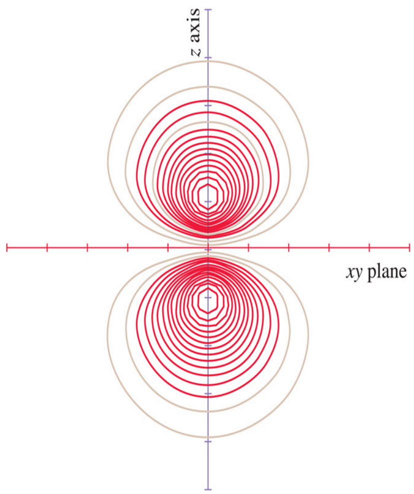
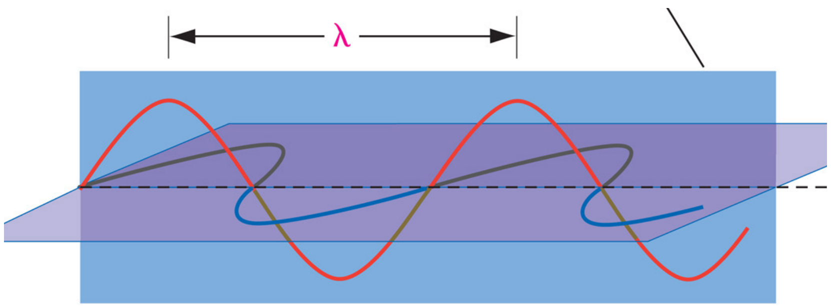
Chapter 6:
Quantum Theory and Atomic Structure





A bit of history…

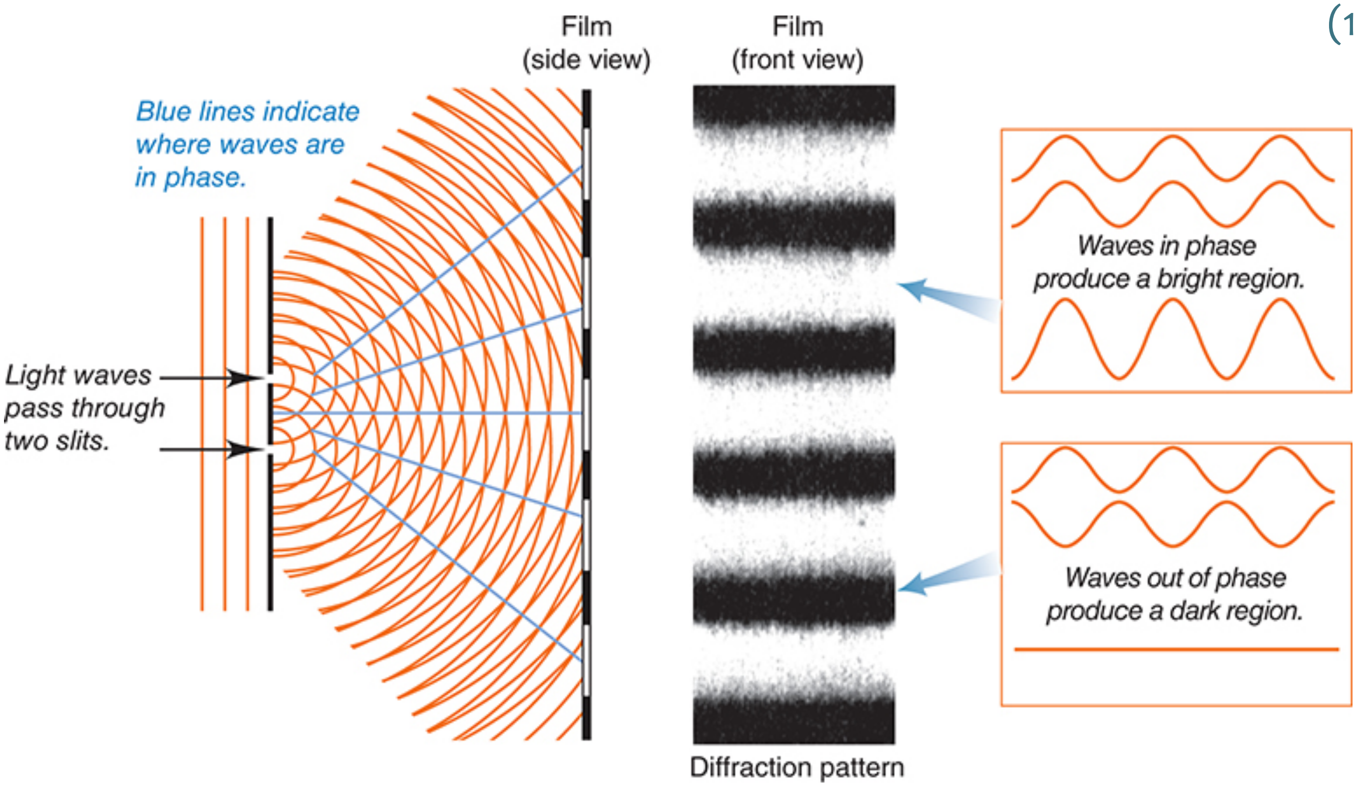
The ideas/evidence that built up to the current theory of atomic structure:

1. light is a wave
2. energy of light is proportional to its frequency
3. light is also a particle
4. atoms have discrete emission spectra
5. electron orbits are quantized

1690: Wave theory of light

- treat light mathematically as waves
- problem: waves propagate through a *medium*
- "solution": the *luminiferous aether*

Christiaan Huygens (1629 – 1695)



Wave Nature of Light

Frequency, ν ("*nu*"):

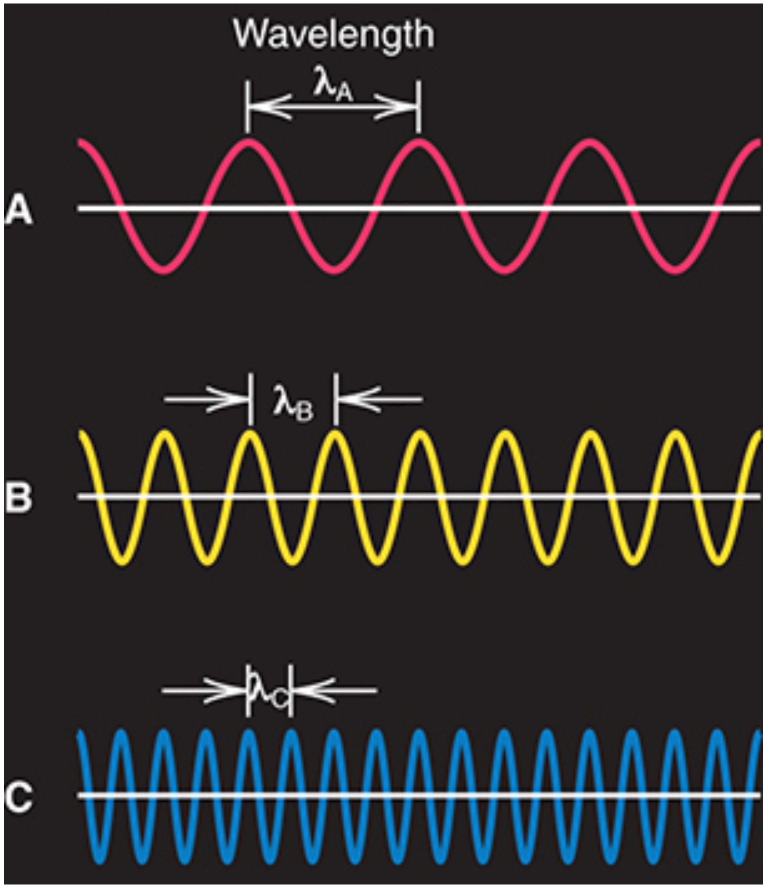
- number of waves passing a given point per second
- unit = s^{-1} (Hz)

Wavelength, λ ("*lambda*"):

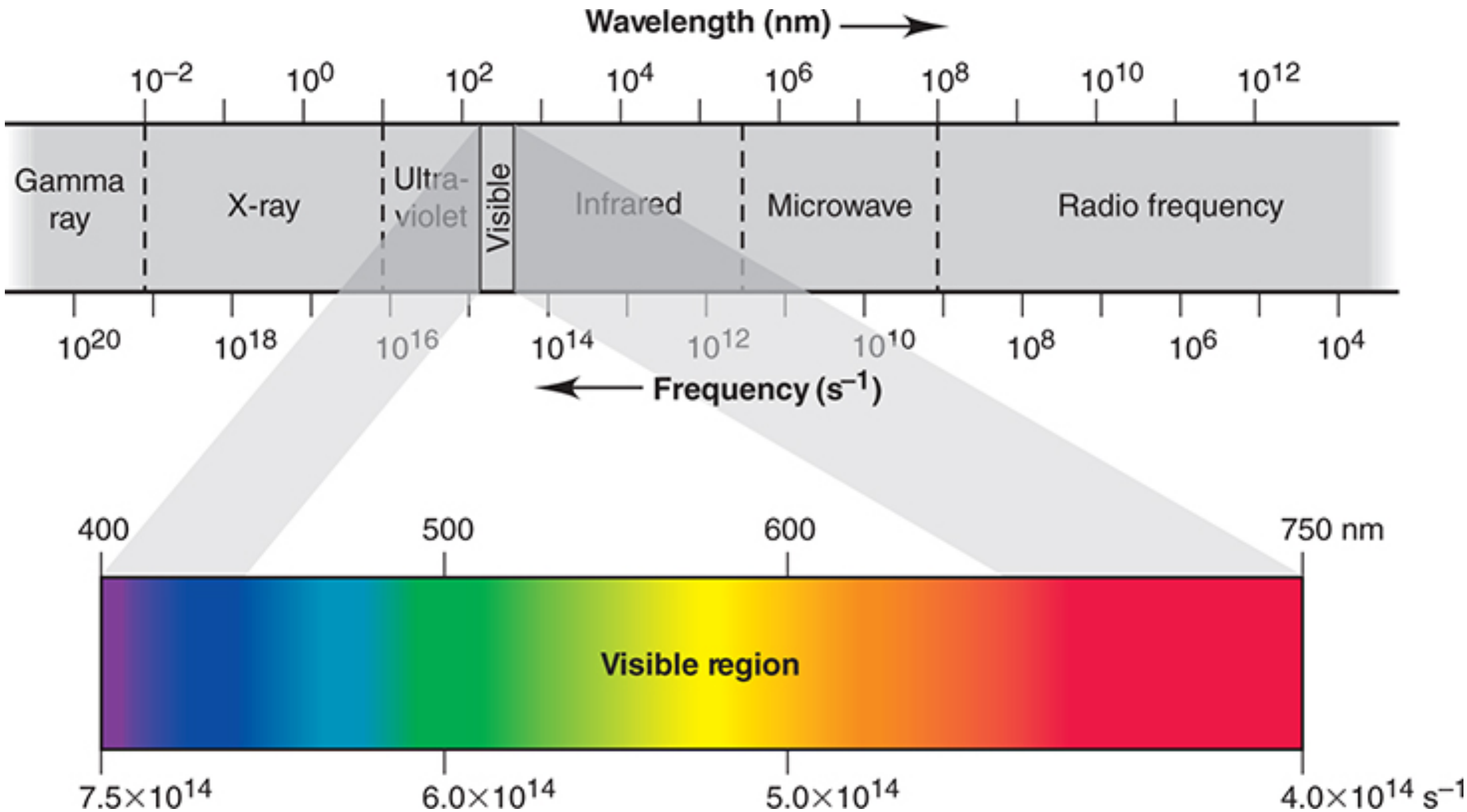
- distance between two successive crests or troughs
- unit = nm or μm

