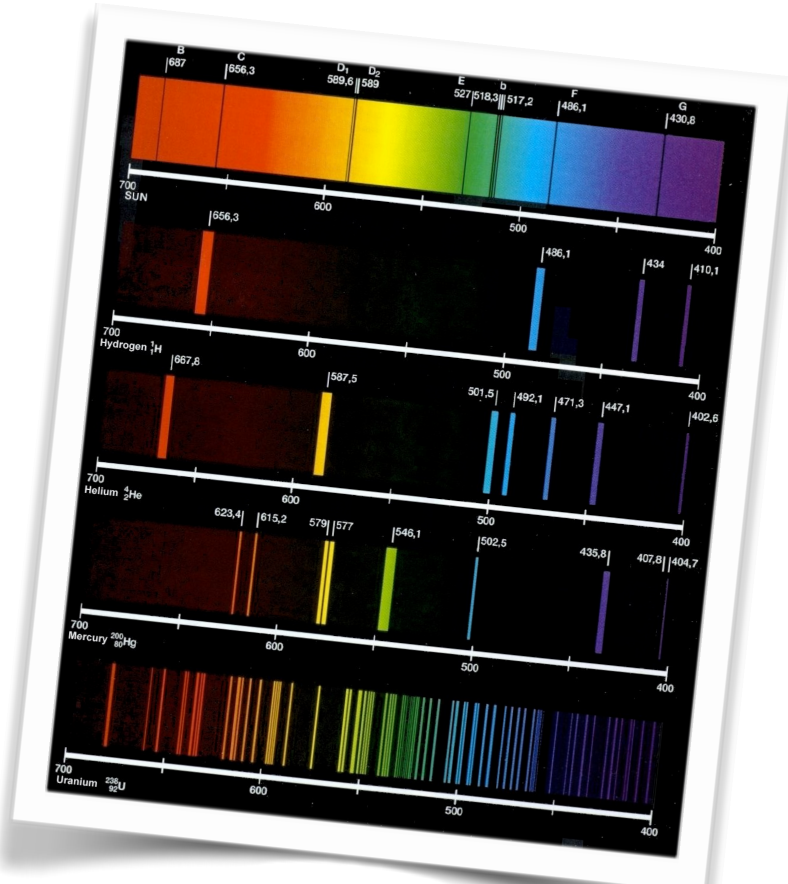
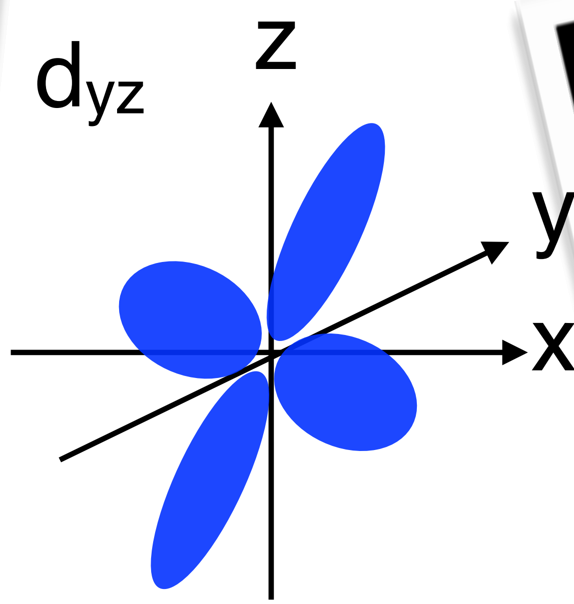
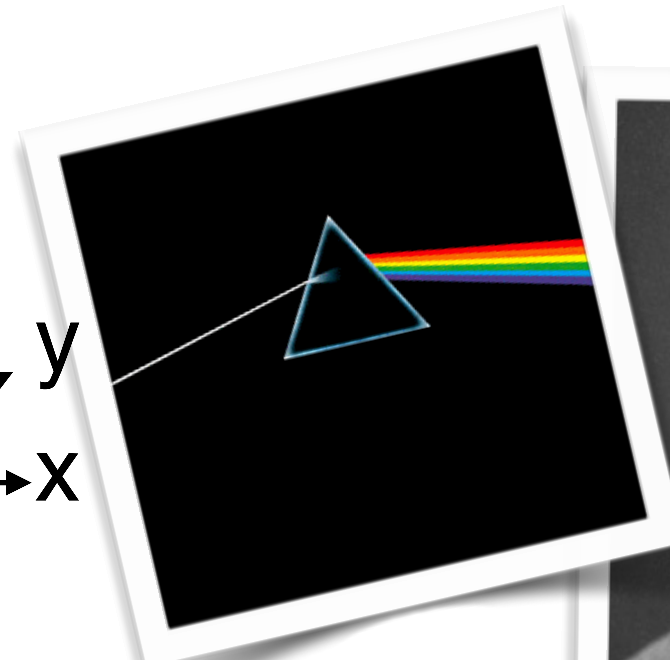
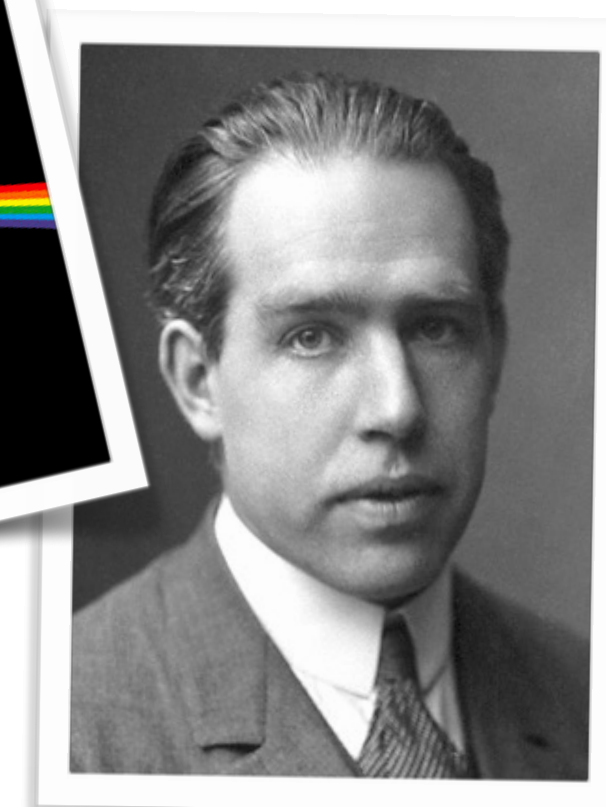
CHEM 100
Principles Of Chemistry





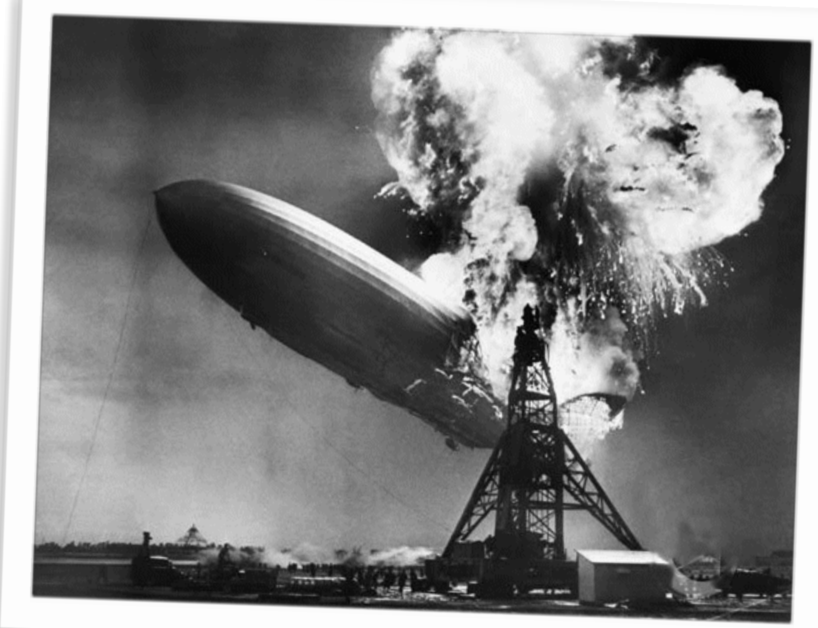




Chapter 7 - Electronic Structure Of Atoms

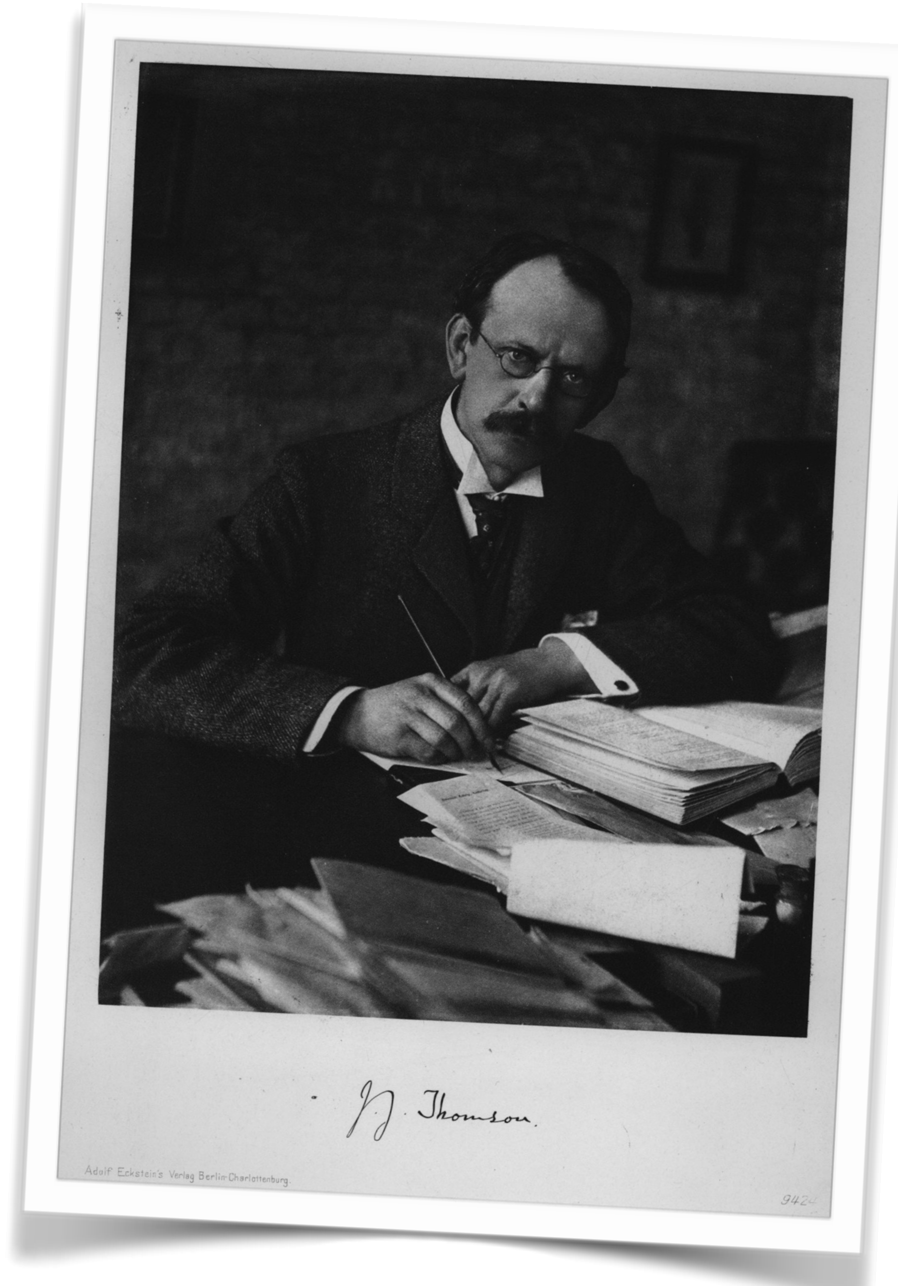
7.1 Balloons and Blimps

- Why is H_2 explosive but He unreactive?
- Why do elements in the same group of the periodic table have similar chemistry?
- Why are some elements metals and some non-metals?
- Why do metals form cations and nonmetals form anions?
- The answers are tied up with the arrangement of electrons in atoms



