Quantum Mechanics and Atomic Physics

Lecture 17:

Hydrogen Atom Probability Distribution

http://www.physics.rutgers.edu/ugrad/361

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Last time

- We solved S.E. for the Coulomb Potential!
- We found the Hydrogen Atom wavefunctions to be:

$$\psi_{n\ell m_\ell}(r,\theta,\varphi) = R(r)\,\Theta(\theta)\,\Phi(\varphi)$$

Table 7.2 Hydrogen Atom Wavefunctions $\psi_{n\ell m}(r,\theta,\phi)$.

$\psi_{100} = \frac{1}{\sqrt{\pi}\,a_o^{3/2}} e^{-r/a_o}$	$\psi_{200} = \frac{1}{4\sqrt{2\pi}\,a_o^{3/2}} (2 - r/a_o) e^{-r/2a_o}$
$\psi_{210} = \frac{1}{4\sqrt{2\pi}\,a_o^{3/2}} (r/a_o) e^{-r/2a_o} \cos\theta$	$\psi_{21\pm1} = \frac{1}{8\sqrt{\pi}\,a_o^{3/2}} (r/a_o) e^{-r/2a_o} \sin\theta\, e^{\pm i\phi}$
$\psi_{300} = \frac{1}{81\sqrt{3\pi}\,a_o^{3/2}} \left[27 - 18\frac{r}{a_o} + 2\frac{r^2}{a_o^2}\right] e^{-r/3a_o}$	$\psi_{310} = \frac{\sqrt{2}}{81\sqrt{\pi}\,a_o^{3/2}} (r/a_o)(6 - r/a_o) e^{-r/3a_o} \cos\theta$
$\psi_{31\pm1} = \frac{1}{81\sqrt{\pi}\,a_o^{3/2}} (r/a_o)(6 - r/a_o) e^{-r/3a_o} \sin\theta\, e^{\pm i\phi}$	
$\psi_{320} = \frac{1}{81\sqrt{6\pi}\,a_o^{3/2}} (r/a_o)^2 e^{-r/3a_o} (3\cos^2\theta - 1)$	
$\psi_{32\pm1} = \frac{1}{81\sqrt{\pi}\,a_o^{3/2}} (r/a_o)^2 e^{-r/3a_o} \sin\theta\cos\theta\, e^{\pm i\phi}$	$\psi_{32\pm2} = \frac{1}{162\sqrt{\pi}\,a_o^{3/2}} (r/a_o)^2 e^{-r/3a_o} \sin^2\theta\, e^{\pm 2i\phi}$

Reed Chapter 7

Last time

- We found that the probability of finding the electron in a volume of space dV

Probability $= \psi^* \psi \, dV = \psi^* \psi r^2 \sin\theta \, dr \, d\theta \, d\phi$

Probability density $= \psi^* \psi$

- We also found that the probability of finding the ground state electron at a distance $r < a_0$, $r<2a_0$, $r<3a_0$ was increasing….

We have an electron cloud around the nucleus.

Cumulative Probability Density

- For the ground state (1,0,0) of Hydrogen:
- As $r \rightarrow \infty$, $P(\leq r) \rightarrow 1$

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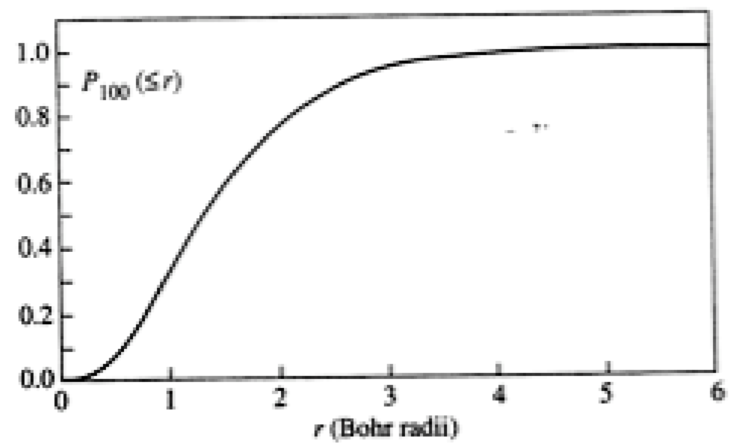


FIGURE 7.5 Cumulative Probability Density for the (1, 0, 0) State of Hydrogen.

- The probability of finding the electron beyond 10 Bohr radii is about 0.003, in other words, very small!

