LECTURE 27 8-7-09

FINISH HYDROGEN : VISUAL/INTUITIVE

HOW BIG ARE ATOMS?

LEGENDRE AND ASSOC. LEGENDRE

The Wave Function Equations

http://panda.unm.edu/Courses/Finley/P262/Hydrogen/WaveFcns.html
http://quantummechanics.ucsd.edu/ph130a/130_notes/node233.html

The Radial Components

http://hyperphysics.phy-astr.gsu.edu/Hbase/hydwf.html#c1
http://www.pha.jhu.edu/~rt19/hydro/img73.gif

The Angular Components

http://oak.ucc.nau.edu/jws8/dpgraph/Yellm.html

Radial times Angular

http://webphysics.davidson.edu/faculty/dmb/hydrogen/intro_hyd.html
http://www.falstad.com/qmatom/
http://quantummechanics.ucsd.edu/ph130a/130_notes/img1944.png

Even More

http://www.pha.jhu.edu/~rt19/hydro/
http://itl.chem.ufl.edu/4412_aa/radwfct.html

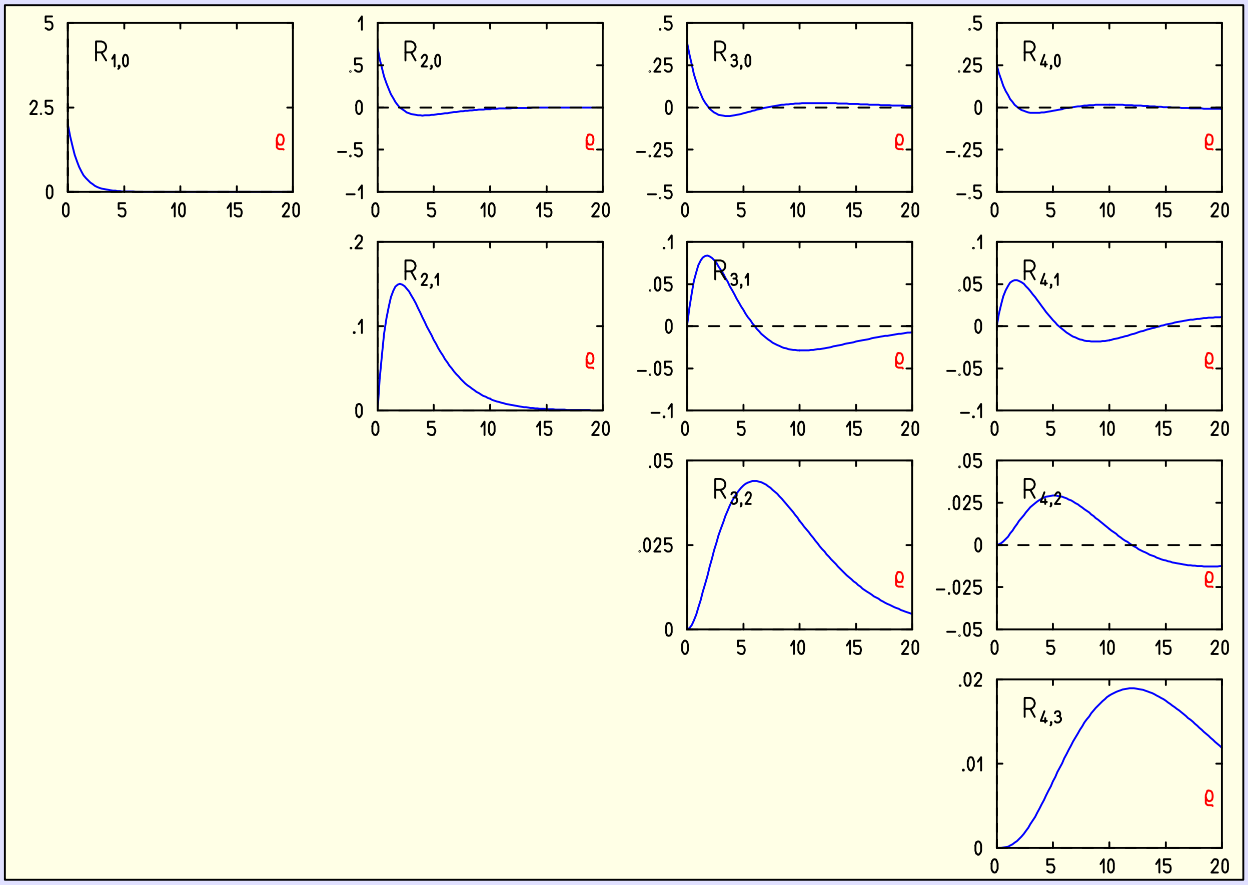
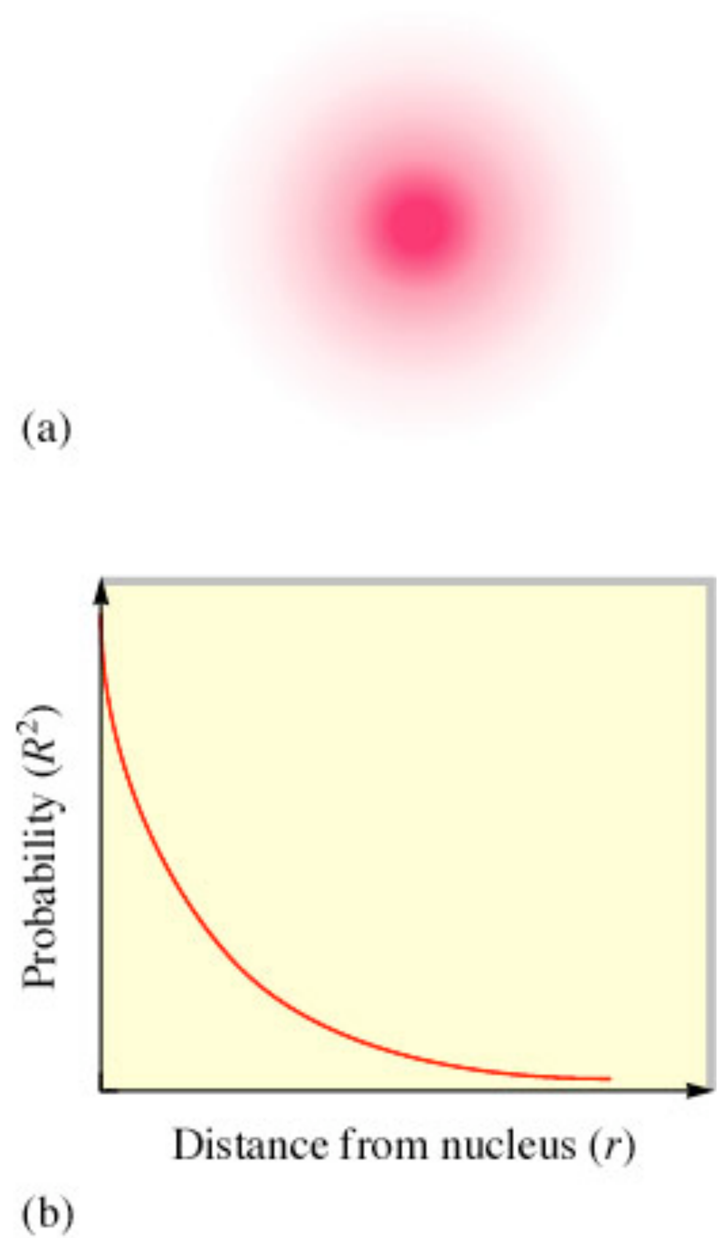


