

Quantum Mechanics and a Preliminary Investigation of the Hydrogen Atom.

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§ 1. *The Algebraic Laws governing Dynamical Variables.*

Although the classical electrodynamic theory meets with a considerable amount of success in the description of many atomic phenomena, it fails completely on certain fundamental points. It has long been thought that the way out of this difficulty lies in the fact that there is one basic assumption of the classical theory which is false, and that if this assumption were removed and replaced by something more general, the whole of atomic theory would follow quite naturally. Until quite recently, however, one has had no idea of what this assumption could be.

A recent paper by Heisenberg* provides the clue to the solution of this question, and forms the basis of a new quantum theory. According to Heisenberg, if x and y are two functions of the co-ordinates and momenta of a dynamical system, then in general xy is not equal to yx . Instead of the commutative law of multiplication, the canonical variables q_r, p_r ($r = 1 \dots u$) of a system of u degrees of freedom satisfy the quantum conditions, which were given by the author† in the form

$$\left. \begin{aligned} q_r q_s - q_s q_r &= 0 \\ p_r p_s - p_s p_r &= 0 \\ q_r p_s - p_s q_r &= 0 \quad (r \neq s) \\ q_r p_r - p_r q_r &= i\hbar \end{aligned} \right\} \quad (1)$$

where i is a root of -1 and \hbar is a real universal constant, equal to $(2\pi)^{-1}$ times the usual Planck's constant. These equations are just sufficient to enable one to calculate $xy - yx$ when x and y are given functions of the p 's and q 's, and are therefore capable of replacing the classical commutative law of multiplication. They appear to be the simplest assumptions one could make which would give a workable theory.

* 'Zeits. f. Phys.,' vol. 33, p. 879 (1925).

† 'Roy. Soc. Proc.,' A, vol. 109, p. 642 (1925). These quantum conditions have been obtained independently by Born, Heisenberg and Jordan, 'Zeit. f. Phys.,' vol. 35, p. 557 (1926).

The fact that the variables used for describing a dynamical system do not satisfy the commutative law means, of course, that they are not numbers in the sense of the word previously used in mathematics. To distinguish the two kinds of numbers, we shall call the quantum variables *q*-numbers and the numbers of classical mathematics which satisfy the commutative law *c*-numbers, while the word number alone will be used to denote either a *q*-number or a *c*-number. When $xy = yx$ we shall say that x commutes with y .

At present one can form no picture of what a *q*-number is like. One cannot say that one *q*-number is greater or less than another. All one knows about *q*-numbers is that if z_1 and z_2 are two *q*-numbers, or one *q*-number and one *c*-number, there exist the numbers $z_1 + z_2$, $z_1 z_2$, $z_2 z_1$, which will in general be *q*-numbers but may be *c*-numbers. One knows nothing of the processes by which the numbers are formed except that they satisfy all the ordinary laws of algebra, excluding the commutative law of multiplication, *i.e.*,

$$z_1 + z_2 = z_2 + z_1,$$

$$(z_1 + z_2) + z_3 = z_1 + (z_2 + z_3),$$

$$(z_1 z_2) z_3 = z_1 (z_2 z_3),$$

$$z_1 (z_2 + z_3) = z_1 z_2 + z_1 z_3, \quad (z_1 + z_2) z_3 = z_1 z_3 + z_2 z_3,$$

and if

$$z_1 z_2 = 0,$$

either

$$z_1 = 0 \quad \text{or} \quad z_2 = 0;$$

but

$$z_1 z_2 \neq z_2 z_1,$$

in general, except when z_1 or z_2 is a *c*-number. One may define further numbers, x say, by means of equations involving x and the z 's, such as $x^2 = z$, which defines $z^{\frac{1}{2}}$, or $xz = 1$, which defines z^{-1} . There may be more than one value of x satisfying such an equation, but this is not so for the equation $xz = 1$, since if $x_1 z = 1$ and $x_2 z = 1$ then $(x_1 - x_2)z = 0$, which gives $x_1 = x_2$ provided $z \neq 0$.

A function $f(z)$ of a *q*-number z cannot be defined in a manner analogous to the general definition of a function of a real *c*-number variable, but can be defined only by an algebraic relation connecting $f(z)$ with (z) . When this relation does not involve any *q*-number that does not commute with z and $f(z)$, one can define $\partial f / \partial z$ without ambiguity by the same algebraic relation as when z is a *c*-number, *e.g.*, if $f(z) = z^n$, then $\partial f / \partial z = n z^{n-1}$ where n is a *c*-number.

In order to be able to get results comparable with experiment from our theory, we must have some way of representing q-numbers by means of c-numbers, so that we can compare these c-numbers with experimental values. The representation must satisfy the condition that one can calculate the c-numbers that represent $x + y$, xy , and yx when one is given the c-numbers that represent x and y . If a q-number x is a function of the co-ordinates and momenta of a multiply periodic system, and if it is itself multiply periodic, then it will be shown that the aggregate of all its values for all values of the action variables of the system can be represented by a set of harmonic components of the type $x(nm) \cdot \exp. i \omega(nm)t$, where $x(nm)$ and $\omega(nm)$ are c-numbers, each associated with two sets of values of the action variables denoted by the labels n and m , and t is the time, also a c-number. This representation was taken as defining a q-number in the previous papers on the new theory.* It seems preferable though to take the above algebraic laws and the general conditions (1) as defining the properties of q-numbers, and to deduce from them that a q-number can be represented by c-numbers in this manner when it has the necessary periodic properties. A q-number thus still has a meaning and can be used in the analysis when it is not multiply periodic, although there is at present no way of representing it by c-numbers.

§ 2. The Poisson Bracket Expressions.

If x and y are two numbers, we define their Poisson bracket expression $[x, y]$ by

$$xy - yx = ih[x, y]. \quad (2)$$

It has the following properties, which follow at once from the definition and make it analogous to the Poisson bracket of classical mechanics.

(i) It contains no reference to any particular set of canonical variables.

(ii) It satisfies the laws

$$\begin{aligned} [x_1 + x_2, y] &= [x_1, y] + [x_2, y], \\ [x_1 x_2, y] &= x_1 [x_2, y] + [x_1, y] x_2, \\ [x, y] &= -[y, x]. \end{aligned}$$

(iii) It satisfies the identity

$$[[x, y], z] + [[y, z], x] + [[z, x], y] = 0.$$

* See particularly, Born and Jordan, 'Zeits. f. Phys.,' vol. 34, p. 858 (1925). Also Born, Heisenberg and Jordan, *loc. cit.*

(iv) The elementary P.B.'s (Poisson brackets) are given, from (1), by

$$\begin{aligned} [p_r, p_s] &= 0, & [q_r, q_s] &= 0, \\ [q_r, p_s] &= 0 \quad (r \neq s), \quad \text{or} \quad 1 \quad (r = s), \end{aligned}$$

and also

$$[p_r, c] = [q_r, c] = 0,$$

when c is a c -number.

