CHM2311
Introduction to Structure & Bonding

Part 1

Atomic Structure and Quantum Theory

Fundamental Particles: Atoms

An ***atom*** is the smallest unit quantity of an element that is capable of existence, either alone or in chemical combination with other atoms of the same or another element.

The fundamental particles of which atoms are composed are the ***proton***, ***electron*** and ***neutron***.

Fundamental Particles: Atoms

Dalton (1808)

- atom/element identities and combinations

Five Main Points of Dalton's Atomic Theory:

1. Elements are made of extremely small particles called atoms.
2. Atoms of a given element are identical in size, mass and other properties; atoms of different elements differ in size, mass and other properties.
3. Atoms cannot be subdivided, created or destroyed.
4. Atoms of different elements combine in simple whole-number ratios to form chemical compounds.
5. In chemical reactions, atoms are combined, separated or rearranged.

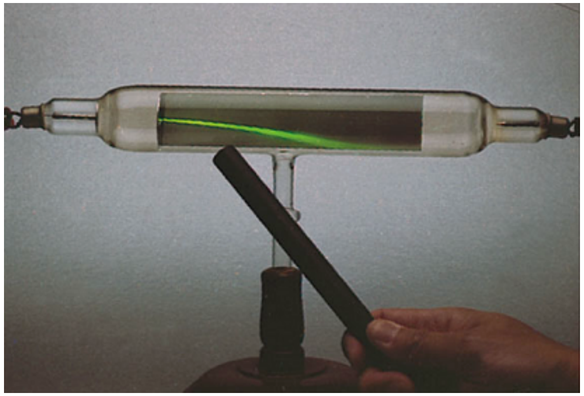
Fundamental Particles: Atoms

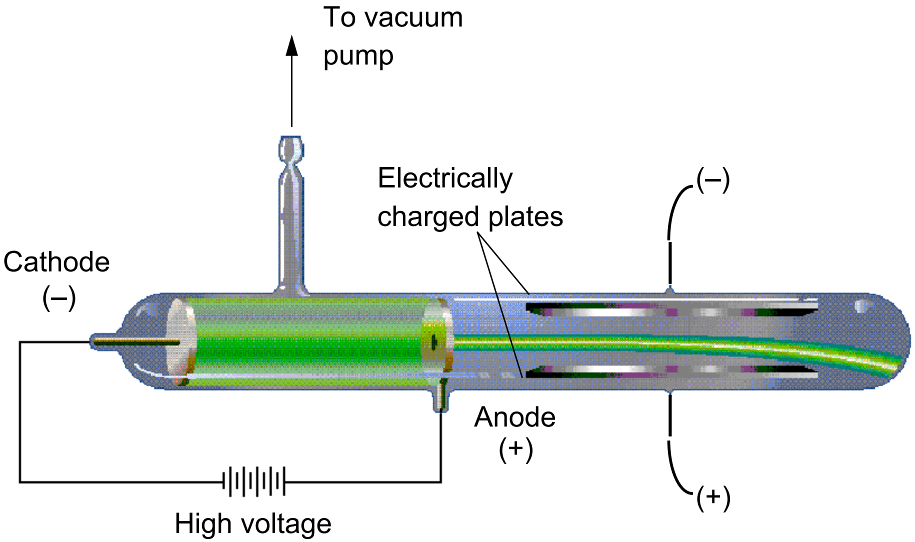
Dalton (1808)

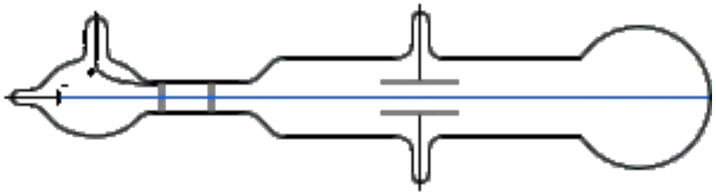
- atom/element identities and combinations

Thomson (1897)

- “cathode rays” consist of negatively charged particles with defined mass
- charge-to-mass (e/m) of electron = -1.759 x 10^8 C/g



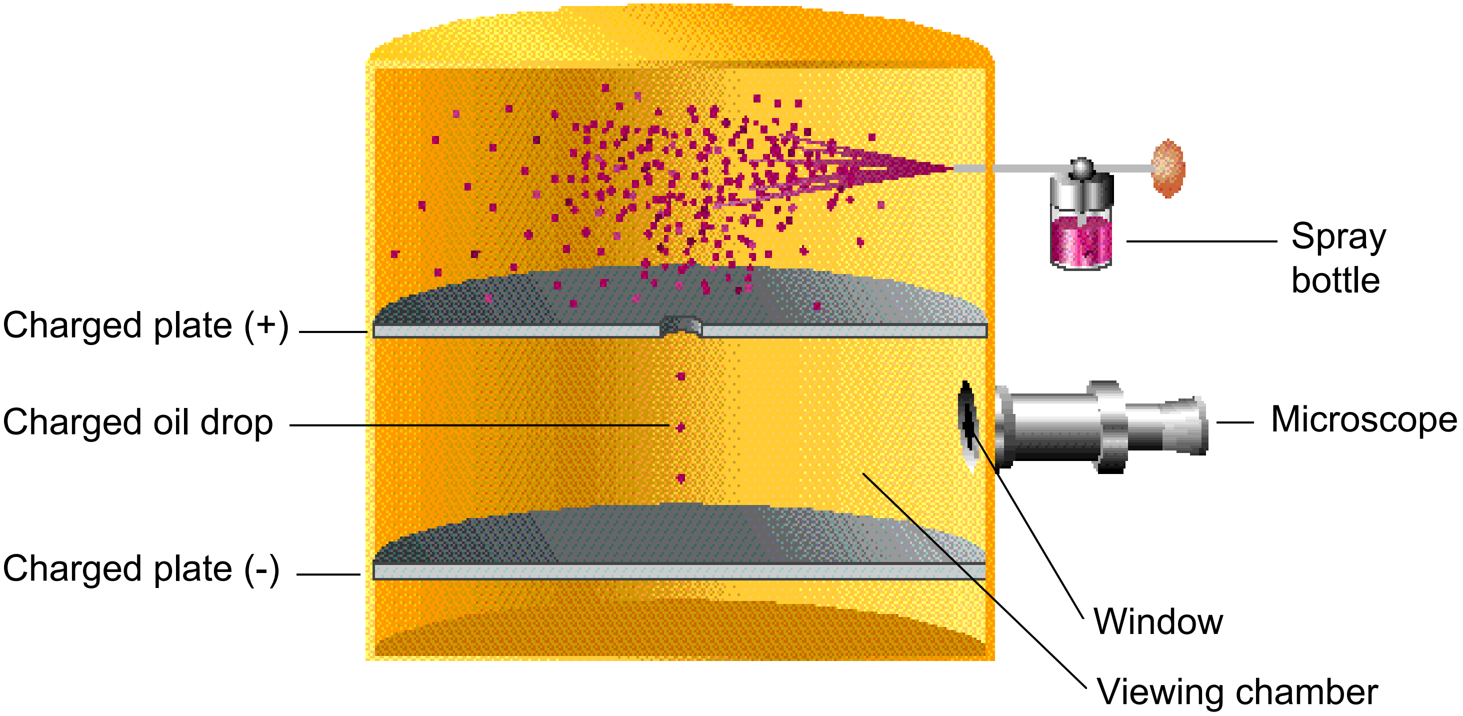




Fundamental Particles: Electrons

Millikan (1909)

- established charge (-1.60 x 10^{-19} C) and, therefore, mass (9.11 x 10^{-31} kg) of an electron

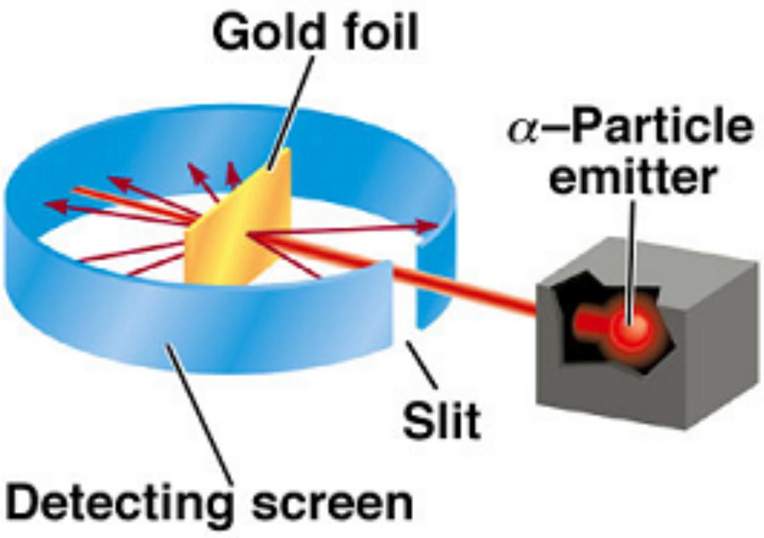


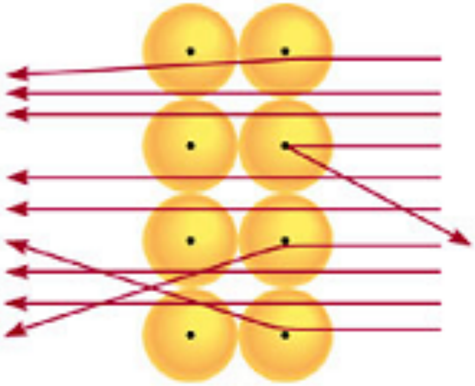
http://www.youtube.com/watch?v=XMfYHag7Liw

Fundamental Particles: Nucleus

Rutherford (1911)

- established the nuclear model of atoms – it's *empty space*!
- gold foil experiment
  - most particles pass straight through the foil
  - Some α-particles were deflected by thin gold foil.
  - Some α-particles rebounded completely





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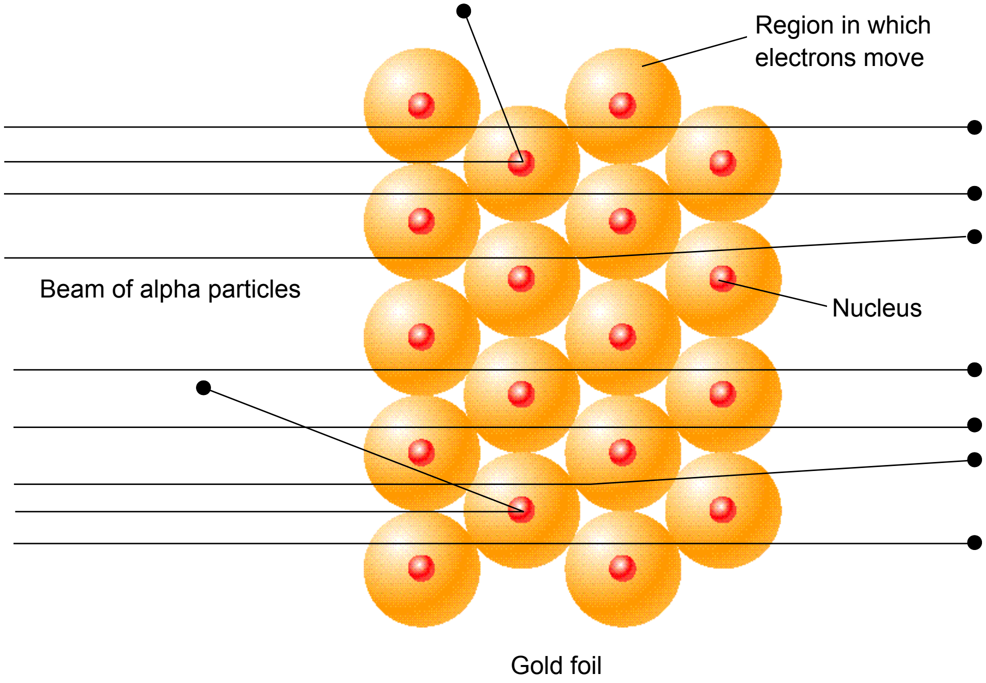


Conclusions: Atoms contain a dense center of positive charge; **NUCLEUS**

Modern View of Atomic Structures

Particle	**Mass (kg)**	**Charge (C)**
Electron	9.11×10^{-31}	-1.602×10^{-19}
Proton	1.67×10^{-27}	$+1.602 \times 10^{-19}$
Neutron	1.68×10^{-27}	no charge

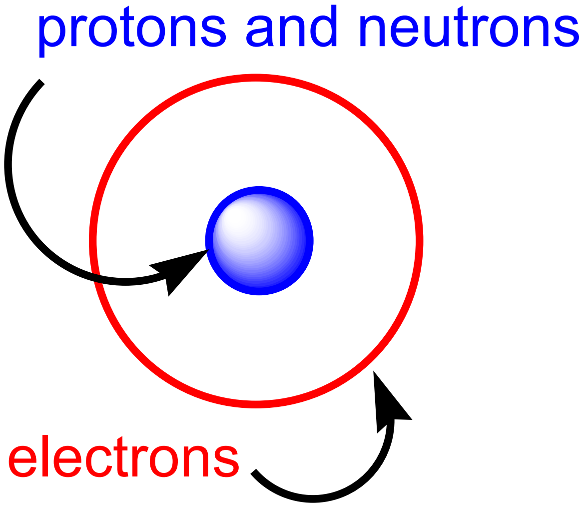
Nuclear radius is 20,000 times smaller than the atomic radius!

Atomic Diameter → **10^{-8} cm**

Nuclear Diameter → **10^{-13} cm**

Nucleus contains protons and neutrons. Electrons balance charge.

Mass of atom is mostly from nucleus, volume of atom is mostly from electron cloud.



Z = Atomic number

= No. of protons

= No. of electrons (neutral atom)

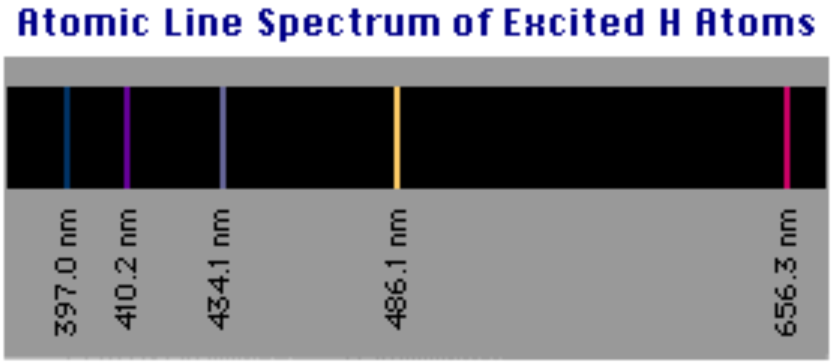
A = Mass number

= No. of protons + neutrons

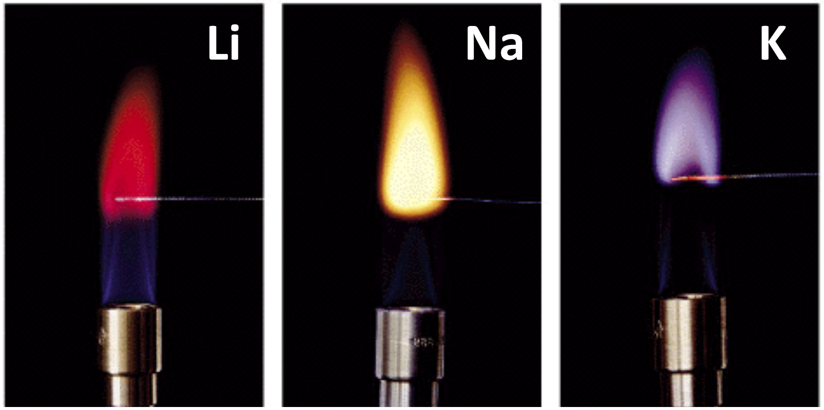
Most chemical properties result from the **number** and **arrangement** of **electrons**.

Emission Spectra from Atoms: A Central Puzzle

Excited (e.g. heat, electric discharge) ***atoms*** in the gas phase produce ***line spectra***: Only specific wavelengths in the visible spectrum are represented.



Excited Group 1 Elements:



Sodium vapour gives off a yellowish light while lithium and potassium generate crimson and violet light, respectively. *Why do these elements radiate different colours?*

Light is Electromagnetic Radiation

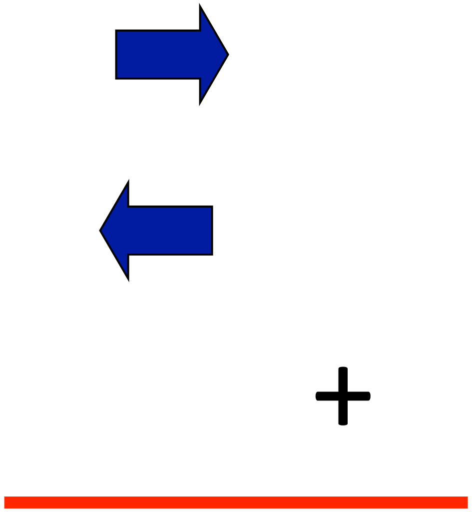
…so are X-rays, radio waves, gamma rays

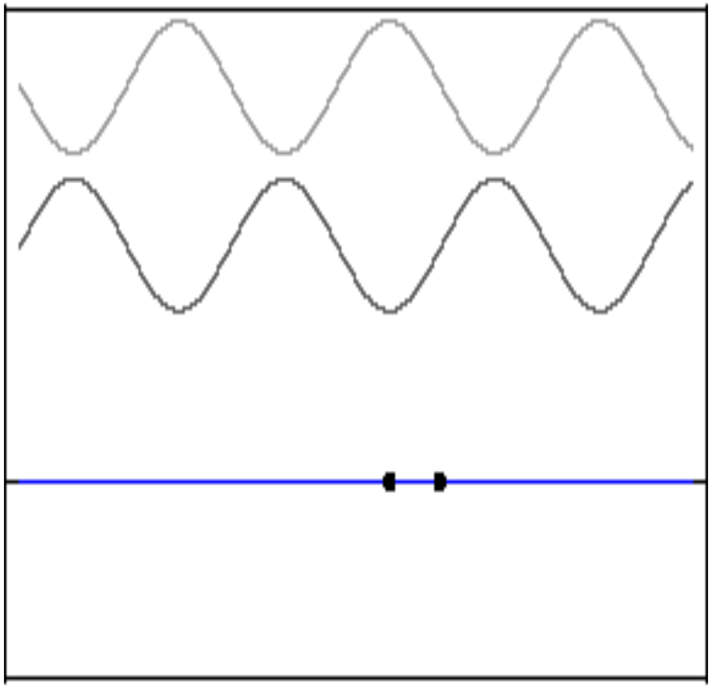
What do they have in common, how do they differ?

A Primer On Wave Motion

Travelling waves

Light, whips, surf, Blue Jay crowds





Standing waves

Skipping ropes, guitar strings

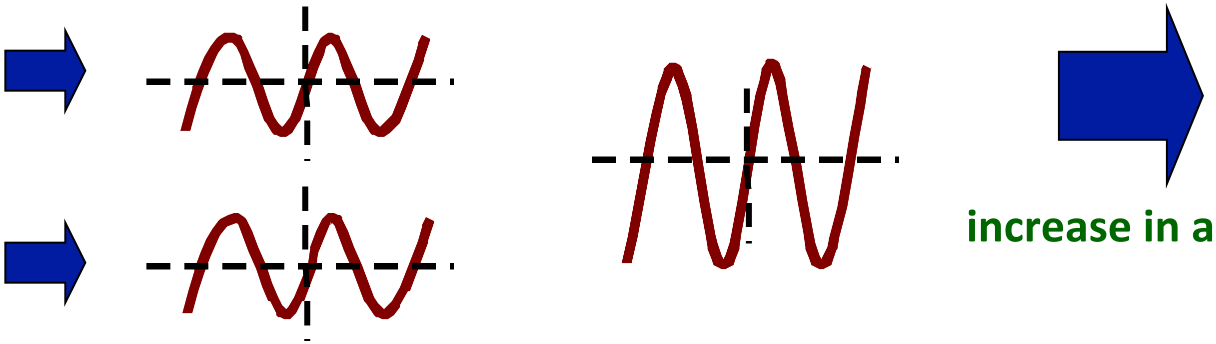
Two opposite *Traveling Waves* superimpose to give a *Standing Wave*.

Wave Motion Continued

Superposition (Interference) of Waves

Constructive Interference

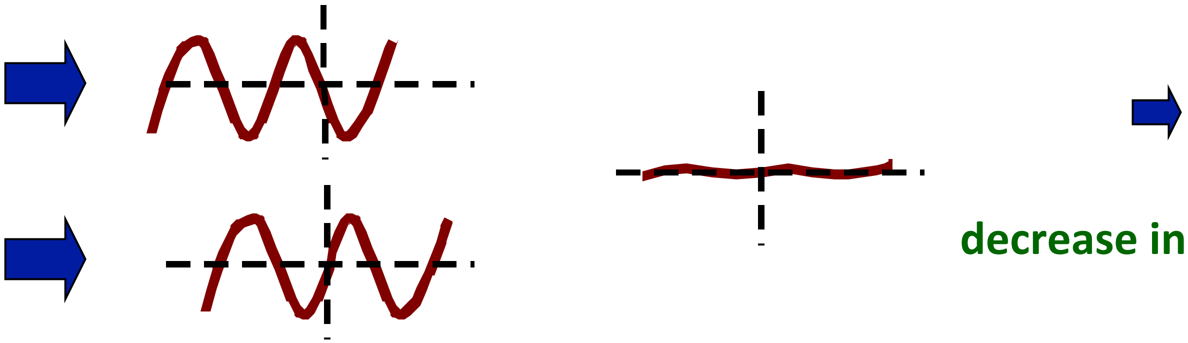
Waves are IN-PHASE



increase in amplitude

Destructive Interference

Waves are OUT-OF-PHASE



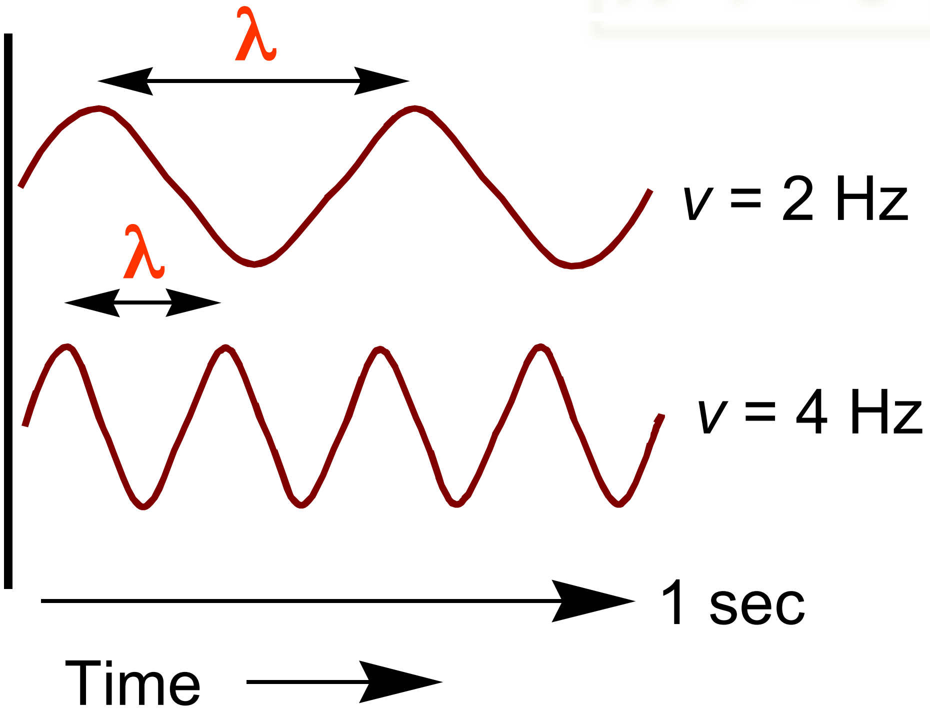
decrease in amplitude

Speed, Wavelength and Frequency

All radiation travels at speed of light, c = 2.997958 x 10^8 m/s

Wavelength λ and frequency ν vary inversely

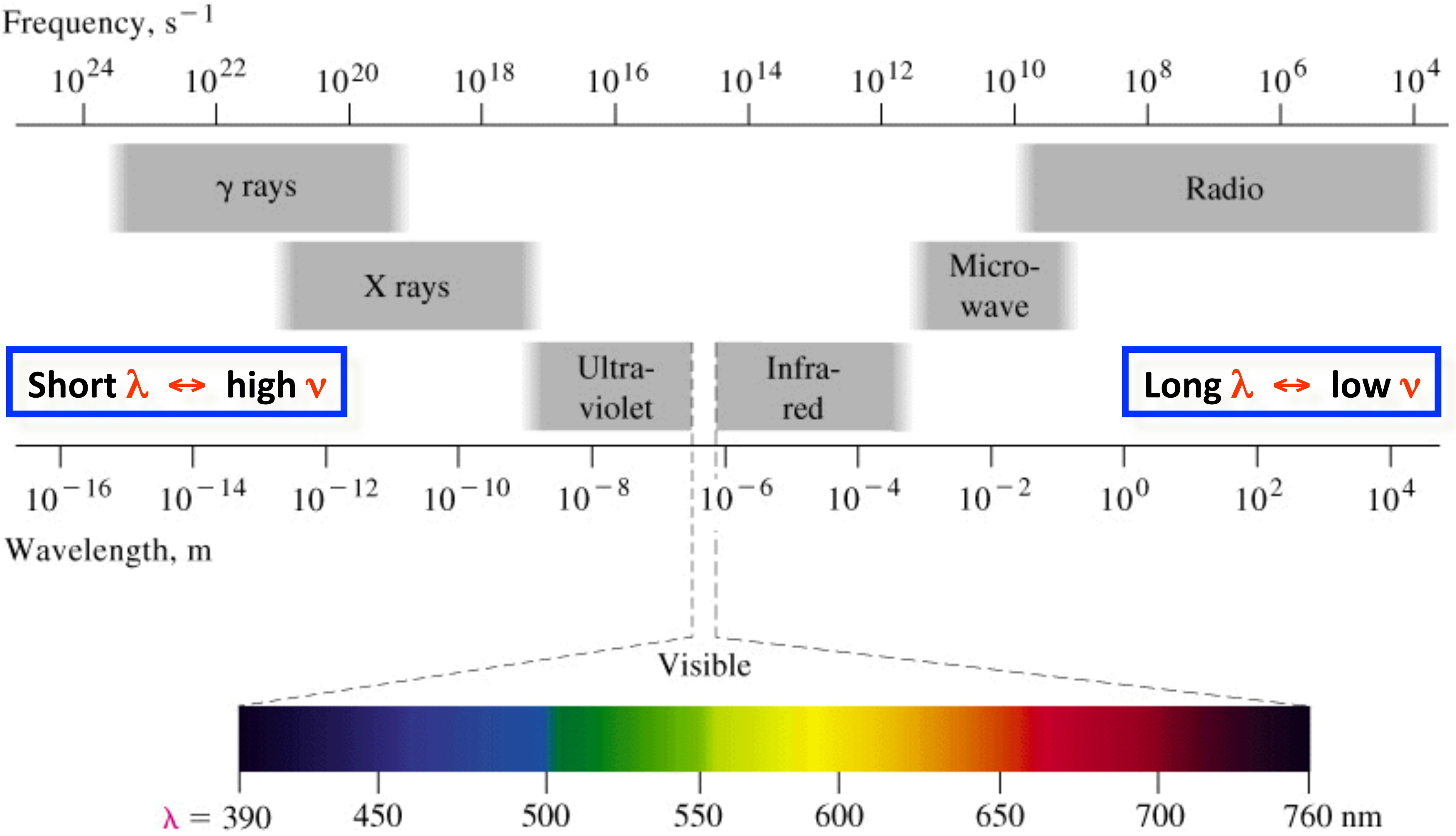
$$\lambda\ \nu = c$$



Long λ ↔ low ν

Short λ ↔ high ν

Electromagnetic Radiation

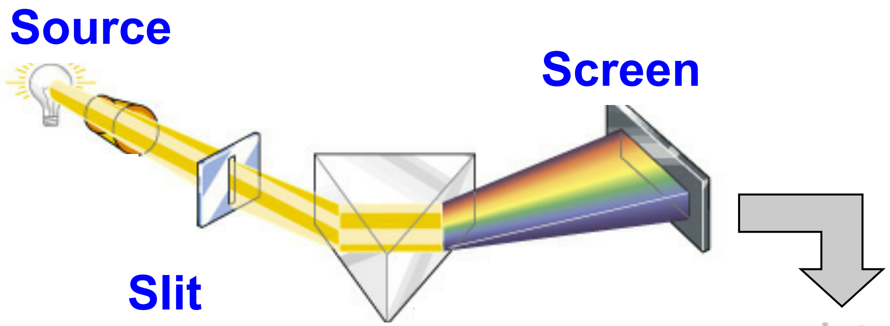


Short λ ↔ high ν

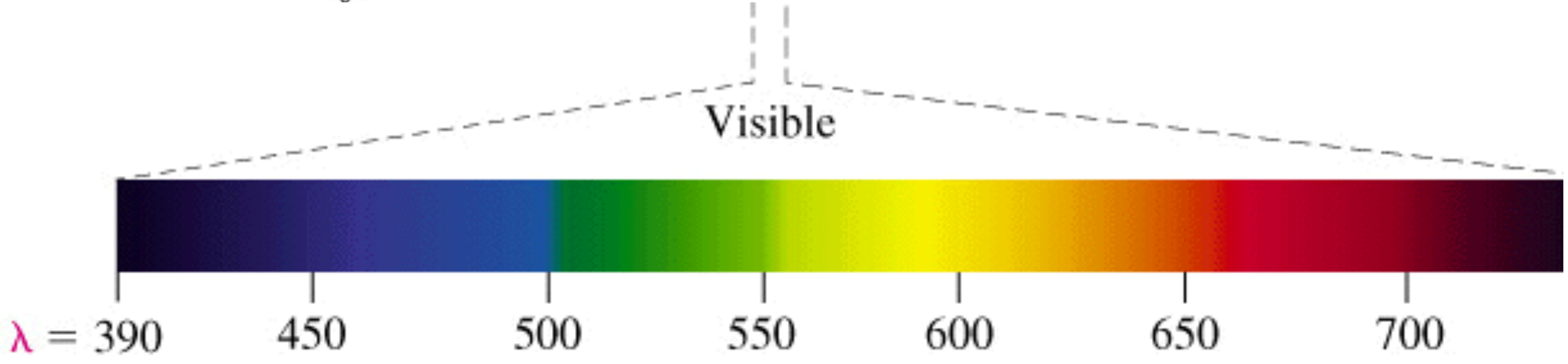
Long λ ↔ low ν

ROYGBIV

The Visible Spectrum



$\boxed{\lambda\ \nu = c}$



Wavelength λ (nanometers, 10^{-9} m)

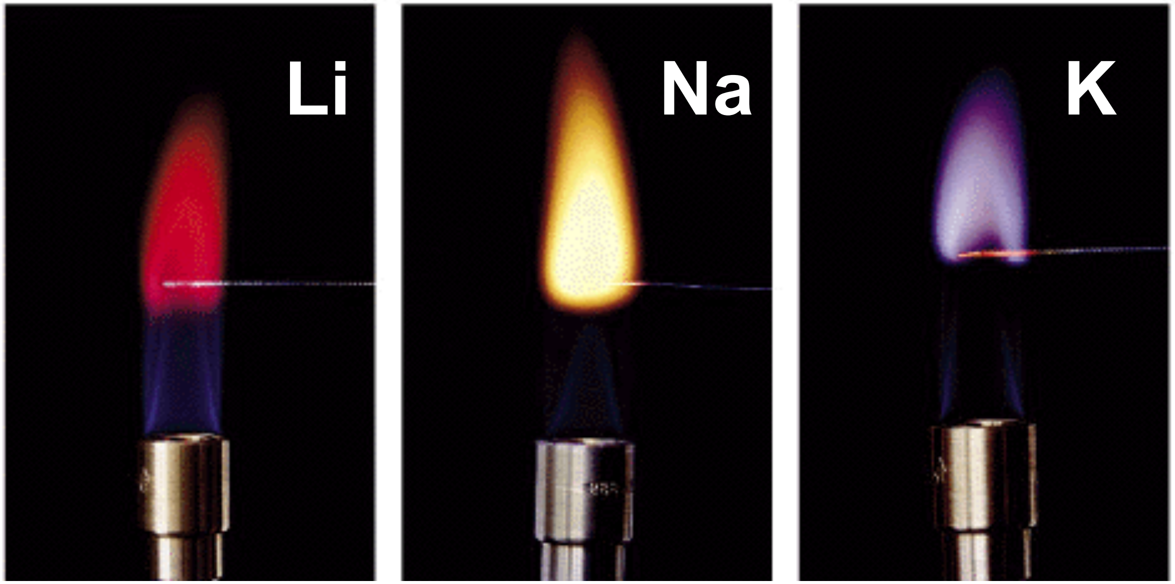
Which colour has the higher frequency?

