

T H E Q U A N T U M T H E O R Y

Present Day Problems and Outstanding
Questions of the Quantum Theory.

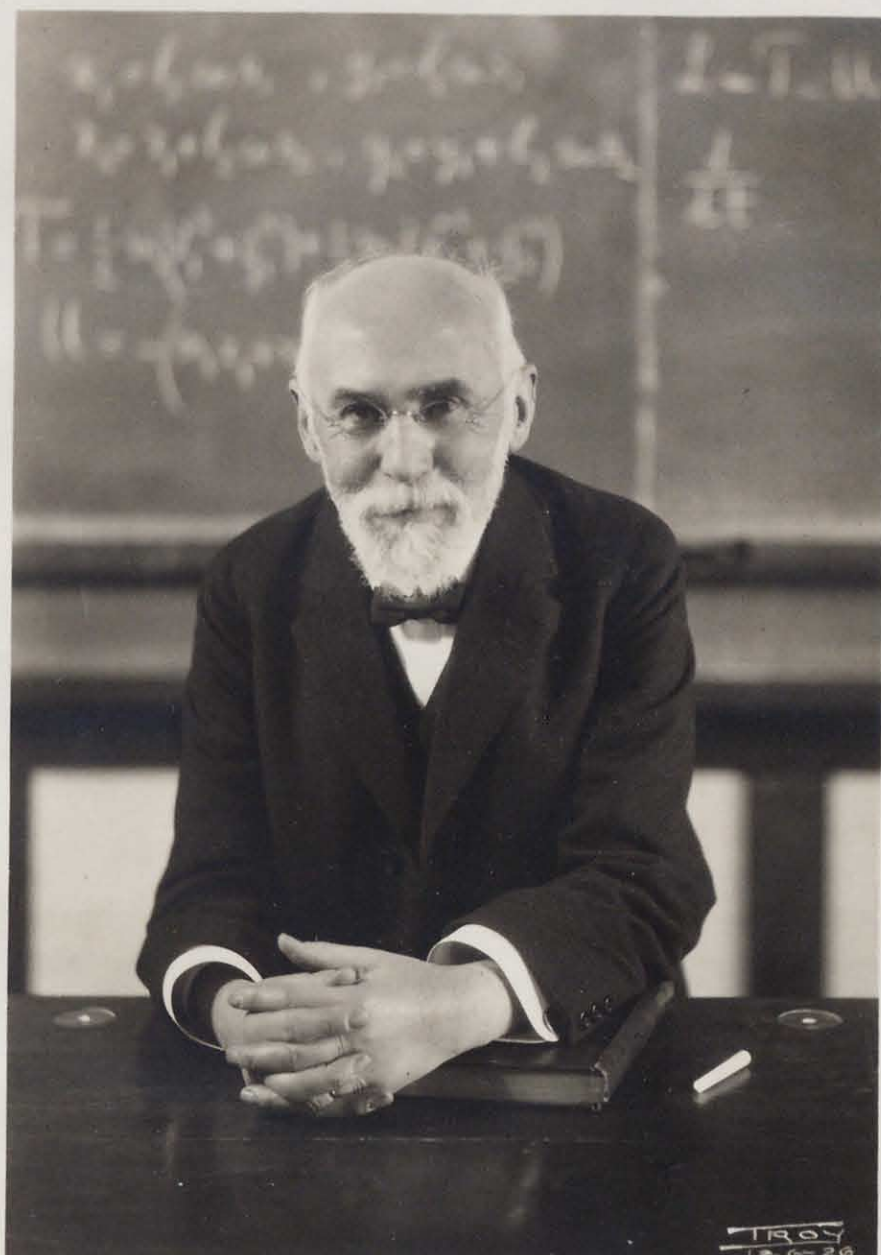
Notes accompanying lectures delivered by

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Theory of Spectral Lines. The frequency of each spectral line is given by the difference of two terms, which represent the energy of the atom in certain "stationary" states, divided by Planck's constant h .

Each stationary state is characterized by particular values of a certain number of quantum numbers. In the theory as it was first developed, these values were integral numbers; in later times, half numbers have been introduced also.

In simple cases the problem may be completely solved. The first step is to integrate the equations of motion, thus finding out the motions that can exist according to the laws of ordinary dynamics. The next step consists in quantizing these motions, i.e. in selecting the stationary states by suitably chosen quantum conditions. For the higher atoms it is impossible exactly to do all this. Yet the principles of the theory allow us to form a general idea of the origin of the different spectral lines and of the relations between them. After all, however, there are many outstanding difficulties, the solution of which will perhaps have to be sought in the new quantum mechanics that has been worked out by Heisenberg, Born, Schrödinger and others. To begin with, there will be no question of this, but only of the theory, the principles of which were laid down by Bohr.

Some General Remarks. The diversity of spectral lines in any case depends on the number of quantum numbers. If there is but one such number n , so that the energy is represented by an equation of the form

$$E = F(n) \quad , \quad .$$

there is a single series of stationary states and of corresponding energy levels and spectral terms. When there are two quantum numbers n_1, n_2 , $E = F(n_1, n_2)$, there will be a double series, and so on.

Any cause that produces a greater diversity in the spectral lines (f.i. a magnetic field that produces a Zeeman effect) does so by giving rise to the introduction of a new quantum number.

The quantum numbers may occur in a number much smaller than that of the constants of integration that would determine the motion of all the electrons. Yet, they must suffice for the determination of the energy. Otherwise, the spectral lines would not be sharp.

Discrepancy Between Bohr's Theory and Classical Dynamics.
Principle of Correspondence. According to the old theory of electricity an electron would radiate energy whenever its velocity is changed either in magnitude or in direction. The electrons revolving around the nucleus of an atom would produce electromagnetic waves spreading outward, whose frequency would be equal to that of the motions to which they are due. Bohr's theory denies the existence of this radiation. The atoms are supposed to radiate only when they pass from one stationary state to the other ("quantum jumps"); the frequency of the radiation determined by Bohr's rule is different from that of the motions existing in the atom.

Never theless, there is a kind of correspondence between the motions and the radiation. Consider the case that in the motion of the electronic system there are a certain number of fundamental periods, the frequencies being

$$p_1, p_2, p_3, \dots$$

Then each of the coordinates of the electrons may be represented by a multiple Fourier series, each term of which has the form

$$a \cos [(s_1 p_1 + s_2 p_2 + s_3 p_3 + \dots) t + q] \quad (1)$$

where s_1, s_2, s_3, \dots are integers. According to classical dynamics the partial motion represented by (1) will give rise to a radiation of the frequency

$$s_1 p_1 + s_2 p_2 + s_3 p_3 + \dots \quad (2)$$

This includes the fundamental frequencies, the upper harmonics and also the combination frequencies. In a case like this, Bohr's theory distinguishes as many quantum numbers n_1, n_2, n_3, \dots as there are fundamental periods, each n corresponding to a p . The relation between the two is expressed by the formula

$$\frac{dE}{dn_1} = h p_1, \quad \frac{dE}{dn_2} = h p_2 \quad \dots \quad (3)$$

Suppose that the number n_1 changes from a to b ($b < a$), the other quantum numbers remaining unaltered, and let the mean value during this transition of any function $f(n_1)$ be determined by

$$\frac{1}{a-b} \int_b^a f(n_1) dn_1$$

Then, one can say that when $b=a-1$ the frequency of the light to which the jump $n_1 = a \rightarrow n_1 = b$ gives rise, is equal to the mean value of p_1 . For this frequency is given by

$$\frac{E_a - E_b}{h} = \frac{1}{h} \int_b^a \frac{dE}{dn_1} dn_1 = \int_b^a p_1 dn_1 = \bar{p}_1 \dots (4)$$

Similary, if $b = a - s_1$ (s_1 an integral number) the emitted frequency will be equal to s_1 times the mean value of p_1 .

Indeed, in this case (4) is to be replaced by

$$\int_b^a p_1 dn_1 = s_1 \bar{p}_1 \quad (5)$$

Suppose now two of the quantum numbers n_1 and n_2 to change simultaneously, the one diminishing by s_1 and the other by s_2 . Imagine these changes to occur in two steps, first the transition from n_1 to $n_1 - s_1$ and then that from n_2 to $n_2 - s_2$. The total change of energy will be equal to the sum of the changes occurring in these steps and therefore the emitted frequency will be the sum of the frequencies that would correspond to the two steps, each taken by itself. This leads to the expression

$$s_1 \bar{p}_1 + s_2 \bar{p}_2$$

and by a similar reasoning, supposing any number of the quantum numbers to be altered, one can obtain a result, much like (2).

It should be especially noted that according to the new theory as well as to the old one, decomposition of lines by any external influence may be considered as due to the appearance of a new fundamental period in the motions of the electrons.

Motion of a Particle Subjected to a Central Force, the Relativity Terms Being Taken into Account. A well known result of the theory of relativity is that the momentum of a particle moving with velocity v is given by

$$m \propto v \quad (6)$$

where

$$\alpha = \frac{1}{\sqrt{1 - \frac{v^2}{c^2}}} \quad (7)$$

In this formula the mass m is a constant. Let U be the potential energy (a function of r). Equations of motion

$$\frac{d}{dt} (m \alpha \dot{x}) = - \frac{dU}{dx}, \quad \frac{d}{dt} (m \alpha \dot{y}) = - \frac{dU}{dy} \quad (8)$$

Equation of energy. Add these equations after having multiplied them by \dot{x} and \dot{y} . Since

$$\begin{aligned} \dot{x} \frac{d}{dt} (m \alpha \dot{x}) + \dot{y} \frac{d}{dt} (m \alpha \dot{y}) &= \frac{d}{dt} (m \alpha v^2) - m \alpha (\dot{x} \ddot{x} + \dot{y} \ddot{y}) = \\ &= \frac{d}{dt} (m \alpha v^2) - m c^2 \frac{d}{dt} \alpha = \frac{d}{dt} (m \alpha c^2) \end{aligned}$$

one finds

$$\frac{d}{dt} (m \alpha c^2) = - \frac{dU}{dt}$$

$$m\alpha c^2 + U = E \quad (\text{constant}) \quad \dots \dots \dots (9)$$

Equation of moment of momentum. Subtract one of the equations (8) from the other after having multiplied the first by y and the second by x .

The result may be written in the form:

$$0 = x \frac{d}{dt} (m\alpha \dot{y}) - y \frac{d}{dt} (m\alpha \dot{x}) = \frac{d}{dt} [m\alpha (x\dot{y} - y\dot{x})] ,$$

Thus

$$m\alpha (x\dot{y} - y\dot{x}) = C \quad (\text{constant}) \quad \dots \dots \dots (10)$$

By the introduction of polar coordinates r, θ eq. (10) takes the form

$$m\alpha r^2 \dot{\theta} = C \quad \dots \dots \dots (11)$$

But

$$v^2 = \dot{r}^2 + r^2 \dot{\theta}^2, \quad \dots \dots \dots (12)$$

so that

$$v^2 = \dot{r}^2 + \frac{C^2}{m^2 \alpha^2 r^2} .$$

If here the values of α and v^2 expressed in terms of r , which can be found from (9) and (7), are introduced, one is led to an equation of the form

$$\dot{r}^2 = f(r), \quad \dots \dots \dots (13)$$

giving

$$dt = \pm \frac{dr}{\sqrt{f(r)}} \quad \dots \dots \dots (14)$$

Integrating this equation one finds the relation between r and t . On the other hand, on account of (11)

$$d\theta = \frac{C}{m\alpha r^2} dt = \pm \frac{C dr}{m\alpha r^2 \sqrt{f(r)}} ,$$

by which the shape of the orbit is determined.

Closed and Open Orbits. Precessional Motion of an Orbit in its Plane. In many cases the function $f(r)$ is found to vanish for two values r_1 and r_2 of the radius vector ($r_1 < r_2$) and to be positive only in the interval between these. This means that there is a perihelium and an aphelium. As to θ it changes continually in the same direction, so that the particle is revolving around the centre.

There are two periods, one in which r changes from r_1 to r_2 and back again, and one in which θ changes by 2π . In the case of an attraction according to Coulomb's law (motion of an electron around a positively charged nucleus), and when the relativity terms are neglected, the two periods are equal, so that the orbit is closed (ellipse). No more than one effective quantum number is to be expected.

In general, however, the periods are unequal so that there will be two quantum numbers. The orbit is not closed but has the form of a rosette. The motion may be described as going on in a closed orbit rotating in its plane.

It ought to be remarked that whereas the number of fundamental periods becomes two, either by a departure from Coulomb's law or by the influence of the relativity terms, it remains two when the two causes are combined.

Quantization of the Motion in an Elliptic Orbit.

When the central force follows Coulomb's law, the potential energy is given by

$$U = - \frac{a}{r}, \quad (15)$$

Whereas, in the absence of relativity terms, the Kinetic energy is given by

$$T = \frac{1}{2} mv^2$$

or

$$T = \frac{1}{2} m(\dot{r}^2 + r^2 \dot{\theta}^2) \quad (16)$$

The partial derivatives of this expression with respect to r and $\dot{\theta}$ are the momenta corresponding to the coordinates r and θ ,

$$p_r = m\dot{r}, \quad p_{\theta} = mr^2\dot{\theta} \quad (17)$$

There are two quantum conditions (though it will be found that there is but one effective quantum number). The first is that p_{θ} , which according to (11) is a constant, must be a multiple of

$$\frac{h}{2\pi},$$

say

$$p_{\theta} = k \frac{h}{2\pi}.$$

This is the azimuthal condition. It may be put in the form

$$\int p_{\theta} d\theta = kh, \quad (18)$$

if the integration is extended to a complete revolution.

The second condition (radial quantum condition) has the similar form

$$\int p_r dr = n^r h, \quad (19)$$

if the integral is again taken for a full period. The numbers k and n^r (k azimuthal, n^r radial quantum number) determine magnitude and shape of the orbit (major axis and excentricity.)

How does the Energy $E = U + T$ depend on the Quantum numbers? Instead of (18) and (19) one can write

$$kh = \int p_{\theta} \dot{\theta} dt = \int m r^2 \dot{\theta}^2 dt \quad (20)$$

$$n^2 h = \int p_r \dot{r} dt = \int m r \dot{r}^2 dt. \quad (21)$$

Adding these equations one finds

$$(k + n^2) h = \int 2 T dt \quad (22)$$

All the integrals have to be taken over a full period.

At this point two well known theorems may be used.

1. Between the period P and the energy E there is the relation

$$P = \pi a \sqrt{\frac{m}{-2E^3}} \quad (23)$$

(E is negative.)

2. If \bar{T} and \bar{U} denote the mean values for a full period

$$\bar{T} = -\frac{1}{2} \bar{U}$$

and therefore

$$\bar{T} + \bar{U} = -\bar{T}$$

or

$$\bar{T} = -E.$$

Eq (22) now becomes

$$(k + n^2) h = -3 EP = \pi a \sqrt{\frac{2m}{-E}}$$

$$E = -\frac{2\pi^2 a^2 m}{(k + n^2)^2 h^2}$$

If $-e$ is the charge of the electron and Ze that of the nucleus

$$E = -\frac{2\pi^2 Z^2 e^4 m}{(k + n^2)^2 h^2}$$

$k + n^2 = n$ is the "Total" quantum number.