If x and y are given functions of the p 's and q 's, then, by successive applications of the laws (ii) the P.B. $[x, y]$ can be expressed in terms of the elementary P.B.'s occurring in (iv), and thus evaluated. It is often more convenient to evaluate a P.B. in this way than by the direct use of (2). For example, to evaluate $[q^2, p^2]$ we have

$$[q^2, p^2] = q [q, p^2] + [q, p^2] q,$$

and

$$[q, p^2] = p [q, p] + [q, p] p = 2p,$$

so that

$$[q^2, p^2] = 2qp + 2pq.$$

One may greatly reduce the labour of evaluating P.B.'s of functions of the p 's and q 's in certain special cases by observing that the classical theory expression for the P.B. $[x, y]$, namely $\sum_r \left(\frac{\partial x}{\partial q_r} \frac{\partial y}{\partial p_r} - \frac{\partial y}{\partial q_r} \frac{\partial x}{\partial p_r} \right)$, may usually be taken over directly into the quantum theory when this does not give rise to any ambiguity concerning order of factors of products, *e.g.*, we can say at once that

$$[f(x), x] = 0,$$

when $f(x)$ does not involve any number that does not commute with x , and also

$$[f(q_r), p_r] = \partial f / \partial q_r, \quad (3)$$

when $f(q_r)$ does not involve any number that does not commute with q_r .

The conditions that a set of variable Q_r, P_r shall be canonical are defined to be that from the relations connecting the Q_r, P_r with the q_r, p_r (which are given to be canonical) one can deduce the equations

$$\begin{aligned} [Q_r, Q_s] &= 0, & [P_r, P_s] &= 0, \\ [Q_r, P_s] &= 0 \quad (r \neq s) \quad \text{or} \quad 1 \quad (r = s). \end{aligned}$$

One could evaluate the P.B. of two functions of the Q_r, P_r , either by working entirely in the variables Q_r, P_r , or by first substituting for these variables in terms of the q_r, p_r . The relations connecting the Q_r, P_r with the q_r, p_r may be put in the form

$$Q_r = bq_r b^{-1}, \quad P_r = bp_r b^{-1},$$

where b is a q -number which determines the transformation, but these formulæ do not appear to be of great practical value.

A dynamical system is determined on the classical theory by a Hamiltonian H , which is a certain function of the p 's and q 's, and the classical equations of motion may be written

$$\dot{x} = [x, H]. \quad (4)$$

We assume that the equations of motion on the quantum theory are also of the form (4), where the Hamiltonian H is now a q -number, and is for the present an unknown function of the p 's and q 's. The representation of a q -number by c -numbers when it is multiply periodic must be such that if x is represented by the harmonic components $x(nm) \exp. i\omega(nm)t$, \dot{x} defined by (4) has the components $i\omega(nm)x(nm) \exp. i\omega(nm)t$.

§ 3. Some Elementary Algebraic Theorems.

In all previous descriptions of natural phenomena the two roots of -1 have always played symmetrical parts. The occurrence of a root of -1 in the fundamental equations (1) means that this is not so in the present theory. For mathematical convenience we shall continually be using in the analysis a root of -1 , j say, which is independent of the i in (1), that is to say, from any equation one can obtain another equation by writing $-j$ for j without at the same time changing the sign of i . From these two equations one can obtain two more equations by reversing the order of the factors of all products occurring in them and at the same time writing $-h$ for h , since if this operation is applied to equations (1) it will give correct results, so that it must still give correct results when applied to any equation derivable from (1). To avoid having two symbols i and j , both denoting roots of -1 , we shall take $j = i$, and must then modify the above rules to read:—From any equation one may obtain another equation by writing $-i$ for i wherever it occurs and at the same time writing $-h$ for h , or by reversing the order of all factors and writing $-h$ for h , or by applying the two previous operations together, which reduces to reversing the order of all factors and writing $-i$ for i . This third operation applied to any number gives what may be defined as the conjugate imaginary number. A number is defined to be real if it is equal to its conjugate imaginary.

The remainder of this section will be devoted to some simple analytical rules which will be of use in the subsequent work.

When forming the reciprocal of a quantity composed of two or more factors, one must reverse their order, *i.e.*,

$$\frac{1}{(xy)} = \frac{1}{y} \cdot \frac{1}{x}. \quad (5)$$

This equation may be verified by multiplying each side by xy either in front or behind.

To differentiate the reciprocal of a quantity x one must proceed as follows:—

$$\frac{d}{dt} \left(\frac{1}{x} \cdot x \right) = \frac{d}{dt} (1) = [1, H] = 0.$$

$$0 = \frac{d}{dt} \left(\frac{1}{x} \cdot x \right) = \frac{d}{dt} \left(\frac{1}{x} \right) \cdot x + \frac{1}{x} \dot{x}.$$

Hence, dividing by x behind, one gets

$$\frac{d}{dt} \left(\frac{1}{x} \right) = -\frac{1}{x} \dot{x} \frac{1}{x}.$$

The binomial expansion for $(1+x)^n$ when n is a c-number is the same as in ordinary algebra. Also one defines e^x by the same power series as in ordinary algebra. The ordinary exponential law, however, is not valid, *i.e.*, e^{x+y} is not in general equal to $e^x e^y$, except when x commutes with y .

If (αq) denotes $\Sigma_r (\alpha_r q_r)$, where the α_r ($r=1 \dots u$) are c-numbers, then from (3)

$$[e^{i(\alpha q)}, p_r] = i\alpha_r e^{i(\alpha q)}.$$

Hence, since

$$e^{i(\alpha q)} p_r - p_r e^{i(\alpha q)} = i\hbar [e^{i(\alpha q)}, p_r],$$

we have

$$e^{i(\alpha q)} p_r = (p_r - \alpha_r \hbar) e^{i(\alpha q)}.$$

More generally, if $f(q_r, p_r)$ is any function of the q 's and p 's,

$$\left. \begin{aligned} e^{i(\alpha q)} f(q_r, p_r) &= f(q_r, p_r - \alpha_r \hbar) e^{i(\alpha q)}, \\ f(q_r, p_r) e^{i(\alpha q)} &= e^{i(\alpha q)} f(q_r, p_r + \alpha_r \hbar). \end{aligned} \right\} \quad (6)$$

To prove this result, we observe that if it is true for any two functions f, f_1 and f_2 , say, it must also be true for $(f_1 + f_2)$ and $f_1 f_2$. Now we have proved it true when $f = p_r$, and it is obviously true when $f = q_r$ since the q 's commute with each other. Hence it is true when f is any power series in the p 's and q 's so that we may take it to be generally true.

