The Elimination of the Nodes in Quantum Mechanics.

By P. A. M. Dirac, St. John's College, Cambridge.

(Communicated by R. H. Fowler, F.R.S.—Received March 27, 1926.)

§ 1. Introduction.

The laws of classical mechanics must be generalised when applied to atomic systems, the generalisation being that the commutative law of multiplication, as applied to dynamical variables, is to be replaced by certain quantum conditions, which are just sufficient to enable one to evaluate xy-yx when x and y are given. It follows that the dynamical variables cannot be ordinary numbers expressible in the decimal notation (which numbers will be called c-numbers), but may be considered to be numbers of a special kind (which will be called q-numbers), whose nature cannot be exactly specified, but which can be used in the algebraic solution of a dynamical problem in a manner closely analogous to the way the corresponding classical variables are used.*

The only justification for the names given to dynamical variables lies in the analogy to the classical theory, e.g., if one says that x, y, z are the Cartesian co-ordinates of an electron, one means only that x, y, z are q-numbers which appear in the quantum solution of the problem in an analogous way to the Cartesian co-ordinates of the electron in the classical solution. It may happen that two or more q-numbers are analogous to the same classical quantity (the analogy being, of course, imperfect and in different respects for the different q-numbers), and thus have claims to the same name. This occurs, for instance, when one considers what q-numbers shall be called the frequencies of a multiply periodic system, there being orbital frequencies and transition frequencies, either of which correspond in certain respects to the classical frequencies. In such a case one must decide which of the properties of the classical variable are dynamically the most important, and must choose the q-number which has these properties to be the corresponding quantum variable.

In the classical treatment of the dynamical problem of a number of particles or electrons moving in a central field of force and disturbing one another, one always begins by making the initial simplification, known as the elimination of the nodes, which consists in obtaining a contact transformation from the

^{* &#}x27;Roy. Soc. Proc.,' A, vol. 110, p. 561 (1926). The method there given in §§ 1-4 is the one used here.

Cartesian co-ordinates and momenta of the electrons to a set of canonical variables, of which all except three are independent of the orientation of the system as a whole, while these three determine the orientation. In the absence of an external field of force, the Hamiltonian, when expressed in terms of the new variables, must be independent of these three, which simplifies the equations of motion. It can be shown that the new variables may be taken to be the following: the distance r of each electron from the centre, with the radial component of momentum p_r as conjugate variable, the component M_r (= p say) of the total angular momentum of the system in a given direction, z sav. with the azimuth about this direction of the direction of total momentum as conjugate variable; and in the case of a system with a single electron the only other new variables may be taken to be the magnitude of the angular momentum k. with the angle 0 in the orbital plane between the radius vector and the line of intersection of the orbital plane with the plane xy as conjugate variable: while in the case of two electrons the remaining new variables may be taken to be the angular momenta k and k' of the two electrons, with, for conjugate variables, the angles θ and θ' between the radius vectors and the line of nodes, and the total angular momentum j with the azimuth ψ of the line of nodes about the direction of j for conjugate variable. The transformation does not involve anything essentially different when there are more than two electrons, as we may consider all the electrons except one as forming an inner system or core which plays the part of the second electron when there are only two, so that the j of the core counts as the k' of the whole system, the ψ of the core counts as the θ' of the whole system, while the magnitude of the resultant of k and k' is the j of the whole system, and the azimuth about the direction of this resultant of the line of intersection of planes perpendicular to the vectors of k and k' is the ψ . All the new variables are independent of the orientation of the system as a whole except p, ϕ and ψ (or θ when there is only one electron). The variables k, k', j and p may be called action variables, and their canonical conjugates angle variables.

The object of the present paper is to perform the corresponding initial simplification in the quantum treatment of the problem by the introduction of certain quantum variables, which will be given the same names r, p_r, k , θ , etc., whose properties upon investigation will be found to be closely analogous to those of the classical variables. The quantum variables, of course, cannot be considered geometrically. The geometrical relations satisfied by the classical variables must be expressed in an analytic form, so that one can then try to obtain quantum variables which satisfy the same algebraic relations. If

a classical variable is independent of the orientation of the system as a whole, the corresponding quantum variable must be invariant under the transformation

$$\bar{x} = l_1 x + m_1 y + n_1 z \qquad \bar{p}_x = l_1 p_x + m_1 p_y + n_1 p_z
\bar{y} = l_2 x + m_2 y + n_2 z \qquad \bar{p}_y = l_2 p_x + m_2 p_y + n_2 p_2
\bar{z} = l_3 x + m_3 y + n_3 z \qquad \bar{p}_z = l_3 p_x + m_3 p_y + n_3 p_z$$
(1)

where the l's, m's and n's are c-numbers satisfying the same relations as the classical coefficients for a rotation of axes. The new variables, of course, must all be real, and also the angle variables θ , θ' , ψ and ϕ must be such that the Cartesian co-ordinates, when expressed in terms of the new variables, are multiply periodic in the θ , θ' , ψ and ϕ of period 2π . Finally, the most essential property of the new variables is that they shall be canonical, which can be verified only by evaluating all their P.B.'s (Poisson bracket expressions) taken two at a time.

In the present paper we are not concerned very much with what the Hamiltonian of the system is. We simply want to find a contact transformation from the Cartesian co-ordinates and momenta to the new variables, namely, the r's, p_r 's and certain variables which we call action and angle variables. These can be true action and angle variables only if the Hamiltonian is a function of the r's, p_r 's and action variables only. In this case, to complete the solution of the dynamical problem, it is necessary only to obtain a contact transformation from the r's and p_r 's to extra action and angle variables, which transformation may require the addition of functions of the r's and p_r 's to the previous angle variables. When the Hamiltonian does not satisfy this condition, the action and angle variables introduced in the present paper form a preliminary system of canonical variables, from which the final uniformising variables may be obtained by a further contact transformation. It can be shown that the kinetic energy of an electron is a function of the r, p_r and action variables only, and hence, if the total field in which the electron moves is approximately central or symmetrical about the z-axis, the Hamiltonian will differ from a function of the r's, p_r 's and action variables only, only by a small quantity, so that the further contact transformation can be made with the help of perturbation theory. In the absence of an external field of force the Hamiltonian must in any case be a function only of those of the new variables that are invariant under the transformation (1), since the Hamiltonian itself is invariant under this transformation.

§ 2. Preliminary Algebraic Relations.

Let x, y, z and p_x , p_y , p_z be the Cartesian co-ordinates and momenta of an electron. Any function of the co-ordinates and momenta of one electron commutes with any function of those of another. Define r and p_r by

$$r = (x^2 + y^2 + z^2)^{\frac{1}{3}},\tag{2}$$

$$rp_r = xp_x + yp_y + zp_z - i\hbar. ag{3}$$

Then we have, since r commutes with x, y and z

 $[r, rp_r] = x [r, p_x] + y [r, p_y] + z [r, p_z].$

Now

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

with similar equations for $[r, p_y]$ and $[r, p_z]$. Hence

 $[r, rp_r] \Rightarrow (x^2 + y^2 + z^2)/r \Rightarrow r,$

or

$$[r, p_r] = 1.$$

Thus r and p_r are canonically conjugate and may be taken to be a pair of the new variables, as they are obviously invariant under the transformation (1). The (-ih) is put in equation (3) for symmetry and to make p_r real, the conjugate imaginary equation, obtained by writing -i for i and reversing all orders of factors of products, being

$$p_r r = p_x x + p_y y + p_z z + i\hbar \tag{3'}$$

which agrees with (3).

The components of angular momentum* of an electron are defined, as on the classical theory, by

$$m_x = yp_z - zp_y$$
, $m_y = zp_x - xp_z$, $m_z = xp_y - yp_x$.

We have at once the identity

$$xm_x + ym_y + zm_z = 0 (4)$$

as on the classical theory. Also

$$[m_x, x] = [xp_y - yp_x, x] = y$$

 $[m_x, y] = [xp_y - yp_x, y] = -x$
 (5)

$$[m_z, z] = [xp_y - yp_x, z] = 0,$$
 (6)

^{*} The angular momentum relations of this section have been obtained independently by Born, Heisenberg and Jordan ('Zeits. f. Phys.,' vol. 35, p. 557 (1926)).

and similarly

$$[m_z, p_x] = p_y, \quad [m_z, p_y] = -p_x,$$
 (7)

$$[m_z, p_z] = 0, \tag{8}$$

with corresponding relations for m_x and m_y . Further,

$$[m_x, m_y] = [m_x, zp_x - xp_z] = [m_x, z] p_x - x [m_x, p_z]$$

$$= -yp_x + xp_y = m_z$$

$$[m_y, m_z] = m_x, [m_z, m_x] = m_y$$

$$(9)$$

and similarly

These relations will be continually used in the subsequent work. Equations (5), (7) and (9) may easily be remembered from the fact that the + sign occurs when the cyclic order $(x \ y \ z \ x)$ is preserved, and the - sign occurs with the reverse order.

From (2), (5) and (6),

$$[r^2, m_z] = [x^2 + y^2, m_z] = -2xy + 2xy = 0,$$

and from (3), (5), (6), (7) and (8),

$$[rp_r, m_z] = [xp_x + yp_y, m_z] = -yp_x - xp_y + xp_y + yp_x = 0,$$

so that r and p_r commute with m_z , and therefore from symmetry also with m_z and m_y , and therefore with any function of the angular momenta.

Put

$$M_r = \Sigma m_r$$
, $M_u = \Sigma m_u$, $M_z = \Sigma m_z$,

the summation being extended over all the electrons. We have at once from (5) and (6) for each electron

$$[M_z, x] = y, \quad [M_z, y] = -x, \quad [M_z, z] = 0.$$
 (10)

Also

$$[\mathbf{M}_x, \mathbf{M}_y] = [\Sigma m_x, \Sigma m_y] = \Sigma [m_x, m_y] = \Sigma m_z = \mathbf{M}_z$$
y (11)

and similarly

$$[\mathrm{M}_{\mathtt{y}},\ \mathrm{M}_{\mathtt{z}}] = \mathrm{M}_{\mathtt{x}}, \quad [\mathrm{M}_{\mathtt{z}},\ \mathrm{M}_{\mathtt{x}}] = \mathrm{M}_{\mathtt{y}}$$

Let

 $m_x^2 + m_y^2 + m_z^2 = m^2.$

We have from (9),

$$[m^2, m_z] = [m_x^2 + m_y^2, m_z] = -m_y m_x - m_x m_y + m_x m_y + m_y m_z = 0,$$

so m commutes with m_x , and hence also with m_x and m_y . Similarly if

$$M_x^2 + M_y^2 + M_z^2 = M^2$$

M commutes with Mz, My and Mz.