Ground State of Hydrogen

- Wave function of the ground state (1,0,0)

$$\psi_{100} = \frac{1}{\sqrt{\pi}\, a_0^{3/2}} e^{-r/a_0}$$

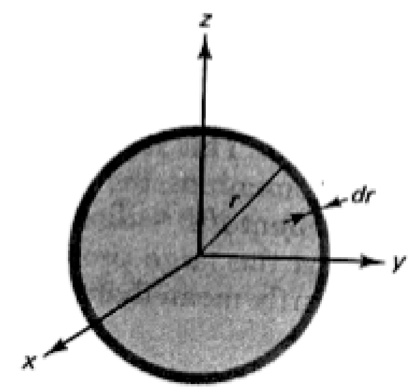
- Probability density is:

$$P_{100} = \psi_{100}^* \psi_{100} = \frac{1}{\pi a_0^3} e^{-2r/a_0}$$

- What is the position of the highest probability density?
  - r=0
- What about the *most likely* radius?
  - Recall that for an infinite spherical well the expectation value of r was <r> = a/2

Radial Probability

- To determine probability of finding the electron within a shell of radius r
  - Imagine the nucleus is surrounded with concentric spherical shells each of thickness Δr
  - Volume of each shell is $4\pi r^2 \Delta r$
  - So,



$$P(\text{electron in shell @ radius } r) = P_{100}(\text{volume of shell})$$

$$= \frac{4}{a_0^3}\left(r^2 e^{-2r/a_0}\right)\Delta r$$

Most Probable Radius

- In what shell are we most likely to find the electron?
- Maximize P with respect to r:

$$\left(\frac{dP}{dr}\right)_{r=r_{mp}} = 0$$

$$\frac{d}{dr}\left(r^2 e^{-2r/a_0}\right) = 2r e^{-2r/a_0} - \left(\frac{2}{a_0}\right) r^2 e^{-2r/a_0} = 0$$

$$\Rightarrow 1 = \frac{1}{a_0} r_{mp} \Rightarrow \underline{r_{mp} = a_0}$$

- r_{mp} in the ground state of Hydrogen is exactly one Bohr radius!
- We will check if: Is $(r_{mp})_{n l m_l} = n^2 a_0$?

Radial Probability Distribution

- The probability of finding an electron in the ground state at radius r is proportional to:

$$P(r) \propto r^2 e^{-2r/a_0}$$

- And more generally: $P(r) = 4\pi r^2 R_{n\ell}^2(r)$

Reed is confused between probability and probability density.

- P(r) vs. r:

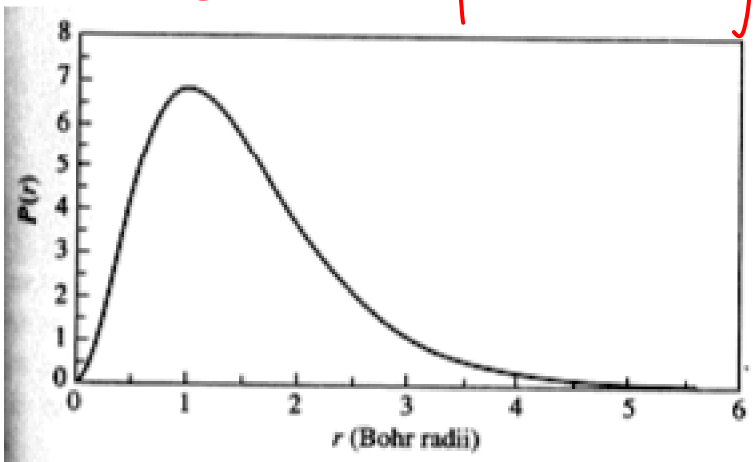


FIGURE 7.4 Radial Probability Distribution for the Ground State of Hydrogen.

P(r) is radial probability density here.

$$\int_0^\infty P(r)\,dr = 1$$

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Expectation value $<r_{100}>$

- We found the most probable radius so now let's find the expectation value of r in ground state:

$$\langle r_{100} \rangle = \langle \psi_{100}^* | r | \psi_{100} \rangle = \int_0^\infty \int_0^\pi \int_0^{2\pi} \psi_{100}^* \, r \, \psi_{100} \, r^2 \sin\theta \, dr \, d\theta \, d\varphi$$

$$= \int_0^\infty \psi_{100}^* \, r \, \psi_{100} \, 4\pi r^2 \, dr$$

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

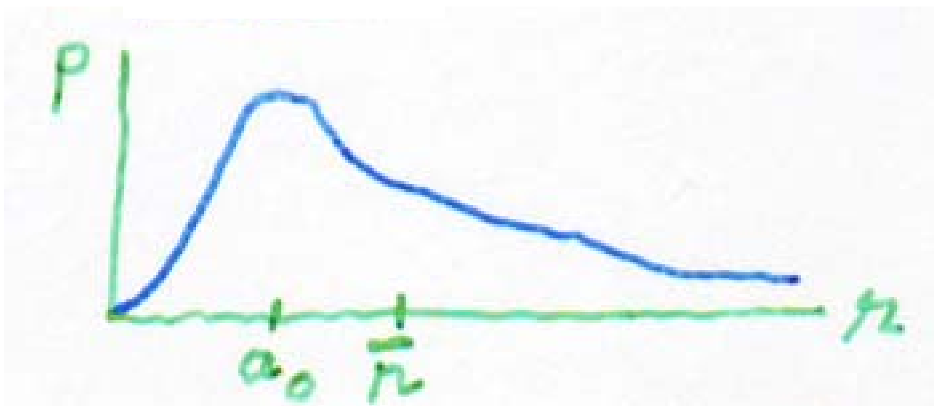
Useful integral (or look in Appendix of your book):

$$\int_0^\infty e^{-ax} x^n \, dx = \frac{n!}{a^{n+1}}$$

$$\Rightarrow \langle r_{100} \rangle = \frac{4}{a_0^3} \frac{3!}{(2/a_0)^4} = \frac{24\, a_0}{16} = \underline{\underline{\frac{3}{2} a_0}}$$

Does this make sense?