Equations (6) show the law of interchange of any function of the p 's and q 's with a quantity of the form $e^{i(\alpha q)}$. They are of great value in the theory of multiply periodic systems. There are, of course, corresponding equations for any set of canonical variables, Q_r, P_r .

§ 4. Multiply Periodic Systems.

A dynamical system is multiply periodic on the quantum theory when there exists a set of uniformising variables J_r, w_r having the following properties :—

(i) They are canonical variables, i.e.,

$$[J_r, J_s] = 0, \quad [w_r, w_s] = 0, \\ [w_r, J_s] = 0 \quad (r \neq s), \text{ or } 1 \quad (r = s).$$

(ii) The Hamiltonian H is a function of the J 's only.*

(iii) The original p 's and q 's that describe the system are multiply periodic functions of the w 's of period 2π , the condition for this being defined to be that a p or q can be expanded in either of the forms

$$\sum_a C_a \exp i (\alpha_1 w_1 + \alpha_2 w_2 + \dots + \alpha_u w_u) = \sum_a C_a \exp i (\alpha w)$$

or

$$\sum_a \exp i (\alpha_1 w_1 + \alpha_2 w_2 + \dots + \alpha_u w_u) C'_a = \sum_a \exp i (\alpha w) C'_a.$$

C'_a , where the C_a 's and C'_a 's are functions of the J 's only and the α 's are integers. We have taken the w 's 2π times as great and the J 's $1/2\pi$ times as great as the usual uniformising variables in order to save writing.

We have at once

$$\dot{J}_r = [J_r, H] = 0$$

from (ii), and

$$\dot{w}_r = [w_r, H] = \partial H / \partial J_r,$$

using (3). The quantities \dot{w}_r are, therefore, constants and may be called the frequencies. There are, however, other quantities that have claims to be called frequencies. We have

$$\frac{d}{dt} e^{i(\alpha w)} = [e^{i(\alpha w)}, H] = \frac{e^{i(\alpha w)} H - H e^{i(\alpha w)}}{i\hbar}.$$

From (6) applied to the J 's and w 's,

$$e^{i(\alpha w)} H(J_r) = H(J_r - \alpha_r \hbar) e^{i(\alpha w)},$$

and

$$H(J_r) e^{i(\alpha w)} = e^{i(\alpha w)} H(J_r + \alpha_r \hbar).$$

Hence

$$\frac{d}{dt} e^{i(\alpha w)} = i(\alpha \omega) e^{i(\alpha w)} = i e^{i(\alpha w)} (\alpha \omega)',$$

where

$$\left. \begin{aligned} (\alpha \omega) \hbar &= H(J_r) - H(J_r - \alpha_r \hbar), \\ (\alpha \omega)' \hbar &= H(J_r + \alpha_r \hbar) - H(J_r), \end{aligned} \right\} \quad (7)$$

* He is not necessarily the same function of the J 's as on the classical theory with the present definition of the J 's.

The quantities w_r correspond to the orbital frequencies on Bohr's theory, while the $(\alpha\omega)$ and $(\alpha\omega)'$ correspond, when the α 's are integers, to the transition frequencies. It must be remembered though that the w_r , $(\alpha\omega)$ and $(\alpha\omega)'$ are q-numbers, and, therefore, they cannot be equated to Bohr's frequencies, which are c-numbers. They are merely the same functions of the present J's, which are q-numbers, as Bohr's frequencies are of his J's, which are c-numbers.

Suppose x can be expanded in the form

$$x = \sum_a x_a e^{i(\alpha w)} = \sum_a e^{i(\alpha w)} x_a', \quad (8)$$

where the α 's are integers and the x_a , x_a' are functions of the J's only. From (6)

$$x_a' (J_r) = x_a (J_r + \alpha_r h).$$

Also

$$\dot{x} = \sum_a x_a i(\alpha\omega) e^{i(\alpha w)} = \sum_a e^{i(\alpha w)} i(\alpha\omega)' x_a' \quad (9)$$

If x and the J's are real and if \bar{x}_a denotes the conjugate imaginary of x_a , then by equating the conjugate imaginaries of both sides of (8) we get

$$x = \sum_a e^{-i(\alpha w)} \bar{x}_a (J_r) = \sum_a \bar{x}_a (J_r + \alpha_r h) e^{-i(\alpha w)}.$$

Comparing this with equation (8) we find that

$$\bar{x}_a (J_r + \alpha_r h) = x_{-a} (J_r).$$

This relation is brought out more clearly if we change the notation. For $x_a (J_r)$ write $x (J, J - \alpha h)$.

Then

$$\bar{x} (J + \alpha h, J) = x (J, J + \alpha h),$$

which shows that there is some kind of symmetry in the way in which the amplitude $x (J, J - \alpha h)$ is related to the two sets of variables to which it explicitly refers. Our expansion for x is now

$$x = \sum_a x (J, J - \alpha h) e^{i(\alpha w)} = \sum_a e^{i(\alpha w)} x (J + \alpha h, J).$$

The expressions (7) for the transition frequencies suggest that we should put

$$(\alpha\omega) (J) = \omega (J, J - \alpha h),$$

and

$$(\alpha\omega)' (J) = \omega (J + \alpha h, J).$$

We should then have from (9)

$$\dot{x} = \sum x (J, J - \alpha h) i\omega (J, J - \alpha h) e^{i(\alpha w)} = \sum e^{i(\alpha w)} i\omega (J + \alpha h, J) x (J + \alpha h, J). \quad (10)$$

Suppose y can also be expanded in the form

$$y = \sum_{\beta} y(J, J - \beta h) e^{i(\beta w)}.$$

Then

$$\begin{aligned} xy &= \sum_{\alpha\beta} x(J, J - \alpha h) e^{i(\alpha w)} y(J, J - \beta h) e^{i(\beta w)}, \\ &= \sum_{\alpha\beta} x(J, J - \alpha h) \cdot y(J - \alpha h, J - \alpha h - \beta h) e^{i[(\alpha+\beta)w]}, \end{aligned}$$

by again using (6), and the fact that the w 's commute; or, the amplitudes of xy are given by

$$xy(J, J - \gamma h) = \sum_{\alpha} x(J, J - \alpha h) \cdot y(J - \alpha h, J - \gamma h). \quad (11)$$

