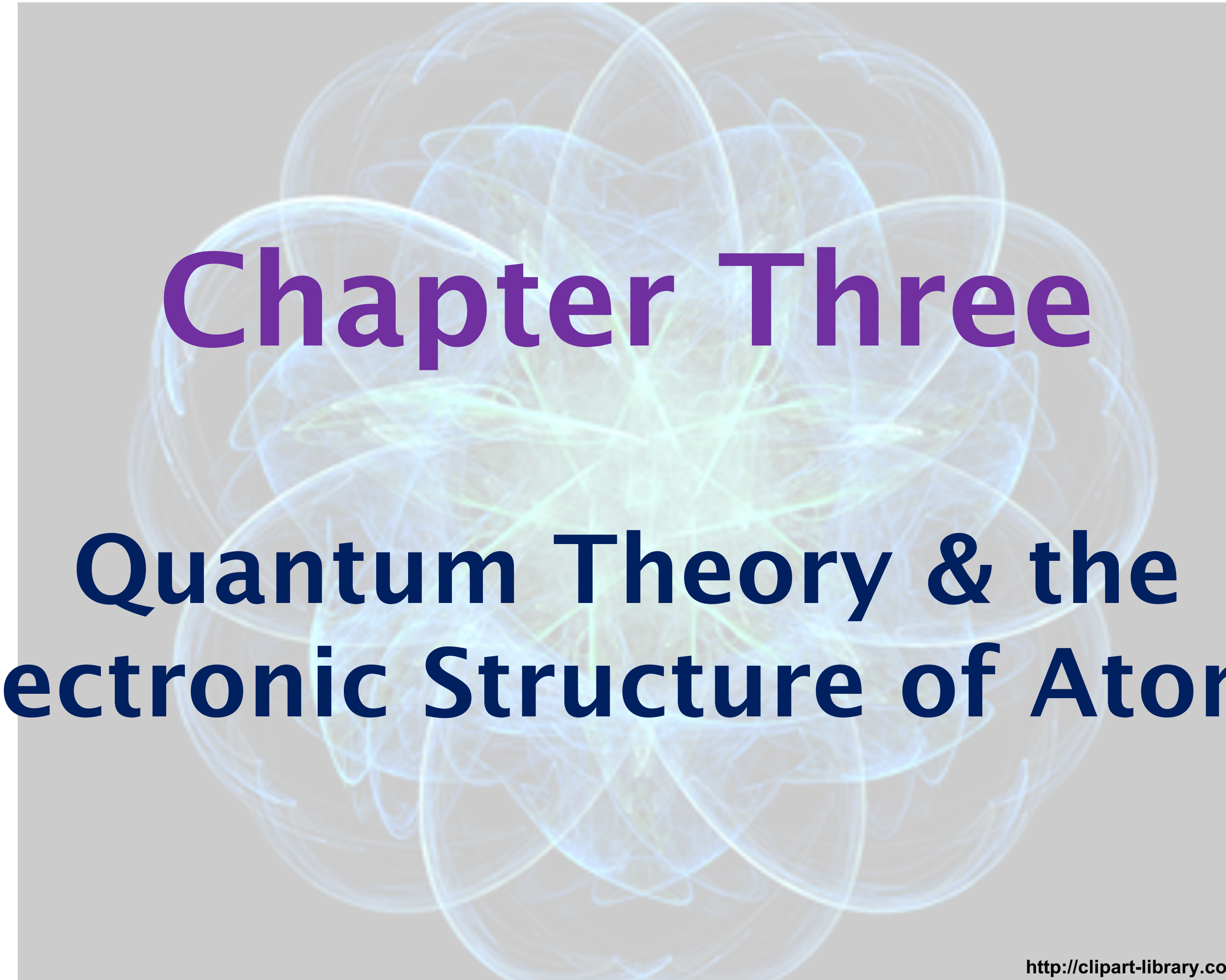


Chapter Three

Quantum Theory & the Electronic Structure of Atoms

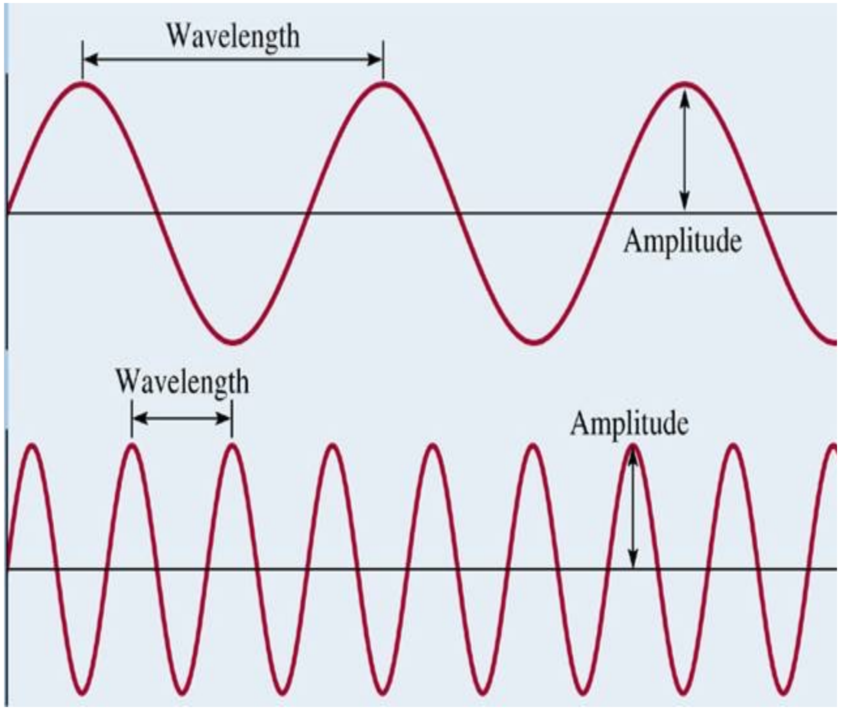
Wave Theory

Wave

- Repeating disturbance spreading out from a defined origin
- Characterized by wavelength, frequency and amplitude

Wavelength (λ)

- Distance between identical pts
- Units some form of meters



Frequency (ν)

