Chapter 6
Electronic Structure and Periodic Properties of Elements

Buffalo State
State University of New York

Jamie Kim
Department of Chemistry
Buffalo State College

Goals

In atoms, there are electrons
(e.g., 8 electrons in neutral oxygen atom).

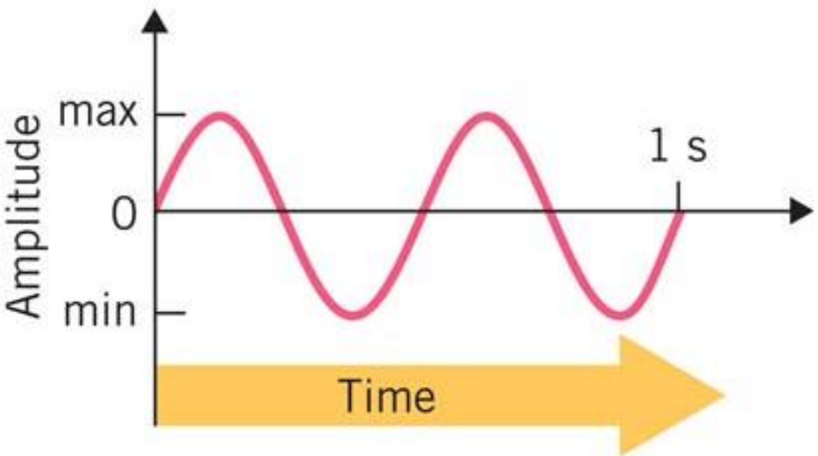
1. Where are they located?

2. How can we describe it?

3. Atomic orbitals (AOs)

Light as Wave: Maxwell

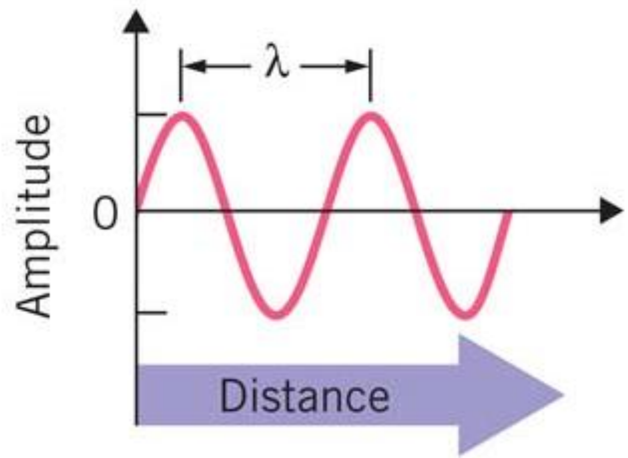
Frequency



Number of complete cycles per second

Unit: Hz (the same as sec^{-1})

Wavelength



Distance between two peaks

Speed of Light

$$c = \lambda \cdot \nu = 3 \times 10^8 \, m/\sec$$

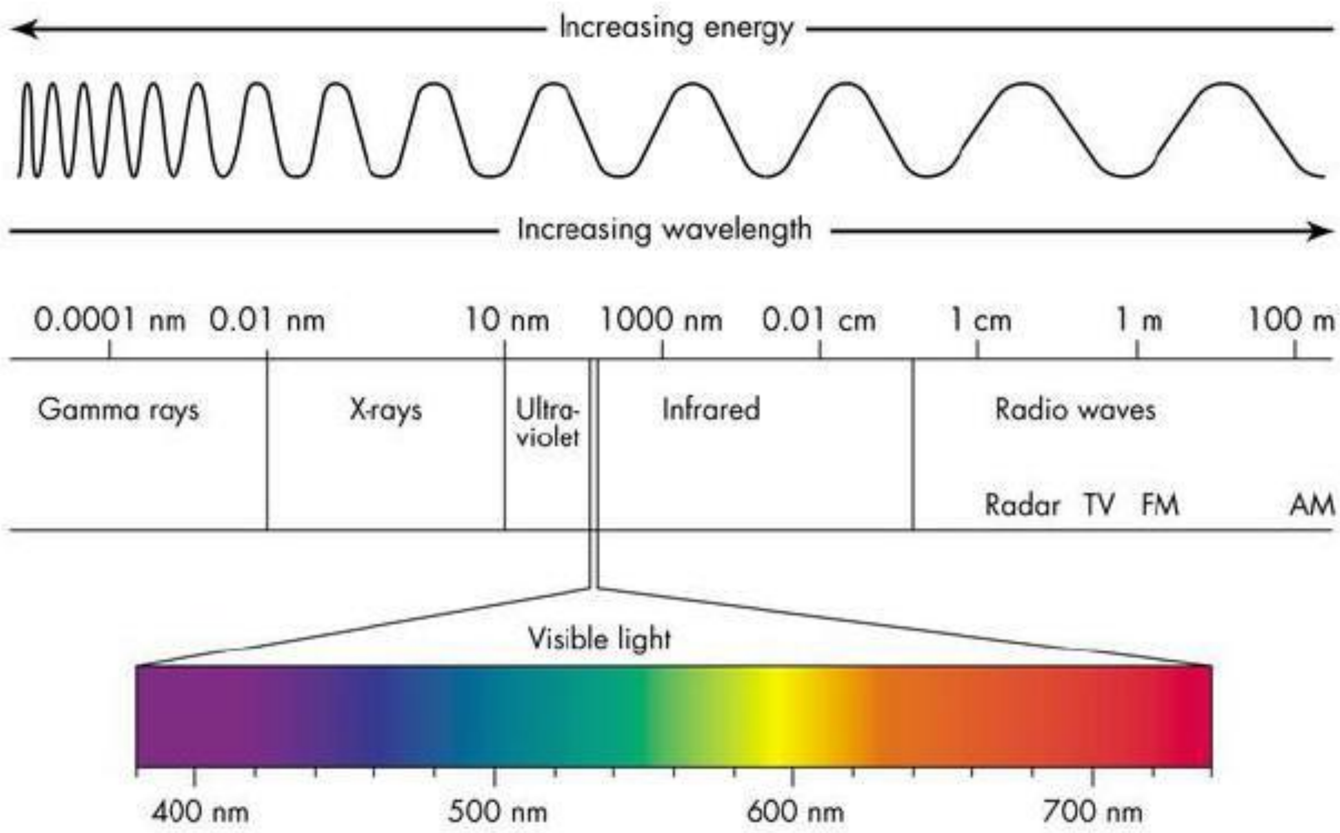
$$\lambda : wavelength$$

$$\nu : \; freqency$$

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

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

Light: Electromagnetic Radiation



- Different energies and wavelengths
- Travels through space at speed of light in vacuum
- ***c*** **= speed of light** = 2.9979×10^8 m/s ≈ 3×10^8 m/s

Light frequency and wavelength

- What is the frequency of 488 nm blue light?

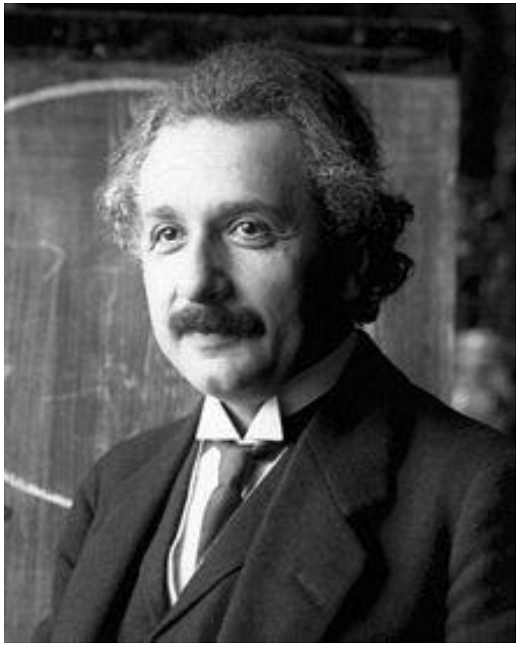
(Note: 1 nm = 10^{-9} m)

Light as Particle (Photons)

- Max Planck

- Einstein

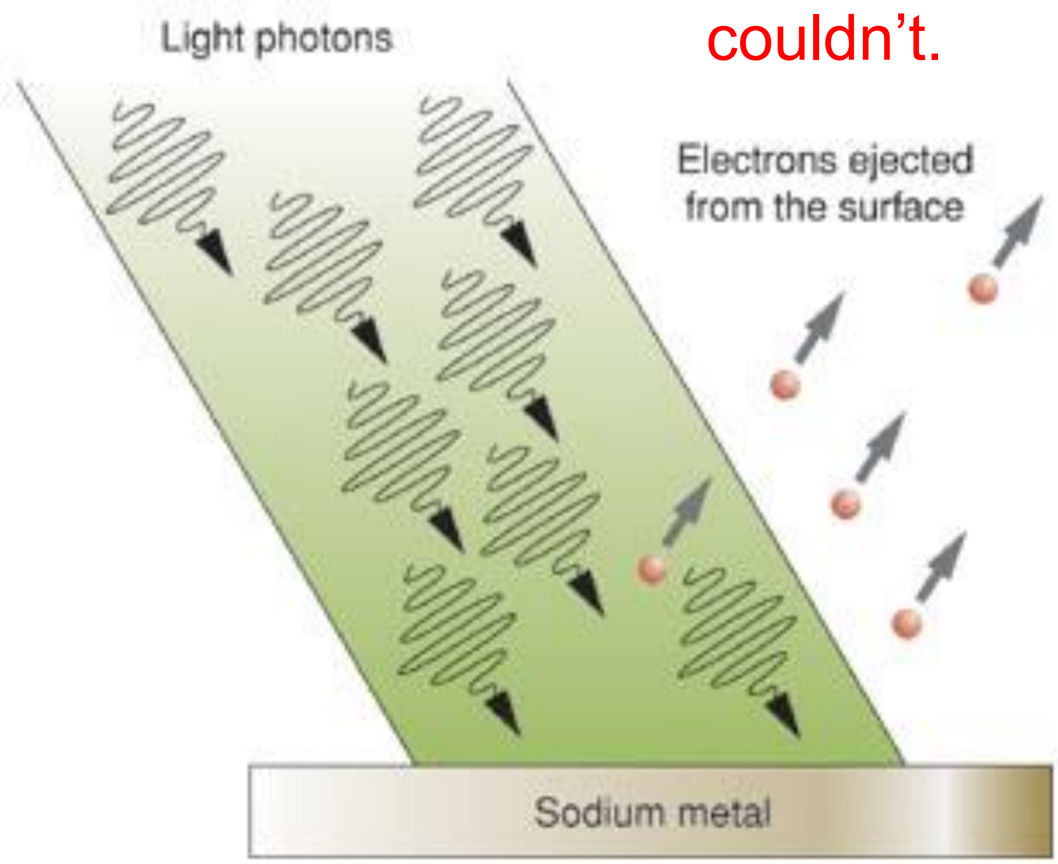
Nobel Prize in Physics
In 1918



Nobel Prize in Physics
In 1921

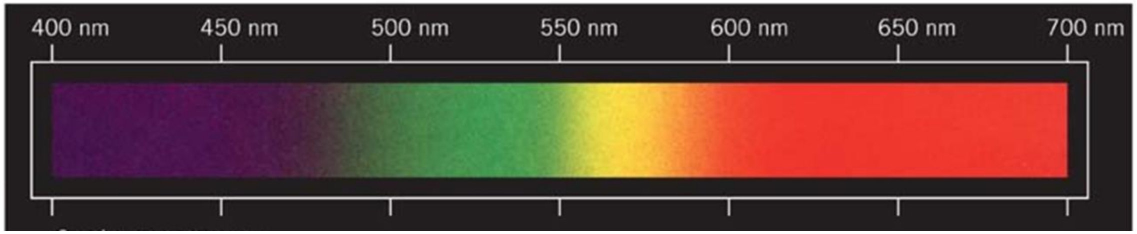
Photoelectric Effect by Einstein

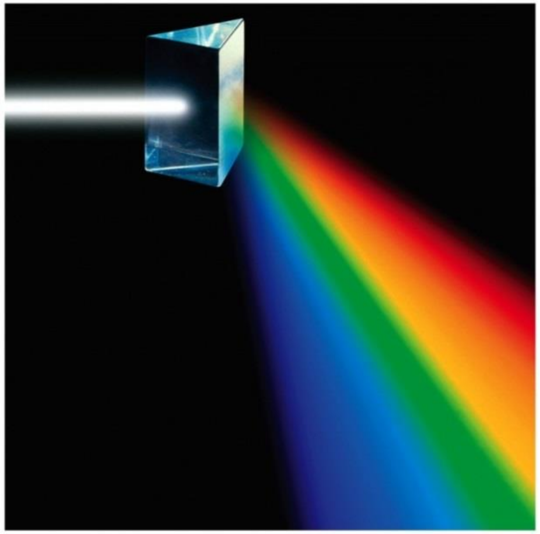
Blue light (high energy) could eject electrons, but red light (low energy) couldn’t.



