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ELECTRON IMPACT BROADENING

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of

SPECTRAL LINES

Bennett Kivel

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ABSTRACT

A quantum mechanical formalism for treating pressure broadening by electron impacts is developed and applied. In particular, the large region of high temperatures and low densities where electron effects are minor is delimited. With diminution of electron temperature and increased density first order corrections to the natural line are found. Here two perturbations are distinguished: 1) change in electron scattering on atomic transition and 2) polarization of the atom. Having developed methods for these regions of small electron effects, application is made to the hydrogen like 2p to 1s transition. By inclusion of a second excited state, namely 2s, polarization is studied.

Some properties of matrix elements involving the form factor which are familiar in scattering theory are studied in detail.

Finally larger broadening effects are considered. An experiment suitable for verification of this electron collision broadening theory is proposed.

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I. INTRODUCTION.

Current investigators of hydrogen line breadths in stellar spectra indicate that Stark broadening by ions is insufficient to account for the observations^{1,2}. They suggest that the difficulties may be obviated by taking into account the electron effects. Another discrepancy is the failure of Holtsmark theory for ions to predict the large shifts of argon spectral lines found by Kantrowitz³ in the study of shock phenomena. Baranger⁴ attributes the difference to electrons. This correction also interests workers using spectral line widths to measure plasma characteristics in discharge tubes⁵. Here the density of charge employed in the Holtsmark theory is taken to be intermediate between the ion density and ion plus electron density⁶.

Reasonable qualitative conclusions about the electron broadening and shift of spectral lines can be found from a semi-classical model⁷. If, for example, the electron density is low and the lifetime of the excited radiator is short, then not many of the atoms will be hit before they emit. By a hit we imply a sufficiently close collision to give a measurable change to the spectral line. In this paper we find the radius for the cross-section of this collision to be essentially the deBroglie wave length of the electron. Thus high energy electrons, which produce small effects, may be considered as passing the atom too quickly to polarize it or be scattered by it.

For a quantitative account we use a quantum mechanical formalism. In particular the large region of high temperatures and low densities where electron effects are minor will be delimited. With decreasing electron temperature and increasing electron density, first order corrections to the natural line are found. Here two perturbations are distinguished: 1) change in the electron energy during an atomic transition (electron

scattering) and 2) distortion of the atomic state-function (polarization) by the electrons. This second effect is important only if the atomic excited state is degenerate. Having developed methods for regions of small electron effects, application is made to the hydrogen-like 2p to 1s transition. By inclusion of the 2s state, the effects of polarization of the excited state can be studied. We consider polarization in the physically interesting situation of a hydrogen atom in a mean electrostatic field due to the ions.

At first we simplify the angular integrals in the matrix elements, saving the details for later sections. Also avoided in the early sections are the diverging matrix elements that couple degenerate atomic states.

In the last section the theory is generalized to encompass broadening larger than the natural width. A novel use of helium spectral line widths to check the theory is proposed.

II. GENERAL CONSIDERATIONS.

In earlier work¹, an approach to the problem of pressure broadening was developed which did not require the perturber to have a classical path. The present analysis is to some extent complementary to the earlier calculations and leads to similar formulas. But it is simpler in conception and places the physics of the problem in better focus.

Electron broadening can be studied as an extension of the Hoyt and Weisskopf-Wigner treatment for the natural line width². The natural decay for a two state atom ($E_1 > E_0$) is described by the growth equations

$$i\hbar \dot{d} = \sum_r J^* b_r e^{i\omega t} \quad (1)$$

and

$$i\hbar \dot{b}_r = J d e^{-i\omega t}, \quad \text{where} \quad (2)$$

$\omega = \omega_{\text{atom}} = \omega_{\text{radiation}}$, $\hbar \omega_{\text{atom}} = E_1 - E_0$, and $\hbar \omega_r$ is the energy of the emitted radiation. In these equations the matrix elements for the atom-radiation interaction (J) couple the probability amplitudes for the excited atom and dark field (d) with the ground state and a single photon (b_r). For exponential damping ($d = e^{-\gamma t}$), (2) yields the natural intensity distribution;

$$I(\omega_r) = |b_r(t = \infty)|^2 = |J/\hbar|^2 / (\gamma^2 + \omega^2). \quad (3)$$

To include a perturber (R) with the atom and the radiation field, we write the Schrodinger equation

$$i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}, R) = H(\mathbf{r}, R) \Psi(\mathbf{r}, R). \quad (4)$$

The Hamiltonian includes terms for unperturbed atom and radiation field ($H_a(\mathbf{r})$); the perturber ($H_e(R)$); an interaction between atom and perturber ($C(\mathbf{r}, R)$); and finally the interaction between atom and radiation ($J(\mathbf{r})$); it neglects the interaction between perturber and radiation.

In our notation symbols referring to the radiation field are suppressed. The wave functions and eigenenergies for the field are contained in the atomic Ψ_n and E_n .

Since we are interested in the extreme of an undistorted atom, we seek a solution which is an expansion of product functions with unperturbed atomic functions--i.e.,

$$\Psi = \sum_n \sum_{\lambda}^n a_{n\lambda}(t) \Psi_n(\underline{r}) \phi_{\lambda}^n(\underline{R}) e^{-i(\epsilon_{\lambda}^n + E_n)t/\hbar}, \quad (5)$$

where \sum_{λ}^n means the sum and/or integral over all states λ corresponding to n . Here the atomic function satisfies

$$H_a(\underline{r}) \Psi_n(\underline{r}) = E_n \Psi_n(\underline{r}), \quad \int |\Psi_n|^2 d\underline{r} = 1; \quad (6)$$

and the normalized electron function for an electron in the coulomb field of an atom in state Ψ_n

$$\left[H_e(\underline{R}) + C_{n,n}(\underline{R}) \right] \phi_{\lambda}^n(\underline{R}) = \epsilon_{\lambda}^n \phi_{\lambda}^n(\underline{R}), \quad (7)$$

$$\int |\phi_{\lambda}^n|^2 d\underline{R} = 1,$$

$$C_{m,n}(\underline{R}) = \int \Psi_m^* C \Psi_n d\underline{r}. \quad (8)$$

To justify the use of this expansion we note that the best product function with neglect of the exchange property is given by the Hartree equations:

$$\left(H_a + \int \phi_{\lambda}^{n*} C \phi_{\lambda}^n d\underline{R} \right) \Psi_n^{\lambda} = E_n^{\lambda} \Psi_n^{\lambda}; \quad (8)$$

$$\left(H_e + \int \Psi_n^{\lambda*} C \Psi_n^{\lambda} d\underline{r} \right) \phi_{\lambda}^n = \epsilon_{\lambda}^n \phi_{\lambda}^n. \quad (9)$$

For high perturber energies (ϵ_λ^n), ϕ_λ^n is to a good approximation a plane wave. Then $|\phi_\lambda^n|^2$ is a constant independent of λ and ψ_n^λ is the atomic state in a uniform charge distribution normalized to the perturber density. Now for low perturber density as a first approximation we neglect the shielding effects of this charge distribution on ψ_n^λ . Thus we ignore the C matrix element in (8) and our equations take the form of equations (6) and (7). Since the product $\psi_n \phi_\lambda^n$ is not a stationary solution for the material system, there will be a perturbation containing C.

On substituting (5) into (4) and using (6) and (7), we find that

$$i\hbar a_{m\mu} e^{-i(\epsilon_\mu^m + E_m)t/\hbar} = \sum_n \sum_\lambda^n a_{n\lambda} J_{mn} \int \phi_\mu^{m*} \phi_\lambda^n d\mathbf{R} e^{-i(\epsilon_\lambda^n + E_n)t/\hbar} + \sum_{(n \neq m)} \sum_n \sum_\lambda^n \int \phi_\mu^{m*} C_{mn} \phi_\lambda^n d\mathbf{R} a_{n\lambda} e^{-i(\epsilon_\lambda^n + E_n)t/\hbar} \quad (12)$$

In this equation we note two additions to the Weisskopf-Wigner equations. First is the exchange of energy between electron and radiation field which enters because of the ϵ_μ^m and ϵ_λ^n factors in the exponent. The likelihood of these shifts depends on the integral factor

$$\int \phi_\mu^{m*} \phi_\lambda^n d\mathbf{R} = \frac{\int \phi_\mu^{m*} (C_{nn} - C_{mm}) \phi_\lambda^n d\mathbf{R}}{\epsilon_\lambda^n - \epsilon_\mu^m} \quad \text{for } (\epsilon_\lambda^n \neq \epsilon_\mu^m). \quad (13)$$

The expression for this integral in terms of eigenvalues is obtained from (7); it is written here to show that small energy exchanges are weighted strongly. Second is the distortion of polarization and quenching of the atom which is introduced by the matrix elements $C_{m,n}$ characteristic of the collision.

These two effects may be treated separately in our case of low electron density and high temperature. Here modification of the spectral line is small.

The first correction, which will be referred to as scattering, is studied with neglect of the off-diagonal elements $C_{m,n}$. This approximation holds for atoms which are not easily polarized or quenched. Hence, it is valid for transitions between two isolated atomic levels. The correction then stems from the atomic transition taking place in the field of the electron. A measure of the change in the spectral line is given by the scattering of the electron beam with the change in atomic state, as might be expected.

For the two state atom with neglect of quenching,

$$i\hbar \dot{a}_\lambda = \sum_r \sum_\mu^0 b_{r\mu} J_r^* e^{i\omega t + i\Omega_{\lambda\mu} t} \int \phi_\lambda^{1*} \phi_\mu^0 dR \quad (13)$$

$$i\hbar \dot{b}_{r\mu} = \sum_\lambda^1 d_\lambda J_r e^{-i\omega t - i\Omega_{\lambda\mu} t} \int \phi_\mu^{0*} \phi_\lambda^1 dR \quad (14)$$

$$\text{with } \hbar\Omega_{\lambda,\mu} = \epsilon_\lambda^1 - \epsilon_\mu^0.$$

We now establish the fact that the exponential decay approximation for the initially excited atom is independent of the electron state. From the second of equations (14) we find an integral for $b_{r\mu}(t)$ which we substitute into the first:

$$i\hbar \dot{a}_\lambda = \sum_r \sum_\mu^0 \frac{|J_r|^2}{i\hbar} \sum_\lambda^1 \int_0^t d_\lambda e^{-i\omega(\tau-t) - i\Omega_{\lambda\mu}(\tau-t)} d\tau e^{i\Omega_{\lambda\lambda} t} \cdot \left[\int \phi_\mu^{0*} \phi_\lambda^1 dR' \cdot \int \phi_\lambda^{1*} \phi_\mu^0 dR \right]. \quad (15)$$

The assertion is that $d_\lambda = a_\lambda^1 e^{-\gamma t}$, where a_λ^1 is a constant. We check by seeing if it reduces the differential equation (15) for d_λ to an identity.

The sum over oscillator states has been replaced by an integral

$$\sum_{\mathbf{r}} \rightarrow \int_0^{\infty} \rho_{\mathbf{r}} d\omega_{\mathbf{r}} \approx \int_{-\infty}^{+\infty} \rho_{\mathbf{r}} d\omega$$

where the symbols for the integration over angles of emission and the sum over polarizations are suppressed into $\rho_{\mathbf{r}}$. Since the integral factor,

$\int \phi_{\mu}^{0*} \phi_{\lambda}^1 d\mathbf{R}_{\mp}$, becomes small for large $\Omega_{\lambda, \mu}$, we can factor $|J_{\mathbf{r}}|^2 \rho_{\mathbf{r}}$ out of the integral over $\omega_{\mathbf{r}}$, provided it remains constant over the spectral line. Integrating over $x = -(\omega + \Omega_{\lambda, \mu})$ and then over τ :

$$\begin{aligned} \int_0^t d_{\lambda} \int_{-\infty}^{+\infty} e^{ix(\tau-t)} dx d\tau &= \int_0^t e^{-\gamma(\tau-t)} 2\pi\delta(\tau-t) d\tau a_{\lambda}^1 e^{-\gamma t} \\ &= \pi a_{\lambda}^1 e^{-\gamma t}. \end{aligned} \quad (16)$$

Then

$$\begin{aligned} \dot{d}_{\lambda} &\approx -\pi |J/h|^2 \rho \sum_{\lambda'} d_{\lambda'} e^{i\Omega_{\lambda\lambda'} t} \sum_{\mu} \int \phi_{\mu}^{0*} \phi_{\lambda}^1 d\mathbf{R}_{\mp} \cdot \int \phi_{\lambda}^{1*} \phi_{\mu}^0 d\mathbf{R}_{\mp} \\ &= -\gamma \sum_{\lambda'} d_{\lambda'} e^{i\Omega_{\lambda\lambda'} t} \delta_{\lambda\lambda'} = -\gamma d_{\lambda} \end{aligned} \quad (17)$$

with $\gamma = \pi \rho |J/h|^2$. With this result

$$ihb_{\mathbf{r}} = \sum_{\mu} ihb_{\mathbf{r}\mu} = J_{\mathbf{r}} e^{-\gamma t - i\omega t} \int \phi_0^* \phi_1 d\mathbf{R}_{\mp} \quad (18)$$

provided that

$$\phi_1 = \sum_{\lambda} a_{\lambda}^1 \phi_{\lambda}^1 e^{-i\epsilon_{\lambda}^1 t/h} \quad \text{and} \quad \phi_0 = \sum_{\mu} \phi_{\mu}^0 e^{-i\epsilon_{\mu}^0 t/h} \quad (19)$$

Both ϕ_0 and ϕ_1 satisfy equations for electron wave packets moving in the Hartree field of the corresponding atomic state. Namely,

$$(H_e + C_{n,n})\phi_n = i\hbar \frac{\partial}{\partial t} \phi_n. \quad (20)$$

Suppose the electron is initially in a single stationary state (λ), so that $a_{\lambda, \lambda}^1 = \delta_{\lambda, \lambda}$. Then we find from (14) for the line intensity

$$I_B(\omega) = \sum_{\mu} |b_{r\mu}(\infty)|^2 = |J/\hbar|^2 \sum_{\mu} \frac{\left| \int \phi_{\mu}^{0*} \phi_{\lambda}^1 d\vec{R} \right|^2}{\gamma^2 + (\omega + \Omega_{\lambda\mu})^2}. \quad (21)$$

We note that the normalization of $I_B(\omega)$ is maintained, ($\int I_B d\omega = \int I d\omega$), since

$$\int_{-\infty}^{+\infty} \frac{d\omega}{\gamma^2 + (\omega + \Omega_{\lambda\mu})^2} \cong \int_{-\infty}^{+\infty} \frac{d\omega}{\gamma^2 + \omega^2} \quad (22)$$

is independent of μ and by the closure property

$$\sum_{\mu} \left| \int \phi_{\mu}^{0*} \phi_{\lambda}^1 d\vec{R} \right|^2 = 1. \quad (23)$$

What can we say about the line shape using equations (21) and (13)?

First we note that

$$\left| \int \phi_{\mu}^{m*} \phi_{\lambda}^n d\vec{R} \right|^2 \leq 1. \quad (24)$$

To see this we expand

$$\phi_{\lambda}^n = \sum_{\mu} a_{\mu} \phi_{\mu}^m \quad (25)$$

where by normalization

$$\int |\phi_{\lambda}^n|^2 d\vec{R} = 1 = \sum_{\mu} |a_{\mu}|^2 \quad (26)$$

so that every

$$|a_{\mu}|^2 \leq 1 \quad (27)$$

and

$$\left| \int \phi_\mu^* \phi_\lambda dR \right|^2 = |a_\mu|^2 \leq 1. \tag{28}$$

Hence, despite the resonance which occurs in (13) as ϵ_λ approaches ϵ_μ none of the elements diverge. However, since functions for free electrons have continuous eigenenergies, we expect a large weight for components in (21) with small energy shifts. Consequently we also expect little broadening.

To evaluate this broadening we expand ϕ as a linear combination of eigenfunctions (u_λ) that are independent of the atomic state. In place of eq. (19) we write

$$\phi_1 = \sum_\lambda d_\lambda u_\lambda e^{-i\epsilon_\lambda t/\hbar} \quad \text{and} \quad \phi_0 = \sum_\lambda b_\lambda u_\lambda e^{-i\epsilon_\lambda t/\hbar}, \tag{29}$$

where $H_e u_\lambda = \epsilon_\lambda u_\lambda$. Equation (20) then leads to

$$i\hbar \dot{d}_\lambda = \sum_\mu (C_{1,1})_{\lambda,\mu} e^{i(\epsilon_\lambda - \epsilon_\mu)t/\hbar} d_\mu = \sum_\mu i\hbar p_{\lambda\mu} d_\mu, \tag{30}$$

and

$$i\hbar \dot{b}_\lambda = \sum_\mu (C_{0,0})_{\lambda,\mu} e^{i(\epsilon_\lambda - \epsilon_\mu)t/\hbar} b_\mu = \sum_\mu i\hbar q_{\lambda\mu} b_\mu; \tag{31}$$

with

$$(C)_{\lambda,\mu} = \int u_\lambda^* (C) u_\mu dR;$$

the p and q matrices are defined by (30) and (31).

Then

$$\int \phi_0^* \phi_1 dR = \sum_\mu b_\mu^* d_\mu = b(t)^\dagger d(t). \tag{32}$$

Here b and d are column vectors. On introducing the unitary time-development matrices T and U, defined by $d(t) = T(t) d(0)$, $b(t) = U(t) b(0)$, which by (19) and (20) satisfy $\dot{T} = pT$ and $\dot{U} = qU$, we find that (32) becomes

$$\int \phi_0^* \phi_1 \frac{dR}{\tau} = b^\dagger a = b(0)^\dagger U^\dagger T d(0). \quad (33)$$

When exponential decay of the initially excited state is assumed, equation (18) takes the form

$$i\hbar \dot{b}_r = J b(0)^\dagger U^\dagger T d(0) e^{-(\gamma+i\omega)t}. \quad (34)$$

For the broadened line intensity we then have,

$$I_B = |b_r(\infty)|^2 = |J/\hbar|^2 \text{Tr} \left[\rho^0 \int_0^\infty d\tau T^\dagger U e^{-(\gamma-i\omega)\tau} \int_0^\infty d\tau U^\dagger T e^{-(\gamma+i\omega)\tau} \right], \quad (35)$$

where

$$\rho^0 = a(0)a(0)^\dagger \quad \text{and} \quad b(0) b(0)^\dagger = E \quad (36)$$

a unit matrix.

The requirement that $b(0)$ shall be unitary is not an arbitrary one (see (19)) and follows from the limiting case in which the interaction between atom and electron vanishes. Here the unmodified spectral line requires

$$\left| \int \phi_0^*(0) \phi_1(0) dR \right|^2 = 1 \quad (37)$$

From this it follows that

$$\sum_\mu |b_\mu(0)|^2 |a_\mu(0)|^2 = 1, \quad (38)$$

since in an average over a random phase distribution the cross terms $b_\mu^*(0) b_\nu(0)$ cancel. The restriction on the $d_\mu(0)$ stems from the initial electron normalization;

$$\int |\phi_1(0)|^2 dR = \sum_{\mu} |d_{\mu}(0)|^2 = 1 \quad (39)$$

Since one can construct $|d_{\mu}(0)|^2 = \delta_{\mu\nu}$, it is required to satisfy (38) that $|b_{\nu}(0)|^2 = 1$. This holds for each ν and justifies our contention that $b(0) b(0)^{\dagger}$ is the unit-matrix.

We now transform

$$d_{\mu} \rightarrow d_{\mu} e^{-i(C_{1,1})_{\mu\mu} t/\hbar} \quad \text{and} \quad b_{\mu} \rightarrow b_{\mu} e^{-i(C_{0,0})_{\mu\mu} t/\hbar}, \quad (40)$$

and thereby remove the diagonal elements from p and q .

For plane waves these diagonal matrix elements are independent of the electron state, since $|u_{\lambda}|^2 \propto |e^{i\mathbf{k}_{\lambda} \cdot \mathbf{R}}|^2 = 1$. Designating such elements by

$$(C_{n,n})_{\lambda\lambda} = C_{n,n} \quad (41)$$

$$\begin{aligned} \int \phi_0^* \phi_1 dR &= \sum_{\lambda} b_{\lambda}^* d_{\lambda} e^{i[(C_{0,0})_{\lambda\lambda} - (C_{1,1})_{\lambda\lambda}]t/\hbar} \\ &= e^{i[C_{0,0} - C_{1,1}]t/\hbar} \sum_{\lambda} b_{\lambda}^* d_{\lambda}. \end{aligned} \quad (42)$$

In computing I_B from (34) and (35) we shall absorb the exponential factor occurring in (42) into $e^{-i\omega t}$ as a line shift. Its magnitude is the change in electrostatic interaction energy of the atomic states with a uniform charge distribution normalized to the free electron density. (IX - (1)).

With this transformation I_B of (35) is identical with equation (5) in Chapter 7 of S. Bloom's dissertation. First he notes that if the perturbation elements as $(C_{1,1})_{\lambda,\mu}$ and $(C_{0,0})_{\lambda,\mu}$ are equal, then no broadening occurs. In this case electron scattering by the atom is the same for the two atomic states. Here no change of the electron energy occurs with the radiative transition and no broadening is expected. To demonstrate this result set $p(t) = q(t)$; then $T = U$; $T^{\dagger}U = E$; and

$$\begin{aligned}
 I_B &= |J/\hbar|^2 \operatorname{Tr} \left\{ \rho^0 \int_0^\infty dt e^{-(\gamma - i\omega)t} \int_0^\infty dt' e^{-(\gamma + i\omega)t'} \right\} \\
 &= \frac{|J/\hbar|^2}{\gamma^2 + \omega^2}, \quad (43)
 \end{aligned}$$

since $\operatorname{Tr}(\rho^0) = 1$.

