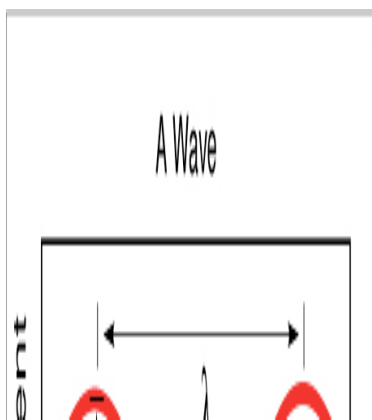


## The Development of Quantum Mechanics

Early physicists used the properties of electromagnetic radiation to develop fundamental ideas about the structure of the atom. A fundamental assumption for their work was that electromagnetic (EM) radiation behaved as waves. Frequency, wavelength, amplitude, phase, displacement and speed are the fundamental measures used for describing waves. For this course we will not be discussing phase.



$\lambda$  (lambda) = wavelength (in m)  
The wavelength is the distance from crest to crest.

$\nu$  (nu) = frequency (in  $s^{-1}$  or hertz)

$c$  = speed of light =  $3.00 \times 10^8$  m/s  
 $c = \lambda\nu$

The amplitude is the maximum displacement.

The frequency ( $\nu$ ) is the number of oscillations per time. For example, if the wave above travels  $10 \lambda$  in 10 seconds, the frequency is  $10 \text{ sec}^{-1}$ .

The following table represents the divisions within the electromagnetic spectrum:

$\lambda$ (m)	$10^{-12}$	$10^{-10}$	$10^{-8}$	$4 \times 10^{-7}$ to $7 \times 10^{-7}$	$10^{-4}$	$10^{-2}$	$10^2$
<b>EM Radiation</b>	Gamma Rays	X-Rays	UV	Visible	IR	Micro-waves	Radio Waves

Commonly the wavelength is expressed in units of nm instead of m.

$$10^9 \text{ nm} = 1 \text{ m} \quad \text{or} \quad 10^{-9} \text{ m} = 1 \text{ nm}$$

Because of rapid developments and progress made in physics toward the end of the 19th century, many physicists were confident that the field had reached maturity and additional developments were unlikely. Physicists assumed that energy was continuous.

However, Planck's law, describing the emission of electromagnetic radiation started a revolution. Planck's Law describes what is known as black body radiation. Any object above 0 K emits radiation; room temperature black objects emit infrared radiation. The assumption of Planck's Law is that the energies of the smallest objects (i.e., the atoms) within a black body are limited to discrete, integer multiples of a fundamental unit of energy. Energy is quantized. Planck did not think there was any physical significance to this assumption. For Planck it was a mathematical trick that allowed him to obtain a single expression that accurately predicted the observed data. Later, Albert Einstein, based on the photoelectric effect, proposed a model in which light is both emitted and

*absorbed* in quantized packets (photons). Einstein's work demonstrated that light has some particle-like properties.

The following expression represents the relationship between the energy of a photon and the frequency of radiation emitted or absorbed.

$$E = h\nu$$

E=energy (in Joules)

$\nu$ =frequency ( $s^{-1}$  or Hz);

$h = 6.626 \times 10^{-34}$  J s (Planck's Constant, in Joule-seconds)

The expression can be rearranged using  $\nu = c/\lambda$ .

Therefore,  $E = hc/\lambda$ . Thus, EM radiation with longer wavelengths is less energetic. What is the most energetic radiation from the table above?

Einstein developed the first mass relationship with energy and radiation. His famous expression often cited is  $E = mc^2$ . In a nuclear reaction, the mass of the products is less than the mass of the reactants. The difference in mass appears as energy (heat and light).

De-Broglie used Planck and Einstein's expression to develop the hypothesis that any moving particle or object has wave-like properties. De-Broglie was the first to conclude that we cannot treat matter as either a wave or a particle, but we have to treat matter as both. Hence, his theory is titled the wave-particle duality of nature.

$$\lambda = h/p$$

$p$  = momentum which is defined as the product of the mass in kg of the particle and its velocity.  $h$  is Planck's constant.

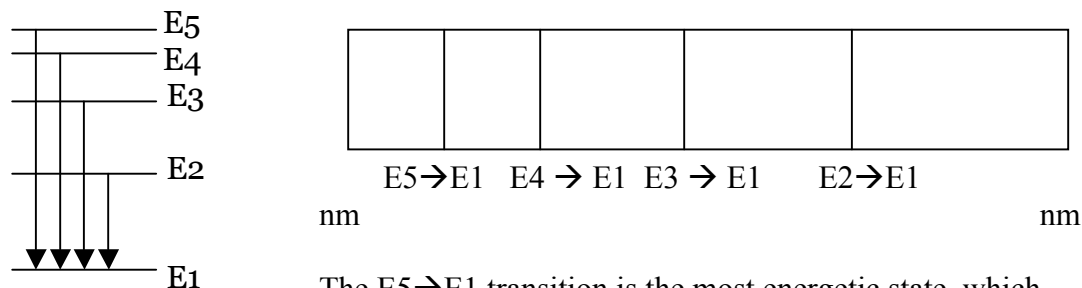
### Atomic Spectrum of Hydrogen

Bohr used the energies observed from black body emission for hydrogen to develop a model for the hydrogen atom.

Bohr used the idea that electrons were confined to specific orbits with specific energies, and he also used the notion that electrons were particles. Bohr's calculations worked well for the hydrogen atom, but failed for other atoms. The Bohr model was not consistent with known physics. An orbiting electron is predicted to fall into the nucleus with the emission of light.

From this research; however, the fundamentals for quantum mechanics emerged. Bohr assumed that electrons could switch between energy levels within the atom. The transition from an "excited" energy level to lower energy states yielded energy (EM

radiation). This models served as the fundamental idea for developing quantum mechanics.



The  $E5 \rightarrow E1$  transition is the most energetic state, which emits the shortest wavelength of light. Wavelength is inversely proportional to the energy.

The transition of an electron from an excited state ( $E2, E3, E4, E5$ ) to the ground state ( $E1$ ) converts electronic energy of the atom to light (EM energy). Because of differences in energy levels within various types of atoms, different energies are yielded for each type of atom; therefore, we can use the emission wavelengths to identify atoms. A line spectrum (shown above) is one method of tabulating the energies produced within the visible region (400 to 700 nm). The different colors yielded are characteristic of the atom-type and provide a positive identification for the atom.

### Modern Quantum Theory

After Bohr's work, the idea of the atom was extended using both a particle and wave properties yielding what has become the most acceptable theory for atomic behavior.

Schrodinger, De-Broglie, and Heisenberg are the names commonly associated with this model for the atom. We have already mentioned De-Broglie's work with identifying the wave-particle duality of nature. Heisenberg emphasized that because the photons and electrons behave as both particles and waves, we cannot identify both position and momentum at any given instance.

$$\Delta x \cdot m \Delta v \geq (h/4\pi) \quad \text{Heisenberg's Uncertainty Principle}$$

$x$  = position

$v$  = velocity

$h$  = Planck's Constant =  $6.6.26 \times 10^{-34}$  Js

$$1 \text{ J} = 1 \text{ kg m}^2/\text{s}^2$$

Schrodinger's work led to a fundamental equation that goes beyond the scope of this course, but it enabled calculations of orbital energies and properties. After Bohr's work, electrons were described as being housed in orbitals, which are specified by their shapes and energies. Each orbital is indicated by three quantum numbers, (roughly) one for energy, one for shape and one for orientation.

### Schrodinger's equation: $H\Psi = E\Psi$

H is the Hamiltonian operator used to alter functions to yield new functions and an additional variable. An operator can be any mathematical operation such as addition, subtraction, etc., but in this case, it is partial differential equations (hence, beyond the scope of the course).

$\Psi$  = Wavefunction. A wavefunction describes an orbital. The best way to understand the physical significance of a wavefunction is to realize that the squares of the absolute values of a wave function give the probability distribution. More simply stated, the shapes of the orbitals (sphere, dumbbell, etc) come from  $\Psi^2$ .

E = Energy.

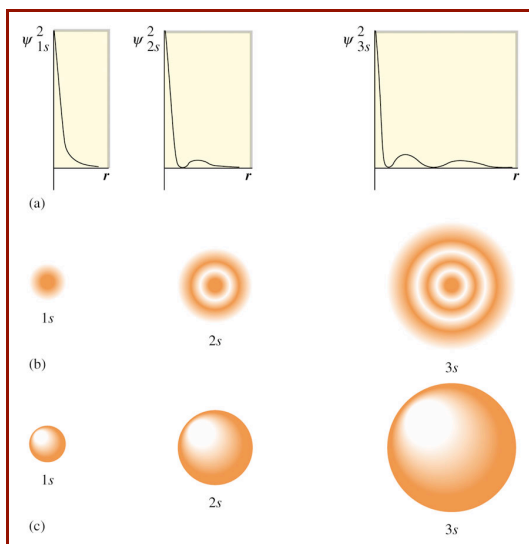
The Hamiltonian operator yields the energy and the wavefunction. A wavefunction describes an orbital, and is characterized by three quantum numbers ( $n, l, m_l$ ). A wave function is usually written as:  $\Psi(n, l, m_l)$ . An orbital can hold no more than two electrons, and these electrons must have opposing spins (+1/2 or -1/2). Electron spin is indicated by the quantum number  $m_s$ , which can be +1/2 or -1/2. So an electron is characterized by four quantum numbers ( $n, l, m_l$ , and  $m_s$ ). The first three indicate which orbital the electron is in, the fourth indicates the electron spin.

**n = principal quantum number.** This is used to describe the energy and size of an orbital. As n increases, the size and energy increases. n can be a positive integer greater than zero ( $n = 1, 2, 3, \dots$ ). n indicates the shell or level. All electrons within a given shell have the same n. [Note: for atoms other than hydrogen n is not the only factor in determining orbital energy.]

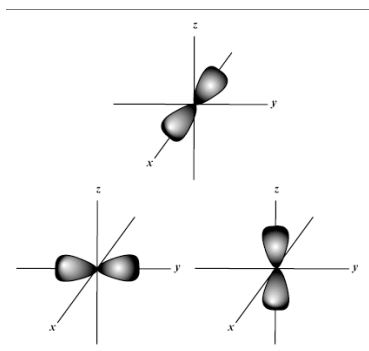
**l = angular quantum number.** This is used to describe the shape of the orbital.  $l = 0, 1, 2, \dots, (n-1)$ . So, n limits the possibilities for l. Within a given shell (n), there can be various subshells with different l's. For  $n=1$ , there is only one subshell ( $l=0$ ) called s. For  $n=2$ , there are two subshells ( $l=0$  and  $l=1$ ) called s and p. For  $n=3$  there are three subshells ( $l=0,1,2$ ), which are s, p and d.

**$m_l$  = magnetic quantum number.** This is used to describe the orientation of the orbital.  $m_l = -l$  to 0 to  $+l$  where l is the angular quantum number. For  $l=1$  (the p subshell),  $m_l$  can be -1, 0, 1. The p orbitals have three orientations.

**n=1.** The simplest orbital is the s orbital ( $l=0$ ), with a spherical shape. This is the only atomic orbital allowed in the first shell ( $n = 1$ ). If  $l=0$ , then  $m_l$  must be 0, too. An s-subshell can hold up to 2 electrons. Examples of s-orbitals are shown in the image below a)  $\Psi(1,0,0)$ , b)  $\Psi(2,0,0)$ , and c)  $\Psi(3,0,0)$ .



**n=2.** The second orbital, introduced in the second shell ( $n=2$ ) is the p-orbital. It has a dumbbell shape. p-Orbitals are only allowed if  $n$  is greater than 1. For  $n=2$ ,  $l$  must be 0 or 1. When  $l=1$  and  $m_l$  can be -1, 0, or 1. These three  $m_l$ 's mean there are three orientations, i.e., 3 p-orbitals are possible, which are sometimes called  $p_x$ ,  $p_y$  and  $p_z$ . The p-subshell can hold up to six electrons.



p-orbitals

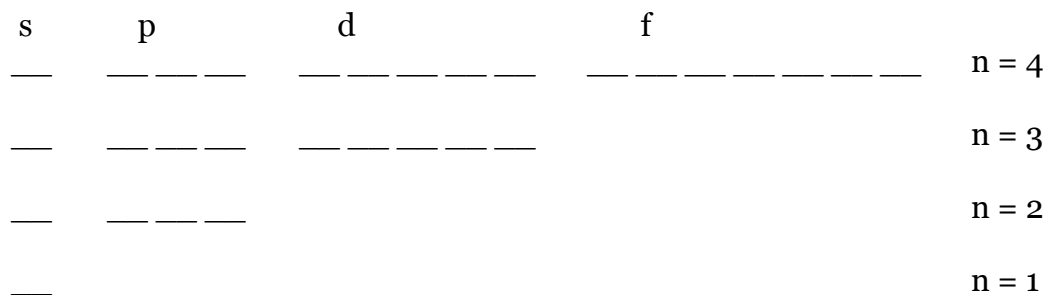
hold up to 14 electrons.

**n=3.** For  $n=3$ ,  $l$  can be 0 (s-orbital), 1 (p orbital) or 2 (d orbital). So the d-orbitals are introduced in the third shell ( $n=3$ ) and have an  $l$  value of 2. If  $l=2$ , the  $m_l = -2, -1, 0, 1, 2$ . So there are five orientations for the d orbitals. The d-subshell can hold up to 10 electrons.

**n=4.** The f-orbitals are introduced in the fourth shell ( $n=4$ ) and have an  $l$  value of 3. The seven f-orbitals can

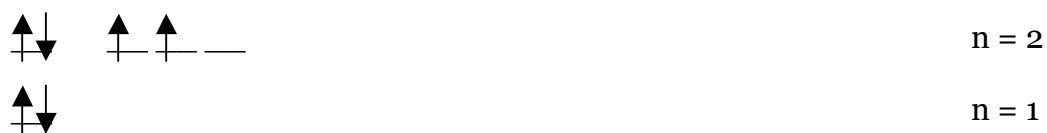
### Adding Electrons to Orbitals

The following summarizes the orbitals for  $n=1$  to  $n=4$ . For hydrogen, the energy of every orbital in a subshell is the same (as indicated in the diagram below). But for other atoms, the degeneracy is lost. For example for heavier atoms the energy of  $4s$  drops below that of  $3d$ .



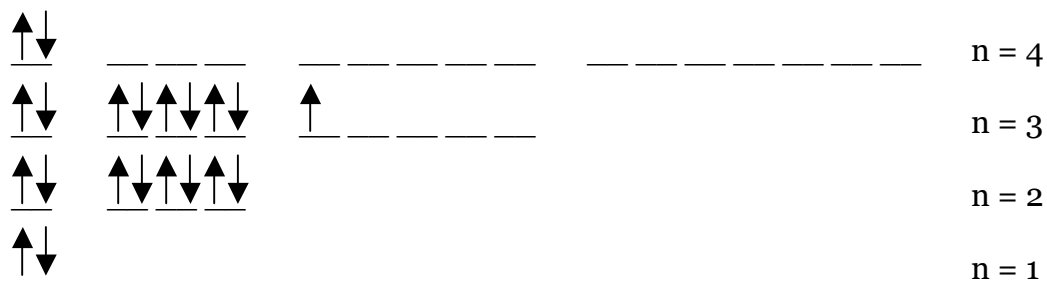
According to Aufbau's principle, electrons are added one at a time to each orbital. The electrons are added such that the lowest configuration possible will be observed according to Hund's rules.

*Carbon (Z = 6)*

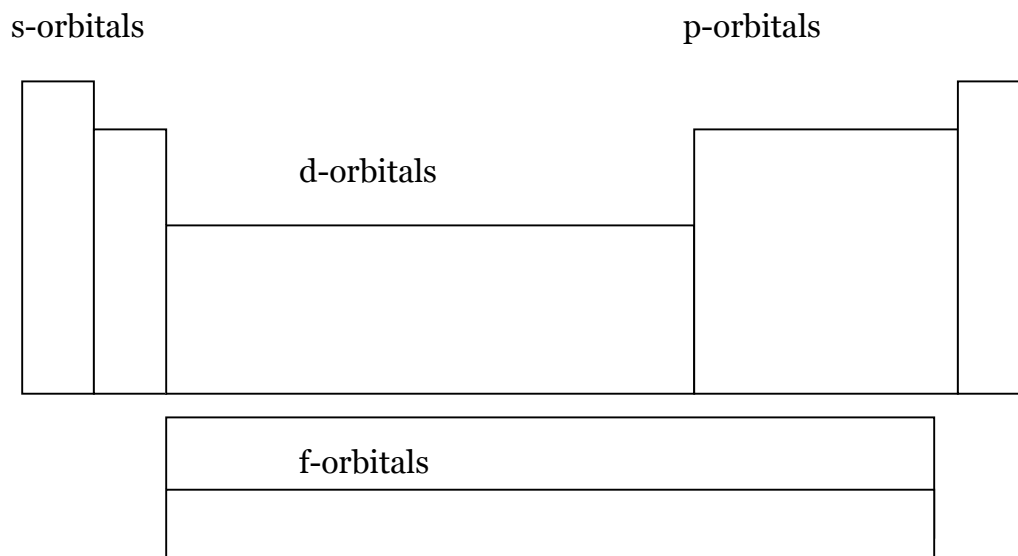


Note that according to Hund's rules, the lowest energy configuration is obtained when each p-orbital is half-filled (with total of three p electrons). The three unpaired electrons have parallel spins. Additional electrons are paired. The pairing of electrons requires energy.

*Scandium (Sc, Z=21)*

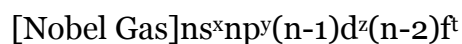


With scandium, note that the  $4s$  orbital is filled before the  $3d$  orbital.



The s-orbitals are filled by alkali and alkaline earth metals, the p-orbitals are filled by nonmetals and metalloids, the d-orbitals are filled by transition metals, and the f-orbitals are filled by lanthanides and actinides.

The electron configuration describes the distribution of electrons.



The row of the periodic table readily identifies the principal quantum number.

For example, Sc ( $Z=21$ ) is in the fourth row, and the maximum quantum number in the electron configuration is 4.

Sc:  $1s^22s^22p^63s^23p^64s^23d^1$  (Sc has 21 electrons; therefore, the superscripts should add to 21).

If we write the quantum numbers for the d-orbital in Sc we have:  
 $\Psi(3,2,0)$ .

Note the 0 could also be -2, -1, 1, or 2. The 0 represents the magnetic quantum number, and it has values from  $-l$  to  $+l$ .

Therefore, other acceptable answers for the quantum numbers would be:  
 $\Psi(3,2,-2)$ ;  $\Psi(3,2,-1)$ ;  $\Psi(3,2,1)$ ; and  $\Psi(3,2,2)$ .

## Ions

Ions are formed by atoms gaining or losing electrons. The most stable chemical species have electron configurations matching those of noble gases (i.e. filled shells). Therefore, whether an atom loses or gains electrons is dependent upon the number of electrons in the highest unfilled shell (the valence electrons). For example, lithium has one electron in its highest shell, therefore, it is most likely that lithium will lose one electron than gain seven electrons. Conversely, nitrogen has five electrons in the highest shell and needs three to obtain a noble gas configuration. Therefore, it is more likely that nitrogen will gain three electrons to become an anion (or negatively charged). In general, for the second row of the periodic table carbon serves as the barrier atom. Carbon will gain electrons to become an anion (carbide) or it will lose electrons to become a cation. Carbon does this because it has 4 valence electrons (gaining or losing 4 electrons yields the same net result).

### Ionization Energy:

This is the process in which electrons are removed from atoms.

This is an endothermic process meaning that energy must be added in order for the process to occur.



The alkali metals have the lowest first ionization energies indicating that they readily lose their one valence electron. An increase in ionization energy is observed thereafter for atoms across a row of the periodic table with two exceptions.

The first exception is observed with alkaline earth metals which have higher first ionization energies than members of the boron family. The alkaline earth metals have a filled s orbital which yields stability. Therefore, removing an electron from this s-orbital will disrupt the observed stability.

Elements with an electron configuration of [Noble Gas] $ns^2np^3$  have higher ionization energies than their adjacent neighbors. Given the p-orbital diagram for one of these elements we have:



This is a half-filled shell and demonstrates more stability than other cases. Because of the increased stability, we observe greater ionization energies for elements such as nitrogen or phosphorus in comparison to their neighbors.

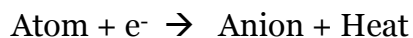
Oxygen has 4 p electrons; therefore, one orbital has a pair of electrons. In this instance, we have electron-electron repulsions because of the pairing. Oxygen has a lower first ionization energy because of this pairing.



### Electron Affinity

This is the counter process to ionization. During this process an electron is added to an atom yielding an anion. This is the most common process by which nonmetals gain noble gas electron configurations. In other words, nonmetals generally form ANIONS.

The chemical process is shown below:



This is an exothermic process because heat is generated as a result of the addition of the electron.

Because heat is produced, the sign convention is negative for electron affinity. The trend for electron affinity is generally, more energy is produced across a row with the exception of members of the alkaline earth and nitrogen families. Noble gases are not considered when discussing electron affinity because they REQUIRE heat or energy for an electron addition.

**Group Exercises and Problems**

1. Define each of the following quantum numbers and state what they tell us about orbitals:
  - a.  $n$
  - b.  $l$
  - c.  $m_l$
  
2. Identify the  $n$ ,  $l$ , and possible  $m_l$  values for each of the following:
  - a. A “d” electron in V
  - b. An “f” electron in Ce
  - c. A “p” electron in Cl
  - d. A “d” electron in Ni
  
3. How do a 2s and a 3s orbital differ?
  
4. Explain the significance of each of the following:
  - a. Pauli Exclusion Principle
  - b. Aufbau Principle
  - c. Hund’s Rule

5. Given the following energies for the associated levels, sketch a line spectrum for this atom:

$$E_4 = 6.41 \times 10^{-19} \text{ J}$$

$$E_3 = 5.61 \times 10^{-19} \text{ J}$$

$$E_2 = 5.10 \times 10^{-19} \text{ J}$$

$$E_1 = 2.00 \times 10^{-19} \text{ J}$$

6. An alpha particle (mass =  $6.6 \times 10^{-24}$  g) emitted by Radium travels at  $3.4 \times 10^7 \pm 0.7 \times 10^7$  mi/h. 1 km = 0.62 miles

- a. Calculate the DeBroglie wavelength.
- b. Calculate the uncertainty in the position.

7. Give all possible  $m_l$  values for orbitals that have each of the following:

- a.  $l = 2$
- b.  $n = 1$
- c.  $n = 4, l = 3$
- d.  $l = 3$
- e.  $n = 6, l = 1$

8. Explain how the Bohr model was proven to be an inaccurate representation for the atom.

9. Explain why the atomic radius of oxygen is larger than the atomic radius of neon.
10. Explain why phosphorus has a greater ionization energy than sulfur.
11. Write an electron configuration for V and  $V^{3+}$ .

**Individual Problems and Exercises**

1. An electron has an uncertainty of  $2.3 \times 10^{-7}$  m in its position. What is the uncertainty of its speed?
2. How fast must a 142 – g baseball travel in order to have a De Broglie wavelength that is equal to that of an x-ray photon with a wavelength of 100 pm?

3. Calculate the energies associated with each of the following wavelengths observed in a line spectrum:

Wavelength 1 = 504 nm

Wavelength 2 = 599 nm

Wavelength 3 = 688 nm

4. How many orbitals and electrons in an atom can have each of the following designations?

a. 1s

b. 4d

c. 3p

d.  $n = 3$

e. 5f

f. 4p

g. 5d

h.  $n = 2$

5. Are the following quantum number combinations allowed? If not, show two ways to correct them:

a.  $n = 2, l = 0, m_l = -1$

b.  $n = 4, l = 3, m_l = -1$

c.  $n = 3, l = 1, m_l = 0$

d.  $n = 5, l = 2, m_l = +3$

6. For each of the following give  $n$  and  $l$  values for the orbitals:

a. 5s

b. 3p

c. 4f

d. 4s

e. 3d