

# Resonance Broadening of Spectral Lines\*

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A formalism introduced previously by the author is used to calculate the shape of an absorption line in a gas, taking account of the "resonance" interaction between like atoms. The most serious approximation is the neglect of the effect of translational motion. An asymmetric line is obtained, with the maximum shifted slightly toward the red. Some simple classical considerations also agree qualitatively with the results. Various properties of the line shape obtained are briefly discussed. The neglect of translational motion makes it impossible to compare the results with experiments performed up to the present time.

## I. INTRODUCTION AND SUMMARY

THE author has previously developed a simple theory of the refractive index of a gas in the absence of absorption.<sup>1</sup> By use of the so-called "damping operators,"<sup>2</sup> it has been possible to extend this to cover the complex refractive index as well.<sup>3</sup> In III, it was shown that the calculation of the complex refractive index for a given frequency could be reduced to the evaluation of a single diagonal matrix element of a damping operator. It is the aim of the present article to carry out this evaluation. Since the absorption intensity is proportional to the imaginary part of the refractive index, this leads to a detailed theory of the absorption line shape, including the effect of the "resonance" interaction between like atoms. The only serious limitation on the theory is that it entirely neglects the effect of translational motion of the atoms; this limitation is, however, sufficiently serious so as to preclude comparison with experiments done to date. It is hoped that it will prove possible in the future to remove this limitation.

Since many readers will probably not wish to familiarize themselves with the properties of the damping operators, Sec. II is devoted to some qualitative remarks based on the simple classical oscillator model. In Sec. III, the damping operators are used to derive an equation which implicitly determines the refractive index as a function of frequency in the region of an absorption, and in Sec. IV certain properties of the solutions of this equation are discussed. Section V gives a qualitative discussion of the effect of translational motion, and briefly discusses the experimental situation. The reader who is interested in line shapes, but not in damping operators, might wish to read Sec. II, and then skip directly to Sec. IV, taking only the final result of Sec. III.

## II. CLASSICAL OSCILLATOR MODEL

Consider an assembly of classical isotropic harmonic oscillators, distributed uniformly over a certain region of space with density  $\mathcal{N}$ . All the oscillators are assumed to have the same mass  $m$ , charge  $q$ , and natural frequency  $\nu_0$ . Now suppose that one of these oscillators is being driven by an oscillating electric field  $E_0 \cos \nu t$ , polarized along the  $x$  axis, where it is assumed that

$$|\nu - \nu_0| \ll \nu_0. \quad (1)$$

The equation of motion obeyed by the displacement of the oscillator is

$$m\ddot{x} = qE_0 \cos \nu t - m\nu_0^2 x - 2m\gamma \dot{x}, \quad (2)$$

where the damping term in  $\gamma$  is supposed to represent in an average way the fact that the oscillator is continually losing energy to the other oscillators with which it is surrounded. If (1) holds, (2) has the steady-state solution

$$x = \frac{qE_0}{2m\nu_0[(\nu_0 - \nu)^2 + \gamma^2]} \{(\nu_0 - \nu) \cos \nu t + \gamma \sin \nu t\}. \quad (3)$$

The average rate at which work is done on the oscillator by the field is

$$\left\langle \frac{dW}{dt} \right\rangle = \langle qE\dot{x} \rangle = \frac{q^2 E_0^2 \gamma}{4m[(\nu_0 - \nu)^2 + \gamma^2]} \equiv \frac{q^2 E_0^2}{4m} \mathcal{J}, \quad (4)$$

where

$$\mathcal{J} \equiv \frac{\gamma}{[(\nu_0 - \nu)^2 + \gamma^2]}. \quad (5)$$

The intensity of absorption is proportional to  $\mathcal{J}$ , and has the familiar Lorentzian shape if  $\gamma$  is a constant. Let us now try to evaluate  $\gamma$ .

If oscillator  $A$  is being driven with amplitude  $x_0$  and frequency  $\nu$ , i.e.,  $x_A = x_0 \cos \nu t$ , it will produce an oscillating electric field at the position of oscillator  $B$ , also with frequency  $\nu$ , and amplitude  $E_{AB}$ , where

$$E_{AB} = \frac{q^2 x_0^2 (1 + 3 \cos^2 \theta)}{|\epsilon| r_{AB}^6}. \quad (6)$$

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<sup>1</sup> C. A. Mead, Phys. Rev. **110**, 359 (1958), hereafter referred to as I.

<sup>2</sup> C. A. Mead, Phys. Rev. **112**, 1843 (1958), hereafter referred to as II.

<sup>3</sup> C. A. Mead, preceding paper [Phys. Rev. **120**, 854 (1960)], hereafter referred to as III.