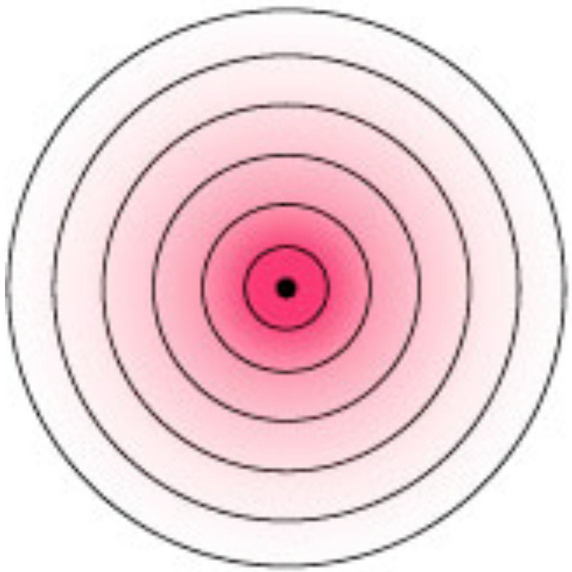
Fig. 13.14. Radial eigenfunctions $R_{n\ell}(\rho)$ for the electron in the hydrogen atom. Their zeros are the $n-\ell-1$ zeros of the Laguerre polynomials $L^{2\ell+1}_{n-\ell-1}(2\rho/n)$. Here the argument of the Laguerre polynomial is $2\rho/n$ with n being the principal quantum number and $\rho = r/a$ the distance between electron and nucleus divided by the Bohr radius a.

A hydrogen atom lost its electron and went to the police station to file a missing electron report. He was questioned by the police: "Haven't you just misplaced it somewhere? Are you sure that your electron is really lost?" *"I'm positive."* replied the atom.

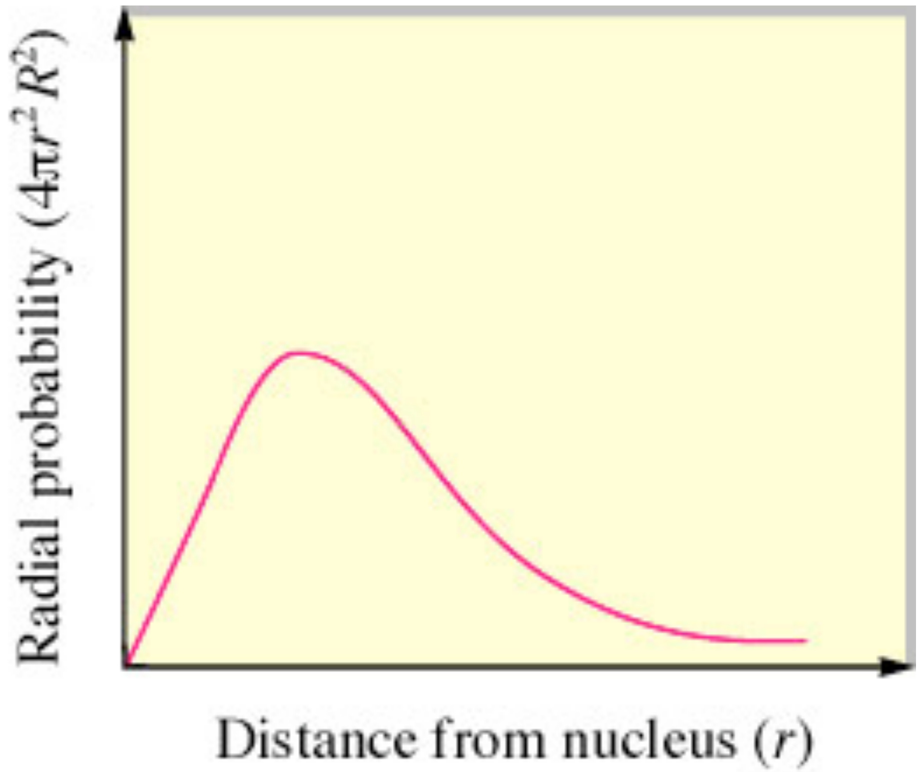
Probability Distribution for the 1s Wave Function



Radial Probability Distribution



(a)

