Received January 17, 1926

16

ON THE HYDROGEN SPECTRUM FROM THE STANDPOINT OF THE NEW QUANTUM MECHANICS

W. PAULI JR

It is shown that the Balmer terms of an atom with a single electron are yielded correctly by the new quantum mechanics and that the difficulties (particularly evident in the case of crossed fields) which arose in the earlier theory through the extra prohibition of singularities in the motion, disappear in the new theory. The influence of external electric and magnetic fields of force, too, on the hydrogen spectrum is discussed from the standpoint of the new quantum mechanics. However, relativistic corrections have not been taken into account and the calculation of transition probabilities (intensities) has for the present been omitted from consideration.

1. The fundamentals of the new quantum mechanics

Heisenberg[1] has recently published a formulation of the principles of quantum theory which represents a considerable advance over the previous theory of multiply-periodic systems. Heisenberg's form of quantum theory completely avoids a mechanical-kinematic visualization of the motion of electrons in the stationary states of an atom. Apart from time averages of classical kinematic quantities, only harmonic partial vibrations are introduced, which are associated with each transition between two stationary states and which are directly related to the spontaneous transition probabilities of the system. If

$$x_m^n = a_m^n \exp\left[2\pi i(\nu_m^n t + \delta_m^n)\right]$$

is the partial vibration of the Cartesian coordinate x of a given electron in an atom, associated with the transition from a state n to another state m, then it contributes an amount

$$\frac{1}{h\nu_m^n}\,\frac{2}{3}\,\frac{e^2}{c^3}\,(2\pi\nu_m^n)^4\,|x_m^n|^2\cdot 2$$

Editor's note. This paper was published as Zs. f. Phys. **36** (1926) 336–363.

[1] W. Heisenberg, Zs. f. Phys. **33** (1925) 879.

to the value of the coefficient of the spontaneous emission probability A^n_m belonging to this transition. Whereas in the earlier theory this relation could, according to the correspondence principle, be regarded only as asymptotically valid in the limit of large quantum numbers, it can now be taken as a universally valid definition of the amplitudes x^n_m. More generally, the partial vibrations assigned to each of the transition processes are physically defined by the intensity and polarization of the emitted radiation. These partial vibrations however can no longer be combined into definite 'orbits' of the atomic electrons, since they are assigned to transition processes, and not to stationary states.

Heisenberg's formulation of the quantum theory was further extended by Born and Jordan,[1] Dirac,[2] and Born, Heisenberg and Jordan.[3] A consistent mathematical system thus ensued, in which all relations formerly taken from classical mechanics were replaced by analogously constructed quantum-theoretical relations between the time averages x^n_n and the partial vibrations x^n_m of the coordinates of each of the atomic particles. In order to formulate these relations, it proved convenient to assign a matrix to each classical kinematic quantity x. The diagonal terms of such a matrix are the time averages x^n_n belonging to the individual stationary states, and the (n, m) and (m, n) elements (nth row, mth column, and mth row, nth column, respectively) are complex conjugate vibrations

$$x^n_m = a^n_m \exp\,[2\pi \mathrm{i}(\nu^m_n t + \delta^n_m)] \quad \text{and} \quad x^m_n = a^m_n \exp\,[2\pi \mathrm{i}(\nu^m_n t + \delta^m_n)], \qquad (1)$$

with a^n_m (equal to a^n_m) positive and real, and

$$\nu^m_n = -\,\nu^n_m, \qquad \delta^m_n = -\,\delta^n_m. \qquad (2)$$

The harmonic vibration x^m_n belongs to the transition from m to n and the harmonic vibration x^n_m to the reverse transition from n to m, so that one of these transitions betokens an emission, and the other an absorption.

To the time derivative $\dot{x}$ we assign the matrix whose individual elements are time derivatives of the corresponding elements of the matrix $\boldsymbol{x}$, i.e.,

$$\dot{x}^n_m = 2\pi \mathrm{i} \nu^n_m x^n_m. \qquad (3)$$

---

[1] M. Born and P. Jordan, Zs. f. Phys. **34** (1925) 858.

[2] P. A. M. Dirac, Proc. Roy. Soc. **109** (1925) 642.

[3] M. Born, W. Heisenberg and P. Jordan, Zs. f. Phys. **35** (1926) 557; hereafter quoted as 'Quantenmechanik II'.

In particular, we have $\dot{x}^n_n=0$, i.e., the diagonal terms of $\dot{x}$ vanish. Since $\nu^m_n=-\nu^n_m$, it also follows that $\dot{x}^n_m$ and $\dot{x}^m_n$ are conjugate complex (the matrices are Hermitian in character). To the energy E we have to assign a diagonal matrix, i.e., one whose off-diagonal terms vanish. The energy value of the quantum state characterized by the index n is given by $E_n=E^n_n$, whence follows the frequency condition,

$$h\nu^n_m = E^n_n - E^m_m, \tag{I}$$

in agreement with the above prescription $\nu^m_n=-\nu^n_m$, $\nu^n_n=0$.

The essential point, as stressed by Heisenberg, lies in the fact that the multiplication of two matrices x and y has now acquired a proper meaning, in view of the frequency condition. The product xy of the two matrices x and y is defined by

$$(xy)^n_m = \sum_l x^n_l y^l_m. \tag{4}$$

From (I) follows the combination rule

$$\nu^n_l + \nu^l_m = \nu^n_m, \tag{5}$$

and therefore the quantity $(xy)^n_m$ indeed again represents a harmonic vibration of frequency ν^n_m, if x^n_l and y^l_m are harmonic vibrations having frequencies ν^n_l and ν^l_m, respectively. For the phases δ^n_m, too, a combination rule

$$\delta^n_l + \delta^l_m = \delta^n_m \tag{6}$$

has to be assumed.

All the normal calculational rules apply to the multiplication of two matrices, with the exception of the commutation law: in general xy differs from yx. Thus, e.g., the difference $\mathsf{Ex}-\mathsf{xE}$ (where E denotes the diagonal energy matrix and products are to be formed according to the general prescription (4)) can be simply related to the matrix $\dot{\mathsf{x}}$, the time derivative of x:

$$\mathsf{Ex} - \mathsf{xE} = \frac{h}{2\pi i}\dot{\mathsf{x}}, \tag{7}$$

using (3) and the frequency condition (I). This relation holds for any arbitrary matrix x.

The requisite relations for calculating the matrices x for a given mechanical system, i.e., the basic physical laws of the new quantum mechanics, have been brought by Born and Jordan into the following form (which we immediately write down for systems having arbitrarily many degrees of freedom). We denote the Cartesian coordinates and the respective momenta of the atomic particles by q_ϱ and p_ϱ, $(\varrho=1\ldots f)$ with $p_x=m\dot{x}$, etc. Then, in addition to the frequency condition (I), we have the 'quantum conditions'

$$p_\varrho p_\sigma - p_\sigma p_\varrho = 0, \qquad q_\varrho q_\sigma - q_\sigma q_\varrho = 0,$$
$$p_\varrho q_\sigma - q_\sigma p_\varrho = \begin{cases} 0 & \text{for} \quad \varrho \neq \sigma, \\ \dfrac{h}{2\pi i}\cdot\mathbf{1} & \text{for} \quad \varrho = \sigma. \end{cases} \tag{II}$$

Here the symbol **1** denotes the unit matrix (whose off-diagonal terms vanish and whose diagonal terms are each equal to 1). As Kramers[1] has shown, these relations can be interpreted from the standpoint of the quantum-theoretical dispersion formulae of Ladenburg, Kramers, and Kramers and Heisenberg, if one postulates that the individual atomic particles behave as free particles with respect to external short-period forces. Finally, as the last of the quantum laws, one has the energy conservation law:

$$H(p, q) = E \ \text{(diagonal matrix)}. \tag{III}$$

The matrix function $H(p, q)$ characterizes a given mechanical system and the most obvious assumption to make is to expect this function to coincide formally with the classical function when Cartesian coordinates are used. It suffices to consider the case in which it comprises two parts, corresponding to kinetic and potential energy, of which the one depends only on p and the other only on q. According to the multiplication rule (4), only those matrix functions are defined in the first instance which can be written in form of a power series in p and q (with positive and negative powers). Born, Heisenberg and Jordan have shown that in this case the basic laws (I), (II) and (III) lead to matrix relations that are completely analogous to the equations of motion in classical mechanics. They can be written as

$$\dot{q}_\varrho = \frac{\partial H(p, q)}{\partial p_\varrho}, \qquad \dot{p}_\varrho = -\frac{\partial H(p, q)}{\partial q_\varrho}, \tag{8}$$

by appropriately defining the partial differential coefficients which occur on the right-hand side.

---

[1] H. A. Kramers, Physica **5** (1925) 369.

