CHEMISTRY XL-14A

NATURE OF LIGHT AND THE ATOM

July 9, 2011

Robert Iafe

Office Hours

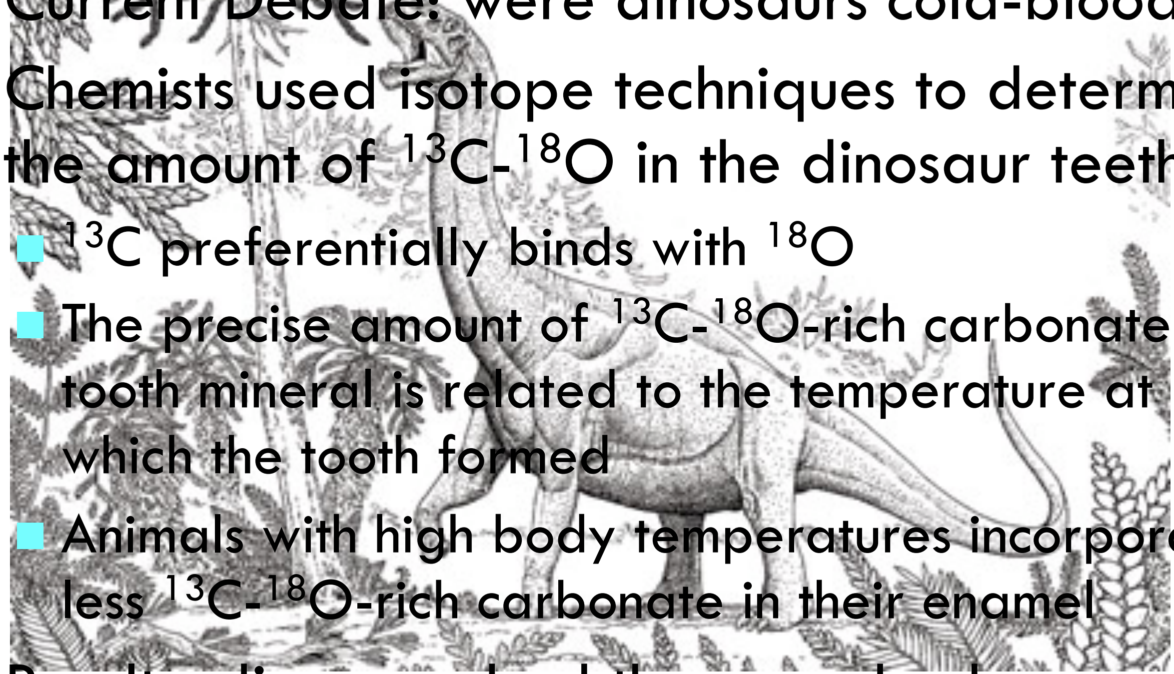
- Sunday, July 10. 11:00a-1:00p. Room MS-B 3234.
- July 11-July 22
  - Monday: 2:00pm in Room MS-B 3114
  - Tuesday-Thursday: 3:00pm in Room MS-B 3114

“Carmageddon 2011”

- 405 will be closed Friday night
- "Stay the heck out of here," said L.A. County Supervisor Zev Yaroslavsky
- Yes, we will have class!
- Beware the impending doom of crazed drivers
- Please drive safely
- Please leave (a lot) earlier than planned
- If you live nearby, I would suggest carpool, taking a bike, or walk

Chemistry in the News

- Dinosaur Thermometry
  - Current Debate: were dinosaurs cold-blooded?
  - Chemists used isotope techniques to determine the amount of ^{13}C-^{18}O in the dinosaur teeth
    - ^{13}C preferentially binds with ^{18}O
    - The precise amount of ^{13}C-^{18}O-rich carbonate in a tooth mineral is related to the temperature at which the tooth formed
    - Animals with high body temperatures incorporate less ^{13}C-^{18}O-rich carbonate in their enamel
  - Results: dinosaurs had the same body temperature as large mammals



Science, DOI: 10.1126/science.1206196

Unit Overview

1. Investigating Atoms
2. Quantum Theory
3. The Hydrogen Atom
4. Many-Electron Atoms
5. Periodicity of Atomic Properties

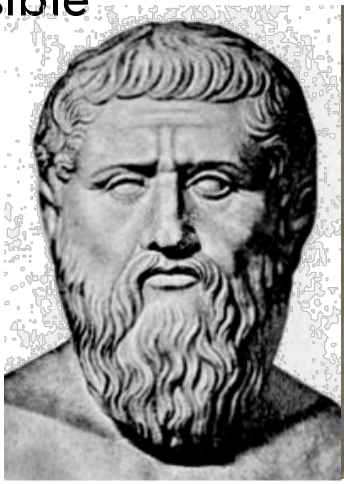
Investigating Atoms

1. The Nuclear Atom
2. Electromagnetic Radiation
3. Atomic Spectra

History of the Atom

Ancient Greece: 2 competing theories

- Democritus
  - Matter is not continuous
  - indivisible particles called atoms (“uncuttable”)
- Plato and Aristotle
  - Matter is continuously and infinitely divisible



Plato and Aristotle “won”

At least until the 19^{th} century…

Dalton's Hypothesis

Around 1800: John Dalton reintroduced the concept of the "atom"

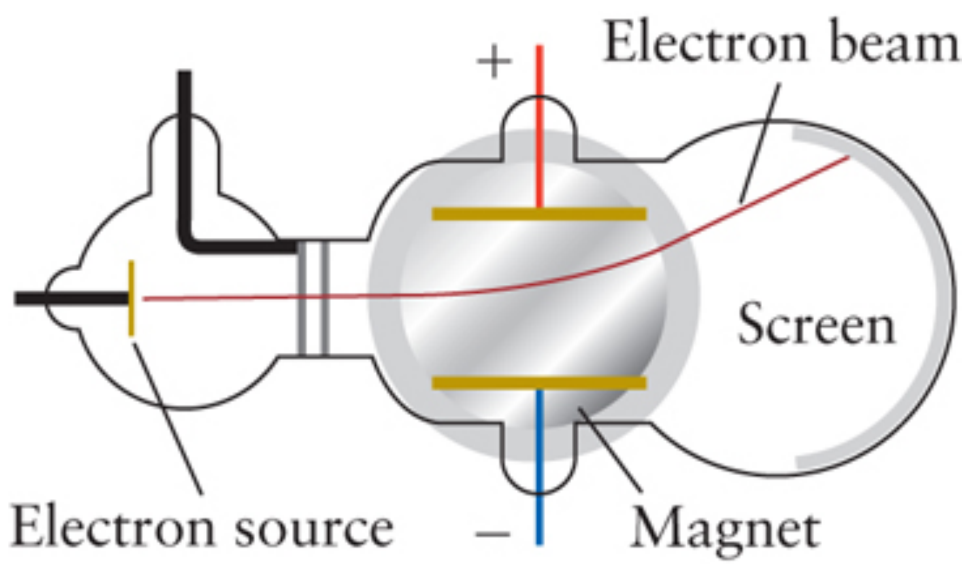
1. All matter is made up of indivisible atoms
2. An element is made up of identical atoms
3. Different elements have atoms with different masses
4. Chemical compounds are made of atoms in specific integer ratios
5. Atoms are neither created nor destroyed in chemical reactions

At the end of the 19th Century a series of experiments began to support this theory

Discovery of the Electron

1897:

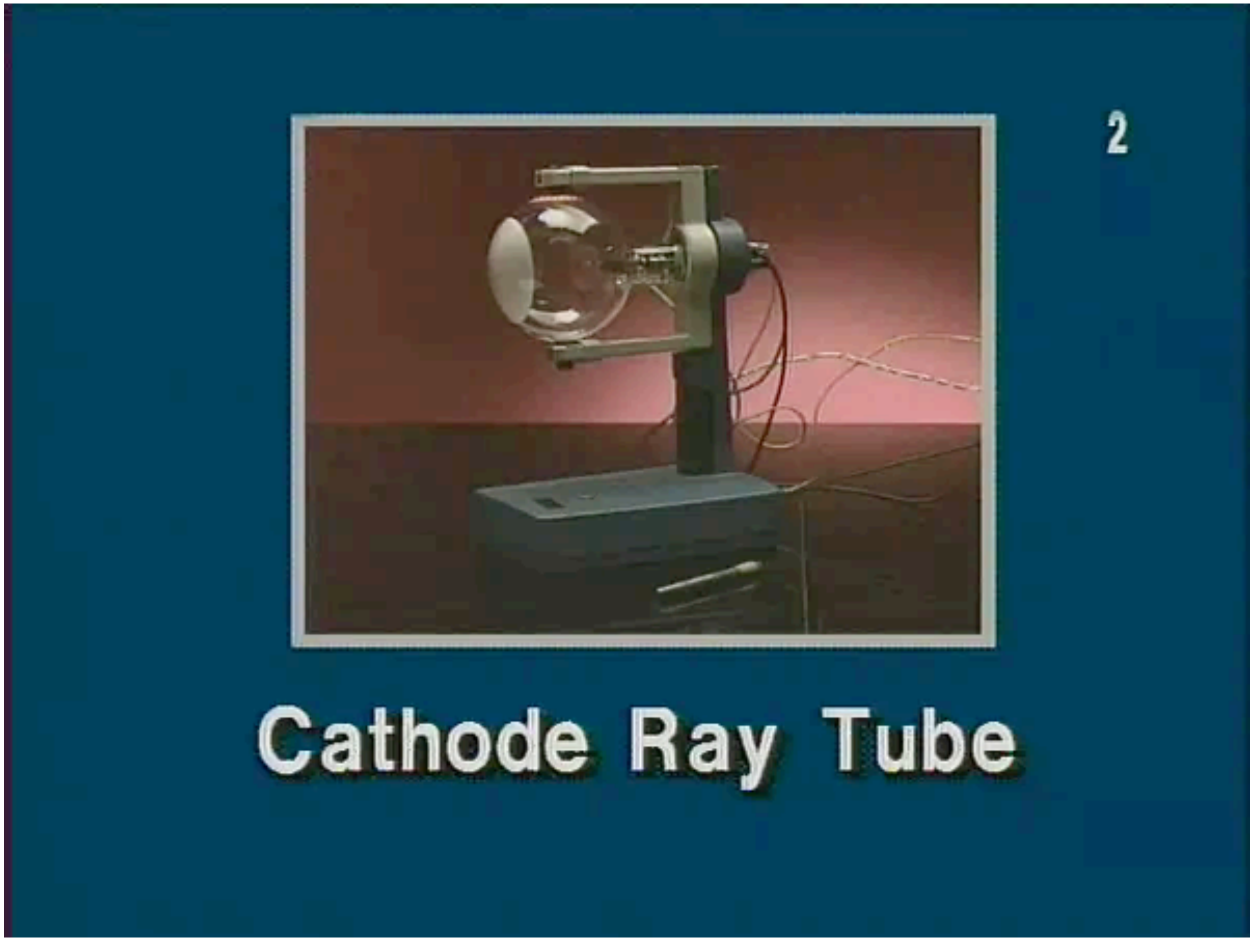
JJ Thomson discovers the electron while studying “cathode rays”



Cathode Rays consist of negatively charged particles → electrons

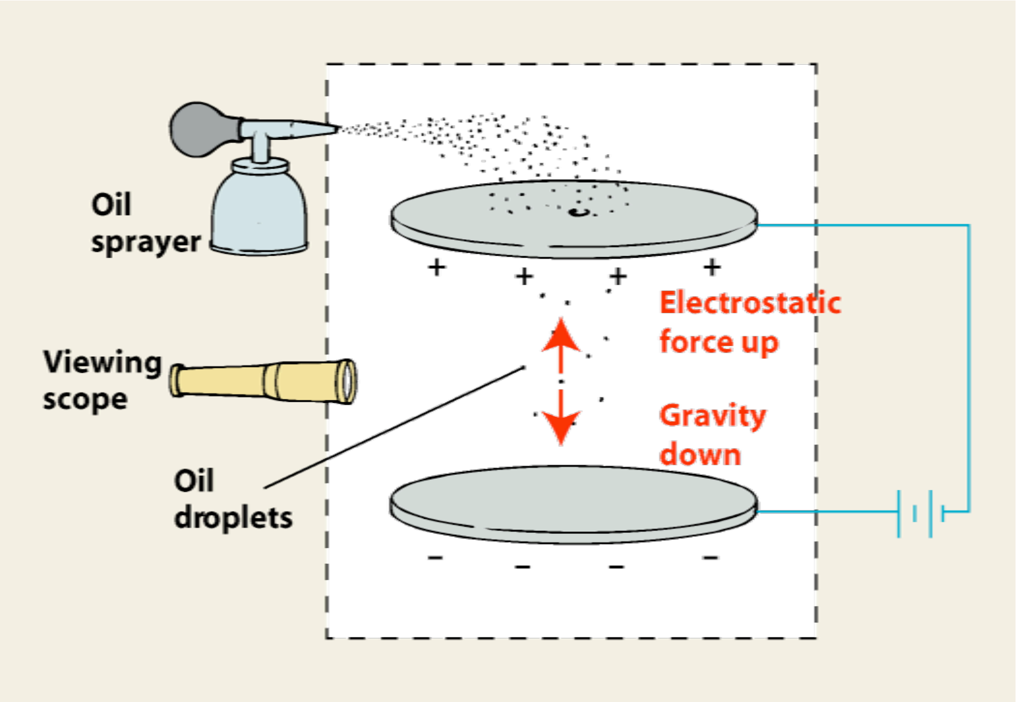
Result: ratio of charge/mass of electron e/m_e

Cathode Ray Tube Movie



Millikan's Oil Droplet Experiment

Sprayed tiny charged droplets of oil sprayed between charged plates



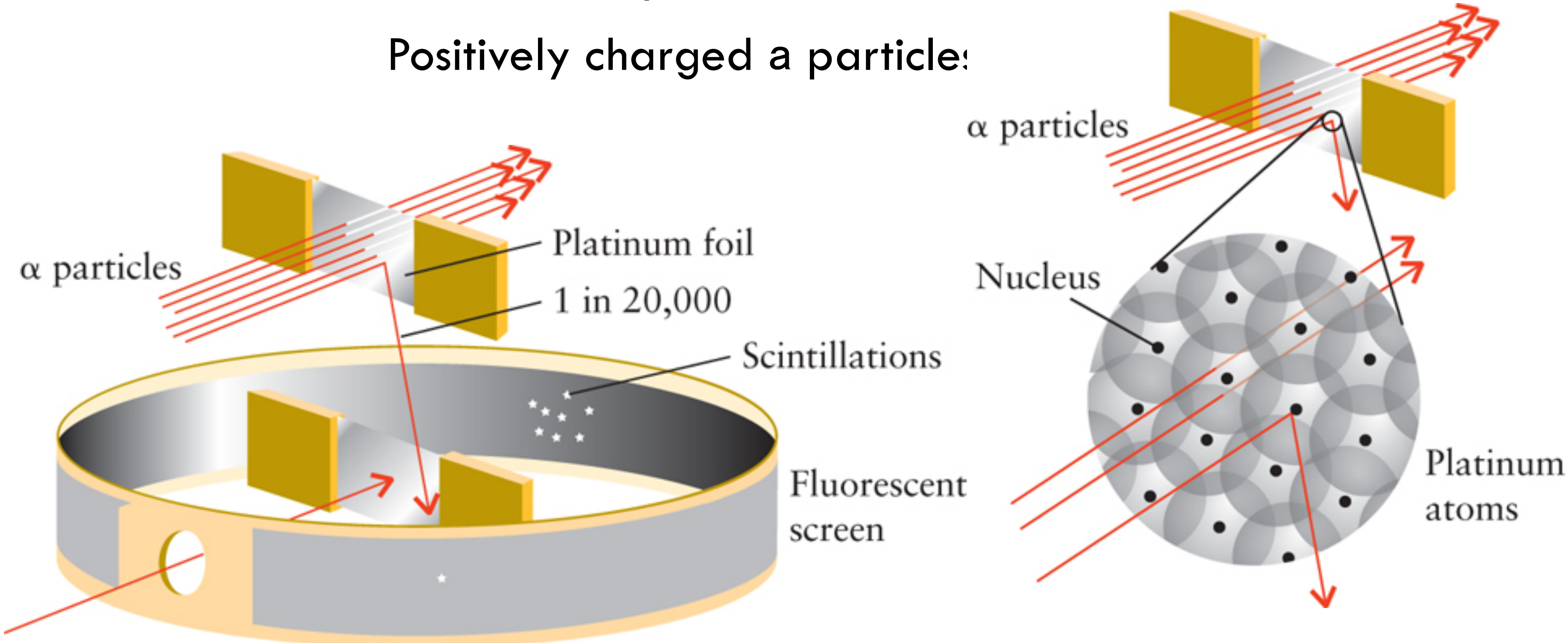
Electrostatic Attraction balanced with gravitational pull

Result: Charge of 1 electron → **$e = 1.602 \times 10^{-19}$ C**

Rutherford's Foil Experiment

Rutherford's Students actually did the work:

Positively charged a particles



1/20,000 deflected by foil

Atoms have small center of mass surrounded by empty space

Structure of the Atom So Far…

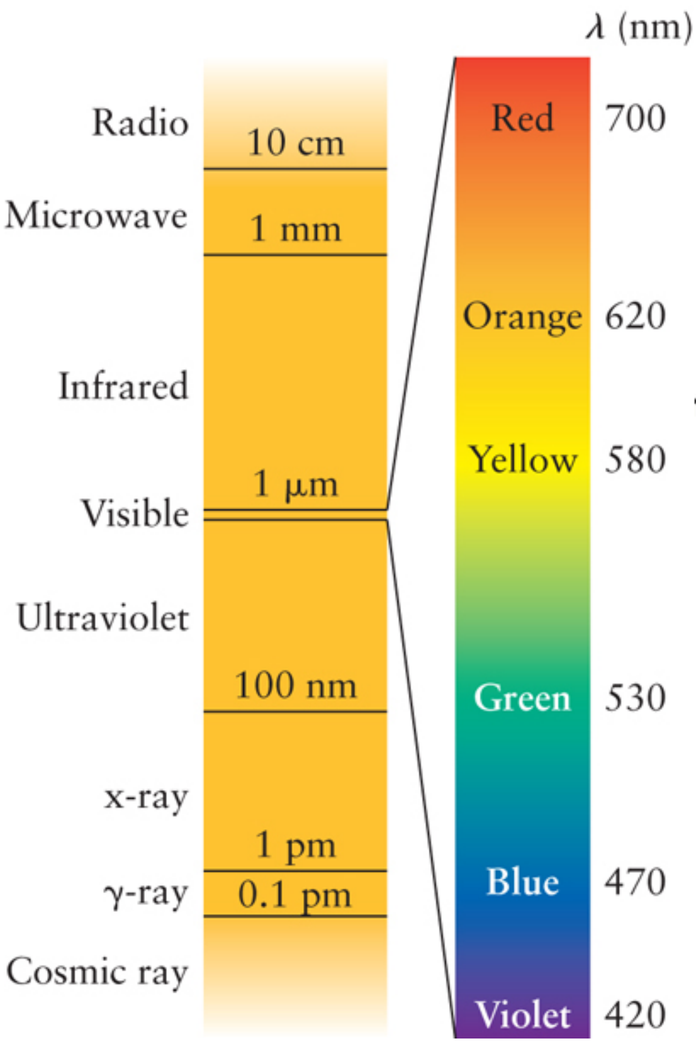
To summarize:

- An atom is mostly empty space
- Most of the mass of an atom located in a small, positively charged nucleus.
- Nucleus is made up of protons (+) and neutrons (0)
- Nucleus is surrounded by electrons (-) with mass m_e and charge $\boldsymbol{e}$

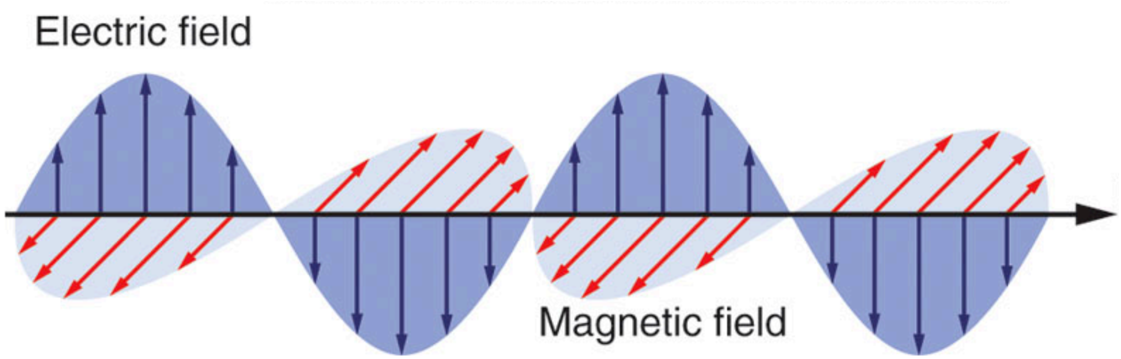
What we don't know

- Behavior of electrons in the atom

Electromagnetic Radiation



Oscillating electric and magnetic fields which travel with time

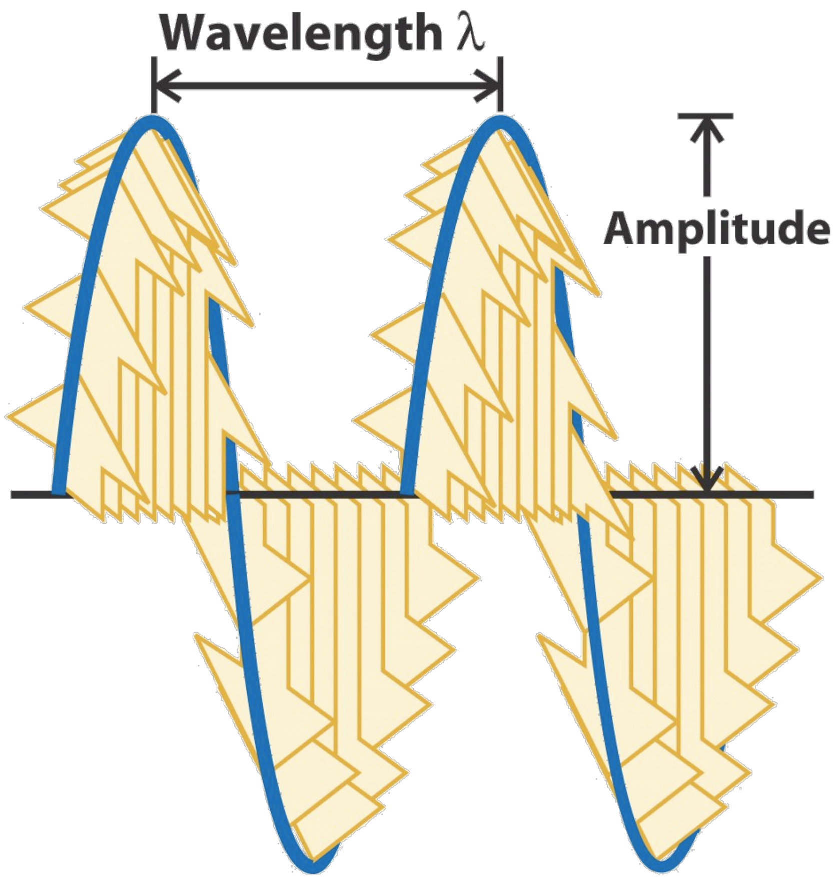


Electric and magnetic field are perpendicular to each other

Speed of radiation in a vacuum is known as “speed of light”

$$c = 2.99792 \times 10^8 \text{ m/s}$$

Characteristics of EM Radiation



Wavelength (λ) – peak-to-peak distance

Units of Length (m)

