Free Motion in the Wave Mechanics.

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The present work is a discussion of a number of simple problems of the free motion of electrons and atoms from the point of view of the wave mechanics. The author has had the advantage of many conversations with Prof. N. Bohr on the subject, and it was composed under this inspiration. Bohr* has recently published his views on the foundations of the theory, and it would be out of place to enter here deeply into the matter, but some review of principles is unavoidable if the technical processes are to be understood. Perhaps the chief point of the work is to show how a simple, even old-fashioned, technique is entirely adequate to deal with these very new problems.

§ 1. General Principles.

The matrix and the wave mechanics have both been already developed to great lengths as a calculus of stationary states, but they have not yet got so far in what we may call dynamics, a description of the progress of events. More and more complicated phenomena have been fitted into the same scheme, but not much has been done in making this scheme intuitively understandable. One of the most important contributions is a recent work by Heisenberg,† who develops an "uncertainty relation" by showing how each observation of a system, say an electron, always itself introduces some disturbance, so that the exact state at the beginning of each new experiment is essentially unknowable. Heisenberg works from the matrix point of view, but Bohr has pointed out that the "uncertainty relation," exhibited by Heisenberg simply as an experimental result, becomes quite natural on wave principles, and is indeed nothing more than an expression of those principles.

The central difficulty of the quantum theory has always been the conflict between waves and particles. On the one hand, we have the theorems of conservation of matter, energy, etc.; these tell us that matter keeps together, and endow a particle or a quantity of energy with individuality, so that we can trace its history. On the other hand, we have the theorems of interference—of light and now of matter as well, which as definitely tell us that the things

* Transactions of Volta Centenary Congress at Como (1927).
which we before regarded as particles must spread, and so must lose their individuality. The recent work of Bohr explains, at any rate in outline, how the apparent contradiction is to be reconciled. The two lines of thought are not contradictory, but complementary. They do not come into conflict because they never meet. To verify conservation we must obviously have an enclosed system, and this excludes observation of what happens in the enclosure. If nothing is observable, it is only proper to say that nothing is happening; the system is settled into a spaceless and timeless stationary state outside our intuitions. On the other hand, if we want to observe what happens we must make a hole in the enclosure and see what leaks out. By the very act conservation is destroyed, but in exchange we get interference phenomena, and these introduce geometry and so a connection with space and time. This very inadequate description shows that we are entitled, when we want to discuss happenings in space and time, to make full use of the wave theory and to pay no attention to the conservation difficulties, because in fact these do not arise.

It is almost impossible to describe the result of any experiment except in terms of particles—a scintillation, a deposit on a plate, etc.—and this language is quite incompatible with the language of waves, which is used in the solution. A necessary part of the discussion of any problem is therefore the translation of the formal mathematical solution, which is in wave form, into terms of particles. We shall call this process the interpretation, and only use the word in this technical sense.

The general treatment of a problem will then fall into three stages. First there is the solution of the appropriate wave equation with the appropriate initial conditions. This gives a Schrödinger function (in general complex) at every time and value of the co-ordinates. Next we multiply this by its conjugate. When dealing with electrons this quantity is usually called the electric density, but it seems better to have a more general name and one not possessing such definite connotations. We shall call it the intensity, extending the meaning, already usual for light and sound, to cover material waves as well. Lastly, there is the interpretation, when we say that the intensity of the wave is a measure of the probability that a particle will be observed. This stage is to be regarded rather as a concession to our ingrained habits of thought than as an essential part of the problem.

As long as they were both concerned only with stationary states, the matrix and wave methods were equivalent and only differed in mathematical convenience. But when the time enters into the question an important distinction arises, for the solution of the wave equation suggests, and our type of problem
requires, that we should not merely take a single solution of the equation, but
that we should build up one by superposition of an infinite number of separate
solutions each of which corresponds to a stationary state. It is a great merit
of the wave theory that it invites this superposition; with matrices the corre­
sponding generalisation does not suggest itself, and has indeed hardly been
used.*

Now the admissibility of superposition has important consequences in
changing our physical outlook. In the older quantum theory we made the
interpretation at the beginning of the discussion, so that a stationary state
meant an orbital motion and it was therefore axiomatic that an atom could only
be in one state at a time. But now we only make the interpretation when some
effect is actually observed, and there is no reason why the atom should not be
in several states simultaneously, for a stationary state is merely a solution of
the wave equation that happens to be harmonic in the time. We are excluding
questions of the emission of radiation (though perhaps the most important and
difficult of the whole quantum theory) and shall take as our guiding principle
that the interpretation is to be delayed as long as possible. For example, in
the Stern-Gerlach experiment we do not say that the field splits the atoms into
two groups and then separates these. We say that a wave goes through the
field, and when we calculate its intensity at the terminal plate we find that it
has two maxima, which we then interpret as two patches of atoms. With
the simple Stern-Gerlach experiment either way of regarding the matter leads
to the same result, but experiments can easily be devised which would dis­
 criminate between them. Consider a stream of silver atoms going along the
direction of $x$. These atoms go through a non-uniform field which polarises
them along the direction $\pm y$ and a slit is arranged so that only the $+y$ ones
emerge. These then enter a uniform field along $z$. According to the older
theory this will instantaneously split them into two groups pointing along $\pm z$,
and if, after emerging from this field, they enter another non-uniform field
along $y$, they will again be split into two groups along $\pm y$, and so will produce
two patches on the terminal plate. But when superposition is allowed the
matter is different, for (as we shall see in § 9) in the uniform field the atoms
simply precess round $z$ at the same rate as given in classical mechanics.
Suppose this field to be so long that the total angle of precession is $180^\circ$. Then
on entering the second non-uniform field they will all be pointing along $-y$.

* Heisenberg's wave packet (loc. cit., p. 188) makes use of it, but this is practically a wave
method. It also perhaps occurs in Dirac's work, but the language is so different that the
relationship is hard to trace.
and there will be only one patch on the terminal plate. On the principle of superposition it is this that we shall expect to observe.

We must now consider the interpretation in more detail, and shall see that rather different things are included under the same name. The solution of any problem takes the following course—one degree of freedom will suffice for illustration. We first solve the wave equation and find a function \( \psi(q, t) \) which conforms to some initial prescribed form, say \( \psi(q, 0) = f(q) \). From this we construct the intensity \( \rho(q, t) = |\psi(q, t)|^2 \), and then we have to begin to think of particles. Now when we think of a particle, we are almost forced to think of a position in space, so our most primitive principle of interpretation must be connected with co-ordinates representing something in space, say \( x \), the position of a free electron (or the centre of gravity of an atom, but not the position of an electron in an atom). In such a case we take as our principle that the intensity \( \rho(x, t) \) is interpreted as giving probability \( \rho(x, t) \, dx \) that the electron will be in the range from \( x \) to \( x + dx \) at the time \( t \). It is perhaps a matter of taste whether we regard this as an observed rule by which the wave theory is verified, or a definition of what we mean by a particle, or even as a definition of what we mean by space.

By making use of Heisenberg's "\( \gamma \)-ray microscope" we may include under the conception of observable quantities the position of an electron in an atom. Hence we may extend the relation of intensity with probability to such co-ordinates, saying that \( \rho(q, t) \, dq \int \rho(q, t) \, dq \) measures the probability of the particle being in the range \( dq \) at \( q \), even though this co-ordinate is only brought into space by such a highly impracticable process as the microscope. A problem of this kind is discussed in § 8.

There is yet another form in which the interpretation has to be made—in fact, that which has been most used in the subject—and this is in determining the probability that the atom is in some one stationary state. Compared to our previous interpretation this is a cross-classification, and the distinction is best appreciated by considering the analogy of light. The intensity of light can be regarded in two different ways, either by measuring the density of electro-magnetic energy at a point and so giving the intensity at that point, or else by making a spectral analysis, not now at a point but in a region of space, and determining the distribution of energy in the spectrum. The former process is analogous to that which we have discussed, and the latter to the analysis into stationary states. In the optical case the two methods of analysis
are united mathematically by equating together expressions for the whole energy in the region, one of which gives it as an integral over the volume, and the other over the frequencies of the spectrum; then the element of the volume integrand is the intensity at a point, and that in the frequency integrand is the spectral intensity. The essential point is that we equate two integral expressions and then pick out terms from the integrands, and this is the method we must pursue here. In a system having stationary states the wave solution takes the form

$$\psi(q, t) = \sum_n c_n \psi_n(q) e^{-\frac{i2\pi \nu}{\hbar}w_m t},$$

where the functions $\psi_n$ are all mutually orthogonal. The integrated intensity will be

$$\int \rho(q, t) dq = \int \sum_n \sum_m c_n c_m^* \psi_n(q) \psi_m^*(q) e^{-\frac{i2\pi \nu}{\hbar}(w_m - w_n) t} dq$$

$$= \sum_n |c_n|^2 \int |\psi_n(q)|^2 dq$$

by virtue of the orthogonality of the $\psi_n$'s. We now pick out the term connected with the $n$th state and say that this is the probability of the atom being in the $n$th state. If the $\psi$'s are normalised to unity, we have $|c_n|^2/\Sigma |c_n|^2$. Incidentally we see why it is so convenient to use normalised functions for stationary states; when considering intensity at a point on the other hand, normalisation would merely consist in multiplying the whole solution by a constant and is quite trivial.

In dealing with the interpretation we have touched on one of the great difficulties which have made it hard to gain physical insight into the wave theory. This is the fact that the wave equation is not in ordinary space but in a co-ordinate space, and the question arises how this co-ordinate space is to be transcribed into ordinary space. It would appear that most of the difficulty has arisen from an attempt to apply it illegitimately to enclosed systems, which are really outside the idea of space. In most of the problems we shall discuss the question hardly arises, but where it does the correct procedure is so obvious that there is no need to deal with it in advance. It is tempting to believe that this will be found to be always the case.

The problems of the present work have been mostly chosen as being the simplest possible, and the methods are almost wholly those of the classical wave theory. As to physical content, there is a very close relationship with the work of Dirac and Heisenberg, but the language is so different that it would not be

† 'Roy. Soc. Proc.,' vol. 113, p. 621 (1927), etc.
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profitable to trace the connections. Following these other methods Kennard* has recently solved some of the same problems, and it is hardly necessary to say has obtained the same results.

§ 2. The Description of Motions.

Our whole outlook on any problem will, of course, be very different from that to which dynamics have accustomed us, and the old habit of thought is so ingrained that it may not be amiss to examine the difference more closely. Thus when we thought of a stream of electrons, we might, for example, have described it by assigning at every point a distribution of velocities, say Maxwellian, round a certain mean velocity. But now all individuality is lost and we think of each electron as itself possessing the whole Maxwellian distribution. It is thus indifferent whether we speak of one electron or of a stream.† If we attempt to contradict this by saying that experiments have been made which prove that the distribution is real, in that some electrons are observed to have velocity higher than the average and some lower, the answer is that the observing instrument has itself created these different velocities, in just the same way as a spectroscope creates coloured light out of white.

Again, consider the free motion of an electron. As a particle it moves along a line, but the wave solution is a set of plane waves without any special line for the motion. This is in conformity with the "uncertainty relation" which, when the direction of motion is accurately given, refuses to define the line of motion at all. Now in all practical problems some sort of spatial limitation is imposed, and to see how this is to be done here we may profitably turn to the analogous case of optics.

