2.5) along with the definitions of λ and ρ_c into (2.13) one finds

$$\frac{T^{1/(\sigma-1)}}{n^{\frac{1}{2}}M^{\frac{1}{2}+1/(\sigma-1)}} \ll \frac{[\gamma_\sigma(C_\sigma/\hbar)]^{2/(\sigma-1)}}{6.90\hbar(3k)^{-\frac{1}{2}+1/(\sigma-1)}}, \tag{2.14}$$

where v, the perturbers' velocity, has been taken to be its rms value

$$v=(3kT/M)^{\frac{1}{2}},$$

M is the mass of the perturber, either a proton or an electron, and the γ_σ are numbers of order unity (e.g., $\gamma_2=\pi$).

This result has the advantage of containing no reference to ρ, which has no experimental meaning. However, inequality (2.14) is a sufficient condition which is in some instances too severe. For hydrogen, the first order Stark effect ($\sigma=2$) involves[18]

$$C_2\approx\tfrac{3}{4}(\hbar^2/m)n'(n'-1),$$

where n' is the principal quantum number of the excited state of the radiating atom and m is the electron mass. This is a sufficient approximation. Accurately, $n'(n'-1)$ should be replaced by $N_{n'}$ such that

$$N_3=4.5,\quad N_4=9.9,\quad N_5=23.6,\quad N_6=31.8.$$

Hence (2.14) becomes

$$\frac{T}{n^{\frac{1}{2}}M^{\frac{1}{2}}} \ll \frac{(\pi C_2)^2}{6.90\hbar^3(3k)^{\frac{1}{2}}}.$$

For the first Balmer line (H_α, $n'=3$), the inequality (2.14) gives Table I. For the higher Balmer lines the temperatures appearing here are multiplied by the factor $[n'(n'-1)/6]^2$, $n'>3$. Hence, for the higher series members the classical-path treatment is valid over a greater temperature range. This increase has practical significance only for the electrons, since they alone are severely limited by the values of the temperature. For a pure hydrogen plasma, thermal ionization begins at about 7000°K, so that appreciable broadening by electrons and protons does not occur at temperatures below this value. Thus much of Table I is purely academic.

For a typical second-order Stark effect in the optical region ($\sigma=4$) $C_4\hbar^{-1}\approx2\times10^{-12}$ esu. Here we obtain from (2.14) $T^{1/3}\ll n^{1/2}M^{5/6}(\gamma_4C_4/\hbar)^{2/3}(3k)^{1/6}/6.9\hbar$ and $\gamma_4=\pi/2$. This leads to the values of n and T shown in Table II. Table II shows that electrons may be treated classically for $n>10^{15}$ cm^{-3} in the second-order Stark effect, while protons and heavier ions always permit such treatment.

B. Criteria for Adiabaticity

We now transfer attention to the radiating system. Perturbation of its states can be treated adiabatically when the inequality (1.11) holds. The state of the system is then maintained throughout a collision except for its alteration through the radiation process. There are two cases of interest: (1) the states of the unperturbed radiator may be classified into groups of degenerate states and (2) the states of the unperturbed radiator are all nondegenerate. In case 1, two questions can be asked: (1a) Does the perturbation cause transitions between two states containing within the same group of degenerate levels? (1b) Does the perturbation cause transitions between a degenerate state in one group and a degenerate state in another group separated from the first by a finite energy? The perturbation may well be adiabatic in the sense of 1b, diabatic in the sense of 1a. In this section, we treat only case 1a, leaving 1b, which is more difficult, for the most part until Sec. V. Only a brief qualitative remark concerning 1b is presented at the end of this part of Sec. II. Existence is assumed of a finite perturbation time τ_p, the rate of change of the perturbation dV/dt being different from zero only during that time which, as we have seen, is of the order d/v. In addition, we here treat single impacts only.

For case 1a the energy differences of the instantaneous states appearing in the condition for adiabaticity are due solely to the perturbation itself, since all other states of the radiator may be ignored because of their much larger energy separations.

As the simplest example, we consider a radiator whose excited initial state has a two-fold degeneracy, and this degeneracy is removed in the first order of the per-

[18] A. Unsöld, *Physik der Sternatmosphären* (Springer-Verlag, Berlin, Germany, 1955), second edition, p. 321.

turbation theory. The adiabatic condition then becomes

$$\left|\int_{-\infty}^{+\infty}\frac{d/dt'\,|V_{12}(t')|}{2|V_{12}(t')|}\times\exp\left[-\frac{i}{\hbar}\int_{-\infty}^{t'}2|V_{12}(t'')|\,dt''\right]dt'\right|\ll 1, \quad (2.15)$$

where $V_{12}(t)=\langle 1|V(t)|2\rangle$, the indices 1 and 2 designating the two states in question.

The phase shift between the states is given by

$$\Delta\varphi(t)=\frac{2}{\hbar}\int_{-\infty}^{t}|V_{12}(t')|\,dt'.$$

When $|\Delta\varphi(t)|\gg 1$, there have been many oscillations of the exponential part of the integrand in (2.15) at time t. These oscillations cause the integral to be quite small provided that

(α) $(d/dt)|V_{12}(t)|/|V_{12}(t)|$ is a slowly varying function of the time during an average period of the oscillation $\hbar/2\langle|V_{12}|\rangle$ (where $\langle|V_{12}|\rangle$ is a time average of $|V_{12}|$ for the whole perturbation,

$$\langle|V_{12}|\rangle=\int_{-\tau_p/2}^{\tau_p/2}|V_{12}(t)|\,dt/\tau_p);$$

and

(β) the perturbation time is much greater than $\hbar/2\langle|V_{12}|\rangle$.

The first requirement α reduces to the second β when the classical-path procedure is used. In that case

$$V_{12}(t)\equiv C_{12}/(\rho^2+v^2t^2)^{\sigma/2}, \quad \tau_p\leqslant t\leqslant\tau_p/2$$
$$\equiv 0, \quad |t|>\tau_p/2$$

and $(d/dt)|V_{12}|/|V_{12}|=(-\sigma v^2t)/(\rho^2+v^2t^2)$. We wish this to vary slowly within an interval of the order of $\hbar/\langle|V_{12}|\rangle$. This can occur only when $|t|\gg\hbar/\langle|V_{12}|\rangle$. To maintain condition α, therefore, the contribution of $(d/dt)\ln|V_{12}|$ coming from small $|t|$ must be inappreciable, and this requires that $\tau_p\gg\hbar/\langle|V_{12}|\rangle$, which is condition β. The two conditions are not independent.

When the degree of degeneracy is greater than 2, E_l-E_m is no longer to be identified with $2|V_{lm}|$, but it is still of the same order of magnitude. The result just obtained is therefore quite general in degenerate situations, and we must depend entirely on long, slow collision processes for the validity of the adiabatic assumption. Our criterion for adiabaticity in case 1a, when written in a more general way, is, therefore,

$$\hbar^{-1}\langle|E_l-E_m|\rangle\tau_p\gg 1. \quad (2.16)$$

But $\hbar^{-1}\langle(E_l-E_m)\rangle$ is the average frequency shift of the initial state during the collision. Neglecting the frequency shift in the lower state of the radiative transition, condition (2.16) takes the form

$$\Delta\varphi\gg 1. \quad (2.17)$$

Hence, in the presence of degeneracy, collisions which fall within the optical radius are adiabatic, others are diabatic. This result has been derived by Spitzer[19] in more detailed calculations for the L_α line.

In the absence of degeneracy, case 2, the energy differences (E_l-E_m) are much larger than those which were considered in case 1. We may thus take $E_l-E_m\approx E_l^0-E_m^0$, where E_l^0 and E_m^0 are the unperturbed states of the radiator. With this understanding, inequality (1.11) reads

$$\frac{1}{|E_l^0-E_m^0|}\left|\int_{-\infty}^{+\infty}\left(\frac{d}{dt'}V_{lm}(t')\right)\times\exp\left[-\frac{i}{\hbar}(E_l^0-E_m^0)t'\right]dt'\right|\ll 1. \quad (2.18)$$

Here it is convenient to distinguish between slow and fast collisions with respect to the oscillatory period $\hbar/|E_l^0-E_m^0|$. For slow collisions, $\tau_p\gg\hbar/|E_l^0-E_m^0|$.

Integrating (2.18) by parts and making use of the fact that $V(\pm\infty)=0$ we have

$$\frac{1}{\hbar}\left|\int_{-\infty}^{+\infty}V_{lm}(t')\exp\left[-\frac{i}{\hbar}(E_l^0-E_m^0)t'\right]dt'\right|\ll 1. \quad (2.19)$$

Therefore, when $V_{lm}(t)$ varies insignificantly over the period $\hbar/|E_l^0-E_m^0|$ the inequality (2.19) will certainly be true provided $\tau_p\gg\hbar/|E_l^0-E_m^0|$, which is our premise. This assumption about V_{lm} holds for times such that $|t|>\hbar/|E_l^0-E_m^0|$ and that the adiabatic criterion reduces merely to $\tau_p\gg\hbar/|E_l^0-E_m^0|$. Hence, all slow collisions are adiabatic.

For fast collisions, $\tau_p\ll\hbar/|E_l^0-E_m^0|$, and we may take the exponential appearing in (2.18) equal to unity. This yields, upon integration of (2.18),

$$|V_{lm}(\infty)-V_{lm}(-\infty)|/|E_l^0-E_m^0|<1,$$

and the quantity on the left is always zero. The adiabatic criterion is therefore satisfied also when the perturbation time is short, provided the radiator has large energy separations.

Thus both very slow and very fast collisions are adiabatic when degeneracy (or near degeneracy) is absent in the levels concerned. In the case of degeneracy only the slow collisions are adiabatic. In this latter instance the condition for adiabaticity is similar to one of the conditions for the classical-path approximation, namely $\Delta\varphi\gg 1$.

Under the subject of degeneracy, case 1a, special attention must be given to *space* quantization, the fact that different orientations of the total angular mo-

[19] L. Spitzer, Phys. Rev. **58**, 348 (1940).

mentum vector correspond to the same energy of the radiating system. The meaning of the term adiabatic is a little confusing in this case, as the following consideration shows.

Suppose the atom is radiating in a $^3P_1$ state, and assume first that an external magnetic field is present. The orientations in space for which $m=-1, 0, 1$ will then have slightly different energies. The passage of a perturber past the atom is said to be adiabatic if the interaction with the perturber does not transfer the radiator from one m value to another or, classically speaking, if the radiator's orientation remains fixed in space during a perturber passage. If we retain this meaning of the word adiabatic even in the absence of an external field, then an adiabatic perturbation is one which does not succeed in turning the radiator about, or in altering the value of m.

The interaction between the radiator and the perturber depends on the value of a quantum number m. However, this m is not identical with the foregoing, which refers to some fixed direction: the interaction depends on space quantization with respect to the line joining radiator and perturber, and this line moves in space as the latter flies by, turning through an angle of 180° during a complete passage. We call the space quantum number relative to this *moving* line, m'. Adiabaticity with respect to m' is clearly different from the former version because it implies rotation of the radiating atom. Spitzer,[19] Lindholm,[20] and Unsöld[18] use the term in the latter sense.

For the present problem this choice is more appropriate because in the derivation of our criterion we have taken $|E_1-E_2|$ to be $|V_{12}|$, and this implies that the radiator is in a state for which the linear combination of m eigenfunctions changes in time while m' remains fixed. With this understanding, inequalities (2.15) and (2.16) tell us under what conditions m' is unaltered by an impact.

But if m' is not changed, so that the impact is adiabatic in the second sense, then, since the radiation has to be analyzed in a fixed coordinate system (the spectrograph does not revolve about the radiating atom), an adiabatic impact corresponds to a phase change of magnitude π. This seems to imply that simple impact theories, like those of Lorentz and Weisskopf, which ignore phase changes resulting from this rotation but consider phase changes of magnitude π produced by dynamic effects as singularly important, contain grave errors. Distant impacts, for example, are not counted in these impact theories; yet they should produce a phase change π if they are adiabatic in the second sense. Physical intuition argues that this cannot be. The resolution of this apparent dilemma is simple: criterion (2.16) shows clearly that distant impacts are *not* adiabatic in the second sense. This means they do not succeed in swinging the radiator around. They *are* adiabatic in the first sense.

This problem, which is practically of minor importance but presents points of fundamental interest, is considered carefully by Spitzer.[19] He shows how the impact theories manage to obtain a reasonable result by compensating errors, the errors being an unwarranted claim of adiabaticity and a neglect of the rotation effect. Further light is shed on the "rotation problem" by an analysis[21] having an entirely different aim, but which indicates nonetheless how and why the Lorentz theory takes correct account of the change in orientation of Debye dipoles induced by collisions.

Before concluding the analysis of adiabatic conditions we take a brief look at case 1b and inquire how one should deal with transitions between one set of degenerate states and another set, separated from the first by a finite energy interval. Suppose that for transitions between any two states of the initial set and also the final set,

$$\Delta\varphi\ll 1.$$

Then the perturbation is diabatic with respect to the (perturbed) degenerate states. In that case a consideration of Unsöld[1c] makes it appear plausible that an optical transition between the two separated level sets can be handled as though each were nondegenerate. The reason is that within the limit of the uncertainty principle the degenerate levels do form a single level even after they have been split by the perturbation.

To see this we remember that the adiabatic hypothesis for transitions between the originally degenerate states of one energy level breaks down when the reverse of (2.16) is true, *viz.*

$$|E_l-E_m|\,\tau_p\hbar^{-1}\ll 1.$$

This implies that the energy uncertainty in the system, of the order of $\hbar/\tau_p$, exceeds the discrete energy shifts due to the instantaneous perturbation $|E_l-E_m|$. The states which are split by the field are therefore not revealed individually through radiation processes involving them since they overlap in energy by large amounts and form what amounts to a single diffuse energy band.

The use of the impact theory when coupled with the suggestion of Unsöld is roughly equivalent to a procedure which takes account of the diffuseness in energy of these states by solving the time-dependent perturbation equations for the probabilities of states formed through quantum transitions that are caused by the collisions. Foley[8d] and Kolb[22] have done this using the classical-path assumption, while Kivel, Bloom, and Margenau,[13] and also Landwehr[23] have carried through the calculation without this assumption.

[20] E. Lindholm, dissertation, Upsala, 1942.

[21] J. H. Van Vleck and H. Margenau, Phys. Rev. **76**, 1211 (1949).

[22] A. Kolb, Thesis, University of Michigan, 1957.

[23] G. Landwehr, Thesis, Yale University, 1956 (unpublished).

In conclusion we call attention to an early calculation by D. Blochinzew[24] who investigated the transition from diabatic to adiabatic behavior of an atom perturbed by a harmonic electric field, $E_0 \cos\omega t$.

C. Construction of Wave Packets

Since the classical-path assumption (Sec. IIA) is not always easy to justify for electron-broadening applications, we discuss this problem in quantum terms.

How can the state function of the perturbing electron be constructed? Inequality (2.9b) is the necessary condition for success of the Born approximation, which is so useful in scattering theory. But (2.9b) is normally satisfied for the plasma electrons, and as (2.9a) leads to (2.10), so (2.9b) leads to its contrary which can roughly be written $\rho \gg \rho_c$. Therefore, when densities are very low and encounters as close as the critical radius are rare, conditions under which one ordinarily employs a plane wave in describing the perturbing electron seem to be satisfied. Nevertheless, the plane wave description, which has received extensive use in problems where collimated beams of particles are directed at scattering centers, is inappropriate to our problem for several reasons.

First, we are here concerned with a single electron encountering the radiator, or, as the density is increased sufficiently, with a number of electrons statistically distributed in momenta and acting simultaneously on the radiator. The single electron hardly acts like a plane wave because the latter is stationary throughout the radiation time, and where in reality the electron has a spectrum of momenta the plane wave possesses a single value. Furthermore, the plane wave does not yield any momentary asymmetry in the charge distribution about the radiator, a situation which practically eliminates the possibility of a Stark effect.[11a] As a description of the many-electron perturbation the plane wave has similar disadvantages for the treatment of broadening, except that in this case the assumption of stationarity of the perturbation is more acceptable. At large densities one would expect the fluctuations in the perturbation to be small and the plane wave picture to become more accurate.

In stellar atmospheres where $n \approx 10^{13}$/cc, the critical radius is only about 10^{-4} times the Debye cutoff at temperatures between 5×10^3 and 10^4 °K. Thus we might expect something like single impacts by the electrons, and strong objections to the use of a plane wave for the electron must arise. For such cases Margenau and Kivel[17] employed a wave packet state function. For simplicity, they construct wave packets in one dimension and determine the width of the packet from the condition of thermal equilibrium.

The quantum-statistical density matrix for the system in a volume V and for states labelled by wave numbers κ and κ', is taken to be

$$S_{\kappa,\kappa'} = P_\kappa \delta_{\kappa,\kappa'},$$
$$P_\kappa = \frac{(2\pi mkT)^{\frac{1}{2}}}{V^{\frac{1}{3}}} \exp\left[-\frac{\hbar^2\kappa^2}{2mkT}\right], \tag{2.20}$$

and the wave packet is defined by

$$\psi(x,t) = \textstyle\sum_\kappa C(\kappa,t) e^{i\kappa x}. \tag{2.21}$$

Correspondence is established between the description (2.20), which is a stationary mixed case, and (2.21), which is a nonstationary pure case, by equating expectation values for the momenta

$$P_\kappa = |C(\kappa,t)|^2, \tag{2.22}$$

This procedure yields the amplitudes but not the phases of the coefficients $C(\kappa,t)$. These are chosen on the basis of a physical argument. If the collision occurs at the time $t=0$, then because at this instant the electron involved in collision has a maximum energy uncertainty, the packet should have its minimum concentration about the radiator at that time. But minimum concentration means equality of all phases, i.e., $P_\kappa = C(\kappa,0)^2$. From (2.22) and (2.21) one then finds (upon carrying out the summation over κ as an integration)

$$\psi(x,0) \leq \exp[-mkTx^2/\hbar^2], \tag{2.23}$$

which represents a Gaussian probability packet whose width is equal to $\hbar/(2mkT)^{\frac{1}{2}}$. This is precisely the mean momentum of the ensemble described by (2.20), and the *diffusion* velocity of this packet is, satisfying enough, the *root-mean-square velocity* of the ensemble. The action of such an electron is to squeeze itself about the atom at the instant of collision and then to diffuse away again after the impact time. More general wave packets of this type, centered about points distant from the radiator and having finite mean momenta, so that they move bodily and diffuse, are even better representations of the electron which may be of assistance in broadening calculations. A paper by the present authors[25] shows how the classical formula for Stark broadening arises out of a wave packet treatment as the wave packets become more and more concentrated.

D. Summary and Appraisal

Section II has dealt with rather basic and intricate matters, and has led to some slightly surprising conclusions which, if true, restrict the validity of classical approaches more severely than might have been anticipated. It may also seem amazing that inequalities of the form $\Delta\varphi > 1$ and $\Delta\varphi < 1$ decide so many different issues. The first defines the range of validity of the classical-path description as well as the domain of adiabaticity (in the case of degeneracy). We also meet

[24] D. Blochinzew, Physik. Z. Sowjetunion 4, 501 (1933).

[25] H. Margenau and M. B. Lewis, Phys. Rev. **106**, 244 (1957).

it again in Sec. IV, as a criterion for the correctness of statistical theories.

The typical structure of the arguments used in this chapter is the following. We carefully specified conditions under which certain conclusion (e.g., "The classical path is a valid assumption") are true. Then we said, quite without logical justification, that when the conditions are violated the conclusion will not be true. All we should have said is that we did not prove it to be true. We did not investigate the conclusions of more general conditions, and have, therefore, no assurance that more general premises will not lead to the interdicted conclusions. Hence all inequalities here encountered are permissive, are sufficient conditions, and mean to say that, under their terms, the type of description in question is certainly adequate. They do not strictly rule out the possibility that the description may be appropriate even when the inequality fails. The logic outlined is not peculiar to our treatment but characterizes most of the arguments found in the literature. They provide guides, but no final solutions.

Fortunately, the criterion derived for classical-path description is at times too limited. But there is no way of discovering this, or of assuring it, short of proceeding with more general premises. This means actually starting with quantum theory in the initial phases of the calculation to show that such treatment does, in fact, yield the same results as the classical-path description.

III. HOLTSMARK THEORY

A. Review of Conventional Treatment

The oldest and, within its limits, most successful theory of line broadening by the particles of a plasma is Holtsmark's; it treats the diffusion of intensities within a line as if each part of the line arose from a Stark effect caused by the electric field associated with a temporary configuration of the moving ions. Most of the older review articles and newer texts deal with this theory in considerable detail; we, therefore, merely sketch its features and develop as much as is needed for present purposes.

A simple approximation gives the frequency distribution at large distances from the line center extremely well. This takes into consideration only close binary encounters between the radiating atom and one ion, leaving out of account the numerous—and therefore highly probable—collaborative but weaker perturbations of many ions further away. Thus it falsifies the center but describes adequately the wings of the line. We call this approximation the *binary* form of the Holtsmark theory and present it as follows.

Selecting the radiating atom as center, we describe a sphere of radius r about it. Denote by $P(r)$ the probability that there is at least one ion within it. To obtain $P(r)$ we first focus attention on its complement $P_-(r)$, namely, the probability that there shall be *no* particles at all within r. Clearly, $P(r)=1-P_-(r)$. By the laws of combination of probabilities,

$$P_-(r+dr)=P_-(r)\cdot p_-, \tag{3.1}$$

where p_- is the probability that there be no ion between r and $r+dr$. But we know p_-: it is 1 less the probability for the presence of particles, one or more, within the shell dr. Hence, if n is the number density of ions,

$$p_-=1-4\pi nr^2dr-(4\pi nr^2dr)^2-\cdots,$$

and the powers of dr beyond the first, which represent the probabilities for the occurrence of 2, $3\cdots$ particles in dr, can be omitted for sufficiently small dr. Thus Eq. (3.1) takes the form

$$P_-(r)+P_-'(r)dr=P_-(r)[1-4\pi nr^2dr],$$

whence on integration $P_-(r)=C\exp[-(4\pi/3)nr^3]$. The constant C must be adjusted so that $P_-(0)=1$ and is therefore 1. Hence $P(r)=1-\exp[-(4\pi/3)nr^3]dr$ and the probability that the shell contain at least one ion is

$$dP(r)=4\pi nr^2\exp[-(4\pi/3)nr^3]dr. \tag{3.2}$$

It is also apparent that this is the *nearest* ion, for the factor $4\pi nr^2dr$ expresses the indiscriminate likelihood of the presence of an ion between r and $r+dr$, while the factor $\exp[-(4\pi/3)nr^3]$ conjoins it with the condition that there be *no* ion *within* r. The latter factor is often insignificant numerically and is sometimes omitted; however, it is necessary if P is to be correctly normalized. Equation (3.2) leads to $\int_0^R dP(r)=1-e^{-N}\to 1$ if R is the volume containing $N=n(4\pi/3)R^3$ particles, whereas $\int_0^R 4\pi nr^2dr=N$.

Introducing the abbreviation

$$(4\pi/3)n=r_0^{-3}. \tag{3.3}$$

Equation (3.2) may be written

$$dP(r)=\exp[-(r/r_0)^3]d(r/r_0)^3. \tag{3.4}$$

The distance r_0 thus defined is the radius of a sphere whose volume equals the mean volume per ion; it is a little smaller than the mean distance between ions, $n^{-\frac{1}{3}}$.

Equation (3.4) is the probability distribution in r. Since a given r defines an electric field, F, and an electric field defines a frequency displacement via the Stark effect, that equation also represents the distribution of the last two quantities. F is given by $F=Ze/r^2$; so substitution $r^2=Ze/F$ in (3.4) converts it to a probability distribution in F

$$\begin{aligned}dP(F)&=\exp[-(F_0/F)^{\frac{1}{2}}]d(F_0/F)^{\frac{1}{2}}\\&=(3/2F)(F_0/F)^{\frac{1}{2}}\exp[-(F_0/F)^{\frac{1}{2}}]dF.\end{aligned} \tag{3.5}$$

Here $F_0=Ze/r_0^2$, and the minus sign was inserted in order that the normalization be correct relative to F, not F_0/F. That is to say, the normalization is such that

$$\int_0^{F=\infty} dP(F)=1.$$

In the *linear* Stark effect,

$$\Delta\omega = sF,$$

s being a constant. Writing $\Delta\omega_0 = sF_0$, Eq. (3.5) leads to

$$dP(\Delta\omega) = -\exp\left[-\left(\frac{\Delta\omega_0}{\Delta\omega}\right)^{\frac{3}{2}}\right] d\left(\frac{\Delta\omega_0}{\Delta\omega}\right)^{\frac{3}{2}}$$

$$= \frac{3}{2\Delta\omega}\left(\frac{\Delta\omega_0}{\Delta\omega}\right)^{\frac{3}{2}} \exp\left[-\left(\frac{\Delta\omega_0}{\Delta\omega}\right)^{\frac{3}{2}}\right] d(\Delta\omega). \quad (3.6)$$

By the fundamental assumption of the statistical theory $dP(\Delta\omega)$ is identical with the intensity distribution:

$$dP(\Delta\omega) = I(\Delta\omega)d(\Delta\omega). \quad (3.7)$$

Hence,

$$I(\Delta\omega) = \frac{3}{2\Delta\omega}\left(\frac{\Delta\omega_0}{\Delta\omega}\right)^{\frac{3}{2}} \exp\left[-\left(\frac{\Delta\omega_0}{\Delta\omega}\right)^{\frac{3}{2}}\right]. \quad (3.8)$$

In the *quadratic* Stark effect,

$$\Delta\omega = tF^2, \quad \Delta\omega_0 = tF_0^2,$$

t being another constant. When this is substituted in (3.5) we obtain, again with the use of (3.7),

$$I(\Delta\omega) = \frac{3}{4\Delta\omega}\left(\frac{\Delta\omega_0}{\Delta\omega}\right)^{\frac{1}{2}} \exp\left[-\left(\frac{\Delta\omega_0}{\Delta\omega}\right)^{\frac{3}{2}}\right]. \quad (3.9)$$

The "normal" frequency $\Delta\omega_0$, though denoted by the same symbol, has different values in the linear and the quadratic Stark effect.

The foregoing elementary considerations, which yield the binary approximations to the intensity distribution Eqs. (3.8) and (3.9), have been superseded by the work of Holtsmark,[26] Verwey,[27] Schmaljohann,[28] and others, who included the cooperative effect of many ions. Their results are most easily derived by a method introduced by Markoff, a good presentation of which is available in a review by Chandrasekhar[5] while its application to other line-width problems is to be found in reference 2e. The treatment under review ignores the Boltzmann factor which attaches to the configuration probability of the moving ions. Effects of this simplification are considered later.

