The expectation values are

$$(\Psi(t), f\Psi(t)) = \sum_{m, n} r_m r_n \exp(i\varphi_n - i\varphi_m) (u(E_m), fu(E_n)) \\ \times \exp(iE_m t - iE_n t),$$

where f is any one of the p's or of the q's.

We must prove that there exists a T such that (for any  $t_0$ ) the following inequalities are verified:

$$| (\Psi(t_0), f\Psi(t_0)) - (\Psi(T), f\Psi(T)) | < \epsilon; (f = p_1, p_2, \cdots; q_1, q_2, \cdots).$$

Now there will exist a number N, such that for every f:

$$\left|\sum_{m,n=N}^{\infty} r_m r_n \exp(i\varphi_n - i\varphi_m)(u(E_m), fu(E_n))\right| \\ \times \exp(iE_m t - iE_n t) \left| \leqslant \sum_{m,n=N}^{\infty} r_m r_n |(u(E_m), fu(E_n))| < \epsilon \right|$$

Therefore it is sufficient to prove that

$$\sum_{n,n=1}^{N} r_m r_n \exp(i\varphi_n - i\varphi_m)(u(E_m), fu(E_n))$$

$$\times \left[ \exp(-iE_n t_0 + iE_m t_0) - \exp(-iE_n T + iE_m T) \right] \right|$$

$$\leqslant \sum_{m,n=1}^{N} r_m r_n |(u(E_m), fu(E_n))|$$

$$\times |\exp(-iE_n t_0 + iE_m t_0) - \exp(-iE_n T + iE_m T)|$$

$$\leqslant 2M \sum_{m,n=1}^{N} |\sin[(E_n - E_m)(T - t_0)/2]| < \epsilon;$$

here M is the greatest of the numbers

$$|(u(E_m), fu(E_n))| (m, n=1, 2, \dots, N; f=p_1, p_2, \dots, q_1, q_2, \dots).$$

But these inequalities can be satisfied.<sup>3</sup>

Of course, the above proof can be repeated formally taking in lieu of f any observable, in particular any macro-observable.

PHYSICAL REVIEW

#### VOLUME 107, NUMBER 2

JULY 15, 1957

# Imprisonment of Resonance Radiation in a Gaseous Discharge

P. J. WALSH

Westinghouse Electric Corporation, Research Department, Lamp Division, Bloomfield, New Jersey (Received February 15, 1957)

Following the theory of Holstein, the density,  $N_r$ , and the imprisonment lifetime of resonance radiation, T, has been investigated for a gaseous discharge between parallel plates. A general solution is given. Two approximate solutions occur according as the number of electronic de-excitations of the resonance state during the imprisonment time of a photon is much less than or much greater than unity. When this number is much less than unity, Nr can be given by a simple relation which compares well with computations based on the exact solution in the case of Doppler broadening. T is then essentially equal to the decay time as calculated by Holstein for the decay of resonance radiation following optical excitation. For large numbers of de-excitations T falls somewhat below the decay value and, as expected, N, is given by its thermodynamic equilibrium value at the temperature of the electrons.

## 1. INTRODUCTION

HE imprisonment of resonance radiation in a gas was originally treated in an approximate manner by considering the imprisonment as a diffusion problem.<sup>1-3</sup> Recently Holstein<sup>4,5</sup> and, independently, Bieberman<sup>6</sup> have presented a rigorous method for handling the imprisonment by the use of an integral equation. These two authors examined the imprisonment in the case of optical excitation. Bieberman studied the steady state conditions while Holstein studied the decay following the optical excitation. Experimental verification of the integral method has been found under both conditions.<sup>7,8</sup> The present paper applies this integral method to the case of the imprisonment of resonance radiation in a gas discharge where the excitation occurs by electron impact within the discharge.

# 2. PARTICLE BALANCE EQUATION FOR THE DENSITY OF RESONANCE ATOMS

Two parameters are of special importance in discussing the resonance imprisonment in a discharge: The density of resonance atoms,  $N_r$ , and the imprisonment lifetime, T, of a resonance photon within the discharge.

338

<sup>&</sup>lt;sup>1</sup>K. T. Compton, Phys. Rev. 20, 288 (1922).
<sup>2</sup>E. A. Milne, J. London Math. Soc. 1, 1 (1926).
<sup>3</sup>C. Kenty, Phys. Rev. 42, 823 (1932).
<sup>4</sup>T. Holstein, Phys. Rev. 72, 1212 (1947).
<sup>5</sup>T. Holstein, Phys. Rev. 83, 1159 (1951).
<sup>6</sup>L. M. Bieberman, J. Exptl. Theoret. Phys. (U.S.S.R.) 17, 16 (1046). 416 (1946).

