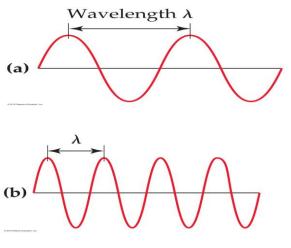# Chapter 6. Electronic Structure of Atoms
Bring CP/HONORS Periodic Table!! (colored)

Ch 6.1 Wave Nature of Light
Read p. 214-216.

Learning Objective	Essential Knowledge
Unit 3.11 **SAP-8.A** Explain the relationship between a region of the electromagnetic spectrum and the types of molecular or electronic transitions associated with that region.	**SAP-8.A.1** Differences in absorption or emission of photons in different spectral regions are related to the different types of molecular motion or electronic transition: a. Microwave radiation is associated with transitions in molecular rotational levels. b. Infrared radiation is associated with transitions in molecular vibrational levels. c. Ultraviolet/visible radiation is associated with transitions in electronic energy levels.

- The **ELECTRONIC STRUCTURE** of an atom refers to the arrangement of electrons.
    - Comes from the analysis of the light either emitted or absorbed by substances.

- The light we see with our eyes, *visible light,* is one type of **_ELECTROMAGNETIC RADIATION_**.
    - Electromagnetic radiation carries energy through space.

- All waves have a characteristic **_WAVELNGTH_**, λ, and **_FREQUENCY_**, ν,
    - The distance between two adjacent peaks (or between two adjacent troughs) is called the **_wavelength_**.
    - The number of complete wavelengths, or *cycles,* that pass a given point each second is the **_frequency_** of the wave.

Notice that the shorter the wavelength, the higher the frequency. The wavelength in (b) is half as long as that in (a), and the frequency of the wave in (b) is therefore twice as great as the frequency in (a).

- All types of electromagnetic radiation move through a vacuum at the ***SPEED OF LIGHT.***

  (c = c speed of light = 3.00×10^8 m/s)

- The wavelength and frequency of electromagnetic radiation have an **inverse relationship**.
  - If the wavelength is long, fewer cycles of the wave pass a given point per second, and so the frequency is low.
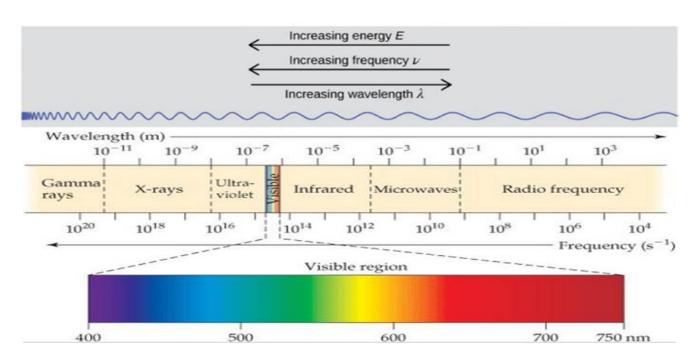 - For a wave to have a high frequency, it must have a short wavelength.

We can calculate the frequency and wavelength of electromagnetic radiation by the following equation:

$$c = \lambda \, \nu$$

  - wavelength = meters, m
  - frequency = **HERTZ** (1 Hz = 1 s^{-1})
  - c = 3.00×10^8 m/s

Why do different types of electromagnetic radiation have different properties?
- **Their differences are due to their different wavelengths.**
- The ***ELECTROMAGNETIC SPECTRUM*** is a display of the various types of electromagnetic radiation arranged in order of increasing wavelength.
  - Notice also that visible light, which corresponds to wavelengths of about 400nm (violet) to 750 nm (red), which is 4×10^{-7} m to 7.5×10^{-7} m, is an extremely small portion of the electromagnetic spectrum.
  - Remember: 1 meter = 1×10^9 nm

Examples

1. The light given off by a sodium vapor lamp used for public lighting has a wavelength of 589 nm. What is the frequency of this radiation? Predict the color associated with this wavelength.

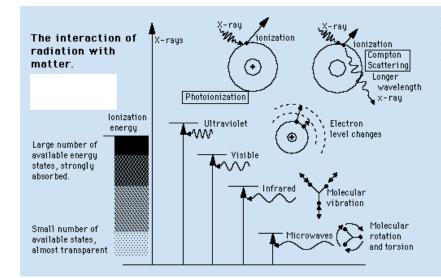2. **(a)** What is the frequency of radiation whose wavelength is 5.0×10^{-5} m?

    (b) What is the wavelength of radiation that has a frequency of 2.5×10^{8} s^{-1} ?

    (c) Would the radiations in part (a) or part (b) be detected by an X-ray detector?

REGION	SPECTROSCOPIC TECHNIQUE	EXAMPLE APPLICATION
TV/Radio (R$_f$)	Nuclear magnetic resonance (NMR)	Measures energy changes in nuclear spin to study molecular structure.
Microwave	Rotational Spectroscopy	Bonding and intermolecular forces
Infrared	IR, FTIR, Raman spectroscopy	Bond vibrations – molecular structure and intermolecular forces
Visible/UV	UV-Vis spectroscopy, Atomic Emission Spectroscopy	Electron transitions
X-ray	Photoelectron spectroscopy (PES)	Electronic structure in an atom

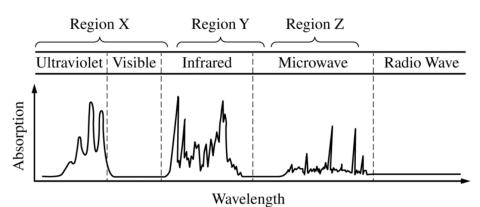**Molecules and Light – PHET website**

Select different molecules and see what happens when different radiations bombard them.

Differences in absorption or emission of photons in different spectral regions are related to the different types of molecular motion or electronic transition:

❏ **Microwave radiation** → transitions in molecular rotational levels

❏ **Infrared radiation** → transitions in molecular vibrational levels

❏ **Ultraviolet and visible radiation** → transitions in electronic energy levels.