Speed, c = ν x λ

- distance travelled per unit time
- 2.998×10^{8} m/s



Electromagnetic Radiation



Your Turn…

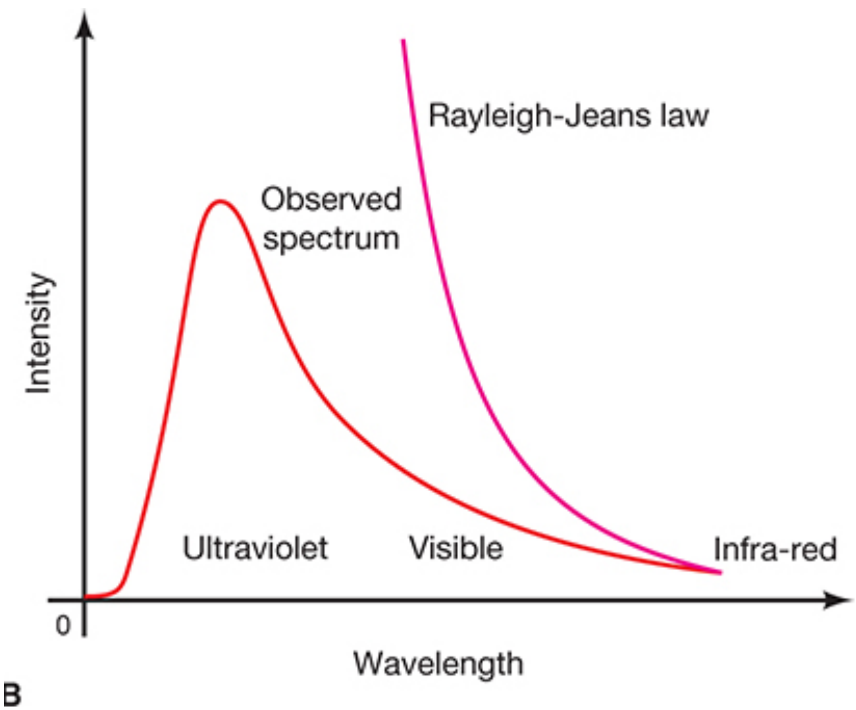
An FM station broadcasts classical music at 93.5 MHz. The corresponding wavelength in nm would be:

A) 3.2×10^{-15}
B) 3.2×10^{-9}
C) 3.2
D) 3.2×10^{9}
E) 3.2×10^{15}

1900: Blackbody radiation

Max Planck
(1858 – 1947)

- the colour of light emitted (i.e. λ) depends on temperature of object
- observed spectra could not be fitted with classical physics



Planck: Energy is *quantized*

- Energy of radiation is proportional to its frequency:

$$\Delta E = \Delta n \cdot h \cdot \nu$$

$$\Delta E = h \cdot \nu$$

- h = Planck's constant = 6.6262×10^{-34} J • s
- Planck won the Nobel Prize 1918

Back to wave theory…

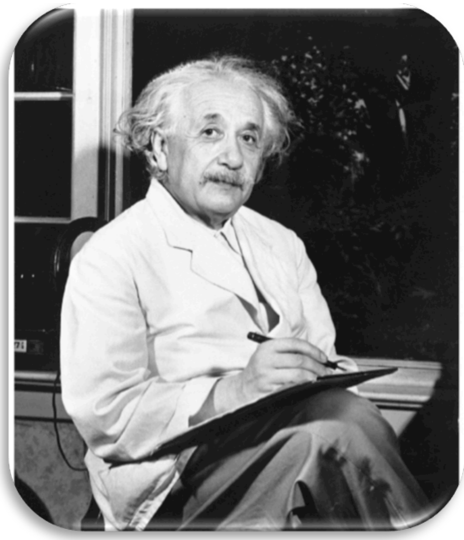
$$\Delta E = \frac{hc}{\lambda} = h\nu$$

Light with <u>long</u> λ (small ν) has a ________ E.

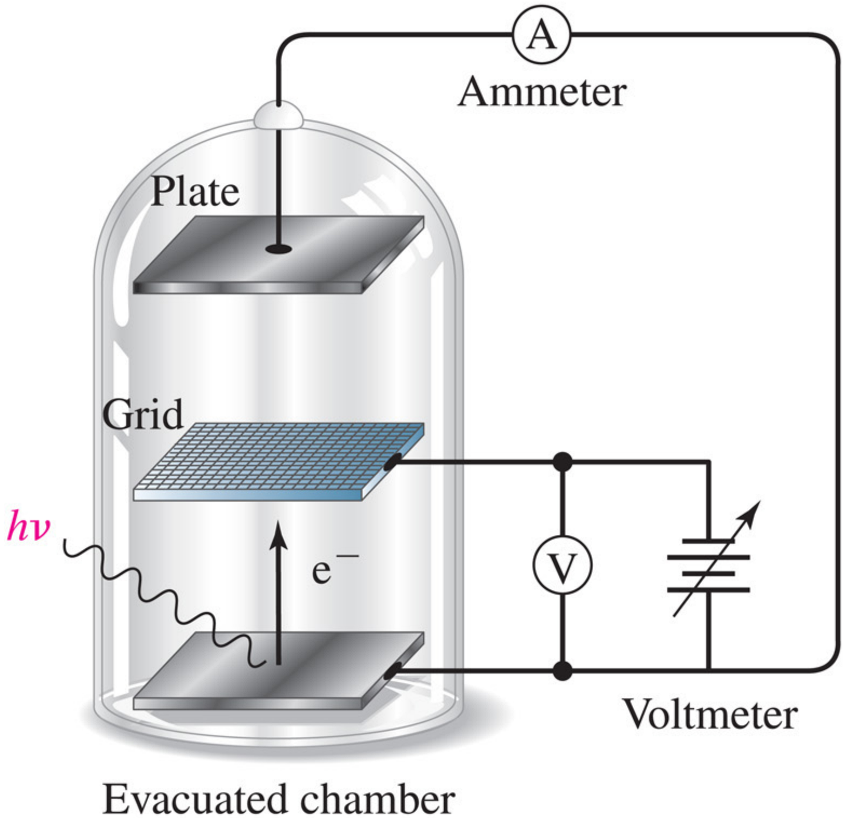
Light with <u>short</u> λ (large ν) has a _________ E.

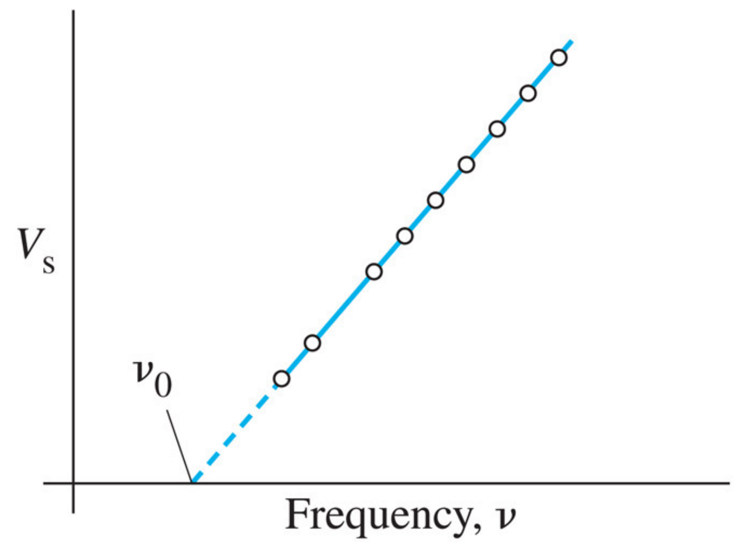
Light behaves like a wave, but its energy is quantized!

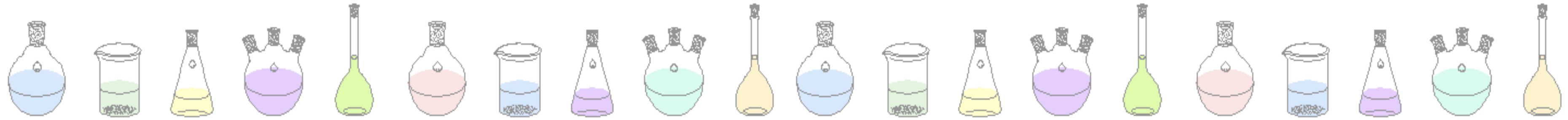
1905: Photoelectric Effect



Albert Einstein
(1879-1955)





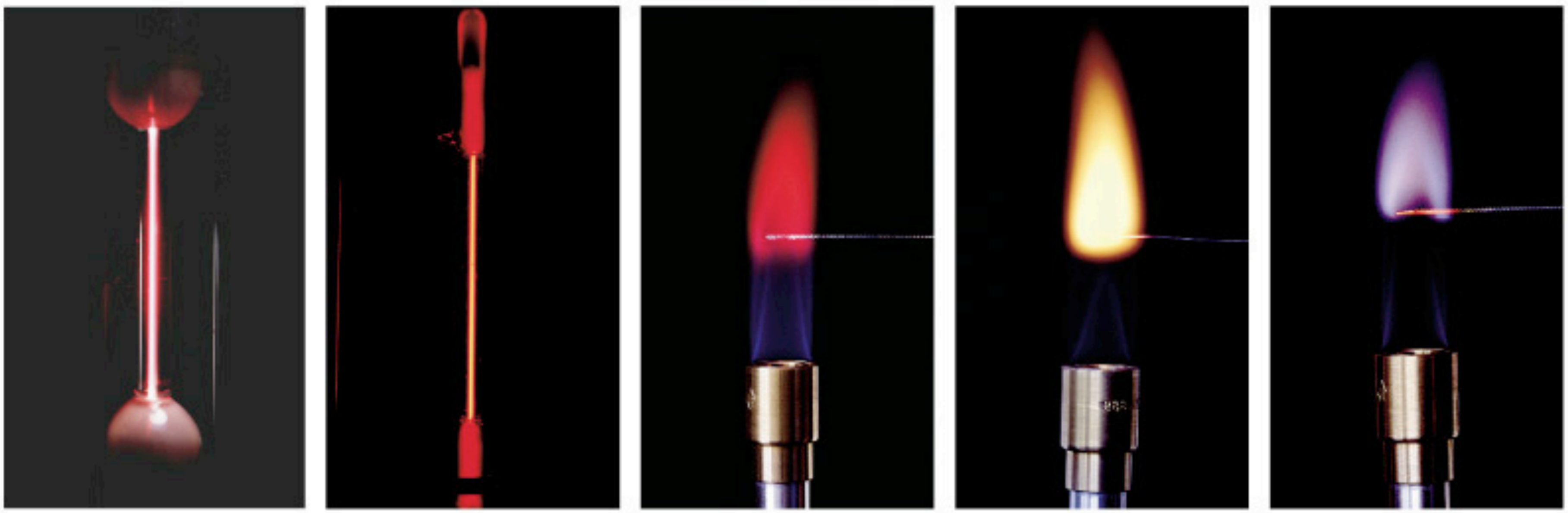


Photoelectric Effect

- Einstein: experimental observations make sense if light consists of particles called photons of discrete energy.

