

Durham E-Theses

Some topics in the theory of electrons

C. C. Barlett

How to cite:

Barlett, C. C. (1952) Some topics in the theory of electrons. Masters thesis, Durham University.

Use policy

The full-text may be used and/or reproduced, and given to third parties in any format or medium, without prior permission or charge, for personal research or study, educational, or not-for-profit purposes provided that:

- a full bibliographic reference is made to the original source
- a <https://etheses.durham.ac.uk/id/eprint/9769/> is made to the metadata record in Durham E-Theses
- the full-text is not changed in any way

The full-text must not be sold in any format or medium without the formal permission of the copyright holders.

Please consult the [full Durham E-Theses policy](#) for further details.

SOME TOPICS IN THE THEORY OF ELECTRONS.

A Thesis for the Degree of Master of Science in the
University of Durham.

Submitted by C.C.Bartlett, October 1952.



SOME TOPICS IN THE THEORY OF ELECTRONS.

The paper is divided roughly into three sections. Section I discusses briefly the considerations which necessitated the introduction of the idea of an intrinsic spin for an electron, and derives the Dirac equation of the electron in an electromagnetic field to show how a term attributable to such a spin appears in this equation.

The validity of such an hypothesis as that of spin depends on the measure of agreement between predicted and empirical results. Section II therefore gives an analysis of the Zeeman effect, using the Dirac equation, to indicate the way in which the new spin term leads to an explanation of observed spectral effects, which had remained unexplained by any previous approach. The analysis is taken to the order of accuracy given by first order perturbation calculation only.

Many difficulties occur, both in the mathematics and in the interpretation of the results of these and other equations in the quantum electrodynamics. Some of these difficulties and inadequacies are discussed in Section III and a brief non-mathematical account is given of various successive modifications which have been made, leading to the present theories of Tomonaga, Schwinger, and Feynman.



Section 1.

The classical electron theory of matter was a form of atomic theory in which the ultimate atoms were regarded as geometrical configurations of electrical charge obeying the classical laws of dynamics. This concept was successful in leading to plausible explanations of many observed phenomena, but was incapable of dealing with many others. Contradictions were found to exist in connection with the electromagnetic theory of light, the specific heats of metals, and the theory of electric conductivity. Many other observed features, such as the "anomalous" Zeeman effect, were unexplained as long as they were treated in terms of ordinary dynamical laws and Maxwell's electromagnetic equations. Other effects were described only within certain small limits. In particular, in the theory of black body radiation, there was a wide divergence between classical theory and observed results for high frequencies. The Rayleigh-Jeans formula, based on the classical theory of "Equipartition of energy", gave the energy E_λ in terms of the temperature T and the wavelength λ by

$$E_\lambda = 8\pi k T \lambda^{-4}$$

The energy should therefore increase to infinity as λ tends to zero. Experiment showed, however, that the intensity per unit frequency rose from zero at very low frequencies

to a maximum, whose position might depend on the temperature, and then fell again at very high frequencies. The Rayleigh-Jeans formula was found to be in accord with experiment only at long wavelengths. Another fundamental difficulty was found in the existence of the observed sharp lines in spectra. The theory was able to describe the "normal" Zeeman effect for a single electron, but to cover the experimental case the average result over a large number of electrons would have to be taken, with, presumably, a corresponding blurring of the lines.

A large accumulation of evidence suggested that a new system of dynamics and a new electron theory was needed, and it was generally supposed that the special feature of this new theory would be that the interaction between electrons and radiation would be of an entirely ^{different} ~~new~~ nature from that pictured by the classical laws. With the introduction of Planck's quantum hypothesis and the Bohr model of the atom, where the electrons moved round a nucleus with certain discrete energy levels only, Planck was able to derive a formula for the intensity of radiation in terms of temperature and frequency, which fitted experimental data. Further, it was now possible to account for the sharpness of the spectral lines, and the new calculated result for the normal Zeeman effect was found to be the same as the classical result which had previously proved to be

satisfactory. With the later formulation of the quantum mechanics and the establishing of Schrödinger's wave equation, some of the lines in the anomalous Zeeman effect were accounted for, using perturbation methods. In the presence of a magnetic field, the Schrödinger non-relativistic equation gives degenerate energy levels splitting into an odd number of levels. For example, in the p-state the z-component of the angular momentum M of an electron has the three values $M_z = \hbar, 0, -\hbar$; the d-state has five values $2\hbar, \hbar, 0, -\hbar, -2\hbar$ and so on, always giving an odd number of levels. However, for all atoms with just one valency electron, splitting into two states was observed. For a full explanation of the anomalous effect, it appeared no longer permissible to say that the magnetic moment was due to orbital motion and proportional to the mechanical moment alone. Another magnetic moment in the atom had to be taken. According to the hypothesis of Uhlenbeck and Goudsmit this moment resided in the "spin" of the electron. It could be described by imagining the electron to have a finite size. It would then have three rotational, as well as three translational, degrees of freedom. An angular momentum about an arbitrary axis in the electron could then be ascribed to the electron. This would necessarily introduce also a magnetic moment. These properties - mechanical and magnetic moment - are called the spin.

A direct mechanical action of the electron spin

can be observed in the magnetisation of ferromagnetic substances. Experiment shows that the ratio

$$\frac{\text{change in the mechanical angular momentum}}{\text{change in magnetic moment}} = \frac{1}{\frac{e\hbar}{mc}} = \frac{\hbar}{2K}$$

(where $K = \frac{e\hbar}{2mc}$) instead of $\frac{\hbar}{K}$ as required if the magnetisation were dependent on the orbital motion of the electron.

2. To explain the anomaly that spin occurs only for ferromagnetic substances, the magnetic moment of the spinning electron must be taken as being twice as great as the magnetic moment of an orbital motion of the same mechanical angular momentum.

Results of the Stern-Gerlach experiments, where a beam of Ag atoms in the ground state are deflected by a magnetic field, show that the spin is quantised and strongly suggest that the magnetic moment of an electron in any direction is $\pm K$ and the spin angular momentum $\pm \frac{1}{2}\hbar$.

If the hypothesis is made that the spin angular momentum is $\frac{1}{2}\hbar$ and its components in any direction can only be $\pm \frac{1}{2}\hbar$, also that spin $\frac{1}{2}\hbar$ implies a magnetic moment K , then a satisfactory explanation of the multiplet structure of spectral terms can be given. Serious difficulties are, however, encountered through the introduction of an electron with finite size.

In particular, if the electro-dynamical equations of Maxwell are used in the mathematical formulation of a theory incorporating spin, contradictions must be expected since Maxwell's equations use the concept of a point electron.

Again, with an electron with "size", if the observed figures

for angular and magnetic moment are to agree with those calculated by classical theory, a point on the surface of the electron would have to move with a velocity greater than that of light. These and other difficulties are discussed in Section III.

The same values for the spin angular momentum and magnetic moment were obtained by Dirac (ref.1.) by purely theoretical arguments, thus tending to confirm the previous hypothesis. His method of procedure was to put the wave equation for the electron in an electromagnetic field into a relativistically invariant form:

Let the four dimensional displacement vector s be given by

$$s^2 = c^2 t^2 - x^2 - y^2 - z^2$$

so that for an infinitesimal displacement

$$ds^2 = c^2 dt^2 - dx^2 - dy^2 - dz^2$$

$$\left(\frac{ds}{dt}\right)^2 = c^2 - \left(\frac{dx}{dt}\right)^2 - \left(\frac{dy}{dt}\right)^2 - \left(\frac{dz}{dt}\right)^2 = c^2 - u^2$$

$$\therefore \frac{ds}{dt} = c \sqrt{1 - \frac{u^2}{c^2}}$$

If the three dimensional momentum vector p has components

$$p_x, p_y, p_z \equiv p^1, p^2, p^3$$

then $p_x = p^1 = m \frac{dx}{dt} = \frac{m_0}{\sqrt{1 - \frac{u^2}{c^2}}} \frac{dx}{ds} \cdot \frac{ds}{dt} = m_0 c \frac{dx}{ds}$

Similarly $p^2 = m_0 c \frac{dy}{ds}$ and $p^3 = m_0 c \frac{dz}{ds}$

If a fourth term p^0 is given by

$$p^0 = m_0 e \frac{dx^0}{ds} = m_0 c^2 \frac{dt}{ds} = \frac{m_0 c}{\sqrt{1 - \frac{u^2}{c^2}}} = m c = \frac{E}{c}$$

then the momentum 4-vector is obtained,

$$p^i = (p^0 p^1 p^2 p^3) \equiv \left(\frac{E}{c} p_x p_y p_z \right)$$

Further $\left(\frac{ds}{ds}\right)^2 = 1 = c^2 \left(\frac{dt}{ds}\right)^2 - \left(\frac{dx}{ds}\right)^2 - \left(\frac{dy}{ds}\right)^2 - \left(\frac{dz}{ds}\right)^2$

so that $\frac{E^2}{c^2} - p_x^2 - p_y^2 - p_z^2 = m_0^2 c^2 \left[c^2 \left(\frac{dt}{ds}\right)^2 - \left(\frac{dx}{ds}\right)^2 - \left(\frac{dy}{ds}\right)^2 - \left(\frac{dz}{ds}\right)^2 \right] = m_0^2 c^2$

which is invariant.

The non-relativistic wave equation is

$$(\text{kinetic energy})\Psi + (\text{potential energy})\Psi = (\text{constant})\Psi$$

This suggests that the relativistic equation will be

$$[p_0^2 - p_1^2 - p_2^2 - p_3^2 - m_0^2 c^2]\Psi = 0 \quad (1)$$

In order to replace the p_i with the appropriate quantum operators it is necessary to factorise this expression into the two linear terms

$$[p_0 + \alpha_1 p_1 + \alpha_2 p_2 + \alpha_3 p_3 + \alpha_0 m_0 c][p_0 - \alpha_1 p_1 - \alpha_2 p_2 - \alpha_3 p_3 - \alpha_0 m_0 c]\Psi = 0$$

This is possible provided

$$\alpha_i \alpha_j = -\alpha_j \alpha_i \quad i, j = 0, 1, 2, 3$$

and $\alpha_i^2 = 1$

This will be so if

$$\alpha_0 = \begin{bmatrix} 1 & & & \\ & 1 & & \\ & & -1 & \\ & & & -1 \end{bmatrix} \quad \alpha_1 = \begin{bmatrix} & & & 1 \\ & & & \\ & & & \\ 1 & & & \end{bmatrix} \quad \alpha_2 = \begin{bmatrix} & & & i \\ & & & \\ & & & \\ i & & & \end{bmatrix} \quad \alpha_3 = \begin{bmatrix} & & & -i \\ & & & \\ & & & \\ -i & & & \end{bmatrix}$$

These are related to the Pauli "spin" matrices

$$\sigma_1 = \begin{bmatrix} & 1 \\ 1 & \end{bmatrix} \quad \sigma_2 = \begin{bmatrix} & -i \\ i & \end{bmatrix} \quad \sigma_3 = \begin{bmatrix} 1 & \\ & -1 \end{bmatrix}$$

by the equations

$$\alpha_1 = \begin{bmatrix} i & \sigma_1 \\ \sigma_1 & \end{bmatrix} \quad \alpha_2 = \begin{bmatrix} i & \sigma_2 \\ \sigma_2 & \end{bmatrix} \quad \alpha_3 = \begin{bmatrix} i & \sigma_3 \\ \sigma_3 & \end{bmatrix}$$

and, if σ'_i is defined by $\sigma'_i = \begin{bmatrix} \sigma_i & \\ & \sigma_i \end{bmatrix}$

$$\left. \begin{aligned} \text{then } \alpha_2 \alpha_3 &= i \sigma'_1 \\ \alpha_3 \alpha_1 &= i \sigma'_2 \\ \alpha_1 \alpha_2 &= i \sigma'_3 \end{aligned} \right\} (2)$$

Consider the equation

$$[p_0 + \alpha_1 p_1 + \alpha_2 p_2 + \alpha_3 p_3 + \alpha_0 m_0 c]\Psi = 0$$

That is,
$$\left[\frac{E}{c} + \alpha \cdot p + \alpha_0 m_0 c \right] \Psi = 0 \quad (3)$$

To put this into a relativistically correct form, for an electron in an electromagnetic field with electrical and magnetic field strengths \underline{E} and \underline{H} , the terms E and p must be replaced by the expressions $(E - e\phi)$ and $(p - \frac{e\mathbf{A}}{c})$ arising from the Lorentz force, (where \mathbf{A} and ϕ are the vector and scalar potentials). \underline{E} and \underline{H} are assumed to obey the Maxwell-Lorentz equations for the electromagnetic field.