Frequency (ν) – # of cycles per sec

Units of 1/s = Hz

$$c = \lambda\nu$$

$c = 2.99792 \times 10^8$ m/s

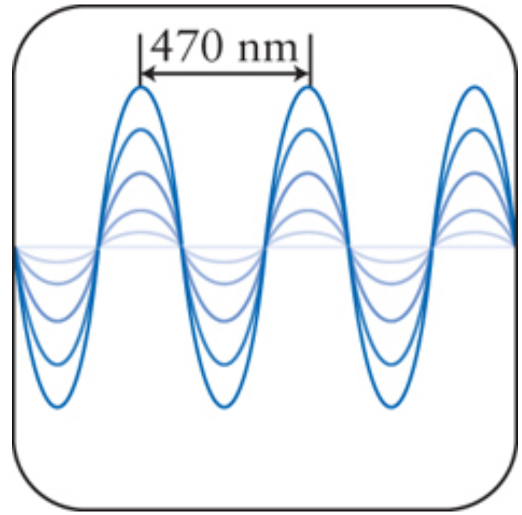
Amplitude (A) – Height of peak from center line

Intensity – Brightness of radiation; proportional to A^2

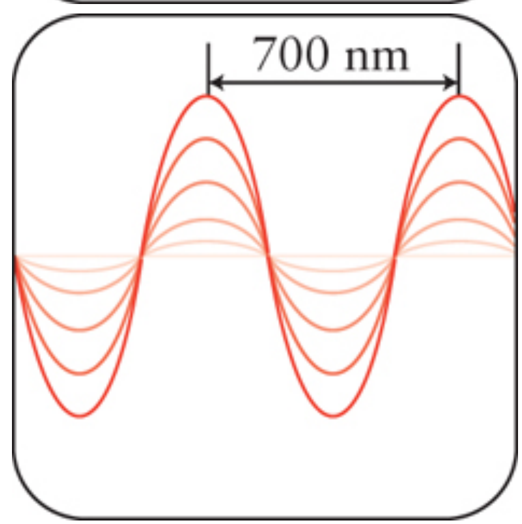
Wavelength vs. Frequency

<u>Wavelength</u> (λ) – peak-to-peak distance

<u>Frequency</u> (ν) – # of cycles per sec



Wavelength and Frequency are inversely proportional



High Frequencies have short Wavelengths and vice versa

Electromagnetic Radiation

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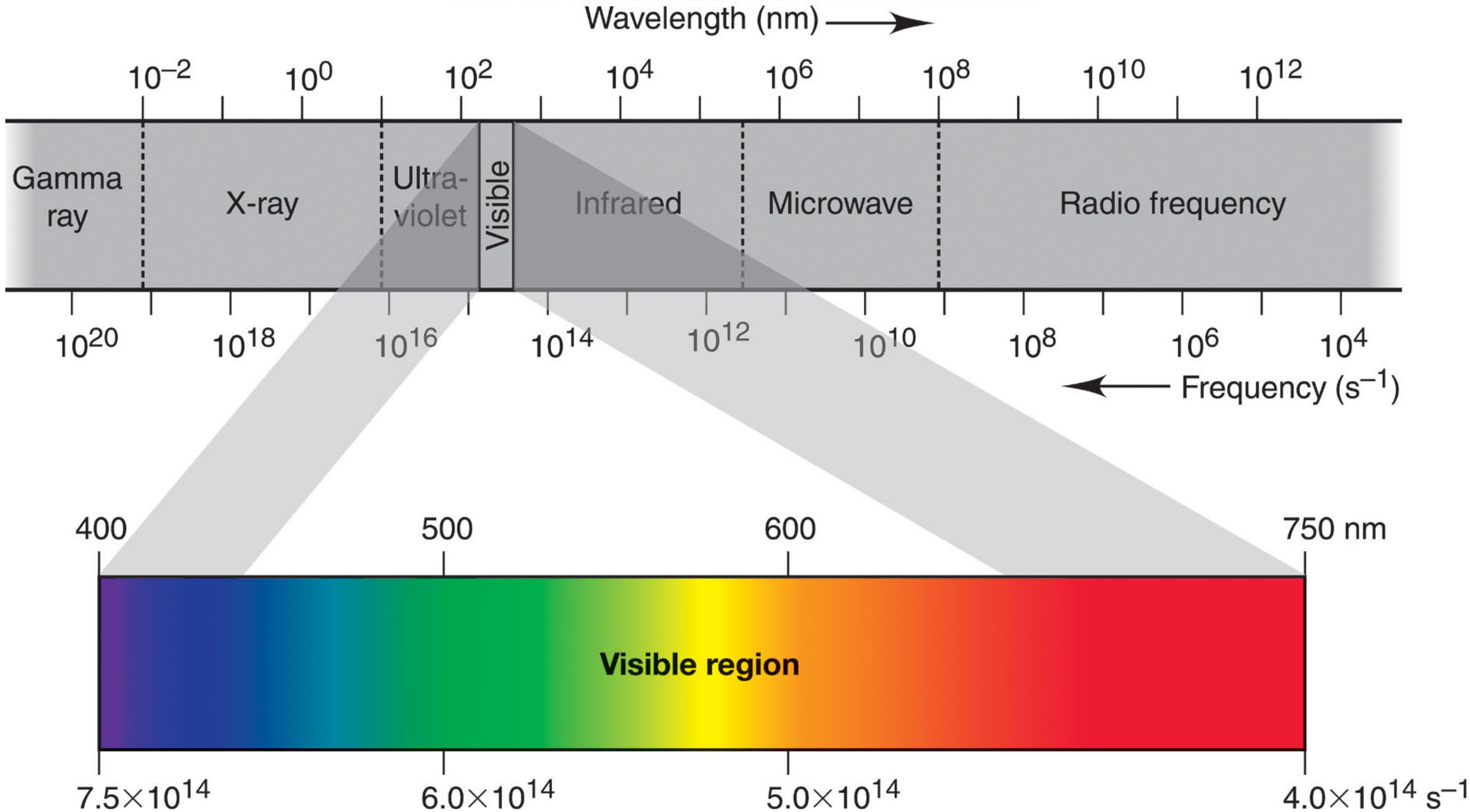


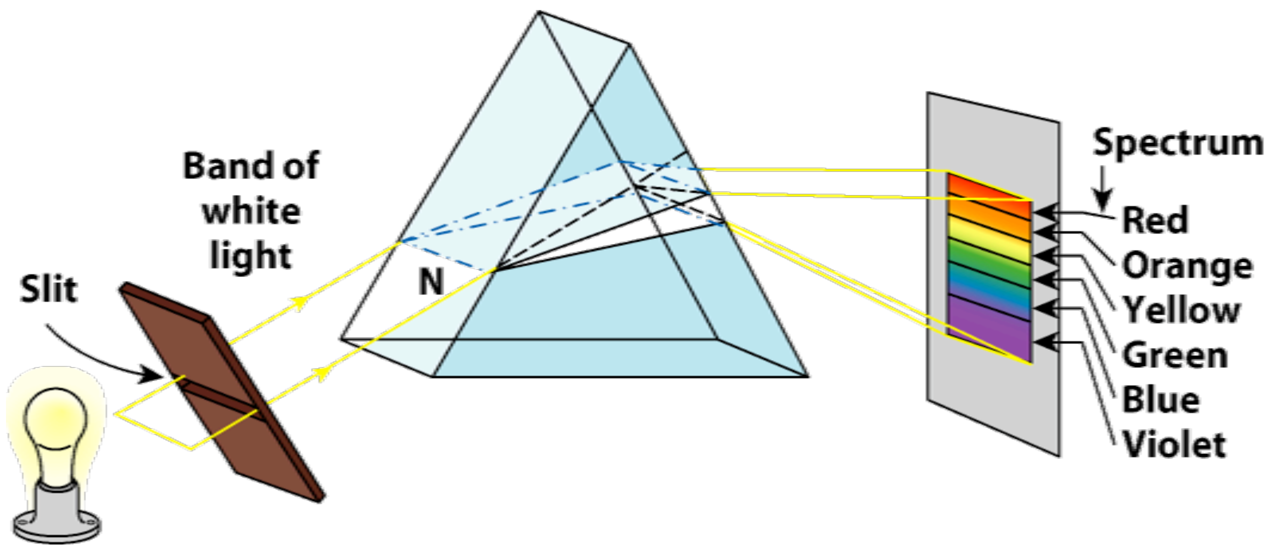
EM Calculations Practice

1. What is the frequency of light with a wavelength of 250 nm?

2. What is the wavelength of light with a frequency of 3.1×10^{15} Hz?

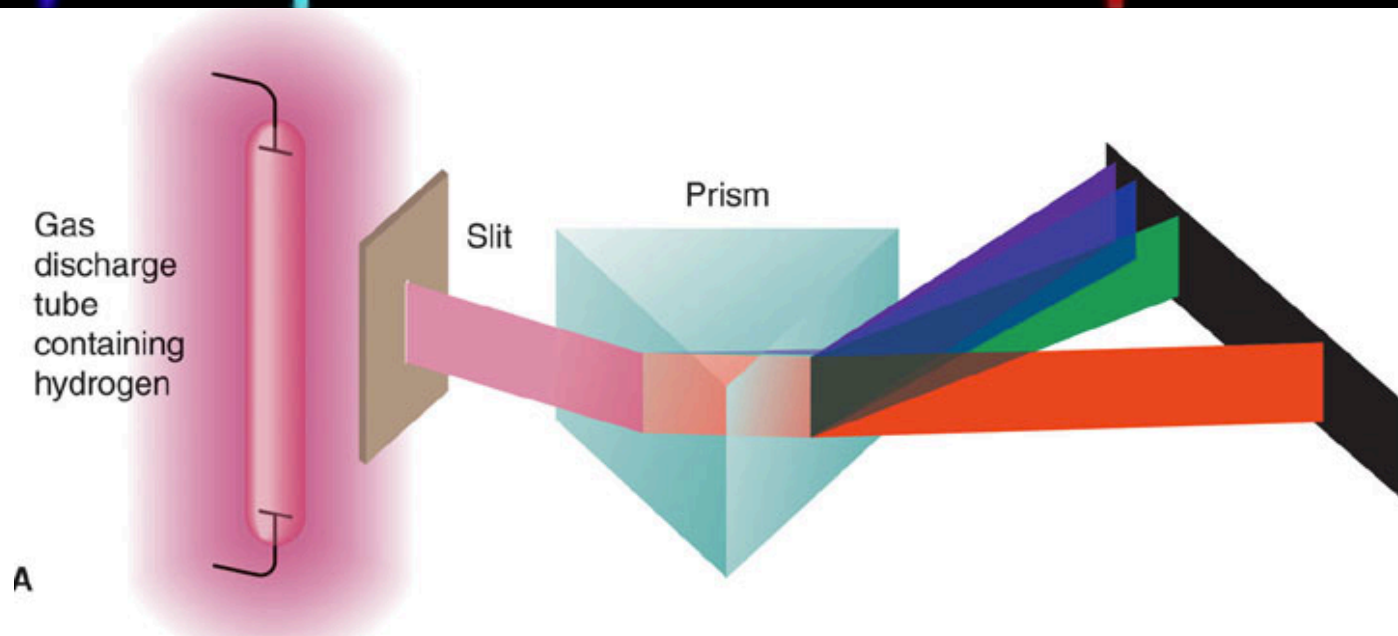
Atomic Spectra

- When white light is passed through a prism, the light is dispersed in a continuous spectrum



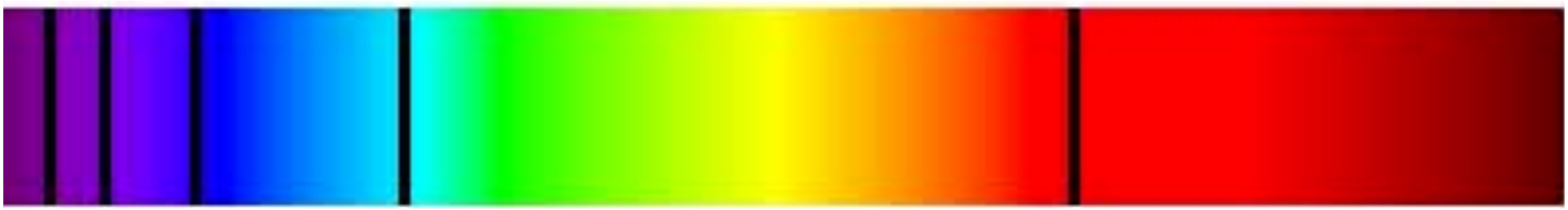
Atomic Spectrum of Hydrogen

- Light emitted from excited H_2 gas produces a <u>Line Spectrum</u>



Atomic Absorption Spectra

- White light passed through an elemental gas will produce an absorption spectrum
- Appears as dark lines on a continuous spectrum

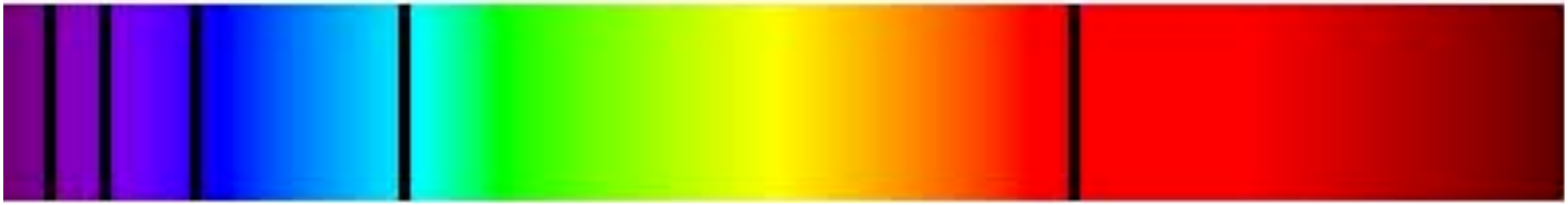


- Absorption lines and emission lines fall at same frequencies
- These spectral lines arise from a transition between energies
- Conclusion → **<u>Electrons in H atom have specific energies</u>**

Emission vs. Absorption Spectra

- Emission Spectrum

- Absorption Spectrum



Atomic Spectra

Lines are not random – there is a pattern

Joseph Balmer → Balmer series

n = 3, 4, …

$$\nu \propto \frac{1}{2^2} - \frac{1}{n^2}$$

More advanced techniques revealed more lines in the H_2 spectrum

Johann Rydberg found the overall pattern

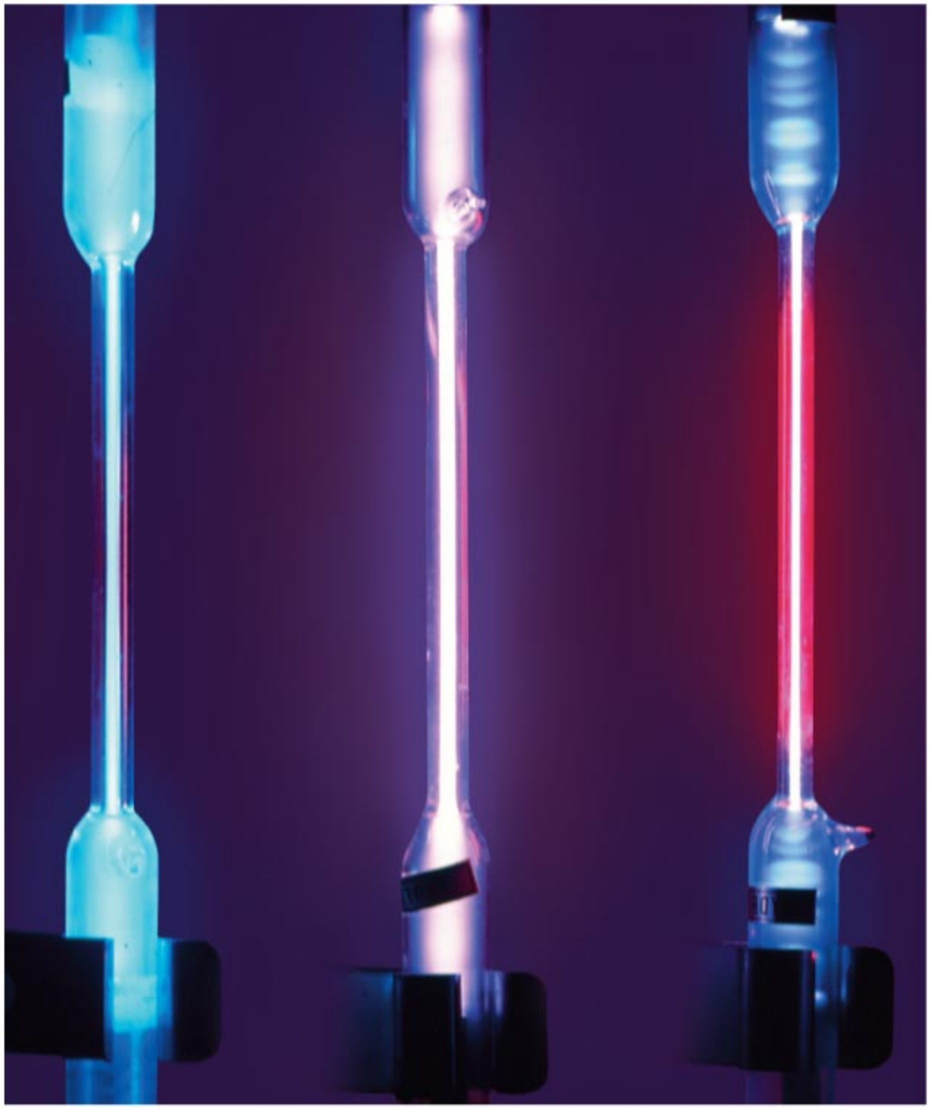
R = Rydberg constant = 3.29×10^{15} Hz

$\mathbf{n_1} = 1, 2, \ldots.$

$\mathbf{n_2} = \mathbf{n_1} + 1, \mathbf{n_1} + 2, \ldots$

$$\nu = \Re\left\{\frac{1}{n_1^2} - \frac{1}{n_2^2}\right\}$$

Atomic Spectrum - Hg, He, H_2



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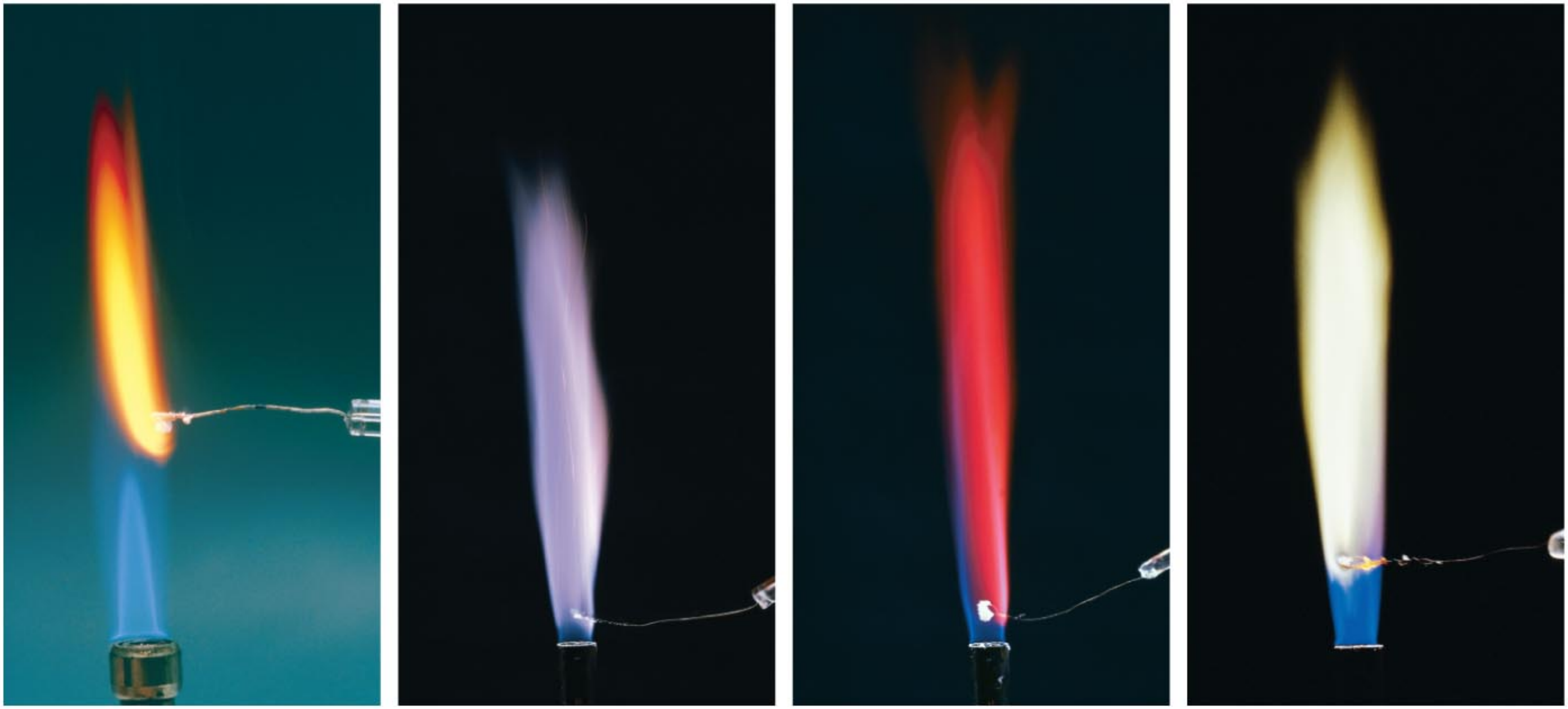
Atomic Spectrum



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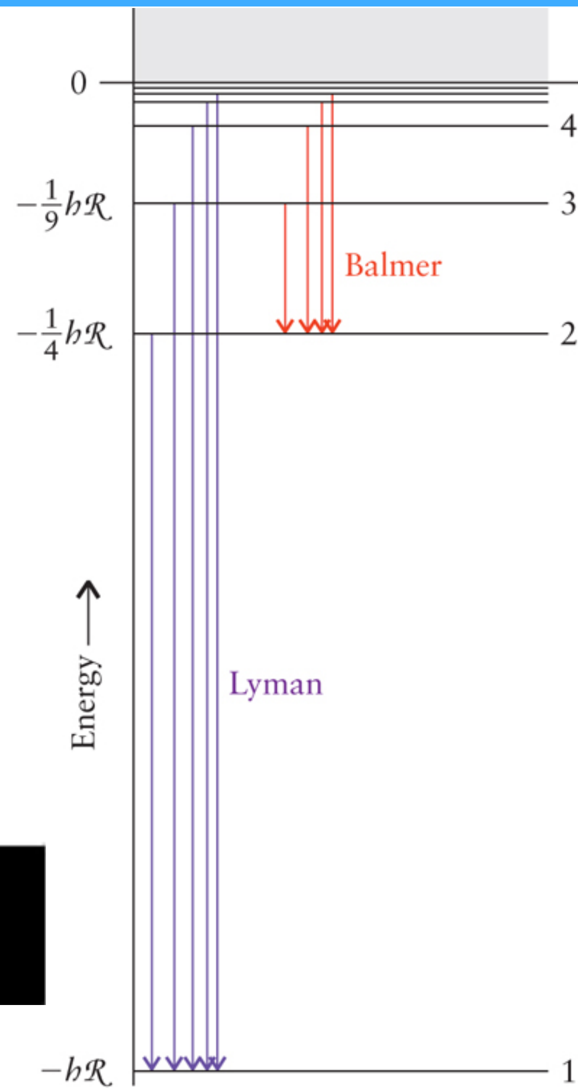
Balmer Series