Electronic Structure Of Atoms

- Many of the properties of the elements can be explained by models of the atoms
- The number of protons and electrons in the atom are fundamentally related to its properties
- Modern descriptions started with the discovery of the electron as a particle by **J.J. Thompson** in 1897



Joseph J. Thompson
1856-1940

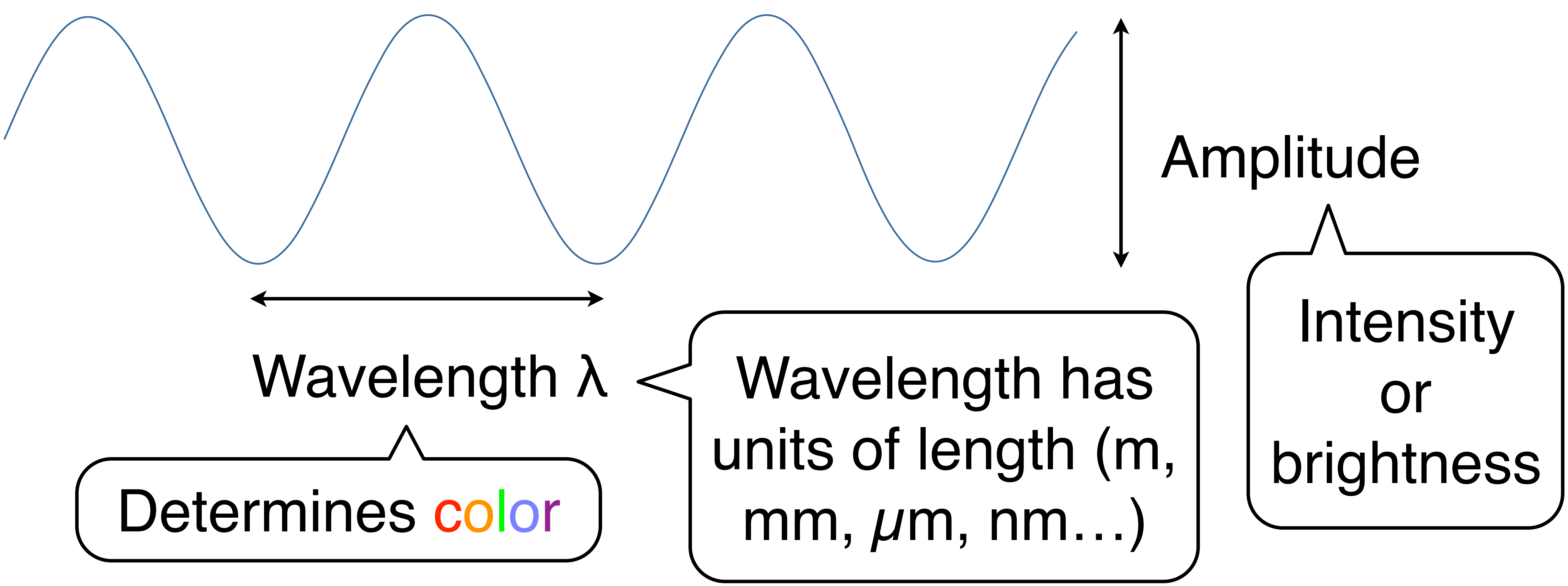
Models Of The Atom

- Several revolutionary concepts developed in the early 1900s followed
- Physicists like **Niels Bohr** (1885-1962), **Albert Einstein** (1879-1955) and **Erwin Schrödinger** (1887-1951) proposed new ideas that were incorporated into new models of the atom

$_{7.2}$ Electromagnetic Radiation

- **Electromagnetic radiation** (light) is not matter (it has no mass)
- It can be described as a wave and defined by its **amplitude** and its **wavelength** (λ)

Greek ‘l’ (lambda)

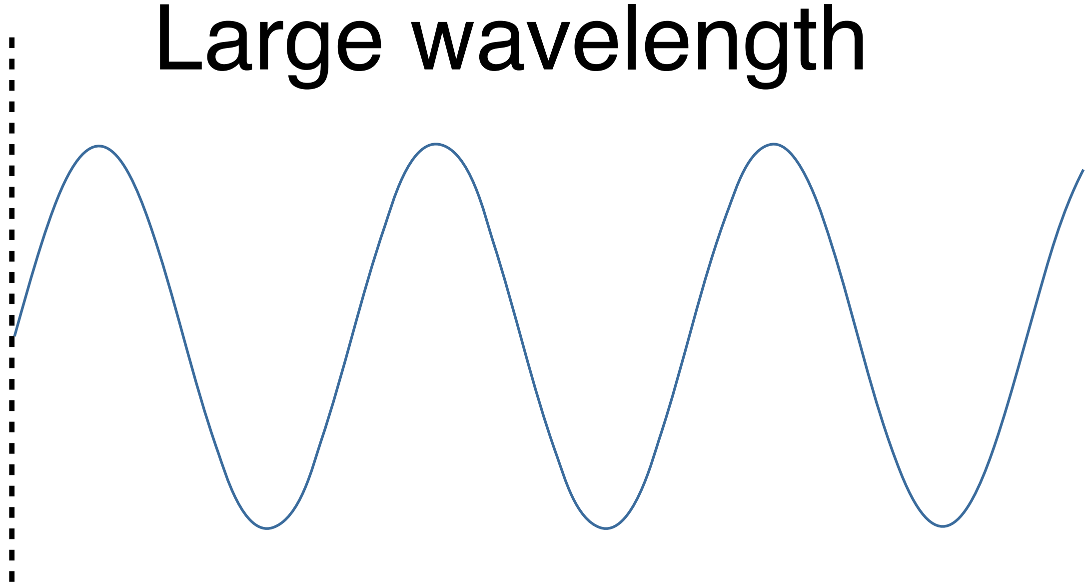


Light As A Wave

Greek ‘n’ (nu)

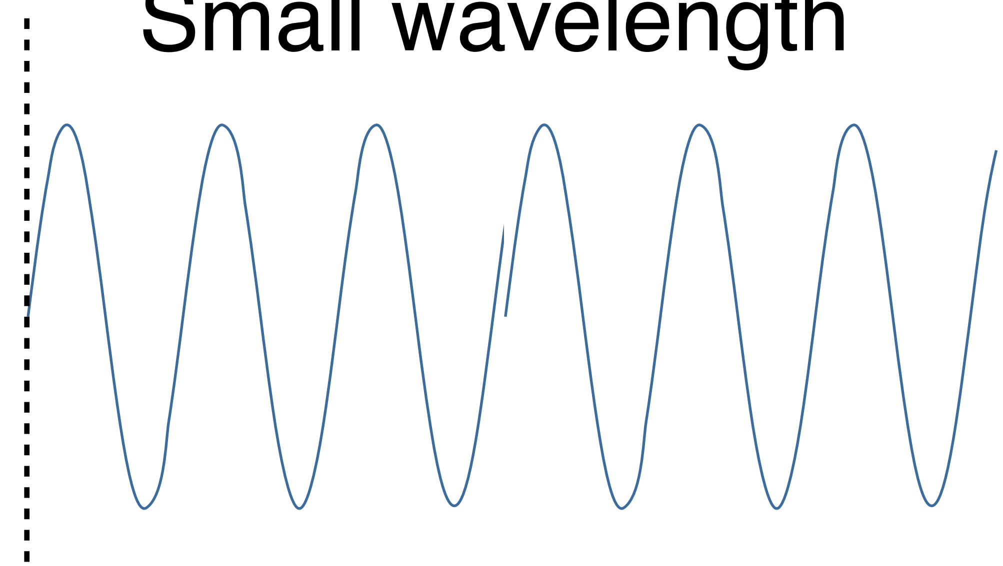
- Another property of a moving wave is **frequency** (ν)
  - Frequency is the number of wave peaks passing a stationary point
  - Units are cycles/s or Hz (Hertz)

Large wavelength



Small frequency

Small wavelength



Large frequency

Wavelength and frequency are inversely proportional

Light As A Wave

- Wavelength and frequency are inversely proportional

$$\nu \propto \frac{1}{\lambda}$$

- We can make this an equality by adding a constant

$$\nu = c \cdot \frac{1}{\lambda} = \frac{c}{\lambda}$$

- The constant is the speed of light ($c = 3.00 \times 10^8$ m/s)

Test Yourself: Electromagnetic Radiation

Q What is the wavelength of an AM radio wave of frequency 1070 kHz?

A Solution map: kHz → Hz (/s) → Wavelength

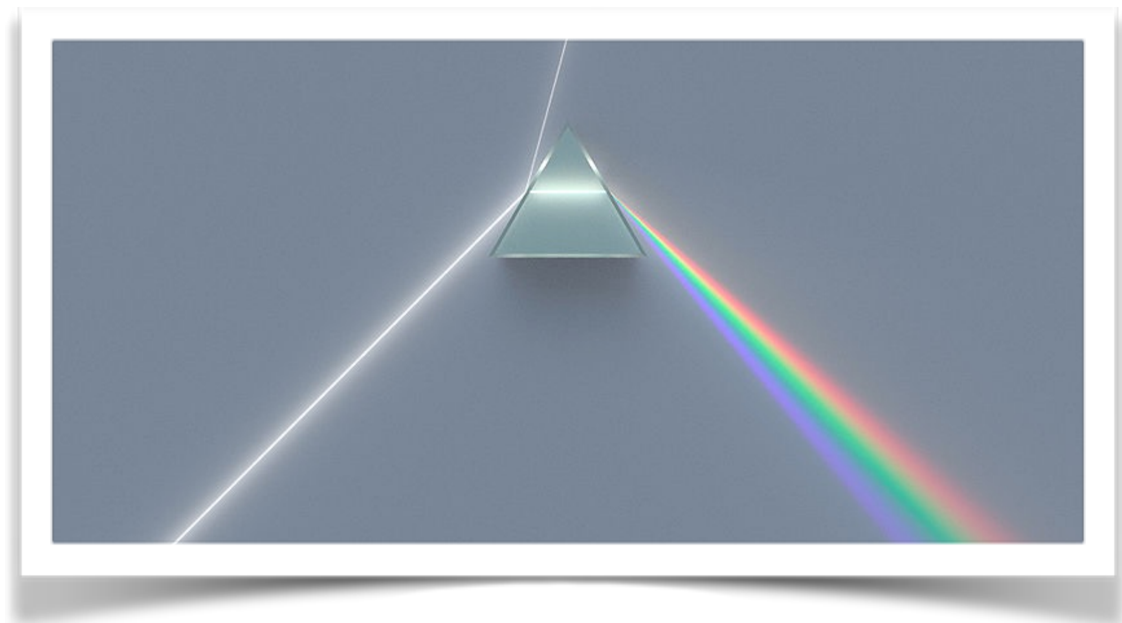
$$1070\ \text{kHz} \times \frac{1000\ \text{Hz}}{1\,\text{kHz}} = 1.070\text{x}10^{6}\ /\ \text{s}$$

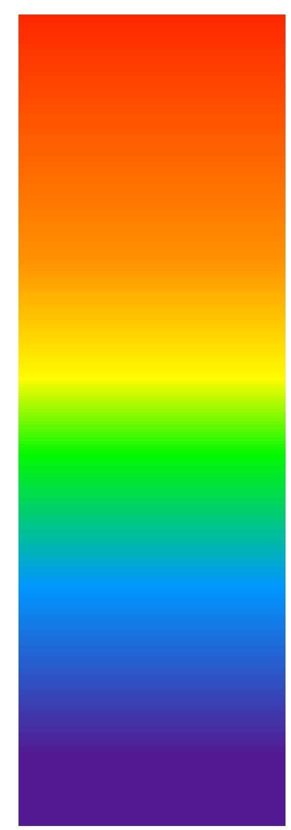
Next, calculate the wavelength

$$\nu = \frac{c}{\lambda} \qquad \lambda = \frac{c}{\nu} = \frac{3.00\text{x}10^{8}\ \text{m}/\text{s}}{1.070\text{x}10^{6}\ /\ \text{s}} = 280\ \text{m}$$