The kinetic energy of an electron is a function of $(p_x^2 + p_y^2 + p_z^2)$. With the help of (2), (3) and (3') we obtain

$$\begin{split} m^2 &= \Sigma_{xyz} \, (yp_z - zp_y)^2 = \Sigma_{xyz} \, (yp_z y p_z + z p_y \, z p_y - y p_z z p_y - z p_y y p_z) \\ &= \Sigma_{xyz} \, (y^2 p_z^2 + z^2 p_y^2 - y p_y p_z z - z p_z p_y y - x p_x p_x x + x^2 p_x^2 - 2ihx p_x) \\ &= (x^2 + y^2 + z^2) \, (p_x^2 + p_y^2 + p_z^2) - (x p_x + y p_y + z p_z) \, (p_x x + p_y y + p_z z + 2ih) \\ &= r^2 \, (p_x^2 + p_y^2 + p_z^2) - (r p_r + ih) \, (p_r r + ih) \\ &= r^2 \, (p_x^2 + p_y^2 + p_z^2) - r^2 p_r^2. \end{split}$$

Hence

$$p_x^2 + p_y^2 + p_z^2 = p_r^2 + m^2/r^2 ag{12}$$

as on the classical theory. Now m^2 is going to be a function of the action variables, and hence the kinetic energy of the system will be a function of the r's, p_r 's and action variables.

We shall not be concerned further with the r's and p_r 's except to verify that they commute with each of the action and angle variables that will be introduced, this being necessary for the variables to be canonical.

§ 3. The Action Variables.

On the classical theory one of the action variables to be introduced, namely, k, is just equal to m. The quantum variable k may not be equal to m, but must be chosen such that x, y and z are periodic functions of its canonically conjugate variable θ of period 2π . On the classical theory, if a co-ordinate, z say, is expanded as a Fourier series in the angle variables, the coefficients of the terms involving $e^{ni\theta}$ all vanish unless $n=\pm 1$. This fact is expressible analytically by the equation $\frac{\partial^2 z}{\partial \theta^2} = -z$, or in P.B.'s by [k, [k, z]] = -z. We try to choose our quantum variable k so as also to satisfy

$$[k, [k, z]] = -z.$$
 (13)

This relation would ensure that when z is expressed in terms of the new variables, it would be periodic in θ of period 2π , and, further, that all the coefficients in the Fourier expansion would vanish except those of $e^{i\theta}$ and $e^{-i\theta}$ terms. The ordinary selection rule for k would then follow.

Equation (13) gives

$$[k^2, [k, z]] = k [k, [k, z]] + [k, [k, z]] k = -(kz + zk),$$

and hence

$$[k^{2}, [k^{2}, z]] = k [k^{2}, [k, z]] + [k^{2}, [k, z]] k = -(k^{2}z + 2kzk + zk^{2})$$

$$= -2 (k^{2}z + zk^{2}) + (k^{2}z - 2kzk + zk^{2})$$

$$= -2 (k^{2}z + zk^{2}) - h^{2} [k, [k, z]]$$

$$= -2 (k^{2}z + zk^{2}) + h^{2}z$$

Or

$$\frac{1}{2}[k^2, [k^2, z]] = -(k^2 - \frac{1}{4}h^2)z - z(k^2 - \frac{1}{4}h^2).$$
 (14)

Now from (5) and (6)

$$\frac{1}{2} [m^2, z] = \frac{1}{2} [m_x^2 + m_y^2, z] = \frac{1}{2} (-ym_x - m_x y + xm_y + m_y x)
= m_y x - m_x y + ihz = m_y x - ym_x = xm_y - m_x y.$$
(15)

Similar relations hold for $\frac{1}{2}$ [m^2 , x] and $\frac{1}{2}$ [m^2 , y]. Hence

$$\frac{1}{2}[m^2, [m^2, z]] = m_y [m^2, x] - m_x [m^2, y] + ih [m^2, z]
= m_y 2 (ym_z - m_y z) - m_x 2 (m_x z - xm_z) + ih [m^2, z]
= 2 (m_x x + m_y y + m_z z) m_z - 2 (m_x^2 + m_y^2 + m_z^2) z + ih [m^2, z]
= -2m^2 z + (m^2 z - zm^2)
= -m^2 z - zm^2.$$
(16)

Comparing this with equation (14) we see that they agree if we take

$$m^2 = k^2 - \frac{1}{4}h^2 = k_1 k_2, \tag{17}$$

where

$$k_1 = k + \frac{1}{2}h, \qquad k_2 = k - \frac{1}{2}h.$$

(In general we shall take the suffix 1 attached to any action variable to denote the value of that variable increased by $\frac{1}{2}h$, and the suffix 2 to denote its value reduced by $\frac{1}{2}h$.)

With k defined by (17), equation (14) follows from equation (16), but equation (13) does not necessarily then follow from equation (14). We may, however, take (13), together with the corresponding equations

$$[k, [k, x]] = -x$$
 $[k, [k, y]] = -y$ (18)

as completing the definition of k, which had previously been defined only through k^2 . It seems probable that in general an algebraic equation in quantum algebra has an infinite number of roots, e.g., the algebraic equation xa - ax = b is analogous to a differential equation on the classical theory, and its general solution contains arbitrary c-numbers. It thus appears to be reasonable for

one to take two or more equations to define a q-number when necessary, provided these equations are consistent, as in the present case.

One may examine the necessity for the further assumptions (13), (18) in the definition of k by the matrix method used by Born, Heisenberg and Jordan.* If one regards (14) as a matrix equation and equates the (nm) components of either side, one obtains a relation effectively the same as Born, Heisenberg and Jordan's equation 22 Kap. 4 (except for the fact that Born, Heisenberg and Jordan are using M instead of m, and X, a linear function of x, y and z, instead of z). From this these authors deduce that all X (nm) components vanish except those related to two k's, a_n and a_m say, that satisfy

$$a_n = \pm a_m \pm 1.$$
 (23) Kap. 4.

But we want each X(nm) to vanish except when

$$a_n = a_m \pm 1.$$
 (23') Kap. 4.

Born, Heisenberg and Jordan state that negative values of k can be ignored without loss of generality, but this is justifiable only if it can be shown that transitions from a positive to a negative k cannot occur. This cannot be done without further assumption, since if there is a matrix representation for which every X(nm) vanishes except when (23') Kap. 4 is satisfied, one can obtain from it others for which this condition is not fulfilled, but only the condition that each X(nm) vanishes except when (23) Kap. 4 is satisfied, by interchanging in the matrix k some of the pairs of rows, and the corresponding pairs of columns, for which the a_n 's are equal in magnitude but opposite in sign, as this process does not affect the validity of any matrix equation that involves k only through k^2 . Equations (13), (18) supply the necessary further assumption.

One can take as another action variable the quantity M_z , equal to p say, since from (10)

$$[p, [p, x]] = [p, y] = -x [p, [p, y]] = -[p, x] = -y$$
(19)

These equations show that x and y are periodic functions of ϕ , the variable conjugate to p, of period 2π , and that all the coefficients in their Fourier expansions vanish except those of $e^{i\phi}$ and $e^{-i\phi}$ terms. Further, since [p, z] = 0, all the coefficients in the Fourier expansion of z vanish except those of terms independent of ϕ . The selection rules for p follow from this.

^{*} Born, Heisenberg and Jordan, loc. cit.

Again, when there is more than one electron in the system, we can define j by

$$M^2 = j^2 - \frac{1}{4}h^2 = j_1, j_2, \tag{20}$$

analogous to (17), and take j as an action variable, because, as we shall show later, quantities μ_x , μ_y , μ_z can be found which satisfy

$$[j, [j, \mu_x]] = -\mu_x, \quad [j, [j, \mu_y]] = -\mu_y, \quad [j, [j, \mu_z]] = -\mu_z.$$
 (21)

From the results of § 2 it is evident that j, p and the k's commute with r and p_r and with one another, and also j and the k's are invariant under the transformation (1).

§ 4. The Angle Variables.

Each of the angle variables w is given on the classical theory by e^{iw} being equal to the square root of the ratio of two quantities that are conjugate imaginaries, *i.e.* by a relation of the type

$$e^{iw} = \left(\frac{a+ib}{a-ib}\right)^{\frac{1}{4}} \tag{22}$$

where a and b are real. This, of course, makes w real, since if one writes -i for i in (22) it remains true. On the quantum theory there are two corresponding ways by which one could define e^{iw} , namely,

$$e^{i\mathbf{w}} = \left\{ (a+ib) \frac{1}{a-ib} \right\}^{\frac{1}{2}}$$
 and $e^{i\mathbf{w}} = \left\{ \frac{1}{a-ib} (a+ib) \right\}^{\frac{1}{2}}$,

but neither of these makes w real. The correct quantum generalisation of (22) is the more symmetrical relation

$$e^{i\mathbf{w}} (a - ib) e^{i\mathbf{w}} = a + ib. \tag{23}$$

This becomes, when one equates the conjugate imaginaries of either side

$$e^{-i\omega}$$
 $(a+ib)$ $e^{-i\omega}=a-ib$,

which is equivalent to (23), so that w defined in this way is real. We may solve equation (23) for e^{iw} in either of two ways, namely,

$$e^{i\omega} (a - ib) e^{i\omega} (a - ib) = (a + ib) (a - ib),$$

giving

$$e^{iw}(a-ib) = \{(a+ib)(a-ib)\}^{\frac{1}{2}} = \{(a+ib)(a-ib)\}^{-\frac{1}{2}}(a+ib)(a-ib),$$

so that

$$e^{i\omega} = \{(a+ib) (a-ib)\}^{-\frac{1}{2}} (a+ib),$$
 (24)

or alternatively

$$(a - ib) e^{iw} (a - ib) e^{iw} = (a - ib) (a + ib),$$

which gives

$$e^{i\omega} = (a+ib) \{(a-ib) (a+ib)\}^{-\frac{1}{2}}.$$
 (25)

VOL. CXI .- A.