Size and Shape of elliptic orbit determined by the Quantum Numbers. Eq. (13) becomes

$$\dot{r}^2 = \frac{2E}{m} + \frac{2a}{mr} - \frac{c^2}{m^2 r^2}.$$

If r_1 and r_2 are the values of r for which the expression on the right hand side vanishes, the semi major axis of the ellipse has the value

$$L = \frac{1}{2} (r_1 + r_2) = - \frac{a}{2E} \quad (\text{relation between}$$

energy and major axis), or

$$L = \frac{n^2 h^2}{4\pi^2 a m} \quad (24)$$

Further

$$r_1 r_2 = - \frac{c^2}{2Em},$$

so that the ordinate p at the focus is given by

$$p = \frac{r_1 r_2}{L} = \frac{k^2 h^2}{4\pi^2 a m} \quad (25)$$

The lengths L and p are therefore determined in the same way by the squares of the numbers n and k .

Eccentricity of the orbit

$$\sqrt{1 - \frac{k^2}{n^2}}$$

Series in the Hydrogen Spectrum. $Z = 1$ and

$$E = - \frac{c h h}{n^2},$$

(c velocity of light), if

$$R = \frac{2\pi^2 e^4 m}{c h^3} \quad (\text{Rydberg's constant}) \quad (26)$$

One obtains Balmer's series, when n is supposed to change from 3 to 2, and from 4 to 3, etc.

Frequencies $cR \left(\frac{1}{4} - \frac{1}{9} \right), \quad cR \left(\frac{1}{4} - \frac{1}{16} \right), \text{ etc.}$

Similarly, the frequencies in Lyman's series are

$$cR \left(1 - \frac{1}{4} \right), \quad cR \left(1 - \frac{1}{9} \right), \text{ etc.}$$

Value of R from observations 109675, calculated by means of
(26) $1.09 \cdot 10^6$.

Justification of the Quantum conditions. According to Planck the energy of a simply harmonic vibrator with the period P must be a multiple of $\frac{h}{P}$. Thus, the time integral of the energy taken over a full period must be a multiple of h. Since, for a simply harmonic vibrator, the mean values of the kinetic and of the potential energy are equal, the time integral of the kinetic energy must be a multiple of $\frac{1}{2} h$.

The quantum conditions that have been applied to the hydrogen atom are simply extensions of this rule to each of the degrees of freedom corresponding to the coordinates r and θ . The corresponding parts of the kinetic energy are

$$\frac{1}{2} m \dot{r}^2 \quad \text{and} \quad \frac{1}{2} m r^2 \dot{\theta}^2$$

and the quantities that have been taken to be multiples of h are just twice the time integrals of these parts.

When the central force follows a law different from that of Coulomb, it is natural to follow the same course and to use eg. (18) and (19) as the quantum conditions. They will serve to determine the constants of the orbit, and the energy, in terms of k and n'. One can still define a principal quantum number by the equation

$$n = k + n',$$

but the energy will not be determined by this number; it will depend in a more complicated way on k and n' (or on k and n).

Eq. (18) and (19) have also been used when the relativity terms are taken into account. Only the momenta p_r and p_θ have in this case been defined by

$$p_r = m\dot{r}, \quad p_\theta = m r^2 \dot{\theta} \quad (27)$$

A Problem that can Serve as an Introduction to the Theorem of Adiabatic Invariants. A ball is suspended by a wire, which is held between two fingers somewhere below its upper extremity, which is fixed. By sliding the fingers up or down one can gradually change the length l of the free portion of the wire. Let θ be the angle which this portion makes with a vertical line.

Coordinates (x vertical, downwards)

$$x = \text{const.} + l(\cos \theta - 1), \quad y = l \sin \theta \quad (28)$$

Equation of motion

$$l\ddot{\theta} + 2\dot{l}\dot{\theta} + l\sin\theta + g\sin\theta = 0 \quad (29)$$

This is found, either by directly considering the accelerations and the forces or by the application of Lagrange's equation.

From (28) one finds for the kinetic energy

$$T = \frac{1}{2} m \left\{ l^2 \dot{\theta}^2 + 2 l \sin \theta \cdot \dot{l} \dot{\theta} + 2(1 - \cos \theta) \dot{l}^2 \right\}$$

whereas the potential energy is

$$U = \text{const.} + mg l(1 - \cos \theta).$$

Substituting these values in Lagrange's equation

$$\frac{d}{dt} \left(\frac{dL}{d\dot{\theta}} \right) - \frac{dL}{d\theta} = 0$$

Where $L = T - U$ (Lagrange's function) one obtains (29).

Simplification. Let ℓ vary so slowly that during a full period, the change is very small in comparison with ℓ itself. Then terms with $\dot{\ell}^2$ or $\ddot{\ell}$ may be neglected. Suppose further that θ is so small that $\sin \theta$ may be replaced by θ and $1 - \cos \theta$ in the expression for U by $\frac{1}{2} \theta^2$. (By the latter assumption the motion is made to be simply harmonic, when ℓ is constant).

Eq. (29) becomes

$$\ell \ddot{\theta} + 2 \dot{\ell} \dot{\theta} + g\theta = 0 \quad (30)$$

If ℓ were constant the solution would have the form

$$\theta = a \cos (nt + p),$$

with constant values of a , n and p . When ℓ changes, (30) can be satisfied by the same expression, provided that a , n and p be taken to be suitable slowly variable quantities. However, the energy only has to be considered.

Define E by

$$E = \frac{1}{2} m \ell^2 \dot{\theta}^2 + \frac{1}{2} mg \ell \theta^2 \quad (31)$$

This will be exactly the energy if ℓ remains constant, and it will represent the energy with any required degree of approximation if $\dot{\ell}$ is small enough.

Calculate the rate of change of $\frac{E}{m}$, using eq. (30) after multiplication by $\dot{\ell}$

$$\begin{aligned} \frac{d}{dt} \left(\frac{E}{m} \right) &= \dot{\ell} \dot{\theta}^2 + \ell^2 \dot{\theta} \ddot{\theta} + \frac{1}{2} g \dot{\ell} \theta^2 + g \ell \dot{\theta} \theta \\ &= \dot{\ell} \left(-\dot{\theta}^2 + \frac{1}{2} g \theta^2 \right) \end{aligned} \quad (32)$$

Since $\dot{\ell}$ is very small, one may calculate the last factor as if ℓ were constant. Even, since ℓ may be considered as not changing during one period, that last factor may be replaced by its

mean value for a full period.

According to a known theorem the mean values of the kinetic and the potential energy are equal in the case of a simple harmonic motion. Thus, if ℓ is constant, the mean values of the terms on the right hand side of (31) are each equal to $\frac{1}{2} E$ and the last factor in (32) may be replaced by

$$- \frac{E}{m\ell} + \frac{1}{2} \frac{E}{m\ell} = - \frac{1}{2} \frac{E}{m\ell}.$$

Thus, multiplying by m

$$\frac{dE}{dt} = - \frac{1}{2} E \frac{\dot{\ell}}{\ell},$$

$$\frac{d(\log E + \frac{1}{2} \log \ell)}{dt} = 0$$

$$E \sqrt{\ell} = \text{const.} \quad (33)$$

Since the period P of the vibrations is proportional to $\sqrt{\ell}$, one may conclude from this that the product EP or the value of E divided by the frequency remains constant when the length of the pendulum is slowly altered.

The quantum condition for a simple harmonic motion is that the energy is a multiple of h times the frequency. Eq. (33) shows that when this condition is fulfilled at a certain moment, it will be continually satisfied.

Eq. (33) can also be found by calculating the work that is required for moving the fingers. Replace these by cylindrical rods held in a horizontal position and having perfectly smooth surfaces. Then the tension of the two parts of the wire must be the same. Let it be S at any moment. Then the two tensions, acting on one of the rods, will give rise to a resulting force having a vertical component

$$S (1 - \cos \theta)$$

(positive when upward) and the work per unit of time will be

$$- S \dot{\ell} (1 - \cos \theta).$$

To the degree of approximation required ($S = mg$) this becomes

$$- \frac{1}{2} mg \dot{\ell}^2,$$

so that

$$\frac{dE}{dt} = - \frac{1}{2} \dot{\ell} mg \dot{\ell},$$

agreeing with what has been found.

Relation between the mean kinetic and the Mean Potential Energy in the case of Forces inversely proportional to the Square of the Distance. This relation, which has been used in the quantization of the motion in elliptic orbits, can be deduced from the so called virial theorem.

Equations of motion for a system of material points

$$m_1 \ddot{x}_1 = X_1, \quad m_1 \ddot{y}_1 = Y_1, \quad m_1 \ddot{z}_1 = Z_1, \quad m_2 \ddot{x}_2 = X_2, \dots$$

Thus

$$\begin{aligned} \sum (xX + yY + zZ) &= \sum m(\ddot{x}x + \ddot{y}y + \ddot{z}z) = \\ &= -2T + \frac{d}{dt} \sum m(\dot{x}x + \dot{y}y + \dot{z}z) \dots \dots \dots (33)' \end{aligned}$$

The sum on the left hand side is called the virial V . Let the motions be exactly periodic and let mean values be taken over a full period. Or, when the state of motion is simply stationary, take mean values over a long interval of time. In both cases, the last term in (33)' vanishes. Thus

$$\bar{V} = -2\bar{T} \quad (34)$$

Now, in the case to be considered, the potential energy U is a homogeneous function of the coordinates of degree -1 , so that

$$V = - \sum \left(x \frac{dU}{dx} + y \frac{dU}{dy} + z \frac{dU}{dz} \right) = U$$

by which (34) becomes

$$\bar{U} = - 2 \bar{T}$$

Adiabatic Invariants. Conservation of quantization.

In the problem of the pendulum it has been found that, if at one time the quantum condition is satisfied, it will remain so forever, when the length of the pendulum is changed very slowly. Ehrenfest has shown that a similar result holds in a great number of cases.

The quantum conditions can be continually fulfilled while the circumstances under which the motions take place, say one or more parameters which ^{define} these circumstances (and which are comparable to the length of the pendulum) are gradually altered. Indeed, it is found that the quantities to which the quantum conditions ascribe certain definite values, are just such that they remain constant during the slow variations in question. These are Ehrenfest's "adiabatic invariants." The theorem may be called that of the conservation of quantization.

Examples of the changes that may be imagined to occur (always very slowly) without violating the quantum conditions. Not only the intensity but also the law of force may be altered. If a force is represented by $f_1(r) + S \{ f_2(r) - f_1(r) \}$, it will change from $f_1(r)$ to $f_2(r)$ if the parameter S varies from 0 to 1. External electric or magnetic fields may change either in direction or magnitude. Moreover, the mass of a particle may be considered as variable. If, in case of a

variable m , the equations of motion are taken to be

$$\frac{d}{dt} (m\dot{x}) = X, \text{ etc.}$$

(and not $\ddot{m}x = X$, etc.) the principle will hold. Finally the relativity terms may be gradually introduced. One may f.i. take for the momenta of a particle the expressions

$$\frac{m \dot{x}}{\sqrt{1 - sv^2}}, \text{ etc.}$$

If the parameter S changes from 0 to $\frac{1}{c^2}$ one passes gradually from the old to the new definition of momentum.

Let A and B be two states of motion of a system, such that one can pass from one of them to the other in the way now under consideration. If it is possible to formulate quantum rules for both cases, the theorem can be proved.

It may also be that the simpler one of the two cases say A admits of quantization, but that one is at a loss how to quantize B . Under these circumstances the stationary states B may be defined as arising by gradual changes from the stationary states A .

Certain restrictions that must be kept in mind will be considered later on.

Change of the Energy of a System When the Circumstances under which it Moves are Slowly Altered. Let the configuration be determined by certain coordinates q_1, q_2 , and let the motion be determined by Lagrange's equations

$$\frac{d}{dt} \left(\frac{dL}{dq} \right) - \frac{dL}{dq} = 0 \quad (\text{for each coordinate}) \quad (35)$$

Lagrange's function L has in simple cases the form $T - U$; it may however be considered now as any function of the coordinates q and the velocities \dot{q} . It will be supposed to contain, in addition to these quantities, one slowly variable parameter s .

The quantities

$$\frac{dL}{d\dot{q}} = p$$

are the momenta of the system.

Equation of energy

$$\dot{q} \frac{d}{dt} \left(\frac{dL}{d\dot{q}} \right) - \dot{q} \frac{dL}{dq} = \frac{d}{dt} \left(\dot{q} \frac{dL}{d\dot{q}} \right) - \ddot{q} \frac{dL}{d\dot{q}} - \dot{q} \frac{dL}{dq}.$$

Thus, if on the right hand side of eq. (35) one had the quantities Q (forces, not included in L) one would have

$$\sum (\dot{q}Q) = \frac{d}{dt} \sum \left(\dot{q} \frac{dL}{d\dot{q}} \right) - \sum \left(\ddot{q} \frac{dL}{d\dot{q}} + \dot{q} \frac{dL}{dq} \right) \dots (36)$$

If s were constant the last term would be $\frac{dL}{dt}$.

Thus, if

$$E = \sum \left(\dot{q} \frac{dL}{d\dot{q}} \right) - L, \dots (37)$$

$$\sum (\dot{q}Q) = \frac{dE}{dt},$$

showing that E is the energy, the sum on the left hand side being the work of the forces Q per unit of time.

Now, let s vary gradually. Still defining the energy by (37) and putting $Q = 0$, one may remark that the last sum in (36) is not equal to $\frac{dL}{dt}$ because the term

$$s \frac{dL}{ds}$$

is wanting.

Thus

$$\frac{dE}{dt} = -s \frac{dL}{ds} \dots \dots \dots (38)$$

Here if s is small the last factor may be calculated as if s were constant.

Let the parameter s first have some constant value, the motion being periodic in this case. If then s is made to change extremely slowly, the relation between the changes of s and E during a full period or during a time comprising a great number of periods will be as follows (if both changes are very small.)

$$dE = -ds \cdot \overline{\frac{dL}{ds}}, \dots \dots \dots (39)$$

the stroke indicating the mean value over a period, calculated for the original motion.

Influence of the Relativity Terms in the Case of an Elliptic Orbit.

Let Lagrange's function be

$$L = \frac{m}{s} \left\{ 1 - \sqrt{1 - sv^2} \right\} + \frac{a}{r} \dots \dots \dots (40)$$

Where s varies slowly from 0 to $\frac{1}{c^2}$

The components of the momentum are

$$\frac{dL}{d\dot{x}} = \frac{m\dot{x}}{\sqrt{1 - sv^2}}, \quad \frac{dL}{d\dot{y}} = \frac{m\dot{y}}{\sqrt{1 - sv^2}}$$

and the energy has the value

$$E = \dot{x} \frac{dL}{d\dot{x}} + \dot{y} \frac{dL}{d\dot{y}} - L = \frac{m}{s} \left[\frac{1}{\sqrt{1 - sv^2}} - 1 \right] - \frac{a}{r}.$$

The first term, the kinetic energy, tends to the limit

$\frac{1}{2} mv^2$ when s diminishes indefinitely, and takes the value

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

for $s = \frac{1}{c^2}$.

Let the original motion, with $s = 0$, be a revolution in an ellipse determined by the quantum numbers k and n' and let now s gradually increase to the value $\frac{1}{c^2}$. One has the relation

$$dE = - ds \cdot \frac{dL}{ds}$$

and if the total change is small, one may therefore calculate it by the formula

$$E - E_0 = - \frac{1}{c^2} \frac{dL}{ds}, \dots \dots \dots (41)$$

where the last factor is given the value which it has in the original motion.