White Light (Sunlight): Produces continuous spectrum

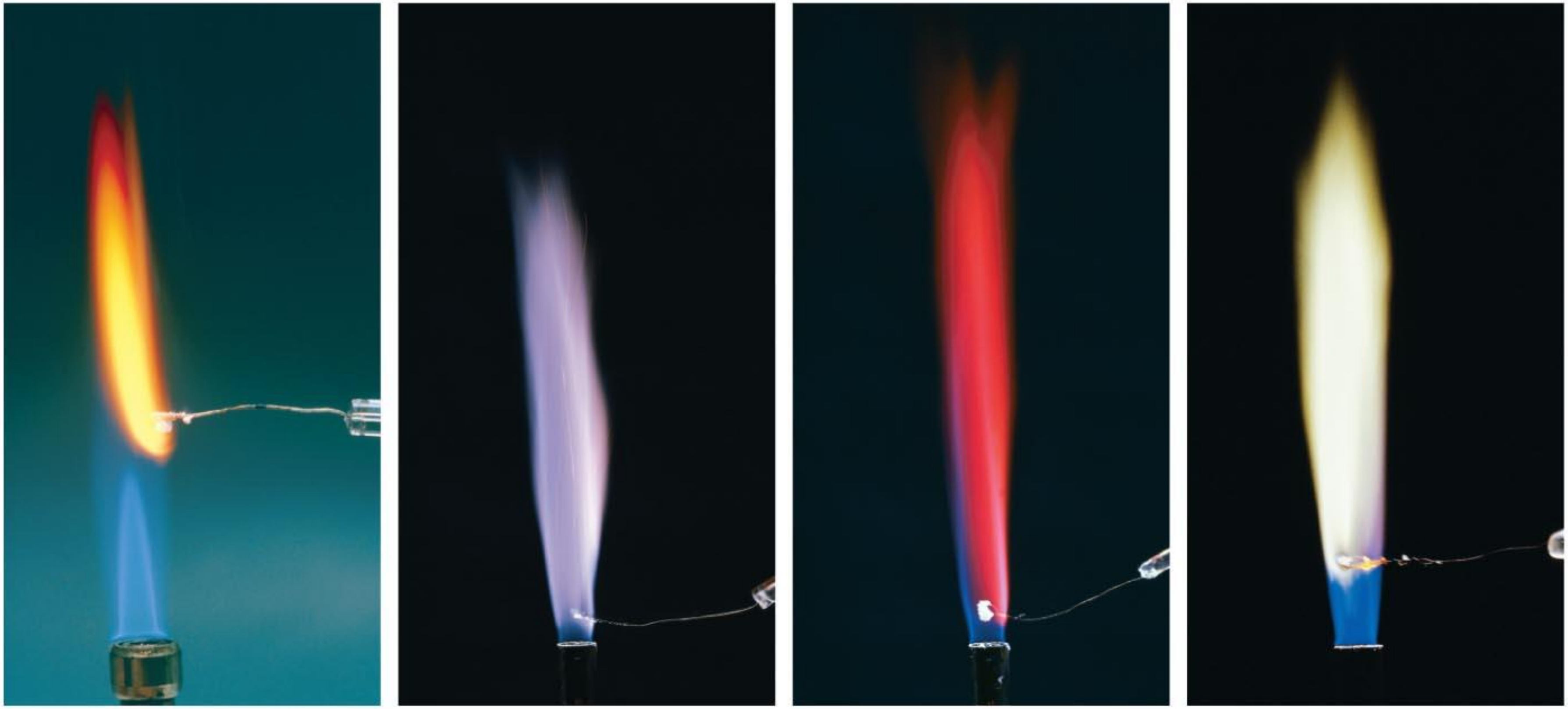
- White light can be separated by prism
- Band of λ's that human eyes can see
- 400 to 700 nm
- Make up spectrum of colors
- 700 nm **ROYGBIV** 400 nm





(c)

Every element produces different colors by flame tests, why?

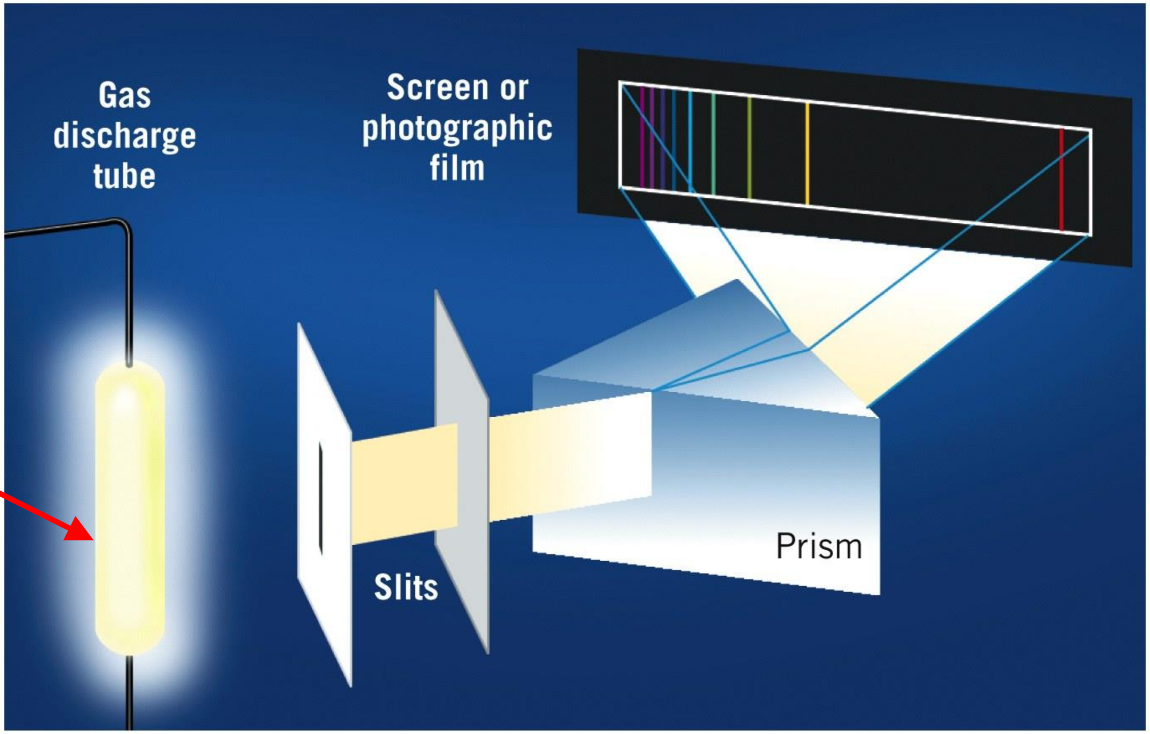


Na K Li Ba

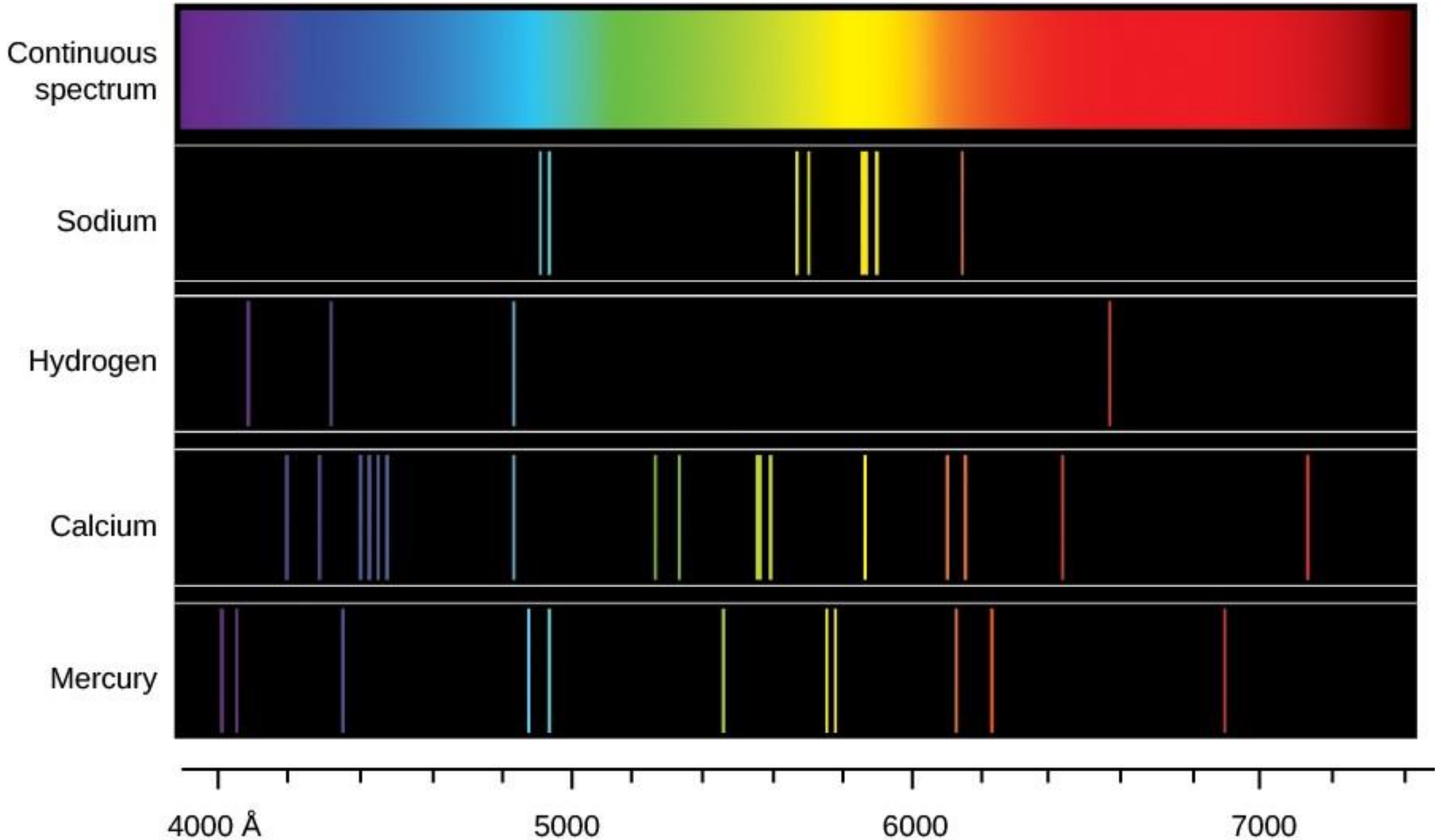
Line Spectrum

- Spectrum that has only a few discrete lines
- Also called **atomic spectrum** or **emission spectrum**
- Each element has unique emission spectrum

hydrogen atoms



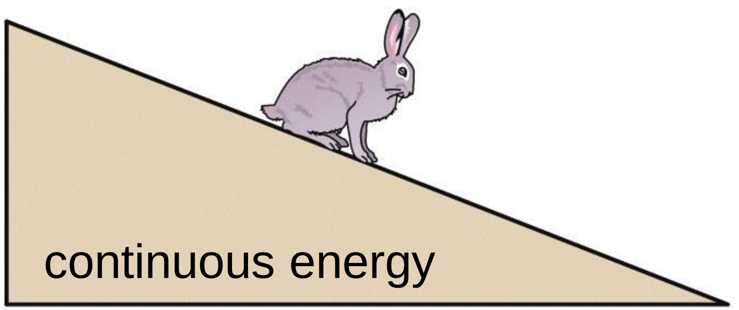
Examples of Spectra



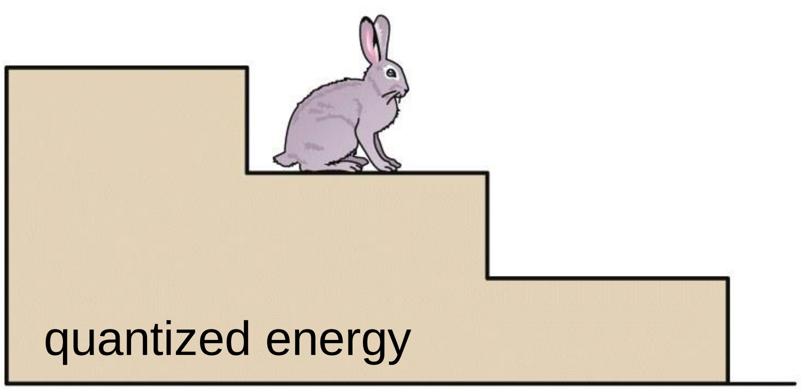
Significance of Atomic Spectra

- Atomic line spectra tells us
  - When excited atom loses energy
    - Only fixed amounts of energy can be lost
    - Only certain **energy** photons are emitted
    - Electron restricted to certain fixed **energy levels** in atoms
  - Energy of electron is **<u>quantized</u>**

What Does “Quantized” Mean?



(*a*) Any potential energy allowed:
energy values are *continuous*



(*b*) Potential energy restricted:
energy values are *discrete*

- Energy is quantized if only certain discrete values are allowed
- Presence of discontinuities makes atomic emission **quantized**

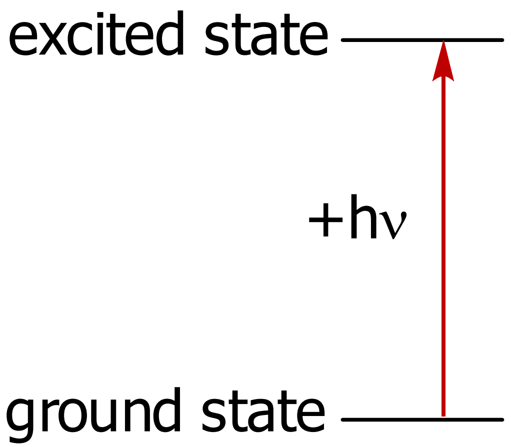
Quantum Mechanical Explanation of Atomic Spectra

- Each wavelength in the spectrum of an atom corresponds to an electron transition between orbitals
- When an electron is **excited**, it transitions from an orbital in a lower energy level to an orbital in a higher energy level
- When an electron **relaxes**, it transitions from an orbital in a higher energy level to an orbital in a lower energy level
- When an electron relaxes, a photon of light is released whose energy equals the energy difference between the orbitals

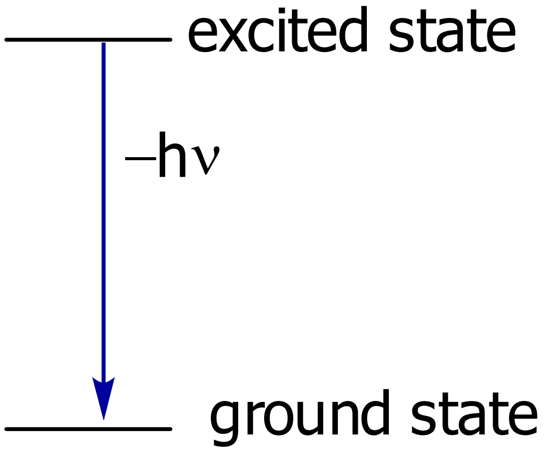
Electronic Structure of Atom

Most information comes from:

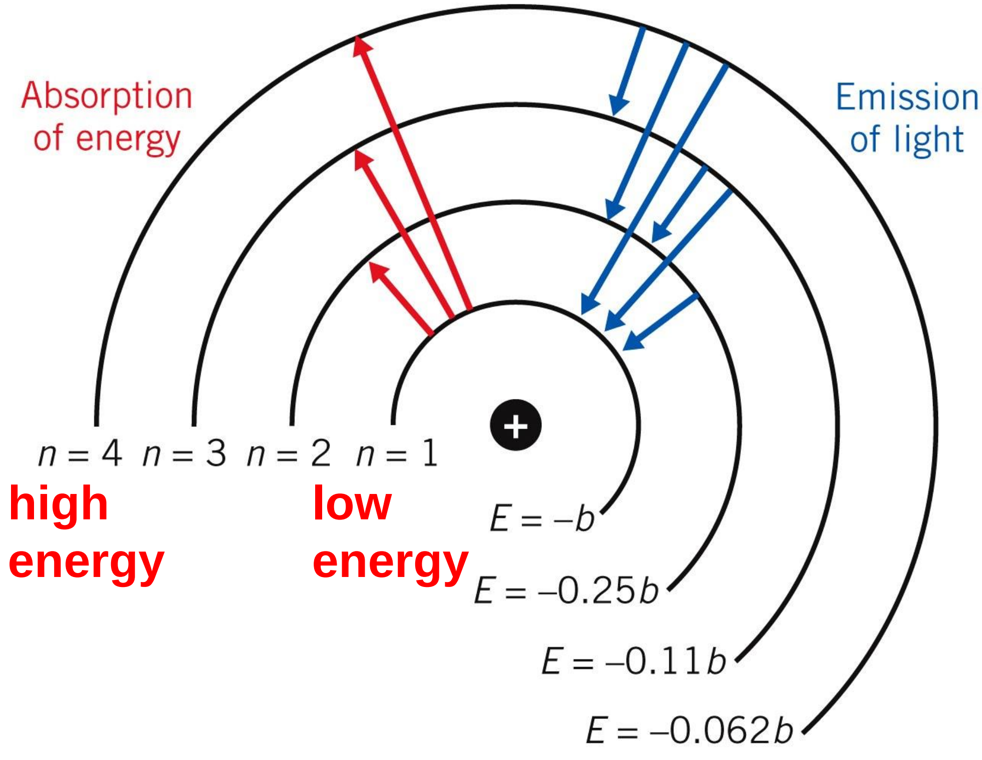
1. Study of light absorption
   - Electron absorbs energy
   - Moves to higher energy "excited state"



2. Study of light emission
   - **e**$^{-}$ loses photon of light
   - Drops back down to lower energy "ground state"



Bohr Model of Hydrogen Atom



- Energy is quantized
- Absorption of photon: Low>high
- Emission of photon: High>low
- Yields line spectra (not continuous)

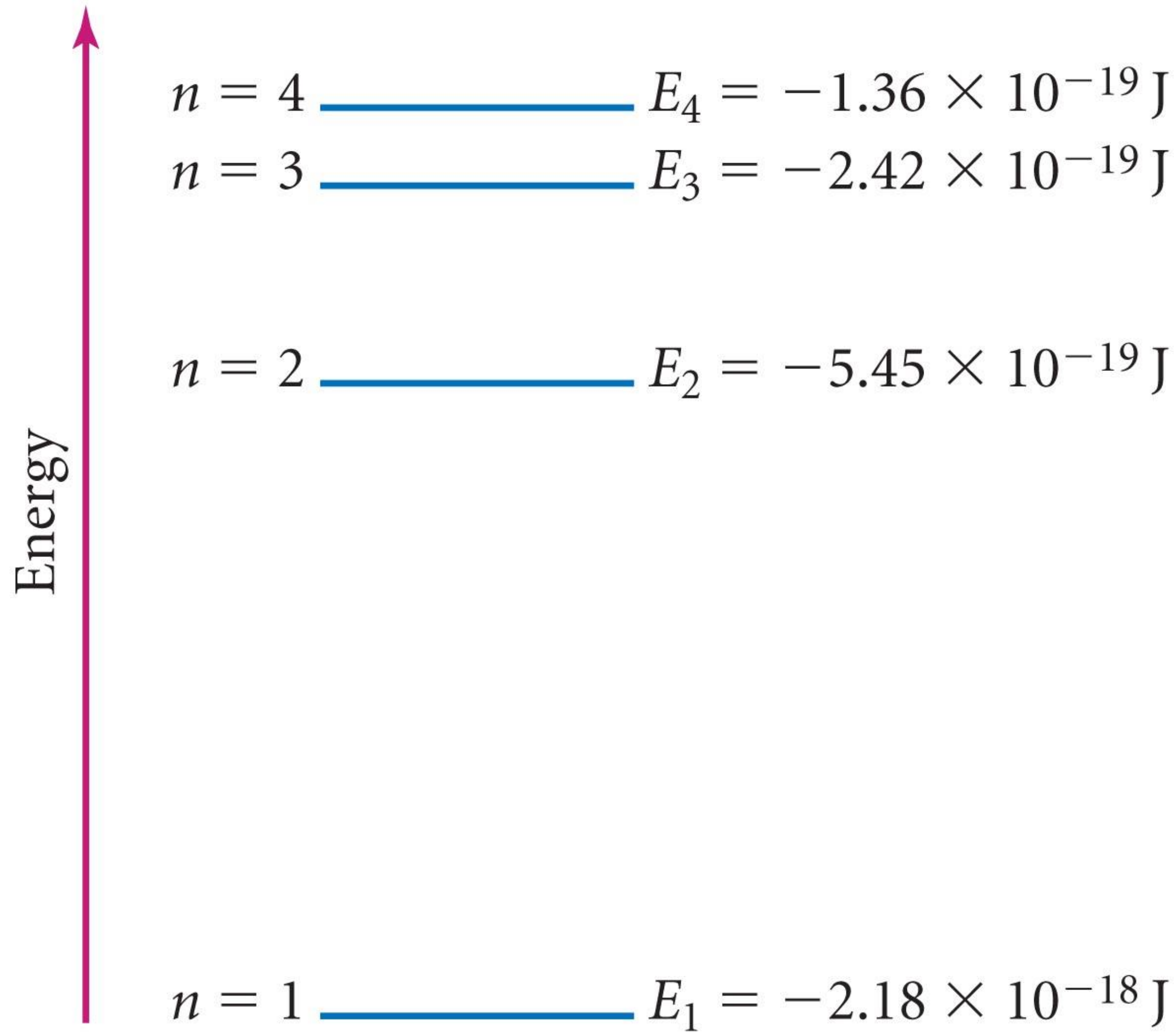
How Do We Describe an Electron?

- So small, it has **both** wave and particle properties
- Confining electron makes its behavior more wavelike (electrons in atoms or molecules)
- Free electrons behave more like particles

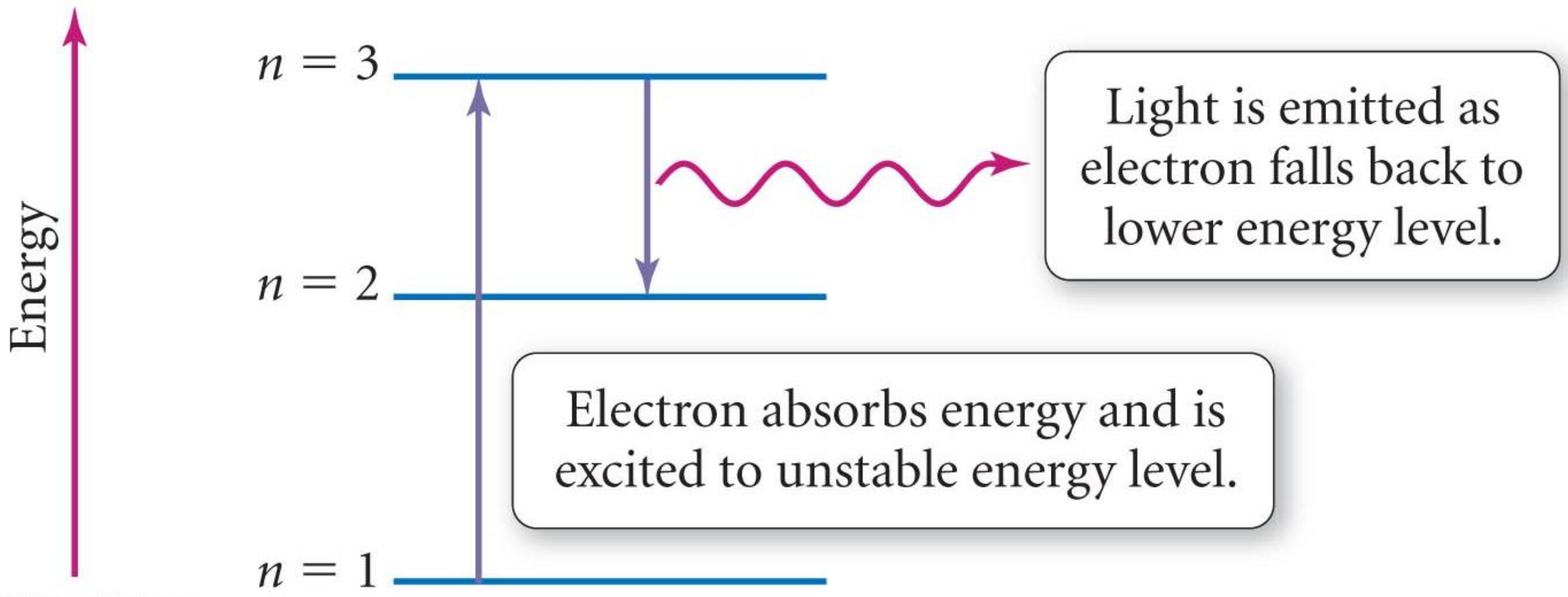
Solutions to the Wave Function, Ψ

- Atomic orbitals: The locations that electrons in atoms/molecules are found
- The size, shape, and orientation of an atomic orbital are determined to be **three integers** in the wave function
- Three integers are called **quantum numbers**
  - principal quantum number, $\boldsymbol{n}$
  - angular momentum quantum number, $\boldsymbol{l}$
  - magnetic quantum number, $\boldsymbol{m_l}$
  - spin quantum number, $\boldsymbol{m_s}$ (it was not proposed this time, but later it was proposed, +1/2 or -1/2)

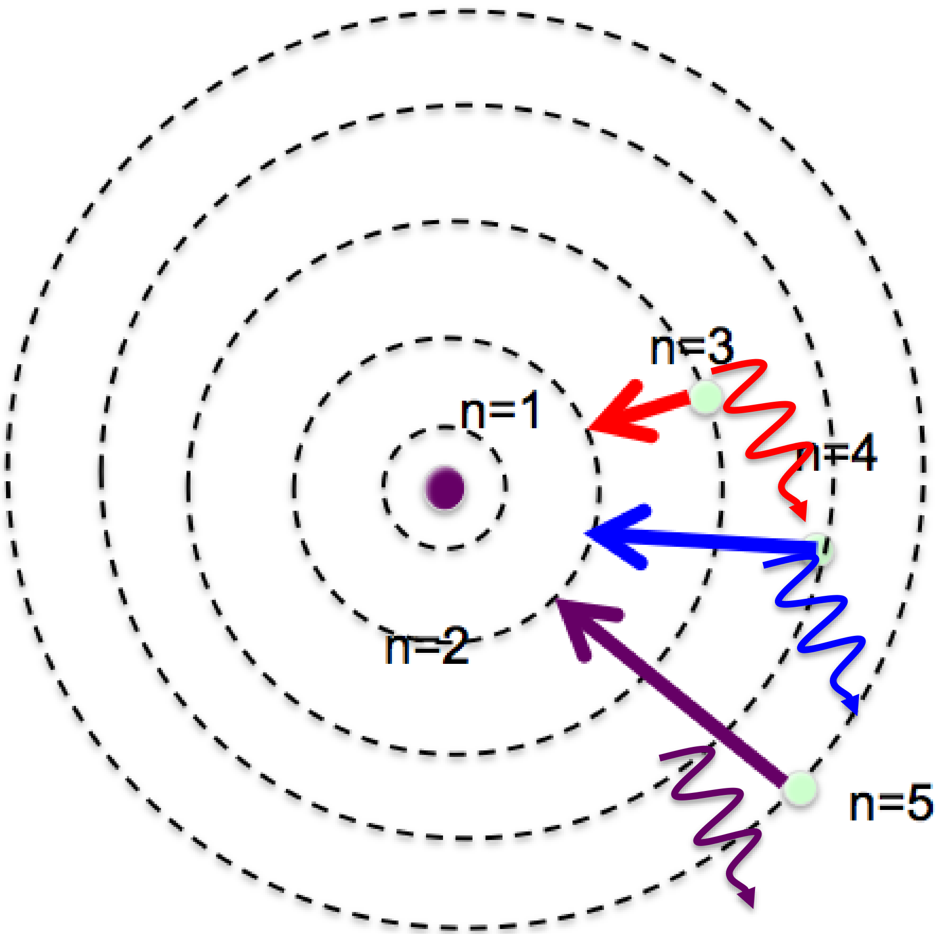
Principal Energy Levels in Hydrogen



Quantum Leaps



Emission spectrum of hydrogen

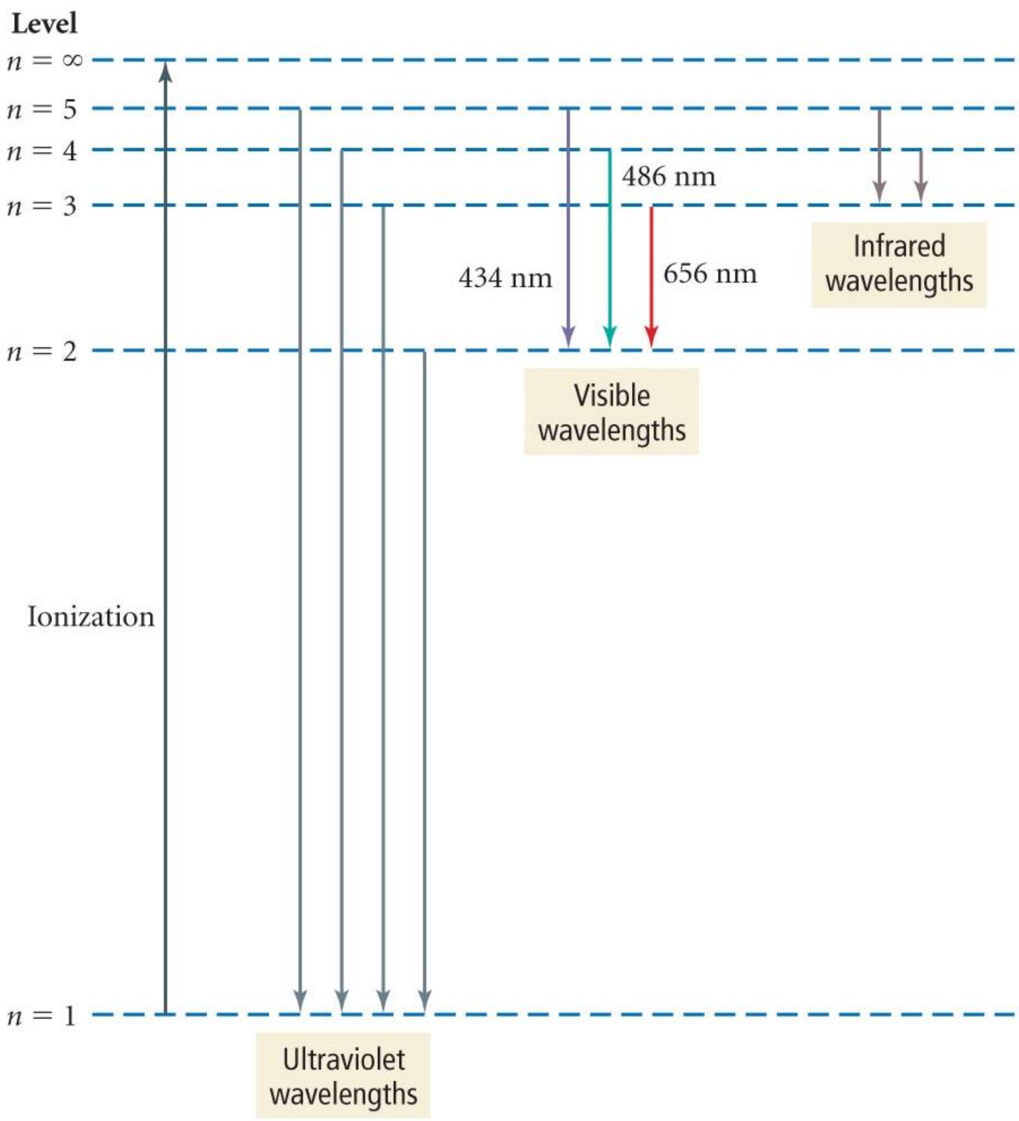


$$\Delta E = E_{high} - E_{low} = \left(\frac{-b}{n_{high}^2}\right) - \left(\frac{-b}{n_{low}^2}\right) = \frac{hc}{\lambda}$$