The field F, which appears in Eq. (3.5), must here be written as a vector sum when it is compounded from the fields of many ions in different places:

$$F = |\textstyle\sum_i \mathbf{F}_i|. \quad (3.10)$$

The analysis leading to (3.5) must be carried out in a configuration space of $3N$ dimensions. In place of (3.5),

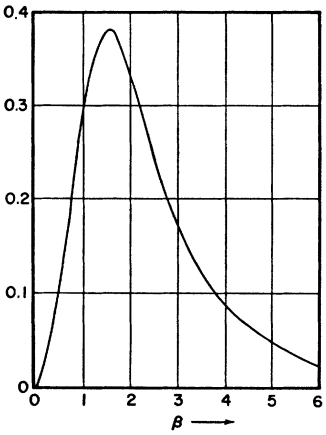

FIG. 2. Graph of $W(\beta)$ *vs* β. See Eq. (3.11b).

it yields

$$dP(F) = W(\beta)d\beta; \quad \beta = F/F_0, \quad (3.11a)$$

$$W(\beta) = \begin{cases} (4/3\pi)\beta^2(1-0.463\beta^2+0.1227\beta^4\cdots) \\ 1.496\beta^{-\frac{5}{2}}(1+5.107\beta^{-\frac{3}{2}}+14.93\beta^{-3}+\cdots). \end{cases} \quad (3.11b)$$

The two alternate expressions are useful for small and large values of β, respectively. Near $\beta=3$, both series converge slowly. According to Schmaljohann and Unsöld $W(3)=0.175$; $W(3.5)=0.122$. In Fig. 2, the function $W(\beta)$ is plotted, showing that

$$\lim_{\beta\to\infty} W = 1.496\beta^{-\frac{5}{2}} = 1.496\left(\frac{F_0}{F}\right)^{\frac{5}{2}}.$$

This is very nearly the same as the limit of Eq. (3.5),

$$\lim_{\beta\to\infty} \frac{dP(F)}{dF}\frac{dF}{d\beta} = \frac{3}{2}\left(\frac{F_0}{F}\right)^{\frac{5}{2}},$$

as asserted earlier.

These statements are not quite correct. In the binary theory F_0 was defined as

$$Ze/r_0^2 = Ze[(4\pi/3)n]^{\frac{2}{3}} = 2.60eZn^{\frac{2}{3}}.$$

The many-ion calculation involves a slightly different parameter,

$$F_0 = 2.61Zen^{\frac{2}{3}},$$

but the change is so small that its importance is quite academic, so we do not trouble to alter notation because of it.

From Eqs. (3.11) we pass to the frequency distribution in the same way as before. In the linear Stark effect $\Delta\omega/\Delta\omega_0 = F/F_0 = \beta$, and since in general

$$I(\Delta\omega)d(\Delta\omega) = W(\beta)d\beta, \quad (3.12)$$

we find

$$I(\Delta\omega) = W(\Delta\omega/\Delta\omega_0)(1/\Delta\omega_0). \quad (3.13)$$

In the *qradratic Stark effect*

$$(\Delta\omega/\Delta\omega_0)^{\frac{1}{2}} = F/F_0 = \beta,$$

[26] J. Holtsmark, Ann. Physik **58**, 577 (1919); Physik Z. **20**, 162 (1919); **25**, 73 (1924).
[27] S. Verwey, Dissertation, Amsterdam, 1936.
[28] P. Schmaljohann, Staatsexamens-Arbeit, Keil, 1936. For comments on this and reference 27, see reference 18, p. 308 ff.

and Eq. (3.5) gives

$$I(\Delta\omega)=W[(\Delta\omega/\Delta\omega_0)^{\frac{1}{2}}]\cdot\tfrac{1}{2}(\Delta\omega_0\cdot\Delta\omega)^{-\frac{1}{2}}. \quad (3.14)$$

The connection between the preceding considerations and what was described in Sec. I as a statistical theory is not altogether clear. For here, we calculate the probability of *fields* and make the passage to an intensity distribution via the Stark effect, whereas the statistical quantum theories fix attention upon the probability of a given *energy perturbation* ϵ, a scalar quantity, and identify this probability with the line intensity at $\hbar\Delta\omega$. Equivalence of the two procedures is intuitively expected. Margenau and Meyerott,[11a] who made a quantum mechanical calculation using the binary approximation for the L_α line of hydrogen, indicate how the equivalence comes about mathematically. Among other things ϵ is not the sum, $\sum_i \epsilon_i$ for individual perturbers but is composed very much like $\mathbf{F}$ from the vectors $\mathbf{F}_i$; hence the Holtsmark theory does not depart from the statistical pattern.

This treatment includes the effect of the nonuniformity of the Stark field produced by ions. In the ordinary theory of the Stark effect, $\mathbf{F}$ is treated as a constant, whereas the ions produce a field which depends on r, the dependence being greater the smaller r. In general the nonuniformity effect is small, increasing in magnitude with ion density, $W(\beta)$ as given by (3.11b) no longer has the asymptotic form $1.5\,\beta^{-\frac{5}{2}}$, but $1.5\,(\beta^{-\frac{5}{2}}+2\beta^{-2}a'/r_0)$, a' being the radius of the lower atomic state (first Bohr radius for L_α). The nonuniformity also causes shifts and widths in Stark components which do not show a first-order effect, the "forbidden" half-widths being of the order a'/r_0 times the regular Holtsmark widths.

B. Effect of Perturber Interactions

In part (A) of this section the probability of a given ion configuration was taken to be proportional to the volume of configuration space assignable to it, the Boltzmann factor $\exp[-V(\mathbf{r}_1,\mathbf{r}_2\cdots,\mathbf{r}_N)/kT]$ being neglected. This factor confers smaller weight upon configurations in which several ions are close together and therefore reduces the probability that many ions shall be situated near the radiating atom. Hence the Holtsmark theory overestimates the likelihood of strong perturbations and therefore the intensity in the wings of a line.

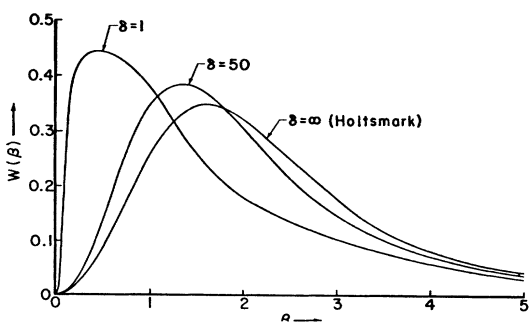

FIG. 3. Graph of $W(\beta)$ for different values of δ.

An accurate calculation with inclusion of the Boltzmann factor has not been made. Broyles[29] considers the problem most carefully, but his results are relevant primarily for the case where the radiator, too, is ionized and repels the perturbing ions by a Coulomb field of its own. His results are examined in the next section. Here we summarize a contribution by Ecker,[30] which deals directly with the problem. He relies upon the Debye-Hückel screening mechanism to provide a semiquantitative solution, which introduces the electrons as well as the ions into the picture.

In the presence of a cloud of ions and electrons the Coulomb field produced by an ion is given by

$$\mathbf{F}=(Ze\mathbf{r}/r^2)[(1/r)+(1/D)]e^{-r/D},$$

as may be seen by differentiating the expression for V, Eq. (5.4). According to (5.5),

$$D=[kT/4\pi ne^2(1+Z^2)]^{\frac{1}{2}}.$$

Analysis of the line-broadening problem even with this simplified potential remains formidable; Ecker chooses as an approximation to $\mathbf{F}$ the form§

$$\mathbf{F}=\begin{cases} Ze^2\mathbf{r}/r^3 & \text{if } r<D \\ 0 & \text{if } r\gtrsim D. \end{cases}$$

Machine computation by the method of part (A) leads to a dependence of the line shape on the parameter

$$\delta=(4\pi D^3/3)n,$$

whose physical meaning is the number of ions within the Debye radius D. Clearly, if $D\to\infty$, the result must agree with Holtsmark's. Figure 3 shows the results of Ecker's calculations for three values of δ. The expected effect, reduction of the intensity in the wing is clearly in evidence.

In principle, a further correction must be made in the Holtsmark distribution. The Debye-Hückel cutoff modifies the effective field at large r. For small r, the Coulomb field breaks down because of *atomic* screening, the potential going to a finite value as $r\to 0$. The theory of this effect is easily developed[31] and predicts a flattening of the Holtsmark curve far from the center of the line. In the region affected, the frequency is pro-

[29] A. A. Broyles, Phys. Rev. **100**, 1181 (1955).
[30] (a) G. Ecker, Z. Physik **148**, 593 (1957); (b) **149**, 254 (1957); (c) Z. Naturforsch. **12**, 346, 517 (1957).
§ A calculation of the shielding correction which avoids this cutoff was made by H. Hoffman and O. Theimer, Astrophys. J. **127**, 477 (1958). Ecker (private communication) has performed a careful machine calculation based on the correct potential and obtains results in substantial agreement with his former approximation and differing from those of Hoffman and Theimer.
[31] H. Margenau, Progress Report AF-18 (603)-15, January 1958.

portional approximately to β^{-1}, not to $\beta^{-\frac{1}{2}}$. But this region lies so far outside the measured range of line widths (hundreds of angstroms for the Balmer lines, as a simple estimate, based on the assumption that the breakdown radius is of atomic dimensions, shows) that this correction is at this time academic.

C. Treatment for Radiating Ions

The analysis leading to Eq. (3.5) is further defective in assuming no potential energy between the moving ions, and none between the radiating atom and the ions. The former is always present but has ordinarily no very profound effect on the frequency distribution. The second potential energy is present when the radiator itself is ionized; in that case its effect is more important. Attention has been called to these shortcomings by Mayer[32] and Broyles,[29] whose interest is primarily in highly ionized exploding plasmas where the ions themselves emit the lines. A completely adequate theory of these effects is not at hand. We develop here first the binary approximation to the many-ion analysis and compare the results with Eq. (3.4). (Our development completes somewhat the treatment of the aforenamed authors who omitted the condition that there be no ion within r and obtained an unnormalized distribution.)

The perturbing ion of charge Z_2e will repel the radiating ion of charge Z_1e with the Coulomb energy $Z_1Z_2e^2/r$. The former p_- will then be $1-4\pi ne^{-a/r}r^2dr$, provided

$$a=(Z_1Z_2e^2)/(kT). \tag{3.15}$$

In place of (3.2) we obtain

$$dP(a,r)=4\pi n\exp[(-a/r)-4\pi nA(a,r)]r^2dr, \tag{3.16}$$

where

$$A(a,r)=\int_0^r e^{-a/r}r^2dr. \tag{3.17}$$

Hence, the ratio of (3.16) to the Holtsmark distribution (3.4) is

$$\begin{aligned}S&=dP(a,r)/dP(0,r)\\&=\exp\{-(a/r)+4\pi n[A(0,r)-A(a,r)]\}.\end{aligned} \tag{3.18}$$

The function $A(a,r)$ is easy to calculate; it may be written

$$\begin{aligned}&A(a,\xi a)=\tfrac{1}{3}a^3\mathfrak{F}(\xi);\\&\mathfrak{F}(\xi)\equiv(\xi^3-\tfrac{1}{2}\xi^2+\xi)e^{-1/\xi}+\tfrac{1}{2}Ei(-1/\xi).\end{aligned} \tag{3.18a}$$

the function $\mathfrak{F}$ is plotted in Fig. 4. Clearly,

$$A(0,r)=r^3/3.$$

For the binary approximation to be valid, the ratio $(r_0/r)^2=\beta$ must be greater than about 7. On the other hand, $r_0=0.62n^{-\frac{1}{3}}$. The last results, then, begin to be useful at values of r in the neighborhood of $1/4n^{-\frac{1}{3}}$ and remain so for smaller radii. At this critical distance, Eq. (3.18) becomes

$$S=\exp\left\{-4an^{\frac{1}{3}}+\frac{\pi}{48}-\frac{4\pi}{3}na^3\mathfrak{F}\left(\frac{1}{4an^{\frac{1}{3}}}\right)\right\}. \tag{3.19}$$

The terms in the exponent become important when $an^{\frac{1}{3}}\approx 1$. This is the condition for equality of mean kinetic energy and Coulomb energy at the mean distance of separation of the ions.

If $4an^{\frac{1}{3}}=0.1$, $S=e^{-0.09}$, the value of $\mathfrak{F}(10)$ being 845. For $4an^{\frac{1}{3}}=1$, $S=e^{-0.952}$ (since $\mathfrak{F}(1)=0.258$), and for larger values of $4an^{\frac{1}{3}}$ only the term $\exp(-4an^{\frac{1}{3}})$ of S remains, the others being negligible.

In the light of these numerical results we consider two cases, first the perturbation of singly ionized helium atoms by protons in a star or a discharge plasma. Here $Z_1=Z_2=1$. The condition that the binary approximation be significant, namely $r<0.62n^{-\frac{1}{3}}$, is easily compatible with the requirement that r be greater than a helium ion, $r>5\times10^{-9}$ cm, since these inequalities merely imply $n<10^{24}$ cm^{-3}. But to have S appreciably smaller than 1, $an^{\frac{1}{3}}$ must be near 1. This means that $T\approx(e^2/k)n^{\frac{1}{3}}=1.7\times10^{-3}n^{\frac{1}{3}}$ °K, which can occur in a shock front or in an arc.

The situation is quite different for atomic explosions. At amosphere of iron ions, each with $Z=23$, and with $T\approx10^7$ °K implies $a=8.4\times10^{-8}$ cm. At normal density

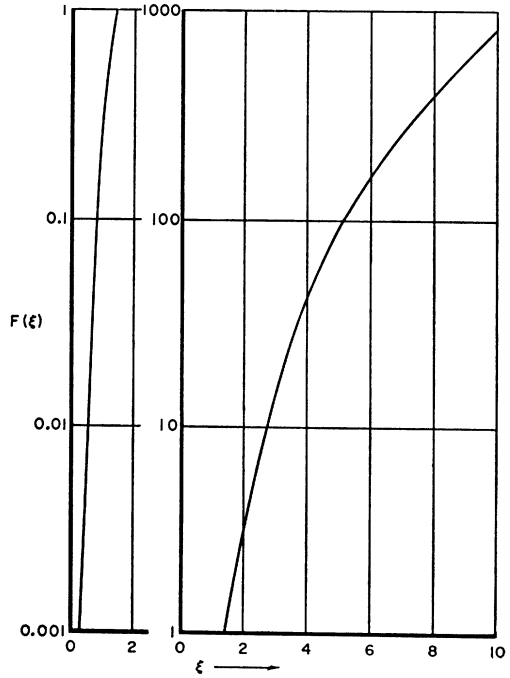

FIG. 4. Graph of $F(\xi)$ *vs* ξ. See Eq. (3.18a).

[32] H. Mayer, Los Alamos Scientific Laboratory Report LA-647, 1947.

$n \approx 10^{23}$ cm^{-3} and the condition upon r is $r < 10^{-8}$ cm. Because of the small size of the iron core this leaves a considerable range in which the binary approximation is correct. Indeed at $r = 1/4n^{\frac{1}{3}}$, for which (3.19) was computed $S \approx 10^{-15}$, indicating that the Holtsmark formula is enormously in error.

We now treat the many-ion problem[33] using the following model: the free electrons form a uniformly smeared out negative charge, and interactions are considered only between the radiating ion and the plasma ions; interaction between plasma ions themselves is ignored. This method avoids some uncertainties inherent in the approximations using the Bohm-Pines approach (see the following), for the approximations are clear in their physical meaning and the analysis is otherwise exact.

With this model, the probability $P(\mathbf{F})$ for an electric field F is given by

$$P(\mathbf{F}) = \frac{\int \cdots \int \exp(-a \sum_{i \to N} r_i^{-1}) \delta(\mathbf{F} - \sum_{i \to N} Q_2 \mathbf{r}_i / r_i^3) d\mathbf{r}_1 \cdots d\mathbf{r}_N}{\int \cdots \int \exp(-a \sum_i r_i^{-1}) d\mathbf{r}_1 \cdots d\mathbf{r}_N}, \tag{3.20}$$

where a is defined by Eq. (3.15). Equation (3.20) can be written in a more convenient form, best obtained through use of Chandrasekhar's method.[5] As before, we denote by $W(\beta)$ the probability of finding a field of strength $\beta = F/F_0$ [see Eq. (3.11a)]

$$F_0 = 2.61 Z_2 e n^{\frac{2}{3}}.$$

F_0 is the quantity introduced previously and represents essentially the field produced on one ion by another ion at the average spacing between ions, and n is the number density of ions. Then

$$W(\beta) = \frac{2}{\pi\beta} \int_0^\infty \exp\left[-\left(\frac{x}{\beta}\right)^{\frac{3}{2}} \eta\right] x \sin x dx, \tag{3.21}$$

$$\eta = \frac{15}{8}\left(\frac{2}{\pi}\right)^{\frac{1}{2}} \int_0^\infty dz z^{-7/2}(z - \sin z) \times \exp\left[-\alpha z^{\frac{1}{2}} \left(\frac{\beta}{x}\right)^{\frac{1}{2}}\right], \tag{3.22}$$

and $\alpha = [Z_1 e (Z_2 e)^{\frac{1}{2}} (kT)] F_0^{\frac{1}{2}}$.

In the limit of large β, the leading term in Eq. (3.21) is the same as that of the binary theory given before [see Eq. (3.16)]. $W(\beta)$ can be computed directly from Eqs. (3.21) and (3.22). However, for certain ranges of α ($\alpha \ll 1$ and $\alpha \gg 1$) the form of $W(\beta)$ can be simplified.

Case 1: $\alpha \ll 1$, $\alpha\beta^{\frac{1}{2}} \ll 1$.

In this case η can be expanded in the ratio $y = x/\beta$:

$$\eta = 1 - c_1 \alpha y^{-\frac{1}{2}} + c_2 \alpha^2 y^{-1} \cdots, \tag{3.23}$$

where

$$c_1 = \frac{15}{16}\left(\frac{\pi}{2}\right)^{\frac{1}{2}}, \quad c_2 = \frac{5}{4}.$$

$W(\beta)$ then becomes

$$W(\beta) = \frac{2}{\pi\beta}\left[I_0(\beta) + \alpha c_1 I_1(\beta) + \alpha^2\left(\frac{c_1^2}{2} I_2(\beta) - c_2 I_{\frac{1}{2}}(\beta)\right) + \cdots\right],$$

where

$$I_p(\beta) = \int_0^\infty \exp\left[-\left(\frac{x}{\beta}\right)^{\frac{3}{2}}\right] x \left(\frac{x}{\beta}\right)^p \sin x dx. \tag{3.24}$$

It is seen that $(2/\pi\beta) I_0(\beta)$ is the Holtsmark distribution, to which Eq. (3.24) reduces in the limit, $T \to \infty$ ($\beta \to 0$).

The integrals in Eq. (3.24) can be expanded in a series and evaluated for $\beta \leqslant 3$ and $\beta \geqslant 6$. The range from 3 to 6 is difficult because of the slow convergence of the series. The coefficients of the first two terms in Eq. (3.24) are listed in Table III.

Case 2: $\alpha \gg 1$, $\beta \ll \alpha$.

For this case, η is expanded in an asymptotic series in y:

$$\eta = \frac{15}{4}\left(\frac{2}{\pi}\right)^{\frac{1}{2}}\left(\frac{1}{3!} y^{\frac{1}{2}} \alpha^{-1} - \frac{4!}{5!} y^{\frac{3}{2}} \alpha^{-5} + \frac{8!}{7!} y^{9/2} \alpha^{-9} - \cdots\right). \tag{3.25}$$

If only the first term is retained, one finds

$$W(\beta) = \frac{\alpha^{\frac{3}{2}} \beta^2 \exp(-\beta^2 \alpha (2\pi)^{\frac{1}{2}}/5)}{2\pi^{\frac{1}{2}}[(5/8)(2/\pi)^{\frac{1}{2}}]^{\frac{3}{2}}} = \frac{\alpha^{\frac{3}{2}} \beta^2 \exp[-0.5\alpha\beta^2]}{1.25}. \tag{3.26}$$

Equation (3.26) is identical with a formula proposed by Mayer[32] on the basis of a different, simpler physical

TABLE III. Coefficients of the first two terms of Eq. (3.24). Values of $(2/\pi\beta) I_0(\beta)$ from reference 5.

β	$(2/\pi\beta) I_0(\beta)$	$(2/\pi\beta) c_1 I_1(\beta)$
0.1	0.004225	0.00745
0.6	0.129598	0.21264
1.0	0.271322	0.3860
2.0	0.33918	0.1791
3.0	0.176	−0.08707
6.0	0.02417	−0.0507
8.0	0.01038	−0.0273
10.0	0.00556	−0.0168

[33] M. B. Lewis and H. Margenau, Phys. Rev. **109**, 842 (1958).

model. Why the two models lead to the same result is not clear.

Broyles[29] has proposed another way of computing the probability $P(F)$ of finding an electric field of magnitude F at a radiating *ion* in a plasma. He uses the method of Pines and Bohm[34] to separate the potential energy and the electric field into a short and a long-range component.

The work is based on a model in which the free electrons are represented as a uniformly smeared out negative charge. The following units are used: unit length is the radius of a sphere whose volume is the volume per ion r_0; unit field strength is F_0, and unit energy is that of two ions separated by unit distance, and the temperature is expressed in the above energy units.

The probability density for occurrence of a field β is [see Eq. (3.11a) for definition of β] in analogy to Eq. (3.20),

$$P(\beta)=\frac{\int\cdots\int \exp(-V/\theta)\delta(\beta-\sum_i \mathbf{r}_i/r_0^3)d\mathbf{r}_1\cdots d\mathbf{r}_N}{\int\cdots\int \exp(-V/\theta)d\mathbf{r}_1\cdots d\mathbf{r}_N}, \tag{3.27}$$

provided V is the potential energy, and δ the Dirac "function." On using the Dirichlet representation for δ one obtains

$$P(\beta)=(2\pi)^{-3}\int T(\mathbf{l})\exp(i\beta\cdot\mathbf{l})d\mathbf{l}, \tag{3.28}$$

$$T(\mathbf{l})\equiv\frac{\int\cdots\int \exp[-(V/\theta)+i\mathbf{l}\cdot\sum_j \mathbf{r}_j/r_j^3]d\mathbf{r}_1\cdots d\mathbf{r}_N}{\int\cdots\int \exp(-V/\theta)d\mathbf{r}_1\cdots d\mathbf{r}_N}.$$

Since $P(\beta)$ depends only on the magnitude of β we have

$$W(\beta)=4\pi\beta^2P(\beta). \tag{3.29}$$

We now employ the Pines-Bohm method to split the potential energy and the electric field into short and long-range components. The *ion* charge density ρ_i is written as

$$\rho_i=\sum_j \delta(\mathbf{r}-\mathbf{r}_j). \tag{3.30}$$

But the total charge density ρ can be expanded into a Fourier series (unit volume per particle) to give

$$\rho=\sum_k{}' \rho(\mathbf{k})\exp(i\mathbf{k}\cdot\mathbf{r}), \tag{3.31}$$

with

$$\rho(\mathbf{k})=\sum_j \exp(-i\mathbf{k}\cdot\mathbf{r}_j),$$

where the prime indicates the omission of $k=0$ from the sum in order that the net charge be zero. The potential and the electric field when expressed as functions of k can each be written as a sum of two terms, one for high and one for low values of k. The high k terms are functions of the individual $\mathbf{r}_i$ and are referred to as the particle or short-range part, the low k terms are expressible as functions of the $\rho(\mathbf{k})$ and are called the wave or long-range part of the respective quantity. With this separation, $T(\mathbf{l})$ can likewise be approximated in consistent fashion; it becomes a product of T_w (wave parts) and T_p (particle part). The wave part can easily be evaluated; the particle part is approximated by Broyles in two ways:

(1) Short-range central interactions (SRCI). In this approximation only the interactions between the radiating ion and the perturbing ions are retained, the interactions among the perturbing ions being neglected. This approximation is similar to the one in the previous section, except that it was there applied to the full Coulomb interactions of the ions whereas it is here restricted to the short range components which arise in the Bohm-Pines method.

(2) Short-range nearest neighbor (SRNN) interactions. Interactions are considered only between the radiating ion and its nearest neighbor.

Broyles[29] has employed his method for iron ions at normal densities, with a charge of 23 electron charges at a temperature of 1 kev, a case already considered earlier in this section. This corresponds to $\theta=0.186$. Under these conditions, α as defined in the previous part of this section [Eq. (3.22)] has a value of 5.5. It is therefore possible to use Eq. (3.26) for $\beta\ll 5.5$. The error attending the use of Eq. (3.26) is less than 10% for $\beta=1$ and decreases for decreasing β. Table IV compares Eq. (3.26) with Broyles' SRNN for $0.3\leqslant\beta\leqslant 1.5$ A more detailed comparison is given in Fig. 2 of reference 29. The curve marked "simple harmonic oscillator" is the result of Mayer's calculation and is identical with Eq. (3.26).

A separate publication by Broyles[35] deals extensively with the approximations involved in using the Pines-Bohm method for this problem and devises an improved procedure[36] which is applicable for $\theta\geqslant 0.6$. It is concluded that $P(\beta)$ is rather well determined by the SRNN approximation for $\theta\geqslant 0.6$.

TABLE IV.

β	Eq. (3.26) $\alpha=5.5$	Broyles' SRNN; $\theta=0.186$
0.3	0.69	0.63
0.5	1.25	1.13
1	0.64	0.66
1.5	0.04	0.147

[34] D. Pines and D. Bohm, Phys. Rev. **85**, 338 (1952).

[35] A. A. Broyles, Phys. Rev. **105**, 347 (1957).

[36] A. A. Broyles, Atomic Energy Commission Report R.M.—1682.

IV. REFINED IMPACT THEORY. FUSION OF IMPACT AND STATISTICAL THEORIES

A. Impact Theory

A consistent and ingenious development of the impact method was carried out by E. Lindholm[8c,15b] who was preceded in several important respects by W. Lenz[8a] and G. Burkhardt.[37] In deriving Lindholm's results we use recent stochastic methods.