It is often possible to separate optical problems into two parts, which we may call the wave problem and the ray problem respectively. In the wave problem an unlimited wave can be used to give the general features of the result, and the question of the limitation of the beam by slits, etc., can be introduced later in determining such things as the resolving power of the instrument. This second part—sometimes called the "theory of optical instruments"—often does not arise or else is very simple and so it tends to be forgotten that it is

† If, regarded as particles, the electrons are so close together that they influence one another's motions, then the wave equation will not be reducible to a set of independent equations for each of them. The system would not be in space, and the method of observation must be described before anything can be said about their relationship to space. In the present paper such very dense streams are excluded.
quite as essential as the first part. This neglect is due to the character of the experiments with which optics have been concerned during the last century; more importance has come to be attributed to the interference fringes seen through a half-wave plate than to the fact that things look double when seen through a crystal. Now the wave aspect of matter is a century behind that of light, and so the class of experiments that have hitherto been done with electrons have not called into play any such complicated interference phenomena. For this reason the ray problem—depending on the limitation of beams—is for electrons quite as important as the wave problem. But that is not all, for electrons have the complication that the wave velocity depends very strongly on the wavelength, so that group velocity is a very important consideration, and the actual motion of rays cannot be directly seen even qualitatively from the solution of the wave problem without a proper consideration of the limitation of the beam. It thus proves more convenient not to attempt to separate the problem into two parts, but to construct solutions of the wave equation which contain the limitations *ab initio*. With this method all that remains of the ray problem is merely the derivation of the intensity from the amplitude by squaring its modulus.

The first attack on a problem of this kind is due to Schrödinger,* who constructed a "wave packet" for a harmonic oscillator. This is exactly the sort of thing we require, but his packet is a very exceptional case without general application. In experiments a beam of electrons is usually limited by passing through a slit, but this gives rise to rather troublesome Fresnel diffraction formulae and so is not mathematically very convenient. For the most part we shall make use of a different limitation, which was introduced by Heisenberg. In the language of particles he supposes that the uncertainty of position is given by a Gaussian error function; corresponding to this we shall look for solutions in which the electron wave is located in a region of space defined by an error function. The chief reason for its use is mathematical convenience, as there is no other form which yields simple mathematical functions for solutions, but in many cases it can be justified physically. For example, if electrons are emitted by a hot filament, their velocities should have a Gaussian distribution, which will be represented in the wave theory by waves of which the amplitude contains an error function. Again, if we determine the position of an electron by means of Heisenberg's "microscope," we shall make an error in fixing it, and may invert the probability and attribute this error to the uncertainty

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* 'Naturwissenschaften,' vol. 14, p. 664 (1926).
relation, and so adopt the error function for the limitation on the initial position of the electron.

In this connection one feature of the present processes perhaps deserves mention, because of its difference from what we are accustomed to in dynamics. There we think of a particle describing a trajectory and can take any point of the trajectory indifferently as starting point of the motion. But in the wave theory the experimental conditions always mark out some special position, say a slit, as starting point, and at other places the waves will have spread. Thus, unlike the case of dynamics, we do not expect to get a solution in which the starting point is quite indifferent.

When de Broglie first developed his wave theory he based it largely on the help of relativity. The consequence is that the wave velocity of an electron is much greater than the velocity of light. This is ultimately correct of course, but it is an unnecessary complication always to have to consider relativity in dealing with quite slow motions. We shall throughout the present work avoid doing so by taking a factor $e^{-\frac{2\pi i m c t}{\hbar}}$ out of our wave functions, which is done by a simple and familiar modification of the wave equation. We shall, of course, get quite a different value for the wave velocity from that of de Broglie. To borrow an analogy from the practice of wireless telephony, we are observing our waves with the help of a heterodyne frequency $mc^2/h$, and when we speak of the phase of a wave we mean the phase of the sound heard in the telephone, not that of the aethereal vibrations.

§ 3. Methods of Solution.

There is no new principle in deriving the wave equation. If the Hamiltonian of our system is $H(\ldots q_s \ldots p_s \ldots)$ we set down as wave equation:

$$H\left(\ldots q_s \ldots \frac{\hbar}{2\pi i} \frac{\partial}{\partial q_s} \ldots \right) \psi = -\frac{\hbar}{2\pi i} \frac{\partial \psi}{\partial t}.$$  

In doing this we need not consider the question of the order of operations in $H$, because it does not arise in any of our problems. We suppose that $\psi$ is given for every value of the $q$'s at $t = 0$, and the solution of the wave problem consists in finding its value everywhere at any other time. We next have the ray problem. We take the conjugate complex quantity $\psi^*$ and form

$$\psi \psi^* = \rho (\ldots q_s \ldots t),$$  

† In practical work I can strongly recommend the convenience of taking $\hbar = 2\pi$. This was used throughout the present work, saves a great deal of writing, and reduces the use of Fourier integrals to the standard form. It is easy to restore $\hbar$ at the end by dimensional principles.
which is the intensity, a real function of the time and co-ordinates. Lastly,
we have the interpretation, when we change our language and speak of particles
instead of waves and probabilities instead of intensities.

To come to details, we will treat of one degree of freedom. We take the
system

$$H(x, p) = \frac{1}{2} p^2 + V(x).$$  \hfill (3.1)

The associated wave equation is

$$\frac{1}{2} \left( \frac{\hbar}{2\pi i} \right)^2 \frac{\partial^2}{\partial x^2} \psi + V(x) \psi = -\frac{\hbar}{2\pi i} \frac{\partial \psi}{\partial t}. \hfill (3.2)$$

We need as solution a function $\psi(x, t)$ which at time $t = 0$ is a given complex
function $f(x)$. The best methods of solving make use of Fourier integrals in
a variety of ways which we must consider. Put

$$\psi(x, t) = \int e^{-i\frac{2\pi}{\hbar} W t} \psi(x, W) \phi(W) dW, \hfill (3.3)$$

where $\phi(W)$ is undetermined. The integration goes from $-\infty$ to $\infty$. Through­
out the paper we shall imply these limits without writing them in the integrals.
Then $\psi(x, W)$ must satisfy Schrödinger's original equation

$$H(x, \frac{\hbar}{2\pi i} \frac{\partial}{\partial x}) \psi = W\psi. \hfill (3.4)$$

The functions $\psi(x, W)$ constitute a complete mutually orthogonal set of
functions, either with $W$ arbitrary or having a discrete set of proper values.
We shall chiefly be concerned with the case where $W$ may be continuous and
shall assume this, though the other case works just as well. The function
$\psi(x, W)$ need not be normalised, but is to be selected as a continuous function
of $W$. The initial condition is

$$f(x) = \int \psi(x, W) \phi(W) dW, \hfill (3.5)$$

and by the orthogonal property we can determine

$$\phi(W) = \int f(x) \psi^*(x, W) dx / \int \left( \int \psi(x, W) \psi^*(x, W) dW \right) dx. \hfill (3.3)$$

(3.3) then gives $\psi(x, t)$ by writing in the value of $\phi(W)$. We can then at once
set down the intensity and make the interpretation.

The functions $\psi(x, t)$ and $\psi(x, W)$ contain as variables the dynamically con­
jugate quantities $t$ and $W$ and are related together by the Fourier integral (3.3).
A similar process can be applied for any other conjugate pair and is very useful.
For example, set

$$\psi(x, t) = \int e^{i\frac{2\pi x p}{\hbar}} \psi(p, t) dp. \hfill (3.6)$$
Here $p$ has been introduced simply as the variable of a Fourier integral, and this is all that momentum really is in the wave mechanics; but we can connect it formally with the dynamical momentum by considering that

$$\frac{\hbar}{2\pi i} \frac{\partial}{\partial x} \psi(x, t) = \int e^{\frac{2\pi i}{\hbar} px} \psi(p, t) \cdot p \cdot dp.$$ 

It is easy to show that $\psi(p, t)$ obeys a wave equation which is obtained by interchanging the roles of co-ordinate and momentum in the Hamiltonian.

More useful than the function $\psi(p, t)$ is the function $\psi(p, W)$ defined by

$$\psi(x, t) = \int e^{\frac{2\pi i}{\hbar} (px - Wt)} \psi(p, W) \, dp \, dW,$$  

since it gives a most convenient way of solving the wave equation in many problems. If we substitute (3.7) in (3.2) we get

$$\int e^{\frac{2\pi i}{\hbar} (px - Wt)} \psi(p, W) \{H(x, p) - W\} \, dp \, dW = 0,$$  

an integral equation that can be set down at once from the Hamiltonian without even writing out the wave equation. It is often easy to solve and in many cases gives the solution in its most convenient form.

Consider, for example, the case of a free electron in one dimension—

$$H = \frac{1}{2m} p^2.$$  

Then for each value of $p$ in the integral choose $W = \frac{1}{2m} p^2$ and (3.8) will be satisfied. This means that we are to omit the $W$ integration in (3.7) and write

$$\psi(x, t) = \int e^{\frac{2\pi i}{\hbar} \left(px - \frac{p^2}{2m}\right)} \phi(p) \, dp,$$  

where $\phi(p)$ is arbitrary. We shall take this as the standard form of the solution. The verification that it satisfies the wave equation is immediate.

A more complicated example is that of uniformly accelerated motion, say,

$$H = \frac{1}{2m} p^2 - mgx.$$  

Pursuing the same course we take (3.7) as solution, where now

$$\int e^{\frac{2\pi i}{\hbar} (px - Wt)} \psi(p, W) \left\{\frac{1}{2m} p^2 - mgx - W\right\} \, dp \, dW = 0.$$  

We integrate the term in $mgx$ by parts, so as to remove the $x$, and reject the integrated term by assuming that the disturbance vanishes for infinite values. Then we have

$$\int e^{\frac{2\pi i}{\hbar} (px - Wt)} \left\{\left(\frac{1}{2m} p^2 - W\right) \psi(p, W) + \frac{\hbar}{2\pi i} mg \frac{\partial \psi}{\partial p}\right\} \, dp \, dW = 0.$$
The factor in brackets vanishes if

\[
\psi(p, W) = e^{i \frac{2\pi}{\hbar} \left( \frac{W}{m} p - \frac{1}{6} \frac{p^3}{m^2} \right)} \phi(W)
\]  
(3.11)

with \(\phi(W)\) arbitrary. So we have

\[
\psi(x, t) = \int \int e^{i \frac{2\pi}{\hbar} \left( px - Wt + \frac{Wp}{m} - \frac{1}{6} \frac{p^3}{m^2} \right)} \phi(W) \, dp \, dW.
\]  
(3.12)

If we solved for \(\psi(x, W)\) directly we should find it a troublesome function, of which even the asymptotic approximations are quite inconvenient. We shall see that the whole problem of accelerated motion can be treated by the present method without any discussion of this function.

The method is, of course, always available, but does not always lead to the simplest solution. For example, in the case of a harmonic oscillator Schrödinger's direct solution for \(\psi(x, W)\) is just as good, as is evident because, for

\[
H = \frac{1}{2} p^2 + \frac{1}{2} \omega^2 x^2,
\]
the wave equation in the \(p\)-space will have the same form as in the \(x\)-space. Nevertheless, similar methods are often useful. For example, in Schrödinger's original solution for the hydrogen atom the substitution

\[
\psi(r, \theta, \phi, t) = S_k(0, \theta) \int \int e^{i \frac{2\pi}{\hbar} (pr - Wt)} \phi(p, W) \, dp \, dW
\]
leads immediately, by means of one integration by parts, to the Laplacian method of solution used by Schrödinger himself.

§ 4. Electrons under No Forces, One Dimension.