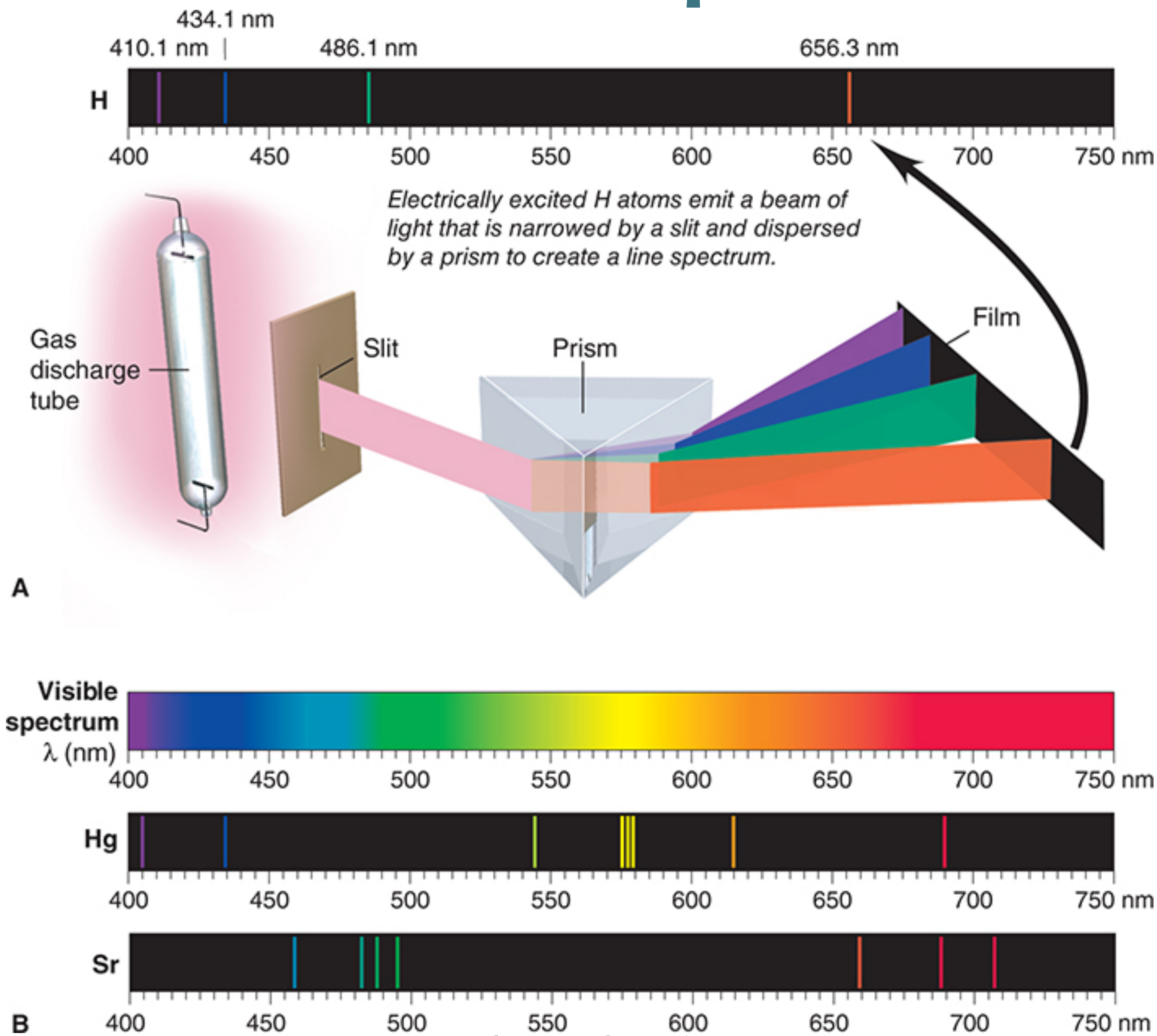
In other words, light is both a wave *and* a particle!

1752: Atomic Spectra

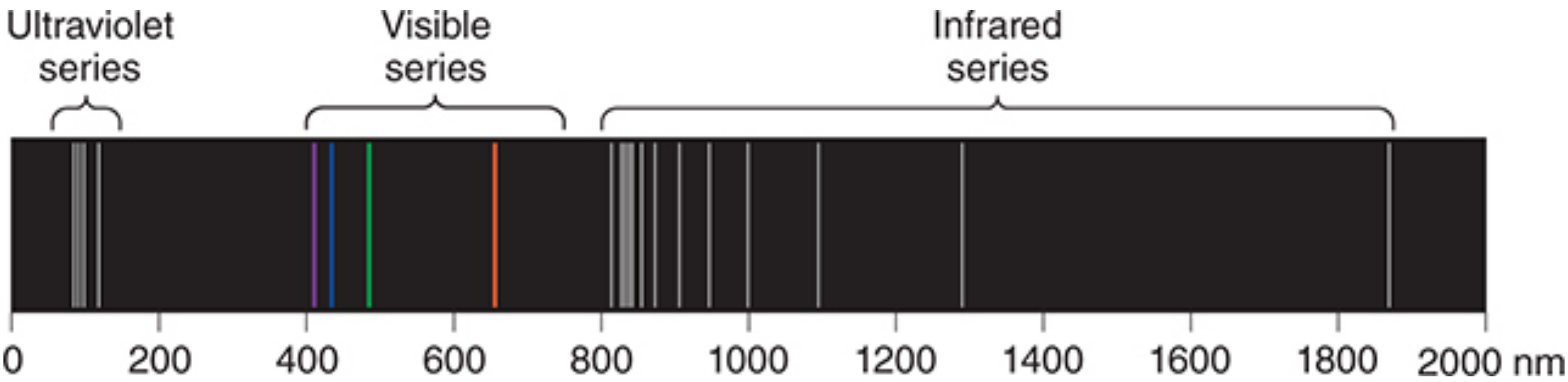


(a) (b) (c) (d) (e)