Visible Light

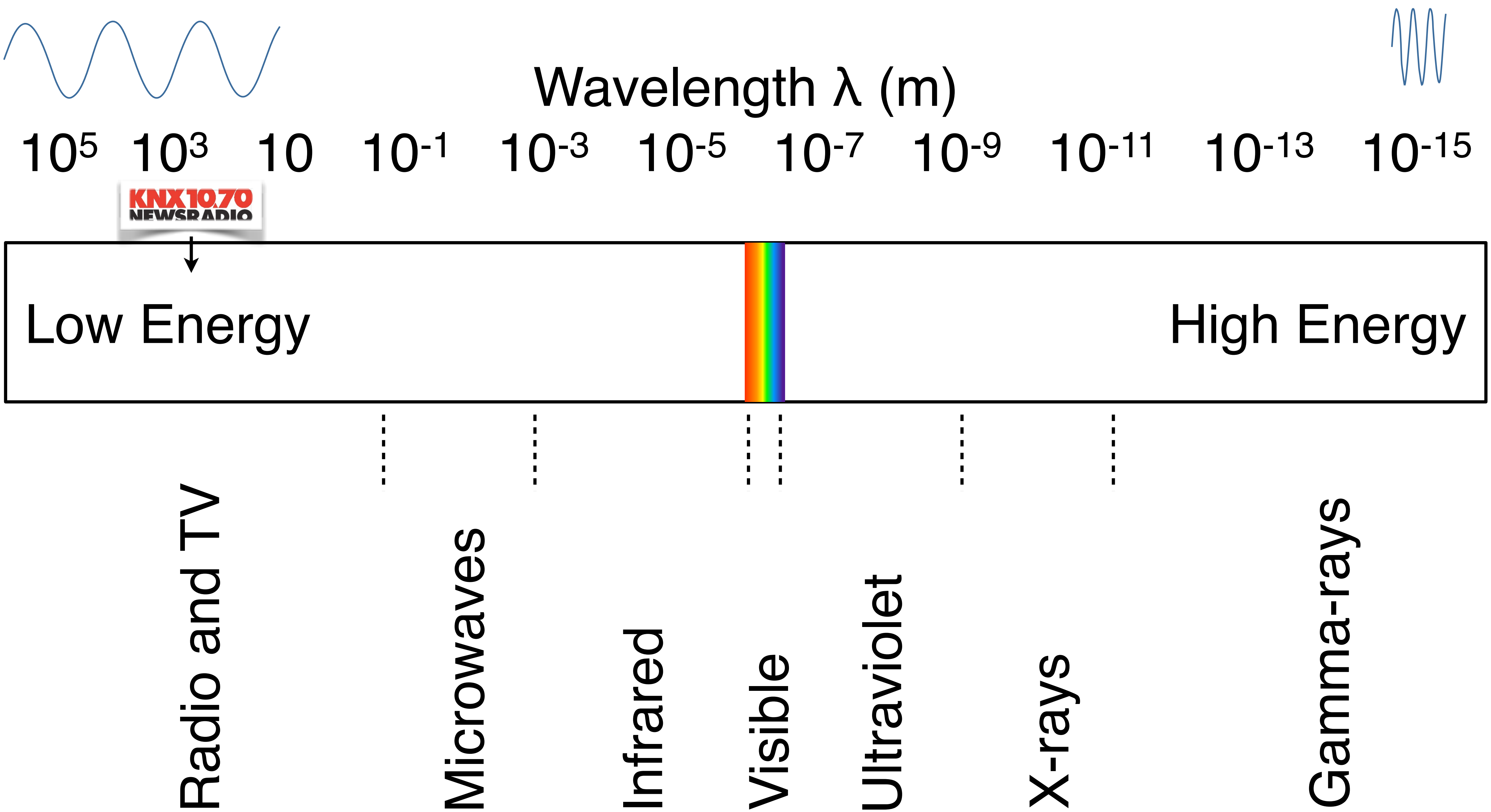
- White (visible) light is split into its component colors by a **prism**
- The human eye perceives a narrow range of wavelengths as a different color
  - The human eye responds from about λ = 750 - 400 nm
- Visible light is only part of the **electromagnetic**





Red (λ ≈ 750 nm)
Orange
Yellow
Green
Blue
Indigo
Violet (λ ≈ 400 nm)

The Electromagnetic Spectrum

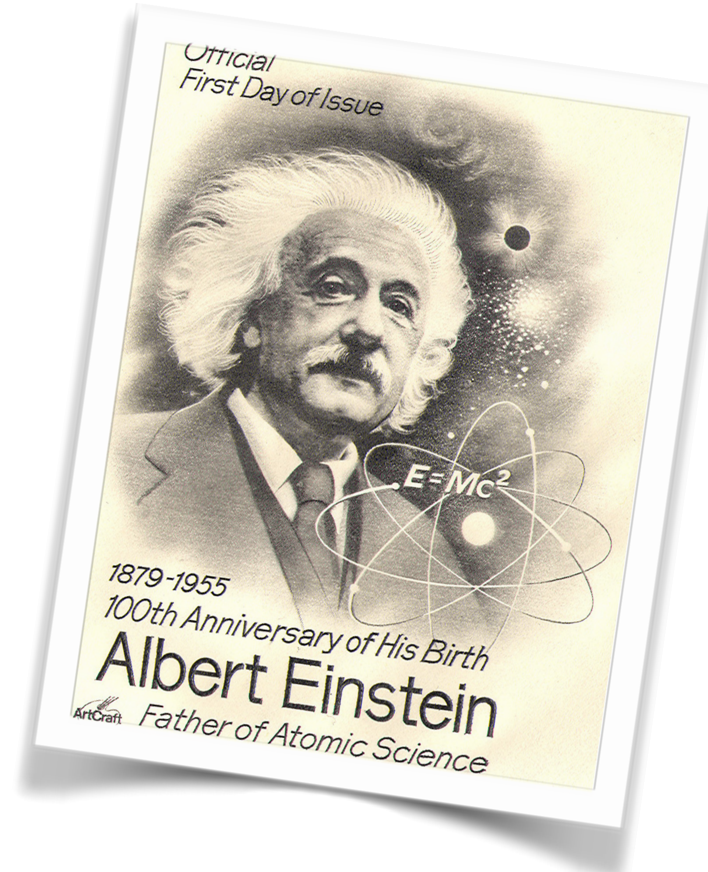


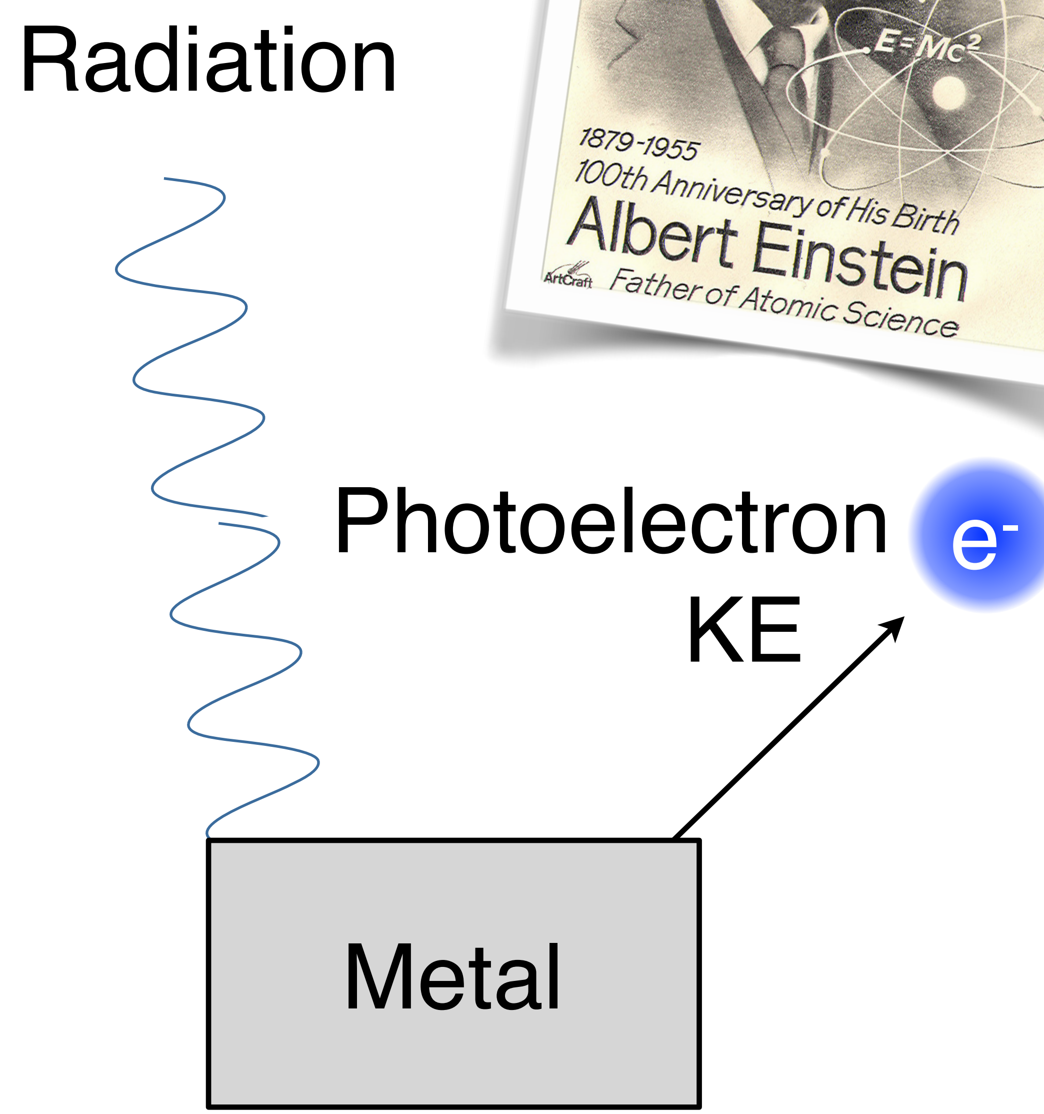
Classes Of Electromagnetic Radiation

- **Gamma rays** - ($\lambda \approx$ pm) produced by stars (cosmic rays) and some radioactive nuclei, kills biological cells
- **X-rays** - travel through most materials, used in x-radiographs, excess causes cancer
- **Ultraviolet** (**UV**) - causes sunburn, excess causes cancer
- **Visible** - causes changes to molecules in the retina responsible for vision, harmless
- **Infrared (IR)** - invisible but can be felt by the skin as heat
- **Microwaves** - causes water molecules to vibrate more intensely, used for ovens and communications

The Photoelectric Effect

- **Albert Einstein** won a Nobel prize for his explanation of the **photoelectric effect**
- Electrons are emitted from a metal when light strikes the metal
  - Electron energy increased with frequency of radiation
  - A minimum frequency is required
  - The number of electrons increased with the brightness



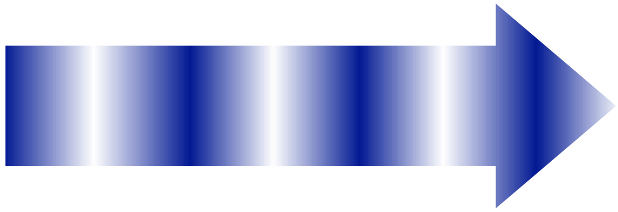


Light As Particles

- Einstein proposed that the photoelectric effect can only be explained if light is a particle
- The light particle is called a **photon**
- The energy of the particle is proportional to its frequency, v

$$E = h \cdot \nu$$

where E is energy (J) and h is **Planck's constant** (6.626×10^{-34} J·s)



