

The enormous departure of  $\Delta\bar{\nu}$  from the hydrogen value for all alkali metals except lithium, in spite of the progressive increase in  $n$ , is in strong contrast with the more moderate departure of the energy levels themselves, as shown by Fig. 67. This may be regarded as resulting from great sensitiveness of the spin-orbit effect to the character of the central field near the nucleus, which is clearly evident from the expression for the spin-orbit energy as given in Eq. (153). Near the nucleus the field of the nucleus itself must predominate, so that, approximately,  $V = -Ze^2/r$ , and

$$\frac{1}{r} \frac{dV}{dr} = \frac{Ze^2}{r^2}$$

which increases much more rapidly than does the numerical value of  $V$  itself as the nucleus is approached. The variation of the spin-orbit effect among the alkalis furnishes an excellent illustration of a general tendency of this effect to be small in atoms of low atomic number but to increase to an enormous magnitude as the atomic number becomes large.

**120. Multiplet Levels for One-electron Atoms.** The theory of the splitting of lines due to the spin-orbit effect as described in the last section should be valid also for atoms containing only a single electron. In the latter case, however, a curious accident occurs. In the nonrelativistic theory, as we have seen in Sec. 104, all states for a given  $n$  have the same energy, regardless of the value of  $l$ . In the relativistic theory this is not quite true. The wave equation contains certain other small relativistic terms besides those giving rise to the spin-orbit effect, and these

other terms cause the energy to vary somewhat with  $l$ . Now, in a one-electron atom this relativistic variation happens to be of the same order of magnitude as the spin-orbit effect itself; in fact, the net result of both effects would be that levels differing in  $l$  but not in  $j$  would coincide. (Actually the coincidence is not exact, at least in the case of  $S$  levels, but this was not discovered until about 1947.) The array of energy levels for one-electron atoms is thus very peculiar. Similar relativistic effects occur also in other atoms, but there the various  $L$

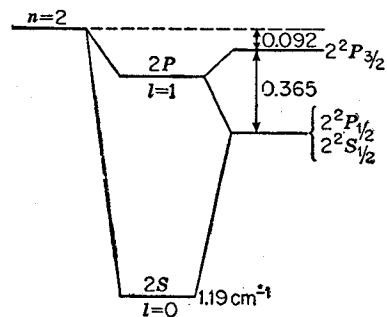


FIG. 73. The fine structure for  $n = 2$  for ordinary hydrogen: at left, nonrelativistic theory; center, as modified by the ordinary relativistic correction; right, as further modified by spin-orbit effects.

terms are so greatly displaced by the effects of the mutual electronic repulsion that the relativistic effects are relatively small.

The theoretical situation in the one-electron atoms as it was understood before 1945 is illustrated in Fig. 73, which represents hydrogen levels for

$n = 2$ . The single line at the left represents the energy as given by Bohr's theory, Eq. (80) in Sec. 81. The two solid lines in the center of the diagram show this level as split into two, a  $P$  and an  $S$  term, in consequence of what is called the "ordinary" relativistic correction. The addition of the spin-orbit effect then splits the  $2P$  term into the usual doublet with  $j = \frac{1}{2}$  or  $\frac{3}{2}$ ; but an additional "special" spin correction raises the  $2S$  level so that it coincides with the  $2P_{\frac{1}{2}}$  level. The net result, as shown at the right in the figure, is just two separate levels, a single one with  $j = \frac{3}{2}$  and a composite level with  $j = \frac{1}{2}$ . In a similar way, the  $3S_{\frac{1}{2}}$  level comes to coincide with the  $3P_{\frac{1}{2}}$  level, and  $3P_{\frac{3}{2}}$  also coincides with  $3D_{\frac{3}{2}}$ , whereas  $3D_{\frac{5}{2}}$  stands alone; and so on. Thus for each value of  $n$  there are only  $n$  different energy levels, with  $j = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots, n - \frac{1}{2}$ ; but all levels except that for the largest  $j, j = n - \frac{1}{2}$ , are double. The lowest level of all, with  $n = 1$ , is still single.

