Chapter 2 -The Structure of Atoms

Chapter 12 Quantum Mechanics and Atomic Theory

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Electromagnetic Radiation

One of the ways that energy travels through space is by **electromagnetic radiation**.

Named so because it has **electrical** and **magnetic** fields that simultaneously oscillate in planes mutually perpendicular to each other and to the direction of propagation through space.
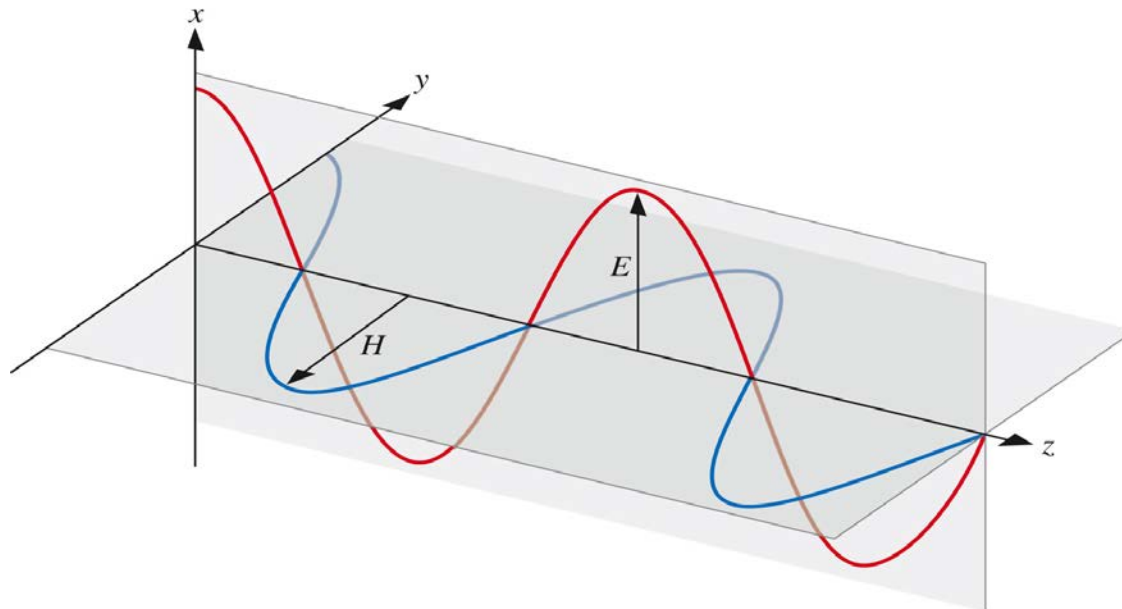

Figure 12.1 - Electromagnetic radiation has oscillating electric (*E*) and magnetic (*H*) fields in planes perpendicular to each other and to the direction of propagation.

Electromagnetic Radiation

Waves are periodic oscillations that transmit energy through space

They are characterized by **wavelength**, **frequency** and **speed**.

Wavelength (λ)

Distance between 2 consecutive peaks or troughs in a wave

Described by any appropriate unit of distance (m, $\mu m = 10^{-6}$ m, $nm = 10^{-9}$m or $pm = 10^{-12}$ m)

Frequency (ν)

Number of waves per second that pass a given point in space.

Units are : oscillations per second or $1/s = s^{-1}$, which is called the *hertz* (Hz)

Since all types of electromagnetic radiation travel through vacuum at the speed of light, short-wavelength must have a high frequency.

$$\lambda \nu = c$$

c = speed of light = 2.99792458×10^8 m/s

Electromagnetic Radiation

$\leftarrow$ 1 second $\rightarrow$

λ_1

$\nu_1 = 4$ cycles/second $= 4$ hertz

λ_2

$\nu_2 = 8$ cycles/second $= 8$ hertz

λ_3

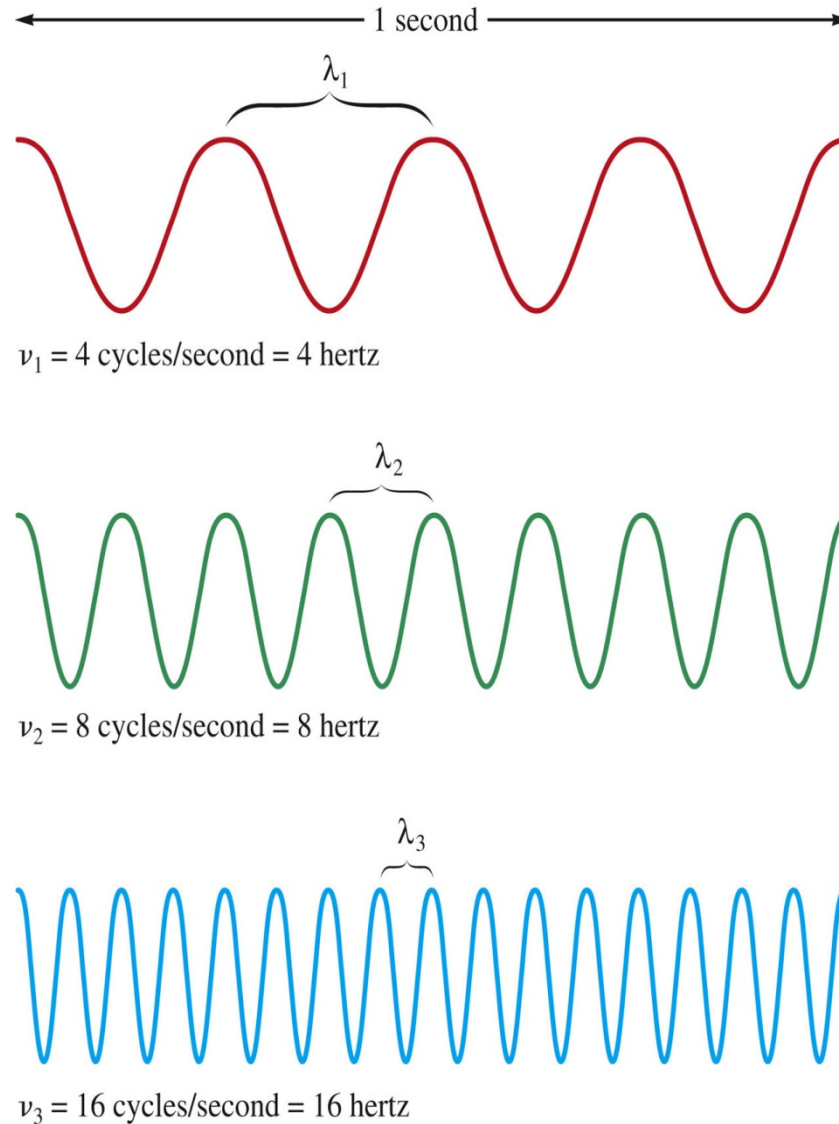$\nu_3 = 16$ cycles/second $= 16$ hertz

Figure 12.2 - The nature of waves. Note that the radiation with the shortest wavelength has the highest frequency. This diagram can represent the oscillating electric or magnetic field of the wave.

Electromagnetic Radiation

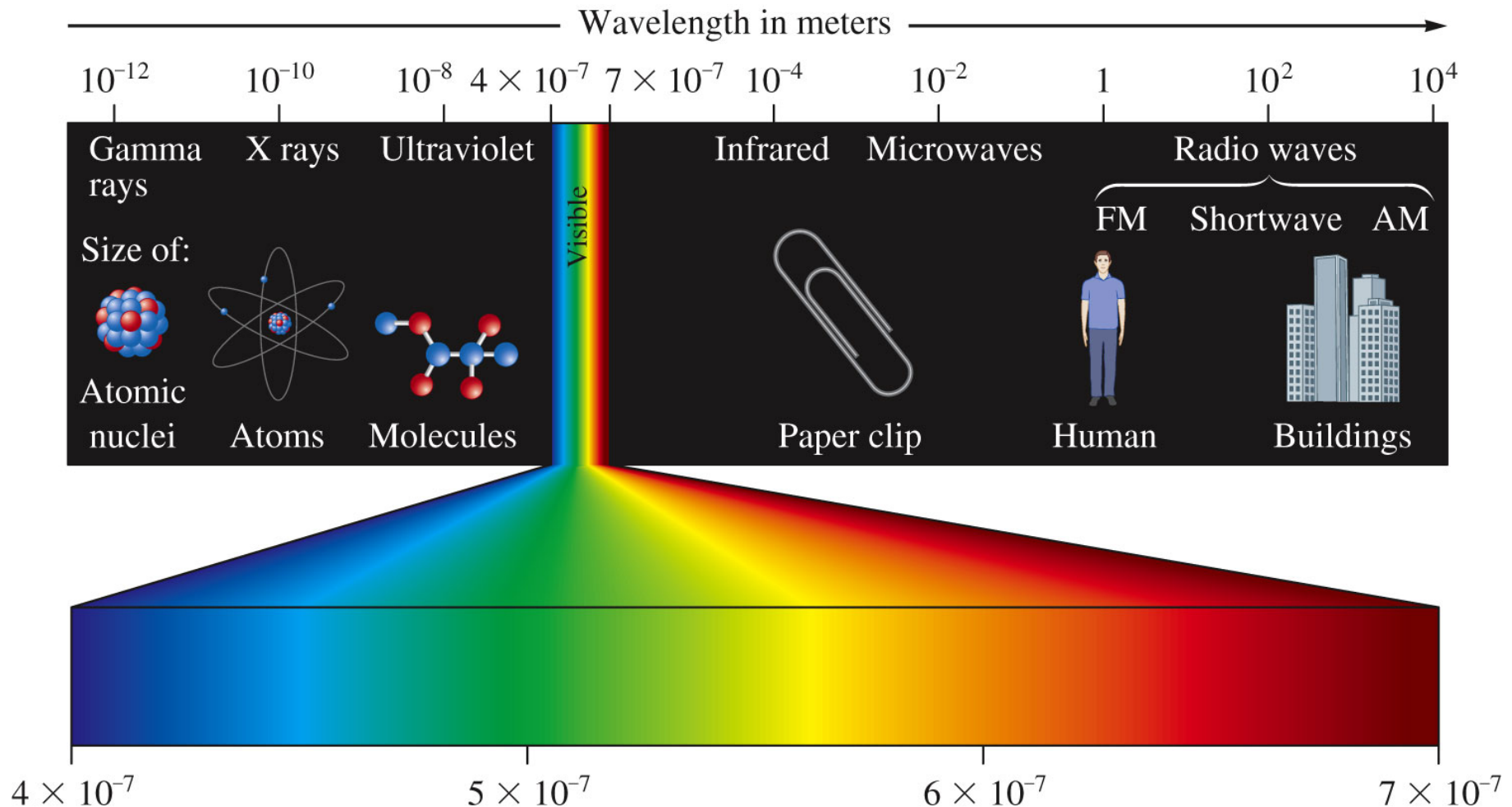Electromagnetic radiation provide an important means of energy transfer

Figure 12.3 - Classification of electromagnetic radiation.

The Nature of Matter

At the end of the 19th century, it was thought that matter and energy were distinct.

Matter was thought to consist of particles (specific mass and position in space) and energy was described as a wave (massless and delocalized).

It was assumed that energy is continuous and that any amount of energy could be released in any radiation process.

The Nature of Matter

In 1901, Max Planck discovered that energy is not continuous. It can be gained or lost in whole-number multiples of the quantity $h\nu$

h (Planck's constant) = 6.626 10^{-34} J.s

The energy is quantized and can be transferred only in discrete units of size $h\nu$. Each of these small "packets" of energy is called *quantum*. A system can transfer energy only in whole *quanta*.

Thus energy seems to have particulate properties.

The Nature of Matter

Example 12.1

The blue color in fireworks is often achieved by heating copper (I) chloride (CuCl) to about 1200°C. The hot compound emits blue light having a wavelength of 450 nm. What is the increment of energy (the quantum) that is emitted at 4.5×10^2 nm by CuCl?

The Nature of Matter

SOLUTION

$\Delta E = h\nu$

$\nu = \dfrac{c}{\lambda} = \dfrac{2.9979 \times 10^8 \text{ m/s}}{450 \times 10^{-9} \text{ m}} = 6.66 \times 10^{14} \text{ s}^{-1}$

So $\Delta E = h\nu = (6.626 \times 10^{-34} \text{ J s})(6.66 \times 10^{14} \text{ s}^{-1}) = 4.41 \times 10^{-19} \text{ J}$

The Nature of Matter

Albert Einstein - The photoelectric effect: phenomenon in which e$^-$ are emitted from the surface of a metal when light strikes it
- No e$^-$ are emitted below a specific threshold frequency ν_0
- Regardless of the intensity of light, no e$^-$ are emitted if $\nu < \nu_0$
- If $\nu > \nu_0$, number of e$^-$ emitted increases with the intensity
- If $\nu > \nu_0$, the KE of e$^-$ emitted increases linearly with ν

⬇

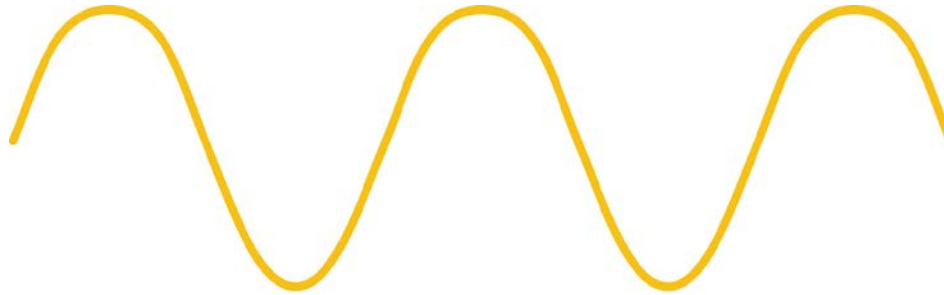electromagnetic radiation is quantized.