Suppose now that J is an action variable such that

$$[J, a] = b, \quad [J, b] = -a.$$
 (26)

We have

$$[J, a+ib] = b - ia = -i(a+ib)$$

[J, a - ib] = b + ia = i (a - ib),

so that

$$J (a + ib) = (a + ib) (J + h)
J (a - ib) = (a - ib) (J - h)$$
(27)

and

$$J(a+ib)(a-ib) = (a+ib)(J+h)(a-ib) = (a+ib)(a-ib)J$$
,

so that J commutes with the product (a+ib) (a-ib). Hence from (24) or (25)

 $Je^{i\omega}=e^{i\omega}(J+\hbar),$

Oľ

$$[e^{iw}, J] = ie^{iw}.$$

It does not follow rigorously that [w, J] = 1, but since w occurs in the analysis only through e^{iw} , the relation $[e^{iw}, J] = ie^{iw}$ is sufficient to show that we can take w to be the variable conjugate to J.

From (26)
$$[J, [J, a]] = -a.$$
 (28)

Hence, to determine the angle variable w canonically conjugate to any action variable J, one must look for a quantity a that satisfies (28) and that commutes with each of the other action variables, and then, if it can be found, define w by (23) with b equal to [J, a]. This will make w real and conjugate to J, and will make it commute with the other action variables. It would, of course, have to be verified that it commutes with r and p_r . (On the classical theory the conditions that a must satisfy are that it must vary periodically according to the cosine law when w increases uniformly and the other new variables are kept constant, and must remain constant when the r's, p_r 's, action variables and w are kept constant and the other angle variables vary arbitrarily.)

To determine, for instance, the angle variable θ canonically conjugate to the k of § 3, we know that [k, [k, z]] = -z and that z commutes with p, and hence for the case of a system with a single electron when there is no other action variable, we can take θ to be defined by

$$e^{i\theta} (z - i [k, z]) e^{i\theta} = z + i [k, z].$$
 (29)

We shall have to take a different value for a when there is more than one electron in the system, since z does not commute with j. It is obvious that θ , defined by (29) or

 $e^{i\theta} = \{(z+i\,[k,\,z])\;(z-i\,[k,\,z])\}^{-\frac{1}{2}}(z+i\,[k,\,z]),$

commutes with r since z and k do so. To prove that it also commutes with p_r we have

$$[z, rp_r] = z$$

or

$$z(rp_r) = (rp_r + ih) z.$$

This equation must still be true when for z is substituted (z + i[k, z]) or (z - i[k, z]) or $\{(z + i[k, z]), (z - i[k, z])\}^{\frac{1}{2}}$.* It follows that $e^{i\theta}$ commutes with rp_r , and hence with p_r . From (27) we have the equation

$$k_2(z + i[k, z]) = (z + i[k, z]) k_1,$$
 (30)

which will be required later.

In the same way we may define ϕ , the angle variable canonically conjugate to p, by taking $a = M_x$, since we know that $[p, [p, M_x]] = -M_x$ and that M_x commutes with each k and with j. We thus have

$$e^{i\phi}(\mathbf{M}_x - i\mathbf{M}_y) e^{i\phi} = \mathbf{M}_x + i\mathbf{M}_y.$$

It is obvious that r and p_r commute with ϕ , since they commute with M_x and M_y .

The equations (23), (24), (25) for the typical angle variable are most useful in the form

$$a + ib = \{(a + ib) (a - ib)\}^{\frac{1}{2}} e^{iw} = e^{iw} \{(a - ib) (a + ib)\}^{\frac{1}{2}}$$

$$a - ib = \{(a - ib) (a + ib)\}^{\frac{1}{2}} e^{-iw} = e^{-iw} \{(a + ib) (a - ib)\}^{\frac{1}{2}} \}.$$
(31)

It is necessary to evaluate the products of (a + ib) and (a - ib) in each case in which these equations are used. For the case when a is M_x and b is M_y we have

$$\begin{split} (\mathbf{M}_x + i\mathbf{M}_y) \ (\mathbf{M}_x - i\mathbf{M}_y) &= \mathbf{M}_x^2 + \mathbf{M}_y^2 - i \ (\mathbf{M}_x\mathbf{M}_y - \mathbf{M}_y\mathbf{M}_x) \\ &= \mathbf{M}^2 - \mathbf{M}_z^2 + h\mathbf{M}_z = j^2 - \frac{1}{4}h^2 - p^2 + hp \\ &= j^2 - p_2^2, \end{split}$$

so that equations (31) become

$$M_x + i M_y = (j^2 - p_2^2)^{\frac{1}{2}} e^{i\phi} = e^{i\phi} (j^2 - p_1^2)^{\frac{1}{2}}
 M_x - i M_y = (j^2 - p_1^2)^{\frac{1}{2}} e^{-i\phi} = e^{-i\phi} (j^2 - p_2^2)^{\frac{1}{2}}$$
(32)

The evaluation of the product $(z + i \ [k, z])$ $(z - i \ [k, z])$ is not so easy. We shall evaluate the more general product $(z + i \ [k, z])$ $(\zeta - i \ [k, \zeta])$, where ξ , η , ζ are three quantities satisfying the relations analogous to (4), (5) and (6)

^{*} This is not rigorous, but appears to be justifiable.

(and the relations corresponding to (5) and (6) for m_y and m_z) in which x, y, zhave been replaced by ξ , η , ζ , as we shall need this piece of analysis later. ξ , η , ζ must satisfy the relations analogous to any of the consequences of (4), (5) and (6) that do not require for their proof the fact that x, y, z commute with one another, such as (15) and (13) [provided the auxiliary assumptions (13), (18) required for the definition of k are true for the ξ , η , ζ].

We have from (15), in which m^2 is replaced by k^2 ,

$$k [k, z] + [k, z] k = [k^{2}, z] = 2 (m_{y}x - m_{x}y + ihz).$$
Also
$$k [k, z] - [k, z] k = ih [k, [k, z]] = -ihz$$
from (13). Hence
$$k [k, z] = m_{y}x - m_{x}y + \frac{1}{2}ihz,$$
and similarly
$$k [k, \zeta] = m_{y}\xi - m_{x}\eta + \frac{1}{2}ih\zeta.$$
From (4)
$$m_{z}zm_{z}\zeta = (m_{x}x + m_{y}y) (m_{x}\xi + m_{y}\eta).$$
(33)

so that

From (4)

Also

$$(m_{y}x - m_{x}y) (m_{y}\xi - m_{x}\eta) + m_{z}zm_{z}\xi$$

$$= m_{y} (xm_{y} + ym_{x}) \xi + m_{x} (ym_{x} + xm_{y}) \eta$$

$$+ m_{x} (xm_{x} - ym_{y}) \xi + m_{y} (ym_{y} - xm_{x}) \eta$$

$$= m_{y} (m_{y}x + m_{x}y) \xi + m_{x} (m_{x}y + m_{y}x) \eta$$

$$+ m_{x} (m_{x}x - m_{y}y) \xi + m_{y} (m_{y}y - m_{x}x) \eta$$

$$= (m_{x}^{2} + m_{y}^{2}) (x\xi + y\eta) - ihm_{z}y\xi + ihm_{z}x\eta.$$

Using these results and also (30) we find

$$k (k - h) (z + i [k, z]) (\zeta - i [k, \zeta])$$

$$= k (z + i [k, z]) k (\zeta - i [k, \zeta])$$

$$= \{k_2 z + i (m_y x - m_x y)\} \{k_1 \zeta - i (m_y \xi - m_x \eta)\}$$

$$= (m_y x - m_x y) (m_y \xi - m_x \eta) + \{k_2 z + i (m_y x - m_x y)\} k_1 \zeta$$

$$- i k_2 z (m_y \xi - m_x \eta)$$

$$= (m_x^2 + m_y^2) (x \xi + y \eta) - m_z^2 z \zeta + i h m_z (x \eta - y \xi)$$

$$+ k_2 \{k_2 z + i (m_y x - m_x y)\} \zeta - i k_2 z (m_y \xi - m_x \eta)$$

$$= (k_1 k_2 - m_z^2) (x \xi + y \eta) + (k_2^2 - m_z^2) z \zeta + i h m_z (x \eta - y \xi)$$

$$- i k_2 \{ - (m_y x - m_x y) \zeta + (m_y z - i h x) \xi - (m_x z + i h y) \eta \}$$

$$= (k_2^2 - m_z^2) (x \xi + y \eta + z \zeta) + i h m_z (x \eta - y \xi)$$

$$- i k_2 \{ m_x (y \zeta - z \eta) + m_y (z \xi - x \zeta) \}. (34)$$

Now take ξ , η , ζ equal to x, y, z. Equation (34) reduces to the simple result

$$k(k-h)(z+i[k,z])(z-i[k,z]) = (k_2^2 - m_z^2)r^2.$$
 (35)

§ 5. The Transformation Equations for the System with a Single Electron.

When the system consists of a single electron, the new canonical variables are, in addition to r and p_r , the action variables k [defined by (17)] and $p = m_z$ and the angle variables θ and ϕ [defined by (29) and (32)]. With the help of (35) the transformation equation (29) may be put in the form (31). The result is

$$z + i[k, z] = rk^{-\frac{1}{2}}(k - h)^{-\frac{1}{2}}(k_{2}^{2} - p^{2})^{\frac{1}{2}}e^{i\theta}$$

$$= rk^{-\frac{1}{2}}(k_{2}^{2} - p^{2})^{\frac{1}{2}}e^{i\theta}k^{-\frac{1}{2}} = rk^{-\frac{1}{3}}e^{i\theta}(k_{1}^{2} - p^{2})^{\frac{1}{2}}k^{-\frac{1}{2}}$$

$$z - i[k, z] = rk^{-\frac{1}{2}}(k_{1}^{2} - p^{2})^{\frac{1}{2}}e^{-i\theta}k^{-\frac{1}{2}} = rk^{-\frac{1}{3}}e^{-i\theta}(k_{2}^{2} - p^{2})^{\frac{1}{2}}k^{-\frac{1}{2}}$$
(36)

We have already shown that the new variables satisfy all the conditions that they ought to satisfy except that $[\theta, \phi] = 0$. This relation is not very easy to prove, but fortunately it is not of any dynamical importance, since if it is not true, our θ and ϕ would differ from the true variables conjugate to k and p only by real quantities that are functions of k and p only, and are, therefore, constants. The amplitude of x, y, z expressed as Fourier series will therefore not be affected.

