of all substances, great fields of equilibria hitherto unsuspected, in which the individual states differ from one another with respect to the new variable, the number of photons. If such a necessity arises and the law of conservation of photons can be established, it may be necessary to revise still further our ideas of thermal radiation, for in that case it would be doubtful whether what is known as black body radiation is as definite a thing as has been supposed.

[1] Lewis, these PROCEEDINGS, 13, 307 (1927).
[2] Lewis, *Nature*, 118, 874 (1926).
[3] Einstein, *Ann. Physik*, 38, 881 (1921); *J. Physique*, 3, 277 (1913).

THE HYDROGEN ATOM WITH A SPINNING ELECTRON IN WAVE MECHANICS

By C. F. RICHTER

CALIFORNIA INSTITUTE OF TECHNOLOGY

Communicated May 9, 1927

In this paper it is shown that the Schrödinger wave mechanics, plus the Uhlenbeck-Goudsmit spinning electron, completely represents the fine structure of hydrogen-like spectra.

The Hamiltonian function of the system in classical mechanics is taken as

$$H = \frac{1}{2m}\left[p_r^2 + \frac{p_\vartheta^2}{r^2} + \frac{p_\varphi^2}{r^2 \sin^2\vartheta}\right] + \frac{1}{2I}\left[p_\theta^2 + \frac{1}{\sin^2\theta}\left(p_\Phi^2 + p_\psi^2 - 2p_\Phi p_\psi \cos\theta\right)\right]$$
$$- \frac{Ze^2}{r} + \frac{Q}{r^3}\left[\cos\alpha p_\vartheta p_\theta - \cot\theta \sin\alpha p_\vartheta p_\psi + \csc\theta \sin\alpha p_\vartheta p_\Phi + \cot\vartheta \sin\alpha p_\varphi p_\theta\right.$$
$$\left. + (1 + \cot\vartheta \cot\theta \cos\alpha) p_\varphi p_\psi - \cot\vartheta \csc\theta \cos\alpha p_\varphi p_\Phi\right] \quad (1)$$

in which r, ϑ, φ are polar coördinates of the center of the electron, referred to the nucleus (of atomic number Z); θ, ψ, Φ are Eulerian angles of the (spherical) electron referred to a parallel polar axis and initial plane; m is the mass of the electron, I its moment of inertia, e its charge, while $Q = \frac{Ze^2}{2m^2c^2}$, and α is an abbreviation for $\psi - \varphi$.

The writer has made use of the above expression for the quantization of the system on the old quantum theory;[1] the results were identical with those of other investigators.[2] It should be remarked that this form is valid only to terms of order v^2/c^2, where v is the velocity of the electron.

Further, the terms due to the relativity change of mass are omitted; it will be shown later that their inclusion leads to the addition of the Sommerfeld correction (with half-integral azimuthal quantum number k) to the energy.

To derive the corresponding wave equation we note that H is equal to the potential energy plus a quadratic form in the momenta. Introducing this quadratic form in Schrödinger's variation principle,[3] we obtain, neglecting terms of order Q^2 and higher,

$$\nabla^2 u + \frac{m}{I}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial u}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\left[\frac{\partial^2 u}{\partial\psi^2} + \frac{\partial^2 u}{\partial\Phi^2} - 2\cos\theta\frac{\partial^2 u}{\partial\psi\partial\Phi}\right]\right\}$$

$$+ \frac{2mQ}{r^3}\left\{\cos\alpha\frac{\partial^2 u}{\partial\vartheta\partial\theta} - \cot\theta\sin\alpha\frac{\partial^2 u}{\partial\vartheta\partial\psi} + \csc\theta\sin\alpha\frac{\partial^2 u}{\partial\vartheta\partial\Phi}\right.$$

$$+ \cot\vartheta\sin\alpha\frac{\partial^2 u}{\partial\varphi\partial\theta} + [1 + \cot\vartheta\cot\theta\cos\alpha]\frac{\partial^2 u}{\partial\varphi\partial\psi}$$

$$\left. - \cot\vartheta\csc\theta\cos\alpha\frac{\partial^2 u}{\partial\varphi\partial\Phi}\right\} + \frac{8\pi^2 m}{h^2}\left[E + \frac{Ze^2}{r}\right]u = 0. \quad (2)$$

We have to treat this by the method of perturbations.[4] Our perturbation is the term with factor $2mQ/r^3$. We put $u = au_0 + 2mQv$, $E = E_0 + 2mQ\epsilon$, where u_0 is a characteristic function of the unperturbed equation, and E_0 is the corresponding parameter.

