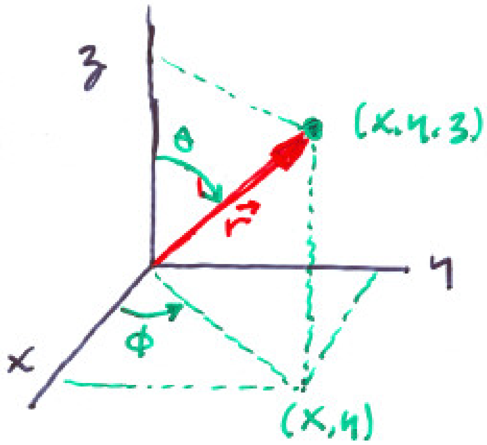
CHAPTER 7 THE HYDROGEN ATOM

The gold-standard calculation of Schrödinger

$$V(r) = -\frac{1}{4\pi\epsilon_0}\frac{e^2}{r} \longrightarrow \text{Sch. Eq.}$$

Cartesian coordinates are not ... helpful



$\theta = \cos^{-1}\left(\frac{z}{r}\right)$ "polar angle"

$\phi = \tan^{-1}\left(\frac{y}{x}\right)$ "azimuthal angle"

$r = \sqrt{x^2+y^2+z^2}$

$x = r\sin\theta\cos\varphi$

$y = r\sin\theta\cos\varphi$

$z = r\cos\theta$

the conversion from Cartesian to spherical coordinates:

$$\frac{-\hbar^2}{2m}\left[\frac{\partial^2\psi(x,y,z)}{\partial x^2} + \frac{\partial^2\psi(x,y,z)}{\partial y^2} + \frac{\partial^2\psi(x,y,z)}{\partial z^2}\right]\psi(x,y,z)$$

$$+\, V(r)\,\psi(x,y,z) = E\,\psi(x,y,z)$$

$$\downarrow$$

$$\frac{-\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\,\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\varphi^2}\right]$$

$$-\frac{e^2}{4\pi\varepsilon_0 r}\,\psi = E\psi \qquad \star$$

In spherical coordinates, the solution is separable

$$\psi(r,\theta,\varphi) = R(r)\,T(\theta)\,\Phi(\varphi)$$

substitute this solution into $\star$

"separation of variables" technique to solving

a differential equation

$$\frac{\sin^2\theta}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{\sin\theta}{T}\frac{d}{d\theta}\left(\sin\theta\frac{dT}{d\theta}\right)+\underline{\frac{1}{P}\frac{d^2P}{d\varphi^2}}$$

$$+\frac{2Mr^2\sin^2\theta}{\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0 r}+E\right)=0$$

notice that the ___ term involves only φ &

no other term involves φ...

$$f(\varphi) = g(\theta, r)$$

changes here don't result in changes here.

$\Rightarrow f(\varphi) = \text{constant.} \rightarrow -m^2$

$$\frac{1}{P}\frac{d^2P}{d\varphi^2} = -m^2$$

$$\frac{d^2P}{d\varphi^2}+m^2P=0 \quad \Rightarrow \quad P(\varphi)=e^{im\varphi}$$

substituting

$$\underbrace{\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2Mr^2}{\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0 r}+E\right)}_{\text{function of only } r}=\underbrace{\frac{m^2}{\sin^2\theta}-\frac{1}{T\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{dT}{d\theta}\right)}_{\text{function of only } \theta}$$

both equal to the same constant $\rightarrow \dfrac{\lambda}{\hbar^2}$

2 equations.

$$-\frac{1}{T\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{dT}{d\theta}\right)+\frac{m^2}{\sin^2\theta}=\frac{\lambda}{\hbar^2}$$

$$-\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{dT}{d\theta}\right)+\frac{m^2}{\sin^2\theta}T(\theta)=\frac{\lambda}{\hbar^2}T(\theta) \qquad (1)$$

and

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\left[\frac{2M}{\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0 r}+E\right)-\frac{\lambda}{\hbar^2 r^2}\right]R=0 \qquad (2)$$

work on (1)

change variables. $\xi\equiv\cos\theta \quad 0<\theta<\pi \Rightarrow -1<\xi<1$

$$T(\theta)\rightarrow f(\xi)$$

new equation

$$\frac{d}{d\xi}(1-\xi^2)\frac{d}{d\xi}f(\xi)+\left(\frac{\lambda}{\hbar^2}-\frac{m^2}{1-\xi^2}\right)f(\xi)=0$$

another well-known differential equation...

