Lecture 15

Everything you should remember about hydrogen forever

QUALITATIVE FIRST

SOLVE TISE FOR HYDROGEN

FIND ev's $\longrightarrow$ EIGENENERGIES

FIND e$\vec{v}$'s $\longrightarrow$ ENERGY EIGENFCNS

STATIONARY STATES

$$|n \, \ell \, m\rangle \longrightarrow \psi_{n\ell m}(\vec{r})$$

$$E_{n\ell m} \longrightarrow E_n$$

TWO POV:

(1) $\nabla^2 \longrightarrow$ RADIAL ∇^2 + ANGULAR ∇^2

SOLN'S $Y_{\ell m}$'s

SEPARATE $\Rightarrow$ RADIAL EQN

(2) $$H = \frac{\vec{p}^{\,2}}{2m} + V(r)$$

$$H = \frac{p_r^2}{2m} + \frac{L^2}{2mr^2} + V(r)$$

SPHERICAL SYMMETRY $V(\vec{r}) = V(x,y,z) = V(r)$

$$H = \frac{\vec{p}^{\,2}}{2m} + V(r)$$

$$\frac{\vec{p}^{\,2}}{2m} = \frac{p_r^2}{2m} + \frac{L^2}{2mr^2}$$

PRODUCT ANSATZ $\psi = R_{n\ell} Y_{\ell m}$

$$\left[\frac{p_r^2}{2m} + \frac{L^2}{2mr^2} + V(r) \right] R_{n\ell} Y_{\ell m} = E_n R_{n\ell} Y_{\ell m}$$

$$\left[\frac{p_r^2}{2m} + \frac{\ell(\ell+1)\hbar^2}{2mr^2} + V(r) \right] R_{n\ell} = E_n R_{n\ell}$$

ANGULAR
MOMENTUM
BARRIER
REPULSIVE

ATTRACTIVE
COULOMB
POTENTIAL

SOLUTIONS TO THE RADIAL EQUATION

$$R_{n\ell}(r) \sim \left(\text{ASYMPTOTIC FORM} \right) \left(\text{LAGUERRE POLYNOMIALS} \right)$$

$\exp(-r/na_0)$
HYDROGEN

HYDROGEN-LIKE
$\exp(-Zr/na_0)$

Ways to solve the radial equation

(1) Solve the differential equation

- Find the asymptotic form
- Separate it
- Differential equation for each value of l
- Make the diff eq dimensionless
- Put highest derivative first
- Set its coefficient equal to 1
- Futz around
- Discover radial equation is Laguerre eqn !!!
- Declare victory
- Normalize the wave functions (caution)

(2) Use the ladder operators

(3) Type “hydrogen atom wavefunctions” into Google

SOLVE RADIAL EQN

TWO METHODS:

(1) DIFF EQN METHOD

- FIND ASYMPTOTIC FORM
- SEPARATE IT
- DIFFERENTIAL EQN for each value of l
- MAKE DIMENSIONLESS
- ORDER HIGHEST DERIVATIVE FIRST
- COEFF OF HIGHEST DERIVATIVE TERM = 1
- FUTZ AROUND
- DISCOVER RADIAL EQN IS EQUIVALENT TO THE ASSOCIATED LAGUERRE EQN
- DECLARE VICTORY
- NORMALIZE WAVEFCNS

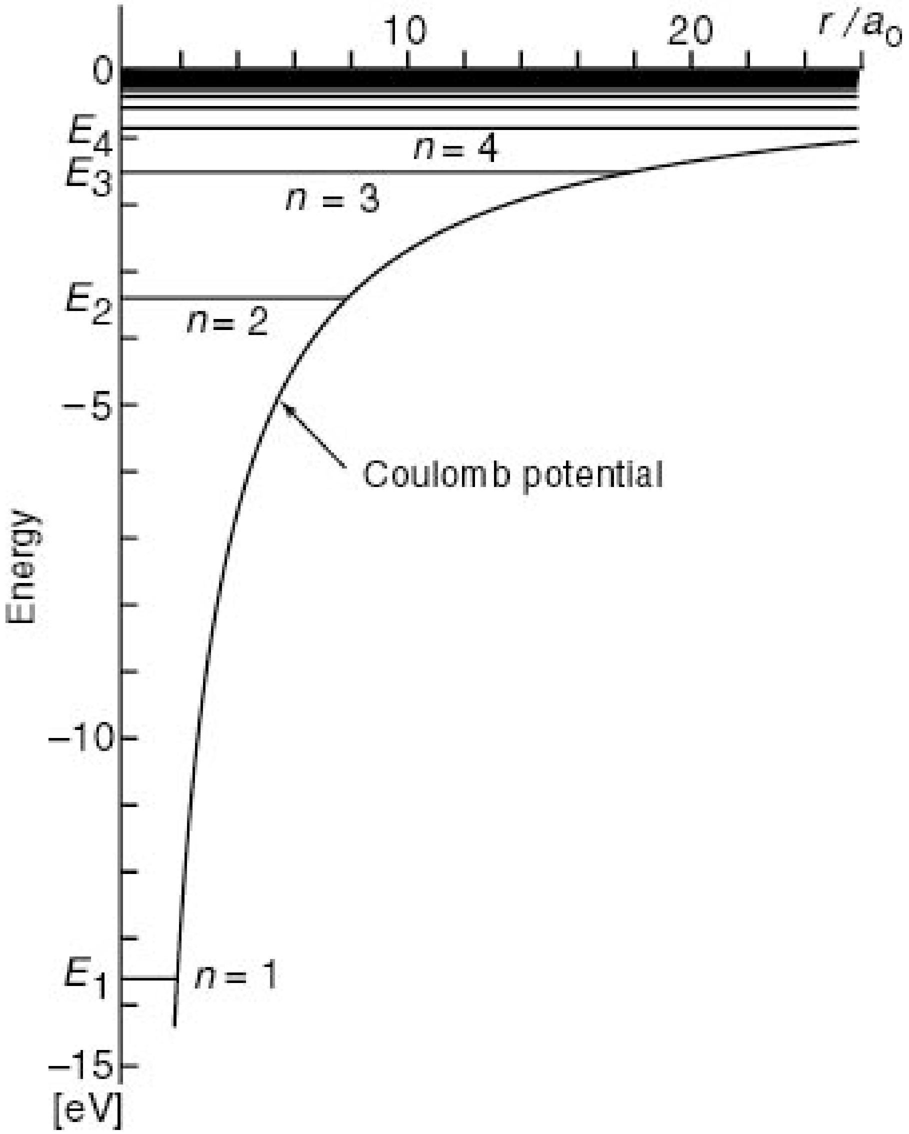
(2) USE LADDER OPERATORS

EIGEN FCNS ⇒ ENERGY EIGEN FCNS

EIGEN VALUES ⇒ EIGEN ENERGIES

$$E_n = \frac{-Ry}{n^2} = \frac{-13.6\ \text{eV}}{n^2}$$ HYDROGEN

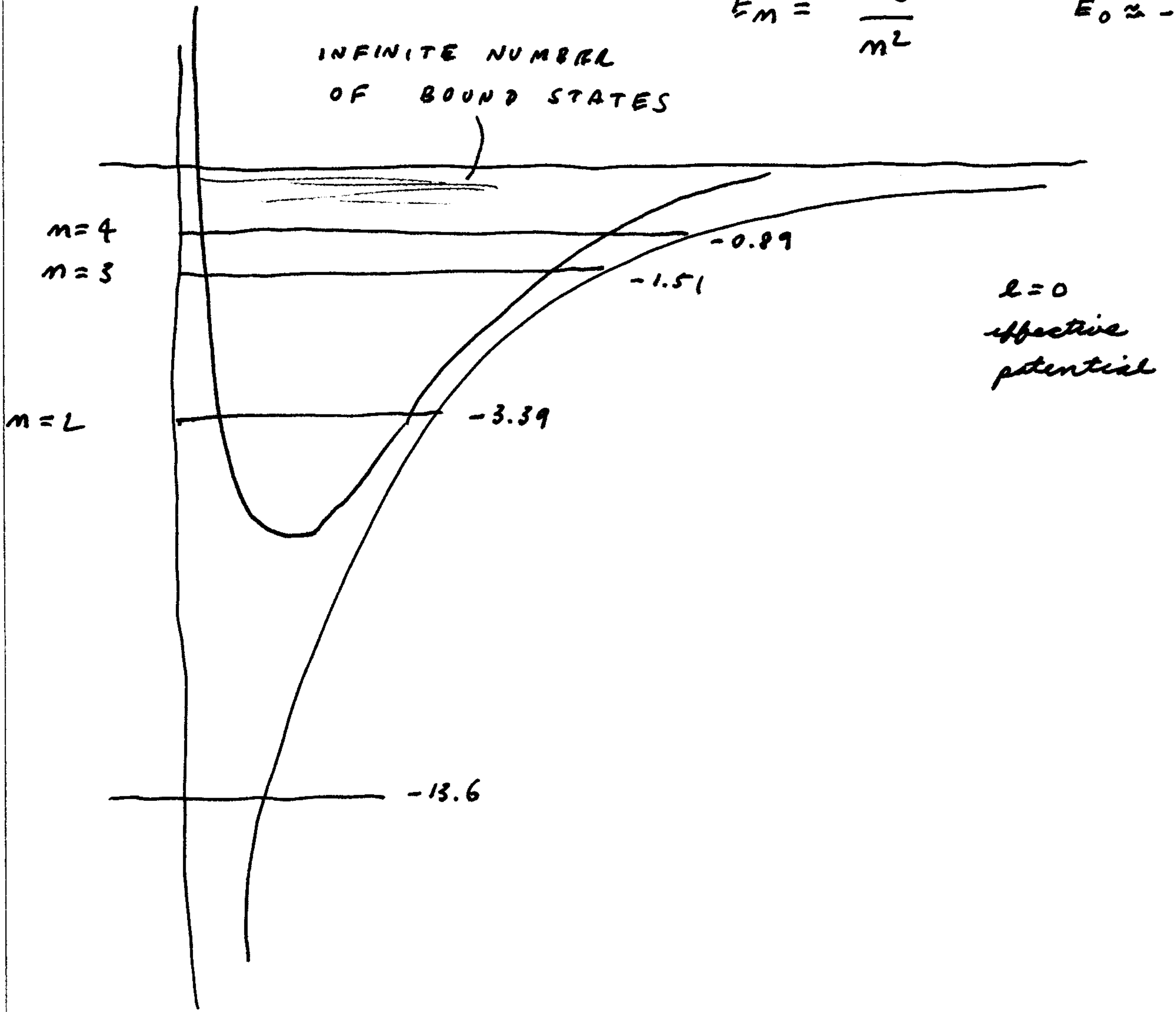
$$E_n' = -\frac{Z^2 Ry}{n^2}$$ HYDROGEN-LIKE



10
20
r / a_0
0
E_4
n = 4
E_3
n = 3
E_2
n = 2
−5
Coulomb potential
Energy
−10
E_1
n = 1
−15
[eV]