A simpler way than the one already given of proving that the transformation from the original variables to the new variables is a contact transformation is to assume that the new variables are canonical and satisfy the quantum conditions, and to deduce from that that the original variables are canonical. It is convenient with this method to introduce the variables

$$\begin{array}{lll} \xi_1 = & (k+p-\frac{1}{2}h)^{\frac{1}{2}}e^{\frac{3}{2}i\,(\theta+\phi)} & = & e^{\frac{3}{2}i\,(\theta+\phi)}(k+p+\frac{1}{2}h)^{\frac{1}{2}},\\ \eta_1 = -i\,(k+p+\frac{1}{2}h)^{\frac{1}{2}}e^{-\frac{1}{2}i\,(\theta+\phi)} & = -ie^{-\frac{1}{2}i\,(\theta+\phi)}(k+p-\frac{1}{2}h)^{\frac{1}{2}},\\ \xi_2 = & (k-p-\frac{1}{2}h)^{\frac{1}{2}}e^{\frac{1}{2}i\,(\theta-\phi)} & = & e^{\frac{3}{2}i\,(\theta-\phi)}(k-p+\frac{1}{2}h)^{\frac{1}{2}},\\ \eta_2 = -i\,(k-p+\frac{1}{2}h)^{\frac{1}{2}}e^{-\frac{1}{2}i\,(\theta-\phi)} & = -ie^{-\frac{1}{2}i\,(\theta-\phi)}\,(k-p-\frac{1}{2}h)^{\frac{1}{2}}, \end{array}$$

which are easily verified to be canonical, and which give

$$\begin{split} \xi_1 \eta_1 &= -i \, (k+p - \tfrac{1}{2} h), & \eta_1 \xi_1 &= -i \, (k+p + \tfrac{1}{2} h), \\ \xi_2 \eta_2 &= -i \, (k-p - \tfrac{1}{2} h), & \eta_2 \xi_2 &= -i \, (k-p + \tfrac{1}{2} h). \end{split}$$

The transformation equations may now be put in the simple form

$$x + iy = -\frac{1}{2}rk^{-\frac{1}{2}} (\xi_{1}^{2} - \eta_{2}^{2}) k^{-\frac{1}{4}}$$

$$x - iy = \frac{1}{2}rk^{-\frac{1}{2}} (\xi_{2}^{2} - \eta_{1}^{2}) k^{-\frac{1}{2}}$$

$$z = \frac{1}{2}rk^{-\frac{1}{2}} (\xi_{1}\xi_{2} + \eta_{1}\eta_{2}) k^{-\frac{1}{2}}$$

$$m_{x} + im_{y} = i\xi_{1}\eta_{2}$$

$$m_{x} - im_{y} = i\xi_{2}\eta_{1}$$

$$m_{z} = \frac{1}{2}i (\xi_{1}\eta_{1} - \xi_{2}\eta_{2})$$

$$xp_{x} + yp_{y} + zp_{z} = rp_{r} + ih,$$

$$(37)$$

from which one can easily verify that x, y, z, p_x , p_y , p_z are canonical when it is assumed that the ξ 's and η 's are canonical. Incidentally this method shows that our previous θ and ϕ do commute.

Equations (37) are also the most convenient ones for evaluating the amplitudes of the various components of vibration, since they give at once

$$x + iy = -\frac{1}{2}r \left\{ \frac{(k+p-\frac{1}{2}h)^{\frac{1}{3}}(k+p-\frac{3}{2}h)^{\frac{1}{3}}}{k^{\frac{1}{2}}(k-h)^{\frac{1}{3}}} e^{i(\theta+\phi)} + \frac{(k-p+\frac{1}{2}h)^{\frac{1}{3}}(k-p+\frac{3}{2}h)^{\frac{1}{3}}}{k^{\frac{1}{2}}(k+h)^{\frac{1}{3}}} e^{i(\phi-\theta)} \right\}$$

$$x - iy = \frac{1}{2}r \left\{ \frac{(k-p-\frac{1}{2}h)^{\frac{1}{3}}(k-p-\frac{3}{2}h)^{\frac{1}{3}}}{k^{\frac{1}{2}}(k-h)^{\frac{1}{3}}} e^{i(\theta-\phi)} + \frac{(k+p+\frac{1}{2}h)^{\frac{1}{3}}(k+p+\frac{3}{2}h)^{\frac{1}{3}}}{k^{\frac{1}{3}}(k+h)^{\frac{1}{3}}} e^{-i(\theta+\phi)} \right\}$$

$$z = \frac{1}{2}r \left\{ \frac{(k+p-\frac{1}{2}h)^{\frac{1}{3}}(k-p-\frac{1}{2}h)^{\frac{1}{3}}}{k^{\frac{1}{3}}(k-h)^{\frac{1}{3}}} e^{i\theta} - \frac{(k+p+\frac{1}{2}h)^{\frac{1}{3}}(k-p+\frac{1}{2}h)^{\frac{1}{3}}}{k^{\frac{1}{3}}(k+h)^{\frac{1}{3}}} e^{-i\theta} \right\}$$

$$-\frac{(k+p+\frac{1}{2}h)^{\frac{1}{3}}(k-p+\frac{1}{2}h)^{\frac{1}{3}}}{k^{\frac{1}{3}}(k+h)^{\frac{1}{3}}} e^{-i\theta} \right\}$$

The simplicity of equations (37) is due to the fact that one can associate each component of vibration of the system with the product of two of the ξ , η variables that are not conjugate. With systems of more than one electron there are too many components of vibration for this to be done, so that there are no equations corresponding to (37) for such systems.

§ 6. The Transformation Equations for the System with Two Electrons.

Consider now the case of a system with two electrons and use dashed letters such as x', p_x' , m_x' , k' to refer to the second electron. We take for our new variables, in addition to r, p_r , r', p_r' , the action variables k [defined by (17)], k', p and j [defined by (20)], and their conjugate angle variables θ , θ' , ϕ and ψ , which will now be defined.

We define ϕ as before by equations (32). To define θ we must replace the z in (29) by some quantity that also satisfies (13) and that commutes with k', p and j. The quantity $xm_x' + ym_y' + zm_z'$ (\Rightarrow \mathbf{q} . \mathbf{m}' say, using the dot to denote a scalar product and \mathbf{q} to denote the vector x, y, z) has the necessary properties, since

from (18), and
$$[k, [k, \mathbf{q} \cdot \mathbf{m}']] = [k, [k, \mathbf{q}]] \cdot \mathbf{m}' = -\mathbf{q} \cdot \mathbf{m}'$$

$$[\mathbf{q} \cdot \mathbf{m}', k'] = 0,$$

owing to the fact that k' commutes with $m_{x'}$, $m_{y'}$ and $m_{z'}$; and further from (4)

$$q \cdot m' = q \cdot (M - m) = q \cdot M,$$

so that

$$[\mathbf{q} \cdot \mathbf{m}', p] = [\mathbf{q} \cdot \mathbf{M}, M_z] = [xM_x + yM_y, M_z]$$

= $-yM_x - xM_y + xM_y + yM_x = 0$,

and from symmetry

$$[\mathbf{q} \cdot \mathbf{m}', \mathbf{M}_x] = 0, \quad [\mathbf{q} \cdot \mathbf{m}', \mathbf{M}_y] = 0,$$

so that

$$[q.m', j] = 0,$$

as required. Thus 0 defined by

$$e^{i\theta} (\mathbf{q} \cdot \mathbf{m}' - i [k, \mathbf{q} \cdot \mathbf{m}']) e^{i\theta} = \mathbf{q} \cdot \mathbf{m}' + i [k, \mathbf{q} \cdot \mathbf{m}']$$
 (39)

is conjugate to k and commutes with k', p and j, and also may be proved, as in the case of a single electron, to commute with r and p_r . In a corresponding way we can define θ' by

$$e^{i\theta'}(\mathbf{q}' \cdot \mathbf{m} - i[k', \mathbf{q}' \cdot \mathbf{m}]) e^{i\theta'} = \mathbf{q}' \cdot \mathbf{m} + i[k', \mathbf{q}' \cdot \mathbf{m}].$$
 (40)

To define ψ we must introduce the quantities

$$\mu_{x} = m_{y}m_{z'} - m_{z}m_{y'} = M_{y}m_{z'} - m_{y'}M_{z} = m_{z'}M_{y} - M_{z}m_{y'}$$

$$\mu_{y} = m_{z}m_{x'} - m_{x}m_{z'} = M_{z}m_{x'} - m_{z'}M_{x} = m_{x'}M_{z} - M_{x}m_{z'}$$

$$\mu_{z} = m_{x}m_{y'} - m_{y}m_{x'} = M_{x}m_{y'} - m_{x'}M_{y} = m_{y'}M_{x} - M_{y}m_{x'}$$
(41)

We have

$$\begin{bmatrix}
M_z, \ \mu_x \end{bmatrix} = [m_z, \ m_y m_z'] + [m_z', -m_z m_y'] = -m_x m_z' + m_z m_x' = \mu_y \\
[M_z, \ \mu_y] = [m_z, -m_x m_z'] + [m_z', m_z m_x'] = -m_y m_z' + m_z m_y' = -\mu_x
\end{bmatrix} (42)$$

$$[M_z, \mu_z] = m_y m_y' + m_x m_x' - m_x m_x' - m_y m_y' = 0,$$
 (43)

and further

$$\mu$$
. $\mathbf{m} = (m_z m_y - m_y m_z) m_x' + (m_x m_z - m_z m_x) m_y' + (m_y m_x - m_x m_y) m_z'$
= $-i\hbar (m_x m_x' + m_y m_y' + m_z m_z')$,

and

$$\mu \cdot \mathbf{m}' = m_x (m_y' m_z' - m_z' m_y') + m_y (m_z' m_x' - m_x' m_z') + m_z (m_x' m_y' - m_y' m_x')$$

$$= ih (m_x m_x' + m_y m_y' + m_z m_z'),$$

so that

$$\mu \cdot \mathbf{m} = 0. \tag{44}$$

The relations (42), (43) and (44) between μ_x , μ_y , μ_z and M_x , M_y , M_z correspond exactly to the relations (5), (6) and (4) between x, y, z and m_x , m_y , m_z , so that any consequences of (5), (6) and (4) that do not require for their proof the fact that x, y, z commute with one another can be applied directly to the μ 's and

M's. The equations (13), (18) are such consequences, and give when applied to the μ 's just equations (21), and thus justify the definition (20) for the action variable j. [The fact that (13), (18) involve an additional assumption, which may be regarded as completing the definition of k, here repeats itself, as (21) involves the corresponding additional assumption, which may be regarded as completing the definition of j.] Equation (33) applied to the μ 's gives in a similar way

 $j[j, \mu_z] = M_y \mu_x - M_x \mu_y + \frac{1}{2} i h \mu_z,$ (45)

which will be required later.