Now, substituting in (40)

$$\sqrt{1 - sv^2} = 1 - \frac{1}{2} sv^2 - \frac{1}{8} s^2 v^4$$

one finds

$$L = \frac{1}{2} mv^2 + \frac{1}{8} msv^4 + \frac{a}{r}.$$

Thus

$$\frac{dL}{ds} = \frac{1}{8} mv^4,$$

by which (41) becomes

$$E - E_0 = - \frac{m}{8c^2} \overline{v^4}.$$

In order to find the mean value of v^4 in the elliptic motion one can use the equation

$$\frac{1}{2} mv^2 - \frac{a}{r} = E_0,$$

which gives

$$v^4 = \frac{4}{m^2} E_0^2 + \frac{8E_0}{m^2} \frac{a}{r} + \frac{4a^3}{m^2} \cdot \frac{1}{r^3}.$$

The first term is constant, and the mean value of the second is

$$- \frac{16}{m^2} E_0^2,$$

because the mean value of the potential energy $-\frac{a}{r}$ is $2 E_0$.

It remains therefore only to calculate the mean value of $\frac{1}{r^3}$.

This is the ratio between the integral

$$\int \frac{1}{r^3} dt$$

taken over a full period, and the period itself. But dt is equal to

$$\frac{r dr}{\sqrt{(r_2-r)(r-r_1)}} \dots \dots \dots (42)$$

multiplied by a constant, and one is therefore led to the ratio between the integrals of the expression

$$\frac{dr}{r \sqrt{(r_2-r)(r-r_1)}} \dots \dots \dots (43)$$

and of (42), both taken between the limits r_1 and r_2 .

The integral of (43) is

$$\frac{\pi}{\sqrt{r_1 r_2}}$$

and that of (42)

$$\frac{1}{2} \pi (r_1 + r_2),$$

so that the mean value of $\frac{1}{r^3}$ becomes

$$\frac{2}{(r_1 + r_2) \sqrt{r_1 r_2}} ,$$

for which, on account of former relations, one may write

$$\frac{4n}{ka^2} E_0^2 .$$

Finally

$$E - E_0 = - \frac{2E_0^2}{mc^2} \left(\frac{1}{4} + \frac{n^2}{k} \right) ,$$

which corresponds to Sommerfeld's formula limited to the first terms.

Influence of the motion of the nucleus. Let the index 1 refer to the nucleus, and 2 to the electron.

$$L = \frac{1}{2} m_1 v_1^2 + \frac{1}{2} m_2 v_2^2 + \frac{a}{r}$$

If m_1 varies slowly,

$$dE = - dm_1 \frac{\overline{dL}}{dm_1} = - \frac{1}{2} v_1^2 dm_1 \dots \dots \dots (44)$$

But the two parts of the kinetic energy are in the ratio

$$T_1 : T_2 = m_2 : m_1 .$$

Thus, since the mean value of the total kinetic energy is

$-E$, that of T_1 is

$$- \frac{m_2}{m_1 + m_2} E$$

and that of $\frac{1}{2} \overline{v_1^2}$

$$- \frac{m_2}{m_1(m_1 + m_2)} E .$$

Eq. (44) therefore becomes

$$\frac{dE}{E} = \frac{m_2}{m_1(m_1 + m_2)} dm_1$$

$$E = \text{const.} \frac{m_1}{m_1 + m_2}.$$

The constant is the value E_0 which the energy has in the simple theory, where the mass of the nucleus is considered as infinite. Therefore, if the mobility of the nucleus is taken into account,

$$E = \frac{m_1}{m_1 + m_2} E_0.$$

Hamilton's Principle in a simple Case.

Let a point

move in a space in which the potential energy U is a given function of the coordinates x, y, z . Consider a "natural" motion (one that can really take place) along some path from a point P_0 to a point P , these points being reached at the times t_0 and t_1 . Let the values of t, x, y, z be altered to an infinitely small extent, the variations being $\delta t, \delta x, \delta y, \delta z$, and suppose these variations to be any continuous functions of the time t . Corresponding to each position $P (x, y, z)$ on the path, there will be a varied position $P' (x + \delta x, y + \delta y, z + \delta z)$ and one can conceive a "varied motion" in which the successive varied positions are just reached at the successive varied times $t + \delta t$. The varied motion needs not be a natural one.

When the variations $\delta t, \delta x, \delta y, \delta z$, have been chosen as functions of the coordinates, not only the coordinates but also the velocities will have definite values in the varied motion, so that for it, as well as for the original motion, Lagrange's function L will have a determinate value.

The problem is to determine the difference between the value of the integral

$$R = \int_{t_0}^{t_1} L dt \quad (45)$$

for the original motion and the corresponding integral R' for the varied motion. $\delta R = R' - R$. The symbol d will serve to denote the change of a quantity in the time dt , and the symbol δ will refer to the variation of a quantity, a definite value of t or a definite range of t being kept in view.

Let t_1, t_2 be two successive instants, t_3, t_4 the corresponding varied times. Then, the original value of dt is $t_2 - t_1$, and its varied value $t_4 - t_3$. Thus:

$$\delta dt = (t_4 - t_3) - (t_2 - t_1).$$

On the other hand, the variation δt is $t_3 - t_1$ at the instant t_1 , and $t_4 - t_2$ at the instant t_2 , so that

$$d\delta t = (t_4 - t_2) - (t_3 - t_1)$$

and

$$\delta dt = d\delta t.$$

Similarly

$$\delta dx = d\delta x, \text{ etc.}$$

The calculation of δR is as follows.

$$\delta \frac{dx}{dt} = \frac{\delta dx}{dt} - \frac{dx}{dt^2} \delta dt = \frac{d\delta x}{dt} - \dot{x} \frac{d\delta t}{dt}, \text{ etc.}$$

$$\delta L = \sum \left[\frac{dL}{dx} \delta x + \frac{dL}{d\dot{x}} \left(\frac{d\delta x}{dt} - \dot{x} \frac{d\delta t}{dt} \right) \right],$$

Or, using Lagrange's equations,

$$\delta L = \frac{d}{dt} \sum \left(\frac{dL}{d\dot{x}} \delta x \right) - \sum \left(\dot{x} \frac{dL}{d\dot{x}} \right) \frac{d\delta t}{dt}$$

$$\begin{aligned}
\delta(Ldt) &= d \sum (p_x \delta x) - \left[\sum \left(\dot{x} \frac{dL}{d\dot{x}} \right) - L \right] d\delta t \\
&= d \sum (p_x \delta x) - E d\delta t \\
\delta R &= \sum (p_x \delta x)_1 - \sum (p_x \delta x)_0 - E \delta(t_1 - t_0) \quad \dots \dots (46)
\end{aligned}$$

From now on, the varied motion will be supposed also to be a natural one, so that two natural motions are compared with each other.

In the given field of force a natural motion will be determined by the initial and the final position and by the time during which the transition from the first point to the second takes place. Eq. (46) shows how the integral R changes, when these data are altered.

Action. Define a new quantity W by

$$W = R + E(t_1 - t_0) = \int_{t_0}^{t_1} L dt + E(t_1 - t_0) \quad \dots \dots (47)$$

Then, in virtue of (46)

$$\delta W = \sum (p_x \delta x)_1 - \sum (p_x \delta x)_0 + (t_1 - t_0) \delta E \quad \dots \dots (48)$$

W is called the "action" along the path, and (47) may be written in the form

$$W = \int_{t_0}^{t_1} 2T dt \quad \dots \dots \dots (49)$$

The motion will now be considered as determined by the initial and the final position and the energy E .

1. Consider all motions that can take place with a given energy E , if the point starts from a chosen initial position P_0 in all possible directions. In one of these motions some given point P_1 , or P (the index 1 now being omitted) can be reached and (49) will have a definite value for the motion up to this point.

This value will depend on the coordinates of P and on the energy E. According to (48)

$$\frac{dW}{dx} = p_x, \quad \frac{dW}{dy} = p_y, \quad \frac{dW}{dz} = p_z \quad \dots \dots \dots (50)$$

$$\frac{dW}{dE} = t - t_0 \quad \dots \dots \dots (51)$$

2. These results also hold in another case. Let S be an arbitrarily chosen surface and consider all the motions starting with a given energy, from points of this surface in directions normal to it. A point P will be reached again by one of the different trajectories, and if W is the action up to P, one is again led to (50) and (51). Indeed the term $\sum (p_x \delta x)_0$ in (48) vanishes when P_0 is displaced in a direction perpendicular to the initial velocity.

In case 1. W is the action reckoned from a fixed point; in case 2. it is the action reckoned from a fixed surface.

Hamilton-Jacobi's Partial Differential Equation. Substituting the values (50) in the energy equation

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

one obtains

$$\left(\frac{dW}{dx}\right)^2 + \left(\frac{dW}{dy}\right)^2 + \left(\frac{dW}{dz}\right)^2 = \frac{1}{2m}(E - U) \quad \dots \dots \dots (52)$$

This equation determines W in function of x, y, z.

As has just been shown the action W reckoned from an arbitrarily chosen fixed surface satisfies the differential equation. Conversely, any solution of the equation, say

$$W = F(x, y, z)$$

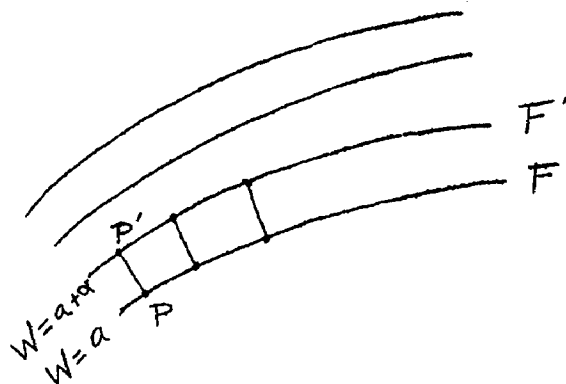
will represent the action up to the point x, y, z, reckoned from a fixed surface, namely from the surface

$$F(x, y, z) = 0.$$

The expression on the left hand side of (52) is the square of the gradient of W , i.e. of $\frac{dW}{dn}$, if n is the direction of the normal to the surface $W = \text{const.}$ Thus, the equation prescribes to the gradient the value

$$\sqrt{\frac{1}{2} m(E - U)}$$

at any point of space.



Hence the following geometrical solution. Let F be a surface in which W is supposed to have some constant value a . Draw normals to F , starting from different points P in the surface and on each of these normals take an infinitely small segment PP' of the length

$$\frac{a}{\sqrt{\frac{1}{2} m(E - U)}}$$

α being a constant infinitely small quantity. Then, at the surface F' passing through the points P' the action W will have the value $a + \alpha$, the same all over the surface.

In a similar way a third surface $W = \text{const.}$ can be deduced from F' and the distribution of W over space can be found step by step.

Hamilton's Principle and the Principle of Least Action.

1. Let the original motion be varied in any way (so that the varied motion needs not be a natural one), but with the restrictions that neither the initial and final positions nor the time $t_1 - t_0$, required for the motion from P_0 to P_1 , shall be altered. Then, on account of (46)

$$\delta R = 0, \quad \delta \int L dt = 0 \quad (53)$$

This is Hamilton's principle. It has been deduced here by assuming the validity of Lagrange's equations of motion, but conversely these equations can be deduced from (53)

2. Let the motion be varied in such a way, the extreme positions again remaining unaltered, that, the energy conserves the same constant value E which it has in the original motion. By this condition, when the varied path has been chosen the velocity at any of its points, and therefore the manner in which it is travelled over in course of time will be completely determined.

Eq. (46) now becomes

$$\delta R = -E\delta(t_1 - t_0).$$

and by (47)

$$\begin{aligned} \delta W &= \delta R + E\delta(t_1 - t_0) = 0 \\ \delta \int 2T dt &= 0 \end{aligned}$$

This is the principle of least action. It may be written in the form

$$\delta \int v ds = 0, \quad \dots \dots \dots (54)$$

if ds is an element of the path.

Propagation of rays of Light (in Isotropic media). The foregoing considerations apply to the motion of the corpuscles of light in Newton's theory. Suppose such corpuscles first to move in vacuum and then to enter a ponderable body, which may be inhomogeneous, or a system of such bodies. Assume further that originally the corpuscles have a definite velocity v_0 . Then, if a corpuscle moves from a point P_0 in vacuum to a point P inside a ponderable body, the velocity v at this latter point will be determined by

$$\frac{1}{2} mv^2 = \frac{1}{2} mv_0^2 + U_0 - U_1$$

when U_0 is the potential energy at P_0 and U that at P . The velocity will be independent of the direction in which P is reached; moreover it will have the same value at all points in the interior of a homogenous body, because U has the same value at all these points.

In any case the motion of corpuscles starting with a given energy from the points of a surface F in directions normal to this surface, can be found by the construction that has been explained. So the course of rays of light is found; they are the orthogonal trajectories to the surfaces F, F' etc. The course of rays of light can also be deduced from eq. (54).

There is a far going analogy between these theorems and those that hold in the undulatory theory of light. Here the successive positions F, F', \dots (see the foregoing figure) of a wave front are found by Huygens' construction which in the case of isotropic media, amounts to this, that the wave front F' at time $t + dt$ is

is found from the wave front F at time t by taking along the normals the segments PP' equal to udt , where u is the velocity of light.

The values of u vary from one point to the other in the inverse ratio as the values of the velocity v that had to be assumed in the corpuscular theory. In connection with this it may be remarked that, whereas the segments PP' between F and F' were just now taken proportional to the velocities u , they were formerly taken inversely proportional to v . So the two theories can lead to the same surfaces F and to the same system of rays, which are perpendicular to them, with this difference, however, that if one starts from F at a definite time, the points of F' will be reached at the same instant in the wave theory but at different instants in the corpuscular theory. Corresponding to eq. (54) one has in the wave theory the theorem

$$\oint \frac{ds}{u} = 0 \quad (55)$$

that can be deduced from Huygens' construction (Fermat's principle).

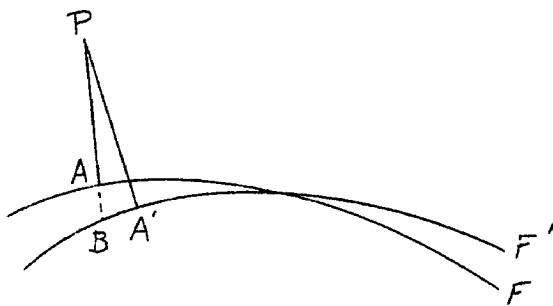
The Solution of a Dynamical Problem can be Made to Depend Entirely on the Hamilton Jacobi Equation. Returning to the motion of a particle in a given field of force, suppose that one has found a function W , satisfying the partial differential equation (52)', and containing (in addition to E) a non-additive arbitrary constant a . Then the quantity

$$\frac{dW}{da}$$

will be a function of x, y, z, E and a . This function has the property that it has the same value all along a path of the point.

Proof: $W(a)$ is the action reckoned from a certain surface F ;
 similarly $W(a + da)$ is the action reckoned from a surface F' in-

finitely little different from F .



Let AP and $A'P$ be the paths leading with the same energy E , from F and F' to point P , the first path starting from A at right angles to F , and the second from A' at right angles

to F' . Let the path PA eventually prolonged, intersect F' at the point B .

Thus, at the point P ,

$$W(a + da) = W(A'P), \quad W(a) = W(AP).$$

But $W(A'P)$ may be replaced by $W(BP)$, because $A'B$ is at right angles to the path $A'P$. (Indeed, if in (46) one supposed the final position to remain unaltered and the initial one to be shifted at right angles to the path, one finds from that equation and (47) $\delta W = 0$)
 Therefore

$$W(a + da) - W(a) = W(BP) - W(AP) \pm W(BA)$$

$$\frac{dW}{da} = \frac{W(BA)}{da},$$

which has the same value for all points P of the path AP . The result is that for any path

$$\frac{dW}{da} = b, \quad \dots \dots \dots (56)$$

where, however the constant b will change from one path to another.