These formulæ provide a way of representing q -numbers by means of c -numbers. Suppose that in the expressions $x(J, J - \alpha h)$ and $\omega(J, J - \alpha h)$, considered merely as functions of the J 's, we substitute for each J_r the c -number $n_r h$, and denote the resulting c -numbers by $x(n, n - \alpha)$ and $\omega(n, n - \alpha)$. We may consider the aggregate of all the c -numbers $x(n, n - \alpha) \exp. i\omega(n, n - \alpha)t$, in which it is sufficient (but not necessary) for the n to take a series of values differing successively by unity, as representing the values of the q -number x for all values of the q -numbers J_r . Equation (10) shows that

$$\dot{x}(n, n - \alpha) = i\omega(n, n - \alpha) x(n, n - \alpha),$$

while equation (11) gives

$$xy(n, n - \gamma) = \sum_{\alpha} x(n, n - \alpha) y(n - \alpha, n - \gamma),$$

which is just Heisenberg's law of multiplication. Also we have obviously

$$(x + y)(n, n - \alpha) = x(n, n - \alpha) + y(n, n - \alpha).$$

Our representation thus satisfies the conditions mentioned in §§ 1 and 2, which proves the sufficiency of this discrete set of n 's.

One gets different representations of the q -numbers x by c -numbers $x(n, m)$ $\exp. i\omega(n, m)t$ by taking different values for the c -numbers, η_r , say, by which the n_r 's differ from integers. Only one of these representations, though, is of physical importance, this being the one (assumed to exist) for which, every $x(n, m)$ vanishes when an m_r is less than a certain value, n_{or} , say, which fixes the normal state of the system on Bohr's theory, and each $n_r \geq n_{or}$. This requires that every coefficient $x(J, J - \alpha h)$ in the expansion of x shall vanish when for each J_r is substituted the c -number $(n_{or} + m_r h)$, where the m_r are integers not less than zero, at least one of which is less than the corresponding α_r .

§ 5. *Orbital Motion in the Hydrogen Atom.*

It is necessary at this point to make some assumption of the form of the Hamiltonian for the hydrogen atom.* We may assume that it is the same function of the Cartesian co-ordinates x, y and their corresponding momenta p_x, p_y as on the classical theory, *i.e.*,

$$H = \frac{1}{2m}(p_x^2 + p_y^2) - \frac{e^2}{(x^2 + y^2)^{\frac{1}{2}}},$$

where e and m are c-numbers.

We transform to polar co-ordinates r, θ by means of the equations

$$x = r \cos \theta, \quad y = r \sin \theta,$$

where $\cos \theta$ and $\sin \theta$ are defined in terms of $e^{i\theta}$ by the same relations as on the classical theory. The momenta p_r and k conjugate to r and θ are given by the equations

$$p_r = \frac{1}{2}(p_x \cos \theta + \cos \theta p_x) + \frac{1}{2}(p_y \sin \theta + \sin \theta p_y) \\ k = xp_y - yp_x.$$

To verify that r, θ, p_r, k defined in this way are canonical variables, we must work out all their P.B.'s taken two at a time. We have at once that x, y, r and θ commute with one another. Also

$$[r, p_x] = [(x^2 + y^2)^{\frac{1}{2}}, p_x] = x/(x^2 + y^2)^{\frac{1}{2}} = \cos \theta,$$

with the help of (3), and similarly

$$[r, p_y] = \sin \theta,$$

so that

$$[r, k] = x[r, p_y] - y[r, p_x] \\ = x \sin \theta - y \cos \theta = 0,$$

and

$$[r, p_r] = \frac{1}{2}[r, p_x] \cos \theta + \frac{1}{2} \cos \theta [r, p_x] + \frac{1}{2}[r, p_y] \sin \theta + \frac{1}{2} \sin \theta [r, p_y] \\ = \cos^2 \theta + \sin^2 \theta = 1.$$

Further

$$r[e^{i\theta}, k] = [re^{i\theta}, k] = [x + iy, xp_y - yp_x] \\ = ix[y, p_y] - y[x, p_x] = ix - y = i r e^{i\theta},$$

so that

$$[e^{i\theta}, k] = i e^{i\theta}.$$

* The hydrogen atom has been treated on the new mechanics by Pauli in a paper not yet published.

The remaining equations, $[e^{i\theta}, p_r] = 0$ and $[k, p_r] = 0$, may be likewise verified by elementary quantum algebra.

If we solve for p_x, p_y in terms of p_r, k , we find that

$$\begin{aligned} p_x + i p_y &= (p_r + i k_2/r) e^{i\theta} = e^{i\theta} (p_r + i k_1/r), \\ p_x - i p_y &= (p_r - i k_1/r) e^{-i\theta} = e^{-i\theta} (p_r - i k_2/r), \end{aligned}$$

where

$$k_1 = k + \frac{1}{2} \hbar, \quad k_2 = k - \frac{1}{2} \hbar,$$

so that

$$k_2 e^{i\theta} = e^{i\theta} k_1, \quad k_1 e^{-i\theta} = e^{-i\theta} k_2$$

by an application of (6). We thus have

$$\begin{aligned} p_x^2 + p_y^2 &= (p_x - i p_y) (p_x + i p_y) = (p_r - i k_1/r) (p_r + i k_1/r), \\ &= p_r^2 + \frac{k_1^2}{r^2} + i k_1 \left(p_r \frac{1}{r} - \frac{1}{r} p_r \right), \end{aligned} \quad (12)$$

Now

$$p_r \frac{1}{r} - \frac{1}{r} p_r = \frac{1}{r} (r p_r - p_r r) \frac{1}{r} = \frac{i \hbar}{r^2}.$$

Hence

$$p_x^2 + p_y^2 = p_r^2 + \frac{k_1^2 - k_1 \hbar}{r^2} = p_r^2 + \frac{k_1 k_2}{r^2},$$

and

$$H = \frac{1}{2m} \left(p_r^2 + \frac{k_1 k_2}{r^2} \right) - \frac{e^2}{r}. \quad (13)$$

If we had originally assumed that the Hamiltonian was the same function of the polar variables as on the classical theory, we should have had instead

$$H = \frac{1}{2m} \left(p_r^2 + \frac{k^2}{r^2} \right) - \frac{e^2}{r}. \quad (13')$$

The only way to decide which of these assumptions is correct is to work out the consequences of both and to see which agrees with experiment.