1 = orange

2 = blue

What is white light?

Excited Group 1 Elements Revisited



Sodium vapour lamps give off a yellowish light (street lighting) with a wavelength of 589 nm.
What is the frequency of this radiation?

But we still haven't determined *why these elements radiate different colours?*

Black Body Radiation

The Concept of Energy Quantization:

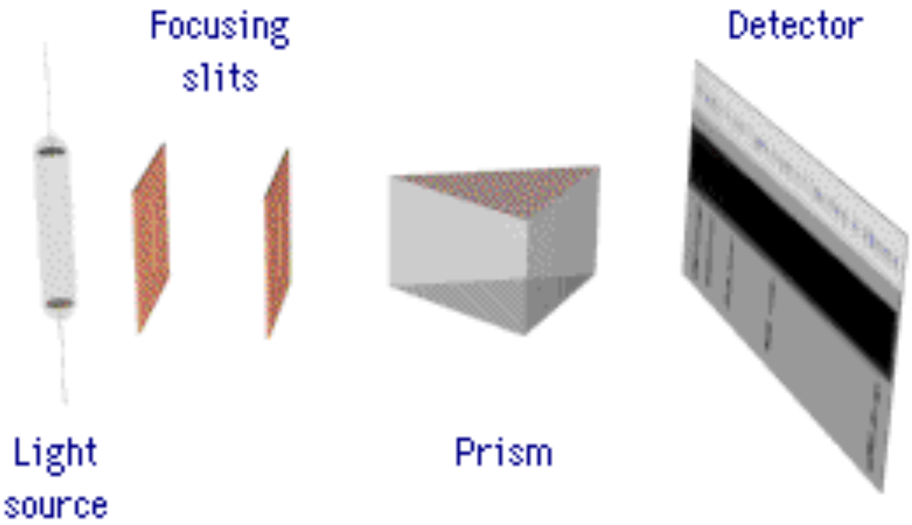
Max Planck studied radiation emitted from black-body spheres. He proposed that matter could be viewed as a bunch of vibrating atoms, each giving off specific (*quantized*) radiant energy that **depended on the frequency of the oscillations.** He suggested that **energy could only be gained or lost in multiples of a fundamental amount – i.e., quantized and only be transferred in units of hν.**

$$E = n(h\nu)$$

ν = Frequency of oscillation
h = Planck's constant = 6.626×10^{-34} J s
n = integer; i.e. 1, 2, 3, 4 etc.

Emission Spectra from Atoms

Every atom has a unique emission spectrum



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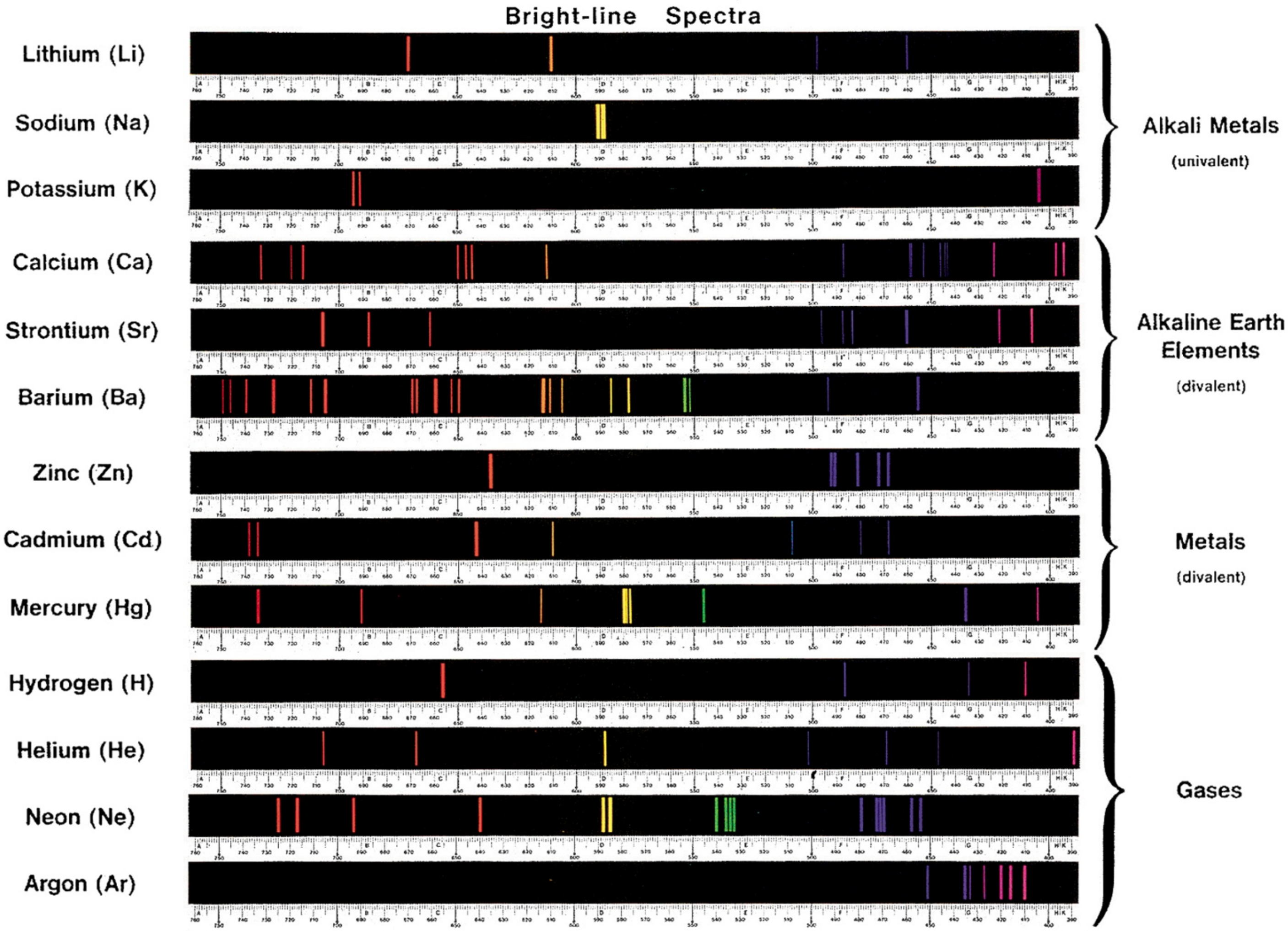


Emission spectra are the ***fingerprint of atoms***

The Line Spectrum of Hydrogen

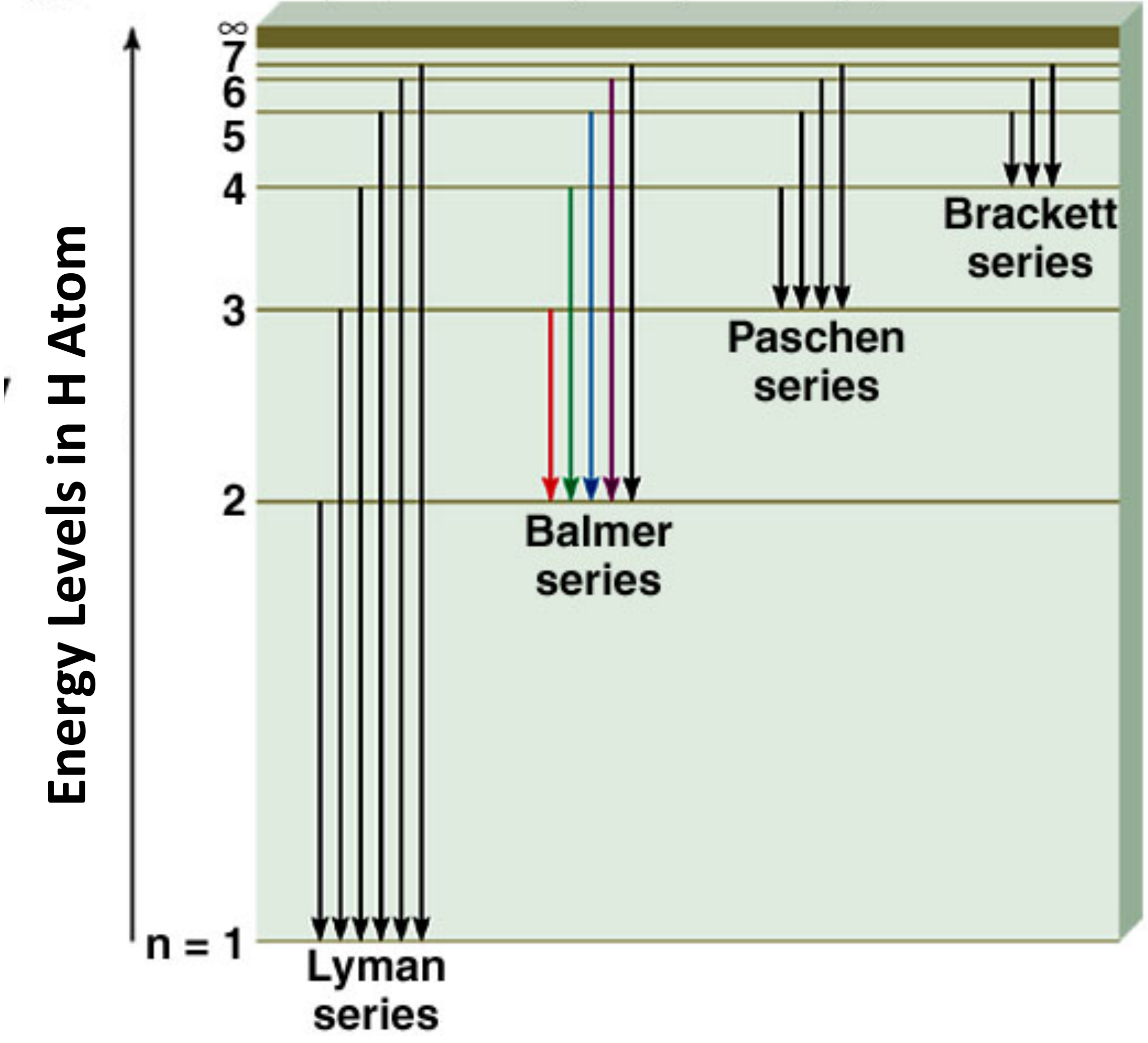
Balmer's original empirical equation: $E = R_H \left(\frac{1}{2^2} - \frac{1}{n^2} \right)$

where E = energy of light emitted from H atom
n = integer greater than 2
R_H = Rydberg constant for hydrogen (2.179×10^{-18} J)

However, Balmer only observed a portion of the spectrum. Generalization to account for spectral lines in the UV and IR regions:

$$E = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad \text{where } n_1 < n_2$$

Electronic Transitions in the Hydrogen Atom



Series are defined by lowest energy state:

Lyman Series
- ↳ Ultraviolet emission ($n_1 = 1$)

Balmer Series
- ↳ Visible emissions ($n_1 = 2$)

Paschen Series
- ↳ Infrared emissions ($n_1 = 3$)

Brackett Series
- ↳ Far Infrared emissions ($n_1 = 4$)

Pfund Series
- ↳ Far Infrared emissions ($n_1 = 5$)

Humphreys Series
- ↳ Far Infrared emissions ($n_1 = 6$)

Explaining the Line Spectra of Atoms

Early 20th Century View of the Atom

The common view of the atom in the early 1900's was the following:

1) Atoms contain protons and electrons
2) Electrons traveled in orbits around the nucleus at high velocities.
   - ↳ With this model, any orbit is possible
   - ↳ Any electron can be in any orbit, so any energy is possible.

This is not consistent with experiment or even with the observation of stable atoms!

It took nearly 100 years of science to explain line spectra of atoms. Major advancements came from:

1) **Niels Bohr (Quantization of electron energies)**
2) **Louis de Broglie (Wave-Particle Duality)**
3) **Werner Heisenberg (Uncertainty Principle)**
4) **Erwin Schrödinger (Wave Equation)**

In explaining the line spectra of atoms, a picture of the *electronic structure of atoms* emerged.

Energy of an Electron in a Bohr Atom

Bohr assumed that the electron was able to stay in an orbit around the nucleus because of a balance between two forces.

Coulombic force of attraction = $Ze^2/4\pi\varepsilon_o r^2$
centrifugal force acting on the electron = mv^2/r

Z = number of charges on the nucleus (1 for H)
e = charge on the electron (C)
r = distance between electron and nucleus
m = mass of the electron
v = velocity of the electron
$4\pi\varepsilon_o$ = permittivity of vacuum

Balancing the two forces gives:

$$Ze^2/4\pi\varepsilon_o r^2 = mv^2/r \quad \Rightarrow \quad v^2 = Ze^2/4\pi\varepsilon_o rm$$

Energy of an Electron in a Bohr Atom

Bohr also assumed that the angular momentum of the electron was *quantized* so that it could only have values given by :

$mvr = nh/2\pi$ where n is an integer = 1,2,3,4 etc.

which leads to:

$$v^2 = n^2h^2/(2\pi)^2(mr)^2$$

And from balancing the Coulombic attraction and centrifugal forces we know:

$$v^2 = Ze^2/4\pi\varepsilon_o rm$$

By equating the two expressions we can calculate the radius of the electron orbit:

$$r = n^2h^2\varepsilon_o/\pi me^2Z$$

Note:
This expression contains a series of constants with only one variable, **n**.

When n = 1 we have the first Bohr radius, a_0 = 0.0529 nm. As n increases, the value of r increases and the electron is further away from the nucleus.

Energy of an Electron in a Bohr Atom

Using kinetic energy (1/2 mv^2) we can find E for each value of n.

$$E = -\frac{2\pi^2\mu Z^2 e^4}{(4\pi\varepsilon_o)^2 h^2}\left(\frac{1}{n^2}\right) = -R_H\left(\frac{1}{n^2}\right)$$

n = quantum number = 1, 2, 3, 4, etc. (integers only!)

μ = reduced mass of electron-nucleus combination

$$\frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{m_{nucleus}}$$

m_e	mass of electron, 9.11×10^{-28} g
$m_{nucleus}$	mass of nucleus
Z	charge of nucleus
e	charge of electron; -1.60×10^{-19} C
h	Planck's constant, 6.626×10^{-34} J•s
$4\pi\varepsilon_o$	permittivity of a vacuum

Constants!

Rydberg Constant, R_H

$$R_H = \frac{2\pi^2 \mu Z^2 e^4}{(4\pi\varepsilon_o)^2 h^2} = 2.179 \times 10^{-18} \text{ J}$$

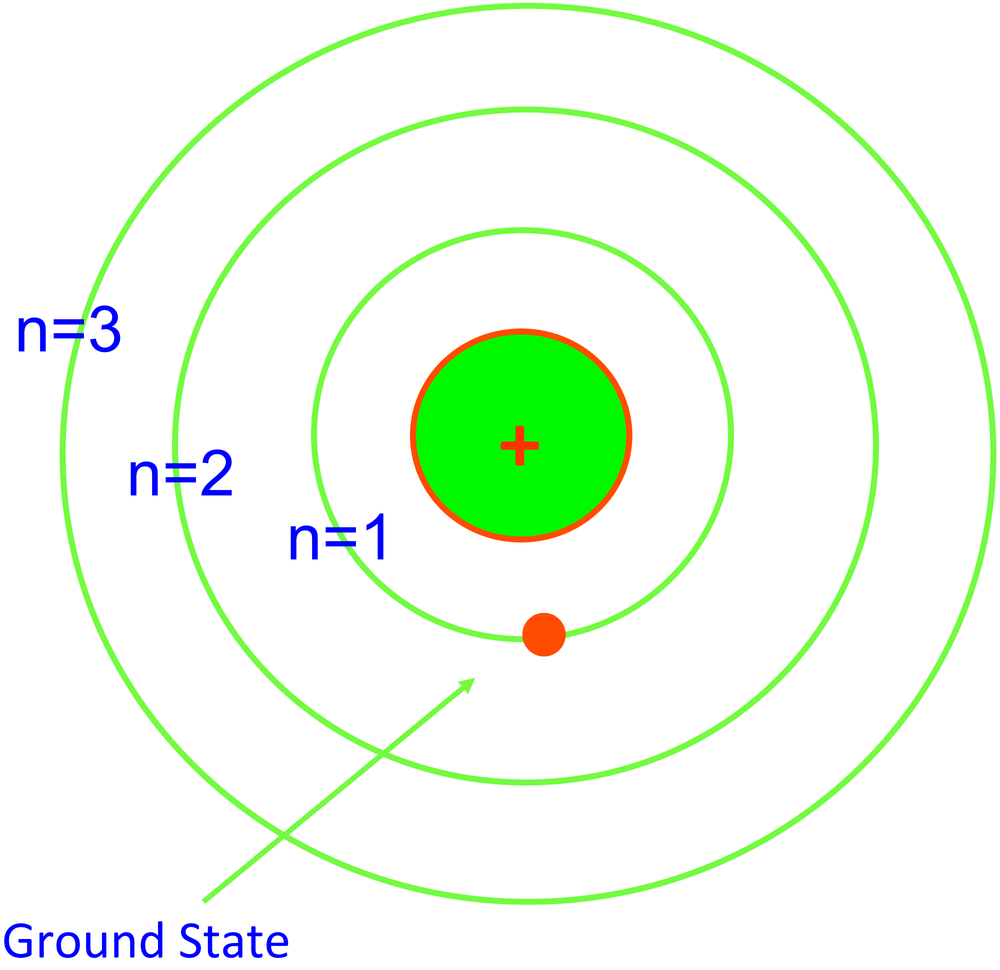
<u>Notes about E (energy of an electron in a hydrogen atom):</u>

1) E is a function of only one variable, n, and a series of constants represented by R_H.
2) n can only have integer values, thus **energy is quantized and can only have certain values**.
3) E is negative due to attractive force between nucleus and electron. Large negative means electron is more stable (closer to nucleus).

$$E_n = -R_H \left(\frac{1}{n^2} \right)$$

The Bohr Model of the Hydrogen Atom

Quantization of electron energies



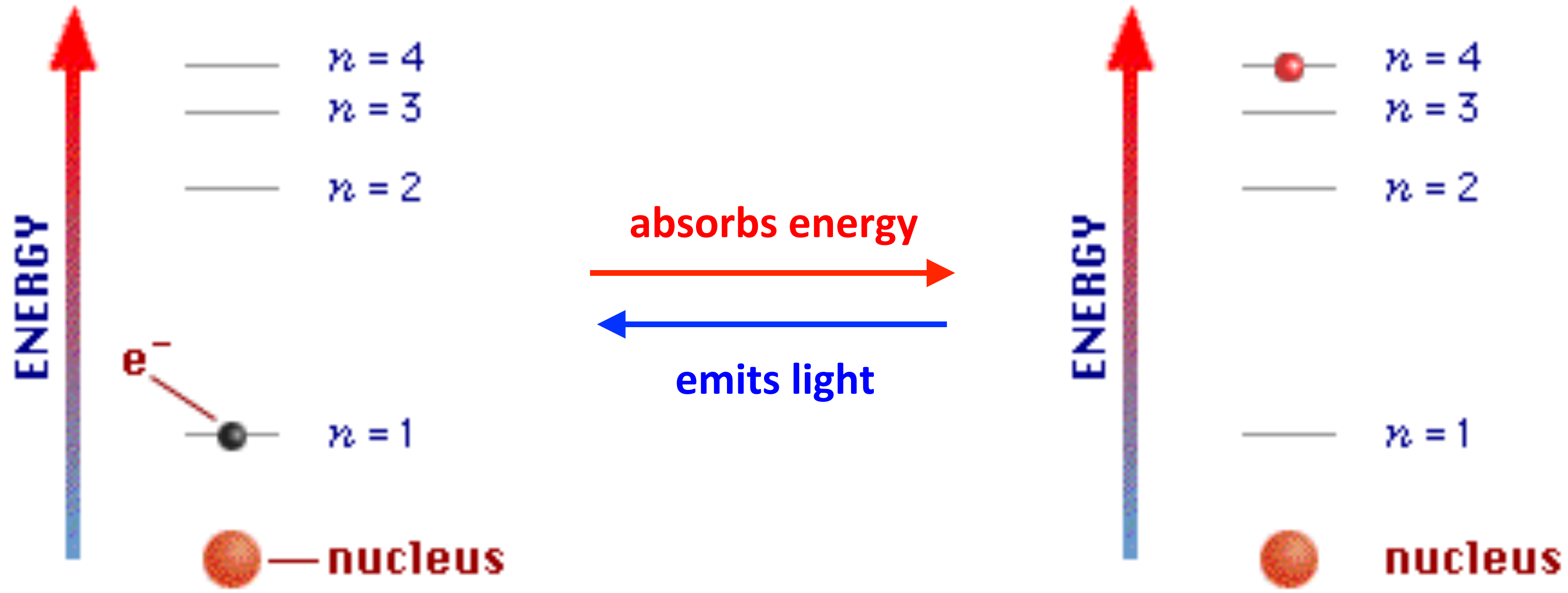
Electrons occupy specific energy levels, identified by a quantum number, n = 1 to ∞.

n = 1 corresponds to the ***lowest energy state*** or ***ground state***.

n > 1 corresponds to

n > ∞ corresponds to

Bohr Model Explanation of Line Spectrum



1. When an atom absorbs energy, an electron jumps from the lower energy ***ground state*** to a higher energy ***excited state***.

2. When the electron returns to the ***ground state*** , it ***emits*** energy in the form of light.

Bohr Model Explanation of Line Spectrum

Energy of light emitted = energy of excited state - energy of ground state

+

$E_n = -R_H\left(\frac{1}{n^2}\right)$

Energy of light = $E_h - E_l = -R_H\left(\frac{1}{n_h^2} - \frac{1}{n_l^2}\right) = R_H\left(\frac{1}{n_l^2} - \frac{1}{n_h^2}\right)$

Example 1: What energy of light is emitted in the electronic transition from n = 2 to the ground state (n = 1) in a hydrogen atom?

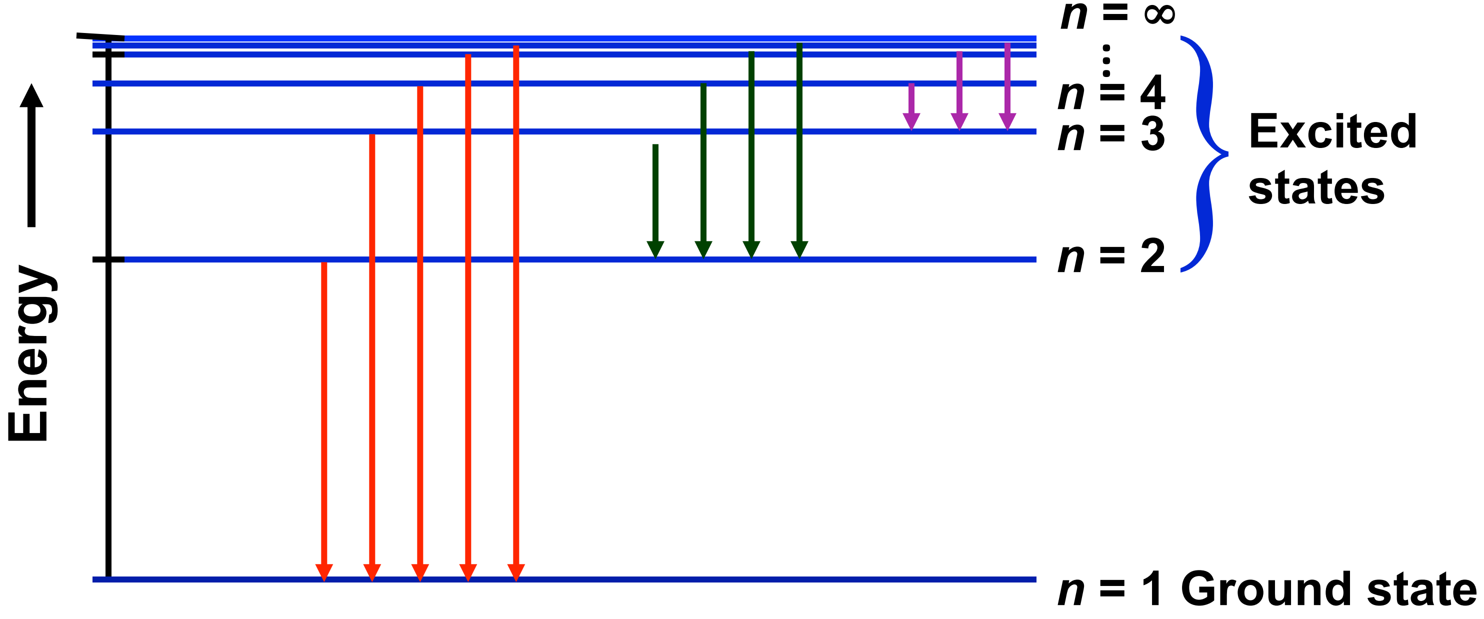
Example 2: What wavelength of light does this energy change correspond to?

Hydrogen Emission Spectrum Revisited

For the **Lyman** series, $n_f = 1$ and $n_i = 2, 3, 4 \ldots$

For the **Balmer** series, $n_f = 2$ and $n_i = 3, 4, 5\ldots$

For the **Paschen** series, $n_f = 3$ and $n_i = 4, 5, 6\ldots$



Spectroscopic Line Frequencies

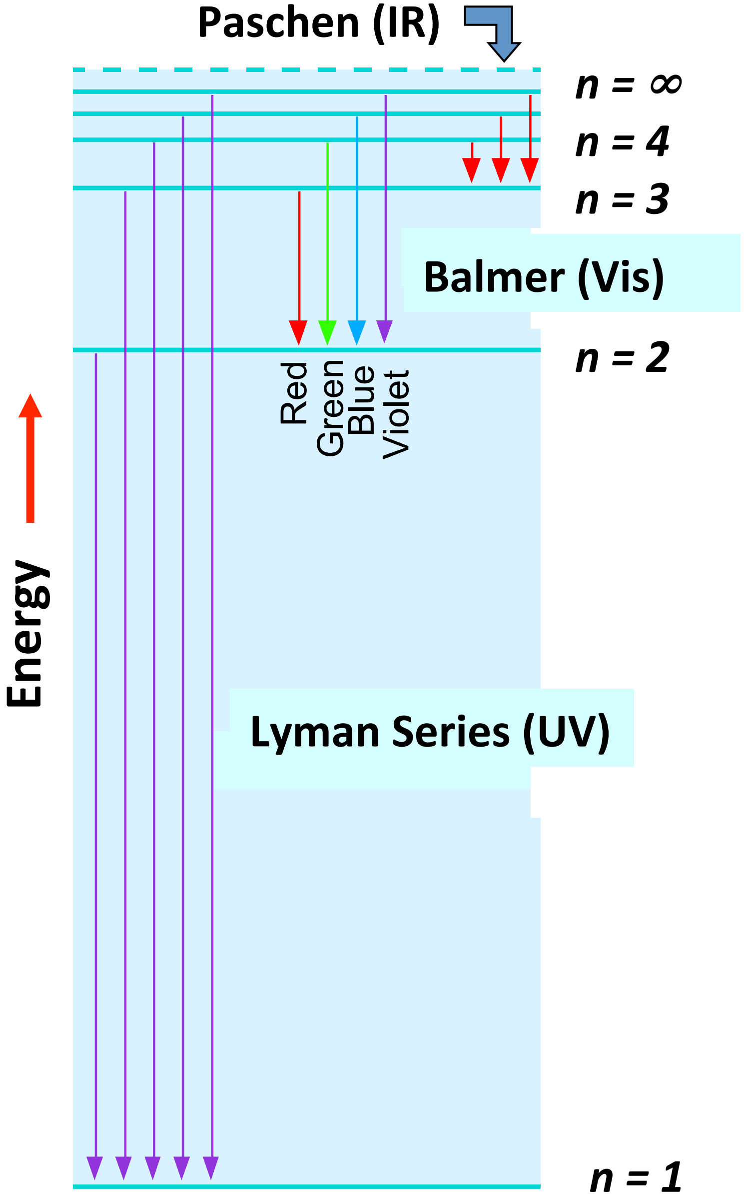
Exercises:

1. Derive the frequency of 1st line of Balmer series for H atoms.

2. Derive the wavelength of 3rd line of Paschen series for H atoms.

3. Calculate the frequency of the 1st Lyman line for H atoms.

4. Predict the ionization energy for H atoms.



Evaluation of the Bohr Model

Success: It explains the observed line spectrum of the hydrogen atom.

Bohr won the Nobel Prize in 1922

Challenges: It does NOT explain the line spectrum of any other element!

The Bohr Conundrum and the de Broglie Solution

Problem: Orbiting electrons should emit light, lose energy and spiral down and "burn up" in the nucleus; *the atom should collapse*.

Solution: *De Broglie* (1924)* proposed that an electron (all matter) is associated with a wavelength - *just like light*.

**Davison and Germer* (in 1927) demonstrated that electrons have wave properties - show interference fringes like X-rays.

de Broglie and Wave-Particle Duality

de Broglie (1924)

- proposed that *all moving objects have wave properties*.

For any particle:

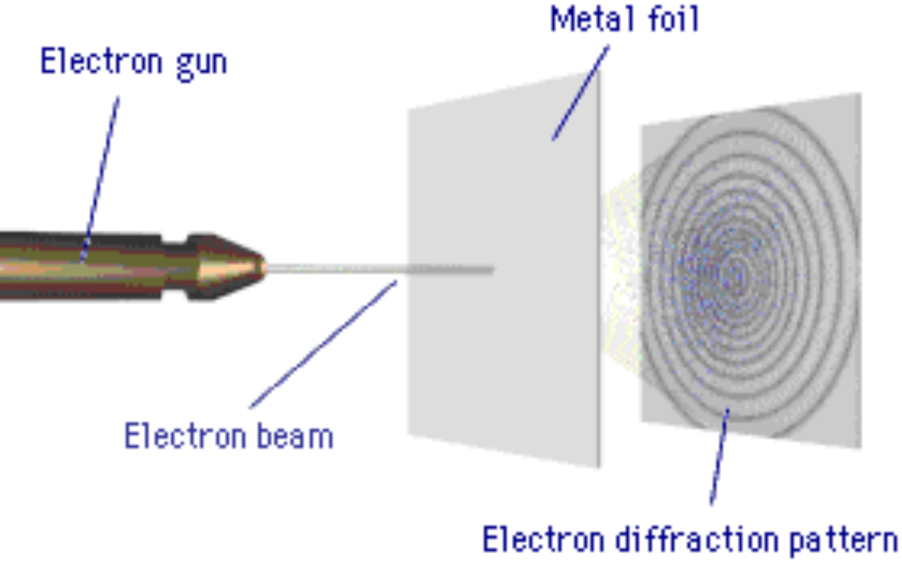
momentum ⇨ $$m\,v = \frac{h}{\lambda}$$

h ⇦ **Planck's constant**

λ ⇦ **wavelength**

The wavelength of a particle is related to its mass and velocity

Experimental Evidence of Wave Properties of Electrons:



When electrons pass through a thin metal foil, they create a diffraction pattern, due to constructive and destructive interference of waves.

