THE HYDROGEN SPECTRUM IN THE NEW QUANTUM THEORY

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Abstract

The *Born and Jordan matrices* representing the "coordinates" of the hydrogen atom are calculated. The model is that of an electron revolving without rotation about a positive nucleus. The computation is based on a method developed independently by the author and by E. Schroedinger. *Half quantum numbers* appear in the formulas for the matrices. It is stated without proof, that they also enter into the formula for the *relativistic fine structure*. This will necessitate the consideration of a more elaborate model for the hydrogen atom (the rotating electron of Uhlenbeck and Goudsmit). The *intensity ratio* of the two brighter components of H_α is calculated and found to be 10:2.1 in contradiction with the observed 10:8. For H_β the calculated ratio is 10:3.6, and the observed 10:9. The discrepancy is too great to be accounted for by the incompleteness of the model, and points to a difficulty in the Born and Jordan theory.

E. SCHROEDINGER[1] and the author,[2] independently, have developed a method for calculating the Born and Jordan matrices. The method is based on an equation proposed in two earlier papers by Schroedinger.[3] In this paper it is proposed to apply it to the determination of the matrices which are supposed to represent the hydrogen spectrum.

The simple model of an electron revolving about a positive nucleus will be the basis for the calculation, in so far as any model is involved. The possibility that the electron itself may be in rotation will not be considered,[4] though it is believed that it will be necessary to make this assumption if a satisfactory account of the fine structure is to be obtained.

The fundamental equation of the theory of the hydrogen atom is, according to the work of Schroedinger (Ref. I):

$$\frac{h^2}{8\pi^2 m}\Delta^2\psi+\left(\frac{e^2}{r}-W\right)\psi=0 \qquad (1)$$

where m and e are the mass and charge of the electron and W the energy of the stationary state. Schroedinger has discussed, in a very elegant

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[1] Schroedinger, Ann. der Physik **79**, 734 (1926) (communicated March 18, 1926). This paper will hereafter be referred to as Ref. II.

[2] Eckart, Proc. Nat. Acad. **12**, 473 (1926) (communicated May 31, 1926); Phys. Rev. **28**, 711 (1926). The last paper will be referred to as Ref. A.

[3] Schroedinger, Ann. der Physik **79**, 361, 481 (1925), hereafter cited as Ref. I.

[4] Uhlenbeck and Goudsmit, Nature **117**, 75 (1926).

manner, the solutions of this equation which are to be considered as physically admissable, so that it will be sufficient to quote his results.

These solutions correspond to values of W in (1) which are given by

$$W=-\frac{2\pi^2me^4}{h^2l^2},\quad l=1,2,3,\cdots. \tag{2}$$

These values are recognized as the Bohr energy levels. The solutions themselves are

$$\Psi=B\chi(nl,r)P_n{}^m(\cos\theta)\exp(im\phi) \tag{3}$$

where $r\theta\phi$ are the usual polar coordinates. The functions $P_n{}^m$ are the functions associated to the Legendre polynomials, and m and n are integers, m ranging from $-n$ to $+n$.[5] The quantity B is an arbitrary constant, whose value will be determined later.

The function χ satisfies the equation

$$\frac{d}{dr}\left(r^2\frac{d\chi}{dr}\right)+\left\{\frac{8\pi^2m}{h^2}(Wr^2+e^2r)-n(n+1)\right\}\chi=0 \tag{4}$$

and may be represented by the integral

$$\chi(nl)=\frac{r^n}{2\pi i}\int\exp(zr)\cdot\left(z-\frac{1}{\rho l}\right)^{l+n}\left(z+\frac{1}{\rho l}\right)^{n-l}dz \tag{5}$$

which is to be evaluated along a closed path, in the complex plane, which encircles the point $z=-1/\rho l$. The quantity ρ has the value $h^2/4\pi^2me^2$. By Cauchy's formula, this integral reduces to zero when $n>l$, and to

$$\chi(nl)=\frac{r^n}{(l-n-1)!}\left(\frac{\partial}{\partial z}\right)^{l-n-1}\left\{\exp(zr)\cdot\left(z-\frac{1}{\rho l}\right)^{l+n}\right\} \tag{6}$$

when $n<l$. In (6), the quantity z is to be given the value $-1/\rho l$ after the differentiation has been carried out.

