state would determine absolute values for the oscillator strengths.

Another quantity of interest is the ratio of the lifetimes of the two states in lead with the (6p7s)-electron configuration. Combining the results of this paper with

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that obtained by Saloman and Happer,<sup>2</sup> a value of 1.15(4) for the ratio  $\tau({}^{3}P_{1}{}^{\circ})/\tau({}^{1}P_{1}{}^{\circ})$  is obtained.

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## Theory of Electron Collision Experiments at Intermediate and High Gas Densities\*

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By means of a two-stream approximation, an analytical solution is obtained to the equation of transfer governing the steady-state concentration of mono-energetic electrons within a slab of gas bounded by two infinite planes, one of which emits a constant current density normal to its surface. The theory places no restriction on the gas pressure and includes the effects of inelastic collisions and partial reflection of scattered electrons at one or both boundaries. The results are applied to electron-beam experiments at intermediate and high pressures where the mean free path of electrons is comparable to or less than the length of the collision chamber. Analytical expressions are obtained for the electron current transmitted through the gas and for the normalized ion currents to be expected in the case of total ion collection and in the case of sampling through a slit. The effect of elastic and inelastic collisions may be represented by an "equivalent length factor" which modifies the equations normally applicable under low-pressure conditions. The results of the present theory are compared with previous theories, with particular reference to their use in interpreting experiments of the Maier-Leibnitz type, designed to measure absolute values of inelastic-collision cross sections.

## I. INTRODUCTION

HIS paper deals with the motion of electrons in gases in the pressure range in which the electron mean free path is comparable with or less than the length of the chamber. One motivation for this work is the recent extension of electron-beam experiments to higher pressures in this<sup>1</sup> and other laboratories.<sup>2</sup> The need for electron-beam experiments at gas pressures higher than those conventionally used (above  $\sim 10^{-3}$ Torr) arises from the desire to obtain higher rates of reaction for the study of (1) ion-molecule reactions involving ions produced in a known excited state by essentially monoenergetic electrons and (2) three-body collision processes involving an electron and two neutral atoms or molecules, e.g., electron attachment to O2 at low-electron energies. It will be shown that the operation of an electron beam at high pressures causes a change in the apparent pressure dependence of ion currents from that found at low pressures.

An additional motivation for this paper is to provide what we believe to be a more accurate analysis of the Maier-Leibnitz<sup>3</sup> type experiment for the determina-

tion of inelastic-scattering cross sections for atoms and molecules. Our analysis is also conceptually simpler than the original analysis of Harries and Hertz<sup>4</sup> or the more recent type of analysis used by McClure<sup>5</sup> and by Fleming.6

In the experiments which we wish to analyze, the electrons are injected into the collision chamber through a relatively small entrance aperture and in a direction normal to the surface containing the aperture. This



FIG. 1. The plane parallel geometry considered in the present problem.

<sup>4</sup> W. Harries and G. Hertz, Z. Physik 46, 177 (1927).

<sup>6</sup> B. T. McClure, Phys. Rev. 130, 1295 (1963).
<sup>6</sup> R. J. Fleming, Proc. Phys. Soc. (London) 83, 890 (1964).

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<sup>1</sup> R. K. Curran, J. Chem. Phys. 38, 2974 (1963).
<sup>2</sup> J. S. Dahler, J. L. Franklin, M. S. B. Munson, and F. H. Field, J. Chem. Phys. 36, 3332 (1962).
<sup>8</sup> H. Maier-Leibnitz, Z. Physik 95, 499 (1935).

geometry is indicated in Fig. 1. The experimentally measured quantities are the gas pressure, the electron current collected at the x=L boundary, and the rate at which excited species or ions are produced in the whole or part of the volume. The rate of production of such species per unit volume will, in general, be proportional to the density of electrons in the collision chamber. It is the purpose of this work to obtain analytic expressions giving the dependence on pressure of the electron density at any point and of the transmitted electron current. In so doing we shall take into account the effects of inelastic collisions by assuming that they cause the electron to be lost, in the sense that it no longer has sufficient energy to cause production of the measured species. In this context, the term inelastic implies excitation or ionization of the target, or attachment of the electron.

For the purpose of this paper we define three regions of pressure. At low pressures, the mean free path for electrons is much greater than the length of the collision chamber. In this region the electrons within the collision chamber consist predominantly of unscattered beam electrons. Their number is independent of pressure, and is related in a simple way to the injected current, which, since there is negligible attenuation, may be measured at the collector.

At high pressures the electron mean free path is much smaller than the length of the collision chamber, and the electrons within the collision chamber are predominantly scattered electrons. The electron beam in this pressure region is strongly attenuated in traversing the collision chamber, providing a source of electrons which gives rise to the spatial distribution of scattered electrons. These scattered electrons are lost by diffusion to the walls and by inelastic collisions.

At intermediate pressures the electron mean free path is comparable to the length of the collision chamber; thus, the number of beam electrons and scattered electrons in the collision chamber are of comparable magnitude.

In some experiments a magnetic field of a few hundred gauss directed parallel to the injected electrons causes spiralling of the scattered electrons and serves to limit their transverse motion to the random walk or diffusion of the electron guiding centers across the magnetic field. In other experiments no magnetic field is used and the electron motion at right angles to the direction of injection is limited only by collisions. For the purposes of analysis, we will assume that the surface at x=0presents a homogeneous boundary to the scattered electrons within the chamber, as though the entrance hole were endowed with the same properties as the rest of the surface. We will also assume that the surface normal to the direction of injection which terminates the collision chamber and serves as an electron collector is large enough to intercept essentially all of the scattered electrons. The collector area required will, in general, be much smaller when a magnetic field parallel

to the direction of injection is used. The collector electrode may, however, be designed to accept only a restricted class of incident electrons. For example, in an experiment of the Maier-Leibnitz type, only electrons which have not suffered inelastic collisions are accepted by the collector.

We also assume that any sampling arrangement located between the source and collector planes, e.g., an ion exit slit in the side wall, is sufficiently large in the y or z direction (see Fig. 1) to collect the products of electron collisions independent of the location of the electrons in the y and z directions. With these assumptions the problem reduces to one involving only the xdimension, and the ratio of any two measured signals can be calculated by considering an infinite parallel plane source and collector, the ratio of interest being obtained from the theory by the ratio of the appropriate quantities calculated per unit area of the infinite geometry considered.

This type of one-dimensional multiple scattering problem has been treated by a large number of investigators in connection with radiative transfer or electron transfer in solids or gases. The results obtained prior to 1950 are summarized by Chandrasekhar<sup>7</sup> and form the basis of our discussion. Unfortunately, many investigators have considered rather specific problems, have used numerical solutions to obtain the desired result, and have not compared their results with the predictions of the theoretical approximations which lead to analytical formulas. Studies relevant to our problem are those of Bartels,<sup>8</sup> Bartels and Noack,<sup>9</sup> of Bartels and Nordstrom,<sup>10</sup> of Goertz,<sup>11</sup> of McKelvey, Longini, and Brody,<sup>12</sup> of Shockley,<sup>13</sup> of McClure,<sup>5</sup> and of Fleming.<sup>6</sup> The work of Bartels, of Bartels and Noack, and of Bartels and Nordstrom uses basic equations similar to ours but resorts to numerical solutions of the integral equation. Their results are compared with ours in the text. The problem treated by McKelvey, Longini, and Brody,<sup>12</sup> and discussed by Shockley<sup>13</sup> is applied to semiconductor problems and is nearly identical to that of the idealized model which we will consider. Unfortunately, their treatment leads to difficulties in relating the parameters of the solution, i.e., diffusion and absorption coefficients, to the conventional scattering and absorption cross sections. No such difficulty is encountered in our treatment. The analyses of McClure<sup>5</sup> and of Fleming<sup>6</sup> are made complicated by the omission of the absorption terms from the basic equations for the electron motion thereby requiring them to solve for the time-dependent and statistical aspects of

<sup>&</sup>lt;sup>7</sup>S. Chandrasekhar, Radiative Transfer (Clarendon Press, Oxford, England, 1950). <sup>8</sup> H. Bartels, Z. Physik 55, 507 (1929).

 <sup>&</sup>lt;sup>10</sup> H. Bartels and H. Noack, Z. Physik 64, 465 (1930).
 <sup>10</sup> H. Bartels and C. H. Nordstrom, Z. Physik 68, 42 (1931).
 <sup>11</sup> A. Goertz, Z. Physik 155, 263 (1959).
 <sup>12</sup> J. P. McKelvey, R. L. Longini, and T. P. Brody, Phys.

Rev. 123, 51 (1961)

<sup>&</sup>lt;sup>13</sup> W. Shockley, Phys. Rev. **125**, 1570 (1962).

the electron motion when actually the problem is time-independent.

The general theory for our idealized model is given in Sec. II. The solutions for the electron density and electrode currents obtained in Sec. II are applied to various experimental arrangements in Sec. III. The results of the present theory are applied to the problem of interpreting experiments of the Maier-Leibnitz type in Sec. IV. In the Appendix we derive an expression for the mean number of collisions suffered by electrons collected at the x=L boundary, for the purpose of comparison with previous estimates.

#### **II. THEORY**

It is convenient at this point to set out the definitions of the various quantities involved in the calculations. These are given in Table I.

The total current density at any plane x consists of the current of scattered electrons  $J_s$ , and the current density of the primary beam  $J_B$  and we can write

$$J_t(x) = J_s(x) + J_B(x)$$
. (2.1)

We can write a similar equation for the total density of electrons

$$n_t(x) = n_s(x) + n_B(x).$$
 (2.2)

The problem of determining  $J_s(x)$  and  $n_s(x)$  is formally identical to that of determining the photon flux and density in a plane parallel medium which absorbs, emits, and scatters radiation.<sup>7</sup>

In the present problem we shall assume that the elastic scattering is isotropic, in which case the appropriate equation of transfer, analogous to Eq. (129) on p. 22 of Ref. 7, is

$$\cos\theta \frac{dI(\theta,x)}{dx} = -\left(\frac{\sigma+\alpha}{L}\right)I(\theta,x) + \frac{\sigma}{L}\int I(\theta',x)\frac{d\omega}{4\pi} + \frac{S(x)}{4\pi}, \quad (2.3)$$

where  $I(\theta, x)$  is the current, due to scattered electrons, crossing unit area of the plane x, within unit solid angle, at a direction  $\theta$  to the positive x axis.