The free motion of an electron in one dimension has already been disposed of by Heisenberg from the point of view of matrices. His process does not have much direct cognizance of phases, and so can to some extent take shortcuts by not working out these unobservable quantities; but this advantage is outweighed by the much more difficult ideas involved.

We take \(H = \frac{1}{2m} p^2\) and have seen that the solution is in the form (3.9). Following Heisenberg, we suppose that the initial disturbance is given by a "wave packet" of the form:

\[
f(x) = \exp \left[ - \frac{1}{2\sigma^2} (x - x_0)^2 + i \frac{2\pi}{\hbar} mv (x - x_0) \right].
\]  
(4.1)

The initial intensity thus is

\[
\varphi(x, 0) = e^{-\frac{1}{\sigma^2} (x-x_0)^2}.
\]  
(4.2)

Making the interpretation, this measures the relative probabilities for the initial
position of the electron, and we may conveniently express it by saying that the
electron is at \( x_0 \pm \sigma \). The complex part of (4.1) has been chosen so that the
velocity is nearly \( v \), as we shall see.

To determine \( \langle \psi \rangle \) we have

\[
\int e^{i\frac{2\pi}{h} px} \phi (p) dp = \exp \left[ -\frac{1}{2\sigma^2} (x - x_0)^2 + i \frac{2\pi}{h} mv (x - x_0) \right],
\]

and so inverting the Fourier integral we get

\[
\phi (p) = \frac{\sigma}{\sqrt{2\pi}} \exp \left[ -\frac{1}{2} \left( \frac{2\pi \sigma}{h} \right)^2 (p - mv)^2 - i \frac{2\pi}{h} px_0 \right].
\]  

(4.3)

As we shall verify, this is interpreted as meaning that the momentum is
\( mv \pm \hbar/2\pi\sigma \), using the \( \pm \) sign in the same sense as above. Substitute in (3.9)
and carry out the integration, and we get

\[
\psi (x, t) = \sigma \sqrt{\frac{\hbar}{2\pi m}} \exp \left[ -\frac{1}{2} \left( x - x_0 - vt \right)^2 + i \frac{\hbar t}{2\pi m} \right].
\]  

(4.4)

It can, of course, be verified by direct substitution that this satisfies the wave
equation.*

We derive the intensity by multiplying by the conjugate and have

\[
\rho (x, t) = \frac{\sigma}{\sqrt{\sigma^2 + (\hbar t/2\pi m)^2}} \exp \left[ -\frac{(x - x_0 - vt)^2}{\sigma^2 + (\hbar t/2\pi m)^2} \right],
\]  

(4.5)

so that the electron at time \( t \) is interpreted as being at

\( x_0 + \pm \sqrt{\sigma^2 + (\hbar t/2\pi m)^2} \).

We explain this by saying that the initial position was \( x_0 \pm \sigma \), and the velocity
is \( v \pm \hbar/2\pi m \), so that at time \( t \) the position will be \( x_0 + \pm \sigma \pm \hbar t/2\pi m \),
and as the two uncertainties are independent they are compounded by squares.
The product of the uncertainties of co-ordinate and momentum is \( \hbar/2\pi \),
which is Heisenberg's uncertainty relation. Observe how the limitation on
the initial position of a stream of electrons of necessity leads to an uncertainty
in their velocity, and so to their "straggling" along the direction of motion.

* The term outside the exponential is necessary in order to satisfy the wave equation, but
is otherwise uninteresting. It would usually be found convenient and sufficient to drop it.
In the present work it has, however, been usually retained for the sake of completeness.
We may write (4.4) (omitting the first factor) as

\[ \exp \left[ -\frac{1}{2} \frac{(x - x_0 - vt)^2}{\sigma^2 + (h/2\pi m)^2} \left( 1 - i \frac{ht}{2\pi m} \right) + i \frac{2\pi}{h} mv (x - x_0 - \frac{1}{2} vt) \right]. \]  

(4.6)

The imaginary part describes the phase. For a short time the quadratic term will be small and so the planes of zero phase will be given by \( x = x_0 + \frac{1}{2} vt + n \frac{h}{mv} \) for integral values of \( n \); that is to say, the phase velocity is half the ray velocity. Later the phase becomes more confused on account of the quadratic terms, which give a contribution like a Fresnel diffraction expression; but there does not seem any point in studying the complicated geometry of these phases until experiments are devised to bring them into evidence.

The error function with which we started ceases to be one in the ordinary sense on account of the imaginary quadratic term. We may conveniently from the mathematical point of view include such complex values of \( \sigma \) under the name of error function, and may if we like regard the motion as starting from such a complex value. But, as pointed out in § 2, there is one outstanding time in the motion, that when \( \sigma^2 + iht/2\pi m \) becomes purely real, which it is natural to regard as the initial time, because that is where the experimental limitation occurs, and where the straggling is less than it is either before or after.

The great advantage of taking the initial disturbance \( f(x) \) as given by an error function (in the extended sense) is that only so is it possible to work out the integrals completely. In the general case we can put down

\[ \psi (x, t) = \frac{1}{h} \int e^{i \frac{2\pi}{h} \left( px - \frac{p^2 x}{2m} t \right)} dp \int e^{i \frac{2\pi}{h} p^2 t} f(\xi) d\xi, \]  

(4.7)

which gives \( \psi (x, 0) = f(x) \). We can then carry out one integration and have

\[ \psi (x, t) = \sqrt{\frac{m}{ht}} e^{-i \frac{\pi}{4}} \int e^{i \frac{2\pi m}{ht} (x - \xi)^2} f(\xi) d\xi. \]  

(4.8)

It is now clear that only when \( f(x) \) is an error function is the other integration simple.

§ 5. Electrons under No Forces, Three Dimensions.

An exactly similar solution holds for three dimensions. If \( p, q, r \) are the components of momentum in directions \( x, y, z \), the Hamiltonian is

\[ H = \frac{1}{2m} (p^2 + q^2 + r^2) \]  

(5.1)
and the wave equation is
\[ \frac{1}{2m} \left( \frac{h}{2\pi i} \right)^2 \Delta \psi = -\frac{h}{2\pi i} \frac{\partial \psi}{\partial t}. \] (5.2)

The form of solution that corresponds to (3.9) is
\[ \psi(x, y, z, t) = \int e^{i \frac{2\pi}{\hbar} \left( px + qy + rz - \frac{p^2 + q^2 + r^2}{2m} t \right)} \phi(p, q, r) \, dp \, dq \, dr. \] (5.3)

When the initial disturbance is given we can evaluate \( \phi \) by putting \( t = 0 \) and using Fourier’s theorem, and can then substitute back into (5.3).

Take as initial disturbance the wave packet
\[ \exp \left[ -\frac{1}{2} \left( \frac{(x - x_0)^2}{\sigma^2} + \frac{(y - y_0)^2}{\tau^2} + \frac{(z - z_0)^2}{\nu^2} \right) \right] + i \frac{2\pi}{\hbar} m \left[ u(x - x_0) + v(y - y_0) + w(z - z_0) \right]. \] (5.4)

Then
\[ \phi = \frac{\sigma \tau \nu}{\hbar^3} (2\pi)^{3/2} \exp \left[ -\frac{1}{2} \left( \frac{2\pi}{\hbar} \right)^2 \left\{ \sigma^2 (p - mu)^2 + \tau^2 (q - mv)^2 + \nu^2 (r - mw)^2 \right\} + \frac{2\pi}{\hbar} \left( px_0 + qy_0 + rz_0 \right) \right] \] (5.5)

and
\[ \psi = \frac{\sigma \tau \nu}{\sigma' \tau' \nu'} \exp \left[ -\frac{1}{2} \left( \frac{(x - x_0 - ut)^2}{\sigma'^2} + \frac{(y - y_0 - vt)^2}{\tau'^2} + \frac{(z - z_0 - wt)^2}{\nu'^2} \right) \right] + i \frac{2\pi}{\hbar} m \left[ u(x - x_0 - \frac{1}{2} ut) + v(y - y_0 - vt) + w(z - z_0 - \frac{1}{2} wt) \right], \] (5.6)

where
\[ \sigma'^2 = \sigma^2 + i\hbar t/2\pi m, \quad \tau'^2 = \tau^2 + i\hbar t/2\pi m, \quad \nu'^2 = \nu^2 + i\hbar t/2\pi m. \]

There is no need for us to write out the intensity, since it too is exactly like the case of one dimension. We have got the wave representing an electron initially at \( x_0 \pm \sigma, y_0 \pm \tau, z_0 \pm \nu, \) and moving with velocity \( u \pm \hbar/2\pi m, v \pm \hbar/2\pi m, \) \( w \pm \hbar/2\pi m. \) If \( v = w = 0, \) we may say that we have roughly represented a stream of electrons emitted by a hot filament so as to have uncertainty \( \hbar/2\pi m \) in their velocity, then rapidly* accelerated to velocity \( u, \) and then passed through a slit of breadth \( 2\tau \) and height \( 2\nu. \) From the similarity of the expressions for \( \sigma' \) and \( \tau', \nu' \) we see that the lateral scattering of the stream obeys the same rule as the longitudinal straggling.

To give a more accurate account of electrons going through a slit, we must

* Rapidly, because otherwise they would straggle during the acceleration.
make use of the Fresnel diffraction formula. This is quite a classical question and need be only shortly touched on. The chief way in which it differs from the diffraction of light arises from the variable wave velocity, which prevents the use of "retarded" wave functions. We are compelled instead to analyse by Fourier integrals.

We suppose that the wave function, together with its differential along the normal, is known at every time and at every point on a closed surface S, and we have to evaluate it at any point inside S. It is best to make a slightly different analysis from that which we had before, by writing

\[ \psi(x, y, z, t) = \int e^{-i \frac{2\pi}{\lambda} \frac{s}{c} t} \psi(x, y, z, s) \, ds, \]

and using \( \psi(x, y, z, s) \). Do the same for \( \frac{\partial}{\partial n} \psi(x, y, z, t) \). Then \( \psi(x, y, z, s) \) and \( \frac{\partial}{\partial n} \psi(x, y, z, s) \) are known for every value of \( s \) and at every point \( x, y, z \) on S. Let \( x_1, y_1, z_1 \) be the point inside S at which we require \( \psi \) and let

\[ r^2 = (x - x_1)^2 + (y - y_1)^2 + (z - z_1)^2. \]

Then the application of Green's theorem in the usual way gives

\[ \psi(x_1, y_1, z_1, t) = \frac{1}{4\pi} \int e^{-i \frac{2\pi}{\lambda} \frac{s}{c} t} \int \left\{ \psi(x, y, z, s) \frac{\partial}{\partial n} \frac{e^{i \frac{2\pi}{\lambda} sr}}{r} - \frac{e^{i \frac{2\pi}{\lambda} sr}}{r} \frac{\partial}{\partial n} \psi(x, y, z, s) \right\} \, dS. \]

This formula makes it easy to work out the effect of a slit or grating by suitable choice of the surface S. We shall not enter into the matter beyond noting that, just as for light, so here, when S is a plane, we get a factor \( i \) representing the quarter wave-length change necessary to give the Huyghenian wave construction, and a factor \( 1 + \cos \theta \) (\( \theta \) being the angle of deviation of the rays) which explains why the wave construction excludes a transmission of the wave backwards.


Our purpose is partly the illustration of a variety of methods, and so we shall treat of the motion of an electron under uniform acceleration in two different ways, the first of which is the more general application of principle, but not quite so simple mathematically. It will suffice to consider the motion in one dimension, as the three can be treated independently.
Free Motion in Wave Mechanics.

