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Determination of the Coefficient of Diffusion and Frequency of Ionization in Microwave Discharges*

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A method is presented for direct determination of the frequency of ionization and of the coefficient of free diffusion for electrons in a microwave discharge. The method is based on determining the rate of growth of the electron density in a microwave cavity in which an electric field larger than that necessary for breakdown is applied. The ionization frequency and the coefficient of free diffusion for electrons in hydrogen were measured in a pressure range of 15 to 45 mm Hg. Comparison is made with existing theory.

INTRODUCTION

MICROWAVE breakdown experiments, in which diffusion is the controlling loss mechanism, can yield the ratio ν_i/D_-, where ν_i is the ionization frequency and D_- is the coefficient of free diffusion for electrons.[1] This paper describes a method for a direct determination of ν_i/p and D_-p as a function of E/p. A breakdown experiment deals with a plasma in which the gain in electron density caused by ionization is just balanced by the loss of electrons that results from diffusion. The proper experimental parameters[2] are E/p, $p\lambda$, and $p\Lambda$, with E the electric-field strength, λ the free-space wavelength of the microwave field, Λ the diffusion length, and p the pressure. The time required for the electron density to build up to some predetermined measurable value is long (theoretically it is infinite), and is not a parameter of the experiment. With field strengths greater by a few percent than the field that is required for breakdown, the time is of the order of a few microseconds. We shall show that by using an experimental parameter (tp), where t is the time, direct determination of the coefficients ν_i/p and D_-p can be obtained, and breakdown fields can be predicted.

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[1] S. C. Brown, *Handbuch der Physik* 22, 531 (1956).
[2] S. C. Brown and A. D. MacDonald, Phys. Rev. 76, 1629 (1949).

THEORY

The rate of growth of electron density, in the absence of space charge, is described by the diffusion equation[3]

$$\partial n/\partial t=\nu_i n+\nabla^2 D_- n. \tag{1}$$

Equation (1) is to be solved for a cylindrical cavity of radius R and length L, with ν_i and D_- independent of position. The solution is subject to the following conditions. At time $t=0$, a single electron is present at $r=0$, $z=z_0$; that is, $n=\delta(z-z_0)\delta(r)/2\pi r$ at $t=0$, where δ is a delta function. For $t>0$, the electron density must vanish at the walls of the cavity; that is, at $r=R$, and $z=0$, and $z=L$. Under these conditions, the solution to Eq. (1) is

$$n(r,z,t)=\frac{2}{V_c}\sum_{ml}\sin\left(\frac{m\pi z_0}{L}\right)\times\sin\left(\frac{m\pi z}{L}\right)\frac{J_0(\beta_{0l}r/R)}{J_1^2(\beta_{0l})}\exp(\gamma_{ml}t), \tag{2}$$

where $\gamma_{ml}=\nu_i-D_-/\Lambda_{ml}^2=\nu_i-D_-[(m\pi/L)^2+(\beta_{0l}/R)^2]$; β_{0l} is the lth root of $J_0(x)=0$; and V_c is the volume of the cavity. The fundamental diffusion mode is given by $m=1$, $l=1$.

In a flat cavity, with $L\ll R$, the higher modes in the axial direction can be neglected, since they last only for times that are much shorter than those observed experimentally. The higher modes in the radial direc-

[3] M. A. Herlin and S. C. Brown, Phys. Rev. 74, 291 (1948).

tion are not negligible. It is, therefore, more convenient to express the solution to the diffusion equation in an alternative form, obtained with the aid of a Green's function,

$$n(r,z,t)=(2/L)\sin(\pi z_0/L)\sin(\pi z/L) \times\exp[\nu_i-D_-(\pi/L)^2]t\exp[(-r^2/4D_-t)]/(4\pi D_-t). \quad (3)$$

Equation (3) satisfies the conditions at $t=0$. At $t>0$ the conditions are satisfied at $z=0$ and $z=L$, but they are not satisfied at $r=R$. However, the experimental conditions are such that $R^2/4D_-t>(p \text{ in mm Hg})>15$. As a result, the density, as given by Eq. (3), is sufficiently small at $r=R$ (although it is not zero) to be negligible.

