

QUANTUM MECHANICS

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(Notes by B. Hoffmann)

Delivered at Princeton University

October, 1931

# LECTURES ON QUANTUM MECHANICS

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Delivered at Princeton University, October, 1931.

In these lectures we shall deal with quantum mechanics from the point of view of general physics; we shall discuss the basic ideas and formalism of the subject and not the most convenient form of the working rules for particular applications; the lectures are for theoretical physicists as distinguished from mathematical physicists.

Formerly we used to think that the formalism of the Newtonian theory would, if pushed far enough, give all the results we wanted; but now we are introducing new formalisms - new ideas - into the scheme of physics; we are changing our axioms.

We shall begin by discussing the meanings of some of the words we shall use; it is not possible to give exact physical definitions of these words; we could, of course, give mathematical definitions, but these must then be supplemented by being given a physical significance. The first term we shall consider is :

A Dynamical System. This is a set of particles interacting according to a definite law of force; it is specified classically by means of a Hamiltonian function,  $H$ , which depends upon the position coordinates of each particle and the corresponding momenta. We shall see that it is possible to specify a dynamical system in the same way in the quantum theory.

State. There will be various possible motions of a given dynamical system, consistent with the laws of motion. We call these motions the states. We shall talk of a system as being in a given state; classically the state is specified if we know the values of the position coordinates and momenta of the particles of the system. It is to a certain extent arbitrary whether we talk of two different states of the same



functions of the time: they involve something that contains  $t$  as a parameter.

Observation. Classically we don't consider observations because the observation doesn't upset the system, but for systems involving very small masses we can't say this in general; there is a theoretical limit to the smallness of the disturbance caused by an observation and this is the point of departure of the quantum theory. The disturbance of the system that we get is connected with the fact that we don't have determinacy in the quantum theory; the disturbance is liable to alter the state of the system. We can only calculate probabilities of any given result being found as a result of an observation.

Observation. An observation often consists in measuring the value of a dynamical variable at some particular time. More generally, an observation consists in setting in motion any piece of apparatus such that a reading is taken which depends upon the state of the system; this definition makes an observation a relativistic concept.

Observable. An observable is what is measured when an observation is made; it is the value of a dynamical variable at a specified time, in the restricted sense, but it is actually a relativistic concept. An observable need not be capable of being measured directly by any apparatus; for example it is doubtful if the quantity

$$x(t) \cdot p_y(t),$$

pertaining to a given particle, could be measured in a single step, but it is nevertheless counted as an observable. An observable is really a more fundamental concept than a dynamical variable; it is to be used together with the four-dimensional meaning for a state, just as a dynamical variable is to be used with the 3-dimensional meaning.

Steady States. Steady states are those such that the probability of getting a given result is independent of the time at which the observation was made; it is only for unsteady states that the distinction here

between three-dimensional and four-dimensional states is necessary.

We now pass onto the formalism underlying the general scheme of quantum mechanics. The basic idea is the principle of superposition. In classical mechanics we have a superposition property - for a vibrating drum for example; this is because the differential equations are linear in the unknown quantities. In quantum mechanics we always have a superposition property.

Consider a single particle in two positions: we may consider this to be two states, A and B, say. Then what are we to mean by the state  $(c_1 A + c_2 B)$ ? The matter is elucidated by means of the indeterminacy of the theory; we only talk of probabilities. The idea of superposition was obtained only in a very roundabout way, but now we put it at the beginning of the subject. Before the observation the particle is partly in each place A and B but after the observation it is only in one of the places. This jump is typical of the quantum theory; we can only calculate the probability of finding the particle in either of the places A and B. We can deal with our states by general mathematical laws that apply whenever we have entities that combine additively to form new entities of the same type.

We take a complete set of independent states,  $\psi_1, \psi_2, \dots, \psi_n$ , and look on them as unit vectors in an n-dimensional space; any state is thus a vector in this space. It is only the direction of the vector that matters; this constitutes a real difference between the superposition properties of the quantum and classical mechanics; it does not hold, for example, in the case of the vibrating membrane. The vector zero doesn't count as a state at all in the quantum theory, unlike in the classical theory. For most practical examples n is infinite; the mathematical theory has not, however, been established rigorously for this case; we usually assume that theorems that hold for finite n will hold for infinite n if the result seems reasonable physically. We allow complex coefficients,  $c_i$ , in the quantum theory, but not in the classical theory.

Each  $\psi$  has a complex imaginary which we shall denote by  $\phi$ ; the relations between the  $\psi$ 's and the  $\phi$ 's is not quite the same as in the ordinary complex variable theory, since we cannot have  $\phi + \psi$ ; it is because of this that we cannot split up a  $\psi$  into its real and imaginary parts; in order to emphasize this difference we use  $\phi$  instead of  $\bar{\psi}$ ; we shall reserve the bar for ordinary complex quantities. We use the phrase conjugate imaginary to denote the relation between  $\psi_r$  and  $\phi_r$  and conjugate complex for that between  $a + ib$  and  $a - ib$ ,  $a$  and  $b$  being ordinary real numbers; the vector space is thus not a complex space in the ordinary sense. We don't try to express the  $\psi$ 's and  $\phi$ 's in terms of quantities previously known; we only require to know the rules of manipulation for them; we shall also need a physical interpretation for them.

We must be able to infer from equations involving the  $\psi$ 's and  $\phi$ 's some physical information, and conversely, we must be able to express physical information by means of conditions to be fulfilled by the  $\psi$ 's and  $\phi$ 's.

A typical calculation in quantum mechanics is as follows: we are given certain information concerning our system; by means of certain rules we are able to express this information in terms of conditions upon the  $\psi$ 's and  $\phi$ 's; then when the results of the mathematics have been obtained we apply our rules to the final equations to find their physical significance.

We now consider the multiplication of  $\phi$ 's and  $\psi$ 's. We allow  $\phi\psi$  to exist; it is analogous to the scalar product of two vectors. We do not allow such quantities as  $\phi\phi$  or  $\psi\psi$ ; we always write the  $\phi$  to the left of the  $\psi$  in a product  $\phi\psi$ ; this is, of course, not an axiom but merely a convenience.

We interpret  $\phi_r \psi_r$ , which is an ordinary number, to be the length of the vector  $\psi_r$ . It is usual to assume that  $\phi_r \psi_r = 1$ , this being merely a question of convenience; this process is called normalisation. When  $L$  is infinite it is not always possible to normalize in this way; we shall consider this point later.

All the preceding applies whether we consider three-dimensional or four-

dimensional states. For three-dimensional states we must, of course, have  $\phi_r \psi_r$  constant; this is actually the case, as we shall see, as a result of the equations of motion.

The fact that the  $\phi$ 's and  $\psi$ 's are conjugate imaginaries implies that if

$$\psi_0 = c_1 \psi_1 + c_2 \psi_2$$

then we require that

$$\phi_0 = \bar{c}_1 \phi_1 + \bar{c}_2 \phi_2,$$

and also that

$$\phi_a \psi_b = \overline{\phi_b \psi_a}$$

and that

$$\phi_a \psi_a \neq 0.$$

These are really further axioms and are easily shown to be consistent with one another; the last condition is necessary in order that we should be able to normalise our symbols.

If we have two different dynamical systems we can put them together and consider them as a single system; we require now to consider what happens to the corresponding  $\psi$ 's. We can put two systems together in two ways; in one way we just consider two distinct systems to be different states of one system; suppose that we have an  $n$ -dimensional vector space for one system and an  $m$ -dimensional vector space for the other, then the resultant system has an  $(n+m)$ -dimensional vector space, a vector in this space merely having the coordinates of the  $\psi$ 's of both original systems as coordinates. Another way of combining two systems is to consider them to exist side by side in the same space but without interacting; in this case the resultant system will have  $n.m$  independent states and  $n.m$  will therefore be the number of dimensions of its vector space; if the coordinates describing states of the two systems are  $a_r$  and  $b_s$  then the coordinates of a state of the resultant system will be  $a_r b_s$ . If there is physical interaction between the two systems the state of the resultant system will not be given by  $a_r b_s$  but the total number of states

of the resultant system will still be  $m_n$ . This problem of interaction has not yet been solved satisfactorily.

We now consider the properties of observables in the symbolical scheme of things; we shall consider the states in their four-dimensional significance. Observables are just linear operators that can operate upon the  $\psi$ 's and  $\phi$ 's; that is to say if  $\alpha$  be a linear operator then

$$\alpha(\psi_1 + \psi_2) = \alpha\psi_1 + \alpha\psi_2.$$

A particular example of an observable is just multiplication by an ordinary number; thus an ordinary number is to be considered as an observable; we shall discuss the physical significance of this number later. We can form the operation of addition of two observables as

$$(\alpha_1 + \alpha_2)\psi = \alpha_1\psi + \alpha_2\psi$$

and similarly for multiplication we write

$$(\alpha_1 \alpha_2)\psi = \alpha_1(\alpha_2\psi);$$

however

$$\alpha_1 \alpha_2 \psi \neq \alpha_2 \alpha_1 \psi$$

in general. The operators must also be able to operate on the  $\phi$ 's; when

$\alpha$  operates on  $\phi$  the resultant is written  $\phi\alpha$ ; we always write the  $\alpha$  to the right of the  $\phi$  but to the left of the  $\psi$ . We need one other axiom; we assume that

$$\phi_a(\alpha\psi_e) = (\phi_a\alpha)\psi_e,$$

and then we can write either of these quantities as  $\phi\alpha\psi$ .

We introduce a coordinate system in the vector space of our  $\psi$ 's, i.e. we take a set of orthogonal unit vectors in the  $\psi$ -space. The coefficients of the unit  $\psi$ 's when we express a given  $\psi$  linearly in terms of them will form an ordered set of numbers which we can write

$$\begin{bmatrix} a_1 \\ a_2 \\ \vdots \\ a_n \end{bmatrix}.$$

An operator  $\alpha$  will then become a square matrix and we operate by using matrix multiplication thus changing one  $\psi$  into another. A  $\phi$  becomes what is con-



veniently written as a horizontal array,

$$\overline{b_1, b_2, \dots, b_b}$$

and matrix multiplication still applies. The product  $\phi \alpha \psi$  is an ordinary number. The above completely represents all the properties of our symbolic algebra. We must consider the relations of conjugate complexes and of conjugate imaginaries; one problem is as follows; what is the conjugate imaginary of the product  $\alpha \psi_a$  ? It is first of all necessary to define the conjugate complex of an observable; we can do this in the symbolic algebra as follows:

$$\phi_r \bar{\alpha} \psi_s = \overline{\phi_s \alpha \psi_r}.$$

We can add  $\alpha$  and  $\bar{\alpha}$  so that we can separate an observable into its real and imaginary parts. In terms of matrices  $\bar{\alpha}$  is the Hermitean conjugate matrix of  $\alpha$ . We return to our problem of finding the conjugate of  $\alpha \psi_a$ ; we know that

$$\phi_b \alpha \psi_a = \overline{\phi_a \bar{\alpha} \psi_b}$$

and that

$$\phi_b \psi_c = \overline{\phi_c \psi_b};$$

hence if  $\psi_c = \alpha \psi_a$  we must have

$$\phi_c = \phi_a \bar{\alpha}$$

so that the conjugate complex of  $\alpha \psi_a$  is  $\phi_a \bar{\alpha}$ . Again what is the conjugate complex observable to the product  $\alpha_1 \alpha_2$  ? We have

$$\phi_a \alpha_1 \alpha_2 \psi_b = \overline{\phi_b \bar{\alpha}_1 \bar{\alpha}_2 \psi_a};$$

but the left hand side is the same as  $(\phi_a \alpha_1)(\alpha_2 \psi_b)$  and is therefore equal to  $\overline{\phi_b \bar{\alpha}_2 \bar{\alpha}_1 \psi_a}$ ;

hence we have

$$\overline{\alpha_1 \alpha_2} = \bar{\alpha}_2 \bar{\alpha}_1;$$

and then we easily see that

$$\bar{\alpha}_1 \bar{\alpha}_2 \bar{\alpha}_3 = \overline{\alpha_3 \alpha_2 \alpha_1},$$

and so on. In general

if we have any product of  $\phi$ 's,  $\alpha$ 's and  $\psi$ 's the conjugate complex or conjugate imaginary quantity is formed by reversing the order of the elements of the product and taking their conjugates. This completes the discussion of the formal properties of the  $\phi$ 's,  $\psi$ 's and  $\alpha$ 's. We must now

make certain rules or assumptions for the physical interpretation of our abstract formalism. The first assumption is the following:-----

We have a system in a given state and consider a certain observation to be made on this state. In general the result will not be determinate but there is a special case in which the result is certain; let the state be  $\psi$  and the observable being measured\* be  $\alpha$ ; when the result is certainly  $a$  we write

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\* This implies that the observable be real.

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$$\alpha \psi = a \psi$$

We say that  $\alpha$  has the value  $a$  for the state  $\psi$ . In classical theory we always use this way of speaking but in the quantum theory we can only use this way of speaking in the very special case in which there is certainty that our observable will have the given value. If we take  $\alpha$  to be an ordinary number, say  $c$ , we always have the equation

$$c \psi = c \psi$$

so that  $c$  is an observable of a very trivial kind, such that when we measure it we always get the same result,  $c$ , whatever the state of the system.

We can already deduce certain physical results;

If

$$\alpha_1 \psi = a_1 \psi$$

and

$$\alpha_2 \psi = a_2 \psi$$

then

$$(\alpha_1 + \alpha_2) \psi = (a_1 + a_2) \psi$$

so that  $\alpha_1 + \alpha_2$  has the value  $a_1 + a_2$ , and similarly we have that  $\alpha_1 \alpha_2$  has the value  $a_1 a_2$ . Again, suppose we have one observable,  $\alpha$ , and two states,

$\psi_1$  and  $\psi_2$ , such that

$$\alpha \psi_1 = a \psi_1$$

and

$$\alpha \psi_2 = a \psi_2 ;$$

then

$$\alpha (c_1 \psi_1 + c_2 \psi_2) = a (c_1 \psi_1 + c_2 \psi_2)$$

and this means that  $\alpha$  will have the value  $a$  for any state given by superposition of the original states for which it had the value  $a$ . This result is not so trivial as the previous one; let us consider it as applied to our former

example of a single particle which may be in either of two positions A and B. Let the two states be such that for each of them the particle is certainly in one position. If the two positions coincide our result implies that for any state obtained by the superposition of the two states the particle will also certainly be found in this position. We need a more general interpretation, however, of the <sup>a</sup>same generality as that of the classical theory. For any interpretation we must obtain pure numbers out of our theory. The general way of obtaining pure numbers is by means of products of the type  $\phi_r \alpha \psi_s$ ; this number refers to two different states which was not the case in the classical theory. We cannot give a direct physical significance to this number but we can to  $\phi_r \alpha \psi_r$ ; this number is quite definite if  $\phi_r \psi_r = 1$ . We cannot say that this number is the value of the observable  $\alpha$  for the state  $\psi_r$  as we can see as follows: let us take two observables  $\alpha_1$  and  $\alpha_2$ ; then the value of  $\alpha_1$  would be, according to this interpretation,

$$\phi \alpha_1 \psi = a_1 \quad (\text{say})$$

and the value of  $\alpha_2$  would be

$$\phi \alpha_2 \psi = a_2 \quad (\text{say});$$

the value of  $(\alpha_1 + \alpha_2)$  would then be given by

$$\phi (\alpha_1 + \alpha_2) \psi = a_1 + a_2$$

which is as it ought to be. But for the product we would expect

$$\phi \alpha_1 \alpha_2 \psi = a_1 a_2$$

whereas in general

$$\phi \alpha_1 \alpha_2 \psi \neq a_1 a_2$$

and thus we cannot look upon  $\phi \alpha \psi$  as the value of  $\alpha$  for the state  $\psi$ .

But we can regard it as the average value of  $\alpha$  for the state  $\psi$ . Thus

we assume that  $\phi_r \alpha \psi_r$  is the average value of  $\alpha$  for the state  $\psi_r$ .

~~Thus we assume that~~ ~~is the average value of~~ ~~for the state~~

This implies an indeterminacy. It should be verified that the assumption

that if

$$\alpha \psi_r = a \psi_r$$

then  $a$  is the value of  $\alpha$  for the state  $\psi_r$  and the assumption that  $\phi_r \propto \psi_r$  is the average value of  $\alpha$  for the state  $\psi_r$  are consistent; this is easily shown since we have

$$\phi_r \propto \psi_r = a \phi_r \psi_r = a.$$

We can actually deduce the first assumption from the second, as we shall show later. If we have a relation

$$\alpha \psi_r = a \psi_r,$$

the quantity  $a$  is called an eigenvalue of the observable for the state  $\psi_r$  and  $\psi_r$  is called an eigen- $\psi$ . If  $\alpha$  is a real observable then all its eigenvalues are real numbers, for

$$\phi_r \alpha \psi_r = a \phi_r \psi_r,$$

but  $\phi_r \psi_r$  is a real number, and  $\phi_r \alpha \psi_r$  is also a real number from the definition of a real observable, so that it follows that  $a$  is a real number.

Again two  $\psi$ 's belonging to two different eigenvalues of a given observable are orthogonal; for if

$$\alpha \psi_r = a_r \psi_r$$

and

$$\alpha \psi_s = a_s \psi_s$$

we have

$$\phi_s(\alpha \psi_r) = a_r \phi_s \psi_r$$

and

$$(\phi_s \alpha) \psi_r = a_s \phi_s \psi_r$$

and hence if  $a_r \neq a_s$  we must have  $\phi_s \psi_r = 0$  which means that  $\psi_s$  and  $\psi_r$  are orthogonal.

With the above material we can already work out certain examples; we shall, as an illustration, consider the problem that corresponds physically to that of the harmonic oscillator; stated abstractly we are given

$$W = \frac{1}{2}(p^2 + q^2)$$

and

$$q p - p q = i \hbar$$

and we require to find the possible eigenvalues of  $W$ . Suppose that  $W'$  is one of the eigenvalues of  $W$ , so that we have

$$1) \quad W \psi = W' \psi$$

Now

$$(p+iq)(p-iq) = p^2 + q^2 + i(qp - pq) \\ = 2W - \hbar$$

and

$$(p-iq)(p+iq) = 2W + \hbar ;$$

hence

$$(p-iq)(p+iq)(p-iq) = (p-iq)(2W - \hbar) \\ = (2W - \hbar)(p+iq)$$

and also

so that

$$(2W + \hbar)(p-iq) = (p-iq)(2W - \hbar)$$

or

$$(p-iq)(W - \hbar) = W(p-iq) ;$$

and in a similar manner we show that

$$(p+iq)(W + \hbar) = W(p+iq) .$$

We have, therefore,

$$W(p-iq)\psi = (p-iq)(W - \hbar)\psi \\ = (W' - \hbar)(p-iq)\psi \quad \text{by (1), and this}$$

shows that  $(W' - \hbar)$  is an eigenvalue of  $W$  for the eigen- $\psi/(p-iq)\psi$ .  
Hence if  $W'$  is an eigenvalue of  $W$  so are  $W' - \hbar$ ,  $W' - 2\hbar$  ... and so on. Again we can show in a similar way that

$$W(p+iq)\psi = (p+iq)(W + \hbar)\psi = (W' + \hbar)(p+iq)\psi$$

so that if  $\psi$  is an eigen- $\psi$  of  $W$  so also are  $W' + \hbar$ ,

$W' + 2\hbar$ , ... and so on. Now since  $p$  is a real operator the eigenvalues of  $p^2$  will be positive or zero, and similarly the eigenvalues of  $q^2$  will not be negative; hence the average value of  $W$  cannot be negative, and therefore the eigenvalues of  $W'$  cannot be negative, since an eigenvalue  $W'$  is always the average value for some state, namely the state for which

$$W\psi = W'\psi .$$

This conclusion doesn't fit in with our previous result which gave us negative eigenvalues; this is because we overlooked the possibility that

$$(p-iq)\psi \equiv 0 ;$$

in this case our argument could not proceed; it should run: if  $W'$  is an eigenvalue of  $W$  then so is  $(W' - \hbar)$  provided  $(\hbar - iq)\psi \neq 0$ . We must therefore look into the question of when  $(\hbar - iq)\psi$  vanishes identically; if

$$(\hbar - iq)\psi = 0$$

we have

$$(\hbar + iq)(\hbar - iq)\psi = 0$$

or

$$(2W - \hbar)\psi = 0$$

i.e.

$$(2W' - \hbar)\psi = 0$$

and hence, since  $\psi$  is by hypothesis, not zero, we must have

$$W' = \frac{1}{2} \hbar.$$

Hence our series of eigenvalues terminates at  $1/2 \hbar$  on the side of small  $W$ .

It is easily shown that  $(\hbar + iq)\psi$  cannot vanish, so that there is no limit to our series of eigenvalues on the side of large  $W$ . The eigenvalues are therefore

$$\frac{1}{2} \hbar, \frac{3}{2} \hbar, \frac{5}{2} \hbar, \dots \text{ to infinity.}$$

The above method appears to work rather by way of a fluke; it surprises us in just the same way that a proof in synthetic geometry surprises us; we can obtain a surer method in the quantum theory, just as in geometry we obtain a surer method by employing analysis, so that in more difficult problems we don't have to think out special tricks for each particular problem.

We shall require the theorem that any  $\psi$  can be expanded in terms of the eigen- $\psi$ 's of a given real operator. If the vector space is of a finite number of dimensions this is easily proved; but a rigorous proof for the case in which the number of dimensions is infinite doesn't appear to have been given. The difficulty lies in the fact that instead of  $\sum_n \psi_n$  we may sometimes have to use  $\int \psi_\hbar d\hbar$  and we should require a lot of new axioms about continuity, limits, and so on, which have not yet been formulated.

We can give an argument that makes the result appear plausible for the

kind of operators used in physics; suppose we consider the equation

$$(2) \quad \frac{\partial}{\partial \tau} \Psi_{\tau} = i \alpha \Psi_{\tau}$$

to have a solution determined when we know the initial value

$$(\Psi_{\tau})_{\tau=0} = \Psi_0;$$

We assume that  $\Psi_{\tau}$  can be expanded as a Fourier integral

$$\Psi_{\tau} = \int e^{i k \tau} \Psi_k d k;$$

substituting in (2) we get

$$\int i k e^{i k \tau} \Psi_k d k = i \alpha \int e^{i k \tau} \Psi_k d k$$

and equating coefficients we get

$$k \Psi_k = \alpha \Psi_k$$

so that  $\Psi_k$  is an eigen- $\Psi$  ~~belonging~~ belonging to the operator  $\alpha$ .

Setting  $\tau = 0$  we have

$$\Psi_0 = \int \Psi_k d k$$

which is the result we required. The weak point in the argument is the assumption of a Fourier integral expansion. For a real observable we can easily show that  $\frac{d}{d\tau} \Psi_{\tau}$  is constant so that the length of the vector doesn't increase <sup>to</sup> infinity as  $\tau$  increases and one possible cause of failure of the Fourier expansion is excluded. The equation (2) is just <sup>like the</sup> equation of motion of a system whose Hamiltonian operator is  $\alpha$  so that physically we should expect that a solution existed for any initial value of  $\Psi_{\tau}$ .

We can now give a general definition of a function of an observable; if we have an observable  $\alpha$  we can form  $\alpha^2$ ,  $\alpha^3$  and so on, and thus any function expressible as a power series; for functions that cannot be so expressed we give a general definition as follows:

Let  $f(x)$  be a single-valued function such that the domain of definition includes all those points which are eigenvalues of the observable  $\alpha$ ; then  $f(\alpha)$  will certainly have a meaning and we can therefore define  $f(\alpha) \Psi_k$  to be equal to  $f(a_k) \Psi_k$  which gives a meaning to  $f(\alpha)$  for every  $\Psi_k$ ; for a general  $\Psi$  we make use of the expansion theorem to express it in

terms of the

$\psi_r$ 's

as

$$\psi = \sum c_r \psi_r$$

and then we have

$$f(\alpha) \psi = \sum c_r f(\alpha_r) \psi_r,$$

so that  $f(\alpha)$  is now defined for any  $\psi$ . It should be noted that

the above only holds for real observables since we have employed the expansion theorem in the definition. We are thus now able to use functions of  $\alpha$

that are not expressible in terms of power series; we shall actually want

to employ such functions, for example  $\frac{1}{\alpha}$  and  $\alpha^{\frac{1}{2}}$ . In general an

observable has quite a number of square roots on account of the ambiguity

of sign of each  $(a_r)^{\frac{1}{2}}$  and to define a square root uniquely we must

state which signs are to be used.

Theorem. If  $\beta$  is such that

$$\beta \alpha = \alpha \beta$$

then

$$\beta f(\alpha) = f(\alpha) \beta.$$

This is obviously true if  $f(\alpha)$  is expressible as a power series; for

the general case we prove the theorem as follows:

Let

$$\alpha \psi_r = a_r \psi_r$$

and

$$\alpha \psi_q = a_q \psi_q,$$

where  $a_r$  and  $a_q$  may be equal. From the second we have

$$\phi_q \alpha = a_q \phi_q.$$

Thus

$$\phi_q \beta \alpha \psi_r = a_r \phi_q \beta \psi_r$$

and

$$\phi_q \alpha \beta \psi_r = a_q \phi_q \beta \psi_r$$

and hence, since  $\beta \alpha = \alpha \beta$ ,

either

$$a_r = a_q$$

or

$$\phi_q \beta \psi_r = 0,$$

that is, either

$$f(a_r) = f(a_q)$$

or

$$\phi_q \beta \psi_r = 0,$$

since our functions are always single-valued; thus we infer that



$$[f(a_r) - f(a_q)] \phi_q \beta \psi_r = 0.$$

We now have

$$\phi_q \beta f(\alpha) \psi_r = \phi_q \beta f(a_r) \psi_q$$

and also

$$\phi_q f(\alpha) \beta \psi_r = f(a_q) \phi_q \beta \psi_r$$

and hence

$$\phi_q [\beta f(\alpha) - f(\alpha) \beta] \psi_r = [f(a_r) - f(a_q)] \phi_q \beta \psi_r = 0,$$

and, since  $\phi_q$  and  $\psi_r$  are arbitrary, it follows that

$$\beta f(\alpha) - f(\alpha) \beta = 0$$

as was to be proved. We can also easily prove the converse theorem that if anything that commutes with  $\alpha$  also commutes with  $f$  then  $f$  is a function of  $\alpha$ . This doesn't mean that  $\alpha$  is necessarily also a function of  $f$  since a function is defined to be single-valued. We can use this property as a definition of a function and this would have its advantages since it doesn't use the expansion theorem.

Suppose we have two commuting observables  $\alpha$  and  $\beta$ ; then there exist certain  $\psi$ 's which are simultaneous eigen- $\psi$ 's of  $\alpha$  and  $\beta$  and moreover there are so many that any  $\psi$  can be expanded in terms of them; for, let

$$\alpha \psi_a = a \psi_a;$$

we can expand  $\psi_a$  in terms of the eigen- $\psi$ 's of  $\beta$  as, say,

$$\psi_a = \sum_b \psi_b;$$

then

$$\begin{aligned} \alpha f(\beta) \psi_a &= \alpha \sum_b f(\beta) \psi_b \\ &= \alpha \sum_b f(b) \psi_b; \end{aligned}$$

but also

$$\begin{aligned} \alpha f(\beta) \psi_a &= f(\beta) \alpha \psi_a \quad (\text{by the previous theorem}) \\ &= a f(\beta) \psi_a \\ &= a \sum_b f(\beta) \psi_b \\ &= a \sum_b f(b) \psi_b \end{aligned}$$

and hence

$$\alpha \sum_b f(b) \psi_b = a \sum_b f(b) \psi_b.$$

Now  $b$  will have as domain all the eigenvalues of  $\beta$  and  $f(\beta)$  will have a certain value for every point of this domain; therefore since  $f(b)$  is a

completely arbitrary function, we can equate the coefficients of each  $f(b)$  in the above, giving

$$\alpha \psi_k = a_{kk} \psi_k$$

so that  $\psi_k$  is an eigen- $\psi$  of  $\alpha$ . Hence every  $\psi$  in our expansion is a simultaneous eigen- $\psi$  of  $\alpha$  and  $\beta$ . This result can be extended to any number of commuting observables. A set of two or more observables that commute with each other may therefore be counted as a single observable; it is in this sense that we can count the position of a particle as a single observable, since the three cartesian coordinates commute with one another.

We shall now discuss representations in more detail; to get a representation we must find a system of independent  $\psi$ 's which satisfy

$$(3) \quad \phi_k \psi_q = \delta_{kq};$$

if  $\psi = \sum c_k \psi_k$  we then say that the coefficients,  $c_k$ , represent this  $\psi$ . Similarly if  $\phi = \sum b_k \phi_k$  the coefficients,  $b_k$ , represent  $\phi$ . If  $\phi$  and  $\psi$  are conjugate,  $\bar{c}_k = b_k$ .

Using (3) we have at once

$$c_k = \phi_k \psi$$

and  $b_k = \phi \psi_k$ .

The matrix elements of an observable,  $\alpha$ , may be obtained as follows: we have

$$\alpha \psi_k = \sum \psi_q a_{qk} \quad (\text{note the order of the suffixes in the coefficient})$$

and therefore

$$\phi_q \alpha \psi_k = a_{qk} \phi_q \psi_k$$

we see at once that if  $\alpha$  is real then  $a_{qp}$  is Hermitian. The diagonal elements are given by

$$a_{kk} = \phi_k \alpha \psi_k$$

which are the average values of  $\alpha$  for the states  $\psi_k$ ; this gives a physical significance to the diagonal elements of the matrix of an observable.

The question arises as to how we are to find a set of  $\psi$ 's that will serve as a base in the vector space. If we have an observable  $\alpha_1$  such that

there is only one eigen- $\psi$  belonging to each eigenvalue of  $\alpha_1$  we can take these eigen- $\psi$ 's as our basis, but if several  $\psi$ 's belong to the same eigenvalues it is best to take a set of observables,  $\alpha_2, \alpha_3, \dots, \alpha_n$ , that commute with  $\alpha_1$  and having the property that the simultaneous eigen- $\psi$ 's of the complete set of observables,  $\alpha_1, \alpha_2, \dots, \alpha_n$ , <sup>is</sup> such that only one belongs to each set of eigenvalues.

We shall use the following notation which is very convenient: we denote the eigenvalues of  $\alpha$  by  $\alpha', \alpha'', \alpha'''$  and so on; the simultaneous eigen- $\psi$ 's of  $\alpha_1, \alpha_2, \dots, \alpha_n$  may be written as  $\psi(\alpha'_1, \alpha'_2, \dots, \alpha'_n)$  and so on since there is just one corresponding to each set of eigenvalues. For the representative of any state we write  $(\alpha'_1, \alpha'_2, \alpha'_3, \dots |)$  or, for brevity,  $(\alpha' |)$ , so that we have

$$\psi_k = \sum_{\alpha'} \psi(\alpha') (\alpha' | k)$$

where we put the  $k$  in to the right of the vertical line to show that the representative belongs to  $\psi_k$ . We have also

$$\phi_k = \sum_{\alpha'} (k | \alpha') \phi(\alpha').$$

For an observable we write  $(\alpha' | \beta | \alpha'')$  and the equation that defines these matrix elements is

$$\beta \psi(\alpha') = \sum_{\alpha''} \psi(\alpha'') (\alpha'' | \beta | \alpha').$$

The symmetric way in which  $k$  and  $\alpha'$  enter the representatives of  $\psi_k$  and  $\phi_k$  will be justified later.

The question arises as to how an  $\alpha$  itself will be represented; we have in general

$$\mathcal{F} \psi(\alpha') = \sum_{\alpha''} \psi(\alpha'') (\alpha'' | \mathcal{F} | \alpha')$$

and if we put  $\mathcal{F} = \alpha_r$  we get

$$\alpha_r \psi(\alpha') = \sum_{\alpha''} \psi(\alpha'') (\alpha'' | \alpha_r | \alpha');$$

but

$$\alpha_r \psi(\alpha') = \alpha'_r \psi(\alpha')$$

so that we have the result ~~and~~ that

$$(\alpha'' | \alpha_r | \alpha') = \alpha'_r \delta_{\alpha' \alpha''};$$

that is, the representation employing the eigen- $\psi$ 's of  $\alpha$  as basic vectors is such that the  $\alpha$ 's are represented by diagonal matrices; the basic  $\psi$ 's are fixed by this property except for a factor of the form  $e^{i f(\alpha)}$  and this involves an uncertainty in the  $(\alpha' | )$ 's and the  $(\alpha' | f | \alpha'')$ 's, the latter being undetermined to the extent of a factor  $e^{[f(\alpha'') - f(\alpha')]}$ ; but in most problems we can ignore this indeterminacy. If we take a complete set of observables it will completely determine one representation, apart from these arbitrary factors of modulus unity, and any function of the  $\alpha$ 's will be represented in it by a diagonal matrix.

We can take a second set of commuting observables,  $\beta$ , and consider what is the connection between the representatives of the  $\psi$ 's etc. in the new and the old representations; we must have a linear relationship, for

$$\begin{aligned} \psi &= \sum_{\alpha'} \psi(\alpha') (\alpha' | ) \\ \text{and} \quad \psi &= \sum_{\beta'} \psi(\beta') (\beta' | ) \end{aligned}$$

so that, since

$$(4) \quad \psi(\alpha') = \sum_{\beta'} \psi(\beta') (\beta' | \alpha'),$$

this equation defining the coefficients  $(\beta' | \alpha')$ , we have

$$\psi = \sum_{\beta' \alpha'} \psi(\beta') (\beta' | \alpha') (\alpha' | )$$

and this gives the result that

$$(\beta' | ) = \sum_{\alpha'} (\beta' | \alpha') (\alpha' | ).$$

From equation (4) we can obtain an explicit expression for  $(\beta' | \alpha')$ , namely

$$(\beta' | \alpha') = \phi(\beta') \psi(\alpha') \quad . \quad \text{The quantities } (\beta' | \alpha') \text{ are called transfor-}$$

mation functions. There is a corresponding transformation for the repre-

sentatives of the  $\phi$ 's, namely

$$(1 \alpha') = \sum_{\beta'} (1 \beta') (\beta' | \alpha')$$

where it can easily be seen that this  $(\beta' | \alpha')$  is the same as the one

for the transformation of  $(\beta' | )$ . We also have the equation

$$(\alpha' | ) = \sum_{\beta'} (\alpha' | \beta') (\beta' | )$$

where  $(\alpha'|\beta')$  is a new transformation function which is the  $\beta$ -representative of  $\psi(\alpha')$  and is given by  $\phi(\alpha') \psi(\beta') = (\alpha'|\beta')$ ;

it thus is the conjugate complex of  $(\beta'|\alpha')$ . There are further relations between the  $(\alpha'|\beta')$  and  $(\beta'|\alpha')$  corresponding to the fact that the transformation is in the nature of a rotation in the vector space; for we have in fact

$$(\beta'|) = \sum_{\alpha'\beta''} (\beta'|\alpha')(\alpha'|\beta'')(\beta''|)$$

so that

$$\sum_{\alpha'} (\beta'|\alpha')(\alpha'|\beta'') = \delta_{\beta'\beta''};$$

and similarly

$$\sum_{\beta'} (\alpha'|\beta')(\beta'|\alpha'') = \delta_{\alpha'\alpha''}.$$

These relations express the conditions that if we regard the transformation functions as matrices they are reciprocal to each other; they are unitary matrices, i.e. matrices that satisfy  $S = S^{-1}$ , and the corresponding transformations are unitary transformations.