The equation for the density of resonance atoms in

<sup>&</sup>lt;sup>7</sup> L. M. Bieberman and I. M. Gourevitch, J. Exptl. Theoret. Phys. (U.S.S.R.) 19, 507 (1949).
 <sup>8</sup> Alpert, McCoubrey, and Holstein, Phys. Rev. 76, 1257 (1949).

the discharge is similar to one discussed by Holstein<sup>4</sup>:

$$\frac{N_{r}(\mathbf{r})}{\tau} + \nu N_{e}(\mathbf{r}) N_{r}(\mathbf{r})$$
$$= \nu' N_{e}(\mathbf{r}) N_{g}(\mathbf{r}) + \int_{\text{vol}} G(\mathbf{r}, \mathbf{r}') \frac{N_{r}(\mathbf{r}')}{\tau} d\mathbf{r}'. \quad (2.1)$$

This equation is a *particle balance equation* in which the creation of resonance states per second per unit volume at some point, r, is equated to the loss at that point. The loss is twofold. First, there is the de-excitation of resonance atoms by spontaneous radiation with a radiating lifetime,  $\tau$ . Second, there is the de-excitation by collisions of electrons of density  $N_e$  with resonance atoms with a rate coefficient  $\nu$ . These two terms are given on the left-hand side of Eq. (2.1). The first term on the right-hand side gives the excitation by collisions of electrons with gas atoms of density  $N_g$  with a rate coefficient  $\nu'$ . The integral term on the right represents the number of resonance atoms created because of the imprisonment effect.

The physical interpretation of the integral term is as follows. At some point r' within the discharge  $N_r(\mathbf{r}')/\tau$ photons are radiated. These photons have a probability  $G(\mathbf{r},\mathbf{r}')$  of being captured at **r**. The product of the number of photons radiated and their probability of being captured, when integrated over the discharge volume, yields the number of photons emitted any place within the tube and captured at r to form resonance atoms.

The main assumption in the particle balance equation is the neglect of the diffusion of resonance atoms directly to the tube walls. When metastable atoms are present the equation again holds if the diffusion of metastable atoms is also negligible. Here, however,  $\nu$ and  $\nu'$  are effective excitation and de-excitation rates and are algebraic functions of the rates of transfer between the metastable, resonance, and ground states. The derivation of the particle balance equation when metastable atoms are present is given in the Appendix. This equation applies quite well to many types of discharges and, in particular, to the mercury-rare gas discharges as found in fluorescent lamps.9,10

The density of electrons used in Eq. (2.1) is taken as the solution of the Schottky diffusion equation for the corresponding geometry, i.e., a cosine function for a parallel plane geometry and a zero order Bessel function for a cylindrical geometry. The geometry also enters into the volume integration.

The electron energy enters into the collision rates  $\nu'$ ,  $\nu$ . With a Maxwellian energy distribution, detailed balancing must occur and then

$$\nu N_{r\epsilon} = \nu' N_g. \tag{2.2}$$

Here  $N_{r\epsilon}$  is the thermal equilibrium density of resonance

atoms at the temperature of the electrons. The density of gas atoms,  $N_g$ , will be taken as constant across the tube. However, we point out that, at high currents,  $N_g$ will vary because of gas heating.

The probability of capture, G, depends on the type of broadening occurring in the discharge. Holstein<sup>5</sup> gives the form for G as follows:

$$G(\mathbf{r},\mathbf{r}') = ma_m/4\pi\rho^{m+3}, \qquad (2.3)$$

where  $\rho = |\mathbf{r'} - \mathbf{r}|$ . For various types of broadening m falls in the range  $0 \le m \le 1$ . In the particular cases of Doppler and pressure broadening, m is 1 and  $\frac{1}{2}$ , respectively, and

$$1/a_1 = k_0 (\pi \ln k_0 x)^{\frac{1}{2}}, \quad 1/a_{112} = (\pi k_P x)^{\frac{1}{2}}, \quad (2.4)$$

where x represents the radius, R, for a cylindrical enclosure and one-half the width, L, of a parallel plate enclosure. In addition,

$$k_0 = \frac{\lambda^3 N_g g_2}{8\pi^{\frac{3}{2}}} \frac{1}{g_1 v_0 \tau n},$$
 (2.5)

$$k_P = \frac{\lambda^3 N_g g_2 \tau_P \mathbf{1}}{2\pi g_1 \tau_n}, \qquad (2.6)$$

$$v_0 = (2k\theta)^{\frac{1}{2}},$$
 (2.7)

where  $\lambda$  is the wavelength of the resonance radiation,  $g_2$  and  $g_1$  are the statistical weights of the resonance and ground states, respectively, n is the multiplicity of the hyperfine structure under the assumption of equal intensity and no overlapping,  $\tau_P$  is the reciprocal of the width of the pressure broadened resonance line, k is Boltzmann's constant, and  $\theta$  is the gas temperature.

