# Atomic Beam Apparatus for Studying the Atomic Spectra of Gases, Especially Hydrogen

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I. Introduction. No consideration appears to have been given in the literature to the design of beam apparatus for studying the atomic spectra of gases. Considering our uniquely complete theoretical knowledge of the spectrum of hydrogen, and the inconclusive nature of our present experimental knowledge of the structure of the alpha-line, atomic beam studies of this line are needed. II. Geometrical consideration. The pressure ratio of the final and initial chambers must be far smaller than the solid angle subtended by the first slit at a point in the field of view; and the region of space in which the atoms are excited should not extend, in the line of view, far beyond the full (nonpenumbral) portion of the beam. III. The Doppler effect. Five independent contributions to the Doppler effect,

#### I. INTRODUCTION

**P**ROFESSOR Meissner has presented an able summary<sup>1</sup> of the spectroscopic applications of atomic beams. On the instrumental side, any such survey must show one remarkable lacuna. While a good deal of attention has been paid to the design of atomic beam apparatus for substances that are solid at liquid-air temperatures, including some special consideration of refractory materials, in the other direction on the volatility scale so far as we know there is nothing in the literature regarding the problem of the design of atomic beam apparatus for the spectroscopic study of the "permanent" gases. There is little regarding atomic beam apparatus of any sort for gases, and as we shall show, what there is,2-5 is not suitable for application to spectroscopy.

Among the several gases to which atomic beam techniques may be applied for spectroscopic fine-structure studies, there is an outstanding need in the case of one element,

<sup>1</sup> K. W. Meissner, Rev. Mod. Phys. 14, 68 (1942).
<sup>2</sup> E. Wrede, Zeits, f. Physik 41, 569 (1927); R. Frisch and O. Stern, Zeits. f. Physik 85, 4 (1933); I. Esterman, O. C. Simpson, and O. Stern, Phys. Rev. 52, 535 (1937).
<sup>3</sup> T. E. Phipps and J. B. Taylor, Phys. Rev. 29, 309 (1927)

for a line emitted from an atomic beam, are studied: (1) Original atomic velocity; (2) atomic velocity gained by excitation (in particular, for hydrogen excited by electron impact); (3) atomic velocity gained by emission; (4) spread of light in the optical system; (5) error of orientation of the optical system with respect to the beam. Some of these factors tend to produce broadening, and some to produce frequency shifts. The broadening can probably be kept low enough for the complete resolution of the electronic structure of the alpha-line,  $\nu/\Delta\nu = 4.2 \times 10^5$ . IV. Design of the apparatus. An atomic beam apparatus is described which has been designed and built with a view to the conditions outlined above.

namely, hydrogen. The spectrum of the light isotope of hydrogen,  $H^1$ , is of extraordinary interest. On the basis of the Dirac<sup>6</sup> theory, the positions and intensities of the components of each line belonging to a system consisting of an electron and a fixed point charge can be predicted<sup>7-9</sup> without resort to any approximation, physical or mathematical-a situation almost if not quite unique among all the problems of physics. Inasmuch as H<sup>1</sup> is almost exactly such a system<sup>10</sup> the experimental study of the spectrum of H<sup>1</sup> can serve as a direct test of the Dirac theory. For the heavy isotope, deuterium, the expected separations are, far within the experimental error, the same as for the light one, so in the summary below the experimental results for the two isotopes are not distinguished in spite of their important difference in behavior with respect to the Doppler effect.

Experimentally, the alpha-line of hydrogen is

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<sup>1.</sup> E. Filipps and J. E. Asyru, (1927).
4. I. Rabi, J. M. B. Kellogg, and J. R. Zacharias, Phys. Rev. 46, 157 (1934); J. M. B. Kellogg, I. I. Rabi, N. F. Ramsey, and J. R. Zacharias, Phys. Rev. 56, 728 (1939).
<sup>5</sup> H. Scheffers and J. Stark, Physik. Zeits. 37, 217 (1936).

<sup>&</sup>lt;sup>6</sup> P. A. M. Dirac, Proc, Roy. Soc. A117, 610 (1928); A118, 351 (1928).

<sup>&</sup>lt;sup>7</sup> C. G. Darwin, Proc. Roy. Soc. A118, 654 (1928).

<sup>&</sup>lt;sup>8</sup> W. Gordon, Zeits. f. Physik 48, 11 (1928) <sup>9</sup> An authoritative summary can be found in H. Bethe,

Handbuch der Physik (J. Springer, Berlin, 1933), second edition, Vol. 24/1, especially Nos. 9, 10, 41-44.

<sup>&</sup>lt;sup>10</sup> The expected influence of the structure and motion of the proton-aside from the elementary matter of the reduced mass correction—is not greater in order of magnitude than  $10^{-3}$  times the fine structure separations. This influence is of the same order of magnitude as the natural breadths of the components of the alpha-line (cf. Table I, below). It is neglected in the discussions in this paper.

the most popular one for study because of its position in that part of the spectrum where silver has a very high reflection coefficient (for Fabry-Perot interferometry) and where photography is possible, and also because, except for the relatively inaccessible Lyman doublets, it is the simplest (five components; resolving power required for complete resolution,  $45/2\alpha^2$  or  $4.2 \cdot 10^5$ , for resolution of the strongest two components,  $180/73\alpha^2$  or  $4.6 \cdot 10^4$ ; cf. Table I, below). Almost all the measurements since the discovery of the complexity of the line<sup>11</sup> have yielded values for the separation between the two unresolved complexes somewhat smaller than would be expected from the theory. Upon examination, especially for the influence of faint unresolved components upon the apparent separation of the two strong components, the results of the seven investigations that have been reported upon in the past decade fall roughly into two classes: those<sup>12-14</sup> in which the separation between the strongest two components,  $2_{1i}-3_{2i}$  and  $2_{i}-3_{1i}$  (in the notation  $n_J$ ), agrees with the theory, and those<sup>15-18</sup> in which it is about  $0.01 \text{ cm}^{-1}$ , or 3 percent, smaller than the theory predicts. Of the five papers that report upon the third most intense component,  $2_{i}-3_{i}$ , two of the former<sup>12, 14</sup> and one of the latter group<sup>16</sup> indicate that it is the predicted position with respect to  $2_{i}-3_{1i}$  and two of the latter<sup>17,18</sup> show it too far from  $2_{i}-3_{1i}$ , by an amount even greater than 0.01 cm<sup>-1</sup>, though not so consistent as the discrepancy in the separation of the strongest two components. The discrepancies among different groups of workers for the strongest two components appear to be greater than one would expect, at least in the most careful experiments. We need not discuss here the proposals that have been set forth to explain the apparent deviations theoretically.