Next he shows that the normalization is maintained; i.e.,

$$\int I_B \rho_r d\omega_r = 1. \quad (44)$$

This follows from (35) if it is noted that

$$\int_{-\infty}^{+\infty} e^{i\omega(t-t')} d\omega = 2\pi\delta(t-t'), \quad (45)$$

$$U(t) U(t)^\dagger = E = T^\dagger(t) T(t), \quad (46)$$

and if ρ_r is approximately a constant over the line's frequency range:

$$\begin{aligned}
 \int_{-\infty}^{+\infty} I_B \rho_r d\omega &\approx \rho \int_{-\infty}^{+\infty} I_B d\omega \\
 &\approx |J/\hbar|^2 \rho \operatorname{Tr} \left\{ \rho^0 \int_0^\infty dt \int_0^\infty dt' T^\dagger(t) U(t) U(t')^\dagger T(t') 2\pi\delta(t'-t) \right. \\
 &\quad \left. \times e^{-\gamma(t+t')} \right\} \\
 &= 2\pi |J/\hbar|^2 \rho \operatorname{Tr} \left\{ \rho^0 \int_0^\infty e^{-2\gamma t} dt \right\} \\
 &= 2\gamma \operatorname{Tr}(\rho^0) \frac{1}{2\gamma} = 1. \quad (47)
 \end{aligned}$$

A useful procedure for reducing I_B to a more tractable form starts by expanding T and U in powers of C ; e.g.,

$$T(t) = 1 + T^{(1)}(t) + T^{(2)}(t) + \dots \quad (48)$$

where

$$T^{(n)}(t) = \int_0^t \int_0^{t_n} \dots \int_0^{t_2} p(t_n) \dots p(t_1) dt_1 \dots dt_{n-1} dt_n. \quad (49)$$

This expansion is more strongly convergent for small C ; i.e., little scattering. The first term, $T = U = 1$, corresponds to no change in the perturber state and leaves the spectral line unchanged. Higher order terms are small if the interaction induces little change in the perturber during the lifetime of the excited atom; i.e., if

$$\sum_{\mu} \delta(\epsilon_{\lambda} - \epsilon_{\mu}) \frac{2\pi}{\hbar^2} |(c_{1,1})_{\mu\lambda}|^2 \ll \gamma \quad (50)$$

These higher terms give a correction to the spectral line which we evaluate to the second order in the elements of C .

On expanding,

$$I_B = |J/\hbar|^2 \text{Tr} \left\{ \rho^0 \left[\int_0^{\infty} dt e^{-a^*t} \left[1 + (U^{(1)})_{+T^{(1)}\dagger} + (U^{(2)})_{+T^{(2)}\dagger} + (U^{(1)})_{+T^{(1)}\dagger} U^{(1)} + \dots \right] \right. \right. \\ \left. \left. * \int_0^{\infty} dt e^{-at} \left[1 + (U^{(1)})_{\dagger T^{(1)}} + (U^{(2)})_{\dagger T^{(2)}} + (U^{(1)})_{\dagger T^{(1)}} + \dots \right] \right] \right\} \quad (51)$$

with $a = \gamma + i\omega$.

Neglecting terms of order C^3 and higher we find

$$\begin{aligned}
I_B = & |J/\hbar|^2 \text{Tr} \left\{ \rho^0 \left\{ \frac{1}{|a|^2} + \frac{1}{a^*} \int_0^\infty dt e^{-at} (U^\dagger(1) + T(1)) \right. \right. \\
& + \frac{1}{a} \int_0^\infty dt e^{-a^*t} (U(1) + T^\dagger(1)) + \int_0^\infty dt e^{-a^*t} (U(1) + T^\dagger(1)) \int_0^\infty dt e^{-at} (U^\dagger(1) + T(1)) \\
& \left. \left. + \frac{1}{a^*} \int_0^\infty dt e^{-at} (U^\dagger(2) + T(2) + U^\dagger(1) + T(1)) + \frac{1}{a} \int_0^\infty dt e^{-a^*t} (U(2) + T^\dagger(2) + T^\dagger(1) + U(1)) \right\} \right\} \quad (52)
\end{aligned}$$

We now specialize to cases where the statistical matrix ρ^0 is diagonal. Thus in the trace the non-diagonal elements $(d_\mu^* d_\nu)$ will not appear. This corresponds to cases where the random phases of d_μ , d_ν , etc., result in the mutual canceling of non-diagonal contributions. Random phases imply a lack of interference patterns or other periodicities in the perturber current. Thus

$$\begin{aligned}
I_B = & |J/\hbar|^2 \left\{ \frac{1}{|a|^2} + \frac{1}{a^*} \sum_\lambda \rho_{\lambda\lambda}^0 \int_0^\infty dt e^{-at} (U_{\lambda\lambda}^{(1)*} + T_{\lambda\lambda}^{(1)}) \right. \\
& + \frac{1}{a} \sum_\lambda \rho_{\lambda\lambda}^0 \int_0^\infty dt e^{-a^*t} (U_{\lambda\lambda}^{(1)} + T_{\lambda\lambda}^{(1)*}) \\
& + \sum_\lambda \rho_{\lambda\lambda}^0 \sum_\mu \int_0^\infty dt e^{-a^*t} (U_{\lambda\mu}^{(1)} + T_{\mu\lambda}^{(1)*}) \int_0^\infty dt e^{-at} (U_{\lambda\mu}^{(1)*} + T_{\mu\lambda}^{(1)}) \\
& + \frac{1}{a} \sum_\lambda \rho_{\lambda\lambda}^0 \int_0^\infty dt e^{-a^*t} (U_{\lambda\lambda}^{(2)} + T_{\lambda\lambda}^{(2)*} + \sum_\mu T_{\mu\lambda}^{*(1)} U_{\mu\lambda}^{(1)}) \\
& \left. + \frac{1}{a^*} \sum_\lambda \rho_{\lambda\lambda}^0 \int_0^\infty dt e^{-at} (U_{\lambda\lambda}^{*(2)} + T_{\lambda\lambda}^{(2)} + \sum_\mu U_{\mu\lambda}^{(1)*} T_{\mu\lambda}^{(1)}) \right\} \quad (53)
\end{aligned}$$

From their defining equation (49), we find for the elements in the expansion of T:

$$\begin{aligned}
 T_{\lambda\lambda}^{(1)} &= 0, & T_{\lambda\mu}^{(1)} &= p_{\lambda\mu}^0 \frac{e^{i\Omega_{\lambda\mu}t} - 1}{i\Omega_{\lambda\mu}}, \\
 T_{\lambda\lambda}^{(2)} &= \sum_{\mu} \frac{p_{\lambda\mu}^0 p_{\mu\lambda}^0}{i\Omega_{\lambda\mu}} \left[t - \frac{e^{i\Omega_{\lambda\mu}t} - 1}{i\Omega_{\lambda\mu}} \right], \\
 T_{\lambda\mu}^{(2)} &= \sum_{\nu} \frac{p_{\lambda\nu}^0 p_{\nu\mu}^0}{i\Omega_{\nu\mu}} \left[\frac{e^{i\Omega_{\lambda\mu}t} - 1}{i\Omega_{\lambda\mu}} - \frac{e^{i\Omega_{\lambda\nu}t} - 1}{i\Omega_{\lambda\nu}} \right]; \quad (54)
 \end{aligned}$$

where $p_{\mu\lambda}^0 = (C_{1,1})_{\mu\lambda}/i\eta$, $q_{\mu\lambda}^0 = (C_{0,0})_{\mu\lambda}/i\eta$.

Using these relations

$$\begin{aligned}
 I_B(\omega) &= \frac{|J/\eta|^2}{\gamma^2 + \omega^2} \left\{ 1 + \sum_{\lambda} p_{\lambda\lambda}^0 \sum_{\mu} \frac{|p_{\lambda\mu}^0 - q_{\lambda\mu}^0|^2}{\gamma^2 + (\omega + \Omega_{\lambda\mu})^2} + \frac{2}{\Omega_{\lambda\mu}^2} \left\{ (|q_{\lambda\mu}^0|^2 - |p_{\lambda\mu}^0|^2) \frac{\omega \Omega_{\lambda\mu}}{\gamma^2 + \omega^2} \right. \right. \\
 &\quad \left. \left. - |q_{\lambda\mu}^0 - p_{\lambda\mu}^0|^2 + |q_{\lambda\mu}^0|^2 \left(\frac{\gamma^2 + \omega^2 + \omega \Omega_{\lambda\mu}}{\gamma^2 + (\omega + \Omega_{\lambda\mu})^2} \right) + |p_{\lambda\mu}^0|^2 \left(\frac{\gamma^2 + \omega^2 - \omega \Omega_{\lambda\mu}}{\gamma^2 + (\omega - \Omega_{\lambda\mu})^2} \right) \right\} \right\} \\
 &\quad - \text{Real} \left(p_{\lambda\mu}^0 q_{\lambda\mu}^{*0} \left[\frac{\gamma^2 + \omega^2 + i\gamma \Omega_{\lambda\mu} + \omega \Omega_{\lambda\mu}}{\gamma^2 + (\omega + \Omega_{\lambda\mu})^2} + \frac{\gamma^2 + \omega^2 - i\gamma \Omega_{\lambda\mu} - \omega \Omega_{\lambda\mu}}{\gamma^2 + (\omega - \Omega_{\lambda\mu})^2} \right] \right) \quad (55)
 \end{aligned}$$

The frequency integral of the correction to the natural line $\left(I_B - \frac{|J/\eta|^2}{\gamma^2 + \omega^2} \right)$ is zero. Thus the line intensity is still normalized.

When the matrix elements are real, I_B has a simpler form. Indeed the matrix elements considered in the next section are real (see III-(17)(27) (28)(29)). Setting

$$p_{\lambda\mu}^0 = -iP_{\lambda\mu} = -iP_{\mu\lambda} \quad (56)$$

$$q_{\lambda\mu}^0 = -iQ_{\lambda\mu} = -iQ_{\mu\lambda} \quad (57)$$

equation (55) reduces to Bloom's equation 8, p. 86:

$$I(\omega) = \frac{|J/\eta|^2}{\gamma^2 + \omega^2} \left\{ 1 + \frac{1}{\gamma^2 + \omega^2} \sum_{\lambda} P_{\lambda\lambda}^0 \sum_{\mu} \left(\frac{P_{\lambda\mu} - Q_{\lambda\mu}}{\gamma^2 + (\omega - \Omega_{\lambda\mu})^2} \left[2P_{\lambda\mu}(\omega^2 - \gamma^2 - \omega\Omega_{\lambda\mu}) \right] \right. \right. \\ \left. \left. + \frac{P_{\lambda\mu} - Q_{\lambda\mu}}{\gamma^2 + (\omega + \Omega_{\lambda\mu})^2} \left[P_{\lambda\mu}(\gamma^2 + \omega^2) - Q_{\lambda\mu}(3\omega^2 - \gamma^2 + 2\omega\Omega_{\lambda\mu}) \right] \right) \right\} \quad (58)$$

III. EVALUATION OF ELECTRON BROADENING FOR A TWO STATE ATOM.

The Redistribution Factor

The present section, being restricted to effects that arise when the atom has but one upper state, is less interesting from the point of view of practical application than its sequels. For the restriction excludes the possibility of degeneracy, and therefore the occurrence of "linear Stark effects." These are numerically larger than the results computed here. The latter, however, are universal, independent of the accident of degeneracy and will therefore be considered first.

The broadened intensity distribution given by Bloom has the form

$$I_B = \frac{|J/\hbar|^2}{\gamma^2 + \omega^2} \left\{ 1 + \frac{R}{\gamma^2 + \omega^2} \right\} . \quad (1)$$

When the statistical matrix is diagonal, the redistribution factor,

$$R = \sum_{\mu} \rho_{\mu\mu}^0 \sum_{\lambda} R_{\mu\lambda} , \quad (2)$$

and depends on the collision matrix elements between the initial (μ) and final (λ) unperturbed electron states. $R_{\mu\lambda}$ contains two resonance terms;

$$R_{\mu\lambda} = \frac{A_{\mu\lambda}}{\gamma^2 + (\omega - \Omega)^2} + \frac{B_{\mu\lambda}}{\gamma^2 + (\omega + \Omega)^2} ; \quad (3)$$

where

$$\pi\Omega = \epsilon_{\mu} - \epsilon_{\lambda} ,$$

represents the perturber energy loss and $\hbar\omega = E_1 - E_0 - \hbar\omega$ radiation. The maximum of the first term occurs when $\omega_{\text{rad}} - \omega_{\text{at}} = -\Omega$, i.e. when the excess of radiation energy over the atomic energy has a sign opposite to that of the energy lost by the perturber; this combination does

not conserve energy. The second, however, corresponds to conservation, since the perturber gain equals the radiation loss. A and B depend on the elements of C;

$$A_{\mu\lambda} = (P-Q)2P(\omega^2 - \gamma^2 - \omega\Omega)$$

and

$$B_{\mu\lambda} = (P-Q)[P(\gamma^2 + \omega^2) - Q(3\omega^2 - \gamma^2 + 2\omega\Omega)],$$

where

$$P = (C_{1,1})_{\mu\lambda} / \hbar \quad \text{and} \quad Q = (C_{2,2})_{\mu\lambda} / \hbar. \quad (4)$$

In the summation over λ the first term in (3) has a resonance at

$$\Omega_{\lambda\mu} = \omega \quad (5)$$

this means

$$\epsilon_\lambda - \epsilon_\mu = \hbar\omega_{\text{atom}} - \hbar\omega_{\text{radiation}} \quad (6)$$

If $\omega_{\text{rad}} > \omega_{\text{at}}$, the radiation has received more energy than the atom possessed (in its excited state, which was assumed to be realized at $t = 0$). Hence the radiation should have drawn energy from the electron. According to (6), however, ϵ_μ must be $> \epsilon_\lambda$, which means the electron, too, has gained energy.

Conversely, if $\omega_{\text{rad}} < \omega_{\text{at}}$, the radiation field did not receive all the energy the atom had. But the electron did not get the excess either, because now $\epsilon_\lambda > \epsilon_\mu$ according to (6), which means the electron lost energy. Therefore this first term (3) represents contributions to the line width which violate conservation of energy.

Characteristically this term is small. At resonance ($\Omega_{\lambda\mu} = \omega$) with respect to λ its coefficient, $\omega^2 - \gamma^2 - \omega\Omega_{\lambda\mu}$ is $-\gamma^2$; it would therefore vanish if we did not include the energy uncertainty resulting from the natural line width.

The second term has a "resonance" (with respect to the λ summation) at

$$\Omega_{\mu\lambda} = \omega, \quad (7)$$

Hence

$$\epsilon_{\mu} - \epsilon_{\lambda} = \hbar\omega_{at} - \hbar\omega_{rad}$$

If $\omega_{rad} > \omega_{at}$, i.e., if the radiation field receives more energy than the atom can supply, then $\epsilon_{\mu} < \epsilon_{\lambda}$; that is, the electron lost energy. The second term therefore represents the energetically proper transfer of energy from the electron to the radiation field.

The greatest term in the summation over λ , defined by (7) has the coefficient

$$P_{\lambda\mu}(\gamma^2 + \omega^2) - Q_{\lambda\mu}(3\omega^2 - \gamma^2 + 2\omega\Omega_{\lambda\mu}) = P_{\lambda\mu}(\omega^2 + \gamma^2) - Q_{\lambda\mu}(\omega^2 - \gamma^2).$$

Interestingly, it survives even if γ is neglected.

Our task is to determine I_B . For simplicity we consider the 2p and 1s states of hydrogen. The perturber density (n) defines the volume per electron $V \equiv n^{-1}$. Using $g = V/(2\pi)^3$, the number of states per unit volume in wave number space, we replace the sum over final states by an integral;

$$\sum_{\lambda} \rightarrow \int g dk_{\lambda}$$

The integrations over direction and magnitude of k_{λ} can be separated, since A and B change slowly with $|k_{\lambda}|$.

We note that P and Q are functions of $K^2 = k_{\mu}^2 + k_{\lambda}^2 - 2k_{\mu}k_{\lambda}\cos\theta$ (see (17)(27)(30)(32)). Hence we write $A = A(k_{\lambda}, \cos\theta)$ and $B = B(k_{\lambda}, \cos\theta)$.

Consequently

$$\begin{aligned} \sum_{\lambda} R_{\mu\lambda} \rightarrow 2\pi g \int_{-1}^{+1} d\cos\theta \int_0^{\infty} k_{\lambda}^2 dk_{\lambda} \left\{ \frac{A(k_{\lambda}, \cos\theta)}{\gamma^2 + (\omega - \Omega)^2} \right. \\ \left. + \frac{B(k_{\lambda}, \cos\theta)}{\gamma^2 + (\omega + \Omega)^2} \right\} \end{aligned}$$

The integrand peaks at $\omega = \pm \Omega$. The value of A and B at these peaks, i.e., where their respective denominators reach a minimum, will be called the "resonance" value of k_λ . These occur at

$$\frac{\hbar^2}{2m} k_{\lambda \pm}^2 = \mp (\hbar \omega_{\text{at}} - \hbar \omega_{\text{rad}} \mp \frac{\hbar^2}{2m} k_\mu^2),$$

where the $- (+)$ sign is for A (B). Now we take advantage of the slow variation of A and B with k_λ and obtain:

$$\begin{aligned} \int R_{\mu\lambda} g dk_{\lambda} = 2\pi g \left\{ -2\gamma^2 \int_0^\pi (P_- (P_- - Q_-) \sin \theta \, d\theta \, k_{\lambda-}^2 G(-) \right. \\ \left. + [(\gamma^2 + \omega^2) \int_0^\pi (P_+ - Q_+) P_+ \sin \theta \, d\theta - (\omega^2 - \gamma^2) \int_0^\pi (P_+ - Q_+) Q_+ \sin \theta \, d\theta] \right. \\ \left. \times k_{\lambda+}^2 G(+), \right. \end{aligned} \quad (8)$$

where

$$G(\pm) = \int_0^\infty \frac{dk_\lambda}{\gamma^2 + (\omega \pm \Omega)^2} \quad (9)$$

and the arguments $+ (-)$ indicate evaluation at the resonance value $k_{\lambda+} (k_{\lambda-})$ which satisfies $\omega + \Omega = 0$ ($\omega - \Omega = 0$). This approximation can not be used if, for example, the radiation gains more energy than the perturber possessed initially. For this case the conservation resonance, $\omega + \Omega = 0$, is not satisfied by a positive k_λ . Similarly for the anti-conservation resonance, the radiation must be restricted to lose less than the initial perturber energy. Thus the present method is not valid in the far wings of the line where $\hbar \omega \gtrsim \epsilon_\mu = \frac{\hbar^2}{2m} k_\mu^2$.

We evaluate the integral in (9);

$$\begin{aligned} \sqrt{\frac{\hbar}{2m}} G(\pm) &= \int_0^{\infty} \frac{dy}{\gamma^2 + (b+iy)^2} = \frac{1}{2\gamma} \int_0^{\infty} \left[\frac{1}{\gamma+i(b+iy^2)} + \frac{1}{\gamma-i(b+iy^2)} \right] dy \\ &= \frac{\pi i}{4\gamma} \left[\frac{-1}{\sqrt{-i\gamma+b}} + \frac{1}{\sqrt{i\gamma+b}} \right], \end{aligned} \quad (10)$$

where

$$y = \sqrt{\frac{\hbar}{2m}} k_{\lambda} \quad \text{and} \quad b = -\frac{\hbar}{2m} k_{\mu}^2 \mp \omega, \quad \text{since} \quad \int \frac{dx}{x^2+c^2} = \frac{1}{c} \tan^{-1} \frac{x}{c}.$$

Ordinarily $\gamma \ll \frac{\hbar k_{\mu}^2}{m}$, and we find on expanding in powers of $\frac{\gamma}{b}$

$$\begin{aligned} G(\pm) &= \sqrt{\frac{2m}{\hbar}} \frac{\pi i}{4\gamma} \frac{1}{\sqrt{b}} \left[\mp \left(1 + \frac{i\gamma}{2b} + \dots \right) \pm \left(1 - \frac{i\gamma}{2b} + \dots \right) \right] \\ &= \sqrt{\frac{2m}{\hbar}} \frac{\pi i}{4\gamma} \frac{1}{\sqrt{b}} \left\{ \begin{array}{l} \mp 2 \\ \pm \frac{i\gamma}{b} \end{array} \right\}, \end{aligned} \quad (11)$$

where the criterion of a real and positive G may be used to select the correct value. This will be done later (cf. eq. 36).