Equation (2.3) applies when the center of the resonance line is thoroughly absorbed. Equations (2.5) and (2.6) hold if there is no overlapping of the hyperfine structure. Thorough discussions covering both the effect of the type of broadening upon the probability of capture and the range of validity of the theory, as will be applied here, are given in references 4 and 5.

The particle balance Eq. (2.1) is a nonhomogeneous integral equation. The exact solution<sup>11</sup> can be given by an eigenfunction expansion in terms of the normalized eigenfunctions,  $N_{rn}$ , and the eigenvalues,  $\lambda_n$  of the corresponding homogeneous equation. This solution is

$$N_{r}(\mathbf{r}) = \nu' N_{g} \tau$$

$$\times \left[ N_{e}(\mathbf{r}) + \sum \frac{\lambda_{n}}{1 - \lambda_{n}} N_{rn}(\mathbf{r}) \int N_{e}(\mathbf{r}') N_{rn}(\mathbf{r}') d\mathbf{r}' \right], \quad (2.8)$$

where the homogeneous equation is

$$\lambda_n N_{rn}(\mathbf{r}) = \int G(\mathbf{r}, \mathbf{r}') N_{rn}(\mathbf{r}') d\mathbf{r}' - \nu N_e(\mathbf{r}) N_{rn}(\mathbf{r}) \tau. \quad (2.9)$$

 <sup>&</sup>lt;sup>9</sup> C. Kenty, J. Appl. Phys. 21, 1309 (1950).
 <sup>10</sup> J. F. Waymouth and F. Bitter, J. Appl. Phys. 27, 122 (1956).

<sup>&</sup>lt;sup>11</sup> H. Margenau and G. M. Murphy, *The Mathematics of Physics and Chemistry* (D. Van Nostrand Company, Inc., New York, 1943), Sec. 14.4. Note difference in nomenclature.

The eigenfunction expansion (2.8) converges quite rapidly because the electron density and the lowest mode eigenfunction have a similar shape. Both are large near the center and fall monotonically to a small value near the walls. The integral of the product of the electron density with any higher eigenfunction will then be small because of the orthogonality of the eigenfunctions.

The equation for the decay following optical excitation which was treated by Holstein has the following form:

$$\lambda_n^0 N_{rn}^0(\mathbf{r}) = \int G(\mathbf{r}, \mathbf{r}') N_{rn}^0(\mathbf{r}') d\mathbf{r}', \qquad (2.10)$$

where

$$1 - \lambda_n^0 = \tau / T_n, \qquad (2.11)$$

and  $T_n$  is the decay time for the *n*th decay mode. Except for the term  $\nu N_e N_{rn} \tau$ , Eqs. (2.9) and (2.10) are the same. This gives a hint as to the method of computation to be used. The decay equation was solved by the variational method used by Holstein to furnish the two lowest mode solutions. The homogeneous equation was then solved by perturbation technique using the term  $\nu N_e N_{rn} \tau$  as the perturbation. Finally, the eigenfunction expansion was used to obtain the solution of the balance equation. Because of the rapid convergence of (2.8) two modes were sufficient for the computation range sought.

The actual computation was carried out for a discharge between parallel plates with Doppler broadening present. The details are given in Sec. 5.

# 3. IMPRISONMENT TIME OF THE RESONANCE RADIATION

The density of resonance atoms discussed in the previous section is the first parameter of special importance. The average length of time a photon is imprisoned within the discharge furnishes the second important parameter. We call this time the imprisonment lifetime, T, and define it by requiring the total number of photons escaping the discharge per unit volume to equal the average density of resonance atoms divided by the imprisonment time. Thus

(Photons escaping)/volume 
$$\equiv \bar{N}_r/T$$
. (3.1)

or .

The bar here indicates an average over the discharge volume.

Since the number of photons escaping per unit volume equals the difference between averages of those radiated within the discharge and those imprisoned, we have

$$T = \bar{N}_{r} / \left\langle \frac{N_{r}}{\tau} - \int G(\mathbf{r}, \mathbf{r}') \frac{N_{r}(\mathbf{r}')}{\tau} d\mathbf{r}' \right\rangle_{AV}, \quad (3.2)$$

or

$$\bar{N}_r/(\nu'N_g\bar{N}_e-\nu\bar{N}_e\bar{N}_r), \qquad (3.3)$$

using (2.1).