- So, <r> > r_{mp}



- The average value of observations of the radial positions of electons in many ground state Hydrogen atoms would be $3a_0/2$ from the nucleus.

The “first excited state” (2,0,0)

- The wavefunction is:

$$\psi_{200} = \frac{1}{\sqrt{32\pi}\, a_0^{3/2}} \left(2 - r/a_0\right) e^{-r/2a_0}$$

- Let’s test the hypothesis that:

$$\text{Is} \quad r_{mp} = n^2 a_0 = 4 a_0 \ ?$$

- We do this by maximizing $4\pi r^2 R^2_{200}$

$$\Rightarrow \frac{d}{dr}\left(r^2(2-r/a_0)^2 e^{-r/a_0}\right) = 0$$

$$2r\left(2-\frac{r}{a_0}\right)^2 e^{-r/a_0} - \frac{2r^2}{a_0}(2-r/a_0)\,e^{-r/a_0} - \frac{r^2}{a_0}\left(2-\frac{r}{a_0}\right)^2 e^{-r/a_0} = 0$$

Divide by $r(2-r/a_0)\,e^{-r/a_0}$

$$\Rightarrow 2(2-r/a_0) - \frac{2r}{a_0} - \frac{r}{a_0}(2-r/a_0) = 0$$

$$4 - \frac{2r}{a_0} - \frac{2r}{a_0} - \frac{2r}{a_0} + \frac{r^2}{a_0^2} = 0$$

$$\left(\frac{r}{a_0}\right)^2 - \frac{6r}{a_0} + 4 = 0$$

- Quadratic equation gives two solutions:

$$r = 2\left(\frac{3}{2}+\frac{\sqrt{5}}{2}\right)a_0 \quad \text{or}$$
$$2\left(\frac{3}{2}-\frac{\sqrt{5}}{2}\right)a_0$$

Inner shell nested within a shell of higher probability density

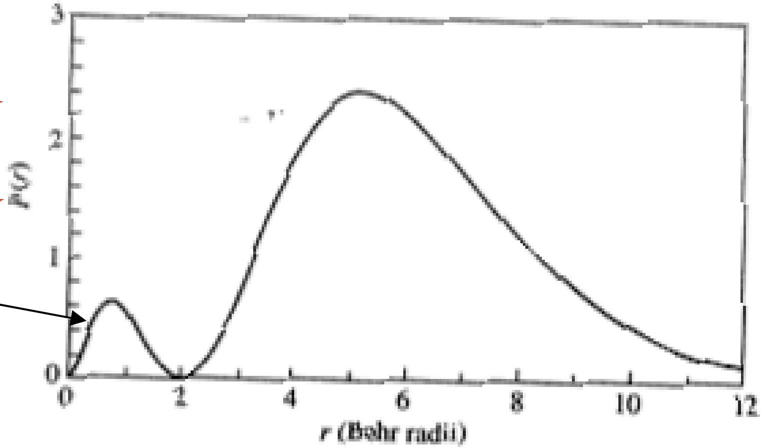


FIGURE 7.6 Radial Probability Distribution for the (2, 0, 0) State of Hydrogen.

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$\Rightarrow (r_{mp})_{200} = 0.764 a_0$ or $5.236 a_0$

$\Rightarrow$ So, $\underline{r_{mp} \neq n^2 a_0}$

- Solution that maximizes the probability density is:

$(r_{mp})_{200} = 5.236 a_0$

- Turns out: $r_{mp} = n^2 a_0$ only for $\underline{\ell = n-1}$

Other Hydrogen States

- P(r) for (n,ℓ) states (m_ℓ does not affect these functions)
- There are a number of radii where P(r) is zero
  - Nodes - where we never expect to find the electron
  - Number of nodes is n - ℓ - 1
- $R_{n\ell}(0)=0$ for $\ell \neq 0$
- $R_{n\ell}(0) \neq 0$ for $\ell = 0$
- Electron will reside closest to the nucleus when ℓ = n-1, for a given n.
  - More on this later.