Emission Spectra



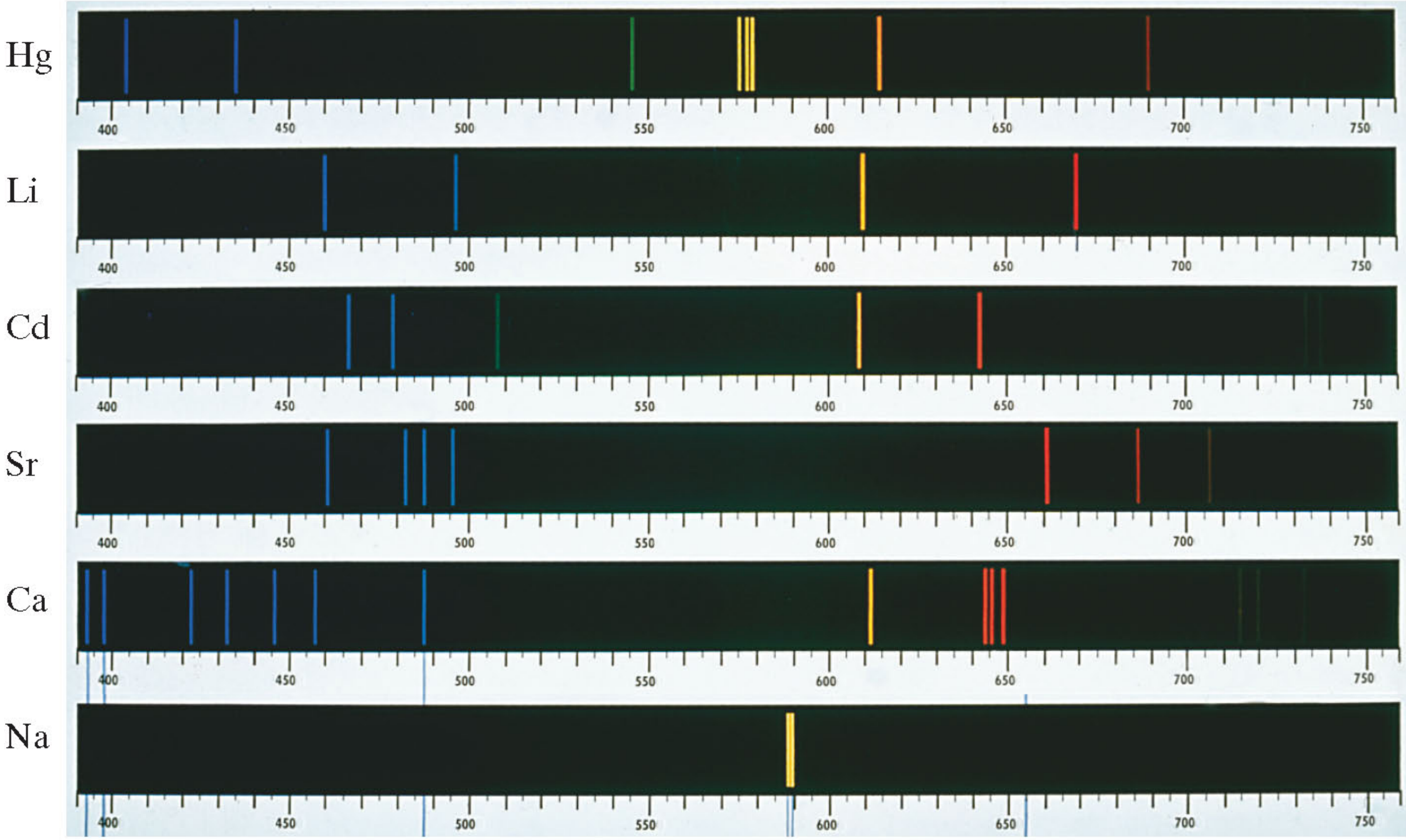
Line Spectrum of Hydrogen



High E
Short λ
High ν

Low E
Long λ
Low ν

Every atom has a unique line spectrum…



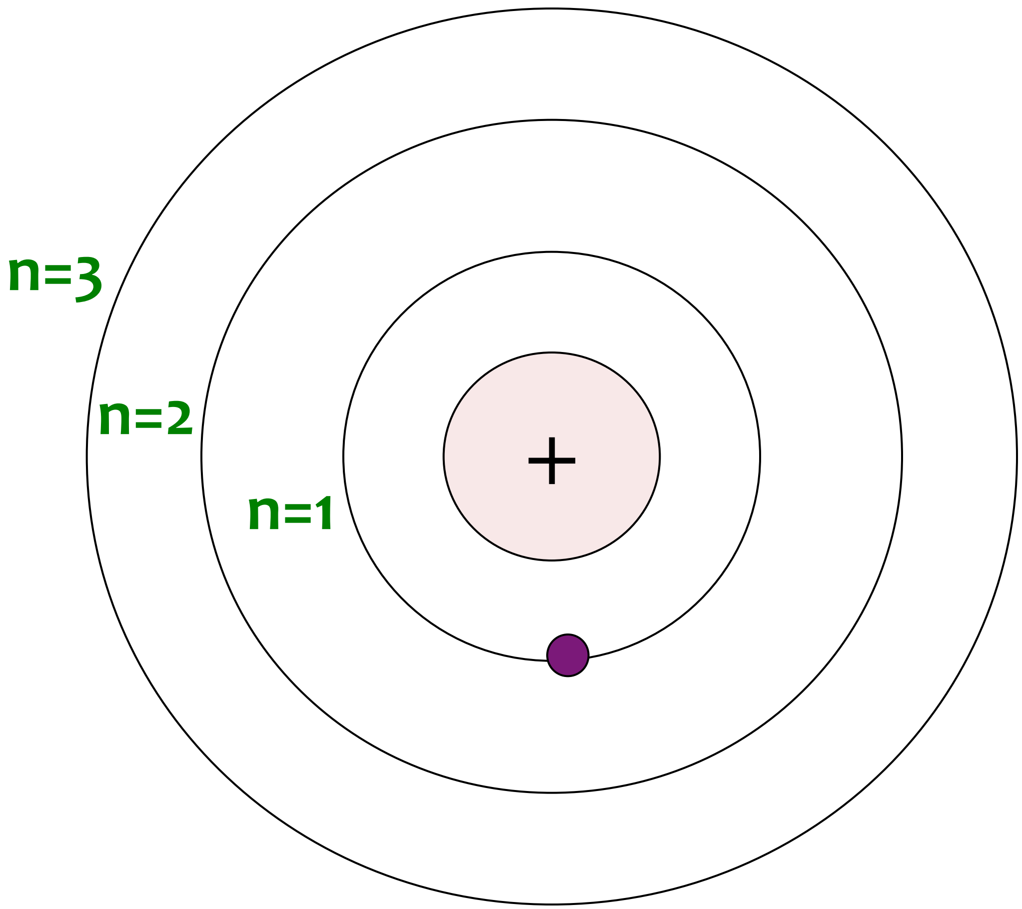
Atomic Spectra

- It took about 150 years to explain the line spectra of elements. The main scientific contributions were:

    1) Niels Bohr (quantization)
    2) Louis de Broglie (wave-particle duality)
    3) Erwin Schrödinger (Schrödinger equation)
    4) Heisenberg (uncertainty principle)

- By seeking to explain the atomic spectra, a whole new perspective on atomic structure was developed!

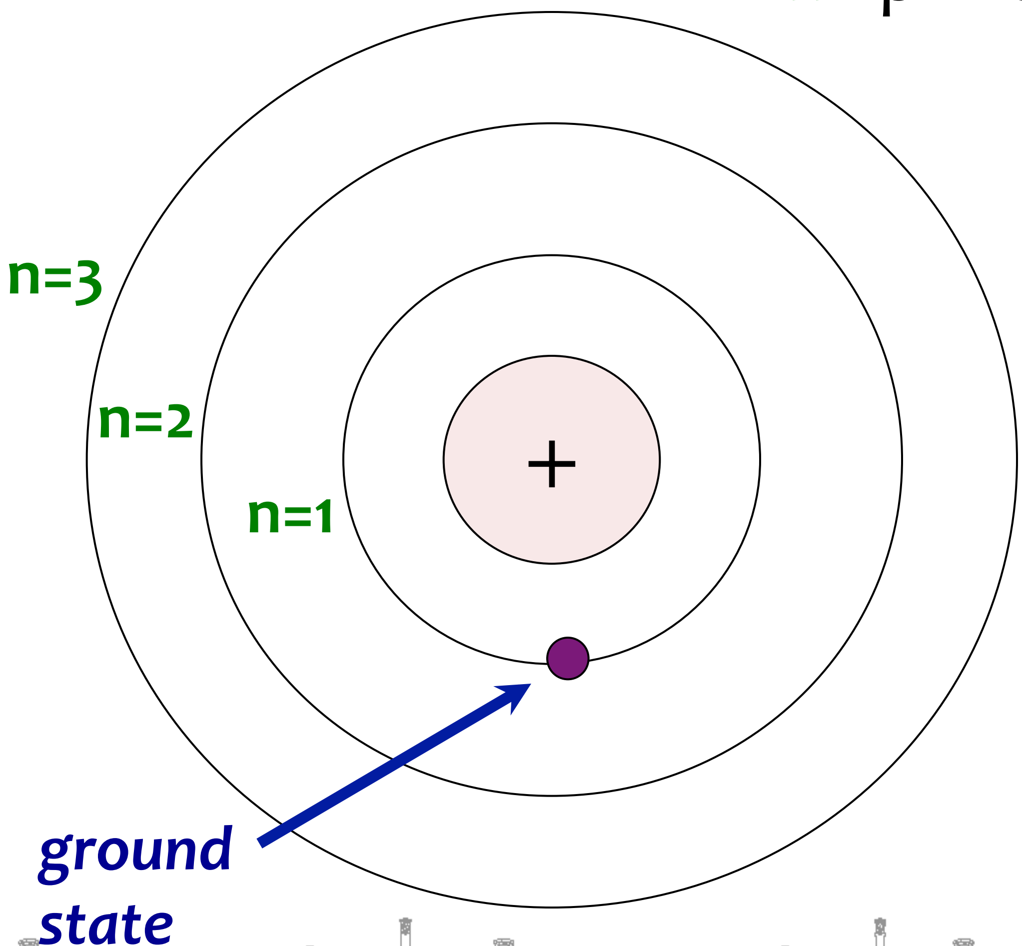
1913: The Bohr Model of the Atom



Niels Bohr
(1885-1962)

Electron orbits cannot just take any value; instead they are "quantized"; only certain orbits, defined by a whole number ***n*** are permitted

The Bohr Model of the Atom



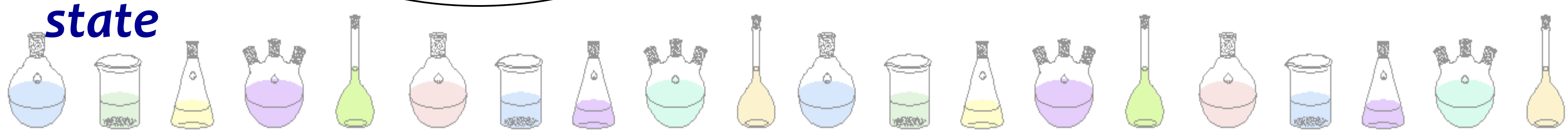
n: principal quantum number

_______ corresponds to the lowest energy state or the *ground state*

ground state

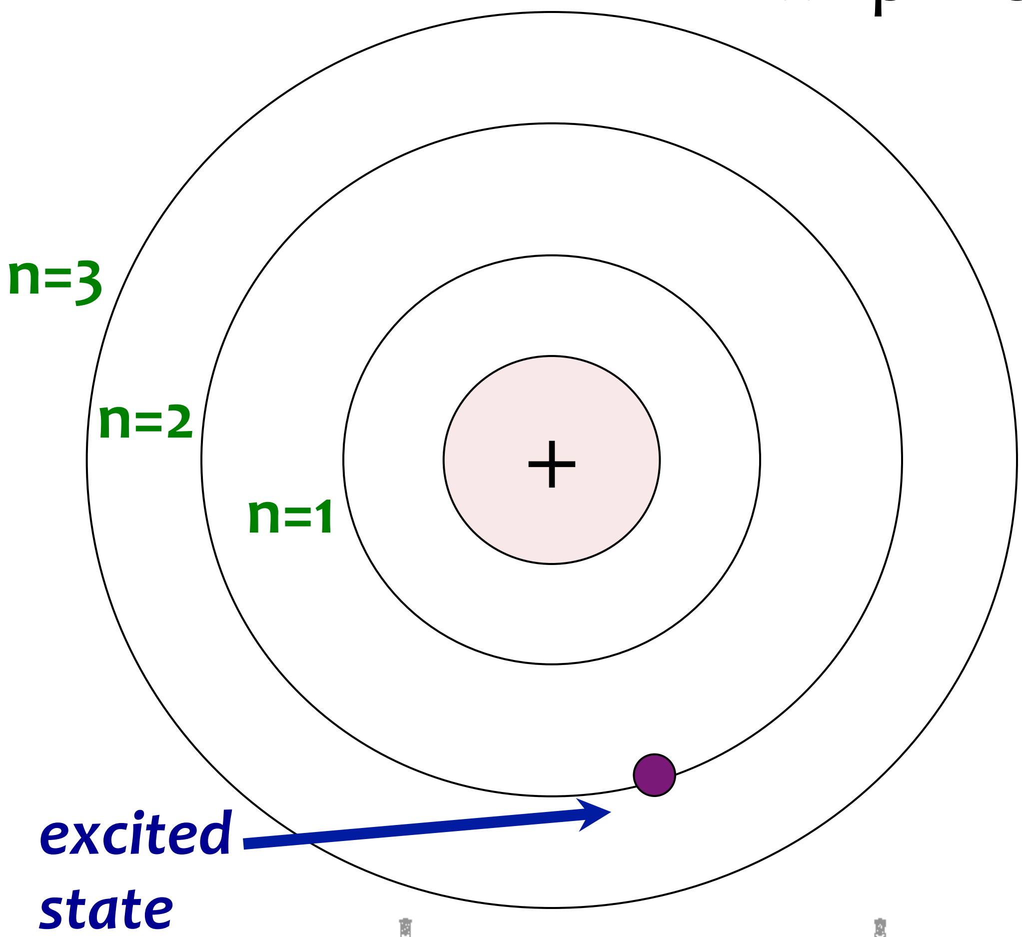
=

the most stable state



The Bohr Model of the Atom

n: principal quantum number



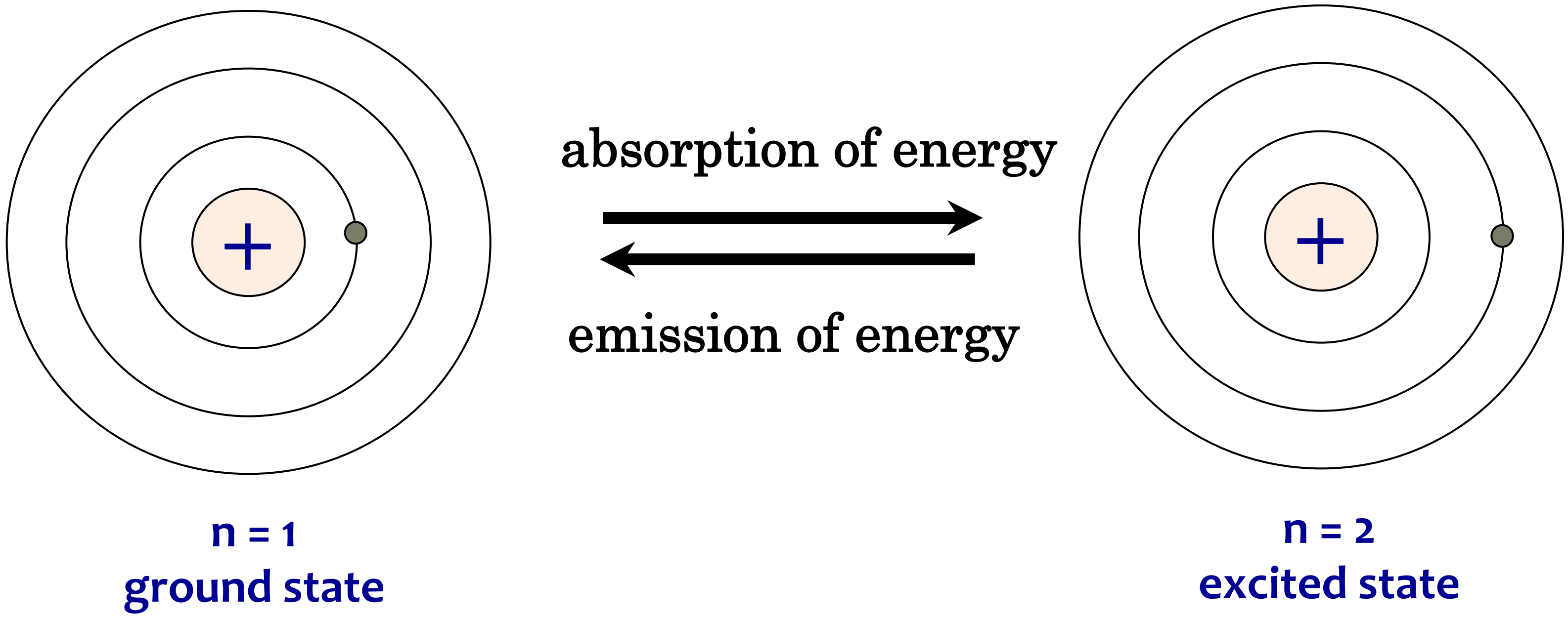
________ corresponds to a higher energy state or an *excited state*