⬇

stream of "particles" called photons.

⬇

The energy of each photon is

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

As λ increases, E decreases

The Nature of Matter

Dual nature of light: wave and particle properties

Light as a wave phenomenon

Light as a stream of photons

Figure 12.6 - Electromagnetic radiation exhibits wave properties and particulate properties. The energy of each photon of the radiation is related to the wavelength and frequency by the equation
$$E_{photon} = h\nu = hc/\lambda.$$

The Nature of Matter

Louis de Broglie - 1923:
- If light was found to have particulate matter characteristics, is the opposite true?
- Does matter that is normally assumed to be particulate exhibit wave properties?

- The particle and the wave properties are related by the expression:

$$\lambda = \frac{h}{mv}$$

λ is the wavelength (m)

h *is the* Planck's constant (J.s or Kg m^2 /s)

M is the mass (Kg)

v is the velocity (m/s)

- The wave properties become observable only for submicroscopic objects due to the smallness of Planck's constant.

The Nature of Matter

Example 12.2

Compare the wavelength for an electron (m= 9.11 x 10^{-31} kg) traveling at a speed of 1 x 10^7 m/s with that for a ball (mass = 0.1 Kg) traveling at 35 m/s.

The Nature of Matter

$$\lambda = \frac{h}{mv}$$

h = 6.26 x 10^{-34} J s = 6.26 x 10^{-34} Kg m²/s

For the electron,

λ = $\dfrac{6.26 \times 10^{-34} \text{ Kg m}^2/\text{s}}{(9.11 \times 10^{-31} \text{ Kg})(10^7 \text{ m/s})}$ = 7.3 x 10^{-11} m

For the ball,

λ = $\dfrac{6.26 \times 10^{-34} \text{ Kg m}^2/\text{s}}{(0.1 \text{ Kg})(35 \text{ m/s})}$ = 1.9 x 10^{-34} m

The Atomic Spectrum of Hydrogen

When a high energy discharge is passed through a sample of hydrogen gas, the H_2 molecules absorb energy, causing some of the H-H bonds to break. The resulting hydrogen atoms are *excited*; that is, they contain excess energy, which they release by emitting light of various wavelengths to produce what is called the *emission spectrum* of the hydrogen atom.

White light – prism – continuous spectrum- all wavelengths of visible light

Hydrogen emission spectrum in the visible – prism – few lines (discrete wavelengths) – line spectrum
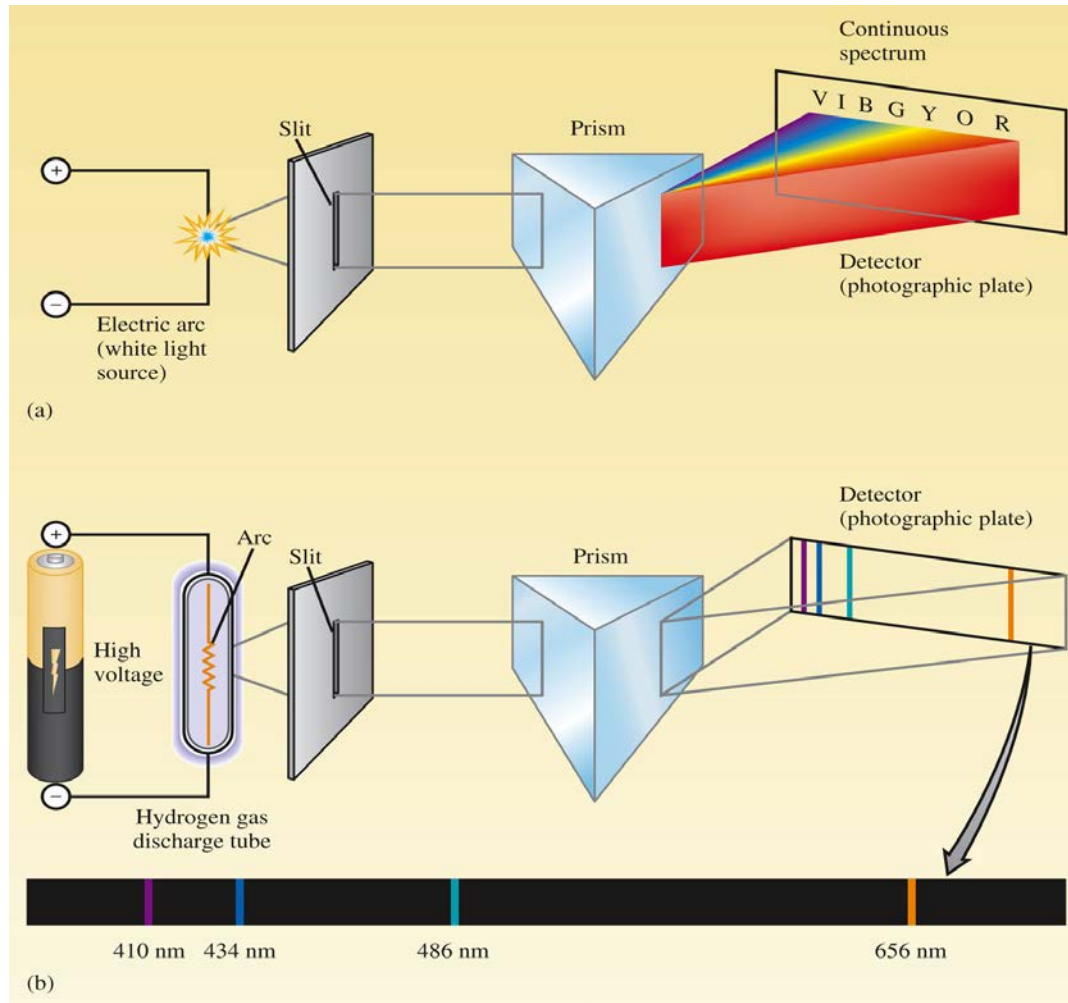
The Atomic Spectrum of Hydrogen

Figure 12.8 - (a) A continuous spectrum containing all wavelengths of visible light (indicated by the first letters of the colors of the rainbow). (b) The hydrogen line spectrum contains only a few discrete wavelengths.
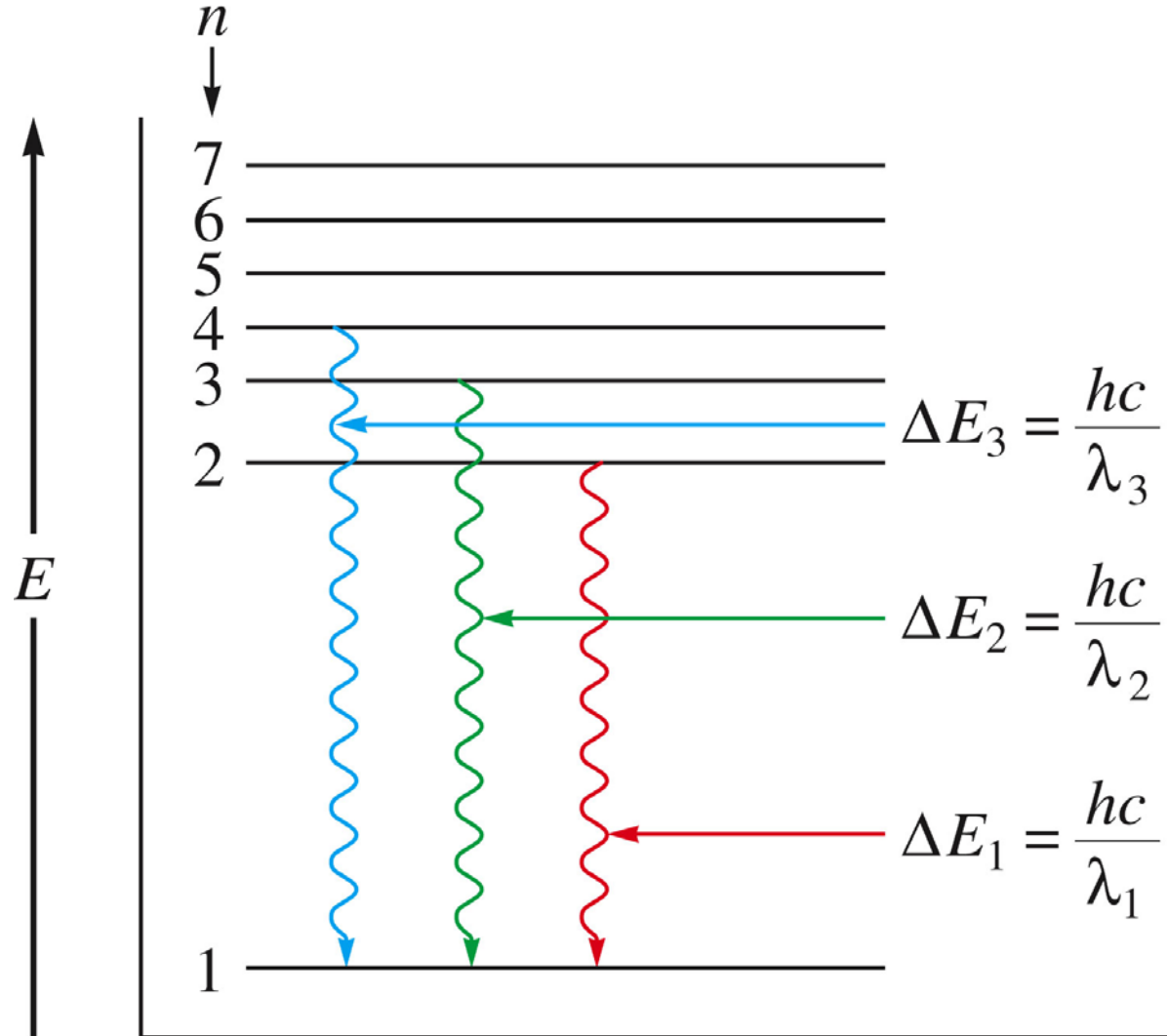
The Atomic Spectrum of Hydrogen

Figure 12.9 - A change between two discrete energy levels emits a photon of light

The Atomic Spectrum of Hydrogen

Significance of the line spectrum of hydrogen:

- Only certain energies are allowed for the electron in the hydrogen atom.
- The energy of the e$^-$ in the hydrogen atom is quantized.
- Changes in energy between discrete energy levels in hydrogen produce only certain wavelengths of emitted light.

