

CHAPTER IX

HYDROGEN FINE STRUCTURE AND THE DIRAC ELECTRON

Even the hydrogen spectrum, the simplest of all systems, is observed to have a fine structure. At an early date Michelson studied the Balmer lines with an interferometer and found that both  $H_\alpha$  and  $H_\beta$  were close doublets with separations of only 0.14 and 0.08 Å, or 0.32 and 0.33  $\text{cm}^{-1}$ , respectively. Many subsequent investigations by others have confirmed these results (see Fig. 9.1).

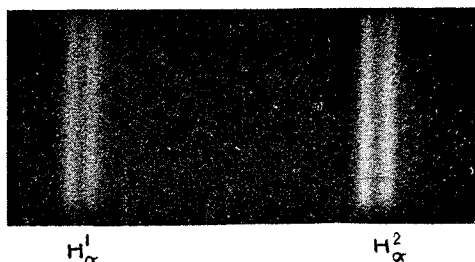


FIG. 9.1.—Photographs of the  $H_\alpha$  line of both of the hydrogen isotopes  $H^1$  and  $H^2$ . (After Lewis and Spedding.)

The most informing observations that have been made on hydrogen-like atoms are those of Paschen<sup>1</sup> on the singly ionized helium line  $\lambda 4686$ . This line (see Fig. 2.8) corresponds to the first member of the so-called *Paschen series of hydrogen*. Historically Paschen's observations were made and published at a most opportune time, for in the next issue of the *Annalen der Physik* Sommerfeld independently predicted just such a fine structure by an extension of the Bohr atom to include elliptic orbits and the special theory of relativity.<sup>2</sup> While the quantum mechanics gives a more perfect account of the observed fine structure, the development of the orbital model is interesting in that it leads to the same energy levels.

**9.1. Sommerfeld Relativity Correction.**—The extension of Bohr's atomic model by Sommerfeld to include elliptic orbits adds no new energy levels to the hydrogen atom (see Sec. 3.3). For a given total quantum number  $n$ , all elliptic orbits  $s$ ,  $p$ ,  $d$ , . . . have just the same

<sup>1</sup> PASCHEN, F., *Ann. d. Phys.*, **50**, 901, 1916.

<sup>2</sup> SOMMERFELD, A., *Ann. d. Phys.*, **51**, 1, 1916.

energy as the Bohr circular orbit with the same  $n$ . This energy in wave numbers is

$$\frac{W}{hc} = -\frac{RZ^2}{n^2} = -T, \quad (9.1)$$

where  $R$  is the Rydberg constant

$$R = \frac{2\pi^2me^4}{ch^3\left(1 + \frac{m}{M}\right)}, \quad (9.2)$$

$h$  is Planck's constant,  $c$  the velocity of light,  $m$  and  $e$  the mass and charge of the electron, and  $M$  the mass of the nucleus with charge  $Ze$ .

Bohr pointed out in his earliest papers that the relativistic change in mass of the orbital electron should be taken into account in computing the energy levels. Introducing elliptic orbits, Sommerfeld applied the special theory of relativity to the electron mass. Due to the different velocity of the electron in orbits of the same  $n$  but differing azimuthal quantum number, the mass of the electron and hence the resultant energy levels are all different. If the rest mass of the electron is  $m_0$ , its mass when moving with velocity  $v$  is given by the special theory of relativity as

$$m = m_0 \left(1 - \frac{v^2}{c^2}\right)^{-\frac{1}{2}}. \quad (9.3)$$

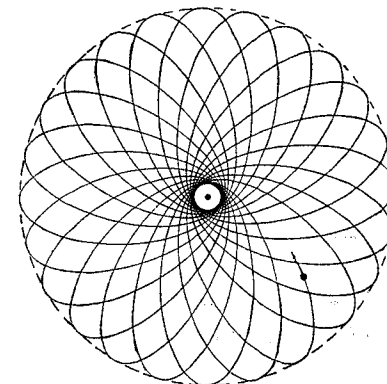


FIG. 9.2.—Schematic representation of the precession of an electron orbit due to the relativity change in mass of the electron with velocity. (After Sommerfeld.)

