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Impact Broadening of Spectral Lines

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An evaluation is made of the error introduced into current impact broadening theory by the two incorrect assumptions usually made,—the adiabatic approximation, and the neglect of the rotation of the adiabatic electron states in the computation of the interaction between these states and the radiation field. A simple case of resonance broadening is examined, with the aid of wave functions in a nonrotating coordinate system, and the emitted intensity is shown to be reduced by a factor of two in the first approximation from the value given by the usual impact formula. This discrepancy is no greater than other errors in the present theory of line broadening, and will be less for dispersion, van der Waals, and other second-order forces since these forces do not vanish on the average and will show little tendency to do so in a single encounter. The Weisskopf formula, despite its theoretical imperfections, may therefore be used to give approximate results for impact broadening. A criterion is also given for the transition between impact and statistical broadening; for resonance forces under normal conditions the impact broadening formulas are shown to be irrelevant, since they apply only within a distance of 10^{-1} angstrom from the line center, and outside this range the statistical formulas must be applied. Although this is substantially the range of Doppler broadening, accurate measurements of line centers at low pressures should provide a qualitative test of the present theory in the case of resonance broadening. The influence of the previously neglected "rotation effect" on the interaction between a hydrogen atom perturbed by a passing ion and the radiation field is calculated with relative exactness for the first excited state.

THE broadening of a spectral line by perturbing atoms in a gaseous assembly has been treated in two limiting cases.[1, 2] When the atomic velocities are sufficiently small the line profile is given by the familiar statistical formulas.[3] When these velocities are large, however, the impact method of Lorentz as modified by Weisskopf[4] and others[5] is usually applied. For this analysis one computes the phase shift ϕ produced in the emitted radiation by the passing perturbing atom; if this is greater than some critical value,—unity in the Weisskopf treatment, $\pi/2$ in the Kallmann and London analysis,—the wave train before the encounter is assumed to be incoherent with that emitted after the encounter. If there are Ω such encounters per second, the line profile is then given by the usual dispersion formula $\Omega/\pi x^2$, where x equals $2\pi(\nu-\nu_0)$ and is simply the distance from the line center in angular frequency units. The term line profile is used throughout to denote $J(x)$, the profile of the line emitted by a thin film of atoms; $J(x)$ is directly proportional to the atomic absorption coefficient.

A different approach to the problem has been given by H. Kuhn,[6] who uses the first derivative of the adiabatic $\nu(t)$ to compute the time T corresponding to a phase shift π. The use of phase shifts to give line broadening directly is an approximation which may lead to serious error.[7] In any case, however, this method of calculating phase shifts is legitimate only when the total phase shift in the course of the encounter is much greater than π and the statistical theory is approximately valid. Hence this aspect of Kuhn's analysis is designed to give a minor correction to the statistical result and refers to a different region of line broadening from that of the Weisskopf impact formula in which we are primarily interested here.

Assumptions of both a mathematical and a physical nature are included in the Weisskopf analysis. From a mathematical standpoint the choice of the critical phase shift is rather arbitrary. More accurately one should compute the broadening produced by a single encounter between the radiating atom and a perturbing one; the true profile would then be given by the appropriate integration over all types of binary encounters.

While this sum could be calculated in the

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[1] H. Kuhn, Phil. Mag. [7] **18**, 987 (1934).

[2] H. Margenau and W. W. Watson, Rev. Mod. Phys. **8**, 22 (1936).

[3] J. Holtsmark, Ann. d. Physik **58**, 577 (1919); Physik. Zeits. **20**, 162 (1919); **25**, 73 (1924).

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

[5] W. Lenz, Zeits. f. Physik **80**, 423 (1933); H. Kallmann and F. London, Zeits. f. physik. Chemie **B2**, 207 (1929).

[6] H. Kuhn, Phil. Mag. [7] **18**, 983 (1934).

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

limiting impact case, if the adiabatic approximation were assumed, such an analysis would not be very useful since the physical assumptions would not correspond to fact. In the first place the adiabatic approximation is definitely incorrect when the phase shift ϕ is as small as unity. For the adiabatic approximation breaks down when transitions between the various atomic states become appreciable. These electronic states are taken in a rotating coordinate system such that the z axis always points towards the moving perturbing atom. Transitions between atomic levels with different unperturbed energies may be neglected, except for the extremely close encounters. In the case of degenerate states of the same level, however,—states differing only in their magnetic quantum number M,—this is not true. In fact it is for the most distant encounters (the smallest values of ϕ) that such nonadiabatic transitions become important. When ϕ is large these transitions become inappreciable.

This may be shown in general by a simple dimensional argument. The change of Ψ with time will be completely determined by the time-dependent Hamiltonian. If we consider only transitions between the states of a particular atomic level, the only dimensional quantities entering the analysis are v, the velocity of the perturbing particle relative to the radiating atom; R, the distance of closest approach; q_s/r^n, the energy perturbation of state s when the perturber is stationary and at a distance r; and of course Planck's constant h. Whether or not the encounter is adiabatic must depend on the value of some dimensionless constant, and the only available one is q_s/hvR^{n-1}, which except for numerical factors of unit order of magnitude, is equal to the adiabatic phase shift ϕ_s for the state s. When v is infinite the adiabatic treatment obviously fails, and one may conclude that an encounter will be adiabatic only if ϕ_s is large compared to unity. A more specific and quantitatively more precise argument is presented in Section 1 below. Since the Weisskopf encounter radius is the value of R when ϕ_s equals unity, it is clear that the adiabatic approximation is not well suited to the determination of this radius or to the treatment of impact broadening in general.