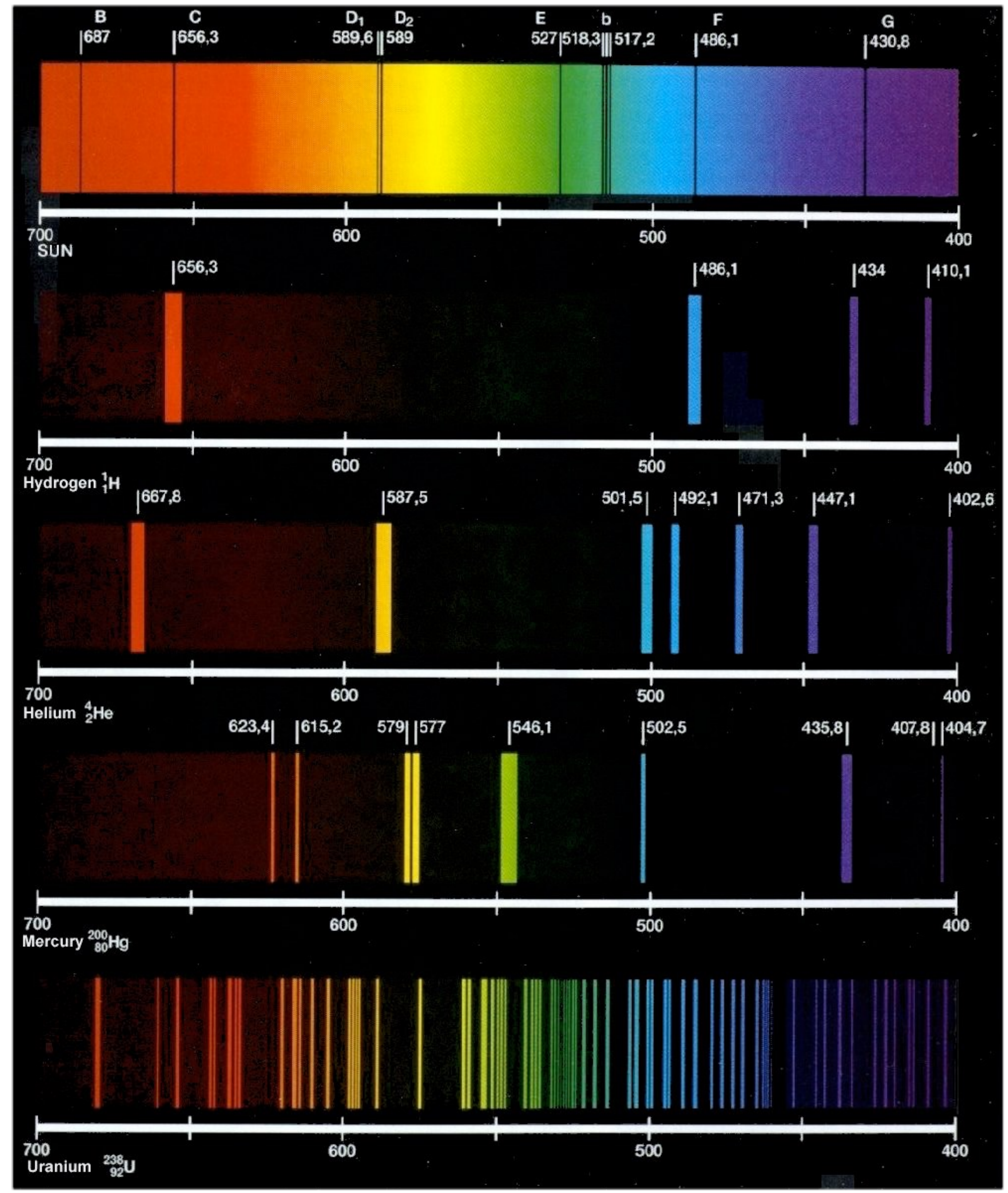
High Energy
Large v
Small λ

Low Energy
Small v
Large λ

Wave-particle duality

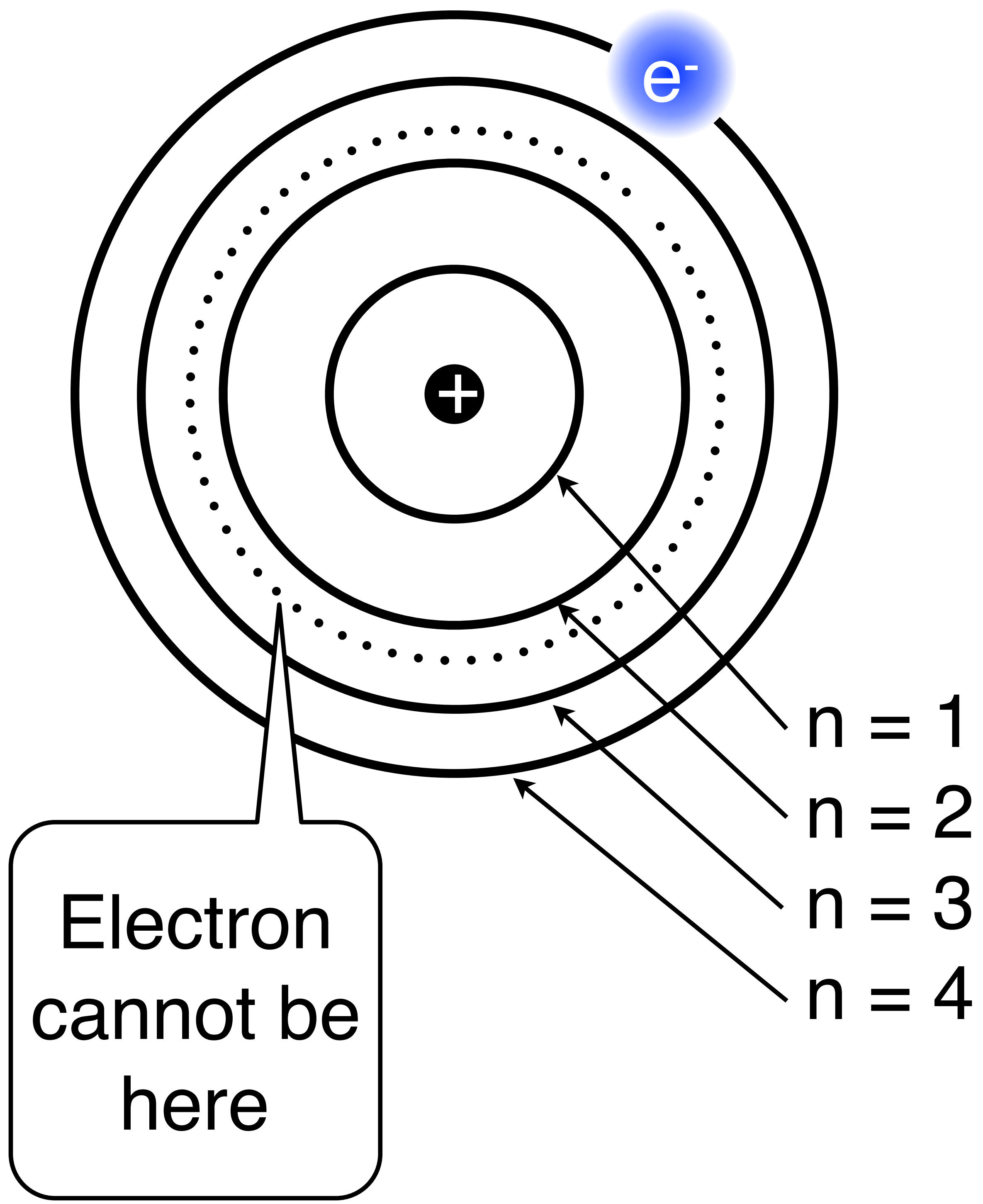
7.3 Absorption And Emission By Atoms

- When atoms **absorb** radiation, they **emit** it again later
- The radiation they absorb or emit is the same and specific to the element
- Atoms emit only certain wavelengths



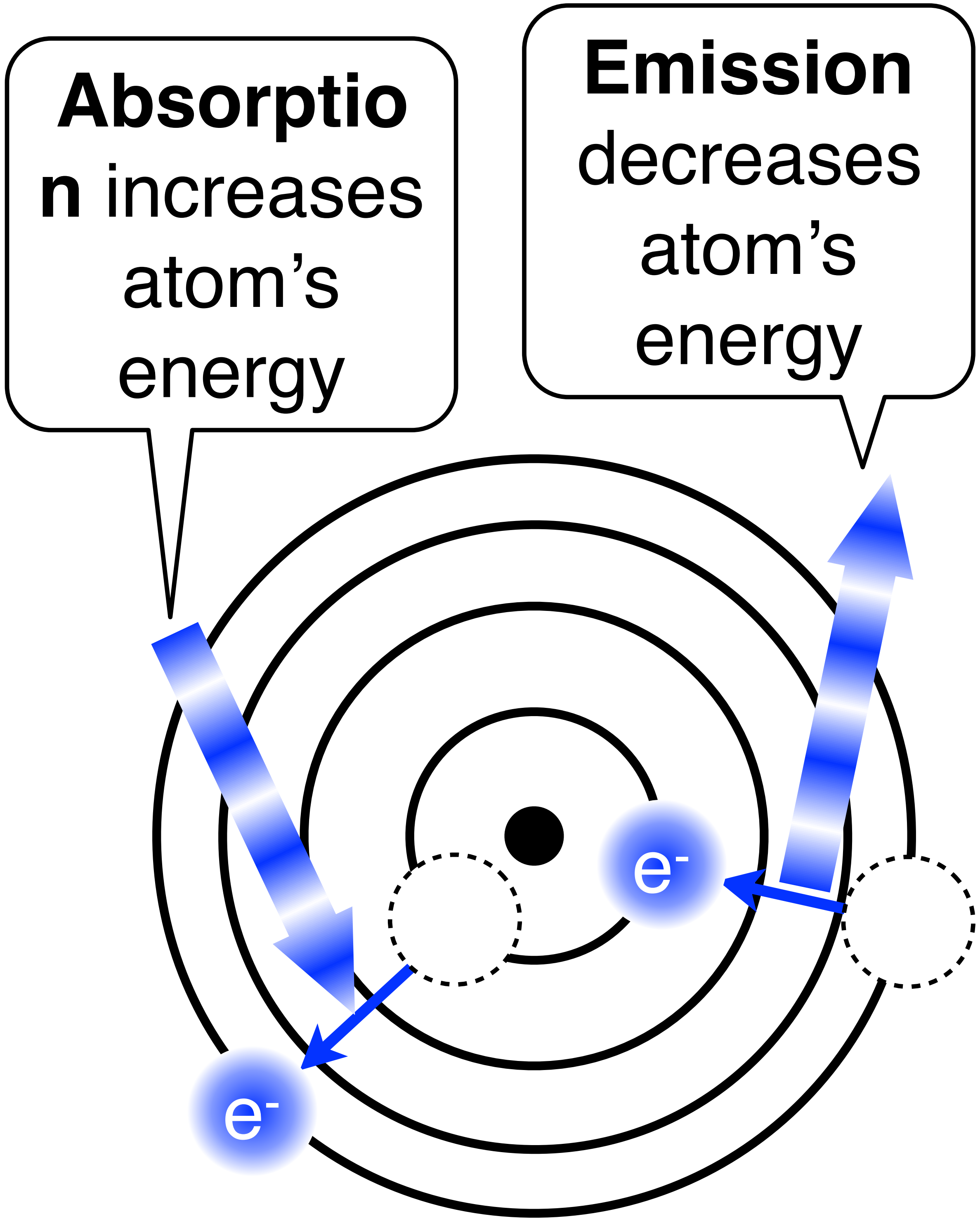
The Bohr Atom

- **Neils Bohr** envisaged the atom with electrons in circular orbits around the nucleus
  - Solar system model
- The potential energy of the orbit increases with distance from the nucleus
- Electrons can only exist in specific energy orbits; their energy is



