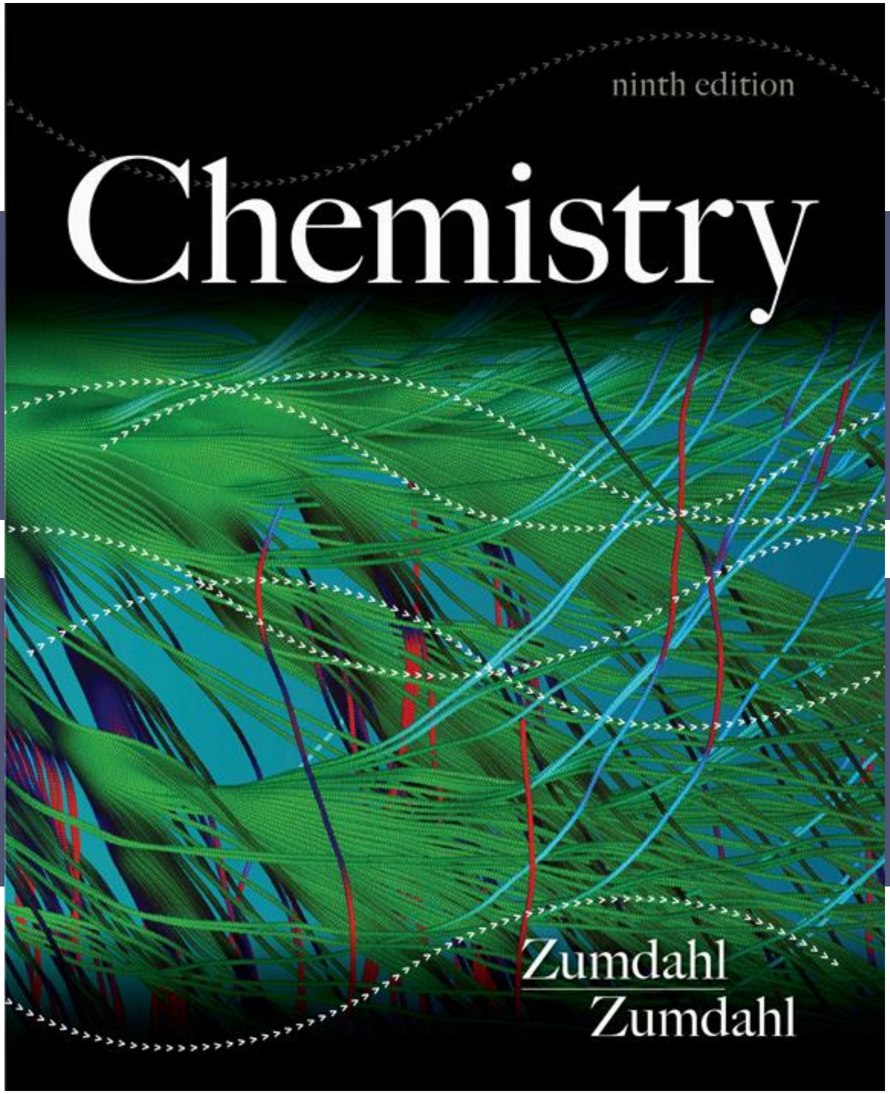

Chapter 7

Atomic Structure and Periodicity

Different Colored Fireworks

Questions to Consider

- Why do we get colors?
- Why do different chemicals give us different colors?

Electromagnetic Radiation

- One of the ways that energy travels through space.
- Three characteristics:
  - Wavelength
  - Frequency
  - Speed

Characteristics

- Wavelength (λ) – distance between two consecutive peaks or troughs in a wave.
- Frequency (ν) – number of waves (cycles) per second that pass a given point in space
- Speed (*c*) – speed of light (2.9979×10^8 m/s)

$$c = \lambda \nu$$


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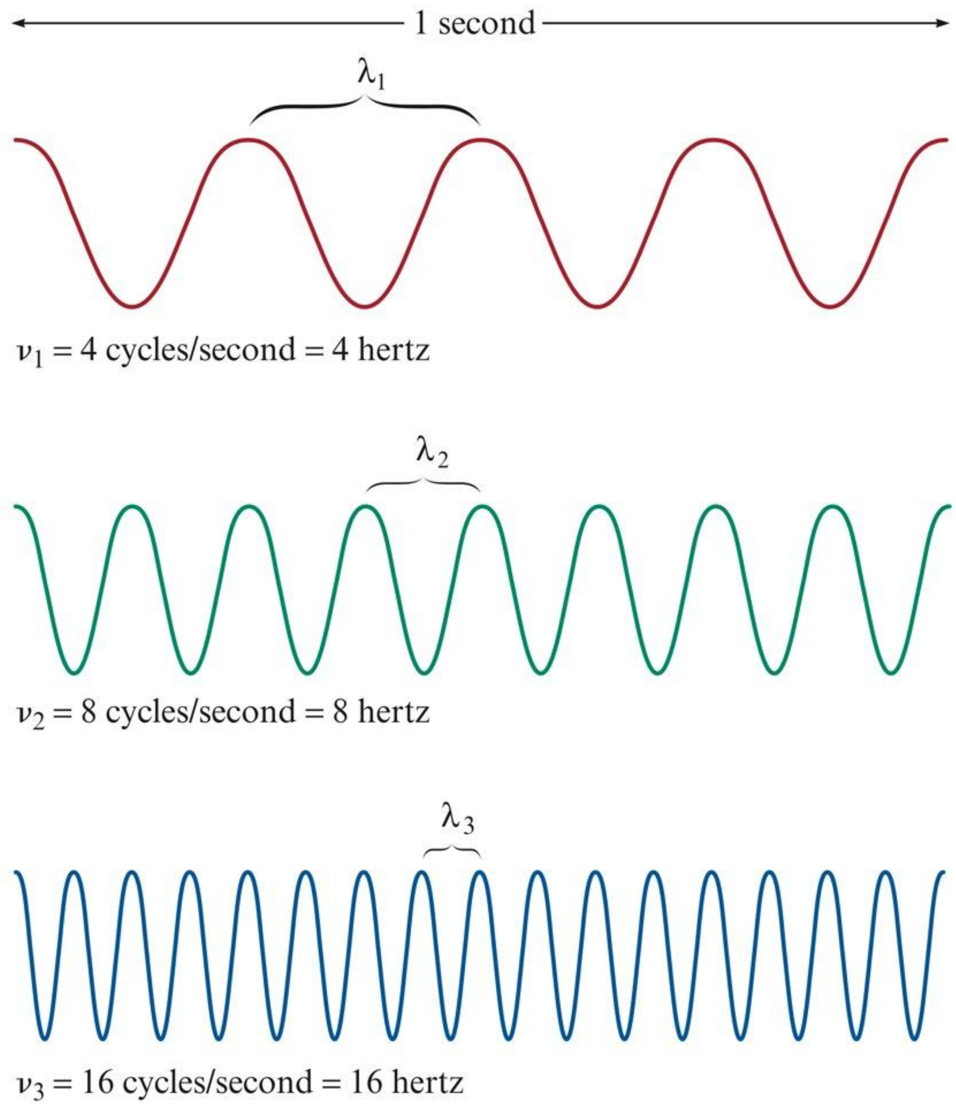
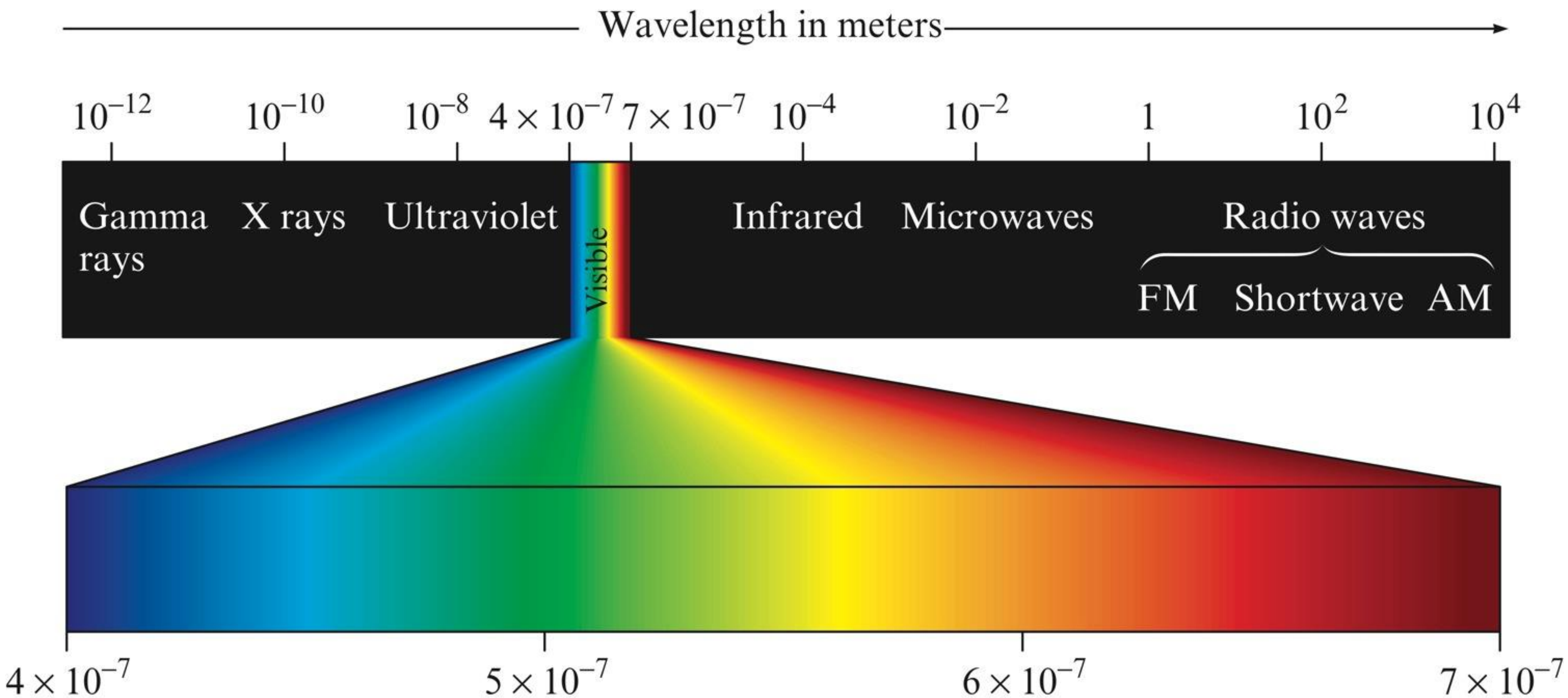
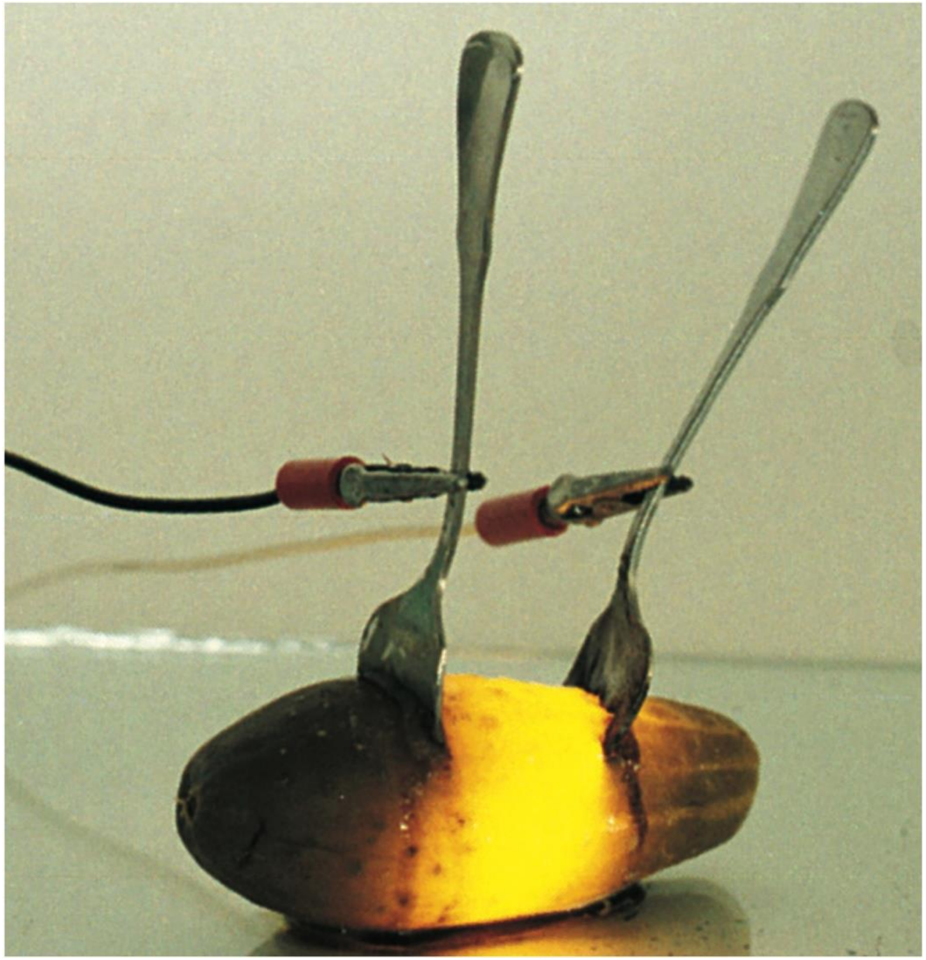
The Nature of Waves