The second assumption involved in the usual analysis of impact broadening is that the interaction between the radiation field and the adiabatically rotating electronic quantum states may be determined as though the states were not rotating. Since the radiation emitted is observed in a stationary coordinate system, one must take the matrix elements not of the electronic coordinates x, y, and z,—which are rotating about the y axis—but rather of $x \sin \theta + z \cos \theta$, y, and $z \sin \theta - x \cos \theta$, where θ is the angle which the moving z axis makes with its direction at the time t_0, when the perturbing atom is at its distance of closest approach R. It is readily shown that if the time-dependent matrix elements of these quantities are used, the perturbation produces a phase shift equal to π even when ΔE is zero or the collision is infinitely rapid. This effect is perhaps most easily seen in the light of its classical analog. A linear oscillator which is rotated through 180° will subsequently emit radiation which is out of phase by the same 180° with the previously emitted wave train, despite the absence of any perturbation to the frequency during the rotation, and despite an arbitrarily fast rotation.

This effect can obviously be taken into account only if departures from the adiabatic assumption are considered, since otherwise all encounters would be said to produce phase shifts greater than π and an enormous line broadening would be predicted. Fortunately these two deviations from the standard treatment of impact broadening tend to offset each other.

We may conclude that current pressure-broadening theory is open to serious criticism on the grounds that it assumes the adiabatic approximation, and that furthermore it does not consider the rotation effect, which should form an integral part of the adiabatic treatment. This neglect would have introduced serious error into the standard impact-broadening analyses, were it not for the fact that the adiabatic approximation was incorrect to begin with. This combination of two separate errors has happily led to results which are not far from the truth.

The simplest approach to a correct treatment of these effects is apparently to take as electronic states the eigenfunctions in a nonrotating, stationary coordinate system. Such a procedure has two advantages. In the first place it eliminates the "rotation effect"; i.e., one need consider only the usual matrix elements of the electronic coordinates x, y, and z to compute the interaction with radiation. Secondly, the nonrotating unperturbed states afford a much better approximation for the case of high velocities and low phase shifts than do the rotating adiabatic states. In other words, if ϕ is as low as unity a Born-type approximation is preferable to the adiabatic one.

When the analysis is carried out for a simple case, the resultant intensity differs from the usual Weisskopf formula by a factor of two, which is scarcely more than the mathematical inaccuracy involved. But the theoretical approach required is rather different, an important fact in the theory of line broadening. While these results justify the use of the Weisskopf model for an order-of-magnitude calculation, it must be emphasized that such a model is not only mathematically approximate but is physically incorrect.

In Section 1 below the general equations for nonadiabatic transitions are examined and the region of validity for the adiabatic approximation is determined. The impact broadening formula is derived in Section 2 from the general Fourier-integral formula for $J(x)$; the conditions under which this derivation is valid lead to a simple criterion for the appearance of impact rather than statistical broadening. Section 3 presents the analysis for the broadening by resonance forces of the line from the level $L=0$ to the level $L=1$; the implications to be drawn for other cases are briefly discussed. In Section 4 a more complete treatment of the $L\alpha$ line of atomic hydrogen is given when this is perturbed by passing ions. This section provides the appropriate modifications—which qualitatively are not great—to the author's previous results,[8] in which the breakdown of the adiabatic approximation was considered, but in which the "rotation effect" was not taken into account.

1.

The general equation for the change of state of a system is

$$i\hbar\partial\Psi(t)/\partial t=H(t)\Psi(t). \tag{1}$$

The state function $\Psi(t)$ may be expressed in terms of any complete set of eigenfunctions. Such a set is provided by the solutions of the adiabatic equation,

$$H(t)\psi_s(t)=E_s(t)\psi_s(t), \tag{2}$$

where t is simply taken as a parameter. We shall assume here and throughout that $E_s(t)$, determined by (2), is given by

$$E_s(t)=q_s/[r(t)]^n, \tag{3}$$

where $r(t)$ is the distance between the atom in question and the perturber. We shall assume for convenience that q_s is positive. Since all particles are assumed to move in straight lines, we have

$$[r(t)]^2=R^2+v^2(t-t_0)^2; \tag{4}$$

t_0 is the time of closest approach.

If we let

$$\Psi(t)=\Sigma_s a_s(t)\psi_s(t), \tag{5}$$

then for a single encounter we find from (1), (2), and (5),

$$\frac{da_s}{dt}+i\frac{E_s(t)}{\hbar}a_s+\sum_r k_{sr}a_r=0, \tag{6}$$

where

$$k_{sr}=\int\psi_s^*\frac{\partial\psi_r}{\partial t}d\tau. \tag{7}$$

Let us introduce the variable θ, defined by

$$d\theta=\frac{vdt/R}{1+v^2t^2/R^2}; \tag{8}$$

from (4) we see that θ is simply the angle which the electronic z axis makes with its position at the time of closest approach t_0.