It may further be remarked that the sequence in which the stationary states of the system under consideration are arranged within the matrices is immaterial and that in the new theory the concept of 'quantum number' does not enter into the basic laws. Furthermore, in the new theory, by contrast with the treatment used hitherto, the values of the transition probabilities are in principle quantitatively determined even for small quantum numbers.

2. General survey of methods and results of subsequent calculations

The present paper sets out to apply the new theory to an atom having a single electron. However, up to the present we have not, in the case of such a hydrogen-like atom, succeeded in developing all the consequences of the basic laws of the new theory, and in particular we have not yet attempted to evaluate transition probabilities for hydrogen-like spectra. We have confined ourselves to calculation of the energy values of stationary states of the hydrogen atom for the unperturbed case, and for the case where external electric and magnetic fields are present (with elimination of the transition probabilities). The relativistic correction terms have for the present not been taken into consideration. As a result, the terms of the Balmer series and the Stark effect are obtained in agreement with observation. Furthermore, difficulties disappear which had arisen in the old theory through the additional exclusion of singular motions in which the electron comes arbitrarily near the nucleus, and which became particularly evident for the case of crossed electric and magnetic fields. In view of this, we explain these difficulties in some detail.

We start by considering the case of parallel electric and magnetic fields. With e and m_0 as the electron charge and mass, Ze the nuclear charge, a the semi-axis of the electron orbit and F and H the field strengths of the electric and magnetic fields, respectively, the Larmor frequency is given by

$$o_H = \frac{eH}{4\pi m_0 c}, \tag{9}$$

and the secular Stark effect frequency, o_F, by

$$o_F = \frac{3}{4\pi}\sqrt{\frac{a}{Zm_0}}\,F = \frac{3}{2}\,eF\,\frac{a_1}{h}\,n, \tag{10}$$

where the quantity a_1, given by

$$a_1 = \frac{h^2}{4\pi^2 Ze^2 m_0},$$

represents the radius of the circular first quantum orbit in the atom. In the presence of external fields, we have two additional quantum conditions which fix the projection z of the distance of the orbit's electric midpoint from the nucleus along the field direction, viz.

$$z = \tfrac{3}{2}a(s/n), \tag{11}$$

and which fix the moment of momentum P_z parallel to the field, viz.

$$P_z = m(h/2\pi). \tag{12}$$

For given n and $|m| \leqq n$, the Stark-effect quantum number s here ranges over the sequence of values[1]

$$s = -(n-|m|), \quad -(n-|m|-2), \ldots, \quad (n-|m|-2), \quad n-|m|, \tag{13}$$

where $|m| \leqq n$, which lie symmetrically with respect to zero and differ by *two* units from one another (for the moment, we have ignored additional restrictions). The extra energy in presence of a field is then given by

$$E_1 = (so_F + mo_H)h. \tag{14}$$

In generalizing this to the case of crossed fields, it is appropriate to introduce frequencies

$$\omega_1 = o_H + o_F, \qquad \omega_2 = |o_H - o_F|$$

in place of o_F and o_H. The relations (13) and (14) are then equivalent to

$$E_1 = (\tfrac{1}{2}n - n_1)\omega_1 h + (\tfrac{1}{2}n - n_2)\omega_2 h \tag{15}$$

with

$$0 \leqq n_1 \leqq n, \qquad 0 \leqq n_2 \leqq n. \tag{16}$$

Since ω_1 and ω_2 are always defined as positive quantities, i.e.,

$$\begin{aligned} \omega_2 &= o_H - o_F \quad \text{for} \quad o_H > o_F, \\ \omega_2 &= o_F - o_H \quad \text{for} \quad o_H < o_F, \end{aligned}$$

---

[1] This follows from the connection between s and n with the quantum numbers n_ξ, n_η of the parabolic coordinates ξ, η, viz.

$$n = n_\xi + n_\eta + |m|, \qquad s = n_\xi - n_\eta,$$
$$0 \leqq n_\xi \leqq n, \qquad 0 \leqq n_\eta \leqq n.$$

the connection between the numbers s and m, and the numbers n_1 and n_2, is given by

$$\begin{aligned} m &= n - (n_1 + n_2), \qquad & s &= n_2 - n_1 \quad \text{for} \quad o_H > o_F, \\ m &= n_2 - n_1, & s &= n - (n_1 + n_2) \quad \text{for} \quad o_H < o_F) \end{aligned} \tag{17}$$

(for $o_H = o_F$ it follows that $\omega_2 = 0$, and the system is degenerate).

Now, in the general case of crossed electric and magnetic fields, the results of Klein[1] and Lenz[2] imply that the expression (15) for the perturbation energy in the quantum states of the system remains valid provided the frequencies ω_1 and ω_2 are defined as follows. We take $\mathfrak{o}_F$ and $\mathfrak{o}_H$ to be *vectors* parallel to the directions of the applied electric and magnetic fields, respectively, whose magnitudes coincide with the secular frequencies (10) or (9) which would be produced by either of these fields alone. We then form the *vectorial* sum and difference of $\mathfrak{o}_F$ and $\mathfrak{o}_H$, and take the respective moduli, to obtain

$$\omega_1 = |\mathfrak{o}_H + \mathfrak{o}_F|, \qquad \omega_2 = |\mathfrak{o}_H - \mathfrak{o}_F|. \tag{18}$$

For parallel electric and magnetic fields, this agrees with the earlier prescription.

This result leads to considerable difficulties if one relates it to the exclusion of such orbits as would cause the electron either to fall into the nucleus or to come arbitrarily near it in the course of its motion. The first of such additional exclusion rules already appeared in Sommerfeld's relativistic theory of fine structure. There, states with vanishing momentum quantum number k, in which the electron would oscillate forwards and backwards along a rectilinear path through the centre of the nucleus, had to be excluded as unsuitable for stationary states:

$$k \neq 0. \tag{19}$$

Correspondingly, in the case of the Stark effect, the value $|s| = n$ of the Stark-effect quantum number represents such a rectilinear oscil-

---

[1] O. Klein, Zs. f. Phys. **22** (1924) 109.

[2] W. Lenz, Zs. f. Phys. **24** (1924) 197. The numbers designated as n_1 and n_2 in that paper are non-integers for odd n; with a common difference of one unit, they run from $-\frac{1}{2}n$ to $\frac{1}{2}n$, including the extreme values (if one adheres to the quantum rules for periodic systems).

latory motion, and empirically it is certain that it can never occur in reality:

$$|s| \neq n. \tag{20}$$

By comparing the number of relativistic fine-structure stationary states under the influence of weak axially-symmetric fields of force with that for the Stark effect, Bohr was able to demonstrate quite generally that all orbits with $m=0$ had to be excluded as well, because of the additional restriction (19) when applied to axially-symmetric fields. Incidentally, for such orbits the electron would in the case of the Stark effect approach the nucleus arbitrarily closely. Thus

$$m \neq 0. \tag{20$'$}$$

Condition (2) is contained in (20′) as a special case, since for $s=n$ the number m can only take the value zero, according to (13). Now, for crossed fields it is possible to carry orbits allowed as stationary states over continuously into orbits excluded by (20) or (20′). For this, one need merely carry out the following adiabatic process: Assume both fields to be parallel in the first instance and o_H to differ from o_F, e.g., $o_H > o_F$. Then, after having slowly rotated the field directions with respect to one another, reduce the magnetic field intensity until a point is reached when $|\mathfrak{o}_H| < |\mathfrak{o}_F|$; finally, re-align the fields parallel to one another. In this process, ω_1 and ω_2 always remain nonzero according to (18) and the quantum numbers n_1 and n_2 therefore retain the same values throughout. Since, however, initially $o_H > o_F$ and finally $o_H < o_F$, it follows from (17) that the process has the effect of transforming into each other states in which *the electric quantum number s and the magnetic quantum number m are interchanged.* In particular, the oscillatory orbit $s=n$, $m=0$ is converted into the circular orbit $s=0$, $m=n$, whose plane lies perpendicular to the field direction. It thus becomes apparent that the additional exclusion rules which have the effect of forbidding rectilinear oscillatory orbits cannot be consistently applied within the framework of a quantum theory of multiply-periodic systems.