The Bohr Model

In 1913, **Bohr** developed a quantum model for the hydrogen atom.
- *e^- in a hydrogen atom moves around the nucleus only in certain allowed circular orbits.*
- by using the theories of classical physics and by making some new assumptions, he gave the expression for the energy levels available to the electron in the hydrogen atom

$$E = -2.178 \times 10^{-18} \text{ J } (1/n^2)$$

- *n* is an integer, the larger its value, the larger is the orbit radius
- The negative sign means that the energy of the e- bound to the nucleus is lower than it would be if the electron were at an infinite distance (*$n = \infty$*).
- This equation can be used to calculate the change in energy when the electron changes orbits.
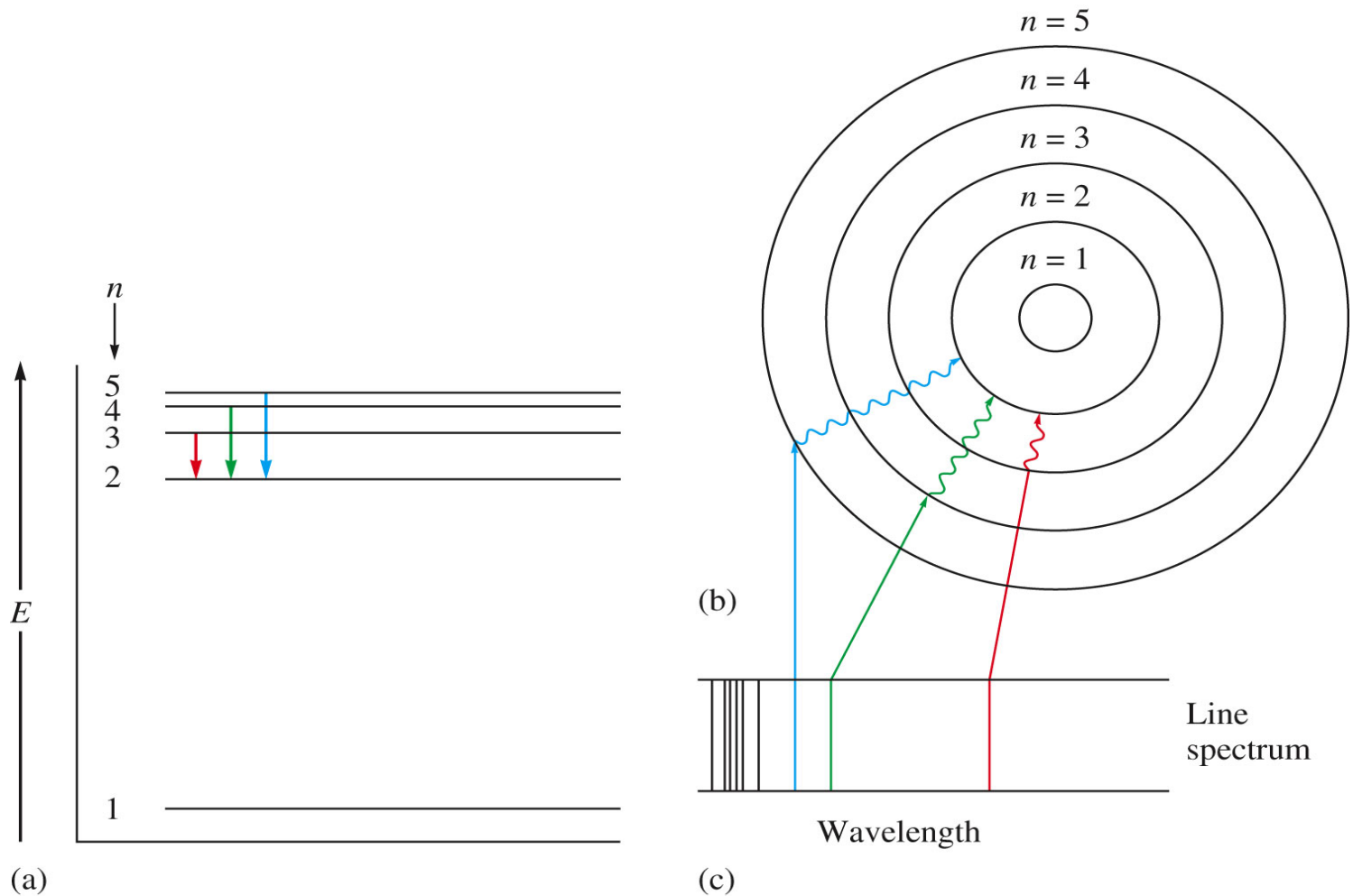
The Bohr Model

Figure 12.10 - Electronic transitions in the Bohr model for the hydrogen atom. (a) An energy level diagram for electronic transitions. (b) An orbit-transition diagram, which accounts for the experimental spectrum. (Note that the orbits shown are schematic. They are not drawn to scale.) (c) The resulting line spectrum on a photographic plate. Note that the lines in the visible region of the spectrum correspond to transitions from higher levels to the $n = 2$ level.

The Bohr Model

Calculate the change in energy when the electron in an excited hydrogen atom falls back from n=6 to n=1.

E_6 = -2.178 x 10^{-18} J (1/6^2) = -6.05 x 10^{-20} J
E_1 = -2.178 x 10^{-18} J (1/1^2) = -2.178 x 10^{-18} J

$\Delta E = E_1 - E_6$ = (-2.178 x 10^{-18}) - (- 6.05 x 10^{-20}) = -2.118 x 10^{-18} J

The negative sign for the change in energy indicates that the atom has lost energy and is now more stable.

The absolute value of ΔE must be used for the calculation of λ.

$$\lambda = \frac{h\,c}{\Delta E} = \frac{(6.626 \times 10^{-34} \text{ J s}) (2.9979 \times 10^8 \text{ m/s})}{2.118 \times 10^{-18} \text{ J}} = 9.379 \times 10^8 \text{ m}$$

The Bohr Model

Two important points about the Bohr model

-The model correctly fits the quantized energy levels of the hydrogen atom as inferred from its emission spectrum.

- As the e$^-$ becomes more tightly bound, its energy becomes more negative relative to the zero-energy reference state ($n=\infty$). As the e$^-$ is brought closer to the nucleus, energy is released from the system.

A general equation for the electron moving from one level ($n_{initial}$) to another level (n_{final}):

$$\Delta E = E_{final} - E_{initial} = (-2.178 \times 10^{-18} \text{ J}) (1/n_{final}^2) - (-2.178 \times 10^{-18} \text{ J}) (1/n_{initial}^2)$$

$$= (-2.178 \times 10^{-18} \text{ J}) (1/n_{final}^2 - 1/n_{initial}^2)$$

The Bohr Model

Example 12.3

Calculate the energy required to excite the hydrogen electron from level n=1 to level n=2. Also calculate the wavelength of light that must be absorbed by a hydrogen atom in its ground state to reach this excited state.

The Bohr Model

SOLUTION

$E_1 = -2.178 \times 10^{-18}$ J $(1/1^2) = -2.178 \times 10^{-18}$ J

$E_2 = -2.178 \times 10^{-18}$ J $(1/2^2) = -5.445 \times 10^{-18}$ J

$\Delta E = E_2 - E_1 = (-5.445 \times 10^{-18}) - (-2.178 \times 10^{-18}) = 1.634 \times 10^{-18}$ J

The positive value of indicates that the system has gained energy.

$$\lambda = \frac{h\,c}{\Delta E} = \frac{(6.626 \times 10^{-34} \text{ J s}) (2.9979 \times 10^{8} \text{ m/s})}{1.634 \times 10^{-18} \text{ J}} = 1.216 \times 10^{-7} \text{ m}$$

The Bohr Model

Example 12.4

Calculate the minimum energy required to remove the electron from a hydrogen atom in its ground state.

The Bohr Model

SOLUTION

$\Delta E = E_{final} - E_{initial} = (-2.178 \times 10^{-18} \text{ J}) (1/n_{final}^2 - 1/n_{initial}^2)$

If no interaction between the nucleus and the e⁻ ➡ E = 0 and n= ∞

$\Delta E = -2.178 \times 10^{-18} \text{ J} (1/\infty - 1/1^2) = 2.178 \times 10^{-18} \text{ J}$

The Bohr Model

Limitations of the Bohr Model

- The energies calculated by Bohr agreed with the values obtained from the hydrogen emission spectrum.

- However, when applied to atoms other than hydrogen, it did not work at all.

The Quantum Mechanical Description

- Since the Bohr model was not a valid model.
- Heisenberg, De Broglie, and Schrödinger developed the **wave mechanics** or **quantum mechanics**.
- De Broglie originated the idea that the e^- shows wave properties.
- Schrödinger decided to explain the atomic structure by emphasizing on the wave properties.
- Using a complicated mathematical technique, he formulated an equation that describes the behavior and energies of submicroscopic particles.
- The Schrödinger equation specifies the possible energy states the e^- can occupy in a hydrogen atom and identifies the corresponding wave functions (Ψ).
- A specific wave function for a given e^- is often called an **orbital**.
- However, an orbital is not a Bohr orbit.

The Quantum Mechanical Description

- The wave function gives us no information about the movements of the e⁻.
- **Heisenberg uncertainty principle:** *There is a fundamental limitation to just how precisely we can know both the position and the momentum (mass x velocity) of a particle at a given time.*
- Quantum mechanics **cannot pinpoint the electron in an atom** it defines a region where the electron might be at a given time.
- *Electron density* is the measure of the **probability** of an *electron* being present at a specific location.
- Regions of high electron density represent a **high probability** of locating the electrons.
- An atomic **orbital is a region around the nucleus where there** is a high probability of finding an electron.

The characteristics of Hydrogen Orbitals

After solving the Schrödinger equation for the hydrogen atom, it was found that many **wave functions** (**orbitals**) satisfy it.

Each of these orbitals is characterized by a set of **quantum numbers**.

Quantum numbers are required to describe the distribution of electrons in hydrogen and other atoms.

1. The principle quantum number (**n**)

2. The angular momentum quantum number (l)

3. The magnetic quantum number (m_l)

4. The spin quantum number (m_s)

The principal quantum number (*n*)

• It can have integral values (1,2,3,...)

• It is related to the **size and energy** of the orbital

• As n increases

- the orbital becomes larger and e$^-$ are farther from the nucleus.

- higher energy because e$^-$ are less tightly bound to the nucleus, and the energy is less negative.

The angular momentum quantum number (*l*)

- It can have integral values from 0 to n-1 for each value of n.
- It is related to the **shape** of the orbital
- The values of *l* are designated by letters s, p, d, f, …
- Each set of orbitals with a given value of *l* is called **subshell**.

Table 12.2

The Angular Momentum Quantum Numbers and Corresponding Letter Symbols

Value	Letter Used
0	s
1	p
2	d
3	f
4	g

The magnetic quantum number (m_l)

- It can have integral values between *l* and *-l,* including zero.

- It is related to the **orientation in space** of the angular momentum associated with the orbital and to the **number of orbitals**.

Table 12.3

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

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

The magnetic quantum number (m_l)

Example 12.7

For principal quantum level $n=5$, determine the number of subshells (different values of l) and give the designation of each.

The magnetic quantum number (m_l)

SOLUTION

For $n=5$,

$l=0$	$l=1$	$l=2$	$l=3$	$l=4$
5s	5p	5d	5f	5g

Orbital Shapes and Energies

Orbitals are presented by the surface that surrounds 90% of the total electron probability.

s orbitals (*l*=0) are spherical

1s

2s

(c)

3s
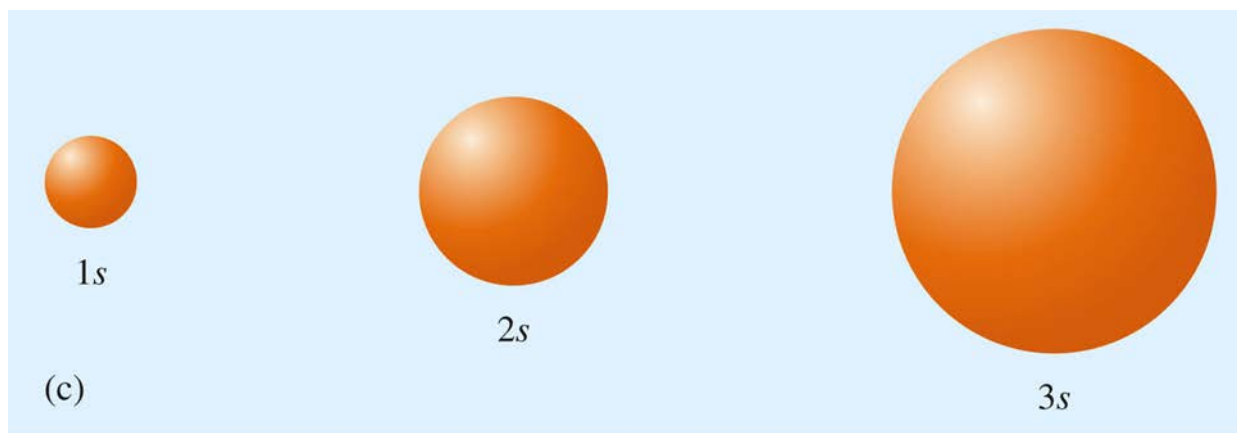
Figure 12.18 - Three representation of the hydrogen 1s, 2s and 3s orbitals

Orbital Shapes and Energies

p orbitals (l=1) have two lobes separated by a node at the nucleus. They are labeled according to the axis along which the lobes lie.
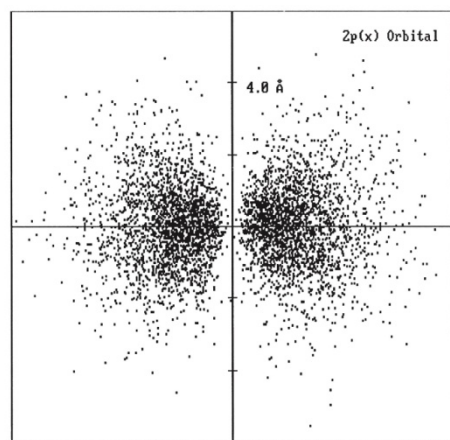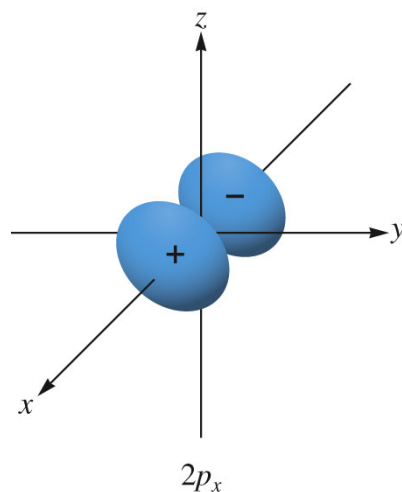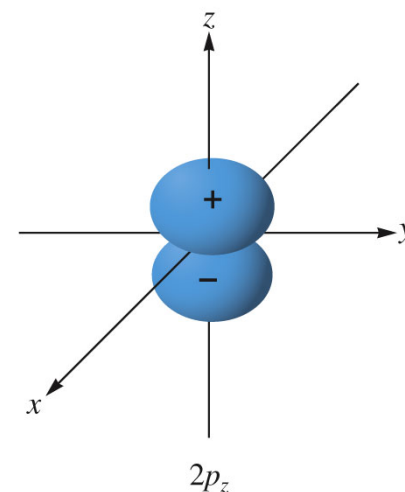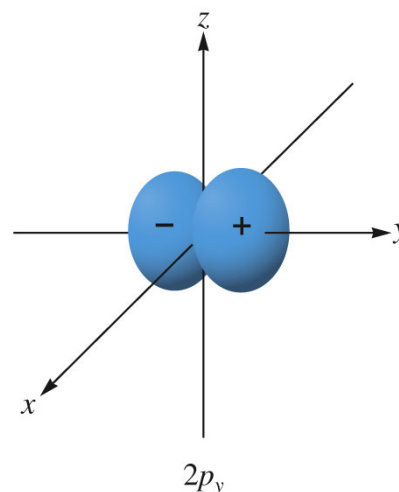

Figure 12.19 - Representation of the 2*p* orbitals.