M. Hayden, Zeits. f. Physik 106, 499 (1937).
 W. V. Houston and Y. M. Hsieh, Phys. Rev. 45, 263

In all the recent studies mentioned above, a cooled discharge tube has been used as the source, and in all except one the high resolving power spectroscope was a Fabry-Perot interferometer; in that one<sup>18</sup> it was a reflection echelon. Clearly there is need for investigation by an independent method. Although several investigators have tried the atomic beam and informally reported failures, and no one has reported success with this method, it remains the most promising to be tried.

We have designed and built an apparatus for the study of the hydrogen alpha-line. Before describing it, we shall point out a consideration essential to the proper geometrical design of the apparatus, and shall consider the Doppler effect with reference to light emitted from the beam. The geometrical consideration concerns the ratio of the number of useful (beam) atoms to the number of harmful (stray) atoms in the field of view of the spectroscope. The main conclusion of this consideration, Eq. (5), is a limitation of the ratio of the pressures in the final and initial chambers of the beam apparatus, depending upon the geometry of the beam. A corollary points out the advantage of limiting the extent of the region of excitation, along the line of sight.

### **II. GEOMETRICAL CONSIDERATION**

We shall confine our discussion to the use of a beam in emission. The general purpose of such a device as we shall describe is to allow excited atoms to travel in one direction (which we shall call the x direction), and with light traveling in a normal direction (the z direction) to image upon the slit of a spectrograph an object field or field of view consisting of a rectangular portion of the beam of length X in the x direction, and of width Y (in the y direction, which is vertical in Figs. 1 and 3).

Let us consider (Fig. 1) a chamber, which we shall designate by the number 1, containing gas at the absolute temperature  $T_1$ , the pressure  $p_1$ , and the corresponding atom density  $n_1$ . We shall suppose the gas to be monatomic, although that is not essential to the argument. In the wall of this chamber is a rectangular slit (slit number 1) of width  $Z_1$  in the z direction and of height  $Y_1$  in the y direction. We shall suppose

<sup>&</sup>lt;sup>11</sup> A. A. Michelson and E. W. Morley, Phil. Mag. 24, 463 (1887).

 <sup>&</sup>lt;sup>12</sup> H. Kopferman, Naturwiss. 22, 218 (1934).
 <sup>13</sup> F. H. Spedding, C. D. Shane, and N. S. Grace, Phys. Rev. 47, 38 (1935).

<sup>(1934).</sup> <sup>16</sup> R. C. Williams and R. C. Gibbs, Phys. Rev. 45, 475

 <sup>(1934).
 &</sup>lt;sup>17</sup> R. C. Williams, Phys. Rev. 54, 558 (1938).
 <sup>18</sup> J. W. Drinkwater, O. Richardson, and W. E. Williams, Proc. Roy. Soc. A174, 164 (1940).



FIG. 1. Geometry of the atomic beam under discussion.

that the slit area  $Y_1Z_1$  is so small and the pressure outside the chamber so low that atomic effusion takes place, i.e., that to a sufficiently close approximation all the motion outside the chamber is in unbroken straight lines. Our atomic beam will consist of those atoms directly effusing from the slit through a second slit or a collimated system of slits 2, 3,  $\cdots k-1$ , into a final chamber which we may designate by the serial number k. Let us suppose that the centers of the slits lie on a line, which will be called the axis of the beam, normal to the plane of slit 1. For the present we shall pay attention only to that portion of the beam in the kth chamber (the "full portion," as distinguished from the penumbral portion) from which the whole boundary of the first slit can be seen through the other slits. The (k-1)th slit may be larger or smaller than the first, but it is required that the width of the full portion of the beam in the y direction be at least as great as that of the field of view Y and it will be shown in the last paragraph of this section that it is best to have the width of the full portion in the z direction at least as great as the width  $Z_e$  of the electron sheet introduced in the discussion below.

We shall now determine the number of beam atoms per unit volume, n(x), in the full portion of the beam in the interval between the planes distant, respectively, x and x+dx from the first slit. The region is to be in the final chamber, so x is at least as great as the distance between slits 1 and k-1; we may consider the angles  $Y_1/x$  and  $Z_1/x$  to be very small. Let us designate by  $\Omega_1(x)$ , or  $\Omega$ , the solid angle  $Y_1Z_1/x^2$  subtended by the first slit when viewed from the distance x. A straightforward calculation<sup>19</sup> yields

$$n(x) = n_1 \Omega / 4\pi. \tag{1}$$

Now suppose that the region under consideration is bombarded by a uniform collimated beam or sheet of electrons traveling in the y direction and covering a sheet thickness or interval  $Z_e$  in the z direction and suppose that the sheet is so aligned that the plane half-way between its faces contains the beam axis. Suppose that the electrons excite to luminescence a certain fraction  $f_b$  of the beam atoms in the region common to the beam and the sheet and a certain fraction  $f_s$  of the other molecules in the sheet. If  $Z_s$  is small enough so that every electron in the sheet invades the full portion of the beam, then when the region is viewed in the z direction, the number of excited beam atoms seen per unit cross section, which we shall call b, is

$$b = f_b n(x) Z_e = f_b n_1 Z_e \Omega / 4\pi.$$
(2)

<sup>&</sup>lt;sup>19</sup> Start, for example, with Eq. (71b) of E. H. Kennard, *Kinetic Theory of Gases* (The McGraw-Hill Book Company, 1938). To find the total number of atoms in the volume element dxdydz, multiply the number of atoms per second by the longitudinal distance dx divided by the speed v, integrate over the speed range 0 to  $\infty$  and the first-slit area  $Y_1Z_1$ , and substitute for the angle integral the solid angle  $dydz/x^2$  subtended at the first slit by the elementary region under consideration. To find n(x), divide by dxdydz. Actually, Eq. (1) is more generally valid than this derivation implies, for it does not require any assumption as to (Maxwell) velocity distribution.