Approximate theoretical formulas for the various shifts are easily obtained by perturbation theory and are as follows. The ordinary relativistic correction to the energy, in  $\text{cm}^{-1}$ , is

$$\Delta_l W = \frac{3}{4} \frac{\alpha^2 R Z^4}{n^4} - \frac{\alpha^2 R Z^4}{n^3(l + \frac{1}{2})} \quad (156)$$

where  $R$  is Rydberg's constant in  $\text{cm}^{-1}$  and  $\alpha$  is the "fine-structure constant":

$$\alpha = \frac{2\pi e^2}{ch} = 0.007297 = \frac{1}{137.04} \quad (157)$$

This correction splits each level for given  $n$  into  $n$  sublevels and accounts for the central part of Fig. 73. Before the advent of wave mechanics, a similar correction was obtained by Sommerfeld but with  $k$  or  $l + 1$  instead of  $l + \frac{1}{2}$ .

The spin-orbit correction is then found to be, at least for  $l > 0$ ,

$$j = l + \frac{1}{2}: \quad \Delta_s W = \frac{1}{l+1} \frac{\alpha^2 R Z^4}{n^3(2l+1)} \quad (158a)$$

$$j = l - \frac{1}{2}: \quad \Delta_s W = -\frac{1}{l} \frac{\alpha^2 R Z^4}{n^3(2l+1)} \quad (158b)$$

For  $l = 0$ , the spin-orbit effect vanishes. The special spin correction is likewise found to vanish for  $l > 0$ , but for  $l = 0$  it is

$$\frac{\alpha^2 R Z^4}{n^3}$$

This latter expression happens to be exactly what we get for  $\Delta_s W$  if we put  $l = 0$  in Eq. (158a). Hence, we can forget the special spin correction entirely provided we drop the restriction that  $l > 0$  in using Eq. (158a). The spin corrections had no analog in the older quantum theory.

Upon adding  $\Delta_l W$  to the proper value of  $\Delta_r W$  and substituting for  $l$  in terms of  $j$ , the total shift in level is found to be, in  $\text{cm}^{-1}$ ,

$$\Delta W_{nj} = \frac{\alpha^2 R Z^4}{n^3} \left( \frac{3}{4n} - \frac{1}{j + \frac{1}{2}} \right) \quad (159)$$

It will be noted that  $\Delta W_{nj}$  depends only on  $j$  and not independently on  $l$ . This formula provides the final net shifts shown in Fig. 73.

It happens, however, that the Dirac relativistic wave equation can also be solved exactly.<sup>1</sup> The energy level for given  $n$  and  $j$  is found to be, in cgs units,

$$W_{nj} = mc^2 \left( \left\{ 1 + \frac{\alpha^2 Z^2}{[n - j - \frac{1}{2} + \sqrt{(j + \frac{1}{2})^2 - \alpha^2 Z^2}]^2} \right\}^{-1/2} - 1 \right) \quad (160)$$

If this expression is expanded in powers of  $\alpha$  and then converted to  $\text{cm}^{-1}$ , it is found that, as far as terms of order  $\alpha^2$ ,  $W_{nj}$  is the sum of Bohr's value,  $-RZ^2/n^2$ , and  $\Delta W_{nj}$  as given by (159). Even the Dirac wave equation is not entirely accurate, however, for reasons described in the

next section. By accident, Sommerfeld's relativistic correction gave the same set of distinct energies as Eq. (159).

**21. Fine Structure of Spectral Lines from One-electron Atoms.** *a. The Original Theoretical Patterns.* If the pair of levels having given values of  $n$  and  $j$  is treated as a single multiple level, no attention need be paid to the selection rule for  $l$  in determining the allowed jumps between such levels; it is sufficient to observe the rule for  $j$  (Sec. 118):

$$\Delta j = 0 \text{ or } \pm 1$$

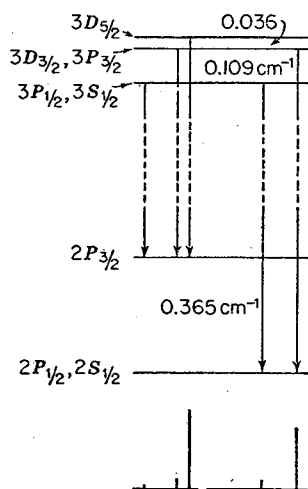
If a jump is allowed by this rule, component quantum states satisfying the condition that  $\Delta l = \pm 1$  can always be selected.