Classification of Electromagnetic Radiation



Pickle Light



Donald W. Clegg

- Energy can be gained or lost only in whole number multiples of $h\nu$.
- A system can transfer energy only in whole quanta (or "packets").
- Energy seems to have particulate properties too.

- Energy is quantized.
- Electromagnetic radiation is a stream of "particles" called photons.

$$E_{\text{photon}} = h\nu = \frac{hc}{\lambda}$$

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

The Photoelectric effect

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- Energy has mass $E = mc^2$
- Dual nature of light:
  - Electromagnetic radiation (and all matter) exhibits wave properties and particulate properties.

- Continuous spectrum (results when white light is passed through a prism) – contains all the wavelengths of visible light
- Line spectrum – each line corresponds to a discrete wavelength:
  - Hydrogen emission spectrum

Refraction of White Light

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The Line Spectrum of Hydrogen

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Significance

- Only certain energies are allowed for the electron in the hydrogen atom.
- Energy of the electron in the hydrogen atom is quantized.

CONCEPT CHECK!

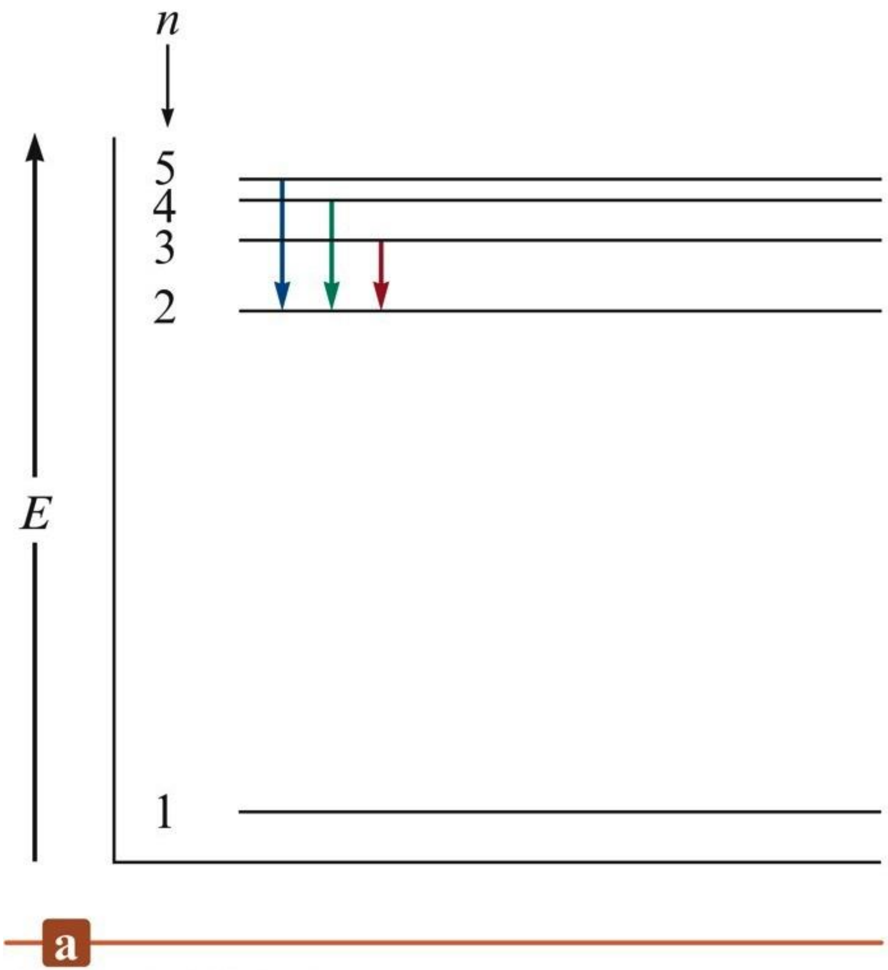
Why is it significant that the color emitted from the hydrogen emission spectrum is not white?

How does the emission spectrum support the idea of quantized energy levels?

- Electron in a hydrogen atom moves around the nucleus only in certain allowed circular orbits.
- Bohr's model gave hydrogen atom energy levels consistent with the hydrogen emission spectrum.
- Ground state – lowest possible energy state ($n = 1$)

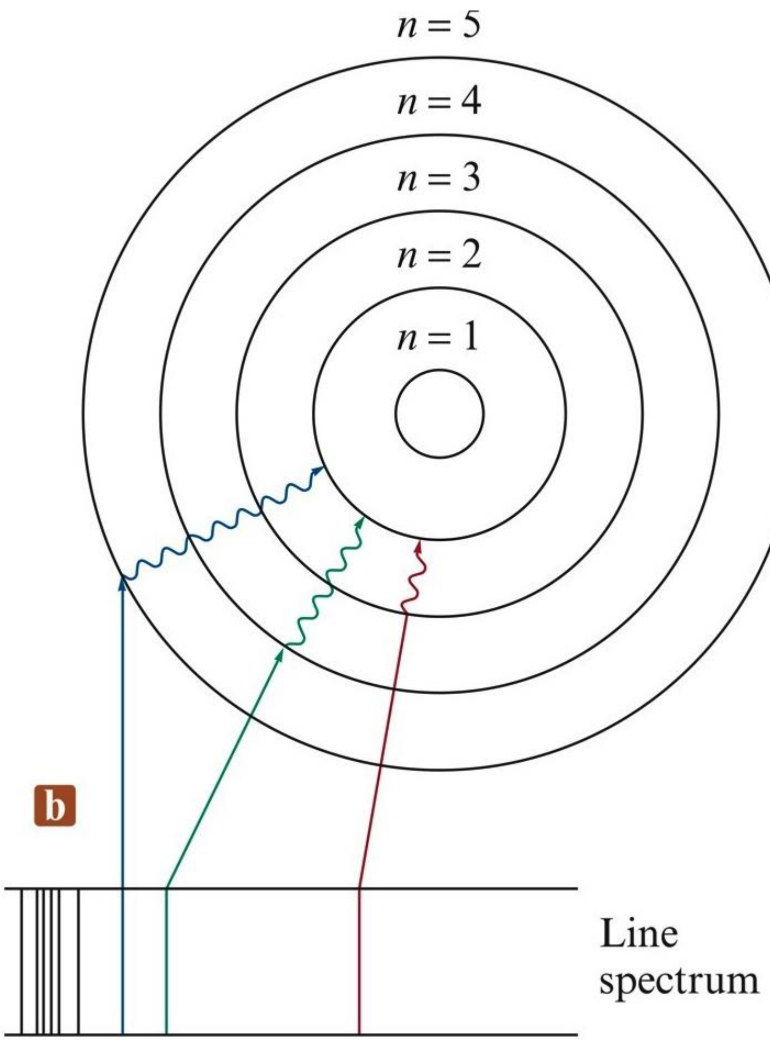
Electronic Transitions in the Bohr Model for the Hydrogen Atom

a) An Energy-Level Diagram for Electronic Transitions



Electronic Transitions in the Bohr Model for the Hydrogen Atom

b) An Orbit-Transition Diagram, Which Accounts for the Experimental Spectrum



- For a single electron transition from one energy level to another:

$$\Delta E = -2.178 \times 10^{-18}\ \mathrm{J}\left(\frac{1}{n_{\text{final}}^2} - \frac{1}{n_{\text{initial}}^2}\right)$$