T =

There are two points of interest concerning this definition for the imprisonment lifetime. First, if we average the particle balance Eq. (2.1), we note that the two radiation terms appear in the same manner as the denominator of (3.2). Thus, this definition of the imprisonment lifetime allows us to replace the radiating terms of an averaged balance equation by a simple term in T and, in essence, changes the equation from an integral equation into an algebraic one. The second point of interest is this. The value of T, for a given type of broadening, depends only on the form of  $N_r$ . This is obvious from (3.2). In particular, if  $N_r$  has the same form as the zero decay mode, (3.2) and (2.10)then yield  $T = T_0$  where  $T_0$  is the zero mode decay time computed by Holstein. If, on the other hand,  $N_r$  is a constant, the denominator of (3.2) occurs in a form already treated by Holstein for several types of broadening and a cylindrical as well as parallel plane geometry. The imprisonment time can then be computed immediately and is found to fall below  $T_0$  to an extent which depends on the type of broadening. These points arise again in the two approximate solutions to the imprisonment problem given in the next section.

### 4. APPROXIMATE SOLUTIONS

The approximate solutions mentioned can best be discussed in terms of the dimensionless parameter  $\bar{N}_{e\nu}T_0$  which represents the number of electron deexcitations of a resonance atom during the time a photon is imprisoned within the tube.  $\bar{N}_{e\nu}T_0$  is a measure of the interaction of the electron energy with the resonance radiation and will be termed the interaction parameter.

## Large Interaction

For  $\bar{N}_{e\nu}T_0$  large compared to unity, many deexcitations occur while the photon is imprisoned and the resonance radiation approaches thermal equilibrium with the electrons because of the strong interaction. To see this result mathematically, we need simply neglect the radiation terms in the balance Eq. (2.1). Then the density of resonance atoms for large interaction,  $N_{rl}$ , is given by

$$N_{e}(\nu'N_{g}-\nu N_{rl})=0,$$
 (4.1)

$$N_{rl} = \nu' N_g / \nu. \tag{4.2}$$

For a Maxwellian distribution of energies, using (2.2),

$$N_{rl} = N_{r\epsilon}. \tag{4.3}$$

The imprisonment time for large interaction,  $T_l$ , is then obtained from (3.2), taking  $N_r$  to be constant across the discharge. Thus

$$T_{l} = \tau \left/ \left\langle 1 - \int G(\mathbf{r}, \mathbf{r}') d\mathbf{r}' \right\rangle_{Av} \right.$$
(4.4)

The denominator is proportional to the  $g_0$  used by Holstein and has been tabulated by him.<sup>12</sup> Table I compiles the results for various values of m [see Eq. (2.3) in terms of the ratio  $T_l/T_0$ .  $T_0$  here indicates the decay time for the particular type of broadening and geometry considered. Note that the difference between  $T_l$  and  $T_0$  will generally be largest for the case of Doppler broadening. The treatment of the Doppler case then represents the extreme case to be found in a gas discharge.

It is quite instructive to compare the resonance radiation output from a Doppler-broadened discharge under the present conditions with that of a blackbody at the temperature of the electrons. We expect them to be equal if we properly specify the width of the resonance line. This is indeed true as elementary calculations show, if we take the resonance line to have a frequency width  $\Delta \omega$  approximately equal to the frequency band between the peaks of the Dopplerbroadened line,13 i.e.,

$$\Delta \omega = 2\omega_0 (v_0/c) [\ln(k_0 L/2)]^{\frac{1}{2}}, \qquad (4.5)$$

where c is the velocity of light. The origin of the dependence of  $T_l/T_0$  on  $\ln(k_0L/2)$  is then seen to arise because of the changing band width of the resonance line with  $\ln(k_0L/2)$ .

## **Small Interaction**

When the interaction parameter  $N_{e\nu}T_0$  is much smaller than unity, the electrons play little part in causing the loss of resonance atoms. The density of resonance atoms falls appreciably below the thermal equilibrium value and the product term,  $\nu N_e N_r$ , in the balance equation (2.1) becomes relatively unimportant. If  $N_e$  is similar to  $N_r$ , as indicated in the discussion after (2.9), we can set

$$N_e(\nu'N_g - \nu N_{rs}) = N_{rs} \cdot \text{const.}$$
(4.6)

Substituting (4.6) into (2.1), neglecting  $\nu N_e N_r$ , and comparing the result with (2.10), we see immediately that  $const = T_0^{-1}$ . The lowest-mode decay time is chosen, because the other modes have shorter decay times and hence die out when the lowest mode occurs in the steady state.

