ELECTRON SPIN

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INTRODUCTION.

Modern theories of atomic structure may be said to have begun with the experimental establishment of the existence of the electron just before the opening of the present century. It was shown to be a negatively charged particle of mass only $\frac{1}{1838}$ that of the hydrogen atom. Lenard in 1903 showed that cathode rays could be made to penetrate a thin aluminium window which led him to conclude that swift cathode rays could pass freely through thousands of atoms, assuming for the size of the atom the magnitude deduced from the kinetic theory of gases. Thus it appeared that the greater part of an atom must be empty. As a result of experiments on the scattering of α particles, Rutherford in 1911 suggested a model of the atom as consisting of a positively charged nucleus, very small compared with the size of the complete atom, surrounded by a distribution of electrons whose number was equal to the nuclear charge (if expressed in units of electron charge). This model may be compared with a planetary system with the central nucleus corresponding to the sun. It was later shown that for an atom of atomic number N (corresponding to its position in Mendelejeff's periodic table), the nucleus would have positive charge Ne where $-e = -4.803 \times 10^{-10}$ e.s.u. is the charge on an electron.

BOHR'S THEORY OF THE ATOM 1913.

Bohr developed his theory of the atom in an attempt to interpret the line spectra of elements.

The Balmer series had been the first series of lines to be discovered in the hydrogen spectrum. Balmer had shown that the frequencies of the four lines occurring in the visible spectrum could be represented by the simple empirical formula

$$\nu_m = R\left(\frac{1}{4} - \frac{1}{m^2}\right)$$

where m could have the values 3, 4, 5, 6 corresponding to the four lines and R was called Rydberg's constant and had the value $3{\cdot}29201 \cdot 10^{15}$.

Later there were discovered other hydrogen series; the Lyman series in the ultraviolet given by the formula

$$\nu_m = R\left(1 - \frac{1}{m^2}\right) \qquad m = 2, 3 \ldots\ldots$$

the Paschen series in the infra red with

$$\nu_m = R\left(\frac{1}{9} - \frac{1}{m^2}\right) \qquad m = 4, 5 \ldots\ldots$$

and the Brackett series with

$$\nu_m = R\left(\frac{1}{16} - \frac{1}{m^2}\right) \qquad m = 5, 6 \ldots\ldots$$

All these formulae could be represented by the general formula

$$\nu = R\left(\frac{1}{n^2} - \frac{1}{m^2}\right)$$

where $n < m$

This suggested that a general law could be stated which since has been shown to be exact for all the spectral lines of all elements. This combination principle of Ritz stated that the frequency of each spectral line was equal to the difference between two spectral terms characteristic of the body emitting the radiation. For hydrogen, the spectral terms would have the form $\frac{R}{n^2}$ where $n = 1, 2 \ldots.$ The problem remained of how to explain these spectral series by means of an atomic model.

In the case of Rutherford's model of the atom, according to the laws of classical mechanics, the system of electrons and nucleus composing an atom, should only have reached final equilibrium when the electrons had fallen into the nucleus. Before the final equilibrium, the electrons would describe orbits of diminishing size about the nucleus, continuously emitting energy as radiation. The frequencies involved in the motion of the electrons would then gradually change during the emission of light, a fact incompatible on the classical theory with the sharply defined frequencies of spectral lines.

Bohr had the idea of applying the quantum laws to Rutherford's model of the atom.

Planck had previously announced (in 1900) that the distribution of energy with frequency of radiation in thermodynamic equilibrium with matter (black body radiation) could be represented by the equation

$$dE = \frac{8\pi^2\nu^2}{c^3}\,\frac{h\nu}{e^{\frac{h\nu}{kT}}-1}\,d\nu$$

in which ν was the frequency of the light, k was Boltzmann's constant, T the absolute temperature and h was a constant called Planck's constant. This equation was not that which was obtained from classical statistical mechanics; Planck showed that it could be derived if the following assumption were made:-

that radiation was not emitted continuously by resonators in equilibrium with radiation but only in discrete portions of magnitude $h\nu$, each portion being called a light quantum. The photoelectric effect was interpreted by Einstein in 1907 and he showed that the maximum velocity of the emitted electrons corresponded to the conversion into kinetic energy of just the energy $h\nu$ of one light quantum. In both these cases, the system emitting or absorbing radiation in quanta changed discontinuously from a state with a given energy to one with energy $h\nu$ greater or less.

Bohr applied the same kind of quantum conditions to the case of an atomic system and his two postulates may be expressed as follows.

(1) An atomic system can exist in certain stationary states, each one corresponding to a definite value of the energy W of the system; and transition from one state

to another is accompanied by the emission or absorption as radiation, or the transfer to or from another system, of an amount of energy equal to the energy difference of the two states.

(2) The frequency of the radiation emitted by a system and associated with the transition from an initial state with energy W_1, to a final state with energy W_2 is

$$\nu = \frac{W_1 - W_2}{h} \qquad (1)$$

In order to determine the energies of stationary states, Bohr assumed that the electron behaved as a point charge obeying the laws of Newtonian dynamics, but he restricted the number of possible motions by introducing the quantum rules. Taking first the simplest case of periodic motion which is defined by a single variable q, then the quantum condition was written

$$\oint p\,dq = nh \qquad n = \text{an integer} \qquad (2)$$

where p is the momentum conjugate to the variable q, h is Planck's constant and the integral is taken over a complete cycle of motion.

Applying this to the circular orbits of the hydrogen atom which consists of a nucleus of charge $+e$ and a planetary electron of charge $-e$ according to the Rutherford atomic model, the following equation is obtained:

$$m_0 r^2 \dot{\theta} = n\frac{h}{2\pi} \qquad (3)$$

where θ is the angle which represents the position of the electron on a circular orbit of radius r and m_0 is the mass of the electron. The angular momentum of an electron on a stable orbit is thus assumed to be a multiple of $\frac{h}{2\pi}$ The laws of dynamics give the relation

$$m_0 r \dot{\theta}^2 = \frac{e^2}{r^2} \qquad (4)$$

The energy of the n^{th} circular quantised motion is given by the sum of the potential and kinetic energies of the electron

$$E_n = \frac{1}{2} m_0 r^2 \dot{\theta}^2 - \frac{e^2}{r} = -\frac{1}{2} m_0 r^2 \dot{\theta}^2 = -\frac{2\pi^2 m_0 e^4}{n^2 h^2} \qquad (5)$$

on substituting from equations (3) and (4).

From equation (1) the frequencies of the hydrogen lines should be given by the general relation

$$\nu_{nn'} = \frac{2\pi^2 m_0 e^4}{h^3}\left(\frac{1}{n^2} - \frac{1}{n'^2}\right) \qquad n' > n \qquad (6)$$

which is seen to agree with the empirical formula

$$\nu_{nn'} = R\left(\frac{1}{n^2} - \frac{1}{n'^2}\right) \qquad n' > n$$

if

$$R = \frac{2\pi^2 m_0 e^4}{h^3} \qquad (7)$$

Good agreement was found between the value of R determined from the hydrogen spectrum and the value $\frac{2\pi^2 m_0 e^4}{h^3}$ calculated from the known values of m_0, e and h.

In order to deal with the more general case of elliptic orbits, the quantum conditions must be applied to a system of two variables, the radius vector r and the azimuth angle θ . The quantum conditions for a system of x degrees of freedom are represented by the x equations

$$\oint p_i \, dq_i = n_i h \qquad n_i = \text{an integer} \qquad i = 1, 2 \ldots\ldots x \tag{8}$$

For an electron on an elliptic orbit, the kinetic energy T is given by

$$T = \frac{1}{2} m_0 \left(\dot{r}^2 + r^2 \dot{\theta}^2 \right)$$

and the momenta conjugate to the variables r and θ are by definition

$$p_r = \frac{\partial T}{\partial \dot{r}} = m_0 \dot{r} \qquad \text{and} \qquad p_\theta = \frac{\partial T}{\partial \dot{\theta}} = m_0 r^2 \dot{\theta} \quad .$$

Applying the quantum conditions of equation (8) gives

$$\oint m_0 r^2 \dot{\theta} \, d\theta = n_1 h \qquad \oint m_0 \dot{r} \, dr = n_2 h \tag{9}$$

n_1 is usually denoted by k and is called the azimuthal quantum number. As the electron is moving in a central field of fone, the angular momentum $m_0 r^2 \dot{\theta}$ is constant, so that the first condition becomes

$$m_0 r^2 \dot{\theta} = n_1 \frac{h}{2\pi} \qquad (10)$$

This is the same as Bohr's condition for circular orbits.

In order to calculate the second integral of equation (9) the energy is expressed as

$$E = \frac{1}{2} m_0 (\dot{r}^2 + r^2 \dot{\theta}^2) - \frac{e^2}{r} = \frac{1}{2m_0}\left[\frac{(m_0 r^2 \dot{\theta})^2}{r^2} + m_0^2 \dot{r}^2\right] - \frac{e^2}{r}$$

and substituting from equation (10)

$$m_0 \dot{r} = p_r = \pm \sqrt{2m_0\left(E + \frac{e^2}{r}\right) - \frac{n_1^2 h^2}{4\pi^2 r^2}}$$

During the motion the radius vector r varies between the values r_1 and r_2. Supposing $r_1 < r_2$

$$\oint p_r\, dr = 2\int_{r_1}^{r_2} \sqrt{2m_0\left(E + \frac{e^2}{r}\right) - \frac{n_1^2 h^2}{4\pi^2 r^2}}\; dr$$

$$= -|n_1| h + \frac{2\pi m_0 e^2}{\sqrt{2m_0 |E|}} = n_2 h$$

Then

$$E_{n_1 n_2} = -\frac{2\pi^2 m_0 e^4}{(|n_1| + n_2)^2 h^2} \qquad (11)$$

where $E_{n_1 n_2}$ is the energy of the stationary state corresponding to quantum numbers n_1 and n_2. As $/n_1/$ and n_2 are positive integers or zero (but not simultaneously zero) one can put

$$|n_1| + n_2 = n \qquad (n = 1, 2 \ldots\ldots) \qquad (12)$$

Substituting this in equation (11) one obtains exactly the same energy levels as in Bohr's early theory of circular orbits.

If the same calculation is carried out for an atom of atomic number N which has been ionized $(N-1)$ times, the frequencies of the spectral lines are given by

$$\nu_{nn'} = \frac{2\pi^2 m_0 e^4}{h^3} N^2 \left(\frac{1}{n^2} - \frac{1}{n'^2}\right) = R N^2 \left(\frac{1}{n^2} - \frac{1}{n'^2}\right) \quad (13)$$

instead of by equation (6).

ANOMALIES.

Rutherford's planetary model of the atom which was made precise by Bohr's theory was able to explain satisfactorily much experimental evidence. It was apparent later however that this model of a hydrogen atom consisting of an electron rotating round the positive nucleus in an elliptic or circular orbit was too simple to explain everything. Anomalies in gyromagnetic experiments, the fine structure of the hydrogen spectrum, thedoublets in the spectra of the alkalies, the anomalous Zeeman effect and certain features in Xray spectra could not be interpreted. It was suggested, perhaps by analogy withthe planetary system of the sun, that the electron had not only an elliptic path about the nucleus but also a rotational motion (or spin) about its own axis. We shall see how the theory of electron spin was brought forward in order to explain the difficulties described above.

EXPERIMENTAL EVIDENCE FOR ELECTRON SPIN.

(1) GYROMAGNETIC ANOMALIES.

Owing to the motion of an electron in an atom, a magnetic moment is produced and the ratio of this to the angular momentum of the motion can easily be calculated.

Let us consider a particle of mass m_0 and charge e traversing a plane closed orbit under a central force towards a point O. Then from classical dynamics, the rate at which area is swept out by the radius vector is constant.

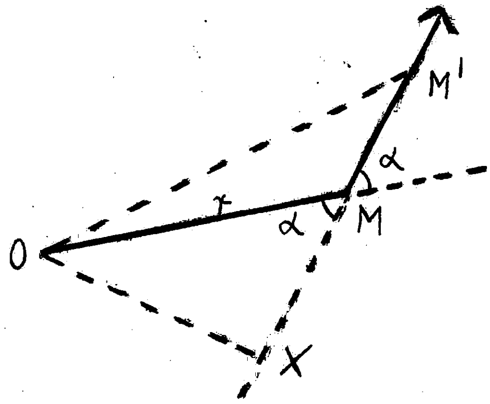

Figure I.

In figure I let M and M^1 represent the positions of the particle at two instants. The area of triangle OMM^1 is

$$\frac{1}{2} MM'.OX = \frac{1}{2} V\,dt\,r\sin\alpha$$

where V = velocity and dt is the small element of time to traverse the distance MM^1

$$dA = \frac{1}{2} v\,dt\,r\sin\alpha$$

$$\frac{dA}{dt} = \text{constant} = \frac{1}{2}\frac{M}{m_0}$$

where M is the angular momentum and equals $m_0 v r \sin\alpha$.
Therefore as M is constant we can integrate over all the period T of the motion

$$A = \frac{M}{2m_0} T \tag{14}$$

where A is the total area of the orbit. The motion of the charge e is equivalent to a current i where

$$i = \frac{e}{T}$$

if e is in electromagnetic units or

$$i = \frac{e}{cT} \tag{15}$$

where e is in electrostatic units. From equations (14) and (15)

$$i = \frac{Me}{2m_0 Ac}$$

From the magnetic point of view, the current is equivalent to a magnetic shell of strength i and area A. Therefore the magnetic moment μ is given by

$$\mu = iA = \frac{eM}{2m_0 c}$$

This relation is valid in magnitude and direction for the vectors $\vec{\mu}$ and $\vec{M}$.

$$\frac{\vec{\mu}}{\vec{M}} = \frac{e}{2m_0 c}$$

It can be demonstrated in a more general way that if one considers an assembly of particles of the same mass m_0 and the same charge e forming a system in a stationary state, the above relation is still valid between the total magnetic moment $\vec{\mu}$ and the total constant angular momentum $\vec{M}$ of the system. By Bohr's theory, atoms contain electrons in motion in stationary states so it should be possible to apply the above relation to atoms. According to Bohr's theory, the total angular momentum of the atom is an integral multiple of $\frac{h}{2\pi}$ Thus

$$\mu = n \cdot \frac{h}{2\pi} \cdot \frac{e}{2m_0c} = n \cdot \frac{eh}{4\pi m_0 c}$$

The magnetic moment of the atom would therefore always be an exact multiple of a certain unit called the "Bohr magneton" and equal to

$$\frac{eh}{4\pi m_0 c}$$

The existence of this unit Bohr magneton was verified by the experiments of Stern and Gerlach from measurements of the deflection of a stream of atoms in a nonhomogeneous magnetic field.

Results of experiments on the gyromagnetic effect do not however verify the relation

$$\frac{\mu}{M} = \frac{e}{2m_0c}$$

in a general and complete way. As an angular momentum is associated with the magnetic moment of each atom, then it seems possible that there may be gyromagnetic effects for matter in bulk.

Let α and β be the magnetic moment and angular momentum of a rod of material, the magnetisation being due to "carriers" of magnetic moment μ and angular momentum M. The rod is assumed to be initially unmagnetised and at rest $(\alpha = 0, \beta = 0)$. The process of magnetisation consists in the partial or complete alignment of the carriers. Let μ' be the resolved magnetic moment of a carrier in the direction of the axis of the rod

$$\alpha = \sum \mu'$$

The change in the resultant angular momentum of the carriers on magnetisation of the rod must be compensated by an equal and opposite change in the angular momentum of the rod as a whole, the total angular momentum communicated by the field being zero.

$$\beta = -\sum M' = -\frac{M}{\mu}\alpha$$

As the magnetisation changes, the couple acting on the rod is given by

$$C = \frac{d\beta}{dt} = -\frac{M}{\mu}\frac{d\alpha}{dt}$$

If the magnetisation of the rod is changed suddenly by an amount $\delta\alpha$, a rotational impulse will be given tothe rod.

$$\int C\,dt = -\frac{M}{\mu}\int\frac{d\alpha}{dt}\cdot dt = -\frac{M}{\mu}\cdot\delta\alpha$$

If the rotational impulse imparted to a rod for a given change of magnetisation can be measured, a value can be obtained for the gyromagnetic ratio $\frac{M}{\mu}$ of the carriers.

