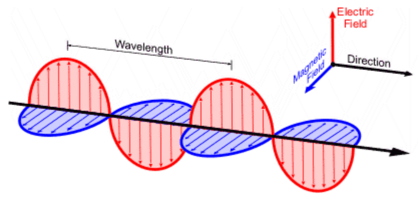
Atomic Structure and Quantum Theory

Light:

- Properties of electromagnetic radiation: "Light"
  Why electromagnetic?
  Wavelength, Frequency,...
- Relationship between energy, frequency, and wavelength:
  "Wave-Particle Duality"



$$E = h\nu = \frac{hc}{\lambda}$$

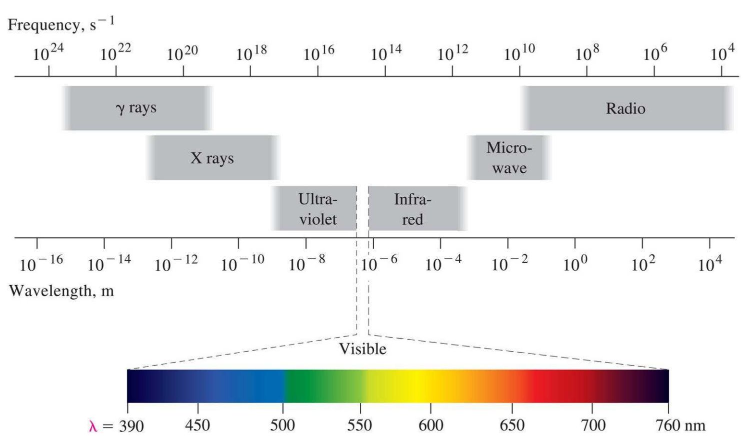
h = Plank's constant = 6.626×10^{-34} Js
c = speed of light = 2.998×10^{8} m/s
Note: units of wavelength must match units of c !

- This energy is in Joules *per photon*
  Photon:

1

Photon Energies

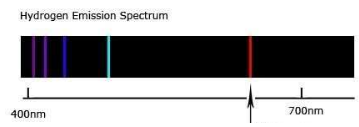
- **Energy is distributed across the *electromagnetic spectrum***
- **Electrons in atoms and compounds occupy a distribution of energy states (both excited and ground states)**



2

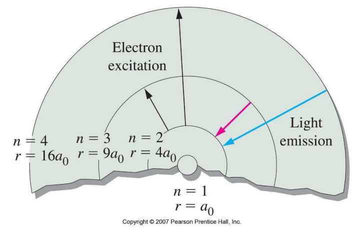
Atomic Structure Based on the Bohr Model

Electrons occupy "shells" or orbits
- These orbits are "quantized"
- Identified by *principle quantum number*, n



Energy of nth level for the hydrogen atom (and ONLY the H atom!):

$$E_n = \frac{-2.178 \times 10^{-18}\ J}{n^2}$$



- Energy must be supplied to promote an electron from the <u>ground state</u> to an <u>excited state</u>.
- Energy is released (often as light) when an electron drops from an excited state to the ground state.

3

The Bohr Model Allows Construction of an Energy-Level Diagram for Hydrogen**

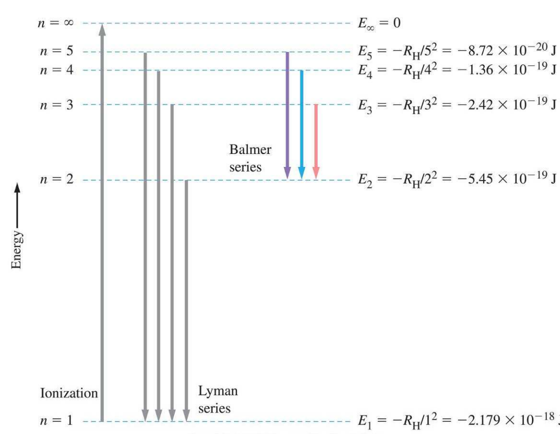
- We can predict (calculate) energy changes for transitions between levels.

$$\Delta E = E_f - E_i = R_H\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

- These energies can be related to photon frequencies

$$\Delta E = h\nu$$

- **This is the foundation of spectroscopy!**



4

Wave Properties of Electrons

Diffraction experiments show that electrons behave in similar fashion as photons.