Equation (3) then becomes

$$\left[(E - e\phi) + \alpha (cp - e\mathbf{A}) + \alpha_0 m_0 c^2 \right] \Psi = 0$$

This will reduce to the form of equation (1) if it is premultiplied by

$$\left[(E - e\phi) - \alpha (cp - e\mathbf{A}) - \alpha_0 m_0 c^2 \right]$$

Then since

$$-\alpha (cp - e\mathbf{A}) \alpha_0 m_0 c^2 - \alpha_0 m_0 c^2 \alpha (cp - e\mathbf{A}) = 0$$

the equation becomes

$$\left\{ \begin{aligned} & (E - e\phi)^2 - [\alpha (cp - e\mathbf{A})]^2 - \alpha_0^2 m_0^2 c^4 \\ & + (E - e\phi) \alpha (cp - e\mathbf{A}) - \alpha (cp - e\mathbf{A}) (E - e\phi) \end{aligned} \right\} \Psi = 0 \quad (4)$$

To simplify this equation the following vector relations will be used:

$$\begin{aligned} 1) \quad (\underline{\alpha} \cdot \underline{B})(\underline{\alpha} \cdot \underline{C}) &= (\alpha_x b_x + \alpha_y b_y + \alpha_z b_z)(\alpha_x c_x + \alpha_y c_y + \alpha_z c_z) \\ &= b_x c_x + b_y c_y + b_z c_z + \alpha_x \alpha_y (b_x c_y - b_y c_x) \\ &\quad + \alpha_y \alpha_z (b_y c_z - b_z c_y) + \alpha_z \alpha_x (b_z c_x - b_x c_z) \\ &= \underline{B} \cdot \underline{C} + i \sigma' (\underline{B} \wedge \underline{C}) \quad \text{by equations (2)} \end{aligned}$$

$$2) \quad (cp - e\mathbf{A})_{\wedge} (cp - e\mathbf{A}) = -ce (\underline{A}_{\wedge} p + p \wedge \underline{A})$$

The i component of $(\underline{A}_{\wedge} p) \Psi$ is $-i\hbar (A_y \frac{\partial \Psi}{\partial z} - A_z \frac{\partial \Psi}{\partial y})$

$$= -i\hbar (A_y \frac{\partial \Psi}{\partial z} - A_z \frac{\partial \Psi}{\partial y})$$

and the \underline{i} component of $(\underline{p}, \underline{A})\Psi$ is $-i\hbar \left[\frac{\partial}{\partial y} (A_z \Psi) - \frac{\partial}{\partial z} (A_y \Psi) \right]$ (9)

$$= -i\hbar \left[\frac{\partial A_z}{\partial y} \Psi - \frac{\partial A_y}{\partial z} \Psi + A_z \frac{\partial \Psi}{\partial y} - A_y \frac{\partial \Psi}{\partial z} \right]$$

Therefore the \underline{i} component of $(\underline{A}, \underline{p} + \underline{p}, \underline{A})\Psi$ is $-i\hbar \left(\frac{\partial A_z}{\partial y} - \frac{\partial A_y}{\partial z} \right) \Psi$

Therefore $-c \underline{e} (\underline{A}, \underline{p} + \underline{p}, \underline{A}) = i \underline{e} \hbar c \text{curl } \underline{A} = i \underline{e} \hbar c \underline{H}$

3) If the energy E is written $E' + m_0 c^2$, then E' is equivalent to the time derivative operator $i\hbar \frac{\partial}{\partial t}$

Then $-c \underline{e} \underline{e} [\underline{E}, \underline{A} - \underline{A}, \underline{E}] \Psi = -c \underline{e} \underline{e} i\hbar \left[\frac{\partial}{\partial t} (A \Psi) - A \frac{\partial \Psi}{\partial t} \right]$

$$= -i \underline{e} \hbar c \underline{e} \frac{\partial A}{\partial t} \Psi$$

4) Similarly, replacing the momentum vector \underline{p} by the operator $\underline{p} = -i\hbar \text{grad}$

$$\begin{aligned} -c \underline{e} \underline{e} [\underline{\phi}, \underline{p} - \underline{p}, \underline{\phi}] \Psi &= -c \underline{e} \underline{e} [\underline{\phi} \text{grad} \Psi - \text{grad}(\underline{\phi} \Psi)] \\ &= -i \underline{e} \hbar c \underline{e} \text{grad} \underline{\phi} \end{aligned}$$

Now considering terms from equation (4)

$$\begin{aligned} \text{a) } [\underline{e} (c\underline{p} - e\underline{A})]^2 &= [\underline{e} (c\underline{p} - e\underline{A})] [\underline{e} (c\underline{p} - e\underline{A})] \\ &= (c\underline{p} - e\underline{A})^2 + i \sigma' (c\underline{p} - e\underline{A})_\lambda (c\underline{p} - e\underline{A}) \quad \text{by relation 1.)} \\ &= (c\underline{p} - e\underline{A})^2 - e \hbar c \sigma' \underline{H} \quad \text{by relation 2.)} \end{aligned}$$

$$\begin{aligned} \text{b) } (\underline{E} - e\phi) \underline{e} (c\underline{p} - e\underline{A}) - \underline{e} (c\underline{p} - e\underline{A}) (\underline{E} - e\phi) &\text{ reduces to} \\ -e \underline{e} (\underline{E}, \underline{A} - \underline{A}, \underline{E}) - c \underline{e} \underline{e} (\underline{\phi}, \underline{p} - \underline{p}, \underline{\phi}) \\ &= -i \underline{e} \hbar c \underline{e} \text{grad} \underline{\phi} - i \underline{e} \hbar c \underline{e} \frac{\partial A}{\partial t} \quad \text{by rel. 3.) + 4.)} \\ &= -i \underline{e} \hbar c \underline{e} \left[\frac{1}{c} \frac{\partial A}{\partial t} + \text{grad} \underline{\phi} \right] \\ &= i \underline{e} \hbar c \underline{e} \underline{E} \end{aligned}$$

since $\text{grad} \underline{\phi} = -\underline{E} - \frac{1}{c} \frac{\partial A}{\partial t}$ by Maxwell's equations.

Equation (4) therefore becomes

$$[(\underline{E} - e\phi)^2 - (c\underline{p} - e\underline{A})^2 - m_0^2 c^4 + e \hbar c \sigma' \underline{H} + i \underline{e} \hbar c \underline{e} \underline{E}] \Psi = 0 \quad (5)$$

The first three terms of this equation are the same as those

of equation (1). The last term is small compared with the other terms and has no classical analogy (ref.2). To the degree of accuracy for which the Dirac equation may be applied, it may be neglected.

The physical significance of the fourth term can be seen by consideration of the non-relativistic limit of the equation: Writing $\mathcal{E} = \mathcal{E}' + m_0 c^2$ and assuming that \mathcal{E}' and $e\phi$ are small compared with $m_0 c^2$, then

$$\begin{aligned} (\mathcal{E} - e\phi)^2 - m_0^2 c^4 &= (\mathcal{E}' + m_0 c^2 - e\phi)^2 - m_0^2 c^4 \\ &\approx 2(\mathcal{E}' - e\phi) m_0 c^2 \end{aligned}$$

Substituting this in equation (5)

$$\begin{aligned} [2(\mathcal{E}' - e\phi) m_0 c^2 - c^2(\mathbf{p} - \frac{e\mathbf{A}}{c})^2 + e\hbar c \boldsymbol{\sigma}' \cdot \mathbf{H} + i e \hbar c \boldsymbol{\alpha} \cdot \underline{\mathcal{E}}] \Psi &= 0 \\ \therefore 2 m_0 c^2 \mathcal{E}' \Psi &= [c^2(\mathbf{p} - \frac{e\mathbf{A}}{c})^2 + 2 m_0 c^2 e\phi - e\hbar c \boldsymbol{\sigma}' \cdot \mathbf{H} - i e \hbar c \boldsymbol{\alpha} \cdot \underline{\mathcal{E}}] \Psi \\ \mathcal{E}' \Psi &= \left[\frac{1}{2 m_0} (\mathbf{p} - \frac{e\mathbf{A}}{c})^2 + e\phi - \frac{e\hbar}{2 m_0 c} \boldsymbol{\sigma}' \cdot \mathbf{H} - \frac{i e \hbar}{2 m_0 c} \boldsymbol{\alpha} \cdot \underline{\mathcal{E}} \right] \Psi \end{aligned}$$

But \mathcal{E}' is equivalent to $i\hbar \frac{\partial}{\partial t}$. Equation (6) is therefore the non-relativistic Schrödinger equation with two additional terms involving $\underline{\mathcal{E}}$ and \mathbf{H} . The term

$$\begin{aligned} \frac{e\hbar}{2mc} \boldsymbol{\sigma}' \cdot \mathbf{H} &= \frac{e}{mc} \frac{\hbar}{2} \boldsymbol{\sigma}' \cdot \mathbf{H} \\ &= \frac{e}{mc} \underline{\mathcal{S}} \cdot \mathbf{H} \quad \text{where } \underline{\mathcal{S}} = \frac{\hbar}{2} \boldsymbol{\sigma}' \quad \text{and } \boldsymbol{\sigma}'^2 = 1 \end{aligned}$$

has the form associated with the energy of a magnetic dipole of moment $\frac{e}{mc} \frac{\hbar}{2} \boldsymbol{\sigma}'$. It is attributed to the effect due to the intrinsic spin of the electron and is precisely the same as that obtained previously by experiment and that used in the hypothesis of Uhlenbeck and Goudsmit. $\underline{\mathcal{E}}$ is taken as the spin angular momentum vector.

Before proceeding to a detailed example of the use of these results, it will be convenient to give here a few results that will be used in the analysis later.

1) The eigenvalues of the squared angular momenta vectors \underline{L}^2 , \underline{S}^2 and \underline{J}^2 are taken as $l(l+1)\hbar^2$, $s(s+1)\hbar^2$ and $j(j+1)\hbar^2$

The derivation of these results is as follows:

Consider an observable quantity represented by a vector whose components obey the commutation relationships

$$J_y J_z - J_z J_y = i\hbar J_x$$

$$J_z J_x - J_x J_z = i\hbar J_y$$

$$J_x J_y - J_y J_x = i\hbar J_z$$

The observables $\underline{L} = r \times p$ and $\underline{S} = \frac{1}{2}\hbar \underline{\sigma}$ and therefore $\underline{J} = \underline{L} + \underline{S}$ are of this form.

Then $J_y (J_y J_z - J_z J_y) + (J_y J_z - J_z J_y) J_y = i\hbar (J_y J_x + J_x J_y)$

i.e. $J_y^2 J_z - J_z J_y^2 = i\hbar (J_y J_x + J_x J_y)$

But $J_x J_z - J_z J_x = -i\hbar J_y$

Therefore $J_x^2 J_z - J_z J_x^2 = -i\hbar (J_x J_y + J_y J_x)$

Also $J_z^2 J_z - J_z J_z^2 = 0$

Therefore, adding $\underline{J}^2 J_z - J_z \underline{J}^2 = 0$

Hence \underline{J}^2 commutes with J_z (and similarly with J_x and J_y and therefore with \underline{J}). Thus there will be simultaneous eigenstates of \underline{J}^2 and J_z .

Suppose that \underline{J}^2 , J_z and a set of observables Γ make up a complete set of independent commuting variables for the system to be considered. If $\gamma, \gamma', \gamma''$ are simultaneous eigenvalues of $\Gamma, \underline{J}^2, J_z$ then $\psi(\gamma, \gamma', \gamma'')$ can be taken as

an eigenstate of the system.

Using the above commutation relationships on the components

$$\begin{aligned} \text{of } \underline{J}, \quad J_z (J_x \pm i J_y) &= (J_z J_x - J_x J_z) \pm i (J_z J_y - J_y J_z) + J_x J_z \pm i J_y J_z \\ &= \pm i J_y J_x + J_x J_z \pm i J_y J_z \end{aligned}$$

$$\text{giving } J_z (J_x \pm i J_y) = (J_x \pm i J_y) (J_z \pm \hbar)$$

$$\begin{aligned} \text{Operating with both sides of this equation on } \psi(\gamma \underline{J}^2 J_z') \\ J_z (J_x \pm i J_y) \psi(\gamma \underline{J}^2 J_z') &= (J_x \pm i J_y) (J_z \pm \hbar) \psi(\gamma \underline{J}^2 J_z') \\ &= (J_z' \pm \hbar) (J_x \pm i J_y) \psi(\gamma \underline{J}^2 J_z') \end{aligned}$$

$$\text{Thus, unless } (J_x \pm i J_y) \psi(\gamma \underline{J}^2 J_z') = 0 \quad (7)$$

this gives an eigenstate of J_z belonging to the eigenvalue

$J_z' \pm \hbar$ in addition to the original eigenvalue J_z' . There will also be the simultaneous eigenvalue \underline{J}^2 of \underline{J}^2 . Hence starting with a given pair of allowed eigenvalues \underline{J}^2 and J_z' a whole series of pairs is obtained,

$$\dots\dots\dots (\underline{J}^2, J_z - 2\hbar); (\underline{J}^2, J_z' - \hbar); (\underline{J}^2, J_z'); (\underline{J}^2, J_z' + \hbar); \dots\dots\dots$$

Denote the lowest and highest members of pairs of this series

by $\underline{J}^2 J_z^l$ and $\underline{J}^2 J_z^h$. Then from equation (7) the

corresponding states must satisfy

$$(J_x - i J_y) \psi(\gamma \underline{J}^2 J_z^l) = 0 \quad (8)$$

$$\text{and } (J_x + i J_y) \psi(\gamma \underline{J}^2 J_z^h) = 0 \quad (9)$$

for otherwise the left hand sides of these equations would be eigenstates belonging to $J_z^l - \hbar$ and $J_z^h + \hbar$ contrary to hypothesis.

Operating on (8) by $(J_x + i J_y)$

$$\begin{aligned} (J_x^2 + J_y^2 + \hbar J_z) \psi(\gamma \underline{J}^2 J_z^l) &= (\underline{J}^2 - J_z^2 + \hbar J_z) \psi(\gamma \underline{J}^2 J_z^l) \\ &= (\underline{J}^2 - (J_z^l)^2 + \hbar J_z^l) \psi(\gamma \underline{J}^2 J_z^l) \\ &= 0 \end{aligned}$$

and since $\Psi (J_z^h J_z^l) \neq 0$,

$$J_z'^2 - (J_z^l)^2 + \hbar J_z^l = 0 \tag{10}$$

Similarly operating on (9) by $(J_x - i J_y)$

$$J_z'^2 - (J_z^h)^2 - \hbar J_z^h = 0 \tag{11}$$

whence $(J_z^h + J_z^l)(J_z^l - J_z^h - \hbar) = 0$

and since $J_z^h \geq J_z^l$,

$$J_z^h = -J_z^l$$

The difference $J_z^h - J_z^l$ must be a positive integer, or zero,

times \hbar . Writing this integer $2j$ where $j = 0, \frac{1}{2}, 1, \frac{3}{2}, \dots$

then $J_z^l = -j\hbar$; $J_z^h = j\hbar$ and from (10) or (11)

$$J'^2 = j(j+1)\hbar^2$$

Therefore the eigenvalues of L^2 , S^2 and J^2 are $l(l+1)\hbar^2$, $s(s+1)\hbar^2$ and $j(j+1)\hbar^2$.