As a result of this change in mass, which is greatest at perihelion and greatest for the most elliptic orbits, there is an advance of the perihelion, or a precession of the electron orbit, similar to that of a penetrating orbit in the alkali metals (see Fig. 7.4), or to that of the planet Mercury moving about the sun. This precession is shown schematically in Fig. 9.2. While the derivation of Sommerfeld's equation for the change in energy due to this precession is out of place here, we shall find use for it in making comparisons with the quantum-mechanical results.<sup>1</sup> According to the Sommerfeld theory the term values of hydrogen-like atoms are given by

$$T = -\frac{W}{hc} = \frac{\mu c}{h} \left\{ 1 + \frac{\alpha^2 Z^2}{(n-k + \sqrt{k^2 - \alpha^2 Z^2})^2} \right\}^{-\frac{1}{2}} + \frac{\mu c}{h}, \quad (9.4)$$

<sup>1</sup> For a derivation of Sommerfeld's relativistic fine-structure formula see "Atomic Structure and Spectral Lines," p. 467, 1923; also A. E. Ruark and H. C. Urey, "Atoms, Molecules and Quanta," p. 132.

where  $\alpha$  is the fine-structure constant

$$\alpha^2 = \frac{4\pi^2 e^4}{h^2 c^2} = 5.30 \times 10^{-5} \quad (9.5)$$

and

$$\mu = \frac{Mm}{M+m}$$

For convenience of evaluation, Eq. (9.4) has been expanded by Sommerfeld into a converging series,

$$\begin{aligned} T = -\frac{W}{hc} = \frac{RZ^2}{n^2} + \frac{R\alpha^2 Z^4}{n^4} \left[ \frac{n}{k} - \frac{3}{4} \right] \\ + \frac{R\alpha^4 Z^6}{n^6} \left[ \frac{1}{4} \left( \frac{n}{k} \right)^3 + \frac{3}{4} \left( \frac{n}{k} \right)^2 - \frac{3}{2} \left( \frac{n}{k} \right) + \frac{5}{8} \right] \\ + \frac{R\alpha^6 Z^8}{n^8} \left[ \frac{1}{8} \left( \frac{n}{k} \right)^5 + \frac{3}{8} \left( \frac{n}{k} \right)^4 + \frac{1}{8} \left( \frac{n}{k} \right)^3 - \frac{15}{8} \left( \frac{n}{k} \right)^2 \right. \\ \left. + \frac{15}{8} \left( \frac{n}{k} \right) - \frac{35}{64} \right] \\ + \dots \end{aligned} \quad (9.6)$$

The first term of this expansion is the same as that derived by Bohr for circular orbits, neglecting relativity, and gives the major part of the energy. With  $n = 1, 2, 3, \dots$ , and with  $Z = 1$  for hydrogen,  $Z = 2$  for ionized helium, and  $Z = 3$  for doubly ionized lithium, this term gives the following values:

TABLE 9.1.—TERM VALUES, NEGLECTING FINE-STRUCTURE CORRECTIONS

	Hydrogen (isotope mass 1) R = 109677.76	Hydrogen (isotope mass 2) R = 109707.56	Ionized helium R = 109722.4	Doubly ionized lithium R = 109728.9
For $n = 1$				
2	109677.76	109707.56	438889.6	987560.1
3	27419.4	27426.9	109722.4	246890.0
4	12186.4	12189.7	48765.5	109728.9
5	6854.8	6856.7	27430.6	61722.5
6	4387.1	4388.3	17555.5	39502.4
7	3046.6	3047.4	12191.3	27432.2
8	2238.3	2238.9	8956.9	20154.4

To each of these values corrections from Eq. (9.6) must be added. For small values of  $Z$  the first term involving  $Z^4$  and  $\alpha^2$  is the only one of importance and the third and succeeding terms may be neglected. In x-ray spectra, however,  $Z$  becomes large for the heavier elements and terms in  $\alpha^4$  and  $\alpha^6$  must be taken into account (see Chap. XVI).

