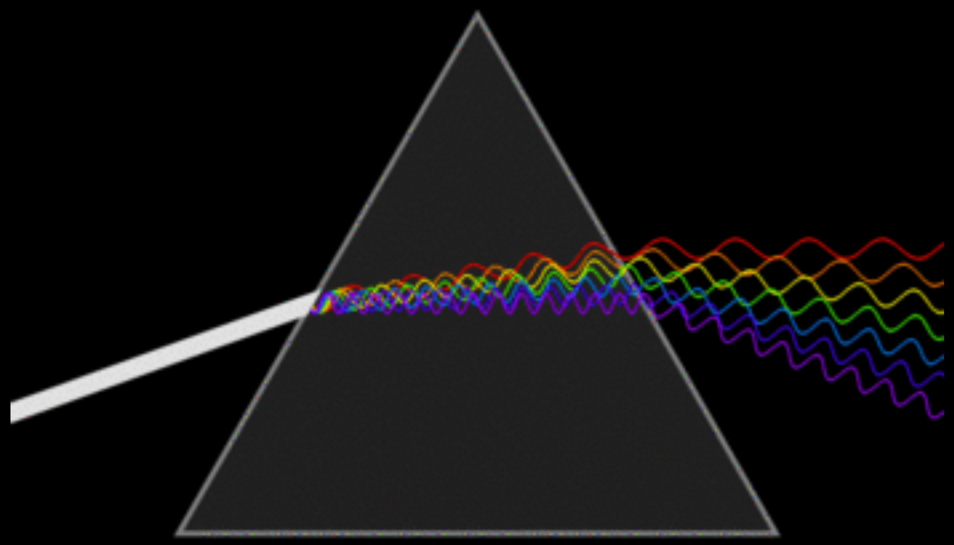
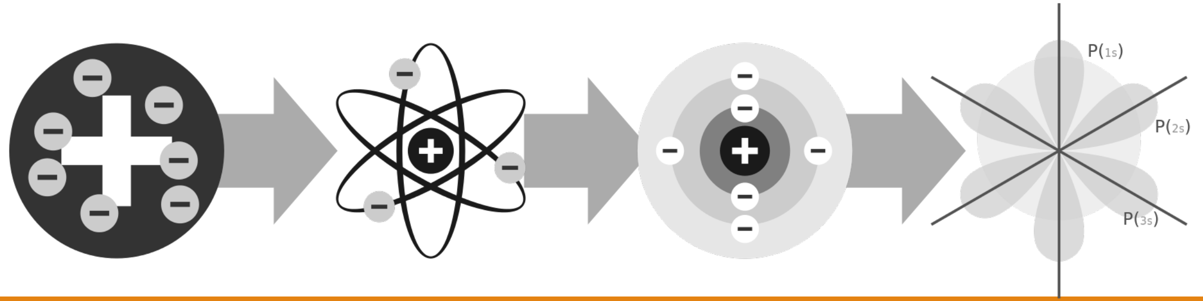


CH301 Unit 2

REVIEW TWO: QUANTUM THEORY

Goals For Today: Quantum Mechanics

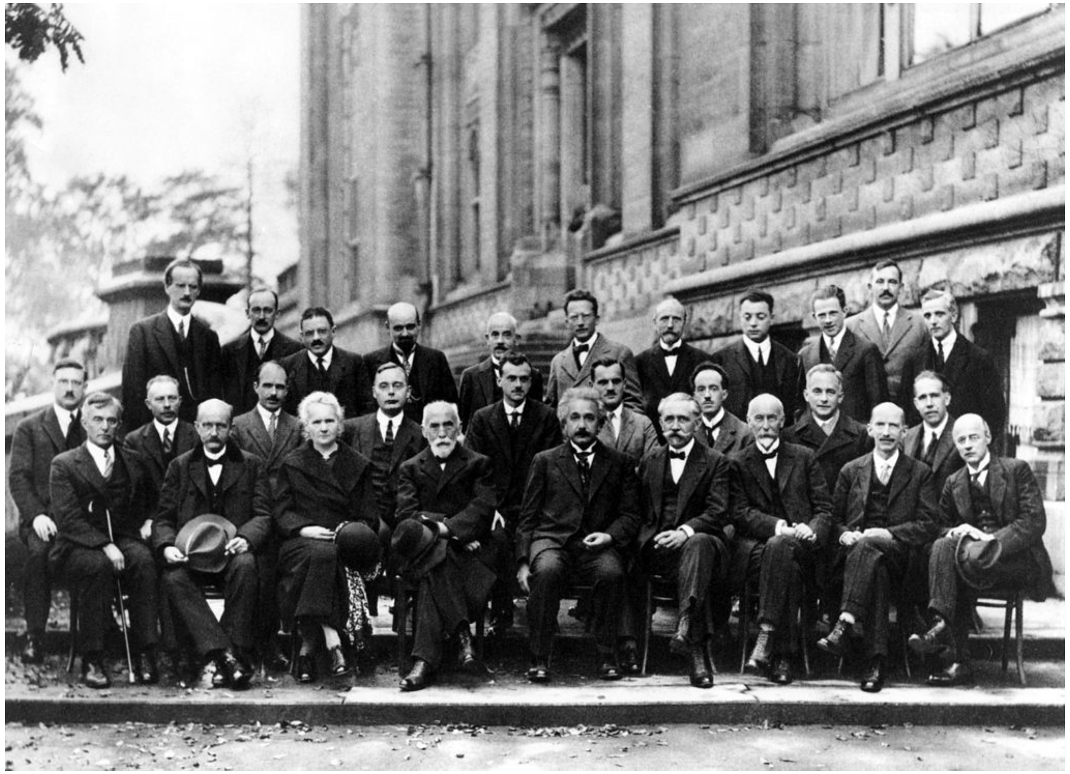
- Briefly discuss the evidence for Quantum Mechanics
- Examine the Rydberg Equation and its relationship to absorption and emission
- Look conceptually into the Schrödinger Equation
- Model the Schrödinger Equation for Hydrogen using Particle in a Box and the Radial Distribution Function
- Discuss the solutions to the Schrödinger Equation and what they mean for the energy, shape, and orientation of atomic orbitals
- Review the basic concepts of non-exception electron configurations



What is Quantum Mechanics?

- Quantum mechanics helps us explain the currently accepted model of the atom using the following empirically derived postulates:

1. Electrons exist in **discrete, quantifiable energy states**.
   - Absorption/Emission spectra: The line spectra for a given gas has characteristic wavelengths
2. Electrons and light (photons) exhibit **wave-particle duality**.
   - Photoelectric effect: Light can act like particles
   - X-Ray diffraction: Small particles (electrons) can act like waves
3. The location and behavior of electrons can be described only with **probabilities**.
   - The Schrödinger Equation: Uses an understanding of probabilities and uncertainty to give us useful information about the electrons of an atom, such as the 4 quantum numbers (n, l, m_l, and m_s)
   - Uncertainty principle: only the position or momentum can be known with certainty at any given time.