1. Calculate the wavelength of light associated with a Balmer transition starting from n=3.



Quantum Theory

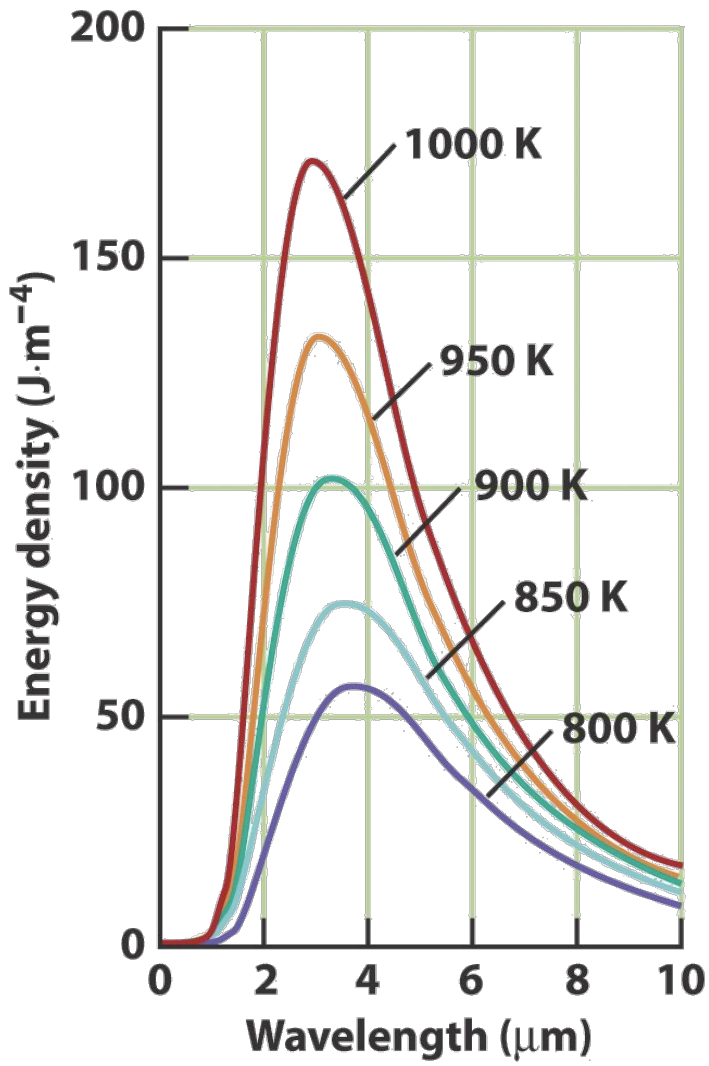
1. Photons and Quanta
2. Wave-Particle Duality of Matter
3. Uncertainty Principle
4. Wavefunctions

Blackbody Radiation

As objects are heated to high temperatures, they begin to glow:

As T↑, both the <u>intensity</u> and <u>color</u> of the emitted light changes

Emitted light from "hot objects" is **<u>black-body radiation</u>**



Blackbody Radiation

Experimental Data showed that:

$$\text{Intensity} \propto T^4$$

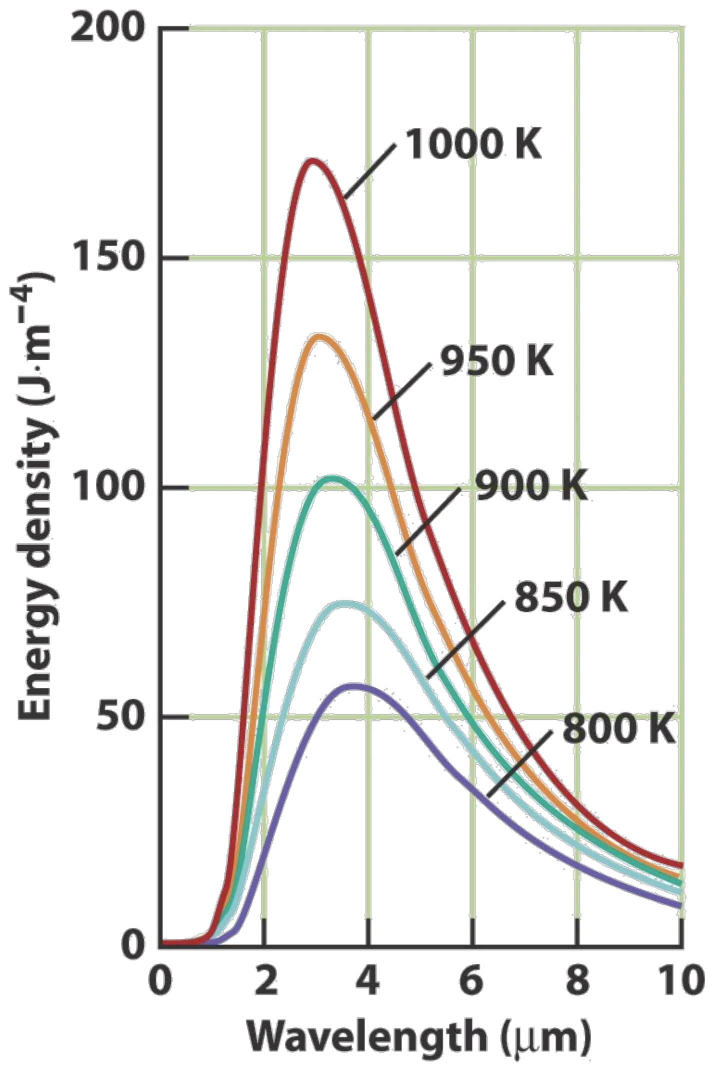
$$\lambda_{max} \propto \frac{1}{T}$$

Classical physics: UV Catastrophe!

Objects at RT will emit dangerous radiation

Gamma Rays, X-Rays, etc…

How can it be explained?



Planck's Quanta

- Until this point, everyone thought energy was continuous…

- In 1900, Max Planck proposed a new idea
  - Matter exchanges energy with surroundings in specific amounts of energy
  - **Quanta** – discrete amount of energy

$$E = h\nu$$

$h = 6.626 \times 10^{-34}$ J·s

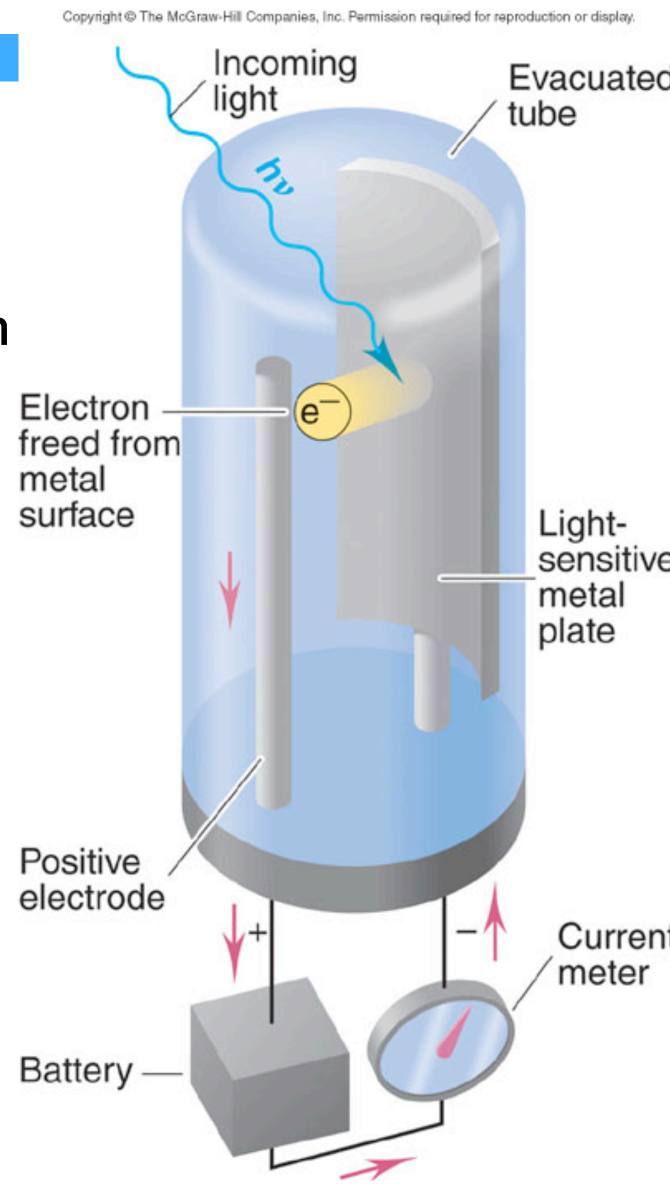
- Planck's concept completely disregarded classical physics
- At this point, no evidence supported this idea

The Photoelectric Effect

- Photoelectric Effect Experiments provides the evidence!
- Basic Idea: Electrons are ejected from a metal when UV light is shone at the surface

<u>Observations</u>:

1. Minimum frequency required to eject electrons
2. Electrons ejected at any intensity of incident light
3. KE of electrons varies linearly with frequency of incident light



Einstein's Proposal

EM radiation is made up of particles (photons)

Each photon is a "packet of energy;"

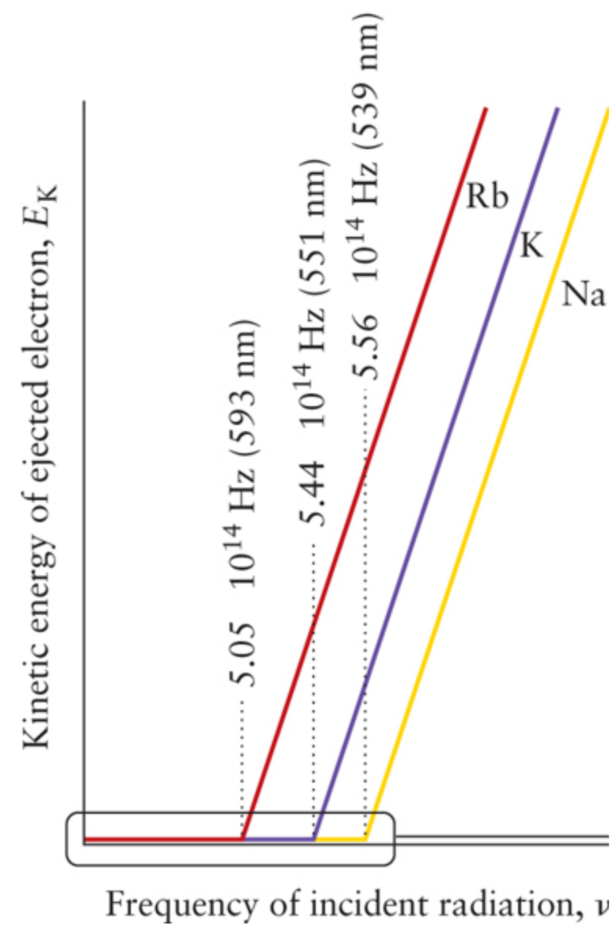
$$E = h\nu$$

The intensity of light is the # of photons

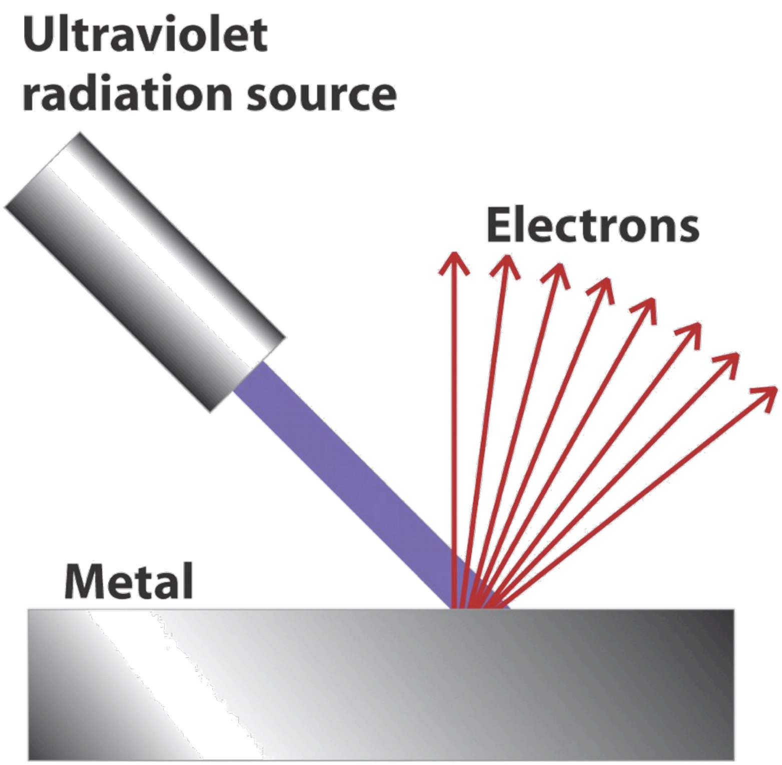
And…

$$h\nu = \Phi + \frac{1}{2}m_e v^2$$

- $h\nu$: Energy of incoming photon
- Φ: Energy to "free" electron (Work Function - F)
- $\frac{1}{2}m_e v^2$: Kinetic Energy



The Photoelectric Effect Explained



$$h\nu = \Phi + \frac{1}{2} m_e v^2$$

Observations:

1. Min frequency to eject electrons

   Incident light will eject e^- when $h\nu \geq \phi$

2. Electrons ejected at any light intensity

   Increasing intensity → increased # of e^- ejected, only if $h\nu \geq \phi$

3. KE of electrons varies linearly with frequency of incident light

   As higher energy photons strike the surface, excess E goes to KE of e^-

Practice

1. Power 106 FM, where hip hop lives, is a radio station in Los Angeles that broadcasts at a frequency of 105.9 MHz. Calculate the wavelength and energy of the radio waves.

Practice

1. The speed of an electron emitted from the surface of a sample of potassium by a photon is 668 km/s.

(a) What is the kinetic energy of the ejected electron?

(b) What is the wavelengh of the radiation that caused the photoejection of the electron?

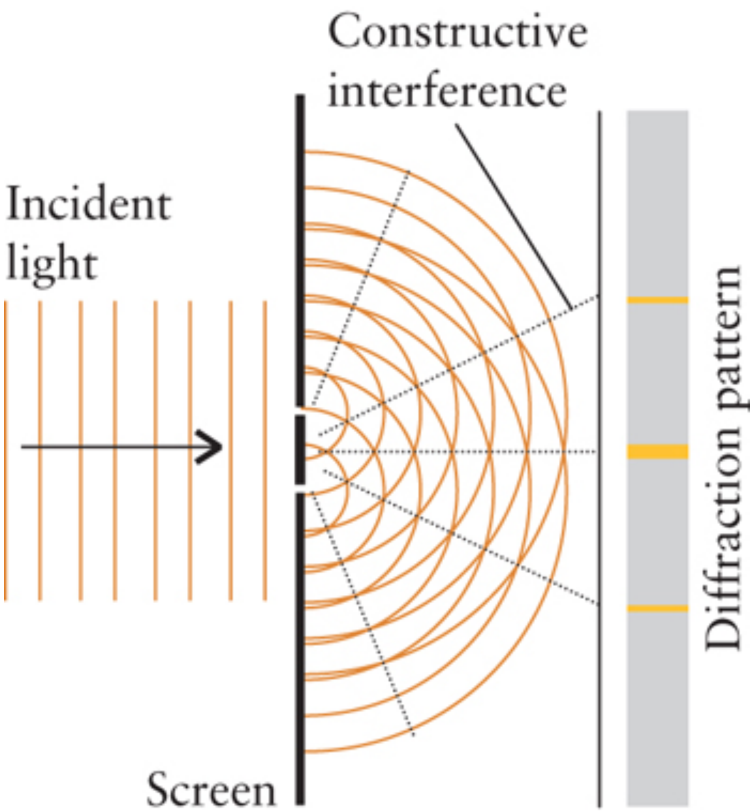
(c) What is the longest wavelength of electromagnetic radiation that could eject electrons from potassium? The work function of potassium is 2.29 eV.

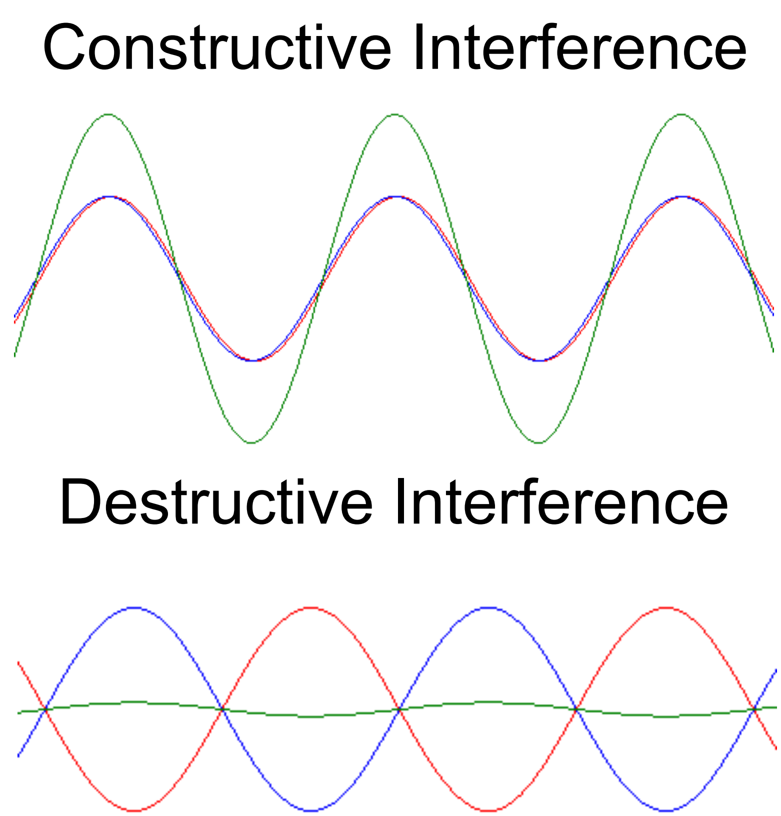
$$(1 \text{ eV} = 1.602 \times 10^{-19} \text{ J})$$

Diffraction of Light

From the Photo-Electric Effect, photons of light behave like particles

Classical Physics: Evidence shows the light behaves like waves



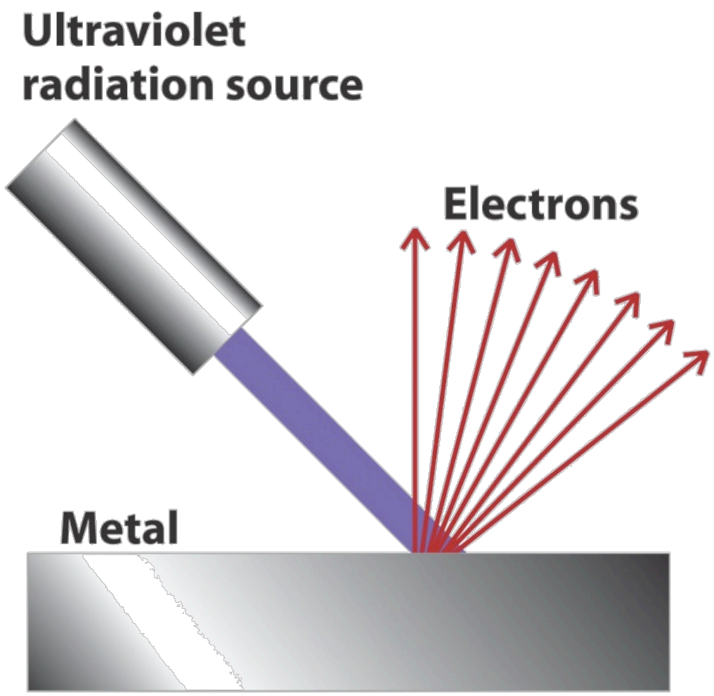


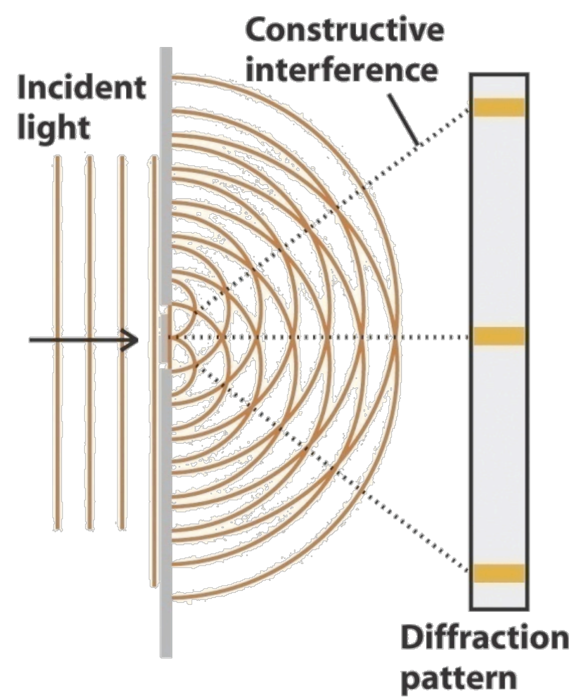
Wave-Particle Duality of Light

According to the Photo-Electric Effect: light behaves like particles
According to the 2-Slit Experiment: light behaves like waves

Modern concept of light:

Light has both wave-like and particle-like behavior

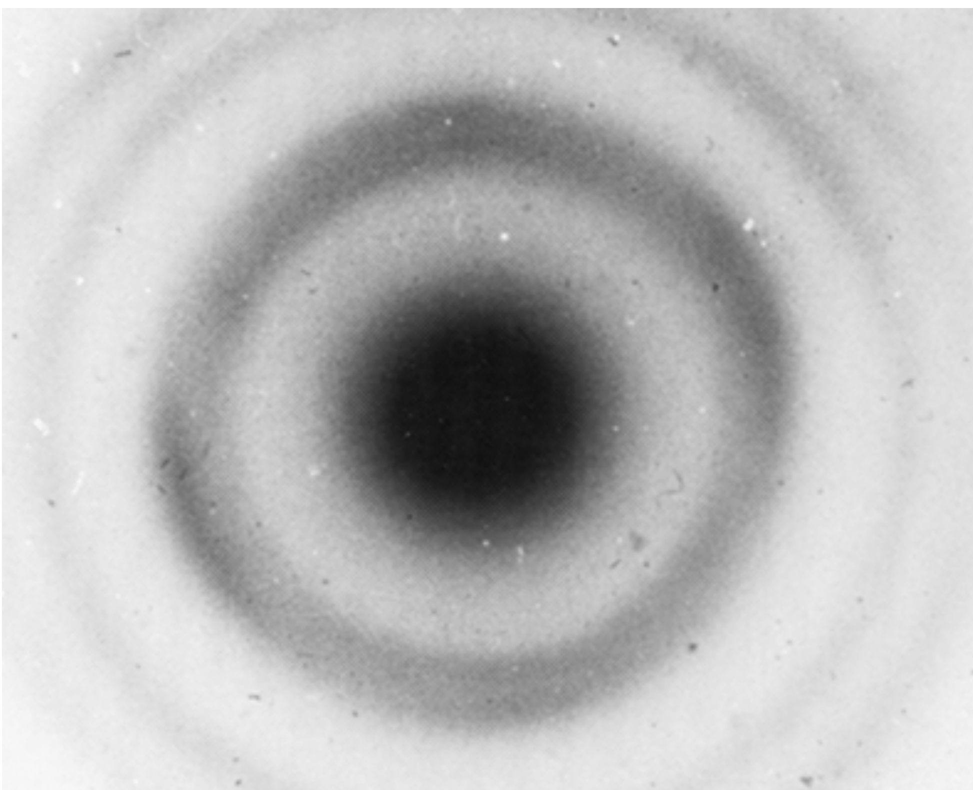




Wave-Particle Duality of Matter

Classical Physics: Electrons have mass, ergo electrons are matter

Modern Physics: Electrons can be diffracted – they can behave like light!



Louis de Broglie: all matter has wavelike properties

de Broglie wavelength:

$$\lambda_{db} = \frac{h}{mv}$$

The Uncertainty of Electrons

Wave-Particle Duality changes the way we think about electrons

Classical physics: matter has a definite location and momentum

But waves are not localized at a specific point

We cannot specify the path of an electron!