Here  $r_{AB}$  is the distance between the two oscillators,  $\theta$  is the angle between the vector  $\mathbf{r}_{AB}$  and the direction of oscillation of  $A$ , and  $\epsilon$  is the (complex) dielectric constant of the intervening "medium" made up of all the other oscillators. Comparing (6) with (4), we see that the average rate at which  $A$  does work on  $B$  is given by

$$\left\langle \frac{dW_{AB}}{dt} \right\rangle = \frac{q^4 x_0^2 \gamma (1 + 3 \cos^2 \theta)}{4m |\epsilon|^2 [(\nu_0 - \nu)^2 + \gamma^2] r_{AB}^6}. \quad (7)$$

The total rate at which  $A$  loses energy to the other oscillators is found by summing (7) over all the oscillators  $B$ . This is easily done by replacing summation by integration over the uniform distribution of oscillators. The resulting integral diverges cubically at the origin, and this divergence is removed by cutting off the integral at a distance  $r_0$ , of the order of the average distance between nearest neighbors. The result is

$$\sum_B \left\langle \frac{dW_{AB}}{dt} \right\rangle = \frac{q^4 x_0^2 \gamma \mathcal{N}^2}{4m \beta^2 |\epsilon|^2 [(\nu_0 - \nu)^2 + \gamma^2]}, \quad (8)$$

where the cutoff is characterized by

$$r_0^3 = (8\pi/3) \beta^2 / \mathcal{N}.$$

$\beta$  is presumably of the order of unity.

Now the energy loss (8) is precisely the process which was to be represented by the damping term in the equation of motion (2). It is easily seen by making use of (1) and (2) that the average rate at which the oscillator does work against the damping force is given by

$$\left\langle \frac{dW}{dt} \right\rangle = m \gamma \nu_0^2 x_0^2. \quad (8a)$$

Since (8) and (8a) are supposed to represent the same process, self-consistency can be obtained only if their right-hand sides are equal. We have therefore

$$m \gamma \nu_0^2 x_0^2 = \frac{q^4 x_0^2 \gamma \mathcal{N}^2}{4m \beta^2 |\epsilon|^2 [(\nu_0 - \nu)^2 + \gamma^2]}. \quad (9)$$

Equation (9) has two solutions:

$$\gamma = 0, \quad (10)$$

and

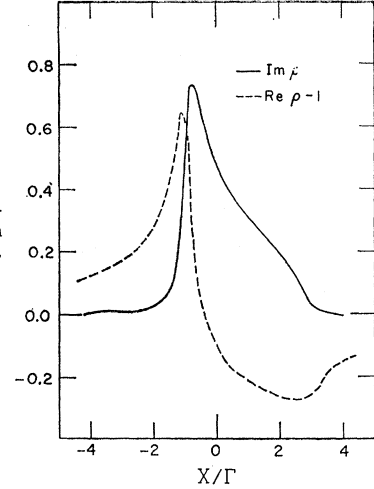
$$\gamma^2 = \gamma_0^2 / |\epsilon|^2 - (\nu_0 - \nu)^2, \quad (11)$$

where

$$\gamma_0 = q^2 \mathcal{N} / 2m \nu_0 \beta.$$

The solution (11) is the one of interest to us. Its frequency dependence is simply due to the fact that an oscillator loses energy to its neighbors more easily if it is oscillating at their natural frequency than at some other frequency. Outside of a certain region, (11) leads to an imaginary value for  $\gamma$  and is therefore meaningless. In this outer region, we must use the solution (10). Thus,

FIG. 1. Plot of refractive index as a function of frequency [from Eq. (39)] for  $a=1$ ,  $\Gamma=10$ .



on the extreme wings of the line, the damping due to electrostatic interaction with the other oscillators becomes ineffective, and pure radiation damping, neglected in this simple treatment, becomes the dominant process. The value of  $\gamma$  due to radiation damping is, of course, just the natural linewidth, and is much smaller than  $\gamma_0$ .

If we substitute (11) into (5), we find

$$\mathcal{G} = \frac{|\epsilon|^2}{\gamma_0^2} \left[ \frac{\gamma_0^2}{|\epsilon|^2} - (\nu_0 - \nu)^2 \right]^{\frac{1}{2}}. \quad (12)$$

The shape of (12) cannot be studied in detail without a knowledge of  $\epsilon$  as a function of frequency, and this in turn depends on a knowledge of the motion of the oscillators. There is no point in trying to carry this through rigorously, since it is of course not completely correct to represent the interaction between the different oscillators entirely in terms of the one quantity  $\gamma$ . Moreover, radiative interactions have been neglected completely, the interaction being considered as purely electrostatic. However, we can get a qualitative idea of the shape by assuming in first approximation that  $\epsilon$  has the Lorentzian form for the dielectric constant in the region near an absorption. In this case, the real part of  $\epsilon$  is greater than unity for  $\nu < \nu_0$ , and becomes less than unity for  $\nu > \nu_0$ ; the imaginary part is symmetrical about  $\nu_0$ , with a maximum at  $\nu_0$ . Thus  $|\epsilon|$  is larger for  $\nu < \nu_0$  than for  $\nu > \nu_0$ , and its derivative with respect to  $\nu$  at  $\nu = \nu_0$  is negative. Now by differentiating (12) with respect to  $\nu$  at the point  $\nu = \nu_0$ , we find

$$\left( \frac{d\mathcal{G}}{d\nu} \right)_{\nu=\nu_0} = - \frac{1}{\gamma_0} \left( \frac{d|\epsilon|}{d\nu} \right)_{\nu=\nu_0} < 0. \quad (13)$$

Thus the maximum of  $\mathcal{G}$  is not at  $\nu_0$ , but to the left of it (i.e., toward the red).