3. SAMPLE PROBLEM (AP STYLE)

ABSORPTION SPECTRUM

Region X		Region Y	Region Z	
Ultraviolet	Visible	Infrared	Microwave	Radio Wave

Wavelength

The diagram above represents the absorption spectrum for a pure molecular substance. What types of molecular motion or electronic transitions would you expect to find in each region labeled? (Region X, Region Y and Region Z)

Check 2013 Pract Exam #41 or 2015 #50

Ch 6.2 Quantized Energy and Photons
Read p. 216-219.

Learning Objective	Essential Knowledge
	SAP-8.B.1 When a photon is absorbed (or emitted) by an atom or molecule, the energy of the species is increased (or decreased) by an amount equal to the energy of the photon.
Unit 3.12 **SAP-8.B** Explain the properties of an absorbed or emitted photon in relationship to an electronic transition in an atom or molecule.	**SAP-8.B.2** The wavelength of the electromagnetic wave is related to its frequency and the speed of light by the equation: EQN: $c = \lambda \nu$ The energy of a photon is related to the frequency of the electromagnetic wave through Planck's equation ($E = h\nu$). EQN: $E = h\nu$ OR $E = hc/\lambda$ **(this one is not on the formula chart)**

Some phenomena cannot be explained using a wave model of light:
1. *BLACKBODY RADIATION* is the emission of light from hot objects.
2. The *PHOTOELECTRIC EFFECT* is the emission of electrons from metal surfaces on which light shines.
3. *EMISSION SPECTRA* are the emissions of light from electronically <u>excited electrons</u>.

Blackbody radiation: Hot Objects and the Quantization of Energy (Planck – Nobel Prize 1918)
- When solids are heated, they emit radiation, as seen in the red glow of an electric stove burner or the bright white light of a tungsten lightbulb.
  - a red-hot object is cooler than a yellowish or white-hot one
- During the late 1800s, a number of physicists studied this phenomenon, trying to understand the **relationship between the temperature and the intensity and wavelength of the emitted radiation.**
- In 1900 a German physicist named **Max Planck** solved the problem by assuming that <u>energy can be either released or absorbed by atoms only in discrete "chunks" of some minimum size.</u>
- Planck gave the name **QUANTRUN** (meaning "fixed amount") to the smallest quantity of energy that can be emitted or absorbed as electromagnetic radiation.
- He proposed that the **ENERGY, E**, of a single quantum equals a constant times the frequency of the radiation:

$$E = h\nu \quad \text{or} \quad E = hc/\lambda$$

  - energy = Joules, J
  - frequency = Hertz $(1 \text{ Hz} = 1 \text{ s}^{-1})$
  - h = **Planck's constant** $(6.626 \times 10^{-34} \text{ J-s})$.

- According to Planck's theory, matter can emit and absorb energy only in whole number multiples.
- Notice that Planck's constant is an extremely small number. Thus, a quantum of energy, hv, is an extremely small amount.
- Planck's rules regarding the gain or loss of energy are always the same, whether we are concerned with objects on the scale of our ordinary experience or with microscopic objects.
- With everyday objects, however, the gain or loss of a single quantum of energy is so small that it goes completely unnoticed.
- **In contrast, when dealing with matter at the atomic level, the impact of QUANTIZED energies is far more significant.**

Examples

1.   Calculate the energy of electromagnetic radiation whose frequency is 5.1 x 10^{-3} s^{-1}?

The Photoelectric Effect and Photons (Einstein – Nobel Prize 1921)

Learning Objective	Essential Knowledge

Unit 1.6
 	
SAP-1.B Explain the relationship between the photoelectron spectrum of an atom or ion and:
  a. The electron configuration of the species.
  b. The interactions between the electrons and the nucleus.
	SAP-1.B.1 The energies of the electrons in a given shell can be measured experimentally with photoelectron spectroscopy (PES). The position of each peak in the PES spectrum is related to the energy required to remove an electron from the corresponding subshell, and the height of each peak is (ideally) proportional to the number of electrons in that subshell.

A few years after Planck presented his quantum theory, scientists began to see its applicability to many experimental observations.
- In 1905, Albert Einstein (1879–1955) used Planck's theory to explain the **photoelectric effect** (**FIGURE 6.7**).
    - **Light shining on a clean metal surface causes the surface to emit electrons.**
    - **A minimum frequency of light, different for different metals, is required for the emission of electrons….because EVERY METAL HAS A DIFFERENT NUMBER OF ELECTRONS!**
    - For example, light with high frequency causes cesium metal to emit electrons, but light of lower frequency has no effect.

To explain the photoelectric effect, Einstein assumed that the radiant energy striking the metal surface behaves like a stream of tiny energy packets.
- Each packet, which is like a "particle" of energy, is called a **PHOTON**.
- Think of a photon as a "bundle of light"
- Under the right conditions, photons striking a metal surface can transfer their energy to electrons in the metal.
    - If the photons striking the metal have low energy, the electrons do not acquire sufficient energy to escape from the metal, even if the light beam is intense.
    - If the photons have higher energy, electrons are emitted.
- The intensity (brightness) of the light is related to the number of photons striking the surface per unit time but not to the energy of each photon.

The idea that the energy of **light depends on its frequency** helps us understand the diverse effects of different kinds of electromagnetic radiation.
- For example, because of the high frequency (short wavelength) of X-rays, X-ray photons cause tissue damage and even cancer. Thus, signs are normally posted around X-ray equipment warning us of high-energy radiation.

Although Einstein's theory of light as a stream of photons rather than a wave explains the photoelectric effect and a great many other observations, it also poses a dilemma.

- Is light a wave, or is it particle-like?
- The only way to resolve this dilemma: We must consider that **light possesses both wave-like and particle-like characteristics** and, depending on the situation, will behave more like waves or more like particles.

Examples

2. Calculate the energy of one photon of yellow light that has a wavelength of 589 nm. (See p. 218 Exercise 6.3)
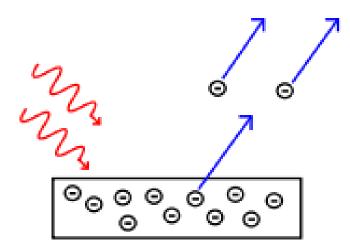
1 mol = 6.02 x 10²³ photons

An experimental technique that measures the relative energies of electrons in atoms and molecules based on the photoelectric effect

- **Photoelectric Effect:** the emission, or ejection, of electrons from the surface of, generally, a metal in response to incident light.
  - ○ **Light shining on the surface of a metal can cause electrons to be ejected from the metal.**
  - ○ The electrons will only be ejected if the photons have sufficient energy (*work function*):
    - Below the threshold frequency no electrons are ejected.
    - Above the threshold frequency, the excess energy appears as kinetic energy of the ejected electrons.

