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Imprisonment of Resonance Radiation in Gases

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It is known that resonance quanta are highly absorbable by normal atoms of the emitting gas; hence, under suitable conditions of gas density the eventual escape of these quanta from a gas-filled enclosure may require a large number of repeated absorptions and emissions. This "radiative" transport of excitation is determined essentially by the probability, $T(\rho)$, that a quantum traverses a layer of gas of thickness, ρ, without being absorbed; the dependence of $T(\rho)$ on the frequency distribution of the resonance line is investigated, and explicit expressions are derived for the cases of Doppler and dispersion broadening. The general transport problem is formulated in terms of a Boltzmann-type integro-differential equation involving $T(\rho)$; the variational method of obtaining steady-state solutions of this equation is discussed. The theory is then applied to the evaluation of the rate of decay of excitation in an infinite slab; the results are compared with Zemansky's measurements of the decay of radiation from an enclosure of mercury vapor. Finally, the application of the theory to a number of problems concerning excited atoms is discussed briefly.

I. INTRODUCTION

The term "resonance" is applied to radiation emitted by an atom in an optical transition from an excited state to the ground state. Examples of such radiation are the sodium doublet (5890, 5896A) and the mercury lines 2537A and 1849A. In contrast to other components of atomic spectra which are emitted in transitions between excited states, the resonance lines are highly absorbable by the gas in its normal state. For instance, in mercury at 1 mm the 2537A line is appreciably absorbed in a distance of the order of 0.001 cm. Other resonance lines are similarly absorbed by small layers of gas.

Under such conditions, it is clear that when a resonance quantum is emitted by an individual atom, it is by no means assured an unimpeded transit to the walls of the enclosure. On the contrary, after traversing a short distance, it is most probably absorbed by another atom, thereby raising the latter to the state originally excited. The result of this process of emission and reabsorption is merely the transfer of excitation energy from atom to atom; the eventual escape of the radiation to the boundary of the enclosure may require a large number of such transfers. In such cases we speak of the radiation as being "imprisoned."

The first theoretical treatment of this phenomenon was given by K. T. Compton.[1] Regarding the transfer of excitation as a type of Brownian motion, Compton obtained, in effect, a diffusion-type equation for the density of excited atoms, n:

$$\partial n/\partial t = D\nabla^2 n, \tag{1.1}$$

with D given in terms of the mean free path of the quantum, λ, and the lifetime of the individual atom, τ, by the relation

$$D = \lambda^2/3\tau. \tag{1.2}$$

In order to compare (1.1) with the conventional kinetic theory expression

$$D = \lambda\bar{v}/3, \tag{1.3}$$

we must take into account an important difference between the motions of resonance quanta and material particles. Namely, in the latter case, the time of collision is always small compared to the mean time *between* collisions, whereas, in the case of quanta, even if one assures λ to be of the order of the dimensions of the enclosure $\sim$1 cm, the time between collisions is much smaller than the time of collision, which for quanta is the lifetime of the excited state, $\tau \sim 10^{-8}$ sec. Denoting by τ' the mean time between collisions, we have the general relation

$$\bar{v} = \lambda/(\tau+\tau'). \tag{1.4}$$

For the case of material particles

$$\bar{v} = \lambda/\tau', \tag{1.5}$$

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[1] K. T. Compton, Phys. Rev. 20, 283 (1922).

whereas, for quanta

$$\bar{v}=\lambda/\tau. \qquad (1.6)$$

Inserting (1.6) into (1.3), we obtain (1.2).

It should be emphasized that the essential feature of the treatment is the assumption of a definite mean free path, λ, for the motion of resonance quanta. This means that the probability of a quantum penetrating a distance ρ in the gas before being absorbed is given by an exponential law, $e^{-\rho/\lambda}$, which, in turn, is true only if the absorption coefficient of the gas varies little over the frequency spectrum of the resonance quantum. Because of the highly selective character of the absorption, however, we expect precisely the opposite; namely, the absorption coefficient varies appreciably over the frequency spectrum of the radiation. Thus, the value of λ to be inserted into (1.2) is uncertain; in fact, as the analysis given below will demonstrate, it is impossible to define a mean free path for the motion of resonance quanta.

The problem was next attacked by Milne,[2] who also assumed the existence of a mean free path. His results were not much different from Compton's.

A noteworthy advance was achieved by Kenty[3] who took the frequency spectrum of the line into account. Assuming a Doppler line to be emitted by each volume element of the gas, he attempted to calculate an average diffusion coefficient essentially by averaging (1.2) over the spectrum of the emitted radiation, but arrived at the surprising result that for an enclosure of infinite size this average was infinite, i.e., one could not define a diffusion coefficient for an infinite region. In treating the finite case Kenty still assumed that the decay was capable of description by a diffusion equation of the type (1.1) and confined himself to calculating an effective coefficient, D. Since, as will be shown below, the phenomenon cannot be formulated in terms of a diffusion equation, D could only be calculated to an order of magnitude. The results, nevertheless, are in fair agreement with those of the more exact theory, to be presented below, and with experimental results[4] over a limited range of pressure.

II. TRANSMISSION OF RESONANCE RADIATION

The essential feature of the treatment presented in this report is the determination of the probability, $T(\rho)$, of the radiation traversing a distance ρ. Once $T(\rho)$ is known, we can readily set up equations describing the transfer of excitation between different volume elements of the enclosure. The basis of Compton's treatment, for example, is the assumption of a uniform absorption coefficient, $1/\lambda$, so that in his case

$$T(\rho)=e^{-\rho/\lambda}. \qquad (2.1)$$

Since, however, the absorption coefficient of the medium, $k(\nu)$, is actually a sensitive function of the frequency in the spectral domain of the resonance radiation, we must average the monochromatic transmission factor:

$$T(\rho,\nu)=e^{-k(\nu)\rho}$$

over the frequency spectrum $P(\nu)$ of the radiation emitted from a given volume element, i.e.,

$$T(\rho)=\int P(\nu)e^{-k(\nu)\rho}d\nu. \qquad (2.3)$$

Equation (2.3) is a crucial formula in our treatment; we therefore discuss it in some detail.

The absorption coefficient $k(\nu)$ is a characteristic of the gas in its normal state. The frequency variation of $k(\nu)$ is dealt with extensively in standard texts.[5] The different forms which it can assume are as follows:

(1) Natural absorption. This type of absorption is characteristic of isolated atoms at rest. The coefficient is given by the "dispersion" formula

$$k(\nu)=\frac{C}{1+[4\pi(\nu-\nu_0)/\gamma]^2}, \qquad (2.4)$$

where ν is the impressed frequency, ν_0 the frequency at which $k(\gamma)$ is a maximum, and γ the reciprocal of the lifetime of the excited state, i.e., the probability per unit time that an excited atom radiates. C is a constant characterized by the density of normal atoms, N, the wave-length of radiation $\lambda_0=c/\nu_0$, and γ; it may be determined

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[2] E. A. Milne, J. Lond. Math. Soc. 1, 1 (1926).

[3] C. Kenty, Phys. Rev. **42**, 823 (1932).

[4] M. W. Zemansky, Phys. Rev. **42**, 843 (1932).

[5] A. C. G. Mitchell and M. W. Zemansky, *Resonance Radiation and Excited Atoms* (The Macmillan Company, New York, 1934), to be referred to hereafter as MZ.

from a very general expression derivable from thermodynamic principles (cf. MZ pages 95–96, formula (28)).

$$\int k(\nu)d\nu=\frac{\lambda_0^2}{8\pi}\frac{g_2}{g_1}\frac{N}{\tau}, \qquad (2.5)$$

where g_1 and g_2 are the statistical weights of the normal and excited atomic energy levels, and $\tau=1/\gamma$. One readily obtains for C the value

$$C=\frac{\lambda_0^2 N}{2\pi}\frac{g_2}{g_1}. \qquad (2.6)$$

In the great majority of cases, natural absorption is unimportant because of the frequency broadening of the absorption line arising from the motion and mutual interaction of the atoms; these effects are described immediately below.

(2) Doppler-broadened absorption. This absorption prevails when the Doppler shift, because of the motion of the atoms, is large compared to the natural width. Each atom may be considered as capable of absorbing a single frequency for a given velocity of the atom and direction of propagation of the incident quantum. This frequency, ν, is given by the well-known relation

$$\nu=\nu_0[1+(v/c)\cos\psi], \qquad (2.7)$$

where ψ is the angle between the directions of motion of the absorbing atom and the quantum. Since the velocity distribution of the atoms is Maxwellian, one can readily obtain the absorption coefficient. This turns out to be (cf. MZ, formulas (32), (34), and (35)):

$$k(\nu)=k_0\exp[-(\nu-\nu_0/\nu_0)^2(c/v_0)^2], \qquad (2.8)$$

where

$$v_0=(2RT/M)^{\frac{1}{2}}, \qquad (2.9)$$

and

$$k_0=\frac{\lambda_0^3 N}{8\pi}\frac{g_2}{g_1}\frac{1}{\pi^{\frac{1}{2}}v_0\tau}. \qquad (2.10)$$

In (2.9) R is the gas constant per mole, T the absolute temperature, and M the gram-molecular weight of the gas. (2.10) is obtained from (2.8) and (2.5).

(3) Pressure-broadened absorption. This type of absorption arises from the interactions between individual atoms; hence it becomes increasingly important as the pressure is raised. For reviews and literature on this subject the reader is referred to the articles of Weisskopf[6] and Margenau and Watson,[7] and to MZ, Chapter IV, Section II. In many cases the dispersion formula

$$k(\nu)=\frac{C'}{1+[4\pi(\nu-\nu_0)/\gamma_p]^2}, \qquad (2.4')$$

first obtained by Lorentz, is valid. Here γ_p varies directly with the pressure and C' is a constant whose value is determined by (2.5). (2.4′) obtains when the main effect of interaction is collision-like, i.e., when atomic frequencies are affected appreciably in a time interval short compared to the average "free" time, during which the atomic frequencies are perturbed negligibly.

At pressures of the order of atmospheres, or for values of $\nu-\nu_0\gg\gamma_p$, the absorption law often departs considerably from (2.4′). These deviations will not be discussed quantitatively in this paper.

(4) A general relation which takes into account the three types of broadening discussed above is (cf. MZ, Chapter III, Section IIc, Eq. (97))

$$k(\nu)=k_0\frac{a}{\pi}\int_{-\infty}^{+\infty}\frac{\exp(-y^2)}{a^2+(x-y)^2}dy. \qquad (2.11)$$

Here, k_0 is given by $a=(\gamma+\gamma_p)\lambda_0/4\pi v_0$ and $x\equiv[(\nu-\nu_0)/\gamma_0](c/v_0)$. In many cases a is small compared to unity; for these cases and for $x\gtrsim 2$, (2.4) may be written approximately (cf. MZ, Appendix) as

$$k(\nu)/k_0\approx\exp(-x^2)+a/\pi^{\frac{1}{2}}x^2. \qquad (2.12)$$

Equation (2.12) shows that, even for $a\ll 1$, the behavior of the absorption coefficient at large $|x|$, i.e., at the edge of the absorption region, is determined by the dispersion distribution.