Electrons have characteristics
of both waves and particles.

This is called ***wave-particle duality***

Wave Properties of Moving Objects

$$\boldsymbol{\lambda = h/mv}$$

Large objects have tiny wavelengths (undetectable):

A 115 g ball moving 100 mph has $\lambda = 1.3 \times 10^{-32}$ cm

Small objects have larger, observable wavelengths:

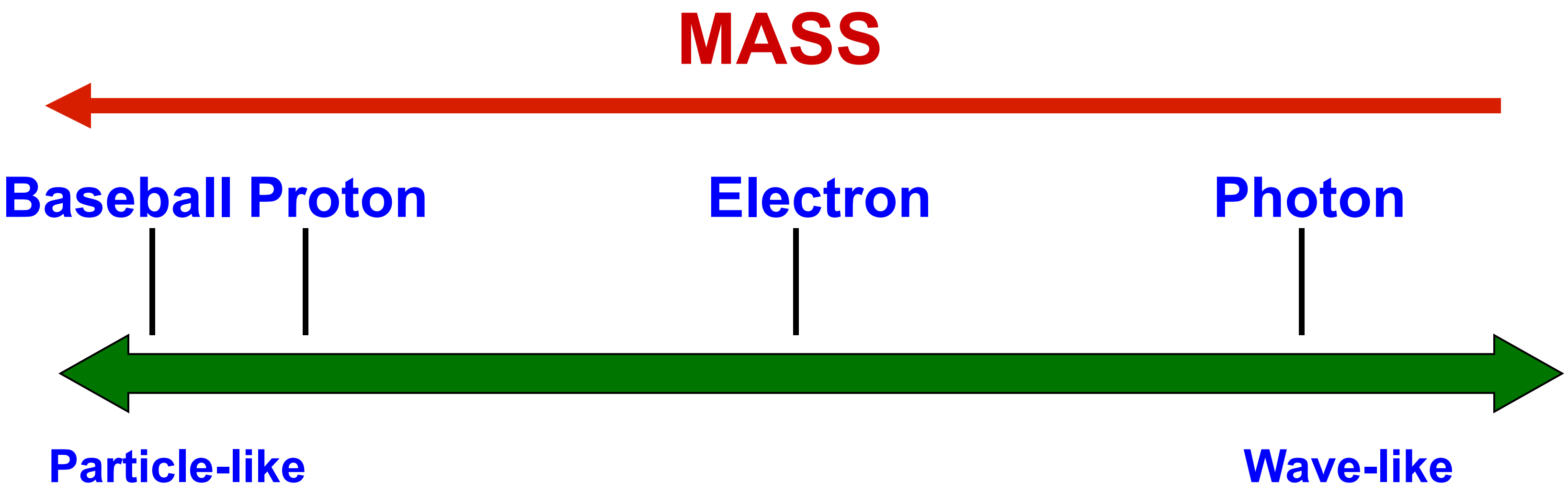
An electron with velocity = 1.9×10^{8} cm/s has $\lambda = 0.383$ nm

The behavior of electrons in atoms can be explained by treating the electrons as waves.

Exercise: Compute the de Broglie Wavelength of (1) a tennis ball (mass 0.1 kg) moving at 10 m/s and (2) an electron (mass 9.11×10^{-31} kg) moving at 10^6 m/s (1% speed of light) in an atom.

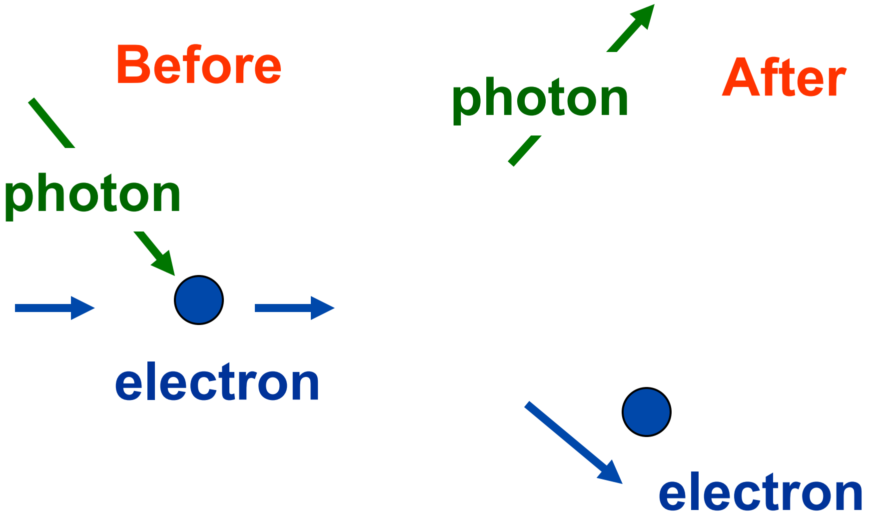
Wave-Particle Duality…A Summary

- All matter and energy shows both particle-like and wave-like properties.
- Large pieces of matter are mainly particle-like, with very short wavelengths.
- Small pieces of matter are mainly wave-like with longer wavelengths.



Heisenberg Uncertainty Principle

Quantum theory puts a limit on the precision of measurements; *the act of measurement changes what you're trying to measure.* We cannot know both the exact position and the exact momentum of a particle. . .



Before

photon

electron

After

photon

electron

$$\underbrace{\Delta\,(mv)}_{\text{Error in momentum}} \times \overbrace{\Delta\,(x)}^{\text{Error in position}} \;\geq\; h/4\pi$$

Speed and direction of electron changes following collision with photon. . . however, they have similar wavelengths (i.e., momentum).

Heisenberg Uncertainty Principle

It is impossible to simultaneously know both the position of a particle and the particle's momentum with certainty.

$$\Delta x \Delta p \geq \frac{h}{4\pi}$$

Δx	uncertainty in position of object
Δp	uncertainty in momentum (mass x velocity) of object

- From spectral lines, we can precisely determine the energies of electrons in atoms.
- From electron energies, we can determine electron momentum with little uncertainty (Δp is small).
- Thus, uncertainty in position of electron (Δx) is large.

If a 145 g baseball has a speed of 22 m/s with an uncertainty of 1.5%, with what precision can we measure the position of the baseball?

If an electron has a speed of 2.05×10^6 m/s with an uncertainty of 1.5%, with what precision can we measure the position of the electron?

Heisenberg Uncertainty Principle

Particle Size:

For large (macroscopic) particles: uncertainty in position or velocity is negligible *relative to the size of the object.*

For small (subatomic) particles: uncertainty in position or velocity is enormous *relative to the size of the object.*

Consequences of Heisenberg Uncertainty Principle:

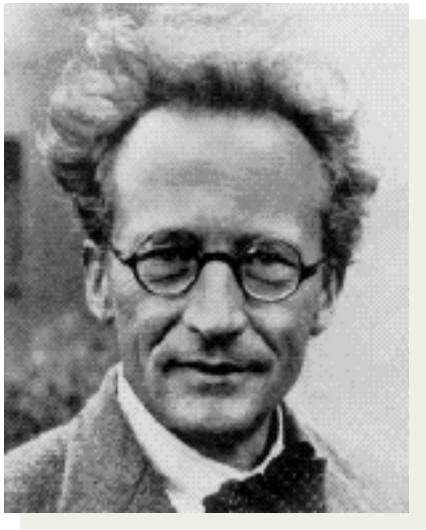
We cannot describe ***precise orbits*** of electrons (as was attempted in the Bohr model).

We can only describe electron ***orbitals***: regions in space where there is a high probability of finding an electron.

From mathematical descriptions of orbitals, we can predict the ***probability*** of finding an electron at a particular location.

The Schrödinger Wave Equation

In its simplest form: $H\,\psi = E\psi$



E. Schrödinger
1887-1961

<u>Premise of equation:</u>
electrons have wave properties

<u>Solutions to equation:</u>

ψ: the ***wave function*** or the ***region*** in space where an electron has some ***probability*** of being found (atomic orbitals)

E: the ***energy*** of the electronic state represented by ψ

The Hamiltonian Operator, H

$$H\psi = E\psi$$

H = the Hamiltonian operator

An ***operator*** is an instruction that explains the mathematical manipulation that should be carried out on the function that follows it.

For example we can define H to mean “divide the function by 2”
Define the function, $\psi = 4x$:

$$H\psi = \psi/2 = (4x)/2 = 2x$$

The Schrödinger Equation

The Schrödinger Equation can be translated as saying:

> *"Find a function ψ which, when the operation specified by H is performed on it, it gives back the same function multiplied by E (the electron's energy)."*

$$H\,\psi = E\psi$$

(operator)(function) = (numerical factor) x (same function)

The operation can be performed on any wave function describing an atomic orbital. Each orbital has its own *characteristic* energy, E, and wave function, ψ.

Example: Suppose the operator was an instruction to differentiate a function twice.
We need to find a function that when differentiated twice, gives us the same function.

e.g., $\psi = \sin x$;

The Hamiltonian Operator

In quantum mechanics, the ***Hamiltonian*** is the *operator* corresponding to the total energy of the system.

$$H = \underbrace{\frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)} + \underbrace{V(x,y,z)}$$

h = Planck's constant

m = mass of the particle

V(x,y,z) = **potential** energy resulting from electrostatic attraction between the electron and nucleus.

The Hamiltonian Operator

The ***Hamiltonian Operator*** instructs us to mathematically manipulate the wave function as follows.

$$\left[\underbrace{\frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)}_{A}\underbrace{+V(x,y,z)}_{B}\right]\psi(x,y,z)=E\psi(x,y,z)$$

A. Take the second derivative of the wave function with respect to x, y, and z then multiply the result by $-h^2/8\pi^2 m$

B. Multiply the wave function by the potential energy

C. Add together the results from A and B to get the wave function multiplied by E

Interpretation of Wave Function, ψ

ψ is a mathematical function, and it is hard to ascribe a physical meaning to it. However,

ψ^2 represents the ***probability of finding an electron at a given point***.

large ψ^2 means greater probability of finding an electron
small ψ^2 means lower probability of finding an electron

Some Conditions on ψ

1. ψ must be single-valued. If ψ had more than one value at a given point, then ψ^2 would have more than one value, meaning there would be two different probabilities of the electron being at one given point. This is nonsense.
2. ψ and its first derivatives must be continuous. The probability must be defined at all positions in space and cannot change abruptly from one point to the next.
3. ψ must approach zero as r (distance from nucleus) approaches infinity. The probability of finding an electron decreases farther from the nucleus.
4. The probability, summed over all space, of finding an electron must be equal to 1. i.e. The electron MUST be somewhere!

How are Electrons Viewed in Atoms?

Bohr: Electrons energies are quantized

De Broglie: Electrons are "matter waves" (wave-particle duality)

Heisenberg: We cannot determine an electron's precise position (Uncertainty Principle)

Schrödinger's Wave Equation: $H\psi = E\psi$

The wave function ψ gives us a description of an electron (as a wave) in an atom.

E gives us the energy of that electron

Solving Wave Equations

The mathematics of the wave equation for the hydrogen atom is very complex
(we won't be solving it here).

HOWEVER

A simple illustration of a wave equation is a *"PARTICLE IN A ONE-DIMENSIONAL BOX."*

3-Dimensional Wave Equation: (electron in an atom)

$$\left[\frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)+V(x,y,z)\right]\psi(x,y,z)=E\psi(x,y,z)$$

Simplify:

1-Dimensional Wave Equation: (particle in a one-dimensional box – a model)

$$\left[\frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2}\right)+V(x)\right]\psi(x)=E\psi(x)$$

Particle has mass, m, and can move only along the x-axis.
("y" and "z" variables are eliminated from 3-D equation)

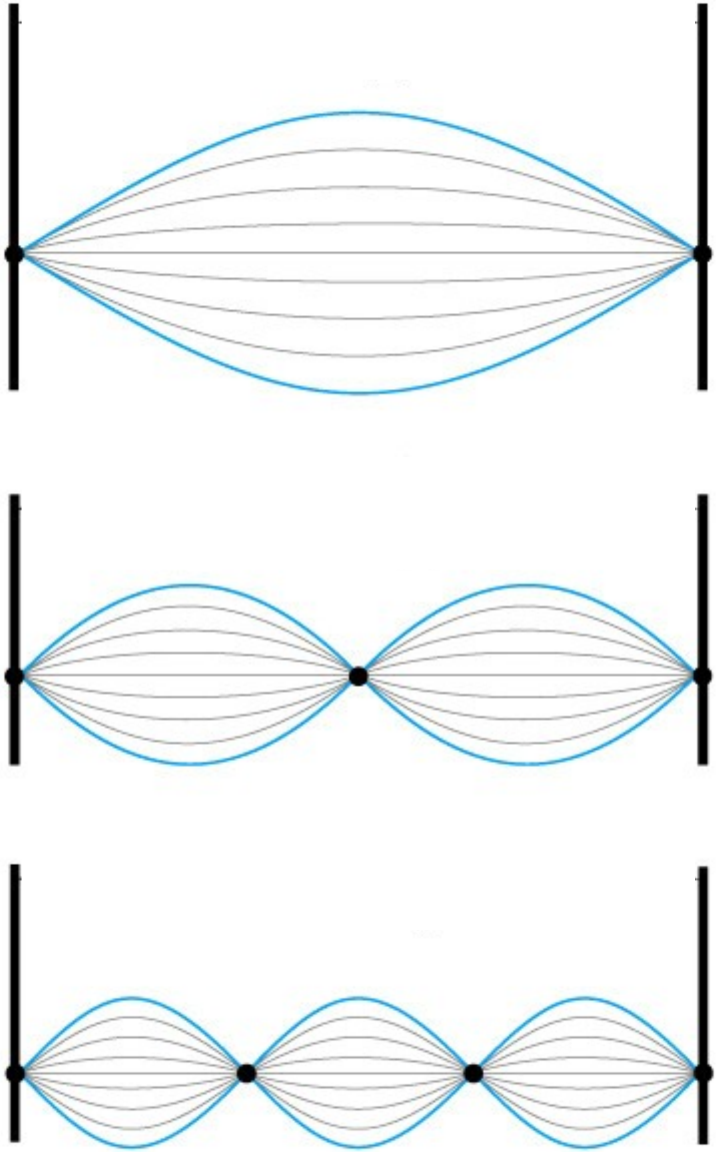
Wave Mechanics

Properties of Standing Waves:

1. Peaks and troughs occur at **<u>fixed</u>** positions (unlike a traveling wave)
2. Amplitude at fixed ends is zero
3. Wave amplitude varies from point to point
4. At points called **<u>nodes</u>** there is no displacement (amplitude = zero)
5. The full length of the string is equal to an ***integral number of ½ wavelengths***

i.e., wavelength is quantized!

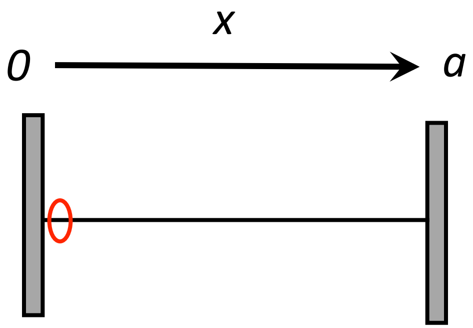
Electrons, as standing waves, must exhibit these characteristics!



A Particle in a One-Dimensional Box

<u>Defined Boundary Conditions (The Box):</u>

1. The particle can only move between the points x = 0 and x = *a* on the x axis.

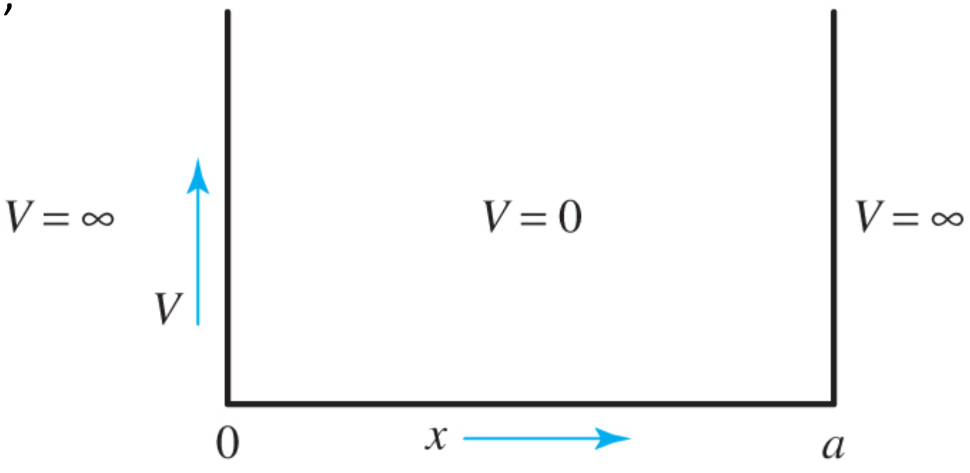


2. Outside of the boundaries x = 0 and x = *a*, V(x) is infinite, preventing the particle from existing in this region.

   $V(x) = \infty$ when $x < 0$ or $x > a$

3. The particle has zero <u>potential</u> energy when it is located anywhere within the points x = 0 and x = *a*.

   $V(x) = 0$ when $x \geq 0$ <u>and</u> $x \leq a$



A Particle in a One-Dimensional Box

Defined Boundary Conditions (The Box):

4. The probability, summed over all space from x = 0 to x = *a*, of finding an electron must be equal to 1. i.e. The electron MUST be somewhere in the box!

$$\int_{allspace} \psi_A^2 dx = 1$$

This is called "normalization" of the wave function.
This is another way of saying that the electron **must be somewhere!**

Examples:
- Tossing a coin
- Rolling a die

Using the Boundary Conditions to Solve the 1D Wave Equation

After applying boundary condition 3, the wave equation simplifies:

$$\left[\frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2}\right)\cancel{+V(x)}\right]\psi(x)=E\psi(x)$$

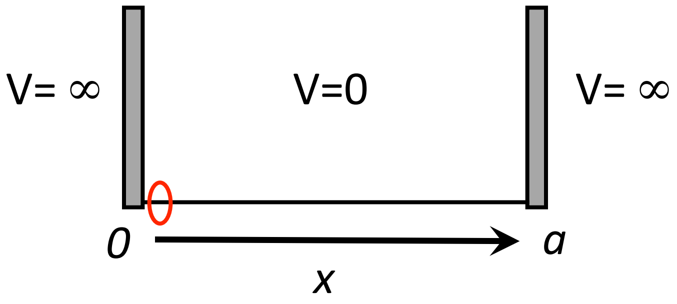
$$\Downarrow$$

$$\frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2}\right)\psi(x)=E\psi(x)$$

Note: Potential Energy is zero in the box. Kinetic energy is NOT zero, and we will determine exactly what it is by solving the equation.

Using the Boundary Conditions to Solve the 1D Wave Equation

Note: The boundary conditions resemble a one-dimensional box

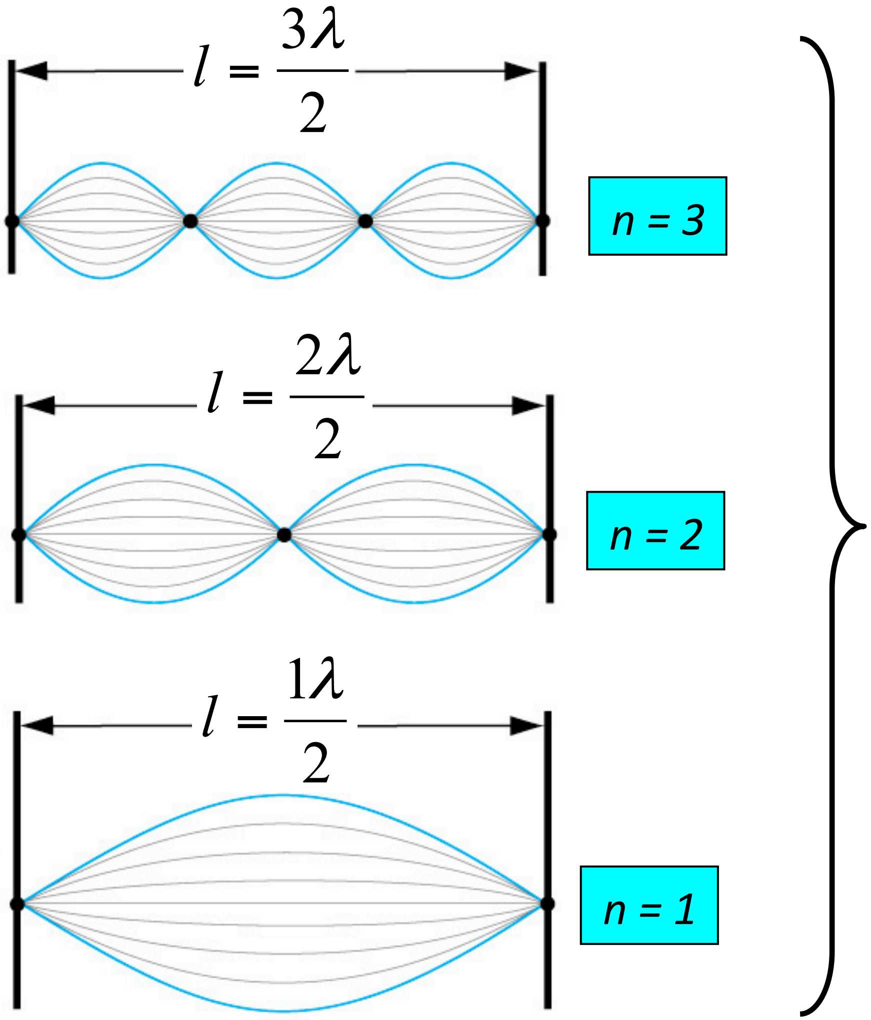


The particle in the box acts as a wave and is described by ψ (which we must determine).

Can you visualize what ψ will look like?

Wave Function for a Particle in a Box

Any standing wave with an ***integral number of ½ wavelengths*** will meet the requirement of being zero at x = 0 and x = a:



n = 3

n = 2

n = 1

$n\,\lambda = 2\,l$

OR

$n\,\lambda = 2a$

Wave Function for a Particle in a Box

The most general function for a one-dimensional wave is:

$$\psi\left(x\right) = A\sin(rx) + B\cos(sx)$$

Where A, B, r, and s are constants

However, the wave function must be zero at x=0, (e.g., $\psi\left(x\right) = 0$) therefore:

$$0 = A\sin(r0) + B\cos(s0)$$

$$0 = A(0) + B(1)$$

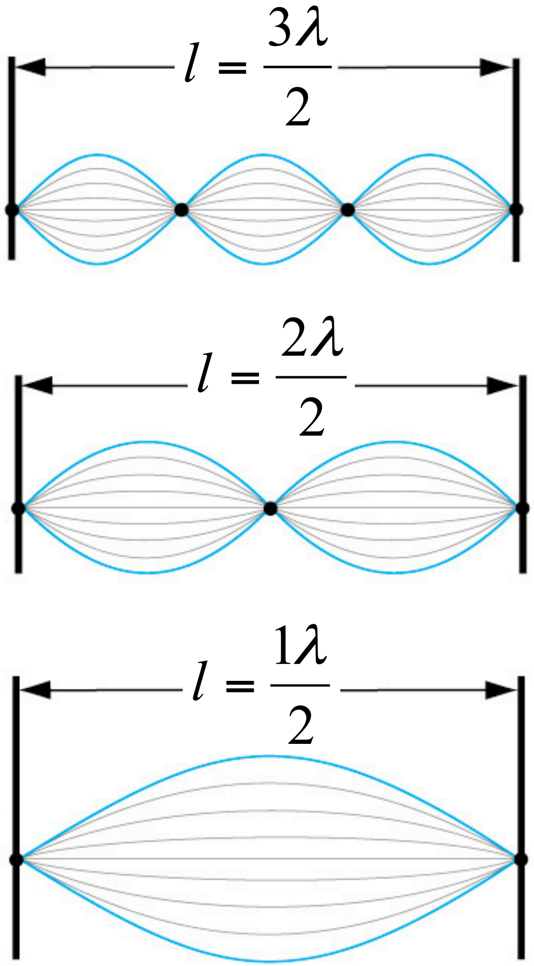
$$0 = B$$

Since B = 0, the wave function simplifies to:

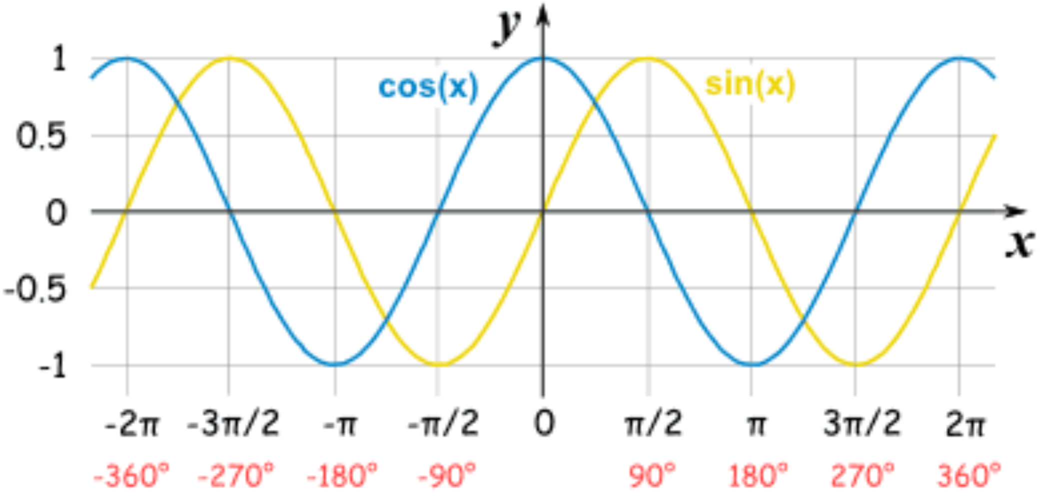
$$\psi\left(x\right) = A\sin(rx)$$

Wave Function for a Particle in a Box

Determination of the wave function can also be done visually. In order to meet the requirement of being zero at x = 0 and x = a, the obvious solution is:



$$\psi(x) = A\sin(rx)$$



Determining the Value of Constants

$$\psi(x) = A\sin(rx)$$

1) Determining r:

Based on the first boundary condition, we know that at $x = a, \psi(x) = 0$

Therefore: $0 = A\sin(ra)$

To solve, we recognize that:

$A\sin(ra) = 0$ when $A = 0$ ***and*** when $\sin(ra) = 0$

But:

If $A = 0$, then $\psi(x) = 0$ at all x!

$$\boxed{\text{Thus } A \neq 0 \text{ and } \sin(ra) = 0}$$

Solving for r

From trigonometry, we know that $\sin(u) = 0$ when u is an integer multiple of π (i.e. π, 2π, 3π, etc..). Thus,

$$\sin(ra) = 0 \quad \text{if} \quad ra = n\pi$$

$$\boxed{r = \frac{n\pi}{a}}$$

n must be an integer and n ≠ 0

This results in QUANTIZATION

(where a is the length of the box)

Substituting this value for r into the wave function, we find:

$$\boxed{\psi(x) = A\sin\left(\frac{n\pi x}{a}\right)}$$

Solving for A

$$\psi(x) = A\sin\left(\frac{n\pi x}{a}\right)$$

Applying boundary condition 4 requires normalization of the wave function such that:

$$\int \psi^2(x)dx = 1$$

(normalization guarantees that the probability of finding the particle ***somewhere*** in the box is 1)

In other words, the probability of finding the electron across all possible space within the box is 100%

Solving for A

Sub the function $\psi(x)$ into the integral:

$$1 = \int_0^a A^2 \sin^2\left(\frac{n\pi x}{a}\right) dx$$

The constant A^2 can be removed from the integral:

$$1 = A^2 \int_0^a \sin^2\left(\frac{n\pi x}{a}\right) dx$$

The integral of a trig. function to an even power can be solved using the following substitution:

$$\left\| \sin^2(u) = \tfrac{1}{2}\left(1 - \cos(2u)\right) \right\|$$

So we can write:

$$\frac{1}{A^2} = \int_0^a \tfrac{1}{2}\left(1 - \cos\left(\frac{2n\pi x}{a}\right)\right) dx$$

Solving for A

Then we can substitute $u = \dfrac{2n\pi x}{a}$ and $du = \dfrac{2n\pi}{a}dx$, which gives:

$$\frac{1}{A^2} = \frac{a}{4n\pi}\int_0^{2n\pi}\left(1-\cos(u)\right)du$$

*Note: the integration limits have changed as the integrand variable, x, is replaced by u. Originally the limits were from 0 to a. Since $u = \dfrac{2n\pi x}{a}$ the new limits are the values of u evaluated at these points: $u\left(0\right) = 0$ and $\mathrm{u}\left(a\right) = \dfrac{2n\pi\ (\cancel{a})}{\cancel{a}} = 2n\pi$

Solving for A

Isolating the integral gives:

$$\frac{4n\pi}{aA^2} = \int_0^{2n\pi} \big(1 - \cos(u)\big)\, du$$

Splitting the integral gives:

$$\frac{4n\pi}{aA^2} = \int_0^{2n\pi} du - \int_0^{2n\pi} \cos(u)\, du$$

Integrating gives:

$$\frac{4n\pi}{aA^2} = u\Big|_0^{2n\pi} - \sin(u)\Big|_0^{2n\pi}$$

$$\frac{4n\pi}{aA^2} = \big(2n\pi - 0\big) - \cancelto{0}{\big(\sin(2n\pi) - \sin(0)\big)}$$

Solving for A

$$\frac{4n\pi}{aA^2} = 2n\pi$$

$$\frac{2}{aA^2} = 1$$

$$\frac{2}{a} = A^2 \quad \Rightarrow \quad \therefore \boxed{A = \sqrt{\frac{2}{a}}}$$

Wave Function for a Particle in a Box

THE FINAL ANSWER!!

$$\boxed{\psi(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right)}$$

where: a is the length of the "box"
n is any integer (1, 2, 3, 4, ...) and n ≠ 0

NOTE: ***n cannot be zero*** because if it were, ψ would be zero for all values of x, meaning the particle does not exist.

Interpretation of Wave Function, ψ

ψ is a mathematical function, and it is hard to ascribe a physical meaning to it. However,

ψ^2 represents the ***probability of finding an electron at a given point***.

large ψ^2 means greater probability of finding an electron
small ψ^2 means lower probability of finding an electron

Energy of a Particle in a Box

Solve for E (energy) by substituting the wave function ψ into the wave equation:

$$\frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2}\right)\psi(x) = E\psi(x)$$

Find the 2nd derivative of ψ, knowing that ψ = A sin (rx) :

$$\frac{\partial^2\psi}{\partial x^2} = \frac{\partial^2}{\partial x^2}[A\sin(rx)]$$

$$\frac{\partial^2\psi}{\partial x^2} = A\frac{\partial^2}{\partial x^2}\sin(rx)$$

$$\frac{\partial^2\psi}{\partial x^2} = -Ar^2\sin(rx)$$

$$\frac{\partial^2\psi}{\partial x^2} = -r^2\psi$$

Keep in mind that:

$A = (2/a)^{1/2}$ and $r = n\pi/a$

However, since these are constants, we can just leave them as "A" and "r" for now, then substitute the actual values back in at the end.