Preliminary Formulas

In the next section, we shall require certain integrals, which will be discussed here, so as not to break the continuity of the later steps. The first integral is

$$\int_0^\infty r^2\chi(nl)\chi(n\lambda)dr \tag{7}$$

It is readily deduced from (4), by partial integration, that it is zero unless $l=\lambda$. In this last case, formula (6), together with the formula

[5] Cf. Byerly, Fourier Series and Spherical Harmonics, p. 195.

$$\int_0^\infty x^n e^{-ax}dx = n!/(a^{n+1}), a>0$$

yields

$$\int_0^\infty r^2[\chi(nl)]^2dr = \frac{(2n+2)!}{[(l-n-1)!]^2}\left(\frac{\partial^2}{\partial z\partial y}\right)^{l-n-1}\frac{\left[\left(z-\frac{1}{\rho l}\right)\left(y-\frac{1}{\rho l}\right)\right]^{l+n}}{(-z-y)^{2n+3}}$$
$$= [c(nl)]^2, \tag{7a}$$

where both z and y are to be replaced by $-1/\rho l$ after the differentiations have been carried out. Substituting $p=l-n-2$, $q=2n+2$, $\zeta=\rho lz$, $\eta=\rho ly$ this becomes

$$\left(\frac{1}{\rho l}\right)^{2n-1}\frac{q!}{[(p+1)!]}\left(\frac{\partial^2}{\partial\zeta\partial\eta}\right)^{p+1}\frac{[(\zeta-1)(\eta-1)]^{p+q}}{(-\zeta-\eta)^{q+1}} \tag{8}$$

Using Leibnitz's formula

$$\left(\frac{\partial}{\partial x}\right)^p AB = \sum_{\alpha=0}^{p}\frac{p!}{\alpha!(p-\alpha)!}\frac{\partial^{p-\alpha}A}{\partial x^{p-\alpha}}\frac{\partial^\alpha B}{\partial x^\alpha} \tag{9}$$

expression (8) reduces to

$$\left(\frac{1}{\rho l}\right)^{2n-1}\frac{(p+q)!}{[(p+1)!]^2}\left(\frac{\partial}{\partial\eta}\right)^{p+1}(\eta-1)^{p+1}\frac{\partial}{\partial\zeta}\frac{(\zeta-1)^q(-\eta-1)^p}{(-\zeta-\eta)^{p+q+1}} \tag{10}$$

The factor involving ζ is

$$\left\{\frac{(\zeta-1)^{q-1}}{(-\zeta-\eta)^{p+q+1}}+(p+q+1)\frac{(\zeta-1)^q}{(-\zeta-\eta)^{p+q+2}}\right\}$$

Substituting $\zeta=-1$ in this, since all the differentiations have been carried out, and the result into (10), we have as the value of the integral

$$-\left(\frac{1}{\rho l}\right)\frac{(p+q)!}{[(p+1)!]^2}\frac{\partial^{p+1}}{\partial\eta^{p+1}}(-\eta+1)^p =$$
$$(2)^{q-1}\left\{q\frac{1}{(1-\eta)}-2(p+q+1)\frac{1}{(1-\eta^2)}\right\} \tag{11}$$

To reduce this further, we evaluate

$$\left(\frac{\partial}{\partial\eta}\right)^{p+1}\frac{(\eta+1)^p}{(1-\eta)^\alpha}$$

for $\eta=-1$. By Cauchy's formula, this is

$$\frac{(p+1)!}{2\pi i}\int\frac{(\eta+1)^p d\eta}{(\eta+1)^{p+2}(1-\eta)^\alpha} = (p+1)!\frac{\partial}{\partial\eta}(1-\eta)^{-\alpha} \tag{12}$$

Evaluating this for $\eta=-1$ and substituting in (11) gives as the value of the integral:

$$[c(nl)]^2=\left(\frac{2}{\rho l}\right)^{2n-1}\frac{2l(l+n)!}{(l-n-1)!} \tag{13}$$

•A second integral which will be needed is

$$A(n,l\lambda)=\int_0^\infty r^3\chi(nl)\chi(n-1\lambda)dr$$

which becomes, on substituting (6),

$$A(n,l\lambda)=\frac{(2n+2)!}{(l-n-1)!(\lambda-n)!}\left(\frac{\partial}{\partial z}\right)^{l-n-1}\left(\frac{\partial}{\partial y}\right)^{\lambda-n}\cdot \tag{14}$$
$$\frac{\left(z-\frac{1}{\rho l}\right)^{l+n}\left(y-\frac{1}{\rho l}\right)^{\lambda+n-1}}{(-z-y)^{2n+3}}$$

