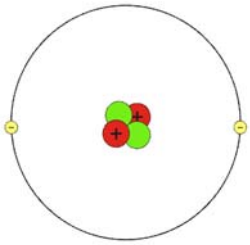
Chapter 2 Electrons and the Periodic Table.

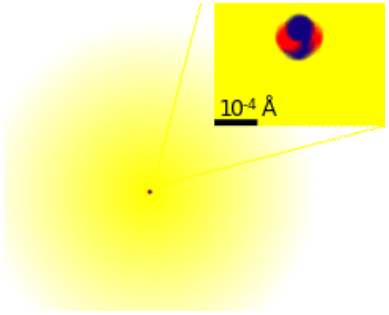
For those of you that watch the Big Bang Theory, you have heard Sheldon Cooper bring up the topic of the dual wave and particle properties of matter. To explain these properties, in the 20th century, Planck, Schrödinger, Dirac, Heisenberg, Einstein and others developed a rather abstract field called quantum mechanics. While Einstein never fully accepted the concepts, experimental results have verified that quantum mechanics has earned the title of being a theory. Quantum mechanics is beyond the scope of this course but the application of quantum mechanics to the electronic structure of atoms gives results that explain and are consistent with the shape of the periodic table.

There are two important and related conclusions from quantum mechanics that we need to consider. First, electrons can only exist in discrete energy states or quantum levels. If there are energy levels designated as 1, 2, 3, 4 ..., the electron cannot exist in level 1.5. As Sheldon indicated, matter has both particle and wave properties. However, the wave properties of large particles are insignificant compared to the particle properties. As the size of the particles decreases, the wave properties become increasingly important. For very small particles, wave properties must be considered when trying to characterize the particle. For the particles of light called photons, the wave and particle properties are comparably important. Wave properties also determine much of the behavior of electrons. Schrödinger was able to develop equations that correctly calculate the properties of electrons. Unfortunately, the calculations become almost prohibitively complex for atoms with more than two electrons although approximations do allow meaningful results to be obtained. The Schrödinger wave equations coupled with other results from quantum mechanics do result in properties of the electrons that enable development of a periodic table consistent with the table derived from experimental results.

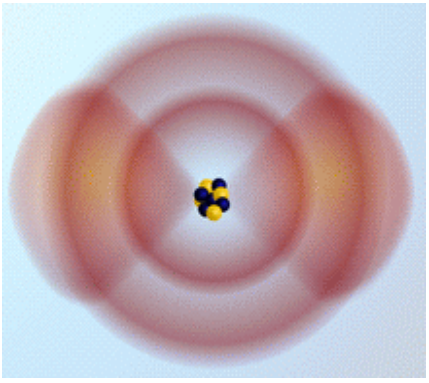
Because of the importance of the wave properties of the electrons, the Bohr orbits are not a good model for multi-electron atoms. Instead, the best we can do is calculate the shape of a region of space that will have the properties of the electron including charge, mass and energy level. For the single electron of hydrogen, the shape of the orbital is a sphere. The size of the sphere can only be calculated for a given probability of finding the electron. As expected the higher the probability, the larger the radius.

Probability	radius (cm)
90%	2.7×10^{-8}
95%	3.1×10^{-8}
97%	3.5×10^{-8}
99%	4.2×10^{-8}





Above you can compare two models for the helium atom. The left one is a Bohr model with the two electrons in circular orbits around the nucleus. Unfortunately, calculations for this model are not consistent with reality. The second model shows the results of wave equation calculations with the two electrons in a spherically shaped region of space. The figure also illustrates that the probability of finding the electron decreases as the distance from the nucleus increases.



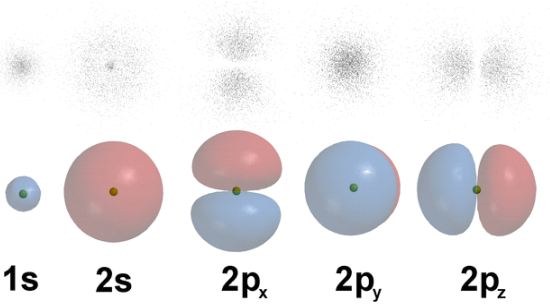
Another consequence of quantum mechanics is that every electron of an atom is in someway distinct from every other electron. Electrons can be characterized with 4 quantum numbers and every electron of an atom has a unique set of quantum numbers. For helium, the 4 quantum numbers for one of the electrons is 1, 0, 0, ½ and the other one has the quantum numbers 1, 0, 0, -½ . Boron with atomic number 5 has 5 electrons. The shapes of the orbitals that contain the 5 electrons are shown in the image to the right. Two electrons occupy the region of the inner sphere called a 1s orbital, two more in the larger sphere called a 2s orbital and one in the 3 dimensional figure 8 orbital that is called a 2p orbital.