The electrostatic interaction,

$$C_{n,n} = -\frac{e^2}{|\underline{R}|} + e^2 \int \frac{|\psi_n(\underline{r})|^2}{|\underline{R}-\underline{r}|} d\underline{r}, \quad (12)$$

provided \underline{r} and \underline{R} represent the positions of atomic and perturbing electrons relative to the nucleus and $\psi_n(\underline{r})$ is the atomic wave function. The unperturbed electron functions are plane waves;

$$u_{\lambda} = \frac{1}{\sqrt{V}} e^{i\mathbf{k}_{\lambda} \cdot \underline{R}} \quad (13)$$

Then the matrix elements between perturber states contain the factor

$$\begin{aligned} \tau &= \int \frac{e^{i\mathbf{K}\cdot\mathbf{R}}}{|\mathbf{R}-\mathbf{r}|} d\mathbf{R} = e^{i\mathbf{K}\cdot\mathbf{r}} \int \frac{e^{i\mathbf{K}\cdot\mathbf{z}}}{|\mathbf{z}|} dz = 2\pi e^{i\mathbf{K}\cdot\mathbf{r}} \int_0^\infty z^2 dz \\ &\quad \times \int_0^\pi \frac{e^{iKz \cos \Theta}}{z} \sin \Theta d\Theta = \frac{4\pi}{K} e^{i\mathbf{K}\cdot\mathbf{r}} \int_0^\infty \sin Kz dz, \quad (14) \end{aligned}$$

where $\mathbf{z} = \mathbf{R}-\mathbf{r}$ and $\mathbf{K} = \mathbf{k}_\lambda - \mathbf{k}_\mu$ is the momentum transfer vector. The indeterminate τ is evaluated by using the artifice of a convergence factor $e^{-\alpha z}$, which leads to

$$\lim_{\alpha \rightarrow 0} \int_0^\infty e^{-\alpha z} \sin Kz dz = \lim_{\alpha \rightarrow 0} \frac{K}{\alpha^2 + K^2} = \frac{1}{K}. \quad (15)$$

Hence

$$\tau = \frac{4\pi}{K^2} e^{i\mathbf{K}\cdot\mathbf{r}}. \quad (16)$$

Using this result and neglecting exchange, we find

$$\begin{aligned} (C_{n,n})_{\mu\lambda} &= \frac{1}{V} \frac{4\pi e^2}{K^2} \int [-1 + e^{i\mathbf{K}\cdot\mathbf{r}}] |\psi_n(\mathbf{r})|^2 d\mathbf{r} \\ &= \frac{1}{V} \frac{4\pi e^2}{K^2} [-1 + F_n]; \quad (17) \end{aligned}$$

where

$$F_n = \int e^{i\mathbf{K}\cdot\mathbf{r}} \rho_n(\mathbf{r}) d\mathbf{r} \quad (18)$$

represents the usual form factor, and ρ_n = the probability density of the atomic electron in state n .

The atomic state and the momentum transfer vector, \underline{K} , determine the form factor (18). Its value is independent of the direction of \underline{K} in the special case of a spherically symmetric charge distribution. Then the polar axis can be oriented along \underline{K} to simplify the evaluation. This is not always possible. The general case will be discussed in detail in section VI. Our computations will be made for the 1s and 2p states of hydrogen. The angular dependence of the 2p states will not trouble us, since in the absence of external fields the orientation probabilities are equal and we may take to a good approximation (see sect. VI)

$$\overline{F}_{2p}^m = \frac{1}{3} \sum_m F_{2p,m} \quad (20)$$

Although this average can be evaluated with the use of the radial function alone, we include for completeness the individual $F_{2p,m}$ in this report.

The atomic functions are

$$\psi_{1s0} = \frac{1}{\sqrt{\pi}} \frac{1}{a^{3/2}} e^{-r/a}; \quad (21)$$

$$\psi_{2p0} = \frac{1}{4\sqrt{2\pi}} \frac{r}{a^{5/2}} e^{-r/2a} \cos \theta; \quad (22)$$

$$\psi_{2p\pm 1} = \frac{1}{8\sqrt{\pi}} \frac{r}{a^{5/2}} e^{-r/2a} \sin \theta e^{\pm i\phi}; \quad (23)$$

where a is the first Bohr radius. To compute the F 's we first consider the fundamental integral

$$\begin{aligned} a_{100} &\equiv \int e^{\alpha r} e^{i\underline{K} \cdot \underline{r}} d\underline{r} = 2\pi \int_0^\infty r^2 dr e^{\alpha r} \int_{-1}^{+1} e^{iKr\mu} d\mu \\ &= \frac{2\pi}{iK} \left[\frac{1}{(\alpha+iK)^2} - \frac{1}{(\alpha-iK)^2} \right] = -\frac{8\pi\alpha}{(\alpha^2+K^2)^2} \end{aligned} \quad (24)$$

In calculating F_{2p0} one encounters

$$\begin{aligned} a_{210} &= \int r^2 e^{\alpha r} \mu^2 e^{iK \cdot r} dr = -\frac{d^2}{dK^2} a_{100} \\ &= -32\pi\alpha \left[\frac{\alpha^2 - 5K^2}{(\alpha^2 + K^2)^4} \right] \end{aligned} \quad (25)$$

Similarly

$$\begin{aligned} a_{21+1} &= \int r^2 (-\mu^2) e^{\alpha r} e^{iK \cdot r} dr = \\ &= 2\pi \int_0^\infty r^2 dr r^2 e^{\alpha r} \left[(1-\mu^2) \frac{e^{iKr\mu}}{iKr} \right]_{-1}^{+1} + \frac{2}{iKr} \int_{-1}^{+1} \mu e^{iKr\mu} d\mu \\ &= 2\pi \int_0^\infty r^2 dr r^2 e^{\alpha r} \frac{2}{iKr} \frac{d}{i r dK} \int_{-1}^{+1} e^{iKr\mu} d\mu \\ &= -\frac{2}{K} \frac{d}{dK} a_{100} = -\frac{\pi\alpha 64}{(\alpha^2 + K^2)^3} \end{aligned} \quad (26)$$

Making use of these relations we find

$$F_1 = F_{100,100} = 1/(1+x/4)^2; \quad (27)$$

$$F_{210,210} = \frac{1-5x}{(1+x)^4}; \quad (28)$$

and

$$F_{21+1, 21+1} = \frac{1}{(1+x)^3}, \text{ where } x = \alpha^2 K^2. \quad (29)$$

$$F_2 = F_{21m,21m}^m = \frac{1-x}{(1+x)^4}. \quad (30)$$

We are now ready to evaluate eq. 8. There are integrals over the scattering angle θ of the type

$$L = \int_0^{\pi} (P-Q)^2 \sin \theta \, d\theta. \quad (31)$$

We can transform from θ to the variable $x = a^2 K^2$ by using the relation

$$K^2 = k_{\lambda}^2 + k_{\mu}^2 - 2k_{\lambda} k_{\mu} \cos \theta. \quad (32)$$

Then $dx = 2a^2 k_{\lambda} k_{\mu} \sin \theta \, d\theta$ and

$$L = \frac{1}{v^2} \frac{(4\pi)^2 e^4}{h^2} \frac{a^2}{2k_{\lambda} k_{\mu}} \int_{\check{x}}^{\hat{x}} \left(\frac{F_1 - F_2}{x} \right)^2 dx, \quad (33)$$

where

$$\hat{x} = a^2 (k_{\mu} + k_{\lambda})^2$$

and

$$\check{x} = a^2 (k_{\mu} - k_{\lambda})^2.$$

For hydrogen $a = \hbar^2/m_e^2$ and

$$L = \frac{2}{v^2} (h/m)^2 \frac{1}{k_{\lambda} k_{\mu}} \int_{\check{x}}^{\hat{x}} \left(\frac{F_1 - F_2}{x} \right)^2 dx. \quad (34)$$

Equation 8 takes a simple form when ω is small, i.e. when the perturber energy changes very little in comparison with its initial value. This is actually a meaningful approximation, as will later be shown. Here

$$k_{\lambda \pm}^2 = k_{\mu \pm}^2 \pm \frac{2m}{\hbar} \omega \approx k_{\mu}^2 \quad (35)$$

and in view of eq. (11)

$$G(\pm) = \frac{\pi m}{\hbar} \frac{1}{\sqrt{k_{\mu}}} \quad (36)$$

Furthermore, when a Taylor expansion is used,

$$\int_{\underline{x}}^{\hat{x}} \frac{(F_1 - F_2)^2}{x^2} dx \approx \int_0^{4a^2 k_\mu^2} \frac{(F_1 - F_2)^2}{x^2} dx \equiv S_B \quad (37)$$

Consequently near the line center all terms in equation 8 become independent of the resonance condition. Equation (8) then reads

$$\begin{aligned} \int R_{\mu\lambda} g dk_\lambda &= 2\pi g (\omega^2 - \gamma^2) k_\mu^2 G \int_0^\pi (P-Q)^2 \sin\theta d\theta = \\ &= 2\pi g (\omega^2 - \gamma^2) k_\mu^2 \frac{\pi m}{\hbar/k_\mu} \frac{2}{v^2} \left(\frac{\hbar}{m}\right)^2 \frac{1}{(k_\mu)^2} \int_0^{4a^2 k_\mu^2} \left(\frac{F_1 - F_2}{x}\right)^2 dx \\ &= f(\omega^2 - \gamma^2) S_B. \end{aligned} \quad (38)$$

We now define symbols and analyze the result.

$$f = 2nv_\mu \sigma_\mu / \gamma;$$

$n = 1/V$, the electron density; v_μ is the electron velocity in the state and σ_μ the cross section associated with its de Broglie wave length,

$$\sigma_\mu = \pi (\hbar/mv_\mu)^2;$$

the function f is a measure of the relative number of atoms hit during the life time of the excited state.

The redistribution factor, R , (cf. eq. 1) has the property of decreasing the intensity within the half maximum and increasing it without. Also it is symmetric. A more detailed investigation which allows ω to be large shows that far from the line center the redistribution factor goes to zero and a very slight shift to the red is introduced.

For large values of fS_B our result indicates that the intensity at the line center can become negative. In this extreme (indeed whenever $fS_B > 0.4$) terms of higher order in the collision matrix elements must be considered.

Evaluation of S_B

Since

$$\frac{F_1 - F_2}{x} = (16u^3 + 17u^2 + 21u + 18)/u^4(3+u)^2, \quad (\text{see (27) and (30)}) \quad (39)$$

where $u = 1+x$, the integral of $(F_1 - F_2)/x^2$ can be transformed into a linear combination of integrals of the form $\int \frac{du}{(3+u)^4 u^m}$. We expand this integrand;

$$\begin{aligned} \frac{1}{(3+u)^4 u^m} &= \frac{1}{(3+u)^4 u^m} \cdot \left(\frac{3+u-u}{3}\right)^{m+2} = \frac{\left[\sum_{t=0}^{m+2} (-1)^t \binom{m+2}{t} (3+u)^{m+2-t} u^t\right]}{(3+u)^4 u^m 3^{m+2}} \\ &= \frac{1}{3^{m+2}} \left[\sum_{t=0}^{m+2} (-1)^t \binom{m+2}{t} W^{t-m} \frac{1}{(3+u)^2}\right], \end{aligned} \quad (40)$$

where

$$W = u/3+u \quad \text{and} \quad \binom{m+2}{t} = \frac{(m+2)!}{t!(m+2-t)!}$$

Integrating each term, using

$$\int \frac{W^{t-m}}{(3+u)^2} du = \frac{1}{3} \int W^{t-m} dW = \begin{cases} \frac{1}{3} \frac{W^{t-m+1}}{t-m+1} & t-m \neq -1 \\ \frac{1}{3} \log W & t-m = -1 \end{cases} \quad (41)$$

we find for the indefinite integral

$$\int \frac{du}{(3+u)^4 u^m} = \frac{1}{3^{m+3}} \left[\sum_{t=0}^{m+2} (-1)^t \binom{m+2}{t} \left\{ \frac{W^{t-m+1}}{t-m+1} \right\}\right], \quad (42)$$

with the understanding that the quantity in the curly brace is to be replaced by $\log W$ when $t-m = -1$. The limits, of course, are $u = 1$ and $u = 1 + \hat{x}$.

When terms with like powers of W are collected,

$$\int \left(\frac{F_1 - F_2}{x} \right)^2 dx = .197W^3 - 1.04W^2 + 2.44W - .798 \log W \quad (10)$$

$$+ .452W^{-1} - .198W^{-2} + .0434W^3$$

$$- 2.51 \times 10^{-3}W^{-4} + 4.12 \times 10^{-3}W^{-5} + .914 \times 10^{-3}W^{-6}$$

$$- .261 \times 10^{-3}W^{-7} + C, \quad (43)$$

C being the constant of integration. This integral between the limits of 0 and \hat{x} , i.e., between $W = \frac{1}{4}$ and $W = \frac{1+\hat{x}}{3+\hat{x}}$, namely S_B , is plotted as a function of the initial electron energy, $\frac{\epsilon_\mu}{e^2/2a} = \frac{\hat{x}}{4} = a^2 k_\mu^2$. (Figure 1).

The integrals in equation 8, when written in their exact form (34) are seen to depend on the final electron energy as well. This dependence enters as the difference between k_λ and k_μ in the limits of integration; and from figure 1, we see that they are quite insensitive to changes in ϵ_λ of the order of the line width $\hbar\gamma \sim 10^{-6}$ e.v., i.e. changes in the abscissa of this amount leave the ordinate unchanged. It is this circumstance which justifies both the resonance approximation and the use of S_B in place of an integral with exact limits in the region near the line center.

Numerical values for R and I_B typical of the positive column of an arc discharge are: $n = 10^{14}/\text{cm}^3$ and $\epsilon_\mu = \frac{1}{25} \frac{e^2}{2a} \sim \frac{1}{2}$ e.v. ($T \sim 5,000^\circ\text{K}$). We treat all of the electrons as if they had this energy and take $\rho_{\nu\nu}^0 = \delta_{\mu\nu}$. As we have shown, the initial direction does not enter in our case. With the value $2\gamma = 6.25 \times 10^8/\text{sec.}^{-1}$ for the chance of spontaneous emission

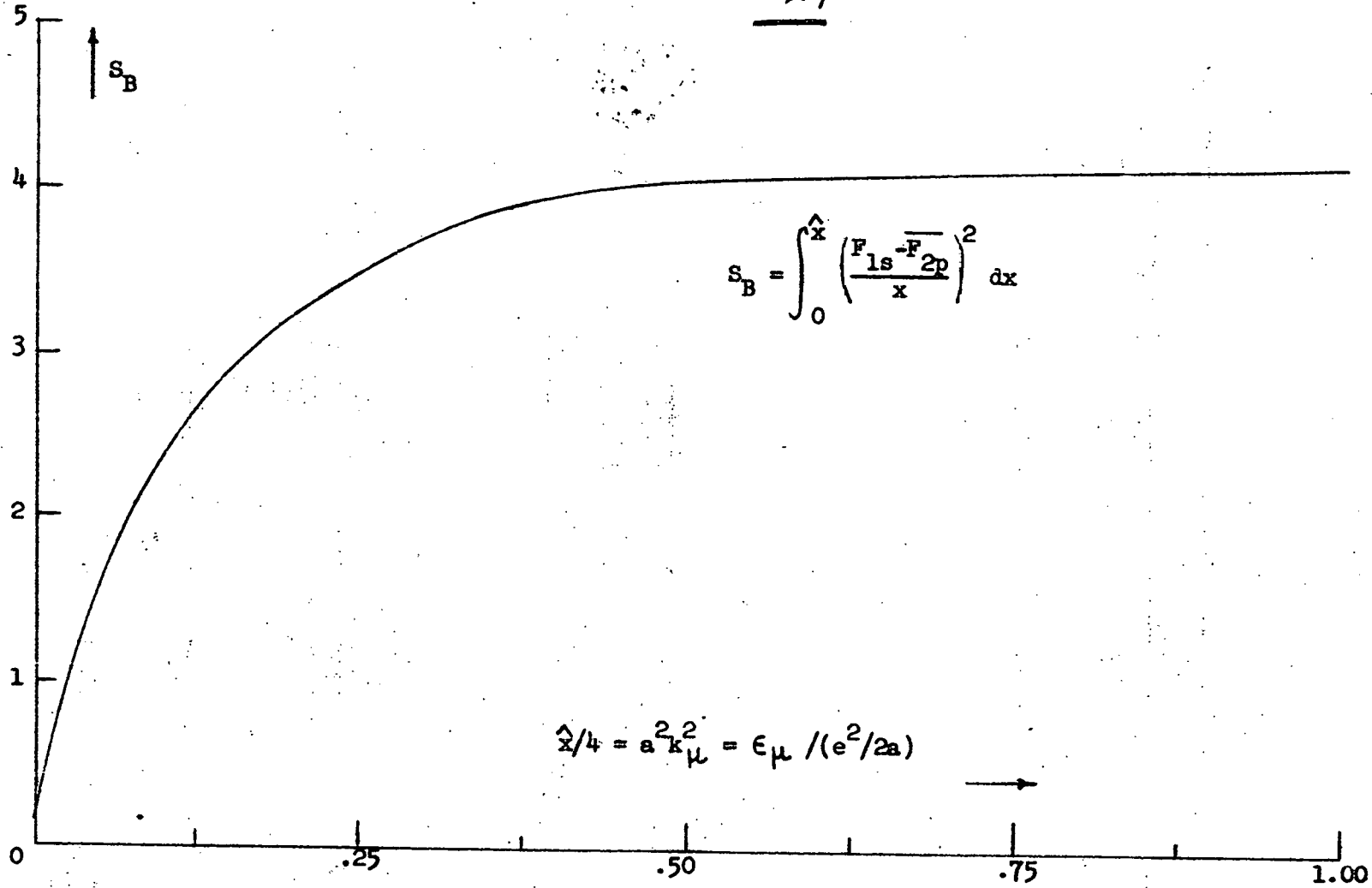


FIGURE 1.

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per unit time,

$$R \cong f(\omega^2 - \gamma^2)S_B \cong .061(\omega^2 - \gamma^2)2.1$$

and

$$I_B \cong \frac{|J/A|^2}{\gamma^2 + \omega^2} \left\{ 1 - .13 \left(\frac{\gamma^2 - \omega^2}{\gamma^2 + \omega^2} \right) \right\} \quad \text{(Figure 2)} \quad (44)$$

Curves for $fS_B = 0.3, 0.5, 0.7$ and 1.0 corresponding to higher electron densities are also included in the graph.

The dotted curves, though given by our theory, are of course spurious because terms beyond the second order in the elements of C are important in these instances.

It may seem surprising that the natural line suffers almost no modification until fS_B reaches a value comparable to 1, at which point the natural line as such is destroyed rather suddenly. But this is merely another aspect of a point previously made: S_B is a number of order 1; $f \sim \frac{nv\sigma}{\gamma}$. Now t_e , the mean time between electron impacts with the atom, is $\frac{1}{nv\sigma}$, and t_a , the life time of the excited atomic state, is of order $\frac{1}{\gamma}$. Hence $f \sim \frac{t_a}{t_e}$. If $f > 1$, the electrons make many collisions during t_a , so that a static perturbation theory is applicable. The region of f under consideration is therefore characterized by the passage from a condition in which the time dependence matters to one in which a steady-state analysis is adequate.

The energy dependence of fS_B is easily obtained, because f is proportional to $(\epsilon\mu)^{-1/2}$ and $S_B(\epsilon\mu)$ has already been calculated. We find that fS_B is zero at both low and high energies because S_B and f vanish respectively at the extremes. (Figure 3).

In Figure 4 we delimit the region of small electron broadening, defined by $\gamma_B \leq \frac{\gamma}{10}$, $\gamma_B = fS_B \gamma$ (see X - (1)).