$$\frac{1}{\lambda} = \frac{b}{hc}\left(\frac{1}{n_{low}^2} - \frac{1}{n_{high}^2}\right)$$

When the excited electron falls to
a lower energy level, light of
a particular energy is emitted.

Hydrogen Energy Transitions



Atomic Orbitals and Quantum Numbers from Schrödinger's Electron Wave Function

- Principal quantum number (n)
  - n is positive integer number (n = 1, 2, 3, …….)
  - As n increases, electron density is further away from the nucleus and electron has higher energy.
- Secondary (angular momentum) quantum number (*l*)
  - 0 to n-1
  - *l* is designated by letter
  - Defines shape of orbital

l	**0**	**1**	**2**	**3**	**4**	**5**
Orbital	s	p	d	f	g	h

Orbitals and Quantum Number

- Magnetic quantum number (m_l)
  - Has integer values: -l, -l+1 …..l-1, l including 0
  - Describes the orientation of orbital in the space

The electron orbitals with a principal quantum number n =1 has the following available values for l and m_l

n	l	Subshell designation	m_l	Number of orbitals
1	0	1s	0	1

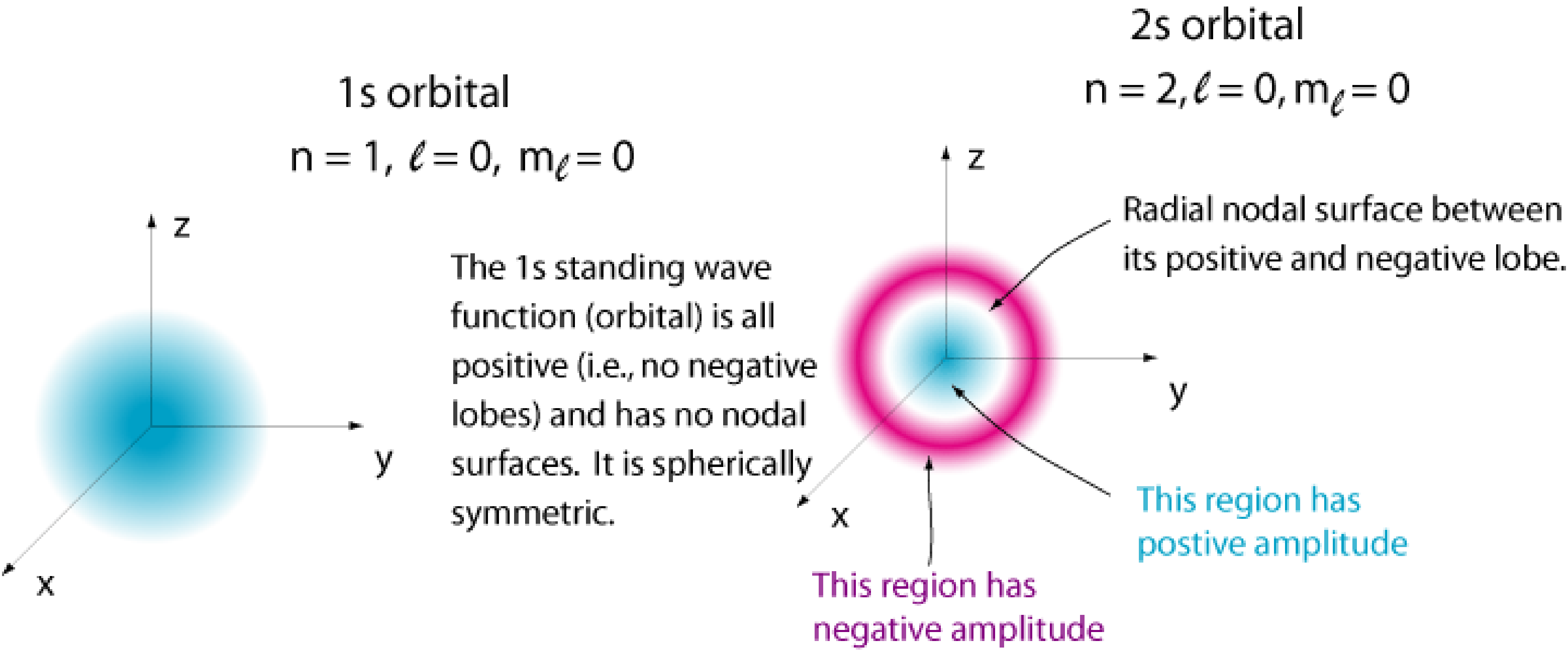
When n=2, possible l and m_l

n	l	Subshell Designation	m_l	Number of Orbitals in a shell
2	0	2s	0	1
	1	2p	-1, 0 , 1	3

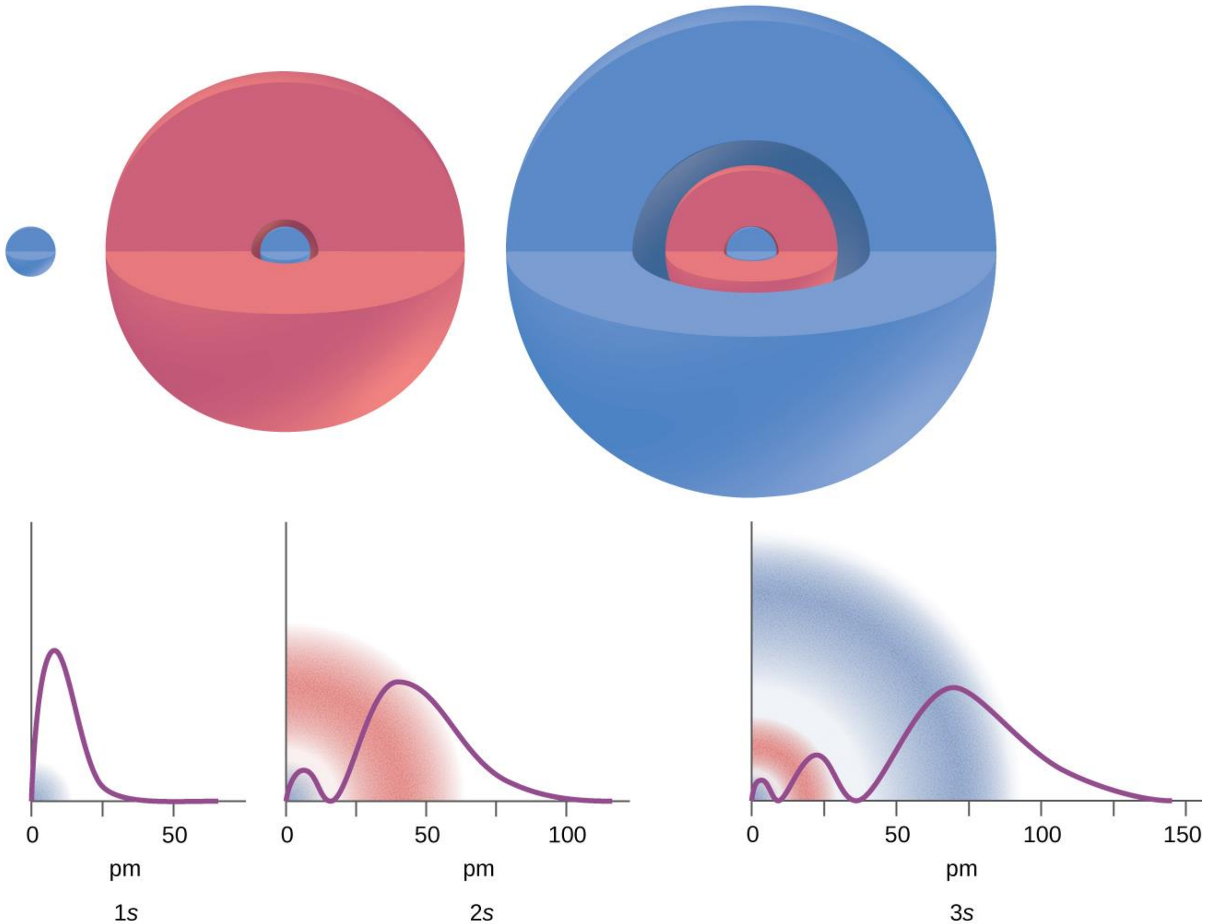
When n=3, possible l and m_l?

What are the quantum numbers and names (for example, 2*s*, 2*p*) of the orbitals in the $n = 3$ principal level? How many orbitals exist?