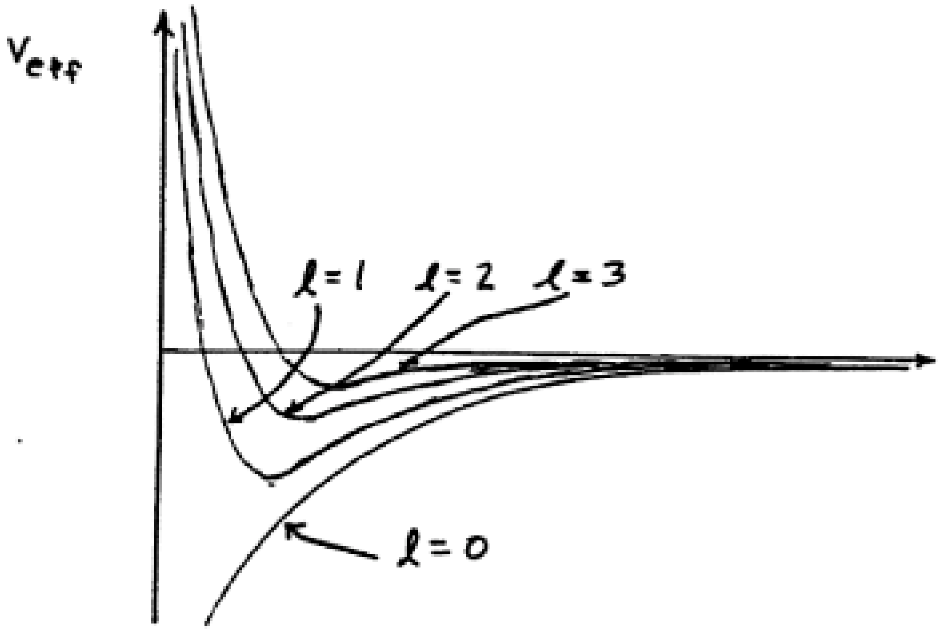
ENERGY DEGENERACY only n

$$E_n = \frac{E_0}{n^2} \qquad E_0 \approx -13.$$

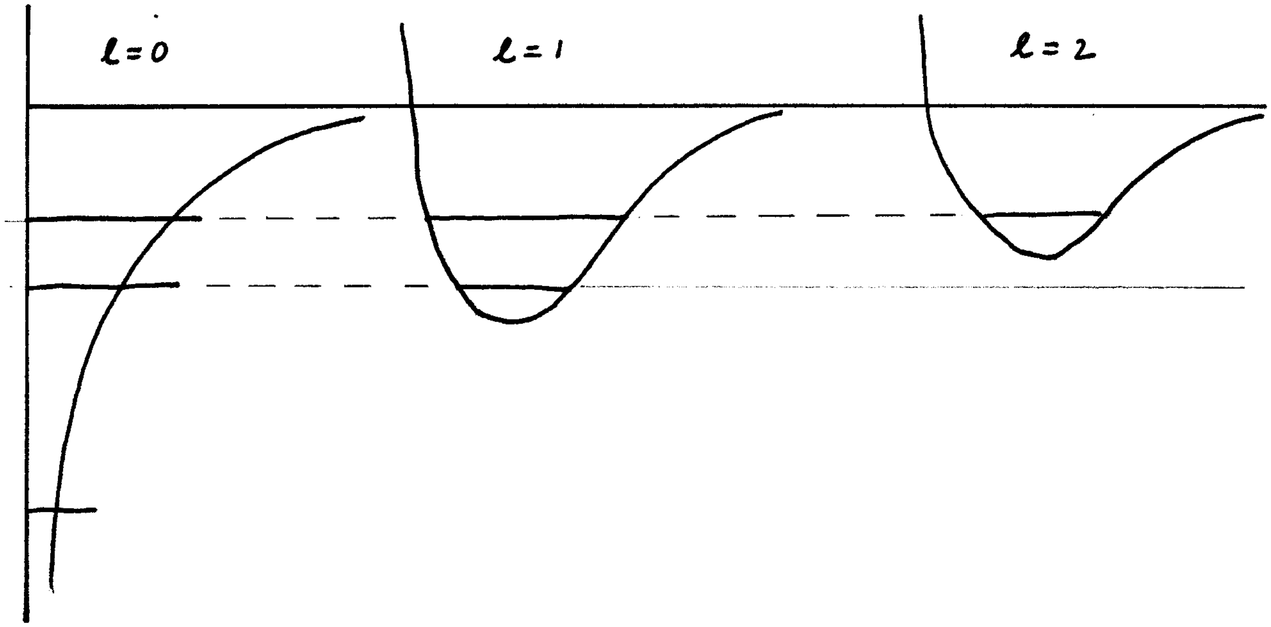


The Effective Potential Depends on the Angular Momentum

=> Series of Nested Wells



Series of States in each Well
Ground, 1st, 2nd, 3rd, ... excited


l=0
l=1
l=2

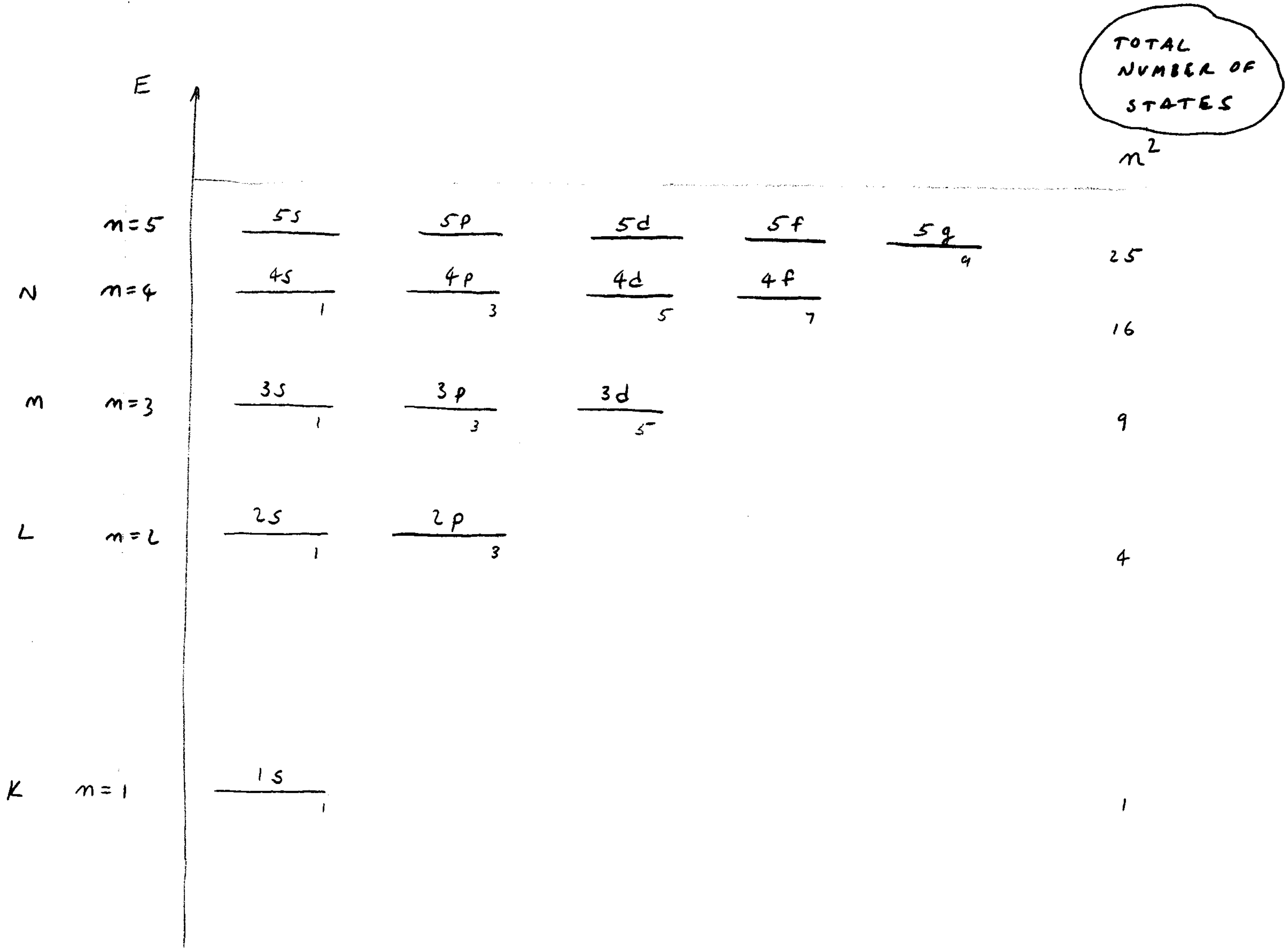
Energy

Degeneracy

$$E_n = - Z^2 \frac{E_0}{n^2}$$

for each n: $l = 0, 1, \ldots, n$

for each l: $m = -l, \ldots, +l$



	$l=0$	$l=1$	$l=2$	$l=3$	$l=4$	
	s	p	d	f	g	h i j k
$(2l+1)$	1	3	5	7	9	

Table 8.5 Spectroscopic Notation for Atomic Shells and Subhells

n	Shell Symbol	ℓ	Shell Symbol
1	*K*	0	*s*
2	*L*	1	*p*
3	*M*	2	*d*
4	*N*	3	*f*
5	*O*	4	*g*
6	*P*	5	*h*
. . .		. . .	

Table 8-5, p.280

FIRST FEW RADIAL WAVEFUNCTIONS $z = Z/a_0$

$n=1$ $$R_{10}(r) = 2\, z^{3/2}\, e^{-zr}$$

$n=2$ $$R_{20}(r) = \frac{1}{\sqrt{2}}\, z^{3/2} \left(1 - \tfrac{1}{2} z r\right) e^{-zr/2}$$

$$R_{21}(r) = \frac{1}{2\sqrt{6}}\, z^{5/2}\, (r)\, e^{-zr/2}$$

$n=3$ $$R_{30}(r) = \frac{2}{3\sqrt{3}}\, z^{3/2} \left(1 - \tfrac{2}{3} z r + \tfrac{2}{27} z^2 r^2\right) e^{-zr/3}$$

$$R_{31}(r) = \frac{8}{27\sqrt{6}}\, z^{5/2} \left(z r - \tfrac{1}{6} z^2 r^2\right) e^{-zr/3}$$

$$R_{32}(r) = \frac{4}{81\sqrt{30}}\, z^{7/2}\, (r^2)\, e^{-zr/3}$$

general form $$(\text{NORM})\,(\text{POLYNOMIAL})\, e^{-Zr/na_0}$$

WHAT DO THE RADIAL WAVEFCNS LOOK LIKE?

" " " RADIAL PROB DISTS " " ?

" " " 3d " " " " ?

$l = 0$ WAVE FCNS

$$R_{\overset{\uparrow}{n}\,\overset{\nwarrow}{l}}$$

energy   orbital angular momentum

$l=0$ R_{n0}'s

ANOTHER NOTATION ns 1s 2s 3s 4s ...

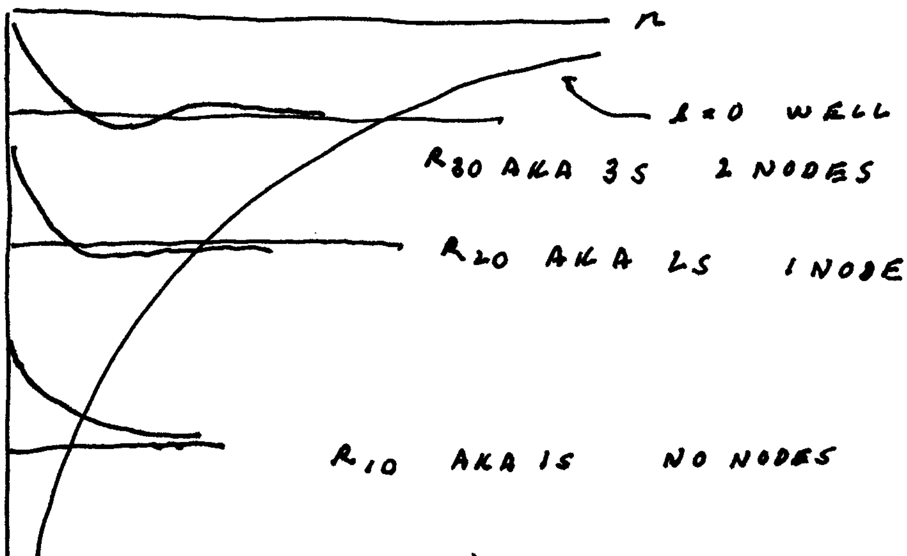
$l=0$ s

$l=1$ p

$l=2$ d

ASYMPTOTIC FORM

AS $x \to \infty$ $\psi \to e^{-r/a_0}$



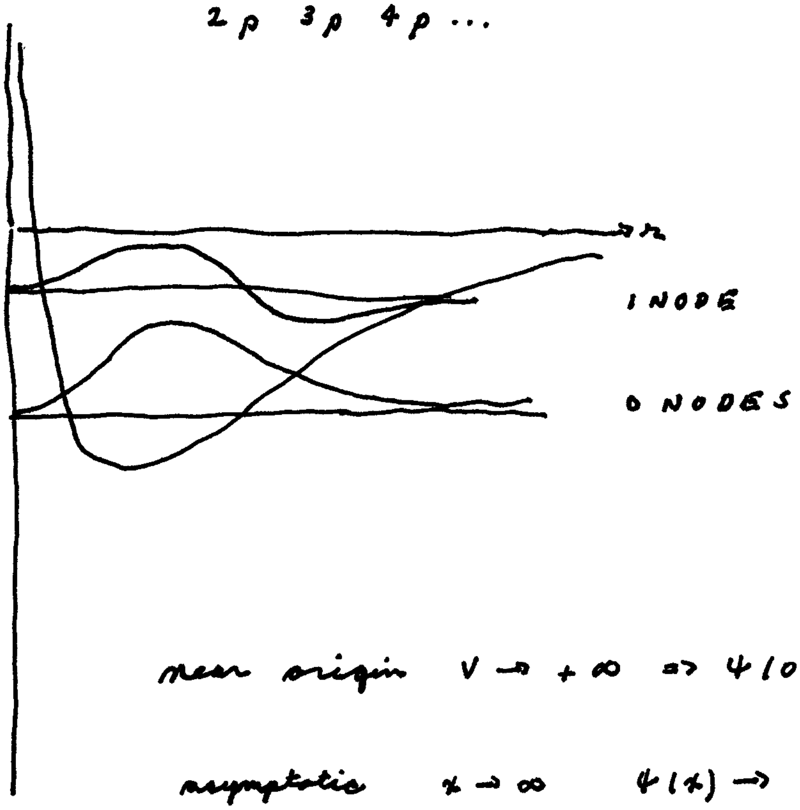
in $l=0$ WELL, $(n-1)$ NODES ⇒ ZEROS OF THE LAGUERRE POLY

POTENTIAL WANTS

$l = 1$ WAVE FCNS

$R_{nl} \to R_{n1}$

2p 3p 4p ...



near origin $V \to +\infty \Rightarrow \psi(0) = 0$

asymptotic $x \to \infty$ $\psi(x) \to e^{-r/na_0}$

TOTAL SOLUTION

$$\psi_n(\vec{r}) = \underset{\substack{\uparrow \\ \text{RADIAL} \\ \text{WAVEFCN}}}{R_{n\ell}(r)} \; \underset{\substack{\uparrow \\ \text{ANGULAR WAVE FCN}}}{Y_{\ell m}(\theta,\varphi)}$$

PROB DENSITIES

$$|\psi(\vec{r})|^2 \, dV$$

PROB TO FIND ELECTRON AT POINT $\vec{r}$

PROB TO FIND ELECTRON AT DISTANCE $|\vec{r}|$ FROM ORIGIN

$$|R_{n\ell}(r)\, Y_{\ell m}(\theta,\varphi)|^2 \, dV$$

$$|R_{n\ell}(r)|^2 \, |Y_{\ell m}(\theta,\varphi)|^2 \, r^2 \, dr \, d\Omega$$

$$\left(|R_{n\ell}(r)|^2 \, r^2 \, dr\right) \left(|Y_{\ell m}(\theta,\varphi)|^2 \, d\Omega\right)$$

$$P_{n\ell}(r) \qquad\qquad P_\ell(\theta)$$

Angular dependence

$$|Y_{\ell m}(\theta,\varphi)|^2 = \Theta(\theta)\, e^{im\varphi}\, \Theta^*(\theta)\, e^{-im\varphi}$$

phase changes as you go around z axis but the prob does not change

$$|\Theta(\theta)|^2$$

Polar plot

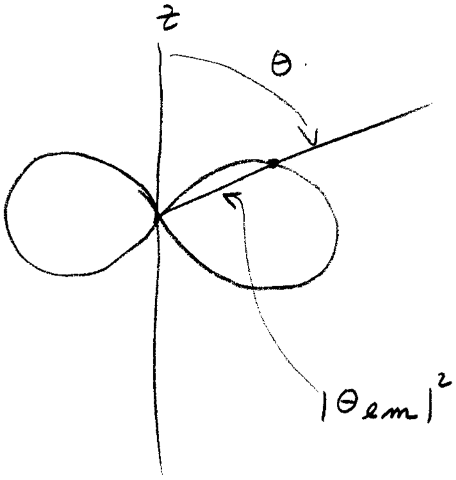
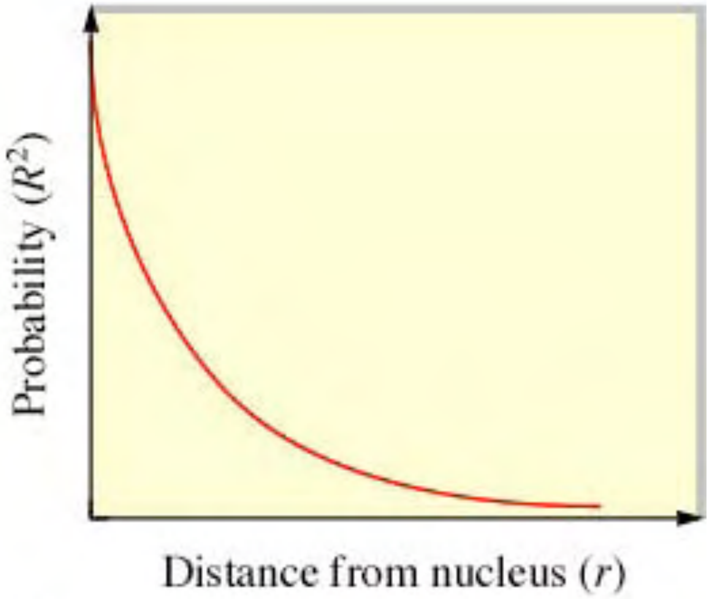


Figure of revolution around z axis

p 271 272 Eisberg

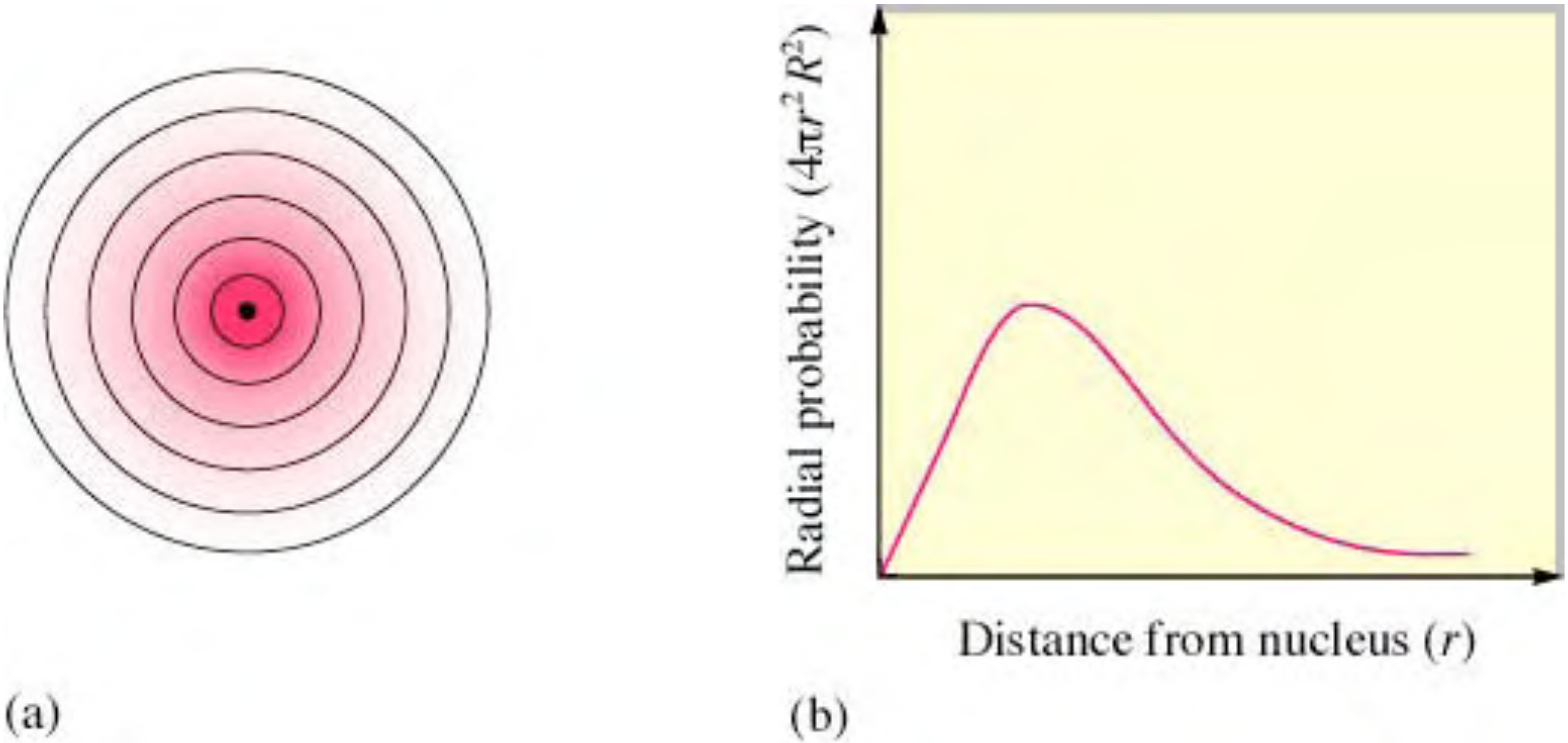
Probability Distribution for the 1s Wave Function

