

Lecture 17

I'd now like to introduce the concept of **formal charge**. The reason that we are interested in formal charge is that it gives us a basis for choosing between different Lewis structures. Often there will be a case where the octet rule gives a Lewis structure that doesn't agree with experiment. For example, using our rules, sulfuric acid will have the structure $\text{H}-\overset{\text{O}}{\parallel}{\text{S}}-\overset{\text{O}}{\parallel}{\text{H}}$. However, if we look at the infrared spectrum of the molecule, it is apparent that the two oxygens that are not attached to hydrogen are more strongly bonded than the two that are. We can make a structure that accounts for this if both of these bonds are double bonds, but we have to violate the octet rule for this. In addition, BeCl_2 , which has the structure $\text{Cl}-\text{Be}-\text{Cl}$ violates the octet rule, since Be is surrounded by only four electrons. **Formal charges give us a tool to predict when we will have to violate the octet rule.**

Formal charge tells us how many more electrons an atom has in a Lewis structure than it would have as an isolated atom. **The formal charge of an atom in a Lewis structure is the charge that atom would have if it were assigned all of its lone pair electrons, plus one half of its bonding electrons.** The sum of the formal charges on all the atoms in a Lewis structure must equal the charge on the molecule or ion. **To calculate the formal charge of an atom in a molecule, you take its group number, and subtract the number of bonds it has and the number of electrons in lone pairs, i.e., the number of electrons not involved in bonds.** Let's look at some of the molecules for which we've just calculated structures. In $\text{H}:\text{C}:::\text{N}:$, H is in group I, has 1 bond, and no lone pairs, so its formal charge is $1 - 1 - 0 = 0$, so H has a formal charge of 0. The C is in group 4, and has four bonds, one triple and one single, and no lone pairs, so its formal charge is $4 - 4 - 0 = 0$. The N is in group 5, has three bonds and two electrons in a lone pair, and a formal charge of $5 - 3 - 2 = 0$. Note that the sum of all the formal charges is equal to the charge

on the molecule, 0. In contrast in carbon monoxide, which has the structure $\text{:C}::\text{O:}$, the C has formal charge $4-3-2 = -1$, while the O in group 6 has formal charge $6-3-2 = +1$. Note again that the sum of the formal charges matches the charge on the molecule, 0.

We can use formal charges to predict the most correct structure, if we say that **in general the best Lewis structure is the one in which the most atoms have a formal charge of zero, and the rest of the atoms have charges as close as possible to zero.** So for the example of H_2SO_4 , for the structure in which all the bonds are single, both H's have a formal charge of 0, but S has a formal charge of +2, and the two O's not bonded to H have formal charges of -1, so three atoms have formal charges. If we double bond both of these oxygens to the sulfur however, we find that all of the atoms in sulfuric acid have a formal charge of zero, and that this second structure is preferable. Thus we can modify our rules for determining Lewis structures so that **step 6 now reads, minimize formal charges by allowing multiple bonding from the outer atoms to the central atom.** Note that as in the case of sulfuric acid, the best structure may be one that violates the octet rule. This is OK, as long as the central atom is from the third period of the periodic table or higher.

Let's consider another case where experiments force us to refine relatively simple minded ideas about chemical bonding. Consider the polyatomic ion CO_3^{2-} . Let's work out its Lewis structure. C has an electronegativity of 2.55, while O's is 3.44, so C is the central atom. C has 4 valence electrons, the three oxygens have six each, and we add two for the negative charge for a total of 24 electrons. We start by making bonds between the C and the O's, which uses up 6 electrons. The remaining electrons we use to fill the octets on the oxygens. Now we're supposed to make multiple bonds to minimize the formal charges, so we had better find out what they are. For each of the oxygens, the formal charge is $\text{group } 6 - 1 \text{ bond} - 6 \text{ electrons in lone pairs} = -1$. For

the carbon, the formal charge is group 4 - 3 bonds = +1, so all four atoms have nonzero formal charges. So we'll make a double bond from one of the oxygens to the carbon. Now the carbon has a formal charge of group 4 - 4 bonds = 0 and the double bonded oxygen has a formal charge of group 6 - 2 bonds - 4 electrons in lone pairs = 0, so we have a better structure. At this point we have a Lewis structure which satisfies all of our rules.

If this structure were the correct one an infrared spectrum would show that there are two types of C-O bonds, one stronger than the other two. However, what infrared spectra show is that all of the bonds have the same strength. What is particularly interesting is that the strength of these bonds is intermediate between single and double bonds.

This is because of a phenomenon called **resonance**. If we look at CO_3^{2-} again, we see that we can draw two other Lewis structures that also satisfy our rules, each by putting the double bond on one of the other two oxygens. Notice that except for the position of the double bond the three Lewis structures are identical. **When we can write two or more correct Lewis structures without altering the positions of the atoms they are called resonance forms.** When we find that a molecule has resonance forms we indicate its structure by drawing two headed arrows between the various resonance structures. But which structure is correct? Well first of all, our spectrum tells us that all the bonds are the same strength, so none of the structures by themselves can be right. Nor can we have a structure in which the double bond switches from one oxygen to the other, because we would still be able to see two types of bonds in our infrared spectrum. The only way that we can make all three bonds equal is if the true structure is the average of the three resonance structures we have drawn. This effectively means that all three of the CO bonds in CO_3^{2-} have a bond order of $1\frac{1}{3}$. Sometimes we represent this by drawing dotted lines to represent the partial bonds.

