QUANTUM THEORY OF THE SPINNING ELECTRON

A Thesis

by

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QUANTUM THEORY OF THE SPINNING ELECTRON.

Abstract.

The following thesis comprises calculations and discussion pertaining to the hypothesis of a spinning electron, chiefly for hydrogen-like atoms.

Part I is a historical introduction.

Part II contains results obtained in the spring of 1926, and presented to the Oakland meeting of the American Physical Society in the following June. The calculations are based on classical mechanics, the final results being obtained by an artificial modification. These results are discussed and shown to completely represent the observations; they are equivalent to those of other investigators.

Part III, which was worked out in 1927 and published in preliminary form in the Proceedings of the National Academy for June of that year, treats the same problem in wave mechanics. The results are not satisfactory, owing to a difficulty also encountered by others.

Part IV is a conclusion, in which some very recent developments are briefly referred to.

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QUANTUM THEORY OF THE SPINNING ELECTRON

Part I. History of the Hypothesis

Sect. 1. Introduction. The writer of this thesis has had the good fortune to be engaged in one of the most actively developing fields of research in modern physics. Since the appearance in print of the fundamental hypotheses of Uhlenbeck and Goudsmit in 1925 and 1926,*[12] the conception of the spinning electron has been extended over the whole of atomic theory, until a bibliography of contemporary papers referring to the spinning electron would be nearly equivalent to a bibliography of the entire subject.

Matters are still more complicated by the circumstance that at the precise moment when it is necessary to bring this thesis to completion, the theory in question has begun a new and rapid development, which is not yet in definitive form.

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*Numbers refer to items in the bibliography.

In view of this situation it seems proper to develop the early portion of the theory historically; next, to present in detail the writer's own calculations on the subject, in their proper relation to the published work of others; and to close with a short summary of the present state of the question.

Following the fundamental papers of Bohr (1913) and Bjerrum (1912) the quantum theory of series and band spectra entered on a course of comparatively rapid development, which began to show signs of slackening at about 1918. In the interim the theory had been applied to practically every atomic phenomenon for which it was capable of giving exact quantitative results. The cases in question were almost exclusively those of atoms with a single electron, which in practice restricts the discussion to the spectra of hydrogen and ionized helium. Besides these the theory had before 1918 found fruitful application to the X-ray spectra of heavy atoms. Even this involved certain approximations; and the main course of the quantum theory from 1918 to 1924 consisted of applications in which it often could give only approximate or even merely qualitative results. This theoretical investigation was accompanied by extensive programs of experimental work, which sometimes verified and sometimes conflicted with the more remote theoretical results, occasionally revealing wholly new phenomena, and with increasing accuaracy uncovering a wealth of minor departures from the theory.

As pointed out by Uhlenbeck and Goudsmit[13] among others, these difficulties were of two distinct types, due to two causes which were initially indistinguishable. The question is still open whether these two sources of discrepancy may not ultimately be reduced to one; but from the standpoint of our present knowledge (May, 1928), we may separate, following Uhlenbeck and Goudsmit, the difficulties due to inaccuracy of the mechanics applied from the difficulties due to incompleteness of the mechanical model. In some physical cases, notably in the anomalous Zeeman effects, these two sets of difficulties appear together, but even in such cases it is possible to study them independently.

We may tabulate the principal difficulties of what has somewhat paradoxically become known as the "classical" quantum theory as follows:

A. Difficulties due to inaccuaracy of the mechanics.
   1. Prediction of intensities.
   2. Theory of dispersion.
   3. The helium atom.
   4. Half quanta in
      a. Band spectra.
      b. Anomalous Zeeman effect.
      c. Multiplet spectra.

B. Difficulties due to incompleteness of the model.

1. Magnetic effects.

a. Anomalous Zeeman effect.

b. Paschen-Back effect.

c. Multiplets

2. Relativity interpretation of X-ray doublets.

3. Fine structure of H and He^{+} spectra.

a. Appearance of forbidden lines.

b. Apparent discrepancy of H_{α} doublet.

c. Paschen-Back effect of H.

Beginning with group A, it should be observed that the very form of the correspondence principle was a constant reminder of the provisional state of the theory. The most obvious case of this was the well-known crudity and uncertainty attached to all theoretical estimates of intensities, contrasting sharply with the precision of the empirical whole number rules of Burgers and Dorgelo.

Closely related to this is the conflict with Kirchhoff's law, into which the quantum theory was led by its assumption of a series of mechanical frequencies in the atom differing from its emitted frequencies. This conflict provided an apparently insuperable obstacle to a rational theory of dispersion.

Of a slightly different character was the failure to develop a theory of the helium atom. The poor success

of early attempts at a solution was natuarally ascribed to the intrinsic difficulties of the three-body problem; but Born and Heisenberg succeeded in demonstrating that the difficulty was not any such purely analytical one, but that the theory in the form then in use was incapable of giving the correct energy levels for either the excited or the normal state of helium.

The appearance of half-quanta was a further symptom of disintegration of the original theory. The half-quanta appearing in band spectra might possibly be explained by special hypotheses; but the peculiar appearance of half-quanta in the anomalous Zeeman effect, in which it is necessary to replace the square of an integer, say j^2, by $(J+\frac{1}{2})(J-\frac{1}{2})$, pointed to the necessity of a far more profound modification. The same remark of course applies to the appearance of half-quanta in multiplet; in fact, multiplets may be regarded as the Zeeman paterns of the series electron in the magnetic field of the whole atom.

We shall not discuss these matters in detail; they have all been cleared up by the introduction of the new quantum dynamics, which, in the form of either matrix or of wave mechanics, appears capable of removing all the difficulties of our first group. The second group of difficulties, those removed by introducing the

hypothesis of a spinning electron or some equivalent, will form the subject of the remainder of this discussion.

Sect. 2. Difficulties leading to the hypothesis of a spinning electron. The anomalous, or better the complex, Zeeman effect is the fundamental phenomenon for an understanding of the empirical and theoretical developments which led to the introduction of the hypothesis of a spinning electron. Its simplest form is that which it takes in the doublet spectra of elements with a single series electron, such as the arc spectra of alkali metals and the first spark spectra of the alkaline earths.

The typical example is that of the D lines, which correspond to 1s-2p of the sodium arc spectrum. The very fact there exist two lines - the phenomenon of multiplets - itself calls for explanation. This is done on the Bohr-Sommerfeld theory by assuming that the principal and aazimuthal quantum numbers determine only the shape of the orbit. A third, the inner quantum number, specifies the orientation. This hypothesis was supported by the Stern-Gerlach experiment (orientation of atoms in a magnetic field). In the case of a hydrogen-like atom it was expected, with apparent experimental verification, that the energy

levels for two such orientations would coincide. In sodium, however, there is the complex "core", consisting of the completed K and L shells of the atom. Different orientations with respect to this core might be expected to correspond to slightly different energies. By a proper choice of the inner quantum number j corresponding to these orientations, and by means of the selection principle $\Delta j = 0$ or ± 1 which would be derived from the correspondence principle, it became possible to account for at least the number of components of most multiplet lines.

The orientations of these orbits must natuarally be with respect to some axis in the atom itself. On the basis of the Stern-Gerlach experiment, and of the consequences here about to be developed, this axis was considered to be that of a magnetic field. It was natural to associate this field with the core; that is, in the case of the sodium atom, with the closed K and L shells.

Apart from the exceptional cases in which the magnetic moment of the core was exactly neutralized by that of the series electron, the whole now became a magnet with all its parts in fixed relation to one another. Associated with the resultant magnetic moment was a resultant

angular momentum about the same axis. Consequently, when placed in a weak homogeneous magnetic field the whole atom would precess about the direction of this field. This motion could be quantized, and it is found that the angle between the magnetic axis of the atom and the direction of the field was restricted to certain fixed values - a space quantization which is confirmed by the Stern-Gerlach experiment.

It was now found that these considerations led to formulae which correctly represented the observed energy levels - but only by introducing two drastic and theoretically unjustified modifications, corresponding precisely to the two groups of difficulties we have mentioned.

On the classical mechanics the ratio of the magnetic moment of an electron moving in an orbit to its angular momentum is a fixed scale or quantity, $e/2mc$; so that to the Bohr unit of angular momentum, $h/2\pi$, corresponds the Bohr magneton $eh/4\pi mc$. This is easily extended to an atom with any number of electrons,* so that in general $\mu/p = e/2mc$, where μ is the magnetic moment and p is the angular momentum.

In order to obtain the above mentioned representation of the energy as derived from a model it is necessary to introduce the magnetic moment μ_c and angular momentum p_c of the core, as well as those of the series electron; and now it is found that the results bear no relation to experiment if μ_c/p_c is given the above normal value, but that the

*Appendix 1.

ratio must be doubled, so that $\mu_c/p_c = e/mc$. This surprising circumstance constitutes the real "anomaly" in the complex Zeeman effect.

A second peculiarity appears as follows. Into the expression for the energy enters the cosine of the angle between the momentum vectors of the core and the series electron. This expression contains the squares of several quantum numbers, associated with various angular momenta. Each of these numbers, say s^2, must be replaced by $s(s+1)$ in Sommerfeld's notation, or by $(S+\frac{1}{2})(S-\frac{1}{2})$ in Landé's, to obtain the correct formula. This clearly involves a modification of dynamical principles, and was one of the starting points for Heisenberg's quantum mechanics.

More significant for our purposes is a further difficulty in the procedure. We have seen that it is necessary to ascribe a magnetic moment to the core in the alkali metals. This core is of identical structure, apart from the increased nuclear charge, with the atom of the preceding noble gas; for lithium it corresponds to the helium atom. Now the noble gases in general, and helium in particular, are known to be diamagnetic; so that it was necessary to assume some unknown disturbing factor in the experiments bearing on this point. Moreover it was pointed out by Pauli[18] that the orbital precession of the series electron, due to such a magnetism in the core,

should result for the heavy elements in a relativity correction to the Zeeman separation which is not found experimentally.

Using the classical mechanics, suppose the applied magnetic field increased. The forces exerted by this field on the series electron will eventually become comparable with those due to the magnetic field of the core. There ensues a curious type of motion, the complexity of which is reflected in the corresponding spectra. Finally, when the intensity of the applied field is very high, its effect dominates over that due to the core. The core and the orbit of the series electron then precess independently and at different rates about the axis of the external field. The energy levels of the electron are given by the Larmor precession. This leads to the levels of the "normal" Zeeman effect, giving the Lorentz triplet in the spectrum. This is the Paschen-Back effect, which in itself involves no new theoretical elements, and consequently no difficulties, beyonf those already introduced.

The general theory of multiplets has not contributed greatly to the development we are studying. The extensive systematization now going on is largely dependent on the use of the spinning electron or of equivalent hypotheses; but the theoretical functions of this subject, which was very imperfectly understood in 1924, have broadly speaking

been two in number. In the first place, several hypotheses, which were adequate to account for doublet spectra, failed when applied to the more complex cases. Secondly, the alternation of even and odd multiplet structure made it impossible to avoid the introduction of half-quanta somewhere in the scheme; but this is a matter of the quantum dynamics, and not of the spinning electron.

A difficulty in the theory of atomic structure of an altogether unexpected character was unearthed by Millikan and Bowen,[17] and was also emphasized by Landé.[16] There appeared a conflict between the established interpretations of X-ray and of visible spectra. In the normal L shell, which is considered to consist of electrons with principal quantum number n=2, there are three energy levels, designated by Sommerfeld as L_{11}, L_{21}, L_{22}. The energy difference $L_{22}-L_{21}$ varies as the fourth power of the atomic number, which is the law to be expected, on Sommerfeld's relativistic theory, for the difference in energy between two orbits having the principal but different azimuthal quantum numbers. On the other hand, the energy difference $L_{21}-L_{11}$ is closely proportional to $(Z-s)^2$, where Z is the atomic number and s is a "screening constant." This led to the following interpretation: Since n=2, the azimuthal quantum number k is either 2(corresponding to a circle) or 1(corresponding to an ellipse). It is

assumed that L_{22} is a circular orbit, and that L_{21} and L_{11} are elipses at different orientations. Consequently L_{22} differs from L_{21} and L_{11} by the large "relativity" term, while L_{21} and L_{11} differ from each other by a small term due to the difference in the screening of the nucleus by the K electrons along two differently inclined paths.

It is a point of importance for later discussion that the L_{22}-L_{21} doublet agrees quantitatively with Sommerfeld's relativistic expression, not merely to terms of order v^2/c^2, (v being the velocity of the electron, c that of light) but also to order v^4/c^4 and probably also to higher orders. Sommerfeld's explanation was therefore accepted with considerable confidence, and the results of Bowen and Millikan occasioned some consternation. It was found that the L-doublet could be traced downward from the X-ray spectra through a whole series of spectra of stripped atoms, without a doubt of identification at any step; and that when this was done the doublet in question proved to be identical with a doublet in optical spectra, on which Bohr, with the strongest kind of evidence, had placed a diametrically opposed interpretation. The level L_{11} corresponds, as it should, to an optical level with azimuthal quantum

number k=1; but both L_{21} abd L_{22} correspond to levels with k=2. L_{21} and L_{22} should therefore correspond to circular orbits; they differ in inclination, not in eccentricity, and should apparently show a "screening-doublet." L_{11} representing an ellipse, should be separated by the relativity doublet from L_{21}. The evidence for each of the two conflicting interpretations was overwhelming; but the conflict was real. The situation, as pointed out by Millikan and Bowen, appeared to demand the assumption of a new non-relativistic cause, which should give rise to a term in the energy of exactly the same form as the relativistic term, so as to restore L_{21} to nearly the level of L_{11}.

A more obscure and less certain, but as later appeared fundamentally important, set of difficulties arose as the observation of the fine structures in the spectra of hydrogen and ionized helium was improved in precision. In the observations of Paschen in 1916, which were accepted as experimental confirmation of Sommerfeld's theory of fine structure, it was found that certain "forbidden" lines in the fine structure of the helium line λ4686 appeared with unexpectedly high intensity. It was attempted, by Kramers especially, to explain this as the result of a Stark effect of stray electric fields; but this was not entirely satisfactory.

Further, for the H_α doublet Sommerfeld's theory predicts $\Delta\nu = 0.365$ cm^{-1}, while direct measurement consistently yields a lower value of about 0.33. Finally, and most significant, was the apparent discovery of a Paschen-Back effect on observing the fine structure of hydrogen in a magnetic field. This result was somewhat uncertain, and was generally questioned, since if true it necessarily implied an additional dynamical degree of freedom in hydrogen-like atoms.

Sect. 3. Origin and Introduction of the Spinning Electron Hypothesis. The hypothesis of a spinning electron had historically an origin and development quite independent of that of the new dynamics. The credit of laying the foundation on which Uhlenbeck and Goudsmit erected their theory belongs to Pauli.[19] In order to avoid the difficulties encountered in ascribing a magnetic moment to the core in the alkali metals, Pauli suggested the association of a fourth quantum number, of unspecified physical meaning, with each individual electron. On the hypothesis that no two electrons in the same atom can have the same set of four quantum numbers, a very considerable measure of order could then be brought into the systematizations of multiplet spectra; in particular, Stoner's scheme[28] for the grouping of electrons in normal atoms was at once derived. This is the celebrated

exclusion principle of Pauli,which has played and is s still playing a leading part in the progress of quantum mechanics. This new contribution was rapidly utilized by a large group of investigators,including Pauli himself,Hund,Goudsmit,Russell,Saunders,and others,and has led to a degree of spectroscopic systematization astounding to those who,like the present writer,have not been in a position to follow these advances very closely.

In constructing the theory of doublet spectra on this new basis it was found by Goudsmit and Uhlenbeck [11] and by Slater [26] that it became possible,and perhaps necessary,to place an entirely new interpretation on the hydrogen fine structure. Moreover,in the theory of the Zeeman effect the anomalous magnetic moment which was previously associated with the core,and for which the ratio μ/p has twice the value expected for orbital motion,could be transferred to the electron itself. Now this "anomalous" ratio is exactly that to be expected for a rotating sphere with a surface charge.* This is the fundamental observation at the bottom of the hypothesis of Uhlenbeck and Goudsmit.

The conclusion,however,is not so obvious as might appear. Compton,[1] for instance,had proposed a spinning electron long before as an explanation of certain

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*Appendix 2.

peculiar phenomena observed in ionization chambers and in X-ray scattering. (This was not known to Uhlenbeck and Goudsmit.) But any such hypothesis, for whatever purpose put forward, encountered at first sight a considerable difficulty. The spinning electron would constitute a small magnet, with a moment of the order of a Bohr magneton. Such a magnetic, moving in the electrostatic field of the nucleus of a hydrogen-like atom, would be deflected by electromagnetic forces. The energy levels would be altered, and the whole Sommerfeld theory of fine structure, beautifully verified as it seemed to be, would apparently be destroyed.

It required no small acumen to observe, as Uhlenbeck and Goudsmit did, that (1) the modifications in the energy levels are of the same order of magnitude as the Sommerfeld second-order fine structure, containing the identical factor $R\alpha^2 z^4$, in which the variation with the fourth power of the atomic number is of the utmost importance; that (2) the combination with the Sommerfeld levels for half-integral azimuthal quantum number k leads precisely to the reinterpretation of the hydrogen fine structure demanded by Pauli's theory; and that (3) a similar reinterpretation, applied to the X-ray levels, removes the conflict discovered by Millikan and Bowen.

The details of these and other applications of this

theory are given in Part II, where the appropriate mathematical apparatus is developed. At this point it is only possible to gove a short summary of results, passing in order over the difficulties discussed in the preceding section. We group these again as referring to (1) magnetic effects, (2) X-ray doublets, and (3) hydrogen and ionized helium.

(1). The hypothesis is introduced precisely to account for the anomalous factor 2 in the Zeeman effect, which was the principal difficulty of the model. It therefore allows a complete theory of this and of the Paschen-Back effect; and, in conjunction with Pauli's exclusion principle, leads to a correct representation of multiplet spectra.

(2). As just mentioned, the Millikan-Bowen difficulty is removed by the exact realization of the expected non-relativity cause producing a "relativity" term. It should be mentioned, however, that this is true only to terms of order v^2/c^2. The exact result is only obtained by the most recent modifications of the theory, in which the spinning electron as a distinct hypothesis no longer appears.

(3). The appearance of "forbidden" lines is explained by the substitution of the selection principle $\Delta j = 0$ or ± 1 for the principle $\Delta k = \pm 1$; this leads to a

reinterpretation of the experimental results on the Hα doublet, which now appear much more nearly in agreement with theory. This is brought about by the theoretical expectation of fine-structure lines previously looked upon as forbidden, which alters the expected distribution of intensity over the fine-structure pattern, and thus changes the relation of this pattern to the observed maxima of intensity. Finally, the Paschen-Back effect in hydrogen-like spectra is explained, as it proves to be of exactly the same character as the similar effect in the alkali-doublet spectra.

Part II. Theory of the Spinning Electron in Classical Mechanics

Sect. 1. Certain difficulties. We shall now proceed to develop as exactly as possible the theory of these phenomena in its original form, based on the classical mechanics and the Bohr form of the quantum theory. The calculations for hydrogen-like atoms are given as worked out by the writer in the spring of 1926. A preliminary report of the results was presented to the Oakland meeting of the American Physical Society in June, 1926.[22] The details were not published; the results are equivalent to those obtained in a different manner by Uhlenbeck and Goudsmit.[13] It should be mentioned that the method here used, as developed by Professor Epstein, is free from arbitrariness in the choice of coördinates for quantization. These coördinates are unambiguously defined by the method itself, involving no assumption beyond that of the Hamiltonian function of the system; this constitutes the decisive advantage of the present method over those employed by others.

Before entering the discussion of the theory proper, mention must be made of three serious difficulties which appeared in the earliest attempts at such a theory. The lightest of these is the following: Consider for simplicity

an isolated electron, which is assumed to have a constant, quantized angular momentum; this should be $h/2\pi$ on the simple quantum theory. To obtain the corresponding magnetic moment of two Bohr magnetons it is assumed* that the electron is a sphere with a surface charge. It follows immediately* that the peripheral velocity of the electron at its equator is 2×10^{13} cm/sec, which is far above that of light. This result has occasioned much discussion — needlessly, in the present writer's opinion. As an analogous case, suppose that we have a problem requiring a body with a rest mass of 10 grams to have a momentum of 10^{12} c.g.s. units. Obviously the velocity 10^{11} cm/sec which we obtain by simple division is meaningless; the true velocity is less than that of light. Similarly in the case of the spinning electron we cannot assume that our simple formulae will hold exactly at high angular velocities. If it be objected that our electromagnetic formulae apparently include a relativity correction, the reply is that an investigation on the basis of general relativity is necessary; this leads to the well-known uncertainties of the theory of relativity for rotation. In spite of these considerations, the following theory retains the simple value $2e^2a/9c^2$ for the moment of inertia.