The corrections to be added to each of the above given terms are therefore given by

$$\Delta T = \frac{R\alpha^2 Z^4}{n^4} \left( \frac{n}{k} - \frac{3}{4} \right) = \frac{R\alpha^2 Z^4}{n^3} \left( \frac{1}{k} - \frac{3}{4n} \right), \quad (9.7)$$

where  $k$  is Sommerfeld's azimuthal quantum number 1, 2, 3, . . . for  $s, p, d, \dots$ . For all allowed values of  $n$  and  $k$  the correction is positive and is to be added to the terms in Table 9.1. For either of the two hydrogen isotopes,

$$\Delta T = 5.819 \left( \frac{1}{n^3} \right) \left( \frac{1}{k} - \frac{3}{4n} \right). \quad (9.8)$$

These corrections are shown graphically in Fig. 9.3. The straight lines at the top of each of the four diagrams represent the first four terms

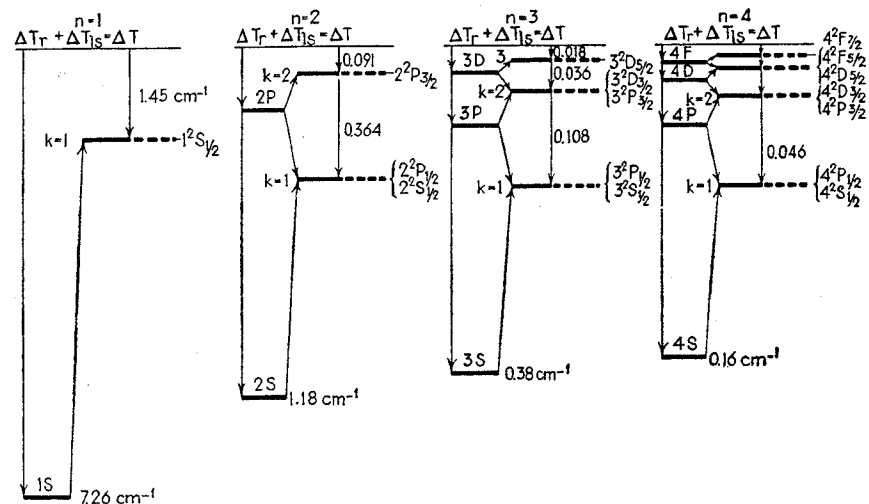


FIG. 9.3.—Fine structure of the hydrogen energy levels.  $\Delta T_r$  and  $\Delta T_{r,s}$  represent the relativity and the spin-orbit corrections respectively. The dashed lines represent Sommerfeld's relativity corrections.

of hydrogen given by Table 9.1. The shifted levels for each value of  $n$  and  $k$  are shown by the dotted lines with the term value increasing downward. The left-hand side of each diagram has to do with the spinning-electron picture of the atom and will be taken up in the following section. For ionized helium and doubly ionized lithium the intervals given in Fig. 9.3 must be multiplied by 16 and 81, respectively.

**9.2. Fine Structure and the Spinning Electron.**—With the introduction of the spinning electron and the quantum mechanics another account of the hydrogen fine structure has been given. Heisenberg and Jordan<sup>1</sup>

<sup>1</sup> HEISENBERG, W., and P. JORDAN, *Zeits. f. Phys.*, **37**, 263, 1926.

have shown from a quantum-mechanical treatment that Sommerfeld's relativity correction for hydrogen-like atoms should be

$$\Delta T_r = \frac{R\alpha^2 Z^4}{n^3} \left( \frac{1}{l + \frac{1}{2}} - \frac{3}{4n} \right), \quad (9.9)$$

where  $l = 0, 1, 2, \dots$  for  $s, p, d, \dots$  electrons. A general comparison of all classical with quantum-mechanical results for the same phenomenon shows that the classical values  $k, k^2$ , and  $k^3$  may usually, but not always, be replaced by  $l + \frac{1}{2}, l(l + 1)$ , and  $l(l + \frac{1}{2})(l + 1)$ , respectively, to obtain the quantum-mechanical results. Sommerfeld's relativity equation is a good example of this;  $k$  in Eq. (9.7) replaced by  $l + \frac{1}{2}$  gives Eq. (9.9).