With the above definition of  $I(\theta, x)$ , we may write

$$I_s(x) = \int I(\theta, x) \cos\theta, d\omega \qquad (2.4)$$

and

$$n_s(x) = \frac{1}{v} \int I(\theta, x) d\omega. \qquad (2.5)$$

The function S(x)dx gives the rate at which the electrons are being fed to the scattered distribution between x and x+dx. In our case these electrons arise from

TABLE	I.	List	of	symbols
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Quantity	
$J_0 J_B(x)$	Electron current density injected at $x=0$ . Electron current density of unscattered elec
$J_s(x)$	trons at $x$ . Net current density of scattered electrons in
$J_t(x)$	the $+x$ direction. Total current density in $+x$ direction.
L	Distance between infinite plane parallel bound aries (e.g., length of collision chamber).
N	Density of gas particles.
Qe	Cross section for elastic scattering of electrons at the energy of the injected beam.
$Q_i$	Cross section for ionization by electrons at the energy of the injected beam.
$Q_x$	Total inelastic cross section for electrons at the
R	energy of the injected beam. Reflection coefficient for scattered electrons a
	x=0 boundary.
R'	Reflection coefficient for scattered electrons at $x=L$ boundary.
ho, ho'	Boundary condition parameters—see Eqs $(2.22)$ and $(2.23)$ .
$n_0$	Density of electrons under vacuum conditions
$n_B(x)$ $n_s(x)$	Density of unscattered beam electrons. Density of scattered electrons.
$n_t(x)$	Total density of electrons.
$N_0 = n_0 L$	Total number of electrons per unit area o emitter under vacuum conditions.
$\mathcal{N}_t = \int n_t(x) dx$	Total number of electrons per unit area o emitter.
v Tro T	Velocity of electrons.
$\begin{array}{l} \alpha = NQ_{x}L\\ \sigma = NQ_{e}L \end{array}$	Inelastic-collision number. Elastic-collision number.
$m = \sigma / \alpha$	Ratio of elastic to inelastic cross section.
$\theta = \sec^{-1} \epsilon$	Angle to $x$ axis at which the two streams are assumed to move.
$q = \epsilon [\alpha (\sigma + \alpha)]^{1/2}$	
$D = Lv[\epsilon^2(\sigma + \alpha)]$	Effective-diffusion coefficient.
go	Equivalent-length factor for normalization to injected current (total ion collection).
gL	Equivalent-length factor for normalization to transmitted current (total ion collection).
g0',gL'	Equivalent-length factors for sampling of ion
h = 1/(1+m)	through slit. Probability that a collision is inelastic.

elastic scattering of the attenuated injected electron beam and S(x) is therefore given by

$$S(x) = \frac{\sigma v}{L} n_B(x) \,. \tag{2.6}$$

#### A. Two-Stream Approximation

An analytical solution of the integrodifferential Eq. (2.3) is not, in general, available. An approximate technique, which in principle permits the solution of Eq. (2.3) to any desired accuracy, is to replace the angular distribution of scattered electrons into 2n representative streams comprised of n pairs. Each pair consists of one stream with intensity  $I_{+i}(i \rightarrow 1 \text{ to } n)$  moving at angle  $\theta_i$  to the +x direction, the other with intensity  $I_{-i}$  moving at  $\theta_i$  to the -x direction. Scattering from  $I_{+i}$  results in the electron remaining in  $I_{+i}$ 

or joining any other stream.<sup>14</sup> By this means Eq. (2.3) is replaced by *n* pairs of coupled linear equations, which may be solved. This approach was first used by Schuster<sup>15</sup> and Schwarzschild<sup>16</sup> who divided the distribution into two streams.

Wick<sup>17</sup> and Chandrasekhar<sup>7</sup> have generalized this approach to any finite number of streams, and have discussed the optimum procedure for choosing the  $\theta_i$ and the weighting factor appropriate to each pair of streams. In the present two-stream approximation we shall postpone choosing the angle  $\theta$ , and obtain an initial solution to the problem which contains  $\epsilon$  (= sec $\theta$ ) as a parameter.

#### **B.** Transfer Equations

In the two-stream approximation Eq. (2.3) is replaced by<sup>7</sup>

and

$$\frac{1}{\epsilon} \frac{dI_{+}}{dx} = -\frac{1}{L} \left( \frac{\sigma}{2} + \alpha \right) I_{+} + \frac{\sigma}{2L} I_{-} + \frac{S}{4\pi}$$
(2.7)

$$-\frac{1}{\epsilon}\frac{dI_{+}}{dx} = -\frac{1}{L}\left(\frac{\sigma}{2} + \alpha\right)I_{-} + \frac{\sigma}{2L}I_{+} + \frac{S}{4\pi}.$$
 (2.8)

Physically, Eq. (2.7) expresses the rate of change with distance of the forward component of the scattered intensity in terms of the depletion of the forward component of intensity (terms involving  $I_+$ ), augmentation from scattering out of the backward component of intensity ( $\sigma I_-/2L$ ), and the component of the unscattered current being scattered between x and x+dx into the appropriate solid angle. Equation (2.8) expresses the rate of change of the backward component of intensity in the same manner. Thus, we see that Eqs. (2.7) and (2.8) can be written from first principles.

The scattered flux  $J_s$  and scattered density  $n_s$  are obtained by substituting the approximation for  $I(\theta)$  into Eqs. (2.4) and (2.5). Thus,

$$J_s = (2\pi/\epsilon)(I_+ - I_-),$$
 (2.9)

$$n_s = (2\pi/v)(I_+ + I_-).$$
 (2.10)

Adding and subtracting Eqs. (2.7) and (2.8) give

$$\frac{1}{\epsilon} \frac{d(I_{+} - I_{-})}{dx} = -\frac{\alpha}{L} (I_{+} + I_{-}) + \frac{S}{2\pi}, \qquad (2.11)$$

$$\frac{1}{\epsilon} \frac{d(I_{+}+I_{-})}{dx} = -\frac{(\sigma+\alpha)}{L} (I_{+}-I_{-}).$$
 (2.12)

<sup>14</sup> The physical model described here corresponds mathematically to the evaluation of the integral in Eq. (2.3) using a polynomial expansion in  $\cos\theta$  for  $I(\theta,x)$ . For further discussion see Chap. 2 of Ref. 7.

<sup>16</sup> K. Schwarzschild, Sitzber. Deutsch. Akad. Wiss. Berlin, Kl. Math., Phys. Tech. 17, 1183 (1914).

<sup>17</sup> G. C. Wick, Z. Physik 120, 702 (1943).

Substituting Eq. (2.11) into the derivative of Eq. (2.12), we obtain

$$\frac{1}{\epsilon} \frac{d^2(I_++I_-)}{dx^2} = \left(\frac{\sigma+\alpha}{L}\right) \epsilon \left[\frac{\alpha}{L}(I_++I_-) - \frac{S}{2\pi}\right].$$

Using Eq. (2.10) this becomes

$$\frac{vL}{\epsilon^2(\sigma+\alpha)}\frac{d^2n_s}{dx^2} = \frac{\alpha v}{L}n_s - S. \qquad (2.13)$$

Similarly, from Eqs. (2.9), (2.12), and the derivative of (2.10), we obtain

$$J_{s} = \frac{2\pi}{\epsilon} (I_{+} - I_{-}) = -\frac{2\pi}{\epsilon} \frac{1}{\epsilon} \frac{L}{(\sigma + \alpha)} \frac{(I_{+} + I_{-})}{dx}$$
$$= -\frac{Lv}{\epsilon^{2}(\sigma + \alpha)} \frac{dn_{s}}{dx}. \quad (2.14)$$

We note that Eqs. (2.13) and (2.14) are identical in form to the diffusion equations for the same problem, provided we define a diffusion coefficient

$$D = Lv/\epsilon^2(\sigma + \alpha). \qquad (2.15)$$

Thus, with suitable choice of  $\epsilon$  we may expect the solution of Eq. (2.13) to accurately predict the contribution of scattered electrons to the total electron density at high pressures where that contribution is predominant. At low pressure we must expect the diffusion equation to be inappropriate, and the solution of it to predict the density of scattered electrons inaccurately. However, at low pressures their contribution to the total electron density is negligibly small, the predominant contribution being from unscattered beam electrons, which is specified exactly at all pressures. Thus, we may expect to obtain a solution for the total density of electrons which is exact in the limits of high and low pressures. At intermediate pressures ( $\sigma \approx 1$ ) we must expect some error, whose magnitude we shall estimate by comparison with the work of Bartels and Noack.

In conventional diffusion theory,  $D = \lambda v/3$ , where  $\lambda$  is the mean free path of the diffusing species. In the presence of both elastic and inelastic collisions  $\lambda$  is given by  $L/(\sigma + \alpha)$ , in which case we may generalize the diffusion coefficient to take into account inelastic collisions by writing

$$D = Lv/3(\sigma + \alpha), \qquad (2.16)$$

with which Eq. (2.15) is to be compared.

#### C. Boundary Conditions for Scattered Electrons

The form of the boundary conditions may be derived in the following way, using the two-stream approximation

<sup>&</sup>lt;sup>15</sup> A. Schuster, Astrophys. J. 21, 1 (1905).

At x=0 we have

$$I_{+}(0) = RI_{-}(0). \qquad (2.17)$$

Using Eq. (2.10) this gives

$$n_s(0) = (2\pi/v)I_{-}(0)(1+R).$$
 (2.18)

From Eqs. (2.10), (2.12), and (2.17), we obtain

$$\left. \frac{dn_s}{dx} \right|_{x=0} = \frac{2\pi}{v} \frac{(\sigma+\alpha)}{\epsilon} I_-(0)(1-R).$$
(2.19)

Hence, using Eqs. (2.18) and (2.19) we obtain

$$\frac{1}{n_s} \frac{dn_s}{dx} \bigg|_{x=0} = \epsilon \frac{(1-R)}{(1+R)} \frac{(\sigma+\alpha)}{L}.$$
 (2.20)

Similarly, at x = L, we obtain

$$\frac{1}{n_s} \frac{dn_s}{dx} \bigg|_{x=L} = -\epsilon \frac{(1-R')}{(1+R')} \frac{(\sigma+\alpha)}{L}.$$
 (2.21)

As will be discussed later (Sec. IIIF), alternative boundary conditions may be derived. They are, however, all of the general form

$$\begin{bmatrix} -1 & dn_s \\ -n_s & dx \end{bmatrix}_0 = \rho \frac{\sigma + \alpha}{L}$$
(2.22)

and

$$\left[\frac{1}{n_s}\frac{dn_s}{dx}\right]_L = -\rho'\frac{\sigma+\alpha}{L},\qquad(2.23)$$

which state that the extrapolated density of scattered electrons goes to zero a distance  $\lambda/\rho$  beyond the physical boundary, where  $\lambda = L/(\sigma + \alpha)$  is the electron mean free path. The quantities  $\rho$  and  $\rho'$  are expected to depend on R and R', respectively, in the way prescribed by Eqs. (2.20) and (2.21). At this stage we shall regard them as variable parameters, and as such they will appear in the solution of Eq. (2.13).