2) It has been shown above that if the vector J is defined as above, then J^2 and J_z can have simultaneous eigenvalues, and that the orbital momentum vector L and the spin angular momentum vector S are of this form. Taking two such vectors L and S whose components commute, there will exist simultaneous eigenvalues of L^2 , S^2 , L_z and S_z . Then L^2, S^2, L_z, S_z together with a set of observables Γ which commute with L and S can be taken to make a complete set of independent commuting variables for a certain system. Let j, j_z, m_l, m_s and γ be quantum numbers specifying the eigenvalues of L^2, S^2, L_z, S_z and Γ . The states of the system can then

be represented in terms of the scheme $\phi(\gamma j, j_2, m_x, m_s)$.

If now a vector $\underline{J} = \underline{L} + \underline{S}$ is introduced, with eigenvalues of \underline{J}_z represented by $m = m_x + m_s$, the set of vectors $\{\underline{J}_1, \underline{J}_2, \underline{J}^2, J_z\}$ is seen to be another set of independent commuting variables which will also be complete. The states of the system can therefore be represented alternatively by $\Psi(\gamma j, j_2, j, m)$ where the relation between the two representations takes the form

$$\Psi(\gamma j, j_2, j, m) = \sum \phi(\gamma j, j_2, m_x, m_s) \langle \gamma j, j_2, m_x, m_s | \gamma j, j_2, j, m \rangle$$

It is sometimes necessary to change over from one representation to the other. A complete formula for the determination of the values of the coefficients $\langle \gamma j, j_2, m_x, m_s | \gamma j, j_2, j, m \rangle$ has been obtained by Wigner (ref.3) but it is rather complex and unwieldy to use. It will be sufficient for the purposes of this paper to quote the values of the particular terms required, (as given by Condon and Shortley)(ref.4).

$$\langle j, \frac{1}{2}, m, m_s | j, \frac{1}{2}, j, m \rangle =$$

$j =$	$m_s = \frac{1}{2}$	$m_s = -\frac{1}{2}$
$j, +\frac{1}{2}$	$\sqrt{\frac{j_1 + m + \frac{1}{2}}{2j_1 + 1}}$	$\sqrt{\frac{j_1 - m + \frac{1}{2}}{2j_1 + 1}}$
$j, -\frac{1}{2}$	$-\sqrt{\frac{j_1 - m + \frac{1}{2}}{2j_1 + 1}}$	$\sqrt{\frac{j_1 + m + \frac{1}{2}}{2j_1 + 1}}$

(12)

3) If \underline{L}^2 and \underline{S}^2 have the eigenvalues $l(l+1)\hbar^2$ and $\frac{1}{2}(\frac{1}{2}+1)\hbar^2$ the matrix component of the product $\underline{L} \cdot \underline{S}$ in the $\phi(\gamma j, j_2, m_x, m_s)$ representation is given by Condon and Shortley as

$$\langle \gamma s l m_s, m_x | \underline{L} \cdot \underline{S} | \gamma s l' m_s', m_x' \rangle = \hbar^2 \left\{ \delta(m_s, m_s') \delta(m_x, m_x') \right. \\ \left. + \frac{1}{2} \delta(m_s', m_s \pm 1) \sqrt{(l-m_x \pm \frac{1}{2})(l+m_x \pm \frac{1}{2})} \right\} \quad (13)$$

4) It will be required to know the values of certain components of the matrix $\langle \alpha j_1 j_2 j_m | \underline{I} | \alpha' j_1' j_2' j_m' \rangle$ where \underline{I} is a vector obeying the commutation relation with respect to any angular momentum \underline{J}

$$[\underline{J}, \underline{I}] = [\underline{I}, \underline{J}] = -i\hbar \underline{I}$$

$\underline{J} = \underline{L} + \underline{S}$ itself obeys this relation. The full investigation of these components is, however, rather long and it will be again sufficient here to quote a result, given by Condon and Shortley.

$$\langle \alpha j_1 j_2 j_m | \underline{I} | \alpha' j_1 j_2 j_m \rangle = \frac{j_1(j_1+1) - j_2(j_2+1) + j(j+1)}{2j(j+1)} m\hbar \quad (14)$$

Section II.

The quantum-mechanical treatment of the Zeeman effect.

Firstly atoms with a single free electron are considered, that is, hydrogen atoms or those with one or more closed shells with an additional free electron. These latter, of which Li having one closed shell and one free electron, and Na with three closed shells and one free electron are examples, behave chemically in many ways similar to those of hydrogen.

For simplicity the atom is first treated in a zero external electromagnetic field. All the energy of the electron will then be due to its Coulomb potential, its orbital and spin angular momenta, and the coupling between these momenta. A

steady electromagnetic field, with electrical and magnetic field strengths \underline{E} and \underline{H} , is then introduced and the effects considered of the additional interaction energy terms, the calculations being given to the order of accuracy given by first order perturbation terms only.

Secondly, the case is considered briefly in which there are two or more free electrons, and it is found that, in general, there is a number of states belonging to the same configuration, which are degenerate in the central field approximation, differing in the assignment of the quantum numbers m_l and m_s ; that is, degenerate if it is assumed that each of the atomic electrons moves in a spherically symmetric potential energy $V(r)$ that is produced by the nucleus and all the other electrons. The theory of complex spectra consists in determining the linear combination of the wave functions of such states that diagonalise the perturbations in the presence of an external field, and the determination of the corresponding perturbed energy levels.

A single electron in a central field.

The case of an atom with a single free electron is treated as that of an electron moving a spherically symmetrical Coulomb potential

The Dirac equation of the electron may be written

$$\left[\frac{1}{c} (E - V) + \underline{\alpha} \left(\underline{p} - \frac{e \underline{A}}{c} \right) + \alpha_0 m_0 c \right] \psi = 0 \quad (15)$$

In the absence of an external field this reduces to

$$\left[\frac{1}{c}(\mathcal{E}-V) + \underline{\sigma} \cdot \underline{P} + 2m_0 c \right] | \rangle = 0 \quad (16)$$

The ket vector $| \rangle$ may be taken in the form

$$\begin{bmatrix} \Psi_1(x, y, z, \sigma) \\ \Psi_2(x, y, z, \sigma) \end{bmatrix}$$

where σ can take the values $\pm \frac{1}{2}$, and Ψ_1 and Ψ_2 together constitute an energy eigenfunction Ψ .

Equation (16) now becomes

$$\left\{ \frac{1}{c}(\mathcal{E}-V) + \begin{bmatrix} \cdot & \sigma \\ \sigma & \cdot \end{bmatrix} \underline{P} + \begin{bmatrix} 1 & \\ & -1 \end{bmatrix} m_0 c \right\} \begin{bmatrix} \Psi_1 \\ \Psi_2 \end{bmatrix} = 0$$

giving

$$\frac{1}{c}(\mathcal{E}-V)\Psi_1 + \underline{\sigma} \cdot \underline{P} \Psi_2 + m_0 c \Psi_1 = 0$$

$$\text{and} \quad \frac{1}{c}(\mathcal{E}-V)\Psi_2 + \underline{\sigma} \cdot \underline{P} \Psi_1 - m_0 c \Psi_2 = 0$$

which, using the approximation $\mathcal{E} \approx m_0 c^2 + \mathcal{E}'$, further reduce to

$$\left. \begin{aligned} \frac{1}{c}(\mathcal{E}'-V)\Psi_1 + \underline{\sigma} \cdot \underline{P} \Psi_2 + 2m_0 c \Psi_1 &= 0 \\ \frac{1}{c}(\mathcal{E}'-V)\Psi_2 + \underline{\sigma} \cdot \underline{P} \Psi_1 &= 0 \end{aligned} \right\} \quad (17)$$

In the first of equations (17) the first term is small compared with the others.

Therefore $\Psi_2 = o\left(\frac{\mathcal{E}'}{V}\right)\Psi_1$,

that is, Ψ_1 is small compared with Ψ_2 .

From this equation

$$\begin{aligned} \Psi_1 &= \frac{-\underline{\sigma} \cdot \underline{P} \Psi_2}{\frac{1}{c}(\mathcal{E}'-V) + 2m_0 c} \\ &= -\frac{1}{2m_0 c} \left[1 + \frac{\mathcal{E}'-V}{2m_0 c^2} \right]^{-1} \underline{\sigma} \cdot \underline{P} \Psi_2 \\ &\approx -\frac{1}{2m_0 c} \left[1 - \frac{\mathcal{E}'-V}{2m_0 c^2} \right] \underline{\sigma} \cdot \underline{P} \Psi_2 \end{aligned}$$

Therefore from the second equation of (17)

$$\frac{1}{c}(\mathcal{E}'-V)\Psi_2 - \underline{\sigma} \cdot \underline{P} \frac{1}{2m_0 c} \left[1 - \frac{\mathcal{E}'-V}{2m_0 c^2} \right] \underline{\sigma} \cdot \underline{P} \Psi_2 \approx 0 \quad (18)$$

It will be convenient at this point to give a few results in vector algebra which we shall require

$$\begin{aligned} \text{(a)} \quad (\underline{\sigma} \cdot \underline{p})(V \cdot F) &= -i\hbar \underline{\sigma} \text{ grad}(VF) \\ &= -i\hbar \underline{\sigma} [V \text{ grad } F + (\text{grad } V) F] \\ &= V(\underline{\sigma} \cdot \underline{p})F - i\hbar (\underline{\sigma} \text{ grad } V) F \end{aligned}$$

$$\begin{aligned} \text{(b)} \quad (\underline{\sigma} \cdot \underline{p})(\underline{\sigma} \cdot \underline{p}) &= (\sigma_x p_x + \sigma_y p_y + \sigma_z p_z)^2 = p_x^2 + p_y^2 + p_z^2 = p^2 \\ &\text{since } \sigma_i^2 = 1 \text{ and the } p\text{'s commute.} \end{aligned}$$

$$\text{(c)} \quad (\underline{\sigma} \text{ grad } V)(\underline{\sigma} \cdot \underline{p})\Psi = (\text{grad } V \cdot \underline{p})\Psi + i \underline{\sigma} (\text{grad } V)_\perp \underline{p} \Psi$$

(d) If $V = V(r)$ is the Coulomb Potential

$$\begin{aligned} \text{grad } V &= \frac{1}{r} \frac{\partial V}{\partial r} \cdot \underline{r} \\ \therefore \text{grad } V \text{ grad } \Psi &= \frac{\partial V}{\partial r} \frac{\partial \Psi}{\partial r} \end{aligned}$$

From equation (17)

$$E' \Psi_2 = V \Psi_2 + \frac{1}{2m} \left[\left(1 - \frac{E'}{2mc^2}\right) (\underline{\sigma} \cdot \underline{p})(\underline{\sigma} \cdot \underline{p}) \Psi_2 + \underline{\sigma} \cdot \underline{p} \frac{V}{2mc^2} (\underline{\sigma} \cdot \underline{p}) \Psi_2 \right]$$

Using the vector relations above, this reduces to

$$\begin{aligned} E' \Psi_2 &= V \Psi_2 + \frac{1}{2m} \left[p^2 \left(1 - \frac{E'}{2mc^2}\right) \Psi_2 + \frac{V}{2mc^2} (\underline{\sigma} \cdot \underline{p})(\underline{\sigma} \cdot \underline{p}) \Psi_2 \right. \\ &\quad \left. - \frac{i\hbar}{2mc^2} \underline{\sigma} (\text{grad } V)(\underline{\sigma} \cdot \underline{p}) \Psi_2 \right] \\ &= V \Psi_2 + \frac{1}{2m} \left[p^2 \left(1 - \frac{E'}{2mc^2}\right) \Psi_2 + \frac{V}{2mc^2} p^2 \Psi_2 - \frac{i\hbar}{2mc^2} (\text{grad } V) \cdot \underline{p} \Psi_2 \right. \\ &\quad \left. - \frac{i\hbar}{2mc^2} i \underline{\sigma} (\text{grad } V)_\perp \underline{p} \Psi_2 \right] \\ &= V \Psi_2 + \frac{1}{2m} \left[p^2 - p^2 \frac{(E'-V)}{2mc^2} - \frac{i\hbar}{2mc^2} (\text{grad } V \cdot \underline{p}) + \frac{\hbar}{2mc^2} \underline{\sigma} (\text{grad } V)_\perp \underline{p} \right] \Psi_2 \end{aligned}$$

But $E' \approx E - m_0 c^2$

and $\frac{E^2}{c^2} - p^2 = m_0^2 c^2$

Therefore $E = c \sqrt{m_0^2 c^2 + p^2} \approx m_0 c^2 \left(1 + \frac{p^2}{2m_0^2 c^2}\right)$

i.e. $E' \approx \frac{p^2}{2m_0}$

giving $E' \Psi_2 = V \Psi_2 + \frac{p^2}{2m} \Psi_2 - \frac{p^4}{8m^3 c^2} \Psi_2 - \frac{\hbar^2}{4m^2 c^2} \frac{\partial V}{\partial r} \frac{\partial \Psi_2}{\partial r} + \frac{\hbar^2}{2m^2 c^2} \frac{1}{r} \frac{\partial V}{\partial r} \underline{s} \cdot \underline{L} \Psi_2$ (19)

where $\underline{s} = \frac{1}{2} \hbar \underline{\sigma}$

and $\underline{L} = \underline{r} \wedge \underline{p}$

The terms on the right hand side of this equation are as follows:

- a) The first and second are the classical non-relativistic terms.
- b) The third is the classical relativistic correction.
- c) The fourth is a relativistic term, having no classical analogy, which is peculiar to the Dirac theory. It can be shown to be a consequence of the approximations adopted above, and to contribute nothing to the Hamiltonian except to the lowest energy terms, the S terms (ref.4.)
- d) The last term is the spin orbit term giving the extra energy due to the coupling between the orbital and spin magnetic momenta.