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*Appendix 2.

A second and more serious source of doubt relates to the mass of the electron. The total energy of rotation, namely the energy of the magnetic field produced, is given in Appendix 2 as $T = 9k^2c^2/16\pi^2e^2a$. Dividing by c^2, this gives an equivalent inertial mass of the order of 10^{-22} grams, which is 10^5 times the observed mass of the electron. This is true on the usual assumption as to the radius of the electron; but matters cannot be much improved unless the electron becomes of nearly atomic size. A way out of this contradiction was suggested by the late H.A. Lorentz in his lectures at this Institute in 1927. If the electron is not distorted by its high angular velocity, it is necessary to assume that it is retained in its spherical form by internal stresses. The potential energy of these stresses may then be such as to compensate the kinetic energy of rotation represented by the magnetic field.

The third and most serious difficulty, empirically stated, is that the correction term, which a simple theoretical consideration of the spin effects introduces into the Hamiltonian function of the system, must be divided by 2 in order to represent the facts of observation. Highly recondite derivations of this factor ½ have been presented by Thomas[29] and Frenkel.[9] It is hardly unfair to suggest that, had the theoretical formulae been thought to correctly

represent the facts, no such considerations as theirs would have been put forward. The very uncertain condition of this theory is well illustrated by the fact that Professor Lorentz, in the series of lectures previously referred to, arrived at a factor of 2 instead of $\frac{1}{2}$. The whole problem, in fact, has a somewhat mystifying fertility in sources of error which multiply the results by 2 and $\frac{1}{2}$. In the present state of the theory these matters are chiefly of historical interest, and it appears advisable to present the line of reasoning originally employed by the writer and others, which leads to a Hamiltonian function from which the desired results can be derived.

Sect. 2. The effect of a dipole in the nucleus. The spinning electron, as we have assumed it, constitutes a magnetic dipole, or elementary magnet. This magnet, moving in the electrostatic field of the nucleus, will be subject to a magnetic force, by reason of which it will deviate from the path of a point electrostatic charge in the given field. Let the charge on the electron by $-e$, that on the nucleus $+Ze$, and the magnetic moment μ. Then it is easily shown* that the force of translation on the electron is exactly that on a non-magnetic electron moving in the field of a nucleus with charge $+Ze$ and magnetic moment $-Z\mu$, the

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*Appendix 3.

negative sign indicating opposite direction.

If we now assume that the axis of the spinning electron is fixed in direction, the problem is easily solved. This assumption is unjustified, as will appear in the next section; but the relations obtained are very close to those in the actual problem, and will be of use in the third part of this discussion, when we attack the corresponding problem in wave mechanics.

According to a well-known theorem due to Schwarzschild, the introduction of the magnetic fields adds to the Lagrangian function a term $-\frac{e}{c}(\bar{A}\cdot\bar{v})$, where $\bar{A}$ is the vector potential of the field in question, and $\bar{v}$ is the velocity of the electron. In this simple case it follows directly that the effect on the Hamiltonian function is the addition of a term $+\frac{e}{c}(\bar{A}\cdot\bar{v})$, plus terms involving A^2, which are here neglected. This perturbation term can then be expressed in terms of the coördinates and momenta of the unperturbed problem; the error introduced is of the second order of small quantities.

For a dipole of moment $-Z\bar{\mu}$, $\bar{A} = -\frac{Z}{r^3}\left[\bar{r}\times\bar{\mu}\right]$.

$$\therefore \frac{e}{c}(\bar{A}\cdot\bar{v}) = -\frac{Ze}{cr^3}\left([\bar{r}\times\bar{\mu}]\cdot\bar{v}\right) = +\frac{Ze}{cr^3}\left(\bar{\mu}\cdot[\bar{r}\times\bar{v}]\right)$$

$$= +\frac{Ze\mu p_\varphi}{mcr^3}$$,if the axis of polar coördinates is taken in the direction of the vector $\bar{\mu}$.

From this

$$H=\frac{1}{2m}\left(p_r^2+\frac{p_\vartheta^2}{r^2}+\frac{p_\varphi^2}{r^2\sin^2\vartheta}\right)-\frac{Ze^2}{r}+\frac{Ze\mu p_\varphi}{mcr^3}=W \qquad (1)$$

p_φ is cyclic. Putting $p_\varphi = p$, and introducing a third constant of integration γ, the equation separates into

$$p_r=\frac{1}{r}\sqrt{2mWr^2+2mZe^2r-\gamma^2-\frac{2Ze\mu p}{c}r}$$

$$p_\vartheta=\sqrt{\gamma^2-\frac{p^2}{\sin^2\vartheta}}$$

$$p_\varphi=p$$

The quantum integrals are of a standard type.*

Their evaluation gives

$$\oint p_r\,dr=2\pi\left(\frac{m^{\frac{1}{2}}Ze^2}{\sqrt{-2mW}}-\gamma\right)-\frac{Ze\mu p}{c}\cdot\frac{2\pi mZe^2}{\gamma^3}=n_1h$$

$$\oint p_\vartheta\,d\vartheta=2\pi(\gamma-p)=n_2h$$

$$\oint p_\varphi\,d\varphi=2\pi p=jh$$

Adding the last two equations, $\gamma=(j+n_2)h/2\pi$.

Putting $j+n_2 = k$, $k+n_1 = n$, and $\mu=\lambda\, eh/4\pi mc$, λ being provisionally left undetermined, we find

$$2\pi Ze^2\sqrt{\frac{m}{-2W}}=(n+Q')h$$

where $Q'=\frac{\lambda j}{2K^3}Z^2\alpha^2$, and $\alpha=\frac{2\pi e^2}{hc}$ is Sommerfeld's fine structure constant. Hence

$$W=-\frac{2\pi^2mZ^2e^4}{h^2(n+Q')^2}$$

As Q' is small, we can expand W in powers of Q'. To the first order

$$W/h=-\frac{RZ^2}{n^2}+\lambda R\alpha^2Z^4\frac{j}{n^3K^3}. \qquad (2)$$

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*Cf. Born, Atommechanik, pp. 346ff.

The factor $R\alpha^2Z^4h$ is the same as that occurring in Sommerfeld's relativistic formula. Since n,k,j are integers, the effect is seen to be of precisely the order of magnitude required.

This procedure has not been discussed in detail, since the neglect of the angular momentum of the rotating electron, and of the consequent precession of its axis in space, raises numerous questions which can only be settled by the more exact treatment which here follows.

Sect. 3. The Legrangian function for hydrogen-like atoms having a rotating spherical electron. The forde on a magnetic pole of strength M moving in an electromagnetic field is given by

$$\bar{F}=M(\bar{H}-\frac{1}{c}\,\bar{v}\times\bar{E}) \qquad (3)$$

The second term can be interpreted to mean that any magnetic system, moving with a velocity $\bar{v}$ through an electrostatic $\bar{E}$, behaves as if in a magnetic field $\bar{H}'=-\frac{1}{c}\,\bar{v}\times\bar{E}$. The rotating electron may be considered as such a system; and now if we put $\bar{E}=\frac{Ze^2\bar{r}}{r^3}$, which is the field due to the nucleus, we have $\bar{H}'=-\frac{Ze}{cr^3}[\bar{v}\times\bar{r}]$, which is precisely the magnetic field of a charge equal to that of the nucleus moving with velocity $-\bar{v}$ through its position. This field can be derived from the vector potential $\bar{A}=-\frac{Ze\bar{v}}{cr}$; and we can now apply Schwarzschild's general theorem, referred to in the previous section, to

the elements de of the charge on the spinning electron; so that we have added to the Legrangian function a term

$$\Delta L = -\iint \frac{de}{c}(\bar{A}\cdot\bar{V}), \qquad (4)$$

where $\bar{V}$ is the velocity of the element of charge with respect to the center of the electron, $\bar{A}$ is the above vector potential, and the integration extends over the surface of the electron. In substituting the value of $\bar{A}$ we take $\bar{v}$ as the velocity of the center of the electron; for r we put r', the distance from the nucleus to the element of charge considered. Further, we may put $\bar{V}=[\bar{\omega}\times\bar{a}]$, where $\bar{\omega}$ is the angular velocity of the spin and $\bar{a}$ is the vector from the center to the surface element. Then

$$\Delta L = \frac{Ze}{c^2}\iint \frac{de\,(\bar{v}\cdot[\bar{\omega}\times\bar{a}])}{r'}$$

The result of the integration is*

$$\Delta L = +\frac{Ze^2a^2}{3c^2r^3}([\bar{v}\times\bar{\omega}]\cdot\bar{r}) \qquad (5)$$

The complete Legrangian function will thus contain (1) the kinetic energy of translation of the electron, (2) the kinetic energy of rotation, (3) the electrostatic potential energy, (4) the above term ΔL divided by 2, and (5) terms representing the relativity correction.

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*Appendix 4.

Of these terms (1) and (3) are the same as for the ordinary theory of hydrogen-like atoms without relativity. (2) is simply $\frac{1}{2}I\omega^2$, where I is the moment of inertia of the spinning electron and ω is the angular velocity of spin. As to (5), we here omit relativity terms. These of course should be included in a complete theory, which would also contain interaction terms between the relativity and spin effects. However the present analysis is carried out only to terms of order v^2/c^2. The interaction terms between the relativity and spin terms of order v^2/c^2 are of order v^4/c^4; accordingly the relativity and spin corrections can be computed separately, and the complete results to the required degree of approximation obtained by their addition. *

The division of ΔL by 2 contains an irremediable arbitrariness. ΔL as computed includes terms only in the velocity of the center of the electron. There are also forces dependent on its acceleration. For the case of a Coulomb field these forces are stated by Thomas to be $-\frac{1}{2}$ times the forces depending on the velocity; accordingly, the total force can by represented as derived from a Legrangian function $\frac{1}{2}\Delta L$. However, as already mentioned, Professor Lorentz arrived at a factor 2 instead of $\frac{1}{2}$; so that it seems best here to follow the procedure adopted by others, and arbitrarily divide ΔL by 2 without attempting a physical

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* *For an additional justification see Section 8 below.

interpretation. We can then write

$$L = \frac{1}{2}mv^2 + \frac{1}{2}I\omega^2 + \frac{Ze^2}{r} - \frac{Ze^2a^2}{6c^2r^3}\left([\bar{v}\times\bar{\omega}]\cdot\bar{r}\right) \qquad (6)$$

To discuss the motion represented by this Legrangian function we introduce the following coördinates:

r, ϑ, φ, polar coördinates of the center of the electron reffered to the nucleus as origin.

θ, Ψ, Φ, Eulerian angles of the electron; polar axis parallel to that of ϑ and φ.

θ = angle between the polar axis and an axis B fixed in the body of the electron.

Ψ = azimuth of the axis B about the polar axis; initial plane parallel to that of φ.

Φ = angle of rotation of the electron about B.

Using these coördinates we have*

$$L = \frac{m}{2}(\dot{r}^2 + r^2\dot{\vartheta}^2 + r^2\sin^2\vartheta\,\dot{\varphi}^2) + \frac{I}{2}(\dot{\theta}^2 + \dot{\Psi}^2 + \dot{\Phi}^2 + 2\cos\theta\,\dot{\Psi}\dot{\Phi})$$
$$+ \frac{Ze^2}{r} - \frac{Ze^2a^2}{6c^2r}\Big\{\cos(\varphi-\psi)\dot{\vartheta}\dot{\theta} - \sin\theta\sin(\varphi-\psi)\dot{\vartheta}\dot{\Phi}$$
$$-\sin\vartheta\cos\vartheta\sin(\varphi-\psi)\dot{\varphi}\dot{\theta} + \sin^2\vartheta\,\dot{\varphi}\dot{\psi}$$
$$+\left[\sin^2\vartheta\cos\theta - \sin\vartheta\cos\vartheta\sin\theta\cos(\varphi-\psi)\right]\dot{\varphi}\dot{\Phi}\Big\}$$

(7)

*Appendix 5.

Sect. 4. The Hamiltonian function. Method of perturbations. Applying the definitions

$$p_i = \frac{\partial L}{\partial \dot{q}_i}\,, \quad H = -L + \sum_i p_i \dot{q}_i\,,$$

we find* that

$$H = H_0 + H_1$$

where

$$H_0 = \frac{1}{2m}\left(p_r^2 + \frac{p_\theta^2}{r^2} + \frac{p_\varphi^2}{r^2 \sin^2\theta}\right) + \frac{1}{2I}\left[p_\Theta^2 + p_\Phi^2 + \frac{1}{\rho \sin^2\Theta}\left(p_\psi - p_\Phi \cos\Theta\right)^2\right] - \frac{Z_0^2}{r}$$

and

$$H_1 = \frac{Z e^2}{2m^2c^2r^3}\Big\{\cos(\varphi-\psi)\, p_\vartheta p_\Theta + \cot\Theta \sin(\varphi-\psi)\, p_\vartheta p_\psi$$
$$- \csc\Theta \sin(\varphi-\psi)\, p_\vartheta p_\Phi - \cot\vartheta \sin(\varphi-\psi)\, p_\varphi p_\Theta \qquad (8)$$
$$+ \left[1 + \cot\vartheta \cot\Theta \cos(\varphi-\psi)\right] p_\varphi p_\psi - \cot\vartheta \csc\Theta \cos(\varphi-\psi)\, p_\varphi p_\Phi \Big\}.$$

For the quantization of the solution of this equation to terms of the order desired we make use of the method of perturbations of **Delaunay**, the application of which to the purposes of the quantum theory has been worked out by Professor Epstein.[6,7] This method, as previously mentioned has the advantage of unambiguously fixing the coördinates for quantization.

The first step is to find the mean value of the perturbation term H_1 over the first intermediate motion, that is, the motion represented by $H=H_0$. In our case this motion is that of an electron moving in an elliptical orbit and simultaneously spinning, the two motions not affecting one another. The plane of the orbit is then fixed; we may choose the polar axis normal to this plane,

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*Appendix 6.

so that $\vartheta = \frac{\pi}{2}$ and $p_\vartheta = 0$. The axis of spin is now fixed in the body of the electron; we choose it as the axis B, and as it is also fixed in space we have $p_\theta = 0, p_\psi = p_\Phi \cos\theta$, where p_ψ, p_Φ, θ are all constant. The perturbation then reduces to

$$H_1 = \frac{Ze^2}{2m^2c^2r^3} \cos\theta\, p_\varphi p_\Phi .$$

The only variable in this expression is $1/r^3$; and, as is well known,* the mean value of $1/r^3$ in a Kepler ellipse is $1/b^3$, where b is the semi-minor axis. Consequently the mean value of H_1 is

$$\tilde{H}_1 = \frac{Ze^2}{2m^2c^2b^3} \cos\theta\, p_\varphi p_\Phi . \quad (9)$$

The Hamiltonian function is now taken as

$$H = H_0 + \tilde{H}_1 ;$$

this completes the first approximation.

Sect. 5. Introduction of angular variables. The next step is to introduce into H_0 and $\tilde{H}_1$ the angular variables and angle momenta of the first intermediate motion; the angle momenta being defined by $u_i = \oint p_i dq_i$, and the angular variables w_i being the canonical conjugates to these with respect to H_0.**

In the ordinary theory of hydrogen-like atoms ($H = H_0$), it is found that $b = (u_r+u_\vartheta+u_\varphi)(u_\vartheta+u_\varphi)/mZe^2$. From the same theory and from the theory of the rotator,

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*Cf. Born, Atommechanik, p.164.

**The properties of these variables are to be found in Appendix 7 and in the papers of Epstein[6,7] referred to.

Lastly, in equation (9) p_φ and p_Φ refer to a particular choice of axes. In general p_φ must be replaced by $u_\vartheta + u_\varphi$, and p_Φ by $u_\Theta + u_\Psi$. For Θ we put Θ', which is the angle between the normal to the plane of the ellipse and the angular momentum of the rotating electron. Computing $\cos\Theta'$ in terms of the variables we are using, and substituting for all the quantities occurring in $H_0 + H_1$, we arrive at the new Hamiltonian function*

$$H = -\frac{m Z^2 e^4}{2(u_1+u_2+u_\varphi)^2} + \frac{(u_\Theta+u_\Psi)^2}{2I} + \frac{m Z^4 e^8}{2c^2}\,\frac{\cos\left[(w_\varphi - w_\vartheta)-(w_\Psi - w_\Theta)\right]\sqrt{\left[(u_\varphi+u_\vartheta)^2-u_\varphi^2\right]\left[(u_\Psi+u_\Theta)^2-u_\Psi^2\right]}}{(u_\vartheta+u_\varphi)^3(u_1+u_2+u_\varphi)^3} - \frac{+u_\varphi u_\Psi}{} \qquad (10)$$

Sect. 6. Canonical Transformations and Solution.

We carry out two canonical transformations in succession. The first of these consists of a transformation already in use in the simple hydrogen problem,[7] together with the analogous transformation for the rotator:

$$p_1 = u_\varphi,\ q_1 = w_\varphi - w_\vartheta;\ p_2 = u_\vartheta + u_\varphi,\ q_2 = w_\vartheta - w_1;\ p_3 = u_1 + u_2 + u_\varphi,\ q_3 = w_1;$$

$$P_1 = u_\Psi,\ Q_1 = w_\Psi - w_\Theta;\ P_2 = u_\Theta + u_\Psi,\ Q_2 = w_\Theta;\ P_3 = u_\Phi,\ Q_3 = w_\Phi.$$

This results in

$$H = -\frac{m Z^2 e^4}{2p_3^2} + \frac{P_2^2}{2I} + \frac{m Z^4 e^8}{2c^2}\,\frac{\cos(q_1-Q_1)\sqrt{(p_2^2-p_1^2)(P_2^2-P_1^2)} + p_1 P_1}{p_2^3 p_3^3} \qquad (11)$$

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*Appendix 7.

The second canonical transformation is as follows:

$$p = P_1, q = Q_1 - q_1; \quad P = p_1 + P_1, Q = q_1.$$

The Hamiltonian function now becomes

$$H = -\frac{mZ^2e^4}{2p_3^2} + \frac{P_2^2}{2I} + \frac{mZ^4e^8}{2c^2p_2^3p_3^3}\left\{\cos q\sqrt{[p_1^2-(P-p)^2][P_2^2-p^2]} + p(P-p)\right\}$$

$$= W. \qquad (12)$$

All the variables are now cyclic except q. The problem is therefore completely separated, and we have as quantum conditions

$$p_3 = \frac{nh}{2\pi}, \; p_2 = \frac{kh}{2\pi}, \; P_2 = \frac{sh}{2\pi}, \; P = \frac{mh}{2\pi}, \; \oint p\,dq = n'h.$$

**

If we write as a definition of F

$$W = -\frac{mZ^2e^4}{2p_3^2} + \frac{P_2^2}{2I} + \frac{mZ^4e^8}{2c^2p_2^3p_3^3}F, \qquad (13)$$

the last quantum condition gives*

$$2\pi\left(\pm\sqrt{p_2^2+P_2^2+2F} - P_2 - p_2\right) = n'h, \quad \sqrt{p_2^2+P_2^2+2F} = (n'+s+k)\frac{h}{2\pi},$$

and putting $n' + s + k = j$

$$F = \frac{h^2}{8\pi^2}(j^2 - k^2 - s^2), \qquad (14)$$

so that finally

$$W = -\frac{2\pi^2mZ^2e^4}{n^2h^2} + \frac{s^2h^2}{8\pi^2I} + \frac{4\pi^4m^4Z^4e^8}{n^3k^2c^2h^4}(j^2 - k^2 - s^2)$$

or

$$\frac{W}{h} = -\frac{RZ^2}{n^2} + \frac{s^2h}{8\pi^2I} + \frac{R\alpha^2Z^4}{2n^3k^3}(j^2 - k^2 - s^2), \qquad (15)$$

$$\alpha = 2\pi e^2/hc$$

In these equations n and k have the same meaning as in the unperturbed Kepler ellipse. j,k,s are $2\pi/h$ times

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*Appendix 8.

**Strictly, the degree of freedom represented by P is degenerate and should not be quantized. Cf.Sect.10.

the total angular momentum, the orbital angular momentum, and the angular momentum of rotation, respectively.* Accordingly the quantization of the resultant angular momentum, which requires a separate discussion in other forms of this theory, here appears as a natural and necessary consequence of the conditions of the problem.