complication: singularities at $\xi=\pm1$ ..

solve for $m=0$

$$\frac{d}{d\xi}(1-\xi^2)\frac{d}{d\xi}f(\xi)+\frac{\lambda}{\hbar^2}f(\xi)=0$$

Legendre Equation

$$\frac{d}{d\xi}(1-\xi^2)\frac{d}{d\xi}f(\xi) + \frac{\lambda}{\hbar^2}f(\xi) = 0$$

Again, use a power-series solution technique.

$$f(\xi) = \sum_n c_n \xi^n$$

just like SHO... substitute and find a recursion solution for the coefficients.

$$c_{n+2} = \frac{n(n+1) - (\lambda/\hbar^2)}{(n+1)(n+2)} c_n$$

As before, argue that for some finite n the series must stop... terminate. Any n beyond that point, $\xi^n = 0$.

call that value of $n = \ell$.

$$n = \ell \Rightarrow \quad \ell(\ell+1) - \lambda/\hbar^2 = 0$$

$$\lambda = \hbar^2 \ell(\ell+1)$$

The polynomial solution now depends on ℓ... call it

$f_\ell(\xi)$ "Legendre Polynomials"

conventionally ...

$$f_\ell(\xi) = \frac{1}{2^\ell \cdot \ell!} \frac{d^\ell}{d\xi^\ell} (\xi^2 - 1)^\ell$$

[usual notation is $P_\ell(\xi)$ or $P_\ell(\cos\theta)$]

first few...

$$f_0(\xi) = 1$$

$$f_1(\xi) = \xi$$

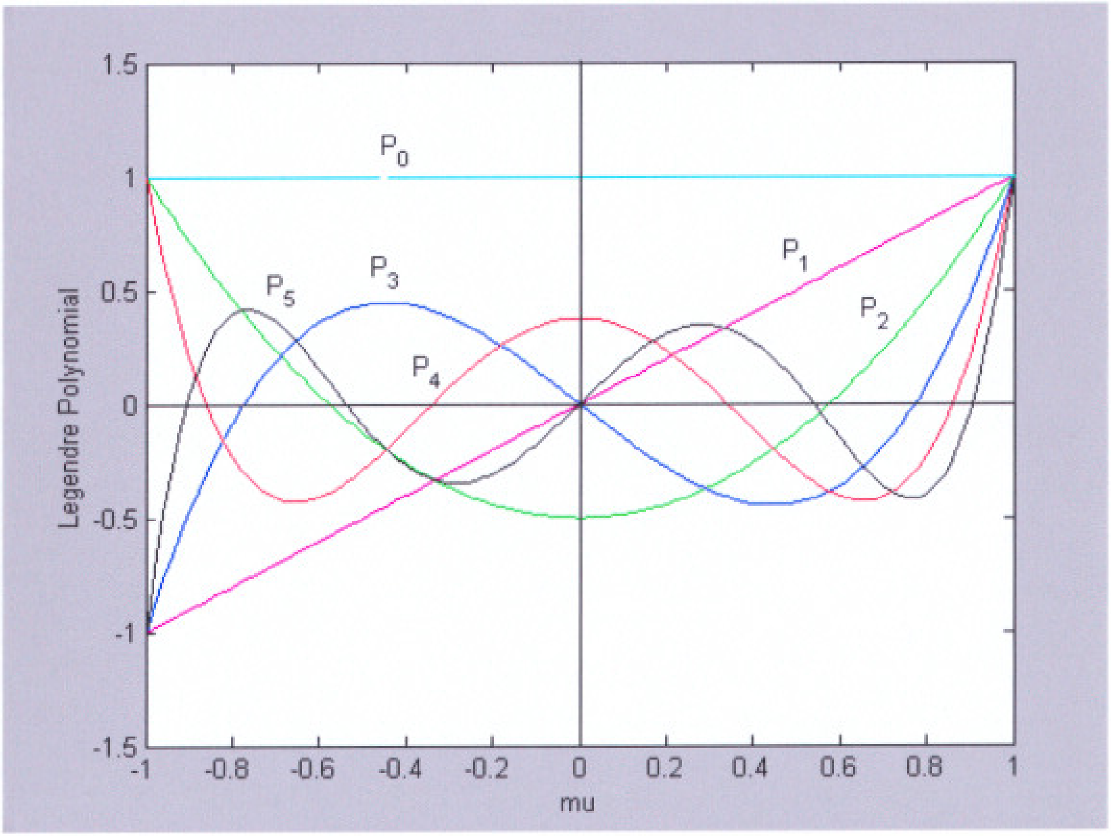
$$f_2(\xi) = \frac{1}{2}(3\xi^2 - 1)$$

We want unnormalized functions. & orthogonal for ℓ, ℓ'