A related, though not strictly converse, effect is obtained by the rotation of a rod. As in the usual treatment of gyroscopes, rotation will tend to align the axes of the carriers in the direction of the axis of rotation, so being equivalent in its effect to a magnetic field. Let ω be the angular velocity of the rod. Since no couple is applied to the carriers, the equation of motion of the carriers relative to fixed axes (denoted by suffix f) will be

$$C_f = \left(\frac{dM}{dt}\right)_f = 0$$

Referred to axes moving with angular velocity (that is, fixed in the rod) the equation becomes

$$\frac{d\vec{M}}{dt} + \left[\vec{\omega}\times\vec{M}\right] = 0$$

where $\left[\vec{\omega}\times\vec{M}\right]$ represents the vector product of $\vec{\omega}$ and $\vec{M}$

$$\frac{d\vec{M}}{dt} = -\left[\vec{\omega} \times \vec{M}\right] = \left[\vec{M} \times \vec{\omega}\right]$$

Now $\frac{d\vec{M}}{dt}$ gives the effective couple on the carriers. This may be alternatively expressed by $\left[\vec{\mu} \times \vec{H}\right]$ The effect of rotation is thus equivalent to a field H such that

$$\left[\vec{\mu} \times \vec{H}\right] = \left[\vec{M} \times \vec{\omega}\right]$$

$$\vec{H} = \left(\frac{M}{\mu}\right) \vec{\omega}$$

Rotation of a rod will result in magnetisation such as would be produced by a field of this magnitude H in a stationary rod. If the values of the fields are found which are required to produce in a stationary rod the same magnetisations as are produced by given speeds of rotation, then the gyromagnetic ratio of the carriers can be determined.

The first experiments to give reasonably definite results (those of Barnett in 1914 and of Einstein and de Haas) showed that $\frac{\mu}{M}$ was negative, the direction of M relative to μ corresponding to the rotation of a negative charge, but that the magnitude of the ratio, for the ferromagnetics investigated was approximately twice that calculated for an orbital electron i.e. $\frac{e}{m_0 c}$ instead of $\frac{e}{2m_0 c}$ This discrepancy between the observed and expected result, the gyromagnetic anomaly, was one of the reasons which led to the idea of an electron having an intrinsic spin and magnetic moment for which the ratio $\frac{\mu}{M}$ was twice that for the orbital motion.

(2) DOUBLETS IN ALKALI SPECTRA.

Rydberg showed that the spectral terms of elements other than hydrogen could be written in the form $\frac{R}{(n+\Delta)^2}$ where R was the same constant as for hydrogen, n was a positive integer and Δ was a number (not an integer) able to take several different values for each element. Ritz suggested a more exact formula $\frac{R}{(n+\Delta+\frac{\delta}{n^2})^2}$ with δ another number. For a given value of n, Δ and δ could in general take several different values, so that to the same value of n would correspond several spectral terms. Spectroscopists designate possible values of Δ by a series of letters s, p, d, f, g, h so that the table of spectral terms is

$$\begin{array}{ccccc} (1s) & (2s) & (3s) & (4s) & (5s) \\ & (2p) & (3p) & (4p) & (5p) \\ & & (3d) & (4d) & (5d) \\ & & & (4f) & (5f) \\ & & & & (5g) \end{array} \qquad (16)$$

As for hydrogen the frequencies of lines of the same spectral series are always obtained by taking the difference between the constant term characteristic of the series and one variable term. It is found that a selection rule applies, that in usual conditions of emission not all possible combinations between spectral terms occur but only those where Δ changes to one or other of its neighbouring values.

Bohr's theory was extended to try to explain the spectra of the alkali metals. The general analagous character of the spectra of all elements and the fact that in each formula the same Rydberg constant R appears, led to the conclusion that the planetary model so useful for the hydrogen atom should be used for other elements.

The first assumption made was that in an atom of atomic number N, the $(N - 1)$ of the planetary electrons should be considered as rotating near the nucleus and forming around it an atomic core, whilst the N^{th} planetary electron called the "optical electron" would have its orbit outside the electronic shell. The passage of an optical electron from one stationary state to another would determine the spectrum of the element. Then it was assumed that the action of the nucleus of charge $+ Ne$ and the shell of charge $-(N - 1)e$ was equivalent approximately to the action of a central charge $+ e$. The problem was thus reduced to the problem of the hydrogen atom with a single quantum number.

To obtain a second approximation, Sommerfeld took account of the fact that near the shell of electricity, the charge of the nucleus and that of the shell would not exactly compensate to a charge + e. He showed that the orbit of the electron would no longer be closed and it would be necessary to introduce a second quantum number k, the azimuthal quantum number corresponding to n, in Bohr's theory of the hydrogen atom. If the orbit penetrated the shell of electricity, it would then consist of a segment of one Kepler ellipse in the outer region and a segment of another Kepler ellipse in the inner region. As a result of the penetration, the outer elliptical segment would then undergo an effective precession about an axis normal to its plane as shown in figure II.

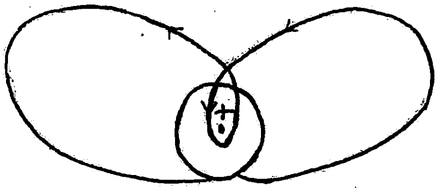

Figure II.

Sommerfeld calculated the term values in this way and obtained again the empirical formula of Rydberg and Ritz given above. By reasoning based on Bohr's correspondence principle, it was shown that the only transitions which should take place were those for which $\delta k = \pm 1$, and this agreed with experiment. Bohr's and Sommerfeld's theories by introducing the two quantum numbers n and k were able to interpret the spectral terms of the Rydberg Ritz formula. Sommerfeld's theory and other versions of the old quantum theory suggested that the azimuthal quantum number k corresponded to the divers values (s, p, d...) in the following way

k = 1 2 3 4 5 6 ....
= s p d f g h ....

Thus each spectral term (n, Δ) could be written in the form (n, k).

However the table (16) obtained from the Rydberg Ritz formula is only a first approximation. Progress in spectroscopy showed that lines considered simple in the Rydberg Ritz scheme were in reality formed by a group of neighbouring lines constituting multiplets. In the alkali spectra, most of the spectral terms of the Rydberg Ritz scheme are doubled. The value s of the quantity Δ always remains single but the values of p, d, f, g ... are all double. Table (16) has therefore to be replaced by the following table:

$$\begin{array}{llll} (1s) & (2s) & (3s) & (4s)\ \ldots \\ & (2p_1) & (3p_1) & (4p_1)\ldots \\ & (2p_2) & (3p_2) & (4p_2)\ldots \\ & & (3d_1) & (4d_1)\ldots \\ & & (3d_2) & (4d_2)\ldots \\ & & & (4f_1)\ldots \\ & & & (4f_2)\ldots \end{array} \tag{17}$$

In order to characterise each of the multiple spectral terms corresponding to the same term of table (17), it would be necessary to introduce a third quantum number. At the time of the old quantum theory, this third quantum number j was introduced in quite an empirical way. The two neighbouring values of Δ which corresponded to a certain value of n and k should be characterised by different values of the quantum number j. To the two neighbouring spectral terms were attributed, the two values of j

$$j = k-1 \pm \frac{1}{2} = l \pm \frac{1}{2}$$

if we put $l = k-1$

There were now two selection rules which gave the possible transitions.

$$\delta k = +1 \text{ or } -1 \qquad\qquad \delta j = +1,\ 0,\ -1$$

In the old quantum theory the meaning of the number j remained unknown. It required the hypothesis of a magnetic and spinning electron to reveal its significance. Thus the reason for the doublet character of the alkali spectra could not be understood without the conception of electron spin.

(3) THE ANOMALOUS ZEEMAN EFFECT.

In the presence of a magnetic field, it is found that a spectral line which is originally single becomes split up into a number of components. On the basis of the old quantum theory, the expected frequencies of these components can be calculated.

Suppose an electron in an atom is in a stable state in the absence of an external magnetic field. Let W_0 be the energy of this electron and μ the magnetic moment corresponding to its orbital motion. In the presence of a uniform external magnetic field H, the energy of the electronic orbit will be

$$W_H = W_0 - (\vec{\mu}.\vec{H})$$

where $(\vec{\mu}.\vec{H})$ represents the scalar product of the two vectors. As

$$\mu = \frac{e}{2m_0c} M$$

this may be written

$$W_H = W_0 + \frac{e}{2m_0c}(\vec{M}.\vec{H})$$

Consider the component of $\vec{M}$ along the direction of the field. This component should be by the old quantum theory, a multiple of $\frac{h}{2\pi}$. Thus

$$(18)$$

where m is a quantum number called the magnetic quantum number.

Consider the spectral line produced by the passage of an electron from a stable state of energy W_0 to a stable state of less energy W_0^1. In the absence of an external magnetic field, this spectral line would have the frequency

$$\nu_0 = \frac{W_0 - W_0'}{h}$$

In the presence of a uniform field this becomes

$$\nu_H = \frac{W_H - W_H'}{h} = \nu_0 + (m - m')\frac{eh}{4\pi m_0 c} H \qquad (19)$$

Under ordinary conditions to account for observations a selection principle must be introduced according to which

$$\Delta m = \pm 1 \text{ or } 0 \qquad (20)$$

This rule is suggested by correspondence principle reasoning.

Classically, the angular momentum M associated with a circularly polarised wave system (that emitted by an electron rotating in a circular orbit with frequency ν) is related to the energy W by the equation

$$\frac{M}{W} = \frac{1}{2\pi\nu}$$

so

so that for a change in momentum of the radiating system

$$\Delta M = \frac{\Delta W}{2\pi\nu}$$

This suggests that, on the quantum theory, since a change in M of $\frac{h}{2\pi}$ (or in m of unity) will result in circularly polarised radiation. On the other hand, radiation arising from a linearly vibrating electron, classically, has no associated angular momentum, suggesting that $\Delta m = 0$ corresponds to linear polarisation. These considerations give some theoretical support for the experimentally justified restriction of (20). The result of the simple quantum theory treatment is then given by (19) and (20); and to these should be added

$\Delta m = \pm 1$ → circular polarisation
$\Delta m = 0$ → linear polarisation

These are exactly the same conclusions as are obtained from the classical theory. The cases in which this theory is verified are called examples of the "normal Zeeman effect".

However it is only verified in a small number of cases, the majority giving a so-called "anomalous" Zeeman effect. The experimental study of this led to two important generalisations. According to Preston's rule (1899), all the lines of the same series of an element undergo the same splitting in a magnetic field, as also corresponding lines of different elements with analogous spectra. Runges rule states that the separation of the components from the zero position (measured in frequencies) is a small multiple of an aliquot part of the normal separation; that is

$$\Delta\nu = \left|\frac{a}{b}\right| \Delta\nu_N$$

where a and b are integral. Landé summarised the results of experiments in a weak magnetic field by the formula

$$(n,l,j)_H = (n,l,j)_0 + mg\frac{eh}{4\pi m_0 c} H \qquad (21)$$

where $(n, l, j)_0$ is the value of a certain spectral term characterised by these quantum numbers in the absence of a magnetic field, $(n, l, j)_H$ is the value in the presence of a uniform field H and the term can take (2j+1) values. g is called the Landé factor and has the value

$$g = 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)}$$

and in the case of an alkali this reduces to

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

as $s = \frac{1}{2}$ and $j = l \pm \frac{1}{2}$

The old quantum theory was no better able to explain than the classical theory the introduction of the factor g. To interpret this requires the introduction of the intrinsic spin and magnetism of the electron. The relation between the magnetic moment and angular momentum which would give the experimental results for the anomalous Zeeman effect is

$$\left|\frac{\mu}{M}\right| = g\,\frac{e}{2m_0c}$$

This leads us to think that connected with angular momentum and magnetic moment, there exists something which is not related by the ratio

$$\frac{\vec{\mu}}{\vec{M}} = -\frac{e}{2m_0c}$$

Thus one can no longer suppose that all the atom's magnetism comes from the circulation of electrons conceived as point charges.

(4) THE FINE STRUCTURE OF THE HYDROGEN SPECTRUM.

On closer examination of the Balmer series of hydrogen it was discovered that the spectral lines originally considered as single really had a fine structure. Bohr's theory, discussed above, was able to explain satisfactorily the frequencies of the lines of the series in general, but it could not explain that each of the lines, at first considered as simple, was in reality a little doublet.

Sommerfeld tried to use relativistic mechanics instead of classical mechanics to explain the effect. This was justified as ~~as~~ in the Bohr atom, the speed of electrons in their orbits was comparable to the velocity of light.

Let m_0 be the rest mass of the electron and V its velocity where

$$V = \sqrt{\dot{r}^2 + r^2\dot{\theta}^2} \qquad (22)$$

if r and θ are the polar co-ordinates of its position relative to the nucleus. If L is the relativistic Lagrangian function, then the momentum p_i conjugate to the variable q_i is defined by

$$p_i = \frac{\partial L}{\partial \dot{q}_i}$$

where

$$L = -m_0c^2\sqrt{1 - \frac{v^2}{c^2}} - U$$

if U is the potential energy. In the problem of the hydrogen atom, the potential energy does not depend on the $\dot{q}_i$'s and one has

$$p_r = \frac{\partial L}{\partial \dot{r}} = \frac{m_0 c^2}{2\sqrt{1-\frac{v^2}{c^2}}} \cdot \frac{\partial\left(\frac{v^2}{c^2}\right)}{\partial \dot{r}} = \frac{m_0 \dot{r}}{\sqrt{1-\frac{v^2}{c^2}}}$$

$$p_\theta = \frac{\partial L}{\partial \dot{\theta}} = \frac{m_0 c^2}{2\sqrt{1-\frac{v^2}{c^2}}} \cdot \frac{\partial\left(\frac{v^2}{c^2}\right)}{\partial \dot{\theta}} = \frac{m_0 r^2 \dot{\theta}}{\sqrt{1-\frac{v^2}{c^2}}} \qquad (23)$$

The quantum conditions

$$\int p_i \, dq_i = n_i h$$

are therefore in this case

$$\int_0^{2\pi} \frac{m_0 r^2 \dot{\theta}}{\sqrt{1-\frac{v^2}{c^2}}} \, d\theta = n_1 h \quad \text{and} \quad \oint \frac{m_0 \dot{r}}{\sqrt{1-\frac{v^2}{c^2}}} \, dr = n_2 h \qquad (24)$$

A detailed study of the motion shows that the electron describes an ellipse with rotation of the perihelion, the ellipse undergoing an effective precession about an axis normal to its plane as shown in figure III.

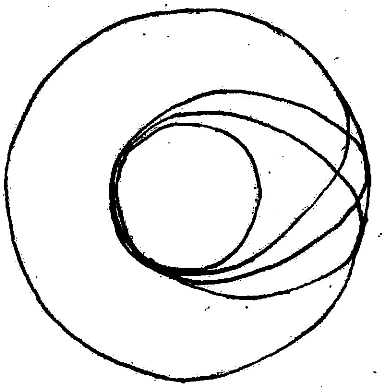

Figure III.