(The Lads, 1927)

Classical Vs. Quantum Mechanics

Classical Mechanics

- Three fundamental particles: protons, neutrons, and electrons
- Light is a wave
- Electrons and light do not interact
- Electrons orbit the nucleus
- Position and momentum are predictable

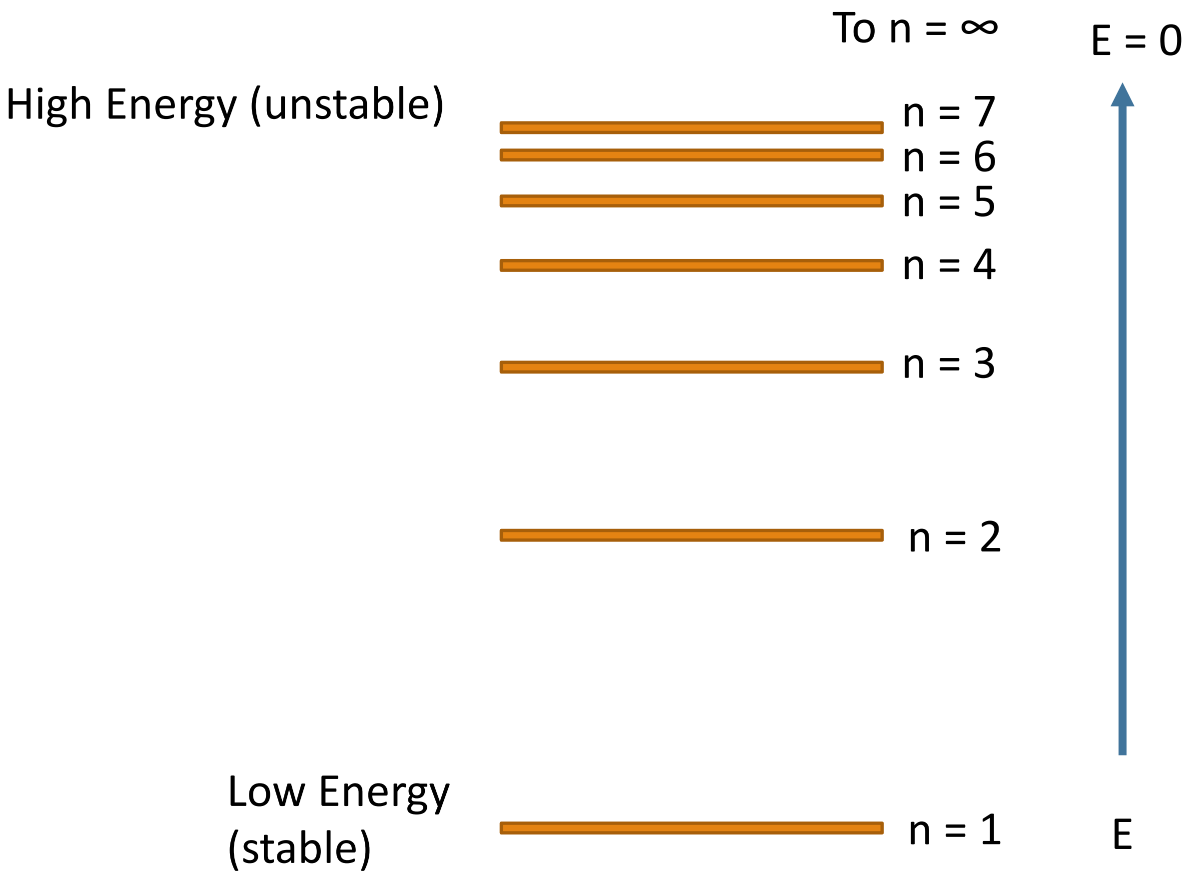
Quantum Mechanics

- Many subatomic particles and growing
- Light exists as tiny packets of energy called photons. Photons exhibit particle-like behavior.
- Electrons and light interact
- Electrons exist in a “cloud-like” shape outside the nucleus and are confined to energy levels (n) of various shapes (l)
- Position and momentum are not simultaneously predictable
- Everything with momentum has a quantifiable wavelength

Why do we need quantum mechanics? Empirical evidence created a need for a unique subset of mechanics to describe interactions on the scale of electrons, light, and subatomic particles.

Quantum Mechanics: Emission vs. Absorption

- The Bohr Model of the atom explained that electrons exist in "energy states," which we now designate the letter "n."
- You can understand n values by following these rules:
  1. n values begin at 1 (closest to the nucleus) and go to infinity (completely out of the influence of the nucleus/ free in space)
  2. The lower n value means more stable (most negative potential energy)
  3. The greatest energy difference between two **consecutive** numbers is 1 and 2.

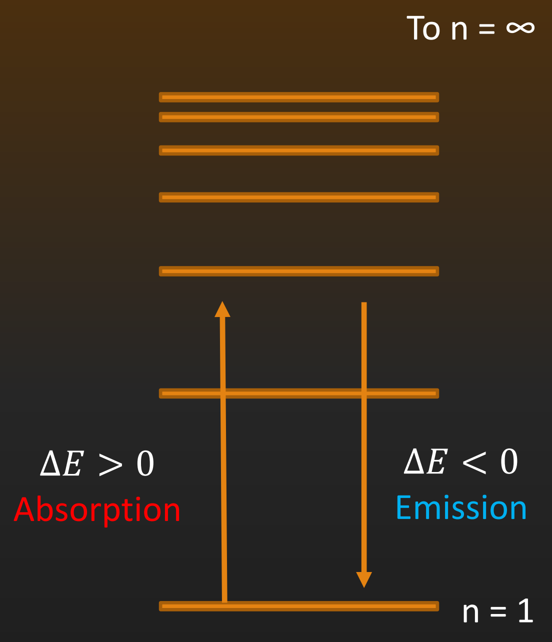


RYDBERG EQUATION

$$\Delta E = \mathcal{R}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

R = 2.18 X 10^{-18} J

$$|\Delta E| = E_{photon} = h\nu = \frac{hc}{\lambda}$$



- This equation calculates the energy difference of an electron going from n_i to n_f
- This equation will always work so long as you follow one conceptual trick: The value for photon energy will always be positive.
- If you are undergoing absorption, ΔE is positive. If you are undergoing emission ΔE is negative. Either way, your photon energy is the absolute value of these energy transitions.

