

## Lecture 13

Last time we said that the distributions of position and the energies of electrons in atoms are correctly described by the solutions of the Schrodinger equation, which are called orbitals. **Each atomic orbital is described by three integers called quantum numbers**, just as Bohr's orbits were described by quantum numbers. Why three? Suppose we have an object, like this marker. If we want to locate it along a line, we use one number, the distance  $x$ , to locate it. To locate it in a square, we use two numbers,  $x$  and  $y$ . To locate it in a sphere, we use three numbers,  $x$ ,  $y$ , and  $z$ . Since atoms are spherical, we are trying to locate electrons inside a sphere, so we need three numbers to describe the positions of electrons, and these are our quantum numbers. Once again, **the three quantum numbers, taken together, yield different average positions, or equivalently, different energies, for the various electrons in atoms.** These energies are typically referred to as **energy levels**.

The first of the three quantum numbers is called the **principle quantum number** and is given the symbol  $n$ .  $n$  can be any integer from 1 to infinity, i.e.,  $n = 1, 2, 3, \dots$ . **For the hydrogen atom,  $n$  determines the energy of the electron. For all other atoms,  $n$  divides the energy levels of an atom into coarse groups called shells.** The larger  $n$  is the larger the average of the energies of the electrons is in that shell. From our previous discussion, this also tells us that as  $n$  increases the average distance between the electrons in a shell and the nucleus also increases. In other words, as  $n$  increases, the size of the orbital increases.

The second quantum number is called the **azimuthal quantum number,  $l$ , also known as the angular momentum quantum number.** What does  $l$  tell us? Each shell is composed of one or more subshells, each of which has a different value of  $l$ .  **$l$  determines the shape of the orbitals in a subshell, and along with  $n$  (for atoms other than hydrogen) determines the energy of an**

**electron and distance of an electron from the nucleus.** The values that  $l$  can take on depend on  $n$ . **The value of  $l$  goes from  $l = 0$  to  $l = n-1$ .** This means that **the number of subshells is determined by the value of  $n$ .** Thus for  $n = 1$ ,  $l$  can only be 0, and  $n = 1$  has only one subshell. For  $n = 2$ ,  $l$  can be 0 or 1 and therefore  $n = 2$  has 2 subshells. What are the allowed values of  $l$  for  $n = 3$ ? [ $l = 0, 1, 2$ ] Therefore  $n = 3$  has three subshells. Notice that the number of subshells in any shell is simply equal to  $n$ . Originally for reasons having to do with the spectroscopy of atoms, but more recently because we're just plain old used to it, the **subshells are most commonly identified by letters.** An orbital with  $l = 0$  is called an s orbital, an orbital with  $l = 1$  is called a p orbital, an orbital with  $l = 2$  is called a d orbital, an orbital with  $l = 3$  is called an f orbital, and for  $l = 4$  or higher the orbital designations just follow alphabetically. The most important subshells for our purposes are s, p, d, and f, because they are the only ones that are used by atoms when they are in their lowest energy states. The subshells s, p, d and f are so important that one member of this department used to use them for his license plate.

When designating the position or energy of an electron, it is important to specify both  $n$  and  $l$ , so we write the number of the shell followed by the letter of the subshell. For example, an orbital with  $n = 1$  and  $l = 0$  is called a 1s orbital; an orbital with  $n = 3$  and  $l = 2$  is called a 3d orbital, and an orbital with  $n = 4$  and  $l = 1$  is called what? [4p]. If an electron occupies an orbital, it is described the same way as the orbital. For example, an electron in a 2p orbital is called a 2p electron.

The third quantum number that describes the position of electrons is called **the magnetic quantum number,  $m_l$ .**  **$m_l$  determines the orientation of an atomic orbital.** It gets its name because if an atom is exposed to a magnetic field new lines appear in its spectrum which correspond to these different orientations. **The values of  $m_l$  depend on  $l$  and range from  $-l$  to  $l$ .**

So for example, for  $n = 1$ ,  $l = 0$  and  $m_l = 0$ , so there is only one orientation of a 1s orbital. For a p subshell,  $l = 1$ , and  $m_l$  can be either 1, 0, or -1, so a p subshell has three orbitals in it each with a different orientation. A d subshell has  $l = 2$ . What are the allowed values of  $m_l$  for a p subshell? [-2, -1, 0, 1, 2] Therefore a d subshell contains 5 orbitals. Using similar arguments, we find that an f subshell will contain 7 orbitals.

Let's practice a little with using quantum numbers.

WHEN  $n = 3$ , THE VALUES OF  $l$  ARE?

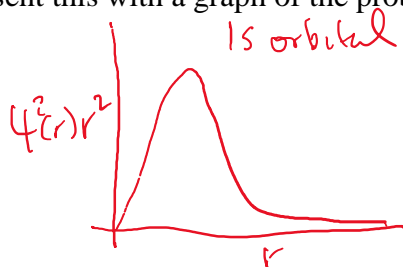
WHEN  $l = 2$ , THE VALUES  $m_l$  CAN BE... AND THE SUBSHELL HAS THE LETTER LABEL

WHEN  $l = 1$ , THIS IS CALLED A ... SUBSHELL.

WHEN A SUBSHELL IS LABELED D, THERE ARE ... ORBITALS WITHIN THAT SUBSHELL

WHEN A SUBSHELL IS LABELED F, THERE ARE ... VALUES OF  $m_l$  AND THERE ARE .....ORBITALS WITHIN THE SUBSHELL.

I said earlier that the  $l$  quantum number determines the shape of an orbital. Let's look at what these shapes are. This is easiest if we start with a 1s orbital. What does it mean if we say an electron is in a **1s orbital**? If we take a picture of the position of an electron again and again, we would see two things. One is that **the electron shows up most often near the nucleus**. When we look farther and farther from the nucleus, we see the electron less and less frequently. We can represent this with a graph of the probability of finding the electron vs. distance.



The other thing we'll notice is that the orbital looks sort of like a ball, or **sphere**. Another way of saying this is that we're likely to find the electron at any angle. It turns out that not just the 1s

orbital, but all s orbitals are shaped like spheres. One way that they differ is that as n increases, the size of the s orbitals increases. Thus a 2s orbital is bigger than a 1s orbital and a 3s orbital is bigger than a 2s orbital.

p orbitals also all have the same basic shape. A p orbital, with  $l = 1$ , is shaped like a double bowling ball. The two bowling balls are separated by a plane that goes through the nucleus. The electron density, the probability of finding the electron, is divided equally between two lobes, one above the nucleus and one below. The plane which separated the two lobes of the orbital is a place where the electron is never found, and is called an **angular node**. Since this plane goes right through the nucleus, we will never find a p electron at the nucleus. The + or - that I wrote on the lobes has to do with a property called the phase of the orbital. We won't be using this now, but when we talk about bonding, it will tell us something about the way orbitals on atoms combine to make bonds.

Let's return to the shapes of orbitals and reconsider the p-orbital. Remember that I told you that there were three p orbitals in the p shell. The only difference between them is in the direction they are pointed. It turns out that one is aligned along the x axis, one along the y axis, and the third along the z axis. They are called  $p_x$ ,  $p_y$ , and  $p_z$  respectively.

Now we'll consider the d-orbitals, of which there are five. Four have very similar shapes, looking more or less like a four leaf clover. This means that d orbitals have two planar nodes, and four lobes. The lobes alternate with + and - phases. The only difference between these four is the direction in which they point. To get the fifth you take one of the other d orbitals, stand it on its end and twirl it and get something which looks like a p orbital with a hula hoop around it. Understanding the shapes of these orbitals will be very important in your understanding of chemistry, so I want very much for you to memorize the shapes of the s, p and d orbitals.

