Outline for Day 13 - 14

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In which we solve the Schrödinger Equation for the hydrogen atom.

- Bohr atom + de Broglie postulate
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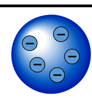
Models of the Atom



- Thomson – "Plum Pudding"
  - Why? Known that negative charges can be removed from atom.
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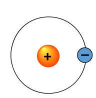

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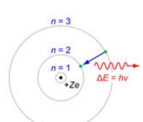
  - Why? Explains spectral lines.
  - Problem: No reason for fixed energy levels



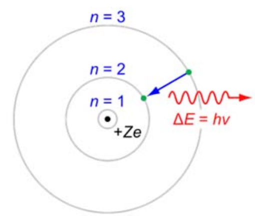
Successes of Bohr Model

- 'Explains' source of Balmer formula and predicts empirical constant *R* (Rydberg constant) from fundamental constants
- Explains why *R* is different for different single electron atoms *(called hydrogen-like ions).*
- Predicts approximate size of hydrogen atom
- Explains (sort of) why atoms emit discrete spectral lines
- Explains (sort of) why electron doesn't spiral into nucleus

Shortcomings of the Bohr model:

- Why is angular momentum quantized yet Newton's laws still work?
- Why don't electrons radiate when they are in fixed orbitals yet Coulomb's law still works?
- No way to know *a priori* which rules to keep and which to throw out…
- Can't explain shapes of molecular orbits and how bonds work
- Can't explain doublet spectral lines

Bohr Atom + de Broglie electron waves



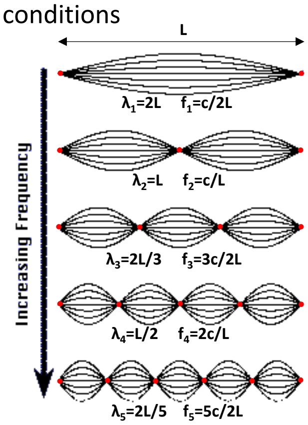
$$+ \qquad \lambda = \frac{h}{p}$$

Waves with boundary conditions

- Boundary conditions mean that waves only have discrete frequencies.
- e.g., guitar strings

$\lambda_n=2L/n \quad f_n=nc/2L$

• = node = fixed point that doesn't move

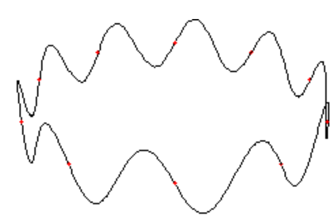


PHET: normal modes

Standing Waves on a Ring

Just like standing wave on a string,
but now the two ends of the string are joined.

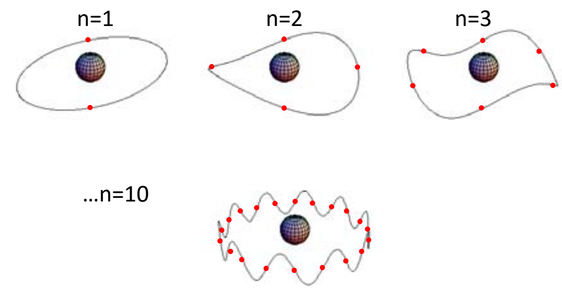
$2\pi r = n\lambda \qquad n = 1, 2, 3, \ldots$



Derive angular momentum of an electron wave

deBroglie electron waves in an atom

$$\lambda = \frac{h}{mv}$$



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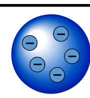
Models of the Atom



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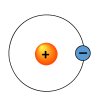

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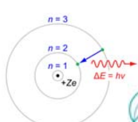
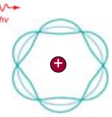


- deBroglie – electron standing waves
  – Why? Explains quantized energy levels
  – Problem: still only works for Hydrogen.



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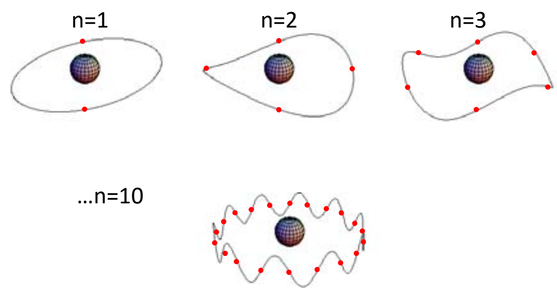