Examples

3. **Photoelectric Effect Guided Practice**

The diagram to the left represents the photoelectric effect for a metal.

There is also a table of wavelength with their respective colors they absorb.

When the metal surface is exposed to light with increasing frequency and energy of photons, electrons first begin to be ejected from the metal when the energy of the photons is 3.3×10^{-19} J. What is the frequency of light with photon energy 3.3×10^{-19} J?

Color	Wavelength
Red	647-760nm
Orange	585-647nm
Yellow	575-585nm
Green	491-575nm
Blue	424-491nm
Violet	300-424nm

What is the color of this light?

Beer - Lambert Law – LAB!!! **(Watch AP Youtube video 3.11-3.13)**

Learning Objective	Essential Knowledge
Unit 3.13 **SAP-8.C** Explain the amount of light absorbed by a solution of molecules or ions in relationship to the concentration, path length, and molar absorptivity.	**SAP-8.C.1** The Beer-Lambert law relates the absorption of light by a solution to three variables according to the equation: **EQN: $A = \varepsilon bc$** The molar absorptivity ε describes how intensely a sample of molecules or ions absorbs light of a specific wavelength. The path length **b** and concentration **c** (in molarity, $mol \cdot L^{-1}$, $mol \cdot dm^{-3}$) are proportional to the number of absorbing species.
	SAP-8.C.2 In most experiments the path length and wavelength of light are held constant. In such cases, the absorbance is proportional only to the concentration of absorbing molecules or ions.

Beer-Lambert Law relates the absorption (A) of light by a solution to three variables according to the equation:
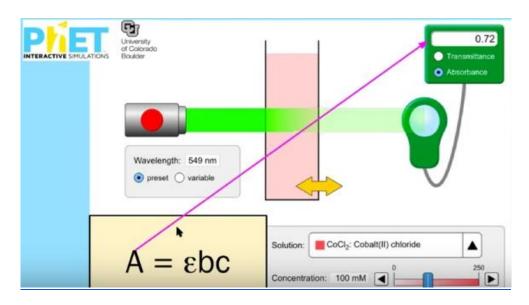
$$A = \varepsilon \, b \, c$$

ε = describes how intensely a sample of molecules or ions absorbs light of a specific wavelength. This is a **constant** unique to the molecule.

b = the path length

c = concentration (M) of solution are proportional to the number of absorbing species.

Beer-Lambert Law PhET Simulation (Linked on Image)

The point of Beer's Law: At a specific wavelength of light is shined through this sample, how much of it is ABSORBED by the sample.

- For this experiment above, when a wavelength of light at 549nm is shined through the sample of cobalt (II) chloride, how much is absorbed by the sample?

- We are going compare how much went into vs how much came out. In this case, the Absorbance was 0.72.

For an experiment, we will typically leave the ε (epsilon), b (path length), and identity of solution the same (constant).

- We usually use a cuvette to put the sample into the detector, so the length of the path (b) doesn't change.

- **Transmittance – how much light is transmitted (100%) – has an indirect relationship with absorbance (0% is absorbed)**

So there is a direct relationship between the absorbance and the concentration.

- **If you increase concentration, absorbance increases. And the color of the solution also increases (gets darker)**

- **If you increase the length of the path (cuvette is bigger), more of the light is absorbed (A increases) because we have MORE solution present.**
    - **So b and A are direct relatiosnhips of each other**

Also notice in this lab that we are only using solutions that have a COLOR.

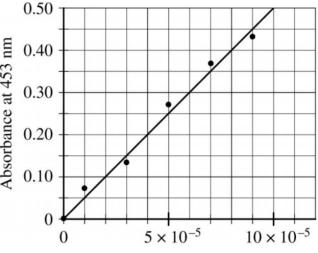- We CANNOT use this method on colorless solutions (like water or NaCl solution)

Examples

3.13 Beer-Lambert Law Guided Practice (Watch AP Youtube video 3.11-3.13 @ ~41mins)

$$Fe^{3+}(aq) + KSCN(s) \rightarrow FeSCN^{2+}(aq) + K^+(aq)$$

4. To determine the moles of $Fe^{3+}(aq)$ in a 100. mL sample of an unknown solution, excess $KSCN(s)$ is added convert all the $Fe^{3+}(aq)$ into the dark red speci $FeSCN^{2+}(aq)$, as represented by the equation above. T absorbance of $FeSCN^{2+}(aq)$ at different concentrations shown in the graph to the right.

The absorbance of the mixture is 0.20 at 453 nm.

1. What is the concentration of $FeSCN^{2+}(aq)$?

2. How many moles of $Fe^{3+}(aq)$ were present in the 125 mL sample?

5. A student uses visible spectrophotometry to determine the concentration of $CoCl_2(aq)$ in a sample solution. First the student prepares a set of $CoCl_2(aq)$ solutions of known concentration. Then the student uses a spectrophotometer to determine the absorbance of each of the standard solutions at a wavelength of 510 nm and constructs a standard curve. Finally, the student determines the absorbance of the sample of unknown concentration

The student made the standard curve below.
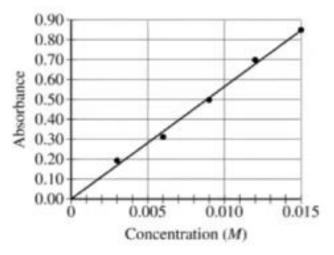
What is a possible experimental error which could have caused the error in the point the student plotted at $0.050 M Co^{2+}(aq)$?

AP EXAM FRQ PRACTICE 3.11-3.13 – HOMEWORK
(Answers in 4.1-4.4 beginning of video)

To spectrophotometrically determine the mass percent of cobalt in an ore containing cobalt and some inert materials, solutions with known $[Co^{2+}]$ are prepared and the absorbance of each of the solutions is measured at the wavelength of optimum absorbance. The data are used to create a calibration plot, shown below.