Remember that I said that the  $n$  and  $l$  quantum numbers together controlled the distance of the electrons from the nucleus. Let's see how this works, by looking at the cross sections of  $s$  orbitals as  $n$  increases. You see that for the  $1s$  orbital the distances are fairly small, with the electron spending most of its time close to the nucleus. If we go to  $2s$ , the electron spends more of its time farther away from the nucleus, but now a node appears as we move away from the nucleus. For  $3s$ , the electron moves even farther out and a second node appears. So you see that there are two effects on the distance of an electron in an  $s$  orbital as  $n$  increases. One is that the electron moves farther out, and the other is that nodes begin to appear in the orbitals. What happens to the  $p$  orbitals? There is no  $p$  orbital in  $n = 1$ , but for the first  $p$  orbital in  $n = 2$  there is no distance node. Similarly, there is no distance node in the first  $d$  shell at  $n = 3$ , or in the first  $f$  shell at  $n = 4$ . However, the second shell of each of these types has one distance node. So for example, the  $3p$  orbitals will have one distance node. If you combine the distance node with the planar node you already have with a  $p$  orbital you get something which looks like this.



In summary, each orbital in an atom, and therefore each electron, has its position in space defined by three quantum numbers,  $n$ ,  $l$ , and  $m_l$ . These quantum numbers together determine the energy, size, shape and orientation of the orbital, the space that an electron can occupy.

In order to complete our description of electrons in atoms we need to introduce a fourth quantum number,  $m_s$ , the **spin quantum number**, which can only take on two values,  $+1/2$  and  $-$

1/2. Why are we treating this fourth quantum number separately, rather than with the other three?

The reason is that the **three other quantum numbers describe an electron's position** or energy within an atom, while  **$m_s$  represents a property of the electron itself**. In effect, an electron behaves like a tiny magnet, i.e., produces a magnetic field. Remember that a magnet has two poles + and -, and therefore has a direction. If the positive pole is pointing up we could say that the magnet is pointing in the positive direction, while if the positive pole is pointing down we could say that it is pointing in the negative direction. Similarly, the electron has a magnetic field which can point up or down. **If  $m_s$  is  $+1/2$ , the electron's magnetic field is pointing up, and if  $m_s$  is  $-1/2$ , the electron's magnetic field is pointing down.**

You should realize that even though this quantum number is called the spin, the electron is not actually spinning. The name spin was chosen because in classical physics a spinning charge produces the kind of magnet that we see the electron produce. Thus spin was a comfortable concept for these physicists when they discovered the magnetic properties of the electron.

The presence of the spin quantum number now means that **each electron in an atom is described by four quantum numbers,  $n$ ,  $l$ ,  $m_l$  and  $m_s$** . Let's just quickly review the meaning of these four quantum numbers.  $n$  is the principle quantum number and can be any integer, 1, 2, 3 ....  $l$  is the azimuthal quantum number. Its value depends on  $n$  and has the range  $l = 0, 1, \dots, n-1$ .  $m_l$  is the magnetic quantum number and ranges from  $-l$  to  $+l$ . Finally,  $m_s$  is the spin quantum number and always has only two values,  $+1/2$  and  $-1/2$ . Thus we can have, for example, two types of 1s electrons. One will have the quantum numbers  $n=1, l=0, m_l = 0$  and  $m_s = 1/2$ , while the other will have  $n=1, l=0, m_l = 0$  and  $m_s = -1/2$ .

## Lecture 14

Why is it important that we know  $m_s$ ? In the late 1920's Wolfgang Pauli came up with a rule called the **Pauli exclusion principle**. In its simplest form, the principle, which is based on experiment, says that **no two electrons in an atom can have the same four quantum numbers**. An atomic orbital is described by the three quantum numbers  $n$ ,  $l$  and  $m_l$ . Let's see what the Pauli exclusion principle says about the number of electrons we can put in an orbital. Let's start by looking at a 1s orbital. When we put an electron in an orbital we label it with the same quantum numbers that the orbital is labeled with. So our first 1s electron will have  $n=1$ ,  $l=0$  and  $m_l = 0$ . Now we have to give it a value of  $m_s$  and we'll arbitrarily choose  $+1/2$ . Now if we want to put a second electron in the orbital,  $n$ ,  $l$ , and  $m_l$  don't change, because they tell us that the orbital is the same. According to the Pauli exclusion principle, the four quantum numbers can't all be the same, so if  $n$ ,  $l$  and  $m_l$  are the same for the two electrons, then  $m_s$  must be different, so the quantum numbers for the second electron must be  $n = 1$ ,  $l = 0$ ,  $m_l = 0$ , and  $m_s = -1/2$ . What would happen if we tried to put a third electron in the 1s orbital? Since it's a 1s orbital, we know that  $n = 1$ ,  $l = 0$  and  $m_l = 0$ , and now we need to find a new value for  $m_s$ . But there is no other value for  $m_s$ , so we can't put a third electron in the 1s orbital, or in fact any orbital, without violating the Pauli exclusion principle. From this example we find that the Pauli exclusion principle tells us two things. First, **an orbital can contain no more than two electrons**. Second, **if the orbital does contain two electrons, the spins of the two electrons must be different**. **When two electrons of different spins are in the same orbital we say that they are paired**.

Let's see what this tells us about **the number of electrons which can fit in a given electronic shell**. The  $n = 1$  shell has only one orbital, the 1s orbital, so it can only hold two electrons. THE  $N = 2$  SHELL HAS HOW MANY ORBITALS? [4, 2s and 3 2p] The 2s can hold two

electrons. The three 2p orbitals can hold two each, so the  $n = 2$  shell can hold up to eight electrons. The  $n = 3$  shell has nine orbitals, one 3s, three 3p and five 3d. HOW MANY ELECTRONS CAN THE 3S ORBITAL HOLD? HOW MANY CAN THE THREE 3P ORBITALS HOLD? WHAT ABOUT THE 5 3D ORBITALS? Therefore, the  $n = 3$  shell can hold eighteen electrons.

You should see from our discussion that we can also talk about the number of electrons which can fit into each type of subshell. There is only one orbital in an s subshell, so it can only hold two electrons. There are three orbitals in a p subshell, so it can hold six electrons. Q: HOW MANY ORBITALS ARE THERE IN A D SUBSHELL? [5] Q: SO HOW MANY ELECTRONS CAN THE D SUBSHELL HOLD? [10] Similarly, the f subshell, which has seven orbitals, can hold 14 electrons.

Notice that the number of electrons that fits into the  $n = 1$  shell, 2, matches the number of elements in the first row of the periodic table, and the number of electrons that can fit into the  $n = 2$  shell matches the number of elements in the second row of the periodic table. This suggests that we can use the Pauli exclusion principle to relate our quantum numbers to the structure of the periodic table.