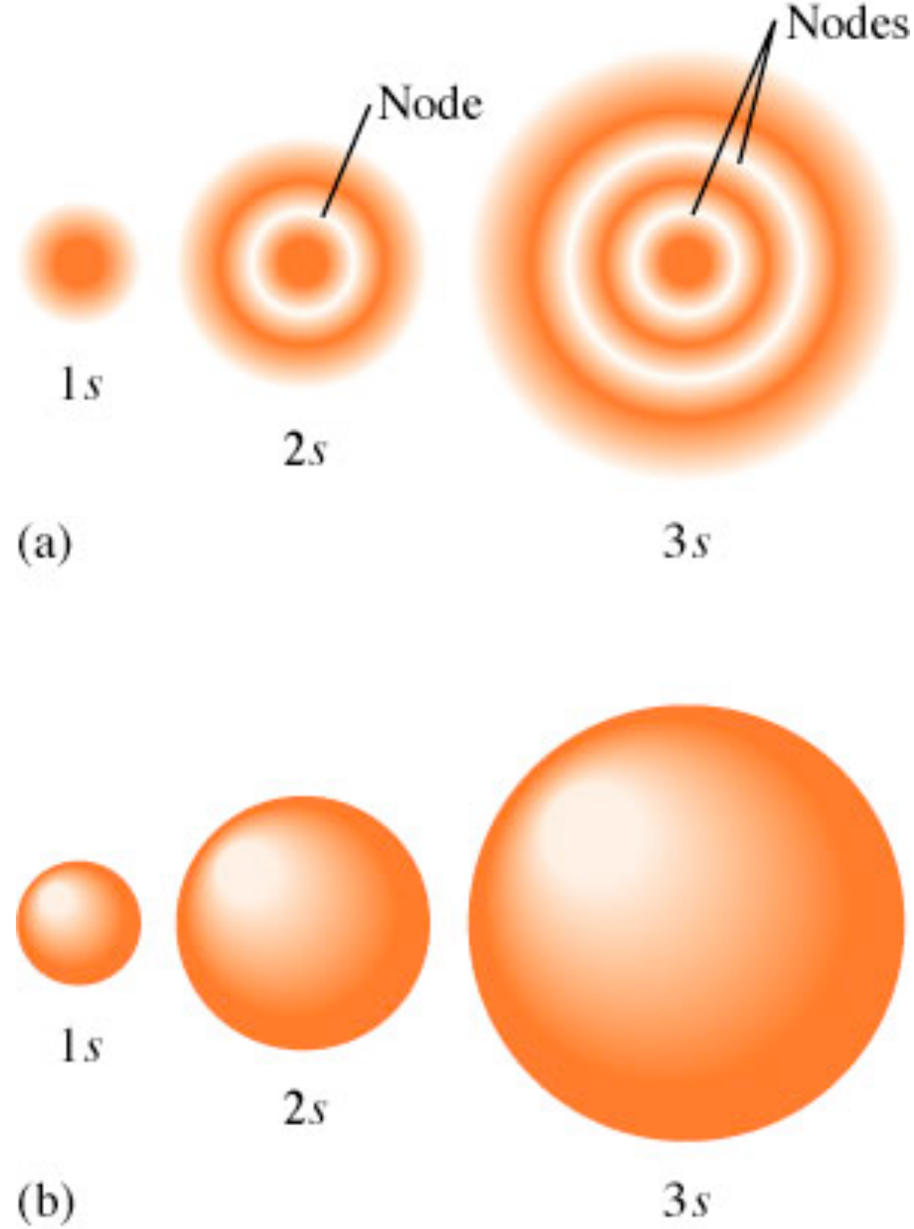


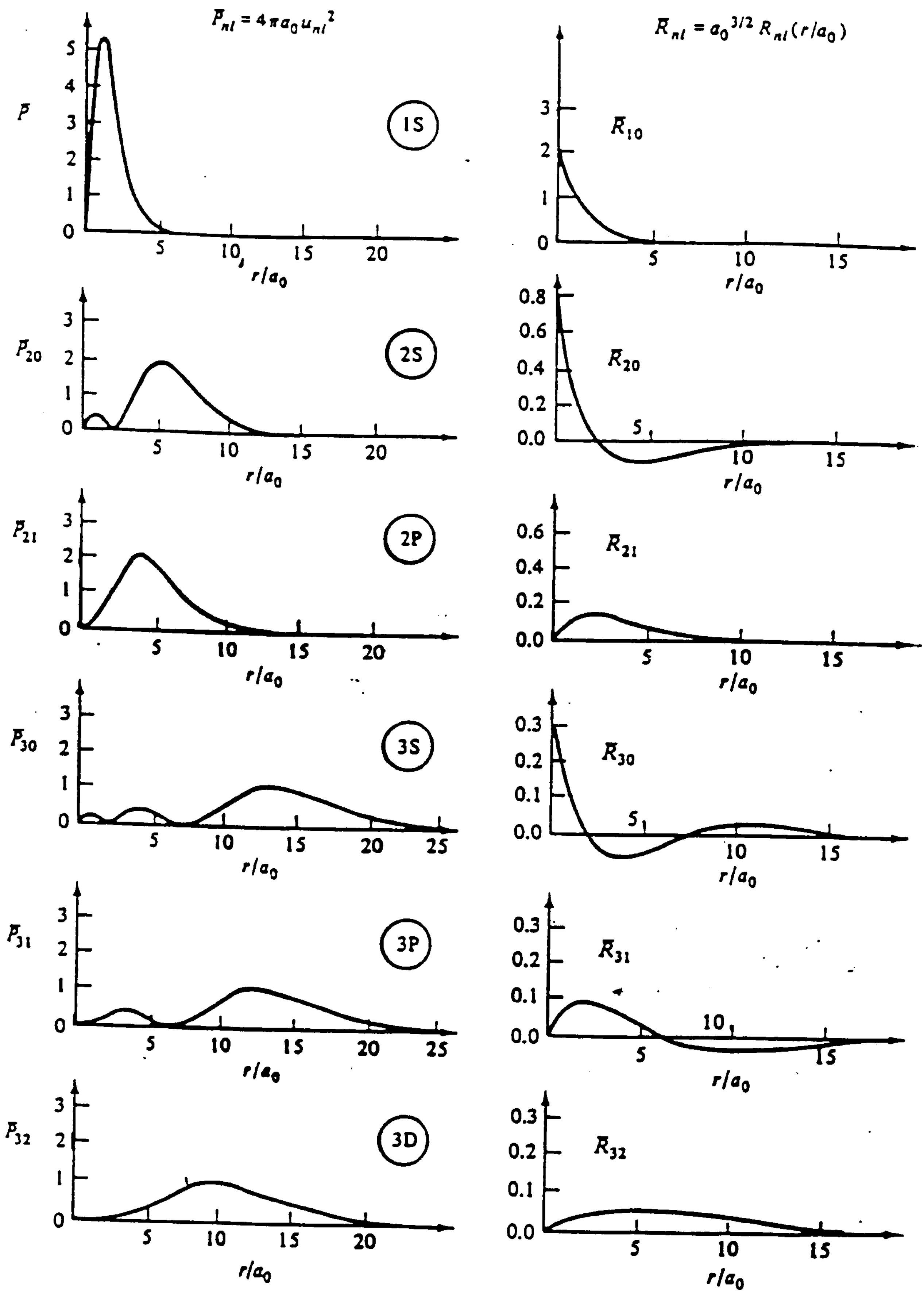
(b)

Probability Distribution

- ✓ square of the wave function
- ✓ probability of finding an electron at a given position
- ✓ Radial probability distribution is the probability distribution in each spherical shell.

Two Representations of the Hydrogen 1s, 2s, and 3s Orbitals




$\bar{P}_{nl} = 4\pi a_0 u_{nl}^2$
$\bar{R}_{nl} = a_0^{3/2} R_{nl}(r/a_0)$
$\bar{P}$
1S
$\bar{R}_{10}$
$\bar{P}_{20}$
2S
$\bar{R}_{20}$
$\bar{P}_{21}$
2P
$\bar{R}_{21}$
$\bar{P}_{30}$
3S
$\bar{R}_{30}$
$\bar{P}_{31}$
3P
$\bar{R}_{31}$
$\bar{P}_{32}$
3D
$\bar{R}_{32}$
r/a_0

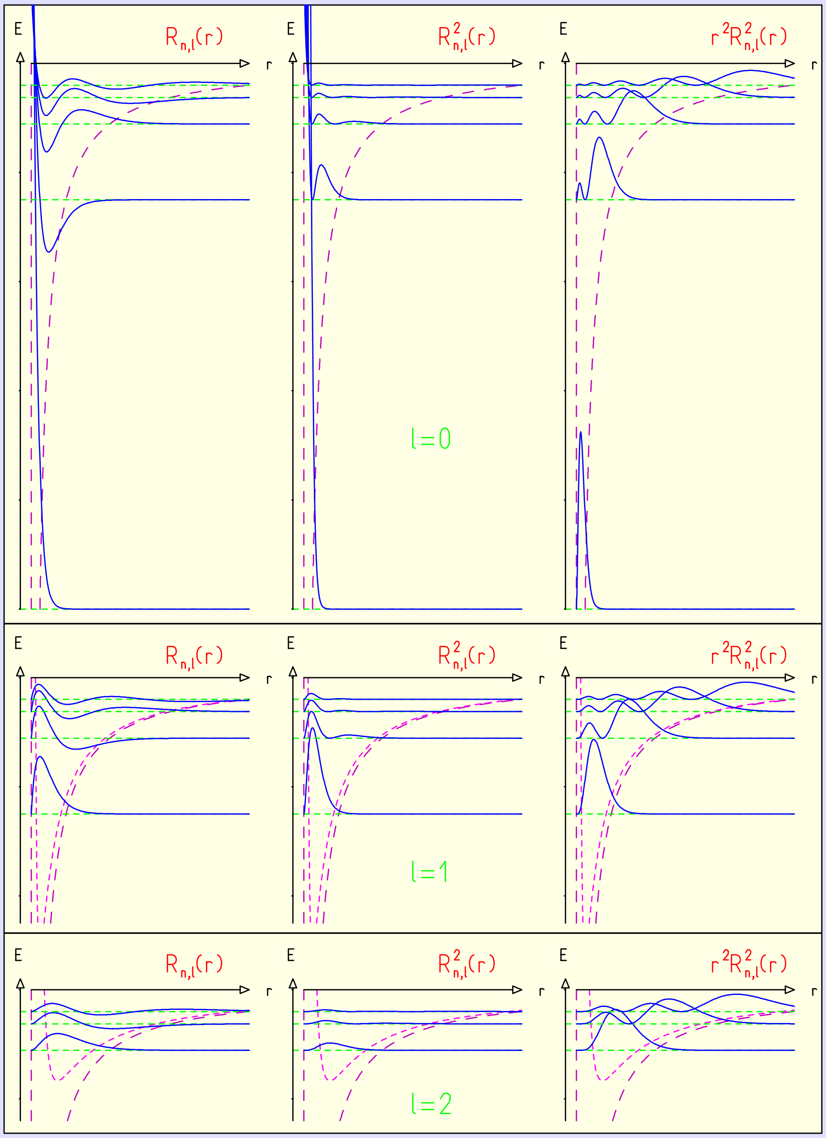
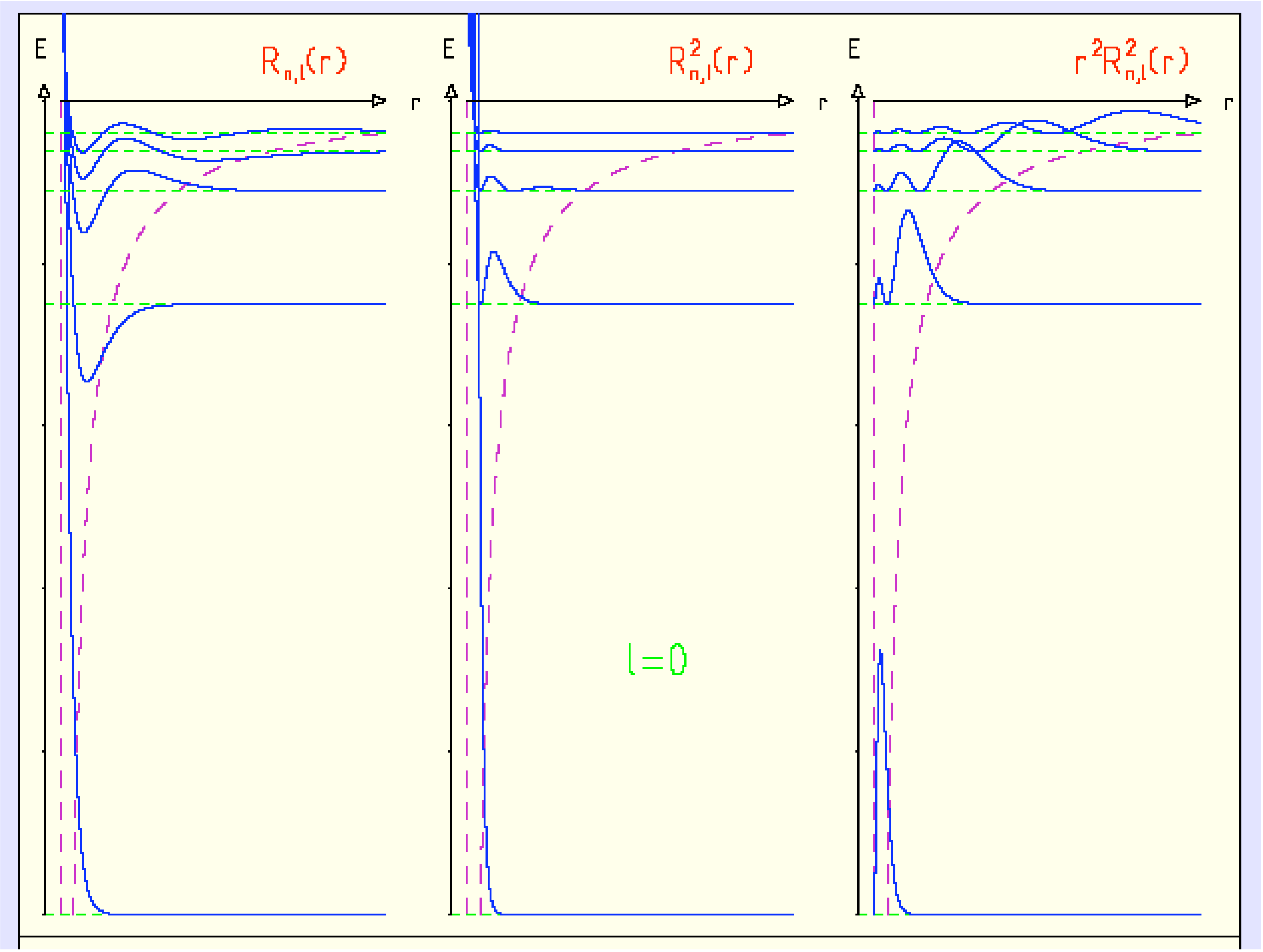
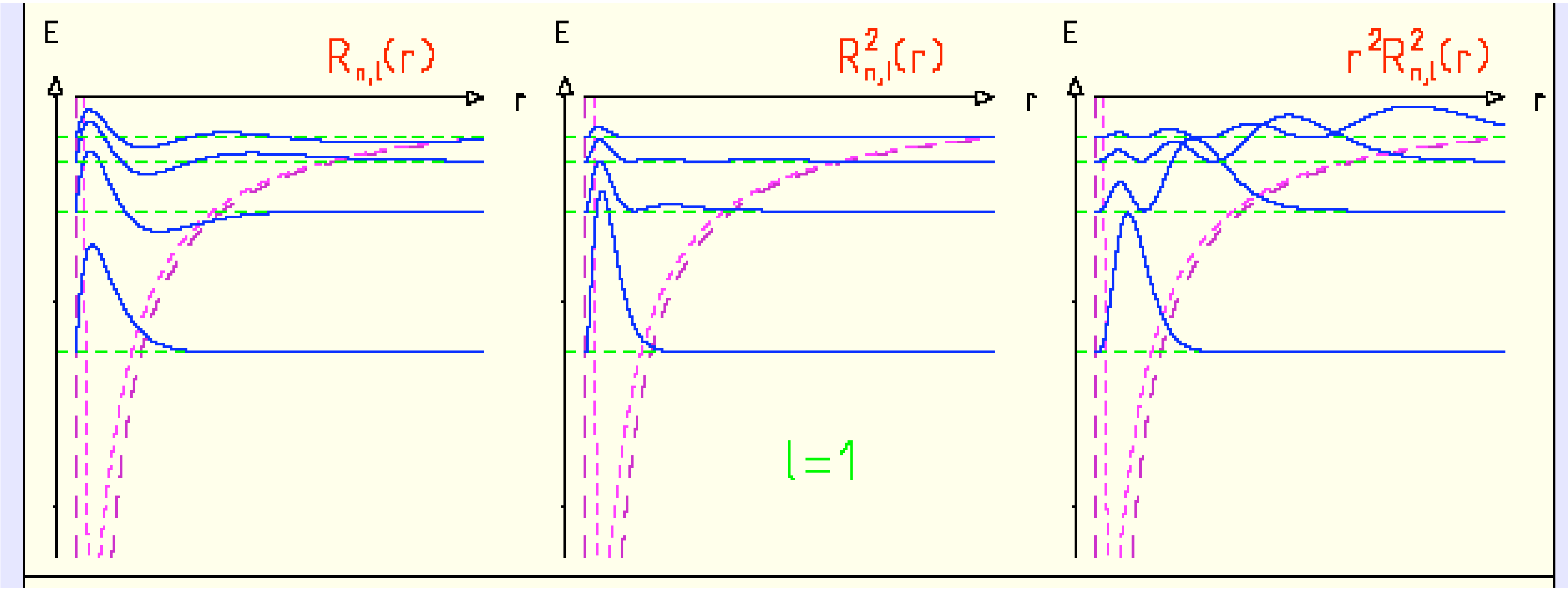


Fig. 13.15. Radial eigenfunctions $R_{n\ell}(r)$, their squares $R^2_{n\ell}(r)$, and the functions $r^2R^2_{n\ell}(r)$ for the lowest eigenstates of the electron in the hydrogen atom and the lowest angular-momentum quantum numbers $\ell = 0, 1, 2$. Also shown are the energy eigenvalues as horizontal dashed lines, the form of the Coulomb potential $V(r)$, and, for $\ell \neq 0$, the forms of the effective potential $V_\ell^{\rm eff}(r)$. The eigenvalue spectra are degenerate for all ℓ values, except that the minimum value of the principal quantum number is $n = \ell + 1$.