We take (3.12) as the form of solution, and (4.1) as initial disturbance. $\phi (W)$ is then determined from

\[
\int e^{i \frac{2\pi}{h} (px + \frac{Wp}{mg} - \frac{1}{6} \frac{p^3}{m^2g})} \phi (W) \, dp \, dW
\]

\[= \exp\left[-\frac{1}{2\sigma^2} (x - x_0)^2 + i \frac{2\pi}{h} \frac{mv (x - x_0)}{p}\right]
\]

by two inversions (involving multiplication by $e^{-i \frac{2\pi}{h} px}$ and integration for $x$, and by $e^{-i \frac{2\pi}{h} \frac{Wq}{mg} q - \frac{1}{6} \frac{q^3}{m^2g}}$ and integration for $q$ respectively). We get

\[
\phi (W) = \frac{\sigma \sqrt{2\pi}}{h^2mg} \exp\left[-\frac{1}{2} \left(\frac{2\pi \sigma^2}{h}\right)^2 (q - mv)^2 - i \frac{2\pi}{h} \left(\frac{Wq}{mg} - \frac{1}{6} \frac{q^3}{m^2g} + qx_0\right)\right] dq.
\]

(6.1)

If this is substituted in (3.12) the integrations can be carried out in the order $W, p, q$. The result is

\[
\psi (x, t) = \frac{\sigma}{\sqrt{\sigma^2 + iht/2\pi m}} \exp\left[-\frac{1}{2} \frac{(x - x_0 - vt - \frac{1}{2} gt^2)^2}{\sigma^2 + iht/2\pi m}\right.
\]

\[+ i \frac{2\pi}{h} \{mv (x - x_0 - \frac{1}{2} vt - \frac{1}{2} gt^2) + mgt (x - \frac{1}{6} gt^2)\}\].

(6.2)

The intensity is

\[
\varphi (x, t) = \frac{\sigma}{\sqrt{[\sigma^2 + (ht/2\pi \sigma m)^2]}} \exp. - \frac{(x - x_0 - vt - \frac{1}{2} gt^2)^2}{\sigma^2 + (ht/2\pi \sigma m)^2}.
\]

We thus see that the ray goes from $x_0 \pm \sigma$ to $x_0 + vt + \frac{1}{2} gt^2 \pm \sigma \pm ht/2\pi \sigma m$, giving the ordinary formula for accelerated motion, and a straggling exactly the same as that of unaccelerated motion. The phase obeys a rather complicated rule, and is of no direct importance, though its various terms are required in order that the wave equation may be satisfied by (6.2). If there were a grating, placed, say, at 45° to the vertical, and if we wished to know the positions of the diffraction maxima after the falling electrons had passed through it, these terms would have to be considered, but such a case is too remote to discuss at present.

Though the above is the most general method of dealing with accelerated motion, it has the disadvantage that $g$ occurs in the denominator, so that the transition to the case of no acceleration is troublesome. The second method is free from this difficulty, being, loosely speaking, an approximative method.
which happens to give an accurate solution. We look for a solution in the form
\[ \psi(x, t) = \int e^{i \frac{2\pi}{\hbar} (px - \frac{p^2}{2m})} \phi(p, t) \, dp. \]  
\hfill (6.3)

Substitute in the wave equation and we have
\[ \int e^{i \frac{2\pi}{\hbar} (px - \frac{p^2}{2m})} \left\{ -mgx \phi + \hbar \frac{\partial \phi}{\partial t} \right\} \, dp = 0. \]

Integrating the term in \( x \) by parts we get
\[ \int e^{i \frac{2\pi}{\hbar} (px - \frac{p^2}{2m})} \left\{ \frac{\hbar}{2\pi i} \frac{\partial \phi}{\partial t} + \frac{\hbar}{2\pi i} mg \frac{\partial \phi}{\partial p} - \frac{gpt \phi}{\partial t} \right\} \, dp = 0; \]

and so the equation is satisfied if we take
\[ \frac{\partial \phi}{\partial t} + \frac{1}{mg} \frac{\partial \phi}{\partial t} = \frac{2\pi i n^{k}}{\hbar m} \phi, \]  
\hfill (6.4)
of which the solution is
\[ \phi(p, t) = \chi(p - mg t) e^{i \frac{2\pi}{\hbar} (2\phi \phi - \frac{1}{2} mg \phi \phi)} \]  
\hfill (6.5)
with \( \chi \) arbitrary. The initial value (4.1) at once determines
\[ \chi(p) = \frac{\sigma}{\hbar} \sqrt{2\pi} \exp \left[ -\frac{1}{4} \left( \frac{2\pi \phi}{\hbar} \right)^2 (p - mg)^2 - i \frac{2\pi}{\hbar} px_0 \right]. \]

We change \( p \) into \( p - mg t \) in this and substitute in (6.5) and then the integration of (6.3) immediately leads to (6.2).

If the acceleration varies slowly, either with time or place, a solution can be constructed by piecing together solutions for regions within which the acceleration is sensibly constant; but we shall not enter into this more complicated question. If the variation of force is so rapid as to give perceptible differences within the region of the wave packet, the motion will differ from that predicted by classical mechanics. The approximative method would then fail and it would be necessary to find a true solution of the wave equation.

\section*{§ 7. Electrons under Constant Magnetic Force.}

In a uniform magnetic field we have of course to show that an electron describes a circle with angular velocity twice the Larmor rotation, and for this purpose the terms in the square of the magnetic force are essential, just as they are in the particle problem. Taking \( p, q, r \) as the momenta and \( \omega \) as the Larmor rotation about \( z \) (magnetic force = \( 2mec \omega / e \)), we have
\[ H = \frac{1}{2m} (p^2 + q^2 + r^2) + \omega (qx - yp) + \frac{1}{2} m \omega^2 (x^2 + y^2), \]  
\hfill (7.1)
so that the wave equation is
\begin{equation}
\frac{1}{2m} \left( \frac{\hbar}{2\pi i} \right)^2 \Delta \psi + \omega \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \psi + \frac{1}{2} m \omega^2 (x^2 + y^2) \psi = - \frac{\hbar}{2\pi i} \frac{\partial \psi}{\partial t}.
\end{equation}

The solution is best found by transforming to rotating axes. Put
\begin{align*}
x &= x' \cos \Omega t' - y' \sin \Omega t' \\
y &= y' \cos \Omega t' + x' \sin \Omega t' \\
t &= t'
\end{align*}
and we get
\begin{equation}
\frac{\partial}{\partial t'} = \frac{\partial}{\partial t} + \omega \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \quad \text{and} \quad \Delta' = \Delta,
\end{equation}
so that the equation becomes:
\begin{equation}
\frac{1}{2m} \left( \frac{\hbar}{2\pi i} \right)^2 \Delta' \psi + \frac{1}{2} m \omega^2 (x'^2 + y'^2) + \frac{\hbar}{2\pi i} \frac{\partial \psi}{\partial t'} = 0.
\end{equation}

The solution separates into products of functions of $x'$, $y'$, $z$. That of $z$ is like the motion without field and represents a gradual spreading of the wave along the direction of the magnetic field. It calls for no further comment. On the other hand, the motion in $x'$ and $y'$ differs from those we have so far considered in that the proper values are discontinuous. Let
\begin{equation}
F_u(z) = e^{\frac{z^2}{2} \left( \frac{d}{dz} \right)^u} e^{-z^2},
\end{equation}
so that
\begin{equation}
\frac{d^2}{dz^2} F_u(z) = [z^2 - (2u + 1)] F_u(z).
\end{equation}

Then our solution can be written as
\begin{equation}
\psi = \sum_{u,v} A_{u,v} F_u(x' \sqrt{\frac{2\pi m \omega}{\hbar}}) F_v(y' \sqrt{\frac{2\pi m \omega}{\hbar}}) e^{-i(u+v+1) \omega t'},
\end{equation}
where $A_{u,v}$ are arbitrary.

The most important feature of this expression is that $\psi$ is unchanged if $t$ is increased by $\pi/\omega$. For consider the point in space $x_0 y_0$. At time $t = \pi/\omega$ the point which overlies it has $x' = -x_0$, and since $F_u(-z) = (-)^u F_u(z)$ we shall have
\begin{equation}
F_u(x' \sqrt{\frac{2\pi m \omega}{\hbar}}) = (-)^u F_u(x_0 \sqrt{\frac{2\pi m \omega}{\hbar}}).
\end{equation}

Similarly for $y$, and the last factor in (7.6) gives another factor $(-1)^{u+v}$, so that altogether $\psi (t = \pi/\omega) = \psi (t = 0)$ for all values of $x$, $y$. Thus, unlike the case of free motion without field, there is no progressive spreading of the waves, but the wave packet returns to its original form in period $\pi/\omega$. The process
may be described in the same way as it is for particles. Schrödinger has shown that for a harmonic oscillator a wave packet can be constructed which, though it spreads in the intermediate states, always returns to its original form at each end of the swing. In the $x'y'$ co-ordinates we have a harmonic oscillator, for which this will be true; but these are rotating co-ordinates, and when the packet has swung across to its extreme position on the other side, the rotation will have carried this position just round to the point from which the motion started. Thus the packet will describe a circle with twice the Larmor rotation, and, though there will be a change in the form of the disturbance in intermediate positions, it will exactly return to its initial form on the completion of the circle.

It is perhaps possible to evaluate the $A_{n,v'}$'s for a wave packet of the Gaussian type that we have been using, but the work would be an unprofitable piece of mathematics which we shall not attempt. We may, however, exhibit a special case which can easily be got by adapting Schrödinger's wave packet. Put $A_m = 0$ when $v' = 0$ and $A_{m,0} = \frac{1}{n!} \left( -\frac{a}{2} \sqrt{\frac{2\pi m \omega}{\hbar}} \right)^m$, and we find on changing over from $x', y'$ to $x, y$ that

$$\psi = \exp \left[ -i\omega t - \frac{2\pi m \omega}{\hbar} \left\{ x^2 + y^2 - 2ae^{-i\omega t} (x \cos \omega t + y \sin \omega t) + \frac{1}{2}a^2 e^{-2i\omega t} \right\} \right], \quad (7.7)$$

an expression exactly satisfying the wave equation. The intensity is

$$\varphi = \exp \left\{ (x - a \cos^2 \omega t)^2 + (y - a \cos \omega t \sin \omega t)^2 - \frac{1}{2}a^2 \right\}. $$

Thus the locus of greatest intensity is the circle with the points, 0, 0 and $a, 0$ as diameter and is described with angular velocity $2\omega$. The packet is, however, not a very concentrated one, since $\omega$ is usually rather small. If we want a packet initially concentrated in a small region, it will during the motion spread over a wide region. This is interpreted by the consideration that the initial concentration corresponds to great uncertainty in the velocity, and so great uncertainty in the radius and tangent of the circle that the electron will describe. The return of the packet to its original size corresponds to the fact that all these circles are described in the same time.