Let's look at another couple of examples. One interesting example is ozone, a molecule that absorbs UV light, and serves to protect the biosphere from damaging solar radiation. It has the formula O_3 . Q: **What's the center atom?** [O]. The dot structure for ozone is $:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:O:$. However this is completely equivalent to the structure $:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:$. The true structure is intermediate between the true structures, with both bonds having a bond order of 1.5.

For another example, NO_2^- , like ozone, has eighteen electrons. We place two in our single bonds, fill out the octets and have two left which go on the N. To minimize formal charge we make a double bond between the N and one O, yielding the structure $:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}::\overset{\cdot\cdot}{\underset{\cdot\cdot}{N}}::\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:$, once again, the alternative structure $:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}::\overset{\cdot\cdot}{\underset{\cdot\cdot}{N}}::\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:$ is just as likely, and the true structure is the average of these.

A particularly important case of resonance is that of benzene, a molecule which is of great importance in organic chemistry. Benzene has the chemical formula C_6H_6 . It is a molecule of unusual stability and its structure eluded chemists for years until Kekulé realized that its carbons were arranged in a ring. A probably fanciful story has it that Kekulé fell asleep in front of his fireplace while thinking about the problem of benzene's structure, and dreamed of the worm Ouroboros, the snake that biteth its own tail, and when he woke up cried, "Of course, its cyclic!" For benzene we can draw two equivalent resonance structures, in both of which the single and double bonds alternate. If we take the average of these two structures, we find that benzene has a bond order of 1.5 for all six of its C-C bonds. It's as if the six electrons that make up the multiple bonds are smeared over all six of the bonds. When electrons are spread over some region this way we say that they are **delocalized**. To represent this, we often draw benzene like this, with a circle inside it to represent the delocalization of the electrons.

One effect that resonance has on molecules is to make them more stable. For example, if

we calculate the heat of formation of benzene based on just one of its resonance structures, it would be 230 kJ/mol. However, the actual measured heat of formation of benzene is 84 kJ/mol. Since a lower heat of formation means a stabler molecule, benzene is stabler than a single Lewis structure would indicate by 146 kJ/mol. We call this energy of stabilization the **resonance energy**. In general, we will find that molecules with resonance structures which result in delocalization of electrons will show some degree of this resonance stabilization.

Now let's consider another special case of bonding. Consider NH_3 . If we draw its Lewis structure we see that the nitrogen has a full octet, while making three bonds. Since it is in the second period of the periodic table, and can't expand its octet, we might expect that nitrogen can't have more than three bonds. However, there are times when nitrogen can have a fourth bond. For example, in the ammonium ion, NH_4^+ , nitrogen has 4 bonds. The reason this comes about is that ammonium ion is formed in a reaction between ammonia and a proton. In this reaction a covalent bond is formed between the lone pair of the nitrogen and the proton, which has no electrons to contribute to the bond. **A covalent bond in which both of the electrons come from one atom is called a coordinate covalent bond or a dative bond.** It is no different than any other covalent bond once formed, since both the electrons in the bond are shared by both atoms, it is just different in that both electrons came from the same atom. In fact, in ammonium, once the bond is formed, you can't tell which is the coordinate bond and which isn't. In this case all four bonds are equivalent. Another example of a coordinate covalent bond is one that is formed between ammonia, with an available lone pair, and boron trichloride, which doesn't have a full octet. Since the product is formed by combining two molecules it is called an **addition compound**. You will find out later that this is a form of acid base chemistry.

Coordinate covalent bonds are particularly important in the chemistry of transition metals.

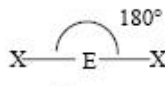
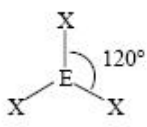
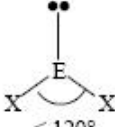
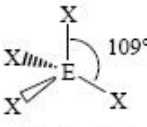
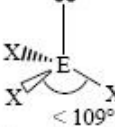
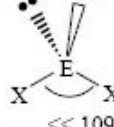
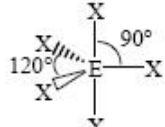
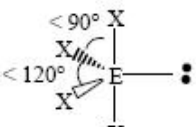
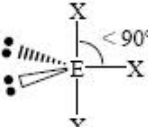
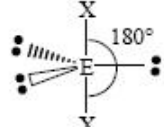
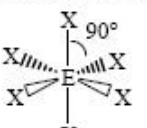
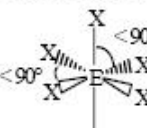
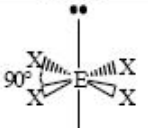
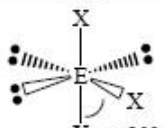
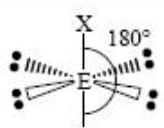
For example, Fe^{+2} reacts with carbon monoxide to form the stable compound $\text{Fe}(\text{CO})_6^{+2}$. In this compound, all six carbon monoxides form coordinate bonds with the iron. A coordinate covalent bond between iron and oxygen is responsible for the ability of hemoglobin to carry oxygen through your bloodstream.

Lecture 18

In the last couple of weeks, we've been discussing the structure of atoms and the bonding of molecules. We started out by talking about how the electrons are organized in an atom, and then continued with crude, but increasingly refined ideas about how electrons are distributed in a molecule, first starting with simple Lewis structures and then adding the concepts of formal charges, and resonance structures. However, in order to understand the reactivity of polyatomic molecules, and to understand how they interact with each other, we need information about the shapes of molecules, the way that the atoms are distributed in space.

The **shapes of molecules** are extremely important in chemistry. The polarity, solubility, stability and reactivity of molecules are critically dependent on their shapes, even to the point where two molecules with exactly the same molecular formula but with different shapes will have drastically different reactivities. We'll begin by discussing the shapes of molecules in which all atoms are bonded to a single central atom, and then move on in later lectures to models which can predict the structure of more complicated molecules.