Hence in zero magnetic field, the Hamiltonian for the electron may be written

$H = H^0 + H^S$ where H^S is the spin orbit coupling term, so that $H^S \propto \underline{L} \cdot \underline{S} = f(r) \underline{L} \cdot \underline{S}$

If a representation is chosen in which H^0, L_x^2, S_x^2, L_z & S_z are diagonal (as on page 13) the wave function can be taken depending on the quantum numbers n, l, m_l, m_s i.e. $\phi(n, l, m_l, m_s)$

The matrix components of the perturbation H^S will be

$$\begin{aligned} & \langle n, l, m_l, m_s | H^S | n', l', m_l', m_s' \rangle \\ &= \langle n, l, m_l, m_s | f(r) \underline{L} \cdot \underline{S} | n', l', m_l', m_s' \rangle \\ &= \sum_{n'', l'', m_l'', m_s''} \langle n, l, m_l, m_s | f(r) | n'', l'', m_l'', m_s'' \rangle \langle n'', l'', m_l'', m_s'' | \underline{L} \cdot \underline{S} | n', l', m_l', m_s' \rangle \end{aligned}$$

Since \hat{V} commutes with \hat{L} and \hat{S} it can be shown that this sum reduces to (reference 4)

$$\delta(\ell\ell') \langle n'l m_s m_\ell | \hat{V} | n'l m_s m_\ell \rangle \langle n'l m_s m_\ell | \hat{L} \cdot \hat{S} | n'l' m_s' m_\ell' \rangle$$

This matrix is strictly diagonal with respect to ℓ . Also although it is not diagonal with respect to n the perturbation theory shows, as follows, that the non-diagonal elements in which the n 's differ need not be considered since the states with the same ℓ but different n have large energy differences. Let the unperturbed Hamiltonian H^0 operating on the vector $|n\rangle$ which represents a state with a particular value of n have eigenvalue E_n .

$$\text{i.e. } H^0 |n\rangle = E_n |n\rangle$$

As n takes all possible values the vectors $|n\rangle$ will represent a complete set of states. Let the perturbed Hamiltonian $H^0 + H^1$ operate on the perturbed state represented by

$$|n'\rangle = \sum a_r |r\rangle$$

where a_r is small except when $r = n$. Let the corresponding eigenvalue be $(E_n + \epsilon_n)$

The energy equation becomes

$$(H^0 + H^1) |n'\rangle = (E_n + \epsilon_n) |n'\rangle$$

$$\text{i.e. } (H^0 + H^1) \left[a_n |n\rangle + \sum_{r \neq n} a_r |r\rangle \right] = (E_n + \epsilon_n) \left[a_n |n\rangle + \sum_{r \neq n} a_r |r\rangle \right]$$

Consider H^1, ϵ_n and $\sum_{r \neq n} a_r |r\rangle$ to be of first order of smallness. Then since

$$H^0 \sum_{r \neq n} a_r |r\rangle = \sum_{r \neq n} E_r a_r |r\rangle$$

this gives to first order of approximation

$$H^1 a_n |n\rangle = \epsilon_n a_n |n\rangle$$

Operating on the left with vector $\langle n, l$ where $n, l \neq n, l$,

$$a_n \langle n, l | H' | n \rangle = E_n a_n \langle n, l | n \rangle$$

$$= 0$$

for normalised vectors.

Thus to first order of approximation, if $n' \neq n$

$$\langle n' l m_s m_l | H' | n l m_s m_l \rangle = 0$$

provided H' is small compared with H^0

The total Hamiltonian is therefore

$$H = H^0 + H^s$$

of which, to the above order of approximation, the eigenstates are not only those of L^2 and S^2 with values $l(l+1)\hbar^2$ and $s(s+1)\hbar^2$ but also of $L \cdot S$.

Further, since $2(L \cdot S) = (S+L)^2 - L^2 - S^2$ because L and S commute,

the eigenstates of H are also those of

$$(L+S)^2 = J^2 \text{ with values } j(j+1)\hbar^2$$

Therefore $2(L \cdot S)$ has eigenvalues $[j(j+1) - l(l+1) - \frac{3}{4}] \hbar^2$

$$= [\pm(l + \frac{1}{2}) - \frac{1}{2}] \hbar^2 \text{ since } j = l \pm \frac{1}{2}$$

If the eigenvalue of the unperturbed Hamiltonian H^0 ,

corresponding to the state characterised by the quantum

numbers n, l is written as E_{nl} then, since

$$H = H^0 + H^s$$

$$= H^0 + f(r) L \cdot S$$

the eigenvalues of H are found to be

$$E_{nl} + \frac{1}{2} l f(r)$$

$$E_{nl} - \frac{1}{2} (l+1) f(r)$$

where $f(r) = \langle n l m_s m_l | f(r) | n l m_s m_l \rangle$

Hence, all configurations characterised by the values of

n and l , except s configurations, split into two levels

corresponding to $j = l \pm \frac{1}{2}$. The s levels are not split since when $l=0$ there is only one value of j , viz $j = \frac{1}{2}$

The effect of applying a magnetic field.

For simplicity in the last section the external field $\underline{H} = \text{curl } \underline{A}$ was taken to be zero. To consider the additional energy due to the presence of a non-zero magnetic field \underline{H} equation (15) must be taken for the electron.

$$\left[\frac{1}{2} (E - V) + \alpha \left(\underline{p} - \frac{e}{c} \underline{A} \right) + \omega_0 m_0 c \right] \psi = 0$$

It has been shown that this reduces to

$$E' \psi = \left[\frac{1}{2m} \left(\underline{p} - \frac{e}{c} \underline{A} \right)^2 + e\phi - \frac{e\hbar}{2mc} \underline{\sigma} \cdot \underline{H} - \frac{ie\hbar}{2mc} \underline{\alpha} \cdot \underline{E} \right] \psi \quad (20)$$

which is the non-relativistic Schrödinger equation with two additional terms involving \underline{H} and \underline{E} directly.

The term involving \underline{H} may be written

$$\frac{-e\hbar}{2mc} \underline{\sigma} \cdot \underline{H} = -\frac{e}{2mc} \underline{H} \cdot 2\underline{S}$$

where $\underline{S} = \frac{\hbar}{2} \underline{\sigma}$

This has the form associated with the energy of a magnetic dipole of moment $\frac{e\hbar}{2mc} \underline{\sigma}$ and is interpreted as the additional energy due to spin.

The only conditions on the vector potential \underline{A} are that it must satisfy the relations

$$\text{div } \underline{A} = 0 \quad \text{and} \quad \text{curl } \underline{A} = \underline{H}$$

It will be convenient at this stage to choose for \underline{A} the relation $\underline{A} = \frac{1}{2} (\underline{H} \wedge \underline{r})$

which certainly satisfies the given relations.

The first term on the right hand side of equation (20) is

$$\frac{1}{2m} \left(p - \frac{eA}{c} \right)^2 = \frac{p^2}{2m} - \frac{e}{2mc} (pA + Ap) + \frac{e^2}{2mc^2} A^2$$

Also $pA\psi = -i\hbar \text{div}(A\psi)$

$$= -i\hbar \psi \text{div} A - i\hbar A \text{grad} \psi$$

$$= 0 + A p \psi$$

Therefore this term becomes

$$\frac{p^2}{2m} - \frac{e}{2mc} 2A p + \frac{e^2}{2mc^2} A^2$$

With zero field, this was $\frac{p^2}{2m}$

Therefore the perturbation of this term due to the field is

$$= \frac{e}{mc} \cdot A \cdot p + \frac{e^2}{2mc^2} A^2 \quad (21)$$

of which the second term $\frac{e^2}{2mc^2} A^2$ is small compared with the

first. Indeed, in a field H as large as 20,000 gauss this term represents an energy of 0.0002cm^2 which is undetectable.

To the order of the present approximations, therefore, it may be neglected. It is worth mentioning, however, that for

very strong fields and large orbits this term becomes

interesting in the theory of diamagnetic susceptibility.

The perturbation term (21) may now be written

$$-\frac{e}{mc} A \cdot p = -\frac{e}{2mc} \int H \cdot \nabla \cdot p$$

$$= -\frac{e}{2mc} \int H \cdot \nabla \cdot p$$

$$= -\frac{e}{2mc} H \cdot L$$

The last term $-\frac{e\hbar}{2mc} \nabla \cdot \underline{E}$ on the right hand side of equation (20)

is easily shown to be of the order $\left(\frac{V}{c}\right)^2$ times the $e\phi$ term

and therefore, to the present order of approximations, may

also be neglected.

Thus in addition to the spin orbit coupling term

$$H^S = f(r) \underline{L} \cdot \underline{S}$$

obtained from the equation for the Hamiltonian with zero field, there are now the terms

$$\begin{aligned} H^M &= -\frac{e}{2mc} \underline{H} \cdot 2\underline{S} - \frac{e}{2mc} \underline{H} \cdot \underline{L} \\ &= -\frac{e}{2mc} \underline{H} \cdot (\underline{L} + 2\underline{S}) \\ &= -\frac{e}{2mc} \underline{H} \cdot (\underline{J} + \underline{S}) \\ &= 0 \cdot (\underline{J} + \underline{S}) \quad \text{where } 0 = -\frac{e\underline{H}}{2mc} \end{aligned}$$

due to the presence of a non-zero field \underline{H}

The term $-\frac{e}{2mc} \underline{H} \cdot 2\underline{S}$ may be interpreted as the energy due to the interaction between the spin magnetic moment and the field. Similarly $-\frac{e}{2mc} \underline{H} \cdot \underline{L}$ may be interpreted as the energy due to the interaction between the orbital magnetic moment and the field. In the present case with a single electron there is no difficulty about the addition of these two terms. When the many-electron case is considered, however, with two such terms appearing for each electron, it becomes necessary to introduce further approximations in order to sum these terms in a form which can be used simply.

The Hamiltonian may now be written

$$H = H^0 + H^S + H^M$$

For a full treatment of the Zeeman splitting due to an external field it will be necessary to consider $(H^S + H^M)$ together as a perturbation. Firstly, however, the two extreme cases are treated:

1. The weak field case in which the Zeeman splitting

is small compared with the spin doubling.

2. The strong field case when the spin orbit interaction is so small that the spin splitting is small compared with the magnetic splitting.

The weak field case.

It appears from the above that both terms of the perturbation H^M due to the external magnetic field are directly proportional to the field strength H . If this is sufficiently small, the Zeeman splitting due to will be small compared with the spin splitting due to the energy term H^S . In dealing with the spin splitting those states were examined which were represented by the quantum numbers n, l, m, m_s for different values of m , and m_s . If H is small the Zeeman splitting is considered as a perturbation of each of the two levels obtained by the spin interaction separately. To do so a state is taken with a particular value of j determined after spin splitting and the further splitting due to H^M examined. Therefore states are taken represented by the quantum numbers n, l, j, m for different values of m . This is a valid choice since it has been shown (page 13) that these will be eigen-states for the unperturbed Hamiltonian $H^0 + H^S$. The matrix components to be evaluated are therefore

$$\langle n, l, j, m | H^M | n, l, j, m' \rangle$$

This is most conveniently done with the aid of the results on page .

If Ψ is written in the form

$$\Psi(nljm) = \sum_{m_1 m_2} \langle nl m_1 m_2 | nljm \rangle \phi(nl m_1 m_2)$$

then with the aid of the table (12) the results are obtained

$$\Psi(nl l+\frac{1}{2} m) = \sqrt{\frac{l+m+\frac{1}{2}}{2l+1}} \phi(nl \frac{1}{2} m-\frac{1}{2}) + \sqrt{\frac{l-m+\frac{1}{2}}{2l+1}} \phi(nl -\frac{1}{2} m+\frac{1}{2})$$

$$\Psi(nl l-\frac{1}{2} m) = \sqrt{\frac{l-m+\frac{1}{2}}{2l+1}} \phi(nl \frac{1}{2} m-\frac{1}{2}) + \sqrt{\frac{l+m+\frac{1}{2}}{2l+1}} \phi(nl -\frac{1}{2} m+\frac{1}{2})$$

Thus

$$\begin{aligned} & \langle n l l \pm \frac{1}{2} m | H^M | n l l \pm \frac{1}{2} m \rangle \\ & = \langle n l l \pm \frac{1}{2} m | O(\bar{J}_z + S_z) | n l l \pm \frac{1}{2} m \rangle \\ & = \left\{ \sqrt{\frac{l \pm m + \frac{1}{2}}{2l+1}} \phi^*(nl \frac{1}{2} m - \frac{1}{2}) \pm \sqrt{\frac{l \mp m + \frac{1}{2}}{2l+1}} \phi^*(nl -\frac{1}{2} m \pm \frac{1}{2}) \right\} O(\bar{J}_z + S_z) \\ & \cdot \left\{ \sqrt{\frac{l \pm m' + \frac{1}{2}}{2l+1}} \phi(nl \frac{1}{2} m' - \frac{1}{2}) \pm \sqrt{\frac{l \mp m' + \frac{1}{2}}{2l+1}} \phi(nl -\frac{1}{2} m' \pm \frac{1}{2}) \right\} \end{aligned}$$

which is diagonal with respect to both \bar{J}_z and S_z and therefore gives

$$\begin{aligned} & \left\{ \sqrt{\frac{l \pm m + \frac{1}{2}}{2l+1}} \phi^*(nl \frac{1}{2} m - \frac{1}{2}) \pm \sqrt{\frac{l \mp m + \frac{1}{2}}{2l+1}} \phi^*(nl -\frac{1}{2} m \pm \frac{1}{2}) \right\} O \hbar \\ & \cdot \left\{ \sqrt{\frac{l \pm m' + \frac{1}{2}}{2l+1}} (m' \pm \frac{1}{2}) \phi(nl \frac{1}{2} m' - \frac{1}{2}) \pm \sqrt{\frac{l \mp m' + \frac{1}{2}}{2l+1}} (m' - \frac{1}{2}) \phi(nl -\frac{1}{2} m' \pm \frac{1}{2}) \right\} \\ & = \hbar O \delta(m m') \left\{ (m \pm \frac{1}{2}) \frac{l \pm m + \frac{1}{2}}{2l+1} + (m - \frac{1}{2}) \frac{l \mp m + \frac{1}{2}}{2l+1} \right\} \\ & = \hbar O m \frac{2l+1 \pm 1}{2l+1} \delta(m m') \end{aligned}$$

Thus displacements of the different Zeeman components of a level specified by a particular set of values of n, l and j are given by this term $\hbar O m g$ where $g = \frac{2l+1 \pm 1}{2l+1}$ is the Landé splitting factor for the case of a single electron. This shows that since m can take $(2j+1)$ possible values

$$m = j, j-1, j-2, \dots, -j$$

each level is split symmetrically into $(2j+1)$ equally spaced states, the splitting being proportional to the field \underline{H} through the symbol $\sigma = \frac{e\hbar}{2mc}$ and independent of the value of the total quantum number n .

