

Chapter Three

Quantum Theory & the Electronic Structure of Atoms

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Wave Theory

Wave

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

Wavelength (λ)

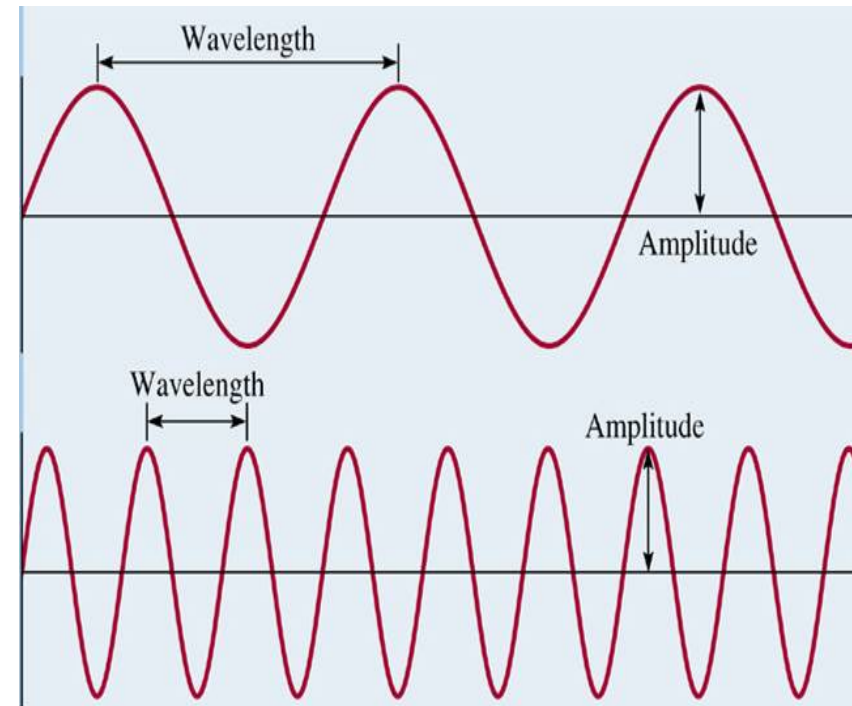
- Distance between identical pts
- Units some form of meters

Frequency (ν)

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

Amplitude

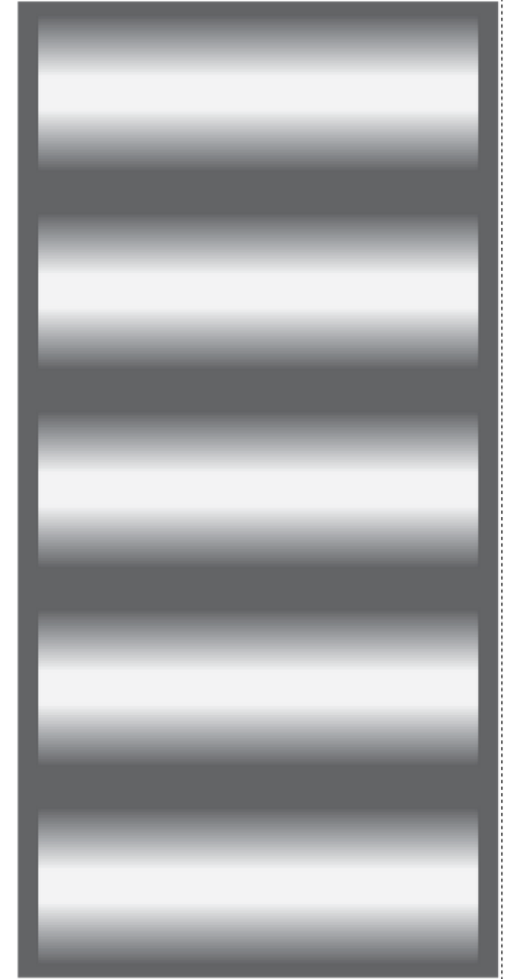
- Height of wave from center point
- Intensity of wave



Wave Theory

Waves exhibit **interference**:

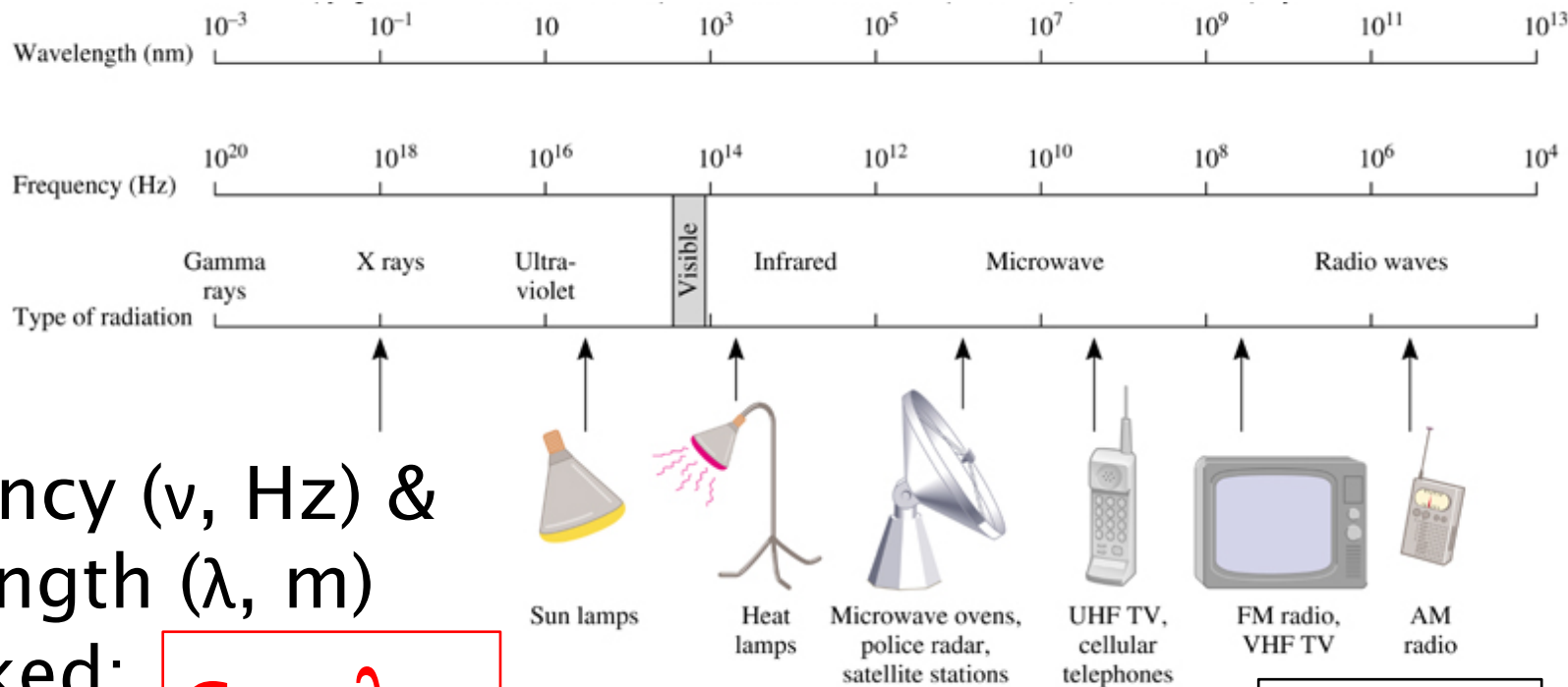
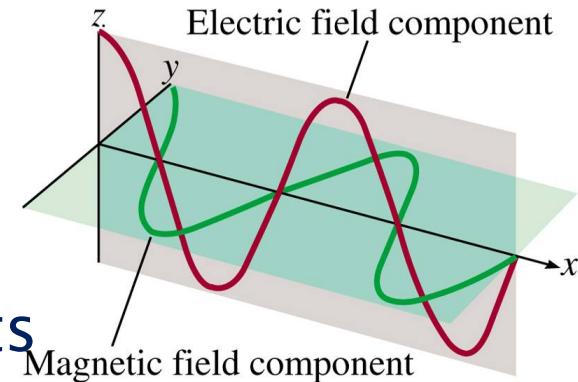
- When light passes through two narrow openings very close to each other, a pattern of light and dark lines is formed
- The lines of light are from **constructive interference** (the high and low points of the waves line up with each other)
- The lines of darkness are from **destructive interference** (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 ($c = 3.00 \times 10^8 \text{ m/s}$)