Now μ_z evidently commutes with r, p_r , r', $p_{r'}$, k and k', and we have proved that it commutes with p, so that we can take it to be the quantity to be substituted for a in (23) for the definition of ψ . We then get

$$e^{i\psi} (\mu_z - i[j, \mu_z]) e^{i\psi} = \mu_z + i[j, \mu_z].$$
 (46)

We have thus established all the relations necessary for the new variables to be canonical except that the angle variables commute with one another, but this, as before for the case of a single electron, is of no dynamical importance. All the new variables except p, ϕ and ψ are obviously invariant under the transformation (1).

To put the transformation equations (39) and (46) in the form (31) it is necessary to evaluate the (a+ib) (a-ib) for each of them. For the case of (46) the analysis leading to equation (34) is directly applicable, and gives, when one writes j for k, M_x and M_y for m_x and m_y , p for m_z , and μ_x , μ_y , μ_s for x, y, z and ξ , η , ζ ,

$$j (j - h) (\mu_z + i [j, \mu_x]) (\mu_z - i [j, \mu_z])$$

$$= (j_2^2 - p^2) (\mu_x^2 + \mu_y^2 + \mu_z^2) + ih p (\mu_x \mu_y - \mu_y \mu_x)$$

$$- ij_2 \{ M_x (\mu_y \mu_z - \mu_z \mu_y) + M_y (\mu_z \mu_x - \mu_x \mu_z) \}.$$
 (47)

We have

$$\begin{split} \mu_{x}^{2} + \mu_{y}^{2} + \mu_{z}^{2} &= \sum_{xyz} \left(m_{y}^{2} m_{z}^{'2} + m_{z}^{2} m_{y}^{'2} - m_{y} m_{z} m_{z}^{'} m_{y}^{'} - m_{z} m_{y} m_{y}^{'} m_{z}^{'} \right) \\ &= \left(m_{x}^{2} + m_{y}^{2} + m_{z}^{2} \right) \left(m_{x}^{'2} + m_{y}^{'2} + m_{z}^{'2} \right) \\ &- \left(m_{x} m_{x}^{'} + m_{y} m_{y}^{'} + m_{z} m_{z}^{'} \right)^{2} \\ &+ \sum_{xyz} \left(m_{y} m_{z} - m_{z} m_{y} \right) \left(m_{y}^{'} m_{z}^{'} - m_{z}^{'} m_{y}^{'} \right) \\ &= m^{2} m^{'2} - \left(\mathbf{m} \cdot \mathbf{m}^{'} \right)^{2} - h^{2} \cdot \mathbf{m} \cdot \mathbf{m}^{'}, \end{split}$$

and

$$\begin{split} \left[\mu_{x}, \ \mu_{y} \right] &= \left[\mu_{x}, \ m_{z} \right] \, m_{x}' + m_{z} \left[\mu_{x}, \ m_{x}' \right] - \left[\mu_{x}, \ m_{x} \right] \, m_{z}' - m_{x} \left[\mu_{x}, \ m_{z}' \right] \\ &= m_{x} m_{z}' m_{x}' + m_{z} \left(m_{y} m_{y}' + m_{z} m_{z}' \right) \\ &- \left(- m_{z} m_{z}' - m_{y} m_{y}' \right) \, m_{z}' + m_{x} m_{x} m_{x}' \\ &= \left(m_{z} + m_{z}' \right) \left(m_{x} m_{x}' + m_{y} m_{y}' + m_{z} m_{z}' \right) \\ &+ \left(m_{x} m_{z} - m_{z} m_{x} \right) \, m_{x}' + m_{y} \left(m_{y}' m_{z}' - m_{z}' m_{y}' \right) \\ &= M_{z} \mathbf{m} \cdot \mathbf{m}', \end{split}$$

as the last two terms cancel, with similar relations for $[\mu_y, \mu_z]$ and $[\mu_z, \mu_z]$. Hence the right-hand side of (47) becomes

$$\begin{split} (j_2{}^2-p^2)\,\{m^2m'^2-(\mathbf{m}\cdot\mathbf{m}')^2-h^2\mathbf{m}\cdot\mathbf{m}'\} -h^2p^2\mathbf{m}\cdot\mathbf{m}'\\ &+hj_2\,(\mathbf{M}_x{}^2+\mathbf{M}_y{}^2)\;\mathbf{m}\cdot\mathbf{m}'\\ =&\,(j_2{}^2-p^2)\,\{m^2m'^2-(\mathbf{m}\cdot\mathbf{m}')^2\}-h^2j_2{}^2\mathbf{m}\cdot\mathbf{m}'+hj_2\,(j_1\,j_2-p^2)\;\mathbf{m}\cdot\mathbf{m}'\\ =&\,(j_2{}^2-p^2)\,\{m^2m'^2-(\mathbf{m}\cdot\mathbf{m}')^2+h\,j_2\,\mathbf{m}\cdot\mathbf{m}'\}. \end{split}$$

Now

$$\mathbf{m} \cdot \mathbf{m}' = \frac{1}{2} (j_1 j_2 - k_1 k_2 - k_1' k_2')$$

$$= \frac{1}{2} (j_2^2 - k_1 k_2 - k_1' k_2' + h j_2)$$

$$\mathbf{m} \cdot \mathbf{m}' - h j_2 = \frac{1}{2} (j_2^2 - k_1 k_2 - k_1' k_2' - h j_2)$$

$$(48)$$

$$\mathbf{m} \cdot \mathbf{m}' - hj_2 = \frac{1}{2} (j_2^2 - k_1 k_2 - k_1 k_2 - hj_2)$$

$$m^2 m'^2 - (\mathbf{m} \cdot \mathbf{m}' - hj_2) \mathbf{m} \cdot \mathbf{m}' = k_1 k_2 k_1' k_2' - \frac{1}{4} \{ (j_2^2 - k_1 k_2 - k_1' k_2')^2 - h^2 j_2^2 \}$$

$$= -\frac{1}{4} \{ j_2^4 - 2 j_2^2 (k_1 k_2 + k_1' k_2' + \frac{1}{2} h^2) + (k_1 k_2 - k_1' k_2')^2 \}$$

$$= -\frac{1}{4} \{ j_2^4 - 2 j_2^2 (k^2 + k'^2) + (k^2 - k'^2)^2 \}$$

$$= \frac{1}{4} \{ k_1 k'_1, j_2 \}.$$

where we have used the notation

$$(a, b, c) = -(a^4 + b^4 + c^4 - 2b^2c^2 - 2c^2a^2 - 2a^2b^2)$$

= $(a + b + c)(a + b - c)(a - b + c)(-a + b + c)$

for three quantities a, b, c that commute. Hence (47) reduces to

$$j(j-h)(\mu_z+i[j,\mu_z])(\mu_z-i[j,\mu_z]) = \frac{1}{4}(j_2^2-p^2)(k,k',j_2).$$
 (49)

The evaluation of the product (a + ib) (a - ib) for equation (39) is more complicated, and the method will only be indicated. The product to be evaluated, namely, $(\mathbf{q} \cdot \mathbf{m}' + i [k, \mathbf{q} \cdot \mathbf{m}'])$ $(\mathbf{q} \cdot \mathbf{m}' - i [k, \mathbf{q} \cdot \mathbf{m}']$, is composed of the sum of three terms like

$$m_x'^2 (x + i [k, x]) (x - i [k, x]),$$

and three terms like

$$\{m_{x'}m_{y'}(x+i[k,x])(y-i[k,y])+m_{y'}m_{x'}(y+i[k,y])(x-i[k,x])\}.$$

The values of the first three terms are given directly by equation (35), while the value of the sum of the quantities (x + i [k, x]) (y - i [k, y]) and (y + i [k, y]) (x - i [k, x]) can be obtained by applying the linear transformation (1) to the z and m_z in (35) and equating the coefficients of l_3m_3 on either side. Proceeding in this way we obtain finally

$$k(k-h)(\mathbf{q} \cdot \mathbf{m}' + i[k, \mathbf{q} \cdot \mathbf{m}'])(\mathbf{q} \cdot \mathbf{m}' - i[k, \mathbf{q} \cdot \mathbf{m}']) = \frac{1}{4}(k_2, k', j) r^2.$$
 (50)

With the help of (49) and (50) the transformation equations (46), (39), (40) may be put in the form (31), and give

$$\mu_{z} + i [j, \mu_{z}] = \frac{1}{2} j^{-\frac{1}{2}} (j_{2}^{2} - p^{2})^{\frac{1}{2}} (k, k', j_{2})^{\frac{1}{2}} e^{i\psi} j^{-\frac{1}{2}}$$

$$= \frac{1}{2} j^{-\frac{1}{2}} e^{i\psi} (j_{1}^{2} - p^{2})^{\frac{1}{2}} (k, k', j_{1})^{\frac{1}{2}} j^{-\frac{1}{2}}$$

$$\mu_{z} - i [j, \mu_{z}] = \frac{1}{2} j^{-\frac{1}{2}} (j_{1}^{2} - p^{2})^{\frac{1}{2}} (k, k', j_{1})^{\frac{1}{2}} e^{-i\psi} j^{-\frac{1}{2}}$$

$$= \frac{1}{2} j^{-\frac{1}{2}} e^{-i\psi} (j_{2}^{2} - p^{2})^{\frac{1}{2}} (k, k', j_{2})^{\frac{1}{2}} j^{-\frac{1}{2}}$$

$$(51)$$

and

$$\mathbf{q} \cdot \mathbf{m}' + i \left[k, \, \mathbf{q} \cdot \mathbf{m}' \right] = \frac{1}{2} r k^{-\frac{1}{2}} \left(k_2, \, k', \, j \right)^{\frac{1}{2}} e^{i\theta} k^{-\frac{1}{2}} = \frac{1}{2} r k^{-\frac{1}{2}} e^{i\theta} \left(k_1, \, k', j \right)^{\frac{1}{2}} k^{-\frac{1}{2}}$$

$$\mathbf{q} \cdot \mathbf{m}' - i \left[k, \, \mathbf{q} \cdot \mathbf{m}' \right] = \frac{1}{2} r k^{-\frac{1}{2}} (k_1, k', j)^{\frac{1}{2}} e^{-i\theta} k^{-\frac{1}{2}} = \frac{1}{2} r k^{-\frac{1}{2}} e^{-i\theta} (k_2, k', j)^{\frac{1}{2}} k^{-\frac{1}{2}}$$
with corresponding relations for θ' .