s Orbital Shape

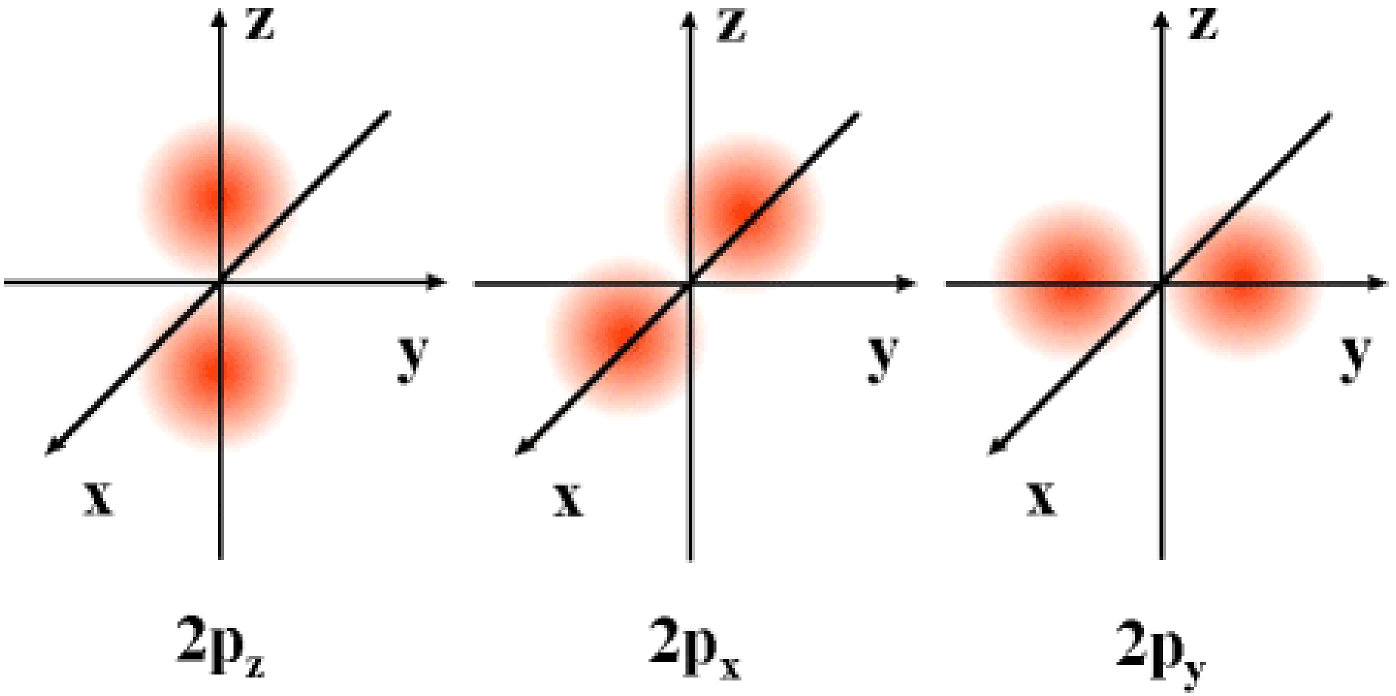


s orbital shape



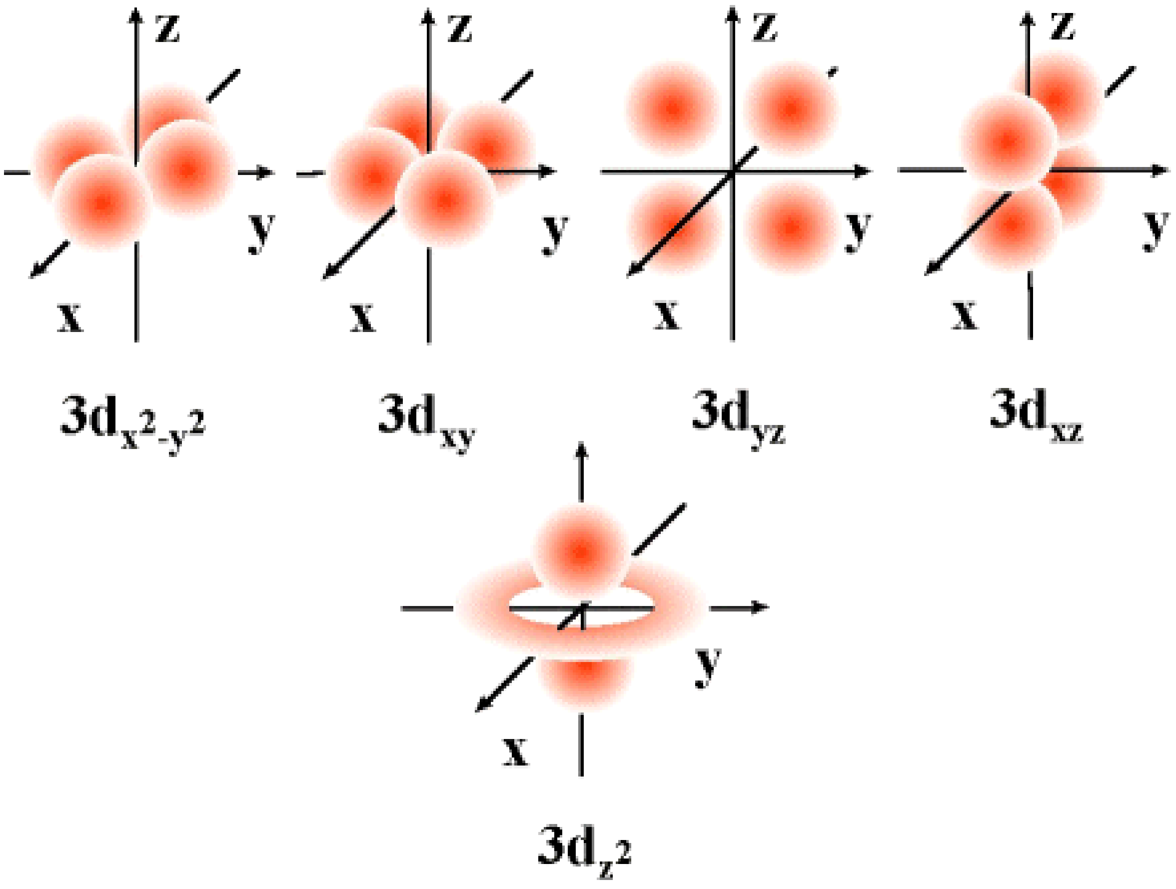
The probability (*y* axis) of finding an electron for the 1*s*, 2*s*, 3*s* orbitals as a function of distance from the nucleus

p Orbital Shape

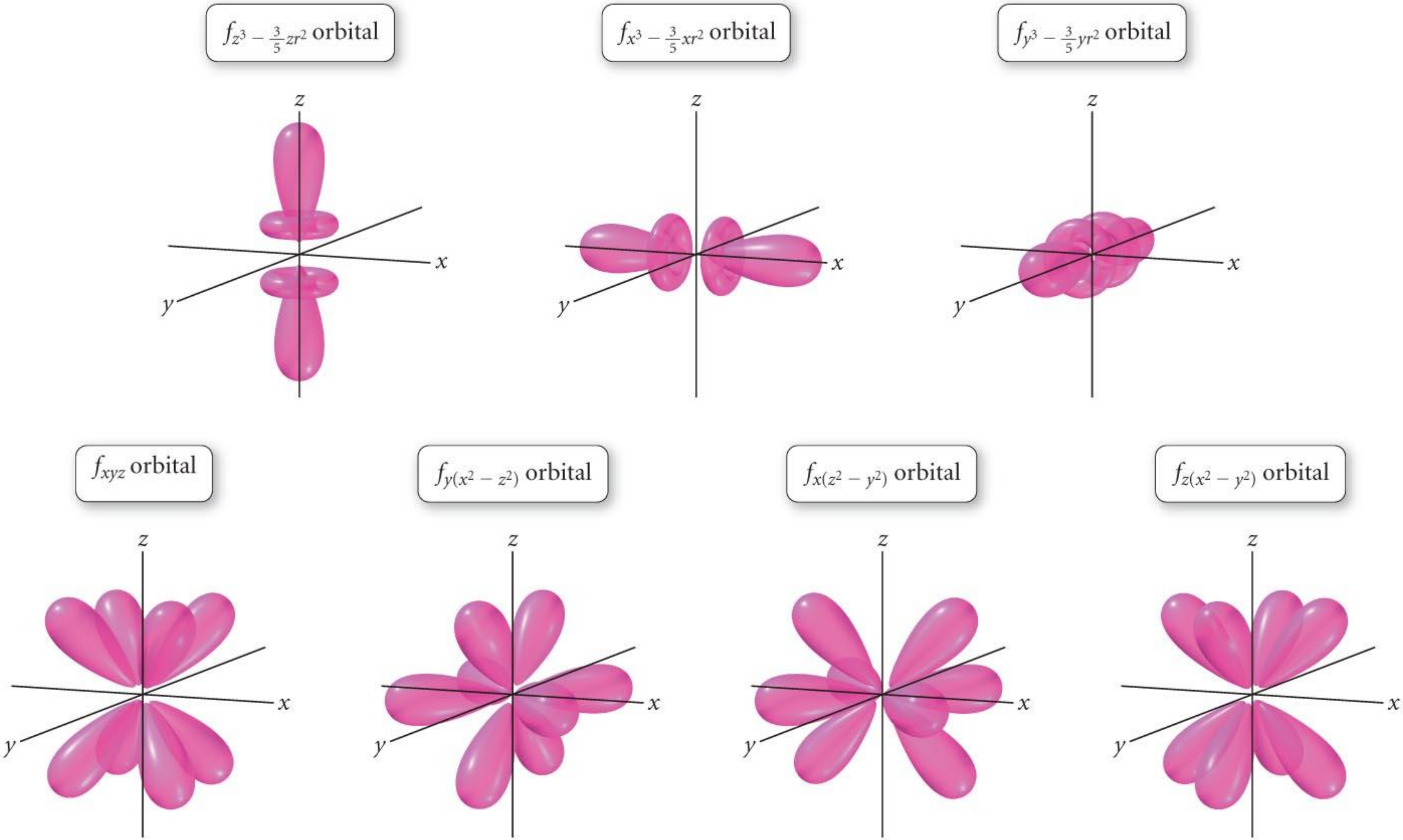


Note that there is **no simple relation** between the m_l values and the x, y, and z direction.

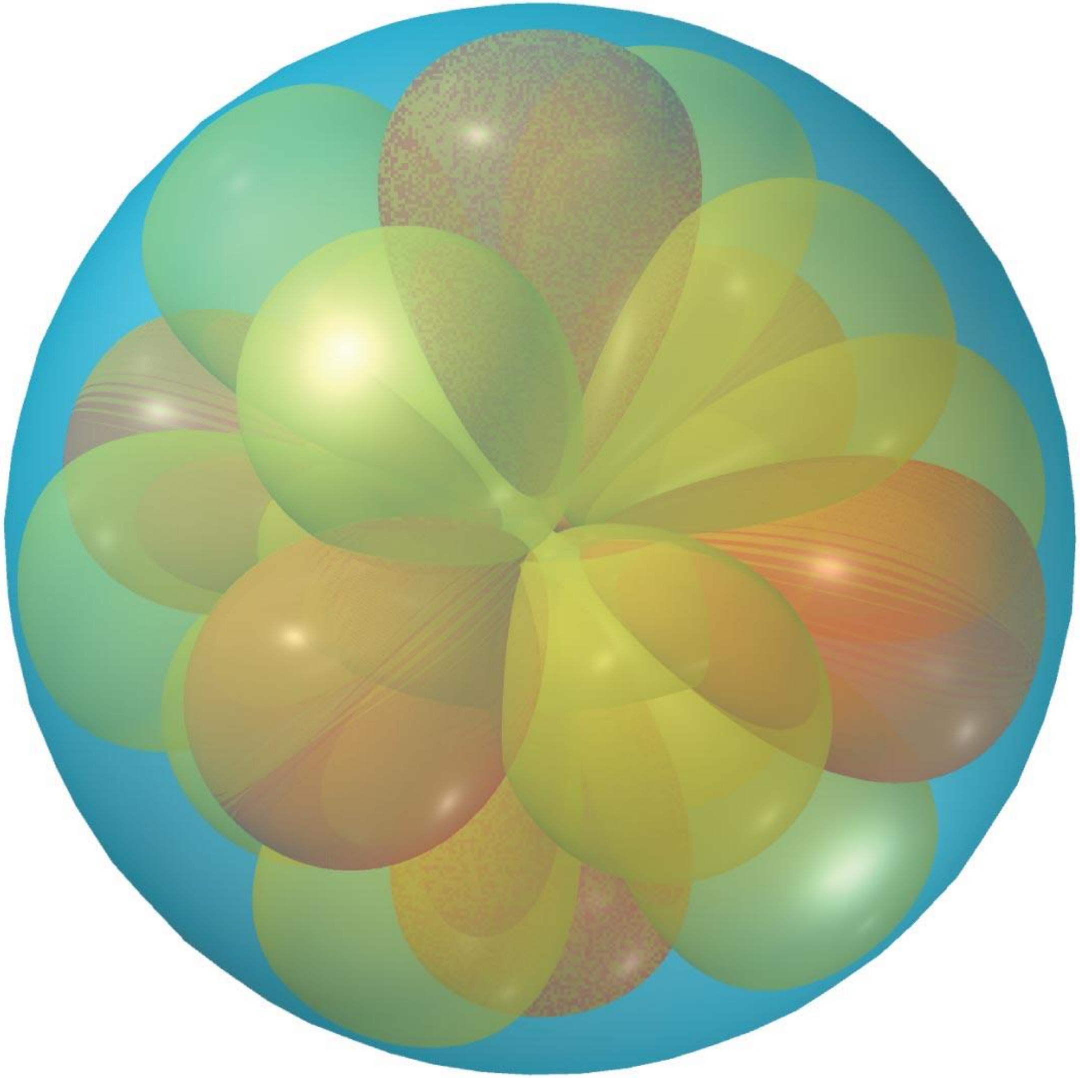
d Orbital Shape



f Orbital Shape



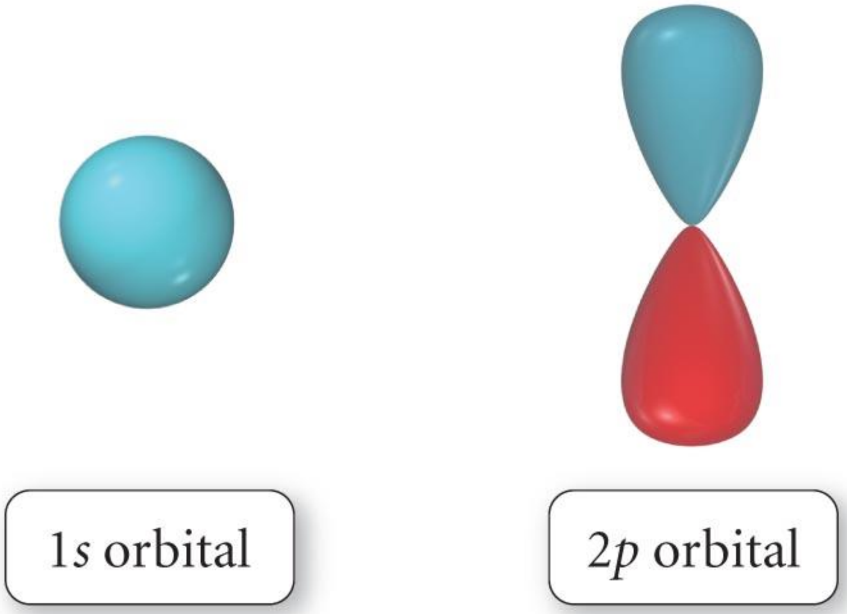
Why are Atoms Spherical?



The Phase of an Orbital

- Orbitals are determined from mathematical wave functions
- A wave function can have positive or negative values
  - as well as nodes where the wave function = 0
- The sign of the wave function is called its **phase**
- When orbitals interact, their wave functions may be in-phase (same sign) or out-of-phase (opposite signs)
  - this is important in bonding
    - as will be examined in a later chapter

Phases



Atomic Orbitals and Quantum Numbers from Schrödinger's Electron Wave Function

- Principal quantum number (n)
  - n is positive integer number (n = 1, 2, 3, …….)
  - As n increases, electron density is further away from the nucleus and electron has higher energy.
- Secondary (angular momentum) quantum number (*l*)
  - 0 to n-1
  - *l* is designated by letter
  - Defines shape of orbital

l	0	1	2	3	4	5
Orbital	s	p	d	f	g	h

Orbitals and Quantum Number

- Magnetic quantum number (m_l)
  - Has integer values: -l, -l+1 …..l-1, l including 0
  - Describes the orientation of orbital in the space

The electron orbitals with a principal quantum number n =1 has the following available values for l and m_l

n	l	Subshell designation	m_l	Number of orbitals
1	0	1s	0	1

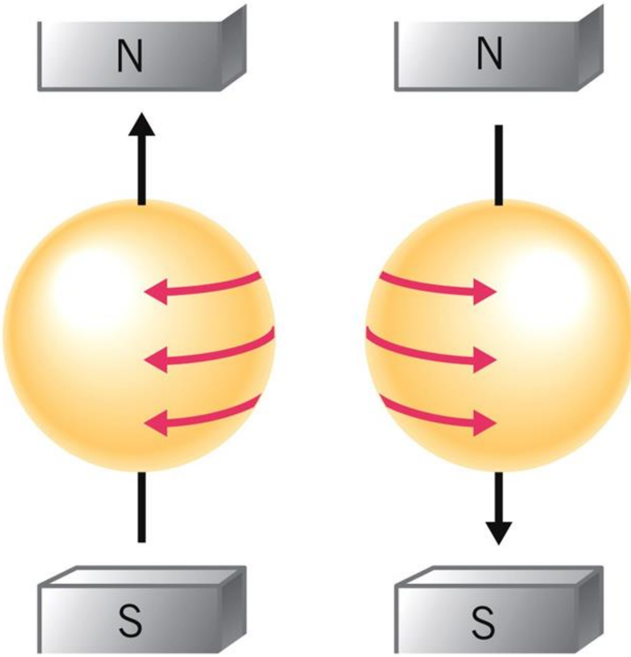
When n=2, possible l and m_l

n	l	Subshell Designation	m_l	Number of Orbitals in a shell
2	0	2s	0	1
	1	2p	-1, 0 , 1	3

When n=3, possible l and m_l?

