PHYSICAL REVIEW VOLUME 98, NUMBER 2 APRIL 15, 1955

Electron Impact Broadening of Spectral Lines*

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(Received August 13, 1954)

Ion densities in electrical discharges and in stars are often determined by observing the widths of spectral lines emitted or absorbed. The Holtsmark theory, usually employed in the interpretation of the data, restricts itself to ions and ignores electron collisions, which are treated in a qualitative way. This paper describes a detailed theory of electron effects upon the Lyman alpha line.

A convenient physical classification of the result is as follows. Electrons produce, first of all, what we have called a *universal* line effect, a broadening occurring regardless of the nature of the atomic transition. Its cause is the transfer of energy from the electrons to one or the other of the two atomic states via scattering. So far as the analogy is proper, this effect is what is sometimes called "second order Stark broadening." It forms the predominating feature when a linear Stark effect is absent.

Secondly, electrons can enforce the optical transition by collisions of the second kind. This mechanism, called *quenching*, broadens the line. It alone has the property of reducing the intensity of the line under normal conditions.

A third possible contribution to the line width results from *polarization*, the counterpart of a first-order Stark effect. It comes about if one of the atomic states (the upper in our example) is degenerate or nearly degenerate. The electron, while flying past the atom, can then induce transitions without much energy transfer, i.e., polarize the atom. A distinction is made between (a) polarization through induction of a temporary dipole moment and (b) polarization through reorientation of an atomic dipole already present by virtue of a neighboring ion. The first of these is a large effect; its calculation requires the removal of divergences which are ordinarily encountered in the matrix elements.

The summary at the end of the paper contains numerical results on the broadening of L_α by these several agencies under conditions approximating the solar photosphere. They are all small in comparison with Holtsmark broadening by ions. But the example is unusual; in general the electron effects are far from negligible.

I. INTRODUCTION

SPECTRAL lines emitted in a plasma are known to be broadened in a manner characteristic of the ion density and the temperature in the discharge. Indeed, line widths are often regarded as "probes" by means of which these two parameters can be determined. Tests of this kind are based upon the theory of line broadening developed long ago by Holtsmark,[1] a theory which assumes that the ions exert Stark effects whose magnitudes vary as the ions move, thereby diffusing the line intensity. The electrons, which are as numerous as the ions, are supposed to produce small effects because of their greater velocity and their ubiquity: they have less time to interact with the radiating atoms, and by being nearly everywhere they affect the atoms like a static distribution of charge, which shifts the lines but does not broaden them.

Despite the plausibility of these considerations, the Holtsmark theory is plagued by an insecurity arising from its failure to include the electrons in its concerns. This has long been felt by astronomers and physicists alike, and many qualitative attempts have been made to treat the electrons. Some of these have had wide attention and interesting use, for the rigorous theory is cumbersome, and the likelihood that it will give answers wholly different from those intuitively expected is small. Probably for these reasons, such a theory has not previously been worked out. In the present paper we undertake to do this, not in the hope of spectacularly new results, but to provide a carefully analyzed instance against which simpler models can be tested. Our approach is via the theory of natural line width; it involves old and familiar ideas. We are not sure, however, that it is the most elegant and the most direct attack upon the problem; in fact it seems to us at times as if our results should be obtainable in simpler ways.

The usual theories of pressure broadening are not applicable to perturbing electrons because the uncertainty principle prevents electrons from pursuing a classical path along which an interaction potential can be defined. It is necessary, therefore, to incorporate them into the quantum mechanical system from the very beginning, a process which leads to the elaborate treatment developed in this paper. Some of the results obtained are intuitively plausible and almost derivable from various simple, classical models. But the consistency of the guesses based on such considerations is difficult to establish unless a comprehensive account is at hand. Aside from being systematic, our treatment also indicates many connections with other physical phenomena, such as scattering, quenching of excited states, etc., and thereby deepens understanding.

To keep the work simple and the methods clear, no extensive applications are given in the present paper. The magnitudes of the various effects are illustrated in the terms of one simple example, the width of the first Lyman line in atomic hydrogen under typical discharge conditions. The analysis dealing with "universal broadening" (by which we mean a transfer of energy to the atomic state via electron scattering in a manner computable without assuming a change in atomic states; this mechanism is always present, whether there is degeneracy of atomic states or not) in Sec. III is limited

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* Part of a dissertation presented for the degree of Doctor of Philosophy in Yale University.

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§ Supported by the Office of Naval Research and the U. S. Atomic Energy Commission.

[1] A. B. Underhill, Astrophys. J. 116, 446 (1953).

to line widths comparable to the natural width. Since this effect is found to be small and our applications fall within the limits of validity of our treatment, we have not thought it necessary to extend it. Subsequent publications will deal with more practical applications, among them the contribution of plasma electrons to the width of the Balmer lines.

Current investigations 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 diffculties 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 Kantrowitz[3] in the study of shock phenomena. Baranger[4] attributes the difference to electrons. The electron effect also interests workers using spectral line widths to measure plasma characteristics in discharge tubes.[5] To account for it the density of charge employed in the Holtsmark theory is often taken to be intermediate between the ion density and ion plus electron density.[6]

Reasonable qualitative conclusions about the electron broadening and shift of spectral lines can be drawn from a semiclassical model.[7] 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, if by a hit we mean a "sufficiently close" collision. In the present paper we find the cross section of this collision; its radius turns out to be essentially the de Broglie wavelength of the electron. Thus high-energy electrons, which produce small effects, may be considered as passing the atom too quickly to polarize it or to be scattered by it.

For the quantitative treatment of the problem quantum theory of radiation is used. On the basis of the results obtained it is possible, first of all, to delimit the large region of high temperatures and low densities where electron effects are minor and ignorable. With decreasing electron temperature and increasing electron density, first-order corrections to the natural line become important and are found. Here two effective broadening mechanisms are distinguished: (1) change in the electron energy during a radiative atomic transition (*universal broadening*) and (2) distortion of the atomic state-function (*polarization*) by the electrons. This second effect is important only if one of the atomic levels is strongly coupled to a neighboring level. 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 by electrons can be studied. Attention will also be given to polarization in the physically interesting situation of a hydrogen atom amid numerous positive ions.

II. GENERAL CONSIDERATIONS[8]

Electron broadening can be studied as an extension of the Hoyt and Weisskopf-Wigner treatment for the natural line width.[9] The natural decay for a two-state atom ($E_1 > E_0$) is described by the growth equations,

$$i\hbar\dot{d}=\textstyle\sum_r J_r^* b_r e^{i\omega t}, \tag{1}$$

and

$$i\hbar\dot{b}_r=J_r d e^{-i\omega t}, \tag{2}$$

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

$$I(\omega_r)=\rho_r|b_r(t=\infty)|^2=\rho_r|J_r/\hbar|^2/(\gamma^2+\omega^2). \tag{3}$$

To include a perturber ($\mathbf{R}$) with the atom and the radiation field, we write the Schrödinger equation

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

The Hamiltonian (H) includes terms for unperturbed atom and radiation field $[H_a(\mathbf{r})]$, the perturber $[H_e(\mathbf{R})]$, an interaction between atom and perturber $[C(\mathbf{r},\mathbf{R})]$, 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 understood to be contained in the atomic ψ_n and E_n.

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

$$\Psi=\textstyle\sum_n\sum_\lambda{}^n a_{n\lambda}(t)\psi_n(\mathbf{r})\phi_\lambda{}^n(\mathbf{R})\exp[-i(\epsilon_\lambda{}^n+E_n)t/\hbar], \tag{5}$$

where $\sum_\lambda{}^n$ means the sum and/or integral over all perturber states λ while the atom is in state n. The atomic function satisfies

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

the normalized electron function for an electron in the

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[2] G. J. Odgers, Astrophys. J. **116**, 444 (1953).

[3] A. Kantrowitz, Phys. Rev. **90**, 368 (1953).

[4] M. Baranger, Phys. Rev. **91**, 436 (1953). See also P. Shultz, Ann. Physik **3**, 280 (1948).

[5] See H. N. Olsen and W. S. Huxford, Phys. Rev. **87**, 922 (1952).

[6] G. Jurgens, Z. Physik **134**, 21 (1952).

[7] See D. R. Inglis and E. Teller, Astrophys. J. **90**, 439 (1939).

[8] H. Margenau and S. Bloom, Oak Ridge National Laboratory Progress Report, March 1, 1952 (unpublished).

[9] See S. Rosseland, *Theoretical Astrophysics* (Clarendon Press, Oxford, 1936), especially Chap. VIII.

field of an atom in state ψ_n obeys

$$[H_e(\mathbf{R})+C_{n,n}(\mathbf{R})]\phi_\lambda{}^n(\mathbf{R})=\epsilon_\lambda{}^n\phi_\lambda{}^n(\mathbf{R}), \tag{7}$$

$$\int|\phi_\lambda{}^n|^2d\mathbf{R}=1,\quad C_{m,n}(\mathbf{R})\equiv\int\psi_m{}^*C\psi_n d\mathbf{r}.$$

To justify the use of the expansion (5), we note that the best product function with neglect of the exchange property is given by the Hartree equations:

$$\left(H_a+\int\phi_\lambda{}^{n*}C\phi_\lambda{}^n d\mathbf{R}\right)\psi_n{}^\lambda=E_n{}^\lambda\psi_n{}^\lambda; \tag{8}$$

$$\left(H_e+\int\psi_n{}^{\lambda*}C\psi_n{}^\lambda d\mathbf{r}\right)\phi_\lambda{}^n=\epsilon_\lambda{}^n\phi_\lambda{}^n. \tag{9}$$

For high perturber energies ($\epsilon_\lambda{}^n$), $\phi_\lambda{}^n$ is to a good approximation a plane wave. Then $|\phi_\lambda{}^n|^2$ is a constant independent of λ, and $\psi_n{}^\lambda$ is the atomic state in a uniform charge distribution normalized to the perturber density. At low perturber density it is proper to neglect the shielding effects of this charge distribution on $\psi_n{}^\lambda$. Thus we ignore the C matrix element in (8) and our equations take the form (6) and (7). Since the product $\psi_n\phi_\lambda{}^n$ is not a stationary solution for the material system, the coefficients will, of course, depend on C.

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

$$\begin{aligned}i\hbar\dot{a}_{m\mu}&\exp[-i(\epsilon_\mu{}^m+E_m)t/\hbar]\\&=\textstyle\sum_n\sum_\lambda{}^n a_{n\lambda}J_{mn}\displaystyle\int\phi_\mu{}^{m*}\phi_\lambda{}^n d\mathbf{R}\exp[-i(\epsilon_\lambda{}^n+E_n)t/\hbar]\\&\quad+\sum_{\substack{n\\(n\neq m)}}\textstyle\sum_\lambda{}^n a_{n\lambda}\displaystyle\int\phi_\mu{}^{m*}C_{mn}\phi_\lambda{}^n d\mathbf{R}\\&\qquad\times\exp[-i(\epsilon_\lambda{}^n+E_n)t/\hbar].\end{aligned} \tag{10}$$

This equation differs in two respects from the Weisskopf-Wigner equations. First it provides for an exchange of energy between electron and radiation field by the presence of the $\epsilon_\mu{}^m$ and $\epsilon_\lambda{}^n$ factors in the exponent of the first expression on the right. These remain because $\phi_\mu{}^m$ and $\phi_\lambda{}^n$ are not orthogonal. The likelihood of these exchanges or shifts depends on the integral factor,

$$\int\phi_\mu{}^{m*}\phi_\lambda{}^n d\mathbf{R}.$$

The second effect additional to the natural line width is inherent in the terms contributed by the C elements on the right of (10). They represent polarization or distortion of the atom when the states m and n are degenerate or nearly degenerate; if n and m denote the levels between which the radiative transition occurs these added terms describe quenching.

Henceforth, we speak of the first additional effect as universal broadening, of the second as polarization or quenching. The two may be treated separately in our case of low electron density and high temperature, where modification of the spectral line is small.

The first correction, to which the remainder of this section and the next are devoted, is found by solving (10) with neglect of the off-diagonal elements $C_{m,n}$. This approximation holds for atomic states which are not easily polarized or quenched, i.e., for transitions between two isolated atomic levels. The correction then comes merely from the fact that the atomic transition takes place in the field of the electron. In view of this, it is not surprising that the results we obtain involve quantities also encountered in the theory of elastic scattering of electrons.

For the two-state atom, then, with neglect of quenching and polarization,

$$i\hbar\dot{d}_\lambda=\textstyle\sum_r\sum_\mu{}^0 b_{r\mu}J_r{}^*\exp(i\omega t+i\Omega_{\lambda\mu}t)\displaystyle\int\phi_\lambda{}^{1*}\phi_\mu{}^0 d\mathbf{R}, \tag{11}$$

$$i\hbar\dot{b}_{r\mu}=\textstyle\sum_{\lambda'}{}^1 d_{\lambda'}J_r\exp(-i\omega t-i\Omega_{\lambda'\mu}t)\displaystyle\int\phi_\mu{}^{0*}\phi_{\lambda'}{}^1 d\mathbf{R}, \tag{12}$$

with $\hbar\Omega_{\lambda'\mu}=\epsilon_{\lambda'}{}^1-\epsilon_\mu{}^0$; the index r refers again to a photon of frequency $\omega_r=\omega_{\text{atom}}-\omega$, and the amplitudes d and b designate "dark" and "bright" states.