As an example, the levels and allowed jumps for  $n = 3$  and  $n = 2$  are shown in Fig. 74. (The spacings between the  $j$  levels are shown to scale, but on the same

Fig. 74. Original theoretical fine structure of the  $H\alpha$  line ( $n = 3 \rightarrow n = 2$ ) for atomic hydrogen.

scale the distance between the two groups would be some 24,000 times larger than as shown.) The selection rule for  $j$  allows five transitions, as shown by the arrows. If changes in  $l$  are considered as well, as a basis for the introduction of standard spectroscopic notation, we

<sup>1</sup> Cf. C. G. Darwin, *Proc. Roy. Soc. (London)*, vol. 118, p. 654, 1928.



find seven transitions, two pairs of them producing identical frequencies, according to the theory so far developed; denoting  $l = 0, 1, 2$  by  $S, P, D$  as usual, we have as transitions:  $3D_{3/2} \rightarrow 2P_{3/2}$ ,  $3D_{3/2} \rightarrow 2P_{1/2}$ ,  $3D_{5/2} \rightarrow 2P_{3/2}$ ,  $3D_{5/2} \rightarrow 2P_{1/2}$ ,  $3P_{3/2} \rightarrow 2S_{1/2}$ ,  $3P_{1/2} \rightarrow 2S_{1/2}$ ,  $3S_{1/2} \rightarrow 2P_{3/2}$ , and  $3S_{1/2} \rightarrow 2P_{1/2}$ . The relative spacing of the five distinct lines is shown in the lower part of Fig. 74, the heights of the lines as drawn representing the theoretical relative intensities of the spectral lines on the assumption that all five quantum states for  $n = 3$  are equally excited (i.e., that as many atoms are excited into one state as into another).

*b. First Comparison with Experiment for Hydrogen.* The "lines" of the Balmer series of hydrogen were early observed as close doublets. In 1887, Michelson and Morley measured the doublet separation for the line of longest wavelength,  $H\alpha$  or  $n = 3 \rightarrow n = 2$ , and found for it  $0.253 \text{ cm}^{-1}$ .

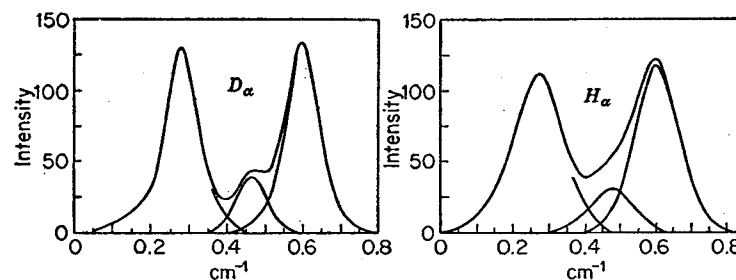


Fig. 75. Typical intensity curves obtained for the  $H\alpha$  line from hydrogen ( $H\alpha$ ) and deuterium ( $D\alpha$ ). Intensity is on an arbitrary scale, and the abscissa is numbered from an arbitrary point. (After Williams.)

Subsequent measurements by other investigators gave values ranging from 0.293 to 0.357. The modern interpretation of the doublet appearance is that the five component lines are smeared together because of the Doppler broadening of all lines due to the thermal motion of the molecules, but two of them are much more intense than the others. The only means of comparing the observations with the theoretical predictions is, therefore, to calculate the contour of the total line from the theory, using the theoretical separations of the fine structure and the theoretical estimates of the relative intensities of the component lines, and then making an approximate allowance for the Doppler effect.

The line  $H\alpha$  has been studied very carefully in this manner. In Fig. 75 are shown typical curves obtained by R. C. Williams<sup>1</sup> for the spectral distribution of intensity in the  $H\alpha$  line from ordinary hydrogen and from deuterium, or heavy hydrogen, the atoms of which are about twice as heavy as those of ordinary hydrogen and ought, therefore, to be influenced less by the Doppler effect. The discharge tube was cooled by liquid air

<sup>1</sup> R. C. Williams, *Phys. Rev.*, vol. 54, p. 558, 1938.

to minimize the broadening. The light from the tube was dispersed by a triple-prism spectrograph containing a quartz Fabry-Perot etalon placed in the parallel beam of the collimator, and photographs were taken of the spectral region containing the  $H\alpha$  line. The blackening on the film was measured with a Moll microphotometer using a thermocouple and galvanometer, and from these measurements the relative distribution of intensity in the line could be determined.