Orbital Shapes and Energies

d orbitals (*l*=2) first occur in level *n* =3
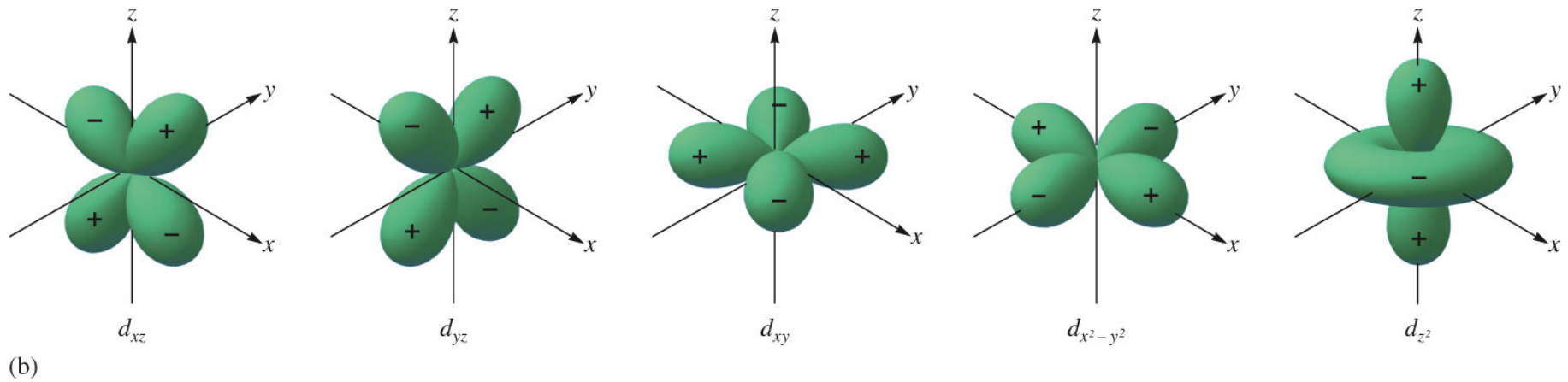

Figure 12.21 - Representation of the 3*d* orbitals.

The spin quantum number (m_s) and the Pauli Principle

- It can only have one of two values, +1/2 or -1/2.

- *Pauli principle:* In a given atom no two electrons can have the same set of four quantum numbers (n, l, m_l, and m_s).

- *An orbital can hold only two electrons, and they must have opposite spins.*

Orbital energy level for the hydrogen atom

• For the hydrogen atom, the energy of a particular orbital is determined by its value of *n*.

• Thus all orbitals with the same value of n have the same energy – they are said to be **degenerate**.

• In the lowest energy state, the **ground state**, the e⁻ resides in the 1s orbital. If energy is put into the atom, the e⁻ can be transferred to a higher-energy orbital, producing an **excited state**.
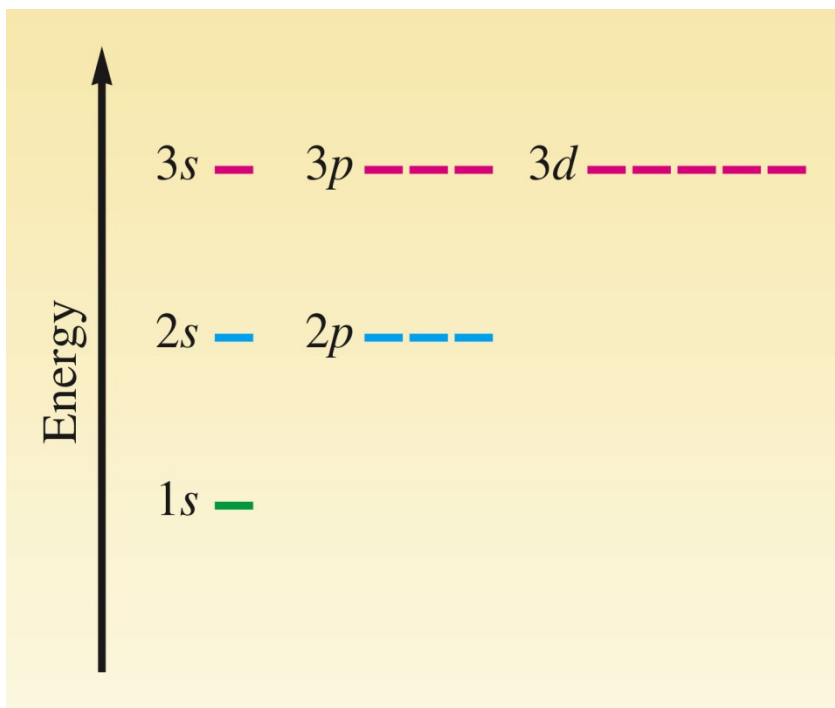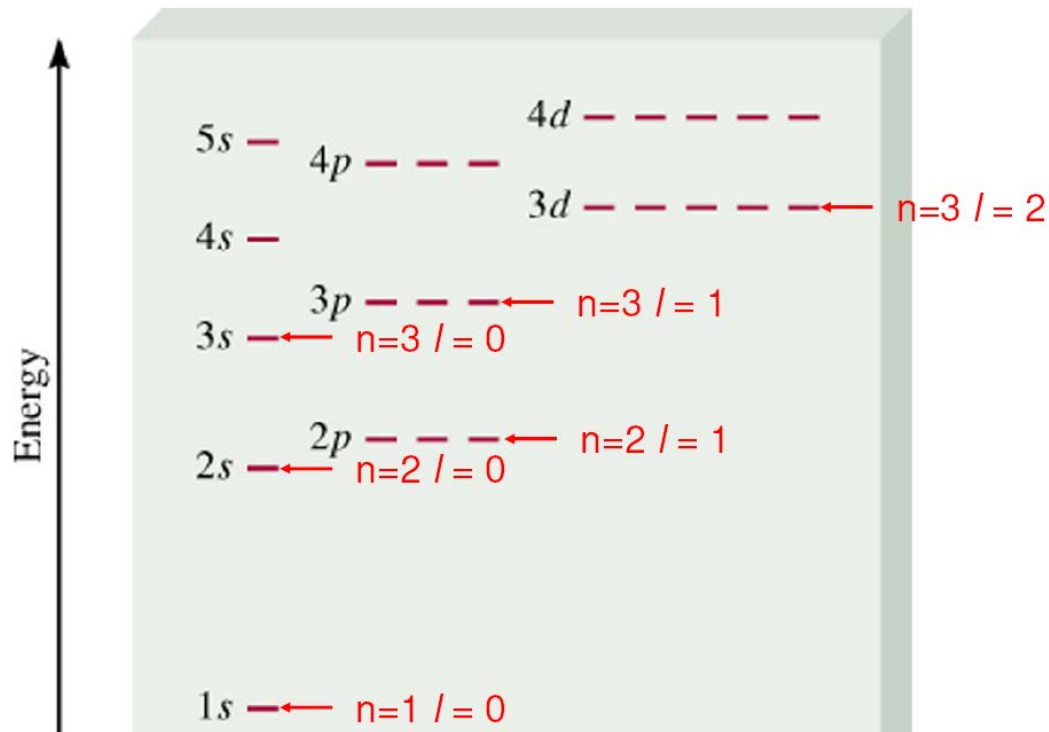

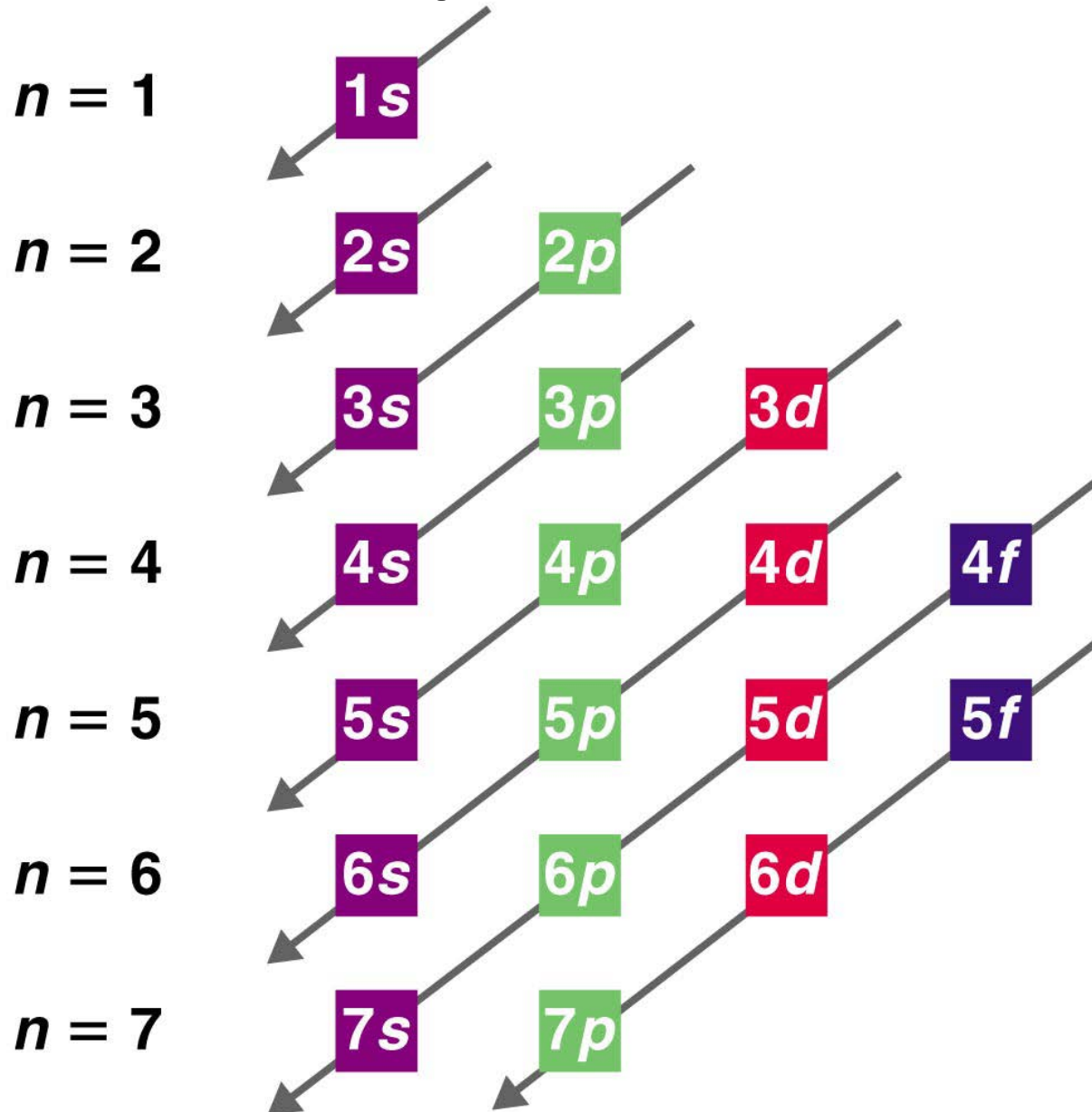**Figure 12.23 - Orbital energy levels for the hydrogen atom.**

The Aufbau Principle and the Periodic Table

The Aufbau Principle: *As protons are added one by one to the nucleus to build up the elements, electrons are similarly added to these atomic orbitals.*

As they are added, they assume their most stable conditions (electron orbitals) with respect to the nucleus and those electrons already there.