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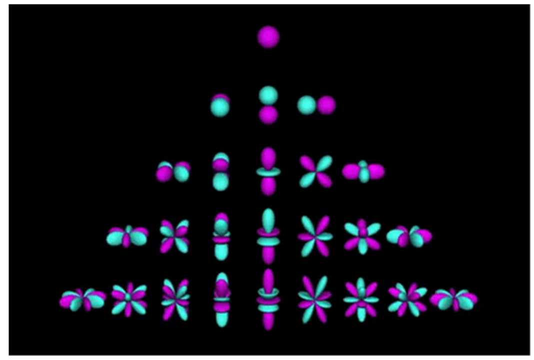

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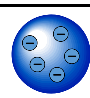
Models of the Atom



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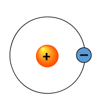

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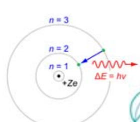

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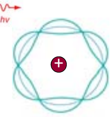
  - Problem: still only works for Hydrogen.



- Schrodinger – quantum wave functions
  - Why? Explains everything!
  - Problem: None (except that it's abstract)

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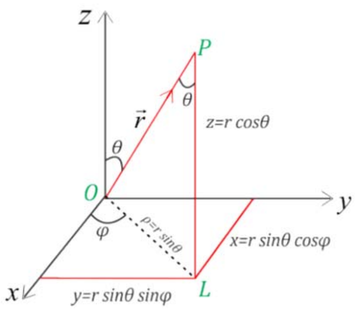
Spherical Coordinates



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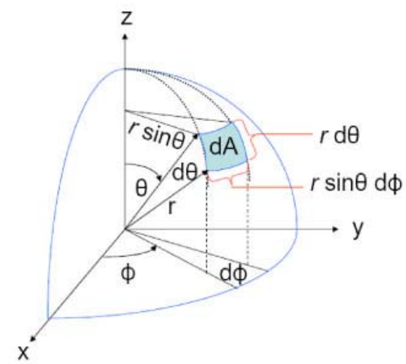

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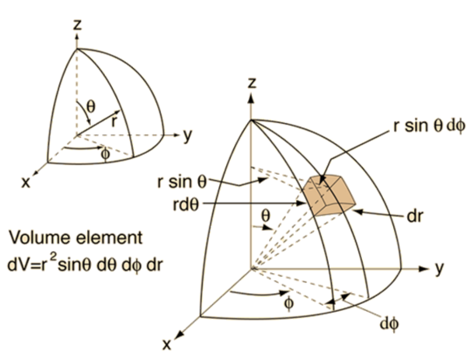

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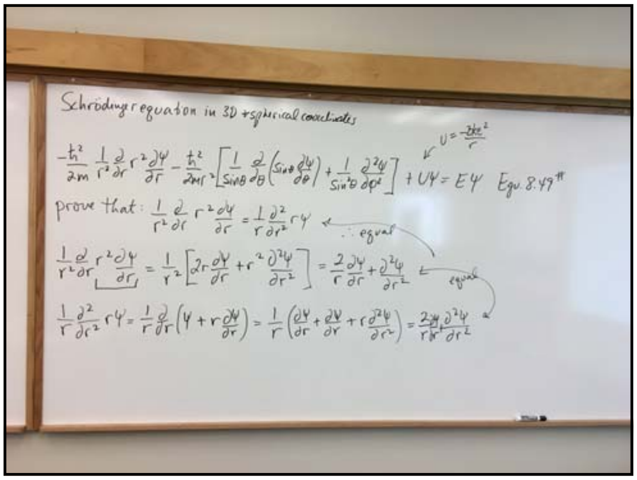

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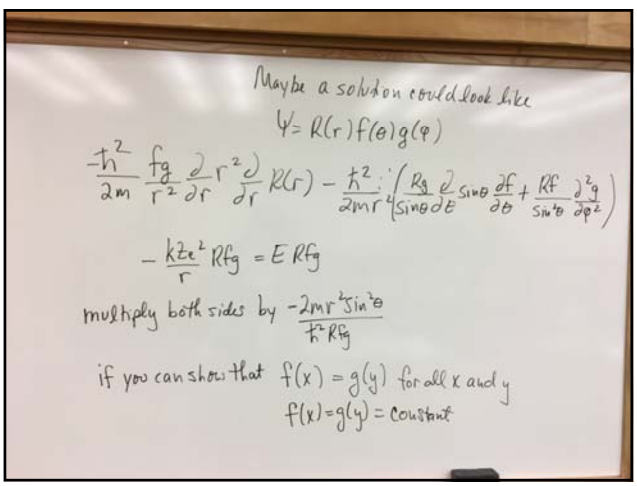

