

We have tabulated for comparison the probability of transition predicted by theory and that which is determined by experiment. Certainly the theoretical value fails to agree in magnitude with the experimental one by an amount much greater than the possible experimental error.

One may say, perhaps, that some factor must still be introduced in the theoretical expression to obtain the correct magnitude of b_{ij} ; and the experimental observations offer a means of evaluating this. But, unfortunately, the theoretical probabilities do not have even the right relative values. They decrease with quantum number while for the experimental values Tolman and Badger found a decided increase. The absolute values which they calculated may be in error for the reasons given above, but more perfect resolution would be expected to increase the trend they observed rather than to eliminate it. It would seem, therefore, that the predictions of the new quantum theory, while they may apply to some ideal system, do not describe the conditions we have experimentally observed in the case of hydrogen chloride.

In conclusion we wish to express our indebtedness to the Carnegie Institution of Washington for funds which made this work possible.

¹ Czerny, *Zeits. f. Physik*, **34**, 227 (1925).

² Tolman and Badger, *Phys. Rev.*, **27**, 383 (1926).

³ Dennison, *Phys. Rev.*, **28**, 318 (1926).

⁴ Reiche, *Zeits. f. Physik*, **41**, 453 (1927).

⁵ Zahn, *Phys. Rev.*, **24**, 400 (1924).

NOTE ON "PENDULUM" ORBITS IN ATOMIC MODELS

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On the simple Bohr theory the orbit of an electron moving in a central field of force about the nucleus is designated by two quantum numbers n and k , of which the first is called the principal quantum number and the second the azimuthal or auxiliary quantum number. These numbers are allowed to take all integral values (for a given orbit $k \leq n$) except zero. It will be seen that for $k = 0$ we get an orbit which is a straight line passing through the nucleus. This type of orbit is commonly known as a "pendulum" orbit and has been usually ruled out of the system of actual orbits because it involves collision of the electron with the nucleus. Nevertheless the fact that the *energy* of an electron orbit under the conditions specified above depends only on the principal quantum number and not on the azimuthal quantum number suggests the possibility of getting

quantized pendulum orbits (in the case of hydrogenic atoms at any rate) which have the correct energy values even though their physical possibility is open to question. In the recent tendency in modern atomic theory (as, for example, the matrix theory of Heisenberg and Born) to get away from pictures in space and time would seem to emphasize the value of utilizing for purposes of calculation the *simplest possible* orbits which have the correct energy values.

Pendulum orbits have been investigated by J. W. Nicholson.¹ He showed that if we write down the quantum condition for straight line motion, viz., $\oint m\dot{x}dx = nh$, substitute therein from the energy equation, disregarding the relativity correction, and integrate from $x = 0$ to $x = a$ we arrive at the usual Balmer energy value, viz., $W = -2\pi^2N^2e^4m/n^2h^2$. The next step was to employ the energy equation for the relativity case, which is as follows:

$$m_0c^2 \left[\frac{1}{\sqrt{1 - \dot{x}^2/c^2}} - 1 \right] - \frac{Ne^2}{x} = W \quad (1)$$

where m_0 is the rest mass of the electron, e its charge, c the velocity of light, W the energy and N the number of charges on the nucleus. The result of the subsequent analysis appears to be that to a first approximation W comes out to have the same value as in the previous simpler case, i.e., we get correctly quantized orbits. However, inspection shows that there is a serious error involved in Nicholson's reasoning. In the quantum condition he used the rest mass m_0 instead of the varying mass m .² It then becomes important to carry through the analysis correcting this error to see what influence it has on the result.

Proceeding as usual³ we have for the momentum

$$p_x^2 = 2m_0W + W^2/c^2 + 2(m_0Ne^2 + WNe^2/c^2)/x + N^2e^4/c^2x^2 \quad (2)$$

whence the quantum conditions becomes

$$\oint \sqrt{A + 2B/x + C/x^2} dx = nh \quad (3)$$

where

$$\left. \begin{aligned} A &= 2m_0W + W^2/c^2 \\ B &= m_0Ne^2 + WNe^2/c^2 \\ C &= N^2e^4/c^2 \end{aligned} \right\} \quad (4)$$

As usual the integration is to be conducted from the larger of the two roots of the radicand to the smaller and back again. Since B and C are both positive quantities and A alone is negative, one of the roots of the radicand is positive and the other negative, i.e., the electron must pass

through the nucleus and penetrate a certain distance on the other side before $p_x = 0$. The difficulty is that the radicand becomes infinite for $x = 0$ and hence the integral is an infinite integral. Examination discloses that the integral does not converge as $x = 0$; hence the quantum condition as stated ceases to have a meaning.

