268(9) : Summary of Concepts

The classical Hamiltonian is:

$$H = \frac{p^2}{2m} - \frac{k}{r} = E \quad -(1)$$

which in two dimensions for a planar orbit gives:

$$\frac{1}{r} = \frac{1}{\alpha}\left(1 + \epsilon\cos\phi\right) \quad -(2)$$

where

$$\alpha = \frac{L^2}{mk}, \quad \epsilon^2 = 1 + \frac{2EL^2}{mk^2} \quad -(3)$$

The Schroedinger quantization of eq. (1) means:

$$H\psi = \left(-\frac{\hbar^2\nabla^2}{2m} - \frac{k}{r}\right)\psi, \quad -(4)$$

$$E = \langle H \rangle = \frac{me^4}{32\pi^2\epsilon_0^2\hbar^2n^2} - \frac{me^4}{16\pi^2\epsilon_0^2\hbar^2n^2}. \quad -(5)$$

The Bohr radius is:

$$r_B = \frac{4\pi\epsilon_0\hbar^2n^2}{me^2} \quad -(5)$$

So

$$E = \langle H \rangle = -\frac{\hbar^2}{2mr_B^2} \quad -(6)$$

and

$$\left\langle \frac{1}{r} \right\rangle = \frac{1}{r_B} \quad -(7)$$

The ϕ ellipse gives the expectation values:

2)

$$\left\langle \frac{1}{r} \right\rangle = \frac{1}{\alpha} \langle 1 + \epsilon \cos\phi \rangle$$

$$= \frac{1}{\alpha} + \epsilon \langle \cos\phi \rangle \quad -(8)$$

$$= \frac{1}{r_B}$$

for all hydrogenic orbitals, with

$$\langle \cos\phi \rangle = 0 \quad -(9)$$

for all orbitals.

Therefore:

$$\langle \alpha \rangle = \alpha = r_B \quad -(10)$$

for all orbitals. From eqs. (3) and (10):

$$\langle L^2 \rangle = m k r_B = n^2 \hbar^2 \quad -(11)$$

for all orbitals.

This means that:

$$\langle \epsilon^2 \rangle = 1 - \frac{k}{r_B} \frac{m k r_B}{m k^2} = 0 \quad -(12)$$

for all orbitals. Note carefully that the classical ϵ^2 is non-zero in general but its expectation value is zero. This result is a consequence of using the ϕ ellipse (2) in a plane. This ellipse also produces:

$$L = n\hbar \quad -(13)$$

) The expectation values for H are :

$$\left\langle \frac{1}{r} \right\rangle = \frac{1}{r_B} \quad -(14)$$

$$\left\langle \frac{1}{r^2} \right\rangle = \frac{1}{r_B^2} \quad -(15)$$

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{1}{r_B^3 \, l(l+1)(l+1/2)} \quad -(16)$$

for $l > 0$.

These results are a consequence of using :

$$\frac{p^2}{2m} = \frac{1}{2} m v^2 = \frac{1}{2} m \left(\left(\frac{dr}{dt} \right)^2 + r^2 \left(\frac{d\phi}{dt} \right)^2 \right). \quad -(17)$$

The assumption (17) produces the result :

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{1}{r_B^3} \quad -(18)$$

for all hydrogenic orbitals, whereas the three dimensional result is eq. (16). The three dimensional kinetic energy is :

$$T = \frac{1}{2} m \left(\left(\frac{dr}{dt} \right)^2 + r^2 \left(\frac{d\theta}{dt} \right)^2 + r^2 \sin^2\theta \left(\frac{d\phi}{dt} \right)^2 \right) \quad -(19)$$

so eq. (17) is a consequence of reducing the 3-D

4)

problem to a 2-D problem. The complete analysis in three dimensions is as follows.

The linear velocity in spherical polar coordinates is:

$$\underline{v} = \dot{r}\,\underline{e}_r + r\dot{\theta}\,\underline{e}_\theta + r\sin\theta\,\dot{\phi}\,\underline{e}_\phi \quad -(20)$$

("Vector Analysis Problem Solver", VAPS, p. 1047).

So the lagrangian is:

$$\mathcal{L} = T - V = \frac{1}{2}mv^2 + \frac{k}{r} \quad -(21)$$

$$= \frac{1}{2}m\left(\dot{r}^2 + r^2\dot{\theta}^2 + r^2\sin^2\theta\,\dot{\phi}^2\right) + \frac{k}{r}$$

The lagrangian variables are r, θ and ϕ. and there are three Euler Lagrange equations.