The Aufbau Principle and the Periodic Table

$n = 1$ 1*s*

$n = 2$ 2*s*   2*p*

$n = 3$ 3*s*   3*p*   3*d*

$n = 4$ 4*s*   4*p*   4*d*   4*f*

$n = 5$ 5*s*   5*p*   5*d*   5*f*

$n = 6$ 6*s*   6*p*   6*d*

$n = 7$ 7*s*   7*p*

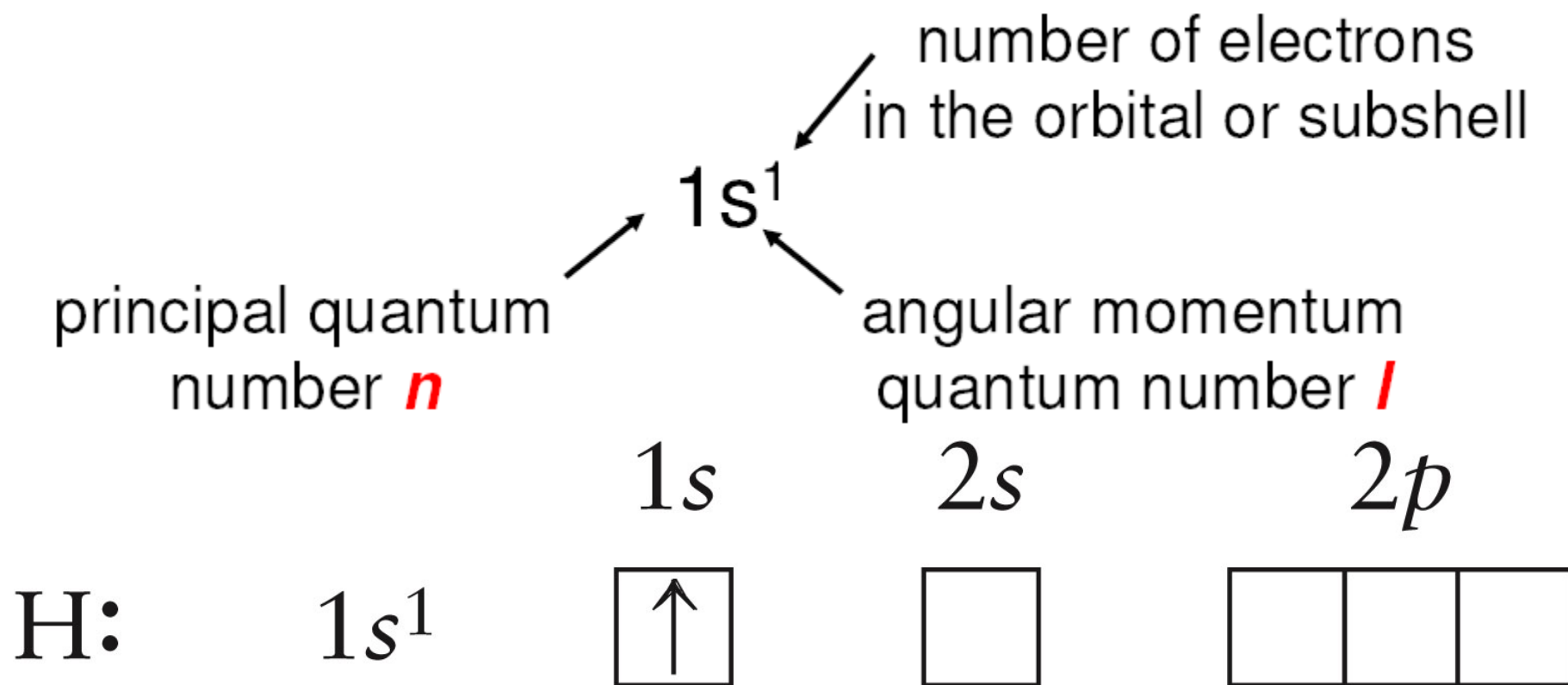1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s

The Aufbau Principle and the Periodic Table

The electronic configuration is the distribution of electrons among the various atomic orbitals.

Pauli Exclusion Principle: *no two electrons in an atom can have the same four quantum numbers.*
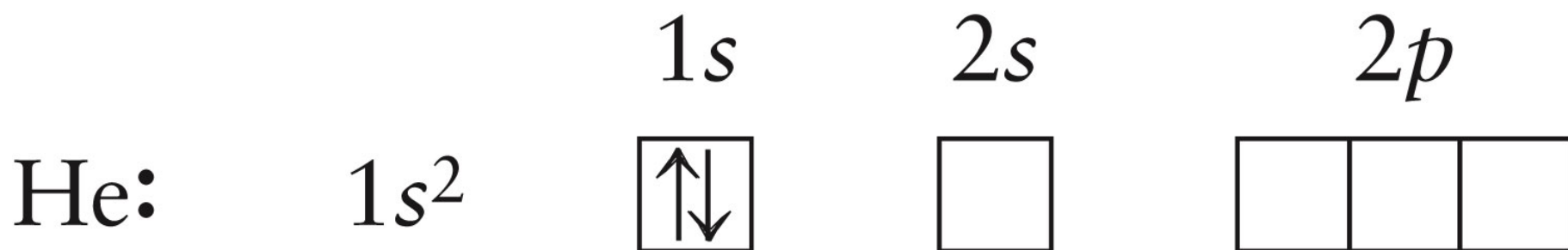
Hund's Rule: *the lowest-energy configuration for an atom is the one having the maximum number of unpaired electrons allowed by the Pauli Principle in a particular set of degenerate orbitals.*

The Aufbau Principle and the Periodic Table

number of electrons
in the orbital or subshell

$1s^1$

principal quantum
number **n**

angular momentum
quantum number **l**

$1s$	$2s$	$2p$

H: $1s^1$ | ↑ | | | | |

The Aufbau Principle and the Periodic Table

Helium has two electrons. Since 2 electrons with opposite spins can occupy an orbital, according to the Pauli exclusion principle, the electrons for Helium are in the 1s orbital with opposite spins.
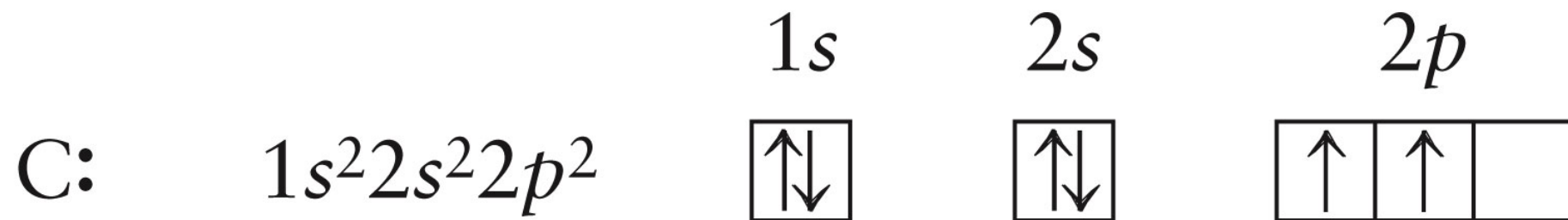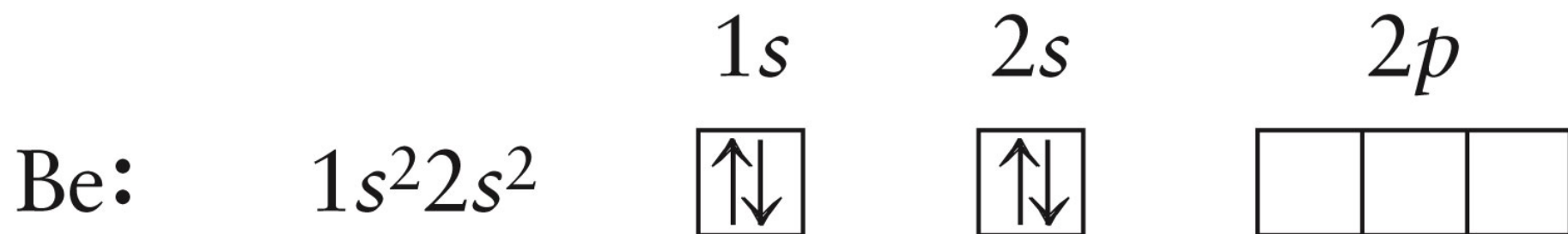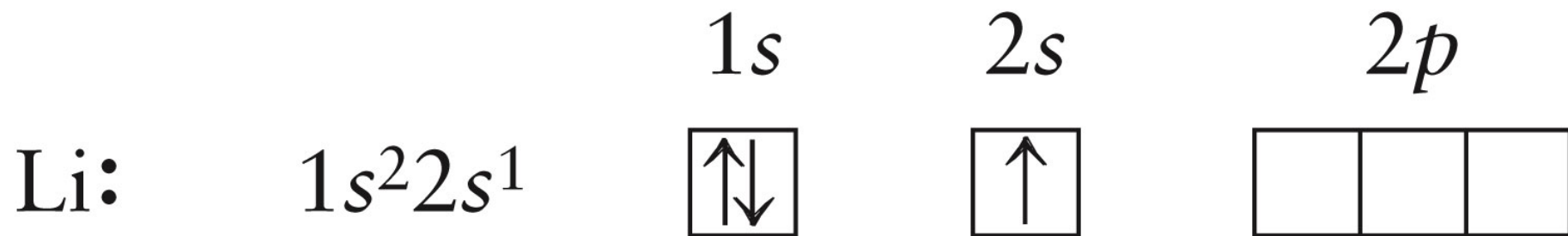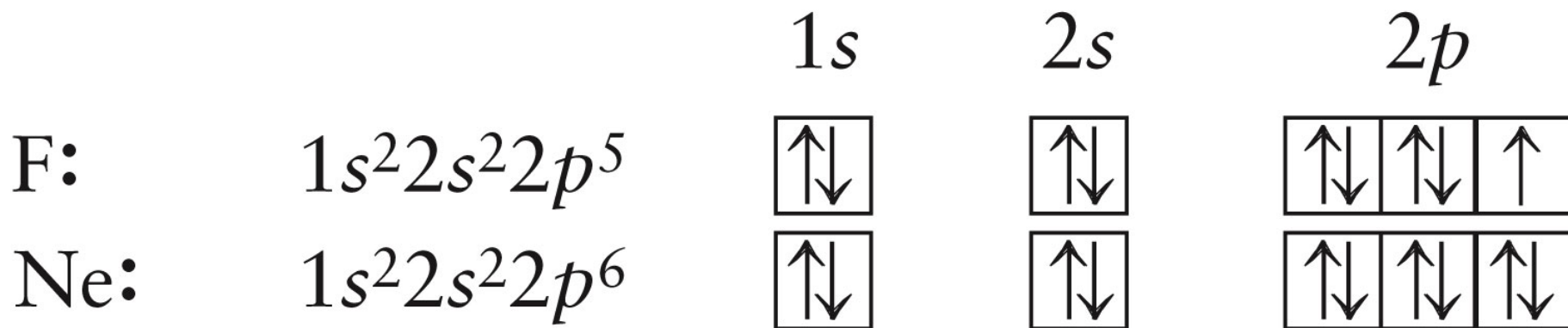
He: $1s^2$

$1s$	$2s$	$2p$
↑↓		

The Aufbau Principle and the Periodic Table

		$1s$	$2s$	$2p$

Li: $1s^2 2s^1$ [↑↓] [↑] [ ][ ][ ]

		$1s$	$2s$	$2p$

Be: $1s^2 2s^2$ [↑↓] [↑↓] [ ][ ][ ]

		$1s$	$2s$	$2p$

C: $1s^2 2s^2 2p^2$ [↑↓] [↑↓] [↑][↑][ ]

The Aufbau Principle and the Periodic Table

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

1s	2s	2p
↑↓	↑↓	↑ ↑ ↑

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

1s	2s	2p
↑↓	↑↓	↑↓ ↑ ↑

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

1s	2s	2p
↑↓	↑↓	↑↓ ↑↓ ↑

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

1s	2s	2p
↑↓	↑↓	↑↓ ↑↓ ↑↓
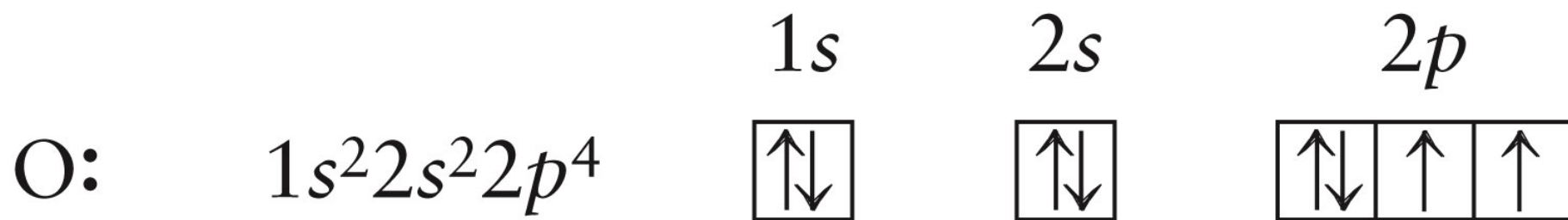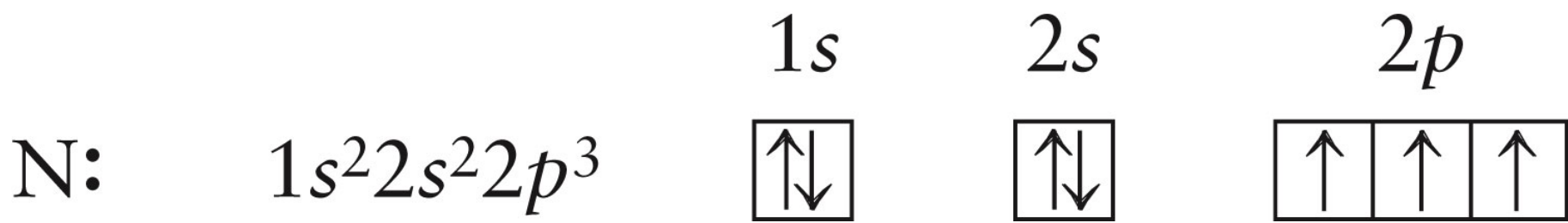
The Aufbau Principle and the Periodic Table

Na: $1s^2 2s^2 2p^6 3s^1$ OR $[Ne]3s^1$

Mg: $1s^2 2s^2 2p^6 3s^2$ OR $[Ne]3s^2$

Abbreviated electronic configuration: to avoid writing the inner-level electrons.