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

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

- h = Planck's constant = $6.626 \times 10^{-34} \text{ J s}$

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

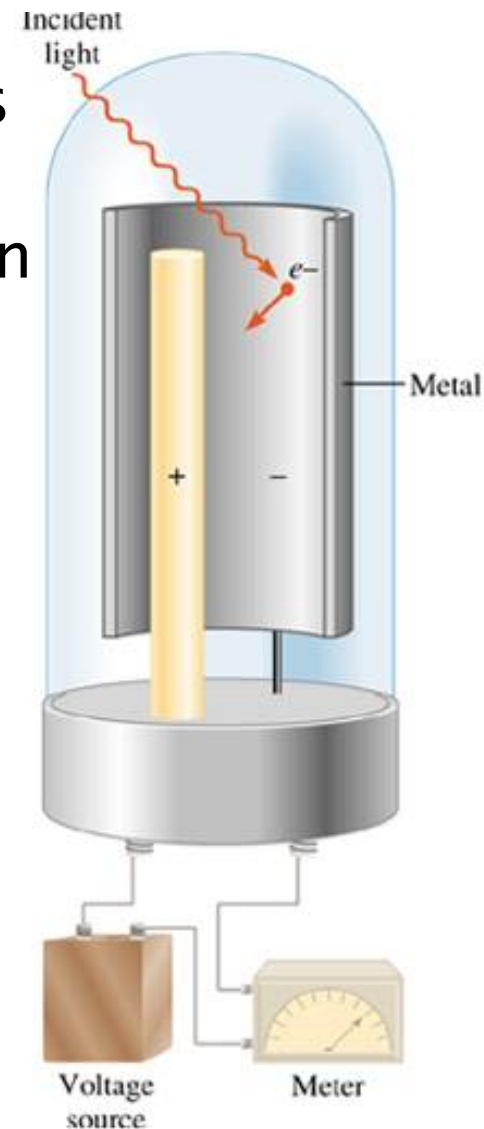
Experiment to prove why $E = h\nu$

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

What is the energy of a radiowave with a frequency of 94.9 MHz? A: $6.29 \times 10^{-26} \text{ J}$

What wavelength has an energy of $1.00 \times 10^{-20} \text{ J}$?

A: $1.99 \times 10^{-5} \text{ m}$
Or $19.9 \mu\text{m}$

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

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

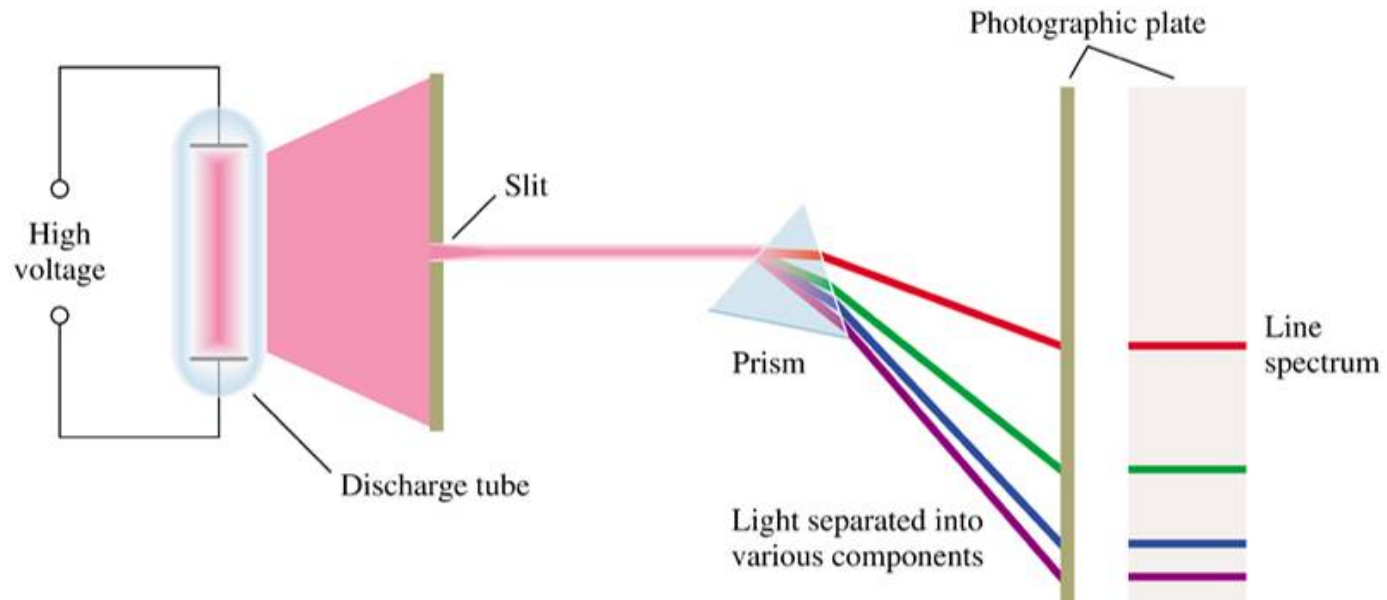
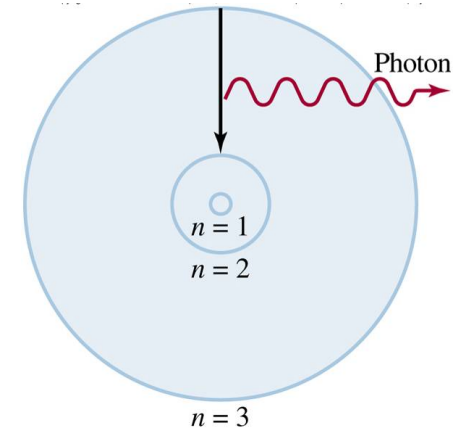
A: $4.79 \times 10^{-19} \text{ J/photon}$
A: $2.88 \times 10^5 \text{ J/mol}$