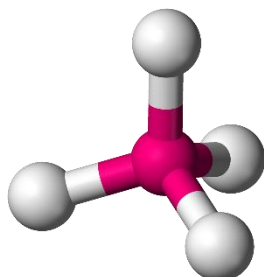
There are five basic shapes that describe almost every molecule with bonding to a central atom. They are called **linear, trigonal planar, tetrahedral, trigonal bipyramidal, and octahedral**. The reason that I call these basic shapes is that all centrally bonded molecules will have structures that are either close to these basic structures or are derived from these basic structures. The basic shapes are shown in the first column of the figure below.

VSEPR Geometries					
Steric No.	Basic Geometry 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs	4 lone pairs
2	 Linear				
3	 Trigonal Planar	 Bent or Angular			
4	 Tetrahedral	 Trigonal Pyramid	 Bent or Angular		
5	 Trigonal Bipyramid	 Sawhorse or Seesaw	 T-shape	 Linear	
6	 Octahedral	 Square Pyramid	 Square Planar	 T-shape	 Linear

A **linear molecule** is one where all of the atoms are in a straight line. If we define the **bond angle as the angle between two bonds connected to a central atom**, then all the bond angles in a linear molecule are 180° . An example of a linear molecule is CO_2 , which has the atomic arrangement OCO , and a bond angle of 180° .

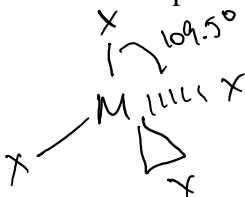
A **trigonal planar molecule**, also known as a triangular planar molecule, has all four atoms in the same plane. The center atom is in the center of a triangle and the three outer atoms are placed at the vertices of a triangle. The bond angles in a trigonal planar molecule are all close to 120° . The triangle could be an equilateral triangle as is the case of BCl_3 , or it could be a nonequilateral triangle, as in the case of BCl_2I .

The first two molecular shapes we've discussed have been planar. The final three are three dimensional. The first of these is **tetrahedral**. A tetrahedron is a pyramid with a triangular base. Here is a three dimensional rendering of a tetrahedral molecule. A tetrahedral molecule has its



center atom at the center of the tetrahedron and the four outer atoms at the vertices. The bond angles in a tetrahedron are all 109.5° .

It's hard to draw three dimensional structures, since the primary medium most of us have to deal with is planar, either a blackboard in my case or paper in your cases, and it may therefore be difficult to visualize three dimensional structures. One solution is the use of molecular model kits, which allow us to build structures in three dimensions. Another thing that chemists have done is to develop a set of symbols which allow us to represent a three dimensional object in three dimensions. Remember that all chemical bonds can be crudely represented as a line. If we look at the position of the line with respect to the plane of the black-board, there are three possible types of orientations. A line can be in the plane of the board, pointing behind the plane of the board, or pointing out from the plane of the board. The trick is to use a different type of line to represent each of these directions. A plain line stands for a bond in the plane of the blackboard. A dashed line is a bond going behind the plane of the board, and an elongated triangle is a bond coming out from the board. Thus, a tetrahedron can be drawn with two of its four bonds in the plane of the board, one going in and one going out, and would look like this.

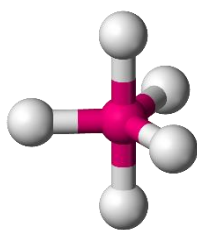


An example of a tetrahedral molecule would be methane, CH_4 .

The next structure is called a **trigonal bipyramid**. It has a central atom surrounded by five

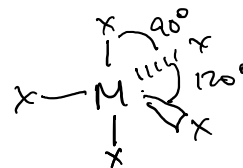
others. The structure has three of the atoms at the vertices of a planar triangle and the other two atoms directly above or directly below the triangle. For this reason the structure is sometimes symbolized by a triangle with a straight line through it. Unlike the other four of our basic structures, the bond angles in the trigonal bipyramid are not all the same. The three bonds in the triangular part have a bond angle of 120° , while the top and bottom bonds are 90° from the bonds in the triangle. Because there are two types of bonds, we have two different names for them. A bond in the triangle is called an **equatorial bond**, while the two bonds that are on top or on the

bottom of the molecule are called **axial**. Here's a three dimensional picture of a trigonal bipyramid.



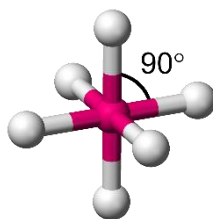
A symbolic rendering

would look like this:



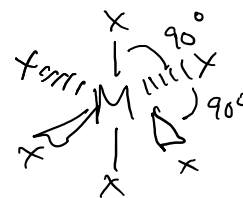
The final one of our basic shapes is called an **octahedron**. It consists of six atoms surrounding a central atom. Four of the atoms form a square around the central atom, while the other two atoms are directly above or directly below the square. For this reason the octahedron is sometimes represented by a square with a straight line running vertically through it. All of the bond angles in an octahedron are

the same and have a value of 90° . Here's a three dimensional picture of an octahedral molecule:



Here is a symbolic

representation of an octahedral molecule:



At this point there are two logical questions to ask. The first is “There are many other possible shapes of molecules. Where do they come from?” The second is “How do we determine which molecules have which shapes?” A model of molecular shapes called VSEPR theory, short for Valence Shell Electron Pair Repulsion, can give the answer to both questions. The idea of

VSEPR should be familiar by now, since it's based on Coulomb's law. The idea is that in any molecule that consists of atoms bonded to a central atom, the central atom is surrounded by electrons, either from covalent bonds, or from lone pairs. According to Coulomb's law, the stablest arrangement of bonds and lone pairs will be the one that keeps the electrons farthest apart. VSEPR simply lists the arrangements of lone pairs and bonds that keep the electrons farthest apart.