<u>Heisenberg Uncertainty Principle</u> – we cannot simultaneously know both the position and momentum of an electron

$$(m\Delta v)(\Delta x) \geq \tfrac{1}{2}\hbar$$

$$\hbar = h/2\pi$$

The Wavefunction

Electrons don't behave as point objects orbiting the nucleus

Erwin Schrödinger: introduced idea of a wavefunction

Wavefunction ψ **(x)**: math function which varies with position

Physical interpretation?

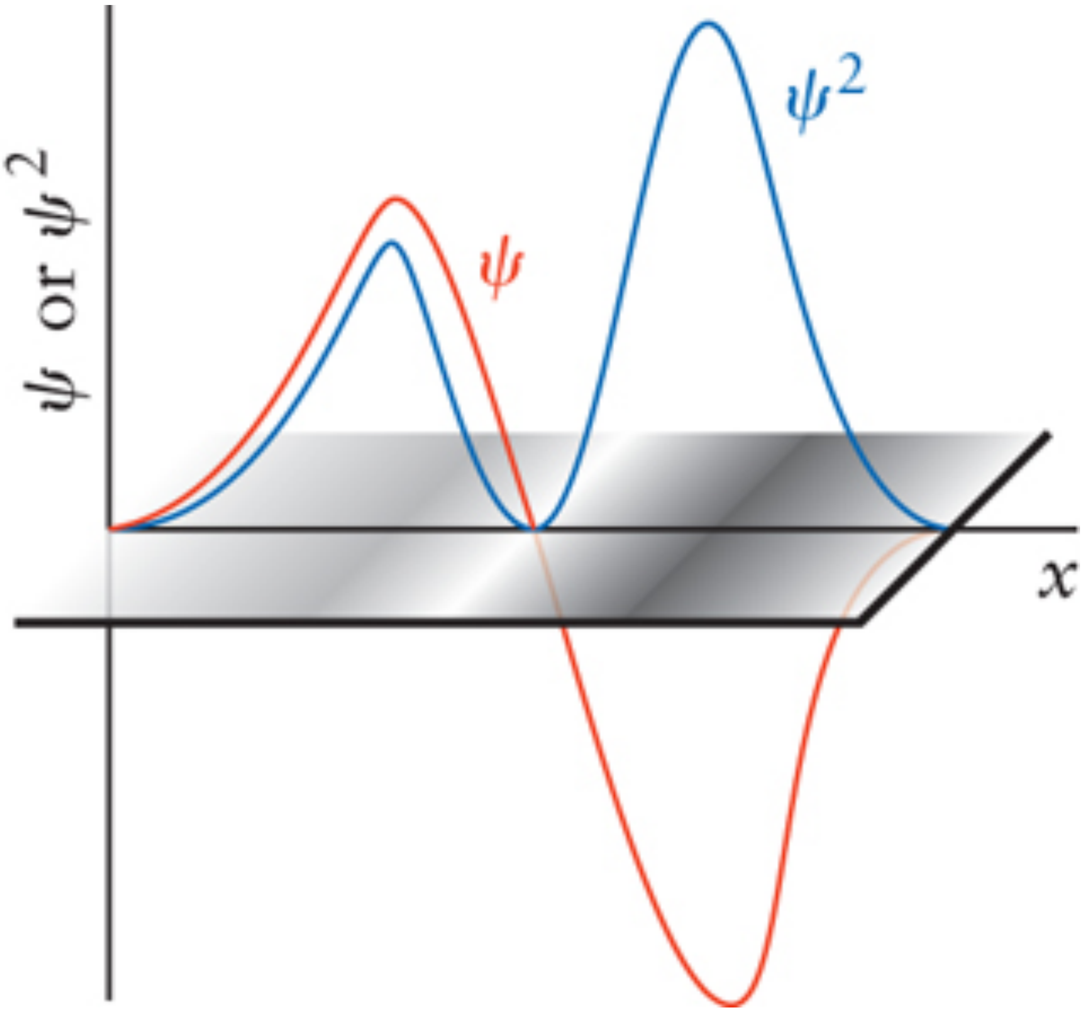
Born interpretation: ψ^2 is the **probability density**

ψ^2 ~ probability of finding the particle in a given Volume.

Wherever $\psi = 0$ → $\psi^2 = 0$, there is zero probability density

A location with zero probability density is called a **node**

The Wavefunction



Schrödinger's Equation

To calculate the wavefunction and energy of a particle, we use the **Schrödinger Equation**:

$$H\psi = E\psi$$

H is an operator called the **Hamiltonian**

E is the energy of the particle with ψ

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)$$

$$-\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2} + V(x)\Psi = E\Psi$$

Particle in a Box

A particle with zero PE in a 1D box

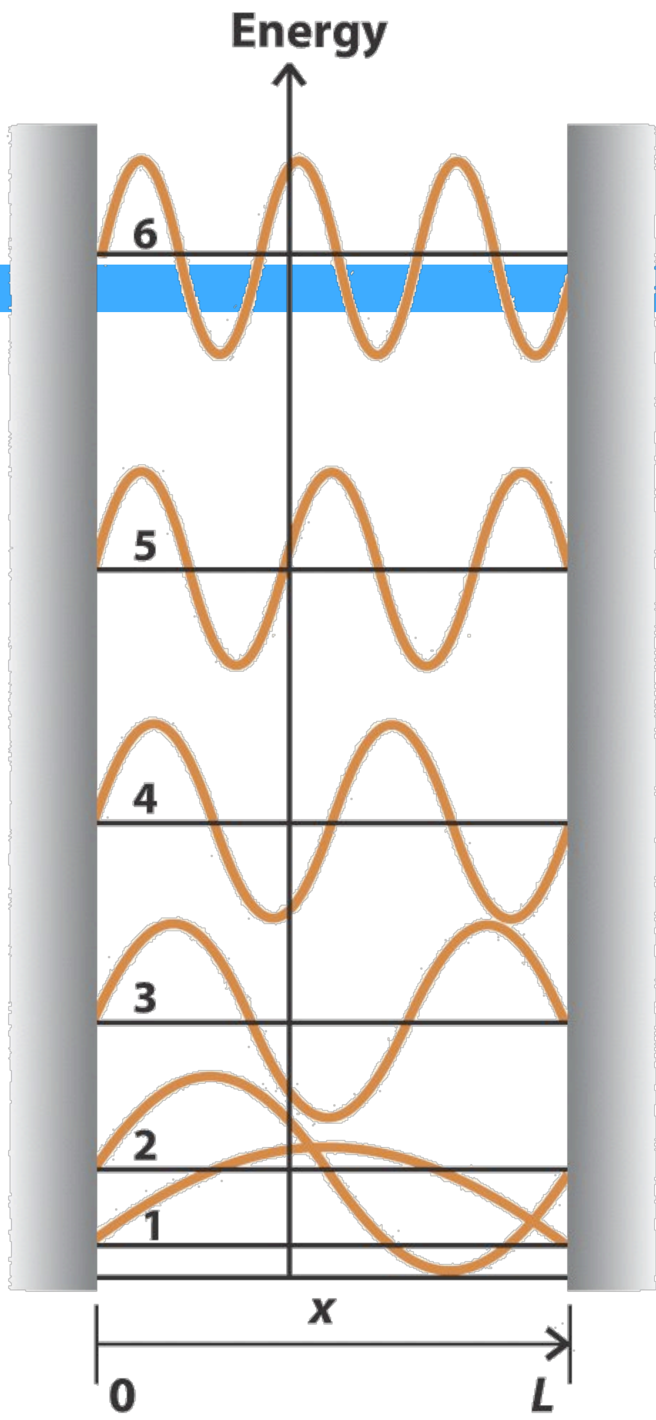
Box has length L

Particle has a mass of m

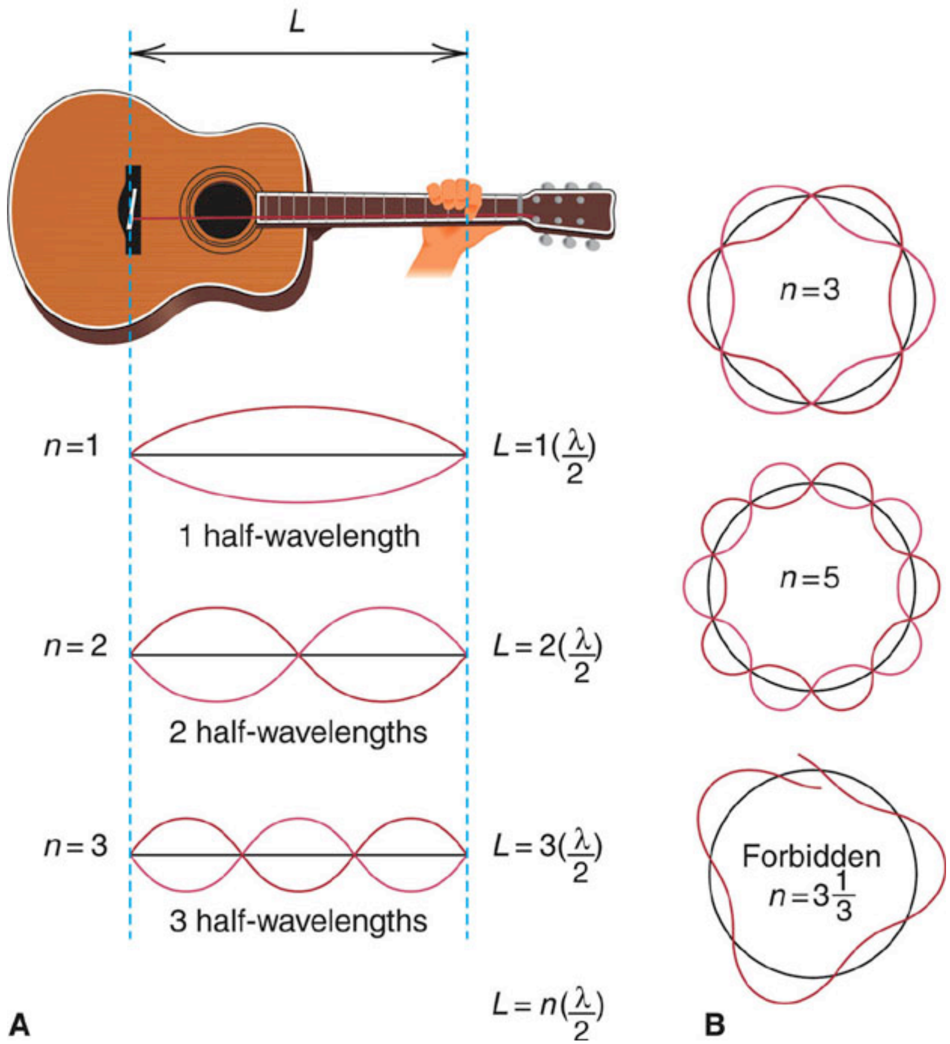
The particle acts as a standing wave; its shape is limited by L

$$\Psi_n(x) = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right)$$

$$-\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2} = E\Psi$$



Particle in a Box



Particle Energy Levels

2 conditions:

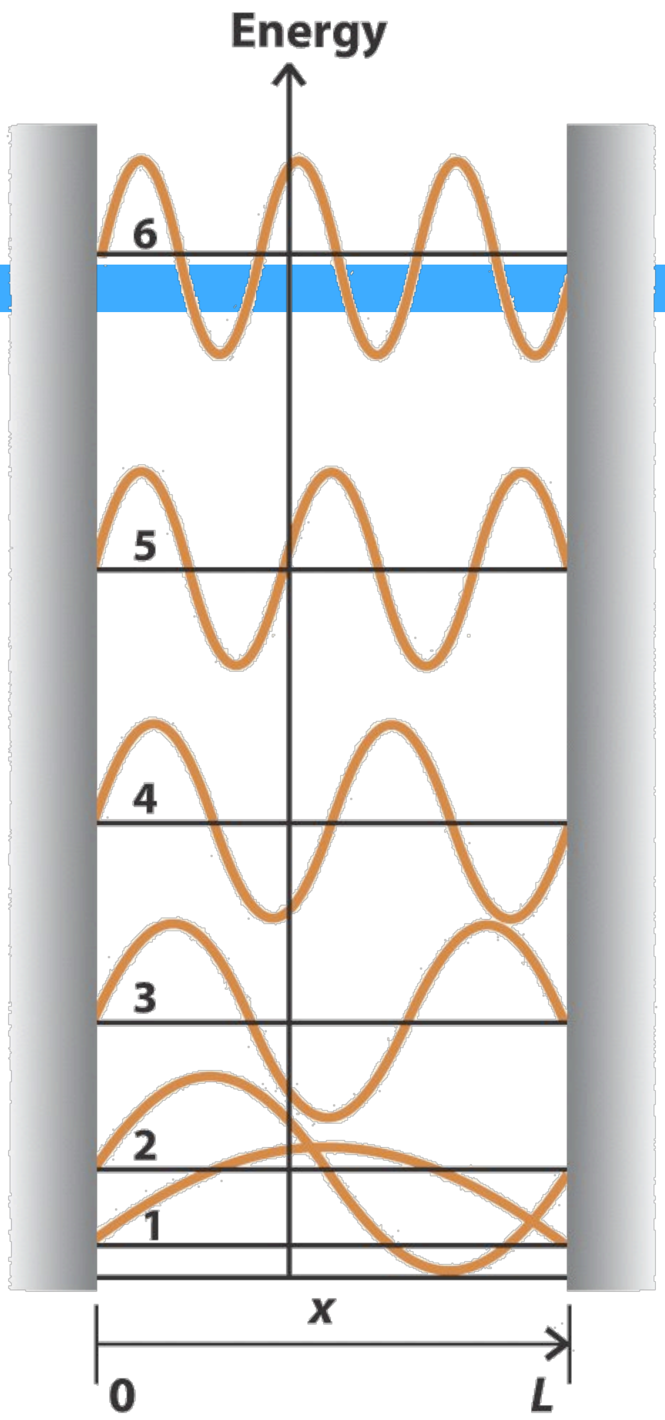
1: $$\frac{d^2\Psi}{dx^2} = C\Psi$$ sin or cos

2: Y = 0 at x = 0, L

- sin (0) = 0 whereas cos(0) = 1
- sin (L) = 0 and sin ($n\pi$) = 0, n = 1,2,3
- kL = $n\pi$

$$\Psi_n(x) = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right) \qquad E_n = \frac{n^2h^2}{8mL^2}$$

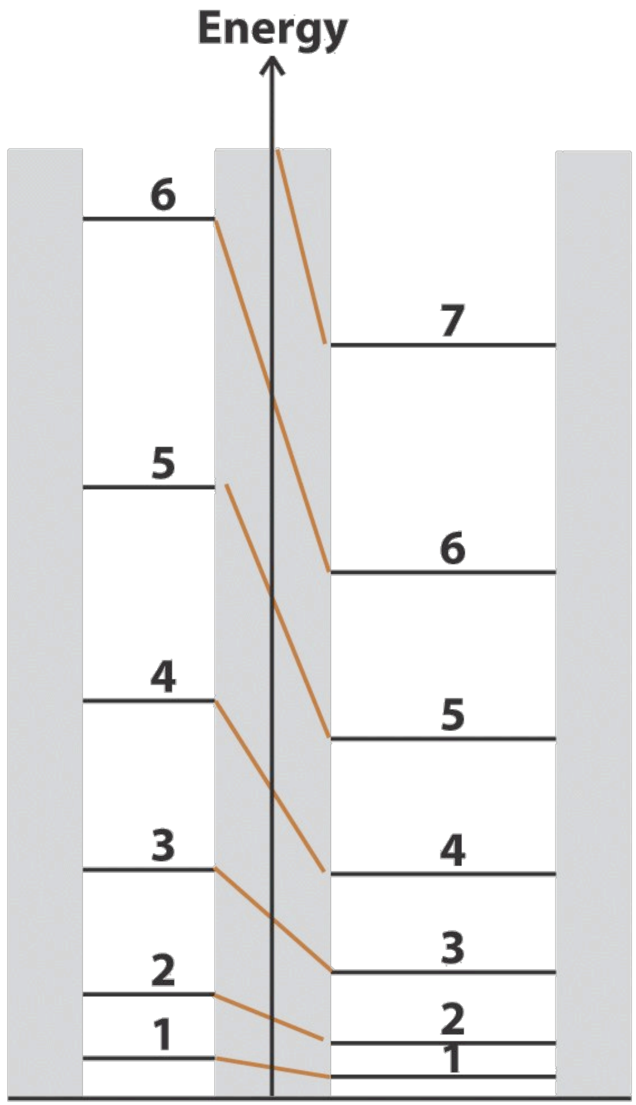
n = 1,2,3, …



Particle Energy Levels

$$\Psi_n(x) = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right) \qquad E_n = \frac{n^2h^2}{8mL^2}$$

- n can only be an integer
- Energy is restricted to specific values
- Energy levels are "quantized"
- As L and/or m increases, energy levels fall and are closer together
- A particle cannot have zero energy
- Zero-point energy = E_1



The Hydrogen Atom

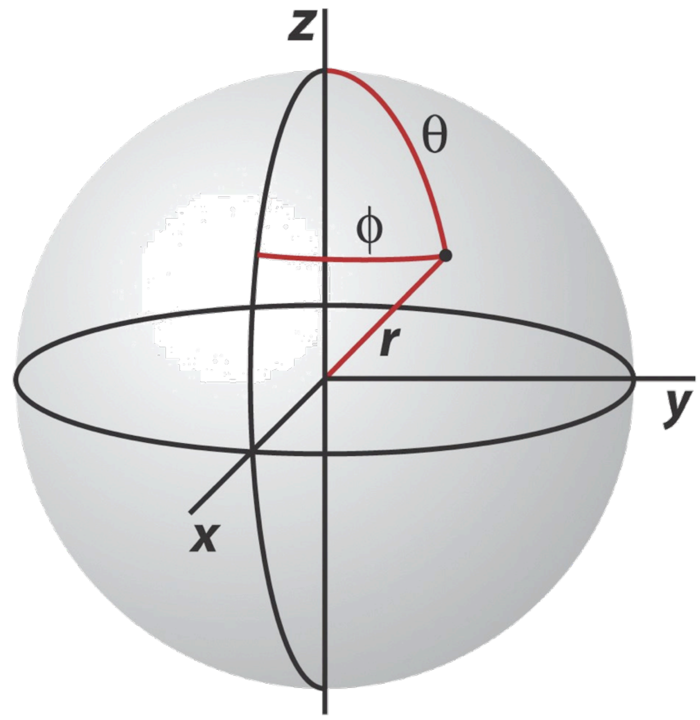
1. Quantum Numbers
2. Atomic Orbitals
3. Electron Spin

Quantum Model of H

- An electron in a H atom is like a particle in a 3D box
- Have to include Coulomb PE in the Hamiltonian

$$V(r) = \frac{(-e)(+e)}{4\pi\varepsilon_0 r} = -\frac{e^2}{4\pi\varepsilon_0 r}$$

$$E_n = -\frac{h\Re}{n^2} \qquad n = 1,2,\ldots$$



Triumph! Schrödinger's $\Re$ fits the experimental Rydberg constant!

Practice

- An electron in a hydrogen atom is initially at 1.5 Å from the proton, and then it moves to a distance of 0.5 Å from the proton. Calculate the change in potential energy between the proton and electron.
  (hint: 1 Å = 10^{-10} m)

Schrödinger's Triumph!

Schrödinger's work can be applied to other 1-electron atoms: He^+, etc…

$$E_n = -\frac{Zh\Re}{n^2} \qquad n = 1,2,\ldots$$

All the energies are negative – an electron in an atom has lower energy than an isolated electron

As Z increases, the electron is more tightly bound to the nucleus

As n increases, Energy becomes less negative

Principal Quantum Number

Energy levels calculated with Schrödinger's equation

Each level labeled with a value of n

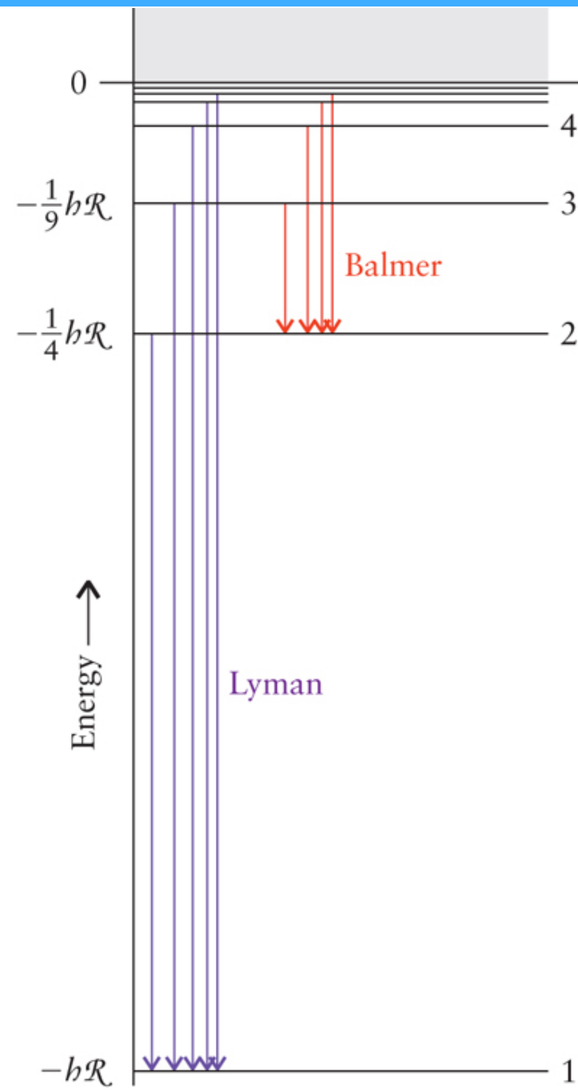
<u>Principal quantum # (n):</u> energy levels of electrons in the atom

n = 1 "**<u>ground state</u>**"

As n↑, Energy of electron ↑

When n → infinity, E = 0: electron is free of the atom

<u>Ionization:</u> removal of electron from an atom

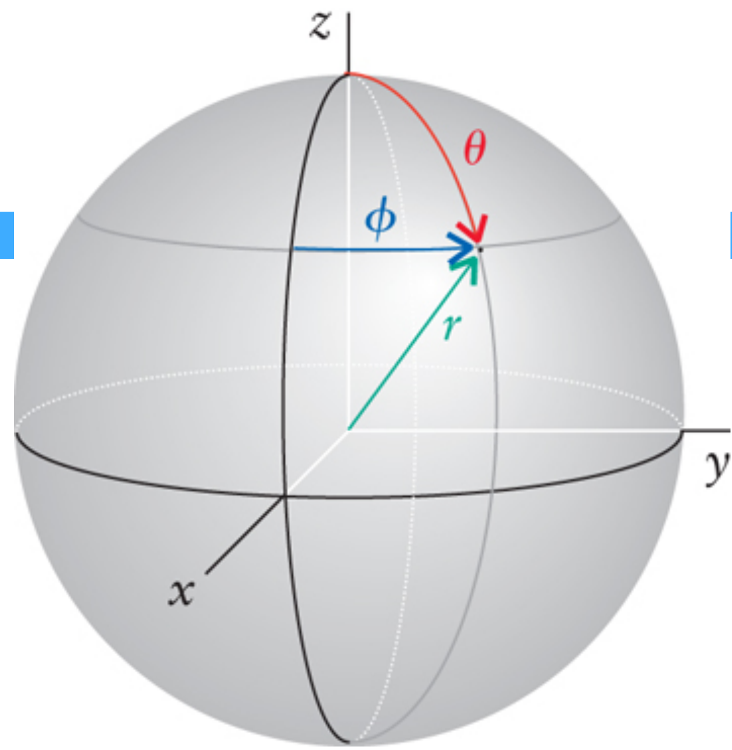


Atomic Orbitals

We know the energies for the H atom.

What about the wavefunctions?

Where do electrons exist in the atom?



- **<u>Atomic Orbitals</u>** - wavefunctions of electrons in atoms
  - Equations are more complicated than Particle in a Box
  - Remember: ψ is the wavefunction and ψ^2 ~ probability density
- Use spherical polar coordinates

  r = distance from center of atom

  θ = "latitude"

  Φ = "longitude"

Radial vs Angular Wavefunction

- Particle in a 1D box → $\psi(x)$; 3D box → $\psi(x,y,z)$
- H atom → $\psi(r,\theta,\Phi)$
- Can isolate r from θ and Φ → $\psi(r,\theta,\Phi) = R(r)\,\psi(\theta,\Phi)$
- Radial wavefunction $R(r)$
  - Change in the wavefunction as you move away from the nucleus
- Angular wavefunction $\psi(\theta,\Phi)$
  - Describes the shape and orientation of the wavefunction
- Ground state of Hydrogen has 1 wavefunction:
- Higher energy levels have more than 1

Quantum Numbers

Principal Quantum Number (n)

- Size of an orbital
- Has values $n = 1, 2, 3\ldots$

Orbital Angular Momentum Quantum Number (ℓ)

- Shape of an orbital
- Has values $\ell = 0, 1, 2, \ldots, n-1$

Magnetic Quantum Number (m_ℓ)

- Orientation of the orbital in space
- Has values $m_\ell = -\ell, -\ell + 1, \ldots, 0, \ldots, \ell - 1, \ell$

Spin Magnetic Quantum Number (m_s)

- Spin state of the electron
- Spin state is either up (↑) or down (↓): $+\frac{1}{2}$ and $-\frac{1}{2}$

Angular Momentum and ℓ

With known n, must specify ℓ and m_ℓ to identify an orbital

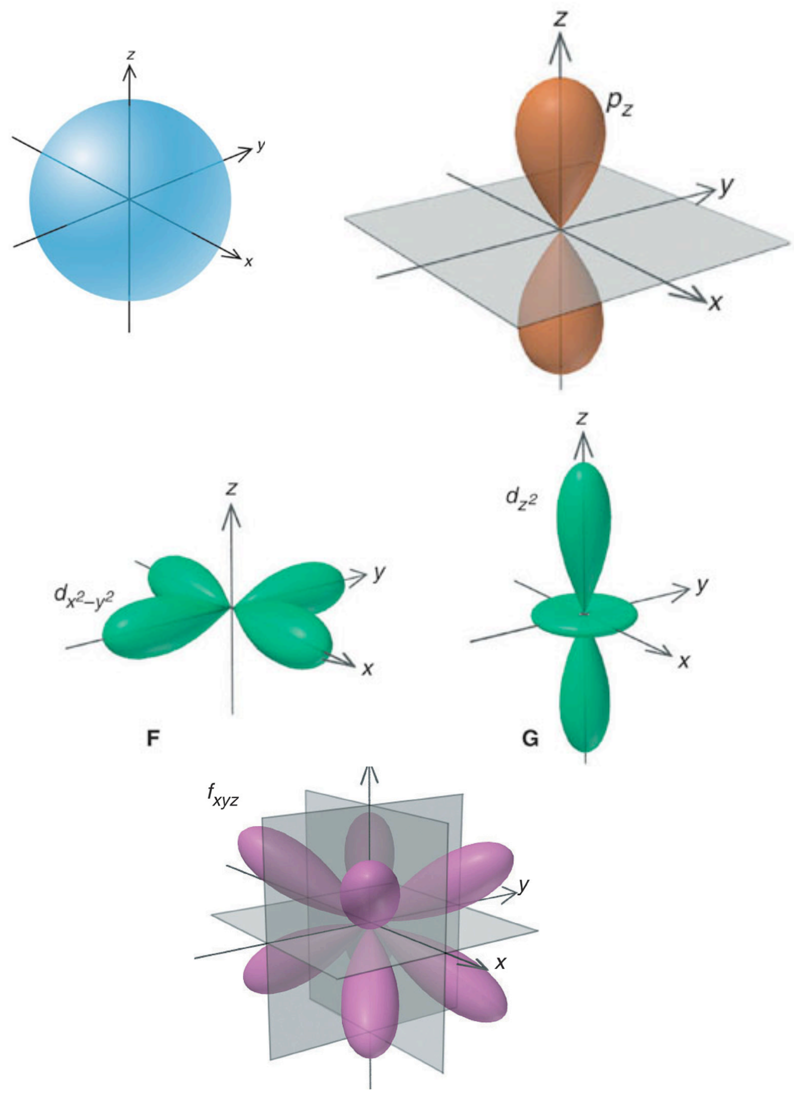
- n values of ℓ for a given energy level
- Possible values: ℓ = 0, 1, 2, … , n-ℓ
- **Subshells**, ℓ, have different Radial functions

n	l	$R_{nl}(r)$
1	0	$2\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$
2	0	$\frac{1}{2\sqrt{2}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2-\frac{Zr}{a_0}\right)e^{-Zr/2a_0}$
	1	$\frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)e^{-Zr/2a_0}$
3	0	$\frac{1}{9\sqrt{3}}\left(\frac{Z}{a_0}\right)^{3/2}\left(3-\frac{2Zr}{a_0}+\frac{2Z^2r^2}{9{a_0}^2}\right)e^{-Zr/3a_0}$
	1	$\frac{2}{27\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2-\frac{Zr}{3a_0}\right)e^{-Zr/3a_0}$
	2	$\frac{4}{81\sqrt{30}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)^2 e^{-Zr/3a_0}$

ℓ	Type
0	s
1	p
2	d
3	f

Visual Depictions of ℓ

ℓ	Type
0	s
1	p
2	d
3	f



Angular Momentum and m_ℓ

Magnetic quantum #, m_ℓ, distinguishes orbitals in a subshell

- $2\ell + 1$ values of m_ℓ in a subshell, ℓ
- Possible values $m_l = -\ell, -\ell + 1, \ldots, 0, \ldots, \ell - 1, \ell$
- m_ℓ identifies the angular wavefunction $\psi(\theta,\Phi)$ of the orbital

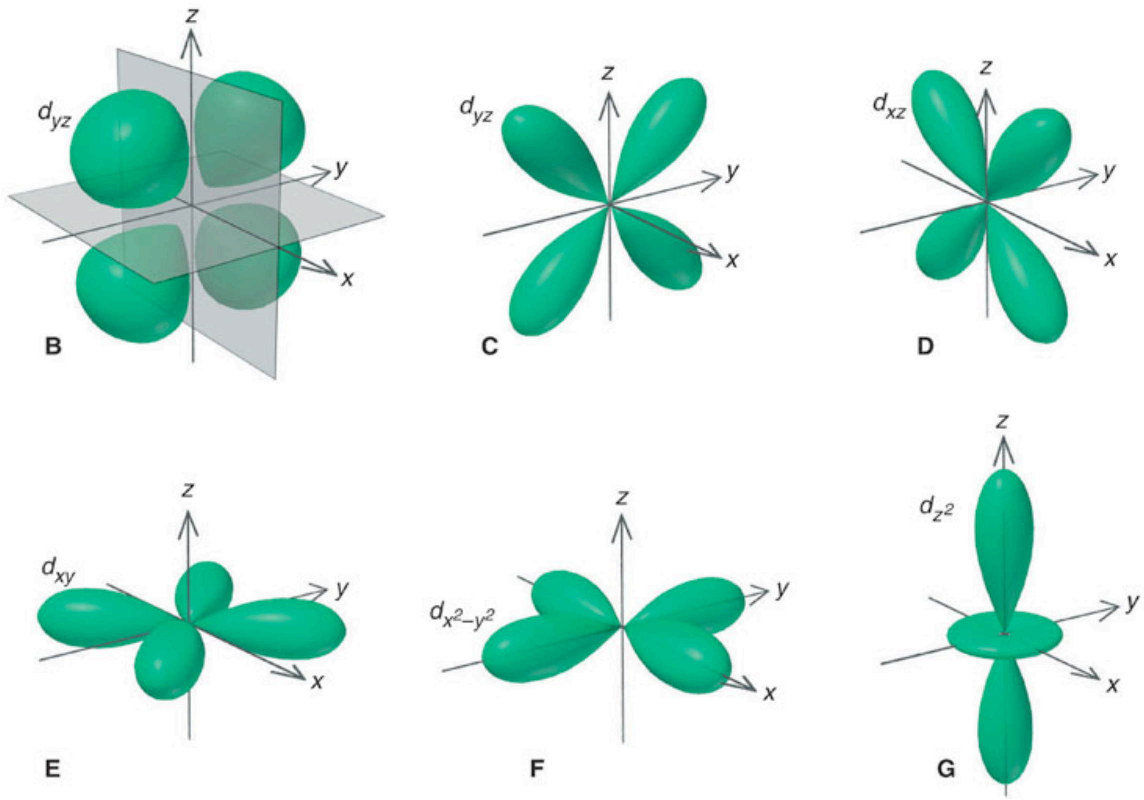
ℓ	Type	m_ℓ
0	s	0
1	p	-1, 0, 1
2	d	-2, -1, 0, 1, 2
3	f	-3, -2, -1, 0, 1, 2, 3

Angular Momentum and m_ℓ

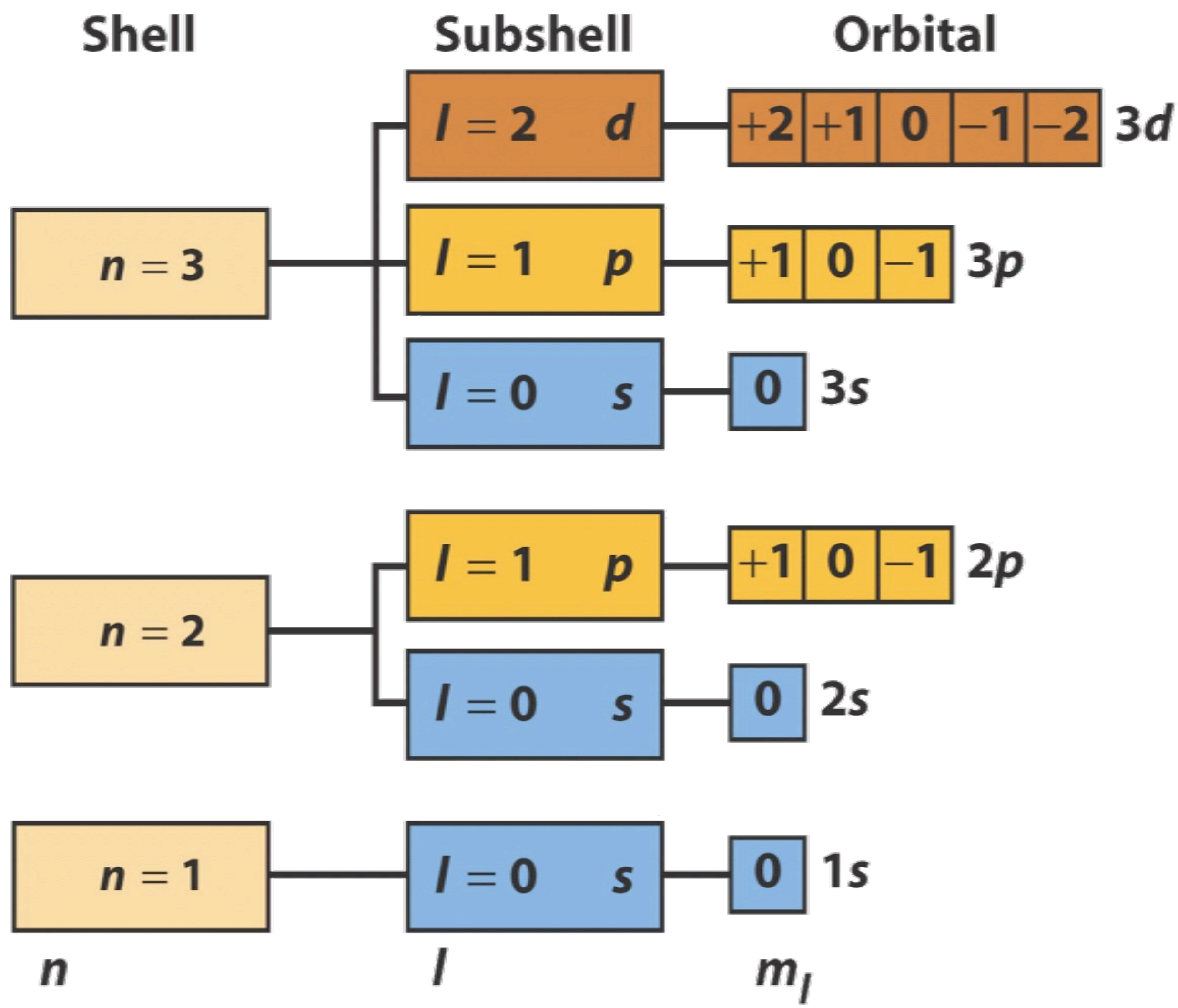
EXAMPLE: For n=3, ℓ can equal 0,1, or 2 (can be a s, p, or d shaped orbital). The different 3d orbitals can have m_ℓ values of -2 -1, 0, 1, 2 that look like this....

(b) Angular wavefunctions, $Y_{lm_l}(\theta,\phi)$

l	"m_l"*	$Y_{lm_l}(\theta,\phi)$
0	0	$\left(\frac{1}{4\pi}\right)^{1/2}$
1	x	$\left(\frac{3}{4\pi}\right)^{1/2} \sin\theta\cos\phi$
	y	$\left(\frac{3}{4\pi}\right)^{1/2} \sin\theta\sin\phi$
	z	$\left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$
2	xy	$\left(\frac{15}{16\pi}\right)^{1/2} \sin^2\theta\cos 2\phi$
	yz	$\left(\frac{15}{4\pi}\right)^{1/2} \cos\theta\sin\theta\sin\phi$
	zx	$\left(\frac{15}{4\pi}\right)^{1/2} \cos\theta\sin\theta\cos\phi$
	x^2-y^2	$\left(\frac{15}{16\pi}\right)^{1/2} \sin^2\theta\sin 2\phi$
	z^2	$\left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1)$



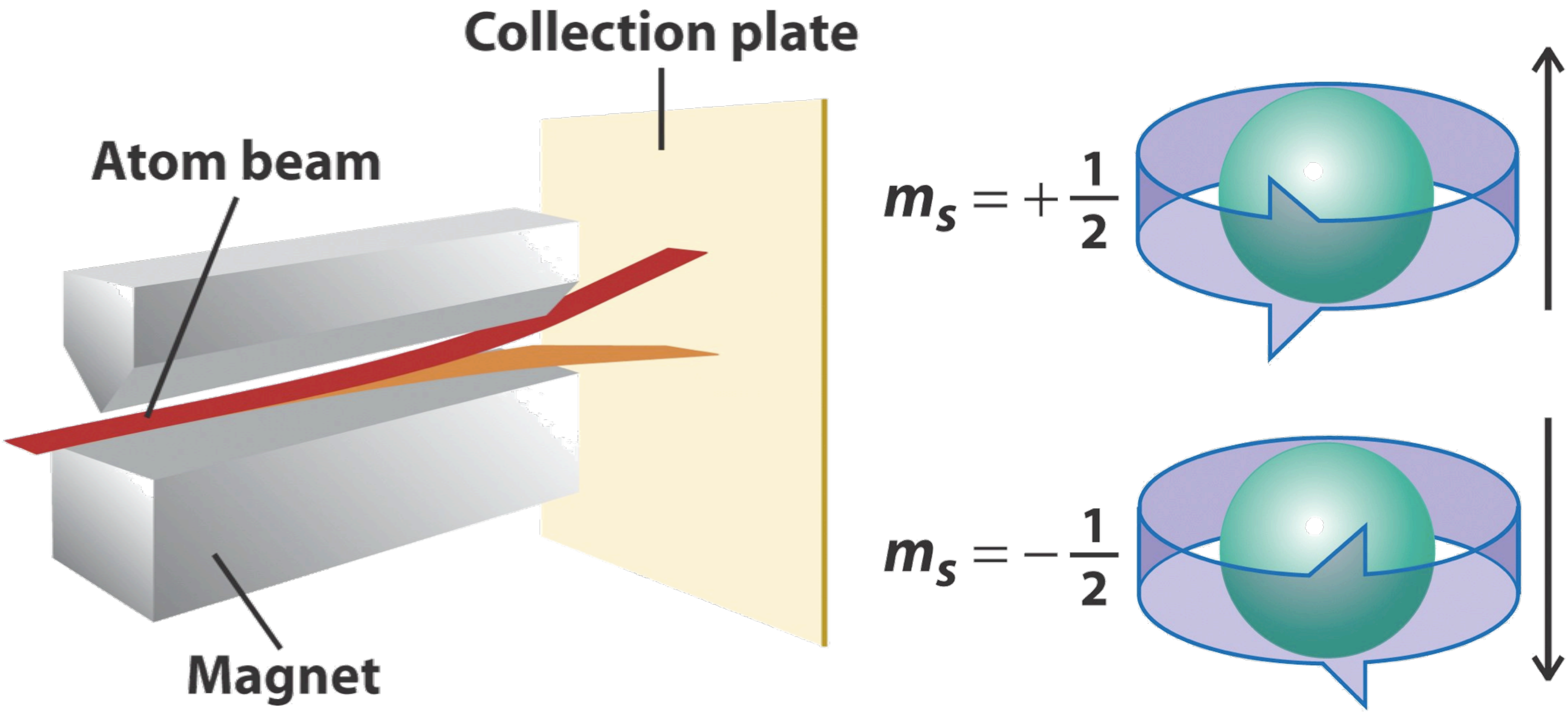
Quantum Number Overview



Electron spin and m_s

Particles with 1 unpaired electron passed through a magnet split into two narrow bands

Electrons have spin, in only 2 possible directions



Quantum Numbers and Atomic Orbitals

- For an energy level n, there are n^2 orbitals

$n = 1$	$n^2 = 1$	$\ell = 0$	$m_\ell = 0$
$n = 2$	$n^2 = 4$	$\ell = 0$	$m_\ell = 0$
		$\ell = 1$	$m_\ell = -1,0,1$
$n = 3$	$n^2 = 9$	$\ell = 0$	$m_\ell = 0$
		$\ell = 1$	$m_\ell = -1,0,1$
		$\ell = 2$	$m_\ell = -2,-1,0,1,2$

- Orbital in energy level n: $n - 1$ nodes

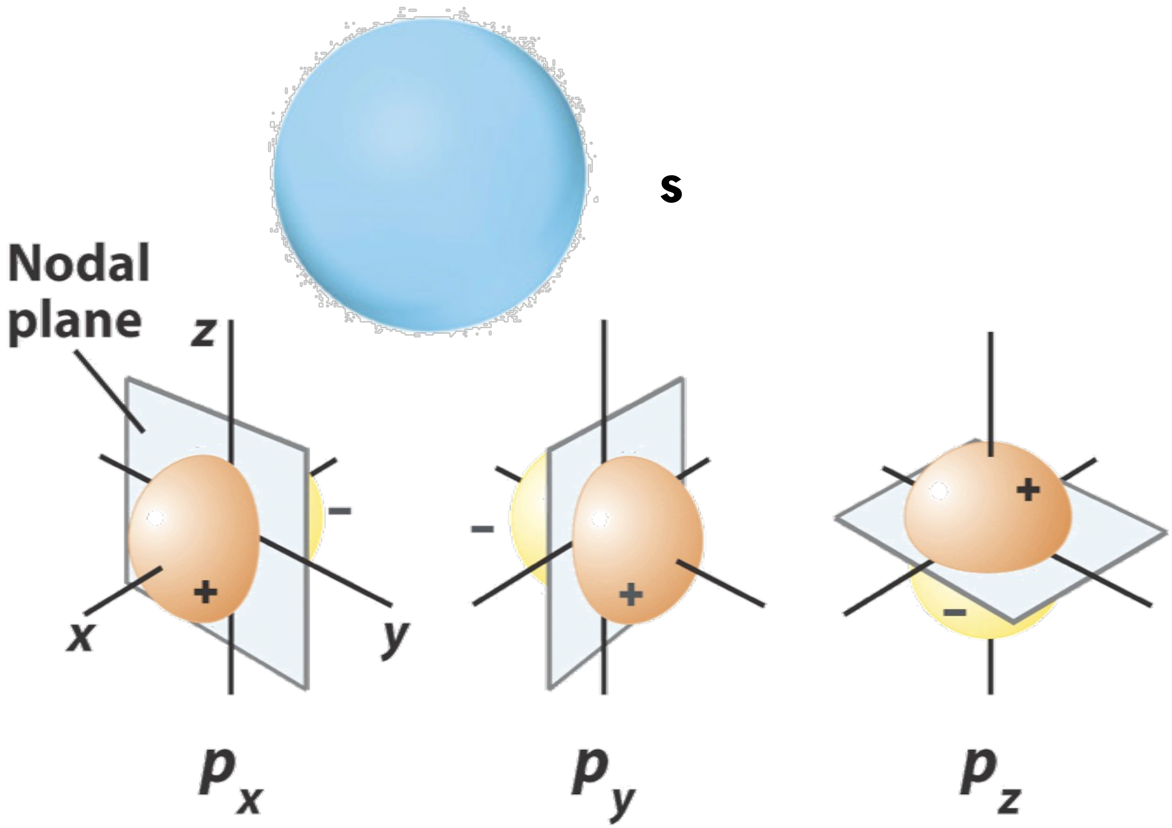
  (node is a region of zero probability density)

- ℓ nodes in the angular wavefunction $\psi(\theta,\Phi)$
- $(n-1) - \ell$ nodes in the radial wavefunction $R(r)$

Shapes of Atomic Orbitals

- For an orbital in energy level n, there are n – 1 nodes
- An orbital has ℓ nodes in the angular wavefunction $\psi(\theta,\Phi)$

ℓ	Type	Nodal Planes
0	s	0
1	p	1
2	d	2
3	f	3



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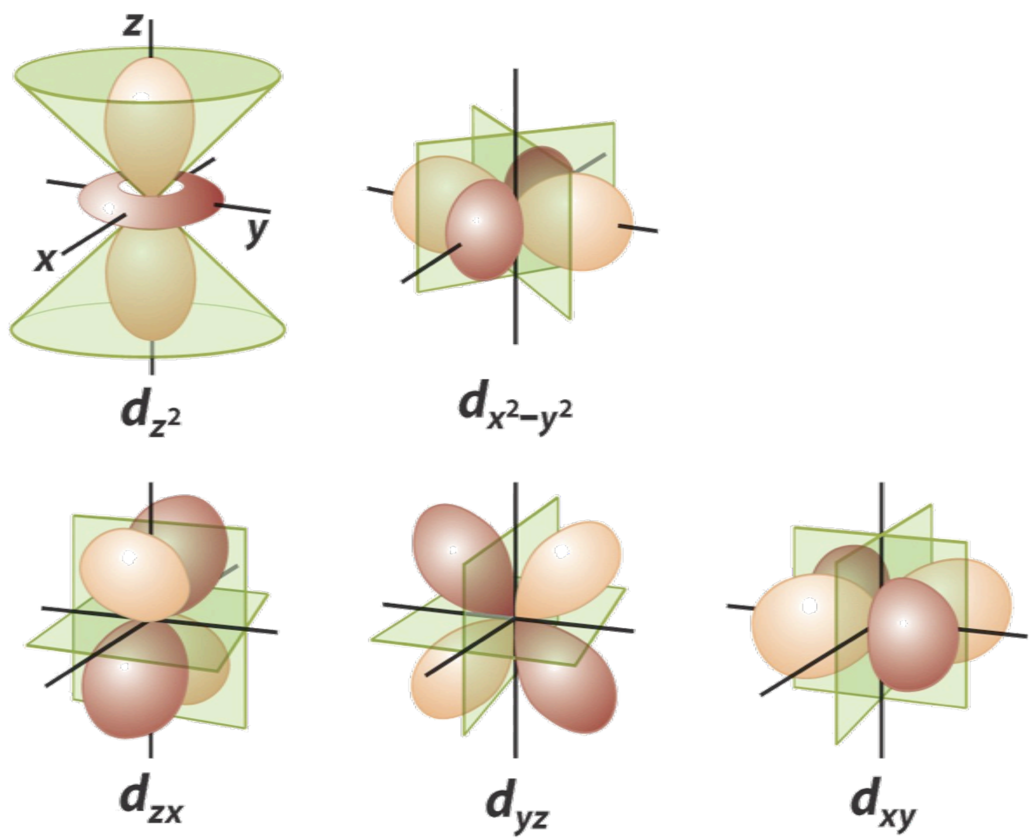