Averaging (4.6) over the discharge volume and comparing with (3.3), we find the imprisonment lifetime at small interaction,  $T_s$ , is given by

$$T_s = T_0.$$
 (4.7)

Using (4.7) in the averaged (4.6) and solving algebraically yields

$$\bar{N}_{rs} = \nu' \bar{N}_{e} T_{0} N_{g} / [1 + (\nu \bar{N}_{e} \bar{N}_{r} T_{0} / \bar{N}_{r})], \quad (4.8)$$

TABLE I. Values of the zero-mode decay time,  $T_0$ , and the ratio of imprisonment time for large interaction,  $T_l$ , to  $T_0$ . See Eqs. (2.4) and (4.4).

	m	ł	ł	1	
Parallel planes	$\frac{a_m T_0/\tau L^m}{T_{l/}T_0}$	0.93 0.96	0.87 0.86	0.544 1.80/ln(k <sub>0</sub> L/2)	
Cylinder	$a_m T_0/ au R^m \ T_l/T_0$	0.94 0.91	0.90 0.81	0.625	

or, for a Maxwellian distribution:

Planar geometry:

$$\frac{\bar{N}_{rs}}{N_{r\epsilon}} = \frac{\nu \bar{N}_{s} T_{0}}{1 + 1.21 \nu \bar{N}_{s} T_{0}}.$$
(4.9)

Cylindrical geometry:

$$\frac{\bar{N}_{rs}}{N_{r\epsilon}} = \frac{\nu \bar{N}_{e} T_{0}}{1 + 1.38 \nu \bar{N}_{e} T_{0}}.$$
(4.10)

In computing (4.9) and (4.10), a parabolic function was used for  $N_{rs}$  and the correct solution of the Schottky diffusion equation for  $N_e$ . This is sufficiently accurate for small values of the interaction parameter. Surprisingly enough, (4.9), and presumably (4.10), are accurate even for large values of interaction as seen in Fig. 3.

# 5. EXACT SOLUTION COMPUTED TO FIRST ORDER

The exact solution proceeds in the manner indicated in Sec. 2 and will be carried out essentially to the first order: the decay Eq. (2.10) is first solved; this solution is then used in treating the homogeneous Eq. (2.9); finally  $N_r$  is obtained from (2.8) and T from (3.2) or (3.3).

The treatment of the decay equation follows Holstein with some modifications. The discharge is taken to occur between parallel planes of infinite extent and of thickness L. The density of resonance atoms is a function of the coordinate, z, perpendicular to the walls placed at  $z=\pm L/2$ . Setting  $\xi=2z/L$ , the following three-parameter function is used to represent the density of resonance atoms:

$$N_{rn}^{0} = a_{n0} + a_{n1}(1 - \xi^{2}) + a_{n2}(1 - \xi^{4})$$
  
=  $a_{n0}n_{0}(\xi) + a_{n1}n_{1}(\xi) + a_{n2}n_{2}(\xi).$  (5.1)

The lowest-mode solution, n=0, is obtained by varying the a's to satisfy the variational principle derived from (2.10). Using this variational principle together with the Ritz variational method, we have<sup>5</sup>

$$\sum_{j=0,1,2} (K_{ij} - \alpha_0 H_{ij}) a_{0j} = 0, \qquad (5.2)$$

or

$$|\mathbf{K} - \alpha_0 \mathbf{H}| = 0, \tag{5.3}$$

<sup>&</sup>lt;sup>12</sup> See Tables I and II and the equation immediately preceding

Eq. (5.19) of reference 5. <sup>13</sup> The frequency spectrum of the Doppler-broadened line as it leaves the tube is described by  $I(x) \sim \exp(-x^2) \exp[-\frac{1}{2}k_0L$   $\times \exp(-x^2)]$ , where  $x = (\omega - \omega_0)c/\omega_0 v_0$ . See reference 4, Eq. (2.19).



FIG. 1. Spatial variation of  $N_r^0$  between parallel planes.

where

$$\alpha_0 = (1 - \lambda_0^0) L/a_1, \tag{5.4}$$

and  $a_1$  is given by (2.4).

**K** and **H** are matrices formed from the coefficients  $K_{ij}$  and  $H_{ij}$ . The integral formulas for these coefficients are given by Holstein<sup>5</sup> and  $K_{00}$ ,  $K_{01}$ ,  $K_{11}$ ,  $H_{00}$ ,  $H_{01}$ , and  $H_{11}$  were calculated by him.  $H_{02}$ ,  $H_{12}$ ,  $H_{22}$ , and  $K_{02}$  are obtained easily. The evaluation of the first integral appearing in  $K_{12}$  and  $K_{22}$  is straightforward, the substitution  $u=1-\xi$  being used. The second integral appearing in  $K_{12}$  and  $K_{22}$  presents some difficulty. The substitutions  $\xi=u-v$  and  $\xi'=u+v$ , however, put the integral into the form of a Dirichlet multiple integral. The details are given in the Appendix. **K** and **H** are then found to be

$$\mathbf{K} = \begin{pmatrix} 2 \ln(k_0 L/2) & 2 & 8/5 \\ 2 & 2 & 20/9 \\ 8/5 & 20/9 & 8/3 \end{pmatrix}, \quad (5.5)$$
$$\mathbf{H} = \begin{pmatrix} 2 & 4/3 & 8/5 \\ 4/3 & 16/15 & 128/105 \\ 8/5 & 128/105 & 32/21 \end{pmatrix}. \quad (5.6)$$