- If this is true, we can treat them similarly

de Broglie wavelength: $\lambda = \frac{h}{mu}$

u = velocity (why not v?)

mu = momentum

In order for wavelength to be measurable, mu must be very small.

SO WHAT? Why care that electrons have wave characteristics!

5

Quantum Mechanics

Theory aimed at understanding atomic behavior

- Based on wave/particle behavior of electrons and electromagnetic radiation (light)

Seeks to answer questions like:

- Why do different atoms emit different colors?
- Why are molecules shaped as they are?

Wave-particle duality causes a problem.

If we consider electrons to have wave properties, how can we pinpoint the position of an electron?

Heisenberg Uncertainty Principle: $\Delta x \bullet \Delta(mu) > h$

- It is impossible to fix both the position and energy of an electron with high certainty (accuracy)
- If you calculate the position with high accuracy, there will be a high level of uncertainty in the energy calculated.
- SO WHAT???

6

Quantum Mechanical Models

What we *think* we know:

- Electrons are small, constantly moving
- Electrons occupy specific (quantized) levels in an atom
- Electrons have properties of BOTH particles and waves
- At any instant, it is impossible to pinpoint the position of an electron of a given energy with high accuracy.

Because of this combination, the best we can do is calculate the <u>probability</u> of finding an electron at a specific point at a given time.

Even calculating probability is tough to do!

7

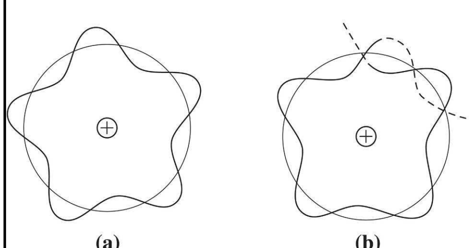
Quantum Mechanical Models

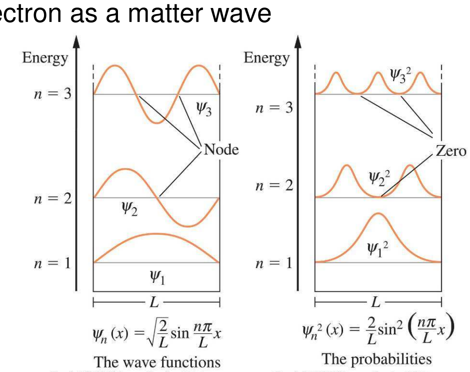
Enter Erwin Schrödinger

One simple equation solves it all! OK its not so simple, but it does work!

$$\hat{H}\psi = E\psi$$

- Solutions to this equations are **wave functions (ψ)**
- Wave functions describe the electron as a matter wave





A Closer Look at Schrödinger

- Solving the Schrodinger equation isn't trivial (even though it looks simple)

$$\hat{H}\psi = E\psi$$

- Here's a functional form for the hydrogen atom:

$$-\frac{h^2}{8\pi^2 m_e}\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}\right)-\frac{Ze^2}{r}\psi = E\psi$$

- Things get even more complex for multi-electron atoms!

9

Schrödinger's Theory in a Nutshell

Only certain wave functions are allowed as solutions to Schrödinger's equation.

- Each ψ corresponds to an allowed energy level for an electron.
- Thus, we say that electron energy levels are *quantized.*

The probability of finding an electron in a given region of space is dependent on ψ^2.

- This probability describes the electron density in this region of space.

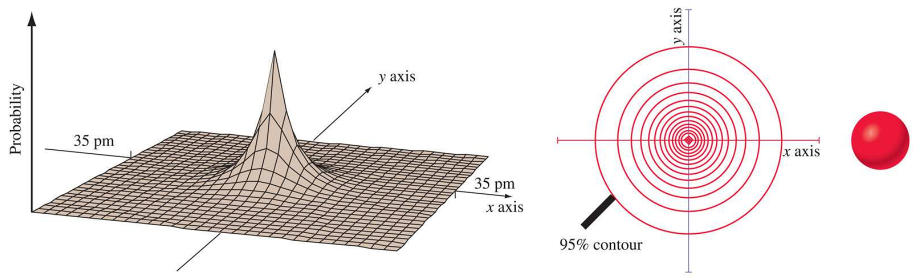
These allowed wave functions map out orbitals for electrons of varying energies.