The radius vector varies between two values r_1 and r_2 but the time that it takes to describe the cycle $r_1 \rightarrow r_2 \rightarrow r_1$ is a little longer than the time taken for θ to increase by 2π. The motion is therefore quasi periodic and the orbit not exactly closed.

The angular momentum p_θ about the nucleus is constant. The first condition of equation (24) therefore gives

$$p_\theta = \frac{m_0 r^2 \dot{\theta}}{\sqrt{1-\frac{v^2}{c^2}}} = n_1 \frac{h}{2\pi} \qquad (25)$$

The total energy W is equal to the sum of the internal energy m_0c^2, the kinetic energy and the potential energy.

$$W = \frac{m_0 c^2}{\sqrt{1-\frac{v^2}{c^2}}} - \frac{e^2}{r} \qquad (26)$$

Using equations (22) and (23) the value of W becomes

$$W = c\sqrt{m_0^2c^2 + p_r^2 + \frac{p_\theta^2}{r^2}} - \frac{e^2}{r} \qquad (27)$$

Let E be the energy W minus the rest energy m_0c^2 so that E is the energy such as defined in classical mechanics. Let W be replaced by $(E + m_0c^2)$ in equation (27) and solve for p_r.

$$p_r = \pm \sqrt{A + \frac{2B}{r} + \frac{C}{r^2}}$$

with the notation

$$A = \frac{E^2}{c^2} + 2m_0E = m_0^2c^2\left[\left(1+\frac{E}{m_0c^2}\right)^2 - 1\right]$$

$$B = \frac{Ee^2}{c^2} + m_0e^2E$$

$$C = \frac{e^4}{c^2} - p_\theta^2 = \frac{e^4}{c^2} - \frac{n_1^2h^2}{4\pi^2}$$

Sommerfeld called $\alpha = \frac{2\pi e^2}{hc}$ the "fine structure constant" and introduced it into the calculation. α^2 is numerically equal to 5.2 x 10^{-5} c.g.s. units.

$$C = -\frac{n_1^2 h^2}{4\pi^2}\left(1 - \frac{\alpha^2}{n_1^2}\right)$$

It is found that

$$\oint \sqrt{A + \frac{2B}{r} + \frac{C}{r^2}}\, dr = -2\pi i\left(\sqrt{C} - \frac{B}{\sqrt{A}}\right)$$

From equation (24) this must equal $n_2 h$. Replacing A, B and C by their values it is found that

$$1 + \frac{E}{m_0 c^2} = \left[1 + \frac{\alpha^2}{\left(n_2 + \sqrt{n_1^2 - \alpha^2}\right)^2}\right]^{-\frac{1}{2}} \qquad (28)$$

This formula gives the enefgy E in a stationary state defined by the quantum numbers n_1 and n_2.

As the quantity α^2 is very small, a first approximation would consist in neglecting the terms of degree greater than one in α^2. The non relativistic formula

$$E_{n_1 n_2} = -\frac{2\pi^2 m_0 e^4}{(|n_1| + n_2)^2 h^2}$$

is obtained again and there is no fine structure.

A better approximation consists in keeping terms in α^4 by writing

$$\left[1 + \frac{\alpha^2}{\left(n_2^2 + \sqrt{n_1^2 - \alpha^2}\right)^2}\right]^{-\frac{1}{2}} = 1 - \frac{\alpha^2}{2(|n_1| + n_2)^2} - \frac{1}{2}\frac{\alpha^4}{(|n_1| + n_2)^4}\left(\frac{1}{4} + \frac{n_2}{|n_1|}\right)$$

Substituting this value into equation (28)

$$E = -\frac{2\pi^2 m_0 e^4}{(|n_1|+n_2)^2 h^2}\left[1 + \frac{\alpha^2}{(|n_1|+n_2)^2}\left(\frac{1}{4}+\frac{n_2}{|n_1|}\right)\right] \quad (29)$$

The third term in the brackets explains the fine structure of the Balmer series as it depends separately on $/n_1/$ and n_2 and not only on $(/n_1/ + n_2)$.

The number $n = /n_1/ + n_2$ is called the "total quantum number" and $k = /n_1/$ is called the "azimuthal quantum number". Each level of quantised energy can be characterised by numbers n and k instead of numbers n_1 and n_2. Formula (29) can then be written

$$E_{n,k} = -\frac{Rh}{n^2}\left[1+\frac{\alpha^2}{n^2}\left(\frac{n}{k}-\frac{3}{4}\right)\right] \quad (30)$$

In the old quantum theory it is assumed that k can never take the value zero; for the circular trajectories $n_2 = 0$ or $n = k$ and for the elliptical trajectories $0 < k < n$. Formula (30) shows that each stationary orbit is characterised by energy E_{nk} which no longer depends only on n but also on k. As α^2 is very small compared to unity, the divers spectral terms corresponding to the same value of n are very close together and thus a fine structure of the line is obtained. The Bohr spectral term corresponding to a given value of n is split up into n neighbouring terms, as with n fixed k can take the n values, 1, 2..... n. The separation of neighbouring terms becomes smaller as n increases because n^2 is in the denominator of the term in α^2

In the Balmer series, the frequencies of lines are given as a first approximation by the formula

$$\nu = R\left[\frac{1}{2^2} - \frac{1}{n^2}\right] \qquad n = 3, 4, \ldots$$

As a second approximation the spectral term $\frac{R}{2^2}$ must be replaced by

$$\frac{R}{2^2}\left[1 + \frac{\alpha^2}{2^2}\left(\frac{2}{k} - \frac{3}{4}\right)\right]$$

and the term $\frac{R}{n^2}$ by

$$\frac{R}{n^2}\left[1 + \frac{\alpha^2}{n^2}\left(\frac{n}{k} - \frac{3}{4}\right)\right]$$

There is therefore in the Balmer series a fine structure with a constant width showing the double level of the first fixed spectral term and another fine structure with decreasing separation on rising in the series due to the complexity of the second variable spectral term. This secondary fine structure is almost inobservable as it is so fine. The first corresponds to a decomposition of each of the lines foreseen by Balmer's formula into a doublet with a constant separation for all the series equal to

$$\Delta\nu_H = \frac{R}{2^2}\left[1 + \frac{\alpha^2}{2^2}\left(\frac{2}{1} - \frac{3}{4}\right)\right] - \frac{R}{2^2}\left[1 + \frac{\alpha^2}{2^2}\left(\frac{2}{2} - \frac{3}{4}\right)\right] = \frac{R\alpha^2}{16}$$

The numerical calculation of $\frac{R\alpha^2}{16}$ gives 0.365cm^{-1}

on replacing frequencies by wave numbers and this value is in quite good agreement with the experimental value. Therefore on completing Bohr's theory by the introduction of relativity, an interpretation is obtained of the existence of doublets in the Balmer series.

However a closer examination of the doublets of the Balmer series showed that these doublets were not correctly interpreted by Sommerfeld's theory. Let us consider the line H_α of the Balmer series which arises from a transition from a stationary state n = 3 to a stationary state n = 2. This line is really multiple and Sommerfeld's theory gives for the fine structure of this line the following scheme shown in figure IV.

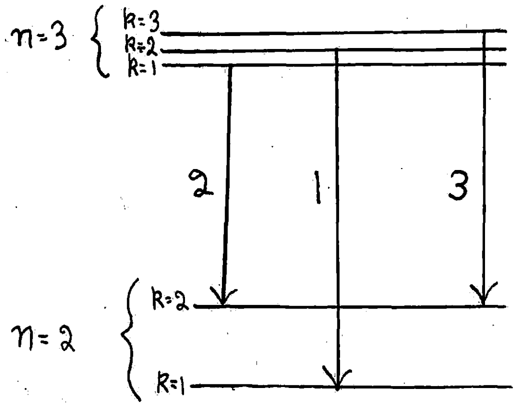

Figure IV.

Applying the selection rule $\delta k = \pm 1$ the three lines shown are predicted for the fine structure of the H_α line. Sommerfeld's doublet is formed by the line 1 and the combination of the two lines 2 and 3 which are of such close frequencies that they cannot usually be distinguished as two lines.

If however a third quantum number j is introduced as was found necessary to explain the occurrence of doublets in the case of the alkali spectra (discussed above), the following scheme of fine structure is predicted as shown in figure V.

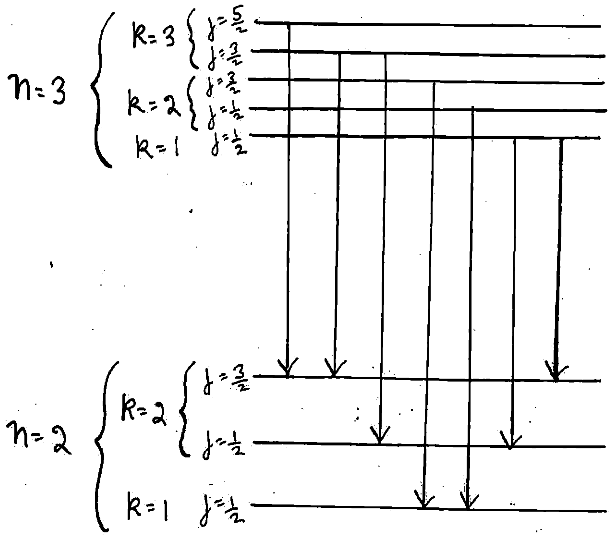

Figure V.

The selection rules

$\delta k = \pm 1$ $\delta j = 0, \pm 1$

allow the seven lines marked on figure V. However in the case of hydrogen, theories of the magnetic and spinning electron show that levels with the same j and different k values should be considered as coming together. The simplified scheme of figure VI is thus obtained.

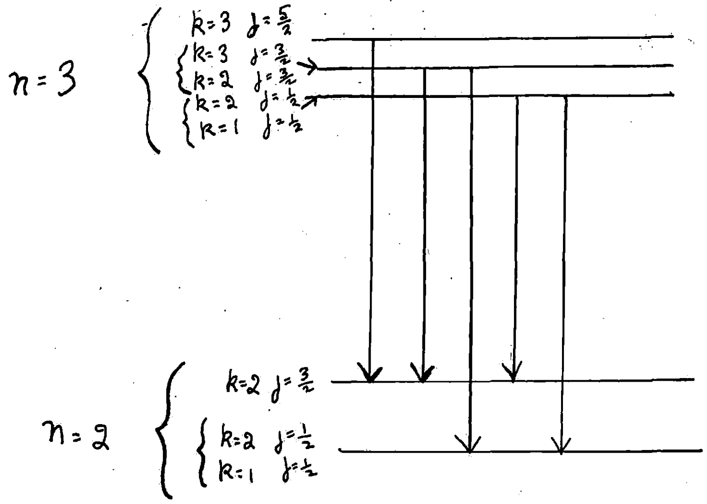

Figure VI.

This theory therefore predicts five components in the fine structure of the H_α line whilst Sommerfeld's theory only predicts three. The careful study of this fine structure has shown that there are more than three lines, thus confirming the new scheme and not that of Sommerfeld.

In the case of ionised helium, the separation of the doublets is sixteen times greater than in the Balmer series, so that the fine structure is much more easily observed. Study of this has confirmed the new theory and not that of Sommerfeld.

Thus it is seen that the fine structure of hydrogen can not be explained simply in terms of a relativity correction to Bohr's simple theory but another factor comes in, dependent on the idea of an electron having magnetic moment and spin.

(5) DOUBLETS OF X RAY SPECTRA.

We shall not discuss Xray spectra in detail here but merely mention the Xray fine structure as one of the lines of evidence which helps to confirm the theory of electron magnetic moment and spin.

Xray spectra show roughly the same general characteristics as optical spectra. The combination principle is applicable to them; series are formed by combining a fixed spectral term with a variable spectral term; selection rules again occur.

To a first approximation Xray spectral terms can be represented by the following expression which is a statement of Moseley's law.

$$\frac{RN^2}{n^2} \qquad n = 1, 2 \ldots. \qquad (31)$$

where R = Rydberg's constant and N = atomic number of emitter. The occurrence of the constant R indicates the close relationship of Xray to optical spectra.

Actually the expression (31) for spectral terms is quite a first approximation and the Xray spectral terms really present the same degree of complexity as the optical spectral terms of the alkalies. The regular doublets which occur, appeared first to be explained by Sommerfeld's theory. He introduced relativity dynamics in the place of classical dynamics, as he did for the case of the hydrogen optical spectrum. A more careful examination of the fine structure showed this theory was insufficient. By only introducing two quantum numbers n and k, the theory does not give enough levels for the Xray spectra.

In order to get a complete theory to explain all the details of the fine structure, the third quantum number J must be introduced. In other words, not only must corrections be made to the simple formula (31) because of relativity, but also another factor must be brought in connected with the magnetic character of the electron.

THEORIES.

(1) UHLENBECK AND GOUDSMIT HYPOTHESIS 1925.

To explain the various anomalies discussed above, Uhlenbeck and Goudsmit supposed that the electron had a spin and thus an intrinsic magnetic moment and angular momentum. Assuming a model of the classical type, the electron was thought of as a sphere of electricity in rotation around one of its diameters, its angular momentum being $M = \frac{1}{2}\frac{h}{2\pi}$ and its magnetic moment μ equal to one Bohr magneton $\frac{eh}{4\pi m_0 c}$ and thus the ratio of these, $\frac{e}{m_0 c}$ is equal to that obtained experimentally in the gyromagnetic effect.

The idea of the electron having spin seems by analogy with the rotation of the planets about their diameters a likely modification of Bohr's simple planetary model of the atom. Uhlenbeck and Goudsmit assumed that the magnetic axis of the electron was always normal to the plane of the trajectory. This allows two possible directions for the electron's angular momentum or spin vector and thus there correspond to each orbit with quantum numbers n and k, two possibilities. As the total angular momentum of the atom equals the sum of the angular momentum of the electron in its orbit $\frac{kh}{2\pi}$ and of the spin $\pm\frac{1}{2}\frac{h}{2\pi}$ the total angular momentum

$$M_{total} = \left(k \pm \frac{1}{2}\right)\frac{h}{2\pi}$$

One would expect to put $j = k \pm \frac{1}{2}$, but the new quantum mechanics leads us to replace k by $\ell = (k-1)$, so that

$$j = k-1 \pm \tfrac{1}{2} = \ell \pm \tfrac{1}{2}$$

THe number j appears as expressing the total angular momentum in units of $\frac{h}{2\pi}$. AS a result of the spin, the orbit of the electron no longer remains plane but the orbital plane itself undergoes uniform precession in space about the total angular momentum vector of the atom, which remains fixed in direction and magnitude.

This theory explains the presence of doublets in both alkali optical spectra and Xray spectra as being due to the different orientation of the spin axis relative to the orbital plane. For the alkali optical spectra to each energy level with quantum numbers n and l, will correspond two levels differing slightly in energy corresponding to $j = l + \frac{1}{2}$ and $j = l - \frac{1}{2}$. However the energy states with $l = 0$, are not split, they are only displaced as with $l = 0$, j can only take the value $+\frac{1}{2}$. This result showing that the s terms are single but all others are double is in agreement with experiment.

The anomalous Zeeman effect can also be explained. The change in energy of an atom in a magnetic field H may be expressed in the form

$$W_H - W_0 = \mu_H \cdot H \tag{32}$$

where μ_H is the resolved magnetic moment in the field direction. If the ratio of magnetic moment to angular momentum is constant and equal to $\frac{e}{2m_0c}$, this is equivalent to the result (18) given above, namely

$$W_H = W_0 + m\frac{eh}{4\pi m_0 c} \cdot H$$

But since the ratio of magnetic moment to angular momentum for electron spin is double that for orbital motion, the ratio of magnetic moment to angular momentum for an atom as a whole will depend on the manner in which the spin and orbital moment are combined to produce the resultant moment.