The calculation carried out below (§ 5) now shows that special additional exclusion rules become superfluous in the new quantum mechanics, in which we have not conceived the stationary states as represented by particular electron orbits; hence the difficulties indicated above disappear automatically. Thus, for the nth quantum state of the unperturbed atom, with energy

$$E_n = -RhZ^2/n^2 \tag{21}$$

(R = Rydberg constant), we obtain once more the values (14) and (15) for the extra energy in presence of external parallel and of crossed electric and magnetic fields, respectively. The quantities o_H and o_F are again given by (9) and (10), and ω_1, ω_2 by (18). However, according to the new mechanics, n has to be replaced throughout by

$$n^* = n - 1 \tag{22}$$

in equations (13), (16) and (17). This value now acts as a maximum limit for the values of s, m and n_1, n_2, so that we now have

$$s = -(n^* - |m|), \quad -(n^* - |m| - 2), \ldots \quad (n^* - |m| - 2), \quad n^* - |m|, \quad \text{with} \quad |m| \leqq n^*, \tag{13*}$$

$$0 \leqq n_1 \leqq n^*, \quad 0 \leqq n_2 \leqq n^*, \tag{16*}$$

$$\left.\begin{aligned} m &= n^* - (n_1 + n_2), & s &= n_2 - n_1, & &\text{for} \quad o_H > o_F, \\ m &= n_2 - n_1, & s &= n^* - (n_1 + n_2), & &\text{for} \quad o_H < o_F. \end{aligned}\right\} \tag{17*}$$

In particular, we have for the Stark effect, according to (10) and (14),

$$E_1 = \tfrac{3}{2} eFa_1 ns, \quad \text{with} \quad 0 \leqq s \leqq n^*, \tag{23}$$

as demanded by experiment. Further, one sees that the set of values taken on by m and s is now entirely symmetric, as required by the above-mentioned adiabatic process for crossed fields.

When the degeneracy of the unperturbed atom is removed by an additional central field of force (e.g., the field arising from the relativistic corrections) and an external magnetic field, the nth quantum state of the atom, whose energy is given by (21), decomposes according to the new quantum mechanics into states which can be characterized by quantum numbers k and m, satisfying the familiar selection rules

$$\Delta k = \pm 1, \qquad \Delta m = 0, \pm 1.$$

The integer m again specifies, according to (12), the atomic momentum component parallel to the field, whereas no such direct dynamical meaning can be ascribed to the number k which determines the value of the perturbation energy of the central field. For a quantized state of order n, the number k takes on $n-1$ consecutive values whose common difference is unity. Thus the number of fine-structure levels comes out correctly in any event, without any additional restrictions being introduced (though we cannot as yet make any predictions about their energy values). We want to normalize the quantum number k in just such a way that for each state characterized by n and k in presence of an external magnetic field, the quantum number m assumes an integral value within the range

$$-k \leqq m \leqq k. \tag{24}$$

In an nth-order quantum state, the number k normalized in this way can take the values

$$k = 0, 1, 2, \ldots, n^*. \tag{25}$$

It is possible to set up a unique correspondence between the states classified by (24) and (25) and those classified by (13*). The weight of the nth-order quantum state is (in each case) equal to n^2.

In particular, it follows from the above set of terms for a hydrogen-like atom in external fields, as furnished by the new theory, that for the ground state of such an atom, where $n=1$, $n^*=0$, the quantum number m can have no value other than $m=0$, and hence that this state is non-magnetic. This conclusion may appear surprising, especially in analogy with the behaviour of alkali atoms. In this connection, it should be stressed that the present version of the new quantum mechanics apparently cannot, as yet, account for the anomalous Zeeman effect (breakdown of Larmor's theorem) and that it might accordingly still require some modification. It may not be impossible that such modifications of the theory could become apparent even in the case of atoms having but a single electron. We shall revert to this point toward the end of this paper (§ 6).

As for the method employed below to solve the matrix equations of the new theory in the case of an atom having only one electron, we must first (in § 3) develop the requisite rules for simultaneously operating with matrices $\mathsf{x}, \mathsf{y}, \mathsf{z}$ of the Cartesian coordinates of the electron (combined into a vector matrix $\mathfrak{r}$), the matrix r of the magnitude of the radius vector, and their time derivatives. The present version of the laws of the new quantum mechanics requires that we avoid the introduction of a polar angle φ. Since this is not confined within finite limits, it cannot, namely, be formally represented as a matrix in the same way as the above-mentioned coordinates, which execute librations in classical mechanics.

For just this reason, the following special integration method, applicable to Coulomb forces in classical mechanics, and previously utilized by Lenz,[1] proves to be particularly suitable for going over to the new quantum mechanics. If

$$\mathfrak{P} = m_0[\mathfrak{r}\mathfrak{v}] \tag{26}$$

denotes the time-independent angular momentum of the electron about the nucleus, and

$$\mathfrak{p} = m_0\mathfrak{v}$$

the linear momentum, then it can be shown directly from the equations of motion in classical mechanics that the vector

$$\mathfrak{A} = \frac{1}{Ze^2 m_0}[\mathfrak{P}\mathfrak{p}] + \frac{\mathfrak{r}}{r} \tag{27}$$

is constant in time. Scalar multiplication with $\mathfrak{r}$ then gives

$$(\mathfrak{A}\mathfrak{r}) = -\frac{1}{Ze^2 m_0}\mathfrak{P}^2 + r. \tag{28}$$

This is the equation of a conic section, and it can from this be seen that $\mathfrak{A}$ lies along the direction from the nucleus to the aphelion of the ellipse and that its magnitude is equal to the numerical eccentricity of the ellipse. Squaring (27), one obtains

$$1 - \mathfrak{A}^2 = -\frac{2E}{m_0 Z^2 e^4}\mathfrak{P}^2, \tag{29}$$

where E represents the energy.

In § 4 it will be shown that in the new mechanics, too, a time-independent vector matrix $\boldsymbol{\mathfrak{A}}$ analogous to (27) can be introduced for which, together with the vector matrix of angular momentum $\boldsymbol{\mathfrak{P}}$ (also constant in time), relations analogous to (28) and (29) hold. If, in addition, one uses the quantum conditions (II) which are characteristic of the new mechanics, together with the relations derived in § 3, one obtains a system of matrix equations that comprise only the time-independent matrices $\boldsymbol{\mathfrak{A}}$, $\boldsymbol{\mathfrak{P}}$ and E; the coordinates (i.e., the transition probabilities) are eliminated. The solution of these latter equations which can be effected by elementary methods (§ 5), then leads to the results already discussed in the present section.

[1] W. Lenz, Zs. f. Phys. **24** (1924) 197.

3. Calculational rules for the radius-vector matrix. Momentum conservation law for central forces

We start by setting up the rules of calculation for the matrices x, y, z of the Cartesian coordinates of the electron, which make up the components of the vector matrix $\mathfrak{r}$, and for the matrix r which represents the magnitude of the radius vector. Obviously, they must satisfy the relation

$$r^2 = x^2 + y + z^2. \tag{30}$$

The quantum conditions (II) not only express the commutability of x and y, of x and $\dot{y}$, and of $\dot{x}$ and $\dot{y}$ (and correspondingly for the remaining coordinates),

$$xy = yx, \ldots; \qquad x\dot{y} = \dot{y}x, \ldots; \qquad \dot{x}\dot{y} = \dot{y}\dot{x}, \ldots. \tag{31a}$$

They also contain relations for the product of x with the momentum component p_x (and similarly for the other canonical quantities):

$$p_x x - x p_x = \frac{h}{2\pi \mathrm{i}}\, \mathbf{1}, \ldots \tag{31b}$$

($p_x = m\dot{x}$ denotes the x-component of the linear momentum $\mathfrak{p} = m\mathfrak{v}$, a vector matrix with the components p_x, p_y, p_z). Here and in what follows, we shall denote by '...' the presence of analogous equations for the remaining coordinates, obtained by cyclic permutation of the coordinates in the expressions cited.

These rules can be extended by the following additional relations, on making use of the matrix r. Firstly, r also commutes with x, y, z. This can be written in the form of a vector equation:

$$r\mathfrak{r} = \mathfrak{r}r. \tag{32}$$

Secondly, for any arbitrary rational function f of r, x, y, z, the relation

$$p_x f - f p_x = \frac{h}{2\pi \mathrm{i}} \frac{\partial f}{\partial x}, \ldots \tag{33}$$

holds, and in particular for $f = r$:

$$\mathfrak{p}r - r\mathfrak{p} = \frac{h}{2\pi \mathrm{i}} \frac{\mathfrak{r}}{r}. \tag{34}$$

Conversely, (33) follows generally from (31) and (34) for every function which can be expressed as a series of positive and negative powers of

x, y, z and r, as can easily be shown by induction. Relation (34) is also in accord with (30). For this reason, the existence of relations (32) and (33) constitutes a necessary requirement for the energy conservation law,

$$\tfrac{1}{2}m\mathfrak{v}^2 + F(x, y, z, r) = E \quad \text{(diagonal matrix)} \tag{35}$$

(for simplicity, we assume here that there is only a single particle), together with the frequency condition (leading to the equation

$$E\Phi - \Phi E = \frac{h}{2\pi i}\dot{\Phi}$$

for any quantity Φ) to yield the equations of motion

$$\frac{\mathrm{d}p_x}{\mathrm{d}t} = -\frac{\partial F}{\partial x}, \ldots. \tag{36}$$

We therefore postulate the existence of a matrix r which satisfies relations (30), (32), (34).