Shapes of Atomic Orbitals

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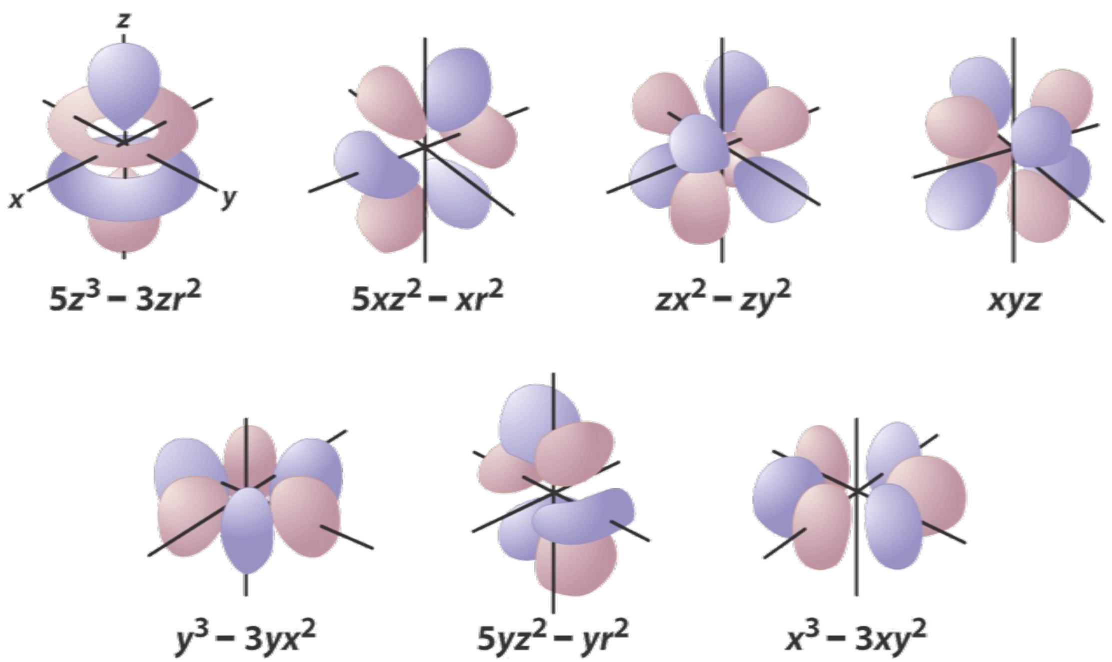
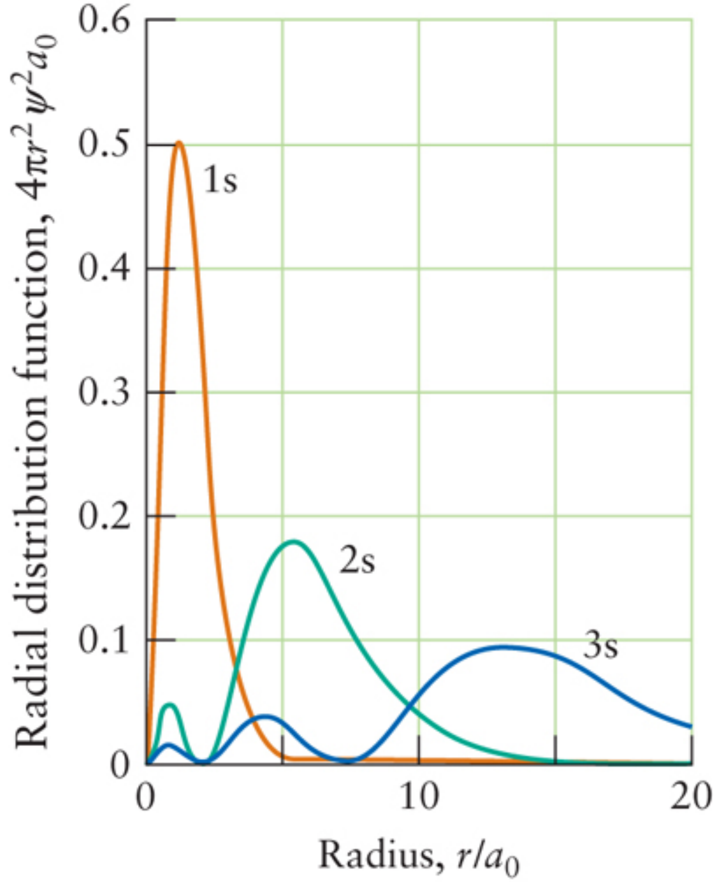
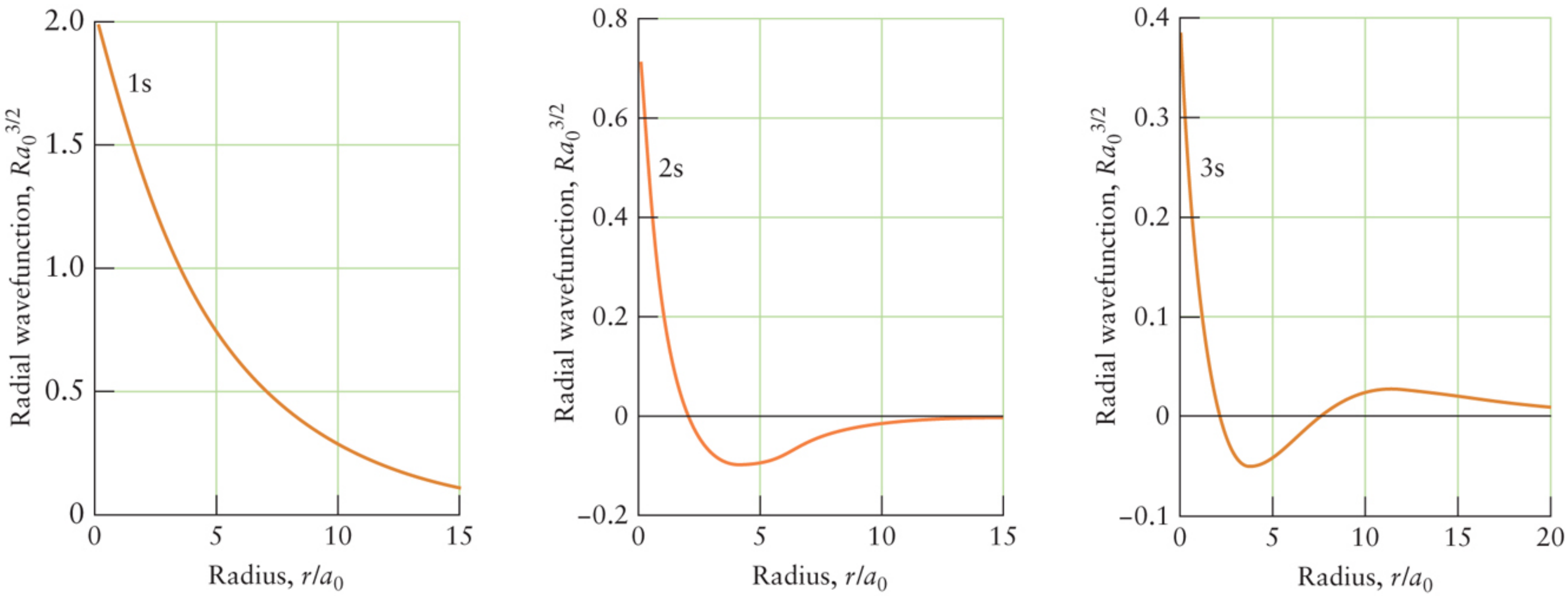


Radial Functions of Orbitals

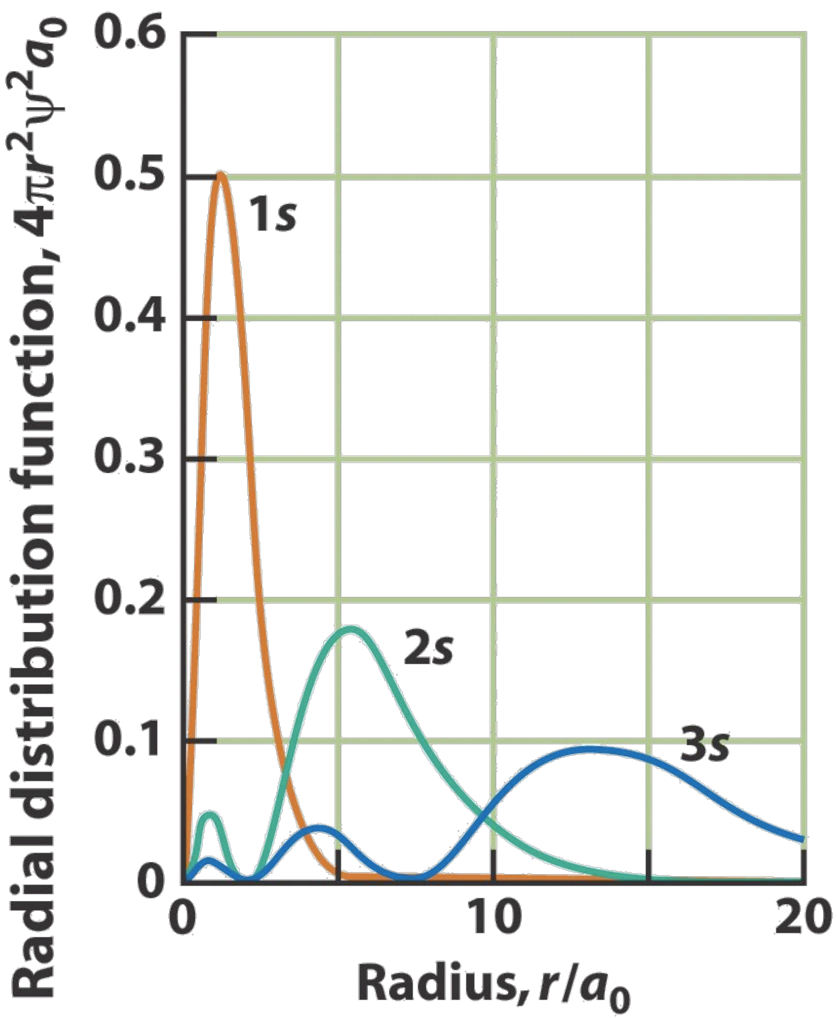
- For an orbital in energy level n, there are n – 1 nodes
- An orbital has (n-1) – ℓ nodes in the radial wavefunction R(r)

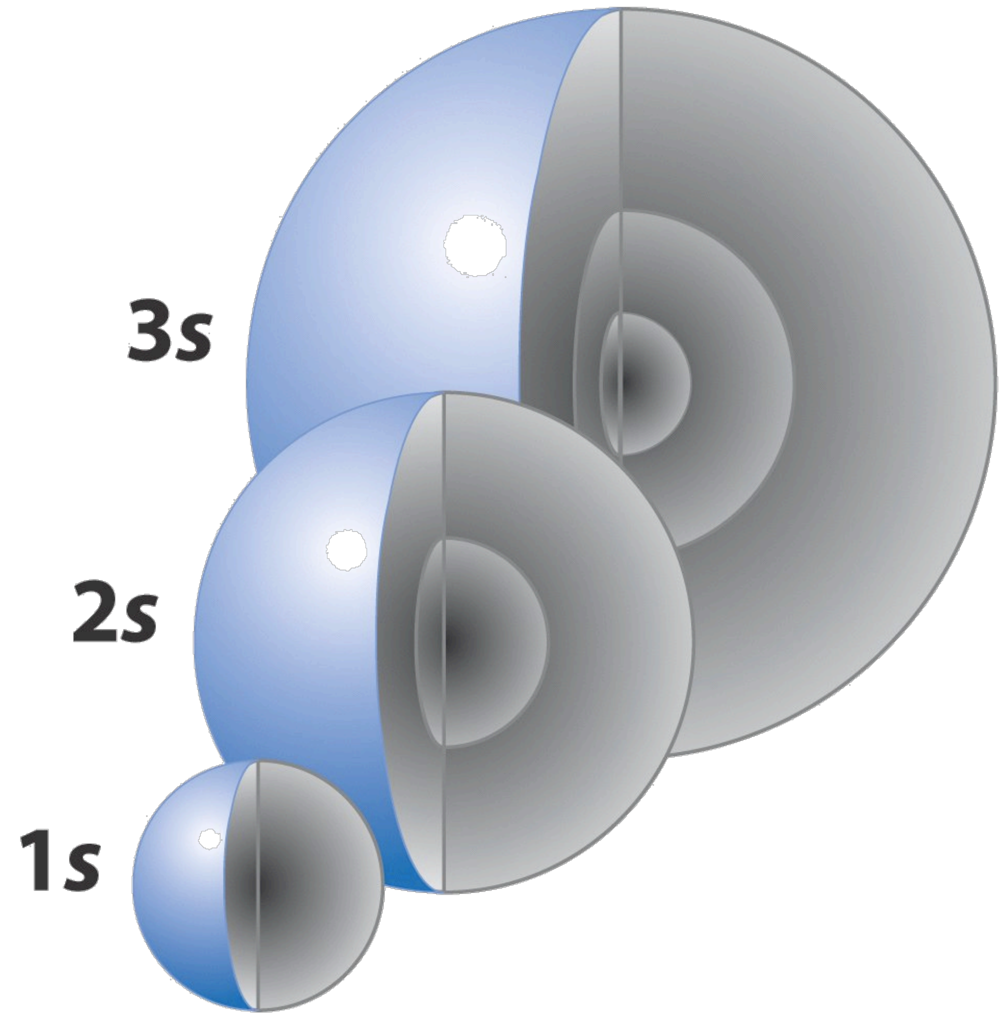


Radial Wavefunctions of s Orbitals



Wavefunctions of s Orbitals





Pauli Exclusion Principle

No two electrons in an atom can have the same four quantum numbers

No more than two electrons may occupy a given orbital. If there are two electrons in an orbital, their spins must be opposite signs

Other Visualization Methods

- See: Orbitron - Gallery of Atomic Orbitals
  http://winter.group.shef.ac.uk/orbitron/

Many-Electron Atoms

1. Orbital Energies
2. Building-Up Principle
3. Electronic Structure

Potential Energy

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)$$

How does the presence of other electrons affect things?

- In 1 e- atoms, simply the attraction of 1 e- to nucleus with charge Z
- Now must take into account repulsion between electrons
- In the Helium atom, the nucleus has a charge of +2, and there are 2 electrons, e_1 and e_2:

Attraction of e_2 to nucleus

$$V = -\frac{2e^2}{4\pi\varepsilon_0 r_1} - \frac{2e^2}{4\pi\varepsilon_0 r_2} + \frac{e^2}{4\pi\varepsilon_0 r_{12}}$$

Attraction of e_1 to nucleus

Repulsion between e_1 and e_2

No more Degeneracy

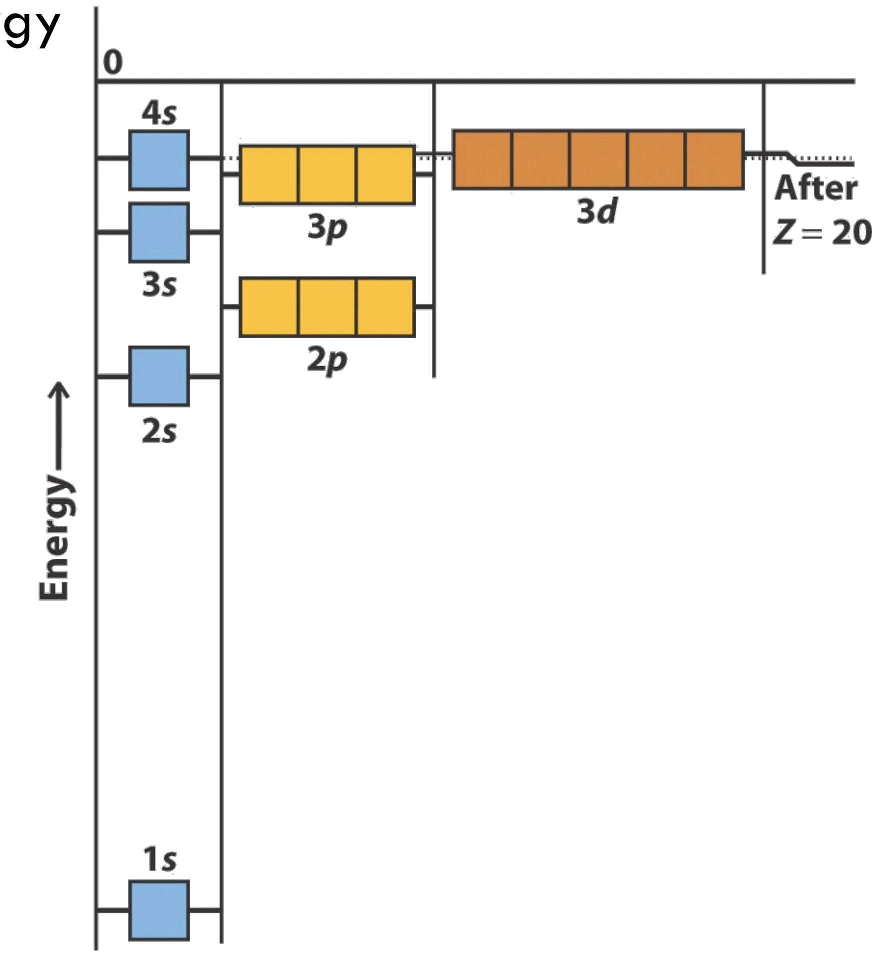
In the Hydrogen atom, all orbitals within an energy level (n) are degenerate; they have the same energy

Electron-electron repulsion removes this degeneracy

Electron-electron repulsion: electrons less tightly bound to the nucleus

Inner electrons **shield** outer electrons from the nucleus.

Shielded electrons do not “feel” Z, they feel $\mathbf{Z_{eff} < Z}$



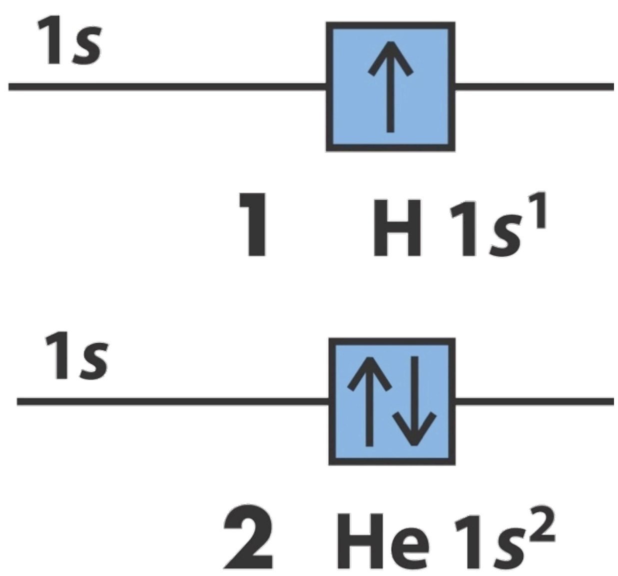
Electron Configurations

Electronic structure of an atom determines its chemical properties

Electron configuration – list of the electrons are in each orbital

Pauli Exclusion Principle:

- No more than 2 electrons in any orbital.
- When 2 electrons do occupy one orbital, their spins are paired
  - 1 is spin up and 1 is spin down.
- No 2 electrons in an atom can have the same set of 4 quantum numbers

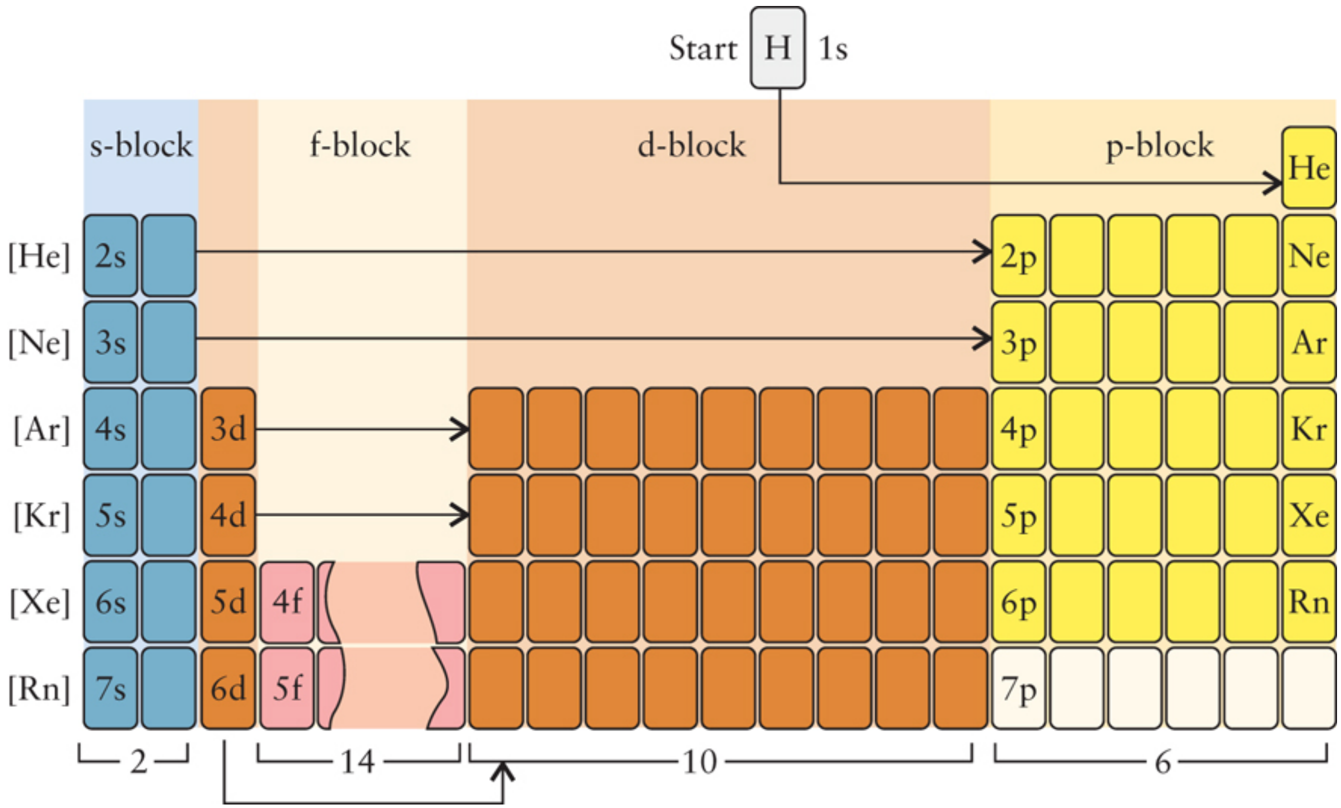


Valence electrons – electrons in the outermost energy level (n)

Ground state – the lowest energy electron configuration for an atom

Building Up Principle

1. Add Z electrons, one after the other, to the orbitals in order of increasing energy. Do not add more than 2 electrons in any orbital
2. If more than one orbital is available in a subshell (p,d,f), add electrons with parallel spins to different orbitals in the subshell before pairing electrons