H $1s^1$								B $2p^1$	C $2p^2$	N $2p^3$	O $2p^4$	F $2p^5$	He $1s^2$ Ne $2p^6$
Li $2s^1$	Be $2s^2$												
Na $3s^1$	Mg $3s^2$							Al $3p^1$	Si $3p^2$	P $3p^3$	S $3p^4$	Cl $3p^5$	Ar $3p^6$

Al through Ar – filling 3 p orbital one electron at a time

The Aufbau Principle and the Periodic Table

Valence electrons: the electrons in the outermost principal quantum level of an atom. They are involved in chemical bonding.

Core electrons: the inner electrons

Example:
Valence electrons of N = 5e$^-$ (electrons in 2s and 2p)
Valence electrons of Na = 1e$^-$ (electrons in 3s)

*The elements in the **same group** have the **same valence electron** configuration.*

*The number of each **period** corresponds to the **outermost energy level that contains electrons** for the elements in that period.*

The Aufbau Principle and the Periodic Table

Transition metals: configurations obtained by adding e⁻ to *3d* orbitals.

Sc: $[Ar]4s^2 3d^1$
Ti: $[Ar]4s^2 3d^2$
V: $[Ar]4s^2 3d^3$

Exception

Cr: $[Ar]4s^1 3d^5$

Cu: $[Ar]4s^1 3d^{10}$

The reason of these irregularities is that half-filled (d^5) and completely filled (d^{10}) orbitals have slightly greater stability.

K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
$4s^1$	$4s^2$	$3d^1$	$3d^2$	$3d^3$	$4s^1\,3d^5$	$3d^5$	$3d^6$	$3d^7$	$3d^8$	$4s^1 3d^{10}$	$3d^{10}$	$4p^1$	$4p^2$	$4p^3$	$4p^4$	$4p^5$	$4p^6$

The Aufbau Principle and the Periodic Table

1- The *(n+1)s* orbitals always fill before the *nd* orbitals.

2- After Lanthanum (La:[Xe]$6s^2 5d^1$), a group of 14 elements, **lanthanides**, occurs.

Lanthanides: filling of the *4f* orbitals. Sometimes one e⁻ occupies a *5d* instead of a *4f* orbital (*4f* and *5d* have similar energies).

3- After Actinium (Ac:[Rn]$7s^2 6d^1$), a group of 14 elements, **actinides**, occurs.

Actinides: filling of the *5f* orbitals. Sometimes one or two e⁻ occupy the *6d* instead of the *5f* (*5f* and *6d* have similar energies).

4- The group labels, 1A, 2A, …, 8A indicate the total number of valence electrons.

The Aufbau Principle and the Periodic Table

Figure 12.28 - the orbitals being filled for elements in various parts of the periodic table. Note that when we move along a horizontal row (a period), the (n + 1)s orbital fills before the nd orbital. The group labels indicate the number of valence electrons (ns plus np electrons) for the elements in each group.

The Aufbau Principle and the Periodic Table

Representative Elements | d-Transition Elements | Representative Elements | Noble Gases

Period number, highest occupied electron level

Group numbers (A-notation and ns configurations):
- 1 / 1A — ns^1
- 2 / 2A — ns^2
- 13 / 3A — ns^2np^1
- 14 / 4A — ns^2np^2
- 15 / 5A — ns^2np^3
- 16 / 6A — ns^2np^4
- 17 / 7A — ns^2np^5
- 18 / 8A — ns^2np^6

Period 1
- 1 H — $1s^1$
- 2 He — $1s^2$

Period 2
- 3 Li — $2s^1$
- 4 Be — $2s^2$
- 5 B — $2s^2 2p^1$
- 6 C — $2s^2 2p^2$
- 7 N — $2s^2 2p^3$
- 8 O — $2s^2 2p^4$
- 9 F — $2s^2 2p^5$
- 10 Ne — $2s^2 2p^6$

Period 3
- 11 Na — $3s^1$
- 12 Mg — $3s^2$
- 13 Al — $3s^2 3p^1$
- 14 Si — $3s^2 3p^2$
- 15 P — $3s^2 3p^3$
- 16 S — $3s^2 3p^4$
- 17 Cl — $3s^2 3p^5$
- 18 Ar — $3s^2 3p^6$

Period 4 (groups 3–12)
- 19 K — $4s^1$
- 20 Ca — $4s^2$
- 21 Sc — $4s^2 3d^1$
- 22 Ti — $4s^2 3d^2$
- 23 V — $4s^2 3d^3$
- 24 Cr — $4s^1 3d^5$
- 25 Mn — $4s^2 3d^5$
- 26 Fe — $4s^2 3d^6$
- 27 Co — $4s^2 3d^7$
- 28 Ni — $4s^2 3d^8$
- 29 Cu — $4s^1 3d^{10}$
- 30 Zn — $4s^2 3d^{10}$
- 31 Ga — $4s^2 4p^1$
- 32 Ge — $4s^2 4p^2$
- 33 As — $4s^2 4p^3$
- 34 Se — $4s^2 4p^4$
- 35 Br — $4s^2 4p^5$
- 36 Kr — $4s^2 4p^6$

Period 5
- 37 Rb — $5s^1$
- 38 Sr — $5s^2$
- 39 Y — $5s^2 4d^1$
- 40 Zr — $5s^2 4d^2$
- 41 Nb — $5s^1 4d^4$
- 42 Mo — $5s^1 4d^5$
- 43 Tc — $5s^1 4d^6$
- 44 Ru — $5s^1 4d^7$
- 45 Rh — $5s^1 4d^8$
- 46 Pd — $4d^{10}$
- 47 Ag — $5s^1 4d^{10}$
- 48 Cd — $5s^2 4d^{10}$
- 49 In — $5s^2 5p^1$
- 50 Sn — $5s^2 5p^2$
- 51 Sb — $5s^2 5p^3$
- 52 Te — $5s^2 5p^4$
- 53 I — $5s^2 5p^5$
- 54 Xe — $5s^2 5p^6$

Period 6
- 55 Cs — $6s^1$
- 56 Ba — $6s^2$
- 57 La* — $6s^2 5d^1$
- 72 Hf — $4f^{14} 6s^2 5d^2$
- 73 Ta — $6s^2 5d^3$
- 74 W — $6s^2 5d^4$
- 75 Re — $6s^2 5d^5$
- 76 Os — $6s^2 5d^6$
- 77 Ir — $6s^2 5d^7$
- 78 Pt — $6s^1 5d^9$
- 79 Au — $6s^1 5d^{10}$
- 80 Hg — $6s^2 5d^{10}$
- 81 Tl — $6s^2 6p^1$
- 82 Pb — $6s^2 6p^2$
- 83 Bi — $6s^2 6p^3$
- 84 Po — $6s^2 6p^4$
- 85 At — $6s^2 6p^5$
- 86 Rn — $6s^2 6p^6$

Period 7
- 87 Fr — $7s^1$
- 88 Ra — $7s^2$
- 89 Ac** — $7s^2 6d^1$
- 104 Rf — $7s^2 6d^2$
- 105 Db — $7s^2 6d^3$
- 106 Sg — $7s^2 6d^4$
- 107 Bh — $7s^2 6d^5$
- 108 Hs — $7s^2 6d^6$
- 109 Mt — $7s^2 6d^7$
- 110 Ds — $7s^2 6d^8$
- 111 Rg — $7s^1 6d^{10}$
- 112 Cn — $7s^2 6d^{10}$
- 113 Uut — $7s^2 6d^{10} 7p^1$
- 114 Uuq — $7s^2 6d^{10} 7p^2$
- 115 Uup — $7s^2 6d^{10} 7p^3$
- 117 Uus — $7s^2 7p^5$
- 118 Uuo — $7s^2 7p^6$

f-Transition Elements

Lanthanides
- 58 Ce — $6s^2 4f^1 5d^1$
- 59 Pr — $6s^2 4f^3 5d^0$
- 60 Nd — $6s^2 4f^4 5d^0$
- 61 Pm — $6s^2 4f^5 5d^0$
- 62 Sm — $6s^2 4f^6 5d^0$
- 63 Eu — $6s^2 4f^7 5d^0$
- 64 Gd — $6s^2 4f^7 5d^1$
- 65 Tb — $6s^2 4f^9 5d^0$
- 66 Dy — $6s^2 4f^{10} 5d^0$
- 67 Ho — $6s^2 4f^{11} 5d^0$
- 68 Er — $6s^2 4f^{12} 5d^0$
- 69 Tm — $6s^2 4f^{13} 5d^0$
- 70 Yb — $6s^2 4f^{14} 5d^0$
- 71 Lu — $6s^2 4f^{14} 5d^1$

**Actinides
- 90 Th — $7s^2 5f^0 6d^2$
- 91 Pa — $7s^2 5f^2 6d^1$
- 92 U — $7s^2 5f^3 6d^1$
- 93 Np — $7s^2 5f^4 6d^1$
- 94 Pu — $7s^2 5f^6 6d^0$
- 95 Am — $7s^2 5f^7 6d^0$
- 96 Cm — $7s^2 5f^7 6d^1$
- 97 Bk — $7s^2 5f^9 6d^0$
- 98 Cf — $7s^2 5f^{10} 6d^0$
- 99 Es — $7s^2 5f^{11} 6d^0$
- 100 Fm — $7s^2 5f^{12} 6d^0$
- 101 Md — $7s^2 5f^{13} 6d^0$
- 102 No — $7s^2 5f^{14} 6d^0$
- 103 Lr — $7s^2 5f^{14} 6d^1$

Figure 12.29 - The periodic table with atomic symbols, atomic numbers, and partial electron configurations.

The Aufbau Principle and the Periodic Table

The Aufbau Principle and the Periodic Table

Example 12.8

Give the electron configurations for sulfur (S), cadmium (Cd), hafnium (Hf), and radium (Ra), using the periodic table.

The Aufbau Principle and the Periodic Table

Example 12.8

Give the electron configurations for sulfur (S), cadmium (Cd), hafnium (Hf), and radium (Ra), using the periodic table.

SOLUTION

^{16}S: $1s^2 2s^2 2p^6 3s^2 3p^4$ or $[Ne]3s^2 3p^4$

^{48}Cd: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10}$ or $[Kr]5s^2 4d^{10}$

^{72}Hf: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^2$

           or $[Xe]6s^2 4f^{14} 5d^2$

^{88}Ra: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^6 7s^2$

           or $[Rn]7s^2$

The Aufbau Principle and the Periodic Table

1. Each shell or principal level of quantum number *n* contains *n* subshells. For example, if n=2, then there are two subshells (two values of *l*) of angular quantum numbers 0 and 1.