The electron density is measured experimentally by observing the relative decrease of the microwave field in the cavity caused by the electron cloud. This decrease is a function of the quantity

$$N=\frac{1}{E_0{}^2}\int_{\substack{\text{volume}\\ \text{of cavity}}} n(r,z,t)E^2dv, \quad (4)$$

where N is the total number of electrons in the cavity averaged over the square of the field. The experimental cavity oscillates in the TM_{010} mode, for which the electric field is given by $E=E_0J_0(\beta_{01}r/R)$, E_0 being the field at the axis of the cavity. Using Eq. (4), we obtain

$$N=\left[\int_0^L \sin\left(\frac{\pi z_0}{L}\right)\sin\left(\frac{\pi z}{L}\right)dz \times\int_0^R \frac{\exp(-r^2/4D_-t)}{4\pi D_-t}J_0{}^2(\beta_{01}r/R)2\pi rdr\right] \times\exp\left[\nu_i-D_-\left(\frac{\pi}{L}\right)^2\right]t. \quad (5)$$

In evaluating the integral in Eq. (5), a negligible error is made in allowing R to go to infinity, since, for $r>R$, the exponential is less than e^{-15}. The result is

$$\begin{aligned}N&=(4/\pi)\sin(\pi z_0/L)\exp(-2\beta^2{}_{01}D_-t/R^2)\\&\quad\times J_0(j\beta^2{}_{01}2D_-t/R^2)\exp[\nu_i-D_-(\pi/L)^2]t\\&=(4/\pi)(1-2\beta^2{}_{01}D_-t/R^2+\cdots)\sin(\pi z_0/L)\\&\quad\times\exp[\nu_i-D_-(\pi/L)^2]t. \quad (6)\end{aligned}$$

Experimentally, we seek the minimum time, t_m, to achieve a predetermined value, N_m. The time will be least if the electron appears at the center of the cavity [$\sin(\pi z_0/L)=1$, $r=0$] because the field is greatest and diffusion least from that point. The rate of appearance of electrons from external sources was observed to be less than one per pulse length, but sufficient breakdown times were observed to assure that for the minimum time the initiating electron arrived within 10% of the breakdown time from the start of the pulse. Furthermore, since the quantities of interest, D_- and ν_i, occur in the exponential, the experimental N_m is of the order of 10^9, and $(2\beta^2{}_{01}D_-t)/R^2<\frac{1}{5}$, an error in time of less than 1% is made by writing

$$N_m=\exp[\nu_i-D_-(\pi/L)^2]t_m. \quad (7)$$

Since the quantities ν_i/p and D_-p are functions of only E/p, we finally write Eq. (7) in the form

$$1/(t_mp)=(1/\ln N_m)[\nu_i/p-(D_-p)/(p\Lambda)^2], \quad (8)$$

where $\Lambda=(L/\pi)$. A plot of $1/(t_mp)$ against $1/(p\Lambda)^2$ at constant E/p should yield a straight line, from which the value of ν_i/p and D_-p can be obtained.

For hydrogen, Eq. (8) is valid only for $p\gtrsim 15$ mm Hg. For pressures of the order of 1 mm Hg, the electron density distribution is sufficiently spread out in the radial direction, so that no simple expression analogous to Eq. (3) could be obtained. The exact form of the density distribution given in Eq. (2) has to be used. For very low pressures, at which only the first radial mode is appreciable, Eq. (8), except for a constant factor, is again correct.

It should be noted that Eq. (8) was derived on the assumption that ν_i and D_- were constant. Actually, this is not so because the microwave field, and hence the electron energy, is a function of the radial position in the cavity. This, and the fact that at high values of N_m the diffusion begins to be limited by space charge, will be discussed later.

EXPERIMENT

A 10-cm magnetron feeds power to a $\frac{7}{8}$-inch coaxial line, which, in turn, is coupled by a loop to a TM_{010} mode cavity. For the determination of wavelength, a probe in the coaxial line is connected to a high-Q wavemeter. An ethylene-glycol attenuator[4] provides a continuously variable control over the power incident on the cavity. A known fraction of the incident power is coupled from the line, by a directional coupler, to a thermistor and a crystal. The output voltage of the crystal is displayed on a Tektronix oscilloscope. The signal is calibrated by an absolute measurement on the thermistor bridge, using cw power. A second loop is used to display on an A/R oscilloscope screen the strength of the electric field in the cavity as a function of time during a pulse. The time between microwave pulses was kept sufficiently long (approximately 1/30 sec) to allow complete decay of the plasma created by the preceding pulse. The vacuum system could reach a pressure of 10^{-9} mm Hg before hydrogen was let into the system. The hydrogen was supplied by uranium hydride contained in a quartz tube.