Substitute the 2nd derivative of ψ into the wave equation:

$$\frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2\psi}{\partial x^2}\right) = E\psi$$

$$\frac{\partial^2\psi}{\partial x^2} = -r^2\psi$$

$$\text{therefore}$$

$$\frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2\psi}{\partial x^2}\right) = \frac{r^2 h^2}{8\pi^2 m}\psi = E\psi$$

$$E = \frac{r^2 h^2}{8\pi^2 m}$$

Substitute in the known value of r:

$$r = \frac{n\pi}{a}$$

$$E = \frac{n^2 h^2}{8ma^2}$$

Energy of a Particle in a Box

$$\boxed{E = \frac{n^2h^2}{8ma^2}}$$

n	integer (1,2, 3, ...)	**QUANTUM NUMBER**
h	Planck’s constant	**constants**
m	mass particle	
a	length of box	

The restriction on the possible values of n results in a restriction on the possible values of E

The energy of a particle in a 1-D box is ***QUANTIZED***

Solutions to the Schrödinger Equation for a Particle in a Box

Wave Function:

$$\psi = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}$$

Energy:

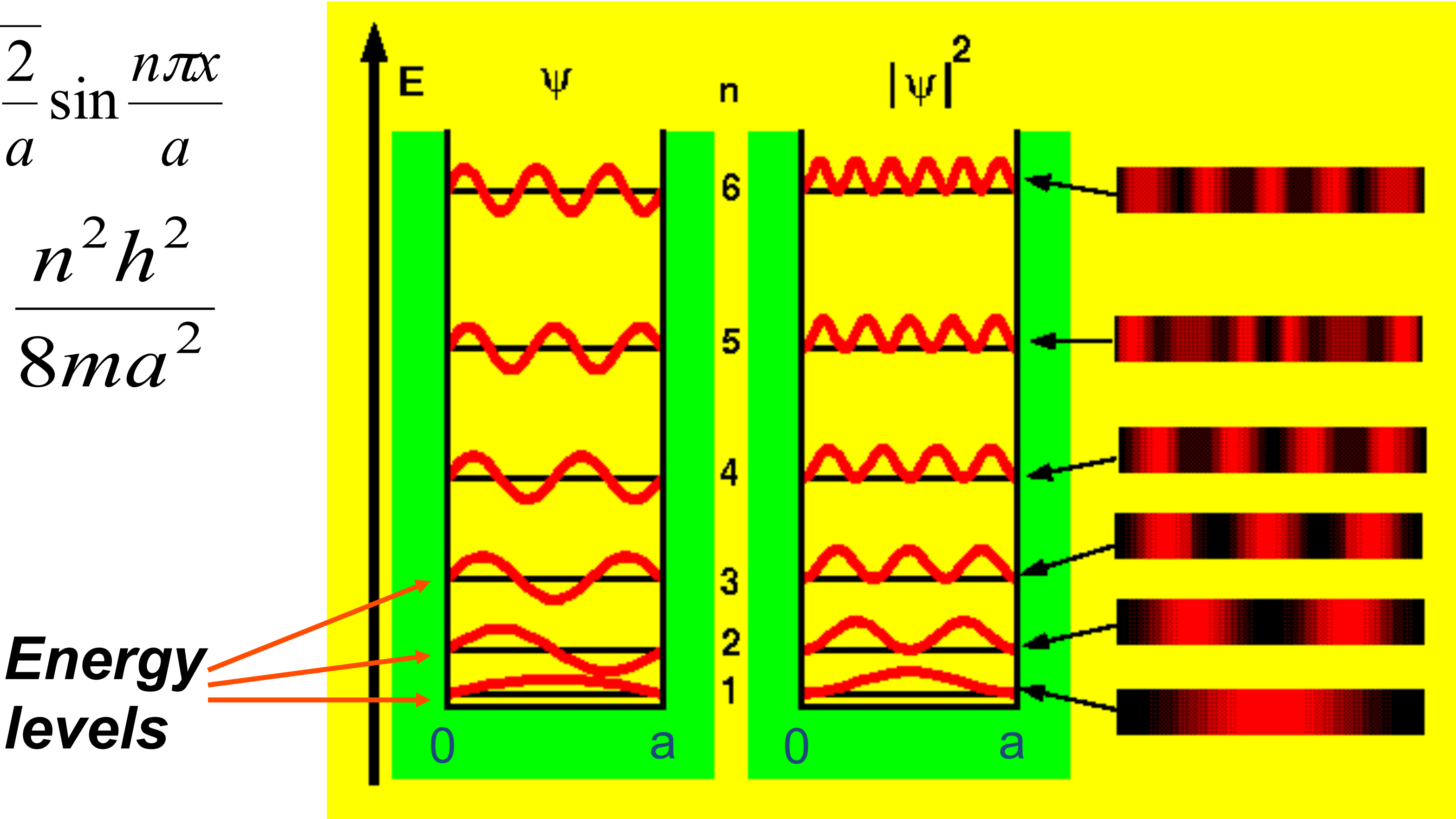
$$E = \frac{n^2 h^2}{8ma^2}$$

n	Wave Function (ψ)	Energy
1	$\psi = \sqrt{\frac{2}{a}} \sin \frac{\pi x}{a}$	$E = \frac{h^2}{8ma^2}$
2	$\psi = \sqrt{\frac{2}{a}} \sin \frac{2\pi x}{a}$	$E = \frac{4h^2}{8ma^2}$
3	$\psi = \sqrt{\frac{2}{a}} \sin \frac{3\pi x}{a}$	$E = \frac{9h^2}{8ma^2}$

Graphical Representations of Wave Functions and Their Energies

$$\psi = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}$$

$$E = \frac{n^2 h^2}{8ma^2}$$

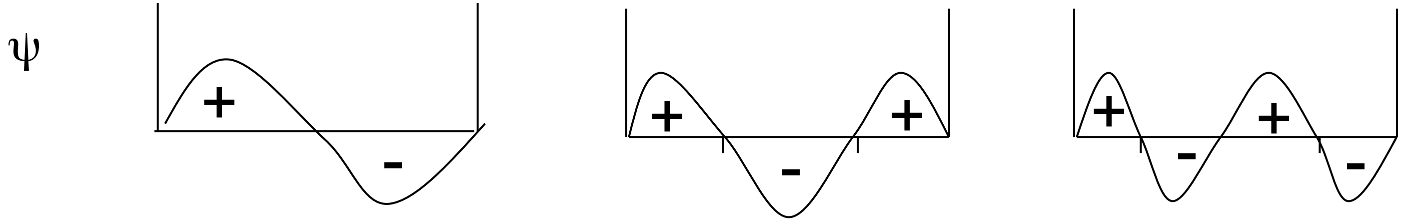


ψ² represents the probability of finding an electron at a given location in the box.

(See also Figure 2-4, p. 25 of Miessler and Tarr)

Wave Functions and Sign

The wave function can have a positive or negative sign.



This has ***nothing*** to do with charge of the particle: it is purely mathematical!
(No physical meaning)

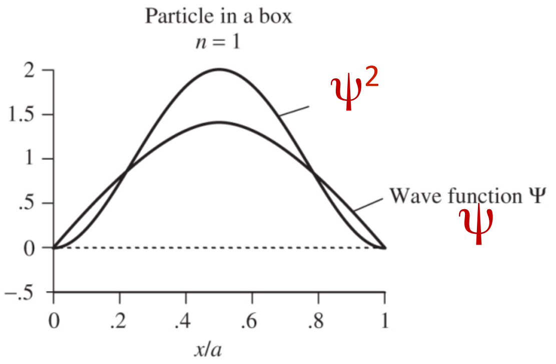
Important Principles Regarding a Particle in a Box

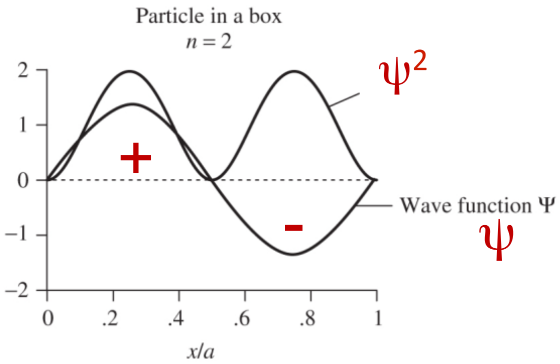
1) ψ (and ψ^2) depends on x (position) and n

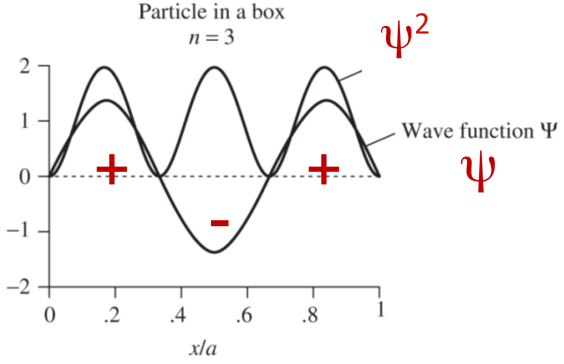
Moving along the x axis, you will find areas of high probability and areas of low probability of finding the particle.

Points of ***zero probability*** ($\psi^2 = 0$) are called ***NODES***.

A ***node*** in a wave function occurs when the wave function changes sign, i.e. when $\psi = 0$.


Particle in a box
$n = 1$

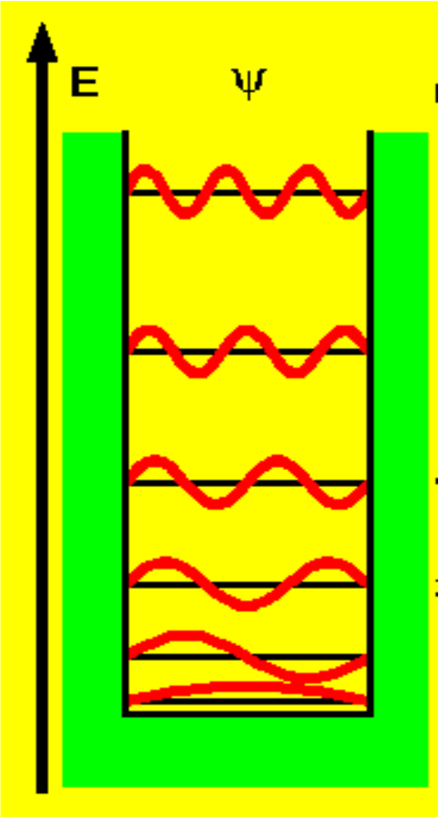

Particle in a box
$n = 2$


Particle in a box
$n = 3$

Probability of finding particle = ψ^2

Important Principles Regarding a Particle in a Box

As n increases, the energy increases, the number of nodes increases.



n = 6

n = 5

n = 4

n = 3

n = 2

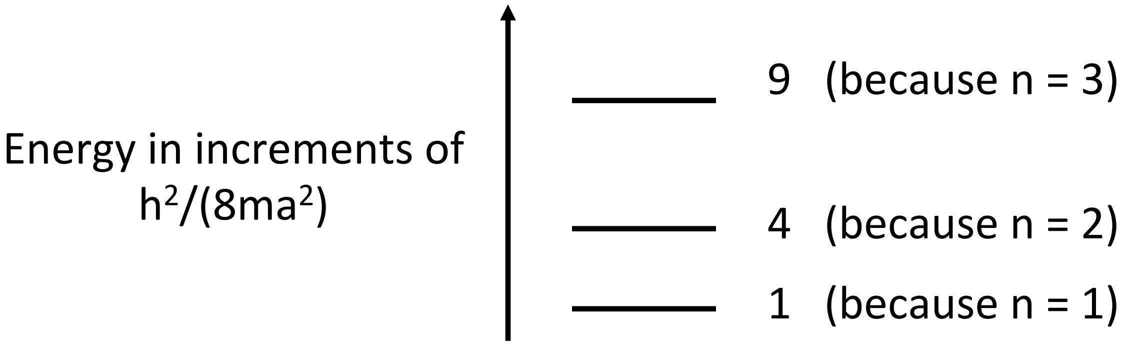
n = 1

Important Principles Regarding a Particle in a Box

2) QUANTIZATION of Energy

The energy is quantized: it can only have very specific values.

$$E = \frac{n^2 h^2}{8ma^2}$$



Energy in increments of $h^2/(8ma^2)$

9 (because n = 3)

4 (because n = 2)

1 (because n = 1)

The particle cannot have energies ***between*** the indicated ***energy levels***.

(Recall that this quantization results from the boundary condition that $\psi = 0$ at $x = a$)

Important Principles Regarding a Particle in a Box

3) ZERO-POINT ENERGY

The energy of the particle in the box is never zero!!

This occurs because the lowest possible value for n is 1.

$$\psi = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}$$

If n = 0, then $\psi = 0$ at all values of x, meaning the particle doesn't exist. Not possible!

If n = 1 is the lowest possible value for n, then the lowest possible energy for the particle is $h^2/(8ma^2)$.

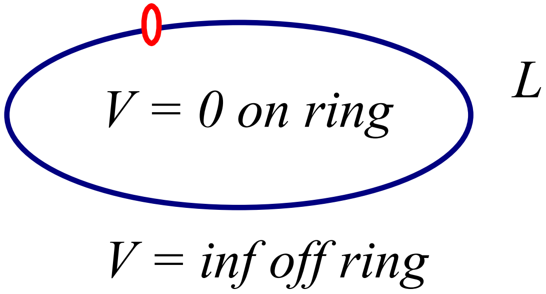
$$E = \frac{n^2 h^2}{8ma^2}$$

where n = 1

This is called the ***ZERO POINT ENERGY***.

A New Dimension…Particle on a Ring

Energy Levels for an Electron confined to a Circular Ring



V = 0 on ring

L

V = inf off ring

Boundary
⇨
conditions

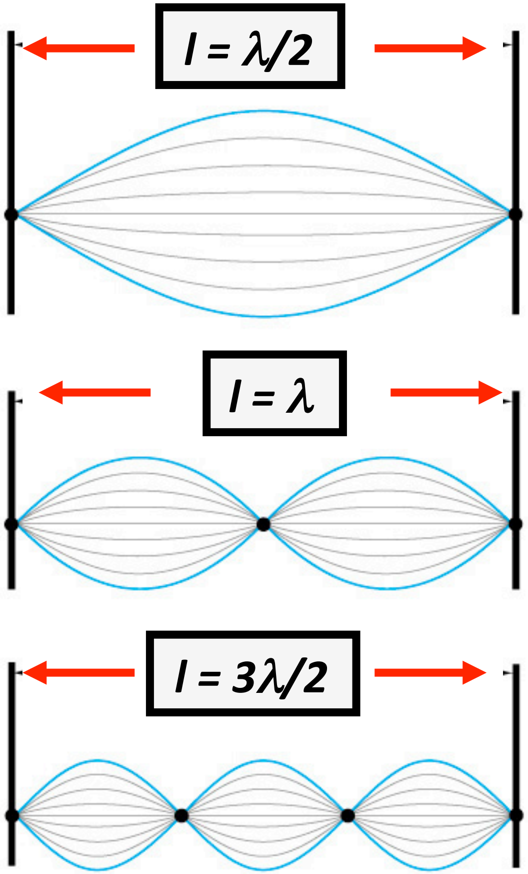
Finite, continuous and single valued → $\psi(x) = \psi(x + L)$

$n\lambda = L = 2\pi r$

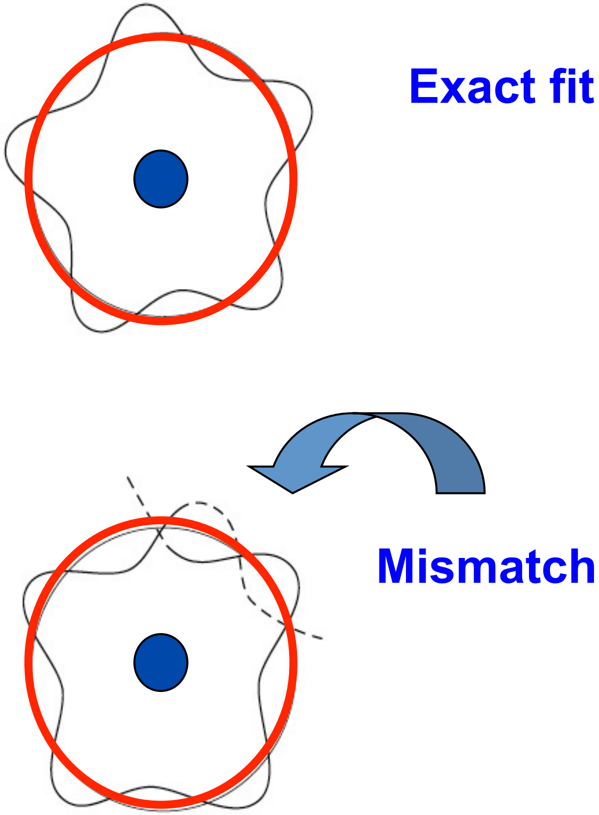
Quantum Confinement of Electron Waves

The Idea

1-D Standing Waves



Circular Standing Waves



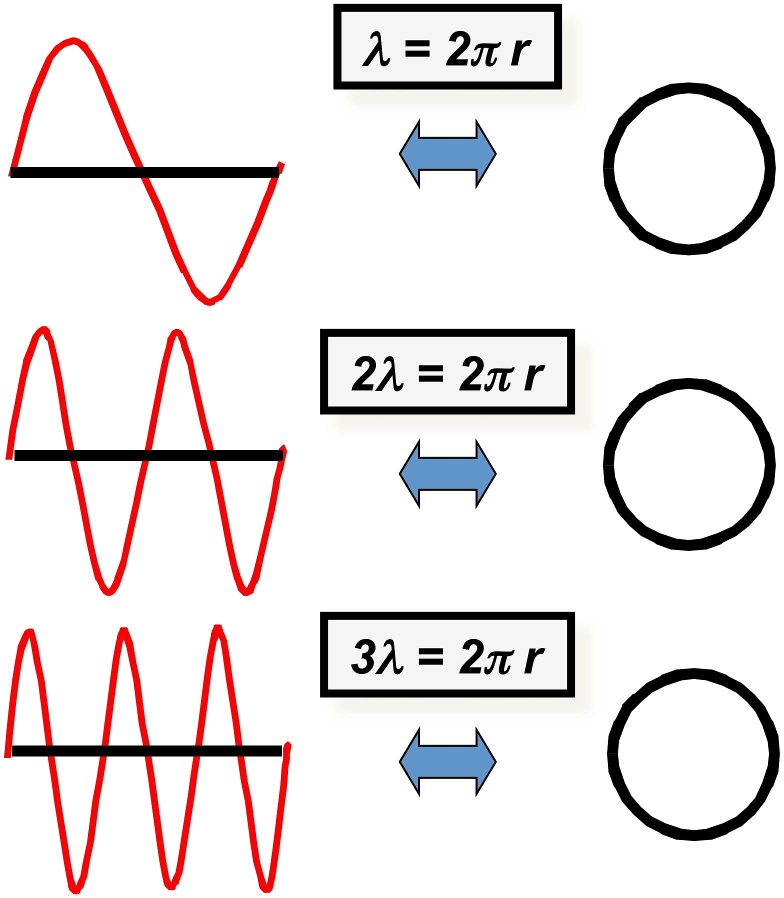
Exact fit ⇨ $n\lambda = 2\pi r$

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

Quantum Confinement of Electron Waves

The Application

Idea: match wavelength of electron to the size its "orbit" size . . .



$\lambda = 2\pi r$

$2\lambda = 2\pi r$

$3\lambda = 2\pi r$

Wave ψ must wrap exactly around circumference $2\pi r$ of its "orbit"

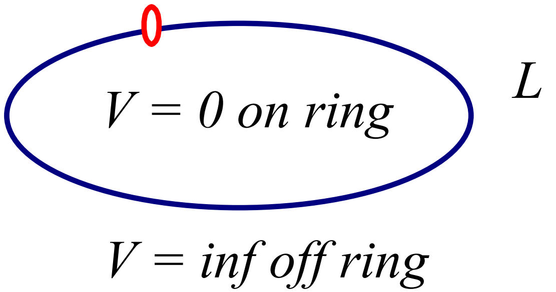
$$n \lambda = 2 \pi r \qquad (n = 1, 2, 3 \ldots)$$

Quantum number n cannot be zero, electron is never at rest.

Square of wave amplitude ψ^2 related to electron density (*probability*).

A New Dimension…Particle on a Ring

Energy Levels for an Electron confined to a Circular Ring



Boundary conditions →

Finite, continuous and single valued → $\psi(x) = \psi(x + L)$

$n\lambda = L = 2\pi r$

Standing waves

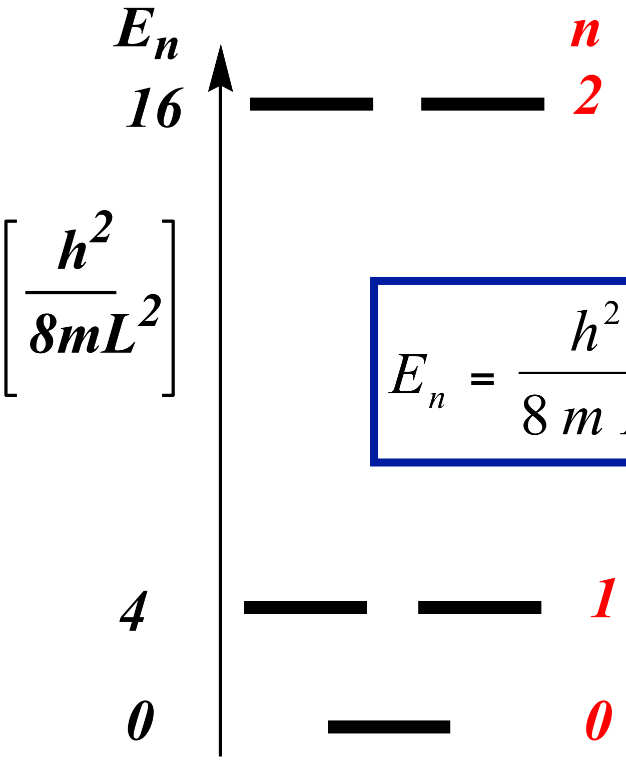
$$\psi_n(x) = A \sin\frac{n\pi x}{L}$$

$$\psi_n(x) = A \cos\frac{n\pi x}{L}$$

(Keep in mind Euler's formula: $e^{ix} = \cos x + i\sin x$)

$$\psi_n(x) = B \exp\frac{in\pi x}{L}$$

$n = 0, \pm 1, \pm 2, \pm 3, \ldots$ and $L = n\lambda$



$$E_n = \frac{h^2}{8\,m\,L^2}(2n)^2$$

Solving the Schrödinger Equation for an Electron in a Hydrogen Atom

In principle, this is similar to solving for a particle in a 1-dimensional box (PIB). In practice, it is mathematically much more complicated due to the following:

1) Electrons in an atom move in three dimensions: x, y, and z. (For PIB, we only used x.)
2) Electrostatic attraction between electron and nucleus gives rise to a potential energy term. (We assumed V = 0 for PIB)
3) The potential energy term is dependent on the electron's position in relation to the nucleus, and is thus a function of all three coordinates: V(x, y, z).

For particle in a box, we simplified the wave equation to the following:

$$\frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2}\right)\psi(x) = E\psi(x)$$

For electrons in a hydrogen atom, the full equation must be used:

$$\left[\frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)+V(x,y,z)\right]\psi(x,y,z) = E\psi(x,y,z)$$

Solving the Schrödinger Equation

Similar to PIB, we must set boundary conditions for an electron in a hydrogen atom.

Boundary Conditions

1. ψ must be single-valued.

   If ψ had more than one value at a given point, then ψ^2 would have more than one value, meaning there would be two different probabilities of the electron being at one given point. This is nonsense.

2. ψ and its first derivatives must be continuous.

   The probability must be defined at all positions in space and cannot change abruptly from one point to the next.

3. ψ must approach zero as r (distance from nucleus) approaches infinity.

   The probability of finding an electron decreases farther from the nucleus.

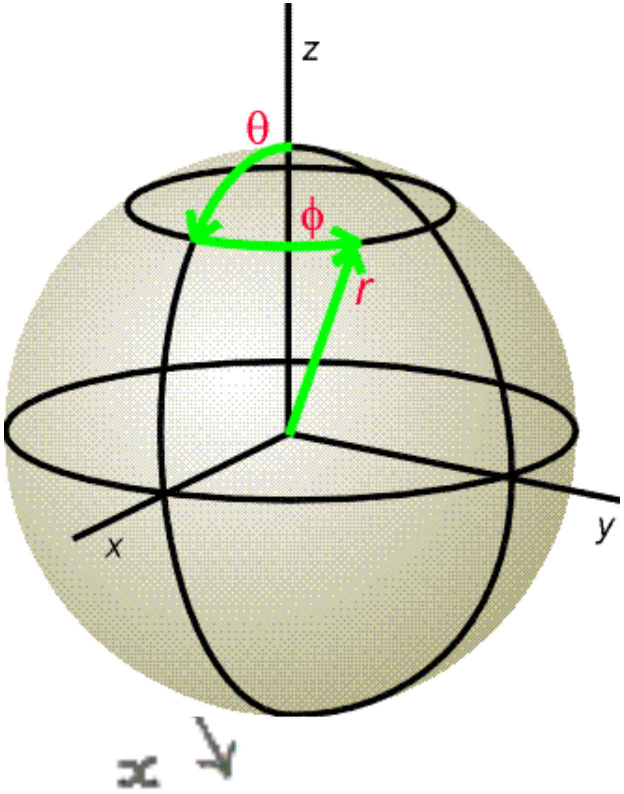
4. The probability, summed over all space, of finding an electron must be equal to 1. i.e. The electron MUST be somewhere!

$$\int_{allspace} \psi_A^2 d\tau = 1$$

⇨ This is called “normalization” of the wave function.

Use of Polar Coordinates

Because we are interested in knowing the distance between the nucleus and the electron, ***polar coordinates*** are more convenient than Cartesian coordinates.



Instead of looking at $\psi(x,y,z)$,
we will look at $\psi(r,\theta,\phi)$

r	distance from nucleus
θ	angle from z-axis (0 to π or 0 to 180°)
φ	angle from x-axis (0 to 2π or 0 to 360°)

(Nucleus is at 0,0,0)

$$x = r \sin\theta \cos\phi$$
$$y = r \sin\theta \sin\phi$$
$$z = r \cos\theta$$

Radial and Angular Functions of ψ

$\psi(r,\theta,\phi)$

For purposes of simplifying the wave equation, the function $\psi(r,\theta,\phi)$ can be broken down into two parts, an ***angular function*** and a ***radial function***:

$$\psi(r,\theta,\phi) = \underbrace{\mathbf{R}(r)}_{\textbf{radial function}}\ \underbrace{\mathbf{Y}(\theta,\phi)}_{\textbf{angular function}}$$

Radial Function **R**(r) :

- Variation of the orbital with distance from the nucleus

Angular Function **Y**(θ,ϕ) :

- The shape of the wave function (or orbital) and its orientation in space.

Quantum Numbers

Recall the particle in a 1-dimensional box:

The boundary restrictions resulted in the emergence of one quantum number, n, where n must be an integer.

PIB: $\psi = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}$ $E = \frac{n^2 h^2}{8ma^2}$

For an electron in a 3-dimensional hydrogen atom:

Solving the wave equation produces ***3 quantum numbers: n, l, m_l*** (instead of just one quantum number).