The unperturbed equation corresponds to a spherical electron moving about the nucleus and simultaneously rotating, the two motions not affecting each other. A particular solution u_0 is then the product of the functions characteristic of these two motions. The first of these is well known.[5] The second is a special case of that worked out by Reiche and Rademacher.[6] The result is

$$\left.\begin{aligned} u_0 &= N\chi_{ne}(r)P_l^{n_1}(\cos\vartheta)T(\theta)e^{i(n_1\varphi + n_2\psi + n_3\Phi)} \\ T(\theta) &= \left(\sin\frac{\theta}{2}\right)^d\left(\cos\frac{\theta}{2}\right)^s F\left(-p, 1 + d + s + p, 1 + d, \sin^2\frac{\theta}{2}\right) \end{aligned}\right\} \quad (3)$$

where N is a normalizing factor, $\chi_{nl}(r)$ is Schrödinger's function for the quantum numbers n and l, $P_l^{n_1}$ is an associated Legendre function, and F a hypergeometric function. n is a positive integer; n_1, n_2, n_3, l, d, s, p are integers or zero; the four latter cannot be negative.

E_0 includes both orbital and spin energy. The latter is constant and does not affect the spectrum; it is proportional to $\sigma(\sigma + 1)$,[7] where

$$\sigma = \frac{1}{2}(d + s) + p.$$

We must take $\sigma = 1$. Moreover, $d = |n_2 - n_3|$, $s = |n_2 + n_3|$. This limits us to the following cases:

p	d	s	n_2	n_3	F
1	0	0	0	0	$\cos\theta$
0	2	0	± 1	∓ 1	1
0	1	1	0	± 1	1
0	1	1	± 1	0	1
0	0	2	± 1	± 1	1

We define

$$Y_l^{n_1}(\vartheta,\varphi) = P_l^{n_1}(\cos\vartheta)e^{in_1\varphi}, \quad Z_{n_3}^{n_2}(\theta,\psi,\Phi) = T(n_2, n_3, \theta)e^{i(n_2\psi + n_3\Phi)} \quad (4)$$

so that

$$u_0 = N\chi_{nl}(r)Y_l^{n_1}(\vartheta,\varphi)Z_{n_3}^{n_2}(\theta,\psi,\Phi). \quad (5)$$

After carrying out our substitutions on the wave equations (2) and performing several reductions, it takes the form.

$$\nabla^2 v + \frac{m}{I}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial v}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\left[\frac{\partial^2 v}{\partial\psi^2} + \frac{\partial^2 v}{\partial\Phi^2} - 2\cos\theta\frac{\partial^2 v}{\partial\psi\partial\Phi}\right]\right\} + \frac{8\pi^2 m}{h^2}\left[E_0 + \frac{Ze^2}{r}\right]V$$

$$= \frac{a}{r^3}N\chi_{nl}(r)X(l, n_1, n_2, n_3) - \frac{8\pi^2 m}{h^2}\epsilon a u_0. \quad (6)$$

$$\left.\begin{array}{l} \text{When } n_2 = \pm 1,\ X(l, n_1, n_2, n_3) = \pm\, y(n_2)Y_e^{n_1+n_2}Z_0^{n_3} - n_1 n_2 Y_l^{n_1}Z_{n_3}^{n_2} \\ \text{When } n_2 = 0,\ X(l, n_1, o, n_3) = \pm\, y(-1)Y_e^{n_1-1}Z_1^{n_3} + Y_l^{n_1+1}Z_{-1}^{n_3} \end{array}\right\} \quad (7)$$

In general, $y(+1) = 1$, $y(-1) = (l - n_1 + 1)(l + n_1)$

but in some cases these values are to be divided by 2; their sign varies from case to case.