The Q value of the cavity was sufficiently low (approximately 1000) to allow the field in the cavity to build up in time that was short compared with the breakdown time. The field measurements were accurate within 5%, pressure within 2%, and the time within

[4] D. Alpert, Rev. Sci. Instr. 20, 779 (1949).

10%. The variation in $p\Lambda$ was effected by varying the pressure of hydrogen from 15 mm Hg to 45 mm Hg and by using two oxygen-free copper vacuum cavities with plate separations of $\frac{1}{8}$ inch and $\frac{1}{16}$ inch.

The quantity observed experimentally was the time required to reach a density N_m at some constant pressure. The quantity N_m was taken as that number of electrons which causes a decrease of 5% in the electric field in the cavity. The electric field in the cavity was determined by measurement of the power that entered the cavity, using microwave techniques described by Brown *et al.*[5]

Figure 1 shows a plot of t_m against the effective field E_e [defined by $E_e^2=E_0^2\nu_c^2/(\nu_c^2+\omega^2)$] with p_0, the pressure at 0°C, as a parameter. The use of the effective field E_e, rather than of the actual field E_0, partly removes the dependence of the parameter $t_m p$ on $p\lambda$. Here ν_c is the collision frequency for momentum transfer and ω the radian frequency of the microwave field.

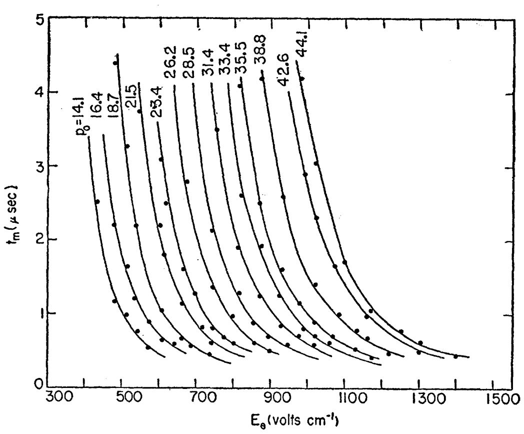

FIG. 1. Minimum time as a function of the effective electric field. $\Lambda=0.1$ cm.

From these plots, a curve of $1/(t_m p)$ against $1/(p\Lambda)^2$ for a constant E_e/p_0 can be obtained. However, the experimental conditions do not quite correspond to the ideal ones for which Eq. (8) was derived.

Experimentally, electron densities reach values sufficiently large, so that space charge limits the diffusion. Following Allis and Rose,[6] the effect of the space charge can be accounted for by the use of an effective diffusion coefficient, D_s, which is a function of the electron density. With space charge present, the observed times, t_{obs}, are shorter than those given by Eq. (8), and can be obtained from the equation

$$t_{\text{obs}}=\int\frac{dn}{n}\bigg/\left[\nu_i-D_s(n)/\Lambda^2\right]. \tag{9}$$

[5] S. C. Brown and D. J. Rose, J. Appl. Phys. **23**, 711 (1952); D. J. Rose and S. C. Brown, J. Appl. Phys. **23**, 719 (1952); **23**, 1028 (1952); L. Gould and S. C. Brown, J. Appl. Phys. **24**, 1053 (1953).

[6] W. P. Allis and D. J. Rose, Phys. Rev. **93**, 84 (1954).

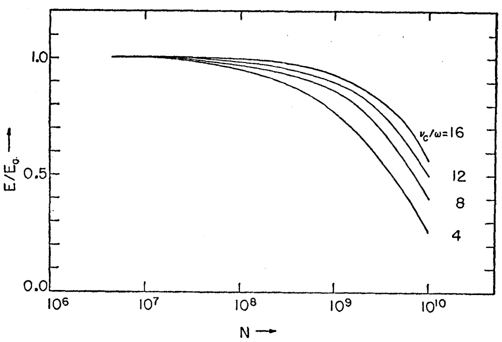

FIG. 2. Fractional change in the microwave field as a function of the total number of electrons. $\Lambda=0.1$ cm.

In the range of pressures that was used, $\nu_i/p\approx 10D_s p/(p\Lambda)^2$; therefore, from Eqs. (9) and (8), the quantity $\Delta t=(t_m-t_{\text{obs}})$ can be written to a good approximation as

$$p\Delta t=\frac{p}{(p\Lambda)^2[(\nu_i/p)-(D_-p)/(p\Lambda)^2]^2}\int(D_--D_s)\frac{dn}{n}. \tag{10}$$

The integral in Eq. (10) was evaluated by fitting an analytical expression to the curves of D_s against n that were computed by Allis and Rose. The observed times were then corrected by the amount Δt. The corrections ranged from approximately 5% at high pressures to 20% at low pressures.