The equations of motion with either Hamiltonian are

$$\begin{aligned} \dot{r} &= [r, H] = p_r/m, \\ k &= [k, H] = 0, \\ \dot{\theta} &= [\theta, H] = k/mr^2, \end{aligned}$$

which give $p_r = m\dot{r}$, $k = \text{constant}$ and $mr^2\dot{\theta} = k$, as on the classical theory, and finally

$$\dot{p}_r = [p_r, H] = \frac{k_1 k_2}{mr^3} - \frac{e^2}{r^2} \quad \text{with (13)} \quad (14)$$

$$= \frac{k^2}{mr^3} - \frac{e^2}{r^2} \quad \text{with (13')} \quad (14')$$

We try to find an integral of the equations of motion of the form

$$1/r = a_0 + a_1 e^{i\theta} + a_2 e^{-i\theta}, \quad (15)$$

where a_0 , a_1 and a_2 are constants, corresponding to the classical equation of elliptic motion

$$l/r = 1 + \varepsilon \cos(\theta - \alpha)$$

in which l is the latus rectum and ε the excentricity.

The rate of change of $e^{i\theta}$ is given with either H by

$$\begin{aligned} \frac{d}{dt} e^{i\theta} &= [e^{i\theta}, H] = [e^{i\theta}, k^2] \frac{1}{2mr^2}, \\ &= \{k[e^{i\theta}, k] + [e^{i\theta}, k]k\}/2mr^2, \\ &= \{kie^{i\theta} + ie^{i\theta}k\}/2mr^2, \\ &= \frac{i}{m} e^{i\theta} \frac{k_1}{r^2} = \frac{i}{m} \frac{k_2}{r^2} e^{i\theta}. \end{aligned}$$

By changing the sign of both i and h we find

$$\frac{d}{dt} e^{-i\theta} = -\frac{i}{m} e^{-i\theta} \frac{k_2}{r^2} = -\frac{i}{m} \frac{k_1}{r^2} e^{-i\theta}.$$

Hence if we differentiate (15) we get

$$-\frac{1}{r} \dot{r} \frac{1}{r} = \frac{i}{m} (a_1 e^{i\theta} k_1 - a_2 e^{-i\theta} k_2) \frac{1}{r^2},$$

or

$$1/r \, p_r r = -i (a_1 e^{i\theta} k_1 - a_2 e^{-i\theta} k_2),$$

which, using

$$p_r = 1/r \cdot p_r r = ih/r,$$

reduces to

$$\begin{aligned} p_r &= -i (a_1 e^{i\theta} k_1 - a_2 e^{-i\theta} k_2) + ih/r, \\ &= -i (a_1 e^{i\theta} k_1 - a_2 e^{-i\theta} k_2) + ih (a_0 + a_1 e^{i\theta} + a_2 e^{-i\theta}), \\ &= i (a_0 h - a_1 e^{i\theta} k_2 + a_2 e^{-i\theta} k_1). \end{aligned} \quad (16)$$

Now differentiate again. The result is

$$\begin{aligned} m\dot{p}_r &= a_1 e^{i\theta} k_1 k_2 / r^2 + a_2 e^{-i\theta} k_2 k_1 / r^2 \\ &= \left(\frac{1}{r} - a_0\right) \frac{k_1 k_2}{r^2} = \frac{k_1 k_2}{r^3} - \frac{a_0 k_1 k_2}{r^2}, \end{aligned}$$

which agrees with the equation of motion (14) if one takes $a_0 = me^2/k_1 k_2$, but will not agree with (14').

We can easily obtain an integral of (14') by making a small change in (15). We transform from the variables r, θ, p_r, k to the variables r, θ', p_r, k' , where

$$k' = (k^2 + \tfrac{1}{4}h^2)^{\frac{1}{2}}, \quad \theta' = \theta k'/k,$$

which are canonical since

$$[\theta', k'] = [\theta, k'] \frac{k'}{k} = \frac{k}{(k^2 + \tfrac{1}{4}h^2)^{\frac{1}{2}}} \frac{k'}{k} = 1,$$

and take

$$1/r = a_0 + a_1 e^{i\theta'} + a_2 e^{-i\theta'}. \tag{15'}$$

Proceeding exactly as before, we find that

$$\frac{d}{dt} e^{i\theta'} = \frac{i}{m} e^{i\theta'} \frac{k_1'}{r^2}, \quad \frac{d}{dt} e^{-i\theta'} = -\frac{i}{m} e^{-i\theta'} \frac{k_2'}{r^2},$$

where

$$k_1' = k' + \tfrac{1}{2}h, \quad k_2' = k' - \tfrac{1}{2}h,$$

and further that

$$m\dot{p}_r = \frac{k_1' k_2'}{r^3} - \frac{a_0 k_1' k_2'}{r^2} = \frac{k^2}{r^3} - \frac{a_0 k^2}{r^2},$$

which agrees with (14') if we take $a_0 = me^2/k^2$.

With the Hamiltonian (13') the orbit of the electron is thus an ellipse with a rotating apse line. If the Cartesian co-ordinates are now expanded in multiple Fourier series, two angle variables will be required, which will give two orbital frequencies. There would therefore necessarily be a two-fold infinity of energy-levels, which disagrees with experiment (when one disregards the relativity fine-structure of the hydrogen spectrum). The assumption of the Hamiltonian (13') is thus untenable.

We therefore assume the Hamiltonian (13), which does give a degenerate motion, and proceed to evaluate the frequencies.

§ 6. Determination of the Constants of Integration.

The equation of the orbit is now given by (15), or

$$1/r = me^2/k_1 k_2 + a_1 e^{i\theta} + a_2 e^{-i\theta}, \tag{17}$$

and from (16)
$$p_r = i (me^2 h/k_1 k_2 - a_1 e^{i\theta} k_2 + a_2 e^{-i\theta} k_1). \tag{18}$$

We must determine the form of the constants of integration a_1 and a_2 .

Since k commutes with r and p_r , it follows from (17) and (18) that it commutes with $(a_1 e^{i\theta} + a_2 e^{-i\theta})$ and $(a_1 e^{i\theta} k_2 - a_2 e^{-i\theta} k_1)$. Hence k must commute with $a_1 e^{i\theta}$ and $a_2 e^{-i\theta}$ separately.