We have

$$\psi = \sum_{\alpha'} \psi(\alpha') (\alpha'|)$$

and the conjugate imaginary equation

$$\phi = \sum_{\alpha''} (|\alpha'') \phi(\alpha'');$$

so

$$\begin{aligned} \phi\psi &= \sum_{\alpha'\alpha''} \phi(\alpha'')(\alpha''|)(|\alpha')\psi(\alpha') \\ &= \sum_{\alpha'\alpha''} \delta_{\alpha'\alpha''} (\alpha''|)(|\alpha') \\ &= \sum_{\alpha'} |(\alpha'|)|^2; \end{aligned}$$

thus  $|(\alpha'|)|^2$  is invariant under these transformations. We can further show that

$$(\beta'|\xi|\beta'') = \sum_{\alpha'\alpha''} (\beta'|\alpha')(\alpha'|\xi|\alpha'')(\alpha''|\beta'').$$

We shall now discuss the physical meaning of these representatives;

they have one very important physical application; if  $\phi\psi = 1$  we can

say that  $|(\alpha'|)|^2$  is the probability that we shall get the result  $\alpha'$

when we observe the observable  $\alpha$ ; we prove this assertion as follows:

The average value of  $\alpha_r$  is  $\phi \alpha_r \psi$  and similarly the average value of any function  $f$  of the  $\alpha$ 's is  $\phi f(\alpha) \psi$ .

Now

$$\phi = \sum (1\alpha') \phi(\alpha')$$

and

$$\psi = \sum \psi(\alpha') (\alpha'|)$$

so

$$f(\alpha) \psi = \sum_{\alpha' \alpha''} \psi(\alpha'') (\alpha''| f | \alpha') (\alpha'|)$$

and therefore

$$\phi f \psi = \sum (1\alpha') (\alpha'| f | \alpha'') (\alpha''|) \dots$$

But

$$(\alpha'| f | \alpha'') = f(\alpha') \delta_{\alpha' \alpha''} \quad \text{so that}$$

$$\begin{aligned} \phi f \psi &= \sum_{\alpha'} (1\alpha') f(\alpha') (\alpha'|) \\ &= \sum_{\alpha'} f(\alpha') |(\alpha')|^2 \end{aligned}$$

Now suppose that  $P(\alpha')$  is the probability that the  $\alpha$ 's shall have the values  $\alpha'$ ; when the  $\alpha$ 's have the values  $\alpha'$   $f$  has the value

$f(\alpha')$  and hence

$$\sum_{\alpha'} P(\alpha') f(\alpha') \text{ is the average value of } f.$$

Hence we must have

$$\sum_{\alpha'} P(\alpha') f(\alpha') = \sum_{\alpha'} f(\alpha') |(\alpha')|^2$$

and since this must be true for arbitrary  $f$  we can equate coefficients of each  $f(\alpha')$  and that gives us

$$P(\alpha') = |(\alpha')|^2$$

which is the result we wanted to prove. It is the most frequently used connection between our mathematics and physics;  $(\alpha'|)$  is actually just the Schrödinger function.

We can now deduce the result that if  $\alpha \psi = \alpha' \psi$  then  $\alpha$  certainly has the value  $\alpha'$ ; we follow the usual method of determining the probability of  $\alpha$  having a specified value for the given state  $\psi$  by expanding  $\psi$  in terms of the eigen- $\psi$ 's of  $\alpha$ ; but here we shall only have one term in the expansion;

$$\psi = \psi(\alpha');$$

hence using our physical result we see that  $\alpha$  certainly has the value  $\alpha'$ .

If we take  $\psi$  to be one of the basic  $\psi$ 's of our second representation  $\beta$ , say  $\psi(\beta')$ , we have

$$\psi(\beta') = \sum_{\alpha'} \psi(\alpha') (\alpha'|\beta')$$

but  $(\alpha'|\beta')$  is just the representative of  $\psi(\alpha')$  <sup>in terms of  $\beta$</sup>  and hence  $P(\alpha') = |(\alpha'|\beta')|^2$ .

But  $\psi(\beta')$  is such that the  $\beta$ 's certainly have the values  $\beta'$  and so

$|(\alpha'|\beta')|^2$  is equal to the probability of getting the result  $\alpha'$  when

we make an observation of  $\alpha$  on the states for which the  $\beta$ 's certainly have the values  $\beta'$ . We have, of course,  $|(\alpha'|\beta')|^2 = |(\beta'|\alpha')|^2$  and this is a

reciprocal theorem which states that the probability of the  $\alpha$ 's having the values  $\alpha'$  when the  $\beta$ 's certainly have the values  $\beta'$  is the same

as the probability that the  $\beta$ 's will have the values  $\beta'$  when the  $\alpha$ 's certainly have the values  $\alpha'$ . On account of this property the  $(\alpha'|\beta')$

have been called by Jordan the probability amplitudes. We now see why we have

the symmetry between  $\alpha'$  and  $k$  in the representative  $(\alpha'|k)$  of  $\psi_k$

since  $(\alpha'|k)$  is symmetric in its physical interpretation between  $k$  and  $\alpha'$ ;

$(\alpha'|k)$  is in fact a transformation function to some representation in which  $\psi_k$  is one of the basic  $\psi$ 's.

We must, before leaving this subject, consider the procedure in the case in which we have a continuous range of eigenvalues of the  $\alpha$ 's. We can approximate to the case of a continuous range by considering a lot of eigenvalues lying very close together; we shall for simplicity consider only one observable,  $\alpha$ , and shall for the present preliminary discussion use

$\psi_{\alpha'}$ , etc. for its eigenvalues. We have the expansion

$$\psi = \sum_{\alpha'} \psi_{\alpha'} c_{\alpha'}$$

and if  $\psi$  is normalized

$$1 = \phi\psi = \sum_{\alpha'} |c_{\alpha'}|^2$$

so that as the number of eigenvalues increases the numbers  $c_{\alpha'}$  must get smaller. Let  $S_{\alpha'}$  be the density of the eigenvalues in the neighborhood of  $\alpha'$ , that is, let  $S_{\alpha'} d\alpha'$  be the number of eigenvalues

in the range  $\alpha'$  to  $\alpha' + d\alpha'$ ; then  $c_{\alpha'}$  is of the order of  $(S_{\alpha'})^{-\frac{1}{2}}$ ;

we can write the expansion for  $\psi$  roughly in the form of an integral as

$$\psi = \int c_{\alpha'} \psi_{\alpha'} s_{\alpha'} d\alpha'$$

and the coefficients of  $\psi_{\alpha'}$ , namely  $(c_{\alpha'} s_{\alpha'})$ , are now of the order

of  $(s_{\alpha'})^{\frac{1}{2}}$  so that they will become infinitely large as we approach the

limiting case of a continuous range of eigenvalues. We must therefore norma-

lize the  $\psi$ 's in a different manner so that they all become divided by

some infinitely large number; we shall require, in fact, that  $\phi_{\alpha'} \psi_{\alpha'} = O(s_{\alpha'})$ .

The choice of normalization process is arbitrary provided it satisfies this

condition but we can find the most convenient one for our purposes by a

consideration of the physical meaning of  $c_{\alpha'}$ ; we have seen that

$|c_{\alpha'}|^2$  is the probability that we shall get the result  $\alpha'$  when we

observe  $\alpha$  on the state  $\psi$ ; when we have a large number of

eigenvalues we are interested only in the probability of getting a result

in the range  $\alpha'$  to  $\alpha' + d\alpha'$  and not of getting a definite result;

let us call this probability  $P(\alpha') d\alpha'$  so that  $P(\alpha')$  will in general

be a finite number even in the limit; then in the limiting case we shall

want to express our normalized  $\psi$  as an integral of the form

$$\psi = \int \psi(\alpha') d\alpha' (x'')$$

where  $\psi(\alpha')$  is so normalized that

$$|\psi(\alpha')|^2 = P(\alpha') d\alpha',$$

$\psi$  being normalized in the usual manner,

$$\phi\psi = 1.$$

One way of determining the appropriate normalization would be to proceed to the

limit of the discontinuous case by straight calculation but we may obtain the

result we want in the following way;

We want  $|\psi(\alpha')|^2$  to be equal to the probability that  $\alpha$  have

a value in the range  $\alpha'$  to  $\alpha' + d\alpha'$  and therefore we want the average

value of  $f(\alpha)$  to be  $\int f(\alpha') |\psi(\alpha')|^2 d\alpha'$  which must consequently be



equal to  $\phi f(\alpha) \psi$ . Thus we have

$$\begin{aligned} \int f(\alpha') |\psi(\alpha')|^2 d\alpha' &= \phi f(\alpha) \psi \\ &= \int (1\alpha') d\alpha' \phi(\alpha') f(\alpha') \int \psi(\alpha'') d\alpha'' (\alpha'') \\ &= \int (1\alpha') d\alpha' \phi(\alpha') f(\alpha') \int \psi(\alpha'') d\alpha'' (\alpha''), \\ &\quad (\text{since } \phi(\alpha') f(\alpha) = \phi(\alpha') f(\alpha')); \end{aligned}$$

and since  $f(\alpha')$  is arbitrary we may equate coefficients of the  $f(\alpha')$  on both sides and get

$$|\psi(\alpha')|^2 = (1\alpha') \phi(\alpha') \int \psi(\alpha'') d\alpha'' (\alpha''),$$

or

$$(\alpha') = \int \phi(\alpha') \psi(\alpha'') d\alpha'' (\alpha''),$$

and this will be the normalizing condition for our basic  $\phi$ 's and  $\psi$ 's in the continuous case. This condition is to hold when  $(\alpha')$  is an arbitrary function and so we must have

$$\phi(\alpha') \psi(\alpha'') = 0 \quad \text{if } \alpha' \neq \alpha''$$

and then, since now

$$(\alpha') = \int \phi(\alpha') \psi(\alpha'') d\alpha'' (\alpha'')$$

we must further have

$$1 = \int \phi(\alpha') \psi(\alpha'') d\alpha''.$$

These two equations are the conditions governing our normalization; we can write them in one equation as

$$\phi(\alpha') \psi(\alpha'') = \delta(\alpha' - \alpha'')$$

where  $\delta(x)$  is an improper function such that

$$\delta(x) = 0 \quad \text{if } x \neq 0$$

and

$$\int_{-|a|}^{+|a|} \delta(x) dx = 1.$$

The introduction and use of this  $\delta$ -function has been known to cause a certain uneasiness among pure mathematicians! It can be regarded as an

abbreviated notation and does not make the mathematics non-rigorous since the argument can be written in full in a rigorous manner, as has been done by von Neumann. We should actually write the above normalization conditions as

$$\iint \psi(x') \psi(x'') dx' dx'' = (\text{the distance through which the domains of integration overlap}).$$

We cannot get along easily without using the  $\delta$ -function; for example it is necessary for the representation of the unit matrix as we shall show; it can easily be proved that the law of matrix multiplication becomes in the continuous case

$$(\alpha' | \xi | \alpha'') = \int (\alpha' | \xi | \alpha''') dx''' (\alpha''' | \eta | \alpha'')$$

and so, setting  $\xi = 1$  we have

$$(\alpha' | 1 | \alpha'') = \int (\alpha' | 1 | \alpha''') dx''' (\alpha''' | \eta | \alpha'')$$

so that

$$(\alpha' | 1 | \alpha''') = \delta(\alpha' - \alpha''').$$

If we want to find the representatives of  $\alpha$  we proceed as follows;

we have

$$\alpha \psi(\alpha') = \int \psi(\alpha'') dx'' (\alpha'' | \alpha | \alpha')$$

and

$$\alpha \psi(\alpha') = \alpha' \psi(\alpha')$$

so that

$$(\alpha'' | \alpha | \alpha') = \alpha' \delta(\alpha' - \alpha'')$$

Thus the  $\delta$ -function is necessary for writing down the elements of a diagonal matrix.

We see that the only difference between the formulae of the discrete case and the continuous case is that  $\delta(\alpha' - \alpha'')$  takes the place of  $\delta_{\alpha' \alpha''}$  and integrals are used instead of sums. The diagonal element is no longer, however, the average value of the observable for the corresponding state since our normalization is not the same as for the discrete case. The rule of

replacing  $\delta_{\alpha' \alpha''}$  by  $\delta(\alpha' - \alpha'')$  holds also for transformation functions; for

$$\int (\alpha' | \beta') d\beta' (\beta' | \alpha'') = \delta(\alpha' - \alpha'')$$

and

$$\int (\beta' | \alpha') d\alpha' (\alpha' | \beta'') = \delta(\beta' - \beta'').$$

We can also make a transformation from a continuous set of eigenvalues,  $\alpha'$ , to a discrete set,  $\beta'$ , in which case the above formulae become

$$\sum_{\beta'} (\alpha' | \beta') (\beta' | \alpha'') = \delta(\alpha' - \alpha'')$$

and

$$\int (\beta' | \alpha') d\alpha' (\alpha' | \beta'') = \delta_{\beta' \beta''},$$

and similar alterations must be made for the various other cases that may arise.

For the case of several commuting observables,  $\alpha_1, \alpha_2, \dots, \alpha_n$ , we require that

$|\langle \alpha' | \rangle|^2 d\alpha'_1 d\alpha'_2 \dots d\alpha'_n$  be equal to the probability that the  $\alpha_r$ 's have values in the ranges  $\alpha'_r$  to  $\alpha'_r + d\alpha'_r$ ; the formulae look exactly as before provided we use the  $\delta$ -function defined by

$$\delta(\alpha' - \alpha'') = \delta(\alpha'_1 - \alpha''_1) \delta(\alpha'_2 - \alpha''_2) \dots \delta(\alpha'_n - \alpha''_n)$$

and understand by  $d\alpha'$  the product  $d\alpha'_1 d\alpha'_2 \dots d\alpha'_n$ . The

normalizing condition  $\phi(\alpha') \psi(\alpha'') = \delta(\alpha' - \alpha'')$  was really chosen

artificially since we assumed that  $|\langle \alpha' | \rangle|^2$  was to be the probability

that  $\alpha$  have a value in the range  $\alpha'$  to  $\alpha' + d\alpha'$ ; it is possible to

introduce a weight function,  $p$ , and define  $|\langle \alpha' | \rangle|^2 p(\alpha') d\alpha'$

to be this probability; this is not really an essential generalization since

it only means that  $\langle \alpha' | \rangle$  becomes multiplied by  $p^{-\frac{1}{2}}$  and similarly  $\langle \alpha' | \rangle \langle \alpha'' |$

by  $\{p(\alpha') p(\alpha'')\}^{-\frac{1}{2}}$ , but it is convenient in certain cases, such as,

for example, when we have two angle variables  $\theta$  and  $\phi$ , it being here

convenient to use a weight factor  $\sin \theta$  so that the probability we obtain

from the formula  $|\langle \alpha' | \rangle|^2 \sin \theta d\theta d\phi$  refers to the element of solid angle.

When the weight function is employed we must alter the law of multiplication

to be

$$(\alpha' | \xi | \alpha'') = \int (\alpha' | \xi | \alpha''') \rho(\alpha''') d\alpha''' (\alpha''' | \eta | \alpha'')$$

and other formulae must be likewise modified.\* The cases we have considered may be generalized by allowing sums and products to occur together in the same formula; for example the equation for the representative of a  $\psi$  for an  $\alpha$  that has a discrete and continuous range of eigen-values is

$$\psi = \sum_k c_k \psi_k + \int \psi(\alpha') d\alpha' (\alpha' |)$$

and the representative of  $\psi$  consists of the continuous set of quantities  $(\alpha' |)$  together with the discrete set  $c_k$ .

. This concludes what we have to say about the general part of the theory.

We now have to come to the dynamical part of the quantum theory. We want to get the analogue of the equations of motion and the like that belong to the classical theory: questions of relativity will arise during the course of the discussion, but so far our theory is perfectly relativistic if we take the four dimensional <sup>view</sup> of a state; when we come to the equations of motion the question of relativistic invariance becomes important and no satisfactory relativistic theory for the general case has been given — the only special case for which a satisfactory theory is known being that of a single particle. Most of our work will be on a non-relativistic basis; we shall use, for example, the pre-relativity concept of instantaneous interaction between particles.

In the historical beginning of quantum mechanics we did everything by analogy with the classical theory, but now we don't look upon the classical theory as being so important but regard the quantum theory as being <sup>capable</sup> of standing by itself, we shall nevertheless first deal briefly with this analogy as it is very helpful.

The classical equations of motion may be written in the Hamiltonian form; we introduce a set of Lagrangian coordinates  $q_r$  and conjugate momenta  $p_r$  and then the Hamiltonian equations of motion are

$$\left. \begin{aligned} \dot{q}_r &= \frac{\partial H}{\partial p_r} \\ \dot{p}_r &= - \frac{\partial H}{\partial q_r} \end{aligned} \right\}.$$

It seems that it is only equations of motion that can be put into this form that have an analogue in the quantum theory. In the quantum theory we shall want a set of equations to replace the Hamiltonian equations and also we shall want some conditions to replace the classical condition that all our variables commute. In the classical theory we have a Poisson-bracket expression (P.B.), for two variables  $\xi$  and  $\eta$  given by

$$[\xi, \eta] = \sum_r \left( \frac{\partial \xi}{\partial q_r} \frac{\partial \eta}{\partial p_r} - \frac{\partial \xi}{\partial p_r} \frac{\partial \eta}{\partial q_r} \right)$$

and in the quantum theory we have the analogous expression

$$[\xi, \eta] = \frac{\xi \eta - \eta \xi}{i \hbar} \quad (\text{where } \hbar = \frac{h}{2\pi}).$$

We note that

$$[\xi_1 \xi_2, \eta] = [\xi_1, \eta] \xi_2 + \xi_1 [\xi_2, \eta]$$

in both cases. If we make the one assumption that  $\frac{\xi \eta - \eta \xi}{i \hbar}$  is the analogue of the classical B. P. of  $\xi$  and  $\eta$ , then the passage from the classical to the quantum theory presents no difficulties. We can express the classical equations of motion in terms of P. B.'s as

$$\left. \begin{aligned} \dot{q}_r &= [q_r, H] \\ \dot{p}_r &= [p_r, H] \end{aligned} \right\},$$

and in general we have

$$\dot{\xi} = [\xi, H].$$

For the commutation rules of the quantum theory we assume that the P. B.'s have the same values as in the corresponding classical case; we thus assume that

$$\left. \begin{aligned} [q_r, q_s] &= 0 \\ [p_r, p_s] &= 0 \\ [q_r, p_s] &= i\hbar \delta_{rs} \end{aligned} \right\}.$$

We may write all our equations now as

$$(5) \quad \left\{ \begin{aligned} q_r q_s - q_s q_r &= 0 \\ p_r p_s - p_s p_r &= 0 \\ q_r p_s - p_s q_r &= i\hbar \delta_{rs} \\ i\hbar \frac{\partial}{\partial t} \psi &= H \psi \end{aligned} \right. \quad \text{and}$$

the last corresponding to the equations of motion. These equations form the fundamental dynamical assumptions of the quantum theory for the class of problems for which there exists a classical analogue.

The P. B. in the quantum theory doesn't involve any reference to canonical variables and this shows one way in which the quantum theory will be more general than the classical since we may deal with systems in which our variables cannot be expressed in terms of canonical variables.

The first type of representation we think of is that for which all the  $q$ 's are diagonal; what are the representatives of the  $p$ 's in this representation? It can easily be shown that

$$p_r \rightarrow -i\hbar \frac{\partial}{\partial q_r}.$$

We can see how this fits in with the conditions (5) by applying the operators

$$-i\hbar \frac{\partial}{\partial q_r}$$

to the representative,  $(q|)$ , of any  $\psi$  and noticing

that the commutability relations, (5), hold. We can show conversely that if (5)

are assumed then  $p_r \rightarrow -i\hbar \frac{\partial}{\partial q_r}$  provided that we choose the phases of

the representation suitably. The result that  $p_r$  is represented by  $-i\hbar \frac{\partial}{\partial q_r}$

when  $q_r$  is diagonal is due to Schrödinger and is very important since it

gives us the most powerful analytical method that we have in the quantum theory.

Any function  $f(qp)$  now becomes a differential operator  $f(q, -i\hbar \frac{\partial}{\partial q})$  and if we

want the eigenvalues of  $f(qp)$  we have only to find the eigenvalues of a diffe-

rential operator for which problem there is an established technique. The

conditions (5) are symmetric in the p's and q's; it is usual to take the q's diagonal in preference to the p's since the q's have a more direct physical meaning; we could however take the p's to be diagonal and then we should have

$$q_i \rightarrow i\hbar \frac{\partial}{\partial p_i}$$

(we no longer get a minus sign), but this is not often convenient since H (which is the <sup>operator</sup> we are chiefly interested in) is a quadratic function of the p's but may be a general function of the q's.

It is sometimes desirable to make a transformation from the q's to the p's, when, for example, we are interested in the momenta rather than in the positions of the particles as in collision problems. The transformation function that connects the q's with the p's is easily found, from the equation of general transformation theory

$$\int (q' | \xi | q'') dq'' (q' | p') = \int (q' | p'') dp'' (p' | \xi | p'),$$

which gives, putting  $\xi = p$ , (taking the one dimensional case)

$$-i\hbar \frac{\partial}{\partial q'} (q' | p') = p' (q' | p')$$

so that

$$(q' | p') = k e^{iq'p'/\hbar}$$

The coefficient, k, is an arbitrary function of  $p'$  but its modulus is determined by the normalizing conditions to be  $1/\hbar^{1/2}$ , so that we have

$$(q' | p') = \frac{1}{\hbar^{1/2}} e^{iq'p'/\hbar}$$

(note that the normalizing factor involves ordinary h.)

when the correct phase is chosen. For the case of n variables we have

$$(q'_1 \dots q'_n | p'_1 \dots p'_n) = \frac{1}{\hbar^{n/2}} e^{i(q'_1 p'_1 + \dots + q'_n p'_n)/\hbar}$$

This result is much used and should be learned by heart

We shall now consider the way in which we could develop the quantum theory without reference to the classical theory; we wish to apply our quantum ideas to a physical system; let us consider a system and displace any state of it bodily in the direction of the x-axis through a distance  $\delta x$ ; this will give us a new state which is, of course, a physically possible one. We must similarly be able to give a meaning to the displacement of any observable;

if the apparatus used to find the value of the observable is moved through  $\delta x$  we say that it then measures the displaced observable. We now make one general physical assumption, we suppose that the various operations of addition, multiplication and so on which are used in the abstract quantum theory are invariant under such displacements; this is a very natural assumption since these operations express physical relations that are not dependent upon any frame of reference. Suppose we have any equation between states and observables such as  $\psi_2 = \alpha \psi_1$  for example; then if the result of applying our displacement to  $\psi_1$ ,  $\psi_2$  and  $\alpha$  is to yield  $\tilde{\psi}_1$ ,  $\tilde{\psi}_2$  and  $\tilde{\alpha}$  our assumption requires that  $\tilde{\psi}_2 = \tilde{\alpha} \tilde{\psi}_1$ . Similarly if  $\psi_1 = \psi_2 + \psi_3$  we require that  $\tilde{\psi}_1 = \tilde{\psi}_2 + \tilde{\psi}_3$  since the superposition relation is a real physical relation and doesn't involve a reference to a frame of reference. It should be realized that we are here dealing with the three-dimensional aspect of a state and the displacement is made on the state at one particular time. To proceed to build up a mathematical theory of these displacements we consider the infinitesimal displacements; the limit  $\lim_{\delta x \rightarrow 0} \frac{\tilde{\psi}_1 - \psi_1}{\delta x}$  will give us some  $\psi$ -symbol which we may call  $D_x \psi_1$ ; we first observe that

$$D_x (\psi_1 + \psi_2) = D_x \psi_1 + D_x \psi_2$$

which follows from our general physical assumption; this shows that  $D_x \psi_1$  is the result of a linear operation operating upon  $\psi_1$  and is therefore the product of an observable, which we may call  $d_x$ , with  $\psi_1$  so that we can write

$$D_x \psi_1 = d_x \psi_1.$$

We must look into one point before proceeding; if we displace our state is the new  $\psi$  quite a definite thing? The new state is certainly quite definite, but the new  $\psi$  may be multiplied by an arbitrary numerical factor so that  $\tilde{\psi}_1$  is not definite. If  $\phi_1 \psi_1 = c$  we must have  $\tilde{\phi}_1 \tilde{\psi}_1 = c$  and this fixed the length of  $\tilde{\psi}_1$  and so the uncertain numerical factor must be of modulus unity; thus  $\tilde{\psi}_1$  is uncertain to the extent of a factor of the form  $e^{iy}$ ; it follows that there will be an uncertainty in  $d_x$ . We must note that the uncertain factor  $e^{iy}$  must be the same for all  $\tilde{\psi}_1^x$ 's



and if it is chosen arbitrarily for one  $\tilde{\psi}$  it becomes determined for all the others, since if  $\psi_1 \rightarrow \tilde{\psi}_1$  and  $\psi_2 \rightarrow \tilde{\psi}_2$  we require that  $\psi_1 + \psi_2 \rightarrow \tilde{\psi}_1 + \tilde{\psi}_2$ .

We now calculate the effect this uncertain factor has upon the operator  $d_x$ ; let us take  $\tilde{\psi}_1 e^{iy}$  and write

$$\lim_{\delta x \rightarrow 0} \frac{\tilde{\psi}_1 e^{iy} - \psi_1}{\delta x} = D_x^* \psi_1 ;$$

now we must have  $\frac{y}{\delta x}$  approach a definite limit, a say, as  $\delta x \rightarrow 0$  since we require  $\psi_1$  to be changed in a continuous manner; we thus have

$$\begin{aligned} D_x^* \psi_1 &= \lim_{\delta x \rightarrow 0} \frac{\tilde{\psi}_1 (1 + iy + \dots) - \psi_1}{\delta x} \\ &= \lim_{\delta x \rightarrow 0} \left( \frac{\tilde{\psi}_1 - \psi_1}{\delta x} + \frac{iy}{\delta x} \tilde{\psi}_1 \right) \\ &= D_x \psi_1 + ia \psi_1 \end{aligned}$$

and hence we have the relation

$$d_x^* = d_x + ia,$$

showing that  $d_x$  is undefined to the extent of an arbitrary additive pure imaginary number.

We could equally well consider the operation of displacing the  $\phi$ 's; we should then write

$$D_x \phi = \lim_{\delta x \rightarrow 0} \frac{\tilde{\phi} - \phi}{\delta x} ;$$

let us take any two states  $\psi_1$  and  $\psi_2$  and form the product  $\phi_1 \psi_2$ ;

if we apply the displacement to this product it must remain invariant; hence we must have

$$\phi_1 \psi_2 = \tilde{\phi}_1 \tilde{\psi}_2$$

or

$$\begin{aligned} 0 &= \frac{\tilde{\phi}_1 \tilde{\psi}_2 - \phi_1 \psi_2}{\delta x} \\ &= \frac{(\tilde{\phi}_1 - \phi_1) \psi_2 + \phi_1 (\tilde{\psi}_2 - \psi_2)}{\delta x} \end{aligned}$$

and proceeding to the limit we get

$$0 = (D_x \phi_1) \psi_2 + \phi_1 (D_x \psi_2)$$

so that

$$\begin{aligned} (D_x \phi_1) \psi_2 &= -\phi_1 (D_x \psi_2) \\ &= -\phi_1 (d_x \psi_2) \\ &= -(\phi_1 d_x) \psi_2 \end{aligned}$$

and hence, since  $\psi_2$  is arbitrary,

$$D_x \phi_1 = -\phi_1 d_x ;$$

the minus sign is to be noted here in comparison with the relation  $D_x \psi_1 = d_x \psi_1$ . Now  $D_x \phi_1$  is the conjugate imaginary symbol to  $D_x \psi_1$  that is, to  $d_x \psi_1$ , and this conjugate imaginary is known to be  $\phi_1 \bar{d}_x$ , so that

$$-\phi_1 d_x = \phi_1 \bar{d}_x$$

or

$$d_x = -\bar{d}_x$$

showing that  $d_x$  is a pure imaginary observable.

We now consider the theory of the displacement of observables; the most interesting observable is  $x$  itself, the  $x$ -coordinate of the C-G of the system; if we have a piece of apparatus that measures  $x$  and we displace it a distance

$$\delta x \text{ it then measures } x - \delta x \text{ so that we must have } \tilde{x} = x - \delta x$$

from which it follows that  $D_x x = -1$ . Now suppose we displace the product  $x\psi$ ; we get

$$D_x (x\psi) = (D_x x) \psi + x (D_x \psi)$$

or

$$d_x x \psi = -\psi + x d_x \psi$$

so that

$$d_x x - x d_x = -1$$

which is a sort of quantum condition connecting  $d_x$  with  $x$ . We can by a similar argument show that

$$d_x y - y d_x = 0$$

and

$$d_x z - z d_x = 0$$

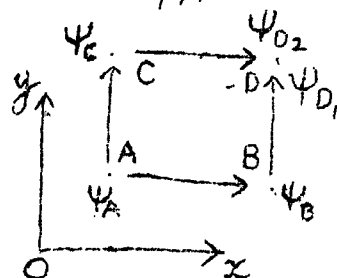
We should like also to find the quantum conditions that connect  $d_x$  with  $d_y$  the question is,

$$\text{is } D_x D_y \psi = D_y D_x \psi ?$$

At first sight this seems obviously true since displacement operations commute

but it is not actually obvious since we have the indeterminacy factor  $e^{iy}$  in the

$\Psi$ -symbols. Let us look into the matter more closely; we displace  $\Psi_A$  to get  $\Psi_B$  and choose the phase arbitrarily; we also displace  $\Psi_A$  to  $\Psi_C$  choosing an arbitrary phase; now, however our phases are fixed for the x and y displacements of any other states and thus we have no further arbitrariness in  $\Psi_B \longrightarrow \Psi_{D_1}$  and



$\Psi_C \longrightarrow \Psi_{D_2}$ . There is no theoretical reason why the two phases at  $D_1$  and  $D_2$  should be the same but in all systems considered so far in practice this has actually been the case.

If we take into account these changes of phase we no longer have

$$D_x D_y \Psi = D_y D_x \Psi \text{ but } (1 + \epsilon_y D_y)(1 + \delta x D_x) \Psi = e^{iy} (1 + \delta x D_x)(1 + \delta y D_y) \Psi$$

where  $y$  is a real number such that  $\frac{y}{\delta x \delta y}$  tends to a definite limit,  $a_z$  say: so

$$D_y D_x \Psi = D_x D_y \Psi + i \left( \frac{y}{\delta x \delta y} \right) \Psi$$

or

$$d_y d_x = d_x d_y + i a_z.$$

For all the applications of the quantum theory that have been considered up to the present  $a_z$  is zero. Let us write

$$p_x = i \hbar d_x;$$

then when  $a_z$  is zero we have

$$\left. \begin{aligned} p_x x - x p_x &= -i \hbar \\ p_x y - y p_x &= 0 \\ p_x z - z p_x &= 0 \end{aligned} \right\} \text{ etc.,}$$

and these are just the quantum conditions for momenta; hence  $i \hbar d_x$  may be defined as the components of the momentum, and this gives us a way of defining momentum without reference to the classical theory. We have been using the three-dimensional meaning of a state so that  $d_x$  must be regarded as a function of the time as a parameter; it is just a dynamical variable. If we have a system that is not acted upon by any external force we can show that  $d_x$  must be a constant; for, after a displacement the motion of the new state must be parallel that of the old and hence the four-dimensional state is displaced as a whole and  $d_x$  will not change in time; ~~hence~~ a system that is not acted upon by external forces has constant momentum.

We can develop a theory similar to the foregoing for rotation

runs closely parallel but differs in one respect, as we shall see; let  $\tilde{\psi}$  represent the state obtained by a bodily rotation of the state represented by  $\psi$  through a small angle  $\delta\theta$  about the x-axis; we introduce  $D_\xi$  by

$$\lim_{\delta\theta \rightarrow 0} \frac{\tilde{\psi} - \psi}{\delta\theta} = D_\xi \psi$$

and we have

$$D_\xi(\psi_1 + \psi_2) = D_\xi \psi_1 + D_\xi \psi_2$$

so that we can consider  $D_\xi \psi$  as the product of some observable with  $\psi$ ; we therefore write

$$D_\xi \psi = d_\xi \psi.$$

We find as in previous case that  $d_\xi$  is not absolutely definite the uncertainty consisting in the addition of an arbitrary pure imaginary number. We find that

$$D_\xi x = 0, D_\xi y = z \quad \text{and} \quad D_\xi z = -y$$

and these equations give

$$\left. \begin{aligned} d_\xi x - x d_\xi &= 0 \\ -d_\xi y - y d_\xi &= z \\ d_\xi z - z d_\xi &= -y \end{aligned} \right\} \text{ etc.}$$

We find also that

$$\left. \begin{aligned} d_\eta d_\xi - d_\xi d_\eta &= d_\xi + i a_\xi \\ d_\xi d_\xi - d_\xi d_\xi &= d_\eta + i a_\eta \\ d_\xi d_\eta - d_\eta d_\xi &= d_\xi + i a_\xi \end{aligned} \right\}$$

where  $a_\xi, a_\eta, a_\xi$  are real numbers which arise on account of the uncertainty of phase of the displaced  $\psi$ , like the  $a_z$  in the equation for

$d_x d_y - d_y d_x$ ; but if we write  $d_\xi^* = d_\xi + i a_\xi, d_\eta^* = d_\eta + i a_\eta, d_\xi^* = d_\xi + i a_\xi$ ,

these become

$$d_\eta^* d_\xi^* - d_\xi^* d_\eta^* = d_\xi^* \quad \text{etc.,}$$

so that these extra constants,  $a_\xi, a_\eta, a_\xi$ , don't make an essential generalization of the theory, although the corresponding constants of the linear displacement theory do.