- Number of waves that pass through a point in 1 second
- Units of cycles/sec or Hz (s^{-1})

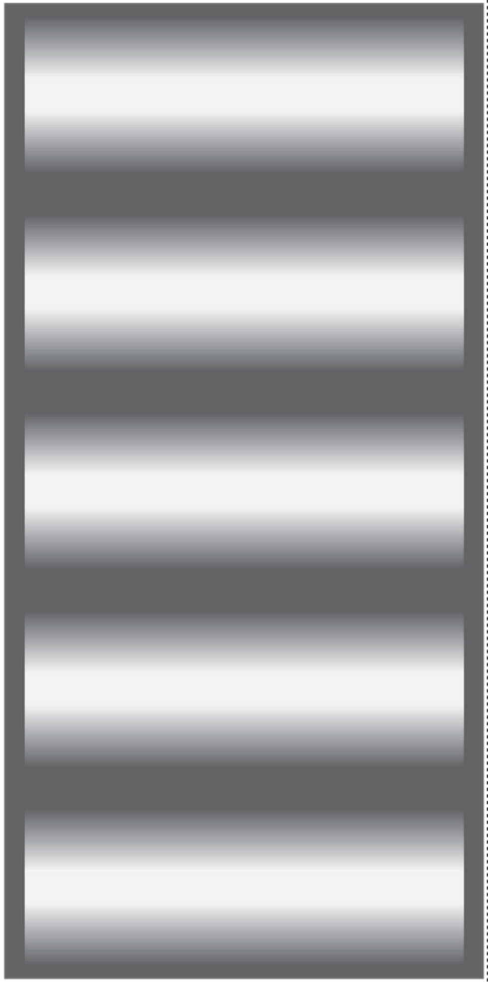
Amplitude

- Height of wave from center point
- Intensity of wave

Wave Theory

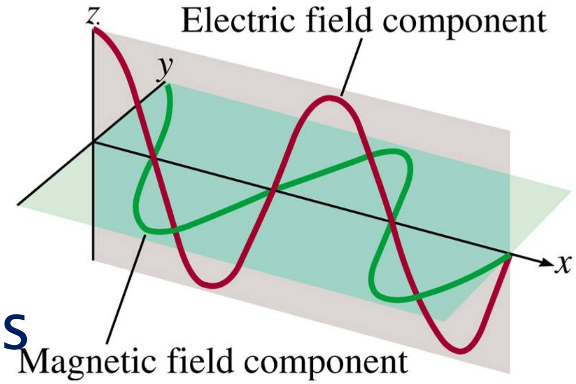
Waves exhibit **interference:**

- When light passes through two narrow openings very close to each other, a pattern of light and dark lines is formed
- The lines of light are from **constructive interference** (the high and low points of the waves line up with each other)
- The lines of darkness are from **destructive interference** (the peak of one wave lines up with the trough (bottom) of another wave, etc.)
- Interference patterns are evidence of light properties

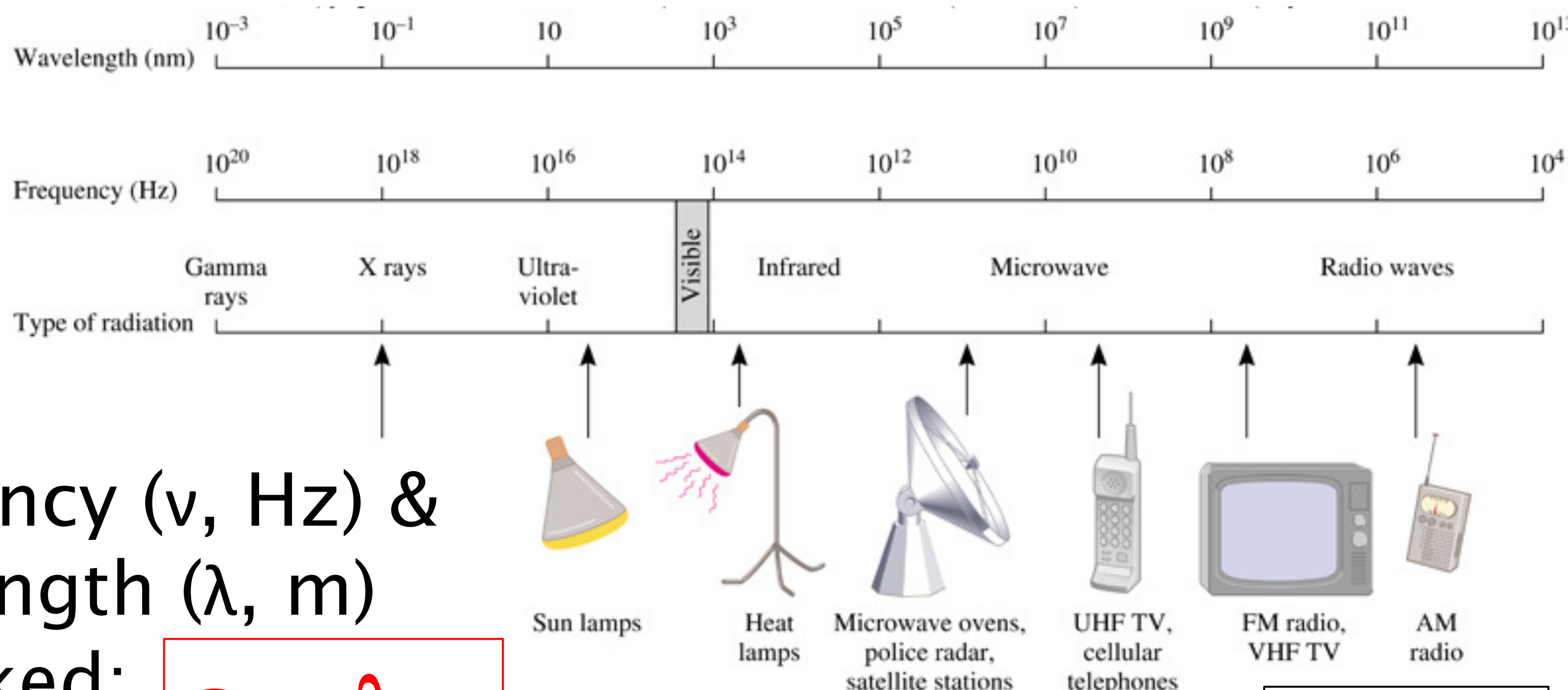


Electromagnetic Radiation

Electromagnetic Radiation



- Emission/transmission of energy
- In form of waves
- Has electrical & magnetic components
- Travels at the speed of light ($c = 3.00 \times 10^8$ m/s)



Frequency (ν, Hz) & wavelength (λ, m) are linked:

$$c = \lambda\nu$$

$\text{Hz} = \text{s}^{-1}$

Using the relationship $c = \lambda\nu$:

What is the wavelength of an FM-radiowave with a 94.9 MHz frequency?