Quantum Numbers

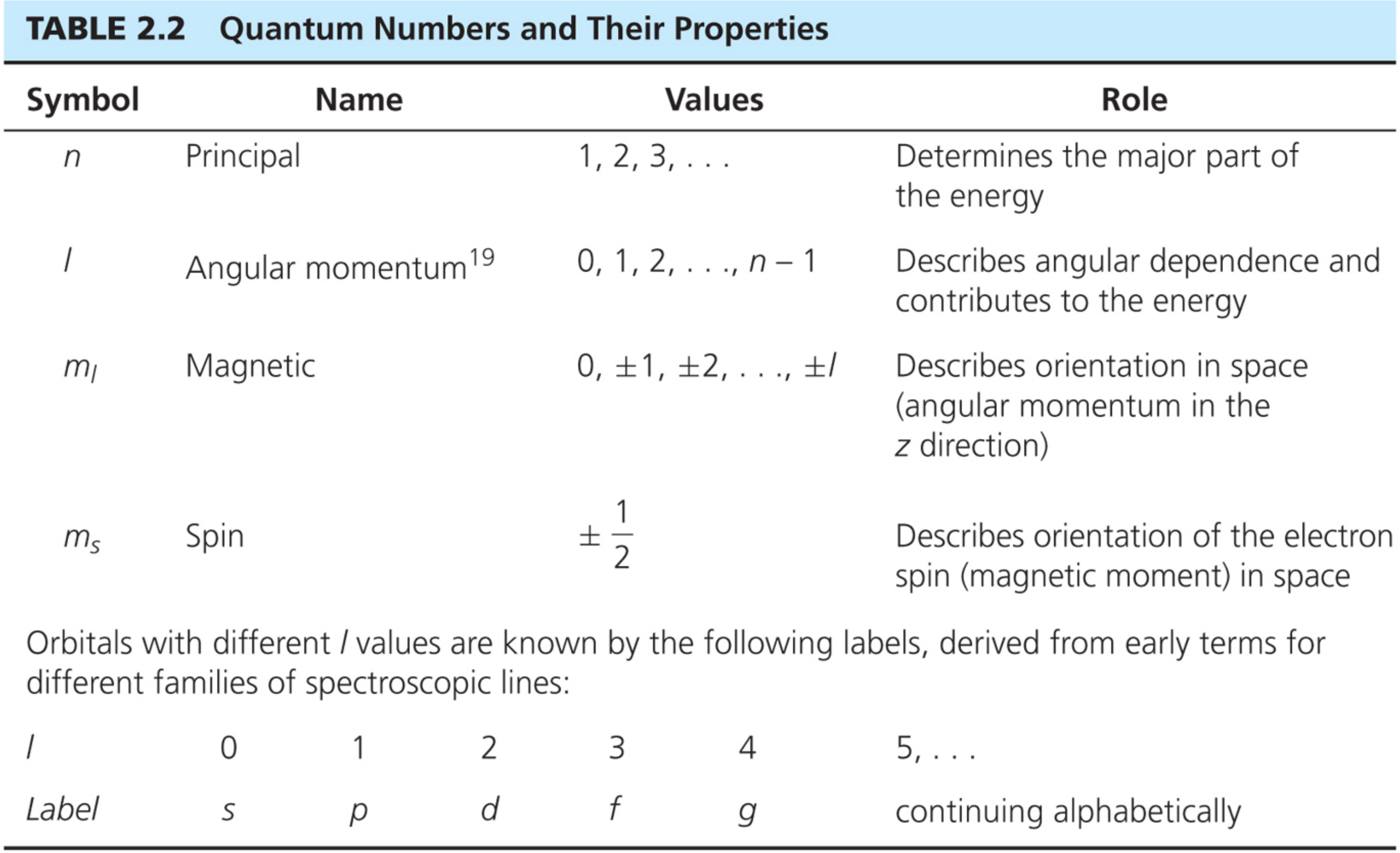


TABLE 2.2 Quantum Numbers and Their Properties

Symbol	Name	Values	Role
n	Principal	$1, 2, 3, \ldots$	Determines the major part of the energy
l	Angular momentum[19]	$0, 1, 2, \ldots, n-1$	Describes angular dependence and contributes to the energy
m_l	Magnetic	$0, \pm 1, \pm 2, \ldots, \pm l$	Describes orientation in space (angular momentum in the z direction)
m_s	Spin	$\pm \frac{1}{2}$	Describes orientation of the electron spin (magnetic moment) in space

Orbitals with different l values are known by the following labels, derived from early terms for different families of spectroscopic lines:

l	0	1	2	3	4	5, . . .
Label	*s*	*p*	*d*	*f*	*g*	continuing alphabetically

Quantum Numbers and Orbital Labels

Quantum Numbers

- n : principal (1, 2, 3,...)
- l : angular momentum (l = 0 (*s*), 1 (*p*), 2 (*d*), 3 (*f*),..., n -1)
- m_l : magnetic (- l, (- l +1),..., (l - 1), + l; total = 2 l + 1)
- m_s : spin (±½)

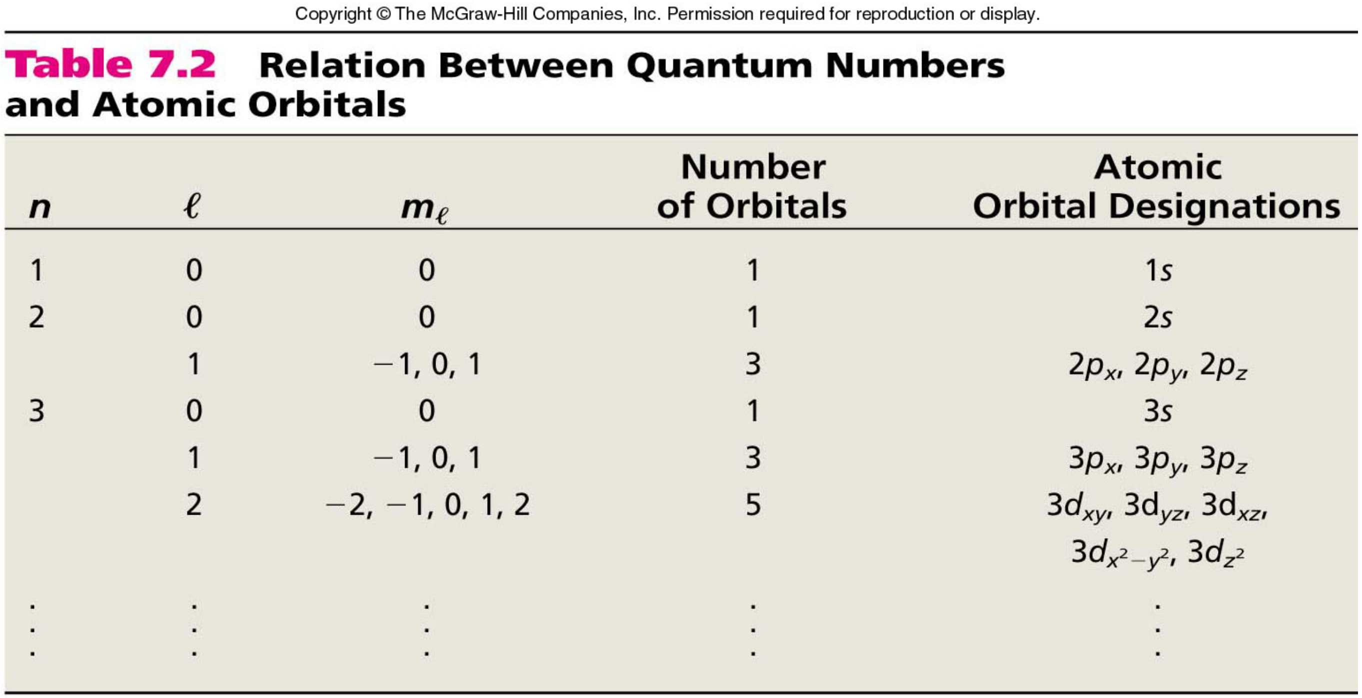


Table 7.2 **Relation Between Quantum Numbers and Atomic Orbitals**

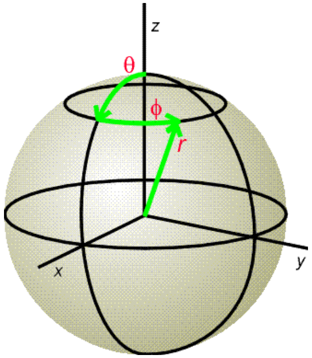
n	ℓ	m_ℓ	Number of Orbitals	Atomic Orbital Designations
1	0	0	1	$1s$
2	0	0	1	$2s$
	1	−1, 0, 1	3	$2p_x$, $2p_y$, $2p_z$
3	0	0	1	$3s$
	1	−1, 0, 1	3	$3p_x$, $3p_y$, $3p_z$
	2	−2, −1, 0, 1, 2	5	$3d_{xy}$, $3d_{yz}$, $3d_{xz}$, $3d_{x^2-y^2}$, $3d_{z^2}$
⋮	⋮	⋮	⋮	⋮

Orbitals are named based on the quantum numbers n, *l*, and m_l

What do the orbitals look like? We'll find out by looking at the solutions to the wave equation!

Solutions to the Wave Equation for an Electron in a Hydrogen Atom

$$\psi(r,\theta,\phi) = \underbrace{\mathbf{R}(r)}_{\text{radial function}}\ \underbrace{\mathbf{Y}(\theta,\phi)}_{\text{angular function}}$$



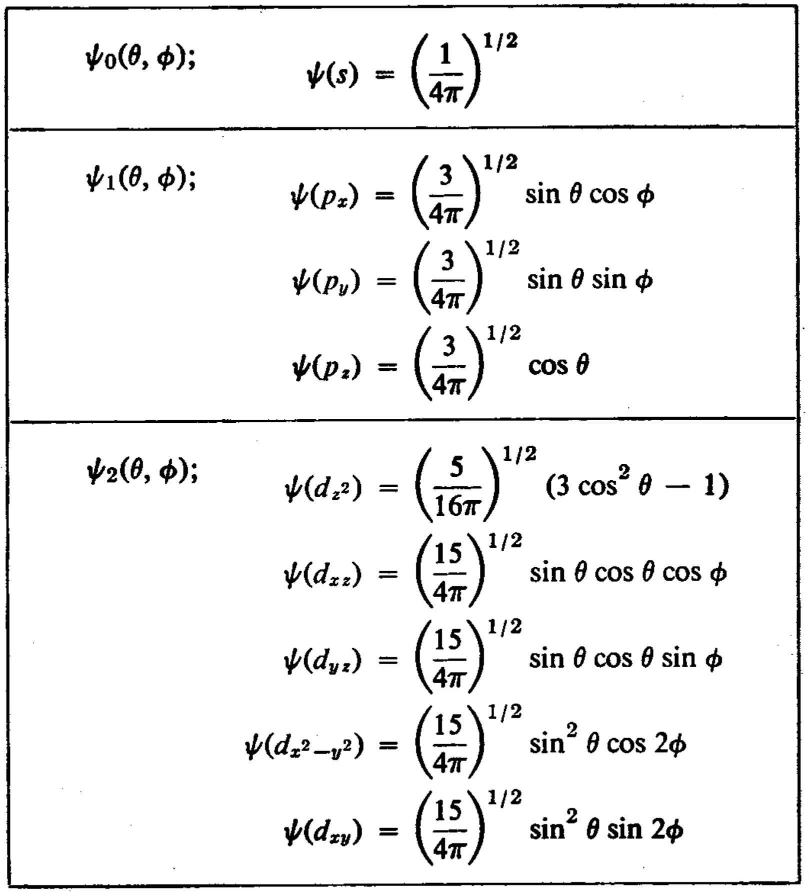
Radial Function R(r):

- Variation of the orbital with distance from the nucleus
- **Depends upon quantum numbers n and *l***

Angular Function Y(θ,ϕ):

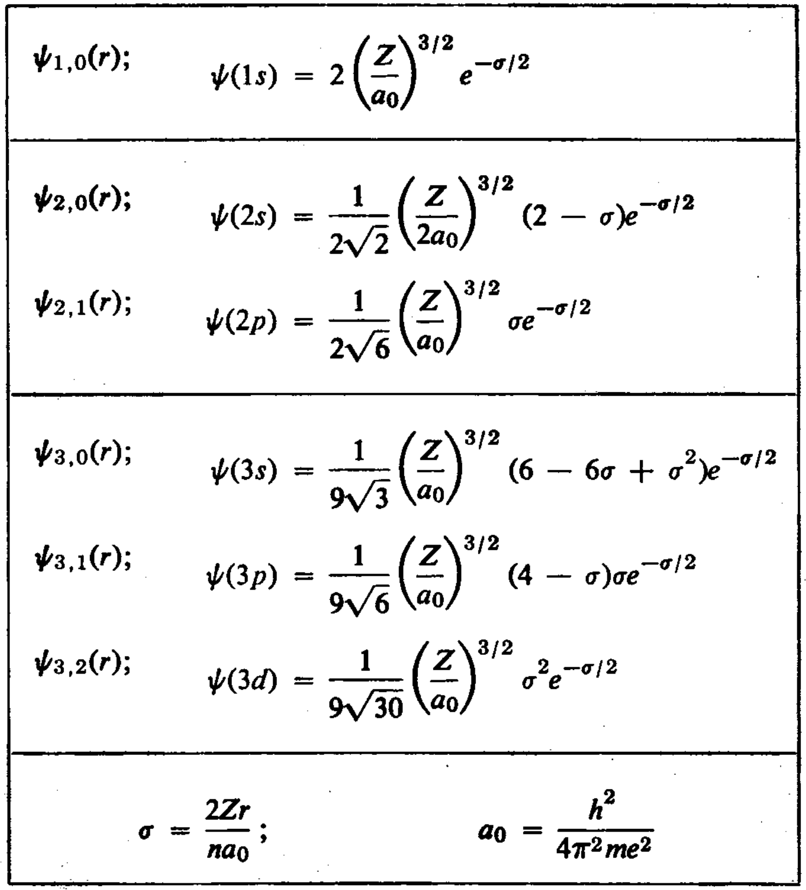
- The shape of the wave function (or orbital) and its orientation in space.
- **Depends upon quantum numbers *l* and m_l**

Hydrogenic Wave Functions in Polar Coordinates



ANGULAR FACTORS $\psi_l\ (\theta, \phi)$ FOR HYDROGENIC WAVE FUNCTIONS

$\psi_0(\theta, \phi)$;	$\psi(s) = \left(\frac{1}{4\pi}\right)^{1/2}$
$\psi_1(\theta, \phi)$;	$\psi(p_x) = \left(\frac{3}{4\pi}\right)^{1/2} \sin\theta\cos\phi$
	$\psi(p_y) = \left(\frac{3}{4\pi}\right)^{1/2} \sin\theta\sin\phi$
	$\psi(p_z) = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$
$\psi_2(\theta, \phi)$;	$\psi(d_{z^2}) = \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1)$
	$\psi(d_{xz}) = \left(\frac{15}{4\pi}\right)^{1/2} \sin\theta\cos\theta\cos\phi$
	$\psi(d_{yz}) = \left(\frac{15}{4\pi}\right)^{1/2} \sin\theta\cos\theta\sin\phi$
	$\psi(d_{x^2-y^2}) = \left(\frac{15}{4\pi}\right)^{1/2} \sin^2\theta\cos 2\phi$
	$\psi(d_{xy}) = \left(\frac{15}{4\pi}\right)^{1/2} \sin^2\theta\sin 2\phi$



RADIAL FACTORS $\psi_{n,l}(r)$ FOR HYDROGENIC WAVE FUNCTIONS

$\psi_{1,0}(r)$;	$\psi(1s) = 2\left(\frac{Z}{a_0}\right)^{3/2} e^{-\sigma/2}$
$\psi_{2,0}(r)$;	$\psi(2s) = \frac{1}{2\sqrt{2}}\left(\frac{Z}{2a_0}\right)^{3/2} (2 - \sigma)e^{-\sigma/2}$
$\psi_{2,1}(r)$;	$\psi(2p) = \frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma e^{-\sigma/2}$
$\psi_{3,0}(r)$;	$\psi(3s) = \frac{1}{9\sqrt{3}}\left(\frac{Z}{a_0}\right)^{3/2} (6 - 6\sigma + \sigma^2)e^{-\sigma/2}$
$\psi_{3,1}(r)$;	$\psi(3p) = \frac{1}{9\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2} (4 - \sigma)\sigma e^{-\sigma/2}$
$\psi_{3,2}(r)$;	$\psi(3d) = \frac{1}{9\sqrt{30}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma^2 e^{-\sigma/2}$
$\sigma = \frac{2Zr}{na_0}$;	$a_0 = \frac{h^2}{4\pi^2 me^2}$

Tables 2.3 & 2.4

Important Points to Wave Functions

1) Plotting these wave functions gives us a visual idea of where the electron may be in a hydrogen atom (i.e. orbitals)
   - The radial wave function tells us ***how far from the nucleus*** the electron is likely to be.
   - The angular function tells us the shapes of the orbitals. (e.g., spherical, peanut-shaped, etc.)

2) By combining the result of the radial functions with the results of the angular functions, we can establish an overall picture of each electronic orbital that includes both size (distance from nucleus) and shape.

The Radial Function R(r)

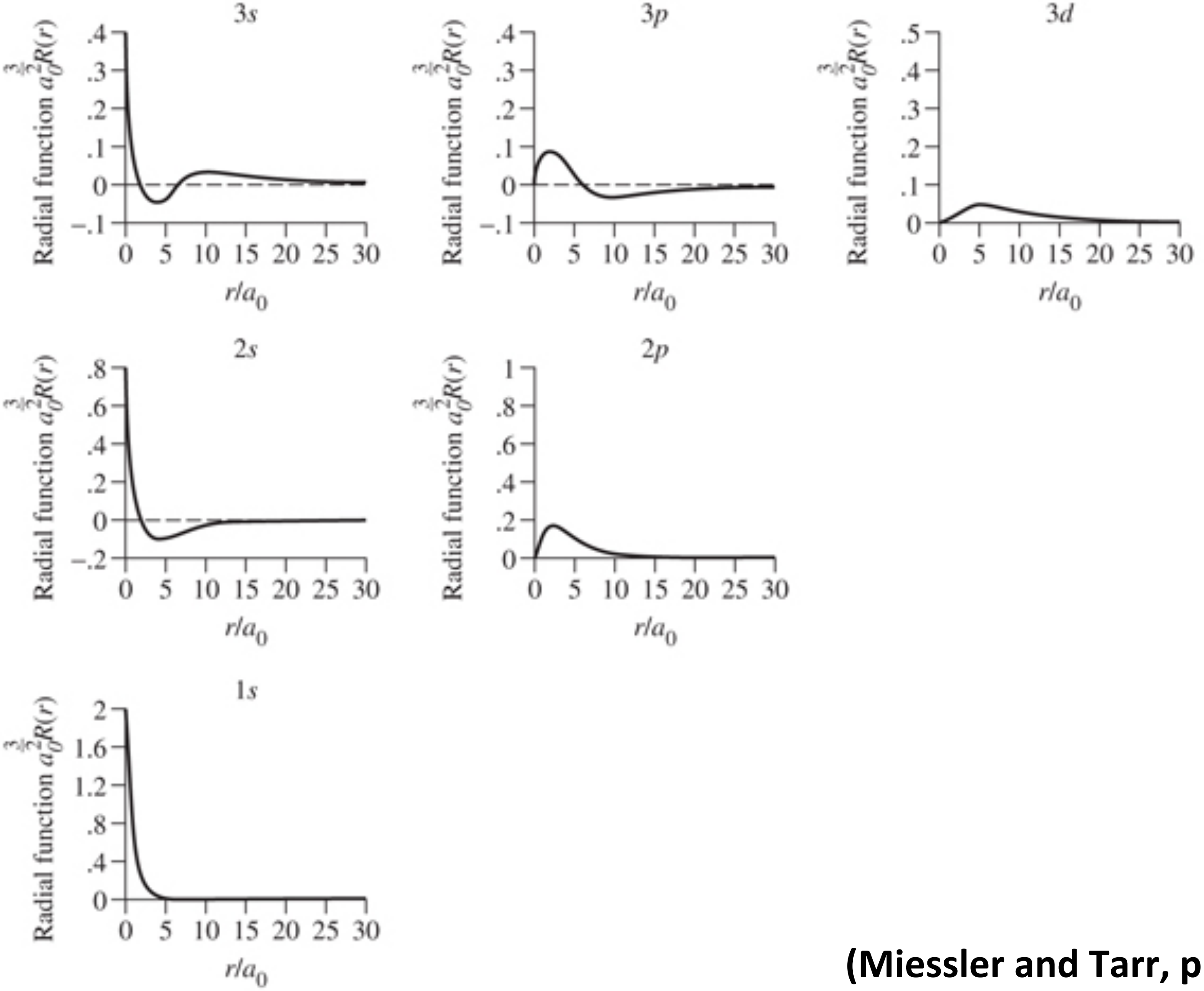
The most important information comes from looking at R^2, not R. But we can note a few things from R:

1) The only variable in R(r) is r (the distance from the nucleus)! It is ***independent*** of θ and ϕ

2) The function R depends on ***both*** n and ***l***, but ***not*** on m_l (i.e., a $2p_x$ orbital and a $2p_y$ orbital have the same R, but a 2p orbital and a 2s orbital have different R.)

3) The Bohr radius, a_0 = 52.9 pm or 0.529 Angstroms is common in quantum mechanics. It is the value of r for which ψ^2 is the greatest in a hydrogen 1s orbital (n=1, ***l***=0).

Plots of Radial Wave Functions



(Miessler and Tarr, p.31 Fig. 2-7)

The Radial Probability Function

$4\pi r^2R^2$

Recall, for ψ :

ψ	wave function
ψ^2	***probability*** of finding an electron at a given location

Likewise, for R:

R	***radial*** wave function
$4\pi r^2R^2$	***radial probability function***
	probability of finding an electron anywhere on a ***spherical surface of radius r*** (where the nucleus is at the center of the sphere).

(where $4\pi r^2$ is the formula for surface area of a sphere)

(also see Fig 2-5, p.28)

The Radial Probability Function

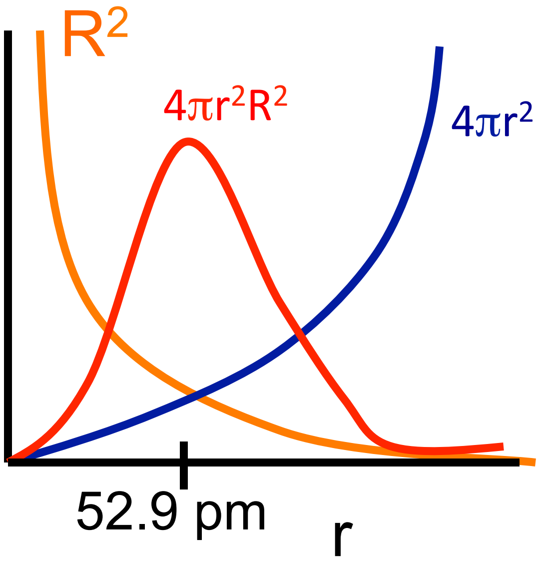
$4\pi r^2 R^2$

For a hydrogen 1s orbital (n=1, ***l***=0) as r increases, $R^2(r)$ ***decreases***.

As r increases, $4\pi r^2$ ***increases***.

Thus, when the two are combined: $4\pi r^2 R^2$ first increases, then decreases, resulting in formation of a maximum.

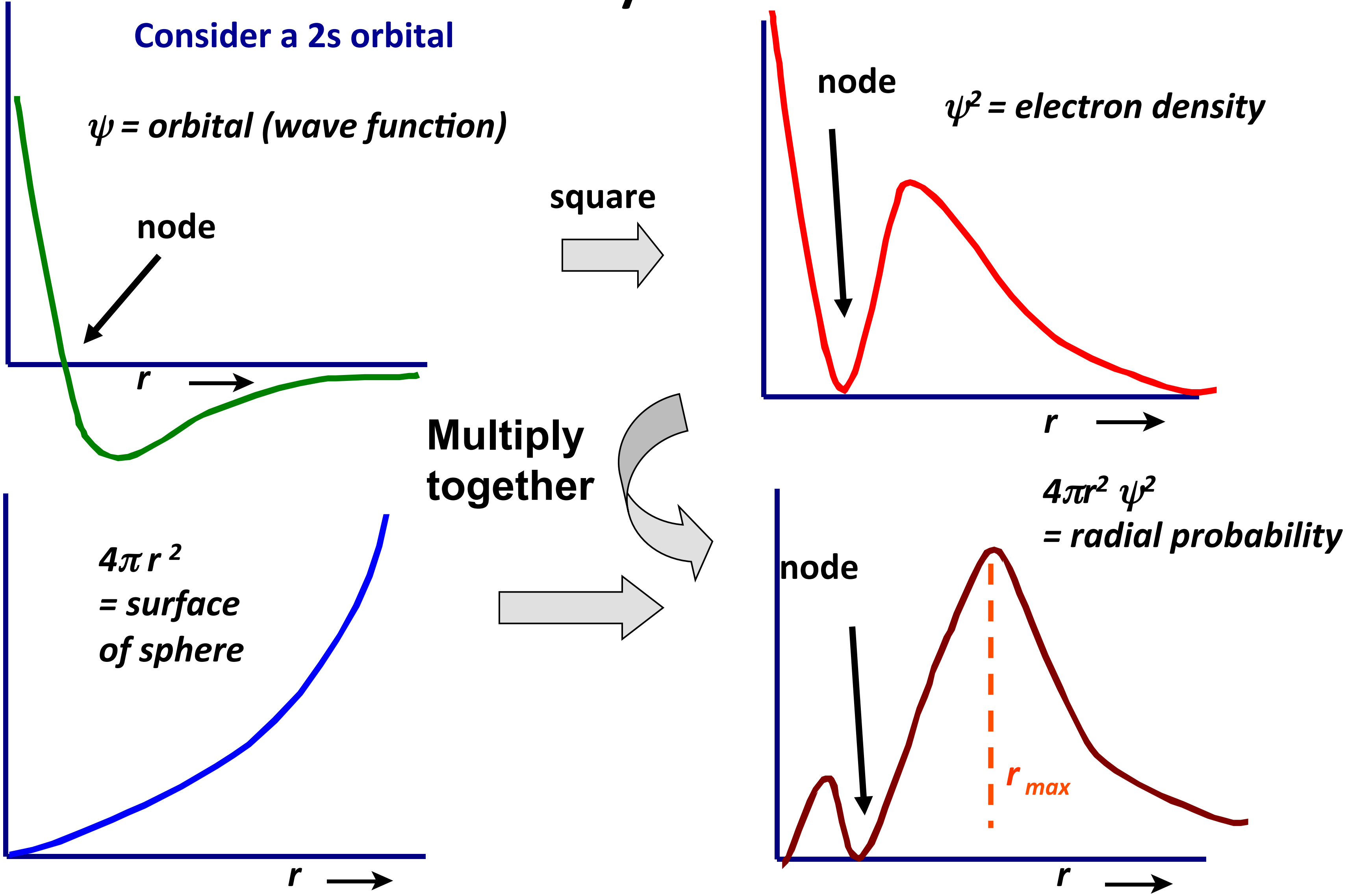
Hydrogen 1s orbital



The maximum represents the distance from the nucleus at which the electron has the greatest probability of being found.

↳ For H 1s, this max is at r = 52.9 pm (the Bohr radius, a_0)

From Wave Function to Radial Probability Distribution

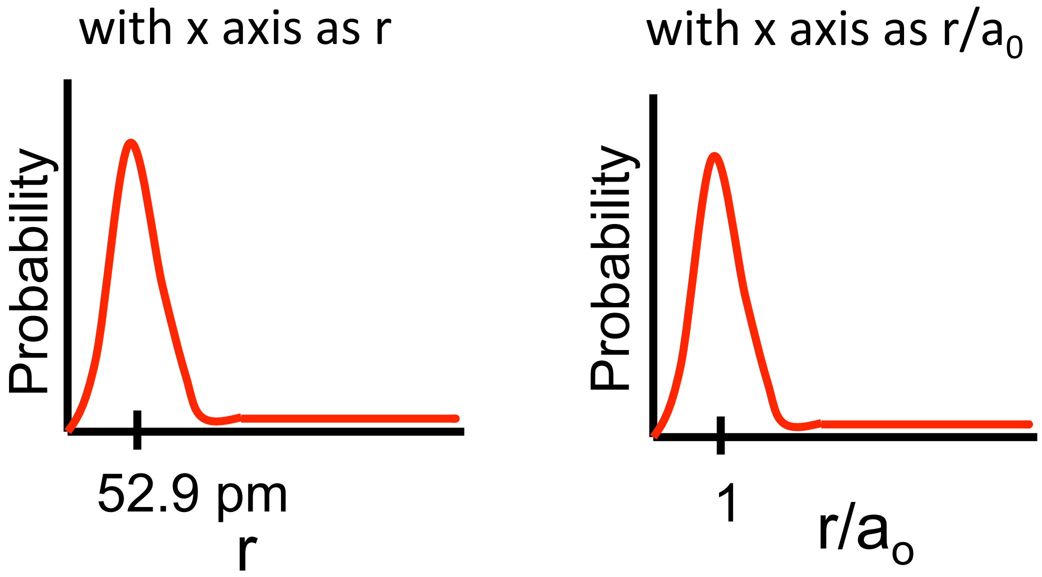


Radial Probability Function Plots

In these plots:
The y-axis represents the probability of finding an electron.

The x-axis represents the distance from the nucleus and is often expressed as r/a_o (i.e. the distance from the nucleus ***relative to*** the Bohr radius).

Hydrogen 1s orbital

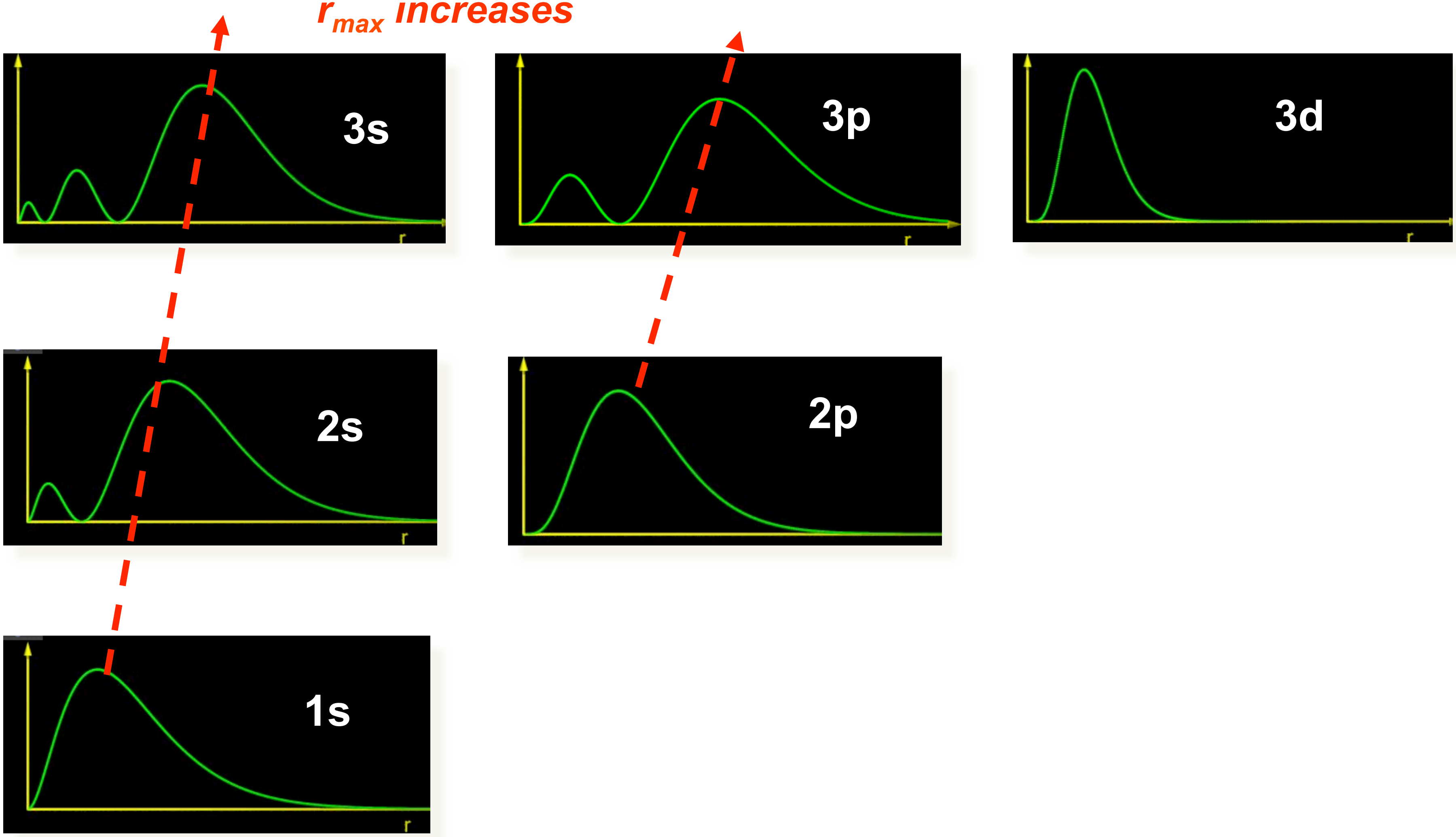


with x axis as r

with x axis as r/a_0

The two plots are identical, but with different x-axis labels.

Radial Probability Function Plots



r_{max} *increases*

(Miessler and Tarr, p.31 Fig. 2-7)

Important Points Regarding Radial Probability Functions

1) For all orbitals, $4\pi r^2 R^2 = 0$ at the nucleus: there is zero probability of finding an electron at the nucleus.

2) ***Radial Nodes*** are spherical surfaces at a given distance, r, from the nucleus upon which there is zero probability of finding an electron (i.e., $4\pi r^2 R^2 = 0$)

   Radial Nodes occur when the radial wave function, $R(r)$, changes sign. i.e. $R(r) = 0$ (which causes $4\pi r^2 R^2 = 0$)

   The nucleus of an s orbital is NOT a radial node!

Why?

Because at the nucleus $R(r)$ does not change sign
(even though in some cases it might be zero.)

Important Points Regarding Radial Probability Functions

3) As n increases, the number of radial nodes increases. (Just like the particle in a box!)

\# radial nodes = n - *l* - 1

e.g. For a 1s orbital n = 1, *l* = 0:

For a 2s orbital n = 2, *l* = 0

For a 2p orbital n = 2, *l* = 1:

NOTE: This formula is only for ***radial*** nodes! There can also be ***angular*** nodes, which we will discuss later.

Important Points Regarding Radial Probability Functions

4) As n increases, the probability of finding an electron ***farther from the nucleus*** increases. (i.e. orbitals get larger)

5) The radial probability function only tell us the probability of finding the electron ***somewhere*** on the spherical surface with radius r.

   The radial probability function ***DOES NOT*** tell us ***WHERE on that spherical surface*** the electron might be found.

   For example, is it more likely to be found on the left side of the sphere than on the right side? Is the probability evenly distributed over the entire surface of the sphere? To answer this we have to look at the ***ANGULAR WAVE FUNCTION***.

Solutions to the Wave Equation for an Electron in a Hydrogen Atom

$$\psi(r,\theta,\phi) = \underbrace{\mathbf{R}(r)}_{\substack{\textbf{radial}\\ \textbf{function}}}\ \underbrace{\mathbf{Y}(\theta,\phi)}_{\substack{\textbf{angular}\\ \textbf{function}}}$$

We have been looking at the solutions to the radial function.