$\Delta E =$ change in energy of the atom (energy of the emitted photon)

$n_{\text{final}} =$ integer; final distance from the nucleus

$n_{\text{initial}} =$ integer; initial distance from the nucleus

- The model correctly fits the quantized energy levels of the hydrogen atom and postulates only certain allowed circular orbits for the electron.
- As the electron becomes more tightly bound, its energy becomes more negative relative to the zero-energy reference state (free electron). As the electron is brought closer to the nucleus, energy is released from the system.

- Bohr's model is incorrect. This model only works for hydrogen.
- Electrons move around the nucleus in circular orbits.

EXERCISE!

What color of light is emitted when an excited electron in the hydrogen atom falls from:

a) n = 5 to n = 2 — blue, λ = 434 nm
b) n = 4 to n = 2 — green, λ = 486 nm
c) $\boxed{\text{n = 3 to n = 2}}$ — orange/red, λ = 657 nm

Which transition results in the longest wavelength of light?

- We do not know the detailed pathway of an electron.
- Heisenberg uncertainty principle:
  - There is a fundamental limitation to just how precisely we can know both the position and momentum of a particle at a given time.

$$\Delta x \cdot \Delta(m\nu) \geq \frac{h}{4\pi}$$

Δx = uncertainty in a particle's position

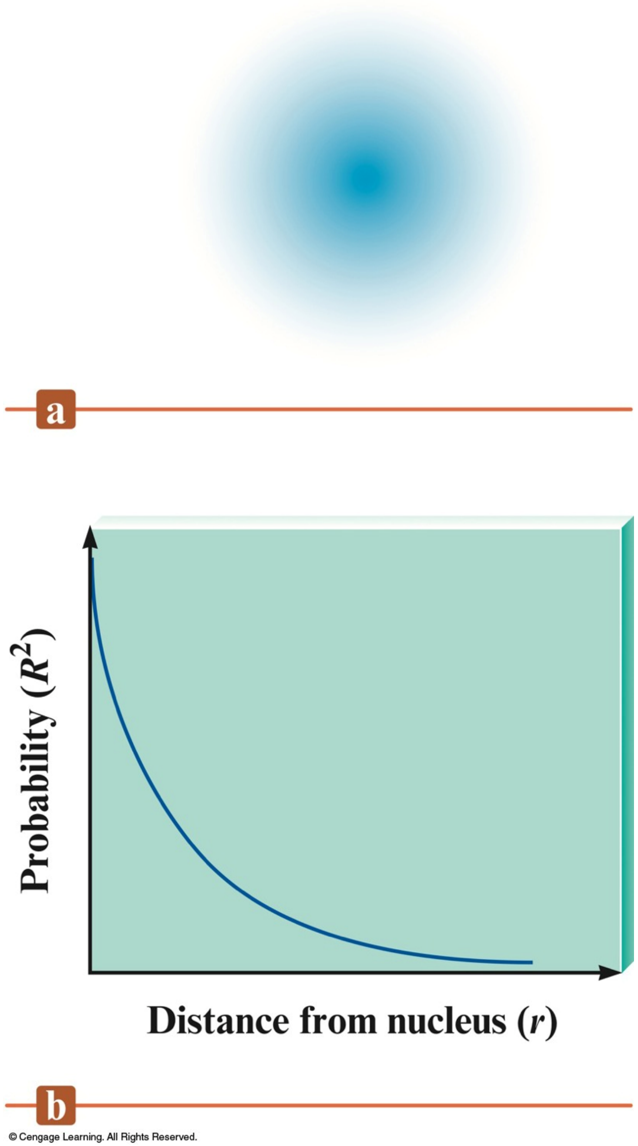
$\Delta(m\nu)$ = uncertainty in a particle's momentum

h = Planck's constant

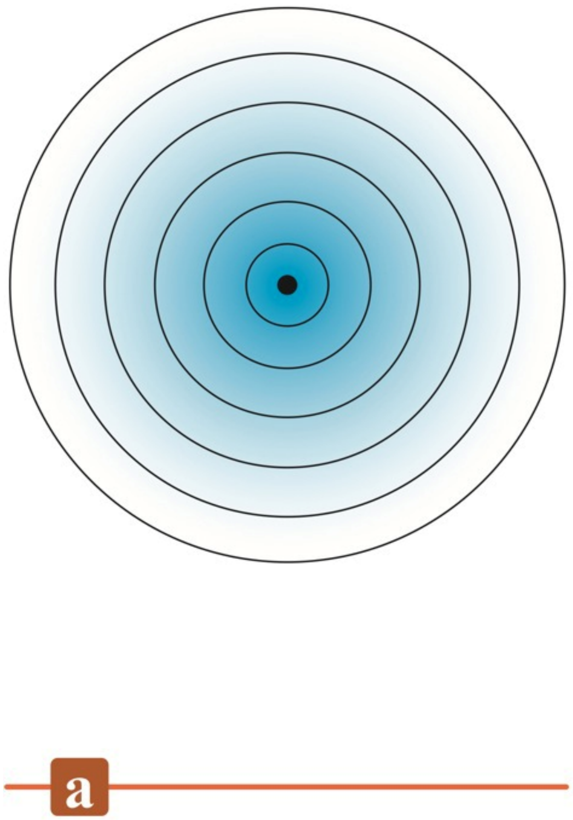
Physical Meaning of a Wave Function (Ψ)

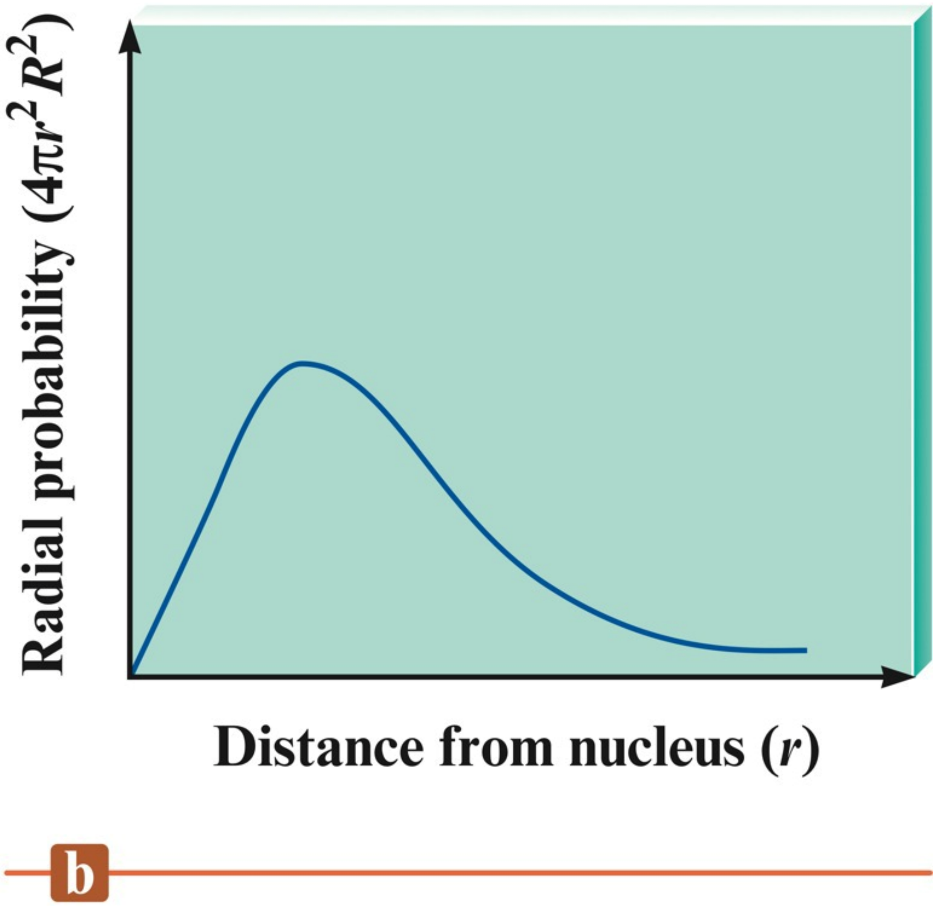
- The square of the function indicates the probability of finding an electron near a particular point in space.
  - Probability distribution – intensity of color is used to indicate the probability value near a given point in space.