Let us return to Eq. (1.13), which represents the true line form, provided only the adiabatic hypothesis holds [see formula (1.11)]. The immediate problem is to calculate the correlation function C. To strip it of irrelevancies, we continue to suppose that the radiator has only two states, and that only one of these is occupied: $S_1=1$, $S_2=0$. We also omit subscripts. Then,

$$C(\tau)=\mu^2\int_{-\infty}^{\infty}e^{-i[\varphi(t+\tau)-\varphi(t)]}dt. \tag{4.1}$$

The phase φ is defined by (1.12). In that expression, E_l and E_m contain constant parts, E_l^0 and E_m^0, plus the perturbations. The constant parts contribute to φ_{lm} the amount $[(E_l^0-E_m^0)/\hbar]t\equiv\omega' t$, ω' being the normal frequency of the line. In this section, *we redefine φ (without changing notation) to mean only the variable part which is contributed by the perturbations*. As a result, we change Eq. (1.13a) to read

$$I(\omega)\propto\int d\tau e^{i(\omega-\omega')\tau}C(\tau). \tag{4.2}$$

Positive φ corresponds to a positive difference ΔE (upper state)$-\Delta E$ (lower state). There is some confusion on this point in the cited literature.

The quantity $\varphi(t+\tau)-\varphi(t)$ represents the perturbational phase change which has occurred in the interval $(t, t+\tau)$. The integrand in Eq. (4.1) is a time series in which this quantity changes from instant to instant t, and we are integrating over t. As is customary (ergodic hypothesis) the one time series is replaced by an ensemble of time series and the *time integral* is identified with an *ensemble average* (except for a constant factor). Thus

$$C(\tau)\propto\langle e^{-i\varphi(\tau)}\rangle_{\text{Av}}\equiv\int_{-\infty}^{\infty}e^{-i\varphi}P_\tau(\varphi)d\varphi, \tag{4.3}$$

where $P_\tau(\varphi)$ is the probability of a phase change φ in the interval τ. It is convenient to make the assumption characteristic of the impact approach, namely that the collisions are sudden and occur singly. The value of φ is then the sum of a whole number of individual phase changes φ_i, each associated with one collision. By the rules of probability, $P_\tau(\varphi)$ is related to the probability $P_\tau(k)$ that k collisions have taken place in τ, by

$$P_\tau(\varphi)=\sum_{k=0}^{\infty}P_\tau(k)\sum_{1,2\cdots k}\left[\prod_{j=1}^{k}P(\varphi_j)\right]\delta\left(\varphi-\sum_{j=1}^{k}\varphi_j\right) \tag{4.4}$$

and

$$P_\tau(k)=(\tau\nu_c)^k e^{-\nu_c\tau}/k!, \tag{4.5}$$

which is Poisson's law. As before, ν_c is the collision frequency $P(\varphi_j)$ the probability for the occurrence of a phase change of magnitude φ_j, and δ is the well-known Dirac "function" which may be replaced by its Dirichlet representation

$$\delta\left(\varphi-\sum_{j=1}^{k}\varphi_j\right)=\frac{1}{2\pi}\int_{-\infty}^{\infty}dy\exp\left[iy\left(\varphi-\sum_{1}^{k}\varphi_j\right)\right]. \tag{4.6}$$

The symbol $\sum_{1,2\ldots k}$ is meant as a summation over all $\varphi_1, \varphi_2, \cdots, \varphi_k$ in every factor that follows it. With the aid of (4.5) and (4.6), one may write Eq. (4.4) in the form

$$P_\tau(\varphi)=\frac{e^{-\nu_c\tau}}{2\pi}\int_{-\infty}^{\infty}dye^{iy\varphi}\sum_{k=0}^{\infty}\frac{\nu_c\tau}{k!}[\sum_j P(\varphi_j)e^{-iy\varphi_j}]^k,$$

and this may be expressed as

$$P_\tau(\varphi)=\frac{e^{-\nu_c\tau}}{2\pi}\int_{-\infty}^{\infty}dye^{iy\varphi+\nu_c\tau\alpha(y)}, \tag{4.7}$$

provided

$$\alpha(y)=\sum_j P(\varphi_j)e^{-iy\varphi_j}. \tag{4.8}$$

On substituting (4.7) in (4.3) we have

$$C(\tau)=\frac{e^{-\nu_c\tau}}{2\pi}\int_{-\infty}^{\infty}e^{-i\varphi}d\varphi\int_{-\infty}^{\infty}dye^{iy\varphi+\nu_c\tau\alpha(y)}$$

$$=e^{-\nu_c\tau}\int dye^{\nu_c\tau\alpha(y)}\left\{\frac{1}{2\pi}\int_{-\infty}^{\infty}e^{i(y-1)\varphi}d\varphi\right\}.$$

The factor { } is $\delta(y,1)$. Hence,

$$C(\tau)=e^{-\nu_c\tau[1-\alpha(1)]}. \tag{4.9}$$

This result is sufficient for many purposes and underlies most of the work on impact broadening. A generalization which allows the collision probability to depend on velocity, and which also gets rid of the usual assumption that the collisions are sudden and occur singly, is contained in Kolb's[22,38] report and is given below, following the lines of the preceding account. The result [Eq. (4.16)] is used in Sec. V.

Let us divide the time interval $(-\infty, \infty)$ into elements Δt_i. The phase change produced by *one* perturber in the time interval τ depends on the time of closest approach, the velocity v, and in general on some impact parameter l. Let us call this phase change $\varphi_{i,v,l}(\tau)$,

[37] G. Burkhardt, Z. Physik **115**, 592 (1940).

[38] A. C. Kolb, AFOSR-TN-57-8, Astia Document No. AD115-400.

where i refers to the time interval $\Delta\tau_i$ which contains the time of closest approach. If the perturbations are *scalarly additive*, the total phase change is

$$\varphi(\tau)=\sum_{iv}\varphi_{iv}(\tau),$$

where $\varphi_{iv}(\tau)$ is the phase change produced in the time interval τ by all perturbers described by (i,v). Clearly,

$$\varphi_{iv}(\tau)=\sum_{j=1}^{\mathfrak{N}(iv)}\varphi_{i,v,l_j}(\tau),$$

if $\mathfrak{N}(iv)$ is the number of perturbers characterized by (i,v) in some effective volume. We first compute $P(\varphi_{iv})$, the probability of a phase change φ_{iv} due to all perturbers in the class (i,v).

Assume that the effective volume of our system is a sphere of radius R and write $n(v)$ for the number per cubic centimeter of perturbers with velocity v (assumed at first to take on discrete values). We designate by $W(l)$ and $W[\mathfrak{N}(i,v)]$ the probability distributions for l and $\mathfrak{N}(i,v)$. The latter is given again by Poisson's distribution,

$$W[\mathfrak{N}(i,v)]=\frac{1}{\mathfrak{N}(i,v)!}(\nu_v\Delta t_i)^{\mathfrak{N}(iv)}e^{-\nu_v\Delta t_i}, \quad (4.10)$$

where ν_v is the collision frequency for particles with velocity v and is given by

$$\nu_v=\pi R^2vn(v). \quad (4.11)$$

We then have

$$P(\varphi_{i,v})=\sum_{\mathfrak{N}(iv)=0}^{\infty}\int_{l_1}\cdots\int_{l_{\mathfrak{N}(i,v)}}W[\mathfrak{N}(i,v)]\times\left\{\prod_{j=0}^{\mathfrak{N}(i,v)}W(l_j)dl_j\right\}\delta\left(\varphi_{iv}-\sum_{j=1}^{\mathfrak{N}(iv)}\varphi_{i,v,l_j}\right). \quad (4.12)$$

Again we replace the δ function by its Dirichlet representation

$$\delta(x-x')=\frac{1}{2\pi}\int_{-\infty}^{\infty}dye^{iy(x-x')}, \quad (4.13)$$

substitute (4.10) into (4.12) and obtain

$$P(\varphi_{iv})=\frac{1}{2\pi}\int_{-\infty}^{\infty}dy\exp\{iy\varphi_{iv}+\nu_v\Delta t_i[\alpha_{i,v}(y)-1]\}, \quad (4.14)$$

provided

$$\alpha_{i,v}(y)=\int W(l)e^{-iy\varphi_{iv}l}dl.$$

Now $P(\varphi)$ can be written

$$\int\cdots\int\left(\prod_{iv}P(\varphi_{iv})d\varphi_{iv}\right)\delta\left(\varphi-\sum_{iv}\varphi_{iv}\right).$$

On using Eqs. (4.13) and (4.14) this becomes, after rearrangement,

$$P(\varphi)=\frac{1}{2\pi}\int_{-\infty}^{\infty}e^{is\varphi}ds\left\{\prod_{iv}\int_{-\infty}^{\infty}dye^{\nu_v\Delta t_i[\alpha_{i,v}(y)-1]}\frac{1}{2\pi}\int d\varphi_{iv}e^{i\varphi_{i,v}(y-s)}\right\}.$$

The last integral is $\delta(y-s)$, so that

$$P(\varphi)=\frac{1}{2\pi}\int_{-\infty}^{\infty}e^{is\varphi}ds\prod_{iv}e^{\nu_v\Delta t_i[\alpha_{iv}(s)-1]}=\frac{1}{2\pi}\int_{-\infty}^{\infty}\exp\{is\varphi+\sum_{i,v}\nu_v\Delta t_i[\alpha_{i,v}(s)-1]\}ds.$$

$C(\tau)$ then becomes proportional to

$$\int_{-\infty}^{\infty}ds\exp\{\sum_{iv}\nu_v\Delta t_i[\alpha_{i,v}(s)-1]\}\cdot\frac{1}{2\pi}\int_{-\infty}^{\infty}d\varphi e^{i(s-1)\varphi}$$

and, therefore,

$$C(\tau)\propto\exp\{\sum_{i,v}\nu_v\Delta t_i[\alpha_{i,v}(1)-1]\}.$$

This finally can be written with the use of Eq. (4.4) and replacement of the sum by integrals, as

$$C(\tau)\propto\exp\left\{\int dv\int_{-\infty}^{\infty}dt\pi R^2vn(v)[\alpha_{t,v}(1)-1]\right\}. \quad (4.15)$$

We now apply this general formula to the special case of impacts. In this approximation, all collisions are assumed to be short enough so that those having their time of closest approach in τ are also completed in τ, and one may disregard the others. This means, in terms of $\varphi_{t,v,l}$, that

$$\varphi_{t,v,l}\begin{cases}=0 \text{ if } t \text{ is not in } \tau\\ =\varphi_{v,l} \text{ if } t \text{ is in } \tau.\end{cases}$$

In the second instance $\varphi_{t,v,l}$ is independent of time, and therefore $\varphi_{v,l}$ represents the total phase change produced by *one* particle with time of closest approach in τ and with impact parameter l. Under these conditions

$$\alpha_{t,v}(1)=1 \text{ if } t \text{ is not in } \tau$$

$$\alpha_{t,v}(1)=\alpha_v(1)=\int dlW(l)e^{-i\varphi_{vl}} \text{ if } t \text{ is in } \tau.$$

Equation (4.15) then leads to

$$C(\tau)\propto\exp\left\{\pi R^2\int dvvn(v)[\alpha_v(1)-1]\tau\right\}. \quad (4.16)$$

This is the general form of $C(\tau)$ for an impact theory

based on scalarly additive perturbations. We return to this equation later (Sec. V). Equation (4.16) reduces to (4.9) under the proper conditions. To show this we first assume that all perturbers have the same velocity v'. This means we replace $n(v)$ by $n\delta(v-v')$, where n is the number of particles per cubic centimeter. In view of Eq. (4.11) and because ν_v is now identical with our former ν_c, we then recover Eq. (4.9)

$$C(\tau) \propto e^{\nu_c[\alpha(1)-1]\tau}.$$

This is the correlation function for perturbers all of which have the same velocity. This derivation shows that its validity rests on the premise of scalarly additive perturbations and does not require the restriction that the impacts fail to overlap in time; this feature was not evident from the simpler proof which led to Eq. (4.9).

We return to calculation of the line intensity, employing the correlation function given by Eq. (4.9). We split $\alpha(1)$ into its real and its imaginary part, $\alpha=\alpha_1+i\alpha_2$ and put

$$\nu_c(1-\alpha_1)\equiv u_1, \quad -\nu_c\alpha_2\equiv u_2 \tag{4.17}$$

so that

$$C(\tau)=e^{-(u_1+iu_2)\tau}. \tag{4.18}$$

The calculation of I in accordance with Eq. (4.2) is then easy. One further detail has to be remembered. It follows from (4.1) that $C(-\tau)=C^*(\tau)$, a relation necessary for the reality of $I(\omega)$ but obscured by the explicit form (4.18) which is valid for $\tau>0$. Thus

$$C(\tau)=C^*(-\tau)=e^{(u_1-iu_2)\tau} \quad \text{for } \tau<0$$

and by (4.2)

$$I(\omega)\propto\left[\int_{-\infty}^{0} e^{u_1\tau+i(\omega-\omega'-u_2)\tau}d\tau+\int_{0}^{\infty} e^{-u_1\tau+i(\omega-\omega'-u_2)\tau}d\tau\right]$$
$$=2u_1[u_1^2+(\omega-\omega'-u_2)^2]^{-1}.$$

To make $\int_0^\infty I(\omega)d\omega=1$ we must write

$$I(\omega)=u_1/\pi[u_1^2+(\omega-\omega'-u_2)^2]^{-1}. \tag{4.19}$$

This represents a dispersion curve with a shift

$$u_2=\nu_c\sum_j P(\varphi_j)\sin\varphi_j \tag{4.20}$$

to the blue of the normal peak at ω', and a half-width

$$\omega_{\frac{1}{2}}=2u_1=2\nu_c[1-\sum_j P(\varphi_j)\cos\varphi_j]. \tag{4.21}$$

Lindholm now falls back upon Eq. (1.5) for a computation of the φ_j, which he identifies with the $\Delta\varphi(\rho,v)$ of that expression. This proficient and simple step is warranted under two conditions: (*a*) The impacts are sudden and do not coincide; (*b*) the perturber has a classical path, so that $\epsilon[(\rho^2+v^2t^2)^{\frac{1}{2}}]$ is meaningful. The first of these had already been discussed; the second is an additional restriction to be examined in the light of Sec. II.

Equation (4.21) distinguishes between phase changes by the arbitrary index j; Eq. (1.5) classifies them by the impact parameter ρ which is the closest distance of approach. The connection is this: If φ_j is taken to be $\varphi(\rho)$ then $P[\varphi(\rho)]=2\pi\rho d\rho/q$, where q is the total collision cross section. On the other hand, $\nu_c=nqv$. Therefore (4.20) and (4.21) become

$$u_2=nv\int 2\pi\rho d\rho\,\sin\Delta\varphi(\rho,v), \tag{4.22}$$

$$\omega_{\frac{1}{2}}=2nv\left[q-\int 2\pi\rho d\rho\,\cos\Delta\varphi(\rho,v)\right]$$
$$=2nv\int(1-\cos\Delta\varphi)2\pi\rho d\rho=4\pi nv\int\sin^2\Delta\varphi\rho d\rho. \tag{4.23}$$

The integrations over ρ are to be carried from 0 to $(q/\pi)^{\frac{1}{2}}$. Because of the rapid decline of $\Delta\varphi$ with ρ it is often permissible to replace the upper limit by ∞. In the case of long-range Coulomb interactions there is the added difficulty of giving a meaning to q.

The evaluation of $\Delta\varphi$ proceeds in accordance with (1.4); it is profitable only for simple force laws of the form

$$\epsilon(r)=\hbar\Omega_\sigma/r^\sigma. \tag{4.24}$$

Here we have replaced the former C_σ by $\hbar\Omega_\sigma$ to save writing. For our purposes the form (4.24) is satisfactory, for we shall be dealing mainly with linear Stark effects (where $\epsilon=\hbar sF=\hbar se/r^2$, whence $\sigma=2$) and quadratic Stark effects (where $\epsilon=\hbar tF^2=\hbar te^2/r^4$, whence $\sigma=4$). Here ϵ is the difference in the Stark displacements of the two states; it refers to the line, not to a given state.

With (4.24) Eq. (1.5) yields

$$\Delta\varphi=\Omega_\sigma\int_{-\infty}^{\infty}dt(\rho^2+v^2t^2)^{-\sigma/2}=\pi^{\frac{1}{2}}\frac{\Gamma[(\sigma-1)/2]}{\Gamma(\sigma/2)}\frac{\Omega_\sigma}{v\rho^{\sigma-1}}.$$

In particular, for $\sigma=2$

$$\Delta\varphi=(\pi\Omega_2)/(v\rho) \tag{4.25}$$

and for $\sigma=4$

$$\Delta\varphi=(\pi\Omega_4)/(2v\rho^3). \tag{4.26}$$

We now compute (4.22) and (4.23) for these two cases.

The shift for the linear Stark effect is not observable as such because the splitting pattern as a whole is symmetric. Lindholm and Unsöld do not compute it for that reason. Nevertheless, it is meaningful as a measure of the shift of each Stark component, and it does manifest itself in each wing of such lines as H_β and H_δ, which have zero intensity at the center. Since q is not well defined, the upper limit in the integrations of (4.22) and (4.23) will be taken as r_0 (see Sec. III: $(4\pi/3)r_0^3n=1$), this being the order of distance beyond which the

Coulomb force is effectively screened.|| When $\sigma=4$ the convergence is fast and the integrations may be carried to ∞. For $\sigma=2$ both integrations are straightforward (see Lindholm); the forms below involve an expansion of the integral sine and cosine. For $\sigma=4$ a graphical integration is necessary to determine the numerical factors. Thus one finds:

Linear Stark effect, $\sigma=2$

$$\text{Shift}=u_2=2\pi^3\Omega_2^2\frac{n}{v}\left(\frac{vr_0}{\pi\Omega_2}-\frac{\pi}{4}+\frac{\pi\Omega_2}{2vr_0}-\cdots\right), \quad (4.27)$$

$$\text{Half-width}=\omega_{\frac{1}{2}}=2\pi^3\Omega_2^2\frac{n}{v}\left(0.923-\ln\frac{\pi\Omega_2}{vr_0}-\frac{\pi^2\Omega_2^2}{24v^2r_0^2}+\cdots\right). \quad (4.28)$$

Quadratic Stark effect, $\sigma=4$

$$\text{Shift}=u_2=9.8\Omega_4^{\frac{2}{3}}v^{\frac{1}{3}}n, \quad (4.29)$$

$$\text{Half-width}=\omega_{\frac{1}{2}}=11.4\Omega_4^{\frac{2}{3}}v^{\frac{1}{3}}n. \quad (4.30)$$

In these formulas v is the speed of the perturbing particle (in the center of gravity system).

Equation (4.27) is somewhat embarassing: it makes the shift depend directly upon the cutoff radius and thereby emphasizes the uncertainty of our assumptions. Numerical considerations even show that for electrons as perturbers, (4.27) is generally much greater than (4.28), and this exposes an inconsistency of the present method. Table V shows the ratio $u_2/\omega_{\frac{1}{2}}$ from (4.27) and (4.28) for different temperatures and electron densities.

Burkhardt,[37] Lindholm,[8c,15b] and particularly Unsöld[18] couple an interesting consideration with the analysis leading to Eqs. (4.29) and (4.30), where no convergence difficulties are encountered. If $\sigma=4$, Eqs. (4.22) and (4.23) read

$$u_2=nv\int \sin(\rho_0/\rho)^3\cdot 2\pi\rho d\rho, \quad (4.31)$$

$$\omega_{\frac{1}{2}}=4nv\int \sin^2\tfrac{1}{2}(\rho_0/\rho)^3\cdot 2\pi\rho d\rho, \quad (4.32)$$

because in this instance $\Delta\varphi$, given by (4.26), takes the form $(\rho_0/\rho)^3$ if we put $\rho_0=(\pi\Omega_4/2v)^{\frac{1}{3}}$. This, is the value of ρ (always in terms of our single-impact analysis) for which the phase change $\Delta\varphi=1$ and therefore corresponds to Weisskopf's critical radius ρ_c.

Consider the integrands in (4.31) and (4.32). Clearly $\sin(\rho_0/\rho)^3$ fluctuates rapidly about zero for small ρ and becomes monotone and decreasing for large ρ. The initial fluctuations practically make u_2 depend on the contributions it gets from large ρ. But as for (4.32), its integrand is never negative; hence, the initial fluctuations contribute greatly to $\omega_{\frac{1}{2}}$ while the small contributions from large ρ are less significant. Now the division between large and small ρ comes at $\rho=\rho_0$, the point beyond which neither integrand oscillates.

|| The Debye-Hückel radius would be a better limit; but the results should not depend critically on this choice if they are to be believed.

TABLE V. Electron broadening. Ratio of shift to half-width in the linear Stark effect.

T(°K)\n	10^{12}	10^{13}	10^{14}	10^{15}	10^{16}
10^2	8.6	3.5	2.6	1.4	1.05
10^3	22	11.7	6.3	3.5	1.9
10^4	58	30	16	8.6	3.5
10^5	158	81	42	22	11.7

All this suggests that perhaps a useful simplification results if we integrate (4.31) from ρ_0 to ∞, and (4.32) from 0 to ρ_0. Furthermore, we replace the sine in (4.31) by its argument and revert to the original form for u_2, Eq. (4.20). It reads

$$u_2=\nu_c\sum_i P(\varphi_j)\varphi_j\equiv\nu_c\bar{\varphi}_j. \quad (4.33)$$

The line shift, which arises primarily from small $\Delta\varphi$ (large ρ) is in effect the average number of phase shifts per second.

The integration of (4.32) from 0 to ρ_0 changes the numerical factor in (4.30) very little; hence, we may conclude that, under conditions in which (4.32) is valid, contributions from $\Delta\varphi$ smaller that 1 may be ignored. This, however, is not the same as saying that (4.32) is valid when $\Delta\varphi\gg1$. Within the limits set by the example of the second-order Stark effect, and for force-law parameters σ greater than 4, one arrives at the qualitative rule that impacts within the optical radius broaden, impacts outside the optical radius shift the line. This somewhat precarious generalization is belied by Eqs. (4.27) and (4.28), and by Table V; hence it has no meaning for first-order Stark effects.

What are the conditions for validity of (4.22) and (4.23) of which (4.31) and (4.32) were special cases? We have derived them by assuming the impacts to be sudden. A little reflection shows that the derivation is essentially unchanged provided the collisions do not overlap, i.e., are binary. The case of multiple collisions has been treated by Lindholm (though in a way which makes no allowance for the *vector* superposition of fields in the Stark-effect problem and which remains within the "classical path" approximation) who succeeded in showing that the foregoing results of this section have wider validity than the present analysis suggests. Some further consideration is given by Krogdahl[39] and, by Kolb.[38]

B. Core and Wing Theorems for Individual Collisions

Under the assumption of binary collisions the criteria for the impact and the statistical theory take special forms.

[39] M. Krogdahl, Astrophys. J. **110**, 355 (1949).

1. Core Theorem

The impact theory (see Sec. I) was established on the assumption that the impacts are sudden and separated in time. The general form for the intensity distribution depends on integrals of the form $\int e^{i[\varphi(t)-\Delta\omega\cdot t]}dt$. A single impact, and therefore the change in φ corresponding to a single impact, are completed in a time of the order of ρ/v. If the change in $\Delta\omega\cdot t$ over this time interval is small compared to unity, i.e., if $\Delta\omega\rho/v\gg 1$ the impact can be considered to be sudden. This inequality can always be satisfied for sufficiently small $\Delta\omega$, hence the impact theory is valid in the core of the line (core theorem).

For *single impacts* the phase change is (see Sec. IIA)

$$\Delta\varphi=\frac{C_\sigma\pi^{\frac{1}{2}}}{\hbar v\rho^{\sigma-1}}\frac{\Gamma[(\sigma-1)/2]}{\Gamma(\sigma/2)}.$$

With the result we can derive[1f] a more specific criterion for validity of the impact theory. If we assume that the important impacts are those that occur within the optical radius ρ_c for which $\Delta\varphi\approx 1$, we have

$$\rho_c\approx(C_\sigma/\hbar v)^{1/\sigma-1}.$$

Combining this equation with the foregoing inequality we have for the range of validity of the impact theory in isolated collisions

$$\Delta\omega\ll v(\hbar v/C_\sigma)^{1/\sigma-1}.$$

In certain cases Kolb[22,38] has shown that this relation is valid under more general conditions than the restrictive ones imposed for this simple derivation.

2. Wing Theorem

The wing theorem, Sec. I, shows that for sufficiently large $\Delta\omega$ (measured from the normal line position) the statistical theory holds, but it does not say beyond what frequency it may be applied. *When the line arises from individual impacts*, a very simple argument covers this point. For there appears in the entire formalism only one time (and hence one frequency) that is characteristic of an impact namely, the duration of the perturbation τ_p. Hence, there is only one frequency τ_p^{-1} to which appeal can be made as a critical limit. The condition, $\Delta\omega\to\infty$, may therefore be replaced by

$$\Delta\omega\cdot\tau_p\gg 1. \tag{4.34}$$

A more pictorial demonstration of the meaning of this inequality has been given by several authors,

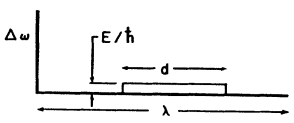

FIG. 5. Idealized representation of collisions. Long and flat rectangles represent gentle impacts of long duration; short and tall rectangle; represent energetic but brief impacts.

among whom Burkhardt[37] seems most explicit and circumspect. He pictures different collisions as producing different rectangles on a perturbation energy *vs* time plot, as drawn in Fig. 5. Distant passages have large τ_p but small $\Delta\omega$, for in this instance we may identify a specific $\Delta\omega$ within the observed line with a specific passage. A given passage is assumed to affect recorded frequencies in two ways, by virtue of the phase jumps occurring at the beginning and the end of a perturbation, and by the actual change of frequency during the perturbation. The former leads to a formula like (4.21) (in which ν_c is strictly *twice* the collision frequency). Empirically, the resulting width is usually small.

The detuning over an interval τ_p requires different treatment in different cases. Taken by itself, a given rectangle in Fig. 5 produces a line at the frequency $\Delta\omega$ and of Lorentz width $1/\tau_p$. Consecutive impacts yield superpositions of such lines, and these superpositions produce a statistical distribution about the different values of $\Delta\omega$ if $1/\tau_p\ll\Delta\omega$, i.e., if the different impact lines do not overlap. Here we discover again the inequality (4.34).

This reasoning is alone perhaps not quite convincing; for it will occur to those with experience in Fourier analysis that the replacement of a set of continuous perturbations by the rectangles of Fig. 5 is a risky practice. Still this demonstration possesses merits, even if rigor is not among them.