excited state

=

less stable state

Bohr's Explanation



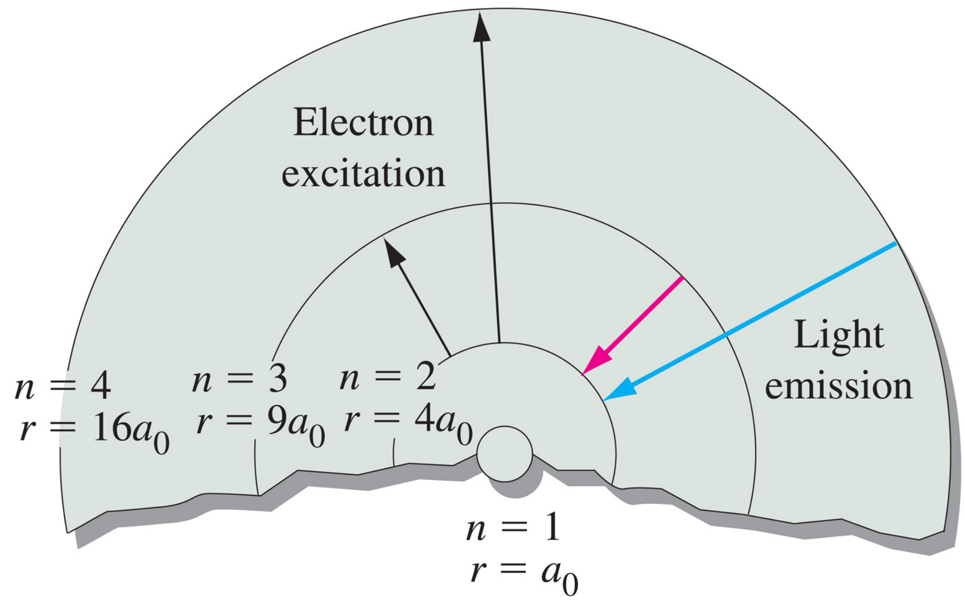
1. When an atom absorbs energy, an electron jumps from the ground state to an excited state.

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

The Bohr Model of the Atom

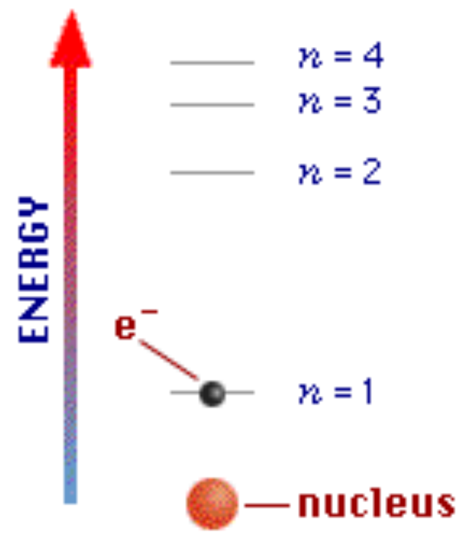
- each orbit is assigned a principal quantum number, which is a whole positive number (n = 1, 2, 3, …)
- the energy associated with each orbit is defined as:

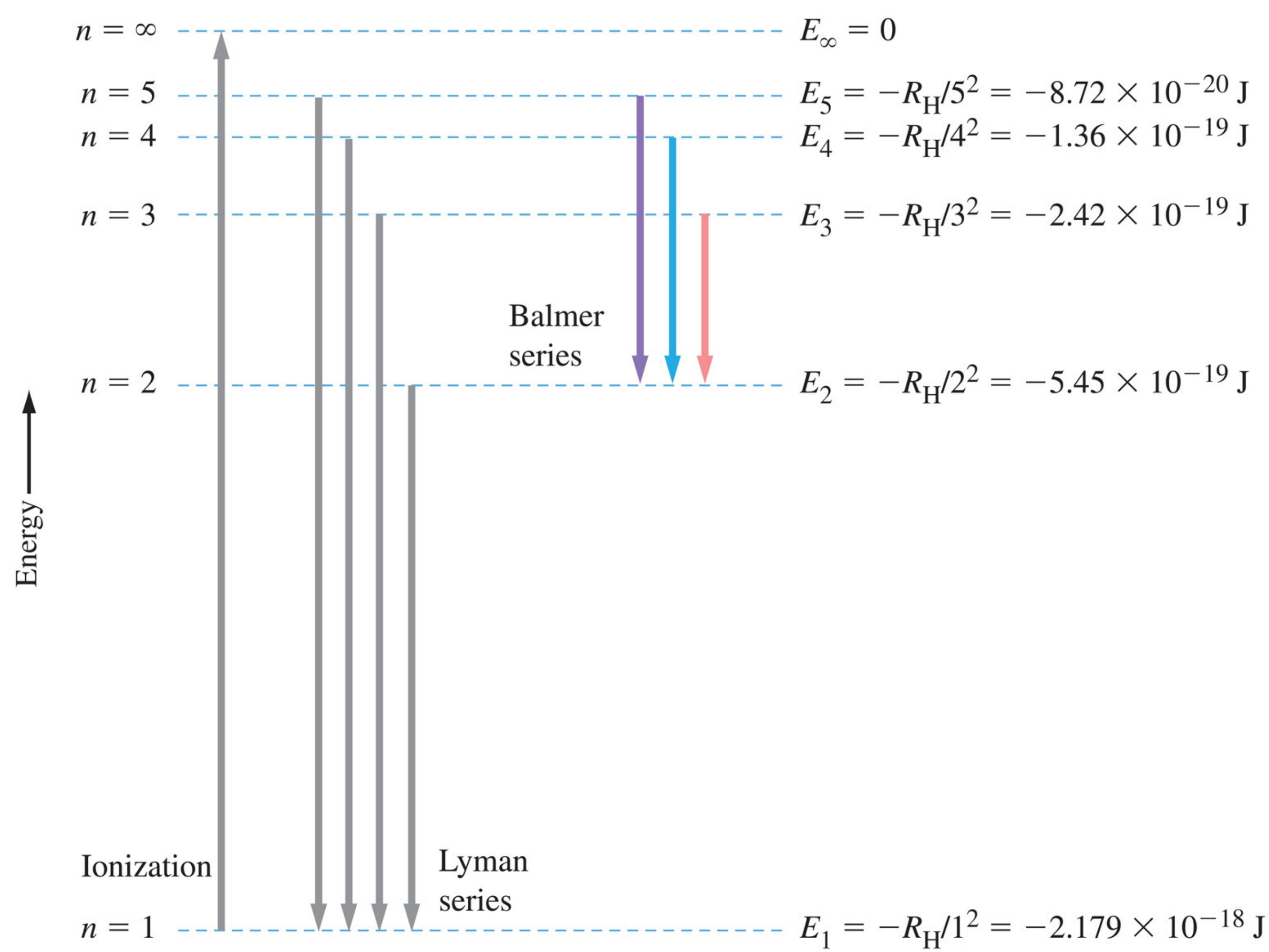
$$E_n = -\frac{R_H}{n^2}$$



- where $R_H = 2.18 \times 10^{-18}$ J

The Bohr Model of the Atom





The Bohr Model of the Atom

- every time the atom absorbs or emits light, an electron moves from one orbital (n_i) to another (n_f)
- the energy of the absorbed or emitted photon is **hν**
- the Bohr equation explains the Lyman, Balmer, Paschen, and Brackett series of lines in the hydrogen spectrum

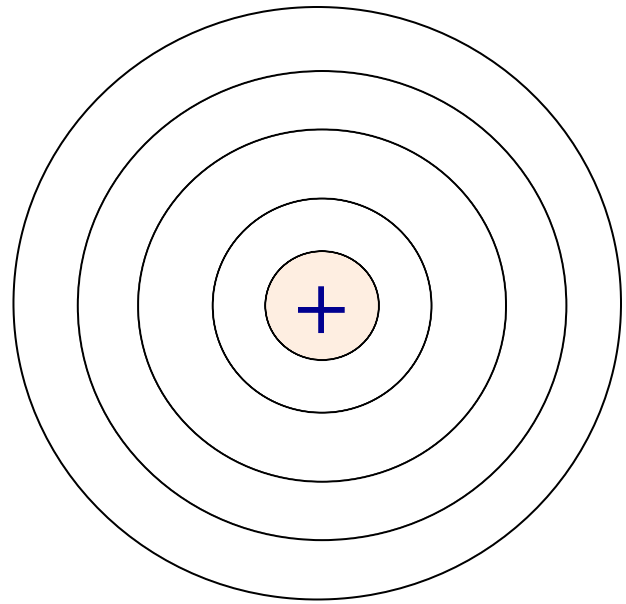
$$\Delta E = E_f - E_i = \left(\frac{-R_H}{n_f^2}\right) - \left(\frac{-R_H}{n_i^2}\right)$$

$$\Delta E = R_H \left(1/n_i^2 - 1/n_f^2 \right)$$

$$\Delta E = h\nu = R_H \left(1/n_i^2 - 1/n_f^2 \right)$$

Your Turn…

For the Bohr Atom shown, what electronic transition would correspond to the **emission** of a photon with the **shortest** wavelength? Answer using a two-digit number to represent the transition. (Ex. n = 0 to n = 1: answer 01)



Atomic Line Spectra and Niels Bohr

- Bohr's theory was a great accomplishment, and he won the Nobel Prize in 1922
- BUT: there was a problem: the theory **only worked for H!**
- Model had to be modified to work for all other elements

…Quantum Mechanics!