We need one more piece of the puzzle if we're going to use our new knowledge of the structure of atoms to try to derive the periodic table. I've said already that the quantum numbers  $n$  and  $l$  determine the energy of the orbital. The best way to illustrate this is using an **energy diagram for an atom**. On the y axis we have the energy. We list the orbitals and show their relative energies. If we draw an orbital higher on the graph, it means that the energy of the orbital is higher, while if it is lower on the graph, it means the energy of the orbital is lower. Lowest in energy is the 1s orbital, the only orbital in the  $n = 1$  shell. Next comes the 2s orbital, then the 2p orbitals. How many 2p orbitals are there? (3) Now come the 3s and the 3p orbitals, but now there's a surprise. If we use the Schrödinger equation to calculate the energy of the orbitals we find that the



next orbital in energy is not 3d but 4s. This will turn out to be important when we use quantum numbers to construct the periodic table. Next comes 3d, then 4p and now 5s, 4d, and 5p. Note that even though 3d is higher in energy than 4s, the energies are very close together. WHICH ORBITAL HAS A HIGHER ENERGY? 3D OR 2S? 5S OR 3D?

How do we use the Pauli exclusion principle and this energy diagram? It is a law of physics that everything is stabler when its energy is lower. For our electrons, this means that **an atom will be stablest when its electrons are in the lowest energy orbitals possible**. This means that when we are trying to figure out which orbitals an atom's electrons belong in, we must start at the lowest energy orbital and work our way up from there. This is called **the aufbau, or building up, principle**.

Let's work out the ground state electronic structures for the elements in the first two rows of the periodic table. These structures are called **ground state** structures since each electron goes into the lowest energy orbital that is available to it. Since one of our requirements is that the orbitals will be filled in order of energy it will help us if I redraw my energy level diagram. [1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d] We start with hydrogen. Hydrogen has one electron, which must go into the lowest energy orbital, 1s. This can be written in two ways. One is to write that hydrogen as a  $1s^1$  configuration, where the superscript indicates the number of electrons in the orbital. The other way is to write the symbol for the element followed by a small line with the orbital written under it and one arrow on the line for each electron. It is conventional to use an up arrow for  $m_s = 1/2$  and a down arrow for  $m_s = -1/2$ . This second method is called an orbital box diagram. For Hydrogen it would be  $\uparrow$ . **What are the quantum numbers for this electron?**

Let's do helium now. Helium has two electrons. We put them into orbitals starting with the orbital with the lowest possible energy. This is 1s, which holds two electrons, so our helium

configuration is  $1s^2$  and our orbital diagram is  $\text{He} \uparrow\downarrow$ . Note that at this point we've filled the shell. Notice also that helium is a noble gas. This suggests a correlation between a filled shell and the unusual stability of a noble gas. We can conclude that **when the placement of the highest energy electron in a configuration fills a shell, we have an especially stable configuration of electrons. We'll have to slightly refine this idea later.**

Our next element is Li, with three electrons. The first two go into a 1s orbital, just like helium. **Can we put a third in the same orbital? What are the quantum numbers for the two 1s electrons?** If we tried to put our third electron in the 1s orbital it would have to have the quantum numbers 1, 0, 0, 1/2 or 1, 0, 0, -1/2, but this would be the same as one of our first two electrons, and would violate the Pauli exclusion principle, so for the third we have to go up to the next energy orbital, which is 2s, so Li has the configuration  $1s^2 2s^1$ .

Be has 4 electrons and has the configuration  $1s^2 2s^2$ . For boron, since the 1s and 2s orbitals are filled, we turn to the 2p orbital, the next highest in energy, and boron has the electron configuration  $1s^2 2s^2 2p^1$ .

Now let's turn to carbon, with six electrons. The first four electrons go into the 1s and 2s orbitals, but when we try to draw an orbital diagram, we find that there are three different ways to draw the orbital diagram for the two 2p electrons,  $\uparrow\downarrow$ ,  $\uparrow \downarrow$ , and  $\uparrow \uparrow$ . In the first, the two electrons are placed in the same p orbital and are paired. In the second, the electrons are placed in two different 2p orbitals and have opposite spins. In the third, the two electrons are placed in different 2p orbitals, and have the same spin. The best configuration will be the one that is lowest in energy. Based on the observed spectra of atoms, a German scientist named Friedrich Hund came up with the following rule: **electrons entering a subshell containing more than one orbital will be spread equally among the orbitals in the subshell with their spins pointing in the same**

**direction.** According to this rule the last configuration that we drew is the best one. We write this as  $1s^2 2s^2 2p_x 2p_y$ .

The next element is nitrogen, with seven electrons. Its electron configuration will be what?  $1s^2 2s^2 2p^3$ . Let's draw its orbital diagram. N  $\uparrow\downarrow \uparrow\downarrow \uparrow \uparrow \uparrow$ . Where will the three p electrons go? [1 in each] Q: WHAT WILL THE SPINS BE? [all up or all down] Next is oxygen with a total of eight electrons. WHAT WILL ITS ELECTRON CONFIGURATION BE? [ $1s^2 2s^2 2p^4$ ] If we draw the orbital diagram, we have as before filled 1s and 2s orbitals, and now we have to deal with the three 2p orbitals again. For the first three electrons we have to follow Hund's rule, and put them in different orbitals, but the fourth electron now has to be paired, since there are no empty 2p orbitals to put it in. Now let's do the last two elements in the second row of the periodic table. WHAT WILL THE ELECTRON CONFIGURATION OF CL BE?  $1s^2 2s^2 2p^5$ . WHAT WILL THE ORBITAL DIAGRAM LOOK LIKE? FINALLY WHAT WILL THE CONFIGURATION OF NE BE?  $1s^2 2s^2 2p^6$ . Notice for this second rare gas, we've filled out all of the orbitals in the 2p shell.

If we move on to Na, we have to start a new shell with 3s, and the electron configuration will be  $1s^2 2s^2 2p^6 3s^1$ . Notice that as we add more electrons, the electron configuration gets longer and longer. It would be nice to have a way to abbreviate these configurations. One fact that helps us do this is that **the electrons in the outermost shell of the atom are the ones that participate most in the chemical reactions of an atom.** These electrons in the outermost shell of the electron are called **valence electrons and the orbitals they occupy are called valence orbitals.** The electrons with principle quantum numbers lower than the outermost shell we call the **core electrons and their orbitals are called core orbitals.** Notice that for Na that we have one valence electron, the 3s electron. Notice also that the other electrons have the same configuration as a noble gas, Ne. We use this fact to come up with our abbreviation. We can abbreviate the Na

configuration as  $[\text{Ne}]3s^1$ . What we are doing is to represent the core electrons by the noble gas with the same configuration, and then writing out the valence electrons in full. This is the same as saying that the sodium electron configuration is the same as neon plus one 3s electron. We call the configuration where we write out all the electrons a **full electron configuration**. We call the abbreviation the **Noble Gas notation**.

Let's look at some other examples of Noble Gas notations. For example, Li's configuration is  $1s^2 2s^1$ . The 2s electron is the only valence electron, and therefore the rest are core electrons. Therefore, Li's configuration can be written  $[\text{He}] 2s^1$ . **In carbon, with the configuration  $1s^2 2s^2 2p^2$  which are the valence electrons?**  $[2s^2 2p^2]$  **Which are the core electrons?**  $[1s^2]$  **So what will be the abbreviation for the carbon configuration?**  $[\text{He}] 2s^2 2p^2$ .