If we are prepared to give up consideration of more than a small arc of the circle, we can treat the problem approximately by neglecting $\omega^2$. For purposes of later reference we shall include the $z$ motion again. We then have in $x', y', z$ a problem just like that of § 5 and can take as the solution

$$\psi(x, y, z, t) = \int e^{\frac{i}{a} \left( px + qy + rz - \frac{p^2 + q^2 + r^2}{2m}t \right)} \phi(p, q, r) \, dp \, dq \, dr. \quad (7.8)$$
It will make a sufficient illustration if we take a rather simpler initial
disturbance than (5.4). We take
\[ \psi(x, y, z, 0) = \exp\left[ -\frac{1}{2\sigma^2} (x^2 + y^2 + z^2) + i \frac{2\pi}{h} \sigma \right]. \] (7.9)
Then
\[ \phi(p, q, r) = \frac{\sigma^3}{h^3} \exp\left[ -\frac{1}{2} \left( \frac{2\pi}{h} \right)^2 \right] \exp\left[ (p - mv)^2 + q^2 + r^2 \right]. \] (7.10)
and
\[ \psi(x, y, z, t) = \frac{\sigma^3}{(\sigma^2 + i\hbar/2\pi m)^{3/2}} \exp\left[ -\frac{1}{2} \left( \frac{x' - v\tau}{\sigma} \right)^2 + \frac{y'^2 + z'^2}{\sigma^2 + i\hbar/2\pi m} \right] \exp\left[ i \frac{2\pi}{h} mv (x' - \frac{1}{2} vt) \right]. \] (7.11)
The ray depends on the first term in the exponent. The greatest intensity is
at
\[ x + y\omega t - vt = 0, \quad y - x\omega t = 0, \quad z = 0, \]
which gives approximately
\[ x = vt, \quad y = \omega t^2, \quad z = 0, \]
representing a velocity \( v \) and radius of curvature \( v/2\omega \), that is, angular velocity \( 2\omega \). The spread is just what it would be without field. It is of interest to
observe the second term in (7.11), which gives the phase of the wave. We
see that just as the wave velocity is half the ray velocity, so the wave
angular velocity is half the ray angular velocity. In fact, the wave turns with
exactly the Larmor rotation.


We shall next consider a problem that falls into a rather different category,
because the motion is in an atom and has no very direct concern with space.
Bohr has shown that Heisenberg's uncertainty relation only applies to a free
electron, and requires modification for one in an atom, where the classification
is by stationary states, not by positions. He considers the conjugacy of energy
and time in a hydrogen atom and uses an argument from an experiment conceived
in optical dispersion. We require to find in which of several quantum states
round about the $n$th the atom is, and the determination will take a certain
time to do.* If $W_1$ is the precision with which we wish to fix the energy,
and $t_1$ the time needed to do so, then $W_1 t_1 \sim n\hbar$, which tends to infinity for high
quantum states, whereas for a free electron $W_1 t_1 \sim \hbar$. This theorem is in the
language of particles and we shall make an inverse interpretation and discuss
what is the corresponding theorem for waves.

An electron is initially concentrated near a field of force in some sort of wave
packet. For example, we may imagine that by means of Heisenberg’s $\gamma$-ray
microscope we have detected an electron near a hydrogen nucleus in the form
of a packet like (5.4) with $x_0$, etc., so adjusted that on the older quantum theory
the particle would describe the $n$th circular quantum orbit. The wave will
propagate itself in a determinate way, and to work this out we only require to
develop the initial disturbance in a series of proper functions appropriate to the
atom and associate with each of these a harmonic time factor. The phases of
the time factors change at different rates, and (apart from special cases like the
harmonic oscillator of Schrödinger) they will gradually fall out of step, so that
they will finally be completely discoordinated. When this has happened we
can no longer speak of a wave packet at all, but only of an atom possessing a
number of stationary states simultaneously. Now make the interpretation.
There is a certain probability of the atom being in any one stationary state, and
as the states have different energies, the energy of the atom is uncertain. We
take this uncertainty for $W_1$. Again, it takes some time for the packet to break
up, and until it does so we cannot speak of a single stationary state at all. So
we take for $t_1$ the length of time that the packet takes to become completely
discoordinated. We shall then show that $W_1 t_1 \sim n\hbar$.

We shall only deal with high quantum states, and this makes it possible to
apply to the wave theory the results of general dynamics. We take the case
of one degree of freedom, a co-ordinate $q$ which is describing a librating

* The argument is briefly this. Consider how long an experiment with a hydrogen atom
must take in order to decide whether the atom is in the $n$th or $(n + 1)$th state. A way of
deciding would be to observe the dispersion of light of such a frequency that it is below
the natural frequency of the line $n \rightarrow (n - 1)$ and above that of $(n + 1) \rightarrow n$. Thus we must
use light of which the frequency is sufficiently definite only to have a “tolerance” of
amount $\Delta \nu = R \left( \frac{1}{(n - 1)^2} - \frac{1}{n^2} \right) - R \left( \frac{1}{n^2} - \frac{1}{(n + 1)^2} \right)$ or approximately $6R/n^4$. This
requires a train containing at least $\nu/\Delta \nu$ waves, and takes a time $t_1 = 1/\Delta \nu$ to pass over the
atom. With such a train we can test whether the energy is $R \hbar/n^2$ or $R \hbar/(n + 1)^2$, that is, we
can measure the energy with precision $R \hbar \left( \frac{1}{n^2} - \frac{1}{(n + 1)^2} \right)$, or approximately $2R \hbar/n^2$. Thus
$W_1 t_1 \sim \frac{1}{2} n \hbar$. 

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Free Motion in Wave Mechanics.

A cyclic movement goes in the same way and is rather simpler. Let $H(q, p)$ be the Hamiltonian and let us suppose that the whole problem is solved according to the methods of the older quantum theory. We then know the solution $S(q, J)$ of the Hamilton-Jacobi equation and can use $S$ to define a contact transformation. This introduces the angle variable $\theta$, which increases by unity every time that $q$ describes a libration. $H$ can be expressed in terms of $J$ without $\theta$ as $W(J)$, and if $\omega = \partial W/\partial J$, the motion of the system is given by $q = \omega t + \varepsilon$. The quantum states are given by $J = n\hbar$.

The solution of the wave equation of $H$ can be expressed asymptotically in terms of $S$. Associated with the proper value $W(J)$ we have

$$\psi(q, W) \sim e^{i \frac{2\pi}{\hbar} S(q, J)} f(q).$$

By substituting in the wave equation we can determine regression formulae for the terms of $f(q)$. The leading term is $(\partial S/\partial q)^{-1}$, and this shows the limitation on the asymptotic series, for $\partial S/\partial q$ vanishes at the turning points of the motion of the librating particle. The series is available well outside this region, where the exponent is real and negative, and well inside where the exponent is pure imaginary, but it fails near the turning points. We shall not investigate this failure, but shall assume that in spite of it we may use $e^{i \frac{2\pi}{\hbar} S(q, J)}$ as solution of the wave equation. The sequence of proper functions is obtained by putting $J = n\hbar$, and we shall write the typical one as $e^{i \frac{2\pi}{\hbar} S_n(q)}$. In order that the coefficients in the expression for intensity may represent actual probabilities, the functions must be normalised. In the present form they are so normalised with sufficient accuracy; for the modulus is unity within the range of the particle’s motion and small outside, and the ranges are nearly of the same extent for all the states near the $n$th.

Consider the expression

$$\psi(q, t) \sim \sum_m \exp \left[ -\frac{1}{2} \alpha^2 (m - n)^2 + i \frac{2\pi}{\hbar} (S_m(q) - S_m(q_0) - W_m t) \right]. \quad (8.1)$$

which satisfies the wave equation approximately. When $t = 0$ every term is real at $q = q_0$, and so, if $\alpha$ is small, the intensity will be very great there, whereas at other places the terms nearly cut out. In fact (8.1) represents a wave packet starting at $q_0$. We must sum the series in order to exhibit the packet, and we shall thus be able to see how it spreads until it disappears. On account of the

* We may take this to be $\frac{1}{2} (\frac{\hbar}{2\pi i})^2 \tilde{\varepsilon}^2 \tilde{\gamma} \tilde{\varepsilon} + V(q) \psi = W\psi.$
first term in the exponent only values of \( m \) near \( n \) contribute to the sum, and for these we may write

\[
S_m(q) = S_n(q) + \hbar (m - n) \frac{\partial S_n(q)}{\partial \J} + \frac{\hbar^2}{2} (m - n)^2 \frac{\partial^2 S_n(q)}{\partial \J^2},
\]

Thus, writing \( w_n \) for \( \partial S_n / \partial \J \), we have

\[
\psi = \sum_m \exp \left[ -\frac{1}{2} \alpha^2 (m - n)^2 + i \frac{2\pi}{\hbar} \left( S_n(q) - S_n(q_0) - W_n \right) + \hbar (m - n) (w_n(q) - w_n(q_0) - \omega_n t) + \frac{\hbar^2}{2} (m - n)^2 \left( \frac{\partial w_n(q)}{\partial \J} - \frac{\partial w_n(q_0)}{\partial \J} - \frac{\partial^2 W_n(q)}{\partial \J^2} \right) \right].
\]

This can now be summed by a well-known theorem of Jacobi,* and gives (apart from an unimportant term outside the exponential)

\[
\psi \sim \exp \left[ -\frac{1}{2 \alpha^2} \left( \frac{2\pi}{\hbar} \right)^2 \frac{\left( w_n(q) - w_n(q_0) - \omega_n t \right)^2}{\frac{\partial w_n(q)}{\partial \J} - \frac{\partial w_n(q_0)}{\partial \J} - \frac{\partial^2 W_n(q)}{\partial \J^2}} \right]. (8.2)
\]

Here the numerator of the second term is many-valued, and the smallest value is to be taken. The intensity is

\[
\varphi \sim \exp \left[ -\frac{\left( \frac{2\pi}{\hbar} \right)^2 \frac{\left( w_n(q) - w_n(q_0) - \omega_n t \right)^2}{\frac{\partial^2 W_n(q)}{\partial \J^2} - \frac{\partial w_n(q)}{\partial \J} + \frac{\partial w_n(q_0)}{\partial \J}}}{\frac{\partial w_n(q)}{\partial \J} - \frac{\partial w_n(q_0)}{\partial \J}} \right]. (8.3)
\]

We may also express this by saying that the electron is at

\[
w_n(q) = w_n(q_0) + \omega_n t \pm \frac{\alpha}{2\pi} \pm \frac{\hbar}{\alpha} \left( \frac{\partial W_n(q)}{\partial \J} - \frac{\partial w_n(q)}{\partial \J} + \frac{\partial w_n(q_0)}{\partial \J} \right). (8.4)
\]

Here \( q \) occurs on both sides, so that we ought really to solve the equation to determine the limits of the wave packet. If, however, \( \hbar/\alpha \) is fairly small, we can see how the packet will behave without doing so. Imagine that we have a \( \gamma \)-ray microscope, with which we can detect the electron at any moment (but in conformity with Heisenberg's principle the observation can only be made once, as its disturbance will spoil the atom for later use). (8.4) then expresses the range in which we shall probably find the electron. At first it will swing to and fro through the range allowed for \( q \) in the \( n \)th quantum state, but the size of the packet will fluctuate a little on account of the term

\[
\frac{\hbar}{\alpha} \left( \frac{\partial w_n(q)}{\partial \J} - \frac{\partial w_n(q_0)}{\partial \J} \right).
\]

* See, for instance, Whittaker and Watson, 'Modern Analysis,' p. 124.
Free Motion in Wave Mechanics.

which for a librating motion vanishes twice in every cycle.* Thus we should locate the electron rather precisely twice in the cycle and not quite so precisely at other times. If we attempted to map out the motion by the study of many similar atoms—remember that each may only be used once—we should get something very like the orbit of the particle in the \( n \)th state; but the discrepancies in the various determinations would be just enough to leave it open which state near the \( n \)th was the exact orbit represented. With the lapse of time, however, the term \( \frac{\hbar}{\alpha} \frac{\partial^2 W}{\partial J^2} t \) grows in importance and spreads out the region in which we may find the electron. This region will finally fill the whole range of \( q \), and then we can no longer speak of a packet at all. To fill the whole range of \( q \), \( \omega \) must be uncertain by unity and this shows that

\[
t_1 = \frac{\hbar}{\alpha} \int \frac{\partial^2 W_n}{\partial J^2}.
\]

(8.5)

To find the uncertainty in the energy we return to (8.1). When the phases have all become discoordinated, the intensity is simply \( \sum_m e^{-\alpha^2 (m-n)^2} \) and the separate terms represent then the probabilities of the atom being in each state. To define the uncertainty of the energy we naturally take a mean-square formula and have

\[
(W_1)^2 = \sum_m (W_m - W_n)^2 e^{-\alpha^2 (m-n)^2} / \sum_m e^{-\alpha^2 (m-n)^2}.
\]

We write \( W_n + \hbar (m-n) \frac{\partial W_n}{\partial J} \) for \( W_m \) and replace the sum by an integral. Then

\[
(W_1)^2 = \frac{1}{2\alpha^2} \left( \hbar \frac{\partial W_n}{\partial J} \right)^2.
\]

(8.6)

Thus

\[
W_1 t_1 = \frac{1}{2\sqrt{2}} \frac{\partial W_n}{\partial J} / \frac{\partial^2 W_n}{\partial J^2}.
\]

(8.7)

This applies to any system that can be quantised. In the case of a harmonic oscillator \( W = \omega J \) and \( \partial^2 W / \partial J^2 = 0 \), so that the wave takes an infinite time to spread. For the hydrogen atom \( W = -\Lambda/2J^2 \) and \( W_1 t_1 = \frac{J}{6\sqrt{2}} \sim nh \). A similar form holds for any case where \( W \) is proportional to a power of \( J \) other than the first.