If  $Z_e$  is so great than the penumbra must be considered, Eq. (2) is no longer valid. We shall refer to this case in the last paragraph of this section.

Now suppose that that gas ("stray gas") in the *k*th chamber which is not part of the beam has the absolute temperature  $T_k$ , the pressure  $p_k$ , and the corresponding molecule density  $n_k$ . When the region is viewed in the *z* direction, the number of excited stray molecules seen per unit cross section, which we shall call *s*, is

$$s = f_s n_k Z_e. \tag{3}$$

The ratio s: b of number per unit area of excited stray molecules to that of excited beam atoms is obtained from expressions (2) and (3) by division:

$$s/b = (f_s/f_b) \cdot (4\pi/\Omega) \cdot (n_k/n_1). \tag{4a}$$

In the important case where atoms of the species constituting the beam are the only molecules that need to be considered as occurring in the *k*th chamber, we have  $f_s=f_b$ , and the expression for the ratio reduces to the simpler one

$$s_b/b = (4\pi/\Omega) \cdot (p_k/p_1) \cdot (T_1/T_k), \qquad (4b)$$

where  $s_b$  is the number seen per unit cross section of excited stray atoms of the species constituting the beam.

The physical significance of Eqs. (4) for the use of atomic beams in the study of the atomic spectra of non-gases, on the one hand, and of gases, on the other, is as follows:

In the study of non-gases,<sup>1</sup> the only requirement upon the pressure  $p_k$  is that it be low enough not to disturb appreciably the collimation of the atomic beam, i.e., that the mean free path in any chamber be great compared with the beam length in the chamber (except that in the final chamber the mean free path need only be great compared with the distance from the last slit to the far end of the field of view). The excitation of stray atoms, producing broad lines, has no effect upon the experiment so long as these lines do not coincide with the lines under study, and stray atoms of non-gases do not persist in the chamber after collision with the cold walls.

In the study of gases, the excitation of stray atoms of the species under study superimposes a broad line upon each of the lines to be analyzed, in the intensity ratio  $s_b : b$ , and it is clearly of importance to keep the ratio  $s_b : b$  far below unity. Upon the assumption that the temperatures  $T_1$  and  $T_k$  in the extreme chambers are approximately the same, the condition imposed upon the apparatus as a consequence of Eq. (4b) can be verbally stated very simply: A necessary condition for the attainment, with gases, of the line sharpness characteristic of the atomic beam, is that the ratio  $p_k/p_1$  of the pressures in the extreme chambers be much smaller than the solid angle  $\Omega/4\pi$ ; or

$$p_k/p_1 \ll \Omega/4\pi$$
, (5)

where  $\Omega$  is the solid angle subtended by the first slit at the field point under consideration.

Equation (5) is the principal conclusion from our geometrical consideration. By way of numerical example, consider the range of the factor  $\Omega/4\pi$  from the near to the far edge of the field, for each of the three pieces of apparatus described below, in Section IV (cf. especially reference 29). From the data given there this range may be seen to extend:

for the first, from  $4.6 \times 10^{-8}$  to  $3.8 \times 10^{-8}$ ; for the second, from  $5.0 \times 10^{-6}$  to  $1.2 \times 10^{-6}$ ; for the third, from  $6.0 \times 10^{-4}$  to  $6.6 \times 10^{-5}$ .

When it is remembered that the pressure  $p_1$  within a discharge tube is usually of the order of 0.1 mm or 1 mm of Hg, and that the slits constitute a large leak from chamber 1, it will be realized that the third system, with fast modern pumps working in every chamber after the first (k equals 3 for the second system, and 4 for the first and third), is the only one of the three with any practical chance of satisfying Eq. (5).

Equation (2) is limited in validity to the case where the full portion of the beam is at least as wide as the electron sheet. If  $Z_e$  is greater than the width of the full portion of the beam, clearly the area density of excited beam atoms is less than the value given in Eq. (2), while Eq. (3) remains valid and the values of the consequent ratios corresponding to Eqs. (4) are greater than those expressed in Eqs. (4). This fact shows that it is advantageous to confine the region of excitation to a sheet not wider, or at most not much wider, than the full portion of the beam. Therefore, unless the inequality (5) can be satisfied in much greater degree than appears possible even with our third system, excitation methods that would excite stray atoms outside the full portion of the beam should be eschewed in favor of a sheet excitation method such as a line source feeding electrons into a cylindrical electron lens.

#### **III. THE DOPPLER EFFECT**

The relative Doppler displacement  $\delta$  for a quantum originating at a beam atom is

$$\delta \equiv (\Delta \nu / \nu) = \beta \sin \theta \doteq \beta \theta, \tag{6}$$

where  $\nu$  is the wave number of the line under consideration,  $\theta$  the angle<sup>20</sup> between the direction of propagation of the light and the plane normal to the direction of motion of the atom, and  $\beta$  the ratio V/c, where V is the speed of the atom and c the speed of light. The angle  $\theta$  will be assumed throughout to be small; hence the last (approximate) equality in Eq. (6). The quantity  $\delta$  is the algebraic sum of five independent contributions:

$$\delta = \delta_1 + \delta_2 + \delta_3 + \delta_4 + \delta_5$$
  
$$\doteq \beta(\theta_1 + \theta_2 + \theta_3 + \theta_4 + \theta_5), \quad (7)$$

where the separate contributions are defined and treated in the corresponding numbered paragraphs below. It might be useful to integrate the intensity over the range of  $\delta$  in order to determine the line shape quantitatively, as undertaken by Minkowski and Bruck<sup>21</sup> with the consideration only of the contribution that we call  $\delta_1$ ; however, we shall content ourselves with a brief consideration of each of the contributions separately and an order-of-magnitude estimate of the whole effect and of the relative importance of the several contributions. Since the atom is supposed to be traveling approximately in the positive x direction and the light approximately in the positive z direction, it will be considered sufficient for our purposes to consider the xzprojection of the relative motion.