Probability Distribution for the 1*s* Wave Function



Radial Probability Distribution





Relative Orbital Size

- Difficult to define precisely.
- Orbital is a wave function.
- Picture an orbital as a three-dimensional electron density map.
- Hydrogen 1*s* orbital:
  - Radius of the sphere that encloses 90% of the total electron probability.

- Principal quantum number (n) – size and energy of the orbital.
- Angular momentum quantum number (l) – shape of atomic orbitals (sometimes called a subshell).
- Magnetic quantum number (m_l) – orientation of the orbital in space relative to the other orbitals in the atom.

Quantum Numbers for the First Four Levels of Orbitals in the Hydrogen Atom

Table 7.2 | Quantum Numbers for the First Four Levels of Orbitals in the Hydrogen Atom

n	ℓ	Sublevel Designation	m_ℓ	Number of Orbitals
1	0	1*s*	0	1
2	0	2*s*	0	1
	1	2*p*	−1, 0, +1	3
3	0	3*s*	0	1
	1	3*p*	−1, 0, 1	3
	2	3*d*	−2, −1, 0, 1, 2	5
4	0	4*s*	0	1
	1	4*p*	−1, 0, 1	3
	2	4*d*	−2, −1, 0, 1, 2	5
	3	4*f*	−3, −2, −1, 0, 1, 2, 3	7

EXERCISE!

For principal quantum level $n = 3$, determine the number of allowed subshells (different values of l), and give the designation of each.

# of allowed subshells = 3

$l = 0$, 3*s*

$l = 1$, 3*p*

$l = 2$, 3*d*

EXERCISE!

For $l = 2$, determine the magnetic quantum numbers (m_l) and the number of orbitals.

magnetic quantum numbers = –2, – 1, 0, 1, 2

number of orbitals = 5

1s Orbital

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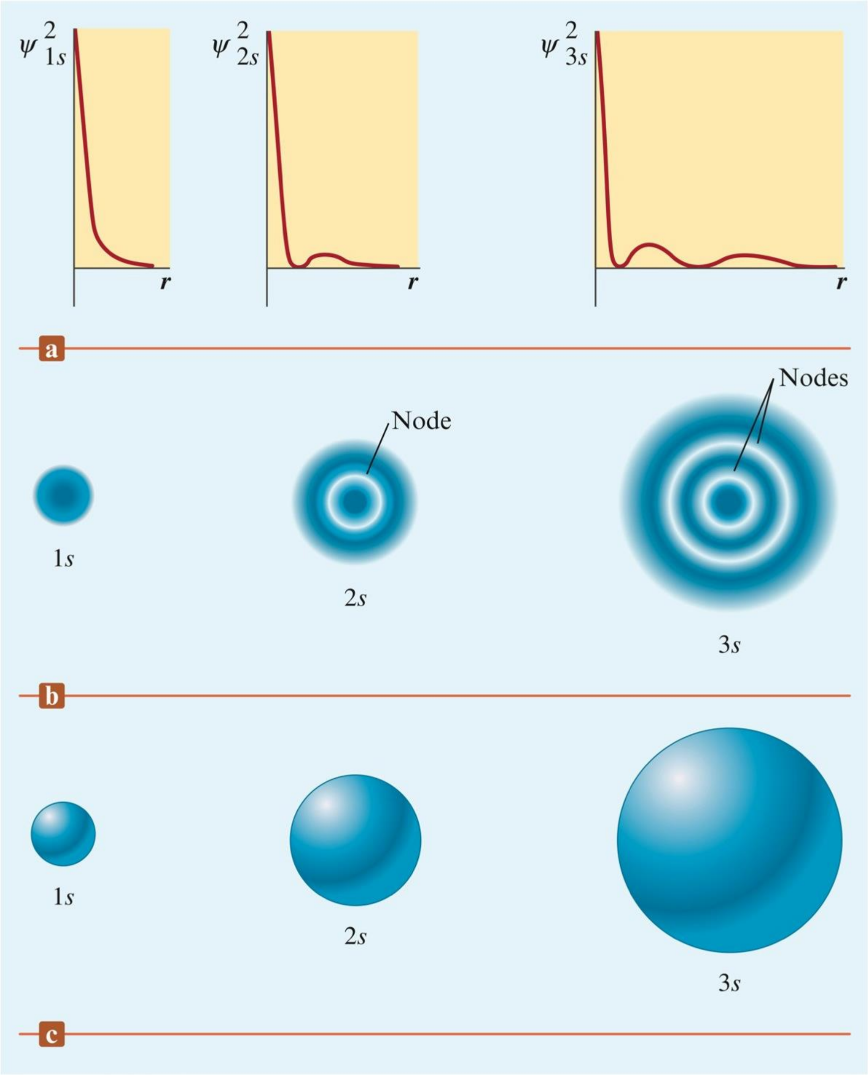
Three Representations of the Hydrogen 1*s*, 2*s*, and 3*s* Orbitals



$2p_x$ Orbital

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$2p_y$ Orbital

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$2p_z$ Orbital

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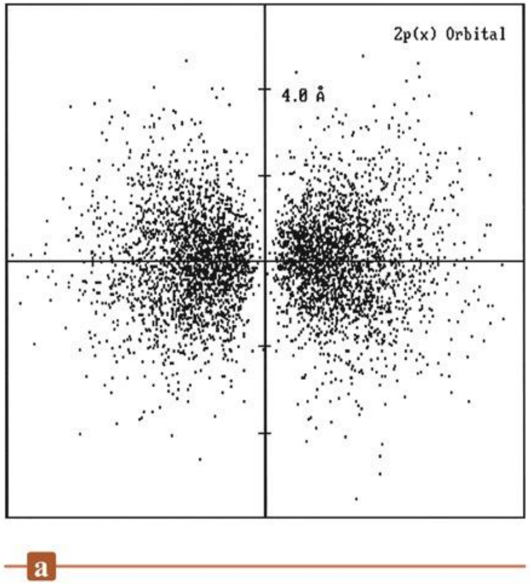
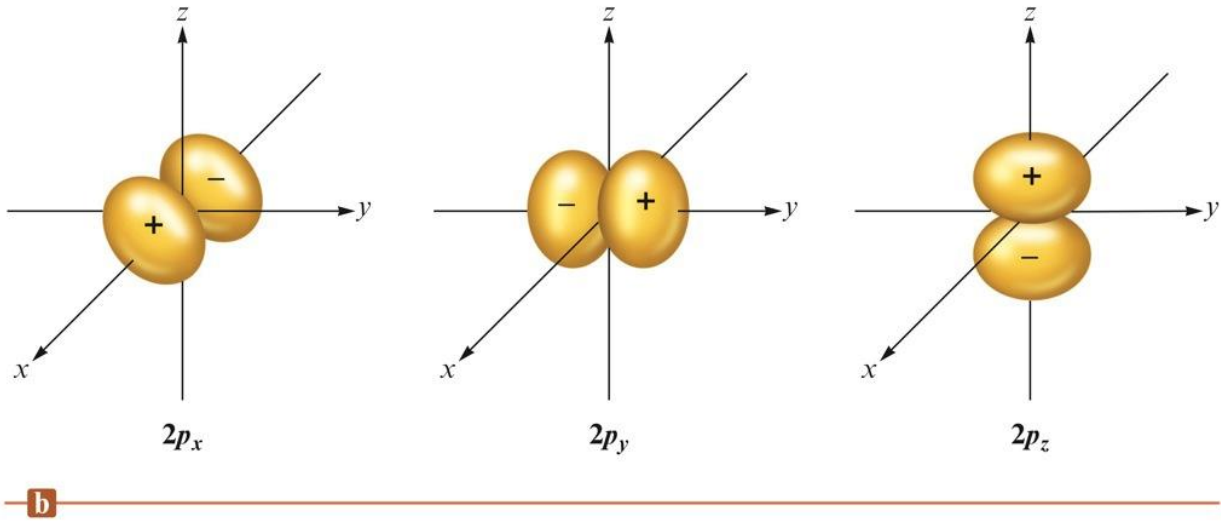
The Boundary Surface Representations of All Three 2*p* Orbitals





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$3d_{x^2-y^2}$ Orbital

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$3d_{xy}$ Orbital

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$3d_{xz}$ Orbital

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3d_{yz} Orbital

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Section 7.7
Orbital Shapes and Energies