To the quantum-mechanical relativity correction [Eq. (9.9)] a second term due to the spin-orbit interaction must be added. This interaction energy has already been calculated in Sec. 8.6 and shown to be given by Eq. (8.17):<sup>1</sup>

$$\Delta T_{l,s} = -\frac{R\alpha^2 Z^4}{n^3 l(l + \frac{1}{2})(l + 1)} \cdot \frac{j^{*2} - l^{*2} - s^{*2}}{2}. \quad (9.10)$$

Applying the first correction  $\Delta T_r$  to the hydrogen terms of Table 9.1, each level  $n$  is split into  $n$  components as shown at the left of each of the four diagrams in Fig. 9.3. Applying now the spin-orbit interaction  $\Delta T_{l,s}$ , each of these terms, with the exception of  $s$  terms, is split into two parts just as in the alkali metals. In each case the level with  $j = l + \frac{1}{2}$  has been shifted up, and the one with  $j = l - \frac{1}{2}$  has been shifted down, to the nearest Sommerfeld level. In other words, levels with the same  $j$  values come together at the older relativity levels  $k$ , where  $k = j + \frac{1}{2}$ . The remarkable fact that Sommerfeld's formula derived from the relativity theory alone should give the same result as the newer theory, where both relativity and spin are taken into account, is a good example of how two incorrect assumptions can lead to the correct result. While the number of numerically different energy levels is the same on both theories, there is an experimental method for showing that the first theory is not correct and that the latter very probably is correct. This will become apparent in Sec. 9.4.

Since the newer theory leads to Sommerfeld's equation, the sum of Eqs. (9.9) and (9.10) should reduce to Eq. (9.7). Since  $j$  takes on values  $l + \frac{1}{2}$  or  $l - \frac{1}{2}$  only, Eq. (9.10) is split into two equations:

$$\Delta T_{l,s} = -\frac{R\alpha^2 Z^4}{n^3 2l(l + \frac{1}{2})(l + 1)} \quad \text{for } j = l + \frac{1}{2}, \quad (9.11)$$

$$\Delta T_{l,s} = +\frac{R\alpha^2 Z^4}{n^3 2l(l + \frac{1}{2})} \quad \text{for } j = l - \frac{1}{2}. \quad (9.12)$$

<sup>1</sup> Equation (9.10) was first derived on the quantum mechanics by W. Heisenberg and P. Jordan, *loc. cit.*

The sign in front of the right-hand side of each of these equations has been changed to conform with Eq. (9.9), where a positive sign means an increase in the term value, or a decrease in the energy. Adding Eq. (9.9) to each of Eqs. (9.11) and (9.12),

$$\begin{aligned} \Delta T &= \Delta T_{l,s} + \Delta T_r = \frac{R\alpha^2 Z^4}{n^3} \left( \frac{1}{l + 1} - \frac{3}{4n} \right) \quad \text{for } j = l + \frac{1}{2}, \\ \Delta T &= \Delta T_{l,s} + \Delta T_r = \frac{R\alpha^2 Z^4}{n^3} \left( \frac{1}{l} - \frac{3}{4n} \right) \quad \text{for } j = l - \frac{1}{2}. \end{aligned} \quad (9.13)$$

If  $k$  in Sommerfeld's equation is replaced by  $l$  and  $l + 1$ , respectively, these equations will result. If again  $k$  is replaced by  $j + \frac{1}{2}$ , which is just

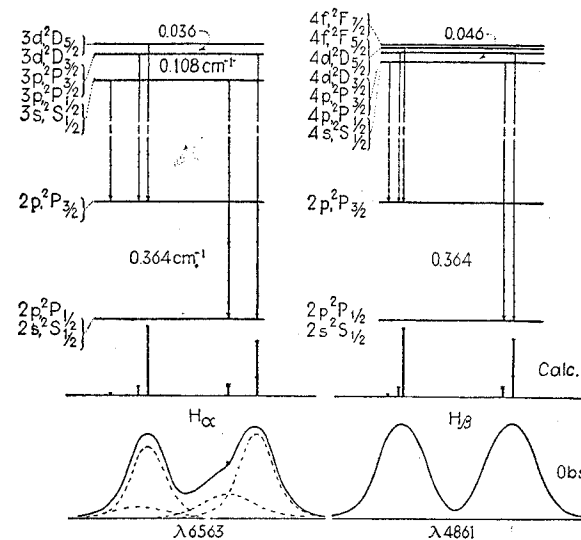


FIG. 9.4.—Schematic diagrams of the lines  $H_\alpha$  and  $H_\beta$ , in the Balmer series of hydrogen. the same as replacing  $l + 1$  and  $l$  of Eq. (9.13) by  $j + \frac{1}{2}$ , we obtain the single equation