2. Each subshell of quantum number *l* contains (*2l+1*) orbitals. For example if *l* =1, then there are three p orbitals

3. No more that two electrons can be placed in each orbital, maximum number of electrons is twice the number of orbitals

4. The total number of *orbitals* = n^2

5. The maximum number of *electrons* an atom can have in a principal level n = $2n^2$

Periodic Trends in Atomic Properties
Ionization Energy

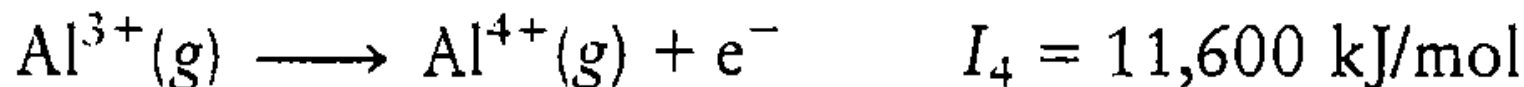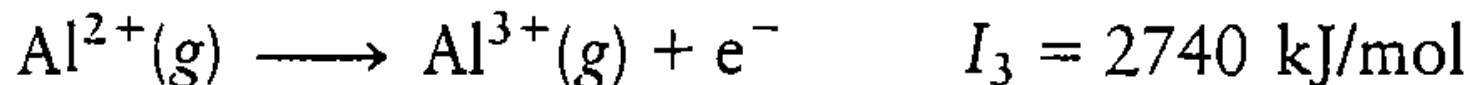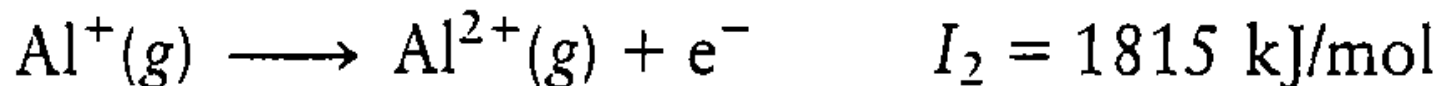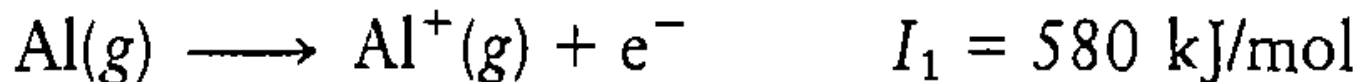**Ionization energy is the minimum energy (kJ/mol) required to remove an electron from a gaseous atom in its ground state.**

It is a measure of the tendency of an atom to **resist the** loss of an electron The **higher the ionization energy the stronger the** attraction between the nucleus and an electron

$$X\ (g) \rightarrow X^+\ (g) + e^-$$

Ionization Energy

$$Al(g) \longrightarrow Al^+(g) + e^- \qquad I_1 = 580 \text{ kJ/mol}$$

$$Al^+(g) \longrightarrow Al^{2+}(g) + e^- \qquad I_2 = 1815 \text{ kJ/mol}$$

$$Al^{2+}(g) \longrightarrow Al^{3+}(g) + e^- \qquad I_3 = 2740 \text{ kJ/mol}$$

$$Al^{3+}(g) \longrightarrow Al^{4+}(g) + e^- \qquad I_4 = 11,600 \text{ kJ/mol}$$
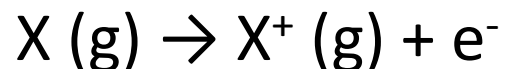
Al [Ne] $3s^2$ $3p^1$

I_1: first ionization energy, energy required to remove the highest energy electron ($3p^1$ electron)

I_2: second ionization energy, corresponds to the removal of one electron from ($3s^2$ orbit)

$I_2 > I_1$: it is harder to remove an electron from a positively charged ion (Al^+)

I_3: third ionization energy, removal of the $3s^1$ electron, the electronic configuration becomes (Al^{3+} $1s^2$ $2s^2$ $2p^6$ = [Ne])

I_4: much higher than I_3, because it corresponds to removing a core electron.

Ionization Energy

Successive Ionization Energies in Kilojoules per Mole for the Elements in Period 3

General increase →

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

← General decrease →

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

Ionization Energy

Table 12.7

First Ionization Energies for the Alkali Metals and Noble Gases

Atom	I_1 (kJ/mol)
Group 1A	
Li	520.
Na	495
K	419
Rb	409
Cs	382
Group 8A	
He	2377
Ne	2088
Ar	1527
Kr	1356
Xe	1176
Rn	1042

Ionization Energy

The core electrons are the electrons between the nucleus and the valence electrons. They are *shielding* the outer electrons from the nuclear charge.

Across a period

The first ionization energy increases from left to right.

Valence electrons do not shield each other from the increased nuclear charge (increase in the atomic number).

Increased attraction between the nuclear charge and the outer electron.

Electrons are bound more tightly from left to right across a period, which means that the ionization energy should increase.

Down a group:

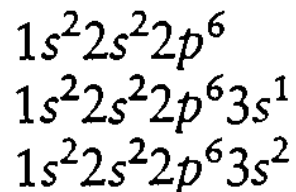Number of core electrons increase, implying increased shielding.

Less attraction between the nuclear charge and the valence electron.

Less energy (ionization energy) is needed to remove the electron.

Ionization Energy

Example 12.10

'

Consider atoms with the following electron configurations:

$$1s^2 2s^2 2p^6$$
$$1s^2 2s^2 2p^6 3s^1$$
$$1s^2 2s^2 2p^6 3s^2$$

Which atom has the largest first ionization energy, and which one has the smallest second ionization energy? Explain your choices.

Ionization Energy

Solution

The atom with the largest value of I_1 is the one with the configuration $1s^2 2s^2 2p^6$ (this is the neon atom), because this element is found at the right end of Period 2. Since the $2p$ electrons do not shield each other very effectively, I_1 will be large. The other configurations given include $3s$ electrons. These electrons are effectively shielded by the core electrons and are farther from the nucleus than the $2p$ electrons in neon. Thus I_1 for these atoms is smaller than I_1 for neon.

The atom with the smallest value of I_2 is the one with the configuration $1s^2 2s^2 2p^6 3s^2$ (the magnesium atom). For magnesium both I_1 and I_2 involve valence electrons. For the atom with the configuration $1s^2 2s^2 2p^6 3s^1$ (sodium), the second electron lost (corresponding to I_2) is a core electron from a $2p$ orbital).
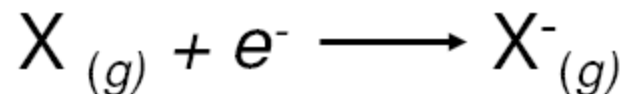
Periodic Trends in Atomic Properties
Electron Affinity

Electron affinity is the energy change associated with the addition of an electron to a gaseous atom.

If the addition of the electron is exothermic, the corresponding value for electron affinity will carry a negative sign.
The more negative the energy, the greater is the quantity of energy released.

$$X_{(g)} + e^- \longrightarrow X^-_{(g)}$$

Periodic Trends in Atomic Properties
Atomic Radius

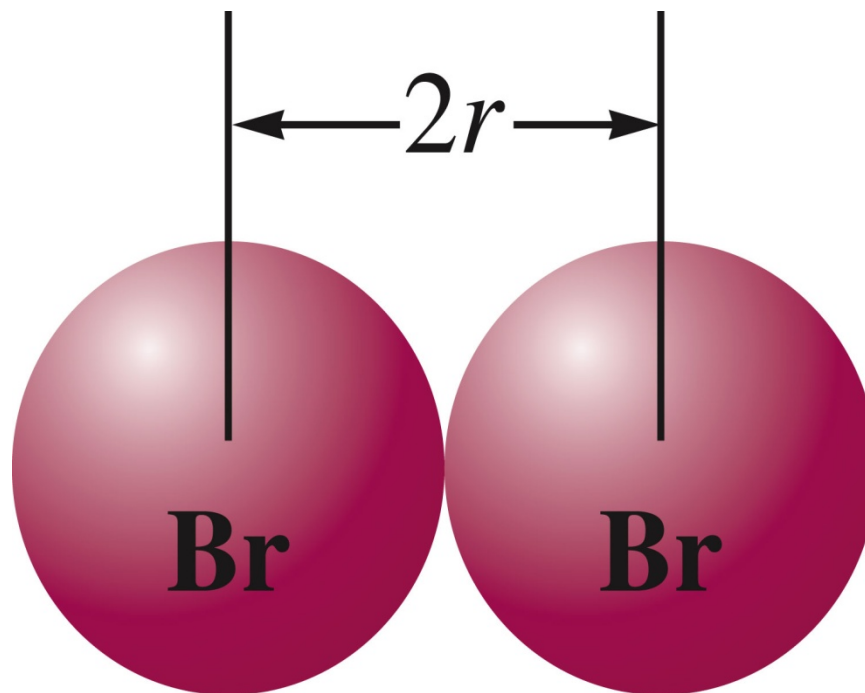**Atomic Radius** is one half the distance between two nuclei

Figure 12.37 - The radius of an atom (*r*) is defined as half the distance between the nuclei in a molecule consisting of identical atoms.

Periodic Trends in Atomic Properties
Atomic Radius

- Atomic radius increases down a group, because of the increases of the orbital sizes in successive principle quantum levels.

- Atomic radius decreases form left to right in the periodic table ("n" same, nb of core electrons the same, increased nuclear charge, increased attraction, less atomic size)
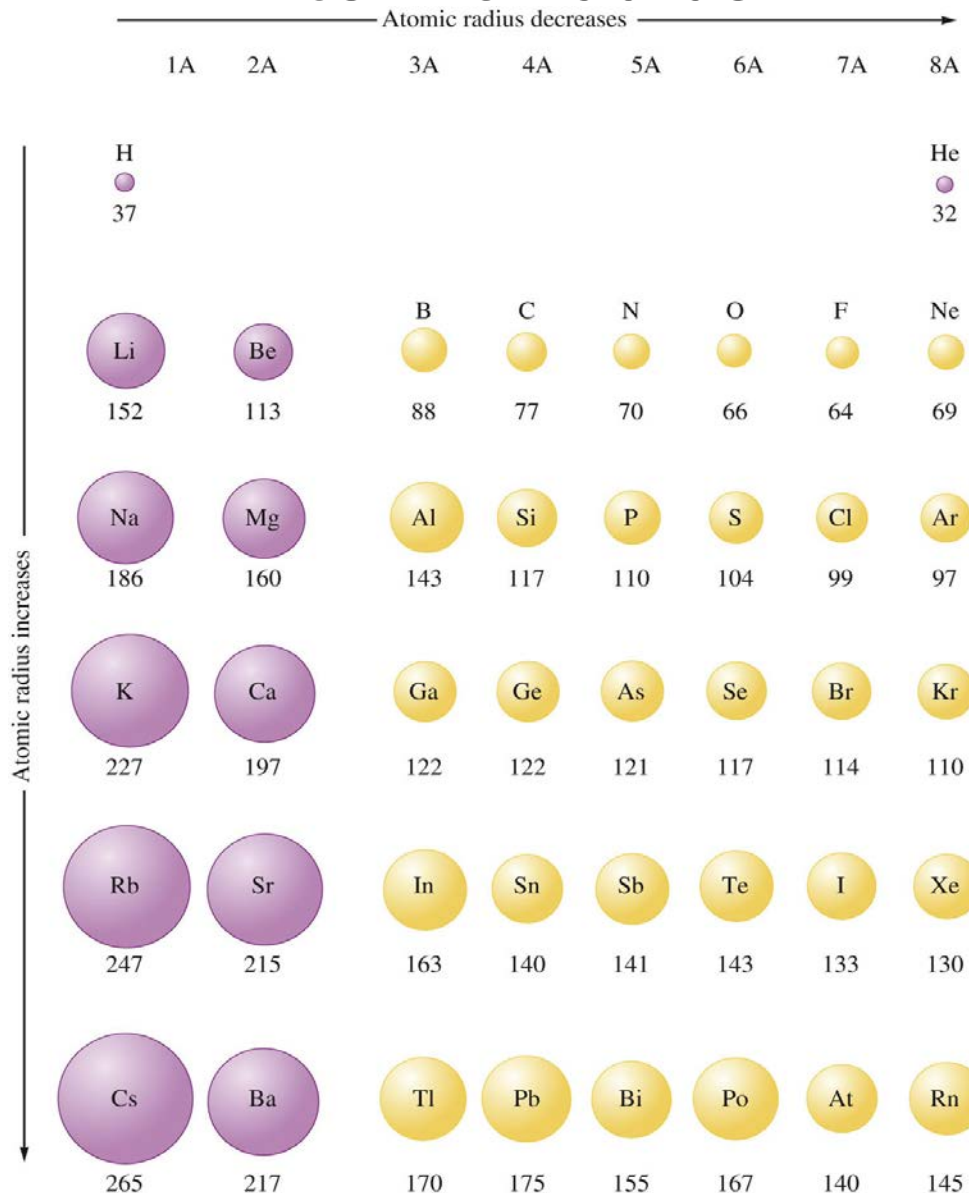
Atomic Radius

Figure 12.38 - Atomic radii (in picometers) for selected atoms. Note that atomic radius decreases going across a period and increases going down a group. The values for the noble gases are estimated because data from bonded atoms are lacking.

Ions: Electron Configurations and Sizes

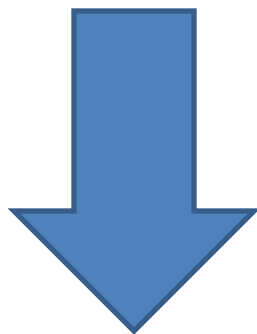Ions derived from **Representative** Elements

Na [Ne]3s^1 Na$^+$ [Ne]

Ca [Ar]4s^2 Ca^{2+} [Ar]

Al [Ne]3s^{2}3p^1 Al^{3+} [Ne]

Atoms **lose electrons so that cation has a noble-gas outer** electron configuration.

