A NOTE ON ENERGY LEVELS OF HYDROGEN ATOM WITH FINITE SIZE NUCLEUS.

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Rose (1951) and others have investigated the effect of the finite size of the nucleus in a number of problems. They take a penetrable model of the nucleus in which the wave functions inside and outside (the nucleus) are made to join analytically at the boundary. We on the other hand for our non-relativistic treatment of the hydrogen atom take an impenetrable model for the nucleus and make the wave function vanish at the boundary. For this the Schroedinger wave function Ψ satisfies here the boundary conditions (i) $\Psi(r)=0$ at $r=a_0$, the radius of the nucleus, (ii) $\Psi(r)\to 0$ as $r\to\infty$ as compared to the conventional case in which (i) $r\,\Psi(r)$ is finite at $r=0$, and (ii) $\Psi(r)\to 0$ as $r\to\infty$. This problem is in a way complementary to that of Sommerfeld and Welker (1938) in which they discuss the solution of Schroedinger equation for a hydrogen atom enclosed in a sphere of finite radius R with the nucleus (proton) at the centre. The problem of the bounded oscillator was considered by Auluck and Kothari (1945). As the energy levels are raised as an effect of the finite size of the nucleus it is likely to have some relevance in connection with the theory of Lamb and Retherford (1947) shift. The shift which is largest for the s levels is in the case of $2s$ of the order of ·23 wave numbers for a_0 of the order of $\frac{\hbar}{MC}=2\times 10^{-14}$ cm.

The Schroedinger equation for the hydrogen atom* is

$$\nabla^2\Psi+\left(E+\frac{2}{r}\right)\Psi=0 \qquad \ldots \quad \ldots \quad \ldots \quad (1)$$

The radial part of Ψ satisfies the usual equation

$$\frac{d^2R}{dZ^2}+\frac{2}{Z}\frac{dR}{dZ}+\left\{-\frac{1}{4}+\frac{k}{Z}-\frac{l(l+1)}{Z^2}\right\}R=0 \quad \ldots \quad \ldots \quad \ldots \quad (2)$$

$$(l=0,1,2,\ldots)$$

where

$$Z=\frac{2r}{k},\quad k=\frac{1}{\sqrt{-E}} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (3)$$

The boundary conditions to be satisfied by R are:

(i) $R(Z)\to 0$ as $Z\to\infty$

(ii) $R(Z_0)=0$ at $Z=Z_0$ $(Z_0>0)$ where $Z_0=\frac{2a_0}{k}$.

The required solution is the confluent hypergeometric function

$$R=W_{k,\,l+\frac{1}{2}(Z)}/Z \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (4)$$

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* Here the unit of r is the Bohr radius a_H and the unit of energy is Rydberg constant $\frac{e^2}{2a_H}$.

as pointed out by Eddington (1927) and Sugiura (1927) and later developed by Hartree (1928)

The vanishing of R at infinity is evident from the asymptotic form for $W_{k,l+\frac{1}{2}(Z)}$ (Whittaker and Watson, 1927) for large Z

$$W_{k,l+\frac{1}{2}(Z)} = e^{-\frac{1}{2}Z}Z^k\left[1+\sum_{n=1}^{\infty}\frac{\{m^2-(k-\frac{1}{2})^2\}\{m^2-(k-\frac{3}{2})^2\}\ldots\{m^2-(k-n+\frac{1}{2})\}}{n!\,z^n}\right]$$

The boundary condition at $Z = Z_0$ requires

$$W_{k,l+\frac{1}{2}(Z_0)} = 0 \quad \ldots \quad (5)$$

The expansion of $W_{k,l+\frac{1}{2}(Z)}$ for small Z (Hartree, 1928) is

$$W_{k,l+\frac{1}{2}(Z)} = \frac{e^{-\frac{1}{2}Z}Z^k}{\Gamma(-k-l)\Gamma(-k+l+1)}\left[\sum_{m=0}^{2l}(-1)^{m+1}\frac{\Gamma(-k-l+m)\Gamma(2l+1-m)}{m!}Z^{-k-l+m}\right.$$
$$\left.-\sum_{m=2l+1}^{\infty}\frac{\Gamma(-k-l+m)Z^{-k-l+m}}{m!\,(m-2l-1)!}\{\log Z+\psi(-n-l+m)-\psi(m-1)-\psi(m-2)\}\right] \quad \ldots \quad (6)$$