Electron Spin and Quantum Number

Spin quantum number (m_s) : +1/2 or -1/2



Possible Values:

+½	−½
↑	↓

Emission spectrum of atoms having odd number of electrons show that lines in the emission spectra split by the application of magnetic field, suggesting the existence of two different electron spins.

Stern-Gerlach Experiment

Nobel prize in physics in 1943

Pauli Exclusion Principle

- No two e^- in same atom can have same set of all four quantum numbers ($\boldsymbol{n}$, l, $\boldsymbol{m_l}$, $\boldsymbol{m_s}$)
- **Can only have 2 e^- per orbital**
- 2 e^- s in same orbital must have opposite spin
  - e^- s are **paired**
- Odd number of e^-s
  - Not all spins paired
  - Have **unpaired** e^-s
- Even number of e^-s
  - Depends on number of orbitals

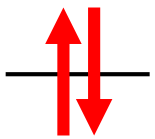
Consequences of Pauli Exclusion Principle

Subshell	Number of Orbitals	Maximum Number of Electrons
s	1	2
p	3	6
d	5	10
f	7	14

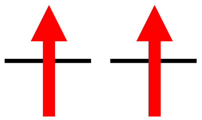
Shell	Subshells	Maximum Shell Population	
1	1*s*	2	
2	2*s* 2*p*	8	(2 + 6)
3	3*s* 3*p* 3*d*	18	(2 + 6 + 10)
4	4*s* 4*p* 4*d* 4*f*	32	(2 + 6 + 10 + 14)

Diamagnetic vs Paramagnetic

- Two e$^-$ s in **same** orbital with **different** spin
  - Spins paired—**diamagnetic**
  - Sample not attracted to magnetic field
  - Magnetic effects tend to cancel each other



- Two e$^-$ s in **different** orbital with **same** spin
  - Spins unpaired—**paramagnetic**
  - Sample pulled into magnetic field
  - Magnetic effects add



- Measure extent of attraction
  - Gives number of unpaired spins

Your Turn!

Which of the following is a **valid** set of four quantum numbers ($\mathbf{n, \ell, m_\ell, m_s}$)?

A. 3, 2, 3, +½

B. 3, 2, 1, 0

C. 3, 0, 0, -½

D. 3, 3, 0, +½

E. 0, -1, 0, -½

Your Turn!

What is the maximum number of electrons allowed in a set of ***4p*** orbitals?

A. 14

B. 6

C. 0

D. 2

E. 10

Ground State Electron Configuration of H

Electron configuration of H

$1s^1$

Number of electrons in the orbital

Principal quantum number (n =1)

Angular momentum quantum number (l= 0)

Orbital diagram of H

$\boxed{\uparrow}$

1s

Box indicates an atomic orbital.

The upward arrow indicates one of the two possible spins (m_s = ½)

Electron Configuration of Atoms Having Many Electrons

Distribution of electrons among the orbitals of an atom that yields the lowest energy for an atom

Electron configuration should be built up by filling electrons in the orbitals from lowest to higher energy orbitals (**Aufbau principle**).

Energy order

1s<2s<2p<3s<3p**<4s<3d**<4p<5s……

Ground State Electron Configuration of He

Then, how about the orbital diagram of He atom?
Which one is correct?

$$He1s^2$$

$\boxed{\uparrow\uparrow}$	$\boxed{\downarrow\downarrow}$	$\boxed{\uparrow\downarrow}$
1s	1s	1s

The two electrons cannot have the same four quantum numbers.
In He example, all three quantum numbers (n, l , m_l) are the same,
but **spin quantum numbers** are different (Pauli Exclusion Principle).

Ground state electron configuration of Li, Be, and B

Li

Be

B

Diamagnetic and Paramagnetic

Paramagnetic substance: contains **net unpaired electrons** and are attracted by a magnet.

Diamagnetic substance: do not contain net unpaired electrons and are slightly repelled by a magnet.

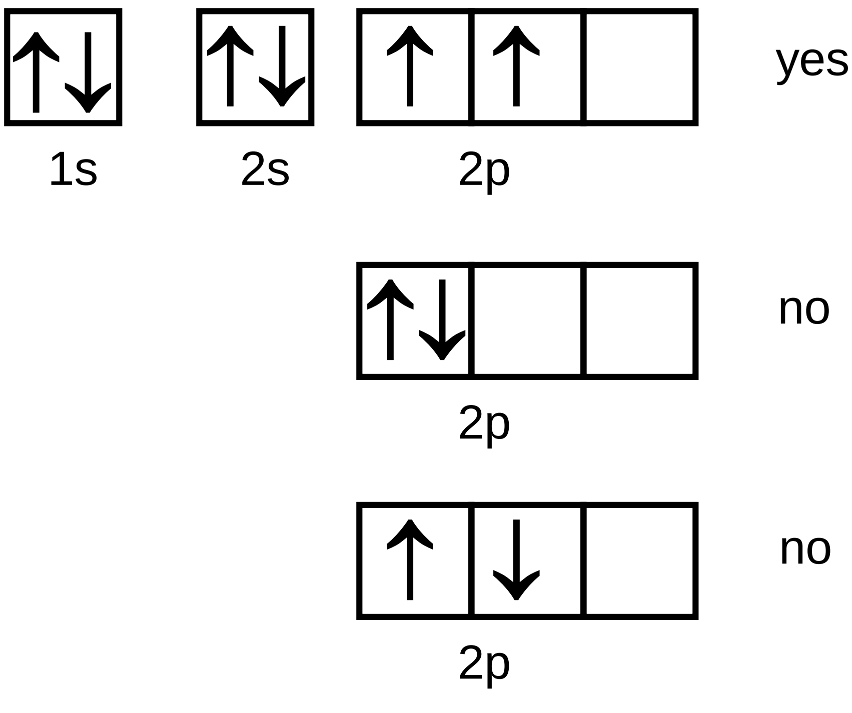
Diamagnetic or paramagnetic?

H
He
Li
Be
B

Hund’s rule

The most stable arrangement of electrons in subshell is the one with **the greatest number of parallel spins**.

C $1s^2 2s^2 2p^2$



N, O, F, and Ne

N $1s^2\ 2s^2\ 2p^3$

O $1s^2\ 2s^2\ 2p^4$

F $1s^2\ 2s^2\ 2p^5$

Ne $1s^2\ 2s^2\ 2p^6$

General Rules for Assigning Electrons to Atomic Orbitals

Each shell (principal level of quantum number n) contains
n subshells (l = 0, 1, 2 , n-1).

Each subshell of quantum number l contains **(2l+1) orbitals**.

No more than two electrons can be placed in each orbital.

The maximum number of electrons that an atom can have
in a principal level n is $\mathbf{2n^2}$.

Electron Configuration Using Noble Gas Core

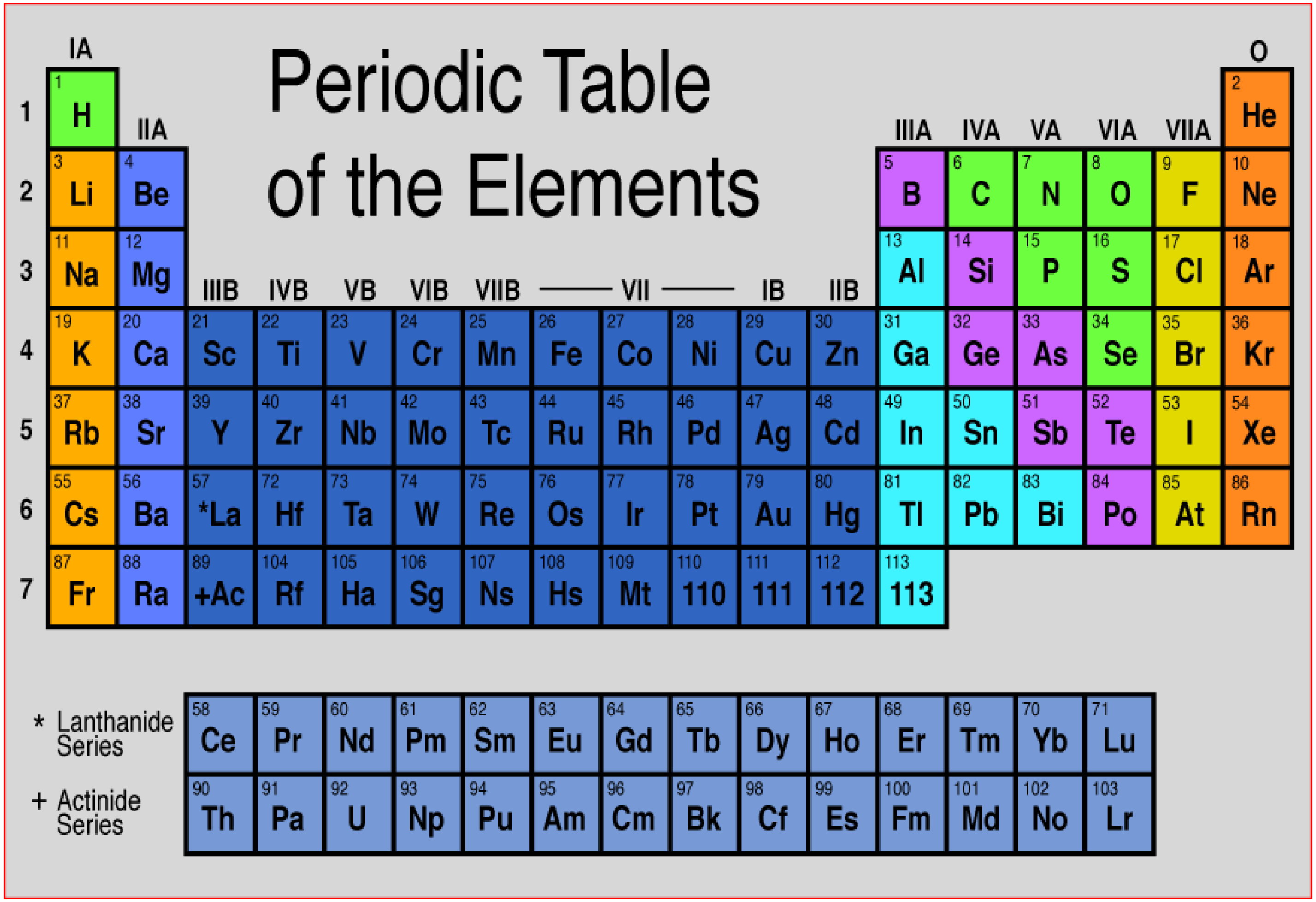
Valence electrons

$_{11}Na$ $1s^2 2s^2 2p^6 3s^1 \rightarrow [Ne]\, 3s^1$

The same electron configuration as "Ne": **core electrons**

$_{12}Mg$ $1s^2 2s^2 2p^6 3s^2 \rightarrow [Ne]\, 3s^2$

Valence electrons



Period 3 elements→ Use Ne
Period 4 elements→ Use Ar
Period 5 elements→ Use Kr
Period 6 elements→ Use Xe
Period 7 elements→ Use Rn

Electron Configuration Using Noble Gas Core

$_{16}S$ $\underbrace{1s^2 2s^2 2p^6}_{[Ne]} 3s^2 3p^4$ → $[Ne]3s^2 3p^4$

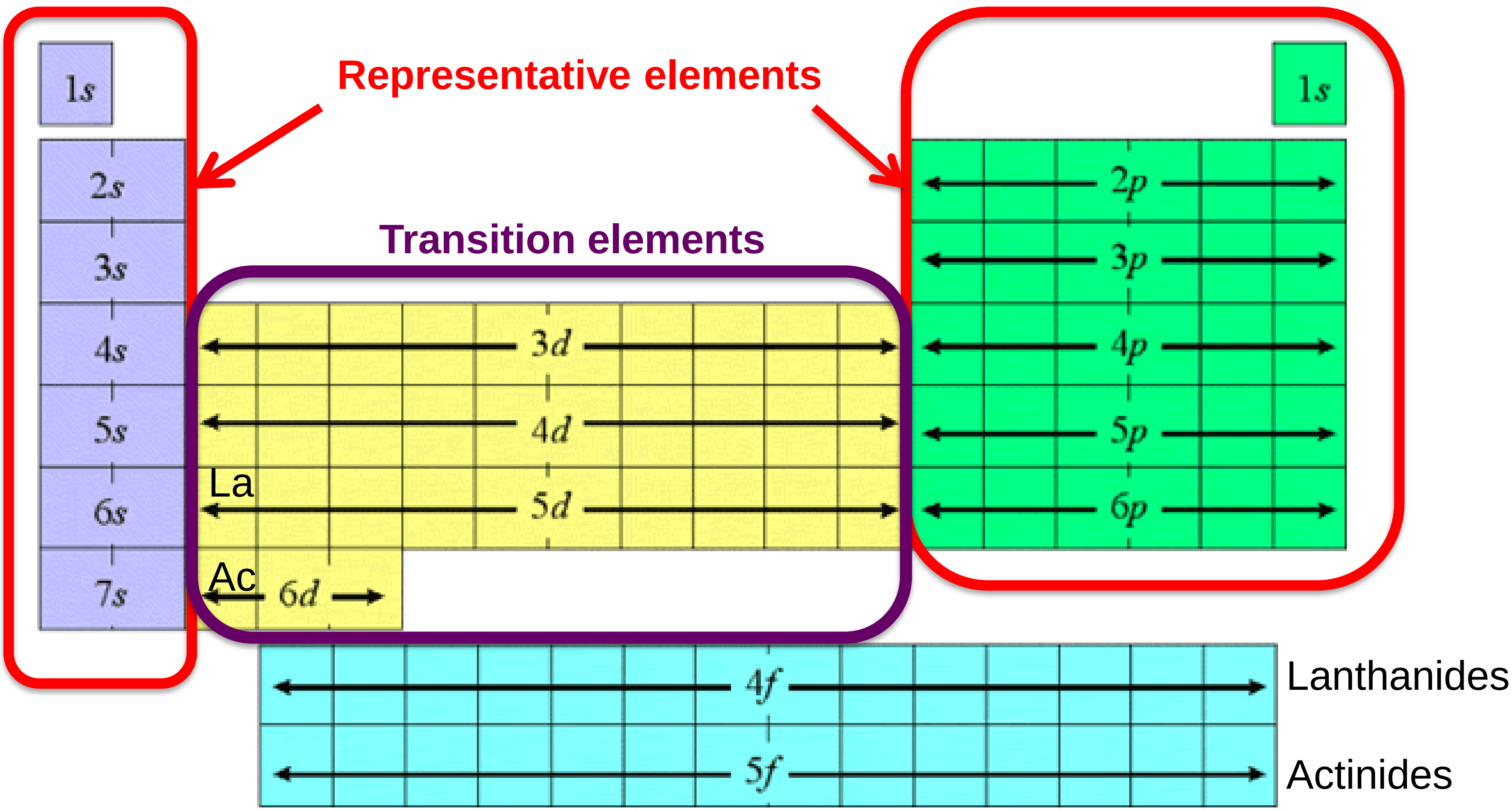
Valence electrons

$_{19}K$ $\underbrace{1s^2 2s^2 2p^6 3s^2 3p^6}_{[Ar]} 4s^1$ → $[Ar]4s^1$

Valence electrons

Try $_{14}Si$ and $_{35}Br$

Electron configuration of transition and rare earth metals (lanthanides)