There is some likelihood of confusion in the criterion (4.34). We noted, in the text following Eq. (4.32), that the condition $\Delta\varphi\gg 1$ selects those encounters which make important contributions to the *impact* width of the line. This same condition is implied by (4.34). But (4.34) is also the condition for validity of the *statistical* theory. If impact broadening and statistical broadening were mutually exclusive or contradictory effects we should encounter here a paradox. This, however, is not the case. Inequality (4.34) means what it says: it permits the use of statistical theory. The earlier information is also true; it means simply that an impact theory, when carefully employed under these conditions (which is in general more difficult to do), must give approximately the same answer. The literature contains many instances showing this to be true.[8d] Lindholm's theory, for instance, leads to Margenau's statistical formula for Van der Waals broadening, a case which has been repeatedly discussed in this connection.

The overlapping of impact and statistical domains is further illustrated by the following coincidence. We saw that the line shift (4.33) arises from small phase changes, which violate the criteria $\Delta\varphi\gg 1$. But if we compute it under certain circumstances, it is nevertheless the statistical shift. Assume, for instance, that every φ_j arises from a perturbation ΔE_j lasting a time t' which is inversely proportional to the velocity v (so that the interaction distance, d, is constant). Then

$\varphi_j=(\Delta E_j/\hbar)(d/v)$. Also, $\nu_c=nqv$ and by (4.33), $u_2=nqd\Delta E/\hbar$, a result which displays the important characteristic of all statistical theories inasmuch as it does not depend on v. In fact, it is exactly the statistical result. In Fig. 6, λ is the mean free path. Along it $\Delta E=0$ except in a region of length d. Hence,

$$\Delta\omega=\frac{\langle\Delta E\rangle}{\hbar}=\frac{1}{\hbar}\frac{0\cdot\lambda+\Delta E\cdot d}{\lambda}=\frac{nqd\Delta E}{\hbar}$$

because $nq\lambda=1$.

C. Some Numerical Estimates, Mainly Regarding the Balmer Lines

The wing theorem for binary collisions says, in effect, that for $\Delta\omega$ greater than ω'', such that $\omega''\tau_p=1$, a statistical description is appropriate. But as we have seen, $\omega''\tau_p$ also equals $\Delta\varphi$ if this simple picture holds.

We now consider the *first-order Stark effect*. Here $\Delta\varphi$ is given by Eq. (4.25). Putting

$$\Delta\varphi=(\pi\Omega_2)/(v\rho_c)=1$$

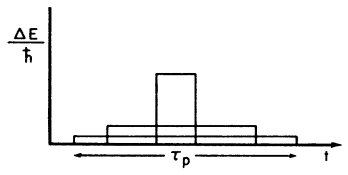

FIG. 6. $\Delta\omega$ *vs* distance travelled by perturber.

we have $\rho_c=\pi\Omega_2/v$. The frequency displacement for this ρ_c is

$$\omega''=\Omega_2/r^2=\Omega_2/\rho_c{}^2=v^2/(\pi^2\Omega_2). \qquad (4.35)$$

This "statistical frequency limit" within the line is independent of the perturber density.

Let us now consider the half-width of the line which would be calculated by means of impact theory, Eq. (4.28):

$$\omega_{\frac{1}{2}}\approx 2\pi^3\Omega_2{}^2n/v. \qquad (4.36)$$

The dependence on v is interesting; the statistical frequency limit moves out farther with increasing v, whereas the impact width becomes smaller.

To make a comparison of (4.35) and (4.36) we need the values of Ω_2. These are discussed by Unsöld (whose C is our $\Omega_2/2\pi$) are are given for the Balmer lines:

	H_α	H_β	H_γ	H_δ	
Ω_2	3.96	10.35	20.5	27.6	(cgs units)

As a typical case we take the H_α line, emitted at a temperature of 10 000°K and an ion density $n=10^{15}$ cm^{-3}. At that temperature v (electron) $=6.23\times10^7$ cm/sec and v (H-ion) $=20.6\times10^5$ cm/sec. From (4.35) and (4.36) one then computes the following values.

TABLE VI. Statistical wavelength limit $\Delta\lambda''$ in Angstroms for the Balmer lines (after Unsöld).

$T=$		25 000°	10 000°	5000°	3000° (K)
H_α	Electrons	580	230	110	70
	Protons	0.63	0.25	0.12	0.08
H_β	Electrons	120	48	24	14
	Protons	0.13	0.05	0.03	0.02
H_γ	Electrons	48	19	9	6
	Protons	0.05	0.02	0.01	0.006
H_δ	Electrons	32	13	6	4
	Protons	0.03	0.01	0.007	0.004

H_α line broadened by

H ions: $\omega_{\frac{1}{2}}=4.8\times10^{11}$ sec^{-1}, $\omega''=1.1\times10^{11}$ sec^{-1}.

electrons: $\omega_{\frac{1}{2}}=1.6\times10^{10}$ sec^{-1}, $\omega''=9.8\times10^{13}$ sec^{-1}.

For all these cases the Holtsmark half width is $\approx10^{12}$ sec^{-1}. The ions, if their broadening effect were computed by the impact theory, would show a half-width greater than ω''. But since for $\Delta\omega\gg\omega''$ the statistical theory is valid one may, so long as one is not interested in the intensity distribution for smaller $\Delta\omega$, disregard $\omega_{\frac{1}{2}}$ for the ions. The electrons, however, produce an ω'' well beyond the limit of interest; hence, a statistical treatment for them is not proper. On the other hand $\omega_{\frac{1}{2}}$ for electrons is very small. The important contribution to the line structure comes from the statistical effects of the ions beyond ω'' and everything else, indeed the entire role of the electrons, can be ignored. The *actual* Holtsmark half width computed for the *ions* under the conditions here assumed is of course greater than ω'' (it is about 8×10^{11} sec^{-1}).

In cases of this sort it is sometimes claimed that the part of the line beyond ω'' can be treated statistically while the inner portion arises from impacts. There is no logical warrant for the second half of this statement despite the core theorem, for the limit of validity of the core theorem need not coincide with that of the wing theorem. Since the interior part has usually been of little interest in line analysis no damage is done by that pleasing supposition.

Table VI, taken from Unsöld,[18] shows the *wave length*, $\Delta\lambda''$, in angstroms from the line center, beyond which the statistical theory is applicable; $\Delta\lambda''=(\lambda^2\omega'')/(2\pi c)$ if λ is the normal frequency of the Balmer line. In all these instances the limit in question is close to the line center for proton broadening, so that Holtsmark's theory may practically be applied throughout the intensity distribution to the protons. The limit for electrons is so far out that they may not be treated statistically. But their impact widths are small, and presumably their entire effect is therefore negligible.

Our logic regarding the electrons contains a blind spot, which we hope the remainder of this article will in part remove. At this point we observe only the proportionality of $\omega_{\frac{1}{2}}$ with n in Eq. (4.36), a feature which

indicates that at higher densities the electrons do become important. Had we chosen $n=10^{16}$ cm^{-3} and $T=10\,000$°K in the example of H_α (see text following Eq. (4.36)) $\omega_{\frac{1}{2}}$ for electrons would have been greater than ω'' for protons.

Before concluding we take a glance at the *second-order* Stark effect. Here $\Delta\varphi$ is given by (4.26), and if this is to be 1, $\rho_c=(\pi\Omega_4/2v)^{\frac{1}{2}}$. The corresponding

$$\omega''=\Omega_4/\rho_c^4=(2v/\pi)^{\frac{1}{2}}\Omega_4^{\frac{1}{2}}.$$

A typical value of Ω_4 is 2×10^{-12} cgs units. Because of the dependence of ω'' on $v^{\frac{1}{2}}$ we encounter here a situation like that presented in Table VI: protons may be treated statistically fairly close to the center of the line, electrons only beyond a large, uninteresting distance from the center. But according to Eq. (4.30) the impact width $\omega_{\frac{1}{2}}=11.4\Omega_4^{\frac{1}{2}}v^{\frac{1}{2}}n$. It is proportional to $v^{\frac{1}{2}}$, not to v^{-1} as in the first-order Stark effect. Impact broadening therefore favors the electrons in the present instance.

A numerical example illustrates the situation. If $T=10\,000$°K, $\omega''=7\times10^{11}$ sec^{-1}. Assume again $n=10^{15}$ cm^{-3}. This makes $\Delta\omega_0$ in the Holtsmark theory $[\Delta\omega_0=\Omega_4(F_0^2/e^2)$, (compare Sec. III)] equal to 1.36×10^9 sec^{-1}. For the frequency ω'', where this theory becomes valid, the parameter $\omega''/\Delta\omega_0\approx500$, and at this value the function $W[(\omega''/\Delta\omega_0)^{\frac{1}{2}}]$ (see Fig. 2) is already quite small. Hence the Holtsmark theory has little to say about the case. The impact width for electrons, however, leads to $\omega_{\frac{1}{2}}=8\times10^{10}$ sec^{-1} which is the dominant contribution.

The formula for the electron contributed to the line width in the case of the quadratic Stark effect may be written more explicitly. For a hydrogen-like atom (if $Z=1$) or an ion of charge Z with principal quantum number g one finds, approximately,

$$\Omega_4\cong\frac{1}{2}\left(\frac{g}{Z}\right)^6\frac{a_0^3e^2}{\hbar}$$

$$=1.4\left(\frac{g}{Z}\right)^6\times10^{-17}.$$

Hence

$$\omega_{\frac{1}{2}}\approx6.6\times10^{-11}\left(\frac{g}{Z}\right)^4nv^{\frac{1}{2}}. \tag{4.37}$$

V. DISAPPEARANCE OF LINES WITH HIGH QUANTUM NUMBERS

Special consideration must be given to the Balmer lines involving high quantum numbers, and in general to lines emitted from highly excited states of atoms or ions within a plasma. The states near the continuum limit have a tendency to disappear for two reasons:

1. Broadening of the levels causes them to merge, which effect begins among the excited states which lie close together on the energy scale. We speak of this as the merging of states.

2. There is also an effective lowering of the continuum limit or, more precisely, an upward displacement of the higher levels because the electron in the atom does not move in a pure Coulomb field. The actual field in a plasma is subject to the Debye-Hückel cutoff. As a result, levels do not approach the energy zero with large quantum number g like $-1/g^2$, but there will be a finite distance between the energy of the level with the largest g (say g^*) and energy zero. This has been recognized in connection with the problem of calculating partition functions, where actually *both* effects, 1 and 2, are important.

Effect 1 has been treated by Inglis and Teller,[40] effect 2 most carefully by Unsöld[41] and by Ecker and Weizel.[42]

The best simple derivation of the formula for the merging of levels (differing only slightly from that of Inglis and Teller) and reliable comments on its precision are found in Unsöld, whose method is followed here. Our analysis will again be applied to the levels of hydrogen, for which $E_g=-e^2/2g^2a_0$ and therefore the undisturbed level separation at large g is

$$\Delta E=e^2/g^3a_0.$$

Here a_0 is the first Bohr radius. The splitting of the levels in the linear Stark effect for the extreme components is approximately

$$\tfrac{3}{2}g^2a_0eF.$$

The most probable value for the ionic field is $4.2\,e^2n^{\frac{2}{3}}$; Inglis and Teller chose the smaller value $3.7\,e^2n^{\frac{2}{3}}$. Merging will take place when the splitting equals $\approx\Delta E/2$. Hence the last discernible level will have the quantum number g^* which is defined by

$$\frac{1}{2}\frac{e^2}{a_0(g^*)^3}=\frac{3}{2}(g^*)^2a_03.7e^2n^{\frac{2}{3}}.$$

When logarithms are taken this becomes

$$\log_{10}n=23.3-7.5\log_{10}g^*. \tag{5.1}$$

This formula has often been used for the determination of the ion density n.

So far we have neglected the electrons. If only their statistical effect is considered (assuming that their impact width is small), Eq. (4.28), which represents the limit beyond which the statistical theory holds, tells what role is played by the electrons. For if $\hbar\omega''$ is much greater than the above $\Delta E/2$, they do not contribute to the ionic breadth when it equals $\Delta E/2$ and may therefore be neglected. But if

$$\hbar\omega''=(\hbar v^2)/(\pi^2\Omega_2)<\Delta E/2$$

[40] D. R. Inglis and E. Teller, Astrophys. J. **90**, 439 (1939). [For experimental verification see F. L. Mohler, Astrophys. J. **90**, 429 (1939).]

[41] A. Unsöld, Z. Astrophys. **24**, 355 (1948).

[42] G. Ecker and W. Weizel, Ann. Physik **17**, 126 (1956).

the electrons must be considered. For large g, the linear Stark constant [defined in Eq. (4.24)] has approximately the value $e^2a_0g^2/\hbar$. The value of v^2 for electrons is taken from

$$\tfrac{3}{2}kT=\tfrac{1}{2}mv^2.$$

Equation (5.1) is therefore subject to modification on account of the electrons when

$$\frac{\hbar}{\pi^2}\frac{3kT/m}{e^2a_0(g^*)^2/\hbar}<\frac{e^2}{2(g^*)^3a_0},$$

or

$$T<\frac{\pi^2me^4}{6\hbar^2kg^*}=\frac{5\times10^5\ ^\circ\mathrm{K}}{g^*}. \tag{5.2}$$

How to include the electrons when this condition holds —and it holds in many cases of physical interest—is, in principle, a difficult problem. The custom seems to be to accord them a role equal to that of the ions and to replace n in Eq. (5.1) by $2n$. Since this adds to $\log_{10}$ only the amount 0.3, and the number 23.3 on the right of (5.1) is hardly certain to within that amount, it is not reasonable to worry about the electrons in this connection.

The second effect, the drowning of the higher levels in the continuum, is treated by Unsöld in a very simple schematic way. The Coulomb potential in which an electron moves never reaches the value zero because another positive ion is situated at a finite distance from it. The electron may slide over into the trough of the other ion, even at a negative total energy, much in the manner in which high atomic levels are depleted by a strong electric field. If the depth of the transfer channel is made to correspond to the mean distance between atom and nearest ion, the highest permitted quantum g^* number is given by

$$(g^*)^2=(Z^{4/3}/6a_0)\left(\frac{4\pi}{3}n\right)^{-\frac{1}{3}}. \tag{5.3}$$

With this simple model, g^* does not depend on the temperature because it ignores the electrons.

The treatment by Ecker and Weizel involves a solution of the Schrödinger equation for an electron moving in a Debye field (or, if the reader is a nuclear physicist, a Yukawa field) of the form

$$V=-(Ze^2/r)\exp(-r/D)+\text{const.} \tag{5.4}$$

The Debye radius is

$$D=[kT/4\pi ne^2(1+Z)]^{\frac{1}{2}}$$
$$\approx10^{-5}\text{ cm for }\begin{cases}T=10\,000^\circ\mathrm{K}\\ n=10^{16}\text{ cm}^{-3}\end{cases} \tag{5.5}$$

in terms of Z, the charge on an ion. The result obtained is simple and agrees with the plausible expectation that the largest orbit of the cited electron shall be smaller than D:

$$(g^*)^2a_0/Z\lesssim[kT/4\pi ne^2(1+Z)]^{\frac{1}{2}}. \tag{5.6}$$

For $Z=1$ this means

$$g^*\cong3\times10^4(n/T)^{-\frac{1}{4}} \tag{5.7}$$

if g^* is the greatest possible quantum number.

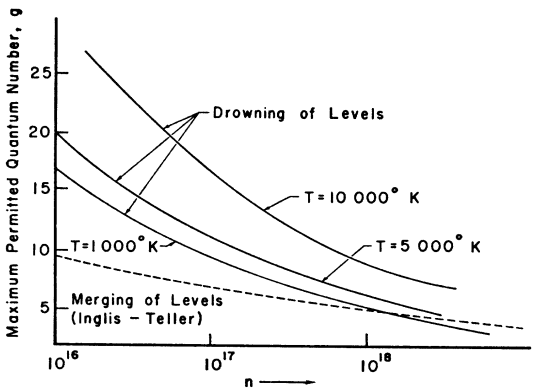

FIG. 7. Disappearance of levels in hydrogen.

Equation (5.7) is plotted for three different temperatures in Fig. 7. On the same figure we have drawn Eq. (5.1). Unsöld's Eq. (3) [Eq. (5.3) of this paper], which is not included, specifies values of g^* which fall slightly below the dotted curve. For high temperatures and low densities the merging of the levels according to Inglis and Teller determines the highest permitted quantum number, whereas in the other extreme the drowning of levels in the continuum is the decisive effect.

The latter has been studied in another way, employing straightforward perturbation theory, in a recent, unpublished calculation.[43] This led to the result

$$(g^*)^2=0.86D, \tag{5.8}$$

which reduces the limiting quantum number slightly below the value given by Eq. (5.6).

Perturbation theory is not strictly applicable since for the last level the perturbation energy is of the same order of magnitude as the unperturbed energy. For this reason we present here the essentials of a parallel variational calculation¶ in which an exponential screening factor $\mathfrak{Z}$ is employed as variable parameter in connection with hydrogen state functions of principal quantum number g. It may be asked why this method should be expected to work, since variation of $\mathfrak{Z}$ might push a hydrogen level initially assigned to the quantum number g down to energies corresponding to lower values of g. The answer is that variation of $\mathfrak{Z}$ does not alter the number of nodes, which is controlled by g, and that therefore a crossing from one g to another cannot occur.

In view of the Debye-Hückel shielding effect the

[43] D. Kelly and H. Margenau, Progress Report, October 1, 1956, Contract Nonr 609 (22).

¶ Contributed by D. Kelly.

atomic electron moves in a potential

$$V=\begin{cases} V_i(r)=-Ze^2\left(\dfrac{1}{r}-\dfrac{1}{b+D}\right) & r\lesssim b \\ V_0(r)=\dfrac{-Ze^2}{1+b/D}\dfrac{\exp[-(r-b)/D]}{r} & r\gtrsim b. \end{cases}$$

The maximum of the radial charge distribution falls at $r=D$, signifying that there is a considerable fraction of the surrounding ion cloud inside the "Debye sphere." We assume $b\ll D$. As a consequence we can use $V(r)=V_0(r)$ with little error. In view of these assumptions concerning b/D and $V(r)$ we write the Schrödinger equation for the optical electron in the form

$$H\psi=-(\hbar^2/2m)\nabla^2\psi-Ze^2(e^{-r/D}/r)\psi=E\psi. \quad (5.9)$$

Choosing functions ψ_g which satisfy the Schrödinger equation for the hydrogen atom of nuclear charge $\mathfrak{Z}$ for quantum number g we compute the integral

$$E_g=\int \psi_g^* H\psi_g d\tau$$

and requires $\partial E_g/\partial\mathfrak{Z}=0$. ($\mathfrak{Z}$ is the variable charge number, Z the fixed ion charge number.) Since

$$-(\hbar^2/2m)\nabla^2\psi_g=[E_g^0+(\mathfrak{Z}e^2/r)]\psi_g$$

and $E_g^0=\mathfrak{Z}^2E_H/g^2$ we have

$$E_g=\frac{\mathfrak{Z}^2}{g^2}E_H-2E_H\int\psi_g^*\left(\frac{\mathfrak{Z}-Ze^{-r/D}}{r/a_0}\right)\psi_g d\tau, \quad (5.10)$$

where $E_H=-e^2/2a_0=-13.53$ ev. Expanding $e^{-r/D}$ in a power series yields

$$\int\left(\frac{\mathfrak{Z}-Ze^{-r/D}}{r/a_0}\right)|\psi_g|^2 d\tau = (\mathfrak{Z}-Z)\frac{\mathfrak{Z}}{g^2}+\kappa\sum_{m=0}^{\infty}\frac{(-1)^m}{m!}\left\langle\left(\frac{\kappa r}{a_0}\right)^m\right\rangle \quad (5.11)$$

$$\kappa\equiv a_0/D$$

$$\langle(\kappa r/a_0)^m\rangle\equiv\int|\psi_g|^2(\kappa r/a_0)^m d\tau.$$

The values of $\langle(\kappa r/a_0)^m\rangle$ are given by Condon and Shortley.[44] For S states,

$$E_g=E_H\{[(-\mathfrak{Z}^2+2\mathfrak{Z}Z)/g^2]-2Z\kappa S(\beta)\}$$
$$\beta\equiv\kappa g^2/\mathfrak{Z} \quad (5.12)$$
$$S(\beta)\approx\frac{3}{4}\beta-\frac{5}{12}\beta^2+\frac{35\beta^3}{192}-\frac{63}{960}\beta^4+\cdots.$$

[44] E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, London, 1957).

The variational constraint, $\partial E_g/\partial\mathfrak{Z}=0$, leads to

$$\mathfrak{Z}-Z+Z\beta^2\partial S(\beta)/\partial\beta=0. \quad (5.13)$$

The principal quantum number of the last level (g^*) is given by the equation $E_g^*=0$. This gives

$$2Z-\mathfrak{Z}-2Z\beta S(\beta)=0. \quad (5.14)$$

Elimination of Z through (5.10) and (5.11) gives an equation involving only β,

$$1-2\beta S(\beta)+\beta^2(\partial S(\beta)/\partial\beta)=0, \quad (5.15)$$

which has $\beta=1.27$ as a root. Thus

$$\beta=[(g^*)^2a_0]/\mathfrak{Z}D=1.27.$$

Reintroducing the true ion charge number, Z, we find

$$(g^*)^2=0.804(ZD/a_0), \quad (5.16)$$

which differs very little from the perturbation result, Eq. (5.8).

We might also inquire how the departure from the hydrogen level structure affects the merging of lines. For this purpose we can apply perturbation theory to all but the last few levels, using hydrogen state functions with $l=l_{\max}=g-1$, since it is for these substates that the Stark splitting is extreme. These functions prove to be very simple and it is not necessary to resort to to the expansion in $\langle(\kappa r/a_0)^m\rangle$. The calculation shows that the first order correction to the hydrogen levels is independent of g and the second order term is so small as to change g^* as given by (5.1) less than one percent.

There are other corrections. Edmonds[45] has calculated, for instance, how the effective mean distance between ions is altered by the Debye shielding effect. For present concerns, relating to the disappearance of the lines, this consideration is of secondary importance.

VI. BROADENING OF DEGENERATE LEVELS

Recently, Kolb[30] has treated the broadening of hydrogen lines in a manner which is more careful than previous treatments in its consideration of the difficulties of degeneracy and which furthermore attempts to include both ions and electrons in their simultaneous actions upon the radiating atom.

We present a synopsis of Kolb's calculations after first discussing certain fundamental ideas of the method and also its principal results. The details given here differ from Kolb's in this respect: our functions [see Eq. (6.8)] are solutions of the *unperturbed* Schrödinger equation, whereas Kolb's are said to be adiabatic functions. The latter choice leads to difficulties which our treatment avoids. Let us recall the meaning of "adiabatic" in the first and second sense discussed in Sec. IIB. The collisions a hydrogen atom can experience with an *electron* can be divided roughly into two extreme groups, namely, (1) *close collisions* that turn the atom around (adiabatic in the second sense) and (2) *distant*

[45] F. N. Edmonds, Astrophys. J. **123**, 95 (1956).

or weak collisions that do not turn the atom (adiabatic in the first sense). We assume that under certain specifiable conditions the weak collisions are mainly responsible for the broadening, so that the analysis can be restricted to collisions of type 2. One can now speak of adiabatic and diabatic in the following sense; an adiabatic collision leaves the atom in, or returns it to, its original state (permitting the energy to change while the collision is in process), a diabatic collision causes transitions to other final states.

Principal conclusions are (*a*) the electron effects are an important factor in the broadening of the hydrogen lines; (*b*) the adiabatic and diabatic electron effects are of comparable magnitude.

A. Mathematical Foundations

The energy radiated and absorbed per second due to transitions between states m and the state n (providing $E_n^0 > E_m^0$) is given by[10]

$$I_n(\omega) \propto \left\langle \sum_m [\rho_m(0)-\rho_n(0)] \times \lim_{T\to\infty} \frac{1}{T}\left|\int_0^T dt \mu_{nm}{}^c(t) e^{-i\omega t}\right|^2 \right\rangle_{\text{Av}}. \quad (6.1)$$

Here $\rho_m(0)$ and $\rho_n(0)$ are Boltzmann factors for the states having unperturbed energies E_m^0 and E_n^0; $\mu_{nm}{}^c(t)$ is the dipole matrix element defined by

$$\mu_{nm}{}^c(t) \equiv \int \chi_n{}^*(t) \mu \chi_n(t) d\tau, \quad (6.2)$$

where μ is the dipole moment operator. The functions χ_n satisfy

$$i\hbar \dot{\chi}_n(t) = [H_0 + H_1(t)]\chi_n(t), \quad (6.3)$$

provided H_0 is the Hamiltonian for the atom and $H_1(t)$ the interaction between the atom and the perturbing ions and/or electrons. Equation (6.1) is valid if $E_n^0 > E_m^0$. For states (m,n) such that $E_m^0 > E_n^0$, $e^{-i\omega t}$ must be replaced by $e^{i\omega t}$.

Equation (6.1) was derived by calculating the increase in population of the nth state due to the action of the light. Since $E_n^0 > E_m^0$ the first term, $\rho_m(0)\left|\int \mu_{nm}{}^c e^{-i\omega t}\right|^2$ is seen to represent absorption, i.e., transitions from m to n; the second term $\rho_n(0) \times \left|\int \mu_{nm}{}^c(t) e^{-i\omega t}\right|^2$ represents induced emission (electromagnetic field was not quantized) i.e., transitions from $n \to m$. Therefore $I_n(\omega)$ is the net absorption. The average in Eq. (6.1) is to be carried out over different collisions.