At most three of the theoretical component lines are evident in Fig. 75; one of the others is too close to the left-hand main line to be resolved, and the remaining one is evidently too weak to be seen. Theoretical line shapes, as influenced by the Doppler effect, are drawn in the figure for the three lines, the assumed strengths of the lines being so adjusted as best to reproduce the observed curve of resultant intensity. The strengths of the lines as thus inferred from the observations agree only roughly with the theoretical predictions. The left-hand line ought to be somewhat stronger and the middle one only about half as strong. Such deviations might be due, however, to unequal excitation of the initial levels ( $S_{1/2}$ ,  $P_{3/2}$ ,  $D_{5/2}$ ). A much more serious discrepancy is that the spacing of the lines does not quite agree with the theoretical predictions. The distance between the two main peaks was found by Williams to be consistently  $0.319$  to  $0.321$   $\text{cm}^{-1}$  for  $D\alpha$ ,  $0.315$  to  $0.319$   $\text{cm}^{-1}$  for  $H\alpha$ , whereas wave-mechanical theory predicts, from the level separations as shown in Fig. 74,  $0.365 - 0.036 = 0.329$ , a difference of  $0.010$   $\text{cm}^{-1}$ . The small central peak seems also to occur at about  $0.134$   $\text{cm}^{-1}$  from the right-hand one, whereas the theory gives for this separation  $0.109$   $\text{cm}^{-1}$ .

*c. Later Experimental Work.* The cause of these discrepancies<sup>1</sup> between existing theory and observation remained a mystery for many years. It was suggested, however, by Pasternak in 1938 that the  $2S_{1/2}$  level might for some unknown reason lie a little higher than the  $2P_{1/2}$  level instead of coinciding with it. The composite bright line of highest frequency,  $3P_{3/2} \rightarrow 2S_{1/2}$  and  $3D_{5/2} \rightarrow 2P_{1/2}$ , would thus appear to be shifted a little closer to the remaining lines.

In 1947 Lamb and Retherford reported observations in support of this explanation.<sup>2</sup> They succeeded in determining the difference between the  $2P_{3/2}$  and the  $2S_{1/2}$  levels, and then even the difference between  $2P_{1/2}$  and  $2S_{1/2}$ , by measuring the frequency of the corresponding spectral line in absorption. The calculated frequency for  $2P_{3/2} \rightarrow 2S_{1/2}$  is  $0.365$   $\text{cm}^{-1}$ , equivalent to a wavelength of  $2.74$   $\text{cm}$ , but methods of generating "micro-

<sup>1</sup> Cf. J. W. Drinkwater, O. Richardson, and W. E. Williams, *Proc. Roy. Soc. (London)*, vol. 174, p. 164, 1940.

<sup>2</sup> W. E. Lamb, Jr., and R. C. Retherford, *Phys. Rev.*, vol. 72, p. 241, 1947; Retherford and Lamb, *Phys. Rev.*, vol. 75, p. 1325, 1949; Lamb, *Repts. Progr. in Phys.*, vol. 14, p. 19, 1951.

waves" of this order of magnitude are now available.<sup>1</sup> A number of difficulties had to be overcome, and elaborate planning was necessary. The investigation is an excellent example of the involved character of much modern experimentation. The apparatus is shown diagrammatically in Fig. 76.

The first problem was to produce excited hydrogen atoms in  $2S_{1/2}$  states. To avoid the complications associated with electrical discharge tubes, use was made of a beam of hydrogen or deuterium issuing from a tungsten oven at about  $2500^\circ\text{C}$ . At this temperature the hydrogen was about 64 per cent dissociated into atoms. An electron beam was allowed to cross the beam of atoms and to excite some of them into higher states, including the  $2S_{1/2}$  state. The latter state is metastable, since no jump can occur by dipole radiation into the normal  $1S$  state ( $\Delta l = 0$ ); thus the excited

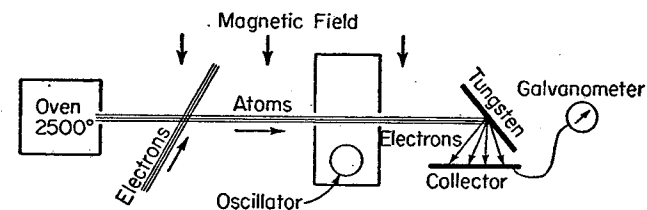


Fig. 76. Diagram of Lamb's apparatus for study of the hydrogen energy levels.