$3d_{z^2}$

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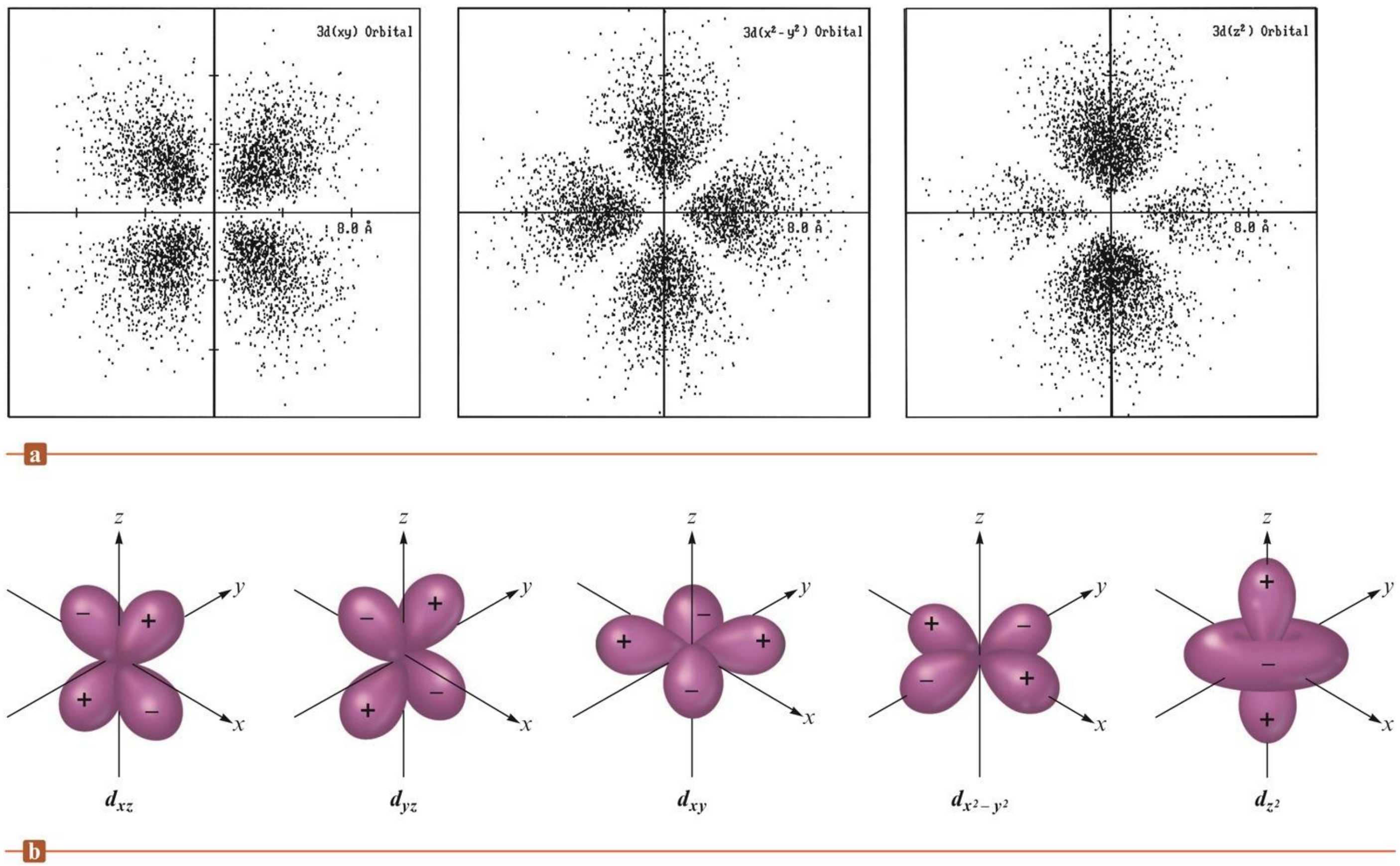
The Boundary Surfaces of All of the 3*d* Orbitals



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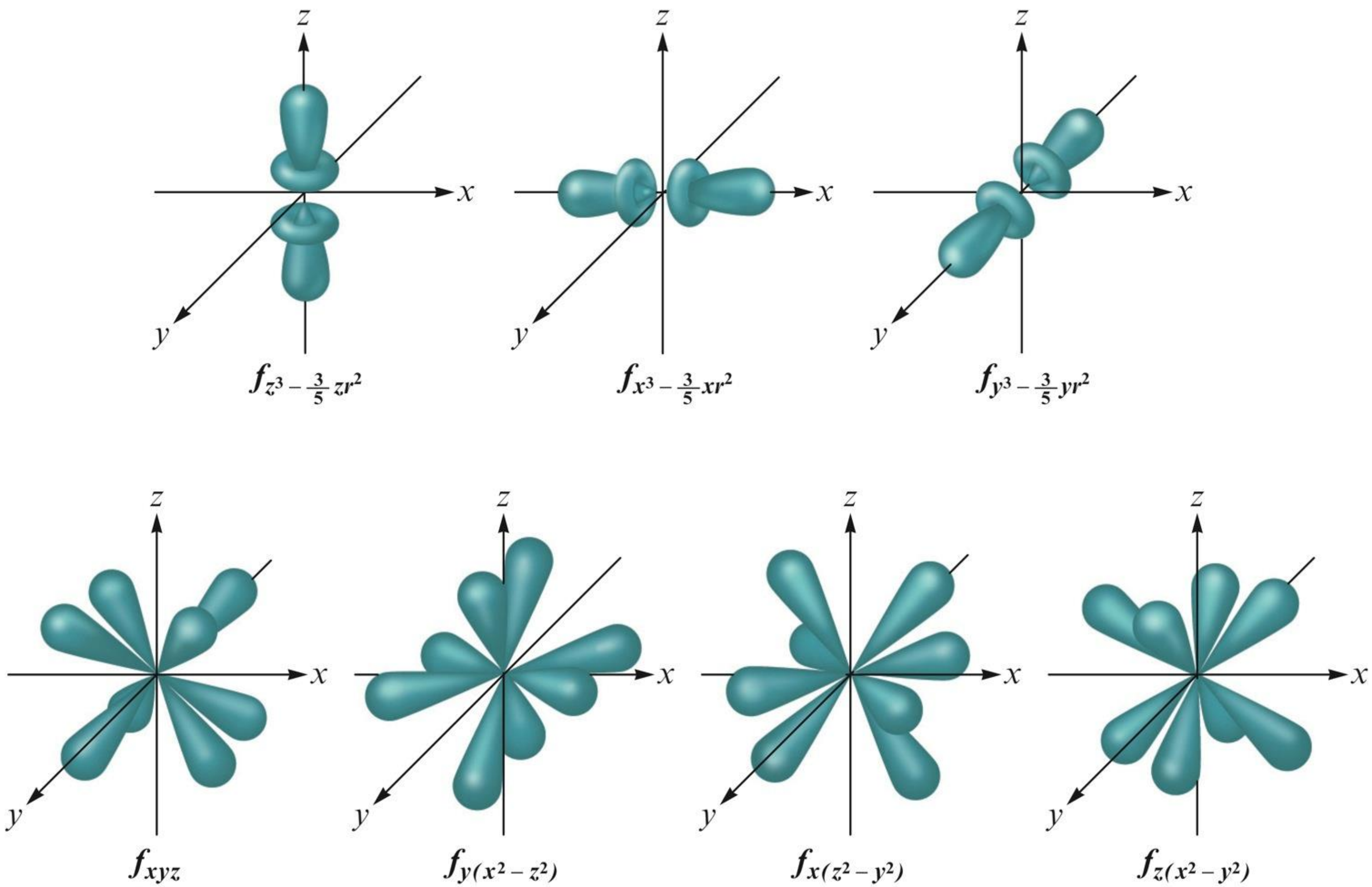
Representation of the 4*f* Orbitals in Terms of Their Boundary Surfaces



Electron Spin

- Electron spin quantum number (m_s) – can be +½ or -½.
- Pauli exclusion principle - in a given atom no two electrons can have the same set of four quantum numbers.
- An orbital can hold only two electrons, and they must have opposite spins.

- Atoms with more than one electron.
- Electron correlation problem:
  - Since the electron pathways are unknown, the electron repulsions cannot be calculated exactly.
- When electrons are placed in a particular quantum level, they "prefer" the orbitals in the order *s*, *p*, *d*, and then *f.*

Penetration Effect

- A 2*s* electron penetrates to the nucleus more than one in the 2*p* orbital.
- This causes an electron in a 2*s* orbital to be attracted to the nucleus more strongly than an electron in a 2*p* orbital.
- Thus, the 2*s* orbital is lower in energy than the 2*p* orbitals in a polyelectronic atom.