From (17) and (18) we find

$$\begin{aligned}\frac{k_1}{r} + ip_r &= \frac{me^2}{k_1 k_2} k_1 + a_1 e^{i\theta} k_1 + a_2 e^{-i\theta} k_1 - \frac{me^2 h}{k_1 k_2} + a_1 e^{i\theta} k_2 - a_2 e^{-i\theta} k_1, \\ &= me^2/k_1 + 2ka_1 e^{i\theta}, \\ &= me^2/k_1 + 2c_1 e^{i\theta},\end{aligned}\quad (19)$$

where $a_1 = k^{-1}c_1$. Multiplying this equation by $e^{i\theta}$ in front and $e^{-i\theta}$ behind we get, since $e^{i\theta}f(k_1)e^{-i\theta} = f(k_2)$,

$$k_2/r + ip_r = me^2/k_2 + 2e^{i\theta}c_1. \quad (20)$$

Hence

$$c_1 e^{i\theta} - e^{i\theta}c_1 = \frac{1}{2} \frac{k_1 - k_2}{r} - \frac{1}{2} me^2 \left(\frac{1}{k_1} - \frac{1}{k_2} \right) = \frac{1}{2} \frac{h}{r} + \frac{me^2 h}{2k_1 k_2}. \quad (21)$$

Similarly, if $a_2 = k^{-1}c_2$, it may be shown that

$$c_2 e^{-i\theta} - e^{-i\theta}c_2 = -\frac{1}{2} \frac{h}{r} - \frac{me^2 h}{2k_1 k_2}, \quad (22)$$

so that

$$c_1 e^{i\theta} + c_2 e^{-i\theta} = e^{i\theta}c_1 + e^{-i\theta}c_2.$$

Hence, as k commutes with $c_1 e^{i\theta}$ and $c_2 e^{-i\theta}$,

$$\frac{1}{r} = \frac{me^2}{k_1 k_2} + \frac{1}{k} (c_1 e^{i\theta} + c_2 e^{-i\theta}) = \frac{me^2}{k_1 k_2} + (e^{i\theta}c_1 + e^{-i\theta}c_2) \frac{1}{k}. \quad (23)$$

We could, of course, have obtained directly from the equations of motion an integral of the form

$$1/r = a_0' + e^{i\theta} a_1' + e^{-i\theta} a_2'.$$

Equations (23) show the relations between the a' 's and the a 's. From (21) and (22) the following two additional forms for $1/r$ are easily obtained:—

$$\frac{1}{r} = \frac{me^2}{k_1^2} + \frac{1}{k_1} (c_1 e^{i\theta} + e^{-i\theta}c_2) = \frac{me^2}{k_2^2} + \frac{1}{k_2} (e^{i\theta}c_1 + c_2 e^{-i\theta}). \quad (24)$$

The equations

$$k_2/r - ip_r = me^2/k_2 + 2c_2 e^{-i\theta}, \quad (25)$$

and

$$k_1/r - ip_r = me^2/k_1 + 2e^{-i\theta}c_2 \quad (26)$$

may be obtained in the same way in which (19) and (20) were obtained. Multiply corresponding sides of equations (19) and (26), putting (19) first. The left-hand side of the result is

$$\begin{aligned}&\left(\frac{k_1}{r} + ip_r \right) \left(\frac{k_1}{r} - ip_r \right) \\ &= k_1 k_2 / r^2 + p_r^2, \\ &= 2m (H + e^2/r),\end{aligned}$$

using (12) and (13), while the right-hand side is

$$\frac{m^2 e^4}{k_1^2} + \frac{2me^2}{k_1} (c_1 e^{i\theta} + e^{-i\theta} c_2) + 4c_1 c_2 = \frac{\Sigma me^2}{r} - \frac{m^2 e^4}{k_1^2} + 4c_1 c_2,$$

using the first of equations (24). Hence

$$2mH = 4c_1 c_2 - m^2 e^4 / k_1^2.$$

Similarly, by multiplying corresponding sides of equations (20) and (25) taking (25) first, we find that,

$$2mH = 4c_2 c_1 - m^2 e^4 / k_2^2.$$

Put

$$2mH = -m^2 e^4 / P^2.$$

P, of course, commutes with k , c_1 and c_2 . We then have

$$\left. \begin{aligned} c_1 c_2 &= \frac{1}{4} m^2 e^4 \left(\frac{1}{k_1^2} - \frac{1}{P^2} \right) = \frac{1}{4} m^2 e^4 \frac{\varepsilon_1^2}{k_1^2}, \\ c_2 c_1 &= \frac{1}{4} m^2 e^4 \left(\frac{1}{k_2^2} - \frac{1}{P^2} \right) = \frac{1}{4} m^2 e^4 \frac{\varepsilon_2^2}{k_2^2}, \end{aligned} \right\} (27)$$

where

$$\varepsilon_1 = \sqrt{1 - \frac{k_1^2}{P^2}}, \quad \varepsilon_2 = \sqrt{1 - \frac{k_2^2}{P^2}}.$$

The excentricities ε_1 and ε_2 are constants, and commute with P and k and with each other.

Put

$$c_1 = \frac{1}{2} m e^2 \varepsilon_1 / k_1 \cdot e^{-i\chi}.$$

χ is a constant and so commutes with P. Since k commutes with $c_1 e^{i\theta}$ and with ε_1 / k_1 , it must commute with $e^{-i\chi} e^{i\theta}$, so that

$$k e^{-i\chi} e^{i\theta} = e^{-i\chi} e^{i\theta} k = e^{-i\chi} (k - h) e^{i\theta}.$$

Hence

$$k e^{-i\chi} = e^{-i\chi} (k - h).$$

This law for the interchange of $e^{-i\chi}$ and k shows that χ is canonically conjugate to k . χ corresponds on the classical theory to the angle between the major axis of the ellipse and the line $\theta = 0$. We now have

$$c_1 = \frac{1}{2} m e^2 \varepsilon_1 / k_1 \cdot e^{-i\chi} = \frac{1}{2} m e^2 e^{-i\chi} \varepsilon_2 / k_2,$$

and from (27)

$$c_2 = \frac{1}{2} m e^2 e^{i\chi} \varepsilon_1 / k_1 = \frac{1}{2} m e^2 \varepsilon_2 / k_2 \cdot e^{i\chi}.$$

The expression (17) for $1/r$ thus takes the form

$$\frac{1}{r} = \frac{me^2}{k_1 k_2} \left\{ 1 + \frac{1}{2} \frac{k_2}{k} \varepsilon_1 e^{-i\chi} e^{i\theta} + \frac{1}{2} \frac{k_1}{k} \varepsilon_2 e^{i\chi} e^{-i\theta} \right\}. \quad (28)$$

§ 7. *Calculation of the Frequencies.*

The easiest frequency to determine is the orbital one \dot{w} , whose evaluation closely follows the classical calculation of the period. The relation between θ and the angle variable w is of the form

$$\theta = w + \sum b_n e^{niw} = w + \sum b_n' e^{ni\theta},$$

where the b 's are constants. On differentiating, this gives

$$\dot{\theta} = \dot{w} + \sum' b_n' \frac{ni}{m} (k - \frac{1}{2}nh) e^{ni\theta} \frac{1}{r^2}.$$

Where \sum' denotes that the term corresponding to $n = 0$ is omitted from the summation. Multiplying both sides by r^2 behind, we get

$$\dot{\theta} r^2 = \dot{w} r^2 + \sum' b_n'' e^{ni\theta},$$

which gives, since $mr^2\dot{\theta} = k$,

$$r^2 = \frac{k}{m\dot{w}} - \sum' \frac{1}{\dot{w}} b_n'' e^{ni\theta}.$$

Hence if r^2 is expanded as a Fourier series in θ with each of the factors $e^{ni\theta}$ behind its respective coefficient, the constant term will be $k/m\dot{w}$, as on the classical theory.