If one had a solution of (52) containing two non-additive constants a and a' the equations (56),

$$\frac{dW}{da'} = b'$$

and (51) would contain the complete integration of the equations of motion. Three relations between x, y, z, t with six constants E, a, b, a', b' and t_0 .

Generalization. The position of the system determined by coordinates q_1, q_2, \dots momenta p_1, p_2, \dots . Lagrange's function $\mathcal{L} = T - U$. Eq. (46) remains true, with the change only that the first two members on the right hand side are replaced by

$$\sum (p \delta q)_1 - \sum (p \delta q)_0$$

Action W again defined by (47). Instead of (50)

$$\frac{dW}{dq_1} = p_1, \quad \frac{dW}{dq_2} = p_2, \quad \dots \quad (57)$$

whereas (51) remains.

The kinetic energy can be expressed as a homogeneous quadratic function of the momenta

$$T = \frac{1}{2} a_{11} p_1^2 + \dots + a_{12} p_1 p_2 + \dots$$

Replacing here p_1, p_2, \dots by their values taken from (57), and remembering that

$$T + U = E$$

one is led to Hamilton Jacobi's equation

$$\frac{1}{2} a_{11} \left(\frac{dW}{dq_1} \right)^2 + \dots + a_{12} \frac{dW}{dq_1} \frac{dW}{dq_2} + \dots + U = E \quad (58)$$

In any special case a_{11}, a_{12}, \dots are known functions of the coordinates.

When one has found a function W satisfying (58) and containing besides E , a sufficient number of non additive constants a, a', \dots (one less than the number of coordinates), the equations

$$\frac{dW}{da} = b, \quad \frac{dW}{da'} = b', \quad \dots \quad (59)$$

together with (51) contain the complete solution of the problem.

Remarks: In the undulatory theory there is a close connection between the course of the rays and the form of the wave fronts, the rays being (in isotropic media) at right angles to the wave fronts.

Similarly, in the case of a particle moving in a constant field of force, the path is always perpendicular to the surfaces $W = \text{const.}$ (whether W be taken from a fixed point or from a fixed surface). This follows from eq. (46) and (47). If f.i. the final position P_1 is displaced in the surface $W = \text{const.}$ passing through it, one has

$$\sum (p_x \delta x)_1 = 0,$$

showing that the direction of the displacement $\delta x, \delta y, \delta z$ is perpendicular to that of the momentum p_x, p_y, p_z , or of the velocity in the path.

When successive positions of a surface $W = \text{const.}$ are found by the construction that has been explained, the infinitely short line PP' being perpendicular to the first surface F , $P'P''$ perpendicular to the second surface F' and so on, the line $PP'P'' \dots$ will be the path of the point when it starts from P at right angles to F and with the energy that has been chosen.

In less simple cases, a system with n degrees of freedom, and n coordinates q the position of the system at any time can be represented by a point P in an n -dimensional space and the system may be said to describe a path or a line in that space. An equation $W = \text{const.}$ represents a "surface" and at any point where such a surface and a path intersect there is a definite relation between their directions.

Hamilton Jacobi's equation, which now has the form (58) again leads to a geometrical solution of the problem. Starting from a surface F one can determine the successive positions of a surface $W = \text{const.}$ and at the same time the paths of systems starting from F with the given amount of energy.

EXAMPLES: 1. A material point free from any force $U = 0$ A solution of Hamilton Jacobi's equation is

$$W = x \sqrt{a} + y \sqrt{a'} + z \sqrt{2mE - a - a'}. \quad \dots (30)$$

Equations of the path

$$\frac{dW}{da} = b, \quad \frac{dW}{da'} = b'$$

or

$$\frac{x}{\sqrt{a}} - \frac{z}{\sqrt{2mE - a - a'}} = 2b, \quad \frac{y}{\sqrt{a'}} - \frac{z}{\sqrt{2mE - a - a'}} = 2b' \quad (61)$$

Further

$$\frac{dW}{dE} = t - t_0$$

or

$$\frac{mz}{\sqrt{2mE - a - a'}} = t - t_0. \quad \dots (62)$$

2. A particle moving in a vertical plane; x horizontal, y positive downward. $U = -mgy$.

A solution of the partial differential equation for W is

$$W = x\sqrt{a} + \frac{1}{3m^2g} \sqrt{(2mE - a + 3m^2gy)^3} \quad \dots (63)$$

From

$$\frac{dW}{da} = b \text{ and } \frac{dW}{dE} = t - t_0$$

$$\frac{x}{\sqrt{a}} - \frac{1}{2m^2g} \sqrt{(2mE - a + 3m^2gy)} = b \quad \dots (64)$$

$$\text{or } y = C \left(\frac{x}{\sqrt{a}} - b \right)^2 + C'$$

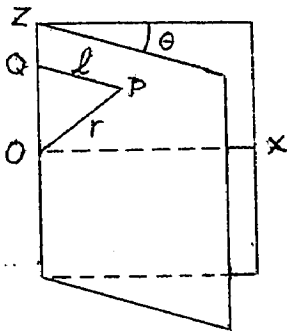
and

$$\frac{1}{mg} \sqrt{(2mE - a + 2m^2 gy)} = t - t_0 \quad \dots \dots \dots (65)$$

or

$$y = \frac{1}{2} g (t - t_0)^2 + \text{const.}$$

Motion of an Electron Around a Nucleus in a New System of Coordinates.



Let θ be the angle between the plane passing through OZ and the position P of the electron, and the fixed plane XOZ ; r the distance from O ; l the distance PQ from the axis OZ ; $OQ = z$ $x = l \cos \theta$, $y = l \sin \theta$

l and z are rectangular coordinates in the plane ZOP , which in general rotates about OZ .

Choose as coordinates

$$u = r + z, \quad v = r - z \quad \text{and} \quad \theta \quad \dots \dots \dots (66)$$

$$l^2 = r^2 - z^2 = uv$$

$$x = \sqrt{uv} \cos \theta, \quad y = \sqrt{uv} \sin \theta, \quad z = \frac{1}{2} (u - v) \quad \dots \dots (67)$$

$$T = \frac{1}{2} m \left(\frac{u+v}{4u} \dot{u}^2 + \frac{u+v}{4v} \dot{v}^2 + uv \dot{\theta}^2 \right) \quad \dots \dots \dots (68)$$

$$p_u = m \frac{u+v}{4u} \dot{u}, \quad p_v = m \frac{u+v}{4v} \dot{v}, \quad p_\theta = muv \dot{\theta} \quad \dots \dots \dots (69)$$

When the potential energy does not contain the angle θ

$$p_\theta = \frac{dW}{d\theta} = C \quad \dots \dots \dots (70)$$

Hamilton Jacobi's equation

$$\frac{4u}{u+v} \left(\frac{dW}{du} \right)^2 + \frac{4v}{u+v} \left(\frac{dW}{dv} \right)^2 + \frac{C^2}{uv} - 2m(E - U) = 0.$$

Attraction by nucleus according to Coulomb's law

$$U = - \frac{a}{r} = - \frac{2a}{u+v}$$

and after multiplication by $\frac{1}{4} (u+v)$

$$u \left(\frac{dW}{du} \right)^2 + v \left(\frac{dW}{dv} \right)^2 + \frac{1}{4} C^2 \left(\frac{1}{u} + \frac{1}{v} \right) - \frac{1}{2} mE (u+v) - am = 0 \dots (71)$$

When there is an external electric field F in the direction of OZ (Stark effect) one has to add to U a term

$$- F \Theta z = - \frac{1}{2} Fe (u - v)$$

and on the left hand side of (71)

$$- \frac{1}{4} mFe (u^3 - v^3) \dots (72)$$

Suppose the electron to be repelled by the line OZ with a force inversely proportional to the cube of the distance. Then, in U there will be a term

$$\frac{a'}{\rho^3} = \frac{a'}{uv}$$

and on the left hand side of (71) a term

$$\frac{1}{2} ma' \left(\frac{1}{u} + \frac{1}{v} \right), \dots (73)$$

which combines with the term with C^2 that refers to the rotation of the plane ZOP .

Separation of the Variables. In all the cases just mentioned one can satisfy the partial differential equation by an expression of the form

$$W = W_1 + W_2 + W_3,$$

in which W_1 is a function of u only, W_2 of v and W_3 of θ

$$W_3 = C\theta, \text{ according to (70)}$$

and in the case of eq. (71) with the addition (72) W_1 and W_2 are determined by

$$u \left(\frac{dW_1}{du} \right)^2 + \frac{1}{4} \frac{C^2}{u} - \frac{1}{2} mEu - \frac{1}{4} mFev^2 - am + f = 0 \quad \dots \dots (73)$$

$$v \left(\frac{dW_2}{dv} \right)^2 + \frac{1}{4} \frac{C^2}{v} - \frac{1}{2} mEv + \frac{1}{4} mFev^2 - f = 0 \quad \dots \dots \dots (74)$$

where f is a constant. These equations lead to expressions of the form

$$\frac{dW_1}{du} = \pm \sqrt{G_1(u)}, \quad \frac{dW_2}{dv} = \pm \sqrt{G_2(v)} \quad \dots (75)$$

so that, W_1 and W_2 are found as integrals.

Quantum Conditions. Consider the case that $G_1(u)$ is positive only in the interval

$$u_1 < u < u_2$$

and $G_2(v)$ only in the interval

$$v_1 < v < v_2.$$

The first variable will continually oscillate between the fixed limits u_1 and u_2 (depending on the values of the constants that occur in the formulae); similarly, v will oscillate between v_1 and v_2 . The third coordinate θ changes continually in the same direction.

Now, since $\frac{dW_1}{du}$ and $\frac{dW_2}{dv}$ are the values of the momenta p_u and p_v , the integrals

$$2 \int_{u_1}^{u_2} p_u du = 2 \int_{u_1}^{u_2} \sqrt{2E_1(u)} du$$

and

$$2 \int_{v_1}^{v_2} p_v dv$$

can be found in terms of the constants. The first and the second quantum conditions are

$$2 \int_{u_1}^{u_2} p_u du = n_1 h, \quad 2 \int_{v_1}^{v_2} p_v dv = n_2 h$$

and the third is

$$C = n_3 \frac{h}{2\pi},$$

or

$$\int_0^{2\pi} p_\theta d\theta = n_3 h.$$

These are the conditions used by Epstein in his theory of the Stark effect.

Interpretation of the quantum conditions. The kinetic energy can be represented by

$$T = \frac{1}{2} \sum p \dot{q}.$$

It may be considered as made up of parts

$$\frac{1}{2} p \dot{q},$$

each of which belongs to one of the coordinates. The quantum conditions mean that the time integral of the part of T which corresponds to a definite coordinate, calculated for a full oscillation of that coordinate, must be a multiple of $\frac{1}{2} h$.

Indeed if q_1 and q_2 are the extreme values of the coordinates considered, this time integral is

$$2 \int_{q_1}^{q_2} \frac{1}{2} p \dot{q} dt = \int_{q_1}^{q_2} p dq.$$

IN the case of the coordinate ϑ a "full oscillation" must be understood to mean a change by 2π .

Different modes of Quantization of an Elliptic Motion. The ordinary quantization (quantization I, or quantization in the plane of the orbit) introduces two quantum numbers k and n' ; the energy is found to depend on the sum $k + n'$.

A quantization (II) can also be based on eq.(71). It introduces three quantum numbers and leads not only to definite elliptical orbits but also to conditions concerning the position of their planes with respect to the line OZ in the last diagram. (Space quantization).

The two modes lead to different results. A motion that satisfies conditions II will not satisfy I.

Yet from I and II one finds the same values for the energy E . This is seen as follows.

Let n_1, n_2, n_3 be the quantum numbers introduced in II. Then the time integrals of the parts of the kinetic energy corresponding to u, v, ϑ , each taken for a full oscillation, will be

$$\frac{1}{2} n_1 h, \quad \frac{1}{2} n_2 h, \quad \frac{1}{2} n_3 h.$$

But in the simple case now considered, the oscillations have one and the same period P . Thus the mean values of the parts in question are

$$\frac{1}{2P} n_1 h, \quad \frac{1}{2P} n_2 h, \quad \frac{1}{2P} n_3 h,$$

giving for the mean value of the kinetic energy

$$\frac{1}{2P} (n_1 + n_2 + n_3) h$$

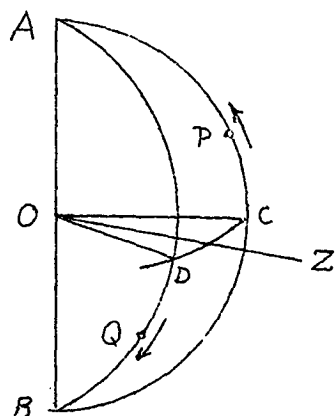
whereas in the quantization I the mean value was found to be
(by an exactly similar reasoning)

$$\frac{1}{2P} (k + n') h.$$

Thus the two quantizations give the same values of \bar{T} and therefore the same values of E , on account of the relation between \bar{T} and E .

When one wants to apply Ehrenfest's theorem to a hydrogen atom placed in an electric field F , first supposing F to be zero and then making it grow up gradually to its final value, the "initial" quantization must be effected, not in the manner I, but in the manner II, with respect to the direction OZ , which the field F is going to have. This is the "restriction" that has been mentioned already.

Helium Atom. Model Proposed by Bohr, Worked out by van Vleck and Kramers.



Let, on a sphere around the nucleus O, ACB and ADB be two meridian circles, intersecting the "equator" at points C and D. Suppose the electrons P and Q at first not to repel each other and to move with equal constant velocities in the two meridians in the directions indicated by the arrows, in such a way that when one is in C, the other is in D. Then they are constantly placed symmetrically with respect to the line which bisects the angle COD and which will be taken as axis of OZ.

This peculiarity of the motion will continue to exist when now the mutual repulsion is made to come up gradually. In the final state also, when the repulsion has reached its full value, there will be this kind of symmetry. Each electron may then be said to be repelled by the line OZ with a force

$$-\frac{e^2}{4l^2} \dots \dots \dots (76)$$

if l is the distance from that line, and it will be sufficient to consider the motion of the electron P only, using the coordinates u, v, Θ that have been introduced in connection with a former diagram.

The vector representing the resulting moment of momentum will constantly have the direction OZ, and in the final state its magnitude will still be what it was initially. The angle

between the circles AC and AD is taken to be 60° , in order that not only the initial moment of momentum may be $\frac{h}{2\pi}$ for each electron separately, but that the total moment of momentum have that same value.

Van Vleck and Kramers have calculated the energy in the final state and have compared their results with the ionization potential, the value of which, as deduced from observations is 24.6 volts.

In order to take into account the force (76) one must introduce a potential energy

$$\frac{e^2}{4\ell}$$

leading to a term

$$\frac{1}{8} m e^2 \left(\sqrt{\frac{u}{v}} + \sqrt{\frac{v}{u}} \right)$$

on the left hand side of eq. (71). The consequence is, however, that the variables can no longer be separated and it was, therefore, necessary to use a method of approximation.