As will be seen later, the effect of the nuclear size on energy levels gets very small for large l, we shall therefore restrict ourselves here to the cases $l = 0$ (s states) and $l = 1$ (p states) for which we can write

$$W_{k,\frac{1}{2}(Z)} = \frac{e^{-\frac{1}{2}Z}}{\Gamma(1-k)}\left[1+\frac{(-k)}{1}\left(\frac{1}{-k}-\frac{1}{1}\right)Z+\frac{(-k)(1-k)}{2\,.\,1^2}\left(\frac{1}{-k}+\frac{1}{1-k}-\frac{2}{1}-\frac{1}{2}\right)Z^2+\ldots\right.$$
$$\left.+\left(\log Z+2\gamma+\psi(1-k)+\frac{1}{k}\right)\left\{(-k)Z+\frac{(-k)(1-k)}{2\,.\,1^2}Z^2+\ldots\right\}\right] \quad \ldots \quad (7)$$

$$W_{k,\frac{3}{2}(Z)} = \frac{e^{-\frac{1}{2}Z}}{\Gamma(2-k)}\frac{1}{Z}\left[2-(-1-k)Z+\frac{(-1-k)(-k)}{2\,.\,1}Z^2+\frac{(-1-k)(-k)(1-k)}{3\,.\,2\,.\,1}\times\right.$$
$$\left\{\frac{1}{1-k}-(\tfrac{1}{3}+\tfrac{1}{2}+1)\right\}Z^3+\ldots+[\log Z+2\gamma+\psi(1-k)]\left\{\frac{(-1-k)(-k)(1-k)}{3\,.\,2\,.\,1}Z^3\right.$$
$$\left.\left.+\frac{(-1-k)(-k)(1-k)(2-k)}{4\,.\,3\,.\,2\,.\,1^2}Z^4+\ldots\right\}\right] \quad \ldots \quad (8)$$

where γ is Euler's constant 0·577.

First for the conventional case,

$$\Psi(r) \text{ is finite at } r = 0\,;$$

we shall show that k must be a positive integer.

For s states :

$$R = \frac{1}{Z}W_{k,\frac{1}{2}(Z)}$$
$$= \frac{e^{-\frac{1}{2}Z}}{\Gamma(2-k)}\left[\frac{1-k}{Z}+\frac{(1-k)(-k)}{1}\left(\frac{1}{-k}-\frac{1}{1}\right)+\ldots-\left\{(1-k)\log Z+2\gamma(1-k)+\right.\right.$$
$$\left.\left.(1-k)\,\psi\,(1-k)+\frac{1-k}{k}\right\}\left\{k-\frac{k(1-k)}{2\,.\,1}Z+\ldots\right\}\right]$$

Now if the above expression is not to diverge at $Z=0$, the coefficients of $\frac{1}{Z}$ and $\log Z$ must vanish, i.e. $k=1$. Similarly it is readily seen that k admits only the other values 2, 3, 4.... Taking now $W_{k,\frac{3}{2}(Z)}$ it similarly follows that the possible values of k are 2, 3, 4...., the lowest value being 2.