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



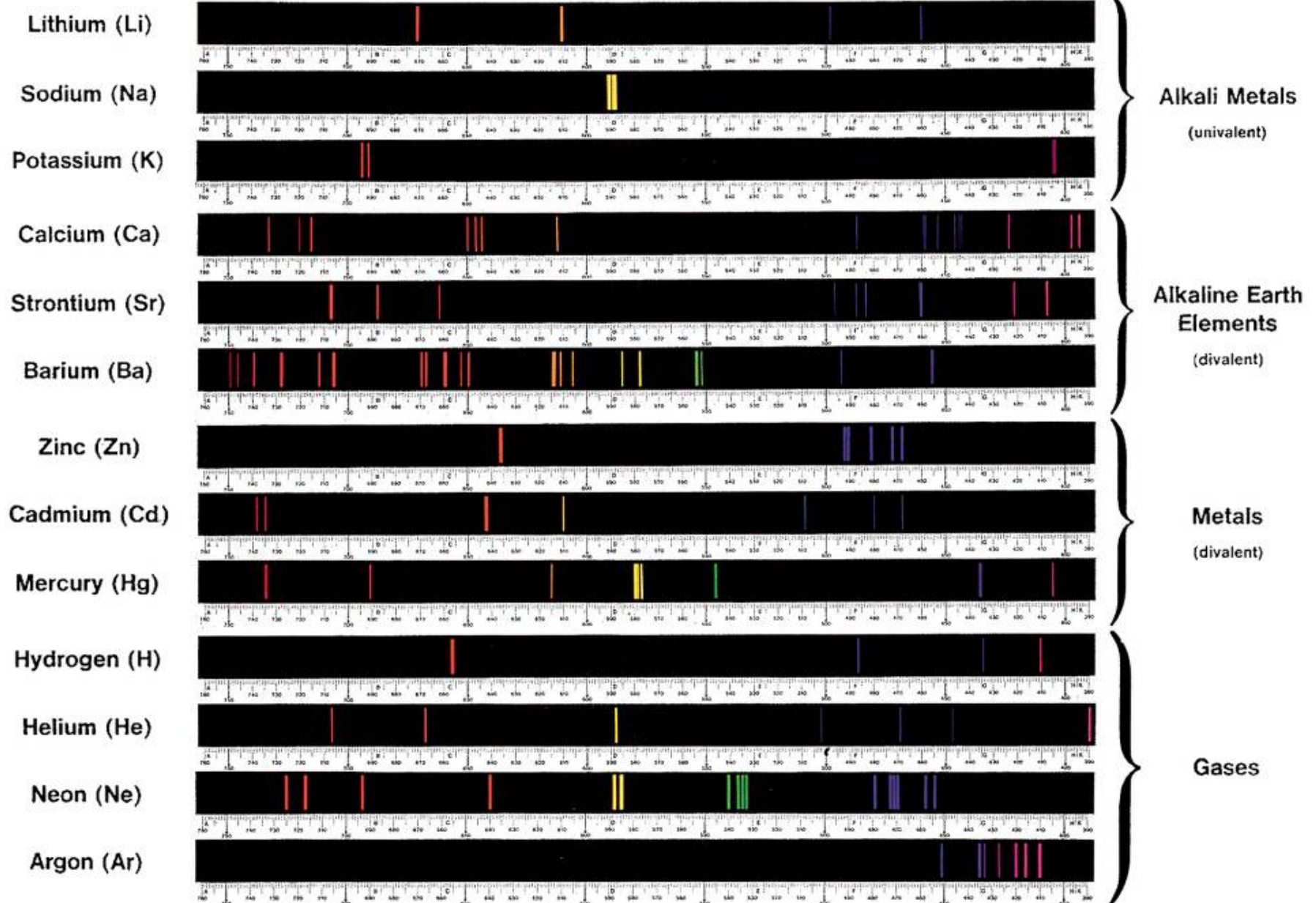
Line Spectrum

- 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

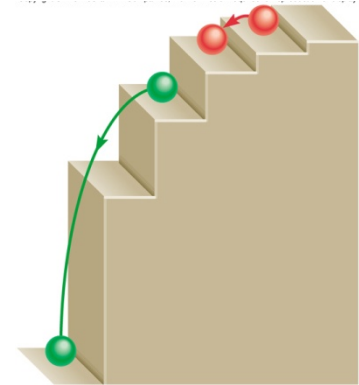
Bright-line Spectra



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 energy levels
- Photon absorbed/released when electron moves from 1 level to another

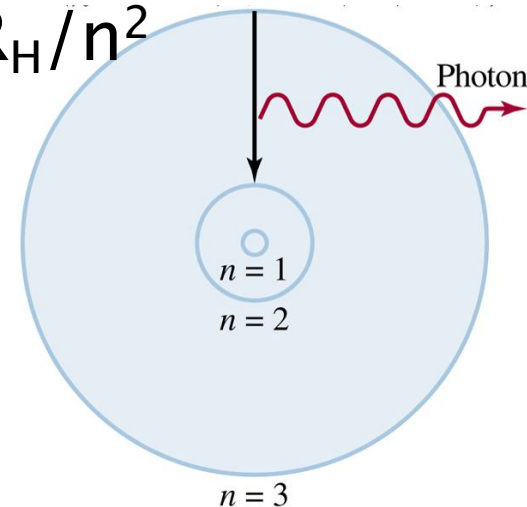