The strong field case.

It is worth looking back for a moment to the procedure that has been followed so far. To examine the splitting due to the spin interaction with no external field present states were examined differing in the quantum numbers m_l and m_s ; that is, matrix components were examined of the form

$$\langle n l m_s m_l | H^S | n l m_s' m_l' \rangle$$

Then with a weak field the Zeeman splitting was treated as a secondary effect superposed on the spin splitting. Therefore a particular value of j determined by the spin splitting was chosen and states differing in the quantum number m only were examined, that is, matrix components of the form

$$\langle n l j m | H^M | n l j m' \rangle$$

With a strong external field when the spin orbit interaction is small compared with the magnetic splitting it will be logical to examine again states differing in both the quantum numbers m_l and m_s , that is to take matrix components

$$\langle n l m_s m_l | H^M | n l m_s' m_l' \rangle$$

and then to consider the spin splitting as superposed upon this effect. This is easily done since H^M is diagonal in this representation;

$$\begin{aligned}
& \langle n l m_s m_l | \circ (\mathcal{J}_z + \mathcal{S}_z) | n l m_s' m_l' \rangle \\
& = (\overline{m_s + m_l + m_s}) \circ \hbar \delta(m_s, m_s') \delta(m_l, m_l') \\
& = \circ \hbar (m + m_s)
\end{aligned}$$

Thus the configuration $n l$ is split up symmetrically into equally spaced components corresponding to the possible values

$$(l+1), l, \dots, -(l+1) \quad d_j (m + m_s) = (m_l + 2m_s)$$

Of these, if a particular value of $m_l + 2m_s$ is considered, say $(l-r)$, it can be formed in two ways,

$$(l-r-1)+1 \quad \text{or} \quad (l-r+1)-1$$

Therefore of the $(2l+3)$ levels all are doubly degenerate except the first two and the last two.

For the non-degenerate terms the effect of superposing a small spin orbit interaction is found by making use of equation (13), giving the perturbation energy as

$$\begin{aligned}
& \langle n l m_s m_l | f(r) \underline{L} \cdot \underline{S} | n l m_s' m_l' \rangle \\
& = \langle n l m_s m_l | f(r) | n l m_s m_l \rangle \langle n l m_s m_l | \underline{L} \cdot \underline{S} | n l m_s' m_l' \rangle \quad \text{from Page 20} \\
& = f(r) \langle n l m_s m_l | \underline{L} \cdot \underline{S} | n l m_s' m_l' \rangle \\
& = f(r) \hbar^2 m_l m_s
\end{aligned}$$

since $m_l' = m_l$ and $m_s' = m_s$ in the non-degenerate case.

Thus the non-degenerate levels are displaced by an amount $f(r) \hbar^2 m_l m_s$. Further for the degenerate levels, because of the $\delta(m_s, m_s')$ in equation (13), there are no matrix components of $\underline{L} \cdot \underline{S}$ joining the two degenerate states, so that each state is displaced by an amount

For the two extreme cases, the weak field and the strong field cases, there are thus these two effects:-

a) A primary splitting of all configurations except s configurations into two levels corresponding to $j = l \pm \frac{1}{2}$ with an evenly spaced Zeeman splitting of each of the two levels into $2j+1$ evenly spaced terms as a subsidiary superposition.

b) A primary splitting of all configurations into levels due to an external magnetic field, all of which except four are doubly degenerate. All of these terms will be displaced by an amount proportional to the product $m_l m_s$ and the degenerate terms may be split into two.

For a full investigation of the Zeeman effect for one electron, to obtain a comprehensive result regardless of the relative values of H^S and H^M it would be necessary to evaluate matrix components when H^S and H^M were taken as simultaneous perturbations. To examine the transition case between the two extreme cases above this is what is done, but H^S and H^M are taken as being of similar order of magnitude. It will clearly be necessary to go back once more to the original set of eigenfunctions labelled $n l m_s m_l$ and investigate the matrix components for a given $n l$,

$$\langle n l m_s m_l | H^S + H^M | n l m_s' m_l' \rangle$$

in which the matrix of $H^M = \mu_B (J_z + S_z)$ is diagonal.

Thus

$$\langle n l m_s m_l | H^S + H^M | n l m_s' m_l' \rangle$$

$$\langle n l m_s m_l | f(r) L_z + \mu_B (J_z + S_z) | n l m_s' m_l' \rangle$$

$$\langle n l m_s m_l | f(r) L_z | n l m_s' m_l' \rangle + \mu_B (2m_s + m_l)$$

To evaluate the first of these two terms the equation (13)

is used: $\langle n l m_s m_l | L_z | n l m_s' m_l' \rangle$

$$f(r) \langle n l m_s m_l | L_z | n l m_s' m_l' \rangle$$

(where $f(r) = \langle n l m_s m_l | f(r) | n' l m_s m_l \rangle$ as on page 21)

$$= f(r) \hbar^2 \delta(m, m') \left[\delta(m_s, m'_s) m_l m_s \pm \frac{1}{2} \delta(m_s, m'_s \pm 1) \sqrt{(l+m \pm \frac{1}{2})(l-m \pm \frac{1}{2})} \right] \text{ using (13)} \quad (22)$$

The highest and lowest values of $m = m_l + m_s$ are $(l + \frac{1}{2})$ and $-(l + \frac{1}{2})$

which may be formed in one way only, that is $m_l = \pm l$, $m_s = \pm \frac{1}{2}$

Substituting these in (22) the energy given by these states is found to be

$$E = \frac{1}{2} l \hbar^2 g(r) + 0 \hbar (l+1) \quad \text{for } m = (l + \frac{1}{2})$$

$$\text{and } E = \frac{1}{2} l \hbar^2 g(r) - 0 \hbar (l+1) \quad \text{for } m = -(l + \frac{1}{2})$$

All other values of m may be formed in two ways. For these values the equation is obtained

$$\left| \begin{array}{cc} -\frac{1}{2} \hbar^2 g (m + \frac{1}{2}) + \hbar (l - \frac{1}{2}) - E & \frac{1}{2} \hbar^2 g \sqrt{(l+m+\frac{1}{2})(l-m+\frac{1}{2})} \\ \frac{1}{2} \hbar^2 g \sqrt{(l+m+\frac{1}{2})(l-m+\frac{1}{2})} & \frac{1}{2} \hbar^2 g (m - \frac{1}{2}) + \hbar (l + \frac{1}{2}) - E \end{array} \right| = 0$$

which has the solutions

$$4E_{\pm} = 4\hbar (l+1) m - \hbar^2 g \pm \sqrt{(4\hbar (l+1) m - \hbar^2 g)^2 - 4[\hbar^2 (l+1) m^2 - 4\hbar^2 g^2 (l+1)]} \quad (23)$$

For these solutions to be satisfactory it will be required that, with appropriate approximations, they agree with the weak field case and similarly for the strong field case.

For a measure of the relative values it is seen that $\hbar^2 g$ represents the magnitude of the spin perturbation and $\hbar (l+1)$ that of the magnetic perturbation. Thus in the weak field case $\frac{0}{\hbar g}$ can be taken as small, and squared terms and terms of higher order can be neglected.

Writing $\frac{0}{\hbar g} = \eta$, equation (23) becomes

$$4E_{\pm} = \hbar^2 g \left[4\eta m - 1 \pm (1 + 4\hbar(l+1) + 8\eta m)^{\frac{1}{2}} \right] \text{ neglecting}$$

$$\approx \hbar^2 g \left[4\eta m - 1 \pm (2l+1) \left(1 + \frac{4\eta m}{2l+1} \right) \right]$$

$$\text{Thus } 4E_{+} = \hbar^2 g \left[4\eta m + 2l + \frac{4\eta m}{2l+1} \right]$$

$$\text{and } 4E_{-} = \hbar^2 g \left[4\eta m - 2 - 2l - \frac{4\eta m}{2l+1} \right]$$

$$\begin{aligned} \text{giving } \epsilon_+ &= \hbar \omega \left(\frac{2l+2}{2l+1} \right) + \frac{1}{2} \hbar^2 \zeta l \\ \epsilon_- &= \hbar \omega \left(\frac{2l}{2l+1} \right) - \frac{1}{2} \hbar^2 \zeta (l+1) \end{aligned}$$

agreeing exactly with the results of the weak field calculation.

Similarly in a strong field squared values of $\frac{\hbar \zeta}{\omega}$ and higher orders are neglected. Equation (23) becomes

$$\begin{aligned} 4\epsilon_{\pm} &= \hbar \omega \left[4m - \eta'_{\pm} (8\eta'_{\pm} m + 4)^{\frac{1}{2}} \right] \quad \text{writing } \frac{\hbar \zeta}{\omega} = \eta' \\ &\quad \left[4m - \eta'_{\pm} \pm 2m(2m-1) \right] \\ \therefore 4\epsilon_+ &= \hbar \omega \left[4m+2 + \eta' (2m-1) \right] \\ \text{or } 4\epsilon_- &= \hbar \omega \left[4m-2 - \eta' (2m+1) \right] \end{aligned}$$

$$\begin{aligned} \text{whence } \epsilon_+ &= \hbar \omega \left(m + \frac{1}{2} \right) + \frac{1}{2} \hbar^2 \zeta \left(m - \frac{1}{2} \right) \\ \epsilon_- &= \hbar \omega \left(m - \frac{1}{2} \right) - \frac{1}{2} \hbar^2 \zeta \left(m + \frac{1}{2} \right) \end{aligned}$$

agreeing again with the previous results.

The many-electron atom.

In extending the above analysis to the case of the atom with more than one electron outside its completed shells it is necessary to introduce a further approximation. If the orbital and spin angular momenta of individual electrons in the atom are denoted by $\underline{L}_1, \underline{L}_2, \underline{L}_3, \dots, \underline{S}_1, \underline{S}_2, \underline{S}_3, \dots$ there will appear spin orbit interaction terms in the Hamiltonian proportional to $\underline{L}_i \underline{S}_i$, making the diagonalisation of the Hamiltonian very complex. However, it is found experimentally that in many atoms the spin orbit interaction is small compared with the Coulomb interaction. The Hamiltonian without the spin orbit interaction terms commutes with all components and therefore with the resultants of the orbital and spin angular momenta $\underline{L} = \underline{L}_1 + \underline{L}_2 + \dots$ and $\underline{S} = \underline{S}_1 + \underline{S}_2 + \dots$ and

and hence with all the components of the total angular momentum

$$\underline{J} = \underline{L} + \underline{S}$$

This Hamiltonian will therefore have no matrix components connecting states labelled by two different precise values of $\underline{S}^2, \underline{L}^2, \underline{J}^2, S_z, L_z$ or J_z

If the spin orbit energy is included, \underline{L} and \underline{S} no longer commute with the Hamiltonian. However, it is sufficient, to the present order of approximation, to assume that the states of different \underline{L}_i and \underline{S}_j are sufficiently well separated by the electrostatic energy H^M that their mixing due to the spin orbit energy can be neglected. This is the "L-S Coupling" scheme which gives an approximation allowing the individual angular momenta to be summed in the form

$$\underline{L} = \underline{L}_1 + \underline{L}_2 + \dots$$

$$\underline{S} = \underline{S}_1 + \underline{S}_2 + \dots$$

$$\underline{J} = \underline{L} + \underline{S}$$

Capital letters S, L, J, M_s, M_L, M are introduced for quantum numbers which refer to the resultant momenta of all the electrons in the atom. Then

$$\underline{S}^2 = S(S+1)\hbar^2 \quad S_z = M_s \hbar$$

$$\underline{L}^2 = L(L+1)\hbar^2 \quad L_z = M_L \hbar$$

$$\underline{J}^2 = J(J+1)\hbar^2 \quad J_z = M \hbar$$

of which only four are independent.

For the weak field case of the one-electron atom for the magnetic perturbation H^M the states investigated were those represented by n, l, j, m for different values of m .

In the same way, to find the weak field perturbation of a level characterised by $\underline{S} \underline{L} \underline{J}$ the matrix component of H^M for this level is calculated where

$$\begin{aligned} H^M &= 0(L_z + 2S_z) \\ \langle SLJM | H^M | SLJM' \rangle \\ &= \langle SLJM | 0(L_z + 2S_z) | SLJM' \rangle \\ &= \langle SLJM | 0J_z | SLJM' \rangle + \langle SLJM | 0S_z | SLJM' \rangle \\ &= 0Mk + \langle SLJM | 0S_z | SLJM' \rangle \end{aligned}$$

If J_z is identified with S and J_z with L in equation (14)

this reduces to

$$\begin{aligned} 0Mk + \frac{1}{2J(J+1)} 0 [S(S+1) - L(L+1) + J(J+1)] Mk \\ = 0k g M \quad \text{where } g = 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)} \end{aligned}$$

Again, the ^{energy levels} ~~energies~~ of the perturbed states are $2J+1$ in number and are distributed symmetrically around that of the unperturbed level. For the singlet terms, $S=0$ and $L=J$ giving g equal to unity. Then, using the selection rule $M = \pm 1, 0$ which will be discussed in the section on radiation theory, the normal Lorentz triplet appears. In other words, the "normal" Zeeman effect applies to lines which are combinations of singlet levels.