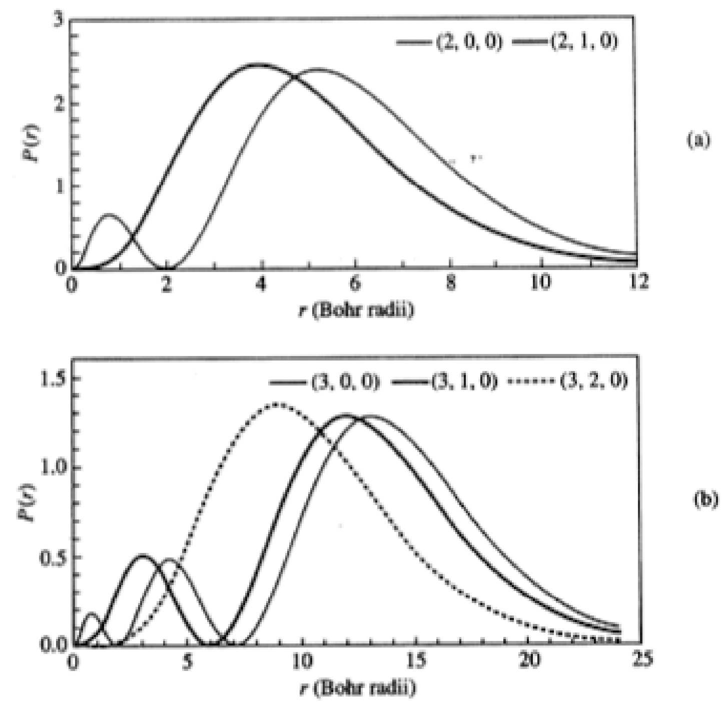

FIGURE 7.7 Hydrogen Radial Probability Distributions for (a) $n = 2$ and (b) $n = 3$.

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Plotting |Ψ|

- $\Psi_{n\ell m\ell}$ also have an angular dependence
- Plot |Ψ| in a plane cutting through the nucleus
  - Usually taken to be $\phi=0$ plane or the xz-plane
  - Remember |Ψ| is rotationally symmetric about the z-axis.
- Since we are representing something that is in 3D onto a 2D surface, think of the figures rotating about the z-axis

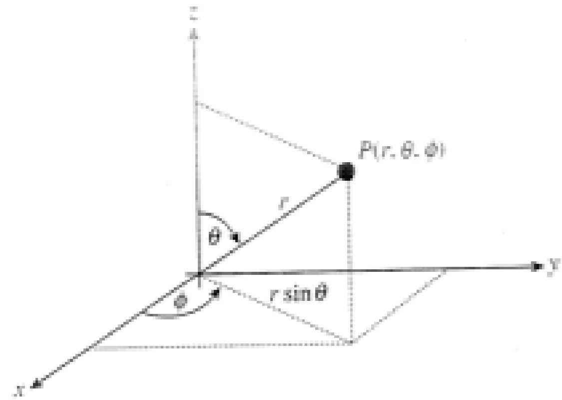

FIGURE 6.4 Spherical coordinates.

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Wave-functions

One radial node
(but non-central)