The energy of each stable orbit: $E_n = -R_H/n^2$

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

Proportionality constant R_H

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



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

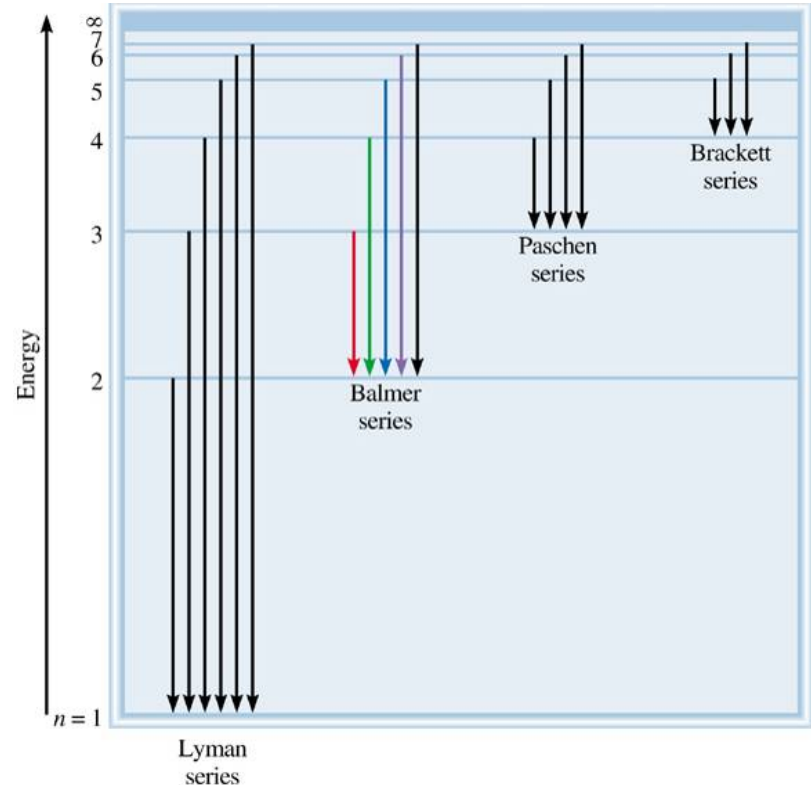
Energy Level Calculations

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

- High to low level:
 - energy released (–)
- Low to high level:
 - energy absorbed (+)