The question remains under what conditions a pendulum-orbit quantized according to $\oint p_x dx = nh$ is possible. Independently of the failure of the integral to converge the idea of the passage of the electron through the nucleus may be distasteful to some. There is a possible way of avoiding this, namely, by the introduction of a repulsive force (in addition to the inverse square attractive force) operative only in the immediate vicinity of the nucleus. This assumption is not so fearfully arbitrary, for the work on α -particle scattering has indicated clearly that the inverse square law breaks down in the close vicinity of the nucleus. Of course, the exact form for a law of the kind indicated is a matter requiring closer investigation. For the purpose of the present work, however, the writer has thought it valuable to see the effect of using the simplest possible law, namely, an inverse cube force. The mathematical analysis in this case is far simpler than in the cases of higher power force laws, and from the result we should be able to infer qualitatively the effect of introducing a more complicated law.

Replacing in equation (1) Ne^2x by $Ne^2/x - \alpha e^2/x^2$ where α is a coefficient, equation (3) becomes

$$\oint \sqrt{A + 2B/x + C'/x^2 + D_1/x^3 + D_2/x^4} dx = nh \quad (5)$$

where A and B are as given in (4) and

$$\begin{aligned} C' &= N^2e^4/c^2 - 2m_0e^2\alpha - 2We^2\alpha/c^2 \\ D_1 &= -2Ne^4\alpha/c^2, \quad D_2 = e^4\alpha^2/c^2. \end{aligned} \quad (6)$$

The limits of integration are obtained as the roots of the equation

$$W + Ne^2/x - \alpha e^2/x^2 = 0. \quad (7)$$

These roots are:

$$\left. \begin{aligned} x_{\max.} &= -Ne^2/W - \alpha/N \\ x_{\min.} &= \frac{\alpha}{N} (1 - \alpha W/N^2e^2) \end{aligned} \right\} \quad (8)$$

both to the second approximation (i.e., $\alpha \ll e^2/W$). Since D_1 and D_2 are correction terms we can evaluate (5) by expanding by the binomial theorem. Then

$$nh = \oint \sqrt{A + 2B/x + C'/x^2} dx + \oint \frac{1}{2} (A + 2B/x + C'/x^2)^{-1/2} (D_1/x^3 + D_2/x^4) dx - \frac{1}{8} \oint (A + 2B/x + C'/x^2)^{-3/2} (D_1/x^3 + D_2/x^4)^2 dx + \dots \quad (9)$$

Since we do not intend to restrict C' to negative values we do not employ the method of complex integration. We have

$$\begin{aligned} \oint \sqrt{A + 2B/x + C'/x^2} dx &= -2\sqrt{X_{\min.}} + \sqrt{\frac{2B}{-A}} \arcsin \left[-\frac{Ax + B}{\sqrt{B^2 - AC'}} \right]_{x_{\min.}}^{x_{\max.}} \\ &+ \frac{2C'}{\sqrt{-C'}} Z_1, \quad \text{for } C' < 0 \\ &(-2)\sqrt{C'} Z_0, \quad \text{for } C' > 0. \end{aligned} \quad (10)$$

In (10) we have set $X = Ax^2 + 2Bx + C'$, whence $X_{\min.} = Ax_{\min.}^2 + 2Bx_{\min.} + C'$. Moreover we also have

$$\left. \begin{aligned} Z_0 &= \log \left[\frac{\sqrt{X} + \sqrt{C'}}{x} + \frac{B}{\sqrt{C'}} \right]_{x_{\min.}}^{x_{\max.}} \\ Z_1 &= \arcsin \left[\frac{Bx + C'}{x\sqrt{B^2 - AC'}} \right]_{x_{\min.}}^{x_{\max.}} \end{aligned} \right\} \quad (11)$$

Proceeding similarly with the first correction term we have

$$\begin{aligned} &\frac{1}{2} \oint (A + 2B/x + C'/x^2)^{-1/2} (D_1/x^3 + D_2/x^4) dx \\ &= \frac{Z_1}{C'\sqrt{-C'}} \left[-BD_1 - \frac{D_2}{2} \left(\frac{3B^2}{C'} - A \right) \right] + \frac{\sqrt{X_{\min.}}}{C'x_{\min.}} \\ &\quad \left[D_1 - \frac{D_2}{2} \left(\frac{3B}{C'} - \frac{1}{x_{\min.}} \right) \right] \text{if } C' < 0 \\ &= \frac{Z_0}{C'\sqrt{C'}} \left[BD_1 - \frac{D_2}{2} \left(\frac{3B^2}{C'} - A \right) \right] + \frac{X_{\min.}}{C'x_{\min.}} \left[D_1 - \frac{D_2}{2} \left(\frac{3B}{C'} - \frac{1}{x_{\min.}} \right) \right] \\ &\quad \text{if } C' > 0 \quad (12) \end{aligned}$$