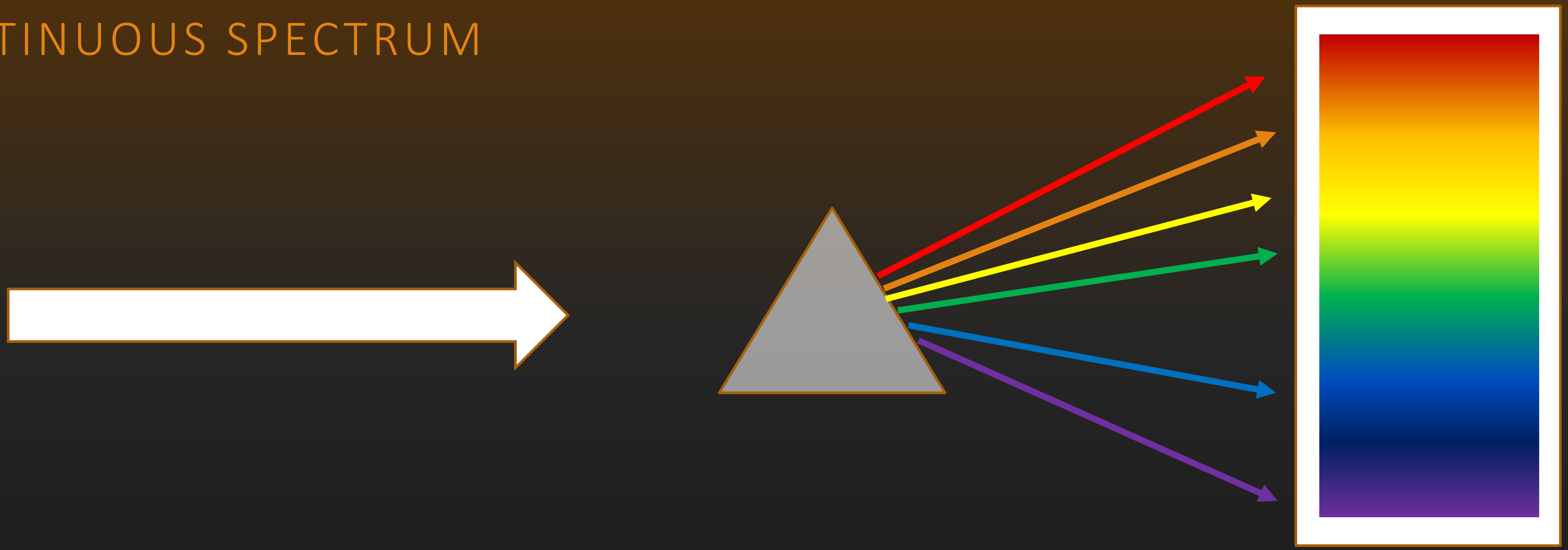
RYDBERG EQUATION: ENERGY

$$\Delta E = \mathcal{R}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

R = 2.18 X 10^{-18}J

Electron energy level transition	**Sign of ΔE**	**Absorption/Emission ($\lvert\Delta E\rvert$)** **(Cause/Effect)**
Low n to high n	Positive (increasing energy)	Light absorbed
High n to low n	Negative (decreasing energy)	Light emitted

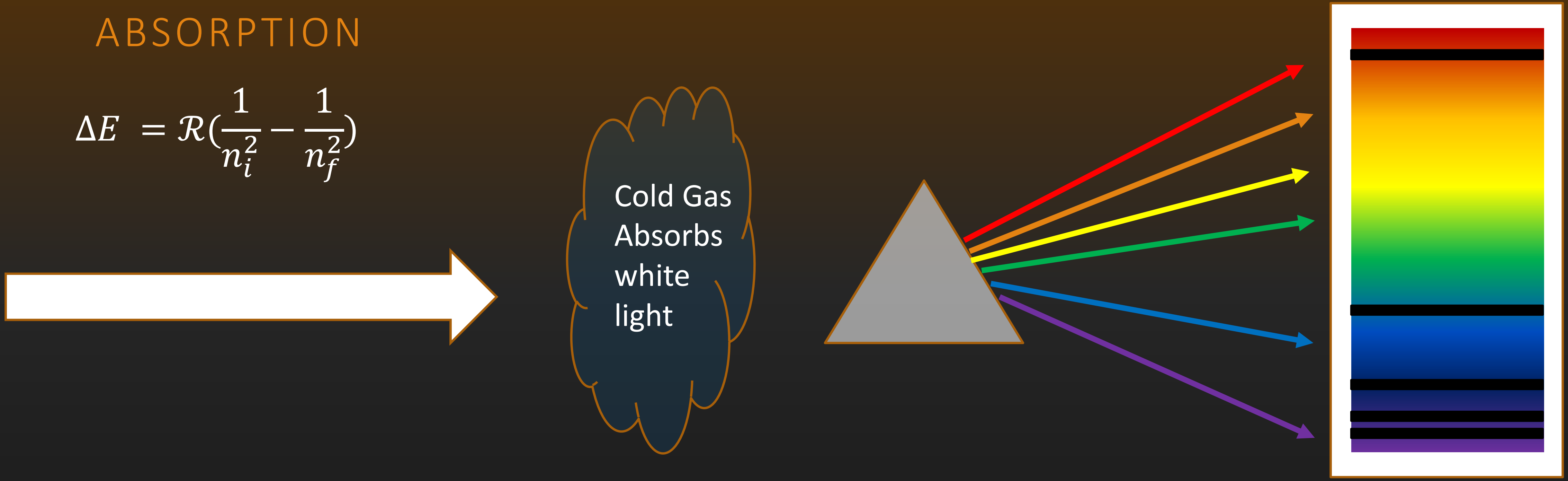
CONTINUOUS SPECTRUM



- WHITE LIGHT ENTERS THE PRISM AND DISPERSES INTO INDIVIDUAL COLORS (ROYGBIV)
- NOTHING SPECIAL IS HAPPENING HERE, EXCEPT TO GIVE US A FRAME OF REFERENCE FOR THE ABSORPTION AND EMISSION SPECTRUM.

ABSORPTION

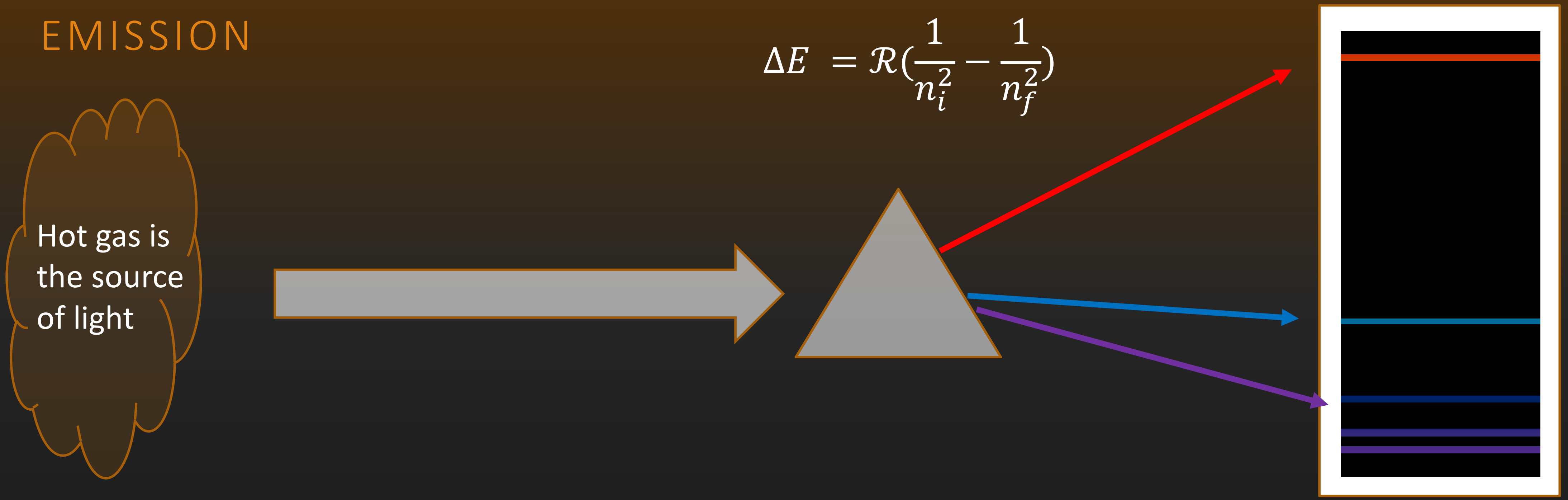
$$\Delta E = \mathcal{R}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$