Suppose that the states n and m are degenerate in the absence of perturbations. For the level n, we call the collection of states f and label the individual states ϵ_f; for the states m we use i and α_i. Occasionally, we omit the subscripts on ϵ and α. Equation (6.1) thus becomes

$$I_{\epsilon f}(\omega) \propto \left\langle \sum_{i,\alpha_i} [\rho_{\alpha i}(0) - \rho_{\epsilon f}(0)] \frac{1}{2\pi} \times \lim_{T\to\infty} \frac{1}{T}\left|\int_0^T dt \mu_{\epsilon f \alpha i}{}^c(t) e^{-i\omega t}\right|^2 \right\rangle_{\text{Av}}. \quad (6.4)$$

Defining

$$I_{\epsilon f \alpha i} \equiv \frac{1}{2\pi} \lim_{T\to\infty} \left|\int_0^T dt \mu_{\epsilon f \alpha i}{}^c(t) e^{-i\omega t}\right|^2_{\text{Av}}, \quad (6.5)$$

we now sum over all degenerate f states, obtaining

$$\sum_{\epsilon f} I_{\epsilon f}(\omega) \propto \sum_i \{\sum_{\epsilon f \alpha i} [\rho_{\alpha i}(0) - \rho_{\epsilon f}(0)] I_{\epsilon f \alpha i}\}. \quad (6.6)$$

The term in brackets represents transitions between the groups of i and f states. The first term represents absorption, and we define the absorption coefficient I_{if} as

$$I_{if} \equiv \sum_{\epsilon f \alpha i} [\rho_{\alpha i}(0) I_{\epsilon f \alpha i}]. \quad (6.7)$$

In keeping with the weak-collision hypothesis, a solution of Eq. (6.3) is written as

$$\chi_\alpha(t) = \sum_{\alpha'} C_{\alpha' \alpha}(t) \varphi_{\alpha'}{}^0 \times \exp\left[-\frac{i}{\hbar}\int_0^t \{E_{\alpha'}{}^0 + (H_1)_{\alpha'\alpha'}\} dt'\right], \quad (6.8)$$

where $\varphi_{\alpha'}{}^0$ and $E_{\alpha'}{}^0$ are eigenfunctions and energies of H_0, and $(H_1)_{\alpha'\alpha'}$ is given by

$$(H_1)_{\alpha'\alpha'} \equiv \int \varphi_{\alpha'}{}^{0*} H_1 \varphi_{\alpha'}{}^0 d\tau.$$

When Eq. (6.8) is substituted into Eq. (6.3), we obtain

$$\dot{C}_{\alpha'' \alpha}(t) = -\frac{i}{\hbar} \sum_{\alpha', \alpha' \neq \alpha''}{}' C_{\alpha' \alpha}(t) (H_1)_{\alpha'' \alpha'} \times \exp[-i\{\omega_{\alpha'\alpha''}{}^0 t + P_{\alpha'\alpha''}\}] \quad (6.9)$$

upon using the following abbreviations:

$$\omega_{\alpha'\alpha''}{}^0 = \omega_{\alpha'}{}^0 - \omega_{\alpha''}{}^0; \quad \omega_{\alpha'}{}^0 = E_{\alpha'}{}^0/\hbar$$
$$P_{\alpha'\alpha''} = P_{\alpha'} - P_{\alpha''}; \quad P_{\alpha'} = \frac{1}{\hbar}\int_0^t (H_1)_{\alpha'\alpha'} dt. \quad (6.10)$$

We take as an initial condition that only the state α is present at $t=0$. With weak collisions only the initial state is appreciable at a later time, i.e.,

$$|C_{\alpha\alpha}(0)| \simeq |C_{\alpha\alpha}(t)| \simeq 1; \quad |C_{\alpha'\alpha}(t)| \ll 1 \quad \text{for } \alpha' \neq \alpha.$$

Hence, Eq. (6.9) can be written

$$C_{\alpha''\alpha}(t) = -\frac{i}{\hbar}\int_0^t (H_1)_{\alpha''\alpha} \times \exp[-i(\omega_{\alpha\alpha''}{}^0 t' + P_{\alpha\alpha''})] dt'. \quad (6.11)$$

In this approximation Eq. (6.8) takes the form

$$\chi_\alpha(t)=\varphi_\alpha{}^0\exp[-i(\omega_\alpha{}^0t+P_\alpha)]+\sum_{\alpha',\alpha'\neq\alpha}{}'C_{\alpha'\alpha}(t)\varphi_{\alpha'}{}^0\exp[-i(\omega_{\alpha'}{}^0t+P_{\alpha'})]. \quad (6.12)$$

When Eq. (6.12) and a similar one for $\chi_\epsilon(t)$ are used to calculate $\mu_{\epsilon\alpha}{}^e(t)$ the result is

$$\mu_{\epsilon\alpha}{}^e(t)=\mu_{\epsilon\alpha}{}^0\exp[i(\omega_{\epsilon\alpha}{}^0t+P_{\epsilon\alpha})]+\sum_{\epsilon'}{}'\mu_{\epsilon'\alpha}{}^0C_{\epsilon'\epsilon}{}^*(t)\exp[i(\omega_{\epsilon'\alpha}{}^0t+P_{\epsilon'\alpha})]+\sum_{\alpha'}{}'\mu_{\epsilon\alpha'}{}^0C_{\alpha'\alpha}(t)\exp[i(\omega_{\epsilon\alpha'}{}^0t+P_{\epsilon\alpha'})], \quad (6.13)$$

where $\mu_{\epsilon\alpha}{}^0=\int\varphi_\epsilon{}^0\mu\varphi_\alpha{}^0d\tau$ and terms of the order C^2 have been neglected. Equation (6.13) together with Eq. (6.5) determines the absorption coefficient. We are now ready to consider two special cases of interest.

B. Adiabatic Approximation

The off-diagonal elements are neglected in this approximation, only the first term in Eq. (6.13) being used. This simplifies the theory so that it can easily be applied to any two states (α,ϵ). The resulting approximation is general enough to include both electrons and ions and serves as a guide for the more complicated theory below, which includes the off-diagonal elements. On substituting Eq. (6.13) into Eq. (6.5) we have, neglecting the off-diagonal elements,

$$I_{\epsilon\alpha}=\frac{|\mu_{\epsilon\alpha}{}^0|^2}{2\pi}\lim_{T\to\infty}\frac{1}{T}\times\left|\int_0^T dt\exp[-i(\Delta\omega_{\epsilon\alpha}{}^0-P_{\epsilon\alpha})]\right|_{\text{Av}}^2, \quad (6.14)$$

where $\Delta\omega_{\epsilon\alpha}{}^0=\omega-\omega_{\epsilon\alpha}{}^0$. Equation (6.14) can be put into the usual correlation form (see Sec. IV)

$$I_{\epsilon\alpha}=\frac{|\mu_{\epsilon\alpha}{}^0|^2}{\pi}\text{Re}\int_0^\infty d\tau\times\exp(i\Delta\omega_{\epsilon\alpha}{}^0\tau)\langle\exp[-iP_{\epsilon\alpha}(\tau)]\rangle_{\text{Av}}. \quad (6.15)$$

The term $P_{\epsilon\alpha}$ contains interactions involving the *ions* and *electrons*. We therefore write

$$P_{\epsilon\alpha}=P_{\epsilon\alpha}{}^i+P_{\epsilon\alpha}{}^e$$

and assume that the ion and electron averages can be calculated separately. The ions are to be treated in the statistical approximation and therefore permit the interaction to be written as time independent. With this understanding

$$P_{\epsilon\alpha}{}^i=(\Omega_2{}^{\epsilon\alpha}/e)F\tau, \quad (6.16)$$

where F is the instantaneous ion field, e the charge on the ion, and $\Omega_2{}^{\epsilon\alpha}$ are terms connected with the Stark shift of the states (ϵ,α).

The electrons are treated by the phase shift (impact) approximation. Consider

$$\langle\exp[-iP_{\epsilon\alpha}{}^e(\tau)]\rangle_{\text{Av}}=\left\langle\exp\left[-\frac{i}{\hbar}\int_0^\tau\{(H_1{}^e)_{\epsilon\epsilon}-(H_1{}^e)_{\alpha\alpha}\}dt\right]\right\rangle_{\text{Av}}, \quad (6.17)$$

where $H_1{}^e$ is the interaction of the atom with all the electrons in the plasma. In the evaluation of (6.17) we employ Eq. (4.15), following Kolb. This does not require that the impacts are sudden or isolated. It is applicable to scalarly additive perturbations, that is perturbations for which

$$H_1{}^e=\sum_p H_1{}^p. \quad (6.18)$$

The sum here is taken over all the electrons contained in some effective volume. The phase change during the time interval τ produced by a single electron depends on the velocity v, the time of closest approach t_i and on some other parameter l. Since

$$H_1{}^e=\sum_{i,v,l}\mathfrak{N}(i,v,l)H_1(i,v,l), \quad (6.19)$$

where $\mathfrak{N}(i,v,l)$ is the number of electrons characterized by (i,v,l) in the effective volume, $P_{\epsilon\alpha}{}^e$ becomes

$$P_{\epsilon\alpha}{}^e=\hbar^{-1}\sum_{i,v,l}\mathfrak{N}(i,v,l)\int_0^\tau[(H_1(i,v,l))_{\epsilon\epsilon}-(H_1(i,v,l))_{\alpha\alpha}]dt, \quad (6.20)$$

$$P_{\epsilon\alpha}{}^e=\sum_{i,v,l}\mathfrak{N}(i,v,l)\varphi_{i,v,l}(\tau),$$

$$\varphi_{i,v,l}(\tau)\equiv\hbar^{-1}\int_0^\tau[(H_1(i,v,l))_{\epsilon\epsilon}-(H_1(i,v,l))_{\alpha\alpha}]dt. \quad (6.21)$$

Using the results developed in Sec. IV we find

$$\langle\exp[-iP_{\epsilon\alpha}{}^e(\tau)]\rangle_{\text{Av}}=\exp\left[\pi R^2\int dvvn_e(v)[\alpha_v(1)-1]\tau\right], \quad (6.22)$$

$n_e(v)$ being the number of electrons with velocity v per cubic centimeter. The effective volume of the system is assumed to be a sphere of radius R and

$$\alpha_v(1)=\int dlW(l)e^{-i\varphi_{v,l}}. \quad (6.23)$$

Here $\varphi_{v,l}$ is the total phase change produced by an electron of velocity v and parameter l which has its time of closest approach in the time interval τ. Now suppose

that the parameter l labels two impact variables ρ and σ, ρ being the distance of closest approach and σ some other characteristic variable defined later. The probability distribution functions for these are

$$W(\rho)d\rho=2\pi\rho d\rho/\pi R^2;\quad W(\sigma)d\sigma=d\sigma/\Sigma, \tag{6.24}$$

where Σ is the total cross section for σ. Then

$$\alpha_v=\int\int W(\rho)W(\sigma)\exp(-i\varphi_{v,\rho,\sigma})d\rho d\sigma, \tag{6.25}$$

and hence

$$\langle\exp[-iP_{\epsilon\alpha}{}^e(\tau)]\rangle_{\text{Av}}=\exp\Big[2\pi\int vn_e(v)dv\int\rho d\rho \times\int(d\sigma/\Sigma)(\exp(-i\varphi_{v,\rho,\sigma})-1)\tau\Big]. \tag{6.26}$$

Finally, we replace $n_e(v)$ by $n_eW(v)$ understanding by n_e the number of electrons per cubic centimeter and by $W(v)$ the Boltzmann distribution function; we write $\varphi_{\epsilon\alpha}(\infty)$ for $\varphi_{v,\rho,\sigma}$, letting (ϵ,α) indicate the two states involved and omitting the (ρ,v,σ) dependence; the symbol (∞) means that the phase change produced by one particle is completed. One then finds

$$\langle\exp[-iP_{\epsilon\alpha}{}^e(\tau)]\rangle_{\text{Av}}=\exp[-(u_1{}^{\epsilon\alpha}+iu_2{}^{\epsilon\alpha})\tau], \tag{6.27}$$

where

$$\begin{pmatrix}-u_1{}^{\epsilon\alpha}\\-u_2{}^{\epsilon\alpha}\end{pmatrix}\equiv\begin{pmatrix}\text{Re}\\\text{Im}\end{pmatrix}2\pi n_e\int_0^\infty vW(v)dv\int_0^R\rho d\rho \times\int_0^\Sigma\frac{d\sigma}{\Sigma}\{\exp[-i\varphi_{\epsilon\alpha}(\infty)]-1\}. \tag{6.28}$$

Substitution of Eqs. (6.27), (6.16) and (6.15′) into (6.15) results in

$$I_{\epsilon\alpha}=\frac{|\mu_{\epsilon\alpha}{}^0|^2}{\pi}\text{Re}\Big\langle\int_0^\infty\exp\Big[i\Big(\Delta\omega_{\epsilon\alpha}{}^0-u_2{}^{\epsilon\alpha}-\frac{\Omega_2{}^{\epsilon\alpha}}{e}F\Big)\tau-u_1{}^{\epsilon\alpha}\tau\Big]d\tau\Big\rangle_{\text{Av(ions)}} \tag{6.29}$$

$$=\frac{|\mu_{\epsilon\alpha}{}^0|^2}{\pi}\Big\langle\frac{u_1{}^{\epsilon\alpha}}{(\Delta\omega_{\epsilon\alpha}{}^0-\Omega_2{}^{\epsilon\alpha}F/e-u_2{}^{\epsilon\alpha})^2+(u_1{}^{\epsilon\alpha})^2}\Big\rangle_{\text{Av(ions)}}. \tag{6.30}$$

We shall return to this equation. At present we wish to develop a formula including the off-diagonal elements, which are taken to be zero in the treatment above.

C. Diabatic Effects in Degenerate Systems

The ions are neglected, so that the atomic states are degenerate, in this approximation. The resulting formulas are useful because they indicate the magnitude of the diabatic effects as far as electron broadening is concerned. In particular, the results of the present development, when applied to the Lyman-α line, and then compared with the adiabatic approximation (when ions are neglected), clearly demonstrate that the adiabatic theory can contain large errors. The method of this section can be generalized to nearly degenerate systems, degeneracy being removed by inclusion of the ions, but the results are difficult to handle and have not been carefully studied.

In the weak collision approximation we assume that $|P_{\epsilon\alpha}{}^e|\ll1$ so that Eq. (6.13) can be written in the form

$$\mu_{\epsilon\alpha}{}^e(t)=\mu_{\epsilon\alpha}{}^0\exp(i\omega_{\epsilon\alpha}{}^0t)\Big\{1+iP_{\epsilon\alpha}{}^e+\sum_{\epsilon'}{}'\frac{\mu_{\epsilon'\alpha}{}^0}{\mu_{\epsilon\alpha}{}^0}C_{\epsilon'\epsilon}{}^*+\sum_{\alpha'}{}'\frac{\mu_{\epsilon\alpha'}{}^0}{\mu_{\epsilon\alpha}{}^0}C_{\alpha'\alpha}\Big\}. \tag{6.31}$$

Since $|P_{\epsilon\alpha}{}^e|\ll1$ and the sum are small, we can write

$$\mu_{\epsilon\alpha}{}^e(t)=\mu_{\epsilon\alpha}{}^0\exp(i\omega_{\epsilon\alpha}{}^0t)\exp(i\Phi_{\epsilon\alpha}), \tag{6.32}$$

with

$$\Phi_{\epsilon\alpha}\equiv P_{\epsilon\alpha}{}^e-i\Big[\sum_{\epsilon'}{}'\frac{\mu_{\epsilon'\alpha}{}^0}{\mu_{\epsilon\alpha}{}^0}C_{\epsilon'\epsilon}{}^*+\sum_{\alpha'}{}'\frac{\mu_{\epsilon\alpha'}{}^0}{\mu_{\epsilon\alpha}{}^0}C_{\alpha'\alpha}\Big]. \tag{6.33}$$

When this is substituted in Eq. (6.5) there results

$$I_{\epsilon\alpha}=\frac{|\mu_{\epsilon\alpha}{}^0|^2}{2\pi}\lim_{T\to\infty}\frac{1}{T}\times\Big|\int_0^T dt\exp(-i\Delta\omega_{\epsilon\alpha}{}^0t)\exp(i\Phi_{\epsilon\alpha})\Big|_{\text{Av}}^2. \tag{6.34}$$

In the weak collision approximation, then, Eq. (6.11) for $C_{\alpha'\alpha}$ becomes

$$C_{\alpha'\alpha}=-\frac{i}{\hbar}\int_0^t(H_1{}^e)_{\alpha'\alpha}\exp(-iP_{\alpha\alpha''}{}^e)dt'\cong-\frac{i}{\hbar}\int_0^t(H_1{}^e)_{\alpha'\alpha}dt'. \tag{6.35}$$

If one assumes, as in the adiabatic case, scalarly additive perturbations [see Eq. (6.19)] then, in view of Eq. (6.35),

$$\Phi_{\epsilon\alpha}\equiv\sum_{i,v,l}\mathfrak{N}(i,v,l)\kappa_{i,v,l},$$

$$\kappa_{i,v,l}(t)=\hbar^{-1}\int_0^t dt'\Big\{\sum_{\epsilon'}\frac{\mu_{\epsilon'\alpha}{}^0}{\mu_{\epsilon\alpha}{}^0}(H_1(i,v,l))_{\epsilon'\epsilon}-\sum_{\alpha'}\frac{\mu_{\epsilon\alpha'}{}^0}{\mu_{\epsilon\alpha}{}^0}(H_1(i,v,l))_{\alpha'\alpha}\Big\}. \tag{6.36}$$

Equation (6.34) is formally the same as Eq. (6.14). On the other hand, Eqs. (6.36) are similar to Eq. (6.21). We can therefore use the results of the adiabatic treatment when the proper replacements are made. Our results in that case do not contain the effects of the ions. Instead of Eqs. (6.35) we thus find

$$I_{\epsilon\alpha}=\frac{|\mu_{\epsilon\alpha}{}^0|^2}{\pi}\frac{u_1{}^{\epsilon\alpha}}{(\Delta\omega_{\epsilon\alpha}{}^0-u_2{}^{\epsilon\alpha})^2+(u_1{}^{\epsilon\alpha})^2}, \tag{6.37}$$

$$\binom{-u_1{}^{\epsilon\alpha}}{-u_2{}^{\epsilon\alpha}}\equiv\binom{\mathrm{Re}}{\mathrm{Im}}2\pi n_e\int_0^\infty vW(v)dv\int_0^R\rho d\rho \times\int_0^\Sigma\frac{d\sigma}{\Sigma}[\exp[-i\kappa_{\epsilon\alpha}(\infty)]-1], \tag{6.38}$$

subject again to the use of the phase shift approximation, which accounts for our writing $\kappa_{\epsilon\alpha}(\infty)$ in place of the $\kappa_{i,v,l}$ appearing in Eq. (6.36). The condition $|P_{\epsilon\alpha}|\ll 1$ is violated after a long enough time, and Eq. (6.37) is valid *only* in the wings. In applications, since $|\kappa_{\epsilon\alpha}(\infty)|\ll 1$, we retain only the first two nonvanishing terms in the expansion of $e^{-i\kappa_{\epsilon\alpha}}$. In the wings (6.37) becomes

$$I_{\epsilon\alpha}=u_1{}^{\epsilon\alpha}/[\pi(\Delta\omega_{\epsilon\alpha}{}^0)^2], \tag{6.39}$$

and

$$u_1{}^{\epsilon\alpha}=2\pi n_e\int_0^\infty W(v)vdv\int_0^R\rho d\rho\int_0^\Sigma\frac{d\sigma}{\Sigma}\frac{1}{2\hbar^2} \times\left[\int_{-\infty}^{+\infty}dt\{\sum_{\epsilon'}\mu_{\epsilon'\alpha}{}^0(H_1)_{\epsilon'\epsilon}-\sum_{\alpha'}\mu_{\epsilon\alpha'}{}^0(H_1)_{\alpha'\alpha}\}\right]^2 \tag{6.40}$$

with the understanding that H_1 refers to one electron with specified ρ, v, σ. We shall now apply the formulas of this and the previous section to line broadening by electrons.

D. Electron Broadening in the Adiabatic Approximation

In this section, the adiabatic theory of part B is applied to broadening by electrons only. Here "adiabatic" means that we retain only the first term in Eq. (6.13). This calculation, although restrictive, is useful in estimating (*a*) the error introduced by the electron collisions that fail to satisfy the conditions for an impact theory; (*b*) the effects of close collisions. The value of $\varphi_{i,v,l}(\infty)$, defined by Eq. (6.21) except that the integration is now extended over all time, is (with suitable changes of indexes)

$$\varphi_{\epsilon\alpha}(\infty)=(2\Omega_2{}^{\epsilon\alpha}/\rho v)\cos\theta, \tag{6.41}$$

where

$$\Omega_2{}^{\epsilon\alpha}=\tfrac{3}{2}(e^2a_0/\hbar)\{[n^\epsilon(k_1{}^\epsilon-k_2{}^\epsilon)]-[n^\alpha(k_1{}^\alpha-k_2{}^\alpha)]\}. \tag{6.42}$$

In this expression n^ϵ, $k_1{}^\epsilon$, $k_2{}^\epsilon$ are quantum numbers, in parabolic coordinates, of the state ϵ and θ of Eq. (6.41) is the polar angle describing the location of the position vector of closest approach ϱ in some fixed coordinate system; θ is the σ parameter mentioned earlier. Equation (6.28) then gives

$$u_2{}^{\epsilon\alpha}=0$$

$$u_1{}^{\epsilon\alpha}=2\pi n_e\int_0^\infty vW(v)dv\int_0^{\rho_m}\rho d\rho \times\left[1-\frac{\sin(2\Omega_2{}^{\epsilon\alpha}/\rho v)}{(2\Omega_2{}^{\epsilon\alpha}/\rho v)}\right], \tag{6.43}$$

where ρ_m is a cutoff distance and is chosen as the Debye length of Sec. II. With the definition

$$\delta_m{}^{\epsilon\alpha}\equiv 2\Omega_2{}^{\epsilon\alpha}/\rho_m v,$$

Eq. (6.43) then becomes

$$u_1{}^{\epsilon\alpha}=8\pi n_e(\Omega_2{}^{\epsilon\alpha})^2\int_0^\infty\frac{W(v)}{v}dv\left[0.2094-\tfrac{1}{6}\ln\delta_m{}^{\epsilon\alpha}+\frac{(\delta_m{}^{\epsilon\alpha})^2}{240}+\cdots\right]. \tag{6.44}$$

The velocity average is approximated by replacing the v^{-1} outside of [ ] by its Boltzmann average $\langle v^{-1}\rangle=(4/\pi)(1/\langle v\rangle)$ in Eq. (6.44). We then obtain, finally,

$$u_1{}^{\epsilon\alpha}=(32/\langle v\rangle)n_e(\Omega_2{}^{\epsilon\alpha})^2G(\delta_m{}^{\epsilon\alpha}),\qquad G(x)\equiv(0.2094-\tfrac{1}{6}\ln x+x^2/240\cdots) \tag{6.45}$$

and $\delta_m{}^{\epsilon\alpha}$ is redefined as

$$\delta_m{}^{\epsilon\alpha}=2\Omega_2{}^{\epsilon\alpha}/(\rho_m\langle v\rangle). \tag{6.45a}$$

Let us now return to the two points mentioned at the beginning of this section.

(*a*) According to the criterion for the validity of the phase shift approximation (Sec. IV B), the velocity must satisfy

$$v\gg(\Omega_2{}^{\epsilon\alpha}\Delta\omega)^{\frac{1}{2}}\equiv v_c$$

for the present results to be acceptable. One can estimate the error resulting from extending the velocity integration from zero to infinity by computing the contribution to $\langle v^{-1}\rangle$ from velocities less than v_c. One obtains

$$\frac{\langle v^{-1}\rangle-\langle v^{-1}\rangle_{v<v_c}}{\langle v^{-1}\rangle}=1-\frac{m(\Delta\omega)\Omega_2{}^{\epsilon\alpha}}{4kT}+\cdots. \tag{6.46}$$

For 10 000°K, and for H_β (4861 A) at 30 A from the line center, 90% of $\langle v^{-1}\rangle$ comes from velocities which satisfy the phase shift approximation.

(*b*) It is reasonable to treat close collisions by the Lorentz formula [Eq. (1.2)]. This leads to an $I_{\alpha\epsilon}$ which is similar to Eq. (6.30) (the ion contribution is again neglected) except that $u_1{}^{\epsilon\alpha}$ is replaced by $\tau_c{}^{-1}$, τ_c being the mean time between collisions. Hence the suggestion that $u_1{}^{\epsilon\alpha}$ can be represented, in an approxi-

mate way, as a sum of two terms

$$u_1^{\epsilon\alpha}=(u_1^{\epsilon\alpha})_{\rho>\rho_c}+(u_1^{\epsilon\alpha})_{\rho<\rho_c}, \tag{6.47}$$

where $(u_1^{\epsilon\alpha})_{\rho>\rho_c}$ is the contribution from the weak collision theory, computed according to Eq. (6.32) except that ρ is now allowed to vary from ρ_c to ρ_m. Here ρ_c is the value of ρ which roughly divides the impacts into strong (close) and weak ones, chosen so that

$$\delta_c^{\epsilon\alpha}\equiv 2\Omega_2^{\epsilon\alpha}/(\rho_c\langle v\rangle)=1 \tag{6.48}$$

or

$$\rho_c=2\Omega_2^{\epsilon\alpha}/\langle v\rangle. \tag{6.49}$$

In view of Eq. (6.41), $\delta_c^{\epsilon\alpha}$ is the maximum phase shift that an electron with velocity $\langle v\rangle$ and distance of closest approach ρ_c can produce. But

$$(u_1^{\epsilon\alpha})_{\rho<\rho_c}=\tau_c^{-1}\equiv\pi\rho_c^2 n_e\langle v\rangle=(4\pi/\langle v\rangle)(\Omega_2^{\epsilon\alpha})^2 n_e \tag{6.50}$$

and

$$\begin{aligned}(u_1^{\epsilon\alpha})_{\rho>\rho_c}&=(32n_e/\langle v\rangle)(\Omega_2^{\epsilon\alpha})^2[G(\delta_m^{\epsilon\alpha})-G(1)]\\&=(32n_e/\langle v\rangle)(\Omega_2^{\epsilon\alpha})^2\\&\quad\times[-0.0042-\tfrac{1}{6}\ln\delta_m^{\epsilon\alpha}+\cdots].\end{aligned} \tag{6.51}$$

Comparing (6.50) and (6.51), the contribution due to close collisions can be neglected if

$$\frac{(u_1^{\epsilon\alpha})_{\rho<\rho_c}}{(u_1^{\epsilon\alpha})_{\rho>\rho_c}}\simeq\frac{3}{4}\pi\frac{1}{\ln(1/\delta_m^{\epsilon\alpha})}\ll 1, \tag{6.52}$$

that is, if

$$\ln(1/\delta_m^{\epsilon\alpha})\gg 1.5. \tag{6.53}$$

When (6.53) is satisfied, the quantities expressed by Eqs. (6.51) and (6.45) are approximately equal.

Example: If $n_e=10^{15}$, $T=20\,000°\mathrm{K}$ and $\Omega_2^{\epsilon\alpha}/A=1.1$ (where $A\equiv\frac{3}{2}e^2a_0/\hbar$) then $\ln(1/\delta_m^{\epsilon\alpha})\approx 6$.