The Bohr Atom: Radiation Absorption

- When an atom absorbs a photon an electron jumps from small orbits to large orbits
- When an atom emits a photon an electron jumps from large orbits to small orbits
- In both cases the energy change is **quantized**



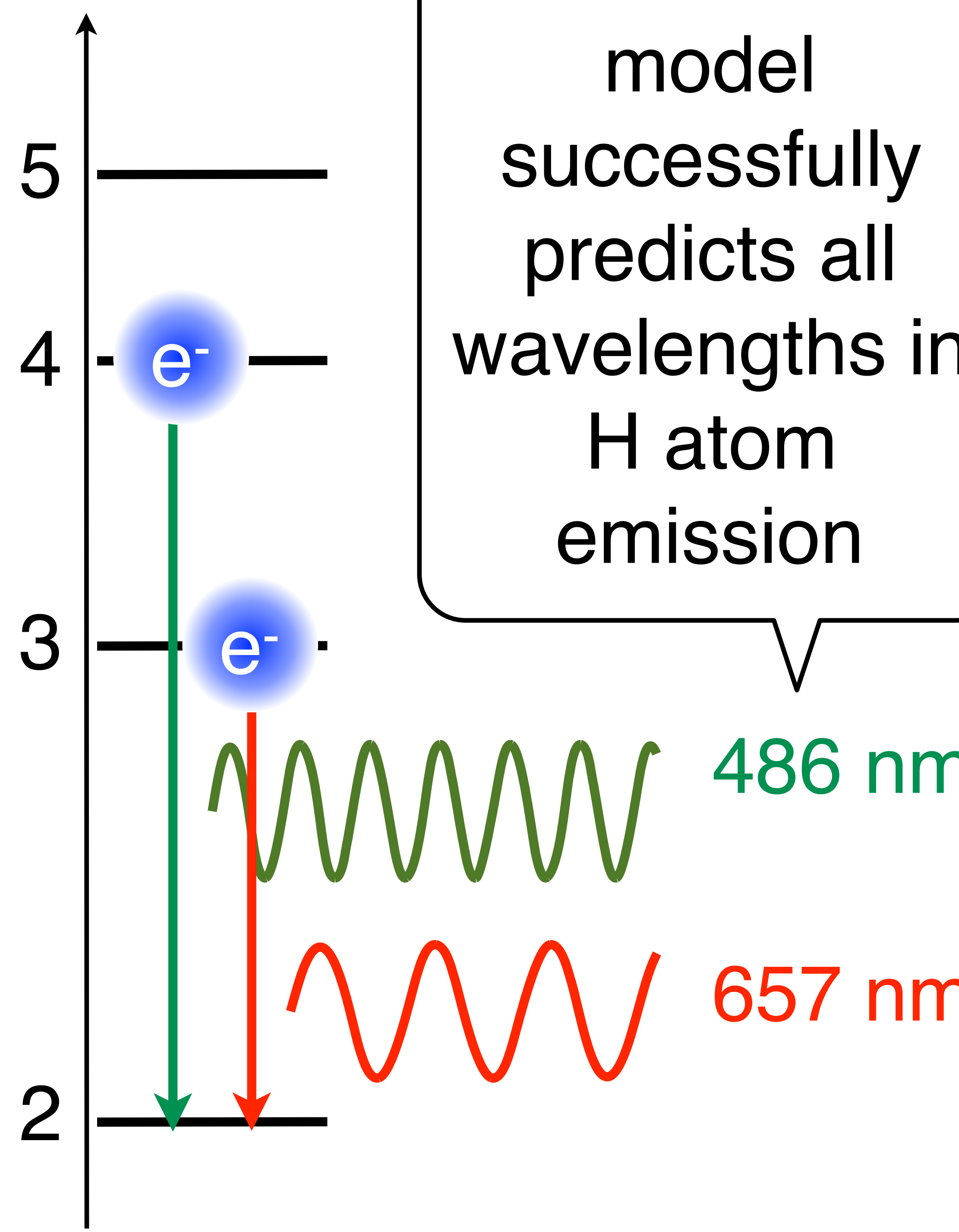
The Bohr Atom

- Each orbit is characterized by a **principal quantum number, n** (1, 2, 3, 4…)
- Each jump between orbits is a fixed amount of energy

$$E_2 - E_4 = \Delta E = h \cdot \nu$$

Large ΔE = Large ν = Small λ

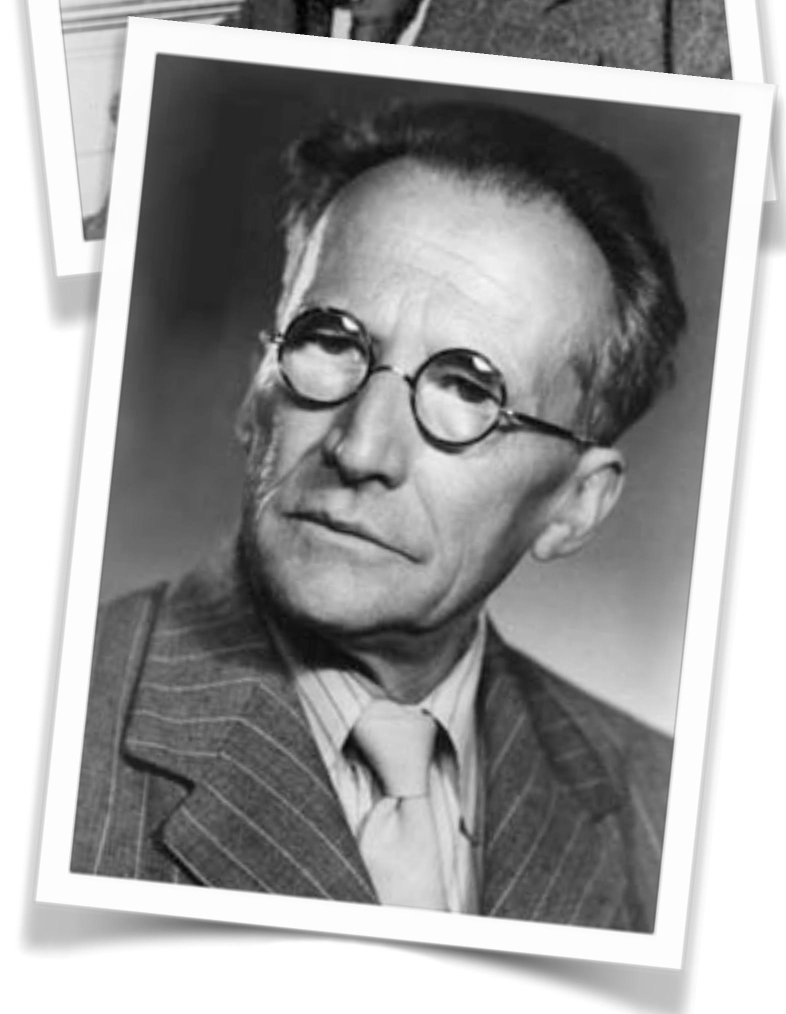
Potential Energy



The Bohr model successfully predicts all wavelengths in H atom emission

7.4 The Quantum-Mechanical Atom

- **Louis de Broglie** (1892-1987) suggested that both electromagnetic radiation and matter can behave like a wave
- These properties were confirmed with electrons
- **Erwin Schrödinger** (1887-1961) developed a mathematical model based on the wave-particle properties of electrons
- The Bohr model was replaced by the **quantum-mechanical**

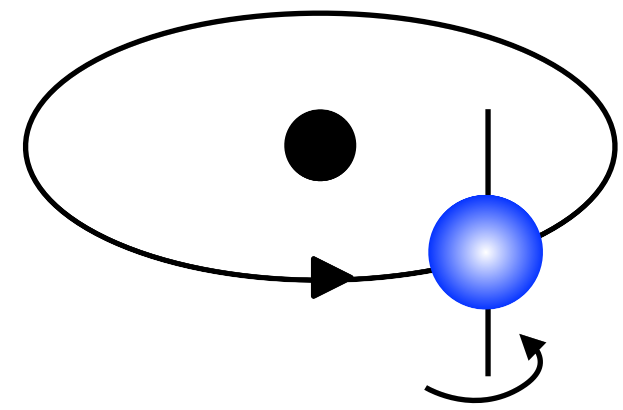


Properties Of Electrons In The Quantum-Mechanical Atom

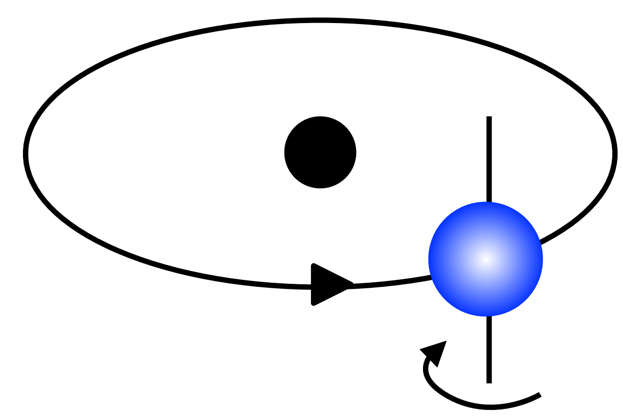
1. Electrons occupy definite energy states characterized by the **principal quantum number** ($n = 1, 2, 3, 4\ldots$)
   - The $n = 1$ state has the lowest potential energy, is most tightly-held and is closest (on average) to the nucleus
   - Electrons occupy the lowest n state preferentially
2. Each state has n **sublevels**, called **orbitals**, designated s, p, d, f
   - For a given state, energy varies $s < p < d < f$
   - Electron motion for a particular orbital is unknown but theory can describe where the electron is likely to be
   - Each sublevel has a specific shape and orientation
3. No more than two electrons of opposite **spin** can occupy each orbital

Properties Of Electrons In The Quantum-Mechanical Atom

- Electrons possess a property called **spin**?
  - Electrons can spin in only two directions, **up** or **down**
- Like the Bohr model, electrons are confined in quantized energy levels but orbits are replaced by orbitals and the motion is much more complex
- The model naturally predicts that electrons have an average distance from the nucleus



Spin up



Spin down

Possible Energy State Combinations

Principal energy level	Possible sublevels	Number of orbitals	Total number of e^-	Designation
n = 1	s	1	2	1s
n = 2	s	1	2	2s
	p	3	6	2p
n = 3	s	1	2	3s
	p	3	6	3p
	d	5	10	3d
n = 4	s	1	2	4s
	p	3	6	4p
	d	5	10	4d
	f	7	14	4f

Test Yourself: Quantum Numbers

Q Which of the following orbitals cannot exist?