Ground state: An e^- 's lowest possible energy level

Excited state: All other levels

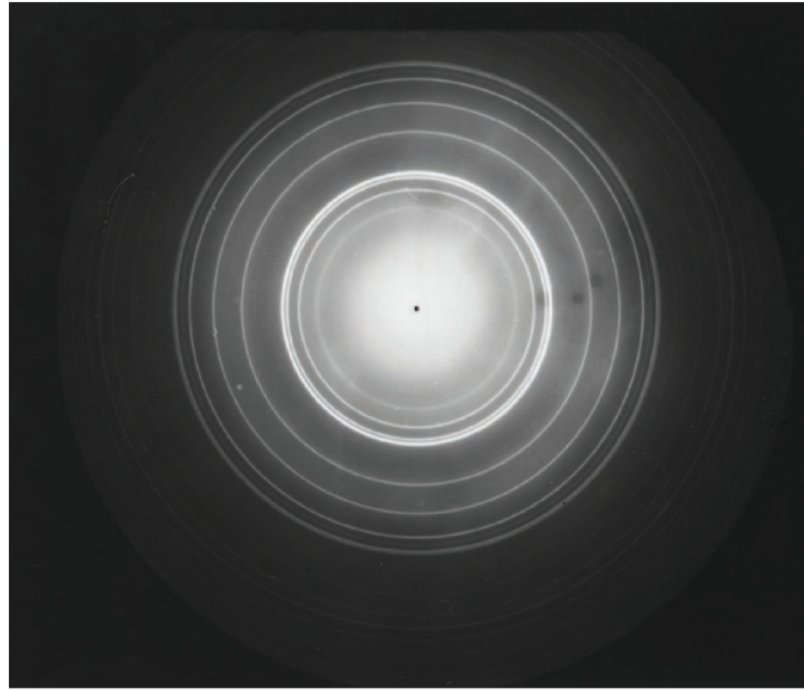
Calculate the wavelength of the electron shift from¹⁵
n = 4 to n = 2. Is light emitted or absorbed?

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

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

A: $\lambda = 486 \text{ nm}$ Visible blue green light is emitted (neg E value)

Wave Properties of Electrons



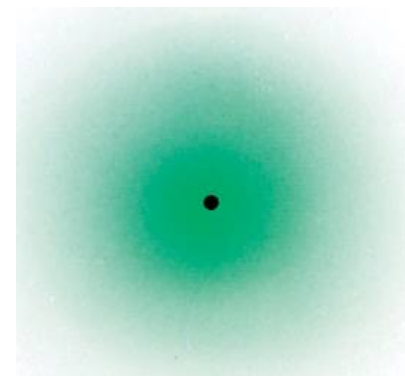
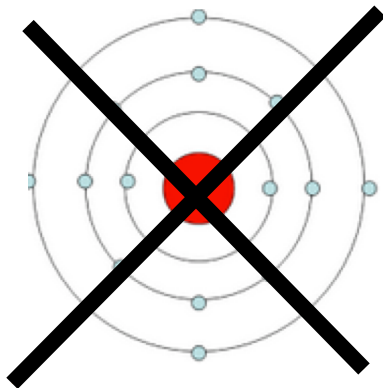
- de Broglie predicted that electrons should have wave properties
- Davisson & Germer successfully showed that electrons produce diffraction patterns like x-rays

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 Uncertainty 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

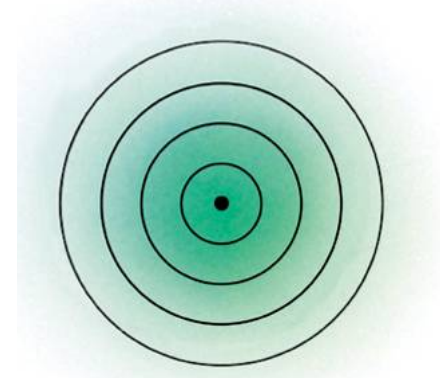
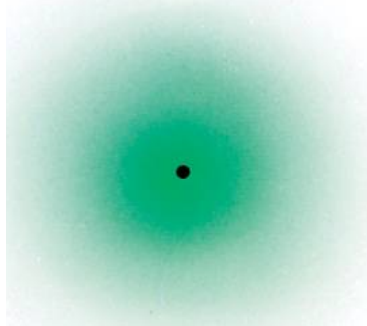
- A region in space with a high probability of finding an electron (high electron density).
- Identified by 4 quantum numbers.

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

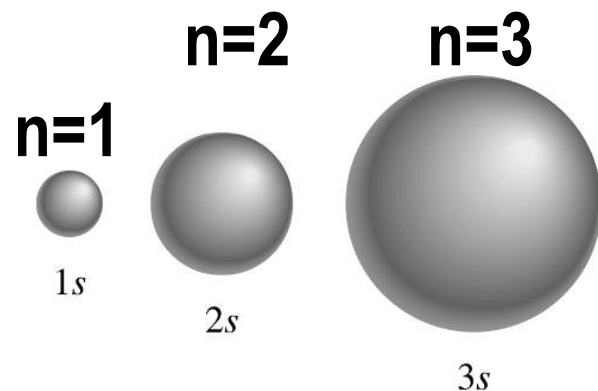
- | | |
|--|----------|
| 1. Principal quantum number (n): | Building |
| 2. Angular momentum quantum number (l) | Floor |
| 3. Magnetic quantum number (m_l) | Room # |
| 4. Electron spin quantum number (m_s) | Bed |