(a)

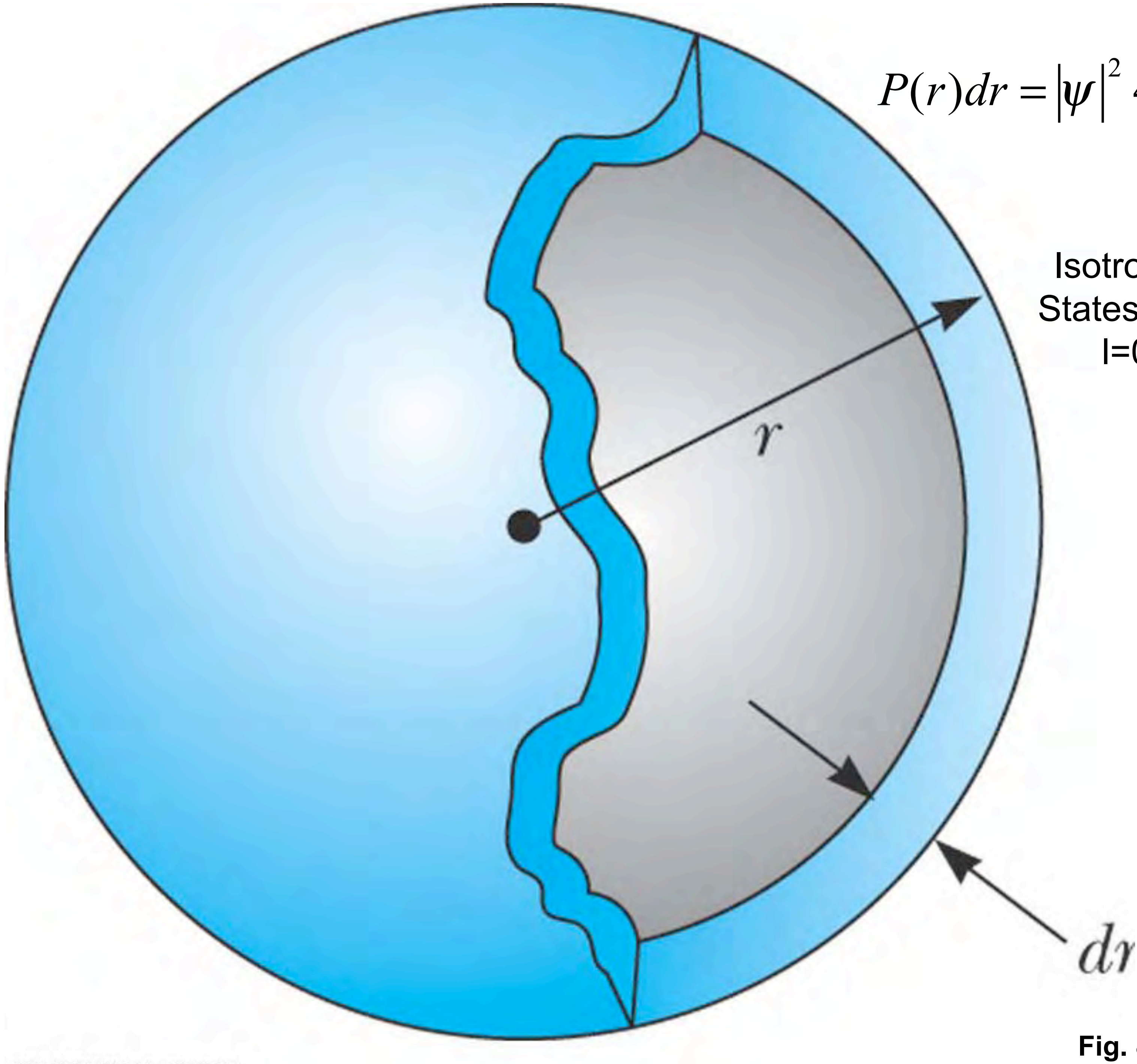


(b)

Radial Probability Distribution

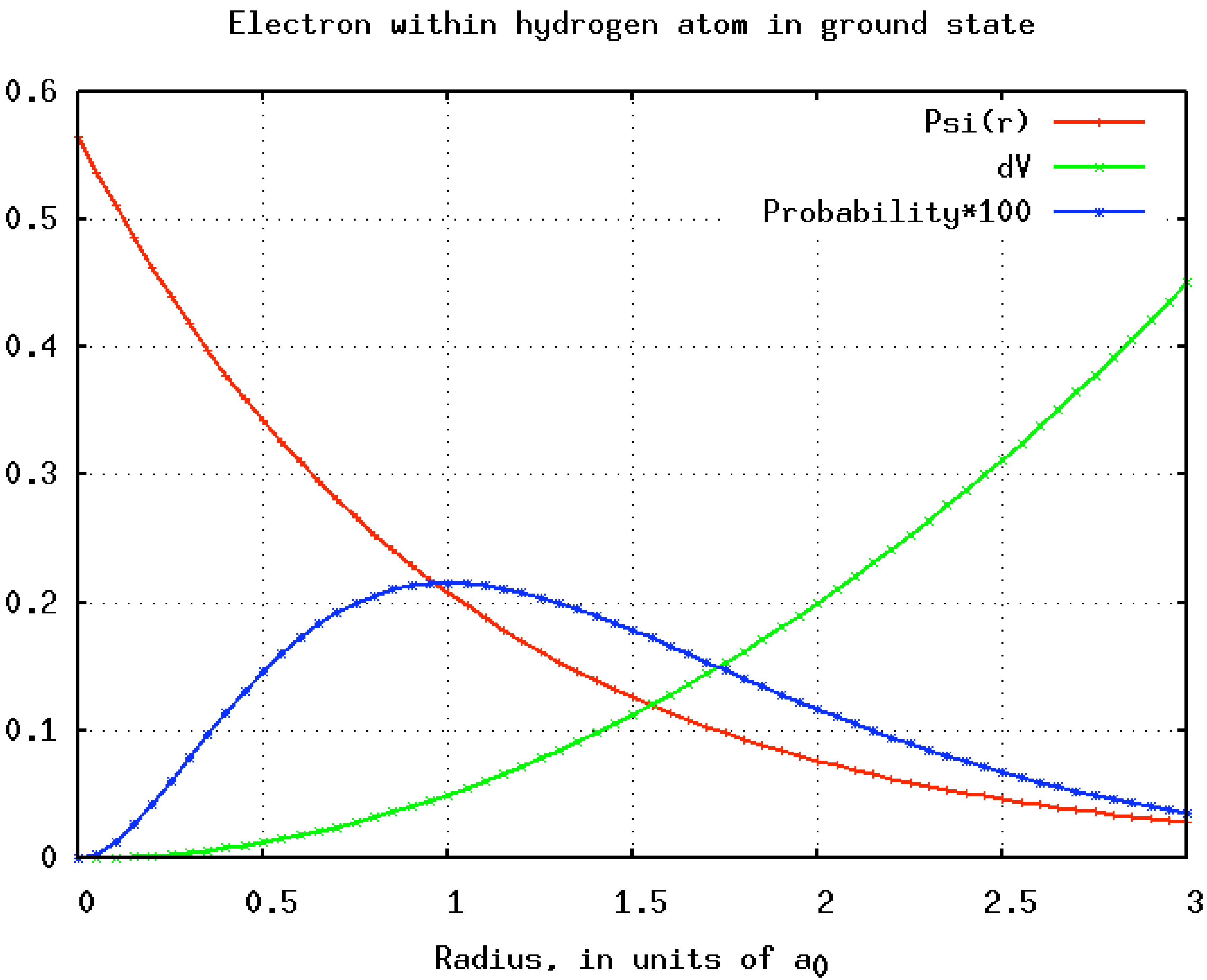


$$P(r)dr = |\psi|^2 4\pi r^2 dr$$



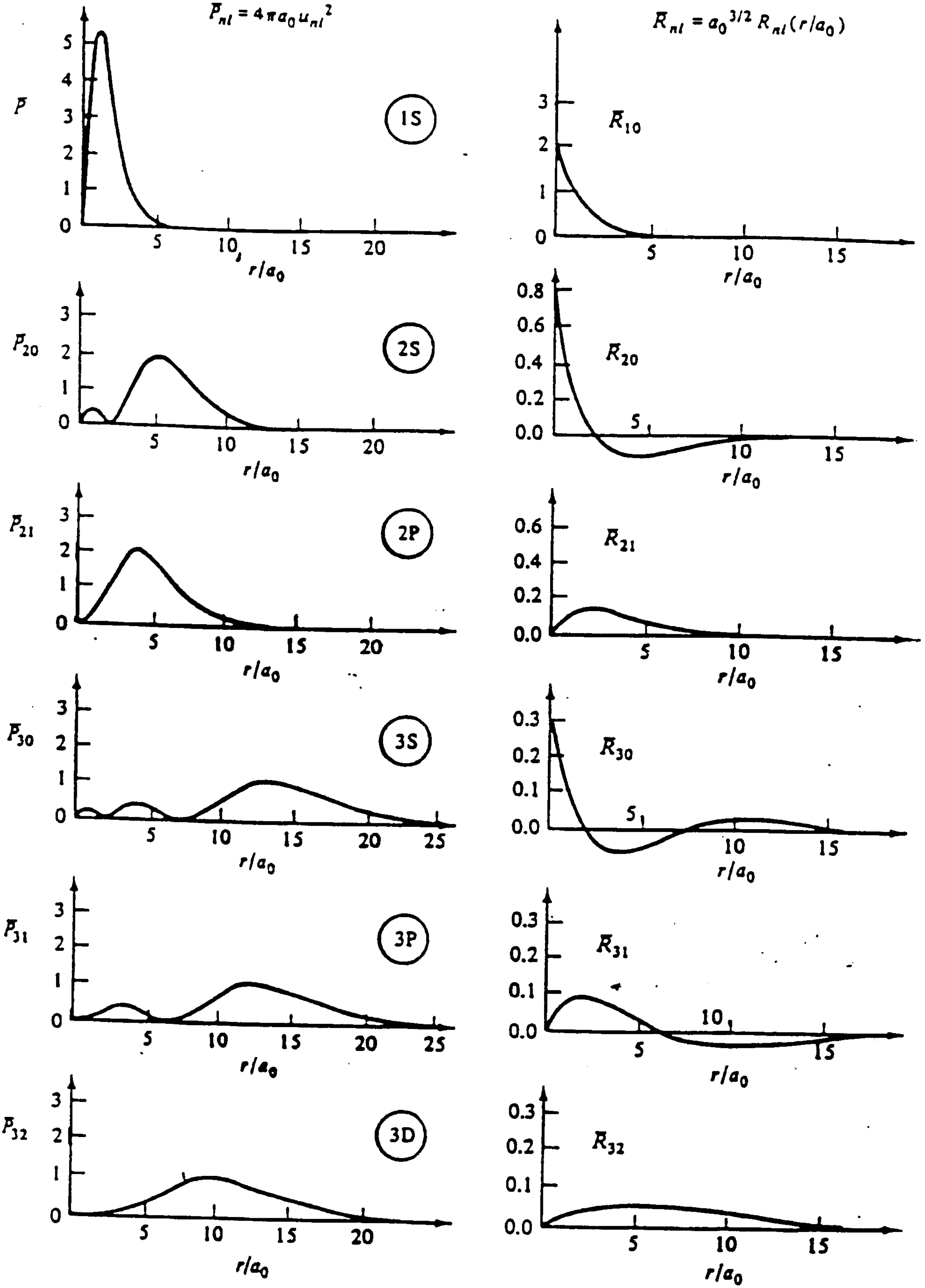
Isotropic
States only
l=0

Fig. 8-9, p.282

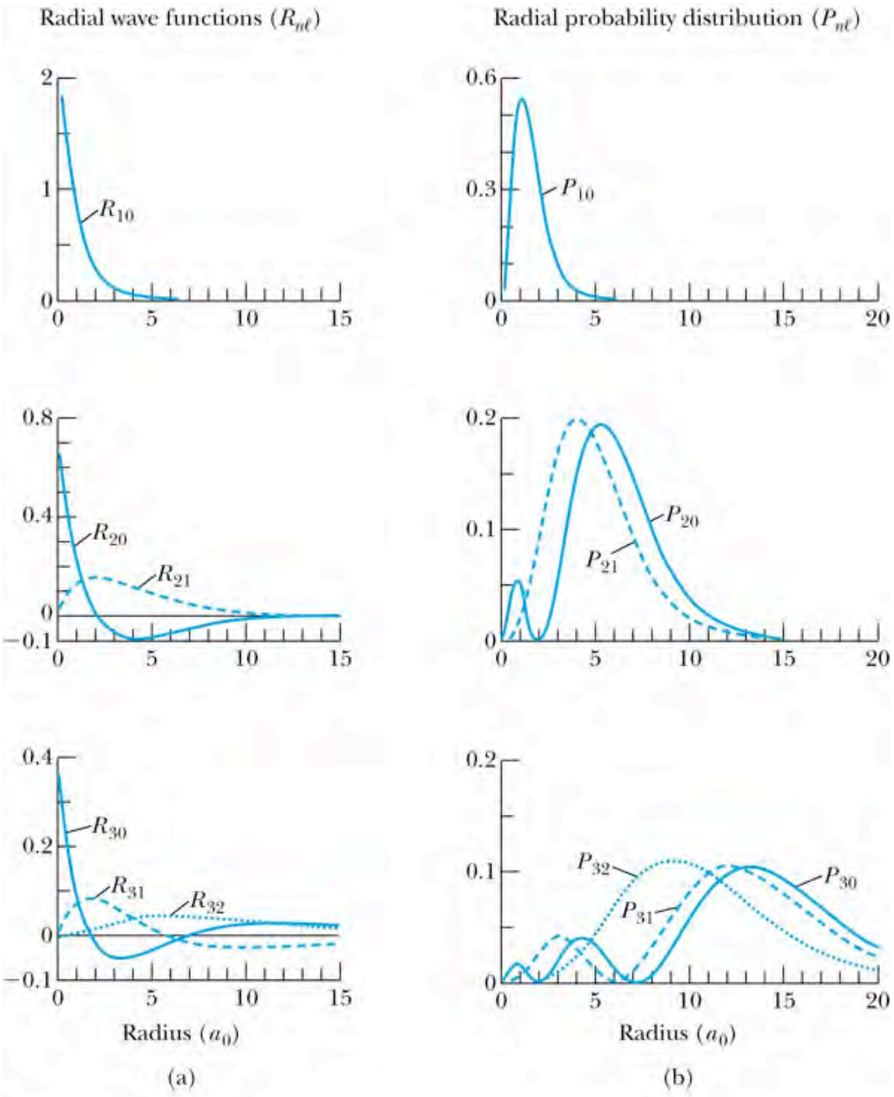

Electron within hydrogen atom in ground state
Psi(r)
dV
Probability*100
0
0.1
0.2
0.3
0.4
0.5
0.6
0
0.5
1
1.5
2
2.5
3
Radius, in units of a_0

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.