We next discuss the frequency spectrum $P(\nu)$ of the radiation emitted from a given volume element. The specification of $P(\nu)$ is not as simple as that of the absorption coefficient $k(\nu)$, since the nature of the excitation is involved. If the system were in temperature equilibrium, the principles of thermodynamics would provide us

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

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

with the simple relation

$$P(\nu)\propto k(\nu), \tag{2.13}$$

which is a form of Kirchhoff's law. In the case at hand, the radiation is certainly not in temperature equilibrium with the gas; nevertheless, if the gas were enclosed within perfectly reflecting walls, we would still be able to consider the system of quanta plus atomic excitation as being in a state of *local* thermodynamic equilibrium, with negligible interaction between it and the mass motion of the atoms. Under such conditions, (2.13) would still be valid. However, in view of the circumstance that, in our case, the radiation leaks out through partially reflecting walls, the thermodynamic argument breaks down; the justification of assumption (2.13) thus requires a special treatment. This treatment is presented in the Appendix, wherein it is shown that the assumption applies to the cases of Doppler and pressure broadening; since these two cases are predominantly encountered in practice, we use (2.13) in the evaluation of $T(\rho)$.

The constant of proportionality in (2.13) is determined with the aid of (2.5). We have, since $\int P(\nu)d\nu=1$,

$$k(\nu)=\frac{\lambda_0{}^2}{8\pi}\frac{g_2}{g_1}\frac{N}{\tau}P(\nu)\equiv\kappa P(\nu). \tag{2.14}$$

For $T(\rho)$ we then obtain the expression

$$T(\rho)=\int P(\nu)e^{-\kappa\rho P(\nu)}d\nu. \tag{2.15}$$

We now evaluate $T(\rho)$ for the two types of spectral distributions: Doppler and dispersion. (1) Doppler distribution. It is convenient to represent the frequency in terms of the variable x defined above, *viz:*

$$x=[(\nu-\nu_0)/\nu_0](c/v_0). \tag{2.16}$$

The normalization of $P(x)$ yields

$$P(x)=\frac{1}{\pi^{\frac{1}{2}}}\exp(-x^2). \tag{2.17}$$

We also obtain

$$k(x)=\kappa P(\nu)=\kappa(\nu_0v_0/c)^{-1}P(x) \\ =k_0\exp(-x^2), \tag{2.18}$$

where k_0 is given by (2.10). Inserting (2.17) and (2.18) into (2.15), we have

$$T(\rho)=\int_{-\infty}^{+\infty}\frac{1}{\pi^{\frac{1}{2}}}e^{-x^2}\exp[-k_0\rho e^{-x^2}]dx. \tag{2.19}$$

To obtain $T(\rho)$ for all values of $k_0\rho$, recourse must be had to numerical integration. However, for many purposes, the asymptotic value of $T(\rho)$ for large $k_0\rho$ suffices. To find this value we first change the variable according to the transformation

$$x=(\log k_0\rho/y)^{\frac{1}{2}} \tag{2.20}$$

and obtain

$$T(\rho)=\frac{1}{k_0\rho\pi^{\frac{1}{2}}}\int_0^{k_0\rho}\frac{e^{-y}dy}{(\log k_0\rho-\log y)^{\frac{1}{2}}}. \tag{2.21}$$

Since the effective region of integration is limited to values of y of the order of magnitude unity, we may, for large values of $k_0\rho$, approximate $(\log k_0\rho-\log y)^{\frac{1}{2}}$ by $(\log k_0\rho)^{\frac{1}{2}}$ and extend the upper limit of integration to infinity. Thus

$$T(\rho)\approx 1/k_0\rho(\pi\log k_0\rho)^{\frac{1}{2}}. \tag{2.22}$$

(2) Dispersion distribution. We associate this distribution with pressure broadening, since natural broadening is in most cases negligible. The normalized distribution may be written as

$$P(u)=\frac{1}{\pi}\frac{1}{1+u^2}, \tag{2.23}$$

where

$$u=4\pi(\nu-\nu_0)/\gamma_p. \tag{2.24}$$

We have

$$k(u)=\kappa P(\nu)=\frac{4\pi\kappa}{\gamma_p}P(u)=\frac{\lambda_0{}^2N}{2}\frac{g_2}{g_1}\frac{\gamma}{\gamma_p}P(u),$$

or

$$k(u)=k_d/(1+u^2), \tag{2.25}$$

with

$$k_d=\frac{\lambda_0{}^2N}{2\pi}\frac{g_2}{g_1}\frac{\gamma}{\gamma_p}. \tag{2.26}$$

Inserting (2.23) and (2.25) into (2.15), and transforming the variable of integration according to (2.24), we obtain

$$T(\rho)=\frac{1}{\pi}\int_{-\infty}^{+\infty}\frac{\exp[-k_d\rho/(1+u^2)]}{1+u^2}du. \tag{2.27}$$

The integral of (2.27) can be evaluated for all values of $k_d\rho$ in terms of modified Bessel functions of zero order; however, for our purposes the asymptotic form for large $k_d\rho$ alone is necessary. Now, for $k_d\rho \gg 1$, the effective region of integration is $u^2 \gg 1$, hence

$$T(\rho) \approx \frac{1}{\pi}\int_{-\infty}^{+\infty} \frac{1}{y^2} \exp(-k_d\rho/u^2)du$$

$$= \frac{2}{\pi}\int_0^{\infty} \exp(-k_d\rho y^2)dy,$$

i.e.,

$$T(\rho) \approx 1/(\pi k_d\rho)^{\frac{1}{2}}. \tag{2.28}$$

Equations (2.22) and (2.28) describe the asymptotic variation of $T(\rho)$ for the cases of Doppler and dispersion distributions, respectively. Since both of these forms differ considerably from the exponential variation of Compton's theory, as given by (2.1), it is obvious that the simple kinetic theory concept of mean free path cannot be applied to quanta.

One way of defining the mean free path is via the introduction of the probability, $K(\rho)d\rho$, that the quantum is captured after traversing a distance between ρ and $\rho+d\rho$ from its emission point. The mean free path, λ, may then be defined as

$$\lambda = \int_0^{\infty} \rho K(\rho)d\rho. \tag{2.29}$$

Now, from elementary laws of probability,

$$K(\rho)d\rho = T(\rho) - T(\rho+d\rho) = -d\rho\partial T/\partial\rho, \tag{2.30}$$

so that

$$\lambda = -\int_0^{\infty} \rho\frac{\partial T}{\partial\rho}d\rho. \tag{2.31}$$

If we, for instance, insert the exponential form (2.1) into (2.31), we obtain an identity. On the other hand, (2.22) or (2.28) both give divergent results. Thus, in the case of Doppler or dispersion spectral distributions, a mean free path cannot be defined.

It can be shown easily that this conclusion holds for an arbitrary spectral distribution $P(\nu)$ which is related to the absorption coefficient $k(\nu)$ of the medium by the relation (2.14). We have, from (2.31) and (2.15),

$$\lambda = \int\int_0^{\infty} P(\nu)\frac{\partial(e^{-\kappa\rho P(\nu)})}{\partial\rho}d\nu d\rho = \int \frac{1}{\kappa}d\nu, \tag{2.32}$$

which diverges, q.e.d.

III. TRANSPORT OF EXCITATION BY RESONANCE RADIATION

The impossibility of defining a mean free path for resonance quanta forces us to relinquish the hope of describing the radiative transport of excitation by a diffusion equation. An adequate description, however, can be achieved by a Boltzmann-type integro-differential equation, which we now derive.

We introduce the probability $G(\mathbf{r}', \mathbf{r})d\mathbf{r}$ that a quantum emitted at $\mathbf{r}'$ is absorbed in a volume element $d\mathbf{r}$ around the point $\mathbf{r}$. Denoting the density of excited atoms by $n(\mathbf{r})$, we have, from the law of conservation of particles,

$$dtd\mathbf{r}\partial n(\mathbf{r})/\partial t = a - b, \tag{3.1}$$

where a and b are the increase and decrease in the number of excited atoms in volume element $d\mathbf{r}$ in time dt. For b we have immediately

$$b = \gamma n(\mathbf{r})d\mathbf{r}dt. \tag{3.2}$$

To obtain a, we must sum over the contributions of all other volume elements. The contribution of $d\mathbf{r}'$ is given by the number of quanta emitted therein in time dt, $\gamma n(\mathbf{r}')d\mathbf{r}'dt$, multiplied by the probability of any one of these quanta being captured in $d\mathbf{r}$, $G(\mathbf{r}', \mathbf{r})d\mathbf{r}$. Integrating over these volume elements, we obtain

$$a = \gamma dtd\mathbf{r}\int n(\mathbf{r}')G(\mathbf{r}', \mathbf{r})d\mathbf{r}'. \tag{3.3}$$

In the derivation of (3.3) we have implicitly assumed that the time of flight of quanta, τ', is negligibly small compared to the atomic lifetime, τ (cf. discussion following Eq. (1.3) of text and preceding Eq. (19A) of Appendix). Inserting (3.2) and (3.3) into (3.1), we arrive at the integral equation

$$\partial n(\mathbf{r})/\partial t = -\gamma n(\mathbf{r}) + \gamma\int n(\mathbf{r}')G(\mathbf{r}', \mathbf{r})d\mathbf{r}', \tag{3.4}$$

where the integral is taken over the volume of the enclosure. (It is here assumed that the walls are non-reflecting.)

Our next step is the specification of $G(\mathbf{r}', \mathbf{r})$ in terms of $T(\rho)$. We require the assumption of isotropic emission. The assumption is valid provided the excited atoms are unpolarized. This situation seems quite likely in view of the large number of absorptions and randomly directed emissions which the average quantum undergoes. In fact, as is stated in MZ, Chapter IV, imprisonment has a strong depolarizing effect on resonance radiation emanating from a region originally excited by a polarized beam. Thus we feel justified in considering polarization effects to be of secondary importance, to be included, perhaps, in a future treatment more refined than that given here.

The assumption of isotropic emission means that the probability of the quantum being propagated in a direction circumscribed by a solid angle $d\omega$ is $d\omega/4\pi$. The probability, then, that it is absorbed in a volume element defined by $d\omega$ and by spheres of radius ρ and $\rho+d\rho$ from the emission point is

$$(1/4\pi)K(\rho)d\omega d\rho,$$

whence we see that, with $\boldsymbol{\varrho}=\mathbf{r}-\mathbf{r}'$, $d\mathbf{r}=\rho^2 d\rho d\omega$, $G(\mathbf{r}, \mathbf{r}')d\mathbf{r}'=G(\boldsymbol{\varrho})d\boldsymbol{\varrho}=(1/4\pi\rho^2)K(\rho)d\rho$, or from (2.30)

$$G(\mathbf{r}, \mathbf{r}')=-(1/4\pi\rho^2)(\partial T/\partial\rho). \tag{3.5}$$

Equation (3.5) shows how the whole problem of the space-time variation of the density of excited atoms is referred back to the nature of the transmission coefficient $T(\rho)$. In this connection it may be pointed out that Compton's diffusion equation can be obtained from (3.4) and (3.5) and the exponential form of $T(\rho)$ given in (2.1) by the Fokker-Planck expansion.[8] In our case, however, in view of the form of $T(\rho)$ as given either by (2.22) or (2.28), we cannot perform this expansion and must hence deal with (3.4) directly.

We first observe that there exist solutions of the type

$$n(\mathbf{r}, t)=n(\mathbf{r})e^{-\beta t}, \tag{3.6}$$

with β and $n(r)$ satisfying the equation

$$(1-\beta/\gamma)n(\mathbf{r})=\int G(\mathbf{r}', \mathbf{r})n(\mathbf{r}')d\mathbf{r}', \tag{3.7}$$

which is a homogeneous integral equation of a standard type treated, e.g., in Courant-Hilbert, Chapter III.[9] We further observe that, in view of (3.5), $G(\mathbf{r}', \mathbf{r})$ is symmetrical in the variables $\mathbf{r}'$ and $\mathbf{r}$, i.e.,

$$G(\mathbf{r}, \mathbf{r}')=G(\mathbf{r}', \mathbf{r}). \tag{3.8}$$

This feature permits us to formulate the problem variationally as is shown in the cited reference.[9] We have, namely,

$$\frac{\beta}{\gamma}=1-\frac{\int\int G(\mathbf{r}, \mathbf{r}')n(\mathbf{r})n(\mathbf{r}')d\mathbf{r}d\mathbf{r}'}{\int n^2(\mathbf{r})d\mathbf{r}}, \tag{3.9a}$$

$$\delta(\beta/\gamma)=0. \tag{3.9b}$$

The application of (3.9b) to (3.9a), with use of (3.8), yields (3.7), as the reader may readily verify.