### (1) Original Atomic Velocity

The transverse component of the original atomic velocity is the quantity which, when considered alone, leads to the usual rough statement that the effective temperature  $T_{\rm eff}$  of an atomic beam source is the true temperature T times the square of the angular spread of the effusing atoms, or in our case  $T_{\rm eff} = T(Z_1+Z)^2/x^2$ , where Z is the smaller of the two quantities,  $Z_e$  and the width in the z direction of the full portion of the beam plus part of the penumbra. If we suppose that the atom under our consideration passes through slit I at the coordinate  $z_1$ and, without being deviated, emits light at the coordinate z(x) or z, then

and

$$|\delta_1| \equiv \beta(Z+Z_1)/2x.$$

(8)

In our final apparatus  $|\delta_1| \sim 0.05\beta = 2.8 \cdot 10^{-7}$ if the value of  $\beta$  used  $(=5.7 \cdot 10^{-6})$  is the one corresponding to the arithmetic mean speed of H<sup>1</sup> atoms at 0°C.

 $\delta_1 = \beta(z-z_1)/x,$ 

## (2) Atomic Velocity Gained by Excitation<sup>22</sup>

We shall consider especially the hydrogen alpha-line. An electron of mass m and of kinetic energy  $E = p^2/2m$ , traveling in the y direction with a momentum p, upon exciting the hydrogen atom, communicates to it a momentum of magnitude P whose projection in the line of sight (z direction) we shall call  $P_z$ . Thus the emitting atom will attain a velocity component  $V_z = P_z/M$ , where M is the mass of the atom, which will cause a relative Doppler shift in the emitted light equal to

$$\delta_2 = (\Delta \nu / \nu) = (V_z / c) = (P_z / M c).$$
(9)

It is clear that the resultant line shape will be of the same form as the curve giving the relative probability that, if the excitation results in the emission of the alpha-line, the atom receives a momentum component  $P_z$  in the range  $dP_z$ . We shall compute this probability, making a series of approximations which tend to overestimate the momentum which is transferred to the atom, and which hence lead to a line width

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<sup>&</sup>lt;sup>20</sup> Our sign convention is such that a positive contribution to  $\theta$  of Eq. (6) produces a shift toward the violet; i.e.,  $\delta$  and  $\theta$  are positive when the angle between the directions of motion of the atom and the light is acute and negative when this angle is obtuse. <sup>21</sup> R. Minkowski and H. Bruck, Zeits. f. Physik **95**, 274

<sup>&</sup>lt;sup>21</sup> R. Minkowski and H. Bruck, Zeits. f. Physik **95**, 274 (1935).

<sup>&</sup>lt;sup>22</sup> We are indebted to Professor Feynman for the essentials of the information in this paragraph.



FIG. 2. Doppler effect for hydrogen atoms excited by electron impact, neglecting everything except the lateral velocity imparted to the atoms by the electrons in inelastic collisions exciting the atoms to the upper level of the alphaline or higher. The main curve shows the shape, Eq. (12), approached asymptotically for large values of  $\Delta \nu / \nu$  by each line contour, according to the Born approximation (electron energy  $\gg$ 13.6 ev). For small momentum transfers the main curve fails to show the true line contour, cf. Eq. (11); in order that the figure be approximately valid the curve is cut off horizontally so as to cover the correct area, Eq. (13). The true line contour for each incident electron energy has a higher central maximum (at  $\Delta \nu / \nu = 0$ ) and a lower value near the sharp corner shown; consequently the true halfintensity half-breadth is less than the one indicated in the lower left corner. The scale of ordinates is such that the top of the graph corresponds to a value of 30 for the integral in Eq. (12). The scales of abscissae are related as follows:  $(\Delta\nu/\nu) = (P_z/p_0) \cdot (m\alpha/M)$ , cf. Eq. (9), where M is the mass of the atom. The abscissae may be compared with the natural breadths and separations in the alpha-line of hydrogen with the aid of Table I.

somewhat greater than would be given by a more accurate calculation.

We assume first that all excitations above the two-quantum levels (n=2) are roughly equally likely to lead to alpha-line emission. By doing this we exaggerate the importance of the larger energy transfers, and hence, by and large, of the larger momentum transfers. We shall further assume that all the momentum lost by the incoming electron is given to the atom. This is correct for collisions which excite discrete levels,

but in ionizing collisions some of the momentum is given to the secondary electron. We are therefore led to compute the cross section for a collision leading to excitation above the n=2levels or to ionization, and resulting in a loss of momentum of the colliding electron whose component is  $P_z$  in the range  $dP_z$ .