Electron configuration of transition and rare earth metals (lanthanides)

Energy order

1s<2s<2p<3s<3p<4s<3d<4p<5s……

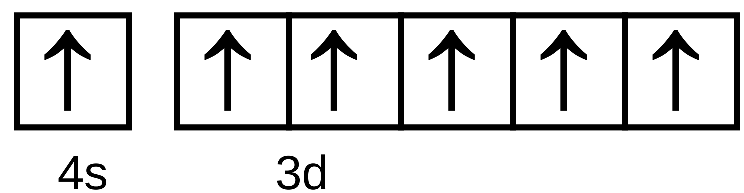
$_{21}Sc \quad \boxed{1s^2 2s^2 2p^6 3s^2 3p^6} 4s^2 3d^1$

[Ar]

$_{22}Ti \quad [Ar]\, 4s^2 3d^2$

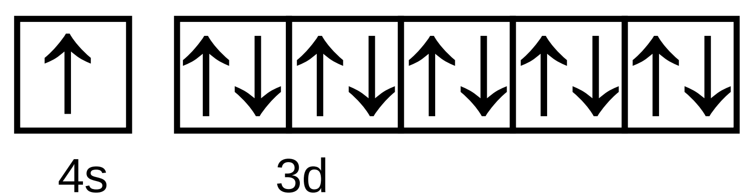
$_{23}V \quad [Ar]\, 4s^2 3d^3$

$\boxed{_{24}Cr \quad [Ar]\, 4s^1 3d^5}$



$_{25}Mn \quad [Ar]\, 4s^2 3d^5$

$\boxed{_{29}Cu \quad [Ar]\, 4s^1 3d^{10}}$



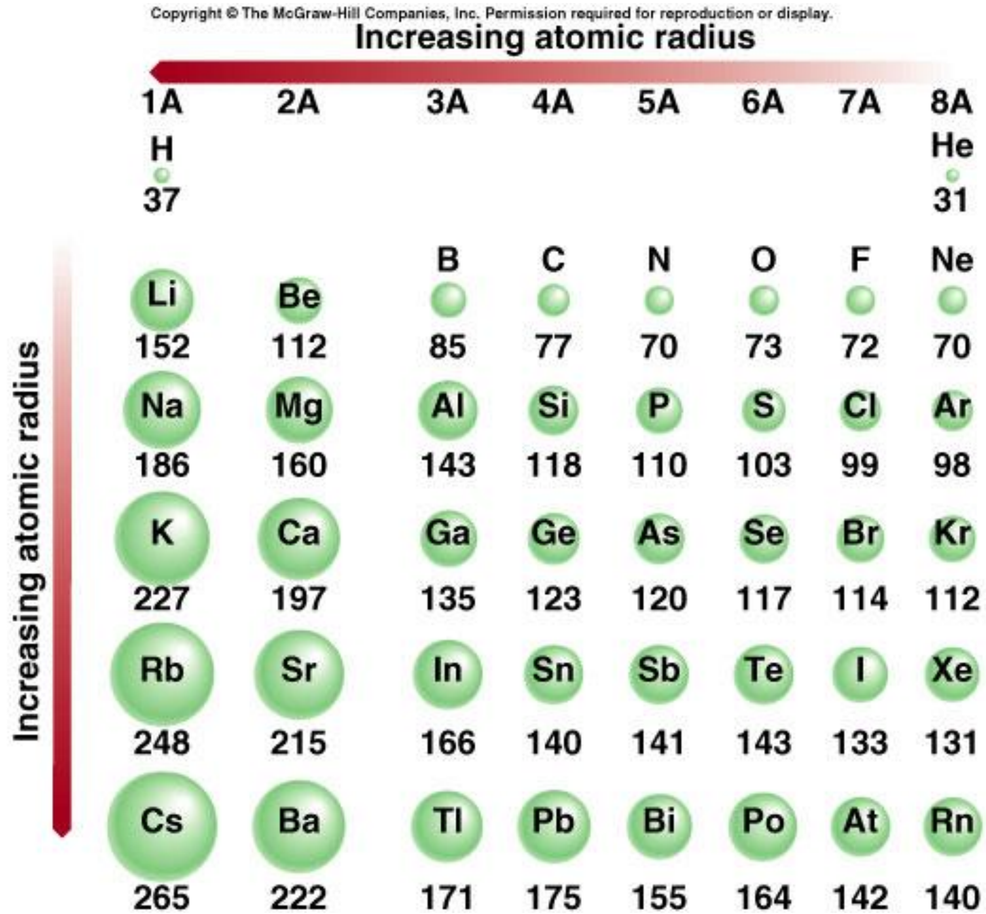
Let's do more practice!

${}_{17}Cl$

${}_{26}Fe$

${}_{32}Ge$

Atomic radii in the periodic table



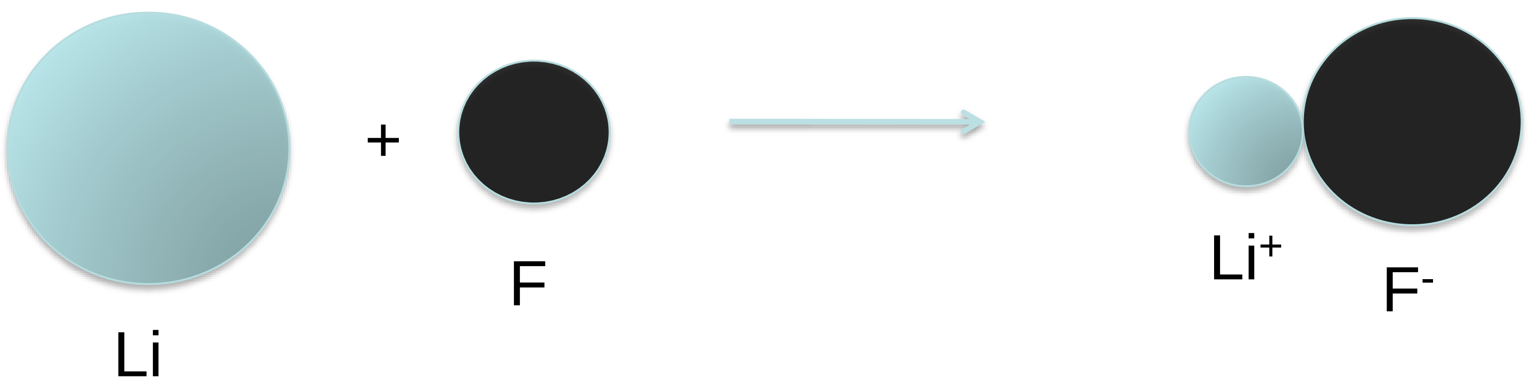
Unit: pm

1 pm = 10^{-12} m

Atomic radius is largely determined by the strength of attraction between the nucleus and the outer-shell electrons.

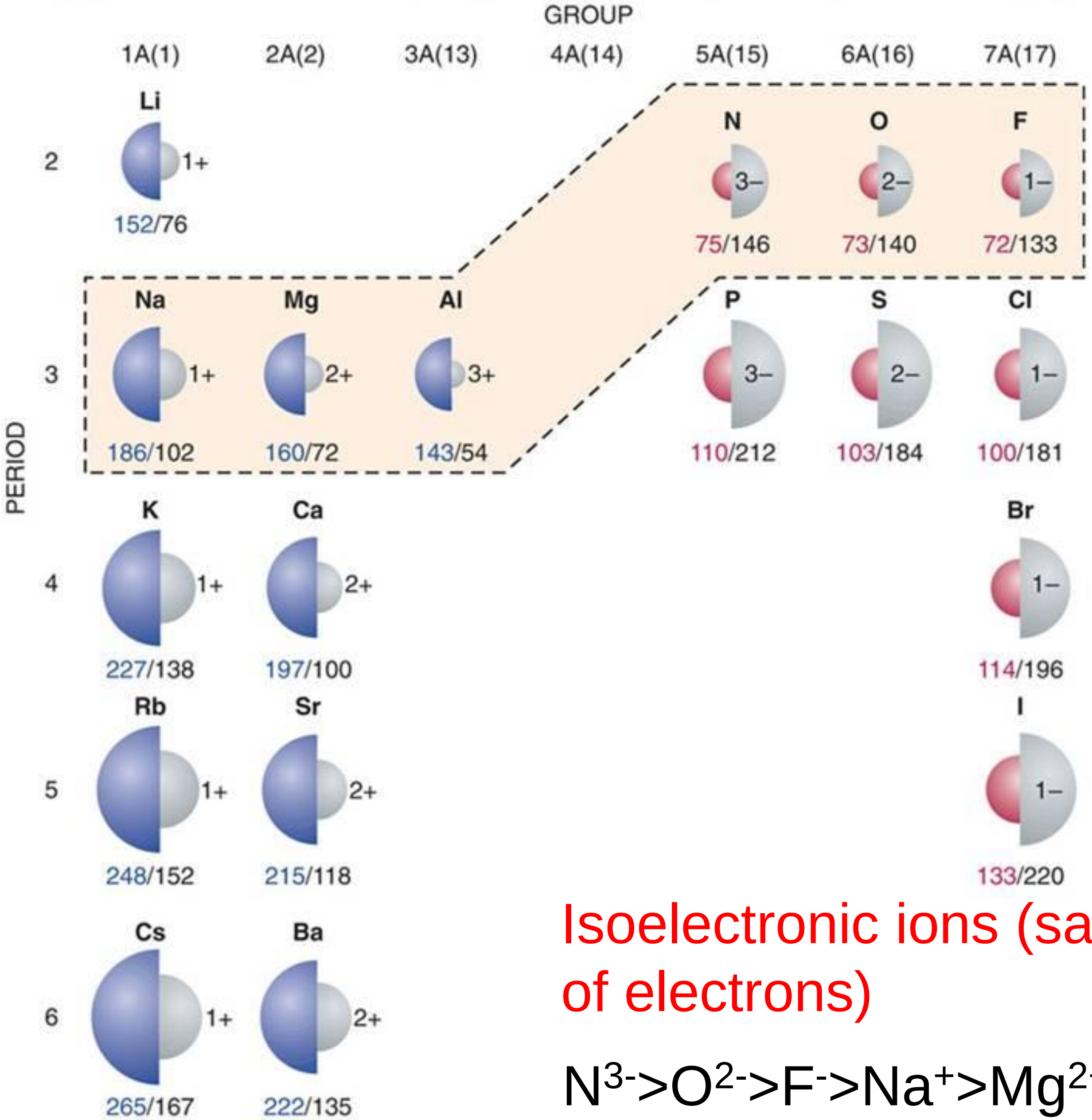
Ionic radii

Changes in the sizes of Li and F when they react to form LiF



If atom forms an anion, its size increases.

If atom forms a cation, its size decrease.



Isoelectronic ions (same number of electrons)

$N^{3-} > O^{2-} > F^{-} > Na^{+} > Mg^{2+} > Al^{3+}$

Ionization Energy

The minimum energy required to remove an electron from a gaseous atom in its ground state

$$\text{energy} + X(g) \rightarrow X^{+}(g) + e^{-}$$

First ionization (I_1)

$$\text{energy} + X^{+}(g) \rightarrow X^{2+}(g) + e^{-}$$

Second ionization (I_2)

$$\text{energy} + X^{2+}(g) \rightarrow X^{3+}(g) + e^{-}$$

Third ionization (I_3)

$$I_1 < I_2 < I_3 < \ldots\ldots$$

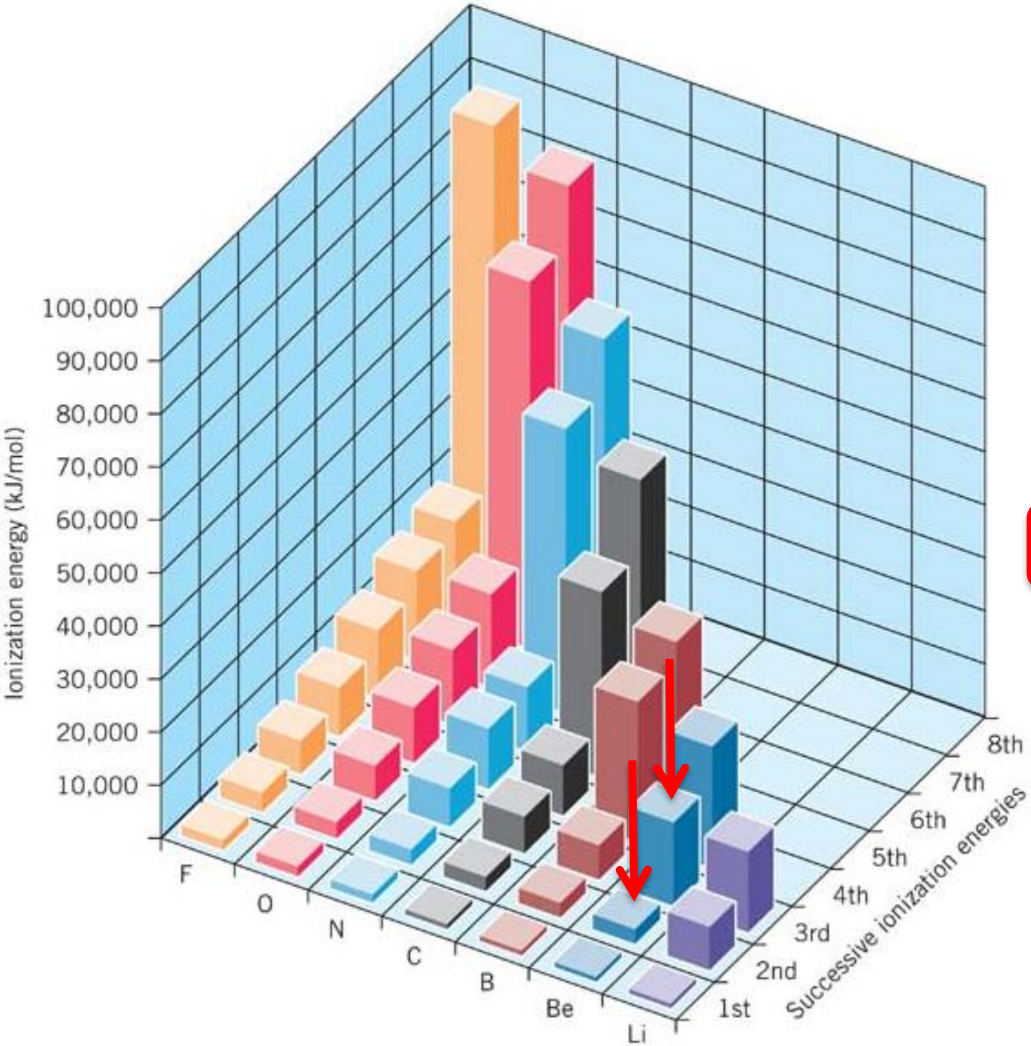
Ionization is always endothermic

Table 8.2 Successive Ionization Energies in kJ/mol for Hydrogen through Magnesium