Section 7. Relativity corrections. The energy levels for the hydrogen-like spectrum. In pursuance of our plan we now add to our expression (15) the terms arising from Sommerfeld's relativity correction. The whole expression then becomes **

$$\frac{W}{h} = -\frac{RZ^2}{n^2} + \frac{s^2 h}{8\pi^2 I} + \frac{R\alpha^2 Z^4}{2n^3 k^3}(j^2 - k^2 - s^2) - \frac{R\alpha^2 Z^4}{n^4}\left(\frac{n}{k} - \frac{3}{4}\right) \quad (16)$$

The correction terms due to spin and relativity can be combined, and written in the form

$$\frac{\Delta W}{h} = R\alpha^2 Z^4 \left(\frac{j^2 - 3k^2 - s^2}{2n^3 k^3} + \frac{3}{4n^4} \right) \quad (17)$$

If n, j, k, s are all integers, as demanded by the simple quantum theory, then of course this does not represent the observed levels, which are then given by Sommerfeld's term alone. But the above formula as it stands cannot be made to represent the observed levels by any reasonable choice of j, k, s, even allowing half-integers; n of course remains unaltered, as it determines the principal term in W.

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*For this interpretation of j see Appendix 8.
**Cf. Born, Atommechanik, p. 233.

The desired result can be obtained, as suggested by Uhlenbeck and Goudsmit, by what they called a "Heisenberg substitution." This was already known from the anomalous Zeeman effect (cf. Sect. // below); as is now known, it corresponds to the relation between an angular momentum in classical dynamics and the corresponding matrix in quantum dynamics. This substitution is made by putting $J^2-\frac{1}{4}, K^2-\frac{1}{4}, S^2-\frac{1}{4}$ for j^2, k^2, s^2 respectively. The k^3 occurring in the denominator is replaced by $K(K^2-\frac{1}{4})$. The first term in parentheses in equation (17) thus becomes

$$\frac{1}{2n^3}\,\frac{J^2-3K^2-S^2+\frac{3}{4}}{K(K^2-\frac{1}{4})}$$

If now, as proposed by Uhlenbeck and Goudsmit, we take $S = 1$, $J = K \pm \frac{1}{2}$, this term reduces to simply $-1/n^3J$. Thus in place of equation (16) we obtain

$$-\frac{W}{h} = -\frac{RZ^2}{n^3} + \frac{3h}{32\pi^2 I} - \frac{R\alpha^2 Z^4}{n^4}\left(\frac{n}{J} - \frac{3}{4}\right). \qquad (18)$$

This is identical with Sommerfeld's original result, except that J occurs in place of k. By assigning integral values to J, we can therefore obtain the whole observed fine structure.

From the interpretation of j, k, s in terms of angular momenta it follows that j must lie between the limits k-s and k+s. If we carry this over to our new quantum numbers and require J to lie between K-S and K+S, then since J is integral, K is half-integral, and S is 1 the restriction $J = K \pm \frac{1}{2}$ follows at once. The case $J = 0$ cannot occur.

This leads to the Uhlenbeck-Goudsmit reinterpretation of the hydrogen-type fine structure. The factor k in k^3, for which we put simply K, has its origin partly in the k of the Sommerfeld term. Accordingly, if the spin terms were not present we should put K for k. We should then obtain levels for half-integral azimuthal quantum numbers, lying between the old Sommerfeld levels. As will be pointed out later (Section //), these levels have a physical significance in connection with the Paschen-Back effect; but under normal circumstances they are masked by the spin terms. Since there are two values of J for every K, each of these relativity levels is split up into two levels due to relativity plus spin, occupying two different levels of the old scheme. Thus for K = 3/2 we have J = 1 and J = 2, corresponding to k = 1 and 2 of the old theory. For K = $\frac{1}{2}$ we have only J = 1; the level J = 0, which the formula would assign an infinite energy, does not exist.

Each of the energy levels in the fine structure, which on the Sommerfeld scheme corresponded only to one state of the atom, here represents two such states.- Each line in the observed spectrum thus may originate in more than one way. Moreover, lines which were "forbidden" on the old scheme are now permitted. For J, being associated with the total angular momentum, obeys the selection principle for the

inner quantum number, $\Delta J = 0$ or ± 1; whereas Sommerfeld's k was restricted to $\Delta k = \pm 1$ only. The lines corresponding to $\Delta J = 0$ are accordingly permitted in the present theory, but forbidden in Sommerfeld's. As mentioned in the introduction, these lines are actually observed with considerable intensity. The present theory removes the apparent contradictions involved in their appearance. Moreover, the general redistribution of theoretically predicted intensities, consequent on the altered interpretation of their origin, leads to results which are in general in better agreement with observation than the previous ones, and which appear to remove at least the larger portions of the inconsistences apparent in experimental determinations of the H_α doublet.

Section 8. Motions in the Model. Correspondence Principle. It is of interest to investigate the exact nature of the motions in the mechanical model we are using, even though recent theory renders this model inapplicable. For this purpose we write out the Hamiltonian function given by equation , with the addition of Sommerfeld's terms expressed in the same variables:

$$H = -\frac{mZ^2e^4}{2p_3^2} + \frac{p_2^2}{2I} + \frac{mZ^4e^8}{2c^2p_2^3p_3^3}\left\{\cos\phi\sqrt{[p_2^2-(p-p_1)^2][p_2^2-p^2]}+p(p-p_1)\right\}+\frac{mZ^4e^8}{2c^2p_3^4}\left(\frac{p_3}{p_2}-\frac{3}{4}\right) \qquad (19)$$

It is obvious that the inclusion of these terms alters nothing in our process of quantization. The equation is

separable in the same variables as before;and if we denote by F the same quantity as previously,the form of the integral $\oint pdq$ will be unchanged. The computed value of F will then be the same as before,and we shall arrive at precisely equation (16) of Section 7. This furnishes an additional justification of our treatment of these relativity terms.

If we introduce $F = \frac{1}{2}(G^2 - p_2^2 - P_2^2)$, G being $jh/2\pi$, we have as the final expression of the Hamiltonian in terms of the angle momenta of the whole problem:

$$H = -\frac{mZ^2e^4}{2p_3^2} + \frac{P_2^2}{2I} + \frac{mZ^4e^8}{4c^2p_2^3p_3^3}(G^2-p_2^2-P_2^2) + \frac{mZ^4e^8}{2c^2p_3^4}\left(\frac{p_3}{p_2} - \frac{3}{4}\right) \quad (20)$$

The angular variables conjugate to these momenta are linear functions of the time. Three of these, q_2, q_3, and Q_2, are known from the first intermediate motion. In the Kepler motion q_2 is the angle between the major axis and the line of ascending nodes;the variation of q_2 is a precession of the ellipse in its plane. q_3 is the mean anomaly in the orbit;its variation is the motion in the ellipse. Q_2 is analogous to q_2;it the angle of rotation of the electron about its axis of rotational angular momentum,measured from the line of nodes in which its equator cuts the plane $\theta = \frac{\pi}{2}$. Its variation constitutes the spin.

The remaining degree of freedom is best treated by

observing that,as the polar axis is arbitrary,we can take it in the direction of the total angular momentum G. Now $P = p_1 + P_1$ is the component of G in the direction of the polar axis;so that in this case G = P. The conjugate angular variable to G,which we may denote by Γ ,then differs from Q only by an easily determined constant;so that the rate of increase of Γ is the same as that of Q,and its physical significance essentially the same. Now $Q = q_1$, and q_1 in the Kepler ellipse is the azimuth of the line of nodes. The variation of Q or of Γ consequently means a precession of the ellipse about the polar axis. This polar axis we have taken to be the direction of the resultant angular momentum,which is fixed. Consequently the normal to the plane of the ellipse and the axis of spin must remain in a plane through the polar axis, about which the whole system precesses uniformly.

Applying to the Hamiltonian (20) the canonical equation $\dot{q}_i = \frac{\partial H}{\partial p_i}$ we find that the frequency $\dot{q}_2$ of precession of the ellipse in its plane is due partly to the spin and partly to relativity;that the orbital frequency $\dot{q}_3$ is affected by both spin and relativity; that the frequency of spin $\dot{Q}_2$ is altered by interaction with the orbital motion;and finally that the precession $\dot{\Gamma}$ is due altogether to the spin effect.

These considerations facilitate an application of Bohr's correspondence principle. As this whole theory has been rendered obsolete by the quantum dynamics, we shall only use it to derive the selection principles.

The problem is that of expanding the three components of the electric moment of the atom in Fourier series in the angle variables. This amounts to finding such an expansion for the Cartesian coördinates x, y, z of the center of the electron, since rotation of the electron cannot alter the moment of the atom. The spin will enter only in so far as it alters the motion of the center. A piece of experimental evidence for this will be pointed out in connection with the Paschen-Back effect (Section ||).

We have seen that three of our angle variables coincide essentially with the angle variables q_1, q_2, q_3 of the Kepler ellipse. The fourth, Q_2, is only an angle of rotation of the electron, and does not concern us here. Accordingly, the required expansions for x, y, z are in form identical with those for the unperturbed Kepler ellipse; the difference is only that for the unperturbed ellipse q_1 and q_2 are constant, while here they are linear functions of the time, like q_3.

The result of this expansion is fairly well known.

If we denote the arguments of the trigonometric terms by $n_1q_1 + n_2q_2 + n_3q_3$, it is found that n_3 may have any value in all three expansions. n_2 takes only the values ± 1, while n_1 is 0 in the expansion for z, and ± 1 in those for y and z. Now as the quantum numbers associated with q_1, q_2, q_3 are j, k, n respectively, this means that $\Delta j = 0$ or ± 1, $\Delta k = \pm 1$, and Δn is unrestricted. Moreover, when $\Delta j = 0$ the light is polarized parallel to the axis of total angular momentum, and when $\Delta j = \pm 1$ the light is circularly polarized at right angles to this axis.

Section 9. Theory of doublets in optical and X-ray spectra. After the discussion of the hydrogen spectrum in Section 7 it is fairly evident that the present theory is adequate to remove the Millikan-Bowen difficulty in the interpretation of X-ray spectra. It will be recalled that the comparison of X-ray and optical doublets demands an interpretation of the former which conflicts with Sommerfeld's relativistic theory. This theory makes use of the fact that the deviation of the electric field about the K and L electrons from Coulomb's law is slight, and that the whole effect of the remaining electrons can be summed up in a "screening constant" subtracted from the atomic number of the nucleus. It follows that the large doublet differences, varying with the fourth power

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of this diminished atomic number,can be explained as due to the difference in energy of two orbits having the same principal quantum number but different azimuthal quantum number,while the small doublet differences are attributed to differences in screening,for different orientations, of two orbits having both azimuthal and principal quantum numbers the same.

On the spinning electron model this interpretation is practically reversed. The large fourth-power differences are seen to be due to differences in our quantum number j,which in fact specifies an orientation with respect to the axis of total angular momentum;the small differences are between states having the same n and j but different k. As in the hydrogen-like spectrum,there are in general two such states. These coincide in hydrogen,but are slightly separated in X-ray spectra,owing to the slight difference in screening between elliptical orbits of differing eccentricity - a much more satisfactory hypothesis than the previous one,which required such orbits to have the same screening constant provided the orientation was unchanged.

Thus the theory of X-ray spectra is cleared of contradictions,provided of course that there is no necessity of altering Bohr's interpretation of the alkali doublets. That this is so appears readily as

follows.

If instead of a Coulomb field we assume that the electron moves in any central field of forces, and neglect the spin effect, the problem is still separable in polar coördinates, and we can introduce the angle variables q_1, q_2, q_3 just as before. The path is confined to a plane; and since the orientation of this plane in space cannot affect the energy, $H=W$ will be independent of p_1.

Now suppose the deviation from a Coulomb field is small. There will then be a small correction to our expression for the spin effect, due to this departure from a Coulomb field; but since the spin effect is already a small term, this correction will be of the second order of small quantities and can be neglected. Finally, since the only correction term admitted depends only on p_2 and p_3 and is independent of p_1, the quantization will be unaffected, just as it is unaffected by the introduction of the relativity term.

The result is that the three effects due to relativity, spin, and deviation from a Coulomb field are additive in the first order, at least for the energy levels. Now the effect of a non-Coulomb field, as exemplified in the spectra of alkali metals, is a very considerable separation of the levels for varying k with constant n; this separation is what distinguishes the

several series of such a spectrum. The small relativity correction is absorbed into these large differences;but at each of the levels thus defined by n and k there is found a doublet,whose separation,allowing for the "screening" and other effects which alter the effective nuclear charge,is precisely that between the two spin levels for which J is $K+\frac{1}{2}$ and $K-\frac{1}{2}$ - K being $k-\frac{1}{2}$. An exception occurs in the case $k=1, K=\frac{1}{2}$. The level J=0 does not exist; as for hydrogen,this level corresponds to infinite energy, and cannot occur. Thus the s levels,for which k=1,are,as is well known,singlets.

Section 10. Degenerate Degrees of freedom. It will be noticed that our final expression of the energy of a hydrogen-like atom (16) contains only the four quantum numbers n,k,s,j, although the original problem is one of six degrees of freedom. This occurrence of only four quantum numbers is in agreement with experiment;but it indicates the existence of two degrees of degeneracy,which we proceed to investigate.

If we return to our first expression (10) for the mean value of the Hamiltonian in terms of the angle momenta of the first intermediate motion,we observe that the momentum u_φ is missing. It follows that the conjugate angle, φ ,is constant;which means that there is no rota-

tion about our axis of reference B fixed in the body of the electron. This is obviously the case; for a sphere is incapable of two simultaneous rotations, and the rotation of the electron is completely specified by u_θ and u_ψ. In other words, we have a degeneracy due to the spherical symmetry, as a result of which all choices of the axis B are equivalent. This degeneracy could only be removed by an inequality in the three axes of inertia, or by the association of some property with an axis fixed in the body of the electron. An argument for the sphericity of the electron is thus provided; an asphericity would introduce an additional degree of freedom and a new quantum number, multiplying the levels beyond those observed.

The second degeneracy is that represented by the momentum P, which appears in the form (12) for the Hamiltonian, and was there set equal to $\frac{m h}{2\pi}$. It will be noticed that P is absent from the energy, and consequently from the final form of the Hamiltonian in terms of angle variables, given in (20). Now P is the component of the total angular momentum G in the direction of the polar axis. Its quantization is accordingly a space quantization, which is justified only when the corresponding degeneracy is removed. This can be done, as in the simple theory of the hydrogen atom, by the introduction of a magnetic field; the number m then enters as the magnetic quantum number.

Sect. 11. Magnetic Effects. The application of a homogeneous magnetic field with lines of force parallel to the polar axis adds two terms proportional to the fields strength $\mathcal{H}$ to our Hamiltonian function. (Terms involving $\mathcal{H}^2$ are neglected.) The first of these, associated with the orbital motion of the electron, is the same term $\frac{e\mathcal{H}}{2mc} p_\varphi$ which occurs in the simple theory of the Zeeman effect.* The second, associated with the spin, is $\frac{e\mathcal{H}}{mc} p_\psi$; the factor 2 arises from the doubled ratio of magnetic moment to angular momentum of spin. Expressed in terms of the angle variables of our problem without magnetic field, these may be written together as

$$\frac{e\mathcal{H}}{2mc}(P+p).$$

This is added to a Hamiltonian function which contains corrections for relativity and spin effects, and also for deviation from a Coulomb field. The result depends on the relative magnitude of these terms to the magnetic correction. We shall first assume that the latter is small compared to all other terms.

If this is so we can again apply the method of perturbations; we have to find the mean value of the magnetic term, taken over the unperturbed motion, express this mean in terms of the angle variables of the unperturbed motion, and quantize the Hamiltonian containing this mean value in place of the above expression.

*Cf. Born, Atommechanik, pp. 237ff., and Appendix 1.

P,as we have seen,is a constant in the unperturbed motion,so that we have only to find the average of p. Now $p = P_1$,which is the component of P_2 in the direction of the polar axis. The vector represented by P_2 precesses uniformly about the vector represented by G;accordingly, the mean value of P_2 is $P_2\cos(P_2,G)$. But the vectors p_2,P_2,G form a vector triangle,so that

$$p_2^2 = P_2^2 + G^2 - 2P_2G\cos(P_2,G).$$

Hence the mean value of P_2 is $(P_2^2 + G^2 - p_2^2)/2G$. The mean value of P_1 is the component of this in the direction of the polar axis;but as P is the component of G in the direction of the axis we find,for the mean value of P_1, $(P_2^2 + G^2 - p_2^2)P/2G^2$,and for the mean value of the whole term which we are seeking

$$\Delta W = \frac{e\mathcal{H}}{2mc} P\left(1 + \frac{G^2+P_2^2-\phi_2^2}{2G^2}\right) \qquad (21)$$

The entire approximate Hamiltonian will now depend only on these momenta,which can accordingly be quantized, giving

$$\Delta W = \frac{e\mathcal{H}}{4\pi mc} \cdot m \cdot \left(1 + \frac{j^2+s^2-k^2}{2j^2}\right) \qquad (22)$$

If now we make the "Heisenberg substitution," we find

$$\Delta W = \frac{e\mathcal{H}}{4\pi mc} \cdot m \cdot \left(1 + \frac{(J^2-\frac{1}{4})+(S^2-\frac{1}{4})-(K^2-\frac{1}{4})}{2(J^2-\frac{1}{4}}\right) \qquad (23)$$

which is Landé's formula for the anomalous Zeeman effect.

Our proof applies only to the case of doublet spectra; but the formula is general.

We have here assumed the magnetic correction small in comparison to the relativity and spin effects. If we now make the opposite assumption, that these effects are small perturbations of the motions produced in the magnetic field - which must be the case if the field strength is sufficiently increased - we have quite different conditions. We have first to solve the motion without the spin and relativity corrections. If the electron moves in a central field, the non-magnetic terms will then depend on p_2, p_3, and P_2, while the magnetic terms are $\frac{e\mathcal{H}}{2mc}(p_1 + 2P_1)$. Consequenttly p_1 and P_1 are quantized; we can write $p_1 = \frac{mh}{2\pi}$, $P_1 = \frac{\Pi h}{2\pi}$.

The effect on the spectrum is clear. Quantum transitions in m and Π occur independently. Those in m split up every non-magnetic line into a "normal" Lorentz triplet. Those in Π should lead, among other things, to lines at double the normal Lorentz displacement. On the correspondence principle the intensity of these lines should be zero, for they do not correspond to a change in the electric moment of the atom; this is so because the omission of the spin terms makes the orbital motion independent of the spin. Lines of this general type are observed, and their intensity drops to zero

for very hgih fields - that is,the probability of such a transition vanishes when it ceases to alter the orbital motion of the electron;this is a partial justification of our use of the correspondence principle.

A further interesting result appears when,after solving the problem with magnetic field,but without spin or relativity terms,we introduce these latter terms as small perturbations. By our general rule,they have to be averaged over the unperturbed motion,and expressed in terms of the angle variables of that motion. For the relativity term this is simple;as it depends only on p_2 and p_3,which are constants of the unperturbued motion, its average is given simply by writing it in terms of p_2 and p_3. The average of the spin term is best obtained from equation (9),by observing that it is a constant multiplied by $1/b^3$ and the scalar product of the orbital and rotational angular momenta. b,the minor axis of the ellipse,is of course a constant of the unperturbed motion (it depends only on p_2,p_3,and constants). For the scalar product we observe that the vectors representing the two angular momenta in question precess uniformly at different rates about the polar axis. The scalar product then reduces to the product of their components in the direction of the axis;this is p_1P_1,so that the required average of the spin term is simply

const.p_1P_1/b^3.

The quantization accordingly consists in putting all the angle momenta of the unperturbed motion equal to quantum numbers times $h/2\pi$. For the relativity term this means adding the Sommerfeld correction;but we must take half-integral K instead of integral k,as explained in Section 7. The spin term is proportional to m/Π. These two energy terms are superposed on those due to the unpertubed motion,including the magnetic effect and the deviation from a Coulomb field,this last being assumed relatively small. The sum represents tthe Pascheh-Back effect of a doublet spectrum for high fields;and it is worth while to examine its relation to the undisturbed doublet discussed in Section 8.