$$\int_{-1}^{1} f_\ell(\xi) f_{\ell'}(\xi)\, d\xi = 0 \qquad \ell \neq \ell'$$

... need ℓ-fold integration by parts.

$$\int_{-1}^{1} f_\ell(\xi)^2\, d\xi = \frac{2}{2\ell+1}$$



P_0
P_1
P_2
P_3
P_4
P_5
Legendre Polynomial
mu
1.5
1
0.5
0
-0.5
-1
-1.5
-0.8
-0.6
-0.4
-0.2
0.2
0.4
0.6
0.8

This was for $m=0$. For $m \neq 0$.. define

$$f_\ell^m(\xi) = (1-\xi^2)^{m/2} \frac{d^m}{d\xi^m} f_\ell(\xi)$$

$$= \frac{1}{2^\ell \cdot \ell!} (1-\xi^2)^{m/2} \frac{d^{\ell+m}}{d\xi^{\ell+m}} (\xi^2-1)^\ell$$

$\underline{m \leq \ell}$

$f_\ell^m(\xi)$ are solutions to the original equation

and

$$\int_{-1}^{1} f_\ell^m(\xi)^2 d\xi = \frac{2}{2\ell+1} \frac{(\ell+m)!}{(\ell-m)!}$$

Going all the way back.. the angular part of ψ

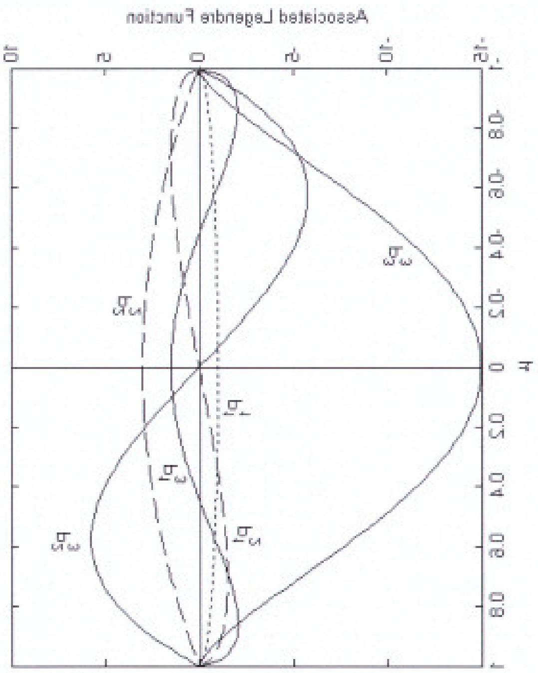
$$\psi(r,\theta,\varphi) = R(r)\,T(\theta)\,\Phi(\varphi)$$

$$= R(r)\,T(\theta)\,e^{im\varphi}$$

$$= R(r)\,Y_{\ell m}(\theta,\varphi)$$

called the "Spherical Harmonics"

$Y_{\ell m}$ --


Associated Legendre Function

$$Y_{\ell m}(\theta,\varphi) = \left[\frac{2\ell+1}{4\pi}\,\frac{(\ell-m)!}{(\ell+m)!}\right]^{1/2} (-1)^m e^{im\varphi} f_\ell^m(\cos\theta)$$

which have the following features.