It can also be shown that β/γ is positive-definite, i.e., its minimum value obtained by applying the variational procedure is positive. One obtains, after some algebraic manipulation,

$$\frac{\beta}{\gamma}=\frac{\int n^2(\mathbf{r})E(\mathbf{r})d\mathbf{r}+\frac{1}{2}\int\int[n(\mathbf{r})-n(\mathbf{r}')]^2G(\mathbf{r}, \mathbf{r}')d\mathbf{r}d\mathbf{r}'}{\int n^2(\mathbf{r})d\mathbf{r}}, \tag{3.10}$$

where

$$E(\mathbf{r})=1-\int G(\mathbf{r}, \mathbf{r}')d\mathbf{r}'; \tag{3.11}$$

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[8] A. D. Fokker, Ann. d. Physik **43**, 812 (1914); M. Planck, Sitz. Preuss. Akad. Wiss. 324 (1917); S. Chandrasekhar, Rev. Mod. Phys. **15**, 1 (1943), Chapter II, Section 4.

[9] R. Courant and D. Hilbert, *Methoden der Mathematischen Physik* (Verlag, Julius Springer, Berlin, 1931).

the domain of integration in all cases is the volume of the enclosure. Since $\int G(\mathbf{r}, \mathbf{r}')d\mathbf{r}'$ gives the total probability of a quantum emitted at $\mathbf{r}$ being caught somewhere in the enclosure, $E(\mathbf{r})$ is the probability of escape of this quantum. From its definition $E(\mathbf{r})$ is a non-negative quantity. Since $G(\mathbf{r}, \mathbf{r}')$ is also non-negative for all values of $\mathbf{r}$ and $\mathbf{r}'$, both terms of (3.10) are non-negative, i.e., β/γ is positive-definite as claimed above.

The eigenvalues of β_n of (3.7) can thus be arranged in an ascending series of positive numbers. (It is also shown in Courant-Hilbert, Chapter III, that these eigenvalues are denumerable, i.e., discrete.) If $n_n(\mathbf{r})$ denotes the solution of (3.7) corresponding to β_n, the most general solution of (3.4) is of the form

$$n(\mathbf{r}, t) = \sum_n c_n n_n(\mathbf{r}) e^{-\beta_n t}, \tag{3.12}$$

where the c_n are constants depending upon the initial conditions. We observe that, after a sufficiently long time,

$$n(\mathbf{r}, t) \approx c_1 n_1(\mathbf{r}) e^{-\beta_1 t}, \tag{3.13}$$

i.e., the solution corresponding to the lowest eigenvalues, β_1, determines the behavior of $n(\mathbf{r}, t)$ for large t. In what follows, we confine our attention to this solution. We note in passing that $n_1(\mathbf{r})$ must be non-negative for all points $\mathbf{r}$ of the enclosure in order that it may represent a density function.

The method which we employ to obtain the lowest eigenvalue, β, and the corresponding eigenfunction, $n(\mathbf{r})$ (we have dropped the subscript in the notation for both of these quantities) is the Ritz variational procedure. This procedure, in the particular form in which we have applied it, consists in approximating $n(\mathbf{r})$ by a finite series of m terms

$$n(\mathbf{r}) = \sum_1^m a_i n_i(\mathbf{r}), \tag{3.14}$$

where the $n_i(\mathbf{r})$ are m known functions of $\mathbf{r}$ and the a_i are to be determined by the minimizing of β. Substituting (3.14) into (3.10), we obtain

$$\frac{\beta}{\gamma} = \sum_{ij} a_i a_j K_{ij} \Big/ \sum_{ij} a_i a_j H_{ij}, \tag{3.15}$$

where

$$K_{ij} = \int n_i(\mathbf{r}) n_j(\mathbf{r}) E(\mathbf{r}) d\mathbf{r} + \tfrac{1}{2} \int\int [n_i(\mathbf{r}) - n_i(\mathbf{r}')] \times [n_j(\mathbf{r}) - n_j(\mathbf{r}')] G(\mathbf{r}, \mathbf{r}') d\mathbf{r} d\mathbf{r}', \tag{3.16a}$$

and

$$H_{ij} = \int n_i(\mathbf{r}) n_j(\mathbf{r}) d\mathbf{r}. \tag{3.16b}$$

We observe that $K_{ij} = K_{ji}$; $H_{ij} = H_{ji}$. β is now a function of the a_i. The minimum conditions are

$$\partial\beta/\partial a_i = 0. \tag{3.17}$$

Performing the differentiations, we obtain

$$\sum_{j=1}^m \left[a_j K_{ij} - \frac{\beta}{\gamma} H_{ij} \right] = 0; \quad i = 1, 2, \cdots, m. \tag{3.18}$$

In order for Eqs. (3.18) to be solved by a nonzero set of the a_i, the determinant of the coefficients must be zero, i.e.,

$$\begin{vmatrix} K_{11} - \frac{\beta}{\gamma} H_{11} & \cdots\cdots & K_{1m} - \frac{\beta}{\gamma} H_{1m} \\ \vdots & & \vdots \\ K_{1m} - \frac{\beta}{\gamma} H_{1m} & \cdots\cdots & K_{\mathrm{mm}} - \frac{\beta}{\gamma} H_{\mathrm{mm}} \end{vmatrix} = 0. \tag{3.19}$$

(3.19) constitutes an algebraic equation of the m'th order in β/γ, and hence possesses m solutions; of these only the lowest one is of interest. Once β/γ has been obtained, any set of $(m-1)$ equations chosen from the m equation of (3.18) can be used to obtain the ratios a_i/a_1, $i = 2, \cdots, m$. One thus determines $n(\mathbf{r})$ to within a multiplicative constant.

It is shown in Courant-Hilbert, pages 149–151, that the Ritz variational approach gives values of β and $n(\mathbf{r})$ which converge towards the true solution of (3.7) as the number, m, of independent functions $n_i(\mathbf{r})$ and adjustable constants a_i, increases. In particular, each addition of a new term involving an adjustable constant to the series (3.14) for $n(\mathbf{r})$ brings both β and $n(\mathbf{r})$ closer to the true solution.

The number of terms which must be chosen to obtain accurate results for β and $n(\mathbf{r})$ depends upon the suitability of the $n_i(\mathbf{r})$ with regard to the representation of the true solution. In many cases the use of two well chosen functions suffices to give values of β which are good to one percent.

It is known that $n(\mathbf{r})$ is not determined as accurately as is β by the Ritz method. Nevertheless, if β is accurate to one percent, $n(\mathbf{r})$ is expected not to deviate too radically from the true function. Indications from calculations of specific cases are that this expectation is fulfilled.

IV. DECAY OF EXCITATION IN AN INFINITE SLAB

We now apply the theory presented above to the calculation of the decay of excitation in a one-dimensional enclosure of gas. The enclosure is in the form of a slab of thickness L, with the other two dimensions infinite. The density of excited atoms is now a function $n(z)$ of the coordinate, z, perpendicular to the walls of the slab. We choose the origin to bisect the perpendicular between the walls so that the coordinates of the latter are $z=\pm L/2$. Equation (3.7) can be simplified by integration over the x and y coordinates, both of which are parallel to the walls. We obtain, after some algebraic manipulation,

$$(1-\beta/\gamma)n(z)=\int_{-L/2}^{+L/2} n(z')H(|z-z'|)dz', \tag{4.1}$$

where

$$H(\zeta)=-\partial\mathcal{E}(\zeta)/\partial\zeta, \tag{4.2}$$

and

$$\mathcal{E}(\zeta)=\frac{1}{4\pi}\int_0^{\pi/2}\int_0^{2\pi} T(\zeta\ \sec\theta)\ \sin\theta d\theta d\varphi. \tag{4.3}$$

$\mathcal{E}(\zeta)$ is the probability that a quantum, emitted at an arbitrary point, will cross a plane situated at a distance ζ from that point. The integral of (4.3) represents a summation over all directions of propagation; in this case the integration goes over the solid angle subtended by the plane at the point, i.e., half the total solid angle. θ and ϕ are polar and azimuthal angles taken with respect to the perpendicular from point to plane as polar axis. The distance from point to plane in the direction given by θ and ϕ is $\rho=\zeta\ \sec\theta$.

In (4.1) $H(|z-z'|)dz$ is the probability that a quantum, emitted at z', is absorbed in a layer between the planes z and $z+dz$. Equation (4.2) is then a statement of conservation of probability.

The variational expression for β/γ, corresponding (3.10) reads

$$\frac{\beta}{\gamma}=\frac{\int n^2(z)E(z)dz+\frac{1}{2}\int\int[n(z)-n(z')]^2H(|z-z'|)dzdz'}{\int n^2(z)dz}, \tag{4.4}$$

where

$$E(z)\equiv 1-\int H(|z-z'|)dz'=\mathcal{E}(\tfrac{1}{2}L+z)+\mathcal{E}(\tfrac{1}{2}L-z). \tag{4.5}$$

In these equations, the limits of integration are $z=\pm L/2$.

Calculations have, up to the present, been carried out only for the Doppler spectrum. Here, according to (2.22), the asymptotic form for $T(\rho)$ is

$$T(\rho)\approx 1/k_0\rho(\pi\ \log k_0\rho)^{\frac{1}{2}}.$$

Inserting this expression into (4.3), we obtain

$$\mathcal{E}(\zeta)=\frac{1}{2}\int_0^{\pi} T(\zeta\ \sec\theta)\ \sin\theta d\theta$$
$$\approx\frac{1}{4k_0\zeta(\pi\ \log k_0\zeta)^{\frac{1}{2}}}\approx\frac{1}{4k_0\zeta(\pi\ \log k_0L/2)^{\frac{1}{2}}}. \tag{4.6}$$

Applying (4.6) to (4.5) and (4.2), we obtain

$$H(\zeta)\approx\frac{1}{4k_0\zeta^2}\frac{1}{(\pi\ \log k_0L/2)^{\frac{1}{2}}}, \tag{4.7}$$

and

$$E(z)\approx\frac{1}{4k_0L(\pi\ \log k_0L/2)^{\frac{1}{2}}}\frac{1}{\frac{1}{4}-(z/L)^2}. \tag{4.8}$$

Inserting (4.7) and (4.8) into (4.4), and changing the variable to $\xi=2z/L$, we obtain

$$\beta'=\frac{\int\frac{n^2(\xi)}{1-\xi^2}d\xi+\frac{1}{4}\int\frac{[n(\xi)-n(\xi')]^2}{(\xi-\xi')^2}d\xi d\xi'}{\int n^2(\xi)d\xi}, \tag{4.9}$$

where

$$\beta' = k_0 L(\pi \log k_0 L/2)^{\frac{1}{2}}\beta/\gamma \tag{4.10}$$

and the limits of integration are $\xi = \pm 1$.