* When a non-periodic motion is treated by the present method, these terms do not fluctuate but increase, and this prevents the useful application of the method to such cases.
We have only treated of one degree of freedom, as other cases are trivial. If there are two non-degenerate degrees the spreading will occur independently with regard to each, and we shall merely have to take the higher quantum number of the two for our theorem. If the system is degenerate, there is no spreading between the degenerate degrees.


In considering the motion of atoms we at once meet a new problem in that the wave equation is not in ordinary space, while the observations must be interpreted in space. It will suffice to consider an atom composed of one electron and one proton. The wave equation will then be an equation in six variables corresponding to the three co-ordinates of each particle, but a transformation can be made which replaces these co-ordinates by \( X, Y, Z \) those of the centre of gravity, and \( x, y, z \) those of the electron relative to the proton. The observation of the atom must be supposed to take place by its producing a scintillation like an \( \alpha \)-particle, or being deposited on a plate as in the experiments of Stern and Gerlach, and this makes it easy to see how the system must be related to space, for we must obviously identify \( X, Y, Z \) with space and suppose \( x, y, z \) to be not directly observable. We shall avoid irrelevant complications by only allowing the atom to be in a \( p \)-state (and indeed the \( p \)-state of lowest energy); it will be clear that this sufficiently illustrates the process. Such an atom would show a Stern-Gerlach pattern of three members, viz.: \( 1, 0, -1 \) Bohr magnetons.

If \( M \) is the total mass and \( 1/m \) the sum of the reciprocals of the masses of proton and electron, the Hamiltonian is

\[
\frac{1}{2M} (P^2 + Q^2 + R^2) + \frac{1}{2m} (p^2 + q^2 + r^2) - \frac{e^2}{s},
\]

where \( s \) is the distance between the particles, and \( P \ldots r \) are the momenta conjugate to \( X \ldots z \). The wave equation is

\[
\left\{ \frac{1}{2M} \left( \frac{\hbar}{2\pi i} \right)^2 \Delta_X + \frac{1}{2m} \left( \frac{\hbar}{2\pi i} \right)^2 \Delta_x - \frac{e^2}{s} \right\} \psi = - \frac{\hbar}{2\pi i} \frac{\partial \psi}{\partial t},
\]

where \( \Delta_X, \Delta_x \) are the usual operators \( \Delta \), referring respectively to the co-ordinates \( X, Y, Z \) and \( x, y, z \). Consider first the equation

\[
\frac{1}{2m} \left( \frac{\hbar}{2\pi i} \right)^2 \Delta_x \psi - \frac{e^2}{s} \psi = W \psi.
\]

If we limit ourselves to the lowest \( p \)-states, we have the following solutions:

\[
W = W_1; \quad \psi = \chi_1, \chi_0, \chi_{-1};
\]
where \( W_1 = -\frac{2\pi^2}{\hbar^2} m e^4 \).

\[
\chi_1 = (x + iy) f(s), \quad \chi_0 = z f(s), \quad \chi_{-1} = (x - iy) f(s) \quad (9.4)
\]

with \( f(s) = e^{-s} \cdot 2\pi^2 me^4/\hbar^2 \).

As the Stern-Gerlach experiment will show in the next section, \( \chi_1, \chi_0, \chi_{-1} \) correspond to atoms with 1, 0, \(-1\) Bohr magnetons. We try as solution of

\[
\psi = \chi_1 \phi_1 (X, Y, Z, t) + \chi_0 \phi_0 (X, Y, Z, t) + \chi_{-1} \phi_{-1} (X, Y, Z, t) \quad (9.5)
\]

and have

\[
\frac{1}{2M} \left( \frac{\hbar}{2\pi i} \right)^2 \Delta_X \psi = -\frac{\hbar}{2\pi i} \frac{\partial \psi}{\partial t} - W_1 \psi.
\]

This is the equation for rectilinear motion, the term in \( W_1 \) simply giving an extra factor \( e^{-\frac{2\pi^2 me^4}{\hbar^2}} \). There is no need to discuss it further.

Consider now the case of motion in the presence of a uniform magnetic field. When the square of the field is negligible, this simply adds on a term \( \omega (xq - yp) \) to the Hamiltonian, where the field is along \( z \) and of strength \( \omega \cdot \frac{2me}{e} \). The wave equation therefore has a term \( \frac{h}{2\pi i} \omega (x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x}) \psi \).

Since

\[
\left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \begin{bmatrix} \chi_1 \\ \chi_0 \\ \chi_{-1} \end{bmatrix} = \begin{bmatrix} i \chi_1 \\ 0 \\ -i \chi_{-1} \end{bmatrix},
\]

we get on substituting (9.5)

\[
\frac{1}{2M} \left( \frac{h}{2\pi i} \right)^2 \begin{bmatrix} \chi_1 \Delta_X \phi_1 + \chi_0 \Delta_X \phi_0 + \chi_{-1} \Delta_X \phi_{-1} + \phi_1 W_1 \frac{\omega}{2\pi} \chi_1 \\ \chi_0 \phi_0 \\ \chi_{-1} \phi_{-1} \end{bmatrix} = -\frac{\hbar}{2\pi i} \frac{\partial \psi}{\partial t}.
\]

Pick out the coefficients of \( \chi_1, \chi_0, \chi_{-1} \) and solve for the \( \phi \)'s.

Then the appropriate solution is

\[
\psi = \int \exp \left\{ \frac{2\pi i}{\hbar} \left[ PX + QY + RZ - \frac{1}{2M} \left( P^2 + Q^2 + R^2 \right) t - W_1 t \right] \right\}
\times \theta (P, Q, R) \left\{ a_1 e^{-\frac{\omega}{\hbar} t} \chi_1 + a_0 \chi_0 + a_{-1} e^{\frac{\omega}{\hbar} t} \chi_{-1} \right\} dP dQ dR. \quad (9.7)
\]

The last factor only contains the internal co-ordinates which are not observed, and the first shows that the motion is rectilinear, just as before.

* Strictly speaking, there are small mixed terms in \( x \) and \( X \) which average out, and the quantity here is not really \( m \) but \( \frac{m_1 m_2}{m_1 - m_2} \), where \( m_1, m_2 \) are the masses of the particles.
This is all that we can strictly say about the motion, and it requires a Stern-
Gerlach experiment to evoke the character of the last bracket in (9.7). But,
by imagining that the uniform field might be followed at will by a suitably
chosen non-uniform one, we may be allowed to make an interpretation of what
is not actually being observed, and we then say that the atom undergoes a
uniform precession at rate $\omega$ about the $z$ axis. Consider, for example, an atom
of which the original state is $(x + iz)f(s)$, which means that it has one Bohr
magneton along $-y$. Then this factor must become

$$\left[\frac{1}{2} (x + iy) e^{-i\omega t} + iz + \frac{1}{2} (x - iy) e^{i\omega t}\right]f(s)$$

and this expresses a magneton turning from $-y$ to $x$, then to $+y$, etc., with
angular velocity $\omega$. Thus, as stated in § 1, the atom behaves exactly as it would
in classical dynamics. We may note that this gives an explanation, though very
incomplete, of why the Langevin formula for magnetic susceptibility is reinstated
by the wave mechanics, as shown by Van Vleck.*

To exhibit the Stern-Gerlach effect we need little more than a combination
of the process of the last section with that of § 6. The wave going through
the non-uniform field, like light going through a crystal, is resolved into com­
ponents which are propagated differently, so that, if the field is long enough and
the terminal plate far enough, the components produce separate patches on the
plate.

We take a pencil of atoms going along the direction of $X$, in a field of com­
ponents $0, -\kappa Y, H + \kappa Z$. This is the simplest non-uniform field satisfying
the electromagnetic equations. We shall suppose that $H$ is so large that near
the origin, in the region passed by the pencil, the resultant magnetic force is
nearly along $Z$, and we shall as usual take the square of the magnetic force to
be negligible. The wave equation now is

$$\frac{1}{2M} \left(\frac{\hbar}{2\pi i}\right)^2 \Delta_x \psi + \frac{1}{2m} \left(\frac{\hbar}{2\pi i}\right)^2 \Delta_x \psi - \frac{e^2}{s} \psi$$

$$+ \frac{e}{2mc} \frac{\hbar}{2\pi i} \left\{ (H + \kappa Z) \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \right.$$ 

$$\left. - \kappa Y \left( \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) \right\} \psi = - \frac{\hbar}{2\pi i} \frac{\partial \psi}{\partial t}. \quad (10.1)$$

We follow the second method of § 6 and so take as solution

$$\psi = \int_{^3} \exp \left( i \frac{2\pi}{\hbar} (PX + QY + RZ - \frac{P^2 + Q^2 + R^2}{2M} t - W_1 t) \right) \times \{ \theta_1 (P, Q, R) \chi_1 + \theta_0 (P, Q, R) \chi_0 + \theta_{-1} (P, Q, R) \chi_{-1} \} \, dP \, dQ \, dR. \quad (10.2)$$

In substituting in (10.1) we have to make use of (9.6) and also of the relations

$$\begin{align*}
\left\{ \frac{z \partial}{\partial x} - x \frac{\partial}{\partial z} \right\} \theta = & \begin{cases} 
\chi_1 & \chi_0 \\
\chi_0 & \frac{1}{2} (\chi_1 + \chi_{-1}) \\
\chi_{-1} & \chi_0
\end{cases}.
\end{align*} \quad (10.3)$$