Finally, we easily obtain the relations

$$\left. \begin{aligned} d_x d_x - d_x d_x &= i a_{11} \\ d_x d_y - d_y d_x &= d_z + i a_{12} \\ d_x d_z - d_z d_x &= -d_y + i a_{13} \end{aligned} \right\} \text{ etc.,}$$

there being nine arbitrary pure numbers  $a_{11}, \dots, a_{33}$ ; three of these may be absorbed in the  $d_x, d_y$  and  $d_z$  but the remaining six constitute an essential generalization of the theory. Once again, however, these  $a$ 's do not appear in the quantum theory as at present developed.

For the present lectures we shall assume that these arbitrary numbers are all zero.

Suppose we now write

$$m_x = i\hbar d_x, \quad m_y = i\hbar d_y, \quad m_z = i\hbar d_z;$$

then we have

$$\left. \begin{aligned} m_x x - x m_x &= 0 \\ m_x y - y m_x &= i\hbar z \\ m_x z - z m_x &= -i\hbar y \end{aligned} \right\} \text{ etc.,}$$

$$\left. \begin{aligned} m_x p_x - p_x m_x &= 0 \\ m_x p_y - p_y m_x &= i\hbar p_z \\ m_x p_z - p_z m_x &= -i\hbar p_y \end{aligned} \right\} \text{ etc.,}$$

and

$$m_x m_y - m_y m_x = i\hbar m_z, \quad \text{etc.,}$$

which are just the same as the commutation relations we would get for the angular momentum if we introduced it as  $m_x = y p_z - z p_y$  etc. by analogy with the classical theory. We have thus been able to introduce quantities that have the properties of momenta and angular momenta without any reference to classical analogy, and in fact our angular momenta are more general than that found from classical analogy as they allow the possibility of a spin.

We get certain properties that we would not expect from the <sup>1</sup>/<sub>classical</sub> analogy; for example, consider a state that is spherically symmetrical about the origin; we then must have no resultant angular momentum so that

$$m_x = m_y = m_z = 0.$$

But we also have the converse theorem; for if  $m_x = m_y = m_z = 0$  we must have  $D_x \psi = 0$  etc. so that  $\lim_{\delta\theta \rightarrow 0} \frac{\tilde{\psi} - \psi}{\delta\theta} = 0$  etc.,

and therefore rotation of this state about the origin can have no effect upon it, so that it is thus necessarily spherically symmetric.

It must be noted that the momenta and angular momenta that we have been discussing are the total momenta and angular momenta of the system; if we want to build up a complete mechanical theory we require to consider the momenta of the individual particles of the system under consideration but there is no satisfactory way, so far, of doing this except by analogy with the classical theory; the method of displacement operators is therefore incomplete.

We now consider the time-displacement operator; we take a three-dimensional section of a four-dimensional state and consider that state,  $\Psi$ , of the system that is exactly the same as the given one but at a time  $\delta t$  later; we define  $D_t \Psi$  to be  $\lim_{\delta t \rightarrow 0} \frac{\Psi - \Psi}{\delta t}$  and then write

$$D_t \Psi = d_t \Psi.$$

We can also give a meaning to  $D_t f$  where  $f$  is a dynamical variable; we write

$$D_t f = \lim_{\delta t \rightarrow 0} \frac{f - f}{\delta t};$$

but  $f$  is a function of the parameter  $t$  so that we may write it as  $f(t)$ ; then  $f$  is  $f(t + \delta t)$ , since we are now displacing the process of observation, and so

$$D_t f = \lim_{\delta t \rightarrow 0} \frac{f(t + \delta t) - f(t)}{\delta t} = \frac{df}{dt} \text{ or } \dot{f}.$$

In contrast this result with the corresponding result in the case of the space displacements where we get

$$D_x f = - \frac{\partial f}{\partial x} \text{ etc. ,}$$

which has a minus sign and moreover involves only partial derivatives; this shows us very clearly the non-relativistic character of our theory.

Suppose now we let  $D_t$  act upon the product  $f\Psi$ ; we then have

$$D_t (f\Psi) = (D_t f)\Psi + f(D_t \Psi)$$

or  
and so we get

$$d_t f\Psi = \dot{f}\Psi + f d_t \Psi$$

$$\dot{f} = d_t f - f d_t;$$

let us now write

$$-i\hbar d_t = H$$

and we get the result that

$$i\hbar \dot{\xi} = [H - H \xi].$$

This is just the equation of motion for the dynamical variable  $\xi$  that we obtained by analogy with the classical theory; this gives us the important result that the equations of motion for any system in the quantum theory must be of the above form whether the system have an analogy in the classical theory or not. The general system that we may deal with in the quantum theory will therefore be one for which we have any Hamiltonian function whatever depending upon any sort of set of dynamical variables.

We can furthermore discuss the equation of motion for  $\psi$  if we look upon  $\psi$  from the three-dimensional viewpoint; we have, by the definition of a derivative,

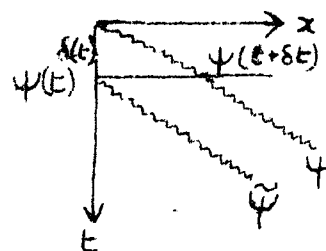
$$\frac{d\psi}{dt} = \lim_{\delta t \rightarrow 0} \frac{\psi(t+\delta t) - \psi(t)}{\delta t};$$

and reference to the figure, in which  $\tilde{\psi}$  is  $\psi$  displaced a time  $\delta t$ , shows that we therefore have

$$\frac{d\psi}{dt} = \lim_{\delta t \rightarrow 0} \frac{\psi - \tilde{\psi}}{\delta t} = -d_t \psi$$

so that

$$i\hbar \frac{d\psi}{dt} = H\psi.$$



This is one form of writing the Schrödinger wave equation; it

shows that we are to picture that the state of a system is a

three-dimensional vector in phase-space which varies with the time according to the

above equation, i.e. that this vector is continually undergoing a rotation. This is

not, however, the usual form of the Schrödinger wave equation; let us rather suppose

that we have a fixed vector referred to a moving set of coordinates in the phase-

space; we get this point of view if we adopt the four-dimensional meaning of a state;

we obtain our moving frame of reference by taking a representation in which the vari-

ables  $q/t$  are diagonal at the time  $t$ ; we have to choose the phases of the repre-

sentation in the proper way so that it doesn't involve explicit dependence upon  $t$ , or,

put in mathematical form, we must have  $(q'_t | \hat{H}_t | q''_t)$  independent of  $t$ . We now have the whole change with time put into the change in our representation; the equations of motion for the coordinates of the fixed vector referred to the moving representation will be <sup>of</sup> the same form as the above but written in the notation

$$i \hbar \frac{d}{dt} (q'_t |) = \int (q'_t | H | q''_t) dq''_t (q''_t |).$$

If we notice that  $(q'_t |)$  is a function of the  $n$  variables,  $q_{1t}, q_{2t}, \dots, q_{nt}$ , and therefore of the  $n+1$  variables,  $q_1, q_2, \dots, q_n, t$ , where  $q_1, \dots, q_n$  are no longer considered as depending on the variable  $t$ , and if we picture  $(q'_t |)$  in this way, the above is then the usual form of the Schrödinger wave equation. Since  $(q'_t |)$  is the representative of  $\psi$  it follows that  $|(q'_t |)|^2 dq'_t$  is the probability that the  $q$ 's have values in the range  $q'_t$  to  $q'_t + dq'_t$ .

Let us consider a dynamical system for which  $H$  doesn't involve  $t$  explicitly, i.e. for which there are no exterior forces varying with the time; then  $(q'_t | H | q''_t)$  doesn't involve  $t$  explicitly so that there are solutions of the Schrödinger equation of the form

$$(q'_t |) = (q' |) e^{-i H' t / \hbar}$$

where  $(q' |)$  is independent of the time and where we must have

$$H'(q' |) = \int (q' | H | q'') dq'' (q'' |);$$

this latter is the standard equation for determining the eigenvalues of  $H$  and hence when  $H$  doesn't involve  $t$  explicitly there exist solutions that are periodic in the time of the above form with  $H'$  an eigenvalue of  $H$ . This sort of state is such that the average value of an observable is independent of the time, for the average value of  $\int$  is given by

$$\iint (q' |) e^{i H' t / \hbar} dq' (q' | \int | q'' ) dq'' (q'' |) e^{-i H' t / \hbar}$$

and the exponents cancel each other so that this value is independent of the time.

It follows that the probability of getting any particular result when we make an observation is independent of the time, since the average value of any function of  $\int$  is independent of the time. Such a state is what we call a Stationary State.



Let us now see what theory of representation we get when we take the stationary states to be the basic states of the representation. There will be certain constants of the motion, i.e. certain observables,  $\alpha_t = f(q_t, p_t)$ , such that

$$\frac{d}{dt} \alpha_t = 0$$

or

$$\alpha_t H = H \alpha_t ;$$

let us take a representation for which these  $\alpha$ 's are represented by diagonal matrices; then the Hamiltonian must also be represented by a diagonal matrix so that

$$(\alpha'_t | H | \alpha''_t) = H' \delta_{\alpha'_t \alpha''_t}$$

where

$$H' = H(\alpha'_t).$$

There remains to be considered the question of how we are to choose the phases in this representation; we might choose them so that they don't involve the time explicitly and in this case the Schrödinger equation will hold in the new variables so that we shall have

$$i\hbar \frac{d}{dt} (\alpha'_t |) = \sum_{\alpha''_t} (\alpha'_t | H | \alpha''_t) (\alpha''_t |) \\ = H'(\alpha'_t |)$$

which gives, on integration,

$$(\alpha'_t |) = (\alpha'_t |)_0 e^{-iH't/\hbar}$$

where  $(\alpha'_t |)_0$  doesn't involve the time. Thus the representative of a state actually varies with the time in this representation.

This result suggests that we introduce a new representation which has different phases from the previous ones such that the representative of a state will not involve the time; we therefore take a new representative,  $(\alpha' |)$ , given by

$$(\alpha' |) = (\alpha'_t |) e^{iH't/\hbar}$$

so that this new representative of a state is a constant. We now have a particularly convenient representation to use—it is in fact a fixed system of coordinates in our vector space. If we have any dynamical variable,  $f_t$ , represented in this new representation by a matrix of the type  $(\alpha' | f_t | \alpha'')$  then

$$\frac{d}{dt} (\alpha' | f_t | \alpha'') = (\alpha' | \frac{df_t}{dt} | \alpha''),$$

which is just another way of expressing the condition that our axes in  $\psi$ -space are fixed. It is of interest to see how this matrix for  $f_t$  will vary with the time; we can calculate this in two ways; using the equations of motion,

$$i\hbar \dot{\xi}_t = \bar{\xi}_t H - H \xi_t,$$

so get

$$i\hbar \frac{d}{dt}(\alpha' | \xi | \alpha'') = (\alpha' | \xi | \alpha'') H'' - H'(\alpha' | \xi | \alpha'')$$

so that

$$(\alpha' | \xi | \alpha'') \propto e^{i(H' - H'')t/\hbar}$$

Another way of getting this result is simply to notice that in the  $(\alpha_t |)$ -representation we must have  $(\alpha'_t | \xi_t | \alpha''_t)$  independent of  $t$  and therefore when we make our change of phase we get just the above equation. Thus our matrix elements will vary with the time according to this equation. This representation was the first one to be found in the quantum theory; it was discovered by Heisenberg in 1925 as a result of a critical discussion of the Bohr theory.

Before leaving this question of equations of motion we wish to discuss the connection between quantum theory and classical theory for the most general dynamical system containing a Hamiltonian which involves the  $q$ 's and  $p$ 's with the only restriction that  $H$  shall be expressible as a power series in the  $p$ 's so that

$H(q, -i\hbar \frac{\partial}{\partial q})$  may be given a meaning; this matter has not been adequately discussed in the literature. We have the equation

$$i\hbar \frac{d}{dt}(q|) = H(q, -i\hbar \frac{\partial}{\partial q})(q|)$$

where we are dropping the primes from the  $q$ 's, which is permissible when this does not lead to confusion. Suppose we try to find a solution of this equation in the form of waves in the coordinate space; we assume that

$$(q|) = e^{iS/\hbar} A$$

where  $S$  and  $A$  are two real functions of the  $q$ 's and  $t$ . Now

$$i\hbar \frac{d}{dt}(q|) = e^{iS/\hbar} \left\{ -\frac{\partial S}{\partial t} + i\hbar \frac{\partial}{\partial t} \right\} A$$

and also

$$-i\hbar \frac{\partial}{\partial q_r}(q|) = e^{iS/\hbar} \left\{ \frac{\partial S}{\partial q_r} - i\hbar \frac{\partial}{\partial q_r} \right\} A$$

which gives

$$(-i\hbar \frac{\partial}{\partial q_r})^2(q|) = e^{iS/\hbar} \left\{ \frac{\partial S}{\partial q_r} - i\hbar \frac{\partial}{\partial q_r} \right\}^2 A$$

and in general

$$f(-i\hbar \frac{\partial}{\partial q_r})(q|) = e^{iS/\hbar} f(q, \frac{\partial S}{\partial q_r} - i\hbar \frac{\partial}{\partial q_r}) A;$$

so, substituting in our original equation we find

$$\left\{ -\frac{\partial S}{\partial t} + i\hbar \frac{\partial}{\partial t} \right\} A = H(q, \frac{\partial S}{\partial q_r} - i\hbar \frac{\partial}{\partial q_r}) A.$$

Thus far our work has been exact, we now make the approximation that  $\hbar$  may be counted as small and we then expand the right-hand side of the above equation by Taylor's theorem as a power series in  $\hbar$  up to the second term; if we equate the zeroth power of  $\hbar$  on each side we get

$$(6) \quad -\frac{\partial S}{\partial t} = H(q, \frac{\partial S}{\partial q})$$

which is just the Hamilton-Jacobi equation of classical mechanics.

Equating the coefficients of  $\hbar$  on each side we would be tempted to write

$$i\hbar \frac{\partial A}{\partial t} = \sum_r \frac{\partial H(q, \frac{\partial S}{\partial q})}{\partial (\frac{\partial S}{\partial q_r})} (-i\hbar \frac{\partial}{\partial q_r}) A$$

which could be the result we would obtain if  $(\frac{\partial S}{\partial q} - i\hbar \frac{\partial}{\partial q})$  were a number and not an operator; but actually the operator  $(-i\hbar \frac{\partial}{\partial q_r})$  will be somewhere in the middle of the factors in each term of  $H$ ; now  $H$  must be a real operator and this means that it must be possible to arrange the terms in it in such a way that the whole operator has symmetry with respect to right and left; i.e. the sort of symmetry exhibited in  $(q\hbar^2 + \hbar^2 q)$  or  $q\hbar^2 q$  so the result we should put down for our operator must be symmetric between left and right and if this symmetry exists it will be permissible (since we are neglecting terms in  $\hbar$ ) to take all the  $\frac{\partial}{\partial q}$ 's to the extreme left of one half of the terms and to the extreme right of the other half without altering the effect of the operator since the alteration caused by the leftward shifts will just balance that caused by the rightward shifts; to illustrate this whole process pictorially we have

$$m \frac{\partial}{\partial q} m = \frac{1}{2} \left( \frac{\partial}{\partial q} m m + m m \frac{\partial}{\partial q} \right).$$

Using this process we see that the equation resulting from equating the coefficients of  $\hbar$  on either side of our original equation must actually be

$$\begin{aligned} -\frac{\partial A}{\partial t} &= \frac{1}{2} \sum_r \left\{ \frac{\partial}{\partial q_r} \frac{\partial H(q, \frac{\partial S}{\partial q})}{\partial (\frac{\partial S}{\partial q_r})} + \frac{\partial H(q, \frac{\partial S}{\partial q})}{\partial (\frac{\partial S}{\partial q_r})} \frac{\partial}{\partial q_r} \right\} A \\ &= \sum_r \left\{ \frac{\partial H(q, \frac{\partial S}{\partial q})}{\partial (\frac{\partial S}{\partial q_r})} \frac{\partial A}{\partial q_r} + \frac{1}{2} A \frac{\partial}{\partial q_r} \frac{\partial H(q, \frac{\partial S}{\partial q})}{\partial (\frac{\partial S}{\partial q_r})} \right\}, \end{aligned}$$

or, multiplying by  $2A$ ,

$$(7) \quad -\frac{dA^2}{dt} = \sum_r \frac{\partial}{\partial q_r} \left\{ \frac{\partial H(q, \frac{\partial S}{\partial q})}{\partial (\frac{\partial S}{\partial q_r})} \cdot A^2 \right\};$$

this, then, is the equation which governs the amplitude,  $A$ , of our wave functions; we wish to get a physical picture of this equation and for this purpose we take a coordinate space,  $(q)$ , and suppose that there is a fluid moving in it such that its

$$\text{Density} = A^2$$

and its

$$q_r\text{-component of current} = \frac{\partial H(q, \frac{\partial S}{\partial q})}{\partial (\frac{\partial S}{\partial q_r})} A^2.$$

Then equation (7) gives just the conservation of this fluid. So we have this fluid moving about in  $q$ -space according to the conservation equation but with no other limitations. Let us take a fixed  $S$  satisfying the first equation and consider that

$A$ 's will then satisfy the second; the velocity of the fluid is then fixed, namely its  $q_r$ -component has the value

$$\frac{\partial H(q, \frac{\partial S}{\partial q})}{\partial (\frac{\partial S}{\partial q_r})}.$$

One possible solution will be the following; we suppose that initially the density vanishes everywhere except in a small region; then, on account of the equation of continuity and the definite velocity, at a later time we shall still

have the density vanishing everywhere except within a small region; this solution is in the nature of a wave packet. There is a limit to how small this region may

be taken since we have made approximations in obtaining our two equations, (6) and

$$(7); \text{ we must have, in fact, } \hbar \frac{\partial}{\partial q} A \ll \frac{\partial S}{\partial q} A,$$

and this condition says that  $A$  must change by an appreciable fraction of itself

only in a distance of several wavelengths. The motion of the wave packet is given

$$\text{by} \quad \text{velocity} = \frac{\partial H(q, \frac{\partial S}{\partial q})}{\partial (\frac{\partial S}{\partial q_r})}$$

and this is just equal to the classical velocity of the particle since the classical formula is

$$\dot{q}_r = \frac{\partial H(q, p)}{\partial p_r};$$

this shows that the wave packet moves according to the same law as given by the trajectory of the classical theory and indicates the way in which the classical theory is to be regarded as a limiting case of the quantum theory for such systems as we have discussed in this section; the limitation upon the smallness of a wave packet leads at once to the Heisenberg Principle of Uncertainty.

This concludes our discussion of the general equations of motion and of the general quantum theory; we shall omit reference to the elementary systems that arise in the applications of the theory and shall proceed directly to more advanced questions.

We shall consider those special properties that arise when we have systems that consist of similar particles. Let us first consider the case of only two similar particles; we have discussed in a general way how we can put two systems together and count them as a single system and two methods were given; the first method, to which we shall refer as method (a), applied when the two systems were considered as alternatives and involved addition of the vector spaces, whilst the second method, method (b), applied when the two systems were both present together and involved multiplication of the vector spaces. When the systems are physically of the same nature method (a) is quite trivial and it is only method (b) that is of physical interest; and if the systems interact we must use method (b).

We shall first of all examine the mathematics of method (b) when there is no interaction, taking the general case when the two systems are not necessarily similar. We shall have a set of dynamical variables,  $\{f_1\}$ , to describe the first system and a set,  $\{f_2\}$ , to describe the second, and we shall require that

$$\mathfrak{F}_1 \mathfrak{F}_2 - \mathfrak{F}_2 \mathfrak{F}_1 = 0$$

as the conditions that the two systems be different (even in the case of interacting systems). The first system will have a Hamiltonian function,  $H_1(\mathfrak{F}_1)$ , depending upon the  $\mathfrak{F}_1$ 's and the second system will have  $H_2(\mathfrak{F}_2)$  as its Hamiltonian. The equations of motion of the individual systems will be

$$\left. \begin{aligned} i\hbar \dot{\mathfrak{F}}_1 &= \mathfrak{F}_1 H_1 - H_1 \mathfrak{F}_1 \\ \text{and } i\hbar \dot{\mathfrak{F}}_2 &= \mathfrak{F}_2 H_2 - H_2 \mathfrak{F}_2 \end{aligned} \right\}$$

We now want to put these two systems together and leave unchanged these equations of motion; we have, since  $\mathfrak{F}_1$  and  $\mathfrak{F}_2$  commute,

$$\left. \begin{aligned} i\hbar \dot{\mathfrak{F}}_1 &= \mathfrak{F}_1 H - H \mathfrak{F}_1 \\ \text{and } i\hbar \dot{\mathfrak{F}}_2 &= \mathfrak{F}_2 H - H \mathfrak{F}_2 \end{aligned} \right\}$$

where

$$H = H_1 + H_2,$$

so that so far as the equations of motion are concerned we merely have to add the two Hamiltonians of the systems when we put them together.

Let us now see what happens to the Schrödinger equation; we want a representation for the two systems and for this purpose we take a complete set of commuting observables,  $q_1$ , out of the observables  $\mathfrak{F}_1$  and a complete set,  $q_2$ , out of the  $\mathfrak{F}_2$  and then, since they commute, we can consider a representation for the whole system such that the  $q_1$ 's and the  $q_2$ 's are diagonal; this corresponds to multiplication of the vector spaces. The wave equation for the first system by itself is

$$i\hbar \frac{\partial}{\partial t} (q_1' |) = \int (q_1' | H_1 | q_1'') dq_1'' (q_1'' |)$$

and for the second system it is

$$i\hbar \frac{\partial}{\partial t} (q_2' |) = \int (q_2' | H_2 | q_2'') dq_2'' (q_2'' |),$$

the matrices above referring to the representatives of the two systems taken separately. As the representative of  $H_1$  in the  $q_1 q_2$  representation we must have

$$(q_1' q_2' | H_1 | q_1'' q_2'') = (q_1' | H_1 | q_1'') \delta(q_2' - q_2'')$$

and similarly for  $H_2$  we must have

$$(q_1' q_2' | H_2 | q_1'' q_2'') = (q_2' | H_2 | q_2'') \delta(q_1' - q_1''),$$

and with the help of these equations we can easily verify the result that

$$i\hbar \frac{\partial}{\partial t} [(q_1' |)(q_2' |)] = \int (q_1' q_2' | H | q_1'' q_2'') dq_1'' dq_2'' (q_1'' |)(q_2'' |),$$

where this  $H$  is  $H_1 + H_2$ . These equations show that the Schrödinger equation holds for the resulting system if we add the Hamiltonians of the original systems and multiply their vector spaces. This result is not really a trivial one; there is no obvious reason why two wave equations should be combined in just this manner; the reason why it does fit in this way is that the Schrödinger equation was derived from a consideration of displacements which is a general method based on group theory considerations of space and time and it must therefore agree with those subsidiary conditions that may further be found necessary; it is essential, in order that this way of putting two systems together should work, that the wave equation be linear in the operator  $\frac{\partial}{\partial t}$ .

There is one important modification that may arise; we may consider in our resulting system only those states for which a special condition such as

$$F\psi = 0$$

holds. This is a very important case in the applications. Let us consider it both from the mathematical and the physical point of view; from the mathematical point of view it means taking a subspace from our total vector space; it is necessary that this subspace remain invariant under the equations of motion if we are to get anything of physical interest; that is to say we take  $\psi$ 's that move according to the law

$$i\hbar \frac{d\psi}{dt} = H\psi$$

and if  $\psi$  lies in the subspace initially it must remain in it; the condition for this is that

if

$$F\psi = 0$$

then

$$F \frac{d\psi}{dt} = 0;$$

we get at once from the second that

$$FH\psi = 0$$

and therefore we must have

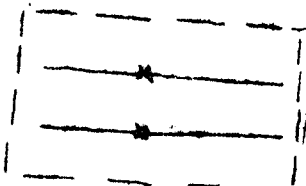
$$(FM - HF)\psi = 0$$

and this usually means that we must have

$$FH - HF = 0$$

when we come to the applications of the theory. So this special way of combining two systems to form a single system is possible whenever we can find some observable,  $F$ , that commutes with  $H$ .

What does this mean physically? It means that there is some kind of coupling between the two systems, but of a nature quite different from that one usually gets from the ordinary forces that act between them; there is thus some kind of constraint between the two systems, but one which is not expressible as a force of interaction and does not conflict with their equations of motion. As an illustration we may take two particles moving each in a one-dimensional domain as shown and consider that the top one must always be vertically above the lower one. Our constraint is to be pictured as of this kind;



it is of great importance in the case of similar particles. From the physical point of view it might be convenient to consider that we have forces, and these constraints are often spoken of as such, but we must remember that mathematically they are quite different from the ordinary forces that arise from an interaction energy.

The above theory applies when we have more than two systems; according to method (b) we have

$$H = H_1 + H_2 + \dots + H_n,$$

where  $H_1, \dots, H_n$  are the Hamiltonians of the original systems.



We shall now discuss special conditions that arise when the systems we put together are all of a similar nature, such as all electrons or all light quanta, and so on. It then becomes necessary to reconsider what we mean by an observable; we have several similar particles which are described individually by observables,  $f_1, f_2, f_3, \dots$ , and so on. If we interchange two of the particles we make no physically observable change and hence we ought not to talk of the  $f$ 's individually as observables; but we can still talk of the probability of a particle being in a given region of space or not; or of two particles being simultaneously in two given regions, and so on, and it is with this different type of observable that we shall have to deal; we might also ask how many particles have a given value for their momentum, or more generally we may take any set of commuting observables,  $q$ , and ask whether there exist particles for which the  $q$ 's have the values  $q'$ , and we can, of course, consider more complicated observables of this nature. What is the general mathematical property of all such quantities? It is plainly that the quantity must be symmetrical <sup>in the</sup> variables of the particles. A particular type of symmetrical function of the  $f$ 's could be the following:

Let us take  $x_r$  to be any variable referring to one of the dynamical systems and let us form  $\sum_{r=1}^n x_r$ , that is, the total value of the variable  $x$  summed for all the systems; this is one of the things we can observe. There are also more complicated things of the type  $\sum_{r \neq s} x_r x_s$  and so on but the  $\sum x_r$  are the most important. If we know the average value of  $\sum x, \sum x^2, \sum x^3, \dots$ , and generally of  $\sum f(x)$ , where  $f$  is an arbitrary function of  $x$ , then we shall know the average number of particles having  $x$  equal to any specified value, and the average number of particles in a small volume of space is a quantity of this nature; it follows by a similar argument that if we know the average values of all quantities of the type  $\sum_{r \neq s} x_r x_s$  we shall know the average number of times two particles exist simultaneously in two specified small regions of space.

We must now develop some mathematical theory that will enable us to deal with observables of the type  $\sum x_r$ ; this theory will be analogous to the theory of the Gibbs Ensemble in classical statistical mechanics. We can build up the theory in the following way;

We can choose the  $q$ 's of our representation in a symmetrical way with respect to the particles and we shall then get a representation that is symmetric with respect to all the particles; each particle will be represented by a wave function,

$(q'/1)$  , and we shall assume for convenience in talking that the  $q'$ 's form a discrete set. Suppose we take an  $x$  and ask what is the average value of  $x$  for one of the particles; this average value will, of course, be

$$\sum_{q', q''} (1/q') (q'/x/q'') (q''/1);$$

we now put all the systems together and ask what is the average total value of  $x$  for all the systems; it must, of course, be given by

$$\sum_{q', q''} \sum_r (r/q') (q'/x/q'') (q''/r),$$

where  $(q/r)$  is the wave function for the  $r$ -th system; now we can take  $(q'/x/q'')$  outside the summation with respect to  $r$  since the operators  $x$  are homologous, and we then get the result that the average total value of  $x$  for all the systems is given by

$$\sum_{q', q''} (q'/x/q'') \sum_r (q''/r) (r/q').$$

It follows that all we want to know about the assembly to answer our question is the quantity  $\sum_r (q''/r) (r/q')$ ; we shall write

$$\sum_r (q''/r) (r/q') = (q''/\rho/q');$$

this quantity,  $\rho$ , plays an important part in the theory; it is the analogue of the density in phase space that enters the classical statistical theory; it may be written as the diagonal sum of  $x$  and  $\rho$ ,  $D(x\rho) = D(\rho x)$ .

There are observables that can't be expressed in terms of  $\rho$ , as for example the symmetrical sum of functions of the dynamical variables of two systems, which is of the form  $\sum_r f(\xi_r, \xi_s)$ ; so it is to a certain limited extent only that we can consider an ensemble to be completely specified by the function  $\rho$ , namely only in regard to averages of quantities defined for the systems at a time.

The total value, then, of a quantity  $x$  for a given ensemble is given by  $D(\rho x)$ ; in the classical theory we have a density function,  $\rho$ , in phase space and the average value of  $x$  is given by

$$\iint x \rho \, d\mathbf{p} \, d\mathbf{q}$$

taken over the whole of phase space. This process of calculating average values is analogous to that of the quantum theory since the double integration corresponds to the double summation of the quantum theory formula.

In the classical theory we have a definite equation of motion for  $\rho$  since the motions of all the particles are determined by the Hamiltonian equations

$$\dot{p} = - \frac{\partial H}{\partial q}, \quad \dot{q} = \frac{\partial H}{\partial p},$$

so that, using the hydrodynamical equation of continuity for  $\rho$ ,

$$\frac{\partial \rho}{\partial t} = - \sum_r \left( \frac{\partial \rho}{\partial q_r} \dot{q}_r + \frac{\partial \rho}{\partial p_r} \dot{p}_r \right) = - [\rho, H].$$

This equation differs from the equation of motion of a dynamical variable only in the minus sign; we shall show that it holds for the quantum theory also; for we have

$$i\hbar \frac{\partial}{\partial t} (q''|s) = \sum_{q'''} (q''|H|q''')(q'''|s)$$

and for the conjugate complex

$$-i\hbar \frac{\partial}{\partial t} (s|q') = \sum_{q'''} (s|q''')(q'''|H|q')$$

so that

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} (q''|\rho|q') &= \sum_{q'''} \sum_s \left\{ \left[ i\hbar \frac{\partial}{\partial t} (q''|s) \right] (s|q') + (q''|s) \left[ -i\hbar \frac{\partial}{\partial t} (s|q') \right] \right\} \\ &= \sum_{q'''} \sum_s \left\{ (q''|H|q''')(q'''|s)(s|q') - (q''|s)(s|q''')(q'''|H|q') \right\} \\ &= \sum_{q'''} \left\{ (q''|H|q''')(q'''|\rho|q') - (q''|\rho|q''')(q'''|H|q') \right\}, \end{aligned}$$

showing that  $\frac{\partial \rho}{\partial t}$  is determined by  $\rho$  itself),

or

$$i\hbar \frac{\partial \rho}{\partial t} = H\rho - \rho H = - [\rho, H].$$

Thus we have corresponding laws of motion for our classical density and our quantum density and this justifies us in saying that our  $\rho$  is the quantum theory analogue of the classical density in phase space; this result is quite remarkable since we have no phase space in the classical sense in the quantum theory. The quantum theory  $\rho$  is a function of just the same number of variables as the classical  $\rho$ .

This theory of the Gibbs ensemble is thus very satisfactory except that it doesn't let us calculate anything that concerns a correlation between two systems.

We shall now consider the way of putting two systems together in which only a subspace of the whole product vector space is used. These are the two important cases in which we use only symmetrical and only antisymmetrical wave functions;

these restrictions are of the linear form

$$F\psi = 0$$

and we must verify that the subspaces in the two cases are actually invariant under the equations of motion; to prove this we have to use the condition that  $H$  is

symmetrical between the particles. We introduce a new notation by writing the

$(q_1' q_2' \dots q_n')$  of the whole system as  $(\tilde{q}|)$  with the primes to the left so that there will be no confusion with the  $(q'|)$  we used previously for the wave function of an individual system; we similarly abbreviate  $(q_1' \dots q_n' | \xi | q_1'' \dots q_n'')$  to  $(\tilde{q}| \xi | \tilde{q})$ .

Then the condition that  $H$  be symmetrical is that

$$(\tilde{q}| H | \tilde{q}) = (P \tilde{q}| H | P \tilde{q}),$$

where  $P \tilde{q}$  is any permutation of the  $\tilde{q}'$ 's. For a wave function

we have the equation of motion

$$i \hbar \frac{\partial}{\partial t} (\tilde{q}|) = \sum_{\tilde{q}} (\tilde{q}| H | \tilde{q}) (\tilde{q}|)$$

and so

$$\begin{aligned} i \hbar \frac{\partial}{\partial t} (P \tilde{q}|) &= \sum_{\tilde{q}} (P \tilde{q}| H | \tilde{q}) (\tilde{q}|) \\ &= \sum_{\tilde{q}} (P \tilde{q}| H | P \tilde{q}) (P \tilde{q}|), \end{aligned}$$

(since  $\tilde{q}$  is in the nature of a dummy suffix),

and therefore for the symmetrical case, in which  $(\tilde{q}|) = (P \tilde{q}|)$ ,

$$\frac{\partial}{\partial t} (\tilde{q}|) = \frac{\partial}{\partial t} (P \tilde{q}|)$$

showing that an initially symmetrical wave function remains symmetrical; in

precisely similar manner it is verified that an initially antisymmetrical wave

function remains antisymmetrical. The notion of symmetry or antisymmetry is in-

variant under a canonical transformation; for if we change from  $q_1, q_2, \dots, q_n$  to  $Q_1, Q_2, \dots, Q_n$  the transformation function,  $(Q_1' Q_2' \dots Q_n' | q_1' q_2' \dots q_n')$ ,

will be of the form

$$(Q_1' | q_1') (Q_2' | q_2') \dots (Q_n' | q_n')$$

where the  $(Q_r' | q_r')$  are all the same function of their arguments, denoting this transformation function by  $(Q | q)$  we therefore have

$$(P \tilde{Q} | P \tilde{q}) = (\tilde{Q} | \tilde{q});$$

the new representative of the state will be given by

$$(\tilde{Q}|) = \sum_{\tilde{q}} (\tilde{Q} | \tilde{q}) (\tilde{q}|)$$

and so

$$\begin{aligned}(P'Q|) &= \sum (P'Q|\psi)(\psi|) \\ &= \sum (P'Q|P\psi)(P\psi|) \\ &= \sum (Q|\psi)(P\psi|)\end{aligned}$$

so that if

$$\begin{aligned}(P\psi|) &= (\psi|) \\ (P'Q|) &= (Q|),\end{aligned}$$

then

and similarly for the antisymmetrical wave functions. This shows that it is permissible to talk about symmetrical and antisymmetrical states, these being such that they are symmetrical or antisymmetrical for any representation.