A: 3.16 m

Max Planck's Quantum Theory

Studied energy emitted by objects (blackbody radiation)

- Amount of energy emitted was directly related to wavelength at which energy was emitted

Theory: Energy is emitted/absorbed in discrete bundles

- Amounts were defined by λ (& ν – they are related!)

$$E = h\nu = hc/\lambda$$

- Can have multiples of these discrete amounts

$$E = h\nu,\ \ E = 2h\nu,\ \ E = 3h\nu\ \ldots$$

- **h = Planck's constant = 6.626×10^{-34} J s**

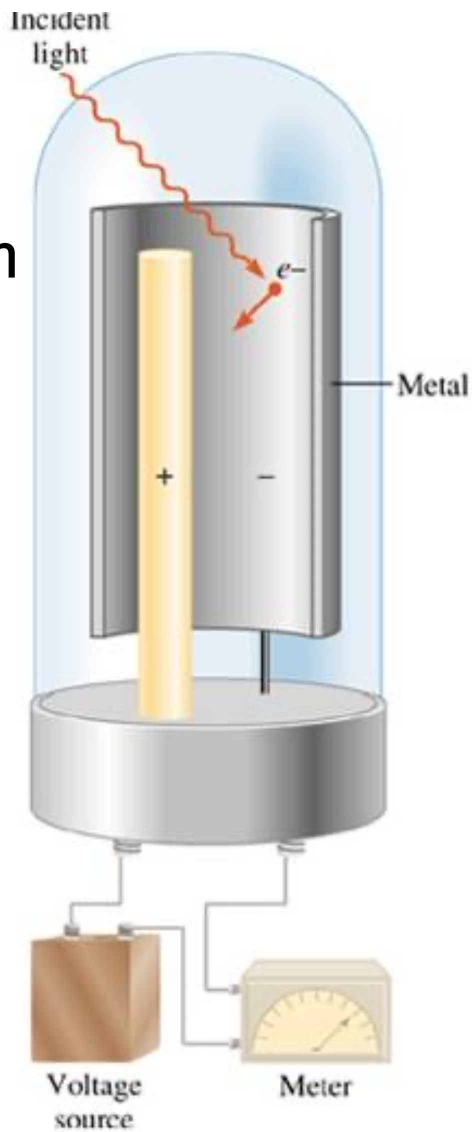
Called the smallest amount of energy a Quantum.

Didn't know why energy was quantized, but math worked over entire spectrum of wavelengths

Einstein and the Photoelectric Effect

Experiment to prove why E= hν

- Light hits metal surface causing electrons to break free
- Light energy must be at or above a certain
- frequency to dislodge electrons
- Intensity of light determines number of electron dislodged
- Intensity of light does not impact energy of dislodged electrons



Conclusion:

Light energy has particle properties in addition to wave properties

Particles of light were later called **"photons"**

Using $E = h\nu$ ($h = 6.626 \times 10^{-34}$ Js)

1. What is the energy of a radiowave with a frequency of 94.9 MHz?

A: 6.29×10^{-26} J

2. What wavelength (in μm) has an energy of 1.00×10^{-20} J?

A: 19.9 μm

Using E = hν (h = 6.626 x 10^{-34} Js)

What is the energy per photon and per mole of photons of violet light, with a wavelength of 415 nm?

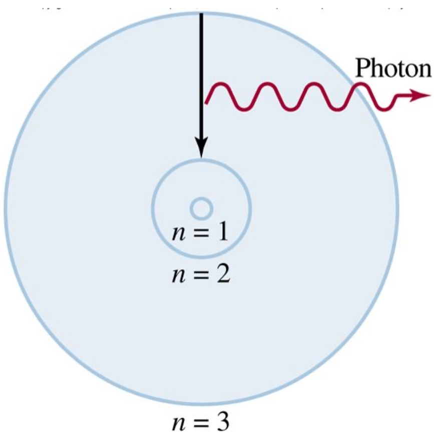
A: 4.79 x 10^{-19} J/photon
A: 2.88 x 10^{5} J/mol