$\bar{P}_{nl} = 4\pi a_0 u_{nl}^2$
$\bar{R}_{nl} = a_0^{3/2} R_{nl}(r/a_0)$
$\bar{P}$
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
0
1
2
3
4
5
0.0
0.1
0.2
0.3
0.4
0.6
0.8
5
10
15
20
25

Probability Distribution Functions



(a)

(b)

- $R(r)$ and $P(r)$ for the lowest-lying states of the hydrogen atom.

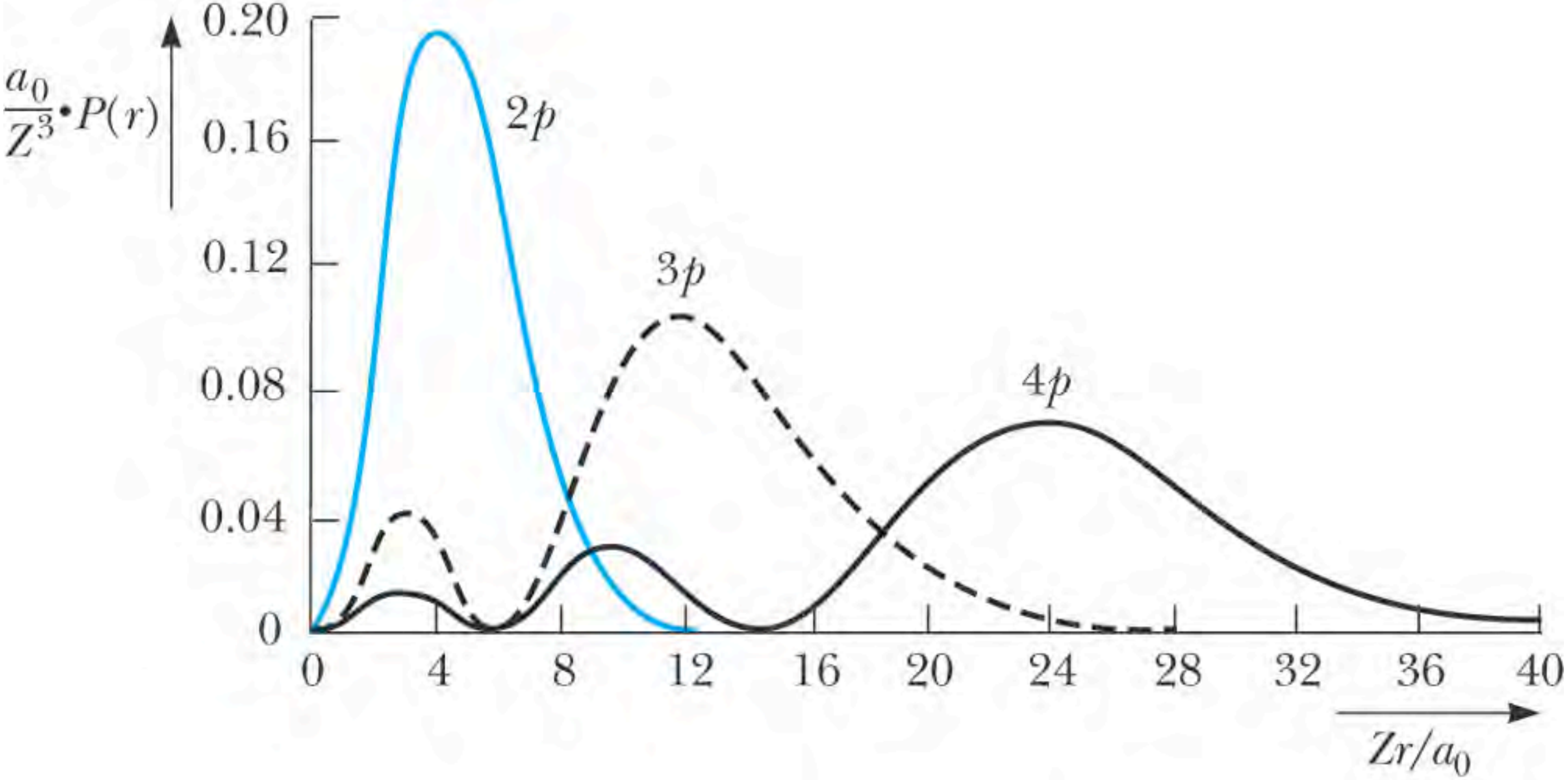
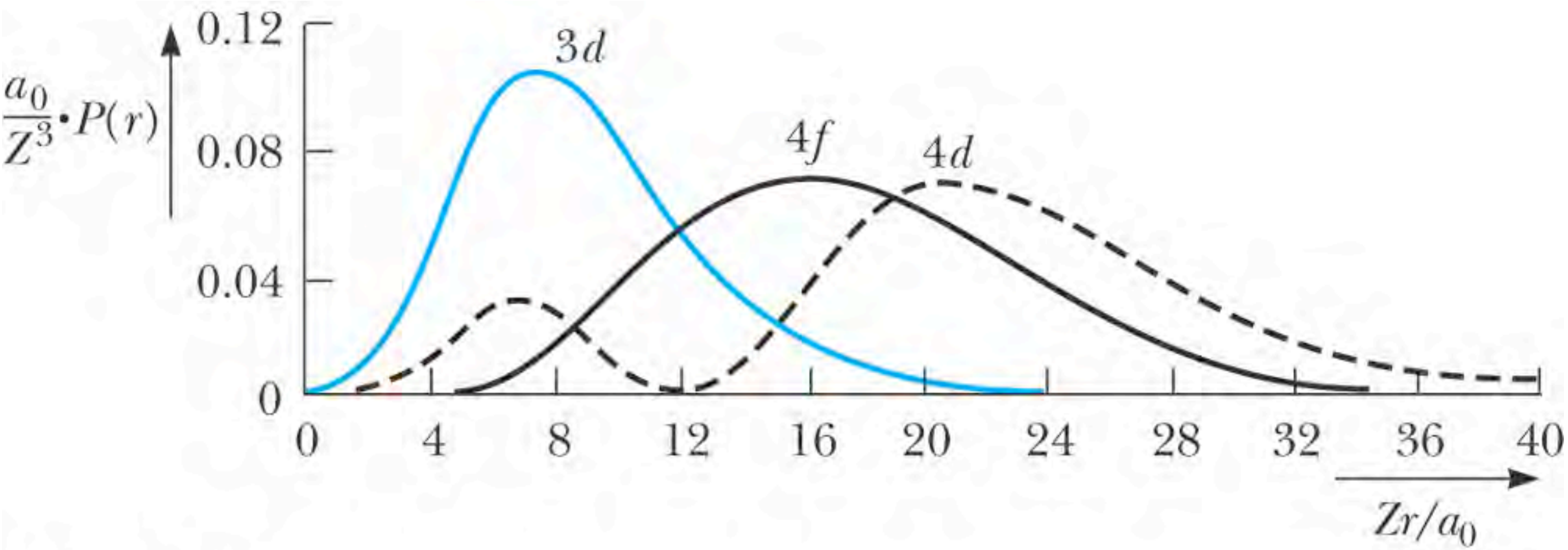
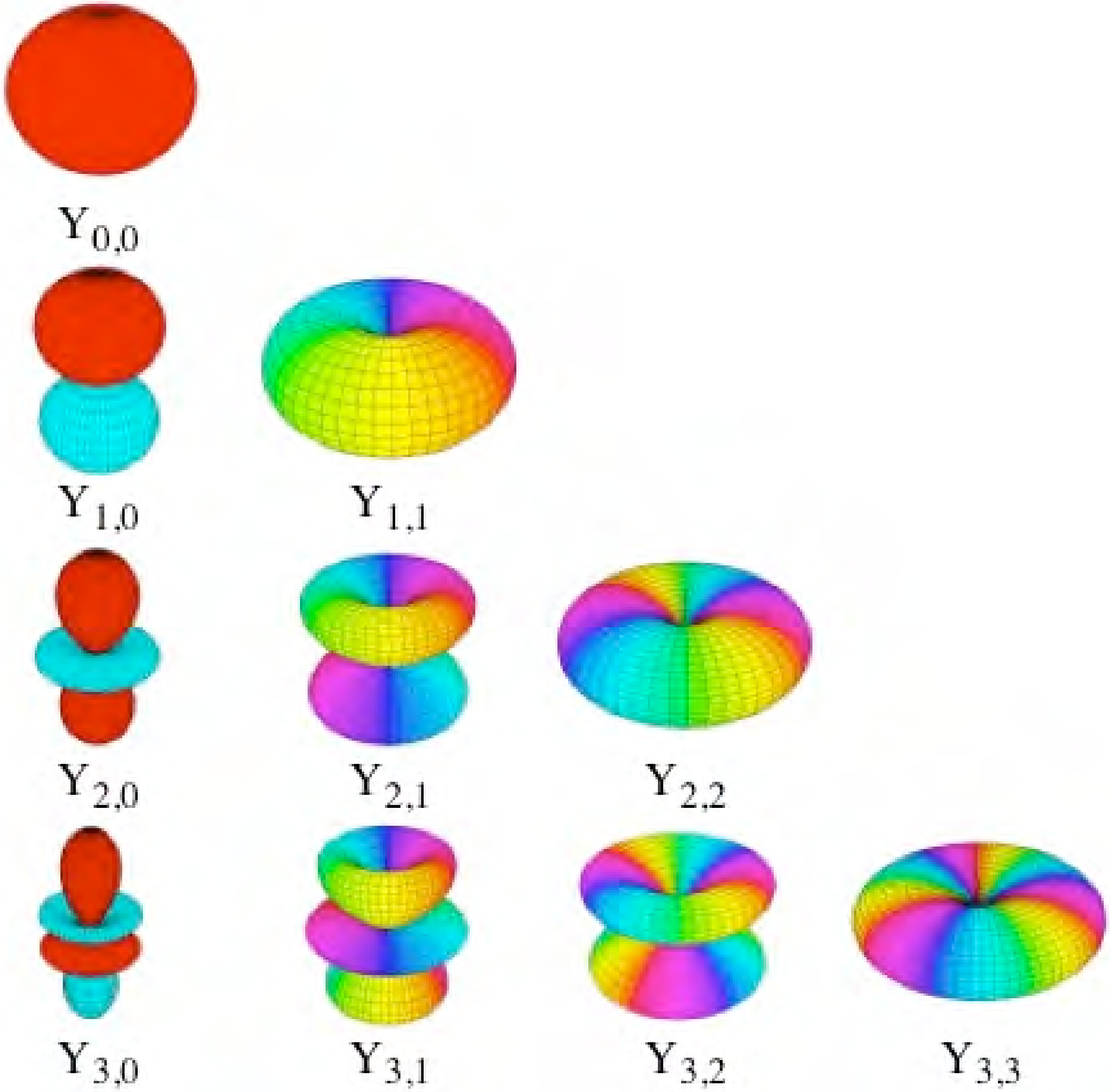


Fig. 8-11b, p.285



l=2

Fig. 8-11c, p.285


$Y_{0,0}$
$Y_{1,0}$
$Y_{1,1}$
$Y_{2,0}$
$Y_{2,1}$
$Y_{2,2}$
$Y_{3,0}$
$Y_{3,1}$
$Y_{3,2}$
$Y_{3,3}$

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

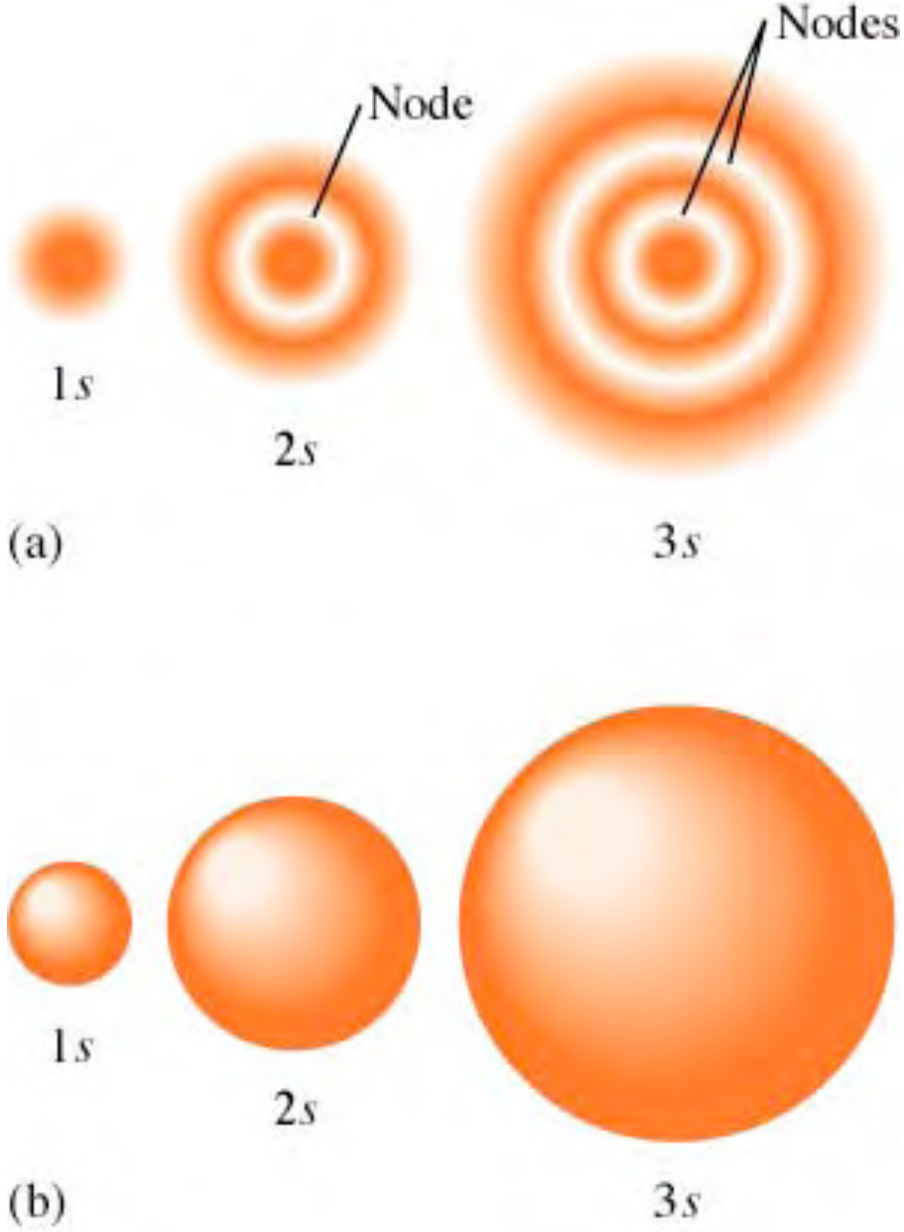
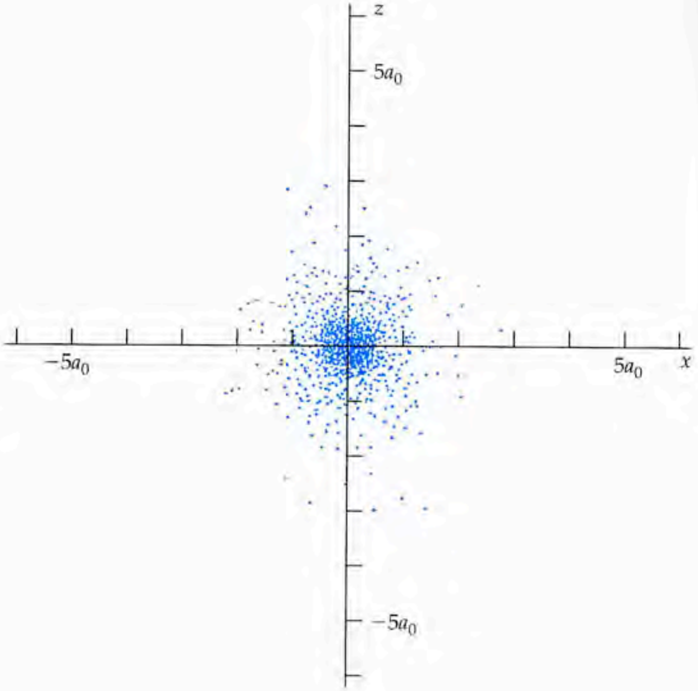
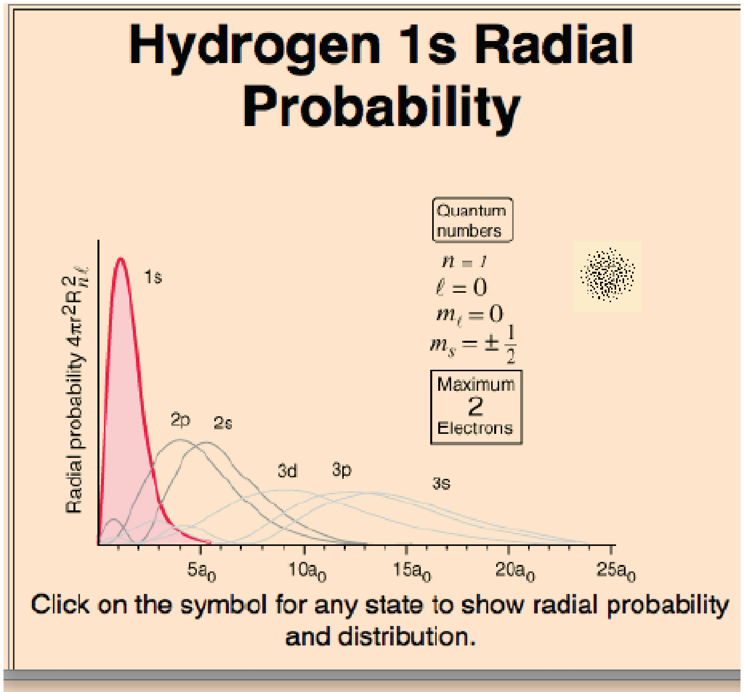


Figure 37-5 Computer-generated dot picture of the probability density ψ^2 for the ground state of hydrogen. The quantity $e\psi^2$ can be thought of as the electron charge density in the atom. The density is spherically symmetric, is greatest at the origin, and decreases exponentially with r.