The theory of the Gibbs ensemble will apply equally well when we restrict ourselves to consider only the symmetrical or only the antisymmetrical wave functions since the analysis makes no reference to the whole <sup>n</sup> ensemble; the case of antisymmetrical wave functions is of special interest since we can now extend the theory of the Gibbs ensemble so as to get rid of the defect we have mentioned; we can see this as follows: The wave function for the whole assembly can be expressed in terms of the wave functions,  $(q^{(n)}|s)$ , of the individual systems in the form of a determinant as

$$\Delta = \begin{vmatrix} (q^{(1)}|1), & (q^{(1)}|1), & \dots, & (q^{(n)}|1) \\ \vdots & \vdots & & \vdots \\ (q^{(1)}|n), & (q^{(1)}|n), & \dots, & (q^{(n)}|n) \end{vmatrix},$$

where  $(q^{(r)}|s)$  refers to the  $r^{th}$  particle in the state  $s$ . This determinant will have the property that if we make a transformation of the wave functions

$$(q^{(r)}|)^* = \sum_s a_{rs} (q^{(s)}|),$$

where  $|a_{rs}|$  corresponds to a rotation, it will have the same value in terms of the  $(q^{(r)}|)^*$  as in the terms of the  $(q^{(r)}|)$ . This is easily seen to be the case geometrically since  $\Delta$  is just proportional to the volume of the  $(n+1)$  simplex formed by the origin and the end points of the  $n$  vectors represented

by the  $(q^{(r)}|s)$  in an  $n$ -dimensional space, such that the coordinates of the  $r^{\text{th}}$  vector are  $(q^{(r)}|1), (q^{(r)}|2), \dots, (q^{(r)}|n)$ , and must therefore be invariant under a rotation of the coordinates in this space. We are therefore only interested in those quantities that remain invariant under these rotations and it is easy to see that all such quantities must be expressible in terms of the scalar products

$$(q'|p|q'') = \sum_s (q'|s)(s|q'').$$

It follows that our  $\rho$  does really give us all the information that is contained in our determinant,  $\Delta$ , so that if we know  $\Delta$  we fix  $\rho$  and if we know  $\rho$  the value of  $\Delta$  is fixed.

Let us now consider this matter analytically in greater detail. If two of the wave functions,  $(q^{(r)}|)$ , are the same  $\Delta$  vanishes and in non-trivial cases we must have them all linearly independent; we may further consider them, without loss of generality, to be orthogonal and separately normalized. We then have

$$\begin{aligned} (q'|p^2|q'') &= \sum_{q'''} \sum_{rs} (q'|r)(r|q''')(q'''|s)(s|q'') \\ &= \sum_{rs} (q'|r) \delta_{rs} (s|q'') \\ &= \sum_r (q'|r)(r|q'') \\ &= (q'|p|q'') \end{aligned}$$

and hence

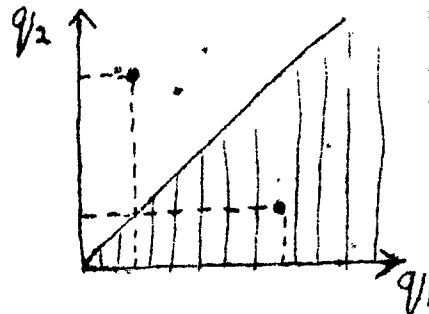
$$\rho^2 = \rho.$$

This corresponds to the fact that the eigenvalues of  $\rho$  are all either zero or unity, which means physically that we can't have more than one particle in a given state.

We should now be able to answer such questions as "what is the probability that we have one particle in the state  $q'$  and another in the state  $q''$ ?" This probability can be calculated in the following way:

We first calculate the probability of all the  $n$  particles being in the states  $q', q'', \dots, q^{(n)}$ ; we then sum this probability over all  $q^{(n)}$  and this gives us the probability of finding  $n-1$  particles in the  $n-1$  states  $q', q'', \dots, q^{(n-1)}$ , and by repeating this process we arrive at the pro-

probability we seek. We must first inquire into the normalisation of our wave function,  $\Delta$ . Let us agree to count two points in configuration space as one and the same point if they differ only in assigning different particles to the same states; or, more explicitly, let us agree, taking the two dimensional case for the purpose of illustration, that the point  $(q_1, q_2)$  in the configuration space is considered as



the same as the point  $(q_2, q_1)$  so that we are here actually dealing with only the shaded portion of the two-dimensional configuration space; and in general

that the point  $(q_1, q_2, \dots, q_n)$  be considered the same as the points  $P(q_1, q_2, \dots, q_n)$ . Then the wave function will be properly normalised for the typical portion of configuration space provided that the wave functions of the individual particles are properly normalised separately. (If we

did not make the above convention regarding the configuration space we should require a normalising factor  $1/\sqrt{n!}$  for  $\Delta$ ). We now continue with our problem; the probability that  $n$  particles be in the states  $q'_1, \dots, q'^{(n)}$  is given by

$$\left| \begin{array}{cccc} (q'_1|1), (q'_1|2), \dots, (q'_1|n) \\ \vdots & \vdots & & \vdots \\ (q'^{(n)}_1|1), (q'^{(n)}_1|2), \dots, (q'^{(n)}_1|n) \end{array} \right| \left| \begin{array}{cccc} (1|q'_1), (1|q'_2), \dots, (1|q'^{(n)}_1) \\ \vdots & \vdots & & \vdots \\ (n|q'_1), (n|q'_2), \dots, (n|q'^{(n)}_1) \end{array} \right|$$

which, by the ordinary rule for the multiplication of two determinants and the definition of the matrix elements  $(q^{(r)}|p|q^{(s)})$  is equal to the determinant

$$\left| \begin{array}{cccc} (q'_1|p|q'_1), \dots, (q'_1|p|q'^{(n)}_1) \\ \vdots & \vdots & & \vdots \\ (q'^{(n)}_1|p|q'_1), \dots, (q'^{(n)}_1|p|q'^{(n)}_1) \end{array} \right|$$

which we shall denote by  $D(n)$ ; Furthermore we shall denote by  $D(r)$  the determinant formed by taking the first  $r$  rows and columns of  $D(n)$ . The determinant  $D(n)$  involves only the matrix elements of  $\rho$  and it therefore follows that all our other probabilities will also be expressible in terms of the matrix elements of  $\rho$  only. To find the probability of  $n-1$  particles being in the states  $q_1^{(1)}, \dots, q_{n-1}^{(n-1)}$  we must sum  $D(n)$  over all  $q_n^{(n)}$ . This turns out to be quite simple on account of the relation  $\rho^2 = \rho$ ; we first expand  $D(n)$  so as to separate out the terms involving  $q_n^{(n)}$ ; we have, expanding by the last row and column,

$$D(n) = (q_n^{(n)} | \rho | q_n^{(n)}) D(n-1) - \sum_{r,s=1}^{n-1} (q_n^{(n)} | \rho | q_r^{(r)}) (q_s^{(s)} | \rho | q_n^{(n)}) K(s, r),$$

where  $K(s, r)$  denotes the cofactor of the element  $(q_s^{(s)} | \rho | q_r^{(r)})$

in the determinant  $D(n-1)$ . Now we have

$$\sum_{q_n^{(n)}} (q_n^{(n)} | \rho | q_n^{(n)}) = \sum_{q_n^{(n)}} \sum_r (q_n^{(n)} | \rho | q_r^{(r)}) \delta_{r, n} = \sum_r \delta_{r, n} = 1$$

and also

$$\begin{aligned} \sum_{q_n^{(n)}} (q_n^{(n)} | \rho | q_r^{(r)}) (q_s^{(s)} | \rho | q_n^{(n)}) &= \sum_{a,b} \sum_{q_n^{(n)}} (q_n^{(n)} | \rho | q_r^{(r)}) (q_s^{(s)} | \rho | q_n^{(n)}) \delta_{a, n} \delta_{b, n} \\ &= \sum_{a,b} (a | \rho | r) (s | \rho | b) \delta_{a, n} \delta_{b, n} \\ &= (q_s^{(s)} | \rho | q_r^{(r)}) \end{aligned}$$

so that summing  $D(n)$  for all  $q_n^{(n)}$  gives

$$\begin{aligned} \sum_{q_n^{(n)}} D(n) &= 1 D(n-1) - \sum_{r,s=1}^{n-1} (q_s^{(s)} | \rho | q_r^{(r)}) K(s, r) \\ &= 1 D(n-1) - (n-1) D(n-1) \\ &= D(n-1). \end{aligned}$$

Thus the determinant  $D(n-1)$  is the probability that  $n-1$  particles be found in the states  $q_1^{(1)}, q_2^{(2)}, \dots, q_{n-1}^{(n-1)}$ . We shall now show by a process of induction that the probability of finding  $m < n$  particles in the states  $q_1^{(1)}, \dots, q_m^{(m)}$



is equal to the determinant  $D(m)$ ; for we have

$$D(m+1) = (q^{(m+1)} | \rho | q^{(m+1)}) D(m) - \sum_{r,s=1}^m (q^{(m+1)} | \rho | q^{(r)}) (q^{(s)} | \rho | q^{(m+1)}) K(s,r)$$

and therefore

$$\begin{aligned} \sum_{q^{(m+1)}} D(m+1) &= n D(m) - m D(m) \\ &= (n-m) D(m). \end{aligned}$$

This factor  $(n-m)$  is just what we want physically since there are  $n-m$  particles

that may occupy our  $(m+1)^{\text{th}}$  state. We therefore have the result that if  $D(m+1)$  is the probability of finding  $m+1$  particles in the states  $q^{(1)}, \dots, q^{(m+1)}$

then  $D(m)$  is the probability of finding  $m$  particles in the states  $q^{(1)}, \dots, q^{(m)}$

and so the induction proof is valid. For the case of a single particle this checks up with our previous work since in this case the probability determinant becomes just a single diagonal element.

The determinant of  $\rho$  thus contains a great deal of physical information; its only mathematical property is that  $\rho^2 = \rho$ , but from this we can deduce that each of our  $D(r)$ 's has the characteristic property of a probability that

$$0 \leq D(r) \leq 1.$$

For example, for the case of  $D(1)$  we have

$$\begin{aligned} (q' | \rho | q') &= (q' | \rho^2 | q') \\ &= \sum_{q^{(r)}} (q' | \rho | q^{(r)}) (q^{(r)} | \rho | q') \\ &= (q' | \rho | q')^2 + \sum_{q^{(r)} \neq q'} (q' | \rho | q^{(r)}) (q^{(r)} | \rho | q') \end{aligned}$$

or

$$(q' | \rho | q') \{ 1 - (q' | \rho | q') \} = \sum (q' | \rho | q^{(r)}) \chi q^{(r)} | \rho | q') \geq 0,$$

since the factors on the right occur in conjugate pairs; it therefore follows that

$$0 \leq (q' | \rho | q') \leq 1.$$

Symmetrical quantities of the type  $\sum_{r,s} V(\xi_r, \xi_s)$  have physical meaning and the average value of such a function can be calculated, and expressed in terms of  $\rho$ ; so the difficulty in our theory of the Gibbs ensemble has been got over for this antisymmetrical case. A theory exists for the case of symmetrical wave functions but it differs in important ways from that for the antisymmetrical wave functions that we have just studied and we shall defer discussing it until a later time.

We now consider the more general theory of the antisymmetrical wave functions that takes account of the interactions between particles. Let us first consider the question of which of the various methods we have discussed for putting together several systems into a single system will be the correct ones for the expression of natural phenomena; there is no satisfactory general way of answering this question from the theoretical point of view and it is necessary, for each kind of particle, to refer to the experimental facts; in the case of electrons the question is decided by Pauli's Exclusion Principle which may be stated as follows:

We can consider that each electron in an atom has its own orbit or state; then no two electrons can have the same state.

This principle was announced by Pauli just before the introduction of the present quantum theory; by "having the same state" we must now mean "having the same wave function". The principle is very necessary if we are to have any theory of chemistry. We obtain just this exclusion principle if we say that only antisymmetrical wave functions are to be allowed in the system resulting from the putting together of several electrons, and thus the Pauli exclusion principle gives quite a definite answer to our question for the case of electrons. Another important case is that of light quanta; the answer is not so obvious here but it turns out that we get a different kind of statistics according as we use symmetrical or antisymmetrical wave functions and that the case of symmetrical

wave functions gives the correct statistical results for light quanta.

There are also other cases such as the nuclei of atoms and so on; in the case of the nuclei of atoms we refer to experimental data regarding molecules to find the correct sort of wave functions to use. It turns out that we can have only symmetrical or only antisymmetrical wave functions in every case.

We shall consider the case of electrons in more detail, but before doing this we shall give a brief resume of the properties of the spin of an electron; we consider for the present that these properties are given purely experimentally. We have already seen that a spherically symmetrical system must have zero angular momentum, and conversely; the case of a spinning electron is the next simple being such that the component of angular momentum about any direction has only the two possible values  $\pm \frac{1}{2} \hbar$ . The electron has, accompanying this spin, a magnetic moment which is very small. For the mathematical description of the spin it is convenient to introduce three components,  $s_x, s_y, s_z$ , of the spin angular momentum which must satisfy the relations

$$[s_x, s_y] = s_z \text{ etc.,}$$

since they are angular momenta, and which must also satisfy

$$s_x^2 = \frac{1}{4} \hbar^2 \text{ etc.,}$$

since the eigenvalues of  $s_x, s_y$  and  $s_z$  are  $\pm \frac{1}{2} \hbar$ . Thus  $s_x^2, s_y^2$  and  $s_z^2$  are pure numbers since they each have only one eigenvalue. If we write

$$s_x = \frac{1}{2} \hbar \sigma_x \text{ etc.,}$$

we have

$$\sigma_x^2 = \sigma_y^2 = \sigma_z^2 = 1$$

and

$$\sigma_x \sigma_y - \sigma_y \sigma_x = 2i \sigma_z \text{ etc.}$$

From these relations we can deduce by straightforward algebra that

$$\sigma_x \sigma_y = -\sigma_y \sigma_x = i\sigma_z \text{ etc.}$$

These are the fundamental relations connecting the components of the spin and should be known by heart, as also should the representation

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

We note that in the wave function of a single electron,  $(xyz\sigma_z)$ , the  $\sigma_z$  has a domain consisting of only two points, and so this is the same as if we had two functions of the three variables  $x, y$  and  $z$ ; it is sometimes convenient to consider that an electron with spin is represented by a wave function depending upon  $x, y$  and  $z$  and having two components rather than by a wave function depending upon  $x, y, z$  and  $\sigma_z$  and having only one component. The two points of view are however equivalent.

Let us now return to the case of several electrons; the spin has a very important effect despite the fact that its effect upon the motion of an electron in a field is extremely small, being of the same order of magnitude as relativistic effects; and since our present theory is non-relativistic we may neglect the spin forces altogether. But we cannot neglect the spin when we apply the exclusion principle. Let  $x_r \sigma_{rz}$  describe the  $r$ th electron,  $\sigma_{rz}$  being the  $z$ -component of the spin; then the wave function for a system of  $n$  electrons will be of the type

$$(x_1 \sigma_{1z} x_2 \sigma_{2z} \dots x_n \sigma_{nz}).$$

The antisymmetry principle means that this quantity must be antisymmetrical in the  $x$ 's and the  $\sigma$ 's together; it is for this reason that we cannot omit the spins when we wish to apply the exclusion principle.

To illustrate the effect of the spin we shall consider the case in which there are only two electrons present. If we neglect the spin forces altogether the Hamiltonian of the resulting system will be given by

$$H = H_1 + H_2 + \frac{e^2}{r},$$

the last term being the Coulomb interaction energy. This Hamiltonian does not involve the spins at all so that we may obtain wave functions of the type  $(x_1 x_2)$  that will satisfy the wave equation. But we may also

have the solutions

$$(x_1, x_2 |) F(\sigma_{1z}, \sigma_{2z})$$

where  $F$  is any function whatever. This is the general type of solution of the wave equation when the spins enter the wave functions but not the Hamiltonian. We must now make the wave functions antisymmetrical; this can be done in two ways, either by taking it antisymmetrical in the  $x$ 's and symmetrical in the spins or by taking it symmetrical in the  $x$ 's and antisymmetrical in the spins. Now  $\sigma_z$  has only two eigenvalues and so there are only two independent functions of it; we shall call these functions  $f_\alpha(\sigma_z)$  and  $f_\beta(\sigma_z)$ , defined by

$$\left. \begin{aligned} f_\alpha(1) &= 1, & f_\alpha(-1) &= 0 \\ f_\beta(1) &= 0, & f_\beta(-1) &= 1 \end{aligned} \right\}$$

and

Any function whatever of  $\sigma_z$  is expressible as a linear function of  $f_\alpha$  and  $f_\beta$ . For two spin variables there are only four independent functions, namely

$$\left. \begin{aligned} f_\alpha(\sigma_{1z}) f_\alpha(\sigma_{2z}) \\ f_\alpha(\sigma_{1z}) f_\beta(\sigma_{2z}) \\ f_\beta(\sigma_{1z}) f_\alpha(\sigma_{2z}) \\ f_\beta(\sigma_{1z}) f_\beta(\sigma_{2z}) \end{aligned} \right\}$$

which we shall denote by  $\alpha_1 \alpha_2$ ,  $\alpha_1 \beta_2$ ,  $\beta_1 \alpha_2$  and  $\beta_1 \beta_2$  respectively; we see that  $\alpha_1 \alpha_2$  is symmetrical,  $\beta_1 \beta_2$  is symmetrical and that  $\alpha_1 \beta_2 + \beta_1 \alpha_2$  is symmetrical while  $\alpha_1 \beta_2 - \beta_1 \alpha_2$  is antisymmetrical. There are, therefore, three symmetrical and one antisymmetrical independent functions of  $\sigma_{1z}$  and  $\sigma_{2z}$  in terms of which any function of them may be expressed. If we take  $(x_1, x_2 |)$  to be symme-

trical in  $x_1$  and  $x_2$  we have, therefore, only one state of the system that will be completely antisymmetrical, and we call such a state a singlet state; if we take  $(x_1, x_2 |)$  to be antisymmetrical we have three symmetrical functions of the spins so that we shall have three antisymmetrical states in this case; such states are said to be triplet states; they will give the same motions of the electrons but will correspond to different orientations of their spins. (If we don't neglect the spin forces the motions of

these three states will be very slightly different from each other).

Let us see what will be the actual orientations of the spins of the electrons in the various cases; it is convenient to introduce the quantity  $s$  given by

$$s(s+1) = \frac{1}{4} [(\sigma_{1x} + \sigma_{2x})^2 + (\sigma_{1y} + \sigma_{2y})^2 + (\sigma_{1z} + \sigma_{2z})^2],$$

this giving the magnitude of the vector  $\underline{\sigma}_1 + \underline{\sigma}_2$ . We then easily find, using the relations satisfied by the  $\underline{\sigma}$ 's that

$$s(s+1) = \frac{3}{4} + \frac{1}{2} (\underline{\sigma}_1, \underline{\sigma}_2),$$

where  $(\underline{\sigma}_1, \underline{\sigma}_2)$  denotes the scalar product of  $\underline{\sigma}_1$  and  $\underline{\sigma}_2$ . Now  $(\underline{\sigma}_1, \underline{\sigma}_2)^2$  can be shown to be equal to  $3 - 2(\underline{\sigma}_1, \underline{\sigma}_2)$  and, hence we have

$$[(\underline{\sigma}_1, \underline{\sigma}_2) + 1]^2 = 4 \quad (6)$$

so that

$$[(\underline{\sigma}_1, \underline{\sigma}_2) + 1] \quad \text{has the eigenvalues } \pm 2.$$

So

$$(\underline{\sigma}_1, \underline{\sigma}_2) \quad \text{has the eigenvalues 1 and -3}$$

and therefore

$s$  has the eigenvalues 1 and 0.

This result is what we would expect from the vector picture that was very much in fashion before we had the accurate theory of quantum mechanics, since we could there have the spins "parallel", as  $\frac{1}{2} \rightarrow \frac{1}{2}$ , or "anti-parallel", as  $\frac{1}{2} \leftarrow \frac{1}{2}$ , giving resultants of 1 and 0 respectively.

It is easy to prove that the singlet state corresponds to the case in which  $s$  has the eigenvalue zero and that the triplet states are those for which  $s$  has the eigenvalue one; for we have

$$\sigma_x f_\alpha = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} = f_\beta$$

and similarly

$$\sigma_y f_\alpha = i f_\beta \quad \text{and} \quad \sigma_z f_\alpha = f_\alpha$$

and also

$$\sigma_x f_\beta = f_\alpha, \quad \sigma_y f_\beta = -i f_\alpha \quad \text{and} \quad \sigma_z f_\beta = -f_\beta.$$

We can then easily prove that

$$S(S+1) f_{\alpha}(\sigma_1) f_{\alpha}(\sigma_2) = 2 f_{\alpha}(\sigma_1) f_{\alpha}(\sigma_2)$$

showing that one of the triplet states corresponds to the eigenvalue 1 of  $S$ , and proceeding similarly we prove the result we stated.

A state that is initially symmetrical or antisymmetrical in  $\sigma_1$  and  $\sigma_2$  will remain so for all time, if we neglect the effect of the spin forces, and hence this division of the totality of states into two sets is a practically permanent one; if we wish to be quite accurate we must say that there is only a small probability of a transition taking place from a state of one set to a state of the other.

We now consider the general case of an atom with any number,  $n$ , of electrons; the most powerful way of attacking this problem would appear to be that which treats permutation operators as observables; let us first take the case of any number of similar particles, not necessarily electrons, forming a single system; then if we have a wave function,  $(q_1, q_2, \dots, q_n)$ , we can apply any permutation on the  $q$ 's and get a new wave function. Since this permutation operation is linear we may look upon our new wave function as the result of an observable,  $P$ , operating upon the original one and we write

$$\begin{aligned} \text{if } (q|) &\rightarrow \psi \\ \text{then } (Pq|) &\rightarrow P\psi. \end{aligned}$$

This observable,  $P$ , is of a new type since it cannot be expressed as a function of the  $q$ 's, but we can nevertheless obtain a representative for it since we must have

$$\begin{aligned} \sum_{\psi'} (q|P|\psi')(\psi'|) &= (Pq|) \\ \text{which gives} \quad (q|P|\psi') &= \delta_{Pq, \psi'} \\ &= \delta_{q, P^{-1}\psi'}. \end{aligned}$$

This representative for  $P$  enables us to find its conjugate complex when  $P$  is counted as an observable, for we have

$$\begin{aligned} (\psi | \bar{P} | \psi) &= (\psi | P | \psi) \\ &= (\psi | P | \psi), \end{aligned}$$

(since these matrix elements are all real),

$$\begin{aligned} &= \delta_{\psi, P^{-1}\psi} \\ &= (\psi | P^{-1} | \psi) \end{aligned}$$

and so

$$\bar{P} = P^{-1}.$$

To divide the permutations up into classes;  $P_a$  and  $P_b$  are said to be in the same class if there is a  $P$  for which

$$P_a = P P_b P^{-1};$$

the meaning of similar permutations is of the following nature; any permutation of  $n$  numbers may be expressed as a set of cyclic permutations as for example

$$(1\ 3\ 4)(2\ 5\ 7\ 6)$$

which expresses the permutation that sends 1 into 3, 3 into 4 and 4 into 1, and also 2, 5, 7 and 6 cyclically in the same way; a permutation similar to this will then be one that is expressible in the form

$$(\times \times \times)(\times \times \times \times),$$

We next show that the permutations are constants of the motion; the quantity  $P$  depends upon the parameter  $t$  and we have to find the value of

$$\frac{dP}{dt}$$

; we have

$$i\hbar \frac{dP}{dt} = PH - HP,$$

but owing to the symmetry of  $H$  the result of operating with  $P$  upon  $H\psi$  must be the same as the result of operating upon  $\psi$  by  $P$  and then operating upon this with  $H$  so that we must have  $PH\psi = HP\psi$  and hence

$$\frac{dP}{dt}$$

must be zero. This result could also be obtained directly

by using the representative of  $P$ . Thus the  $P$ 's are constants of the motion.



It is really very convenient when we can find constants of the motion of a dynamical system since they constitute a partial integration of the equations of motion; when we have a constant of the motion,  $\alpha$ , for any dynamical system we can divide all the states of the system into sets, the members of each set being such that  $\alpha$  has the same given value for each of them, and this classification will hold for all time. In the present case we have  $(n!-1)$  non-trivial constants of the motion and this is too much riches since we cannot give numerical values to all the  $P$ 's simultaneously because they don't all commute; what is the correct procedure in such a case? We look for functions of the  $P$ 's that commute with each of the  $P$ 's and therefore commute with each other; these functions, which we denote by  $\chi_r$ , can be given numerical values simultaneously and will thus serve to classify the states in the manner we require.

Let us see what this classification means physically for the case of stationary states; for the purposes of this discussion we shall assume that the energy levels form a discrete set and that the system is degenerate, i.e. that there are several states for which  $H$  has the same eigenvalue. In this case the  $\chi$ 's will have the property that each will have a definite numerical value corresponding to each energy level of the system; that is, if we make a classification of the states by means of the  $\chi$ 's all states belonging to one energy level go into the same class; for, let us consider what is the most general method of classifying the states in order that this property should hold; we must look for some observable,  $\beta$ , that is a constant of the motion and which will have the same numerical value for all states having the same energy level; this means that  $\beta$  may be regarded

as a function of  $H$  according to our definition of a function of an observable. So we have to look for functions of the  $P$ 's that are functions of  $H$ ; but  $f(H)$  must commute with  $H$  and with everything that commutes with  $H$ , so that the functions we seek must commute with all the  $P$ 's. An example of such a function is

$$\chi = \frac{1}{n_{\text{class}}} \sum_{\text{class}} P_{\text{class}}$$

and this gives us one  $\chi$  for each class of the permutations. We can see that this gives all of the  $\chi$ 's since any function of the  $P$ 's can be expressed as a linear function of the  $P$ 's and if this linear function of the type  $\sum_r c_r P_r$  commutes with all the  $P$ 's we have

$$P(\sum_r c_r P_r)P^{-1} = \sum_r c_r P_r$$

which requires that all the  $c$ 's multiplying  $P$ 's of the same class must be equal and hence our function is expressible as a linear function of the  $\chi$ 's.

We can verify that

$$\frac{1}{n_{\text{class}}} \sum_{\text{class}} P_{\text{class}} = \frac{1}{n!} \sum P P_c P^{-1};$$

for we have merely to show that each permutation occurs the same number of times in the summation on the right; we ask how many  $P$ 's satisfy

$$P P_c P^{-1} = P_a;$$

let us assume that  $P$  and  $P_0$  are two solutions; then we have

$$P_0 P_c P_0^{-1} = P_a;$$

then, eliminating  $P_a$ , we get

$$P_0 P_c P_0^{-1} = P P_c P^{-1}$$

or

$$P^{-1} P_0 P_c P_0^{-1} P = P_c$$

so that

$$P^{-1} P_0$$

commutes with  $P$ . To keep  $P_0$

fixed and enquire how many  $P$ 's satisfy this condition; the number of such

P's will plainly be independent of  $P_a$ , and hence the number of P's satisfying the condition

$$P_0 P_c P^{-1} = P_a$$

will be independent of  $P_a$  and therefore each  $P_a$  similar to  $P_c$  will occur

the same number of times in our sum.

We now have a set of  $\chi$ 's each of which is a constant of the motion and commutes with all the P's. Let us put

$$\chi_r = \lambda_r'$$

where  $\lambda_r'$  are numbers; this will then give us a classification of the states such that all stationary states belonging to the same energy level will go into the same class. There will be certain restrictions upon the numerical values that may be given to the  $\chi$ 's since the  $\chi$ 's must satisfy certain algebraic relations; for, any product of two  $\chi$ 's,  $\chi_r \chi_s$ , being a function of the P's, must be expressible as a linear function of the P's, and, since it further must commute with all the P's, it must be expressible as a linear function of the  $\chi$ 's. Hence we must have relations of the type

$$\chi_r \chi_s = a_1 \chi_1 + a_2 \chi_2 + \dots + a_n \chi_n,$$

and when we give numerical values to the  $\chi$ 's they must be consistent with these algebraic relations.

For the sake of illustration let us take the case of three particles; there are now six permutations which fall into three classes as follows;

The trivial permutation,  $P_0$ , equal to the identity,

The interchanges,  $P(23)$ ,  $P(31)$  and  $P(12)$ , and

The cyclical permutations,  $P(123)$  and  $P(132)$ .

Our  $\chi$ 's are given by

$$\chi_0 = 1,$$

$$\chi_1 = \frac{1}{3} (P(12) + P(13) + P(23))$$

and

$$\chi_2 = \frac{1}{3} (P(123) + P(132)),$$

and so we have, since  $\{P(12)\}^2$  etc. and  $P(12)P(13) = P(231)$  etc.,

$$\chi_1^2 = \frac{1}{9} (3 + 6\chi_2) = \frac{1}{3} + \frac{2}{3}\chi_2,$$

and similarly

$$\chi_2^2 = \frac{1}{3}\chi_2 + \frac{1}{3}$$

and

$$\chi_1\chi_2 = \chi_1,$$

these being the algebraic relations that must be satisfied by the numerical

values we give to the  $\chi$ 's. We easily find that the only possibilities are

$\chi_2$	1	1	$-\frac{1}{2}$
$\chi_1$	1	-1	0

these giving a classification of the states into three classes. The class

for which  $\chi_1 = \chi_2 = 1$  corresponds to the states that are symmetrical, that

for which  $\chi_1 = -\chi_2 = -1$  to the states that are antisymmetrical and that for

which  $\chi_1 = 0, \chi_2 = -\frac{1}{2}$  to states that are neither completely symmetrical

nor completely antisymmetrical, such states not arising in the corresponding

classification for a system consisting of only two particles.

There are two obvious solutions to the algebraic relations that must

be satisfied by the  $\chi$ 's in the general case; the first is that for which

$\chi = 1$  for every  $\chi$  and corresponds to the case of symmetrical wave functions;

the other is that for which  $\chi = 1$  for even permutations and  $\chi = -1$  for odd

permutations and this corresponds to the case of antisymmetrical wave func-

tions. The other solutions correspond to wave functions that are neither

wholly symmetric nor antisymmetric.

We can easily find how many solutions there are for the  $\chi$ 's

for the general case of  $n$  particles; let there be  $m$   $\chi$ 's of which one

is the trivial  $\chi, \chi_0 = P_0 = 1$ . Let us consider a linear function of the  $\chi$ 's,

$$B = b_0\chi_0 + b_1\chi_1 + \dots + b_{m-1}\chi_{m-1};$$

then  $B^2$  must also be expressible as a linear function of the  $\chi$ 's, say,

$$B^2 = b_{02}\chi_0 + b_{12}\chi_1 + \dots + b_{m-1,2}\chi_{m-1},$$

and we can continue to express  $B^3, B^4, \dots, B^n$  as linear functions of the

$\chi$ 's . With the relation

$$1 = \chi_0$$

we now have  $m + 1$  equations from which we may eliminate the  $\chi$ 's so as to give, say,

$$z_0 + z_1 B + z_2 B^2 + \dots + z_m B^m = 0;$$

this can be regarded as an ordinary algebraic equation since its coefficients are numbers; we can solve this equation to obtain  $m$  roots which, we shall see, must all be distinct; each root will be a linear function of the  $b_r$ , corresponding to a set of numerical values for the  $\chi$ 's so that we shall obtain  $m$  such sets and there are therefore at most  $m$  different sets. We can see that the roots of the equation in  $B$  must be distinct since if we had fewer than  $m$  different sets of values for the  $\chi$ 's we could construct something of the type

$$a_0 \chi_0 + a_1 \chi_1 + \dots + a_{m-1} \chi_{m-1}$$

which would vanish for all these sets of values; this quantity would thus have all its eigenvalues zero and must therefore be equal to the number zero which would mean that the  $\chi$ 's were not linearly independent. That the  $\chi$ 's must have real eigenvalues follows from the fact that  $P$  and  $P^{-1}$  are in the same class and  $P + P^{-1}$ , which is the same as  $P + \bar{P}$ , must be real. The number  $m$  is equal to the number of partitions of the number  $n$ .

We have now completed our discussion of the way in which the states of a system of  $n$  similar particles fall into classes; let us proceed to apply this theory to the case of electrons. We may now only have antisymmetrical wave functions and so the direct application of our mode of classification leads to the trivial result that there is only one class of states, namely those that have antisymmetrical wave functions. But there is a different way in which we may apply the previous theory which will not lead to trivial

results; the wave function,  $(x_1 \sigma_1 x_2 \sigma_2 \dots x_n \sigma_n)$ , must be antisymmetrical in both the  $x$ 's and the  $\sigma$ 's. We consider the permutations,  $P$ , that act on the  $x$ 's only, and the permutations,  $P^\sigma$ , that act only upon the  $\sigma$ 's; any permutation of the  $x$ 's and  $\sigma$ 's together is then of the form  $P P^\sigma$ . We must have

$$P P^\sigma = \pm 1$$

where the positive sign is taken if  $P P^\sigma$  is an even permutation and the negative sign if it is an odd one. So we have

$$P^{-1} = \pm P^\sigma$$

Let us once again neglect the spin forces and take the Hamiltonian,  $H$ , of the system to be independent of the  $\sigma$ 's; it must be a symmetrical function of the  $x$ 's and so

$$P H = H P$$

showing that the  $P$ 's are constants of the motion; we can therefore apply our preceding theory to the  $P$ 's and this will give us results that are not trivial.

Since  $P P^\sigma = \pm 1$  it follows that the  $P^\sigma$ 's are also constants of the motion. We now wish to establish a connection between the  $P^\sigma$ 's and the  $\sigma$ 's themselves; let us consider the spin vectors,  $\underline{\sigma}_1$  and  $\underline{\sigma}_2$ , of two of the electrons; we write

$$\frac{1}{2} \{ (\underline{\sigma}_1, \underline{\sigma}_2) + 1 \} = O_{12}$$

and we shall show that  $O_{12}$  must be identified with the interchange,  $P_{12}^\sigma$ .