$\ell \geq m$ but the same f's work for both $+m$ and $-m$ -- so need the $e^{im\varphi}$ to distinguish

$\downarrow$

~~$\ell \leq |m|$~~ $\ell \geq m$

explicitly:

$$m = -\ell,\ -\ell+1,\ -\ell+2, \ldots\ \ell-1,\ \ell$$

and, recall -- the ℓ's also vary

$$\ell = 0, 1, 2 \ldots$$

when

$\ell = 0$	$m = 0$
$\ell = 1$	$m = -1, 0, 1$
$\ell = 2$	$m = -2, -1, 0, 1, 2$
$\vdots$	$\vdots$

a few..

$$Y_{00} = \left(\frac{1}{4\pi}\right)^{1/2}$$

$$Y_{10} = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$$

$$Y_{1\pm1} = \mp\left(\frac{3}{8\pi}\right)^{1/2} e^{\pm i\varphi} \sin\theta$$

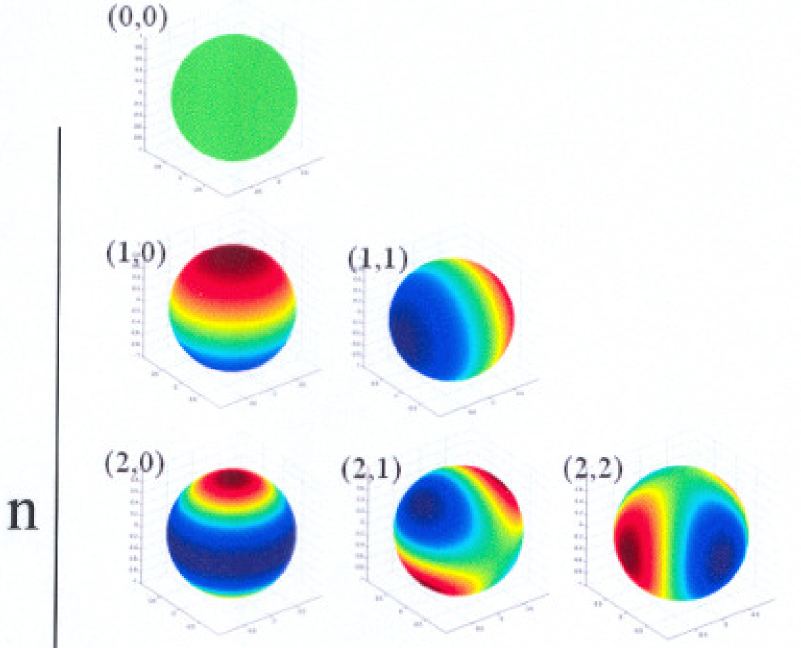
$$Y_{20} = \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1)$$

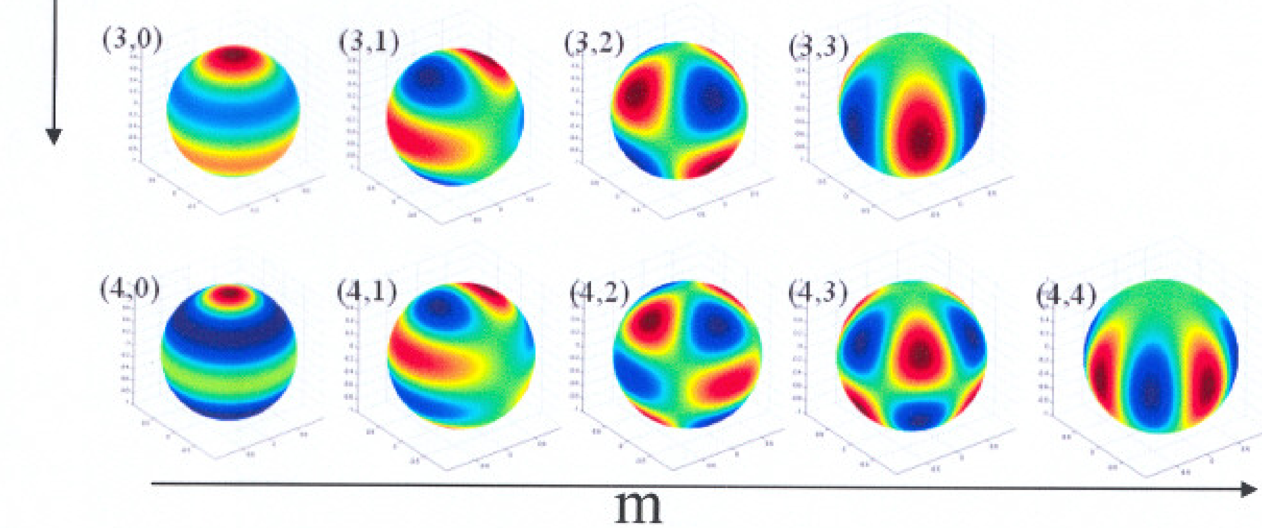
$$Y_{2\pm1} = \mp\left(\frac{15}{8\pi}\right)^{1/2} e^{\pm i\varphi} \cos\theta \sin\theta$$