We now introduce a vector matrix $\mathfrak{P}$, which represents the angular momentum of the particle about the origin. Let us first of all remark that we shall define, as in ordinary vector algebra, the scalar product of two vector matrices $\mathfrak{A}$ and $\mathfrak{B}$ as the expression

$$(\mathfrak{A}\mathfrak{B}) = \mathfrak{A}_x\mathfrak{B}_x + \mathfrak{A}_y\mathfrak{B}_y + \mathfrak{A}_z\mathfrak{B}_z,$$

and the vector product $[\mathfrak{A}\mathfrak{B}]$, as a new vector matrix having components

$$[\mathfrak{A}\mathfrak{B}]_x = \mathfrak{A}_y\mathfrak{B}_z - \mathfrak{A}_z\mathfrak{B}_y, \ldots. \tag{37}$$

In general, the order of the factors for $\mathfrak{A}$ and $\mathfrak{B}$ is important: the expressions $(\mathfrak{A}\mathfrak{B})-(\mathfrak{B}\mathfrak{A})$ and $[\mathfrak{A}\mathfrak{B}]+[\mathfrak{B}\mathfrak{A}]$ do not in general vanish here, since the commutation law for multiplication does not apply. Also, the components of the vector product $[\mathfrak{A}\mathfrak{A}]$ of a matrix $\mathfrak{A}$ with itself are in general different from zero:

$$[\mathfrak{A}\mathfrak{A}]_x = \mathfrak{A}_y\mathfrak{A}_z - \mathfrak{A}_z\mathfrak{A}_y, \ldots. \tag{37'}$$

However, a special case is obtained if we form the vector product $[\mathfrak{r}\mathfrak{v}]$, since this is equal to $-[\mathfrak{v}\mathfrak{r}]$ because of the commutability of x with $\dot{y}$. We can thus define the vector matrix

$$\mathfrak{P} = m[\mathfrak{r}\mathfrak{v}] = -m[\mathfrak{v}\mathfrak{r}] \tag{38}$$

to be the angular momentum of the particle.

This matrix satisfies the following commutation rules, which are a direct consequence of (31a) and (31b):

$$xP_x = P_x x, \dots; \qquad xP_y - P_y x = P_x y - yP_x = -\frac{h}{2\pi i} z, \dots; \qquad (\mathfrak{r}\mathfrak{P}) = (\mathfrak{P}\mathfrak{r}) = 0, \tag{39}$$

and also

$$\begin{gathered} p_x P_x = P_x p_x, \dots; \\ p_x P_y - P_y p_x = P_x p_y - p_y P_x = -\frac{h}{2\pi i} p_z, \dots; \\ (\mathfrak{P}\mathfrak{p}) = (\mathfrak{p}\mathfrak{P}) = 0. \end{gathered} \tag{40}$$

From this it follows that $v^2 = \dot{x}^2 + \dot{y}^2 + \dot{z}^2$ commutes[1] with P_x, P_y, P_z:

$$v^2 \mathfrak{P} = \mathfrak{P} v^2. \tag{41}$$

Further, we deduce from (34) the commutability of r with P_x, P_y, P_z,

$$r\mathfrak{P} = \mathfrak{P} r; \tag{42}$$

therefore every function $F(r)$ of r alone commutes with $\mathfrak{P}$. If we are dealing with a central force, for which the potential energy depends only on r,

$$\tfrac{1}{2} m \mathfrak{v}^2 + F(r) = E \qquad \text{(diagonal matrix)}, \tag{35'}$$

it follows that

$$E\mathfrak{P} = \mathfrak{P}E,$$

and hence the vector matrix $\mathfrak{P}$ remains constant with time (angular momentum integral).

For the vector product of $\mathfrak{P}$ with itself (cf. (37′)), it is easy to obtain a relation which will be of use[2] later on,

$$[\mathfrak{P}\mathfrak{P}] = -\frac{h}{2\pi i} \mathfrak{P}. \tag{43}$$

For example, from (39) and (40) we obtain for the z-component of $[\mathfrak{P}\mathfrak{P}]$:

$$\begin{aligned} P_x P_y - P_y P_x &= P_x(zp_x - xp_z) - (zp_x - xp_z)P_x \\ &= (P_x z - zP_x)p_x - x(P_x p_z - p_z P_x) \\ &= \frac{h}{2\pi i}(yp_x - xp_y) = -\frac{h}{2\pi i} P_z. \end{aligned}$$

---

[1] Note the identity $a^2 b - ba^2 \equiv a(ab - ba) + (ab - ba)a$.

[2] Cf. 'Quantenmechanik II', p. 597, eq. (3). The quantities denoted by M_x, M_y, M_z there, represent the *negative* angular momentum components.

We are now in a position to evaluate the radial momentum $p_r = m\dot{r}$, for this is in fact equal to

$$p_r = \frac{2\pi i}{h} m(Er - rE) = \frac{2\pi i}{h} \tfrac{1}{2}[(p_x^2 + p_y^2 + p_z^2)r - r(p_x^2 + p_y^2 + p_z^2)]$$

$$= \frac{2\pi i}{h} \tfrac{1}{2}[p_x(p_x r - r p_x) + p_y(p_y r - r p_y) + p_z(p_z r - r p_z)$$

$$+ (p_x r - r p_x)p_x + (p_y r - r p_y)p_y + (p_z r - r p_z)p_z],$$

and hence, because of (34),

$$p_r = \frac{1}{2}\left[\left(\mathfrak{p}\,\frac{\mathfrak{r}}{r}\right) + \left(\frac{\mathfrak{r}}{r}\,\mathfrak{p}\right)\right]. \tag{44}$$

Now, from (33)

$$\left(\mathfrak{p}\,\frac{\mathfrak{r}}{r}\right) - \left(\frac{\mathfrak{r}}{r}\,\mathfrak{p}\right) = \frac{h}{2\pi i}\,\mathrm{div}\,\frac{\mathfrak{r}}{r} = \frac{h}{2\pi i}\,\frac{2}{r},$$

so that (44) can also be written

$$p_r = (\mathfrak{p}\mathfrak{r})\,\frac{1}{r} - \frac{h}{2\pi i}\,\frac{1}{r} = \frac{1}{r}\,(\mathfrak{r}\mathfrak{p}) + \frac{h}{2\pi i}\,\frac{1}{r}. \tag{44'}$$

Multiplying this by r, we obtain, first, the relation

$$p_r r + r p_r = (\mathfrak{p}\mathfrak{r}) + (\mathfrak{r}\mathfrak{p}), \tag{45}$$

which is also obtained directly by differentiating (30) with respect to time. Also

$$p_r r - r p_r = (\mathfrak{p}\mathfrak{r}) - (\mathfrak{r}\mathfrak{p}) - \frac{h}{2\pi i}\,\mathbf{2}.$$

The meaning of $(\mathfrak{p}\mathfrak{r}) - (\mathfrak{r}\mathfrak{p})$ is now $(p_x x - x p_x) + (p_y y - y p_y) + (p_z z - z p_z)$. From (31b), each of the bracketed terms has the value

$$\frac{h}{2\pi i}\,\mathbf{1}.$$

We thus obtain the overall result

$$p_r r - r p_r = \frac{h}{2\pi i}\,\mathbf{1}. \tag{46}$$

Finally, in preparation for the application which follows, we evaluate the time-derivative of $\mathfrak{r}/r$. For example, for the x-component we make use of (34) to obtain

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\,\frac{x}{r} &= \frac{2\pi \mathrm{i}}{h}\left(E\frac{x}{r} - \frac{x}{r}E\right) = \frac{2\pi \mathrm{i}}{h}\,\frac{1}{2m}\left(\mathfrak{p}^2\frac{x}{r} - \frac{x}{r}\mathfrak{p}^2\right)\\ &= \frac{2\pi \mathrm{i}}{h}\,\frac{1}{2m}\left\{\mathfrak{p}\left(\mathfrak{p}\,\frac{x}{r} - \frac{x}{r}\,\mathfrak{p}\right) + \left(\mathfrak{p}\,\frac{x}{r} - \frac{x}{r}\,\mathfrak{p}\right)\mathfrak{p}\right\}\\ &= \frac{1}{2m}\left\{\left(p_x\frac{y^2+z^2}{r^3} - p_y\frac{xy}{r^3} - p_z\frac{xz}{r^3}\right)\right.\\ &\qquad\left.+\left(\frac{y^2+z^2}{r^3}\,p_x - \frac{xy}{r^3}\,p_y - \frac{xz}{r^3}\,p_z\right)\right\}\\ &= \frac{1}{2m}\left\{\left(P_y\frac{z}{r^3} - P_z\frac{y}{r^3}\right) + \left(\frac{z}{r^3}P_y - \frac{y}{r^3}P_z\right)\right\}.\end{aligned}$$