An additional complication arises from the fact that N_m is a function of ν_c/ω. This can be seen by realizing that the decrease of the electric field in the cavity is the result of the shift of the resonant frequency of the cavity and the change in the Q value caused by the electron cloud. These are given by

$$\begin{aligned}\frac{\Delta\omega}{\omega}&=\frac{1}{2}\frac{e^2}{m\epsilon_0\omega^2}\frac{1}{[1+(\nu_c/\omega)^2]}\int nE^2dv\bigg/\int E^2dv,\\ \frac{1}{Q}-\frac{1}{Q_0}&=\frac{e^2}{m\epsilon_0\omega^2}\frac{(\nu_c/\omega)}{[1+(\nu_c/\omega)^2]}\int nE^2dv\bigg/\int E^2dv,\end{aligned} \tag{11}$$

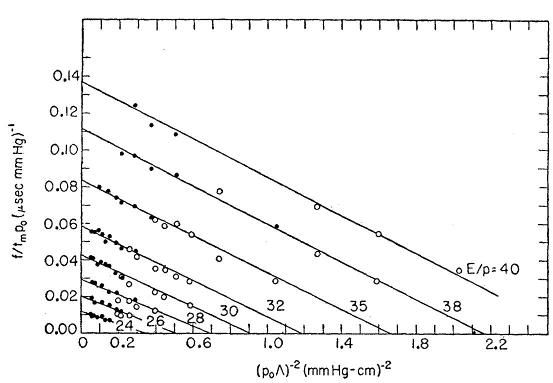

FIG. 3. Plot of $f/(t_m p)$ (f as defined) against $1/(p\Lambda)^2$. ●—, $\Lambda=0.1$ cm; ○—, $\Lambda=0.05$ cm.

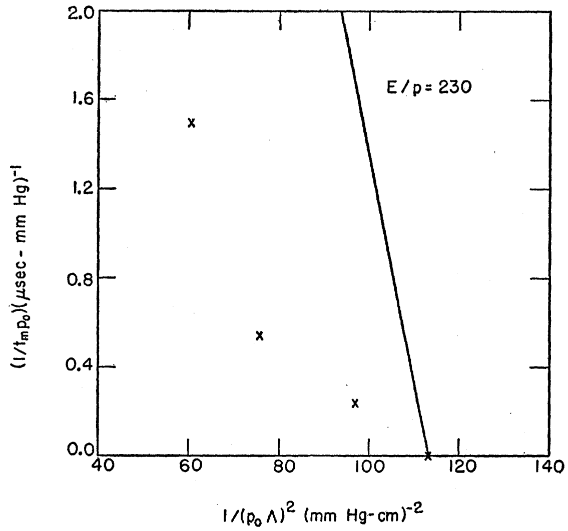

FIG. 4. Plot of $1/(t_m p)$ against $1/(p\Lambda)^2$ at low pressures.

where Q_0 is the unloaded Q-value of the cavity in the absence of the plasma. From Eq. (11) and the results of Brown *et al.*,[5] a plot of the field in the cavity as a function of N, with (ν_c/ω) as a parameter, is obtained for a constant input power. (See Fig. 2.) Since N_m appears in a logarithm in Eq. (8), it is convenient to express the dependence of N_m on (ν_c/ω) by writing $N_m=(N_{m0})^{f(\nu_c/\omega)}$. The function $f(\nu_c/\omega)$ was determined, from the plots of Fig. 2, to be a straight line. The constant N_{m0} was taken to be 5×10^8. The values of $f(\nu_c/\omega)$ range from 1.01 for high pressures to 0.95 for low pressures. Thus, the dependence of N_m on pressure is accounted for by plotting $f(\nu_c/\omega)/(t_m p)$, rather than $1/t_m p$, against $1/(p\Lambda)^2$. The plots of $f/(t_m p)$ against $1/(p\Lambda)^2$ are shown in Fig. 3, for a pressure range of 15–45 mm Hg. It is seen that the plots are straight lines, in agreement with Eq. (8).

The experiments were repeated in the pressure range around 1 mm Hg. As previously mentioned, Eq. (8) is not expected to hold in this range of pressure, because the electron loss in the radial direction is not negligible during the time required for the discharge to build up. As a result, the time required to reach a specified density is greater than that predicted by Eq. (8). Figure 4 shows the experimental points, together with a curve obtained from Eq. (8).