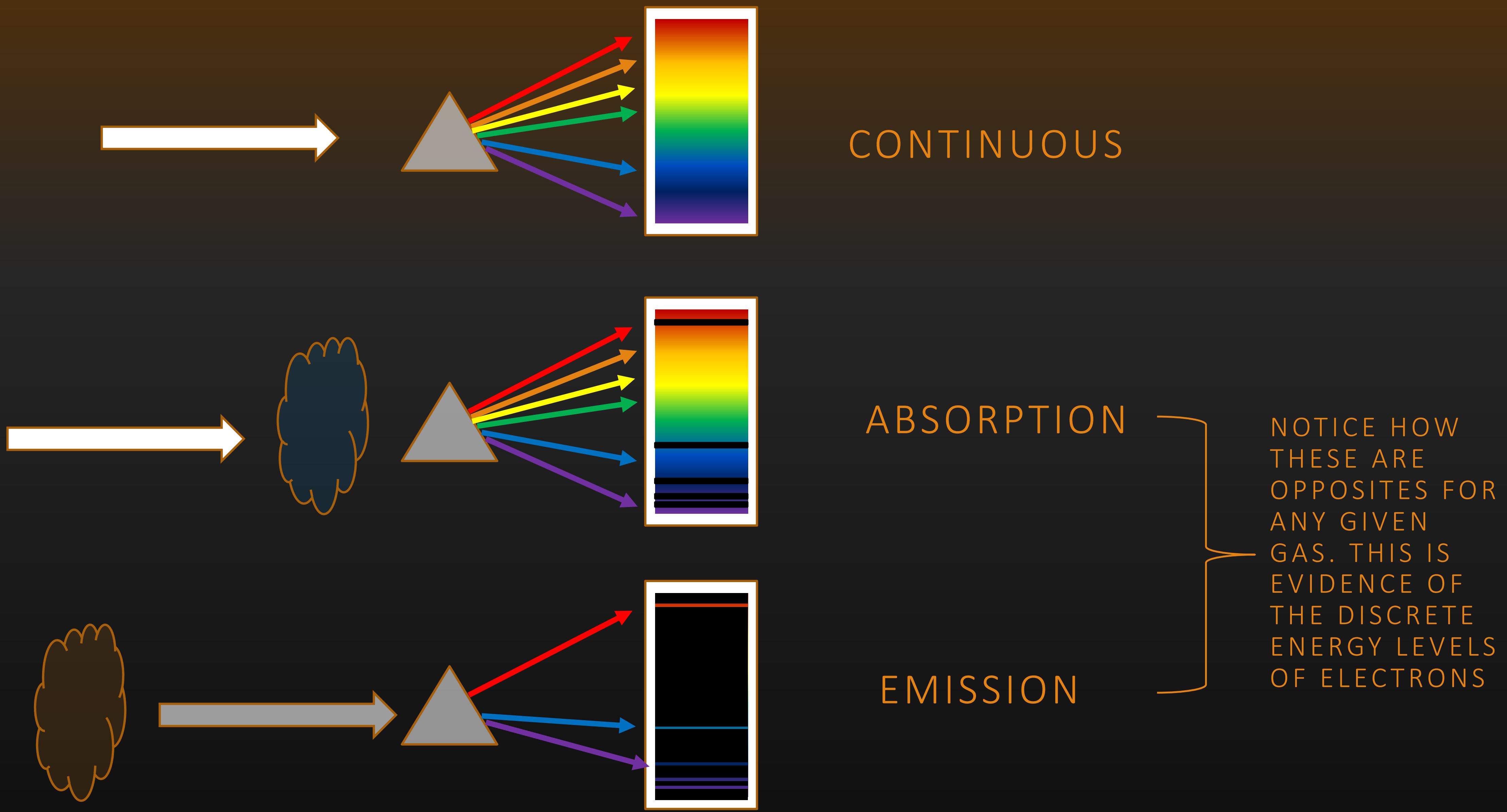
- YOU WILL SEE THE CONTINUOUS ("WHITE LIGHT") SPECTRUM MINUS THE CHARACTERISTIC FREQUENCIES OF HYDROGEN
- THE LIGHT ABSORBED IS "LAUNCHING" THE ELECTRONS FROM A LOW N VALUE TO A HIGHER N VALUE. THIS ABSORPTION REQUIRES ENERGY THAT CORRESPONDS TO THE FREQUENCIES OF LIGHT THAT ARE MISSING

EMISSION

$$\Delta E = \mathcal{R}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$



- YOU SEE ONLY THE CHARACTERISTIC FREQUENCIES OF HYDROGEN EMISSION
- THE LIGHT EMITTED HAS THE ENERGY OF THE FREQUENCIES SEEN IN THE COLORED LINES. THIS CORRESPONDS TO ELECTRONS FALLING FROM A HIGH N TO A LOWER N


CONTINUOUS
ABSORPTION
EMISSION
NOTICE HOW THESE ARE OPPOSITES FOR ANY GIVEN GAS. THIS IS EVIDENCE OF THE DISCRETE ENERGY LEVELS OF ELECTRONS

Rydberg Equation Question

A hydrogen electron emits a photon in the Lyman Series when it falls from n = 3.

a. What is the difference in energy for the electron in this process? Answer in Joules
b. What is the wavelength of the photon emitted? Answer in nm
c. What is the color of light emitted?