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) ²⁰

- Indicates orbital shape

- Designation: s, p, d or f

level	0	1	2	3
Name	s	p	d	f

- Designates the **subshell**

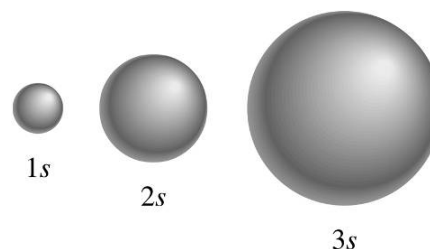
- Values range from 0 to $n-1$
- 0-6 theoretically, but realistically 0-3
- Give rise to “Blocks” in periodic table

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

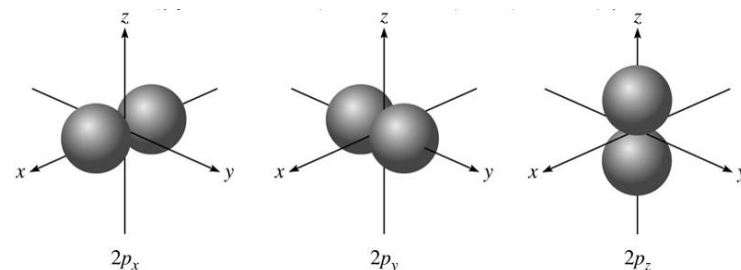
$\ell = 0$: s orbitals

- Spherical
- **One** per energy level



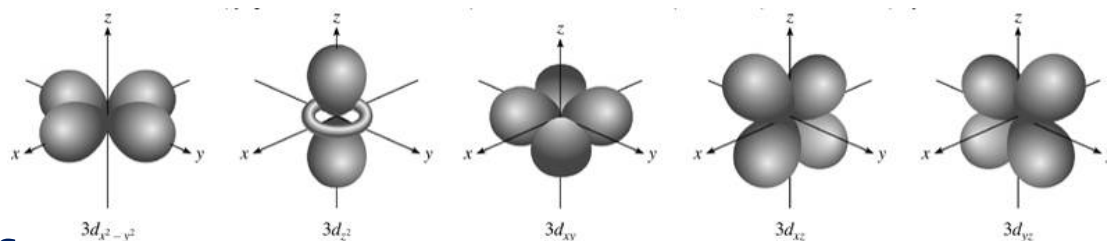
$\ell = 1$: p orbitals

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



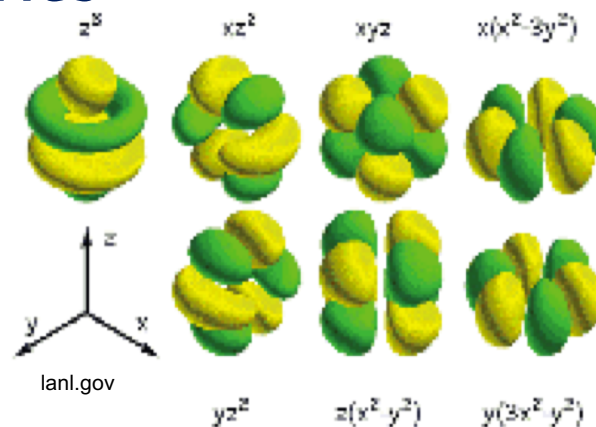
$\ell = 2$: d orbitals

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



$\ell = 3$: f orbitals.

- Complicated shapes
- **Seven** 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)

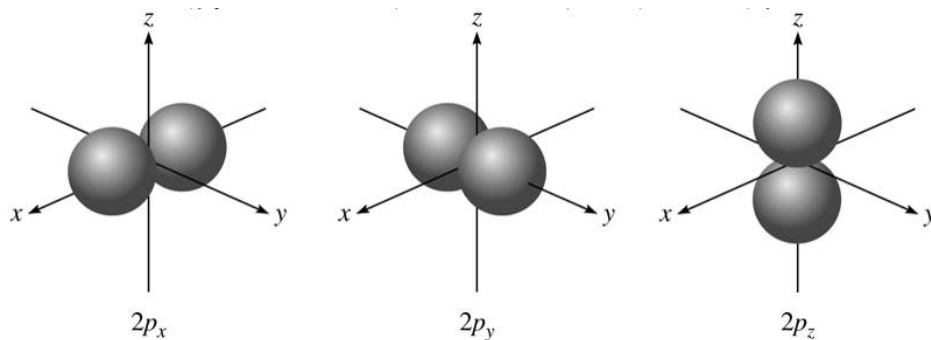
Possible quantum numbers for an electron in a 4p orbital:

$$n = 4$$

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

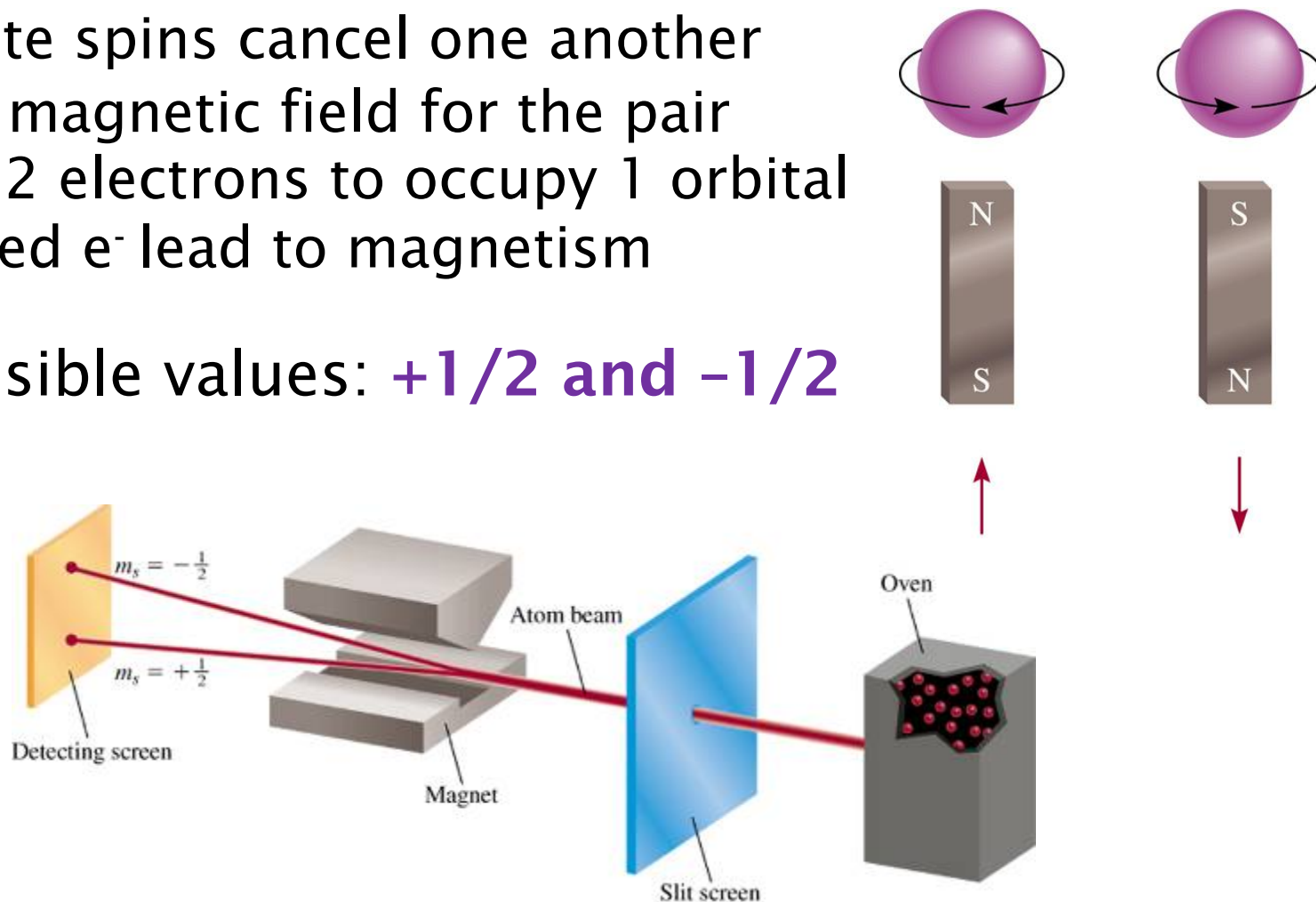
m_ℓ can be $+\ell$ to $-\ell = -1, 0, +1$

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**

Electrons in the outermost energy level are the valence electrons.

1s			1s
2s			2p
3s			3p
4s	3d		4p
5s	4d		5p
6s	5d		6p
7s	6d		7p
		4f	
		5f	

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 :