Now as we go along the periodic table we'll fill the orbitals in the order in which they appear in our energy diagram, so the next orbital to be filled will be 3p, then 4s, not 3d, because the 4s is lower in energy. Next come the 3d orbitals, and the 4p orbitals. So for example let's work out the configuration of Fe. **HOW MANY ELECTRONS ARE THERE?** 26. **WHAT IS THE CORE CONFIGURATION GOING TO BE?**  $[\text{Ar}]$  **HOW MANY CORE ELECTRONS ARE THERE THEN?** [18] **SO HOW MANY VALENCE ELECTRONS ARE THERE?** [8] **WHAT WILL BE THE ELECTRON CONFIGURATION OF THE VALENCE ELECTRONS?**  $4s^2 3d^6$ . **WHAT WILL THE ORBITAL BOX DIAGRAM OF THE VALENCE ELECTRONS LOOK LIKE?**

We can come up with a new way of naming the groups in the periodic table based on their electronic configurations. If the last electron in an atom's ground state electron configuration goes in an s orbital we call the atom an **s block element**. H, Li, Mg and Ba are all s block elements. If the last electron in an atom's ground state electron configuration goes in a p orbital we call it a **p block element**. O, Cl, As, Sn and Ga are all p block elements. S and p block elements together

are called **representative elements**. If the last electron in a ground state electron configuration goes into a d orbital, we call the element a **transition metal**. Ti, Mn, Os, Pt, and Zr are all transition metals. Let's make sure we have this down. Q: WHAT IS S? K? Y? RU? TE? BR?

You should be aware that **there are some exceptions to this relatively simple plan for filling the atomic orbitals**. Take for example the element Cr. It has 24 e<sup>-</sup>, with 18 core electrons and 6 valence electrons. According to our rules it should have the configuration, [Ar] 4s<sup>2</sup> 3d<sup>4</sup>, but instead we find that it actually has the configuration [Ar] 4s<sup>1</sup> 3d<sup>5</sup>. If we look at the orbital box diagram for Cr we see that this configuration puts one electron into each of the s and d orbitals. This type of configuration is called a half-filled subshell. It turns out that half-filled subshells are particularly stable (not as stable as rare gases, though). In fact, atoms with half-filled shells are stable for the same reasons that rare gases with their filled shells are stable. The reason is simply that because electrons are all negative and like repels like, electrons will repel each other. The atom will be stablest when the electrons are farthest apart. Electrons tend to be spread farthest apart when they are divided evenly among orbitals of the same or at least similar energies. In fact this tendency to have distributions of electrons that are as even as possible is what causes chemical bonds to form, as we will discuss later.

## Lecture 15

Earlier in the semester we talked about the ways that many atoms form ions. How do we determine the **electron configurations of ions**? For anions, the answer is simple - we just keep on adding electrons to orbitals. So for example, Cl has the configuration  $[\text{Ne}]3s^2 3p^5$ . To find the configuration of  $\text{Cl}^-$  we just add one more electron to get the configuration  $[\text{Ne}] 3s^2 3p^6$ . Q: WHAT WOULD THE CONFIGURATION OF  $\text{O}^{2-}$  BE? WHAT ABOUT  $\text{P}^{3-}$ ?

The **electron configurations of cations** of s and p block elements are also simple to figure out. You just take the configuration of the neutral atom and remove the highest energy electrons. So for example, suppose we want to find the configuration for  $\text{Mg}^{+2}$ . We start with the configuration of neutral Mg,  $[\text{Ne}]3s^2$ , and remove two electrons to get  $[\text{Ne}]$ . Let's say we had Cl and wanted to work out the configuration of  $\text{Cl}^+$ . We take the Cl configuration,  $[\text{Ne}]3s^2 3p^5$  and remove an electron to get  $3s^2 3p^4$ . Let's draw a diagram and see how the electrons will be distributed in the p orbitals. Remember that here, just as in a neutral atom, we must follow Hund's rule so the p electrons are in the configuration  $\uparrow\downarrow \uparrow \uparrow$ . What would the configuration of  $\text{N}^{+2}$  be?  $\text{S}^{+1}$ ?

**Transition metals follow a different rule for forming cations.** When we are figuring out the electron configuration of transition metal ions we begin with the neutral atom, but rather than beginning by removing the electrons with the highest energies, we remove the electrons with the highest value of n. Thus if we are going to figure out the electronic configuration of  $\text{Fe}^{+2}$ , we begin with the configuration of Fe,  $[\text{Ar}]4s^2 3d^6$ . We need to remove two electrons, and according to our new rule, we remove the 4s electrons first because they have the highest n. Thus the electronic configuration for  $\text{Fe}^{+2}$  is  $[\text{Ar}]3d^6$ . Let's do a couple of others.  $\text{Cr}^{+3}$ ,  $\text{Zr}^{+2}$ .

Why do these transition metal ions follow a different rule than main group ions? To see

this let's consider what makes an electron configuration stable. WHAT IS THE STABLEST GROUP IN THE PERIODIC TABLE? [Noble gases] Let's look at the electronic configurations of Ne, Ar, Kr and Xe. Ne has the configuration  $[\text{He}]2s^2 2p^6$ . Ar has the configuration  $[\text{Ne}] 3s^2 3p^6$ . Kr has the configuration  $[\text{Ar}] 4s^2 3d^{10} 4p^6$ . Xe has the configuration  $[\text{Kr}] 5s^2 4d^{10} 5p^6$ . Notice that all of these atoms have the configuration  $ns^2 n-1d^{10} np^6$ . Any atom or ion with this configuration is said to have a **noble gas configuration**, and will be especially stable. All of our noble gases have 2s electrons and 6 p electrons, and since these add up to eight, we deduce the eight-electron rule, that atoms or ions with eight electrons in the s and p valence orbitals will have special stability.

Let's look at the periodic table. Most transition metals can't fulfill the 8-electron rule, since they don't have any valence p electrons. However, there is another configuration that is almost as stable as the noble gas configuration, which transition metals can achieve. To see this let's look at the configuration of  $\text{Zn}^{+2}$ . According to our rules this has the configuration  $[\text{Ar}] 3s^2 3d^{10} 3p^6$ . Notice that this is not a noble gas configuration, since the noble gases with d electrons have a configuration  $ns^2 n-1d^{10} np^6$ . Nonetheless this configuration of  $\text{Zn}^{+2}$  has a special stability. We conclude that a configuration in which all of the orbitals in a shell, like  $n=3$ , are filled has special stability also. We call a configuration where all of the orbitals in a shell are filled a **pseudo noble gas configuration**. Since it takes 18 electrons to fill a shell with s, p and d electrons, the pseudo noble gas configuration leads to an **18-electron rule - a transition metal achieves special stability when surrounded by 18 electrons in its outermost shell**.

How do we know how many of our electrons are paired and how many are not? The answer is because of a phenomenon called **paramagnetism**. If we put a magnet next to any substance it will always react to the magnet. There are three different types of reactions to magnets, and paramagnetism is one of them. The first type is ferromagnetism. If you take a ferromagnetic

material, most usually iron, and put it next to a magnet, the iron is strongly attracted to the magnet. I'm sure you're all familiar with this. In addition to being strongly attracted to the magnet, a ferromagnetic material also has the property that it can be made into a permanent magnet. Again, I'm sure that you are all familiar with iron magnets.

The other extreme is **diamagnetism**. A diamagnetic material is one that has no apparent reaction when we bring a magnet near. Actually if very sensitive instruments are used to measure the response of a diamagnetic substance, we find that there is a tiny, tiny repulsion - **diamagnetic substances have a small tendency to push away from magnets**. Experimentation has shown that **diamagnetic substances are ones in which all electrons are paired**.