R = 2.18 X 10^{-18}J

(Provided)

$$\Delta E \; = \mathcal{R}(\frac{1}{n_i^2} - \frac{1}{n_f^2})$$

(Memorize)

$n = 3 \longrightarrow n = 1$

UV emission

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

$$\left(2.18 \times 10^{-18}\ \text{J}\right)\left(\frac{1}{9} - \frac{1}{1}\right)$$

$$= -1.938 \times 10^{-18}\ \text{J}$$

$$E_{photon} = 1.938 \times 10^{-18}\ \text{J}$$

$$E_{photon} = h\nu = \frac{hc}{\lambda}$$

$$\lambda = \frac{h \cdot c}{E_{photon}} \times \frac{10^9\ \text{nm}}{\text{m}} = 102.6\ \text{nm}$$

Rydberg Conceptual Question

Which of the following represents the greatest (in magnitude) energy transition?

a. n = 3 to n=1
b. n = 5 to n=2
c. n = 2 to n = 1
d. n = 3 to n = 2
e. n = 5 to n = 1

Which of the following represents the greatest (in magnitude) energy transition between consecutive energy levels?

a. n = 3 to n = 2
b. n = 5 to n = 6
c. n = 10 to n = 9
d. n = 4 to n = 3

Rydberg Conceptual Question

Which of the following represents the greatest (in magnitude) energy transition?

a. n = 3 to n=1
b. n = 5 to n=2
c. n = 2 to n = 1
d. n = 3 to n = 2
e. n = 5 to n = 1

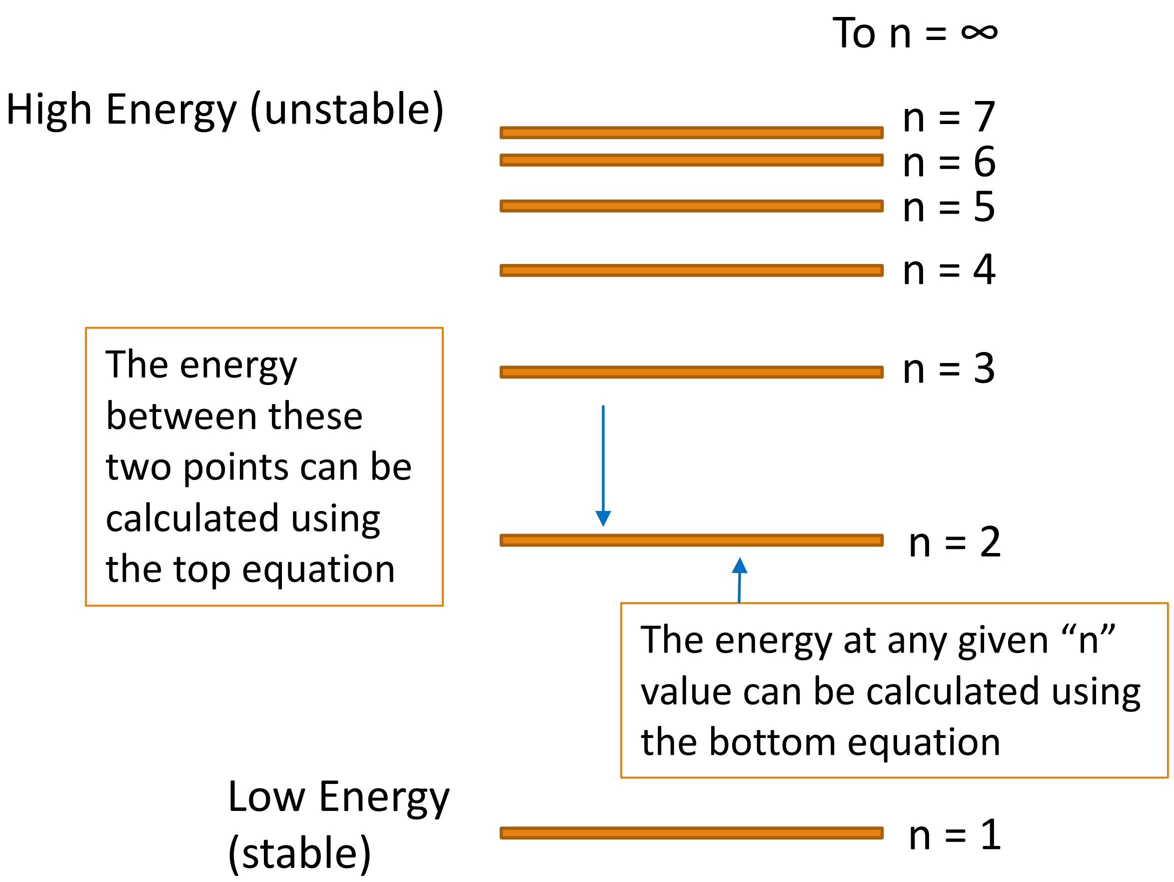
Which of the following represents the greatest (in magnitude) energy transition between consecutive energy levels?

a. n = 3 to n = 2
b. n = 5 to n = 6
c. n = 10 to n = 9
d. n = 4 to n = 3

Calculations with the Rydberg Equation

- Two equations you should know:
  - $\Delta E = \mathcal{R}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$
  - The change in energy is proportional to the difference of the inverse square of "n" values
  - $E_n = -\mathcal{R}\left(\frac{1}{n^2}\right)$
  - The potential energy of a given energy level is proportional to the inverse square of its "n" value

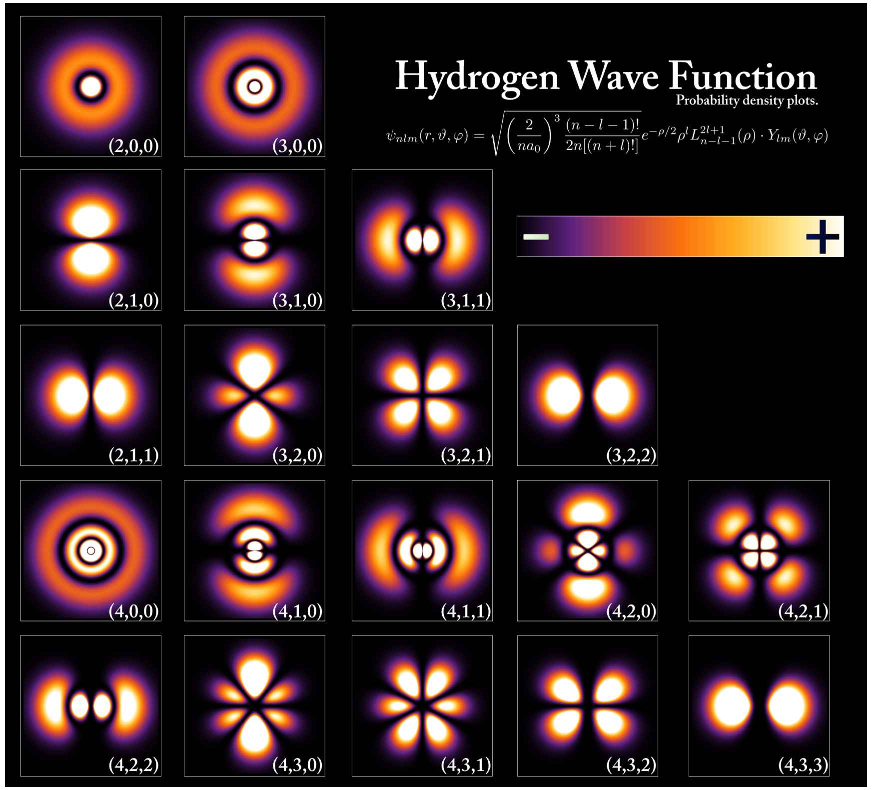
Remember, if you have the energy change, you can also solve for the wavelength of the light emitted using E = hv and $c = \lambda \nu$