- These allowed orbitals are described in three-dimensional space by three quantum numbers.

10

Bohr + Heisenberg + Schrödinger = ???

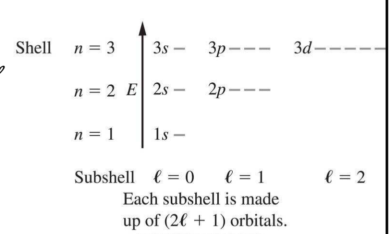
- Energy of an electron is quantized
- Schrödinger Eqn.: Calculate ψ for a given E
- Allows prediction of the probability of finding an electron in a given spot at a given time



Defining Wave Functions

For three-dimensional space, need three variables
Define three **Quantum Numbers**

1. Principle Quantum Number, **n**
   - Relates to “size”
   - Only positive, nonzero integers
2. Angular Momentum Quantum Number, ℓ
   - Relates to “shape”
   - Only integers, ℓ = 0, 1, 2, 3…n-1
   - n possible values
   - Spectroscopic notation (s, p, d, f…)
3. Magnetic Quantum Number, $\mathbf{m}_\ell$
   - Relates to orientation
   - Only integers, $m_l = -\ell, (-\ell+1), \ldots, -1, 0, 1, \ldots (\ell+1), \ell$
   - $2\ell+1$ possible values



Degenerate Orbitals

Defining Wave Functions

The combination of these quantum numbers allows us to visualize orbitals.

- Why do we care?
- Electrons control chemistry!
- Orbital size and shape → **BONDING**

How the *%&&@#$ do we do this?

- Need wave function (solution to Schrödinger Equation)
- Calculate ψ^2 (probability density)
- Plot ψ^2 in three dimensions – "shape"
- Need to consider *radial* and *angular* components
- In some instances, ψ^2 goes to zero (ψ changes sign)
  - **nodes:** planar (angular) or spherical (radial)

13

Hydrogen-like Wave Functions

- Wave function is a mathematical combination of the angular and radial components.

$$\psi(1s) = R(r) \times Y(\theta,\phi) = \frac{2e^{-r/a_0}}{a_0^{3/2}} \times \frac{1}{\sqrt{4\pi}} = \frac{e^{-r/a_0}}{\sqrt{(\pi a_0^3)}}$$

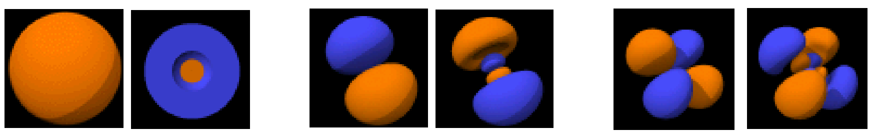
- Nodes occur when either the radial or angular parts of the wavefunction = 0

TABLE 8.1 The Angular and Radial Wave Functions of a Hydrogen-like Atom

Angular Part $Y(\theta, \phi)$	Radial Part $R_{n,\ell}(r)$
$Y(s) = \left(\frac{1}{4\pi}\right)^{1/2}$	$R(1s) = 2\left(\frac{Z}{a_0}\right)^{3/2} e^{-\sigma/2}$
	$R(2s) = \frac{1}{2\sqrt{2}}\left(\frac{Z}{a_0}\right)^{3/2}(2 - \sigma)e^{-\sigma/2}$
	$R(3s) = \frac{1}{9\sqrt{3}}\left(\frac{Z}{a_0}\right)^{3/2}(6 - 6\sigma + \sigma^2)e^{-\sigma/2}$
$Y(p_x) = \left(\frac{3}{4\pi}\right)^{1/2} \sin\theta\cos\phi$	$R(2p) = \frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2}\sigma e^{-\sigma/2}$
$Y(p_y) = \left(\frac{3}{4\pi}\right)^{1/2} \sin\theta\sin\phi$	$R(3p) = \frac{1}{9\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2}(4 - \sigma)\sigma e^{-\sigma/2}$
$Y(p_z) = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$	
$Y(d_{z^2}) = \left(\frac{5}{16\pi}\right)^{1/2}(3\cos^2\theta - 1)$	$R(3d) = \frac{1}{9\sqrt{30}}\left(\frac{Z}{a_0}\right)^{3/2}\sigma^2 e^{-\sigma/2}$
$Y(d_{x^2-y^2}) = \left(\frac{15}{16\pi}\right)^{1/2} \sin^2\theta\cos 2\phi$	
$Y(d_{xy}) = \left(\frac{15}{16\pi}\right)^{1/2} \sin^2\theta\sin 2\phi$	$\sigma = \frac{2Zr}{na_0}$
$Y(d_{xz}) = \left(\frac{15}{4\pi}\right)^{1/2} \sin\theta\cos\theta\cos\phi$	
$Y(d_{yz}) = \left(\frac{15}{4\pi}\right)^{1/2} \sin\theta\cos\theta\sin\phi$	