No radial node
one angular node

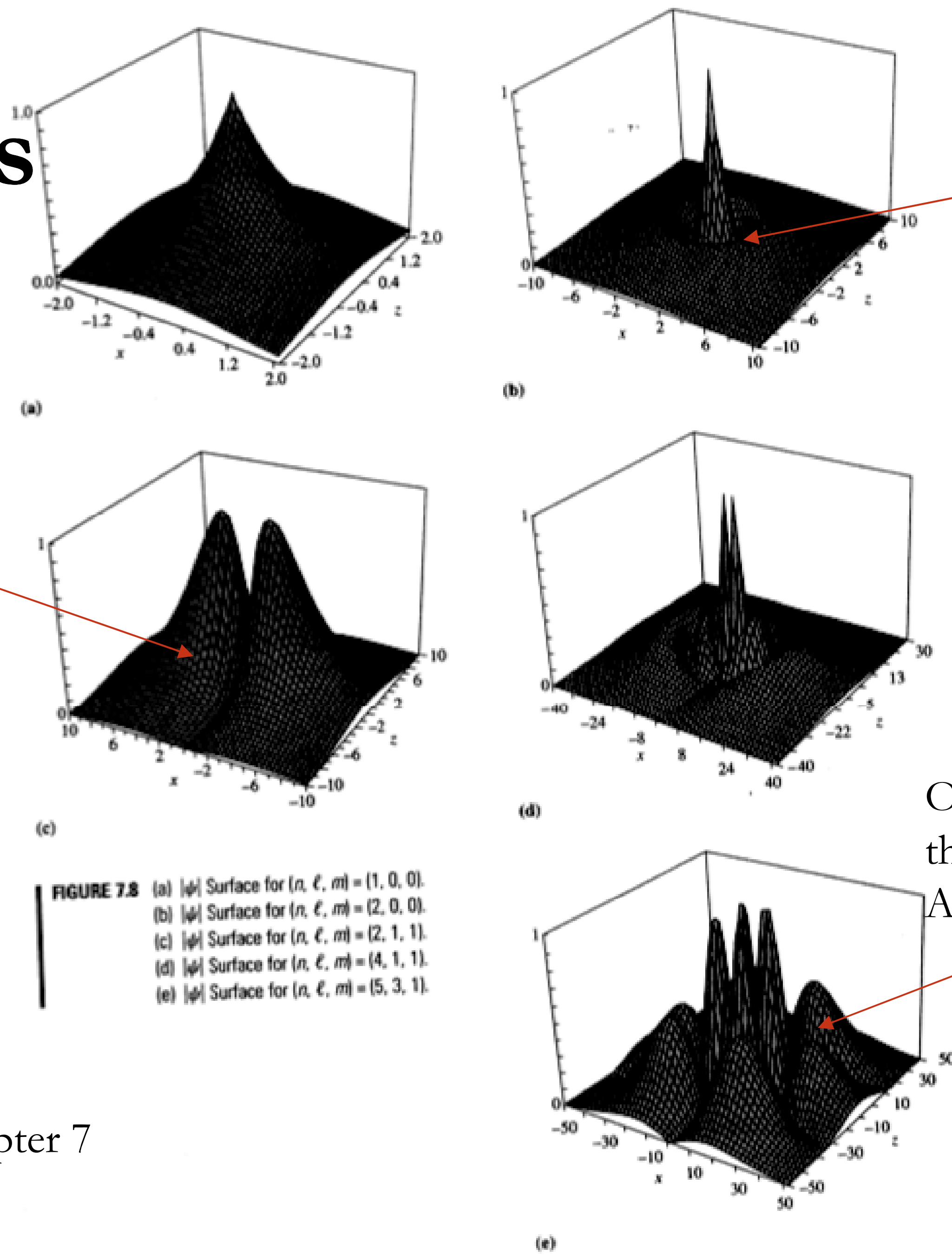

FIGURE 7.8 (a) $|\psi|$ Surface for $(n, \ell, m) = (1, 0, 0)$.
(b) $|\psi|$ Surface for $(n, \ell, m) = (2, 0, 0)$.
(c) $|\psi|$ Surface for $(n, \ell, m) = (2, 1, 1)$.
(d) $|\psi|$ Surface for $(n, \ell, m) = (4, 1, 1)$.
(e) $|\psi|$ Surface for $(n, \ell, m) = (5, 3, 1)$.

One radial node excluding
the central one
And three angular nodes.

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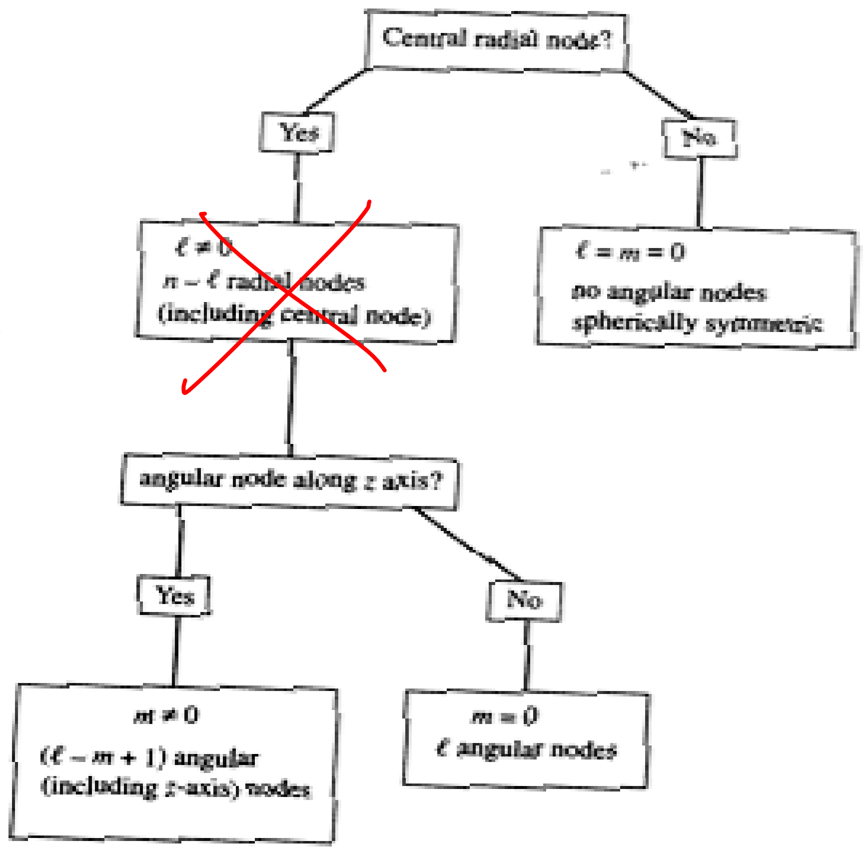


FIGURE 7.9 Flowchart for Analysis of |ψ| (x, z) Plots.

This table is a little confusing. See the examples in the next slide.
Do not include the origin (r=0) when counting radial nodes; it is confusing.