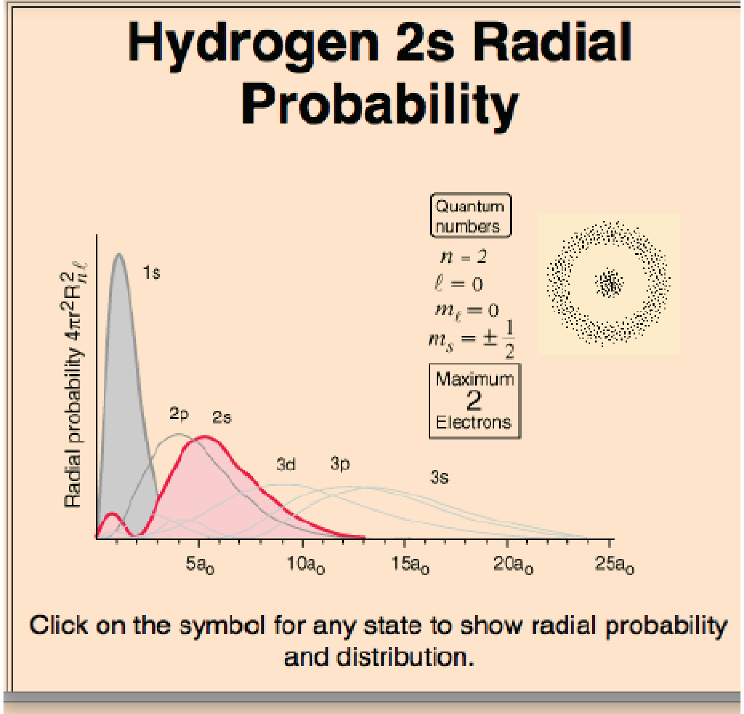
Hydrogen 1s Radial Probability

$n = 1$
$\ell = 0$
$m_\ell = 0$
$m_s = \pm\frac{1}{2}$

Maximum 2 Electrons

Click on the symbol for any state to show radial probability and distribution.

$Y_{0,0}$



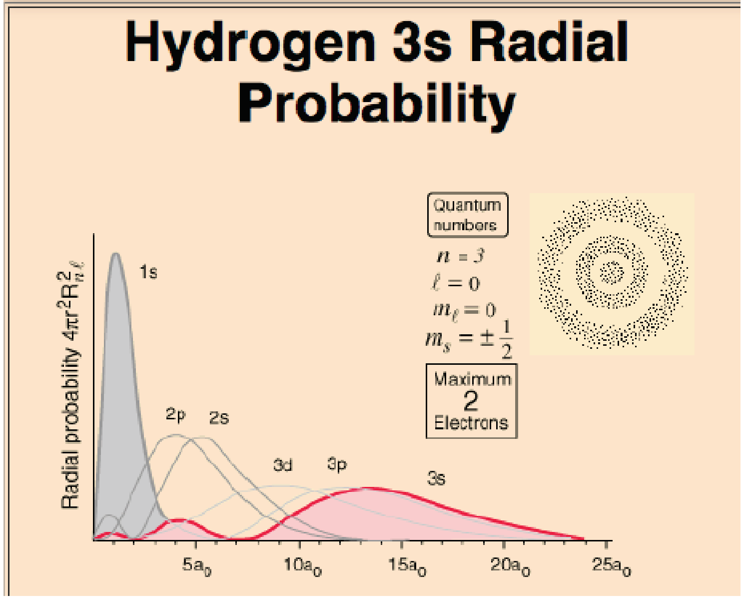
Hydrogen 2s Radial Probability

$n = 2$
$\ell = 0$
$m_\ell = 0$
$m_s = \pm\frac{1}{2}$

Maximum 2 Electrons

Click on the symbol for any state to show radial probability and distribution.

$Y_{0,0}$

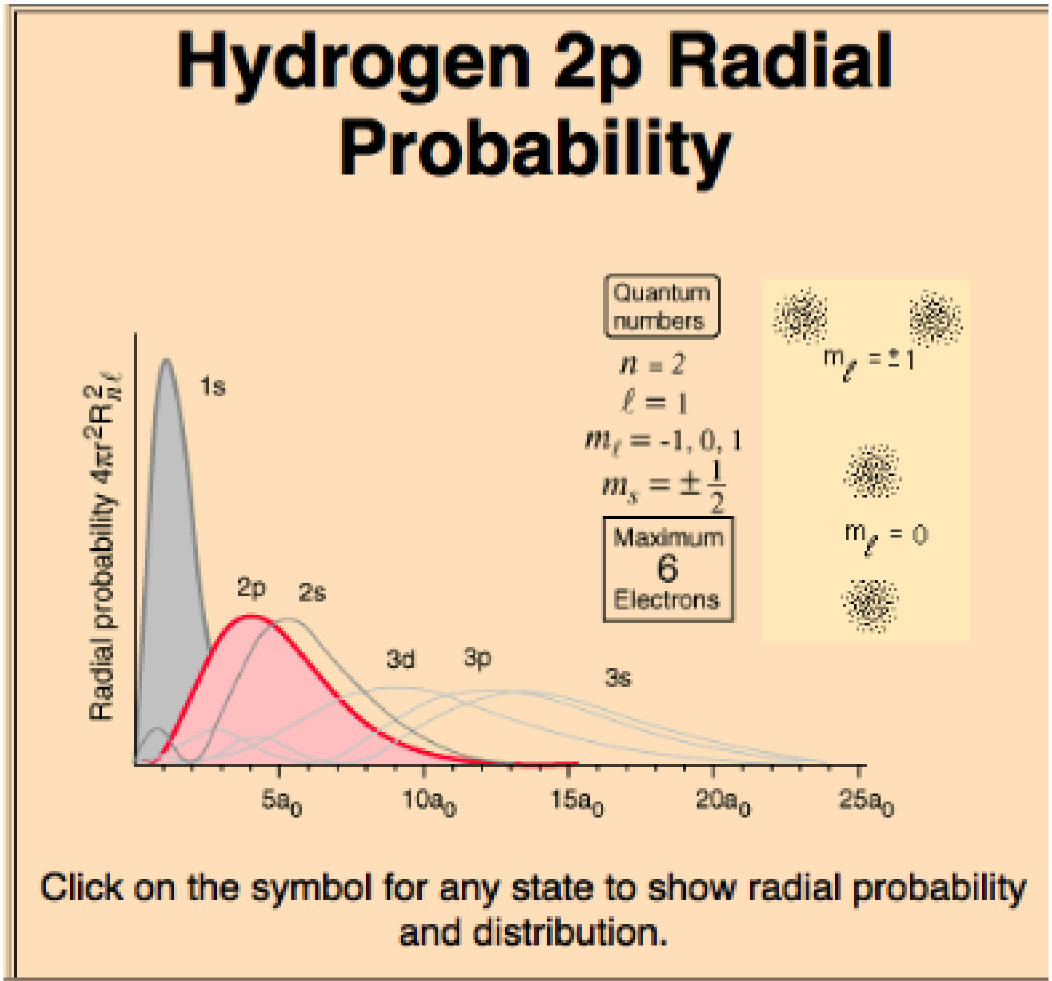


Hydrogen 3s Radial Probability

$n = 3$
$\ell = 0$
$m_\ell = 0$
$m_s = \pm\frac{1}{2}$

Maximum 2 Electrons

$Y_{0,0}$



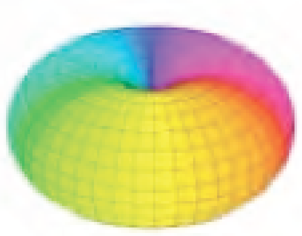
Hydrogen 2p Radial Probability

Quantum numbers

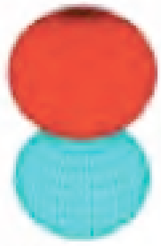
$n = 2$
$\ell = 1$
$m_\ell = -1, 0, 1$
$m_s = \pm\frac{1}{2}$

Maximum 6 Electrons

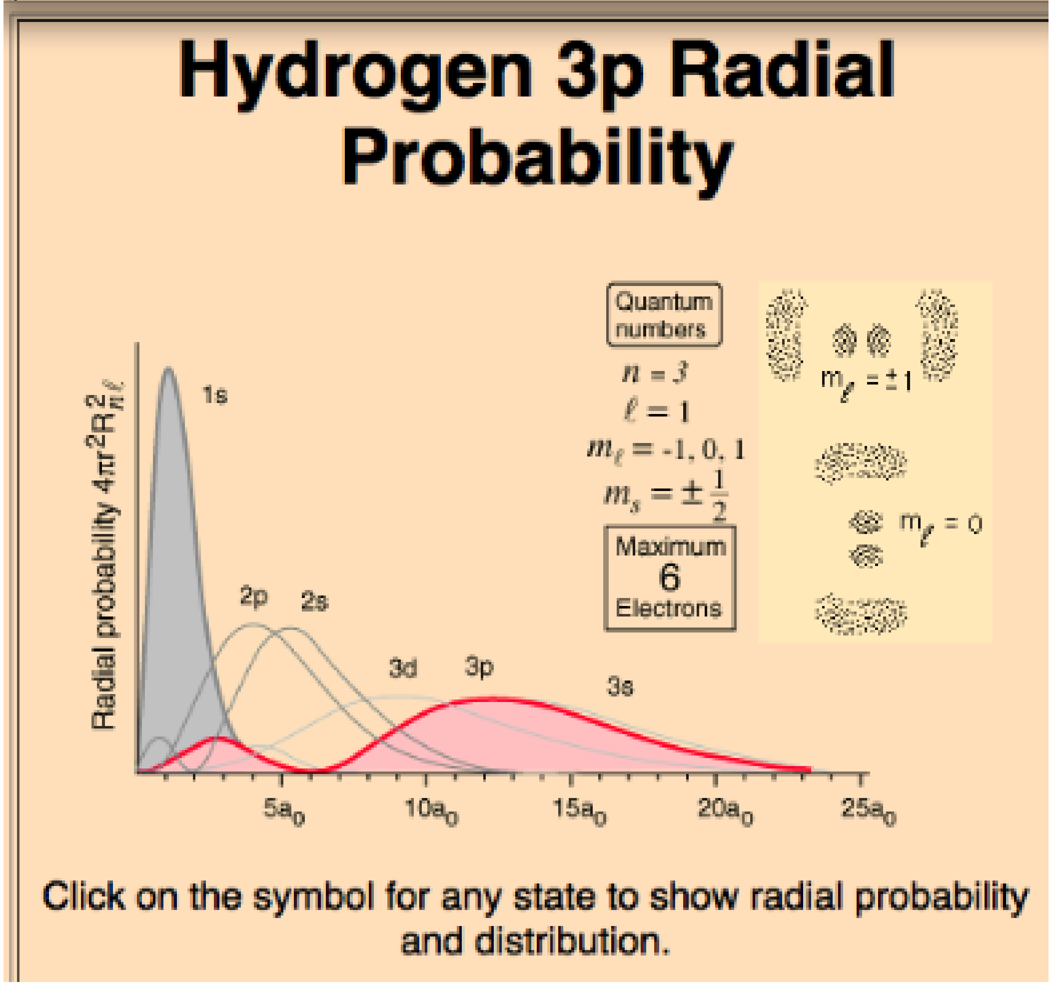
Click on the symbol for any state to show radial probability and distribution.



$Y_{1,1}$



$Y_{1,0}$



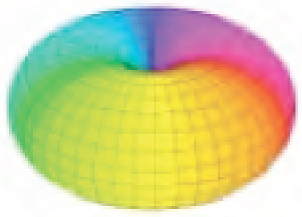
Hydrogen 3p Radial Probability

Quantum numbers

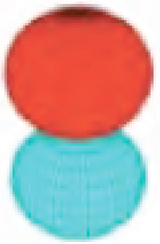
$n = 3$
$\ell = 1$
$m_\ell = -1, 0, 1$
$m_s = \pm\frac{1}{2}$

Maximum 6 Electrons

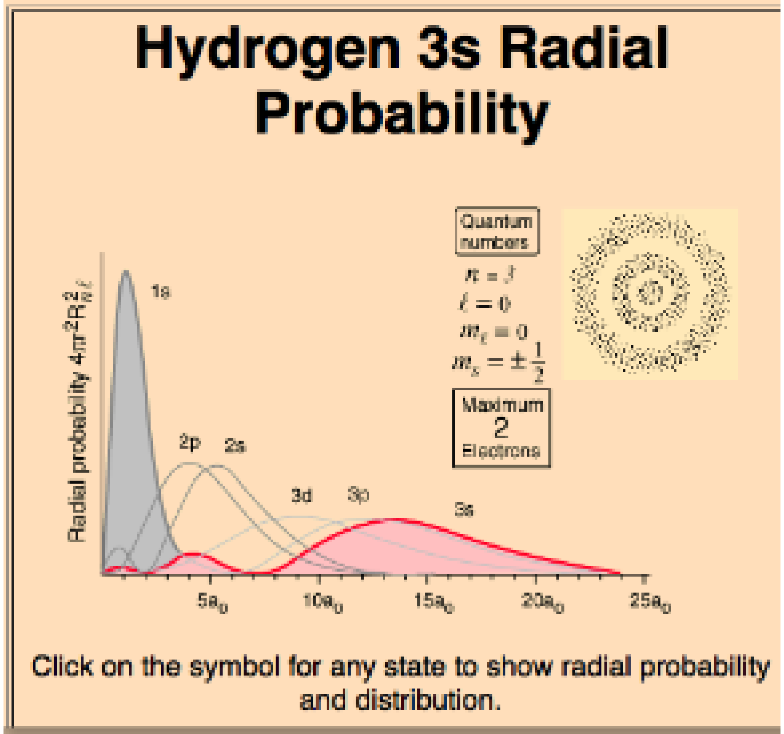
Click on the symbol for any state to show radial probability and distribution.