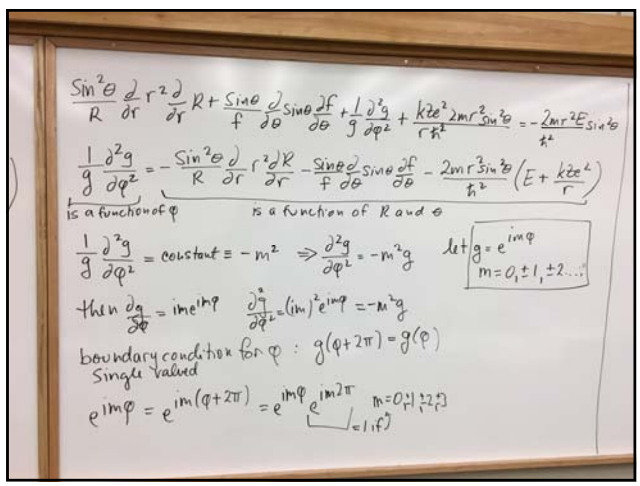

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move all r dependence to one side

$$\underbrace{\frac{1}{R}\frac{\partial}{\partial r} r^2 \frac{\partial R}{\partial r} + \frac{2mr^2}{\hbar^2}\left(E + \frac{kZe^2}{r}\right)}_{\text{depends only on } r} = \underbrace{-\frac{1}{f\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial f}{\partial\theta} - \frac{1}{\sin^2\theta\, g}\frac{\partial^2 g}{\partial\phi^2}}_{\text{depends only on } \theta + \phi}$$

$$= \ell(\ell+1)$$

multiply both sides by $\frac{R}{r^2}$

*use the identity for r derivative term

$$\frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial R}{\partial r} = \ell(\ell+1)\frac{R}{r^2}\cdot\frac{2m}{\hbar^2}\frac{\hbar^2}{2m} - \frac{2mr^2}{\hbar^2}\frac{R}{r^2}\left(E + \frac{kZe^2}{r}\right)$$

$$\frac{\partial^2}{\partial r^2} rR = \frac{2m}{\hbar^2}\left[-\frac{kZe^2}{r} + \frac{\ell(\ell+1)\hbar^2}{2mr^2} - E\right] Rr \quad \text{Equ 8.70}$$

Equ. 8.70 is a differential equation
that has solutions tabulated in Table 8.2
boundary conditions (not shown)
require: $\ell < n$ ℓ and n integers
so $n = 1 \Rightarrow \ell = 0$
$n = 2 \Rightarrow \ell = 0, 1$
that the energy is quantized

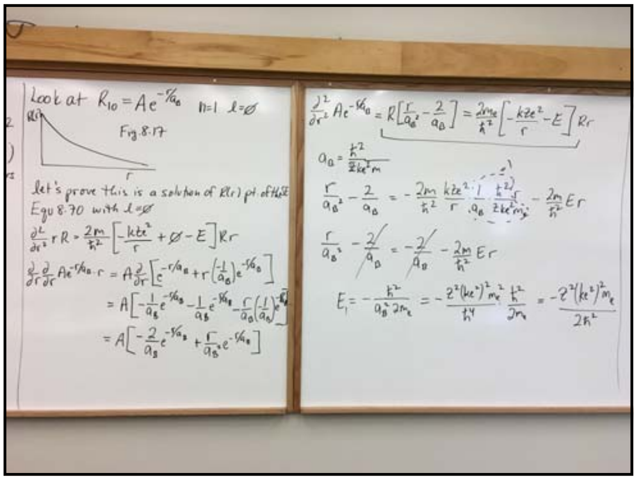
$$E_n = -\frac{m_e(ke^2)^2}{2\hbar^2}\frac{1}{n^2} = -13.6\,\text{eV}\frac{1}{n^2} \quad \text{Equ 8.74}$$

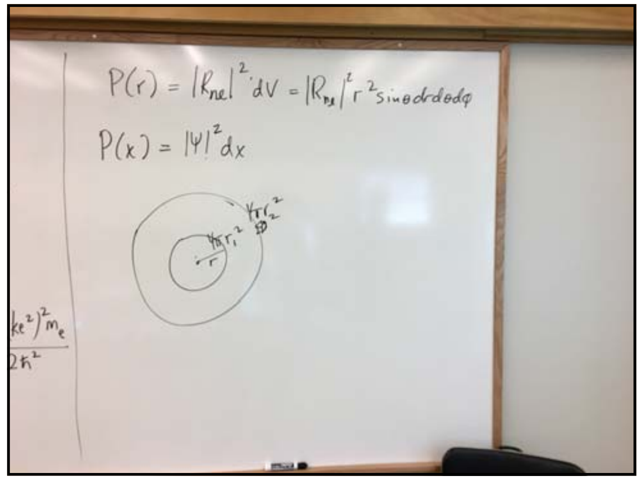
$R_{nl}(r)$: The Radial Wave Functions for the atom

TABLE 8.2

The first few radial functions $R_{nl}(r)$ for the hydrogen atom. The variable ρ is an abbreviation for $\rho = r/a_B$ and a stands for a_B.