Orbital Energies

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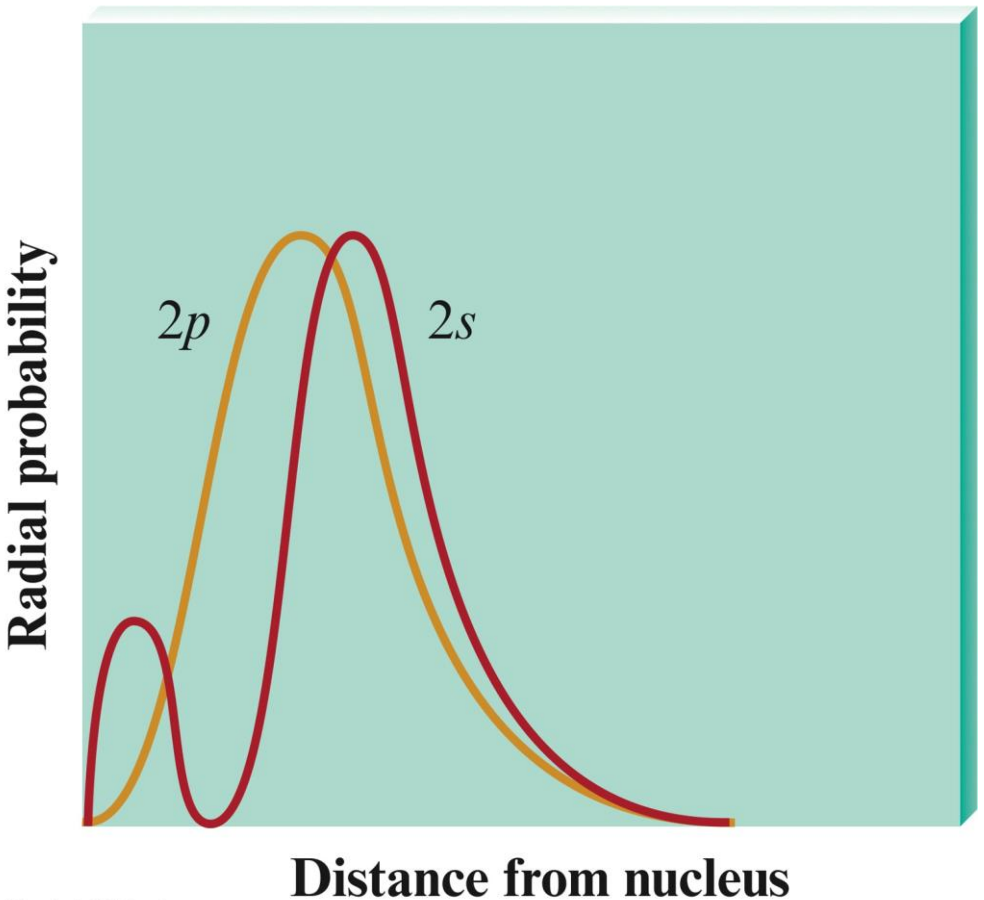
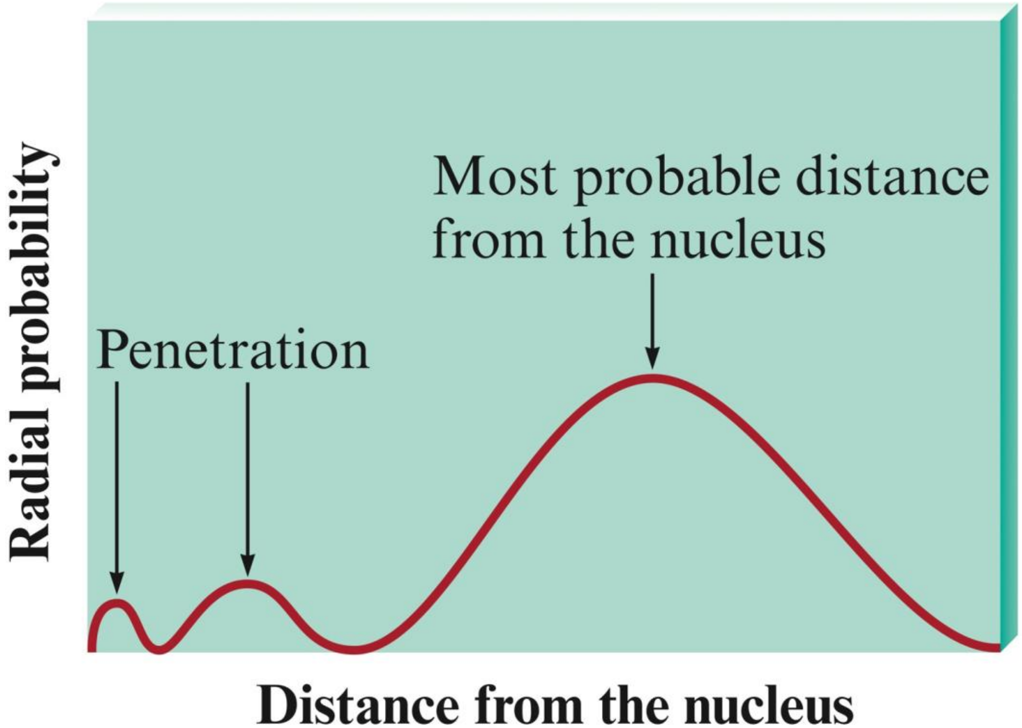
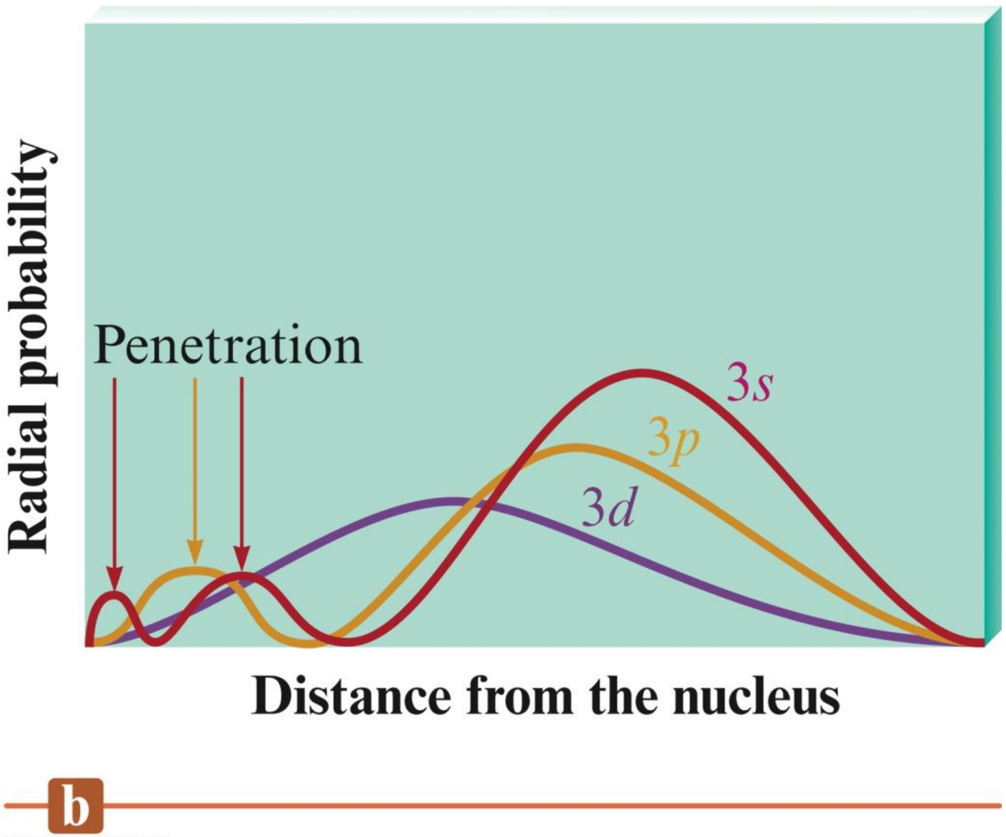
A Comparison of the Radial Probability Distributions of the 2*s* and 2*p* Orbitals



The Radial Probability Distribution of the 3*s* Orbital



A Comparison of the Radial Probability Distributions of the 3*s*, 3*p*, and 3*d* Orbitals



- Originally constructed to represent the patterns observed in the chemical properties of the elements.
- Mendeleev is given the most credit for the current version of the periodic table because he emphasized how useful the periodic table could be in predicting the existence and properties of still unknown elements.

Aufbau Principle

- As protons are added one by one to the nucleus to build up the elements, electrons are similarly added to hydrogen-like orbitals.
- An oxygen atom has an electron arrangement of two electrons in the 1*s* subshell, two electrons in the 2*s* subshell, and four electrons in the 2*p* subshell.

Oxygen: $1s^2 2s^2 2p^4$

Hund's Rule

- The lowest energy configuration for an atom is the one having the maximum number of unpaired electrons allowed by the Pauli principle in a particular set of degenerate (same energy) orbitals.

Orbital Diagram

- A notation that shows how many electrons an atom has in each of its occupied electron orbitals.

Oxygen: $1s^2 2s^2 2p^4$

Oxygen: $1s$ $2s$ $2p$

↑↓	↑↓	↑↓	↑	↑

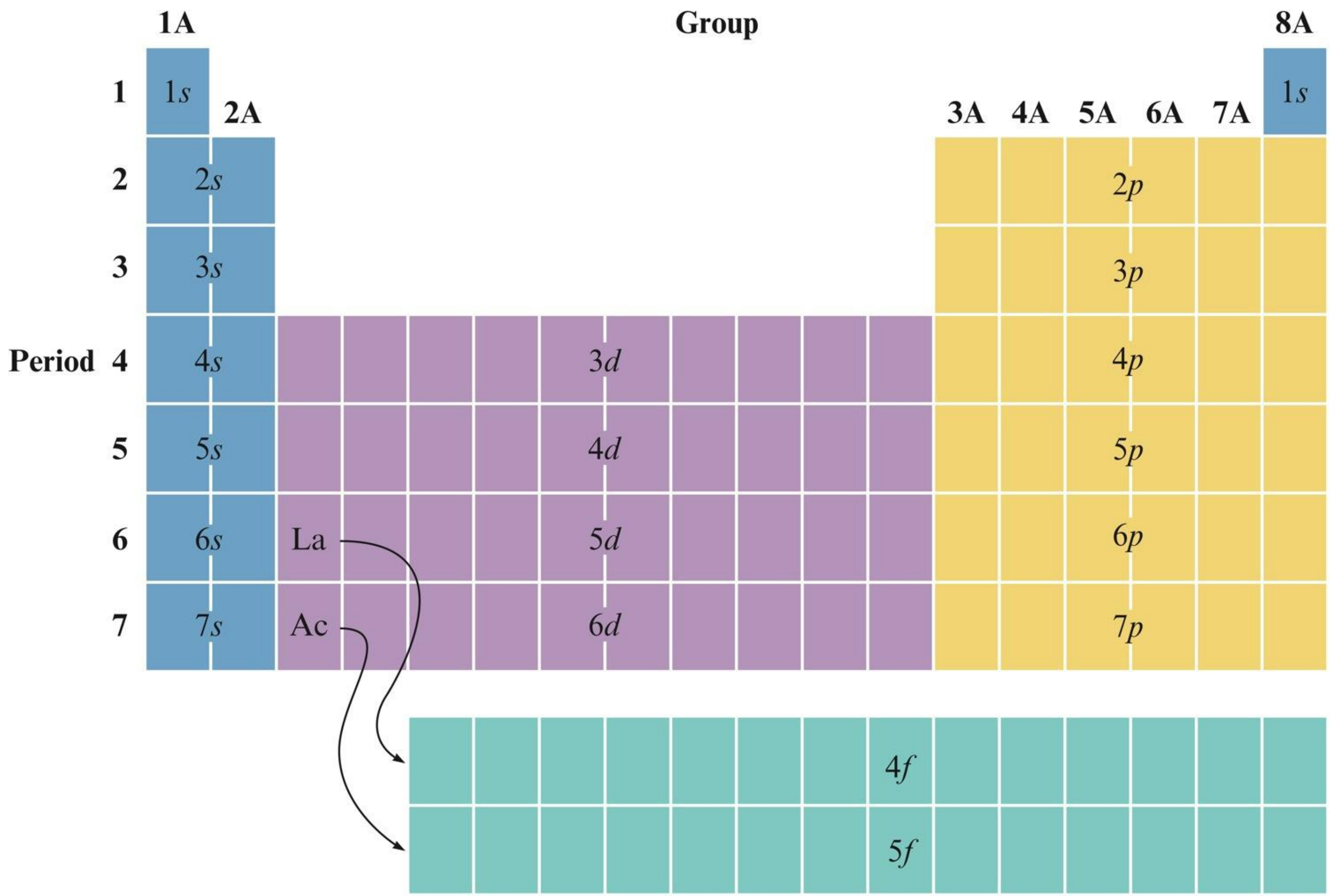
Valence Electrons

- The electrons in the outermost principal quantum level of an atom.