Next we will look at the solutions to the angular function.

Finally, we will see how the radial and angular functions combine to give us the overall wave functions (which we call orbitals).

Angular Wave Functions

- The shape of the wave function (or orbital) and its orientation in space.
- Depends upon quantum numbers l and m_l

---

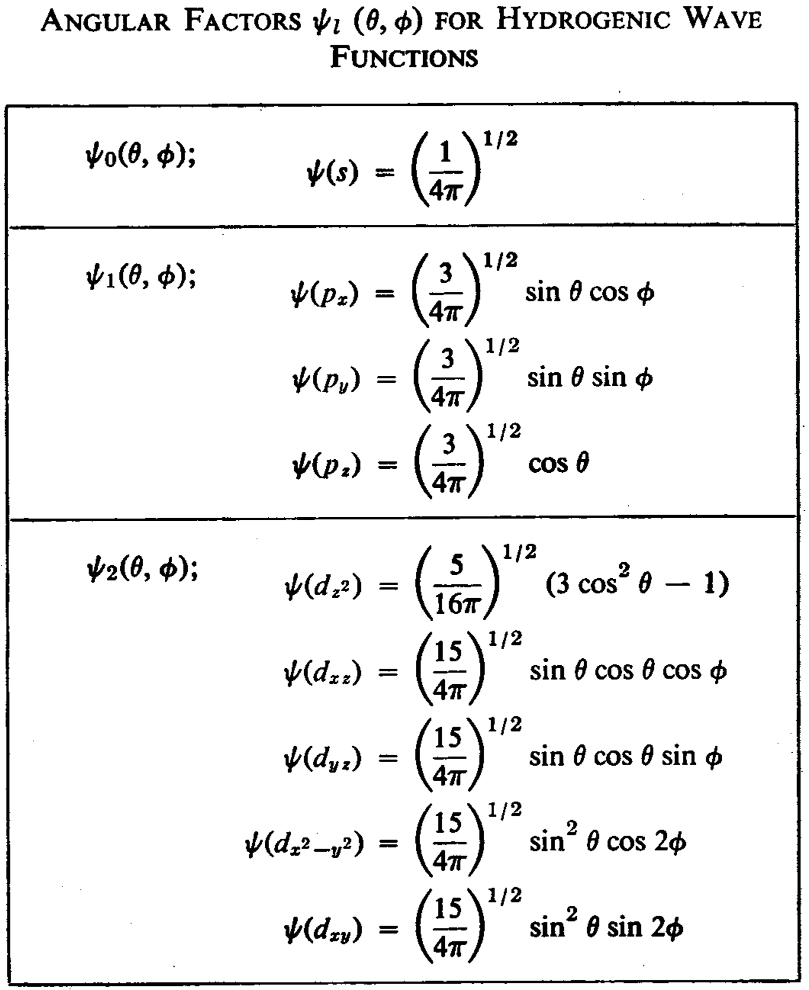
s-orbitals: $l = 0$, $m_l = 0$

$$\Theta\Phi(x, y, z) = \frac{1}{2\sqrt{\pi}}$$

⇨

Notice that this is expressed in Cartesian coordinates!

Hydrogenic Wave Functions in Polar Coordinates



ANGULAR FACTORS $\psi_l\ (\theta, \phi)$ FOR HYDROGENIC WAVE FUNCTIONS

$\psi_0(\theta, \phi)$;	$\psi(s) = \left(\frac{1}{4\pi}\right)^{1/2}$
$\psi_1(\theta, \phi)$;	$\psi(p_x) = \left(\frac{3}{4\pi}\right)^{1/2} \sin\theta\cos\phi$
	$\psi(p_y) = \left(\frac{3}{4\pi}\right)^{1/2} \sin\theta\sin\phi$
	$\psi(p_z) = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$
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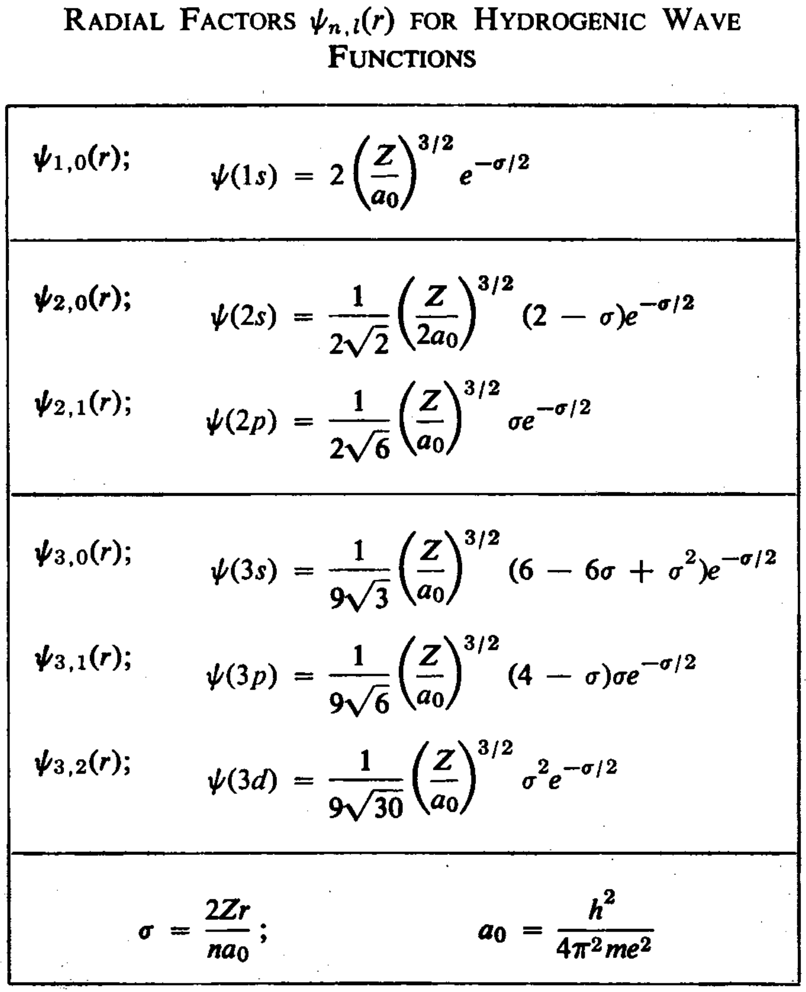
	$\psi(d_{xz}) = \left(\frac{15}{4\pi}\right)^{1/2} \sin\theta\cos\theta\cos\phi$
	$\psi(d_{yz}) = \left(\frac{15}{4\pi}\right)^{1/2} \sin\theta\cos\theta\sin\phi$
	$\psi(d_{x^2-y^2}) = \left(\frac{15}{4\pi}\right)^{1/2} \sin^2\theta\cos 2\phi$
	$\psi(d_{xy}) = \left(\frac{15}{4\pi}\right)^{1/2} \sin^2\theta\sin 2\phi$



RADIAL FACTORS $\psi_{n,l}(r)$ FOR HYDROGENIC WAVE FUNCTIONS

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$\psi_{2,1}(r)$;	$\psi(2p) = \frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma e^{-\sigma/2}$
$\psi_{3,0}(r)$;	$\psi(3s) = \frac{1}{9\sqrt{3}}\left(\frac{Z}{a_0}\right)^{3/2} (6 - 6\sigma + \sigma^2)e^{-\sigma/2}$
$\psi_{3,1}(r)$;	$\psi(3p) = \frac{1}{9\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2} (4 - \sigma)\sigma e^{-\sigma/2}$
$\psi_{3,2}(r)$;	$\psi(3d) = \frac{1}{9\sqrt{30}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma^2 e^{-\sigma/2}$
$\sigma = \frac{2Zr}{na_0}$;	$a_0 = \frac{h^2}{4\pi^2 me^2}$

Tables 2.3 & 2.4

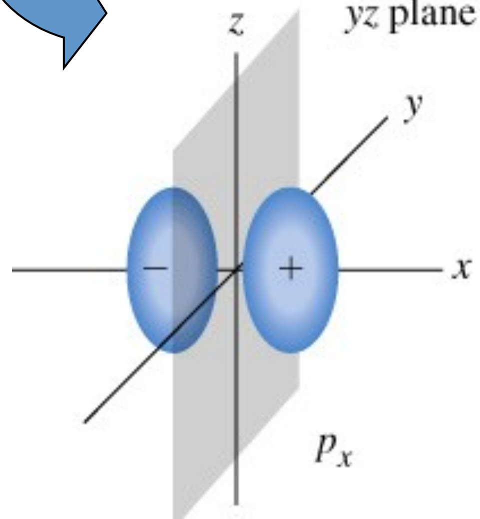
Angular Wave Functions

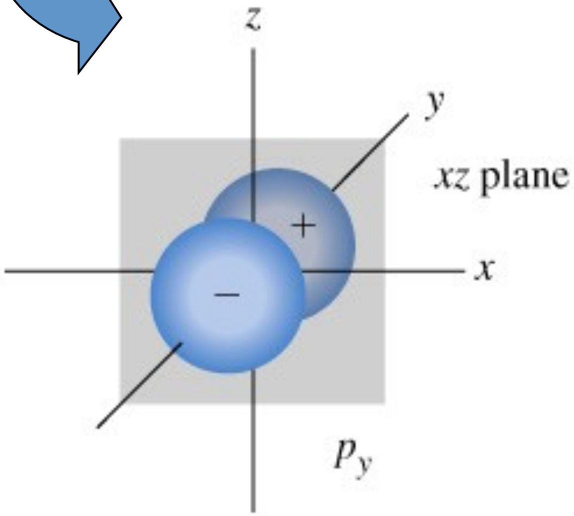
p-orbitals: $l = 1$, $m_l = -1, 0, +1$

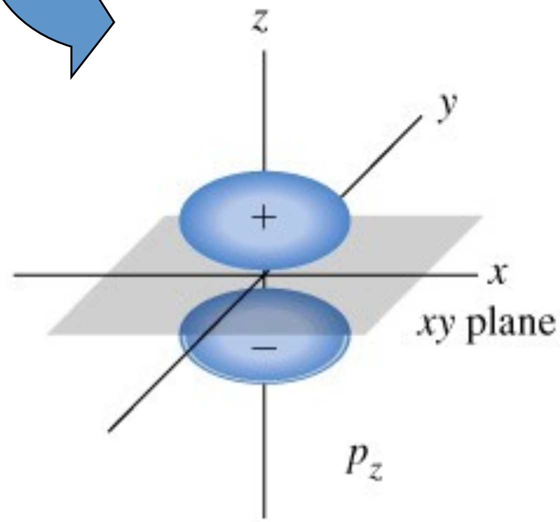
Angular Wave Functions: ΘΦ (x,y,z)

$$\frac{1}{2}\sqrt{\frac{3}{\pi}}\frac{x}{r} \qquad \frac{1}{2}\sqrt{\frac{3}{\pi}}\frac{y}{r} \qquad \frac{1}{2}\sqrt{\frac{3}{\pi}}\frac{z}{r}$$

p_x $\qquad$ p_y $\qquad$ p_z







(For the polar coordinate expression see Table 2-3)

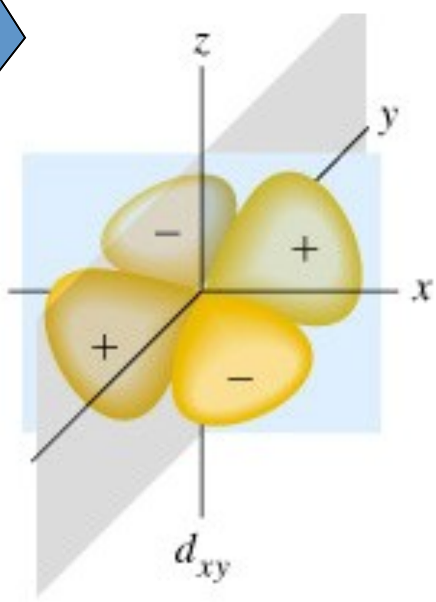
Angular Wave Functions

d-orbitals: $l = 2$, $m_l = -2, -1, 0, +1, +2$

Angular Wave Functions: $\Theta\Phi\ (x,y,z)$

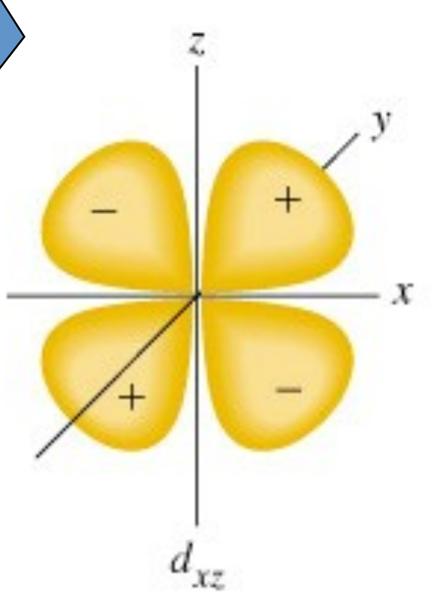
$$\frac{1}{4}\sqrt{\frac{15}{\pi}}\frac{xy}{r^2}$$

d$_{xy}$



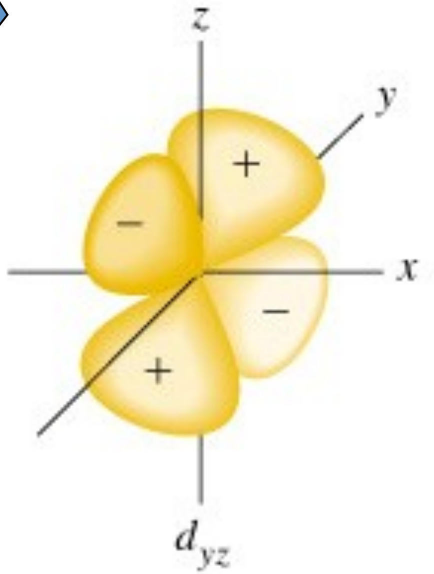
$$\frac{1}{2}\sqrt{\frac{15}{\pi}}\frac{xz}{r^2}$$

d$_{xz}$



$$\frac{1}{2}\sqrt{\frac{15}{\pi}}\frac{yz}{r^2}$$

d$_{yz}$



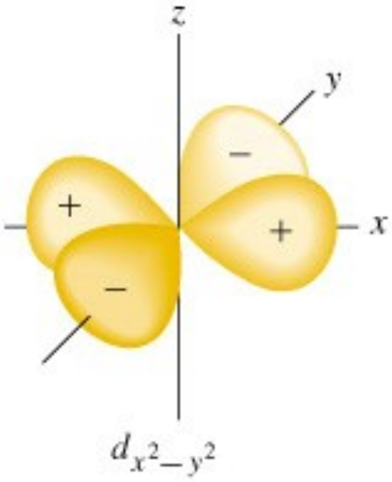
Angular Wave Functions

d-orbitals: $l = 2$, $m_l = -2, -1, 0, +1, +2$

Angular Wave Functions: $\Theta\Phi\ (x,y,z)$

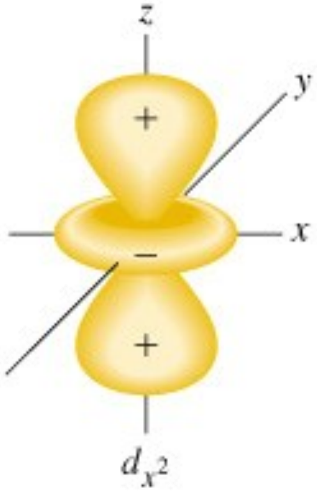
$$\frac{1}{4}\sqrt{\frac{15}{\pi}}\,\frac{(x^2 - y^2)}{r^2}$$

$d_{x^2-y^2}$



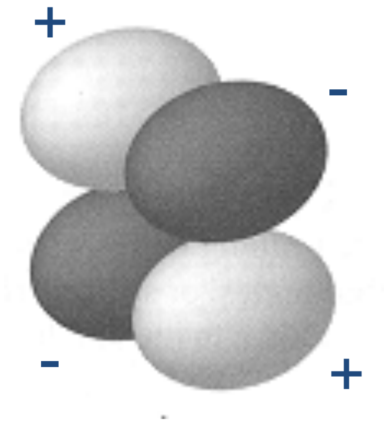
$$\frac{1}{4}\sqrt{\frac{5}{\pi}}\,\frac{\left(2z^2 - x^2 - y^2\right)}{r^2}$$

d_{z^2}



Sign of the Angular Wave Function

Often, orbitals are shaded to indicate the opposite signs of the wave function.



(which color is + and which color is – is arbitrary)

The probabilities of finding an electron are the same in shaded and non-shaded regions because probability is equal to Ψ^2, which is always positive.

Nodes

surfaces upon which the probability of finding and electron is zero

Radial Nodes

- *Spherical* surfaces of radius r upon which the probability of finding an electron is zero.
- Occur when the ***radial*** wave function changes sign (when $R(r) = 0$).

Angular Nodes

- Either *planar* or *conical* surfaces upon which the probability of finding an electron is zero.
- Occur when the ***angular*** wave function changes sign (when $\mathbf{Y}(\theta,\phi) = 0$).

Angular Node of a p_z Orbital

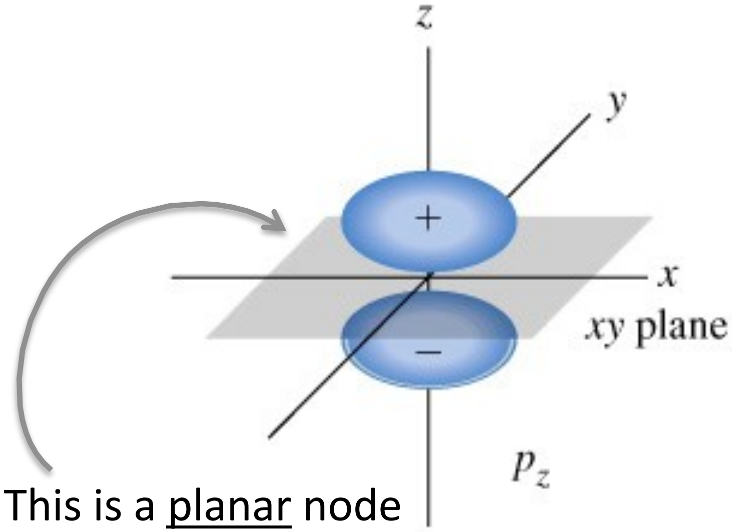
Example: Describe the angular nodal surface for a p_z orbital.

The angular wave function for a p_z orbital: $\frac{1}{2}\sqrt{\frac{3}{\pi}}\frac{z}{r}$

At an angular nodal surface, $Y(\theta,\phi) = 0$

Therefore, $\frac{1}{2}\sqrt{\frac{3}{\pi}}\frac{z}{r} = 0$

This is solved by making z = 0. ***Thus, an angular node exists where z = 0 (i.e., the xy plane)***



This is a planar node

Angular Node of a d_{z^2} Orbital

Example: Describe the angular nodal surface for a d_{z^2} orbital.

The angular wave function for a d_{z^2} orbital: $\frac{1}{4}\sqrt{\frac{5}{\pi}}\frac{\left(2z^2-x^2-y^2\right)}{r^2}$

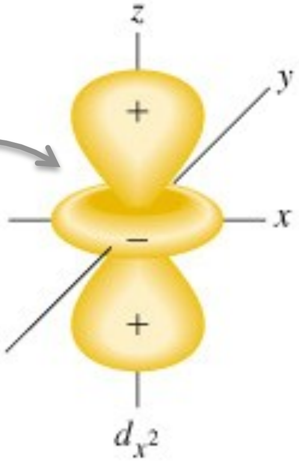
At an angular nodal surface, Y(θ,ϕ) = 0

Therefore,

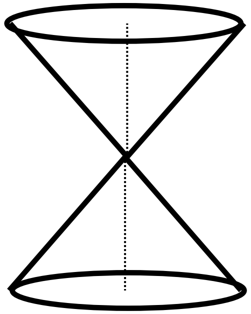
$$\frac{1}{4}\sqrt{\frac{5}{\pi}}\frac{\left(2z^2-x^2-y^2\right)}{r^2}=0$$

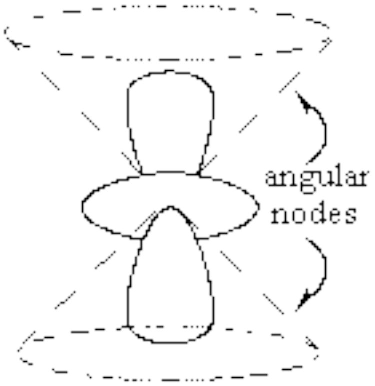
This is solved by making $2z^2 = x^2 + y^2$ which is the equation for a cone.

Thus, an angular node of the conical type exists where $2z^2 = x^2 + y^2$



This is a conical node

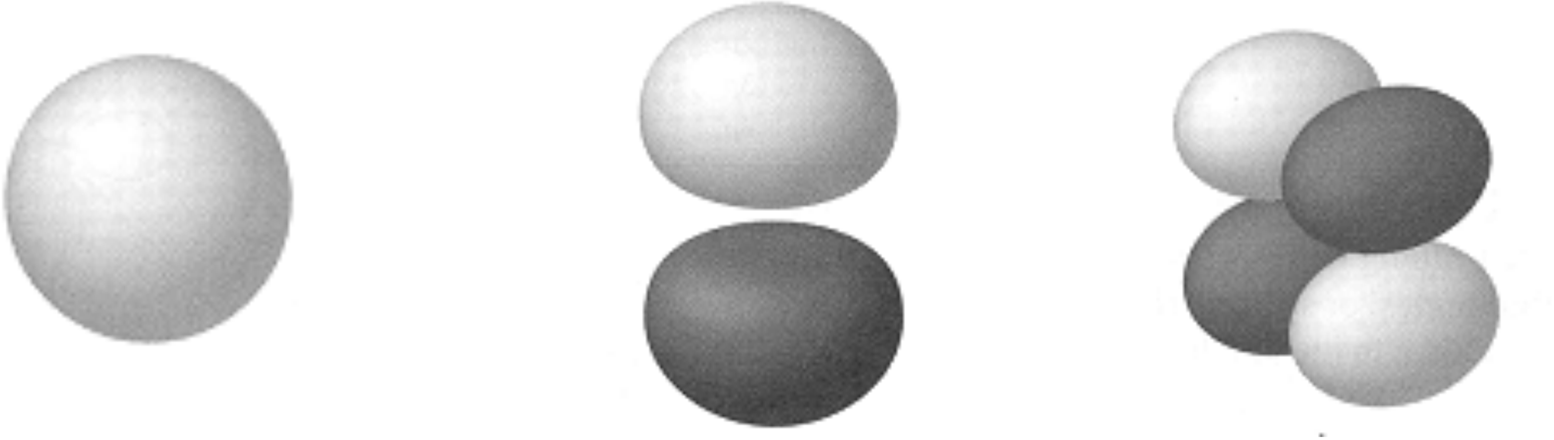




Counting Nodes

radial nodes = n - *l* - 1

angular nodes = *l*



s orbitals (*l*=0):	0 angular nodes
p orbitals (*l*=1):	1 angular node
d orbitals (*l*=2):	2 angular nodes

Total # nodes (radial + angular) = n - 1

Practice Exercises

1) Describe the angular nodal surface for a $d_{x^2-y^2}$ orbital, which has the following angular wave function

$$Y = \frac{1}{4}\sqrt{\frac{15}{\pi}}\frac{(x^2 - y^2)}{r^2}$$

2) In a $3d_{x^2-y^2}$ orbital
   a) how many angular nodes are there?
   b) how many radial nodes are there?

3) In a $5d_{x^2-y^2}$ orbital
   a) how many angular nodes are there?
   b) how many radial nodes are there?

Combining Radial and Angular Wave Functions

$$\psi(r,\theta,\phi) = \underbrace{\mathbf{R}(r)}_{\text{radial function}} \; \underbrace{\mathbf{Y}(\theta,\phi)}_{\text{angular function}}$$

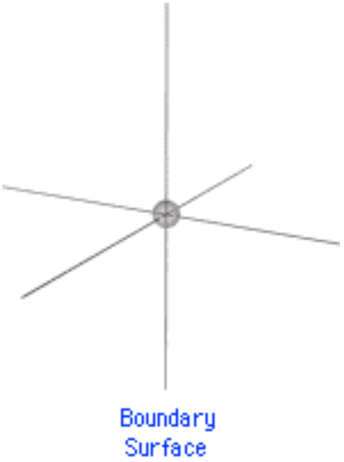
Radial Function R(r):

- Variation of the orbital with distance from the nucleus
- **Depends upon quantum numbers n and *l***

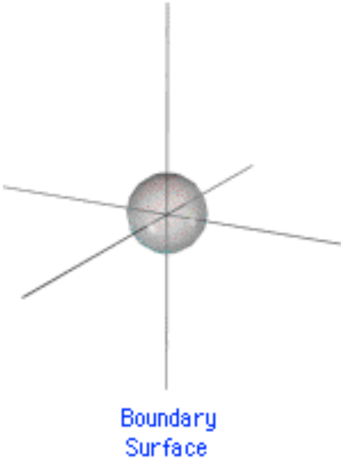
Angular Function Y(θ,ϕ):

- The shape of the wave function (or orbital) and its orientation in space.
- **Depends upon quantum numbers *l* and m_l**

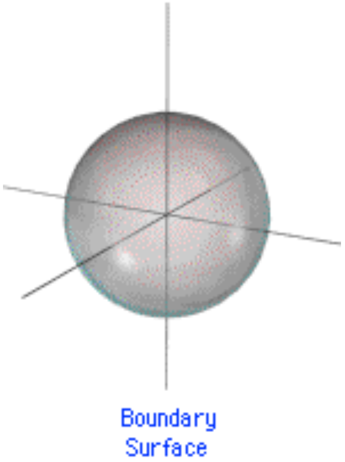
s-Orbitals ($l = 0$)



1s



2s



3s

Size: as n increases, size increases

Nodes: angular nodes = $l = 0$ (results in spherical shape)
radial nodes = $n - l - 1$ → 1s = 0; 2s = 1; 3s = 2

Where are these radial nodes? Why don't we see them?

Boundary Surfaces

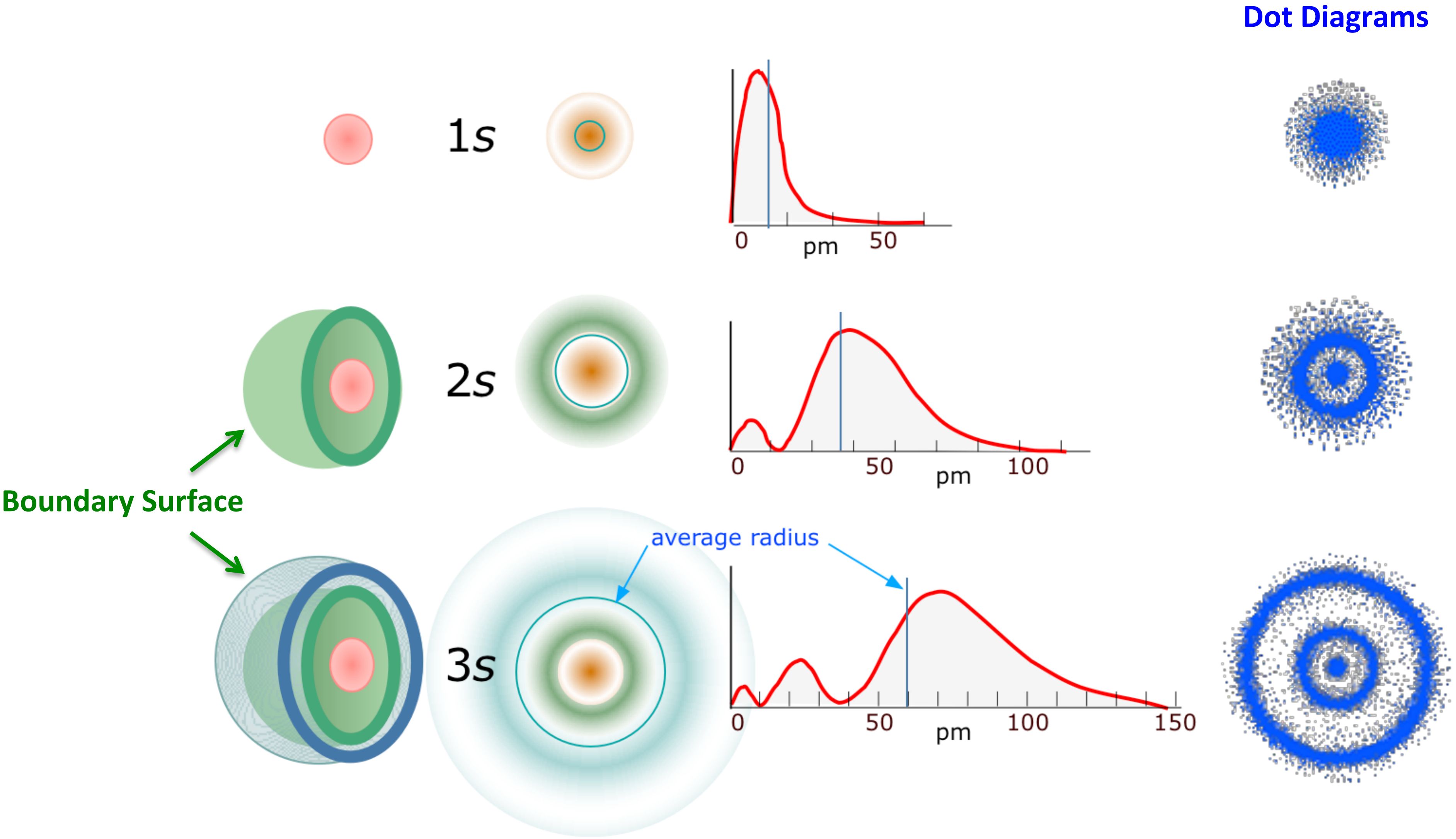
We represent orbitals using ***boundary surfaces***: regions in space within which the probability of finding the electron is 90%.

Boundary surfaces only show us the outer surface. There can be nodes on the interior layers that we don't see.

↳ think of the layers within an onion

By looking at orbital cross-sections, we can see interior nodes.