A 0.630 g sample of the ore is completely dissolved in concentrated $HNO_3(aq)$. The mixture is diluted with water to a final volume of 50.00 mL. Assume that all the cobalt in the ore sample is converted to $Co^{2+}(aq)$.

(a) What is the $[Co^{2+}]$ in the solution if the absorbance of the sample of the solution is 0.74?

(b) Calculate the number of moles of $Co^{2+}(aq)$ in the 50.00 mL solution.

(c) Calculate the mass percent of Co in the 0.630 g sample of the ore.

The student in the previous problem used a spectrophotometer to determine the absirbance of each of the standard solutions at a wavelength of 510 nm. A wavelength of 510 nm corresponds to an approximate frequency of $6 \times 10^{14} \, s^{-1}$.

(d) What is the approximate energy if one photon of this light?
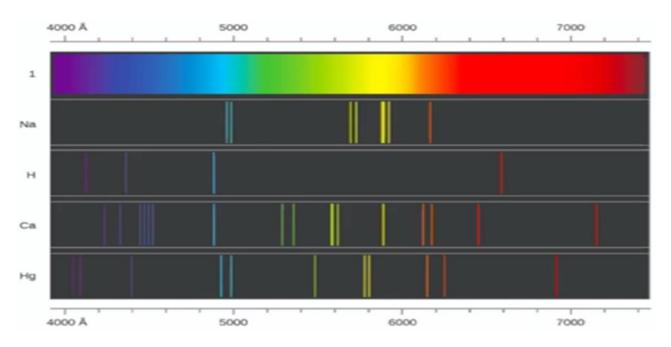
(e) What is the color of this light?

Ch 6.3 Line Spectra and the Bohr Model
Read p. 219-223.

In 1913, the Danish physicist **Niels Bohr** offered a theoretical explanation of *line spectra,* another phenomenon that had puzzled scientists during the nineteenth century.

- Radiation composed of a single wavelength is ***monochromatic***.
- However, most common radiation sources, including lightbulbs and stars, produce radiation containing many different wavelengths and is ***polychromatic***.
- A **spectrum** is produced when radiation from such sources is separated into its component wavelengths, as shown in **FIGURE 6.9**.
- The resulting spectrum consists of a continuous range of colors—violet, indigo, blue, green, yellow, orange, red - <u>with no blank spots.</u>
- This rainbow of colors, containing light of all wavelengths, is called a **CONTINUOUS SPECTRUM**.
  - Example of a continuous spectrum is the rainbow produced when raindrops or a prism for sunlight.

Not all radiation sources produce a continuous spectrum.
- When a high voltage is applied to tubes that contain different gases under reduced pressure, the gases emit different colors of light (**FIGURE 6.10**).
  - neon gas is the familiar red-orange glow of many "neon" lights
  - sodium vapor emits the yellow light of some streetlights.
- When light coming from such tubes is passed through a prism, only a few wavelengths are present in the resultant spectra (**FIGURE 6.11**).
  - Each colored line in such spectra represents light of one wavelength.
  - A spectrum containing radiation of only specific wavelengths is called a **LINE SPECTRUM**. (We did this lab/demo in CP/Honors)

When scientists first detected the line spectrum of hydrogen in the mid-1800s, they were fascinated by its simplicity. At that time, only four lines at wavelengths of 410 nm (violet), 434 nm (blue), 486 nm (blue-green), and 656 nm (red) were observed (**Figure 6.11).**

Bohr's Model – Nobel Prize in 1922

To explain the line spectrum of hydrogen, Bohr assumed that electrons in hydrogen atoms move in circular orbits around the nucleus, but this assumption posed a problem.

- According to classical physics, a charged particle (such as an electron) moving in a circular path should continuously lose energy.
- As an electron loses energy, therefore, it should spiral into the positively charged nucleus.
- This behavior, however, does not happen— hydrogen atoms are stable.
- And this is an apparent violation of the laws of physics! Oh no!

Bohr assumed that the prevailing laws of physics were inadequate to describe all aspects of atoms. **Furthermore, he adopted Planck's idea that energies are quantized.**
Bohr based his model on three postulates:

1. Only orbits of certain radii, corresponding to certain specific energies, are permitted for the electron in a hydrogen atom.
2. An electron in a permitted orbit is in an "allowed" energy state. An electron in an allowed energy state does not radiate energy and, therefore, does not spiral into the nucleus.
3. Energy is emitted or absorbed by the electron only as the electron changes from one allowed energy state to another. This energy is emitted or absorbed as a photon that has energy $(E = h\nu)$.

The Energy States of the Hydrogen Atom

Starting with his three postulates and using classical equations for motion and for interacting electrical charges, Bohr calculated the energies corresponding to the allowed orbits for the electron in the hydrogen atom.

- Bohr showed mathematically that **(NOT ON AP EXAM 😊)**

$$E = -(hcR_\text{H})\left(\frac{1}{n^2}\right) = (-2.18x10^{-18}J)\left(\frac{1}{n^2}\right)$$

  - where **n is the *principal quantum number* (n = 1, 2, 3, ….)**
  - R_H is the **Rydberg constant.**
  - The product $hcR_\text{H} = 2.18 \times 10^{-18}$ J.

Each orbit corresponds to a different value of n, and the **radius of the orbit gets larger as n increases.**
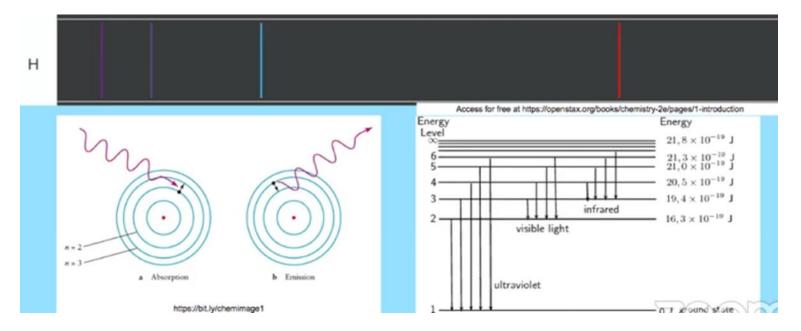
- The first allowed orbit (the one closest to the nucleus) has n=1 , the next allowed orbit (the one second closest to the nucleus) has n=2, and so forth.
- The electron in the hydrogen atom can be in any allowed orbit, and Bohr's Equation tells us the energy the electron has in each allowed orbit.

