71(8): Wavefunctions of the H Atom from the New Quantization Method

From the previous note

$$-\hbar^2 \nabla^2 \phi = p^2 \phi = \frac{L^2}{\alpha}\left(\frac{2}{r} - \frac{1}{a}\right)\phi \quad -(1)$$

where:

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

$$+ \frac{1}{r^2 \sin^2\theta}\frac{\partial^2 \phi}{\partial \phi^2}$$

$$:= \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial \phi}{\partial r}\right) + \frac{1}{r^2}\Lambda^2 \phi \quad -(3)$$

In the H atom:

$$\phi = RY \quad -(4)$$

where R are the radial functions and Y the spherical harmonics defined by:

$$\Lambda^2 Y = -l(l+1)Y \quad -(5)$$

It follows that -(6)

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial YR}{\partial r}\right) + \frac{1}{r^2}\Lambda^2 YR = -\frac{L^2}{\alpha \hbar^2}\left(\frac{2}{r} - \frac{1}{a}\right) YR \quad -(7)$$

i.e.

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial R}{\partial r}\right) - \frac{l(l+1)}{r^2}R + \frac{2L^2}{\alpha \hbar^2}\frac{R}{r} = \frac{L^2}{a\alpha\hbar^2}R$$

-(7)

Now consider the Hamiltonian method of quantization:

$$-\frac{\hbar^2}{2m}\nabla^2\psi - \frac{e^2}{4\pi\epsilon_0 r}\psi = E\psi \quad -(8)$$

here E is the total energy, a constant of motion.

From eqs. (4), (5) and (8):

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) - \frac{l(l+1)}{r^2}R + \frac{me^2}{2\pi\epsilon_0\hbar^2}\frac{R}{r} = -\frac{2mE}{\hbar^2}R \quad -(9)$$

It is seen that eqs. (7) and (9) are the same provided that:

$$-2mE = \frac{L^2}{a\alpha} \quad -(10)$$

and

$$\frac{me^2}{2\pi\epsilon_0} = \frac{2L^2}{\alpha} \quad -(11)$$

The total energy is negative valued so eq. (10) is

$$\frac{L^2}{a\alpha} = 2m|E| \quad -(12)$$

i.e.

$$\frac{L^2}{2m|E|} = a\alpha = \frac{\alpha^2}{1-\epsilon^2} \quad -(13)$$

This is the definition of the semi minor axis b of ellipse (Marion and Thornton eq. (7.43)):

$$b = \frac{\alpha}{(1-\epsilon^2)^{1/2}} = \frac{L}{(2m|E|)^{1/2}} \quad -(14)$$

Q.E.D.

Eq. (11) defines the constant of motion:

3)
$$\boxed{L^2 = \alpha m \frac{e^2}{4\pi\epsilon_0}} \quad -(15)$$

The ellipse is defined by:

$$r = \frac{\alpha}{1+\epsilon\cos\beta} \quad -(16)$$

where α is the half right latitude and ϵ the eccentricity. Here:

$$\dot{\beta}^2 = \dot{\theta}^2 + \dot{\phi}^2 \sin^2\theta \quad -(17)$$

Therefore the hamiltonian and lagrangian both produce the wave functions of the H atom given eqs. (14) - (16).

This is a completely new result of quantum mechanics.

The lagrangian is:

$$\mathcal{L} = \frac{1}{2} m \left(\dot{r}^2 + r^2\dot{\beta}^2\right) - U \quad -(18)$$

where U is the potential energy. In the H atom:

$$U = -\frac{e^2}{4\pi\epsilon_0 r} \quad -(19)$$

The proper Lagrange variables are r and β. The Euler Lagrange equations are:

$$\frac{\partial\mathcal{L}}{\partial r} = \frac{d}{dt}\left(\frac{\partial\mathcal{L}}{\partial\dot{r}}\right) \quad -(20)$$

and

$$\frac{\partial \mathcal{L}}{\partial \beta} = \frac{d}{dt}\left(\frac{\partial \mathcal{L}}{\partial \dot{\beta}}\right) \quad -(21)$$

Eqs. (20) and (21) produce eq. (16). In other [w]ords [at]oms and molecules U can become very complicated, [s]o a numerical method is needed. The new lagrangian [q]uantization is well suited for numerical methods, [w]hich in computational chemistry are highly developed. Eq. (1) is the result of using eq. (19). More generally,

$$-\hbar^2 \nabla^2 \phi = m^2 v^2 \phi = m^2\left(\left(\frac{dr}{dt}\right)^2 + r^2 \dot{\beta}^2\right)\phi$$

$$= m^2\left(\dot{r}^2 + r^2 \dot{\beta}^2\right)\phi \quad -(22)$$

In general, $\dot{r}$ and $\dot{\beta}$ can be found from eqs. (18), (20) and (21) for any potential:

$$U = U(r, \theta, \phi) \quad -(23)$$

The wavefunctions ϕ can therefore be computed for any atom or molecule, QED.