In the variational calculation of β' as given by (4.9), linear combinations of the functions

$$\begin{aligned} n_0(\xi) &= 1/2, \\ n_1(\xi) &= (3/4)(1-\xi^2), \\ n_2(\xi) &= (5/8)(1-\xi^4), \end{aligned} \tag{4.11}$$

were used. (The $n_i(\xi)$ are normalized according to the relation

$$\int_{-1}^{+1} n_i(\xi) d\xi = 1, \tag{4.12}$$

as is customary for probability functions.)

The K_{ij} and H_{ij} are, with the exception of K_{∞}, all readily evaluated from the one-dimensional analogs of (3.16a) and (3.16b), which read

$$K_{ij} = \int_{-1}^{+1} \frac{n_i(\xi)n_j(\xi)}{1-\xi^2} d\xi + \frac{1}{4}\int_{-1}^{+1}\int_{-1}^{+1} \frac{[n_i(\xi)-n_i(\xi')][n_j(\xi)-n_j(\xi')]}{(\xi-\xi')^2} d\xi d\xi', \tag{4.13a}$$

$$H_{ij} = \int_{-1}^{+1} n_i(\xi) n_j(\xi) d\xi. \tag{4.13b}$$

The calculation of K_{00} cannot be carried out in this way since (4.13a) gives a divergent result. This divergence owes its origin to our replacement of $T(\rho)$, $\mathcal{E}(\zeta)$, and $E(z)$ by their asymptotic values. The rigorous expression for K_{00} reads (cf. (4.13a), (4.11), and (4.8))

$$K_{00} = \frac{k_0[\pi \log(k_0 L/2)]^{\frac{1}{2}}}{2} \int_{-L/2}^{+L/2} E(z) dz,$$

which, in view of (4.5), may be written as

$$K_{00} = k_0(\pi \log k_0 L/2)^{\frac{1}{2}} \int_{-L/2}^{+L/2} \mathcal{E}(\tfrac{1}{2}L+z) dz. \tag{4.14}$$

For $\mathcal{E}(\frac{1}{2}L+z)$, we have from (4.3) and (2.19),

$$\mathcal{E}(\tfrac{1}{2}L+z) = \int_0^{\pi/2}\int_0^{\infty} \frac{\exp(-x^2)}{\pi^{\frac{1}{2}}} \times \exp[-k_0 \sec\theta(\tfrac{1}{2}L+z)e^{-x^2}] \sin\theta d\theta dx. \tag{4.15}$$

The insertion of (4.15) into (4.14) gives the complete expression for K_{00}. Integrating this expression with respect to z, we obtain

$$K_{00} = (\log k_0 L/2)^{\frac{1}{2}} \int_0^{\pi/2}\int_0^{\infty} \cos\theta \times \{1-\exp[-k_0 L \sec\theta e^{-x^2}]\} \sin\theta d\theta dx. \tag{4.16}$$

We next consider the integration over x. We perform this operation approximately by taking the factor in curly brackets equal to unity for $x < \log^{\frac{1}{2}}(k_0 L \sec\theta)$ and zero for x greater than this value. Thus,

$$K_{00} \approx (\log k_0 L/2)^{\frac{1}{2}} \int_0^{\pi/2} \cos\theta \log^{\frac{1}{2}}(k_0 L \sec\theta) \sin\theta d\theta.$$

We introduce the further approximations of replacing both $\log k_0 L/2$ and $\log(k_0 L \sec\theta)$ by $\log k_0 L$. These approximations partly cancel each other and are also small in magnitude because of the slow variation of the logarithmic factors. We then obtain

$$K_{00} \approx \tfrac{1}{2} \log k_0 L. \tag{4.17}$$

Once the K_{ij} and H_{ij} have been evaluated, β' and the coefficients a_i in the Ritz approximations of $n(\xi)$ are readily obtained by solution of (3.18) and (3.19).

In the first three calculations $n(\xi)$ was successively equated to $n_1(\xi)$, $n_2(\xi)$, and $n_3(\xi)$; the corresponding eigenvalues, β_0', β_1', and β_2', were found to be $2 \log k_0 L$, 15/8, and 15/8, respectively.

Next, the two-parameter combinations

$$\begin{aligned} n_{01}(\xi) &= a_0 n_0(\xi) + a_1 n_1(\xi), \\ n_{02}(\xi) &= a_0 n_0(\xi) + a_2 n_2(\xi), \\ n_{12}(\xi) &= a_1 n_1(\xi) + a_2 n_2(\xi) \end{aligned}$$

were tried; these gave the following expressions for β':

$$\begin{aligned} \beta_{01}' &= (15/8)\left(1 - \frac{1/16}{\log k_0 L - 5/4}\right), \\ \beta_{02}' &= (15/8)\left(1 - \frac{1/48}{\log k_0 L - 3/2}\right), \\ \beta_{12}' &= (15/8)(0.986). \end{aligned} \tag{4.18}$$

Taking for $\log k_0 L$ a typical value, say 5, we have

$$\begin{aligned} \beta_{01}' &= (15/8)(0.983), \\ \beta_{02}' &= (15/8)(0.994), \end{aligned} \tag{4.19}$$

whence we see that, although the best two-parameter result is achieved with $n_{01}(\xi)$, the total improvement over the one-parameter value, 15/8, is only 1.7 percent.

In view of the approximations which have already been introduced in the evaluation of $E(z)$ and $H(\zeta)$, discrepancies of this order of magnitude are rather inconsequential. We therefore omit the calculation of β' for three-parameter function

$$n_{012}(\xi) = a_0 n_0(\xi) + a_1 n_1(\xi) + a_2 n_2(\xi),$$

which can only lead to a small additional improvement of the order of a percent.

The coefficients a_i of the function $n_{01}(\xi)$, which gives the best two-parameter result, are found to be

$$a_0 = \frac{3/8}{\log k_0 L - 3/2}; \quad a_1 = 1 - a_0, \tag{4.20}$$

which, for $\log k_0 L = 5$, give $a_0 = 0.107$; $a_1 = 0.893$. These numbers correspond to a ratio of density at the edge of the container to that in the center

$$n_{01}(\pm 1)/n_{01}(0) = 0.071. \tag{4.21}$$

For the comparison of theory with experiment we ignore the 1.7 percent difference between β_{01}' and β_1' and take $\beta' = 15/8$. The value of β/γ corresponding to this choice is

$$\beta/\gamma = \frac{1.06}{k_0 L (\log k_0 L/2)^{\frac{1}{2}}}. \tag{4.22}$$

V. COMPARISON WITH EXPERIMENT

Although the imprisonment of radiation has been observed in a number of ways, the sole reliable, direct measurement known to the author is that of Zemansky,[10] who obtained β for the 2537A line of Hg as a function of gas density, N. The comparison of his results with the theory of this paper encounters a number of complications.

1. Geometry of the enclosure. The experiment consisted in measuring the decay of radiation from two disks of thickness 1.30 cm and 1.95 cm, both of diameter 5.1 cm. It is obvious that the correspondence of this geometry to the one-dimensional idealization of the theory is only approximate.

2. Hyperfine structure. The theoretical calculations are based upon the assumption that the resonance line is simple. Actually, the 2537A line consists of five, hyperfine structure components. The change in β arising from this structure is analyzed immediately below. The main results of the treatment are: (a), $T(\rho)$ may be considered as the average of the transmission functions, $T_i(\rho)$, of the individual components, each taken as an isolated line, and (b), (4.22) is still approximately valid with the sole modification that k_0 is to be replaced by $k_0/5$.

In the evaluation of $T(\rho)$ the first question which arises is whether the absorption bands of the different components overlap. By "absorption band" we mean a continuous aggregate of frequencies which are appreciably absorbed in the traversal of a layer of length L in the gas. If the absorption bands do overlap, it becomes necessary to consider the composite line structure in detail.

The edge of an absorption band is given roughly by the relation

$$k(\nu)L = 1. \tag{5.1}$$

For the case of Doppler-broadened spectral distributions, we have

$$k_0 L e^{-x^2} = 1,$$

or

$$x = (\log k_0 L)^{\frac{1}{2}}. \tag{5.2}$$

Combining (5.2) with (2.16), we obtain for the half-breadth of the absorption band in frequency units

$$\Delta\nu = \frac{v_0}{c}\nu_0 (\log k_0 L)^{\frac{1}{2}}$$

or in wave-length units

$$\Delta\lambda = \frac{c}{\nu_0^2}\Delta\nu = \lambda_0 \frac{v_0}{c}(\log k_0 L)^{\frac{1}{2}}. \tag{5.3}$$

For mercury at room temperature $v_0 = (2RT/M)^{\frac{1}{2}} = 1.57 \times 10^4$ cm/sec.; with $\lambda = 2537\text{A}$ we obtain

$$\Delta\lambda = (\log k_0 L)^{\frac{1}{2}} 1.33 \text{ mA}. \tag{5.4}$$

Now, in Zemansky's experiments, as will be seen below, the maximum value of $k_0 L$, for which quantitative comparison with the theory is at-

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[10] M. W. Zemansky, Phys. Rev. **20**, 283 (1922).

tempted, is 1000. Since $(\log 1000)^{\frac{1}{2}}=2.67$, we have

$$\Delta\lambda_{\max}=3.5\text{ mA}.$$

On the other hand, the minimum separation of the hyperfine structure lines is about 10 mA (MZ, p. 38, Fig. 12); hence, there is a band of 3 mA between the two components in which negligible absorption takes place.

Actually, the non-overlap of absorption bands is not a sufficient criterion to permit us to consider the hyperfine components as isolated; this can be seen by consideration of the transmission factor $T(\rho)$. For a line possessing hyperfine structure

$$P(\nu)=\sum_i P_i(\nu) \tag{5.5a}$$

and

$$k(\nu)=\sum_i k_i(\nu), \tag{5.5b}$$

where the P_i's and k_i's are the spectral distribution and absorption coefficients of the individual components. We introduce

$$N_i\equiv\int P_i(\nu)d\nu, \tag{5.6a}$$

$$\sum N_i=1. \tag{5.6b}$$

N_i gives essentially the intensity of the i'th hyperfine component. We then have, according to (2.3),

$$T(\rho)=\sum_i N_i T_i'(\rho), \tag{5.7a}$$

where

$$T_i'(\rho)=\int[P_i(\nu)/N_i]\exp[-\sum_j k_j(\nu)\rho]d\nu. \tag{5.7b}$$

Now, if over the range in which $P_i(\nu)$ contributes appreciably to $T(\rho)$, all the $k_j(\nu)\rho$, $j\neq i$, are small compared to unity, we obtain

$$T_i'(\rho)=T_i(\rho), \tag{5.8a}$$

where

$$T_i(\rho)=\int[P_i(\nu)/N_i]e^{-k_i(\nu)\rho}d\nu. \tag{5.8b}$$

$T_i(\rho)$ is the transmission coefficient of an isolated line. We thus have

$$T(\rho)=\sum_i N_i T_i(\rho). \tag{5.9}$$

$T(\rho)$ represents a composite or average transmission factor of all the components. Against the introduction of this average transmission, one might raise the objection that each line ought to be treated separately, so that one should obtain different values of β. The answer to this objection is twofold:

(1) All the lines which emanate from a common state of the atom must actually be averaged since their relative intensities are fixed atomic constants. This is the case of the sodium hyperfine structure.