It has not been possible to effect any essential reduction of this expression, but its numerical value may be obtained from the expansion of (14):

$$A(n_1l\lambda)=(l+n)!(\lambda+n-1)!\sum_{\alpha=0}^{\lambda-n}\sum_{\beta=0}^{l-n-1}\frac{(2n+2+\alpha+\beta)!\left(-\frac{2}{\rho\lambda}\right)^{2n-1+\alpha}}{\alpha!(\lambda-n-\alpha)!(2n-1+\alpha)!} \tag{14a}$$
$$\frac{\left(-\frac{2}{\rho l}\right)^{2n+1+\alpha}}{\beta!(l-n-1-\beta)!(2n+1+\beta)!}$$

which is readily obtained by carrying out the differentiation.

The value of the constant B is to be determined in such a way that the matrices are Hermite. The author has shown (Ref. A) this is equivalent to the condition that

$$\iiint\psi(mnl)\psi(-mnl)dv=1 \tag{15}$[6]$$

where the integral is to be extended over all space.
Since this integral may be separated into the product of three, and it is readily seen that

$$B=1/[\sqrt{2\pi}c(nl)D(mn)] \tag{16}$$

[6] The appearance of a negative sign in this formula is a consequence of the use of the function $\exp(im\phi)$ instead of the more usual sin or cos. The former notation has certain advantages for our purposes, and is permissible if the convention that $P_n^{-m}=P_n^m$ is agreed upon.

where $c\,(nl)$ has the value given by (7a) and (13), while

$$[D(mn)]^2=\int_{\pi/2}^{\pi/2}[P_n{}^m(\cos\theta)]^2\sin\theta d\theta=\frac{(n+m)!}{(n-m)!}\,\frac{2}{2n+1}$$

Certain formulas relative to the functions $P_n{}^m$ will also be needed[7]:

$$(2n+1)\cos\theta P_n{}^m=(n-m-1)P_{n+1}^{\ m}+(n-m)P_{n+1}^{\ m}$$

$$\begin{aligned}(2n+1)\sin\theta P_n{}^m&=-(n-m+1)(n-m+2)P_{n+1}^{\ m}+(n+m-1)(n+m)P_{m-1}^{\ m-1}\\&=P_{n+1}^{\ m+1}-P_{n-1}^{\ m+1}\end{aligned}\tag{18}$$

These functions also constitute an orthogonal set:

$$\int_{\pi/2}^{\pi/2}P_n{}^mP_\nu{}^m\sin\theta d\theta=0\ ;\ n\neq\nu.\tag{19}$$

Calculation of the Matrices

Since three quantum numbers enter into the function ψ, the matrices will have six indices, three, mnl, for the initial state, and three, $\mu\nu\lambda$, for the final state of the atom. There will be a matrix for each of the rectangular coordinates x, y, and z. However, it will be more convenient not to calculate these matrices, but rather those corresponding to $x+iy$, $x-iy$ and z. These will be denoted by $R(mnl,\ \mu\nu\lambda)$, and $S(mnl,\ \mu\nu\lambda)$, and $Z(mnl,\ \mu\nu\lambda)$, respectively.

The calculation of R will be carried out in detail. It is defined by (Ref. A and II)

$$R(mnl,\mu\nu\lambda)=\int\int\int r^2(x+iy)\psi(mnl)\psi(\mu\nu\lambda)dv\tag{20}$$

where the integral is to be extended throughout all space. Since $x+iy=r\sin\theta\exp(i\phi)$, this integral is the product of three:

$$\begin{gathered}\frac{1}{2\pi}\int_0^{2\pi}\exp i(m+1-\mu)\phi d\phi\\ \frac{1}{D(mn)D(\mu\nu)}\int_{-\pi/2}^{+\pi2}\sin^2\theta P_n{}^mP_\nu{}^\mu\,d\theta\end{gathered}\tag{21}$$

and

$$\frac{1}{c(nl)c(\nu\lambda)}\int_0^\infty r^3\chi(nl)\chi(\nu\lambda)dr$$

The first integral is zero except when $\mu=m+1$ and then has the value unity. Hence the second need only be evaluated for $\mu=m+1$, and its

[7] I am indebted to Professor Epstein's notes for these formulas. They are due to C. Neumann, but the reference is not available.

value is readily obtained by multiplying the third of (18) by $\sin\theta\, P_\nu^{m+1}$ and integrating. From (19) it follows that it is zero except when $\nu = n \pm 1$ and from (17) that it is equal to

$$\frac{1}{2n+1}\,\frac{D(m+1\ n+1)}{D(mn)} \tag{22}$$

when $\nu = n+1$
and

$$\frac{-1}{2n+1}\,\frac{D(m+1\ n-1)}{D(mn)}$$

when $\nu = n-1$.