$Y_{1,1}$



$Y_{1,0}$



Hydrogen 3s Radial Probability

Quantum numbers

$n = 3$

$\ell = 0$

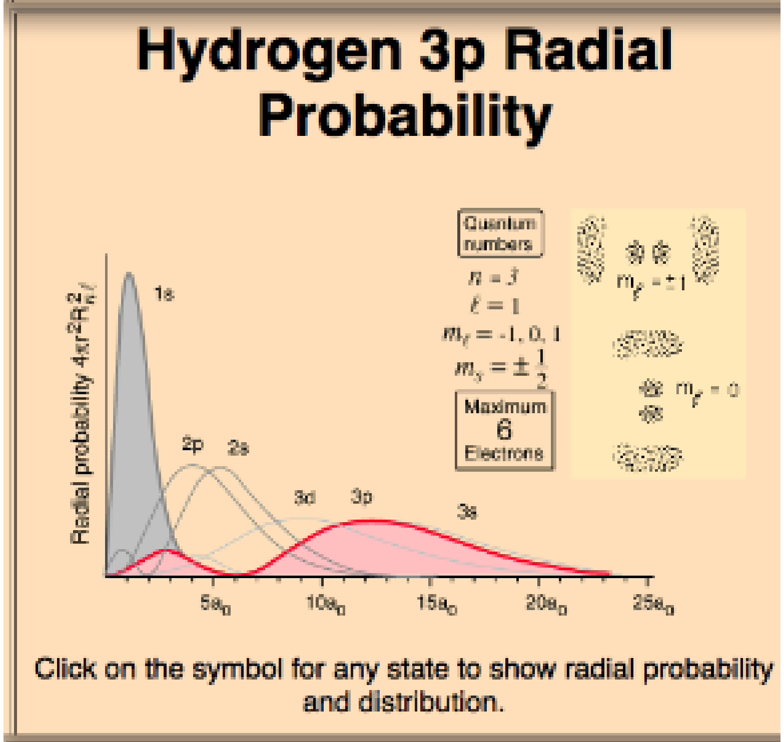
$m_\ell = 0$

$m_s = \pm\frac{1}{2}$

Maximum 2 Electrons

Click on the symbol for any state to show radial probability and distribution.

$Y_{0,0}$



Hydrogen 3p Radial Probability

Quantum numbers

$n = 3$

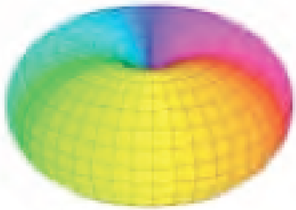
$\ell = 1$

$m_\ell = -1, 0, 1$

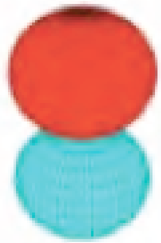
$m_s = \pm\frac{1}{2}$

Maximum 6 Electrons

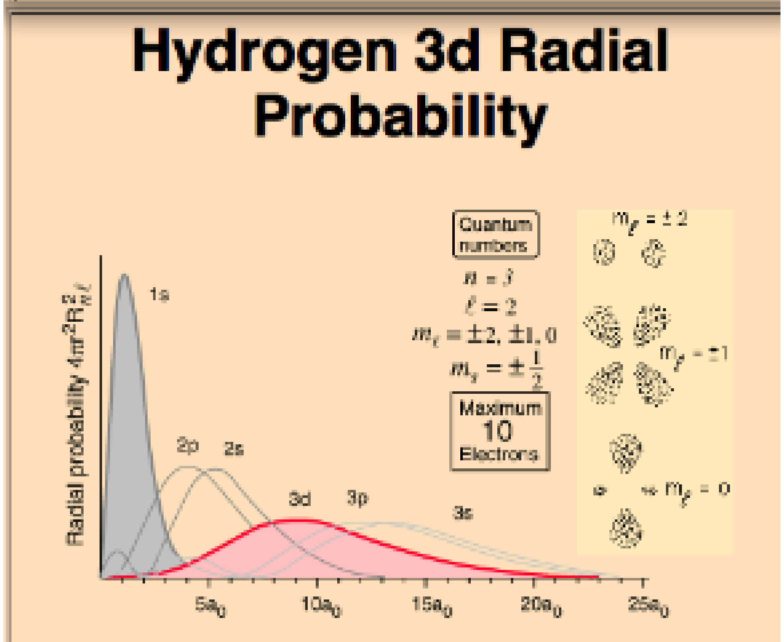
Click on the symbol for any state to show radial probability and distribution.