1s, 2s, 3s, 3p, 2d, 4f, 3f, 2p, 4p, 4d

A Write out all the possible combinations

n = 1: 1s

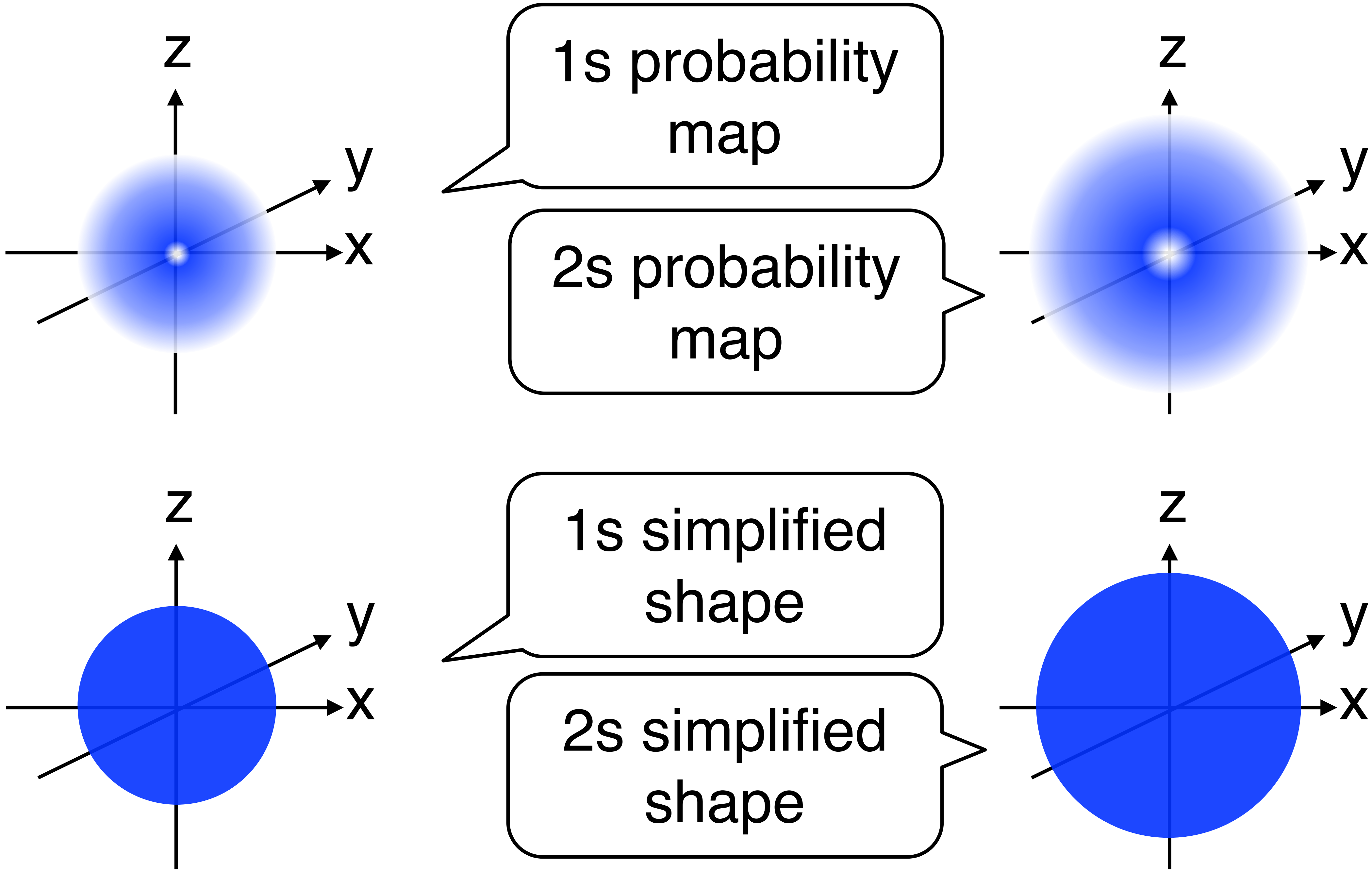
n = 2: 2s, 2p

n = 3: 3s, 3p, 3d

n = 4: 4s, 4p, 4d, 4f

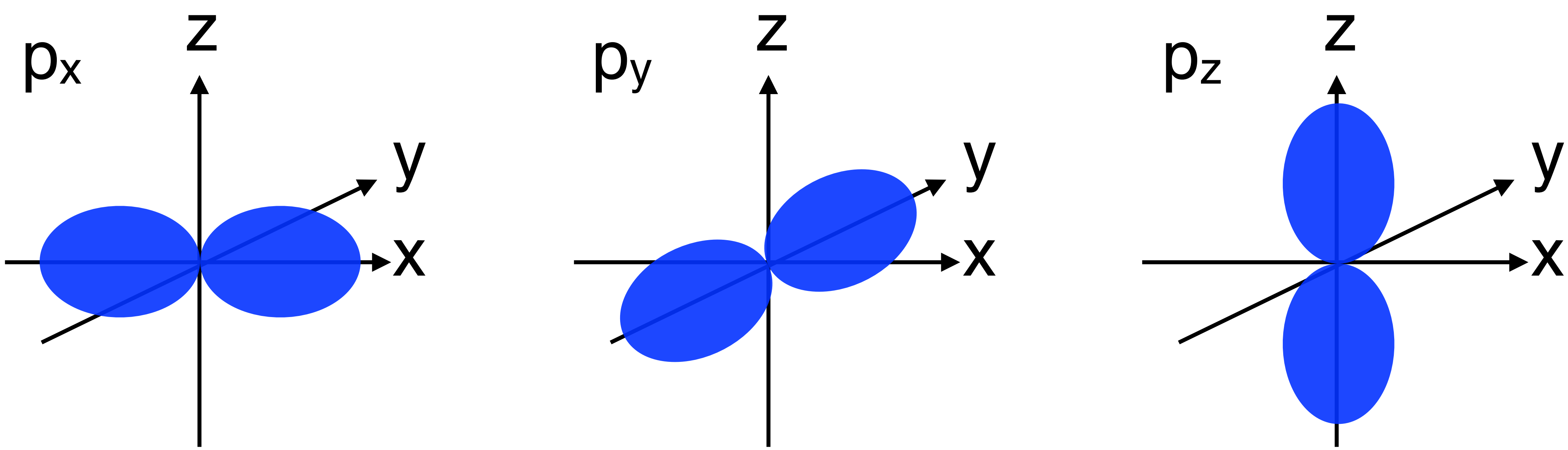
The orbitals that cannot exist are the 2d and 3f

Shapes Of Orbitals



- All s orbitals are <u>spherical</u>

Simplified Shapes Of p Orbitals



- All p orbitals are "<u>peanut</u> <u>shaped</u>"
- There are **three** equivalent-energy **p orbitals** pointed in different directions in space
- Similarly, there are **five** equivalent-energy **d orbitals** and **seven** equivalent-energy **f orbitals**

7.5 Electron Configurations

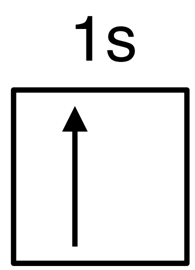
- Electrons add to orbitals in order of lowest energy to highest energy
  - When all electrons are in the lowest possible combination of orbitals, we say the electrons are in the **ground state**
  - When some electrons are in higher energy orbitals, we say the electrons are in the **excited state**
- Electrons occupy orbitals in pairs
  - Two electrons fit in each orbital with opposite spins
- The ground state **electronic configuration** of H is written as $1s^1$

Means 1 electron in the 1s orbital

Electron Configurations

- We could also write the electron configuration as an **orbital diagram**

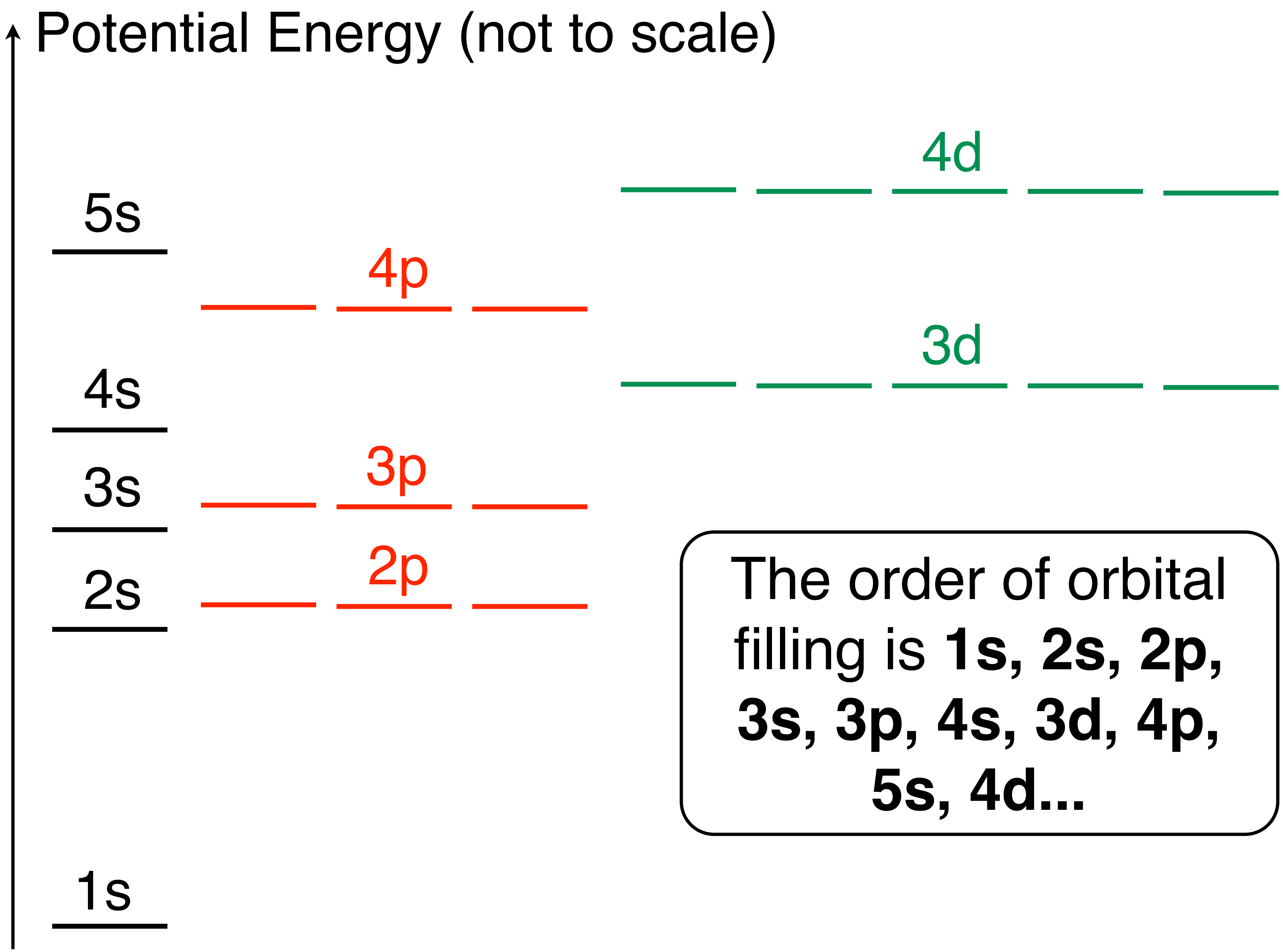
$1s^1$ =



Only space for 1 more electron ($1s^2$)

- The arrow represents the electron spin (spin up)
- Remember, each orbital can hold a maximum of two electrons only (with opposing spins)