## D. Boundary Conditions for Unscattered Electron Beam

The role of the unscattered electron beam in the present problem is twofold, in that it provides the source function S(x) to be used in solving Eq. (2.13) and at the same time contributes directly to the electron density,  $n_t(x)$  and to the current collected at the boundary  $J_t(L)$ . The functions S(x),  $n_B(x)$ , and  $J_B(L)$  depend on the choice of boundary conditions, which depends in turn on the experimental arrangement to which the theory is to be applied. If, for example, the beam is

specularly reflected<sup>18</sup> at the x=L boundary, with reflection coefficient  $R_B'$ , and with subsequent reflection at the x=0 boundary with reflection coefficient  $R_B$ , we sum the infinite series involved and obtain

$$n_B(x) = \frac{J_0}{v [1 - R_B R_B' e^{-2(\sigma + \alpha)}]}$$

 $\times \left[ e^{-(\sigma+\alpha)x/L} + R_B' e^{-(\sigma+\alpha)(2-x/L)} \right], \quad (2.24)$ 

$$J_B(L) = \frac{J_0(1 - R_B')e^{-(\sigma + \alpha)}}{1 - R_R R_B' e^{-2(\sigma + \alpha)}}.$$
 (2.25)

From (2.24) we may obtain  $n_0$  by setting  $(\sigma + \alpha) = 0$ . If the beam is completely absorbed at the x=L boundary we set  $R_B'=0$  and obtain

 $n_0 =$ 

$$n_B(x) = n_0 e^{-(\sigma + \alpha)\mu/L},$$
 (2.26)

where

and

and

$$J_0/v$$
, (2.27)

$$J_B(L) = J_0 e^{-(\sigma + \alpha)}$$
. (2.28)

If the beam is diffusely reflected at x=L, then this effect may be treated as an additional planar source term in the transfer equation.

#### E. Solution for Electron Density

To proceed further with the solution of Eq. (2.13) it is necessary to write S(x) explicitly. For the purpose of this derivation, we shall assume that  $R_{B'}$  is zero,<sup>19</sup> in which case we may apply Eqs. (2.26), (2.27), and (2.28) which have the advantage of simplicity. The results at high pressure are in any case expected to be independent of  $R_{B'}$  as may be seen by allowing  $(\sigma + \alpha)$  to become large in the expressions for  $n_B(x)$  given in **D** above.

With the assumption then that  $R_B'=0$ , S(x) is obtained by substituting Eq. (2.26) into Eq. (2.6). Using also Eq. (2.15), we obtain from Eq. (2.13):

$$D\frac{d^2n_s}{dx^2} = \frac{\sigma v}{L} n_s - \frac{\sigma}{L} J_0 e^{-(\sigma+\alpha)x/L}.$$
 (2.29)

<sup>18</sup> We may expect this case to be appropriate to ion sources of the Heil type in which electrons are made to oscillate back and forth through the gas. For details see G. P. Barnard, *Modern Mass Spectrometry* (The Institute of Physics and the Physical Society, London, 1953).

<sup>19</sup> In practice, the assumption is reasonable for most electronbeam experiments in which the unscattered portion of the beam passes through a small hole in the x=L boundary to be subsequently collected on a positively biased electrode. In experiments of the Maier-Leibnitz type,  $R_B$  is expected to be small provided unscattered electrons reach the collector with energies in excess of 10 eV, which is usually the case. The solution of (2.29), subject to (2.22), is

$$n_{s}(x) = n_{s}(0) \bigg[ \cosh((\alpha v/LD)^{1/2}x) + \rho(\sigma + \alpha) \bigg(\frac{D}{\alpha vL}\bigg)^{1/2} \sinh((\alpha v/LD)^{1/2}x) \bigg] + \frac{\sigma L J_{0}}{[\alpha vL - D(\sigma + \alpha)^{2}]} \\ \times \bigg[ (\sigma + \alpha) \bigg(\frac{D}{\alpha vL}\bigg)^{1/2} \sinh((\alpha v/LD)^{1/2}x) - \cosh((\alpha v/LD)^{1/2}x) + e^{-(\sigma + \alpha)x/L} \bigg].$$
(2.30)

By differentiation of (2.30) and substitution into (2.23), n(0) may be obtained explicitly. Introducing the parameters q and m, defined in Table I, we have the complete solution for  $n_s(x)$ 

$$n_{s}(x) = \frac{J_{0} \epsilon^{2} m (1+m)^{1/2}}{v (m+1-\epsilon^{2})} \\ \times \left\{ \frac{(\rho+1) [\epsilon \cosh q (1-x/L) + \rho'(1+m)^{1/2} \sinh q (1-x/L)] + (\rho'-1) [\epsilon \cosh q (x/L) + \rho (1+m)^{1/2} \sinh q (x/L)] e^{-(\sigma+\alpha)}}{[\epsilon^{2} + \rho \rho'(1+m)] \sinh q + \epsilon (\rho+\rho') (1+m)^{1/2} \cosh q} - \left(\frac{1}{1+m}\right)^{1/2} e^{-(\sigma+\alpha)x/L} \right\}. \quad (2.31)$$

Using Eq. (2.2), we may obtain the spatial dependence of the total electron density

$$n_{\ell}(x) = \frac{\int_{0}^{0} \epsilon^{2}m(1+m)^{1/2}}{(m+1-\epsilon^{2})} \\ \times \left\{ \frac{(\rho+1)[\epsilon \cosh q(1-x/L)+\rho'(1+m)^{1/2}\sinh q(1-x/L)]+(\rho'-1)[\epsilon \cosh q(x/L)+\rho(1+m)^{1/2}\sinh q(x/L)]e^{-(\sigma+\alpha)}}{[\epsilon^{2}+\rho\rho'(1+m)]\sinh q+\epsilon(\rho+\rho')(1+m)^{1/2}\cosh q} \right\}$$

$$\frac{(\epsilon^2 - 1)(1+m)^{1/2}}{\epsilon^2 m} e^{-(\sigma+\alpha)x/L} \bigg\} . \quad (2.32)$$

If inelastic collisions are neglected ( $\alpha = 0$ ), we obtain

$$n_{t}(x)|_{\alpha=0} = \frac{J_{0}}{v} \epsilon^{2} \left\{ \frac{(\rho+1)[1+\rho'\sigma(1-x/L)] + (\rho'-1)[1+\rho\sigma(x/L)]e^{-\sigma}}{\rho\rho'\sigma + \rho + \rho'} - e^{-\sigma x/L} \right\} + \frac{J_{0}}{v} e^{-\sigma x/L}.$$
(2.33)

In this expression the last term represents the contribution from the unscattered beam. We note that the shape of the density profile of scattered electrons, the first term of (2.33), is independent of  $\epsilon$ , while its magnitude is directly proportional to  $\epsilon^2$ .

For large  $\sigma$ , Eq. (2.33) becomes

$$n_t(x) \bigg|_{\alpha=0} \sim \frac{J_0}{v} \frac{\int_0^{\infty} (\rho+1) [1+\rho'\sigma(1-x/L)]}{\rho\rho'\sigma} . \quad (2.34)$$

## F. Current Collected at the Boundary x = L

In general, the current collected at the boundary x=L will consist of three components, whose relative contributions will depend strongly on the elastic and inelastic collision numbers,  $\sigma$  and  $\alpha$ . At low pressures the major contribution will be from the unscattered beam, given by  $J_0 \exp[-(\sigma+\alpha)]$ . As  $\sigma$  is increased this contribution will decrease, while that due to the diffusion of scattered electrons to the boundary will increase.

The third component is due to the diffusion of electrons which have suffered inelastic collisions.<sup>20</sup> In the present theory no account is kept of these electrons, the effect of inelastic collisions having been treated as an absorption term in the basic transfer equation. This procedure is desirable from the point of view of predicting the number of electrons which are capable of causing ionization near threshold. It also gives directly the transmitted electron current in an experiment of the Maier-Leibnitz type, in which the inelastically scattered electrons are purposely prevented from reaching the collector by the presence of a suitable retarding voltage. In many electron-beam experiments, however, this provision does not exist, and certain difficulties arise in relating the measured transmitted electron current to that predicted by the theory in its present form. (See Sec. III).

 $<sup>^{20}</sup>$  The electrons produced by ionizing collisions constitute a fourth component whose contribution is assumed here to be always negligible.

In principle the contribution of inelastically scattered electrons to the transmitted current may be calculated by solving a transfer equation for each velocity group involved, the source functions being given by  $(\alpha_i/L) \times vn_i(x)dx$  where  $\alpha_i$  refers to the inelastic process which gives rise to the group having velocity  $v_i$ , and  $n_i(x)dx$  is given by Eq. (2.32). The solution of these equations is difficult because of the complicated source function involved, and has not been attempted.

An alternative approximate approach to calculating the total transmitted current is to assume that the contribution from inelastically scattered electrons is unaffected by their changed velocity, in which case the total transmitted current may be derived by taking  $\alpha=0$ .

In what follows it is therefore to be understood that

the transmitted electron current predicted for the case  $\alpha \neq 0$  is expected to apply only to measurements in which inelastically scattered electrons are prevented from reaching the collector by a suitable potential barrier. In the absence of such a barrier the transmitted current derived on the assumption that  $\alpha = 0$  is expected to represent more closely the measured current, even when in fact  $\alpha \neq 0$ .

Using Eqs. (2.1), (2.14), and (2.15), we write for the transmitted current,

$$J_t(x) = J_0 e^{-(\sigma+\alpha)x/L} - D \frac{dn_s(x)}{dx}.$$

The second term on the right-hand side may be obtained from Eq. (2.31). Evaluating the resulting expression at x=L, we obtain

$$J_{t}(L) = \frac{J_{0}m\epsilon}{(m+1-\epsilon^{2})} \left\{ \frac{(\rho+1)\rho'(1+m)^{1/2} - (\rho'-1)[\epsilon \sinh q + \rho(1+m)^{1/2}\cosh q]e^{-(\sigma+\alpha)}}{[\epsilon^{2} + \rho\rho'(1+m)]\sinh q + \epsilon(\rho+\rho')(1+m)^{1/2}\cosh q} - \frac{\epsilon^{2} - 1}{m\epsilon}e^{-(\sigma+\alpha)} \right\}.$$
 (2.35)

In the limit of low pressures this behaves as

$$J_t(L) \sim J_0\{1 - \alpha - \left[\rho/(\rho + \rho')\right]\sigma\}. \qquad (2.36)$$

With the assumption that inelastic collisions may be neglected ( $\alpha = 0$ ), we obtain<sup>21</sup>

$$J_{t}(L)|_{\alpha=0} = J_{0} \left\{ \frac{\rho'(\rho+1) - \rho(\rho'-1)e^{-\sigma}}{\rho + \rho' + \rho\rho'\sigma} \right\} . \quad (2.37)$$

We note that this quantity is independent of  $\epsilon$ . At high pressures

$$J_t(L)|_{\alpha=0} \sim J_0 \left(\frac{\rho+1}{\rho}\right) \frac{1}{\sigma}$$
(2.38)

and we note that the dependence on  $\rho'$ , the boundary conditions at x=L, has been removed.