The principal lines observed will be those of the Normal Lorentz triplets,corresponding to transitions in alone. Other lines will be weak,since the effect of the spin on the orbital motion is by hypothesis small. The energy differences corresponding to the outer lines of these triplets,for which $\Delta m = \pm 1$,will contain spin terms,so that there will be slight deviations from the normal separation of the Zeeman pattern. The central line,on the other hand,is given by $\Delta m = 0$;and for this line the spin effect vanishes,so that its position is determined by the principal energy levels and the rela-

tivity terms. These lines accordingly appear as if they were transitions between the Sommerfeld levels for half-integral K,while the original doublet lines appear as transitions between these levels for integral k (=J). The two values of J corresponding to a doublet with given K are $J_1 = K-\frac{1}{2}, J_2 = K+\frac{1}{2}$. It easily seen that $J_1(1/J_1 - 1/K) = J_2(1/K - 1/J_2)$; in other words,if we assign the weights Jl and J_2 to the corresponding doublet levels,and find the resulting center of gravity, this center coincides with the level which enters into the central line of the Paschen-Back triplet. (This neglects the spin term,which drops out of the energy difference and thus cannot be observed.) This is a well-known fact of observation;and by means of these centers of gravity the relativity levels for half-integral K acquire a direct physical significance.

It is well known that the Paschen-Back effect is frequently partial. Since the separation of doublets with different K's,say of a p and a d term,may have quite different values,it is possible for the same magnetic field to be large with respect to one term and small with respect to the other. The first then shows a Paschen-Back effect,the second an anomalous Zeeman effect,and the combination of the two gives a system of spectral lines intermediate between the two types.

This result is familiar; but it is not so well known that the Paschen-Back effect as observed for s-p doublets, even when carried through to the appearance of a normal Zeeman triplet, as by Kent,[15] is still only the partial effect. On the old theory this is not the case; the s state is a singlet, and the phenomena of the Paschen-Back transformation enter the s-p lines only through the p term. Accordingly, the appearance of a Lorentz triplet with its central component at the "center of gravity" of the original pattern- between the two doublet lines- is taken as the final effect. But for an s level J = 1, while K = ½; so that a sufficiently high field should produce a Paschen-back effect of the s-term, in the sense that the center of the triplet should shift from its position between the original doublet lines to a position considerably outside; for 1/½ - 1/1 = 1, while the separation of the p doublet on the same scale is 1/1 - 1/2 = ½. This effect is probably not accessible to experiment; for in the most favorable case, that of lithium,[15] the separation of the p-doublet is sufficiently large, so that extremely high fields are required to produce the partial effect; and the separation of the levels J = 1 and K = ½ is probably even greater than the above result would indicate, owing to an increase in the effective quantum number.

Section 12. Other results. This Part will now be concluded with a brief mention of certain further consequences of the theory which have been developed by various investigators.

The discussion of magnetic effects in the preceding section referred only to the two extreme cases in which the effect of the magnetic field is small (anomalous Zeeman effect) or very large (Paschen-Back transformation) in comparison with the spin terms. It is also possible to discuss the intermediate Paschen-Back effect, in which the magnetic and spin terms are of the same order of magnitude. This has been carried out on the matrix dynamics by Heisenberg and Jordan,[14] in a paper which handles the whole subject matter of the present part from that point of view.

It is also possible to discuss the behaviour of the hydrogen-like fine structure in a magnetic field. Here what corresponds to the anomalous Zeeman effect can scarcely be observed. The intervals between the separate non-magnetic lines are already near the limit of observation, so that a Zeeman pattern small in comparison to these intervals is hardly accessible to experiment. If now the field is increased, the magnetic effect becomes simultaneously of the same order of magnitude as the interval between levels of differing J and of differing K,

which gives a very complex intermediate Paschen-Back effect;while for high fields,in which the experimental technique becomes difficult,there is a complicated overlapping of the Lorentz triplets due to the various values of K;these triplets should overlap with out disturbing one another.

Sommerfeld and Unsöld [27] have attempted an application of the summation rules of Burgers and Dorgelo to the intensities in the fine structure,treating it as a special case of a doublet system. However,the theoretical foundation of these rules implies the whole of the new dynamics;and as the equations representing the system are now undergoing a fundamental revision,these results must be regarded as provisional.

Finally,the hypothesis of a spinning electron,in conjunction with Pauli's exclusion principle,has been applied to the systematization of practically all multiplet spectra,involving the theory of atoms with more than one valence electron. This is a vast subject which can only be referred to here;the most available systematic presentation is Hund,Linienspektren.

Part III. Theory of the Spinning Electron in Wave Mechanics.

Sect. 1. Introduction. The formulae for energy levels derived in Part II actually represent the observed facts, and the discussion there givem of their physical consequences is substantially correct. Such a discussion, being stated in terms of classical mechanics, has the advantage of greater clearness, owing to the simple and familiar character of the principles employed; but it is theoretically unsatisfactory, since we now know that classical dynamics is not strictly applicable to atomic processes. It is even logically unsatisfactory, since the physically significant results are obtained by the highly arbitrary device of a "Heisenberg substitution," a procedure which can only be justified by theoretical considerations based on quantum dynamics.

A less objectionable procedure is to introduce a modification corresponding to the spinning electron into the equations of quantum dynamics, and to derive the required formula by the methods in use in that subject. Until recently, this has been done by taking the Hamiltonian equation (8) used in Part II (including the Thomas factor $\frac{1}{2}$), and translating this into quantum dy-

namics by the rules in use for such purposes. Not only is this method subject to all the uncertainties, discussed in Section 1 of Part II, which attend the setting up of the Hamiltonian function in question, but, as shortly will appear, it gives rise to new and unexpected difficulties of its own.

The most adequate theory of this type is that given by Heisenberg and Jordan in the paper already referred to.[14] The given Hamiltonian function is translated into a matrix expressions, and the energy levels are then derived by matrix operations. The authors thus derive the formulae found in Part II, as well as others, such as those for the intermediate Paschen-Back effect. No additional assumptions beyond those of Part II are involved.

The advent of Schrödinger's wave mechanics naturally gave rise to numerous attempts at stating the theory of Part II in this physically interesting and mathematically attractive form. The writer at one time believed he had succeeded in such an attempt, and published a preliminary report of his results;[23] subsequently an error was discovered, due to a difficulty clearly stated in a paper by Darwin.[2]

As the writer's investigations coincide with part of Darwin's, the presentation of the method will take a con-

siderably more abbreviated form than would have been proper for Part II, which contains much unpublished material. The method is again to take the Hamiltonian equation of Part II, but now to translate this into wave mechanics by the use of a rule due to Schrödinger. The resulting problem can be solved, but gives rise to the difficulty mentioned above, namely that the boundary conditions of the equation require the quantum number associated with the spin to be an integer, while in order to obtain doublet spectra - or any spectra of even multiplicity - it is necessary to take it as a half integer.

Devices for avoiding this difficulty were given by Pauli [20] and by Darwin [3]. These form the incomplete foundation on which Dirac has very recently [5] set up a theory of an entirely new type, which not only eliminates the trouble just mentioned, but also disposes of the difficulties in setting up the Hamiltonian function, by dispensing with the mechanical model of a spinning electron.

Before taking up the writer's now superseded investigations we shall consider a problem corresponding to that studied in Section 2, Part II.

Sect. 2. The effect of a dipole in the nucleus.

Schrödinger's general equation for an electron moving in an electromagnetic field independent of time, neglecting the effect of relativity, is

$$\nabla^2\psi + \frac{4\pi i e}{hc}(\bar{A}\cdot\nabla\psi) + \frac{8\pi^2 m}{h^2}[E - eV]\psi = 0 \qquad (24)$$

where $\bar{A}$ is the vector potential and V the scalar potential. The equation for the case when the magnetic field is due to a dipole in the nucleus was first given by Fock ; we derive it as follows. Let the dipole have a magnetic moment $Z\mu$, the vector representing this moment being fixed in the direction of the negative z-axis. (This is the dipole substantially equivalent in its classical effect to the spin. See Appendix 3.) Then

$$A_x = -\frac{Z\mu}{r^3}y, \quad A_y = +\frac{Z\mu x}{r^3}, \quad A_z = 0$$

and

$$A\cdot\nabla\psi = -\frac{Z\mu}{r^3}\left(y\frac{\partial\psi}{\partial x} - x\frac{\partial\psi}{\partial y}\right) = \frac{Z\mu}{r^3}\frac{\partial\psi}{\partial\varphi}$$

We now put $\mu = eh/4\pi mc$, supposing the electron to have an angular momentum of half a quantum unit, i.e. $h/4\pi$. Then

$$\nabla^2\psi + \frac{iZe^2}{mc^2r^3}\frac{\partial\psi}{\partial\varphi} + \frac{8\pi^2 m}{h^2}\left(E + \frac{Ze^2}{r}\right)\psi = 0 \qquad (25)$$

Professor Epstein [8] has discussed this problem, with the additional refinement of allowing for the effect of relativity, using a method current previous to the recent theory of Dirac. He also introduces the Thomas factor $\frac{1}{2}$ into the dipole term.

His equation can be put in the form

$$\nabla^2\psi+\left(A+\frac{2B}{r}+\frac{C}{r^2}+\frac{imQ}{r^3}\frac{\partial}{\partial\varphi}\right)\psi=0 \qquad (26)$$

in which the abbreviations are

$$A=\frac{4\pi^2E}{h^2c^2}(E+2mc^2),\ B=\frac{4\pi^2Ze^2}{h^2c^2}(E+mc^2),\ C=\frac{4\pi^2Z^2e^4}{h^2c^2},\ Q=\frac{Ze^2}{2m^2c^2},$$

and terms depending on the time and the square of the vector potential are omitted. He finds for the energy levels, to the first order of approximation,

$$E=-\frac{RhZ^2}{n^2}-\frac{Rh\alpha^2Z^4}{n^4}\left(\frac{n}{l+\frac{1}{2}}-\frac{3}{4}\right)+\frac{Rh\alpha^2Z^4}{2n^3}\frac{n_1}{l(l+\frac{1}{2})(l+1)} \qquad (27)$$

in which n is a positive integer, l is a positive integer or zero, and n_1 is an integer or zero. If now $n_1=+l$ or $-l-1$ the two last terms combine, and

$$E=-\frac{RhZ^2}{n^2}+\frac{Rh\alpha^2Z^4}{2n^3}\left(\frac{n}{j}-\frac{3}{4}\right),\quad j=\begin{cases} l \text{ if } n_1=-l-1 \\ -l-1 \text{ if } n_1=l \end{cases} \qquad (28)$$

which represents the observed fine structure.* Since the characteristic values of the equation with relativity correction but no dipole terms are, as worked out by Epstein, Schrödinger, and others,

$$E_n=-\frac{RhZ^2}{n^2}+\frac{Rh\alpha^2Z^4}{n^4}\left(\frac{n}{l+\frac{1}{2}}-\frac{3}{4}\right) \qquad (29)$$

it is evident that the characteristic values of our present equation (25) are

$$E_d=-\frac{RhZ^2}{n^2}+\frac{Rh\alpha^2Z^4}{2n^3}\cdot\frac{2n_1}{l(l+\frac{1}{2})(l+1)}.$$

This solution bears a simply demonstrable relation to that of the general equation of the spinning electron problem, to be set up in the next section, and will be used to obtain the result more readily.

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*Note that this demands a half quantum for the spin. The relation of E to the similar expression on classical mechanics (Sect. 2 Part II) is interesting.

Sect. 3. The Schrödinger wave equation for hydrogen-like atoms having a rotating spherical electron. We begin by rewriting the Hamiltonian equation used in Part II in the form

$$H = \frac{1}{2m}\left[p_r^2 + \frac{p_\theta^2}{r^2} + \frac{p_\varphi^2}{r^2\sin^2\theta}\right] + \frac{1}{2I}\left[p_\theta^2 + \cot^2\theta\left(p_\psi^2 + p_\Phi^2 - 2p_\psi p_\Phi \cos\theta\right)\right]$$
$$- \frac{Ze^2}{r} + \frac{Q}{r^3}\left[\cos\alpha\, p_\vartheta p_\theta - \cot\theta\sin\alpha\, p_\vartheta p_\psi + \csc\theta\sin\alpha\, p_\theta p_\Phi\right. \qquad (31)$$
$$\left. + \cot\vartheta\sin\alpha\, p_\varphi p_\theta + (1 + \cot\vartheta\cot\theta\cos\alpha) p_\varphi p_\psi - \cot\vartheta\csc\theta\cos\alpha\, p_\varphi p_\Phi\right]$$

in which all the symbols have the meanings with which they were there employed, and we have introduced the two additional abbreviations $\alpha = \psi - \varphi$ and $Q = Ze^2/2m^2c^2$.

The part of H which depends on the momenta is a quadratic form, so that we can at once derive the corresponding wave equation from Schrödinger's variation principle.[25] The result* proves to be the same as that easily obtained by the operational method. Calling the wave function u, since ψ is in use as a coordinate, we have

$$\nabla^2 u + \frac{m}{I}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial u}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\left[\frac{\partial^2 u}{\partial\psi^2} + \frac{\partial^2 u}{\partial\Phi^2} - 2\cos\theta\frac{\partial^2 u}{\partial\psi\partial\Phi}\right]\right\}$$
$$+ \frac{2mQ}{r^3}\left\{\cos\alpha\frac{\partial^2 u}{\partial\vartheta\partial\theta} - \cot\theta\sin\alpha\frac{\partial^2 u}{\partial\vartheta\partial\psi} + \csc\theta\sin\alpha\frac{\partial^2 u}{\partial\vartheta\partial\Phi}\right.$$
$$+ \cot\vartheta\sin\alpha\frac{\partial^2 u}{\partial\varphi\partial\theta} + \left[1 + \cot\vartheta\cot\theta\cos\alpha\right]\frac{\partial^2 u}{\partial\varphi\partial\psi}$$
$$\left. - \cot\vartheta\csc\theta\frac{\partial^2 u}{\partial\varphi\partial\Phi}\right\} + \frac{8\pi^2 m}{h^2}\left[E + \frac{Ze^2}{r}\right]u = 0 \qquad (32)$$

*The calculation is given in Appendix 9.

By introducing two very obvious abbreviations we may write

$$\nabla^2 u + \frac{m}{I}\nabla'^2 u + \frac{2mQ}{r^3} f(u) + \frac{8\pi^2 m}{h^2}\left[E + \frac{Ze^2}{r}\right]u = 0. \quad (33)$$

Section 4. The solutions of the unperturbed equation.

We have now to treat the above wave equation by the method of perturbations, taking $\frac{2mQ}{r^3} f(u)$ as the perturbing term. A theory of perturbations for this type of problem is given by Schrödinger[24]; the method used in what follows is a modification due to Professor Epstein.

We begin in the usual way by considering the solutions of the unperturbed equation

$$\nabla^2 u_0 + \frac{m}{I}\nabla'^2 u_0 + \frac{8\pi^2 m}{h^2}\left[E_0 + \frac{Ze^2}{r}\right]u_0 = 0. \quad (34)$$

This equation corresponds to a spherical electron revolving about the nucleus and simultaneously rotating, the two motions not affecting one another. A characteristic function u_0 is then the product of functions characteristic of these two motions, and E_0 is the sum of the corresponding energy parameters.

The first of these two partial solutions is the well-known solution due to Schrödinger; ~~already used in Section 2 of this Part~~; the second is a special case of the solution for the symmetrical top, worked out by Reiche and Rademacher.[21] Combining these, we have

$$u_0 = \chi_n^{\ell}(r)\, P_\ell^{n_1}(\cos\vartheta)\, T(\theta)\, e^{i(n_1\varphi + n_2\psi + n_3\Phi)} \qquad (35)$$

$$T(\theta) = \left(\sin\tfrac{\theta}{2}\right)^d \left(\cos\tfrac{\theta}{2}\right)^s F\left(-p,\, 1+d+s+p,\, 1+d,\, \sin^2\tfrac{\theta}{2}\right) \qquad (36)$$

$$E_0 = -\frac{Rh}{n^2} + \frac{h^2}{8\pi^2 I}\sigma(\sigma+1) \qquad (37)$$

Here $\chi_n^{\ell}(r)$ is ~~again~~ Schrödinger's function for the quantum numbers n and ℓ, $P_\ell^{n_1}$ is an associated Legendre function, and F is a hypergeometric function. n is a positive integer. $n_1, n_2, n_3, \ell, d, s, p$ are intergers or zero, of which the four last cannot be negative; in fact, $d = |n_2 - n_3|$ and $s = |n_2 + n_3|$. Finally $\frac{1}{2}(d+s) + p = \sigma$, so that σ is a positive integer or zero.

From the expression of E_0 it appears that $\sigma(\sigma+1)$ takes the place of s^2 in the theory of Part II. This is the ordinary relation of the manner, in which a quantum number of the type associated with an angular momentum enters the energy in the quantum dynamics, to the manner in which it enters in the classical dynamics. Since we took $s = 1$, it is natural, and in fact almost compulsory, to take $\sigma = 1$. This leads to difficulties, as we shall see.

This choice of σ has the advantage of bringing about a great simplification in our expressions. The writer has worked out the relations for any general value of σ; but as the results are only a part of those which Darwin [2] has published in a more finished form, they are scarcely

worth inclusion in this thesis. The relations become extremely complicated and cumbersome to handle, and the results contribute nothing to the solution of the difficulties in hand. They do not even represent the physical facts to a first approximation; for Darwin[2] has shown that to obtain the observed results for doublet spectra we must take $\sigma = \frac{1}{2}$, which is excluded by the boundary conditions. The writer's work was exclsuively with integral values of σ, and consequently failed of even this result.

The choice of $\sigma = 1$ limits the choice of p, d, s, n_2, and n_3, and greatly simplifies the expression for T. We are limited to the following cases:

p	d	s	n_2	n_3	F	T
1	0	0	0	0	cosθ	cosθ
0	2	0	±1	∓1	1	$\frac{1}{2}(1-\cos\theta)$
0	1	1	0	±1	1	$\frac{1}{2}\sin\theta$
0	1	1	±1	0	1	$\frac{1}{2}\sin\theta$
0	0	2	±1	±1	1	$\frac{1}{2}(1+\cos\theta)$

Section 5. Introduction of method of perturbations. Into equation (32) we now substitute $u = u_0 + 2mQv$ and $E = E_0 + 2mQ\epsilon$. We assume that v and ϵ are small, so that their product can be neglected; the result, correct to the first order of small quantities, is then

$$\nabla^2 v + \frac{m}{I}\nabla'^2 v + \frac{8\pi^2 m}{h^2}\left[E_0 + \frac{Ze^2}{r}\right]v + \frac{8\pi^2 m}{h^2}\epsilon u_0$$
$$+ \frac{1}{r^3}\left[\cos\alpha \frac{\partial^2 u_0}{\partial\theta\partial\theta} - \cot\theta \sin\alpha \frac{\partial^2 u_0}{\partial\theta\partial\psi} + \operatorname{cosec}\theta \sin\alpha \frac{\partial^2 u_0}{\partial\theta\partial\Phi}\right. \qquad (38)$$
$$\left. + \cot\theta \sin\alpha \frac{\partial^2 u_0}{\partial\varphi\partial\theta} + \left\{1 + \cot\theta\cot\theta\cos\alpha\right\}\frac{\partial^2 u_0}{\partial\varphi\partial\psi} - \cot\theta\operatorname{cosec}\theta\cos\alpha \frac{\partial^2 u_0}{\partial\varphi\partial\Phi}\right] = 0$$

Substituting for u_0 its value

$$\nabla^2 v + \frac{m}{I}\nabla'^2 v + \frac{8\pi^2 m}{h^2}\left[E_0 + \frac{Ze^2}{r}\right]v$$
$$= -\frac{1}{r^3}\chi_n^{\ell}(r)\, e^{i(n_1\varphi + n_2\psi + n_3\Phi)}\left[\cos\alpha\, P'\Pi' - i n_2 \sin\alpha\, P'\Pi\cot\theta\right.$$
$$\left. + i n_3 \sin\alpha\, P'\Pi\operatorname{cosec}\theta + i n_1 \sin\alpha\, P\cot\theta\,\Pi' - n_1 n_2 \cos\alpha\cot\theta\cot\theta\, P\Pi\right.$$
$$\left. + n_1 n_3 \cos\alpha\cot\theta\operatorname{cosec}\theta\, P\Pi - n_1 n_2 P\Pi'\right] - \frac{8\pi^2 m}{h^2}\epsilon\chi_n^{\ell}(r) P\Pi\, e^{i(n_1\varphi + n_2\psi + n_3\Phi)}$$
$$= 0 \qquad (39)$$

where $P' = \dfrac{dP_\ell^{n_1}}{d\theta}$ and $\Pi' = \dfrac{d\Pi_{n_2}^{n_3}}{d\theta}$. By putting the cosine and sine of α into exponentials this reduces to

$$\nabla^2 v + \frac{m}{I}\nabla'^2 v + \frac{8\pi^2 m}{h^2}\left[E_0 + \frac{Ze^2}{r}\right]v$$
$$- \frac{1}{2r^3}\chi_n^{\ell}(r)\, e^{i(n_1\varphi + n_2\psi + n_3\Phi)}\left[e^{i\alpha}(P' + n_1 P\cot\theta)(\Pi' - n_2\Pi\cot\theta + n_3\Pi\operatorname{cosec}\theta)\right.$$
$$\left. + e^{-i\alpha}(P' - n_1 P\cot\theta)(\Pi' + n_2\Pi\cot\theta - n_3\Pi\operatorname{cosec}\theta) - 2n_1 n_2 P\Pi\right]$$
$$- \frac{8\pi^2 m}{h^2}\epsilon\chi_n^{\ell}(r)\, P\Pi\, e^{i(n_1\varphi + n_2\psi + n_3\Phi)} = 0 \qquad (40)$$

We now apply the reduction formulae* for $P_\ell^{n_1}$:

$$\left.\begin{aligned} P_\ell^{n_1+1} - n_1\cot\theta\, P_\ell^{n_1} &= \xi P_\ell^{n_1+1}, \\ P_\ell^{n_1\,\prime} + n_1\cot\theta\, P_\ell^{n_1} &= \eta(\ell + n_1)(\ell - n_1 + 1)\, P_\ell^{n_1-1} \end{aligned}\right\} \qquad (41)$$

where ξ is -1 if $n_1 \geq 0$, and $+1$ if $n_1 < 0$, while η is $+1$ if $n_1 > 0$, and -1 if $n_1 \leq 0$.