1) The equation $$\frac{\partial \mathcal{L}}{\partial r} = \frac{d}{dt}\frac{\partial \mathcal{L}}{\partial \dot{r}} \quad -(22)$$

gives $$m\ddot{r} = mr\left(\dot{\theta}^2 + \sin^2\theta\,\dot{\phi}^2\right) - \frac{k}{r^2} \quad -(23)$$

2) The equation: $$\frac{\partial \mathcal{L}}{\partial \theta} = \frac{d}{dt}\frac{\partial \mathcal{L}}{\partial \dot{\theta}} \quad -(24)$$

gives: $$\frac{d}{dt}\left(mr^2\dot{\theta}\right) = 0 \quad -(25)$$

and the constant angular momentum:

$$L_1 = mr^2\dot{\theta} \quad -(26)$$

The equation:

$$\frac{\partial \mathcal{L}}{\partial \phi} = \frac{d}{dt}\frac{\partial \mathcal{L}}{\partial \dot{\phi}} \quad -(27)$$

gives:

$$\frac{d}{dt}\left(mr^2 \dot{\phi} \sin^2\theta\right) = 0 \quad -(28).$$

and the constant angular momentum:

$$L_2 = mr^2 \dot{\phi} \sin^2\theta \quad -(29)$$

So

$$\dot{\theta} = \frac{d\theta}{dt} = \frac{L_1}{mr^2} \quad -(30)$$

$$\dot{\phi} = \frac{d\phi}{dt} = \frac{L_2}{mr^2 \sin^2\theta} \quad -(31)$$

Therefore:

$$m\ddot{r} = \frac{L_1^2}{mr^3} + \frac{L_2^2}{mr^3 \sin^2\theta} - \frac{k}{r^2} \quad -(32)$$

$$= \frac{L^2}{mr^3} - \frac{k}{r^2}$$

where the total angular momentum is:

$$L^2 = L_1^2 + \frac{L_2^2}{\sin^2\theta}. \quad -(33)$$

The total classical L^2 is quantized

) as:

$$L^2 \phi = \hbar^2 \ell(\ell+1)\phi \quad -(34)$$

as is well known.

In transforming eq. (32) into a Binet equation note that:

$$\frac{d}{d\theta}\left(\frac{1}{r}\right) = -\frac{1}{r^2}\frac{dr}{d\theta} = -\frac{1}{r^2}\frac{dr}{dt}\frac{dt}{d\theta} \quad -(35)$$

in which $d\theta / dt$ is defined by eq. (30):

$$\frac{d\theta}{dt} = \frac{L_1}{mr^2} \quad -(36)$$

So

$$\frac{d}{d\theta}\left(\frac{1}{r}\right) = -\frac{m}{L_1}\frac{dr}{dt} \quad -(37)$$

and

$$\frac{d^2}{d\theta^2}\left(\frac{1}{r}\right) = -\frac{m}{L_1}\frac{d}{d\theta}\frac{dr}{dt} \quad -(38)$$

Now use:

$$\frac{d}{d\theta} = \frac{dt}{d\theta}\frac{d}{dt} \quad -(39)$$

so

$$\frac{d^2}{d\theta^2}\left(\frac{1}{r}\right) = -\frac{m^2}{L_1^2} r^2 \frac{d^2 r}{dt^2} \quad -(40)$$

and

$$m\ddot{r} = -\frac{L_1^2}{mr^2}\frac{d^2}{d\theta^2}\left(\frac{1}{r}\right) \quad -(41)$$

Eq. (32) therefore becomes <u>the three dimensional</u>

) Binet equation:

$$F = -\frac{k}{r^2} = -\frac{L_1^2}{mr^2}\left(\frac{d^2}{d\theta^2}\left(\frac{1}{r}\right)+\frac{1}{r}\right) - \frac{L_2^2}{mr^3\sin^2\theta}$$

The relevant ellipse is therefore the theta ellipse $-(42)$:

$$\frac{1}{r} = \frac{1}{\alpha_1}\left(1+\epsilon_1\cos\theta\right) \quad -(43)$$

in which:

$$\alpha_1 = \frac{L_1^2}{mk}, \quad \epsilon_1^2 = 1 + \frac{2E_1L_1^2}{mk^2} \quad -(44)$$

and

$$E_1 = \frac{1}{2}m\left(\frac{dr}{dt}\right)^2 + \frac{L_1^2}{mr^3} \quad -(45)$$