The lower (more negative) the energy is, the more stable the atom is.
- The energy is lowest (most negative) for n=1.
- **As *n* gets larger, the energy becomes less negative and therefore increases.**
  - **The greater the value of), the higher the energy!**

Bohr assumed that the electron can "jump" from one allowed orbit to another by either absorbing or emitting photons.
- The electron must absorb energy in order to move to a higher-energy state (higher value of *n*).
  - The atom is said to be in an **EXCITED state**.
- The energy is emitted when the electron jumps to a lower-energy state (lower value of *n*).
  - The lowest-energy state is called the **GROUND state** of the atom.

Access for free at https://openstax.org/books/chemistry-2e/pages/1-introduction

Electrons are jumping around.
LEFT PIC: Photons of light (Energy) comes in and hits an electron, the electron **ABSORBS** the energy and can jump up to higher energy levels = **EXCITED STATE.**

RIGHT PIC: After a certain amount of time, electron will **EMIT** that energy (same energy it absorbed) and falls back down to lower energy level = **GROUND STATE**

Limitations of the Bohr Model

Although the Bohr model explains the line spectrum of the hydrogen atom, <u>it cannot explain the spectra of other atoms.</u>

- Bohr also avoided the problem of why the negatively charged electron would not just fall into the positively charged nucleus by simply assuming it would not happen.
- Also, there is a problem with describing an electron merely as a small particle circling the nucleus.

In Section 6.4, the electron exhibits wavelike properties!

- The Bohr model was only an important step along the way toward the development of a more comprehensive model.
- What is most significant about Bohr's model is that it introduces two important ideas that are also incorporated into our current model (Quantum Mechanics):
    1. *Electrons exist only in certain discrete energy levels, which are described by quantum numbers.*
    2. *Energy is involved in the transition of an electron from one level to another.*

Several scientists after Bohr took a closer look at the wave behavior of matter:

- Louis de Broglie (momentum = mv): he proposed that the wavelength of the electron, or of any other particle, depends on its mass, m, and on its velocity,
- Werner Heisenberg (uncertainty principle – Nobel Prize 1933): we cannot determine the exact position, direction of motion, and speed of subatomic particles simultaneously. For electrons: we cannot determine their momentum and position simultaneously.
- Erwin Schrödinger (Schrödinger's wave equation): incorporates both the wave-like behavior of the electron and its particle-like behavior. His work opened a new approach to dealing with subatomic particles, an approach known as *quantum mechanics* or *wave mechanics*. (You may know his name from the theory of Schrodinger's cat)

Ch 6.5 Quantum Mechanics and Atomic Orbitals
Read p. 226-230.

Learning Objective	Essential Knowledge
Unit 1.5 **SAP-1.A** Represent the electron configuration of an element or ions of an element using the Aufbau principle.	**SAP-1.A.1** The atom is composed of negatively charged electrons and a positively charged nucleus that is made of protons and neutrons.
	SAP-1.A.3 In atoms and ions, the electrons can be thought of as being in "shells (energy levels)" and "subshells (sublevels)," as described by the electron configuration. Inner electrons are called core electrons, and outer electrons are called valence electrons. The electron configuration is explained by quantum mechanics, as delineated in the Aufbau principle and exemplified in the periodic table of the elements.
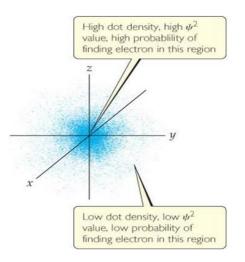
Orbitals (Enrgy levels) and Quantum Numbers

Orbitals and Orbits do NOT mean the same!

- **ORBITS –** path of an electron that moves around the nucleus in an atom.

- **Atomic ORBITAL -** the space or region around the nucleus where the electron are calculated to be present.

Probability of finding the electron.
- At best, we can only determine location by 90%!!!
- A region of high electron density is one where there is a high probability of finding an electron.

Each orbital has a characteristic shape and energy

The quantum mechanical model uses **3 QUANTUM NUMBERS** (n, l, and m_l) to describe an orbital.

==*AP tips: There are 4 quantum numbers, however AP only requires that you understand and determine the principal quantum # (n) and angular momentum quantum # (l)*==

1. *PRINCIPAL QUANTUM NUMBER, n.* This is the same as Bohr's n.

   - **SIZE of the orbital** – also known as the period #, energy level
   - **As n increases, the orbital becomes larger, and the electron is farther from the nucleus.**
   - **An increase in n also means that the electron has a higher energy and is therefore less tightly bound to the nucleus.**

2. *ANGULAR MOMENTUM QUANTUM NUMBER, l.*

   - **SHAPE of the orbital – s, p, d, f……**
   - This quantum number depends on the value of n!
   - The values of l begin at 0 and increase to $n - 1$.
   - We usually use letters for l (s, p, d and f for $l = 0$, 1, 2, and 3).

==Electrons are found in **shells (energy levels)** and **subshells (sublevels)**==
A collection of orbitals with the same value of n is called an **electron shell**.
   - A set of orbitals with the same *n but different l* is called a **subshell**.
       - For example, $3p$ orbitals have $n = 3$ and $l = 1$.
Think of it like a peanut M&M… the outside shell candy shell is the electron "shell", the chocolate candy layer would be the electron subshell (maybe the s subshell) and then the peanut can be another subshell (p)

3. **Magnetic quantum number, m_l – not tested on AP Exam**
    • Magnetic quantum numbers give the <u>three-dimensional orientation of each orbital.</u>
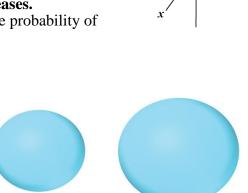
n = (Principal Quatrum #)	1	2	3	4
l = (shape)	0	0,1	0,1,2	0,1,2,3
Total number of subshells	1	3	5	7

Ch 6.6 Shapes of Orbitals
Read p. 230-234.
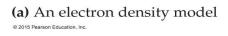
The *s* Orbitals
   • There is only **1 orbital for s orbitals.**
   • All *s* orbitals are **spherical**.
   • **As *n* increases, the *s* orbitals get larger.**
   • **As *n* increases, the number of nodes increases.**
       ○ A node is a region in space where the probability of finding an electron is zero.