Similarly, following the lines of the argument of the calculation for the one-electron system in a strong external field, but using the quantum numbers $S L M_S M_L$ results for the many-electron problem may be obtained for the strong-field case. Since, however, the calculations are somewhat cumbersome and the results have little

applicability in spectroscopy, the details will be omitted here.

Note on the "fine structure" and "hyperfine structure" in spectra.

If the classical relativistic correction is taken into account an additional term H'' appears in the total energy where $H'' \propto \left(\frac{n}{l+1} - \frac{3}{4} \right)$ and l may take any of the values $0, 1, 2, \dots, n-1$. The effect of this additional energy will be to split the state corresponding to any given n into n components, the order of splitting being very small. This result is confirmed empirically in the observed fine structure of spectral lines.

To explain the "hyperfine" structure exhibited by many spectral lines the concept of nuclear spin was introduced. Pauli assumed that the nucleus itself possessed angular momentum and therefore also magnetic moment in an external field. The nuclear spin magnetic moment takes the form

$$\mu_n = \rho \frac{e}{2Mc} \hbar$$

where ρ is an undetermined constant of proportionality, and e and M are the electric charge and mass associated with the nucleus. But the orbital magnetic moment is

$$\mu_l = \frac{e}{2mc} \hbar \cdot l$$

Thus the ratio $\frac{\text{nuclear spin magnetic moment}}{\text{angular spin magnetic moment}}$ is of the

order $\frac{m}{M}$. The effect of nuclear spin will therefore be very small compared with those of the orbital motion and

electron spin. Let \underline{i} be the nuclear spin quantum number. Then the resultant vector $\underline{i} + \underline{j} = \underline{f}$ represents the total angular momentum of the atom. \underline{f} is the "hyperfine" quantum number. This further assumption leads to frequency differences of the proper order of magnitude.

Radiation theory.

The discussion so far has been about the possible energy levels of the electrons in an atom and their alterations due to the application of steady external magnetic fields. The Zeeman effect itself is, however, a phenomenon of radiation. To complete the picture it will therefore be necessary to give a brief discussion on certain aspects of radiation theory. The work is divided roughly into two sections. Firstly a general perturbation H' of an unperturbed Hamiltonian H^0 is considered where H^0 is not time dependent, while H' may be some function of time. With these terms acting upon some wave function the probability of a transition from one state to another is investigated. Secondly, considering two different states the relations are determined which must exist between their quantum numbers in order that a transition from one to the other may be possible.

Let the unperturbed Hamiltonian for the electron of an hydrogen atom, or the free electron of a hydrogen-like atom be H^0 and let it satisfy the time dependent wave equation

$$H^0 \Phi = i\hbar \frac{\partial \Phi}{\partial t}$$

with the normalised solutions

$$\Phi_1, \Phi_2, \Phi_3, \dots$$

where ϕ_r is time dependent in the manner

$$\phi_r = \phi_r e^{-\frac{i}{\hbar} E_r t}$$

Now introduce an unspecified perturbation H' which is small compared with H^0

$$\text{Then } (H_0 + H') \Psi = i\hbar \frac{\partial}{\partial t} \Psi \quad (25)$$

where Ψ may be written

$$\Psi(\mathbf{r}, t) = \sum a_n(t) \phi_n(\mathbf{r}, t) \quad (26)$$

Since H' is not, in general, independent of time, a_n must be written as a function of t . If H' is small, the a_n 's will be expected to vary slowly with time.

Then $|a_n(t)|^2$ will represent the probability that, at any time, the system is in the state ϕ_n .

It is required to determine in what way $a_n(t)$ changes with time, that is, in what way the probability of the state ϕ_n changes. If the a_n 's vary little with respect to time there will be no major change in the system during any small period of time.

From equation (24)

$$H_0 \sum (a_n \phi_n) = i\hbar \sum (a_n \frac{\partial \phi_n}{\partial t}) \quad (27)$$

Therefore using equations (25) and (27)

$$\begin{aligned} (H_0 + H') \sum (a_n \phi_n) &= i\hbar \frac{\partial}{\partial t} \sum (a_n \phi_n) \\ &= i\hbar \sum \left(\frac{da_n}{dt} \phi_n + a_n \frac{d\phi_n}{dt} \right) \end{aligned}$$

$$\therefore H' \sum (a_n \phi_n) = i\hbar \sum \left(\frac{da_n}{dt} \phi_n \right)$$

Multiply on the left by ϕ_n^* and integrate. Since the ϕ_n 's are normalised the equation reduces to

$$\int \phi_n^* H' \Psi d\tau = i\hbar \frac{da_n}{dt}$$

That is $\frac{da_n}{dt} = \frac{1}{i\hbar} \int \phi_n^* H' \Psi d\tau$.

Since H^0 has been taken as large compared with H' , Ψ is approximately equal to ϕ_0 where ϕ_0 is used to denote the initial state of the system when the perturbation was first applied.

Then

$$\begin{aligned} \frac{da_n}{dt} &\approx \frac{1}{i\hbar} \int \phi_n^* H' \phi_0 d\tau \\ &= \frac{1}{i\hbar} \int \phi_n^* H' \phi_0 e^{\frac{i}{\hbar}(E_n - E_0)t} dq \\ &= \frac{1}{i\hbar} \langle \phi_n | H' | \phi_0 \rangle e^{\frac{i}{\hbar}(E_n - E_0)t} \\ \text{Therefore } a_n(t) &= \frac{1}{i\hbar} \int \langle \phi_n | H' | \phi_0 \rangle e^{\frac{i}{\hbar}(E_n - E_0)t} dt \end{aligned}$$

It is immediately clear that, if H' is a constant or varies so slowly that many oscillations of the exponential term take place while H' remains sensibly constant, the transition probability $|a_n(t)|^2$ will be zero or very small. Thus if H' is the perturbation due only to the presence of a constant magnetic field there will be no induced radiation at all. In other words, for the Zeeman effect to be observed, the above approximation indicates that there must be, in addition to a constant magnetic field causing splitting and shifting levels, a further perturbation varying with time which will induce the radiation necessary for the effect to be observed. Such a perturbation will usually be given by an electromagnetic field \mathcal{H} defined by a vector potential \underline{A} and a scalar potential ϕ .

Given such a time dependent perturbation H' , a_n takes the form

$$\begin{aligned} a_n &= \frac{1}{i\hbar} \int \langle \phi_n | H' | \phi_0 \rangle e^{\frac{i}{\hbar}(E_n - E_0)t} dt \\ &= \frac{1}{i\hbar} \int \langle \phi_n | H' | \phi_0 \rangle e^{2\pi i \nu_{n0} t} dt \end{aligned}$$

where ϕ_n and ϕ_0 are independent of time.

The non-relativistic Hamiltonian may be written

$$\begin{aligned} H &= \frac{p^2}{2m} \left(1 - \frac{e}{c} \underline{A} \right)^2 + e\phi \\ &= \frac{p^2}{2m} - \frac{e}{2mc} \cdot 2\underline{A}p + \frac{e^2}{2mc^2} \underline{A}^2 + e\phi \quad (\text{c.f. page 23}) \end{aligned}$$

To the present order of approximation the term $\frac{c^2}{2mc^2} \underline{A}^2$ is to be neglected. Writing H in the form

$$H = H^0 + H' \quad \text{where} \quad H^0 = \frac{p^2}{2m}$$

the time dependent perturbation due to the electro-magnetic field is $H' = e\phi - \frac{e}{mc} \underline{A} \cdot p$

If in the field defined by ϕ and \underline{A} the electric charge density ρ is taken equal to zero, then ϕ may be set equal to zero and the required results derived using \underline{A} alone. This is a usual procedure for dealing with electro-magnetic waves at points far from their source.

The wavelength of radiation is great compared with the size of an atom, and since the motion being considered is that of an electron in an atom, \underline{A} may be taken as approximately equal to $\underline{A}_0 e^{-2\pi i \nu t}$ where \underline{A}_0 is constant in the space of the system and in time. For example, suppose the perturbation is due to a plane electro-magnetic wave

$$\underline{A} = \text{real part of } \underline{A}_0 e^{2\pi i(kr - \nu t)}$$

where \underline{A}_0 is constant in time and space. Since \underline{v} is just an atomic distance,

$$v \leq \lambda, \text{ that is, } v \leq \frac{1}{k}$$

giving

$$kr \leq 1$$

and therefore

$$e^{2\pi i k r} \approx 1$$

Therefore

$$\underline{A} \approx \underline{A}_0 e^{-2\pi i \nu t}$$

and

$$\underline{H}' \approx -\frac{e}{mc} \underline{A}_0 \cdot p e^{-2\pi i \nu t}$$

Therefore

$$a_{n'} \approx \frac{1}{i\hbar} \int \langle \phi_{n'} | -\frac{e}{mc} \underline{A}_0 \cdot p e^{-2\pi i \nu t} | \phi_0 \rangle e^{-2\pi i \nu t} dt$$

$$= \frac{1}{i\hbar} \langle \phi_{n'} | -\frac{e}{mc} \underline{A}_0 \cdot p | \phi_0 \rangle t$$

The transition probability is therefore proportional to

$$|\langle \phi_n | A_0 \rho | \phi_0 \rangle|^2$$

that is, $\propto A_0^{-1} |\langle \phi_n | \rho | \phi_0 \rangle|^2$

Thus it is necessary to investigate the non-vanishing components of the matrix

$$\langle n \ell j m | \rho | n' \ell' j' m' \rangle$$

It has already been shown (page 20) that this is diagonal with respect to ℓ and that terms differing in n need not be considered. To examine those differing in j and m consider first the commutation bracket $[A, B] = AB - BA$. With this definition of $[A, B]$ the commutator of a single observable with the product of two is given the formula

$$[A, B, C] = [A, C] B + A [B, C]$$

The cartesian coordinates x_1, x_2, x_3 and the conjugate momenta p_1, p_2, p_3 then satisfy the relations

$$[x_i, x_j] = x_i x_j - x_j x_i = 0$$

$$[p_i, p_j] = p_i p_j - p_j p_i = 0$$

$$[x_i, p_j] = x_i p_j - p_j x_i = i\hbar \delta_{ij}$$

The orbital angular momentum vector $\underline{L} = \underline{r} \wedge \underline{p}$ has the three components

$$L_x = y p_z - z p_y$$

$$L_y = z p_x - x p_z$$

$$L_z = x p_y - y p_x$$

If the quantities Π and Π' are given by

$$\Pi = p_x - i p_y$$

$$\Pi' = p_x + i p_y$$

$$\begin{aligned}
\text{Then } [L_z, \Pi] &= [L_z, p_x] - i [L_z, p_y] \\
&= [x p_y, p_x] - [y p_x, p_x] - i [x p_y, p_y] + i [y p_x, p_y] \\
&= [x, p_x] p_y + x [p_y, p_x] - [y, p_x] p_x - y [p_x, p_x] \\
&\quad - i [x, p_y] p_y - i x [p_y, p_y] + i [y, p_y] p_x + i y [p_x, p_y] \\
&= [x, p_x] p_y + i [y, p_y] p_x \\
&= i \hbar p_y - \hbar p_x \\
&= -\hbar \Pi
\end{aligned}$$

Similarly, if \underline{S} is the spin angular momentum vector

$$[S_z, \Pi] = -\hbar \Pi$$

and therefore, since $J = L_1 + L_2 + \dots + S_1 + S_2 + \dots$

$$[J_z, \Pi] = -\hbar \Pi$$

that is $(J_z \Pi - \Pi J_z) = -\hbar \Pi$

Taking the $n l j m, n l j' m'$ components of both sides,
 $m \hbar \langle n l j m | \Pi | n l j' m' \rangle - \langle n l j m | \Pi | n l j' m' \rangle m' \hbar$
 $= -\hbar \langle n l j m | \Pi | n l j' m' \rangle$

that is $(m - m' + 1) \langle n l j m | \Pi | n l j' m' \rangle = 0$

Therefore $\langle n l j m | \Pi | n l j' m' \rangle = 0$ unless $m' = m + 1$

Similarly $\langle n l j m | \Pi | n l j' m' \rangle = 0$ unless $m' = m - 1$

Hence the non-zero components of $p_x = \frac{1}{2}(\Pi + \Pi')$ and $p_y = \frac{1}{2}i(\Pi - \Pi')$
are those for which $m' = m \pm 1$

$$\begin{aligned}
\text{Further } [L_z, p_z] &= [x p_y - y p_x, p_z] \\
&= [x p_y, p_z] - [y p_x, p_z] \\
&= [x, p_z] p_y + x [p_y, p_z] - [y, p_z] p_x - y [p_x, p_z] = 0
\end{aligned}$$

That is, L_z commutes with p_z and similarly S_z commutes
with p_z . Therefore J_z commutes with p_z giving

$$m \hbar \langle n l j m | p_z | n l j' m' \rangle - \langle n l j m | p_z | n l j' m' \rangle m' \hbar = 0$$

for which the only non-zero components are those for which

$$m' = m$$

Thus all the matrix components

$$\langle n l j m | p | n l j m' \rangle$$

are zero unless

$$m' - m = \pm 1, 0$$

Thus, in the presence of an electro-magnetic field defined by \underline{A} and ϕ the probability of transition between two states with quantum numbers m and m' is zero unless $m' - m = \pm 1, 0$.

Applying these selection rules to the results calculated earlier for the perturbed energy levels, it is found that the theory is able to account for all the observed spectral lines and to predict their energies to the degree of accuracy already specified. It therefore represents a big advance on previous attempts at description. The theory contains, however, some apparent contradictions and other undesirable features and some of the predicted results are not entirely satisfactory. These difficulties are discussed in Section III.

SECTION III.

The real criterion for any theory of physics is the measure of agreement between the calculated results it gives and empirical observations. The general structure of the theory of energy levels to first order of approximation as outlined above possesses so many points of close contact with experimental data that one feels safe in assuming that more accurate analysis and further modifications of the quantum theory will not affect the main conclusions to any great degree. It should likewise be possible to develop the theory of radiation along the general lines indicated with considerable assurance that future alterations brought by a revision of the theory of the electro-magnetic field will not appreciably change the calculated results. Indeed, the satisfactory results of the theory outlined above suggest that, if improvements are to be attempted, they will probably be made most satisfactorily by modifying the existing theory, rather than by looking for a fresh approach to the problems.