## G. Choice of $\varepsilon$ , and of $\varrho$ and $\varrho'$

The work of previous authors is often formulated in terms of two streams directed forward and backward along the chosen axis, but in which the scattering coefficient is multiplied by a factor  $\epsilon$  to take approximate account of the angular distribution of the carrier velocity. This formulation is equivalent to the twostream model adopted here, in which the streams are assumed to move at some chosen angle  $\theta = \sec^{-1}\epsilon$ . Thus, the various treatments may be compared in terms of the value of  $\epsilon$  used. Schuster<sup>15</sup> first used the two-stream approximation to obtain an approximate solution to the problem of radiation transport through a scattering and absorbing layer, and used  $\epsilon = 1$ . The same problem, but excluding absorption, was considered in greater detail by Schwarzschild<sup>16</sup> who adopted Schuster's approach but chose  $\epsilon = 2$  to take account of the mean obliquity of the rays. The formally identical problem of electron transport through a scattering but nonabsorbing gas has been treated in the same way by Allis.<sup>22</sup> McKelvey, Longini, and Brody<sup>12</sup> assume an isotropic distribution of electron velocities to derive  $\epsilon = \frac{3}{2}$  for treating elastic scattering, and  $\epsilon = 2$  for treating absorption effects. Their derivation has been discussed by Shockley.<sup>13</sup>

According to Chandrasekhar<sup>23</sup> the best choice of  $\epsilon$ in the two-stream approximation is  $\sqrt{3}$ . This choice becomes mandatory if we require that the effective diffusion coefficient, defined by Eq. (2.15), correspond to the conventional diffusion coefficient generalized to take into account inelastic collisions, Eq. (2.16). We shall therefore use

$$\epsilon = \sqrt{3}$$
. (2.39)

Thus, with the appropriate choice of  $\epsilon$  Eq. (2.13) becomes identical with the diffusion equation for the same problem, emphasizing the equivalence of the twostream approximation and diffusion theory.<sup>24</sup> This shows that the difficulties encountered by McKelvey, Longini, and Brody in relating these theories are not fundamental, but arise from their choice of  $\epsilon$ .

The dependence of  $\rho$  and  $\rho'$  on the reflection coefficients at the boundaries has already been derived and is given in Eqs. (2.20) and (2.21), which contain  $\epsilon$  as a coefficient. With the choice of  $\epsilon$  made previously

<sup>&</sup>lt;sup>21</sup> Equation (2.37) actually applies for any value of x, as is expected in the case of no absorption. In the case of  $\rho = 0$ , complete reflection at x=0, and any value of  $\sigma$ , one obtains the expected result  $J_t(x)=J_0$ . The fact that Eq. (2.37) is independent of  $\epsilon$  suggests that it may be an exact result. Its independence of the order of the 2n stream approximation used has, however, not been demonstrated.

<sup>&</sup>lt;sup>22</sup> W. P. Allis (private communication).

<sup>&</sup>lt;sup>23</sup> S. Chandrasekhar, see Ref. 7, Chap. 2.

<sup>&</sup>lt;sup>24</sup> For further discussion of this point, see Refs. 13 and 25.



FIG. 2. Transmitted current as a function of the elastic collision number  $\sigma$  for the case of complete absorption at the boundaries and negligible inelastic losses ( $\alpha = 0$ ). The circles are the results of Fleming (Ref. 26). The full curve is obtained from Eq. (2.37) using  $\rho = \rho' = 1.41$ . The broken curve is the result of Bartels and Noack, and is indistinguishable from the full curve below  $\sigma = 2$ . Equation (2.37) gives a curve indistinguishable from that of Bartels and Noack if  $\rho = \rho' = 2$  is used.

[Eq. (2.39)], we obtain

$$\rho = \sqrt{3} \frac{(1-R)}{(1+R)}; \quad \rho' = \sqrt{3} \frac{(1-R')}{(1+R')}. \tag{2.40}$$

It is important to bear in mind that the value of  $\epsilon$ was chosen to ensure agreement between the present theory and conventional diffusion theory, and does not necessarily provide the best prescription for relating  $\rho$  and  $\rho'$  to R and R'. We could, for example, obtain the relationship

$$\rho = \frac{3}{2} \frac{(1-R)}{(1+R)}; \quad \rho' = \frac{3}{2} \frac{(1-R')}{(1+R')}$$
(2.41)

by requiring that as R, or R', approaches one (complete reflection) the current to the boundary given by conventional diffusion theory equals the random current, nv(1-R)/4.

According to Davison<sup>25</sup> the exact solution of the case of a completely absorbing plane boundary of a semi-

TABLE II. Ratio of transmitted electron current to injected current,  $J_t(L)/J_0$  for case  $\alpha = 0$ .

Authors	Boundary parameters $\rho = \rho'$	Elast 4	tic collisio 5	on numbe 6.67	er, σ 10
Bartels and Noack (Ref. 9)	(1996)/Harrison atom files h	0.30	0.25	0.18	0.135
Fleming (Ref. 26)		0.31	0.27	0.21	0.15
CPS, Eq. (2.37)	1.41	0.314	0.266	0.211	0.150
	1.50	0.311	0.263	0.208	0.147
	$\sqrt{3}$	0.305	0.256	0.202	0.141
	2	0.298	0.249	0.195	0.136

<sup>25</sup> B. Davison, *Neutron Transport Theory* (Clarendon Press, Oxford, England, 1957), Chap. 6.

infinite medium gives  $\rho = 1.41$  provided  $\alpha \ll \sigma$ . From this we infer that in the problem of interest here the choice of

$$\rho = 1.41 \frac{(1-R)}{(1+R)}; \quad \rho' = 1.41 \frac{(1-R')}{(1+R')}$$
(2.42)

will be exact for the case of  $\alpha = 0$  in the limit of large  $\sigma$ , i.e., when the two boundaries effectively see a semiinfinite medium.

Substitution of Eq. (2.42) into (2.37) is therefore expected to provide an analytic expression which is exact in the limit of large  $\sigma$ . The dependence of Eq. (2.37) on  $\rho$  and  $\rho'$  is in fact rather weak, particularly at low values of  $\sigma$ , as shown in Table II, where the value of  $J_i(L)/J_0$  has been calculated from Eq. (2.37) for the cases  $\rho = \rho' = 1.41$ ; 1.5;  $\sqrt{3}$ ; and 2. Also shown are the recent results of Fleming<sup>26</sup> obtained using Monte Carlo techniques for which an accuracy of  $\pm 2\%$  is claimed and the results of Bartels and Noack,9 which were obtained by solving the integral formulation of the problem by numerical methods, and which should be exact.<sup>27</sup> All results refer to the case of complete absorption at both boundaries (R=R'=0). The agreement between the present results, using  $\rho = \rho' = 1.41$ , and the Monte Carlo calculations is seen to be well within the limits of error of the latter. Comparison of the various results is also made in Fig. 2. The broken curve is the result of Bartels and Noack, and is indistinguishable from the



FIG. 3. Spatial dependence of normalized electron density for  $\sigma = 1, \alpha = 0$ . The dashed curve is from Bartels and Noack (Ref. 9). The other curves are plots of Eq. (2.33), using the values of  $\epsilon$ ,  $\rho$ , and  $\rho'$  indicated.

<sup>26</sup> R. J. Fleming, Proc. Phys. Soc. (London) **87**, 153 (1966). <sup>27</sup> The degree of accuracy to which the numerical calculations were carried is not given in Ref. 9. full curve below  $\sigma=2$ . Equation (2.37) essentially reproduces Bartels and Noack's result if  $\rho=\rho'=2$  is used. We conclude that Eqs. (2.37) and (2.42) serve to determine  $J_t(L)/J_0$  exactly for the case of no inelastic collisions at high pressures, and with an accuracy of probably better than  $\pm 2\%$  over the whole range.

The spatial dependence of the electron density, normalized to its value in vacuum, is shown in Fig. 3 for  $\sigma = 1$  and in Fig. 4 for  $\sigma = 8$ , given by Eq. (2.33), and using various values of  $\epsilon$  and of  $\rho$ ,  $\rho'$ . In both these figures inelastic collisions are neglected. Also shown are the results of Bartels and Noack.9 We note that, for  $\sigma = 1$ , better agreement is obtained with Bartels and Noack's result when  $\epsilon$  is chosen to be 2 instead of  $\sqrt{3}$ . This choice of  $\epsilon$ , however, leads to very large errors at higher  $\sigma$ , as is to be expected, since only  $\epsilon = \sqrt{3}$  can give agreement with diffusion theory, which will be essentially correct at large  $\sigma$ . This can be seen from Fig. 4, where, for  $\sigma = 8$  we find good agreement with the results of Bartels and Noack for  $\epsilon = \sqrt{3}$ . The possibility of using a coefficient  $\epsilon$  which is a function of  $\sigma$  to cover more accurately the whole pressure range has been considered. The function  $\epsilon = (\sqrt{3}\sigma^2 + 2)/(\sigma^2 + 1)$  has been found to provide values of  $\epsilon$ , which when used in the present theory together with the boundary conditions specified by Davison [Eq. (2.42)] give very good agreement



FIG. 4. Spatial dependence of normalized electron density for  $\sigma = 8, \alpha = 0$ . The dashed curve is from Bartels and Noack (Ref. 9). The other curves are plots of Eq. (2.33), using the values of  $\epsilon, \rho, \rho'$  indicated.



FIG. 5. Spatial dependence of normalized electron density with 1/m as parameter. The solid curves are the results of the present theory, using  $\rho = \rho' = \sqrt{3}$ . The dashed curves are from Bartels and Noack.

with the data of Bartels and Noack over the whole pressure range. The generating function for  $\epsilon$  was chosen to give  $\epsilon = 2$  for  $\sigma = 0$  and  $\epsilon = \sqrt{3}$  for large  $\sigma$ .

If inelastic collisions are possible the spatial distribution of electrons which have not suffered such collisions is given by Eq. (2.32) and is plotted in Fig. 5 for the cases  $\sigma=1$ , 3, 5, and 8, and using  $\epsilon=\sqrt{3}$ ,  $\rho=\rho'=\sqrt{3}$ . Comparison is made between the present data and those of Bartels and Noack for 1/m=0, and in the case of  $\sigma=3$  also for 1/m=0.25.

The effect on the spatial distribution of reflecting half the scattered electrons incident on one or other of the boundaries is demonstrated in Fig. 6 where Eq. (2.33) has been plotted using  $\epsilon = \sqrt{3}$ , and various values of R and R' from which  $\rho$  and  $\rho'$  have been calculated using Eq. (2.40). It is clear that the spatial distribution is much more sensitive to R than to R'. In fact, at very high pressures the distribution becomes independent of R', as shown by Eq. (2.34).