We now establish the fact that the exponential decay approximation for the initially excited atom is valid and independent of the electron state. From (12) we find an integral for $b_{r\mu}(t)$ which we substitute into Eq. (11):

$$\begin{aligned}i\hbar\dot{d}_\lambda=\textstyle\sum_r\sum_\mu{}^0\dfrac{|J_r|^2}{i\hbar}\sum_{\lambda'}{}^1\displaystyle\int_0^t d_{\lambda'}&\\\times\exp[-i\omega(\tau-t)-i\Omega_{\lambda'\mu}(\tau-t)]d\tau\exp(i\Omega_{\lambda\lambda'}t)&\\\times\left[\int\phi_\mu{}^{0*}\phi_{\lambda'}{}^1,\ d\mathbf{R}\cdot\int\phi_\lambda{}^{1*}\phi_\mu{}^0 d\mathbf{R}\right].&\end{aligned} \tag{13}$$

The assertion is: $d_{\lambda'}=a_{\lambda'}{}^1e^{-\gamma t}$, where $a_{\lambda'}{}^1$ is a constant. The proof is to note that it reduces the differential Eq. (13) for d_λ to an identity. The sum over oscillator states in (13) can be replaced by an integral.

$$\textstyle\sum_r\rightarrow\displaystyle\int_0^\infty\rho_r d\omega_r\cong\int_{-\infty}^{+\infty}\rho_r d\omega_r,$$

where the symbols for the integration over angles of emission and the sum over polarization are compressed into ρ_r. Since the integral, $\int\phi_\mu{}^{0*}\phi_{\lambda'}{}^1 d\mathbf{R}$, is small for large $\Omega_{\lambda'\mu}$, we can take $\rho_r|J_r|^2$ out of the integral over ω_r, understanding that it remains constant over the spectral line, and replace it by its value $\rho|J|^2$ at $\omega=0$. Integrating over $x\equiv-(\omega+\Omega_{\lambda'\mu})$ and then over τ, we obtain

$$\int_0^t d_{\lambda'}(\tau)\int_{-\infty}^{+\infty} e^{ix(\tau-t)}dxd\tau$$
$$=\int_0^t e^{-\gamma(\tau-t)}2\pi\delta(\tau-t)d\tau a_{\lambda'}{}^1 e^{-\gamma t}=\pi a_{\lambda'}{}^1 e^{-\gamma t}.$$

Returning to (13), we find

$$\dot{d}_\lambda=-\pi\rho|J/\hbar|^2\sum_{\lambda'}{}^1 d_{\lambda'}\exp(i\Omega_{\lambda\lambda'}t)$$
$$\times\sum_\mu{}^0\int\phi_\mu{}^{0*}\phi_{\lambda'}{}^1 d\mathbf{R}'\int\phi_\lambda{}^{1*}\phi_\mu{}^0 d\mathbf{R}$$
$$=-\gamma\sum_{\lambda'}{}^1 d_{\lambda'}\exp(i\Omega_{\lambda\lambda'}t)=-\gamma d_\lambda, \tag{14}$$

with $\gamma\equiv\pi\rho|J/\hbar|^2$. In establishing Eq. (14) the closure relation of the functions $\phi_\mu{}^0$ is used. This proves the exponential dependence of d_λ on time.

Equation (12) can be written

$$i\hbar\dot{b}_r\equiv\sum_\mu i\hbar\dot{b}_{r\mu}=J_r e^{(-\gamma-i\omega)t}\int\phi_0{}^*\phi_1 d\mathbf{R}, \tag{15}$$

provided we define

$$\begin{aligned}\phi_1&\equiv\sum_\lambda{}^1 a_\lambda{}^1\phi_\lambda{}^1\exp(-i\epsilon_\lambda{}^1 t/\hbar),\\ \phi_0&\equiv\sum_\mu{}^0\phi_\mu{}^0\exp(-i\epsilon_\mu{}^0 t/\hbar).\end{aligned} \tag{16}$$

Both ϕ_0 and ϕ_1 represent electron wave packets moving in the Hartree field of the corresponding atomic state; in view of Eq. (9) they satisfy

$$(H_e+C_{n,n})\phi_n=i\hbar(\partial/\partial t)\phi_n. \tag{17}$$

The function ϕ_0 is, of course, not normalized.

Suppose the electron is initially in a single stationary state (λ), so that $a_{\lambda'}{}^1,=\delta_{\lambda'\lambda}$. Then we find from (12) for the line intensity

$$I_U(\omega)=\rho_r\sum_\mu|b_{r\mu}(\infty)|^2$$
$$=\rho_r|J_r/\hbar|^2\sum_\mu\left|\int\phi_\mu{}^{0*}\phi_\lambda{}^1 d\mathbf{R}\right|^2\Big/\gamma^2+(\omega+\Omega_{\lambda\mu})^2. \tag{18}$$

A theory based on a formula of this type was developed by Rudkjobing[10]; his paper contains applications to the H and K doublets of Ca^+ and to the $4S$–$4P$ doublet of Si^{+++} at 4100 A.

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

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

is independent of μ and, by the closure property,

$$\sum_\mu\left|\int\phi_\mu{}^{0*}\phi_\lambda{}^1 d\mathbf{R}\right|^2=1.$$

To evaluate this broadening quantitatively, we expand ϕ in eigenfunctions (u_λ) that are independent of the atomic state. In place of Eq. (16), we write (using a slightly modified definition of d and b)

$$\phi_1=\sum_\lambda d_\lambda u_\lambda\exp(-i\epsilon_\lambda t/\hbar)$$

and

$$\phi_0=\sum_\lambda b_\lambda u_\lambda\exp(-i\epsilon_\lambda t/\hbar), \tag{19}$$

where $H_e u_\lambda=\epsilon_\lambda u_\lambda$. Equation (17) then leads to

$$i\hbar\dot{d}_\lambda=\sum_\mu(C_{1,1})_{\lambda,\mu}\exp[i(\epsilon_\lambda-\epsilon_\mu)t/\hbar]d\mu\equiv\sum_\mu i\hbar p_{\lambda\mu}d_\mu, \tag{20}$$

and

$$i\hbar\dot{b}_\lambda=\sum_\mu(C_{0,0})_{\lambda,\mu}\exp[i(\epsilon_\lambda-\epsilon_\mu)t/\hbar]b_\mu\equiv\sum_\mu i\hbar q_{\lambda\mu}b_\mu; \tag{21}$$

with

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

the p and q matrices are defined by (20) and (21).

Then

$$\int\phi_0{}^*\phi_1 d\mathbf{R}=\sum_\mu b_\mu{}^*d_\mu\equiv b(t)^\dagger d(t), \tag{22}$$

where b and d are column vectors. We now introduce time-development matrices T and U, defined by $d(t)=T(t)d(0)$, $b(t)=U(t)b(0)$; $T(0)=U(0)=E$. By (20) and (21) they satisfy $\dot{T}=pT$ and $\dot{U}=qU$. Since p and q are anti-Hermitean, T and U are unitary. Equation (22) then becomes

$$\int\phi_0{}^*\phi_1 d\mathbf{R}=b^\dagger d=b(0)^\dagger U^\dagger Td(0).$$

With exponential decay of the initially excited state Eq. (15) takes the form

$$i\hbar\dot{b}_r=J_r b(0)^\dagger U^\dagger Td(0)e^{-(\gamma+i\omega)t}. \tag{23}$$

For the broadened line intensity we then have,

$$I_U=\rho_r\sum_\mu|b_{r\mu}(\infty)|^2=\rho_r|\sum_\mu b_{r\mu}(\infty)|^2=\rho_r|b_r(\infty)|^2$$
$$=\rho_r|J_r/\hbar|^2\,\mathrm{Tr}\Big[\rho^0\int_0^\infty d\tau T^\dagger Ue^{-(\gamma-i\omega)\tau}$$
$$\times\int_0^\infty d\tau' U^\dagger Te^{-(\gamma+i\omega)\tau'}\Big], \tag{24}$$

where

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

a unit matrix. Several steps in the preceding development require comment. First, we prove the equality of the sum of squares and the squared sum of the $b_{r\mu}$. It holds if

$$\sum_{\substack{\mu\\ \mu\neq\nu}} b_{r\mu}{}^*b_{r\nu}=0.$$

This is not true in general; e.g., when there are correlations between the phases of the individual $b_{r\mu}$. But in the absence of correlations every term $b_{r\mu}{}^*b_{r\nu}$ will vanish when supplied with the phase factor $\exp i(\alpha_\mu-\alpha_\nu)$ and averaged over some ensemble of phases.

The relation

$$b(0)b(0)^\dagger=E$$

rests on a similar argument. From (16) and (19) at

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[10] M. Rudkjobing, Ann. astrophys. **12**, 229 (1949).

$t=0$,

$$\phi_0=\sum_\mu \phi_\mu{}^0=\sum_\lambda b_\lambda(0)u_\lambda.$$

It follows that

$$b_\lambda(0)=\sum_\mu\int u_\lambda{}^*\phi_\mu{}^0 d\mathbf{R};$$

and

$$b_\nu{}^*(0)b_\lambda(0)=\left(\sum_{\mu'}\int u_\nu\phi_{\mu'}{}^{0*}d\mathbf{R}'\right)\left(\sum_\mu\int u_\lambda{}^*\phi_\mu{}^0 d\mathbf{R}\right)$$

$$=\sum_\mu\int u_\nu\phi_{\mu'}{}^{0*}d\mathbf{R}'\int u_\lambda{}^*\phi_\mu{}^0 d\mathbf{R}=\delta_{\nu\lambda};$$

if cross-terms containing $\phi_{\mu'}{}^{0*}\phi_\mu{}^0$ with factors

$$\exp[i(\alpha_\mu-\alpha_{\mu'})]$$

are assumed to vanish on being averaged over phases.

We now transform

$$d_\mu\rightarrow d_\mu\exp[-i(C_{1,1})_{\mu\mu}t/\hbar]$$

and

$$b_\mu\rightarrow b_\mu\exp[-i(C_{0,0})_{\mu\mu}t/\hbar]$$

and thereby remove the diagonal elements from p and q.

For plane waves these diagonal matrix elements are independent of the electron state, since

$$|u_\lambda|^2\propto|\exp(i\mathbf{k}_\lambda\cdot\mathbf{R})|^2=1.$$

Designating such elements by

$$(C_{n,n})_{\lambda\lambda}\equiv C_{n,n},$$

we have

$$\int\phi_0{}^*\phi_1 d\mathbf{R}=\sum_\lambda b_\lambda{}^*d_\lambda\exp\{i[(C_{0,0})_{\lambda\lambda}-(C_{1,1})_{\lambda\lambda}]t/\hbar\}$$

$$=\exp\{i[C_{0,0}-C_{1,1}]t/\hbar\}\sum_\lambda b_\lambda{}^*d_\lambda. \quad (25)$$

In computing I_U from (23) and (24), we shall absorb the exponential factor occurring in (25) 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.

Some interesting implications of Eq. (24) are easily established. First, if the perturbation elements $(C_{1,1})_{\lambda,\mu}$ and $(C_{0,0})_{\lambda,\mu}$ are equal, then no broadening occurs. This is reasonable, for in this case electron scattering by the atom is the same for the two atomic states; 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

$$I_U=\rho_r|J_r/\hbar|^2\,\mathrm{Tr}\left\{\rho^0\int_0^\infty dte^{-(\gamma-i\omega)t}\int_0^\infty dte^{-(\gamma+i\omega)t}\right\}$$

$$=\frac{\rho_r|J_r/\hbar|^2}{\gamma^2+\omega^2},$$

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

Second, the normalization is maintained; i.e.

$$\int I_U d\omega_r=1.$$

This follows from (24) and a little algebra.

To prepare for the detailed work of the following section we now consider a specific expansion of the matrices T and U. As we shall see, this limits the range of validity of our results and restricts us to broadening effects comparable with the natural line width. We solve for T by iteration, writing

$$T(t)=E+T^{(1)}(t)+T^{(2)}(t)+\cdots,$$

where

$$T^{(n)}(t)=\int_0^t\int_0^{t_n}\cdots\int_0^{t_2}p(t_n)\cdots p(t_1)dt_1\cdots dt_{n-1}dt_n. \quad (26)$$

A similar expansion holds for U. This expansion is more strongly convergent for small C; i.e., little scattering. The first term, $T=U=E$, 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. These higher terms give a correction to the spectral line which we evaluate to the second order in the elements of C.