The region of appreciable absorption ends when the right-hand side of (11) becomes negative. This happens

somewhat sooner on the red side of  $\nu_0$  than on the blue, since  $|\epsilon|$  is greater on the red side.

The considerations of this section, therefore, suggest that the resonance-broadened line shape will have the following properties: First, the maximum will be displaced somewhat toward the red; second, the region of appreciable absorption will extend farther on the blue side of  $\nu_0$  than on the red side. The curve might therefore be expected to have a "saw-toothed" shape somewhat like the solid line of Fig. 1.

Of course, there has been no attempt to be rigorous in this section, but only to give an intuitive basis for the qualitative results to be derived later. In the next section, a detailed quantum mechanical determination of the refractive index as a function of frequency is presented.

### III. DETERMINATION OF THE REFRACTIVE INDEX

The situation to be considered here is the same as that of III, and the notation will be the same. The excited state to be considered is again a triply degenerate  $p$  state, the density of atoms is  $\mathfrak{N}$ ; here we assume that the atoms are distributed over the entire box in which the field is quantized, i.e.,  $\alpha=1$  in the language of III. It is easy to convince oneself that this will not affect the results, which depend only on the assumption that the linear dimensions of the region occupied by the gas are large compared with all wavelengths, etc.

Now by combining (III-17) and (III-20), we find that the refractive index  $\rho$  for frequency  $\nu_\lambda$  is given by<sup>4</sup>

$$\rho^2 - 1 = -4\pi\mathfrak{N}\mu^2/\hbar(\nu_\lambda - \nu_0 - \Delta). \quad (14)$$

It is assumed that

$$|\nu_0 - \nu|/\nu_0 \ll 1, \quad (15)$$

and

$$|\nu_0 - \nu|/\nu_0 \ll |\rho^2 - 1|. \quad (16)$$

The Hamiltonian matrix elements which we shall need are given by (III-8) and (III-9a).

Equation (14) reduces the task of calculating  $\rho$  to that of calculating  $\Delta$ . Using (III-12) and (II-19a), we see that

$$\begin{aligned} \hbar\Delta = \langle A_i | \mathfrak{D} | A_i \rangle = \sum_{\eta}' \frac{\langle A_i | \mathfrak{K} | \eta \rangle \langle \eta | \mathfrak{D} | A_i \rangle}{\hbar(\nu_\lambda - \nu_\eta + i\xi)} \\ + \sum_{B,j} \frac{\langle A_i | \mathfrak{K} | B_j \rangle \langle B_j | \mathfrak{D} | A_i \rangle}{\hbar(\nu_\lambda - \nu_0 - \Delta)}. \end{aligned} \quad (17)$$

We can use (II-19a) to eliminate the matrix elements  $\langle \eta | \mathfrak{D} | A_i \rangle$  from (17), with the result

$$\begin{aligned} \hbar\Delta = \sum_{\eta}' \frac{\langle A_i | \mathfrak{K} | \eta \rangle \langle \eta | \mathfrak{K} | A_i \rangle}{\hbar(\nu_\lambda - \nu_\eta + i\xi)} \\ + \sum_{B,j} \frac{\langle A_i | \mathfrak{K} | B_j \rangle \langle B_j | \mathfrak{D} | A_i \rangle}{\hbar(\nu_\lambda - \nu_0 - \Delta)}, \end{aligned} \quad (18)$$

where  $\mathfrak{K}$  is defined by (III-15) and evaluated in (III-16).

The first summation on the right-hand side of (18) is independent of the presence of the other atoms. If we choose the width of our energy shell  $|\epsilon| \gg |\nu_\lambda - \nu_0|$ , and also make use of (15), and (III-8), we easily find, apart from terms of a smaller order of magnitude,

$$\sum_{\eta}' \frac{\langle A_i | \mathfrak{K} | \eta \rangle \langle \eta | \mathfrak{K} | A_i \rangle}{\hbar(\nu_\lambda - \nu_\eta + i\xi)} = -i\hbar\sigma, \quad (19)$$

where

$$\sigma = 2\nu_0^3\mu^2/3\hbar c^3 \quad (20)$$

is the natural linewidth. Combining (18) and (19), we have

$$\hbar\Delta = -i\hbar\sigma + \sum_{B,j} \frac{\langle A_i | \mathfrak{K} | B_j \rangle \langle B_j | \mathfrak{D} | A_i \rangle}{\hbar(\nu_\lambda - \nu_0 - \Delta)}. \quad (21)$$