The cross section for a transfer of momentum of magnitude P in the range dP when levels above n=2 are excited may be found<sup>23</sup> according to the Born approximation (valid if  $p \gg p_0$ , say  $E \approx 150$  volts) to be

$$d\sigma(E, P) = \pi a_0^2 \cdot 8p_0^2 \frac{E_0}{E} \frac{dP}{P^3} \times \left[1 - \frac{2^8 p_0^8}{(4p_0^2 + P^2)^4} - \frac{2^{15} p_0^8 P^2}{(9p_0^2 + 4P^2)^5}\right], \quad (10)$$

where  $a_0 = \hbar^2/me^2$  is the radius,  $p_0 = \hbar/a_0$  is the momentum, and  $E_0 = e^2/2a_0$  is the ionization energy of the first Bohr orbit of hydrogen. This expression, which does not contain the direction, shows immediately that all the energetically possible momentum transfer vectors with the same magnitude P are equally probable. The cross section for an inelastic collision with  $P_z$  in the range  $dP_z$  is  $d\sigma(E, P)$  times the probability that, when P is in the range dP,  $P_z$  is between  $P_z$  and  $P_z + dP_z$ . If we consider the spherical shell segment of radius P in momentum space, which represents the energetically possible values of the momentum transfer vector, the latter probability is found to be the fraction of this segment that lies between the planes,  $P_z$ and  $P_z + dP_z$ , normal to the z axis. We suppose P to be small compared with p and large enough so that the limitation of energy transfer (to discrete levels, or to the continuum above ionization) does not seriously limit the angular range possible for the vector momentum transfer. This requires that P be considerably larger than the smallest momentum  $P_{\min}$  which can be transferred and still result in ionization. Thus we must have

$$P_{\min} \ll P \ll p$$
,

where  $P_{\min}$  must satisfy

$$(p^2/2m) - [(p - P_{\min})^2/2m] = E_0 = p_0^2/2m,$$

<sup>23</sup> H. Bethe, Ann. d. Physik 5, 325 (1930).

so that  $P_{\min} \doteq p_0^2/2p$ , or

$$p_0^2/2p \ll P \ll p. \tag{11}$$

Under these circumstances, the spherical segment is almost a hemisphere, and the fraction between the planes  $P_z$  and  $P_z+dP_z$  is  $dP_z/2P$  for  $P>P_z$ , and zero otherwise. Thus the cross section when  $P_z$  lies in the range  $dP_z$  is

$$d\sigma_{z}(E, P_{z}) = \pi a_{0}^{2} \cdot 8p_{0}^{2} \cdot \frac{dP_{z} \cdot E_{0}}{E} \int_{P_{z}}^{\infty} \frac{dP}{2P^{4}} \\ \times \left[ 1 - \frac{2^{8}p_{0}^{8}}{(4p_{0}^{2} + P^{2})^{4}} - \frac{2^{15}p_{0}^{8}P^{2}}{(9p_{0}^{2} + 4P^{2})^{5}} \right].$$
(12)

The upper limit is of the order of the maximum possible transfer, but this is so large that no appreciable error is made by assuming the upper limit to be infinite. This integral has been evaluated, and the result plotted in Fig. 2 (for positive  $P_z$ ; the curve is, of course, symmetrical about the  $P_z=0$  axis). Three scales of abscissae are shown:  $P_z/p_0$ , and  $\delta_2$  for H<sup>1</sup> and H<sup>2</sup>. The fact that the shape of this curve is independent of the incident electron energy E arises from the fact that p or E enters into Eq. (12) only as a scale factor.

Equation (12) is incorrect for small momentum transfers  $(P \approx p_0^2/2p)$  by Eq. (11), so that this curve is meaningless below about  $p_0^2/2p$ . We may, however, obtain a fairly good idea of its behavior for these small transfers by noting that the entire area under the curve must equal the total cross section for excitation above the n=2 levels. That is, the integral of  $d\sigma_z(E, P_z)$  over all  $P_z$  must equal the total cross section for inelastic collisions minus the cross section for excitation of the n=2 levels. Taking for these cross sections the values calculated by Bethe,<sup>24</sup> we find the total cross section for excitation above n=2 to be

$$\pi a_0^2 \cdot (E_0/E) [1.780 \ln E/E_0 + 5.813].$$
 (13)

The curves have been completed for small momentum transfers, for several values of the incident electron energy E, by arbitrary horizontal cut-offs at ordinates chosen to satisfy Eq. (13). The half-intensity breadths resulting from this arbitrary procedure are indicated for

the various electron energies.<sup>25</sup> The true halfintensity breadths are certainly smaller than those shown.

Paradoxically, smaller half-breadths arise from excitation by more energetic electrons; in fact the line breadth varies approximately as the inverse square root of the bombarding voltage. It is to be noted also, that insofar as the hemisphere treatment is approximately valid, the curves for the components of the transfer of momentum in directions other than the zdirection would be very similar; and that therefore, since the atoms in the beam are traveling slowly compared with the electrons, the contribution of the excitation process to the Doppler effect is almost independent of the relative orientation of the atomic beam, the electron sheet, and the line of sight.

## (3) Atomic Velocity Gained by Emission

The contribution of this velocity to the relative Doppler effect is exceedingly small, and it differs from the other contributions previously considered in that it has the same value for all the light of a certain line, regardless of the source and the optical system used. It constitutes a shift and not a spread of the line. The atomic velocity is a recoil velocity arising from the emission of a quantum of momentum  $h/\lambda$ , where h is Planck's constant and  $\lambda$  is the wave-length of the light. If M is the mass of the emitting atom,  $\delta_3 = -h/2\lambda Mc = -1.0 \times 10^{-9}$  for the alphaline of H<sup>1</sup>.<sup>14</sup>

The effect of this minute red shift is to require a correction with the relative value of  $+1.0 \times 10^{-9}$ to the wave number of the alpha-line. This correction is far within the present error of measurement for any line, and is significant only when applied to the most meticulously calculated quantities.<sup>26</sup>

### (4) Spread of Light in the Optical System

We shall suppose that the light from the field X, Y is to be collimated for an interference

<sup>&</sup>lt;sup>24</sup> H. Bethe, reference 23, page 356.

<sup>&</sup>lt;sup>25</sup> The half-intensity breadths similarly calculated for the Lyman line  $1_{i}-2_{j,1i}$  by omitting the last term of the trinomial of Eqs. (10), (12) are about two-thirds as great as those indicated in Fig. 2.

<sup>&</sup>lt;sup>36</sup> For instance, Birge's value, R. T. Birge, Rev. Mod. Phys. 13, 233 (1941), for the Rydberg constant  $R_{\rm H}$ , should be corrected only from (109677.5812±0.0075) cm<sup>-1</sup> to 109677.5813 cm<sup>-1</sup> on account of this recoil.