Ions: Electron Configurations and Sizes

H $1s^1$ H^- $1s^2$ or [He]

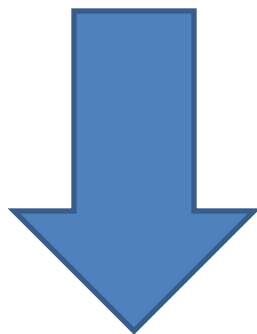F $1s^2 2s^2 2p^5$ F^- $1s^2 2s^2 2p^6$ or [Ne]

O $1s^2 2s^2 2p^4$ O^{2-} $1s^2 2s^2 2p^6$ or [Ne]

N $1s^2 2s^2 2p^3$ N^{3-} $1s^2 2s^2 2p^6$ or [Ne]

Atoms **gain electrons** so that **anion has a noble-gas outer** electron configuration

Ions: Electron Configurations and Sizes

O^{2-}, F^-, Na^+, Mg^{2+}, and Al^{3+} all have the **same number of** electrons, the **same ground state electron configuration.**

Ions and atoms that have the **same number of electrons** are called **isoelectronic.**

The number of electrons is 10 in each case.
Electron repulsions should therefore be about the same.
However the number of protons increases from 8 to 13 as we go from O^{2-} to Al^{3+}.
More attraction between the 10 electrons and the increasing positive charge of the nucleus.
Ions become smaller

Ions: Electron Configurations and Sizes

Table 13.5

Common Ions with Noble Gas Electron Configurations in Ionic Compounds

Group 1A	Group 2A	Group 3A	Group 6A	Group 7A	Electron Configuration
H^-, Li^+	Be^{2+}				[He]
Na^+	Mg^{2+}	Al^{3+}	O^{2-}	F^-	[Ne]
K^+	Ca^{2+}		S^{2-}	Cl^-	[Ar]
Rb^+	Sr^{2+}		Se^{2-}	Br^-	[Kr]
Cs^+	Ba^{2+}		Te^{2-}	I^-	[Xe]

Ions: Electron Configurations and Sizes

Ionic radius is the radius of a cation or an anion

Li   +   F   →   Li⁺   F⁻
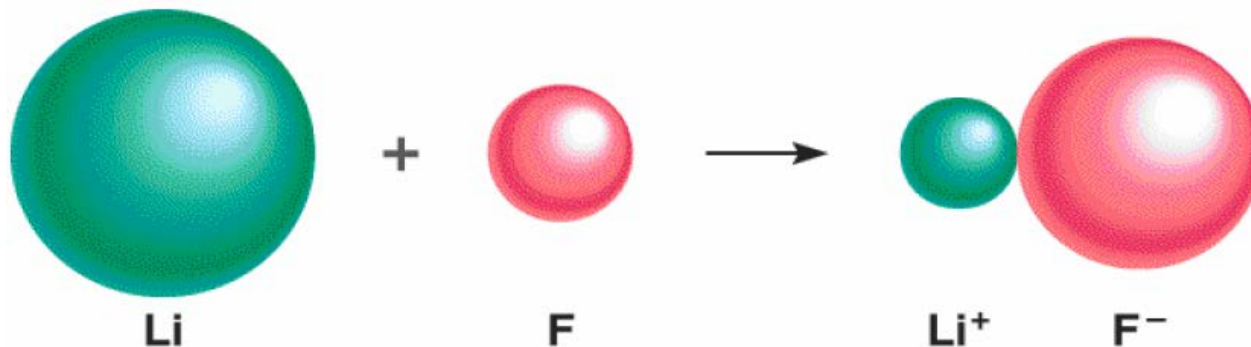
Cation is always **smaller** than atom from which it is formed.

Anion is always **larger** than atom from which it is formed.

For *isoelectronic* ions: Cations are smaller than anions

$$Na^+ < F^-$$

Ions: Electron Configurations and Sizes

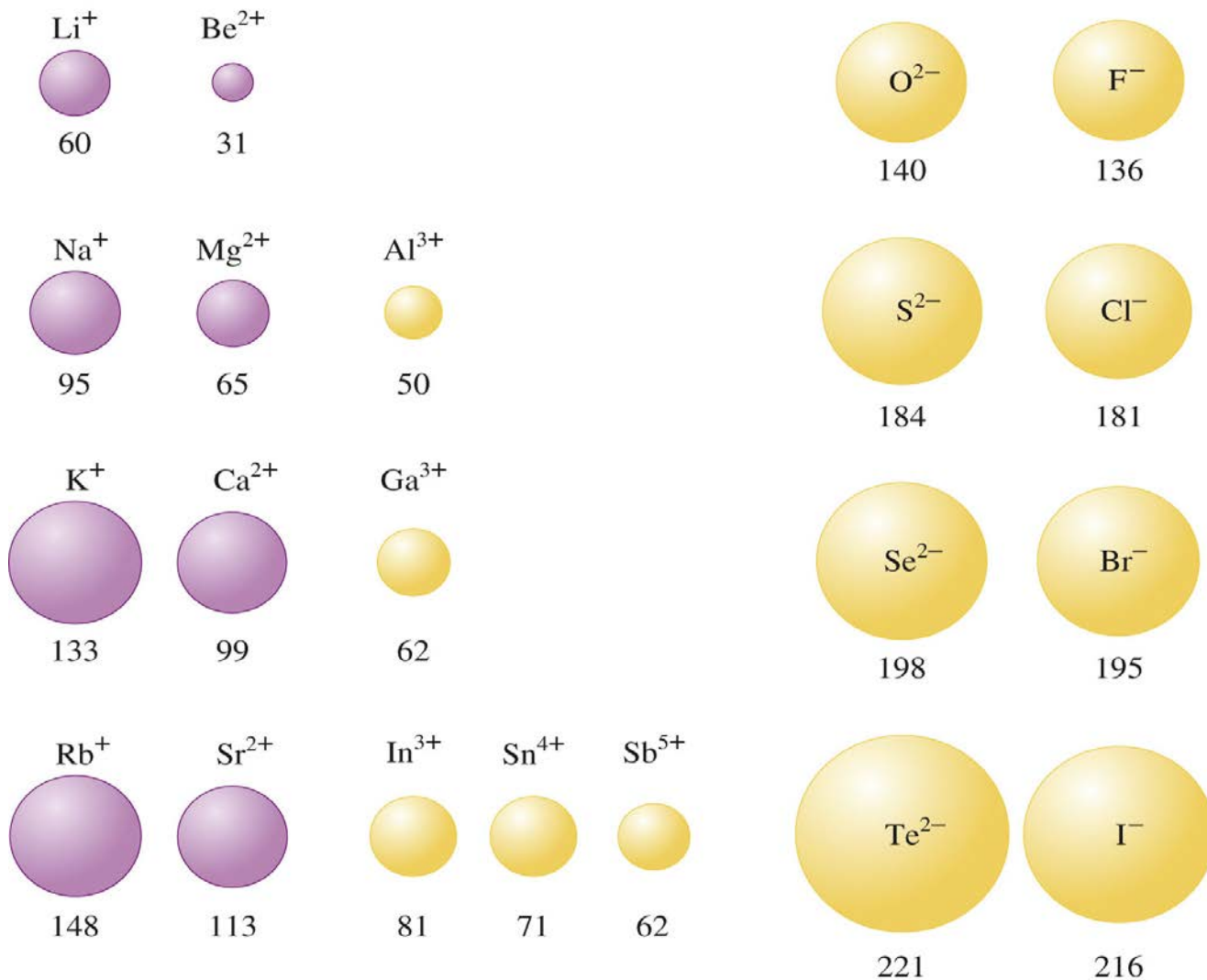|						
Li^+	Be^{2+}				O^{2-}	F^-
60	31				140	136
Na^+	Mg^{2+}	Al^{3+}			S^{2-}	Cl^-
95	65	50			184	181
K^+	Ca^{2+}	Ga^{3+}			Se^{2-}	Br^-
133	99	62			198	195
Rb^+	Sr^{2+}	In^{3+}	Sn^{4+}	Sb^{5+}	Te^{2-}	I^-
148	113	81	71	62	221	216
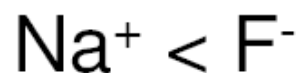
Figure 13.8 - Sizes of ions related to positions of elements in the periodic table. Note that size generally increases down a group. Also note that in a series of isoelectronic ions, size decreases with increasing atomic number. The ionic radii are given in units of picometers.

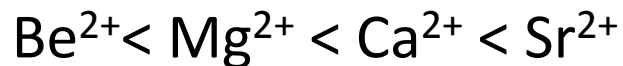# Ions: Electron Configurations and Sizes

Example 12.11

Predict the trend in radius of the following ions: Be^{2+}, Mg^{2+}, Ca^{2+}, and Sr^{2+}.

Ionic Radius

Example 12.11

Predict the trend in radius of the following ions: Be^{2+}, Mg^{2+}, Ca^{2+}, and Sr^{2+}.

SOLUTION

$Be^{2+} < Mg^{2+} < Ca^{2+} < Sr^{2+}$

Ions: Electron Configurations and Sizes

Example 13.3

Arrange the ions Se^{2-}, Br^-, Rb^+, and Sr^{2+} in order of decreasing size.

Ions: Electron Configurations and Sizes

Example 13.3

Arrange the ions Se^{2-}, Br^-, Rb^+, and Sr^{2+} in order of decreasing size.

SOLUTION

$Se^{2-} > Br^- > Rb^+ > Sr^{2+}$

Ions: Electron Configurations and Sizes

Example 13.4

Choose the largest ion in each of the following groups.

a. Li^+, Na^+, K^+, Rb^+, Cs^+

b. Ba^{2+}, Cs^+, I^-, Te^{2-}

Ions: Electron Configurations and Sizes

Example 13.4

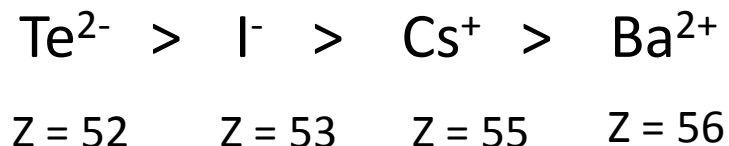Choose the largest ion in each of the following groups.

a. Li^+, Na^+, K^+, Rb^+, Cs^+

b. Ba^{2+}, Cs^+, I^-, Te^{2-}

SOLUTION

a. The ions are all from Group 1A elements. Since size increases down a group, Cs^+ is the largest ion.

b. This is an isoelectronic series of ions, all of which have the xenon electron configuration. The ion with the smallest nuclear charge is the largest ion.

$$Te^{2-} \ > \ I^- \ > \ Cs^+ \ > \ Ba^{2+}$$

$$Z = 52 \qquad Z = 53 \qquad Z = 55 \qquad Z = 56$$

HOMEWORK

<u>Chap.12:</u> 32, 36, 43, 66, 75, 78, 87, 97, 98
<u>Chap.13:</u> 29

Calculate the velocities of electrons with de Broglie wavelengths of 1.0×10^2 nm and 1.0 nm, respectively.

Calculate the wavelength of light emitted in each of the following spectral transitions in the hydrogen atom. What type of electromagnetic radiation is emitted in each transition?

a. n=4 → n=3

b. n=5 → n=4

c. n=5 → n=3

An excited hydrogen atom emits light with a wavelength of 397.2 nm to reach the energy level for which $n = 2$. In which principal quantum level did the electron begin?

66

Which of the following sets of quantum numbers are not allowed in the hydrogen atom? For the sets of quantum numbers that are incorrect, state what is wrong in each set.

a) $n = 3$, $l = 2$, $m_l = 2$

b) $n = 4$, $l = 3$, $m_l = 4$

c) $n = 0$, $l = 0$, $m_l = 0$

d) $n = 2$, $l = -1$, $m_l = 1$

75

What is the maximum number of electrons in an atom that can have these quantum numbers?

a. $n = 4$

b. $n = 5$, $m_\ell = +1$

c. $n = 5$, $m_s = +\frac{1}{2}$

d. $n = 3$, $\ell = 2$

e. $n = 2$, $\ell = 1$

f. $n = 0$, $\ell = 0$, $m_\ell = 0$

g. $n = 2$, $\ell = 1$, $m_\ell = -1$, $m_s = -\frac{1}{2}$

h. $n = 3$

i. $n = 2$, $\ell = 2$

j. $n = 1$, $\ell = 0$, $m_\ell = 0$

The elements of Si, Ga, As, Ge, Al, Cd, S, and Se are all used in the manufacture of various semiconductor devices. Write the expected electron configurations for these atoms.

How many unpaired electrons are present in each of the following in the ground state: O, O^+, O^-, Os, Zr, S, F, Ar?

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Arrange the following groups of atoms in order of increasing size.

a)   Te, S, Se

b)   K, Br, Ni

c)   Ba, Si, F

d)   Rb, Na, Be

e)   Sr, Se, Ne

f)   Fe, P, O

Arrange the atoms in exercise 97 in order of increasing first ionization energy.

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For each of the following groups, place the atoms and ions in order of decreasing size.

a. Cu, Cu^+, Cu^{2+}

b. Ni^{2+}, Pd^{2+}, Pt^{2+}

c. O, O^-, O^{2-}

d. La^{3+}, Eu^{3+}, Gd^{3+}, Yb^{3+}

e. Te^{2-}, I^-, Cs^+, Ba^{2+}, La^{3+}