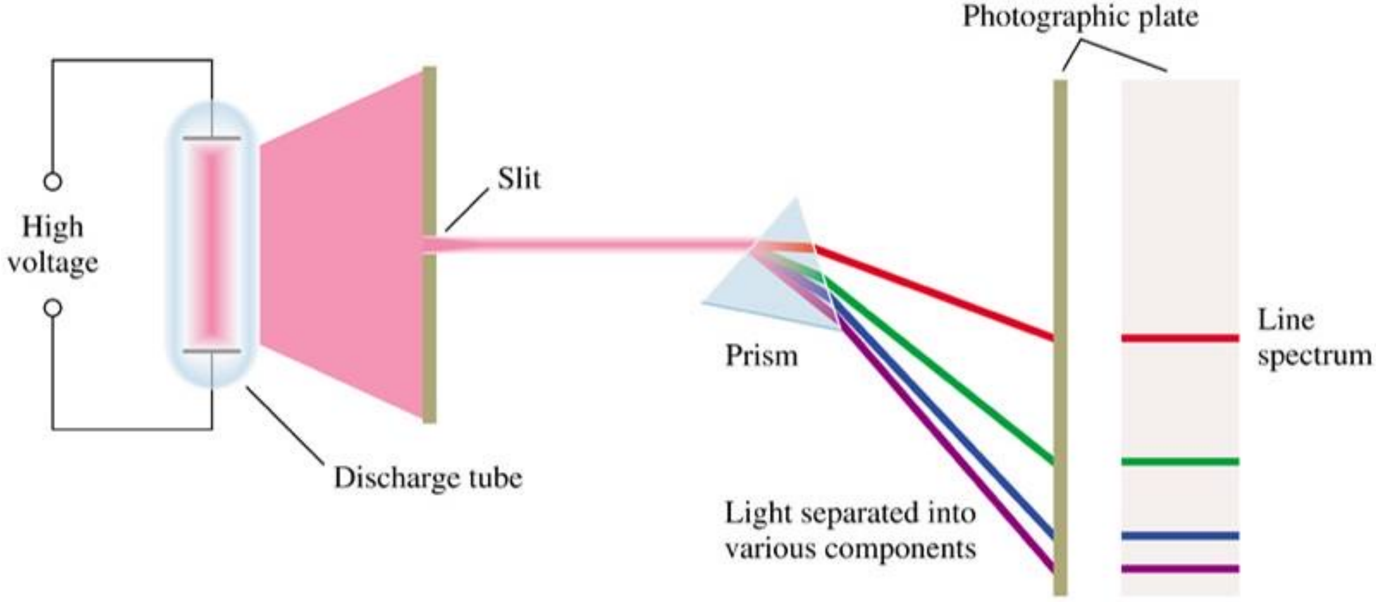
Elemental Line Spectra

Emission Spectra: Pattern of radiation that is emitted when photons are released from a substance.

Procedure

- Add energy to an element
- Photons are emitted as a beam of light
- Separate wavelengths through a prism
- Record pattern on a photographic plate





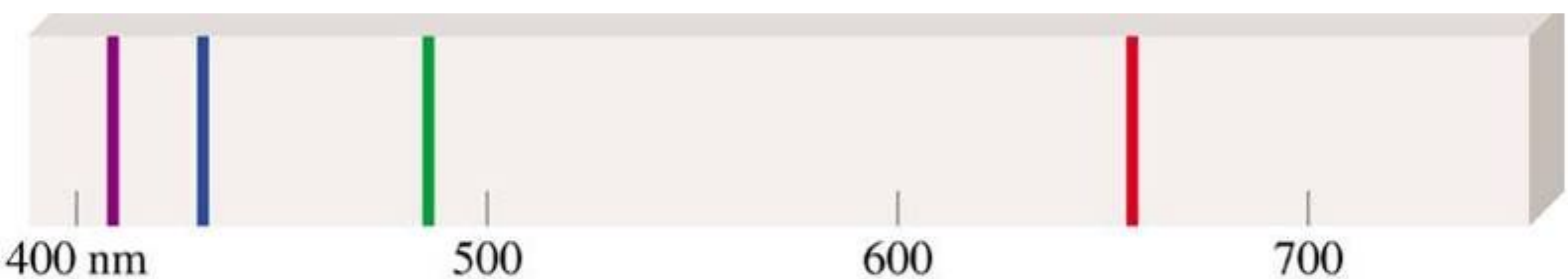
Continuous vs. Line Spectra

Continuous spectrum:

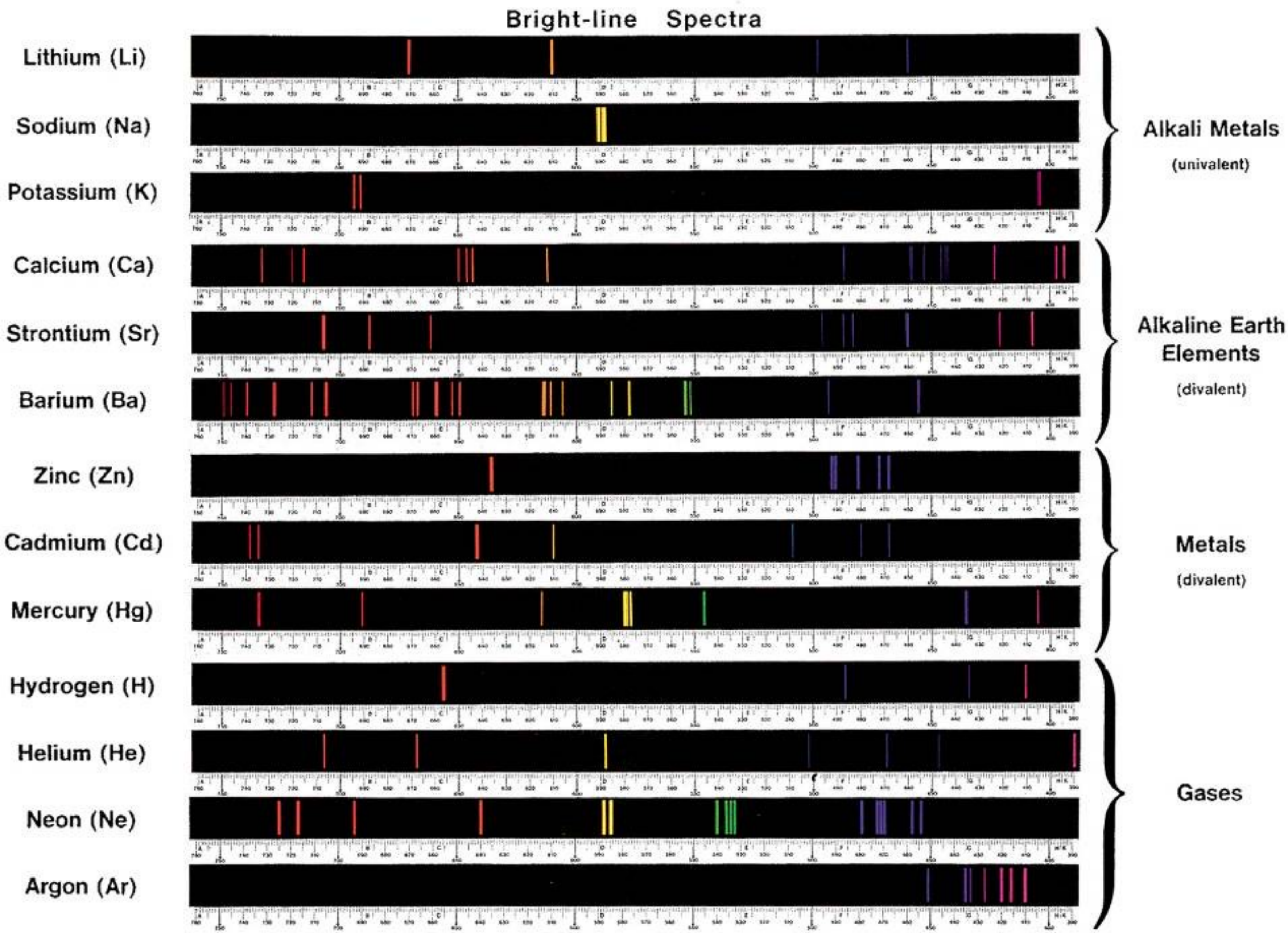
- Occurs when all visible light is present: white light