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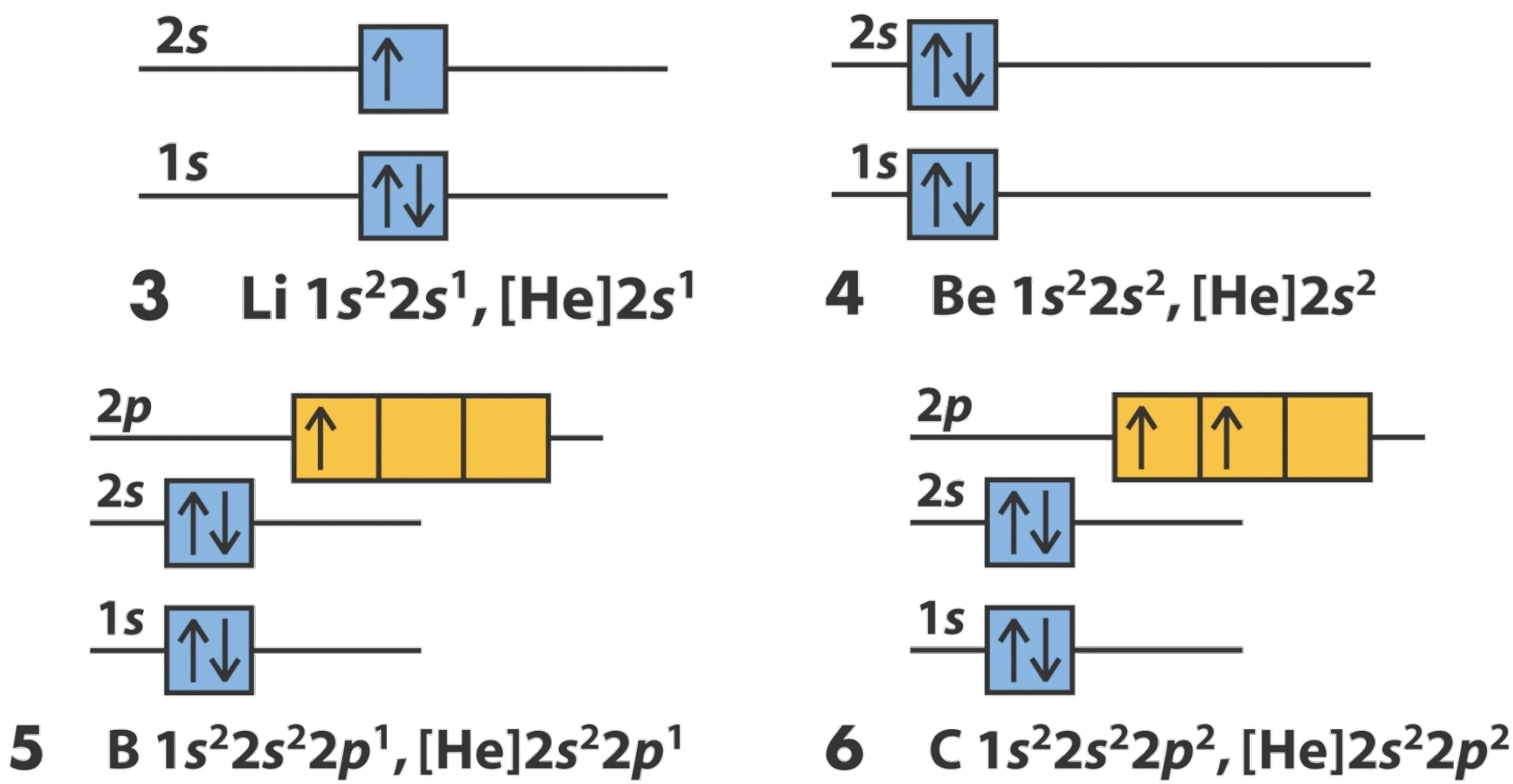

Building Up Principle

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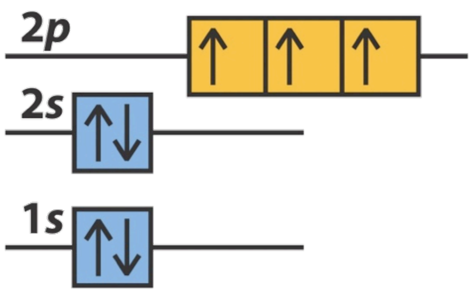
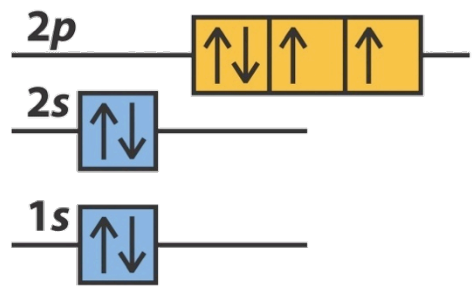
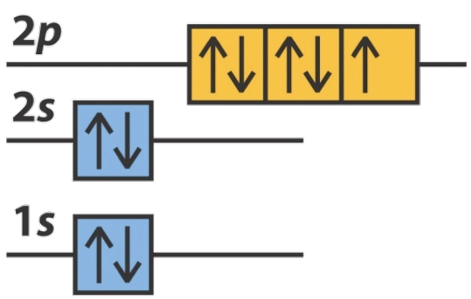


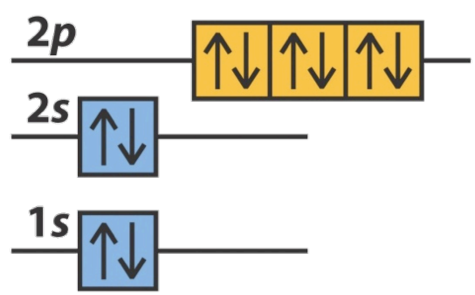
7 N $1s^2 2s^2 2p^3$, [He]$2s^2 2p^3$



8 O $1s^2 2s^2 2p^4$, [He]$2s^2 2p^4$



9 F $1s^2 2s^2 2p^5$, [He]$2s^2 2p^5$



10 Ne $1s^2 2s^2 2p^6$, [He]$2s^2 2p^6$

Building Up Principle

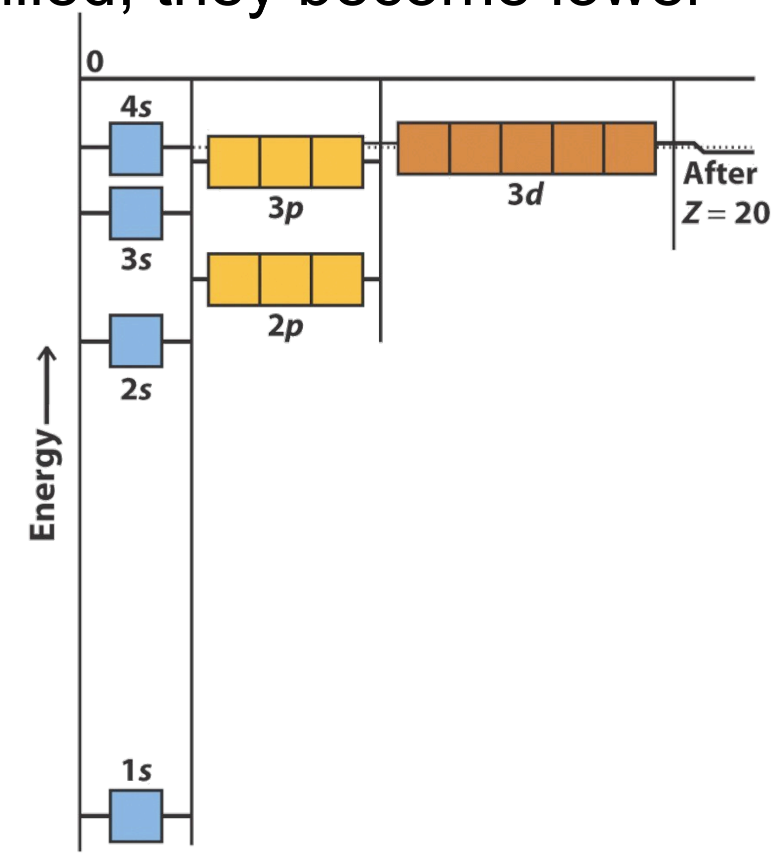
1. Add Z electrons, one after the other, to the orbitals in order of increasing energy. Do not add more than 2 electrons in any orbital.
2. Add electrons with parallel spins to different orbitals in the subshell before pairing electrons.

3. These Principles are known as the Aufbau Principle, Hund’s Rule, and Pauli Exclusion Principle

Trickiness in Electron configurations…

When unoccupied, 4s orbital is slightly lower in energy than 3d orbitals

Once the 3d orbitals start to get filled, they become lower in energy than the 4s orbital.



K Z = 19 [Ar]$4s^1$

Ca Z = 20 [Ar]$4s^2$

Sc Z = 21 [Ar]$3d^1 4s^2$

Trickiness in Electron configurations…

Exceptions to the Building-Up Principle

- Filled subshells are the most energetically favorable
- ½ filled subshells are good too! Ex. p^3 or d^5

Cr **$[Ar]3d^5 4s^1$**

Cu **$[Ar]3d^{10} 4s^1$**

<u>Excited state</u> electron configurations:

If the electron configuration does not follow the building-up principle, the electron is in an excited state

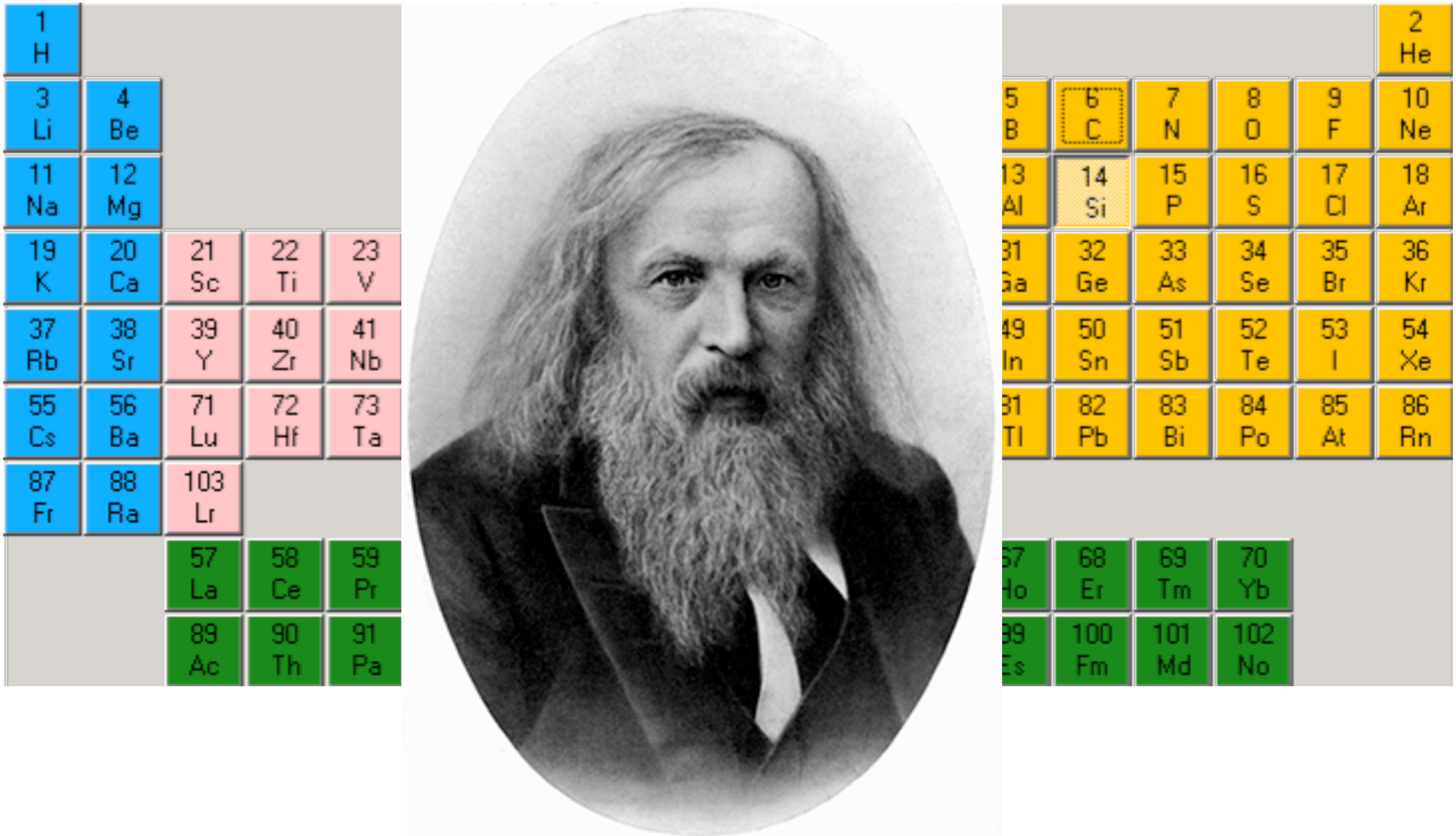
Cations and Anions

- Cations: remove electron from highest valence
  - Be : $1s^2 2s^2$
  - Be^{2+} : $1s^2$
  - Ti : $[Ar]4s^2 3d^2$
  - Ti^{2+} : $[Ar]3d^2$
- Anions: follow Building-Up Property
  - N : $1s^2 2s^2 2p^3$
  - N^{3-} : $1s^2 2s^2 2p^6$

Isoelectronic

- Atoms that have the same electron configuration
  - C^{4-}
  - N^{3-}
  - O^{2-}
  - F^{1-}
  - Ne
  - Na^{1+}
  - Mg^{2+}
  - Al^{3+}

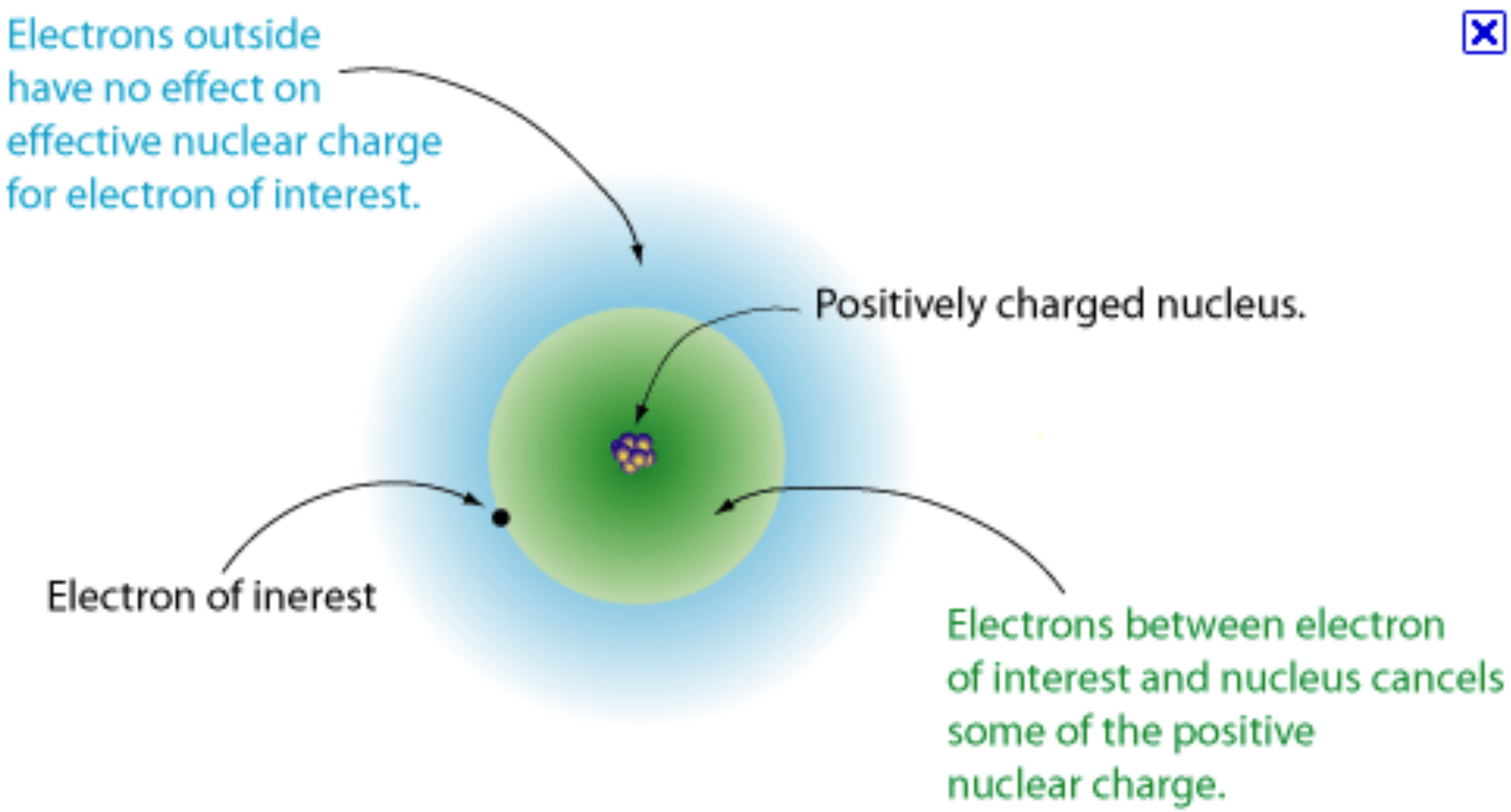
Organization of the Periodic Table



Periodicity of Atomic Properties

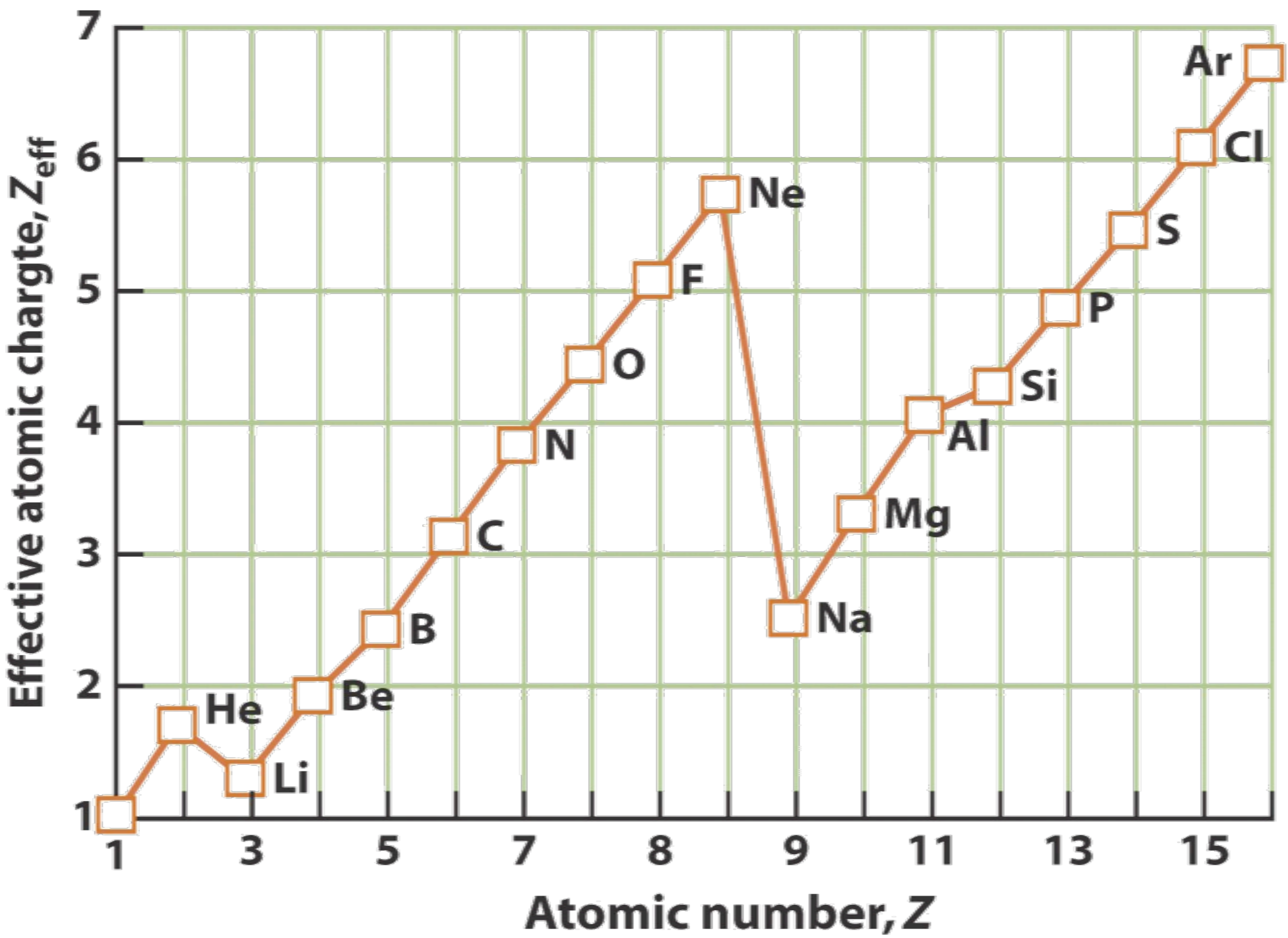
1. Atomic Radius
2. Ionic Radius
3. Ionization Energy
4. Electron Affinity

Effective Nuclear Charge



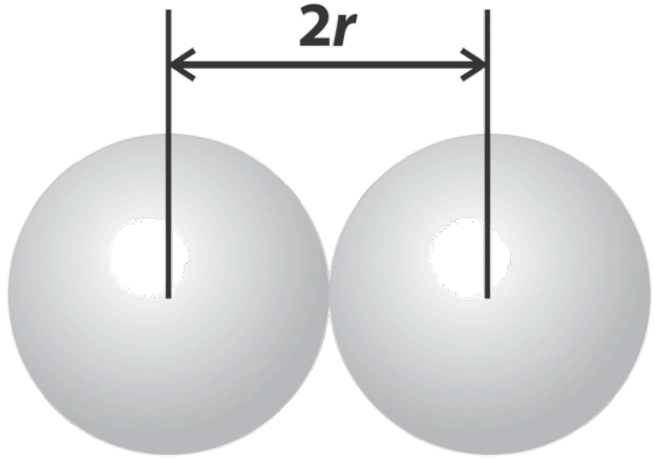
Shielded electrons do not "feel" Z, they feel $\underline{Z_{eff} < Z}$

Effective Nuclear Charge - Z_{eff}



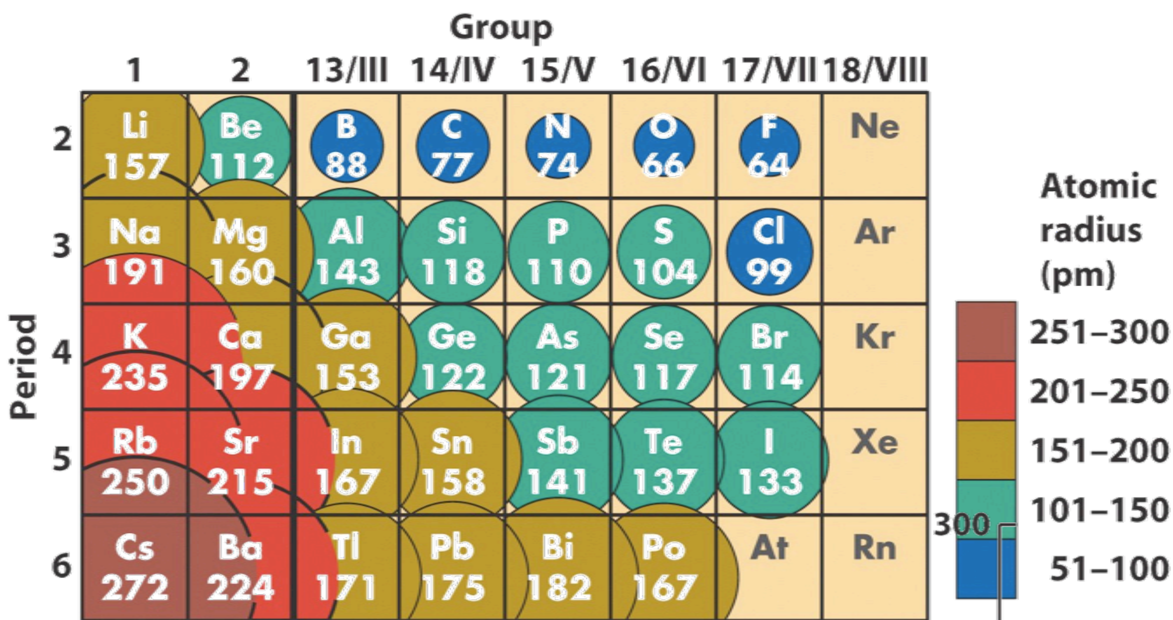
Atomic Radius

Atomic Radius – half the distance between the centers of neighboring atoms of an element