The way we use VSEPR is first to do a Lewis structure for the molecule we are interested in. Then we count the total number of bonds and lone pairs that surround the center atom. For this purpose, we count multiple bonds, if any, as one bond, and any single unpaired electrons will have the same effect as a lone pair. **The number of bonds and lone pairs determines which of the basic structures we will see. The actual structure we see will be the basic structure if the central atom is surrounded only by bonds, and will be derived from the basic structure if the central atom is surrounded by a combination of bonds and lone pairs.**

Let's go through all the cases. We will identify each case by a number n , where n is the total number of bonds and lone pairs surrounding the central atom. Your handout calls this the steric number.

The simplest case is for $n=2$. The only way that n can equal 2 is for a triatomic molecule with two bonds and no lone pairs, as in the case of BeCl_2 or CO_2 . The basic structure and actual structure for $n = 2$ are the same, and are both **linear**.

The next cases are for $n = 3$. **For molecules with $n = 3$, the basic structure is trigonal planar.** If all three electron pairs are in bonds, the actual structure will also be trigonal planar. An example of this is BCl_3 , which has the Lewis structure. $\begin{array}{c} \text{Cl} \\ | \\ \text{B} \\ | \\ \text{Cl} \end{array}$. We call a molecule like BCl_3 an MX_3 molecule, where M stands for the center atom and the X for outer atoms. The outer atoms

are not necessarily all the same element.

The other $n = 3$ case is one where the center atom is surrounded by two bonds and a lone pair. In this case the actual structure is different from the basic structure. This is because **the actual structure is a description of the arrangement of the atoms in the molecule**. In this case the lone pair and the two outer atoms are arranged in a trigonal planar structure, but the three atoms, whose positions are the ones we are interested in, are arranged in a bent structure. The bond angle in this case will be slightly less than the 120° we expect for a trigonal planar basic structure, because a lone pair of electrons takes up more space than electrons in a bond. We call this case MX_2E , where the E indicates a lone pair. A classic example of this is the radical methylene, CH_2 , which is important in the chemistry of flames.

The next group is for $n = 4$. We will consider three cases, MX_4 , MX_3E and MX_2E_2 . **The basic structures of all three will be tetrahedral**. For MX_4 the actual structure will be tetrahedral as well. Another example of this type of molecule is carbon tetrachloride, CCl_4 . For MX_3E one of the positions is occupied by a pair of electrons, and the structure of the atoms is called a trigonal pyramid. It looks like a squashed tetrahedron, except the center atom is at one of the vertices of the tetrahedron instead of in the center. Again, because the lone pair takes up more space than the bond, the bond angles are somewhat smaller than the 109.5° expected for a normal tetrahedron. An example of this is ammonia, NH_3 . For MX_2E_2 , two of the vertices are occupied by electron pairs, so the result is a bent molecule with bond angle slightly less than 109.5° . An example of this is water, H_2O .

Our next case is $n=5$. We will consider 4 cases here, MX_5 , MX_4E , MX_3E_2 , and MX_2E_3 . **The basic structure for all of these cases is the trigonal bipyramid**. For the case of MX_5 , the

actual structure is the same as the basic structure, the trigonal bipyramid. For MX_4E , one of the positions is taken by a lone pair. Remember that **we have two types of positions in a trigonal bipyramid, the axial and equatorial, which are not equivalent**. So which gets the lone pair? The answer is that the lone pair will go in the position that gives the greatest distance from the other electrons. If we put it in an equatorial position, it is 120° away from two atoms and 90° away from two atoms. If it is in an axial position it is 90° away from three atoms, so there is more space in an equatorial position, and that's where the lone pair goes. In fact, for MX_3E_2 both electron pairs will go in equatorial positions, and for MX_2E_3 all three electron pairs will go in equatorial positions. The resulting structures are called a see saw for MX_4E , as in the case of SF_4 , T shaped for MX_3E_2 , as in the case of ClF_3 , and linear for MX_2E_3 , as in the case of I_3^- . A special case we need to consider is the case of MX_5 where there are two types of outer atoms, as in PCl_3I_2 . In this case the less electronegative atom, I, goes in the equatorial position. If you have a case like MX_4E , with two different types of outer atom, as in the case of SF_2Br_2 , the electron pair goes in the first equatorial position and is joined there by the less electronegative atoms, the Br's.

This leaves, **$n = 6$, which will have the octahedral basic structure**. The cases here are MX_6 , MX_5E , MX_4E_2 . There are two other possible combinations, MX_3E_3 , and MX_2E_4 but they are never found to occur in nature. MX_6 will simply have an octahedral structure as in the case of SF_6 . MX_5E has an electron pair in any one of the positions and results in a structure called a square pyramid, where four of the atoms are at the vertices of a square and the fifth is directly above the center. An example of this is BrF_5 . For MX_4E_2 it is important for the electron pairs to be as far apart as possible, so one will go above the plane and one below, yielding a square planar structure, as in the case of XeF_4 .

Let's do two quick examples. PO_4^{3-} has the Lewis structure. $\left[\begin{array}{c} \text{O} \\ | \\ \text{O} = \text{P} - \text{O} \\ | \\ \text{O} \end{array} \right]^{-3}$. There are 4

bonds, and no lone pairs, so this is an MX_4 case and will be tetrahedral. For another example, we have XeO_3 , which has the structure $\begin{array}{c} \text{O} \\ | \\ \text{Xe} = \text{O} \\ | \\ \text{O} \end{array}$. This is the case MX_3E , and means that XeO_3 will be a trigonal pyramid.