(2) If different excited states or the excited states of different isotopes are involved, radiationless transfers of excitation energy between all such states will take place readily because of the extremely small energy differences between the levels. For pressures of the order of those involved in Zemansky's experiment, this exchange is much more rapid than the decay rates of the individual resonance lines. Hence the relative concentrations of the excited states are in constant thermodynamic equilibrium. We are thus justified in considering $T(\rho)$ to be the common transmission factor for all the components. Now, for the Doppler broadening, we have

$$k_i(\nu)=k_i\exp[-(x-x_i)^2], \tag{5.10}$$

where x_i denotes the frequency center of the i'th component; with use of (2.14), we obtain

$$k_i=k_0N_i, \tag{5.11}$$

with k_0 given by (2.10). Using the asymptotic formula (2.22) for $T(\rho)$, we find

$$T(\rho)\approx\frac{1}{k_0\rho}\sum_i\frac{1}{(\pi\log N_ik_0\rho)^{\frac{1}{2}}}. \tag{5.12}$$

Now the logarithmic factor is slowly varying; hence, unless the intensities of the different components are very unequal, we may replace N_i by an average without incurring much error. If the number of components is m, we take $N_i=1/m$ and obtain

$$T(\rho)\approx\frac{1}{k_e\rho}\frac{1}{(\pi\log k_e\rho)^{\frac{1}{2}}}, \tag{5.13a}$$

where

$$k_e=k_0/m. \tag{5.13b}$$

Since β is determined by $T(\rho)$, we obtain the correct result by replacing k_0 by k_e in (4.22).

This "averaging" procedure of considering the lines to be of equal strength has been used by Zemansky in evaluating Kenty's theory, as well as in other connections (cf., MZ, p. 234, 125).

We now have to show that the fundamental condition for the validity of (5.8a) and hence of (5.13a), namely, the smallness of $k_j(\nu)\rho$, $i \neq j$, in the region in which $P_i(\nu)$ contributes effectively to $T(\rho)$, prevails in the case at hand. Here, as we have found above, there exists a domain of 3mA between absorption bands. This corresponds to a Δx of 2.2. Now, for $k_eL = 1000$ (the k_0L of the above numerical estimate should be written k_eL), we have for the edge of the absorption band at $x = 2.67$, $\exp(-x^2) = 10^{-3}$. At the edge of the adjacent band $x = 2.67 + 2.2 = 4.89$; the corresponding value of $\exp(-x^2)$ is e^{-24}, which is altogether negligible. The validity of our basic assumption, as expressed by (5.8a), is thus established.

3. Natural broadening. A small correction to (4.22) may arise from natural broadening due to the relatively slow decrease of the dispersion distribution at large x, as is indicated by (2.12) and the discussion immediately following. The correction does not affect the absorption appreciably. Namely, for $k_0\rho$ as high as 1000, the important contributions to $T(\rho)$ come from values of $|x|$ in the neighborhood of $x_1 = (\log k_0\rho)^{\frac{1}{2}} = 2.67$; taking $a_N = \gamma\lambda_0/4\pi v_0 = 0.0011$ (Hg at 90°C), we obtain

$$k_0\rho/\pi^{\frac{1}{2}}x_1^2 = 0.086,$$

which is a small correction to the Doppler absorption, $k_0\rho \exp(-x_1^2) = 1$.

However, if we assume (2.13), i.e., $P(x) \propto k(x)$, the change in $T(\rho)$, $\Delta T_N(\rho)$ is not negligible; we have from (2.12), (2.13), and (2.17)

$$\Delta P_N(x) = a_N/\pi x^2,$$

and hence,

$$\Delta T_N(\rho) = \int_{-\infty}^{+\infty} \exp(-k_0\rho e^{-x^2}) \frac{a_N}{\pi x^2} dx \approx \frac{2a_N}{\pi(\log k_0\rho)^{\frac{1}{2}}},$$

which, in view of the slow variation of the logarithmic factor, may be approximated by

$$\Delta T_N(\rho) = \frac{2a_N}{\pi(\log k_0 L/2)^{\frac{1}{2}}}. \tag{5.14}$$

Since (93) is independent of ρ, $n(z)$ is left unaltered and β is increased by an amount $\Delta\beta_N = \Delta T_N$.

The presence of the hyperfine structure causes a diminution of $\Delta\beta_N$; a rough estimate of this effect gives a reduction factor of 0.8, which, when combined with (5.14), yields

$$\Delta\beta_N \approx \frac{0.5\gamma}{(\log k_0 L/2)^{\frac{1}{2}}}. \tag{5.15}$$

With $a_N = 0.0011$, $\gamma = 10^7$ sec.$^{-1}$, and $\log k_0L/2 = 4$ (corresponding to $k_0L = 110$) we obtain

$$\Delta\beta_N \approx 3 \times 10^3 \text{ sec.}^{-1} \tag{5.16}$$

which, although not negligible, is small as far as the comparison between theory and experiment is concerned.

The above analysis is based on assumption (2.13), the validity of which in the case of natural broadening is rather doubtful. However, it seems quite likely that (2.13) gives at least an upper limit for the contribution of natural broadening to $P(x)$. First of all, the radiation from a given volume element contained in the spectral region $|x| \gtrsim x_1$ possesses a preferentially large escape probability. Secondly, as pointed out in the beginning of the Appendix, the absorption-emission process, in the absence of Doppler shift and pressure-broadening interactions, does not alter frequencies and hence cannot contribute to a replenishment of the dispersion component, $\Delta P_N(x)$, in the spectral region $|x| \gtrsim x_1$. Thus, the actual $\Delta P_N(x)$ may be expected to be smaller than $a_N/\pi x^2$; hence, in our opinion, (5.15) represents an upper limit to the natural broadening correction.

4. Pressure broadening. The detailed treatment of the transition from Doppler to pressure broadening in the case of the 2537A line is quite involved due to the hyperfine structure. Here we discuss only the initial manifestation of this transition.

Assuming an absorption law of the form of (2.12), we may take over the results for natural broadening presented immediately above. In the case of pressure broadening we note that: (a), (2.13) is valid as is shown in the Appendix, and (b), a_N is to be replaced by $a_p = a_N\gamma_p/\gamma_N$.

For γ_p we use the result of Furssov and

Vlassov:[11]

$$\gamma_p = \frac{8\pi}{3} \frac{e^2}{m\omega} fN, \qquad (5.17)$$

where N is the density of atoms and f the "oscillator" strength for the absorption of the resonance line (cf., MZ, page 96). Equation (5.17) assumes the absence of hyperfine structure.

We also have (cf., MZ, page 97)

$$\gamma = \frac{8\pi e^2}{mc} \frac{g_1}{g_2} f/\lambda_0^2.$$

For the 2537A line $g_2/g_1 = 3$; we thus obtain

$$\gamma_p/\gamma = N\lambda_0^3/2\pi^2 = 0.83 \times 10^{-15} N. \qquad (5.18)$$

We now consider the effect of hyperfine structure on the magnitude of γ_p. As in the Appendix, we represent the atoms by classical harmonic oscillators whose natural frequencies coincide with those of the actual resonance lines. In this case we must consider oscillators of five different frequencies corresponding to the five hyperfine components; the density of each type of oscillator is proportional to the intensity of the associated component. Now, for collisions between oscillators of the same natural frequency, the usual phase-shift calculation of impact broadening is valid; the contribution of these collisions to γ_p is of the form of (5.17) with the sole modification that f here represents the oscillator strength for the absorption of one hyperfine component. When, on the other hand, oscillators of different natural frequencies collide, the perturbation of the frequencies of both oscillators by the interaction is reduced; in order for a given phase shift to be achieved, the oscillators must approach closer with the result that the rate of effective collision is diminished.

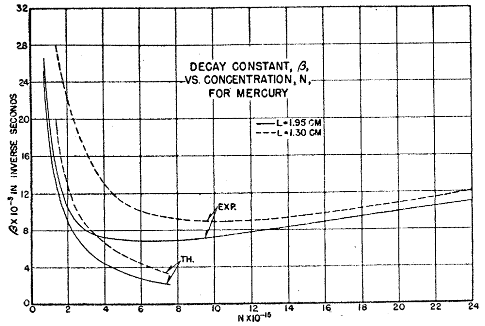

FIG. 1. Decay constant, β, *vs.* concentration, N, for mercury.

A preliminary calculation of this effect indicates that the hyperfine separation cuts down γ_p by a factor of the order of 2. The insertion of this result into (5.18) gives

$$\gamma_p/\gamma \approx \tfrac{1}{2} 10^{-15} N. \qquad (5.19)$$

Combining (5.19) with (5.15), we obtain for the increase in β due to pressure broadening, $\Delta\beta_p$, the order-of-magnitude estimate

$$10^{-3}\Delta\beta_p \approx 1.5(N \times 10^{-15}) \text{ sec.}^{-1}. \qquad (5.20)$$

We now proceed to the comparison of theory with experiment. Since Zemansky has already evaluated k_eL (in his notation, k_0l) as a function of the experimental conditions of gas density, temperature, and slab thickness (MZ, page 234, Table 40), we need only insert these values into (4.22). The resultant theoretical expressions for β are given in Fig. 1 together with Zemansky's experimental results.

We observe that the left-hand portion of the experimental curves agree in order of magnitude with the theoretical prediction. Quantitatively, the agreement for $L = 1.95$ is quite good while that for $L = 1.30$ is not as satisfactory; the reason for the discrepancy in the latter case is not clear.

It should, at this point, be mentioned that Kenty's results show a similar agreement with the left-hand part of the experimental curves (MZ, Table 40).

The slow rise of Zemansky's curves with increasing N for gas densities greater than 10^{16} atoms/cc is not explained by the theory. Two possible causes are: (1) pressure broadening, and (2) non-radiative transitions from the radiating 6^3P_1 state to the metastable 6^3P_0 state 0.218 volt lower.

With regard to the first agency, an order-of magnitude estimate of its initial effect is given by (5.20). According to this equation the increase in β due to pressure broadening becomes appreciable for $N \gtrsim 3 \times 10^{15}$/cc. Beyond $N \sim 7 \times 10^{15}$/cc we encounter the complications associated with the overlap of the absorption bands of the hyperfine components.

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[11] W. Furssov and A. Vlassov, Phys. Zeits. Sowjetunion **10**, 378 (1936).

At densities high enough so that the separation of the components is small compared to the absorption band, we may consider the line to be simple. Assuming a dispersion distribution we have

$$T(\rho) \approx 1/(\pi k_d \rho)^{\frac{1}{2}}, \qquad (2.28)$$

where

$$k_d = (\lambda_0^2 N/2\pi)(g_2/g_1)(\gamma/\gamma_p). \qquad (2.26)$$

Now, γ_p, the line breadth resulting from pressure broadening, varies linearly with N; hence k_d and $T(\rho)$ become independent of the gas density. Since $T(\rho)$ determines the decay factor, β, the latter should also become independent of the density.

It should be pointed out that, at the high density extreme of absorption band large compared to the separation of the components, the absorption band must cover a spectral range at least of the order of 0.2A. Now according to Kuhn,[12] the pressure-broadened spectrum at distances $\gtrsim$0.6A from the center of the line is no longer of the dispersion type. Since in the determination of $T(\rho)$ the important spectral region is in the neighborhood of the edge of the absorption band ~0.1A from the center of the line, the validity of a treatment based on the dispersion distribution is rather doubtful.

Recently[13] the method of nuclear transmutation has been applied to the production of the pure mercury isotope 198, which by itself shows no hyperfine structure since its spin is zero. Experiments with this isotope should prove quite informative, since the complications due to hyperfine structure do not exist.

In this connection, experiments with the sodium D lines would also be of interest since the element exists in only one isotopic form. Both of the lines are split into only two hyperfine components, the separation of which is small compared to the absorption bands which would be encountered in radiation-decay experiments of the type performed by Zemansky. On the other hand, the 6A separation of the D lines themselves permits the avoidance of overlap complications over a large range of pressure. Whether or not the lines decay independently is an additional question which can be investigated both experimentally and theoretically.