Investigation of the order of magnitude of the correction terms D_1 and D_2 indicates that it will not be necessary for the approximation desired in this work to use the second order correction term. Substitution of the limits and replacement of A, B, C', D_1, D_2 by their values as given in (4) and (6) yield finally

$$\frac{2\pi e^2}{c} \left[-1 + (1 + W/m_0c^2)^{-2} \right]^{-1/2} \cdot \left[1 - \frac{1}{\pi} \left\{ -\frac{2W}{m_0c^2} (1 + (N - 1)\lambda) \right\}^{1/2} \right] = nh + \Psi \quad (13)$$

where Ψ represents a correction term different according as $C' < 0$ or $C' > 0$. Thus we have

$$\begin{aligned} \Psi_{C' < 0} = & Ne^2/c \cdot [1 + (N - 1)\lambda]^{1/2} \cdot [2 + 2/N(1 - \lambda) - 1/2N^2(1 - \lambda) \\ & + 3\lambda/2N(1 - \lambda)^2] \\ & + \frac{Ne^2/c}{(\lambda - 1)^{1/2}} \cdot \left[\pi/2 - \arcsin \frac{N - 2}{N} \left(1 + \frac{2}{(N - 2)\lambda} \right) \right] \cdot \\ & [2(\lambda - 1) - 2\lambda/(1 - \lambda) - 3\lambda^2/8(1 - \lambda)^2] \quad (14) \end{aligned}$$

and

$$\begin{aligned} \Psi_{C' < 0} = & Ne^2/c \cdot [1 + (N - 1)\lambda]^{1/2} \cdot [2 + 2/N(1 - \lambda) - 1/2N^2(1 - \lambda) \\ & + 3\lambda/2N(1 - \lambda)^2] \\ & - \frac{Ne^2/c}{(1 - \lambda)^{1/2}} \cdot [2(1 - \lambda) + 2\lambda/(1 - \lambda) + 3\lambda^2/8(1 - \lambda)^2] \log [1 + 2(1 - \lambda)^{1/2}/N\lambda \\ & \cdot \{1 + N(1 - \lambda)^{1/2}\}] \quad (15) \end{aligned}$$

In the expressions (14) and (15) we have set $\lambda = 2m_0c^2\alpha/N^2e^2$. The quantity λ is of the order of unity, and it is clear that for (14) $\lambda > 1$, while for (15) $\lambda < 1$.

Now returning to (13) we have, after the usual transpositions, the following expression for the energy

$$\begin{aligned} W = & \frac{-2\pi^2N^2m_0e^4}{n^2h^2} \{1 - 2(\Psi + 2Ne^2/c \cdot \sigma)/nh \\ & - [(\Psi - 6Ne^2/c \cdot \sigma)(\Psi + 2Ne^2/c \cdot \sigma) + 3\pi^2N^2e^4/c^2]/n^2h^2\} \quad (16) \end{aligned}$$

wherein we set $[1 + (N - 1)\lambda]^{1/2} = \sigma$. In order that (16) should be equivalent to the Balmer formula with the addition of a correction term of the same sign and the same order as that of the relativity term, it is essential that we have

$$\begin{aligned} -2(\Psi + 2Ne^2/c \cdot \sigma) - [(\Psi - 6Ne^2/c \cdot \sigma)(\Psi + 2Ne^2/c \cdot \sigma) + 3\pi^2N^2e^4/c^2]/nh \\ = \pi^2N^2e^4/c^2nh \quad (17) \end{aligned}$$

whence we must have:

$$\Psi = -2Ne^2/c \cdot \sigma \{1 + \pi^2Ne^2/c\sigma nh \cdot (1 + 4Ne^2\sigma/cnh)\}. \quad (18)$$