E. Broadening of the Lyman-α Line by Electrons

In this section we treat the broadening of the Lyman lines by electrons only. Both adiabatic and diabatic effects are considered. The wave functions used are the Stark wave functions with the Z axis fixed in space

$$\varphi_+=\frac{1}{\sqrt{2}}(\varphi_{200}+\varphi_{210}),\quad \varphi_-=\frac{1}{\sqrt{2}}(\varphi_{200}-\varphi_{210}),$$

$$\varphi_{21\pm1},\quad \varphi_{100},$$

the subscripts on φ denoting, in spherical coordinates, the quantum numbers nlm.

We use Eqs. (6.39) and (6.40), dropping $\sum_{\alpha'}$ in Eq. (6.40) because of the nondegeneracy of the ground state (100). Letting α designate the state (100), ϵ the states

$$(21\pm1),\quad (+),\quad (-),$$

one finds

$$u_1^{211,100}=u_1^{21-1,100}=0,\quad u_1^{+,100}=u_1^{-,100} \tag{6.54}$$

so that

$$\begin{aligned}&I_{211,100}=I_{21-1,100}=0,\\&I_{+,100}=\frac{u_1^{+,100}}{\pi(\Delta\omega_{+,100})^2};\quad I_{-,100}=\frac{u_1^{-,100}}{\pi(\Delta\omega_{-,100})^2},\\&u_1^{+,100}=u_1^{-,100}=\tfrac{1}{2}|\mu_{+,100}^{0}|^2\langle 6e^2a_0/v\rho\hbar\rangle,\end{aligned} \tag{6.55}$$

and

$$\left(\frac{6e^2a_0}{\rho v\hbar}\right)\equiv 2\pi n_e\int_0^\infty vW(v)dv\int_\rho^{\rho_m}\rho d\rho\left(\frac{6e^2a_0}{v\rho\hbar}\right). \tag{6.56}$$

The off-diagonal elements contribute twice as much as the diagonal elements to Eq. (6.55). We may therefore write Eq. (6.54) in the form

$$I_{+,100}=\frac{3(u_1^{+,100})_{\mathrm{ad}}}{\pi(\Delta\omega_{+,100})^2}, \tag{6.57a}$$

$$I_{-,100}=\frac{3(u_1^{-,100})_{\mathrm{ad}}}{\pi(\Delta\omega_{-,100})^2}, \tag{6.57b}$$

where $(u_1^{+,100})_{\mathrm{ad}}$ is given by Eq. (6.40) with only the diagonal term, $\mu_{+,100}^{0}(H_1)_{++}$ appearing in the sum. Finally, then,

$$\begin{aligned}(u_1^{+,100})_{\mathrm{ad}}&=(u_1^{-,100})\\&=\frac{|\mu_{+,100}^{0}|^2}{3}\frac{144a_0^2e^4}{\hbar^2}\frac{n_e}{\langle v\rangle}\ln\left(\frac{\rho_m}{\rho_c}\right).\end{aligned} \tag{6.58}$$

This result for $(u_1^{+\,100})_{\mathrm{ad}}$ agrees with the corresponding one obtained from the adiabatic theory of part D of this section, Eq. (6.51) with $\Omega_2^{\epsilon\alpha}/A=2$ and definitions of (6.49), (6.45a), and (6.42). Thus a pure adiabatic treatment (part D) which ignores collision-induced transitions underestimates the broadening by a factor of 3, a conclusion which is important later when an attempt is made to introduce both ions and electrons. Such an attempt succeeds simply only in an adiabatic theory. But with the information now at hand one can estimate the contribution to $u_1^{\epsilon\alpha}$ from the off-diagonal elements (diabatic effects) by using the results of this section.

F. Simultaneous Broadening by Ions and Electrons in the Adiabatic Approximation

In this section both electrons and ions are taken into account in the adiabatic approximation to the theory. The basic formulas are Eqs. (6.27), (6.28), and (6.30). The u_1's are treated in the manner explained in part D. So far as the ions are concerned the averaging process indicated in Eq. (6.30) can be performed with the use of the Holtsmark distribution for the field F since the ions are to be treated in the statistical approximation. Thus, define $W(\Omega)$ to be the probability distribution for

the quantity $\Omega \equiv F/e$; Eq. (6.30) then becomes

$$I_{\epsilon\alpha}=\frac{|\mu_{\epsilon\alpha}{}^0|^2}{\pi}\int_0^\infty W(\Omega)d\Omega \times\left\{\frac{u_1{}^{\epsilon\alpha}}{(\Delta\omega_{\epsilon\alpha}{}^0-\Omega_2{}^{\epsilon\alpha}\Omega)^2+(u_1{}^{\epsilon\alpha})^2}\right\} \quad (6.59)$$

and, according to the adiabatic theory for electrons, is $u_2{}^{\epsilon\alpha}$ zero, and $u_1{}^{\epsilon\alpha}$ is independent of Ω. Using the Holtsmark distribution for $W(\Omega)$ and adding together a pair of lines that satisfy $\Omega_2{}^{\epsilon\alpha}=-\Omega_2{}^{\epsilon'\alpha'}$ [this simplifies the results and makes $I(\Delta\omega)$ symmetric] one gets after some mathematical manipulation (see Kolb)

$$I_{\epsilon\alpha}=\frac{2}{\pi}\frac{|\mu_{\epsilon\alpha}{}^0|^2}{(\Omega_2{}^{\epsilon\alpha})^2}\int_0^\infty \xi d\xi \exp[(-4.21\Omega_2{}^{\epsilon\alpha}n_i\xi^{\frac{3}{2}}-u_1{}^{\epsilon\alpha}\xi)/\Omega_2{}^{\epsilon\alpha}] \times\left[\Delta\omega_{\epsilon\alpha}{}^0\sin\left(\frac{\Delta\omega_{\epsilon\alpha}{}^0\xi}{\Omega_2{}^{\epsilon\alpha}}\right)+u_1{}^{\epsilon\alpha}\cos\left(\frac{\Delta\omega_{\epsilon\alpha}{}^0\xi}{\Omega_2{}^{\epsilon\alpha}}\right)\right], \quad (6.60)$$

where n_i is the number of ions per cubic centimeter. This equation can be expanded for large and small frequencies ($\Delta\omega_{\epsilon\alpha}{}^0$). We present here only the large frequency expansion, since the other is subject to too many invalidating uncertainties. For convenience we make the following changes in notation:

$$Z_{\epsilon\alpha}\equiv 4.52\Omega_2{}^{\epsilon\alpha}n_i^{\frac{2}{3}}/A, \quad A\equiv \tfrac{2}{3}e^2a_0/\hbar,$$

i.e., $Z_{\epsilon\alpha}$ is the Stark shift (in radians per second) resulting from the mean Holtsmark field strength, and

$$B\equiv\Delta\omega_{\epsilon\alpha}{}^0/Z_{\epsilon\alpha},$$

i.e., B is the shift in units of $Z_{\epsilon\alpha}$ while

$$R\equiv Z_{\epsilon\alpha}/u_1{}^{\epsilon\alpha},$$

i.e., R is a measure of the relative importance of ion and electron broadening. With these changes in notation, for large frequencies ($\Delta\omega_{\epsilon\alpha}{}^0$), Eq. (6.60) becomes

$$I_{\epsilon\alpha}(B)dB=|\mu_{\epsilon\alpha}{}^0|^2dB\frac{2}{\pi}\left\{\frac{1}{R(B^2+1/R^2)}+\sum_{n=2}^{\infty}\frac{(-1)^{n-1}}{(n-1)!} \times\frac{\Gamma[(3n+1)/2]}{B^{(3n-1)/2}}\frac{\cos[\{(3n-1)/2\}\tan^{-1}(BR)]}{[1+1/(BR)^2]^{(3n-1)/4}}\right\}. \quad (6.61)$$

Equation (6.61) reduces to the Holtsmark distribution for ions if we set $u_1{}^{\epsilon\alpha}=0$ ($R=\infty$), for in this limit

$$I_{\epsilon\alpha}(B)dB=|\mu_{\epsilon\alpha}{}^0|^2dB\frac{2}{\pi}\sum_{n=2}^{\infty}\frac{(-1)^{n-1}}{(n-1)!}\frac{\Gamma[(3n+1)/2]}{B^{(3n-1)/2}} \times\cos[\{(3n-1)/4\}\pi]. \quad (6.62)$$

This agrees with Eq. (3.11b) when the coefficients are evaluated. Equation (6.61) reduces to the results of the adiabatic electron theory if $Z_{\epsilon\alpha}=0$.

The electron effects are revealed by comparison of Eqs. (6.61) and (6.62). In addition to the correction factors in each term of the sum in Eq. (6.61), there is a term that depends only on the electrons. In the wings of the line this is dominant since it is of the order B^{-2} whereas the mixed electron ion effects are of the order $B^{-\frac{5}{2}}$. This feature is present in all theories which attempt the fusion of statistical and impact features: the intensity in the statistical theory for large B is proportional to $B^{-\frac{5}{2}}$ that in all impact theories B^{-2}.

Equation (6.61) is applicable to any two pairs of states (ϵ,α), (ϵ',α') for which $\Omega_2{}^{\epsilon\alpha}=\Omega^{2\epsilon'\alpha'}$ since it neglects collision-induced transitions (off-diagonal elements of C). Formally, Kolb does generalize Eq. (6.1) to include the off-diagonal elements. This leads to mathematical difficulties because the $u_1{}^{\epsilon\alpha}$ are then dependent on the ion field strength, which complicates the ion-averaging process. The dependence arises through the $C_{\alpha'\alpha}$ (where $\alpha'\neq\alpha$) (taken as zero in the adiabatic approximation). Under certain conditions, these can be neglected. If, for instance, the average ion field is large the degenerate states are split far enough apart so that the off-diagonal elements vanish. Under other conditions, the term in $C_{\alpha'\alpha}$ that causes the difficulty, namely $\exp(i\omega_{\alpha'\alpha}{}^0t)$ (where $\omega_{\alpha\alpha'}{}^0$ is the separation of two degenerate levels due to the ions) can be replaced by unity. This will be true if the collisions are fast enough, i.e., if the collision time is small compared to $(\omega_{\alpha'\alpha}{}^0)^{-1}$. In this latter case, one can employ the adiabatic theory of Sec. E and estimate the diabatic contribution to $u_1{}^{\epsilon\alpha}$ from a knowledge of the diabatic electron effects, using the procedure given in the treatment of the Lyman-α line. That is, one first determines $u_1{}^{\epsilon\alpha}$ (adiabatic and diabatic) by considering only electrons and then uses this $u_1{}^{\epsilon\alpha}$ in the formula for broadening by ions and electrons in the adiabatic approximation.

As an example of this procedure, Kolb considers the following situation. For $n_e=n_i=10^{16}$ cm^{-3}, $T=15\,000$ °K, and $\Omega_2{}^{\epsilon\alpha}/A=10$. While an analysis of this line to determine the diabatic effects has not been carried out, Kolb estimates that they are of the same order of magnitude as the Lyman-α line. He takes the contribution to the weak collision to be twice the adiabatic contribution Eq. (6.51):

$$(u_1{}^{\epsilon\alpha})_{\rho>\rho_c}\simeq -2\left[\frac{16}{3}\frac{n_e}{\langle v\rangle}(\Omega_2{}^{\epsilon\alpha})^2\ln\delta_m{}^{\epsilon\alpha}\right] \quad (6.63)$$

and for the close collisions

$$(u_1{}^{\epsilon\alpha})_{\rho<\rho_c}=\left[4\pi\frac{n_e}{\langle v\rangle}(\Omega_2{}^{\epsilon\alpha})^2\right] \quad (6.64)$$

assuming that

$$u_1{}^{\epsilon\alpha}=(u_1{}^{\epsilon\alpha})_{\rho<\rho_c}+(u_1{}^{\epsilon\alpha})_{\rho>\rho_c}.$$

The result is shown graphically in Fig. 8.

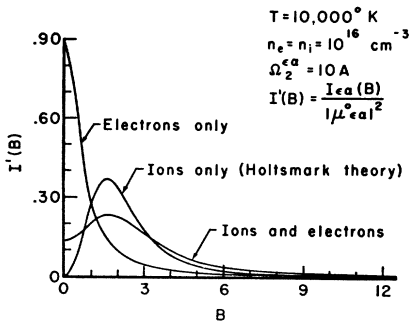

FIG. 8. Line contours produced by different agencies (after Kolb).

This result may be compared with that obtained from the classical theory. Lindholm's result [see Eq. (4.28)] is

$$(u_1{}^{\epsilon\alpha})_{\mathcal{L}} \equiv \omega_{\frac{1}{2}}/2 = \pi^3(\Omega_2{}^{\epsilon\alpha})^2(n_e/\langle v\rangle) \times[0.923 - \ln(\pi\Omega_2{}^{\epsilon\alpha}/\langle v\rangle\rho_m)\cdots].$$

We have replaced the cutoff r_0 by the Debye cutoff ρ_m and v by $\langle v\rangle$. The ratio is then

$$\frac{u_1{}^{\epsilon\alpha}}{(u_1{}^{\epsilon\alpha})_{\mathcal{L}}} \approx 0.345\left[\frac{\ln(\rho_m\langle v\rangle/\Omega_2{}^{\epsilon\alpha})+0.485}{\ln(\rho_m\langle v\rangle/\Omega_2{}^{\epsilon\alpha})-0.212}\right]. \quad (6.65)$$

For large $\ln(\rho_m\langle v\rangle/\Omega_2{}^{\epsilon\alpha})$, therefore,

$$u_1{}^{\epsilon\alpha} \approx 0.345(u_1{}^{\epsilon\alpha})_{\mathcal{L}}. \quad (6.66)$$

The quantity $\ln(\rho_m\langle v\rangle/\Omega)$ is in general large enough so that the difference between Eqs. (6.66) and (6.65) is within the uncertainties of Kolb's method.

For the condition which led to Eqs. (6.63) and (6.64)

$$\ln(\rho_m\langle v\rangle/\Omega_2{}^{\epsilon\alpha}) \approx 3.25.$$

Equation (6.65) then gives

$$u_1{}^{\epsilon\alpha} \approx 0.43(u_1{}^{\epsilon\alpha})_{\mathcal{L}}.$$

This is the line width of a single Stark component which is unobservable. The disparity between u_1 and $(u_1)_{\mathcal{L}}$, however, will remain no matter how the components are combined into a resultant contour. Because of the numerous approximations and inherent uncertainties involved in either of the classical path calculations it is difficult to say which formula is numerically preferable, even though Kolb's approach is the more circumspect and realistic one. Later we compare the result of the quantum-mechanical treatment with $(u_1)_{\mathcal{L}}$ (after compounding of Stark states) and find closer agreement.

VII. EXPERIMENTAL RESULTS AND CLASSICAL INTERPRETATIONS

A. Experimental Determination of Plasma Properties

Among the important physical parameters characterizing a plasma are the concentrations of various ions n_i, the electron concentration n_e and the temperature T. In a simple plasma, i.e., one containing but a single type of ion, $n_i = n_e$. The remarks of this section are confined to this case. In complex cases, Dalton's law of total pressure must be employed in addition to the equations discussed below,[46] but otherwise nothing fundamentally new emerges in the analysis of lines from complex plasmas.

A common temperature T exists for all constituents of a plasma if it is in thermal equilibrium. This is not necessarily true in the presence of agencies (discharge currents, ionizing radiations, shocks in rarefied media) which are not part of the thermal mechanism. In such instances it is customary to assign different temperatures to different components (neutral molecules, ions, electrons, photons) and to find ways of measuring each. The limitations of such an approach should, however, be apparent; for the external agencies just mentioned do not always produce a Maxwellian distribution of particle speeds,[47] and a temperature is definable only for a Maxwellian distribution. In a discharge plasma at low electron densities ($n_e < 10^{13}$ cm^{-3}) the temperature concept is known to break down, but it becomes meaningful once more at higher densities when long-range Coulomb forces among the ions and electrons begin to randomize the distribution toward its canonical form. This report does not deal with the pathologies of T, and we assume for the most part that a common T exists.

It has been standard practice to determine $n_i = n_e$ by measuring the intensity distribution of the Balmer lines and comparing it with the Holtsmark formula. Since the temperature does not enter in this procedure, simplicity strongly recommends it. Recent investigations by Edels and Craggs,[48] Lochte-Holtgreven and Nissen,[49] and by Olsen and Huxford[50] are based on it. The risks involved in this method are evident from our earlier theoretical considerations (and from numerous experimental findings of more recent date): reliance on the Holtsmark theory alone is permissible at low ion and electron densities ($n_e < 10^{16}$ cm^{-3}). At high densities, repulsion between perturbing ions produces a smaller intensity in the line wing (where measurements and theory are usually compared), but the electrons add to it. It is likely that a fortunate, rough cancellation between these opposing errors has sometimes led to correct values of n_i even when the method was not strictly valid.

Ion densities obtained by Edels and Craggs and by Lochte-Holtgreven and Nissen in hydrogen arcs were

[46] See, for instance, W. Lochte-Holtgreven, *Temperature, its Measurement and Control in Science and Industry* (Reinhold Publishing Corporation, New York, 1955), Vol. 2. Also Reports on Progress in Physics **21**, 312, 1958.

[47] Druyvesteyn, Physica **10**, 61 (1930); **1**, 1003 (1934); H. Margenau, Phys. Rev. **69**, 508 (1946).

[48] H. Edels and J. D. Craggs, Proc. Phys. Soc. (London) **A64**, 575 (1951).

[49] W. Lochte-Holtgreven and W. Nissen, Z. Physik **133**, 124 (1952).

[50] N. H. Olsen and W. S. Huxford, Phys. Rev. **87**, 922 (1952).

of the order 10^{16} cm^{-3}, in a range where the simple method can hardly fail. Those reported by Olsen and Huxford are somewhat higher (condensed flash discharge) and very probably subject to some error. One should also mention that "fitting a Holtsmark contour" is not a wholly obvious matter. It involves the composition of many Stark-broadened component lines into a single distribution with appropriate weights. The weighting has not always been performed correctly; there are differences, for example, in Olsen and Huxford[50] and Craggs and Hopwood[51] (factor 2 for perpendicular Stark components).

When n_i has been determined, it is a relatively easy matter to find T from the Saha equation (see the following), the relative intensity of different Balmer lines and other known effects involving n_i and T.[46,49] However, since line broadening is strictly also a function of T (mainly through the electron effect), and since we are furthermore interested in *testing* line broadening theories, it behooves us to discuss briefly some available methods for determining n_i and T that are independent of the details of plasma broadening.

1. Saha-Eggert Equation (Mass-Action Law)

This is a relation correcting n_e and T as follows:

$$\frac{n_i n_e}{n_0}=\frac{2Z_i}{Z_0}\frac{(2\pi m_e kT)^{\frac{3}{2}}}{h^3}\exp\left\{-\frac{\chi-\Delta\chi}{kT}\right\}. \quad (7.1)$$

Z_0 and Z_i are partition functions for neutral atoms and ions, n_0 and n_i their concentrations. For protons, Z_i has the classical form $(2\pi M_p kT)^{\frac{3}{2}}/h^3$; for neutral H atoms, however, Z_0 consists of two factors, the one just written (since $M_H \approx M_p$) and the sum of states $\sum_n g_n \exp(-E_n/kT)$ with weights $g_n=2n^2$ and E_n =hydrogen energy for principal quantum number n. This sum diverges because $E_n \propto n^{-2}$. Physically, however, this divergence is prevented by the drowning of levels discussed in Sec. V. A good practice, established on theoretical and experimental grounds, is to cut off the sum at $n=6$ or 7.

The quantity χ is the ionization potential for the ion, and $\Delta\chi$ is a correction resulting from the drowning of the high levels or, to put it another way, by the lowering of the ionization potential in the presence of ions. It has been computed by Unsöld, Weizel and Ecker, and others (see Sec. V).

Equation (7.1) holds in thermal equilibrium. Strictly speaking, this means that radiative processes as well as corpuscular collision processes, both those generating ions and destroying ions (recombination), must be balanced in detail.[52] If, for instance, radiation escapes partly from the medium, the equation is not exact. There is some evidence that for low n_e photoionization and recombination by triple collisions are not fully effective. The Saha-Eggert equation is then impaired, and Elwert[53] has proposed its replacement by

$$\frac{n_e}{n_0}=\frac{8.4\times10^5}{n\chi}\frac{kT}{g}e^{-\chi/kT}, \quad n_e<7\times10^{16}\text{ cm}^{-3}, \quad (7.2)$$

where g is a number around 2 given in reference 53.

Saha's equation is sometimes used when the temperatures of different plasma components are different. It is then said to define an ionization temperature T_i. The physical meaning of this concept is far from clear; still it may be a useful parameter. But if the energy distribution of the electrons is not Maxwellian (e.g., discharges with $n_e \approx 10^{14}$ cm^{-3}) the Saha equation may be vastly in error. E. Dewan[54] has derived the analog of (7.1) for electron distribution functions given in references 47 and found departures from Eq. (7.1) by large factors.

2. Absolute Intensity of a Line

The temperature alone is involved in the formula for the absolute intensity of the Balmer lines (in emission):

$$I=\frac{2\pi e^2 h f n^2}{m_e\lambda^3}n_0 l\exp\left(-\frac{E_n-E_0}{kT}\right) \quad (7.3)$$

(λ = wavelength of line, f = oscillator strength, quantum number, n and E_n refer to upper state of line, l is the thickness of the radiating layer, which must be small, i.e., optically thin). If l and n_0 can be determined with precision, this formula is the most direct and reliable means for determining T.

3. Relative Intensity of Different Lines

Two Balmer lines, one originating in the state of principal quantum number n', the other in state n, and of frequencies $\nu_{n'}$ and ν_n, have an intensity ratio

$$\frac{I_n}{I_{n'}}=\frac{n^2\nu_n A_n}{n'^2\nu_{n'}A_{n'}}\exp\left\{\frac{E_{n'}-E_n}{kT}\right\} \quad (7.4)$$

if all excited states are in thermal equilibrium. A_n is the coefficient of spontaneous emission. Again, in the absence of external agencies, and at high electron-ion concentration even in their presence, this condition is satisfied. Recent measurements in a hydrogen arc discharge by Edels and Craggs,[55] who compared H_α, H_β, and H_γ, have revealed large departures from formula (7.4).

[51] J. D. Craggs and W. Hopwood, Proc. Phys. Soc. (London) **A59**, 755 (1947).

[52] For a simple discussion see W. Finkelnburg and H. Maecker in *Handbuch der Physik* (Springer-Verlag, Berlin, 1956), Vol. XXII, p. 308.

[53] G. Elwert, Z. Naturforsch. **7a**, 432, 703 (1952).

[54] E. Dewan, Dissertation, Yale, 1957 (unpublished).

[55] See reference 48, p. 562.

4. *Intensity of the Balmer Continuum*

The intensity of radiation at a wavelength λ below the Balmer continuum limit of 3646 A is given by the formula[56]

$$I_\lambda=\gamma\frac{16\pi^4 m_e e^{10}}{3^{\frac{3}{2}}c^2h^5\lambda^2}n_0 l\exp\left\{\frac{E_1-E_2}{kT}-\frac{hc}{\lambda kT}\right\}\times\left[1+\sum_{n=3,4}\left(\frac{2}{n}\right)^3\exp\left\{\frac{E_2-E_n}{kT}\right\}+\frac{4kT}{Rhc}\exp\left\{\frac{E_2-E_5}{kT}\right\}\right], \quad (7.5)$$

where n_0 is again the concentration of H atoms, l the layer thickness, E_n=energy of nth quantum state $=-Rhc/n^2$, and R=Rydberg constant. The last two terms in [ ] represent contributions of higher continua in the region of the Balmer continuum.

5. *Temperature in Shocks*

Shocks are an increasingly important agency for producing high temperatures of short duration, yet long enough to emit measurable spectra lines. Temperatures and ion densities obtainable in shocks surpass by far the limitation of most electrical discharges.[57] Formulas for the temperature in shocks may be derived from the Rankine-Hugoniot equations, are given in Turner's dissertation[57] and, in a more elaborate manner, in Courant and Friedrichs.[58]

Of the five methods thus far surveyed only the first presents means for determining n_e; the remainder are independent ways of finding T. The Saha equation, involves both n_e and T; hence it must always be coupled with one or more of the later formulas. Unfortunately, a determination of n_e from Eq. (7.1) is highly inaccurate because $\Delta\chi$ and T appear in an exponent; the error in T resulting from an uncertainty in a given value of n_e would be much less.

A higher degree of confirmation can be given to a Saha n_e if use is made of the Inglis-Teller formula (Sec. V) which involves n_i $(=n_e)$ and only n_i directly. Although it depends on line widths, details do not enter that equation, and the action of electrons affects it in a minor way. But of course it yields only an estimate.

B. Some Recent Experimental Results

The need for modifications of the statistical theory because of the impacts of electrons was recognized by Unsöld and Lochte-Holtgreven at Kiel where, in consequence, a systematic series of experiments were recently performed on the Balmer series by Jürgens,[56] Griem,[59] Dieter-Henkel,[60] and Bogen.[61] High-intensity carbon electrode arcs maintained in a water channel and supporting currents up to 200 amp were used as sources of radiation, the first six series members being observed for various values of temperature and electron density. Although their experiments were done independently, the sum total of work of the Kiel group exhibits a large measure of unity, justifying a discussion of their findings as a whole.

In these experiments, the perturbations arise from protons and electrons acting together in the discharge; these always occur in equal numbers so that $n_e=n_p$ where n_p is the density of protons per cubic centimeter.

In order to allow the application of a theory of broadening to given experimental contours, values of T and n_e must first be determined, for as we have seen in Sec. II, the validity of a particular broadening theory in general depends upon the values of these parameters. Several independent methods for determining the temperature were employed, such as: measurement of the relative intensities of the successive lines of the series emitted from optically thin portions of the discharge, measurement of the degree of inversion of the lines when emitted from optically thick portions of the discharge, and variation of the intensity of the series continuum. The temperatures calculated by these several methods were found (doubtless in part by good fortune) to agree within a few percent, the values ranging from about 5×10^3 to 1.4×10^4 °K. The determination of n_e was made by the single method of matching the observed contours to an intensity distribution. Two distributions were used, the first being the statistical distribution of Holtsmark and the second a distribution formed by smearing the statistical distribution over the Lindholm impact distribution.