DISCUSSION OF RESULTS

From the slope of the plots in Fig. 3, the values of D_-p are obtained as a function of E_e/p. The intercepts with the ordinate yield ν_i/p, while the intercepts with the abscissa, since they correspond to infinite times, give the values of $(p\Lambda)$ as a function of E_e/p for breakdown. Breakdown fields that were predicted in this way are compared with experimental and theoretical results in Fig. 5. The agreement is seen to be good. In Fig. 6, the values of D_-p are plotted against E_e/p. For comparison, values of D_-p, obtained from Varnerin and Brown's[7] measurements of D_-/μ and from Bradbury and Nielson's[8] measurements of the mobility μ, are also plotted. In Fig. 6 the values of ν_i/p against E_e/p and the theoretical values of Allis and Brown[9] are also plotted. The theoretical values are subject to a 20% variation as a result of the uncertainty in the experimentally obtained ionization cross section.[10] In

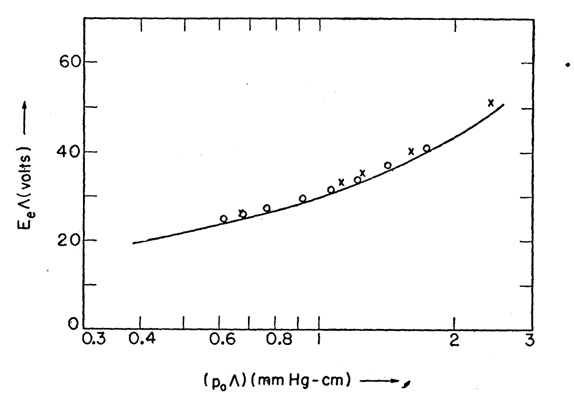

FIG. 5. Breakdown voltage as a function of $(p\Lambda)$. —, theory; o, present experiment; ×, breakdown experiment.

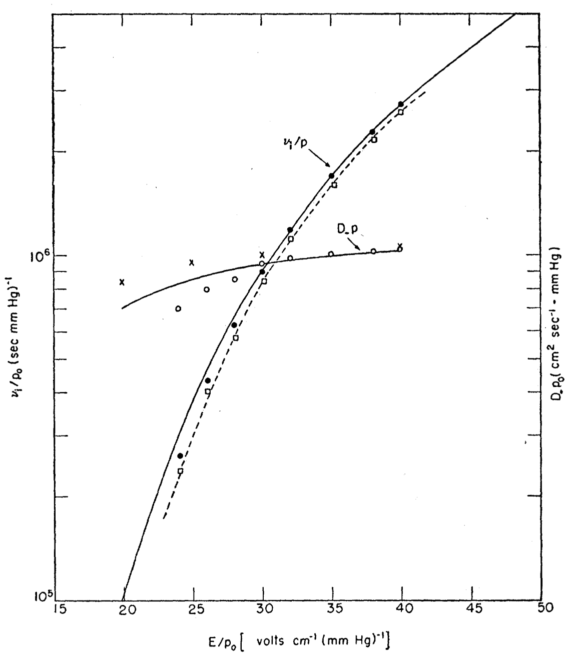

FIG. 6. Experimental and theoretical values of (D_-p) and ν_i/p as a function of E/p. o, experimental values of D_-p; ×, experimental values of D_-p (Varnerin and Brown). □, experimental values of ν_i/p; ●, experimental values of ν_i/p corrected for the variation of the field over the radius of the cavity. The solid line represents theoretical values in both cases.

[7] L. J. Varnerin and S. C. Brown, Phys. Rev. **79**, 946 (1950).
[8] N. W. Bradbury and R. A. Nielsen, Phys. Rev. **49**, 388 (1936).
[9] W. P. Allis and S. C. Brown, Phys. Rev. **87**, 419 (1952).
[10] H. Ramien, Z. Physik **70**, 353 (1931).

addition, Fig. 6 exhibits values of ν_i/p corrected for the nonuniformity of the electric field. The correction is obtained as follows.

In Eq. (7), the coefficient ν_i is interpreted as an effective ionization frequency ν which takes into account the variation of the field with the radius of the cavity and the loss of electrons by radial diffusion. The value of ν lies between the value of ν_i at the axis of the cavity where E_e/p is determined, and the value of ν associated only with the lowest radial diffusion mode. The value of ν associated with the lowest diffusion mode is obtained by a variational calculation.[11] The maximum correction is the difference between ν_i at the axis of the cavity and ν for the lowest diffusion mode. The corrected values are obtained by applying the maximum correction.