If one introduces the potential energy

$$s \frac{e^2}{4\ell} \dots \dots \dots (77)$$

and supposes s to increase very slowly from 0 to 1, the energy of the system can be found in the form of a series

$$E = E_0 + sE_1 + s^2E_2 + \dots \dots \dots$$

The term sE_1 can be easily found from the initial motion by means of the theorem expressed in eq. (39). The next step is much more difficult to make. Eq. (39) can still be applied but it is necessary to determine, up to terms of the order s , the changes in the motion that are due to the potential energy (77). Van Vleck made the two steps. Kramers, on the other hand, used a

device by which the first step already led to a result which he considers as sufficiently accurate. Having remarked that the motion can be rigorously determined when the electron is repelled by OZ with a force, inversely proportional to the cube of the distance so that there is a potential energy

$$\frac{e^2}{\ell^2} \dots \dots \dots (78)$$

he first works out this case, and he then introduces an additional potential energy

$$s \left(\frac{e^2}{4\ell} - \frac{a'}{\ell^2} \right),$$

where s increases from 0 to 1. When the constant a' is chosen in such a way that in the mean during a revolution of the electron the force deduced from (78) differs as little as can be from the real force, the approximation is very satisfactory. Kramer's result for the ionization potential is 20.7 volts.

Precessional Motion of the Planes in which the two Electrons Move.

The problem now under consideration presents itself also when there are two valence electrons moving around the core of the atom.

Consider again the problem that was treated by means of the coordinates u, v, θ . If there is only the attraction by the nucleus the motion determined by (71) will be the ordinary one in some ellipse whose plane makes a certain angle with the axis OZ. The formula

$$\dot{\theta} = \frac{C}{m\ell^2} \dots \dots \dots (79)$$

that follows from (69) and (70) determines the rotation of the plane OZP which, combined with the changes of u and v (or r and z) in that plane, give rise to such an elliptical motion.

When there is the repulsion resulting from (78), the third term in (71) is replaced by

$$\frac{1}{4} C'^2 \left(\frac{1}{u} + \frac{1}{v} \right),$$

where
$$C'^2 = C^2 + 2ma'.$$

If now the plane OZP rotated with the angular velocity

$$\frac{C'}{m \rho^2}$$

the orbit would be a stationary ellipse described in the ordinary way. But the velocity of rotation is still given by (79). Hence, there will now be a motion in a stationary ellipse, combined with a rotation of the whole system about OZ, with the angular velocity

$$\frac{C - C'}{m \rho^2}.$$

In the real case of two electrons their orbits will both show this precessional motion (in the same direction) about the axis OZ, which has the direction of the vector representing the resulting moment of momentum.

If there is such a precession in the case of two particles whose mutual repulsion is inversely proportional to the cube of the distance, it may also be expected to exist when the repulsion follows Coulomb's law. Assuming that initially the circular motions go on with an angular velocity n , one finds by an approximate calculation (for the helium atom) that the velocity of the precession will be of the order of magnitude of $0.14n$.

Mutual actions Between the Electrons due to their Magnetic Fields. This question is more or less connected with that of the relativity terms. These latter are of the order of magnitude $\frac{v^2}{c^2}$ compared with the other terms in the equations of motion. Similarly, the forces between two electrons arising from their magnetic

fields, are of the order of magnitude $\frac{v_1 v_2}{c^2}$. The factor $\frac{v_1}{c}$ occurs in the expression for the magnetic force which the first electron produces at the place of the second, and the factor $\frac{v_2}{c}$ is introduced when, from this magnetic force one deduces the force acting on the second electron.

When higher terms are neglected, the problem of the motion of a system of charged particles may be made to depend on the following form of Lagrange's function:

$$\mathcal{L} = \sum mc^2 \left\{ 1 - \sqrt{1 - \frac{v^2}{c^2}} \right\} - \sum \frac{ee'}{4\pi r} \left\{ 1 - \frac{(v \cdot v')}{2c^2} - \frac{v_r v'_r}{2c^2} \right\}. \quad (80)$$

(rational units). The first sum refers to all the particles and the second to all the pairs of particles. The symbol $(v \cdot v')$ represents the scalar product of the velocities v and v' of the particles e and e' , whereas v_r and v'_r are the components of v and v' in the direction of the line joining the particles, these components being taken with the same sign when they are in the same direction. Replacing $\frac{1}{c^2}$ by s and making s change very slowly from 0 to $\frac{1}{c^2}$ one can, after having effected an initial quantization, determine the influence of the magnetic action on the energy in a stationary state by means of eq. (39).

This method can be applied to an electron circulating around a core that has a certain magnetic moment. In calculations of this kind one has to take into consideration that if all moving particles have the same $\frac{e}{m}$ (nucleus at rest) the magnetic moment of a system is equal to the moment of momentum multiplied by

$$\frac{e}{2mc}$$

Conservation of the Moment of Momentum. The momenta of one of the particles are

$$p_x = \frac{d\mathcal{L}}{d\dot{x}}, \quad p_y = \frac{d\mathcal{L}}{d\dot{y}}, \quad p_z = \frac{d\mathcal{L}}{d\dot{z}},$$

and the first component of the total moment of momentum is

$$\mathcal{M}_x = \sum \left(y \frac{d\dot{L}}{dz} - z \frac{d\dot{L}}{dy} \right) \dots \dots \dots (81)$$

Proof that $\mathcal{M}_x = \text{const.}$

$$\frac{d\mathcal{M}_x}{dt} = \sum \left(\dot{y} \frac{d\dot{L}}{dz} - \dot{z} \frac{d\dot{L}}{dy} \right) + \sum \left(y \frac{d}{dt} \frac{d\dot{L}}{dz} - z \frac{d}{dt} \frac{d\dot{L}}{dy} \right),$$

or, using Lagrange's equations,

$$\frac{d\mathcal{M}_x}{dt} = R + S,$$

where

$$R = \sum \left(\dot{y} \frac{d\dot{L}}{dz} - \dot{z} \frac{d\dot{L}}{dy} \right)$$

$$S = \sum \left(y \frac{d\dot{L}}{dz} - z \frac{d\dot{L}}{dy} \right).$$

It is easily seen that $S = 0$ insofar as only a factor depending on r is differentiated, and that $R = 0$ insofar as it depends on the first term in (80). One has therefore to show that $R + S = 0$, when one substitutes for \mathcal{L} (considering one pair of particles) either

$$(v \cdot v') = \dot{x}\dot{x}' + \dot{y}\dot{y}' + \dot{z}\dot{z}' \dots \dots \dots (82)$$

or QQ' , when

$$Q = (x-x') \dot{x} + (y-y') \dot{y} + (z-z') \dot{z}$$

$$Q' = (x'-x) \dot{x}' + (y'-y) \dot{y}' + (z'-z) \dot{z}'$$

Substituting (82) one finds for the two particles

$$P = (\dot{y}\dot{z}' - \dot{z}\dot{y}') + (\dot{y}'\dot{z} - \dot{z}'\dot{y}) = 0$$

On the other hand, when $\mathcal{L} = QQ'$, the contributions of the first particle to R and S become

$$\left\{ \dot{y} (z - z') - \dot{z} (y - y') \right\} Q'$$

and $(y\dot{z} - z\dot{y}) Q' - (y'\dot{z}' - z'\dot{y}') Q,$

the sum of which is

$$(y'\dot{z} - z'\dot{y}) Q' - (y\dot{z}' - z\dot{y}') Q.$$

If the contribution that is due to the second particle (obtained by interchanging symbols with and without primes) is added to this, the result is zero. It is to be remarked that the expression (8) is somewhat different (so far as higher powers of v are concerned) from the ordinary value

$$\sum m (y\dot{z} - z\dot{y})$$

that is related in a simple way to the magnetic moment of the system.

The vector with the components μ_x, μ_y, μ_z remains constant in course of time. It remains somewhat doubtful however whether it be appropriate to speak of a precession of the system around a line having the direction of μ . This would be the case if the equations of motion would become simpler when transformed to axes that rotate about this line with a suitably chosen velocity.

Larmor's Theorem. Theory of the Normal Zeeman Effect.

Consider a system for all the movable particles of which $\frac{e}{m}$ has the same value (nucleus at rest). Let there be no external magnetic field at first, and let the system have a certain motion relatively to a stationary system of axes OX, OY, OZ . Then, when an external magnetic field (uniform all through the system) gradually comes up, the motion will continually be the same with respect to the axes OX, OY, OZ , provided that these are made to rotate at any instant with the velocity

$$\mathbf{g} = - \frac{e}{2mc} \mathbf{H} \quad \dots \dots \dots (83)$$

Here \mathbf{H} , representing the magnetic force, and \mathbf{g} are vectors.

The theorem is true so long as quantities of the order of H^2 may be neglected. It holds for any change of \mathbf{H} , either in magnitude or direction, or in both together.

Suppose now that the field H has constantly the same direction. Let μ be the moment of momentum of an atom, and μ_H its component in the direction of H . Let the initial quantum conditions ($H = 0$) be

$$\mu_H = n \frac{h}{2\pi} \dots \dots \dots (84)$$

(n magnetic quantum number). Then change of energy produced by gradually starting the magnetic field will be

$$g \mu_H = -n \frac{eh}{4\pi mc} H. \dots \dots \dots (85)$$

This leads to the explanation of the Zeeman effect in its simplest form. The change of (85) for a change of n by $+1$ or -1 , after division by h , determines the separation of the lines in a normal triplet.

Spinning Electrons. For the sake of simplicity the electron is considered as a sphere of invariable radius R , having a charge e , uniformly distributed over the surface and no other mass but the "electromagnetic" one

$$m = \frac{e^2}{6\pi c^2 R}$$

Let the sphere rotate with the angular velocity g (a vector).

Magnetic moment:

$$M_a = \frac{eR^2}{3c} g$$

"Moment of Inertia": $Q = \frac{e^2 R}{18\pi c^2}$

Moment of momentum: Qg

Energy: $\frac{1}{2} Qg^2$.

The ratio between the magnetic moment and the moment of momentum is

$$\frac{e}{mc}$$

twice as great as it is for α system of revolving electrons.

Let the electron be placed in a magnetic field, the strength H of which is a given function of the time. It is acted on by two couples, the one $[M_a H]$ (the vector product of M_a and H) and the other

$$- \frac{eR^2}{3c} \dot{H}.$$

When the magnetic field gradually grows up from $H = 0$, and when the electron has initially a magnetic moment $M_{a'o}$, the magnetic moment at any later time will consist of two parts, one with the magnitude

$$- 2\pi R^3 H$$

in the direction of H , and the other the original moment M_{ao} such as it will be when it has constantly been rotating with the angular velocity

$$- \frac{e}{mc} H.$$

Now apply the same quantization as in the case of the revolving electrons. Taking (84) as the quantum condition, μ now being the moment of momentum of the spinning electron in the initial state, one finds for the change of energy produced by the magnetic field

$$- n \frac{eh}{2\pi mc} H,$$

twice the change (85).

General form of Lagrange's function for Moving Electric Charges. The electromagnetic field depends on two potentials, the scalar potential V and the vector potential A . Let μ be the volume density of the electric charge, v its velocity. Then, at a certain point P , and at a chosen instant t , the potentials are determined by the equations

$$V = \frac{1}{4\pi} \int \frac{[\mu]}{r} ds,$$

$$A = \frac{1}{4\pi c} \int \frac{[\mu v]}{r} ds,$$

where ds is an element of volume and r its distance from P . The brackets $[]$ serve to indicate the values of μ and μv which existed in ds at the time $t - \frac{r}{c}$ (Retarded potentials):

In the last equation μv and A are vectors.

From the two potentials one can deduce the electric force E and the magnetic force H , by means of the vector equations

$$E = - \frac{1}{c} \dot{A} - \text{grad } V$$

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

The function $\mathcal{L} = - \frac{1}{2} \int \mu V ds + \frac{1}{2c} \int \mu (v \cdot A) ds \dots \dots (86)$ plays the part of Lagrange's function. Only those parts of space in which there is an electric charge contribute to its value.

Application to an Electron Revolving Around a nucleus and having at the same time a rotation about a diameter. From (86) one can deduce the following expression for the Lagrangian function

$$\mathcal{L} = \frac{1}{2} m v^2 + \frac{1}{2} Q g^2 - \frac{e e'}{4\pi r} + \mathcal{L}' \dots \dots (87)$$

where \mathcal{L}' is an additional term depending on the simultaneous existence of the two motions.

$$\mathcal{L}' = - \frac{\pi Q}{2c^2} (\mathbf{v} \cdot [\dot{\mathbf{v}} \cdot \mathbf{g}]),$$

$$\mathcal{L}' = - \frac{\pi Q}{2c^2} \begin{vmatrix} v_x, v_y, v_z \\ \dot{v}_x, \dot{v}_y, \dot{v}_z \\ g_x, g_y, g_z \end{vmatrix} \dots \dots \dots (88)$$

In the first term of \mathcal{L} the relativity quantities have now been neglected.

e' charge of the nucleus.

Q moment of inertia of the electron.

\mathbf{g} , with components g_x, g_y, g_z , its angular velocity.

Certain higher terms (with $\ddot{\mathbf{v}}, \dot{\mathbf{g}}$) have been neglected.

Equation of Motion for the Translation of the Electron.

The above form of \mathcal{L} differs from the ordinary one in so far as it contains not only the velocity but also the acceleration. The equations of motion can still be derived from the theorem that

$$\delta \int_{t_0}^{t_1} \mathcal{L} dt = 0,$$

when all variations are zero for t_0 and t_1 . But, when \mathcal{L} contains x, \dot{x} and \ddot{x} , $\delta \mathcal{L}$ will contain

$$\frac{d\mathcal{L}}{dx} \delta x + \frac{d\mathcal{L}}{d\dot{x}} \delta \dot{x} + \frac{d\mathcal{L}}{d\ddot{x}} \delta \ddot{x}$$

the second term can be replaced by

$$\frac{d}{dt} \left(\frac{d\mathcal{L}}{d\dot{x}} \delta x \right) - \frac{d}{dt} \left(\frac{d\mathcal{L}}{d\ddot{x}} \right) \delta \dot{x}$$

and similarly the third one by

$$\frac{d}{dt} \left\{ \frac{d\mathcal{L}}{d\ddot{x}} \delta \dot{x} - \frac{d}{dt} \left(\frac{d\mathcal{L}}{d\ddot{x}} \right) \delta x \right\} + \frac{d^2}{dt^2} \left(\frac{d\mathcal{L}}{d\ddot{x}} \right) \delta x$$

Remembering that terms of the form $\frac{dK}{dt}$ vanish when the integration with respect to the time is performed and equating to zero the coefficient of δx , one finds

$$-\frac{d\mathcal{L}}{dx} + \frac{d}{dt}\left(\frac{d\mathcal{L}}{dx}\right) - \frac{d^2}{dt^2}\left(\frac{d\mathcal{L}}{dx}\right) = 0$$

After substitution of (87) and (88) this becomes

$$m\ddot{x} = \frac{ee'x}{4\pi r^3} + \frac{\pi Q}{2c^2} \left\{ \frac{d}{dt} (\dot{v}_y g_z - \dot{v}_z g_y) + \frac{d^2}{dt^2} (v_y g_z - v_z g_y) \right\}$$

etc.

The last term in these equations represents an additional force acting on the electron and due to the combination of the two motions.

Omitting terms in \dot{g} and \ddot{g} one finds for the components of the additional force

$$\frac{\pi Q}{c^2} (\ddot{v}_y g_z - \ddot{v}_z g_y), \text{ etc.}$$

It is at right angles to \ddot{v} and g , being in fact determined by the vector product of these two vectors. In the case of a circular motion \ddot{v} has a direction opposite to that of v ; hence, if g is normal to the plane of the orbit, the additional force is directed towards the center or away from it.