As $W_{k,l+\frac{1}{2}(Z)}$ vanishes at $Z=Z_0$ ($Z_0>0$), we have from the series expansions (7) and (8)

$$\Big[1+\frac{(-k)}{1}\left(\frac{1}{-k}-\frac{1}{1}\right)Z_0+\frac{(-k)(1-k)}{2.1^2}\left(\frac{1}{-k}+\frac{1}{1-k}-\frac{2}{1}-\frac{1}{2}\right)Z_0^2+\ldots$$
$$+\left(\log Z_0+2\gamma+\psi(1-k)+\frac{1}{k}\right)\left\{(-k)Z_0+\frac{(-k)(1-k)}{2.1^2}Z_0^2+\ldots\right\}\Big]=0$$

(for $l=0$)

and

$$\Big[2+\frac{k+1}{1}Z_0+\frac{(-k)(-k-1)}{2.1}Z^2+\frac{(1-k)(-k)(-k-1)}{3.2.1}Z_0^3\left(\frac{1}{1-k}-(\tfrac{1}{3}+\tfrac{1}{2}+1)\right)+\ldots$$
$$+\frac{(1-k)(-k)(-1-k)}{3.2.1}\left(\log Z_0+2\gamma+\psi(1-k)\right)\left\{Z_0^3+\frac{2-k}{4.1}Z_0^4+\ldots\right\}\Big]=0$$

(for $l=1$)

Writing for convenience $2a_0=\sigma$ and noting that

$$kZ_0=2a_0=\sigma$$

we obtain

$$1+\frac{1+k}{k}\sigma+\frac{2+k-5k^2}{4k^2}\sigma^2+\ldots=(\log\sigma+2\gamma-\log k+\frac{1}{k}+\psi(1-k))\left\{\sigma+\frac{1-k}{2k}\sigma^2+\ldots\right\}$$

(for $l=0$) .. (9)

and

$$2+\frac{1+k}{k}\sigma+\frac{k+k^2}{2k^2}\sigma^2+\ldots=\frac{(1-k)(-1-k)}{6k^2}\sigma^3(\log\sigma/k+2\gamma+\psi(1-k))\left\{1+\frac{2-k}{4k}\sigma+\ldots\right\}$$

(for $l=1$) .. (10)

Writing $k=1+\beta$ we have, as $\sigma\ll 1$, the following approximate expressions [from equations (10) and (11)] for

$$\beta=\sigma+\sigma^2(\log\sigma+\gamma-1)+O(\sigma^3) \quad \text{.. .. .. (9a)}$$

(1s state)

Similarly for the next level ($k=2$) we have, writing $k=2+\beta$,

$$\beta=\sigma+\sigma^2(\log\sigma+\gamma-\log 2-\tfrac{1}{4})+O(\sigma^3) \quad \text{.. .. (9b)}$$

(2s state)

$$\beta=\tfrac{1}{16}\sigma^3+O(\sigma^4) \quad \text{.. .. .. (10b)}$$

(2p state)

and for the next ($k=3$) writing $k=3+\beta$

$$\beta=\sigma+\sigma^2(\log\sigma+\gamma-\log 3-\tfrac{1}{6})+O(\sigma^3) \quad \text{.. .. (9c)}$$

(3s state)

$$\beta=\tfrac{2}{27}\sigma^3+O(\sigma^4) \quad \text{.. .. .. (10c)}$$

(3p state)

Numerical values for the shifts in the energy levels are given in the following table for (i) $a_0 = \hbar/MC$, (ii) $a_0 = \frac{e^2}{MC^2}$, where M is the mass of the proton.

Table for level-shifts in Rydberg units.

Level	$a_0 = \frac{\hbar}{MC}$	$a_0 = \frac{e^2}{MC^2}$
1s	$1{\cdot}6 \times 10^{-5}$	$1{\cdot}2 \times 10^{-7}$
....	....	....
2s	2×10^{-6}	$1{\cdot}5 \times 10^{-8}$
2p	8×10^{-18}	3×10^{-24}
3s	6×10^{-7}	$4{\cdot}4 \times 10^{-9}$
3p	3×15^{-18}	1×10^{-24}

(It may be noted that the observed Lamb-Retherford shifts for the $2s-2p$ levels is 3×10^{-7} Rydberg units.)

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ABSTRACT.

In this paper the solution of the Schroedinger equation for a hydrogen atom with a finite size impenetrable nucleus is worked out.

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