We thus get

$$\int_{^3} dP \, dQ \, dR \exp \left( i \frac{2\pi}{\hbar} (PX + QY + RZ - \frac{P^2 + Q^2 + R^2}{2M} t - W_1 t) \right) \times \left\{ e^\frac{\hbar}{2\pi i} \left[ (H + \kappa Z) (i \theta_1 \chi_1 - i \theta_{-1} \chi_{-1}) - \kappa Y (\theta_i \chi_0 - \frac{1}{2} \theta_0 \chi_1 + \chi_{-1} + \theta_{-1} \chi_0) \right] + \frac{\hbar}{2\pi i} \left[ \frac{\partial \theta_1}{\partial t} \chi_1 + \frac{\partial \theta_0}{\partial t} \chi_0 + \frac{\partial \theta_{-1}}{\partial t} \chi_{-1} \right] \right\} = 0. \quad (10.4)$$

Integrate by parts the terms in Y and Z; and equate to zero the coefficients of the \(\chi\)'s and we have

$$\begin{align*}
\frac{\partial \theta_1}{\partial t} = & \frac{eH}{2mc} \theta_1 + \frac{e\kappa}{2mc} \left[ - \frac{\hbar}{2\pi i} \frac{\partial \theta_1}{\partial R} + \frac{R}{M} t \theta_1 + \frac{1}{2} \frac{\hbar}{2\pi i} \frac{\partial \theta_0}{\partial Q} - \frac{i Q}{2 M} t \theta_0 \right] \\
\frac{\partial \theta_0}{\partial t} = & \frac{e\kappa}{2mc} \left[ - \frac{\hbar}{2\pi i} \left( \frac{\partial \theta_1}{\partial Q} + \frac{\partial \theta_{-1}}{\partial Q} \right) + \frac{Q}{M} t \left( \theta_1 + \theta_{-1} \right) \right] \\
\frac{\partial \theta_{-1}}{\partial t} = & - \frac{eH}{2mc} \theta_{-1} + \frac{e\kappa}{2mc} \left[ \frac{\hbar}{2\pi i} \frac{\partial \theta_{-1}}{\partial R} - \frac{R}{M} t \theta_{-1} + \frac{1}{2} \frac{\hbar}{2\pi i} \frac{\partial \theta_0}{\partial Q} - \frac{i Q}{2 M} t \theta_0 \right]
\end{align*} \quad (10.4)$$

These equations differ from (6.4) in the presence of the cross-terms (those involving Q). This is due to the fact that the direction of the magnetic force varies from point to point, so that the \(\chi\)'s do not represent exactly the proper functions suitable to each position, and with waves, unlike particles, we cannot treat of each position separately. It is physically fairly obvious that this little complication will have no effect, but to demonstrate it we must use the fact that \(H\) is great compared to the variations of the field in the region traversed by the waves. If \(\kappa\) were to vanish we should have

$$\theta_1 = \theta_1' e^{-\frac{eH}{2mc} t}, \quad \theta_0 = \theta_0', \quad \theta_{-1} = \theta_{-1}' e^{\frac{eH}{2mc} t}. \quad (10.4)$$
We form the equation for $\theta_1'$

$$i \frac{\partial \psi'}{\partial t} = \frac{ek}{2mc} \left( -\frac{h}{2\pi i} \frac{\partial \psi'}{\partial R} + \frac{R}{M} t \theta_1' \right) + \frac{1}{2} \cdot \frac{ek}{2mc} e^{i \frac{eh}{2mc} t} \left( \frac{h}{2\pi i} \frac{\partial \theta_1'}{\partial Q} - i \frac{Q}{M} t \theta_1' \right).$$

The last expression in this undergoes rapid fluctuations on account of the exponential factor, and if we only ask for the average of $\theta_1'$ over the period of a Larmor rotation, it will be insignificant in its effect. Thus, since we only want averaged results, we may drop out from (10.4) all the cross terms, and this reduces those equations to the form (6.4), which has been solved. In writing down the solution we may omit the terms in $k^2$, and have

$$\theta_1 = \theta_1^0 (P, Q, R - \frac{ek}{2mc} \frac{h}{2\pi M} t) \exp \left[ -i \frac{eH}{2mc} t - \frac{ek}{2mc} \frac{1}{2} \frac{R}{M} \left( \frac{1}{t^2} \right) \right].$$

$$\theta_0 = \theta_0^0 (P, Q, R)$$

$$\theta_{-1} = \theta_{-1} (P, Q, R - \frac{ek}{2mc} \frac{h}{2\pi M} t) \exp \left[ i \frac{eH}{2mc} t + i \frac{ek}{2mc} \frac{1}{2} \frac{R}{M} \left( \frac{1}{t^2} \right) \right].$$

(10.5)

We take as initial disturbance

$$\psi = (a_1 \chi_1 + a_0 \chi_0 + a_{-1} \chi_{-1}) \exp \left[ -\frac{1}{2} \left( \frac{X^2}{\sigma^2} + \frac{Y^2}{\sigma^2} + \frac{Z^2}{v^2} \right) + i \frac{2\pi}{h} MVX \right],$$

(10.6)

which may be taken as a stream of atoms, of arbitrary orientation given by $a_1 a_0 a_{-1}$, with velocity $V = \frac{h}{2\pi \sigma M}$ along the X-direction, passing, roughly speaking, through a slit of breadth $2\tau$ and height $2v$. By the method of (5.5) we immediately have as initial values

$$\theta_1^0 = a_1 S, \quad \theta_0^0 = a_0 S, \quad \theta_{-1}^0 = a_{-1} S,$$

where

$$S = \frac{\sigma \tau^0}{h^3} \left( 2\pi \right)^{3/2} \exp \left[ -\frac{1}{2} \left( \frac{2\pi}{h} \right)^2 \left[ \sigma^2 (P - MV)^2 + \frac{e^2}{2} Q^2 + \frac{v^2 R^2}{} \right] \right].$$

We change the arguments of the $\theta$'s in conformity with (10.5), substitute in (10.2) and carry out the integrations. The result is

$$\psi = \frac{\sigma \tau^0}{\sigma^2 \tau v^2} \exp \left[ -\frac{1}{2} \left( \frac{X - \frac{1}{3} Vb}{\sigma^2} \right)^2 - \frac{1}{2} \frac{Y^2}{\sigma^2} + i \frac{2\pi}{h} MV \left( X - \frac{1}{3} Vb \right) - i \frac{2\pi}{h} W_1 t \right]$$

$$\times \left\{ a_1 \chi_1 \exp \left[ -i \frac{e}{2mc} \left( H + \kappa Z \right) t - \frac{1}{2} \left( Z + \frac{1}{2} \frac{ek}{2mc} \frac{h}{2\pi M} t \right)^2 / \left( v^2 \right) \right] \right\}$$

$$+ a_0 \chi_0 \exp \left[ -\frac{1}{2} \cdot Z^2 / v^2 \right]$$

$$+ a_{-1} \chi_{-1} \exp \left[ i \frac{e}{2mc} \left( H + \kappa Z \right) t - \frac{1}{2} \left( Z - \frac{1}{2} \frac{ek}{2mc} \frac{h}{2\pi M} t \right)^2 / \left( v^2 \right) \right] \right\}.$$ 

(10.7)

where $\sigma^2 = \sigma^2 + ihl/2\pi M$, etc. From this we form the intensity by
multiplying by the conjugate and integrating over the internal co-ordinates. Let
\[ J_1 = \int \chi_1 \chi_2 \, dx \, dy \, dz, \]
etc., and writing \( \sigma' \sigma'' \) for \( \sigma^2 + (\hbar t/2\pi\sigma M)^2 \), etc., we have
\[ \varphi (X, Y, Z, t) = \frac{\sigma' \sigma''}{\sigma' \sigma''} \exp \left[ - \frac{(X - Vt)^2}{\sigma' \sigma''} \right] \left| a_1 \right|^2 J_1 \exp \left( Z + \frac{1}{3} \frac{ek}{2mc} \frac{\hbar}{2\pi M} t^2 \right) \right|_{\sigma' \sigma''}
\[ + \left| a_0 \right|^2 J_0 \exp \left( - Z^2 / \sigma' \sigma'' \right) \]
\[ + \left| a_{-1} \right|^2 J_{-1} \exp \left( Z - \frac{1}{3} \frac{ek}{2mc} \frac{\hbar}{2\pi M} t^2 \right) \right|_{\sigma' \sigma''} \}.

There are thus three rays, one of which accelerates upwards at rate \( \frac{ek}{2mc} \frac{\hbar}{2\pi M} \), one goes straight, and one downwards also at rate \( \frac{ek}{2mc} \frac{\hbar}{2\pi M} \). This acceleration corresponds to a force \( \frac{ek}{2mc} \frac{\hbar}{2\pi} \) acting on a particle of mass \( M \), and as \( \kappa \) is the differential of the magnetic force, this force would be called into play by attributing to the particle magnetic moment \( \frac{e}{2mc} \frac{\hbar}{2\pi} \). In fact, we have exactly the three components of the Stern-Gerlach effect as it would be observed with our atomic model.

\( \S 11. \) The Spinning Electron.

Our last problem will be the motion of the spinning or polarised electron. The wave theory of this was recently developed by the present writer* for motion in an atom, but the case of free motion was deferred. In a recent paper Pauli† has discussed the matter, and it will be well first to consider his results, which are rather different from those we shall have here. Pauli treats the following problem: An assembly of electrons are all pointing along and none away from a magnetic field. The field suddenly changes in direction through angle \( \theta \). Then he claims that the electrons will divide into two groups, one along and one away from the new field, and their numbers will be in the ratio
\[ \cos^2 \frac{\theta}{2} : \sin^2 \frac{\theta}{2}.
\]
In the first place it is very questionable whether it is legitimate to postulate a sudden change of field. To produce it we should have to construct a set of rapidly changing electromagnetic forces. These could be analysed into electric

waves, and if the change is to be very abrupt, some of these waves will have very high frequency. It can hardly be right to make the sudden change without considering the Compton effect of these waves, which would be an elaborate business, and anyhow was not contemplated. But even if we admit the sudden change, on our present view it will not split the electrons into two groups, for we have seen (with atoms) that in a uniform field they will simply precess round the axis of the new field. It requires a non-uniform field to separate them, and in that case Pauli’s result is valid. The magnetic moment is initially \( \cos \theta \), and the assembly is separated into two parts of moment \( \pm 1 \), and the ratio of the intensities, or the number of the electrons, must be in the ratio \( (1 + \cos \theta) : (1 - \cos \theta) \).

The polarised electron has four wave equations. We shall take these from the paper cited (equations (5.2)), but make the modification that excludes relativity. This means that we remove a factor \( e^{-i\frac{2\pi mc^2}{\hbar}} \) from the wave function, and omit terms involving \( 1/c^2 \). The interaction between the wave components was represented by means of a vector operator \( U \) involving both electric and magnetic forces, but the electric terms are of order \( 1/c^2 \) and so fall out here. The equations are only accurate to the first order in the magnetic field, so that we must only look for solutions to this degree of precision; we have no right to follow an electron round the complete circle in a uniform magnetic field.

