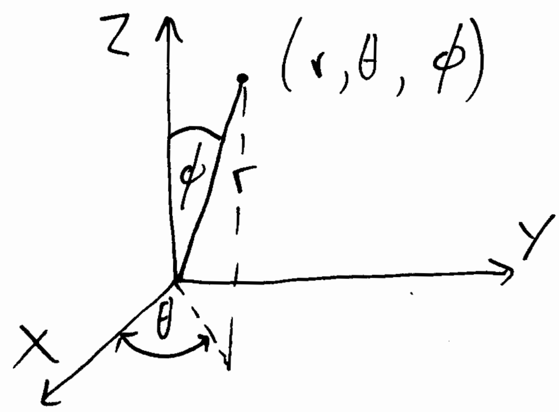
267(3): Relation between x Theory and Schroedinger Orbitals for the H Atom

The coordinate notation used here is defined in "Vector Analysis Problem Solver", p. 1047:

$$x = r\sin\phi\cos\theta \quad -(1)$$
$$y = r\sin\phi\sin\theta \quad -(2)$$
$$z = r\cos\phi \quad -(3)$$



When:

$$\phi = \frac{\pi}{2} \quad -(4)$$

it reduces to the plane polar:

$$X = r\cos\theta \quad -(5)$$
$$Y = r\sin\theta \quad -(6)$$
$$Z = 0. \quad -(7)$$

The volume element is:

$$dV = r^2 \sin\phi \, dr \, d\phi \, d\theta \quad -(8)$$

and

$$V = \int_0^r r^2 dr \int_0^{2\pi} d\theta \int_0^{\pi} \sin\phi \, d\phi \quad -(9)$$

The area is:

$$A = \pi r^2 = \pi(x^2 + y^2) \quad -(10)$$

and

$$V = -\frac{r^3}{3} \cdot 2\pi \cdot \cos\phi \Big|_0^{\pi} = \frac{4}{3}\pi r^3 \quad -(11)$$

The classical equation, using the notation of previous notes and papers, is:

$$\frac{p^2}{2m} - \frac{e^2}{4\pi\epsilon_0 r} = E \quad -(12)$$

This quantizes to the Schroedinger equation:

$$-\frac{\hbar^2}{2m}\nabla^2\psi - \frac{e^2}{4\pi\epsilon_0 r}\psi = E\psi \quad -(13)$$

where

$$\psi = R(r)\,Y(\phi, \theta) \quad -(14)$$

The spherical harmonics are defined by:

$$\Lambda^2 \underline{Y} = -\ell(\ell+1)\underline{Y} \quad -(15)$$

in the usual notation, and the radial functions are defined by:

$$E = -\frac{\hbar^2}{2mR}\frac{d^2R}{dr^2} + \frac{\ell(\ell+1)\hbar^2}{2mr^2} - \frac{e^2}{4\pi\epsilon_0 r} \quad -(16)$$

$$= \frac{1}{2m}\left(\frac{dr}{dt}\right)^2 + \frac{L^2}{2mr^3} - \frac{e^2}{4\pi\epsilon_0 r} \quad -(17)$$

Therefore

$$\boxed{L^2 = \ell(\ell+1)\hbar^2} \quad -(18)$$

3) and:

$$\frac{p^2}{m} = \left(\frac{dr}{dt}\right)^2 = -\frac{\hbar^2}{P}\frac{d^2P}{dr^2} \quad -(19)$$

Here

$$\underline{P} = r R_{nl} \quad -(20)$$

where R_{nl} are the associated Laguerre functions, where:

$$n = 1, 2, 3, \ldots \quad -(21)$$

$$l = 0, 1, 2, \ldots, n-1 \quad -(22).$$

The table gives the first few associated Laguerre functions.

n	l	$R_{nl}(r)$
1	0 (1s)	$2\left(\frac{1}{r_B}\right)^{3/2} \exp\left(-\frac{r}{nr_B}\right)$
2	0 (2s)	$\frac{1}{\sqrt{2}}\left(\frac{1}{r_B}\right)^{3/2}\left(1-\frac{r}{nr_B}\right)\exp\left(-\frac{r}{nr_B}\right)$
2	1 (2p)	$\frac{1}{\sqrt{6}}\left(\frac{1}{r_B}\right)^{3/2}\frac{r}{nr_B}\exp\left(-\frac{r}{nr_B}\right)$
3	0 (3s)	$\frac{1}{9\sqrt{3}}\left(\frac{1}{r_B}\right)^{3/2}\left(6-12\frac{r}{nr_B}+4\left(\frac{r}{nr_B}\right)^2\right) \cdot \exp\left(-\frac{r}{nr_B}\right)$

4)

n	ℓ	$R_{n\ell}$
3	1 (3p)	$\frac{1}{9\sqrt{6}}\left(\frac{1}{r_B}\right)^{3/2}\left(4-\frac{2r}{nr_B}\right)\left(\frac{2r}{nr_B}\right) \cdot \exp\left(-\frac{r}{nr_B}\right)$
3	2 (3d)	$\frac{1}{9\sqrt{30}}\left(\frac{1}{r_B}\right)^{3/2}\left(\frac{2r}{nr_B}\right)^2 \exp\left(-\frac{r}{nr_B}\right)$

where
$$r_B = \frac{4\pi\epsilon_0\hbar^2}{me^2} \quad -(23)$$
is the Bohr radius.