atoms were able to move an appreciable distance while remaining in the  $2S_{1/2}$  state. It was necessary, however, to avoid the presence of electric fields, which, by a form of Stark effect, would modify the quantum states in such a way that, instead of pure  $2S_{1/2}$  and  $2P_{1/2}$  states, there would be two states each having as a wave function a combination of  $2S_{1/2}$  and  $2P_{1/2}$  wave functions; dipole jumps would then be possible out of both states by the process  $2P_{1/2} \rightarrow 1S_{1/2}$ , resulting in a quick loss of the excited atoms. This effect of an electric field is appreciable even when the  $2P_{1/2}$  and  $2S_{1/2}$  levels are slightly separated. Since entire freedom from electric fields is difficult to secure, a magnetic field was applied at right angles to the beam; each level was thus broken up into Zeeman components liberally separated from each other in proportion to the field strength, thereby minimizing any effects due to stray electric fields.

In the apparatus, the excited atoms next traversed a small metal tube, entering and leaving through openings in its walls. The tube, together with a metal strip down its center (not shown in Fig. 76), served as a wave guide for microwaves generated in a small oscillator at one end of the tube. The atoms then fell upon a tungsten plate, in which, by a collision process, those arriving in the  $2S_{1/2}$  state were returned to their normal

<sup>1</sup> Cf. J. C. Slater, "Microwave Electronics," 1950; H. J. Reich, P. F. Ordung, and H. L. Skalnik, "Microwave Theory and Techniques," 1953.

states with the simultaneous emission of an electron. The stream of electrons thus generated was collected and measured. Typically, this stream amounted to about  $10^{-14}$  ampere, and it was observed to be decreased by  $\frac{13}{20}$  when a strong steady electric field was applied between the conductors of the wave-guide tube; this fraction  $\frac{13}{20}$  was assumed to represent the atoms arriving in  $2S_{\frac{1}{2}}$  states, which were caused by the electric field to undergo transitions into other states. The remaining  $\frac{7}{20}$  of the electron beam was ascribed to stray ultraviolet light generated somehow in the tungsten plate by the *exciting* electron beam located on the opposite side of the wave guide.

The method of observation was to set the frequency of the microwaves at a suitable fixed value, this frequency being hard to adjust continuously, and then to vary the strength of the magnetic field and observe the intensity of the final electron beam. Narrow minima were found, and these were ascribed to transitions induced by absorption of the microwaves, out of the  $2S_{\frac{1}{2}}$  state into  $2P_{\frac{1}{2}}$  or  $2P_{\frac{3}{2}}$ . The energy differences for these transitions as calculated from the microwave frequencies were plotted against the strength of the magnetic field, and, for a final result, the curve thus obtained was extrapolated to zero magnetic field.

The first set of observations indicated clearly that the difference between the  $2P_{\frac{3}{2}}$  and  $2S_{\frac{1}{2}}$  levels was not 10,095 Mc per sec (megacycles per second) or  $0.365 \text{ cm}^{-1}$ , as was predicted by existing theory, but about 1,000 Mc per sec or  $0.0332 \text{ cm}^{-1}$  less. The  $2S_{\frac{1}{2}}$  level would thus lie roughly  $0.033 \text{ cm}^{-1}$  above  $2P_{\frac{3}{2}}$ , provided the latter level is not shifted. With new apparatus, using microwaves of about 30 cm wavelength, it was found possible also to induce transitions from  $2S_{\frac{1}{2}}$  to  $2P_{\frac{1}{2}}$  (by forced emission) and so to measure this energy difference directly. Later work gave as the observed difference 1,057.8 Mc per sec or  $0.0353 \text{ cm}^{-1}$  for hydrogen, and 1,059.0 Mc per sec for deuterium.<sup>1</sup>

The line  $3P_{\frac{3}{2}} \rightarrow 2S_{\frac{1}{2}}$  thus no longer coincides exactly with  $3D_{\frac{3}{2}} \rightarrow 2P_{\frac{1}{2}}$ . If the  $3P_{\frac{3}{2}}$  and  $3D_{\frac{3}{2}}$  levels were equally excited, it can be calculated that the intensity ratio of these lines would be 2.08:5.0, so that the two would actually be observed as a single line shifted

$$\frac{2.08}{7.08} 0.0353 = 0.010 \text{ cm}^{-1}$$

in good agreement with Williams's observations.