$$\Delta T = \frac{R\alpha^2 Z^4}{n^3} \left( \frac{1}{j + \frac{1}{2}} - \frac{3}{4n} \right). \quad (9.14)$$

**9.3. Observed Hydrogen Fine Structure.**—Schematic diagrams of the theoretical fine structure of the first two lines of the Balmer series of hydrogen are shown in Fig. 9.4. Applying selection and intensity rules, both  $H_\alpha$  and  $H_\beta$  should be composed of two strong components and three weaker ones. Neither one of these patterns has ever been resolved into more than two components. The best results to date are those of Lewis, Spedding, Shane, and Grace,<sup>1</sup> obtained from  $H^2$ , the behavior of

<sup>1</sup> LEWIS, G. N., and F. H. SPEDDING, *Phys. Rev.*, **43**, 964, 1933; also SPEDDING, F. H., C. D. SHANE, and N. S. GRACE, *Phys. Rev.*, **44**, 58, 1933.

the two known hydrogen isotopes. Using Fabry and Perot étalons, photographs similar to the one shown in the center of Fig. 9.5 have been obtained. For this photograph the first order of a 30-ft. grating mounting (of the Littrow type) was used as the auxiliary dispersion instrument. Microphotometer curves of both  $H^1$  and  $H^2$  are reproduced above and below each pattern. It is to be noted that the components of  $H^2_\alpha$  are considerably sharper than  $H^1_\alpha$ , and that a third component is beginning to show up. The broadening is due to the Doppler effect and should be greater for the lighter isotope.

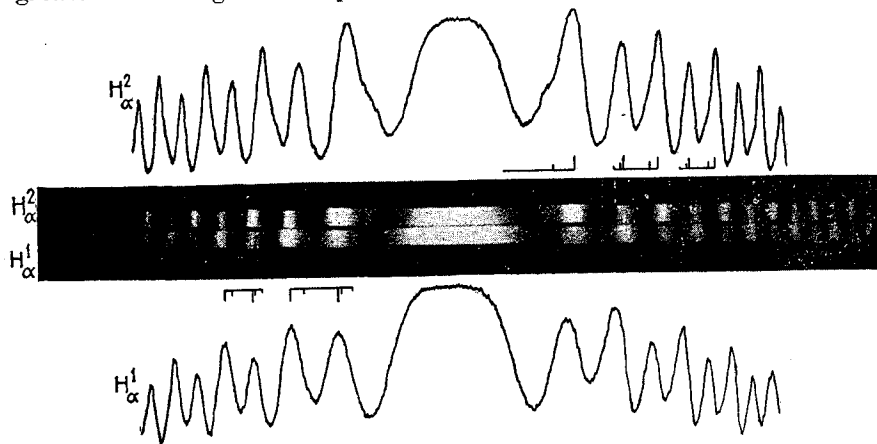


FIG. 9.5.—Fine structure of  $H^2_\alpha$  and  $H^1_\alpha$  from the Balmer series of the two hydrogen isotopes. Microphotometer curves above and below were made from the interference patterns in the center. (After Spedding, Shane, and Grace.)

Theoretical intensities for the fine structure of hydrogen were first calculated by Sommerfeld and Unsöld<sup>1</sup> in 1926. Experimentally it is found that the relative intensities of the two main components, the only ones resolved, depend largely upon the conditions of excitation. In some instances the supposedly weaker of the two lines will be the stronger, as it is in Fig. 9.5.

In going to higher members of the Balmer series the separation of the two strong components of each member approaches theoretically and experimentally the separation of the common lower state,  $0.364 \text{ cm}^{-1}$ . This interval occurs in each doublet between the fainter of the two strong lines and the next to the weakest satellite.