Orbital Cross-Sections

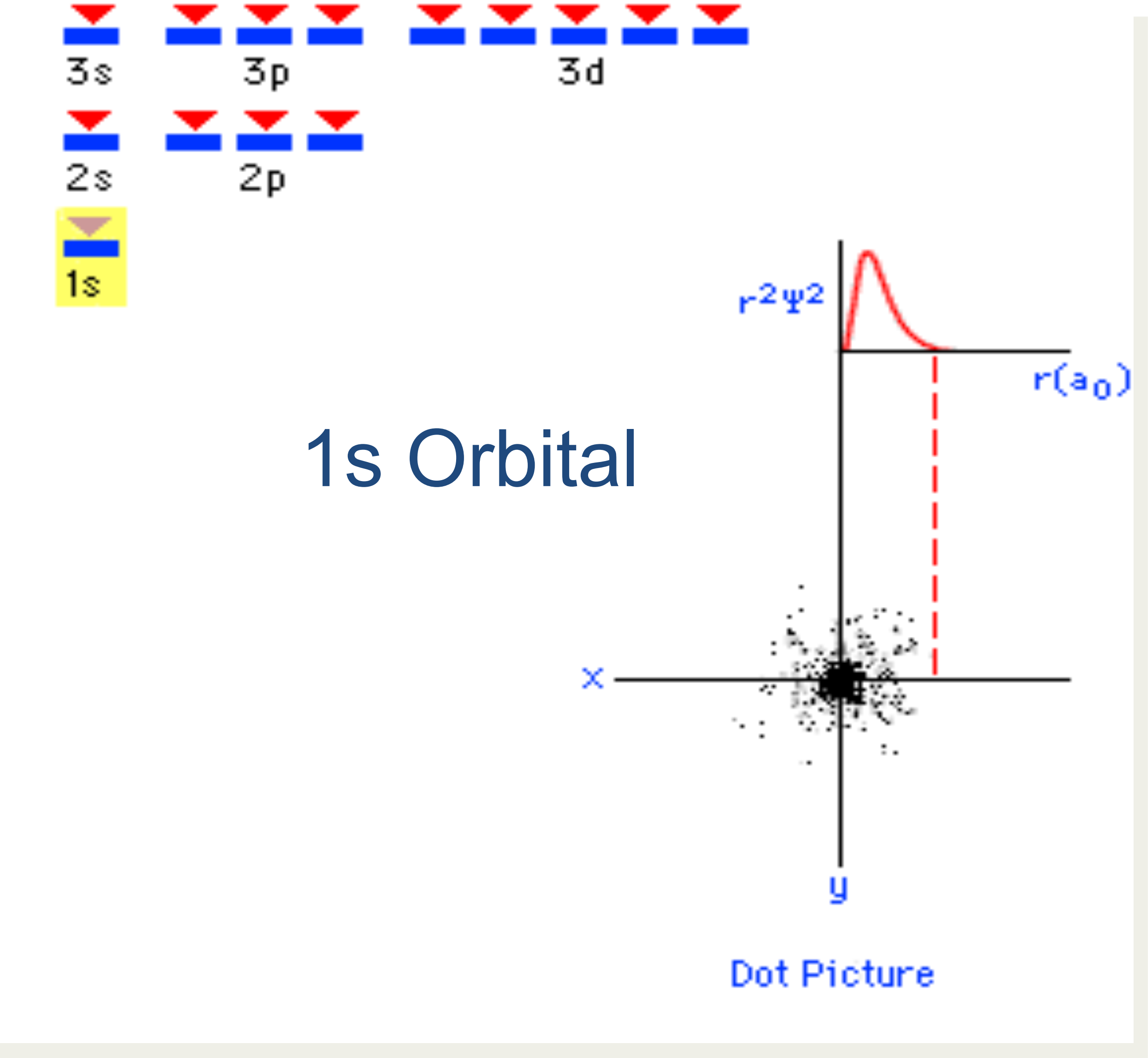


Dot Diagrams

Boundary Surface

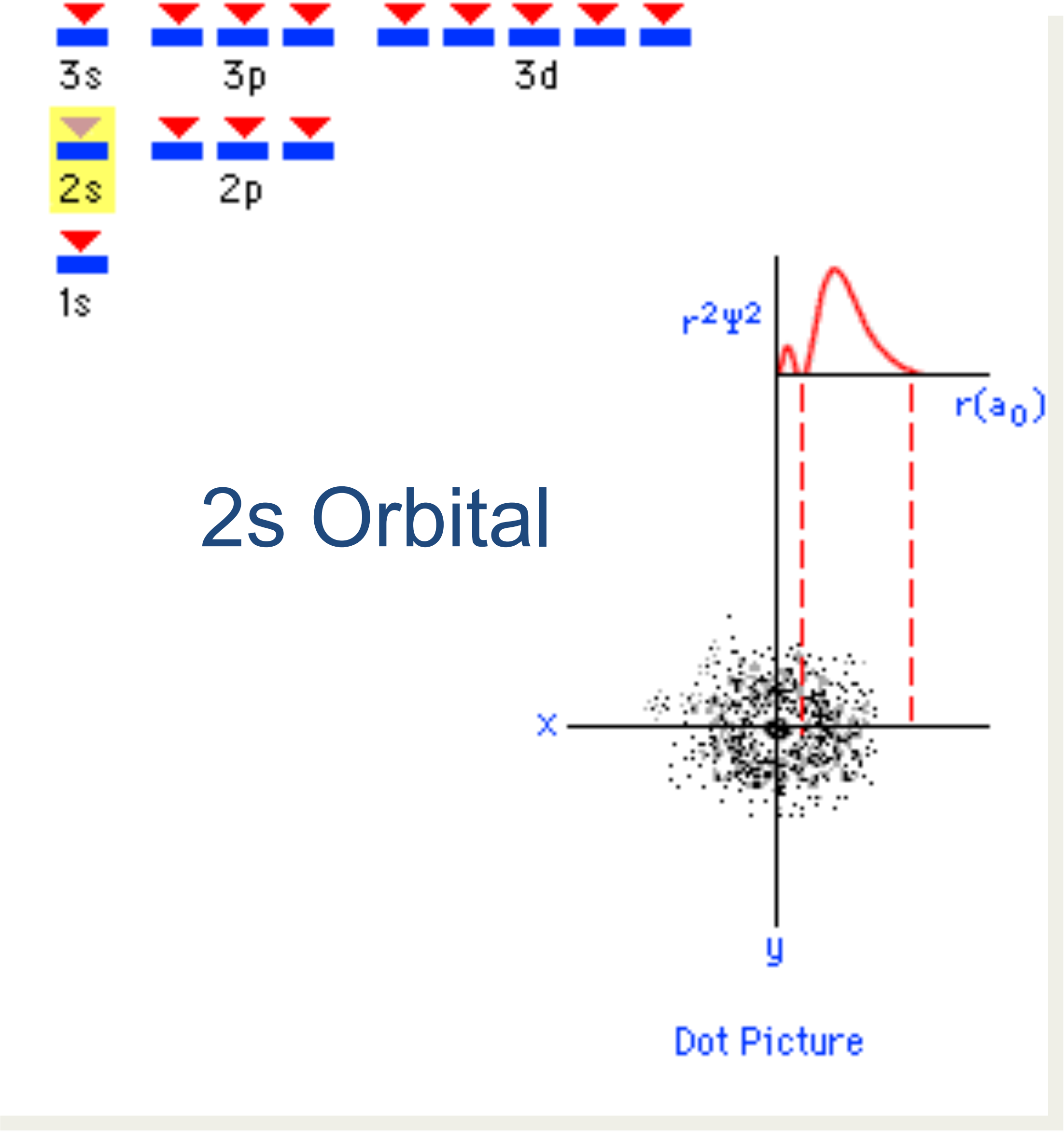
average radius

Radial Nodes in s-Orbitals



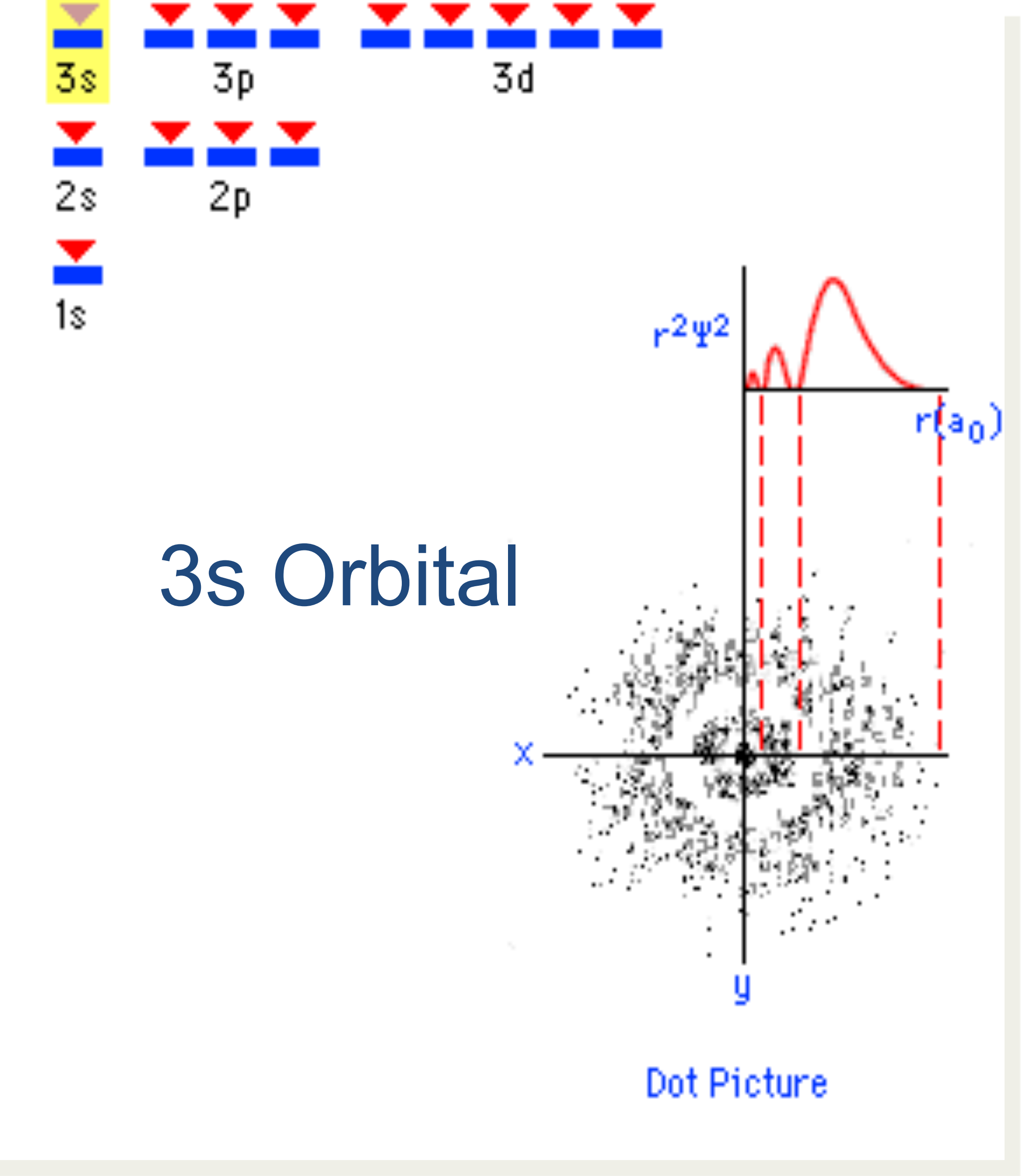
1s Orbital

Radial Nodes in s-Orbitals



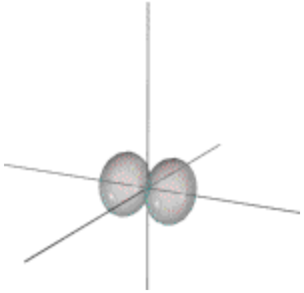
2s Orbital

Radial Nodes in s-Orbitals

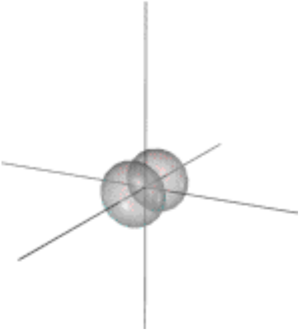


3s Orbital

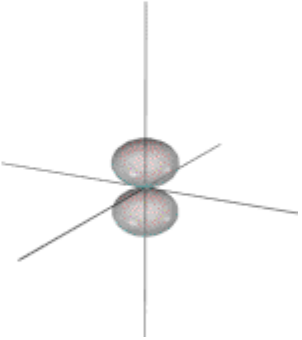
p-Orbitals (*l* = 1)



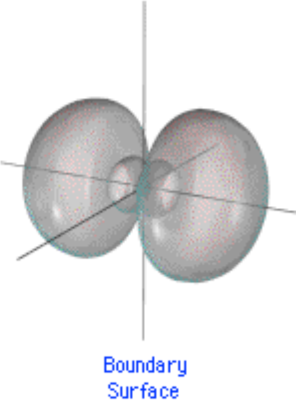
$2p_x$



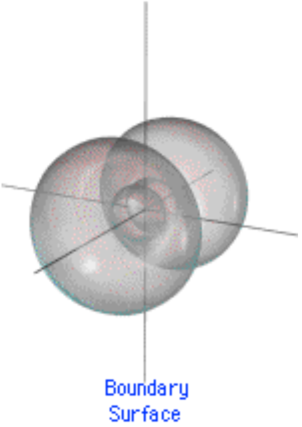
$2p_y$



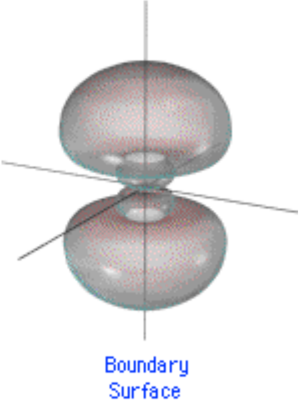
$2p_z$



$3p_x$



$3p_y$

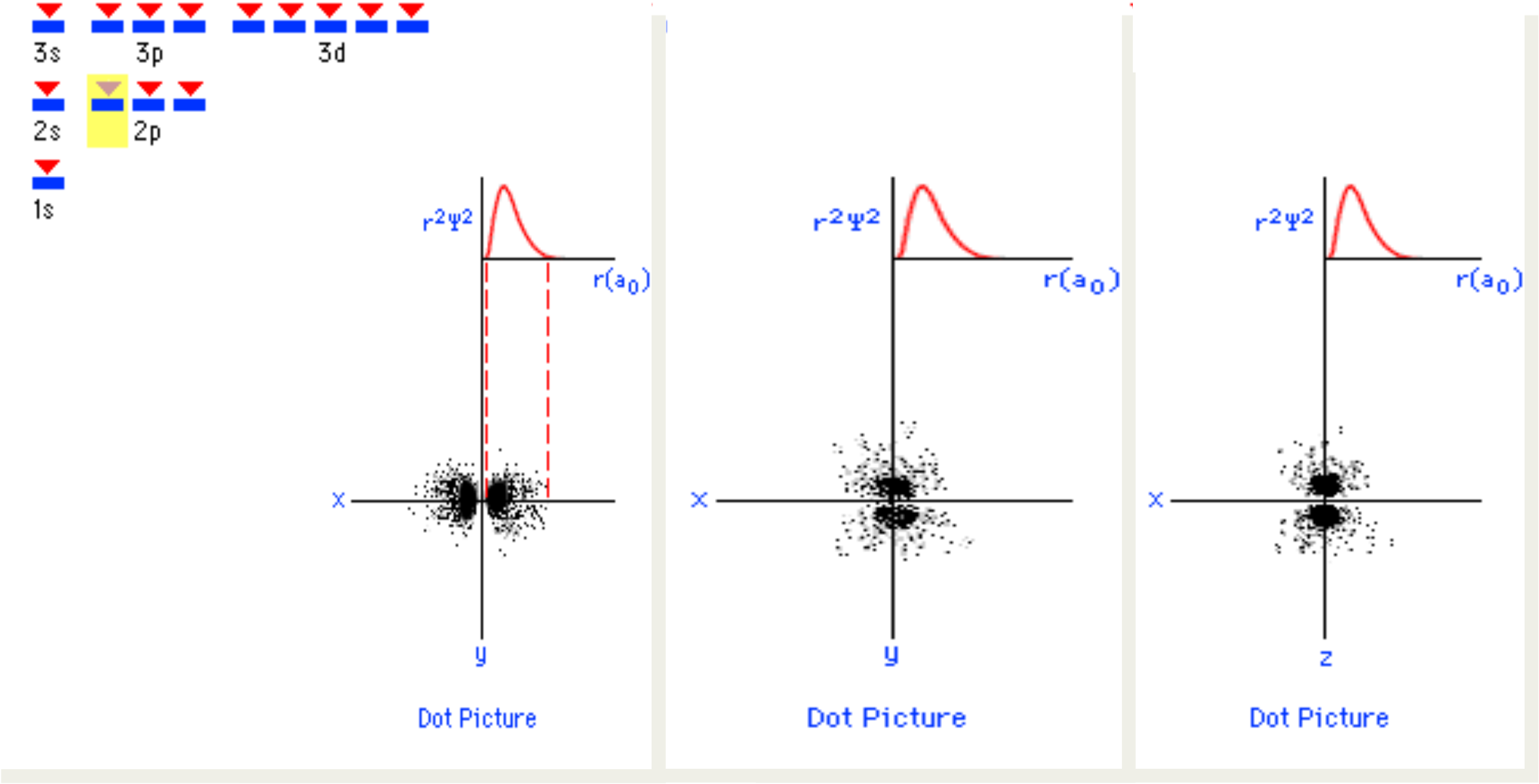


$3p_z$

Size: as n increases, size increases

Nodes: angular nodes = *l* = 1 (results in barbell or dumbbell shape)
radial nodes = n – *l* – 1 → 2p = 0; 3p = 1; 4p = 2

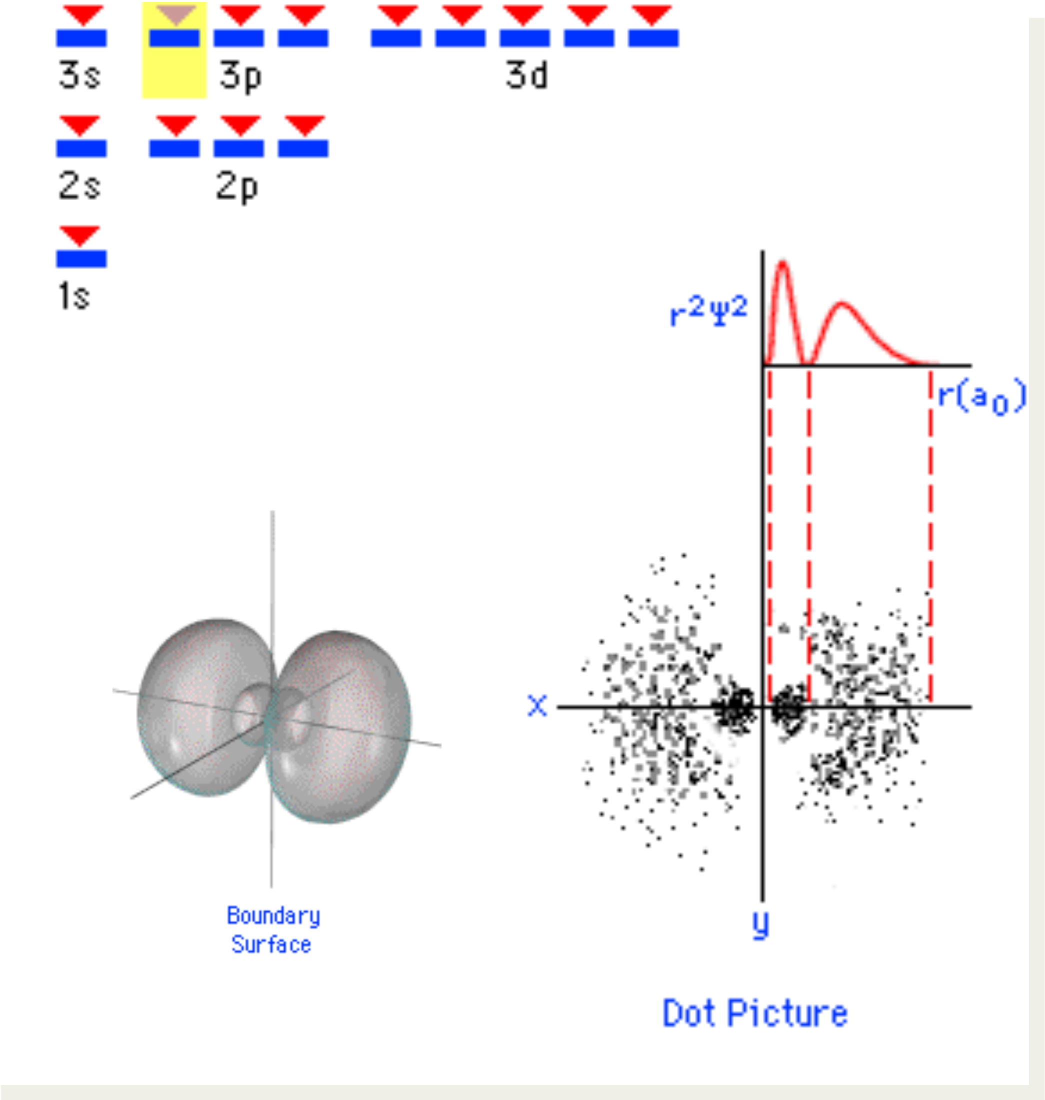
Nodes in p-Orbitals



$2p_x$ $2p_y$ $2p_z$

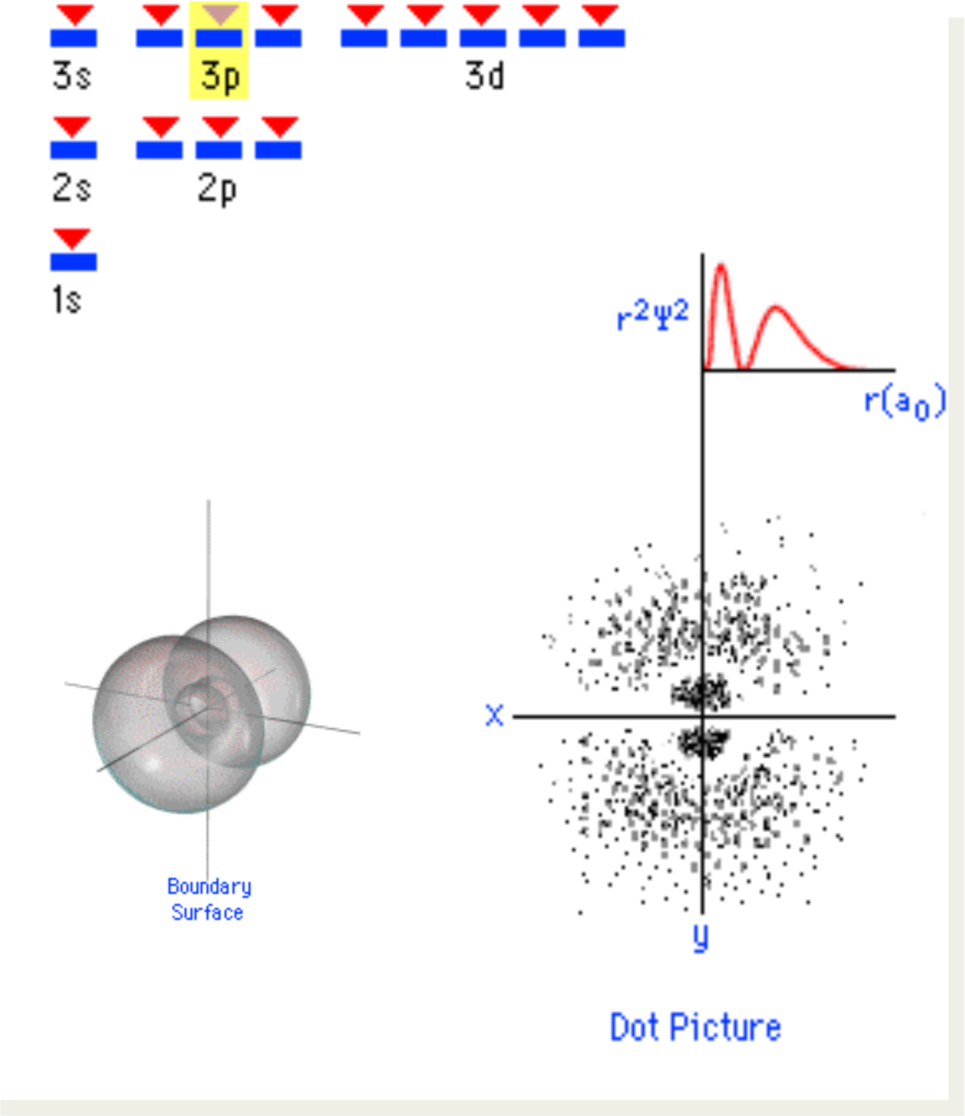
From the radial probability plots, you can see that the radial wave function is identical for p_x, p_y, and p_z. The only thing that changes is the angular wave function.

Nodes in p-Orbitals



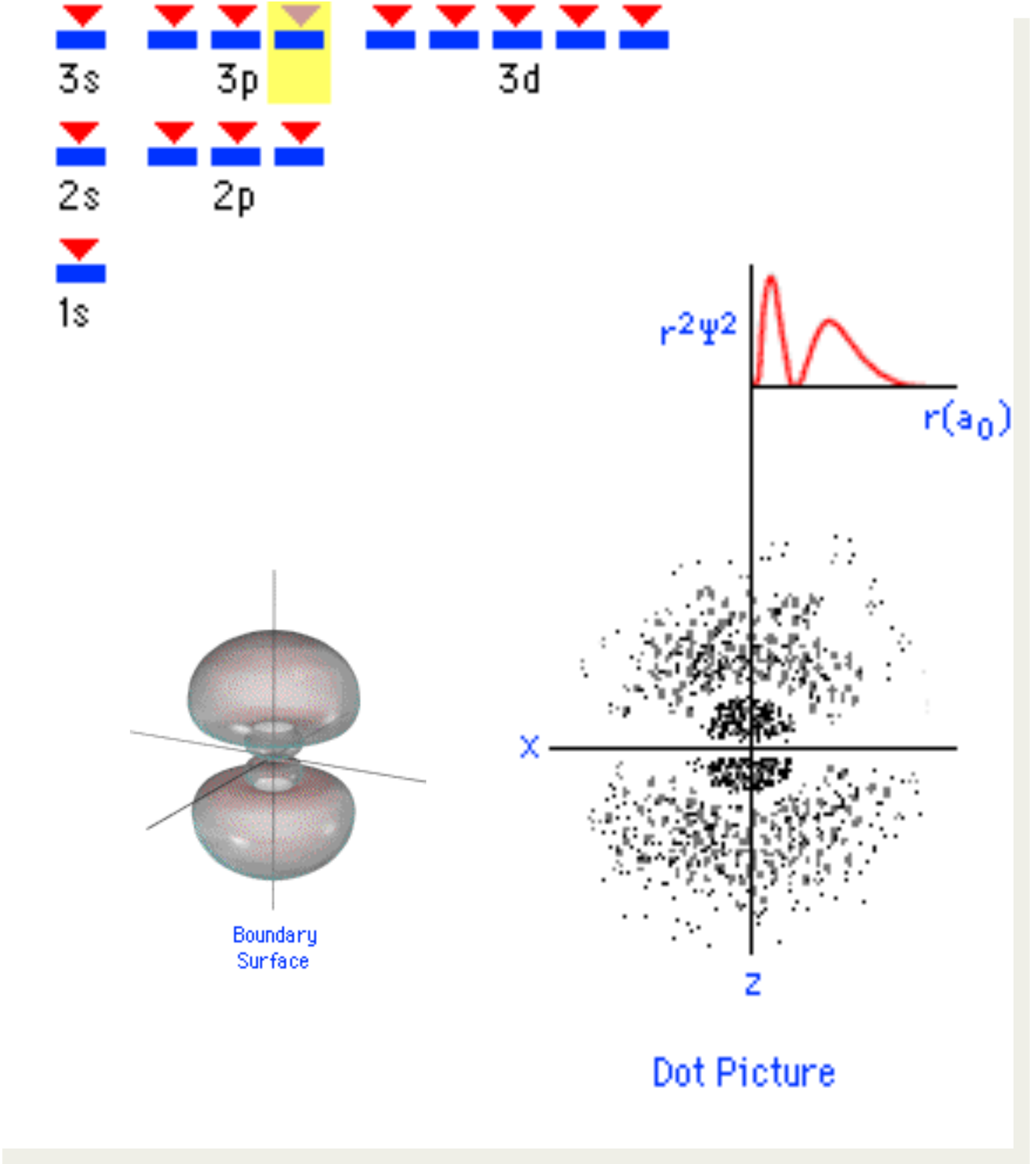
$3p_x$

Nodes in p-Orbitals



3p$_y$

Nodes in p-Orbitals

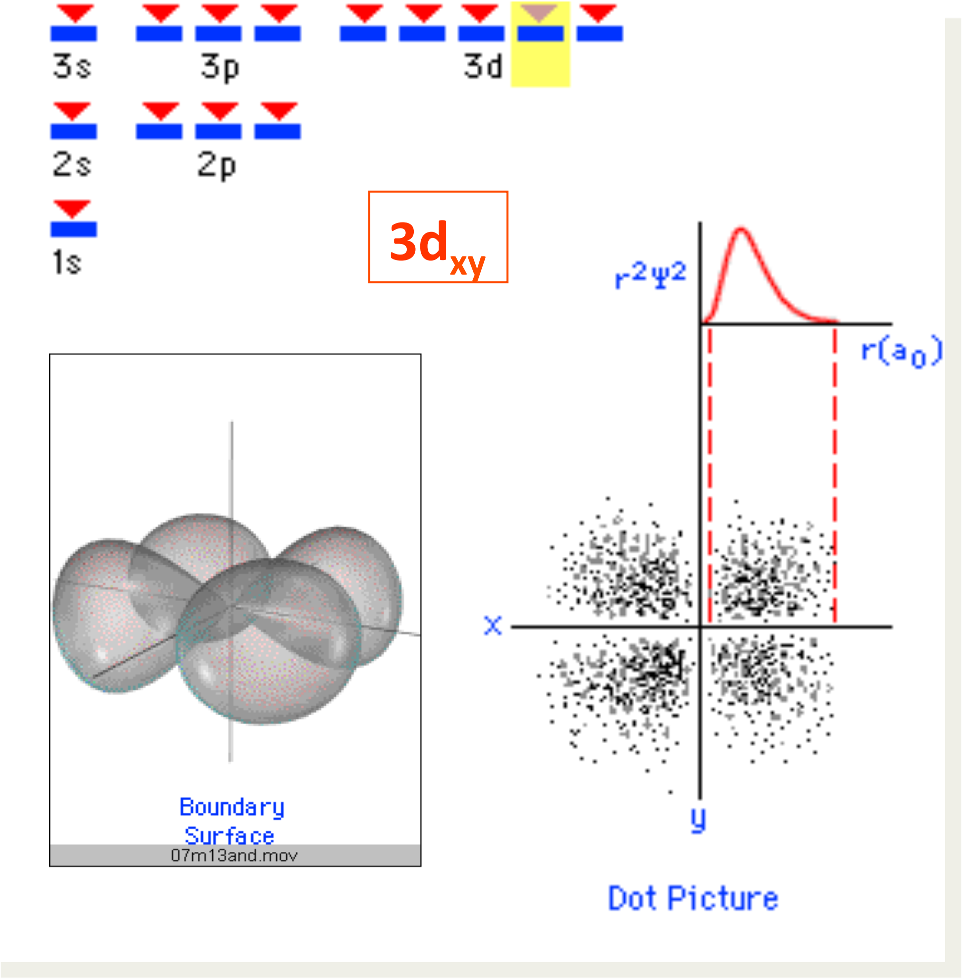


$3p_z$

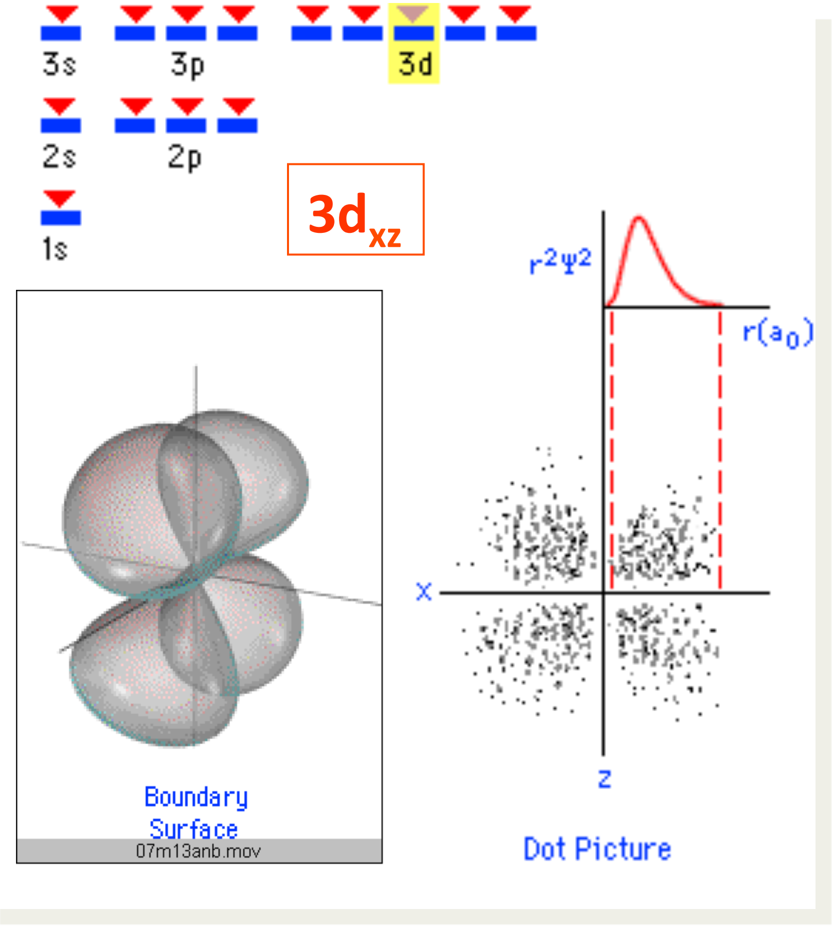
Nodes in d-Orbitals (*l* = 2)

Nodes: angular nodes = *l* = 2

radial nodes = n – *l* – 1 → 3d = 0; 4d = 1, etc.