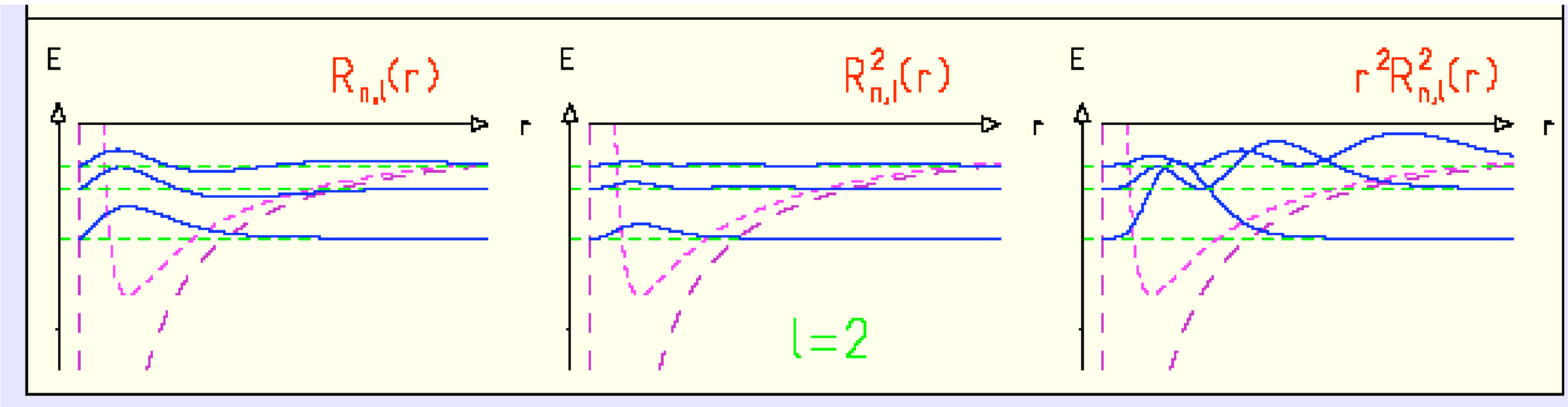
1s, 2s, 3s, 4s, 5s

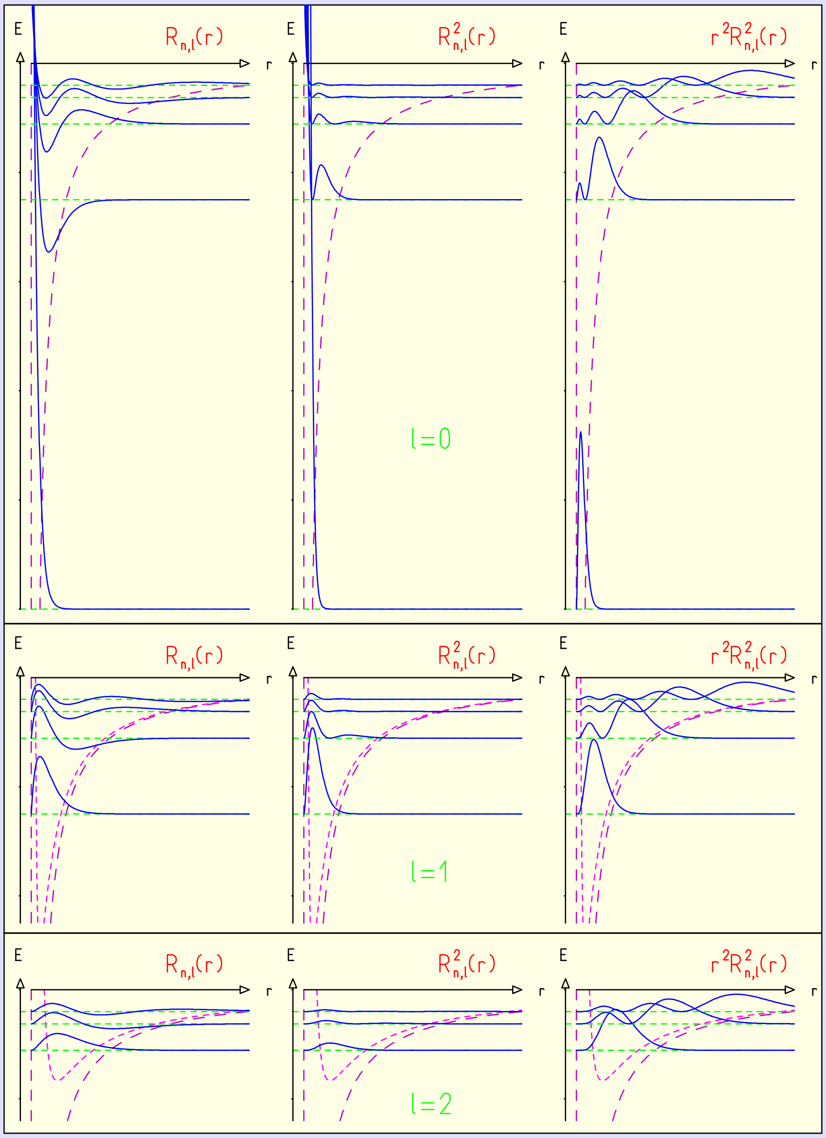


2p, 3p, 4p, 5p



3d, 4d, 5d





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http://itl.chem.ufl.edu/4412_aa/radwfct.html

How big are atoms?

HOW BIG ARE ATOMS?

HOW BIG ARE THE ORBITS?

TWO WAYS TO CHARACTERIZE RADIUS

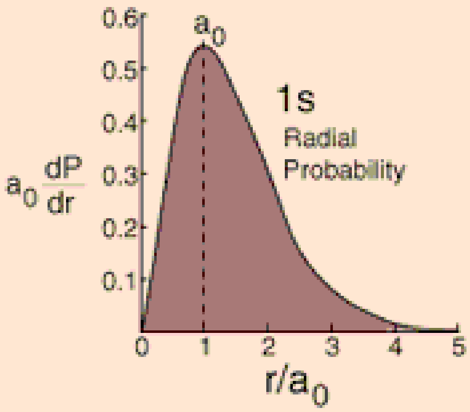
(1) MAX PROBABILITY r_{MAX}

(2) EXPECTATION VALUE $\langle r \rangle$

HOW SPREAD OUT ARE THE ORBITS

$$\Delta r = \sqrt{\langle r^2 \rangle - \langle r \rangle^2}$$

The Most Probable Radius Hydrogen Ground State



The radial probability density for the hydro ground state is obtained by multiplying the square of the wavefunction by a spherical s volume element.

$$dP = \left[\frac{1}{\sqrt{\pi} a_0^{3/2}} e^{-r/a_0} \right]^2 4\pi r^2 dr = \frac{4}{a_0^3} r^2 e^{-2}$$

It takes this comparatively simple form bec the 1s state is spherically symmetric and no angular terms appear.