1924: Wave-Particle Duality of Electrons

Louis de Broglie
1892 – 1987

- proposed that all moving objects have wave properties
- for light: $E = mc^2$ and $E = hc/\lambda$
- therefore, $mc = h/\lambda$, or:

$$\lambda = h/mv$$

- thus, electrons (and all objects!) can be treated as both a wave and a particle

1926: Birth of Quantum Mechanics

E. Schrodinger
1887-1961

- mathematically treat e^- as waves
- developed the WAVE EQUATION
- Solution to wave equation gives set of mathematical expressions called

WAVE FUNCTIONS, Ψ

- Each describes an allowed energy state of an e^-
- Quantization introduced naturally

WAVE FUNCTIONS, Ψ

- each Ψ corresponds to an ORBITAL — the region of space within which an electron is found.
- Ψ does NOT describe the exact location of the electron.
- $\mathbf{\Psi^2}$ is proportional to the **probability of finding an electron** at a given point.

Wave Functions and QUANTUM NUMBERS

- Each orbital is a function of 3 quantum numbers: n, ℓ, and m_ℓ
- Electrons are arranged in shells and subshells.
  - n → shell
  - ℓ → subshell
  - m_ℓ → designates an orbital within a subshell

Quantum Numbers

$$\Psi = \mathrm{f}(n, \ell, m_\ell)$$

n principal quantum number (energy and size)

ℓ angular momentum q. number (shape)

m_ℓ magnetic quantum number (orientation)

Only specific values of n, ℓ, and m_l are allowed

(i.e. electronic states are *quantified!*)

Quantum Numbers: the Rules

Quantum Number	Values	Description
n	1, 2, 3, 4…	energy and size of the orbital
ℓ	0 to $n - 1$	shape of the orbital, number of nodes
m_ℓ	$-\ell$ to $+\ell$	number and orientation of the orbitals in the subshell

Quantum Numbers

TABLE 6.2 The Hierarchy of Quantum Numbers for Atomic Orbitals

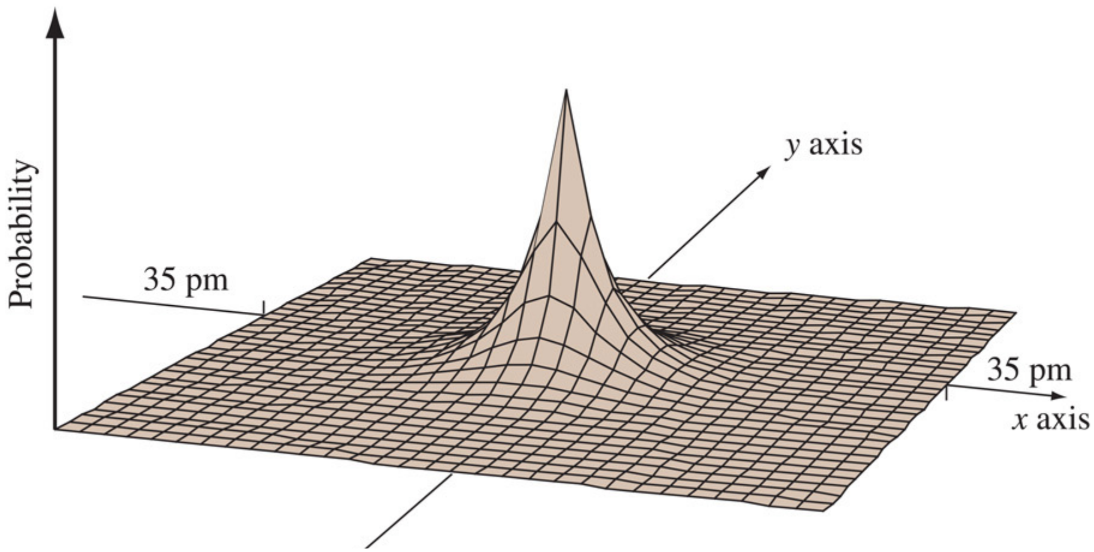
Name, Symbol (Property)	Allowed Values	Quantum Numbers		
Principal, n (size, energy)	Positive integer (1, 2, 3, . . .)	1	2	3
Angular momentum, l (shape)	0 to $n - 1$	0	0, 1	0, 1, 2
Magnetic, m_l (orientation)	$-l, \ldots, 0, \ldots, +l$	0	0; −1 0 +1	0; −1 0 +1; −2 −1 0 +1 +2

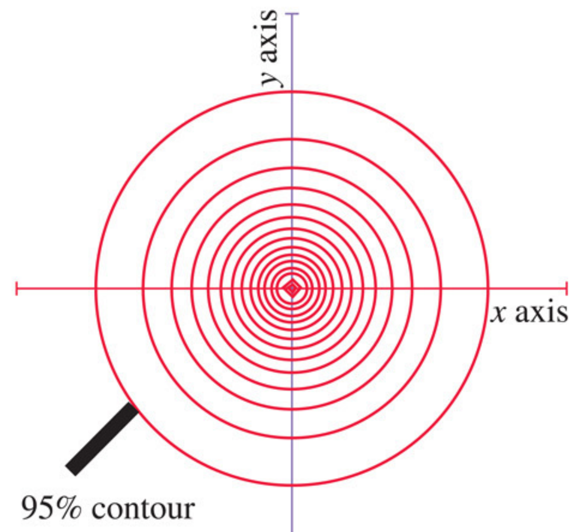
Shells and Subshells

- When n = 1, then ℓ = 0 and m_ℓ = 0
- Therefore, in n = 1, there is 1 type of subshell and that subshell has a single orbital (m_ℓ has a single value → 1 orbital)
- This subshell is labeled ____
- Each shell has 1 orbital labeled s, and it is **SPHERICAL** in shape.