	1st	2nd	3rd	4th	5th	6th	7th	8th
H	1312							
He	2372	5250						
Li	520	7297	11,810					
Be	899	1757	14,845	21,000				
B	800	2426	3659	25,020	32,820			
C	1086	2352	4619	6221	37,820	47,260		
N	1402	2855	4576	7473	9442	53,250	64,340	
O	1314	3388	5296	7467	10,987	13,320	71,320	84,070
F	1680	3375	6045	8408	11,020	15,160	17,860	92,010
Ne	2080	3963	6130	9361	12,180	15,240	—	—
Na	496	4563	6913	9541	13,350	16,600	20,113	25,666
Mg	737	1450	7731	10,545	13,627	17,995	21,700	25,662

Note the sharp increase in ionization energy when crossing the "staircase," indicating that the last of the valence electrons has been removed.

Why big jump from second to third ionization energy in Be?



$\mathrm{Be} + \mathrm{energy} \rightarrow \mathrm{Be}^{+} + \mathrm{e}^{-}$: first ionization

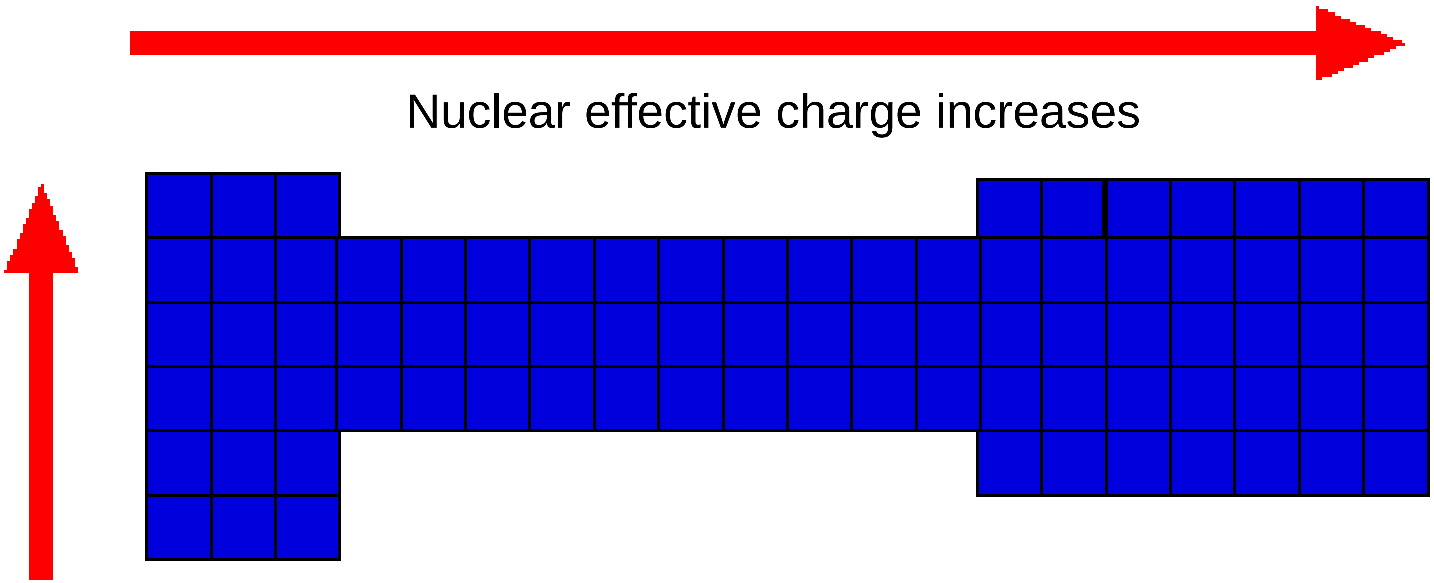
$\mathrm{Be}^{+} + \mathrm{energy} \rightarrow \mathrm{Be}^{2+} + \mathrm{e}^{-}$: second ionization

$\boxed{\mathrm{Be}^{2+}} + \mathrm{energy} \rightarrow \mathrm{Be}^{3+} + \mathrm{e}^{-}$: third ionization

The same electronic configuration as noble gas "He"

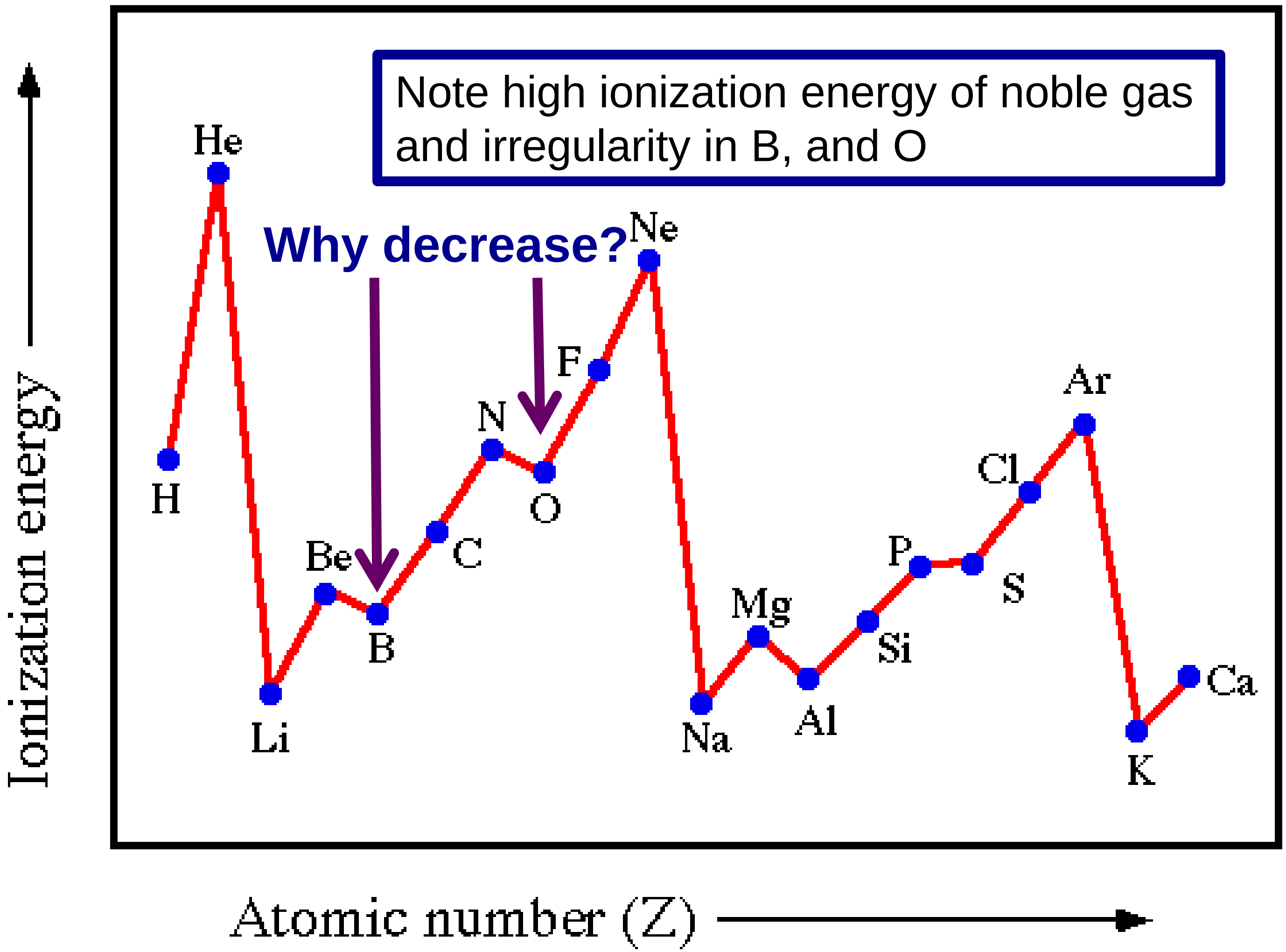
The first ionization in the periodic table

Ionization energy increases with arrows



As principal number decreases, the distance between a valence electron and nucleus decreases.

First Ionization Energy



Electron affinity

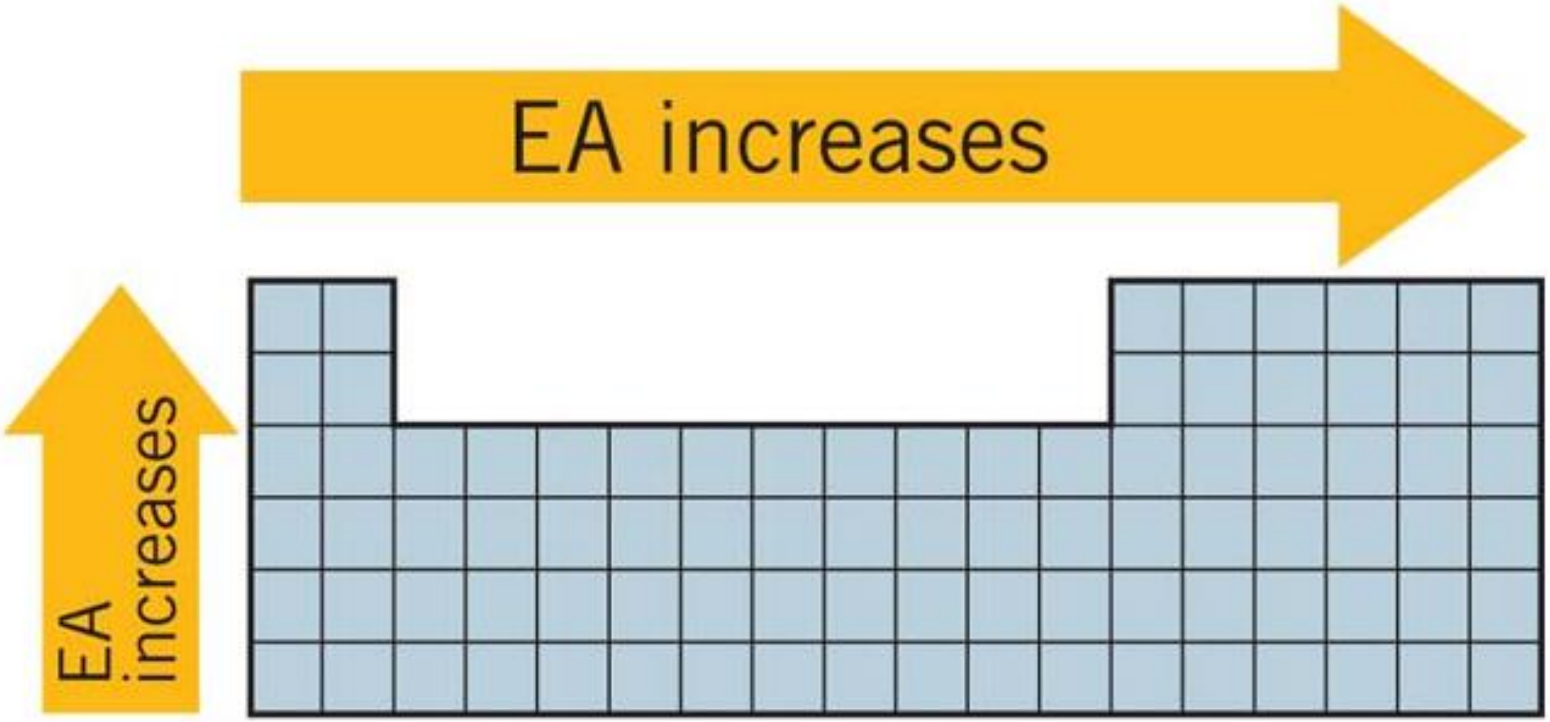
The energy change that occur when **an electron is accepted by an atom** in the gaseous state to form an anion

$$F(g) + e^{-} \rightarrow F^{-}(g) \ \Delta H = -328 kJ/mol$$

More negative, more electron affinity
(loves electron more)

Table 8.3	Electron Affinities of the Representative Elements (kJ/mol)					
1A	2A	3A	4A	5A	6A	7A
H						
−73						
Li	Be	B	C	N	O	F
−60	+238	−27	−122	~ +9	−141	−328
Na	Mg	Al	Si	P	S	Cl
−53	+230	−44	−134	−72	−200	−348
K	Ca	Ga	Ge	As	Se	Br
−48	+155	−30	−120	−77	−195	−325
Rb	Sr	In	Sn	Sb	Te	I
−47	+167	−30	−121	−101	−190	−295
Cs	Ba	Tl	Pb	Bi	Po	At
−45	+50	−30	−110	−110	−183	−270

Electron affinity trend



Homework

TBA