Nodes

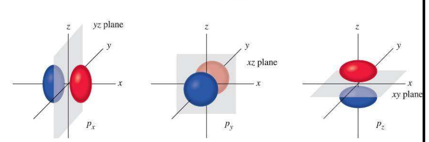
- Places where the Probability of finding the Electron is Zero (ψ = 0 so ψ^2 = 0)
- When ψ_{radial} is zero, called a *radial (or spherical) node*
  - There are n - ℓ - 1 radial nodes
- When $\psi_{angular}$ is zero, called an *angular node* (or a *nodal plane*)
  - There are ℓ angular nodes



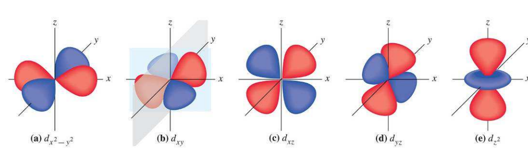
Orbital Shapes

s orbitals
- spherical
- as n ↑, size ↑

p orbitals
- "dumbbell" shaped, 1 nodal plane
- three orientations
- node at nucleus



d orbitals
- two nodal surfaces
- five orientations



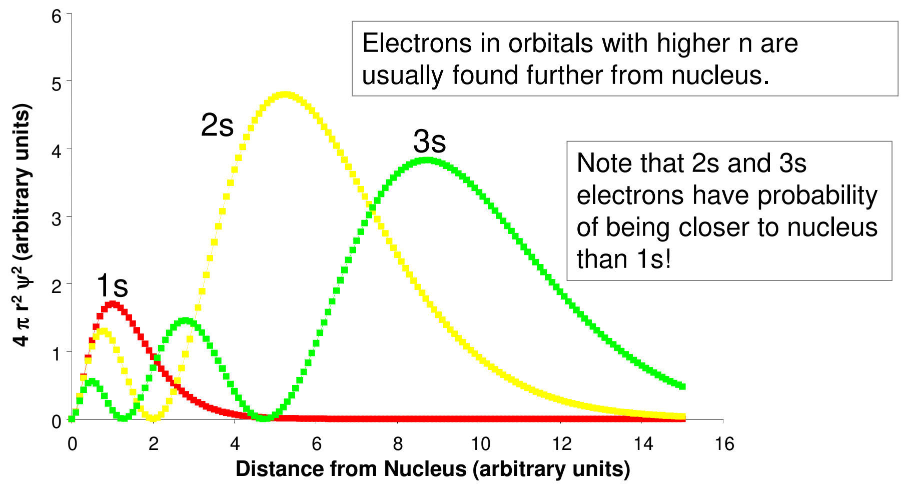
f orbitals
- three nodal surfaces
- seven orientations

- Total # nodes depends on n and l: http://www.orbitals.com/orb/orbtable.htm#table3

16

Radial Distribution Function

- Problem with ψ^2, it over estimates probability close to nucleus and under estimates it further out
  - Radial Distribution Function corrects for this.



Multi-electron Atoms

What does an electron "see" from its orbital? What keeps it in the orbital? What impact do other electrons have?

Penetration and Shielded Nuclear Charge:

Depends on:

- Number of protons (charge) in nucleus
- Number of electrons in lower energy shells

Effective Nuclear Charge (Z_{eff}):

Average shielded charge "felt" by an electron.

– The higher the Z_{eff}, the stronger the attraction for the nucleus.