With regard to the second possibility for the rise of Zemansky's curves at higher values of N, namely, the radiationless conversion of the radiating state into the metastable state, the sole evidence known to the present author consists of an experiment performed by Orthmann and Pringsheim.* They find that, as the pressure of mercury is raised to about one atmosphere, the diffuse resonance radiation from a chamber illuminated with the resonance line 2537A is almost completely quenched, whereas the radiation of a small admixture of thallium (2×10^{-2} mm), the atoms of which can be excited upon collision with metastable mercury atoms, loses none of its original intensity. These results indicate that the radiating 6^3P_1 state produced by the incident beam is converted to the 6^3P_0 metastable state, which in turn, lives long enough to make a relatively infrequent collision with a thallium atom.

The conversion from radiating to metastable state should be capable of a more direct and quantitative investigation than that of Orthmann and Pringsheim. However, this has not yet to our knowledge been achieved.

In the light of the above discussion, a further advantage of experiments with sodium vapor is that non-radiative quenching of excitation should not take place in sodium since the only level below the resonance level is the ground state 2.1 volts lower in energy. The conversion of this amount of energy into kinetic energy of nuclear motion is extremely unlikely; hence, the decay should be due entirely to the escape of resonance radiation.

VI. ADDITIONAL PROBLEMS

In conclusion we present a brief discussion of additional problems suggested by the theory.

1. Lines of various spectral distributions. The above theory may be amplified to include various types of spectral distributions arising both from pressure broadening and the existence of hyperfine structure. Concerning the dispersion distribution, the first step has already been taken in the derivation of (2.28). As we have remarked above, in the discussion of pressure broadening,

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[12] H. Kuhn, Proc. Roy. Soc. **A158**, 230 (1937).

[13] J. H. Wiens, Phys. Rev. **70**, 910 (1946).

* W. Orthmann and P. Pringsheim, Zeits. f. Physik **35**, 626 (1926).

distributions other than the dispersion distribution occur. Probably the most important is the "statistical" distribution[14] which for large $(\nu_0-\nu)$ is given by the formula

$$P(\nu)=\frac{\frac{2}{3}\pi(-b)^{\frac{1}{2}}N}{(\nu_0-\nu)^{\frac{3}{2}}},$$

in which the sign of $(\nu_0-\nu)$ is opposite to that of b (for $(\nu_0-\nu)b$ positive, $P(\nu)=0$).

The presence of hyperfine structure will, as we have seen above, also give rise to new effects, particularly when the absorption bands overlap.

2. Equilibrium between an excited radiating state and electrons. Here two additional processes must be included.

(a). The creation of excited atoms by electron collision with normal atoms. The contribution of this process to the rate of increase of excitation is given by

$$An_e(\mathbf{r}),$$

where $n_e(\mathbf{r})$ is the electron density and A a constant proportional to the density of normal atoms and otherwise dependent on the cross section for excitation of the level and the energy distribution of the electrons.

(b). The destruction of excited atoms by collisions of the second kind with electrons. The rate of decrease of excitation due to this cause is represented by the term

$$-Bn(\mathbf{r})n_e(\mathbf{r}),$$

where B is a function of the cross section for such collisions and the electron-energy distribution.

The equation describing the equilibrium set up by these two collision processes, together with the radiative transport of excitation, reads

$$0=An_e(\mathbf{r})-Bn_e(\mathbf{r})n(\mathbf{r})-\gamma n(\mathbf{r})+\gamma\int G(\mathbf{r},\mathbf{r}')n(\mathbf{r}')d\mathbf{r}'. \quad (6.1)$$

We observe two limiting cases:

(a). At very low electron densities the second term becomes negligible and we have approximately

$$0\approx An_e(\mathbf{r})-\gamma n(\mathbf{r})+\gamma\int G(\mathbf{r},\mathbf{r}')n(\mathbf{r}')d\mathbf{r}',$$

from which we see that $n(\mathbf{r})$ is proportional to the number of electrons.

(b). At very large electron densities, the last two terms may be neglected and we have

$$n(\mathbf{r})=A/B, \quad (6.2)$$

i.e., $n(\mathbf{r})$ is independent of electron density. We observe here that, if the electron energy distribution is Maxwellian, with a temperature T_e, we must have in case (b)

$$n(\mathbf{r})=Ne^{-\epsilon/kT_e}g_2/g_1, \quad (6.3)$$

where N is the normal atom density, ϵ the excitation energy, and g_2/g_1 the ratio of the statistical weights of the excited and ground states. Equation (6.3) follows from thermodynamic principles which apply to case (b), since the only processes involved are reversible exchanges of energy between free electrons and bound atomic electrons. Now (6.2) and (6.3) must be identical; hence,

$$A/B=(g_2/g_1)e^{-\epsilon/kT_e},$$

when the electrons have a Maxwell distribution in energy.

In order to obtain quantitative results for the general case, we must solve (6.1). This problem was attacked a number of years ago by de Groot,[15] who erroneously assumed the transmission function $T(\rho)$ for light quanta to be exponential; the results were retracted in a subsequent paper.[16]

The approach which seems most feasible at present is the variational method. The application of this method to the solution of linear inhomogeneous integral equations is indicated in Courant-Hilbert[9] (Chapter IV, page 176).

(3) Decay of excited states in noble gases: In noble gases (and to some extent in metallic vapors such as cadmium and mercury) radiating and metastable states are separated by small energy differences. Hence, the conversion from one to the other upon collision with normal atoms, with simultaneous change in the kinetic energy of nuclear motion, may take place readily. It has often been tacitly assumed that once a metastable atom is converted into a radiating atom, the excitation energy is immediately radi-

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[14] Reference 7, Section 8, Eq. (2).

[15] W. de Groot, Physica 12, 289 (1932), (old series).

[16] W. de Groot, Physica 1, 28 (1934).

ated from the enclosure. Because of the long lifetimes of radiating states caused by imprisonment of radiation, this assumption must be revised. A schematic treatment of the decay problem from the new point of view has been given by de Groot and Penning in their *Handbuch* article. A more accurate analysis will require the solution of integral equations of the type encountered above.

(4) The Penning effect. This phenomenon is the ionization of impurity atoms by excited atoms of the main constituent of a gas mixture; the most notable example is the ionization of argon atoms by excited neon atoms.[17] Since the ionization process must complete with other forms of destruction of excited atoms, the radiative transport of excitation is of crucial importance. A correct treatment of the problem must therefore consider imprisonment of resonance radiation.

APPENDIX I

The purpose of this appendix is the justification of the assumption

$$P(\nu) \propto k(\nu). \tag{1A}$$

The validity of (1A) is by no means universal; one can readily imagine cases for which it fails. For instance, let us suppose that "monochromatic" radiation (whose spectral width is small compared to the natural width) is incident on a medium whose absorption coefficient is characterized by natural broadening, i.e., the atoms are at rest and do not interact with each other. Then it is well known[18] that the spectrum of the emitted radiation is identical with that of the incident beam.

A similar, though less drastic situation prevails in the case of Doppler broadening. Here, a monochromatic beam excites only those atoms whose velocity component in the direction of the incident beam satisfies the Doppler relation (2.7). Since these atoms emit radiation in all directions, the spectral distribution of this radiation is obviously not monochromatic; nevertheless, it will certainly deviate greatly from the Doppler form as given by (2.17).

Since, as these examples demonstrate, (1A) is not universal, its applicability must be examined for the particular situations of interest. In this appendix we show that (1A) may be used in the cases of pressure and Doppler broadening; the case of natural broadening presents difficulties which have not yet been overcome.

A. Pressure Broadening

For this case we demonstrate that atoms, even when excited by a monochromatic beam, emit radiation whose spectral distribution is essentially proportional to $k(\nu)$. For the sake of simplicity the treatment will be classical throughout; i.e., the atoms are considered to be classical harmonic oscillators whose resonance frequency is identical with that of the resonance line; the corresponding quantum-mechanical approach does not present any essentially new features and will hence not be given here.

We first assume that the interaction of a given oscillator with its environment may be represented by quenching collisions, after each of which the oscillator is de-excited, i.e.,

$$\mathbf{u}(t_c) = \dot{\mathbf{u}}(t_c) = 0, \tag{2A}$$

where $\mathbf{u}$ is the oscillator displacement and t_c the time at which the collision takes place. This assumption will later be modified to deal with the actual case of non-quenching collisions. In the time between collisions, the oscillator does not interact with its neighbors; hence, in the presence of an incident field, $Ee^{i\omega t}$, the displacement $\mathbf{u}$ obeys the well-known oscillator equation, which, with neglect of radiation damping, reads

$$\ddot{\mathbf{u}} + \omega_0^2 \mathbf{u} = -(eE/m)e^{i\omega t}, \tag{3A}$$

where $\omega_0 = 2\pi\nu_0$ and the other symbols have their conventional significance.

It is permissible to neglect the damping term in (3A) because of the circumstance that when pressure broadening predominates the mean free time between collisions, τ_p, is much smaller than the radiative lifetime, $\tau = 1/\gamma$; since we integrate (3A) only over times of the order of τ_p, the effect of the damping term, $\gamma\dot{\mathbf{u}}$, can easily be shown to be negligible.

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[17] M. J. Druyvesteyn and F. M. Penning, Rev. Mod. Phys. 12, 87 (1940).

[18] Max Born, *Optik* (Verlag, Julius Springer, Berlin, 1933), Chapter VIII, Section 91.

The solution of (3A) subject to (2A) is

$$\mathbf{u}=-\frac{eE}{m}\frac{e^{i\omega t}}{\omega_0^2-\omega^2}\left[1-\frac{1}{2}\left(1+\frac{\omega}{\omega_0}\right)e^{-i(\omega-\omega_0)(t-t_i)}-\frac{1}{2}\left(1-\frac{\omega}{\omega_0}\right)e^{-i(\omega+\omega_0)(t-t_i)}\right],\qquad(4\text{A})$$

where t_i is the time at which the last collision previous to time t has occurred. In the neighborhood of resonance (4A) may be approximated by the expression

$$\mathbf{u}=-(Ee/m)\frac{e^{i\omega t}}{2\omega_0(\omega_0-\omega)}\left[1-e^{-i(\omega-\omega_0)(t-t_i)}\right].\qquad(5\text{A})$$

Because of the random nature of the collision process, $\mathbf{u}(t)$ is only partly coherent with the impressed field. The coherent component is gotten by averaging $\mathbf{u}(t)$ over all collision times $t_i=t-\theta$ with the weight factor

$$W(\theta)=e^{-\theta/\tau_p}.\qquad(6\text{A})$$

We then obtain the well-known result

$$\langle\mathbf{u}\rangle_{\text{Av}}=-(eE/m)\frac{e^{i\omega t}}{2i\omega_0}\frac{1}{1/\tau_p+i(\omega_0-\omega)}.\qquad(7\text{A})$$

The incoherent component of $u(t)$ is given by

$$\Delta\mathbf{u}\equiv\mathbf{u}-\langle\mathbf{u}\rangle_{\text{Av}}.\qquad(8\text{A})$$

Now, the field of the emitted radiation has the same time dependence as $\mathbf{u}(t)$; hence, to obtain the spectral distribution of the emitted radiation, it is sufficient to perform a Fourier analysis of $u(t)$. This analysis, which involves the evaluation of the Fourier components of $\mathbf{u}(t)$ for specified times of collision, t_1, t_2, $\cdots$, t_i, $\cdots$, and the averaging of these components and their absolute squares over all properly weighted values of t_1, t_2, $\cdots$, t_i, $\cdots$, will not be presented here; we confine oursevles to stating the results.