The general theory[4] shows that we can perform the following expansions:

$$\frac{N}{r^3}\chi_{nl}(r) = \frac{1}{r}\sum_{n'} A_{n'}\chi_{n'l}, \quad Nr\chi_{nl}(r) = \frac{1}{r}\sum_{n'} B_{n'}\chi_{n'l}$$

where the summation extends over all possible values of n', so that the right side of our equation can be expressed as the series

$$\frac{a}{r}\sum_{n'}\left[X(l, n_1, n_2, n_3)A_{n'} - \frac{8\pi^2 m}{h^2}\epsilon Y_l^{-n_1}Z_{n_3}^{n_2}B_{n'}\right]\chi_{n'l}.$$

X, in general, contains two terms, in one or both of which the indices of the functions Y and Z differ from l, n_1, n_2, n_3. If there is a term in X

in which these indices do not differ from l, n_1, n_2, n_3, there is then one term of the above expansion in which all five indices have the particular values n, l, n_1, n_2, n_3; and the theory[4] shows that the coefficient of this term must vanish. Since the coefficient of $Y_l^{n_1} Z_{n_2}^{n_3}$ in X is always $-n_1 n_2$, it follows that

$$\epsilon = -\frac{h^2}{8\pi^2 m} n_1 n_2 . \frac{An}{Bn} . \qquad (8)$$

But if $n_2 = -1$ this is of precisely the same form as the result obtained by applying the same method of perturbations to the wave equation discussed by Professor Epstein,[8] which corresponds to a non-magnetic electron revolving about a nucleus containing a fixed magnetic dipole of moment Z times that of the spinning electron. This equation has been shown by Professor Epstein[8] to give the energy levels which, when added to the relativity correction (in the form for the new mechanics, with apparent half-quanta), produce the observed fine structure, on the assumption that the condition $n_1 = l + 1$ or $-l$ is satisfied.

Now, it can be shown by considerations too lengthy for inclusion here that we are actually restricted to the cases in which $n_2 = -1$ and $n_1 = l + 1$ or $-l$. Our wave equation thus gives the correct energy levels, provided that the relativity correction is additive; and this is now evident. For the characteristic function of the hydrogen-like atom without spin is affected by the relativity correction only in the form of the function $\chi_{nl}(r)$. We have made no use of the explicit form of this function, so that all our considerations still apply in the case including relativity; the energy terms which appear here as additive corrections will play the same part there.

With this the outline of the demonstration is completed; a more detailed account of the method will be published later. The writer wishes to express his deep indebtedness to Professor P. S. Epstein, whose constant advice and encouragement have made this work possible, and whose own investigations have contributed largely to its successful conclusion.

[1] *Physical Review*, **28**, 1926, p. 849 (Abstract). The same or an equivalent form has been used by others (see note 2). In a course of lectures recently delivered by Professor H. A. Lorentz at this Institute it was shown that this is not *strictly* the rigorous expression, since terms involving the accelerations are omitted. However, it is certain that within the approximation used (terms of order v^2/c^2) the rigorous expression leads to the same result. (In my equation, loc. cit., interchange j and k.)

[2] Heisenberg, W., and Jordan, P., *Zeits. Physik*, **37**, 1926, p. 263.

[3] *Ann. Physik*, **79**, 1926, p. 748.

[4] Cf. Schrödinger, *Annalen*, **80**, 1926, pp. 440ff; and for the method used here refer especially to Epstein, P. S., these PROCEEDINGS, **13**, June, 1927, p. 432.

[5] Schrödinger, *Annalen*, **80**, 1926, p. 479.

[6] *Zeits. Physik*, **39**, 1926, p. 444.

[7] *Ibid.*, p. 449.

[8] Epstein, P. S., these PROCEEDINGS, **13**, April, 1927, p. 232.