We could prove this result directly by getting a representation for  $O_{12}$  and  $P_{12}^\sigma$  but we can get a neater method by using general algebraic reasoning; we have

$$O_{12}^2 = 1 \quad (\text{from (6)})$$

and also

$$P_{12}^{\sigma^2} = 1;$$

again we have

$$O_{12} \sigma_{1x} = \frac{1}{2} \{ -i \sigma_{1z} \sigma_{2y} + i \sigma_{1y} \sigma_{2z} + \sigma_{1x} + \sigma_{1y} \}$$

and

$$\sigma_{2x} O_{12} = \frac{1}{2} \{ \sigma_{1x} + i \sigma_{1y} \sigma_{2z} - i \sigma_{1z} \sigma_{2y} + \sigma_{2x} \}$$

so that

$$O_{12} \sigma_{1x} = \sigma_{2x} O_{12}$$

with similar results for the y- and z- components of the spins; we

may therefore write these results as

$$\text{and since } O_{12}^2 = 1 \quad O_{12} \sigma_1 = \sigma_1 O_{12} \quad \text{we have from this equation that}$$

$$\left. \begin{aligned} O_{12} \sigma_1 &= \sigma_1 O_{12} \\ \text{and } O_{12} \sigma_2 &= \sigma_2 O_{12} \end{aligned} \right\};$$

these properties are just the same as those possessed by  $P_{12}^\sigma$  and

since  $O_{12}$  and  $P_{12}^\sigma$  must each commute with  $\sigma_3, \sigma_4, \dots, \sigma_n$ ,

it follows that

$$O_{12} = c P_{12}^\sigma$$

where  $c$  is a number; and since we have  $O_{12}^2 = P_{12}^{\sigma^2}$  it follows that

$c = \pm 1$ . To determine the correct sign to use we consider the average of the eigenvalues of  $O_{12}$  and also of  $P_{12}^\sigma$ ; now the average of the eigenvalues of  $(\sigma_1, \sigma_2)$  must be zero so that the average of the eigenvalues of  $O_{12}$  is  $\frac{1}{2}$ . For the  $P_{12}^\sigma$ 's, since we have three symmetric and one antisymmetric independent functions of  $\sigma_1$  and

$\sigma_2$ , the average eigenvalue is  $\frac{1}{4}(1+1+1-1) = \frac{1}{2}$ . Hence we have to take the positive sign and thus have the result that

$$O_{12} = P_{12}^\sigma.$$

In general we have

$$P_{rs}^\sigma = \frac{1}{2} \{ (\sigma_r, \sigma_s) + 1 \}.$$

We can now carry on with the classification of the states of our system of  $n$  particles; we have

$$\chi = \frac{1}{n_{\text{class}}} \sum_{\text{class}} P_{\text{class}}$$

and since  $P^{-1} = \pm P^\sigma$  we have

$$\chi = \pm \frac{1}{n_{\text{class}}} \sum_{\text{class}} P_{\text{class}}^\sigma$$

and so we can use the  $P_{\text{class}}^\sigma$ 's instead of the  $P$ 's for determining the

values of the  $\chi$ 's; this is more convenient than employing the  $P$ 's since

we have an expression for the  $p\sigma's$  in terms of the  $\sigma's$  about whose properties we know quite a lot; we have, for example, that  $\chi_{(12)}$  is the average of  $-\frac{1}{2}\{(\sigma_r, \sigma_s) + 1\}$ . so that

$$\chi_{(12)} = -\frac{1}{2} \left\{ 1 + \frac{\sum_{r \neq s} (\sigma_r, \sigma_s)}{n(n-1)/2} \right\};$$

we can express this in terms of the variable,  $s$ , that describes the magnitude of the total spin and which is defined by

$$s(s+1) = \frac{1}{4} \{ (\sum \sigma_x)^2 + (\sum \sigma_y)^2 + (\sum \sigma_z)^2 \};$$

for, we have

$$2 \sum_{r \neq s} (\sigma_r, \sigma_s) = (\sum \sigma_r, \sum \sigma_s) - \sum (\sigma_r, \sigma_s).$$

and hence

$$\chi_{(12)} = - \frac{n(n-4) + 4s(s+1)}{2n(n-1)}.$$

Thus  $\chi_{(12)}$  is describable in terms of the number of particles and just the one quantity  $s$ , which determines the magnitude of the total spin. This holds true for all the  $\chi's$ . It follows that there will be one set of numerical values for the  $\chi's$  corresponding to each value we can give to the variable  $s$ . The number of sets of numerical values is now very much restricted since the  $p\sigma's$  operate upon quantities the domain of each of whose eigenvalues consists of two points only. We have one class of states corresponding to each numerical value we can give to  $s$ ; the permissible values of  $s$  are known from a general theorem applying to any angular momentum observable; we find actually that the permissible values of form the arithmetic series  $\frac{n}{2}, \frac{n}{2}-1, \frac{n}{2}-2, \dots$  ending with either  $\frac{1}{2}$  or  $0$ ; the value  $\frac{n}{2}$  corresponds to the case in which all the spins are parallel. Thus each class corresponds to a definite numerical value of the resultant spin. This is, however, not an accurate statement since we have neglected the spin forces; if we don't neglect these forces the  $s$  is no longer a constant of the motion and so there is a small transition probability from one value of  $s$  to another, that is, from one class to another according to the above scheme of classification.



One could proceed to build up a perturbation theory to deal with the Coulomb interaction forces, but we shall not discuss it in these lectures; we shall, however, deal with this problem by a method which has recently been much employed and which is based upon a variational principle. As soon as we have interaction between the particles of our system the problem becomes extremely difficult and in general involves equations that are so complicated that exact solutions cannot be found by present analytical methods; to attack these problems we must therefore make use of approximate methods; approximate methods do not necessarily have to be ugly and those we shall describe are based on general laws; all of physics is only approximation.

The method consists in assuming eigen- $\psi$ 's that are restricted to be of a certain definite form and finding which of these eigen- $\psi$ 's gives the best approximation to the solution of the wave equation. It is applicable to the general atomic system and not merely to the case of systems consisting of a number of electrons only. The first question that arises is what is the special form for  $\psi$  that one should choose, but to answer this question we must be guided by physical considerations and we shall therefore not consider the answer at this point. If we assume a given form for the wave functions how do we set about choosing the various arbitrary things that occur in this special form in order to obtain the best approximation? Let us first consider this question for the case of stationary states and later give the general theory; when stationary states exist the Hamiltonian,  $H$ , must not contain the time explicitly and to find the stationary states we must determine the eigen- $\psi$ 's of  $H$ . We shall prove the theorem that if  $\phi\psi = 1$ ,  $\phi$  being the conjugate complex of  $\psi$ , then the necessary and sufficient condition that  $\psi$  be an eigen- $\psi$  of  $H$  is that  $\phi H\psi$  be

stationary for all variations of  $\psi$  that leave  $\phi\psi$  equal to unity;  
for we have

$$\delta(\phi H \psi) = 0$$

provided that

$$\delta(\phi\psi) = 0,$$

so that we must have

$$\delta(\phi H \psi) = E \delta(\phi\psi)$$

for all variations of  $\psi$ ,  $E$  being a number. Thus

$$\delta[\phi(H-E)\psi] = 0$$

or

$$\delta\phi \cdot (H-E)\psi + \phi(H-E)\delta\psi = 0.$$

Now  $\delta\phi$  and  $\delta\psi$  are not independent variations since they are conjugate imaginary quantities, but we shall show that we may nevertheless equate the two terms in the above equation individually to zero; for, if we take a new  $\delta\psi$  which is  $i$  times the old one the new  $\delta\phi$  is  $-i$  times the old and we have

$$-i \delta\phi \cdot (H-E)\psi + \phi(H-E)i \delta\psi = 0$$

and comparing this with the previous equation we find that

$$\delta\phi \cdot (H-E)\psi = 0$$

and

$$\phi(H-E)\delta\psi = 0$$

which proves our statement;\* since  $\delta\psi$  is arbitrary we have

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\* We shall often use in future work this property that we get the right answer if we assume  $\delta\phi$  and  $\delta\psi$  to be independent and we shall just quote the result without going through the proof every time.

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$$(H-E)\psi = 0$$

showing that  $\psi$  is an eigen- $\psi$  of  $H$ ,  $E$  being the corresponding eigenvalue. It is not difficult to show that the condition is necessary as well as sufficient. We note that the eigenvalue,  $E$ , is equal to the quantity,  $\phi H \psi$ , that we varied.

The above theorem forms the foundation of our method of approximation; we assume for this method that the wave function is of a special form,  $\psi_1$  ;

this means that we are limiting the approximate solution to lie in a definite subspace of the  $\Psi$ -space; : we now have to choose

$\Psi_1$  so that it will be the best approximation to the solution of the problem; we must thus have  $\phi_1 H \Psi_1$  stationary for all variations of  $\Psi_1$  that retain its special form and the condition for this is that

$$\delta \phi_1 E \Psi_1 = \delta \phi_1 H \Psi_1 ; \quad (7)$$

the approximate eigenvalue is then given by  $\phi_1 H \Psi_1$  provided that  $\Psi_1$  is properly normalised.

We now generalize this theory to the case of non-stationary states; the work doesn't look exactly parallel to that given above but is actually a little more direct. The equation that must be satisfied in the exact theory is

$$i\hbar \frac{d\Psi}{dt} = H\Psi$$

where we are taking the three-dimensional view of a state; If  $\Psi$  is given arbitrarily at time  $t_0$  it is determined for all other times by this equation; let us take the initial  $\Psi$  at time  $t_0$  to be of the special form,  $\Psi_1(t_0)$ ; the condition that  $\Psi_1(t)$  be a good approximation is that

$$i\hbar \frac{d}{dt} \Psi_1(t) = H\Psi_1(t) + \Psi_2(t) \quad (8)$$

where  $\Psi_2(t)$  is small. This can be written as

$$i\hbar \Psi_1(t_0 + dt) = i\hbar \Psi_1(t_0) + H\Psi_1(t_0) dt + \Psi_2(t_0) dt$$

and we want  $\Psi_1(t_0 + dt)$  to be such that  $\Psi_2(t_0)$  is the smallest possible vector with  $\Psi_1(t_0)$  fixed. If we make any variation in  $\Psi_1$  it will induce an equal variation in  $\Psi_2$  since the other terms in (8) are fixed; so we have

$$i\hbar \delta \Psi_1(t_0 + dt) = \delta \Psi_2(t_0) dt. \quad (9)$$

Now the condition that  $\Psi_2$  be as small as possible is that  $\phi_2 \Psi_2$  be a minimum so that we must have

$$\delta(\phi_2 \psi_2) \rightarrow 0$$

or\*

$$\delta \phi_2 \cdot \psi_2 = 0.$$

\* See previous footnote.

But from (9) we have

$$-i\hbar \delta \phi_1(t_0 + dt) = \delta \phi_2(t_0) dt$$

and hence we get the condition that

$$\delta \phi_1(t_0 + dt) \cdot \psi_2(t_0) = 0$$

and taking the limit as  $dt \rightarrow 0$  this becomes

$$\delta \phi_1(t_0) \cdot \psi_2(t_0) = 0;$$

if this be satisfied  $\psi_2$  will be the smallest possible. Multiplying (7)

by  $\delta \phi_1$  we have

$$i\hbar \delta \phi_1 \frac{d\psi_1}{dt} = \delta \phi_1 H \psi_1 \quad (10)$$

which is the condition that  $\psi_1$  be the best approximation to the solution of the wave equation.

Let us consider this method from the purely geometrical point of view; the diagram represents the space of the  $\psi$ 's and the subspace occupied by

the  $\psi$ 's of the given form  $\psi_1$  is denoted by the curve  $\overline{PRS}$ .

Let the vector  $OP$  be  $\psi_1(t_0)$

and let the broken line  $\overline{PQK}$

denote the motion of the end of

this vector according to the exact

equation of motion,  $i\hbar \frac{d\psi}{dt} = H\psi$ . This curve will in general not

lie in the subspace of the  $\psi_1$ 's; we go for a time  $dt$  along  $\overline{PQK}$  to

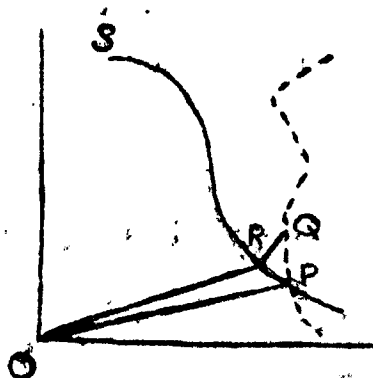
the point  $Q$  so that  $Q$  is the end, at time  $t_0 + dt$ , of the vector that

satisfies the exact wave equation; from  $Q$  we drop a perpendicular  $QR$  onto

the subspace of the  $\psi_1$ 's and the vector  $OR$  is then  $\psi_1(t_0 + dt)$ . To see

the relation between this picture and our analysis we note that  $PQ$  is the

vector  $H\psi_1 dt / i\hbar$  and  $QR$  is  $\psi_2 dt / i\hbar$ ; the perpendicularity



of  $Q R$  to the subspace of the  $\psi_i$ 's is a geometrical expression of the equation

$$\delta \phi(t_0 + dt), \psi_2(t_0) = 0$$

that we have used in the analysis.

Suppose we take  $\psi_i$  to be initially normalized according to the equation  $\phi, \psi_i = 1$ ; the question is will this  $\psi_i$  remain so normalized when its motion is determined by the above method? We can easily verify that this will be so provided that the special form of  $\psi_i$  doesn't involve any restriction upon the normalization of  $\psi_i$ ; i.e. if  $\psi_i$  is of the special form so also must  $c\psi_i$  be, where  $c$  is an arbitrary number (geometrically this means that the subspace of the  $\psi_i$ 's is to be a cone having the origin as vertex). We prove this as follows: if  $c\psi_i$  is of the special form  $\psi_i$  a permissible variation will be

$$\delta \psi_i = \epsilon \psi_i$$

where  $\epsilon$  is a small number; substituting in (10) we now have

$$i\hbar \bar{\epsilon} \phi, \frac{d\psi_i}{dt} = \bar{\epsilon} \phi, H \psi_i$$

or

$$i\hbar \phi, \frac{d\psi_i}{dt} = \phi, H \psi_i;$$

the conjugate complex equation is

$$-i\hbar \frac{d\phi}{dt} \psi_i = \phi, H \psi_i$$

and subtracting this from the above we get

$$\phi, \frac{d\psi_i}{dt} + \frac{d\phi}{dt} \psi_i = 0$$

so that  $\phi, \psi_i$  remains constant.

The method for non-stationary states actually includes the method for stationary states as a special case since if we take  $\psi_i$  such that

$$i\hbar \frac{d\psi_i}{dt} = E \psi_i$$

equation (9) becomes just the equation

$$\delta \phi, E \psi_i = \delta \phi, H \psi_i$$

that was found in the method applicable to stationary states.

We shall now apply the general method to the approximate solution of the problem of several interacting systems and in particular to that of several

interacting electrons. We take first of all the case of several interacting systems, not necessarily similar systems; let the set of commuting observables  $q_1$  describe the first system,  $q_2$  the second, ..., and  $q_n$  the  $n^{\text{th}}$ ; there is no homology between these sets of observables in the general case. We shall have an exact wave function  $(q_1, q_2, \dots, q_n |)$ ;

let us take the special form for the approximate wave function to be

$$\{f_1(q_1), f_2(q_2), \dots, f_n(q_n)\} \quad \text{which we shall write as } \prod_r f_r(q_r).$$

We first of all take the case of stationary states and apply our method of approximation; now

$$\delta\phi = \delta[\prod_r \bar{f}_r(q_r)] \quad ??$$

and so

$$\begin{aligned} \delta\phi, H\psi &= \sum_s \left\{ \delta \bar{f}_s(q'_s) \cdot \prod_{r \neq s} \bar{f}_r(q_r) \cdot \prod_{r \neq s} f_r(q_r) \right\} \\ &= \sum_s \left\{ \delta \bar{f}_s(q'_s) \cdot \prod_{r \neq s} \bar{f}_r(q_r) \cdot \prod_{r \neq s} f_r(q_r) \right\} \end{aligned}$$

where

$$(q'_s | H_s | q''_s) = \left\{ \prod_{r \neq s} \bar{f}_r(q_r) \cdot \prod_{r \neq s} f_r(q_r) \right\} (q'_s | H_s | q''_s) \left\{ \prod_{r \neq s} \bar{f}_r(q_r) \cdot \prod_{r \neq s} f_r(q_r) \right\}$$

This quantity is a function only of  $q'_s$  and  $q''_s$ ; we have carried out an integration for all the variables except these. Again we have

$$\delta\phi, E\psi = E \sum_s \left\{ \delta \bar{f}_s(q'_s) \cdot \prod_{r \neq s} \bar{f}_r(q_r) \cdot \prod_{r \neq s} f_r(q_r) \right\};$$

we may assume without any loss of generality that each of the  $f$ 's is individually normalized so that

$$\int \bar{f}_r(q_r) dq_r f_r(q_r) = 1.$$

Then we can carry out the integration in the previous equation for all the variables except  $q'_s$  and we get

$$\delta\phi, E\psi = E \sum_s \left\{ \delta \bar{f}_s(q'_s) \cdot f_s(q'_s) \right\}.$$

Thus from (7), equating coefficients of  $\delta \bar{f}_s$ , we have

$$\int (q'_s | H_s | q''_s) dq''_s f_s(q''_s) = E f_s(q'_s) \quad (11)$$

and these are our final equations for the individual functions  $f_s$ ; these equations say that each of the functions  $f_s$  must be an eigenfunction of the corresponding operator  $H_s$  belonging to the eigenvalue  $E$ . We have,

using the normalisation condition on the  $f$ 's,

$$E = \int \bar{f}_s(q'_s) d\tilde{q}_s' (q'_s | H_s | q_s'') dq_s'' \cdot f_s(q_s'')$$

which expresses  $E$  symmetrically for all the systems when we make use of the equation that defines  $(q'_s | H_s | q_s'')$ .

We can give a simple physical meaning to the above results; for we can interpret  $H$  as a Hamiltonian belonging to the  $s^{\text{th}}$  system alone; this Hamiltonian is obtained from the accurate Hamiltonian by a sort of averaging process applied to all systems except the  $s^{\text{th}}$  system. This simple picture was really thought of and the above equations obtained by Hartree from physical grounds long before their justification by the present method was obtained by Fock.

Let us now consider what happens in the case of non-stationary states; we have

$$\begin{aligned} i\hbar \delta \phi &= i\hbar \left( \sum_s \delta \bar{f}_s(q_s) \cdot \prod_{r \neq s} \bar{f}_r(q_r) \cdot \prod dq_r \cdot \sum_u \frac{d f_u(q_u)}{dt} \cdot \prod_{v \neq u} f_v(q_v) \right) \\ &= i\hbar \sum_s \int \delta \bar{f}_s(q_s) dq_s \cdot \frac{d f_s(q_s)}{dt} + \sum_s \sum_{u \neq s} a_u \int \delta \bar{f}_s(q_s) dq_s \cdot f_s(q_s), \end{aligned}$$

where

$$a_u = i\hbar \int \bar{f}_u(q_u) dq_u \cdot \frac{d f_u(q_u)}{dt},$$

provided that each  $f_s$  is normalised at the particular time that we are considering. Thus from equation (10), equating coefficients of  $\delta \bar{f}_s$ , we have

$$i\hbar \frac{d}{dt} f_s(q'_s) + \sum_{u \neq s} a_u f_u(q'_u) = \int (q'_s | H | q_s'') dq_s'' \cdot f_s(q_s'') \quad (12)$$

and these equations are the generalisation for the case of non-stationary states of the equations (11) that hold for stationary states. We have to

consider the meaning of the numbers  $a_u$ ; in the first place we can get

an expression for the sum of all the  $a$ 's; for multiplying (12) by  $\bar{f}_s(q'_s) dq'_s$  and integrating over  $q'_s$  we have at once

$$\sum_u a_u = \int \bar{f}_s(q'_s) dq'_s \cdot (q'_s | H | q_s'') dq_s'' \cdot f_s(q_s'')$$

and the right hand side is the same as the symmetrical form for E that we found for the case of stationary states; apart from this we can say nothing about the a's and our equations are accordingly to a certain degree arbitrary so that if we know the f's at a given time we cannot find their values at a later time. This degree of arbitrariness is just what we should expect since we can multiply the f's by numerical coefficients whose product is unity without altering the total wave function. It is possible to reduce the arbitrariness in the f's by insisting that they remain individually normalised for all time, but there will still be some arbitrariness left corresponding to the arbitrary numerical factors of modulus unity by which the f's may still be multiplied; we can show that this restriction upon the f's causes the a's to be real numbers; for we must now have

$$i\hbar \frac{d}{dt} \int \bar{f}_r(q_i') dq_i' f_r(q_i') = 0$$

or

$$i\hbar \int \frac{d\bar{f}_r(q_i')}{dt} dq_i' f_r(q_i') + i\hbar \int \bar{f}_r(q_i') dq_i' \frac{df_r(q_i')}{dt} = 0$$

which is just

$$-a_r + a_r = 0$$

so that  $a_r$  must be real.

The above theory is quite general; when we come to apply it to physical problems the Hamiltonian will be of the form

$$H = \sum_r U_r + \sum_r \sum_{s < r} V_{rs},$$

the first group of terms referring to the systems one at a time and the second group to the interactions between pairs of systems; interactions involving more than two particles do not occur in nature. In this case it is interesting to see what our general equations reduce to: we have now

$$(q_s' | H_s | q_s'') = (q_s' | U_s | q_s'') + \sum_{r \neq s} \delta(q_s' - q_s'') (r | U | r) + \sum_{r \neq s} (q_s' | V_{rs} | q_s'') + \sum_{r \neq s} \sum_{\substack{t < r \\ t \neq s}} \delta(q_s' - q_s'') (r | V_{rt} | r)$$



where

$$\begin{aligned} \langle r | U_r | r \rangle &= \iint \bar{f}_r(q'_r) dq'_r \cdot (q'_r | U_r | q''_r) dq''_r \cdot f_r(q''_r); \\ \langle q'_s | \beta_{rs} | q''_s \rangle &= \iint \bar{f}_r(q'_r) dq'_r \cdot (q'_r q'_s | V_{rs} | q''_r q''_s) dq''_r \cdot f_r(q''_r) \\ \text{and} \\ \langle r' | V_{rt} | r \rangle &= \iiint \bar{f}_r(q'_r) \bar{f}_s(q'_s) dq'_r dq'_s \cdot (q'_r q'_s | V_{rs} | q''_r q''_s) dq''_r dq''_s \cdot f_r(q''_r) f_s(q''_s). \end{aligned}$$

Also our expression for E can be written in this notation as

$$E = \sum_r \langle r | U_r | r \rangle + \sum_r \sum_{s < r} \langle rs | V_{rs} | rs \rangle.$$

Substituting these results in (11) we now have

$$\{ \langle s | U_s | s \rangle + \sum_{r \neq s} \langle rs | V_{rs} | rs \rangle \} f_s(q'_s) = \int (q'_s | U_s + \sum_{r \neq s} \beta_{rs} | q''_s) dq''_s \cdot f_s(q''_s).$$

This equation is an easy one to interpret physically; the operator  $\beta_{rs}$  in  $(V_s + \sum_{r \neq s} \beta_{rs})$  is the contribution to the Hamiltonian of the  $S^{th}$  system that arises from the interaction of the  $r^{th}$  system; it is just the value of the interaction energy of the  $r^{th}$  and  $S^{th}$  systems averaged for the  $r^{th}$  system assuming it to have the special state represented by the wave function  $f_r$ .

For the non-stationary states we have the equation

$$\begin{aligned} i\hbar \frac{d}{dt} f_s(q'_s) + \{ \langle s | U_s | s \rangle + \sum_{r \neq s} \langle rs | V_{rs} | rs \rangle - a_s \} f_s(q'_s) &= \\ &= \int (q'_s | V_0 + \sum_{r \neq s} \beta_{rs} | q''_s) dq''_s \cdot f_s(q''_s). \end{aligned}$$

This completes what we have to say about this general theory; the analysis is complicated but it is possible to see the physical meaning of each term that enters into it; the method is merely a process of averaging.

We shall now consider an improvement in this method that can be made in the case of electrons; for, the wave function of several electrons must be antisymmetric and we therefore cannot express it as a product of the form

$\prod_r f_r(q_r)$ . We shall use the notation that the operation A operating upon a function F of all the q's gives the result

$$A \{ F(q_1 \dots q_n) \} = \frac{1}{\sqrt{n!}} \sum_p [ \pm F(pq) ]$$

the positive sign being taken for even and the negative for odd permutations;

$A \{ F(q_1 \dots q_n) \}$  is therefore antisymmetrical.

The special form of the wave function that we shall now consider will

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$$A \{ \prod_r f_r(q_r) \}$$

which is just the previous special form of the wave function made antisymmetrical. The application of the method of approximation will be very complicated if we take a general Hamiltonian and we shall therefore only consider the case in which

$$H = \sum_r U_r + \sum_{r < s} V_{rs}$$

In a representation in which the  $q$ 's are diagonal  $U$  will have a representative  $(q'_r | U_r | q''_r)$  but since the  $q$ 's are homologous we need not specify which set we are using and may write the above representative merely as  $(q'_r | U | q''_r)$ ; in a similar way we may write the representative of  $V_{rs}$  as  $(q'_r q''_s | V | q'''_r q''''_s)$ .

In carrying out the computations involved in the method of approximation we must make as many simplifying assumptions as we can without loss of generality; one such assumption is that the  $f$ 's are normalized and orthogonal to each other; we therefore assume that the  $f$ 's satisfy

$$\int \bar{f}_s(q) dq f_r(q) = \delta_{rs}. \quad (13)$$

We can further assume without loss of generality for the case of antisymmetrical wave functions that the varied  $f$ 's will still satisfy these conditions; thus we assume that

$$\int \delta \bar{f}_s(q) dq f_r(q) = \delta_{rs}. \quad (14)$$

The following simple property of the operator  $A$  will be much used in the later work, namely, if  $F(q)$  and  $G(q)$  are any function of the  $q$ 's

$$\begin{aligned} A \{ F(q) \} \prod dq A \{ G(q) \} &= \sqrt{n!} \int F(q) \prod dq A \{ G(q) \} \\ &= \sqrt{n!} \int A \{ F(q) \} \prod dq G(q). \end{aligned}$$

This is easily seen to be true since on the left we have  $(n!)^2$  terms in the integrand of which only  $n!$  are different, each of these occurring  $n!$  times; this  $n!$  combines with the  $\frac{1}{\sqrt{n!}}$  that enters the definition of  $A$  to give just the  $\sqrt{n!}$  written above.

Let us first take the case of stationary states; our main work will consist in evaluating the quantity  $\delta\phi, H\psi$  and to do this we first consider the quantity  $\phi, H\psi$ , reduce it as far as possible by means of the relations (13) and then perform the variation; this is allowable since we have assumed that the varied  $f$ 's are still normalised and orthogonal. We have

$$\begin{aligned}\phi, H\psi &= \int \int A \{ \pi_r \bar{f}_r(q'_r) \} \pi dq'_r (q'_1 \dots q'_n | H | q''_1 \dots q''_n) \pi dq''_r A \{ \pi_u f_u(q''_u) \} \\ &= \int A \{ \{ \pi_r \bar{f}_r(q'_r) \} \pi dq'_r (q'_1 \dots q'_n | H | q''_1 \dots q''_n) \} \pi dq''_r A \{ \pi_u f_u(q''_u) \}, \\ &\quad (\text{since } H \text{ is symmetrical in the } q' \text{'s and } q'' \text{'s together}), \\ &= \sqrt{n!} \int \int \pi_r \bar{f}_r(q'_r) \pi dq'_r (q'_1 \dots q'_n | H | q''_1 \dots q''_n) \pi dq''_r A \{ \pi_u f_u(q''_u) \}\end{aligned}$$

and we can show that this reduces to

$$\begin{aligned}&\sum_s \left( \int \int \bar{f}_s(q'_s) dq'_s (q'_1 \dots q'_n | U | q''_1 \dots q''_n) dq''_s \bar{f}_s(q''_s) + \right. \\ &\quad \left. + \sum_r \sum_{s < r} \int \int \int \int \bar{f}_r(q'_r) \bar{f}_s(q''_s) dq'_r dq''_r (q'_1 \dots q'_n | U | q''_1 \dots q''_n) dq''_s dq''_r [f_r(q''_r) f_s(q''_s) - f_s(q''_s) f_r(q''_r)] \right) \\ &\text{for, we must have the representative of } U_s \text{ of the form}\end{aligned}$$

$$(q'_s | U_s | q''_s) \pi_{r \neq s} \delta(q'_r - q''_r)$$

and so for this part of the total Hamiltonian we can immediately perform the integration with respect to all the variables except  $q'_s$  and  $q''_s$  and we find that any permutation of the set A other than the identity will produce a zero integral on account of the conditions (13) and when we take this identity permutation term we obtain the  $3^{\text{th}}$  term of the first sum of the above result. The second term comes in a similar way except that now we have for each pair (r,s) <sup>two</sup> permutations that will not lead to a zero integral, namely the identity and the interchange of  $q'_r$  and  $q'_s$ , the remnants of these two terms being shown in the square parentheses in the second term.

We now make the variation upon  $\phi, H\psi$  and this leads at once to the result

$$\begin{aligned}\delta\phi, H\psi &= \sum_s \left( \int \int \delta \bar{f}_s(q'_s) dq'_s (q'_1 \dots q'_n | U | q''_1 \dots q''_n) dq''_s \bar{f}_s(q''_s) + \right. \\ &\quad \left. + 2 \sum_r \sum_{s < r} \int \int \int \int \bar{f}_r(q'_r) \delta \bar{f}_s(q''_s) dq'_r dq''_r (q'_1 \dots q'_n | U | q''_1 \dots q''_n) dq''_s dq''_r [f_r(q''_r) f_s(q''_s) - f_s(q''_s) f_r(q''_r)] \right).\end{aligned}$$

In simpler form we have

$$\delta \phi_i \cdot H \psi_i = \sum_s \left( \int \delta \bar{f}_s(q') dq' (q' | U + B - A | q'') dq'' f_s(q'') \right) \quad (15)$$

where B and A are two matrices defined by

$$(q'' | B | q'') = \sum_r \left( \int \bar{f}_r(q') dq' (q' q'' | V | q'' q'') \right) dq'' f_r(q'')$$

and

$$(q'' | A | q''') = \sum_r \left( \int \bar{f}_r(q') dq' (q' q'' | V | q''' q'') \right) dq' f_r(q'').$$

Now we want  $\delta \phi_i \cdot H \psi_i = 0$  for variations satisfying (14); this means

that the coefficients of  $\delta \bar{f}_s$  in (15) must be a linear combination of the

coefficients of  $\delta \bar{f}_s$  in the equations (14); so we have the conditions

$$\int (q' | U + B - A | q'') dq'' f_s(q'') = \sum_r a_{sr} \bar{f}_r(q'),$$

the  $a_{sr}$  being Lagrangian multipliers. These are our final results for

the stationary states; they are a little simpler than the corresponding ones

for the general case considered previously <sup>since</sup> we have the same operator operat-

ing upon all the f's. The term B corresponds to the  $\sum_r \beta_{rs}$  of the

general theory and we may say that B is the contribution to the Hamiltonian

of the  $s^{\text{th}}$  electron due to the interaction of all the electrons upon the

$s^{\text{th}}$  electron; it includes the interaction of the  $s^{\text{th}}$  electron with

itself and this isn't really right physically since it is quite meaningless

to talk of the interaction of an electron with <sup>its</sup> own field; but this is

taken account of by the term A which makes just the proper allowance for

the fact that there is no interaction of the electron with itself and which

also contains exchange terms which could not be found from ordinary physical

arguments.

For the case of non-stationary states we have to work out also the

quantity  $i \hbar \delta \phi_i \cdot \frac{d\psi_i}{dt}$ . The easiest way is to simplify  $i \hbar \phi_i \frac{d\psi_i}{dt}$

as far as possible by means of (13) and then to perform the variation; we

have

$$\begin{aligned}
 i\hbar \phi \frac{d\psi}{dt} &= i\hbar \left\{ A \{ \pi_r \bar{f}_r(q_r) \} \pi dq, A \left\{ \sum_s \frac{df_s(q_s)}{dt} \pi_{u \neq s} f_u(q_u) \right\} \right\} \\
 &= i\hbar \sqrt{n!} \int A \{ \pi_r \bar{f}_r(q_r) \} \pi dq \sum_s \left[ \frac{df_s(q_s)}{dt} \pi_{u \neq s} f_u(q_u) \right] \\
 &= i\hbar \sum_s \int \bar{f}_s(q) dq \frac{df_s(q)}{dt} \quad (\text{by (13)})
 \end{aligned}$$

and making the variation we have

$$i\hbar \delta \phi \frac{d\psi}{dt} = i\hbar \sum_s \int \delta \bar{f}_s(q) dq \frac{df_s(q)}{dt}.$$

Our condition is now that

$$i\hbar \delta \phi \frac{d\psi}{dt} = \delta \phi H \psi$$

where  $\delta \phi$  are subject to the conditions (14); so we get

$$i\hbar \frac{df_s(q')}{dt} + \sum_r b_{rs} f_r(q') = \int (q' | U + B - A | q'') dq'' f_s(q''), \quad (16)$$

the  $b_{rs}$  being the Lagrangian multipliers. We can obtain some information about the  $b_{rs}$  corresponding to the information we found for the  $a$ 's in the general theory; we can choose the  $b_{rs}$  so that the

$f$ 's always remain normalized and orthogonal and it is then easily seen that

this requires the  $b_{rs}$  considered as a matrix to be Hermitian; for, we

must have

$$\frac{d}{dt} \int \bar{f}_s(q) dq f_r(q) = 0,$$

that is

$$\int \frac{d\bar{f}_s(q)}{dt} dq f_r(q) + \int \bar{f}_s(q) dq \frac{df_r(q)}{dt} = 0$$

so that the matrix

$$\left[ i\hbar \int \bar{f}_s(q) dq \frac{df_r(q)}{dt} \right]$$

is Hermitian; but if we multiply (16) by  $\bar{f}_r$  and integrate with respect to

$q'$  we get

$$i\hbar \int \bar{f}_r(q') dq' \frac{df_s(q')}{dt} + b_{rs} = \int \bar{f}_r(q') dq' \int (q' | U + B - A | q'') dq'' f_s(q'');$$

now the right hand side is evidently a Hermitian matrix and we have just

shown that the first term on the left is so that it follows that  $b_{rs}$  forms

a Hermitian matrix. This condition corresponds to the condition that the

$a$ 's be real in the general theory.