Dropping off the constant terms and taking the derivative with respect to setting it equal to zero gives the radius for maximum probability.

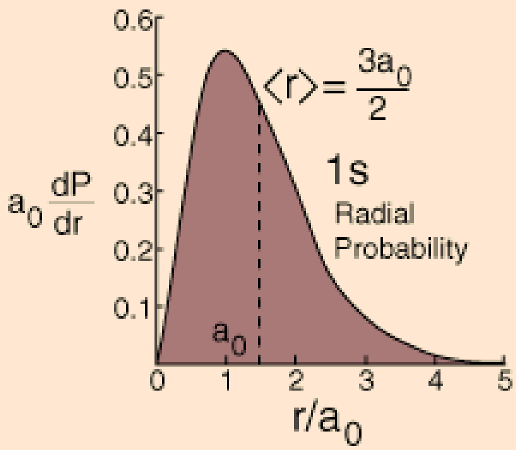
$$2re^{-2r/a_0} - \frac{2}{a_0} r^2 e^{-2r/a_0} = 0$$

$$2re^{-2r/a_0} \left[1 - \frac{r}{a_0} \right] = 0$$

which gives

$$r = a_0$$

The Expectation Value for Radius Hydrogen Ground State



The average or "expectation value" of the radius for the electron in the ground state of hydrogen is obtained from the integral

$$\langle r \rangle = \int_0^\infty r \frac{dP}{dr} dr = \frac{4}{a_0^3} \int_0^\infty r^3 e^{-2r/a_0} dr$$

This requires integration by parts. The solution is

$$\langle r \rangle = \frac{4}{a_0^3} \left[e^{-2r/a_0} \left(\frac{-a_0 r^3}{2} - \frac{3a_0^2 r^2}{4} - \frac{3a_0^3 r}{4} - \frac{3a_0^4}{8} \right) \right]_{r=0}^{r \to \infty}$$

All the terms containing r are zero, leaving

$$\langle r \rangle = \frac{3a_0}{2}$$

It may seem a bit surprising that the average value of r is 1.5 x the first Bohr radius, which is the most probable value. The extended tail of the probability density accounts for the average being greater than the most probable value.

CALCULATING EXPECTATION VALUES

$$\langle r^k \rangle = \int R_{n\ell}^*(r)\, r^k\, R_{n\ell}(r)\, r^2\, dr = \int r^{k+2} (R_{n\ell})^2\, dr$$

$$\langle r \rangle = \langle n \ell m | r | n \ell m \rangle$$

k=1 $$\langle r \rangle = \frac{1}{2}\left[3n^2 - \ell(\ell+1)\right] a_0$$

does not depend on m

does depend on n and ℓ

$$\langle r^2 \rangle = \langle n \ell m | r^2 | n \ell m \rangle$$

k=2 $$\langle r^2 \rangle = \frac{1}{2} n^2 \left[5n^2 + 1 - 3\ell(\ell+1)\right] a_0^2$$

$$\left\langle \frac{1}{r} \right\rangle = \frac{1}{a_0 n^2}$$

$$\left\langle \frac{1}{r^2} \right\rangle = \frac{1}{a_0^2 n^3 (\ell + 1/2)}$$

does not depend on m

does depend on n and ℓ

CALCULATING THE MAXIMUM PROBABILITY RADIUS

$$P_{n\ell}(r)\, dr = |R_{n\ell}(r)|^2 r^2\, dr$$

$$\int_0^\infty P_{n\ell}(r)\, dr = 1$$

EXAMPLE MAX PROBABILITY POINT

$$P_{21}(r) = r^2 \, | R_{21}(r) |^2$$

$$= \frac{1}{24 a_0^5} \, r^4 e^{-r/a_0}$$

$$\left. \frac{d P_{21}}{dr} \right|_{r = r_{20}} = 0 \quad \Rightarrow \quad 4 r_{20}^3 - \frac{r_{20}^4}{a_0} = 0$$

$$\boxed{r_{20} = 4 a_0}$$

GENERAL EXPRESSION

$$\left. \frac{d P_{n,n-1}}{dr} \right|_{r_n} = 0$$

$$2 n \, r_n^{2n-1} - \frac{2 \, r_n^{2n}}{n a_0} = 0$$

$$\Rightarrow \boxed{r_n = n^2 a_0}$$

MAX $\qquad n^2 a_0$

$$\langle r \rangle = \frac{1}{2}\left[3n^2 - l(l+1)\right] a_0$$

$$\langle r^2 \rangle = \frac{1}{2} n^2 \left[5n^2 + 1 - 3\, l(l+1)\right] a_0^2$$

$$(\Delta r) = \sqrt{\langle r^2 \rangle - \langle r \rangle^2}$$

$$\langle r \rangle \gtrsim r_{MAX}$$

$n\ l$	$n^2 a_0$	$\frac{1}{2}\left[3n^2 - l(l+1)\right] a_0$	$\frac{n^2}{2}\left[5n^2+1-3\right.$
1 0	a_0	$1.5\, a_0$	$3 a_0^2$
2 0	$4a_0$	$6\, a_0$	
2 1	"	$4\, a_0$	$30\, a_0^2$
3 0	$9\, a_0$		
3 1	"		
3 2	"		