Line Spectrum

- Occurs when light is produced through an element
- Pattern of lines is characteristic of the element
- Can be used for identification of elements



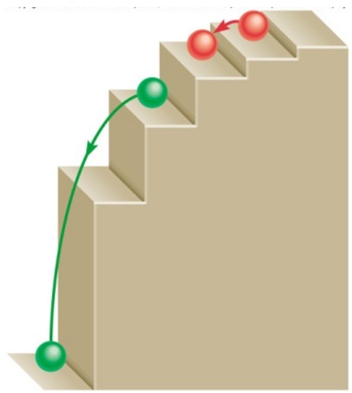
Elemental Line Spectra



Bohr's Hydrogen Atom

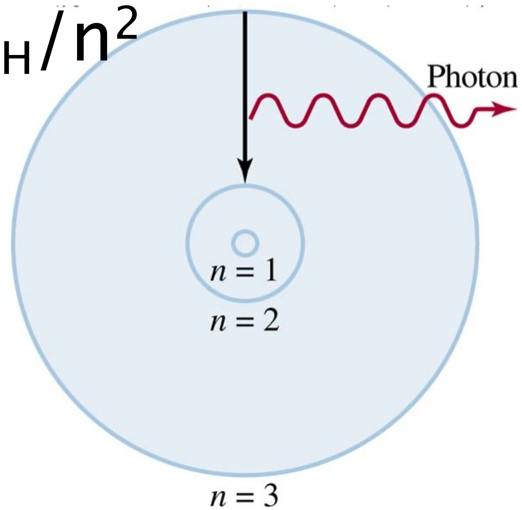
Niels Bohr (1913): Electron energy (E_n) was quantized

- Similar to light/photons
- Only certain specified values allowed
- Stable levels called <u>energy levels</u>
- Photon absorbed/released when electron moves from 1 level to another



The energy of each stable orbit: $E_n = -R_H/n^2$

- *n* is the quantum number of the level
- *n* is always an integer, 1,2,3,...etc.



Proportionality constant R_H

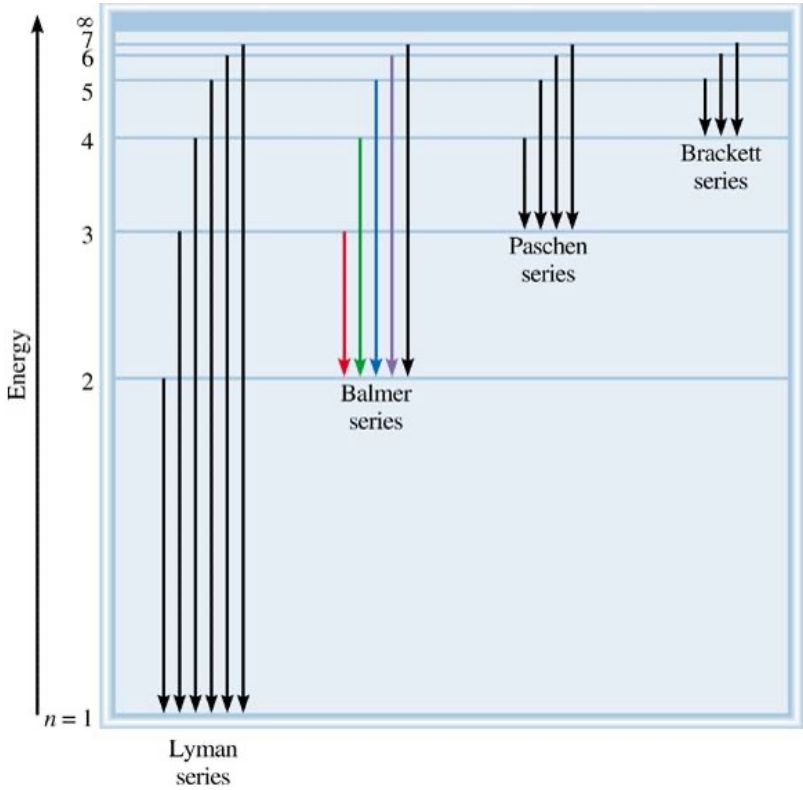
- Rydberg constant
- **$R_H = 2.18 \times 10^{-18}$ J**

Leads to orbit description of atoms – we know today this is not accurate

Energy Level Calculations

All calculations done by comparing energy levels

- Electron moves between levels
- $E = -R_H (1/n_f^2 - 1/n_i^2)$



Energy emitted or absorbed

- <u>High to low level:</u>
  - energy released (–)
- <u>Low to high level:</u>
  - energy absorbed (+)

Ground state: An e⁻ 's lowest possible energy level
Excited state: All other levels