The formula for the ratio will be here derived by applying the appropriate quantum mechanical modification to the formula obtained on a vector model basis. Consider a vector model atom in which the usual coupling relations hold; let L and S be the resultant orbital and spin moments and J the total resultant moment (in units $\frac{h}{2\pi}$).
Let μ' be the magnetic moment of the atom (in units $\frac{eh}{4\pi m_0 c}$).
The relation between the vectors is shown in figure VII.

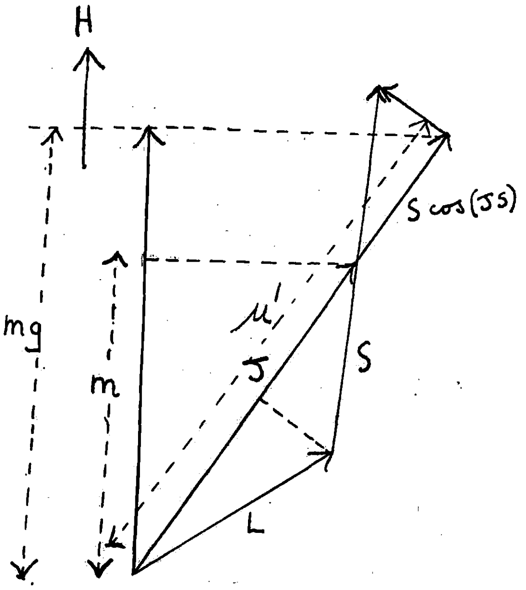

Figure VII.

Since the ratio of the magnetic moment to the angular momentum for the spin is double that for the orbital moment

$$J = L\cos(JL) + S\cos(JS)$$

$$\mu' = L\cos(JL) + 2S\cos(JS)$$

$$\frac{\mu'}{J} = 1 + \frac{S\cos(JS)}{J}$$

Now $L^2 = J^2 + S^2 - 2JS\cos(JS)$

Substituting for cos (JS)

$$\frac{\mu'}{J} = 1 + \frac{J^2 + S^2 - L^2}{2J^2}$$

Since μ' and J are in the same direction, we have for the component μ'_H along the direction of the field

$$\mu'_H = \frac{\mu'}{J} \cdot J_H = \frac{\mu'}{J} \cdot m$$

Using the expression (32) and remembering the different units for μ' and J

$$W_H - W_0 = m.\frac{ehH}{4\pi m_0 c}\left(1 + \frac{J^2 + S^2 - L^2}{2J^2}\right)$$

The quantum mechanical value for the mean square of the angular momentum is given by $j(j+1)\left(\frac{h}{2\pi}\right)^2$ and it is legitimate to make analogous substitutions in the above expression; with the result

$$W_H - W_0 = m\frac{eh}{4\pi m_0 c}H\left(1 + \frac{j(j+1) + s(s+1) - \ell(\ell+1)}{2j(j+1)}\right)$$

Thus

$$W_H = W_0 + mg\frac{eh\,H}{4\pi m_0 c}$$

where

$$g = 1 + \frac{j(j+1) + s(s+1) - \ell(\ell+1)}{2j(j+1)}$$

This expression for the splitting factor is strictly valid only when the normal coupling relations hold, and when the applied field is weak; that is when its effect is smaller than that of the interactions of the spin and orbital moments in the atom. A measure of the atomic interactions is provided by the natural multiplet width, and of the effect of the field by the Zeeman separation. A field is to be considered weak when the Zeeman separations are small compared with the multiplet width.

In the case of the alkali spectra, g reduces to $\frac{2j+1}{2l+1}$ in the equation

$$W_H = W_0 + mg.\frac{eh H}{4\pi m_0 c} \quad .$$

Thus the empirical formula (21) is obtained.

It has been shown how the hydrogen fine structure could be explained if the quantum number j is introduced. The spinning electron hypothesis explains the significance of j and therefore gives an interpretation of the fine structure.

Thus the original hypothesis of Uhlenbeck and Goudsmit applied to the old quantum theory had considerable success. However, owing to reasons that we shall explain below, the old quantum theory was replaced by a wave mechanical theory. In spite of the great success of the hypothesis of the spinning electron in the theory of spectra, there are grave difficulties encountered in interpreting it in terms of the wave theory.

THE PRINCIPLES OF WAVE MECHANICS.

The old quantum theory tried to combine classical mechanics with certain quantum conditions, the reason for which could not be explained by classical mechanics. Thus the quantum conditions appeared artificial and the theory did not seem complete. Although at first it had a striking success in accounting for the fine structure, Stark effect and Zeeman effect of hydrogen and ionised helium, it was later found to be insufficient. Several predictions made using the old quantum theory were found to be in definite contradiction with observation. This showed that the old quantum theory would have to be abandoned in favour of a more powerful and accurate theory.

In 1924 De Broglie had suggested that matter might have a wave nature. Light had already been shown to possess both wave and corpuscular aspects and it seemed natural to suppose that matter might also have this double character. The energy E of the particles was supposed related to the frequency ν by the same relationship as for light photons.

$$E = h\nu$$

The relationship between the magnitude of the momentum $|p|$ and the wavelength λ was supposed given by

$$|p| = \frac{h}{\lambda}$$

A comparison between the principle of least action in classical mechanics and Fermat's principle for geometrical optics leads to this relationship. Fermat's principle states that a ray of light in passing from a point A to a point B will describe a path for which the time of transit has a stationary value. If V denote the velocity of light and ds an element of the path:

$$\delta \int_A^B \frac{ds}{V} = 0$$

If ν is the frequency and λ the wavelength.

$$V = \nu \lambda$$

Substituting for V

$$\frac{1}{\nu} \delta \int \frac{ds}{\lambda} = \frac{1}{\nu} \delta \int \left(\frac{dx}{\lambda_x} + \frac{dy}{\lambda_y} + \frac{dz}{\lambda_z} \right) = 0 \qquad (33)$$

if the wave number $\frac{1}{\lambda}$ is supposed to have components ($\frac{1}{\lambda_x}$ $\frac{1}{\lambda_y}$ $\frac{1}{\lambda_z}$) in the same way as ds has components (dx, dy, dz).

The principle of least action in classical mechanics states that the integral $\int (p_x dx + p_y dy + p_z dz)$

when taken between two points along a mechanically possible path is less than when taken between the same two points along a neighbouring path with which the same amount of energy is associated. p_x p_y p_z represent components of the momentum p of the particle.

$$\delta \int (p_x\,dx + p_y\,dy + p_z\,dz) = 0 \qquad (34)$$

Comparing equations (33) and (34) one would conclude that

$$p_x \propto \frac{1}{\lambda_x} \quad p_y \propto \frac{1}{\lambda_y} \quad p_z \propto \frac{1}{\lambda_z} \qquad |p| \propto \frac{1}{\lambda}$$

We might suppose by analogy that just as the theory of diffraction comes to the aid of geometrical optics when the dimensions of the objects considered are of the same order as the wavelength of light, wave mechanics should be used to aid classical mechanics when dimensions are of the order of the mechanical wavelength (i.e. of atomic dimensions).

Experiments by Davisson and Germer (1927), G.P. Thomson (1928) and Rupp (1928) on the diffraction of electrons gave direct experimental verification of the above relations. Dempster and Stern showed that not only cathode rays but also atomic and molecular beams were associated with waves, and verified the De Broglie relation between momentum and wavelength.

We shall derive the propagation equation of wave mechanics for a particle in a constant field of force in the non relativistic form in the simple case of one dimension by using the above relation between wavelength and momentum. The general equation for wave propagation in one dimension is

$$\frac{\partial^2\psi}{\partial x^2} = \frac{1}{V^2}\frac{\partial^2\psi}{\partial t^2}$$

where V is the velocity of the wave, ψ the wave amplitude and the direction of propagation is along the X axis. Now

$$V = \nu\lambda$$

where ν is the frequency. Assuming ψ depends on the time by the relation

$$\psi = Ae^{2\pi i\nu t}$$

then

$$\frac{\partial^2\psi}{\partial t^2} = -4\pi^2\nu^2\psi$$

$$\frac{\partial^2\psi}{\partial x^2} = -\frac{4\pi^2\nu^2}{V^2}\psi = -\frac{4\pi^2}{\lambda^2}\psi = -\frac{4\pi^2 p^2}{h^2}\psi$$

as $\lambda = \frac{h}{|p|}$

If E represents the total energy of the particle and U the potential energy then

$$E = \frac{1}{2} m_0 v^2 + U$$

where v is the velocity of the particle

$$p^2 = m_0^2 v^2 = 2m_0(E-U)$$

and substituting for p, the propagation equation becomes

$$\frac{\partial^2 \psi}{\partial x^2} = - \frac{8\pi^2}{h^2} m_0 (E-U) \psi$$

In three dimensions this equation becomes the equation below, which is known as Schroedinger's equation (published 1926)

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2}{h^2} m_0 (E-U) \psi = 0$$

if ψ represents the wave function in this case.

This equation may be obtained from the energy equation

$$E = \frac{1}{2m_0} (p_x^2 + p_y^2 + p_z^2) + U$$

where p_x p_y p_z are the components of the momentum $\vec{p}$ if one replaces p_x by the operator $- \frac{h}{2\pi i} \frac{\partial}{\partial x}$

p_y by $- \frac{h}{2\pi i} \frac{\partial}{\partial y}$

and p_z by $- \frac{h}{2\pi i} \frac{\partial}{\partial z}$

When the energy is expressed as a function of the coordinates of the particle and the components of momenta, it is called the Hamiltonian function $H(x, y, z, t, p_x, p_y, p_z)$. If p_x p_y p_z are replaced by the corresponding operators then

$$H\left(x, y, z, t\ -\frac{h}{2\pi i}\frac{\partial}{\partial x} - \frac{h}{2\pi i}\frac{\partial}{\partial y} - \frac{h}{2\pi i}\frac{\partial}{\partial z}\right)$$

is called the Hamiltonian operator. The wave equation is expressed by

$$H(\psi) = \frac{h}{2\pi i}\frac{\partial \psi}{\partial t}$$

where $\psi(x, y, z, t)$ is the wavefunction of the particle, or more explicitly

$$\nabla^2\psi - \frac{8\pi^2 m_0}{h^2}U(x,y,z,t)\psi = \frac{4\pi i m_0}{h}\frac{\partial \psi}{\partial t}$$

If U is not dependent on the time so that the external field is constant, the wave equation has monochromatic solutions which only depend on the time by a factor of the form $e^{\frac{2\pi i}{h}Et}$

Such a monochromatic wave satisfies Schroedinger's equation

$$\nabla^2\psi + \frac{8\pi^2 m_0}{h^2}(E - U)\psi = 0$$

We suppose the wave function ψ is always "normalised" by the condition $\int \psi\psi^* d\tau = 1$

(where ψ^* represents the quantity which is the complex conjugate of ψ). This expresses the fact that the particle must be present somewhere in space.

Using Schroedinger's equation we shall determine the energy values for the hydrogen spectrum on the basis of wave mechanics. Assuming the hydrogen atom consists of a central nucleus of positive charge e and an electron of charge -e at a distance r from it, then the potential energy U of the electron will be $-\frac{e^2}{r}$ if we assume a Coulomb law of attraction. Substituting in Schroedinger's equation we obtain

$$\nabla^2\psi + \frac{8\pi^2 m_0}{h^2}\left(E + \frac{e^2}{r}\right)\psi = 0$$

On transforming $\nabla^2\psi$ into polar coordinates r, θ and ϕ this becomes

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}$$
$$+ \frac{8\pi^2 m_0}{h^2}\left(E + \frac{e^2}{r}\right)\psi = 0$$

To solve this equation one substitutes

$$\psi = R(r)\,\Theta(\theta)\,\Phi(\phi)$$

where R is a function of r only, Θ is a function of θ only and Φ of ϕ only. The equation becomes

$$\frac{1}{Rr^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{1}{\Theta r^2\sin\theta}\cdot\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{1}{\Phi r^2\sin^2\theta}\frac{\partial^2\Phi}{\partial\phi^2}$$
$$+\frac{8\pi^2 m_0}{h^2}\left(E+\frac{e^2}{r}\right)=0 \qquad (35)$$

Multiplying by $r^2\sin^2\theta$ the equation becomes

$$\frac{\sin^2\theta}{R}\frac{d}{dr}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2}$$
$$+\frac{8\pi^2 m_0}{h^2}r^2\sin^2\theta\left(E+\frac{e^2}{r}\right)=0$$

The only term in this equation which contains ϕ is $\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2}$ so that in solving for Φ this must equal a constant say $-d_0^2$

$$\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2}=-d_0^2$$

and solving

$$\Phi=A\cos d_0\phi+B\sin d_0\phi$$

where A and B are constants. The wave function ψ must be single valued and therefore Φ must be single valued and the condition for this is that d_0 must be an integer. Multiplying equation (35) by r^2 and substituting for Φ

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\left[\frac{1}{\Theta\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)-\frac{d_0^2}{\sin^2\theta}\right]+\frac{8\pi^2 m_0 r^2}{h^2}\left(E+\frac{e^2}{r}\right)=0 \qquad (36)$$

The only terms in θ are

$$\frac{1}{\Theta\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)-\frac{d_0^2}{\sin^2\theta}$$

so in solving for Θ this must equal a constant. Let this constant be $-f(f+1)$, then for Θ to be a single valued function of θ, f must be an integer. On substituting in equation (36) this becomes

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\left[-f(f+1)+\frac{8\pi^2 m_0 r^2}{h^2}\left(E+\frac{e^2}{r}\right)\right]=0$$

or

$$\frac{d^2R}{dr^2}+\frac{2}{r}\frac{dR}{dr}+\left[\frac{8\pi^2 m_0}{h^2}\left(E+\frac{e^2}{r}\right)-\frac{f(f+1)}{r^2}\right]R=0$$

When r is very large the equation reduces to

$$\frac{d^2R}{dr^2}+\frac{8\pi^2 m_0 E}{h^2}R=0$$

with solution

$$R=\text{constant}\, e^{\frac{1}{2}a_1 r} \quad \text{where} \quad \frac{8\pi^2 m_0}{h^2}E=-\frac{a_1^2}{4}$$

Thus for r not very large we should expect a solution of the form

$$R=X(r)\,e^{\frac{1}{2}a_1 r}$$

where $X(r)$ is a function of r and tends to a constant value when $r \rightarrow \infty$. Substituting this, the equation becomes

$$\frac{d^2X}{dr^2} + \left(a_1 + \frac{2}{r}\right)\frac{dX}{dr} + \left[\frac{\left(a_1 + \frac{8\pi^2 m_0}{h^2} e^2\right)}{r} - \frac{f(f+1)}{r^2}\right] X = 0$$

This equation is of the form

$$\frac{d^2X}{dr^2} + \left(a_1 + \frac{b_1}{r}\right)\frac{dX}{dr} + \left(\frac{a_0}{r} + \frac{b_0}{r^2}\right) X = 0$$

where

$$\frac{a_1^2}{4} = -\frac{8\pi^2 m_0 E}{h^2} \qquad a_0 = -a_1 + \frac{8\pi^2 m_0 e^2}{h^2}.$$

$$b_1 = 2 \qquad b_0 = -f(f+1)$$

This equation in X may be solved by series, by putting

$$X = A_0 r^{g_0} + A_1 r^{g_0+1} + A_2 r^{g_0+2} + \ldots\ldots \quad A_{s_0} r^{g_0+s_0}$$

Substituting for X in the equation and equating the coefficient of the term in r^{g_0-2} to zero we find

$$g_0(g_0+1) = f(f+1)$$

so that

$$g_0 = f \quad \text{or} \quad -(f+1)$$

Equating the coefficient of the term in $r^{g_0+s_0-2}$ to zero we find

$$A_{s_0} = -\frac{a_1(g_0+s_0-1) + a_0}{(g_0+s_0)(g_0+s_0+1) + b_0} A_{s_0-1}$$

The condition for the series to terminate is for one of the coefficients to be zero, so that all subsequent terms will be zero.