The determination of the  $\lambda_0^0$  and  $N_{r0}^0$  is as follows. Equation (5.3) was solved numerically for  $\alpha_0$  and then (5.4) was used to determine  $\lambda_0$ . With  $\alpha_0$  known, (5.2) is solved to obtain the *a*'s, and from these and (5.1),  $N_{r0}$  is determined. The computation was carried out for  $\ln(k_0L/2) = 2$ , 3, 5,  $\infty$ . From these values the following equations are deduced:

$$\alpha_0 = 1.8491 \left[ 1 - \frac{0.0329}{\ln(k_0 L/2) - 1.5836} \right], \quad (5.7)$$

$$a_{00} = 0.193 / [\ln(k_0 L/2) - 1.570],$$
 (5.8)

$$a_{02} = 0.464 \left[ 1 - \frac{0.940}{\ln(k_0 L/2) - 1.572} \right], \tag{5.9}$$

$$a_{01} = 1 - a_{00} - a_{02}. \tag{5.10}$$

The normalization here is such that  $N_{r0}^{0}(0)=1$ . The equations are accurate for  $\ln(k_0L/2)>2$ . Below this value, the theory loses validity. Figure 1 depicts the shape of  $N_{r0}^{0}$  for several values of  $\ln(k_0L/2)$ .

The improvement in the value of  $\lambda_0^0$  or  $\alpha_0$  over that determined by Holstein using a two-parameter function is negligible. The importance of using the threeparameter function lies in the accurate determination of the  $\alpha_0$ 's, and consequently of the eigenfunction  $N_{r0}^0$ , and of the possibility of determining, variationally,  $N_{r1}^0$  and  $\lambda_1^0$ .

The second eigenvalue and eigenfunction of the decay equation (2.10) are determined by choosing new a's such that  $N_{r1}^0$  is orthogonal to  $N_{r0}^0$ . This determines one a in terms of the other two. Since  $N_{r1}^0$  is indeterminate within a multiplier, one of the remaining a's was chosen as unity and the last a was used to minimize  $\alpha_1$  by trial and error. The method, though tedious, is straightforward. Table II summarizes the results. Note that  $\alpha_1 \cong 3.8\alpha_0$  for all values  $\ln(k_0L/2)$ .

Once the decay Eq. (2.10) is solved, the nonhomogeneous Eq. (2.9) can be treated, in the range desired, by first-order perturbation theory. The eigenvalues and eigenfunctions of (2.9) are then<sup>14</sup>

$$\lambda_n = \lambda_n^0 - \nu \tau \bar{N}_e \psi_{nn^0}, \qquad (5.11)$$

$$N_{rn} = \phi_n^0 + \sum_{n \neq m} \frac{\phi_n^0 \nu \tau}{\lambda_n^0 - \lambda_m^0} \psi_{nm^0}, \qquad (5.12)$$

where

$$\phi_n^0 \equiv N_{rn}^0 \left/ \left( \int_{-1}^1 (N_{rn}^0)^2 d\xi \right)^{\frac{1}{2}}$$
 (5.13)

is the normalized eigenfunction of the decay equation, and

$$\psi_{nm^0} \equiv \int \phi_n^0 \phi_m^0 N_e d\xi / \bar{N}_e.$$
 (5.14)

We note for future reference that

$$\psi_n^{0} \equiv \int \phi_n^{0} N_e d\xi / \bar{N}_e. \tag{5.15}$$

 $N_r$  is now determined by the eigenfunction expansion (2.8). In particular the average density of resonance

TABLE II. Values of the eigenvalues  $\alpha_n$ , and eigenfunction multipliers  $a_{nm}$ , for the first two decay modes (n=0, 1) as a function of  $\ln(k_0L/2)$ .