Equations of Motion for the Rotation of the Electron.

Here, in the function \mathcal{L} , one is only concerned with velocities.

Now, Lagrange's equation

$$\sum \left\{ \frac{d}{dt} \left(\frac{d\mathcal{L}}{dq} \right) \delta q - \frac{d\mathcal{L}}{dq} \delta q \right\} = 0$$

may be replaced by

$$\frac{d}{dt} (\delta' \mathcal{L}) - \delta \mathcal{L} = 0, \dots \dots \dots (89)$$

where $\delta \mathcal{L}$ is the change of \mathcal{L} when one passes from the original to the varied motion, and

$$\delta' \mathcal{L} = \sum \frac{d\mathcal{L}}{dq} \delta q$$

is the change that would occur, when the variations that are in reality applied to the coordinates were applied to the velocities.

Let OA be a diameter of the electron, having a fixed position in this particle and whose direction constants at the time t are j, k, ℓ . Then, on account of the rotation

$$\frac{dj}{dt} = \ell g_y - k g_z, \text{ etc} \quad \dots \dots \dots (90)$$

Let the variation of the position or the virtual displacement be an infinitely small rotation a about OA, a being independent of t . Then $\delta \mathcal{L} = 0$, and $\delta' \mathcal{L}$ will be the change of \mathcal{L} when g_x, g_y, g_z are given the variations $ja, ka, \ell a$. Thus

$$\delta' \mathcal{L} = (j \frac{d\mathcal{L}}{dg_x} + k \frac{d\mathcal{L}}{dg_y} + \ell \frac{d\mathcal{L}}{dg_z}) a$$

and, on account of (90)

$$\frac{d}{dt} (\delta' \mathcal{L}) = \left\{ j \frac{d}{dt} \left(\frac{d\mathcal{L}}{dg_x} \right) + \text{etc.} + (\ell g_y - k g_z) \frac{d\mathcal{L}}{dg_x} + \text{etc.} \right\} a$$

Substituting in (89) and separating the terms in j, k, ℓ one finds the equations of motion

$$\frac{d}{dt} \left(\frac{d\mathcal{L}}{dg_x} \right) + g_z \frac{d\mathcal{L}}{dg_y} - g_y \frac{d\mathcal{L}}{dg_z} = 0. \quad \dots \dots \dots (91)$$

If one omits the additional term \mathcal{L}' in the expression (87) for Lagrange's function, one has simply

$$\frac{d\mathcal{L}}{dg_x} = Qg_x, \quad \frac{d\mathcal{L}}{dg_y} = Qg_y, \quad \frac{d\mathcal{L}}{dg_z} = Qg_z$$

and (91) becomes

$$Q\dot{g}_x = 0, \quad Q\dot{g}_y = 0, \quad Q\dot{g}_z = 0,$$

showing that the angular velocity of the electron remains constant in direction and magnitude.

Introducing now the additional term \mathcal{L}' one has

$$\frac{d\mathcal{L}'}{dg_x} = -\frac{\pi Q}{2c^2} (v_y \dot{v}_z - v_z \dot{v}_y), \text{ etc.}$$

or

$$\frac{d\mathcal{L}'}{dg_x} = K_x, \quad \frac{d\mathcal{L}'}{dg_y} = K_y, \quad \frac{d\mathcal{L}'}{dg_z} = K_z.$$

when the vector K is defined by

$$K = -\frac{\pi Q}{2c^2} [\mathbf{v} \cdot \dot{\mathbf{v}}] \quad \dots \dots \dots (92)$$

The last vector meaning the vector product of the velocity \mathbf{v} and the acceleration $\dot{\mathbf{v}}$.

The equations of motion (91) for the rotation are now

$$Q\dot{g}_x = -\frac{dK_x}{dt} - K_y g_z + K_z g_y, \text{ etc.}$$

or

$$Q\dot{\mathbf{g}} = -\dot{\mathbf{K}} - [\mathbf{K} \cdot \mathbf{g}] \quad \dots \dots \dots (93)$$

The additional Terms Which Depend on \mathcal{L}' Compared with the Principal Terms. The additional term \mathcal{L}' , defined by (88) is of the order of magnitude

$$\frac{\pi Q}{2c^2} v \dot{v} g,$$

where the last three factors indicate the absolute values.

Hence the ratio of \mathcal{L}' to $\frac{1}{2}mv^2$ is of the order of magnitude

$$\frac{\pi Qg}{mvc^2} \dot{v} = \pi \frac{Qg}{mvr} \cdot \frac{\dot{v}}{c^2}.$$

But $\dot{v}r$ is of the same order of magnitude as v^2 . Therefore, when the momenta of momentum Qg and mvr are of the same order of magnitude (as they are on account of the quantum conditions applied to them) the ratio between \mathcal{L}' and $\frac{1}{2}mv^2$ will be of the order $\frac{v^2}{c^2}$.

The additional terms will lead to small displacements or separations of spectral lines.

Moment of Momentum of the System. To a first approximation this is

$$\mathcal{M} = m[r.v] + Qg \dots \dots \dots (94)$$

(r means the vector drawn from the nucleus to the electron), compounded of the momenta due to the translation and to the rotation. But there are additional terms. In the first component the additional term is (when terms of the order $\frac{v^4}{c^4}$ are neglected)

$$y \frac{d\mathcal{L}'}{dz} - z \frac{d\mathcal{L}'}{dy} - y \frac{d}{dt} \left(\frac{d\mathcal{L}'}{dz} \right) + z \frac{d}{dt} \left(\frac{d\mathcal{L}'}{dy} \right) + \dot{y} \frac{d\mathcal{L}'}{dz} - \dot{z} \frac{d\mathcal{L}'}{dy} \dots (95)$$

Effect of the Additional Terms on the Motion of the Electron

The additional force whose first component is

$$\frac{\pi Q}{c^2} (\ddot{v}_y g_z - \ddot{v}_z g_y)$$

leads to a slow precessional motion of the plane of the orbit, due to the rotation of the electron, the angular velocity of this precession being

$$\frac{\pi Q n^2}{2c^2 m} g, \dots \dots \dots (96)$$

where n is the frequency of the motion in the orbit.

This result has been obtained for the case of a circular orbit but probably it will be possible to generalize it.

As to the motion of rotation, the first term on the right hand side of (93) will produce a small variation in the angular velocity g , which however is zero after a complete revolution in the orbit. In the case of a circular orbit at any instant $\dot{K} = 0$.

The last term in (93) produces a precessional motion of the spinning electron, the angular velocity of this precession being $-\frac{K}{Q}$, or, according to (92)

$$\frac{\pi}{2c^2} [\mathbf{v} \cdot \dot{\mathbf{v}}] \dots \dots \dots (97)$$

consider again the case of a circular orbit. Then

$$\dot{\mathbf{v}} = -n^2 \mathbf{r},$$

so that (97) becomes

$$\frac{\pi n^2}{2c^2} [\mathbf{r} \cdot \mathbf{v}]$$

and the two precessions (96) and (97) are

if μ_1 and μ_2 are the two parts of (94). The precessional motion may therefore (nearly) be replaced by a common precession

$$\frac{\pi n^2}{3c^2 m} \mu$$

The precession (97) of the spinning motion can be compared with the precession that would take place if the nucleus had a certain velocity w and thereby produced a magnetic field H at the place of ^{the} electron.

Let V be the scalar potential produced by the nucleus.

Then the magnetic force in question would be

$$H = -\frac{1}{c} [w \cdot \text{grad } V],$$

giving rise to a precession

$$\begin{aligned} -\frac{e}{mc} H &= \frac{e}{mc^2} [\mathbf{w} \cdot \text{grad } V] , \\ \text{or} \quad -\frac{1}{c^2} [\mathbf{w} \cdot \dot{\mathbf{v}}] \end{aligned}$$

because $\dot{\mathbf{v}} = -\frac{e}{m} \text{grad } V$. The result would agree with (97) if

$$\mathbf{w} = -\frac{1}{2} \pi \mathbf{v} . \quad \dots \dots \dots (98)$$

Equation of Energy. When Lagrange's function \mathcal{L} contains coordinates q , velocities \dot{q} and accelerations \ddot{q} , the equations of motion are

$$\frac{d}{dt} \left(\frac{d\mathcal{L}}{d\dot{q}} \right) - \frac{d\mathcal{L}}{dq} - \frac{d^2}{dt^2} \left(\frac{d\mathcal{L}}{d\ddot{q}} \right) = 0 , \quad \dots \dots \dots (99)$$

and the energy has the value

$$E = \sum \left\{ \dot{q} \frac{d\mathcal{L}}{d\dot{q}} + \ddot{q} \frac{d\mathcal{L}}{d\ddot{q}} - \dot{q} \frac{d}{dt} \left(\frac{d\mathcal{L}}{d\dot{q}} \right) \right\} - \mathcal{L} . \quad \dots \dots \dots (100)$$

Indeed, one finds by differentiating this, taking (99) in to account,

$$\frac{dE}{dt} = \sum \left(\dot{q} \frac{d\mathcal{L}}{d\dot{q}} + \ddot{q} \frac{d\mathcal{L}}{d\ddot{q}} + \ddot{q} \frac{d\mathcal{L}}{d\ddot{q}} \right) - \frac{d\mathcal{L}}{dt} = 0 .$$

If the function \mathcal{L} contained, besides q , \dot{q} , \ddot{q} , a slowly variable parameter s , the last equation would become

$$\dot{E} = -\dot{s} \frac{d\mathcal{L}}{ds}$$

giving for a small change of s

$$dE = -ds \frac{\overline{d\mathcal{L}}}{ds} , \quad \dots \dots \dots (101)$$

where $\frac{\overline{d\mathcal{L}}}{ds}$ is the mean value calculated for the original motion.

From eq. (100) one can infer that the energy of the system under consideration consists of the principal part

$$\frac{1}{2} m v^2 + \frac{1}{2} Q g^2 + \frac{e e'}{4 \pi r}$$

and an additional part which depends on \mathcal{L}' and will be found to be

$$2 \mathcal{L}' \quad \dots \dots \dots (102)$$

Quantization of the Motions.

The difficulty of finding

suitable quantum conditions for an atom in which an electron is revolving around the nucleus and rotating at the same time can be avoided by remembering that the interaction between the two motions depends solely on the additional part \mathcal{L}' of Lagrange's function. replace the factor $\frac{1}{c^2}$ in eq. (88) by an parameter s and suppose this to change slowly from 0 to $\frac{1}{c^2}$. Then, at first, there is no interaction at all between the two motions, and one can easily lay down appropriate quantum conditions, prescribing f.i. definite values not only to each of the parts μ_1 and μ_2 of the momentum (94), but also to μ itself. When the initial quantization has been performed in this way, the energies of the stationary motions in the final state, when $s = \frac{1}{c^2}$ will be known. Since the changes produced by the additional terms are small, one may infer from (101) that the change in energy when one passes from an initial to the corresponding final stationary state, is given by

$$-\overline{\mathcal{L}'} \quad \dots \dots \dots (103)$$

the mean value of \mathcal{L}' in the initial motion, with the opposite sign. It would be possible by means of this result to calculate or to estimate the separations of the multiplets.

Determination of the Change in the Energy of a Stationary State, Caused by the Spinning Motion of the Electron.

Eq. (83) for \mathcal{L}' may be written in the form

$$\mathcal{L}' = - \frac{\pi Q}{2c^2} (g. [\mathbf{v} \cdot \dot{\mathbf{v}}])$$

Let \mathbf{r} be the vector drawn from the nucleus to the electron. Then

$$\dot{\mathbf{v}} = - \frac{Ze^2}{mr^3} \mathbf{r},$$

where, in the first factor r means simply the length of \mathbf{r} . Thus

$$\mathcal{L}' = \frac{\pi Q}{2c^2} \cdot \frac{Ze^2}{mr^3} (g. [\mathbf{v} \cdot \mathbf{r}]).$$

But

$$m [\mathbf{v} \cdot \mathbf{r}] = -\mu_1 \text{ and } Qg = \mu_2$$

Hence

$$\mathcal{L}' = - \frac{\pi Ze^2}{2c^2 m^2} (\mu_1 \cdot \mu_2) \frac{1}{r^3}$$

and

$$-\mathcal{L}' = \frac{\pi Ze^2}{2c^2 m^2} (\mu_1 \cdot \mu_2) \cdot \frac{1}{r^3} \dots\dots\dots (104)$$

The mean value of $\frac{1}{r^3}$ in the elliptic motion is equal to the ratio between the integrals

$$\int_{r_1}^{r_2} \frac{dr}{r^2 \sqrt{(r_2-r)(r-r_1)}} \quad \text{and} \quad \int_{r_1}^{r_2} \frac{r dr}{\sqrt{(r_2-r)(r-r_1)}}$$

The first of these is

$$\frac{1}{3} \pi \frac{r_1 + r_2}{\sqrt{(r_1 r_2)^3}}$$

and the second

$$\frac{1}{2} \pi (r_1 + r_2)$$

so that the mean value of $\frac{1}{r^3}$ is

$$\frac{1}{\sqrt{(r_1 r_2)^3}}.$$

Now (104) can be expressed in terms of the quantities belonging to the stationary state as it would be if there were no interaction between the two motions of the electron, energy E_0 , quantum numbers k and n . Put

$$\mu_1 = k \frac{h}{2\pi}, \quad \mu_2 = \ell \frac{h}{2\pi},$$

k and ℓ being eventually considered as vectors. The final result for the energy is

$$E = E_0 \left[1 + \frac{2\pi n}{k^3} \frac{E_0}{mc^2} (k \cdot \ell) \right] \dots \dots \dots (105)$$

It may be remarked that the additional term contains the factor E_0^2 and therefore Z^4

Action of an External Magnetic Field. This gives rise to two new terms in Lagrange's function, namely

$$\mathcal{L}_m = \frac{e}{c} (\mathbf{v} \cdot \mathbf{A}) + \frac{eR^2}{3c} (\mathbf{g} \cdot \mathbf{H}), \dots \dots \dots (106)$$

where H is the magnetic force in the field and A the vector potential from which it can be derived. The first term leads to a new force acting on the electron. Its first component is found by substituting the value

$$\frac{e}{c} (\mathbf{v} \cdot \mathbf{A})$$

for \mathcal{L} in the expression

$$\frac{d\mathcal{L}}{dx} - \frac{d}{dt} \left(\frac{d\mathcal{L}}{dx} \right)$$

The result is

$$\frac{e}{c} \left(v_x \frac{dA_x}{dx} + v_y \frac{dA_y}{dx} + v_z \frac{dA_z}{dx} \right) - \frac{e}{c} \frac{dA_x}{dt}. \quad (107)$$

Let \dot{A}_x be the rate of change of A_x at a fixed point in space. Then at the place of the moving electron

$$\frac{dA_x}{dt} = \dot{A}_x + v_x \frac{dA_x}{dx} + v_y \frac{dA_x}{dy} + v_z \frac{dA_x}{dz}$$

Substituting this value in (107) and remembering that $-\frac{1}{c} \dot{A}_x$ is the first component F_x of the electric force, and that $H = \text{curl } A$,

one finds

$$eF_x + \frac{e}{c} (v_y H_z - v_z H_y) \dots \dots \dots (108)$$

Similarly the last term in (106) leads to a new couple acting on the electron. It consists of the parts

$$- \frac{eR^2}{3c} \dot{H} \dots \dots \dots (109)$$

and

$$\frac{ek^2}{3c} [g.H] = [\mu_a.H] \dots \dots \dots (110)$$

The expression (106) does not lead to any new term in the equation for the energy.