To go further, we must evaluate the off-diagonal matrix element  $\langle B_j | \mathfrak{D} | A_i \rangle$ . Using (II-19a), and again eliminating  $\langle \eta | \mathfrak{D} | A_i \rangle$ , one finds

$$\begin{aligned} \langle B_j | \mathfrak{D} | A_i \rangle = \langle B_j | \mathfrak{K} | A_i \rangle \\ + \sum_{C,k} \frac{\langle B_j | \mathfrak{K} | C_k \rangle \langle C_k | \mathfrak{D} | A_i \rangle}{\hbar(\nu_\lambda - \nu_0 - \Delta)}. \end{aligned} \quad (22)$$

Equation (22) may be solved by Fourier analysis. We write

$$\begin{aligned} \langle B_j | \mathfrak{D} | A_i \rangle = \frac{\mu^2}{V} \sum_{\eta} \epsilon_{\eta j} \epsilon_{\eta i} \mathfrak{D}_t(\eta) \exp[i\mathbf{k}_\eta \cdot (\mathbf{r}_B - \mathbf{r}_A)] \\ + \frac{\mu^2}{V} \sum_{\kappa} \frac{\kappa_j \kappa_i}{\kappa^2} \mathfrak{D}_t(\kappa) \exp[i\mathbf{k}_\kappa \cdot (\mathbf{r}_B - \mathbf{r}_A)]. \end{aligned} \quad (23)$$

When we substitute (III-16) and (23) into (22), the summation over  $C, k$  can be immediately carried out (by replacing it with integration), and because of orthogonality the equation breaks up into separate equations for the coefficients. Also making use of (14), (15), and (16), one easily finds

$$\mathfrak{D}_t(\kappa) = 4\pi/\rho^2, \quad (24)$$

$$\mathfrak{D}_t(\eta) = 4\pi\nu_0^2/(\rho^2\nu_\lambda^2 - \nu_\eta^2). \quad (25)$$

We can now substitute (23), (24), (25), and (III-16) into (21). The summation over  $B, j$  can be carried out immediately, with the cross terms again dropping out because of orthogonality. The result is

$$\hbar\Delta = -i\hbar\sigma + \mathfrak{D}_t + \mathfrak{D}_t, \quad (26)$$

<sup>4</sup> (III-17) means Eq. (17) of III.

where

$$\begin{aligned} \mathcal{D}_i &= \frac{1}{\hbar(\nu_\lambda - \nu_0 - \Delta)} \\ &\times \sum_{B,j} \left\{ \frac{4\pi}{V} \nu_0^2 \mu^2 \sum_\eta \frac{\epsilon_{\eta i} \epsilon_{\eta j} \exp[i\mathbf{k}_\eta \cdot (\mathbf{r}_A - \mathbf{r}_B)]}{(\nu_\lambda + i\xi)^2 - \nu_\eta^2} \right\} \\ &\times \left\{ \frac{4\pi}{V} \nu_0^2 \mu^2 \sum_\xi \frac{\epsilon_{\xi i} \epsilon_{\xi j} \exp[i\mathbf{k}_\xi \cdot (\mathbf{r}_B - \mathbf{r}_A)]}{\rho^2 \nu_\lambda^2 - \nu_\xi^2} \right\} \\ &= \frac{16\pi^2 \mathcal{N} \nu_0^4 \mu^4}{V \hbar(\nu_\lambda - \nu_0 - \Delta)} \sum_\eta \frac{\epsilon_{\eta i}^2}{[(\nu_\lambda + i\xi)^2 - \nu_\eta^2][\rho^2 \nu_\lambda^2 - \nu_\eta^2]} \\ &= i\hbar\sigma(1 - \rho). \end{aligned} \quad (27)$$

Since the longitudinal Fourier component (24), representing the electrostatic dipole-dipole interaction, is a constant, it is a simple matter to evaluate  $\mathcal{D}_i$  in coordinate space. We find

$$\begin{aligned} \mathcal{D}_i &= \frac{\mu^4}{\hbar(\nu_\lambda - \nu_0 - \Delta)\rho^2} \sum_{B,j} \frac{1}{r_{AB}^6} \left\{ \delta_{ij} - \frac{3r_{ABi}r_{ABj}}{r_{AB}^2} \right\}^2 \\ &= \frac{\mu^4}{\hbar(\nu_\lambda - \nu_0 - \Delta)\rho^2} \sum_B \frac{1}{r_{AB}^6} (1 + 3 \cos^2\theta), \end{aligned} \quad (28)$$

where  $\theta$  is the angle between  $\mathbf{r}_{AB}$  and the  $i$  axis. If we replace summation by integration in (28), and cut off the diverging integral at some distance  $r_0$ , of the order of the average distance between nearest neighbors, we find

$$\mathcal{D}_i = (2\mu^2/3r_0^3)[(1 - \rho^2)/\rho^2]. \quad (29)$$

In arriving at (29), we have also used (14). For later purposes it is convenient to rewrite (29) as

$$\mathcal{D}_i = 4\pi \mathcal{N} a \mu^2 [(1 - \rho^2)/\rho^2], \quad (30)$$

where the parameter now characterizing the cutoff is

$$a = 1/6\pi r_0^3 \mathcal{N} = 2/9\nu_0 \mathcal{N}. \quad (31)$$

If we determine the cutoff by the requirement

$$\frac{4}{3}\pi r_0^3 = \nu_0 = 1/\mathcal{N},$$

then we obtain  $a = 2/9$ . On the other hand, if we make the cutoff in wave-number space in such a way that the total number of allowed wave numbers is  $\mathcal{N}V$ , then  $a = \frac{1}{3}$ . Probably both of these are too small. A more sophisticated method is the following: Assume that the  $\mathcal{N}V$  atoms other than atom  $A$  may be anywhere in the volume  $V$  with equal probability except that they are excluded from a sphere of volume  $\omega$  about atom  $A$ . Let  $v$  be the volume of the largest sphere that can be drawn around atom  $A$  which does not contain any other atoms, and define  $v_0$  by

$$1/v_0 = \langle 1/v \rangle,$$

where the average is taken over all allowed distributions of the other atoms. With this model, if  $\mathcal{N}\omega \ll 1$ , one finds

$$\begin{aligned} a &= (2/9)(C - \ln \mathcal{N}\omega), \\ C &= 0.577 \dots \end{aligned}$$

If  $\omega$  is of the order of the cube of an atomic radius, this leads to values of  $a$  in the range 1–10 for ordinary densities.

We now define a dimensionless quantity  $\Gamma$  by means of the equation

$$4\pi \mathcal{N} \mu^2 = \Gamma \hbar \sigma. \quad (32)$$

By using (20), it may easily be verified that  $\Gamma$  is equal to  $(3/4\pi^2)$  times the number of atoms per cubic wavelength of radiation in vacuum at frequency  $\nu_0$ . Combining (26), (27), (30), and (32) gives

$$\Delta = -i\rho\sigma + a\Gamma\sigma[(1 - \rho^2)/\rho^2]. \quad (33)$$

We also have, from (14) and (32),

$$\rho^2 - 1 = -\Gamma\sigma/(\nu_\lambda - \nu_0 - \Delta). \quad (34)$$

With the further change of variables

$$\begin{aligned} \Delta &= \alpha\sigma, \\ \nu_\lambda - \nu_0 &= x\sigma, \end{aligned} \quad (35)$$

we obtain

$$\rho^2 - 1 = -\Gamma/(x - \alpha) \quad (36)$$

which may be solved for  $\alpha$ :

$$\alpha = x + \Gamma/(\rho^2 - 1). \quad (37)$$

There are now two convenient ways of rewriting (33). First, by making the substitution (35), we find

$$\alpha = -i\rho + a\Gamma[(1 - \rho^2)/\rho^2]. \quad (38)$$

With the further substitution (37), we obtain

$$x + \Gamma/(\rho^2 - 1) = -i\rho + a\Gamma[(1 - \rho^2)/\rho^2]. \quad (39)$$

Equation (39) can be solved numerically for  $\rho$  as a function of  $x$ . The result is plotted in Fig. 1 for the case  $a = 1$ ,  $\Gamma = 10$ . Note that the shape of the absorptive part (solid line) has the qualitative properties expected from the considerations of Sec. II.

#### IV. PROPERTIES OF THE REFRACTIVE INDEX

##### A. Limiting Properties; Linewidth

It is easy to see from (38) or (39) together with (36) that in the limit  $|x| \gg \Gamma$ , the refractive index is given approximately by

$$\rho^2 - 1 \approx -\Gamma/(x + i). \quad (40)$$

By looking at the imaginary part of (40), we see that the absorption in the extreme wings of the line has the Lorentzian form, with the width parameter being equal to the natural linewidth,  $\sigma$ . The physical reason for this is the same as for the similar effect in Sec. II: If an atom is excited at a frequency (energy) different from its

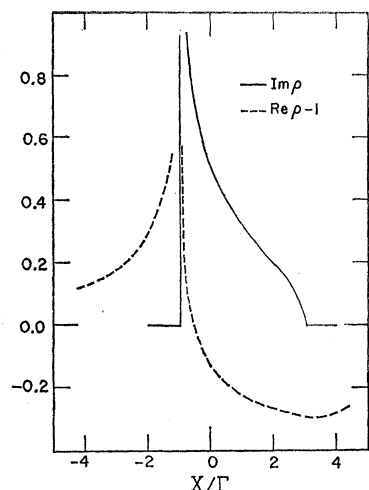


FIG. 2. Plot of refractive index as a function of frequency in the limit  $\Gamma \rightarrow \infty$ , [from Eq. (43)], with  $a=1$ .

natural frequency (energy of excitation), it cannot lose energy to its like neighbors as easily as at the resonance. The only mechanism for energy loss which is equally effective at all frequencies is the pure radiative damping, which is represented by the natural linewidth.

Another limiting solution which is of interest is the limit  $\Gamma \gg |\rho|$ . In this case, by writing

$$\alpha = \gamma\Gamma, \quad x = \xi\Gamma,$$

we obtain from (36)

$$\rho^2 - 1 = -1/(\xi - \gamma). \quad (41)$$

By substituting (41) into (38), dividing through by  $\Gamma$ , and neglecting  $i\rho/\Gamma$ , we find

$$\gamma = a/(\xi - 1 - \gamma). \quad (42)$$

Equation (42) may easily be solved for  $\gamma$ , and the result substituted into (41) to find  $\rho$ . The result is

$$\rho = \begin{cases} \frac{\xi - 1 - [(\xi - 1)^2 - 4a]^{\frac{1}{2}}}{\xi + 1 - [(\xi - 1)^2 - 4a]^{\frac{1}{2}}}, & \xi < -2a^{\frac{1}{2}} + 1, \\ \frac{1}{\sqrt{2}} \left\{ \frac{2[a(\xi + a)]^{\frac{1}{2}} + (\xi + 2a + 1)}{2(\xi + a)} \right\} \\ + \frac{i}{\sqrt{2}} \left\{ \frac{2[a(\xi + a)]^{\frac{1}{2}} - (\xi + 2a - 1)}{2(\xi + a)} \right\}, & -2a^{\frac{1}{2}} + 1 < \xi < 2a^{\frac{1}{2}} + 1, \end{cases} \quad (43)$$

$$\rho = \begin{cases} \frac{\xi - 1 + [(\xi - 1)^2 - 4a]^{\frac{1}{2}}}{\xi + 1 + [(\xi - 1)^2 - 4a]^{\frac{1}{2}}}, & \xi > 2a^{\frac{1}{2}} + 1. \end{cases}$$

Figure 2 shows a plot of Eq. (43) for  $a=1$ . The singularity is, of course, integrable, and where it occurs the neglect of the term  $i\rho/\Gamma$ , which was necessary in the derivation of (43), becomes self-contradictory. Therefore, the singularity is not real, and should not cause alarm. Furthermore, it is smoothed out for values of  $a$

different from unity. A comparison of Figs. 1 and 2 shows that except in the region of the singularity, the behavior of the absorption line for  $\Gamma=10$  already resembles closely its limiting behavior.

Due to the rather sharp peak, it appears that the width at half maximum is not a very appropriate quantity to indicate the spread in absorption intensity. It would seem more convenient to use the entire range in which the absorption is nonzero in the limit (43). Translating this into frequency units, this gives a width

$$\delta\nu = 4a^{\frac{1}{2}}\Gamma\sigma, \quad (44)$$

which is the same order of magnitude as the linewidths for resonance broadening found by other authors.<sup>5</sup>

## B. Total Absorption Intensity

We are interested in evaluation of the integral

$$I = \int_{-\infty}^{\infty} (\rho - 1) dx, \quad (45)$$

the imaginary part of which is equal to the total absorption intensity, apart from trivial constant factors.

To evaluate  $I$ , we rewrite (39) as

$$(x + i\rho + a\Gamma)\rho^2(\rho^2 - 1) + \Gamma(1 - a)\rho^2 + a\Gamma = 0. \quad (46)$$

Now differentiate (46) with respect to  $x$ , denoting differentiation by a prime:

$$(1 + i\rho')\rho^2(\rho^2 - 1) + 2(x + i\rho + a\Gamma)\rho'(2\rho^2 - \rho) + 2\rho\rho'\Gamma(1 - a) = 0,$$

or

$$\rho' = - \frac{\rho(\rho + 1)(\rho - 1)}{i\rho(\rho^2 - 1) + 2(2\rho^2 - 1)(x + i\rho + a\Gamma) + 2\Gamma(1 - a)}. \quad (47)$$

Equation (47) may be solved for  $(\rho - 1)$ :

$$\rho - 1 = -\rho' \times \left\{ \frac{i\rho(\rho^2 - 1) + 2(2\rho^2 - 1)(x + i\rho + a\Gamma) + 2\Gamma(1 - a)}{\rho(\rho + 1)} \right\}. \quad (48)$$

From (46) we see that

$$(x + i\rho + a\Gamma) = - \frac{\Gamma[a + (1 - a)\rho^2]}{\rho^2(\rho^2 - 1)}. \quad (49)$$

We can now substitute (49) into (48), and the result into (45), obtaining

$$I = - \oint dz \left\{ iz - \frac{2\Gamma a}{z(z+1)(z+2)^2} - \frac{2\Gamma a}{(z+1)^3(z+2)} - \frac{2\Gamma(1-a)(z+1)}{z(z+2)^2} \right\}, \quad (50)$$

<sup>5</sup> R. G. Breene, Jr., *Revs. Modern Phys.* **29**, 94 (1957).

where  $z = \rho - 1$ . When  $x$  goes from minus to plus infinity,  $z$  describes a closed curve in the counterclockwise sense in the upper half of the complex plane, which is tangent to the real axis at the origin. The contour integral (50) can easily be evaluated, with only the second and fourth terms contributing. The result is

$$I = i(\pi/2)\Gamma. \quad (51)$$

Thus the absorption intensity is strictly proportional to the density of atoms in the gas. It should be emphasized that (51) is by no means a trivial result. For instance, it is not a direct consequence of the dipole sum rule, or any similar rule, since the theory presented here takes into account indirect mechanisms of absorption involving an arbitrary number of intermediate states on the energy shell. It is, therefore, not obvious that the total absorption intensity is proportional to a sum of squared dipole matrix elements.

#### V. EFFECT OF TRANSLATIONAL MOTION; DISCUSSION OF EXPERIMENTS

The theory developed in the last two sections ignores completely any effect of the translational motion of the atoms making up the gas. The most important result in this case is that the damping due to the resonance interaction has a strong frequency dependence, due to the fact that (speaking classically) an oscillator cannot lose energy to its neighbors as easily if it is being driven at a frequency other than its natural frequency as it does at the natural frequency.

However, if the atoms are moving rapidly with respect to one another, their interaction will be explicitly time-dependent, and may contain Fourier components corresponding to frequencies large enough to make up the difference between the frequency at which an oscillator is being driven and the natural frequency. The order of magnitude of this effect may be estimated as follows: Suppose two atoms experience a "collision," in which they pass within a distance  $R$  of each other with relative velocity  $v$ , of the order of the root-mean-square velocity of the atoms in the gas. Their time-dependent interaction will then have appreciable Fourier coefficients for frequencies up to the order of

$$\delta\nu \sim v/R. \quad (52)$$

If we choose  $R$  to be of the order of an "optical collision diameter,"<sup>6</sup>

$$R \sim (\mu^2/v\hbar)^{1/2}, \quad (53)$$

then we have, combining (52) and (53),

$$\delta\nu \sim \delta\nu_D (\Delta\nu_D/\sigma)^{1/2}, \quad (54)$$

where  $\delta\nu_D \sim \nu_0 v/c$  is the Doppler width. Equation (54) indicates that if the Doppler width is much larger than the natural width, the frequency dependence of the resonance interaction may only become effective at

distances from the peak center one or two orders of magnitude greater than the Doppler width. The distortion of the line predicted by (39) should not be noticeable unless the right-hand side of (54) is less than the resonance width (44).

All experiments on resonance broadening known to the author have been conducted on the alkali metals at rather high temperatures and low densities. In the earlier experiments, the procedure was to assume a Lorentzian shape, and then determine the width by observing only the outer wings of the line.<sup>6-9</sup> The width thus calculated was in agreement as to order of magnitude with (44). According to the theory presented here, it should be impossible to get this result by looking at the wings of the line [see Eq. (40)]; but the result may be explained by the effect of the translational motion, as shown by (54). The more recent experiments of Tomiser,<sup>10</sup> and Moser and Schultz,<sup>11</sup> observe the line profile directly, and find a half-width considerably greater than that given by (44). This also may be due to some such mechanism as that used in the derivation of (54), but we can give no detailed explanation at this time. In any case, their results cannot be compared directly with the theory given here in Sec. III and IV, because of the high temperature and consequent importance of considering translational motion.

It appears, therefore, that the theory presented in this paper cannot be compared with experiment at this time, because it neglects translational motion, and experiments done to date have been at such high temperatures and low densities that translational motion cannot be neglected. It would seem advisable to try to extend the theory to include the effect of translational motion, and also to perform experiments on gases at low temperatures and high densities, if possible.

Finally, we briefly compare this work with previous theories of resonance broadening.<sup>5</sup> Most of these may be divided into two basic methods. The first method is to consider a single atom as initially excited, and calculate the evolution of the state with time, including the effect of interatomic interactions, and sometimes the interaction with a quantized radiation field. This is basically a theory of emission rather than absorption, and suffers from an ambiguity in the definition of the initial state, since an excited state cannot be unambiguously defined without reference to the conditions of excitation.<sup>12</sup> In the other method, one attempts to use degenerate perturbation theory to calculate the energy levels of the assembly of interacting atoms. Due to the very high degeneracy, this method can usually be used only to obtain the first

<sup>6</sup> D. S. Hughes and P. E. Lloyd, *Phys. Rev.* **52**, 1215 (1937).

<sup>7</sup> S.-Y. Ch'en, *Phys. Rev.* **58**, 884 (1940).

<sup>8</sup> K. Watanabe, *Phys. Rev.* **59**, 151 (1941).

<sup>9</sup> C. Gregory, *Phys. Rev.* **61**, 465 (1942).

<sup>10</sup> J. Tomiser, *Acta Phys. Austriaca* **8**, 198 (1953); **8**, 276 (1954); **8**, 323 (1954); **9**, 18 (1954).

<sup>11</sup> H. Moser and H. Schultz, *Ann. Physik* **7**, 243 (1959).

<sup>12</sup> See, e.g., W. Heitler, *The Quantum Theory of Radiation* (Clarendon Press, Oxford, 1954), 3rd ed., pp. 196-204.

one or two moments of the line, and not the detailed shape. It is difficult to include the effect of the transverse radiation field in this method. Our approach is in some respects more fundamental than either of these, as we attempt to directly construct stationary states of the whole system consisting of field and matter. There is no ambiguity in the definition of states, and radiative processes on the energy shell are taken into account in all orders. The main new physical effect is the frequency dependence of the damping term in the resonance

denominator, which is easily overlooked in the above two methods.

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## Applicability of Roothaan's Self-Consistent Field Theory\*

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Roothaan's open-shell self-consistent field theory is extended in such a way that it can cover a number of important classes of atomic and molecular states which are not included in the range of applicability originally claimed.

## I. INTRODUCTION

IN a recent paper<sup>1</sup> Roothaan described a new self-consistent field (SCF) theory for electronic systems which can accommodate open shells as well as the closed shells. However, his paper made a rather modest claim on the range of applicability. The purpose of the present paper is to extend the applicability of the theory in such a way that it includes a number of open-shell cases of practical importance which are not accommodated in the original form of Roothaan's scheme.

The relevant points of Roothaan's open-shell SCF theory are as follows. It is stated that the scheme is of practical value if the total energy can be represented by the following equation:

$$E = 2 \sum_k H_k + \sum_{kl} (2J_{kl} - K_{kl}) + f[2 \sum_m H_m + f \sum_{mn} (2aJ_{mn} - bK_{mn}) + 2 \sum_{km} (2J_{km} - K_{km})]. \quad (1)$$

This is the expectation value of the total Hamiltonian (in a.u.),

$$\mathcal{H} = \sum_{\mu} H^{\mu} + \frac{1}{2} \sum_{\mu \neq \nu} (1/r^{\mu\nu}). \quad (2)$$

$H^{\mu}$  is the nuclear field plus kinetic energy operator for the  $\mu$ th electron, and  $r^{\mu\nu}$  the distance between the  $\mu$ th and the  $\nu$ th electron. In Eq. (1),  $H_i$ ,  $J_{ij}$ , and  $K_{ij}$  are defined as usual by using Dirac's notation:

$$\begin{aligned} H_i &= \langle \varphi_i | H | \varphi_i \rangle, \\ J_{ij} &= \langle \varphi_i | J_j | \varphi_i \rangle = \langle \varphi_j | J_i | \varphi_j \rangle, \\ K_{ij} &= \langle \varphi_i | K_j | \varphi_i \rangle = \langle \varphi_j | K_i | \varphi_j \rangle, \end{aligned} \quad (3)$$

where

$$\begin{aligned} J_i^{\mu} \varphi^{\mu} &= \left[ \int \bar{\varphi}_i^{\nu} \varphi_i^{\nu} (1/r^{\mu\nu}) dV^{\nu} \right] \varphi^{\mu}, \\ K_i^{\mu} \varphi^{\mu} &= \left[ \int \bar{\varphi}_i^{\nu} \varphi^{\nu} (1/r^{\mu\nu}) dV^{\nu} \right] \varphi_i^{\mu}. \end{aligned} \quad (4)$$

$J_i$  and  $K_i$  are commonly called the Coulomb and exchange operators, respectively, associated with the orbital  $\varphi_i$ . In referring to the individual orbitals, the indices  $k, l$  are used for the closed-shell orbitals and  $m, n$  for the open-shell orbitals in Eq. (1).  $a, b$ , and  $f$  are numerical constants depending on the specific case. The first two sums in Eq. (1) represent the closed-shell energy, the next two sums the open-shell energy, and the last sum the interaction energy of the closed and open shell. The number  $f$  is, in general, the fractional occupation of the open shell, that is, it is equal to the number of occupied open-shell spin orbitals divided by the number of available open-shell spin orbitals. The numbers  $a$  and  $b$  differ for different states of the same configuration.

Two alternative formulations of the SCF problem are given in Roothaan's paper.<sup>1</sup> The first is the following set of equations:

$$\begin{aligned} F_C \varphi_k &= \eta_k \varphi_k, \\ F_O \varphi_m &= \eta_m \varphi_m, \end{aligned} \quad (5)$$

where

$$\begin{aligned} F_C &= H + 2J_C - K_C + 2J_O - K_O + 2aL_O - \beta M_O, \\ F_O &= H + 2J_C - K_C + 2aJ_O - bK_O + 2aL_C - \beta M_C, \end{aligned} \quad (6)$$

$$\begin{aligned} \alpha &= (1-a)/(1-f), \\ \beta &= (1-b)/(1-f). \end{aligned} \quad (7)$$

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<sup>1</sup> C. C. J. Roothaan, *Revs. Modern Phys.* **32**, 179 (1960).