Conceptual look into the Schrödinger Equation

$$\underbrace{-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}}_{\text{kinetic energy}} + \underbrace{V(x)\psi}_{\text{potential energy}} = \underbrace{E\psi}_{\text{total energy}}$$

- The Schrödinger Equation gives us infinite wave functions (solutions) for the Hydrogen atom.
- The wave functions are classified by the quantum numbers:
  - Principle Quantum Number, n (Energy)
  - Angular Momentum Quantum Number, l (Shape)
  - Magnetic Quantum Number, m_l (Orientation)
- **This ultimately tells us the energy of an electron and the probable location of that electron in three dimensional space.**



Particle in a Box

- The Schrödinger Equation gives us insight to the **energy of an electron** and the **probability of finding that electron** (location, correlates with shape) in a given range of three dimensional space.
- Particle in a Box is useful because it conceptualizes the simplest solutions to the Schrödinger equation (1 particle, 1 dimension, no potential energy):
  - Given any n-value, where can I find the particle? Where is there zero probability of finding the particle?
- The Radial Distribution Function helps bring it all together in three-dimensional space by answering:
  - Where are my electrons most likely to be found?

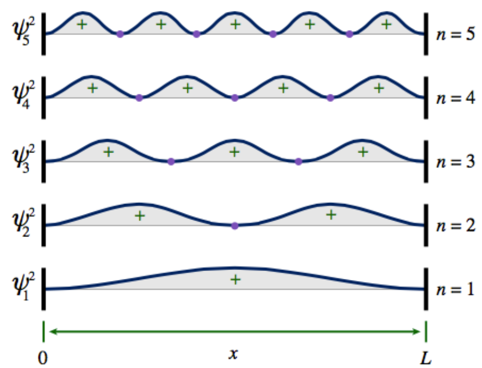
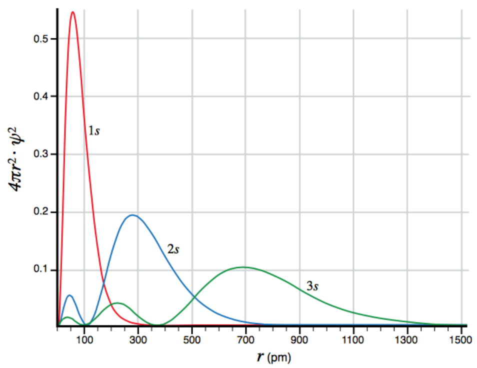


figure 2



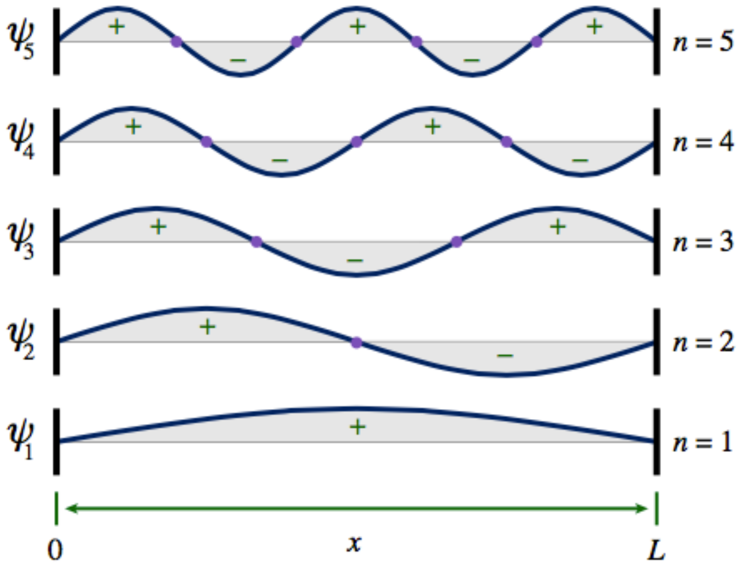
Particle in a Box

Some helpful rules:

- # of full wavelengths = n/2
- # of distributions (“humps”) = n
- # of nodes = n-1

- Given any n-value, where can I find the electrons?
  - Where the graph gives you a non-zero value
- Where is there zero probability of finding an electron?
  - At the nodes (y=0)

$$\psi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi}{L}\right)x$$



Multiply by Ψ to get all positive values

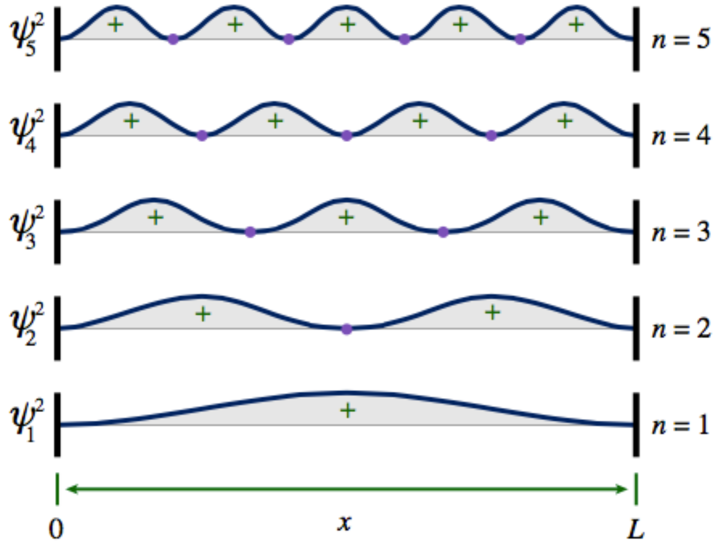
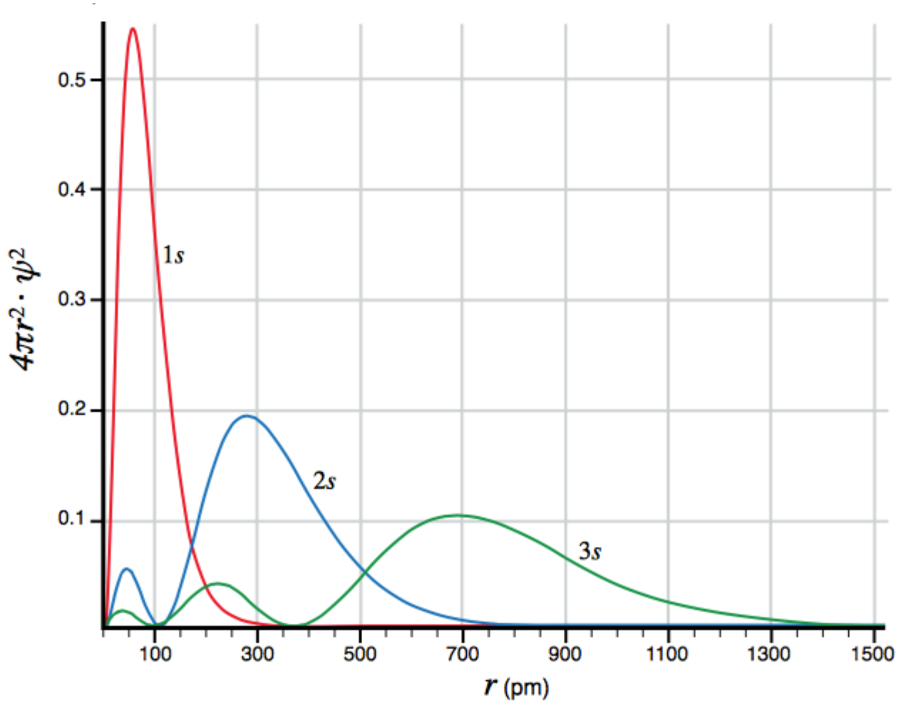