TABLE I. Natural half-intensity relative half-breadths,  $\delta_{\text{nat}}$ , and relative separations,  $\Delta \nu / \nu$ , of the components of the hydrogen (H<sup>1</sup> or H<sup>2</sup>) alpha-line. The components are listed in order of frequency, starting at the violet end.

Component	21-311	21-31	$2_{14} - 3_{24}$	211-311	211-31
Usual designation	ż	3	1 -	4 .	5 '
Relative intensity	7.08	1.14	9.00	1.00	0.20
$\delta_{nat} \times 10^8$	9.0	3.9	12.0	12.0	11.0
$\Delta \nu / \nu$	$\frac{2}{15}$	$\frac{\alpha^2}{18}$	$\frac{1}{2}\alpha^2 = \frac{2}{45}$	$\frac{\alpha^2}{15} - \frac{2}{15}$	$\alpha^2$
$\Delta \nu / \nu  imes 10^8$	7	10 14	50 2	37 7	10

spectroscope with the aid of a lens of focal length f, opened to the f-number N. Let the axis of the optical system (z axis) intersect the axis of the beam (x axis) normally at a coordinate  $x_0$  in the center of the field length X and consider the light emanating from an atom at coordinate x (where  $|x-x_0| \leq \frac{1}{2}X$ ) and striking the lens at the coordinate  $x_L = x_0 + qf/2N$  (where  $|q| \leq 1$ ). This light gives rise to a relative Doppler shift of

 $\delta_4 = \delta_{4a} + \delta_{4b},$ 

 $\delta_{4a} = -\beta(x-x_0)/f$ 

where

and

$$\delta_{4b} = \beta q/2N. \tag{15b}$$

(15a)

It will be noticed that the x-dependent part 4agives rise primarily not to a spread but to a shift that varies from point to point of the field so that the light from points with increasing xis successively redder. Accompanying the shift  $\delta_{4\alpha}$  is a spread with a half-intensity half-breadth of about  $\frac{1}{2}\delta_{4a}$  arising from the velocity distribution of the atoms in the obliquely viewed beam. Thus, not only are the ends of the spectrum line (e.g., the fringes far from the center, in the case of a Fabry-Perot interferometer) of different colors from the center, but they are broader, all on account of part 4a of the Doppler shift. Part 4b gives rise to a general shift. It can be decreased indefinitely at the expense of exposure speed and of the smoothing-out effect of the use of a large area of the Fabry-Perot plates.

In our case X=2 cm, and with our f:6 collimating lens of focal length 30 cm,  $\delta_{4a} = +1.9 \times 10^{-7}$  at the end of the field nearest the first slit and  $\delta_{4a} = -1.9 \times 10^{-7}$  at the other end, and  $\delta_{4b} = 4.7 \times 10^{-7}$  for full aperture for the alphaline, if  $\beta = 5.7 \times 10^{-6}$ .

# (5) Error of Orientation of the Optical System with Respect to the Beam

If the axis of the optical system is not normal to that of the beam there is introduced an angular shift of

 $\theta_5 = \delta_5 / \beta = \pi/2 - (\text{angle between the optical system axis and the beam axis}).$  (16)

Just as in case 4a, this shift  $\delta_5$  is accompanied by a broadening effect with a half-breadth of about  $\frac{1}{2}\delta_5$ , arising from the velocity distribution within the beam; but in this case the spread is common to the whole length of the line.

If we estimate that there is in our apparatus an uncertainty of  $\pm 0.1$  mm in the z coordinate of the second slit with respect to the third, this uncertainty gives rise to a possible  $\delta_5 = \beta \theta_5$  $= \pm 8 \times 10^{-8}$  for the alpha-line, if  $\beta = 5.7 \times 10^{-6}$ . We have made no great effort to minimize the quantity  $\delta_5$  in our apparatus; if it were to become important it could be reduced greatly by increased care in alignment, for instance with the aid of refined optical methods.

### Summary of Doppler Effect

In summary, under the conditions of our experiment the following orders of magnitude may be expected for the values of the contributions to  $\delta$ , in the experiment upon H<sup>1</sup>:  $|\delta_1| \approx 2.8 \times 10^{-7}$ ;  $|\delta_2| \sim 10^{-6}$ ;  $\delta_3 = -1.0 \times 10^{-9}$ ;  $|\delta_{4a}| \leq 1.9 \times 10^{-7}$ ;  $|\delta_{4b}| \leq 4.7 \times 10^{-7}$ ;  $\delta_5 = \pm 8 \times 10^{-8}$ . Each component of the alpha-line can be expected to exhibit a half-breadth at its center of the order of magnitude<sup>27</sup> of

central half-breadth

$$\sim (\delta_1^2 + \delta_2^2 + \delta_{4b}^2 + \frac{1}{4} \delta_5^2)^{\frac{1}{2}} \sim 1.2 \times 10^{-6} \text{ for } \mathrm{H}^1$$
(17a)

and an extreme half-breadth at its ends of

terminal half-breadth

$$\sim (\delta_1^2 + \delta_2^2 + \frac{1}{4} \delta_{4a}^2 + \delta_{4b}^2 + \frac{1}{4} \delta_{5}^2)^{\frac{1}{2}}$$
  
  $\sim 1.3 \times 10^{-6} \text{ for } \mathrm{H}^1$  (17b)

and the center of each component to be shifted

<sup>&</sup>lt;sup>27</sup> In these order-of-magnitude considerations there is no need to distinguish by separate symbols the displacement  $\delta_1$ , etc., of a single quantum and the half-breadth or shift of the line that arises from the random distribution of such displacements.