*d. Refinement of the Theory.* A theoretical explanation of the shift of the  $2S_{\frac{1}{2}}$  level was put forward almost simultaneously with the observations by Bethe.<sup>2</sup> It had long been suspected that a more thoroughgoing

<sup>1</sup> S. Triebwasser, E. S. Dayhoff, and W. E. Lamb, Jr., *Phys. Rev.*, vol. 89, p. 98, 1953.

<sup>2</sup> H. A. Bethe, *Phys. Rev.*, vol. 72, p. 339, 1947.

application of the wave-mechanical theory of the electromagnetic field, described briefly in Sec. 108, might lead to a slight revision of the theoretical values of atomic energy levels. In the usual theory of the hydrogen atom, the interaction between the nucleus and the electron is represented by a simple potential-energy term. This term, however, really represents the effect of an electromagnetic field of very simple type, and for consistency this field should be treated by the same general method that is used in dealing with the emission of radiation. When such a treatment is attempted, however, a divergent integral is obtained for the energy of an electron in the presence of a nucleus. The integral diverges, in fact, even for the energy of a free electron!

In classical electromagnetic theory, a similar difficulty had been encountered when the electron was treated as a point charge, but it had been possible to overcome this difficulty by assigning to it a finite size. If the electron were a sphere with all its charge on the surface, its electromagnetic mass would be equal to the observed mass  $m$  provided the radius of the sphere were  $2e^2/3mc^2$  or  $1.9 \times 10^{-13} \text{ cm}$ . Thus the hypothesis became possible that all mass is of electromagnetic origin. The inertia of charged particles would then arise from essentially the same electromagnetic action as that which is responsible for the inductive inertia of ordinary electric circuits.

An analogous wave-mechanical theory of electronic mass has never been achieved. Bethe pointed out, however, that the divergent integral that is obtained for the energy of a stationary free electron should represent its rest energy  $m_0c^2$  and that allowance for this part of the energy has really already been made by introducing the constant  $m = m_0$  into the wave equation. He proposed, therefore, to take as the binding energy of an electron in an atom the difference between the divergent integral obtained for the energy of the electron in the atom and the divergent integral for its energy when free, and he gave reasons for believing that the difference would be a convergent integral that could be evaluated.

This surmise was confirmed by more exact calculations. The result in the case under discussion is a slight correction to the accepted formulas for the binding energy, which is very much larger on the  $S$  states of a one-electron atom than on other states because for  $S$  states  $\psi$  does not vanish at the nucleus. The final theoretical values obtained are 1,057.2 Mc per sec for hydrogen and 1,058.5 for deuterium.<sup>1</sup> These values are only 0.5 Mc per sec below the experimental values, an extraordinary agreement (unless in some way fortuitous!).

It appears, therefore, that in Figs. 73 and 74 the  $2S_{\frac{1}{2}}$  level should be drawn to lie above the  $2P_{\frac{1}{2}}$  level by  $0.035 \text{ cm}^{-1}$  or about  $\frac{1}{10}$  of the space between  $2P_{\frac{1}{2}}$  and  $2P_{\frac{3}{2}}$ . In ionized helium the same shift was measured

<sup>1</sup> E. E. Salpeter, *Phys. Rev.*, vol. 89, p. 92, 1953.

experimentally as 14,000 Mc per sec, being 1.4 per cent greater than the calculated value.<sup>1</sup>

**122. Many-electron Wave Theory.** When an atom contains two or more electrons outside closed subshells, it is still true, as a rule, that in a radiative transition only one electron is active, but the atomic energy levels between which the jump occurs are themselves influenced by the presence of the other electrons. As a basis for the discussion of such cases, it may be worth while to describe briefly the wave equation for complex atoms, although no actual mathematical developments can be attempted.

The complete relativistic wave equation for two or more electrons is not known, but an approximate equation can be written down that is adequate for most purposes. The terms that occur in this equation may be classified as follows:

1. Terms representing kinetic energy and containing derivatives of  $\psi$
2. Terms due to the nuclear field
3. Terms representing the mutual energy of the electrons due to their electrostatic repulsion
4. Spin-orbit terms representing interaction between the magnetic moment of each electron and its own orbital motion
5. Mixed spin-orbit terms representing interaction between each spin magnetic moment and the orbital motions of other electrons
6. Spin-spin interactions between the spin magnetic moments of the electrons
7. Other relativistic corrections, only partly known
8. Terms allowing for nuclear motion