With this change of variable (6) assumes the form

$$da_s/d\theta+i\lambda_s\delta\cos^{n-2}\theta\, a_s+\Sigma_r K_{sr}a_r=0, \tag{9}$$

where

$$K_{sr}=k_{sr}\bigg/\frac{d\theta}{dt}, \tag{10}$$

$$q_s=\lambda_s q, \tag{11}$$

and

$$\delta=q/\hbar vR^{n-1}. \tag{12}$$

The quantity q is chosen so that $|\lambda_s-\lambda_r|\,(s\neq r)$ has unity as its lowest value. For most cases of importance λ_s will assume values of unit order of magnitude.

Values of K_{sr} for a rotating system have been calculated by J. Schwinger[9] for the case in which

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[8] L. Spitzer, Jr., reference 7; Phys. Rev. **56**, 39 (1939), referred to here as II.

[9] J. Schwinger, Phys. Rev. **51**, 648 (1937).

the total angular momentum J is quantized. Only the rotation is relevant in the present connection, since the change in $E_s(t)$ with time gives rise only to matrix elements connecting $a_s(t)$ with states of the same M but of different unperturbed energies. As long as ΔE, the difference in unperturbed energies, is greater than hv/R, such matrix elements lead to negligible transition probabilities, and may therefore be disregarded. Since this criterion will be satisfied for most of the cases in which we are interested, we may use Schwinger's values, derived on the assumption that $E_s(t)$ is constant; from his formula (26), with ϕ set equal to zero, we find

$$K_{sr}=\tfrac{1}{2}\{(J-M)(J+M+1)\}^{\frac{1}{2}}\delta_{M,\,M+1} -\tfrac{1}{2}\{(J+M)(J-M+1)\}^{\frac{1}{2}}\delta_{M,\,M-1}, \quad (13)$$

where $\delta_{\mu\nu}$ is zero or unity as μ is different from or equal to ν. Hence $|K_{sr}|$ lies between $2^{-\frac{1}{2}}$ and $(J+1)/2$.

On the adiabatic approximation we neglect K_{sr} and solve (9) for the probability amplitude of state s; this becomes

$$a_s(t)=A_s\exp\left(-i\lambda_s\delta\int_0^{\theta(t)}\cos^{n-2}\varphi d\varphi\right), \quad (14)$$

where A_s is a constant. If we set A_s equal to unity and use (14) to calculate the first-order transition probability to another state, for which the probability amplitude was initially zero, we have from (9)

$$|a_r(\infty)|=2K_{rs} \times\left|\int_0^{\pi/2}d\theta\cos\left\{(\lambda_r-\lambda_s)\delta\int_0^{\theta}\cos^{n-2}\varphi d\varphi\right\}\right|. \quad (15)$$

It is obvious from (15) that when $|(\lambda_r-\lambda_s)\delta|$ is less than unity the argument of the cosine is always smaller than π; $|a_r(\infty)|$ may therefore be of unit order of magnitude and for such a case the adiabatic approximation is clearly invalid. When $|(\lambda_r-\lambda_s)\delta|$ is greater than K_{rs}, on the other hand, the cosine term oscillates rapidly, $|a_r(\infty)|$ is small, transitions are negligible, and the adiabatic approximation is more nearly correct. The fact that A_s, or $a_s(t_0)$, is actually less than unity does not affect these conclusions.

The adiabatic phase shift for the state s, which we shall denote by ϕ_{as}, is given by the relationship

$$\phi_{as}=\int_{-\infty}^{+\infty}\frac{2\pi E_s(t)}{h}dt=\frac{q_s}{\hbar}\int_{-\infty}^{+\infty}\frac{dt}{(R^2+v^2t^2)^{n/2}}, \quad (16)$$

provided that (3) is used for $E_s(t)$. Carrying out the integration, we find

$$\phi_{as}=c_n\lambda_s\delta, \quad (17)$$

where λ_s and δ are defined in (11) and (12), and

$$c_n=\pi^{\frac{1}{2}}\Gamma[\tfrac{1}{2}(n-1)]/\Gamma(\tfrac{1}{2}n). \quad (18)$$

Combining (17) with the results derived from (15), we see that the adiabatic approximation is valid if

$$\phi_{as}>c_nK_{sr}\left|\frac{\lambda_s}{\lambda_s-\lambda_r}\right|, \quad (19a)$$

and is wholly invalid if

$$\phi_{as}<c_n\left|\frac{\lambda_s}{\lambda_s-\lambda_r}\right|. \quad (19b)$$

Since c_n is of unit order of magnitude, we see that when ϕ_{as} is unity (19a) will not be satisfied and the adiabatic approximation definitely fails.

2.