s Orbitals

- All s orbitals are spherical in shape





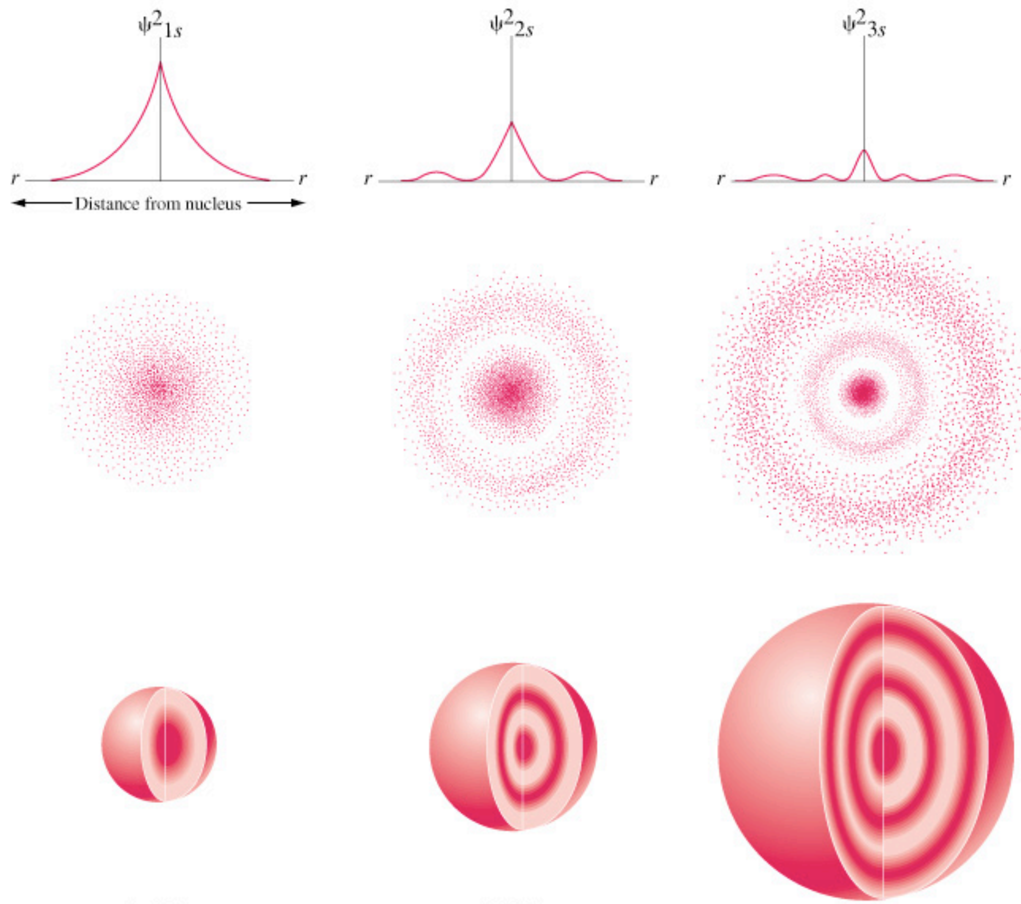
s Orbitals

n = 1 **n = 2** **n = 3**

Ψ^2 = Probability

2-D Dot Picture

3-D Picture



(a) 1s (b) 2s (c) 3s

p Orbitals

When n = 2, then ℓ = 0 and 1

- Therefore, in n = 2 shell there are 2 types of orbitals → 2 subshells

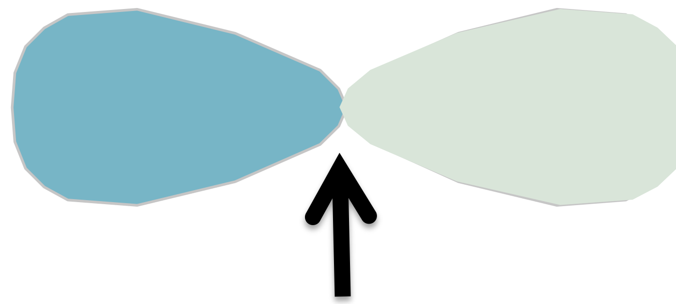
- For $\ell = 0$ $m_\ell = 0$

  this is a **s** subshell

- For $\ell = 1$ $m_\ell = -1, 0, +1$

  this is a ____ subshell with 3 orbitals

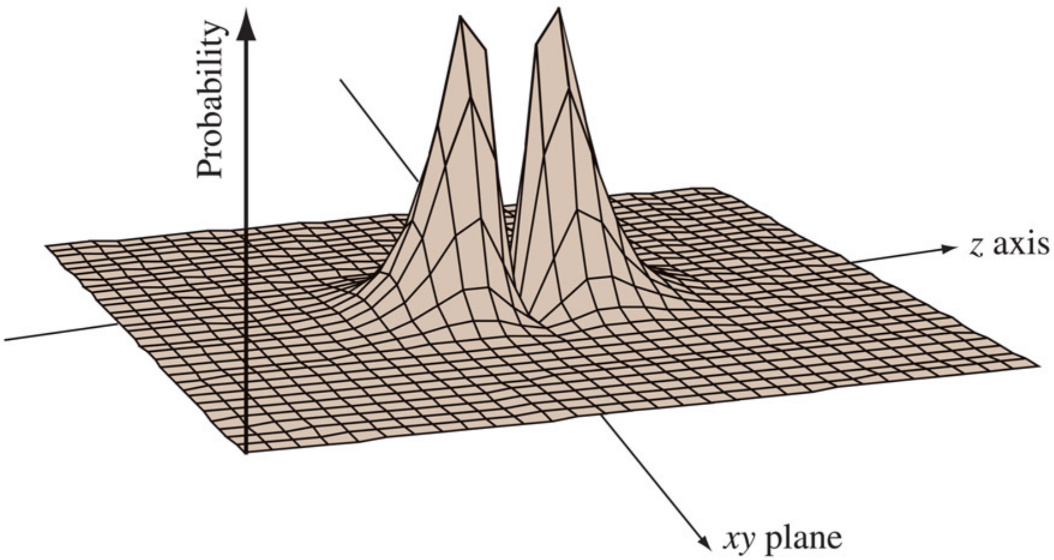
Typical p orbital

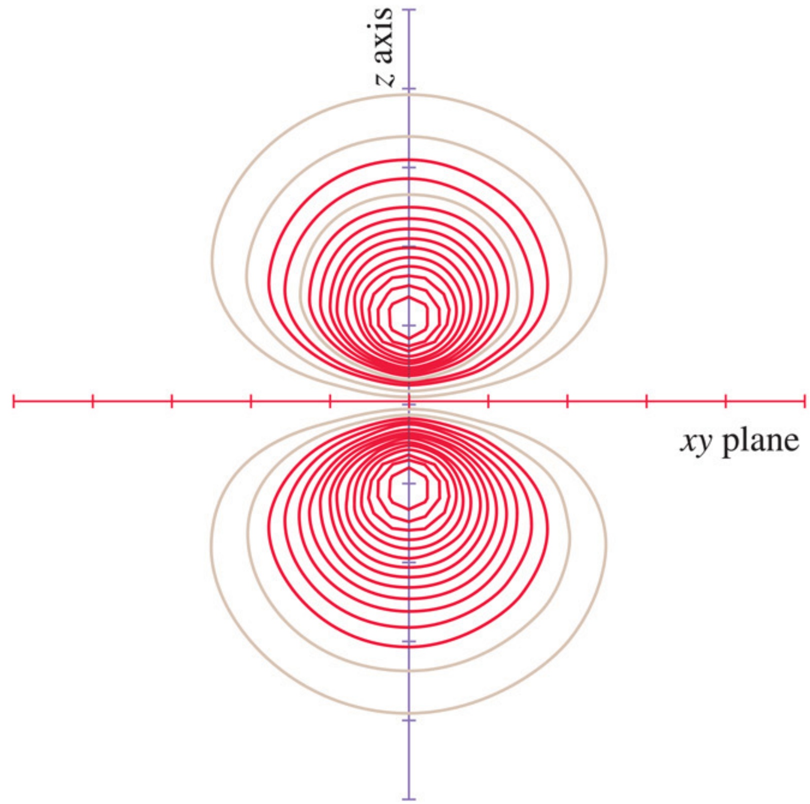


planar node

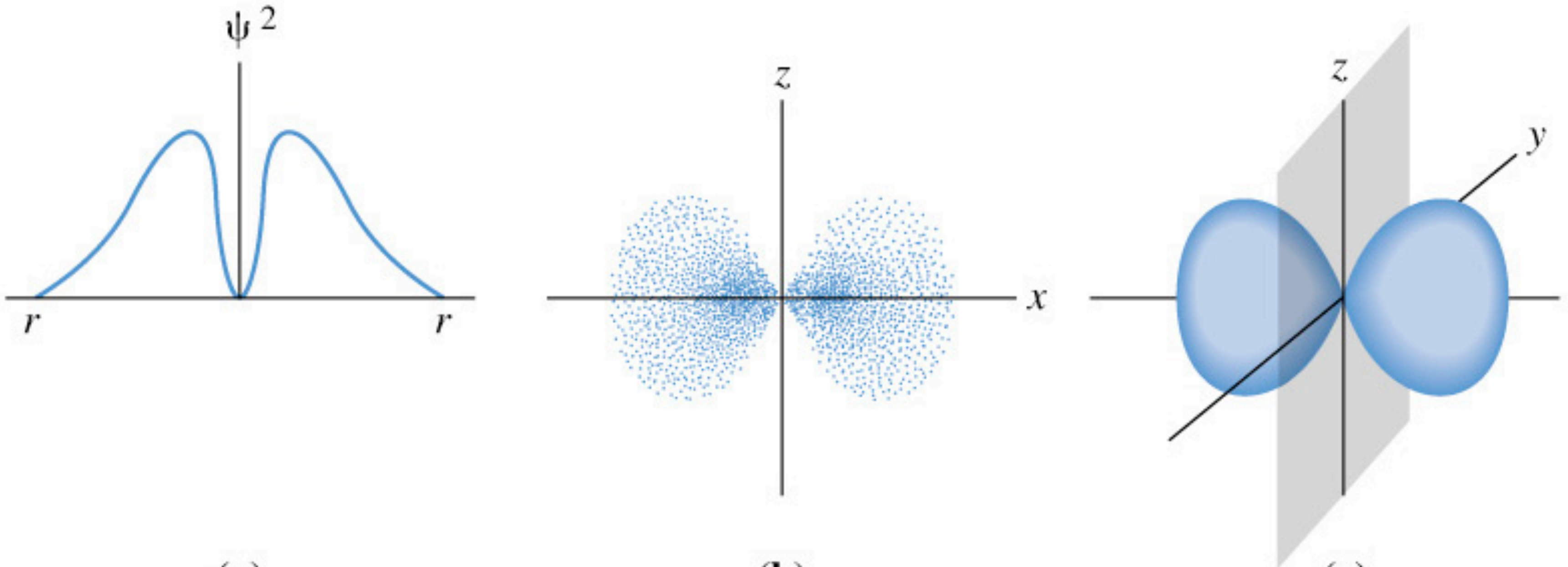
When ℓ = 1, there is a PLANAR NODE through the nucleus.

p Orbitals



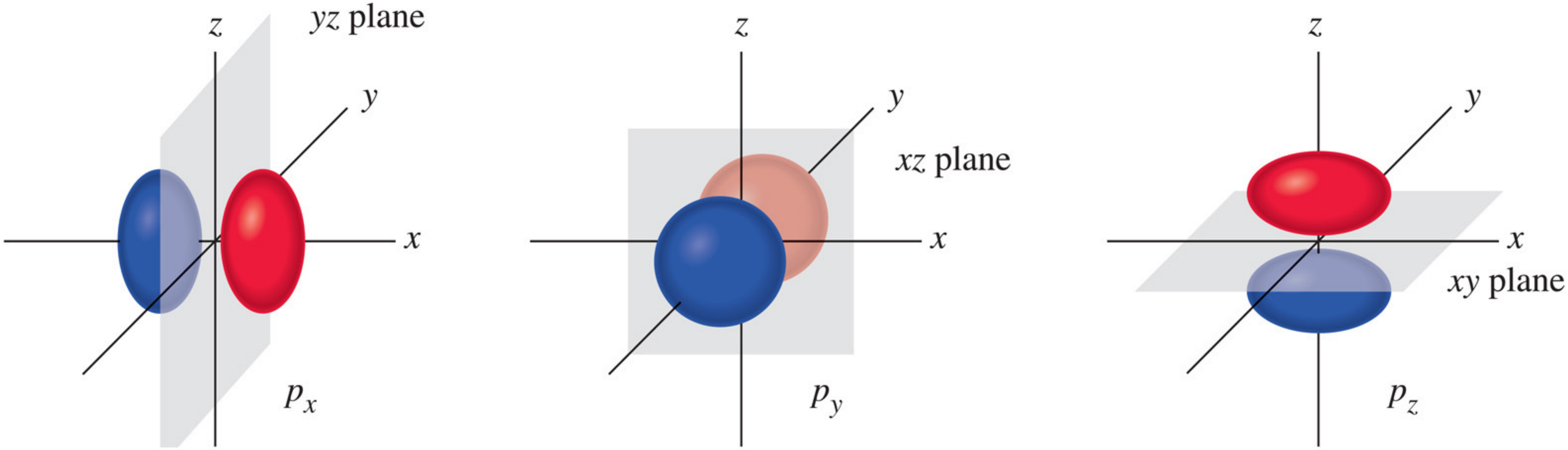


p Orbitals

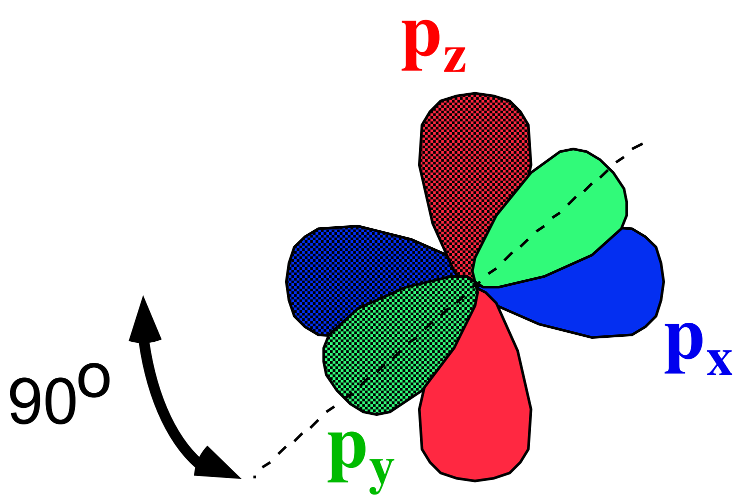


(a) (b) (c)

p Orbitals
Three orientations



p Orbitals



The three p orbitals lie 90^o apart in space

d Orbitals

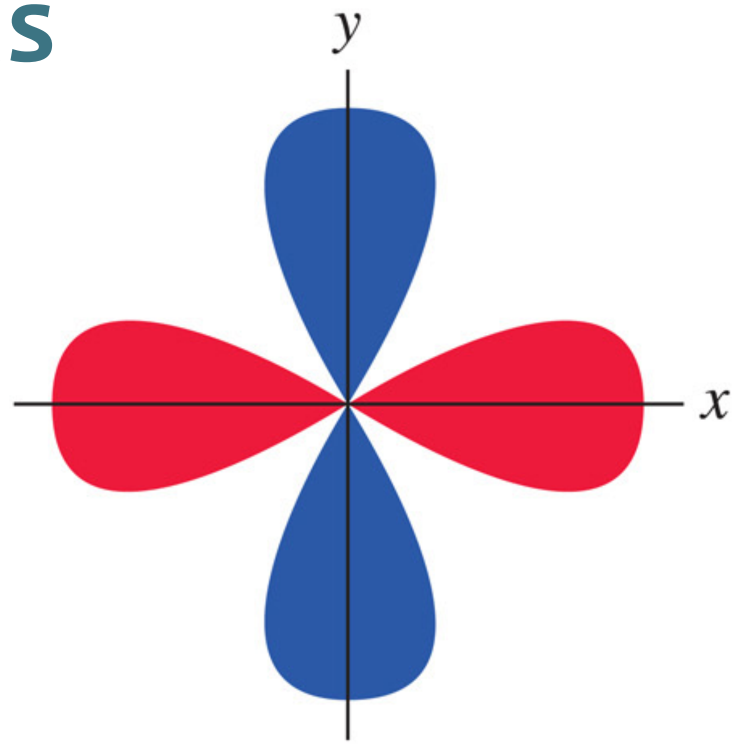
- When n = 3, what are the values of ℓ?
- ℓ = 0, 1, 2 and so there are 3 subshells in the shell