If $A_{s_0} = 0$, there are s_0 terms in the series and

$$a_1(g_0 + s_0 - 1) = -a_0 \qquad \text{or}$$

$$(g_0 + s_0)^2 = \left(\frac{a_1 - a_0}{a_0}\right)^2$$

and substituting for a_1 and a_0

$$(g_0 + s_0)^2 = -\frac{\left(\frac{8\pi^2 m_0}{h^2} e^2\right)^2}{4 \cdot \frac{8\pi^2 m_0}{h^2} E}$$

or

$$(g_0 + s_0)^2 = -\frac{2\pi^2 m_0}{h^2}\,\frac{e^4}{E}$$

We have seen $g_0 = f$ or $-(f+1)$ and is an integer and s_0, being the number of terms in the series must be an integer. $n = (g_0 + s_0)$ must therefore be an integer. Then

$$E = -\frac{2\pi^2 m_0 e^4}{n^2 h^2} \qquad \text{where n is an integer}$$

This gives exactly the energy values for E of Bohr's theory. However instead of the arbitrary quantum conditions of Bohr's theory, the discrete energy values appear here naturally as the only ones for which a solution of the wave equation is possible.

The point of view of wave mechanics is quite different from that of classical mechanics. In classical mechanics one considers particles as having at each instant a well defined position in space so that using the laws of motion and knowing the fones acting on the particle and certain initial conditions, it is possible to predict the whole course of the motion of the particle. In wave mechanics however, the quantities associated with the particle such as its coordinates, its energy, its momentum components have not in general exactly determined values. It is no longer possible to speak of its exact position at each instant One can only assign at each instant to each of the quantities associated with the particle a certain number of possible values, each having a certain probability. This point of view is expressed in Heisenberg's "uncertainty relations" which will be mentioned later.

INCOMPLETENESS OF EARLY FORM OF WAVE MECHANICS.

Whilst wave mechanics explains naturally the Bohr energy levels of hydrogen, it does not in this early form explain the fine structure of the hydrogen spectrum nor the various anomalies we have enumerated above, which have led to the idea of spin and magnetic moment associated with the electron. Thus wave mechanics must remain incomplete whilst it does not contain some element corresponding to electron spin. However whilst the model of a rotating electron is permissible with the conceptions of the old quantum theory, one cannot transpose such into wave mechanics because in this theory one cannot state precisely that there is an electron at a particular place at a particular time. Instead of assuming Uhlenbeck and Goudsmit's hypothesis, it is necessary somehow to introduce the idea of spin into the framework of wave mechanics.

Schroedinger's wave equation is evidently also not completely satisfactory as it is not in accordance with the principle of relativity. Early attempts to slightly modify the equation to make it conform to the relativity principle were not successful. To obtain the wave equation of relativistic wave mechanics, one would expect to apply a similar method to that shown above for the derivation of Schroedinger's equation, but instead of starting from the formulae of classical dynamics to start from those of relativistic mechanics. For a particle of charge e in an electromagnetic field the relativistic equation obtained in this way is

$$\frac{1}{c^2}\frac{\partial^2\psi}{\partial t^2} - \nabla^2\psi - \frac{4\pi i}{h}\frac{eV}{c^2}\frac{\partial\psi}{\partial t} - \frac{4\pi i}{h}\frac{eA_x}{c}\frac{\partial\psi}{\partial x} \qquad (37)$$

$$- \frac{4\pi i}{h}\frac{eA_y}{c}\frac{\partial\psi}{\partial y} - \frac{4\pi i}{h}\frac{eA_z}{c}\frac{\partial\psi}{\partial z} + \frac{4\pi^2}{h^2}\left[m_0^2c^2 + \frac{e^2}{c^2}(V^2 - A^2)\right]\psi = 0$$

where the electric field $\vec{E}$ and the magnetic field $\vec{H}$ can be defined by the potential scalar $V(x, y, z, t)$ and the potential vector $\vec{A}(x, y, z, t)$ according to the relations

$$\vec{H} = \text{curl}\ \vec{A} \qquad \text{and} \qquad \vec{E} = -\,\text{grad}\, V - \frac{1}{c}\frac{\partial \vec{A}}{\partial t}$$

We shall discuss later the reason for A_x A_y A_z and V occurring in this manner in the equation.

When there is no electromagnetic field so that V and $\vec{A}$ are zero the equation becomes

$$\nabla^2\psi - \frac{1}{c^2}\frac{\partial^2\psi}{\partial t^2} = \frac{4\pi^2}{h^2} m_0^2 c^2 \psi$$

The equation (37) is not satisfactory as not only does it predict results not in agreement with experiment but also this equation is of the second order with respect to time whilst Dirac has shown that the correct propagation equation should be of the first order with respect to time.

PAULI'S THEORY 1927.

Remaining in the framework of classicalconceptions, Uhlenbeck and Goudsmit had imagined the electron as a little sphere of negative electricity in rotation about a diameter with angular momentum $\frac{1}{2}\frac{h}{2\pi}$ and magnetic moment about the same ax is equal to one Bohr magneton $\frac{eh}{4\pi m_0 c}$

In wave mechanics it appears that one must not represent the electron so precisely but must always introduce the idea of probabilities.

In order to discuss an analogous problem we may consider the meaning of the polarisation of a light quantum according to the principles of wave mechanics. Let us imagine a plane polarised beam of light to be propagated in the direction OZ. Let OX and OY be two axes perpendicular to OZ. The light vector normal to OZ will be of the form

$$\vec{a}_0 \sin 2\pi\nu\left(t - \frac{z}{c} + \varphi\right)$$

and its components along OX and OY will have amplitudes given by

$$a_x = a_0 \cos\theta \qquad a_y = a_0 \sin\theta$$

if θ is the angle between the light vector and OX. The intensity of the beam is a_0^2. If a nicol which allows only vibrations parallel to OX to pass is placed in the path of the beam, the light vector after traversing the nicol is reduced to $a_x \sin 2\pi\nu(t-\frac{z}{c}+\varphi)$ and the intensity is $a_0^2\cos^2\theta$ If the nicol is then turned through 90°, the light vector in the waves transmitted will be parallel to OY and equal to $a_y \sin 2\pi\nu(t-\frac{z}{c}+\varphi)$ the transmitted intensity being $a_0^2\sin^2\theta$

The question arises as to how all this should be interpreted if one assumes the existence of photons. If one attributes a polarisation to each individual photon, an explanation of the cause of the phenomenon becomes impossible. In that case one must attribute in some way to the incident photon a polarisation dependent on the light vector of the incident wave and it becomes very difficult to explain why certain photons do not traverse the nicol whilst others do. However from the probability point of view of wave mechanics, one cannot attribute an exactly determined polarisation to the incident photon. One can only define with the help of the associated light wave, the probability for the photon after crossing the nicol to be revealed as having a polarisation parallel to OX. This probability is $\cos^2\theta$ One can say that when the photon has passed through the nicol, it has a probability $\cos^2\theta$ of being revealed with polarisation parallel to OX and probability $\sin^2\theta$ of being revealed with polarisation parallel to OY.

Let us now return to the case of the spin of the electron. The hypothesis of the magnetic and spinning electron leads one to associate with an electron, two directed quantities proportional to one another, the magnetic moment and angular momentum. Whilst for the photon polarisation is defined by direction but no sense is specified, for the vector spin of the electron, both direction and sense must be stated. However in the same way that we cannot attribute to a photon a definite direction of polarisation, we also should not in making the theory of the magnetic electron conform to the general principles of wave mechanics, attribute a definite spin to an individual electron. We can only state the probability that an experiment made to determine the direction of spin of the electron should give such and such result. On this essential idea, Pauli founded a first tentative theory of the spinning electron in the framework of wave mechanics.

If one considers a system of rectangular axes, all experiments which permit one to assign a value to the component of the spin angular momentum of the electron along OZ will give the result either $+\frac{h}{4\pi}$ or $-\frac{h}{4\pi}$ from Uhlenbeck and Goudsmit's hypothesis. Pauli showed that to find the probabilities for the two possible values of spin, one must consider a wave function with two components ψ_1, and ψ_2 such that $|\psi_1|^2$ dx dy dz is the probability of finding the particle in the element of volume dx dy dz with spin $+\frac{h}{4\pi}$ along OZ and that $|\psi_2|^2$ dx dy dz is the probability of finding the particle in the volume dx dy dz with spin $-\frac{h}{4\pi}$ along OZ.

A rather closer analogy to electron spin can be obtained if we consider instead of linear polarisation, the circular polarisation of light. In the case of light, to find the probability of a photon having one kind of circular polarisation after passage through an analyser of circularly polarised light, we should decompose the incident wave into a wave ψ_R with right circular polarisation and a wave ψ_L with left circular polarisation. Then $(\psi_R)^2$ would give us the probability of right circular polarisation of the photon. One might think therefore that the two possible senses of spin along OZ would perhaps correspond to circular polarisations in opposite senses in the plane XOY.

Pauli thus introduced the idea that to take account of the spin of the electron, one must increase the number of functions ψ. Naturally the normalisation condition becomes here

$$\iiint (|\psi_1|^2 + |\psi_2|^2)\, dx\, dy\, dz = 1$$

Pauli's theory for introducing spin into wave mechanics was incomplete. Firstly it was not in accordance with the principle of relativity; it only envisaged changes in space coordinates and not transformations of space time coordinates in the relativistic sense. Further it did not lead to quite correct predictions in the case of the hydrogen spectrum. However it indicated clearly the way to follow to take account of spin and guided Dirac in the development of his more complete theory.

DIRAC'S THEORY 1928

Introduction.

We have seen that in nonrelativistic wave mechanics, the general equation of propagation of a particle is

$$H\left(x, y, z, -\frac{h}{2\pi i}\frac{\partial}{\partial x}, -\frac{h}{2\pi i}\frac{\partial}{\partial y}, -\frac{h}{2\pi i}\frac{\partial}{\partial z}, t\right)\psi = \frac{h}{2\pi i}\frac{\partial \psi}{\partial t} \qquad (38)$$

where H is the Hamiltonian operator. In the case of a particle of mass m_0 displaced in a field of potential energy U, this equation becomes

$$-\frac{h^2}{8\pi^2 m_0}\nabla^2\psi + U(x, y, z, t)\psi = \frac{h}{2\pi i}\frac{\partial \psi}{\partial t} \qquad (39)$$

If the particle carries a charge e and moves in an electrostatic field of electric potential V(x, y, z, t) one has

$$U = eV$$

and the equation becomes

$$-\frac{h^2}{8\pi^2 m_0}\nabla^2\psi + eV(x, y, z, t)\psi = \frac{h}{2\pi i}\frac{\partial \psi}{\partial t} \qquad (40)$$

If the charged particle is an electron we can put above $e = -e^1$. In this non relativistic theory, the necessarily positive quantity $\psi\psi^*$ represents the probability density for the presence of the particle at a point. The total probability is conserved in the course of time and is equal to unity.

We have seen (from equation (37)) that the early attempt to obtain a relativistic propagation equation gave the following equation for a particle of mass m_0 and charge e displaced in an electromagnetic field with scalar potential V(x, y, z, t) and vector potential $\vec{A}$(x, y, z, t)

$$\frac{1}{c^2}\left(\frac{h}{2\pi i}\frac{\partial}{\partial t} - eV\right)^2\psi - \sum_{x,y,z}\left(\frac{h}{2\pi i}\frac{\partial}{\partial x} + \frac{e}{c}A_x\right)^2\psi = m_0^2c^2\psi \tag{41}$$

For an electron this takes the form

$$\frac{1}{c^2}\left(\frac{h}{2\pi i}\frac{\partial}{\partial t} + e'V\right)^2\psi - \sum_{x,y,z}\left(\frac{h}{2\pi i}\frac{\partial}{\partial x} - \frac{e'}{c}A_x\right)^2 = m_0^2c^2\psi$$

Introducing the notation

$$\begin{aligned} P_1 &= -\frac{h}{2\pi i}\frac{\partial}{\partial x} + \frac{e'A_x}{c} & \qquad P_2 &= -\frac{h}{2\pi i}\frac{\partial}{\partial y} + \frac{e'A_y}{c} \\ P_3 &= -\frac{h}{2\pi i}\frac{\partial}{\partial z} + \frac{e'A_z}{c} & \qquad P_4 &= \frac{h}{2\pi i}\frac{1}{c}\frac{\partial}{\partial t} + \frac{e'V}{c} \end{aligned} \tag{42}$$

we obtain the equation

$$\left(P_4^2 - \sum_1^3 P_i^2 - m_0^2c^2\right)\psi = 0 \tag{43}$$

It is seen that in the presence of an electromagnetic field, the momentum operators P_1 P_2 P_3 are modified. Instead of $P_1 = -\frac{h}{2\pi i}\frac{\partial}{\partial x}$ as in the case of no field

$$P_1 = -\frac{h}{2\pi i}\frac{\partial}{\partial x} + \frac{e'A_x}{c}$$

and thus contains an extra term dependent on the x component of the vector potential. We shall consider the reason for this

MODIFICATION OF MOMENTUM OPERATORS IN THE PRESENCE OF AN ELECTROMAGNETIC FIELD.

It is first necessary to consider some generalised principles of classical mechanics. The equations of motion for a system of free particles may be expressed by the equations

$$\frac{d}{dt}\left(m_k \vec{V}_k\right) = \vec{K}_k \qquad (44)$$

where m_k denotes the mass of the k_{th} particle, $\vec{V}_k$ its velocity and $\vec{K}_k$ the force acting on it. In many cases the system of equations (44) are equivalent to a variation principle, Hamilton's principle which is expressed by the statement

$$\int_{t_1}^{t_2} L\, dt = \text{stationary value} \qquad (45)$$

Lagranges equations

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{x}_k} - \frac{\partial L}{\partial x_k} = 0 \qquad (46)$$

and the two similar equations in y and z can be derived from this variation principle. L has to be determined so that these equations (46) agree with the Newtonian equations (44).