FIG. 3. Design of the apparatus described in Section IV. The "gun" is schematic. The heavy dashed line represents a removable funnel; cf. reference 32.

from its "true" value, at the center of the line by an amount of the order of

central shift

$$\sim \delta_3 + \delta_5 \sim \pm 8 \times 10^{-8} \text{ for } \mathrm{H}^1$$
 (18a)

and at its ends by an amount of the order of

terminal shift

$$\sim \delta_3 + \delta_{4a} + \delta_5$$
  
  $\sim (-2 \pm 1) \times 10^{-7}$  and  
  $(+2 \pm 1) \times 10^{-7}$  for H<sup>1</sup>. (18b)

Numerical values considerably smaller than those given in Eqs. (17) and (18) are attainable. The principal contribution to the half-width,  $\delta_2$ , may be reduced by increasing the energy of the bombarding electrons, and, while it might be inconvenient to reduce  $\delta_{4a}$ , the principal contribution to the shift, this field angle effect can always be corrected for by a simple calculation with Eq. (15a), and the second largest contribution  $\delta_5$  can be reduced by improvements in the methods of aligning the beam with respect to the axis of the optical system.

For H<sup>2</sup> the quantities  $\delta_2$  and  $\delta_3$  have  $\frac{1}{2}$  the values that they have for H<sup>1</sup>, and the other  $\delta$ 's have  $2^{-\frac{1}{2}}$  times the values they have for H<sup>1</sup>. With  $\delta_2$  predominant in Eqs. (17) and  $\delta_{4a}$  and  $\delta_5$  in Eqs. (18), one may expect that for H<sup>2</sup> the half-breadths will be about half as great and the shifts about seven-tenths as great as for H<sup>1</sup>.

The relationship of these relative shifts and half-intensity half-breadths to the hydrogen alpha-problem can best be seen by comparing them with the separations and natural halfintensity half-breadths<sup>28</sup> of the several components of the alpha-line. These quantities are shown in Table I. It will be noticed that the

<sup>&</sup>lt;sup>28</sup> Cf. H. Bethe, reference 9, p. 444.

numerical values of the half-breadths expressed for H<sup>1</sup> in Eqs. (17) are of the order of 10 times the natural half-breadths and that the separations  $\Delta \nu / \nu$  are from 2 to 12 times the half-breadths expressed in Eqs. (17).

### IV. DESIGN OF THE APPARATUS

We have successively designed and built three systems. The first two<sup>29</sup> have been tested and abandoned as failures, but before it was possible to complete the test of the third the work was interrupted and its early resumption is a doubtful possibility. Because we believe that our final (third) system is designed on a sounder basis than any other apparatus of which we know for the spectroscopic investigation of atomic beams of gases, and may consequently at least be useful as a guide toward future designs, we are describing it in spite of its untested condition.

The final apparatus consists primarily of four chambers connected by three slits, each 0.50 mmin the z direction and 1.5 mm in the y direction, with facilities for maintaining a hydrogen discharge in the first chamber and with an electron gun in the fourth chamber, designed to throw a thin sheet of electrons through the beam. Figures 3 and 4 show the structure of the apparatus. The second and third slits are, respectively, 0.3 cm and 1.0 cm from the first. Almost all other considerations are sacrificed to that of the speed of pumping from the last three chambers.

Hydrogen is generated by electrolysis in alkaline solution, with nickel electrodes, and

admitted through a needle valve to one end of a U-shaped, water-cooled Geissler-Wood<sup>30</sup> tube 3 meters long. The tube is slowly pumped out through a controlled constriction. The central portion of the tube, containing the first chamber (1, Fig. 3), closely follows Rabi's<sup>4</sup> design, except that the slit was produced in a nipple-shaped tube of glass by pinching the glass down over a piece of copper ribbon of the right cross section and dissolving the ribbon. The outer surface of the glass was ground to a thickness small compared with the slit width. The nipple tube was waxed onto the Rabi tube and grounded electrically by Aquadag, a metal sleeve, and a chain dropped to the brass tube below the glass. The end of the horizontal tube far from the nipple is ground flat and covered with a piece of microscope cover glass. All the fine adjustment of the slits is accomplished by aligning the first slit with the other two. The slit is made vertical with the aid of a telescope during the waxing of the nipple tube. The slit is adjusted vertically with the aid of the screw collar (shown in Fig. 3) that holds the first chamber in the second, and horizontally by moving the tube in the conical ground joint of the same collar. In order to allow adjustment without the necessity of delay for glass blowing and the renewal of the hydrogen supply, the whole Geissler tube is mounted on an axis coincident with the axis of the threaded collar and ground joint. After the adjustment of the slit the tube may be clamped in place by



FIG. 4. The apparatus described in Section IV.

<sup>30</sup> R. W. Wood, Proc. Roy. Soc. A97, 455 (1920).

<sup>&</sup>lt;sup>29</sup> In the first system, the beam arrangement was much like that of Rabi and his co-workers (reference 4). There were three slits, ranging in approximate size from 0.028 mm by 0.9 mm to 0.09 mm by 5 mm. The second and third slits were, respectively, about 1 cm and 8 cm from the first. The field of view extended from about 21 cm to about 23 cm from the first slit. A well-defined beam of atomic hydrogen was found by the molybdenum oxide test, but no trace of the alpha-line was detected. In the second system there were two slits, respectively 0.028 mm by 0.9 mm and 0.08 mm by 1.4 mm only 1 cm apart and the field extended from about 2 cm to about 4 cm from the first slit. In both these systems the pumping arrangements were quite primitive compared with that of the third system. Fabry-Perot photographs taken with the second system showed, not several components as expected, but a single broad line, which probably arose from the Doppler spread of mutually repellent atoms produced by the dissociation of molecular hydrogen in the final chamber. A study of these photographs led to the geometrical consideration given in Section II, as a basis for the design of the third system.

means of another metal collar near the ground joint.