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*For these reduction formulae see Appendix 10.

and also the reduction formulae for T * in the case when σ is 1*

$$T' + (n_2 \cot\theta - n_3 \operatorname{cosec}\theta) T = \lambda_{n_2}^{n_3} T_{n_2-1}^{n_3},$$
$$T' - (n_2 \cot\theta - n_3 \operatorname{cosec}\theta) T = \mu_{n_2}^{n_3} T_{n_2+1}^{n_3}. \qquad (42)$$

in which the values of $\lambda_{n_2}^{n_3}$ and $\mu_{n_2}^{n_3}$ are given in the following tables:

$\lambda_{n_2}^{n_3}$

n_3 \ n_2	1	0	-1
1	-2	-1	0
0	1	-2	0
-1	2	1	0

$\mu_{n_2}^{n_3}$

n_3 \ n_2	1	0	-1
1	0	1	2
0	0	-2	1
-1	0	-1	-2

(43)

If we introduce the further notation

$$P_\ell^{n_1} e^{i n_1 \varphi} = Y_\ell^{n_1}, \quad T_{n_2}^{n_3} e^{i(n_2\psi + n_3\Phi)} = Z_{n_2}^{n_3}, \qquad (44)$$

so that $u_0 = \chi_n^\ell Y_\ell^{n_1} Z_{n_2}^{n_3}$, (45)

the final form of the equation is

$$\nabla^2 V + \frac{m}{I}\nabla'^2 V + \frac{8\pi^2 m}{h^2}\left[E_0 + \frac{Ze^2}{r}\right] V$$
$$- \frac{1}{2r^3}\chi_n^\ell(r)\Big[\eta(n_1)\mu_{n_2}^{n_3} Y_\ell^{n_1-1} Z_{n_2+1}^{n_3} (\ell+n_1)(\ell-n_1+1)$$
$$+ \xi(n_1)\lambda_{n_2}^{n_3} Y_\ell^{n_1+1} Z_{n_2-1}^{n_3} - 2n_1 n_2 Y_\ell^{n_1} Z_{n_2}^{n_3}\Big]$$
$$- \frac{8\pi^2 m}{h^2}\epsilon\chi_n^\ell(r) Y_\ell^{n_1} Z_{n_2}^{n_3} = 0. \qquad (46)$$

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*Appendix 10.

We now introduce into this and equation (3γ) the quantity $\beta = -4\pi^2 mZe^2/nh^2$, whereupon we obtain

$$\nabla^2 u_0 + \frac{m}{I}\nabla'^2 u_0 - \left[\beta^2 + \frac{2\beta n}{\lambda} + \frac{m}{I}\sigma(\sigma+1)\right] u_0 = 0 \qquad (47)$$

$$\nabla^2 v + \frac{m}{I}\nabla'^2 v - \left[\beta^2 + \frac{2\beta n}{\lambda} + \frac{m}{I}\sigma(\sigma+1)\right] v$$
$$= \frac{1}{2\lambda^3}\left[\eta(n_1)\mu_{n_2}^{n_3}(\ell+n_1)(\ell-n_1+1)\, u_0(n,\sigma,\ell,n_1-1,n_2+1,n_3)\right.$$
$$+ \xi^*(n_1)\lambda_{n_2}^{n_3} u_0(n,\sigma,\ell,n_1+1,n_2-1,n_3) - 2n_1 n_2 u_0(n,\sigma,\ell,n_1,n_2,n_3)$$
$$\left. + 8\pi^2 m \in u_0(n,\sigma,\ell,n_1,n_2,n_3)\right) \qquad (48)$$

Our present problem is the expansion of the right side of (48) in terms of the solutions of (47) for varying n; if we succeed in carrying out this expansion, a large body of general theory becomes available for our use. Now if β has the value given above, it is different for the different forms of u_0; the functions defined by (47) are simply the product of the Schrödinger and Reiche functions. But it is equally possible to regard β in (47) as a constant independent of n. The equation is still of the Sturm-Liouville type,* so that the solutions satisfying the boundary conditions still form a complete orthogonal system, though of course a different system from that with variable β. The dependence on r, that is the form of the function $\chi_n^{\ell}(\rho)$, is changed; the factors depending on the other coordinates are unaltered. The orthogonal property is modified only with respect to r; in place of $\int_0^\infty \chi_n^{\ell}\chi_{n'}^{\ell} r^2 dr = 0$ we now have $\int_0^\infty \chi_n^{\ell}\chi_{n'}^{\ell}\, r\, dr = 0$ *. With this understanding the possibility of expansion

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*Appendix 11. This highly ingenious device is due to Professor Epstein.

in terms of the functions u_o is retained. Onw futther property calls for remark: β ,being a fixed constant,is to some extent arbitrary. It is then possible to take $\beta = -4\pi^2 mZe^2/h^2 n$,where n is the value of the quantum number n occurring on the left side of (47). One of the functions u_o then coincides with a particular one of the original set.*

Now it easily shown from general considerations** that if the right side of such an equation as (48) be expanded in a series of 1/r times the functions u_o the coefficient of the term which contains the same function as that appearing on the left must vanish; otherwise v cannot satisfy the requirements of finiteness.

The original problem is degenerate;the parameter E depends only on the two indices n and σ . This means that u_o,and consequently the quantity on the right of (48) which is derived from it,will in general consist of a linear combination of partial solutions of the type indicated by (33) and (45),involving all the combinations of the indices ℓ ,n_1,n_2,n_3 which are consistent with the values of n and σ appearing on the left of (48). However, since only n1 and n2 are altered in the terms on the

*It has not been thought necessary to intmduce a new notation for these modified functions.

** Appendix 12.

right, it will be unnecessary to consider u_0 as composed of terms with varying ℓ or n_3; the equations obtained for the energy levels would simply break up into a set of independent equations, one for each level with constant ℓ and n_3. (It will appear that the energy is independent of n_3.)

We introduce the following three expansions, the first of which is assumed with undetermined coefficients, while the last two must be constructed by integration.

$$(1)\quad u_0(n,\sigma,\ell,n_1,n_2,n_3) = \sum_{n_1' n_2'} K\ u_0(n,\sigma,\ell,n_1',n_2',n_3) \qquad (49)$$

where u_0 on the right represents the partial solution given by $\chi_n^\ell Y_\ell^{n_1} Z_{n_2}^{n_3}$.

$$(2)\ \frac{1}{\Omega^3}\chi_n^\ell = \frac{1}{\Lambda}\sum_{n'} A_{n'}\chi_{n'}^\ell \qquad ;(3)\quad \Lambda\chi_\eta^\ell = \sum_{n'} B_{n'}\chi_{n'}^\ell \qquad (50)$$

This gives

$$\nabla^2 V + \frac{m}{I}\nabla'^2 V - \left[\beta^2 + \frac{2\rho n}{\Lambda} + \frac{m}{I}\sigma(\sigma+1)\right]V$$

$$= \frac{1}{\Lambda}\sum_{n_1', n_2'} K_{n_1'}^{n_2'}\left\{\left(\frac{8\pi^2 m\epsilon}{h^2}B_{n'} - n_1' n_2' A_{n'}\right)u_0(n',\sigma,\ell,n_1',n_2',n_3')\right.$$

$$\tfrac{1}{2}\eta(n_1')\,\mu_{n_2'}^{n_3}(\ell+n_1')(\ell-n_1'+1)\,A_{n'}\,u_0(n',\sigma,\ell,n_1'-1,n_2'+1,n_3)$$

$$\left.+\tfrac{1}{2}\xi(n_1')\lambda_{n_2'}^{n_3}A_{n'}\,u_0(n',\sigma,\ell,n_1'+1,n_2'-1,n_3)\right\} \qquad (51)$$

$$= \frac{1}{\Lambda}\sum_{n_1', n_1', n_2'}\left\{K_{n_1'}^{n_2'}\left(\frac{8\pi^2 m\epsilon}{h^2}B_{n'} - n_1' n_2' A_{n'}\right) + \frac{1}{2}K_{n_1'+1}^{n_2'-1}\eta(n_1'+1)\mu_{n_2'-1}^{n_3}(\ell+n_1'+1)(\ell-n_1')A_{n'}\right.$$

$$\left.+\tfrac{1}{2}K_{n_1'-1}^{n_2'+1}\xi(n_1'-1)\lambda_{n_2'+1}^{n_3}A_{n'}\right\}u_0(n',\sigma,\ell,n_1',n_2',n_3). \qquad (52)$$

According to theory*, the coefficient on the right having indices the same as on the left must vanish.

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*Appendix 12.

This leads to a set of $3(2\ell + 1)$ homogeneous linear equations in the $3(2\ell + 1)$ unknowns $K_{n_1}^{n_2}$;for from Schrödinger's theory $-\ell \leqslant n_1 \leqslant \ell$,while we have seen that n_2 in our case is -1,0,or 1.

In order that these equations may be consistent the determinant of the coefficients of the K's must vanish. This gives a set of $2\ell + 1$ cubic equations in ϵ ,* which are easily solved,all having the roots

$$\epsilon = -\frac{h^2}{8\pi^2 m}\frac{A_n}{B_n}, \epsilon = +\ell\frac{h^2}{8\pi^2 m}\frac{A_n}{B_n}, \epsilon = -(\ell+1)\frac{h^2}{8\pi^2 m}\frac{A_n}{B_n}. \quad (53)$$

The existence of such a triplet of levels instead of the expected doublet indicated that something is wrong with our procedure;but there remains the possibility that the explicit expressions of A_n and B_n may in some way remove the difficulty.

The next step in order would be to compute these coefficients A_n and B_n by integration,using the orthogonal properties of the functions χ_n^ℓ ;this is an easy matter for individual states of low quantum number,and such a case is accordingly computed in an appendix* for the sake of an example. For any quantum numbers in general the process is less simple,and we shall take refuge in a special device.

The equation for the case of a fixed dipole in the

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*Appendix 14.

nucleus may be treated by applying the same method of perturbations which we have been using to equation of Section 2. The result has a very close relation to that of our present problem, and it will be shown that we can apply Professor Epstein's solution of the dipole problem to our more complex case.

Section 6. Application of the same method to the fixed-dipole problem. Equation (25) is so much simpler than those which we have been discussing that we can obtain the results we need by little more than a specialization of those already in hand. We rewrite the equation in the form

$$\nabla^2 u + \frac{i \cdot 2mQ}{r^3}\frac{\partial u}{\partial \varphi} + \frac{8\pi^2 m}{h^2}\left(E + \frac{Ze^2}{r}\right)u = 0 \qquad (54)$$

and substitute $u = u_0 + 2mQv$, $E = E_0 + 2mQ\epsilon$, where

$$\nabla^2 u + \frac{8\pi^2 m}{h^2}\left(E_0 + \frac{Ze^2}{r}\right)u_0 = 0 \qquad (55)$$

We find

$$\nabla^2 v + \frac{8\pi^2 m}{h^2}\left(E_0 + \frac{Ze^2}{r}\right)v = -i\frac{\partial u_0}{\partial \varphi} - \frac{8\pi^2 m\epsilon}{h^2}u_0 \qquad (56)$$

Now $u_0 = \chi_n^{\ell}(r)\, P_{\ell}^{n_1}(\cos\vartheta)\, e^{i n_1 \varphi}$.

so that $\frac{\partial u_0}{\partial \varphi} = i n u_0$; substituting this and introducing our two expansions in terms of modified functions* (50)

$$\nabla^2 v + \frac{8\pi^2 m}{h^2}\left(E_0 + \frac{Ze^2}{r}\right)v = \frac{1}{r}\sum_{n'}\left(n_1 A_{n'} - \frac{8\pi^2 m\epsilon}{h^2}B_{n'}\right)u_0(n', \ell, n_1) \qquad (57)$$

Since again the coefficient of $u_0(n, \ell, n_1)$ on the right must vanish,

$$\epsilon = \frac{h^2}{8\pi^2 m}\, n_1 \frac{A_n}{B_n} \qquad (58)$$

*The justification of this procedure is even simpler than in the complicated case.

From this

$$2mQ\epsilon = E_1' = 2mQ \frac{An}{Bn} \frac{h^2}{8\pi^2 m} n_1 \qquad (59)$$

But from Professor Epstein's results we have seen that we must have

$$E_1' = \frac{R\alpha^2 Z^4 h}{n^3} \cdot \frac{n_1}{\ell(\ell+\frac{1}{2})(\ell+1)}, \qquad (60)$$

so that the two quantities on the right must be equal. This is a mere mathematical identity, which we can now apply to our problem.*

Section 7. Final solution of the spinning electron problem for $\sigma = 1$. From the results of Section 5 we have for our problem $E_1 = 2mQ \frac{A_n}{B_m} \frac{L\, h^2}{8\pi^2 m}$, in which L may have any of the three values $-1, \ell, -\ell - 1$. Applying the above identity

$$E_1 = -\frac{R\alpha^2 Z^4 h}{n^3} \frac{L}{\ell(\ell+\frac{1}{2})(\ell+1)}. \qquad (61)$$

We have derived this result from an equation in which relativity is neglected. It is obvious that a general equation including relativity effects would bear the same relation to ours that the equation solved by Professor Epstein does to our dipole equation (54). The result will be the addition to our E of the same terms as form the difference between the characteristic values of (25) and (26).

*This agrees exactly with the result of Appendix 14.

For the complete expression of the energies of our problem we have

$$E = -\frac{Rh\alpha^2 Z^4}{n^2} - \frac{Rh\alpha^2 Z^4}{n^4}\left(\frac{n}{\ell+\frac{1}{2}} - \frac{3}{4}\right) + \frac{Rh\alpha^2 Z^4}{n^3}\frac{L}{\ell(\ell+\frac{1}{2})(\ell+1)} \quad (62)$$

L again has the three values $-l, \ell, -\ell - 1$; the energy level is a triplet instead of the expected doublet. There is no way out of this difficulty. We could, indeed, represent the observed spectra by assuming that the spin contribution must still be divided by 2, and throwing out the value L = 1 as spurious; but as our original equation already included the Thomas factor $\frac{1}{2}$, such a procedure would be altogether without justification.

Darwin has shown that in general any integral choice of σ leads to an odd multiplicity, of order $2\sigma + 1$. For doublets we must have $\sigma = \frac{1}{2}$; but this conflicts with the conditions that u is single-valued. It has been suggested that we might allow double-valued functions, reserving single-valuedness for u^2, which is the physically important quantity; but this allows n_1 to take half-integral values, which introduces new energy levels corresponding to half-integral values of n, which conflicts with observation. The difficulty is only to be removed by a complete revision of the theory, as will be sketched in the Conclusion.

Part IV. Conclusion.

From the discussion presented in Part II it must be evident that, in spite of numerous uncertainties and inaccuracies, the hypothesis of Uhlenbeck and Goudsmit has proved one of the most fruitful in modern physics. It has served to bring order into what was previously a puzzling mass of complicated phenomena.

The spinning electron has been of most importance in the theory of atomic structure, though it enters into the discussion of every subdivision of the quantum theory. In view of the fact that the rapid growth of the quantum dynamics has widened and deepened our conceptions of quantum phenomena to such an extent that visualization of the mathematical relations involved is usually difficult and sometimes apparently impossible, it is well to remember that progress in physics, especially in experimental physics, depends largely on a geometrical representation of the phenomena being studied. It is for this reason that those investigators who are actively engaged in applying the hypothesis to atomic theory continue to use the clearer mechanical model, despite the fact that quantum dynamics renders such an interpretation incomplete.

The efforts to state the hypothesis in terms of the new dynamical principles are of course necessary and of the highest importance. Until recently the only nearly compleye success in this direction was that of Heisenberg and Jordan,[14] although most of the uncertainties attaching to the theory of Part II remain associated with their work.

All attempts to represent the spinning electron in wave mechanics at first came to grief on the difficulties explained at the close of Part III. The first escape from this blind alley occurs in a paper by Pauli,[20] in which he adopts the device of setting up a wave equation involving the three components of angular momentum of the electron instead of the three Eulerian angles of rotation. Pauli's work was open to the objection that no reason appears why this method should succeed where the more obvious one fails. An equivalent mathematical procedure was interpreted by Darwin[3] as meaning that the Schrödinger wave of the electron is a transverse wave, specified by two amplitudes instead of one.

These two theories still failed in one respect dommon to all discussions of the spinning electron previous to the present year. The equations set up not being invariant, the facts of observation were represented correctly only to the first order of approximation, that is, to

terms of the order v^2/c^2, where v is the velocity of the electron on the Bohr theory. Moreover, one would expect from a complete theory some explanation of the curious fact that the spin correction comes out with exactly the same coefficient as the relativity term.

Both these points are settled by the new theory of Dirac.[5] Much of the mathematical apparatus developed to handle problems in the new dynamics depends on the fact that the Schrödinger wave equation is linear in the energy parameter E. As will be seen from equation (Section 2, Part III), this was no longer true of the relativistic generalization of the equation formerly in use. Presupposing the necessity of such a linearity in E, and adding thw requirement of relativistic invariance, Dirac has been able to set up a system of equations which correctly represent all the phenomena ascribed to the spinning electron and to the relativity change of mass; in particular, as shown by Darwin [4] and by Gordon,[10] they lead without approximation to the experimentally verified Sommerfeld expression for the energy levels of the fine structure and of X-ray spectra. Thus the mechanical hypothesis of an electron with a given angular momentum and magnetic moment has apparently disappeared; the present writer believes that this is a temporary eclipse, and expects that a geometrical interpretation will shortly be brought forward.

Appendix 1.

Magnetic moment of a system of electrons.

By a theorem due to Schwarzschild the Lagrangian function for a system of electrons of charge -e and mass m, moving in a fixed electromagnetic field in which the vector potential is $\bar{A}$ and the total electrostatic potential energy (including mutual repulsions) is U, has the form

$$L = \frac{1}{2m}\sum(\dot{x}^2+\dot{y}^2+\dot{z}^2) - U - \frac{e}{c}\sum(\bar{A}\cdot\bar{v})$$

where the sum extends over all the electrons.

From this, neglecting terms in A^2, there follows

$$H = \frac{1}{2m}\sum(p_x^2+p_y^2+p_z^2) + U + \frac{e}{c}(\bar{A}\cdot\bar{v})$$

H is thus increased by the term $\sum \frac{e}{c}(\bar{A}\cdot\bar{v})$.

Now for a homogenous magnetic field $\bar{\mathcal{H}}$, $\bar{A} = \frac{1}{2}[\bar{\mathcal{H}}\times\bar{r}]$

We have $\frac{e}{c}\sum(\bar{A}\cdot\bar{v}) = \frac{e}{c}\sum\frac{1}{2}(\bar{\mathcal{H}}\cdot[\bar{r}\times\bar{v}]) = \frac{e\mathcal{H}}{2mc}p_\varphi$

if the axis of polar coördinates is in the direction of $\bar{\mathcal{H}}$.