- Metals – half the nearest neighbor distance in a solid sample
- Non-metals: **Covalent radius** - half the distance between nuclei of atoms joined by chemical bond
- Noble Gas – **van der Waals radius** – half the distance between centers of neighboring atoms in a sample of solidified gas

Atomic Radius



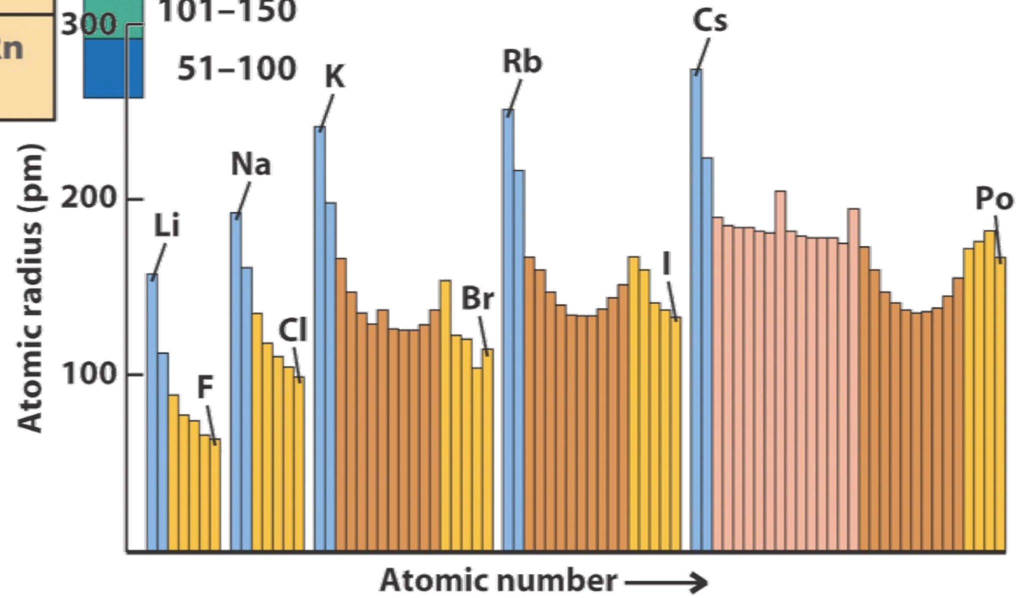
In General:

Increases as you move down the table

Decreases as you move left to right

As n increases, outermost electrons farther from nucleus

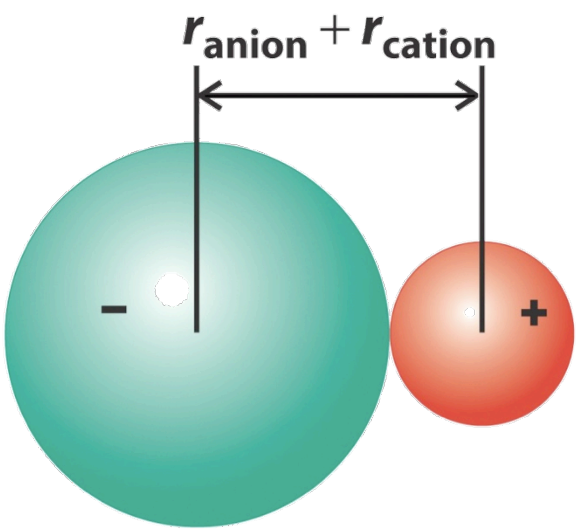
Within a period, Z_{eff} increases from left to right, nucleus pulls electrons closer

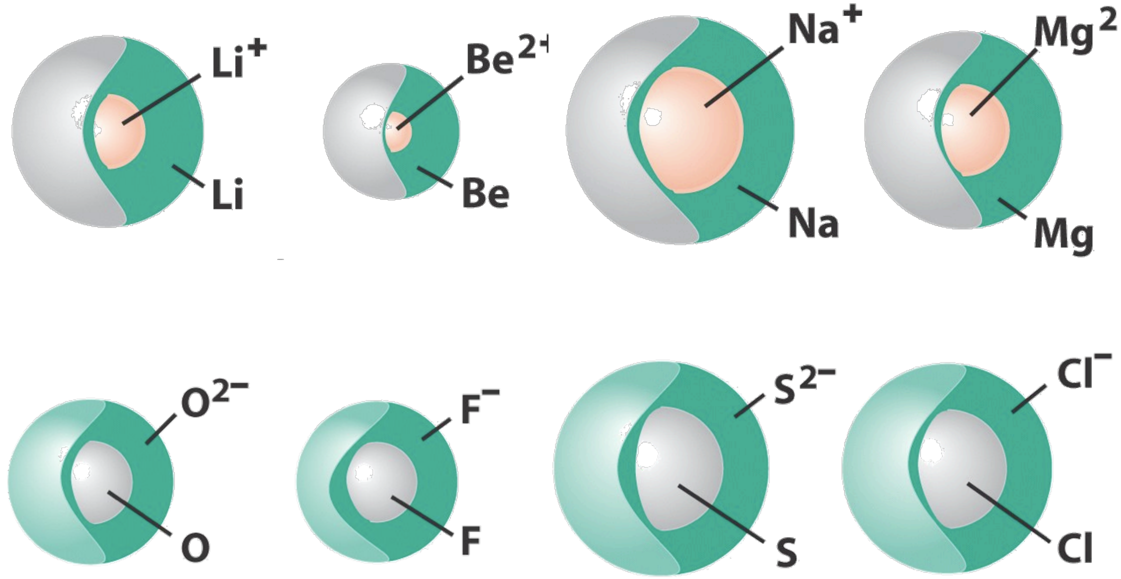


Ionic Radius

<u>Ionic Radius</u> – an ions share of the distance between neighboring ions in an ionic solid

- Values of all ions in reference to that of the oxide ion, r = 140. pm

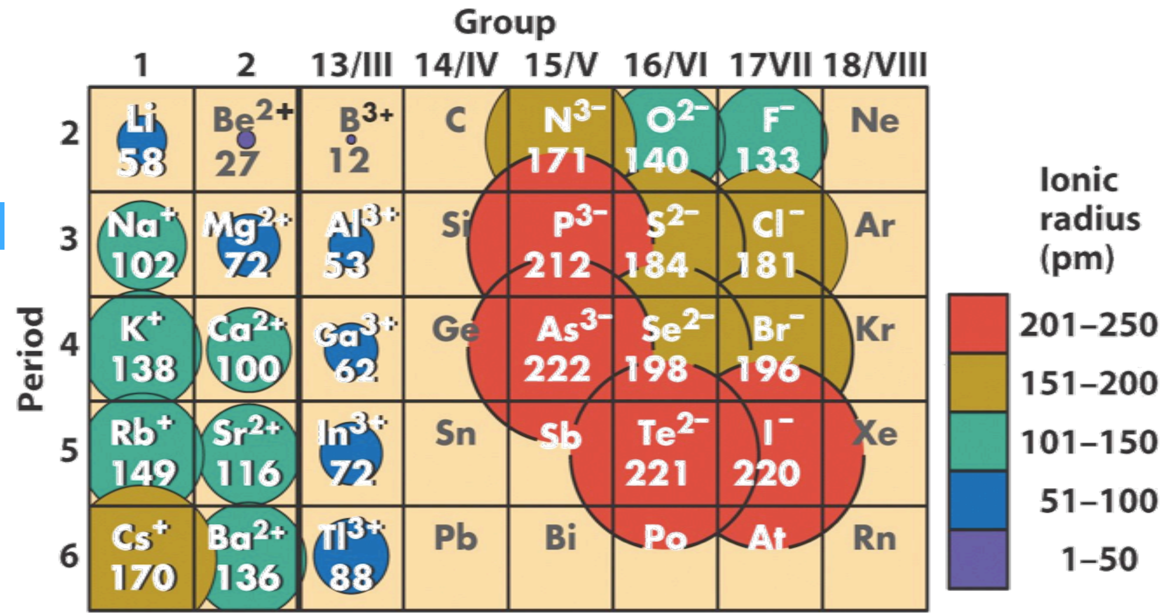




Cations (+) are always smaller than the neutral atom

Anions (-) are always larger than the neutral atom

Ionic Radius



Cations (+): always smaller than neutral atom

- As electrons are removed, core of atom is exposed
- Pull of nucleus is greater on remaining electrons

Anion (-): always larger than neutral atom

- Increased # electrons leads to greater electron-electron repulsion

Atoms and ions with same # electrons are called **isoelectronic**

- Ex. Na^+, F^- and Mg^{2+} are isoelectronic
- Radii decrease with increasing nuclear charge

Ionization Energy

Ionization Energy (I) – energy needed to remove an electron from an atom in gas phase:

$$X_{(g)} \rightarrow X^{+}_{(g)} + e^{-}_{(g)} \qquad I = E(X^{+}) - E(X)$$

1st Ionization Energy (I_1)

$$Cu_{(g)} \rightarrow Cu^{+}_{(g)} + e^{-}_{(g)} \quad I_1 = 7.73 \text{ eV}$$

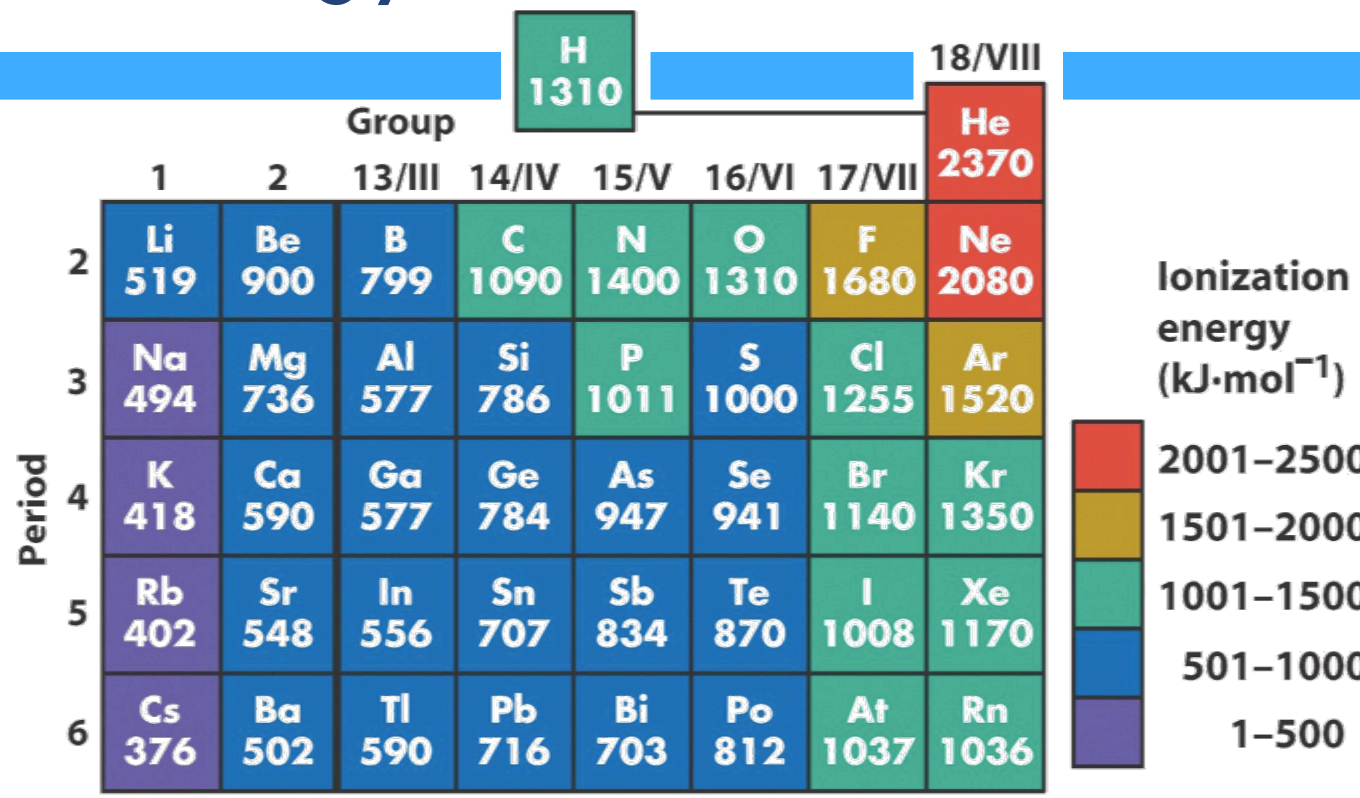
2nd Ionization Energy (I_2)

$$Cu^{+}_{(g)} \rightarrow Cu^{2+}_{(g)} + e^{-}_{(g)} \qquad I_2 = 20.29 \text{ eV}$$

Elements with low ionization energies form cations easily, conduct electricity in solid form; i.e. metals

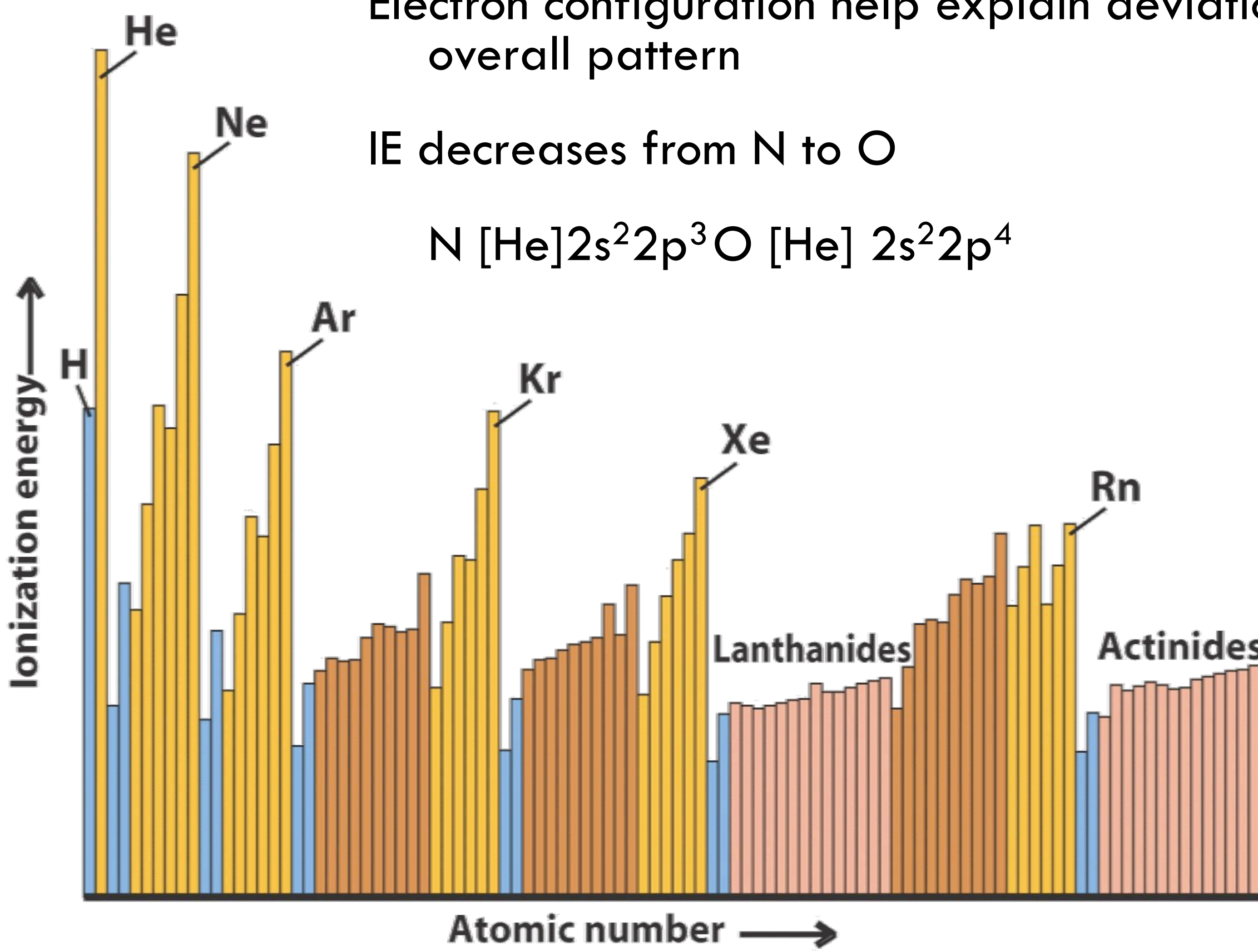
Elements with high ionization energies are unlikely to form cations and unlikely to conduct electricity

Ionization Energy



- 1^{st} IE generally decrease down a group
  - Outermost electron is further (less tightly bound) from nucleus
- 1^{st} IE generally increases from left to right across a period
  - Z_{eff} increases, gripping electrons more tightly

Ionization Energy



Electron configuration help explain deviations from overall pattern

IE decreases from N to O

N [He]$2s^2 2p^3$ O [He] $2s^2 2p^4$

Electron Affinity

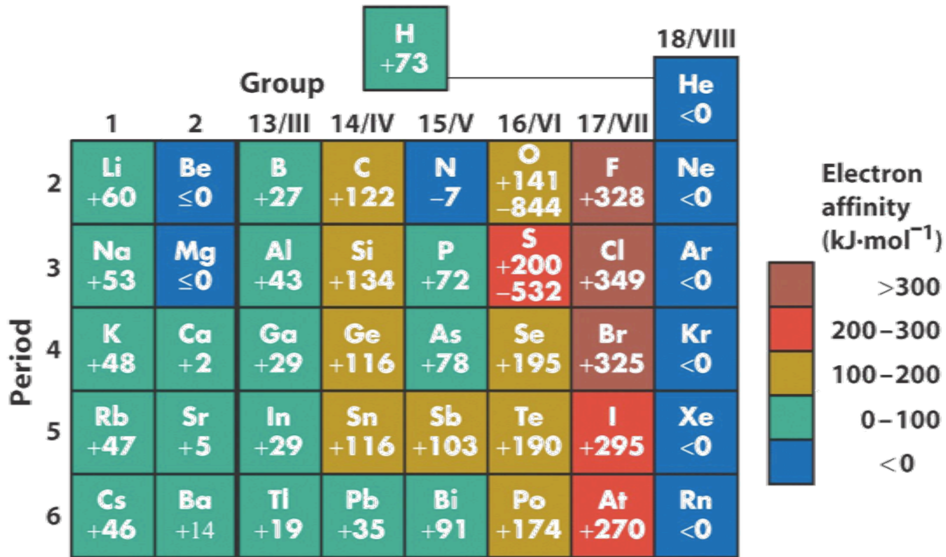
Electron Affinity (E_{ea}) – energy released when an electron is added to a gas-phase atom

$X_{(g)} \;+\; e^-_{(g)} \;\rightarrow\; X^-_{(g)}$

$E_{ea}(X) = E(X) - E(X^-)$

$Cl_{(g)} \;+\; e^-_{(g)} \;\rightarrow\; Cl^-_{(g)}$

$E_{ea} = 3.62 \text{ eV}$

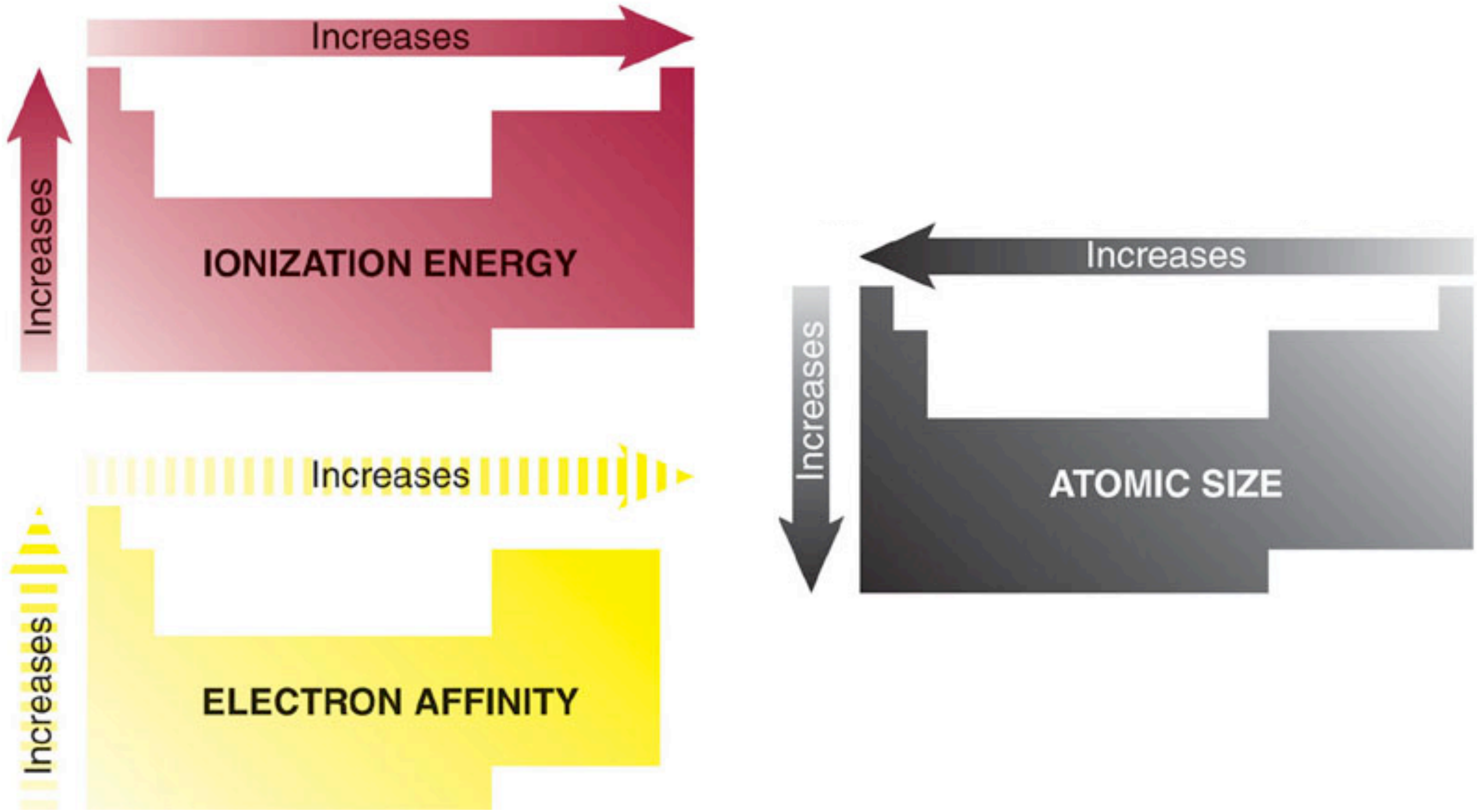


Much less periodic than the other trends

Highest towards right side of the periodic table, and most prominently towards the upper right

p orbital close to the nucleus with a high effective charge

Summary of Periodic Trends



For Next Week

- Do the assigned questions for the Ch. 2
- Read chapter 2
- Prepare for quiz on Ch. 1
- Beware “Carmageddon 2011”