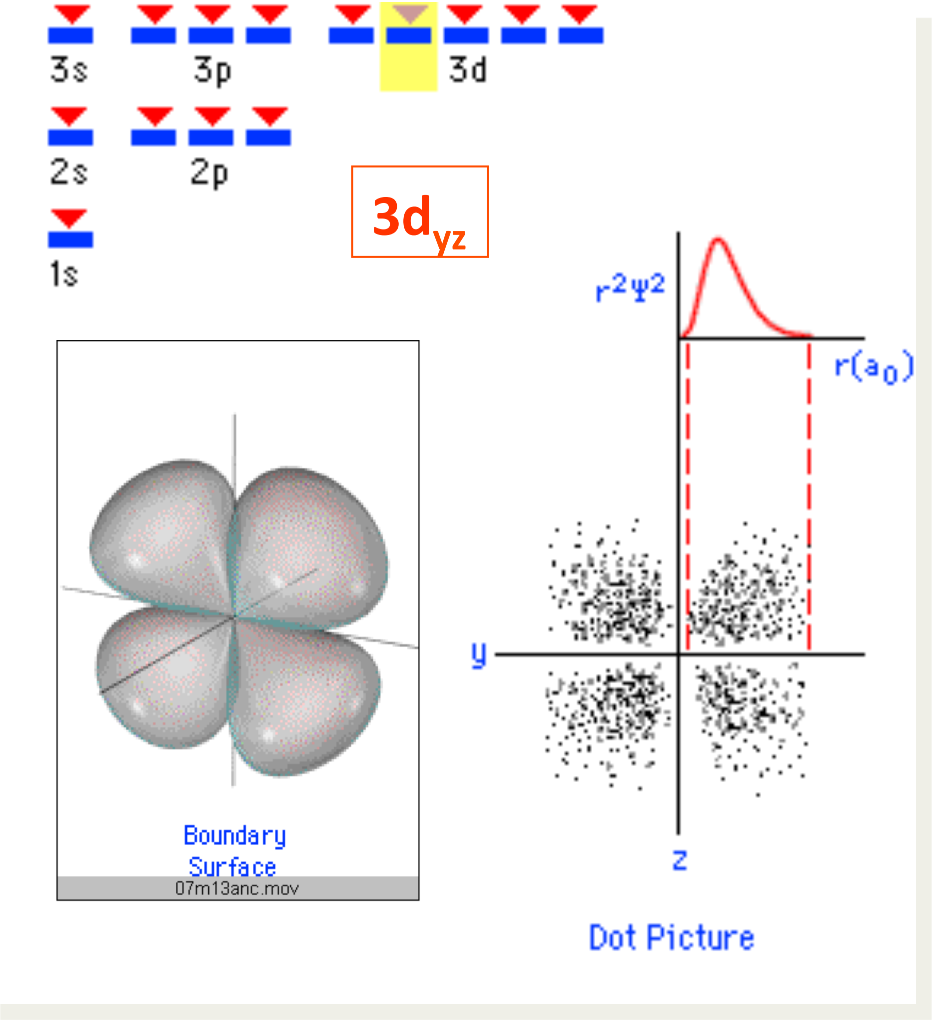


Nodes in d-Orbitals

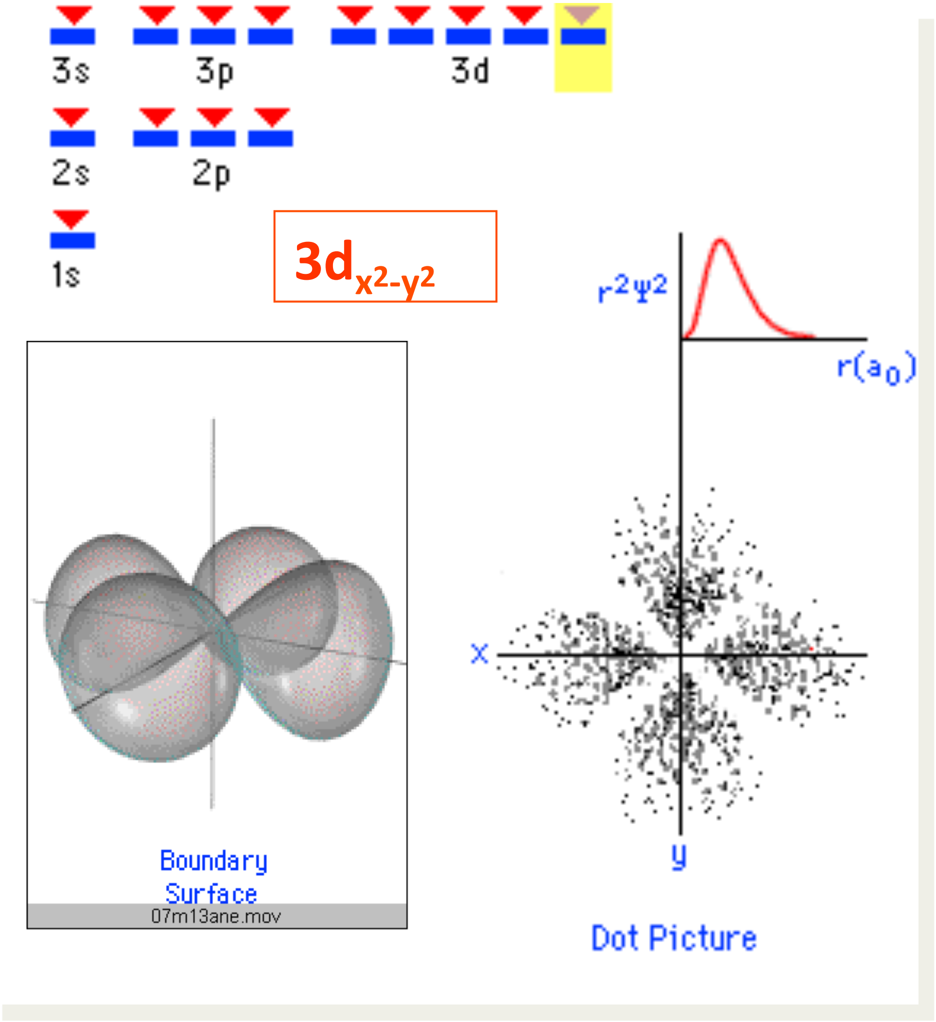


$3d_{xz}$

Nodes in d-Orbitals

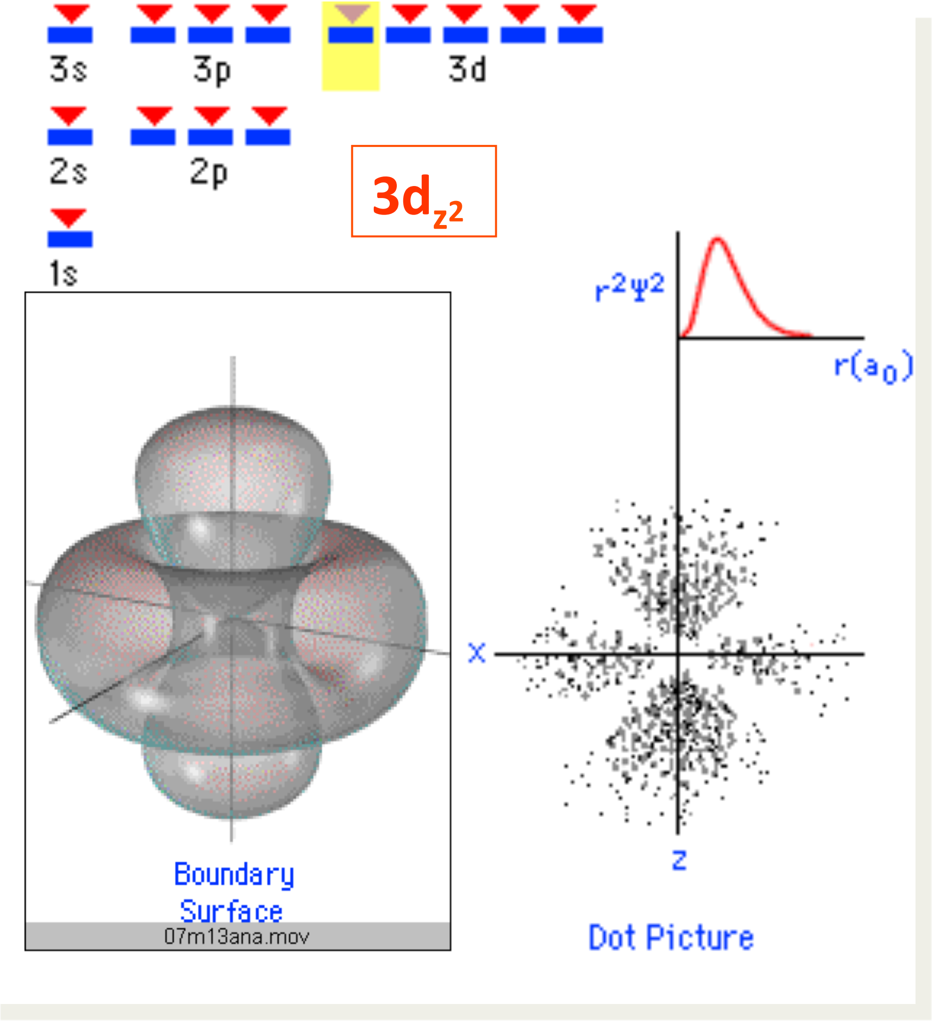


Nodes in d-Orbitals



$3d_{x^2-y^2}$

Nodes in d-Orbitals

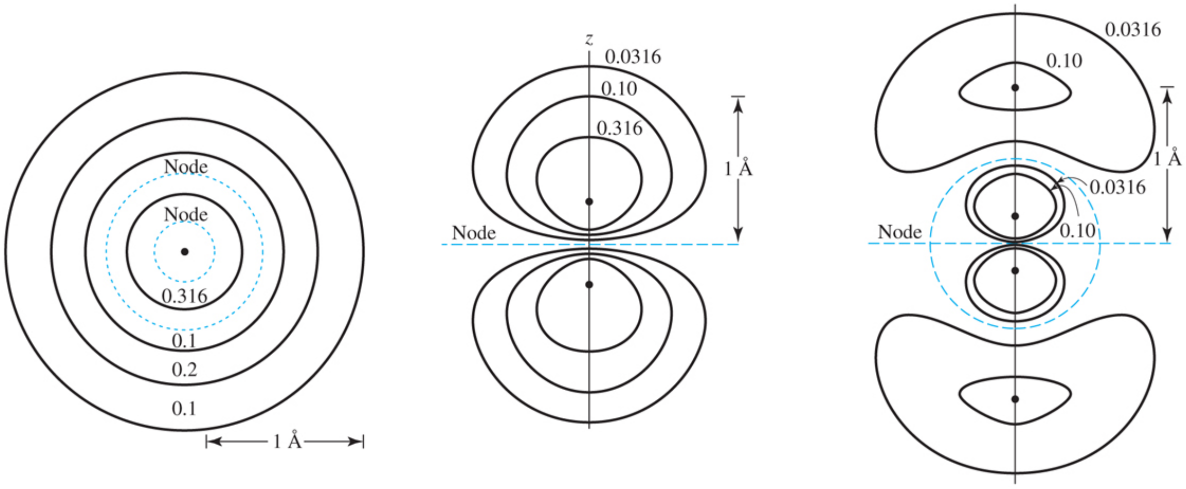


Contour Maps of Orbitals

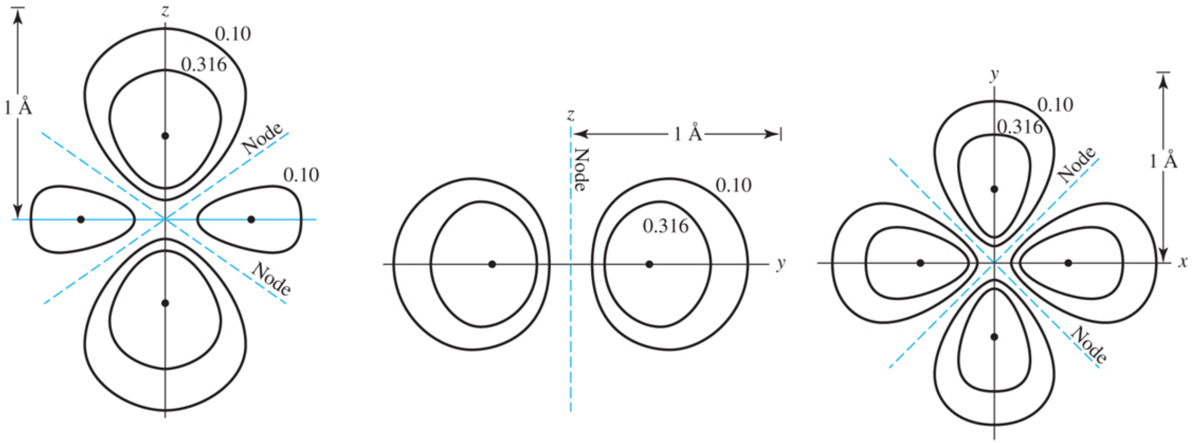
Contour maps show lines of constant electron density in a cross section of an atomic orbital.

These diagrams can make it easier to see nodes.

Which nodes are radial and which are angular?



(a) Cl:$3s$ (b) C:$2p_z$ (c) Cl:$3p_z$



(d) Ti^{3+}:$3d_{z^2}$ (e) Ti^{3+}:$3d_{x^2-y^2}$ (f) Ti^{3+}:$3d_{x^2-y^2}$

Online Resource: The Orbitron

http://winter.group.shef.ac.uk/orbitron/

A gallery of atomic orbitals and molecular orbitals on the web.

- images representing atomic orbitals and molecular orbitals
- animated plots of wave functions
- animated plots of electron density
- “dot-density” plots of electron density
- plots of radial distribution functions

Energies from the Schrödinger Equation

$$\left[\frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)+V(x,y,z)\right]\psi(x,y,z)=E\psi(x,y,z)$$

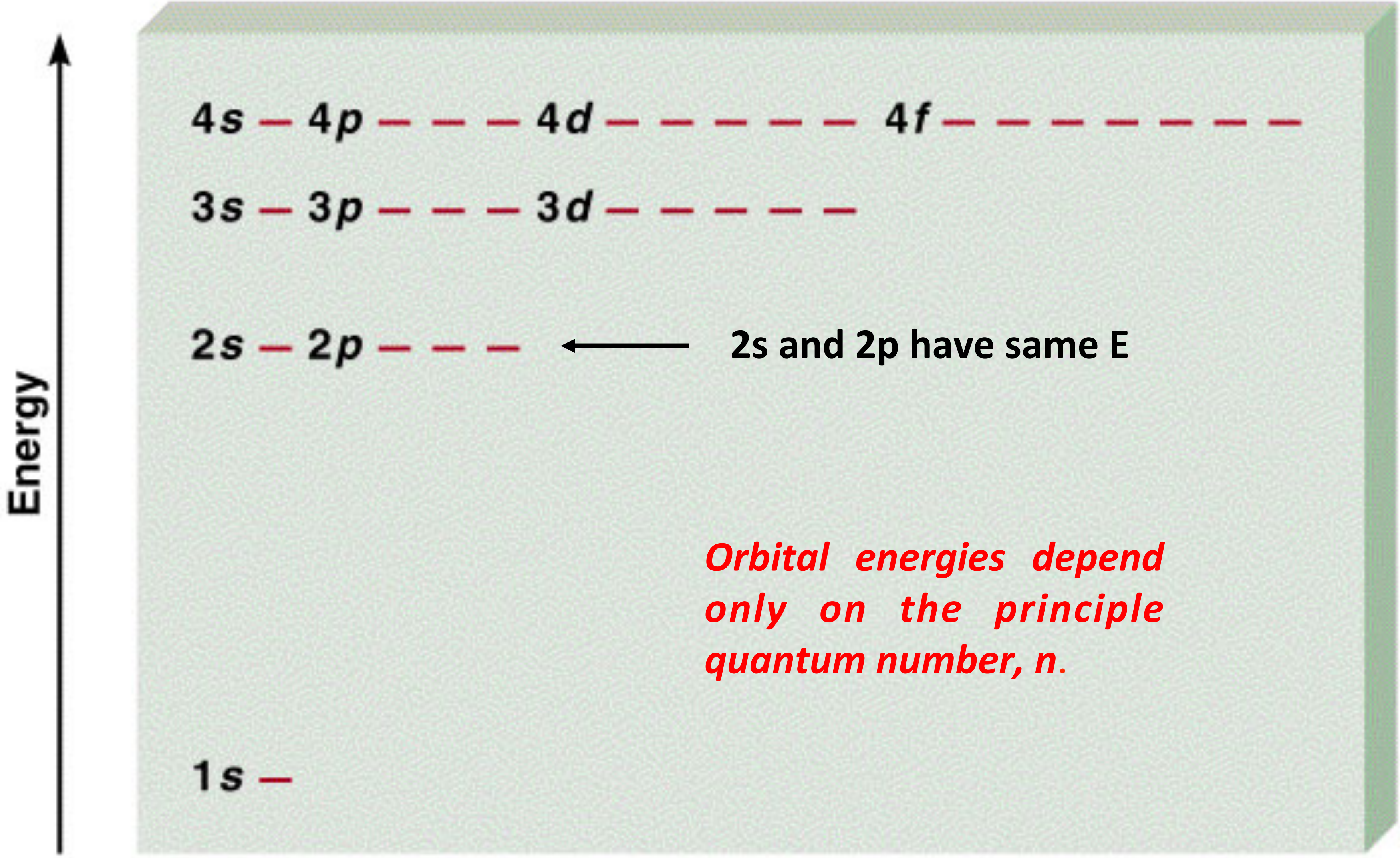
In solving the Schrodinger Equation, we find:

1) Values for ψ (orbital description)
2) Energies associated with each orbital – these depend only on n

The Schrödinger Energy: $E_n = -R_H\left(\frac{1}{n^2}\right)$

(Same as Bohr Model!)

Orbital Energy Level in the Hydrogen Atom



2s and 2p have same E

Orbital energies depend only on the principle quantum number, n.

Multi-Electronic Atoms

Adding electrons to an atom makes the Schrödinger equation more complicated:

For 1 electron atoms:

- ➥ Potential energy depends only on electron-nuclear attraction
- ➥ Thus, the potential energy depends only on r (distance from nucleus)

For multi-electron atoms:

- ➥ Potential energy depends on:
  a) electron-nuclear attractions
  b) electron-electron repulsions
- ➥ Thus, the potential energy portion of the equation becomes very complicated.

Multi-Electronic Atoms

The Schrödinger equation can not be exactly solved for multi-electronic atoms!

Why?

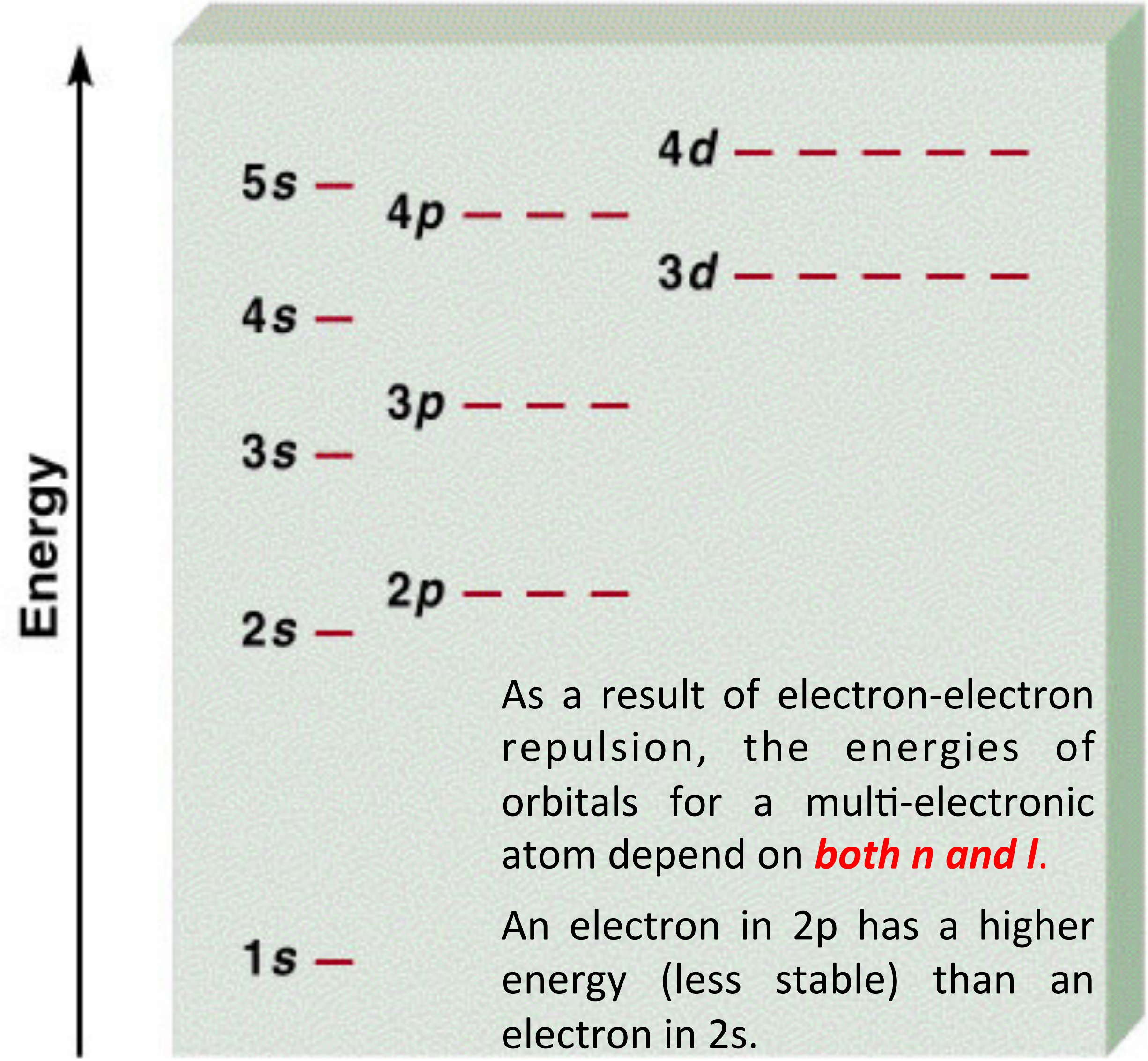
The electron-electron repulsion factor depends upon the distance between two electrons.

To solve it, it would be necessary to know the exact location of each electron, which we can not know!

Therefore, the electron-electron repulsion term can be, at best, an approximation.

There are many ways to carry out this approximation, and you can learn them in a computational chemistry class. Some methods of approximation give better results than others. The better approximations consume more computer time.

Orbital Levels in a Many Electron Atom



As a result of electron-electron repulsion, the energies of orbitals for a multi-electronic atom depend on ***both n and l***.

An electron in 2p has a higher energy (less stable) than an electron in 2s.

Summary of the Schrödinger Equation for a Hydrogen Atom

1) The Schrödinger equation treats electrons as waves.
2) The Schrödinger equation is the expressed as the following:

$$\left[\frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)+V(x,y,z)\right]\psi(x,y,z)=E\psi(x,y,z)$$

3) Solving the Schrödinger equation gives the wave function for an electron (ψ) and its associated energy.
4) The wave function may be divided into radial and angular components as follows:

$$\psi(r,\theta,\phi) = \underbrace{\mathbf{R}(r)}_{\text{radial function}}\ \underbrace{\mathbf{Y}(\theta,\phi)}_{\text{angular function}}$$

Summary of the Schrödinger Equation for a Hydrogen Atom

5) The radial function shows how the electron distribution in the atom changes at different distances from the nucleus. (i.e. the size of the orbital).
   - Radial functions depend on n and l
   - For a given orbital, there are n-l-1 radial nodes.
   - These radial nodes occur when $R(r) = 0$

6) The angular function shows the shape of the orbital.
   - Angular functions depend on l and m_l
   - For a given orbital, there are l angular nodes.
   - These angular nodes occur when $Y(\theta,\phi) = 0$

7) In solving the Schrodinger Equation for a hydrogen atom, three quantum numbers emerge: n, l, m_l. We define the orbitals based on the set of these three quantum numbers

Quantum Numbers

- n : principal (1, 2, 3,...) → *radial distribution, orbital size, energy*
- l : angular momentum (l = 0 (*s*), 1 (*p*), 2 (*d*), 3 (*f*),..., n -1) → *orbital shape*
- m_l : magnetic (- l, (- l +1),..., (l - 1), + l; total = 2 l + 1) → *orbital orientation*

Summary of the Schrödinger Equation for a Hydrogen Atom

8) The square of the wave function (ψ^2) gives the probability of finding an electron at a given location in the atom.

- ➥ Orbitals are visualized by their *boundary surfaces*. These are surfaces within which there is a 90% probability of finding the electron.
- ➥ Orbital energies
  - ↳ in a single-electron atom, E depends only on the quantum number n.
  - ↳ in a multi-electron atom, E depends on n and l
  - ↳ n and l are quantized (have restricted values) resulting in ***quantization of E.***

Returning to the Original Question

How can the line spectra of atoms be explained?

Line Emission Spectrum of Hydrogen Atoms

Schrödinger Model Explanation of Line Spectrum for Hydrogen

Schrӧdinger's wave equation gives the same orbital energies as does Bohr's model.

$$E_n = -R_H \left(\frac{1}{n^2} \right)$$

An electron absorbs energy and jumps to a higher energy orbital. When it returns to a lower energy orbital it emits light.

Comparing Bohr and Schrödinger Models?

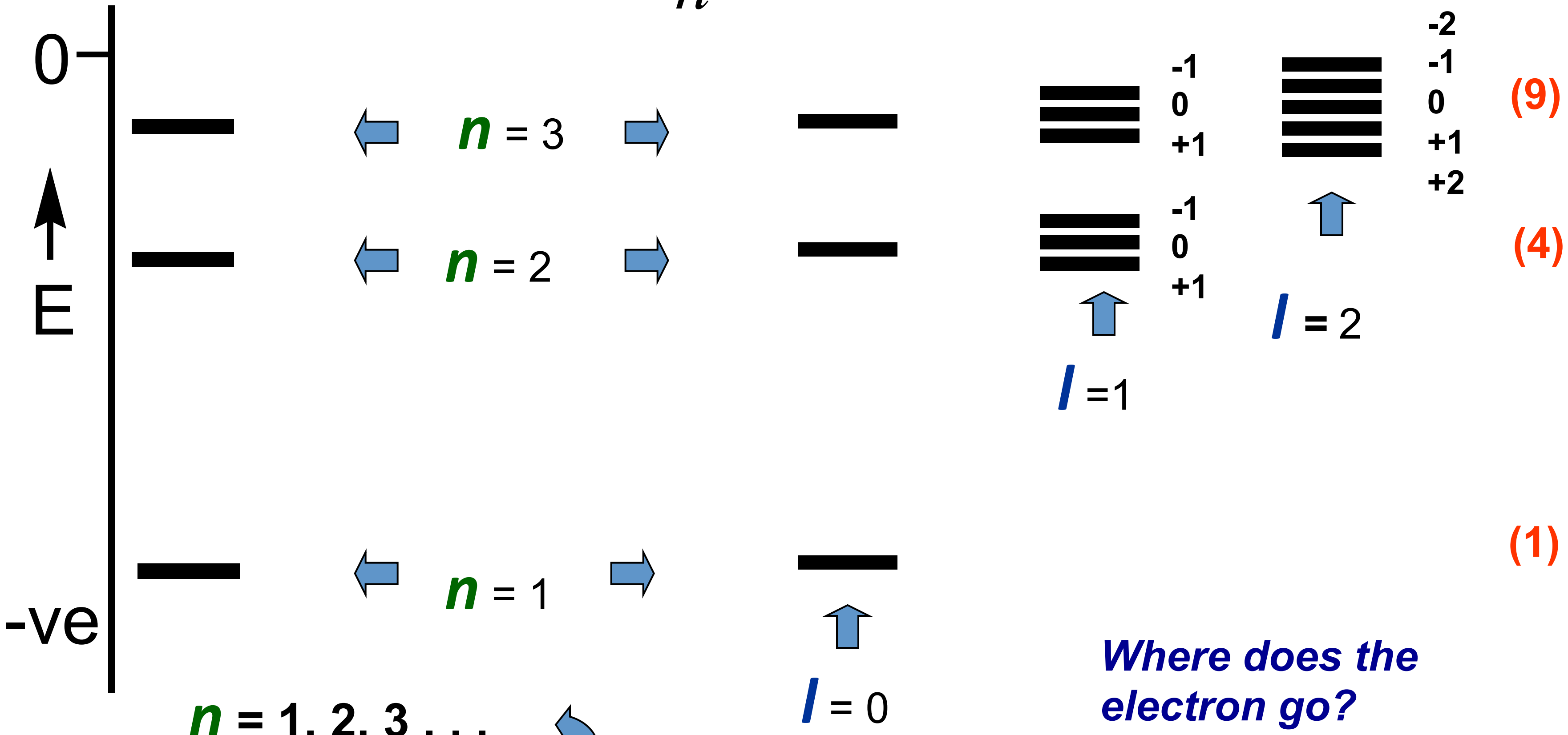
The energies for a single-electron hydrogen atom turn out the be the same. Everything else is different.

- Bohr model describes electrons as particles.
- Schrödinger model describes electrons as waves.

- Bohr describes electrons as orbiting around the nucleus: location and velocity can be calculated.
- Schrödinger gives probable locations of electrons (orbitals), but it is impossible to determine exact locations (Heisenberg Uncertainty Principle). Electrons DO NOT ORBIT the nucleus!!!

- Bohr model cannot be extended to polyelectronic atoms
- Schrödinger model can be extended to polyelectronic atoms, albeit with mathematical difficulty).

Bohr Hydrogen ⇐ $E_n = \frac{R_H}{n^2}$ ⇒ **Schrodinger Hydrogen**



Where does the electron go?

n = 1, 2, 3 . . .

One quantum number

Three quantum numbers

n = 1, 2, 3 . . .

l = 0, 1, 2 . . .(n - 1) ***(n values)***

m_l = 0, ±1, . . ± l ***(2l + 1 values)***