If the forces $\vec{K}_k$ have a potential U then

$$\vec{K}_{kx} = -\frac{\partial U}{\partial x_k}$$

and we determine a function T^1 of the velocity components so that

$$\frac{\partial T'}{\partial \dot{x}_k} = m_k \dot{x}_k \qquad \frac{\partial T'}{\partial \dot{y}_k} = m_k \dot{y}_k \qquad \frac{\partial T'}{\partial \dot{z}_k} = m_k \dot{z}_k$$

Equations (44) can then be written in the form

$$\frac{d}{dt}\frac{\partial T'}{\partial \dot{x}_k} - \frac{\partial(-U)}{\partial x_k} = 0$$

or

$$\frac{d}{dt}\frac{\partial(T'-U)}{\partial \dot{x}_k} - \frac{\partial(T'-U)}{\partial x_k} = 0$$

Therefore in the variation principle (45) we can put

$$L = T' - U \tag{47}$$

If taking no account of the theory of relativity, m_R is regarded as constant, T^1 is equal to the kinetic energy T. On the other hand, if in accordance with relativity, we write

$$m = \frac{m_0}{\sqrt{1-\frac{v^2}{c^2}}}$$

where m_0 is the rest mass we have

$$T' = m_0 c^2 \left(1 - \sqrt{1-\frac{v^2}{c^2}}\right)$$

T^1 being a function which differs from the kinetic energy T

$$T = m_0 c^2 \left(\frac{1}{\sqrt{1-\frac{v^2}{c^2}}} - 1\right)$$

If besides the component $\vec{K}$ which can be derived from a potential U, the forces alsocontain a component $\vec{K}^1$ depending on the velocities (as for example in the case of magnetic forces acting on electric charges) then the above theory has to be modified. We must determine a function M so that

$$\frac{d}{dt}\frac{\partial M}{\partial \dot{x}} - \frac{\partial M}{\partial x} = K_x^{1}$$

and the expression

$$L = T^{1} - U - M \tag{48}$$

is substituted in the variation principle (45). Lagranges equations (46) then become

$$\frac{d}{dt}\frac{\partial T^{1}}{\partial \dot{x}} + \frac{\partial U}{\partial x} - \frac{d}{dt}\frac{\partial M}{\partial \dot{x}} + \frac{\partial M}{\partial x} = 0$$

and the variation principle is in fact equivalent to the Newtonian equations of motion

$$\frac{d}{dt}(m\dot{x}) - \vec{K}_x - \vec{K}_x^{1} = 0$$

Let us apply this general theory to the case of an electron of charge $e = -e^1$ in a magnetic field H. It will be subject to the so called Lorentz force given by

$$\vec{K}^1 = -\frac{e^1}{c}[\vec{V} \times \vec{H}]$$

We have to determine a function M such that

$$\frac{d}{dt}\frac{\partial M}{\partial \dot{x}} - \frac{\partial M}{\partial x} = \vec{K}_x^{1}$$

We find that the function

$$M = \frac{e^1}{c} (\vec{A}.\vec{V}) = \frac{e^1}{c} (A_x \dot{x} + A_y \dot{y} + A_z \dot{z})$$

has this property. $\vec{A}$ is the vector potential of the magnetic field defined by

$$\vec{H} = \text{curl } \vec{A}$$

We have

$$\frac{\partial M}{\partial \dot{x}} = \frac{e'}{c} A_x$$

$$\frac{d}{dt}\frac{\partial M}{\partial \dot{x}} = \frac{e'}{c}\frac{dA_x}{dt} = \frac{e'}{c}\left[\frac{\partial A_x}{\partial t} + \frac{\partial A_x}{\partial x}\dot{x} + \frac{\partial A_x}{\partial y}\dot{y} + \frac{\partial A_x}{\partial z}\dot{z}\right]$$

$$\frac{\partial M}{\partial x} = \frac{e'}{c}\left[\frac{\partial A_x}{\partial x}\dot{x} + \frac{\partial A_y}{\partial x}\dot{y} + \frac{\partial A_z}{\partial x}\dot{z}\right]$$

$$\frac{d}{dt}\frac{\partial M}{\partial \dot{x}} - \frac{\partial M}{\partial x}$$

$$= \frac{e'}{c}\left[\frac{\partial A_x}{\partial t} + \frac{\partial A_x}{\partial x}\dot{x} + \frac{\partial A_x}{\partial z}\dot{z} + \frac{\partial A_x}{\partial y}\dot{y} - \frac{\partial A_x}{\partial x}\dot{x} - \frac{\partial A_y}{\partial x}\dot{y} - \frac{\partial A_z}{\partial x}\dot{z}\right]$$

If A_x does not contain the time explicitly as in the usual case of a constant field

$$\frac{d}{dt}\frac{\partial M}{\partial \dot{x}} - \frac{\partial M}{\partial x} = -\frac{e'}{c}\left[\dot{y}\left(\frac{\partial A_x}{\partial y} - \frac{\partial A_y}{\partial x}\right) + \dot{z}\left(\frac{\partial A_x}{\partial z} - \frac{\partial A_z}{\partial x}\right)\right]$$

$$= -\frac{e'}{c}\left(\dot{z} H_y - \dot{y} H_z\right)$$

$$= -\frac{e'}{c}\left[v \times H\right]_x = \vec{K}'_x$$

as H = curl A

The total force on an electron in an electromagnetic field is

$$\left(\vec{E} - \left[\frac{\vec{v}}{c} \times \vec{H}\right]\right) e'$$

where E is the electric field. The lagrangian function by equation (48) is in this case equal to

$$L = T - U - \frac{e^1}{c}\left[A_x\dot{x} + A_y\dot{y} + A_z\dot{z}\right]$$

Taking the Newtonian approximation

$$p_x = \frac{\partial L}{\partial \dot{x}} = \frac{\partial T}{\partial \dot{x}} - \frac{e'}{c}A_x = m\dot{x} - \frac{e'}{c}A_x$$

$$p_y = m\dot{y} - \frac{e'}{c}A_y$$

$$p_z = m\dot{z} - \frac{e'}{c}A_z$$

Thus instead of the momentum component $m\dot{x}$ being equal to p_x, in this case it will equal $p_x + \frac{e^1}{c}A_x$

The momentum operator $-\frac{h}{2\pi i}\frac{\partial}{\partial x}$ is then replaced by

$$-\frac{h}{2\pi i}\frac{\partial}{\partial x} + \frac{e' A_x}{c}$$

$$P_1 = -\frac{h}{2\pi i}\frac{\partial}{\partial x} + \frac{e' A_x}{c} \qquad P_2 = -\frac{h}{2\pi i}\frac{\partial}{\partial y} + \frac{e' A_y}{c}$$

$$P_3 = -\frac{h}{2\pi i}\frac{\partial}{\partial z} + \frac{e' A_z}{c}$$

No additional term occurs in the energy corresponding to the magnetic field, since the magnetic forces do no work. The electron will however have potential energy in the electric field which will equal $e^1 V$ in an electromagnetic field of scalar potential V. Thus P_4 in this case will equal $\frac{h}{2\pi i}\frac{1}{c}\frac{\partial}{\partial t} + \frac{e' V}{c}$ instead of $\frac{h}{2\pi i}\frac{1}{c}\frac{\partial}{\partial t}$

DIRAC'S EQUATIONS IN THE ABSENCE OF ANY FIELD OF FORCE.

For the relativistic equations of propagation (43), the probability density for the presence of the electron at a point can no longer be taken as $\psi\psi^*$, as in the non relativistic case, because the integral of this quantity throughout all space is no longer necessarily constant in the course of time. Instead a more complicated expression for the probability density must be used

$$\rho = -\frac{h}{4\pi m_0 c^2}\left(\psi\frac{\partial\psi^*}{\partial t} - \psi^*\frac{\partial\psi}{\partial t}\right) + \frac{e'}{m_0 c^2} V\psi\psi^* \qquad (49)$$

which reduces to $\psi\psi^*$ when the Newtonian approximation is sufficient.

Dirac criticised these equations (41) (43) and (49) especially the equation (49) for the probability density. In this equation ρ is not necessarily positive whilst negative values of ρ could evidently have no meaning. Also the general principles of quantum mechanics require that whatever the form of propagation equation adopted, the probability of finding the particle in the small volume between x and x + dx, y and y + dy, z and z + dz should be $\psi\psi^*\,dx\,dy\,dz$ and this requirement does not agree with formula (49). Dirac said that the probability ought to have always the positive form $\psi\psi^*$ or if the existence of several wave functions ψ_i

is assumed the form $\sum_i \psi_i \psi_i^*$

The non relativistic differential equation (40) is of the first order with respect to time and the corresponding expression for probability density is $\psi\psi^*$ Given the initial form ψ (x, y, z, 0) of the wave function, the later evolution of the probability density will be completely determined by the propagation equation. However in the case of the relativistic equation (41) as it is the second order in t, it would be necessary to give values both of ψ and of $\frac{\partial\psi}{\partial t}$ at the initial instant for the wave function to be determined. In this case there is no automatic conservation of the probability in the course of time. Dirac thus concluded that the propagation equation should be of the first order in t; and as by the principle of relativity, it must always be symmetrical in the coordinates of space and time, it oughtto be of the first order with respect to the four variables x, y, z, t. The same reasoning and conclusions are valid if there are several functions ψ and several simultaneous propagation equations.

Dirac first considered the case of the free motion of an electron in the absence of any electromagnetic field. Then $V = \vec{A} = 0$ and the operators P_i of equation (42), (if small letters are used to denote the p's in this case) become

$$p_1 = -\frac{h}{2\pi i}\frac{\partial}{\partial x} \quad p_2 = -\frac{h}{2\pi i}\frac{\partial}{\partial y} \quad p_3 = -\frac{h}{2\pi i}\frac{\partial}{\partial z} \quad p_4 = \frac{h}{2\pi i}\frac{1}{c}\frac{\partial}{\partial t} \qquad (50)$$

The propagation equation (43) becomes

$$\left(p_4^2 - \sum_1^3{}_i\, p_i^2 - m_0^2 c^2\right)\psi = 0$$

which, if one uses the Newtonian approximation, reduces in this case to the same form as the ordinary Schroedinger equation. Dirac supposed that there were several wave functions $\psi_1\ \psi_2 \cdots \psi_N$ each satisfying the equation

$$\left(p_4^2 - \sum_1^3{}_i\, p_i^2 - m_0^2 c^2\right)\psi_k = 0 \qquad (k = 1 \ldots\ldots N) \qquad (51)$$

These second order equations should be derived from the true propagation equations which are of the first order and which Dirac wrote in the symbolic form

$$\left(p_4 + \alpha_1 p_1 + \alpha_2 p_2 + \alpha_3 p_3 + \alpha_4 m_0 c\right)\psi_k = 0 \qquad (52)$$

The α_i are matrices of N rows and N columns and the operation $\alpha_i\,\psi_k$ is defined by the formula

$$\alpha_i \psi_k = \sum_1^N{}_l\, \alpha_{i,\,kl}\, \psi_l$$

where $\alpha_{i,\,kl}$ designates an element of the matrix α_i with indices k, l. The equation (52) should lead to the equations (51) and this imposes certain conditions on the α_i matrices. Applying the operator

$$\left(p_4 - \sum_1^3{}_i\, \alpha_i p_i - \alpha_4 m_0 c\right)$$

to equation (52) we have

$$\left(p_4 - \sum_{1\,i}^{3} \alpha_i p_i - \alpha_4 m_0 c\right)\left(p_4 + \sum_{1\,i}^{3} \alpha_i p_i + \alpha_4 m_0 c\right) \psi_k = 0$$

For this equation on expansion to coincide with equation (51) we must have for all the α_i's

$$\alpha_i^2 = 1 \qquad \text{and} \qquad \alpha_i \alpha_j + \alpha_j \alpha_i = 0 \tag{53}$$

For N less than four, it is not possible to find four hermitian matrices which satisfy the conditions (53). For N = 4 several of these matrices are possible and in the following theory we shall use the matrices α_i given by

$$\alpha_1 = \begin{pmatrix} 0&0&0&1 \\ 0&0&1&0 \\ 0&1&0&0 \\ 1&0&0&0 \end{pmatrix} \quad \alpha_2 = \begin{pmatrix} 0&0&0&+i \\ 0&0&-i&0 \\ 0&+i&0&0 \\ -i&0&0&0 \end{pmatrix} \quad \alpha_3 = \begin{pmatrix} 0&0&1&0 \\ 0&0&0&-1 \\ 1&0&0&0 \\ 0&-1&0&0 \end{pmatrix} \quad \alpha_4 = \begin{pmatrix} 1&0&0&0 \\ 0&1&0&0 \\ 0&0&-1&0 \\ 0&0&0&-1 \end{pmatrix}$$

Dirac assumed there were four functions ψ_i satisfying the four simultaneous equations (52) of the first order. Using the above α_i matrices and assuming the wave functions form a matrix $\begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{pmatrix}$ these four equations may be written explicitly.

$$\begin{aligned}
(p_4 + m_0 c)\psi_1 + (p_1 + i p_2)\psi_4 + p_3 \psi_3 &= 0 \\
(p_4 + m_0 c)\psi_2 + (p_1 - i p_2)\psi_3 - p_3 \psi_4 &= 0 \\
(p_4 - m_0 c)\psi_3 + (p_1 + i p_2)\psi_2 + p_3 \psi_1 &= 0 \\
(p_4 - m_0 c)\psi_4 + (p_1 - i p_2)\psi_1 - p_3 \psi_2 &= 0
\end{aligned} \tag{54}$$

The equations (54) are only suitable for the case where there is no field.

DIRAC'S EQUATIONS IN AN ELECTROMAGNETIC FIELD - MAGNETIC MOMENT OF ELECTRON.

Dirac next considered the case of an electron moving in a field defined by a scalar potential V and a vector potential $\vec{A}$. For this he replaced the operators p_i of the formulae (50) by the operators P_i of formulae (42) in the symbolic equation (52). The propagation equations in an electromagnetic field are then symbolically written

$$(P_4 + \alpha_1 P_1 + \alpha_2 P_2 + \alpha_3 P_3 + \alpha_4 m_0 c)\psi_k = 0 \tag{55}$$

with

$$P_1 = -\frac{h}{2\pi i}\frac{\partial}{\partial x} + \frac{e' A_x}{c} \qquad P_2 = -\frac{h}{2\pi i}\frac{\partial}{\partial y} + \frac{e' A_y}{c}$$

$$P_3 = -\frac{h}{2\pi i}\frac{\partial}{\partial z} + \frac{e' A_z}{c} \qquad P_4 = \frac{h}{2\pi i}\frac{1}{c}\frac{\partial}{\partial t} + \frac{e' V}{c}$$

Explicitly equation (55) may be written

$$\begin{aligned}
(P_4 + m_0 c)\psi_1 + (P_1 + iP_2)\psi_4 + P_3\psi_3 &= 0\\
(P_4 + m_0 c)\psi_2 + (P_1 - iP_2)\psi_3 - P_3\psi_4 &= 0\\
(P_4 - m_0 c)\psi_3 + (P_1 + iP_2)\psi_2 + P_3\psi_1 &= 0\\
(P_4 - m_0 c)\psi_4 + (P_1 - iP_2)\psi_1 - P_3\psi_2 &= 0
\end{aligned} \tag{56}$$

We shall see that these equations which have been obtained by general considerations quite independently of any electron spin hypothesis, contain properties of the magnetic and spinning electron. We shall try to obtain from these equations the general second order equation (43) for the case of an electromagnetic field. Applying to the symbolic equation (55) the operator $P_4 - \left(\sum_{1}^{3} {}_i \alpha_i P_i + \alpha_4 m_0 c\right)$ we obtain

$$\left(P_4 - \sum_{1}^{3} {}_i \alpha_i P_i - \alpha_4 m_0 c\right)\left(P_4 + \sum_{1}^{3} {}_i \alpha_i P_i + \alpha_4 m_0 c\right)\psi = 0$$

$$\Big[P_4^2 + \sum_{1}^{3} \alpha_i \left(P_4 P_i - P_i P_4\right) - \sum_{1}^{3} {}_i P_i^2 - \sum_{i \neq j} \left(\alpha_i \alpha_j P_i P_j + \alpha_j \alpha_i P_j P_i\right) \qquad (57)$$

$$- m_0^2 c^2\Big]\psi = 0$$

On expanding this and remembering the conditions (53) obeyed by the α_i's we find

$$\left(P_4 P_i - P_i P_4\right) \cancel{\psi} = \frac{h}{2\pi i} \frac{1}{c} \left[e' \frac{\partial V}{\partial x_i} + \frac{e'}{c} \frac{\partial A_i}{\partial t}\right] = -\frac{h e'}{2\pi i} \frac{E_i}{c}$$

where E_1 is a component of the electric field. Then

$$\sum_{1}^{3} {}_i \alpha_i \left(P_4 P_i - P_i P_4\right) = -\frac{h}{2\pi i} \frac{e'}{c} \left(\alpha_1 E_x + \alpha_2 E_y + \alpha_3 E_z\right)$$

$$\alpha_2 \alpha_3 \left(P_2 P_3 - P_3 P_2\right) = -\frac{h}{2\pi i} \frac{e'}{c} \alpha_2 \alpha_3 \left(\frac{\partial A_z}{\partial y} - \frac{\partial A_y}{\partial z}\right)$$

$$= -\frac{h}{2\pi i} \frac{e'}{c} \alpha_2 \alpha_3 H_x$$

where H_x is the x component of the magnetic field. Then

$$\sum_{i \neq j} \alpha_i \alpha_j \left(P_i P_j - P_j P_i\right) = -\frac{h}{2\pi i} \frac{e'}{c} \left(\alpha_2 \alpha_3 H_x + \alpha_3 \alpha_1 H_y + \alpha_1 \alpha_2 H_z\right)$$