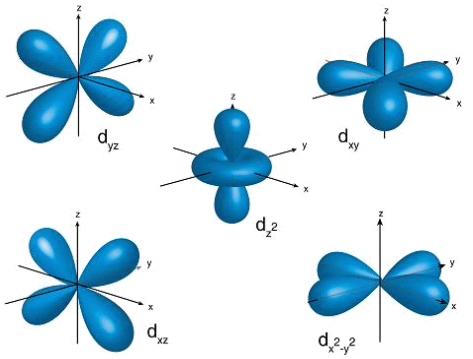
It is the restrictions on the values of the quantum numbers that yield a shape for the periodic table consistent with experimental results. You have already learned that each electron must have a unique set of quantum numbers. In addition, n is the principal quantum number and gives the approximate energy level of the electron. An electron in n = 2 is at a higher energy than an electron in n = 1. Except for s, the quantum numbers must be integers. n restricts the values of ℓ and m. s can only be ½ or -½. Using these limitations results in the following list of possible quantum numbers:

n	ℓ	m	s	total electrons possible
	$0 \le \ell \le n-1$	$-\ell \le m \le \ell$	1/2, -1/2	
1	0	0	1/2, -1/2	2
2	0	0	1/2, -1/2	2
2	1	-1, 0, 1	1/2, -1/2	6
3	0	0	1/2, -1/2	2
3	1	-1, 0, 1	1/2, -1/2	6
3	2	-2, -1, 0, 1, 2	1/2, -1/2	10
4	0	0	1/2, -1/2	2
4	1	-1, 0, 1	1/2, -1/2	6
4	2	-2, -1, 0, 1, 2	1/2, -1/2	10
4	3	-3, -2, -1, 0, 1, 2,3	1/2, -1/2	14
5	0	0	1/2, -1/2	2
5	1	-1, 0, 1	1/2, -1/2	6
5	2	-2, -1, 0, 1, 2	1/2, -1/2	10
5	3	-3, -2, -1, 0, 1, 2, 3	1/2, -1/2	14
5	4	-4,-3, -2, -1, 0, 1, 2, 3, 4	1/2, -1/2	18
6	0	0	1/2, -1/2	2
6	1	-1, 0, 1	1/2, -1/2	6
6	2	-2, -1, 0, 1, 2	1/2, -1/2	10
6	3	-3, -2, -1, 0, 1, 2, 3	1/2, -1/2	14
6	4	-4,-3, -2, -1, 0, 1, 2, 3, 4	1/2, -1/2	18

This table could be continued but elements with more electrons have not been discovered or synthesized and probably will never be. Some of the hypothetical elements near the bottom also will not ever be synthesized There is another complication in this model. While n represents the general energy level of the orbital, ℓ gives energy sublevels. In some cases the sublevels overlap with sublevels of higher values of n. In other words, an electron with n = 3 and $\ell = 2$ is higher in energy than an electron with n = 4 and $\ell = 0$. In addition to having a significant role in determining the energy of a sublevel, the value of ℓ determines the shape of the orbital. For communication purposes, letters have been assigned to designate the value of ℓ.

ℓ	letter designation	orbital shape
0	s	spherical
1	p	3d figure 8 (see image)
2	d	(see image)
3	f	complex
4	g	complex





http://commons.wikimedia.org/wiki/File:D_orbitals.png

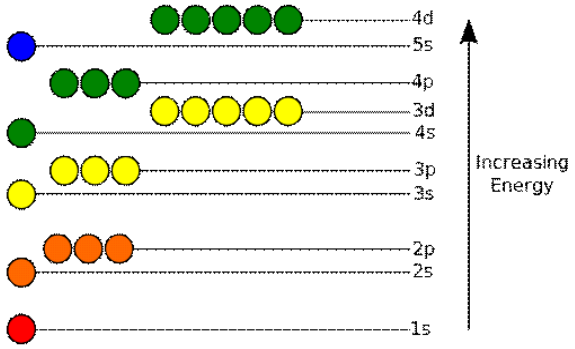
orbitals arranged according to increasing energy

n	ℓ	m	s	total electrons	total electrons =
	$0 \le \ell \le n-1$	$-\ell \le m \le \ell$	1/2, -1/2	possible	atomic number
1	0	0	1/2, -1/2	2	2
2	0	0	1/2, -1/2	2	4
2	1	-1, 0, 1	1/2, -1/2	6	10
3	0	0	1/2, -1/2	2	12
3	1	-1, 0, 1	1/2, -1/2	6	18
4	0	0	1/2, -1/2	2	20
3	2	-2, -1, 0, 1, 2	1/2, -1/2	10	30
4	1	-1, 0, 1	1/2, -1/2	6	36
5	0	0	1/2, -1/2	2	38
4	2	-2, -1, 0, 1, 2	1/2, -1/2	10	48
5	1	-1, 0, 1	1/2, -1/2	6	54
6	0	0	1/2, -1/2	2	56
4*	3	-3, -2, -1, 0, 1, 2,3	1/2, -1/2	14	70
5	2	-2, -1, 0, 1, 2	1/2, -1/2	10	80
6	1	-1, 0, 1	1/2, -1/2	6	86
7	0	0	1/2, -1/2	2	88
5*	3	-3, -2, -1, 0, 1, 2, 3	1/2, -1/2	14	102
6	2	-2, -1, 0, 1, 2	1/2, -1/2	10	112
7	1	-1, 0, 1	1/2, -1/2	6	118

*The 5d and 4f (and the 6d and 5f) are extremely close in energy. One electron goes into the 5d and then 14 electrons go into the 4f before the remaining 5d orbitals fill.

The table above lists the orbitals ranked from lowest to highest energy. The orbitals fill in order of increasing energy. The next image gives you a pictorial representation of the orbitals up through Xenon (element 54).

http://commons.wikimedia.org/wiki/File:Atomic_orbital_energy_levels.svg



We are now ready to compare the model derived above from quantum mechanics to the periodic table. Notice that only 2 electrons are allowed in the n = 1 level thus hydrogen and helium form the first period. For n = 2, there are both s and p sublevels giving a total of 8 possibilities. We find 8 elements in the second period. The next period also has 8 possibilities as the 3d level is higher in energy than the 4s and therefore fills after the 4s. We notice after the first two elements in the 4th period, the 10 transition metals that follow involve filling the 3d level. Next 6 more electrons fill the 4p level before the table goes to the next quantum level, the 5s. At this point, you can compare the remainder of the periodic table with the energy levels from the model and see if you can find the consistency.

We observed earlier that Mendeleev started new rows to make formulas and reactivities line up. The formulas and reactivities of the elements are determined by the highest energy electrons only. Once orbitals are filled, considerable stability is achieved. This is especially true each time the p orbitals are filled. Notice that each time the p orbitals are filled, the elements on the far right of the chart have been reached. These elements go by the name noble or inert gases. It is only under extreme conditions that inert gases can be forced into reacting. Their electronic structures result in so much stability that it is not energetically favorable for the inert gases to react. While not previously stated, the energetics of a potential reaction determine whether the reaction is possible without energy input or whether energy will have to be provided to cause a reaction. The inert gases are about as stable as possible as simple atoms and do not undergo chemical reactions.

Notice that the first element (group 1) of each period (lithium, sodium, potassium, rubidium, cesiuim) each has one electron in the highest quantum level. Since filled orbitals are the most energetically stable, there is a strong tendency for the group 1 elements to react and transfer an electron to its reaction partner. This leaves the group 1 elements with the same number of electrons as the preceding inert gas and this is a very stable electronic state. On the other side of the chart, the elements that precede each inert gas (group 7A or 17) are one electron short of the number required for filled orbitals. It is not surprising then that if a sodium atom were to encounter a chlorine atom, the sodium atom transfers an electron to the chlorine. This results with a sodium ion or Na^+ and a chloride ion or Cl^- and both have filled orbitals and the same electronic configuration

as an inert gas. Since positive and negative charges are strongly attracted to each other, a compound of NaCl is formed. **The strong attractive force of opposite charges is a significant part of the reason that the overall energetics for this process are very favorable. The result is called an ionic bond.** Notice also that all of the group 1 compounds form 1:1 compounds with chlorine (LiCl, NaCl, KCl, RbCl, CsCl) as a result of the favorable energetics involved with the loss of one electron. For the group 2 elements, the compounds that result from a reaction with chlorine are $BeCl_2$, $MgCl_2$, $CaCl_2$, $SrCl_2$, $BaCl_2$ as these elements need to transfer 2 electrons to achieve filled orbital status. Likewise the elements near the top of group 6A or 16 tend to gain two electrons. As a result, a compound of sodium and oxygen has the formula Na_2O. While group 3 elements tend to donate 3 electrons, prediction of which ions should be formed is much more difficult for elements that are not near an inert gas. It is rare for elements to donate or gain 4 or more electrons as it is energetically unfavorable to have a big difference between the number of protons and electrons. For this reason, near the center of the chart such as group 4, electrons are not donated or gained when bonds are formed. Instead electrons are shared in ways that give the elements a pseudo inert gas structure of electrons or 8 electrons in the highest energy level orbitals. Bonds formed from sharing are called covalent bonds. Elements with partially filled d or f orbitals such as the transition metals and the rare earths would have too lose too many electrons to acquire the electronic structure of an inert gas. These elements still strive to achieve filled or next best half filled orbitals. However, predictions of how many electrons will be donated is difficult even for experts and the best way to determine oxidation states is by experiment. The most common oxidation states are +2 and +3.

The concept that chemical reactivity is largely due to the electrons in the highest orbitals and the stability attained by the atom acquiring an electronic structure identical to the electronic structure of an inert gas is worthy of a little more discussion. This discussion will only be about elements that have partially filled s and p orbitals and not those with partially filled d and f orbitals. These electrons are commonly called valence electrons. These elements are commonly labeled in periodic tables in the U.S. with an "A" after the group number. Elements with partially filled d and f orbitals have a B after the group number. This results in the U.S with groups IA through VIIIA and IB through VIIIB (actually 10 elements as three elements in each period are labled VIIIB). In the European system, the groups are numbered 1 through 18 without distinguishing the A and B groups.

Going from left to right for A group elements, the number of electrons in the outer orbitals increases from 1 to 8 for the filled inert gas. Although these electrons all go into the same principal quantum level (same value of n), they go into two different sublevels with ℓ values of 0 and 1 and these are designated as s and p orbitals. A chemist would use the valence electron structure below to symbolize these electrons:

Group #	1A	2A	3A	4A	5A	6A	7A	8A
# valence electrons	1	2	3	4	5	6	7	8 (stable)
valence electron structure	s^1	s^2	s^2p^1	s^2p^2	s^2p^3	s^2p^4	s^2p^5	s^2p^6
Lewis structure	Li·	Be:	·B:	·C:	·N:	·O:	:F:	:Ne:

Groups 1A, 2A and 3A tend to transfer their valence electrons to their bonding partners giving them the same electronic structure as the previous inert gas (helium in this case). 7A, 6A and in some cases, the 5A elements tend to gain electrons to achieve the electronic structure of the next inert gas (in this case, Neon). Carbon has too many electrons to either lose or gain and instead shares with a partner so that the carbon has 8 electrons in atomic and molecular orbitals. Notice that a new concept has been introduced in the table. An alternative method used to focus on the valence electrons was developed by UCBerkeley chemist, Gilbert Lewis. To draw Lewis structures of an element (this method is only used for group A elements and not group B elements), the symbol of the element is imagined to be surrounded on four sides by 4 orbitals. Since each orbital as a result of spin can have two electrons, this method corresponds to providing a simple view of the 8 valence electrons. The resulting Lewis structures for the second period elements are shown in the table. The Lewis structures for all of the elements in any group would be identical to the above except the elemental symbol would change. This method provides another rationale for the similar reactivities for all the elements in a group. Please note that many texts use a slightly different method for drawing Lewis structure. Using the alternative method, going across the period, one electron is added to each side before the electrons are paired up. The advantage of the latter method is that it does provide a good model for the way the element reacts. However, the method used here correlates better with the model for the electronic structure of an atom of the element as provided by the quantum mechanics approach to electronic structures. This method was used here for consistency reasons.

Lewis structures are even more useful when it comes to drawing molecular structures especially for organic compounds. We will develop this technique in a later chapter.