Probability Densities

of radial nodes (excluding $r=0$) in Blue

$= n - \ell - 1$

# of angular nodes

$= \begin{cases} \ell - m + 1, & \text{if } m \neq 0 \\ \ell, & \text{if } m = 0 \end{cases}$

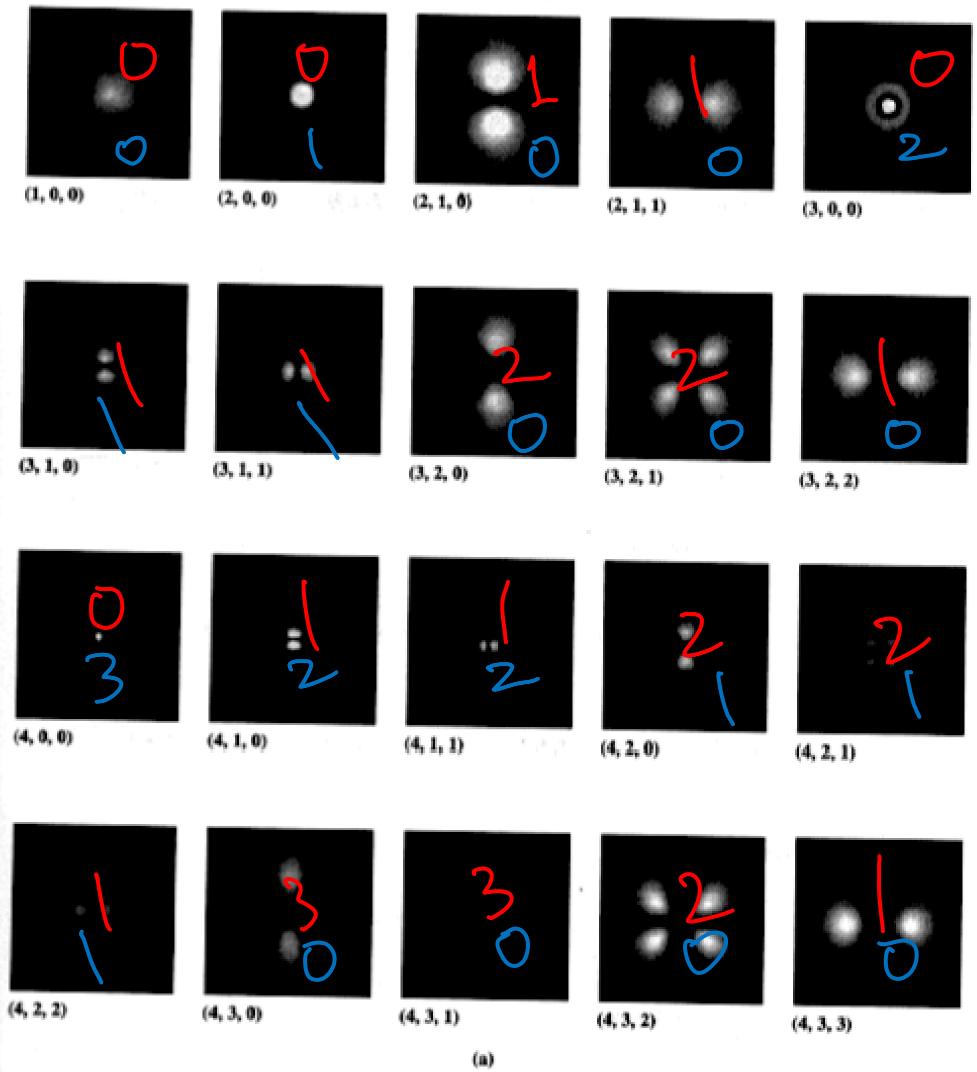


FIGURE 7.10 (a) Grayscale Representations of $|\psi|$ (x, z) for Hydrogen states to $n = 4$. (b) Grayscale Representations of $|\psi|$ (x, z) for Hydrogen $n = 5$ states.

- http://phet.colorado.edu/simulations/sims.php?sim=Quantum_Bound_States
- http://phet.colorado.edu/simulations/sims.php?sim=Models_of_the_Hydrogen_Atom