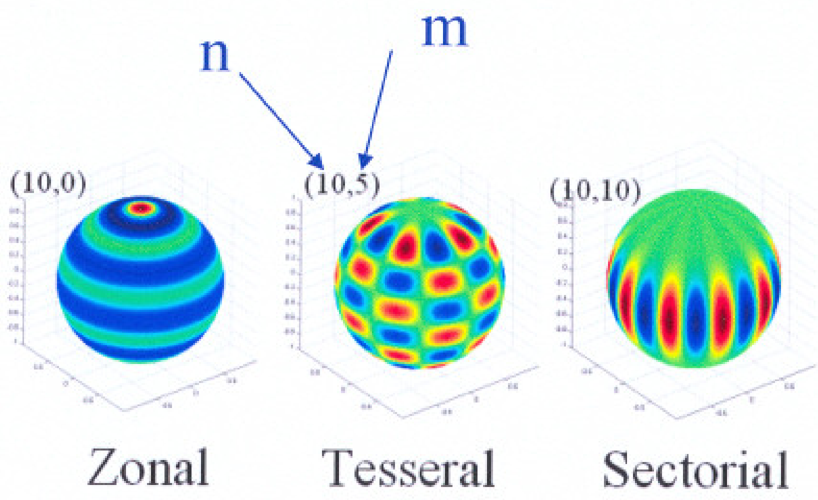
$$Y_{2\pm2} = \left(\frac{15}{32\pi}\right)^{1/2} e^{\pm 2i\varphi} \sin^2\theta$$

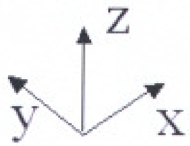
$$\vdots$$

$$Y_{\ell m}(\pi-\theta, \varphi+\pi) = (-1)^{\ell}\, Y_{\ell m}(\theta, \varphi)$$









$$Y_n^{-m}(\theta,\varphi) = \overline{Y_n^m(\theta,\varphi)}.$$

$$Y_0^0(\theta,\varphi) = \text{const} = \sqrt{\frac{1}{4\pi}}.$$

The radial equation 2 was

$$\left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr}\right)R(r) + \frac{2M}{\hbar^2}\left(E + \frac{e^2}{4\pi\epsilon_0 r} - \frac{\hbar^2 \ell(\ell+1)}{2Mr^2}\right)R(r) = 0$$

put in the λ found before.

E can be + or − !

free states like Rutherford scattering with an electron

bound states .. like Hydrogen atom ✓

$E \to -|E|$

new variables ..

$$\rho \equiv \left(\frac{8M|E|}{\hbar^2}\right)^{1/2} r$$

$$\lambda \equiv \frac{e^2}{\hbar}\left(\frac{M}{2|E|}\right)^{1/2}\frac{1}{4\pi\epsilon_0}$$

so, 2 becomes:

$$\frac{d^2R}{d\rho^2} + \frac{2}{\rho}\frac{dR}{d\rho} - \frac{\ell(\ell+1)}{\rho^2}R + \left(\frac{\lambda}{\rho} - \frac{1}{4}\right)R = 0$$

yet another famous differential equation ..

The Laguerre Equation

$$\frac{d^2R}{d\rho^2} + \frac{2}{\rho}\frac{dR}{d\rho} - \frac{\ell(\ell+1)}{\rho^2}R + \left(\frac{\lambda}{\rho} - \frac{1}{4}\right)R = 0$$

asymptotically for large ρ --

$$\frac{d^2R}{d\rho^2} - \frac{1}{4}R = 0$$

with solutions

$$R \sim e^{-\rho/2}$$

so, for a general solution try

$$R(\rho) = e^{-\rho/2}G(\rho)$$

Substituting... get a differential equation in $G(\rho)$:

$$\frac{d^2G}{d\rho^2} - \left(1 - \frac{2}{\rho}\right)\frac{dG}{d\rho} + \left[\frac{\lambda-1}{\rho} - \frac{\ell(\ell+1)}{\rho^2}\right]G = 0$$