The hamiltonian is:

$$H = \frac{1}{2}m\left(\dot{r}^2 + r^2\dot{\theta}^2 + r^2\sin^2\theta\,\dot{\phi}^2\right) - \frac{k}{r} \quad -(46)$$

$$= \frac{1}{2}m\dot{r}^2 + \frac{L_1^2}{2mr^2} + \frac{L_2^2}{2mr^2\sin^2\theta} - \frac{k}{r}$$

$$= \frac{p_r^2}{2m} + \frac{L^2}{2mr^2} - \frac{k}{r}$$

$$= \frac{p^2}{2m} - \frac{k}{r}.$$

Upon quantization:

$$\hat{H}\psi = -\frac{\hbar^2}{2m}\nabla^2\psi - \frac{k}{r}\psi \quad -(47)$$

where:

$$\nabla^2\psi = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} \quad -(48)$$

In the H atom:

$$-\frac{\hbar^2}{2m}\langle\nabla^2\psi\rangle = -\frac{\hbar^2}{2m}\int\psi^*\nabla^2\psi\, d\tau \quad -(49)$$

$$= \frac{me^4}{32\pi^2\epsilon_0^2\hbar^2n^2}$$

$$= \left\langle\frac{p^2}{2m}\right\rangle = \left\langle\frac{p_r^2}{2m}\right\rangle + \frac{L_1^2}{2m}\left\langle\frac{1}{r^2}\right\rangle + \frac{L_2^2}{2m}\left\langle\frac{1}{r^2\sin^2\theta}\right\rangle$$

The total energy levels are:

$$E = \left\langle\frac{p^2}{2m}\right\rangle - \left\langle\frac{k}{r}\right\rangle \quad -(50)$$

$$= -\frac{me^4}{32\pi^2\epsilon_0^2\hbar^2n^2}$$

In order to introduce relativistic effects the angle θ is changed to $x\theta$.

) The ellipse (43) becomes :

$$\frac{1}{r} = \frac{1}{\alpha_1}\left(1+\epsilon_1\cos(x\theta)\right) \quad -(51)$$

and the energy levels are changed to :

$$E = -\frac{\hbar^2}{2m}\langle\nabla^2\psi\rangle - k\left\langle\frac{1}{r}\right\rangle \quad -(52)$$

where

$$k\left\langle\frac{1}{r}\right\rangle = \frac{me^4}{16\pi^2\epsilon_0^2\hbar^2n^2} \quad -(53)$$

and :

$$\langle\nabla^2\psi\rangle = \int\psi^*\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)d\tau$$

$$+\int\frac{\psi^*}{r^2\sin(x\theta)}\frac{\partial}{\partial(x\theta)}\left(\sin(x\theta)\frac{\partial\psi}{\partial(x\theta)}\right)d\tau$$

$$+\int\frac{\psi^*}{r^2\sin^2(x\theta)}\frac{\partial^2\psi}{\partial\phi^2}d\tau \quad -(54)$$

in which :

$$\int\frac{\psi^*}{r^2\sin(x\theta)}\frac{\partial}{\partial(x\theta)}\left(\sin(x\theta)\frac{\partial\psi}{\partial(x\theta)}\right)d\tau \quad -(55)$$

$$= \frac{1}{x^2}\int\frac{\psi^*}{r^2\sin(x\theta)}\frac{\partial}{\partial\theta}\left(\sin(x\theta)\frac{\partial\psi}{\partial\theta}\right)d\tau$$

) The integral in eq. (54) may not be analytical, but it is possible to proceed by evaluating the effect of x on eq. (49)

$$\left\langle \frac{p^2}{2m} \right\rangle = \left\langle \frac{p_r^2}{2m} \right\rangle + \frac{L_1^2}{2m} \left\langle \frac{1}{r^2} \right\rangle + \frac{L_2^2}{2m} \left\langle \frac{1}{r^2 \sin^2\theta} \right\rangle \quad -(56)$$

by using:

$$\theta \rightarrow x\theta \quad -(57)$$

so:

$$\left\langle \frac{p_r^2}{2m} \right\rangle = -\frac{\hbar^2}{2m} \int \psi^* \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) d\tau \quad -(58)$$

$$\left\langle \frac{1}{r^2} \right\rangle = -\frac{\hbar^2}{2m} \int \psi^* \frac{1}{r^2} \psi \, d\tau$$

$$\left\langle \frac{1}{r^2 \sin^2(x\theta)} \right\rangle = -\frac{\hbar^2}{2m} \int \psi^* \frac{1}{r^2 \sin^2(x\theta)} \psi \, d\tau \quad -(59)$$

and

$$\left\langle \frac{k}{r} \right\rangle = k \int \psi^* \frac{1}{r} \psi \, d\tau \quad -(60)$$

The final hydrogenic energy levels are changed to:

$$E = \left\langle \frac{p^2}{2m} \right\rangle_x - \left\langle \frac{k}{r} \right\rangle \quad -(61)$$

and can be compared with results from atomic fine structure such as spin orbit splitting.