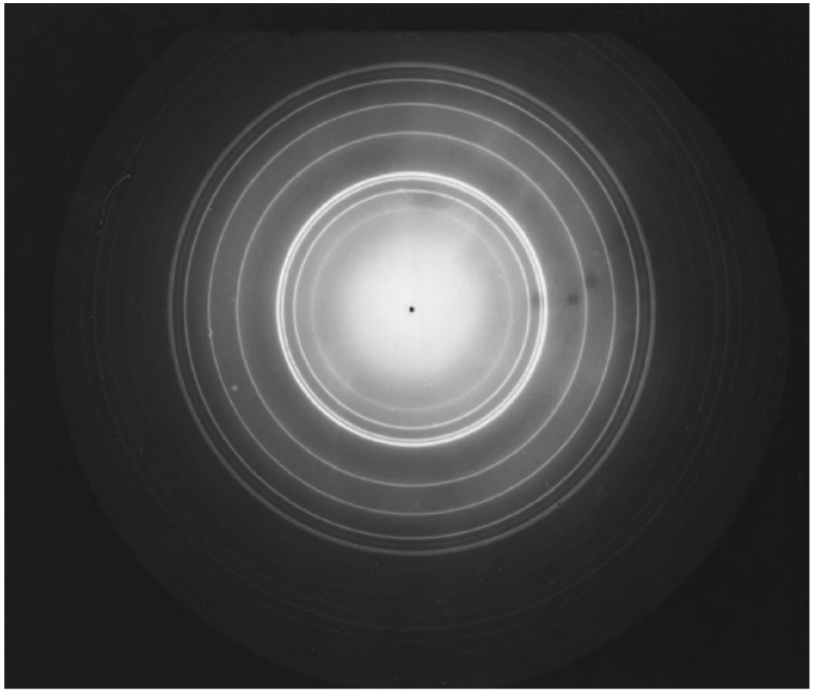
Calculate the wavelength, in nm, of the electron shift from n = 4 to n =2. Is light emitted or absorbed?

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

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

A: λ = 486 nm Visible blue green light is emitted (neg E value)

Wave Properties of Electrons

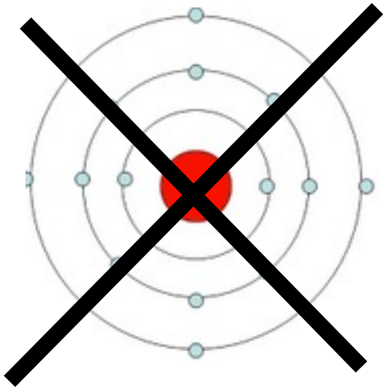


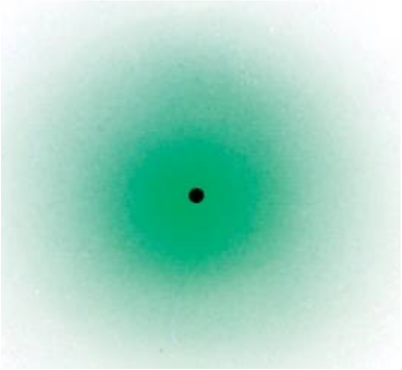
- de Broglie predicted that electrons should have wave properties
- Davisson & Germer successfully showed that electrons produce diffraction patterns like x-rays

Electrons, like light, are both particles & waves

Modern View of the Atom: Quantum Mechanics – a very brief intro

- (Nucleus in center, protons & neutrons in nucleus)
- Electrons outside nucleus
  - located in "cloud" surrounding the nucleus
  - likely location based on probability functions
  - quantum numbers used to describe probable location
  - impossible to know both position and velocity (momentum) of an electron at the same time (Heisenberg Uncertainly Principle)





$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi + [V_1(x) + iV_2(x)]\Psi$$

Quantum Numbers and Atomic Orbitals

Atomic orbital

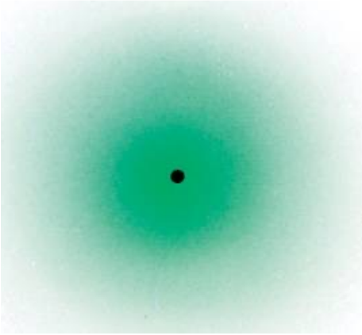
- A region in space with a high probability of finding an electron (high electron density).
- Identified by 4 quantum numbers.

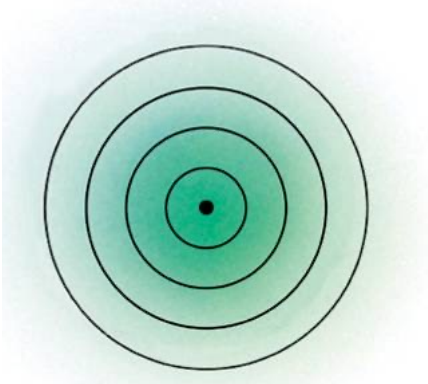
4 Quantum Numbers (think of it as a dorm address)

1. Principal quantum number (n):	Building
2. Angular momentum quantum number (*l*)	Floor
3. Magnetic quantum number (m_l)	Room #
4. Electron spin quantum number (m_s)	Bed

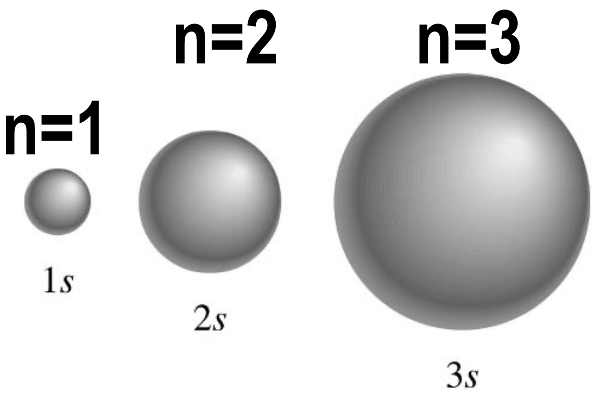
The Principal Quantum Number (n)

- Restricted to the positive integers: 1, 2, 3, 4, 5, 6, 7
- The shell or energy level of the orbital





- Indicates the size of the orbital
  - max distance e^- can travel from nucleus
- Integers correspond to row numbers in Periodic Table
  - row an element is in tells you the highest energy level in the ground state



The Angular Momentum Quantum Number (ℓ)

- Indicates orbital shape
  - Designation: s, p, d or f

*l*evel	0	1	2	3
Name	s	p	d	f

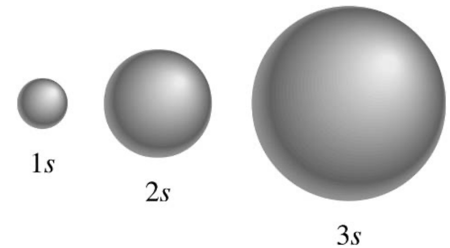
- Designates the subshell
  - Values range from 0 to n-1
  - 0-6 theoretically, but realistically 0-3
  - Give rise to “Blocks” in periodic table