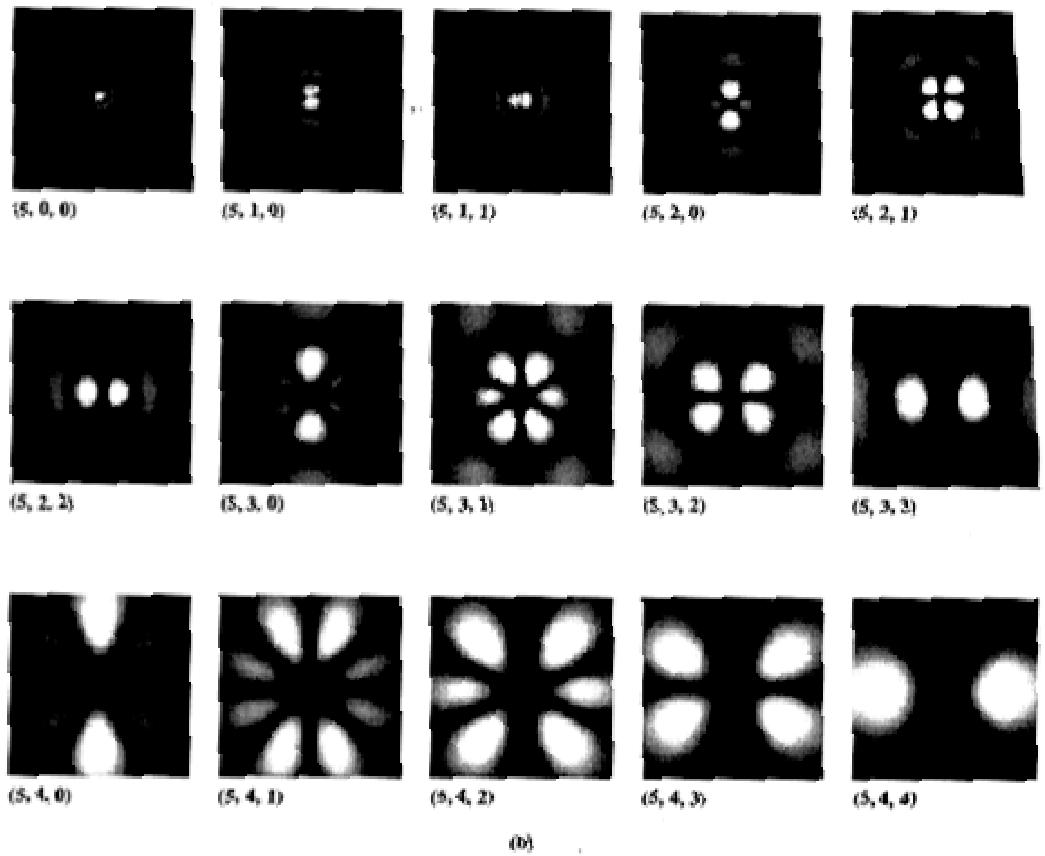


FIGURE 7.10 (continued)

Try to count the number of radial and angular nodes yourself on these figures and find the relationship with n, l, m values

More figures

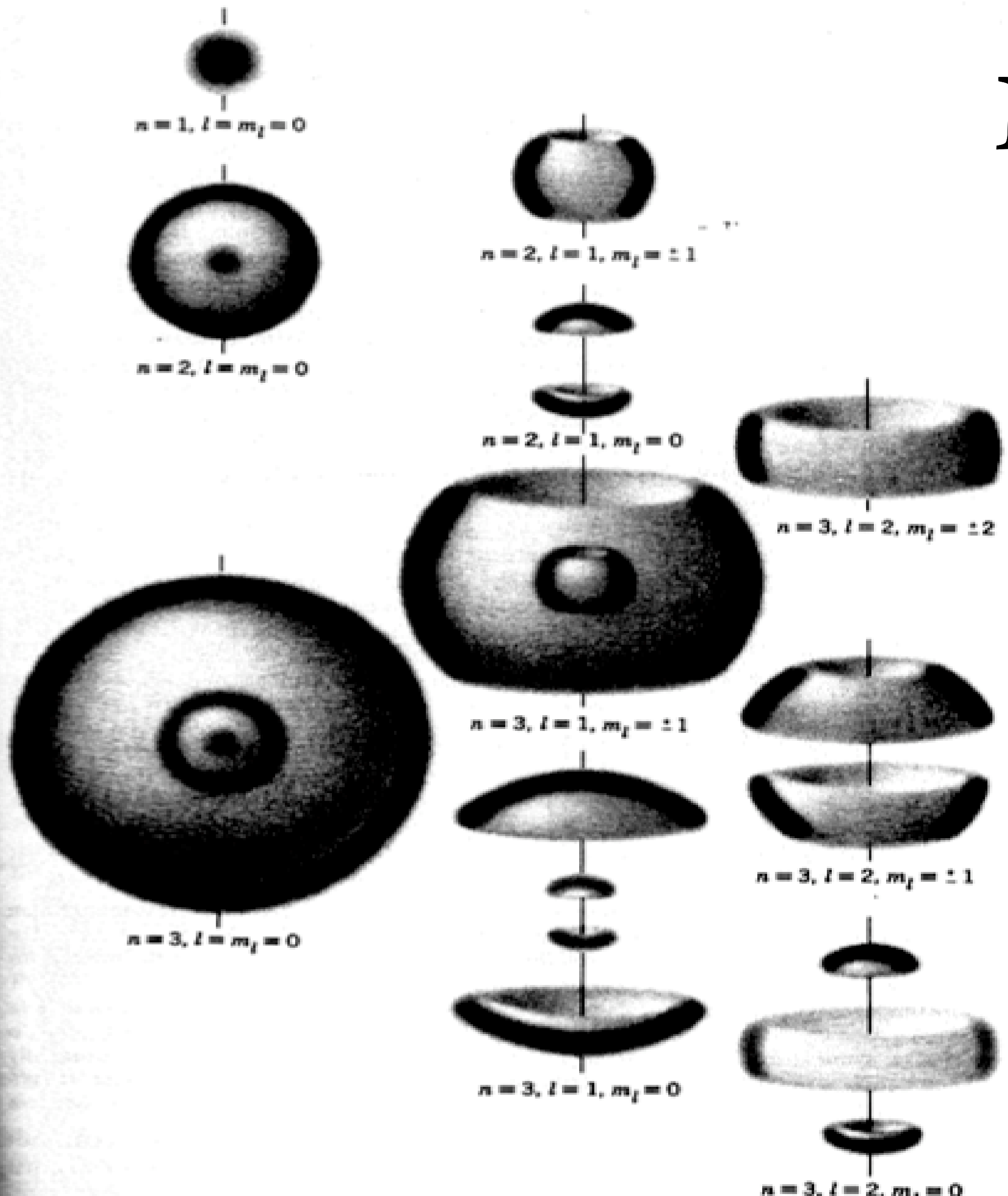
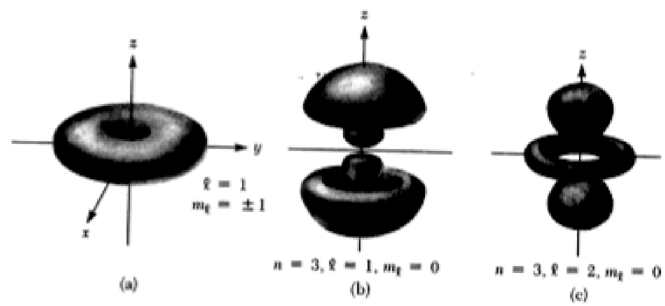