§ 7. Systems with more than Two Electrons.

The extension of the transformation to systems of more than two electrons may be made as on the classical theory, as explained in § 1. The M_x, M_y, M_z of the core form the m_x' , m_y' , m_z' of the whole system and the j of the core forms the k' of the whole system. A slight change must be made in the ψ of the core in order to change it into the θ' of the whole system, since the ψ of the core has to commute with the M_z of the core or m_z' of the whole system, while the θ' of the whole system need not do this, as m_z' is not an action variable, but must instead commute with the p and j of the whole system. This change is made by substituting for μ_z in the defining equation (46) the scalar product of the (μ_x, μ_y, μ_z) of the core and the (m_x, m_y, m_z) of the outer electron, in the same way in which the definition of 0 was changed on passing from the case of one electron to the case of two electrons by substituting \mathbf{q} . \mathbf{m}' for the z in (29). This change also makes θ' invariant under the transformation (1), while the ψ of the core was not. On the classical theory the geometric meaning of the change is that the \(\psi\) of the core is its azimuth about the direction of the j of the core measured from the plane containing this j and the z axis, while the θ' of the whole system is the same azimuth, but measured from the plane containing the j of the core and the j of the whole system.

There are alternative ways of treating the system of more than two electrons, as one may add the angular momenta together according to different plans; for instance, one could first add the angular momenta of the two outer electrons, and then add this sum to the resultant angular momentum of the remaining ones. The suitability of the different methods depends on the relative importance of the different perturbation terms in the Hamiltonian. The action variables (except p) are always related to the magnitudes of angular momenta by

equations of the type (17) and (20), while the method of § 4 can always be used to find the angle variables.

§ 8. Applications. The Boundary Values of the Action Variables.

The applications which are now to be made are valid only when the Hamiltonian is such that the k, k', j, p are the true action variables or approximately so.

To obtain physical results from the present theory one must substitute for the action variables a set of c-numbers which may be regarded as fixing a stationary state. The different c-numbers which a particular action variable may take form an arithmetical progression with constant difference h, which must usually be bounded, in one direction at least, in order that the system may have a normal state. All the terms in the Fourier expansions of the Cartesian co-ordinates that correspond to transitions from a stationary state inside the boundary to one outside must vanish. It may seem that these conditions are difficult to satisfy, and that in general there would be no way of choosing the arithmetical progression to satisfy them. In practice it appears to be a general rule that the conditions can be satisfied in a way of which the following example is typical.

Suppose that w is an angle variable and J the conjugate action variable, and that wherever e^{iw} occurs in the transformation equations it has immediately in front of it the factor (J_2-c) , where c is a c-number, and wherever e^{-iw} occurs it has immediately behind it the factor (J_2-c) , which is equivalent to the factor (J_1-c) immediately in front. Then we take J to have the series of values $c+\frac{1}{2}h$, $c+\frac{3}{2}h$, $c+\frac{5}{2}h$, ..., which terminates at $(c+\frac{1}{2}h)$. The amplitude related to $(c+\frac{1}{2}h, c-\frac{1}{2}h)$ is given by one putting $J=c+\frac{1}{2}h$ in the coefficient in front of e^{iw} or in the coefficient behind e^{-iw} , and therefore vanishes on account of the factor (J_2-c) . The amplitudes related to $(c+\frac{1}{2}h, c-\frac{3}{2}h)$ and $(c+\frac{3}{2}h, c-\frac{1}{2}h)$ are given by one putting $J=c+\frac{1}{2}h$ and $J=c+\frac{3}{2}h$ in the coefficient in front of e^{2iw} , or the coefficient behind e^{-2iw} . Now e^{2iw} can occur only through

 $\{(\mathbf{J}_2 - e) e^{iw}\}^2 = (\mathbf{J}_2 - c) e^{iw} (\mathbf{J}_2 - c) e^{iw} = (\mathbf{J} - c - \frac{1}{2}h) (\mathbf{J} - c - \frac{3}{2}h) e^{2iw},$ so that its coefficient vanishes when $\mathbf{J} = c + \frac{1}{2}h$ or $c + \frac{3}{2}h$, and similarly e^{-2iw} can occur only through

$$\{e^{-iw}(\mathbf{J}_2-c)\}^2 = e^{-2iw}(\mathbf{J}-c-\tfrac{1}{2}h)(\mathbf{J}-c-\tfrac{3}{2}h).$$

In the same way e3iw can occur only through

$$\{(J_2-c)e^{iw}\}^3 = (J-c-\frac{1}{2}h)(J-c-\frac{5}{2}h)(J-c-\frac{5}{2}h)e^{3iw},$$

and its coefficient vanishes when $J=c+\frac{1}{2}h$, $c+\frac{3}{2}h$, or $c+\frac{5}{2}h$, and so on. Thus all the amplitudes in the Fourier expansions that are related to a value of J greater than c and a value less than c vanish, which justifies the series we have chosen for J. We could equally well have taken the series $c-\frac{1}{2}h$, $c-\frac{3}{2}h$, $c-\frac{5}{2}h$, We may call the value J=c the boundary value of either series.

In the same way when there is more than one action variable, J and J' say, if e^{iw} is always preceded in the transformation equations by a coefficient with the factor $f(J_2, J')$, and e^{-iw} is preceded by $f(J_1, J')$ we may take f(J, J') = 0 to be a boundary value for J. This equation, though, may also be considered as fixing a boundary value for J', and it is therefore necessary that the factor $f(J, J_2')$ should always occur in front of $e^{iw'}$ and $f(J, J_1')$ in front of e^{-iw} .

Now consider (32) and (36), the transformation equations that involve the angle variables for the system with a single electron. We see that $e^{i\phi}$ is preceded by the factors $(j-p_2)^{\frac{1}{2}}$, $(j+p_2)^{\frac{1}{2}}$, which are the same as $(k-p_2)^{\frac{1}{2}}$, $(k+p_2)^{\frac{1}{2}}$, and $e^{i\phi}$ by $(k-p_1)^{\frac{1}{2}}$, $(k+p_1)^{\frac{1}{2}}$, and, further, that $e^{i\theta}$ is preceded by $(k_2-p)^{\frac{1}{2}}$, $(k_2+p)^{\frac{1}{2}}$ and $e^{-i\theta}$ by $(k_1-p)^{\frac{1}{2}}$, $(k_1+p)^{\frac{1}{2}}$. All the conditions are therefore satisfied for k-p=0 and k+p=0 to be boundary values of the action variables. Hence for a given k, p takes the 2 |k| values ranging from $|k|-\frac{1}{2}h$ to $-|k|+\frac{1}{2}h$. It may be shown that k takes half integral quantum values when the central field consists of an inverse square field of force with a small inverse cube field of force superposed (with non-relativity mechanics), and thus has the values $\pm \frac{1}{2}h$, $\pm \frac{3}{2}h$, $\pm \frac{5}{2}h$..., corresponding to the S, P, D... terms of spectroscopy. There will thus be 1, 3, 5... stationary states for S, P, D... terms when the system has been made non-degenerate by a magnetic field, in agreement with observation for singlet spectra.

We have already shown the selection rules for k and p. It remains to be proved that transitions from $k = \frac{1}{2}h$ to $k = -\frac{1}{2}h$ cannot occur, as these would appear experimentally as $S \to S$ transitions. When k is $\pm \frac{1}{2}h$, the only possible value for p is zero, so that we have to consider only transitions for which p does not change. From (36) or (38) we see that the coefficient in front of $e^{i\theta}$ in the Fourier expansion of z vanishes when one puts $k = \frac{1}{2}h$, p = 0, so that the transition $k = \frac{1}{2}h$ to $k = -\frac{1}{2}h$ cannot occur.

For a system with two or more electrons, we see from equations (32) and (51) that $j \pm p = 0$ are boundary values for j and p, and from equations (51), (52) and the equations corresponding to (52) for θ' , that $k \pm k' \pm j = 0$ are boundary values for k, k' and j. Hence p takes the values from $|j| - \frac{1}{2}h$ to $-|j| + \frac{1}{2}h$,

while j takes the values, when k and k' are positive, from $k + k' - \frac{1}{2}h$ to $|k - k'| + \frac{1}{2}h$, in agreement with experiment. This rule applies generally for the addition of any two angular momenta.

The transition $k = \frac{1}{2}h$ to $k = -\frac{1}{2}h$ is still forbidden, since when $k = \pm \frac{1}{2}h$, j can take only the value k', so that j cannot change during this transition, and from (52) the coefficient in front of $e^{i\theta}$ vanishes when one puts $k = \frac{1}{2}h$, j = k', on account of the factors $(k_2 + k' - j)^{\frac{1}{2}}$ or $(k_2 - k' + j)^{\frac{1}{2}}$.

§ 9. The Anomalous Zeeman Effect.