(a) An electron density model   (b) Contour models

© 2015 Pearson Education, Inc.
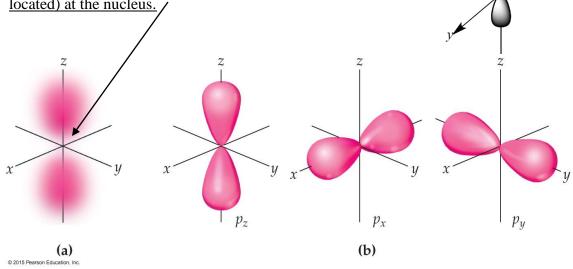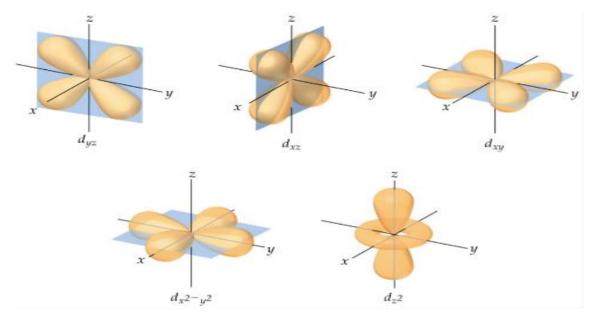
The *p* Orbitals

- **There are three *p* orbitals:** p_x, p_y and p_z.
- The orbitals are **dumbbell** shaped; each has **two *lobes*.**
- **As *n* increases, the *p* orbitals get larger.**
- All *p* orbitals have a **node** (a region where no electrons are located) at the nucleus.

(a)

(b)

© 2015 Pearson Education, Inc.

p_z p_x p_y

The *d* and *f* Orbitals

- **There are five *d (clovers)* and seven f orbitals.**
  - Three of the *d* orbitals lie in a plane bisecting the *x*-, *y*-, and *z*-axes.
  - Two of the *d* orbitals lie in a plane aligned along the *x*-, *y*-, and *z*-axes.
  - Four of the *d* orbitals have four lobes each.
  - One *d* orbital has two lobes and a collar.

d_{yz} d_{xz} d_{xy}

$d_{x^2-y^2}$ d_{z^2}

Ch 6.7 Many Electron Atoms
Read p. 234-236.
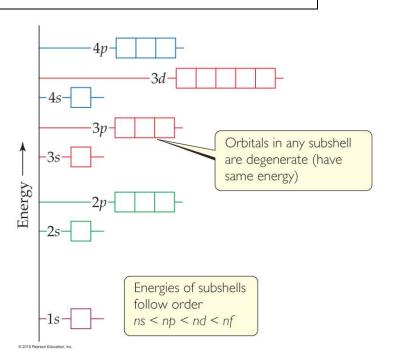
Orbitals and Their Energies

In a many-electron atom: for a given value of n, the energy of an orbital increases with increasing value of l.

For example, notice in Figure 6.24 that the n = 3 orbitals increase in energy in the order
3s < 3p < 3d.

Notice also that all orbitals of a given subshell (such as the five 3d orbitals) have the same energy as one another.

Orbitals with the same energy are said to be **degenerate**.

Orbitals in any subshell are degenerate (have same energy)

Energies of subshells follow order ns < np < nd < nf

© 2015 Pearson Education, Inc.

- **So, the energy of an orbital increases with increasing value of *l*. (ns < np < nd < nf).**
- **Spacing is different between orbitals – gets closer as n increases!**
  - **Notice the spacing between 1s&2s and the spacing between 3d&4s. Not the same spacing as n increases.**

Electron Spin and the Pauli Exclusion Principle

When scientists studied the line spectra of many-electron atoms in great detail, they noticed a very puzzling feature: Lines that were originally thought to be single were actually closely spaced pairs.

- This meant, in essence, that there were twice as many energy levels as there were "supposed" to be.
- Scientists proposed that electrons have an intrinsic property, called **electron spin**, that causes each electron to behave as if it were a tiny sphere spinning on its own axis.
- By now it probably does not surprise you to learn that **electron spin is quantized.**
- This observation led to the assignment of a new quantum number for the electron, in addition to *n, l,* and m_l, which we have already discussed.

The 4th new quantum number, the **SPIN MAGNETIC quantum number**, is denoted m_s (the subscript *s* stands for *spin*).

- Two possible values are allowed for m_s, + ½ or – ½, which was first interpreted as indicating the two opposite directions in which the electron can spin.
- A spinning charge produces a magnetic field. The two opposite directions of spin therefore produce oppositely directed magnetic fields (_ **FIGURE 6.25**).*

Electron spin is crucial for understanding the electronic structures of atoms.

- In 1925, Wolfgang Pauli discovered the principle that governs the arrangements of electrons in many-electron atoms.

The **Pauli exclusion principle** states that *an orbital can hold a maximum of two electrons* and they must have *opposite spins*.

- *By this principle: **no two electrons in an atom can have the same set of four quantum numbers n, l, m_l, and m_s.***

| Ch 6.8-6.9 Electron Configurations and the Periodic Table |
| Read p. 237-245. |

ELECTRON CONFIGURATION – it's a model that shows us the arrangements of electrons in the orbitals of an atom.

The **most stable electron configuration—the ground state**—is that in which the electrons are in the **lowest energy states.**
- The Pauli exclusion principle tells us, however, that there can be at most two electrons in any single orbital.
- **Thus,** *the orbitals are filled in order of increasing energy, with no more than two electrons per orbital.*
- For example, consider the lithium atom, which has three electrons.
    o Recall that the number of electrons in a neutral atom equals its atomic number.
    o The l*s* orbital can accommodate two of the electrons. The third one goes into the next lowest energy orbital, the 2*s*.

We can represent any electron configuration by writing the symbol for the occupied **subshell** and adding a **superscript** to indicate the number of electrons in that subshell. For example, for lithium we write $1s^2 \, 2s^1$.