The method of procedure above was to set up equations for a system described in classical terms in space and time - the system described above was one in which particles interacted with each other - and then to "quantize" the equations. This process of quantisation may be defined as an attempt to set up within the framework of quantum mechanics a set of equations describing the system which, in the limit of large quantum numbers, will go back into the original classical equations. This process is not unique in that there may be several quantum

theoretical equations corresponding to the classical picture; for example, the Dirac equation or the Klein-Gordon equation of the electron. There may also be more than one classical picture of the result, obtained by going to the limit of macroscopic dimensions in different ways. The process of quantisation has been applied with success to systems of particles and wave fields, but, in the theory as outlined above, the success has been limited to applications involving lowest order perturbation theory only. So long as it is required to deal with the normal interactions of matter that act instantaneously at long distances, the quantised equations lead to consistent results and describe experiments with fair accuracy, indicating that the theory is satisfactory for non-relativistic particle energies. Serious difficulties are encountered, however, when it becomes necessary to deal with particles having relativistic energies, or with phenomena in the analysis of which linear dimensions occur which are comparable with, or smaller than, the so-called classical electron radius

$$r_0 = \frac{e^2}{mc^2}$$

This is not surprising since the quantum equations are derived directly from the classical theory which itself contains singularities, as mentioned earlier. The most important classical difficulty arose from the problem of the initial description of the electron. The choice lay between describing it as a small charged sphere, (or some such configuration,) or as a point charge. The first of these presents two serious

difficulties:

- 1). Size and shape are not relativistically invariant.
- 2). A finite charge distribution would explode if acted on by purely electromagnetic forces.

It was found more satisfactory, therefore, to adopt the second description and to regard the electron as a point charge.

That is the basis of the Maxwell-Lorentz equations which have been used above. A point charge is found, however, to have infinite "self-energy". The classical theory gives the total force \underline{K} on a single point charge e in an electromagnetic field as

$$\underline{K} = e \left(\underline{E} + \frac{1}{c} [\underline{v} \cdot \underline{H}] \right)$$

The field given by \underline{E} and \underline{H} which must be inserted in this equation is the external field together with the field produced by the point charge itself. This self produced field will itself react on the motion of the particle and, in order to give a correct account of the conservation of energy, the reaction of the field produced by the charge on its own motion must be considered, i.e. the self-force. Considering the electron as a finite spherical distribution of radius r_0 this self force can be expressed classically in

the form $\underline{K}^s = \underline{K}_0 + \underline{K}_s$

where $\underline{K}_0 = -\frac{2}{3} \frac{\dot{\underline{v}}}{c^2} \cdot \frac{1}{2} \int \frac{de de'}{r}$

the integration being taken over all charge elements, de, de' ,

and $\underline{K}_s = \frac{2}{3} \frac{e^2}{c^3} \ddot{\underline{v}}$ (ref.5.)

The factor $\frac{1}{2} \int \frac{de de'}{r}$ is shown to represent the electrostatic self energy contained in the static field of the particle.

For a point particle r tends to zero and the self energy becomes infinite. It is worth noting here that for a charge with radius r , the self energy is of the order of magnitude

$$\mu_0 = \frac{e^2}{r_0}$$

This term is not distinguishable from the inertia term, and since the nature of the inertial mass is not observable, the two terms could just as well be taken together, assuming that the self force \underline{V}_0 is contained in the definition of the mass m . Such a step would be very similar to the process of "mass renormalisation" mentioned later in this paper.

The point charge used in the Maxwell-Lorentz equations is described, then, as having infinite self energy. If these equations are carried over directly into the quantum mechanics corresponding singularities must therefore be expected to appear. This is indeed so and, in addition, other singularities appear in the quantum equations which are essentially a result of the quantum-theoretical formulation.

Several formal remedies have been invented to remove or circumvent the classical singularities in a relativistically invariant way. If, for example, the electron is not regarded as the limit of a finite charge but as an "elementary particle" then it will not have self energy. The potential energy of a system is the result of the displacement of the system from some position, and obviously an elementary particle in free space cannot be regarded as displaced from any position. The

infinities arising from the self energy terms should therefore not appear.

One way of removing these classical singularities, which achieved some success, was the λ -limiting process of Dirac. In this, a "Hamiltonian" for each set of interacting particles is formed which is the same as the classical Hamiltonian except that the vector potential A is defined by

$$\underline{A}(x) = \frac{1}{2} \left\{ \underline{A}_c(x+\lambda) + \underline{A}_c(x-\lambda) \right\}$$

where \underline{A}_c is the classical vector potential and λ is a time-like 4-vector. At the end of the calculations λ is allowed to tend to zero and the same results are obtained as in the classical theory except that the classical singularities no longer appear. In the transition to the quantum theory this process is still consistent under certain restrictions. Further, on applying the perturbation theory to the resulting equations, the perturbation integrals are, with certain conventions of interpretation, convergent, and transition probabilities for all types of process can be calculated. Difficulties arise, however, in the physical interpretation:

- 1). The particle has negative as well as positive energy states,
- 2). If the particle has spin, negative states occur with negative probabilities,
- 3). When applied to photons the corresponding wave equations contain divergent integrals.

Another difficulty is that some of the calculated results have been proved wrong. The success of this process when dealing

with the classical singularities suggests, however, that a further modification of some other detail of classical relativistic theory may give further improvements.

One such modification can be made by the use of the "retarded" and "advanced" field potentials which occur in the classical theory. Electric and magnetic fields are propagated with a finite velocity c . Consider a charge moving through positions P_i creating a field at some point Q . The field at Q at a time t will be that due to the charge at a position P_i at time $t - \frac{r}{c}$ where r is the radius-vector between P_i and Q . If after leaving P_i the charge were to change its motion, the field at Q at the time t would be unaffected. Thus in the case of non-uniform motion it is better to describe the field at a time t in terms of its motion at a time $t - \frac{r}{c}$, called the retarded time, where r is the radius vector drawn from the retarded position P_i to the point of measurement Q . Maxwell's equations then give the retarded scalar potential ϕ_{ret} in terms of ρ ,

$$\phi_{ret} = \phi(x'y'z't') = \int \frac{\rho(xyzt)}{r} dx dy dz$$

in which $t = t' - \frac{r}{c}$ and r is the distance between the volume element $dx dy dz$ and the point $x'y'z'$. A similar formula gives the retarded vector potential A_{ret} in terms of \underline{I} . Consider now the general equation for the propagation of electromagnetic waves in an uncharged medium. It can be reduced to the form (ref.6)

$$\frac{1}{a^2} \frac{\partial^2 h}{\partial t^2} = \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{\partial h}{\partial r} \right)$$

which has the solution

$$\lambda = \frac{1}{r} [f(at-r) + g(at+r)]$$

where f and g are arbitrary functions representing two waves,

f diverging, and g converging. Classical theory neglects the term g representing the convergent waves, as having no physical significance, and defines $t_0 = t - \frac{r}{a}$ as the "retarded time", thence obtaining the retarded potentials. If instead

f were neglected, $t_1 = t + \frac{r}{a}$ could be regarded as an "advanced time" and corresponding "advanced potentials" obtained, although their physical significance would be somewhat obscure.

In his earlier work Dirac assumed that the retarded field would give the only physical interpretable solution. In view of some of the defects of the resulting equations it seemed worth while, however, trying to use the advanced field or perhaps a combination of the retarded and advanced fields. A brief comparison is given below between some results obtained by using retarded potentials alone and the corresponding results found by using a combination for the field of the electron of the form

$$F_{el} = F_{ret} + k [F_{ret} - F_{adv}] \text{ where } 2k+1 \text{ is negative (ref 7)}$$

A) Classical theory, using retarded potentials alone:

1) Dirac obtains the equations of motion of a free electron in the form

$$a \ddot{v}_\mu - \frac{d\dot{v}_\mu}{ds} - \dot{v}^2 v_\mu = 0$$

having the general solution

$$v_\mu = A_\mu \exp(Ce^{as}) + B_\mu \exp(-Ce^{as})$$

where $A_\mu, B_\mu + c$ are arbitrary except that $A_\mu^2 = B_\mu^2 = 0$, $[A, B] = \frac{1}{2}$. This solution corresponds to motion in which the velocity of the electron tends to the velocity of light and the electron loses energy rapidly by radiation. He concludes that the solution is non-physical. A particular solution is $v_\mu = c_\mu$ where $c_\mu c^\mu = 1$, giving motion in a straight line with uniform velocity. This is a possible physical solution, but it requires a knowledge of initial position and velocity and the final acceleration.

2) For an electron disturbed by a pulse of electromagnetic radiation passing over it the classical equation of motion may be expressed

$$a \frac{dv}{dt} - \frac{d^2x}{dt^2} = k \delta(t)$$

A particular solution is

$$\left. \begin{aligned} v &= \frac{k}{a} e^{at} & t < 0 \\ v &= \frac{k}{a} & t > 0 \end{aligned} \right\}$$

which corresponds to motion in which the electron is gradually building up acceleration before it meets the pulse. This contains an apparent contradiction to the ideas of causality in that the electron appears to anticipate the pulse. Dirac got round this by supposing that the electron behaved as though it had finite size, which implies, unfortunately, that it is possible for a signal to be transmitted faster than light through the interior of the electron.

3) In the classical picture of the hydrogen atom one would expect that, taking into account radiation damping, the electron

would spiral into the proton. The Lorentz-Dirac equations applied to this problem show that there may be no solutions corresponding to such spiralling motion. Even when an electron is moving directly towards the proton it would be brought to rest before it reached the proton and would eventually go off to infinity. Similarly two particles of unlike charges do not come into collision while two particles of like charges could possibly spiral inwards towards each other. The equations suggest that near a nucleus the Coulomb inverse square law of attraction is not true but there exists a repulsive force on the electron. This may be interpreted as the effect of radiation damping. When the electron is projected towards the nucleus it acquires an acceleration away from the nucleus due to radiation damping.

B) Classical theory, using a combination of retarded and advanced potentials of the form

$$F_{el} = F_{ret} + k [F_{ret} - F_{adv}] \quad \text{where } (2k+1) \text{ is negative.}$$

- 1) The equations of motion of a free electron have a general solution which shows that, whatever the initial conditions of projection of the electron, it quickly settles down to a uniform velocity, in contrast to Dirac's self acceleration. The solution only requires a knowledge of the initial velocity and acceleration.
- 2) The new equations for an electron disturbed by a pulse of electromagnetic radiation allow the velocity to be zero until $t=0$. The velocity then increases to a constant maximum

which agrees with that given by the previous result.

3) The new equations for the hydrogen atom allow the electron to fall into the nucleus by spiralling.

It seems surprising that a theory using advanced potentials, where therefore the physical mechanism is by no means clear, should lead to equations having physically understandable results while a theory using retarded potentials alone should give results which appear ~~satisfactory~~^{unsatisfactory}. However, the use of a combination of retarded and advanced potentials does appear to give in the cases considered, and in other problems, a picture more like the classical picture than the previous theory. It is worth proceeding to the quantum formulation, therefore, using these modified classical equations in Hamiltonian form, the classical infinities having been removed by the λ -limiting process. This is accomplished in the usual way, by replacing momenta by the appropriate Hermitian operators satisfying certain commutation relations, and then attempting a solution by perturbation methods. Again improved results are obtained in that some of the divergences of a purely quantum-mechanical nature no longer appear. For example the divergent terms in the theory of the interaction of hydrogen-like atoms with a radiation field are all eliminated. The general solution of the wave equation for an electron in a magnetic field still contains some divergent integrals but there is a particular solution, corresponding to outgoing waves of the electron, free from divergence to all orders of approximation in the perturbed theory.

However, considerable difficulties in physical interpretation appear. If the same method of physical interpretation is followed as in non-relativistic quantum theory, particles are found having negative energies. The negative energy states cannot be excluded because, even if initially the particle is in a state of positive energy, there exists the possibility of a quantum jump into a state of negative energy. Negative probabilities also appear.

An attempt to avoid the difficulty of negative energy states was made by Dirac in the formulation of his "Hole theory", which found substantial agreement with experiment (ref.1). He made two fundamental assumptions:

1) In the absence of an external field all negative energy states with energies ranging from $-\infty$ to $-\infty$ are filled up with electrons. No electron can therefore jump into one of these occupied states.

2) No external field is produced by this sea of electrons and they do not contribute to the total energy of the system.

A hole in the distribution of negative energy electrons will then appear to have a positive charge and positive energy. It will behave like an ordinary particle with electronic mass but with positive charge - a positron. Thus positrons are represented as holes in the sea of electrons filling the negative energy states. The possibility of a quantum jump into a state of negative energy can now be interpreted using the concept of creation or annihilation of positron - electron pairs. Consider a state in which there is initially no

particle present. An external field acting on the electrons in the negative energy states may cause a transition of one of these electrons with negative energy to a state with positive energy leaving a hole in the sea of negative energy electrons, i.e. leaving a positron-electron pair. Conversely if initially there is a positron-electron pair present, the electron can jump into the hole representing the positron and the pair is annihilated. A quantum jump into a state of negative energy is therefore interpreted as the annihilation of such a pair.

Such electronic particles with positive charge have, of course, been found experimentally. They can be created, together with a negative electron, by rapidly changing electron-magnetic fields, for example, in the collision of two fast particles.

Feymann suggests that this creation of electron-positron pairs is closely connected with the self energy problem. The expression for the total energy of a system must include terms representing the mutual interaction of a pair of charges. Similar terms representing the interaction of a charge with itself must also be included. "For under some circumstances what appears to be two distinct electrons may be viewed also as a single electron, namely, in the case when one electron was created in a pair with a positron destined to annihilate the other electron. Thus to the interaction between such electrons must correspond the possibility of the action of an electron on itself..... This interaction is the heart of the self energy problem."

(Feymann. Theory of positrons, Phys. Rev. Vol. 76 No.6).