We can collect up these equations and put them in a very much neater form by the use of the density function we introduced in the theory of the Gibbs ensemble: this will then give us an approximate extension of our previous theory of the Gibbs ensemble in order to take into account the interaction of the similar systems. We shall show that it is possible to express our results in terms of  $\rho$  alone; we have  $\rho$  defined by

$$(q' | \rho | q'') = \sum_r f_r(q') \bar{f}_r(q'')$$

and it thus contains all the information contained in the  $f$ 's that is invariant under those rotations in  $f$ -space that we considered when we previously discussed the quantity  $\rho$  for the case of antisymmetrical wave function. We

shall first express  $\frac{d\rho}{dt}$  in terms of  $\rho$  alone; we have

$$i\hbar \frac{d}{dt} (q' | \rho | q'') = \sum_s \left\{ i\hbar \frac{d f_s(q')}{dt} \bar{f}_s(q'') + i\hbar f_s(q') \frac{d \bar{f}_s(q'')}{dt} \right\}$$

and substituting the value we have found for  $df/dt$  this becomes equal to

$$\sum_s \left\{ \left[ -\sum_r \bar{f}_r(q') \right] + \int (q' | V+B-A | q''') dq''' f_s(q''') \bar{f}_s(q'') \right\} \\ - \sum_s f_s(q') \left\{ \left[ -\sum_r \bar{f}_r(q'') \right] + \int (q'' | V+B-A | q''') dq''' \bar{f}_s(q''') \right\};$$

the terms in square brackets cancel each other since  $\bar{f}_{rs}$  is Hermitian, so that the Lagrangian multipliers disappear from the expression for  $\frac{d}{dt} (q' | \rho | q'')$ ;

this is just what we should expect since the Lagrangian multipliers express the arbitrariness in the  $f$ 's due to the fact that their values at a given time do not completely determine their values at a later time (owing to the possibility of applying the rotations mentioned above) and there is no such arbitrariness in  $\rho$ . We have, then

$$i\hbar \frac{d}{dt} (q' | \rho | q'') = \int (q' | V+B-A | q''') dq''' (q''' | \rho | q'') - \\ \int (q' | \rho | q''') dq''' (q'' | V+B-A | q''),$$

since  $(q' | V+B-A | q'')$  is Hermitian; the  $f$ 's have now completely disappeared explicitly from our expression for  $\frac{d}{dt} (q' | \rho | q'')$  and we can write the result symbolically in the form

$$i\hbar \frac{d}{dt} \rho = (U+B-A)\rho - \rho(U+B-A);$$

and so it appears that this  $\rho$  satisfies the usual type of equation that a density function satisfies, the Hamiltonian being  $(U+B-A)$ ; there is this difference, however, that  $(U+B-A)$  is not a given quantity but is itself a linear function of  $\rho$ , as is seen when we express B and A in terms of

$\rho$ ; for, from the definitions of these quantities we get at once

$$(q''|B|q'') = \iint (q'q''|V|q'''q''') dq' dq''' (q'''|\rho|q')$$

and

$$(q'|A|q''') = \iint (q'q''|V|q'''q''') dq' dq''' (q''|\rho|q').$$

The f's have now disappeared completely from all our formulas and we have expressed everything in terms of  $\rho$ .

If we take the interaction between electrons to be the ordinary Coulomb interaction we have

$$(q'q''|V|q'''q''') = \delta(q'-q''')\delta(q''-q''') \frac{e^2}{r(q'q''')}$$

where  $r(q'q''')$  is the distance between the points  $q'$  and  $q'''$  (taking these to be cartesian coordinates and ignoring the spin). The matrices B and A

now take the values

$$(q'|B|q'') = e^2 \delta(q'-q'') \int \frac{(q'''|\rho|q''')}{r(q'q''')} dq'''$$

and

$$(q'|A|q'') = e^2 \frac{(q'|\rho|q'')}{r(q'q'')}.$$

The quantity  $(q'''|\rho|q''')$  that enters the formula for  $(q'|B|q'')$  is a diagonal element of  $\rho$  and therefore gives the probable density at the point  $q'''$  so that if we suppose that we have a distribution of electricity given by this density, the integral  $e^2 \int \frac{(q'''|\rho|q''')}{r(q'q''')} dq'''$  is just the classical potential at the point  $q'$  that would be produced by this distribution, and the matrix

$(q'|B|q'')$  therefore represents the contribution to the Hamiltonian of this potential. There is no such simple meaning for the quantity A. The Hamiltonian for the motion of  $\rho$  now consists of a part, U, that is the

Hamiltonian of a single electron without interaction, plus a part, B, that is due to the whole distribution of charge, minus a part, A, that is a correction term for the term B so as to cancel the interaction of the electron with itself and which also contains exchange terms due to the antisymmetry of the approximate wave function.

To make the approach to the classical theory we may neglect A and treat  $q$  and  $p$  as classical variables and we then get just the classical picture in phase space; the equation  $i\hbar \frac{d\rho}{dt} = (U+B-A)\rho - \rho(U+B-A)$  means that the classical  $\rho$  must be 0 or 1 for each point of phase space so that there will be a sharp boundary between those parts of phase space where  $\rho = 1$  and those parts where  $\rho = 0$ . If we took the spin into account we should find that  $\rho$  must have one or other of the values 0, 1, 2 at each point of phase space ( $\rho$  is here the diagonal sum over the spin variables). Let us see how a boundary between parts of phase space for which  $\rho$  has different values will move; the equation

$$i\hbar \frac{d\rho}{dt} = (U+B-A)\rho - \rho(U+B-A)$$

must now be written in the P. B. form, neglecting A, as

$$\frac{d\rho}{dt} = [U+B, \rho].$$

It is convenient to consider that the value of  $\rho$  changes continuously, though very rapidly, at the boundary in order that we may differentiate at these places. Let the boundary be given by

$$F(p, q, t) = 0;$$

we may now regard  $\rho$  as a function of  $F$ , that is

$$\rho = r(F),$$

since the value of  $\rho$  at any point depends on which side of the boundary the point is, and this is determined by whether  $F$  is positive or negative at the point. We now have

$$\frac{d\rho}{dt} = \frac{d\rho}{dF} \frac{\partial F}{\partial t}$$

but



$$\frac{dp}{dt} = [U+B, f(F)] \stackrel{-88-}{=} \frac{df}{dF} [U+B, F]$$

by the usual rule for a P. B. involving a function of a function; so comparing these two values of  $\frac{dp}{dt}$  we get

$$\frac{\partial F}{\partial t} = [U+B, F];$$

in particular, for a stationary state we have  $\partial F / \partial t = 0$  so that the boundary must satisfy

$$[U+B, F] = 0.$$

This method is easily applied to get a rough idea of the distribution of the electrons in an atom having many electrons. For a state of minimum energy there will be no region for which  $\rho = 1$ . The electrons will all crowd in to the region of phase space of lowest energy and will saturate this region with  $\rho = 2$  everywhere in it.

It is significant that the quantity  $(q'q''|V|q'''q^{iv})$  always occurs in the combination

$$\{(q'q''|V|q'''q^{iv}) - (q'q''|V|q^{iv}q''')\}$$

in all the equations that have physical meaning; for example although  $V$  doesn't enter in this way in the definitions of  $B$  and  $A$  it is only  $B - A$  that enters the physical equations and this quantity contains  $V$  only in the above combination. This fact is true not only for the approximate method but also for the exact theory as we can easily see since if  $\psi$  be antisymmetrical the value of the quantity

$$(\sum_{r < s} V_{rs}) \psi$$

will depend only upon the value of  $\{(q'q''|V|q'''q^{iv}) - (q'q''|V|q^{iv}q''')\}$ . This means that any new  $V$  such that the value of  $\{(q'q''|V|q'''q^{iv}) - (q'q''|V|q^{iv}q''')\}$  is the same as before will give the same physical results as before: this shows the unsatisfactory position of the present theory regarding the interaction between electrons since we assume more about the interaction than is necessary to give the results; a satisfactory theory would give the value of  $\{(q'q''|V|q'''q^{iv}) - (q'q''|V|q^{iv}q''')\}$  without giving the value of

$$\{(q'q''|V|q'''q''') + (q'q''|V|q''q''')\}.$$

We shall now consider the other kind of systems of similar particles that is of importance, namely that kind for which only symmetrical wave functions occur in nature. The important practical physical application is to the theory of light quanta.

The basis of the theory of symmetrical wave functions is a certain transformation that one can make; we have a wave function

$$(q_1 \dots q_n |)$$

such that if we permute any of the  $q$ 's we may suppose that we still get the same point in the domain of the wave function; we can therefore make a passage to a different set of coordinates that will be symmetrical in the  $q$ 's. Let  $q^{(a)}$  be any one of the permissible values of the  $q$ 's and write

$$n_a = \text{the number of } q\text{'s equal to } q^{(a)};$$

if there are  $n$  particles we must thus have  $\sum_a n_a = n$ . We can now regard each point of the domain of the wave function as specified by the  $n$ 's instead of the  $q$ 's; they are just a set of symmetrical function of the  $q$ 's. We may now write the symmetrical wave function  $(q_1 q_2 \dots q_n |)$  as a wave function of the form  $(n_a n_b \dots |)$  and we shall have to find the appropriate transformation that connects them; the number of variables,  $n$ , is equal to the number of eigenvalues of  $q$ , which is in general infinite. The transformation in question is of a rather trivial kind since each <sup>point</sup> of the domain of the wave function  $(q_1 \dots q_n |)$  corresponds to a point of the domain of the wave function  $(n_a n_b \dots |)$ ; and we must therefore have

$$(q_1 q_2 \dots q_n |) = C (n_a n_b \dots |)$$

where  $C$  is a number, where we regard the  $n$ 's as functions of the  $q$ 's; we take the connection between the two wave functions to be such that if one is normalized the other will be also and this means that we must have

$$\sum_{q_1 \dots q_n} |(q_1 q_2 \dots q_n |)|^2 = \sum_{n_a n_b \dots} |(n_a n_b \dots |)|^2;$$

now each term of the summation on the left corresponds to one term of the summation on the right but one term of the latter summation corresponds to several terms in the summation on the left; let us count the number of terms that correspond to a given term on the right; it is the same as the number of ways we can choose the  $q$ 's so that  $n_a$  of them are  $q^{(a)}$ ,  $n_b$  are  $q^{(b)}$ , and so on, and this is just

$$n! / n_a! n_b! \dots$$

Hence we must have

$$|(q_1 q_2 \dots q_n)|^2 = \frac{n_a! n_b! \dots}{n!} |(n_a n_b \dots)|^2$$

so that

$$(q_1 q_2 \dots q_n) = \left( \frac{n_a! n_b! \dots}{n!} \right)^{1/2} (n_a n_b \dots),$$

(neglecting the possibility of an arbitrary phase).

The next question we should like to consider is the way in which we are to make a passage from a symmetrical observable represented in terms of the  $q$ 's to its representative in terms of the  $n$ 's. It is easiest to work with the transformation of wave functions, for, if  $H$  be a symmetrical operator, and  $\psi$  a symmetrical state  $H\psi$  will be a symmetrical state, say  $\psi_1$ , and we know both sides of the equation

$$H\psi = \psi_1$$

in terms of both the  $q$  - and the  $n$  - representation; from which, since  $\psi$  is arbitrary, we may infer the  $n$ -representative of  $H$ . We shall apply this to the special case in which  $H$  is of the form

$$H = \sum_r U_r$$

where  $U_r$  is a function only of the variables of the  $r^{\text{th}}$  particle.

In the  $q_r$  -representation for the  $r^{\text{th}}$  particle  $U_r$  will have matrix elements,

$$(q_r' | U_r | q_r''),$$

and we may write this as

$$(q^{(a)} | U | q^{(b)})$$

since  $U$  is the same for each particle; we shall also write it as  $U_{ab}$  for the sake of brevity. If we take a representation for the whole assembly the representative of  $U_r$  will be given by

$$(q_1' q_2' \dots q_n' | U | q_1'' q_2'' \dots q_n'') = (q_r' | U_r | q_r'') \delta_{q_1' q_1''} \delta_{q_2' q_2''} \dots \delta_{q_n' q_n''}$$

in which  $\delta_{q_r' q_r''}$  is omitted from the set of Kronecker  $\delta$ 's on the right.

Let us now take an arbitrary  $\Psi$  having the representatives

$$(q_1' \dots q_n' |) \quad \text{and} \quad (n_a n_b \dots |) \quad \text{respectively in terms of the } q\text{- and } n\text{-representations. The equation}$$

$$\Psi = H \Psi$$

in the  $q$ -representation is

$$(q_1' \dots q_n' | 1) = \sum_r (q_r' | U_r | q_r') (q_1' q_2' \dots q_n' |) + \sum_r \sum_{q_r'' \neq q_r'} (q_r' | U_r | q_r'') (q_1' q_2' \dots q_{r-1}' q_r'' q_{r+1}' \dots q_n' |);$$

now  $U_{aa}$  occurs  $n_a$  times in the first summation and the  $U_{cd}$  term in the second summation (that is the term for which  $q_r' = q^{(c)}$ ,  $q_r'' = q^{(d)}$ ) occurs  $n_a$  times so that in terms of the  $n$ -representation our equation becomes

$$\left( \frac{n_a! n_b! \dots}{n!} \right)^{1/2} (n_a n_b \dots | 1) = \left( \frac{n_a! n_b! \dots}{n!} \right)^{1/2} (n_a n_b \dots |) \sum_a n_a U_{aa} + \sum_{c \neq d} \left( \frac{n_a! n_b! \dots (n_c-1)! (n_d+1)! \dots}{n!} \right)^{1/2} (n_a n_b \dots n_c-1, n_d+1, \dots |) n_c U_{cd};$$

the wave function  $(n_a n_b \dots n_{c-1}, n_{d+1}, \dots |)$  arises because the corresponding wave function of the  $q$ -representation differs from  $(q_1' q_2' \dots q_n' |)$  only in that  $q_r''$  replaces  $q_r'$  so that the number of particles in state  $q_r' (= q^{(c)})$  is reduced by unity and the number in  $q_r'' (= q^{(d)})$  increased by unity; it is then necessary to give the wave function its appropriate normalisation factor, namely  $\left( \frac{n_a! n_b! \dots (n_c-1)! (n_d+1)! \dots}{n!} \right)^{1/2}$ , so that we obtain

the result given above. This result simplifies to

$$(n_a n_b \dots | 1) = \sum_a n_a U_{aa} (n_a n_b \dots | 1) + \sum_{c \neq d} n_c^{1/2} (n_d + 1)^{1/2} (n_a n_b \dots n_c - 1, n_d + 1, \dots | 1),$$

and we can say that H will be just that operator that changes  $(n_a n_b \dots | 1)$  into  $(n_a n_b \dots | 1)$ .

In order to see what this equation means we shall write it symbolically; a suitable symbolical notation is suggested by the properties of the harmonic oscillator, for  $n_a$  etc. can only take on the values 0, 1, 2, 3, ... and these, as we have seen, are precisely the eigenvalues of

$$J = \frac{1}{2} (p^2 + q^2) - \frac{1}{2}$$

when

$$q p - p q = i.$$

We shall want to introduce some kind of variable that will be a sort of canonical conjugate to an  $n$  and to do this we shall make use of the known theory of the harmonic oscillator; for we may regard  $J$  as like an action variable of the classical theory and as having therefore a canonical conjugate like an angle variable. In a representation in which  $J$  is diagonal it is given by the matrix

$$J = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 & \dots \\ 0 & 1 & 0 & 0 & 0 & 0 & \dots \\ 0 & 0 & 2 & 0 & 0 & 0 & \dots \\ 0 & 0 & 0 & 3 & 0 & 0 & \dots \\ 0 & 0 & 0 & 0 & 4 & 0 & \dots \\ 0 & 0 & 0 & 0 & 0 & 5 & \dots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix};$$

we introduce the quantity  $e^{i\omega}$  defined by being represented in this representation by the matrix,

$$e^{i\omega} = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 & \dots \\ 1 & 0 & 0 & 0 & 0 & 0 & \dots \\ 0 & 1 & 0 & 0 & 0 & 0 & \dots \\ 0 & 0 & 1 & 0 & 0 & 0 & \dots \\ 0 & 0 & 0 & 1 & 0 & 0 & \dots \\ 0 & 0 & 0 & 0 & 1 & 0 & \dots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix},$$

having ones just below the main diagonal and all other elements zero;  $\omega$  is then the quantum analogue of the angle variable canonical to  $J$ . The complex conjugate of  $e^{i\omega}$ , namely  $e^{-i\omega}$ , is given in the representation

by

$$e^{-i\omega} = \begin{pmatrix} 0 & 1 & 0 & 0 & 0 & \dots \\ 0 & 0 & 1 & 0 & 0 & \dots \\ 0 & 0 & 0 & 1 & 0 & \dots \\ 0 & 0 & 0 & 0 & 1 & \dots \\ 0 & 0 & 0 & 0 & 0 & \dots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}$$

These matrices that we have introduced have certain simple properties that should be noted: firstly we have

$$e^{-i\omega} e^{i\omega} = 1,$$

but

$$e^{i\omega} e^{-i\omega} \neq 1$$

being equal to the unit matrix bordered on top and at the left by a row and a column of zeros. We also have the relations

$$e^{i\omega} J = (J-1) e^{i\omega}$$

and

$$e^{-i\omega} J = (J+1) e^{-i\omega},$$

and in general

$$e^{i\omega} f(J) = f(J-1) e^{i\omega}$$

and

$$e^{-i\omega} f(J) = f(J+1) e^{-i\omega}$$

Let us now introduce  $w$ 's canonically conjugate to our  $n$ 's,  $w_a$  being the conjugate of  $n_a$  and so on;  $e^{i w_a}$  will be represented by a matrix that is diagonal with regard to  $n_b$  if  $b \neq a$  and that is like the  $e^{i\omega}$  above for the elements corresponding to the eigenvalues of  $n_a$ , and similar statements hold for all the other  $n$ 's and  $w$ 's; it follows that  $e^{i w_a}$  and  $e^{i w_b}$  will commute. The equation we are considering may now be written symbolically in the form

$$H = \sum_a n_a U_{aa} + \sum_{c \neq d} n_c^{1/2} (n_d + 1)^{1/2} e^{i(w_c - w_d)} U_{cd},$$

giving  $H$  in terms of the new variables  $n$  and their conjugate  $w$ 's; we may

write this also in the form

$$H = \sum_{c,d} n_c^{1/2} (n_d + 1 - \delta_{cd})^{1/2} U_{cd} e^{i(w_c - w_d)}$$

$$= \sum_{c,d} n_c^{1/2} e^{i w_c} U_{cd} (n_d + 1)^{1/2} e^{-i w_d}$$

By the same argument we could carry through this transformation for a more general observable such as  $\sum_{r < s} V_{rs}$ , where  $V_{rs}$  refers to two particles; in this particular case we find the result

$$\sum_{r < s} V_{rs} = \sum_{a,b,c,d} n_a^{1/2} e^{i\omega_a} n_b^{1/2} e^{i\omega_b} V_{ab,cd} (n_c+1)^{1/2} e^{-i\omega_c} (n_d+1)^{1/2} e^{-i\omega_d},$$

where  $V_{ab,cd}$  is the matrix element of  $V$  that refers to  $q^{(a)}$ ,  $q^{(b)}$  for the row and  $q^{(c)}$ ,  $q^{(d)}$  for the column.

We can write these transformations in a concise form by introducing new variables  $\{$  defined by

$$\{_a = (n_a+1)^{1/2} e^{-i\omega_a} = e^{-i\omega_a} n_a^{1/2}$$

and the conjugate complex

$$\bar{\{}_a = n_a^{1/2} e^{i\omega_a} = e^{i\omega_a} (n_a+1)^{1/2}$$

the  $\{_a$  correspond to the quantity  $(p + iq)$  that enters the analysis of the harmonic oscillator. In terms of the  $\{$  we now have

$$\sum_r U_r = \sum_{ab} \bar{\{}_a U_{ab} \{_b$$

and

$$\sum_{r < s} V_{rs} = \sum_{abcd} \bar{\{}_a \bar{\{}_b V_{ab,cd} \{_c \{_d.$$

There is one point of interest to be noted; we might change from

the  $q$ -representation to a new representation for which, say,  $Q$ 's were diagonal; the wave function  $(q_1 q_2 \dots q_n | )$  would then be written  $(Q_1 Q_2 \dots Q_n | )$ ; we may now introduce new  $n$ 's defined by

$$n_A = \text{the number of } Q\text{'s having the value } Q^A,$$

and so on, and then introducing  $\omega_A$  etc conjugate to these  $n_A$ 's we could define  $\{_A$ 's for this representation; what is the connection between these  $\{_A$ 's and the old  $\{_a$ 's? It turns out to be quite a simple one; for we have

$$\sum_r U_r = \sum_{ab} \bar{\{}_a U_{ab} \{_b = \sum_{AB} \bar{\{}_A U_{AB} \{_B$$

for arbitrary  $U$ ; but we know that

$$U_A^{(B)} = \sum_{ab} (Q^A | q^a) U_{ab} (q^b | Q^B),$$

the  $(q | Q)$  and  $(Q | q)$  being transformation functions for a single particle of the assembly, and substituting in the previous relation we get

$$\sum_{ab} \bar{f}_a U_{ab} f_b = \sum_{AB} \bar{f}_A (Q^A | q^a) U_{ab} (q^b | Q^B) f_B$$

which gives, on equating coefficients of  $U_{ab}$ ,

$$\left. \begin{aligned} \bar{f}_a &= \sum_A \bar{f}_A (Q^A | q^a) \\ f_a &= \sum_B (q^b | Q^B) f_B \end{aligned} \right\} \quad (17)$$

and also

which are the transformation laws for the  $f$ 's.

There are one or two other properties of the  $f$ 's that are to be noted; we have from the definition of the  $f$ 's that

$$\left. \begin{aligned} \sum_a \bar{f}_a f_a &= n_a + 1 \\ \sum_a f_a \bar{f}_a &= n_a \end{aligned} \right\} \quad (18)$$

and

these following since  $e^{i\omega} e^{-i\omega}$  acts essentially like the unit matrix when multiplying  $n^{1/2}$  on account of the fact that  $n^{1/2}$  has the form

$$n^{1/2} = \begin{pmatrix} 0 & 0 & 0 & 0 & - \\ 0 & 1 & 0 & 0 & - \\ 0 & 0 & \sqrt{2} & 0 & - \\ 0 & 0 & 0 & \sqrt{3} & - \end{pmatrix},$$

zero being the first element of the main diagonal.

Again, since the  $f$ 's are observables they will have equations of motion of the form

$$i\hbar \dot{f} = fH - Hf$$

where  $H$  is a Hamiltonian. Let us assume that  $H$  is here of the form  $\sum_r U_r$ , this being the case for light quanta since there is no interaction between them; we then have as the equation of motion for  $f_a$ ,

$$i\hbar \dot{f}_a = \sum_b U_{ab} f_b, \quad (19)$$

since  $f_a$  commutes with all  $f_b$  and with all  $f_c$  except  $f_a$ .



These equations, (17) and (19), are like the equations that govern the motion of one of the particles of the assembly considered by itself, the only difference being that the wave function,  $(q^a |)$ , of a single particle is an ordinary function whilst the  $\mathcal{F}'$ 's are operators. Let us consider the limiting case in which there is an infinite number of particles in each state so that the  $n$ 's are infinite; in virtue of (18) we may now consider the  $\mathcal{F}'$ 's as commuting with each other so that they may be taken as ordinary numbers; if we normalise the  $(q^a |)$  that refers to a single particle by taking

$$\sum_a (q^a |)(|q^a) = n$$

instead of unity,  $n$  being the total number of particles, so that  $|(q^a |)|^2$  is then the probably number of particles in the state  $q^a$ , i.e.  $n_a$ , we may in the limit look on this as corresponding to the equations (18) so that the equations for the  $\mathcal{F}'$ 's and for the  $(q^a |)$ 's are exactly similar. This result is rather remarkable since the  $\mathcal{F}'$ 's represent an Einstein-Bose assembly whilst the  $(q^a |)$ 's represent an assembly of classically independent particles and these are two different assemblies physically. There is, however, one important difference between the mathematics involved in the two cases, for we know all about a classical assembly if we know how many of the systems are in a given state, the phases of the  $(q^a |)$ 's being therefore indeterminate, (if we do have to introduce some phases in the course of the mathematics we must average over all possible values for these phases in order to obtain a physical result); for an Einstein-Bose assembly, however, to know all that is permissible about the assembly we must be given the phases as well as the number of systems in each state as the  $\mathcal{F}'$ 's are observables; the phases can have specified numerical values for a given state of an Einstein-Bose assembly. If the  $n$ 's are not all large the difference between the two assemblies of course becomes greater since the  $\mathcal{F}'$ 's are not just numbers like the  $(q^a |)$ 's but are observables satisfying definite commutability relations; the

process of passing from the  $(q^a)'s$  to the  $\{f^a's\}$  is often referred to as a process of second quantisation.

This is the essential underlying theory for a system of similar particles that are representable only by symmetrical wave functions; can we obtain a similar theory for the case of a system of particles having only antisymmetrical wave functions? This is possible and has been worked out by Jordan; we shall proceed to consider the case of antisymmetrical wave functions; we introduce variables,  $n_a, n_b, \dots$ , as before defined by

$n_a$  = the number of  $q$ 's having the value  $q^{(a)}$ , etc,

but now, since  $(q_1 q_2 \dots q_n)$  is antisymmetrical, the  $n$ 's may take on only the values 0 or 1. We must now try to set up a wave function of the form  $(n_a n_b \dots |)$ ; to each set of values of the  $q$ 's there will be one definite set of values for the  $n$ 's and for each set of values of the  $n$ 's there will be one set of values for the  $q$ 's, but we shall not know in what order these  $q$ 's will occur in the wave function; all we may infer, therefore, is that

$$(q_1 q_2 \dots q_n) = \pm (n_a n_b \dots |),$$

(a normalizing coefficient not being necessary in the present case). To get over this ambiguity of sign we make some arbitrary convention concerning the order of the  $q$ 's, as, say,

$$q^1, q^2, q^3, \dots, q^u, \text{ (u = number of eigenvalues for } q),$$

and make the convention that if the  $q$ 's occur in the wave function in the same order as they occur in this series we take the positive sign.

We can now follow through the same analysis as we did in the symmetrical case and we find that if

$$\psi \rightarrow (n_a n_b \dots |)$$

and

$$\psi_i = \sum_r U_r \psi$$

we get

$$\psi_1 = \sum_c n_c U_{cc} (n_a n_b \dots n_{c-1}, n_{c+1}, \dots) + \sum_c \sum_{d \neq c} \pm U_{cd} (n_a n_b \dots n_{c-1}, n_{d+1}, \dots),$$

where we make the convention that if either  $(n_{c-1})$  or  $(n_{d+1})$  have any other value than 0 or 1 the corresponding wave function on the extreme right is to be counted as zero. This equation is similar to that that arose in the symmetrical case except for the ambiguity of sign and the absence of certain numerical coefficients; we have to take the positive sign if the set of  $q$ 's corresponding to the set of  $n$ 's,  $n_a, n_b, \dots, n_{c-1}, n_{d+1}, \dots$ , that is the set of  $q$ 's that differs from the set in the initial wave function,  $(q_1 q_2 \dots q_n)$ , by having  $q^c \rightarrow q^d$ , can be brought into the arbitrary ordering we have decided upon by an even number of permutations, and if not we must take the negative sign. If, then, in the arbitrary series  $q^1, q^2, \dots$ , we find that  $q^c$  and  $q^d$  are separated by an even number of  $q$ 's which actually occur in the set  $q_1, \dots, q_n$  corresponding to  $n_a, n_b, \dots$  we must take the positive sign and if by an odd number the negative sign. Thus we have the + sign when  $\sum_e n_e$  is even, the sum being taken over all  $e$  for which  $q^{(e)}$  lies between  $q^{(c)}$  and  $q^{(d)}$ , and the - sign otherwise.

It is possible to express the above equation in operational form in a manner analogous to that employed in the symmetrical case; we must introduce operators conjugate to (i.e. that do not commute with) the  $n$ 's; we note that the  $n$ 's are analogous to operators that occur in the description of the spin of the electron, for, since  $n_a$  has the eigenvalues 0 and 1, the quantity  $(2n_a - 1)$  has the eigenvalues  $\pm 1$ ; hence we may write

$$(2n_a - 1) = -\sigma_z a,$$

where  $\sigma_z a$  is a spin operator, with similar equations for  $b, c, \dots$ ,  $\sigma_z a$  and  $\sigma_z b$  commuting. As the conjugate operators to these  $\sigma_z$ 's we take  $\frac{1}{2}(\sigma_x - i\sigma_y)$  and  $\frac{1}{2}(\sigma_x + i\sigma_y)$ , which, when we take

the usual representation for  $\sigma_x$ ,  $\sigma_y$  and  $\sigma_z$ , are given by

$$\frac{1}{2}(\sigma_x - i\sigma_y) = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$$

and  $\frac{1}{2}(\sigma_x + i\sigma_y) = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}$ ;

these operators have the properties that

$$\frac{1}{2}(\sigma_{xc} - i\sigma_{yc})(n_a n_b \dots n_c |) = (n_a n_b \dots, n_c - 1, \dots |)$$

and

$$\frac{1}{2}(\sigma_{xc} + i\sigma_{yc})(n_a n_b \dots n_c |) = (n_a n_b \dots, n_c + 1, \dots |),$$

where, of course, in the first case we must have  $n_c = 1$  and in the second  $n_c = 0$  or otherwise the right hand side must be taken as zero. Using these operators our equation may be written in the form

$$\sum_r U_r = \sum_c n_c U_{cc} + \sum_c \sum_{d \neq c} \pm U_{cd} \frac{1}{2}(\sigma_{xc} - i\sigma_{yc})(\sigma_{xd} + i\sigma_{yd}).$$

This corresponds to the similar equation that was obtained for the symmetrical case; the  $\pm$  sign is an ugly feature of this equation and we shall introduce new operators in order to get rid of it. We define  $\mathcal{F}_d$  by

$$\mathcal{F}_d = \sigma_{z1} \sigma_{z2} \dots \sigma_{zd} \cdot \frac{1}{2}(\sigma_{xd} + i\sigma_{yd})$$

where the  $\sigma_z$ 's that occur as factors to the left correspond in order to the  $q$ 's of our arbitrary series as far as the term  $q^d$ . The conjugate complex of  $\mathcal{F}_c$  may be written as

$$\overline{\mathcal{F}_c} = \frac{1}{2}(\sigma_{xc} - i\sigma_{yc}) \cdot \sigma_{z1} \sigma_{z2} \dots \sigma_{zc}$$

since the  $\sigma_z$ 's commute. We now have, since  $\sigma_z^2 = 1$ ,

$$\overline{\mathcal{F}_c} \mathcal{F}_d = \frac{1}{2}(\sigma_{xc} - i\sigma_{yc}) \cdot \left\{ \begin{matrix} \sigma_{z,c+1} \sigma_{z,c+2} \dots \sigma_{zd} \\ \sigma_{z,d+1} \sigma_{z,d+2} \dots \sigma_{zc} \end{matrix} \right\} \cdot \frac{1}{2}(\sigma_{xd} - i\sigma_{yd})$$

where the upper line in the curly parentheses is to be taken if  $c < d$  and the lower if  $d < c$ . Since

$$\sigma_{zd} \cdot \frac{1}{2}(\sigma_{xd} + i\sigma_{yd}) = \frac{1}{2}(i\sigma_{yd} + \sigma_{xd})$$

and

$$\frac{1}{2}(\sigma_{xc} - i\sigma_{yc}) \sigma_{zc} = \frac{1}{2}(-i\sigma_{yc} + \sigma_{xc})$$

we may write the above formula as

$$\bar{\xi}_c \xi_d = \frac{1}{2} (\sigma_{xc} - i \sigma_{yc}) \left\{ \sigma_{z,c+1} \sigma_{z,c+2} \dots \sigma_{z,d-1} \right\} \frac{1}{2} (\sigma_{xd} - i \sigma_{yd})$$

and we may now consider the curly parenthesis as being on the right of the factor  $\frac{1}{2} (\sigma_{xd} - i \sigma_{yd})$  since each term of it commutes with this factor; Now the eigenvalues of each  $\sigma_z$  are  $\pm 1$  being  $-1$  if the corresponding  $n$  is 1 and  $+1$  if the corresponding  $n$  is 0; so if there is an even number of  $n$ 's between  $n_c$  and  $n_d$  equal to unity the curly parenthesis will produce a positive sign and if an odd number a negative sign; this is just the rule we had for determining the correct sign to use in our previous equation for  $\sum_r U_r$  so that we may now write it in terms of the  $\xi$ 's as

$$\sum_r U_r = \sum_c n_c U_{cc} + \sum_c \sum_{d \neq c} U_{cd} \bar{\xi}_c \xi_d$$

which is our final formula for this transformation; it is these  $\xi$ 's that are to be regarded as the real analogues of the  $\xi$ 's of the symmetrical case; they have rather interesting properties; we notice that

$$\xi_c \xi_d + \xi_d \xi_c = 0 \quad \text{if } c \neq d$$

since, for example, if  $c > d$  there will be a factor  $\sigma_{zd}$  in the expression for  $\xi_c$  which will anticommute with the factor  $\frac{1}{2} (\sigma_{xd} + i \sigma_{yd})$  that enters  $\xi_d$  and all the other factors will commute. Also we have

$$\xi_c^2 = 0$$

since  $(\sigma_{xc} + i \sigma_{yc})^2 = 0$  and hence we may combine these two results into the single formula

$$\xi_c \xi_d + \xi_d \xi_c = 0;$$

it follows that we also have

$$\bar{\xi}_c \bar{\xi}_d + \bar{\xi}_d \bar{\xi}_c = 0.$$

We may compare these results with corresponding results that arose in the symmetrical case, namely

$$\xi_c \xi_d - \xi_d \xi_c = 0$$

and

$$\bar{\xi}_c \bar{\xi}_d - \bar{\xi}_d \bar{\xi}_c = 0.$$

Again, we have in the same way

$$\sum_c \sum_d + \sum_d \sum_c = 0 \quad \text{if } c \neq d$$

but

$$\begin{aligned} \sum_c \sum_c &= \frac{1}{4} (\sigma_{xc} - i \sigma_{yc}) (\sigma_{xc} + i \sigma_{yc}) \\ &= \frac{1}{2} (1 - \sigma_{zc}) = n_c, \end{aligned}$$

(which we compare with the corresponding

$$\sum_c \sum_c = n_c$$

of the symmetrical case),

and

$$\sum_c \sum_c = \frac{1}{2} (1 + \sigma_{zc}) = 1 - n_c,$$

(which we compare with the corresponding

$$\sum_c \sum_c = 1 + n_c$$

of the symmetrical case),

so that we have

$$\sum_c \sum_c + \sum_c \sum_c = 1$$

which combines with the previous result to give

$$\sum_c \sum_d + \sum_d \sum_c = \delta_{cd};$$

the corresponding formula for the symmetrical case is

$$\sum_c \sum_d - \sum_d \sum_c = \delta_{cd}.$$

We thus see that there is a very close correspondence between the formalism of symmetrical and antisymmetrical assemblies, the difference lying only in changes of sign, although the analysis by which our results were obtained was quite different in the two cases. The similarity between the two cases is further brought out by the fact that we can write  $H$  for the antisymmetrical case in the form

$$H = \sum_{a,b} \sum_a U_{ab} \sum_b$$

which is exactly the same as the form we had in the symmetrical case.