Examination of (14) and (15) in connection with (18) shows that for $C' < 0$ it is in general not possible to find a value of λ such that the corresponding value of Ψ satisfies (18). However, this does prove always to be possible for $C' > 0$. In the particular case of the hydrogen atom where $N = 1$ and $\sigma = 1$, it develops that the proper value of λ is $\lambda = 0.179$ which corresponds to $\alpha = 0.25 \times 10^{-13}$. For hydrogen, then, we have

$$x_{\min.} = 0.25 \times 10^{-13} [1 - 0.5 \times 10^{-13} \pi^2 m_0 e^2 / n^2 h^2]$$

or roughly 0.25×10^{-13} cm. This result cannot be looked upon as unreasonable, though unfortunately there is no experimental data available for comparison. However, from the expression for λ on page (5) it is seen that α varies as N^2 (though, of course, it will also depend on λ which will vary slightly with N). Hence $x_{\min.}$ will increase roughly proportionally with N (for small values of N , at any rate). Actual calculation for the case of He ($N = 2$) shows $x_{\min.} = 0.62 \times 10^{-13}$ cm. while for the case of Al ($N = 13$) we get $x_{\min.} = 2 \times 10^{-13}$ cm. This latter value is at any rate qualitatively in agreement with Bieler's value for the effective radius of the Al nucleus, namely 3.3×10^{-13} cm. as estimated from the analysis of experiments⁴ on α -ray scattering by Al nuclei. Unfortunately, there is no record of electron scattering at such close distances. Thus Schonland⁵ finds that in the case of electron scattering by Al foils the inverse square law holds down to 1.8×10^{-11} cm. In any case there seems to be no experimental data which would militate *against* the assumption underlying the above work.

It may be pertinent to introduce here a few remarks concerning the relation between the kind of pendulum orbit used in this work and the newer theories of atomic structure. In the Schrödinger wave mechanics⁶ the azimuthal quantum number has been put equal to $l + 1$, where l can take only the values 0, 1, 2, 3, Hence $l = 0$ would not lead to the vanishing of the angular momentum, and so Schrödinger concludes that paths for which the angular momentum vanishes do not exist. The difficulty with this conclusion, as it seems to the present writer, is that there seems no definite assurance that the angular momentum of the electron in an actual orbit must be represented by the quantum number $l + 1$. More generally, the Schrödinger theory does not fix electron orbits in time and space as we have previously understood them; it fixes only the value of a certain function (the eigen-funktion ψ) in the configuration space. It thus seems that the new theory affords a considerable amount of latitude in the choice of electron orbits corresponding to a given distribution of the ψ function. The same comment applies to the matrix mechanics of Born and Heisenberg, which is mathematically equivalent to the wave mechanics. If modern atomic theory is going to retain atomic models at all (which seems likely if only for the pictorial advantage afforded by them) then all

that is required of an electron orbit in such a model is that it shall have the proper energy value and be of the right order of magnitude for atomic dimensions. It may well be that pendulum orbits which satisfy these conditions will still prove useful in atomic theory.

¹ J. W. Nicholson, *Phil. Mag.*, **45**, 804 (1923).

² This fact was first called to the attention of the present writer by Prof. A. E. Ruark.

³ A. Sommerfeld, *Atombau und Spektral linien*, 3rd German ed., page 735.

⁴ E. S. Bieler, *Proc. Roy. Soc.*, **105**, 434 (1924).

⁵ B. F. J. Schonland, *Proc. Roy. Soc.*, **113**, 87 (1926).

⁶ E. Schrödinger, *Ann. Physik*, **79**, 371 (1926). The number l here used corresponds to n in the paper referred to, in conformity with more recent usage.

MEASUREMENT OF THE MO.K DOUBLET DISTANCES BY MEANS OF THE DOUBLE X-RAY SPECTROMETER

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The doublet which should be present in the $K\beta$ radiation has only been observed in the case of a few elements; between $Z = 41$ and $Z = 50$.¹ Their separation is so small that they appear as a single line except with an instrument of high resolving power.

We have recently found that the double X-ray spectrometer possesses high resolving power when properly arranged. We have obtained a considerable separation of the $K\beta$ doublet of Mo as shown in figure 3.

The geometry of the arrangement used will be easily understood from figure 1. The two slits between the X-ray tube and the crystal Z are quite wide (1.5 mm.) so that a divergent beam comes through to crystal A . Crystal A may be regarded as the collimator and crystal B as the analyzer. If these crystals are nearly perfect, such as split calcite, only one wave-length is reflected at a given angle of incidence. This is not strictly true as it has been found from previous experimental work that some energy is reflected at about $4''$ of arc each side the proper angle for reflection of a given wave-length, λ .

A radiation of certain wave-length, say λ_1 represented by full lines in figure 1, falls on crystal A at proper angle θ for reflection. Any other wave-length proceeding along same path will not be reflected. But radiation of another wave-length such as λ_2 of the figure coming through the slits at a different angle ($\theta + d\theta$) will be reflected at its proper angle