At this point it is reasonable to look at our covalent bonds and ask the question “Even if two atoms share the electrons in a covalent bond do they always share them equally?” For example, consider hydrogen fluoride, HF. It's a covalent compound, but if you look at your electronegativity charts you will find that F is considerably more electronegative than H. Remember that electronegativity is the tendency of an atom in a molecule to pull electrons toward itself. So we could imagine that even though the H and the F are sharing the electrons, since the F is pulling on them harder, they spend more of their time near the F than near the H. In other words, F is getting a bigger share of the electrons in the bond. This means that the F will have a small negative charge and the H will have a small positive charge, which we indicate by writing a δ^- over the F and a δ^+ over the H, where the δ 's indicate a fractional charge. In fact we will find that in any bond in which the electronegativities of the atoms are different, that the sharing of the electrons will be somewhat unequal. We say **that a bond in which the sharing of electrons is unequal is polar.**

This distribution of electrons between the atoms in a bond is very important in chemistry. It determines the melting point of solids made up of covalent compounds, it determines what solutes dissolve in what solvents, and it even determines some of the ways that light is absorbed or emitted by molecules. For this reason, it is useful to have some means of quantifying just how polar a molecule or bond is. The quantity that we use is called the **dipole moment**, defined as the product of the charge on the positive end of the molecule with the bond length. We show that a molecule or bond has a dipole moment schematically by drawing an arrow from the positive end

of the bond to the negative end of the bond. A molecule like HF, where there is a large difference in electronegativity between the atoms, has a large dipole moment and is very polar. A molecule like I_2 , where the two atoms have no difference in electronegativities, will have no dipole moment and is called a **non-polar** molecule.

When we deal with a molecule with 3 or more atoms we determine the dipole moment of the molecule by adding the arrows which show the dipole moments of each bond. This uses a technique that some of you may have learned called vector addition. For example, in H_2O , O has a higher electronegativity than H, so both bonds will be polar. We can draw two arrows to indicate the dipole moments for the bonds. **To get the dipole moment of the molecule we add the arrows by placing them head to tail and drawing a line from the tail of the first arrow to the head of the second arrow.** So we see from this that the water molecule is also polar.

One of the implications of this way of determining the dipole moment of a molecule is that **there will be molecules with polar bonds that have no overall dipole moment and will therefore be non-polar.** Consider for example carbon dioxide, which has the structure $O=C=O$. Since C is less electronegative than O, both bonds will have dipole moments. The arrow for each bond will go from the positive end of the bond, the carbon, to the negative end, the oxygen. To determine the dipole moment of the overall molecule we place the head of the first arrow at the tail of the second, and draw a line to connect. However, since the arrows are the same length, and are pointed in exactly the opposite directions, the arrows cancel and carbon dioxide has no dipole moment, and therefore is non-polar. This should make qualitative sense to us, if we think about what's going on. On one side of the C, an O is pulling electrons toward itself. On the other side the same thing is happening. Since the O's are identical, they pull with the same intensity, and the polarities cancel out.

Lecture 19

VSEPR theory is very nice, because it gives qualitative geometries for a wide variety of molecules, and you only need to know the Lewis structure. However, it doesn't tell you exact geometries, for example the exact bond angles of the NH bonds in ammonia, it doesn't tell you bond lengths, it doesn't tell you anything about how strong the bonds are and most importantly it produces an anomaly: the structure of the trigonal bipyramid. Remember that the simple rationale for VSEPR is that we find structures where the electrons are as far apart as possible. In all such structures the bond angles of all the atoms should be the same. Yet in the trigonal bipyramid we have two drastically different bond angles, 90° and 120° . Experiments show that this structure is correct, yet VSEPR cannot predict this structure but must take it as a given. Clearly, to explain this we need a more sophisticated theory of chemical bonding.

One useful theory of chemical bonding which can explain many of the things which VSEPR can't and in addition can predict the structure of the trigonal bipyramid is the **Valence Bond Theory**, developed in its earliest forms by Heitler and London, and championed in this country by Linus Pauling. His book, The Nature of the Chemical Bond, provided the title for an advanced chemistry course that Dr. Donald teaches, and is still considered a classic.

We start our treatment of the valence bond theory by asking a simple question. We know from the Lewis theory that a chemical bond forms when two electrons are shared by two atoms. We know that when the electrons are on the atoms, they reside in certain areas in space called orbitals. For example, an electron in a 1s orbital resides in a sphere, while a 2p electron resides in a double bowling ball arrangement. But where do the electrons in a chemical bond reside? We know that they sit somewhere between the two atoms but what can we say beyond that? It is logical to extend the idea of orbitals, which we introduced for atoms, and say that **the electrons in**

a bond are also located in an orbital. This should make sense, since this is just another way of saying that the electrons are limited to some region of space, and we already know that they have to stay somewhere between the two atoms. Since this new orbital is the space in which we find the electrons when they form a chemical bond, we call it a **bonding orbital**.

What does a bonding orbital look like? To answer this, let's consider two H atoms. Each of them has one electron in a 1s orbital. What happens as we bring them together to form a bond? If we don't bring them close enough that the two orbitals touch, nothing happens. If the two electrons are not somehow in the same region of space, they can't be paired and can't form a bond. Now let's bring them close enough together that the orbitals overlap just a little bit. We can draw a new orbital for the atoms by combining the two 1s orbitals. The space between the two hydrogen nuclei now consists of three regions. The region closest to each nucleus will have only one electron in it just like the hydrogen atom. The little region where the two orbitals overlap is a space that can have both electrons in it. In other words, this region of overlap can have paired electrons, i.e., a bond. Since the space where the electrons are paired is only a tiny bit of the space between the nuclei, the electrons will only be paired a small portion of the time and the bond will be weak.