**9.4. Fine Structure of the Ionized Helium Line  $\lambda 4686$ .**—A better detailed agreement between observation and theory has been found in the hydrogen-like spectrum of ionized helium. A microphotometer curve of the line  $\lambda 4686$  is given at the bottom of Fig. 9.6. This line corresponds with the first line of the Paschen series in hydrogen (see Fig. 2.8). With

<sup>1</sup> SOMMERFELD, A., and A. UNSÖLD, *Zeits. f. Phys.*, **36**, 259, 1926; **38**, 237, 1926; see also SCHRÖDINGER, E., *Ann. d. Phys.*, **80**, 437, 1926.

$Z = 2$  the fine-structure separations should be 16 times as great as in hydrogen [see Eqs. (9.13) and (9.14)]. The predicted fine structure shown above in Fig. 9.6 was first given by Sommerfeld and Unsöld. At least four and possibly five of the predicted components may be said to have been resolved by Paschen.<sup>1</sup> The appearance of certain component lines in this pattern, which are not allowed on Sommerfeld's original theory of hydrogen fine structure, are strong points in favor of the newer theory of the coincidence of levels having the same  $j$  values.

**9.5. The Dirac Electron and the Hydrogen Atom.**—On Dirac's<sup>2</sup> theory a single electron in a central force field is specified by a set of four wave functions  $\psi_1, \psi_2, \psi_3,$  and  $\psi_4$ , in place of just one as in the case of the Schrödinger theory. Each of these functions is a solution of a wave equation. Although the setting up of the equations is out of place here we shall accept the solutions arrived at by Darwin and Gordon<sup>3</sup> and show in what way they correspond to the earlier theories and, at the same time, get some picture of the new atom model.

With each wave function  $\psi_1, \psi_2, \psi_3,$  and  $\psi_4$  properly normalized, the probability density, just as in the case of Schrödinger's theory (see Chap. IV), is given by

$$P = \psi\psi^*, \quad (9.15)$$

where

$$\psi\psi^* = \psi_1\psi_1^* + \psi_2\psi_2^* + \psi_3\psi_3^* + \psi_4\psi_4^*. \quad (9.16)$$

For given values of the azimuthal quantum number  $l$  and the magnetic quantum number  $m$  ( $m = u + \frac{1}{2}$ ), there are two sets of solutions corresponding to  $j = l + \frac{1}{2}$  and  $j = l - \frac{1}{2}$ , respectively ( $j$  equals inner quantum number).

$$j = 1 + \frac{1}{2}$$

$$\begin{aligned} \psi_1 &= -iM_o P_{l+1}^u \cdot M_r F_l \\ \psi_2 &= -iM_o P_{l+1}^{u+1} \cdot M_r F_l \\ \psi_3 &= (l + u + 1) \cdot M_o P_l^u \cdot M_r G_l \\ \psi_4 &= -(l - u) \cdot M_o P_l^{u+1} \cdot M_r G_l \end{aligned} \quad (9.17)$$

<sup>1</sup> PASCHEN, F., *Ann. d. Phys.*, **82**, 692, 1926.

<sup>2</sup> DIRAC, P. A. M., *Proc. Roy. Soc.*, **A**, **117**, 610, 1928; **A**, **118**, 351, 1928; see also DARWIN, C. G., *Proc. Roy. Soc.*, **A**, **118**, 654, 1928.

<sup>3</sup> GORDON, W., *Zeits. f. Phys.*, **48**, 11, 1928.

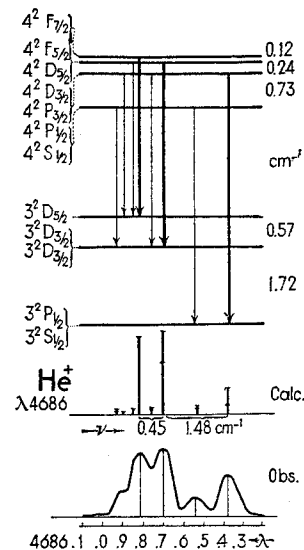


FIG. 9.6.—Diagram of the fine structure of the ionized helium line  $\lambda 4686$ . (After Sommerfeld, Unsöld, and Paschen.)