Energy Level (n)	Math	Allowed ℓ values	Orbitals
1	1-1 = 0	0	s only
2	2-1 = 1	0, 1	s & p
3	3-1 = 2	0, 1, 2	s, p, & d

Orbital Shapes = ℓ quantum number

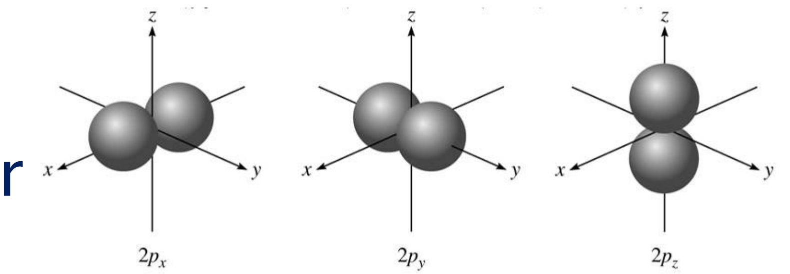
ℓ = 0: s orbitals

- Spherical
- **One** per energy level



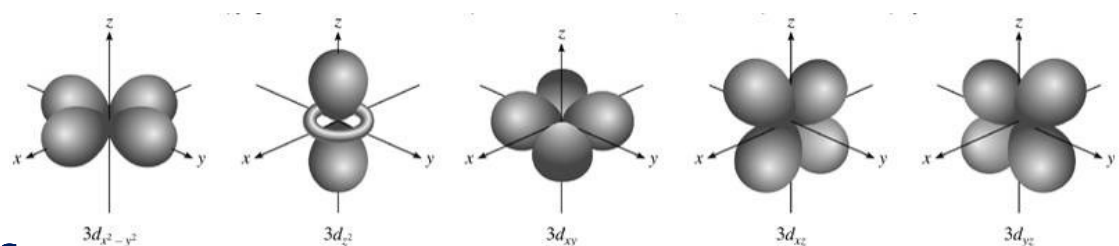
ℓ = 1: p orbitals

- 2 teardrops joined at center
- **Three** per energy level



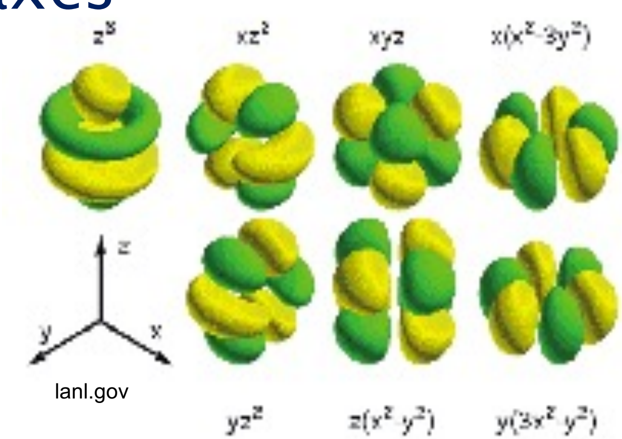
ℓ = 2: d orbitals

- Most are like two p orbitals along different axes
- **5** per energy level



ℓ = 3: f orbitals.

- Complicated shapes
- **7** per energy level



The Magnetic Quantum Number (m_ℓ):

Determines the orientation in space of the orbitals

- "orientation" refers to proximity to axes (x, y, z)
- Integers from $-\ell$ to $+\ell$

Determines the number of orbitals in a subshell

- The number of possible values for $m_\ell = 2\ell + 1$

Orbital	ℓ value	Allowed m_ℓ values	Number of Orbitals per Energy Level
s	0	0	1
p	1	-1, 0, 1	3
d	2	-2, -1, 0, 1, 2	5
f	3	-3, -2, -1, 0, 1, 2, 3	7

Orbitals with same n & ℓ values are "degenerate"

degenerate = same energy

(Note: In some cases there are slight energy differences)

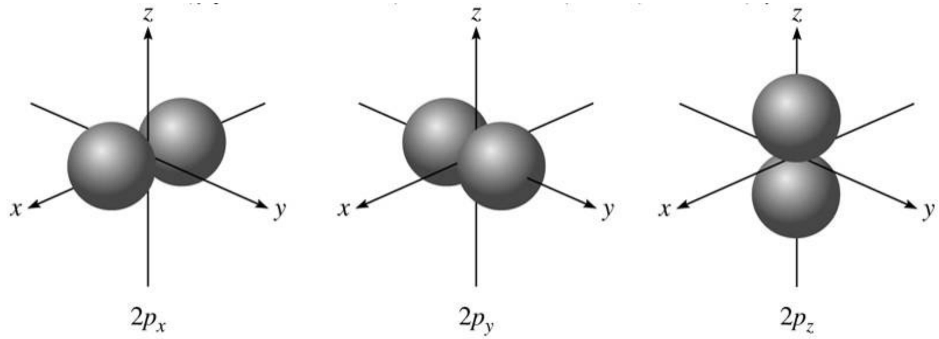
Possible quantum numbers for an electron in a 4p orbital:

n = 4

ℓ can be 0 to 4-1 (0, 1, 2, 3) BUT if it is a p orbital ℓ = 1

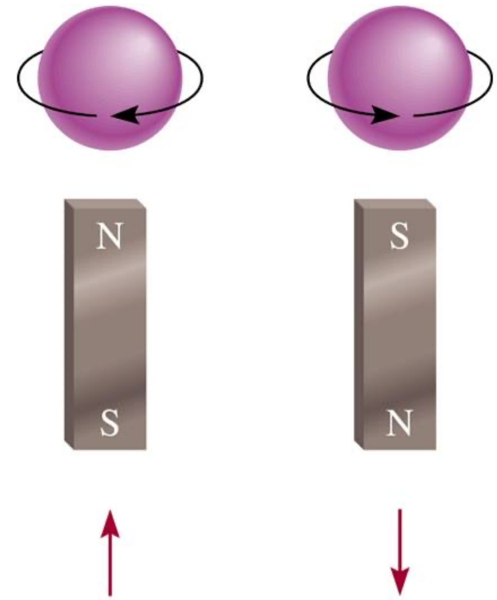
m_ℓ can be $+\ell$ to $-\ell$ = -1, 0, +1