$Y_{1,1}$



$Y_{1,0}$



Hydrogen 3d Radial Probability

Quantum numbers

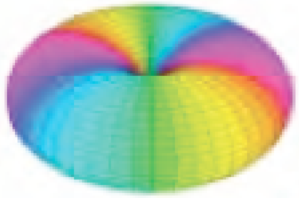
$n = 3$

$\ell = 2$

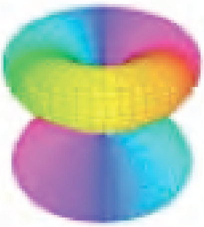
$m_\ell = \pm 2, \pm 1, 0$

$m_s = \pm\frac{1}{2}$

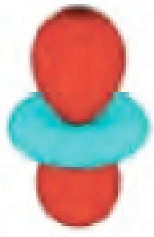
Maximum 10 Electrons



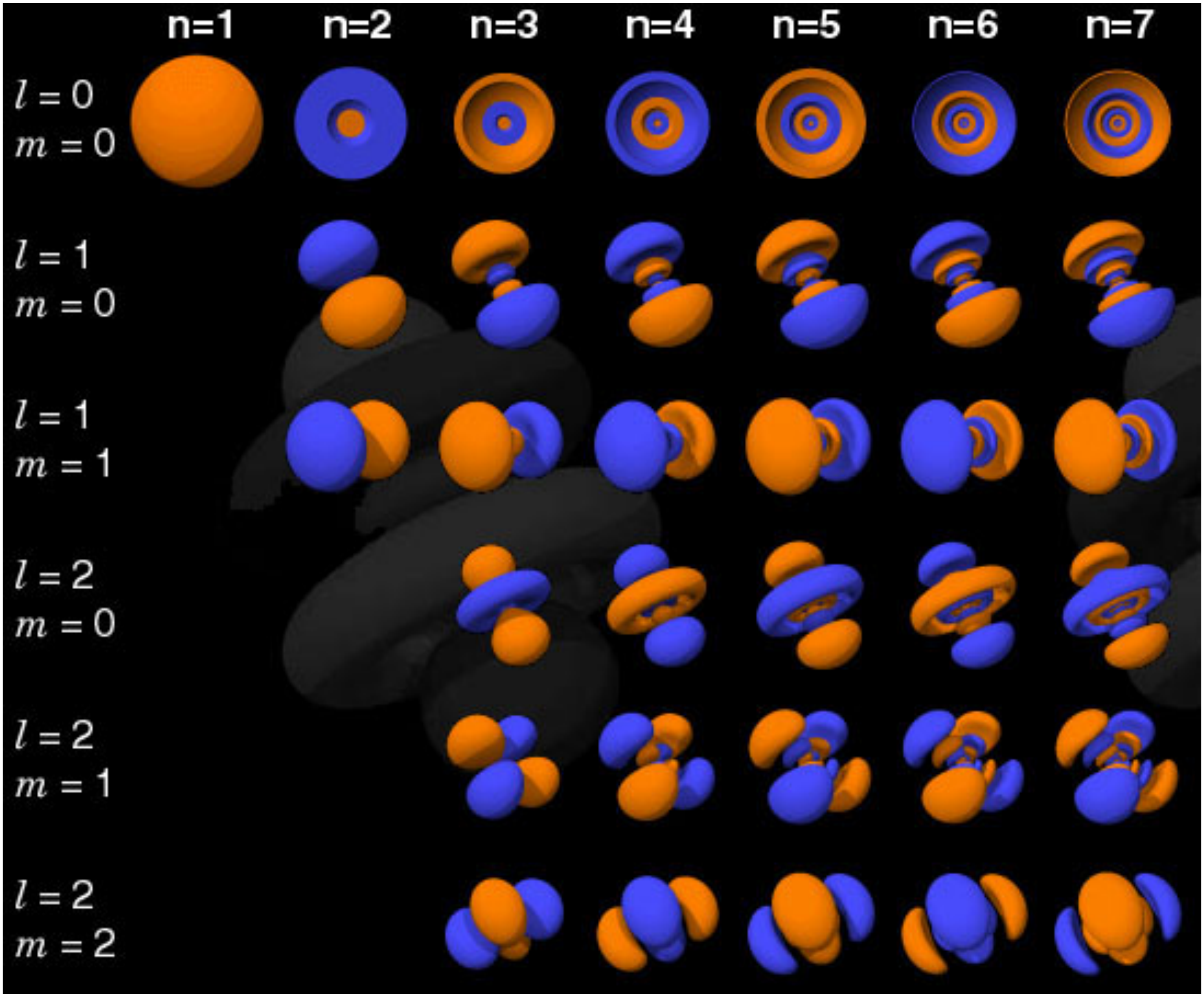
$Y_{2,2}$

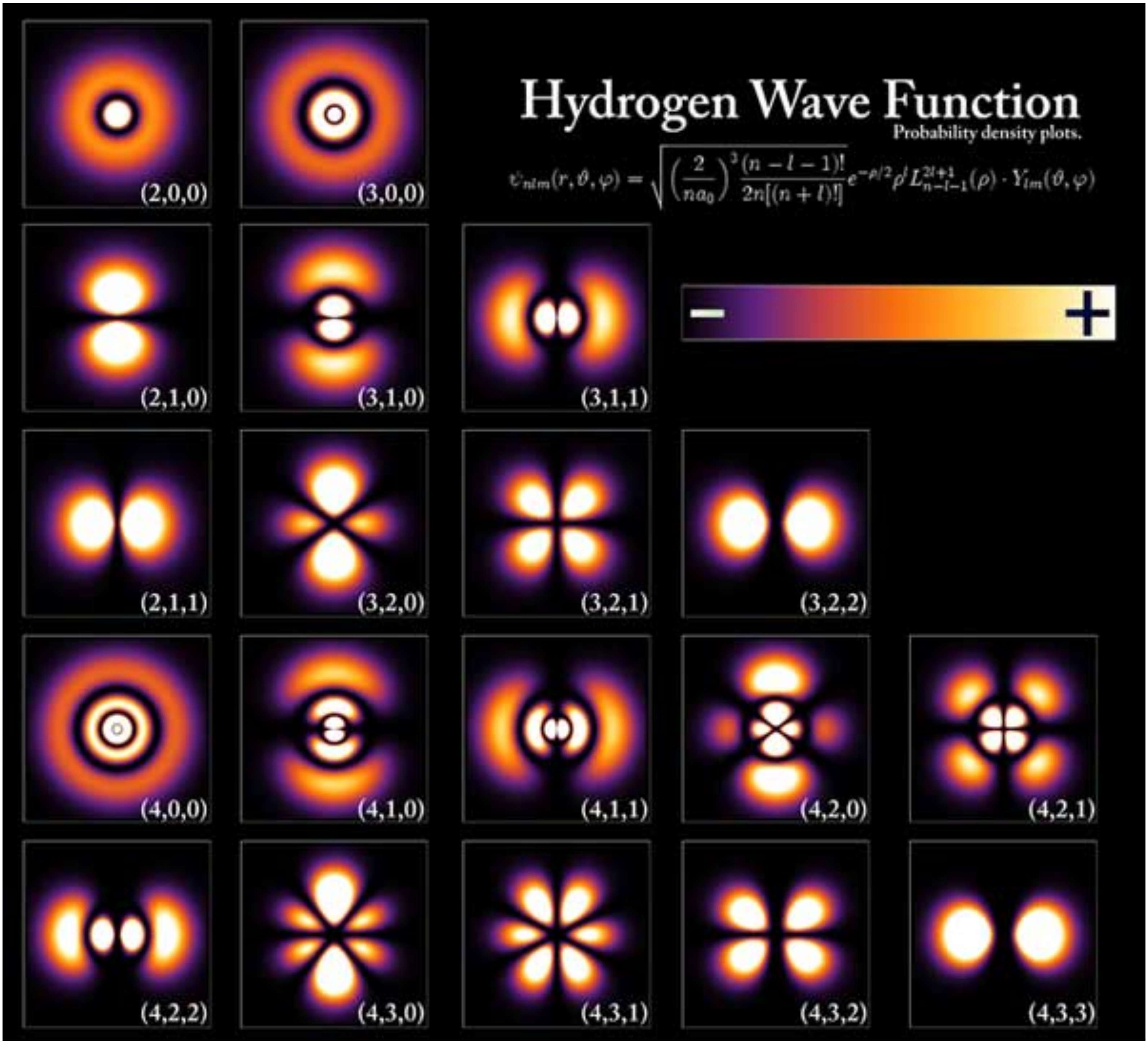


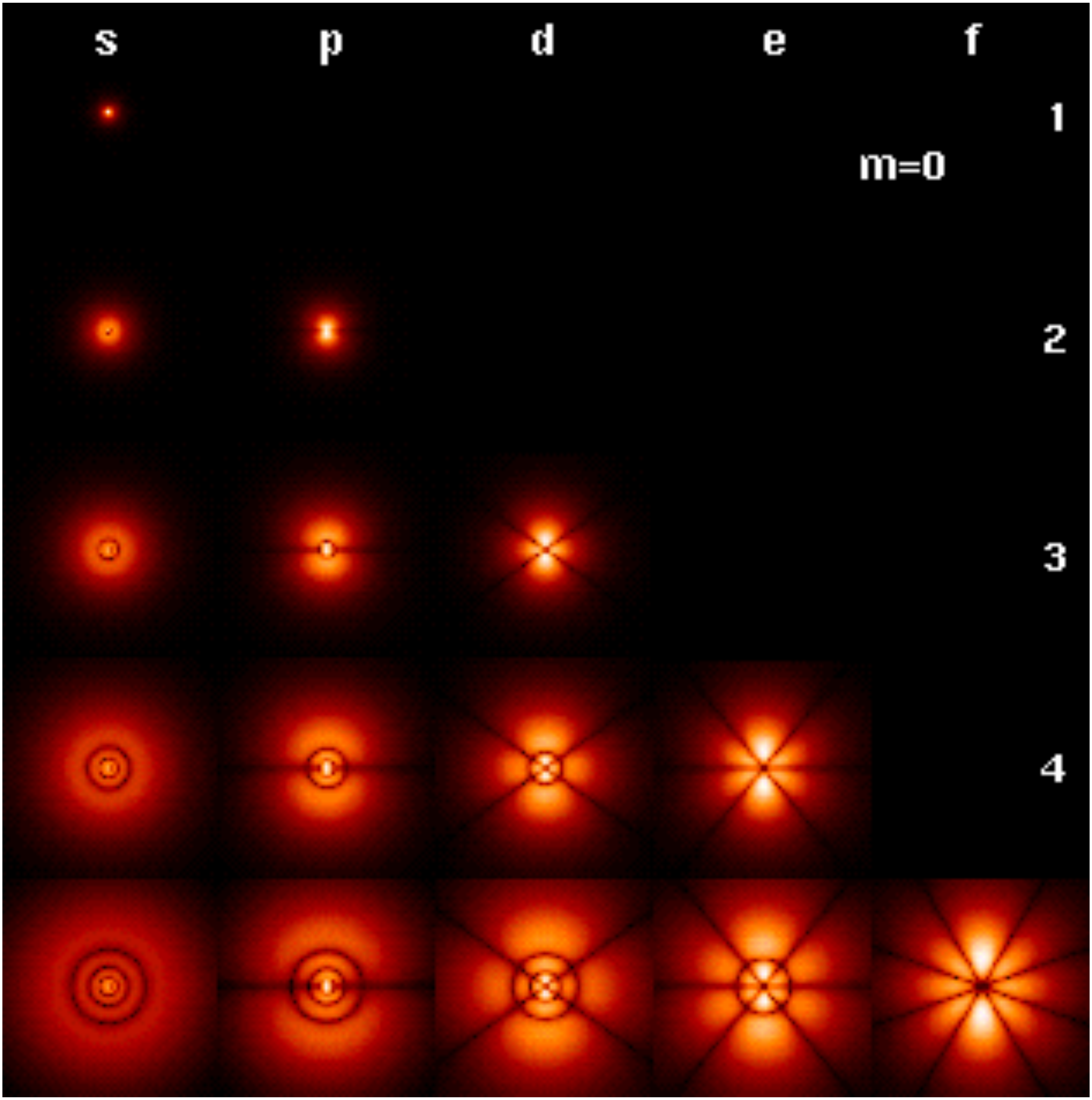
$Y_{2,1}$



$Y_{2,0}$

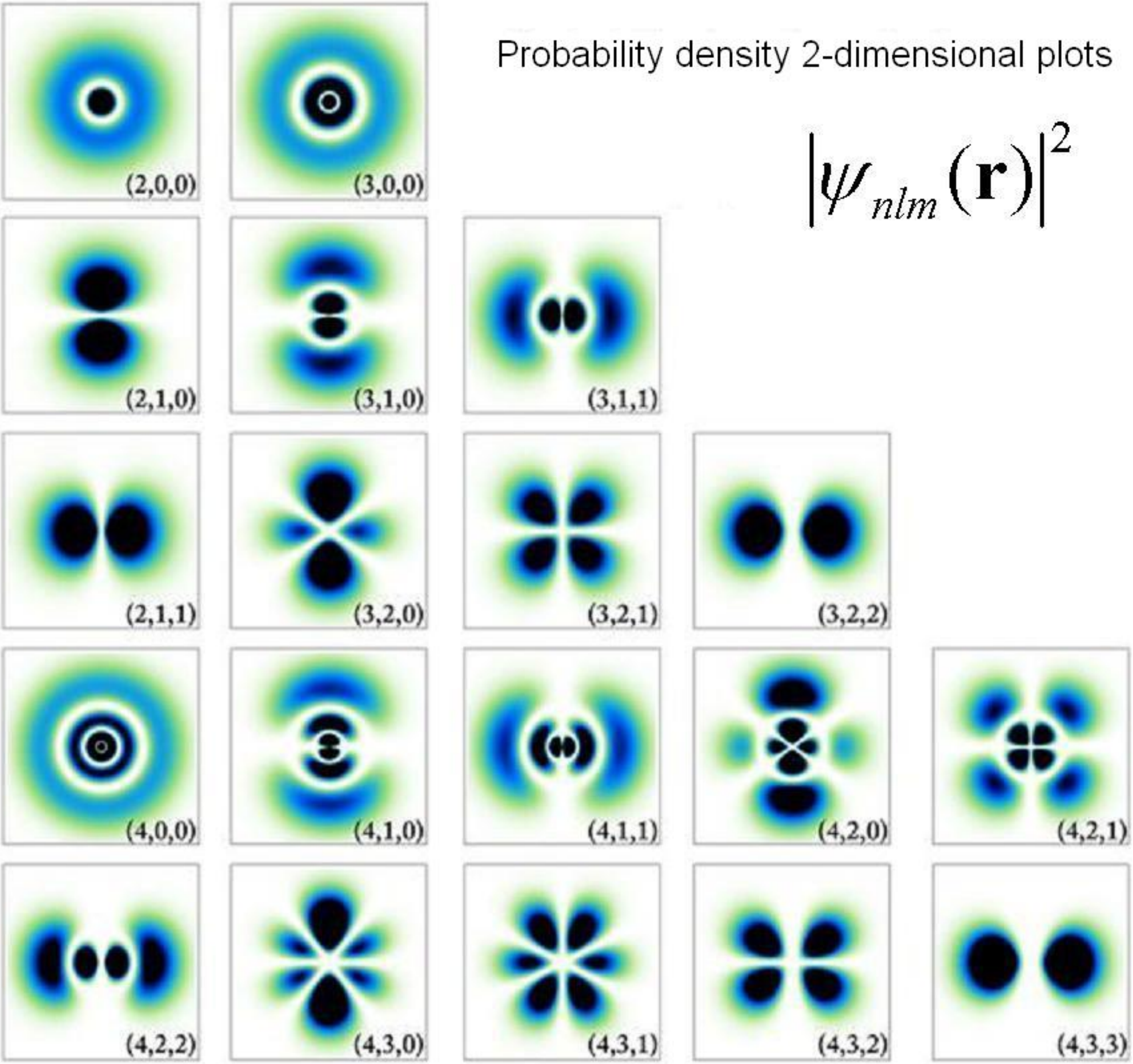

n=1
n=2
n=3
n=4
n=5
n=6
n=7
$l = 0$
$m = 0$
$l = 1$
$m = 0$
$l = 1$
$m = 1$
$l = 2$
$m = 0$
$l = 2$
$m = 1$
$l = 2$
$m = 2$

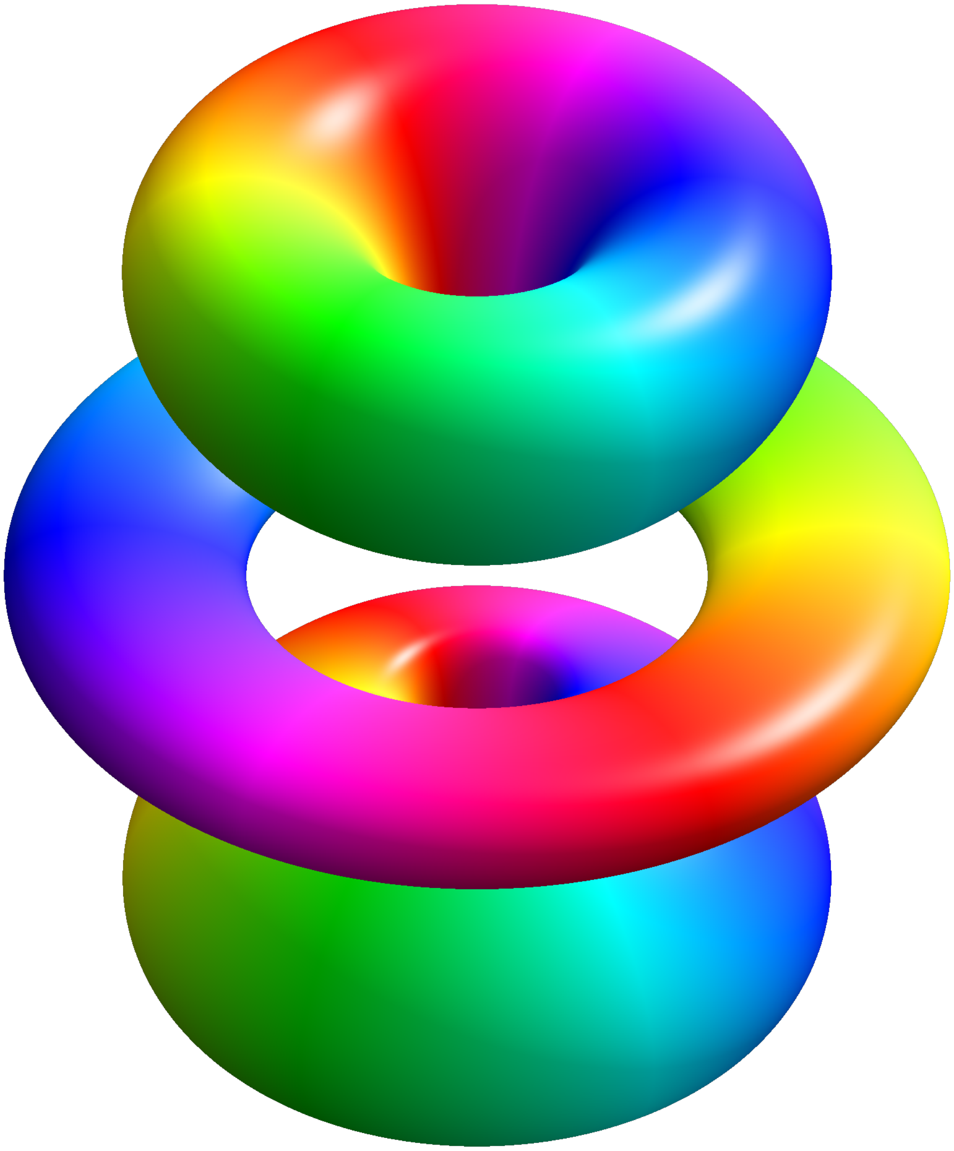

Hydrogen Wave Function
Probability density plots.
$\psi_{nlm}(r,\vartheta,\varphi) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]}} e^{-\rho/2} \rho^l L_{n-l-1}^{2l+1}(\rho) \cdot Y_{lm}(\vartheta,\varphi)$
−
+
(2,0,0)
(3,0,0)
(2,1,0)
(3,1,0)
(3,1,1)
(2,1,1)
(3,2,0)
(3,2,1)
(3,2,2)
(4,0,0)
(4,1,0)
(4,1,1)
(4,2,0)
(4,2,1)
(4,2,2)
(4,3,0)
(4,3,1)
(4,3,2)
(4,3,3)

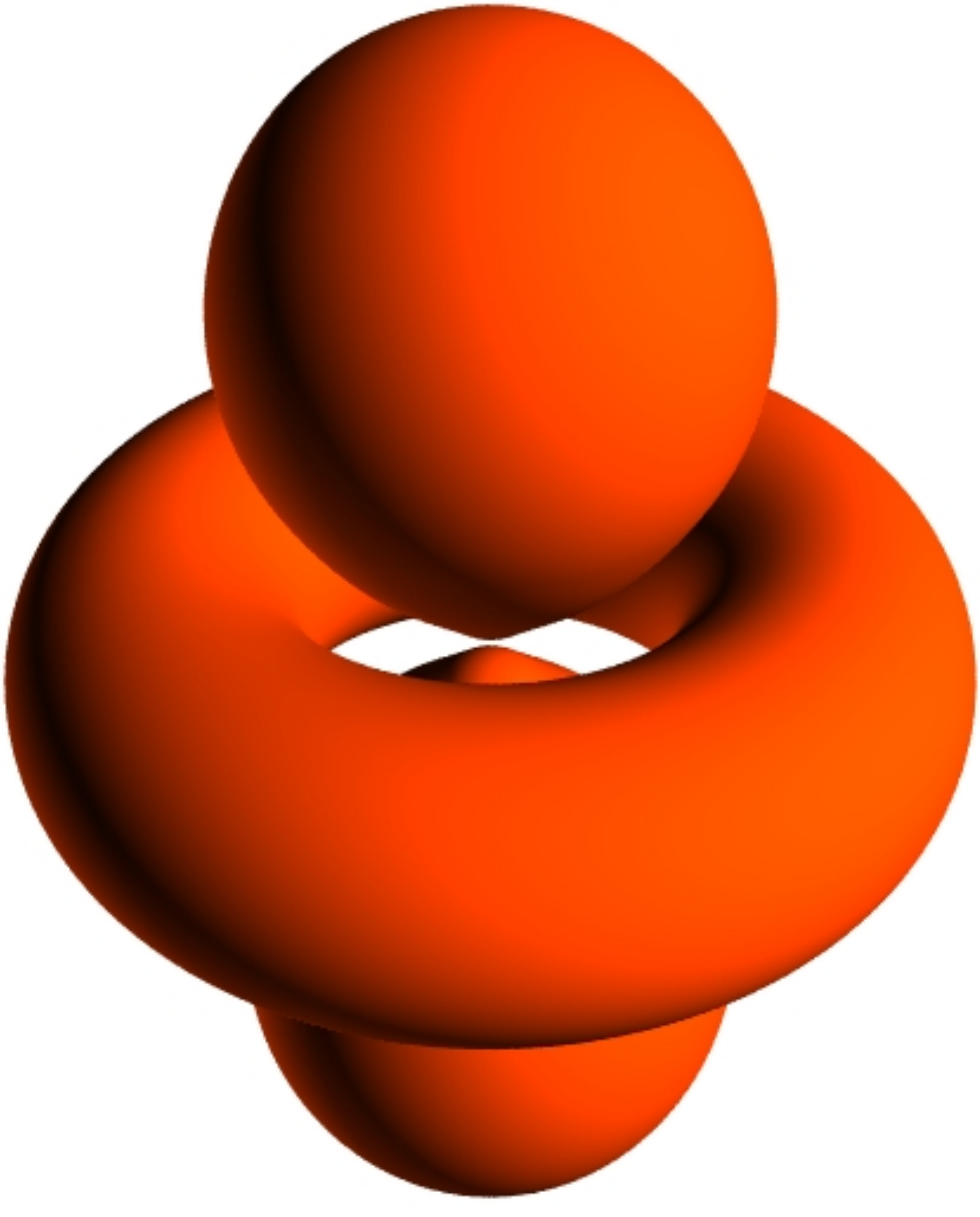

s
p
d
e
f
1
m=0
2
3
4

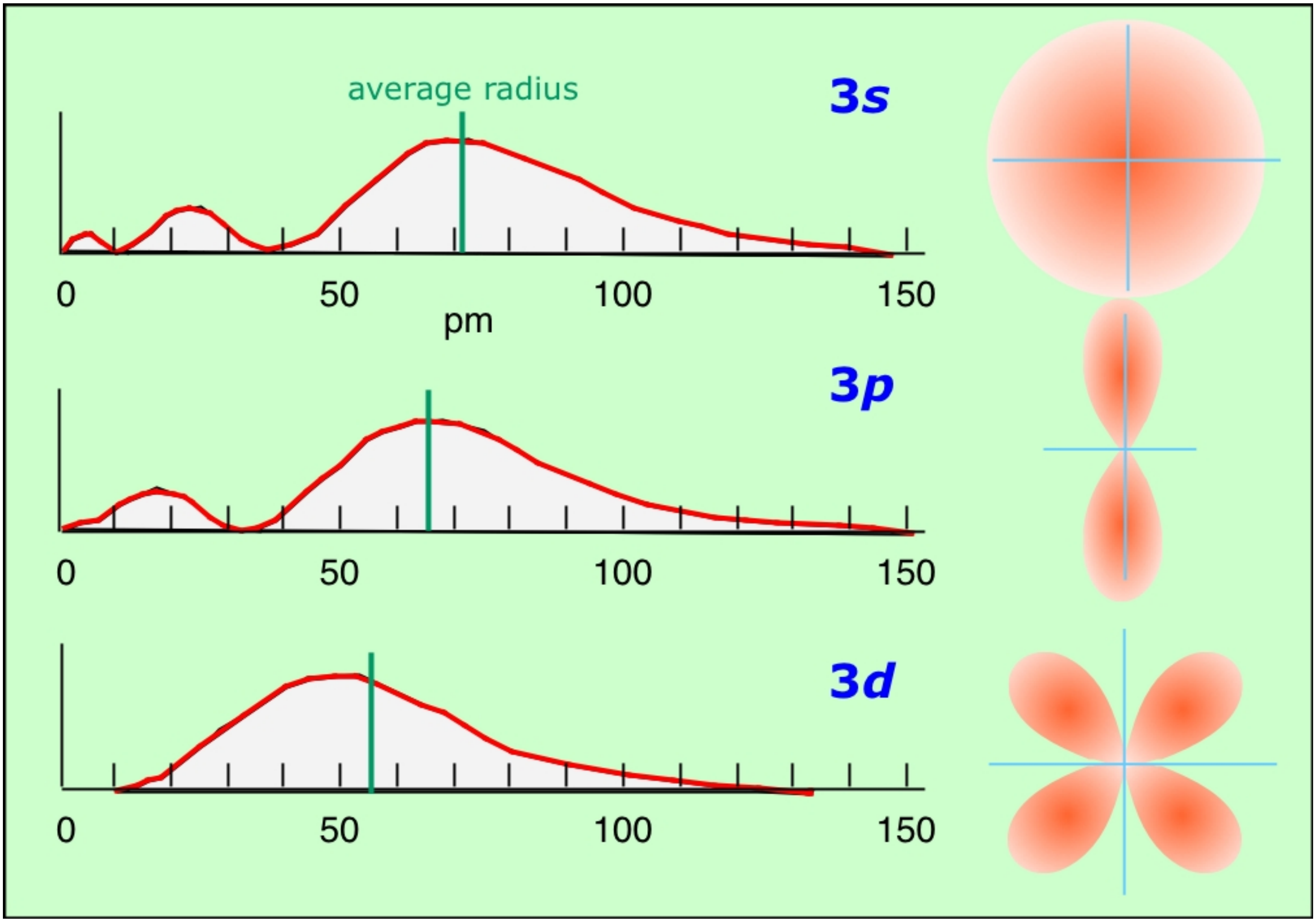
Probability density 2-dimensional plots

$$\left|\psi_{nlm}(\mathbf{r})\right|^2$$









average radius
3s
0
50
100
150
pm
3p
0
50
100
150
3d
0
50
100
150

The Functional Form
http://panda.unm.edu/Courses/Finley/P262/Hydrogen/WaveFcns.html