  $1s^22s^22p^6$ (valence electrons = 8)

- The elements in the same group on the periodic table have the same valence electron configuration.

The Orbitals Being Filled for Elements in Various Parts of the Periodic Table



EXERCISE!

Determine the expected electron configurations for each of the following.

a) S

$1s^2 2s^2 2p^6 3s^2 3p^4$ or $[Ne]3s^2 3p^4$

b) Ba

$[Xe]6s^2$

c) Eu

$[Xe]6s^2 4f^7$

Periodic Trends

- Ionization Energy
- Electron Affinity
- Atomic Radius

Ionization Energy

- Energy required to remove an electron from a gaseous atom or ion.
  - $X(g) \rightarrow X^+(g) + e^-$

$Mg \rightarrow Mg^+ + e^-$ $I_1 = 735$ kJ/mol(1st IE)

$Mg^+ \rightarrow Mg^{2+} + e^-$ $I_2 = 1445$ kJ/mol (2nd IE)

$Mg^{2+} \rightarrow Mg^{3+} + e^-$ $I_3 = 7730$ kJ/mol *(3rd IE)

*Core electrons are bound much more tightly than valence electrons.

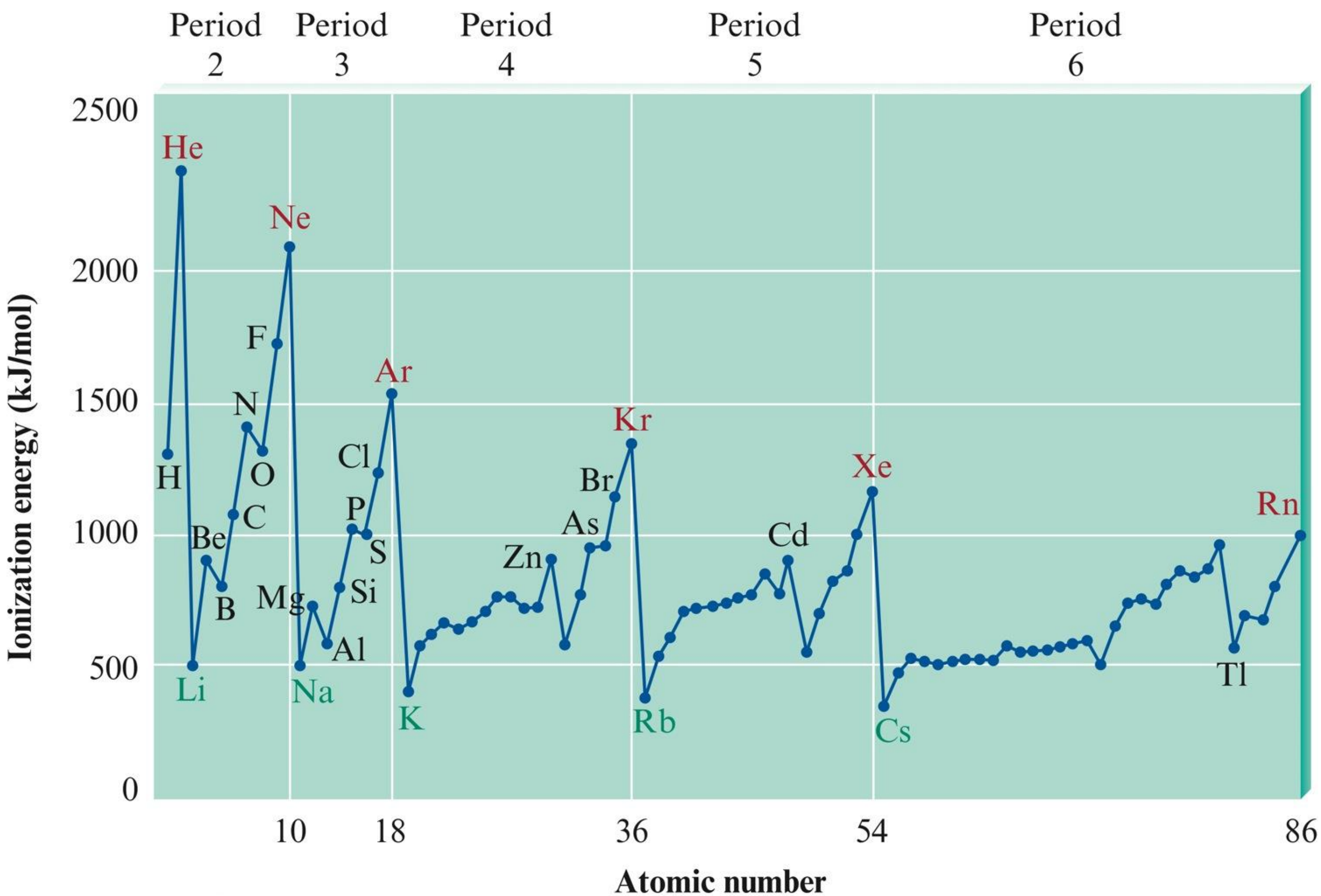
Ionization Energy

- In general, as we go across a period from left to right, the first ionization energy increases.
- Why?
  - Electrons added in the same principal quantum level do not completely shield the increasing nuclear charge caused by the added protons.
  - Electrons in the same principal quantum level are generally more strongly bound from left to right on the periodic table.

Ionization Energy

- In general, as we go down a group from top to bottom, the first ionization energy decreases.
- Why?
  - The electrons being removed are, on average, farther from the nucleus.

The Values of First Ionization Energy for the Elements in the First Six Periods



CONCEPT CHECK!

Explain why the graph of ionization energy versus atomic number (across a row) is not linear.

electron repulsions

Where are the exceptions?

some include from Be to B and N to O

CONCEPT CHECK!

Which atom would require more energy to remove an electron? Why?

Na $\boxed{\text{Cl}}$

CONCEPT CHECK!

Which atom would require more energy to remove an electron? Why?

$\boxed{\text{Li}}$ Cs

CONCEPT CHECK!

Which has the larger second ionization energy? Why?

Lithium or Beryllium

Successive Ionization Energies (KJ per Mole) for the Elements in Period 3

Table 7.5 | Successive Ionization Energies (kJ/mol) for the Elements in Period 3

Element	I_1	I_2	I_3	I_4	I_5	I_6	I_7
Na	495	4560					
Mg	735	1445	7730	Core electrons*			
Al	580	1815	2740	11,600			
Si	780	1575	3220	4350	16,100		
P	1060	1890	2905	4950	6270	21,200	
S	1005	2260	3375	4565	6950	8490	27,000
Cl	1255	2295	3850	5160	6560	9360	11,000
Ar	1527	2665	3945	5770	7230	8780	12,000

*Note the large jump in ionization energy in going from removal of valence electrons to removal of core electrons.

General decrease

General increase

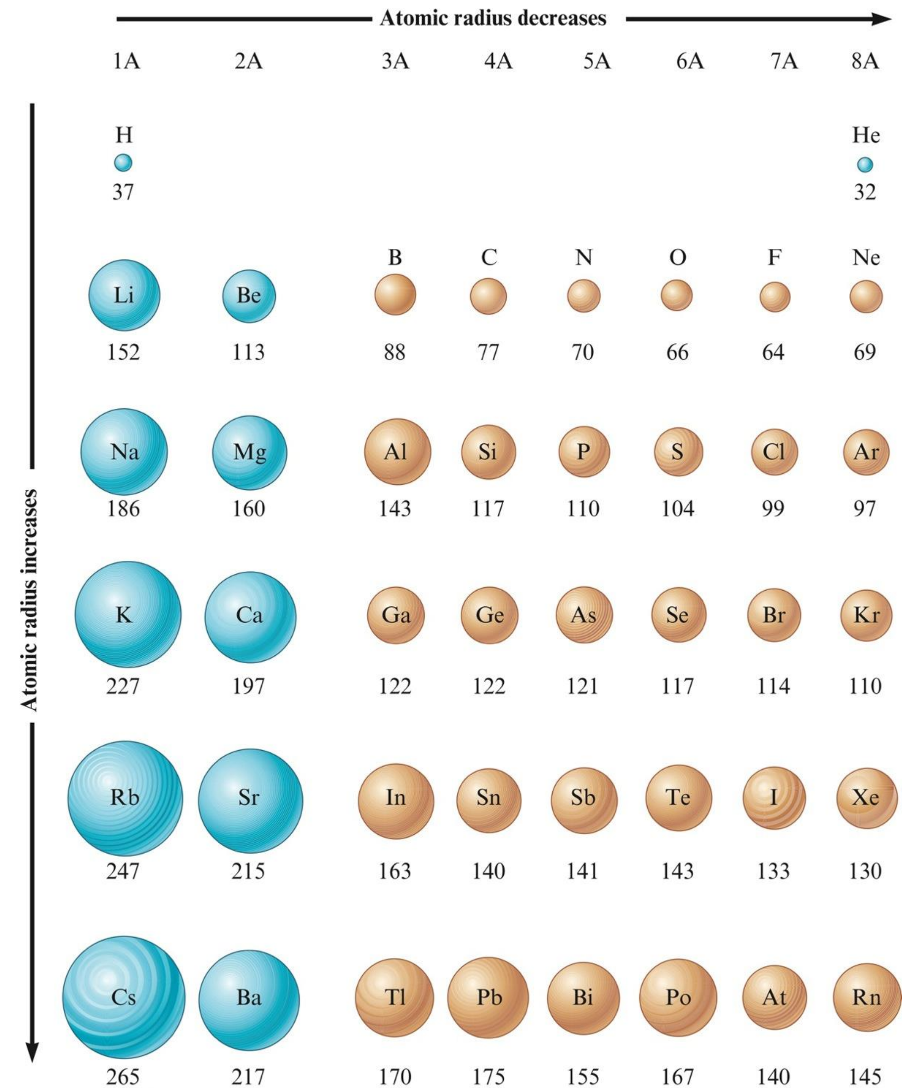
Electron Affinity

- Energy change associated with the addition of an electron to a gaseous atom.
  - $X(g) + e^{-} \rightarrow X^{-}(g)$
- In general as we go across a period from left to right, the electron affinities become more negative.
- In general electron affinity becomes more positive in going down a group.