	$n = 1$	$n = 2$	$n = 3$
$l = 0$	$\frac{2}{\sqrt{a^3}}e^{-\rho}$	$\frac{1}{\sqrt{2a^3}}\left(1 - \frac{1}{2}\rho\right)e^{-\rho/2}$	$\frac{2}{\sqrt{27a^3}}\left(1 - \frac{2}{3}\rho + \frac{2}{27}\rho^2\right)e^{-\rho/3}$
$l = 1$		$\frac{1}{\sqrt{24a^3}}\rho e^{-\rho/2}$	$\frac{8}{27\sqrt{6a^3}}\left(1 - \frac{1}{6}\rho\right)\rho e^{-\rho/3}$
$l = 2$			$\frac{4}{81\sqrt{30a^3}}\rho^2 e^{-\rho/3}$

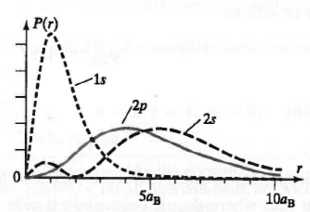




Radial Probability Density

$$P(r) = |R_{nl}|^2 r^2$$

FIGURE 8.22
The radial probability density for the $2p$ states (solid curve). The most probable radius is $r = 4a_B$. For comparison, the dashed curves show the $1s$ and $2s$ distributions to the same scale.



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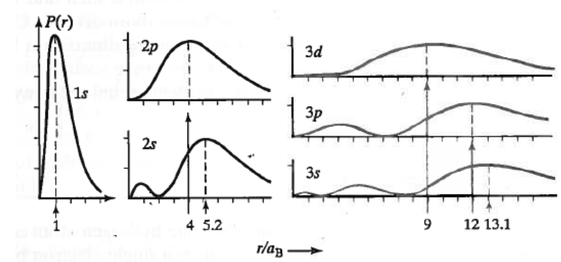
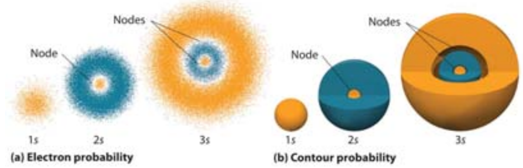
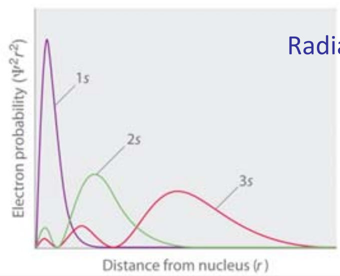


most probably radius indicated for each state





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$$l(l+1) = -\frac{1}{f\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial f}{\partial\theta} - \frac{1}{\sin^2\theta}(-m^2)$$

Solutions are in table 8.1

boundary conditions restrict values of m and l such that:

$l \geq 0$ $|m| \leq l$ m, l integers

Often angular functions are written together

$$Y_{lm}(\theta,\varphi) = f_{lm}(\theta) g_m(\varphi) = f_{lm}(\theta) e^{im\varphi}$$

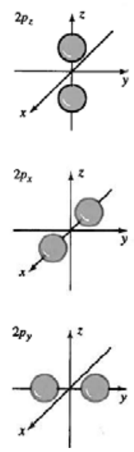
$Y_{lm}(\theta)$: The spherical harmonic wave functions

TABLE 8.1 Θ(θ) = f(θ) in our derivation in class

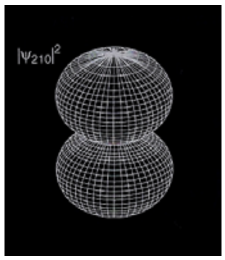
The first few angular functions $\Theta_{l,m}(\theta)$. The functions with m negative are given by $\Theta_{l,-m} = (-1)^m \Theta_{l,m}$.