Equations (3.1) and (5.2) of the other paper are modified to conform to the present usage. If the external magnetic field has components \( \frac{2mc}{e} \{ \omega_1, \omega_2, \omega_3 \} \) and if the operator \( D \) means

\[
\frac{1}{2m} \left( \frac{\hbar}{2\pi i} \right)^2 \Delta + \frac{\hbar}{2\pi i} \left( \frac{\partial}{\partial \ell} + \omega_1 \left( y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) + \omega_2 \left( z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) + \omega_3 \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \right),
\]

the equations are

\[
\begin{align*}
\text{DX}_1 &= -\frac{\hbar}{2\pi i} \omega_1 X_4 - \frac{\hbar}{2\pi i} \omega_2 X_3 + \frac{\hbar}{2\pi i} \omega_3 X_2 = 0 \\
\text{DX}_2 &= -\frac{\hbar}{2\pi i} \omega_2 X_4 - \frac{\hbar}{2\pi i} \omega_3 X_1 + \frac{\hbar}{2\pi i} \omega_1 X_3 = 0 \\
\text{DX}_3 &= -\frac{\hbar}{2\pi i} \omega_3 X_4 - \frac{\hbar}{2\pi i} \omega_1 X_2 + \frac{\hbar}{2\pi i} \omega_2 X_1 = 0 \\
\text{DX}_4 &= +\frac{\hbar}{2\pi i} \omega_1 X_1 + \frac{\hbar}{2\pi i} \omega_2 X_2 + \frac{\hbar}{2\pi i} \omega_3 X_3 = 0
\end{align*}
\]

(11.1)
Of the four X’s, \(X_1, X_2, X_3\) are the components of a vector and \(X_4\) is scalar. When there are electric forces, their potential must be added to \(D\) in the usual way, but we shall have no occasion to do so here.

The wave functions which are a solution of (11.1) have the peculiarity that they are partly indeterminate, that is to say, a number of different solutions will give results that are physically indistinguishable. In fact, equations can be set down for two fully determinate quantities \(f, g\), and then with any fixed arbitrary constants \(\alpha, \beta\) (but constants that must be transformed when the axes are changed) we can take

\[
X_1 = \alpha f + \beta g, \quad X_2 = i\alpha f - i\beta g, \quad X_3 = -\beta f + \alpha g, \quad X_4 = i\beta f + izg.
\]

In consequence of these relations the X’s must obey the relation

\[
X_1^2 + X_2^2 + X_3^2 + X_4^2 = 0
\]

(not, be it observed \(|X_1|^2, \text{ etc.}\); but as long as complex quantities are retained in the wave theory, it is not easy to see a physical meaning in this relation.†)

The use of \(f\) and \(g\) often abbreviates the mathematics, but if we are to endow the wave with any sort of physical reality, we must suppose that some two things are being carried by it; \(f\) and \(g\) are then inadmissible, because they obey a rather complicated law of transformation for changes of axes, and we cannot suppose that things carried by the wave have a knowledge of the axes we happen to be using. Nothing in theory as it at present stands compels us to prefer any special values of \(\alpha, \beta\), as all known conditions are satisfied anyhow, but by examining a free electron we shall see that a certain special choice is appropriate.

The equations (11.1) determine the wave amplitudes. To determine the intensity we have to form the quantity

\[
\rho = X_1 X_1^* + X_2 X_2^* + X_3 X_3^* + X_4 X_4^*.
\]

(11.4)

This measures the chance of finding the electric charge at a point. We also have to consider the magnetic moment, which is composed of two parts. The first is the magnetism due to the convection of electricity, which we may disregard as being unconnected with the spin and fully explained. The second part is the intensity of intrinsic magnetic moment and its components are proportional to

\[
\mu_1 = -i (X_2^* X_3 - X_2 X_3^* - X_1^* X_4 + X_1 X_4^*),
\]

(11.5)

e tc. These quantities should bear an absolute ratio \(\hbar/4\pi mc\) to the electron

† If we simply separate the X’s into real and imaginary parts, (11.3) implies that the two four-vectors are of equal magnitude and perpendicular. But this does not get us much farther.
intensity, but by supposing a suitable unit of magnetic moment, we need not consider this.

The interpretation into terms of particles brings in a slightly different conception from that which we have hitherto had; for we have four intensities now, but they are all to be interpreted as belonging to the same electron. We might, for example, have wave functions such that \( \rho \) has a maximum at a point \( A \), whereas \( \mu \) has a maximum at a different point \( B \). There is no discrepancy in this; it means that the particle is most likely to be found at \( A \), but if it is found there its axis is rather uncertain. On the other hand, the electron is less likely to be at \( B \), but if it is found there it is very certain how it will be pointing. Thus our formulae give just the necessary flexibility in describing the uncertainty relation for the spinning electron.

With these preliminaries we may now return to the solution. If there is no magnetic field, each of the four equations (11.1) is independent, apart from the condition (11.3). To represent a stream of electrons all having the same polarisation, we only require to multiply the expression (5.6) by four arbitrary constants, provided these satisfy (11.3). This suggests the possibility of giving the wave components a canonical form by a special choice of \( \alpha, \beta \) in (11.2). In the motion there are two directions which are of pre-eminent importance, the direction of the polarisation, and the direction of motion; the latter must be included because, as they stand, our equations do not admit of the relativity transformation. If there is any canonical form for the vector, it must be related to one or both of these directions. Trial shows that it is best to consider only the polarisation, and that any solution can be brought into the form

\[
X_1 = \varphi_1 P, \quad X_2 = \varphi_2 P, \quad X_3 = \varphi_3 P, \quad X_4 = P, \quad (11.6)
\]

where \( P \) is the expression (5.6), and \( \varphi_1, \varphi_2, \varphi_3 \) are real and, in order that (11.3) may hold, \( \varphi_1^2 + \varphi_2^2 + \varphi_3^2 = 1 \). If we substitute in (11.5) we immediately see that the magnetic moment is along the line of direction cosines \( l_1 : l_2 : l_3 \). This special solution of the wave equations we shall call the canonical form.

We will next apply a uniform magnetic field along \( z \). The equation (11.1) become

\[
\begin{align*}
D X_1 - \frac{\hbar \omega}{2\pi i} X_2 &= 0, \\
D X_3 - \frac{\hbar \omega}{2\pi i} X_4 &= 0, \\
D X_2 - \frac{\hbar \omega}{2\pi i} X_1 &= 0, \\
D X_4 + \frac{\hbar \omega}{2\pi i} X_3 &= 0
\end{align*}
\]

(11.7)

where \( D \) is now

\[
\frac{1}{2m} \left( \frac{\hbar}{2\pi i} \right)^2 \Delta + \frac{\hbar}{2\pi i} \left[ \frac{\partial}{\partial t} + \alpha \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \right]
\]
Free Motion in Wave Mechanics.

the operator used, by itself, in the last part of § 7. We can form four separated equations in $X_1 \pm iX_2$, $X_3 \pm iX_4$, and then the solution is so like (7.11) that we need only give the result. We take as initial disturbance the form (11.6), in which $P$ stands for (7.9). This represents a stream of electrons polarised along the direction $l_1 : l_2 : l_3$ and projected from the origin along the $x$-axis with velocity $v$. Let $P'$ represent (7.11), so that it satisfies $DP' = 0$. Then the solution of (11.7) is

$$X_1 = i \left( l_1 \cos \omega t - l_2 \sin \omega t \right) P'$$
$$X_2 = i \left( l_2 \cos \omega t + l_1 \sin \omega t \right) P'$$
$$X_3 = i \left( l_3 \cos \omega t - i \sin \omega t \right) P'$$
$$X_4 = \left( \cos \omega t - il_3 \sin \omega t \right) P'$$

The associated four intensities are

$$\rho = 2 |P'|^2$$
$$\mu_1 = \left( l_1 \cos 2\omega t - l_2 \sin 2\omega t \right) 2 |P'|^2$$
$$\mu_2 = \left( l_2 \cos 2\omega t + l_1 \sin 2\omega t \right) 2 |P'|^2$$
$$\mu_3 = l_3 2 |P'|^2$$

We thus see that the magnetic moment turns at rate $2\omega$ just as the ray itself does, so that the magnets preserve their direction relative to the direction of motion of the electrons. We also see that a similar principle holds for the waves. The phase turns at rate $\omega$, as we saw in § 7, and we now see that the wave vector turns at this rate too. This is exactly true for the components perpendicular to the magnetic field, but requires qualification for that along the field, since this has an interaction with the scalar part of the wave $X_4$. If we may disregard this complication, we may express the magnetic character of the electron very simply by saying that in a magnetic field the wave vector turns with the wave front at the rate of the Larmor precession. From this statement all the properties of the spinning electron follow; the ratio of magnetic moment to angular momentum is $e/mc$ and not $e/2mc$, and finally the anomalous Zeeman effect is not at all anomalous!

The Stern-Gerlach effect for an electron is rather more troublesome than for an atom, because of the difficulty of devising a suitable non-uniform field; for the wave packet will approximately describe a circle and so rapidly pass out of the central region of such a field as that used in § 10. It will suffice here to show that it reduces to the same process as for the atom. If in (11.1) the $\omega$'s are regarded as constant, it is always possible to recombine the equations into
four in separated variables. For example, with the force along $z$ the equations are to be taken in $X_1 \pm iX_2, X_3 \pm iX_4$; in the general case the combinations are given by simple algebra which we need not work out. Apply this analysis to the non-uniform field, taking as direction for the resolution that of the field at the centre of the instantaneous position of the wave packet. For simplicity, let us suppose that this is the $z$ direction. Then just as in § 10 we can see that the transverse non-uniformity does not matter, so that we can regard $\omega$ as varying with $z$ and apply the method of § 6. This then shows that the rays split into two, and we have the Stern-Gerlach effect.

We have seen that an undesirable feature in the present way of treating the spinning electron is the ambiguity in the vector and invariant which together represent it. This ambiguity does not affect observed results, but is unsatisfactory when we try to make a physical picture of the wave. In the case of a free electron not acted on by forces, we have seen that there is a natural way of resolving it by the introduction of the canonical form, and it is much to be desired that this form should be extended to other cases. I have not hitherto had any success in doing this.

One way of attempting it is to take a polarised wave packet starting in free space and passing into a field of force. Then if we start with the canonical form in free space, the $X$'s are all given initially and the whole solution will therefore be definite. It would then be natural to call the solution inside the field canonical. (Observe that on this principle there is no reason to believe that (11.8) is the canonical solution for a constant magnetic field.) But the matter is not so simple as this; for if the canonical form is to have any utility, we must suppose that when the electrons emerge into free space they will, if completely polarised, again have a wave solution in canonical form. For example, imagine that we have a non-uniform field, roughly speaking along $z$, and that a stream of electrons pointing along $x$ enters it. On emerging there will be two streams pointing along $z$, and these ought automatically to come into canonical form. It seems at first sight very improbable that they would do so, but the following consideration perhaps tells the other way. Take the simple electron of § 7 and send it near the field of a magnet. Before it approaches the field the wave front is perpendicular to the ray. We may presumably imagine the field pieced together out of parts each sensibly constant, and in each of these the wave front turns at half the rate of the ray, and yet on emergence into free space the wave front must again be perpendicular to the ray, for that is the only solution corresponding to rectilinear propagation in free space. It would be interesting to see how this comes about, but a cursory examination of the
present material does not help much, because the quadratic term in the phase factor (see (4.6)) enormously outweighs the linear and confuses the matter. In fact, the waves become so involved that it seems impossible to follow them through in detail without much more elaborate mathematics. If in this case we know, without being able to prove, that the wave front must return to a position perpendicular to the ray, it seems not impossible that in our more complicated process the vector should return to the canonical form. If it should be proved to do so, we might claim to have a good line of attack on the question of finding the general canonical form. But at present we must conclude that nothing can be done to remove the ambiguity in the vector wave of the electron.

Summary.

Whereas hitherto the wave mechanics has mostly been applied to a study of stationary states, the present paper deals with its application to cases where there is a progress of events. After a review of principles and a description of the new way in which motion must be regarded, the following problems are discussed:

The free motion of an electron under no forces.
The motions of an electron in uniform electric and magnetic fields.
The motion of an electron in an atom.
The motion of an atom in a uniform magnetic field.
The Stern-Gerlach effect.
The motion of the spinning electron.