$\ln(k_0L/2)$					~	4			
	<i>α</i> 0	α1	$a_{00}$	<i>a</i> <sub>01</sub>	$a_{02}$	$a_{10}$	<i>a</i> 11	$a_{12}$	
2	1.703	6.5	0.414	1.019	-0.512	-22	4 5	1 3	
3	1.806	6.9	0.113	0.673	0.132	-0.2	74	6.2	
5	1.831	6.9	0.051	0.551	0.306	-0.0	74	64	
~	1.849	6.9	0.000	0.487	0.402	0.0	7.4	6.4	

<sup>14</sup> L. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1955), pp. 151 ff. atoms is of practical importance. Averaging (2.8), using (2.11) and (5.11), we have

$$\frac{\bar{N}_{r}}{N_{g}\nu'\bar{N}_{e}T_{0}} = \left[\frac{\tau}{T_{0}} + \frac{\sum\{(T_{n}/T_{0}) - (\tau/T_{0})(1 - r_{n}\psi_{nn})\psi_{n}\bar{N}_{rn}\}}{1 - r_{n}\psi_{nn}}\right],$$
(5.16)

$$r_n \equiv N_e T_n \nu. \tag{5.17}$$

 $\psi_{nm}$  and  $\psi_n$  are similar to  $\psi_{nm}^0$  and  $\psi_n^0$  being evaluated, however, with the eigenfunctions of the nonhomogeneous equation. They can obviously be obtained directly from the  $\psi_{nm}^0$  and  $\psi_n^0$  by using (5.12).

With a Maxwellian distribution of energies, (5.16) can be used to give the ratio of the average density of resonance states to the thermal equilibrium value:  $\bar{N}_r/N_{r\epsilon}$ . The resultant curve is given in Fig. 2. For a non-Maxwellian distribution, the ordinate is interpreted as  $\nu \bar{N}_r / \nu' N_q$ , i.e., the ratio of the number of de-excitations of resonance atoms to the number of excitations per second per unit volume. The agreement between the approximate expression (4.9) and the exact computations is within 10% over the range shown. Indeed, the exact value of the ratio must have an asymptotic value, for large interaction, of unity while the approximate expression has an asymptote 20% lower. The two curves must consequently cross again at some value of  $N_e \nu T_0$ , beyond which the exact calculations are given. Thus, the exact and approximate expressions agree well even in the range in which agreement is not at first expected.

The imprisonment time is given by Eq. (3.3) in the form:





FIG. 2. Ratio of resonance atom density to its equilibrium density vs the interaction parameter. The approximate expression is derived from Eq. (4.9).



FIG. 3. Ratio of imprisonment time to decay time vs the interaction parameter.

where

$$\frac{r\bar{N}_{e}\bar{N}_{r}}{\nu'\bar{N}_{g}} = \nu\bar{N}_{e}^{2}T_{0} \times \left[\frac{\tau}{T_{0}} + \frac{\sum\{(T_{n}/T_{0}) - (\tau/T_{0})(1 - r_{n}\psi_{nn})\psi_{n}\bar{N}_{rn}^{2}\}}{1 - r_{n}\psi_{nn}}\right],$$
(5.19)

and  $\bar{N}_r/\nu' N_g$  is given by (5.16).

Figure 3 gives the results of the computation of  $T/T_0$  for a discharge between parallel plates with Doppler broadening as a function of the interaction parameter,  $\nu \bar{N}_e T_0$ , for several values of  $\ln(k_0 L/2)$ . The results are independent of the type of energy distribution. For small interaction, the imprisonment lifetime approximately equals the decay time. The difference is due to the somewhat different forms of  $N_e$  and  $N_r$ . The asymptotic values of T for large interaction are also indicated.

The effect of the diffusion of resonance atoms to the tube walls under the equations given is easily seen. Diffusion causes the resonance density to resemble the lowest order decay mode for reasons already discussed. Thus, the diffusion will tend to improve the convergence of the series. The imprisonment time for the range of computation used can thus change but slightly. The density of resonance states will fall but in a manner which should be well represented by (4.9) or (4.10) with a term added in the denominator to represent the diffusion loss of resonance atoms. This term would be approximated to  $T_0D_r/\Lambda^2$ , where  $D_r$  is the diffusion coefficient for resonance atoms and  $\Lambda^2$  is the diffusion length for the geometry in question.

### 6. CONCLUSION

An exact computation has been carried out to first order for the density of resonance atoms and the imprisonment lifetime of a photon within the discharge. The particular case of a discharge between parallel plates with Doppler broadening was investigated, and good agreement was found between the exact computation and the approximate expressions given. Since Doppler broadening represents an extreme type of broadening (see Sec. 4), the approximate expressions should yield valid results when applied to other geometries and types of broadening. The inclusion of the diffusion of resonance atoms should offer no special problem, and the results to be expected in this case have been indicated.

## APPENDIX I

The mercury atom is taken as the model for computing the effect of metastable atoms on the particle balance equation for the resonance atoms. In mercury the two metastable states ( $6 {}^{3}P_{0}, 6 {}^{3}P_{2}$ ) bracket the resonance states ( $6 {}^{3}P_{1}$ ). No other excited states are close enough to require consideration in determining transitions among the states.