Now the potential energy of a dipole of moment $\bar{\mu}$ in this field is $(\bar{\mathcal{H}}\cdot\bar{\mu})$; so that the additional energy is exactly that of a dipole of moment $\mu = ep/2mc$, with its axis in the direction of the total angular momentum p.

Appendix 2.

Theory of the rotating sphere with a surface charge.

The initial problem is to find the magnetic fields produced. The magnetic vector potential at any point is given by $\bar{A} = -\frac{1}{c}\int\int \frac{d\epsilon \cdot \bar{v}}{r'}$,

where $d\epsilon = \frac{e}{4\pi}\sin\vartheta' d\vartheta' d\varphi$ is an element of surface charge, $\bar{v}$ is the vector velocity of this element, and r' is the distance from the element $d\epsilon$ to the point at which the vector potential is being computed. Let the distance of this point from the center be r, and choose the polar axis so as to pass through the point. Then we may write $\frac{1}{r'} = \frac{1}{a}\sum_n \left(\frac{r}{a}\right)^n P_n(\cos\vartheta')$, $r < a$, and $\frac{1}{r'} = \frac{1}{r}\sum_n \left(\frac{a}{r}\right)^n P_n(\cos\vartheta')$, $r > a$.

Further, $\bar{v} = [\bar{\omega} \times \bar{a}]$, where $\bar{\omega}$ is the vector angular velocity of rotation and $\bar{a}$ is the vector from the center to $d\epsilon$.

That is, $v_{x'} = \omega_{y'} z' - \omega_{z'} y'$, $v_{y'} = \omega_{z'} x' - \omega_{x'} z'$, $v_{z'} = \omega_{x'} y' - \omega_{y'} x'$

in which $\omega_{x'}, \omega_{y'}, \omega_{z'}$ are all constants independent of the integration. Moreover, the initial plane can be so chosen that $\omega_{y'} = 0$; and finally, the terms in y' and x' will give no contribution to the integral, as they contain $\sin\varphi'$ and $\cos\varphi'$. The ultimate result is that $A_{x'} = A_{z'} = 0$, while

$$A_{y'} = \frac{e a}{4\pi}\int\int \frac{1}{r'}\omega_{x'}\cos\vartheta'\sin\vartheta' d\vartheta' d\varphi'$$

Now since $\cos\vartheta P_n(\cos\vartheta) = \frac{1}{2n+1}\left[(n+1)P_{n+1}(\cos\vartheta) + n P_{n-1}(\cos\vartheta)\right]$

only the term in the expansion of $1/r'$ for which $n = 1$

will contribute to the integral, giving a numerical factor 2/3. The integration over φ' gives a factor 2π, so that

$$A_{y'} = \frac{e\pi\omega_{x'}}{3a}, \; r < a \; ; = \frac{e a^2 \omega_{x'}}{3r^2}, \; r > a.$$

We now have all three components of $\bar{A}$, and can pass to a system of coördinates with polar axis or z-axis in the direction of $\bar{\omega}$. We find in every case $A_z = 0$.

For $r < a$, $A_x = -\frac{2e\pi}{3ca^2} \omega \sin\vartheta \sin\varphi$ and $A_y = \frac{2e\pi}{3ca^2} \omega \sin\vartheta \cos\varphi$.

For $r > a$, $A_x = -\frac{2ea}{3cr^3} \omega \sin\vartheta \sin\varphi$ and $A_y = \frac{2ea}{3cr^3} \omega \sin\vartheta \cos\varphi$.

This can be put in the form

For $r < a$, $A_x = -\frac{e\omega}{3ac} y$, $A_y = \frac{e\omega}{3ac} x$, $A_z = 0$.

For $r > a$, $A_x = -\frac{e\omega a^2}{3cr^3} y$, $A_y = \frac{e\omega a^2}{3cr^3} x$, $A_z = 0$.

These are the vector potentials of a uniform magnetic field of strength $\frac{2e\omega}{3ac}$, and of a dipole of moment $\frac{e\omega a^2}{3c}$, respectively.

The magnetic field is given by $\bar{H} = \text{curl } \bar{A}$; the energy density is then given by $E = \frac{H^2}{8\pi}$. The total magnetic energy within the sphere is found by integrating the value of E found from the first form of $\bar{A}$ over the interior; the result is $T_1 = \frac{2}{27} \frac{e^2\omega^2 a}{c^2}$.

The total energy outside the sphere is found by integrating the second form of E over all exterior space; this is

$$T_0 = \frac{1}{27} \frac{e^2\omega^2 a}{c^2}$$

Finally, the total magnetic energy, or kinetic energy of rotation, is given by

$$T = T_0 + T_1 = \frac{1}{9} \frac{e^2\omega^2 a}{c^2}.$$

We can now derive all the results used in this thesis.

(1) T can be written in the ordinary form of a kinetic energy of rotation, $T = \frac{1}{2}I\omega^2$; whence $I = 2e^2a/9c^2$. (If we introduce the "electromagnetic mass" $m = 2e^2/3ac^2$, we have $I = ma^2/3$.) The momentum p is $I\omega$; μ, as we have seen, is $e\omega a^2/3c$. From this $\mu/p = e/mc$, as we require.

(2) If the rotation is quantized, $p = I\omega = h/2\pi$. Since the equatorial velocity is $v_0 = a\omega$, we have $v_0 = ah/2\pi I$. Substituting, $v_0 = 9hc^2/4\pi e^2 = 9c/2\alpha$ $= 617\ c = 1.85 \times 10^{13}$ cm/sec. Note that this result depends only on universal constants.

(3) Since $T = \frac{1}{2}I\omega^2$ and $I\omega = h/2\pi$, $T = \omega h/4\pi$. Remembering that $\omega = v_0/a$, we have from (2) the result $T = 9h^2c^2/16\pi^2e^2a$.

Appendix 3.

Force of translation on the spinning electron.

A magnetic particle in an electrostatic field $\bar{E}$ moves as if subject to a magnetic field $\bar{H} = -\frac{1}{c}[\bar{v} \times \bar{E}]$, where $\bar{v}$ is the velocity of the particle. If the nucleus has charge $+Ze$ its field is $\bar{E} = +Ze\bar{r}/r^3$. Hence $\bar{H} = -\frac{1}{c}[\bar{v} \times \bar{E}]$. If the magnetic moment of the electron is represented by the vector $\bar{\mu}$ the force of translation $\bar{F}$ is given by

$$F_x = (\bar{\mu} \cdot \nabla H_x), \quad F_y = (\bar{\mu} \cdot \nabla H_y), \quad F_z = (\bar{\mu} \cdot \nabla H_z)$$

Substituting the value of $\bar{H}$ and reducing

$$\bar{F} = \frac{Ze}{cR^3}[\bar{v} \times \bar{\mu}] - \frac{3Ze}{cR^5}(\bar{\mu} \cdot \bar{R})[\bar{v} \times \bar{R}]$$

$$= -\frac{e}{c}[\bar{v} \times \bar{H}']$$

where $\bar{H}' = -\frac{Z}{R^3}\left[\bar{\mu} - 3\frac{(\bar{\mu} \cdot \bar{R})}{R^2}\bar{R}\right]$.

But $\bar{H}'$ is precisely the magnetic field of a dipole of moment $-Z\bar{\mu}$, the negative sign indicating that its direction is opposite to that of $\bar{\mu}$. $\bar{F}$ is exactly the force on a charge $-e$ moving in the field of this dipole; which was to be proved.

Appendix 4.

Evaluation of Δ L.

The procedure is similar to that used in Appendix 2.

We have to evaluate the integral

$$\iint \frac{de(\bar{v}\cdot[\bar{\omega}\times\bar{a}])}{r'}.$$

$(\bar{v}\cdot[\bar{\omega}\times\bar{a}]) = ([\bar{v}\times\bar{\omega}]\cdot\bar{a})$. Let $[\bar{v}\times\bar{\omega}] = \bar{\sigma}$; then the integral becomes (taking the z-axis parallel to r)

$$\frac{e}{4\pi}\iint \sin\vartheta\, d\vartheta\, d\varphi \left[\frac{1}{r}\sum_n \left(\frac{a}{r}\right)^n P_n(\cos\vartheta)\right]\left[\sigma_x a\sin\vartheta\cos\varphi + \sigma_y a\sin\vartheta\sin\varphi + \sigma_z a\cos\vartheta\right]$$

$$= \frac{eq\sigma_z}{4\pi z}\iint \sum \left(\frac{q}{r}\right)^n P_n(\cos\vartheta)\cos\vartheta\sin\vartheta\, d\vartheta$$

$$= \frac{2}{3}\frac{ea\sigma_z}{4\pi z}\cdot 2\pi\cdot\frac{a}{r}$$

$$= \frac{1}{3}\frac{ea^2}{r^2}\sigma_z .$$

$$\therefore \Delta L = -\frac{\Sigma e^2 a^2}{3c^2 r^2}[\bar{v}\times\bar{\omega}]_z$$

$$= -\frac{\Sigma e^2 a^2}{3c^2 r^3}\left([\bar{v}\times\bar{\omega}]\cdot\bar{r}\right)$$

Appendix 5.

Introduction of coördinates into the Lagrangian function.

The expressions of the kinetic energy of translation $\frac{1}{2}mv^2$ in terms of polar coördinates, and of the kinetic energy of rotation $\frac{1}{2}I\omega^2$ in terms of the Eulerian angles, are well known. (For the latter see Born, Atommechanik, p.31.) There remains the expression $([\bar{v}\times\bar{\omega}]\cdot\bar{r})$. This is equal to the determinant

$$\begin{vmatrix} v_x & v_y & v_z \\ x & y & z \\ x & y & z \end{vmatrix}$$

Using $x = r\sin\vartheta\cos\varphi$
$y = r\sin\vartheta\sin\varphi$
$z = r\cos\vartheta$

and $\omega_x = \sin\theta\cos\psi\dot{\Phi} - \sin\psi\dot{\theta}$
$\omega_y = \sin\theta\sin\psi\dot{\Phi} + \cos\psi\dot{\theta}$
$\omega_z = \cos\theta\dot{\Phi} + \dot{\psi}$

the determinant reduces to

$$r^2\{\cos(\varphi-\psi)\dot{\vartheta}\dot{\theta} - \sin\theta\sin(\varphi-\psi)\dot{\vartheta}\dot{\Phi}$$
$$-\sin\vartheta\cos\vartheta\sin(\varphi-\psi)\dot{\varphi}\dot{\theta}$$
$$+[\sin^2\vartheta\cos\theta - \sin\vartheta\cos\vartheta\sin\theta\cos(\varphi-\psi)]\dot{\varphi}\dot{\Phi}$$
$$+\sin^2\vartheta\dot{\varphi}\dot{\psi}\}.$$

Appendix 6.

Derivation of the Hamiltonian function from the Lagrangian.

$$L = \frac{m}{2}(\dot r^2 + r^2\dot\vartheta^2 + r^2\sin^2\vartheta\dot\varphi^2) + \frac{I}{2}(\dot\theta^2 + \dot\psi^2 + \dot\Phi^2 + 2\cos\theta\,\dot\psi\dot\Phi) + \frac{Ze^2}{r}$$
$$- \frac{Ze^2a^2}{6c^2r}\Big\{\cos(\varphi-\psi)\dot\vartheta\dot\theta - \sin\theta\sin(\varphi-\psi)\dot\vartheta\dot\Phi - \sin\vartheta\cos\vartheta\sin(\varphi-\psi)\dot\varphi\dot\theta$$
$$+ \big[\sin^2\vartheta\cos\theta - \sin\vartheta\cos\vartheta\sin\theta\cos(\varphi-\psi)\big]\dot\varphi\dot\Phi + \sin^2\vartheta\,\dot\varphi\dot\Psi\Big\}.$$

We may introduce T merely as an abbreviation for the part of L which depends on the velocities: L = T - U.

Then by definition $H = -T + U + \sum_i \frac{\partial T}{\partial \dot q_i}\dot q_i$

Since T is a homogenous quadtatic form in the velocities, it follows by Euler's theorem that

$$H = T + U = \tfrac{1}{2}\sum p_i\dot q_i + U.$$

For the momenta we find

$$\left.\begin{aligned}
p_r &= m\dot r\\
p_\vartheta &= mr^2\dot\vartheta + A_\vartheta\\
p_\varphi &= mr^2\sin^2\vartheta\,\dot\varphi + A_\varphi\\
p_\theta &= I\dot\theta + A_\theta\\
p_\Psi &= I(\dot\Psi + \cos\theta\dot\Phi) + A_\psi\\
p_\Phi &= I(\dot\Phi + \cos\theta\dot\psi) + A_\Phi
\end{aligned}\right\} \quad (a)$$

where

$$\left.\begin{aligned}
A_\vartheta &= -\frac{Ze^2a^2}{6c^2r}\{\cos(\varphi-\psi)\dot\theta - \sin\theta\sin(\varphi-\psi)\dot\Phi\}\\
A_\varphi &= -\frac{Ze^2a^2}{6c^2r}\{-\sin\theta\cos\vartheta\sin(\varphi-\psi)\dot\theta + \sin^2\vartheta\,\dot\psi\\
&\quad + [\sin^2\vartheta\cos\theta - \sin\vartheta\cos\vartheta\sin\theta\cos(\varphi-\psi)\dot\Phi\}\\
A_\theta &= -\frac{Ze^2a^2}{6c^2r}\{\cos(\varphi-\psi)\dot\vartheta - \sin\vartheta\cos\vartheta\sin(\varphi-\psi)\dot\varphi\}\\
A_\psi &= -\frac{Ze^2a^2}{6c^2r}\{\sin^2\vartheta\dot\varphi\}\\
A_\Phi &= -\frac{Ze^2a^2}{6c^2r}\{-\sin\theta\sin(\varphi-\psi)\dot\vartheta + [\sin^2\vartheta\cos\theta - \sin\theta\cos\vartheta\sin\theta\cos(\varphi-\psi)]\dot\varphi\}
\end{aligned}\right\} \quad (b)$$

Solving equations (a) for the velocities, we find

$$\dot{r} = p_r/m,$$
$$\dot{\vartheta} = (p_\vartheta - A_\vartheta)\, m r^2$$
$$\dot{\varphi} = (p_\varphi - A_\varphi)/m r^2 \sin^2\vartheta$$
$$\dot{\theta} = (p_\theta - A_\theta)/I$$
$$\dot{\Psi} = \left[(p_\psi - \cos\theta\, p_\Phi) - (A_\psi - \cos\theta\, A_\Phi)\right]/I \sin^2\theta$$
$$\dot{\Phi} = \left[(p_\Phi - \cos\theta\, p_\Psi) - (A_\Phi - \cos\theta\, A_\Psi)\right]/I \sin^2\theta$$

These values may now be substituted in (b). Neglecting higher order terms, the result is

$$A_\vartheta = -\frac{Ze^2a^2}{\vartheta c^2 r}\left\{\cos(\varphi-\psi)\frac{p_\theta}{I} - \sin\theta\sin(\varphi-\psi)\frac{p_\Phi - \cos\vartheta\, p_\psi}{I\sin^2\theta}\right\}$$

$$A_\varphi = -\frac{Ze^2a^2}{\vartheta c^2 r}\left\{-\sin\vartheta\cos\vartheta\sin(\varphi-\psi)\frac{p_\theta}{I} + \sin^2\vartheta\,\frac{p_\psi - \cos\theta\, p_\Phi}{I\sin^2\theta}\right.$$
$$\left. + \left[\sin^2\vartheta\cos\theta - \sin\vartheta\cos\vartheta\sin\theta\cos(\varphi-\psi)\right]\frac{p_\Phi - \cos\theta\, p_\psi}{I\sin^2\theta}\right\}$$

$$A_\theta = -\frac{Ze^2a^2}{\vartheta c^2 r}\left\{\cos(\varphi-\psi)\frac{p_\vartheta}{mr^2} - \sin\vartheta\cos\vartheta\sin(\varphi-\psi)\frac{p_\varphi}{mr^2\sin^2\vartheta}\right\}$$

$$A_\varphi = -\frac{Ze^2a^2}{\vartheta c^2 r}\left\{\sin^2\vartheta\cdot\frac{p_\varphi}{mr^2\sin^2\vartheta}\right.$$

$$A_\Phi = -\frac{Ze^2a^2}{\vartheta c^2 r}\left\{-\sin\theta\sin(\varphi-\psi)\frac{p_\vartheta}{mr^2} + \left[\sin^2\vartheta\cos\theta - \sin\vartheta\cos\vartheta\sin\theta\cos(\varphi-\psi)\right]\frac{p_\varphi}{mr^2\sin^2\vartheta}\right.$$

Substituting equations (c) into the Hamiltonian,

$$H = \frac{1}{2m}\left\{p_r^2 + \frac{p_\vartheta^2}{mr^2} + \frac{p_\varphi^2}{mr^2\sin^2\vartheta} + \frac{p_\theta^2}{I} + \frac{p_\psi(p_\psi - \cos\theta\, p_\Phi)}{I\sin^2\theta} + \frac{p_\Phi(p_\Phi - \cos\theta\, p_\psi)}{I\sin^2\theta}\right.$$
$$\left. - \frac{2Ze^2}{r} - \frac{1}{2}\left\{\frac{p_\vartheta A_\vartheta}{mr^2} + \frac{p_\varphi A_\varphi}{mr^2\sin^2\vartheta} + \frac{p_\theta A_\theta}{I} + \frac{p_\psi(A_\psi - \cos\theta A_\Phi)}{I\sin^2\theta} + \frac{p_\Phi(p_\Phi - \cos\theta A_\psi)}{I\sin^2\theta}\right\}\right\}$$
$$= \frac{1}{2m}\left(p_r^2 + \frac{p_\vartheta^2}{r^2} + \frac{p_\varphi^2}{r^2\sin^2\vartheta}\right\} + \frac{1}{2I}\left\{p_\theta^2 + \frac{1}{\sin^2\theta}\left(p_\psi^2 + p_\Phi^2 - 2\cos\theta\, p_\psi p_\Phi\right)\right\}$$
$$- \frac{2Ze^2}{r} - \frac{1}{2}\left\{\frac{p_\vartheta A_\vartheta}{mr^2} + \frac{p_\varphi A_\varphi}{mr^2\sin^2\vartheta} + \frac{p_\theta A_\theta}{I} + \frac{p_\psi A_\psi + p_\Phi A_\Phi - \cos\theta(p_\psi A_\Phi + p_\Phi A_\psi)}{I\sin^2\theta}\right.$$
$$= H_0 - \frac{1}{2}\left\{\frac{p_\vartheta A_\vartheta}{mr^2} + \frac{p_\varphi A_\varphi}{mr^2\sin^2\vartheta} + \frac{p_\theta A_\theta}{I} + \frac{p_\psi A_\psi + p_\Phi A_\Phi - \cos\theta(p_\psi A_\Phi + p_\Phi A_\psi)}{I\sin^2\theta}\right.$$

Substituting the values of the A's from (d)

$$H = H_0 + \frac{Ze^2}{6c^2r}\left\{\cos(\varphi-\psi)\frac{p_\vartheta p_\theta}{mr^2I} - \sin(\varphi-\psi)\frac{p_\vartheta(p_\Phi - \cos\theta\, p_\psi)}{mr^2I\sin^2\theta}\right.$$
$$- \cot\vartheta\sin(\varphi-\psi)\frac{p_\varphi p_\theta}{mr^2I} + \frac{p_\varphi(p_\psi - \cos\theta\, p_\Phi)}{mr^2I\sin^2\theta}$$
$$\left.+\left[\cot\theta - \cot\vartheta\cos(\varphi-\psi)\right]\frac{p_\varphi(p_\Phi - \cos\theta\, p_\psi)}{mr^2I\sin^2\theta}\right\}$$

Taking out the common factor $1/mr^2I$ we have a coefficient $Ze^2a^2/6mc^2r^3I$. By Appendix 2 $I = ma^2/3$, so that the expression becomes $Ze^2/2m^2c^2r^3$. Simplifying,

$$H = H_0 + \frac{Ze^2}{2m^2c^2r^3}\left\{\cos(\varphi-\psi)\,p_\vartheta p_\theta + \cot\theta\sin(\varphi-\psi)\,p_\vartheta p_\psi\right.$$
$$- \csc\theta\sin(\varphi-\psi)\,p_\vartheta p_\Phi - \cot\vartheta\sin(\varphi-\psi)\,p_\varphi p_\theta$$
$$\left.+\left[1+\cot\vartheta\cot\theta\cos(\varphi-\psi)\right]p_\varphi p_\psi - \cot\vartheta\csc\theta\cos(\varphi-\psi)\,p_\varphi p_\Phi\right\}.$$

The spproximations involved in this derivation are equivalent to neglecting terms in the square of the vector potential. Since the terms in the first power are oforder v^2/c^2, these neglected terms are of order v^4/c^4.