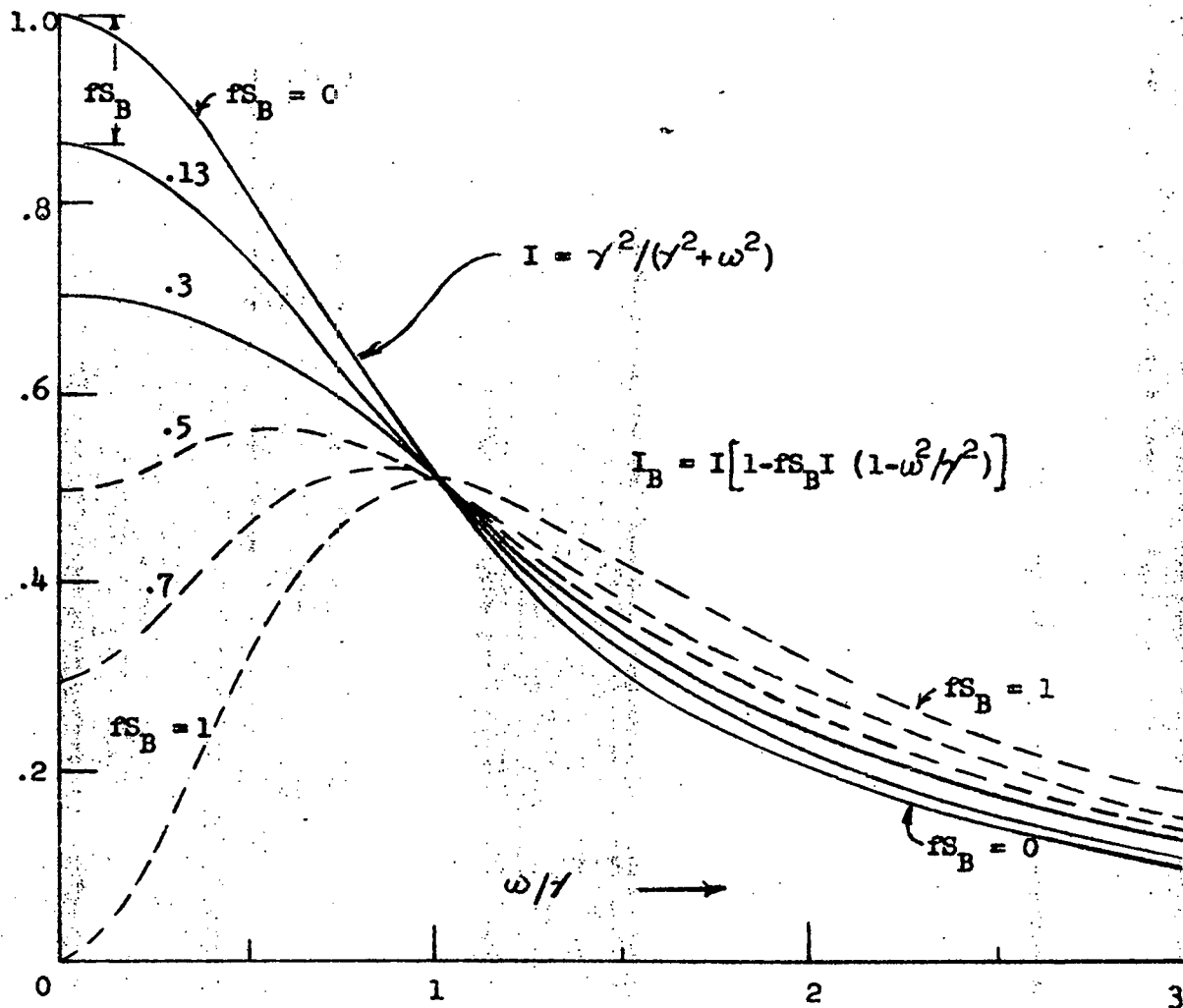


FIGURE 2

32

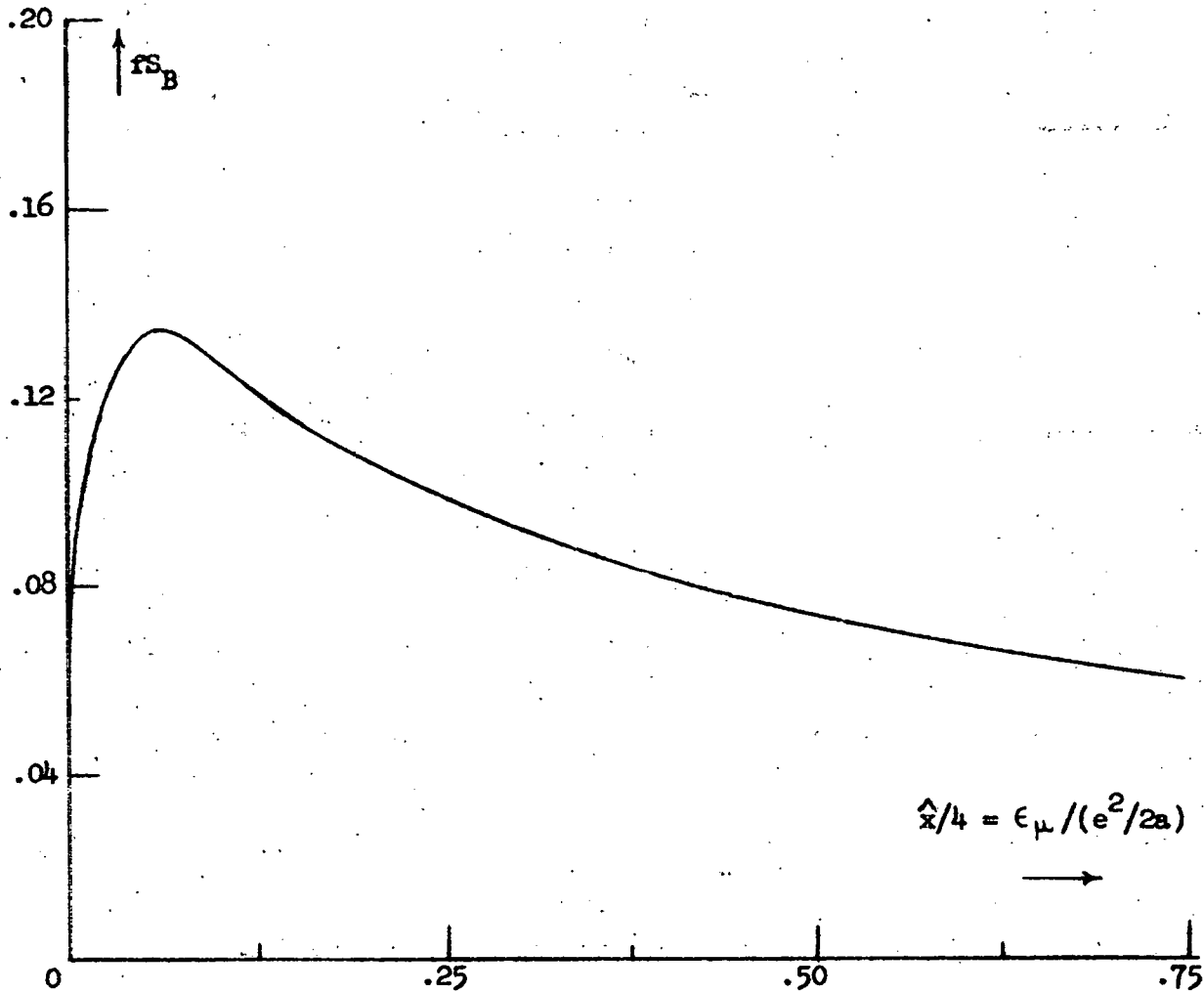


FIGURE 3.

556 036

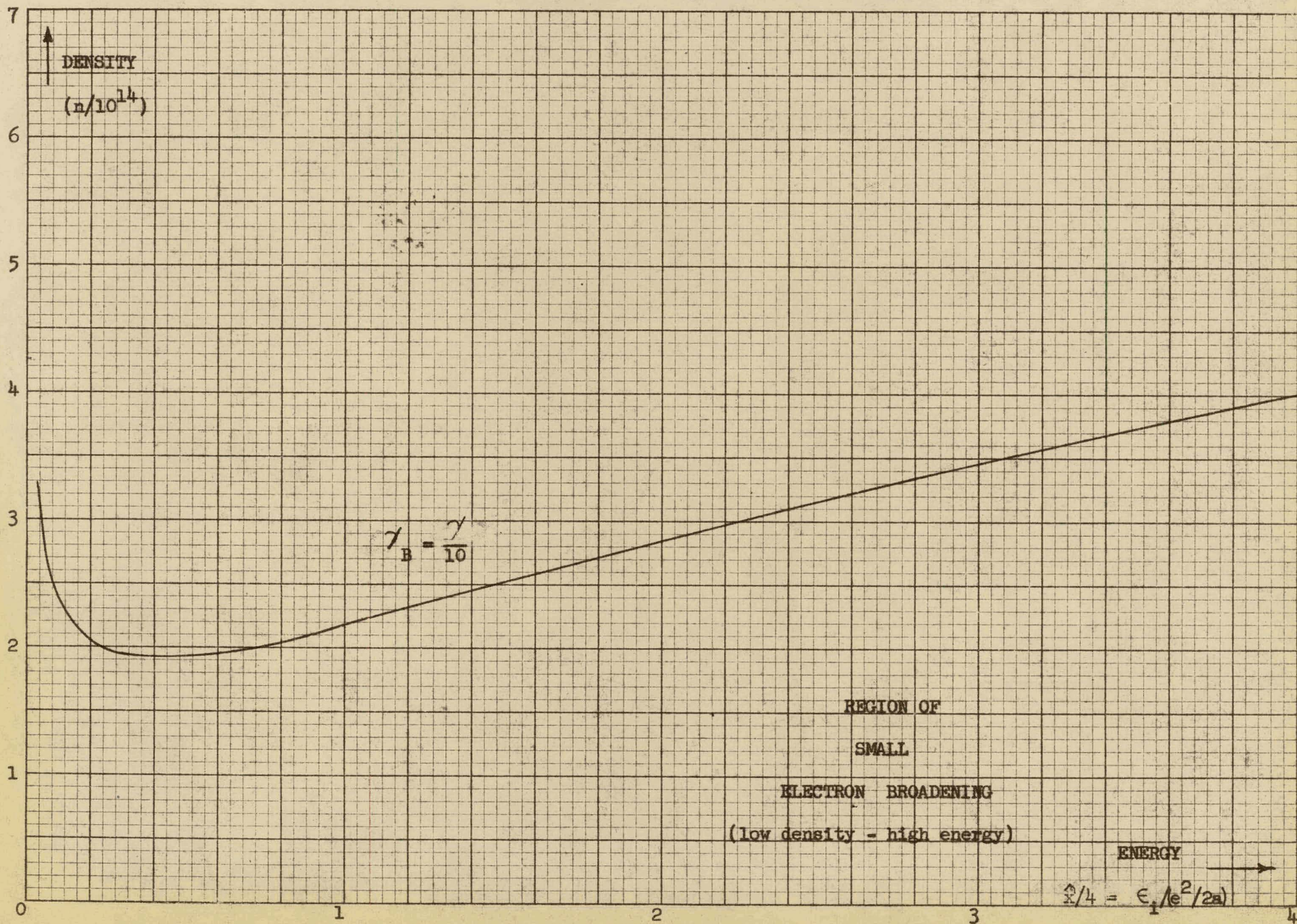


FIGURE 4.

536 037

For negligible effects

$$\frac{n}{10^{14}} < \frac{8.2}{S_B} \sqrt{\frac{\epsilon \mu}{e^2/2a}} \quad (45)$$

The theory developed here holds in the region below the curve of Figure 4. Immediately above it our theory is not adequate because of the neglect of higher powers of C . In Section XI we comment on cases where broadening can be greater than the natural width. Far above this curve (e.g., at very high densities where several electrons interact simultaneously with the atom) a statistical or time-independent type of treatment seems to be required. In an unpublished report by H. Margenau and R. Meyerott, it is shown that such treatment leads to shifts and not to appreciable line widths.

IV. COMPARISON WITH QUENCHING AND STARK BROADENING.

A. Quenching

The results of the preceding section are not altogether academic.

Let us compare them with the effect of quenching by electron collisions.

For quenching, the intensity distribution¹ is

$$I_q(\omega) = \gamma^2 / [\omega^2 + (\nu + \gamma_q)^2], \quad (1)$$

provided γ_q is the contribution to the decay constant resulting from quenching. γ_q is equal to half the transition probability per unit time induced by electron impacts:

$$\gamma_q = \frac{1}{2} n v_\mu Q_\mu \quad ; \quad (2)$$

for initial electron velocity v_μ . Here Q_μ is the quenching cross section for hydrogen,²

$$Q_\mu(2p \rightarrow 1s) = \int d\Omega \frac{k_\lambda}{k_\mu} \left(\frac{m}{2\pi n^2} \right)^2 \left(\frac{4\pi e^2}{K^2} \right)^2 |F_{1s,2p}|^2 \quad (3)$$

Now k_λ is fixed by conservation of energy, and

$$\gamma_q = \frac{2n v_\lambda}{a^2} \int \frac{|F_{1s,2p}|^2}{K^4} d\Omega = \frac{2n v_\lambda}{k_\mu} \left(\frac{n}{m} \right) \int_{\frac{v}{x}}^{\frac{\lambda}{x}} \frac{|F_{1s,2p}|^2}{x^2} dx. \quad (4)$$

The form factor is evaluated as before

$$\begin{aligned} F_{100,210} &= \int \psi_{100}^* \psi_{210} e^{i\mathbf{K} \cdot \mathbf{r}} d\mathbf{r} \\ &= \frac{1}{4\sqrt{2}\pi a^4} \int e^{-3r/2a} \cos \theta r e^{i\mathbf{K} \cdot \mathbf{r}} d\mathbf{r} \\ &= \frac{1}{4\sqrt{2}\pi a^4} \frac{d}{dK} \int e^{-3r/2a} e^{iKr \cos \theta} d\mathbf{r} \\ &= \frac{1}{4\sqrt{2}\pi a^4} \frac{d}{dK} \left(\frac{-8\pi [-3/2a]}{[(-3/2a)^2 + K^2]^2} \right) \\ &= \frac{3iKa^7 \cdot \sqrt{2}}{[9+4K^2 a^2]^3} \end{aligned} \quad (5)$$

Furthermore,

$$F_{100,21+1} = 0, \text{ since } \int_0^{2\pi} e^{-i\phi} d\phi = 0.$$

This means that only 1/3 of the atoms will be so oriented as to allow a quenching transition. Therefore one can use $F_{100, 210}$ in equation 6 and multiply by the factor 1/3.

The integral over x , $\int \frac{|F_{1,2}|^2}{x^2} dx$ contains the factor

$$\int \frac{dx}{x(9+4x)^6} = -\frac{1}{9^6} \left[-\log(S) + 5x4S + \frac{10x4^2}{2} S^2 + \frac{10x4^3}{3} S^3 - \frac{5x4^4}{4} S^4 + \frac{4^5}{5} S^5 \right], \text{ where}$$

$$S = x/(9+4x). \quad (6)$$

For

$$\epsilon_{\mu} = \frac{1}{25} \frac{e^2}{2a} \quad \text{and} \quad n = 10^{14}, \quad k_{\mu} = \frac{1}{5a}$$

and

$$\gamma_q = \frac{h}{m} \frac{n}{k_{\mu}} \times \frac{1}{3} \times .15 = .95 \times 10^6 / \text{sec}. \quad (7)$$

Under these conditions γ_q is sufficiently smaller than γ to permit the use of an expansion for I_q in powers of γ_q/γ . We note that $I_q \approx I(1-2I\gamma_q/\gamma)$, and this is in a form very similar to that for I_B . A more striking similarity is found upon using equation 4; $\gamma_q/\gamma = fS_q$ where $S_q = \int_{\frac{1}{x}}^{\hat{x}} \frac{|F_{1,2}|^2}{x^2} dx$.

The comparison between quenching and broadening impacts can then be made in terms of S_B and S_q . For the case studied $S_B = 2.1$ and $S_q = .05$.

B. Stark Broadening by Ions

Subject to later refinement and analysis, we give here a qualitative estimate of relative magnitudes of the "universal" electron effect of the preceding section and Stark broadening. The latter results from variations of the electric field at the atom produced by the moving ions. The mean field for the ions given by Holtsmark is $F = 3.26en^{2/3}$, where n is the ion density. This splits the degenerate hydrogen $n = 2$ states into three components. The separation of the outer two, $6Fea$, is linear in F . Using this to estimate the half width of the broadened line, we find

$$\gamma_{\text{Stark}} = 3.26en^{2/3} \times 3ea/n = 2.5 \times 10^{10}/\text{sec} \quad (8)$$

for $n = 10^{14}/\text{cm}^3$. Consequently Stark broadening by ions is at least 10 times larger than the electron broadening.

A comment on the mass dependence of the broadening effect computed in this section is in order. The effect is expected to be small for heavy ions since it arises from elastic scattering collisions, and the ions are scattered less. This is indeed borne out by our formulas.

Broadening is proportional to $fS_B = 2nv \frac{\sigma}{\gamma} S_B$. Let the ions have a reduced mass (with respect to the radiating atom) M . Now $v \propto M^{-1/2}$ for ions of the same energy, $\sigma = \pi \lambda^2 \propto \left(\frac{h}{Mv}\right)^2 \propto M^{-1}$; hence $f \propto M^{-3/2}$. On the other hand, S_B depends on M through the upper limit of eq. II-37, and it decreases with k_μ^2 . At low energy its variation with k_μ^2 is approximately linear. However, $k_\mu^2 \propto \frac{1}{M^2 v^2} \propto M^{-1}$. In all, therefore, $fS_B \propto M^{3/2+c}$ ($0 < c < 1$). Protons are thus less effective in broadening the hydrogen lines by a factor between 3×10^{-5} and 3×10^{-8} .

We proceed to show, however, that protons at this density can have individual particle effects. Hence they will produce the Holtsmark-Stark broadening discussed above.

Critique of the 'wave approximation'

In the foregoing sections the perturber function is not taken as a wave packet representing a localized particle. Had we formed packets for individual perturbers, the results would have been very different, as for instance, in Spitzer's classical path approximation for broadening by protons. We now consider criteria for choosing between wave packets (particle approximation) and individual waves (wave approximation). First we sketch the essential features of the two methods.

Proton broadening is generally explained classically (particle approximation). This approach is valid when the perturber packet remains localized. If furthermore this packet moves slowly it polarizes the atom in a manner describable by means of an ordinary potential. Quantum mechanically this situation is described with adiabatic functions (stationary functions for the atom in the field of a fixed perturber) as used in the Born-Oppenheimer theory of molecules.

Our treatment of electron broadening does not localize the perturbers. Instead of knowledge of the electron position we know its initial energy or momentum state (wave approximation). Changes in this momentum result from the atom-electron interaction. There is a corresponding broadening which was just considered. The effect depends on the difference of electron scattering by the two atomic states. Other modifications of emitted radiation arising from collision-induced, non-radiative atomic transitions will be discussed in ensuing sections.

Now one must find a criterion for knowing when to use the classical treatment for the perturber. From scattering considerations we expect the classical method to become applicable where the Born approximation fails, i.e., at low energies.¹ This agrees with the failure of our wave mechanical treatment for low energy protons.

The larger Holtsmark broadening effects occur when the perturber that determines the atomic distortion can be treated as a localized particle. That is, the packet must diffuse little during the lifetime of the atomic state ($1/\gamma$). Now the rate of diffusion depends on the localization. The smallest spread occurs during a time t if the initial packet dimension $(\Delta x)_{t=0} \sim \sqrt{\frac{\hbar t}{2m}}$. Since for reasonable localization

$$(\Delta x)_{t \sim 1/\gamma}^3 \lesssim \frac{1}{1000} \frac{1}{n},$$

where n is the perturber density; we require

$$2(\Delta x)_{t=0}^2 \sim (\Delta x)_{t \sim 1/\gamma}^2 \frac{\hbar}{m\gamma} \leq \frac{n^{-2/3}}{100}.$$

Our intent is that for individualization to be insured the packet must remain a small fraction of the volume per perturber. Thus to use packets we restrict:

$$n \lesssim \gamma^{3/2} 10^{-3} \quad (\text{for electrons of mass } m)$$

$$n \lesssim \left(\frac{M}{m}\right)^{3/2} 10^{-3} \gamma^{3/2} \quad (\text{for protons of mass } M);$$

or where

$$\gamma \sim 10^9/\text{sec}, \left(\frac{M}{m}\right)^{3/2} \sim 10^5,$$

$$n \lesssim 10^{10}/\text{cm}^3 \quad (\text{for electrons})$$

$$n \lesssim 10^{15}/\text{cm}^3 \quad (\text{for protons}).$$

Perhaps these inequalities are a little too severe and should be considered only as being qualitative. They do manifest the large factor $[(M/m)^{3/2} \sim 10^5]$ which differentiates the regions in which packets are valid for electrons and for protons. This also shows how localization can depend on the atomic lifetime and the perturber density.

Throughout this paper it is assumed that the densities are sufficiently high to disallow treating the electron perturbers as single particles.

V. INCLUSION OF POLARIZATION¹

Polarization effects arise when the perturber is able to induce a dipole moment in the radiator or to orient an existing dipole moment. They depend, of course, on the speed and localizability of the perturbing ion or electron. Fixed ions give rise to the Stark shifted lines. As the perturber moves, the atom may or may not have time to be deformed or to reorient itself. A measure of this failure to follow the changing field is given by the probability of non-adiabatic transitions. For very fast collisions, unpolarized, randomly oriented atoms are expected, and electron effects are usually negligible. We seek a criterion for the setting in of these polarization effects as the electron density increases and temperature decreases.

Here we study polarization effects as a correction to Holtsmark broadening. We consider a Stark shifted component of the first Lyman line from a hydrogen atom in the mean Holtsmark ion field. ($F_{ion} = 3.26 n_{ion}^{2/3}$) Only three atomic states are considered: $\psi_+ = \frac{1}{2}(\psi_{2s0} + \psi_{2p0})$, $\psi_- = \frac{1}{2}(\psi_{2s0} - \psi_{2p0})$ and ψ_{1s0} . The excited states correspond to dipoles ($3ea$) oriented along the z axis of the atom which point at the ion. Their energies are displaced by $\pm 3ea F_{ion}$ from $E_2 = -\frac{1}{4} \frac{e^2}{2a}$.

Clearly so long as electrons can not reorient the atom -- i.e., induce appreciable transitions between ψ_+ and ψ_- , polarization effects by the electron are small. Coupling to other states should be still smaller, because of the larger energy separations. An exception is the undisplaced states $\psi_{2p\pm 1}$, which will be considered in Section VIII.

The basic equation for the expansion coefficients is II-(12):

$$i\hbar a_{mj} e^{-i(\epsilon_{\mu}^m + E_m)t/\hbar} = \sum_n \sum_{\lambda} a_{n\lambda} J_{mn} \int \phi_{\mu}^{m*} \phi_{\lambda}^n d\mathbf{r} e^{-i(\epsilon_{\lambda}^n + E_n)t/\hbar} \tag{1}$$

$$+ \sum_{n \neq m} \sum_{\lambda} \int \phi_{\mu}^{m*} C_{m,n} \phi_{\lambda}^n d\mathbf{r} a_{n\lambda} e^{-i(\epsilon_{\lambda}^n + E_n)t/\hbar}$$

The electron functions satisfy (II-(7)):

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + C_{n,n}\right) \phi_\lambda^n = \epsilon_\lambda^n \phi_\lambda^n \quad (2)$$

In order to neglect the effects of scattering broadening we must replace $C_{n,n}$ by a function which is independent of the atomic state; i.e.

$$C_{n,n} \cong C_{m,m} \longrightarrow C.$$

Below where plane waves are used for the ϕ we imply that $C \equiv 0$ has been used in equation 2. As a consequence of this approximation

$$\int \phi_\mu^{m*} \phi_\lambda^n dR \cong \int \phi_\mu^{*} \phi_\lambda dR = \delta_{\mu\lambda}, \quad (3)$$

with the equation determining ϕ_μ

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + C\right) \phi_\mu = \epsilon_\mu \phi_\mu \quad (4)$$

One correction for the electron-atom interaction is retained. It corresponds to the changes induced in the atom by the second sum in equation (1). The effect of these non-radiative transitions is referred to as polarization broadening. To see how it enters, we start with the growth equations for the three state atom.

$$\begin{aligned} i\hbar \dot{a}_{+\mu} e^{-i(\epsilon_u + E_+)t/\hbar} &= \sum_r b_{r\mu} J_e^{-i(\epsilon_\mu + E_{1s} + h\nu_r)t/\hbar} \\ &+ \sum_\lambda d_{-\lambda} \int \phi_\mu^{*} C_{+,-} \phi_\lambda dR e^{-i(\epsilon_\lambda + E_-)t/\hbar}; \end{aligned} \quad (5)$$

$$i\hbar \dot{d}_{-\nu} e^{-i(\epsilon_{\nu} + E_{-})t/\hbar} = \sum_{\mathbf{r}} b_{\mathbf{r}\nu} J e^{-i(\epsilon_{\nu} + E_{1s} + \hbar\nu_{\mathbf{r}})t/\hbar} \quad (6)$$

$$+ \sum_{\lambda} d_{+\lambda} \int \psi_{\nu}^{*} c_{-,+} \phi_{\lambda} d\mathbf{r} e^{-i(\epsilon_{\lambda} + E_{+})t/\hbar};$$

$$i\hbar b_{\mathbf{r}\mu} = J^{*} \left[d_{+\mu} e^{i(E_{1s} + \hbar\nu_{\mathbf{r}} - E_{+})t/\hbar} + d_{-\mu} e^{i(E_{1s} + \hbar\nu_{\mathbf{r}} - E_{-})t/\hbar} \right]; \quad (7)$$

where the absolute square of the radiative matrix element is

$$|J|^2 = \frac{1}{2} \left| (\psi_{2p_0} \pm \psi_{2s_0}) | J | (\psi_{1s_0}) \right|^2 = \frac{1}{2} \left| (\psi_{2p_0} | J | \psi_{2s_0}) \right|^2 \quad (8)$$

and

$$c_{+,-} = \int \psi_{+}^{*} c \psi_{-} d\mathbf{r}.$$

In the approximation of exponential radiative decay these equations

become:--

$$i\hbar \dot{d}_{+\mu} = -i\hbar \gamma_{+} d_{+\mu} + \sum_{\lambda} d_{-\lambda} (c_{+,-})_{\mu\lambda} e^{i(\omega_{+,-} + \Omega_{\mu\lambda})t} \quad (9)$$

$$i\hbar \dot{d}_{-\nu} = -i\hbar \gamma_{-} d_{-\nu} + \sum_{\lambda} d_{+\lambda} (c_{-,+})_{\nu\lambda} e^{i(\omega_{-,+} + \Omega_{\nu\lambda})t} \quad (10)$$

$$i\hbar b_{\mathbf{r}\mu} = J^{*} \left[d_{+\mu} e^{i\omega_{+}t} + d_{-\mu} e^{i\omega_{-}t} \right] \quad (11)$$

with

$$\gamma_{+} = \gamma_{-} = \frac{1}{2} \gamma_{2p_0 \rightarrow 2s_0} = \frac{1}{2} \times 3.12 \times 10^8 / \text{sec}. \quad (12)$$

according to (8). Here

$$\hbar\omega_{+,-} \equiv E_+ - E_-, \quad (13)$$

$$\hbar\omega_+ \equiv E_{1s} - E_+ + h\nu_r, \quad (14)$$

$$\hbar\omega_- \equiv E_{1s} - E_+ + h\nu_r, \quad (15)$$

and

$$(c_{+,-})_{\mu\lambda} = \int \phi_{\mu}^*(c_{+,-}) \phi_{\lambda} d\mathbf{R}. \quad (16)$$

To solve these equations we put

$$d_{+\mu} \equiv D_{+\mu} e^{-\gamma_+ t} \quad \text{and} \quad d_{-\mu} \equiv D_{-\mu} e^{-\gamma_- t}. \quad (17)$$

This reduces the growth equations to:

$$i\hbar \dot{D}_{+\mu} = \sum_{\lambda} D_{-\lambda} (c_{+,-})_{\mu\lambda} e^{i(\omega_{+,-} + \Omega_{\mu\lambda})t - (\gamma_- - \gamma_+)t} \quad (18)$$

$$i\hbar \dot{D}_{-\nu} = \sum_{\lambda} D_{+\lambda} (c_{-,+})_{\nu\lambda} e^{i(\omega_{-,+} + \Omega_{\nu\lambda})t + (\gamma_- - \gamma_+)t} \quad (19)$$

$$i\hbar \dot{D}_{r\mu} = J^* \left[D_{+\mu} e^{-(\gamma_+ + i\omega_+)t} + D_{-\mu} e^{-(\gamma_- + i\omega_-)t} \right]. \quad (20)$$

As the initial conditions we consider an excited atom in state ψ_+ , no radiation present and the perturbing electron's function to be

$$\phi_i^+ = \frac{1}{V} e^{i\mathbf{k}_i \cdot \mathbf{R} - i\epsilon_i t/\hbar}. \quad (21)$$

Further all $d_{+\lambda}$ are assumed to remain small compared to d_{+i} during the lifetime of the excited state. That is, polarizing transitions which return the atom to the initial state before the atom radiates are unlikely. Then

$$i\hbar \dot{D}_{+i} = \sum_f (C_{+,-})_{if} D_{-f} e^{i(\omega_{+,-} + \Omega_{if})t - (\gamma_- - \gamma_+)t} \quad (22)$$

$$i\hbar \dot{D}_{-f} = \sum_\lambda (C_{-,+})_{f\lambda} D_{+\lambda} e^{i(\omega_{-,+} + \Omega_{f\lambda})t + (\gamma_- - \gamma_+)t} \quad (23)$$

$$\cong (C_{-,+})_{fi} D_{+i} e^{i(\omega_{-,+} + \Omega_{fi})t + (\gamma_- - \gamma_+)t}$$

$$I(\omega) = \sum_\mu |b_{r\mu}(t=\infty)|^2 = |J/\hbar|^2 \left\{ \left| \int_0^\infty e^{(-\gamma_+ + i\omega_+)t} D_{+i} dt \right|^2 \right. \quad (24)$$

$$\left. + \sum_f \left| \int_0^\infty e^{(-\gamma_- + i\omega_-)t} D_{-f} dt \right|^2 \right\}.$$

As a check consider the case where all of the C matrix elements vanish. Then the D are constants: $D_{+i} = 1$ and $D_{-f} = 0$. From (24) $I(\omega)$, as expected, contains only the + component of the spectrum and this line has the natural breadth.

For small coupling induced by elements of C, it will be shown that

$$D_{+i} \cong e^{-\gamma_P t} \quad (25)$$

The spectral line is thus broadened according to the uncertainty principle; γ is replaced by $\gamma + \gamma_p$. The reoriented atoms emit in the opposite component which has the same broadened width.

To find γ_p we substitute D_{-f} found from (23) into (22):

$$D_{+i} = -\gamma_p D_{+i} \quad (26)$$

$$\approx -\frac{1}{\hbar^2} \sum_f |c_{+,-} f_1|^2 \int_0^t D_{+i}(\tau) e^{[i(\omega_{+,-} + \Omega_{f1}) + (\gamma_{-} - \gamma_{+})](\tau-t)} d\tau. \quad ($$

To take account of the random orientation of the direction of motion of the incident electron with respect to the atom, we average over directions of the atomic z axis for a given k_i . Hence we replace $\psi_{-}^* \psi_{+}$ by the spherically symmetric

$$\begin{aligned} \overline{\psi_{-}^* \psi_{+}} &= \frac{1}{4\pi} \int_0^{2\pi} d\phi \int_0^{\pi} \sin \theta d\theta \psi_{-}^* \psi_{+} = \frac{1}{4} \int_{-1}^{+1} [|\psi_{2s0}|^2 - |\psi_{2p0}|^2] du \\ &= \frac{1}{2} \left[(R_{2s0})^2 - \frac{1}{3} (R_{2p})^2 \right], \quad (27) \end{aligned}$$

with

$$(R_{2p})^2 \equiv \frac{r^2}{32\pi} \frac{e^{-r/a}}{a^5},$$

$$(R_{2s0})^2 \equiv \frac{[2-(r/a)]^2}{32\pi} \frac{e^{-r/a}}{a^3}$$

Then with the use of plane waves

$$\begin{aligned}
 |(c_{+,-})_{fi}|^2 &\approx \left| \int \int \frac{e^{i\mathbf{K}\cdot\mathbf{R}}}{V} \left(\frac{e^2}{|\mathbf{R}-\mathbf{r}|} - \frac{e^2}{|\mathbf{R}|} \right) \psi_-^* \psi_+ \, d\mathbf{r} \, d\mathbf{R} \right|^2 \\
 &= \left| \frac{4\pi e^2}{K^2} \cdot \frac{1}{2} \int \frac{e^{i\mathbf{K}\cdot\mathbf{r}}}{V} \left[(R_{2s0})^2 - \frac{1}{3}(R_{2p})^2 \right] d\mathbf{r} \right|^2.
 \end{aligned} \tag{28}$$

The interaction with the nucleus $e^2/|\mathbf{R}|$ contributes nothing to γ_p , since ψ_+ is orthogonal to ψ_- ; i.e., $\int \psi_-^* \psi_+ \, d\mathbf{r} = 0$. The integral (28) over the atomic coordinates is independent of the direction of \mathbf{K} which we take along the polar axis, as follows:

$$\begin{aligned}
 &\int e^{i\mathbf{K}\cdot\mathbf{r}} \left\{ (R_{2s0})^2 - \frac{1}{3}(R_{2p})^2 \right\} d\mathbf{r} \\
 &= 2\pi \int_{-1}^{+1} d\mu \int_0^\infty dr \, e^{iKr\mu} \frac{[4-4(r/a) + \frac{2}{3}(r^2/a^2)]}{32\pi a^3} e^{-r/a} r^2 \\
 &= \frac{1}{(1+x)^2} - \frac{(3-x)}{(1+x)^3} + \frac{2(1-x)}{(1+x)^4} = \frac{2x(x-1)}{(1+x)^4}.
 \end{aligned} \tag{29}$$

Here we have made use of the following earlier results. The integral is considered as the sum of three integrals corresponding to the three terms in the square brace (29). The first is related to $F_{100,100}$ and is adapted from the integral a_{100} (see III-(24)). The third is just $2F_2$ (see III-(30)). The second we evaluate (setting $a = 1$, $K^2 a^2 = x$):

$$\begin{aligned}
& -\frac{1}{4} \int_{-1}^{+1} d\mu \int_0^{\infty} dr e^{iKr\mu} r^3 e^{-r} = -\frac{1}{4} \int_0^{\infty} \frac{[e^{iKr} - e^{-iKr}]}{iKr} e^{-r} r^3 dr \\
& = -\frac{1}{4iK} \left[\frac{2}{(-iK-1)^3} - \frac{2}{(iK-1)^3} \right] = -\frac{3-K^2}{(1+K^2)^3} = -\frac{3-x}{(1+x)^3}. \quad (30)
\end{aligned}$$

Thus from (28) and (29)

$$|(c_{+,-})_{fi}|^2 = \left(\frac{4\pi e^2 a^2}{V} \frac{(x-1)}{(x+1)^4} \right)^2, \quad (31)$$

which is a function of the momentum transfer

$$K^2 = k_1^2 + k_f^2 - 2k_1 k_f \cos \theta.$$

A simplification for evaluation of the sum over states f in (26) is possible, because of the small change in the matrix element as $\epsilon_f = \frac{\hbar^2}{2m} k_f^2$ varies from $\epsilon_1 + \hbar\omega_{+,-}$ by $\hbar(\gamma_p + \gamma_+ - \gamma_-)$. The time integral, however, peaks in this region of ϵ_f . Hence we can factor the integrals over the magnitude and direction of k_f ; i.e., from (26)

$$\begin{aligned}
\dot{D}_{+1} &= -\frac{1}{\hbar^2} \sum_f |(c_{+,-})_{fi}|^2 \int_0^t \dots dt \\
&\cong \frac{V k_f}{(2\pi)^2 \hbar^2} \int_0^\pi |(c_{+,-})_{f,1}|^2 \sin \theta d\theta \int_0^\infty \left[\int_0^t \dots dt \right] k_f dk_f, \quad (32)
\end{aligned}$$

where (see section III)

$$\Sigma_f \rightarrow \int \frac{v}{(2\pi)^3} dk_f$$

and

$$\frac{\hbar^2}{2m} k_f^2 \cong \hbar\omega_{-,+} + \epsilon_i.$$

By inverting the order of integration over τ and k_f , replacing $k_f dk_f$ by $\frac{m}{\hbar} d(\omega_{+,-} + \Omega_{fi})$ and using

$$\int_{-\infty}^{+\infty} e^{i(\omega_{+,-} + \Omega_{fi})(\tau-t)} d(\omega_{+,-} + \Omega_{fi}) = 2\pi \delta(\tau-t);$$

the last integral factor in (32) becomes

$$\int_0^t D_{+i}(\tau) e^{+(\gamma_- - \gamma_+)(\tau-t)} \frac{2 \cdot m \pi}{\hbar} \delta(\tau-t) d\tau = \frac{\pi m}{\hbar} D_{+i}(t). \quad (33)$$

This leads to the result

$$\gamma_p = 2m v_i \sigma_i S_p, \quad (34)$$

with

$$S_p \equiv \int_0^{\hat{x}} \left[\frac{(x-1)}{(1+x)^4} \right]^2 dx = \frac{11}{105} - \frac{1}{5(1+\hat{x})^5} + \frac{2}{3(1+\hat{x})^6} - \frac{4}{7(1+\hat{x})^7},$$

$$\hat{x} = a^2 (k_i + k_f)^2 \cong 4(k_i a)^2 = 4\epsilon_i / (e^2 / 2a),$$

$$\sigma_i \equiv \pi (\hbar / m v_i)^2.$$

Figure 1 is a graph of S_p as a function of the initial electron energy (ϵ_1).

Our (arbitrary) criterion for neglecting polarization is

$$\gamma_P < \frac{\gamma}{10} . \quad (35)$$

The region of low electron density and high energy where this occurs is delimited by the curve in Figure 2. The value $\gamma = \frac{1}{2} \times 3.12 \times 10^8 / \text{sec}$ (see (12)) has been used to determine the expression for this curve:

$$\frac{n}{10^{14}} = \left(\frac{\epsilon_1}{(e^2/2a)} \right)^{1/2} \frac{4.05}{S_p} \quad (36)$$

To return to our example at $\epsilon_1 \sim \frac{1}{2} \text{ev}$, densities of electrons $n \lesssim 10^{15}$ induce few reorientations of the (three state) radiating atom and hence the polarization effect can be neglected. If $\epsilon_1 = \frac{1}{2} \text{ev}$ and $n = 10^{14}$, then $\frac{\gamma_P}{\gamma} = fS_p \sim .013$. The inclusion of other atomic states (esp. ψ_{2P+1}) is carried out later.

Since the low energy limit to the validity of this treatment is not definite, we have extended both curves to zero. Certainly this extreme should not be taken seriously.

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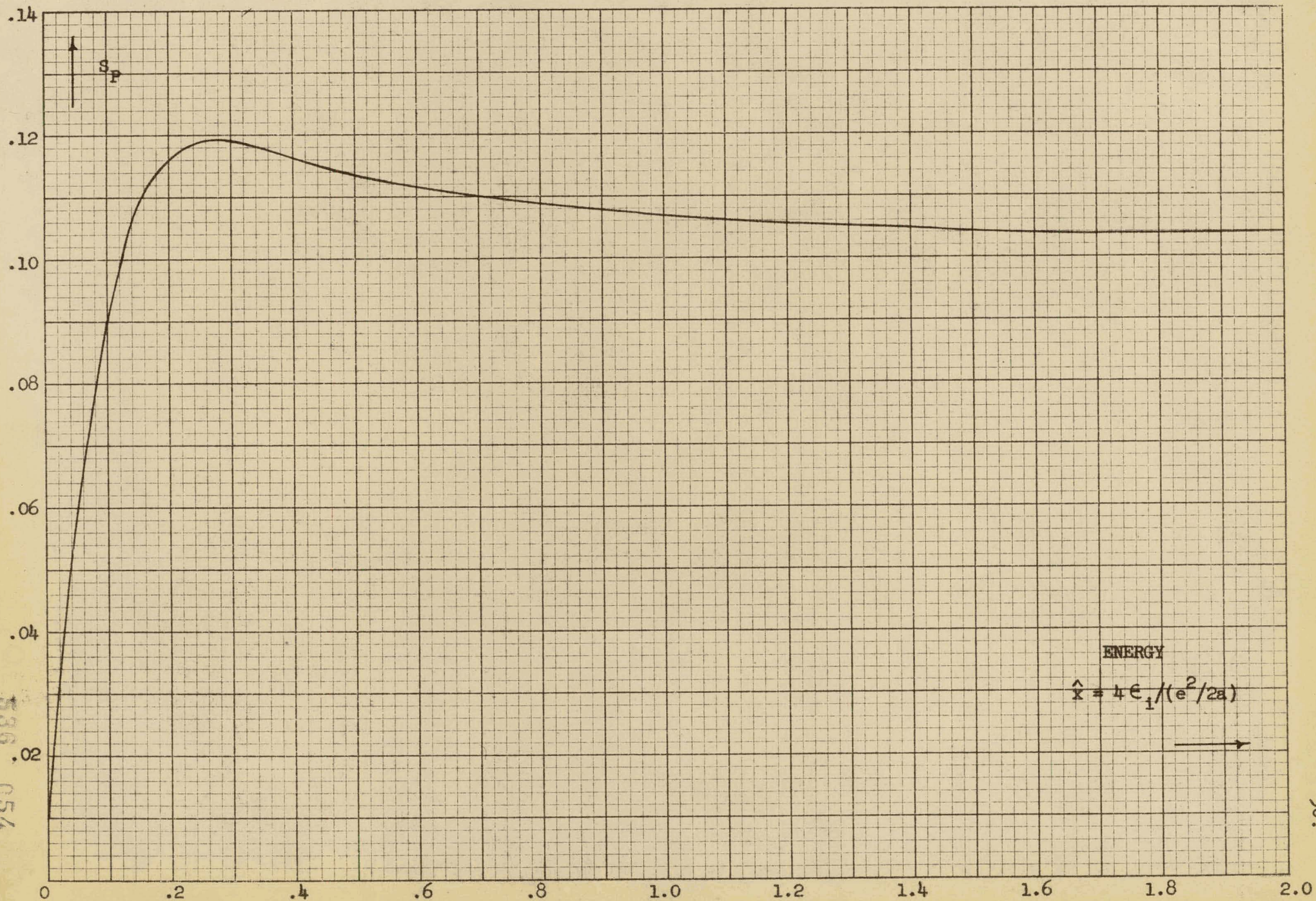


FIGURE 1.

51

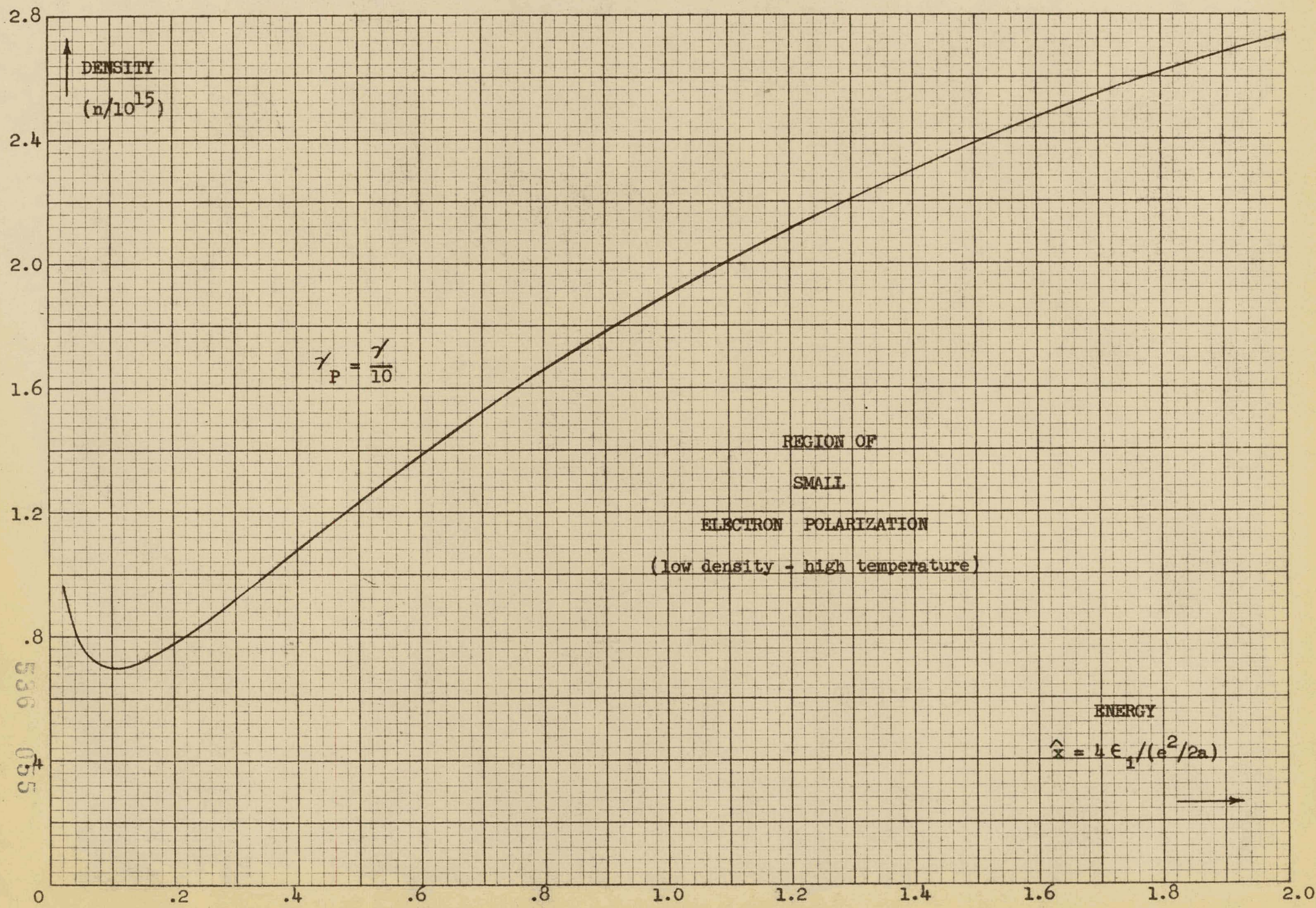


FIGURE 2.

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055

VI. ANGULAR DEPENDENCES IN THE FORM FACTORS.

In the preceding work we have made much use of the form factor

$$F_{n,m}(\underline{K}) = \int e^{i\underline{K}\cdot\underline{r}} \psi_n^* \psi_m d\underline{r}. \quad (1)$$

Throughout we simplified these integrals by taking the momentum transfer vector \underline{K} to be directed along the z axis of the atom. Of course, where the product of the atomic functions $\psi_n^* \psi_m$ is spherically symmetric, this makes no difference. However, since spherical symmetry is not the general case, we took advantage of the random directions of the incident electron to average out angular dependences. In the next few paragraphs we demonstrate that the orientation of the atom with respect to the momentum transfer vector is not critical for small Ka .

We evaluate

$$F_{2p_0,2p_0} = \int e^{i\underline{K}\cdot\underline{r}} \left| \psi_{2p_0}^{z'} \right|^2 d\underline{r}, \quad (2)$$

where the superscript z' (or z) specifies the direction of the polar axis for the wave function, $\psi_{2p_0}^{z'}$. The direction of \underline{K} is the polar (z) axis of $\psi_{2p_0}^z$. The angles Θ , Φ define the orientation of z' with respect to z . In terms of these angles we expand

$$\begin{aligned} \psi_{2p_0}^{z'} &= R_{2p} \cos \Theta' = R_{2p} \left[\cos \Theta \cos \theta + \sin \Theta \sin \theta \cos (\phi - \Phi) \right] \\ &= \cos \Theta \psi_{2p_0}^z + \frac{\sin \Theta}{\sqrt{2}} \left[e^{-i\Phi} \psi_{2p+1}^z + e^{i\Phi} \psi_{2p-1}^z \right], \quad (3) \end{aligned}$$

$$\text{with } R_{2p} = \frac{1}{4\sqrt{2\pi}} \frac{r}{a^{5/2}} e^{-r/2a}.$$

We can also expand in the Legendre Polynomials¹

$$e^{iKz} = \sum_{L=0}^{\infty} (2L+1) i^L P_L(\cos \theta) f_L(Kr) \quad (4)$$

where

$$f_0(r) = \frac{1}{Kr} \sin Kr ,$$

$$f_L(r) = \sqrt{\frac{\pi}{2Kr}} J_{L+1/2}(Kr).$$

Integration over ϕ results in the vanishing of all terms in $F_{2p_0, 2p_0}$ containing ϕ - dependent factors. This reduces the integral to

$$\begin{aligned} F_{2p_0, 2p_0} &= 2\pi \int_{-1}^{+1} d\mu \int_0^{\infty} r^2 dr e^{iKz} \left\{ \left[\cos^2 \theta \left| \Psi_{2p_0}(z) \right|^2 \right. \right. \\ &\quad \left. \left. + \frac{\sin^2 \theta}{2} \left(\left| \Psi_{2p+1}(z) \right|^2 + \left| \Psi_{2p-1}(z) \right|^2 \right) \right] \right\} \\ &= 2\pi \int_{-1}^{+1} d\mu \int_0^{\infty} r^2 dr (R_{2p})^2 e^{iKz} \left\{ \cos^2 \theta \cos^2 \theta \right. \\ &\quad \left. + \frac{1}{2} \sin^2 \theta \sin^2 \theta \right\} . \end{aligned} \quad (5)$$

When we replace e^{iKz} by its expansion, most of the terms contribute nothing, because of the orthogonality of the Legendre Polynomials. To proceed we need the relations²

$$\int_{-1}^{+1} P_L(\mu) P_{L'}(\mu) d\mu = \frac{2}{2L+1} \delta_{L,L'} \quad (6)$$

and

$$\mu P_L(\mu) = \frac{1}{2L+1} \left[(L+1) P_{L+1}(\mu) + L P_{L-1}(\mu) \right] , \quad (7)$$

where $\mu = \cos \theta = P_1$.

In view of them

$$\int_{-1}^{+1} \mu^2 P_L(\mu) d\mu = \frac{2}{3} \delta_{L,0} + \frac{4}{15} \delta_{L,2} \quad (8)$$

and

$$\int_{-1}^{+1} (1 - \mu^2) P_L(\mu) d\mu = \frac{4}{3} \delta_{L,0} - \frac{4}{15} \delta_{L,2}. \quad (9)$$

Consequently

$$\begin{aligned} F_{2p_0, 2p_0} &= 2\pi \int_0^{\infty} r^2 dr (R_{2p})^2 \left\{ \cos^2 \Theta \left(\frac{2}{3} f_0 - \frac{4}{3} f_2 \right) \right. \\ &\quad \left. + \frac{1}{2} \sin^2 \Theta \left(\frac{4}{3} f_0 + \frac{4}{3} f_2 \right) \right\} \\ &= \frac{4\pi}{3} \int_0^{\infty} r^2 dr (R_{2p})^2 \left\{ f_0 + f_2 \left[\sin^2 \Theta - 2 \cos^2 \Theta \right] \right\}. \quad (10) \end{aligned}$$

Our task is almost finished. The radial integrals require the use of

$$\int_0^{\infty} x^n e^{-ax} dx = \frac{n!}{a^{n+1}} \quad (11)$$

and a little algebra. The radial integral for f_0 ,

$$\begin{aligned} \int_0^{\infty} \frac{\sin Kr}{Kr} r^4 e^{-r} dr &= \frac{1}{2iK} \int_0^{\infty} r^3 \left(e^{iKr} - e^{-iKr} \right) e^{-r} dr \\ &= \frac{24(1-x)}{(1+x)^4} \quad (12) \end{aligned}$$

where $x \equiv (Ka)^2$. And for f_2

$$f_2 = \frac{1}{Kr} \left[\left(\frac{3}{(Kr)^2} - 1 \right) \sin Kr - \frac{3}{Kr} \cos Kr \right], \quad (13)$$

$$\begin{aligned}
& \int_0^{\infty} r^4 e^{-r} P_2(Kr) dr \\
&= \frac{3}{K^3} \int_0^{\infty} r e^{-r} \sin Kr dr - \frac{1}{K} \int_0^{\infty} r^3 e^{-r} \sin Kr dr - \frac{3}{K^2} \int_0^{\infty} r^2 e^{-r} \cos Kr dr \\
&= \frac{6}{x(1+x)^2} - \frac{24(1-x)}{(1+x)^4} - \frac{6(1-3x)}{x(1+x)^3} \\
&= \frac{48x}{(1+x)^4} \quad (14)
\end{aligned}$$

Combining these results, we find

$$F_{2po,2po} = \frac{(1-x)}{(1+x)^4} + \left[\sin^2 \Theta - 2 \cos^2 \Theta \right] \frac{2x}{(1+x)^4} \quad (15)$$

Two observations can now be made. First, it is good to check our earlier calculations. At $\Theta = 0$ we have

$$F_{2po,2po} (\Theta = 0) = \frac{1-5x}{(1+x)^4} \quad (16)$$

as found directly for K along the (z') polar axis of the atom (III-(28)). Further, if we average over random angles of collisions (i.e. over Θ) the term in brackets vanishes, and the result is the quantity used in our study (III-(30)):

$$F_{2,2} \equiv \overline{F_{2po,2po}(\Theta)} = \frac{1-x}{(1+x)^4} \quad (17)$$

Proceeding now more rigorously we use the sum over initial states to average over orientations of collisions (i.e., $\sum_i \rho_{ii}^0 \rightarrow \frac{1}{2} \int_0^\pi \sin \Theta d\Theta$) (III-(21)). Here

$$\frac{1}{2} \int_0^\pi [F_1 - F_{2p_0, 2p_0}(\Theta)]^2 \sin \Theta d\Theta = (F_1 - F_2)^2 + \Delta \quad (18)$$

where the deviation from our earlier result is

$$\Delta = \left[\frac{2x}{(1+x)^4} \right]^2 \frac{1}{2} \int_0^\pi [\sin^2 \Theta - 2 \cos^2 \Theta]^2 \sin \Theta d\Theta \quad (19)$$

Corresponding to Δ there is a difference added to S_B , namely,

$$\begin{aligned} \Delta S &= \int_0^{\hat{x}} \frac{\Delta}{x^2} dx \\ &= \frac{16}{35} \left(1 - \frac{1}{(1+\hat{x})^7} \right) = .29 < S_B = 2.1 \end{aligned} \quad (20)$$

for $\hat{x} = \frac{4}{25}$. This correction is limited $(0 < \Delta S < \frac{16}{35})$

depending on the value of \hat{x} . Its inclusion would not change appreciably the results of our simpler approach.

We can also show that our treatment of quenching is rigorous. The form factor is

$$\begin{aligned} F_{12_0, 2p_0}(\Theta) &= \int e^{i\mathbf{K} \cdot \mathbf{r}} \psi_{1s_0}(z') \psi_{2p_0}(z')^* d\mathbf{r} \\ &= \int e^{i\mathbf{K} \cdot \mathbf{r}} \psi_{1s_0}(z) \left[\cos \Theta \psi_{2p_0}(z) + \frac{\sin \Theta}{\sqrt{2}} \left(e^{-i\Phi} \psi_{2p+1}(z) + e^{i\Phi} \psi_{2p-1}(z) \right) \right] d\mathbf{r} \\ &= \cos \Theta \int e^{i\mathbf{K} \cdot \mathbf{r}} \psi_{1s_0}(z) \psi_{2p_0}(z) d\mathbf{r} = \cos \Theta F_{1s_0, 2p_0}^2(0) \end{aligned} \quad (21)$$

and the transition probability averaged over orientations is proportional to

$$\frac{1}{2} \int_0^\pi \cos^2 \Theta \sin \Theta d\Theta F_{1s_0, 2p_0}^2(0) = \frac{1}{3} F_{1s_0, 2p_0}^2(0)$$

This is the value used previously (IV-(7)).

VII. MATRIX ELEMENTS WITH SPURIOUS DIVERGENCES.

Some quenching collision matrix elements appear to be imaginary and to diverge if the momentum transfer vector (\underline{K}) is zero. In this limit a contradiction arises, for the integrals are obviously real. We shall see that they do not diverge if the colliding electron charge is distributed over a finite volume.

We investigate a matrix element for the electrostatic interaction between a free electron and a bound hydrogen-like electron. In particular

$$C(\underline{K})_{2p0,2s0} = \frac{4\pi e^2}{K^2 V} F_{2p0,2s0}, \quad (1)$$

where

$$F_{2p0,2s0} = \int e^{i\underline{K}\cdot\underline{r}} \psi_{2p0}^* \psi_{2s0} d\underline{r}$$

and

$$\underline{K} = \underline{k}_\mu - \underline{k}_\lambda.$$

Use has been made of the formula

$$\int \frac{e^{i\underline{K}\cdot\underline{R}}}{|\underline{r}-\underline{R}|} d\underline{R} = \frac{4\pi}{K^2} e^{i\underline{K}\cdot\underline{r}}. \quad (2)$$

The procedure for finding (2), is:

$$\begin{aligned} \int \frac{e^{i\underline{K}\cdot\underline{R}}}{|\underline{R}-\underline{r}|} d\underline{R} &= e^{i\underline{K}\cdot\underline{r}} \int \frac{e^{i\underline{K}\cdot\underline{\rho}}}{|\underline{\rho}|} d\underline{\rho} \\ &= 2\pi e^{i\underline{K}\cdot\underline{r}} \int_0^\infty \rho^2 d\rho \int_{-1}^{+1} \frac{e^{iK\rho\mu}}{\rho} d\mu = \frac{4\pi e^{i\underline{K}\cdot\underline{r}}}{K} \int_0^\infty \sin K\rho d\rho, \quad (3) \end{aligned}$$

with

$$\underline{\rho} = \underline{R} - \underline{r}.$$

The indeterminate integral was evaluated with the use of a convergence factor; i.e. we put

$$\lim_{\alpha \rightarrow 0} \int_0^\infty e^{-\alpha\rho} \sin K\rho d\rho = \lim_{\alpha \rightarrow 0} \frac{K}{\alpha^2 + K^2} = \frac{1}{K}. \quad (4)$$

The form factor, $F_{2p0,2s0}$ (evaluated in atomic units) contains

$$\psi_{2s0} = \frac{1}{4\sqrt{2\pi}} (2-r)e^{-r/2} \text{ and } \psi_{2p0} = \frac{1}{4\sqrt{2\pi}} re^{-r/2} \cos \theta.$$

In performing the integral over θ we can see that the form factor is pure imaginary, as follows. Taking \underline{K} along the polar axis of the atom and letting $\mu = \cos \theta$, we have

$$\begin{aligned} \int_{-1}^{+1} e^{iKr\mu} \mu d\mu &= e^{iKr\mu} \left[\frac{\mu}{iKr} - \frac{1}{(iKr)^2} \right] \Bigg|_{-1}^{+1} \\ &= \frac{1}{(Kr)^2} \left[e^{iKr} - e^{-iKr} \right] + \frac{1}{iKr} \left[e^{iKr} + e^{-iKr} \right] \\ &= \frac{1}{\text{real}} [\text{imaginary}] + \frac{1}{\text{imaginary}} [\text{real}], \end{aligned} \quad (5)$$

where \underline{K} is in atomic units. That is

$$\begin{aligned} F_{2p0,2s0} &= \frac{1}{16} \int_0^{\infty} (2r^3 - r^4) \left\{ \frac{1}{K^2 r^2} \left[e^{-(1-iK)r} - e^{-(1+iK)r} \right] \right. \\ &\quad \left. + \frac{1}{iKr} \left[e^{-(1-iK)r} + e^{-(1+iK)r} \right] \right\} dr \\ &= \frac{3iK(x-1)}{(1+x)^4}, \text{ where } x = K^2. \end{aligned} \quad (6)$$

Finally, converting back from atomic units:

$$C(\underline{K})_{2p0,2s0} = \frac{4\pi e^2}{VK^2} \left[\frac{3iKa(x-1)}{(1+x)^4} \right], \text{ } x = K^2 a^2. \quad (7)$$

This element diverges as $1/K$ when K goes to zero and is imaginary. A look at the integral (1) for $\underline{K} = 0$ tells us that the result should be real. We note that the form-factor alone does not introduce this difficulty, since it becomes zero. This suggests that the $1/K^2$ factor in (2) is the culprit.

We now view this matrix element as the electrostatic interaction energy between atomic charge, $dq_a(\underline{r}) = e \psi_n^* \psi_n d\underline{r}$, and an electron charge density $dq_e = \frac{e^{i\mathbf{K}\cdot\mathbf{R}}}{V} e d\underline{R}$. The integral (2)

$$\frac{e}{V} \int \frac{e^{i\mathbf{K}\cdot\mathbf{R}}}{|\underline{r}-\underline{R}|} d\underline{R} = \frac{4\pi e}{V K^2} e^{i\mathbf{K}\cdot\mathbf{r}} \quad (8)$$

then plays the roll of the potential at \underline{r} due to the charge density distribution $\frac{e}{V} \cdot e^{i\mathbf{K}\cdot\mathbf{R}}$. It satisfies Poisson's equation;

$$\nabla^2 \left(\frac{4\pi e}{V K^2} e^{i\mathbf{K}\cdot\mathbf{r}} \right) = - \frac{4\pi e}{V} e^{i\mathbf{K}\cdot\mathbf{r}}. \quad (9)$$

In order to understand the trouble, we take $\underline{K} = 0$. Think of the free electron distribution as uniform spherical charge shells with their origin at the nucleus. If $R < r$, then for the potential at r the charge $4\pi e R^2 dR/V$ on the shell dR at R can be treated as if it was at the nucleus. This corresponds to inner shielding in a Hartree atom calculation. The potential energy of dq_a at r is

$$V_{in}(\underline{r}) = \int_0^r dq_a(\underline{r}) \frac{4\pi e}{rV} R^2 dR = \frac{4\pi e dq_a(\underline{r})}{3V} r^2. \quad (10)$$

If $R > r$, then the potential of dq_a is independent of r and has the value, akin to outer shielding,

$$V_{out} = dq_a \int_r^{\hat{R}} \frac{4\pi e R^2}{VR} dR = dq_a \left(\frac{4\pi e \hat{R}^2}{2V} - \frac{4\pi e r^2}{2V} \right). \quad (11)$$

The upper limit is introduced as a means of terminating the free electron charge. In practice there is a finite cut off because of polarization of the plasma.

The total energy is given by the integral over the atomic charge dq_a :

$$C_{n,n}(\underline{K}=0) = \int \psi_n^* \psi_n \left[\frac{2\pi e^2}{V} \hat{R}^2 - \frac{4\pi e^2 r^2}{6V} \right] d\underline{r}$$

$$= \frac{2\pi e^2}{V} \left[\hat{R}^2 \delta_{n,n'} - \frac{(r^2)_{n,n'}}{3} \delta_{l_m, l_{m'}} \right], \quad (12)$$

with

$$(r^2)_{n,n'} = \int \psi_n^* r^2 \psi_{n'} dr.$$

For $n = 2p0$ and $n' = 2s0$, this vanishes. If $n' = n$, it is a very classical case; i.e.,

$$C_{n,n}(K=0) = \frac{2\pi e^2}{V} \left[\hat{R}^2 - \frac{(r^2)_{n,n}}{3} \right]. \quad (13)$$

The first term corresponds to the interaction energy, if the atomic charge is concentrated at the origin.

$$\int \frac{e^2}{|\underline{r}-\underline{R}|} \frac{dR}{V} = \frac{4\pi e^2}{V} \frac{\hat{R}^2}{2}. \quad (14)$$

The second term is a correction because of the distribution of the atomic charge. It is this second part that varies from state to state and gives a relative shift to the energy levels.

The evaluation of (13) can be made a little more formal. Using the expansion

$$\frac{1}{|\underline{r}-\underline{R}|} = \sum_{L=0}^{\infty} \frac{r_{<}^L}{r_{>}^{L+1}} P_L(\cos \theta_{rR}), \quad (15)$$

where $r_{>}$ ($r_{<}$) is the larger (smaller) of R and r , and integrating

$$C_{n,n'}(K=0) = e^2 \int \frac{\psi_n^* \psi_{n'}}{|\underline{r}-\underline{R}|} d\underline{r} d\underline{R} \quad (16)$$

over the angular space of \underline{R} with \underline{r} as the polar axis;

$$C_{n,n'}(K=0) = 4\pi e^2 \int \frac{dr}{r} \int_0^{\infty} R^2 dR \psi_n^* \psi_{n'} \frac{1}{r}, \text{ since} \quad (17)$$

$$\int_{-1}^{+1} P_L(\mu) P_{L'}(\mu) d\mu = \frac{2}{2L+1} \delta_{L,L'}. \quad (18)$$

This reduces to (12).

We now want to use the finite cut off, \hat{R} , to modify the result (2) for $K \neq 0$. In this derivation there was an indeterminate integral (4)

$$\int_0^{\hat{\rho}} \sin K\rho \, d\rho,$$

which for finite $\hat{\rho}$ and small enough K is known. At large values $\rho \approx R$, which goes to \hat{R} . We assume $K\hat{R} \ll 1$ and then

$$\int_0^{\hat{\rho}} \sin K\rho \, d\rho \approx \int_0^{\hat{R}} K\rho \, d\rho = K\hat{R}^2/2. \quad (19)$$

Thus

$$\int \frac{e^{iK \cdot \frac{R}{r}}}{|r-R|} dR \approx e^{iK \cdot \frac{r}{r}} \frac{4\pi}{K} \cdot \frac{K\hat{R}^2}{2} = 2\pi e^{iK \cdot r} \hat{R}^2, \quad K\hat{R} \ll 1. \quad (20)$$

Consequently

$$C_{n,n'}(K\hat{R} \ll 1) = \frac{2\pi \hat{R}^2 e^2}{V} F_{n,n'} \quad (21)$$

and

$$C_{n,n'}(K=0) = \frac{2\pi \hat{R}^2 e^2}{V} \delta_{n,n'} \quad (22)$$

which agrees with (13) with neglect of the second term, (the correction for the distributed charge). Evidently we have made an approximation in the transformation from $\frac{R}{r}$ to $\frac{r}{r}$ (see equation 3), by which this term is lost. This was done by inexact treatment of the upper limit of integration, which depends on the angle θ_{rR} . If done correctly

$$\int \frac{e^{iK \cdot \frac{R}{r}}}{|R-r|} dR \approx 2\pi e^{iK \cdot r} \left[\hat{R}^2 - \frac{r^2}{3} \right],$$

provided $K \cdot (\hat{R}-r) \ll 1$.

Thus the problem of the divergence as $K \rightarrow 0$ can be avoided by introduction of a plasma cut off \hat{R} .

VIII. POLARIZATION AND DEGENERATE LEVELS.

In section V an attempt was made to treat the small broadening resulting from polarization for a three state atom. The matrix elements were chosen deliberately to avoid the divergences associated with the near degenerate levels which were discussed in section VII. Now we are prepared to study collisions which couple the initial state ψ_+ to all atomic states.

Excitation to higher principal quantum numbers is not energetically possible for low electron energies such as that considered in our example ($\epsilon_1 \sim \frac{1}{25} \frac{e^2}{2a}$). For these transitions the electron must supply a minimum of about $(\frac{1}{4} - \frac{1}{9}) \frac{e^2}{2a}$. Even where they are possible, they should introduce no new features. On the other hand quenching--transitions to the ground state--occur. As seen in section IV, the divergence poses no problem for them; the large amount of energy given to the electron, keeps the minimum momentum transfer far enough from zero to avoid this difficulty. The resulting contribution to polarization broadening is

$$\begin{aligned} \frac{(\gamma_P)_{+,1s0}}{\gamma} &= \frac{f}{2} \left\{ (S_P)_{2s0,1s0} + \frac{1}{3} (S_P)_{2p0,1s0} \right\} \\ &\approx \frac{.061}{2} \left\{ .036 + \frac{1}{3} \times .15 \right\} = 2.6 \times 10^{-3} \end{aligned} \quad (1)$$

provided $n = 10^{14}$ and $\epsilon_1 = \frac{1}{25} \frac{e^2}{2a}$. This should be compared with the previous

$$\frac{(\gamma_P)_{+,-}}{\gamma} = 6.7 \times 10^{-3}. \quad (2)$$

The situation is not so simple for near degenerate levels. Here the minimum momentum transfer approaches zero and we enter the region of spurious divergences. We meet this problem when considering the two undisplaced states, $\psi_{2P_{\pm 1}}$.

In order to treat collisions which couple the polarized state ψ_+ to these states we define these states in terms of functions with a polar axis z along the direction of the momentum transfer vector \mathbf{K} , as follows,

$$\psi_{2p+1}^{z'} = -\frac{\sin \Theta}{\sqrt{2}} \psi_{2p0}^z + \frac{1}{2} (1 + \cos \Theta) e^{-i\Phi} \psi_{2p+1}^z + \frac{1}{2} (\cos \Theta - 1) e^{i\Phi} \psi_{2p-1}^z \quad (3)$$

and

$$\psi_{2p-1}^{z'} = -\frac{\sin \Theta}{\sqrt{2}} \psi_{2p0}^z + \frac{1}{2} (\cos \Theta - 1) e^{-i\Phi} \psi_{2p+1}^z + \frac{1}{2} (\cos \Theta + 1) e^{i\Phi} \psi_{2p-1}^z \quad (4)$$

The angles Θ and Φ determine the direction of z with respect to z' . Thus

with $\psi_+^{z'} = \frac{1}{\sqrt{2}} (\psi_{2s0}^{z'} + \psi_{2p0}^{z'})$ and $\psi_-^{z'}$ there are four states for the

principal quantum number $n = 2$, which are normalized and orthogonal. They

serve to describe this level completely. We rewrite similar expansions

for $\psi_{2s0}^{z'}$ and $\psi_{2p0}^{z'}$:

$$\psi_{2s0}^{z'} = \psi_{2s0}^z \quad (5)$$

$$\psi_{2p0}^{z'} = \cos \Theta \psi_{2p0}^z + \frac{1}{\sqrt{2}} \sin \Theta e^{-i\Phi} \psi_{2p+1}^z + \frac{1}{\sqrt{2}} \sin \Theta e^{i\Phi} \psi_{2p-1}^z \quad (6)$$

First, consider the form factor:

$$\begin{aligned} F_{2p+1,+}^{(\Theta, \Phi)} &= \int e^{i\mathbf{K} \cdot \mathbf{r}} \psi_{2p+1}^{z*} \psi_+^z d\mathbf{r} \\ &= \frac{1}{\sqrt{2}} \left[F_{2p+1,2s0}^{(\Theta, \Phi)} + F_{2p+1,2p0}^{(\Theta, \Phi)} \right], \end{aligned} \quad (7)$$

with

$$F_{2p+1,2s0}^{(\Theta, \Phi)} = -\frac{\sin \Theta}{\sqrt{2}} F_{2p0,2s0}^{(0)} = -\frac{\sin \Theta}{\sqrt{2}} \left[\frac{31K(x-1)}{(1+x)^4} \right] \quad (8)$$

and

$$\begin{aligned} F_{2p+1,2p0}^{(\Theta, \Phi)} &= -\frac{1}{\sqrt{2}} \sin \Theta \cos \Theta F_{2p0,2p0}^{(0)} + \frac{1}{2\sqrt{2}} (1 + \cos \Theta) \sin \Theta F_{2p+1,2p+1}^{(0)} \\ &\quad + \frac{1}{2\sqrt{2}} (\cos \Theta - 1) \sin \Theta F_{2p-1,2p-1}^{(0)} \\ &= -\frac{1}{\sqrt{2}} \sin \Theta \cos \Theta \left[\frac{1-5x}{(1+x)^4} \right] + \frac{1}{\sqrt{2}} \sin \Theta \cos \Theta \left[\frac{1}{(1+x)^3} \right] \\ &= \frac{1}{\sqrt{2}} \sin \Theta \cos \Theta \frac{6x}{(1+x)^4} \end{aligned} \quad (9)$$

We note that if $\Theta = 0$ this form factor vanishes. This tells us that collisions in which the momentum transfer is along the polar z' axis can not change the atom from $\psi_{2p+1}^{z'}$ to $\psi_{2p+1}^{z'}$.

The transition probability is proportional to the absolute square of the form factor averaged over collision orientations:

$$\frac{1}{4\pi} \int_0^{\pi} \int_0^{2\pi} |F_{2p+1,+}(\Theta, \Phi)|^2 \sin \Theta d\Theta d\Phi$$

$$= \frac{1}{6} \left\{ |F_{2p0,2s0}(0)|^2 + \frac{1}{5} \left[\frac{6x}{(1+x)^4} \right]^2 \right\}, \quad (10)$$

where $F(0)$ indicates that $\Theta = 0$ and \vec{k} is along the polar axis of the atom. As before we can write

$$(\gamma_P)_{+,2p+1} = 2nv_i \sigma_i(S_P)_{+,2p+1} \quad (11)$$

with

$$(S_P)_{+,2p+1} = \frac{1}{6} \int_{\check{x}}^{\hat{x}} \frac{|F_{2p0,2s0}(0)|^2}{x^2} dx + \frac{6}{5} \int_0^{\hat{x}} \frac{dx}{(1+x)^8} = \frac{1}{6}(S_P)_{2p0,2s0}$$

$$+ \frac{6}{35} \left[1 - \frac{1}{(1+x)^7} \right]. \quad (12)$$

The false divergence of $(S_P)_{2p0,2s0}$ at small x appear in this term.

The magnitude of

$$\check{x} = a^2 (k_i - k_f)^2 \quad (13)$$

is limited by the requirement of energy conservation. By the artifact of a static ion field we have removed the atomic degeneracy and \check{x} does not vanish. However, to avoid the region of small x where (12) becomes invalid, we must restrict

$$\check{x} \left(\frac{a}{a} \right)^2 \gg 1. \quad (14)$$

In that case the integral

$$\int_0^{\hat{R}} \sin \sqrt{KR} dR = \frac{1 - \cos \sqrt{K\hat{R}}}{\sqrt{K}} \quad (15)$$

may be averaged over a sufficient range in \hat{R} to eliminate $\cos \sqrt{K\hat{R}}$ so that the integral is $\frac{1}{\sqrt{K}}$, where $K^2 a^2 = \chi$.

This is the value obtained earlier with a convergence factor (VII-(4)).

How large must the energy separation ΔE of the atomic levels be to satisfy (14)? To answer this question \hat{R} must be defined. For definiteness we take $\hat{R} \sim n^{-1/3}$ -- a quantity which must be revised to suit the physical situation. The results will be found insensitive to this choice. Thus

$$\chi \gg a^2 n^{2/3}. \quad (16)$$

For $\Delta E \ll \epsilon_1$,

$$k_p \approx k_1 \left(1 + \frac{\Delta E}{2\epsilon_1}\right) \quad (17)$$

and for (14)

$$\chi = a^2 k_1^2 \left(\frac{\Delta E}{2\epsilon_1}\right)^2 = \left(\frac{\epsilon_1}{e^2/2a}\right) \left(\frac{\Delta E}{2\epsilon_1}\right)^2 \gg a^2 n^{2/3}. \quad (18)$$

What ion density produces a Holtmark field sufficiently strong to satisfy this inequality?

For $n = 10^{14}$ and $\epsilon_1 = \frac{1}{25} \left(\frac{e^2}{2a}\right)$,

$$\frac{\Delta E}{(e^2/2a)} = \frac{3ea(3.26n_{ion}^{2/3})}{(e^2/2a)} \gg 2an^{1/3} \sqrt{\frac{\epsilon_1}{(e^2/2a)}};$$

and thus

$$n_{ion} \gg \frac{1}{(50)^{3/2}} \cdot \frac{n^{1/2}}{a^{3/2}} \sim 10^{17}. \quad (19)$$

If we also restrict $n_{ion} \sim n$, then

$$n_{ion} \gg \frac{1}{(50a)^3} \sim .6 \times 10^{20}. \quad (20)$$

Both of these are higher densities than we are considering.

Before going further let us point out that the appropriate inequality is, in fact, satisfied for quenching. Here $\Delta E \gg \epsilon_1$ and we approximate

$$\frac{y}{x} \sim a^2 k_f^2 \sim \left(\frac{\Delta E}{e^2/2a} \right) \sim \frac{3}{4} \gg a^2 n^{2/3} \sim 5.4 \times 10^{-8}. \quad (21)$$

Thus it becomes necessary to consider the region of small x more carefully. Here (VII - (23))

$$\int \frac{e^{iK \cdot R}}{|R-r|} dR \approx 2\pi e^{iK \cdot r} \left[\frac{\hat{R}^2}{R} - \frac{r^2}{3} \right]. \quad (22)$$

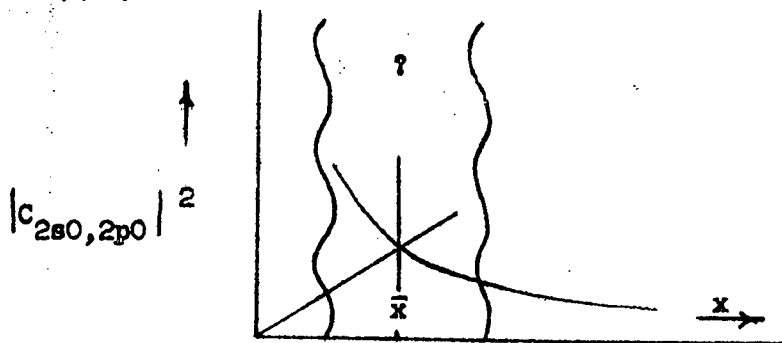
If we neglect the $r^2 \sim a^2$ contribution as being small compared to \hat{R} , then (VII - (12))

$$c_{2s0,2p0} = \frac{4\pi e^2}{V} \left(\frac{\hat{R}^2}{2} \right) F_{2s0,2p0} \quad (23)$$

so that $\frac{\hat{R}^2}{2}$ has taken the place of $\frac{1}{K^2}$. This change prevents the divergence. We now have a better appreciation of the matrix element -- at least at the extremes of x . As long as $x \ll 1$ the matrix element has a simple form; viz.

$$|c_{2s0,2p0}|^2 \approx \left(\frac{4\pi e^2 a^2}{V} \right)^2 x \begin{cases} \left(\frac{\hat{R}}{a} \right)^4 \frac{x}{4} & x \left(\frac{\hat{R}}{a} \right)^2 < 1 \\ \frac{1}{x} & x \left(\frac{\hat{R}}{a} \right)^2 \gg 1 \end{cases} \quad (24)$$

with $x \ll 1$.



Sketch 1

Following the considerations of section VII it can be shown that

$|C_{2s0,2p0}|^2$ is bounded in the uncertain region. Consider (VII - (19))

$$\left| \int_0^{\hat{p}} \sin K\rho d\rho \right| = \left| \frac{1 - \cos K\hat{p}}{K} \right| \leq \left| \frac{2}{K} \right|$$

so that

$$|C_{2s0,2p0}|^2 \leq 4 \left| \frac{4\pi e^2}{VK^2} F_{2s0,2p0} \right|^2 \approx 4 \left(\frac{4\pi e^2 a^2}{V} \right)^2 \frac{1}{x}.$$

In sketch 1 the curves for $|C|^2$ are extrapolated into the region of uncertainty. To avoid a detailed treatment of this intermediate region we use the extrapolated curves to their intersection. This intersection \bar{x} occurs where

$$\left(\frac{\hat{R}}{a} \right)^4 \frac{\bar{x}}{4} = \frac{1}{\bar{x}}; \quad (25)$$

$$\bar{x} \sim 2a^2 n^{2/3} \sim 10^{-7}.$$

Consequently, neglecting x compared to 1, we find

$$\begin{aligned} (S_p)_{2p0,2s0} &\approx \frac{1}{4} \left(\frac{\hat{R}}{a} \right)^4 \int_0^{\bar{x}} |F_{2s0,2p0}|^2 dx + \int_{\bar{x}}^{\hat{x}} \left| \frac{F_{2s0,2p0}}{x} \right|^2 dx \\ &\approx \frac{9}{x^2} \int_0^{\bar{x}} x dx + 9 \int_{\bar{x}}^{\hat{x}} \frac{dx}{x} \\ &\approx 9 \left\{ \frac{1}{2} + \ln \frac{\hat{x}}{\bar{x}} \right\} = 9 \left\{ \frac{1}{2} + \ln \frac{.16}{10^{-7}} \right\} \\ &\approx 133, \end{aligned} \quad (26)$$

$$\text{since } |F_{2s0,sp0}|^2 = \frac{9x(x-1)^2}{(1+x)^8}.$$

And finally

$$\frac{(\gamma_p)_{+,2p+1}}{\gamma} \sim f \left\{ \frac{1}{6} 133 + .11 \right\} = .061x22 \approx 1.3. \quad (27)$$

The main uncertainty introduced in this number arises from the manner in which we obtained \bar{x} . If we require $\bar{x} \gg a^{2/3} n^{2/3}$ so as to stop the rapid rise at the region of uncertainty, then there is a decrease in γ_p . However, an increase in \bar{x} by a factor 100 decreases

$$\frac{(\gamma_p)}{\gamma} +, 2p+1 \text{ by only}$$

$$\frac{3}{2} \ln 100 \approx .4.$$

(28)

This leaves the order of magnitude of the effect unchanged. In the other direction \bar{x} cannot be pushed far, since $\bar{x} \left(\frac{\hat{R}}{a}\right)^2 \sim 2$ has been used (25) and the logarithmic divergence is limited by $\bar{x} \left(\frac{\hat{R}}{a}\right)^2 \sim 1$. However, \hat{R} may be larger than $n^{-1/3}$. An increase of \hat{R} by factor 100 decreases \bar{x} by 10^{-4} but increases γ_p by only .8.

We conclude that coupling between ψ_+ and ψ_{2p+1} gives rise to a polarization effect about 100 times as large as the other states. This is because the coupling involves the matrix elements between ψ_{2p0} and ψ_{2s0} . However, the effect certainly does not diverge.

In summary we compare the several effects for the hydrogen

$2p \rightarrow 1s$ transition. Using $\gamma = 3.12 \times 10^8 \text{ sec}^{-1}$, $n = 10^{14}$, $\epsilon_1 = \frac{1}{25} \left(\frac{e^2}{2a}\right)$:

[III - (44)] scattering or universal broadening	$\frac{\gamma_B}{\gamma} = .13,$
[IV - (7)] quenching ($2p0 \rightarrow 1s0$)	$\frac{\gamma_q}{\gamma} = .003,$
[VIII - (27)] polarization ($2p0 \rightarrow 2s0$)	$\frac{\gamma_p}{\gamma} = 1.3,$
[IV - B - (8)] Stark (ion)	$\frac{\gamma_{\text{Stark}}}{\gamma} = 80.$

IX. SPECTRAL LINE SHIFT.

The spectral line shift for the two state atom is given by

(VII - (13))

$$\begin{aligned} \hbar\omega_s &= C_{1,1}(K=0) - C_{2,2}(K=0) = \frac{e^2}{V} \int \frac{|\psi_1|^2 - |\psi_2|^2}{\left| \frac{r}{r} - \frac{R}{r} \right|} dr dR \\ &= \frac{2\pi e^2}{3V} [(r^2)_{2,2} - (r^2)_{1,1}] = \frac{18\pi e^2 a^2}{V}, \end{aligned} \quad (1)$$

where we consider the hydrogen $2p \rightarrow 1s$ transition and use¹

$$(r^2)_{nl, nl} = \frac{n^2}{2} [5n^2 + 1 - 3l(l+1)] a^2.$$

This agrees with the result obtained from our earlier form factors

(section III)

$$\hbar\omega_s = \frac{4\pi e^2 a^2}{V} \left(\frac{F_1 - F_2}{x} \right) \Bigg|_{K=0} = \frac{18\pi e^2 a^2}{V}. \quad (2)$$

In units of the natural width $\gamma = 3.1 \times 10^8$ /sec., and with $n = 10^{14}$

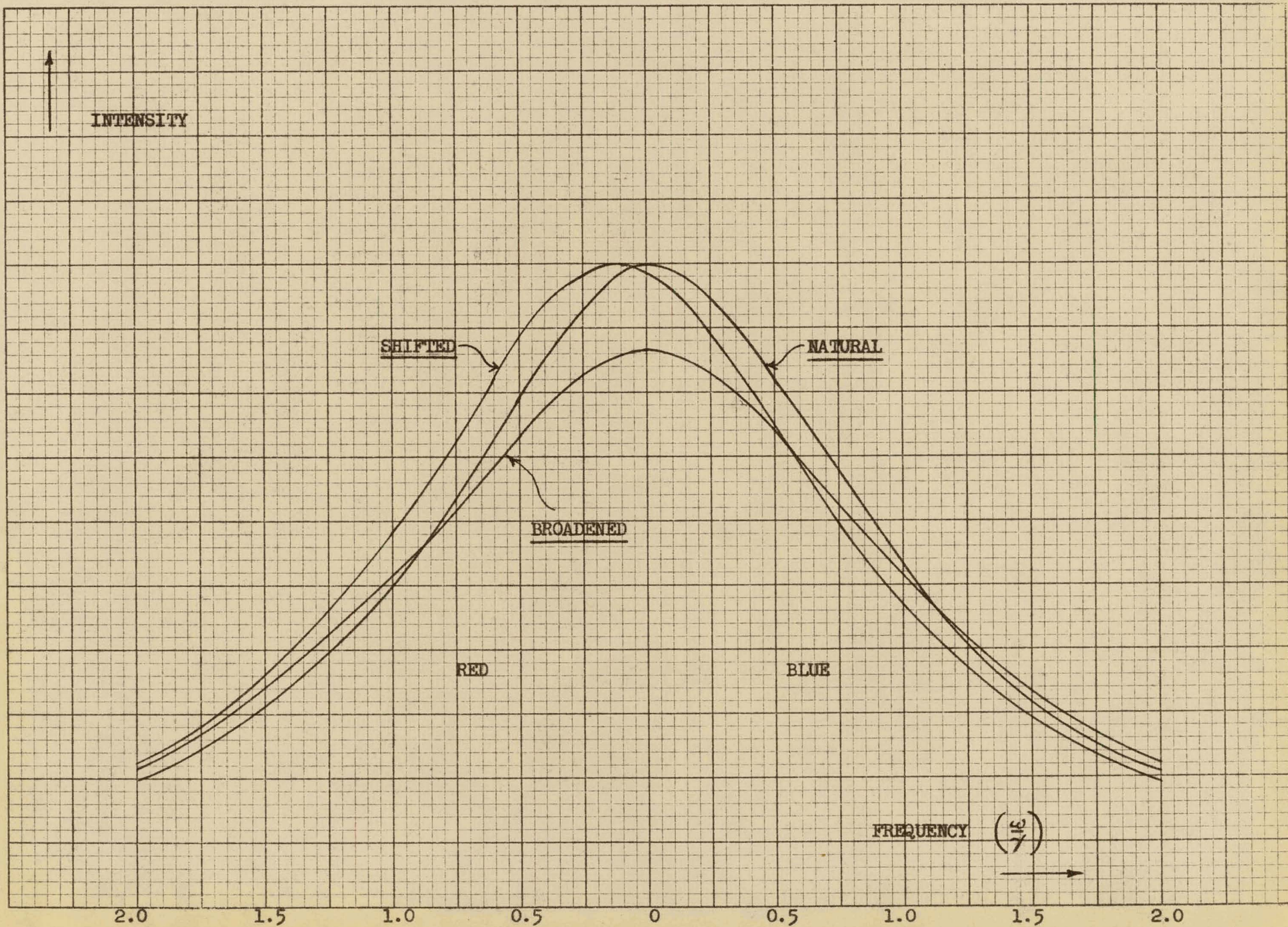
$$\frac{\hbar\omega_s}{\hbar\gamma} = .11, \quad (3)$$

a shift to the red.