The numerical results presented in the remaining sections of this paper will be evaluated using  $\epsilon = \sqrt{3}$  throughout, together with the boundary conditions specified by Eq. (2.42). By virtue of this choice the expressions so obtained are expected to be accurate at high pressures. Reference to Fig. 3 shows that at intermediate pressures the contribution of scattered electrons is underestimated, as will be the case at low pressures. We expect the error in estimating the total density of electrons to be greatest in the region of  $\sigma = 1$ , since at low pressures the contribution from scattered electrons is in any case small. At  $\sigma = 1$ , the discrepancy



FIG. 6. Spatial dependence of normalized electron density showing the effect of reflecting half of the incident electrons at one or other boundary. In all cases 1/m=0. Values of  $\rho$  and  $\rho'$  were obtained from Eq. (2.40).

between the present data, using  $\epsilon = \sqrt{3}$  and the chosen boundary conditions, and that of Bartels and Noack may be seen in Fig. 3 to be nowhere greater than 11%.

## **III. PRESSURE DEPENDENCE OF ION CURRENTS**

We have already pointed out that at intermediate and high pressures (as defined in Sec. I) the pressure dependence of measured ion currents or other signals resulting from electron collisions depart from the pressure dependence observed at low pressure. In this section we develop the equations necessary for interpreting the pressure dependence of ion currents resulting from the behavior of electrons in the collision chamber. Other possible causes of departures from the normally expected pressure dependence, such as charge transfer during subsequent mass analysis, will not be considered.

It is convenient to divide electron beam experiments into those in which all the products formed in the collision chamber are being measured ("total collection") and into those in which only a sample of the products are collected (e.g., mass spectrometer ion sources, photoexcitation chambers). In either of these two cases, an additional complexity arises when we consider that the electron-beam current to which the measured ion current is normalized may itself be related to the electron density in a pressure-dependent manner. There are generally two choices available: we can normalize (i) against the injected current,  $J_0$  or (ii) against the current collected on the electron collector,  $J_t(L)$ . In general, we can say that we normalize against some measured electron current,  $J_M$ . When we normalize against injected current, or against collec-



FIG. 7. The equivalent length factors  $g_0$  and  $g_0'$ , for total ion collection and for ion sampling through a centrally located slit, respectively, with normalization to the injected electron current. The values of 1/m are indicated. In all cases  $\epsilon = \sqrt{3}$  and  $\rho = \rho' = 1.41$ .

tor current,  $J_M$  assumes the values  $J_0$  and  $J_t(L)$ , respectively.

#### A. Total Ion Collection

The measured total ion current is proportional to the total electron density integrated over the length of the collision chamber  $N_i$ . For the case of direct electron impact ionization we can write for the ion current  $J_i$ , normalized to the measured electron current  $J_M$ ,

$$\frac{J_i}{J_M} = \frac{N_t}{N_0} \frac{J_0}{J_M} NQ_i L = g NQ_i L, \qquad (3.1)$$

where we have defined the equivalent length factor  $g = (N_t/N_0)J_0/J_M$ . In the case that we normalize against the injected electron current,  $J_M = J_0$  and the equivalent length factor becomes  $g_0 = N_t/N_0$ . For normalization at the electron collector  $J_M = J_t(L)$  and we have  $g_L = (N_t/N_0)J_0/J_t(L)$ .

We can consider the factor g as the parameter which multiplies the path length of the electrons at intermediate and high pressures so that gL is the equivalent length of the collision chamber under these conditions. Thus, we can describe the effect of gas scattering on the electron beam in terms of the departure from unity of the equivalent length factor g.

## (i) Normalization to Injected Current

By integration of Eq. (2.32) we obtain the expression for the equivalent length factor  $g_0$ .

$$g_{0} = \frac{N_{t}}{N_{0}} = \frac{m^{2}\epsilon}{\sigma(m+1-\epsilon^{2})} \left\{ \frac{(\rho+1)[\epsilon \sinh q - \rho'(1+m)^{1/2}(\cosh q - 1)] + (\rho'-1)[\epsilon \sinh q + \rho'(1+m)^{1/2}(\cosh q - 1)]e^{-(\sigma+\alpha)}}{[\epsilon^{2} + \rho\rho'(1+m)]\sinh q + \epsilon(\rho+\rho')(1+m)^{1/2}\cosh q} - \frac{(\epsilon^{2}-1)}{m\epsilon} [1-e^{-(\sigma+\alpha)}] \right\}. \quad (3.2)$$

Equation (3.2) is shown by the full curves in Fig. 7 in which  $g_0$  is plotted as a function of  $\sigma$  for various values of m. It can be seen that  $g_0$  equals unity at low pressure and increases to values greater than unity, owing to elastic scattering. At higher pressures inelastic scattering causes electrons to lose energy so that these electrons cannot participate in ion production near the threshold of ionization (or another process being measured, such as excitation) and  $g_0$  reaches a maximum and thereafter decreases monotonically with pressure.

At very high pressures for m not too large,<sup>28</sup> Eq. (3.2) approximates to

$$g_{0} \sim \left\{ \frac{3m(1+\rho)+2\{\rho+[3(1+m)]^{1/2}\}}{[3+\rho(3(1+m))^{1/2}]\{m+2[(1+m)/3]^{1/2}\}} \frac{m}{\sigma} \right\} .$$
(3.3)

This expression is also plotted in Fig. 7. In the case of m=10 the agreement is seen to be reasonably good for  $\sigma > 6$ ; for m = 100 it is good for  $\sigma > 20$ .

For the case of no inelastic collisions  $(\alpha = 0, m \rightarrow \infty)$ Eq. (3.2) reduces to

$$g_{0}|_{\alpha=0} = \frac{3}{2} \left\{ \frac{(\rho+1)(2+\rho'\sigma) + (\rho'-1)(2+\rho\sigma)e^{-\sigma}}{\rho+\rho'+\rho\rho'\sigma} - \frac{4}{3\sigma}(1-e^{-\sigma}) \right\}.$$
 (3.4)

At very high pressures we can write

$$g_0|_{\alpha=0} \sim \frac{3}{2} \left\{ \frac{(\rho+1)(2+\rho'\sigma)}{\rho+\rho'+\rho\rho'\sigma} \right\} ,$$
 (3.5)

provided that both  $\rho$  and  $\rho'$  are greater than zero. Equation (3.5) tends to the constant value<sup>29</sup>  $3(\rho+1)/2\rho$ as  $\sigma$  approaches infinity. In the case of complete absorption at both boundaries we use  $\rho = \rho' = 1.41$ , in which case the limiting value is  $g_0 = 2.56$ , as shown in Fig. 7. For complete reflection on both boundaries, we set  $\rho = \rho' = 0$  and obtain  $g_0|_{\alpha=0} \rightarrow \infty$  at all  $\sigma$ , which is ex-



FIG. 8. The equivalent-length factors  $g_L$  and  $g_L'$  for total ion collection and for ion sampling through a centrally located slit, respectively, with normalization to the transmitted electron current. The values of 1/m are indicated and the high- and lowpressure asymptotes for the case 1/m = 0 are shown intercepting at  $\sigma = \frac{2}{3}$ . In all cases  $\epsilon = \sqrt{3}$  and  $\rho = \rho' = 1.41$ .

pected since we have removed both sinks for scattered electrons.

## (ii) Normalization to the Transmitted Current

We shall assume that in the type of experiment under discussion provision does not exist for preventing inelastically scattered electrons from reaching the electron collector. In this case (see Sec. IIF), the measured transmitted current is given approximately by  $J_t(L)|_{\alpha=0}$ , even when in fact  $\alpha \neq 0$ . Thus, the quantity required is

$$g_L = g_0 \times \frac{J_{\theta}}{J_t(L)|_{\alpha=0}}, \qquad (3.6)$$

where  $g_0$  is given in general by Eq. (3.2), and

$$J_t(L)|_{\alpha=0}/J_0$$

is given by Eq. (2.37). The dependence of  $g_L$  on  $\sigma$  is shown for various values of m in Fig. 8. In the case of  $\alpha = 0$  we have, without the assumption regarding  $J_t(L)$ , the relation.

$$g_{L}|_{\alpha=0} = \frac{3}{2} \left\{ \frac{(\rho+1)(2+\rho'\sigma) + (\rho'-1)(2+\rho\sigma)e^{-\sigma} - (4/3\sigma)(\rho+\rho'+\rho\rho'\sigma)(1-e^{-\sigma})}{\rho'(\rho+1) - \rho(\rho'-1)e^{-\sigma}} \right\} ,$$
(3.7)

which may be obtained from Eqs. (3.4) and (2.37). At very high pressures this behaves as<sup>30</sup>

$$g_L|_{\alpha=0} \sim \frac{3}{2}\sigma - \frac{2\rho}{\rho+1} + \frac{3}{\rho'}.$$
 (3.8)

Thus, if one linearly extrapolates the high- and lowpressure behaviors to intermediate pressures, in a plot such as Fig. 8 they will  $cross^{31}$  at  $\sigma = \frac{2}{3}$ .

In Fig. 9 direct comparison is made between the predictions of the present theory and experimental data obtained in a "total ionization tube"<sup>32</sup> in which the total production rate of O<sup>-</sup> from O<sub>2</sub> was measured as a function of pressure. The electron energy was 5 eV,

<sup>&</sup>lt;sup>28</sup> This restriction is necessary in order that  $\sigma \gg 1$  gives  $q \gg 1$ , allowing the approximation to be made.

<sup>&</sup>lt;sup>29</sup> In the special case of complete reflection at x=0, this constant limit no longer applies. Instead one obtains  $g_0 \sim 3\sigma/2$ .

<sup>&</sup>lt;sup>30</sup> In the case of complete absorption at both boundaries  $(\rho = \rho' = 1.41)$ , Eq. (3.8) is accurate at intermediate and high pressures. For example, at  $\sigma = 1$ , the discrepancy between Eqs. (3.7) and (3.8) is only 11%.

<sup>&</sup>lt;sup>31</sup> Had we used linear scales in Fig. 8 the crossing point would have been at  $\sigma = \frac{2}{3} [1 - 3\rho/\rho + 2\rho/(\rho+1)]$ . <sup>32</sup> G. J. Schulz, Phys. Rev. **128**, 178 (1962).

close to the threshold for the two-body process  $e + O_2 \rightarrow$  $O+O^-$ , where the cross section for all inelastic processes<sup>33</sup> is sufficiently small that we may assume  $\alpha = 0$ and use Eq. (3.7).