The present theory does not give any explanation of those atomic phenomena that come under the heading of duplexity, namely, the peculiar relationships of the relativity and screening doublets in the X-ray spectra, the branching rule of spectroscopy, and the anomalous Zeeman effect. If, however, one adopts the usual model of the atom, consisting of a normal series electron and a core in which the ratio of magnetic moment to mechanical angular momentum is double the normal Lorentz value, then the present theory gives the correct g-formula for the energy of the stationary states in a weak magnetic field without further assumption.

The energy of the atom in a magnetic field in the direction of the z-axis is proportional, with this model, to

$$m_z + 2m_z' = M_z + m_z'$$

instead of to M_z , as with the normal model. If the field is weak we may use perturbation theory, according to which the change in energy of the stationary states is given, to the first order, by the constant term in the Fourier expansion of the energy of the perturbation in terms of the uniformising variables for the undisturbed system. We must therefore obtain the constant term in the Fourier expansion of $(M_z + m_z')$ in terms of the θ , θ' , ϕ and ψ . We have from (45) and (41)

$$\begin{split} j\left[j,\,\mu_{z}\right] &= \mathrm{M}_{y}\left(\mathrm{M}_{y}m_{z}' - m_{y}'\mathrm{M}_{z}\right) - \mathrm{M}_{x}\left(m_{x}'\mathrm{M}_{z} - \mathrm{M}_{x}m_{z}'\right) + \frac{1}{2}ih\mu_{z} \\ &= \left(\mathrm{M}_{x}^{2} + \mathrm{M}_{y}^{2} + \mathrm{M}_{z}^{2}\right)m_{z}' - \left(\mathrm{M}_{x}m_{x}' + \mathrm{M}_{y}\,m_{y}' + \mathrm{M}_{z}\,m_{z}'\right)\mathrm{M}_{z} + \frac{1}{2}ih\mu_{z}. \end{split}$$

From equations (51) the Fourier expansions of μ_z and $[j, \mu_z]$ contain no constant terms. Hence the constant term in the expansion of m_z' is

$$rac{{{
m M}_x}{m_x}^{'}+{{
m M}_y}{m_y}^{'}+{{
m M}_z}{m_z}^{'}}{{{
m M}_x}^2+{{
m M}_y}^2+{{
m M}_z}^2}{{
m M}_z}=rac{k_1^{'}k_2^{'}+rac{1}{2}\left(j_1j_2-k_1k_2-k_1^{'}k_2^{'}
ight)}{j_1j_2}{
m M}_z,$$

using (48), and the constant term in the expansion of $M_z + m_z'$ is

$$\left(1 + \frac{1}{2} \frac{j_1 j_2 - k_1 k_2 + k_1' k_2'}{j_1 j_2}\right) M_z.$$

The coefficient of M_z in this expression is the g-value, and agrees with Landé's formula.*

§ 10. The Relative Intensities of the Lines of a Multiplet.

The amplitude of vibration of an atom corresponding to transitions from the state $J_r = n_r h$ to the state $J_r = (n_r - \alpha_r) h$ is obtained by one putting $J_r = n_r h$ in the coefficient in front of exp. $i \Sigma \alpha_r w_r$ in the Fourier expansion of the total polarisation of the atom, or by putting $J_r = (n_r - \alpha_r) h$ in the coefficient behind this exponential. We cannot actually determine the amplitudes at present because we do not know the action and angle variables corresponding to the r's and p_r 's. If, however, we assume that the Fourier expansion of r does not involve p, j, ϕ or ψ , then when x/r, y/r, z/r are expanded as Fourier series in $e^{i\phi}$, $e^{i\psi}$, the ratios of the coefficients will give the ratios of the corresponding amplitudes. We can thus determine the relative intensities of the lines of a multiplet and of the components into which these lines are split in a weak magnetic field. \dagger

For the case of a system with a single electron, equations (38) give at once the relative amplitudes of the components in a magnetic field. For the case of the core-series electron atom we must obtain the Fourier expansions of x, y, z from (32), (51) and (52). It is convenient to introduce the quantities

$$\begin{split} &\lambda_x = \, \mathrm{M}_y z - y \mathrm{M}_z = z \mathrm{M}_y - \mathrm{M}_z y = \mathrm{M}_y z - \mathrm{M}_z y - i h x \\ &\lambda_y = \, \mathrm{M}_z x - z \mathrm{M}_x = x \mathrm{M}_z - \mathrm{M}_x \, z = \mathrm{M}_z x - \mathrm{M}_z z - i h y \\ &\lambda_z = \, \mathrm{M}_z y - x \mathrm{M}_y = y \mathrm{M}_x - \mathrm{M}_y x = \mathrm{M}_x y - \mathrm{M}_y x - i h z \end{split}$$

We have

$$\mathbf{M}_{x}\lambda_{x} + \mathbf{M}_{y}\lambda_{y} + \mathbf{M}_{z}\lambda_{z} = \sum_{xyz} \left\{ (\mathbf{M}_{z}\mathbf{M}_{y} - \mathbf{M}_{y} \mathbf{M}_{x})z - ih\mathbf{M}_{z}z \right\} = 0$$
 (53)

and

$$[M_z, \lambda_x] = [M_z, M_y z - y M_z] = -M_x z + x M_z = \lambda_y$$

$$[M_z, \lambda_y] = [M_z, M_z x - z M_x] = M_z y - z M_y = -\lambda_x$$
(54)

$$[M_z, \lambda_z] = [M_z, M_x y - x M_y] = M_y y - M_x x - y M_y + x M_x \Rightarrow 0.$$
 (55)

The relations (53), (54), (55) between the λ 's and M's correspond exactly to the relations (4), (5), (6) between the x, y, z and m's or relations (44), (42), (43) between the μ 's and M's. We can therefore apply results deduced from (4), (5), (6) directly to the λ 's. We thus obtain, corresponding to (33) or (45)

$$j[j, \lambda_z] = M_y \lambda_x - M_x \lambda_y + \frac{1}{2} i h \lambda_z, \tag{56}$$

^{*} Landé, 'Zeits. f. Phys.,' vol. 15, p. 189 (1923).

[†] The relative intensities of the components of a line in a magnetic field have been obtained by Born, Heisenberg and Jordan (loc. cit.) by their matrix method.

and also we can take λ_x , λ_y , λ_z to be the ξ , η , ζ of equation (34) and can write μ_x , μ_y , μ_z for x, y, z, provided we replace m_x , m_y , m_z , k by M_x , M_y , M_z , j. This gives

$$j (j - h) (\mu_z + i [j, \mu_z]) (\lambda_z - i [j, \lambda_z])$$

$$= (j_2^2 - p^2) (\mu_x \lambda_x + \mu_y \lambda_y + \mu_z \lambda_z) + ih M_z (\mu_x \lambda_y - \mu_y \lambda_x)$$

$$- i j_2 \{ M_x (\mu_y \lambda_z - \mu_z \lambda_y) + M_y (\mu_z \lambda_x - \mu_x \lambda_z) \}.$$
 (57)

Now

$$\begin{split} \mu_x \lambda_x + \mu_y \lambda_y + \mu_z \lambda_z &= \Sigma_{xyz} \left(m_z' m_y - m_y' m_z \right) \left(\mathbf{M}_y z - \mathbf{M}_z y - i h x \right) \\ &= \Sigma_{xyz} \left\{ \left(m_z' m_y - m_y' m_z \right) \; \mathbf{M}_y - \left(m_x' m_z - m_z' m_x \right) \; \mathbf{M}_x \\ &- i h \; (m_y' m_x - m_x' m_y) \right\} z \\ &= \Sigma_{xyz} \left\{ m_z' \left(m_x \mathbf{M}_x + m_y \mathbf{M}_y + m_z \mathbf{M}_z \right) \\ &- \left(m_x' \; \mathbf{M}_x + m_y' \; \mathbf{M}_y + m_z' \; \mathbf{M}_z \right) m_z \right\} z \\ &= \Sigma_{xyz} \left\{ \left(m_x \mathbf{M}_x + m_y \mathbf{M}_y + m_z \mathbf{M}_z \right) \; m_z' \\ &+ m_x \left(m_z' \mathbf{M}_x - \mathbf{M}_x m_z' \right) + m_y \left(m_z' \mathbf{M}_y - \mathbf{M}_y m_z' \right) \right\} z \\ &= \mathbf{m} \cdot \mathbf{M} \quad \mathbf{m}' \cdot \mathbf{q} + i h \; \mu \cdot \mathbf{q}. \end{split}$$

Also

$$\begin{split} \mu_{x}\lambda_{y} - \mu_{y}\lambda_{x} &= \mu_{x} \left(xM_{z} - M_{x}z\right) - \mu_{y} \left(M_{y}z - yM_{z}\right) \\ &= \left(\mu_{x}x + \mu_{y}y + \mu_{z}z\right)M_{z} - \left(\mu_{x}M_{x} + \mu_{y}M_{y} + \mu_{z}M_{z}\right)z \\ &= \mu \cdot qM_{z}, \end{split}$$

and similarly

$$\mu_{\mathbf{v}}\lambda_{\mathbf{z}} - \mu_{\mathbf{z}}\lambda_{\mathbf{v}} = \boldsymbol{\mu} \cdot \mathbf{q}\mathbf{M}_{\mathbf{x}}$$

$$\mu_{\mathbf{z}}\lambda_{\mathbf{z}} - \mu_{\mathbf{z}}\lambda_{\mathbf{z}} = \boldsymbol{\mu} \cdot \mathbf{q}\mathbf{M}_{\mathbf{v}},$$

while

$$\boldsymbol{\mu}$$
 . $\mathbf{q} = \sum_{xyz} (m_y m_z' - m_z m_y') x = \sum_{xyz} (m_y x - m_x y) m_z'$
= $k [k, \mathbf{q} \cdot \mathbf{m}'] - \frac{1}{2} i h \mathbf{q} \cdot \mathbf{m}'$

from (33). Using these results and the fact that M_x , M_y , M_z commute with μ . q (since they commute with k and with q. m'), equation (57) becomes