The frequency distribution of quanta emitted by an atom in a certain excited level may be expressed as the square of a sum of the Fourier integrals of each $b_s(t)$, the probability amplitude of state s of that level;[10] one must stipulate, however, that state s is an eigenstate in a stationary coordinate system, and that the lower level of the radiative transition is undegenerate. The problem of line broadening is the evaluation of these Fourier integrals when the radiating atom is perturbed in various ways. This problem in the general case is one of great complexity and several approximations are necessary if an analysis is to be carried through.

The first simplification made in the impact case is to assume that the perturbations are very

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[10] See H. Margenau and W. W. Watson, reference 2, V. Weisskopf, reference 4, and the author, I, reference 7, for proofs of this procedure under various different simplifying conditions. A general analysis for the case where both upper and lower levels are degenerate and perturbed has apparently not been given.

rapid compared to the mean life of each atomic state. Then each $b_s(t)$ may be expressed as the product of $a_s(t)$ and the radiation damping factor, where $a_s(t)$ is given by the solution of the perturbation equations, neglecting the interaction with radiation. The second approximation is to neglect all but binary encounters; this will be valid for frequencies far in the wings of the line. On this approximation the change in $a_s(t)$ at any one time is always produced by a single binary encounter; the values of a_s at the end of each encounter are taken as the initial values of a_s for the next encounter. Since the Fourier integral of $b_s(t)$ may be reduced to one of da_s/dt, this integral may be regarded as the sum of Fourier integrals, one for each separate encounter.

With these approximations, then, there are three distinct steps involved in the computation of line broadening by moving atoms. First one must set up and solve the general quantum-mechanical equation of state for the atom in the field of some passing perturber,—ion, atom, or molecule. If the state function Ψ is expanded in terms of ψ_s, a complete set of eigenfunctions, the coefficients $a_s(t)$ in the expansion will represent the solution to this first problem.

Next one must compute the Fourier integral or transform of each da_s/dt. The squared sum of these Fourier integrals over different values of s yields the broadening of the line profile for a single encounter. Finally the third step consists of integrating such profiles over encounters at all velocities and at all relevant distances of closest approach to yield the final profile $J(x)$.

If we assume, then, that the lower state is an undegenerate S state, and normalize $J(x)$ to unity for a single component of the spectral line, we have, accordingly,

$$J(x)=\frac{\Gamma}{2\pi}\sum_s\left|\int_0^\infty b_s(t)e^{ixt}dt\right|^2, \tag{20}$$

where Γ is the damping constant for the upper level (the same for all the states in a given level). The summation sign has been taken outside the brackets since the transitions from the different upper states to the lower S state will give quanta with different polarization vectors, and will therefore not interfere with each other. Following the assumption made above, we may set

$$b_s(t)=e^{-\frac{1}{2}\Gamma t}a_s(t)\,; \tag{21}$$

$a_s(t)$ is the coefficient of ψ_s found from the perturbation equations for the encounters without regard for the interaction with the radiation field. Any perturbation to the energy of the lower state may be taken into account by a simple change in the equation for $a_s(t)$. If we substitute (21) into (20) and integrate by parts we find

$$J(x)=\frac{\Gamma}{2\pi}\frac{1}{x^2+\frac{1}{4}\Gamma^2}\sum_s\left|a_s(0)+\int_0^\infty e^{-\frac{1}{2}\Gamma t}\frac{da_s}{dt}e^{ixt}dt\right|^2. \tag{22}$$

The integral in (22) may be regarded as the sum of separate integrals, one for each encounter. If t_0 represents the midpoint in time of each encounter and if we let $\tau=t-t_0$ and neglect the damping factor inside the integral, we have

$$J(x)=\frac{\Gamma}{2\pi}\frac{1}{x^2+\frac{1}{4}\Gamma^2}\sum_s\left|a_s(0)+\sum_{t_0}\exp\left(-\tfrac{1}{2}\Gamma t_0+ixt_0\right)\times\int_{-\infty}^{+\infty}\frac{da_s}{d\tau}(\tau)e^{ix\tau}d\tau\right|^2; \tag{23}$$

the sum over t_0 is a sum over all collisions. Since the cross-product terms vanish on the average if x is not too small, we have, finally, neglecting the radiation damping term, and integrating over t_0,

$$J(x)=\frac{1}{2\pi x^2}\sum_s\sum{}'\left|\int_{-\infty}^{+\infty}\frac{da_s}{d\tau}e^{ix\tau}d\tau\right|^2, \tag{24}$$

where Σ' denotes the sum over all encounters within an interval of one second.

One may now see the conditions under which the Weisskopf treatment is legitimate. If R represents the distance of closest approach and v the velocity of the perturbing particle relative to the atom under consideration, the encounter will last roughly $2R/v$ seconds; i.e., the value of the integral in

(24) will come largely from this range. If Rx/v is less than unity the exponential in (24) may therefore be neglected and the integral becomes simply the total change in a_s produced by the encounter.

The error introduced by this procedure may be evaluated. We introduce the dimensionless variables u and ξ, defined by

$$u = v\tau/R \tag{25}$$

$$\xi = Rx/v. \tag{26}$$

Then we find that

$$\begin{aligned}\int_{-\infty}^{+\infty}\frac{da_s}{d\tau}e^{ix\tau}dt &= \int_{-\infty}^{+\infty}\frac{da_s}{du}du+\int_{-\infty}^{+\infty}(e^{i\xi u}-1)\frac{da_s}{du}du. \\ &= \Delta a_s + Q.\end{aligned} \tag{27}$$

From the principle of spectroscopic stability it follows that the sum over s of $|da_s/du|^2$ must equal the corresponding sum in the adiabatic case; hence we may set $|da_s/du|$ equal to its adiabatic counterpart in finding an approximate upper limit for Q.

From (9) we have in the adiabatic case

$$\frac{da_s}{du} = -\frac{i\lambda_s\delta}{(1+u^2)^{n/2}}a_s. \tag{28}$$

Taking absolute values we see from (27) that

$$|Q| \leq \int_{-\infty}^{+\infty}|e^{i\xi u}-1|\left|\frac{da_s}{du}\right|du. \tag{29}$$

If we take for $|da_s/du|$ the expression in (28) and equate $|a_s|$ to unity, (29) becomes

$$|Q| \leq 4\lambda_s\delta\int_0^{\infty}\frac{|\sin\frac{1}{2}\xi u|}{(1+u^2)^{n/2}}du. \tag{30}$$

The numerator of (30) is always less than $\frac{1}{2}\xi u$. With this substitution (30) may be integrated at once, provided that n is greater than 2. Substituting from (17) for δ and from (18) for c_n, we find

$$|Q| < K_n\phi_{as}|\xi|, \tag{31}$$

where

$$K_n = \Gamma(\tfrac{1}{2}n-1)/\pi^{\frac{1}{2}}\Gamma[\tfrac{1}{2}(n-1)]; \tag{32}$$

K_n decreases steadily from 1.00 for $n=3$ to 0.424 for $n=6$. The case $n=2$, in which we are not interested here, must be treated separately.

Formula (31) gives a useful limit on Q when $|\xi|$ is less than unity. When ϕ_{as} is sufficiently large the Lenz[11] criterion for the appearance of statistical broadening is automatically satisfied, and the usual statistical formulas may be used in place of the Fourier integral in (24). We shall neglect Q entirely in the determination of $J(x)$ and investigate later the error introduced by this approximation.

Returning, then, to (24) we see that since the maximum change in a_s is two, we may define a phase shift ϕ_s by the relationship

$$\int_{-\infty}^{+\infty}\frac{da_s}{d\tau}d\tau = \Delta a_s = 2\sin\phi_s; \tag{33}$$

the ϕ_s so defined will clearly vanish for very distant encounters, and will become large for close encounters, when it will in fact equal the adiabatic phase shift ϕ_{as}. From (24) and (33) we have

$$J(x) = \frac{2}{\pi x^2}\sum_s\sum{}'\sin^2\phi_s. \tag{34}$$

Following the mathematics of the Weisskopf analysis, we may replace $\sin^2\phi_s$ by its average value $\frac{1}{2}$, and set

$$J(x) = (1/\pi x^2)\Sigma_s\Omega_s, \tag{35}$$

where Ω_s is the number of encounters per second for which ϕ_s is greater than unity. This approximation is possible only when n is greater than two, since otherwise the more distant encounters become more important than the closer ones.

As a rough indication of the amount by which (35) is in error we may take Q_1, the upper limit on Q given by (31) when ϕ_{as} equals unity. From (12), (17), and (26) we find that

$$Q_1 = K_n\left(\frac{c_nq_s}{\hbar v^n}\right)^{1/(n-1)}|x|. \tag{36}$$

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[11] W. Lenz, reference 5; also Zeits. f. Physik **83**, 139 (1933).

More accurately we should average $|\Delta a_s+Q|^2$ over all encounters to find a rigorous upper limit for the error in (35). Although the upper limit given by (31) becomes infinite as R approaches zero, it is possible to show that as R decreases, the adiabatic approximation becomes more nearly correct, and if Q_1 is less than unity the left-hand side of (27) becomes small; Q can therefore not become greater than two. Hence if we replace Q by its upper limit in (31) or by two, which ever is the smaller, the appropriate average can be roughly carried out.

The results of this calculation show that when n is equal to three, the average error in $|\Delta a_s|^2$ is not greater than five times Q_1. Since (31) gives an upper limit which is probably too great by a similar factor, we may take $2Q_1$ as the approximate error. Since also the average value of $|\Delta a_s|^2$ equals two, Q_1 becomes the relative error in $J(x)$. This procedure is approximately valid when n equals four, but will not be accurate when n is equal to or greater than five, since in such a case Q may increase very rapidly with decreasing R and the actual error of (35) may be quite large. This is particularly true if Q_1 is very small. An order of magnitude result may, however, be obtained in this manner.

Thus (36) gives an upper limit of x for which (35) is accurate to within some definite relative error. If we neglect the factor K_n, as this is of unit order of magnitude, and set Q_1 less than some preassigned relative error P, we find that this upper limit becomes

$$|\nu-\nu_0|<\frac{P}{2\pi}\left(\frac{\hbar v^n}{c_n q_s}\right)^{1/(n-1)}. \qquad (37)$$

This condition, which does not seem to have been generally realized, must be satisfied for all s if the impact broadening analysis is to have any relevance. It should be pointed out that these results depend on the assumption that ϕ_s is small when R is equal to the average interionic or interatomic distance, since otherwise ϕ_s will always be greater than unity and the limits for the sum in (35) must be changed.

Another condition which must be satisfied if (35) is to be valid is that x must be greater than Ω_s. It is evident that Ω_s plays the role of a collision damping factor, and for values of $2x$ less than the half-width $2\Omega_s$, (35) is clearly an incorrect approximation for $J(x)$. Also $1/\Omega_s$ is the difference in t_0 between encounters producing a phase shift of unity; i.e., the time elapsed between the midpoints of such encounters. If x/Ω_s is less than unity the cross products of successive integrals in (23) will include a phase factor less than unity and will not cancel out when an average is taken over neighboring values of this phase factor. This lower limit Ω_s for x will be less than the upper limit in (37) provided that ϕ_s is again less than unity when R is equal to the average distance of the nearest perturber. Hence if ϕ_s is greater than unity at this point, not only is the derivation of (35) incorrect, but there is no region of x to which it applies; in such a case $J(x)$ is in fact given by the usual statistical formula.

3.

We consider next the approximate determination of ϕ_s in the simplest case of resonance broadening, that of the $L=1$ level. Let A and B denote the two atoms in question, and 1, 2, and 3 the states with $M=1$, 0, and -1, respectively. The interaction potential V is given[12] by the formula

$$V=\frac{e^2}{r_{AB}^3}[x_Ax_B+y_Ay_B-2z_Az_B], \qquad (38)$$

provided that the coordinates are taken rotating about the y axis so that the z axis lies along the line connecting the two atoms. In stationary coordinates (38) becomes

$$V=\frac{e^2}{r_{AB}^3}[\mathbf{r}_A\cdot\mathbf{r}_B-3\{z_Az_B\sin^2\theta+x_Ax_B\cos^2\theta+(z_Ax_B+x_Az_B)\sin\theta\cos\theta\}]; \qquad (39)$$

θ, defined in (8), is identical with the quantity w used in I.

Let Λ, χ_1, χ_2, and χ_3 denote the wave functions for the ground state ($L=0$), and the three states of the upper level; each χ_s is an eigenfunction in a nonrotating, stationary coordinate system. Then for the ψ_s functions we have the usual combinations

$$\psi_s=\Lambda_A\chi_{sB}+\Lambda_B\chi_{sA}. \qquad (40)$$

The choice of sign in (40) affects this and the adiabatic analyses in the same manner, and is

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[12] H. Margenau, Rev. Mod. Phys. 11, 1 (1939).

therefore immaterial in this connection. If we assume that

$$\Psi(t)=\Sigma_s a_s(t)\psi_s, \tag{41}$$

and make the substitutions

$$\begin{aligned} a_5&=(a_1-a_3)/\sqrt{2},\\ a_6&=(a_1+a_3)/\sqrt{2}, \end{aligned} \tag{42}$$

then Eq. (1) yields the formulas

$$\frac{1}{\cos\theta}\frac{da_5}{d\theta}+2i\delta a_5=0, \tag{43}$$

$$\frac{1}{\cos\theta}\frac{da_6}{d\theta}-i\delta a_6(1+3\cos 2\theta)+i\delta a_2\sin 2\theta=0, \tag{44}$$

$$\frac{1}{\cos\theta}\frac{da_2}{d\theta}-i\delta a_2(1-3\cos 2\theta)+i\delta a_6\sin 2\theta=0, \tag{45}$$

where

$$\delta=e^2\bar{r}^2/\hbar vR^2; \tag{46}$$

$\bar{r}$ is the matrix element of r between the $L=0$ and the $L=1$ quantum states.

The state represented by a_5 follows the adiabatic equation rigorously. For states a_2 and a_6 we may find a first approximation for the change in $a(t)$ as θ increases from $-\pi/2$ to $+\pi/2$. Let a_{s0} denote the initial value of a_s; remembering (33), we see that when the change in a_s is small, $\sin\phi_s$ may be replaced by ϕ_s. A simple integration yields

$$\phi_5=2i\delta a_{50};\quad \phi_6=2i\delta a_{60};\quad \phi_2=0. \tag{47}$$

Since the number of encounters per second closer than a fixed R is proportional to R^2 it is also proportional to $1/\delta$, as we see from (46). Hence if we substitute for δ from (47), setting each ϕ_s equal to unity, and equating a_{50} to a_{60}, we see that

$$\Sigma_s\Omega_s=(2+2+0)K=4K, \tag{48}$$

where K is a constant.

On the adiabatic approximation, however, one finds to the same approximation

$$\Sigma_s\Omega_s=(2+2+4)K=8K. \tag{49}$$

We see that $J(x)$ will be less than calculated on the adiabatic approximation by a factor of two. This error is not very large compared to the other uncertainties in the analysis. This decreased value of $J(x)$ arises directly from the fact that resonance forces are zero on the average and tend accordingly to cancel out even in a single encounter. A similar effect of comparable magnitude has been pointed out in II for the hydrogen lines, where again the perturbations occur in the first approximation. The neglect of the more distant collisions, which for hydrogen can become very important, is not serious here.

Higher exponents in the perturbation formula q_s/r^n correspond primarily to second approximations, and give perturbations which do not cancel out on the average. For such perturbations, in fact, the average algebraic value of the perturbation energy, taken over all states, should be approximately equal to the root mean square value. One may therefore expect the Weisskopf formula to hold more accurately for dispersion and van der Waals forces than for resonance ones.

A comparison of theory with experiment would of course be desirable. A lack of accurate knowledge of the matrix elements involved makes such a check difficult for the most part. In the case of resonance forces, however, a comparison is ideally possible. It is well known that in such a case the statistical and the adiabatic impact formulas lead to essentially the same result, independently of the velocity.[13] Hence the true impact dispersion curve should lie somewhat below the statistical one.

Unfortunately the statistical formula for this case holds even when $|\nu-\nu_0|$ is very small, corresponding to a wave-length difference of about a tenth of an angstrom. If we set q equal to $e^2\hbar f/4\pi m\nu_0$ in (37) and assume that v does not exceed 10^5 cm/sec., we find that $|\Delta\lambda|$ must not exceed $0.30Pf^{-\frac{1}{2}}$ angstrom unit or the K resonance line, if the broadening is to follow the impact laws with a relative error not greater than P. Since the oscillator strength f is nearly unity for such lines it is clear that impact broadening is relevant only to the core of the line; i.e., roughly a tenth of an angstrom on each side of the center. Since the width produced by Doppler broadening is of the same order of magnitude, an experimental test of the present theory would be difficult but not impossible. Accurate observations with high dispersion should show significant deviations from the normal line con-

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[13] H. Margenau and W. W. Watson, reference 2, pp. 41, 43.

tour given by integrating a dispersion curve over a Doppler curve. The measurements would have to be carried out at low pressures to eliminate the effect of multiple encounters which would otherwise be important in the line core.

4.

In the hydrogenic case an exact solution may be given for the profile of the line perturbed by a single encounter between the atom and an ion. The analysis has, therefore, considerable theoretical interest. In previous papers[7, 8] by the author the "rotation effect" was not considered. The results in I are correct for large and small ϕ, however, since when δ is small the equations derived for a stationary coordinate system in Section 3-I provide a check on the formulas used, while for large δ the statistical theory is valid. For intermediate values of δ, on the other hand, the results must be slightly changed.

Let us consider as before the first excited state of the hydrogen atom. Following the notation of Section 2-I we may let ψ_1, ψ_2, ψ_3, and ψ_4 represent the states in which k_1, k_2, and m are equal to 100, 001, 00–1, and 010, respectively. These functions are taken in a rotating coordinate system and are the eigenfunctions on the adiabatic approximation. The solution of Eqs. (46-I) is still valid, and shows that the a_s have the form $\exp i\sigma\theta$, $\exp -i\sigma\theta$, and a constant, where

$$\sigma^2=1+\delta^2 \tag{50}$$

and

$$\delta=-\frac{e^2z_{11}}{\hbar vR}=\frac{\phi_1}{\pi}. \tag{51}$$

More specifically the complete Ψ function may be expressed in the form

$$\begin{aligned}\Psi=&A_1\times(e^{i\sigma\theta}/2\sigma)\left\{\frac{i}{\sigma-\delta}\psi_1-\frac{i}{\sigma+\delta}\psi_4+\psi_2+\psi_3\right\}\\ &+A_2\times2^{-\frac{1}{2}}\{\psi_2-\psi_3\}\\ &+A_3\times(2^{-\frac{1}{2}}/\sigma)\{i(\psi_1+\psi_4)-\delta(\psi_2+\psi_3)\}\\ &+A_4\times(e^{-i\sigma\theta}/2\sigma)\left\{-\frac{i}{\sigma-\delta}\psi_1\right.\\ &\left.\qquad+\frac{i}{\sigma+\delta}\psi_4+\psi_2+\psi_3,\right\},\end{aligned} \tag{52}$$

where the A_s are constants such that the sum of the squares of their absolute values is unity. One must next take the matrix components of $i(z+ix)e^{i\theta}$, $i(z-ix)e^{-i\theta}$, and y, which equal $z+ix$, $z-ix$, and y, respectively, in stationary coordinates. The line profile may be computed in a manner similar to that used in I, and in place of (20-I) and (21-I), we find

$$J(x)=\frac{\Gamma}{2\pi x^2}\left\{6+\frac{\Omega(\delta,\,\xi)}{\Gamma}\delta^2\{g_\sigma{}^2(\xi)+g_\sigma{}^2(-\xi)\}\right\}, \tag{53}$$

where ξ equals xR/v and

$$g_\sigma{}^2(\xi)=\frac{\delta^2\{\frac{1}{2}f_{\sigma+1}{}^2(\xi)+\frac{1}{2}f_{\sigma-1}{}^2(\xi)\}+f_1{}^2(\xi)}{\delta^2+1}; \tag{54}$$

and, as before,

$$f_\delta(\xi)=\int_{-\infty}^{+\infty}\frac{e^{i(\xi u-\delta\tan^{-1}u)}}{1+u^2}du. \tag{55}$$

Other symbols have the same meaning as in I. Formula (53) includes the effect of all four components of $L\alpha$; if (21-I), which applies to only a single component, is summed over all four, a formula identical with (53) is found, except that $g_\sigma(\xi)$ is replaced by $f_\delta(\xi)$ or, in accordance with Section 2-I, by $f_\sigma(\xi)$. The function $f_\delta(\xi)$ is shown graphically in Fig. 1 of I.

The rotation effect manifests itself here in two ways. In the first place it replaces $f_\sigma{}^2(\xi)$ by the average of $f_{\sigma+1}{}^2(\xi)$ and $f_{\sigma-1}{}^2(\xi)$. In the second place it introduces the term $f_1{}^2(\xi)/\sigma^2$, arising from the state function of which A_3 is the coefficient in (52). This state is completely unperturbed in the rotating coordinate system. Yet it is responsible for all the impact broadening when δ is small, and for $\frac{2}{3}$ of it when δ is greater than unity! This case is unusual, however, and can arise only when most of the transitions between two levels are between such "unperturbed" states,—in this case such transitions make up $\frac{2}{3}$ the total number. Formulas (53) and (54) may also be derived, of course, from a consideration of the functions in a stationary coordinate system.

The replacement of $f_\sigma(\xi)$ by $g_\sigma(\xi)$ decreases the contributions of states A_1 and A_4 to the line profile, however, almost as much as it increases that of state A_3; as a result the observable profiles given in II are changed only in detail. This result arises from the fact that $g_\infty(\xi)$ and $g_1(\xi)$ are equal to $f_\infty(\xi)$ and $f_1(\xi)$, respectively. For intermediate values of σ the difference between $f_\sigma(\xi)$ and $g_\sigma(\xi)$ will not be very large, and we may as before take for $L(x, u)$ the two asymptotic forms; these now become

$$L(x, u)=\pi u^{\frac{1}{2}}/\gamma_1^{\frac{1}{2}} \tag{56}$$

for large u,—the same as (22a-II),—and for small u,

$$L(x, u)=4 \ln u/\gamma_1+3.77. \tag{57}$$

This substitution of 3.77 for -0.69 in the asymptotic form of $L(x, u)$ changes somewhat the final results for $H'(x)$. In particular the values of $H(x)$ when γ_1 is of unit order of magnitude or when γ_2 is only slightly less than unity may differ considerably from those given in II. The asymptotic results portrayed in Fig. 2–II, however, should still be correct within at least twenty percent.

These results are valid for the lowest Lyman line. For higher lines a separate investigation would be required for rigorous results. The main features of Fig. 2-II depend primarily, however, on the two asymptotic results,—for δ large and for δ small,—which are known to be correct for all the hydrogen lines. The results of II, summed over all components of each line, may therefore be applied to all hydrogen or hydrogenic lines.

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The Phenomenological Theory of Superconductors

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Proceeding from the idea that the superconducting electrons are free, classical particles under the influence solely of the electric field, London found it necessary to make an integration constant vanish arbitrarily in order to obtain agreement with the Meisner effect. A variation principle constructed from the same classical ideas gives the experimental result without resorting to an additional assumption. The very precise, linear approximation results in London's equations; the rigorous theory has the same qualitative character. Unlike Mie's theory, the present theory has a satisfactory gauge invariance.

THE LONDON THEORY

THE first attempt to formulate a system of equations for a superconducting medium proceeded from the assumption that the conduction electrons are free, classical particles under the influence solely of the electric field. According to this idea, the Maxwell equations for the fields are to be supplemented by the Newtonian force equation for each electron. It is assumed that the dielectric constant and the magnetic susceptibility are unity since this is very nearly true for the metals in their normally conducting states. The equations are then:

$$\nabla\times\mathbf{H}-\mathbf{E}'=\mathbf{J}, \quad \nabla\cdot\mathbf{E}=\rho, \tag{1}$$

$$\nabla\times\mathbf{E}+\mathbf{H}'=0, \quad \nabla\cdot\mathbf{H}=0, \tag{2}$$

$$m(dVi/dt)=-eE. \tag{3}$$

The summation of the Newtonian Eqs. (3) over the N conduction electrons per unit volume gives the macroscopic equation

$$\mathbf{E}-\lambda\mathbf{J}'=0, \quad \lambda=\frac{1}{N}\cdot\frac{m}{e^2}=\left(\frac{10^{23}}{N}\right)\cdot 10^{-11}\ \mathrm{cm}^2. \tag{4}$$

This equation is in agreement with the experimental finding that e.m.f.'s are required not to maintain a current but only to change one. Its substitution in the second Maxwell equation results in

$$\frac{\partial}{\partial t}(\mathbf{H}+\lambda\nabla\times\mathbf{J})=0 \quad \text{or} \quad \mathbf{H}+\lambda\nabla\times\mathbf{J}=\mathbf{H}_0(x), \tag{5}$$

where $\mathbf{H}_0(x)$ is independent of the time. Now, since λ is very small, $\mathbf{H}(x, t)-\mathbf{H}_0(x)$ is practically