problem.. singular at $\rho = 0$ .. try

$$G(\rho) = \rho^s \sum_m a^m \rho^m = \rho^s H(\rho)$$

Substituting... get another equation

$$\rho^2\frac{d^2H}{d\rho^2} + \rho\left[2(s+1) - \rho\right]\frac{dH}{d\rho} + \left[\rho(\lambda - s - 1) + s(s+1) - \ell(\ell+1)\right]H = 0$$

if $\rho = 0$ $\quad [\;] = 0 \quad \Rightarrow \quad s = \ell$

so, the equation for H: $\quad s=\ell$

$$\frac{d^2H}{d\rho^2} + \left(\frac{2\ell+2}{\rho} - 1\right)\frac{dH}{d\rho} + \frac{\lambda-\ell-1}{\rho}\,H = 0$$

use the series solution technique again

$$H(\rho) = \sum_m a_m \rho^m$$

substitute

$$\sum_{m=0}^{\infty}\left[m(m-1)a_m\rho^{m-2} + m a_m \rho^{m-1}\left(\frac{2\ell+2}{\rho}-1\right) + (\lambda-\ell-1)a_m\rho^{m-1}\right] = 0$$

$$\sum_{m=0}^{\infty} \rho^{m-1}\left\{(m+1)\left[m+2\ell+2\right]a_{m+1} + (\lambda-1-\ell-m)a_m\right\} = 0$$

$\{\} = 0$ required

$$a_{m+1} = \frac{m+\ell+1-\lambda}{(m+1)(m+2\ell+2)}\,a_m$$

again, the series must terminate at some $m = n_r$

$$\lambda = n_r + \ell + 1$$

λ is called the principle quantum number

Typically called .. $n = \lambda = n_r + \ell + 1$ $\quad$ ~~(stupid! not n in series!)~~

note: $n_r \geq 0$ so n is + integer and

$n \geq \ell + 1$

so, $\ell \leq n - 1$

From the definition of λ -- now n --

$$\lambda = n = \frac{e^2}{4\pi\epsilon_0 \hbar}\left(\frac{M}{2E}\right)^{1/2}$$

solve for E:

$$E_n = \frac{e^4}{(4\pi\epsilon_0)^2}\frac{M}{\hbar^2 2n^2}$$ The Bohr energy!

I mean... how neat is that?

still need the wavefunctions...

The series defines the $H(\rho)$'s --

but they are very close in form to the so-called Laguerre Polynomials $L_q(x) = e^x \frac{d^q}{dx^q}(x^q e^{-x})$

Actually define the Associated Laguerre Polynomials

$$L_q^p(x) = \frac{d^p}{dx^p} L_q(x)$$

a few...

$$L_0(x) = 1$$

$$L_1(x) = 1 - x \qquad \text{so} \qquad L_1^1(x) = -1$$

$$L_2(x) = 2 - 4x + x^2 \qquad \text{so} \qquad L_2^1(x) = -4 + 2x$$

$$L_2^2(x) = 2$$

$$\vdots \qquad\qquad \vdots$$

related to the $H(\rho)$'s:

$$H(\rho) = -L_{n+\ell}^{2\ell+1}(\rho)$$

So, the complete, unnormalized, radial functions are:

$$R_{n\ell}(\rho) = -e^{-\rho/2} \rho^\ell L_{n+\ell}^{2\ell+1}(\rho)$$

The normalization is very complicated...

$$\int_0^\infty \rho^2 e^{-\rho} \rho^{2\ell} \left[L_{n+\ell}^{2\ell+1}(\rho) \right]^2 d\rho = \frac{2n\left[(n+\ell)!\right]^3}{(n-\ell-1)!}$$

and:

$$R_{n\ell}(r) = -\left[\left(\frac{2}{na_0}\right)\frac{(n-\ell-1)!}{2n[(n+\ell)!]^3}\right]^{1/2}\left(\frac{2r}{na_0}\right)^{\ell} e^{-r/na_0} L^{2\ell+1}_{n+\ell}\left(\frac{2r}{na_0}\right)$$

where $a_0 = \dfrac{4\pi\epsilon_0\hbar^2}{Me^2}$ the "Bohr radius"

the WHOLE ENCHILADA is

$$\psi_{n\ell m}(r,\theta,\varphi) = R_{n\ell}(r)\, Y_{\ell m}(\theta,\varphi)$$

Hydrogenic Wave functions

few.. (inserting Ze for the nuclear charge).. radial guys.