Hence the third need only be evaluated for $\nu = n \pm 1$ and is readily seen to be

$$\frac{A(n,l\lambda)}{c(nl)c(n-1,\lambda)} \tag{23}$$

when $\nu = n-1$

$$\frac{A(n+1,\lambda l)}{c(nl)c(n+1,\lambda)}$$

when $\nu = n+1$.

where A is the integral (14). The conclusion is that $R(mnl,\mu\nu\lambda)$ is zero except in the cases included in the formulae

$$\begin{aligned} R(mnl\,m+1\ n+1\,\lambda) &= \frac{1}{2n+1}\,\frac{D(m+1\,n+1)}{D(mn)}\,\frac{A(n,l\lambda)}{c(nl)c(n-1,\lambda)} \\ R(mnl\,m+1\ n-1\,\lambda) &= \frac{-1}{2n+1}\,\frac{D(m+1\,n-1)}{D(mn)}\,\frac{A(n+1,\lambda l)}{c(nl)c(n+1,\lambda)} \end{aligned} \tag{24}$$

The matrices S and Z may be computed in the same manner. Writing

$$J(nl\lambda) = \frac{A(n,l\lambda)}{c(nl)c(n-1,\lambda)} \tag{25}$$

and substituting for D its value, the result is that all the terms of the matrices are zero except the following, in which the substitution $k = n+\frac{1}{2}$ has been made:

$$R(mnl,m+1\,n+1\,\lambda) = \sqrt{\frac{(k+m+3/2)(k+m+\frac{1}{2})}{k(k+1)}}\cdot\tfrac{1}{2}J(k+\tfrac{1}{2},\lambda l)$$

$$R(mnl,m+1\,n-1\,\lambda) = -\sqrt{\frac{(k-m-\frac{1}{2})(k-m-3/2)}{k(k-1)}}\cdot\tfrac{1}{2}J(k-\tfrac{1}{2},l\lambda)$$

$$S(mnl,m-1\,n+1\,\lambda) = -\sqrt{\frac{(k-m+3/2)(k-m+\frac{1}{2})}{k(k+1)}}\cdot \tfrac{1}{2}J(k+\tfrac{1}{2},\lambda l) \qquad (26)$$

$$S(mnl,m-1\,n-1\,\lambda) = \sqrt{\frac{(k+m-\frac{1}{2})(k+m-3/2)}{k(k-1)}}\cdot \tfrac{1}{2}J(k-\tfrac{1}{2},l\lambda)$$

$$Z(mnl,m\,n+1\,\lambda) = \sqrt{\frac{(k+m+\frac{1}{2})(k-m+\frac{1}{2})}{k(k+1)}}\cdot \tfrac{1}{2}J(k+\tfrac{1}{2},\lambda l)$$

$$Z(mnl,m\,n-1\,\lambda) = \sqrt{\frac{(k+m-\frac{1}{2})(k-m-\frac{1}{2})}{k(k-1)}}\cdot \tfrac{1}{2}J(k-\tfrac{1}{2}),l\lambda)$$

Were the half quantum-numbers not used, the symmetry which is very evident in (27) would be quite obscured. This notation also brings out the Heisenberg "square," $\bar{k}^2 = k(k+1)$, which is so characteristic in the description of the Zeeman effect.

Discussion of the Matrices

According to the original definition of the matrices, each term of the matrix represents the amplitude of a partial oscillation of the electric moment of the atom. The matrix term $Z(mnl,\mu\nu\lambda)$, for example, represents the z-component of the amplitude of a partial oscillation of frequency $(1/h)(W_\lambda - W_l)$. Using a somewhat mixed terminology, it is the amplitude of the oscillation due to a transition from the state mnl to the state $\mu\nu\lambda$.