The hole theory found substantial agreement with experiment but other difficulties were introduced by it. In the theory of particles with integral spin Pauli and Weisskopf were able to remove negative energies and negative probabilities by their process of "second quantisation". Operators of admission into or absorption from states were introduced. Then by replacing operators of admission into and absorption from negative energy states by operators of absorption from and emission into positive energy states respectively, the difficulty of negative energy states was removed. Again, this was partly successful, but solutions of the wave equations in series form still involved divergent integrals after the second term.

It appears therefore that although the above alterations of the classical equations have introduced considerable improvements, both in the elimination of some infinities and in the correlation between calculated and empirical results, every Hamiltonian containing interactions has so far given some divergent results and contained some features difficult to interpret. A possible explanation is that for such problems there may be no true Hamiltonian at all, or at least that the present methods of expression do not permit the correct formulation of such a Hamiltonian. Heisenberg (ref.8.) has suggested that this situation has arisen from the supposition that the correspondence between the classical equations and their quantum-theoretical analogue

should be close even at the shortest wavelengths, or, in the particle picture, at the shortest distances between the particles. This appears not to be so. From considerations of dimensions it is not possible to derive the mass of an elementary particle from the two universal constants \hbar and c . It is likely therefore that a third universal constant of dimensions of a length, (of the order of magnitude $l \sim 10^{-13}$ cm), will be required in any future theory of elementary particles. It will then be necessary to assume that the classical wave description and quantum theory based on it, as described above, will be limited to the description of phenomena in the analysis of which no linear dimensions occur less than or comparable with this universal length.

A further source of possible error is indicated by the experimental evidence that explosion processes occur, notably in cosmic radiation, in which many interpenetrating particles have been created in one single act. It seems therefore that all particles are related at high energies, and any theory not containing all particles, or their corresponding wave fields, simultaneously must necessarily fail at high energies. If, then, a Hamiltonian can be found to represent the whole group of elementary particles of a system, it will certainly not bear much resemblance to any of the Hamiltonians derived from a correspondence to classical pictures.

A new approach was therefore initiated by Heisenberg, (ref.8.) the aim of which was to create a frame sufficiently

wide for a consistent theory of atomic phenomena by limiting the description more explicitly to directly observable features. Such a concept as orbits would be rejected as unobservable and hence operationally meaningless. Assuming that the Hamiltonian will lose its predominate position, the problem is the specification of the new functions which will define atomic systems or, more generally, the quantities which will be observable in the new theory. For this specification Heisenberg defined his S-matrix, the elements of which were the amplitudes of the wave functions of the scattered or emitted particles (final state) for given momenta of the incident particles (initial state). The absolute square of these matrix elements would determine directly the observable cross-sections of scattering, emission and absorption processes. The S-matrix would represent the asymptotic behaviour of the wave function at large distances and would be directly connected with observable quantities only. Heisenberg did not, however, give any law or rule to determine the S-matrix mathematically in the region where the usual theory failed.

A more recent approach, however, while not setting out with the specific aim of finding such a matrix, obtains a quantity which satisfies the requirements exactly. This approach due to Tomonaga, Schwinger and Feynmann has achieved spectacular success in eliminating or circumventing the previous difficulties and in giving a complete set of rules for calculating each term in a series, equivalent to the

previous perturbation series, as a divergence-free expression (ref.9.) The question of calculating results to a higher order of approximation has acquired a more immediate importance in view of conclusive evidence that the Dirac wave equation does not give completely accurate results even for the simplest case - that of the hydrogen atom. Fine structure measurements on hydrogen as well as on deuterium and ionized helium have shown displacements in energy levels which imply the existence of a weak short range repulsive interaction between electron and proton. Further, experiments on the hyperfine structure of hydrogen and deuterium prove that the electron possesses a small additional spin moment. A provisional non-relativistic calculation lent support to the view that the most probable explanation would be found in higher order electrodynamic effects, but a completely relativistic treatment would be required to demonstrate that these higher order effects could account simultaneously for the two apparently unrelated deviations from the Dirac electron theory.

The success of the Tomonaga, Schwinger and Feynmann theories has been due mainly to their ability to express the wave equations of their systems in a relativistically invariant form. In the Schrödinger representation an essential property of the wave function ϕ is that, given the ϕ of a system at a particular time, the results of all measurements made on the system at that time are statistically determined. A relativistic system, however, requires a more general kind of

measurement than the simultaneous measurement of field quantities at different points of space, because it is possible to measure independently field quantities at different points of space at different times, provided that the points of space at which the measurements are made lie outside each others light cones. The Schrödinger representation is not, therefore, relativistically invariant. In particular, consider the total Hamiltonian $H(r)$ expressed as a function of the purely spatial coordinate \underline{r} . Write it in the form

$$H(r) = H_0(r) + H_1(r)$$

where $H_0(r)$ is the energy density of the free electro-magnetic and electron fields, and $H_1(r)$ is that of their interaction with each other and with any external disturbing forces that may be present. In Dirac's analysis $H_1(r)$ is expressed in terms of emission and absorption operators by the process of second quantisation and is put into a relativistically invariant form. An expression is obtained for $H_0(r)$ from the classical energy density $\frac{1}{8\pi} (\underline{E}^2 + \underline{H}^2) d\tau$. This appears as one term only in the invariant electromagnetic stress energy tensor and is therefore not itself invariant. The analysis is therefore based on Hamiltonian $H(r)$ which is not wholly relativistically invariant.

The new theory begins by defining a family of 3-dimensional surfaces σ_i which are space-like. Every pair of points on a particular surface σ_i is separated by a space-like interval and any two surfaces σ_i and σ_j are separated by

a time-like interval. σ_i cover all time from the infinite past to the infinite future. The Hamiltonian H for the total energy density of a system is now reformulated in terms of χ_0 , a point in space-time, whose coordinates are $(\mathbf{r}, t(\mathbf{r}))$. Again H is divided into the components

$$H(\chi_0) = H_1(\chi_0) + H_2(\chi_0)$$

A new wave function $\Psi(\sigma)$ is established which depends on σ and a "constant vector" Ψ_0 is defined by saying that "a system has a constant state vector" shall mean "a system consists of photons, electrons and positrons, travelling freely through space without interaction or external disturbance." It appears at once that $H_1(\chi_0)$ and $H_2(\chi_0)$ operating on $\Psi(\sigma)$ both give relativistically invariant equations.

An operator $U = U(\sigma)$ which is a function of $H_1(\chi_0)$ is defined by $\Psi(\sigma) = U(\sigma)\Psi_0$, where Ψ_0 is a constant vector. Then the operator $U(\infty)$, formed by taking σ in the infinite future is found to have matrix components corresponding only to real transitions of the system, that is, transitions which conserve energy and momentum. $U(\infty)$ is, in fact, identifiable with the Heisenberg S-matrix. Further, when it is expanded as a power series in H_1 , the use of a finite number of terms, neglecting higher terms, is the equivalent in the new theory to the use of perturbation methods in the older electrodynamics.

To avoid the difficulty of the infinite self energy of an electron the theory supposes that previous theories have been mistaken in trying to represent the observed electron,

together with its electromagnetic self-energy by a wave field with the same characteristic rest-mass as that of the "bare" electron. To allow for a difference between these two masses an arbitrary quantity δm is introduced, which, being an unobservable quantity, must not appear in the final description of observable phenomena. By a suitable choice of δm the self-energy effects are cancelled out. The mass is said to have been re-normalised. Thus again the divergence is eliminated by formal mathematical manipulation as in Dirac's λ -limiting process and the other methods of "extraction physics". This is unfortunate, since the theory as a whole cannot be put into a finally satisfactory form so long as these divergences occur in it, however skilfully they may be circumvented. Once more the treatment must be regarded as justified by its success in application rather than by its theoretical derivation. A measure of this success is indicated by calculations of Schwinger. Using a series derived from that of $U(\sigma)$ and taking the first three terms he calculated the second order radiative corrections to the equations of motion of an electron in an external field, and obtained satisfactory agreement with experimental results.

The infinite integrals arising in the phenomenon of vacuum polarisation are avoided by the process of "charge renormalisation". The terms denoting the effects of vacuum polarisation are found to be multiplied by certain factors k_1 and k_2 , which are divergent. It is believed that all

n^{th} order matrix elements will involve these factors only in the form of a multiplier $(\ell k_1 k_2)^n$. Now, the only possible experimental determination of ℓ is by means of measurements of the effects described by various matrix elements and the directly measured quantity will not be ℓ but $\ell k_1 k_2^{\frac{1}{2}}$. Therefore, in practice the letter ℓ is used to denote this measured quantity and the multipliers k no longer appear explicitly in the matrix elements. The effect is to replace the divergent factors k by unity and an unambiguous interpretation can then be given to the phenomenon of vacuum polarisation.

Using the renormalised expressions for mass and charge the theory is now able to give a complete set of rules for calculating each term in the series for $U^{(\infty)}$ as a divergence free expression which is a function of the observed mass m and the observed charge ℓ , of the electron, m and ℓ , being taken to have their empirical values. The divergent terms appearing in the series are irrelevant to the calculation of $U^{(\infty)}$ being absorbed in the unobservable constants δm and ℓ . The rules are divergence free and unambiguous. Thus, without using any fresh techniques, the theory has successfully arrived at an **S-matrix** $U^{(\infty)}$ from which the divergences which have previously been so troublesome, have been eliminated. This convergence of the integrals appears to be connected essentially with the fact that, in obtaining the rules, the electron and positron parts of the electron-positron field are never separated. That is, what amounts to a new physical hypothesis has been introduced,

namely that the electron-positron field always acts as a unit and not as a combination of two separate fields. A similar hypothesis is made for the electro-magnetic field, namely that this field also acts as a unit and not as a sum of one part representing photo emission and another part representing photo absorption. All the terms of $U^{(\infty)}$, when it is expanded as a power series in \hbar , can in theory be calculated to any required degree of accuracy, and those results which have been calculated have been in agreement with empirical results.

This method of procedure, and indeed all methods so far obtained for dealing with problems of quantum electro-dynamics, give results in the form of a power series in \hbar in which some of the coefficients may be zero. When the process of mass and charge renormalisation has been carried out, all the individual coefficients in the series are finite. If then, the series converges, its sum will represent a finite physical quantity. However, Dirac has shown quite generally that such a series cannot be convergent (ref.10.). The approach to the problems has been first to attempt to set up a definite wave of function Ψ . To do this a representation must be chosen. This is usually done by choosing as commuting variables the coordinates of the electrons with suitable spin variables for the electrons, and the numbers of the photons with particular momentum values and particular states of polarisation. The wave function is then expanded in the form

$$\Psi = \Psi_0 + \hbar \Psi_1 + \hbar^2 \Psi_2 + \hbar^3 \Psi_3 + \dots$$

and it is found that Ψ_2 and all the later terms in the series involve divergent integrals. In this procedure two arbitrary steps have been taken:

- 1) The choosing of the representation,
- 2) The assumption of the existence of a power series in ℓ .

By using a representation referring to other field variables, all such divergent integrals can be avoided and all the individual terms in the power series in ℓ become finite. However, the new power series representing the wave function is now found to be divergent, and Dirac has shown that this divergency is independent of any representation. The conclusion must be that, although the wave function may exist, it certainly cannot be represented exactly by a power series in ℓ . The difficulties seem to be essentially mathematical rather than physical. The series for $U(\infty)$ appears in the form of a power series in ℓ^2 and so will be divergent, even after renormalisation. A very rough numerical calculation has indicated, indeed, that successive terms in the series will decrease to a minimum and then increase again without limit.

$U(\infty)$ cannot therefore be a correct operator. That does not, however, prevent practical applications being made of the series using the first terms only. Such applications that have been made have given results in agreement with experiment to the limit of the accuracy of the experimental measurements. By taking sufficient terms a degree of accuracy

could be obtained far greater than anything at present required or even contemplated.

The present theory of electrodynamics is thus certainly incomplete and will remain so while it is necessary to remove the divergent integrals in such an arbitrary way and while the wave function is represented by a divergent series. This, however, is not so unfortunate as it might at first appear. Experimentally it is recognised that two types of phenomena occur, one type which is accurately in agreement with the present quantum electrodynamics, and another of which there is, as yet, no understanding. It is not possible to abandon completely the theory which accounts so well for the first type, and yet if this theory were complete and closed the second type would constitute a serious difficulty. The two possibilities present themselves:

1) The present theory will remain incomplete and sufficiently flexible to allow for the future inclusion of the phenomena not at present understood.

2) The difficulties will be cleared up and the present theory become closed. In this case a new theory, independent of but compatible with the present theory will have to be evolved to contain the remaining phenomena.

Of these two, the first is clearly the more desirable and the present approach seems to be following along these lines. The theory is certainly incomplete but, as shown by the agreement between calculation and observation, it is no

longer certainly incorrect.

BIBLIOGRAPHY:

- Ref.1. Dirac, "The principles of quantum mechanics"
(Oxford, New York, 1935)
2. Schiff, "Quantum mechanics"
(McGraw-Hill, 1949)
3. Wigner, "Gruppentheorie" und ihre Anwendung auf die
Quantenmechanik der Atomspektren"
(F.Vieweg, 1931)
4. Condon &
Shortley, "The theory of atomic spectra"
(C.U.P. 1935)
5. Heitler, "The quantum theory of radiation"
(O.U.P. 1944)
6. Jeans, "Electricity and magnetism"
(C.U.P. 1927)
7. Eliezer, Phys. Rev. Vol 71, 1947 (?)
8. Heisenberg, "The present situation in the theory of
elementary particles"
(C.U.P. 1949)
9. Dyson, Phys. Rev. Vol 75, Feb 1949. "Radiation Theories"
Phys. Rev. Vol. 85 No.4. "Divergence
of the perturbation theory in quantum
electro-dynamics."
Proc. Royal Soc., N1090 Vol.207 (1951)
10. Dirac Conference on fundamental particles,
1946.
(The difficulties in quantum electro-
dynamics."