We can also show the arrangement of the electrons in a diagram called **ORBITAL DIAGRAM** (ARROWS).
- *Ea*ch orbital is denoted by a box and each electron by an arrow (can be a full or half arrow).
- An arrow pointing up (↑) represents an electron with a positive spin magnetic quantum number ($m_s = +\frac{1}{2}$) and an arrow pointing down (↓) represents an electron with a negative spin magnetic quantum number ($m_s = +\frac{1}{2}$).
- Electrons having **opposite spins** are said to be *PAIRED* when they are in the same orbital (↑↓).
- An *UNPAIRED electron* is one not accompanied by a partner of opposite spin.
- In the lithium atom the two electrons in the 1*s* orbital are paired and the electron in the 2*s* orbital is unpaired.

unpaired | ↑ | paired | ↑ ↓ |

Electron Configurations of Several Lighter Elements

Element	Total Electrons	Orbital Diagram						Electron Configuration
		1s	2s	2p			3s	
Li	3	↑↓	↑					$1s^2 2s^1$
Be	4	↑↓	↑↓					$1s^2 2s^2$
B	5	↑↓	↑↓	↑				$1s^2 2s^2 2p^1$
C	6	↑↓	↑↓	↑	↑			$1s^2 2s^2 2p^2$
N	7	↑↓	↑↓	↑	↑	↑		$1s^2 2s^2 2p^3$
NE	10	↑↓	↑↓	↑↓	↑↓	↑↓		$1s^2 2s^2 2p^6$
Na	11	↑↓	↑↓	↑↓	↑↓	↑↓	↑	$1s^2 2s^2 2p^6 3s^1$

Consider now how the electron configurations of the elements change as we move from element to element across the periodic table. Let's look at some examples in period 2.

- Boron, atomic number 5, has the electron configuration . The fifth electron must be placed in a 2p orbital because the 2s orbital is filled. Because all the three 2p orbitals are of equal energy, it does not matter which 2p orbital we place this fifth electron in.
- With the next element, carbon, we encounter a new situation. We know that the sixth electron must go into a 2p orbital. However, does this new electron go into the 2p orbital that already has one electron or into one of the other two 2p orbitals? Hund's Rule comes to the rescue for this!

Hund's rule states that *for degenerate orbitals, the lowest energy is attained when the number of electrons having the same spin is maximized.*
Each subshell should have one electron filled (with the same spin) before any are doubled up (with opposite spin).
By placing electrons in different orbitals, electron-electron repulsions are minimized.
(Rodriguez name for it: School Bus Rule)

- For a carbon atom to achieve its lowest energy, the two 2p electrons must have the same spin. For this to happen, the electrons must be in different 2p orbitals, as shown in Table above. So, a carbon atom in its ground state has two unpaired electrons.
- When you get to oxygen ($1s^2\ 2s^2\ 2p^4$), the fourth electron in the 2p orbital will now pair up with an electron already in the 2p orbital, but with OPPOSITIE SPIN!

Aufbau Principle

- Aufbau means "to build up"
- Electrons are added to the lowest subshells first (1s, 2s, 2p, 3s, 3p, ….)
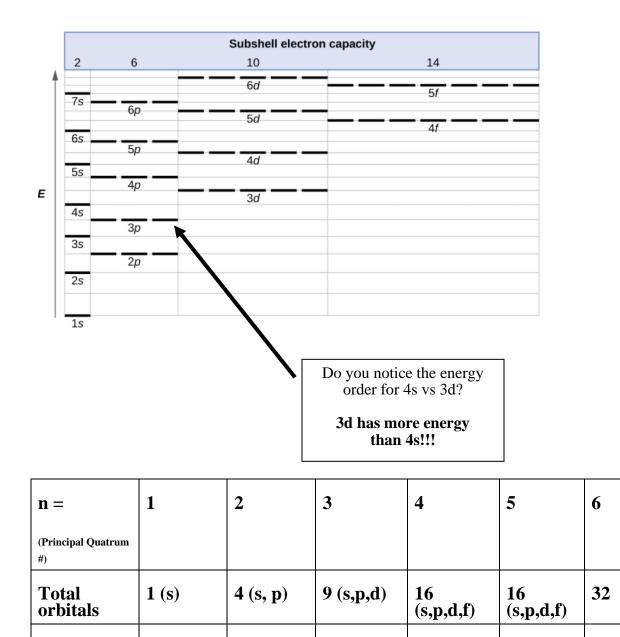
Orbitals can be ranked in terms of energy to yield an **Aufbau diagram**.
- Note that this Aufbau diagram is for a <u>single electron system</u>.
- As *n* increases note that the spacing between energy levels becomes smaller.

Do you notice the energy order for 4s vs 3d?

3d has more energy than 4s!!!
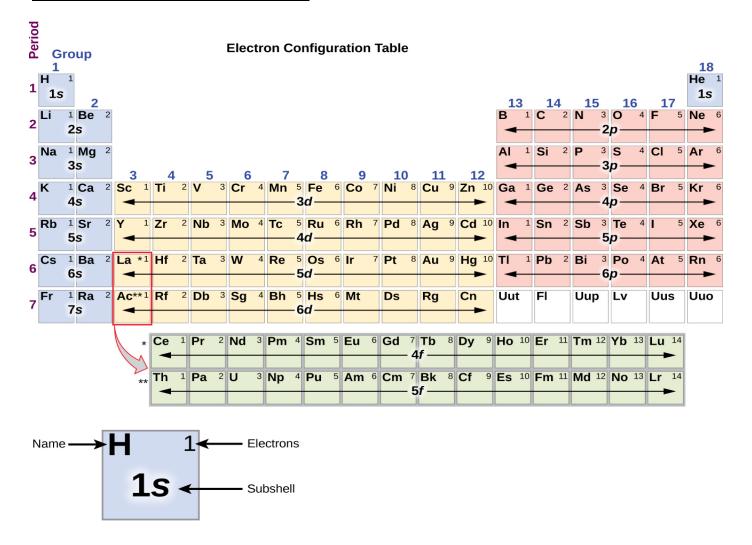
n = (Principal Quatrum #)	1	2	3	4	5	6
Total orbitals	1 (s)	4 (s, p)	9 (s,p,d)	16 (s,p,d,f)	16 (s,p,d,f)	32
Total electrons	2	8	18	32	32	64

Let's label and color our Periodic Table!