Appendix 7.

Angle Variables of the Unperturbed Motion.

I. Angle variables of the Kepler motion.

For further details and for demonstrations not given here refer to the following:

P.S. Epstein, Zs. f. Physik 9,92,1922.

Born, Atommechanik, pp. 158ff.

Van Vleck, Quantum Principles and Line Spectrs, pp. 193ff.

Of these Van Vleck's treatment is the most detailed.

The Kepler motion is the solution of the equation

$$H = \frac{1}{2m}\left(p_r^2 + \frac{p_\vartheta^2}{r^2} + \frac{p_\varphi^2}{r^2 \sin^2\vartheta}\right) - \frac{Ze^2}{r}.$$

This separated into

$$p_r = \sqrt{2mW + \frac{2mZe^2}{r} - \frac{\gamma^2}{r^2}}$$

$$p_\vartheta = \sqrt{\gamma^2 - \frac{p^2}{\sin^2\vartheta}}$$

$$p_\varphi = p$$

where W, γ, p are constants of integration. Applying the definition of the angle momenta we find

$$u_r = \frac{1}{2\pi}\oint p_r\, dr = \frac{mZe^2}{\sqrt{-2mW}} - \gamma,$$

$$u_\vartheta = \frac{1}{2\pi}\oint p_\vartheta\, d\vartheta = \gamma - p$$

$$u_\varphi = \frac{1}{2\pi}\oint p_\varphi\, d\varphi = p$$

The three constants of integration then become

$$W = -\frac{mZ^2e^4}{2(u_r + u_\vartheta + u_\varphi)^2}, \quad \gamma = u_\vartheta + u_\varphi, \quad p = u_\varphi.$$

The angular variables $w_r, w_\vartheta, w_\varphi$ are now founrd by setting up $S = \int p_r dr + \int p_\vartheta d\vartheta + \int p_\varphi d\varphi$, expressing the constants W, γ, p which occur in the momenta in terms of $u_r, u_\vartheta, u_\varphi$, and differentiating with respect to r, ϑ, and φ respectively.

If simultaneously we introduce the abbreviations

$$\frac{1}{r} = \frac{2\mu e^2}{(u_\vartheta + u_\varphi)^2}(1 + \epsilon \cos\psi), \quad \cos\vartheta = \frac{\sqrt{(u_\vartheta + u_\varphi)^2 - u_\varphi^2}}{u_\vartheta + u_\varphi} \cos\chi$$

where ϵ is the eccentricity of the ellipse the results may be stated in the form

$$w_\varphi - w_\vartheta = \varphi - \tan^{-1}\left(\frac{u_\vartheta + u_\varphi}{u_\varphi} \tan\chi\right)$$

$$w_\vartheta - w_r = \chi - \psi$$

$$w_r = \sin^{-1}\left(\frac{\sqrt{1-\epsilon^2}\sin\psi}{1+\epsilon\cos\psi}\right) + \epsilon\frac{\sqrt{1-\epsilon^2}\sin\psi}{1+\epsilon\cos\psi}$$

The physical meaning of the variables may be discussed as follows: $u_\varphi = p_\varphi = p = mr^2\sin^2\vartheta\,\dot{\varphi}$;that is, u is the component of angular momentum in the direction of the polar axis. Further, the total angular momentum is $\sqrt{p_\vartheta^2 + p_\varphi^2 + p_\varphi^2 \cot^2\vartheta}$. Comparing this witht the expression for p_ϑ we find that $\gamma = u_\vartheta + u_\varphi$ is the total angular momentum. It follows that the angle between the polar axis and the hormal to the plane of the orbit has for its cosine $u_\vartheta/(u_\vartheta + u_\varphi)$. The equantity $u_r + u_\vartheta + u_\varphi$ is connected with the eccentricity by the relation

$$\sqrt{1-\epsilon^2} = \frac{u_\vartheta + u_\varphi}{u_r + u_\vartheta + u_\varphi}$$

We add the expressions for the semi-major and minor axes:

$$a = \frac{(u_1+u_\vartheta+u_\varphi)^2}{mZe^2}, \quad b = \frac{(u_\vartheta+u_\varphi)(u_1+u_\vartheta+u_\varphi)}{mZe^2}.$$

The nodes are the points in which the orbit intersects the plane $\vartheta = \frac{\pi}{2}$. Consequently for a node $\cos\vartheta = 0$, $\cos\chi = 0$, $\tan\chi = \infty$, and $w_\varphi - w_\vartheta = \varphi - \tan^{-1}\infty = \varphi \pm \frac{\pi}{2}$; whence for a node $\varphi = w_\varphi - w_\vartheta \pm \frac{\pi}{2}$. The azimuth of the normal to the plane of the orbit must lie midway between that of the nodes; hence this azimuth is precisely $w_\varphi - w_\vartheta$.

It will be noticed that our relation between r and ψ is the equation of an ellipse in polar coördinates of its plane. r is a minimum when $\psi = 0$, so that ψ is the azimuth in the plane of the orbit, measured from the perihelion. w_1 is a linear function of time which vanishes when ψ vanishes and increases by 2π when does so; accordingly, w_1 is the mean anomaly in the orbit. χ can be shown to be the azimuth in the orbit measured from a node, so that $w_\vartheta - w_1$ is the "longitude" of the node measured from perihelion.

II. Angle variables of the spherical top.

In this case

$$H = \frac{1}{2I}\left[p_\theta^2 + \frac{1}{\sin^2\theta}(p_\varphi^2 + p_\psi^2 - 2\cos\theta\, p_\varphi p_\psi)\right]$$

which separates into

$$p_\theta = \sqrt{2IW - \frac{1}{\sin^2\theta}(p^2 + p''^2 - 2\cos\theta\, p' p'')}$$
$$p_\psi = p'$$
$$p_\phi = p''$$

Hence

$$u_\theta = \frac{1}{2\pi}\oint p_\theta \, d\theta = \sqrt{-2IW} - p'$$
$$u_\psi = p'$$
$$u_\phi = p''$$

W is the energy; therefore $W = -\gamma'^2/2I$, where γ' is the total angular momentum. From this $\gamma' = u_\theta + u_\psi$. Further, $p_\psi = p' = u_\psi$ is by definition the component of angular momentum parallel to the polar axis; so that the cosine of the angle which the resultant angular momentum makes with this axis is $u_\psi/(u_\theta + u_\psi)$.

The angular coördinates w are closely related to those of the Kepler motion, so that $w_\psi - w_\theta$ proves to be the azimuth of the axis of angular momentum.

III. Calculation of cos θ'.

The angle θ' is that between the normal to the plane of the ellipse and the axis of rotation (which for a sphere coincides with the axis of angular momentum) of the spinning electron. Let λ, μ be the polar angle and azimuth of the normal to the plane of the ellipse, and Λ, M, those of the spin axis. Then by spherical trigonometry

$$\cos\theta' = \cos(\mu - M)\sin\lambda\sin\Lambda + \cos\lambda\cos\Lambda .$$

Substituting our values for the various functions,

$$\cos\theta' = \cos\left[(w_\varphi - w_\vartheta) - (w_\psi - w_\theta)\right] \frac{\sqrt{\left[(u_\varphi+u_\vartheta)^2 - u_\varphi^2\right]\left[(u_\psi+u_\theta)^2 - u_\psi^2\right]}}{(u_\varphi+u_\vartheta)(u_\psi+u_\theta)} + \frac{u_\varphi u_\psi}{(u_\varphi+u_\vartheta)(u_\psi+u_\theta)}.$$

We can now substitute into the mean value of the perturbation found in Section 8 our values of the angular momenta, the angle between them, and the semi-minor axis:

$$H = -\frac{m Z^2 e^4}{2(u_2+u_\vartheta+u_\varphi)^2} + \frac{(u_\psi+u_\vartheta)^2}{2I}$$

$$+ \frac{Z\alpha^2}{2m^2c^2} \cdot \frac{m^3 Z^3 e^6}{(u_\vartheta+u_\varphi)^3(u_2+u_\vartheta+u_\varphi)^3} \Bigg\{ \cos\left[(w_\varphi - w_\vartheta) - (w_\psi - w_\theta)\right] \cdot$$

$$\cdot \frac{\sqrt{\left[(u_\varphi+u_\vartheta)^2 - u_\varphi^2\right]\left[(u_\psi+u_\theta)^2 - u_\psi^2\right]}}{(u_\varphi+u_\vartheta)(u_\psi+u_\theta)} + \frac{u_\varphi u_\psi}{(u_\varphi+u_\vartheta)(u_\psi+u_\theta)} \Bigg\} (u_\varphi+u_\vartheta)(u_\psi+u_\theta).$$

This is readily reduced to the form in the text.

Appendix 8.

Evaluation of the quantum integral.

The problem of quantizing the motion represented by

$$H = -\frac{m Z^2 e^4}{2 p_3^2} + \frac{P_2^2}{2I} + \frac{m Z^4 e^8}{2 c^2 h^3 p_3^3}\left\{\cos q\sqrt{[P_2^2-(P-p)^2][P_2^2-p^2]} + p(P-p)\right\} = W$$

reduces to the evaluation of the cyclic integral $\oint p\,dq$. To facilitate computation we set the quantity in curly brackets equal to F. As an abbreviation we also restore the previous notation $P - p = p_1$. Then

$$\cos q = \frac{F - pp_1}{\sqrt{(P_2^2-p^2)(p_2^2-p_1^2)}}$$

This equation is of a decidedly awkward form if we wish to extract p as an explicit function of q. Instead of attempting this, we make a transformation which allows of evaluating our integral in the complex plane of p. We observe that $dq = -d\cos q \,/\sqrt{1-\cos^2 q}$. Substituting the above value of cosq, it is found that

$$p\,dq = \frac{p_1 - p + (F - pp_1)\left(\frac{p_1}{P_2^2-p_1^2} - \frac{p}{P_2^2-p^2}\right)}{\sqrt{(P_2^2-p^2)(p_2^2-p_1^2) - (F-pp_1)^2}}\,p\,dp$$

Now $(P_2^2 - p^2)(p_2^2 - p_1^2) - (F - pp_1)^2 = a + bp + cp^2$, where $a = P_2^2 p_2^2 - P_2^2 p^2 - F^2$; $b = 2P(P_2^2 + F)$; $c = -(P_2^2 + p_2^2 + 2F)$. Our integral is accordingly of a standard type. It has two branch points at the roots of $a + bp + cp^2 = 0$, and five other singularities at $p_2 = \pm p_1$, $P_2 = \pm p$, and $p = \infty$. The problem then becomes one in the

calculus of residues.

To calculate the residue at infinity we put $p = 1/\sigma$. Simplifying slightly, we obtain

$$p\,dq = -\frac{d\sigma}{\sigma\sqrt{a\sigma^2+b\sigma+c}}\left[\frac{P}{\sigma} - \frac{2}{\sigma^2} + \left(F - \frac{P}{\sigma} + \frac{1}{\sigma^2}\right)\left(\frac{1-P\sigma}{1-2P\sigma+(P^2-p_2^2)\sigma^2} + \frac{1}{1-P^2\sigma^2}\right)\right]$$

The residue depends on the terms of zero degree in σ within the square brackets. Such terms can only occur in the product of the two parentheses. Expanding the second parenthesis in ascending powers of σ, we find that we have to take the terms of zero degree in

$$\left(F - \frac{P}{\sigma} + \frac{1}{\sigma^2}\right)\left[2 + P\sigma + (p_2^2 + P_2^2 + P^2)\sigma^2\right]$$

These terms are $2F - P^2 + p_2^2 + P_2^2 + P^2 = p_2^2 + P_2^2 + 2F$.

$$\therefore \mathrm{Res}_\infty = -\frac{2\pi i\,(p_2^2+P_2^2+2F)}{\sqrt{c}} = \frac{-2\pi i\,(p_2^2+P_2^2+2F)}{\pm i\sqrt{p_2^2+P_2^2+2F}} = \pm 2\pi\sqrt{p_2^2+P_2^2+2F}.$$

The sign of the radical is in general indeterminate, but does not affect the results.

The calculation of the residues at the four finite poles is simpler, but in these cases the determination of the sign is essential. This sign depends on the position of these poles with respect to the branch points. The general method, it will be recalled, is to connect the two branch points, which are the roots of $a + bp + cp^2 = 0$, by a cut along the real axis (assuming both roots real). The path of integration then passes in the positive sense around this branch cut, the sign of the radical being taken as positive below the real axis and negative above, and consequently as positive imaginary on the real axis

to the right of the branch cut, negative imaginary on the real axis to the left of the cut. Accordingly, it is necessary for our purposes to establish that the roots of our quadratic are real and that the poles of the integrand do not lie between them, and to determine on which side of the branch cut these poles lie.

Apparently the case of complex roots can occur in our problem; but the results we require are given by the case of real roots. In this case it is readily shown that the poles lie outside the branch cut; for if either $p_2^2 = p_1^2$ or $p^2 = P_2^2$ we have $a + bp + cp^2$ reduced to $-(F - pp_1)^2$, and the radical is imaginary, while between the branch points it is real.

If we put $y = a + bp + cp^2$, this represents a parabola in the py-plane, with its axis parallel to the y-axis. The intersections of this parabola with the p-axis are the branch points; two values of p for which y' has opposite signs, and which lie outside the branch cut, must consequently be on opposite sides. Now

$$y' = b + 2cp = 2P(P_2^2 + F) - 2p(P_2^2 + p_2^2 + 2F).$$

In the special case when $P = 0$ the sign of y' changes when that of p changes, so that the poles $p = \pm P_2$ are on opposite sides of the branch cut; and as when $P = 0$ $p_1 = -p$, the other two poles are $p = \pm p_2$, and also lie on opposite sides of the branch cut. Now P is quantizable,

so that it is a constant of the motion; but $P = u_\varphi + u_\psi$; that is, it is the component of the total angular momentum in the direction of the polar axis. Now this direction is arbitrary, which proves the conservation of angular momentum for the system in this approximation; and as it is arbitrary it is always possible to choose it so that P = 0. Consequently, since the mere choice of a coördinate system cannot affect the motions, the poles of our integrand always have the relation to the branch points which we have just found.

To find the residue at $p = +P_2$ we take the coefficient of $1/(p-P_2)$ in $p\,dq$, substituting P_2 for p. The result is $\frac{P_2 (F - pP_1)}{2\sqrt{-(F-pP_1)^2}}$, which is $+P_2/2i$, since this pole is to the right of the branch cut. The contribution to our integral is $-2\pi i$ times this, or $-\pi P_2$. The pole $p = -P_2$ also contributes $-\pi P_2$; it lies to the left of the cut, and the radical has therefore been taken as negative imaginary.

For the pole $p = P - p_2$ we find the contribution $\pi(P-p_2)$, and for the pole $p = P + p_2$, $-\pi(P+p_2)$.

Adding all our results,

$$2\pi\left(\pm\sqrt{P_2^2+P_2^2+2F} - P_2 - P_2\right) = n'h$$

or $$\pm\sqrt{P_2^2+P_2^2+2F} = (n'+s+k)\frac{h}{2\pi} = \frac{jh}{2\pi}$$

whence $F = \frac{h^2}{8\pi^2}(j^2 - k^2 - s^2)$.

It remains to establish the physical meaning of j,

or of its associated angle momentum $G = jh/2\pi$. This can be done by comparing our definition of F with the expression of the mean value of the pertubation (Section 5,Part II, equation (9)). The quantities there written as p_φ and p_Σ have the same physical meaning as p_2 and P_2. Accordingly

$$F = p_2P_2 \cos(p_2P_2).$$

But $G^2 = p_2^2 + P_2^2 + 2F = p_2^2 + P_2^2 + 2p_2P_2 \cos(P_2p_2)$. This is the ordinary form for the absolute value of a vector sum. But the vector sum of p_2 and P_2 is the resultant angular momentum of the system,with which G must therefore be identified.

The quantization of the total angular momentum,which in other discussions of this problem is taken as a starting point,here appears as a natural result of the general theory of quantization,necessitating no special theory whatever.

Appendix 9.

Derivation of the Wave Equation.

The general result of Schrödinger's variation process may be stated as follows: [25]

Given a Hamiltonian function in the form H= T + U, where T is a quadratic form in the momenta and U depends only on the coördinates, the wave equation takes the form, in which p_k is to be replaced by $\partial u/\partial q_k$,

$$\Delta^{\frac{1}{2}} \sum_k \frac{\partial}{\partial q_k}\left(\Delta^{-\frac{1}{2}} \frac{\partial T(p_1, p_2, \cdots)}{\partial p_k}\right) + \frac{8\pi^2 m}{h^2}(E - U)\, u = 0$$

where Δ is the determinant of the quadratic form. In our case

$$\Delta = \begin{vmatrix}
\frac{1}{2m} & 0 & 0 & 0 & 0 & 0 \\
0 & \frac{1}{2mr^2} & 0 & \frac{Q}{2}\frac{\cos\alpha}{r^3} & -\frac{Q}{2}\frac{\cot\vartheta\sin\alpha}{r^3} & \frac{Q}{2}\frac{\cos\vartheta\sin\alpha}{r^3} \\
0 & 0 & \frac{1}{2mr^2\sin^2\vartheta} & \frac{Q}{2}\frac{\cot\vartheta\sin\alpha}{r^3} & \frac{Q}{2}\frac{1+\cot\vartheta\cot\vartheta\cos\alpha}{r^3} & -\frac{Q}{2}\frac{\cot\vartheta\cos\vartheta\cos\alpha}{r^3} \\
0 & \frac{1}{2}\frac{Q\cos\alpha}{r^3} & \frac{Q}{2}\frac{\cot\vartheta\sin\alpha}{r^3} & \frac{1}{2I} & 0 & 0 \\
0 & -\frac{Q}{2}\frac{\cot\vartheta\sin\alpha}{r^3} & \frac{Q}{2}\frac{1+\cot\vartheta\cot\vartheta\cos\alpha}{r^3} & 0 & \frac{1}{2I\sin^2\vartheta} & -\frac{1}{2I}\frac{\cos\vartheta}{\sin^2\vartheta} \\
0 & \frac{Q}{2}\frac{\cos\vartheta\sin\alpha}{r^3} & -\frac{Q}{2}\frac{\cot\vartheta\cos\vartheta\cos\alpha}{r^3} & 0 & -\frac{1}{2I}\frac{\cos\vartheta}{\sin^2\vartheta} & \frac{1}{2I\sin^2\vartheta}
\end{vmatrix}$$

Those elements of Δ which are due to the spin effect are all multiplied by the factor Q, and are none of them on the principal diagonal. They will give rise in Δ, and consequently in the wave equation, to terms only of order Q^2 or higher. These we neglect, and accordingly we may take for Δ the same value as for the unperturbed system:

$$\Delta = 1/64\, m^3 I^3 r^4 \sin^2\vartheta \sin^2\theta .$$

We find

$$\frac{\partial T'}{\partial p_r} = \frac{p_r}{m} \; ; \; \frac{\partial T'}{\partial p_\vartheta} = \frac{1}{mr^2} + \frac{Q}{r^3}\left[\cos\alpha\, p_\theta - \cot\theta \sin\alpha\, p_\psi + \operatorname{cosec}\theta \sin\alpha\, p_\Phi\right]$$

$$\frac{\partial T'}{\partial p_\varphi} = \frac{1}{mr^2\sin^2\vartheta} + \frac{Q}{r^3}\left[\cot\vartheta \sin\alpha\, p_\theta + \{1+\cot\vartheta\cot\theta\cos\alpha\}\, p_\psi - \cot\vartheta \operatorname{cosec}\theta\, p_\Phi\right]$$

$$\frac{\partial T'}{\partial p_\theta} = \frac{1}{I} + \frac{Q}{r^3}\left[\cos\alpha\, p_\vartheta + \cot\vartheta \sin\alpha\, p_\varphi\right]$$

$$\frac{\partial T'}{\partial p_\psi} = \frac{p_\psi - p_\Phi\cos\theta}{I\sin^2\theta} + \frac{Q}{r^3}\left[-\cot\theta\sin\alpha\, p_\theta + \{1+\cot\vartheta\cot\theta\cos\alpha\}\, p_\varphi\right]$$

$$\frac{\partial T'}{\partial p_\Phi} = \frac{p_\Phi - p_\psi\cos\theta}{I\sin^2\theta} + \frac{Q}{r^3}\left[\operatorname{cosec}\theta\sin\alpha\, p_\theta - \cot\vartheta\operatorname{cosec}\theta\cos\alpha\, p_\varphi\right]$$

Putting $U = -Ze^2/r$, and introducing the derivatives,

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial u}{\partial r}\right) + \frac{1}{r^2\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\frac{\partial u}{\partial\vartheta}\right) + \frac{1}{r^2\sin^2\vartheta}\frac{\partial^2 u}{\partial\varphi^2} + \frac{m}{I}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial u}{\partial\theta}\right)$$
$$+ \frac{m}{I\sin^2\theta}\left[\left(\frac{\partial^2 u}{\partial\psi^2} - \cos\theta\frac{\partial^2 u}{\partial\Phi\partial\psi}\right) + \left(\frac{\partial^2 u}{\partial\Phi^2} - \cos\theta\frac{\partial^2 u}{\partial\varphi\partial\Phi}\right)\right]$$
$$+ \frac{mQ}{r^3}\left[\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\cos\alpha\frac{\partial u}{\partial\vartheta} - \sin\vartheta\cot\theta\sin\alpha\frac{\partial u}{\partial\psi} + \sin\vartheta\operatorname{cosec}\theta\sin\alpha\frac{\partial u}{\partial\Phi}\right)\right.$$
$$+ \frac{\partial}{\partial\varphi}\left(\cot\theta\sin\alpha\frac{\partial u}{\partial\theta} + \{1+\cot\vartheta\cot\theta\cos\alpha\}\frac{\partial u}{\partial\psi} - \cot\vartheta\operatorname{cosec}\theta\cos\alpha\frac{\partial u}{\partial\Phi}\right)$$
$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\cos\alpha\frac{\partial u}{\partial\vartheta} + \sin\theta\cot\vartheta\sin\alpha\frac{\partial u}{\partial\varphi}\right)$$
$$+ \frac{\partial}{\partial\psi}\left(-\cot\theta\sin\alpha\frac{\partial u}{\partial\vartheta} + \{1+\cot\vartheta\cot\theta\cos\alpha\}\frac{\partial u}{\partial\varphi}\right)$$
$$\left. + \frac{\partial}{\partial\Phi}\left(\operatorname{cosec}\theta\sin\alpha\frac{\partial u}{\partial\theta} - \cot\vartheta\operatorname{cosec}\theta\cos\alpha\frac{\partial u}{\partial\varphi}\right)\right] + \frac{8\pi^2 m}{h^2}\left[E + \frac{Ze^2}{r}\right]u = 0$$

which easily reduces to equation (32) of the text.