The Holtsmark fitting is performed in the far wings of the line where the inequality, Eq. (4.27), holds. Large discrepancies between this distribution and the observed contours were found, especially in the cases of H_α and H_γ, both of which have undisplaced central components in their Stark patterns which contain large fractions of the total intensities of the lines (38% for H_α and 16% for H_γ). The H_β line, having no undisplaced component, lends itself best to a fit by the statistical distribution. An application of the conditions, Eq. (5.2) to the last resolved member of the series shows that the electrons may be neglected as statistically broadening particles at the temperatures calculated. Hence the perturber density determined by the statistical fit is interpreted as that of the protons only.

The dashed curves of Fig. 9 show the contours as found for the first three lines of the series along with their Holtmark wing fits; these curves were taken from

[56] G. Jürgens, Z. Physik **134**, 21 (1952).
[57] See, for instance, Petschek, Rose, Glick, Kane, and Kantrowitz, J. Appl. Phys. **26**, 83 (1955); E. B. Turner, Dissertation, University of Michigan, 1956.
[58] R. Courant and K. O. Friedrichs, *Supersonic Flow and Shock Waves* (Interscience Publishers, Inc., New York, 1948).
[59] H. Griem, Z. Physik **137**, 280 (1954).
[60] W. Dieter-Henkel, Z. Physik **137**, 295 (1954).
[61] P. Bogen, Z. Physik **149**, 62 (1957).

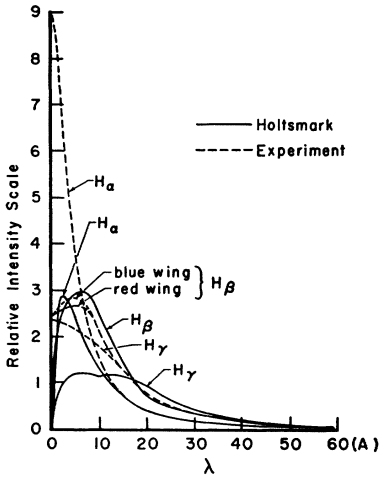

FIG. 9. Comparison of experimental with Holtsmark contours (after Jürgen).

Jürgens and correspond to $T=12\,300$ °K and $n_e=8.4\times10^{16}/\text{cm}^3$.

According to these findings, the experimental contours agree with the statistically calculated ones beyond 30 A, and the agreement occurs for a value of n_e identical with that obtained from the Saha equation. This was disquieting to theorists when the data appeared, for it seemed to show the old but unjustifiable belief in the unimportance of the electrons (at these wavelengths) to be correct. But the later work of P. Bogen[61] has changed this picture.

In his painstaking investigation, which includes a good discussion of errors, Bogen first measures the absolute intensity of the H_β line and uses formula (7.3) to find T. This requires knowledge of n_0, the number of hydrogen atoms, which for the water-stabilized arc employed in these experiments is not readily at hand. It is obtained from a previous study[62] of the properties of this arc, which resulted in the determination of n_0 as a function of T (with use of the Saha equation). Bogen then substitutes T in the Saha equation and obtains $n_e=2.1\times10^{16}$ cm^{-3} for the most fully documented example. When the intensity in the wing of the Balmer lines is plotted one obtains for each of the Balmer lines a graph such as Fig. 10. In the indicated wavelength range the experimental curve lies between two Holtsmark curves, one drawn for $n_e=2.2\times10^{16}$ cm^{-3}, the other for twice that value. For H_α, but not for the higher Balmer lines, the experimental curve approaches the upper Holtsmark curve at about 60 A, and the indication is that the higher Balmer lines likewise show this feature, but the approach takes place at higher wavelengths. Bogen concludes that for large λ the Holtsmark theory is correct for all lines, provided one lets ions and electrons have independent additive effects, i.e., one chooses $2n_e$ instead of n_e as the number of perturbers. The range of correctness coincides with that in which the binary statistical theory (see Sec. III A) is valid. Electron effects appear to be confined to the center of the Balmer lines, and they extend to greater distances from the line center in the higher series members.

We end this review of experimental results with a graphical summary of the shock tube work at Michigan. The latest data of this group may be found in the dissertation of Turner,[57] analyzed by Kolb,[22] from whose thesis Fig. 11 is taken. Again the experimental curve falls outside the Holtsmark distribution for the proper n_e at large distances from the line center. The dashed curve marked "ion and electron theory" represents Kolb's calculation (see Sec. VI), adapted in a suitable way to the Balmer lines, for which a complete calculation is still missing.

C. Classical Interpretations

The electrons must be included in an adequate theory. Their effect, according to all the foregoing developments, is most pronounced in the center of the lines. A simple way to incorporate it is to fold an impact distribution for the electrons into a statistical (Holtsmark) contour. This method, suggested in another connection by Margenau, Burkhardt, and doubtless others, was employed by Griem and Henkel in their data analyses. Griem adopts the use of the distribution:

$$I(\lambda)=\frac{\Delta}{\pi}\frac{I_0(\lambda)}{\lambda^2+\Delta^2}+\frac{\Delta}{\pi F_0}\int_{-\infty}^{+\infty}\frac{\bar{W}(x/F_0)dx}{(\Delta-x)^2+\Delta^2}. \quad (7.6)$$

Here 2Δ is the half-width computed for the electron impacts by the Lindholm theory; $\bar{W}(x/F_0)$ is the statistical distribution for a normal field strength F_0. This is taken from the work of Verwey and Schmaljohann (see Sec. III), which excludes the central undisplaced component of a Balmer line. Hence the central component, whose total intensity is I_0, must be added in via the first term of Eq. (7.1), which shows only an impact width. In Eq. (7.1), λ is measured from the normal position of the line. The bar over $\bar{W}$ is to indicate that a proper average over different Stark components has been taken. Much better representations of the data are obtained through the use of (7.6) as can be seen from the curves of Fig. 12 which are taken from the paper of Henkel.

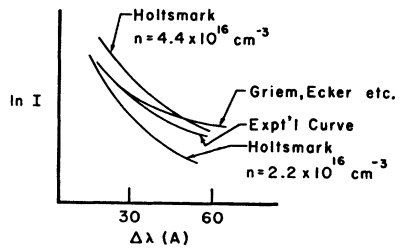

FIG. 10. Comparison of wing intensities (schematic, after Bogen).

[62] Burhorn, Maecker and Peters, Z. Physik **131**, 28 (1951).

A plausibility argument in favor of smearing the distributions takes a form similar to the one used in earlier sections. When a perturbation of the radiator contains two components, one of which acts slowly and the other quickly, the action of the slow one is to produce discrete shifts in energy which may be considered to be constant over time intervals in which many broadening collisions involving the fast component occur. Hence, in our example, each discretely shifted frequency of the statistical theory, produced by the protons, is broadened by the many impacts of the electrons. The condition under which many electron collisions occur during a time in which the ions are essentially motionless is:

$$t_e \ll t_p, \tag{7.7}$$

where t_e is the time between successive electron collisions and t_p is the time during which a proton collision occurs. For classically describable particles we have the definitions,

$$t_e = 1/(n\pi d^2 v_e), \quad t_p = d/v_p, \tag{7.8}$$

where d is defined by Eq. (2.5); v_e and v_p are, respectively, the mean speeds of the electrons and the protons. The inequality (7.2) thus becomes:

$$[(6.90)^3 \pi T^{\frac{3}{2}}/n^{\frac{1}{2}}](m_p/m_e)^{\frac{1}{2}} \gg 1, \tag{7.9}$$

where m_p is the mass of the proton and m_e is the mass of the electrons. This inequality holds for many important applications of electron broadening, both stellar and terrestrial.

It was shown in Sec. II that the classical-path assumption of the impact theory is not necessarily valid for collisions producing phase shifts less than unity. Such phase shifts, however, contribute most of the shift and broadening, as calculated by that theory, for the first order Stark effect [see Eqs. (4.27) and (4.28) and Table V]. Since this is the case, there exists no *a priori* justification for employing the Lindholm distribution, as Griem does in his folding procedure; instead one should replace it with the results of a quantum mechanical calculation. For the quadratic Stark effect this is not the case because the large contributions to the broadening result from collisions falling within the critical radius as has been shown by Unsöld[18] and in Sec. IV of this article.

The peculiarity in the behavior of the first-order Stark effect is connected with the nonconvergence of the broadening when collision parameters out to infinity

TABLE VII. Densities for which $d=\rho_c$ for the first-order Stark effect in hydrogen.

	n^*
H_α	$6.2 \times 10^{18}/\text{cm}^3$
H_β	$1.6 \times 10^{18}/\text{cm}^3$
H_γ	$5.48 \times 10^{17}/\text{cm}^3$
H_δ	$2.52 \times 10^{17}/\text{cm}^3$

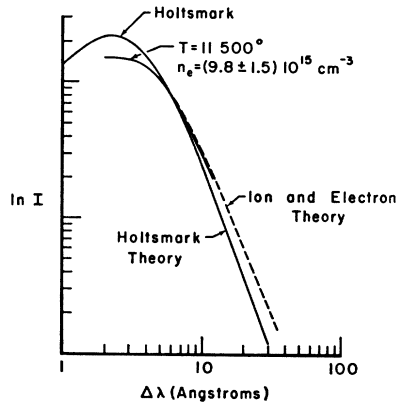

FIG. 11. Comparison of wing intensities (after Kolb).

are considered. The arbitrary cutoff in the collision parameter, taken usually at d or $n^{-\frac{1}{3}}$, introduces an uncertainty in the final broadening; but, more important even, the nonconvergence leads to the phenomenon of the most distant collisions producing the greatest amount of broadening. Griem, in establishing the applicability of the Lindholm distribution to his broadening results, states that only phase shifts greater than unity are important and points to the improbability of multiple impacts within ρ_c, in order to validate the single-impact theory. His arguments, therefore, ignore the long-range contributions to the broadening. In the cases where $d \leqslant \rho_c$, the Lindholm theory may indeed be used. At the temperature of the Kiel experiments $T \approx 10^4$ °K, and we find the values in Table VII

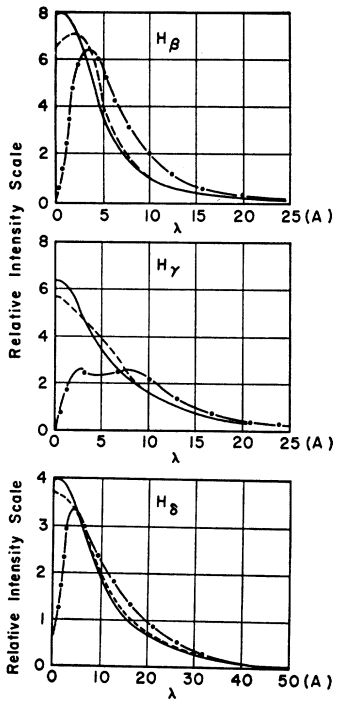

FIG. 12. Comparison of Holtsmark theory jor $F_0=100$ esu, and the folded distribution, with experiment for H_β, H_γ, and H_δ.

for n^*, the density above which all impacts occur within ρ_c. Thus, for the observed densities, $n \approx 5 \times 10^{16}$ cm^{-3}, the Lindholm theory should not be expected to be strictly valid, except for the very close collisions.

Aside from these details, there is a very general defect of the folding procedure when it involves a statistical distribution varying more rapidly with λ than λ^{-2}, such as Holtsmark's, in that it forces the asymptotic dependence of intensities, as $\lambda \to \infty$, to be proportional to λ^{-2}, which contradicts the wing theorem. Hence, one should not expect a line folded in accordance with Eq. (7.1) to agree with observations at very large λ. This criticism also applies to the use of Eq. (6.30) and all applications based on it.

Ecker[30b] has discussed the desirability of including in the calculation of intensities both the electron effect and the modification of the statistical theory at large distances. He dealt with the latter in reference 30, where the parameter δ is introduced to effect the correction. In reference 30b he folds an impact distribution into a statistical one. But he does this for $\delta = \infty$ and, therefore, obtains results which do not go beyond those of Griem and are in essential agreement with them.

Another result obtained by the Kiel investigators demonstrates that electron collision effects increase at a more rapid rate than do the statistical effects as one proceeds to higher series members. This is in agreement with both the Lindholm theory and the quantum mechanical calculation. Difficulties in the inclusion of the electron effects are implied even in the early work of the Kiel group, as one may see from the following discrepancy. Henkel's fit with the folded distribution leads to values of the perturber density which are about $\frac{1}{3}$ of those derived from the Holtsmark wing fits, i.e., the method employed by Jürgens. When this result is applied to the data of Jürgens, which antedated the suggestion for the use of (7.6), the Saha[59] equation no longer yields his measured value of the temperature.

VIII. QUANTUM TREATMENT OF THE LYMAN-α LINE

The Lyman-α or resonance line of H, because of its position in the spectrum ($\lambda = 1216$ A), has not been the object of experimental line-width work. Its basic nature and the simplicity of the spectral terms it involves, however, have been inviting to theorists, and calculations regarding its behavior have been made. Much of Spitzer's[15a,19,63] work has reference to this line, a review of which is found in Breen's[64] article. An extended study specifically of the effects of electrons in broadening the Lyman-α line was made by Kivel, Bloom, and Margenau.[13]

Quantum radiation theory is applied from the beginning, and numerous details of little practical importance are discussed. In essence, however, three rather typical effects are distinguished. The first is called *universal* broadening. It results from a schematic calculation in which only two levels are included, the lower and the upper states of the line. In the case of L_α, the upper state is actually degenerate, but this degeneracy is not taken into consideration at this stage of the analysis. The results are therefore not specific to the line in question and have a very general meaning. They ignore the first-order Stark effect by not including linear combinations of the degenerate states; and they ignore the second-order Stark effect by neglecting higher energy levels whose virtual excitation normally accounts for the distortion of the radiating atom. What the universal effect describes, then, is broadening by electrons which are scattered nearly elastically, as is apparent in the following.

Polarization of the radiating atom is introduced by properly combining the degenerate states of the upper level. The four correct combinations are known from the theory of the linear Stark effect; they are

$$\psi_+ = \frac{1}{\sqrt{2}}(\psi_{200} + \psi_{210}); \quad \psi_- = \frac{1}{\sqrt{2}}(\psi_{200} - \psi_{210});$$

$$\psi_{21-1}; \quad \psi_{21+1}.$$

The subscripts on ψ denote, in spherical coordinates, the quantum numbers nlm. The first and second of these correspond to different energies $[(-e^2/8a_0) \pm 3ea_0F]$ whereas the last two belong in first approximation to the unchanged energy $-e^2/8a_0$. Moreover, the states ψ_+ and ψ_- have permanent dipole moments in the field F. Transitions between them involve, therefore, spatial *reorientations* of the atomic dipoles occurring as a result of the perturbing electrons. The effect of ψ_{21-1} and ψ_{211} is more subtle; it represents the *induction* of a dipole moment by the passing electron. The calculation which includes only ψ_+ and ψ_- is easy because it does not lead to divergent matrix elements. Its results on the line width were termed "polarization broadening by reorientation." The inclusion of ψ_{21+1} and ψ_{21+1} produces divergences which must be dealt with more carefully. It results in much larger effects, here called "polarization broadening by induction."

Finally, there is an effect connected with matrix elements of the electron perturbation between the states $2p$ and $1s$. These obviously represent quenching by electron collisions, a problem for which the theory had already been given by Wentzel.[65]

Polarization and quenching are strongly dependent on the nature of the quantum levels entering the calculation. The results computed are, therefore, not capable of immediate generalization to other cases and are here only cited as numerical examples. The universal effect, however, presents certain features of wider interest, even though it is small in the case of the Lyman-α line.

[63] L. Spitzer, Phys. Rev. **56**, 39 (1939).
[64] R. G. Breene, Geophys. Research Papers No. 41 (1955).
[65] G. Wentzel in *Handbuch der Physik* (see reference 52), Vol. 24/1, p. 738.

The lengthy calculations in reference 13 concerning the universal effect lead to the same result as a much simpler picture,[17] which we use here. While this analysis standing by itself is perhaps not convincing, its plausibility is fairly high. Instead of considering atom, radiation field, and electron as the quantum system, we concentrate attention on the electron alone and investigate the change in its motion as it meets the radiating atom. If it loses an energy ΔE while it passes the atom, one may say that the atom gains ΔE and therefore emits a frequency shifted to the blue by $\omega_{if}=\hbar^{-1}\Delta E$. What this picture does not suggest is the potential exerted by the radiating atom upon the electron as it moves near it, for the atom has a finite probability of being in the upper as well as the lower state during the emission of radiation.

Here our earlier reflections are helpful. All through Sec. I it was evident that the perturbation responsible for line widths is ϵ, the difference between the upper and the lower energy levels as a function of the position of the perturbing particle. This is the quantity that alters the phase of the radiation in the impact theories and causes the shifts in the statistical theory. Reference 13 bears out the expectation that ϵ, in the form proper for a Coulomb interaction, should be used as the perturbation in the present problem. If the Coulomb interactions between the atomic electron at $\mathbf{r}_R$ and the perturbing electron at $\mathbf{r}$ are denoted by $C(\mathbf{r}_R,\mathbf{r})$, and $C_{ii}(r)$ is the diagonal element of $C(\mathbf{r}_R,\mathbf{r})$ with respect to the ith state of the atom, then

$$\epsilon(r)=C_{22}-C_{11}, \tag{8.1}$$

provided 2 is the upper and 1 the lower state of the line.

In accordance with the usual procedure in (time-dependent) perturbation theory it is now supposed that the electron, before the interaction, has an anergy E_i and its state is represented by a probability amplitude a_i, whereas afterward these quantities are changed to E_f and a_f. We take the states to be those of a free electron: $E_s=(\hbar^2/2m)k_s^2$, $\psi_n\propto\exp(i\mathbf{k}_n\cdot\mathbf{r})$. The amplitude a_f is then a function of t as well as of ω_{if}, and the intensity of the spectral line at a frequency ω_{if} beyond its normal frequency is given by

$$I(\omega_{if})\propto\lim_{t\to\infty}|a_f(\omega_{if})|^2. \tag{8.2}$$

Strictly, the limit $t\to\infty$ is meaningless because the radiative process lasts only for a finite time which is the reciprocal of the natural line width in cycles per second. This natural width is being neglected in the passage to an infinite limit.

The equations for the amplitudes are

$$i\hbar\dot{a}_i=\textstyle\sum_f a_f\epsilon_{fi}e^{-i\omega_{fi}t}, \tag{8.3}$$

$$i\hbar\dot{a}_f=a_i\epsilon_{if}e^{-i\omega_{if}t},\qquad \omega_{if}\equiv\hbar^{-1}(E_i-E_f). \tag{8.4}$$

If we put $a_i=\exp(-\gamma_u t)$, integrate (8.4) and substitute in (8.3) we find

$$\gamma_u=\sum_f\frac{|\epsilon_{if}|^2}{\hbar^2}\frac{e^{i\omega_{if}t+\gamma_u t}-1}{i\omega_{if}+\gamma_u}. \tag{8.5}$$

The sum over final states is converted to an integral in a well-known manner:

$$\sum_f\rightarrow\int\frac{V}{(2\pi)^3}\cdot 2\pi k_f^2dk_f\sin\theta d\theta,$$

where θ is the angle between the wave-number vectors of the electron, $\mathbf{k}_i$ and f_f, and V is the volume per electron. If ω_n is written for $\hbar k_n^2/2m$, the integration over ω_f in (8.5) can be carried out according to the formula[66]

$$\int f(\omega_f)\frac{e^{i(\omega_i-\omega_f)t+\gamma_u t}-1}{i(\omega_i-\omega_f)+\gamma_u}d\omega_f\doteq\pi f(\omega_i),$$

and (8.5) results in

$$\gamma_u=\frac{V}{(2\pi)^2}\frac{m\pi k_i}{\hbar^3}\int|\epsilon_{if}|^2\sin\theta d\theta, \tag{8.6}$$

with the understanding that the remaining integrand is evaluated at $k_f\cong k_i$. This shows that the scattering which leads to γ_u is essentially elastic.

Now ϵ_{if} is easily computed; it is expressible in terms of other atomic integrals frequently encountered in scattering theory, namely,

$$F_{ss}(\boldsymbol{\kappa})\equiv\int\exp(i\boldsymbol{\kappa}\cdot\mathbf{r}_R)|\psi_s(\mathbf{r}_R)|^2d\mathbf{r}_R.$$

Thus

$$\epsilon_{if}=\frac{4\pi e^2}{V\kappa^2}(F_{22}-F_{11})$$

and

$$\kappa^2=k_i^2+k_f^2-2k_ik_f\cos\theta. \tag{8.7}$$

From this last relation $\sin\theta d\theta$ is computed, and Eq. (8.6) then gives

$$\gamma_u=\frac{2\pi e^4}{V}\frac{a_0^2m}{\hbar^2k_i}\int_0^{x'}\left(\frac{F_{22}-F_{11}}{x}\right)dx. \tag{8.8}$$

The variable x here stands for κ^2a_0 and a_0 is the first Bohr radius; F_{11} and F_{22} refer, of course, to the $1s$ and to the weighted mean of the $2p$ states of hydrogen. The upper limit, $x'=4k_i^2a_0^2$, represents the maximum value permitted by (8.7) when $k_i=k_f$.

Let us call the remaining integral in (8.8) $2\pi^2Y$; it is a function of the initial energy of the perturbing electron through x'. In Fig. 13 it is plotted for the L_α line, E_i being in units equal to the ground-state energy

[66] W. Heitler, *Quantum Theory of Radiation* (Oxford University Press, 1936), first edition, p. 112.

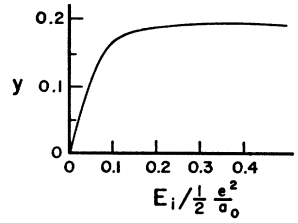

FIG. 13. Graph of the efficiency factor Y *vs* electron energy. See Eq. (8.9).

of hydrogen. If now we replace V in Eq. (8.8) by n^{-1} and $\hbar k_i$ by mv_i, that equation reduces to

$$\gamma_u = nv_i\pi(h/mv_i)^2 Y(v_i). \tag{8.9}$$

From Eq. (8.4)

$$-ih a_f = \epsilon_{if}\frac{e^{-\gamma_u t - i\omega_{if}t}-1}{\gamma_u + i\omega_{if}}$$

because $a_i = e^{-\gamma_u t}$. Hence, (8.2) yields a dispersion curve of half-width $2\gamma_u$; from (8.9), therefore

$$\omega_{\frac{1}{2}}(u) = 2n[\pi(h/mv_i)^2]Y(v_i)\cdot v_i. \tag{8.10}$$

A comparison of this result with Lorentz' formula, (1.3), is interesting, for both are of the same form. Evidently the collision cross section for this type of electronic broadening is $\pi\lambda^2$ times an efficiency factor $Y(v_i)$, λ being the DeBroglie wavelength. The rise of $Y(v_i)$ from small values at small v_i illustrates again that a perturbing electron, if it is to produce effects other than shifts described by a static theory, must have sufficient velocity. The development here sketched, and also the work in reference 13, relies upon the Born approximation. When the energy of the impinging electrons is of the order of magnitude of 1 volt, as in the examples under study, this approximation may be greatly in error and the numerical results (e.g., Fig. 13 and Table VIII) may be inaccurate. When good experimental data are at hand, recalculation with better wave functions is desirable.

Meyerott and Margenau[67] computed the analog of Eq. (8.10) with the use of Lindholm's impact theory, basing the work on (4.16). But instead of using a schematic potential of the form (4.17) they employed the potentials ϵ_{2p} and ϵ_{1s} which the electron actually experiences in its approach to the hydrogen atom. The result, plotted in Fig. 14, shows moderate agreement with Eq. (8.10).

TABLE VIII. Broadening of L_α by *electron impacts* at an electron concentration $n=10^{14}$ cm^{-3}, mean energy $(1/25)(e^2/2a_0)(\approx\frac{1}{2}$ ev). The quantity $\omega_{\frac{1}{2}}^0$ is the natural line width, 3.12×10^8 sec^{-1}.

Effect, i	$\omega_{1/2}^{(i)}/\omega_{1/2}^0$
"Universal" broadening	0.13
Polarization by	
reorientation	0.027
induction	2.7
Quenching	0.0013
(Stark broadening by ions	80)

In several publications[68] Sobel'man has shown that Eqs. (8.8) and (8.10) can also be derived in a simple way from scattering theory. His method is quite similar to that employed in reference 67, and he gives useful criteria for the applicability of the scattering approach to line-width problems.

We now turn to the polarization effects, in which electrons cause transitions between the initially degenerate states. Here, the calculation is troubled by the occurrence of spurious divergences in the matrix elements, divergences which can only be avoided by the choice of a cutoff radius like the d encountered in Sec. II. The uncertainties introduced by this somewhat arbitrary procedure are not serious, however. Polarization brings the greatest contribution to the line width so far as the effect of the electrons is concerned.

Kolb, on applying his classical-path theory to the line, has made a careful comparison between his results and those of reference 13. While he reaches numerically different conclusions (resulting from omission of one matrix element in Kivel *et al.*,[13] and also from the fact that Kolb averages the Stark components of L_α with proper weight factors whereas Kivel *et al.* do not average), he is able to show that even the polarization effects can be calculated for the conditions under study with the use of classical-path theory instead of the completely quantum mechanical theory here summarized. The only effect not appearing in Kolb's work is the one called polarization by reorientation, and this is seen to be very small. In Sec. IX it appears that a similar conclusion holds for the Balmer lines—a fortunate fact likely to obviate the need for further detailed calculations.

Finally, there is the width caused by quenching. This, for L_α, turns out to be negligible. In illustration of orders of magnitude the various results are collected in Table VIII, where all quantities refer to a special situation that is approximately realized in the photosphere of the sun. The last line in the table represents the Holtsmark width produced by the ions which in this instance quite evidently outweighs all electron effects.

In judging these results and in appraising the role of the electrons at higher charge densities and for other lines, two facts need to be borne in mind. First, electron effects increase with n, ion effects only with $n^{\frac{1}{4}}$ (see Sec. III). Secondly, lines involving states of higher excitation than L_α offer larger targets to the impinging electrons, and this enhances their sensitivity to broadening impacts. The enhancement is, in fact, greater than the accompanying increase in static polarizability which accounts for the Holtsmark width. While this is not apparent from the present discussion, it manifests itself

[67] R. E. Meyerott and H. Margenau, Phys. Rev. **99**, 1851 (1955).

[68] I. Sobel'man, Optika i Spektroskopiya **1**, 617 (1956); Fortschr. Physik **5**, 175 (1957).

in our treatment of the Balmer lines in the following section, where the electrons begin to play a role that is no longer subordinate to that of the ions at attainable concentrations. There the work is limited to the effect which was here found to be predominant, namely polarization. In the terminology of Sec. IV, the adiabatic hypothesis is abandoned and full consideration is given to the degenerate states that go into the formation of a broadened line.