From (28) we have

$$r^2 = \left\{ \frac{me^2}{k_1 k_2} \left(1 + \frac{1}{2} \frac{k_2 \varepsilon_1}{k} e^{-i\chi} e^{i\theta} + \frac{1}{2} \frac{k_1 \varepsilon_2}{k} e^{i\chi} e^{-i\theta} \right) \right\}^{-2},$$

$$= \{ \alpha_0 + \alpha_1 e^{-i\chi} e^{i\theta} + \alpha_2 e^{i\chi} e^{-i\theta} \}^{-2},$$

say. We can expand the right-hand side by the binomial theorem. This will give a series of terms containing $e^{i\theta}$'s mixed up with α 's, which cannot easily be evaluated. A more satisfactory way of proceeding is as follows:

It can be shown that r^n is equal to the expression obtained by expanding $(\alpha_0 + \alpha_1 e^{-i\chi} + \alpha_2 e^{i\chi})^{-n}$ in powers of $e^{i\chi}$, and inserting after each term of the form $\beta_s e^{si\chi}$, where β_s is independent of χ , the requisite power of $e^{i\theta}$, namely $e^{-si\theta}$. To prove this theorem we assume it to be true for some value of n , and deduce from that, that it is true for $n + 1$. Suppose for instance that

$$(\alpha_0 + \alpha_1 e^{-i\chi} + \alpha_2 e^{i\chi})^{-n} = \sum \beta_s e^{si\chi}, \quad (29)$$

and

$$r^n = \sum \beta_s e^{si\chi} e^{-si\theta}. \quad (30)$$

Let

$$r^{n+1} = \sum \gamma_s e^{si\chi} e^{-si\theta},$$

then

$$r^n = \sum \gamma_s e^{si\chi} e^{-si\theta} \frac{1}{r} = \sum \gamma_s e^{si\chi} \frac{1}{r} e^{-si\theta},$$

$$= \sum \gamma_s e^{si\chi} (\alpha_0 + \alpha_1 e^{-i\chi} e^{i\theta} + \alpha_2 e^{i\chi} e^{-i\theta}) e^{-si\theta}.$$

Comparing this with (30), we see that

$$\beta_s e^{si\chi} = \gamma_s e^{si\chi} \alpha_0 + \gamma_{s+1} e^{(s+1)i\chi} \alpha_1 e^{-i\chi} + \gamma_{s-1} e^{(s-1)i\chi} \alpha_2 e^{i\chi};$$

but this is just the condition that

$$\Sigma \beta_s e^{si\chi} = \Sigma \gamma_s e^{si\chi} (\alpha_0 + \alpha_1 e^{-i\chi} + \alpha_2 e^{i\chi}).$$

(Note that a term like $\gamma_{s+1} e^{(s+1)i\chi} \alpha_1 e^{-i\chi}$ is equal to something independent of χ multiplied by $e^{si\chi}$, owing to the special nature of the laws of interchange of the α 's with the $e^{i\chi}$'s.) Hence from (29)

$$\Sigma \gamma_s e^{si\chi} = (\alpha_0 + \alpha_1 e^{-i\chi} + \alpha_2 e^{i\chi})^{-n-1},$$

which proves the theorem.

Our problem thus reduces to the determination of the term independent of χ in the expansion of $(\alpha_0 + \alpha_1 e^{-i\chi} + \alpha_2 e^{i\chi})^{-2}$. To do this we first factorise the expression $(\alpha_0 + \alpha_1 e^{-i\chi} + \alpha_2 e^{i\chi})$. We have

$$\begin{aligned} (\alpha_0 + \alpha_1 e^{-i\chi} + \alpha_2 e^{i\chi}) &= \frac{me^2}{2kk_1} \left(2 \frac{k}{k_2} + \varepsilon_1 e^{-i\chi} + \varepsilon_2 \frac{k_1}{k_2} e^{i\chi} \right), \\ &= \frac{me^2}{2kk_1} \left\{ \left(1 + \frac{k_1}{P} \right) + \frac{k_1}{k_2} \left(1 - \frac{k_2}{P} \right) \right. \\ &\quad \left. + \varepsilon_1 e^{-i\chi} + e^{i\chi} \varepsilon_1 \frac{k_1 + h}{k_1} \right\}, \\ &= \frac{me^2}{2kk_1} \left\{ \sqrt{1 + \frac{k_1}{P}} + e^{i\chi} \frac{k_1 + h}{k_1} \sqrt{1 - \frac{k_1}{P}} \right\} \\ &\quad \left\{ \sqrt{1 + \frac{k_1}{P}} + \sqrt{1 - \frac{k_1}{P}} e^{-i\chi} \right\}, \\ &= \frac{me^2}{2kk_1} \sqrt{1 + \frac{k_1}{P}} \left\{ 1 + \frac{k_1}{k_2} \sqrt{\frac{P - k_2}{P + k_1}} e^{i\chi} \right\} \\ &\quad \left\{ 1 + e^{-i\chi} \sqrt{\frac{P - k_2}{P + k_1}} \right\} \sqrt{1 + \frac{k_1}{P}}. \end{aligned}$$

We must now express $(\alpha_0 + \alpha_1 e^{-i\chi} + \alpha_2 e^{i\chi})^{-1}$ in the form of partial fractions. Putting for brevity $(P + k_1)^{\frac{1}{2}} = \lambda_1$, $(P + k_2)^{\frac{1}{2}} = \lambda_2$, $(P - k_1)^{\frac{1}{2}} = \mu_1$, $(P - k_2)^{\frac{1}{2}} = \mu_2$, we have, remembering (5),

$$\begin{aligned} (\alpha_0 + \alpha_1 e^{-i\chi} + \alpha_2 e^{i\chi})^{-1} &= \frac{2P}{me^2} \cdot \frac{1}{\lambda_1} \cdot \frac{1}{1 + e^{-i\chi} \mu_2 / \lambda_1} \cdot \frac{1}{1 + k_1 \mu_2 / k_2 \lambda_1 e^{i\chi}} \cdot \frac{k k_1}{\lambda_1}, \\ &= \frac{2P}{me^2} \cdot \frac{1}{\lambda_1} \cdot \frac{1}{e^{i\chi} + \mu_2 / \lambda_1} \cdot e^{i\chi} \cdot \frac{1}{1 + k_1 \mu_2 / k_2 \lambda_1 \cdot e^{i\chi}} \cdot \frac{k k_1}{\lambda_1}. \end{aligned}$$