Thus, generally,

$$\frac{\mathrm{d}}{\mathrm{d}t}\,\frac{\mathfrak{r}}{r} = \frac{1}{2m}\left\{\left[\mathfrak{P}\,\frac{\mathfrak{r}}{r^3}\right] - \left[\frac{\mathfrak{r}}{r^3}\,\mathfrak{P}\right]\right\}. \tag{47}$$

4. Introduction of the vector matrix $\mathfrak{A}$, constant in time, for Coulomb forces. Elimination of the coordinates

Let us now consider an atom consisting of a fixed nucleus having charge $+Ze$ and exerting a Coulomb attraction on a single orbital electron of mass m_0 and charge $-e$. For the Hamiltonian, we have to set

$$\frac{1}{2m_0}\,\mathfrak{p}^2 - \frac{Ze^2}{r} = E \quad \text{(diagonal matrix)}, \tag{48}$$

i.e., for this special case we set

$$F(r) = -\,Ze^2/r$$

in (35′). The equations of motion (36) derived from energy-conservation with the aid of the quantum rules assume the same form here as in classical mechanics:

$$\dot{\mathfrak{p}} = m_0\ddot{\mathfrak{r}} = -\,\frac{Ze^2}{r^3}\,\mathfrak{r}. \tag{49}$$

Analogously to classical mechanics (cf. (27)), it follows from (47) that the vector matrix $\mathfrak{A}$ defined by

$$\mathfrak{A} = \frac{1}{Ze^2m_0}\,\frac{1}{2}\{[\mathfrak{P}\mathfrak{p}] - [\mathfrak{p}\mathfrak{P}]\} + \frac{\mathfrak{r}}{r} \tag{50}$$

is constant with time in the special case of a Coulomb field of force. Using (40), we can also write

$$\begin{aligned}\mathfrak{A} &= \frac{1}{Ze^2m_0}\left\{[\mathfrak{P}\mathfrak{p}] + \frac{h}{2\pi i}\,\mathfrak{p}\right\} + \frac{\mathfrak{r}}{r}\\ &= -\frac{1}{Ze^2m_0}\left\{[\mathfrak{p}\mathfrak{P}] + \frac{h}{2\pi i}\,\mathfrak{p}\right\} + \frac{\mathfrak{r}}{r}.\end{aligned} \tag{51$'$}$$

The remaining calculations are quite elementary when use is made of the rules collected in the preceding section. In the first instance, in analogy with equation (28) of a conic in classical mechanics, we obtain the relation

$$\tfrac{1}{2}[(\mathfrak{A}\mathfrak{r}) + (\mathfrak{r}\mathfrak{A})] = -\frac{1}{Ze^2m_0}\left[\mathfrak{P}^2 + \frac{3}{2}\,\frac{h^2}{4\pi^2}\right] + r, \tag{51}$$

and also the commutation rule

$$\tfrac{1}{2}([\mathfrak{A}\mathfrak{r}] + [\mathfrak{r}\mathfrak{A}]) = -\frac{h}{2\pi i}\,\frac{3}{2}\,\frac{1}{Ze^2m_0}\,\mathfrak{P}. \tag{52}$$

Furthermore, the following relations are found to be valid, in which the coordinates x, y, z, r have been entirely eliminated, leaving only the matrices $\mathfrak{A}$, $\mathfrak{P}$ and E which are constant with time:

$$[\mathfrak{P}\mathfrak{P}] = -\frac{h}{2\pi i}\,\mathfrak{P}. \tag{I}$$

$$\left.\begin{aligned}&A_xP_x = P_xA_x, \ldots,\\ &A_xP_y - P_yA_x = P_xA_y - A_yP_x = -\frac{h}{2\pi i}A_z, \ldots,\\ &(\mathfrak{A}\mathfrak{P}) = (\mathfrak{P}\mathfrak{A}) = 0\end{aligned}\right\} \tag{II}$$

$$[\mathfrak{A}\mathfrak{A}] = \frac{h}{2\pi i}\,\frac{2}{m_0Z^2e^4}\,E\mathfrak{P}. \tag{III}$$

$$1 - \mathfrak{A}^2 = -\frac{2}{m_0Z^2e^4}\,E\left(\mathfrak{P}^2 + \frac{h^2}{4\pi^2}\right). \tag{IV}$$

Equation (I) is identical with equation (43) of the previous section, (II) is analogous with (39) in form, (IV) is analogous to the classical equation (29), though the occurrence of the additional term $h^2/4\pi^2$ (as also of the additional term $\frac{3}{2}h^2/4\pi^2$ in (51)) is characteristic of the new mechanics.

From the existence of the vector matrix $\mathfrak{A}$, constant in time, we can infer that an atom with a single electron constitutes a degenerate system, even apart from the spatial orientation of the atom (a situation similar to Kepler motion in classical mechanics). Namely, we can readily conclude from the relations derived above that in general $\mathfrak{A}\mathfrak{P}^2-\mathfrak{P}^2\mathfrak{A}$ cannot vanish. Since, on the other hand, $\mathfrak{A}E-E\mathfrak{A}$ vanishes, it is obvious that for every value of the energy E there is not just a single value of $\mathfrak{P}^2$; the system is thus in fact degenerate.

As discussed in detail by Born, Heisenberg and Jordan,[1] when such a system is treated from the standpoint of the new quantum mechanics the amplitudes of the various partial vibrations belonging to transitions between states of predetermined energy are not uniquely established by the quantum-mechanical equations. Furthermore, matrices which are constant with time need not in general be diagonal, inasmuch as non-zero elements can occupy positions (n, m) which correspond to a vanishing frequency $\nu^n_m=(E_n-E_m)/h=0$. In our case, to each energy value (to each value of the principal quantum number) there belongs a matrix which contains the time-independent parts of a quantity (e.g., x or r) and whose number of rows or columns is equal to the weight of that particular energy state. This matrix is obtained by setting equal to zero all those elements in the original matrix that are located in positions relating to a transition process associated with a change in the energy value. It is called the time-average of the corresponding quantity and is denoted by a bar above that quantity, (e.g., $\bar{x}$ or $\bar{r}$).

Even though in the case of a degenerate system the individual partial vibrations of a kinematic quantity which belong to the same frequency ν^n_m are not uniquely determined, nevertheless the energy values and statistical weights of these states are.[2] Thus in principle it should be possible to derive the Balmer terms and the corresponding statistical weights from equations (I) to (IV) without any further specifying assumptions as to the type of solution. This we have, regrettably, not succeeded in doing and in the following we sidestep

---

[1] Quantenmechanik II, Chapter 2, § 2.

[2] Quantenmechanik II, Chapter 2, § 2 and Chapter 3.

this difficulty by introducing additional requirements (in various ways) which render the solution of equations (I) to (IV) unique.

If the degeneracy is removed by an additional perturbing field whose Hamiltonian is H_1, then the time-average of the perturbation function $\overline{H}_1$, taken over the unperturbed motion, must be a diagonal matrix, as can be shown by carrying through the perturbation calculation according to the method of Born, Heisenberg and Jordan.[1] In our case, this mean value depends in general not only on the energy E of the unperturbed motion but also on $\mathfrak{P}$ and $\mathfrak{A}$.

If, in particular, the perturbing field is due to an additional non-Coulomb central force, the above time average depends only on $\mathfrak{P}^2$ (apart from its E-dependence), since there exists no preferred direction in space here. Further, the perturbation energy of a magnetic field in the z-direction depends only on the momentum component P_z, which is parallel to the field. The requirement that $\mathfrak{P}^2$ *and* P_z are to be *diagonal* matrices therefore leads to a special solution of equations (I) to (IV), adapted to the relativistic fine structure and to an additional weak magnetic field. We shall treat this case in the next section.

A second case of particular interest is furnished by the Stark effect. Here, we are concerned with the existence of a diagonal matrix $\bar{z}$ which is the component in the field direction (z-direction) of the time-independent vector matric $\bar{\mathfrak{r}}$ representing the electrical centre of the orbit. It can, however, be shown that this matrix $\bar{\mathfrak{r}}$ is connected with the matrix $\mathfrak{A}$ in just the same way as in classical theory, viz. by the relation

$$\bar{\mathfrak{r}} = \frac{3}{2}\,\frac{Ze^2}{2|E|}\,\mathfrak{A}, \tag{53}$$

(classically, $Ze^2/2|E|$ represents the semi-major axis a of the Kepler ellipse). Namely, in the first place the same commutation rules apply to $\bar{\mathfrak{r}}$ and $\mathfrak{P}$ as to $\mathfrak{A}$ and $\mathfrak{P}$, from (39) and (II). Further, if we next compare (52) with (III), we obtain the relations

$$\left[\mathfrak{A}, \bar{\mathfrak{r}} - \frac{3}{2}\,\frac{Ze^2}{2|E|}\,\mathfrak{A}\right] = 0$$

involving the difference

$$\bar{\mathfrak{r}} - \frac{3}{2}\,\frac{Ze^2}{2|E|}\,\mathfrak{A}.$$

---

[1] Quantenmechanik II, Chapter 2, § 2 and Chapter 3.