IX. QUANTUM THEORY OF THE BALMER LINES

An entirely quantum-mechanical treatment of the broadening of the Balmer lines *due to electrons* has been given by Landwehr.[23] A system composed of the radiator (i.e., an atom or molecule), a number N of perturbing electrons, and the quantized radiation field all confined to a volume V, is described by the Schrödinger equation

$$H\Psi = i\hbar\dot{\Psi}. \tag{9.1}$$

The Hamiltonian H is decomposed into an unperturbed part H^0 representing the total energy of the isolated components of the system, and a part H' which accounts for their mutual interaction. We write

$$H^0 = H_R{}^0 + H_f{}^0 + \sum_{j=1}^{N} H_{pj}{}^0, \tag{9.2}$$

where $H_R{}^0$, $H_{pj}{}^0$, and $H_f{}^0$ are, respectively, the unperturbed Hamiltonians of the radiator, the jth perturbing electron and the radiation field. The perturbation

$$H' = J_{Rf} + \sum_{j=1}^{N} C_{Rj}, \tag{9.3}$$

where J_{Rf} is the interaction between the radiation field and the radiator, and C_{Rj} the Coulomb interaction between the jth electron and the radiator. The Coulomb interactions between the perturbing electrons has been neglected.

Landwehr's method of calculation is similar to that of Weisskoff and Wigner[69] for the problem of the natural line width. It starts with an initial condition in which an excited atom but no photons are present and then derives the probability of finding a photon of a given frequency after a time long enough so that the atom has certainly radiated. At zero time the perturbations are "turned on" suddenly. We then have at $t=0$:

$$\psi(0) = \psi_{n_0}{}^R \psi_0{}^f \psi_{\lambda_0}{}^p,$$

where $\psi_{n_0}{}^R$ is the n_0th eigenstate of $H_R{}^0$, $\psi_0{}^f$ the null state of $H_f{}^0$, and $\psi_{\lambda_0}{}^p$ the λ_0th eigenstate of $\sum H_{pj}{}^0$. The function $\psi_{\lambda_0}{}^p$ is taken to be a product of plane waves. The momentum distribution of the N electrons is assumed to be the equilibrium distribution of the particles at the temperature T (i.e., the Boltzmann distribution).

The solution of (9.1), corresponding to the initial conditions given above, can be expanded over the eigenfunctions of H^0 to give

$$\Psi(t) = \sum_{n\lambda\nu} a_{n\lambda\nu}(t)\psi_n{}^R\psi_\lambda{}^p\psi_\nu{}^f \times \exp\left[-\frac{i}{\hbar}(E_m{}^R + E_\lambda{}^p + E_\nu{}^f)t\right], \tag{9.4}$$

with $a^{(0)}_{n_0,\lambda_0,0} = 1$. The determination of the coefficients a is extremely unwieldy; hence, it is assumed that a satisfactory approximation can be obtained by neglecting all matrix elements of H' that do not involve the initial state. This means that only the initial state can radiate a photon and all collision-induced transitions are from and into the initial state. With this assumption, the equations for the amplitudes become

$$\begin{aligned}
\dot{a}_{n_0,\lambda_0,0}(t) &= -\frac{i}{\hbar}\left\{\sum_{n\lambda}\left(n_0\lambda_0\left|\sum_{j=1}^{N} C_{Rj}\right|n\lambda\right)a_{n,\lambda,0}(t)\right. \\
&\quad \times\exp\left[-\frac{i}{\hbar}(E_n{}^R + E_\lambda{}^p - E_{n_0}{}^R - E_{\lambda_0}{}^p)t\right] \\
&\quad \left.+\sum_{n'\nu}(n_0,0|J_{Rf}|n'\nu)a_{n',\lambda_0,\nu}(t)\right. \\
&\quad \left.\times\exp\left[-\frac{i}{\hbar}(E_{n'}{}^R + E_\nu{}^f - E_{n_0}{}^R)t\right]\right\}, \\
\dot{a}_{n,\lambda,0}(t) &= -\frac{i}{\hbar}\left(n\lambda\left|\sum_{j=1}^{N} C_{Rj}\right|n_0\lambda_0\right)a_{n_0,\lambda_0,0}(t) \\
&\quad \times\exp\left[-\frac{i}{\hbar}(E_{n_0}{}^R + E_{\lambda_0}{}^p - E_n{}^R - E_\lambda{}^p)t\right], \\
\dot{a}_{n,\lambda_0,\nu}(t) &= -\frac{i}{\hbar}(n'\nu|J_{Rf}|n_0 0)a_{n_0,\lambda_0,0}(t) \\
&\quad \times\exp\left[-\frac{i}{\hbar}(E_{n_0}{}^R - E_{n'}{}^R - E_\nu{}^f)t\right].
\end{aligned} \tag{9.5}$$

The approximations have not interfered with the correct normalization, as the solutions of Eq. (9.5) retain the property

$$\sum_{n\lambda\nu} |a_{n\lambda\nu}(t)|^2 = 1.$$

For J_{Rf} we take the single-photon operator

$$J_{Rf} = -(e/m)\mathbf{p}_R \cdot \mathbf{A}_f,$$

where $\mathbf{p}_R$ is the momentum of the radiator's atomic electron and $\mathbf{A}_f$ is the vector potential of the field. The Coulomb interaction, C_{Rf}, is cut off at the distance d

[69] V. Weisskopf and E. Wigner, Z. Physik **63**, 54 (1930).

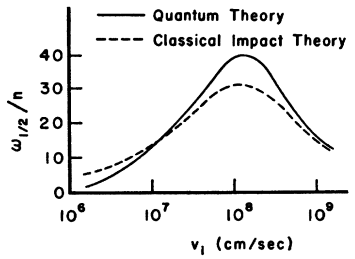

FIG. 14. "Universal" broadening. Graph of half-width *vs* electron velocities.

from the center of the radiator and given by

$$C_{Rj}=\begin{cases}-\dfrac{e^2}{r_j}+\dfrac{e^2}{|\mathbf{r}_j-\mathbf{r}_R|} & \text{for } 0\leqslant r_j\leqslant d\\ 0 & \text{for } r_j<d.\end{cases}$$

It develops that the solution of (9.5) for the initial state amplitude, is of the decaying exponential form when the following conditions hold:

$$\frac{3}{2}\frac{kT}{\hbar}\gg\Gamma_C+\Gamma_J,\quad \omega'\gg\Gamma_C+\Gamma_J.$$

Here ω' is again the frequency of the undisplaced line and $\Gamma_C+\Gamma_J$ is the total decay constant of the initial state, a sum of the contribution from electron scattering Γ_C and from spontaneous emission Γ_J. The inequalities above are both satisfied over wide ranges of interest; the case of electron broadening of the Balmer lines will be analyzed with respect to them below.

There results, for the distribution of amplitudes corresponding to frequency ω due to transitions from an initial state $(n_0,\lambda_0,0)$ to a final state (n',λ_0,ω), the simple formula

$$|a_{n'\lambda_0\omega}(\infty)|^2=\frac{(\Gamma_C+\Gamma_J)/\pi}{(\omega-\omega')^2+(\Gamma_C+\Gamma_J)^2}. \qquad (9.6)$$

Here $\Gamma_J=\sum_{n''}\Gamma^J_{n_0,n''}$ is the total radiative decay constant of the upper state, the sum being taken over all states into which the atom can radiate; $\Gamma_C=\sum_{n'''}\Gamma^C_{n_0,n'''}$ is the total collisional decay constant

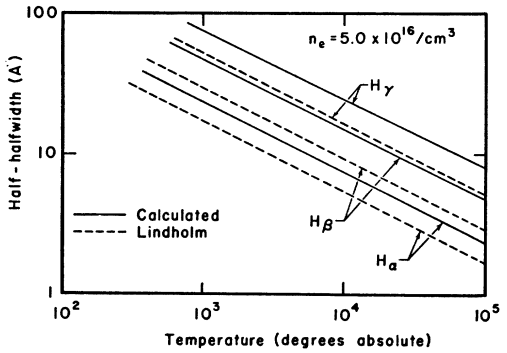

FIG. 15. Broadening of H_α, H_β, and H_γ as calculated by Landwehr, compared with classical impact theory.

of the upper state, and the sum is over all states to which the atom can pass by collisional transitions. The Γ_C depends on the transition matrix elements,

$$\Gamma_C\propto F(\boldsymbol{\kappa})\sum_{n'''}|[n_0|1-\exp(i\boldsymbol{\kappa}\cdot\mathbf{r}_R)|n'']|^2,$$

where $F(\boldsymbol{\kappa})$ is a function of $\boldsymbol{\kappa}$, the wave-number difference between the initial and final states of the colliding electron ($\boldsymbol{\kappa}=\boldsymbol{\kappa}_i-\boldsymbol{\kappa}_f$), and $\mathbf{r}_R$ is the coordinate of the atomic electron.

When degeneracy exists in the states of the radiator, the largest contribution to Γ_C comes from matrix elements of the states that are degenerate with the initial state. In addition, $F(\boldsymbol{\kappa})$ is highly weighted for values of $\boldsymbol{\kappa}$ which correspond to elastic scattering. The evaluation of Γ_C is, therefore, restricted to those states that are degenerate with the initial state. These matrix elements may be summed approximately in a convenient manner by using known sum rules.

The method leads to a spectral contour associated with a particular radiative transition between given initial and final states. In order to form a single spectral line, such as a Balmer line of hydrogen, it is necessary to combine the results obtained for each transition from one of the initial degenerate states with one of the final degenerate states. In this procedure each of the initial states is assumed to be equally populated and each transition is weighted by the relative transition probabilities per unit time in the dipole approximation. The line formed in this manner is symmetric about ω' but is not of strict resonance shape, being lower in the line core and higher in the wings.

The diagonal matrix elements of H' have been neglected in Eq. (9.6). These represent shifts in the individual line components but are presumably small because of the uniformity of the perturber's charge distribution. These neglected matrix elements, of course, are responsible for the line width and shifts in a purely adiabatic theory; however, in the extreme diabatic case (collision-induced transitions) they contribute only to the shift.

Landwehr has applied this theory to the first three Balmer lines. The half-width Γ_C arising from collision broadening of the atomic state $(n_0l_0m_0)$ is expressible in the form

$$\Gamma^C_{n_0l_0m_0}=n_0^2\left(\frac{2\pi m}{kT}\right)^{\frac{1}{2}}e^4n_ea_0^2\left\{A-B\ln\left(\frac{\hbar^2}{n_e^{\frac{1}{3}}2mkTn_0a_0}\right)+C\mathfrak{E}(\hbar^2/2mkTn_0^2a_0^2)\right\}, \qquad (9.7)$$

where A, B, and C are constants dependent on $(n_0l_0m_0)$ and $\mathfrak{E}(x)$ is the exponential integral of x.

Table IX, calculated for $n_e=5\times10^{16}$ cm^{-3} and $T=10^4$ °K, lists the ratio $\Gamma^C_{n_0l_0m_0}/\Gamma^C_{n_022}$ for the first three Balmer lines.

The form of Eq. (9.7) is strikingly similar to Eq. (4.28) for the impact half-width. Indeed when comparison is made of the results of the two theories we find exactly the same variation with temperature and electron density, as shown in Fig. 15. The dotted line is an application of the Lindholm theory, as adapted to the Balmer lines by Griem.[59] Griem treats the normally degenerate states in a given excited level as one state using an average splitting factor for this composite state. The quantum mechanical values of the half-width of the lines exceed those of the classical impact theory, by hardly more than the possible error introduced by Landwehr's use of sum rules in the evaluation of matrix elements. Thus the two theories yield about the same results, the major difference being that the Lindholm theory produces a resonance contour and the quantum mechanical theory a less peaked distribution.

The form of the variation of the collision damping constant with T and n_e

$$\Gamma^C \propto n_e T^{-\frac{1}{2}}$$

is a quite general result and has been found also by Rudkjobing[70] in a quantum mechanical calculation of a different sort.

TABLE IX. $\Gamma^C_{n_0 l_0 m_0}/\Gamma^C_{n_0 22}$ for $n_e = 5\times10^{16}$ cm^{-3} and $T = 10^4$ °K.

		(l_0, m_0)								
		(2,2)	(2, −2)	(2,1)	(2, −1)	(2,0)	(1,1)	(1, −1)	(1,0)	(0,0)
n_0	3	1	1	1.7	1.7	3.4	1.9	1.9	5.5	3.6
	4	1	1	2.8	2.8	2.9	1.3	1.3	4.7	2.8
	5	1	1	3.0	3.0	3.7	1.5	1.5	4.1	2.4

Figure 16 shows the complete quantum contour of H_β taken at $n_e = 5\times10^{16}$ cm^{-3} and $T = 1.25\times10^4$ °K as compared with a resonance curve (as predicted by Lindholm theory) of the same half-width and total integrated intensity. The solid curve in this figure results from a superposition of curves based on Eq. (9.6) for the different degenerate upper state.

Figure 17 compares the values of the half-width of H_β produced by electrons with that produced by ions (Holtsmark theory) where the average broadening is given by[59]

$$\Gamma_H \approx (3\hbar/\pi m)7.8n^{\frac{2}{3}}.$$

For stellar applications at $n \leqslant 10^{15}$ cm^{-3}, $T > 5\times10^3$ °K the electrons do not contribute much broadening of the line and may be omitted from consideration. In some interesting terrestrial applications, such as those discussed in Sec. VII B, the electrons do contribute large effects to the line. Electron broadening becomes inappreciable for extremely large values of the temperature if the number density of electrons is held fixed.

[70] M. Rudkjobing, Ann. astrophys. **12**, 229 (1949).

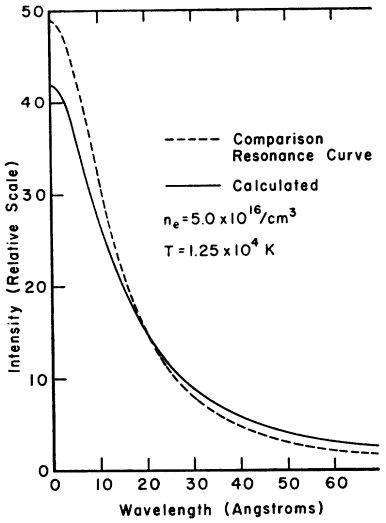

FIG. 16. Comparison of line shapes. Landwehr calculation against resonance curve.

X. SHIFTS PRODUCED BY ELECTRON COLLISIONS**

Argon spectra from high-temperature plasmas produced in shock tubes by Petschek, Rose, Glick, Kane, and Kantrowitz at Cornell proved surprising at first because the lines were not at their expected wavelengths. It seemed that the shifts were greater than could be accounted for by the usual Holtzmark theory of static ion fields and the consequent Stark shifts.†† Hence the results were attributed to line shifts induced by the free electrons in the plasma. Baranger[71] made a quantitative calculation based on the theory of Lindholm (see Sec. IV) which showed that this interpretation was reasonable.

At the same time the group at Yale[13] had been working out the details of the quantum mechanical theory of electron effects. Their predictions of hydrogen line broadening have been shown by Meyerott and Margenau[67] to agree with semiclassical broadening

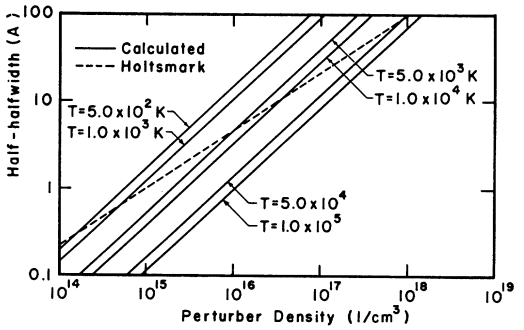

FIG. 17. Broadening of H_β, as calculated quantum mechanically, compared with Holtsmark theory.

** We are greatly indebted to Dr. B. Kivel for a draft of this section.

†† This point has not been entirely clarified; for the asymmetry of the statistical background can introduce a shift.

[71] M. Baranger, Phys. Rev. **91**, 436 (1953).

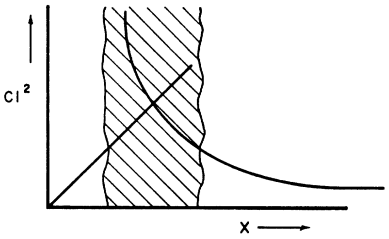

FIG. 18. Matrix element $|C(2p0 \rightarrow 2s0)|^2$ as a function of $x \equiv a_0^2K^2$. The shaded portion is uncertain.

theories. This agreement and the calculation by Baranger led Kivel[72] to expect that the quantum mechanics will also predict an electron-induced shift. The situation in hydrogen is obscured because the atomic levels are nearly degenerate, distant collisions become important, and an artifact such as the Debye shielding to cut off distant collisions must be employed in the calculations. On the other hand, argon presents the difficulty of unknown matrix elements. Helium, having hydrogenlike atomic wave functions and nondegenerate eigenvalues is free of these two problems. The experiment in pure helium, however, is not easy because for elements of low molecular weight it is difficult to heat gas to 20 000 °K and obtain the high free electron densities (10^{17}/cm^3) required. Nevertheless, Seay and Seely[73] of Los Alamos have largely succeeded in carrying it out by using a high explosive driver for their shock tube. The preliminary results are in agreement with the theory when an algebraic error in reference 72 is corrected.

An interesting aspect of this work is that the Born approximation used in the theory gives a reasonable result. Though perhaps somewhat surprising, this reflects the fact that the approximation requires only that the energy of the electron be large compared to the atomic energy separation, and not the atomic binding energies. Also, while the Born approximation fails to some extent for slow electron scattering, in our problem a small error in the electron trajectory is not serious. This same circumstance accounts in general for the success of the classical theories in line-broadening problems, i.e., the Born approximation is close to the classical correspondence limit.

A. Quantum Theory

The line shift might be expected as a matter of course since it arises from the coupling of two states by a perturbation (electron-atom interaction), and such perturbations generally cause coupled states to separate in energy. To deal with this shift quantitatively, we apply a simple correction to the theory of the line width in Sec. VIII where we used the approximation

$$\int f(\omega_f)\frac{e^{i(\omega_i-\omega_f)t+\gamma t}-1}{i(\omega_i-\omega_f)+\gamma}d\omega_f \doteq \pi f(\omega_i). \qquad (10.1)$$

In this formula $f(\omega_f)$ is the collision matrix element integrated over the scattering angle; it depends on $\omega_f \equiv (h/2m)k_f^2$ through the quantity κ, defined in (8.7), which appears in ϵ_{if} and therefore in $f(\omega_f)$. As an example, we reproduce the sketch of $|C(2p0 \rightarrow 2s0)|^2$, which is proportional to $f(\omega_f)$ as a function of the momentum transfer $a_0^2\kappa^2 \equiv x$ given in reference 13 (see Fig. 18). The region of interest in helium is that of large momentum transfers, since the atomic states are not degenerate. Here the close collisions matter, the Debye cutoff does not enter, and the $|C|^2$ dependence on x is known. For hydrogen, however, where the energy levels are close together and the distant collisions become important, the problem is more complicated and is not worked out at this time.

The physical meaning of the decrease in the matrix element with x is that the electron prefers to minimize its momentum change. Consequently, if the electron causes an atomic transition which requires energy (excites the atom) some of this energy will come from the photon (red shift) since the electron is stingy with its own energy change. Similarly for de-exciting collisions the photon will gain energy (blue shift). This is in agreement with simple expectation based on first order perturbation theory where coupled levels repel each other. Figure 19 shows this schematically: the perturbation C changes the optical transitions J in the indicated manner.

Now we return to Eq. (10.1). In view of the slow variation of $f(\omega)$ with ω, Eq. (10.1) is not strictly valid. A more careful evaluation yields an extra, imaginary term on the right, and this term gives rise to a shift, δ_i, of the line.

Quantitatively,[72] the shift (assumed small compared to energy separation; hence the formula given is not valid for hydrogen) is a sum over all coupled states

$$\hbar\delta_i = (hnv_\lambda\sigma_\lambda/3)\sum_{n\neq i}(\omega_{ni}/|\omega_{ni}|)(|\mathbf{r}_{ni}|/a_0)^2, \qquad (10.2)$$

where n=electron density, v_λ=electron velocity, $\sigma_\lambda = \pi(\hbar/mv_\lambda)^2$, $|r_{ni}|^2 = |x_{ni}|^2 + |y_{ni}|^2 + |z_{ni}|^2$, ψ_n=free atom function for eigenvalue E_n with space vector $\mathbf{r}$, and $\hbar\omega_{ni} = E_n - E_i$.

The error in Bethe[74] was the use of $|z_{ni}|^2$ instead of the correct $|\mathbf{r}_{ni}|^2$, as given above. It is interesting that the shift does not depend on the magnitude of the energy separation if the electron has enough energy to excite the transition. For a Maxwell-Boltzmann dis-

[72] B. Kivel, Phys. Rev. **98**, 1055 (1955).
[73] G. E. Seay and L. B. Seely, Jr., Bull. Am. Phys. Soc. **1**, 227 (1956), Washington Meeting, 1956.
[74] H. Bethe in *Handbuch der Physik* (see reference 52), Vol. 24/1, p. 433.

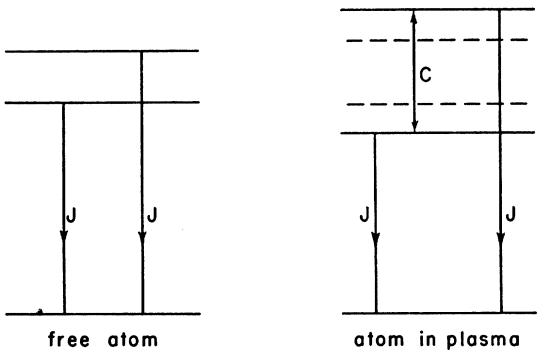

FIG. 19. Energy levels in a plasma.

tribution of velocities we find (δ is in units of sec^{-1}):

$$\hbar\delta_i = 4.55\times10^{-8}\hbar n\left(\frac{e^2}{2a_0kT}\right)^{\frac{1}{2}}\left\{\sum_{E_n>E_i}\left|\frac{\mathbf{r}_{ni}}{a_0}\right|^2 \times\exp(-\hbar\omega_{ni}/kT)-\sum_{E_n<E_i}\left|\frac{\mathbf{r}_{ni}}{a_0}\right|^2\right\}. \quad (10.3)$$

This assumes the Born approximation even for the zero energy electrons.

B. Application to Helium

As a sample application we consider the He line $4s\rightarrow 2p$ at $\lambda=4713$ A. This is one of the lines studied by Seay and Seely at Los Alamos and has a measured shift to the red estimated to be 25 A when the electron density is $n=4\times10^{17}/\text{cm}^3$ and the temperature is $T=20\,000$ °K. This shift is far too large to be accounted for by ions, which produce only a few angstroms. On the other hand, Eq. (10.3) predicts a line shift of about 35 A, as shown below. Considering that the measurement is preliminary and that the calculation uses the Born approximation, this seems to establish the electron effect.

To evaluate Eq. (10.3) we note that the sum over the magnetic quantum number removes the angular dependence[74]; i.e.,

$$\sum_{m'}|\mathbf{r}_{nlm}{}^{n'l+1\,m'}|^2=\frac{l+1}{2l+1}(R_{nl}{}^{n'l+1})^2$$

and

$$\sum_{m'}|\mathbf{r}_{nlm}{}^{n'l-1m'}|^2=\frac{l}{2l+1}(R_{nl}{}^{n'l-1})^2.$$

The radial integrals R are tabulated for hydrogenic wave functions in the quantum mechanical literature.

For the $4s\rightarrow 2p$ transition the most important term in the curly brace is the $4s\rightarrow 4p$ term for which $(R_{4s}{}^{4p})^2=540$, $(l+1)/(2l+1)=1$ and the exponential in Eq. (10.3) is 0.9360, so that there is a contribution of $+505$ (to the red); similarly the transition $4s\rightarrow 5p$ contributes $+56$; $4s\rightarrow 6p$, $+8.4$, $2p\rightarrow 3d$, -4 (to blue); and $2p\rightarrow 2s$, $+9$. The net of all terms with principal quantum number $\leqslant 8$ is 573. The corresponding wavelength shift for $n=4\times10^{17}$ and $T=20\,000$ °K ($kT=1.72$ ev) is

$$\Delta\lambda=\lambda^2\delta/2\pi c=35\text{ A}.$$

C. Comparison with Lindholm's Theory

It is interesting to compare this result with that of Lindholm's theory. From Eq. (4.22) we find for the line shift according to Lindholm:

$$u_2=9.8\Omega_4{}^{\frac{1}{2}}v^{\frac{1}{2}}n.$$

Considering only the main contributions of $4s-4p$ to the polarization, one finds

$$u_2=\pi^2nva_0{}^2\left[\frac{|z_{4s,4p}|^2}{a_0{}^2}\frac{e^2/a_0}{hc\Delta\nu}\frac{\alpha c}{v}\right]^{\frac{1}{2}}. \quad (10.4)$$

Since $\alpha=1/137$, $|z_{4s,4p}|^2=180a_0{}^2$, $\Delta\nu_{4s,4p}=919$ cm^{-1} the line shift for the same values of n and T as in B is about 24 A. We have written (10.4) so that it can be compared with the quantum result, Eq. (10.3), which reads, with retention of the same matrix element,

$$\delta=\pi nva_0{}^2\left[2\frac{|z_{4s,4p}|^2}{a_0{}^2}\left(\frac{\alpha c}{v}\right)^2\right]. \quad (10.5)$$

This gives a shift of 28 A.

Lindholm's theory assumes that the perturber can be localized sufficiently long so that it is reasonable to consider a polarized atom. This is in contrast with our calculation, which assumes the particles to be moving so quickly that the atom is at all times essentially free. Also our treatment which uses the Born approximation is restricted to perturbers with kinetic energy large compared to the atomic energy level separations (e.g., $\Delta\nu_{4s,4p}$).

These two extreme assumptions predict similar effects, since the physical situations being considered lie between their separate provinces. Their agreement makes the magnitude of the result more secure, especially since they are reasonably close to the experimental value.

ACKNOWLEDGMENT

This paper evolved from a technical memorandum written two years ago by Margenau and Landwehr. To Dr. Landwehr we are indebted for the first draft of Secs. II and IX. Dr. Kivel's contribution (see Sec. X) is gratefully acknowledged. After this article had been written, a manuscript and a research memorandum by M. Baranger were received. Unfortunately, their contents, though of great relevance to the problems here discussed, could not be included in this survey.