In Fig. 9 the points show the measured ratios of the O<sup>-</sup> current to the transmitted electron current as a function of the measured gas pressure. At low pressures they exhibit linear, and at high pressures a quadratic pressure dependence. According to the present theory (see Fig. 8) the extrapolated linear and quadratic segments intersect at  $\sigma = \frac{2}{3}$ , providing a relation between  $\sigma$  and the measured pressure, and allowing us to calculate  $Q_{e_1}$  since  $\sigma = NQ_{e_2}L$ . The density of  $O_2$  molecules N is given by the measured pressure, and L is the known length of the collision chamber. The result,  $Q_e = 6.4$  $\times 10^{-16}$  cm<sup>2</sup> is in excellent agreement with that of Brüche.34

The ratio of negative-ion current to transmitted electron current is predicted in the present theory by the quantity  $NQ_{-}g_{L} = \sigma g_{L}Q_{-}/Q_{e}$ , where  $Q_{-}$  is the dissociative attachment cross section. In the linear lowpressure region  $g_L = 1$ , and  $Q_-/Q_e$  is determined directly, with the result  $Q_{-}/Q_{e} = 2.2 \times 10^{-4}$ . Using the value of  $Q_e$  determined independently above, we obtain  $Q_{-}=1.4$  $\times 10^{-19}$  cm<sup>2</sup> for 5-eV electrons. The calculated value of  $\sigma g_L Q_-/Q_e$  is shown as a function of  $\sigma$  by the full curve, giving excellent agreement with experiment over the whole pressure range. Especially satisfying is the agreement between theory and experiment in the transition range, between  $\sigma = 0.1$  and  $\sigma = 4$ .

It should be noted that the extra power of p in the pressure dependence of the O<sup>-</sup> current at high pressure is the result of the chosen normalization to the transmitted electron current. This may be seen by comparing the curves for  $g_0$  and  $g_L$  in Figs. 7 and 8 for the case 1/m = 0.

#### B. Sampling of Ions

Let us now consider the type of experiment in which a sample of the ions is extracted through a slit in the side wall of the collision chamber. For maximum collection efficiency, a slit having its longer dimension parallel to the electron beam is often used. However, when the source is to be operated at intermediate and high pressures, there are advantages in the use of a slit with its longer dimension transverse to the electron beam. With such a slit the collection efficiency is much less likely to be affected by the transverse diffusion of scattered electrons, which may place some of the electrons contributing to ion formation outside the region sampled by a longitudinal slit. Moreover, with a transverse slit, the profile of the ion beam extracted will remain symmetrical with the maximum density at its center so that focusing requirements in the mass spectrometer are less severe. This would not be the case if one used a longitudinal slit. We shall therefore consider only the case of a transverse slit, and assume that its length is sufficient that the effects of transverse diffusion of electrons may be neglected, and that it is sufficiently narrow that the electron density does not change significantly across the slit. As was done in the case of total collection, we can define the equivalent length factor

$$g' = \frac{n_t(s)}{n_0} \frac{J_0}{J_M},$$
 (3.9)

where  $n_t(s)$  is the electron density opposite the sampling slit (at x=s) and  $J_M$  again assumes the value  $J_0$  and  $J_t(L)|_{\alpha=0}$  when normalization is performed with respect to the injected or collector current, respectively.

## (i) Normalization to Injected Current

For a centrally located slit (s=L/2) we obtain from Eq. (2.32)

 $\epsilon^2 m$ 

$$g_{0}' = \frac{n_{t}(s)}{n_{0}(s)} = \frac{\epsilon^{2}m(1+m)^{1/2}}{(m+1-\epsilon^{2})} \times \left\{ \frac{(\rho+1)[\epsilon \cosh(q/2) + \rho'(1+m)^{1/2}\sinh(q/2)] + (\rho'-1)[\epsilon \cosh(q/2) + \rho(1+m)^{1/2}\sinh(q/2)]e^{-(\sigma+\alpha)}}{[\epsilon^{2} + \rho\rho'(1+m)\sinh q] + \epsilon(\rho+\rho')(1+m)^{1/2}\cosh q} - \frac{(\epsilon^{2}-1)(1+m)^{1/2}}{\epsilon^{2}m}e^{-(\sigma+\alpha)/2} \right\}.$$
 (3.10)

With the restrictions discussed previously in deriving Eqs. (3.3)-(3.5) from (3.2), we obtain the following corresponding approximations to (3.10). At high pressures

$$g_0' \sim \frac{m[3(1+m)]^{1/2}}{m-2} \left\{ \frac{\rho+1}{1+\rho[(1+m)/3]^{1/2}} \right\} e^{-q/2}.$$
(3.11)

 <sup>&</sup>lt;sup>33</sup> G. J. Schulz and J. T. Dowell, Phys. Rev. 128, 174 (1962).
 <sup>34</sup> E. Brüche, Ann. Physik 83, 1065 (1927).

In the case of no elastic collisions we obtain

$$g_{0}'|_{\alpha=0} = \frac{3}{2} \left\{ \frac{(\rho+1)(2+\rho'\sigma) - (\rho'-1)(2+\rho\sigma)e^{-\sigma}}{\rho+\rho'+\rho\rho'\sigma} - \frac{4}{3}e^{-\sigma/2} \right\} .$$
(3.12)

At very high pressures  $g_0'|_{\alpha=0}$  approaches the same limit as  $g_0|_{\alpha=0}$ , given in Eq. (3.5), whose dependence on  $\rho$  and  $\rho'$  has already been discussed.

#### (ii) Normalization to Transmitted Current

In case of normalization of the sample ion current to the transmitted electron beam, we once again assume that the measured transmitted current is given by  $J_t(L)|_{\alpha=0}$  for all  $\alpha$ . Thus, we require

$$g_{L}' = g_{0}' \frac{J_{0}}{J_{t}(L)|_{\alpha=0}}$$
(3.13)

where  $g_0'$  is given in general by Eq. (3.10) and  $J_t(L)|_{\alpha=0}/J_0$  by (2.37). The dependence of  $g_L'$  on  $\sigma$  is shown for various values of m in Fig. 8. Once again, in the case of  $\alpha = 0$  we have, without the assumption regarding  $J_t(L)$ , the relation

$$g_{L'}|_{\alpha=0} = \frac{3}{2} \left\{ \frac{(\rho+1)(2+\rho'\sigma) + (\rho'-1)(2+\rho\sigma)e^{-\sigma} - (8/3)(\rho+\rho'+\rho\rho'\sigma)e^{-\sigma/2}}{\rho'(\rho+1) - \rho(\rho'-1)e^{-\sigma}} \right\} ,$$
(3.14)

obtained from Eqs. (3.12) and (2.37).

At very high pressures this behaves as ...

$$g_{L'}|_{\alpha=0} \sim \frac{3}{2}\sigma + 3/\rho'.$$
 (3.15)

#### C. Precautions for High-Pressure Mass Spectrometry

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We conclude from the preceding discussion that in the case of no inelastic collisions, at sufficiently high pressures, the ion current observed using either type of collection system, when normalized to the transmitted electron current, will exhibit a power-law pressure dependence whose power is greater by 1 than that observed at low pressures. Reference to Eqs. (2.38), (3.8), and (3.15) reveals however that the additional dependence on pressure arises simply because of the method of normalization. The ion current normalized to the transmitted electron current, although containing information regarding the pressure dependence of the electron density within the source, reflects predominantly the pressure dependence of the transmitted electron current, which is not of direct interest.

On the other hand, the ion current normalized to the injected electron current reflects directly the behavior of the electron density within the source, the interpretation of experimental data then requiring the prediction of only this one quantity. The latter procedure is therefore to be preferred. Measurement of the injected electron current does, however, present certain difficulties, especially at high collision chamber pressures.<sup>35</sup>

It is hoped that the equations derived in this section will be of value to the practice of mass spectrometry at the high-source pressures often necessary for the study of complex molecular ion formation, three-body attach-

ment processes and two-body reactions having only small cross sections. They should also be of value in photoexcitation experiments in which relatively high pressures are often employed, for example, in the study of excitation transfer processes.<sup>36</sup> In mass-spectrometer



FIG. 9. Comparison of the predictions of the present theory with experimental results for  $O^-$  production from  $O_2$  by electrons of 5-eV energy. The measured pressure is related to the  $\sigma$  scale by requiring that the break point occur at  $\sigma = \frac{2}{3}$ , and gives a value of  $Q_e = 6.4 \times 10^{-16}$  cm<sup>2</sup>. The full curve is a plot of  $g_L \sigma Q_-/Q_e$ , where  $\rho_{-}$ , the dissociative attachment cross section, is determined by the low-pressure data, and  $g_L$  is given by Eq. (3.7) using  $\rho = \rho' = 1.41$ . The points are experimental.

<sup>&</sup>lt;sup>85</sup> R. K. Asundi, G. J. Schulz, and P. J. Chantry (to be published).

<sup>&</sup>lt;sup>36</sup> R. Wolf and W. Maurer, Z. Physik 115, 410 (1940).



FIG. 10. Predicted ratio of sample ion current to total ion current when both have the same true pressure dependence, normalized to the value at low pressures. The value of 1/m is indicated on each curve. In all cases  $\epsilon = \sqrt{3}$  and  $\rho = \rho' = 1.41$ .

work attempts have been made<sup>2</sup> to circumvent the difficult problems of understanding the behavior of the electron beam at high pressures by normalizing the secondary ion sample to the primary ion sample. This procedure is generally unsatisfactory for the following reasons. Because the total inelastic cross section (and therefore the equivalent length factor g) may well be a strong function of electron energy, it is necessary to measure the primary and secondary samples at the same electron energy. In many cases, however, the secondary process of interest lies below the threshold for primary ion production. Moreover, assuming that a primary ion sample is available at the electron energy of interest, the primary and secondary ion samples are likley to be reduced by significantly different amounts because of charge transfer processes occurring in the analysis section of the instrument. In these circumstances, the only safe procedure is to obtain an understanding of the observed pressure dependence of the individual ion sample and thereby deduce the true pressure dependence of the process of ion formation. The expressions for the equivalent length factor g, derived in this section, enable estimates to be made of the extent to which scattering of the electron beam is affecting the apparent pressure dependence of the ion formation process.

## D. An Alternative Method of Normalization Applicable to Mass-Spectrometer Ion Sources

In a mass spectrometer, it is often possible to normalize the ion current measured through the central slit to that collected on the repeller with appropriate reversal of the extraction field. If we consider first the case when the process of formation of the mass-analyzed sample ion has the same pressure dependence as the process of formation of the majority ion, assumed predominant in the total current,<sup>37</sup> the ratio of the two currents will be independent of pressure at low pressures. If we further normalize the ratio to its value at low pressures, we expect its dependence on pressure to be given by the ratio  $g_0'/g_0$ , shown in Fig. 10 for various values of *m*. It is seen that for *m* not too small  $g_0'$  never departs from  $g_0$  by more than 11% over a large pressure range. Thus the sample ion current normalized to the total ion current will be rather insensitive to the effects of electron beam scattering. This fact becomes of value in the situation where a minority ion is being sampled under conditions where the true pressure dependence of the majority ion responsible for the total ion current is known. For example, if the total ion current is known to consist predominantly of parent ions, which have a linear pressure dependence, and the sample ion current normalized to the total is observed to have a quadratic dependence on pressure, one may conclude that the true pressure dependence of the sample ion is cubic. The advantage of this method over that involving normalization to a mass-analyzed sample of the parent ion discussed in Sec. IIIC, is that the effects of charge transfer in the analysis section of the mass spectrometer are in general much less severe for secondary ions than for parent ions. The effects of charge transfer within the source will of course not falsify the total ion-current measurement.