For $\ell = 0$, $m_\ell = 0$ → ____ subshell with ________orbital

For $\ell = 1$, $m_\ell = -1, 0, +1$ → ____ subshell with _____ orbitals

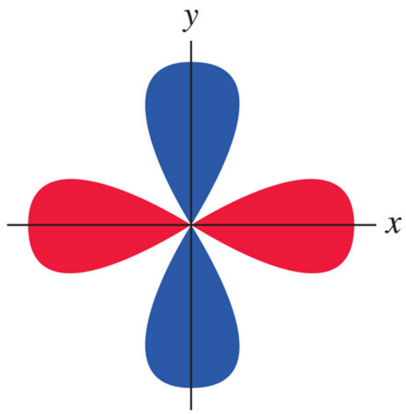
For $\ell = 2$, $m_\ell = -2, -1, 0, +1, +2$ → ____ subshell with _____ orbitals

d Orbitals

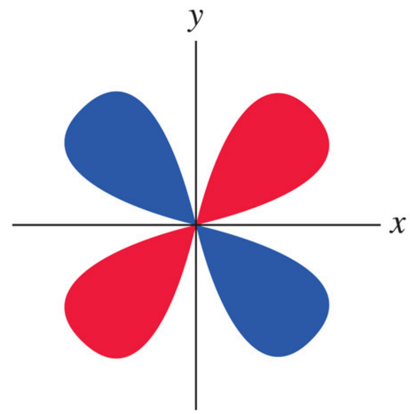


- s orbitals have no planar node (______) and so are spherical.
- p orbitals have ______, and have 1 planar node, and so are "dumbbell" shaped.
- d orbitals (with _____) have 2 planar nodes

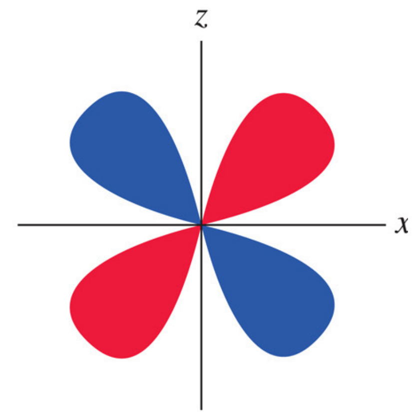
d Orbitals



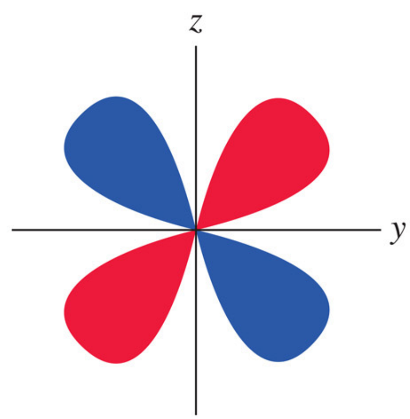
(a) $d_{x^2-y^2}$



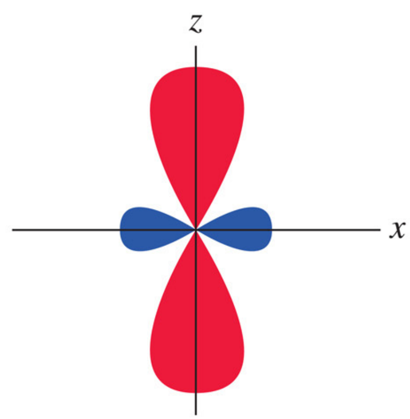
(b) d_{xy}



(c) d_{xz}

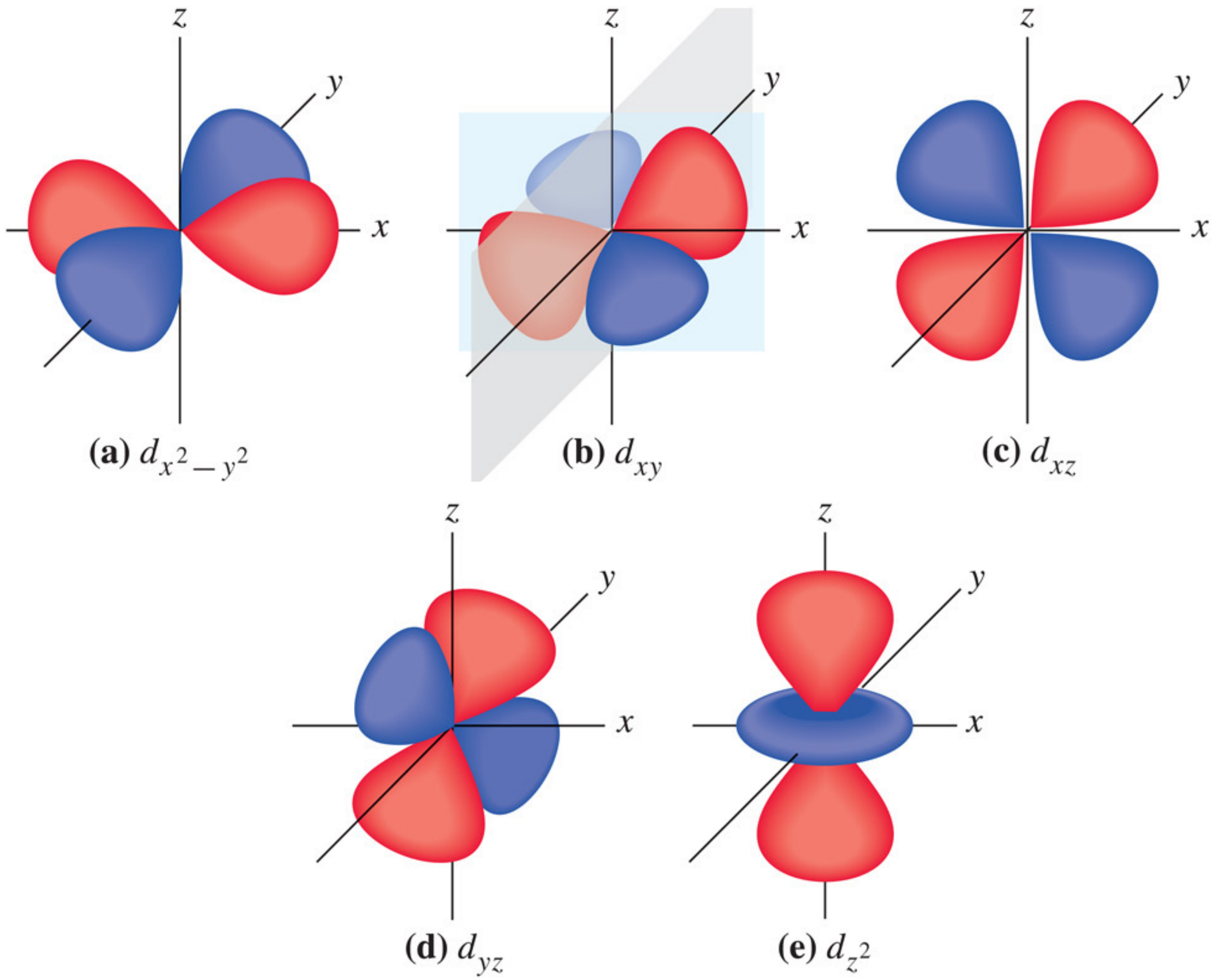


(d) d_{yz}



(e) d_{z^2}

d Orbitals – another view



Example: Quantum Numbers

How many orbitals are available with the following sets of quantum numbers?

a) n = 4

b) n = 5, ℓ = 2

c) n = 3, ℓ = 1, m_ℓ = 2

n	ℓ	m_ℓ
1	0	0
2	0	0
	1	-1, 0, +1
3	0	0
	1	-1, 0, +1
	2	-2, -1, 0, +1, +2
4	0	0
	1	-1, 0, +1
	2	-2, -1, 0, +1, +2
	3	-3, -2, -1, 0, +1, +2, +3

Your Turn…

Which of the following is a correct set of quantum numbers for an electron in a 3d orbital?

A) $n = 3, \ell = 0, m_\ell = -1$

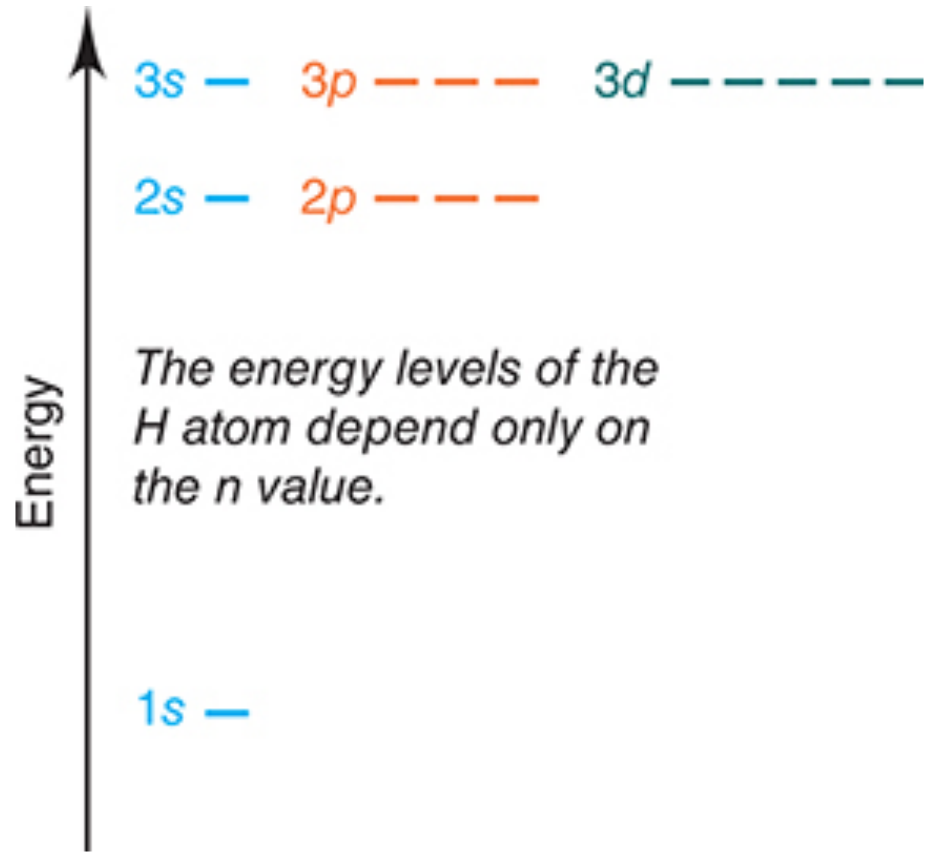
B) $n = 3, \ell = 1, m_\ell = +3$

C) $n = 3, \ell = 2, m_\ell = +3$

D) $n = 3, \ell = 3, m_\ell = +2$

E) $n = 3, \ell = 2, m_\ell = -2$

A one-electron atom



Chapter 6: Key Concepts

1. Development of Quantum Mechanics
2. The Bohr Model
3. The 3 Quantum Numbers

Chapter 6 Suggested Problems

6.7, 6.11, 6.23, 6.27, 6.29, 6.31, 6.34, 6.48, 6.49, 6.51, 6.53, 6.55, 6.57, 6.59, 6.72