$$R_{10}(r) = 2\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$$

$$R_{20}(r) = \left(\frac{Z}{2a_0}\right)^{3/2} 2\left(1-\frac{Zr}{2a_0}\right)e^{-Zr/2a_0}$$

$$R_{21}(r) = \left(\frac{Z}{2a_0}\right)^{3/2} 3^{-1/2}\,\frac{Zr}{a_0}\, e^{-Zr/2a_0}$$

R_{32} ⋮ ⋮

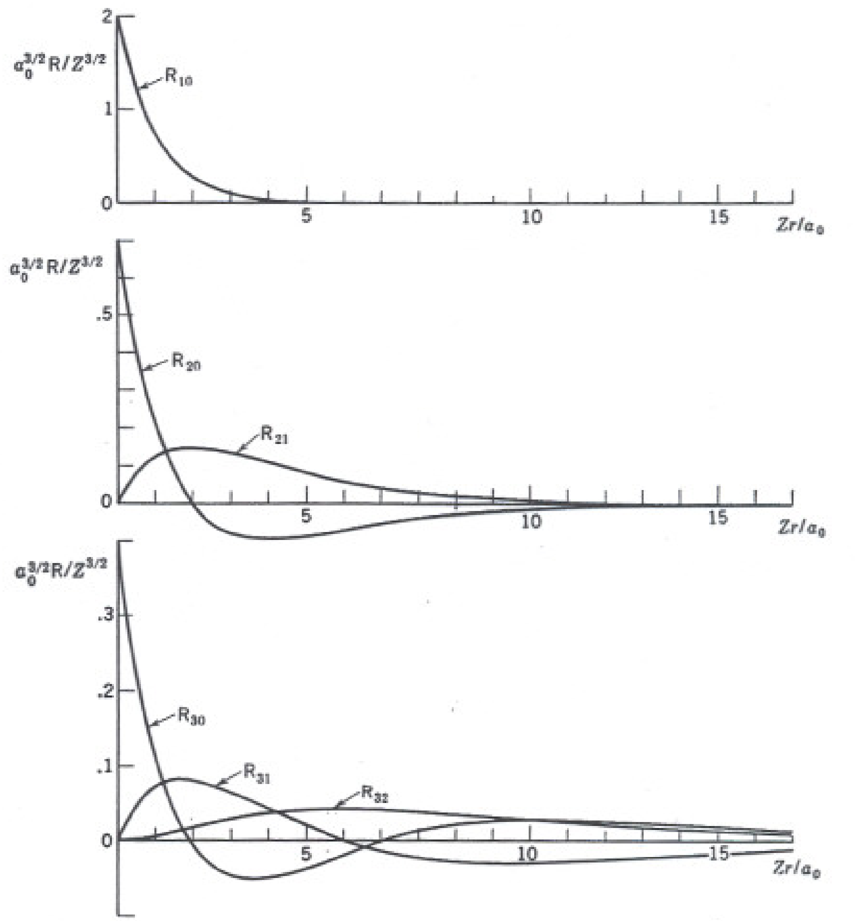


Figure 7-6 Graphs of the radial wave functions $R_{n\ell}(r)$ for $n = 1, 2,$ and 3 and $\ell = 0, 1, 2$. (From *Principles of Modern Physics* by R. B. Leighton. Copyright 1959 by McGraw-Hill Book Company. Used with permission of McGraw-Hill Book Company.)

The radial solutions obtained above should be recognized as the energy eigenfunctions for the hydrogenic atom. This result could have been anticipated from Equations 7.9 and 7.10, where the energy is seen to appear only in the radial equation. The energy eigenvalues corresponding to the radial solutions are readily obtained from Equation 7.74. Thus:

$$\lambda = \frac{1}{\hbar}\sqrt{2\mu\,|E_n|} = \frac{Z}{na_0},$$

or,

$$E_n = -\frac{Z^2e^2}{2a_0n^2} = -\frac{w_0Z^2}{n^2}.$$

The allowed energies are precisely the same as those obtained for circular Bohr orbits and for Sommerfeld's non-relativistic elliptical orbits. Such good agreement between classical and quantum mechanical calculations is fortuitous in the case of the Coulomb potential, and should not be expected in general.