1. The coherent component, $\langle\mathbf{u}\rangle_{\text{Av}}$, obviously has a non-zero Fourier amplitude for only one frequency, the impressed frequency ω, i.e., the spectrum of $\langle\mathbf{u}\rangle_{\text{Av}}$ is a line spectrum.

2. The incoherent component, $\Delta\mathbf{u}$, possesses non-vanishing Fourier amplitudes for all frequencies, ω'. These amplitudes are uncorrelated with each other. The average spectral distribution, $P(\omega')$, which is proportional to the average absolute square of the Fourier amplitude at ω', varies with frequency according to the relation

$$P(\omega')\sim\frac{1}{1+(\omega'-\omega_0)^2\tau_p^2},\qquad(9\text{A})$$

which, if we define $\gamma_p=2/\tau_p$, is identical with (2.4′), i.e., the spectrum of the incoherent component obeys (1A).

We now show that the average magnitudes of the coherent and incoherent components of the total displacement are equal. With the aid of (6A) we readily obtain

$$\langle|\mathbf{u}|^2\rangle_{\text{Av}}=\left|\frac{eE}{2m\omega_0}\right|^2\frac{2}{(1/\tau_p)^2+(\omega_0-\omega)^2}.\qquad(10\text{A})$$

From (10A) and (7A) we then find that

$$\langle|\Delta\mathbf{u}|^2\rangle_{\text{Av}}=\langle|\mathbf{u}|^2\rangle_{\text{Av}}-|\langle\mathbf{u}\rangle_{\text{Av}}|^2=|\langle\mathbf{u}\rangle_{\text{Av}}|^2.\qquad(11\text{A})$$

Thus, the spectrum of the total displacement, and hence of the emitted radiation, may be resolved into two equal parts of which one is a line spectrum whose frequency is equal to that of the incident beam, whereas the other obeys (1A).

The above result is obtained on the basis of assumption (2A), which states that every collision quenches the oscillation. Since the quenching action of collisions is by no means universal, and, in fact, is very rarely observed if only one type of atom is present, the assumption requires modification. According to the present point of view,[19] a collision need not extinguish the motion of the classical oscillator; in the absence of quenching its chief effect is the introduction of a random phase shift into this motion with the consequence that immediately after collision the phase of the oscillator displacement is uncorrelated with that of the incident field. Thus, at any time t the total displacement $\mathbf{u}(t)$ may be written as

$$\mathbf{u}(t)=\mathbf{u}_1(t)+\mathbf{u}_2(t),\qquad(12\text{A})$$

where $\mathbf{u}_1(t)$ is given by (4A) or (5A), and $\mathbf{u}_2(t)$ is uncorrelated in phase with the incident field or with $\mathbf{u}_1(t)$. The coherent part of the total oscillation is thus left unaltered, whereas the intensity of the incoherent component is increased by

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[19] V. Weisskopf, Physik. Zeits. **34**, 1 (1933); H. Margenau and W. W. Watson, Rev. Mod. Phys. **8**, 22 (1936).

$|\mathbf{u}_2(t)|^2$. Now, the time dependence of $\mathbf{u}_2(t)$ is that of free oscillation interspersed with the random phase shift due to collisions; as is demonstrated in standard texts,[18] the spectrum associated with this time variation is given by (9A) and, hence, by (1A). Therefore, if we are able to show that

$$\langle|\mathbf{u}_2|^2\rangle_{\text{Av}} \gg \langle|\mathbf{u}_1|^2\rangle_{\text{Av}}, \tag{13A}$$

we shall have established the validity of (1A) for the case of pressure broadening.

Two processes enter into the determination of $\langle|\mathbf{u}_2|^2\rangle_{\text{Av}}$. One of these is the relatively slow decrease due to radiation damping, heretofore neglected in our treatment. The rate of decrease per unit time arising from this mechanism is

$$-\gamma\langle|\mathbf{u}_2|^2\rangle_{\text{Av}}.$$

The other process is the transformation of $\mathbf{u}_1$ to $\mathbf{u}_2$ which takes place with each collision because of the introduction of the random phase shift; the rate of the resultant increase of $\langle|\mathbf{u}_2|^2\rangle_{\text{Av}}$ is

$$\frac{1}{\tau_p}\langle|\mathbf{u}_1|^2\rangle_{\text{Av}}.$$

Equating these two rates, we have

$$\langle|\mathbf{u}_2|^2\rangle_{\text{Av}} = \frac{1}{\gamma\tau_p}\langle|\mathbf{u}_1|^2\rangle_{\text{Av}},$$

which, in view of the inequality $\gamma\tau_p \ll 1$, immediately gives (13A).

The above treatment establishes the validity of (1A) for the "impact" type of pressure broadening associated with the dispersion-type absorption law (2.4′). As stated in the text, deviations from impact broadening may occur at pressures above 1 mm and for frequency differences $\nu-\nu_0 \gg \gamma_p$. Since these cases have not been treated in the text, we shall not analyze the applicability of (1A) to them.

B. Doppler Broadening

From the standard treatments of Doppler-broadened emission spectra it is apparent that the validity of (1A) requires the velocity distribution of the excited atoms to be Maxwellian. In the investigation of this velocity distribution two cases are of interest.

1. Non-radiative transfer of excitation between atoms takes place before radiation. This transfer owes its origin essentially to dipole-dipole interaction between an excited and a normal atom. The cross sections for such reactions, classified as collisions of the second kind, are generally much larger than kinetic cross sections, because of the fact that no energy transfer between electronic excitation and nuclear motion is required. It has been shown, first by Fursov and Vlassov[20] and later by Houston,[21] that the non-radiative exchange of excitation is connected quite intimately with pressure broadening; in fact, at the pressure such that the mean free time between exchanges is equal to the radiative lifetime, pressure broadening is of the same order of magnitude as natural broadening. Another characteristic of the collisions is that the radius of collision varies inversely with the square root of the relative velocity of the colliding atoms, with the result that the mean free time is independent of the relative velocity.

If, now, pressure broadening exceeds natural broadening, both remaining small compared to Doppler broadening, non-radiative exchange of excitation takes place with equal likelihood between atoms of arbitrary velocities in preference to radiation. Hence the velocity distribution of the emitting atoms approaches that of the normal atoms, which is Maxwellian.

2. The radiative time is short compared to the mean free time between excitation transfers. In this case we cannot assume *a priori* that the velocity distribution of the excited atoms is Maxwellian and must, therefore, fall back on a more general formulation of the problem which presents both this velocity distribution and the frequency spectrum of the radiation as unknowns to be solved by analysis.

In describing the frequency spectrum of the radiation we introduce the frequency variable $x=(\nu-\nu_0/\nu_0)c/v_0$. The energy in a positional volume element, $d\mathbf{r}$, radiation whose direction of propagation is contained in an element of solid angle $d\omega$ and whose frequency lies in a range between x and $x+dx$, is represented by

$$h\nu f(\mathbf{r}, x, \mathbf{n})d\mathbf{r}dxd\omega,$$

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[20] W. Furssov and A. Vlassov, Physik. Zeits. Sowjetunion **10**, 378 (1936).

[21] W. V. Houston, Phys. Rev. **54**, 884 (1938).

where $\mathbf{n}$ is a unit vector in the direction of propagation. $f(\mathbf{r}, x, \mathbf{n})d\mathbf{r}dxd\omega$ may be regarded as the number of quanta in the positional volume element $d\mathbf{r}$ and within the specified range of solid angle and frequency. Furthermore, we designate by $N(\mathbf{r}, \mathbf{v})$ the density of excited atoms in six-dimensional, velocity-position space. We may then describe the time variation of $f(\mathbf{r}, x, \mathbf{n})$ and $N(\mathbf{r}, \mathbf{v})$ by two "probability-conservation" integro-differential equations. The first reads

$$\partial f/\partial t = -c\mathbf{n}\cdot\mathrm{grad}_{\mathrm{r}} f - ck(x)f + (\gamma/4\pi)\int N(\mathbf{r}, \mathbf{v})\delta\left(\frac{\mathbf{n}-\mathbf{v}}{v_0} - x\right)d\mathbf{v}. \quad (16\mathrm{A})$$

Here $k(x)$ is the absorption coefficient of quanta of frequency x, dv an element of volume in velocity space, and δ the Dirac delta-function, defined by the equations

$$\delta(x-x_1) = 0;\ x \neq x_1, \qquad \int_{x_1-a}^{x_1+b} \delta(x-x_1)dx = 1. \quad (17\mathrm{A})$$

Equation (17A) describes the generation, transport, and absorption of light quanta. The transport and absorption are obviously given by the first and second terms of the right-hand side. To see that the integral term represents the generation of quanta, we note the following:

(a). The integral is proportional to the density of emitting atoms, $N(\mathbf{r}, \mathbf{v})$.

(b). The delta-function restricts the emissive contribution to those atoms for which $x = \mathbf{n}\cdot\mathbf{v}/v_0$, which, in view of the definition of x, is the Doppler equation.

(c). If we integrate the term over all values of x and $\mathbf{n}$, i.e., over all possible emission frequencies and directions, we should obtain the total rate of emission per unit positional volume. Performing this integration we find for this rate the expression $\gamma N(\mathbf{r}, \mathbf{v})d\mathbf{v}$ which is obviously valid.

(d). Finally, it should be remarked that isotropic emission is assumed. This assumption is discussed in the text.

The second equation reads

$$\frac{\partial N(\mathbf{r}, \mathbf{v})}{\partial t} + \gamma N(\mathbf{r}, \mathbf{v}) = \frac{k_0 \exp(-v^2/v_0^2)}{\pi v_0^2} \times \int \delta\left(\frac{\mathbf{n}\cdot\mathbf{v}}{v_0} - x\right) f(r, x, \mathbf{n})d\omega dx. \quad (18\mathrm{A})$$

Here, k_0 represents, as in the text, the absorption coefficient at the center of the Doppler line, $x = 0$. In (18A) the transport of excitation due to the velocities of the excited atoms is neglected so that the equation represents the change in N due to absorption and emission of radiation alone. The emission is obviously given by the second term of the left; to show that the term on the right describes the absorption process, we note that (a), the integrand is proportional to the density of quanta, $f(\mathbf{r}, x, \mathbf{n})$, and of normal atoms $\propto \exp(-v^2/v_0^2)$, (b), the delta-function takes care of the Doppler effect, and (c), integration over all velocities gives the total rate per unit volume of absorption of light quanta, i.e.,

$$\int k_0 \exp(-x^2) f(\mathbf{r}, x, \mathbf{n})d\omega dx = \int k(x) f(\mathbf{r}, x, \mathbf{n})dxd\omega.$$

In proceeding further we find it convenient to neglect the retardation effect arising from the finite velocity of propagation of light. This effect is contained analytically in the $\partial f/\partial t$ term on the left-hand side of (16A). As we shall show in detail below, the neglect of this term gives $f(\mathbf{r}, x, \mathbf{n})$ at time t as an integral involving $N(\mathbf{r}', \mathbf{v})$ the "source" function, evaluated at the same time, t; on the other hand, consideration of the $\partial f/\partial t$ term would give $f(\mathbf{r}, x, \mathbf{n})$ as an integral containing $N(\mathbf{r}', \mathbf{v})$ evaluated at the retarded time, $t' = t - (|\mathbf{r}-\mathbf{r}'|)/c$. The neglect of retardation is permissible because of the circumstance that as long as we deal with enclosures whose dimensions are of the order of centimeters and radiative lifetimes, $\tau \gtrsim 10^{-8}$ sec, the time of flight of the quanta is much smaller than τ; we may therefore, to a good approximation, regard their motion within the enclosure as instantaneous.