Equation (57) therefore becomes

$$\Big[P_4^2 - \sum_{1}^{3} {}_i P_i^2 - m_0^2 c^2 - \frac{e'}{c} \frac{h}{2\pi i} \left(\alpha_1 E_x + \alpha_2 E_y + \alpha_3 E_z\right)$$

$$+ \frac{e'}{c} \frac{h}{2\pi i} \left(\alpha_2 \alpha_3 H_x + \alpha_3 \alpha_1 H_y + \alpha_1 \alpha_2 H_z\right)\Big]\psi = 0 \qquad (58)$$

If the first three terms only of the bracket were present we should again obtain equation (43)

$$\left(P_4^2 - \sum_1^3{}_i\, p_i^2 - m_0^2c^2\right)\psi = 0$$

which would be valid for each ψ_k The new element introduced by Dirac's theory is the addition of supplementary terms in equation (58). To understand the meaning of these supplementary terms, let us consider the nonrelativistic equation

$$-\frac{h^2}{8\pi^2 m_0}\nabla^2\psi + U(x,y,z,t)\psi = \frac{h}{2\pi i}\frac{\partial\psi}{\partial t}$$

which can be written in the form

$$\left(2m_0 c p_4 - \sum_1^3{}_i\, p_i^2 - 2m_0 U\right)\psi = 0 \qquad (59)$$

Comparing equation (59) with equation (58) we see the supplementary terms can be considered as terms of potential energy if we divide them by $-2m_0$. The potential energy for the magnetic field terms is therefore

$$-\frac{he'}{4\pi m_0 c}\left(i\alpha_2\alpha_3 H_x + i\alpha_3\alpha_1 H_y + i\alpha_1\alpha_2 H_z\right)$$

and for the electric field terms

$$\frac{he'}{4\pi m_0 c}\left(i\alpha_1 E_x + i\alpha_2 E_y + i\alpha_3 E_z\right)$$

The potential energy terms for the electric field are imaginary and so may be neglected as not representing anything of physical significance. For the potential energy terms of the magnetic field, let us put

$$\sigma_x = i\alpha_2\alpha_3 \qquad \sigma_y = i\alpha_3\alpha_1 \qquad \sigma_z = i\alpha_1\alpha_2 \tag{60}$$

Then the energy is expressed as $-\frac{he'}{4\pi m_0 c}(\sigma \cdot H)$ which corresponds to the potential energy of a body of magnetic moment μ in a magnetic field H where

$$\mu = -\frac{he'}{4\pi m_0 c}\sigma \tag{61}$$

Thus Dirac's equations attribute automatically to the electron a magnetic moment related to the Bohr magneton.

It can be proved that Dirac's equations remain invariant for any general Lorentz transformation, the new wave functions being related to the old ones by a linear transformation and thus the equations conform to the principle of relativity.

CONSERVATION OF ANGULAR MOMENTUM IN DIRAC'S THEORY - SPIN ANGULAR MOMENTUM OF ELECTRON.

It can be shown that the time derivative of any operator A is given by

$$\frac{DA}{Dt} = \frac{\partial A}{\partial t} + \frac{2\pi i}{h}(AH - HA)$$

where $\frac{\partial A}{\partial t}$ represents the partial derivative with respect to time if the operator A contains the time explicitly, and H is the Hamiltonian operator. The condition for the physical quantity represented by the operator A to be a constant is that $\frac{DA}{Dt}$ is zero. Let us apply this result to the case of the angular momentum of an electron about the OZ axis if the electron is moving in a field of force which has cylindrical symmetry about the Z axis. We should expect from the conservation of angular momentum that this would be a constant. If M_z is the operator $\frac{h}{2\pi i}\left(y\frac{\partial}{\partial x} - x\frac{\partial}{\partial y}\right)$

corresponding to the angular momentum about the OZ axis, then we should expect $\frac{DM_z}{Dt}$ to be zero. If $\frac{DM_z}{Dt}$ equalled zero then we should have

$$\frac{\partial M_z}{\partial t} + \frac{2\pi i}{h}(M_z H - H M_z) = 0$$

$\frac{\partial M_z}{\partial t} = 0$ as M_z does not depend explicitly on the time.

We shall therefore investigate whether or not $\frac{2\pi i}{h}(M_z H - H M_z)$ is zero. Now from Dirac's equations

$$H = \frac{h}{2\pi i}\frac{\partial}{\partial t} = -e'V + c\alpha_1\left(\frac{h}{2\pi i}\frac{\partial}{\partial x} - \frac{e'A_x}{c}\right) + c\alpha_2\left(\frac{h}{2\pi i}\frac{\partial}{\partial y} - \frac{e'A_y}{c}\right)$$
$$+ c\alpha_3\left(\frac{h}{2\pi i}\frac{\partial}{\partial z} - \frac{e'A_z}{c}\right) + m_0 c^2 \alpha_4$$

$$M_z H = \frac{h}{2\pi i}\left(y\frac{\partial}{\partial x} - x\frac{\partial}{\partial y}\right)\left(-e'V + c\alpha_1\frac{h}{2\pi i}\frac{\partial}{\partial x} + c\alpha_2\frac{h}{2\pi i}\frac{\partial}{\partial y} + c\alpha_3\frac{h}{2\pi i}\frac{\partial}{\partial z}\right.$$
$$\left. - c\alpha_1\frac{e'A_x}{c} - c\alpha_2\frac{e'A_y}{c} - c\alpha_3\frac{e'A_z}{c} + m_0 c^2\alpha_4\right)$$

$$H M_z = \frac{h}{2\pi i}\left(-e'V + c\alpha_1\frac{h}{2\pi i}\frac{\partial}{\partial x} + c\alpha_2\frac{h}{2\pi i}\frac{\partial}{\partial y} + c\alpha_3\frac{h}{2\pi i}\frac{\partial}{\partial z} - c\alpha_1\frac{e'A_x}{c}\right.$$
$$\left. - c\alpha_2\frac{e'A_y}{c} - c\alpha_3\frac{e'A_z}{c} + m_0 c^2\alpha_4\right)\left(y\frac{\partial}{\partial x} - x\frac{\partial}{\partial y}\right)$$

Expanding these expressions we find

$$M_z H - H M_z = -\frac{h}{2\pi i}e'y\frac{\partial V}{\partial x} + \left(\frac{h}{2\pi i}\right)^2 c\alpha_2\frac{\partial}{\partial x} + \frac{h}{2\pi i}e'x\frac{\partial V}{\partial y}$$
$$-\left(\frac{h}{2\pi i}\right)^2 c\alpha_1\frac{\partial}{\partial y}$$

$$\frac{DM_z}{Dt} = \frac{2\pi i}{h}\left(M_z H - H M_z\right) = e'\left(x\frac{\partial V}{\partial y} - y\frac{\partial V}{\partial x}\right) + \frac{h}{2\pi i}c\left(\alpha_2\frac{\partial}{\partial x} - \alpha_1\frac{\partial}{\partial y}\right)$$

As the field has cylindrical symmetry about the OZ axis

$$x\frac{\partial V}{\partial y} - y\frac{\partial V}{\partial x}$$

$$\frac{DM_z}{Dt} = \frac{h}{2\pi i}c\left(\alpha_2\frac{\partial}{\partial x} - \alpha_1\frac{\partial}{\partial y}\right)$$

Thus $\frac{DM_z}{Dt}$ is not zero and the angular momentum about OZ is not constant as we expected.

Let us consider the operator $N_z = M_z - \alpha_1\alpha_2\frac{h}{4\pi i}$ instead of M_z. N_z is a hermite operator and we shall show that N_z is a constant in the case considered. It can be shown by expanding and because of the properties of the α_i's that

$$\frac{2\pi i}{h}\left(\alpha_1\alpha_2\frac{h}{4\pi i}H - H\alpha_1\alpha_2\frac{h}{4\pi i}\right) = \frac{h}{2\pi i}c\left(\alpha_2\frac{\partial}{\partial x} - \alpha_1\frac{\partial}{\partial y}\right)$$

and therefore it must equal

$$\frac{2\pi i}{h}\left(M_z H - H M_z\right)$$

One concludes that

$$\frac{2\pi i}{h}\left[\left(M_z - \alpha_1\alpha_2\frac{h}{4\pi i}\right)H - H\left(M_z - \alpha_1\alpha_2\frac{h}{4\pi i}\right)\right] = 0$$

or $$\frac{2\pi i}{h}\left(N_z H - H N_z\right) = 0$$

Thus $\frac{DN_z}{Dt}$ = 0 and N_z will be a constant. Similar reasoning can be applied to the angular momentum about the OX and OY axes.

Therefore in Dirac's theory the total angular momentum of the electron must be a vector with components

$$N_x = M_x + S_x \qquad N_y = M_y + S_y \qquad N_z = M_z + S_z$$

the operators corresponding to M_x etc. being

$$M_x = \frac{h}{2\pi i}\left(z\frac{\partial}{\partial y} - y\frac{\partial}{\partial z}\right) \qquad M_y = \frac{h}{2\pi i}\left(x\frac{\partial}{\partial z} - z\frac{\partial}{\partial x}\right) \qquad M_z = \frac{h}{2\pi i}\left(y\frac{\partial}{\partial x} - x\frac{\partial}{\partial y}\right)$$

$$S_x = -\alpha_2\alpha_3\frac{h}{4\pi i} \qquad S_y = -\alpha_3\alpha_1\frac{h}{4\pi i} \qquad S_z = -\alpha_1\alpha_2\frac{h}{4\pi i}$$

M_x M_y and M_z are the components of the "orbital" angular momentum of the electron and one is led to consider S_x S_y S_z as components of the intrinsic angular momentum or "spin".

If as in equation (60) we let

$$\sigma_x = i\alpha_2\alpha_3 \qquad \sigma_y = i\alpha_3\alpha_1 \qquad \sigma_z = i\alpha_1\alpha_2$$

then the spin angular momentum is $\frac{h}{4\pi}\sigma$ In equation (61) we found the intrinsic magnetic moment of the electron to be $-\frac{he'}{4\pi m_0 c}\sigma$ The ratio of the two is seen to be $\frac{-e'}{m_0 c}$ that which is assumed in Uhlenbeck and Goudsmit's hypothesis to explain gyromagnetic anomalies and the anomalous Zeeman effect. Dirac's equations thus automatically endow the electron with properties that account for the phenomena previously ascribed to a hypothetical spinning motion of the electron.

SUMMARY OF RESULTS OBTAINED BY DIRAC'S THEORY.

Let us take the case of an electron moving in a constant central field derived from a potential $V(r)$. Thus in Dirac's equations

$$A_x = A_y = A_z = 0$$

As the field is constant the energy also will be constant, equal to W say. Dirac's equations (44) written out explicitly then become

$$\frac{2\pi i}{h}\left(\frac{W+eV}{c}+m_0c\right)\psi_1-\left(\frac{\partial}{\partial x}+i\frac{\partial}{\partial y}\right)\psi_4-\frac{\partial}{\partial z}\psi_3=0$$

$$\frac{2\pi i}{h}\left(\frac{W+eV}{c}+m_0c\right)\psi_2-\left(\frac{\partial}{\partial x}-i\frac{\partial}{\partial y}\right)\psi_3+\frac{\partial}{\partial z}\psi_4=0$$

$$\frac{2\pi i}{h}\left(\frac{W+eV}{c}-m_0c\right)\psi_3-\left(\frac{\partial}{\partial x}+i\frac{\partial}{\partial y}\right)\psi_2-\frac{\partial}{\partial z}\psi_1=0$$

$$\frac{2\pi i}{h}\left(\frac{W+eV}{c}-m_0c\right)\psi_4-\left(\frac{\partial}{\partial x}-i\frac{\partial}{\partial y}\right)\psi_1+\frac{\partial}{\partial z}\psi_2=0$$

Dirac solved these equations in the case of the hydrogen atom and found a formula for fine structure which is very similar to Sommerfeld's. The approximate formula for the energy levels of hydrogen to the second order in α^2 is

$$E=-\frac{Rh}{n^2}\left[1+\frac{\alpha^2}{n^2}\left(\frac{n}{j+\frac{1}{2}}-\frac{3}{4}\right)\right] \qquad (62)$$

where α is the fine structure constant. Sommerfeld's corresponding formula (30) was

$$E=-\frac{Rh}{n^2}\left[1+\frac{\alpha^2}{n^2}\left(\frac{n}{k}-\frac{3}{4}\right)\right]$$

The azimuthal quantum number k of the old quantum theory has been replaced by the whole number $(j+\frac{1}{2})$ Sommerfeld's doublets therefore occur between levels whose j values differ by unity. Levels only differing by the azimuthal quantum number (k or l) will coincide. This is in complete agreement with the actual fine structure of the lines of the Balmer series e.g. the H_α line as we have seen.

For a hydrogen like atom (i.e. an atom of atomic number N ionised (N - 1) times) the formula instead of (62) becomes

$$E = -\frac{RhN^2}{n^2}\left[1+\frac{\alpha^2 N^2}{n^2}\left(\frac{n}{j+\frac{1}{2}}-\frac{3}{4}\right)\right]$$

This formula explains satisfactorily the fine structure of the He^+ spectrum.

Dirac's formulae have permitted the interpretation of Xray spectra and in particular the existence and value of the regular doublets without coming across the difficulties which Sommerfeld's old theory encountered.

Dirac's theory also gives a completely satisfactory interpretation of the anomalous Zeeman effect for the alkalies. It gives the same formula as Lande's empirical formula (21)

$$W_H(n,l,j) = W_0(n,l,j) + mg\frac{ehH}{4\pi m_0 c}$$

with $g = \frac{j+\frac{1}{2}}{l+\frac{1}{2}}$ in the case of an alkali. For atoms where it is not possible to consider a single "optical" electron, Dirac's theory cannot predict the Zeeman effect rigorously as this theory is not able to deal with the case of a system of interacting electrons.

Thus the results of Dirac's theory are in agreement with those previous theories based on the spinning electron model. Dirac's theory however applies quantum mechanics to the point charge electron so that the whole of the duplicity phenomena follow without arbitrary assumptions. The incompleteness of previous theories which led to the necessity for these arbitrary assumptions was due to their disagreement with the principle of relativity or alternatively the general transformation theory of quantum mechanics.

NEGATIVE ENERGY STATES IN DIRAC'S THEORY.

However one important difficulty arises in Dirac's theory; namely, that for the electron, negative energy states become possible. This occurs when one attempts to explain the phenomena previously attributed to spin, on the basis of quantum mechanics and in conformity with the principle of relativity.