The Radial Components
http://hyperphysics.phy-astr.gsu.edu/Hbase/hydwf.html#c1

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

Radial times Angular
http://www.falstad.com/qmatom/
http://webphysics.davidson.edu/faculty/dmb/hydrogen/intro_hyd.html

The Story Continues
http://www.pha.jhu.edu/~rt19/hydro/

http://webphysics.davidson.edu/faculty/dmb/hydrogen/

http://hyperphysics.phy-astr.gsu.edu/Hbase/quantum/hydcn.html#c1

http://cronodon.com/Atomic/AtomTech4.html

http://www.evilmadscientist.com/article.php/atomiccookies

http://mareserinitatis.livejournal.com/tag/food

Spherical Harmonics

The Meaning of the Spherical Harmonics

http://infovis.uni-konstanz.de/research/projects/SimSearch3D/images/harmonics_img.jpg

The Spherical Harmonics

http://oak.ucc.nau.edu/jws8/dpgraph/Yellm.html
http://www.bpreid.com/applets/poasDemo.html
http://www.du.edu/~jcalvert/math/harmonic/harmonic.htm

Encyclopedia

http://en.wikipedia.org/wiki/Spherical_harmonics
http://en.wikipedia.org/wiki/Table_of_spherical_harmonics
http://mathworld.wolfram.com/SphericalHarmonic.html

Applications of Spherical Harmonics

http://www.falstad.com/qmrotator/
http://www.falstad.com/qmatom/
http://www.falstad.com/qmatomrad/
http://www.falstad.com/qm2dosc/
http://www.falstad.com/qm3dosc/

Legendre Polynomials

The Meaning of the Legendre Polynomials

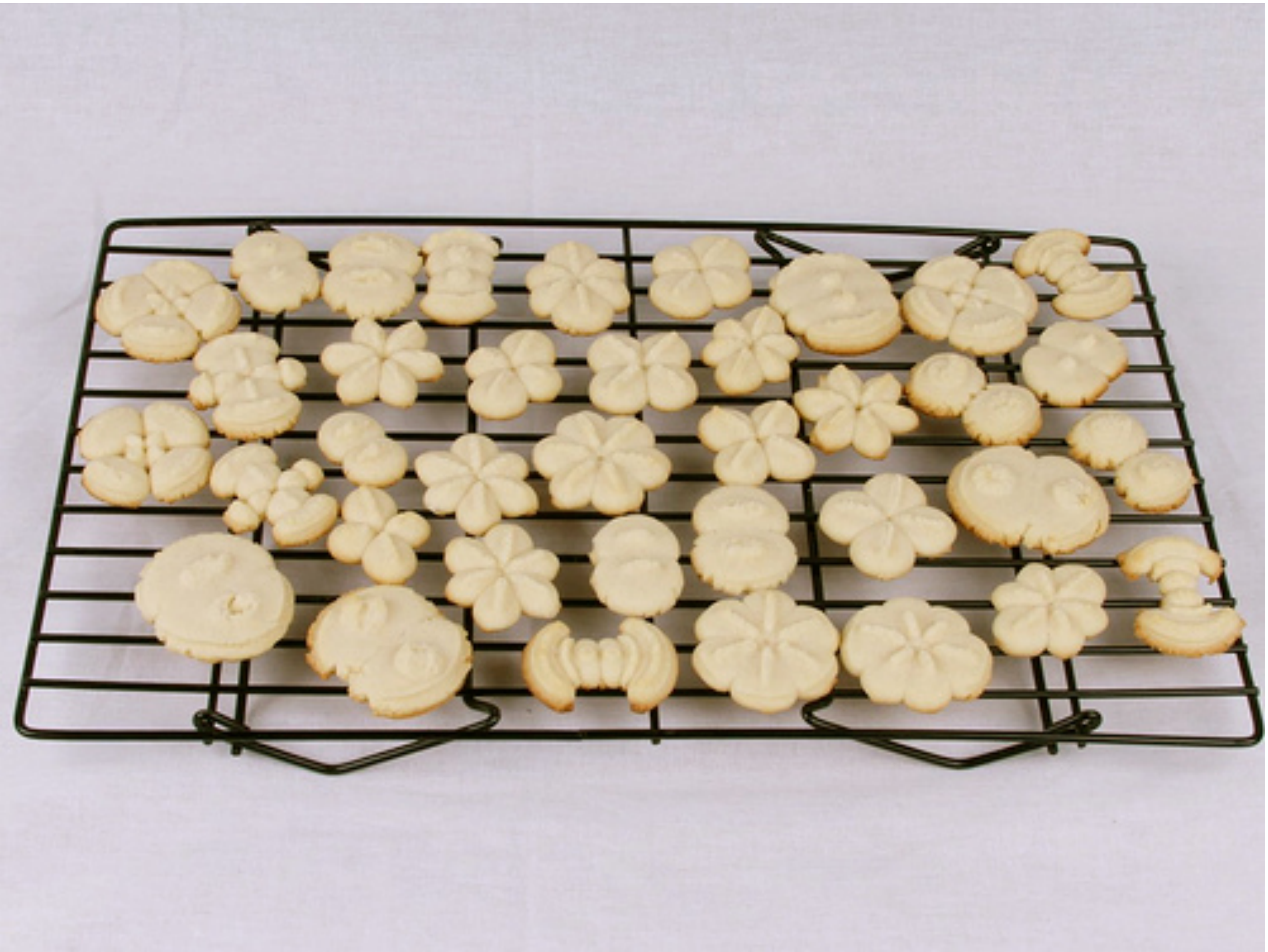
http://physics.unl.edu/~tgay/content/multipoles.html

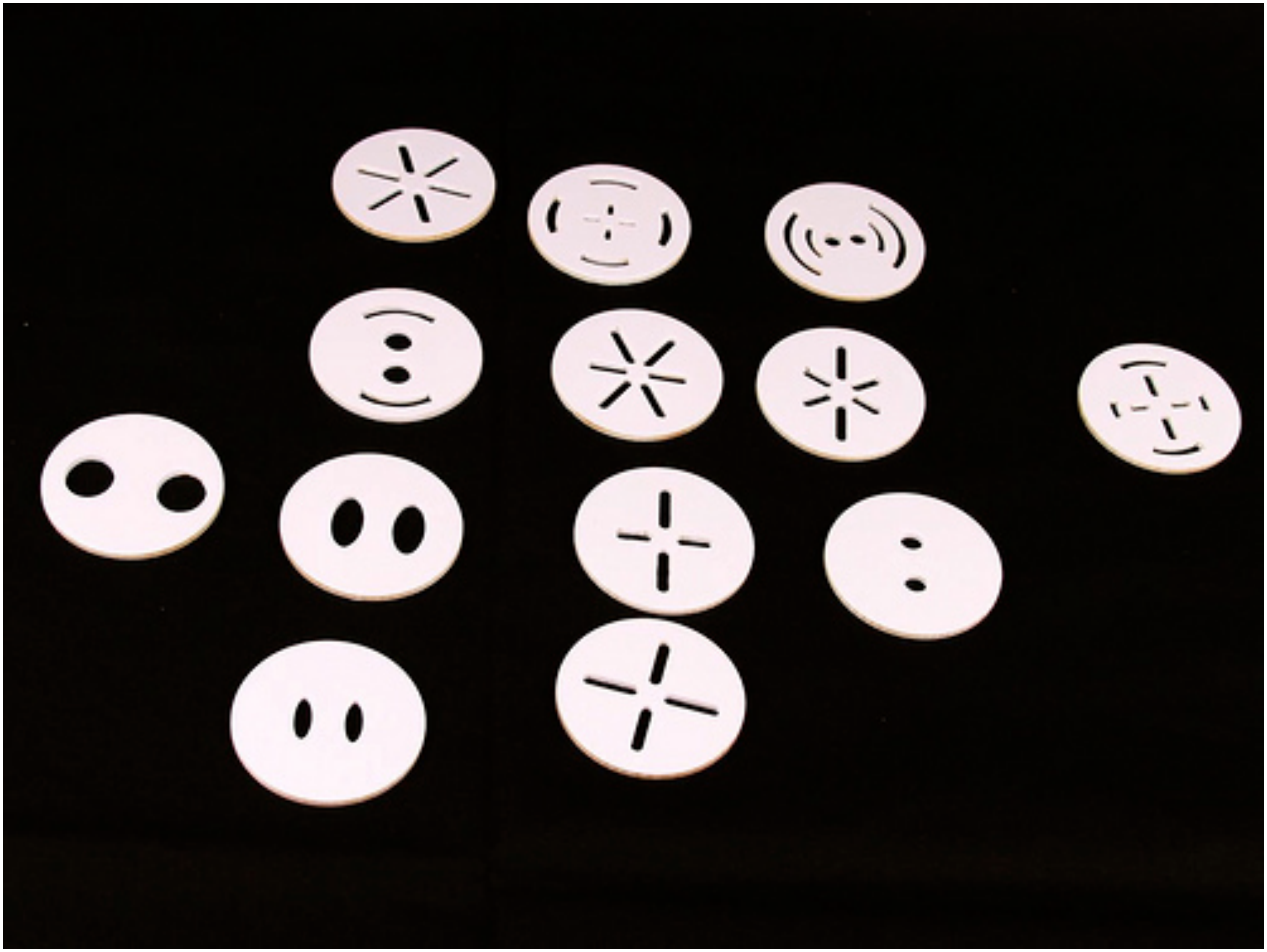
Encyclopedia

http://en.wikipedia.org/wiki/Legendre_polynomials
http://mathworld.wolfram.com/LegendrePolynomial.html

Wolfram Demonstrations

http://demonstrations.wolfram.com/SphericalHarmonics/
http://demonstrations.wolfram.com/VisualizingAtomicOrbitals/
http://demonstrations.wolfram.com/HydrogenOrbitals/
http://demonstrations.wolfram.com/PlotsOfLegendrePolynomials/
http://demonstrations.wolfram.com/PolarPlotsOfLegendrePolynomials/
http://demonstrations.wolfram.com/DipoleAntennaRadiationPattern/





Associated Laguerre Polynomials

Some wag once said the nice thing about standards is that there are so many to choose from. I have been trying to come to grips with the difference between what I presented in class and the formulae in Sakurai. It is easy to explain the differences on the basis of different conventions about the associated Laguerre polynomials.

If you want to skip details, a main result is that Sakurai and *Mathematica* use different conventions. If we call $\mathcal{L}_n^q(\rho)$ the convention of Sakurai and $L_p^{(q)}(\rho)$ the convention of *Mathematica*, we have

$$\mathcal{L}_{p+q}^q(\rho) = (p+q)!(-1)^q L_p^{(q)}(\rho) \ .$$

Below are the details. They are presented somewhat in the order of my investigation and not according to the shorted derivation of the above result.

Differential equation

I have consulted two well known books on mathematical functions that adhere to the same index convention, but have different normalization conventions. The first book that I consulted by Abramowitz & Stegun states on pg 778, Eqs. (22.5.16) and (22.5.17):

$$L_n^{(0)}(x) = L_n(x)$$

$$L_n^{(m)}(x) = (-1)^m \frac{d^m}{dx^m}[L_{n+m}(x)]$$

Also, on pg 781, in Eq. (22.6.15), the differential equation is given.

$$x\frac{d^2}{dx^2}L_n^{(\alpha)}(x) + (\alpha+1-x)\frac{d}{dx}L_n^{(\alpha)}(x) + nL_n^{(\alpha)}(x) = 0 \ .$$

The differential equation is very valuable, but being linear, does not tell us anything about the normalization.

Another well known book by Morse & Feshbach on pg 784, in an unnumbered equation three lines from the bottom of the page gives their convention for the associated Laguerre polynomials.

$$L_n^m(z) = (-1)^m \frac{d^m}{dx^m}[L_{n+m}^0(z)] \ .$$

The differential equation is also given a few lines above:

$$z\frac{d^2}{dz^2}L_n^a(z) + (a+1-z)\frac{d}{dz}L_n^a(z) + nL_n^a(z) = 0 \ .$$

Morse & Feshbach do not put the upper index in parentheses, otherwise, it looks like these conventions might agree. We can be pretty certain that in these two books the $L_n^{(a)}$ is a polynomial of degree n. However, we will soon see that the normalizations don't agree in the two books.

Sakurai convention

Now, let's turn to Sakurai. On pg 454 in Eq. (A.6.4), we find

$$L_p^q(\rho) = \frac{d^q}{d\rho^q} L_p(\rho) \ .$$

This leads us to conclude that L_p^q is of degree $p-q$, and makes the result above plausible. In fact, if the normalizations were the same, we would expect:

$$\mathcal{L}_{p+q}^q(\rho) = \frac{d^q}{d\rho^q} L_{p+q}(\rho) = (-1)^q L_p^{(q)}(\rho) \qquad \textbf{Not quite correct!} \ .$$

Class Derivation

In class, I presented the differential equation for the associated Laguerre polynomials as stated by *Mathematica*,

$$xy'' + (a+1-x)y' + ny = 0 \ .$$

This is the same convention as Abramowitz & Stegun and Morse & Feshbach.

In class, we found we needed to solve this differential equation:

$$\rho L'' + (2(l+1) - \rho)L' + (\lambda - l - 1)L = 0 \ ,$$

but $\lambda = n$, the total quantum number, and $n - l - 1 = n'$ the radial quantum number. So, we have

$$\rho L'' + (2l + 1 + 1 - \rho)L' = n'L = 0 \ .$$

In the notation of Abramowitz & Stegun, *Mathematica* or the Morse & Feshbach index convention, the solution to the differential equation is

$$L_{n'}^{(2l+1)}(\rho) = L_{n-l-1}^{(2l+1)}(\rho) \ .$$

In Sakurai notation, $L_{n-l-1}^{(2l+1)}(\rho) = (-1)^{2l+1}\mathcal{L}_{n+l}^{2l+1} = -\mathcal{L}_{n+l}^{2l+1}$. This explains the indices for R_{nl} in Sakurai in the equation above (A.6.3).

Pinning Down the Normalizations

We still need to consider normalization conventions, and that can be done from the generating function or from what is know as Rodrigues' formula. In fact, in retrospect, it seems that just looking at the Rodrigues' formulae in the three books might have been the easiest way to proceed.

In Abramowitz & Stegun, we find on pg 785, Eq. (22.11.6)

$$L_n^{(\alpha)}(x) = \frac{1}{n!} e^x x^{-\alpha} \frac{d^n}{dx^n}[x^{n+\alpha} e^{-x}] \ .$$

On pg 784 of Morse & Feshbach, we find

$$L_n^a(z) = \frac{\Gamma(a+n+1)}{\Gamma(n+1)} \frac{e^z}{z^\alpha} \frac{d^n}{dz^n}[z^{a+n}e^{-z}] \ .$$

If we set α and a to zero, we can compare with Sakurai, which states in Eq. (A.6.5)

$$L_p(\rho) = e^\rho \frac{d^p}{d\rho^p}(\rho^p e^{-\rho}) \ .$$

We immediately see that Sakurai agrees in normalization with Morse & Feshbach, at least for the Laguerre polynomials, if not for the associated Laguerre polynomials. However, the two books on mathematical methods differ by a factor of $(n+a)!$ in their normalizations with Abramowitz & Stegun convention being smaller by division by that factor. Morse & Feshbach include a small table of associated Laguerre polynomials at the bottom of page 784. They have $L_0^n = n!$, whereas Abramowitz & Stegun according to Eq. (22.4.7) have $L_0^{(\alpha)} = 1$. The only remaining mystery is which normalization convention *Mathematica* obeys. With this command

$$\mathrm{Table}[\{\mathrm{n}, \mathrm{LaguerreL}[0, \mathrm{n}, \mathrm{x}]\}, \{\mathrm{n}, 0, 6\}]$$

you will easily find that all results are 1 and *Mathematica* follows the Abramowitz & Stegun normalization.

Further, I coded up the Rodrigues' formula with the Sakurai convention and compared with $(p+q)!(-1)^q L_p^{(q)}$ where the I used the *Mathematica* function `LaguerreL[p,q,x]`. They were in agreement.

Mystery solved! Quantum mechanics and children can now sleep soundly at night.