Now let's bring the atoms together so that there is a high degree of overlap between the 1s orbitals. When we draw a new orbital for the molecule, we find that the electrons are paired almost everywhere between the two nuclei. Since the space where the electrons are paired is most of the space between the two nuclei, the electrons spend most of their time paired, and a strong bond is formed.

This is the basis of the Valence Bond Theory, which can be stated as three postulates. 1)

When two atoms form a covalent bond, a valence atomic orbital on one of them overlaps

with a valence atomic orbital on the other. By overlap we mean that the two orbitals share some region of space. The orbital that results from this overlap is called a bonding orbital. **2) A maximum of two electrons with their spins paired can be shared in a single bonding orbital, and the electrons will spend most of their time between the two nuclei.** This should make sense - if we have a Pauli exclusion principle for orbitals in atoms it seems natural that we should have one for orbitals in molecules. **3) The strength of the bond depends on the amount of overlap - the more overlap the stronger the bond.**

These three rules can explain the formation of our bond between two H atoms to form H₂. As we've already shown, the 1s orbitals on the H atoms overlap to form a new orbital, and when two electrons occupy this new orbital a bond is formed. **When a new orbital is formed from two s orbitals it is called a σ orbital.**

The rules can also explain the bonding in HF. Fluorine's electronic structure is 1s² 2s² 2p⁵. To form a bond, we first create a new orbital for the bonding electrons by overlapping the H 1s orbital with one of the valence orbitals and then putting the electrons into it. But which orbital do we use? If we use the 2s orbital or one of the filled 2p orbitals, we can create the new orbital but then we would have to put three electrons into it, the two originally in the orbital + the hydrogen electron. Since our Pauli exclusion principle says that we can only have two electrons in an orbital this won't work. This means that our bond will be formed between the half filled p orbital on the F and the half filled 1s orbital on the H. Notice that this use of the Pauli exclusion principle extends our idea of bonding from the dot structures. In that case we learned that bonding occurs from the sharing of electrons between electron deficient atoms. Now we extend it to the idea that **bonding occurs between the electron deficient parts of atoms. This bond between an s orbital and a p orbital is also called a σ orbital.** In the valence bond model of bonding all single bonds are σ

bonds.

We begin to run into trouble when we consider H₂O, water. Oxygen has the structure O $\frac{\uparrow\downarrow}{1s} \frac{\uparrow\downarrow}{2s} \frac{\uparrow\downarrow \uparrow \uparrow}{2p}$, with two unpaired p electrons. According to our new model, we can form two bonding orbitals by overlapping a hydrogen 1s orbital with each of the two unfilled p orbitals of O. So far, so good. But remember that the 3p orbitals are along the x, y and z axes, and are therefore 90° from each other. This means that if our bonds formed between H 1s and O 2p orbitals that they would be 90° apart. Experiment tells us that they are actually 104.5° apart. To deal with this discrepancy, we need to refine the Valence Bond Theory by introducing the idea of **hybrid orbitals**.

To see how hybrid orbitals come about consider C. It has the atomic valence structure C $\frac{\uparrow\downarrow}{2s} \frac{\uparrow\downarrow \uparrow \uparrow}{2p}$. If we use our simple bonding theory, we would predict that bonds would form between the two half-filled 2p C orbitals and hydrogen atoms to form CH₂. However, this molecule is extremely unstable and the simplest stable compound made of carbon and hydrogen turns out to be CH₄, methane. We could deal with this problem if we spread the four electrons out to get C $\frac{\uparrow\downarrow}{1s} \frac{\uparrow}{2s} \frac{\uparrow \uparrow \uparrow}{2p}$, which has 4 half-filled orbitals and can form 4 bonds. There's still a problem with this, though. The three p orbitals are all at right angles to each other. If we make three bonding orbitals with the p's they'll be at right angles to each other too, while the bonding orbital made with the 2s orbital could be in any direction. In other words, we expect that the 2s and 2p orbitals of carbon will make bonds that are different in some way, since they are formed from different atomic orbitals. There are two problems with this. First, VSEPR predicts, and experiments confirm, that the bond angles between the four CH bonds in methane are 109.5°, and that methane has the shape of a tetrahedron. In addition, experiment shows that all four CH bonds

in methane are the same in every way.

We can solve this problem completely if we combine the four available orbitals on carbon, the 2s and the 3 2p's, to make four new completely equivalent orbitals. The four new orbitals are called **sp³ orbitals**, since they are made from 1 s and three p orbitals. All four sp³ orbitals are made up of 1/4 of an s orbital and 3/4 of a p orbital. These new orbitals are one type of **hybrid orbital**. Each of the sp³ orbitals looks like a cross between an s orbital and a p orbital. [Draw s orbital, p orbital and sp³ orbital]. Each of the four sp³ orbitals is now identical, except that they point in different directions. The directions of the four sp³ orbitals form a tetrahedron, exactly the structure predicted by VSEPR.

I'd like to point out three things here. First, these hybrid orbitals only form when the carbon atom is bonding with other atoms. If the hydrogen atoms were not present, the hybrid orbitals would not form. Second, notice that **we started out with four orbitals, the s orbital and the three p orbitals, and ended up with four orbitals, the 4 sp³ orbitals**. It will always be the case that **after making hybrid orbitals we always end up with the same number of orbitals we started out with**. Finally note that these hybrid orbitals are still atomic orbitals. They can be used to form bonding orbitals, but are themselves just new types of atomic orbitals.