Of these many terms, however, those in class 8 scarcely ever have appreciable effects, and classes 6 and 7 are important only for a few levels of light atoms, such as the  $2^3P$  levels of neutral helium and ionized lithium. With inclusion of only the remaining five classes, the wave equation may be written down as follows:

$$-\frac{\hbar^2}{8\pi^2m} \sum_{j=1}^N \nabla_j^2 \psi - e^2 Z \sum_{j=1}^N \frac{1}{r_j} \psi + e^2 \sum_{j=2}^N \sum_{k=1}^{j-1} \frac{1}{r_{jk}} \psi + P\psi = W\psi \quad (161)$$

Here  $h$ ,  $e$ ,  $m$ ,  $Z$ , and  $W$  are as in Eq. (133) and  $c$  is the speed of light;  $\nabla_j^2$  denotes  $\nabla^2$  (Sec. 96) expressed in terms of the coordinates of the  $j$ th electron, whose distance from the nucleus is  $r_j$ ; and  $N$  is the number of electrons in the atom, equal to the atomic number  $Z$  for a neutral atom but less than  $Z$  for an ion. The units are cgs with  $e$  in electrostatic units. The terms in  $r_{jk}$  represent the mutual potential energy of the electrons; the term  $P\psi$  represents the spin-orbit energies (Sec. 118).

<sup>1</sup> W. E. Lamb and M. Skinner, *Phys. Rev.*, vol. 78, p. 539, 1950.

Unfortunately, this equation cannot be solved in terms of ordinary functions; hence the perturbation approach is usually employed. Let us omit the spin-orbit term and replace the electrostatic-interaction terms by the central field described in Sec. 109, which includes a rough average of the electrostatic effects of the electrons on each other. If  $\phi$  is the electrostatic potential due to the entire electronic charge cloud, the potential energy of an additional electron in this field is  $V = -e\phi$ ; for an electron belonging to the atom itself, however, we substitute  $(N-1)V/N$ . The zero-order approximate wave equation thus derived reads as follows:

$$H_0\psi = -\frac{\hbar^2}{8\pi^2m} \sum \nabla_j^2 \psi - e^2 Z \sum \frac{1}{r_j} \psi + \frac{N-1}{N} \sum V_j \psi = W^0\psi \quad (162)$$

$V_j$  denoting  $V$  expressed in terms of the coordinates of the  $j$ th electron.

In this equation the electronic variables occur separated, that is, each term contains the coordinates of only one electron. For this reason the solutions can be written as products of solutions of the simpler one-electron wave equation

$$-\frac{\hbar^2}{8\pi^2m} \nabla^2 \psi - \frac{e^2 Z}{r} \psi + \frac{N-1}{N} V\psi = W\psi \quad (163)$$

If  $\psi_1, \psi_2, \dots, \psi_N$  are solutions of this equation with associated electronic energies  $W_1, W_2, \dots, W_N$ , then it is easily verified by substitution that a solution of (162) is the product  $\psi = \psi_1\psi_2 \cdots \psi_N$  with  $W^0 = W_1 + W_2 + \cdots + W_N$ . Here  $\psi_j$  is written in terms of the coordinates of the  $j$ th electron. Each of the  $W_j$ 's represents the negative of the work required to remove one electron out of state  $\psi_j$  in the atom to rest at infinity, thereby ionizing the atom.

The potential field  $V$  is required to be such that the cloud charge arising from electrons with respective wave functions  $\psi_1, \psi_2, \dots, \psi_N$  just suffices, together with the nucleus, to reproduce the field itself. It is called for this reason a "self-consistent" field. Since the electronic wave functions cannot be found until the field is known, the problem might seem to be circular, but methods of handling it have been developed.<sup>1</sup> An example was shown in Fig. 62, and the calculated charge-cloud density for sodium was shown in Fig. 68.

Proceeding with perturbation theory, the correct wave equation (161) is then written in this form:

$$H_0\psi + \left( e^2 \sum_{j=2}^N \sum_{k=1}^{j-1} \frac{1}{r_{jk}} - \frac{N-1}{N} \sum_{j=1}^N V_j \right) \psi + P\psi = W\psi \quad (164)$$

<sup>1</sup> Cf. D. R. Hartree, *Proc. Cambridge Phil. Soc.*, vol. 24, p. 189, 1928; and E. U. Condon and G. H. Shortley, "Theory of Atomic Spectra," 1935, reprinted with corrections in 1951.