Ithaca, Feb. 1923, p. 207; May 1923, p. 483; June 1923, p. 715; *Phil. Mag. London*, Nov. 1923, p. 897.

[3] Ross, these PROCEEDINGS, July 1923, and June 1924.

[4] Duane and others, these PROCEEDINGS, Dec. 1923, p. 419; Jan. 1924, p. 41; March 1924, p. 92; April 1924, p. 148.

COULOMB'S LAW AND THE HYDROGEN SPECTRUM

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Communicated, July 3, 1924

In the Bohr theory of the hydrogen atom restricted, let us say, to circular orbits so as to deal only with the simplest case, Coulomb's law has been assumed to hold. This is carrying over to the microcosm our molar laws of electricity and might seem a doubtful procedure in the face of our giving up so much of our mechanics just as it seems to some questionable, after taking the electron as the indivisible electric unit, to talk of the distribution of electricity over or through the electron.[1] In favor of Coulomb's law for the microcosm we have our general tendency to carry over and apply old laws whenever they work and insofar as they work. Further in favor are the scattering experiments of Rutherford dealing with the positive nuclei.[2] And it may be that best of all our evidence is the success with which theories of spectra have been worked out by combining Coulomb's law with elementary mechanics plus the quantum hypothesis.

Is then the law of Coulomb really implied by the quantum theory? The equations of motion for the electron in its circle are

$mrw^2 = -F = dV/dr$	force equation	(1)
$mr^2w = nh/2\pi$	quantum condition	(2)
$E_2 - E_1 = h\nu$	frequency condition	(3)
$\nu = N(1/n_1^2 - 1/n_2^2)$	spectral law	(4)

Here F is the central force, V is the potential energy, r is the orbital radius, m is the mass, w is the angular velocity, E is the total energy, etc.

$$E = V + \frac{1}{2} mr^2w^2 \qquad \text{energy equation} \qquad (5)$$

From (4) and (3) we have

$$E_1 + Nh/n_1^2 = E_2 + Nh/n_2^2 \qquad (6)$$

For all subscript combinations arising from $n_1 = 1,2,\ldots$, $n_2 = 2,3,\ldots$, $n_1 < n_2$. Hence

$$V_i + \frac{1}{2} mr_i^2 w_i^2 + Nh/n_i^2 = \text{constant}, \; i = 1,2,\ldots \tag{7}$$

As V may contain an additive constant we may write

$$V + \frac{1}{2} mr^2 w^2 + Nh/n^2 = 0 \tag{8}$$

This equation must hold for all values of r which occur in the orbits. Let us assume it holds identically for all values of r, as it surely holds for all those in which we are interested and as the use of $-F = dV/dr$ implies other values of r at least in the vicinity of the orbital radii.

Now equations (1), (2), (8) contain in addition to r and V the unknown or variable quantities w and n. We shall eliminate them to obtain a relation between V and r. First introduce the auxiliary variable $u = 1/r^2$. Then

$$\frac{1}{2} mw^2 = -u^2 dV/du \qquad \text{from (1)}$$

$$2\pi mw = unh \qquad \text{from (2)}$$

$$V + \frac{1}{2} mw^2/u + Nh/n^2 = 0 \qquad \text{from (8)}$$

Hence $$V - udV/du = -Nh/n^2 \qquad \text{from (1) and (8)}$$

But $$-\frac{1}{n^2} = -\frac{u^2h^2}{4\pi^2 m^2 w^2} = \frac{h^2}{8\pi^2 m}\frac{du}{dV} \qquad \text{from (2) and (1)}$$

If we write $p = dV/du$ the equation for V takes the Clairaut form

$$V = up + A/p, \qquad A = Nh^3/8\pi^2 m \tag{9}$$

The solution is

$$V = Cu + A/C, \qquad C = \text{integration constant} \tag{10}$$

$$V = \frac{C}{r^2} + \frac{A}{C}, \qquad F = -\frac{dV}{dr} = \frac{2C}{r^3} \tag{11}$$

It appears therefore that the force should be as the inverse cube and involves a (negative) constant C as yet undetermined.[3]

If we eliminate w between (1) and (2) we have

$$mr^3 = -n^2h^2/4\pi^2 F = -n^2h^2r^3/8\pi^2 C$$

Hence it appears that r cancels out and the quantum condition imposes no restriction on the size of the orbit—a fact well known for the law of the inverse cube. Then

$$-C = n^2h^2/8\pi^2m = An^2/Nh \tag{12}$$

The force and potential energy therefore are

$$F = -\frac{2An^2}{Nhr^3} = -\frac{h^2n^2}{4\pi^2mr^3} \tag{13}$$

$$V = -\frac{An^2}{Nhr^2} - \frac{Nh}{n^2} = -\frac{h^2n^2}{8\pi^2mr^2} - \frac{Nh}{n^2} \tag{14}$$

It appears therefore that the force and potential energy depend on the quantum number; it is the force that is quantized and not the orbit.[4]

The differential equation (9) has, however, another solution, namely, the singular solution obtained by eliminating the constant between (10) and its derivative with respect to the constant.

$$V = \frac{C}{r^2} + \frac{A}{C} \qquad 0 = \frac{1}{r^2} - \frac{A}{C^2}$$

$$V = -\sqrt{\frac{Nh^3}{2\pi^2m}}\,\frac{1}{r} = -\frac{e^2}{r} \qquad \text{since } e^4 = \frac{Nh^3}{2\pi^2m}$$

This is Coulomb's law. From the general line of argument which leads to this result, it would appear that if we had given the quantum equations (2) and (3), the spectral law (4) and if we assume so much of elementary mechanics as the energy equation (5) and the force equation for circular orbits (1) and further assume that equation (8), therefrom deduced and known to hold for an infinity of orbits, holds identically, then we are led either to a quantized force (13) or to the Coulomb law.[5]

[1] Cf. G. N. Lewis, *Valence*, especially p. 42 and p. 50.

[2] To be sure, the experiments of Nicholson and Merton on the radii of the atomic orbits in mixtures of hydrogen and helium relative to the distance between molecules and of Ramsauer on the long free paths of electrons in argon and other gases do not favor Coulomb's law. It may be that the repulsion between nuclei and the attraction between nucleus and electron follow different laws.

[3] The inverse cube has been used in tentatives toward atomic theory by J. J. Thomson.

[4] We do not have here the quantized force of G. C. Evans, these PROCEEDINGS, 9, 1923, p. 234; for his term in the inverse cube represents repulsion and not attraction.

[5] This does not get us ahead much; but we may observe that of (1)–(5) only (4) is an experimental fact, (1) and (5) are definitions, (2) and (3) are hypotheses. There is some advantage in replacing the hypothetical Coulomb law by an experimental fact.