Let  $\nu_{nm}$  denote the transition rate by electron collision from the *n*th to the *m*th level. Using the subscripts 0, 2, *r*, *g* to denote the  ${}^{3}P_{0}$ ,  ${}^{3}P_{2}$ , resonance, and ground states, respectively, we can equate transitions to and from each metastable level as follows:

$$N_0(\nu_{0r} + \nu_{02} + \nu_{0g}) = \nu_{g0}N_g + \nu_{20}N_2 + \nu_{r0}N_r, \quad (I.1)$$

$$N_2(\nu_{2r} + \nu_{20} + \nu_{2g}) = \nu_{g2}N_g + \nu_{02}N_0 + \nu_{r0}N_r. \quad (I.2)$$

Diffusion of metastable atoms directly to the walls has been neglected.

Solving (I.1) and (I.2) algebraically, we obtain

$$N_0 = \nu^{r_0} N_r + \nu^{g_0} N_g, \qquad (I.3)$$

$$N_2 = \nu^{r^2} N_r + \nu^{g^2} N_g, \qquad (I.4)$$

where

$$\nu^{r_0}\Delta = \nu_{r_0}(\nu_{2r} + \nu_{20} + \nu_{2g}) + \nu_{20}\nu_{r_2},$$
  

$$\nu^{g_0}\Delta = \nu_{g_0}(\nu_{2r} + \nu_{2g} + \nu_{2g}) + \nu_{20}\nu_{g_2},$$
  

$$\nu^{r_2}\Delta = \nu_{r_2}(\nu_{0r} + \nu_{02} + \nu_{0g}) + \nu_{02}\nu_{r_0},$$
  

$$\nu^{g_2}\Delta = \nu_{g_2}(\nu_{0r} + \nu_{02} + \nu_{0g}) + \nu_{02}\nu_{g_0},$$
  
(I.5)

and

 $\Delta = (\nu_{0r} + \nu_{02} + \nu_{0g})(\nu_{2r} + \nu_{20} + \nu_{2g}) - \nu_{20}\nu_{02}.$ 

The particle balance for resonance atoms, including metastable transitions, is

$$N_{r} [N_{e}(\nu_{r0} + \nu_{r2} + \nu_{rg}) + \tau^{-1}]$$
  
=  $(\nu_{gr}N_{g} + \nu_{0r}N_{0} + \nu_{2r}N_{2})N_{e} + \tau^{-1} \int GN_{r}' d\mathbf{r}'.$  (I.6)

$$\nu' = \nu_{gr} + \nu_{0r} \nu^{g0} + \nu_{2r} \nu^{g2}, \qquad (I.7)$$

$$\nu = \nu_{r0} + \nu_{r2} + \nu_{rg} - (\nu_{0r}\nu^{r0} + \nu_{2r}\nu^{r2}). \tag{I.8}$$

The statement of detailed balancing (2.2) is still valid. This can be verified in a straightforward, though lengthy, manner by using detailed balancing for the individual transitions and the definition of the  $\nu$ 's with superscripts given in (I.5).

#### APPENDIX II

Let  $I_{ij}$  denote the second integral appearing in the definition of  $K_{ij}$  as given by Eq. (5.11a) of reference 5. Then, with m=1,

$$I_{12} = \int_{-1}^{1} \int_{-1}^{1} \frac{(\xi'^2 \xi^2) (\xi'^4 - \xi^4)}{|\xi' - \xi|^2} d\xi d\xi'.$$
(II.1)

Take

$$\xi = (u - v), \quad \xi' = (u + v), \quad 4dudv = d\xi'd\xi;$$
 then

$$I_{12} = 16 \int_{u-v=1}^{u+v=1} \int_{u-v=1}^{u+v=1} \frac{u^2 v^2 (u^2+v^2)}{|v|^2} du dv. \quad (\text{II.2})$$

The integration boundaries enclose a diamond-shaped area. Since the integrand is even in u and v, the integral is four times the integration in the upper right quadrant of the diamond. Therefore

$$I_{12} = 64 \int_0^1 du \int_0^{1-u} \frac{u^2 v^2 (u^2 + v^2)}{v^2} dv.$$
 (II.3)

The integral is now in the form of a Dirichlet multiple integral<sup>15</sup>:

$$\int_{0}^{1} du \int_{0}^{1-v} u^{p} v^{q} dv = \frac{\Gamma(p+1)\Gamma(q+1)}{\Gamma(p+q+3)}.$$
 (II.4)

We then obtain  $I_{12}=112/45$ . In a completely analogous manner we find  $I_{22}=96/35$ .

<sup>15</sup> P. Franklin, *Methods of Advanced Calculus* (McGraw-Hill Book Company, Inc., New York, 1944), Sec. 99.