1)

268(1): Calculation of the Energy levels of the H Atom and Elliptical Representation

The energy levels of the hydrogen atom are given by:

$$E = \int \phi^* \hat{H} \phi \, d\tau \quad -(1)$$

where

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 - \frac{k}{r} \quad -(2)$$

and

$$k = \frac{e^2}{4\pi\epsilon_0} \quad -(3)$$

In spherical polar coordinates:

$$\nabla^2 \phi = \frac{\partial^2 \phi}{\partial r^2} + \frac{2}{r}\frac{\partial \phi}{\partial r} + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta \frac{\partial \phi}{\partial \theta}\right) + \frac{1}{r^2 \sin^2\theta}\frac{\partial^2 \phi}{\partial \phi^2} \quad -(4)$$

A hand calculation can be carried out for the 1s wavefunction and the energy levels can be calculated for all wavefunctions using the computer. The analysis can then be extended to

$$\frac{1}{r} = \frac{1}{\alpha}(1 + \epsilon\cos\theta) \quad -(5)$$

and

$$\frac{1}{r} = \frac{1}{\alpha}(1 + \epsilon\cos\phi) \quad -(6)$$

2) The 1s wavefunction is radial:

$$\psi = \psi^* = \frac{1}{\pi^{1/2}} \left(\frac{1}{r_B}\right)^{3/2} \exp(-r/r_B) \quad -(7)$$

So
$$\nabla^2 \psi = \frac{\partial^2 \psi}{\partial r^2} + \frac{2}{r}\frac{d\psi}{dr} \quad -(8)$$
$$= \frac{1}{\pi^{1/2}} \left(\frac{1}{r_B}\right)^{3/2} e^{-r/r_B} \left(\frac{1}{r_B^2} - \frac{2}{r r_B}\right)$$

and:
$$\psi^* \nabla^2 \psi = \frac{1}{\pi r_B^3} e^{-2r/r_B} \left(\frac{1}{r_B^2} - \frac{2}{r r_B}\right) \quad -(9)$$

So
$$\langle E_1 \rangle = -\frac{\hbar^2}{2m} \frac{1}{\pi r_B^3} \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta \, d\theta \int_0^{\infty} r^2 \psi^* \nabla^2 \psi \, dr$$
$$= -\frac{\hbar^2}{2m} \cdot \frac{4}{r_B^3} \int_0^{\infty} r^2 \left(\frac{1}{r_B^2} - \frac{2}{r r_B}\right) e^{-2r/r_B} dr \quad -(10)$$
$$= -\frac{\hbar^2}{2m} \left[\frac{4}{r_B^5} \int_0^{\infty} r^2 e^{-2r/r_B} dr - \frac{8}{r_B^4} \int_0^{\infty} r e^{-2r/r_B} dr \right]$$

Now use:
$$\int_0^{\infty} r^2 e^{-2r/r_B} dr = \frac{r_B^3}{4} \quad -(11)$$
$$\int_0^{\infty} r e^{-2r/r_B} dr = \frac{r_B^2}{4} \quad -(12)$$

So:

3)

$$\langle E_1 \rangle = -\frac{\hbar^2}{2m r_B^2}(1-2) = \frac{\hbar^2}{2m r_B^2} \quad -(13)$$

Similarly:

$$\langle E_2 \rangle = -\frac{e^2}{4\pi \epsilon_0} \int \psi^* \frac{1}{r} \psi \, d\tau \quad -(14)$$

$$= -k \left(\frac{4}{r_B^3} \int_0^\infty r e^{-2r/r_B} dr \right)$$

$$= -\frac{e^2}{4\pi \epsilon_0 r_B} \quad -(14)$$

The total expectation value is:

$$\langle E \rangle = \langle E_1 \rangle + \langle E_2 \rangle$$

$$\boxed{\langle E \rangle = \frac{\hbar^2}{2m r_B^2} - \frac{e^2}{4\pi \epsilon_0 r_B}} \quad -(15)$$

The Bohr radius is:

$$r_B = \frac{4\pi \epsilon_0 \hbar^2}{m e^2} \quad -(16)$$

So

$$\langle E \rangle = \frac{m e^4}{32 \pi^2 \epsilon_0^2 \hbar^2} - \frac{m e^4}{16 \pi^2 \epsilon_0^2 \hbar^2} \quad -(17)$$

4)

i.e.

$$\langle E \rangle = -\frac{me^4}{32\pi^2\epsilon_0^2\hbar^2} \quad -(18)$$

The 1s wavefunction is defined by:

$$n = 1, \; l = 0, \; m_l = 0 \quad -(19)$$

So eq. (18) is:

$$\langle E \rangle = -\frac{me^4}{32\pi^2\epsilon_0^2\hbar^2 n^2} \quad -(20)$$

with

$$n = 1.$$

If the computation is carried out with the higher order wavefunctions of H then for the ns wave functions eq. (20) should be obtained. The same result (20) is obtained for the Bohr atom using:

$$E = \frac{1}{2}mv^2 - \frac{k}{r} \quad -(21)$$

whose solution is:

$$r = \frac{\alpha}{1+\epsilon\cos\phi} \quad -(22)$$

Here

$$\alpha = \frac{L^2}{mk} \quad -(23)$$

5) and

$$\epsilon^2 = 1 + \frac{2EL^2}{mk^2} \quad -(24)$$

The Bohr energy levels are obtained when:

$$\epsilon = 0 \quad -(25)$$

so

$$E = -\frac{mk^2}{2L^2}, \quad -(26)$$

and the Bohr quantization is:

$$L = n\hbar. \quad -(27)$$

The Schroedinger quantization is:

$$\hat{L}\phi = m_e \hbar \phi \quad -(28)$$

and

$$L^2\phi = \ell(\ell+1)\hbar^2\phi. \quad -(29)$$

Therefore it is logical to quantize eq. (21) using eq. (22) of x theory, i.e.:

$$
\begin{aligned}
E &= \frac{p^2}{2m} - \frac{k}{r} \\
&= \frac{p^2}{2m} - \frac{k}{\alpha}\left(1 + \epsilon\cos\phi\right)
\end{aligned}
\quad -(30)
$$

and:

6)
$$E\psi = -\frac{\hbar^2\nabla^2}{2m}\psi - \frac{k}{\alpha}(1+\epsilon\cos\phi)\psi \quad -(31)$$

Therefore:
$$\langle E\rangle = -\frac{\hbar^2}{2m}\int\psi^*\nabla^2\psi\, d\tau - \frac{k}{\alpha}\int\psi^*(1+\epsilon\cos\phi)\psi\, d\tau \quad -(32)$$

$$= -\frac{\hbar^2}{2m}\int\psi^*\nabla^2\psi\, d\tau - \frac{k}{\alpha}\int\psi^*\psi\, d\tau - \frac{\epsilon k}{\alpha}\int\psi^*\cos\phi\,\psi\, d\tau$$

in which
$$\int\psi^*\psi\, d\tau = 1 \quad -(33)$$

In the 1s orbital of H:
$$\langle E_2\rangle = -k\int\psi^*\frac{1}{r}\psi\, d\tau = -\frac{k}{r_B} \quad -(34)$$

so
$$\int\psi^*\frac{1}{r}\psi\, d\tau = \int\psi^*\frac{1}{\alpha}(1+\epsilon\cos\phi)\psi\, d\tau = \frac{1}{r_B} \quad -(35)$$

Therefore
$$\frac{1}{\alpha} + \frac{\epsilon}{\alpha}\int\psi^*\cos\phi\,\psi\, d\tau = \frac{1}{r_B} \quad -(36)$$

7) In the Bohr atom:

$$\alpha = r_B \quad -(37)$$

so the Schroedinger atom differs from the Bohr atom through the second term on the left hand side of eq. (36):

$$\boxed{\int \phi^* \cos\phi \, \phi \, d\tau = \frac{\alpha}{\epsilon}\left(\frac{1}{r_B} - \frac{1}{\alpha}\right) \quad -(38)}$$

Eq. (38) is true for any orbital.

A hand calculation can be made for the 1s orbital (7). In this case:

$$\int \phi^* \cos\phi \, \phi \, d\tau = \frac{1}{\pi r_B^3} \int_0^{2\pi} \cos\phi \, d\phi \int_0^{\pi} \sin\theta \, d\theta \int_0^{\infty} r^2 e^{-2r/r_B} dr$$

$$= 0 \quad -(39)$$

Therefore for the ellipse:

$$r = \frac{\alpha}{1 + \epsilon \cos\phi}, \quad -(40)$$

$$\langle \cos\phi \rangle = 0, \text{ and } \alpha = r_B \quad -(41)$$

8) However for the ellipse :

$$r = \frac{\alpha}{1+\epsilon\cos\theta} \quad -(42)$$

$$\langle \cos\theta \rangle = \int \phi^* \cos\theta \, \phi \, d\tau$$

$$= \frac{1}{\pi r_B^3} \int_0^{2\pi} d\phi \int_0^{\pi} \cos\theta \sin\theta \, d\theta \int_0^{\infty} r^2 e^{-2r/r_B} dr$$

$$-(43)$$

$$= \frac{1}{2} \int_0^{\pi} \cos\theta \sin\theta \, d\theta = \frac{1}{2} \quad -(44)$$

So

$$\langle \cos\phi \rangle = 0, \quad \langle \cos\theta \rangle = \frac{1}{2} \quad -(45)$$

There are two types of eq. (38) :

$$\langle \cos\phi \rangle = \frac{\alpha_1}{\epsilon_1} \left(\frac{1}{r_B} - \frac{1}{\alpha_1} \right) \quad -(46)$$

and

$$\langle \cos\theta \rangle = \frac{\alpha_2}{\epsilon_2} \left(\frac{1}{r_B} - \frac{1}{\alpha_2} \right) \quad -(47)$$

From eqs. (45) and (46) :

$$\alpha_1 = r_B \quad -(48)$$

and from eqs. (45) and (47) :

$$\frac{\alpha_2}{\epsilon_2}\left(\frac{1}{r_B}-\frac{1}{\alpha_2}\right)=\frac{1}{2} \quad -(49)$$

So:

$$\epsilon_2 = 2\alpha_2\left(\frac{1}{r_B}-\frac{1}{\alpha_2}\right)$$

$$= 2\left(\frac{\alpha_2}{r_B}-1\right) \quad -(50)$$

The expectation values of $\cos\phi$ and $\cos\theta$ can now be evaluated by computer for any orbital and tabulated. On the classical level the solutions of

$$E = \frac{p^2}{2m} - \frac{k}{r} \quad -(51)$$

are in general:

$$r = \frac{\alpha_1}{1+\epsilon_1\cos\theta} = \frac{\alpha_2}{1+\epsilon_2\cos\phi} \quad -(52)$$

but in the H atom the expectation values of $\cos\theta$ and $\cos\phi$ are different for each orbital.

This again gives a new way of describing quantum mechanics in general.