In the middle we have paramagnetism. **Paramagnetic substances are attracted by magnets, but only weakly**. Paramagnetic substances never can make permanent magnets. In other words, paramagnets only exhibit magnetic behavior at the time they are exposed to magnetic fields. It turns out that **paramagnetic substances are ones in which at least one electron is not paired**. So for example, a chlorine atom is paramagnetic, since there is one unpaired electron. However,  $\text{Cl}^-$ , in which all electrons are paired, is not paramagnetic. **In paramagnetism, the more unpaired electrons there are, the bigger the attraction to the magnet**. So for example,  $\text{Sc}^{+2}$  has the configuration  $3s^2 3p^6 3d^1$ , and is slightly paramagnetic. Let's look at  $\text{Fe}^{+2}$ , which is strongly paramagnetic. It has the electronic configuration  $3s^2 3p^6 3d^6$  and according to Hund's rule has four unpaired electrons.

Paramagnetism can change, however, when an atom bonds with other substances. For example, when paramagnetic Cl atoms bond with paramagnetic Na atoms, the product is diamagnetic! This tells us that when Na and Cl react, it results in all the electrons being paired. This is easy to understand in this case, since we know that NaCl is made of  $\text{Na}^+$  and  $\text{Cl}^-$ , both of



which have noble gas configurations. However, it also happens when two Cl atoms bond to form  $\text{Cl}_2$ . The atoms are paramagnetic, but the molecule is diamagnetic. This means that when two Cl atoms bond their electrons pair. So you see by considering paramagnetism, we've already learned something about the bonding of atoms when they make molecules.

Our discussion of the structure of atoms should help us understand the periodic properties that we began to discuss earlier. Let's talk about size first. **The size of an atom increases as we go down a group.** Well we just discovered that **as we go down a group that the principle quantum number increases.** Remember that **as the principle quantum number increases, the distance from the nucleus increases.** Therefore, going down a group should increase the size of atoms. What happens as we go across a group? The electrons are added to the same valence shell, but as the nuclear charge increases, the electrons are pulled closer and closer to the nucleus, so as we go across a period, the size of the atom shrinks.

**How do the sizes of ions compare to the sizes of other atoms?** It depends on what their electronic configuration is. Let's look at K and  $\text{K}^+$ . K has the configuration  $[\text{Ar}] 4s^1$ .  $\text{K}^+$  has the configuration  $[\text{Ar}]$  This means that K has an electron with  $n=4$ , while the outermost electron in  $\text{K}^+$  is in  $n=3$ . Therefore,  $\text{K}^+$  will be smaller than K. Here's a good question. Which will be smaller,  $\text{K}^+$  or Ar? They have identical electron configurations. Atoms or molecules with identical electronic configurations are said to be **isoelectronic**. However, K has a nucleus with a +19 charge, while Ar has a nucleus with a +18 charge. Since  $\text{K}^+$  has a higher charge, its electrons are pulled in more tightly and it will be smaller.

Let's take a quick look at **anions**. Which will have a smaller radius,  $\text{O}^{2-}$ ,  $\text{F}^-$  or Ne? Notice that all have the same electronic configuration. Again, we'll answer the question by looking at the charges on the nuclei. O has a nuclear charge of +6, F has a nuclear charge of +7 and Ne has a

nuclear charge of +8. Since the electronic configurations are the same, Ne, the one with the largest charge, will be the smallest. Let's do a couple together,  $K^+$ ,  $Ca^{+2}$ ;  $Se^{2-}$ , Ar.

Another important property is **ionization energy**. We define ionization as the process of removing an electron from an atom or ion. An example of ionizing an atom would be  $Ca \rightarrow Ca^+ + e^-$ . An example of ionizing an ion would be  $Ca^+ \rightarrow Ca^{+2} + e^-$ . The energy it takes to remove an electron from an atom or ion is called the ionization energy. If the electron is the first one removed, as in our first equation, the energy is called the **first ionization energy**. If the electron is the second one removed, the energy is called the **second ionization energy**. The tendency for ionization energies is that the first ionization energy of an atom goes down as you go down a group, and goes up as you go across the periodic table. The first trend is easy to understand if we look at our energy level chart. Say we want to remove an electron from Cs and an electron from Li. The Cs electron is in a 6s orbital, and the Li electron is in a 2s orbital. The 6s electron already has a much higher energy than the 2s electron and is much farther from the nucleus, so it takes less energy to remove it. It is also easy to understand why the ionization energy goes up as you go across a period. In this case the charge on the nucleus keeps increasing, so the atom holds on to its electrons more tightly, and it takes more energy to take them away. Thus F has a +9 nuclear charge, and O has a +8 nuclear charge, and the first ionization energy of F is larger than the first ionization energy of O.

We should also note that it is always harder to take a second electron off of an atom than the first, and it gets increasingly harder as you try to take more and more electrons off of an atom. Thus **the second ionization energy of an atom is always greater than the first ionization energy**.

A pair of related concepts are those of **electron attachment energy and electron affinity**.

The electron attachment energy is the energy change when an electron is added to an atom or anion. An example would be  $\text{Cl} + \text{e}^- \rightarrow \text{Cl}^-$ . These can be negative or positive depending on the atom involved. A negative attachment energy means that the anion which results from adding the electron is stabler than the original atom. It also means that energy is released when the electron is attached. A positive attachment energy means that the anion is less stable than the original atom. It also means that energy is required for the electron to be added. An example of an atom with a negative electron attachment energy is Cl. Adding an electron to Cl releases 349 kJ/mol, ie,  $\text{Cl} + \text{e}^- \rightarrow \text{Cl}^- + 349 \text{ kJ}$ . Most electron attachment energies are negative. For the simple reason that most of us are more comfortable dealing with positive numbers than negative ones, the electron affinity is defined as the negative of the electron attachment energy. Thus a positive electron affinity means that formation of an anion is favored. We would therefore write that  $\Delta E_{\text{EA}} = 349 \text{ kJ}$ . The electron affinity of an atom increases as you go up a group, and also increases as you go across a period. The halogens have the highest electron affinities, but generally elements on the right side of the periodic table will tend to have high electron affinities, and thus will tend to become anions. The big exception to this is N, which has a negative electron affinity, and thus requires energy before it will form  $\text{N}^-$ .

**Why do we care about these ionization energies and electron affinities?** They tell us why alkali metals form ions with charges of +1 and the alkaline earths have charges of +2. They tell us why the halogens usually have charges of -1 and why group 6A atoms usually have charges of -2. To see this let's look at the first, second and third ionization energies of Na and Mg. For Na the first IE is 496 kJ/mol, the second is 4562 kJ/mol, and the third is 6912 kJ/mol. Why the big jump from first to second? Notice that when we take an electron from Na, we're taking away a 3s electron, but that when we take an electron from  $\text{Na}^+$ , we have to go down one level lower,

and disrupt a noble gas configuration. That takes lots of energy.

For Mg, the first ionization energy is 738 kJ/mol, the second is 1451 kJ/mol and the third is 7733 kJ/mol. Once again the reason for the large increase between the second and third ionization energy is that removing the third electron means removing an electron from a lower shell, and disrupting a noble gas configuration. Taken together, we can conclude, that the energy it takes to disrupt a noble gas configuration is so prohibitively large that cations will be formed by removing electrons only until a noble gas configuration can be achieved. This explains why group 1 loses 1 electron, group 2 loses two and so on. Similar considerations involving electron affinity tell us that F will tend to gain one electron to achieve a noble gas configuration as will the other halogens, while group 6 elements will tend to pick up two electrons. Thus our knowledge of ionization energies and electron affinities allows us to understand some of the trends we discussed earlier.

## Lecture 16

Last time, I suggested that the structure of the outer shell of electrons in an atom was in some way responsible for its ability to form chemical bonds. What we'll be talking about for the next two weeks is **chemical bonding and the structures of molecules**. We'll be spending much of our time relating these structures to what we just learned about the structure of atoms.

**A chemical bond is any kind of attachment between atoms.** Why do these atoms attach to each other? Remember that for an atom, the best electronic configuration is a noble gas configuration, where all the s and p orbitals in the valence shell are filled. Remember that the **valence shell** is the outermost shell in which an atom has electrons. For example, in Na, the electron configuration is  $1s^2 2s^2 2p^6 3s$ . The highest shell in which there are electrons is  $n = 3$ , so the 3s electron is a valence electron. The rest of the electrons are called **core electrons**. Let's look at a couple of other quick examples together. Q: FOR CA, WHICH ARE THE VALENCE ELECTRONS? WHICH ARE THE CORE ELECTRONS? FOR SI?

GN Lewis came up with yet another way to abbreviate the electron configurations of atoms and molecules, called **Lewis symbols for atoms**, and **Lewis dot structures for molecules**. The structures are very simple. **The Lewis symbol of an atom simply takes the symbol for the atom and surrounds it with one dot for each s and p valence electron.** Let's quickly do the dot structures for the second row of the periodic table. { Li, Be, B, C, N, O, F, Ne} Notice that the first four electrons are added as single electrons, and the fifth through the eighth are used to create pairs of electrons, so that Ne is represented as being surrounded by four pairs of electrons. Notice also that our noble gas, with filled s and p subshells, has eight electrons around it. This is another representation of the **octet rule - "The stablest electronic configuration of an atom is when it has eight s and p electrons around it."** There are exceptions to this rule, but we will go over the

most important of these later in the chapter.

The problem is that only the noble gases start out with these configurations. We can give the other atoms a noble gas configuration by adding electrons or by taking them away, but then we are left with ions. Ions are not stable by themselves very long, so **atoms that don't have noble gas configurations will combine in a way that each gets a noble gas configuration.** This combination of atoms is a molecule. The forces that hold them together come from the way the electrons and nuclei in the molecules are arranged. **The forces that hold the molecules together are called chemical bonds.**

There are three types of bonds we'll mainly be concerned with. These are **ionic bonds, covalent bonds, and metallic bonds.** Of these we will deal with metallic bonds only briefly. The types of bonds depend on the way that the electrons are shared between the atoms.

The three types of bonds each have different properties. **Ionic compounds** generally are solids at room temperature with very high melting points, often around 1000°C. They are made up of combinations of metallic and nonmetallic elements. If we make solutions of ionic compounds or melt them they conduct well. **Their formation involves the transfer of electrons between atoms.**

The second type of bonding is **covalent bonding.** A covalent compound can be a gas, a liquid, or a solid at room temperature. Examples of covalent compounds are methane, the major component of natural gas; water, a liquid; and naphthalene, the major component of moth balls, a solid. They are usually composed of two or more nonmetals, but sometimes will be combinations of metals and nonmetals. Generally, solutions or liquids of these compounds do not conduct electricity. **A covalent compound is formed when electrons are shared between two atoms.**

The third type of bond is a **metallic bond**. Metals are almost always solid at room temperature. They are formed when large numbers of metal atoms share large numbers of electrons. Metals are excellent conductors of heat and electricity. This is because in the special types of bonds that occur in metals, electrons are especially mobile.

A useful question to ask at this point is whether there is any way that we **can predict whether a compound will be ionic or covalent**. The answer is that we can use electronegativities for crude predictions of this sort. Look in your book on page 228 in chapter 7 of the Seventh Edition, and on page 221 in Chapter 7 of the Sixth Edition and you'll see a periodic table with electronegativities assigned to each element. The **electronegativity is a measure of an atom's tendency to attract electrons to itself when combining with another atom**. The larger the electronegativity, the greater the tendency of the atom to attract electrons to itself. When we use electronegativities to predict bond types, the general rule of thumb is that **if there is a large difference between the electronegativities of the atoms in a compound that it will be ionic**. For example, Li has an electronegativity of 1.0 and F of 4.1, so the difference is 3.1 and the molecule is ionic. In contrast a molecule like  $F_2$  is completely covalent, since both atoms have the same electronegativity. A compound like HI would also be very covalent, since the electronegativity of H is 2.1 and I 2.2. If the difference in electronegativities is about halfway between 0 for completely covalent molecules and 3.2 for completely ionic molecules, then the compounds have some of the characteristics of both ionic and covalent compounds.

Using the electronegativity scale this way leads us to an interesting question - what does the difference in electronegativities have to be for a compound to be ionic. The crude rule here is that **if the atoms have an electronegativity difference greater than 1.7 the molecule will be more ionic than covalent, less than 1.7 more covalent than ionic**. Let's look at a few examples.

NaCl, NO, GeI<sub>2</sub>.

What determines **when an ionic bond will form, and when one won't form?** Let's consider the reaction to form NaCl. The reaction to form NaCl can be looked at as containing three steps, ionization of sodium,  $\text{Na} [\text{Ne}]3s^1 \rightarrow \text{Na}^+ [\text{Ne}] + e^-$ , adding an electron to Cl to form  $\text{Cl}^-$ ,  $\text{Cl} [\text{Ne}] 3s^2 3p^5 + e^- \rightarrow \text{Cl}^- [\text{Ne}] 3s^2 3p^6 = \text{Cl}^- [\text{Ar}]$  and finally, formation of the ionic compound from the ions -  $\text{Na}^+ + \text{Cl}^- \rightarrow \text{NaCl}$ . **If the overall process has a negative energy, i.e., energy is given off, then the ionic compound will form, while if the overall process has a positive energy, i.e. energy is required, then it won't form.** The energy of the first step is the **ionization energy**. This step always requires energy, but the energy required is relatively small if one is only removing one or two valence electrons from a metal. The energy of the second step is called the **electron attachment energy**, and this process usually releases energy if the atom has a high electronegativity. However, taken together the first two steps usually require energy. The energy of the final step is called the **lattice energy** and always releases energy. **If the energy released in the final step is large enough to overcome the energy required by the first two steps, then the overall reaction will release energy, and the ionic bond will form.**

We can represent the **formation of ionic compounds by using Lewis dot structures**. Let's look at the structure of LiCl. When we start out we have a Li atom with Lewis dot structure  $\text{Li}\cdot$  and a Cl atom with Lewis dot structure  $\cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{Cl}}}\cdot$ . Remember that when we form an ionic compound, the metal, which is less electronegative, loses an electron to the nonmetal. When this happens, our atoms are transformed into the ions  $\text{Li}^+$  and  $\text{Cl}^-$  with Lewis structures  $\text{Li}^+$  and  $\left[ \overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{Cl}}} \right]^-$ . If we combine these to form LiCl we get a Lewis structure for the ionic compound.

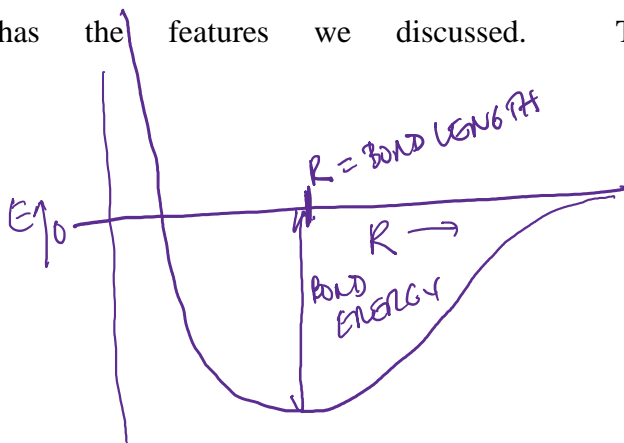
One way to determine the **strength of an ionic bond** is by measuring **the enthalpy of**



**dissociation,  $\Delta H_{\text{diss}}$ .**  $\Delta H_{\text{diss}}$  is the heat change when a gas phase salt molecule is dissociated into ions. In other words, if we have an ionic compound,  $\Delta H_{\text{diss}}$  is the heat change for the process  $\text{MX}(\text{g}) \rightarrow \text{M}^+(\text{g}) + \text{X}^-(\text{g})$ . For example, for the reaction  $\text{NaCl}(\text{g}) \rightarrow \text{Na}^+(\text{g}) + \text{Cl}^-(\text{g})$ ,  $\Delta H_{\text{diss}} = 548$  kJ/mol. The larger  $\Delta H_{\text{diss}}$  is, the stronger the attraction between the two ions, and the stabler the compound is.  **$\Delta H_{\text{diss}}$  shows some periodic behavior.** For example if we look at  $\Delta H_{\text{diss}}$  for the compounds of the halogens with Li, we find that that  $\Delta H_{\text{diss}}$  decreases as we go down the group from F to I. Similarly if we look at  $\Delta H_{\text{diss}}$  for compounds of F with the alkali metals we find that  $\Delta H_{\text{diss}}$  decreases as you go from LiF to KF. Let's see if we can figure out why. **OF THE THREE CATIONS WHICH IS SMALLEST?** So when we look at the trend in alkali metals, the stablest compounds form when the cation is smallest. **WHAT ABOUT THE HALOGENS? WHICH IS THE SMALLEST ANION?** So here again it is the smallest anion which yields the stablest ionic compound. We conclude that **an ionic compound is stablest when its two ions are as small as possible, and grows less stable as the ions increase in size.** Thus the stablest alkali halide is LiF, while the least stable would be FrAt. (Fr and At seem to be correlated to instability in college students as well.) **WHICH WOULD BE STABLER NABR OR RBI? KCL OR CSBR? NA CL OR MGO?** Notice in this last example, that another factor that affects the stability of ionic compounds is the magnitude of the charges on the ions. Since Mg and O have charges of +2 and -2 respectively, and attraction between charged species gets bigger when the charges get bigger, MgO will be stabler than NaCl.

Our second type of bond is a covalent bond. **In a covalent bond, electrons are shared between two or more atoms.** The electrons hold the atoms together because they sit between the two nuclei, and therefore can exert attractive forces on both nuclei. This attraction depends on the distance that the atoms are from each other. For example, if I hold two atoms at arm's length they can't have much effect on each other. On the other hand, if the atoms are too close together, they

repel each other because of the positive charges of the nuclei. In general, there is one distance called the **bond length**, at which the attraction of the two atoms is maximized. This is symbolized by a potential energy diagram, below. This is a graph of bond energy as a function of distance between the atoms. The zero of energy is taken to be the energy of the two separated atoms. Notice that it has the features we discussed. Two separated atoms



don't interact. If we bring the atoms closer together the bond forms, and the energy drops until it reaches a minimum energy, called the **bond energy**. The distance between the atoms at this energy is called the **bond length**. If we move the atoms closer together than the bond length they begin to repel and the energy increases. Notice that if we are at the bond length and move to either longer or shorter distances between the atoms, the energy increases. This means that if we move the atoms in a molecule away from their bond length, they will tend to move back.

It is important to realize that **when two electrons form a covalent bond they become paired**. In fact, the simplest model of a covalent bond, the electron pair model, due to G.N. Lewis, simply says that a covalent bond is created when one or more pairs of electrons is localized between a pair of atoms. For the case of two hydrogen atoms, when they form a chemical bond each hydrogen completes its valence shell. To see this, we look at the reaction using Lewis symbols.  $\text{H}\cdot + \text{H}\cdot \rightarrow \text{H}:\text{H}$ . We call a molecular structure made up from Lewis symbols a **Lewis**

**structure.** In the Lewis structure **the pair of electrons between the atoms represents the bond.** The bond is also often represented by a single line connecting the atoms. The line has the exact same meaning as the pair of dots.


Remember that the electrons are shared equally by the two H atoms. Since they are between the two atoms each atom feels almost the same effect as if it had two electrons all to itself. **To see if an atom in a molecule satisfies the octet rule, we count all the electrons that are around it, even if they are shared with another atom.** For example, in our structure of  $H_2$  both electrons are counted as belonging to the first hydrogen, so that it has a full two electrons, but both electrons are also counted as belonging to the second hydrogen.

**Let's see how many bonds can be formed by an atom.** To do this let's look at some elements in the second row of the periodic table and see how many bonds each can form with hydrogen. Li has one unpaired e- and can make one bond with H to form LiH. The Lewis structure is Li:H. Be has two unpaired electrons in its Lewis symbol and can make two bonds, to give  $BeH_2$ , with the dot structure H:Be:H. Boron has three unpaired electrons in its Lewis symbol and can make three bonds to form  $BeH_3$ , with dot structure  $H:\overset{\overset{H}{\cdot}}{\underset{\cdot}{B}}:H$ . Carbon has four unpaired electrons in its Lewis symbol and can make four bonds, to make  $CH_4$  with dot structure  $\overset{\overset{H}{\cdot}}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{C}}}}:H$ . We can see a pattern forming. **The number of bonds a main group atom can form is equal to the number of unpaired electrons it has in its Lewis symbol.** Let's go on to N and see if this holds. N has three unpaired electrons and one pair. It can make three bonds and our rule holds. We call the pair of electrons a **lone pair**. Notice that in our last two examples, our atoms have ended up with eight electrons surrounding them, in line with our octet rule.

So far in each molecule we've talked about the atoms have shared only one pair of electrons.

A bond in which one pair of electrons is shared is called a **single bond**. Sometimes two atoms will share two or even three pairs of electrons. For example, in carbon dioxide, the carbon shares two pairs of electrons with each atom. The dot structure is  $\text{:}\ddot{\text{O}}\text{:C:}\ddot{\text{O}}\text{:}$ . **A bond in which two pairs of electrons are shared is called a double bond**. Notice that since all four electrons in the double bond are shared, each atom still has a full octet. In carbon monoxide, carbon shares three pairs of electrons with the oxygen and has the Lewis structure  $\text{:C::O:}$ . This bond is called a **triple bond**. Again both the atoms in this bond still have a full octet.

There are two types of exceptions to the octet rule. The first is that sometimes an atom will form a stable compound without a full octet. For example, Be and Cl form the compound  $\text{BeCl}_2$ , which has the Lewis structure  $\text{:}\ddot{\text{Cl}}\text{:Be:}\ddot{\text{Cl}}\text{:}$ . We also saw this for the hydrides of Li, Be and B.

The other, more common, **type of exception is when an atom has more than eight electrons in its valence shell**. For example in the compound  $\text{SF}_6$ , with the dot structure , sulfur has 12 valence electrons. This can happen in the third row of the periodic table and above, because the d electrons allow the accommodation of up to 18 electrons for elements in these rows. **This exception is never found in the first or second row of the periodic table.**

Most of the examples so far have been compounds of two elements where one of the elements was hydrogen. We need to learn how to make Lewis structures for just about any compound. There are two reasons for this. The first is that these Lewis structures are our first introduction to bonding, and we can learn basic information about the structures of various molecules, most importantly, whether the bonds in the molecule are single, double or triple bonds. Secondly, at the end of this chapter, we'll learn a theory of the shape of molecules which is based

primarily on Lewis structures.

Determining the Lewis structure of a molecule shows two things, what is bonded to what, and where the valence electrons go. Unfortunately, the question of what is bonded to what is not always simple to determine. This is usually determined either by chemical means or by some form of spectroscopy, and is outside of what we'll be covering in this course. Nonetheless, before we start assigning electrons we have to know what is bonded to what, or, to put it differently, what the central atom is. For example,  $\text{CO}_2$  could have the arrangement  $\text{COO}$  or  $\text{OCO}$ . There is a **simple rule we can use to determine the central atom for most compounds**. You just **put the least electronegative one in the center**. So for example with  $\text{CO}_2$ , C has an electronegativity of 2.55 and O has an electronegativity of 3.44, so the C is in the center. For another example, in  $\text{SCN}^-$ , S has an electronegativity of 2.58, C has an electronegativity of 2.55 and N has an electronegativity of 3.04, so the C goes in the center. Finally in  $\text{PCl}_5$ , P has an electronegativity of 2.19 and Cl has an electronegativity of 3.16, so which one will be in the center? [P] Now if you look at the table of electronegativities in your books, you will notice that the rare gases don't have an electronegativity listed, and we will have to do Lewis structures for compounds involving rare gases. In this case the rare gas will always go in the center. Another exception is hydrogen, which almost never goes in the middle, for the simple reason that there are very very few cases in which H is capable of making more than one bond. So for example in  $\text{H}_2\text{O}$  and  $\text{H}_2\text{S}$ , the O and S will be the center atoms.

Notice that in cases like  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ ,  $\text{PCl}_5$ , and  $\text{SF}_6$ , if we arrange the other atoms around the center atom, that the distributions are very symmetric. There is a beautiful tendency in nature to favor these symmetric arrangements of atoms. However, we shouldn't take this too far. For example, in  $\text{N}_2\text{O}$ , the symmetry argument suggests that the structure would be  $\text{NON}$ , while the

actual structure is the one predicted by our electronegativity rule, NNO. In cases where the choice is between symmetry and the electronegativity rule, go with the electronegativity.

Once we work out the arrangement of the atoms, we have to decide on the distribution of electrons. There are six simple rules.

1) Arrange the atoms around the center atom.

2) Count all the valence electrons of the atoms. If the species is an ion add one electron for each negative charge, or subtract one electron for each positive charge.

3) Make single bonds between the central atom and all other atoms. This means that we put two electrons between them. Subtract the electrons you've used from the total.

4) Fill the octet on all remaining outer atoms. (Except for hydrogen.) HOW MANY ELECTRONS SHOULD HYDROGEN GET? [2]

5) If there are any remaining electrons put them around the central atom.

6) If the central atom still doesn't have an octet fill out its octet by creating double bonds, taking the extra electrons to make the double bond from the outer atom.

Let's do some examples. First HCN. H has an electronegativity of 2.2, C has an electronegativity of 2.55, and N has an electronegativity of 3.04, the arrangement will be HCN. Now we count valence electrons. H has one, C has 4 and N has 5 for a total of 10. We make single bonds between the C and H and C and N giving us H:C:N. We've used four electrons which leaves us with 6. Now we complete the octet around N with our 6 electrons. At this point C has only 4 electrons around it so we need to make a multiple bond between the C and the N. It is important to remember that when we make our multiple bonds we never take the electrons from the central

atom. We always use electrons from one of the outer atoms to make the multiple bond. So first we try moving two electrons from the N to the bond giving  $\text{H}:\text{C}::\overset{\cdot\cdot}{\text{N}}:$ . C still has only 6 electrons around it so we move another pair of electrons from the N to the bond to give  $\text{H}:\text{C}:::\text{N}:$ . Now the H has its two electrons and the C and N have their eight so we're done.

For a second example let's take  $\text{PCl}_3$ . We've already shown that P will be the central atom here, so the arrangement of the atoms will be  $\text{Cl}-\overset{\text{Cl}}{\text{P}}-\text{Cl}$ . Now we count the valence electrons. P has 5 valence electrons and the 3 Cl's have seven each, so the total is 26. We put two electrons between the P and each of the Cl's, which leaves us with twenty. Now we complete the octet around each of the Cl's, which leaves us with two remaining electrons which go on the P. At this point all of our atoms have octets so we're done.

Now let's look at another compound of P and Cl,  $\text{PCl}_5$ . Again P goes in the center. We count the valence electrons. P has 5, and the 5 Cl's have seven each for a total of 40. We make single bonds between the P and each of the Cl's, which uses 10 electrons and leaves us with 30. When we complete the octets around the Cl's we find we've used all of our electrons. The P has 10 electrons around it so it has more than an octet, so we're done. WHY CAN P HAVE MORE THAN AN OCTET AROUND IT? [d orbitals] COULD N HAVE MORE THAN AN OCTET AROUND IT? [No]

I'll do one final example of how to figure out a Lewis structure, with a rare gas compound  $\text{XeOF}_4$ . Remember that in rare gas compounds the rare gas goes in the center. WHAT'S OUR FIRST STEP? [Count valence electrons] Xe has 8, O has 6, and the 4 F's have 7 each for a total of 42. WHAT'S THE NEXT STEP? [Make single bonds between Xe and each of the outer atoms] This takes up 10 electrons leaving 32. WHAT'S THE NEXT STEP? [Complete octets on each of the outer atoms] This leaves 2 electrons that go on the center atom. Since the center atom has more than an octet,

we're done.

One of the things that our Lewis structures do is to tell us whether a compound has a single bond or a multiple bond. Why do we care? The answer is that **many of a molecule's properties, and much of its reactivity depend on the kind of bonds it has.** For example, in carbon compounds, triple bonds are more reactive than double bonds, which are in turn more reactive than single bonds. For example, acetylene, which is used in welding torches, burns with a tremendous release of heat precisely because it has a triple bond. We call the number of pairs of electrons involved in the bond the bond order. This is what we're referring to when we speak of a triple bond, a double bond or a single bond. Another property that is related to bond order is the bond length. As bond order increases, the bonds get shorter. So for example if we look at the series  $C_2H_6$ ,  $C_2H_4$ , and  $C_2H_2$ , the carbon-carbon bond length goes from 154 pm to 133 pm to 120 pm. In addition, as bond order goes from single to double to triple, the total bond energy increases and therefore the bond gets stronger. For example, if we look at the series  $C_2H_6$ ,  $C_2H_4$ , and  $C_2H_2$ , the carbon carbon bond energy goes from 347 kJ/mol to 620 kJ/mol to 812 kJ/mol.

We can experimentally determine bond order using **infrared spectroscopy.** **Infrared spectroscopy measures the frequency with which bonds vibrate.** In turn, **the frequency with which bonds vibrate can tell us what kind of bond we have.** To see this, realize that a bond connecting two atoms has a similar effect to a spring. If you have two balls attached to a spring and pull on one both start vibrating. The stronger the spring, the faster the balls vibrate. Since a triple or double bond represents a stronger spring, doubly or triply bonded molecules will vibrate faster, and will therefore absorb light of a higher frequency.