Electron Configuration Table

Period

Group

Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H 1 1s																	He 1 1s
2	Li 1 2s	Be 2											B 1	C 2	N 3	O 4 2p	F 5	Ne 6
3	Na 1 3s	Mg 2	3	4	5	6	7	8	9	10	11	12	Al 1	Si 2	P 3	S 4 3p	Cl 5	Ar 6
4	K 1 4s	Ca 2	Sc 1	Ti 2	V 3	Cr 4	Mn 5 3d	Fe 6	Co 7	Ni 8	Cu 9	Zn 10	Ga 1	Ge 2	As 3	Se 4 4p	Br 5	Kr 6
5	Rb 1 5s	Sr 2	Y 1	Zr 2	Nb 3	Mo 4	Tc 5 4d	Ru 6	Rh 7	Pd 8	Ag 9	Cd 10	In 1	Sn 2	Sb 3	Te 4 5p	I 5	Xe 6
6	Cs 1 6s	Ba 2	La *1	Hf 2	Ta 3	W 4	Re 5 5d	Os 6	Ir 7	Pt 8	Au 9	Hg 10	Tl 1	Pb 2	Bi 3	Po 4 6p	At 5	Rn 6
7	Fr 1 7s	Ra 2	Ac**1	Rf 2	Db 3	Sg 4	Bh 5 6d	Hs 6	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo

*	Ce 1	Pr 2	Nd 3	Pm 4	Sm 5	Eu 6	Gd 7	Tb 8 4f	Dy 9	Ho 10	Er 11	Tm 12	Yb 13	Lu 14
**	Th 1	Pa 2	U 3	Np 4	Pu 5	Am 6	Cm 7	Bk 8 5f	Cf 9	Es 10	Fm 11	Md 12	No 13	Lr 14

Name → **H** 1 ← Electrons

1s ← Subshell

The periodic table can be used as a guide for electron configurations.
- The period number is the value of n.
- Groups 1A and 2A have their s orbitals being filled.
- Groups 3A – 8A have their p orbitals being filled.
- Valence e-: The s-block and p-block of the periodic table contain the representative, or main-group, elements.
- Groups 3B – 2B have their d orbitals being filled.
- The lanthanides and actinides have their f orbitals being filled.
- Note that the $3d$ orbitals fill after the $4s$ orbital. Similarly, the $4f$ orbitals fill after the $5d$ orbitals.

EXCEPTION TO RULE: SEE CHRONIUM & COPPER'S GROUPS
(NOT TESTED ON AP EXAM)

There are many elements that appear to violate the electron configuration guidelines.
- 2 groups in the d-orbital block: Group 6 (Cr, Mo, W) and Group 11 (Cu, Ag, Au)
- Examples:
  - Chromium is **[Ar]$3d^5 4s^1$** instead of [Ar]$3d^4 4s^2$.
  - Copper is **[Ar]$3d^{10} 4s^1$** instead of [Ar]$3d^9 4s^2$.

Examples

1. Write the electron configuration for sodium. How many unpaired electrons does a Na atom possess?

2. Write the electron configuration for phosphorus. How many unpaired electrons does a P atom possess?

3. Write the electron configuration for calcium. How many unpaired electrons does a Ca atom possess?

Condensed Electron Configurations (Short-hand or Noble gas configurations)

Electron configurations may be written using a shorthand notation.
- **Noble-gas or condensed electron configuration**
- Why noble gas? All orbitals are completely filled up. No unpaired e-.

CORE electrons are the electrons that are filled up to the noble gas in brackets.
- **Core electrons** are electrons in the inner shells. (inner electrons)
- These are generally not involved in bonding

VALENCE electrons are electrons in the outer shell. (outer electrons)
- Valence e- are only located in the **s & p orbitals only! (d & f orbital electrons are not valence e-)**
- **Maximum valence e-: 8!**
  - **s orbitals can hold 2 e- and p orbitals can hold 6 e-.**
- These electrons are gained and lost in reactions. THESE ARE THE ELECTRONS WORKING DURING A CHEMICAL RXN!!!

Rules:

Locate the noble-gas **BEFORE** the element you are looking at.
- Put the noble-gas in brackets [X].
- Write the remaining e- configuration after the nearest noble gas configuration.

Example: Aluminum
- Al is **$1s^2 2s^2 2p^6 3s^2 3p^1$**
- **Ne** is **$1s^2 2s^2 2p^6$**.
- Therefore, the noble gas configuration for Al   **[Ne]$3s^2 3p^1$**.
- Core e-: 10
- Valence e-: 3

Examples

4. Write the condensed electron configuration for sodium.

5. Write the condensed electron configuration for phosphorus.

6. Write the condensed electron configuration for calcium.

Transition Metals: n (period -1)
- After Ar, the 4s orbitals fill THEN the $3d$ orbitals begin to fill.
  - Why not 3d not 4d? **The d-orbitals "n" number is the (period – 1).**
- After the $3d$ orbitals are full, the $4p$ orbitals begin to fill and so on.

Inner Transition Metals: n (period -2)
- The electron configuration of La is [Xe]$6s^2 5d^1$.
- After La comes Ce, which starts the 4f orbitals.
  - Why not 4f not 6f? **The f-orbitals "n" number is the (period – 2).**
- The $4f$ orbitals are filled for the elements Ce – Lu, which are called **lanthanide elements** (or rare earth elements).
- The $5f$ orbitals are filled for the elements Th – Lr, which are called **actinide elements**.

Examples

7. Write the electron configuration and noble gas configuration for vanadium. How many unpaired electrons does a V atom possess?

8. Write the electron configuration and noble gas configuration for bromine. How many unpaired electrons does a Br atom possess?

9. Write the electron configuration and noble gas configuration for cadmium. How many unpaired electrons does a Cd atom possess?

10. Write the electron configuration and noble gas configuration for tin. How many unpaired electrons does a Sn atom possess?

11. Write the electron configuration and noble gas configuration for xenon. How many unpaired electrons does a Xe atom possess?