The experimental values of ν_i/p do not agree with dc measurements of the Townsend ionization coefficient α that was determined by Rose[12] when the two coefficients are compared by the use of the relation[1] $\nu_i/p = \alpha\mu E/p$. The values of mobility were obtained from reference 8. The discrepancy is greatest at small values of E/p. The values of ν_i/p that are plotted in Fig. 6 are not affected by taking into account the fluctuations of the average electron energy with the time variation of the microwave field.

[11] P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill Book Company, Inc., New York, 1953), Chap. 6; S. J. Buchsbaum, Quarterly Progress Report, Research Laboratory of Electronics, Massachusetts Institute of Technology, January 15, 1957 (unpublished), p. 10.

ACKNOWLEDGMENTS

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[12] D. J. Rose, Phys. Rev. **104**, 273 (1956).

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Statistical Mechanical Theory of Transport Phenomena in a Fully Ionized Gas

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Nonequilibrium statistical mechanics, as developed by Kirkwood, Irving, and Zwanzig, is applied to a system of charged particles interacting via the electromagnetic field. Particles and field are treated statistically both from the classical and quantal points of view. It is shown that Maxwell's equations are valid for the quantum statistical ensemble-averaged fields. An exact form for the hydromagnetic equations is derived, and it is shown that these equations differ from those which are customarily considered to be exact.

I. CLASSICAL THEORY

We consider a system composed of N charged particles subjected to external forces and interacting via the electromagnetic field. Let r: $\mathbf{r}_1, \cdots \mathbf{r}_N$ be the position vectors of the particles and $e_1, \cdots e_N$ their electric charges. It is assumed that apart from the masses $m_1, \cdots m_N$ the particles have no further electrical or mechanical structure. The electric field $\mathbf{E}$ is decomposed into a transverse internal part $\mathbf{E}^T$, an instantaneous Coulomb part $\mathbf{E}^C$, and an external part $\mathbf{E}^{\text{ext}}$:

$$\mathbf{E} = \mathbf{E}^T + \mathbf{E}^C + \mathbf{E}^{\text{ext}}, \tag{1.1}$$

where

$$\mathbf{E}^C = \sum_{k=1}^{N} e_k(\mathbf{r}-\mathbf{r}_k)/|\mathbf{r}-\mathbf{r}_k|^3, \tag{1.2}$$

and

$$\nabla\cdot\mathbf{E}^T = 0. \tag{1.3}$$

Similarly the magnetic field $\mathbf{B}$ is expressed as the sum of an internal and an external part:

$$\mathbf{B} = \mathbf{B}^{\text{int}} + \mathbf{B}^{\text{ext}}. \tag{1.4}$$

The system is enclosed in a large volume $V = L^3$ so that the electromagnetic field may be described by a denumerable set of coordinates. Following Heitler,[1] a set of real vector functions $\mathbf{A}_\lambda(\mathbf{r})$ is introduced, complete with respect to transverse vector fields and with the following properties:

$$\int_V \mathbf{A}_\lambda\cdot\mathbf{A}_\mu d\mathbf{r} = 4\pi c^2\delta_{\mu\nu}, \tag{1.5}$$

$$\nabla^2\mathbf{A}_\lambda + k_\lambda^2\mathbf{A}_\lambda = 0, \tag{1.6}$$

$$\nabla\cdot\mathbf{A}_\lambda = 0, \tag{1.7}$$

where $k_\lambda^2 \equiv \omega_\lambda^2/c^2$, $\mathbf{k}_\lambda = 2\pi\mathbf{n}/L$, and $\mathbf{n}$ is a vector having non-negative integral components. The fields $\mathbf{E}^T$ and $\mathbf{B}^{\text{int}}$ are expressed in terms of the field coordinates q_λ by the equations

$$\mathbf{E}^T = -(1/c)\textstyle\sum_\lambda \dot{q}_\lambda\mathbf{A}_\lambda, \tag{1.8}$$

$$\mathbf{B}^{\text{int}} = \textstyle\sum_\lambda q_\lambda\nabla\times\mathbf{A}_\lambda. \tag{1.9}$$

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[1] W. Heitler, *The Quantum Theory of Radiation* (Oxford University Press, New York, 1954), p. 39.