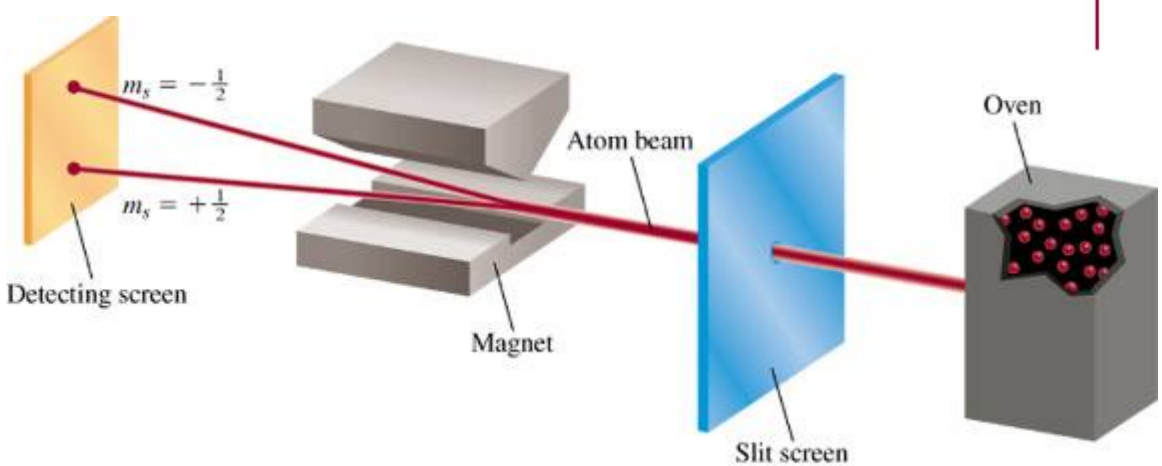
Since the three 4p orbitals are degenerate, any of the three m_ℓ values could be correct



Electron Spin Quantum Number (m_s)

- A magnetic field is induced by the moving electric charge of an electron as it spins
  - Opposite spins cancel one another
  - No net magnetic field for the pair
  - Allows 2 electrons to occupy 1 orbital
  - Unpaired e^- lead to magnetism
- Two possible values: **+1/2 and –1/2**





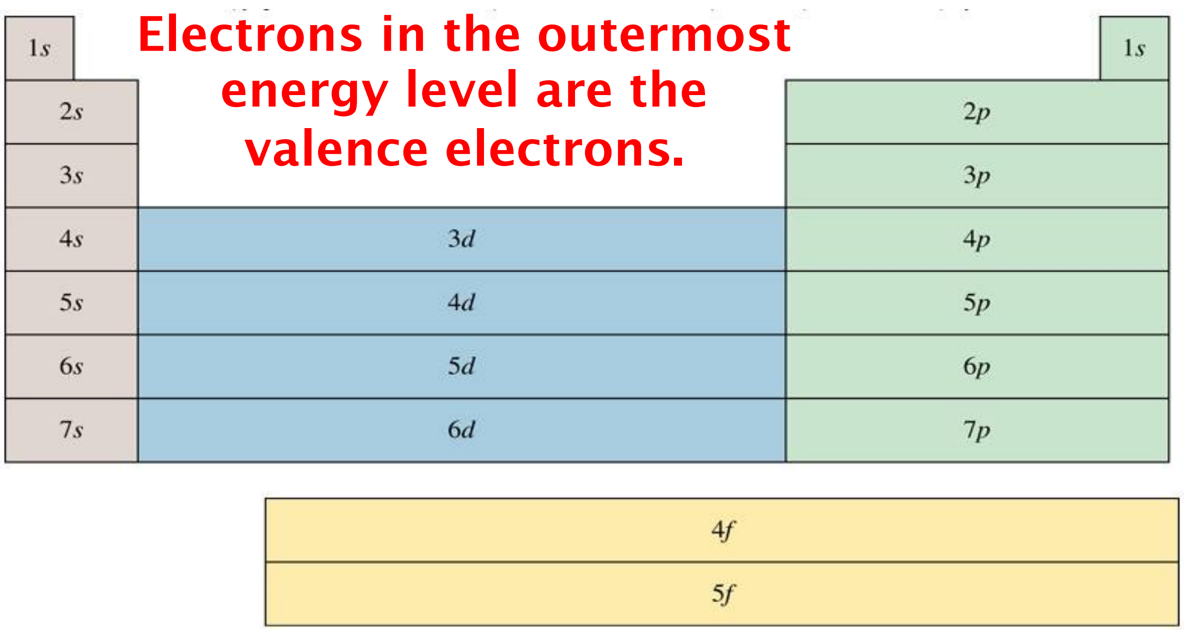
Quantum Numbers Summary

TABLE 3.2 Allowed Values of the Quantum Numbers n, ℓ, and m_ℓ

When n is	ℓ can be	When ℓ is	m_ℓ can be
1	only 0	0	only 0
2	0 or 1	0	only 0
		1	−1, 0, or +1
3	0, 1, or 2	0	only 0
		1	−1, 0, or +1
		2	−2, −1, 0, +1, or +2
4	0, 1, 2, or 3	0	only 0
		1	−1, 0, or +1
		2	−2, −1, 0, +1, or +2
		3	−3, −2, −1, 0, +1, +2, or +3

Quantum Numbers & the Periodic Table

- **Principle quantum number, n**
  - Row number of periodic table, values of 1-7
- **Angular momentum quantum number, ℓ**
  - Specific area of periodic table, spdf "blocks"
- **Can follow the periodic table to fill e^- configuration**
- **Can use location on Periodic Table to determine where e^- configuration will end**



A possible set of quantum numbers for the last electron added to complete an atom of selenium would be:

n:

l:

m_l:

m_s: