## Chapter 6 – Electronic Structure and Periodic Properties of the Elements

Chapters 4 and 5 discussed types of reactions and the energy changes associated with them, respectively. We now begin a look at atoms and molecules at a fundamental level. Earlier we saw that energy is consumed or released when a chemical reaction occurs. Why? Because during reactions some bonds break and others form and all will have different strengths. For example, stronger bonds replace weak bonds and energy is released in most chemical reactions. Chemical bonds involve the interaction of electrons between atoms. For this reason, we must understand the interaction of electrons with nuclei and with each other. That is what this chapter is all about.

6.1   Electromagnetic Energy

When a fire burns, you can feel the heat from the flames without touching them. The reaction between wood and oxygen releases this energy. Electromagnetic radiation carries energy through space and is sometimes called radiant energy. There are a number of different kinds of such energy including: visible light, X-rays, and radio waves, as well as the infrared radiation coming from the fire. They all share the property of traveling in waves at **3.00 x 10⁸ m/s** in a vacuum (*memorize this value*).
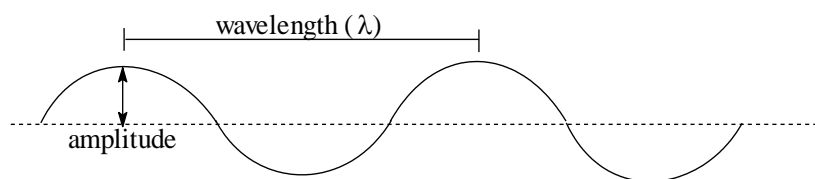
Wavelength, λ, is the distance between successive peaks. Amplitude is the distance from the center point to the top of the wave crest. The distance covered by one wavelength is sometimes called a wave cycle or more simply, a cycle. The (wave)cycle is frequently used as a counting term. For example, 5 wave cycles passed this point in one second.

It is important to remember that when waves move through a medium they don't carry the medium with them. This is a demonstration you can do at home. First, fill a bathtub a few inches

deep with water. (The deeper the better.) Place a cork (or small floating ball) at one end, but at least 6 inches from the nearest wall. Position yourself so you are looking straight down at the cork from above. Have someone else drop an object (e.g. a tennis ball) at the other end at roughly the same position. (It is important that there be 2-3 feet between the cork and the dropped object.) As the waves travel past the cork, you will see it bob up and down, but it should not move much towards or away from the dropped object. (It may move a little because the cork and dropped object will be near each other.) This demonstration works better in a lake with greater distances between the balls.

Frequency, ν, is the number of wave cycles that pass a given point in one second. Thus, the velocity of the wave is $\lambda\nu$. Since we know that all radiant energy travels at the speed of light, this becomes $c = \lambda\nu$. Does this make sense? For high frequency light, many wave cycles pass a given point in one second. If this is the case, the wavelengths must be short to get them through in the allotted time since the speed is fixed.

Most light (e.g. from an incandescent light bulb or the sun) contains many wavelengths and can be separated into individual components. (Radiation consisting of a single wavelength is called monochromic.) A rainbow results from water droplets breaking sunlight up into its constituent wavelengths. A prism does the same thing. This collection of wavelengths is called a spectrum. Figure 6.3 (p. 284) shows the entire electromagnetic spectrum. You can see wavelengths ranging from picometers (γ-rays) to meters (radio waves). Electromagnetic radiation with wavelengths shorter than visible light (higher frequencies) is generally thought of as high energy light. You don't have to know the exact wavelengths of each type of light, but you should know the energetic ordering.

The interaction of waves with one another is discussed on pp. 286 and this has important implications for understanding how atoms really work. Wikipedia has a nice description of why

light refracts under [Refraction](). The 'do at home' experiment on diffraction takes a little practice but is interesting. The discussion on interference concerns us most, but we'll delay that discussion until we're ready to use it.

Blackbody Radiation

Your personal, everyday experiences tell you that energy changes come in a continuous (i.e. gradual) manner. When you turn the stove on, it slowly gets hot. A ball rolling down a smooth hill gives up its energy continuously.

By the late 1800s, problems had arisen in the description of certain physical phenomena using a continuous model. For example, hot metal stove burners initially emit an orange glow. As the coil gets hotter, the light next becomes yellow, then white. Competing theories at that time only partially accounted for this observation.

In 1900, Max Planck proposed that atoms and molecules could absorb or emit energy only in discreet quantities or packets. He called each packet a quantum and calculated the energy of a single light wave to be where h = 6.626 x 10^{-34} J•s, ν is the frequency of emitted or absorbed light.

$$E = h\nu$$

We will shortly discuss why quanta arise. The reason we "see" a continuum is that on the macroscopic scale the quantities of energy are so large that we don't see the very small steps between quanta. It would be like looking at a staircase from a hundred yards away.

The Photoelectric Effect

It has long been known that shining very high energy light on a metal surface causes the surface to eject electrons. Low frequency light causes the ejection of no electrons, but as frequency increases, the metal suddenly begins to release electrons. As the frequency increases further, the energy of the ejected electrons increases, but not their numbers. As the intensity (brightness) of the light increases, the number of electrons ejected increases, but not their energy. Below the

threshold frequency, light intensity has no effect. Classical physics predicted that no threshold frequency would exist and that both the numbers and energies of ejected electrons would increase with both increasing frequency and intensity.

In 1905, Albert Einstein explained the photoelectric effect by suggesting that light travels as energy packets called photons. In other words, when a photon hits an electron, the photon can knock the electron off the atom if the photon has sufficient energy. Each photon interacts with just one electron. Since brighter light has more photons than dim light, it can knock more electrons off atoms. Higher energy light will knock off electrons more forcefully.

To explain the photoelectric effect, consider the surface of a metal sheet. There are innumerable atoms on the surface. Shine a low intensity, low frequency light on it. Nothing happens because the light doesn't have enough energy to force electrons off the atoms. (A minimum energy is required to overcome the attraction by the electron for the nucleus.) As frequency increases, we reach the minimum energy needed to knock electrons off, and that is observed. As the energy of the photons increases, the ejected electrons fly off with the difference in energy. As intensity increases there are more photons, so more electrons are ejected. A reasonable analogy is to think of a pool table with a ball lightly glued to the surface. A softly tapped cue ball would bounce off the target ball with no effect. At some point, as you hit the cue ball harder it would dislodge the target ball. Hitting the cue ball harder would cause the target ball to move with greater speed but some of the energy of the cue ball would be used to dislodge the target ball.

Line Spectra

Broadly speaking, there are two types of spectra, absorption and emission. Absorption spectra are the kind we typically think of. Here a light shines on a sample and either passes through it or reflects off it. The light is the collected and compared to the source light. The difference is the absorption spectrum and shows the wavelengths of light absorbed by the sample. The other type

of spectrum is the emission spectrum in which the sample first absorbs energy. The sample then emits some of the energy in the form of light, which yields a spectrum. Thus, the absorption spectrum measures what wavelengths of light are removed from a sample, while the emission spectrum measures the wavelengths of light that are produced.

Continuous spectra contain all wavelengths of light between two values. The sun and incandescent light bulbs produce continuous spectra. When samples of elements or pure compounds emit light, discreet wavelengths are observed yielding a line spectrum. (For example, this happens when an electrical discharge is passed through a gaseous sample of an element. Fluorescent and neon lights work this way.) The line spectrum of each element is unique and can be used for identification purposes. Think of it as an elemental fingerprint. Since the intensity of the light emission depends on the amount of material emitting, line spectra also provide information about the quantity of the element present. This is how astronomers determine the composition of stars.

By 1885, the line spectrum of hydrogen had been known for quite some time. In that year J.J. Balmer related some of the lines to each other by the equation:

$$\nu = C\left(\frac{1}{4} - \frac{1}{n^2}\right)$$

Over the next several years, this equation was generalized to include all of the lines using the following formula (Rydberg equation):

$$E = R_H\left(\frac{1}{n_1^{\,2}} - \frac{1}{n_2^{\,2}}\right)$$

where n_1 and n_2 are whole numbers and $n_2 > n_1$. R_H is the Rydberg constant = 2.18×10^{-18} J. A problem with this equation was that, while it worked, there was no explanation of why it did.

6.2   The Bohr Model

Rutherford's discovery of the nucleus (pp. 3-4, Chapter 2 notes) led scientists to view the atom as a mini-solar system. Yet in this model, classical physics predicted the electron should spiral into the nucleus and emit energy in the process, but clearly this doesn't happen. In 1913, Danish physicist Niels Bohr proposed a model of the atom to account for this apparent inconsistency. It retained the solar system model, but placed the following restrictions on it.

1) The hydrogen atom could have only a limited number of energy levels (states); each of which corresponded to a circular orbit. The lowest energy state (the orbit closest to the nucleus) is called the <u>ground state</u>. All others are called <u>excited states</u>. Intermediate energy states (orbits) are <u>not</u> possible. This is called <u>quantization</u>, following Planck's model, and the energy levels (see equations below) are described by <u>quantum numbers</u>.

2) Electrons move between energy states emitting or absorbing energy (as photons) in fixed quantities, depending on whether the electron was getting closer to or farther from the nucleus.

From the Rydberg equation, the energy for any state is given by:

$$E_n = -R_H\left(\frac{1}{n^2}\right)$$

When $n = \infty$, the electron is free from the nucleus ($E_\infty = 0$). (It is ionized.) Since the electron and nucleus possess opposite charges and the particles become more stable as they move closer to each other, in any orbit closer to the nucleus the electron is more stable ($E < 0$).

The energy gap between any two orbits (or states) is given by:

$$E = R_H\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) = h\nu.$$

where n_i is the initial state of the electron and n_f the final state. While this is similar to the Rydberg equation, it differs slightly. Look carefully.

This model has two problems, however. First, it worked only for hydrogen atoms. All

attempts to generate similar equations for other elements were unsuccessful. Second, no theoretical justification for the equation or its application to the hydrogen atom exists.

6.3   <u>Development of Quantum Theory</u>

So if the Bohr atom is wrong; what is correct? Before we get to the modern model of the atom, we should examine one intermediate model that helped physicists determine the correct model. A question that immediately follows from the previous section is "Why only certain orbits?" In answering this question, Louis de Broglie reasoned that if waves could have particle-like properties, then particles might have wave-like properties. de Broglie thus proposed that the electron was essentially a traveling wave in a circular orbit around the nucleus (the wave plane is perpendicular to the orbit plane, see Fig. 6.17, p. 302). (You can see this by drawing a sine wave on the outside of a metal can.) If true, two possible scenarios exist.

i) An *in-phase* wave. Here the wave exactly superimposes on itself as it repeatedly goes around the nucleus. This can occur only if the circumference is a whole number multiple of the wavelength (nλ).

ii) An *out-of-phase* wave. When the wave completes one trip around the atom, it does not line up perfectly. In this case, the wave eventually self-destructs. To illustrate this, consider a wave that on the second trip around the nucleus has its maxima line up with the minima the first time around (180º out-of-phase, see below).
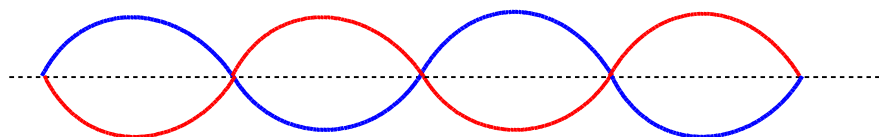
Adding the blue curve to the red curve causes them to cancel out, leaving the dotted line. This is called destructive interference and leads to the elimination of the wave. It's a little difficult to see this, but destructive interference would occur in any situation where the wave repeated passes

over itself and the waves were not exactly in-phase with each other. (To test this, try putting the waves 90° out-of-phase. It takes four cycles for the wave to self-destruct.)

Mathematically, the in-phase relationship is $n\lambda = 2\pi r$ ($2\pi r$ is the circumference of a circle). Since n is a whole number, r may have only certain values and, hence, is quantized. We also know for a wave $E = h\nu$ and for a particle $E = mv^2$. Setting them equal yields: $h\nu = mv^2$. For any particle: $v = \lambda\nu$ (very similar to the speed of light equation). Substituting this equation into the one before it and rearranging yields:

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

Thus, knowing the mass and velocity of a particle allows the calculation of its wavelength (even if it is not traveling in a circular path). This equation assumes that every moving particle has a wavelength. So why don't we see moving things bob up and down as they move? First, we know nothing of the wave amplitude, but beyond that, begin by looking at the equation. Planck's constant is very small (*ca.* 10^{-34}) so the denominator must even smaller to make the wavelength visible in the macroscopic world. Since the objects we can see have very large masses, they have wavelengths many orders of magnitude smaller than an atomic diameter.

The Heisenberg Uncertainty Principle

One major difference between classical and quantum physics concerns the knowledge of position and momentum. Classical physics (i.e. Newton's laws of motion) calculates both exactly. The Heisenberg uncertainty principle tells us this is impossible. It states that the more accurately we know either the position or momentum of a moving object, the less accurately we know the other. (The associated math gives an upper limit to the accuracy.) Why is this? The first thing to realize is that this principle ignores experimental error. The uncertainty principle states that even with no experimental error, determination of absolutely accurate values of both position and momentum would still be impossible.

To explain the uncertainty principle, we simplify by using velocity in place of momentum. Let's say I throw a baseball across the room and ask you how fast it is traveling. The moment it leaves my fingers you would start a timer and stop it when the ball hits the wall on the other side of the room. Knowing the distance from my fingers to the wall you could calculate the velocity of the ball exactly. A necessary question that would not ordinarily occur to you is: How do you know when the ball leaves my hand? You see it, right? If the lights were off, you wouldn't know when the ball left my hand so you wouldn't know when to start the timer. Light reflects off the ball and strikes your eyes, but its effect on the ball is so small that in the real world it can't be measured. Now consider the same process with an electron ejected from a source. Using the same process, could you determine its velocity exactly? Here the question of the interaction of light is not trivial. If electromagnetic radiation can have particle-like properties, and electrons can have wave-like properties, they are energetically similar. The result is that any photon you use to gather information about an electron, will perturb the electron in a substantive way. Thus, the information you gather will have an inherent inaccuracy.

Think of this analogy. Imagine a billiard table with one ball (**A**) moving randomly about the table. You are blindfolded and have a second, identical ball (**B**) that you can slide across the table. Further, whenever you release ball **B**, it will head straight for ball **A**, collide with it, and bring back to you ball **A**'s position and momentum. There exist two limiting choices for how you throw the ball: very fast or very slow. If you throw it fast, it will reach ball **A** quickly and return quickly giving the position of ball **A** accurately (ball **A** won't have had much time to move). However, it will strike ball **A** hard, which will change ball **A**'s momentum, so that value will be relatively inaccurate. In the other extreme, if you release ball **B** slowly when it strikes ball **A**, its momentum won't change much so that information will be quite accurate, but it will take so long to return, the position value of ball **A** will be very inaccurate.

This is why, even for the baseball, we cannot know its position and momentum exactly.

There will be the tiniest of errors induced by measurement.

The Quantum-Mechanical Model of an Atom

De Broglie brought us a step closer to what the atom really looks like, but the best model of the atom to date throws out the concept of circular orbits for the electron altogether. Erwin Schrödinger developed an equation that treats the electron entirely as a wave and only at the very end takes into account its mass. When this is done, something very remarkable happens.

1) The electron no longer travels in circular paths or is constrained to a certain distance from the nucleus. Rather the electron now occupies certain, general 3-D regions of space (volumes) with characteristic shapes called orbitals.

2) The mathematical function that describes the movement of the electron is called a wave function, ψ, and the motion of the electron is physically best described as a standing wave. Each electron has a different wave function. Standing waves stay within a fixed region of space and basically fold back in on themselves. They differ from the more familiar traveling waves, which begin at a fixed point and move outwards indefinitely (e.g. a lightbulb).

3) Solving the wave function yields only certain energies, so the atom is quantized. (i.e. It is a result of the theory, not a precondition. Bohr assumed quantization, Schrödinger derived it.)

4) Since the electron is a wave, it no longer has a defined physical location. (Even thought of as a particle, the uncertainty principle says we can't define its location precisely.) To see how this works, imagine a box containing only a single hydrogen atom in its ground state. Now imagine a plane passing through the center of the atom. You probably (correctly) guessed that the electron spends half of the time on each side of the plane. Thus, if you had to guess which side of the plane the electron was on at any given moment, you'd have a 50/50 chance of being correct. If a second plane, perpendicular to the first, were also there, you'd have a 1-in-4 chance of guessing where the electron was. Here, the electron spends 25% of the time in each of the 4

quadrants. Now erase the planes and put the nucleus in the center of a medium sized ball. Does the electron spend more time in the ball or outside? This question is more difficult because it depends on the size of the ball. The negative charge on the electron causes it to spend more time near the nucleus than far from it, so we don't expect the chance of finding the electron to be equal everywhere as you move away from the nucleus. If we erase the ball, and put the nucleus at the center of a giant 3-D grid with very tiny boxes, we can come up with how quantum mechanics describes the location of the electron. Think of the electron as a particle whizzing around the atom and every time it passes through a grid box, the electron trips a counter. If we wait a long time and shade each box according to the number of counts (say dark = many counts, light = few counts) we get something similar to a charcoal sketch of the atom. The darker the volume, the more time the electron spends there. There is such a picture at the website "The Orbitron" that shows this view. This is done mathematically by squaring ψ, the wave function that describes the electron, with the result being called <u>electron density</u>, which provides the probability of finding the election at any given location. Thus, scientists refer to the electron density in a region of space rather than the location of an electron. (This description treats the electron as a particle. To treat it as a standing wave (which is more correct, but also more difficult to visualize) the density corresponds to the wave amplitude in each of the boxes. That is, the darker areas have larger amplitudes.)

<u>Quantum Numbers of an Atomic Orbital</u>

A result of this theory is that we now have three quantum numbers (q.n.), with each representing a different aspect of the orbital's identity.

n - <u>principal q.n.</u> - has values of 1, 2, 3, ..., The energy of the electron depends only on n for hydrogen atoms. Larger n values result in larger orbitals with the electron spending time further from the nucleus on average. It corresponds to the Bohr q.n.

ℓ - <u>angular momentum q.n.</u> - whole number values from 0 to (n-1). This quantum number defines

   the shape of the orbital. (Figure 6.21, p. 308)

   $0 = s$ = spherical, $1 = p$ = 2 lobes, $2 = d$ = 4 lobes, $3 = f$ = 8 lobes (N.B. # lobes = 2^{ℓ})

m_{ℓ} - <u>magnetic q.n.</u> - integral values of ℓ to -ℓ. Describes the orientation in space of the orbital. (for

   $\ell = 1$ and higher, it describes where the lobes point)

   A collection of all of the orbitals with the same principal quantum number is called a <u>shell</u>. A

collection of orbitals with the same n and ℓ quantum numbers is called a <u>subshell</u>. A shell has n

subshells, but some may be empty. A subshell contains $2\ell + 1$ orbitals. Thus, there are 1 s orbital,

3 p orbitals, 5 d orbitals, or 7 f orbitals in any subshell where they are allowed. The book uses the

word "level" in place of "shell," which is technically better, but the word "shell" will likely be more

familiar to you

<u>Shapes of Atomic Orbitals</u>

   The *Orbitron* provides high quality, animated images of orbitals and is linked on the class

webpage as well as here.

s orbitals –   Electrons with an $\ell = 0$ occupy these orbitals. They possess a spherical shape (see Fig.

   6.20), meaning that at any distance, x, from the nucleus, the probability of finding

   the electron (or the electron density) is the same, no matter what direction you travel.

   This is the most stable (lowest energy) type of orbital at any given n value. The

   graphs for each orbital in 6.20 are important. Going back to the grid discussion in

   these notes on pp. 10-11, we need to do a thought experiment. We know that opposite

   charges attract and The Orbitron picture suggests something reasonable, which is

   that the closer one approaches the nucleus, the more likely we are to find the electron.

   Unfortunately, that leads to a logical conflict, which is that the most likely location

   for the electron is on the surface of the nucleus. This inconsistency between a

reasonable assumption and an illogical outcome is solved by realizing that as we approach the nucleus, each successive slice of the atom decreases in volume as a cubic function. Imagine a marble, then put a 1 mm thick layer on it. Now consider a volleyball and put a 1 mm layer on it. Think about how much larger the volume of the layer is on the volleyball than the marble and you have the path to solving the problem. Basically, the attraction between the nucleus and electron increases linearly as they approach, but the volume occupied by the electrons drops off as a cube root. The result is that starting from a long way away from the nucleus the attraction is so small that the volume makes no difference and there is scant attraction. As the electron approaches the nucleus the product of volume and charge attraction increases, but at some point, the volume drops precipitously, and the corresponding product drops too.

p orbitals – The orbitals occur when $\ell = 1$ and have 2 lobes oriented in a dumbbell shape. A nodal plane exists between the two lobes passing through the nucleus. They begin at the *n* = 2 energy level.

d orbitals – The orbitals occur when $\ell = 2$ and have 4 lobes oriented in a cloverleaf shape (except the d_{z^2}, which we'll discuss in class). There are 2 nodal planes between the lobes that pass through the nucleus. They begin at the *n* = 3 energy level.

A <u>node</u> is a place where the electron cannot exist (if you think of it as a particle). That is, the probability of finding the electron there is zero. If you think of the electron as a wave, the node is the place where the wave passes from a positive to a negative amplitude.
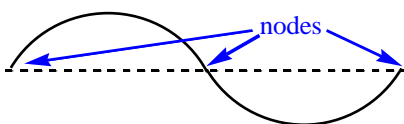
There are 3 *p* orbitals (Fig. 6.21) and each is located along one of the coordinate axes (*x*, *y*, *z*).

There is no correlation between the axis designation and the magnetic q.n. (-1, 0, 1). If called for, any axis may be assigned to any magnetic q.n., however, once a pairing is designated it must be maintained throughout the discussion or problem. For example, if $2p_z$ has $\ell = 0$, then $3p_z$ is also $\ell = 0$.

d/f orbitals – Although their shapes suggest otherwise (Fig. 6.21), the 5 *d* orbitals are <u>all</u> energetically equivalent. Each has 2 nodal surfaces. There are 7 *f* orbitals (all energetically equivalent). Beyond this we will not discuss *f* orbitals in this course.

You should be able to sketch any of the *s*, *p*, or *d* orbitals.

Until now, all of what we have covered has concerned only the hydrogen atom. This is both for historical reasons and for simplicity's sake. Hydrogen atoms consist of only two particles: a proton and an electron. For the physicists trying to describe mathematically the atom, this was ideal because you could exactly describe the physical motions going on in the atom because if you held the nucleus fixed in space, all you had to do is track the electron. For a physicist, one body moving and one variable gives a simple calculation. When one progresses to the helium atom, now you have two bodies moving (2 e⁻) and what one atom ago was easy, now, quite literally, is impossible to solve exactly. Fortunately, the math doesn't concern us and, more fortunately still, the results of the math are nearly identical for many electron atoms as they are for hydrogen atoms.

Adding another electron requires us to introduce a fourth quantum number, spin, m_s. Electrons behave as if they were particles rotating about an axis. Spinning charged bodies set up a magnetic field around themselves and electrons have such a magnetic field. The result is a new quantum number, the magnetic q.n.: $m_s = \pm\frac{1}{2}$. (read "spin up" ($+\frac{1}{2}$) or "spin down" ($-\frac{1}{2}$)). Orbitals hold up to 2 electrons. In orbitals with 2 electrons, the electrons will always have opposite spins and are said to be paired. This leads to the Pauli exclusion principle: No two

electrons in any atom may have the same four quantum numbers.

Finally a note of trivia, why are there 4 q.n.? The Schrödinger equation was mentioned earlier, but not provided because it is a complex equation to solve and well beyond what you need for an introduction to chemistry. That said, it's an equation that examines the relationship of the electron to the atom and so basically maps out the 3-dimensional movement of the electron. Thus, there are 3 variables (i.e. x, y, z or r, θ, ϕ) to be solved for. Three inputs require three outputs and hence you get 3 q.n.s. Now the electron moves and the position of any electron is affected by the electrons around it so at a later time, the electronic field changes. That means that time is now a variable and that requires a 4th q.n. This is where the idea that time is the 4th dimension comes from.

6.4   Election Structure of Atoms

At this point, we have the physical locations in which the electrons will reside. The next question is how do we populate those locations? The goal is to place the electrons in the lowest energy arrangement we can.

The arrangement of electrons in an atom or ion is called its electron configuration and is very important in predicting how atoms will bond to each other and otherwise behave chemically. There are two important, initial rules to consider:

1) Fill the lowest energy orbitals first (Aufbau principle).

2) The Pauli exclusion principle

Working examples provides the simplest way to show this, beginning with hydrogen: hydrogen has only one electron and it goes into the lowest energy orbital, $1s$.

$$\underline{\uparrow} \quad \text{or} \quad 1s^1$$
$$1s$$
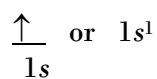
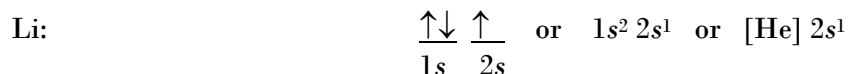The electron is said to be 'unpaired' because there is only one in the orbital.

In helium, a second electron is added. There are two possibilities here: i) to pair the electrons in the $1s$ orbital or ii) to promote the new electron to the $2s$ orbital, which is higher in energy because it has a higher q.n. The question is: which costs less energy?

<u>It always costs less energy to pair electrons than to move an electron to a higher energy</u> (n) level so the electron configuration of He is:
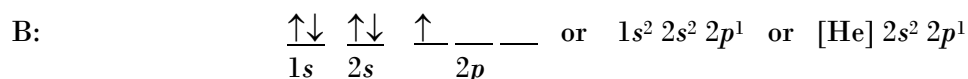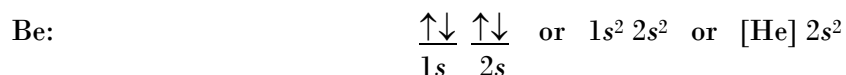
$$\uparrow\downarrow \quad \text{or} \quad 1s^2$$
$$\overline{}$$
$$1s$$
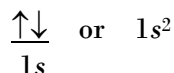
In the hydrogen atom, all orbitals with the same n value have equal energies. <u>Degenerate</u> orbitals possess equal energies. All other atoms have more than one electron and for these atoms only the orbitals within a subshell are degenerate. There are two reasons for this. The first is the basic shape of the orbitals. If you look at the pictures of the s, p, and d in your book, you will see that adding nodal planes forces electron density away from the nucleus. For example, on average, an electron in a $2s$ orbital lies closer to the nucleus than a $2p$ electron. Thus, the $2s$ electron experiences greater nuclear attraction and is more stable (lower energy) than the $2p$ electron. The other reason for the difference in energies is discussed in Section 8.1. For any multielectron atom (or ion), within any shell the energy ordering of orbitals goes as $s < p < d < f$.
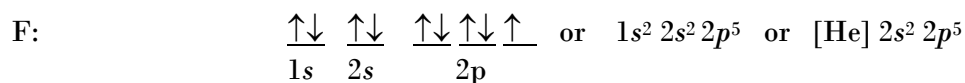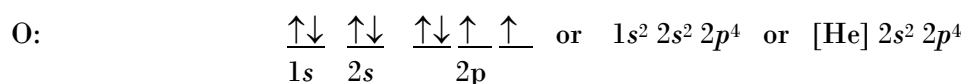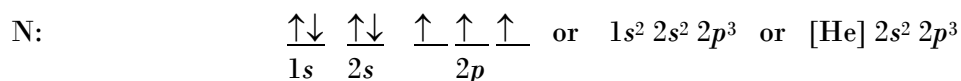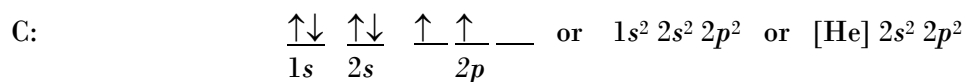
Likewise in lithium, the next electron goes in the most stable orbital at the next principal quantum number, 2, because the n $=$ 1 subshell is filled.

Li: $\qquad\qquad\qquad\qquad \uparrow\downarrow \ \ \uparrow \quad$ or $\quad 1s^2\, 2s^1 \ $ or $\ $ [He] $2s^1$
$$\qquad\qquad\qquad\qquad\quad \overline{1s} \ \ \overline{2s}$$

As in shells, it always costs less energy to pair electrons than to promote one to a higher energy subshell, so

Be: $\qquad\qquad\qquad\qquad \uparrow\downarrow \ \ \uparrow\downarrow \quad$ or $\quad 1s^2\, 2s^2 \ $ or $\ $ [He] $2s^2$
$$\qquad\qquad\qquad\qquad\quad \overline{1s} \ \ \overline{2s}$$

B: $\qquad\qquad\qquad\qquad \uparrow\downarrow \ \ \uparrow\downarrow \ \ \uparrow \ \_\_ \ \_\_ \quad$ or $\quad 1s^2\, 2s^2\, 2p^1 \ $ or $\ $ [He] $2s^2\, 2p^1$
$$\qquad\qquad\qquad\qquad\quad \overline{1s} \ \ \overline{2s} \quad \overline{2p}$$

The next electron entering the atom will go into a $2p$ orbital, the question is: Does it go into a vacant orbital or spin pair with the other electron? Two electrons in the same orbital spend much of the time relatively close to one another. Since electrons repel one another, their energy increases. Electrons placed in other orbitals have no such energy increase, so electrons pair only after each orbital in the subshell contains one electron. A second question is will the spins align or oppose? Remember that a spinning charge has an associated magnetic field. The magnetic fields of electrons spinning in the same direction reinforce one another, while those spinning in opposite directions offset one another. Thus, unpaired electrons will align their spins to maximize the resulting magnetic field (Hund's Rule).

C: $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow$ $\uparrow$ ___ or $1s^2\,2s^2\,2p^2$ or [He] $2s^2\,2p^2$
    1s   2s   2p

N: $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow$ $\uparrow$ $\uparrow$ or $1s^2\,2s^2\,2p^3$ or [He] $2s^2\,2p^3$
    1s   2s   2p

O: $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow$ $\uparrow$ or $1s^2\,2s^2\,2p^4$ or [He] $2s^2\,2p^4$
    1s   2s   2p

F: $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow$ or $1s^2\,2s^2\,2p^5$ or [He] $2s^2\,2p^5$
    1s   2s   2p

Electrons in the outer (valance) shell are referred to as <u>valence</u> electrons. Once a shell is completed, the electrons are referred to as <u>core electrons</u> (except the outermost electrons in the noble gases and anions, which are still valence electrons). Valence electrons are the chemically active electrons, while core electrons are chemically inert.

$$[\text{Ne}]\,3s^1$$
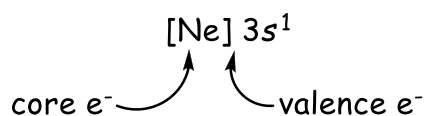
core e⁻ ⟋ ⟍ valence e⁻

It is important to remember that it is not acceptable to write [Ne] for F⁻ because the valence electrons are still chemically active. There are some discontinuities from what you'd expect in the filling of orbitals. The most important set occurs on the fourth row. The rules predict that the $3d$

electrons should follow the $3p$. Instead, the $4s$ electrons follow $3p$. The rationale behind this is beyond the scope of this course. Skip the discussion of "elements with completely filled orbitals" on p. 321. Likewise, skip any discussion of the "inner transition elements" (the lanthanides and actinides).

The periodic table shown on p. 255 displays a common way chemists think about the elements. As you can see, the periodic table can be broken up into 4 sections: (1) on the left side: a pair of columns (representative or main group elements), (2) on the right: a set of 6 columns (more representative or main-group elements), (3) in the center: a group of 10 columns (transition metals) and (4) at the bottom: two rows of 14 elements each (lanthanides & actinides, respectively). This corresponds to 2 electrons in each of the s, p, d, and f orbitals, respectively. Each grouping is called a "block" hence the green elements are sometimes called the "s-block" elements.

Electron Configurations of Ions

The electron configurations of ions are very similar to the atoms from which they are derived. For example, the electron configuration for the sodium atom is [Ne] $3s^1$. For the sodium ion (Na^+), one electron is removed, yielding a configuration of [Ne]. Likewise, chlorine is [Ne] $3s^2 3p^5$ and chloride is [Ne] $3s^2 3p^6$. Thus, electrons are simply added to or subtracted from the valence shell as necessary, following the same rules for filling as the atoms from which they are derived.

Transition metals can all form ions of more than one charge (except Zn and Cd: +2 only). The +2 and +3 oxidation states occur most commonly. The +2 oxidation state is common because of the way transition metals form ions. The $4s$ orbitals are filled before the $3d$ orbitals, so you'd guess that the $3d$ orbitals would empty first. That turns out not to be true. The $4s$ orbital always empties first, leading to a common +2 charge on transition metals. For charges greater than +2, electrons next come from the d subshell until the appropriate charge is attained. For example Fe(II) has an electron configuration of [Ar] $3d^6$ and Fe(III) has an electron configuration of [Ar] $3d^5$.

6.5   Periodic Variations in Element Properties

Variation in Covalent Radius

In large part, the energy of an electron depends on the charge of the nucleus to which it is attracted. The higher the charge on a nucleus, the stronger the attraction and the lower the energy of the electron bound to it. (i.e. the more stable the electron is)

$$E = -R_H\left(\frac{Z^2}{n^2}\right)$$

However, all electrons on an atom do not experience the same nuclear charge. Electrons that are closer to the nucleus diminish the interaction between the nucleus and electrons further away. Imagine a hypothetical two electron atom where electron **A** is always closer to the nucleus than electron **B**. Whenever electron **A** passes between the nucleus and electron **B**, electron **B** experiences the pull of only one net proton. When electron **A** is on the opposite side of the nucleus, electron **B** feels the pull of both protons. Since electron **A** is always inside of electron **B** the former always feels the pull of two protons. However, electron **B** experiences an average charge between +1 and +2. In real atoms, electrons with small principal quantum numbers spend most of the time close to the nucleus, while those with large *n* values spend most of the time further from the nucleus. Thus, different electrons within the same atom are acted on by different net nuclear charges. Effective nuclear charge, Z_{eff}, is the nuclear charge *actually* experienced by an electron. As a result, outer electrons have a higher energy than would be the case in the absence of such screening/shielding. Effective nuclear charges are always smaller than actual nuclear charges.

The shapes of orbitals also play a role in this shielding process. All other things being equal, electrons in *s* orbitals shield best and those in *f* orbitals most poorly. The addition of nodes accounts for the change in shielding. The nodal surfaces in higher orbitals force electrons away from the nucleus.

Three results from this follow for multi-electron atoms on effective nuclear charge:

1) For electrons at the same n value, the energies of the electrons increase $s < p < d < f$. The result is that it requires less energy to remove f electrons than d electrons, etc. with the same principal quantum number.

2) As Z values increase, electrons in the same orbital (e.g. the $1s$ orbitals for all of the alkali metals) tend to have larger effective nuclear charges.

3) Within an atom, as n increases for a particular type of orbital (e.g. s orbitals), effective nuclear charge decreases. (e.g. For lithium: $Z_{eff}(1s) > Z_{eff}(2s)$)

Chemistry revolves around the movement of electrons. As you know, ions result from the adding or removing of electrons to or from neutral species. Molecules are held together by the nuclei of atoms attracting the electrons on adjacent atoms. Thus, understanding the behavior of electrons on atoms is quite important.

We've just seen that orbitals with relatively low principal quantum numbers shield electrons with high n values. The result is that as the atomic number increases, core electrons are pulled closer to the nucleus, while valence electrons move away from the nucleus because of the higher n value. This will be important in explaining many physical properties.

Atoms don't have sharp boundaries like baseballs, so their size is somewhat arbitrary. When comparing atomic sizes, the method of describing the size of an atom doesn't matter, so long as the same method is used for all atoms. Most commonly, we use one-half the distance between two atoms of the same element bound together in the pure element (e.g. Cl_2). This gives the atomic radius. The radius of metals is determined by examining a crystal of the metal to yield its metallic radius. [A different way to measure atomic radii is to use one-half the distance between to atoms of the same element not bonded to one another. As you might imagine this yields different values, but the trends are identical.]

With this as our measure, we find two trends:

1) As expected, radius increases down a group. New higher energy shells go outside the existing shells, making atoms larger.

2) Radii **decrease** from left to right across a period. This is surprising at first and it happens because electrons with the same principal quantum number shield each other poorly. Thus, the charge experienced by each added electron increases (remember a proton is added with each electron) and the electrons are pulled closer to the nucleus.

Variation in Ionic Size

There are both similarities and differences between trends in atomic and ionic radii. Points 1 and 2 mirror atomic radii trends for the same reasons, the other 3 are unique to ions.

1) Radii increase down a group if ionic charge remains constant. (e.g. Na^+ is larger than Li^+.)

2) All other things equal (e.g. charge), radii decrease left to right across a period.

3) For a given cation, radii decrease as charge increases because the same number of protons will attract fewer electrons. There are also fewer electron-electron repulsions in the valence shell. (e.g. Iron(II) is larger than iron(III).)

4) Almost all anions are larger than almost all cations.

5) For a given anion, radii increase as charge becomes more negative because the same number of protons attracts more electrons and electron-electron repulsions increase. (e.g. O^{2-} is larger than O^-.)

6) Atoms with the same total number of electrons are called isoelectronic. Within an isoelectronic series of electrons, size decreases with increasing (more positive) charge.

   e.g. $O^{2-} > F^- > Ne > Na^+ > Mg^{2+}$ (all [He] $2s^2\ 2p^6$)
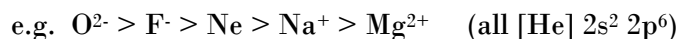
Variations in Ionization Energies

Ionization energy is the energy required to completely remove a mole of electrons from a mole of gas phase atoms or ions.

1st IE: $Ca(g) \rightarrow Ca^+(g)\ +\ e^-$

2nd IE: Ca+(g) $\rightarrow$ Ca2+(g) + e-
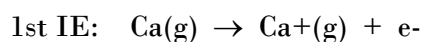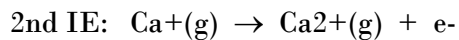
As expected, each successive electron is more difficult to remove (e.g. 2nd IE > 1st IE) than the previous one. This is because the first ionization removes an electron from a neutral atom. The second ionization results in an ion with the same number of protons as the neutral atom, but now they now pull on one fewer electron. Also, fewer electrons now repel one another. Finally, this will involve separating an electron from an already positively charged ion. In general:

1) Ionization energy decreases down each group. The radius of an atom increases more rapidly than does its charge. Thus, electrons are held less tightly and can be removed more easily.

2) Within each period, ionization energy generally increases left to right for the same reason that size decreases.

Ionization energies always increase sharply upon an atom reaching a noble gas configuration. See Figure 6.33 (p. 327). (It is difficult to remove electrons from a noble gas.) Hence, valence electrons always have much lower ionization energies than do core electrons. (See Table 6.3, p. 328-9 for examples.) Don't worry about irregularities or the differences between various blocks of elements.

<u>Variation in Electron Affinities</u>

The energy change that occurs when one mole of electrons is added to a mole of gas phase atoms or ions is called <u>electron affinity</u>.

1st EA: $Cl_{(g)}$ + e^- $\rightarrow$ $Cl^-_{(g)}$
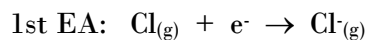
Electron affinities are negative when energy is released on addition of the electron. First electron affinities are almost always negative, with closed shell groups as the exceptions. Can you reason out why?

Imagine an atom in isolation. Now start moving an electron towards the atom so that it will pass near the atom, but not directly collide with it. As the electron approaches the atom, it will begin to experience electrostatic attraction to the nucleus, just as any valence electron already on the atom does. This stabilizes the electron relative to being separated from the nucleus and results in a release of energy when it adds to the atom.

All second electron affinities and higher are positive because an electron is being added to an anion. Here, there is electrostatic repulsion between two negatively charged entities and this results in the need for additional energy to force the electron onto the anion.

First electron affinities tend to become more negative moving left to right. As before, this occurs because the atom contracts and electrons in the valence orbital lie closer to the nucleus. Thus, electrostatic attraction increases.

Electron affinities don't change much down a group, although they do become a little smaller because in larger atoms the electrons are more spread out. An added electron would experience less electrostatic repulsion from other electrons, but increased electron-nuclear distance offsets this. The result is not much change in electron affinity.

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