Influence of the Magnetic Field on the Energy of a Stationary State. Let the field be produced by a current of intensity s in a coil and let s gradually grow from 0 to the final value; A and H will increase proportionally to s . The change in the energy of a stationary state is found when the final value of s is multiplied by the mean value of

$$- \frac{d\mathcal{L}}{ds}$$

taken for the original motion. The result depending solely on (106) is

$$- \frac{e}{c} (\overline{v.A}) - \frac{eR^2}{3c} (\overline{g.H}) \dots \dots \dots (111)$$

The mean values in (111) can be calculated in two steps; first average as if the precessional motions of the orbit and the axis of rotation did not exist, and then take the mean of the results for all positions of the orbit and the axis that occur in the precessional motions.

First step. Take into account the relation $Qg = \mu_2$ and the values of Q and m one finds for the last term in (111)

$$- \frac{e}{cm} (\mu_2 \cdot H)$$

Further, let N be the normal to the plane of the orbit, drawn in the direction that corresponds to that of the revolution and is also the direction of μ_1 . Let P be the period, ds an element of the orbit, dS an element of the plane limited by it, then

$$(\overline{v \cdot A}) = \frac{1}{P} \int A_s ds = \frac{1}{P} \int H_N dS.$$

Since H_N has the same value at all points, the integral is equal to the product of H_N and the area of the ellipse. But, since the area described by the radius vector in unit of time is $\frac{\mu_1}{2m}$, the area of the ellipse is $\frac{P\mu_1}{2m}$, Finally, the first term in (111) becomes

$$- \frac{e}{2cm} \mu_1 H_N = - \frac{e}{2cm} \mu_1 \cdot H$$

If E_0 is the energy in the initial stationary state ($H = 0$), the energy in the corresponding state in the magnetic field will be

$$E = E_0 - \frac{e}{2cm} \{ (\overline{\mu_1 \cdot H}) + 2 (\overline{\mu_2 \cdot H}) \} \dots \dots (112)$$

where the strokes indicate mean values during the precessional motions

The vectors μ_1 and μ_2 both turn around the resultant vector μ . Let this have the magnitude

$$j \frac{h}{2\pi}$$

and let it make an angle θ with the direction of H . Further, let a be the angle between μ_1 and μ , b that between μ_2 and μ .

The mean $\bar{\mu}$, is a vector of magnitude $\frac{k}{2\pi} \cos. a$ in the direction of μ and similarly $\bar{\mu}_2$ is a vector $\frac{l}{2\pi} \cos. b$ in the same direction. Thus (112) becomes

$$E = E_0 - \frac{he}{4\pi cm} H \cos \theta (k \cos a + 2 l \cos b),$$

or, after substitution of the values of $\cos a$ and $\cos b$ in the triangle formed of the vectors k, l, j , namely

$$\cos a = \frac{k^2 + j^2 - l^2}{2kj}, \quad \cos b = \frac{l^2 + j^2 - k^2}{2lj}$$

$$E = E_0 - \frac{he}{4\pi cm} H \cos \theta \frac{3j^2 - k^2 + l^2}{2j},$$

a result similar to Lande's formula.

Introduction to Schrödinger's "undulatory" dynamics.

Equation of motion of a stretched string.

$$\frac{d^2 f}{dx^2} = \frac{1}{u^2} \frac{d^2 f}{dt^2} \quad \dots \dots \dots (113)$$

(f displacement of a point from its position of equilibrium).

Similarly for a stretched membrane

$$\frac{d^2 f}{dx^2} + \frac{d^2 f}{dy^2} = \frac{1}{u^2} \frac{d^2 f}{dt^2} \quad \dots \dots \dots (114)$$

In three dimensions one can have vibrations determined by an equation of the form

$$\frac{d^2 f}{dx^2} + \frac{d^2 f}{dy^2} + \frac{d^2 f}{dz^2} = \frac{1}{u^2} \frac{d^2 f}{dt^2}, \quad \dots \dots \dots$$

or

$$\Delta f = \frac{1}{u^2} \frac{d^2 f}{dt^2} \quad \dots \dots \dots (115)$$

Here f may mean f.i. a small change of density (contraction or dilation) that exists in an isotropic elastic medium.

The coefficient $\frac{1}{u^2}$ depends on the stresses as they are called forth or modified by the displacements and on the density. It may change from point to point.

The velocity of propagation of waves is given by u ; it also may be a function of the coordinates, but since in (114) and (115) the system has been supposed to be isotropic, u will be, at a given point, independent of the direction. It therefore also represents the velocity of rays.

The course of a ray is determined by condition (Fermat's theorem) that between fixed points

$$\delta \int \frac{ds}{u} = 0 \quad \dots \dots \dots (116)$$

There are cases in which $\frac{1}{u^2}$ must be considered as depending on the frequency n (dispersion). Then the "group velocity" v is given by

$$\frac{1}{v} = \frac{d}{dn} \left(\frac{n}{u} \right) \quad \dots \dots \dots (117)$$

In what follows eq. (116) and (117) are considered as definitions of ray and of group velocity. These latter words will be used even if circumstances would be such that the words lose their original physical meaning.

Schrödinger's Theory. Hydrogen atom.

1. Choose a definite value E for the energy of the electron. The potential energy is taken to be 0 when the electron is at infinite distance from the nucleus. When, in the course of its motion, the electron reaches a given point P , its velocity at that point will be entirely determined.

$$\frac{1}{2} mv^2 - \frac{e^2}{r} = E$$

$$v^2 = \frac{2}{m} \left(E + \frac{e^2}{r} \right) \quad \dots \dots \dots (118)$$

The path of the electron between given points is determined by the principle of least action.

$$\delta \int v ds = 0 \quad \dots \dots \dots (119)$$

2. Schrödinger supposes, following de Broglie, that in the space around the nucleus there is a system in which vibrations can exist

and waves can be propagated, the disturbance of equilibrium being represented by some quantity f ., and the velocity of propagation by u .

Let it be required that the course of a ray in this system coincides with a path of the electron. From (116) and (119) it is seen that the condition for this is that, when one passes from one point to another, the velocity u changes in the inverse ratio as v

$$u = \frac{a}{v}, \quad \dots \dots \dots (120)$$

where a is independent of the coordinates.

3. Schrödinger further supposes that the frequency (which of course must be the same all through the system) is given by

$$n = \frac{E_0 + E}{h} \quad \dots \dots \dots (121)$$

Here E_0 is a positive quantity whose magnitude far surpasses that of E . One may take f.i. $E_0 = mc^2$.

4. Let it finally be required that the velocity v of the electron is just equal to the group velocity in the medium. By this the quantity a in (120) which may depend on E or n , is determined.

Indeed, on account of (117) and (120)

$$\frac{1}{v} = \frac{d}{dn} \left(\frac{n}{a} v \right),$$

or, multiplying by $\frac{2n}{a} v$

$$2 \frac{n}{a} = \frac{d}{dn} \left(\frac{n^2}{a^2} v^2 \right).$$

Since, according to (118) v^2 contains a term depending on r , the condition can only be satisfied if $\frac{n}{a}$ is independent of n . In this case the equation becomes

$$2 \frac{a}{n} = \frac{d}{dn} (v^2) = \frac{2}{m} \frac{dE}{dn}$$

or if (121) is used,

$$a = \frac{n}{m} \frac{dE}{dn} = \frac{E_0 + E}{m},$$

so that the velocity (120) of the waves must be

$$u = \frac{E_0 + E}{mv} = \frac{E_0 + E}{\sqrt{2m(E + \frac{e^2}{r})}} \dots (122)$$

This determines the form of the equation of motion (115) for the vibrating system. Since

$$\frac{d^2 f}{dt^2} = -4\pi^2 n^2 f = -4\pi^2 \frac{(E_0 + E)^2}{h^2} f$$

the equation becomes

$$\Delta f + \frac{8\pi^2 m}{h^2} \left(E + \frac{e^2}{r}\right) f = 0 \dots (123)$$

This is Schrödinger's "wave equation." It determines the way in which f depends on the coordinates.

It must be remarked that with a given energy E (supposed to be negative) the electron can never get beyond a certain distance from the nucleus; for greater distance (118) would give a negative value of v^2 . Never the less eq. (123) is applied through all space, even to indinite distance.

Just^{as} in the case of a string, or a vibrating membrane or an elastic body there are boundary conditions. Here they are simply that f must remain finite at the origin $r = 0$ and must vanish at infinite distance.

Schrödinger has shown that these conditions can be satisfied only when the constant E has one of certain definite values, namely

$$E = -\frac{2\pi^2 m e^4}{h^2} \frac{1}{\ell^2}, \dots (124)$$

where ℓ is an integer. These are exactly the values that are found in Bohr's theory of the hydrogen atom.

. Remarks About Schrödinger's Theory. From the values of the velocity of propagation u and the frequency n one finds for the wave-length

$$\frac{u}{n} = \frac{h}{\sqrt{2m \left(E + \frac{e^2}{r}\right)}}$$

This may be written (if for E one takes one of its particular values E_l)

$$2\pi \sqrt{\frac{r_1 r_l}{-1 + \frac{2r_l}{r}}}$$

where r_1 and r_l are the radii of the one-quantum and l -quantum circular orbits in Bohr's theory.

The result shows that the wave length is by no means very small. It is in many cases of the same order of magnitude as the distance r from the nucleus. For this reason not only the words "ray" and "group velocity" have lost their original physical meaning but even u can scarcely be said to be the velocity of propagation of waves. It is difficult to attach a clear physical meaning to Schrödinger's wave equation however interesting and fruitful may be the consequences that are drawn from it.

Frequency of the Emitted Radiations. Let f_a and f_b be two solutions of the wave equation, in which E has different values E_a and E_b . Let the vibratory states represented by f_a and f_b , with the frequencies

$$n_a = \frac{E_o + E_a}{h} \quad \text{and} \quad n_b = \frac{E_o + E_b}{h}$$

exist simultaneously, and suppose that for some reason or another, their superposition produces "combination vibrations", with the frequencies $n_a + n_b$ and $n_a - n_b$. The first of these may be considered to be so high that it escapes observation. Schrödinger considers the "difference vibrations" as the direct source of the emitted light. Their frequency

$$n_a - n_b = \frac{E_a - E_b}{h}$$

corresponds exactly to Bohr's fundamental assumption.

Solutions of Schrödinger's Wave Equation. That the energy E must have one of the definite values that have been mentioned was shown by Schrödinger by really working out the solution of the wave equation. This equation can be satisfied by a function of the form

$$\psi = Y_n F(r),$$

where Y_n is a spherical harmonic of order n , arbitrarily chosen, and $F(r)$ a function of r only, determined by

$$\frac{d^2 F}{dr^2} + \frac{2}{r} \frac{dF}{dr} - n(n+1) \frac{F}{r^2} + \frac{8\pi^2 m}{h^2} \left(E - \frac{e^2}{r} \right) F = 0$$

A necessary condition appears to be $\ell > n$.

Some Theorems on Spherical Harmonics. Among all the spherical harmonics of order n one can select a number of $2n + 1$, in such a way that any other Y_n can be expressed as a linear homogeneous function of the selected ones. These may be called the "independent" spherical harmonics.

Examples. $n = 1$. Independent spherical harmonics f.i.

$$\frac{x}{r}, \quad \frac{y}{r}, \quad \frac{z}{r}$$

$n = 2$. Independent spherical harmonics f.i.

$$1 - \frac{3x^2}{r^2}, \quad \frac{y^2 - z^2}{r^2},$$

$$\frac{xy}{r}, \quad \frac{yz}{r}, \quad \frac{zx}{r},$$

Let $d\Omega$ be the opening of an infinitely narrow cone and let the integrations extend to all directions.

With the exception of Y_0 (which is a constant) any spherical harmonic has the property

$$\int Y_n d\Omega = 0$$

Moreover the independent spherical harmonics, for a given n , can (and will) be chosen in such a way that, if Y_n and Y'_n are two of them

$$\int Y_n Y'_n d\Omega = 0$$

This condition is satisfied in the above example.

Finally, if Y_n and $Y_{n'}$ are any two spherical harmonics of different orders n and n' one has always

$$\int Y_n Y_{n'} d\Omega = 0$$

Normal Functions in Schrödinger's Theory. Give to ℓ all possible integral values, and, after having chosen ℓ , give to n all values compatible with it. Finally, when n has been chosen, select for Y_n a set of independent spherical harmonics. By this, all the independent solutions of the wave equation with its boundary conditions will be found. These solutions f are called the "normal" functions. A normal solution can be specified by three numbers (comparable to quantum numbers). The first is ℓ the second n and the third number s indicates with which one of the $2n + 1$ independent functions Y_n one is concerned. A normal function can therefore be represented by $f_{\ell ns}$. But it is more convenient to distinguish them by one single index, writing f_a (or f_b , f_c . . . as the case may be), as if they were all put in one row. The suffix a now stands for ℓns , and the equality of two suffixes a and b will mean that each of the values ℓ , n , s contained in a is equal to the corresponding one in b .

Theorem. If f_a and f_b are any two different normal functions

$$\int f_a f_b dS = 0$$

dS is an element of space and the integration is extended over all space.

If the number ℓ and therefore E , has the same value in the two functions, the theorem follows from what has been said about the spherical harmonics.

When E_a and E_b are different, the proof is as follows

$$\Delta f_a + \frac{8\pi^2 m}{h^2} \left(E_a + \frac{e^2}{r} \right) f_a = 0$$

$$\Delta f_b + \frac{8\pi^2 m}{h^2} (E_b + \frac{e^2}{r}) f_b = 0.$$

multiply the first equation by f_b , the second by f_a , subtract and integrate over space. Since

$$f_b \Delta f_a - f_a \Delta f_b = \frac{d}{dx} (f_b \frac{df_a}{dx} - f_a \frac{df_b}{dx}) + \text{etc.}$$

the integral of this expression vanishes. Thus,

$$(E_a - E_b) \int f_a f_b dS = 0 \quad \text{and} \quad \int f_a f_b dS = 0$$

By the introduction of suitably chosen constant coefficients the normal functions may be made such that for each of them

$$\int f_a^2 dS = 1. \dots \dots \dots (125)$$

Development of a Given Function $P(x,y,z)$ of the Coordinates in a Series of Normal Functions Each Multiplied by a Constant Coefficient. With certain restrictions that need not be considered here one can say that any function $P(x,y,z)$ can be represented by an infinite series of the form

$$P = A_1 f_1 + A_2 f_2 + \dots + A_a f_a + \dots$$

If the possibility of this expansion is assumed, the coefficients are easily determined.

Multiply by $f_a dS$ and integrate over all space. On the right-hand side all terms with the exception of that with f_a disappears, and on account of (125)

$$A_a = \int P f_a dS. \dots \dots \dots (126)$$

This has a definite numerical value when $P(x,y,z)$ is a given function (because f_a is a known function).

Matrices. In quantum mechanics as it was developed by Heisenberg, Born and Jordan, the ordinate x (and similarly $y, z, r, \dot{x}, \dot{y}, \dot{z}$ and other quantities occurring in the formulae) is replaced by an ensemble of an infinite number of quantities each of which x_{ab} is distinguished by two numbers a and b , analogous to quantum numbers (or by two

sets of numbers, a standing f.i. for ℓ, n, s and b for ℓ', n', s' .) They form together what is called a "matrix" in which they are simply juxtaposed, not being connected by any mathematical operation. The symbol x will serve to denote the quantity in its ordinary and original meaning, and the matrix will be represented by (x) . The quantities x_{ab} or eventually $(x)_{ab}$ are the "elements" of the matrix.