What are the energies of these hybrid orbitals? If we draw an energy level diagram, the 2p orbitals will be at a higher energy than the 2s. When we make our hybrid orbitals, just as their shape is in between the shape of an s orbital and a p orbital, so is their energy. Notice that **all four sp³ orbitals have the same energy**.

Now that we have these four sp³ orbitals, we can use them to make bonds just as we used atomic orbitals earlier. For example, in CH₄, we place our four valence electrons in the hybrid

orbitals according to Hund's rule. We now make our CH_4 molecule by overlapping each carbon sp^3 orbital with a hydrogen $1s$ orbital. It turns out that if we do this not only are all four bonds equivalent, but the shape of the molecule is tetrahedral, the shape we get from VSEPR for a MX_4 molecule.

We can also use this hybridization for molecules where some of the electrons are in lone pairs. For example, in H_2O , we combine the $2s$ and $2p$ orbitals to make 4 sp^3 hybrid orbitals. When we place our six valence electrons in the four orbitals, two of the orbitals are filled. We now use the remaining two to form two bonds by overlapping their orbitals with the hydrogen $1s$ orbital.

There are many different orbitals in valence bond theory, but only **five hybrid orbitals** are necessary to describe the vast majority of molecules. Each of the five yields a different molecular shape. They are named for the atomic orbitals they are formed from. The first of these five orbitals is the **sp orbital** which comes from combining one s orbital and one p orbital. The two sp orbitals are pointed 180° from each other, and can hold two electrons each, so an atom with sp hybridization can make two sigma bonds. If we look at our energy level diagram, we start out with an s orbital and three p orbitals. After we make our sp orbitals we have the two sp orbitals with energy intermediate between s and p , and two p orbitals, at their original energy. The two p orbitals will either stay empty or will be used in multiple bonding, which we will talk about shortly.

The second type of hybrid orbital is formed from 1 s and 2 p orbitals and is called **sp²**. There are three of these sp^2 orbitals and they have a trigonal planar geometry, each 120° from the next. If we look at the energies for these orbitals, we find that we have three sp^2 orbitals with energies in between s and p , and the remaining p orbital at its original energy.

The third is formed from 1 s and 3 p orbitals and is called sp^3 . The four sp^3 orbitals are arranged in a tetrahedron, with angles of 109.5° separating them.

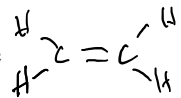
Now we want to consider hybrid orbitals for compounds that make more than four bonds. What does an atom need in order to make more than four bonds? [d orbitals] So our fourth type of hybrid orbital is formed from 1 s, 3 p and 1 d orbital and is called sp^3d . The five resulting orbitals have the shape of the trigonal bipyramid, with the three central orbitals separated by 120° and the top and bottom orbitals at 90° from the trigonal plane.

The final type is formed from 1 s 3 p and 2 d orbitals and is called sp^3d^2 . The six resulting orbitals are all ninety degrees apart and form an octahedron. Note that in forming our five types of hybrid orbitals we've reproduced the five types of basic structures we used in VSEPR theory.

How do we tell which type of hybrid orbital to use? For molecules with a central atom bonded to outer atoms, we only have to look at the number of valence electrons. An example is BeH_2 . The Be has the valence configuration $Be \begin{array}{c} \uparrow\downarrow \\ 1s \end{array} \begin{array}{c} \uparrow\downarrow \\ 2s \end{array} \underbrace{\quad \quad \quad}_{2p}$, but to make two bonds, we first need to form two half filled sp orbitals, by combining the 2s and 2p orbitals. We now create the BeH bonds by overlapping the sp orbitals with the 1s orbital of H. In addition, for all other elements in group 2A, we have two valence electrons and we can make two bonds, so we'll have sp hybridization.

Let's look at BCl_3 . Since the boron has three valence electrons, we need to make three hybrid orbitals so we can make three bonds. The three orbitals we use to form the hybrid orbitals will be one s and two p orbitals, so our hybridization will be sp^2 . For the rest of group 3, we'll have sp^2 hybridization as well. For group 4, we can make 4 bonds, so the hybridization will be sp^3 . An example is methane, which we treated earlier.

For higher groups it depends on what period we are in. In the second period, we have no d orbitals, so the rest of the atoms, C, O, and F, will all use sp^3 orbitals to make their bonds. In the third period, however, the d orbitals are available. For these atoms in the third period and above, the only way to determine the hybridization is to count the number of orbitals necessary to make the number of bonds we need. For example, S can form two compounds with F, SF_4 and SF_6 . S has the configuration $[Ne] \uparrow\downarrow \uparrow\downarrow \uparrow \uparrow$. To make SF_4 , we need 4 half filled orbitals so we promote 1 electron, and use the 5 orbitals to make 5 sp^3d orbitals. Four of the orbitals are used to bond the F's, while the fifth accommodates the lone pair. SF_6 needs 6 bonds, so we promote two electrons to create 6 half filled orbitals, and now use them to create 6 sp^3d^2 orbitals, all of which are now used to make bonds with F.

Valence bond theory has the added advantage that it can explain **multiple bonding**. Remember that in a multiple bond two or three pairs of electrons are located between two atoms. An example is the organic molecule ethylene which has the Lewis structure . How can we explain its bonding? If we sp^3 hybridize our carbon atoms, and overlap two of the orbitals, we can still put only two electrons between the two carbons! This is because the Pauli Exclusion principle holds for bonding orbitals just as it does for atomic orbitals. We can get a hint if we look at the structure of ethylene. Experiments show that all the bond angles in ethylene are 120° . WHAT HYBRIDIZATION DOES THIS MEAN THE ETHYLENE CARBONS HAVE? [sp^2] This means that each carbon will have 3 sp^2 orbitals and one unhybridized p orbital. We still need four bonds for each carbon, the two CH bonds and the C=C double bond, so we'll put one electron in each orbital. Now we can overlap an sp^2 orbital from each carbon to make a CC single bond, and overlap hydrogen 1s's with the other sp^2 's to make the four CH bonds.