$$\begin{split} j \left(j - h \right) \left(\mu_z + i \left[j, \, \mu_z \right] \right) \left(\lambda_z - i \left[j, \, \lambda_z \right] \right) \\ &= \left(j_2{}^2 - p^2 \right) \left(\mathbf{m} \cdot \mathbf{M} \cdot \mathbf{q} \cdot \mathbf{m'} + i h \boldsymbol{\mu} \cdot \mathbf{q} \right) + i \left\{ h \mathbf{M}_z{}^2 - j_2 \left(\mathbf{M}_z{}^2 + \mathbf{M}_y{}^2 \right) \right\} \boldsymbol{\mu} \cdot \mathbf{q} \\ &= \left(j_2{}^2 - p^2 \right) \left(\mathbf{m} \cdot \mathbf{M} \cdot \mathbf{q} \cdot \mathbf{m'} + i h \boldsymbol{\mu} \cdot \mathbf{q} - i j_1 \boldsymbol{\mu} \cdot \mathbf{q} \right) \\ &= \frac{1}{2} \left(j_2{}^2 - p^2 \right) \left\{ \left(j_1 j_2 + k^2 - k'^2 \right) \mathbf{q} \cdot \mathbf{m'} \right. \\ &\qquad \qquad \left. - 2 i j_2 \left(k \left[k, \, \mathbf{q} \cdot \mathbf{m'} \right] - \frac{1}{2} i h \mathbf{q} \cdot \mathbf{m'} \right) \right\} \\ &= \frac{1}{4} \left(j_2{}^2 - p^2 \right) \left\{ \left(k + k' + j_2 \right) \left(k - k' + j_2 \right) \left(\mathbf{q} \cdot \mathbf{m'} - i \left[k, \, \mathbf{q} \cdot \mathbf{m'} \right] \right) \right\}. \end{split}$$

Now substitute for $\mu_z + i[j, \mu_z]$, $\mathbf{q} \cdot \mathbf{m}' - i[k, \mathbf{q} \cdot \mathbf{m}']$ and $\mathbf{q} \cdot \mathbf{m}' + i[k, \mathbf{q} \cdot \mathbf{m}']$ their values given by (51) and (52).

After cancelling certain factors and taking the $e^{i\psi}$ over to the right-hand side, we obtain

$$\lambda_{z} - i[j, \lambda_{z}] = r \frac{(j_{1}^{2} - p^{2})^{\frac{1}{2}} j_{1}^{\frac{1}{2}}}{j^{\frac{1}{2}} (j+h)^{\frac{1}{2}}} \{ \mathbf{F}_{+1} e^{-i(\theta+\psi)} - \mathbf{F}_{+1}' e^{i(\theta-\psi)} \}, \quad (58)$$

where

$$\begin{split} \mathbf{F}_{+1} &= \tfrac{1}{4} \, (k + k' + j + \tfrac{1}{2}h)^{\frac{1}{2}} \, (k - k' + j + \tfrac{1}{2}h)^{\frac{1}{2}} \, (k + k' + j + \tfrac{3}{2}h)^{\frac{1}{2}} \, (k - k' + j + \tfrac{3}{2}h)^{\frac{1}{2}} \\ & \div \, (j + \tfrac{1}{2}h)^{\frac{1}{2}} \, k^{\frac{1}{2}} \, (k + h)^{\frac{1}{2}}, \\ \mathbf{F}_{+1}' &= \tfrac{1}{4} \, (k + k' - j - \tfrac{1}{2}h)^{\frac{1}{2}} \, (-k + k' + j + \tfrac{1}{2}h)^{\frac{1}{2}} \, (k + k' - j - \tfrac{3}{2}h)^{\frac{1}{2}} \, (-k + k' + j + \tfrac{3}{2}h)^{\frac{1}{2}} \\ & \div \, (j + \tfrac{1}{2}h)^{\frac{1}{2}} \, k^{\frac{1}{2}} \, (k - h)^{\frac{1}{2}} \end{split}$$

Similarly it may be shown that

$$\lambda_z + i [j, \lambda_z] = r \frac{(j_2^2 - p^2)^{\frac{1}{2}} j_2^{\frac{1}{2}}}{j^{\frac{1}{2}} (j+h)^{\frac{1}{2}}} \{ F_{-1}' e^{i(\theta+\psi)} - F_{-1} e^{-i(\theta-\psi)} \}$$
 (59)

where F_{-1} , F_{-1} are the quantities obtained by writing -h for h in F_{+1} , F_{+1} , respectively. Also from (52)

$$\mathbf{q} \cdot \mathbf{m}' = r (j_1 j_2 / j)^{\frac{1}{2}} (\mathbf{F}_0 e^{-i\theta} + \mathbf{F}_0' e^{i\theta})$$
 (60)

where

$$\begin{split} \mathbf{F}_0 &= \tfrac{1}{4} j^{\frac{1}{4}} (k + k' + j + \tfrac{1}{2} h)^{\frac{1}{4}} (k + k' - j + \tfrac{1}{2} h)^{\frac{1}{4}} (k - k' + j + \tfrac{1}{2} h)^{\frac{1}{4}} (-k + k' + j - \tfrac{1}{2} h)^{\frac{1}{4}} \\ & \div j_1^{\frac{1}{4}} j_2^{\frac{1}{4}} k^{\frac{1}{4}} (k + h)^{\frac{1}{4}} \end{split}$$

and F_0 is the quantity obtained by writing -h for h in F_0 . From (56)

$$egin{aligned} j\left[j,\,\lambda_{z}
ight] &= \mathrm{M}_{y}\left(\mathrm{M}_{y}z - y\mathrm{M}_{z}\right) - \mathrm{M}_{x}\left(x\mathrm{M}_{z} - \mathrm{M}_{x}z\right) + rac{1}{2}ih\lambda_{z} \ &= \left(\mathrm{M}_{x}^{2} + \mathrm{M}_{y}^{2} + \mathrm{M}_{z}^{2}\right)z - \left(\mathrm{M}_{x}x + \mathrm{M}_{y}y + \mathrm{M}_{z}z\right)\mathrm{M}_{z} + rac{1}{2}ih\lambda_{z}. \end{aligned}$$

Hence

$$j_1j_2z = \mathbf{q} \cdot \mathbf{m}' p - \frac{1}{2}ih\lambda_z + j[j, \lambda_z].$$

or

$$z = \frac{p}{j_1 j_2} \mathbf{q} \cdot \mathbf{m}' + \frac{1}{2} i \frac{1}{j_1} (\lambda_z - i [j, \lambda_z]) - \frac{1}{2} i \frac{1}{j_2} (\lambda_z + i [j, \lambda_z]).$$
 (61)

Also we have

$$\begin{split} (x+iy)\left(\mathbf{M}_{x}-i\mathbf{M}_{y}\right) &= x\mathbf{M}_{x}+y\mathbf{M}_{y}+i\left(y\mathbf{M}_{x}-x\mathbf{M}_{y}\right)\\ &= \mathbf{q}\cdot\mathbf{m}'-pz+i\left(\lambda_{z}-ihz\right)\\ &= \frac{j_{1}j_{2}-p\left(p-h\right)}{j_{1}j_{2}}\mathbf{q}\cdot\mathbf{m}'+\frac{1}{2}i\frac{j_{1}-(p-h)}{j_{1}}(\lambda_{z}-i\left[j,\lambda_{z}\right])\\ &+\frac{1}{2}i\frac{j_{2}+p-h}{j_{2}}(\lambda_{z}+i\left[j,\lambda_{z}\right]) \end{split}$$

using (61). Now take the factor $(M_x - iM_y)$ over to the right-hand side, and substitute for $(M_x - iM_y)^{-1}$ its value from equations (32), namely, $(j^2 - p_2^2)^{-\frac{1}{2}} e^{i\phi}$. The result after rearrangement of the factors is

$$x + iy = \left\{ \frac{(j^2 - p_2^2)^{\frac{1}{2}}}{(j^2 - \frac{1}{4}h^2)} \mathbf{q} \cdot \mathbf{m}' + \frac{1}{2}i \frac{(j - p + \frac{3}{2}h)^{\frac{1}{2}}}{j_1(j + p + \frac{1}{2}h)^{\frac{1}{2}}} (\lambda_z - i[j, \lambda_z]) + \frac{1}{2}i \frac{(j + p - \frac{3}{2}h)^{\frac{1}{2}}}{j_2(j - p - \frac{1}{2}h)^{\frac{1}{2}}} (\lambda_z + i[j, \lambda_z]) \right\} e^{i\phi}.$$
(62)

To obtain the Fourier expansions of x/r, y/r, z/r it is now only necessary to substitute for the factors $\mathbf{q} \cdot \mathbf{m}'$, $\lambda_z - i [j, \lambda_z]$, and $\lambda_z + i [j, \lambda_z]$ in (61) and (62), their values given by (60), (58) and (59). The ratios of the amplitudes obtained in this way are in complete agreement with those previously obtained by Kronig and others* by means of certain special assumptions, and in agreement with experiment. The F_{+1} , F_{-1} , F_0 of the present paper are proportional to the square roots of Kronig's F_{+1} , F_{-1} , $\frac{1}{2}F_0$.

My thanks are due to Mr. R. H. Fowler, F.R.S., for his criticism and help in the writing of this paper.

Summary.

The new quantum mechanics which involves non-commutative algebra is applied to the problem of a number of electrons moving in an approximately central field of force, a contact transformation being obtained to a set of variables which includes the k for each electron and the j of the whole system. It is found that each k is not equal to m, the magnitude of the angular momentum of the electron, as on the classical theory, but must be related to m by the formula $m^2 = (k + \frac{1}{2}h)$ $(k - \frac{1}{2}h)$, and a similar relation holds between j and the resultant angular momentum of the whole system.

It is shown that the theory gives the correct boundary values for the j of the resultant of two angular momenta whose k's are given, and also gives the correct g-formula for the energy levels of an atom in a weak magnetic field on the assumption of the usual magnetic anomaly of the core of the atom. The theory also gives Kronig's results for the relative intensities of the lines of a multiplet and their components in a weak magnetic field.

^{*} Kronig, 'Zeits. f. Phys.,' vol. 31, p. 885 (1925); Sommerfeld and Hönl, 'Sitz. d. Preuss. Akademie,' p. 141 (1925); Russell, 'Proc. Nat. Academy Sciences, U.S.A.,' vol. 11, p. 314 (1925).