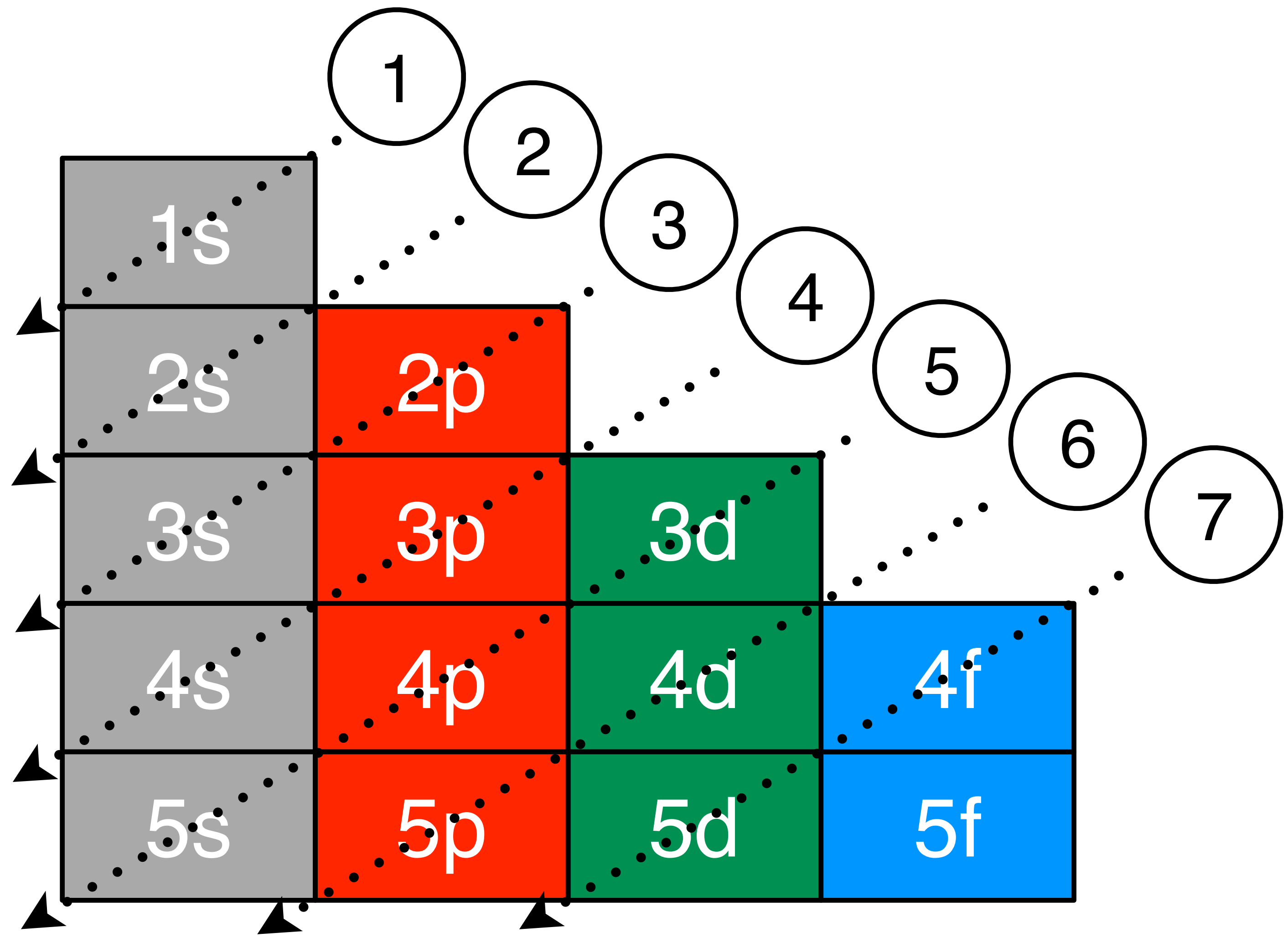
Energy Of Orbitals And Order Of Filling



The order of orbital filling is **1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d...**

Energy Of Orbitals And Order Of Filling

1. Add electrons to orbitals starting at the lowest energy
2. Add two electrons to each orbital with opposite spins
3. Keep electrons unpaired if energy-equivalent orbitals are available (**Hund's rule**)



The order of orbital filling is **1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d...**

7.6 Electron Configurations: H to C

Element	Number Of Electrons	Orbital diagram					Electron Configuration
		1s	2s	2p			3s	
H	1	↑						$1s^1$
He	2	↑↓						$1s^2$
Li	3	↑↓	↑					$1s^2 2s^1$
Be	4	↑↓	↑↓					$1s^2 2s^2$
B	5	↑↓	↑↓	↑				$1s^2 2s^2 2p^1$
C	6	↑↓	↑↓	↑	↑			$1s^2 2s^2 2p^2$

Electron Configurations: N to Mg

Element	Number Of Electrons	Orbital diagram				Electron Configuration
		1s	2s	2p	3s	
N	7	↑↓	↑↓	↑ ↑ ↑		$1s^22s^22p^3$
O	8	↑↓	↑↓	↑↓ ↑ ↑		$1s^22s^22p^4$
F	9	↑↓	↑↓	↑↓ ↑↓ ↑		$1s^22s^22p^5$
Ne	10	↑↓	↑↓	↑↓ ↑↓ ↑↓		$1s^22s^22p^6$
Na	11	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑	$[Ne]3s^1$
Mg	12	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	$[Ne]3s^2$

Test Yourself: Electron Configurations

Q What is the electron configuration of Cl?

A Cl (Z = 17) has 17 electrons

$1s^2 2s^2 2p^6 3s^2 3p^5$ or $[Ne]3s^2 3p^5$

Q What is the electron configuration of Mg^{2+}?

A Mg^{2+} (Z = 12) has 10 electrons

$1s^2 2s^2 2p^6$ or [Ne]

Q What is the electron configuration of S^{2-}?

A S^{2-} (Z = 16) has 18 electrons

$1s^2 2s^2 2p^6 3s^2 3p^6$ or [Ar]

17	12	16
Cl	Mg	S
35.45	24.31	32.07

Valence Electrons And The Periodic Table

- The outer electrons of an atom are held least tightly
  - These electrons are involved in chemical bonding and reactions
- **Valence electrons** are electrons in the highest n shell
- All other electrons are **core electrons**

F $\underbrace{1s^2}_{\text{core}}\overbrace{2s^2 2p^5}^{\text{valence}}$

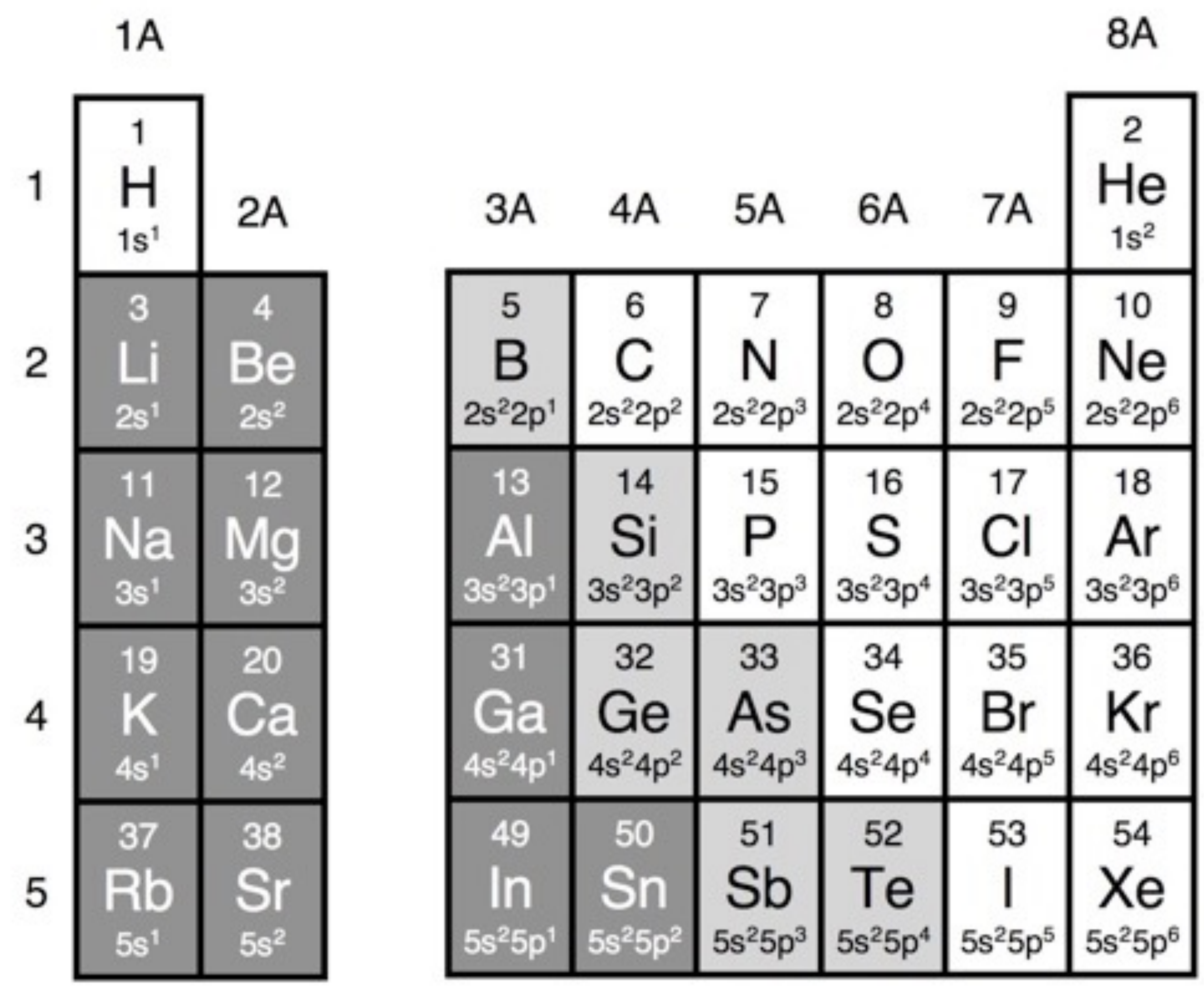
Na $\underbrace{1s^2 2s^2 2p^6}_{\text{core}}\ \overbrace{3s^1}^{\text{valence}}$

Fluorine has 7 valence electrons

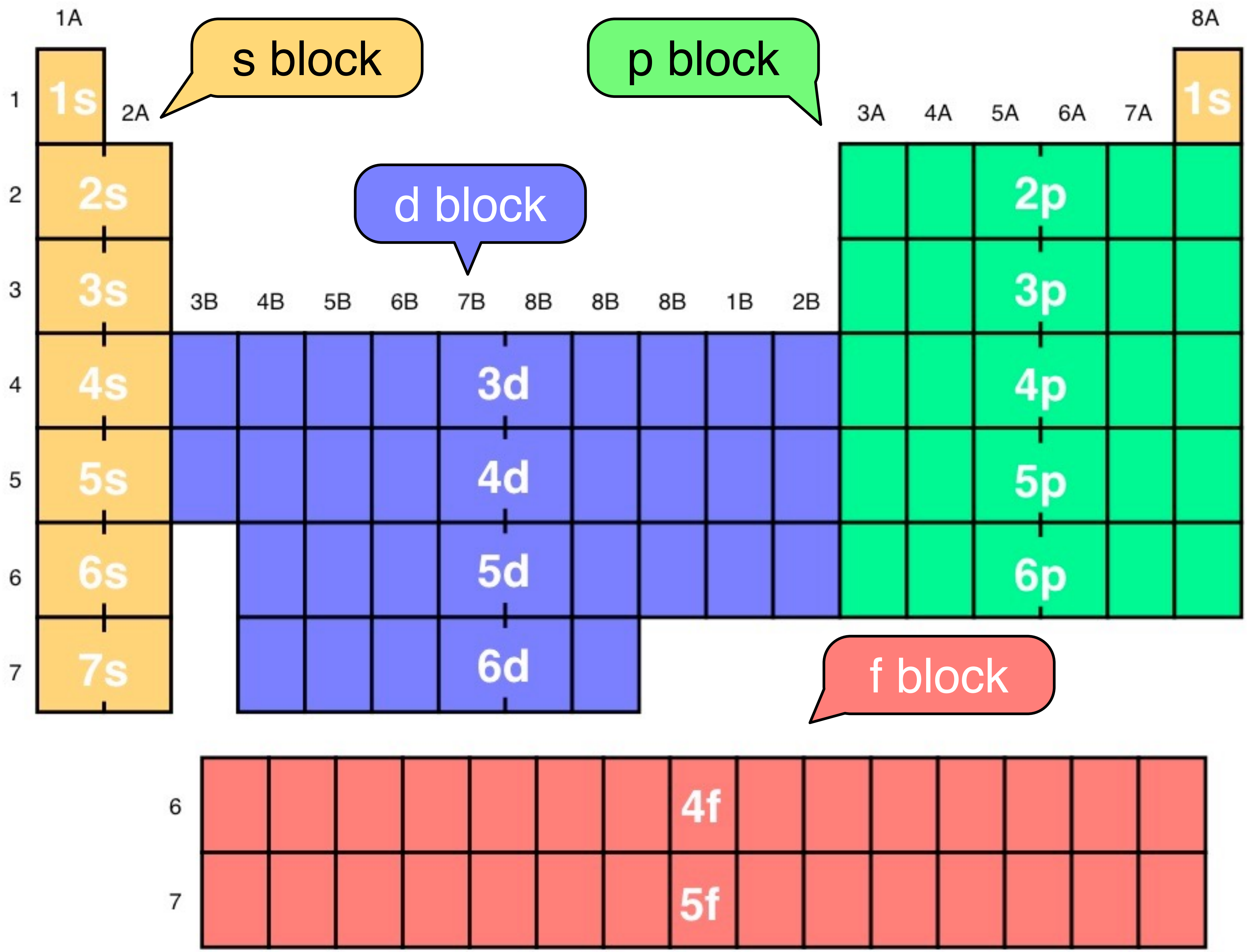
Ti $\underbrace{1s^2 2s^2 2p^6 3s^2 3p^6}_{\text{core}}\ \overbrace{4s^2}^{\text{valence}}\ \underbrace{3d^2}_{\text{core}}$