On expanding,

$$I_U=\rho_r|J_r/\hbar|^2\,\mathrm{Tr}\Big\{\rho^0\Big[\int_0^\infty dte^{-a^*t}[E+(U^{(1)}+T^{\dagger(1)})$$

$$+(U^{(2)}+T^{\dagger(2)}+T^{\dagger(1)}U^{(1)})+\cdots]$$

$$\times\int_0^\infty dte^{-at}[E+(U^{\dagger(1)}+T^{(1)})$$

$$+(U^{\dagger(2)}+T^{(2)}+U^{\dagger(1)}T^{(1)})+\cdots]\Big]\Big\},$$

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

Neglecting terms of order C^3 and higher, we find

$$I_U=\rho_r|J_r/\hbar|^2\,\mathrm{Tr}\Big\{\rho^0\Big[\frac{E}{|a|^2}+\frac{1}{a^*}\int_0^\infty dte^{-at}(U^{\dagger(1)}+T^{(1)})$$

$$+\frac{1}{a}\int_0^\infty dte^{-a^*t}(U^{(1)}+T^{\dagger(1)})$$

$$+\int_0^\infty dte^{-a^*t}(U^{(1)}+T^{\dagger(1)})\int_0^\infty dte^{-at}(U^{\dagger(1)}+T^{(1)})$$

$$+\frac{1}{a^*}\int_0^\infty dte^{-at}(U^{\dagger(2)}+T^{(2)}+U^{\dagger(1)}T^{(1)})$$

$$+\frac{1}{a}\int_0^\infty dte^{-a^*t}(U^{(2)}+T^{\dagger(2)}+T^{\dagger(1)}U^{(1)})\Big]\Big\}.$$

In practice, the statistical matrix ρ^0 is diagonal because the random phases of the d_μ, result in the cancellation of nondiagonal $d_\mu d_\nu^*$. Random phases imply a lack of interference patterns or other periodicities in the perturber current. Thus, on expanding the trace,

$$I_U=\rho_r|J_r/\hbar|^2\left\{\frac{1}{|a|^2}+\frac{1}{a^*}\sum_\lambda \rho_{\lambda\lambda}{}^0\left[\int_0^\infty dte^{-at}(U_{\lambda\lambda}{}^{(1)*}+T_{\lambda\lambda}{}^{(1)})+\frac{1}{a}\int_0^\infty dte^{-a^*t}(U_{\lambda\lambda}{}^{(1)}+T_{\lambda\lambda}{}^{(1)*})\right.\right.$$
$$+\sum_\mu\int_0^\infty dte^{-a^*t}(U_{\lambda\mu}{}^{(1)}+T_{\mu\lambda}{}^{(1)*})\int_0^\infty dte^{-at}(U_{\lambda\mu}{}^{(1)*}+T_{\mu\lambda}{}^{(1)})+\frac{1}{a}\int_0^\infty dte^{-a^*t}(U_{\lambda\lambda}{}^{(2)}+T_{\lambda\lambda}{}^{(2)*}+\sum_\mu T_{\mu\lambda}{}^{(1)*}U_{\mu\lambda}{}^{(1)})$$
$$\left.\left.+\frac{1}{a^*}\int_0^\infty dte^{-at}(U_{\lambda\lambda}{}^{(2)*}+T_{\lambda\lambda}{}^{(2)}+\sum_\mu U_{\mu\lambda}{}^{(1)*}T_{\mu\lambda}{}^{(1)})\right]\right\}.$$

From their defining Eq. (26), we find for the elements in the expansion of T:

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

where $p_{\mu\lambda}{}^0\equiv(C_{1,1})_{\mu\lambda}/i\hbar$, $q_{\mu\lambda}{}^0\equiv(C_{0,0})_{\mu\lambda}/i\hbar$. Because of these relations,

$$I_U(\omega)=\frac{\rho_r|J_r/\hbar|^2}{\gamma^2+\omega^2}\left\{1+\sum_\lambda\rho_{\lambda\lambda}{}^0\sum_\mu\left[\frac{|p_{\lambda\mu}{}^0-q_{\lambda\mu}{}^0|^2}{\gamma^2+(\omega+\Omega_{\lambda\mu})^2}+\frac{2}{\Omega_{\lambda\mu}{}^2}\left\{(|q_{\lambda\mu}{}^0|^2-|p_{\lambda\mu}{}^0|^2)\frac{\omega\Omega_{\lambda\mu}}{\gamma^2+\omega^2}-|q_{\lambda\mu}{}^0-p_{\lambda\mu}{}^0|^2\right.\right.\right.$$
$$+|q_{\lambda\mu}{}^0|^2\left(\frac{\gamma^2+\omega^2+\omega\Omega_{\lambda\mu}}{\gamma^2+(\omega+\Omega_{\lambda\mu})^2}\right)+|p_{\lambda\mu}{}^0|^2\left(\frac{\gamma^2+\omega^2-\omega\Omega_{\lambda\mu}}{\gamma^2+(\omega-\Omega_{\lambda\mu})^2}\right)$$
$$\left.\left.\left.-\mathrm{Real}\left(p_{\lambda\mu}{}^0q_{\lambda\mu}{}^{0*}\left[\frac{\gamma^2+\omega^2+i\gamma\Omega_{\lambda\mu}+\omega\Omega_{\lambda\mu}}{\gamma^2+(\omega+\Omega_{\lambda\mu})^2}+\frac{\gamma^2+\omega^2-i\gamma\Omega_{\lambda\mu}-\omega\Omega_{\lambda\mu}}{\gamma^2+(\omega-\Omega_{\lambda\mu})^2}\right]\right)\right\}\right]\right\}.\quad(27)$$

The frequency integral of the correction to the natural line $I_U-\rho_r|J_r/\hbar|^2/(\gamma^2+\omega^2)$ is zero. Thus the line intensity is still normalized; there is no quenching of the radiation.

When the matrix elements are real, I_U has a simpler form. Since the matrix elements considered in the next section are all real we avail ourselves of this advantage. On putting

$$p_{\lambda\mu}{}^0=-iP_{\lambda\mu}=-iP_{\mu\lambda},\quad q_{\lambda\mu}{}^0=-iQ_{\lambda\mu}=-iQ_{\mu\lambda},$$

Eq. (27) reduces to[11]

$$I_U(\omega)=\frac{\rho_r|J_r/\hbar|^2}{\gamma^2+\omega^2}\left\{1+\frac{1}{\gamma^2+\omega^2}\sum_\lambda\rho_{\lambda\lambda}{}^0\sum_\mu\left(\frac{P_{\lambda\mu}-Q_{\lambda\mu}}{\gamma^2+(\omega-\Omega_{\lambda\mu})^2}[2P_{\lambda\mu}(\omega^2-\gamma^2-\omega\Omega_{\lambda\mu})]\right.\right.$$
$$\left.\left.+\frac{P_{\lambda\mu}-Q_{\lambda\mu}}{\gamma^2+(\omega+\Omega_{\lambda\mu})^2}[P_{\lambda\mu}(\gamma^2+\omega^2)-Q_{\lambda\mu}(3\omega^2-\gamma^2+2\omega\Omega_{\lambda\mu})]\right)\right\}.\quad(28)$$

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

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 II-(28) has the form

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

We shall refer to R as the *redistribution factor*. It is

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

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

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

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[11] S. Bloom, dissertation, Yale University, 1952 (unpublished).

where

$$\hbar\Omega = \epsilon_\lambda - \epsilon_\mu$$

represents the perturber energy loss and $\hbar\omega = E_1 - E_0 - \hbar\omega_r$. The maximum of the first term occurs when $\omega_r - \omega_a = -\Omega$; 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;

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

and

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

where

$$P = (C_{1,1})_{\lambda\mu}/\hbar \quad \text{and} \quad Q = (C_{0,0})_{\lambda\mu}/\hbar.$$

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

$$\Omega_{\lambda\mu} = \omega,$$

which means

$$\epsilon_\lambda - \epsilon_\mu = \hbar\omega_a - \hbar\omega_r. \tag{4}$$

If $\omega_r > \omega_a$, 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 (4), however, ϵ_μ must be $> \epsilon_\lambda$, which means the electron, too, has gained energy.

Conversely, if $\omega_r < \omega_a$, 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 (4), which means the electron lost energy. Therefore this first term of (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 μ, 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 variable λ) at

$$\Omega_{\mu\lambda} = \omega. \tag{5}$$

Hence,

$$\epsilon_\mu - \epsilon_\lambda = \hbar\omega_a - \hbar\omega_r.$$

If $\omega_r > \omega_a$, i.e., if the radiation field receives more energy than the atom can supply, then $\epsilon_\lambda > \epsilon_\mu$; that is, the electron looses 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 μ, defined by (5), 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.

To calculate I_U for a specific and simple case, 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:

$$\sum_\mu \to \int g d\mathbf{k}_\mu.$$

The integrations over direction and magnitude of $\mathbf{k}_\mu$ can be separated, since A and B change slowly with $|\mathbf{k}_\mu|$.

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

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

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

$$\frac{\hbar^2}{2m} k_{\mu\mp}{}^2 = \mp\left(\hbar\omega_a - \hbar\omega_r \mp \frac{\hbar^2}{2m} k_\lambda{}^2 \right),$$

where the $-$ $(+)$ sign is for $A(B)$. We now take advantage of the slow variation of A and B with k_μ and obtain

$$\int R_{\lambda\mu} g d\mathbf{k}_\mu = 2\pi g \left\{ -2\gamma^2 \int_0^\pi P_-(P_- - Q_-) \sin\Theta d\Theta k_{\mu-}{}^2 G_- + \left[(\gamma^2+\omega^2) \int_0^\pi (P_+ - Q_+) P_+ \sin\Theta d\Theta - (\omega^2 - \gamma^2) \int_0^\pi (P_+ - Q_+) Q_+ \sin\Theta d\Theta \right] k_{\mu+}{}^2 G_+, \right. \tag{6}$$

where

$$G_\pm = \int_0^\infty \frac{dk_\mu}{\gamma^2 + (\omega\pm\Omega)^2}, \tag{7}$$

and the arguments $+$ $(-)$ indicate evaluation at the resonance value $k_{\mu+}(k_{\mu-})$ which satisfies $\omega+\Omega=0$ $(\omega-\Omega=0)$. This approximation cannot 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_μ. Similarly, for the nonconservative 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 $|\hbar\omega| > \epsilon_\lambda = (\hbar^2/2m)k_\lambda{}^2$.

Direct evaluation of the integral in (7) yields

$$G_{\pm}=\left(\frac{2m}{\hbar}\right)^{\frac{1}{2}}\frac{\pi i}{4\gamma}\left[\frac{-1}{(-i\gamma+b)^{\frac{1}{2}}}+\frac{1}{(i\gamma+b)^{\frac{1}{2}}}\right],$$

where

$$b=-(\hbar/2m)k_{\lambda}^{2}\pm\omega.$$

Ordinarily $\gamma\ll\epsilon_{\lambda}/\hbar$, and we find on expanding in powers of γ/b:

$$G_{\pm}=\left(\frac{2m}{\hbar}\right)^{\frac{1}{2}}\frac{\pi i}{4\gamma}\frac{1}{b^{\frac{1}{2}}}\left[\mp\left(1+\frac{i\gamma}{2b}+\cdots\right)\pm\left(1-\frac{i\gamma}{2b}\cdots\right)\right]$$

$$=\left(\frac{2m}{\hbar}\right)^{\frac{1}{2}}\frac{\pi i}{4\gamma}\frac{1}{b^{\frac{1}{2}}}\begin{cases}\pm 2\\ \pm i\gamma/b,\end{cases}\tag{8}$$

where the criterion of a real and positive G may be used to select the correct value. This will be done later [see Eq. (21)].

The electrostatic interaction is

$$C_{n,n}=-\frac{e^{2}}{|\mathbf{R}|}+e^{2}\int\frac{|\psi_{n}(\mathbf{r})|^{2}d\mathbf{r}}{|\mathbf{R}-\mathbf{r}|},$$

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

$$u_{\lambda}=(1/V^{\frac{1}{2}})\exp(i\mathbf{k}_{\lambda}\cdot\mathbf{R}).$$

Then the matrix elements between perturber states contain the factor

$$Z=\int\frac{e^{i\mathbf{K}\cdot\mathbf{R}}}{|\mathbf{R}-\mathbf{r}|}d\mathbf{R}=e^{i\mathbf{K}\cdot\mathbf{r}}\int\frac{\exp(i\mathbf{K}\cdot\mathbf{z})}{|\mathbf{z}|}d\mathbf{z}$$

$$=2\pi e^{i\mathbf{K}\cdot\mathbf{r}}\int_{0}^{\infty}z^{2}dz\int_{0}^{\pi}\frac{e^{iKz\cos\theta}}{z}\sin\theta d\theta$$

$$=\frac{4\pi}{K}e^{i\mathbf{K}\cdot\mathbf{r}}\int_{0}^{\infty}\sin Kz dz,\tag{9}$$

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

$$\lim_{\alpha\to 0}\int_{0}^{\infty}e^{-\alpha z}\sin Kz dz=\lim_{\alpha\to 0}\frac{K}{\alpha^{2}+K^{2}}=\frac{1}{K}.\tag{10}$$

Hence,

$$Z=(4\pi/K^{2})e^{i\mathbf{K}\cdot\mathbf{r}}.\tag{11}$$

Using this result and neglecting exchange, we find

$$\frac{1}{V}\int e^{i\mathbf{K}\cdot\mathbf{R}}C_{n,n}d\mathbf{R}\equiv(C_{n,n})_{\lambda\mu}=\frac{1}{V}\frac{4\pi e^{2}}{K^{2}}[F_{n,n}-1],$$

where

$$F_{n,n}\equiv\int e^{i\mathbf{K}\cdot\mathbf{r}}|\psi_{n}(\mathbf{r})|^{2}d\mathbf{r}\tag{12}$$

represents the usual form factor.

The atomic state and the momentum transfer vector, $\mathbf{K}$, determine the form factor (12). Its value is independent of the direction of $\mathbf{K}$ for a spherically symmetric charge distribution, in which case polar axis can be oriented along $\mathbf{K}$ to simplify the evaluation. The general situation will be discussed in detail in Sec. VI, where the shortcomings of the present simplified treatment are removed. The angular dependence of the $2p$ states will not trouble us, since in the absence of external fields the probabilities for the degenerate states are equal and we may take to a good approximation.

$$F_{2}\equiv\tfrac{1}{3}\sum_{m}F_{2pm,\,2pm}.$$

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

The atomic functions are

$$\psi_{1s,0}=\frac{1}{\pi^{\frac{1}{2}}}\frac{1}{a^{3/2}}e^{-r/a},$$

$$\psi_{2p,0}=\frac{1}{4(2\pi)^{\frac{1}{2}}}\frac{r}{a^{5/2}}e^{-r/2a}\cos\theta,$$

$$\psi_{2p,\pm1}=\frac{1}{8\pi^{\frac{1}{2}}}\frac{r}{a^{5/2}}e^{-r/2a}\sin\theta e^{\pm i\phi},$$

a being the first Bohr radius. To compute the F's we consider the integral

$$a_{100}\equiv\int e^{\alpha r}e^{i\mathbf{K}\cdot\mathbf{r}}d\mathbf{r}=2\pi\int_{0}^{\infty}r^{2}dre^{\alpha r}\int_{-1}^{+1}e^{iKr\mu}d\mu$$

$$=-\frac{8\pi\alpha}{(\alpha^{2}+K^{2})^{2}};\quad(\alpha<0).\tag{13}$$

In calculating F_{2p0}, one encounters

$$a_{210}\equiv\int r^{2}e^{\alpha r}\mu^{2}e^{i\mathbf{K}\cdot\mathbf{r}}d\mathbf{r}=-\frac{d^{2}}{dK^{2}}a_{100}$$

$$=-32\pi\alpha\left[\frac{\alpha^{2}-5K^{2}}{(\alpha^{2}+K^{2})^{4}}\right].\tag{14}$$

Similarly,

$$a_{21\pm1}\equiv\int r^{2}(1-\mu^{2})e^{\alpha r}e^{i\mathbf{K}\cdot\mathbf{r}}d\mathbf{r}$$

$$=-\frac{2}{K}\frac{d}{dK}a_{100}=-\frac{64\pi\alpha}{(\alpha^{2}+K^{2})^{3}}.\tag{15}$$

Making use of these relations, we find

$$F_1 \equiv F_{100,100} = 1/(1+\tfrac{1}{4}x)^2, \tag{16}$$

$$F_{210,210} = (1-5x)/(1+x)^4, \tag{17}$$

and

$$F_{21\pm1,21\pm1} = 1/(1+x)^3, \tag{18}$$

where

$$x = a^2K^2, \quad F_2 \equiv \langle F_{21m,21m}\rangle_m = (1-x)/(1+x)^4, \tag{19}$$

where $\langle\ \rangle_m$ means the average over m.

We are now ready to evaluate Eq. (6). There are integrals over the scattering angle Θ of the type

$$L \equiv \int_0^\pi (P-Q)^2 \sin\Theta d\Theta.$$

Transformation from Θ to the variable $x = a^2K^2$ proceeds by the relation

$$K^2 = k_\lambda^2 + k_\mu^2 - 2k_\lambda k_\mu \cos\Theta.$$

Thus $dx = 2a^2k_\lambda k_\mu \sin\Theta d\Theta$, and

$$L = \frac{1}{V^2}\frac{(4\pi)^2e^4}{\hbar^2}\frac{a^2}{2k_\lambda k_\mu}\int_{x_-}^{x_+}\left(\frac{F_1-F_2}{x}\right)^2 dx, \tag{20}$$

where

$$x_+ = a^2(k_\lambda + k_\mu)^2$$

and

$$x_- = a^2(k_\lambda - k_\mu)^2.$$

For hydrogen, $a = \hbar^2/me^2$ and

$$L = \frac{2}{V^2}(\hbar/m)^2\frac{1}{k_\lambda k_\mu}\int_{x_-}^{x_+}\left(\frac{F_1-F_2}{x}\right)^2 dx.$$

Equation (6) 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 indeed a meaningful approximation, as will later be shown. Here

$$k_{\mu\pm}^2 = k_\lambda^2 \pm (2m/\hbar)\omega \cong k_\lambda$$

and, in view of Eq. (8),

$$G_\pm = (m/\hbar)(1/\gamma k_\lambda). \tag{21}$$

Furthermore, when a Taylor expansion is used,

$$\int_{x_-}^{x_+}\frac{(F_1-F_2)^2}{x^2}dx \cong \int_0^{4a^2k_\lambda^2}\frac{(F_1-F_2)^2}{x^2}dx \equiv S_U. \tag{22}$$

Consequently, near the line center all terms in Eq. (6) become independent of the resonance condition. Equation (6) then reads

$$\int R_{\lambda\mu}g d\mathbf{k}_\mu = 2\pi g(\omega^2-\gamma^2)k_\lambda^2 G\int_0^\pi (P-Q)^2 \sin\Theta d\Theta$$

$$= 2\pi g(\omega^2-\gamma^2)k_\lambda^2 \frac{\pi m}{\hbar\gamma k_\lambda}\frac{2}{V^2}\left(\frac{h}{m}\right)^2\frac{1}{(k_\lambda)^2}$$

$$\times\int_0^{4a^2k_\lambda^2}\left(\frac{F_1-F_2}{x}\right)^2 dx \equiv f(\omega^2-\gamma^2)S_U,$$

and

$$I_U = \frac{\rho_r|J_r/\hbar|^2}{\omega^2+\gamma^2}\left\{1+fS_U\frac{\omega^2-\gamma^2}{\omega^2+\gamma^2}\right\}. \tag{23}$$

We now define symbols and analyze the result.

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

$n = 1/V$, the electron density; v_λ is the electron velocity in the state λ and σ_λ the cross section associated with its de Broglie wavelength,

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

the function f is a measure of the relative number of atoms struck during the lifetime of the excited state.

The redistribution factor, R, [see Eq. (1)] has the property of decreasing the intensity within the half maximum and increasing it without. It is symmetric in ω. 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_U our result indicates that the intensity at the line center can become negative. In this case (indeed whenever $fS_U > 0.4$) terms of higher order in the collision matrix elements must be considered.

Evaluation of S_U

Since

$$(F_1-F_2)/x = (16u^3+17u^2+21u+18)/u^4(3+u)^2$$

[see (16) and (19)], 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 $\int du/[(3+u)^4u^m]$. We expand this integrand:

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

where

$$W = u/(3+u).$$

Integrating each term, using

$$\int\frac{W^{t-m}}{(3+u)^2}du = \frac{1}{3}\int W^{t-m}dW = \begin{cases}\dfrac{1}{3}\dfrac{W^{t-m+1}}{t-m+1} & t-m\neq-1\\ \tfrac{1}{3}\ln W & t-m=-1\end{cases},$$

we find for the indefinite integral:

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

with the understanding that the quantity in the curly brace is to be replaced by $\ln W$ when $t-m=-1$. The limits are $u=1$ and $u=1+x_+$.

When terms with like powers of W are collected, there results

$$\int \left(\frac{F_1 - F_2}{x} \right)^2 dx = 0.197W^3 - 1.04W^2 + 2.44W$$
$$-0.799 \ln W + 0.452W^{-1} - 0.198W^{-2} + 0.0434W^{-3}$$
$$-2.52\times 10^{-3}W^{-4} - 4.11\times 10^{-3}W^{-5} + 0.914$$
$$\times 10^{-3}W^{-6} - 0.261\times 10^{-3}W^{-7} + C,$$

C being the constant of integration. This integral between the limits of 0 and x_+, i.e., between $W=\frac{1}{4}$ and $W=(1+x_+)/(4+x_+)$, namely S_U, is plotted as a function of the initial electron energy $\epsilon_\lambda/(e^2/2a)=\frac{1}{4}x_+=a^2k_\lambda{}^2$ (Fig. 1). The integrals in equation (6), when written in their exact form (20) 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 Fig. 1, we see that they are quite insensitive to changes in ϵ_μ of the order of the line width $\hbar\gamma \sim 10^{-6}$ ev, 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_U in place of an integral with exact limits in the region near the line center.

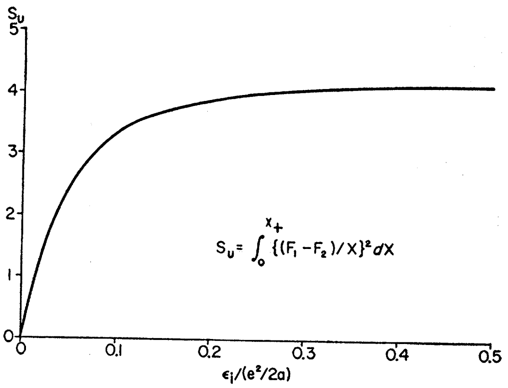

FIG. 1. S_U, the factor in universal broadening which depends on the atomic states, as a function of the initial electron energy, ϵ_i.

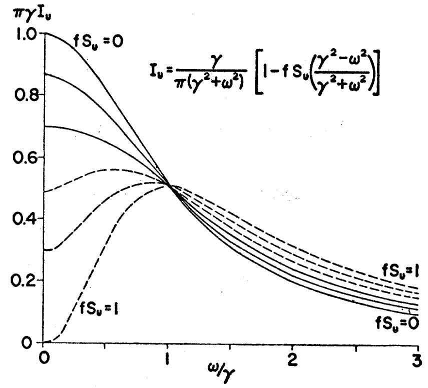

FIG. 2. Intensity profiles for universal broadening: $fS_U=0$, 0.13, 0.3, 0.5, 0.7, 1.0. The dashed curves represent cases for which the present theory does not hold.

Numerical values to be used, typical of the positive column of an arc discharge, are: $n=10^{14}/\text{cm}^3$ and $\epsilon_\lambda=(1/25)(e^2/2a)\sim\frac{1}{2}$ ev ($T\sim 5000$°K). We treat all the electrons as if they had this energy and take $\rho_{\nu\nu}{}^0=\delta_{\lambda\nu}$. As we have shown, the initial direction does not enter in our case. With the value $\gamma=3.12\times 10^8/\text{sec}$[12] for the chance of spontaneous emission

$$I_U \cong \frac{\rho_r |J_r/\hbar|^2}{\gamma^2+\omega^2} \left\{ 1 - 0.13 \left(\frac{\gamma^2-\omega^2}{\gamma^2+\omega^2} \right) \right\}. \tag{24}$$

This is plotted in Fig. 2. Curves for $fS_U=0.3$, 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.

We note that the half-width of I_U [Eq. (23)] under the condition in which our approximation is valid (small fS_U) is given by

$$\gamma_{\frac{1}{2}} = \gamma(1+fS_U).$$

It is therefore suggested that we define the half-width for universal broadening as

$$\gamma_U \equiv fS_U\gamma.$$

Formula (23) can then be shown to be an approximation to first powers in γ_U/γ of

$$I_U = \frac{\rho_r |J_r/\hbar|^2 (\gamma+\gamma_U)/\gamma}{\omega^2 + (\gamma+\gamma_U)^2}, \tag{25}$$

which we expect to be valid even if γ_U/γ is large.

It may seem surprising that the natural line suffers almost no modification until fS_U reaches a value comparable to 1, at which point the natural line as such is destroyed rather suddently. But this is merely another aspect of a point previously made: S_U is a number of order 1; $f\sim nv\sigma/\gamma$. Now t_e, the mean time between electron impacts with the atom, is $1/nv\sigma$, and t_a, the lifetime of the excited atomic state is of order $1/\gamma$. Hence $f\sim t_a/t_e$. If $f>1$, the electrons make many col-

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[12] H. Bethe, *Handbuch der Physik* (Verlag Julius Springer, Berlin, 1933), second edition, Vol. 24, p. 444.

lisions during t_a, so that a static perturbation theory is applicable. The region of f under consideration seems to be 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_U is easily obtained, because f is proportional to $(\epsilon_\lambda)^{-\frac{1}{2}}$ and $S_U(\epsilon_\lambda)$ has already been calculated. We find that fS_U is zero at both low and high energies because S_U and f vanish respectively at the extremes (Fig. 3).

In Fig. 4 we delimit the region of small electron broadening (of the universal kind here discussed) defined by $\gamma_U \leqslant \gamma/10$.

For negligible effects,

$$\frac{n}{10^{14}} < \frac{8.2}{S_U}\left(\frac{\epsilon_\lambda}{e^2/2a}\right)^{\frac{1}{2}}.$$

The theory developed here holds strictly in the region below the curve of Fig. 4. Immediately above it our theory is not adequate because of the neglect of higher powers of C. Far above this curve a statistical or time-independent type of treatment is appropriate.[13]

To remove the restriction to small n, distorted waves must be used to describe the electrons. This refinement is under consideration. The result is likely to be Eq. (25) with a γ_U not differing appreciably from that computed with plane waves.

IV. INCLUSION OF POLARIZATION[14]

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 re-orient itself. A measure of this failure to follow the changing field is given by the probability of nonadiabatic transitions. For very fast and frequent collisions, unpolarized, randomly oriented atoms are expected, and electron effects are negligible. We seek a criterion for the setting in of these polarization effects as the electron density increases and temperature decreases.

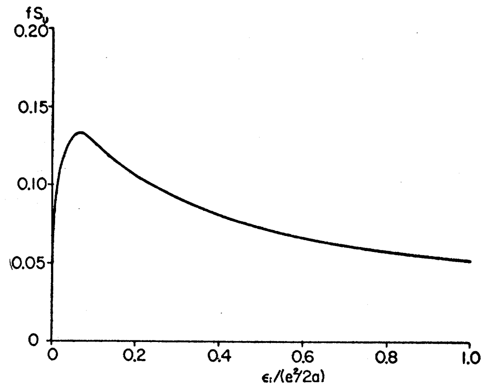

FIG. 3. fS_U, which is proportional to universal broadening, as a function of the initial electron energy, ϵ_i.

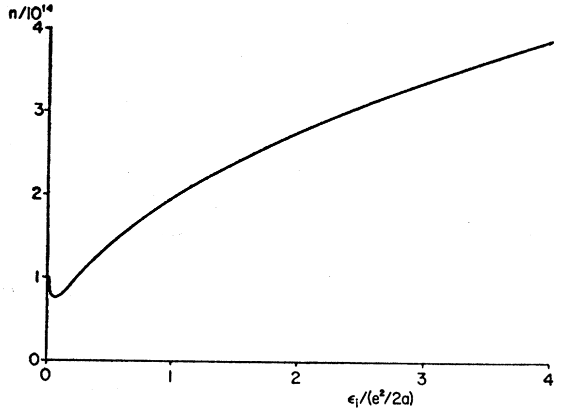

FIG. 4. Curve of density (n) *vs* electron energy (ϵ_i) delimiting the region of small n and large ϵ_i where universal broadening is negligible compared to the natural width (γ); the curve is the locus of points satisfying $fS_U = \gamma_U/\gamma = 1/10$.

We study polarization effects as a correction to Holtsmark broadening and consider the Stark-shifted components of the first Lyman line from a hydrogen atom in the mean Holtsmark ion field, $F_{\text{ion}} = 3.26en_{\text{ion}}^{\frac{2}{3}}$. *Only three atomic states are considered:* $\psi_+ = (1/\sqrt{2}) \times (\psi_{2s,0} + \psi_{2p,0})$, $\psi_- = (1/\sqrt{2})(\psi_{2s,0} - \psi_{2p,0})$, and $\psi_{1s,0}$. The excited states correspond to dipoles ($3ea$) oriented along the z-axis of the atom which points at the ion. Their energies are displaced by $\pm 3eaF_{\text{ion}}$ from $E_2 \equiv -\frac{1}{4}(e^2/2a)$.

Deliberate exclusion of the states $\psi_{2p\pm1}$ is a very unrealistic procedure. Our reason is this. The two omitted states give rise to divergences requiring special treatment. Since we do not wish to encumber the basic analysis of the present section with mathematical difficulties, it seems indicated that the degenerate states, though present and far more effective in broadening the line, be first ignored.

Physically, a transition between ψ_+ and ψ_- corresponds to the re-orientation of a dipole, while a mixing-in of $\psi_{2p,+1}$ and $\psi_{2p,-1}$ represents induction of a dipole moment. In the present section, then, we make a somewhat artificial distinction between polarization by *re-orientation* and polarization by *induction*, and we treat here only the former effect.

The mathematical difficulties arising in connection with induction are removed in Sec. VII. This will prepare the way for the study of polarization by induction in Sec. VIII.

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[13] H. Margenau and R. E. Meyerott (to be published).

[14] G. Wentzel, *Handbuch der Physik* (Verlag Julius Springer, Berlin, 1933), second edition, Vol. 24, p. 767. L. Spitzer, Phys. Rev. **55**, 699 (1939).

The basic equation for the expansion coefficients is

$$i\hbar\dot{a}_{m\mu}\exp[-i(\epsilon_\mu{}^m+E_m)t/\hbar]$$
$$=\sum_n\sum_\lambda{}^n a_{n\lambda}J_{mn}\int\phi_\mu{}^{m*}\phi_\lambda{}^n d\mathbf{R}\exp[-i(\epsilon_\lambda{}^n+E_n)t/\hbar]$$
$$+\sum_{\substack{n\\ n\neq m}}\sum_\lambda{}^n a_{n\lambda}\int\phi_\mu{}^{m*}C_{m,n}\phi_\lambda{}^n d\mathbf{R}$$
$$\times\exp[-i(\epsilon_\lambda{}^n+E_n)t/\hbar].\quad(1)$$

The electron functions satisfy (II–(7))

$$[-(\hbar^2/2m)\nabla^2+C_{n,n}]\phi_\lambda{}^n=\epsilon_\lambda{}^n\phi_\lambda{}^n.\quad(2)$$

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

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

Below, where plane waves are used for the ϕ, we imply that $C\equiv 0$ in Eq. (2). As a consequence of this approximation,

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

with the equation

$$[-(\hbar^2/2m)\nabla^2+C]\phi_\mu=\epsilon_\mu\phi_\mu\quad(4)$$

determining the ϕ_μ. The part of the electron-atom interaction retained corresponds to the changes induced in the atom by the second sum in Eq. (1), and the effect of these nonradiative transitions will be called polarization broadening. To see how it enters, we start with the growth equations for the three-state atom. In fairly obvious notation,

$$i\hbar\dot{d}_{+\mu}\exp[-i(\epsilon_\mu+E_+)t/\hbar]$$
$$=\sum_r b_{r\mu}J_r{}^*\exp[-i(\epsilon_\mu+E_{1s}+h\nu_r)t/\hbar]$$
$$+\sum_\lambda d_{-\lambda}\int\phi_\mu{}^*C_{+,-}\phi_\lambda d\mathbf{R}$$
$$\times\exp[-i(\epsilon_\lambda+E_-)t/\hbar];\quad(5)$$

$$i\hbar\dot{d}_{-\nu}\exp[-i(\epsilon_\nu+E_-)t/\hbar]$$
$$=\sum_r b_{r\nu}J_r{}^*\exp[-i(\epsilon_\nu+E_{1s}+h\nu_r)t/\hbar]$$
$$+\sum_\lambda d_{+\lambda}\int\phi_\nu{}^*C_{-,+}\phi_\lambda d\mathbf{R}$$
$$\times\exp[-i(\epsilon_\lambda+E_+)t/\hbar];\quad(6)$$

$$i\hbar\dot{b}_{r\mu}=J_r\{d_{+\mu}\exp[i(E_{1s}+h\nu_r-E_+)t/\hbar]$$
$$+d_{-\mu}\exp[i(E_{1s}+h\nu_r-E_-)t/\hbar]\};\quad(7)$$

and

$$C_{+,-}\equiv\int\psi_+{}^*C\psi_- d\mathbf{r}.$$

We know that the effect of the terms with J in the equations for $\dot{d}$ can be approximated by an exponential decay; therefore Eqs. (5)–(7) become

$$i\hbar\dot{d}_{+\mu}=-i\hbar\gamma_+d_{+\mu}+\sum_\lambda d_{-\lambda}(C_{+,-})_{\mu\lambda}$$
$$\times\exp[i(\omega_{+,-}+\Omega_{\mu\lambda})t],\quad(8)$$

$$i\hbar\dot{d}_{-\nu}=-i\hbar\gamma_-d_{-\nu}+\sum_\lambda d_{+\lambda}(C_{-,+})_{\nu\lambda}$$
$$\times\exp[i(\omega_{-,+}+\Omega_{\nu\lambda})t],\quad(9)$$

$$i\hbar\dot{b}_{r\mu}=J_r[d_{+\mu}e^{-i\omega_+t}+d_{-\mu}e^{-i\omega_-t}].\quad(10)$$

Here

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

and

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

To solve these equations we first put

$$d_{+\mu}\equiv D_{+\mu}e^{-\gamma_+t}\quad\text{and}\quad d_{-\mu}\equiv D_{-\mu}e^{-\gamma_-t}.\quad(11)$$

This reduces the growth equations to

$$i\hbar\dot{D}_{+\mu}=\sum_\lambda D_{-\lambda}(C_{+,-})_{\mu\lambda}$$
$$\times\exp[i(\omega_{+,-}+\Omega_{\mu\lambda})t-(\gamma_--\gamma_+)t],\quad(12)$$

$$i\hbar\dot{D}_{-\nu}=\sum_\lambda D_{+\lambda}(C_{-,+})_{\nu\lambda}$$
$$\times\exp[i(\omega_{-,+}+\Omega_{\nu\lambda})t+(\gamma_--\gamma_+)t],\quad(13)$$

$$i\hbar\dot{b}_{r\mu}=J_r\{D_{+\mu}\exp[-(\gamma_++i\omega_+)t]$$
$$+D_{-\mu}\exp[-(\gamma_-+i\omega_-)t]\}.\quad(14)$$

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

$$\phi_i{}^+\cong\frac{1}{\sqrt{V}}\exp(i\mathbf{k}_i\cdot\mathbf{R}-i\epsilon_it/\hbar).\quad(15)$$

Further, all amplitudes $d_{+\lambda}$, 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

$$i\hbar\dot{D}_{+i}=\sum_\mu(C_{+,-})_{i\mu}D_{-\mu}$$
$$\times\exp[i(\omega_{+,-}+\Omega_{i\mu})t-(\gamma_--\gamma_+)t];\quad(16)$$

$$i\hbar\dot{D}_{-\mu}=\sum_\lambda(C_{-,+})_{\mu\lambda}D_{+\lambda}$$
$$\times\exp[i(\omega_{-,+}+\Omega_{\mu\lambda})t+(\gamma_--\gamma_+)t]$$
$$\cong(C_{-,+})_{\mu i}D_{+i}\exp[i(\omega_{-,+}+\Omega_{\mu i})t+(\gamma_--\gamma_+)t].\quad(17)$$

From (14) and because cross-terms with random phase factors cancel,

$$I(\omega)=\sum_\mu \rho_r|b_{r\mu}(t=\infty)|^2$$
$$=\rho_r|J_r/\hbar|^2\left\{\left|\int_0^\infty \exp[-(\gamma_++i\omega_+)t]D_{+i}dt\right|^2\right.$$
$$\left.+\sum_\mu\left|\int_0^\infty \exp[-(\gamma_-+i\omega_-)t]D_{-\mu}dt\right|^2\right\}. \quad (18)$$

Clearly, when all of the C matrix elements vanish, the D are constants: $D_{+i}=1$ and $D_{-\mu}=0$. Then $I(\omega)$, as expected, contains only the $+$ component of the spectrum, and this line has the natural breadth.

It will now be shown that

$$D_{+i}\cong e^{-\gamma_P t}. \quad (19)$$

The spectral line is then broadened in accordance with the uncertainty principle, γ being replaced by $\gamma+\gamma_P$.

To find γ_P we substitute $D_{-\mu}$ found from (17) into (16):

$$\dot{D}_{+i}=-\gamma_P D_{+i}\cong-\frac{1}{\hbar^2}\sum_\mu|(C_{+,-})_{i\mu}|^2\int_0^t D_{+i}$$
$$\times\exp\{[i(\omega_{-,+}+\Omega_{\mu i})+(\gamma_--\gamma_+)](\tau-t)\}d\tau. \quad (20)$$

This result is general and free from the limitation to a single large d_{+i}. Had we retained all terms on the right of (17), then the place of (20) would be taken by

$$i\hbar\dot{D}_{+i}e^{i\alpha_i}=\sum_\mu\sum_\lambda(C_{+,-})_{i\mu}(C_{-,+})_{\mu\lambda}$$
$$\times\int_0^t D_{+\lambda}\exp(i\alpha_\lambda)\exp\{[i(\omega_{-,+}+\Omega_{\mu\lambda})$$
$$+(\gamma_--\gamma_+)](\tau-t)\}d\tau\exp(i\Omega_{i\lambda}t), \quad (21)$$

where the phase factors $\exp(i\alpha_\lambda)$ are written explicitly. When we average over random phases (21) reduces to (20), since the average of $\exp[i(\alpha_\lambda-\alpha_i)]$ is zero unless $\lambda=i$.

Before summing over μ we evaluate the matrix elements.

Preliminary account is taken of the random orientation of the direction of motion of the incident electron with respect to the atom by averaging over directions of the atomic z axis for a given $\mathbf{k}_i$. (See Sec. VI for an accurate treatment of the angular dependence of form factors.) Hence we replace $\psi_-^*\psi_+$ by the spherically symmetric

$$\langle\psi_-^*\psi_+\rangle_{\text{Av}}=\frac{1}{4\pi}\int_0^{2\pi}d\phi\int_0^\pi\sin\theta d\theta\psi_-^*\psi_+$$
$$=\tfrac{1}{4}\int_{-1}^{+1}[|\psi_{2s,0}|^2-|\psi_{2p,0}|^2]d\mu$$
$$=\tfrac{1}{2}[(R_{2s})^2-\tfrac{1}{3}(R_{2p})^2], \quad (22)$$

where

$$(R_{2p})^2\equiv\frac{r^2}{32\pi}\frac{e^{-r/a}}{a^5},\quad (R_{2s})^2\equiv\frac{[2-(r/a)]^2}{32\pi}\frac{e^{-r/a}}{a^3}.$$

Then, with the use of plane waves,

$$|(C_{+,-})_{\mu i}|^2$$
$$\cong\left|\int\int\frac{e^{i\mathbf{K}\cdot\mathbf{R}}}{V}\left(\frac{e^2}{|\mathbf{R}-\mathbf{r}|}-\frac{e^2}{|\mathbf{R}|}\right)\langle\psi_-^*\psi_+\rangle_{\text{Av}}d\mathbf{r}d\mathbf{R}\right|^2$$
$$=\left|\frac{4\pi e^2}{K^2}\cdot\tfrac{1}{2}\int\frac{e^{i\mathbf{K}\cdot\mathbf{r}}}{V}[(R_{2s})^2-\tfrac{1}{3}(R_{2p})^2]d\mathbf{r}\right|^2. \quad (23)$$

The interaction with the nucleus, e^2/R, contributes nothing to γ_P, since ψ_+ is orthogonal to ψ_-. The integral (23) over the atomic coordinates is independent of the direction of $\mathbf{K}$ which is along the polar axis;

$$\int e^{i\mathbf{K}\cdot\mathbf{r}}\{(R_{2s})^2-\tfrac{1}{3}(R_{2p})^2\}d\mathbf{r}$$
$$=2\pi\int_{-1}^{+1}d\mu\int_0^\infty dre^{iKr\mu}\frac{[4-4(r/a)+\frac{2}{3}(r/a)^2]}{32\pi a^3}e^{-r/a}r^2$$
$$=\frac{1}{(1+x)^2}-\frac{(3-x)}{(1+x)^3}+\frac{2(1-x)}{(1+x)^4}=\frac{2x(x-1)}{(1+x)^4}. \quad (24)$$

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 (24). The first is related to $F_{100,100}$ and is adapted from the integral a_{100} [see III-(13)]. The third is just $2F_2$ [see III-(19)]. The second was not previously encountered but is evaluated in a similar way and yields

$$-\frac{1}{4iKa}\left[\frac{2}{(-iKa-1)^3}-\frac{2}{(iKa-1)^3}\right]=-\frac{3-x}{(1+x)^3}. \quad (25)$$

Thus, from (23) and (24),

$$|(C_{+,-})_{i\mu}|^2=\left(\frac{4\pi e^2a^2}{V}\frac{(x-1)}{(x+1)^4}\right)^2, \quad (26)$$

which is a function of the momentum transfer through

$$x=a^2K^2=a^2(k_i^2+k_\mu^2-2k_ik_\mu\cos\Theta).$$

The evaluation of the sum over states μ in (20) can be simplified because the change in the matrix element, as $\epsilon_\mu=(\hbar^2/2m)k_\mu^2$ deviates from $\epsilon_i+\hbar\omega_{+,-}$ by $\hbar(\gamma_P+\gamma_+-\gamma_-)$, is very small. The time integral, however, peaks in this region of ϵ_μ. Hence we can factor the integrals over the magnitude and direction of $\mathbf{k}_\mu$; i.e., from (20)

$$\frac{dD_{+i}}{dt}=-\frac{1}{\hbar^2}\sum_\mu|(C_{+,-})_{i\mu}|^2\int_0^t\cdots d\tau$$
$$\cong\frac{-V}{(2\pi\hbar)^2}\int_0^\pi|(C_{+,-})_{i\mu 0}|^2k_{\mu 0}\sin\Theta d\Theta$$
$$\times\int_0^\infty\left[\int_0^t\cdots d\tau\right]k_\mu dk_\mu, \quad (27)$$

where (see Sec. III)

$$\sum_{\mu}\rightarrow\int\frac{V}{(2\pi)^3}d\mathbf{k}_{\mu}$$

and

$$(\hbar^2/2m)k_{\mu0}{}^2\equiv\hbar\omega_{+,-}+\epsilon_i.$$

By inverting the order of integration over τ and k_{μ}, replacing $k_{\mu}dk_{\mu}$ by $(m/\hbar)d(\omega_{-,+}+\Omega_{\mu i})$, and using

$$\int_{-\infty}^{+\infty}\exp[i(\omega_{-,+}+\Omega_{\mu i})(\tau-t)]d(\omega_{-,+}+\Omega_{\mu i})=2\pi\delta(\tau-t),$$

the last integral factor in (27) becomes

$$\int_0^t D_{+i}(\tau)\exp[+(\gamma_{-}-\gamma_{+})(\tau-t)]\frac{2m\pi}{\hbar}\delta(\tau-t)d\tau$$
$$=\frac{\pi m}{\hbar}D_{+i}(t).\qquad(28)$$

Hence

$$\dot{D}_{+i}=-\gamma_P D_{+i}=-\frac{V}{(2\pi\hbar)^2}\int_0^{\pi}|(C_{+,-})_{i\mu0}|^2k_{\mu0}$$
$$\times\sin\Theta d\Theta\cdot\frac{\pi m}{\hbar}D_{+i}.$$

This leads to the result

$$\gamma_P=2nv_i\sigma_iS_P,\qquad(29)$$

with

$$S_P\equiv\int_0^{x_+}\left[\frac{(x-1)}{(1+x)^4}\right]^2dx$$
$$=\frac{11}{105}-\frac{1}{5(1+x_+)^5}+\frac{2}{3(1+x_+)^6}-\frac{4}{7(1+x_+)^7},$$
$$x_+=a^2(k_i+k_{\mu})^2\cong4(k_ia)^2=4\epsilon_i/(e^2/2a),$$
$$\sigma_i\equiv\pi(\hbar/mv_i)^2.$$

If we say, somewhat arbitrarily, that polarization by orientation can be neglected when

$$\gamma_P<\gamma/10,\qquad(30)$$

there is defined region of low electron density and high energy delimited by

$$\frac{n}{10^{14}}=\left(\frac{\epsilon_i}{(e^2/2a)}\right)^{\frac{1}{2}}\frac{8.2}{S_P}.\qquad(31)$$

But this is of theoretical interest only, for it will be seen that the orientation effect we have here considered contributes far less to the line width than the states thus far omitted. To return to our example: at $\epsilon_i\sim\frac{1}{2}$ ev, an electron density of the order $n\leqslant10^{15}$ induces few reorientations of the (three-state) radiating atom and hence this polarization effect can be neglected. If $\epsilon_i=\frac{1}{2}$ ev and $n=10^{14}$, then with $\gamma=3.12\times10^8$, $S_P=0.081$ and

$$\gamma_P/\gamma=fS_P\cong0.0049.\qquad(32)$$

This result is subject to modification because of the angular dependence of the form factors, which is discussed in Sec. VI. Other atomic states (especially $\psi_{2p,\pm1}$) are included later.

V. QUENCHING AND STARK BROADENING

A. Quenching

For quenching, the intensity distribution is the same as for polarization broadening:

$$I_Q(\omega)\propto[\omega^2+(\gamma+\gamma_Q)^2]^{-1},\qquad(1)$$

provided γ_Q is equal to half the transition rate from the initial atomic level induced by electron impacts. That is,

$$\gamma_Q=\tfrac{1}{2}nv_iQ_i\qquad(2)$$

for initial electron velocity v_i. Here Q_i is the quenching cross section for hydrogen,[15]

$$\underset{(2p\rightarrow1s)}{Q_i}=\int\frac{k_\lambda}{k_i}\left(\frac{m}{2\pi\hbar^2}\right)^2\left(\frac{4\pi e^2}{K^2}\right)^2F_{1s,\,2p}{}^2\sin\Theta d\Theta d\Phi.\qquad(3)$$

Now k_λ is fixed by conservation of energy, and (see Appendix)

$$\gamma_Q=2nv_i\sigma_i\int_{x_-}^{x_+}\frac{|F_{1s,\,2p}|^2}{x^2}dx=\gamma f_iS_Q.\qquad(4)$$

The form factor is evaluated as before:

$$F_{100,\,210}=\frac{1}{4\sqrt{2}\pi a^4}\int e^{-3r/2a}\cos\theta re^{i\mathbf{K}\cdot\mathbf{r}}d\mathbf{r}$$
$$=3iKa2^{15/2}/[9+4K^2a^2]^3.\qquad(5)$$

Furthermore,

$$F_{100,\,21\pm1}=0,\quad\text{since}\quad\int_0^{2\pi}e^{\pm i\phi}d\phi=0.$$

This means that only $\frac{1}{3}$ of the atoms will be so oriented as to allow a quenching transition. Therefore one can use $F_{100,\,210}$ in (4) and multiply by the factor $\frac{1}{3}$.

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

$$\int\frac{dx}{x(9+4x)^6}=-\frac{1}{9^6}\Bigg[-\ln(S)+5\times4S-\frac{10\times4^2}{2}S^2$$
$$+\frac{10\times4^3}{3}S^3-\frac{5\times4^4}{4}S^4+\frac{4}{5}S^5\Bigg],$$

where

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

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[15] G. Wentzel, *Handbuch der Physik* (Verlag Julius Springer, Berlin, 1933), second edition, Vol. 24, p. 738.

For $\epsilon_i = (1/25)(e^2/2a)$ and $n = 10^{14}$, $k_i = 1/5a$, $S_Q = 0.021$, and

$$\gamma_Q/\gamma = 0.0013. \tag{7}$$

B. Stark Broadening by Ions[16]

Stark broadening by ions results from variations of the electric field intensity at the atom. The mean field for the ions given by Holtsmark is $F = 3.26 e n_i^{\frac{2}{3}}$, where n_i 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 estimate the half-width of the broadened line, we find

$$\gamma_{\mathrm{Stark}} = 3.26 e n^{\frac{2}{3}} \times 3ea/\hbar = 2.5 \times 10^{10}/\mathrm{sec} \tag{8}$$

for $n = 10^{14}/\mathrm{cm}^3$. Consequently, Stark broadening by ions is at least 100 times larger than the universal 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 $fS_U = 2nv\sigma S_U/\gamma$. Let the ions have a reduced mass (with respect to the radiating atom) M. Now $v \propto M^{-\frac{1}{2}}$ for ions of the same energy, $\sigma = \pi \lambda\!\!\!^{-2} \propto (\hbar/Mv)^2 \propto M^{-1}$; hence $f \propto M^{-\frac{3}{2}}$. On the other hand, S_U depends on M through the upper limit of Eq. III-(22), and it increases with k_μ^2. At low energy its variation with k_μ^2 is approximately linear. However, $k_\mu^2 \propto M$. In all, therefore, $fS_U \propto M^{-\frac{1}{2}}$.

Protons are thus less effective in broadening the line by a factor of at least 30.

VI. ANGULAR DEPENDENCES IN THE FORM FACTORS

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

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

Throughout we simplified these integrals by taking the momentum transfer vector $\mathbf{K}$ to be directed along the z-axis of the atom. When the product of the atomic functions $\psi_n^*\psi_m$ is spherically symmetric, this is of no consequence. We now extend the calculation and demonstrate that the orientation of the atom with respect to the momentum transfer vector is generally unimportant for small Ka.

Let us evaluate

$$F_{2p0,2p0} = \int e^{i\mathbf{K}\cdot\mathbf{r}} |\psi_{2p,0}{}^{z'}|^2 d\mathbf{r}, \tag{2}$$

where the superscript z' specifies the direction of the polar axis for the wave function, $\psi_{2p,0}{}^{z'}$. The direction of $\mathbf{K}$ is the polar (z) axis of $\psi_{2pm}{}^{z}$. The angles Θ, Φ define the orientation of z' with respect to z. In terms of these angles, we expand

$$\begin{aligned}\psi_{2p,0}{}^{z'} &= R_{2p} \cos\Theta' \\ &= R_{2p}[\cos\Theta \cos\theta + \sin\Theta \sin\theta \cos(\phi - \Phi)] \\ &= \cos\Theta \psi_{2p,0}{}^{z} + (\sin\Theta/\sqrt{2})[e^{-i\Phi}\psi_{2p,+1}{}^{z} + e^{i\Phi}\psi_{2p,-1}{}^{z}],\end{aligned} \tag{3}$$

with

$$R_{2p} \equiv \frac{1}{4(2\pi)^{\frac{1}{2}}} \frac{r}{a^{5/2}} e^{-r/2a}.$$

Furthermore,[17]

$$e^{iKz} = \sum_L (2L+1) i^L P_L(\cos\theta) f_L(Kr), \tag{4}$$

where

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

Integration over Φ annuls all terms in $F_{2p0,2p0}$ which contain Φ-dependent factors. Hence the integral reduces to

$$\begin{aligned}F_{2p0,2p0} = 2\pi \int_{-1}^{+1} d\mu \int_0^\infty & r^2 dr e^{iKz} \{[\cos^2\Theta |\psi_{2p,0}(z)|^2 \\ & + \tfrac{1}{2}\sin^2\Theta (|\psi_{2p,+1}(z)|^2 + |\psi_{2p,-1}(z)|^2)]\} \\ & + 2\pi \int_{-1}^{+1} d\mu \int_0^\infty r^2 dr (R_{2p})^2 e^{iKz} \\ & \times \{\cos^2\Theta \cos^2\theta + \tfrac{1}{2}\sin^2\Theta \sin^2\theta\}.\end{aligned} \tag{5}$$

When we replace e^{iKz} by its expansion, most of the terms contribute nothing because of the orthogonality of the Legendre polynomials. On using well-known relations[18] between these polynomials, we find

$$\begin{aligned}F_{2p,0;2p,0} &= 2\pi \int_0^\infty r^2 dr (R_{2p})^2 \{\cos^2\Theta[\tfrac{2}{3} f_0 - (4/3) f_2] \\ &\qquad + \tfrac{1}{2}\sin^2\Theta[(4/3) f_0 + (4/3) f_2]\} \\ &= \frac{4\pi}{3} \int_0^\infty r^2 dr (R_{2p})^2 \\ &\qquad \times \{f_0 + f_2[\sin^2\Theta - 2\cos^2\Theta]\}.\end{aligned} \tag{6}$$

The radial integral for f_0,

$$\frac{1}{a^5} \int_0^\infty \frac{\sin Kr}{Kr} r^4 e^{-r/a} dr = \frac{24(1-x)}{(1+x)^4}, \tag{7}$$

where $x \equiv (Ka)^2$. Further,[19]

$$\frac{1}{a^5} \int_0^\infty r^4 e^{-r/a} f_2(Kr) dr = \frac{48x}{(1+x)^4}. \tag{8}$$

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[16] For a discussion of the quantum theory of broadening by ions see reference 13.

[17] N. F. Mott and H. S. W. Massey, *Atomic Collisions* (Clarendon Press, Oxford, 1949), second edition, p. 22.

[18] H. Margenau and G. M. Murphy, *Mathematics of Physics and Chemistry* (D. Van Nostrand Company, Inc., New York, 1943), Chap. 3, Secs. 4 and 5.

[19] See reference 18, Chap. 3, Sec. 8.

Combining these results, we find

$$F_{2p,\,0;\,2p,\,0}=\frac{(1-x)}{(1+x)^4}+[\sin^2\Theta-2\cos^2\Theta]\frac{2x}{(1+x)^4}.$$

Clearly, at $\Theta=0$ we have

$$F_{2p,\,0;\,2p,\,0}=(1-5x)/(1+x)^4, \tag{9}$$

which is the result found directly for $\mathbf{K}$ along the (z') polar axis of the atom [III-(17)]. 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 earlier study [III-(19)]:

$$\langle F_{2p0,\,2p0}\rangle_\Theta=(1-x)/(1+x)^4=F_2. \tag{10}$$

To proceed more rigorously, we use the sum over initial states to average over orientations of collisions (i.e., $\sum_i \rho_{ii}^0\rightarrow\frac{1}{2}\int_0^\pi \sin\Theta d\Theta$). Let us put

$$\tfrac{1}{2}\int_0^\pi [F_1-F_{2p0,\,2p0}(\Theta)]^2\sin\Theta d\Theta=(F_1-F_2)^2+\Delta, \tag{11}$$

so that the deviation from our earlier result is

$$\Delta\equiv\left[\frac{2x}{(1+x)^4}\right]^2\tfrac{1}{2}\int_0^\pi[\sin^2\Theta-2\cos^2\Theta]^2\sin\Theta d\Theta. \tag{12}$$

A corresponding difference is added to S_U, namely,

$$\Delta S=\int_0^{x_+}\frac{\Delta}{x^2}dx=\frac{16}{35}\left(1-\frac{1}{(1+x_+)^7}\right)=0.29 \tag{13}$$

for $x_+=4/25$. This is to be compared with S_U which has the value 2.1. The correction is limited $(0<\Delta S<16/35)$, depending on the value of x_+. Its inclusion would not change appreciably the results of our simpler approach.

For polarization broadening $F_1-F_{2p,\,0;\,2p,\,0}$ is replaced by $(1/2)F_{2s,\,0;\,2s,\,0}-F_{2p,\,0;\,2p,\,0}$. Since $\psi_{2s,\,0}$ like $\psi_{1s,\,0}$ is spherically symmetric, $(1/4)\Delta S$ is to be added to S_P of Sec. IV. Here the correction is not negligible and

$$\gamma_P/\gamma=0.061[0.081+(0.29/4)]=0.0094 \tag{14}$$

in place of (IV-32).

Our earlier treatment of quenching is rigorous. The form factor is

$$\begin{aligned}F_{1s,\,0;\,2p,\,0}&=\int e^{i\mathbf{K}\cdot\mathbf{r}}\psi_{1s,\,0}{}^{z'}\psi_{2p,\,0}{}^{z'*}d\mathbf{r}\\&=\int e^{i\mathbf{K}\cdot\mathbf{r}}\psi_{1s,\,0}{}^{z}\bigg[\cos\Theta\psi_{2p,\,0}{}^{z}\\&\qquad+\frac{\sin\Theta}{\sqrt{2}}(e^{-i\Phi}\psi_{2p,+1}{}^{z}+e^{i\Phi}\psi_{2p,-1}{}^{z})\bigg]d\mathbf{r}\\&=\cos\Theta\int e^{i\mathbf{K}\cdot\mathbf{r}}\psi_{1s,\,0}{}^{z}\psi_{2p,\,0}{}^{z}d\mathbf{r}\\&=\cos\Theta F_{1s,\,0;\,2p,\,0}(\Theta=0),\end{aligned}$$

and the transition probability averaged over orientations is proportional to

$$\tfrac{1}{2}\int_0^\pi\cos^2\Theta\,\sin\Theta d\Theta[F_{1s,\,0;\,2p,\,0}(0)]^2=\tfrac{1}{3}[F_{1s,\,0;\,2p,\,0}(0)]^2.$$

This is the value used previously [V-(7)].

VII. MATRIX ELEMENTS WITH SPURIOUS DIVERGENCES

Some matrix elements occurring in the analysis of polarizing collisions appear to be imaginary and to diverge if the momentum transfer vector ($\mathbf{K}$) is zero. Hence a contradiction arises, for the integrals are obviously real. We shall see that they do not diverge if the perturbing electron charge is distributed over a finite volume.

This obviates the difficulty which prevented us from including all degenerate states in the polarization problem. Polarization by induction involves electron-enforced transitions between $\psi_\pm$ and $\psi_{2p,\,\pm1}$ (see Sec. IV). These contain a matrix element which we now single out for study. It is

$$C(\mathbf{K})_{2p,\,0;\,2s,\,0}=\frac{4\pi e^2}{K^2V}F_{2p,\,0;\,2s,\,0}, \tag{1}$$

where

$$F_{2p,\,0;\,2s,\,0}=\int e^{i\mathbf{K}\cdot\mathbf{r}}\psi_{2p0}{}^*\psi_{2s0}d\mathbf{r}.$$

Use has here been made of the formula

$$Z\equiv\int\frac{e^{i\mathbf{K}\cdot\mathbf{R}}}{|\mathbf{r}-\mathbf{R}|}d\mathbf{R}=\frac{4\pi}{K^2}e^{i\mathbf{K}\cdot\mathbf{r}}, \tag{2}$$

which was derived by [III-(9, 11)].

The form factor $F_{2p,\,0;\,2s,\,0}$ contains

$$\psi_{2s,\,0}=\frac{1}{4(2\pi)^{\frac{1}{2}}a^{\frac{3}{2}}}(2-r/a)e^{-r/2a}$$

and

$$\psi_{2p,\,0}=\frac{1}{4(2\pi)^{\frac{1}{2}}a^{5/2}}re^{-r/2a}\cos\theta.$$

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

$$\int_{-1}^{+1}e^{iKr\mu}\mu d\mu=2i\left[\frac{\sin Kr}{(Kr)^2}-\frac{\cos Kr}{Kr}\right].$$

This yields

$$F_{2p,\,0;\,2s,\,0}=3iKa(x-1)/(1+x)^4; \tag{3}$$

and

$$C(K)_{2p,\,0;\,2s,\,0}=\frac{4\pi e^2}{VK^2}\left[\frac{3iKa(x-1)}{(1+x)^4}\right],\quad x=K^2a^2. \tag{4}$$

This element diverges as $1/K$ when K goes to zero, and it is imaginary. A look at the integral (1) for $\mathbf{K}=0$ 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 may view $C(\mathbf{K})_{n,n'}$ as the electrostatic interaction energy between atomic charge, $dq_a(\mathbf{r})=e\psi_n{}^*\psi_{n'}d\mathbf{r}$ and an electron charge density $dq_e=(e^{i\mathbf{K}\cdot\mathbf{R}}/V)ed\mathbf{R}$. The integral (2), when multiplied by e/V, then plays the role of the potential at $\mathbf{r}$ due to the charge density distribution $(e/V)e^{i\mathbf{K}\cdot\mathbf{R}}$. It satisfies Poisson's equation[20]:

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

For $K=0$, therefore, it is proper to evaluate $C_{nn'}$ by ordinary electrostatics, taking q_e to be a uniform spherical distribution extending to R_+. The mutual potential energy between q_e and $dq_a(\mathbf{r})$ is

$$dU=\frac{2\pi e}{V}(R_+{}^2-\tfrac{1}{3}r^2)dq_a(\mathbf{r}).$$

This leads to

$$C_{nn'}(K=0)=\int dU=\frac{2\pi e^2}{V}(R_+{}^2\delta_{nn'}-\tfrac{1}{3}(r^2)_{nn'}). \quad (5)$$

V is the volume per free electron, R_+ some finite cut-off radius introduced by the over-all neutrality of the plasma. For $n=2p,0$ and $n'=2s,0$, the term $(r^2)_{nn'}$ vanishes and therefore $C_{nn'}=0$.

To obtain $C_{nn'}$ for small K, we modify the calculation of formula (2), heeding the suggestion implied by the electrostatic consideration and using a finite cut-off radius. By the previous substitutions, (2) becomes

$$Z=\frac{4\pi}{K}e^{i\mathbf{K}\cdot\mathbf{r}}\int_0^{\rho_+}\sin K\rho d\rho,$$

where $\boldsymbol{\rho}=\mathbf{R}-\mathbf{r}$.

At large values $\rho\cong R$, which goes to R_+. We assume $KR_+\ll 1$; then

$$\int_0^{\rho_+}\sin K\rho d\rho\cong\int_0^{R_+}K\rho d\rho=KR_+{}^2/2.$$

Thus

$$Z\cong 2\pi e^{i\mathbf{K}\cdot\mathbf{r}}R_+{}^2, \quad KR_+\ll 1.$$

Consequently,

$$C_{n,n'}(KR_+\ll 1)=(2\pi R_+{}^2e^2/V)F_{n,n'} \quad (6)$$

and

$$C_{n,n'}(K=0)=(2\pi R_+{}^2e^2/V)\delta_{n,n'}, \quad (7)$$

which agrees with (5) with neglect of the second term, (the correction for the distributed charge). Evidently we have made an approximation in the transformation from $\mathbf{R}$ to $\boldsymbol{\rho}$ [in Eq. (2)], 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

$$Z\cong 2\pi e^{i\mathbf{K}\cdot\mathbf{r}}[R_+{}^2-\tfrac{1}{3}r^2], \quad (8)$$

provided $\mathbf{K}\cdot(\mathbf{R}_+-\mathbf{r})\ll 1$.

Thus the problem of the divergence as $K\rightarrow 0$ can be avoided by introduction of a plasma cutoff R_+.

VIII. POLARIZATION AND DEGENERATE LEVELS

Section V treated the small broadening effect resulting from polarization for a three state atom, i.e., polarization by reorientation. The matrix elements were selected deliberately to avoid the divergences associated with the degenerate levels of the preceding section. 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 $[\epsilon_i\approx(1/25)e^2/2a]$. Even where they are possible, they introduce no new features. On the other hand, quenching-transitions to the ground state do occur. As seen in Sec. V, 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 results obtained in Sec. V for quenching are slightly modified when we regard the upper state, not as a random combination of degenerate states, but as the one corresponding to ψ_+. Our present concern with polarization requires this latter choice. The line width in question is

$$(\gamma_P)_{+;1s,0}/\gamma=\tfrac{1}{2}f\{(S_P)_{2s,0;1s,0}+\tfrac{1}{3}(S_P)_{2p,0;1s,0}\}$$
$$=\tfrac{1}{2}(0.061)\{0.032+0.021\}=0.0016, \quad (1)$$

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

$$\gamma_Q/\gamma=0.0013. \quad (2)$$

Only for degenerate levels does the minimum momentum transfer approach zero, and we enter the region of spurious divergences. We meet this problem when considering the two undisplaced states, $\psi_{2p,\pm 1}$. 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:

$$\psi_{2p,+1}{}^{z'}=-\frac{\sin\Theta}{\sqrt{2}}\psi_{2p,0}{}^z+\tfrac{1}{2}(\cos\Theta+1)e^{-i\Phi}\psi_{2p,+1}{}^z$$
$$+\tfrac{1}{2}(\cos\Theta-1)e^{i\Phi}\psi_{2p,-1}{}^z,$$

and

$$\psi_{2p,-1}{}^{z'}=-\frac{\sin\Theta}{\sqrt{2}}\psi_{2p,0}{}^z+\tfrac{1}{2}(\cos\Theta-1)e^{-i\Phi}\psi_{2p,+1}{}^z$$
$$+\tfrac{1}{2}(\cos\Theta+1)e^{i\Phi}\psi_{2p,-1}{}^z.$$

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[20] H. S. W. Massey and C. B. O. Mohr, Proc. Roy. Soc. (London) **A132**, 605 (1931).

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

$$\psi_+^{z'} \equiv (1/\sqrt{2})(\psi_{2s,0}^{z'} + \psi_{2p,0}^{z'})$$

and $\psi_-^{z'}$, there are four states of principal quantum number $n=2$, which are normalized and orthogonal. We write similar expansions for $\psi_{2s,0}^{z'}$ and $\psi_{2p,0}^{z'}$:

$$\psi_{2s,0}^{z'} = \psi_{2s,0}^{z},$$

$$\psi_{2p,0}^{z'} = \cos\Theta\psi_{2p,0}^{z} + (1/\sqrt{2})\sin\Theta e^{-i\Phi}\psi_{2p,+1}^{z} + (1/\sqrt{2})\sin\Theta e^{i\Phi}\psi_{2p,-1}^{z}.$$

First, consider the form factor:

$$F_{2p,+1;+}(\Theta,\Phi) = \int e^{i\mathbf{K}\cdot\mathbf{r}}\psi_{2p,+1}^{z*}\psi_+^{z}d\mathbf{r}$$

$$= (1/\sqrt{2})[F_{2p,+1;2s,0}(\Theta,\Phi) + F_{2p,+1;2p,0}(\Theta,\Phi)],$$

with

$$F_{2p,+1;2s,0}(\Theta,\Phi) = -(\sin\Theta/\sqrt{2})F_{2p,0;2s,0}(0)$$

$$= -(\sin\Theta/\sqrt{2})[3iKa(x-1)/(1+x)^4]$$

and

$$F_{2p,+1;2p,0}(\Theta,\Phi) = -(1/\sqrt{2})\sin\Theta\cos\Theta F_{2p,0;2p,0}(0)$$

$$= (1/2\sqrt{2})(\cos\Theta+1)\sin\Theta F_{2p,+1;2p,+1}(0) + (1/2\sqrt{2})(\cos\Theta-1)\sin\Theta F_{2p,-1;2p,-1}(0)$$

$$= \frac{1}{\sqrt{2}}\sin\Theta\cos\Theta\frac{6x}{(1+x)^4}.$$

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 cannot change the atom from $\psi_+^{z'}$ to $\psi_{2p,\pm1}^{z'}$.

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

$$\frac{1}{4\pi}\int_0^{2\pi}\int_0^{\pi}|F_{2p,+1;+}(\Theta,\Phi)|^2\sin\Theta d\Theta d\Phi = \tfrac{1}{6}\{|F_{2p,0;2s,0}(0)|^2 + \tfrac{1}{5}[6x/(1+x)^4]^2\},$$

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

$$(\gamma_P)_{+;2p,+1} = 2nv_i\sigma_i(S_P)_{+;2p,+1}, \tag{3}$$

with

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

$$= \tfrac{1}{6}(S_P)_{2p,0;2s,0} + \frac{6}{35}\left[1 - \frac{1}{(1+x_+)^7}\right]. \tag{4}$$

The false divergence of $(S_P)_{2p,0;2s,0}$ at small x appears in this term.

It might be thought that it can be avoided because x_- is not zero but $a^2(k_i-k_f)^2$, and k_i cannot equal k_f in view of the shift which the $+$ level has undergone relative to $2p,+1$; for conservation of energy requires $k_f^2 - k_i^2 = (2m/\hbar^2)\Delta E$. Inspection shows, however, that this is not the case for reasonable ion densities. Nor would the removal of a mathematical difficulty by the artifact of a static ion field be altogether satisfactory.

We therefore turn to the development of Sec. VII. From (VII-8),

$$\int\frac{e^{i\mathbf{K}\cdot\mathbf{R}}}{|\mathbf{R}-\mathbf{r}|}d\mathbf{R} \cong 2\pi e^{i\mathbf{K}\cdot\mathbf{r}}\left[R_+^2 - \frac{r^2}{3}\right]. \tag{5}$$

If we neglect the $r^2 \sim a^2$ contribution as being small compared to R_+ then [VII-(6)] gives

$$C_{2s,0;2p,0} = (4\pi e^2/V)(\tfrac{1}{2}R_+^2)F_{2s,0;2p,0}, \tag{6}$$

so that $R_+^2/2$ has taken the place of $1/K^2$, as is seen from (VII-1). This change prevents the divergence. We now know the matrix element at the two extremes of x. In these two regions,

$$|C_{2s,0;2p,0}|^2 = (4\pi e^2a^2/V)^2|F_{2s,0;2p,0}|^2 \times\begin{cases}\tfrac{1}{4}(R_+/a)^4 & \text{if } x(R_+/a)^2<1\\ 1/x^2 & \text{if } x(R_+/a)^2>1,\end{cases}$$

in view of VIII-(6) and VII-(1).

In order to average over orientations of $\mathbf{K}$ we use the previous expansions. Setting $\mu=\cos\Theta$,

$$\langle|F_{2s,0;2p,0}|^2\rangle_{\text{Av}} \equiv \tfrac{1}{2}\int_{-1}^{+1}|F_{2s,0;2p,0}(\Theta)|^2d\mu$$

$$= \tfrac{1}{2}\cdot\tfrac{2}{3}|F_{2s,0;2p,0}(0)|^2 = \tfrac{1}{3}[9x(x-1)^2/(x+1)^8],$$

since $F_{2s,0;2p,0}$ is given by [VII-(3)]. Hence, when $x \ll 1$, $\langle|F_{2s,0;2p,0}|^2\rangle_{\text{Av}} \cong 3x$ and the matrix elements have the simple form:

$$\langle|C_{2s,0;2p,0}|^2\rangle_{\text{Av}} = (4\pi e^2a^2/V)^2\begin{cases}\tfrac{3}{4}x(R_+/a)^4 & \text{if } x(R_+/a)^2<1\\ 3/x & \text{if } x(R_+/a)^2>1.\end{cases}$$

Following the considerations of Sec. VII, it can be shown that $|C_{2s,0;2p,0}|^2$ is bounded in the middle region. Since

$$\left|\int_0^{\rho_+}\sin K\rho d\rho\right| \leqslant \left|\frac{2}{K}\right|,$$

we have

$$|C_{2s,0;2p,0}{}^{(0)}|^2 \leqslant 4\left|\frac{4\pi e^2}{VK^2}F_{2s,0;2p,0}(0)\right|^2 \cong 4\left(\frac{4\pi e^2a^2}{V}\right)^2\frac{9}{x}.$$

In Fig. 5, 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 $(R_+/a)^4(\bar{x}/4)=1/\bar{x}$; $\bar{x}\sim 2a^2n^{\frac{2}{3}}\sim 10^7$ for $n=10^{14}$ cm^{-3}. Consequently, neglecting x against 1, we find

$$(S_P)_{2p,0;2s,0}(0)\cong\tfrac{1}{4}(R_+/a)^4\int_0^{x}|F_{2s,0;2p,0}(0)|^2dx$$

$$+\int_{\bar{x}}^{x+}\left|\frac{F_{2s0,2p0}(0)}{x}\right|^2dx$$

$$\cong\frac{9}{\bar{x}^2}\int_0^{\bar{x}}xdx+9\int_{\bar{x}}^{x_+}\frac{dx}{x}$$

$$\cong 9\left\{\frac{1}{2}+\ln\frac{x_+}{\bar{x}}\right\}\cong 9\left\{\frac{1}{2}+\ln\frac{0.16}{10^{-7}}\right\}$$

$$\cong 133, \tag{7}$$

since $|F_{2s,0;2p,0}(0)|^2=9x(x-1)^2/(1+x)^8$. And finally, in view of Eq. (4) (with $x_+=0.16$),

$$(\gamma_P)_{+;2p,+1}/\gamma\sim f\{\tfrac{1}{6}\times 133+0.11\}=0.061\times 22\cong 1.3.$$

The main uncertainty in this number arises from the manner in which we obtained $\bar{x}$. We note, however, that an increase in $\bar{x}$ by a factor 100 decreases $(\gamma_P)_{+;2p,+1}/\gamma$ by only $\frac{3}{2}f\ln 100\cong 0.4$. This leaves the order of magnitude of the effect unchanged. In the other direction $\bar{x}$ cannot be pushed very far, since $\bar{x}(R_+/a)^2\sim 2$ has been used in (7) and the logarithmic divergence is limited by $\bar{x}(R_+/a)^2\sim 1$. R_+ may, of course, be larger than $n^{-1/3}$. An increase of R_+ by factor 100 decreases $\bar{x}$ by 10^{-4} but increases γ_P/γ by only 0.8.

We conclude that coupling between ψ_+ and $\psi_{2p,+1}$ gives rise to a polarization effect about 100 times as large as inclusion of the other states. This is because the coupling involves the matrix elements between $\psi_{2p,0}$ and $\psi_{2s,0}$. However, the effect does not diverge.

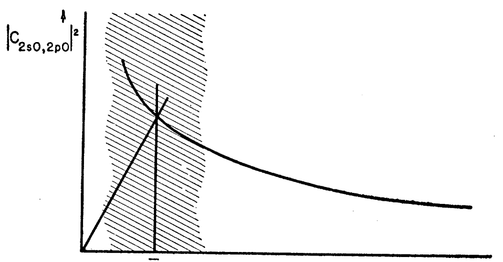

FIG. 5. A sketch of $|C_{2s0,2p0}|^2$, known at large and small $x=a^2K^2$ (K = momentum transfer). The matrix element in the shaded area is found by extrapolation from the extremities. The point of intersection is called $\bar{x}$.

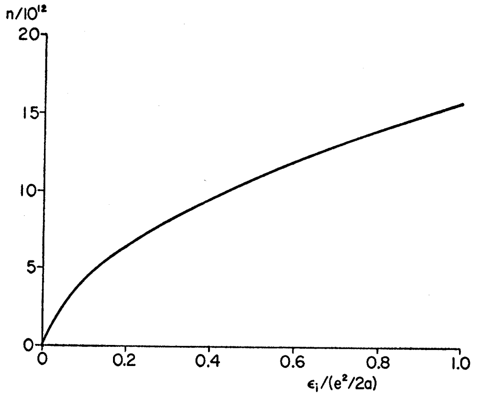

FIG. 6. Curve of density (n) *vs* electron energy (ϵ_i) delimiting the region of small n and large ϵ_i where electron broadening is negligible compared to the natural width (γ). The curve is the locus of points satisfying $(\gamma_P)_{2p0,2s0}=\gamma/10$.

In Fig. 6, we plot the locus of $\gamma_P/\gamma=1/10$ in order to indicate the region of electron densities and velocities in which their broadening may be neglected.

A word is in order about the line shifts, which are neglected in this treatment. The use of the resonance approximation, which ignores the variation of the matrix elements C with change in electron energy Ω, makes γ_P real. When this dependence is properly considered, an imaginary term is added to γ_P. This produces a line shift which will be discussed in a separate publication.

As a summary, we compare the several effects for the hydrogen $2p,0\rightarrow 1s,0$ transition, using $\gamma=3.12\times 10^8$ sec^{-1}, $n=10^{14}$ cm^{-3}, $\epsilon_i=(1/25)e^2/2a$:

III-(38)	Universal broadening	$\gamma_U/\gamma=$ 0.13
VIII-(16)	Polarization by re-orientation (involving the matrix elements $2p0\rightarrow 2p\pm 1$)	$\gamma_P/\gamma=$ 0.027
V-A-(7)	Quenching ($2p0\rightarrow 1s0$)	$\gamma_Q/\gamma=$ 0.0013
VIII-(16)	Polarization by induction (involving the large element $2p0\rightarrow 2s0$)	$\gamma_P/\gamma=$ 2.7
V-B-(8)	Stark broadening by ions	$\gamma_{\text{Stark}}/\gamma\cong 80$

Thus for the Lyman α line, where there is a linear Stark effect, the ion broadening is the dominant effect, as expected. But in other instances, to be treated in further publications, the electrons can make important contributions.

APPENDIX

The principal symbols used in this paper are as follows: E = energy of atomic state; ϵ = energy of electron: ϵ_i = initial energy, ϵ_μ = final energy; $\mathbf{k}$ = wave-number vector for electron; $\mathbf{K}=\mathbf{k}_\mu-\mathbf{k}_i$ = momentum-transfer vector; $\mathbf{v}$ = velocity of electron; $a=\hbar^2/me^2$;

$x=a^2K^2$; $x_+=a^2(k_\mu+k_i)^2$; $x_-=a^2(k_\mu-k_i)^2$; n=number density of electrons.

Throughout the paper, line widths resulting from different causes are written in the Lorentz form:

$$\gamma=2nv\sigma S,$$

where σ is a cross section and S a numerical efficiency factor. In particular,

$$S_U\equiv\int_0^{x+}\frac{|F_{11}-F_{22}|^2}{x^2}dx,\quad S_P\equiv\int_0^{x+}\frac{|F_{nm}|^2}{x^2}dx,$$

and

$$F_{nm}=\int e^{i\mathbf{K}\cdot\mathbf{r}}\psi_n{}^*(r)\psi_m(r)d\mathbf{r}.$$

PHYSICAL REVIEW VOLUME 98, NUMBER 2 APRIL 15, 1955

Extension of Hund's Rule*

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(Received September 20, 1954)

In this note we show that in an n-electron system, if we assume that these n electrons occupy n orthogonal one-electron orbitals, the state of highest multiplicity has the lowest energy.

One of the interesting results that comes out of the calculation of the energy levels of atoms, molecules, and crystals is the total spin (multiplicity) of the ground state. In general the question of the multiplicity of the ground state cannot be answered without lengthy calculations. It is, however, sometimes possible to answer this question without any calculation at all (at least to within a certain approximation). We know of Hund's rule of atomic spectra. Part of this rule states that of all the levels arising from a given spatial configuration, the state of highest multiplicity lies lowest. A rule similar to this can be proved quite generally.[1]

We imagine that we have n distinct one-electron spatial orbitals $u_1, u_2, \cdots u_n$. In each of these we put one electron with either spin up or spin down. (The presence of other orbitals which are doubly filled does not influence the validity of the arguments given below and will be dropped from consideration.) We also assume that the orbitals under consideration are orthogonal.

$$\int u_i{}^*(\mathbf{r})u_j(\mathbf{r})d\tau=\delta_{ij}. \tag{1}$$

For our n-electron problem, by taking products of these one-electron states with spin up or down, we can form 2^n product functions which we use as the basis of approximation for the wave function for our n electron system. We must now form the correct linear combinations of these product functions to form states which are antisymmetric with respect to permutations of all of the electron coordinates and which have definite multiplicities. The multiplicities will range from singlets (n even) to states of multiplicity $n+1$. We shall lose no generality by restricting ourselves to all those states with the same z component of total spin. Of these only one corresponds to the state of highest multiplicity, whereas for any other multiplicity there is, in general, more than one state of this multiplicity. We shall now show that there is no state that lies lower in energy than the state of highest multiplicity. The problem which confronts us now is to diagonalize the matrix of our Hamiltonian between states of a given multiplicity in the basis of antisymmetric functions. (There is, of course, no interaction between the states of different multiplicities.) We assume that our Hamiltonian in this case is spin-free and is given by

$$H=\sum_1^n(i)[-\nabla_i{}^2+f(i)]+\tfrac{1}{2}\sum_1^n(i\neq j)g_{ij}. \tag{2}$$

Here $f(i)$ is the one-electron potential and g_{ij} is the interelectronic Coulomb interaction.

The problem as stated above is in just the form which can easily be set up in terms of the Dirac vector model.[2] For a given multiplicity the matrix of the Hamiltonian is given by

$$\mathcal{H}_{\lambda\sigma}{}^S=\text{const}+\tfrac{1}{2}\sum(i\neq j)[-J_{ij}(P_{ij}{}^S)_{\lambda\sigma}]. \tag{3}$$

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* The research in this paper was supported jointly by the Army, Navy, and Air Force under contract with the Massachusetts Institute of Technology.

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[1] This extension of Hund's rule has been published in the Quarterly Progress Report of the Solid-State and Molecular Theory Group at Massachusetts Institute of Technology, July 15, 1953, p. 37. P.-O. Löwdin [Phys. Rev. **97**, 1474, 1490, 1509 (1955)] has also presented a proof by a different method.

[2] P. A. M. Dirac, Proc. Roy. Soc. (London) **A123**, 714 (1929). For further references and a complete discussion of this method see F. M. Corson, *Perturbation Methods in the Quantum Mechanics of n-Electron Systems* (Hafner Publishing Company, New York, 1950).