The formulas (26) therefore show that only those transitions in which m changes by ± 1 or 0 and k by ± 1 actually occur. When m does not change, only the matrix Z has a non-zero term, and the oscillation has therefore no x or y component—the light emitted is linearly polarized, in the usual sense of the term in spectroscopy. When m changes by 1 the R matrix has the non-vanishing term, and since R corresponds to $x+iy$, this represents emitted light which is circularly polarized. The change of m by -1 results in light which is also circularly polarized, but in the opposite sense.

These polarization rules correspond to those for the three components of the normal Zeeman effect, and a preliminary treatment of this effect shows that the separation is also given, in this theory, by the usual formula, the number m playing the usual rôle. There are still several fundamental questions to be answered before the discussion of this problem can be completed, however.

The quantum number k which changes only by ± 1 is evidently the azimuthal. This identification is rendered certain by a calculation of the

relativistic fine-structure (subject to the same uncertainty of theoretical interpretation, however, as the Zeeman effect). The additional term-value is

$$\Delta\nu=\frac{R\alpha^2}{l^4}\left\{\frac{l}{k}-\frac{3}{4}\right\}, \quad R=\text{Rydberg constant},$$

which is identical in form with the expression given by the Sommerfeld theory. Since k in that theory takes on the values 1,2,3 . . . . , while in this theory it takes the values $\frac{1}{2},\frac{3}{2}$ . . . . , however, the levels will not coincide. This difference is apparently just that which is required by the theory of the rotating electron.[8]

Thus much for the identification of the quantum numbers. Since the intensity of the light emitted by an oscillating dipole is proportional to the square of the amplitude, the expressions (26) furnish the means of calculating this quantity. Since the atomic system under consideration is degenerate, the total intensity of the light of a given frequency emitted will be proportional to

$$I(l\lambda)=\sum_m\sum_k(\tfrac{1}{2}R^2+\tfrac{1}{2}S^2+Z^2)$$

$$m=-(k-\tfrac{1}{2})\to k-\tfrac{1}{2}, \qquad k=\tfrac{1}{2}\to l-\tfrac{1}{2} \tag{28}$$

The factors $\frac{1}{2}$ appear because the R and S terms represent circularly polarized light.

An approximation to the relative intensity of the components of the relativistic fine structure may also be obtained. The intensity of the line corresponding to a transition from $\kappa\lambda$ to kl will be

$$I(kl,\kappa\lambda)=\sum_m(\tfrac{1}{2}R^2+\tfrac{1}{2}S^2+Z^2) \tag{29}$$

Carrying out the summation, it is found that

$$I(k-1\,l,k\lambda)=(k-\tfrac{1}{2})[J(k-\tfrac{1}{2}\lambda l)]^2$$
$$I(kl,k-1\,\lambda)=(k-\tfrac{1}{2})[J(k-\tfrac{1}{2}l\lambda)]^2$$

all others being zero. On calculating the quantities I for H_α, $(l=2,\ \lambda=3)$, the intensities of the three components are given as proportional to

$$I(1/2\ \ 3,3/2\ \ 2)= \quad .879\rho^2$$
$$I(3/2\ \ 3,1/2\ \ 2)= \quad 9.42\rho^2$$
$$I(5/2\ \ 3,3/2\ \ 2)= \quad 45.2$$

These values are not in accordance with observation. According to experiments of W. V. Houston, the actual ratio of the intensities of the two brighter components is more nearly 8:10 than 2:10. For H_β

[8] Note added Oct. 23, 1926. Cf. Schroedinger, Ann. d. Physik **81**, 132 (1926).

$$I(1/2\ \ 4, 3/2\ \ 2) = .146\rho^2$$
$$I(3/2\ \ 4, 1/2\ \ 2) = 1.64\rho^2$$
$$I(5/2\ \ 4, 3/2\ \ 2) = 5.88\rho^2$$

whereas observation yields 9:10 for the ratio of the two brighter.

In how far this lack of agreement is to be laid to the general theory, and how far to the model on which the calculations are based, is not certain. The model is certainly incomplete, as is shown by the energy levels of the fine-structure predicted by this theory. The rotation of the electron, which is expected to remove this discrepancy, is also expected to predict a fourth component whose intensity is included in that of the fainter of the two components observed. It does not appear likely, however, that its intensity will be sufficient to account for all the difference.

This theory, so far as its determination of the energy levels and selection principles is concerned, is unimpeachable. It must be emphasized, however, that the identification of the matrix terms with dipole amplitudes constitutes an independent hypothesis.

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