## IV. INTERPRETATION OF EXPERIMENTS FOR MEASUREMENTS OF ABSOLUTE VALUES OF INELASTIC CROSS SECTIONS (MAIER-LEIBNITZ TYPE)

In this section we use our theory for the interpretation of a class of experiments designed to measure the absolute value of inelastic cross sections. The experiments we wish to discuss, generally called Maier-Leibnitz-type experiments, are conceptually very simple and represent one of the few ways of measuring the absolute value of the inelastic cross section.<sup>38</sup> This type of experiment has been used by Harries<sup>39</sup> and by Haas<sup>40</sup> for measurement of the vibrational cross section in N<sub>2</sub>, by Ramien<sup>41</sup> for the vibrational and electronic cross section in H2 and by Maier-Leibnitz3 and by Fleming and Higginson<sup>42</sup> for the electronic excitation of helium and other rare gases. We will also compare the results of our theory with the theories used by these authors.

The experiment of Maier-Leibnitz is designed to measure the inelastic cross section by observing the

<sup>&</sup>lt;sup>37</sup> In most cases this will be the parent ion formed by the direct two-body process  $e+X \to X^++2e$ . <sup>38</sup> For a review see H. S. W. Massey and E. H. S. Burhop,

Electronic and Ionic Impact Phenomena (Clarendon Press, Oxford, <sup>40</sup> R. Haas, Z. Physik **148**, 177 (1957).
 <sup>41</sup> H. Ramen, Z. Physik **148**, 177 (1957).

<sup>&</sup>lt;sup>42</sup> R. J. Fleming and G. S. Higginson, Proc. Phys. Soc. (London) 84, 531 (1964).

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reduction in the electron current transmitted through a collision chamber as the electron energy is varied around the threshold of an inelastic process. Electrons which have suffered inelastic collisions are prevented from reaching the collector by a retarding voltage between the collision chamber and the collector. The experiment provides data in the form of the ratio of the transmitted electron current to that which would have been collected had the inelastic collisions been absent.<sup>43</sup> Unfortunately, interpretation of the data has suffered from the absence of a rigorous theoretical treatment of the problem.

#### A. Interpretation Using Present Theory

The present theory gives directly the desired currents whose ratio is measured experimentally. We introduce the parameter h=1/(1+m), which is the probability of a collision being inelastic. By making this substitution in Eq. (2.35) we obtain a general expression for the current transmitted in the presence of inelastic collisions

$$J_{t}(L,h) = \frac{(1-h)}{(1-3h)} \left\{ \frac{\rho'(\rho+1)(3/h)^{1/2} - (\rho'-1)[3\sinh q + \rho(3/h)^{1/2}\cosh q]e^{-\sigma/(1-h)}}{(3+\rho\rho'/h)\sinh q + (\rho+\rho')(3/h)^{1/2}\cosh q} - \frac{2h}{(1-h)}e^{-\sigma/(1-h)} \right\}, \quad (4.1)$$

where in terms of h,  $q = [h\sigma/(1-h)](3/h)^{1/2}$ . The current transmitted in the absence of inelastic collisions,  $J_t(L,0)$ , is given directly by Eq. (2.37), providing an analytic expression for the experimentally determined ratio  $J_t(L,h)/J_t(L,0)$ . The solid curves of Fig. 11 show plots of this ratio as a function of h for various values of  $\sigma$ , in the case of complete absorption at the boundaries.

#### B. Interpretation Used by Maier-Leibnitz

Maier-Leibnitz made use of earlier theoretical work by Harries and Hertz<sup>4</sup> which provided an estimate of the average number of collisions,  $\bar{c}$ , made by electrons which reach the collector. For the case of plane-parallel geometry, Harries and Hertz predict  $\bar{c} = \sigma^2/2$ . Knowing  $\bar{c}$ , Maier-Leibnitz made the assumption that the ratio of the current collected to the current that would have been collected were h=0 is given by

$$\frac{J_t(L,h)}{J_t(L,0)} = \exp(-h^{\bar{c}}).$$
(4.2)

Apart from the experimental difficulties<sup>44</sup> which may give rise to systematic errors in the data, the cross sections obtained by Maier-Leibnitz in this way are affected by errors of interpretation arising from the following sources: (a) The Harries and Hertz theory, used to estimate  $\bar{c}$ , is valid only for values of  $\sigma$  much larger than those generally used for the experiment, and under conditions when electrons are completely absorbed on reaching the boundaries. Theoretical work<sup>10,27</sup> subsequent to that of Harries and Hertz has provided more accurate values of  $\bar{c}$ . (b) Even with the correct value of  $\bar{c}$ , Eq. (4.2) is an approximation which is expected to be correct only in the limit of small  $h\bar{c}$ , where it behaves in the same way as the formally exact expression (see Appendix). The degree of smallness required of  $h\bar{c}$  has been considered by McClure,<sup>5</sup> who derives a more general expression for the case of spherical geometry, but it is applicable only at high pressures.

# C. Comparison of Present Interpretation with that Used by Maier-Leibnitz

For the case of complete absorption at both boundaries, the current ratio  $J_t(L,h)/J_t(L,0)$  predicted by the present theory and by the use of the Harries and Hertz theory are shown in Fig. 11 as a function of hfor various values of  $\sigma$ . We note that, in general, the initial slope of the curves given by the present theory is greater than that predicted using the Harries and Hertz



FIG. 11. Ratio of transmitted current to its value with zero inelastic collision probability. The full curves are the predictions of the present theory, the broken lines are the predictions of the Harries and Hertz theory, as used by Maier-Leibnitz. All curves refer to the case of complete absorption at both boundaries.

<sup>&</sup>lt;sup>43</sup> Two methods are generally used to estimate the current which would have been collected at the collector if no inelastic collisions were present, i.e.,  $J_t(L,0)$ . Maier-Leibnitz extrapolates the current collected below the inelastic threshold (in helium) to energies above the inelastic threshold. Haas and Ramien use a buffer gas (He) which does not have inelastic processes in the energy range they study, to determine  $J_t(L,0)$  and then add a small partial pressure of the gas to be studied (N<sub>2</sub> or H<sub>2</sub>) to obtain  $J_t(L,h)$ . The latter procedure is particularly useful for a determination of vibrational cross sections.

<sup>&</sup>lt;sup>44</sup> For example, the currents measured at the collector may contain contributions from electrons ejected from the surface by impinging metastable atoms. This effect has been considered in some detail by Fleming and Higginson (Ref. 42).



FIG. 12. Ratio of the value of h, obtained from  $J_t(h,L)/J_t(L,0)$  by application of the Harries and Hertz formula, to the value obtained from present theory. The full curves refer to the case of complete absorption at both boundaries ( $\rho = \rho' = 1.41$ ), the dashed curves to partial reflection at the collector ( $\rho = 1.41$ ,  $\rho' = 0.775$ ) and the dotted curves to partial reflection at both boundaries ( $\rho = 1.15$ ,  $\rho' = 0.775$ ).

theory, and secondly, that the dependence on h is only approximately exponential, the slope decreasing with increasing h. From this we conclude that the values of  $\bar{c}$  predicted by the Harries and Hertz theory are in general too small, and that the assumption of an exponential dependence on  $h\bar{c}$  is unjustified.

The interpretation of an experiment of the Maier-Leibnitz type requires that one deduce the value of h from a knowledge of  $\sigma$  and of  $J_t(L,h)/J_t(L,0)$ . If in so doing use is made of the Harries and Hertz theory one will obtain values which are usually too large.<sup>45</sup> The ratio of this value to the value of h calculated using the results of the present theory is shown in Fig. 12 for various values of  $\sigma$ , and for various boundary conditions.

For the purpose of comparing the results of various theories we have so far restricted ourselves to the situation in which electrons are completely absorbed at both boundaries. In practice, the retarding potential applied between the collision chamber and the collector in order to reject inelastically scattered electrons also reflects some of the elastically scattered electrons. In the interpretation used by Maier-Leibnitz no account is taken of this effect. The retarding potential used by Maier-Leibnitz was in general  $\frac{1}{3}$  the primary electron energy. For a perfectly transparent grid and randomly oriented trajectories of arriving scattered electrons, this corresponds to R'=0.58.

In practice the grid will collect some fraction of those electrons which would have been reflected<sup>46</sup> by a perfectly transparent grid, thereby decreasing R'. If for example, this fraction is one-half, the effective value of R' is decreased from 0.58 to 0.29. The ratio of  $J_t(L,h)/J_t(L,0)$  has been computed for various values of  $\sigma$  for the case R=0, R'=0.29. The effect of increasing R' is in general to decrease the ratio  $J_t(L,h)/J_t(L,0)$ , giving rise to further departure from the Harries and Hertz theory. This effect is shown in Fig. 12. Fleming and Higginson<sup>47</sup> have observed experimentally that such a decrease occurs in the current ratio when the collector retarding voltage is increased, and regarded the observation as evidence that metastable atoms were causing electron ejection from the collector. They conclude that the departure of the experimental data from the predictions of the Harries and Hertz theory is minimized by using the smallest possible retarding voltage. While one could argue from the present theory that their experimental observations arise at least in part from their having varied the boundary conditions, one reaches the same conclusion as to the best operating conditions for application of the Harries and Hertz theory.

In Fig. 12 we show also the effect of reflecting 10% of the electrons backscattered to the x=0 boundary. It gives rise to a further decrease in the current ratio, and consequently to a further departure from the Harries and Hertz theory.

## D. Accuracy of Present Results

It has already been pointed out that, while the general problem considered in this paper has been formulated in terms of a two-stream approximation, with the choice of  $\epsilon = \sqrt{3}$ , we have in effect obtained diffusion solutions for the electron density and current involved. The prediction of  $J_t(L,h)/J_t(L,0)$  is one aspect of these solutions. Its superiority to the interpretation used by Maier-Leibnitz, which employed diffusion theory in estimating  $\bar{c}$ , derives from the following features:

(a) The effects of inelastic collisions are included in the initial transfer equation, which gives directly the desired transmitted currents without the need to introduce the average number of collisions  $\bar{c}$ . Consequently, there is no limitation on the magnitude of  $h\bar{c}$ .

(b) The fact that the electrons are injected normal to the boundary has been properly taken into account.

(c) The boundary conditions are expected to provide more accurate results at intermediate pressures than given by the Harries and Hertz treatment, which

<sup>&</sup>lt;sup>45</sup> The fact that such errors may arise was discussed by Maier-Leibnitz with reference to the work of Bartels and Nordstrom (Ref. 10). The data presented in Figs. 11 and 12 do not apply directly to Maier-Leibnitz's experiment, since he used cylindrical geometry, but are indicative of the errors involved. The extension of the present theory to cylindrical geometry simply involves the solution of the diffusion equation including absorption in cylindrical coordinates subject to boundary conditions similar to those discussed in Sec. IIG. This will be the subject of a separate publication.