As is shown by the more detailed discussion based on the solutions of equations (I) to (IV) derived in the next section, these constitute a sufficient number of homogeneous linear equations to permit us to conclude that

$$\bar{\mathfrak{r}} - \frac{3}{2}\,\frac{Ze^2}{2|E|}\,\mathfrak{A}$$

vanishes. If we supplement the electric field in the z-direction by a parallel magnetic field along the same direction, we can use (53) to characterize this case by stipulating that A_z *and* P_z are *diagonal matrices.*

Finally, at the end of the next section we also treat the case of crossed electric and magnetic fields. As explained in detail in § 2, this is of especial interest because of the occurrence of additional exclusion conditions for singular motions, which appeared in the earlier theory.

5. Solution of equations (I) to (IV). Derivation of the Balmer terms

(a) P_z *and* $\mathfrak{P}^2$ *are diagonal matrices.* For this first case, where the degeneracy is removed by superimposing an additional central field and a weak magnetic field in the z-direction, we make the following *Ansatz* in order to satisfy equations (I) and (II). For a given value of $\mathfrak{P}^2$, let the possible values of P_z be

$$P_{z\,k,m}^{\,k,m} = mh/2\pi, \tag{54}$$

where m runs from $-k$ to $+k$:

$$-\,k \leqq m \leqq k. \tag{54'}$$

Further, let the partial vibrations of $\mathfrak{P}$, which belong to a change in m by ± 1, be left- and right-circular in the (x, y)-plane:

$$P_{y\,k,m\pm1}^{\,k,m} = \pm\, iP_{x\,k,m\pm1}^{\,k,m}. \tag{55}$$

It then follows from (I) that

$$\begin{aligned} |P_{x\,k,m\mp1}^{\,k,m}|^2 = |P_{y\,k,m\mp1}^{\,k,m}|^2 &= \frac{1}{4}\,\frac{h^2}{4\pi^2}\,[k(k+1) - m(m\mp 1)] \\ &= \frac{1}{4}\,\frac{h^2}{4\pi^2}\,(k\pm m)(k+1\mp m). \end{aligned} \tag{56}$$

$$(\mathfrak{P}^2)_{k,m}^{k,m} = \frac{h^2}{4\pi^2}\,k(k+1). \tag{57}$$

Next we set for the matrix $\mathfrak{A}$,

$$A_{yk',m\pm1}^{k,m} = \pm\, \mathrm{i} A_{xk',m\pm1}^{k,m} \qquad (k' = k+1 \quad \text{or} \quad k-1), \tag{58}$$

$$|A_{xk,m\pm1}^{k+1,m}|^2 = |A_{yk,m\pm1}^{k+1,m}|^2 = \tfrac{1}{4} C_k^{k+1} (k \mp m)(k \mp m + 1), \tag{59}$$

in accordance with the Hönl–Kronig formula for the intensity of the Zeeman components. When m is replaced by $m-1$ or $m+1$, it further follows that

$$|A_{xk+1,m\pm1}^{k,m}|^2 = |A_{yk+1,m\pm1}^{k,m}|^2$$

$$= \tfrac{1}{4} C_{k+1}^{k} (k \pm m + 1)(k \pm m + 2). \tag{59a}$$

Finally, we have for A_z,

$$|A_{zk,m}^{k+1,m}|^2 = C_k^{k+1}[(k+1)^2 - m^2]. \tag{60}$$

It still remains to be seen whether m (and thus also k) is an integer or half-integer; also, the C_k^{k+1} remain for the time being undetermined functions of k which can never take on negative values and which satisfy the symmetry relation

$$C_k^{k+1} = C_{k+1}^{k}. \tag{61}$$

A further remark concerning the signs of $\mathfrak{A}$ relative to those of $\mathfrak{P}$: if P_x and A_z are assumed to be positive and real, then A_x has to be taken as positive or negative (and real) depending on whether one is dealing with transitions that correspond to changes of k and m in the opposite sense (as for $A_{xk+1,m-1}^{k,m}$ and $A_{xk-1,m+1}^{k,m}$) or in the same sense (as for $A_{xk+1,m+1}^{k,m}$ and $A_{xk-1,m-1}^{k,m}$). When the calculations are carried through, it is evident that this approach satisfies equations (I) and (II) of the previous section. Moreover, it follows conversely from considerations by Born, Heisenberg and Jordan[1] that if $\mathfrak{P}^2$ and P_z are assumed to be diagonal matrices, the expression chosen here for $\mathfrak{A}$ and $\mathfrak{P}$ is a necessary consequence of (I) and (II).

In order now to determine the normalization of m and k and the function C_{k+1}^{k}, we make use of equation (III) from the preceding section. It suffices, however, to use just the z-component,

$$A_x A_y - A_y A_x = \frac{h}{2\pi \mathrm{i}} \frac{2}{m_0 Z^2 e^4} E P_z. \tag{62}$$

---

[1] Quantenmechanik II, Chapter 4, § 1. Cf. also the discussion of the Zeeman effect in Chapter 4, § 2.

Namely, if we form the expression

$$P_y(A_xA_y - A_yA_x) - (A_xA_y - A_yA_x)P_y = \frac{h}{2\pi i}\,\frac{2}{m_0Z^2e^4}\,E(P_yP_z - P_zP_y)$$

and use (I) and (II), we obtain an equation which agrees with the x-component of (III). Similarly, the y-component of (III) also follows from the z-component of this vector equation and equations (I) and (II).

If we form the element of equation (62) which occupies the (k, m) position in the diagonal series, we first obtain, for the left-hand side, from (58) and (59),

$$\begin{aligned}(A_xA_y - A_yA_x)_{k,m}^{k,m} &= 2i\{|A_{x\,k+1,m-1}^{\;k,m}|^2 - |A_{x\,k+1,m+1}^{\;k,m}|^2 \\ &\quad + |A_{x\,k-1,m-1}^{\;k,m}|^2 - |A_{x\,k-1,m+1}^{\;k,m}|^2\} \\ &= im\{-(2k+3)C_k^{k+1} + (2k-1)C_{k-1}^k\}.\end{aligned}$$

Noting further that E has a negative sign, and introducing the Rydberg constant

$$R = 2\pi^2e^4m_0/h^3 \tag{63}$$

together with the value of P_z given by (54), we see that equation (62) yields the condition

$$m\{-(2k+3)C_k^{k+1} + (2k-1)C_{k-1}^k\} = \frac{|E|}{RhZ^2}\,m. \tag{64}$$

Let us first of all consider the smallest possible value of k for a given $|E|$. Obviously the contribution from the transition $k \rightarrow k-1$ on the left-hand side vanishes for this value of k, and the coefficient of m on the left-hand side can therefore certainly not be positive, whereas the coefficient of m on the right-hand side is positive. Hence equation (64) can be satisfied for the minimum value of k only if $m=0$. But according to (54), this means that the minimum value of k must itself vanish, since otherwise m could assume other, non-zero, values. *Hence k and m are necessarily integer*, and k assumes the values

$$k = 0, 1, 2, \ldots n^*, \tag{65}$$

the integer n^* being the largest value of k that can be attained for a given $|E|$. Now (64) implies

$$(2k-1)C_{k-1}^k - (2k+3)C_k^{k+1} = \frac{|E|}{RhZ^2} \quad \text{for} \quad k = 1, \ldots n^*. \tag{64'}$$

Furthermore, we have to set

$$C_{n^*}^{n^*+1} = 0, \tag{64''}$$

since obviously the contribution from the transition $k+1 \to k$ (second term) disappears for $k=n^*$. Beginning with $k=n^*$ and reducing k stepwise, we can successively calculate the values of

$$C_{n^*-1}^{n^*},\ C_{n^*-2}^{n^*-1},\ \ldots,\ C_0^1$$

from (64′). The result can be expressed by the formula

$$\begin{aligned} C_k^{k+1} &= \frac{|E|}{RhZ^2}\,\frac{n^*(n^*+2)-k(k+2)}{(2k+1)(2k+3)} \\ &= \frac{|E|}{RhZ^2}\,\frac{(n^*-k)(n^*+k+2)}{(2k+1)(2k+3)}. \end{aligned} \tag{66}$$

Replacing k by $k-1$, we also obtain

$$\begin{aligned} C_{k-1}^{k} &= \frac{|E|}{RhZ^2}\,\frac{n^*(n^*+2)-(k-1)(k+1)}{(2k-1)(2k+1)} \\ &= \frac{|E|}{RhZ^2}\,\frac{(n^*-k+1)(n^*+k+1)}{(2k-1)(2k+1)}. \end{aligned} \tag{66'}$$

With the help of these formulae, we can confirm directly that relations (64′) and (64″) are satisfied.