From eqn (19), computer algebra can be used to work out dr/dt for each orbital. From Eq. (17) it is known that:
$$r = \frac{\alpha}{1+\epsilon\cos\theta}, \quad -(24)$$

so
$$\frac{dr}{dt} = \frac{dr}{d\theta}\frac{d\theta}{dt} = \frac{L}{mr^2}\frac{dr}{d\theta} \quad -(25)$$

Here
$$\frac{dr}{d\theta} = \frac{\epsilon r^2}{\alpha}\sin\theta \quad -(26)$$

So
$$\boxed{\frac{dr}{dt} = \frac{L}{m}\frac{\epsilon}{d}\sin\theta} \quad -(27)$$

For example, for $n = 1$, $\ell = 0$:
$$R_{10} = 2\left(\frac{1}{r_B}\right)^{3/2} \exp\left(-\frac{r}{r_B}\right) \quad -(28)$$

so
$$P_{10} = r R_{10} = 2\left(\frac{1}{r_B}\right)^{3/2} r \exp\left(-\frac{r}{r_B}\right) \quad -(29)$$

$$\frac{dP_{10}}{dr} = \left(\frac{1}{r} - \frac{1}{r_B}\right) P_{10} \quad -(30)$$

$$\frac{d^2 P_{10}}{dr^2} = \left(\frac{1}{r} - \frac{1}{r_B}\right)\frac{dP_{10}}{dr} - \frac{1}{r^2} P_{10} \quad -(31)$$

$$= \left(\left(\frac{1}{r} - \frac{1}{r_B}\right)^2 - \frac{1}{r^2}\right) P_{10}$$

$$= \frac{\not{\ell}^2}{r_B}\left(\frac{1}{r_B} - \frac{2}{r}\right) P_{10}$$

Fm eqs. (19), (27) and (31):
$$\left(\frac{dr}{dt}\right)^2 = \left(\frac{L\epsilon}{md}\sin\theta\right)^2 = \frac{\not{\ell}^2}{r_B}\left(\frac{1}{r_B} - \frac{2}{r}\right)$$

$$-(32)$$

6) This is an equation for the radial velocity of the electron in the 1S orbital of the hydrogen atom:

$$\boxed{\begin{aligned} v_r^2 &= -\frac{\hbar^2}{r_B}\left(\frac{2}{r} - \frac{1}{r_B}\right) \quad -(33) \\ &= \left(\frac{L\epsilon}{m\alpha}\sin\theta\right)^2 \end{aligned}}$$

In this case v_r is structurally similar to the total velocity equation of an elliptical orbit.

<u>Suggested Computer Work</u>

The radial velocity can be plotted against r and against θ for each of the radial orbitals in Table One.

Eq. (33) can be developed further as follows:

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

and

$$\sin^2\theta = 1 - \cos^2\theta \quad -(35)$$

where from eq. (24):

$$\cos\theta = \frac{1}{\epsilon}\left(\frac{\alpha}{r} - 1\right) \quad -(36)$$

so

$$l(l+1)\left(\frac{\epsilon}{md}\sin\theta\right)^2 = -\frac{1}{r_B}\left(\frac{2}{r} - \frac{1}{r_B}\right) \quad -(37)$$

i.e.

$$l(l+1)\left(\frac{\epsilon}{md}\right)\left[1 - \frac{1}{\epsilon}\left(\frac{d}{r} - 1\right)\right] = -\frac{1}{r_B}\left(\frac{2}{r} - \frac{1}{r_B}\right) \quad -(38)$$

This is an equation for r in terms of the other parameters.

For s orbitals:

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

so

$$\frac{2}{r} = \frac{1}{r_B} \quad -(40)$$

and

$$r = 2r_B \quad -(41)$$

for the 1s orbital. However, for a 2p orbital,

$$n = 2,\ l = 1 \quad -(42)$$

and

$$\left(\frac{dr}{dt}\right)^2 = -\frac{\hbar^2}{P}\frac{d^2P}{dr^2} \quad -(43)$$

where:

$$P = rR_{10} = \frac{1}{\sqrt{6}}\left(\frac{1}{r_B}\right)^{3/2}\frac{r^2}{2r_B}\exp\left(-\frac{r}{2r_B}\right)$$