figure 2

Node: any time the sinusoidal function crosses from (-) to (+) or (+) to (-)

Radial Distribution

- If we further apply this concept, we can answer the more specific question: where are the electrons **most likely** to be found?

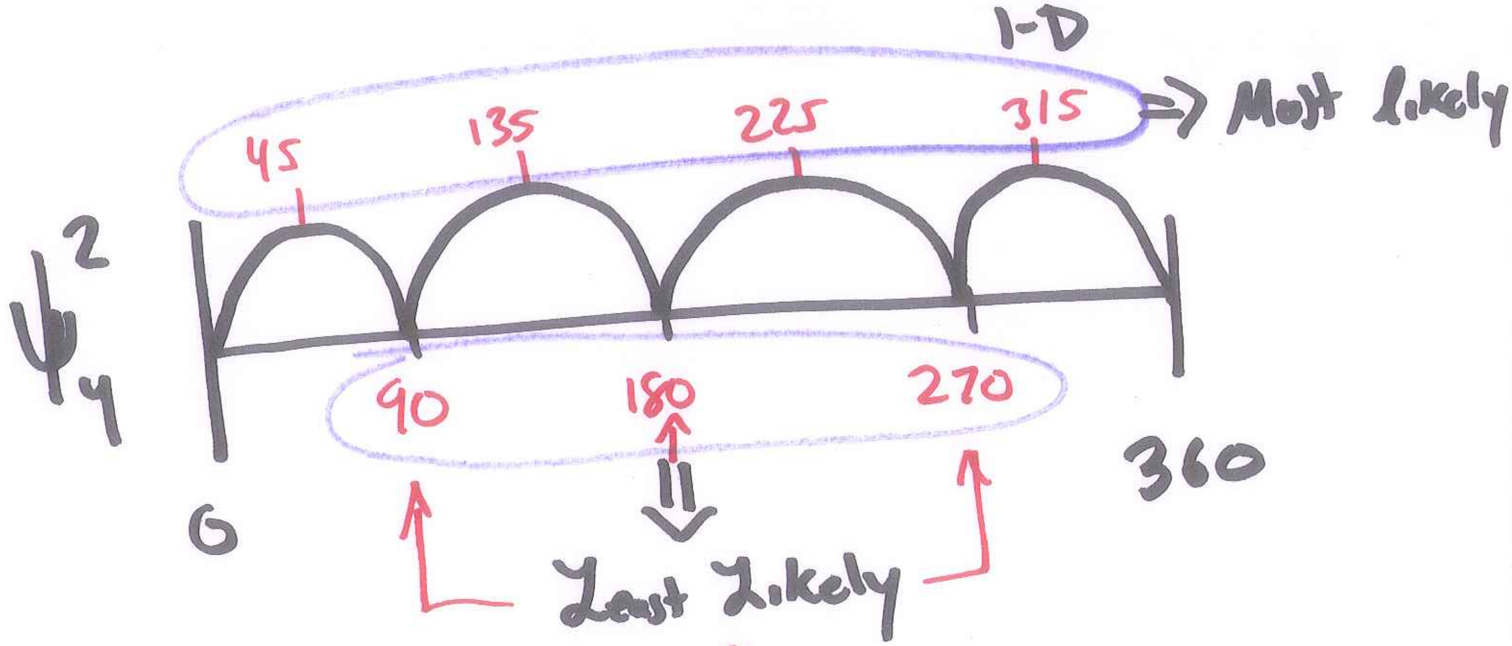


- Radial distribution curves show the same number of nodes as particle in a box, but they also show the actual probability of finding an electron in **three-dimensional space**.
- The number of distributions is equal to the n-value. It is always most probably that electrons are found in the furthest hump from the nucleus (r=0)