Finally, in order to derive the energy value itself, we make use of the last equation (IV). First of all, we determine the value of $\mathfrak{A}^2$ at the (k, m) position of the diagonal series. Because of (59) and (60), we obtain

$$\begin{aligned} (\mathfrak{A}^2)_{k,m}^{k,m} &= 2|A_{x\,k+1,m+1}^{k,m}|^2 + 2|A_{x\,k+1,m-1}^{k,m}|^2 + |A_{z\,k+1,m}^{k,m}|^2 \\ &\quad + 2|A_{x\,k-1,m+1}^{k,m}|^2 + 2|A_{x\,k-1,m-1}^{k,m}|^2 + |A_{z\,k-1,m}^{k,m}|^2 \\ &= (k+1)(2k+3)C_k^{k+1} + k(2k-1)C_{k-1}^{k}, \end{aligned}$$

and on substitution from (66), (66′),

$$(\mathfrak{A}^2)_{k,m}^{k,m} = \frac{|E|}{RhZ^2}\,[n^{*2} + 2n^* - k(k+1)]. \tag{67}$$

This expression for $\mathfrak{A}^2$ and the expression (57) for $\mathfrak{P}^2$ now have to be substituted in (IV), giving

$$1 = \frac{|E|}{RhZ^2}(n^{*2} + 2n^* + 1) = \frac{|E|}{RhZ^2}(n^* + 1)^2,$$

and hence

$$|E| = \frac{RhZ^2}{(n^* + 1)^2} = \frac{RhZ^2}{n^2}, \tag{68}$$

(setting $n = n^* + 1$), as in § 2. This demonstrates that the Balmer terms result correctly from the new quantum mechanics and that the weight n^2 is associated with the nth quantum state in the new theory.

(b) *A_z and P_z are diagonal matrices* (*Stark effect*). If a homogeneous electric field of strength F acts in the z-direction, the time-average of the perturbation energy is given by (53),

$$E_1 = \tfrac{3}{2}eF\bar{\mathsf{z}} = \tfrac{3}{2}eF\frac{Ze^2}{2|E|}\mathsf{A}_z. \tag{69}$$

For this case, therefore, we seek a solution of equations (I) to (IV) for which A_z is a diagonal matrix. The added condition that P_z, too, should be a diagonal matrix has the physical meaning that we consider the degeneracy of the secular perturbation of the Stark effect to be removed by an additional weak magnetic field parallel to the electric field.

We shall confine ourselves here simply to quoting the result, without going through the individual calculations in detail and without supplying the proof that the given solution of equations (I) to (IV) is the only one meeting the requirement that A_z and P_z be diagonal matrices. The states which belong to a definite value of the unperturbed energy as given by (68), have to be classified by two quantum numbers s and m, of which the former determines the value of A_z (and of the additional energy E_1), according to

$$A_{zs,m}^{s,m} = s/n, \qquad E_1 = \tfrac{3}{2}eFa_1ns \qquad (0 \leqq s \leqq n^*), \tag{70}$$

(where $a_1 = h^2/4\pi^2Ze^2m_0$) and the latter determines that of P_z, according to

$$P_{zs,m}^{s,m} = mh/2\pi. \tag{71}$$

The range of values taken on by s and m has already been given in § 2 by the relation (13*). The matrices P_x, P_y, A_x, A_y have non-zero elements only in those positions which correspond to a change of ± 1 in s and m. Their values are given by

$$P_{y_{s',m\pm 1}}^{s,m} = \pm \mathrm{i} P_{x_{s',m\pm 1}}^{s,m}, \qquad A_{y_{s',m\pm 1}}^{s,m} = \pm \mathrm{i} A_{x_{s',m\pm 1}}^{s,m} \tag{72}$$

$$(s' = s + 1 \quad \text{or} \quad s - 1).$$

$$A_{x_{s\pm 1,m\pm 1}}^{s,m} = + \frac{2\pi}{h} \frac{1}{n} P_{x_{s\pm 1,m\pm 1}}^{s,m},$$

$$A_{x_{s\mp 1,m\pm 1}}^{s,m} = - \frac{2\pi}{h} \frac{1}{n} P_{x_{s\mp 1,m\pm 1}}^{s,m}, \tag{73}$$

(in these last relations either the upper or the lower sign is to be taken throughout), and

$$\begin{aligned} |P_{x_{s-1,m-1}}^{s,m}|^2 &= |P_{y_{s-1,m-1}}^{s,m}|^2 \\ &= \frac{1}{16} \frac{h^2}{4\pi^2} [n^* + 2 - (m + s)][n^* + (m + s)], \\ |P_{x_{s+1,m-1}}^{s,m}|^2 &= |P_{y_{s+1,m-1}}^{s,m}|^2 \\ &= \frac{1}{16} \frac{h^2}{4\pi^2} [n^* + 2 - (m - s)][n^* + (m - s)]. \end{aligned} \tag{74}$$

It is easy to verify that equations (I) to (IV) are indeed satisfied when expressions (70) to (74) are used.

(c) *Crossed fields.* If the vectors $\mathfrak{E}$ and $\mathfrak{H}$ represent the strengths of the external electric and magnetic field respectively, the time-average of the perturbation energy when both fields are simultaneously present is given by

$$E_1 = \tfrac{3}{2} ea(\mathfrak{E}\mathfrak{A}) + \frac{e}{2m_0c} (\mathfrak{H}\mathfrak{P}). \tag{75}$$

The quantity a, which in the earlier theory represented the semi-axis of the Kepler ellipse, is now to be regarded simply as an abbreviation for

$$a = \frac{Ze^2}{2|E|}. \tag{76}$$

We introduce the vectors $\mathfrak{o}_F$ and $\mathfrak{o}_H$, which are respectively parallel to $\mathfrak{E}$ and $\mathfrak{H}$ and whose magnitudes are equal to the secular frequencies that would be obtained if just one of the homogeneous external fields were to act by itself, so that (cf. (9) and (10))

$$\mathfrak{o}_H = \frac{e\mathfrak{H}}{4\pi m_0 c}, \qquad \mathfrak{o}_F = \frac{3}{4\pi}\sqrt{\frac{a}{Zm_0}}\,\mathfrak{E} = \frac{3}{4\pi}\,\frac{e\mathfrak{E}}{\sqrt{(2m_0|E|)}}. \tag{77}$$

We can then write (75) in the form

$$E_1 = \sqrt{\frac{Z^2Rh}{|E|}}\,(\mathfrak{A}\mathfrak{o}_F)h + 2\pi(\mathfrak{P}\mathfrak{o}_H). \tag{75a}$$

It is now expedient[1] to introduce vector matrices $\mathfrak{J}_1$ and $\mathfrak{J}_2$ which are defined by

$$\begin{aligned} 2\mathfrak{J}_1 &= \frac{2\pi}{h}\,\mathfrak{P} + \sqrt{\frac{Z^2Rh}{|E|}}\,\mathfrak{A}, \\ 2\mathfrak{J}_2 &= \frac{2\pi}{h}\,\mathfrak{P} - \sqrt{\frac{Z^2Rh}{|E|}}\,\mathfrak{A}, \end{aligned} \tag{78}$$

so that

$$\frac{2\pi}{h}\,\mathfrak{P} = \mathfrak{J}_1 + \mathfrak{J}_2, \qquad \sqrt{\frac{Z^2Rh}{|E|}}\,\mathfrak{A} = \mathfrak{J}_1 - \mathfrak{J}_2, \tag{78a}$$

and to introduce the two vectors

$$\mathfrak{o}_1 = \mathfrak{o}_H + \mathfrak{o}_F, \qquad \mathfrak{o}_2 = \mathfrak{o}_H - \mathfrak{o}_F, \tag{79}$$

whose absolute magnitudes have in § 2 been denoted by ω_1 and ω_2 (cf. equation (18)). The perturbation energy (75a) can then simply be written as

$$E_1 = (\mathfrak{J}_1\mathfrak{o}_1)h + (\mathfrak{J}_2\mathfrak{o}_2)h. \tag{80}$$