EXAMPLE : WIDTH OF PROB DIST

$$R_{21}(r) = r\, e^{-r/2a_0} \Big/ \sqrt{24 a_0^5}$$

$$\langle r \rangle = \frac{1}{24 a_0^5} \int_0^\infty r^5 e^{-r/a_0}\, dr$$

$$= \frac{a_0}{24} \int_0^\infty u^5 e^{-u}\, du = \frac{120\, a_0}{24}$$

$$\boxed{\langle r \rangle = 5 a_0} \qquad \int_0^\infty x^n e^{-x}\, dx = n!$$

$$r_{MAX} = 4 a_0 \qquad \langle r \rangle \approx n^2 a_0$$

$$\langle r^2 \rangle_{21} = \int_0^\infty r^3 R_{21}^2(r)\, dr$$

$$= \frac{1}{24 a_0^5} \int r^6 e^{-r/a_0}\, dr$$

$$= \frac{6!\, a_0^7}{24 a_0^5} = 30\, a_0^2$$

SO, WIDTH

$$\Delta r_{21} = \sqrt{\langle r^2 \rangle - \langle r \rangle^2}$$

$$= \sqrt{30 a_0^2 - (5 a_0)^2}$$

$$= \sqrt{5}\, a_0$$

Orthonormal Basis Functions for the hydrogen atom problem

Legendre Polynomials

Spherical Harmonics

Laguerre Polynomials

BASIC IDEA: $H\psi = E\psi$

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right]\psi = E\psi$$

$$\nabla^2 = \left(\frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} - \frac{L^2}{r^2}\right)$$

spherical harmonics

$$\psi(r,\theta,\varphi) = R(r)\,\Omega(\theta,\varphi)$$

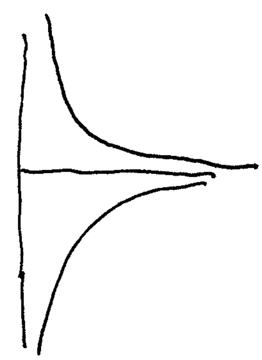
→ effective potential

$$V(r) - \frac{\hbar^2}{2m}\frac{-\ell(\ell+1)}{r^2}$$

asymptotic solution

times

Laguerre polynomials



$L_0(x) = 1$

$L_1(x) = 1 - x$

$L_2(x) = 1 - 2x + \frac{x^2}{2}$

$$x\frac{d^2y}{dx^2} + (1-x)\frac{dy}{dx} + ny = 0$$

$$\int_0^\infty L_m^*(x)\,L_n(x)\,e^{-x}\,dx = \delta_{mn}$$

SPHERICAL HARMONICS

LEGENDRE EXPANSIONS

$m \geq 0$

$$Y_{\ell m}(\theta, \varphi) = (-1)^m \sqrt{\frac{(2\ell+1)\,(\ell-m)!}{4\pi\,(\ell+m)!}}\; P_{\ell m}(\cos\theta)\, e^{im\varphi}$$

ASSOCIATED LEGENDRE FUNCTIONS

$m < 0$ $\quad Y_{\ell\,-m} = (-1)^m \left(Y_{\ell m}\right)^*$

GENERATOR FOR LEGENDRE POLYNOMIALS

$$P_\ell(u) = \frac{(-1)^\ell}{2^\ell\,\ell!}\,\frac{d^\ell}{du^\ell}\,(1-u^2)^\ell$$

ASSOCIATED LEGENDRE FUNCTIONS

$$P_{\ell m}(u) = \sqrt{(1-u^2)^m}\;\frac{d^m}{du^m}\,P_\ell(u)$$

THE LEGENDRE DIFF EQ

$$(1-x^2)\frac{d^2y}{dx^2} - 2x\frac{dy}{dx} + n(n+1)y = 0$$

LEGENDRE POLYNOMIALS

$$P_n(x) = \frac{1}{2^n n!}\left(\frac{d}{dx}\right)^n (x^2-1)^n$$

$P_0(x) = 1$

$P_1(x) = x$

$P_2(x) = \frac{1}{2}(3x^2-1)$

$P_3(x) = \frac{1}{2}(5x^3-3x)$

$P_4(x) = \frac{1}{8}(35x^4-30x^2+3)$

$P_5(x) = \frac{1}{8}(63x^5-70x^3+15x)$

ASSOCIATED ~~LEGENDRE FCNS~~

$$P_{nm}(x) = (1-x^2)^{m/2}\left(\frac{d}{dx}\right)^m P_n(x)$$

ASSOCIATED LEGENDRE DIFF EQ

$$(1-x^2)\frac{d^2y}{dx^2} - 2x\frac{dy}{dx} + \left[\ell(\ell+1) - \frac{m^2}{1-x^2}\right]y = 0$$

⇒ ASSOCIATED LEGENDRE FCNS

$$P_{\ell m}(x) = (1-x^2)^{m/2}\left(\frac{d}{dx}\right)^m P_\ell(x)$$

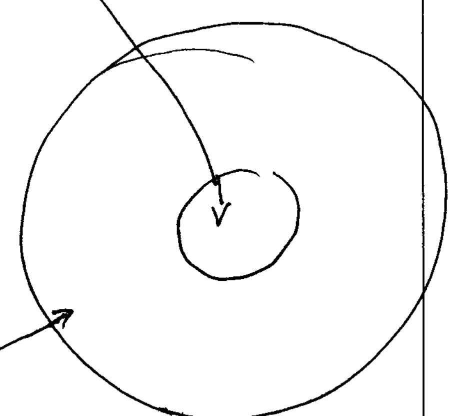
LEGENDRE POLYNOMIALS

ARE THE SPECIAL

m=0 CASE (m=0) OF

THE ASSOCIATED

LEGENDRE FCNS



ASSOCIATED LAGUERRE POLYNOMIALS

$$L_{ml}(x) = (-1)^l \left(\frac{d}{dx}\right)^l L_{m+l}(x)$$

$$x \frac{d^2 y}{dx^2} + (l+1-x)\frac{dy}{dx} + my = 0$$

$$L_{ml}(x) = \frac{x^{-l} e^x}{m!}\left(\frac{d}{dx}\right)^m \left(x^{m+l} e^{-x}\right)$$

$$\int_0^\infty L^*_{ml} \, L_{ml} \, \underline{x^l e^{-x}} \, dx = \frac{(m+l)!}{m!} \delta_{nm}$$

ORTHONORMAL
WRT THIS
WEIGHT
FUNCTION

FOR HYDROGEN

$$\int [L_{ml}]^2 \, x^{l+1} e^{-x} \, dx = (2m+l+1)\frac{(m+l)!}{m!}$$

7''