This Jordan theory for the antisymmetrical wave functions has not been applied practically to the case of electrons; it is not convenient to work with in practice since it involves so many variables; it is, however, of great interest theoretically on account of the way in which the results we obtain correspond to those of the symmetrical case.

We now go back to the symmetrical case and apply the theory to the particular case of light quanta interacting with an atom; this involves our making a slight generalisation since the previous theory <sup>applied</sup> to the case of only an assembly of similar particles. The generalisation is to make it apply to an assembly interacting with some other system, for example an assembly of photons interacting with an atom. The total Hamiltonian will be of the form

$$H = H_p + \sum_r U_r$$

where  $H_p$  refers to the atom and  $U_r$  is the proper energy of a light quantum together with its interaction energy with the atom. We take a set of commuting variables  $\{q\}$  to describe the atom, and then the representative of  $U$  will be

$(\{q'\} | U | \{q''\})$  and since we have called  $q', q''$  etc.  $q^a, q^b$  etc., we may write this as  $(\{q^a\} | U | \{q^b\})$  or as  $(\{q^a\} | U_{ab} | \{q^b\})$  which we regard as a matrix in  $\{q^a\}$  and  $\{q^b\}$ .

We can now proceed to introduce  $\{q\}$  as before and we shall obtain exactly the same results as in the previous symmetrical case except for the one difference that the  $U_{ab}$  are no longer pure numbers but are functions of the variables that describe the atom; since the  $U$ 's commute with the  $\{q\}$ 's our previous result for  $\sum_r U_r$  can be taken over directly for the present case and gives

$$H = H_p + \sum_{ab} \{q^a\} U_{ab} \{q^b\}.$$

It is necessary to make one further generalisation; the total number of photons is not conserved since an atom may emit or absorb a photon; our theory of Einstein-Bose assemblies didn't apply to this case but the necessary modification is quite trivial; we merely postulate the existence of some new state, the zero state, such that when the photon is in the zero state it cannot be observed at all; if a photon is absorbed by an atom we

say that it jumps into the zero state and if it is emitted we say that it jumps from the zero state into some other state; we assume that the number of photons in the zero state is infinite.

To fix our ideas we wish to say what our  $q$ 's shall be: we shall take  $q$  to be such that when  $q = q^a$  the particle is in a stationary state, which means that  $q$  is a constant of the motion; for a single particle the constants of the motion are the components of the momentum and so we shall take the  $q$ 's to be the components of the momenta of the light quanta. We must also introduce one more variable, having only two eigenvalues, in order to express the state of polarisation of the light quantum; we take this new variable to refer to the states of linear polarisation rather than to the states of circular polarisation since the former leads to slightly simpler formulae.

We can now write down explicitly what the form of  $U$  will be; it must consist of the proper energy of the photon together with a certain term that describes its interaction with the atom. The proper energy is known to be proportional to the frequency and we thus have

$$U_{ab} = h \nu_a \delta_{ab} + V_{ab}$$

where  $V_{ab}$  is still unknown. We have now

$$H = H_P + H_Q + H_R$$

where  $H_P$  is the Hamiltonian of the atom alone,

$H_R$  is the Hamiltonian of the radiation field alone, namely  $\sum_a n_a h \nu_a$ ,

and  $H_Q$  is the interaction term, given by

$$H_Q = \sum_{ab} n_a^{1/2} e^{i i \omega_a t} V_{ab} (n_b + 1)^{1/2} e^{-i i \omega_b t}.$$

We should now like to separate out of  $H_Q$  the terms that refer to the zero state and treat them apart from the other terms. Using 0 to denote the zero state the corresponding terms in  $H_Q$  are



$$\sum_b n_b^{1/2} e^{i\omega_b} V_{ob} (n_b+1)^{1/2} e^{-i\omega_b} + \sum_a n_a^{1/2} e^{i\omega_a} V_{ao} (n_a+1)^{1/2} e^{-i\omega_a}$$

In order to deal with finite terms here we must introduce new coefficients instead of  $V_{ob}$  and  $V_{ao}$  that differ from them by infinite factors; we write

$$n_b^{1/2} e^{i\omega_b} V_{ob} = \overline{V}_b$$

and then

$$(n_a+1)^{1/2} e^{-i\omega_a} V_{ao} = V_a,$$

where  $\overline{V}_b$  is the conjugate complex of  $V_b$ , and now the zero state terms in  $H_Q$  may be written as

$$\sum_a \{ V_a n_a^{1/2} e^{i\omega_a} + \overline{V}_a (n_a+1)^{1/2} e^{-i\omega_a} \}.$$

The introduction of the zero state has thus allowed terms involving the  $e^{i\omega_a}$ 's and  $e^{-i\omega_a}$ 's singly to enter the Hamiltonian instead of only terms containing the combinations  $e^{i\omega_a} e^{-i\omega_b}$  etc.. This is what we should expect since it is only the latter type of operator involving the  $\omega$ 's that conserves the number of photons.

The total interaction energy is now

$$H_Q = \sum_{ab} n_a^{1/2} e^{i\omega_a} V_{ab} (n_b+1)^{1/2} e^{-i\omega_b} + \sum_a \{ V_a n_a^{1/2} e^{i\omega_a} + \overline{V}_a (n_a+1)^{1/2} e^{-i\omega_a} \},$$

where now  $a$  and  $b$  are taken over all states except the zero state.

To get a theory of the interaction of light quanta with an atom all that remains to be done is to determine what the interaction matrix  $V_{ab}$  shall be. The only way we have for determining the Hamiltonians that we have used so far is to make use of the analogy of the classical theory, and we can do this in the present case; we have to pass to the limiting case in which the  $n$ 's become infinite and then compare the result with the classical result. The real reason why this works is that an assembly of light quanta is dynamically equivalent to a set of harmonic oscillators, this equivalence

still applying when we have an interacting atom. (The number of harmonic oscillators is very large since we have one for each state of the photons, including incidentally, the zero state). It is this that gives us the reconciliation between the wave and particle aspects of light since we can regard waves in a continuous medium as equivalent to a set of harmonic oscillators corresponding to the Fourier components of the wave.

Now our states are such that the momentum has a definite value so that we ought to take the case of a continuous range of eigenvalues and must therefore pass from the sums to integrals; this would in general be quite complicated; we should in fact have to set up a new kind of mathematics because of the fact that the number of the variables  $n$  and  $w$  is equal to the number of points on a line; however, we don't really need to do this in the general case since we are only concerned with the case in which the  $n$ 's are large in which case we can neglect the non-commutability of the  $n$ 's and  $e^{i n w}$ ; we can make the passage from sums to integrals by assuming that the discrete eigenvalues for  $h$  lie very closely together and then make a transition to a different notation that refers only to certain ranges  $dh$  of momentum space rather than to discrete eigenvalues  $h^a$ . For this purpose we have to introduce quantities  $\sigma_a$  that give the density of these eigenvalues in momentum space; we say that  $\sigma_a$  is the number of discrete eigenvalues of  $h$  per unit volume of momentum space about the point  $h^a$ ; this  $\sigma_a$  is therefore infinitely large in the limit and so we introduce  $\eta_a$  given by

$$\eta_a = n_a \sigma_a$$

which is the number of light quanta per unit of momentum space about  $h^a$ . If we take polarisation into account we must say that  $\eta_a$  is the number of photons per unit of momentum space for a fixed polarisation.

We now have to use different matrix elements,  $(h' | V | h'')$ , referring to the case of continuous ranges of eigenvalues for the momentum; these will

differ from the previous ones referring to discrete eigenvalues for the momentum only in the introduction of a weight function; in the discrete theory the weight is  $\sigma_a d\hbar$  ; in the continuous case we should like to attach the weight  $d\hbar$  itself and so we must change the weight function by the factor  $\sigma$  ;

we can apply our general rule for changing the weight function and we get

$$V_{ab} (\sigma_a \sigma_b)^{1/2} = (\hbar^a |V| \hbar^b).$$

For the  $V_a$  , since the weight attached to the zero state is not changed, we have the transformation

$$V_a \sigma_a^{1/2} = (\hbar^a |V| 0)$$

and

$$\overline{V}_a \sigma_a^{1/2} = (0 | V | \hbar^a).$$

We can now rewrite our interaction energy, taking the n's to be large, in the form

$$H_Q = \sum_a \left\{ (\hbar^a |V| 0) \eta_a^{1/2} e^{i\omega_a} + (0 | V | \hbar^a) \eta_a^{1/2} e^{-i\omega_a} \right\} \sigma_a^{-1} \\ + \sum_{ab} (\hbar^a |V| \hbar^b) \eta_a^{1/2} \eta_b^{1/2} e^{i(\omega_a - \omega_b)} \sigma_a^{-1} \sigma_b^{-1}$$

or, in terms of integrals, as

$$H_Q = \iint \left\{ (\hbar^a |V| 0) \eta_a^{1/2} e^{i\omega_a} + (0 | V | \hbar^a) \eta_a^{1/2} e^{-i\omega_a} \right\} d\hbar_a \\ + \iint (\hbar^a |V| \hbar^b) \eta_a^{1/2} \eta_b^{1/2} e^{i(\omega_a - \omega_b)} d\hbar_a d\hbar_b, \quad (20)$$

since  $\sigma_a^{-1}$  is now the same as  $d\hbar_a$  ; these integrals also imply summation over both states of the polarisation.

We may now proceed to compare this expression with the analogous one of the classical theory and so obtain the values of the matrix elements of V. We shall merely indicate the lines along which it is necessary to proceed in order to bring the classical expression for the interaction energy into a form in which it can be compared with the quantum form, (20).

We may consider the classical electromagnetic field to consist of waves that we can resolve into plane waves, which means that we can express it in the form of a Fourier integral; we have

$$\underline{E} = \int \underline{E}_h \cos\left(\frac{(\underline{x}, \underline{h})}{h} - 2\pi \nu_h t - \gamma_h\right) d\mathbf{h}$$

and

$$\underline{H} = \int \underline{H}_h \cos\left(\frac{(\underline{x}, \underline{h})}{h} - 2\pi \nu_h t - \gamma_h\right) d\mathbf{h},$$

$\underline{E}$  and  $\underline{H}$  being the electric and magnetic force vectors, and  $\gamma_h$  the phases,  $\nu_h$  the frequencies and  $\underline{E}_h$  and  $\underline{H}_h$  the amplitudes of the Fourier components.  $\underline{E}_h$  and  $\underline{H}_h$  are of equal magnitude and each is perpendicular to the other and to the vector  $\underline{h}$ . The total energy is

$$\frac{1}{8\pi} \int (\underline{E}^2 + \underline{H}^2) d\mathbf{x} = \frac{h^3}{8\pi} \int \underline{E}_h^2 d\mathbf{h},$$

the integrals being taken over the whole of space.

Now since the energy of a light quantum is  $h\nu$ , the total energy must be  $\int \eta_h h\nu_h d\mathbf{h}$  and so we must have the connection

$$\frac{h^3}{8\pi} \int \underline{E}_h^2 d\mathbf{h} = \int \eta_h h\nu_h d\mathbf{h} \quad (21)$$

between  $\underline{E}_h$  and the number of light quanta per volume element of momentum space; this gives at once the relation

$$\underline{E}_h^2 = \frac{8\pi}{h^2} \nu_h \eta_h.$$

We must also introduce the vector potential  $\underline{A}$  which we express in the form

$$\underline{A} = \int \underline{A}_h \sin\left(\frac{(\underline{x}, \underline{h})}{h} - 2\pi \nu_h t - \gamma_h\right) d\mathbf{h} \quad (22)$$

where  $\underline{A}_h$  is connected with  $\underline{E}_h$  by the relation

$$\underline{A}_h^2 = \left(\frac{c}{2\pi \nu_h}\right)^2 \underline{E}_h^2 = \frac{2c^2}{\pi h^2 \nu_h} \eta_h \text{ from (21).} \quad (23)$$

Let us for simplicity make the assumption that the atom has only one electron or at least that it has only one electron that is of importance for the present discussion; then the classical expression for the interaction energy of this atom with the field of radiation will be the total energy of the atom when the field is present minus the energy of the atom when there is no field so that this interaction energy is equal to

$$\begin{aligned} \frac{1}{2m} \left( \underline{p} + \frac{e}{c} \underline{A} \right)^2 - \frac{1}{2m} \underline{p}^2 \\ = \frac{e}{mc} (\underline{p}, \underline{A}) + \frac{e^2}{2mc^2} \underline{A}^2 \\ = \frac{e}{c} (\underline{\dot{x}}, \underline{A}) - \frac{e^2}{2mc^2} \underline{A}^2, \end{aligned} \quad (24)$$

since  $\underline{p} = m \underline{\dot{x}} - \frac{e}{c} \underline{A}$ .

Let us write

$$\omega_{\underline{p}} = - \frac{(\underline{x}, \underline{p})}{\hbar} + 2\pi \nu_{\underline{p}} t + \gamma_{\underline{p}} + \frac{\pi}{2} \quad (25)$$

so that (22) becomes

$$\underline{A} = \int \underline{A}_{\underline{p}} \cos \omega_{\underline{p}} d\underline{p}; \quad (26)$$

the quantities  $\omega_{\underline{p}}$  increase uniformly with the time and are of the same nature as the  $\omega$ 's we introduced in the quantum theory of photons being the angle variables corresponding to the components of the harmonic oscillations of the Fourier expansion. Substituting in (24) from (26) we find that the classical interaction energy may be written in the form

$$\frac{e}{c} \int (\underline{\dot{x}}, \underline{A}_{\underline{p}}) \cos \omega_{\underline{p}} d\underline{p} - \frac{e^2}{2mc^2} \iint (\underline{A}_{\underline{p}}, \underline{A}_{\underline{p}'}) \cos \omega_{\underline{p}} \cos \omega_{\underline{p}'} d\underline{p} d\underline{p}'$$

and using the value of  $\underline{A}_{\underline{p}}$  given by (23) this becomes

$$\begin{aligned} \frac{e}{\hbar} \int \left( \frac{2}{\pi \nu_{\underline{p}}} \right)^{1/2} \eta_{\underline{p}}^{1/2} \underline{\dot{x}}_{\underline{p}} \cdot \frac{1}{2} (e^{i\omega_{\underline{p}}} + e^{-i\omega_{\underline{p}}}) d\underline{p} \\ - \frac{e^2}{\pi m \hbar} \iint \left( \frac{1}{\nu_{\underline{p}} \nu_{\underline{p}'}} \right)^{1/2} \eta_{\underline{p}}^{1/2} \eta_{\underline{p}'}^{1/2} \cos \theta_{\underline{p}\underline{p}'} \cdot \frac{1}{4} (e^{i\omega_{\underline{p}}} + e^{-i\omega_{\underline{p}}}) (e^{i\omega_{\underline{p}'}} + e^{-i\omega_{\underline{p}'}}) d\underline{p} d\underline{p}', \end{aligned} \quad (27)$$

where  $\underline{\dot{x}}_{\underline{p}}$  denotes the scalar product of  $\underline{\dot{x}}$  with the unit vector along  $\underline{A}_{\underline{p}}$  and is thus the components of  $\underline{\dot{x}}$  in this direction, and where  $\theta_{\underline{p}\underline{p}'}$  is the angle between the electric vectors of the components  $\underline{p}$  and  $\underline{p}'$ .

We now compare the two expressions (20) and (27), that we have obtained for the interaction energy of the atom with the radiation field. The single integral terms in the two expressions will coincide if we choose the matrix elements  $(\underline{p}|V|0)$  and  $(0|V|\underline{p})$  to be such that

$$(h|V|0) = (0|V|h) = \frac{e}{h} \left( \frac{1}{2\pi\nu_h} \right)^{\frac{1}{2}} \dot{x}_h. \quad (28)$$

The double integral terms are not similar in the two cases since there is nothing in (20) to correspond to the terms in (27) containing quantities like  $e^{i(\omega_h + \omega_{h'})}$  and  $e^{-i(\omega_h + \omega_{h'})}$  if we wish the other terms of the double integral in (27) to coincide with the terms of the double integral of (20) we must choose the matrix elements  $(h|V|h')$  to be such that

$$(h|V|h') = \frac{-e^2}{2\pi m h^2} \left( \frac{1}{\nu_h \nu_{h'}} \right)^{\frac{1}{2}} \cos \theta_{hh'}.$$

The extra terms in (27) are not important physically and can be neglected in the ordinary applications; they correspond to the emission or absorption of two light quanta simultaneously which processes are not physically important; however the existence of these terms means that the foregoing theory of photons has not been as complete as it might and we could actually get terms in (20) that would correspond to these extra terms in (27) if we took the interaction energy of the assembly of photons with the atom to contain terms that refer simultaneously to two light quanta.

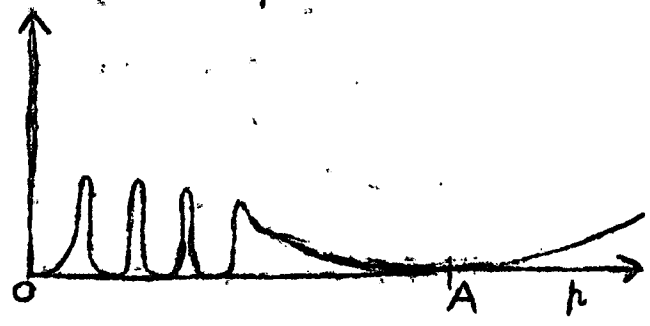
The above is the essential theory of the light quantum and it shows how we can obtain explicitly the interaction energy between a light quantum and an atom. Our interaction energy, obtained by considering a large number of photons, can now be applied to the case of a single photon interacting with an atom. The quantum interaction energy for a single photon is not at all like any classical expression; the matrix elements  $(h|V|h')$  are given by an entirely different analytical formula from that giving the matrix elements  $(0|V|h)$  and  $(h|V|0)$  so that we cannot hope to be able to express the whole matrix in terms of canonical coordinates and momenta; it should be remembered that  $(0|V|h)$  and  $(h|V|0)$  are not matrix elements really but are functions of the observable describing the atom; we should really introduce the commuting variables  $\{$  describing the atom and should replace the equation (28) by

$$(f|V|0f') = \frac{e}{h} \left( \frac{1}{2\pi\nu_f} \right)^{1/2} (f|\dot{x}_f|f')$$

but the notation we have been using is quite unambiguous if we remember this point.

We can now work out the problems of the absorption, emission and scattering of a photon by an atom; there is one difficulty in the working out of this theory since the wave equation with this kind of interaction energy is not really convergent and we therefore cannot give an exact meaning to the Hamiltonian; we can, however, still operate with it and get sensible results since it possesses a property of semi-convergence; if we plot the importance of  $(0|V|h)$  in the wave equation against increasing  $h$  we obtain

a curve containing several sharp peaks initially, as shown, followed by a decline and a subsequent slow rise to infinity; the peaks give the resonance frequencies of the atom the  $(0|V|h)$  being



Very important for these frequencies. In practice, at least for frequencies corresponding to visual light, we can cut off the interaction energy at some value of  $h$ , such as at the point A in the diagram, so that all the resonance frequencies are retained and the infinite part to the right of A is ignored.

We shall now consider Heisenberg's development of this theory of radiation to make it into a field theory. E and H have at present no meaning in the quantum theory and Heisenberg has given a theory in which we can introduce electric and magnetic vectors into the quantum theory and in which we can give commutability relations between them. This part of the theory can easily be made relativistic since we can treat our Fourier components

as harmonic oscillators to obtain the commutability relations and by making the Fourier resolution in a relativistic way we can obtain commutability relations that will be relativistically invariant. Physically  $\underline{E}$  and  $\underline{H}$  at one point ought to commute with  $\underline{E}$  and  $\underline{H}$  at another point at the same time, since the principle of relativity implies that no effect can travel with velocity greater than that of light and thus a measurement of  $\underline{E}$  or  $\underline{H}$  at one point at a given time cannot disturb the measurement of  $\underline{E}$  or  $\underline{H}$  at another point at the same time so that we must expect commutation between  $\underline{E}$  and  $\underline{H}$  at one point and  $\underline{E}$  and  $\underline{H}$  at another. We actually find that this is the case in the Heisenberg theory if the two points are a finite distance apart, but not if they are an infinitesimal distance apart. Our problem is to find the general commutability relations in connecting the field quantities at a particular time. If our theory is to be complete we must know the commutability relations connecting the field quantities at different times but if we combine our limited information with the equations of motion we can infer the more general commutability relations. It is therefore sufficient to work with one particular time and this does not mean that our theory is not really relativistic.

For time  $t = 0$  we may write

$$\underline{E}(x) = \int \underline{E}_k \cos\left(\frac{(x, k)}{r} - y_k\right) dk$$

and

$$\underline{H}(x) = \int \underline{H}_k \cos\left(\frac{(x, k)}{r} - y_k\right) dk$$

and we have also the relation

$$\underline{E}_k^2 = \frac{8\pi}{h^2} y_k \eta_k$$

we want to regard  $\eta$  and  $y$  as in some way conjugates since  $\eta$  describes the strength of a particular oscillation and  $y$  describes its phase; we cannot, however, have a relation of the type

$$\eta_k y_k - y_k \eta_k = \text{constant}$$

since the  $k$ 's have a continuous range of values and we must have



$$\eta_{h'} \eta_{h''} - \eta_{h''} \eta_{h'} = 0$$

if  $h' \neq h''$  however closely  $h'$  and  $h''$  be together. We therefore pass to the case of discrete eigenvalues very close to each other; we take  $\sigma_h$  as the number of eigenvalues per unit of momentum space and then we may write our formulae in the form

$$\underline{E} = \sum_h \underline{E}_h \cos \left( \frac{(x, h)}{\hbar} - \gamma_h \right) \sigma_h^{-1}$$

and

$$\underline{H} = \sum_h \underline{H}_h \cos \left( \frac{(x, h)}{\hbar} - \gamma_h \right) \sigma_h^{-1}$$

with  $\eta$  given by

$$\eta_h = n_h \sigma_h.$$

To pass over to the quantum theory we only have to assume that  $n_h$  and  $\gamma_h$  satisfy the quantum conditions

$$n_h e^{i\gamma_h} = e^{i\gamma_h} (n_h + 1),$$

with the conditions that  $\eta_{h'}$  and  $e^{i\gamma_{h''}}$  commute if  $h' \neq h''$ . These conditions are quite definite in the discrete case and we have no difficulty at all in applying them.

Let us now express  $\underline{E}$  and  $\underline{H}$  in terms of the  $n$ 's and the  $\gamma$ 's; we have, writing  $\alpha_h$  to denote the unit vector in the direction of  $\underline{E}_h$ , and  $\beta_h$  for that in the direction  $\underline{H}_h$ ,

$$\underline{E}_h = \frac{2}{\hbar} (2\pi\nu_h)^{1/2} (n_h \sigma_h)^{1/2} \alpha_h$$

and

$$\underline{H}_h = \frac{2}{\hbar} (2\pi\nu_h)^{1/2} (n_h \sigma_h)^{1/2} \beta_h,$$

and substituting in our expression for  $\underline{E}$  we obtain

$$\underline{E} = \frac{1}{\hbar} \sum_h (2\pi\nu_h)^{1/2} \alpha_h n_h^{1/2} \left[ e^{i(x, h)/\hbar} e^{-i\gamma_h} + e^{-i(x, h)/\hbar} e^{i\gamma_h} \right] \sigma_h^{-1/2},$$

but this formula does not make  $\underline{E}$  a real observable and so it cannot be correct for the quantum theory and must be modified in such a way as to become Hermitian;

this can be done if we merely write it as

$$\underline{E} = \frac{1}{\hbar} \sum_h (2\pi\nu_h)^{1/2} \alpha_h \left[ e^{i(x, h)/\hbar} e^{-i\gamma_h} n_h^{1/2} + e^{-i(x, h)/\hbar} n_h^{1/2} e^{i\gamma_h} \right] \sigma_h^{-1/2}.$$

$\alpha_p$  above.

introduce the following notation;

Em.

commutability relations between  $E_\ell(x')$  and  $E_m(x'')$  ; our formula for

$$\underline{C}(x)$$

becomes

$$\underline{\underline{C}}(x) = \frac{1}{h}$$

and so we have, since

over 100

$$\mathcal{E}_\ell(x') \mathcal{E}_m(x'') - \mathcal{E}_m(x'') \mathcal{E}_\ell(x') =$$

Now the  $\hbar$  refers to the polarisation as well as to the momentum; we first of all sum over the two states of the polarisation; let us suppose we have fixed a direction of motion for the photon, which must be perpendicular to  $\alpha$  and  $\beta$ ; when we sum for both states of the polarisation we have to sum only the part

$\alpha_{\ell e} \alpha_{\ell m}$  of the above formula since these are the only quantities that have to do with the state of polarisation; we write  $\gamma$  for the unit vector in the direction of the vector  $\ell$ ;  $\alpha$  and  $\beta$  are each perpendicular to  $\gamma$  and to each other so that we have to sum for the two cases  $\alpha = \alpha$  and  $\alpha = \beta$  thus getting

$$\sum_{\text{polarisation}} \alpha_{\ell e} \alpha_{\ell m} = \alpha_{\ell e} \alpha_{\ell m} + \beta_{\ell e} \beta_{\ell m} \\ = \cos \theta_{\ell m} - \gamma_{\ell e} \gamma_{\ell m}$$

since  $\alpha_{\ell e}$ ,  $\beta_{\ell e}$  and  $\gamma_{\ell e}$  etc. are just the direction cosines of the directions  $\ell$  and  $m$  referred to  $\alpha, \beta$  and  $\gamma$  as axes. We now have to substitute this value for the effect of summation over the polarisation into our expression above and then to sum for all values of the momentum of the photon; we can turn this sum into an integral again and we see at once that this integral vanishes since the integrand is an odd function of  $\ell$ . It follows that

$$E_{\ell}(x') E_m(x'') - E_m(x'') E_{\ell}(x') = 0.$$

A similar result holds for the components of the magnetic field. The remaining problem is to determine the commutability relations connecting  $E_{\ell}(x')$

with  $H_m(x'')$ ; we have

$$E_{\ell}(x') H_m(x'') - H_m(x'') E_{\ell}(x') = \begin{cases} \text{the same ex-} \\ \text{pression as for the} \\ \text{case of } E_{\ell}(x') \\ \text{and } E_m(x'') \text{ except} \\ \text{that } \alpha_{\ell e} \text{ is replaced} \\ \text{by } \beta_{\ell e} \end{cases}$$

and writing this expression in the form of integrals it becomes

$$\frac{2\pi}{\hbar^2} \int \sum_{\text{polarisation}} v_{\ell} \alpha_{\ell e} \beta_{\ell m} \{ e^{i(\underline{x}' - \underline{x}'', \ell)/\hbar} - e^{-i(\underline{x}' - \underline{x}'', \ell)/\hbar} \} d\ell.$$

Now when we sum over the polarisation we have the two cases  $\alpha = \alpha$ ,  $\beta = \beta$

and  $\alpha \rightarrow \beta$ ,  $\beta \rightarrow -\alpha$ , the latter being the

result of turning the former polarisation through a right-angle, and so we get

$$\sum_{\text{polarisation}} \alpha_{\ell e} \beta_{\ell m} = \alpha_{\ell e} \beta_{\ell m} - \beta_{\ell e} \alpha_{\ell m}.$$

If we now want to continue without having to consider very complicated formulae

we must specify what  $\ell$  and  $m$  are to be. In the first case let us take  $\ell$  and  $m$

to be parallel; then  $\sum \alpha_{\ell e} \beta_{\ell m}$  vanishes so that we have the result that  $E_{\ell}(x')$

and  $\mathcal{H}(x'')$  commute if they are parallel. The other interesting case is when  $\mathcal{E}(x')$  and  $\mathcal{H}(x'')$  are perpendicular and if we also know the commutability relations for this case we shall know the commutability relations concerning  $\mathcal{E}$  and  $\mathcal{H}$  for arbitrary directions; let us, then, take  $l$  and  $m$  perpendicular and each perpendicular to the direction  $n$ . Then we have

$$\sum_{\text{polarisation}} \alpha_{\ell} \beta_{\ell m} = \alpha_{\ell} \beta_{\ell m} - \beta_{\ell} \alpha_{\ell m} = \chi_{\ell m}$$

since  $(\alpha \beta \gamma)$  and  $(l m n)$  form two sets of mutually perpendicular triads.

Also instead of  $\chi_{\ell m}$  we can write  $\hbar z / |\hbar|$ , where we take  $n$  to be the direction of the  $z$ -axis which is allowable since  $n$  is a fixed direction. Substituting

in our integral we now have

$$\begin{aligned} \mathcal{E}(x') \mathcal{H}(x'') - \mathcal{H}(x'') \mathcal{E}(x') &= \\ &= \frac{2\pi c}{\hbar^2} \int \frac{\hbar_z}{|\hbar|} \left\{ e^{i\{(x'-x'')\hbar_x + (y'-y'')\hbar_y + (z'-z'')\hbar_z\}/\hbar} - e^{-i\{(x'-x'')\hbar_x + (y'-y'')\hbar_y + (z'-z'')\hbar_z\}/\hbar} \right\} d\hbar \\ &= \frac{2\pi c}{\hbar^2} \hbar^2 \delta(x'-x'') \delta(y'-y'') \int \hbar_z \left\{ e^{i(z'-z'')\hbar_z/\hbar} - e^{-i(z'-z'')\hbar_z/\hbar} \right\} d\hbar_z, \\ &\text{(since } \frac{\hbar_z}{|\hbar|} = \frac{c}{\hbar} \text{ because the momentum of a light quantum is equal to } \hbar\nu/c, \text{ and} \\ &\text{since we have the result } \int e^{i\alpha\hbar/\hbar} d\hbar = \hbar \delta(\alpha) \end{aligned}$$

$$= \frac{2\pi c}{\hbar} \delta(x'-x'') \delta(y'-y'') (-2i) \hbar \hbar \delta'(z'-z'')$$

(since, by differentiating the integral in the previous parenthesis with respect

$$\text{to } \alpha, \text{ we have } \frac{i}{\hbar} \int \hbar e^{i\alpha\hbar/\hbar} d\hbar = \hbar \delta'(\alpha) )$$

$$= -2i\hbar c \delta(x'-x'') \delta(y'-y'') \delta'(z'-z'')$$

$$= -2i\hbar c \frac{\partial}{\partial z'} \delta(x'-x''),$$

where

$$\delta(x'-x'') = \delta(x'-x'') \delta(y'-y'') \delta(z'-z'') ;$$

the direction  $z$  is here to be understood as the direction that is perpendicular to both  $l$  and  $m$ . Using suffixes  $x, y$  and  $z$  to denote the directions  $l$  and  $m$  these commutability relations are

$$[E_x(x'), H_y(x'')] = -4\pi c \frac{\partial}{\partial z'} \delta(x' - x'')$$

and similarly

$$[E_x(x'), H_z(x'')] = +4\pi c \frac{\partial}{\partial y'} \delta(x' - x'')$$

with similar results for the other components of  $\underline{E}$  and  $\underline{H}$ .

We shall now show that these commutability relations lead to Maxwell's equations for the field if we take as the Hamiltonian just the classical quantity for the energy, that is if we take

$$H = \frac{1}{8\pi} \int (\underline{E}^2 + \underline{H}^2) d\underline{x};$$

for the motion of  $\underline{E}$  we have, for example,

$$\begin{aligned} \frac{d}{dt} E_x(x') &= [E_x(x'), H] \\ &= \frac{1}{8\pi} \int [E_x(x'), E^2(x'') + H^2(x'')] d\underline{x}'', \end{aligned} \quad (29)$$

(since "[ ]" and " $\int d\underline{x}''$ " are commuting operations).

Now the components of  $E^2(x'') + H^2(x'')$  all commute with

$E_x(x')$  except  $H_y(x'')$  and  $H_z(x'')$ ; and we have

$$\begin{aligned} [E_x(x'), H_y^2(x'')] &= 2[E_x(x'), H_y(x'')] H_y(x'') + H_y(x'') [E_x(x'), H_y(x'')] \\ &= -8\pi c \frac{\partial}{\partial z'} \delta(x' - x'') H_y(x''), \end{aligned}$$

(since the P.B.'s are ordinary numbers and thus commute with  $H_y(x'')$ ),

and integrating over all space with regard to  $\underline{x}''$  we get

$$\int [E_x(x'), H_y^2(x'')] d\underline{x}'' = -8\pi c \frac{\partial}{\partial z'} H_y(x');$$

similarly we obtain the result

$$\int [E_x(x'), H_z^2(x'')] d\underline{x}'' = +8\pi c \frac{\partial}{\partial y'} H_z(x');$$

and substituting these two results in (29) we obtain

$$\frac{d}{dt} E_x = -c \frac{\partial}{\partial z} H_y + c \frac{\partial}{\partial y} H_z$$

which is just one of the Maxwell equations. The other Maxwell equations

came out in the same way and this shows that the commutability relations

we have obtained for the field components do lead to the correct equations

of motion if we take the above Hamiltonian. Attempts have been made to

bring the potentials into this theory but it doesn't seem to be possible to give any commutability relations for them which will be consistent with the above commutability relations for the field quantities and which will be relativistically invariant. This is as far as the radiation theory will really go satisfactorily.

We shall now consider briefly the question of relativistic quantum mechanics; the whole of the original theory of states and observables was relativistic when we considered the four-dimensional meaning of a state and the relativistic meaning of an observable. One of the main difficulties in obtaining a satisfactory relativistic theory is to find suitable relativistic observables to work with; in the case of a system containing more than one particle we have no really satisfactory relativistic theory at present; if we take as our observables the positions of the particles at a particular instant of time we find that they are very unrelativistic quantities and their transformation laws are so complicated that we have very little chance of obtaining a relativistic theory in terms of them. The only case in which a theory that is at all satisfactory has been given is when we have only one particle.