Appendix 10.

Reduction Formulae.

I. Formulae for $P_\ell^{n_1}(\cos\vartheta)$.

When n_1 is positive it is easily shown by differentiating the definition

$$P_\ell^{n_1} = \sin^{n_1}\vartheta \frac{d^{n_1} P_\ell(\cos\vartheta)}{[d(\cos\vartheta)]^{n_1}}$$

that

$$\frac{dP_\ell^{n_1}}{d\vartheta} - n_1 \cot\vartheta P_\ell^{n_1} = -P_\ell^{n_1+1}$$

By differentiating Legendre's equation

$$(1-x^2)\frac{d^2P_\ell}{dx^2} - 2x\frac{dP_\ell}{dx} + \ell(\ell+1)P_\ell = 0$$

n_1-1 times with respect to x, putting $x = \cos\vartheta$, and finally applying the above definition, there results

$$2n_1 \cot\vartheta P_\ell^{n_1} = (\ell-n_1+1)(\ell+n_1) P_\ell^{n_1-1} + P_\ell^{n_1+1}$$

which added to the relation above gives

$$\frac{dP_\ell^{n_1}}{d\vartheta} + n_1 \cot\vartheta P_\ell^{n_1} = (\ell-n_1+1)(\ell+n_1) P_\ell^{n_1-1}$$

When n_1 is negative we make use of the form

$$P_\ell^{n_1}(x) = \frac{(\ell+n_1)!}{n_1!(\ell-n_1)!}\left(\frac{1-x}{1+x}\right)^{\frac{n_1}{2}} F\left(\ell+1, -\ell, n_1+1, \frac{1-x}{2}\right)$$

from whichbit follows that

$$P_\ell^{-n_1}(x) = \frac{(\ell-n_1)!}{(\ell+n_1)!} P_\ell^{n_1}(x)$$

Applying this to the above relations we find

$$\frac{dP_\ell^{n_1}}{d\vartheta} - n_1 \cot\vartheta P_\ell^{n_1} = \xi P_\ell^{n_1+1},$$

$$\frac{dP_\ell^{n_1}}{d\vartheta} + n_1 \cot\vartheta P_\ell^{n_1} = \eta(\ell+n_1)(\ell-n_1+1) P_\ell^{n_1-1}$$

in which $\xi = -1$ if $n_1 \geqslant 0$, and $+1$ if $n_1 < 0$,
while $\eta = +1$ if $n_1 > 0$, and -1 if $n_1 \leqslant 0$.

II. Formulae for $T(n_2, n_3, \sigma)$

T is given as a hypergeometric function; it is not difficult on principle to apply the known properties of these functions for obtaining the formulae needed. The writer has worked this out for any value of σ; but the result is not capable of simple statement, and the calculations are long and awkward. Darwin,[2] by a change of notation, has put the results in a workable form. Here we shall use the writer's original means of attacking the problem - namely, of taking $\sigma = 1$.

The following table is easily constructed; T' is dT/dθ, and D is an abbreviation for $n_2 \cot\theta T - n_3 \csc\theta\, T$.

$[\sigma = 1]$

n_2	n_3	T'	D	T'-D	T'+D	T
1	1	$-\frac{1}{2}\sin\theta$	$-\frac{1}{2}\sin\theta$	0	$-\sin\theta$	$\frac{1}{2}(1+\cos\theta)$
1	0	$\frac{1}{2}\cos\theta$	$\frac{1}{2}\cos\theta$	0	$\cos\theta$	$\frac{1}{2}\sin\theta$
1	-1	$\frac{1}{2}\sin\theta$	$\frac{1}{2}\sin\theta$	0	$\sin\theta$	$\frac{1}{2}(1-\cos\theta)$
0	1	$\frac{1}{2}\cos\theta$	$-\frac{1}{2}$	$\frac{1}{2}(1+\cos\theta)$	$-\frac{1}{2}(1-\cos\theta)$	$\frac{1}{2}\sin\theta$
0	0	$-\sin\theta$	0	$-\sin\theta$	$-\sin\theta$	$\cos\theta$
0	-1	$\frac{1}{2}\cos\theta$	$\frac{1}{2}$	$-\frac{1}{2}(1-\cos\theta)$	$\frac{1}{2}(1+\cos\theta)$	$\frac{1}{2}\sin\theta$
-1	1	$\frac{1}{2}\sin\theta$	$-\frac{1}{2}\sin\theta$	$\sin\theta$	0	$\frac{1}{2}(1-\cos\theta)$
-1	0	$\frac{1}{2}\cos\theta$	$-\frac{1}{2}\cos\theta$	$\cos\theta$	0	$\frac{1}{2}\sin\theta$
-1	-1	$-\frac{1}{2}\sin\theta$	$\frac{1}{2}\sin\theta$	$-\sin\theta$	0	$\frac{1}{2}(1+\cos\theta)$

Now since $T'-D = \mu_{n_2}^{n_3} T_{n_2+1}^{n_3}$ and $T' + D = \lambda_{n_2-1}^{n_3} T_{n_2-1}^{n_3}$, the values of λ and μ used in the text are easily read off.

Appendix 11.

Properties of the modified functions.

We are considering the equation

$$\nabla^2 u_0 + \frac{m}{I}\nabla^2 u_0 - \left[\beta^2 + \frac{2\beta n}{r} + \frac{m}{I}\sigma(\sigma+1)\right] u_0 = 0$$

The solution can obviously be obtained as a product of a Reiche function, a surface spherical harmonic, and a function of r, which is found to satis-f fy the equation

$$\frac{d^2\chi}{dr^2} + \frac{2}{r}\frac{d\chi}{dr} - \left(\beta^2 + \frac{2\beta n}{r} + \frac{\ell(\ell+1)}{r^2}\right)\chi$$

If now we put $\beta = -4\pi^2 mZe^2/nh^2$ this becomes the ordinary equation for Schrödinger's functions; but if β is kept constant for varying n the equation has déifferent properties. If we multiply by r^2

$$r^2\frac{d^2\chi}{dr^2} + 2r\frac{d\chi}{dr} - \left[\beta^2 r^2 + \ell(\ell+1)\right]\chi - 2\beta n r\chi = 0$$

This is of the standard form of the Sturm-Liouville equation

$$py'' - p'y' - qy + \lambda\rho y = 0$$

if we put $y = \chi$, $p = r^2$, $p' = 2r$, $q = \beta^2 r^2 + \ell(\ell+1)$, $\rho = r$, $\lambda = -2\beta n$.

From the general theory of such equations the functions χ_n^ℓ must then have the property $\int_0^\infty \chi_n^\ell \chi_{n'}^\ell r\,dr = 0$ if $n \neq n'$. This is easily proved directly by combining two such equations and integrating. The theory shows that the functions form a complete orthogonal system, which justifies our expansions in terms of them.

Appendix 12.

Application of theory of inhomogeneous equations.

To show that if

$$F(n,\sigma,v) = \nabla^2 v + \frac{m}{I}\nabla'^2 v - \left[\beta^2 + \frac{2\beta n}{r} + \frac{m}{I}\sigma(\sigma+1)\right]$$

$$= \frac{1}{r}\sum K(n',\sigma,\ell,n_1',n_2',n_3)\,u_0(n',\sigma,\ell,n_1',n_2',n_3)$$

where $F(n,\sigma,u_0) = 0$

so that $u_0 = \chi_n^{\ell} Y_{\ell}^{n_1} Z_{n_2}^{n_3}$

then in order to satisfy the conditions of finiteness $K(n,\sigma,\ell,n_1,n_2,n_3) = 0$.

Since the equation is linear v can be built up from a sum of solutions of the equations of type

$$F(n,\sigma,v) = \frac{1}{r}K(n',\sigma,\ell,n_1',n_2',n_3)\,u_0(n',\sigma,\ell,n_1',n_2',n_3)$$

If in this we put $v = Cu_0(n',\sigma,\ell,n_1',n_2',n_3)$

we find that $$C = \frac{K}{2\beta(n'-n)}$$

so that if $n' \neq n$ C does not vanish unless K does. This method fails if $n' = n$; we have then to solve

$$F(n,\sigma,v) = \frac{1}{r}K(n,\sigma,\ell,n_1,n_2,n_3)\,u_0(n,\sigma,\ell,n_1,n_2,n_3)$$

χ_n^{ℓ} is a solution of the equation

$$\frac{d^2\chi}{dr^2} + \frac{2}{r}\frac{d\chi}{dr} - \left[\beta^2 + \frac{2\beta n}{r} + \frac{\ell(\ell+1)}{r^2}\right]\chi = 0.$$

Let $\overline{\chi}_n^{\ell}$ be the second independent solution of this equation, which of course does not satisfy the conditions of finiteness; put $U_0 = \overline{\chi}_n^{\ell} Y_{n_1}^{n_2} Z_{n_2}^{n_3}$, and substitute

$$v = A\dot{u}_0 + BU_0,$$

where A and B are undetermined funnctions of r. As we require only a particular solution we may impose one further restriction, namely

$$u_0 \frac{dA}{dr} + U_0 \frac{dB}{dr} = 0$$

We find $$\frac{dA}{dr}\frac{\partial u_0}{\partial r} + \frac{dB}{dr}\frac{\partial U_0}{\partial r} = 0$$

and solving the last two equations simultaneously

$$\frac{dB}{dr} = -\frac{K u_0^2 / r}{U_0 \frac{\partial u_0}{\partial r} - u_0 \frac{\partial U_0}{\partial r}} \qquad \text{(a)}$$

Now $F(r, \sigma, u_0) = 0$

and $F(r, \sigma, U_0) = 0$

from which, taking into account the form of u_0 and U_0, we obtain

$$U_0 \frac{\partial^2 u_0}{\partial r^2} - u_0 \frac{\partial^2 U_0}{\partial r^2} + \frac{2}{r}\left(U_0 \frac{\partial u_0}{\partial r} - u_0 \frac{\partial U_0}{\partial r}\right) = 0$$

and since u_0 and U_0 contain the same factors depending on the five angles,

$$\bar{\chi} \frac{d^2\chi}{dr^2} - \chi \frac{d^2\bar{\chi}}{dr^2} + \frac{2}{r}\left(\bar{\chi} \frac{d\chi}{dr} - \chi \frac{d\bar{\chi}}{dr}\right) = 0$$

Putting $W = \bar{\chi} \frac{d\chi}{dr} - \chi \frac{d\bar{\chi}}{dr}$

we have $$\frac{dW}{dr} + \frac{2W}{r} = 0$$

whence $W = D/r2$, D being a constant of integration.

From (a), because of the character of the dependence on the angles, $$\frac{dB}{dr} = -\frac{K\chi^2}{rW}$$

whence $$B = -\frac{C}{D}\int r\chi^2 dr.$$

Now as χ is real χ^2 is positive, and B cannot vanish identically unless K = 0. But unless B does vanish v cannot satisfy the conditions of finiteness, and consequently K must vanish; which was to be proved.

Appendix 13.

Final solution for energy levels, wave mechanics.

Equation (52), page 67, leads to the following set of equations for the coefficients $K^{n_2}_{n_1}$:

$$K^{n_2}_{n_1}\left(\frac{8\pi^2 m\epsilon}{h^2}B_n - n_1 n_2 A_n\right) + \frac{1}{2}K^{n_2-1}_{n_1+1}\eta(n_1+1)\mu^{n_3}_{n_2-1}(\ell+n_1+1)(\ell-n_1)A_n$$
$$+\frac{1}{2}K^{n_2+1}_{n_1-1}\xi(n_1-1)\lambda^{n_3}_{n_2+1}A_n = 0,$$

for every possible combination of n_1 and n_2. The condition that these equations shall be consistent is the vanishing of the determinant of the quantities multiplying the K's. This determinant is of order $3(2\ell+1)$; but it will be observed that in each equation there occur only the three K's for which $n_1 + n_2$ is a constant-m, say. There are then three equations for each value of m, independent of all the remaining equations; these equations can be treated separately, and we shall see that the result is independent of m.

For a given value of m these equations are

$$K^{1}_{m-1}\left[\frac{8\pi^2 m\epsilon}{h^2}B_n - (m-1)A_n\right] + \frac{1}{2}K^{0}_{m}\eta(m)\mu^{n_3}_{0}(\ell+m)(\ell-m+1)A_n = 0,$$

$$K^{0}_{m}\cdot\frac{8\pi^2 m\epsilon}{h^2}B_n + \frac{1}{2}K^{-1}_{m+1}\eta(m+1)\mu^{n_3}_{-1}(\ell+m+1)(\ell-m)A_n + \frac{1}{2}K^{1}_{m-1}\xi(m-1)\lambda^{n_3}_{1}A_n = 0,$$

$$K^{-1}_{m+1}\left[\frac{8\pi^2 m\epsilon}{h^2}B_n + (m+1)A_n\right] + \frac{1}{2}K^{0}_{m}\xi(m)\lambda^{n_3}_{0}A_n = 0.$$

The condition that they shall be consistent becomes

$$\begin{vmatrix} \frac{8\pi^2 m\epsilon}{h^2} B_n - [m-1]A_n, & \frac{1}{2}\eta(m)\mu_0^{n_3}(\ell+m)(\ell-m+1)A_n, & 0 \\ \frac{1}{2}\xi(m-1)\lambda_1^{n_3}A_n, & \frac{8\pi^2 m\epsilon}{h^2}B_n, & \frac{1}{2}\eta(m+1)\mu_{-1}^{n_3}(\ell+m+1)(\ell-m)A_n \\ 0, & \frac{1}{2}\xi(m)\lambda_0^{n_3}A_n, & \frac{8\pi^2 m\epsilon}{h^2}B_n + (m+1)A_n \end{vmatrix} = 0.$$

Dividing by A_n, setting $\frac{8\pi^2 m\epsilon}{h^2}\frac{B_n}{A_n} = x$, and expanding,

$$[x-(m-1)]\left\{x[x+(m+1)] - \frac{1}{4}\xi(m)\eta(m+1)\lambda_0^{n_3}\mu_{-1}^{n_3}(\ell+m+1)(\ell-m)\right\}$$

$$-\frac{1}{4}\xi(m-1)\eta(m)\lambda_1^{n_3}\mu_0^{n_3}(\ell+m)(\ell-m+1)[x+(m+1)] = 0$$

It will be found on examining the values of the coefficients $\xi, \eta, \lambda_{n_2}^{n_3}, \mu_{n_2}^{n_3}$ (Appendix 10 or pages 63-64) that $\lambda_0^{n_3}\mu_{-1}^{n_3} = \lambda_1^{n_3}\mu_0^{n_3} = -2$ for all values of n_3, and that $\xi(n_1)\eta(n_1+1) = \xi(n_1-1)\eta(n_1) = -1$ for all values of n_1.

Substituting these results and reducing,

$$x^3 + 2x^2 - [\ell(\ell+1) - 1]x - \ell(\ell+1) = 0;$$

the roots of which are

$$x = -1, \ell, -\ell-1.$$

From this

$$\epsilon = -\frac{h^2}{8\pi^2 m}\frac{A_n}{B_n}, \ell\frac{h^2}{8\pi^2 m}\frac{A_n}{B_n}, -(\ell+1)\frac{h^2}{8\pi^2 m}\frac{A_n}{B_n}.$$

Appendix 14.

Calculation of An/Bn.

Given the two expansions (50)

$$\frac{\chi_n^\ell}{r^2} = \sum A_{n'} \chi_{n'}^\ell \quad , \quad r\chi_n^\ell = \sum B_{n'} \chi_{n'}^\ell$$

in which χ_n^ℓ are the modified functions with constant β, we wish to find the ratio of the two particular coefficients A_n and B_n.

Since $\int_0^\infty \chi_n^\ell \chi_{n'}^\ell dr = 0$ when $n \neq n'$, we have

$$A_n = \frac{\int_0^\infty r^{-1} (\chi_n^\ell)^2 dr}{\int_0^\infty r^{-2} (\chi_n^\ell)^2 dr} \quad , \quad B_n = \frac{\int_0^\infty r^2 (\chi_n^\ell)^2 dr}{\int_0^\infty r^2 (\chi_n^\ell)^2 dr}$$

or $A_n/B_n = \int_0^\infty r^{-1} (\chi_n^\ell)^2 dr \Big/ \int_0^\infty r^2 (\chi_n^\ell)^2 dr$.

This calculation is not easy to carry out in general; but it is very simple for the cases in which $\ell = n - 1$. The functions χ_n^ℓ then take the form

$$\chi_{\ell+1}^\ell = e^{\beta r} r^\ell$$

and consequently $A_n/B_n = \dfrac{\int_0^\infty e^{2\beta r} r^{2\ell-1} dr}{\int_0^\infty e^{2\beta r} r^{2\ell+1} dr}$

$$= \frac{(2\ell-1)!/(-2\beta)^{2\ell}}{(2\ell+2)!/(-2\beta)^{2\ell+3}} = -\frac{8\beta^3}{2\ell(2\ell+1)(2\ell+2)}$$

$$= -\frac{\beta^3}{\ell(\ell+\tfrac{1}{2})(\ell+1)} = \frac{e^4 \pi^6 m^3 Z^3 e^6}{\eta^3 h^6} \frac{1}{\ell(\ell+\tfrac{1}{2})(\ell+1)}.$$

While this has here been derived only for special cases, it chances to be the general expression; for since $E_1 = 2mQ\epsilon$, $Q = Ze^2/2m^2c^2$, and $\epsilon = \frac{L\,h^2}{8\pi^2 m}\,\frac{An^*}{B_n}$, we find on reduction that

$$E_1 = \frac{Rh\alpha^2 Z^4}{n^3}\,\frac{L}{l(l+\frac{1}{2})(l+1)}$$

which is the general result given in the text. (61)

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*Appendix 13, putting L = -1, , or - - 1.

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