Atomic Radius

- In general as we go across a period from left to right, the atomic radius decreases.
  - Effective nuclear charge increases, therefore the valence electrons are drawn closer to the nucleus, decreasing the size of the atom.
- In general atomic radius increases in going down a group.
  - Orbital sizes increase in successive principal quantum levels.

Atomic Radii for Selected Atoms



CONCEPT CHECK!

Which should be the larger atom? Why?

$\boxed{\text{Na}}$ Cl

CONCEPT CHECK!

Which should be the larger atom? Why?

Li $\boxed{\text{Cs}}$

CONCEPT CHECK!

Which is larger?

- The hydrogen 1s orbital
- The lithium 1*s* orbital

Which is lower in energy?

- The hydrogen 1*s* orbital
- The lithium 1*s* orbital

Atomic Radius of a Metal

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Atomic Radius of a Nonmetal

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EXERCISE!

Arrange the elements oxygen, fluorine, and sulfur according to increasing:

- Ionization energy

  S, O, F

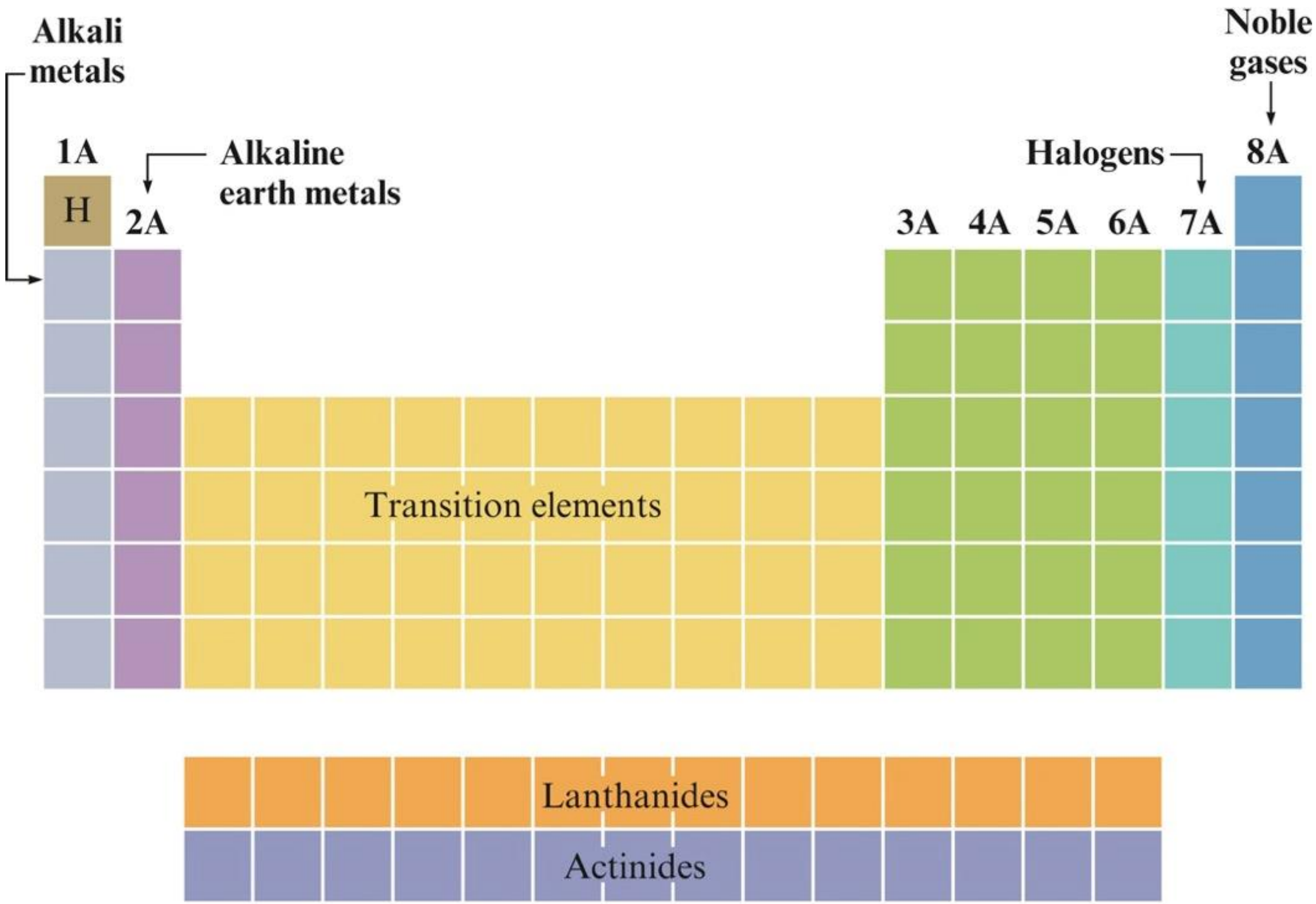
- Atomic size

  F, O, S

The Periodic Table – Final Thoughts

1. It is the number and type of valence electrons that primarily determine an atom's chemistry.
2. Electron configurations can be determined from the organization of the periodic table.
3. Certain groups in the periodic table have special names.

Special Names for Groups in the Periodic Table

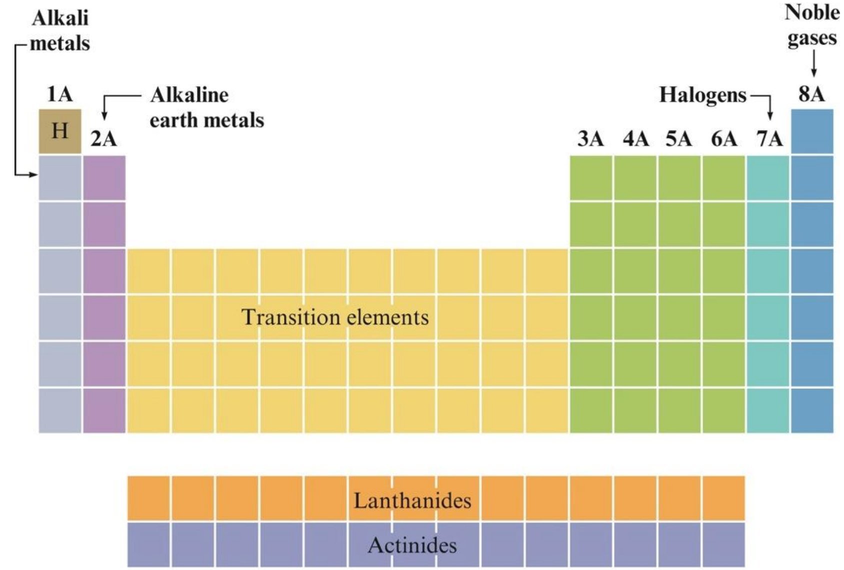


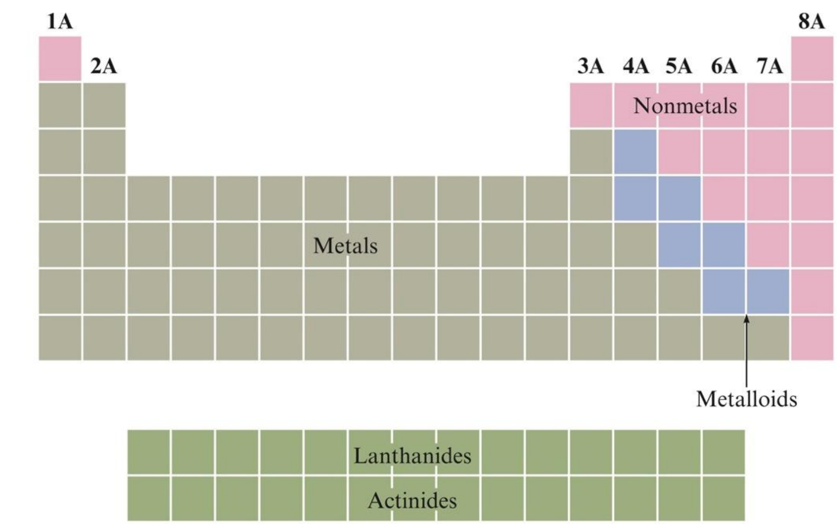
The Periodic Table – Final Thoughts

4. Basic division of the elements in the periodic table is into metals and nonmetals.

Section 7.13
The Properties of a Group: The Alkali Metals

Metals Versus Nonmetals





The Alkali Metals

- Li, Na, K, Rb, Cs, and Fr
  - Most chemically reactive of the metals
    - React with nonmetals to form ionic solids
  - Going down group:
    - Ionization energy decreases
    - Atomic radius increases
    - Density increases
    - Melting and boiling points smoothly decrease