Similarly, we introduce into equations (I) to (IV) the new vector matrices $\mathfrak{J}_1$ and $\mathfrak{J}_2$ (as given by (78a)) in place of $\mathfrak{A}$ and $\mathfrak{P}$. A simple calculation then yields the following relations:

$$\boldsymbol{I}_{1x}\boldsymbol{I}_{2x} = \boldsymbol{I}_{2x}\boldsymbol{I}_{1x}, \ldots, \quad \boldsymbol{I}_{1x}\boldsymbol{I}_{2y} = \boldsymbol{I}_{2y}\boldsymbol{I}_{1x}, \quad \boldsymbol{I}_{2x}\boldsymbol{I}_{1y} = \boldsymbol{I}_{1y}\boldsymbol{I}_{2x}, \ldots \tag{81}$$

$$[\mathfrak{J}_1\mathfrak{J}_1] = \mathrm{i}\mathfrak{J}_1, \qquad [\mathfrak{J}_2\mathfrak{J}_2] = \mathrm{i}\mathfrak{J}_2, \tag{82}$$

$$\mathfrak{J}_1^2 = \mathfrak{J}_2^2 = \tfrac{1}{4}(RhZ^2/|E| - 1) = \tfrac{1}{4}(n^2 - 1) = \tfrac{1}{2}n^*(\tfrac{1}{2}n^* + 1). \tag{83}$$

Relations (81) state that each component of $\mathfrak{J}_1$ commutes with each component of $\mathfrak{J}_2$. Relations (82) are quite analogous in structure to

---

[1] The following should be compared with the papers of Klein and Lenz quoted in footnotes $^{1)}$ and $^{2)}$, following eqs. (17), § 2.

equations (I); in the last part of (83), the energy values (68) were used.

It follows from (80) that the case of crossed fields is characterized by the fact that $(\mathfrak{J}_1\mathfrak{o}_1)$ and $(\mathfrak{J}_2\mathfrak{o}_2)$ or, what amounts to the same, the *components of* $\mathfrak{J}_1$ *and* $\mathfrak{J}_2$ *parallel to* $\mathfrak{o}_1$ *and* $\mathfrak{o}_2$ (written as $\mathfrak{J}_{1\parallel}$ and $\mathfrak{J}_{2\parallel}$), *are diagonal matrices*. The solution of equations (82) is in this case completely analogous to the solution of equations (I) if we assume P^2 and P_z to be diagonal matrices. Here, $\frac{1}{2}n^*$ appears instead of k, and we have to replace m (following the notation of § 2, eqs. (15) and (16)) by the numbers $\frac{1}{2}n^*-n_1$ and $\frac{1}{2}n^*-n_2$, which can run from $-\frac{1}{2}n^*$ to $+\frac{1}{2}n^*$. We then obtain

$$\begin{aligned}
&(\mathfrak{J}_{1\parallel})^{n_1}_{n_1} = \tfrac{1}{2}n^* - n_1, \qquad (\mathfrak{J}_{2\parallel})^{n_2}_{n_2} = \tfrac{1}{2}n^* - n_2,\\
&\qquad\qquad\qquad\qquad 0 \leqq n_1 \leqq n^*, \qquad 0 \leqq n_2 \leqq n^*,\\
&E_1 = (\tfrac{1}{2}n^* - n_1)\omega_1 h + (\tfrac{1}{2}n^* - n_2)\omega_2 h\\
&\qquad\qquad\qquad\qquad (\omega_1 = |\mathfrak{o}_1|, \quad \omega_2 = |\mathfrak{o}_2|).
\end{aligned} \tag{84}$$

The projections $\mathfrak{J}_{1\perp}$ and $\mathfrak{J}_{2\perp}$ in the planes perpendicular to the directions of $\mathfrak{o}_1$ and $\mathfrak{o}_2$ respectively, describe circular oscillations and are therefore represented by matrices which are analogous to those described by (56) for P_x and P_y (one has to replace k by $\frac{1}{2}n^*$ and m by $\frac{1}{2}n^*-n_1$ or $\frac{1}{2}n^*-n_2$; $\mathfrak{J}^2_\perp$ corresponds to the sum of P^2_x and P^2_y):

$$\begin{aligned}
|\mathfrak{J}_{1\perp}{}^{n_1}_{n_1+1}|^2 &= \tfrac{1}{2}(n_1 + 1)(n^* - n_1),\\
|\mathfrak{J}_{2\perp}{}^{n_2}_{n_2+1}|^2 &= \tfrac{1}{2}(n_2 + 1)(n^* - n_2).
\end{aligned} \tag{85}$$

Equations (81) and (82) are thereby satisfied, and since, analogously to (57),

$$(\mathfrak{J}^2_1)^{n_1}_{n_1} = (\mathfrak{J}^2_2)^{n_2}_{n_2} = \tfrac{1}{2}n^*(\tfrac{1}{2}n^* + 1),$$

equation (83), too, is satisfied by the energy values (68).

Thus all the results given in § 2 have been derived from the new mechanics.

6. On the relationship between the hydrogen spectrum and the alkali spectra

It has already been mentioned in § 2 that the modifications to the basic foundations of the new quantum mechanics which would still be necessary in order to interpret the anomalous Zeeman effects might possibly make themselves felt even in the case of atoms with a single electron; in particular, the result that the ground state of such an atom should be non-magnetic might well not be regarded as conclusive. A suggestion of a special kind, aimed at taking account of the anomalous Zeeman effect, has recently been put forward by Goudsmit and Uhlenbeck.[1] According to this suggestion, the electron is no longer regarded as a point charge, but instead has a preferred axis, angular momentum and (doubly anomalous) magnetism associated with it. Whether this assumption, when combined with the new quantum mechanics, suffices to explain all the empirical results, will probably be decided only when the calculation of relativistic fine structure, too, has been carried out on the basis of the new mechanics. This calculation had to be left, for the present, because we have as yet been unable to effect the requisite evaluation of the time-average $\overline{1/r^2}$.

Independently of the conception of any particular model one is, however, prompted to ask whether the hydrogen spectrum (including the fine-structure and the influence of external fields) could be regarded as a limiting case of the alkali spectra or X-ray spectra for a vanishing central force exerted by the rest of the atom on the valency electron or, respectively, for vanishingly small screening numbers (so that the levels forming a screening doublet coincide).[2] The fine structure of the Balmer lines would then differ from that predicted by the earlier theory, not by the position of the energy levels and line components, but by their intensities: instead of the selection rule $\Delta k=\pm 1$, we should now have the selection rule $\Delta j=0, \pm 1$, which permits the occurrence of components that had been forbidden in the earlier theory. Goudsmit and Uhlenbeck[1] were able to show that the observed results would make such an alteration of the selection rule appear quite probable. At the same time, however, they draw attention to the fact that the following difficulty stands in the way of a complete analogy between the hydrogen spectrum and alkali spectra: the Zeeman effect for spectra of single-electron atoms in magnetic fields that are weak (relative to the fine structure) does not at all seem to resemble that for alkali spectra according to the available observations.

Although therefore the question as to how far one may pursue the above-mentioned relationship between hydrogen- and alkali-spectra cannot yet be regarded as resolved, one may nevertheless be justified

---

[1] S. A. Goudsmit and G. E. Uhlenbeck, Naturwiss. **13** (1925) 953.

[2] S. Goudsmit and G. E. Uhlenbeck, Physica **5** (1925) 266. Similar arguments were communicated to me in a letter by Mr. A. Landé a considerable time ago.

in letting oneself be guided by this analogy, at least for all those cases in which the relativistic (or doublet) fine structure can be left out of consideration. This would lead us to assume that, in magnetic fields in which the Zeeman splitting is large compared with the separation of the fine-structure components, the magnetic energy levels in the spectra of single-electron atoms agree with the Paschen–Back terms of the alkali elements, as far as the number and position of these levels is concerned. One would then have to assign twice as many states to the hydrogen atom in an external field of force as were derived in the preceding sections on the present basis of the new quantum mechanics (i.e., $2n^2$ states instead of n^2). In an external magnetic field, to each value of the quantum number m (lying between $-n^*$ and $+n^*$) would have to belong the two magnetic energy values $(m \pm 1)o_H h$ (where o_H=Larmor frequency); in the same way, for the case of crossed fields, each state characterized by n^*, n_1, n_2 would have to split into two states whose energy values would differ from those given by (84) by an amount $\pm o_H h$. According to the correspondence principle, only those transitions would then occur which leave the sign of the additional term $\pm o_H h$ unchanged.

One possible way of differentiating between the term manifold derived in the previous section (for which the ground state of the hydrogen atom is non-magnetic) and the manifold considered here in analogy with the Paschen–Back terms of the alkali elements (for which energy values $\pm o_H h$ are assigned to the ground state of a hydrogen atom in a magnetic field) may be offered by investigations of the Stern–Gerlach type on the deflection of atomic hydrogen beams in an inhomogeneous magnetic field.