The second chamber (2, Fig. 3) is a vertical brass cylinder, truncated diagonally at the bottom to facilitate the pumping in the third chamber. The second chamber is co-axial with the first but eccentrically mounted with respect to the third. At the level of the slit the tube is externally turned thin in a ring 6 mm wide. On the side opposite the slit is a window, fitted into a recessed plug to allow the cylinder to pass without hindrance through its receiving hole in the top plate of the third chamber. A hole for the slit is countersunk from the inside of the tube. The slit itself is punched with a special tool in a thin copper sheet, which is inserted in the thinned ring. A rough control over the position of the slit is afforded in the punching and placement of the slit, and in the rotational adjustment of the chamber; this control, of the order of a few tenths of a millimeter, is sufficient to allow the beam axis to be made nearly enough coincident with the axis of the horizontal tube of the fourth chamber, for convenience. The chamber is evacuated through a 2.5-cm outlet near the top by means of a Hypervac pump or a mercury diffusion pump  $P_2$ . The pressure in chamber 2 may be determined by means of a McLeod gauge.

The third chamber (3, Fig. 3) is a vertical brass cylinder which is merely a short extension of a 4-inch 3-jet vertical fractionating oil diffusion pump  $P_3$ ;<sup>31</sup> so that the second chamber is effectively hanging in  $P_3$ . The third slit, like the second, is punched in a thin copper sheet. This sheet is soldered to a narrow 6-mm ring which fits singly into a 6-mm hole in the wall between the third and fourth chambers, and is fastened there, with the sheet in the fourth chamber, by means of a screw 2 cm below the slit, where the wall is thickened for the purpose by a small block soldered in the third chamber. Opposite the slit in the third chamber is a hand hole (which we have not had to use) and a centered glass window. The pressure in chamber 3 may be read by means of a McLeod gauge or an ionization gauge.

The fourth chamber (4, Fig. 3) is a horizontal cylinder fitted with an oil diffusion pump  $P_4$ , of the same kind as  $P_3$  and a removable elbow leading to another oil diffusion pump  $P_{4+}$ . The structure of this chamber can best be seen from Fig. 4. An electron gun is mounted on cleats against the wall of chamber 3 above the slits so as to send electrons vertically downward in a sheet striking the atomic beam normally;  $P_4$  is placed so that the electron discharge takes place nearly straight down  $P_4$ . The pressure in chamber 4 is read by an ionization gauge above  $P_4$ .

The elbow is attached to the horizontal cylinder by a tongue-and-groove joint sealed by a Duprene gasket of  $\frac{1}{16}$ -inch square cross section. The removal of the elbow allows convenient access to the chamber. The elbow<sup>32</sup> contains a glass window in the line of the beam axis, which completes a train of slits and windows from one end of the system to the other.

The electron gun is mounted in chamber 4 on a three-point support in such a way as to be adjustable and subject to easy removal and return to a repeatable position. It is mounted against a sheet of mica in contact with the wall of the third chamber so that the excited portion of the beam constituting the field of view XY(Figs. 1, 3) may start at as low a value of x and consequently as large a value of  $\Omega$ , Eq. (5), as possible. In this apparatus X extends 2 cm, starting 1 cm and ending 3 cm from the first slit. The gun consists essentially of a filament, a long slotted grid, and a long slotted plate. The filament is made of Konel metal ribbon 2.5 mm wide with a hot length of 2 cm, activated by the application of a mixed solution of SrCO<sub>3</sub> and BaCO<sub>3</sub>. The filament is mounted in a slot 3 mm wide recessed in a metal block, which is kept at the potential of one end of the filament. The hot surface of the filament is about  $\frac{1}{2}$  mm behind the face of the block. The filament itself is fastened at the end nearest the wall of chamber

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<sup>&</sup>lt;sup>31</sup> A modified form of the pump described by L. Malter and N. Marcuvitz, Rev. Sci. Inst. 9, 92 (1938).

<sup>&</sup>lt;sup>22</sup> The elbow has been fitted with a removable funnel (dashed lines, Fig. 3) shaped and adjusted to collect all of the beam, including the penumbra, and lead it, after one collision, to  $P_{4+}$  while reducing as little as possible the effective aperture of  $P_{4}$ ; since the helpfulness or harm-fulness of this funnel is a complicated function of geometry and pumping speeds, whether it is used will depend upon experience. The elbow is fitted with an outlet for an ionization gauge in the geometric shadow, from the beam, of the face plate.

3, and passes over two small porcelain cylinders to a spring clip that keeps it taut. The grid consists of a nickel sheet 5 cm square with a slot 3 mm wide by 2 cm long mounted against mica spacers on the recessed block so that the plane of the grid is about 1 mm from that of the filament. An attempt to use a grid with the slot crossed by fine wires every 0.5 mm was abandoned after it was found to increase the grid current greatly without appreciably affecting the current through the final slot. The plate is a pair of nickel sheets 2 cm long with a slot 0.5 mm wide between them, mounted about 6 mm from the plane of the grid and kept at the potential of the ground, i.e., of the chamber. Our incomplete tests indicate that as much slot current ( $\sim 20$  ma, when the applied potential is 300 volts) can be obtained by connecting the grid and plate to run at the same high potential with respect to the filament, as by putting the grid at an intermediate potential, according to

the proposal in Klemperer's<sup>33</sup> discussion of the optics of cylindrical electron lenses. In connection with this result it will be remembered that we are using the focusing system of the gun as a condensing, rather than an image-forming lens.

A pair of transverse windows of 4.5-cm aperture, 11 cm apart, for the observation and photography of the beam, lies symmetrically across the beam axis. Their line of centers (lying in the z direction) crosses the beam 1.2 cm beyond the third slit. This design allows the placement of a spherical concave mirror behind the beam, imaging it in itself, so that (for perfect reflectance) the relative values of the brightness calculated with the aid of Eq. (1) for the near end, center, and far end of the field, instead of being 36:9:4, are 40:18:40.

<sup>&</sup>lt;sup>33</sup> O. Klemperer, *Electron Optics* (Cambridge Physical Tracts No. 4; The University Press, Cambridge, 1939), p. 96.



FIG. 4. The apparatus described in Section IV.