Figure 7-10 An artist's conception of the three-dimensional appearance of several one-electron atom probability density functions. For each of the drawings a line represents the z axis. If all the probability densities for a given n and l are combined, the result is spherically symmetrical.



The Effective Potential

- Recall the radial equation with the Coulomb Potential:

$$\frac{\hbar^2}{2\mu}\frac{d^2 U(r)}{dr^2} + \left(E - V(r) - \frac{\ell(\ell+1)\hbar^2}{2\mu r^2}\right)U(r) = 0$$

with $V_{eff}(r) \equiv V(r) + \frac{\ell(\ell+1)\hbar^2}{2\mu r^2}$

$$\Rightarrow \frac{\hbar^2}{2\mu}\frac{d^2 U(r)}{dr^2} + \left(E - V_{eff}(r)\right)U(r) = 0$$

$$\left[\text{ or } \quad -\frac{\hbar^2}{2\mu}\frac{d^2 U(r)}{dr^2} + V_{eff}(r)\,U(r) = E\,U(r)\right]$$

- This looks like the 1D S.E.!

V_{eff}

- V_{eff} vs. ρ, where $\rho = r/a_0$
- Striking difference between ℓ=0 and $\ell \neq 0$
  - When $\ell \neq 0$ the combination of the two terms in the effective potential leads to potential wells with infinite walls as $r \rightarrow 0$ (see that the wavefuncion is zero for $\ell \neq 0$ in Fig. 7.10)
- V_{eff}=0 as $r \rightarrow \infty$
  - Bohr energy levels get closer together as $n \rightarrow \infty$

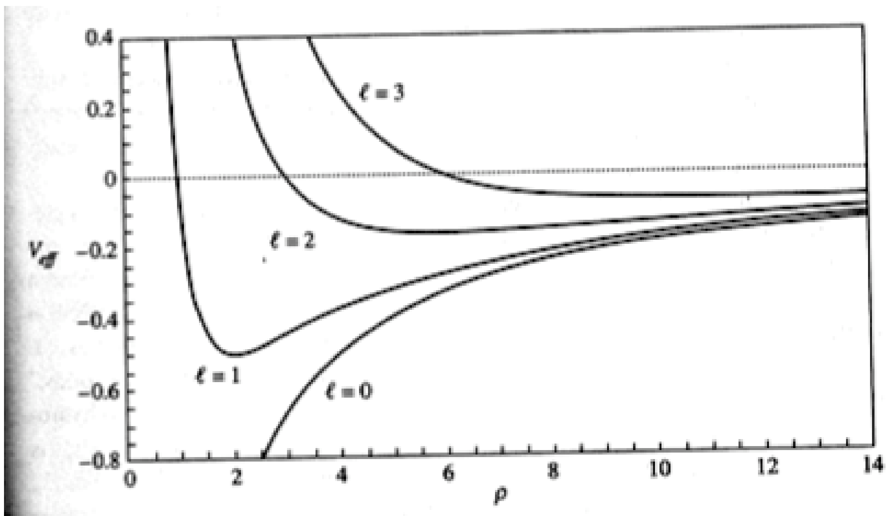


FIGURE 7.11 Effective Potential Curves for the Coulomb Potential.

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Centrifugal term

$$V_{eff}(r) = -\frac{e^2}{4\pi\epsilon_0}\frac{1}{r} + \frac{\ell(\ell+1)\hbar^2}{2\mu r^2}$$

- The $\ell(\ell+1)/r^2$ term is known as the "centrifugal" term
- Contributes a repulsive potential - drives the electron away from the nucleus
- Stronger repulsion as ℓ increases and we expect to find the electron further from the nucleus.

Summary/Announcements

- Next time:

  Angular Momentum Raising and Lowering Operators

- Time for Quiz.