<sup>&</sup>lt;sup>46</sup> The grid will also collect some fraction of those electrons which, with a perfect grid, would have reached the collector. Because we are interested here in the ratio of two currents the value of this fraction, provided it is constant, is unimportant.

<sup>&</sup>lt;sup>47</sup> R. J. Fleming and G. S. Higginson, in *Proceedings of the* Sixth International Conference of Ionization Phenomena in Gases (S.E.R.M.A., Paris, 1964), Vol. II, p. 183.

assumed that the density of scattered electrons goes to zero at the physical boundaries.

(d) The boundary conditions have the added advantage that they allow the inclusion of reflection effects in a direct manner.

The absolute accuracy of the ratio  $J_t(L,h)/J_t(L,0)$ predicted by the present theory cannot be readily estimated. It is shown in the Appendix that for hsufficiently small, the current ratio is related in a simple manner to  $\bar{c}$ , and that  $\bar{c}$  predicted by the present theory is in excellent agreement with other reliable estimates. We may therefore conclude that, in the limit of small h, the present estimates of  $J_t(L,h)/J_t(L,0)$  are probably accurate to better than  $\pm 5\%$  provided  $\sigma \gg 2$ . Since the method by which inelastic collisions are taken into account in the theory is in itself rigorous, it is to be expected that this estimate of the absolute accuracy applies without restricting h to small values.

## **V. CONCLUSIONS**

The two-stream approximation to the distribution of elastically scattered electrons in a plane parallel medium which scatters both elastically and inelastically has been applied to the problem in which an electron beam of well-defined energy is injected normal to one of the boundaries. This approach has been shown to be entirely compatible with diffusion theory provided that a suitable choice is made for the angle to the axis at which the two streams are assumed to move. The contributions of unscattered beam electrons and of elastically scattered electrons to the density and current are evaluated separately, and added to give analytic expressions for these quantities which are exact in the limits of both high and low pressure. At intermediate pressure the total electron density is underestimated by probably less than 11%.

The results have been applied to the problem of interpreting electron-beam experiments conducted at pressures at which multiple electron collisions become important. In order to facilitate the use of the theory, an "equivalent length factor" has been introduced into the equation normally used to relate the ion production rate to the collision chamber length, the target number density, collision cross section, and measured electron current. The dependence of this "equivalent length factor" on pressure and on the ratio of elastic to total inelastic collision cross sections has been derived for the cases of normalization to the injected electron current and for normalization to the transmitted electron current. This equivalent length factor, which should be useful for the interpretation of electron-beam experiments at intermediate and high pressure is given in closed form and typical cases are plotted in Figs. 7 and 8. Where possible, normalization to the injected current is to be preferred in most electron-beam experiments.

A new method of interpreting experiments of the Maier-Leibnitz type has been presented which includes inelastic processes *a priori* and gives directly the ratio of currents for comparison with experiment. This approach eliminates the restriction to small inelastic cross sections implicit in the usual *a posteriori* approach using the mean number of collisions. The present theory is valid in an extended range of gas density.

## ACKNOWLEDGMENT

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## APPENDIX: DERIVATION OF $\overline{c}$

As demonstrated in Sec. IV, a knowledge of the mean number of collisions  $\bar{c}$  made by electrons reaching the collector is not a necessary step in interpreting the experimental data. Moreover, a knowledge of  $\bar{c}$  alone is inadequate for the interpretation of  $J_t(L,h)/J_t(L,0)$ unless h is extremely small. We shall calculate it here merely for the purpose of comparison with the results obtained by Bartels and Nordstrom, 10 and by Fleming, 26 in order to judge the accuracy of the present results. The geometry treated by these authors is the same as here, and comparison is justified in the case of complete absorption at both boundaries. The work of Bartels and Nordstrom is based on an exact<sup>48</sup> numerical solution of the integral form of the transfer equation. Fleming has estimated  $\bar{c}$  by Monte Carlo techniques in which "the accuracy aimed at was  $\pm 2\%$ ."

The value of  $\bar{c}$  is obtained from the present theory through the relationship<sup>49</sup>

$$\frac{J_t(L,h)}{J_t(L,0)} = \sum_{o=0}^{\infty} A_o(1-h)^o,$$
 (A1)

where, if  $J_t(L,h)$  arises from conditions specified by  $\sigma$  and h,  $J_t(L,0)$  is the current that would have been col-

$$\tilde{\sum} A_c (1-h)^c.$$

If we now specify that collisions of type X in effect cause the electron to disappear, which will be the case in our practical problem, this will not affect the probability of an electron not making collisions of type X, since we have not changed the relative probabilities of a collision being of type X or Y nor the total collision number  $\sigma_T$  on which  $A_c$  depends. We are indebted to J. A. Marshall for a critical examination of the validity of Eq. (A1).

<sup>&</sup>lt;sup>48</sup> See, however, Fig. 2 and footnotes 27 and 52.

<sup>&</sup>lt;sup>49</sup> Equation (A1) is derived in the following way. If electrons can make only elastic collisions, the elastic-collision number being  $\sigma_T$ , let the probability that a collected electron made c collisions before being collected be  $A_c$ . We specify that, while they can still only be elastic, collisions can in some other respect be classified into two types, X and Y. Let the probability that a collision be of type X be h; that it be of type Y is therefore (1-h). If an electron makes c collisions, all of type Y, is  $A_c(1-h)^c$ . The over-all probability that an electron makes an unspecified number of collisions, but all of type Y, is therefore

lected if all collisions had been elastic,<sup>50</sup> i.e., with  $\sigma$  taking on the value  $\sigma_T = \sigma/(1-h)$ .  $A_c$  is the probability that a collected electron made c collisions before being collected, under the conditions giving rise to  $J_t(L,0)$ . In the binomial expansion of (A1) the first two terms are

$$\frac{J_t(L,h)}{J_t(L,0)} = \sum A_c(1-ch) = 1 - \bar{c}h.$$
 (A2)

In order to obtain an expression for  $\bar{c}$  from the present theory we therefore make a corresponding expansion of Eq. (4.1) and write the first two terms in the form<sup>51</sup>

$$J_t(L,h) = J_t(L,0) [1 - f(\sigma_T)h],$$
 (A3)

where  $J_t(L,0)$  is given by Eq. (2.37) with  $\sigma = \sigma_T$ , and  $f(\sigma_T)$  is identified as  $\bar{c}$ , the mean number of collisions suffered by transmitted electrons in the case of only elastic collisions, the elastic collision number being  $\sigma_T$ . In the above we have made use of  $\sigma_T$  simply to obtain the function "f". For general use we write as if  $f(\sigma)$ , it being understood that the identity  $\bar{c} = f(\sigma)$  applies to the case of no inelastic collisions. Thus we obtain:

$$\bar{c} = \frac{\sigma \left[3 + \frac{3}{2}(\rho + \rho')\sigma + \frac{1}{2}\rho\rho'\sigma^{2}\right]}{\rho + \rho' + \rho\rho'\sigma} + \frac{\left\{2(\rho + \rho') + \sigma \left[3(\rho' - 1)(1 + \frac{1}{2}\sigma\rho) + 2\rho\rho'\right]\right\}e^{-\sigma}}{\rho'(\rho + 1) - \rho(\rho' - 1)e^{-\sigma}} - 2.$$
(A4)

If there is complete reflection of scattered electrons at the collector we expect  $\bar{c}=0$ , which may be shown to be the case by putting  $\rho'=0$  in Eq. (A4). In the limit of very low pressures we obtain from Eq. (A4)

$$\bar{c} \sim \sigma \left( \frac{\rho'}{\rho + \rho'} \right).$$
 (A5)

If we put  $\rho = \rho'$ , as in the case of complete absorption

TABLE III. Values of  $\bar{c}$ .

Authors	Elastic collision number, $\sigma$								
	$\mathbf{Ref}$	. 1	2	3	4	5	6.67	10	
Harries and Hertz	4	0.5	2	4.5	8	12.5	22.2	50	
Bartels and Nordstrom	10	1.18	3.40	6.78	10.8	16.4	31.5	61.0	
Fleming	26				11.9	17.6	30.1ª	63.6	
Equation (6.4) using $\rho = \rho' = 1.41$		1.06	3.34	6.83	11.5	17.3	29.2	61.8	

\* Revised value supplied by R. J. Fleming (private communication).

at both boundaries, we obtain  $\bar{c} = \frac{1}{2}\sigma$  as expected. If there is complete reflection at x=0 we obtain  $\bar{c}=\sigma$ in this limit, which is also to be expected.

In the limit of very high pressures we obtain from Eq. (A4)

$$\bar{c} \sim \frac{1}{2} \sigma^2 - 2 \quad (\rho, \rho' > 0),$$
(A6)

$$\bar{c} \sim \frac{3}{2} \sigma^2 - 2 \quad (\rho' > 0, \rho = 0).$$
 (A7)

The fact that the high-pressure limit does not depend on the reflection coefficients at the boundaries (provided neither is identically zero) arises from the fact that, at very high pressure, an electron reflected by either boundary has a very high probability of being returned to the same boundary, and a very small probability of reaching the other boundary.

One may show that the constant term (-2) appearing in Eq. (A4) arises from the fact that the electrons are injected normal to the boundaries. When  $\sigma=4$  the second term contributes 0.2 to  $\bar{c}$ , and may therefore be neglected for  $\sigma \ge 4$ . The values of  $\bar{c}$  computed from (A3) are compared with the results of Fleming,<sup>26</sup> and of Bartels and Nordstrom<sup>52</sup> in Table III. The present data agree with those of Fleming to better than 4%. For values of  $\sigma$  less than 4 comparison may be made only with the results of Bartels and Nordstrom. For  $\sigma \ge 2$  the agreement is seen to be good. For  $\sigma=1$ , in the region of which the present theory is expected to provide its least accuracy, the discrepancy is still only 10%.

<sup>&</sup>lt;sup>50</sup> This definition of  $J_t(L,0)$  is slightly different from that given in Sec. IV, where it was defined to correspond to the experimental situation.

<sup>&</sup>lt;sup>51</sup> In order to obtain the required form we first make the substitution  $\sigma_T = \sigma/(1-h)$  in Eq. (4.1), and in making the expansion regard  $\sigma_T$  as a constant.

<sup>&</sup>lt;sup>52</sup> According to these authors (Ref. 10)  $\bar{c} = \sigma C_B(\sigma) J_0/J_t(L)$ , where  $C_B(\sigma)$  is given as a function of  $\sigma$  in graphical form. The ratio  $J_t(L)/J_0$  is given also in graphical form, and has been compared in Table II with the predictions of the present theory. In making the present comparison the values of  $C_B(\sigma)$  and  $J_t/J_0$ were read from small published figures. It is estimated that the error involved in so doing is not more than  $\pm 5\%$ .