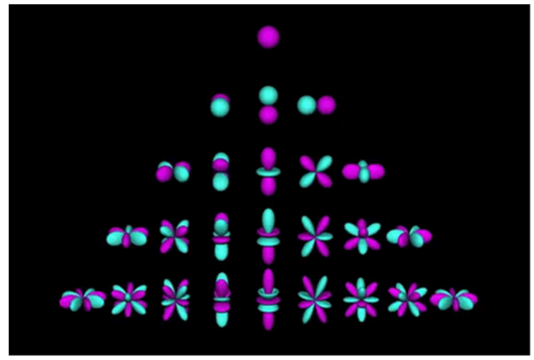
	$l = 0$	$l = 1$	$l = 2$
$m = 0$	$\sqrt{1/4\pi}$	$\sqrt{3/4\pi}\cos\theta$	$\sqrt{5/16\pi}(3\cos^2\theta - 1)$
$m = 1$		$-\sqrt{3/8\pi}\sin\theta$	$-\sqrt{15/8\pi}\sin\theta\cos\theta$
$m = 2$			$\sqrt{15/32\pi}\sin^2\theta$

$$Y_{lm}(\theta,\phi) = \Theta_{lm}(\theta)e^{im\phi}$$



$|Y_{21m}|^2$





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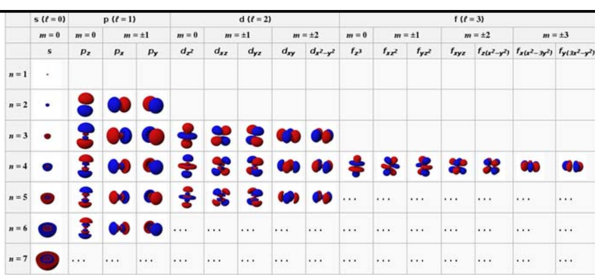

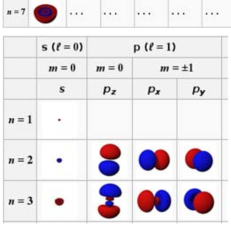

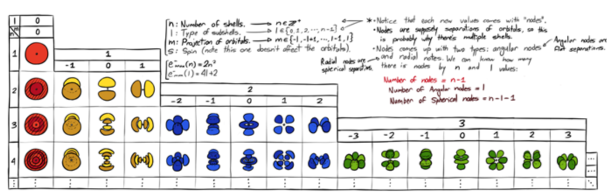

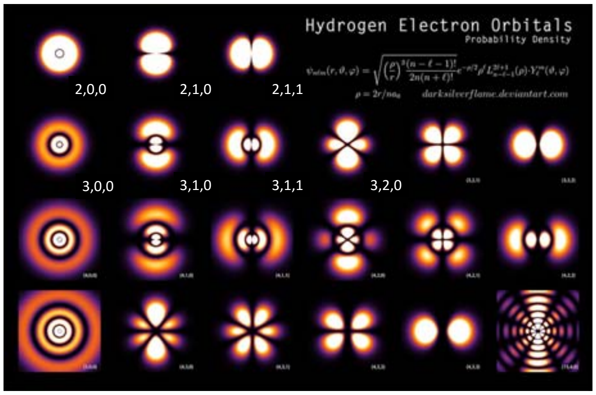

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Altogether then

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

normalization constant   table 8.2   table 8.1 $e^{im\varphi}$

$n = 1, 2, 3, \ldots$

s p d f

$\ell \geq 0 \quad \ell < n \quad \ell = 0, 1, 2, 3 \ldots (n-1)$

$|m| \leq \ell \quad m = -\ell, (-\ell+1), (-\ell+2) \ldots 0, 1, 2, \cdots +\ell$

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$$Y_{lm}(\theta, \phi) = \Theta_{lm}(\theta)e^{im\phi}$$

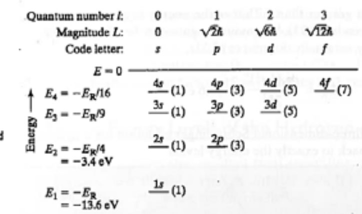

FIGURE 8.16
Energy-level diagram for the hydrogen atom, with energy plotted upward and angular momentum to the right. The letters $s, p, d, f, \cdots$ are code letters traditionally used to indicate $l = 0, 1, 2, 3, \cdots$. (Energy spacing not to scale.)

code letter:	s	p	d	f	g	h	i
quantum number l:	0	1	2	3	4	5	6

$n = 1, 2, 3\ldots$

$\ell < n$

$|m| \leq \ell$