Now it is easily verified that

$$e^{ix} = \left(e^{ix} + \frac{\mu_2}{\lambda_1} \right) \frac{\lambda_1^2}{2k_1} - \frac{\lambda_1 \mu_2}{2k_1} \left(1 + \frac{k_1 \mu_2}{k_2 \lambda_1} e^{ix} \right).$$

Hence

$$\begin{aligned} (\alpha_0 + \alpha_1 e^{-ix} + \alpha_2 e^{ix})^{-1} &= \frac{P}{me^2} \frac{\lambda_1}{k_1} \frac{1}{1 + k_1 \mu_2 / k_2 \lambda_1 \cdot e^{ix}} \frac{k k_1}{\lambda_1} \\ &\quad - \frac{P}{me^2} \frac{1}{\lambda_1} \frac{1}{e^{ix} + \mu_2 / \lambda_1} \mu_2 k. \end{aligned} \quad (31)$$

We must now square the expression on the right, which will give four terms, and must expand each of them by the binomial theorem and take out the part independent of χ . The term

$$\left[\frac{P}{me^2} \frac{\lambda_1}{k_1} \frac{1}{1 + k_1 \mu_2 / k_2 \lambda_1 \cdot e^{ix}} \frac{k k_1}{\lambda_1} \right]^2$$

will contribute $(Pk/me^2)^2$. The term

$$\left[\frac{P}{me^2} \frac{1}{\lambda_1} \frac{1}{e^{ix} + \mu_2 / \lambda_1} \mu_2 k \right]^2$$

will contribute nothing, since $(e^{ix} + \mu_2 / \lambda_1)^{-1} = e^{-ix} (1 + \mu_2 / \lambda_1 \cdot e^{-ix})^{-1}$, which, when expanded, consists only of terms of the form e^{-nix} with $n > 0$. The remaining two terms may best be evaluated by using partial fractions again. It is easily verified that

$$\begin{aligned} & - \frac{P}{me^2} \frac{\lambda_1}{k_1} \frac{1}{1 + k_1 \mu_2 / k_2 \lambda_1 \cdot e^{ix}} \frac{k k_1}{\lambda_1} \cdot \frac{P}{me^2} \frac{1}{\lambda_1} \frac{1}{e^{ix} + \mu_2 / \lambda_1} \mu_2 k \\ &= - \frac{P^2}{m^2 e^4} \frac{\lambda_1}{k_1} \left\{ \frac{1}{\frac{1}{2} k_1 e^{ix} + \mu_2 / \lambda_1} - \frac{1}{1 + k_1 \mu_2 / k_2 \lambda_1 \cdot e^{ix}} \frac{1}{2} \frac{k_1 \mu_2}{\lambda_1} \right\} \mu_2 k, \end{aligned}$$

and

$$\begin{aligned} & - \frac{P}{me^2} \frac{1}{\lambda_1} \frac{1}{e^{ix} + \mu_2 / \lambda_1} \mu_2 k \cdot \frac{P}{me^2} \frac{\lambda_1}{k_1} \frac{1}{1 + k_1 \mu_2 / k_2 \lambda_1 \cdot e^{ix}} \frac{k k_1}{\lambda_1} \\ &= - \frac{P^2}{m^2 e^4} \frac{1}{\lambda_1} \left\{ - \frac{\lambda_1^2 \mu_1^2}{2k_1} \frac{1}{1 + k_1 \mu_2 / k_2 \lambda_1 \cdot e^{ix}} + \frac{1}{e^{ix} + \mu_2 / \lambda_1} \frac{\lambda_1 \lambda_2^2 \mu_2}{2k_1} \right\} \frac{k k_1}{\lambda_1}. \end{aligned}$$

The first of these thus contributes

$$\frac{P^2}{m^2 e^4} \frac{\lambda_1}{k_1} \cdot \frac{1}{2} \frac{k_1 \mu_2}{\lambda_1} \cdot \mu_2 k = \frac{P^2 k}{2m^2 e^4} (P - k_2),$$

and the second

$$\frac{P^2}{m^2 e^4} \frac{1}{\lambda_1} \cdot \frac{\lambda_1^2 \mu_1^2}{2k_1} \cdot \frac{k k_1}{\lambda_1} = \frac{P^2 k}{2m^2 e^4} (P - k_1).$$

We therefore have for the term independent of χ in the expansion of $(\alpha_0 + \alpha_1 e^{-i\chi} + \alpha_2 e^{i\chi})^{-2}$ the sum of the three contributions

$$\frac{P^2 k^2}{m^2 e^4} + \frac{P^2 k}{2m^2 e^4} (P - k_2) + \frac{P^2 k}{2m^2 e^4} (P - k_1) = \frac{P^3 k}{m^2 e^4}.$$

This is the value of $k/m\dot{w}$. Hence

$$\dot{w} = me^4/P^3,$$

which happens to be the same function of P as on the classical theory. Now since $H = -me^4/2P^2$, we have

$$\dot{w} = \partial H/\partial P,$$

which proves that P is canonically conjugate to w and is therefore an action variable. The transition frequencies are now given by

$$\frac{H(P + n\hbar) - H(P)}{\hbar} = \frac{me^4}{2\hbar} \left\{ \frac{1}{P^2} - \frac{1}{(P + n\hbar)^2} \right\}. \tag{32}$$

The expansion of r is given by the expansion of the right-hand side of (31) in which the appropriate power of $e^{i\theta}$ has been inserted behind each term. The coefficient of every term in it vanishes when one puts $P = 0$, which makes each of the amplitudes $x(nm)$ in the c-number representation of the Cartesian co-ordinates vanish when n or m is zero. This suggests, according to the principles of § 4, that the state $J = \hbar$ is the normal state. (To prove this completely it would be necessary to show that $x(nm) = 0$ when n is a negative integer and m a positive integer.) If this is so, one would have to put P equal to an integral multiple of \hbar in (32), and one would then obtain the observed frequencies of the hydrogen spectrum.

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