Valence Electrons And The Periodic Table

- The period number corresponds with n for the outer electrons
- The A group number corresponds with the total number of valence electrons
- All elements in the same group have the same number and type of valence



All halogens have the outer electron configuration ns^2np^5

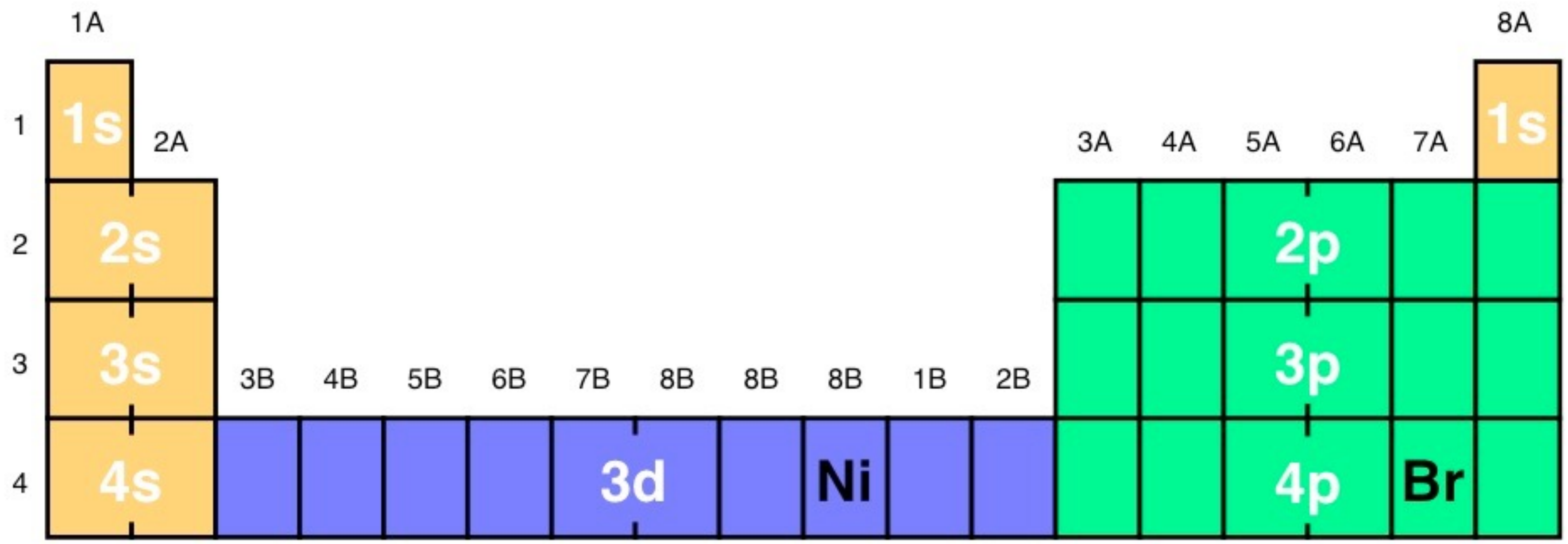

s block
p block
d block
f block
1A
8A
2A
3A
4A
5A
6A
7A
3B
4B
5B
6B
7B
8B
8B
8B
1B
2B
1
2
3
4
5
6
7
1s
2s
3s
4s
5s
6s
7s
2p
3p
4p
5p
6p
3d
4d
5d
6d
6
7
4f
5f

Energy Of Orbitals And Order Of Filling

- We can use the periodic table to determine the electron configuration (and orbital filling order) very easily

Q What are the electron configurations of Ni and Br?

A

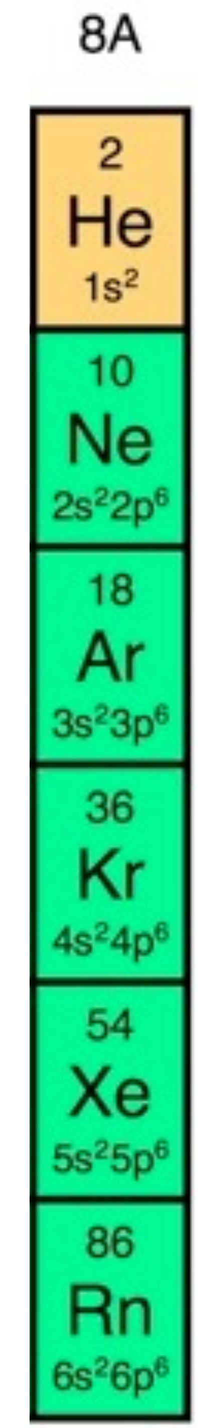


Ni = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^8$

Br = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^5$

Electron Configurations And The Periodic Table

- The chemical properties of an element are largely determined by the number of valence electrons
- For example, the noble gases (group 8A) all have very low reactivity and are associated with filled subshells
- A filled subshell is associated with special stability
- Elements near the noble gases are reactive because by gaining or losing a few electrons they can achieve this special stability



Electron Configurations And The Periodic Table

Q What are the electron configurations of Na^+ and Ne?

A Na^+ (Z = 11) has 10 electrons: $1s^2 2s^2 2p^6$

Ne (Z = 10) has 10 electrons: $1s^2 2s^2 2p^6$

Q What are the electron configurations of S^{2-} and Ar?

A S^{2-} (Z = 16) has 18 electrons: $1s^2 2s^2 2p^6 3s^2 3p^6$

Ar (Z = 18) has 18 electrons: $1s^2 2s^2 2p^6 3s^2 3p^6$

- Atoms tend to form stable ions with the <u>same electron configuration as the nearest noble gas</u>
  - Works best for groups 1A, 2A, 3A, 6A, 7A

10
Ne
20.18

11
Na
22.99

16
S
32.07

18
Ar
39.95

Explaining Chemical Properties With The Periodic Table

- We know that metals form **cations** by losing electrons and nonmetals form **anions** by gaining electrons
- We can use the periodic table to explain why
  - The explanation is based on **Coulomb's law**: the attraction between the electron and nucleus
- The energy to remove a valence e^- depends on the number of positive nuclear charges (atomic number Z)
  - If Z is high, the electron will be less likely to be removed
- But intervening electrons reduce the effect of the nuclear charge by '**shielding**' it

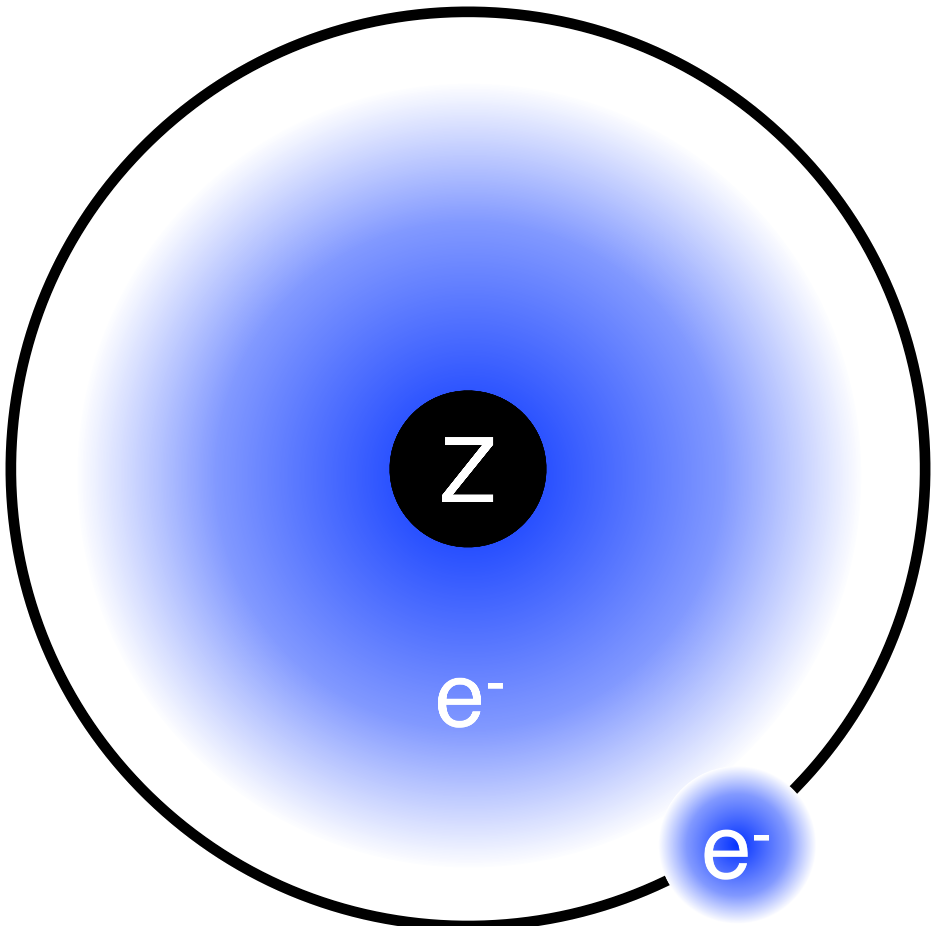
Explaining Element Properties With The Periodic Table

- The nuclear charge experienced by the valence e^- is not Z but the smaller **effective nuclear charge Z_{eff}**

$$Z_{eff} = Z - \sigma$$

  where σ ~ number of lower n electrons

- Z_{eff} determines the attraction between e^- and nucleus



This e^- experiences reduced nuclear charge, Z_{eff}, partly cancelled out by inner e^-

Explaining Element Properties With The Periodic Table

Q What is Z_{eff} for Na and Cl?

A Na = $1s^2\ 2s^2\ 2p^6\ 3s^1$

Z = 11 and σ = 10 ($1s^2\ 2s^2\ 2p^6$)

So Z_{eff} = 11 - 10 = <u>1</u>

Cl = $1s^2\ 2s^2\ 2p^6\ 3s^5$

Z = 17 and σ = 10 ($1s^2\ 2s^2\ 2p^6$)

So Z_{eff} = 17 - 10 = <u>*7*</u>

- Note that it is much easier to remove a valence electron from Na than Cl!

Na holds its valence electrons weakly

Cl holds its valence electrons tightly

Explaining Element Properties With The Periodic Table

- The large Z_{eff} applies to all elements on the right side of the periodic table (the nonmetals)
- In the case of Cl, the large Z_{eff} attracts electrons towards itself, even those from other nearby atoms
- When Na and Cl atoms are close, the Cl atom attracts the valence electron of Na more strongly than Na can hold onto it
  - An electron is **transferred** and an **ionic bond** is formed