With neglect of the $\partial f/\partial t$ term, we integrate (15A), obtaining

$$f(\mathbf{r}, x, \mathbf{n}) = \frac{\gamma}{4\pi c}\int_0^{\rho_m}\int N(\mathbf{r}-\mathbf{n}\rho, \mathbf{v}') \times \delta\left(\frac{\mathbf{n}\cdot\mathbf{v}'}{v_0} - x\right) e^{-k(x)\rho} d\rho d\mathbf{v}', \quad (19\mathrm{A})$$

where ρ_m corresponds to a point $r - \mathbf{n}\rho_m$ situated on the boundary of the enclosure. Inserting (19A) into (18A) and introducing the "source-point" vector, $\mathbf{r}'=\mathbf{r}-\mathbf{n}\rho$, with $d\mathbf{r}'=\rho^2 d\rho d\omega$ representing the positional volume element around the source point, we obtain

$$\frac{\partial N}{\partial t}+\gamma N(\mathbf{r},\mathbf{v})=\gamma\exp(-v^2/v_0^2)\times\int\int K(\mathbf{r},\mathbf{v};\mathbf{r}',\mathbf{v}')N(\mathbf{r}',\mathbf{v}')d\mathbf{r}'d\mathbf{v}',\qquad(20\text{A})$$

where

$$K(\mathbf{r},\mathbf{v};\mathbf{r}',\mathbf{v}')=\int_{-\infty}^{+\infty}\frac{k_0 e^{-k(x)|\mathbf{r}-\mathbf{r}'|}}{4\pi c\pi v_0^2|\mathbf{r}-\mathbf{r}'|^2}\times\delta\left(\frac{\mathbf{v}\cdot\mathbf{n}}{v_0}-x\right)\delta\left(\frac{\mathbf{v}'\cdot\mathbf{n}}{v_0}-x\right)dx.\qquad(21\text{A})$$

We observe in passing that

$$K(\mathbf{r},\mathbf{v};\mathbf{r}',\mathbf{v}')=K(\mathbf{r}',\mathbf{v}';\mathbf{r},\mathbf{v}).\qquad(22\text{A})$$

Also, in (20A) the integrations go over all velocities and over the volume of the enclosure.

As in the text treatment, we are interested in steady-state solutions of the form $N(\mathbf{r},\mathbf{v},t)\sim e^{-\beta t}N(\mathbf{r},\mathbf{v})$, which satisfy the equation

$$(-\beta+\gamma)N(\mathbf{r},\mathbf{v})=\gamma\exp(-v^2/v_0^2)\times\int\int K(\mathbf{r},\mathbf{v};\mathbf{r}',\mathbf{v}')N(\mathbf{r}',\mathbf{v}')d\mathbf{r}'d\mathbf{v}'.\qquad(23\text{A})$$

Furthermore, we confine our attention to the solution of (23A) which gives the smallest value of β, since, after a sufficiently long time, that solution alone is capable of experimental observation. We note that (23A) is equivalent to the following variational problem

$$\frac{\beta}{\gamma}=1-\frac{\int\int\int\int K(\mathbf{r},\mathbf{v};\mathbf{r}',\mathbf{v}')N(\mathbf{r},\mathbf{v})N(\mathbf{r}',\mathbf{v}')d\mathbf{r}'d\mathbf{v}'d\mathbf{r}d\mathbf{v}}{\int\int\exp(+v^2/v_0^2)N^2(\mathbf{r},\mathbf{v})d\mathbf{r}d\mathbf{v}};\delta(\beta/\gamma)=0,\qquad(24\text{A})$$

as can easily be verified with use of (22A). Our problem is then to find the minimum of β/γ as given by (24A).

To solve this problem we have at our disposal the Ritz variational procedure. The value of β obtained by this method is always higher than the true value, and converges towards it as the number of variable parameters increases.

We now try a solution of the form $N(\mathbf{r},\mathbf{v})=N(\mathbf{r})\exp(-v^2/v_0^2)$; inserting this expression into (24A), we obtain

$$\frac{\beta}{\gamma}=1-\frac{\int\int G(\mathbf{r},\mathbf{r}')N(\mathbf{r})N(\mathbf{r}')d\mathbf{r}'d\mathbf{r}}{\int N^2(\mathbf{r})d\mathbf{r}},\qquad(25\text{A})$$

where

$$G(\mathbf{r},\mathbf{r}')=\frac{\int\int K(\mathbf{r},\mathbf{v};\mathbf{r}'\mathbf{v}')\exp[-(v^2+v'^2)/v_0^2]d\mathbf{v}d\mathbf{v}'}{\int\exp(-v^2/v_0^2)d\mathbf{v}}.\qquad(26\text{A})$$

The evaluation of (26A) yields

$$G(\mathbf{r},\mathbf{r}')=\int_{-\infty}^{+\infty}\frac{k(x)\exp(-x^2)e^{-k(x)|\mathbf{r}-\mathbf{r}'|}}{\pi^{\frac{1}{2}}4\pi|\mathbf{r}-\mathbf{r}'|^2}dx,\qquad(27\text{A})$$

which is easily seen to be equivalent to (3.5) and (2.19). For the determination of $N(r)$ and β we now apply the variational method to (25A); since this form is identical with (3.9a) the further analysis is the same as that of the text problem.

The above treatment shows that the assumption of a Maxwellian distribution for the velocities of the excited atoms leads to a variational approximation of the exact solution. In particular, the value of β obtained with the Maxwell distribution is always higher than the true value. Thus the text calculation gives an upper limit for β.

Unfortunately, this procedure cannot give quantitative information as to how far off the upper limit is until other more general forms for $N(\mathbf{r}, \mathbf{v})$ have been tried. Such calculations are rather tedious. Another possible approach is that of iteration. One inserts an assumed function for $N(\mathbf{r}, \mathbf{v})$, e.g., the Maxwellian form, into the right-hand side of (23A); the evaluation of the integral gives a new value of $N(\mathbf{r}, \mathbf{v})$, which may be substituted into (14A) for a repetition of the process. The correspondence of the new $N(\mathbf{r}, \mathbf{v})$ to the original function gives an indication as to the validity of the latter as a solution of the problem. Using this approach, we have made some preliminary semiquantitative studies; the essential physical picture which emerges from these studies may be described as follows.

For an infinite vessel, in which $N(\mathbf{r}, \mathbf{v})$ is rigorously Maxwellian (as can be verified by substitution into 23A), the radiation density function, $f(\mathbf{r}, x, \mathbf{n})$ as determined from (19A) is independent of frequency and propagation direction (as well as of position). This independence is linked up with the circumstance that, with increasing x, the diminution in the emissivity of each volume element is compensated by a longer free path, $1/k(x)$, which permits more volume elements to contribute to the radiation density at $\mathbf{r}$. For the finite case this behavior is still realized for those frequencies x such that $1/k(x)$ is much smaller than the linear dimensions of the enclosure; furthermore, in its $\mathbf{r}$ variation $f(\mathbf{r}, x, \mathbf{n})$ is proportional to the density of excited atoms at $\mathbf{r}$.

However, when $1/k(x)$ approaches the linear dimensions of the enclosure, this picture changes. In the central region the radiation density drops, since contributions from outlying regions diminish because of the lower density of excited atoms in those regions. When $1/k(x)$ exceeds the dimensions of the container, no new volume elements are brought into play with the result that the decrease in the emissivity of individual volume elements is now uncompensated; hence the radiation density drops off rapidly with further increase of x.

In the outer portion of the enclosure the x dependence of the radiation is somewhat more complicated. Here, as $1/k(x)$ gets large enough so that quanta emitted in the central regions can penetrate to the boundary, the radiation density at first *increases* with frequency; when, however, $1/k(x)$ exceeds the dimensions of the container, no new volume elements can contribute and the radiation density drops rapidly to zero. The phenomenon of enhanced intensity in the wings of the frequency distribution of the radiation density is often encountered in spectroscopy, where it is designated by the term "self-reversal."

As a result of the above described behavior of $f(\mathbf{r}, x, \mathbf{n})$, it turns out that in the central region the wings of the velocity distribution of excited atoms drop below the Maxwell form. It is also probable, though at the present time not definitely established, that in the boundary regions the self-reversal of the radiation density is duplicated to a certain extent in the velocity distribution of the excited atoms.

Here it should be pointed out that the behavior in the central region is of decisive importance in the estimation of the error in β. Namely, a deficiency of high velocity excited atoms gives rise to a cutting off of the wings of the emission spectrum from the individual volume elements and hence leads to a reduction $T(\rho)$ and β. On the other hand, by an analogous chain of events, the self-reversal, characteristic of the outer regions, may be expected to provide an increase in β. Now, the variational theory states that the true eigenvalue is lower than that obtained from the Maxwell distribution. Hence, in obtaining an upper limit for the error we neglect the possible increase in β due to the self-reversal in the periphery and confine our attention solely to the central region, where the correction results in a diminution.

Preliminary iteration-type calculations following this approach indicate that the emission spectrum of individual volume elements closely approximates the Doppler distribution, e^{-x^2}, up to a value x_1 such that

$$x_1 \sim (\log(k_0L/2))^{\frac{1}{2}}.$$

For $x > x_1$ the Doppler distribution is to be multiplied by a factor roughly of the form x_1/x.

These results may now be introduced into (2.3) to calculate, e.g., $T(L/2)$; it is then found that the new value is smaller than the text value

$$T_1(L/2) = \frac{1}{k_0\rho(\pi \log(k_0L/2))^{\frac{1}{2}}},$$

by an amount

$$\Delta T \sim \frac{T_1(L/2)}{2 \log(k_0L/2)},$$

which, for $k_0L \sim 200$, is of the order of 10 percent.

We may thus expect that the error in β arising from the use of (1A) is less than, say, 20 percent. On the other hand, the error in the functional form of $N(\mathbf{r}, \mathbf{v})$, or even of $N(\mathbf{r})$, is undoubtedly much greater; in particular, for these quantities the contrast between the central region and the periphery of the enclosure is more significant.

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Paramagnetic Resonance Absorption in Salts of the Iron Group[*]

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When a paramagnetic salt is placed in a high frequency alternating magnetic field which is perpendicular to a static magnetic field, energy may be absorbed by the salt in a resonant fashion for a range of values of the steady field. These paramagnetic losses have been investigated for three manganous, two cupric, and one chromic salt at a frequency of 9375 mc/sec. Well-defined absorption maxima were obtained in all cases, and absolute values of χ'', the imaginary part of the high frequency magnetic susceptibility, are presented.

I. INTRODUCTION

Absorption of energy from a high frequency alternating magnetic field by a paramagnetic salt placed in the field was first demonstrated by Gorter[1] in 1936. He found that this absorption can be influenced by the application of a static magnetic field either parallel or perpendicular to the alternating field. He and his colleagues have carried on an extensive investigation of both types of absorption during the last decade.[2,3] The perpendicular field case has been further investigated by Zavoisky[4,5] and by two of the present authors.[6]

Purcell and co-workers[7] have recently demonstrated that when paraffin is put into a cavity resonator and a static magnetic field of the correct magnitude is applied perpendicularly to the high frequency magnetic field in the paraffin-filled cavity, energy is absorbed from the alternating field. This absorption shows sharp resonance characteristics and is associated with reorientations of the magnetic moments of the protons in the paraffin. Such nuclear absorptions are several orders of magnitude smaller than the absorptions referred to above, which are ionic in character.

In the earlier experiments[2–4] which were limited by the unavailability of oscillators of sufficiently high frequency,[***] the strength of the static magnetic field corresponding to the maximum absorption was less than the absorption half-width, so that the maxima were not very clearly

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[***] Zavoisky's most recent work,[5] carried out at 3000 mc/sec., has only recently been available to us.