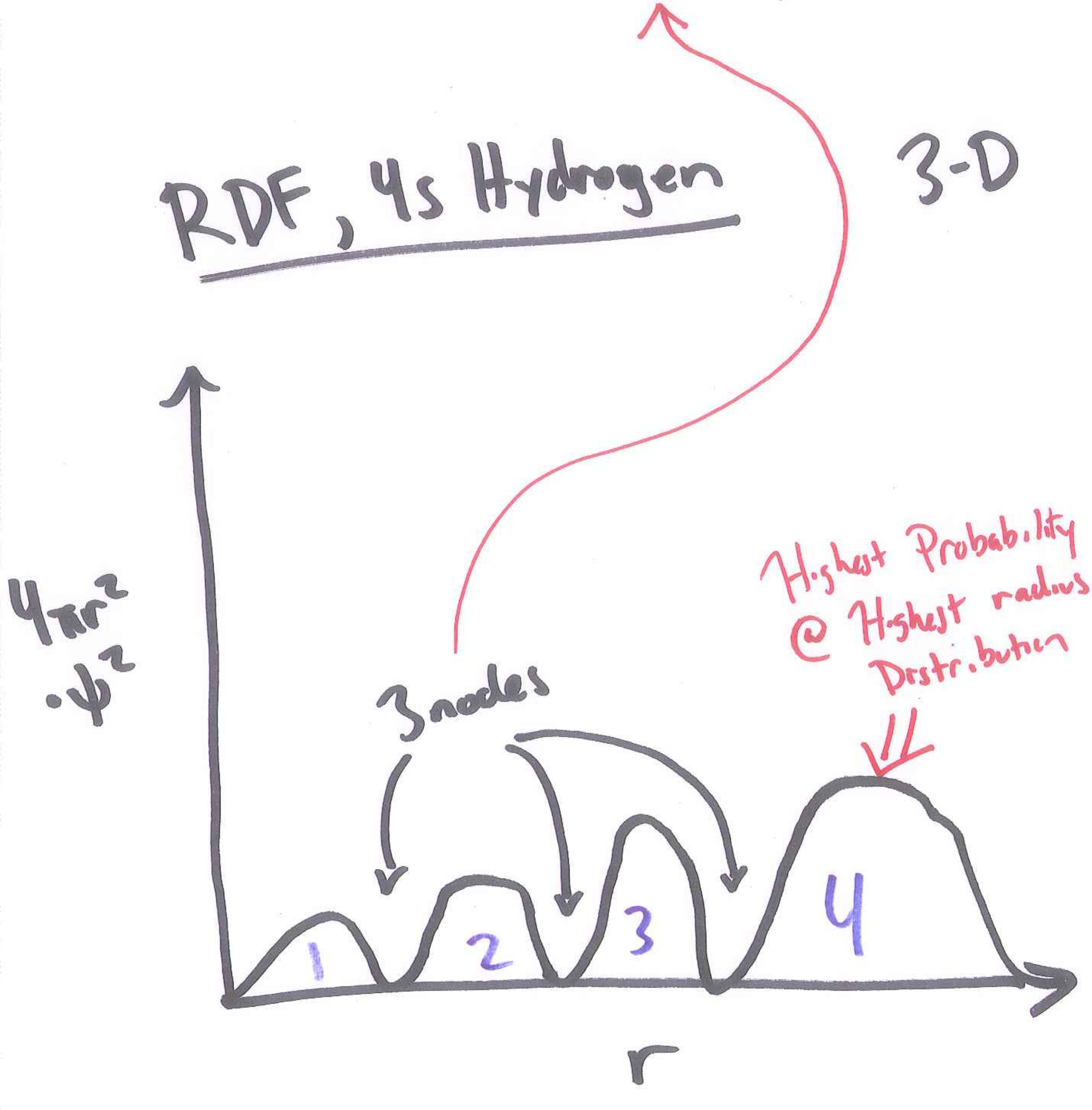
PIB to Radial Distribution Example

Suppose you have a single particle confined to a one-dimensional “box” of length 360 pm.

1. At what distances are you most likely to find the particle if n = 4?
2. At what distances do you have zero probability of finding this particle?
3. How many wavelengths are in the box?
4. Lastly, if this particle is a hydrogen atom electron in the 4s orbital, what does the radial distribution function tell you about the location of the electrons?



RDF, 4s Hydrogen



Quantum Numbers

- The Quantum Numbers (n, l, m_l, and m_s) stem from the solutions of the Schrödinger Equation and represent the following:

1. **Principle Quantum Number (n):** the size and energy of the shell; mostly corresponds to the row of the periodic table (exception: d, f block).
2. **Angular Momentum (l):** the shape of the subshell; corresponds to the region on the periodic table.
   - 0= s subshell; 1 = p subshell; 2 = d subshell; 3 = f subshell
3. **Magnetic (m_l):** the orbitals of the subshell; mathematically indicates the orientation of the subshell shape
   - The number of possible m_l values is equal to the number of orientations possible in space, which therefore represents the number of orbitals available
4. **Spin Magnetic (m_s):** the spin of the electrons in a subshell
   - Can equal ½ or - ½, but all that really matters is that no two electrons in the same orbital have the same value

Quantum Numbers: Rules

We are mostly interested in assigning possible quantum numbers to the electrons of a given species. To do this, we must understand the rules for assigning quantum numbers:

Principle Quantum Number (n) = 1,2,3, …to n = ∞

Angular Momentum (l) = 0,1,2,… to n-1

Magnetic (m_l) = -l to l

Spin Magnetic (m_s) = $\pm\frac{1}{2}$

Example:

If n = 4

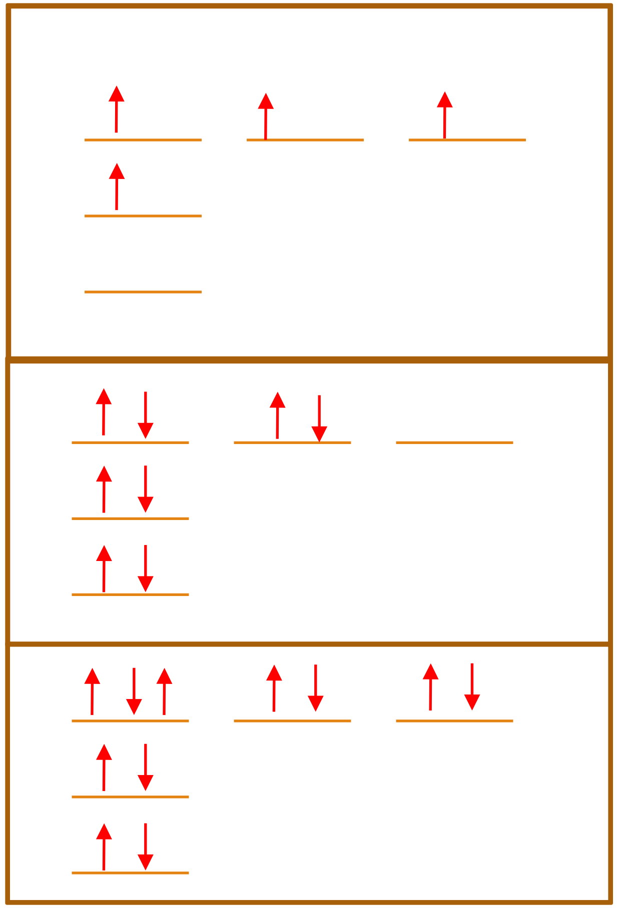
l can equal 0,1,2,3

m_l can equal -3,-2,-1,0,1,2,3

m_s = +/- 1/2

Electron Configurations: Rules

- There are three main rules to abide by when filling out electron configurations. It is important to follow these rules when doing your own electron configurations and be able to identify the rule that an incorrect electron configuration breaks
- **Aufbau Principle:** fill electrons from the bottom (lowest energy) up
- **Hund's rule:** fill each orbital in a given subshell with a single electron before doubling up
  - Technically this refers to the idea that you should maximize the multiplicity of your configuration
- **Pauli's Exclusion Principle:** no electrons can occupy the same orbital with the same spin and a maximum of two electrons can exist in a single orbital



Note: these are all examples of these rules violated

Exam Question

For the chlorine anion that is isoelectric with argon,

a. What is the electron configuration? Shorthand notation?
b. What are ALL possible quantum numbers for the highest energy electron(s) in chloride?

Isoelectronic*

$Cl: 1s^2 2s^2 2p^6 3s^2 3p^5$

$Cl^-: 1s^2 2s^2 2p^6 3s^2 3p^6 = [Ar]$

$3p \rightarrow l = 1$

$n = 3$

$l = 1$

$m_l: -1, 0, 1$

$m_s: +/- \frac{1}{2}$

s = l is 0

p = l is 1

d = l is 2