This shift was suppressed in our earlier work when the exponent in the factor $\exp(i [C_{1,1}(K=0) - C_{2,2}(K=0)] t/\hbar)$ was absorbed into $\exp(i\omega t)$. In the graph are illustrated the natural, broadened and shifted lines.

Before leaving this matter we note that the shift here computed is quite negligible in comparison with the large Holtmark-Stark shifts resulting from the use of localized wave packets. The shift obtained here corresponds to the difference in interaction energy of the atomic state charge clouds with a uniform space distribution of the free electron charge. The use of Coulomb functions, which increase the free electron concentration near the nucleus and change the inner shielding, should not produce any major change in the situation. On the other hand, the interaction with localized packets is expected to give different results.

70



536 074

FIGURE 1.

X. COMPLEMENTARY DERIVATION OF BROADENING FOR A TWO STATE ATOM.

Once the work of the preceding sections is completed, it is illuminating to obtain the same results by a more direct though not as conscientious a procedure. Again we consider the two state atom and one electron per volume V . At $t = 0$ the atom is excited and remains excited until $t \sim 1/\gamma$. During this interval electron transitions are induced destroying the initially excited state (i.e., state of combined electron-atom system). This has the effect of decreasing the lifetime of the initial state and increasing its energy uncertainty. We write at once from the same arguments as used in the discussion of polarization effects:

$$I_B = N |J/\hbar|^2 / [\omega^2 + (\gamma + \gamma_B)^2], \quad (1)$$

provided $\gamma_B (\ll \gamma)$ is one-half of the chance that the electron quantum numbers change per unit time. The normalization factor N adjusts I_B so that each atom still emits one photon.

To demonstrate this we consider the factor in the expansion coefficient in which changes are induced by the collision perturbation, P .

$$i\hbar \dot{d}_1 = \sum_f d_f(P)_{f1} e^{-i\Omega_{f1}t}$$

$$i\hbar \dot{d}_f = d_1(P)_{1f} e^{-i\Omega_{1f}t} + \text{small terms with factors } d_k \ll d_1. \quad (2)$$

From these equations we can show exponential decay:

$$i\hbar \dot{d}_1 = \sum_f \frac{1}{i\hbar} |P_{f1}|^2 \int_0^t e^{-\gamma_B(\tau-t) - i\Omega_{f1}(\tau-t)} dt d_1, \quad (3)$$

that is

$$d_1 = e^{-\gamma_B t}, \quad (4)$$

provided

$$\gamma_B = \frac{1}{n^2} \sum_f |P_{fi}|^2 \pi \delta(\Omega_{fi}). \quad (5)$$

Now we treat the perturbation as a sudden brief change in the Hamiltonian for the free electron. Distortion of the atom is neglected. Before the atom is excited and after emission the Hamiltonian is $H_e + C_{1,1}$. However, while the atom is excited, this becomes $H_e + C_{2,2}$. The perturbation¹ which modifies the initial stationary state of the free electron is $P = C_{11} - C_{22}$. One might not be certain of his choice without a more detailed study as given above.

Then, using a plane wave approximation and replacing the sum over final states by an integral, we find

$$\begin{aligned} \gamma_B &= \frac{1}{n^2} \int \frac{v}{(2\pi)^3} dK_f \frac{1}{v^2} \left(\frac{4\pi e^2}{K^2} \right)^2 (F_{11} - F_{22})^2 \pi \delta(\Omega_{fi}) \\ &= f S_B \gamma \end{aligned} \quad (6)$$

where $f = 2nv_1 \pi \left(\frac{\hbar}{mv_1} \right)^2 \frac{1}{\gamma}$,

$$S_B = \int_0^{\Omega} \left(\frac{F_{11} - F_{22}}{x} \right)^2 dx.$$

As long as $\frac{\gamma_B}{\gamma} \ll 1$ we can expand

$$I_B = \frac{N |J/\hbar|^2}{(\gamma^2 + \omega^2)} \left\{ 1 - \frac{2\gamma/\gamma_B}{\gamma^2 + \omega^2} \right\}; \quad (7)$$

and N is found to be $1 + \gamma_B/\gamma$ by requiring

$$\int_{-\infty}^{+\infty} I_B d\omega = \int_{-\infty}^{+\infty} \frac{|J/\hbar|^2}{\gamma^2 + \omega^2} d\omega. \quad (8)$$

Thus this somewhat more direct approach leads to our earlier goal;

$$I_B = \frac{|J/\pi|^2}{\gamma^2 + \omega^2} \left\{ 1 - f_{S_B} \left(\frac{\gamma^2 - \omega^2}{\gamma^2 + \omega^2} \right) \right\}. \quad (9)$$

X1. LARGE BROADENING AND EXPERIMENTAL VERIFICATION

The previous arguments can be extended to instances of larger broadening. It will be found that the line width may be expressed as the sum of the natural (γ) scattering (γ_B) and polarization (γ_P) widths even when γ_B and γ_P are greater than γ . We now turn to this generalization:

A. Large γ_P .

The changing field of the electron at the atom can induce transitions between the atomic levels. This shortens the lifetime of the state and broadens the level according to the uncertainty principle. Although the atom may be returned to this level by a second collision, this should not extend the lifetime. Rather the return can be thought of as the start of a new life.

Let us see how this follows from our equations for polarization (V-(18), (19))

$$i\hbar \dot{D}_{+\lambda} = \sum_{\mu} (C_{+-})_{\lambda\mu} D_{-\mu} e^{i(\omega_{+-} + \Omega_{\lambda\mu})t} - (\gamma_- - \gamma_+)t \quad (1)$$

$$i\hbar \dot{D}_{-\mu} = \sum_{\lambda} (C_{-+})_{\mu\lambda} D_{+\lambda} e^{i(\omega_{-+} + \Omega_{\mu\lambda})t} + (\gamma_- - \gamma_+)t \quad (2)$$

In the earlier treatment, (Sec. V), all terms on the right of the second equation (2) were neglected in comparison with the initial state which had the large probability amplitude. Here we retain all terms. An argument concerning the random phase associated with each $D_{+\lambda}$, is used to eliminate all but one.

Integrating the second equation (2) and substituting into the first (1) we find

$$i\hbar \dot{D}_{+\lambda} = \sum_{\mu} \sum_{\lambda'} (C_{+-})_{\lambda\mu} \frac{1}{i\hbar} (C_{-+})_{\mu\lambda'} \int_0^t dz D_{+\lambda'} e^{(\gamma_- - \gamma_+) + i(\omega_{-+} + \Omega_{\mu\lambda'}) (\tau - t)} \times e^{i\Omega_{\lambda\lambda'} t} \quad (3)$$

Since the electrons come from different sources, the $D_{+\lambda}$, have factors $\exp(i\phi_{\lambda})$ containing unrelated arbitrary phases ϕ_{λ} . An average over these phases leads to the cancelation of all terms on the right of (3) except that with $D_{+\lambda}$. For consider the parallel example:

$$\dot{a}e^{i\phi} = Ae^{i\phi} + Be^{i\phi'} \quad (4)$$

assumed true when averaged over ϕ and ϕ' . Multiplying first by $e^{-i\phi}$ and then averaging

$$\dot{a} = A + \overline{Be^{i(\phi'-\phi)}} = A, \quad (5)$$

since the average $\overline{\exp[i(\phi'-\phi)]}$ vanishes.

Consequently, following the same procedure as in sect. V:¹

$$\begin{aligned} \dot{D}_{+\lambda} &= -\frac{1}{\hbar^2} \sum_{\mu} |C_{+-}(\mu\lambda)|^2 \int_0^t D_{+\lambda} e^{[(\gamma_- - \gamma_+) + i(\omega_{-+} + \Omega_{\mu\lambda})](\tau-t)} d\tau \\ &= -2\nu\sigma S_p D_{+\lambda} = -\gamma_p D_{+\lambda} \end{aligned} \quad (6)$$

This result is not restricted to γ_p small compared to γ .

B. Large γ_B .

The arguments just used for large γ_p can be applied to the complementary derivation of scattering broadening (sect. X). This leads to the same result-- γ_B is not restricted to be small compared to γ . A similar conclusion probably can be reached using the general expression for I_B (II-(21))

$$I_B(\omega) = |J/\hbar|^2 \sum_{\mu} \frac{\left| \int \phi_{\mu}^{0*} \phi_{\lambda}^1 d\vec{R} \right|^2}{\gamma^2 + (\omega + \Omega_{\lambda\mu})^2} \quad (7)$$

A treatment of this problem is given by Rudkjobing². Since the experimentally interesting case has large γ_p because of near degenerate levels, we do not concern ourselves further with γ_B in this section.

C. Experimental Verification.

Knowledge of electron or ion densities and temperatures is not easily obtained. Consequently, an experiment which is independent of these parameters is desired. The comparison of different line widths in a spectrum of radiators in the same plasma, where all the atoms emit in a given though perhaps uncertain temperature and density, has this property. An especially interesting case presented by the relative widths of the $n^3D \rightarrow 2^3P$ lines in the helium spectrum. For example, we will show that the width ratio for lines from the principal quantum levels $n = 4$ and $n = 3$ is ~ 150 for Holtsmark ion broadening while it is only ~ 10 for electron collision broadening. This difference stems from the fortuitous fact that there is no 3^3F level.

For the higher principal quantum numbers the F level is the nearest neighbor of the D level and leads to much larger Stark shifts and Holtsmark broadening than occurs for $n = 3$. On the other hand, the collision width receiving a contribution from the more distant P level, which is comparable to that from F, remains relatively unchanged with n .

The energy separations of interest are given in Table 1.

Table 1. Energy Separations.

ΔE		
n	$(E_{nF} - E_{nD}) / (e^2/2a)$	$(E_{nD} - E_{nP}) / (e^2/2a)$
3		.00481
4	.0000726	.00212
5	.0000437	.00107
6	.0000252	.00062
		536 080

where the energy levels are determined using [B-p. 421] ³.

$$E_{nl} = \frac{(e^2/2a)}{(n - \delta_{nl})^2} \quad (8)$$

and approximate quantum defects δ_{nl} (Table 2) for orthohelium. Since

Table 2. δ_{nl}

n	δ_{nF}	δ_{nD}	δ_{nP}
3		.00217	.0650
4	.00017	.00249	.0684*
5	.00017*	.00290*	.0684*
6	.00017*	.00290*	.0684*

the table in Bethe's Handbuch article [B-p. 347] is incomplete, we have extrapolated from the nearest values to fill out Table 2. The values not in Bethe's table are indicated by an asterisk.

The matrix elements which enter both Stark shift broadening and collision broadening is $Z_{nlm, n'l'm'}$. In particular we will consider [B-p. 420]

$$(Z_{n,l,0;n,l-1,0})^2 = \frac{9n^2}{4} \left(\frac{(n^2 - l^2)l^2}{4l^2 - 1} \right) a^2 \equiv Z_{nl}^2 \quad (9)$$

for $l = 3$ and 2 (Table 3). We see that for $n = l = 3$ this vanishes.

Table 3. $(z_{n0;n1-10})^2 \equiv z_{n1}^2$

n	$\frac{z_{n3}^2}{a^2}$	$\frac{z_{n2}^2}{a^2}$
3	0	27.0
4	64.8	115.2
5	231.4	315.0
6	562.4	691.2

1. Estimate of Holtmark Broadening (Stark Shift).

For a uniform electric field (F) the component with the value (for the angular momentum projection quantum number) $m = 0$ has the largest energy shift. Because the levels of helium are non-degenerate one obtains in weak fields the quadratic Stark shift [B-p. 421] for the D levels with $m = 0$:

$$E_{nD0}^{(2)} = -e^2 F^2 \left(\frac{z_{n3}^2}{E_{nF} - E_{nD}} - \frac{z_{n2}^2}{E_{nD} - E_{nF}} \right) \quad (10)$$

With the values in Tables 1 and 3 we find these shifts (Table 4):

Table 4. Stark Shifts.

$E_{nD0}^{(2)} / e^2 F^2$	$- 5.6 \times 10^3$	$+ 8.38 \times 10^5$	$+ 5.00 \times 10^6$	$+ 2.12 \times 10^7$
n	3	4	5	6

The very small shift for $n = 3$ is a result of the absence of a 3^3F level.

To estimate the width we follow Holtsmark and take

$$F = 3.26 en^{2/3}; \quad (11)$$

and for the ion broadening width (Table 5)

$$h(\gamma_{ion})_{nD} = 4 \cdot (3.26)^2 (e^2/2a)^2 n^{4/3} a^4 \left[\frac{Z_{n3}^2}{E_{nF} - E_{nD}} - \frac{Z_{n2}^2}{E_{nD} - E_{nF}} \right] \quad (12)$$

Table 5. Ion broadening width and width ratios
for $n = 10^{15}$.

n	$(\gamma_{ion})_{nD}$ (sec ⁻¹)	$\frac{(\gamma_{ion})_{n+1,D}}{(\gamma_{ion})_{n,D}}$
3	6.03×10^7	149
4	9.018×10^9	6.0
5	5.381×10^{10}	4.2
6	2.281×10^{11}	

2. Collision Broadening.

The collision matrix elements can be written as (III-(17))

$$C_{nlm, n'l'm'} = \frac{4\pi e^2}{VK^2} \left[-\delta_{nlm, n'l'm'} + F_{nlm, n'l'm'} \right] \quad (13)$$

provided plane waves are used for the free electron functions. The elements $C_{nso, n'p_0}$ diverge as K^{-1} and give particularly large polarization broadening (sect. VIII). To generalize this observation we develop an approximate form for the C elements.

The momentum transfer vector \underline{K} will be oriented along the polar axis of the atom. It was seen (sect. VI) that $|C|^2$ with this orientation did not differ greatly from an average of $|C|^2$ over the orientation of the incident plane wave. In fact the difference vanished as \underline{K} became zero.

When K is small the exponential factor of the integrand of F is expanded:

$$e^{i\mathbf{K}\cdot\mathbf{r}} = 1 + i\mathbf{K}\cdot\mathbf{r} - \frac{1}{2}(\mathbf{K}\cdot\mathbf{r})^2 + \dots \quad (14)$$

In this way an expansion in increasing powers of K starting with K^{-2} is obtained. The leading term in K^{-2} survives in the diagonal elements. These entered in scattering and again in the element $C_{+,-}$ (sections III and V). However, here these terms canceled each other.

The elements

$$C_{n'l'm, n'l'+1m} = \frac{4\pi e^2}{VK^2} \left[iK(r \cos \theta)_{n'l'm, n'l'+1m} + \dots \right], \quad (15)$$

where the leading term diverges at small K , interest us most. The divergence does not actually occur because of the finite distance from which an electron can perturb the atom. Still these elements give the largest contributions to broadening (section VIII).

The divergence at small K makes the expansion (14) useful. Because of this divergence an integral as $S = \int \left(\frac{F}{x} \right)^2 dx$ receives its major contribution from the region of small K . Hence, while (14) is incorrect at larger K , its use does not cause much error in S .

We conclude that to a good approximation the electron broadening of n^3D is given by (VIII)

$$(\gamma_P)_{nD} = 2\pi v_i \sigma_i \sum_{l=2,3} z_{nl}^2 \left\{ \begin{array}{l} \frac{1}{x^2} \int_{\check{x}_{nl}}^{\bar{x}} x dx + \int_{\bar{x}}^{\hat{x}} \frac{dx}{x} \\ \int_{\check{x}_{nl}}^{\hat{x}} \frac{dx}{x} \end{array} \right. \text{for } \left\{ \begin{array}{l} \bar{x} > \check{x}_{nl} \\ \bar{x} < \check{x}_{nl} \end{array} \right. , \quad (16)$$

where

$$\hat{x} \cong 4\epsilon_1 / (e^2/2a),$$

$$\check{x}_{nl} = \left(\frac{\epsilon_1}{e^2/2a} \right) \left(\frac{E_{nl} - E_{nl-1}}{2\epsilon_1} \right)^2 \quad \text{for } E_{nl} - E_{nl-1} \ll \epsilon_1,$$

$$\bar{x} \sim a^2 n^{2/3},$$

n = electron density,

ϵ_1 = initial energy of the free electron,

v_i = initial velocity of the free electron,

$$\sigma_i = \pi \left(\frac{h}{mv_i} \right)^2.$$

Thus electron collision broadening depends on the same matrix elements as the Stark shift. However, it does not depend so strongly on the associated energy separations. Consequently the vanishing of Z_{33}^2 only changes $(\gamma_P)_{3D}$ by about a factor 1/2.

Use of (16) requires knowledge of \bar{x} and the plasma radius. In order to avoid the uncertain details of these quantities, we find $(\gamma_P)_{nP}$ for two extremes: $\bar{x} = 0$ and $\bar{x} = a^2 n^{2/3}$. The latter places an upper limit on $(\gamma_P)_{nD}$ as \check{x} vanishes. The former is independent of the plasma cut off.

In Table 6 are the values of \check{x}_{nl} corresponding to the energy separations in Table 1.

Table 6. \check{x} for $\epsilon_1 = \frac{1}{25} \frac{e^2}{2a}$

n	3	4	5	6
\check{x}_{n3}		3.29×10^{-8}	1.19×10^{-8}	3.97×10^{-9}
\check{x}_{n2}	1.45×10^{-4}	2.80×10^{-5}	7.17×10^{-6}	2.39×10^{-6}

In Table 7 are $(\gamma_P)_{nD}$ values and their successive ratios. Comparison with the ion effect is facilitated by reproducing the ratio values from Table 5.

Table 7. $(\gamma_P)_{nD}$ and ratios for $n = 10^{15}$ and $\epsilon_1 = \frac{1}{25} \frac{e^2}{2a}$.

$\bar{x} = 0$ (no plasma cut off)

n	Contributions to $(\gamma_P)_{nD}$ from		$(\gamma_P)_{nD}$ sum (sec ⁻¹)	$\frac{(\gamma_P)_{n+1,D}}{(\gamma_P)_{nD}}$	$\frac{(\gamma_{ion})_{n+1,D}}{(\gamma_{ion})_{n,D}}$
	$l=P$ (sec ⁻¹)	$l=F$ (sec ⁻¹)			
3	3.60×10^{10}	0	3.60×10^{10}	10.5	149
4	1.90×10^{11}	1.89×10^{11}	3.80×10^{11}	3.5	6.0
5	6.00×10^{11}	7.23×10^{11}	1.32×10^{12}	2.5	4.2
6	1.46×10^{12}	1.87×10^{12}	3.34×10^{12}		

$$\bar{x} = a^2 n^{2/3} = 2.79 \times 10^{-7}$$

n	Contribution to $(\gamma_P)_{nD}$ from		$(\gamma_P)_{nD}$ sum (sec ⁻¹)	$\frac{(\gamma_P)_{n+1,D}}{(\gamma_P)_{nD}}$
	$l=P$ (sec ⁻¹)	$l=F$ (sec ⁻¹)		
3	3.60×10^{10}	0	3.60×10^{10}	10.0
4	1.90×10^{11}	1.70×10^{11}	3.60×10^{11}	3.4
5	6.00×10^{11}	6.06×10^{11}	1.21×10^{12}	2.4
6	1.46×10^{12}	1.47×10^{12}	2.93×10^{12}	

It is seen that at the density $n \sim 10^{15}$ the use of the plasma cut off ($\bar{x} \sim a^2 n^{2/3}$) does not alter the result appreciably.

Unlike hydrogen, where there is a large linear Stark effect, in helium the electron broadening is larger than ion broadening. Another advantage to the use of helium is the possible appearance of the forbidden transitions

$4^3F \longrightarrow 2^3P$ and $4^3P \longrightarrow 2^3P$. Since the uniform field intensity for their appearance is known [B-p.427], this may serve as an indicator of the ion density.

Although the results are contained in Table 7, we point out that the ion broadening ratio for lines from 3D and 4D is 150 while the corresponding electron broadening ratio is 10. The difference should be easily observed.

We have kept ion and electron effects separate although they of course occur simultaneously. In our example the sum of electron and ion broadening is approximately the same as the larger electron effect alone.

It is likely that our calculation overestimates γ_p . The electrons have been assumed monoenergetic and represented by plane waves. Actually the electrons are distributed in energy and our calculation is poor for the slower ones (failure of the Born approximation). If the very slow electrons produce ion-like (Stark) effects, then we may expect that the electron density to be used in γ_p is less than the actual density. This diminution of our calculated γ_p may mean that electron effects are less important than ion effects for the lines $nd \rightarrow 2p$ ($n > 3$). Hence these lines would have contours predictable from Stark shifts and the appearance of forbidden lines (as $4p \rightarrow 2p$). On the other hand $3d \rightarrow 2p$ can still have the anomalous electron broadening shape; i.e., the Lorentz shape $([(\gamma + \gamma_p)^2 + \omega^2]^{-1})$. Also this line should be broader than expected on comparison with the other members of the series when only ion effects are considered. The ions present should, however, introduce a slight shift and asymmetry toward the violet. Thus electron effects as treated in this report may find a fairly simple experimental verification.

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