The elements with equal suffixes x_{aa} are constant numbers. An element with different suffixes x_{ab} consists of two factors one of which represents a vibration, containing $\cos. 2\pi n_{ab}t$ or $\sin. 2\pi n_{ab}t$. Let this factor be

$$e^{2\pi i n_{ab}t}, \quad \dots \dots \dots (127)$$

so that

$$x_{ab} = e^{2\pi i n_{ab}t} \chi_{ab} \quad \dots \dots \dots (128)$$

the last factor being a constant.

The factor (127) will also be represented by q_{ab} . Corresponding to every element x_{ab} there is another element x_{ba} . It belongs to the definition of the kind of matrices now considered that

$$n_{ba} = -n_{ab} \quad \dots \dots \dots (129)$$

and that the quantities χ_{ab} and χ_{ba} , when real, are equal to each other and that they are conjugate when they have complex values. This amounts to saying that x_{ab} and x_{ba} are conjugate complex quantities. The frequencies n are subjected to the rule that, if a, b, c are any three suffixes

$$n_{ab} + n_{bc} = n_{ac} \quad \dots \dots \dots (130)$$

Eq. (129) and (130) imply that $n_{aa} = 0$, so that the elements x_{aa} are independent of t . Also that all the frequencies can be expressed in the form

$$n_{ab} = K_a - K_b, \quad \dots \dots \dots (131)$$

where K_a , K_b etc. are a series of constant quantities. The idea is that the frequencies n_{ab} are those of the light that is emitted by the atom, so that the element x_{ab} (together with x_{ba}) may be considered as representing something like a vibrator having the frequency n_{ab} .

In all matrices replacing quantities that occur in the same problem the frequencies n_{ab} have the same values

Mathematical Operations Performed on Matrices. Some of these are defined by the following formulae

$$(u + v)_{ab} = u_{ab} + v_{ab}$$

$$(u - v)_{ab} = u_{ab} - v_{ab}$$

$$(ku)_{ab} = k (u)_{ab} \quad (k \text{ a constant factor})$$

$$\left(\frac{d}{dt} u\right)_{ab} = \frac{d}{dt} (u)_{ab} = 2\pi i n_{ab} (u)_{ab}$$

A matrix may be written in a form similar to that of a determinate.

Ei., with the smallest number of elements

$$(u) = \begin{vmatrix} u_{11} & u_{12} \\ u_{21} & u_{22} \end{vmatrix}$$

If this were a determinant and if v_{11} , v_{12} , v_{21} and v_{22} where the elements of a second determinant, their product would be the determinant

$$(uv) = \begin{vmatrix} u_{11} v_{11} + u_{12} v_{21} & u_{11} v_{12} + u_{12} v_{22} \\ u_{21} v_{11} + u_{22} v_{21} & u_{21} v_{12} + u_{22} v_{22} \end{vmatrix}$$

The product of two matrices is defined as a matrix, the elements of which are deduced from the elements of the given matrices by the same rule that applies in the case of determinants. It can be expressed by the formula

$$(uv)_{ab} = \sum (c) u_{ac} v_{cb} \quad \dots \dots \dots (132)$$

where the sign of summation refers to all values of the suffix c.

A matrix (1) is a matrix whose elements with equal suffixes are all 1, all other elements being 0.

The inverse to a matrix (u), represented by $(\frac{1}{u})$ or $(\frac{1}{u})$ is defined by the equation

$$(u) (\frac{1}{u}) = 1 \quad \dots \dots \dots (133)$$

A consequence of the way in which the multiplication has been defined is that the products (uv) and (vu) are not in general equal. The commutative law of multiplication does not hold in this case. If, in a special case the two products are equal, the matrices (u) and (v) are said to be interchangeable. The mathematical operations that have now been mentioned never introduce new frequencies.

Fundamental Assertion (for the Case of the Hydrogen Atom).

The equations of motion of the electron are

$$m \frac{d^2 x}{dt^2} = - e^2 \frac{x}{r^3} \quad \text{etc.} \quad \dots \dots \dots (134)$$

The new theory asserts that matrices (x), (y), (z), (r) can be found which satisfy the equations of the same form

$$m \frac{d^2 (x)}{dt^2} = - e^2 \left(\frac{x}{r^3} \right), \quad \text{etc.} \quad \dots \dots \dots (135)$$

the matrix (r) being defined by

$$(r)^2 = (x)^2 + (y)^2 + (z)^2 \quad \dots \dots \dots (136)$$

Moreover, that when (leaving aside some conditions of minor importance) these matrices are subjected to the conditions

$$(\dot{x} x) - (x \dot{x}) = \frac{h}{2\pi m i} (1), \text{etc.} \quad \dots \dots \dots (137)$$

their elements are determined in so far that the frequencies n_{ab} all become known.

Eq. (137) are the only quantum conditions. The frequencies of the emitted radiations can in this way be determined without any further quantization of motions and without any consideration about quantum jumps.

Or, when the omitted factors are again introduced

$$(uv)_{ab} = \sum (c) u_{ac} v_{cb}$$

This agrees with (132)

3. The elements of the matrix (\dot{x}) are determined by

$$(\dot{\bar{x}})_{ab} = \frac{h}{2\pi mi} \int f_a \frac{df_b}{dx} dS \dots\dots\dots (143)$$

or, since

$$(f_a \frac{df_b}{dx} + f_b \frac{df_a}{dx}) dS = \int \frac{d(f_a f_b)}{dx} dS = 0,$$

$$(\dot{\bar{x}})_{ab} = \frac{h}{4\pi mi} \int (f_a \frac{df_b}{dx} - f_b \frac{df_a}{dx}) dS.$$

It must now be shown that the matrix (\dot{x}) thus defined is the same that is obtained by differentiating (x) with respect to t , i.e.

$$(\dot{x})_{ab} = 2\pi i n_{ab} x_{ab} \dots\dots\dots (144)$$

Proof: One has the equations

$$\Delta f_a + \frac{8\pi^2 m}{h^2} (E_a + \frac{e^2}{r}) f_a = 0 \dots\dots\dots (145)$$

$$\Delta f_b + \frac{8\pi^2 m}{h^2} (E_b + \frac{e^2}{r}) f_b = 0 \dots\dots\dots (146)$$

Multiply (145) by $x f_b$ and (146) by $x f_a$, subtract and integrate over all space. It is found that the difference between the expressions

$$x (f_b \Delta f_a - f_a \Delta f_b) \dots\dots\dots (147)$$

and

$$f_a \frac{df_b}{dx} - f_b \frac{df_a}{dx} \dots\dots\dots (148)$$

consists of three terms, each of which is the derivative of some expression with respect to one of the coordinates and therefore vanishes on integration. The integral of (147) may therefore be replaced by that of (148) and the result of the operation is

$$\int (f_a \frac{df_b}{dx} - f_b \frac{df_a}{dx}) dS = - \frac{8\pi^2 m}{h^2} (E_a - E_b) \int x f_a f_b dS \dots\dots (149)$$

Combining this with the rule expressed in (139) and with the above value of $(\bar{x})_{ab}$ one finds

$$(\bar{x})_{ab} = 2\pi i n_{ab} \bar{x}_{ab},$$

which leads to (144) if the factor c_{ab} is again introduced.

Proof that the Matrices Constructed by Schrodinger Satisfy the Equation of Motion (135) and the quantum Conditions (137).

1. Differentiate (146) with respect to x , multiply by f_a and subtract the resulting equation from eq. (145) after having multiplied the latter by $\frac{df_b}{dx}$.

$$\begin{aligned} \frac{df_b}{dx} \Delta f_a - f_a \Delta \frac{df_b}{dx} + \frac{8\pi^2 m}{h^2} (E_a - E_b) f_a \frac{df_b}{dx} + \\ + \frac{8\pi^2 m c^2}{h^2} \frac{x}{r^3} f_a f_b = 0 \end{aligned}$$

Now integrate over all space. The first two terms vanish and one finds, taking into account (143) and the rule expressed in (139)

$$2\pi m i \frac{E_a - E_b}{h} (\bar{x})_{ab} = - e^2 \left(\frac{x}{r^3} \right)_{ab}.$$

Hence

$$2\pi i n_{ab} m \left(\frac{d(x)}{dt} \right)_{ab} = - e^2 \left(\frac{x}{r^3} \right)_{ab}$$

or

$$m \frac{d^2(x)}{dt^2}{}_{ab} = - e^2 \left(\frac{x}{r^3} \right)_{ab}$$

in which (135) is proved.

Note that the proof could have been given just as well if in (134) and (135) there had been $\frac{dU}{dx}$ instead of $e^2 \frac{x}{r^3}$ and in (145) and (146) $-U$ instead of $\frac{e^2}{r}$.

2. According to (143)

$$\frac{2\pi m i}{h} (\bar{x})_{ab} = \frac{2\pi m i}{h c_{ab}} \dot{x}_{ab}$$

is the coefficient of f_a in the expansion of $\frac{df_b}{dx}$. ⁷⁷ Thus

$$\frac{df_b}{dx} = \frac{2\pi mi}{h} \sum (a) \frac{\dot{x}_{ab}}{q_{ab}} f_a \dots \dots \dots (150)$$

Similarly, according to (139)

$$xf_c = \sum (d) \frac{x_{cd}}{q_{cd}} f_d \dots \dots \dots (151)$$

Multiply (150) and (151) and integrate.

$$\sum (a) \frac{\dot{x}_{ab}}{q_{ab}} \cdot \frac{x_{ca}}{q_{ca}} = \frac{h}{2\pi mi} \int xf_c \frac{df_b}{dx} dS \dots \dots (152)$$

In the second factor on the left hand side the suffixes may be interchanged (follows from (139)) and the same may be done in the first factor if the sign is inverted at the same time (follows from (144)). If finally, after having made these two changes, one interchanges b and c, one obtains

$$-\sum (a) \frac{x_{ab}}{q_{ab}} \cdot \frac{\dot{x}_{ca}}{q_{ca}} = \frac{h}{2\pi mi} \int xfb \frac{df_c}{dx} dS \dots \dots (153)$$

Now add (152) and (153). On the right hand side

$$\int x \frac{d(f_b f_c)}{dx} dS = - \int f_b f_c dS$$

On the left hand side, remembering that

$$q_{ab} q_{ca} = q_{cb}$$

and that, in virtue of (132),

$$\begin{aligned} \sum (a) \dot{x}_{ab} x_{ca} &= (x\dot{x})_{cb} \\ \sum (a) \dot{x}_{ab} \dot{x}_{ca} &= (\dot{x}x)_{cb} \end{aligned}$$

one obtains

$$-(\dot{x}x - x\dot{x})_{cb} \frac{1}{q_{cb}}$$

Thus

$$(\dot{x}x - x\dot{x})_{cb} = \frac{hq_{cb}}{2\pi mi} \int f_b f_c dS.$$

This shows that the elements of the matrix

$$(\dot{x}x - x\dot{x})$$

are zero when the two suffixes are different and that they have the value

$$\frac{h}{2\pi mi}$$

when the suffixes are equal, exactly what is expressed by (137).

The "Energy" in quantum Dynamics. Like all other quantities

the energy

$$E = \frac{1}{2} m [\dot{x}^2 + \dot{y}^2 + \dot{z}^2] - \frac{e^2}{r}$$

is replaced by a matrix

$$(E) = \frac{1}{2} m [(\dot{x})^2 + (\dot{y})^2 + (\dot{z})^2] - \left(\frac{e^2}{r}\right).$$

The question now is to find its elements E_{ab} . In order to have in the first place the elements of $\left(\frac{e^2}{r}\right)$ multiply (145) by f_b and integrate. This gives

$$\frac{1}{q_{ab}} \left(\frac{e^2}{r}\right)_{ab} = -E_a \int f_a f_b dS - \frac{h^2}{8\pi^2 m} \int f_b \Delta f_a dS \dots (154)$$

For the last integral one can write

$$-\int \left(\frac{df_a}{dx} \frac{df_b}{dx} + \frac{df_a}{dy} \frac{df_b}{dy} + \frac{df_a}{dz} \frac{df_b}{dz} \right) dS \dots (155)$$

Now using (150)

$$\frac{df_a}{dx} = \frac{2\pi m i}{h} \sum (c) \frac{\dot{x}_{ca}}{q_{ca}} f_c = -\frac{2\pi m i}{h} \sum (c) \frac{\dot{x}_{ac}}{q_{ac}} f_c$$

$$\frac{df_b}{dx} = \frac{2\pi m i}{h} \sum (d) \frac{\dot{x}_{db}}{q_{db}} f_d$$

Multiply and integrate, using (132)

$$\int \frac{df_a}{dx} \frac{df_b}{dx} dS = \frac{4\pi^2 m^2}{h^2} \sum (c) \frac{\dot{x}_{ac}}{q_{ac}} \frac{\dot{x}_{cb}}{q_{cb}} = \frac{4\pi^2 m^2}{h^2 q_{ab}} (\dot{x}^2)_{ab}$$

There are similar formulae for the other parts of (155). Finally

(154) becomes

$$(E)_{ab} = q_{ab} E_a \int f_a f_b dS$$

Thus the elements of (E) with different suffixes are 0, and for

$b = a$, since $q_{aa} = 1$,

$$(E)_{aa} = E_a$$

The elements of (E) are therefore the energy values E_1, E_2 , etc., that occur in Schrödinger's theory.

Mathematical Operations in the Dynamics of Matrices, Independent of Schrodinger's Normal Functions. Starting from the equations of motion

$$m(\ddot{x}) = -e^2 \left(\frac{x}{r^3}\right), \quad m(\ddot{y}) = -e^2 \left(\frac{y}{r^3}\right), \text{ etc. (156)}$$

one can prove theorems similar to those of ordinary dynamics.

1. In the first place

$$m \left\{ (\dot{x} \ddot{x} + \ddot{x} \dot{x}) + \text{etc.} \right\} = -e^2 \left(\dot{x} \frac{x}{r^3} + \frac{x}{r^3} \dot{x} + \text{etc.} \right)$$

Using relation like (137) one can deduce from this

$$\frac{d(E)}{dt} = 0,$$

the energy equation.

2. Multiply the second of the equations (156) by z and the third by y and subtract. This gives

$$m(y\ddot{z} - z\ddot{y}) = 0. \dots \dots \dots (157)$$

But

$$\frac{d}{dt}(y\dot{z} - z\dot{y}) = (\dot{y}\dot{z} + y\ddot{z} - \dot{z}\dot{y} - z\ddot{y}) = (y\ddot{z} - z\ddot{y})$$

since y and z are found to be interchangeable. By this (157) becomes

$$\begin{aligned} \frac{d}{dt} \left\{ m(y\dot{z} - z\dot{y}) \right\} &= 0 \\ m(y\dot{z} - z\dot{y}) &= \text{const. say} = P_x \end{aligned}$$

Similarly

$$m(z\dot{x} - x\dot{z}) = P_y, \quad m(x\dot{y} - y\dot{x}) = P_z$$

These matrices represent the components of the moment of momentum.

Pauli has shown that the elements of the matrix (P^2) are of the form

$$k(k+1) \frac{h^2}{4\pi^2}$$

The End.