We take the wave equation in the absence of an electromagnetic field (gravitational effects are so very small that they may be neglected; indeed it may be that gravitation has only a statistical significance) to be of the form

$$\left\{ \frac{W}{c} + \sum_r \alpha_r p_r + \alpha_4 mc \right\} \psi = 0$$

where

$$W = i\hbar \frac{\partial}{\partial t}$$

and

$$p_r = -i\hbar \frac{\partial}{\partial x_r}, \quad r = 1, 2, 3.$$

We are led to this form simply by the requirement that the wave equation be linear in the operator  $W = i\hbar \frac{\partial}{\partial t}$ , which we found to be a necessary condition from group theoretic considerations of the displacements of states; if

we want some kind of symmetry between space and time, as we do in a relativistic theory, we must thus have the wave equation linear in the  $h$ 's also. We want the Hamiltonian in the above wave equation to be something like the second order relativistic Hamiltonian of a free particle and this means that we want the  $\alpha$ 's to satisfy

$$\alpha_\mu \alpha_\nu + \alpha_\nu \alpha_\mu = 2 \delta_{\mu\nu} \quad (\mu, \nu = 1, 2, 3, 4),$$

since then if we evaluate

$$\left\{ \frac{W}{c} - \sum_r \alpha_r h_r - \alpha_4 mc \right\} \left\{ \frac{W}{c} + \sum_r \alpha_r h_r + \alpha_4 mc \right\}$$

we get just the classical Hamiltonian. Our wave equation doesn't look completely relativistic since the  $W/c$  has no coefficient although the  $h$ 's have, but this is not important since by multiplication by an  $\alpha$  we can give  $W/c$  a coefficient and leave one of the  $h$ 's without one. It can quite easily be shown that this wave equation leads to relativistic results, the best method of showing this being by the use of spinors; we shall not pause to discuss this point here. We shall proceed to show how this equation leads us to ascribe spin to the electron; when there is an electromagnetic field we generalise our wave equation by writing

$$\text{and} \quad \begin{array}{ll} h_r + \frac{e}{c} A_r & \text{for } h_r \\ \frac{W}{c} + \frac{e}{c} A_0 & \text{for } \frac{W}{c} \end{array}$$

where  $(A_r, A_0)$  is the potential of the field. The equation thus becomes

$$\left\{ \left( \frac{W}{c} + \frac{e}{c} A_0 \right) + \sum_r \alpha_r \left( h_r + \frac{e}{c} A_r \right) + \alpha_4 mc \right\} \psi = 0.$$

For a discussion of this equation we shall need to put it into a different form and this will require some knowledge of the properties of the  $\alpha$ 's. We have already found quantities that obey commutability relations like those satisfied by the  $\alpha$ 's, namely  $\sigma_x$ ,  $\sigma_y$  and  $\sigma_z$ ; there are however only three of these and to obtain the  $\alpha$ 's we must introduce a similar set of three quantities,  $\rho_1$ ,  $\rho_2$  and  $\rho_3$  that commute with the  $\sigma$ 's and obey the same commutation rules. We cannot obtain four matrices,  $\alpha$ , in terms of two-rowed

square matrices and we have to go to at least four rows and columns to represent them\*. We take a representation of the  $\sigma$ 's and  $\rho$ 's together, for which

\* We cannot use three-rowed square matrices since the eigenvalues of  $\alpha_1$  are the same as those of  $\alpha_2$ ,  $\alpha_2^{-1} = \alpha_2 \alpha_1 \alpha_2 = -\alpha_1$  and hence to every positive eigenvalue of an  $\alpha$  corresponds an equal negative one so that we must have an even number of eigenvalues and therefore an even number of rows and columns.

we shall require four rows and columns in our matrices, and write

$$\left. \begin{aligned} \alpha_1 &= \rho_1 \sigma_x \\ \alpha_2 &= \rho_1 \sigma_y \\ \alpha_3 &= \rho_1 \sigma_z \\ \text{and } \alpha_4 &= \rho_3 \end{aligned} \right\} ;$$

these  $\alpha$ 's then have the properties we desire; the above is merely a particular way of representing the  $\alpha$ 's and there are several other ways; the present method is convenient because we may treat  $\alpha_1$ ,  $\alpha_2$  and  $\alpha_3$  as the components of  $\rho_1$  times the vector  $\underline{\sigma}$ .

In terms of the  $\rho$ 's and  $\sigma$ 's the wave equation becomes

$$\left\{ \left( \frac{W}{c} + \frac{e}{c} A_0 \right) + \rho_1 (\underline{\sigma}, \underline{p} + \frac{e}{c} \underline{A}) + \rho_3 mc \right\} \psi = 0.$$

One of the most direct ways of getting physical information from this equation is to make it into a second order wave equation that looks something like the wave equation formed from the classical relativistic Hamiltonian. We therefore consider the equation

$$\left\{ \left( \frac{W}{c} + \frac{e}{c} A_0 \right) - \rho_1 (\underline{\sigma}, \underline{p} + \frac{e}{c} \underline{A}) - \rho_3 mc \right\} \left\{ \left( \frac{W}{c} + \frac{e}{c} A_0 \right) + \rho_1 (\underline{\sigma}, \underline{p} + \frac{e}{c} \underline{A}) + \rho_3 mc \right\} \psi = 0,$$

this being the way in which we can change the linear equation into a second order equation that looks as closely as possible like the second order equation using the classical Hamiltonian. To evaluate the operator entering this equation we make use of the general theorem that if  $\underline{X}$  and  $\underline{Y}$  commute with  $\underline{\sigma}$  then

$$(\underline{\sigma}, \underline{X})(\underline{\sigma}, \underline{Y}) = (\underline{X}, \underline{Y}) + i(\underline{\sigma}, \underline{X} \times \underline{Y})$$



where  $\underline{X} \times \underline{Y}$  denotes the vector product of  $\underline{X}$  and  $\underline{Y}$ . Applying this theorem to a particular case that arises in our evaluation we have, since

$$\begin{aligned} (\underline{p}_x + \frac{e}{c} A_x) \times (\underline{p}_y + \frac{e}{c} A_y) &= \frac{e}{c} (\underline{p}_x A_y - \underline{p}_y A_x - A_y \underline{p}_x + A_x \underline{p}_y) \\ &= -i \hbar \frac{e}{c} \left( \frac{\partial}{\partial x} A_y - \frac{\partial}{\partial y} A_x \right) \\ &= -i \hbar \frac{e}{c} \mathcal{H}_z, \end{aligned}$$

the result that

$$(\underline{\sigma}, \underline{p} + \frac{e}{c} \underline{A})^2 = (\underline{p} + \frac{e}{c} \underline{A})^2 + \hbar \frac{e}{c} (\underline{\sigma}, \underline{\mathcal{H}});$$

again we have the result that

$$(\frac{W}{c} + \frac{e}{c} A_0)(\underline{\sigma}, \underline{p} + \frac{e}{c} \underline{A}) - (\underline{\sigma}, \underline{p} + \frac{e}{c} \underline{A})(\frac{W}{c} + \frac{e}{c} A_0) = -i \rho_1 \hbar \frac{e}{c} (\underline{\sigma}, \underline{\mathcal{E}});$$

so, using these results, our second order wave equation becomes

$$\left\{ (\frac{W}{c} + \frac{e}{c} A_0)^2 - (\underline{p} + \frac{e}{c} \underline{A})^2 - m^2 c^2 - \hbar \frac{e}{c} (\underline{\sigma}, \underline{\mathcal{H}}) - i \rho_1 \hbar \frac{e}{c} (\underline{\sigma}, \underline{\mathcal{E}}) \right\} \psi = 0.$$

The first two parentheses are the same as the terms that enter the classical Hamiltonian; we have here extra terms involving  $\underline{\mathcal{H}}$  and  $\underline{\mathcal{E}}$ . The difference has arisen from the fact that the coefficients of the  $\alpha$ 's no longer commute with each other when a field is present. The extra terms may be interpreted as some additional energy that the electron has in the electromagnetic field; to get the actual magnitude of this extra energy we must of course divide the equation by  $2m$  in order that the part that corresponds to the classical energy have the correct factor; thus our extra terms correspond to the extra potential energy

$$\frac{\hbar e}{2mc} (\underline{\sigma}, \underline{\mathcal{H}}) + i \rho_1 \frac{\hbar e}{2mc} (\underline{\sigma}, \underline{\mathcal{E}}).$$

The first term may be attributed to the electron having a small magnetic moment of magnitude

$$-\frac{\hbar e}{2mc} \underline{\sigma}.$$

The other term corresponds to the electron having an imaginary electric moment

$$-i \rho_1 \frac{\hbar e}{2mc} \underline{\sigma}.$$

The magnetic moment seems to have a physical meaning but the electric moment being imaginary does not seem to have physical significance; it appears necessary

to regard it as a mathematical fiction, since the linear Hamiltonian was real and so the imaginary term must have come in from our having changed to a second order equation. If there were no electric field the imaginary part would disappear and so an electron moving in a purely magnetic field would behave as though it had a magnetic moment of the above magnitude.

We now consider the other way in which the spin of the electron comes in, namely in the angular momentum of the electron. In the ordinary way the angular momentum of the electron about the x-axis would be defined by

$$m_x = y p_z - z p_y.$$

Now when there is no field we have

$$H = -c \{ \rho_1 (\underline{\sigma}, \underline{p}) + \rho_3 mc \}$$

and so

$$\begin{aligned} i\hbar \dot{m}_x &= m_x H - H m_x \\ &= -c \rho_1 (\underline{\sigma}, m_x \underline{p} - \underline{p} m_x) \\ &= -i\hbar c \rho_1 (\sigma_z p_y - \sigma_y p_z) \end{aligned}$$

and this does not vanish. Thus the ordinary angular momentum is not a constant of the motion!

But we have

$$\begin{aligned} i\hbar \dot{\sigma}_x &= \sigma_x H - H \sigma_x \\ &= -c \rho_1 (\sigma_x \underline{\sigma} - \underline{\sigma} \sigma_x, \underline{p}) \\ &= -2ic \rho_1 (\sigma_z p_y - p_y \sigma_z) \end{aligned}$$

and hence it follows that

$$\dot{m}_x + \frac{1}{2} \hbar \dot{\sigma}_x = 0$$

so that

$$m_x + \frac{1}{2} \hbar \sigma_x = \text{const.}$$

This suggests that this expression is the real angular momentum integral for the problem so that the ordinary angular momentum must be supplemented by  $\frac{1}{2} \hbar \sigma_x$ ; we ascribe this extra angular momentum to the spin of the electron.

We shall now consider the complete integration of the equations of motion in the case of no field; although the quantities involved do not commute the equations are sufficiently simple to admit of complete integration, as was shown by Schrödinger. By performing the integration we obtain an insight into the motion of an electron according to the present theory. We shall change the sign of the Hamiltonian for convenience and write

$$H = c \{ \rho(\underline{\sigma}, \underline{p}) + \rho_3 mc \}$$

or, in terms of the  $\alpha$ 's,

$$H = c \{ (\underline{\alpha}, \underline{p}) + \alpha_4 mc \};$$

we consider first the equations of motion for the momentum; we have

$$\begin{aligned} \dot{p}_r &= [p_r, H] \\ &= 0 \end{aligned}$$

and so

$$p_r = \text{const.}$$

which is what one would expect in the case of a particle moving freely in no field.

Again we have

$$\begin{aligned} \dot{x}_r &= [x_r, H] \\ &= [x_r, c \alpha_r p_r] \end{aligned}$$

(since  $x_r$  commutes with every quantity in  $H$  except  $p_r$ )

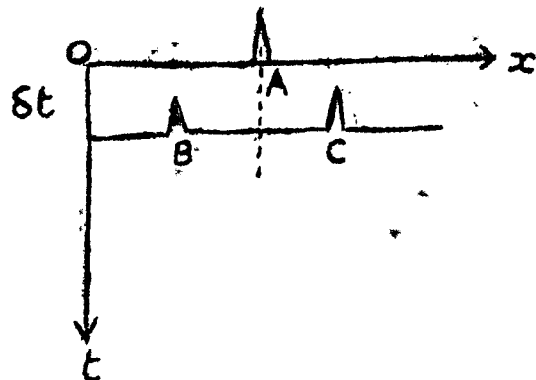
$$= c \alpha_r$$

and so  $c \alpha_r$  is the expression for the velocity according to the relativistic theory of the electron. This is at first sight a surprising result since it means that the velocity of the electron is always equal to that of light on account of the fact that the eigenvalues of  $c \alpha_r$  are  $\pm c$ ; this result, however, is not really so surprising as it appears to be since in order to measure the velocity, there being no simple connection between the velocity and the momentum in the present case, we must observe the position of the electron at two times very near together; when we observe the exact position the first time the momentum, according to the uncertainty principle, becomes completely undetermined

and is therefore practically certain to be infinite, corresponding to a velocity equal to that of light.

We can also see that this result is what one should expect by referring to the wave equation; if we start with a wave function that is just the  $\delta$ -function at the position A. at time  $t = 0$ , then at time

$\delta t$ , by the well-known properties of the wave equation the  $\delta$ -function will have spread out into a spherical shell, indicated by B C in the figure, of radius  $c \delta t$ . The relativity principle requires that the electron cannot be outside this shell at time  $\delta t$ , the special form that the wave equation has tells us further that neither can it be within it. Thus at time  $\delta t$  the electron will certainly have moved through a distance  $c \delta t$ .



The velocity of the electron is not a constant since it keeps on changing its direction; we shall now show that its average value is connected with the momentum by the usual relation between velocity and momentum. For, let us consider the way in which the velocity changes; we have

$$i\hbar \dot{\alpha}_r = \alpha_r H - H \alpha_r;$$

now

$$\alpha_r H + H \alpha_r = \alpha_r c \hat{p}_r + c \hat{p}_r \alpha_r = 2c \hat{p}_r$$

and so

$$i\hbar \dot{\alpha}_r = 2\alpha_r H - 2c \hat{p}_r$$

and also  $= -2\alpha_r H + 2c \hat{p}_r;$

the  $\hat{p}_r$  is a constant of the motion and  $H$  is also constant so that we now have a linear differential equation with constant coefficients. Following Schrödinger we introduce

$$\eta_r = \alpha_r - c \frac{\hat{p}_r}{H},$$

(it is permissible to write  $\frac{\hat{p}_r}{H}$  since  $\hat{p}_r$  and  $H$  commute),

and then we have

$$i\hbar \dot{\eta}_r = i\hbar \dot{\alpha}_r = 2\eta_r H \quad (30)$$

which is a differential equation for  $\eta_r$ . Integrating we get

$$\eta_r = \text{const. } e^{-2iHt/\hbar}$$

(since if we differentiate this expression for  $\eta_r$  we get

$$\dot{\eta}_r = \text{const. } e^{-2iHt/\hbar} \left( -\frac{2iH}{\hbar} \right) ) ;$$

the constant of integration is not necessarily an ordinary number and so its position in the formula is of importance and in the above it must be placed first.

We have for this constant the value

$$(\eta_r)_{t=0} = \eta_r^0 \text{ (say)}$$

and thus our integral is

$$\eta_r = \eta_r^0 e^{-2iHt/\hbar}$$

this equation will show us how the velocity varies with the time. We could have proceeded by an alternative method; we could have used the relation

$$i\hbar \ddot{\alpha}_r = -2H\dot{\alpha}_r + 2c\dot{p}_r$$

instead of

$$i\hbar \dot{\alpha}_r = 2\alpha_r H - 2c p_r ;$$

if we do this we obtain

$$i\hbar \dot{\eta}_r = -2H\eta_r$$

(Note, by comparing this with equation (30), that  $\eta_r$  anticommutes with H)

and this leads to

$$\eta_r = e^{2iHt/\hbar} \eta_r^0$$

We thus have two different expressions for  $\eta_r$  but they are actually equivalent since when we change the order of  $\eta_r^0$  and H we must change the sign of H because  $\eta_r^0$ , like  $\eta_r$ , anticommutes with H. In fact we can see the equations are equivalent since  $\eta_r$  is a real observable and therefore the two equations are conjugate complex.

We thus have

$$\begin{aligned} \dot{x}_r &= c \dot{\alpha}_r \\ &= c \eta_r + c^2 \frac{p_r}{H} \\ &= c \eta_r^0 e^{-2iHt/\hbar} + c^2 \frac{p_r}{H} \end{aligned}$$

The last term is what the velocity would be according to classical ideas; so the mean value of the velocity is just the classical value and we have in addition the high frequency velocity given by the first term which results in the actual magnitude of the velocity being always equal to the velocity of light.

We now have

$$x_r = c \eta_r^0 \frac{i\hbar}{2\pi} e^{-2iHt/\hbar} + c^2 \frac{p_r}{H} t + a_r$$

where  $a_r$  is a constant of integration which will be an observable. Following Schrödinger we split up  $x_r$  into two terms

$$x_r = \tilde{x}_r + f_r$$

where

$$\tilde{x} = \frac{c^2 p_r}{H} t + a_r$$

and

$$f_r = \frac{i\hbar c}{2} \eta_r^0 e^{-2iHt/\hbar} \frac{1}{H}$$

$$= \frac{i\hbar c}{2} \eta_r \frac{1}{H}$$

$$\text{and also} = -\frac{i\hbar c}{2} \frac{1}{H} \eta_r$$

since  $\eta_r$  anticommutes with  $H$ .

The part  $\tilde{x}_r$  gives the motion of the electron according to classical relativistic ideas; the  $f_r$  gives the high frequency part of the motion. Now  $H$  has very big eigenvalues of the order of  $mc^2$  so that  $f_r$  is of very high frequency indeed; its amplitude however is very small since it is given by

$$\frac{\hbar c}{2} \eta_r^0 \frac{1}{H}$$

and the eigenvalues of  $\eta_r^0$  are of the order of unity as we see from the definition of  $\eta_r$ , the eigenvalues of  $\alpha_r$  being  $\pm 1$  and of  $c \frac{p_r}{H}$  being not greater than unity on account of the relativistic relation between  $p$  and  $H$ , so that the amplitude of  $f_r$  is of order  $\frac{\hbar}{2mc}$  which is a very small quantity even in the theory of the atom. Thus the motion of our electron

is to be pictured as a high frequency wiggle about a straight line as shown below;



We can get a simple formula for the magnitude of the oscillating part;

for

$$\begin{aligned} p_r^2 &= \left(-\frac{i\hbar c}{2} \frac{1}{H} \eta_r\right) \left(\frac{i\hbar c}{2} \eta_r \frac{1}{H}\right) \\ &= \frac{\hbar^2 c^2}{4} \frac{1}{H} \eta_r^2 \frac{1}{H}; \end{aligned}$$

now

$$\alpha_r = \eta_r + \frac{c p_r}{H}$$

and so, squaring this relation, we get

$$1 = \eta_r^2 + \frac{c^2 p_r^2}{H^2},$$

the cross terms vanishing since  $\eta_r$  commutes with  $p_r$  and anticommutes with  $H$ .

Hence we have

$$p_r^2 = \frac{\hbar^2 c^2}{4} \frac{1}{H} \left(1 - \frac{c^2 p_r^2}{H^2}\right) \frac{1}{H}$$

in which the order of the factors on the right hand side no longer matters. So

we have

$$\begin{aligned} p_1^2 + p_2^2 + p_3^2 &= \frac{\hbar^2 c^2}{4} \frac{1}{H^2} \left\{ 3 - \frac{c^2 (p_1^2 + p_2^2 + p_3^2)}{H^2} \right\} \\ &= \frac{\hbar^2 c^2}{4 H^2} \left( 2 + \frac{m^2 c^4}{H^2} \right) \end{aligned}$$

and this is always small since  $\frac{m^2 c^4}{H^2} \leq 1$  and  $\frac{\hbar^2 c^2}{4 H^2}$  is small.

We have been considering the motion of the centre of gravity of the electron; we can treat the spin in the same way; the spin angular momentum is  $\frac{1}{2} \hbar \sigma$  and we have

$$\frac{1}{2} \hbar \dot{\sigma}_r = -\frac{1}{2} i (\sigma_r H - H \sigma_r);$$

now we notice

$$\begin{aligned} (\sigma_r H - H \sigma_r) H + H (\sigma_r H - H \sigma_r) &= \sigma_r H^2 - H^2 \sigma_r \\ &= 0, \end{aligned}$$

since  $H^2$  is independent of  $\sigma$ , and hence we have the result that  $(\sigma_r H - H \sigma_r)$  anticommutes with  $H$ . So

$$\frac{1}{2} \hbar \dot{\sigma}_r \text{ anticommutes with } H.$$

We may now treat  $\frac{1}{2} \hbar \dot{\sigma}_r$  as we treated  $\eta_r$  since each anticommutes with  $H$ .

We have

$$\begin{aligned} i \hbar \frac{d}{dt} (\sigma_r H - H \sigma_r) &= (\sigma_r H - H \sigma_r) H - H (\sigma_r H - H \sigma_r) \\ &= 2 (\sigma_r H - H \sigma_r) H \end{aligned}$$

which is the same as the differential equation we had for  $\eta_r$ ; integrating we obtain

$$\sigma_r H - H \sigma_r = (\sigma_r H - H \sigma_r)_{t=0} e^{-2iHt/\hbar}$$

which gives us explicitly the value of  $\dot{\sigma}_r$ , and integrating once again we get

$$\frac{1}{2} \hbar \sigma_r = \frac{\hbar}{4} (\sigma_r H - H \sigma_r)_{t=0} \frac{1}{H} e^{-2iHt/\hbar} + \frac{1}{2} \hbar \tilde{\sigma}_r$$

(where  $\tilde{\sigma}_r$  is a constant of integration),

$$= \frac{\hbar}{4} (\sigma_r H - H \sigma_r) \frac{1}{H} + \frac{1}{2} \hbar \tilde{\sigma}_r$$

and we now have the spin variable expressed as a high frequency varying part together with a constant part. We can try to interpret the variable part of the spin in the following way; suppose we evaluate the quantity  $(\mathbf{r} \times \mathbf{p})$ ;

we have

$$\begin{aligned} (\mathbf{r} \times \mathbf{p})_1 &= \int_2 p_3 - \int_3 p_2 \\ &= \frac{i\hbar c}{2} (\gamma_2 p_3 - \gamma_3 p_2) \frac{1}{H} \\ &= \frac{i\hbar c}{2} (\alpha_2 p_3 - \alpha_3 p_2) \frac{1}{H}, \quad (\text{from the definition of the } \gamma\text{'s}). \end{aligned}$$

and this quantity we shall show to be equal to the 1-component of the varying part,  $\frac{\hbar}{4} (\sigma_r H - H \sigma_r)$ , of the spin, except for sign; for

$$\begin{aligned} \frac{\hbar}{4} (\sigma_r H - H \sigma_r) \frac{1}{H} &= \frac{\hbar}{4} p_1 c \{ \sigma_1 (\sigma_2 p_3 + \sigma_3 p_2) - (\sigma_2 p_3 + \sigma_3 p_2) \sigma_1 \} \frac{1}{H} \\ &= \frac{i\hbar c}{2} p_1 (\sigma_3 p_2 - \sigma_2 p_3) \frac{1}{H} \\ &= -\frac{i\hbar c}{2} (\alpha_2 p_3 - \alpha_3 p_2) \frac{1}{H}; \end{aligned}$$

we may therefore say that the variable part of the spin is just

$$- (\mathbf{r} \times \mathbf{p})$$

and we may interpret this as meaning that the variable part arises from the small radius vector  $\mathbf{r}$  moving with the momentum  $\mathbf{p}$  attached to the end of it. Schrödinger tried very hard to give a similar meaning to the constant part of the spin but it doesn't seem to be possible to obtain a simple picture in this case. This completes the discussion of the equations of motion for the relativistic theory of the electron; it shows us how each of our variables



varies with the time; each has a small high frequency term in addition to the part that would be expected from classical ideas.

We shall now consider the difficulties of the relativistic theory; for the case of stationary states in the absence of an electromagnetic field the energy is given by

$$E = c(\alpha_1 p_1 + \alpha_2 p_2 + \alpha_3 p_3 + \alpha_4 mc)$$

so that

$$E^2 = c^2(p_1^2 + p_2^2 + p_3^2 + m^2 c^2)$$

and therefore any eigenvalue of  $E^2$  will be just equal to the right hand side of the above expression when some particular eigenvalues are given to the  $p$ 's.

It follows that any eigenvalue of  $E^2$  must be such that

$$E'^2 \geq m^2 c^4$$

and so

$$\begin{aligned} \text{either } E' &\geq mc^2 \\ \text{or } E' &\leq -mc^2. \end{aligned}$$

In practice we always find the result  $E' \geq mc^2$  and this really gives rise to a discrepancy between theory and observation since, as we shall see, we cannot ignore the negative energy states. Let us take any representation for which  $E$ , amongst other observables, is diagonal; there will be certain points in the domain of the wave function for which  $E' \geq mc^2$  and others for which  $E' \leq -mc^2$  and this means that the domain of the wave function divides up into two regions quite distinct and separate from each other. A wave function that vanishes everywhere in its domain except in the region where  $E' \geq mc^2$  we shall call, following Schrödinger, a positive wave function, and one that is zero except where  $E' \leq -mc^2$

will be called a negative wave function; then we may say that only positive wave functions have been observed to occur in nature. So long as we deal with an electron in the absence of a field a wave function that is initially positive will remain positive, since  $E$  is a constant of the motion in the absence

of a field; but if there is a field such is no longer the case in general and this gives rise to a real difficulty in the theory since it means that there is a small probability of a transition from a positive to a negative energy state and we can therefore no longer ignore the negative energy states. We can discuss these transition probabilities in the following way; let  $V$  denote the extra terms that arise in the Hamiltonian when there is a field present; then the general theory of transitions shows that

$$(E' | V | E''), \quad (\text{omitting the other observables that should accompany } E),$$

is the matrix element that is responsible for a transition from a state of energy  $E'$  to one of energy  $E''$ , or vice versa, and if this matrix element vanish we shall not get such transitions. There are four kinds of matrix element of the above type according as  $E'$  and  $E''$  are positive or negative and the matrix elements that cause the trouble will be those in which  $E'$  and  $E''$  are of opposite sign. We can split up any observable into two parts, one of which contains, in this representation, only matrix elements for which  $E'$  and  $E''$  are both positive or both negative and the other elements for which  $E'$  and  $E''$  have different signs. We shall call these two parts respectively the even and odd parts of the observable. If we could arrange that the matrix elements have only even parts we should get over our difficulty and this is what Schrödinger tried to do. We can easily see how this should be done; let us consider the observable  $x_y$  first of all; we enquire what are the even and odd parts of  $x_y$ . Our previous resolution of  $x_y$  into two parts,  $\tilde{x}_y$  and  $\xi_y$ , turns out to be the same as its resolution into even and odd parts; for we have

$$\xi_y E + E \xi_y = 0$$

and this means, since  $E$  is diagonal, that

$$(E' | \xi_y | E'') (E'' + E') = 0$$

so that  $(E' | \xi_y | E'')$  must vanish unless  $E' = -E''$ ;  $\xi_y$  is thus odd.

We now consider the part  $\tilde{x}_r$ ; this can only be defined through the relation

$$x_r = \tilde{x}_r + \xi_r \quad \text{and thus we have}$$

$$\begin{aligned} \tilde{x}_r E - E \tilde{x}_r &= x_r E - E x_r - (\xi_r E - E \xi_r) \\ &= i\hbar c \alpha_r - \xi_r \\ &= i\hbar c \alpha_r - i\hbar c \eta_r \\ &= i\hbar c^2 \frac{p_r}{H} = i\hbar c^2 \frac{p_r}{E} \end{aligned}$$

and so, taking a representation in which  $p_r$  is also diagonal, as we may since

$$\begin{aligned} p_r \text{ commutes with } E, \text{ we have} \\ (E' | \tilde{x}_r | E'') (E'' - E') &= i\hbar c^2 (E' | \frac{p_r}{H} | E'') \\ &= 0 \quad \text{unless } E' = E'', \end{aligned}$$

and thus  $(E' | \tilde{x}_r | E'') = 0$  unless  $E' = E''$ , so that  $\tilde{x}_r$  is even. Hence

$\tilde{x}_r$  is the even part of  $x_r$  and  $\xi_r$  the odd.

It is now easy to express any function of  $x$  in terms of an even and an odd part; we first notice that  $F(\tilde{x}_r, \xi_r)$  and  $F(\tilde{x}_r, -\xi_r)$  must have the same even parts and opposite odd parts. Thus

$$\begin{aligned} F(\tilde{x}_r, \xi_r) + F(\tilde{x}_r, -\xi_r) &\text{ is even} \\ \text{and } F(\tilde{x}_r, \xi_r) - F(\tilde{x}_r, -\xi_r) &\text{ is odd.} \end{aligned}$$

This enables us to express any function of  $x$  in terms of its even and odd parts as

$$\begin{aligned} f(x) &= f(\tilde{x} + \xi) \\ &= \frac{1}{2} [f(\tilde{x} + \xi) + f(\tilde{x} - \xi)] + \frac{1}{2} [f(\tilde{x} + \xi) - f(\tilde{x} - \xi)], \end{aligned}$$

the terms in the first square parentheses constituting the even part and those in the second the odd. We see that the odd part will be very small on account of the smallness of  $\xi$ . Schrödinger proposes to get over the difficulty of the negative energies by neglecting the odd parts altogether, and he has shown that this makes an alteration in the calculated spectrum of Hydrogen that is much too small to be observed. However, this method doesn't seem to be very satisfactory since the new wave equation is no longer relativistic; so probably this is not

really the correct line upon which one should proceed in order to resolve the difficulty of the negative energy levels.

Another way in which one might proceed is to assume that all the negative energy states are occupied by electrons; then by the Pauli principle the electrons that are left over in the positive energy states can never jump into the states of negative energy. This would be a formal way of getting over the difficulty but it does, of course, introduce the idea of an infinite number of electrons in the negative energy states; this infinitely need not give rise to any immediate difficulties in the theory; a perfect vacuum will be a space in which all the negative energy states are filled and all the positive energy states are empty.

7. In the Maxwell equations we have the relation

$$\text{div. } \underline{E} = -4\pi\rho$$

and we must then interpret  $\rho$  as being only the difference between the electric density in the case under consideration and in the case of a vacuum as defined above. If one wanted actually to write down equations for this theory one may get infinities coming in but similar infinities have already appeared in the theory of radiation and it seems reasonable to suppose that one should first get over these infinities in the radiation theory and then employ the ideas thus discovered to overcome any infinities that occur in the theory of the negative energy electrons.

These negative energy electrons are not to be considered as a mathematical fiction; it should be possible to detect them by experimental means. It ought to be possible to lift up one of the electrons in a negative energy state to bring it into a positive energy state; this would leave a vacancy in the series of negative energy states and we ask ourselves what such a vacancy would be like. Let us first consider what one electron alone in a negative energy state would be like; this can be best seen by referring to the classical theory;

(the negative energy states exist in the classical theory but we don't get jumps from positive to negative energy states so that the negative energy states may be ignored). Classically the Hamiltonian that describes the motion of an electron is of the form

$$F = \left( \frac{W}{c} + \frac{e}{c} A_0 \right)^2 - \left( \mathbf{h} + \frac{e}{c} \mathbf{A} \right)^2 - m^2 c^2$$

the equations of motion according to this Hamiltonian being

$$\frac{dx_\mu}{ds} = \frac{\partial F}{\partial h_\mu} = -2 \left( h_\mu + \frac{e}{c} A_\mu \right)$$

and

$$\frac{dh_\mu}{ds} = - \frac{\partial F}{\partial x_\mu} = \sum_\nu \pm \left( h_\nu + \frac{e}{c} A_\nu \right) \frac{\partial A_\nu}{\partial x_\mu};$$

where  $\mu, \nu = 1, 2, 3, 4$ ,  $x^4 = ct$ , and we have to take the positive sign in the second equation for  $\nu = 1, 2, 3$  and the negative sign for  $\nu = 4$ .

Let us now consider a new Hamiltonian function  $F^*$  defined as

$$F^* = \left( \frac{W^*}{c} - \frac{e}{c} A_0 \right)^2 - \left( \mathbf{h}^* - \frac{e}{c} \mathbf{A} \right)^2 - m^2 c^2;$$

the corresponding equations of motion are

$$\frac{dx_\mu^*}{ds^*} = -2 \left( h_\mu^* - \frac{e}{c} A_\mu \right)$$

and

$$\frac{dh_\mu^*}{ds^*} = \sum_\nu \mp \left( h_\nu^* - \frac{e}{c} A_\nu \right) \frac{\partial A_\nu}{\partial x_\mu}.$$

These two sets of equations of motion will become the same if we take

$$\text{and } \left. \begin{aligned} x^* &= x \\ h^* &= -h \\ W^* &= -W \\ S^* &= -S \end{aligned} \right\}.$$

Thus if we take an electronic trajectory corresponding to  $F$  and to a positive value for the energy it will be the same trajectory as that corresponding to  $F^*$  for an electron of negative energy, and conversely. Now  $F^*$  is the same as  $F$  except that it has  $-e$  instead of  $+e$ ; so an electron of negative energy will move in just the same way as an electron of positive energy having charge  $+e$  instead of  $-e$ . The same result also holds for the quantum theory. Thus if we take an electron in a quantum state of negative energy it will move in an electromagnetic field in just the same way as an ordinary electron would move if it had

a positive instead of a negative charge.

Let us now pass from the case of a single electron to that of the whole set of negative electrons; any hole in these states will move in exactly the same way as that electron would move that would just fill up this hole (neglecting the interaction between the electrons) and it would furthermore have a positive energy so that this hole would not be anything unreasonable; we shall refer to such a hole as an anti-electron; an anti-electron ought to have the same mass as an electron and this appears to be unavoidable; we should prefer to get a much larger mass so as to identify the anti-electrons with the protons, but this does not seem to work even if we take a Coulomb interaction into account. The above theory does not lead to a violation of the principle of the conservation of electricity since if an electron of positive energy jumps into a hole it disappears but also causes an anti-electron to vanish, and similarly if an electron of negative energy jumps to a state of positive energy the effect is to produce an electron and an anti-electron.

The theory enables one to calculate the probability for an electron jumping down into one of the holes and filling it up; it is necessary that two light quanta be emitted in such a process on account of the principles of the conservation of energy and momentum since we may take a Lorentz frame of reference in which the electron and anti-electron in question have together no resultant momentum and thus after their coalescence and disappearance the light emitted must also have no resultant momentum which is impossible with only one light quantum.

This idea of the anti-electrons doesn't seem to be capable of experimental test at the moment; it could be settled by experiment if we could obtain two beams of high frequency radiation of a sufficiently great intensity and let them interact.