For a plane monochromatic wave corresponding to the case where there is no field, the potential energy will be zero and a solution of Dirac's equations may be given in the form

$$\psi_k = a_k e^{\frac{2\pi i}{h}(Wt - p_x x - p_y y - p_z z)}$$

where W is the constant energy and p_x p_y p_z are the components of the momentum. Substituting in Dirac's equations (54) these become

$$\begin{aligned} (\tfrac{W}{c} + m_0c)a_1 + (p_x + ip_y)a_4 + p_z a_3 &= 0 \\ (\tfrac{W}{c} + m_0c)a_2 + (p_x - ip_y)a_3 - p_z a_4 &= 0 \\ (\tfrac{W}{c} - m_0c)a_3 + (p_x + ip_y)a_2 + p_z a_1 &= 0 \\ (\tfrac{W}{c} - m_0c)a_4 + (p_x - ip_y)a_1 - p_z a_2 &= 0 \end{aligned} \qquad (63)$$

These linear and homogeneous equations for the a_k's can only be satisfied simultaneously, (assuming that all the a_k's are not zero) if the determinant

$$\begin{vmatrix} \left(\frac{W}{c} + m_0c\right) & 0 & p_z & (p_x + ip_y) \\ 0 & \left(\frac{W}{c} + m_0c\right) & (p_x - ip_y) & - p_z \\ p_z & (p_x + ip_y) & \left(\frac{W}{c} - m_0c\right) & 0 \\ (p_x - ip_y) & - p_z & 0 & \left(\frac{W}{c} - m_0c\right) \end{vmatrix} \qquad (64)$$

is zero. This determinant is equal to

$$\left(\frac{W^2}{c^2} - m_0^2c^2 - p_x^2 - p_y^2 - p_z^2\right)^2$$

and will equal zero if W p_x p_y and p_z are related by the well known equation of relativistic mechanics.

$$\frac{W^2}{c^2} - p_x^2 - p_y^2 - p_z^2 = m_0^2c^2 \qquad (65)$$

If this relation is satisfied, then not only is the determinant (64) zero but also all its minors will also be zero. Thus two of the four a_k's may be arbitrarily chosen. For example, giving arbitrary values A and B to a_3 and a_4, then equations (63) will determine a_1 and a_2. We find by putting

$$W = + c\sqrt{m_0^2c^2 + p_x^2 + p_y^2 + p_z^2} \qquad (66)$$

that

$$a_1 = \frac{- p_zA + (p_x + ip_y)B}{\frac{W}{c} + m_0c} \qquad a_2 = \frac{-(p_x - ip_y)A - p_zB}{\frac{W}{c} + m_0c}$$

But condition (63) can also be satisfied by putting

$$W = -c\sqrt{m_0{}^2c^2 + p_x{}^2 + p_y{}^2 + p_z{}^2}$$

In this case the solution, if C and D are complex arbitrary constants, will be

$$a_1 = C \qquad a_2 = D \qquad a_3 = \frac{p_zC + (p_x + ip_y)D}{m_0c - \frac{W}{c}}$$

$$a_4 = \frac{(p_x - ip_y)\,C - p_zD}{m_0c - \frac{W}{c}} \qquad (67)$$

If the notation is now slightly modified and for given values of p_x p_y p_z we in future always define W by formula (66) with positive sign, then to take account of solution (67) we can say that we have to consider at the same time a wave of energy $+W$ and a wave of energy $-W$. With this new convention it will be necessary in equations (67) tochange $+W$ into $-W$.

Thus for a given value of p_x p_y and p_z, W being defined by relation (66), we have to consider the plane monochromatic waves of positive energy $+W$ defined by

$$\psi_k = a_k e^{\frac{2\pi i}{h}(Wt - p_x x - p_y y - p_z z)}$$

with

$$a_1 = \frac{-p_zA + (p_x + ip_y)B}{\frac{W}{c} + m_0c} \qquad a_2 = -\frac{(p_x - ip_y)A - p_zB}{\frac{W}{c} + m_0c}$$

$$a_3 = A \qquad\qquad a_4 = B$$

and the plane monochromatic wave with negative energy -W defined by

$$\psi_k = b_k e^{\frac{2\pi i}{h}(-Wt - p_x x - p_y y - p_z z)}$$

with

$$b_1 = C \qquad b_2 = D \qquad b_3 = \frac{p_z C + (p_x + i p_y) D}{\frac{W}{c} + m_0 c}$$

$$b_4 = \frac{(p_x - i p_y) C - p_z D}{\frac{W}{c} + m_0 c}$$

For the waves of positive energy, the wave functions ψ_1 and ψ_2 which are zero if the velocity is zero, only take on importance for velocities comparable with the velocity of light, so that the wave functions ψ_3 and ψ_4 predominate. The conclusions are exactly opposite in the case of waves of negative energy as here ψ_1 and ψ_2 are preponderant and ψ_3 and ψ_4 only take on importance when the velocity approaches that of light.

The existence of negative energy states in Dirac's theory constitutes a grave difficulty as a particle in such a state would have strange properties which have never been observed in practice. Such a particle when placed in an electric field would have an acceleration in an opposite direction to the force; its speed would be increased on withdrawing energy; its velocity would be in the opposite direction to its momentum. However these negative energy states cannot be easily eliminated from the theory.

In non relativistic wave mechanics, for the case of no field of force, any solution of the non relativistic wave equation for a free material point can be represented by a superposition of plane monochromatic waves i.e. the plane monochromatic waves constitute a "complete" system.

In Dirac's theory this is not in general the case, if only the waves with positive energy are considered. If however the plane waves of negative energy are also considered, a "complete" system of plane monochromatic waves is obtained.

One might think that the difficulty of negative energy states exists even in classical relativity where energy is defined as a function of momentum in the absence of a field of force by the equation

$$\frac{W^2}{c^2} = m_0^2c^2 + p_x^2 + p_y^2 + p_z^2$$

This equation would give two values for W, namely

$$W = \pm\sqrt{c^2\left(m_0^2c^2 + p_x^2 + p_y^2 + p_z^2\right)}$$

However from this equation the possible values of W are comprised in two separated regions of $+\infty$ to $+m_0c^2$ and $-m_0c^2$ to $-\infty$ The interval $+m_0c^2$ to $-m_0c^2$ does not correspond to any possible value of energy. In classical relativistic dynamics, mechanical quantities and in particular energy, vary in a continuous way. Thus if at the beginning the electrons had energies in the positive region $+m_0c^2$ to $+\infty$ no value in the negative region $-m_0c^2$ to $-\infty$ could appear since the two regions are separated by the interval $+m_0c^2 \rightarrow -m_0c^2$. Therefore in classical relativistic mechanics, the difficulty of negative energy states is removed in this way.

However in quantum mechanics, the possibility of abrupt transitions between states of different energy is admitted. Thus it appears that the passage of an electron from a region of positive energies to a region of negative energies might be possible.

THE IMPOSSIBILITY OF MEASURING EITHER THE SPIN ANGULAR MOMENTUM OR THE MAGNETIC MOMENT OF THE ELECTRON DIRECTLY.

From the general principles of wave mechanics it can be shown that two mechanical quantities associated with a particle can only be simultaneously measured with precision if for the corresponding operators A and B,

$$AB = BA$$

The simplest and most important example of quantities which are not simultaneously measurable is that of a coordinate and the corresponding component of momentum of a particle because

$$x p_x - p_x x = \frac{h}{2\pi i}\left(\frac{\partial}{\partial x}.x - x\frac{\partial}{\partial x}\right) = \frac{h}{2\pi i}$$

which is not zero. A coordinate and the corresponding momentum component can therefore never be known at a given instant except with a particular uncertainty Δx and Δp_x which cannot both be zero at the same time. It can be shown that the following relation holds, at least as to order of magnitude.

$$\Delta x . \Delta p_x \geqslant h$$

This relation and the two analogous relations for y and z

$$\Delta y . \Delta p_y \geqslant h \qquad \Delta z . \Delta p_z \geqslant h$$

constitute the Heisenberg "uncertainty relations". They were derived by Heisenberg from other considerations.

From arguments based on the "uncertainty relations" Bohr has shown that it must be impossible to measure the magnetic moment of the electron due to its spin, because the effects produced cannot be distinguished from those due to the translational motion of the electron.

In order to find the magnetic moment of the electron one might either try to measure its effect on a magnetometer or one might make the electron cross a non uniform magnetic field and try to observe the effect of this field on the electron magnet.

Considering the first method, let us imagine the direction of motion of the electron to be along the X axis and that a magnetometer is placed on the Y axis at a point with ordinate y.

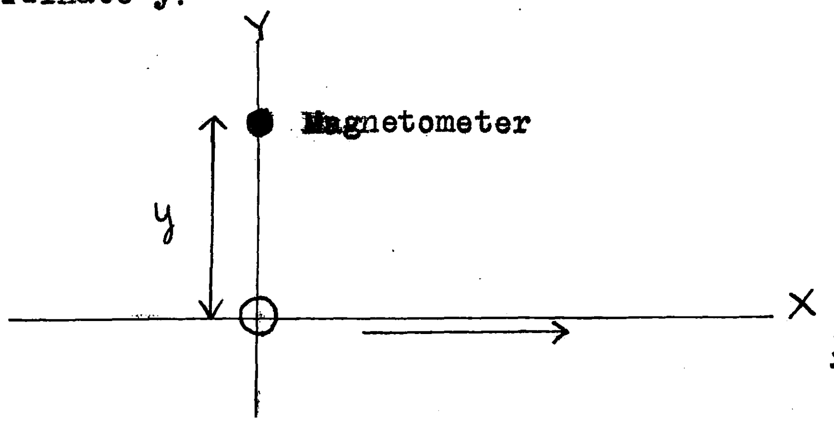

Figure VIII.

In order that the action on the magnetometer can be known exactly, it must be supposed that the electron is sufficiently well localised; that is that the electron is associated with a train of waves ψ with dimensions which are small compared with the distance y. If Δx is the length of the train of waves along the OX axis this giving the uncertainty in the x coordinate of the electron, one must have

$$\Delta x \ll y \qquad (68)$$

In the same way if Δy is the length of the wave train in the OY direction one must have

$$\Delta y \ll y$$

On passing near the origin of coordinates, the electron will produce two effects on the magnetometer. One of these is due to the magnetic field caused by the translational motion of the electron. Its value is

$$H_1 = \frac{eV_x}{cy^2}$$

where V_x is the x component of the electron's velocity.

The second action is due to the magnetic moment of the electron which produces at the magnetometer, the magnetic field

$$H_2 = \frac{eh}{4\pi m_0 c} \frac{1}{y^3} \qquad (69)$$

The value of H_1 is not known however precisely. The uncertainty in this quantity is given by

$$\Delta H_1 = \frac{e}{c}\left(\frac{\Delta V_x}{y^2} + \frac{V_x}{y^3}\Delta y\right) \tag{70}$$

since there must be an uncertainty ΔV_x in the x component of velocity of the electron and an uncertainty Δy in its ordinate Y. From Heisenberg's relations, using the Newtonian approximation, one has

$$\Delta V_x \geqslant \frac{h}{m_0 \Delta x} \qquad \Delta V_y \geqslant \frac{h}{m_0 \Delta y} \tag{71}$$

Also one must suppose

$$\Delta V_y << V_x \tag{72}$$

as otherwise the motion would not be approximately along the X axis. Comparing equations (69) and (70)

$$\frac{\Delta H_1}{H_2} = \frac{4\pi m_0}{h}\left(y\,\Delta V_x + V_x\,\Delta y\right)$$

From this and using equations (71) (68) and (72)

$$\frac{\Delta H_1}{H_2} \geqslant \left(\frac{y}{\Delta x} + \frac{V_x}{\Delta V_y}\right) \geqslant 1$$

The uncertainty in the field H_1 is therefore always much greater than the value of the field H_2. Thus the magnetic moment of the electron cannot be measured with the magnetometer.

In a similar way it can be shown that the action of a non uniform magnetic field on the electron magnet is completely masked by the Lorentz force so that one cannot measure the electron's magnetic moment by this method.

Darwin has pointed out that the same kind of considerations apply to the electron's angular momentum due to its spin

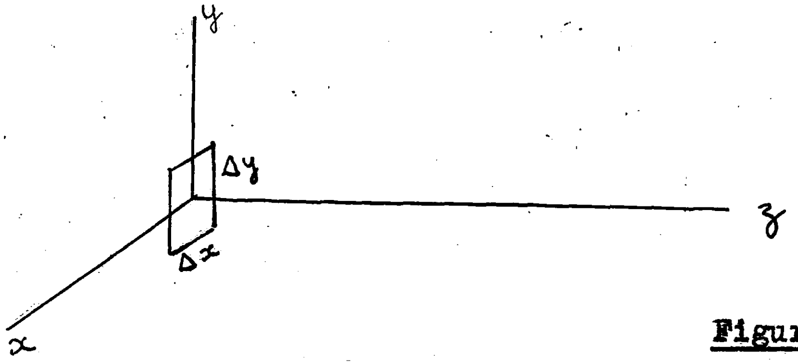

Figure IX.

Let us imagine a rectangular opening with sides of length Δx and Δy in a plane screen. We also suppose that a plane monochromatic wave associated with an electron falls on the left hand side of the screen, the wave train of the electron to the right of the screen having dimensions Δx and Δy. The x and y components of the momentum of the electron after passing through the screen will have the uncertainties

$$|\Delta p_x| \geq \frac{h}{\Delta x} \qquad |\Delta p_y| \geq \frac{h}{\Delta y} \qquad (73)$$

The z component of the angular momentum due to the translational motion of the electron is

$$M_z = xp_y - yp_x$$

The uncertainty Δ Mz lies therefore between zero and

$$\Delta M_z = \Delta x \, |\Delta p_y| + \Delta y \, |\Delta p_x|$$

From equation (73)

$$\Delta M_z \geqslant h\left(\frac{\Delta x}{\Delta y} + \frac{\Delta y}{\Delta x}\right) = h\,\frac{\Delta x^2 + \Delta y^2}{\Delta x \Delta y}$$

As the fraction $\frac{\Delta x^2 + \Delta y^2}{\Delta x \, \Delta y}$ is greater than unity, one deduces

$$\Delta M_z > \frac{h}{4\pi}.$$

The uncertainty in the z component of the angular momentum due to translational motion is therefore greater than the z component of the spin angular momentum so that it is not possible to measure the latter quantity in this way.

The same reasoning can be applied to the components x and y of the spin angular momentum.

It has been shown more generally that an experiment in which it is possible to treat the electron as a material point cannot lead to a measurement of its magnetic moment or spin. It would be contradictory tosuppose that both the old mechanics dealing with point particles could be valid and at the same time effects characteristic of spin could be shown.

SUMMARY.

Bohr's theory of the atom, particularly when modified by Sommerfeld to conform to the principle of relativity was able to give a good explanation of the general properties of optical and Xray spectra. However, certain anomalies of the gyromagnetic effect, doublets in the alkali spectra, the anomalous Zeeman effect, certain features of the fine structure of the hydrogen spectrum could not be explained by it. Bohr's model of the atom consisted of electrons rotating round the nucleus in circular or elliptic orbits. But if as Uhlenbeck and Goudsmit supposed, the electrons were also to have a spin and magnetic moment, these anomalies could be explained.

This hypothesis was a useful modification of the old quantum theory but with the replacement of this theory by wave mechanics, the idea of an electron being a sphere rotating about a diameter could no longer be directly applied. In the early form of wave mechanics, Schroedinger's wave equation was not able to explain the anomalies nor did it conform to the principle of relativity. Pauli in his theory, tried to give a wave mechanical interpretation of the electron's spin but he was only partially successful. Dirac reformed Schroedinger's equation, taking account of the principle of relativity and also of

magnetic forces which depend not only on the position of the particle but also upon its velocity. The solution of Dirac's first order differential equations gave a satisfactory explanation of the anomalies mentioned above. The results were then in agreement with those previous theories based on the spinning electron model. Dirac's theory however applied quantum mechanics to the point charge electron so that all the duplicity phenomena followed without arbitrary assumptions.

It was shown from Heisenberg's uncertainty relations that it is not possible to directly measure the spin motion apart from the orbital motion. Thus it seems that the spin motion has no real existence as something independent of translational motion but is actually a certain aspect of it.

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