This leaves two electrons sitting in the p orbitals. They're sitting right next to each other.

What happens is that their orbitals are close enough that they overlap sideways to make the second carbon-carbon bond. So you see a double bond contains two different kinds of bonds, one where the two orbitals overlap by pointing at each other, called a σ bond, and the other where the bonding orbitals overlap sideways, called a π bond. It is important to realize that in the valence bond model, we never make a π bond unless we have already made a σ bond.

Now remember that the p orbitals have a node, where you never find the electron, so it seems logical that a π bond, which is made from p orbitals, will also have a node. We can see this if we draw the bond sideways. Notice that the node is exactly where the electrons from the single bond would be, so that we aren't putting more than two electrons in the same space.

Let's see if we can figure out how triple bonding works. Acetylene, HCCH, is the simplest triple bonded compound. It is a completely linear molecule. WHAT MUST THE HYBRIDIZATION OF ITS CARBONS BE? [sp] This means that the 4 valence electrons sit in 2 sp orbitals and 2 unhybridized p orbitals. We can make our C-C bond by bringing two C sp orbitals together, and then our two CH bonds by overlapping the H 1s with the other two C sp orbitals. This leaves 4 p orbitals with 1 electron each. We can overlap two sideways to make 1 π bond as before. This leaves two p electrons, right next to each other, pointing out of the board. They can make a π bond too! Just as the two p orbitals on the original carbon are at right angles to each other, the two π bonds are at right angles to each other.

We see that for a single bond we just have a sigma bond, with the orbitals pointing at each other. These sigma bonds can be made up of any two kinds of orbital as long as they point at each other. A double bond has one σ bond and 1 π bond, and a triple bond one σ bond and two π bonds.

Lecture 20

We see that Valence Bond Theory has many successes. It yields the structures of many molecules based only on first principles and teaches us much about the nature of bonds and especially of multiple bonds. Furthermore, the simple relationship between the bonding orbitals and the geometries of molecules is particularly clear in Valence Bond Theory. Unfortunately, when dealing with double bonds Valence Bond Theory has one of the same drawbacks as Lewis structures - it is still necessary to average resonance structures to obtain realistic structures for molecules like benzene, NO_2^- or CO_3^{2-} . Furthermore, if one does experiments that measure the energies of the electrons in bonds, one finds that valence bond theory gives incorrect results. Note that once again we are being motivated to bring up new theories by results of increasingly more sophisticated experiments.

The theory which best explains chemical bonding is called the **Molecular Orbital Theory**, developed primarily by Robert Mulliken of the University of Chicago, and Friedrich Hund, of Hund's Rule. To see where this theory is coming from, let's do a brief history of orbitals. In the beginning, there were **atomic orbitals**. They were portions of space in which we could find the electrons of an atom. And the electrons in the orbitals were the first day.

Then we wanted to describe the way that atoms combine to make molecules. To do this we took the valence orbitals of two atoms, and combined them to make bonding orbitals. This is where we get the name valence bond theory, because only the valence electrons sit in new orbitals and only the **valence orbitals** are involved in bonding. And the electrons in the valence orbitals were the second day.

Then we discovered that if we made bonds using our atomic valence orbitals they didn't

give the right molecular shape. In order to get the right shape, we had to combine the valence orbitals to give **hybrid orbitals**. The hybrid orbitals on two or more atoms are then combined to make bonding orbitals. Notice, however, that when we make bonding orbitals, we are still only using the valence orbitals. So the electrons in the valence hybrid orbitals were the third day.

Molecular orbital theory says that it's not just the valence orbitals that change when a molecule is formed, but all of the orbitals in the atom. When you bring two atoms together to make a molecule, **all of the atomic orbitals combine** to make a new set of orbitals called **molecular orbitals**. Unlike valence bond theory, in which all electrons either sit on atoms or are involved in bonds, in molecular orbital theory, orbitals extend over the whole molecule, and therefore electrons are not limited to the same small volume of space that they resided in in atomic form. So the electrons in the molecular orbitals were the fourth day. Before I go on I'd like to point out that we're only up to the fifth day right now, and the fifth day is something called electron correlation, but you probably won't see this until graduate school.

Another name for Molecular Orbital Theory is Linear Combination of Atomic Orbitals (LCAO). The LCAO theory says that we get molecular orbitals by adding or subtracting atomic orbitals. To see how this works we'll first look at hydrogen. The Lewis structure says that its structure is H:H. Hydrogen is composed of two hydrogen atoms, each of which has an electron in a 1s orbital. The LCAO says that we combine these two 1s orbitals to make a σ bond with two electrons in it.

As was the case with atomic orbitals and VSEPR theory, there are some rules we need to follow in adding together atomic orbitals to get molecular orbitals.

- 1) We can get molecular orbitals by either adding or subtracting atomic orbitals.

2) The number of molecular orbitals equals the number of atomic orbitals used to make them. In other words, if I use two atomic orbitals to make molecular orbitals, I get two molecular orbitals out. This is often referred to as conservation of orbitals.

3) When you add atomic orbitals to make molecular orbitals the atomic orbitals must be as close in energy as possible. For example, when we make molecular orbitals for O_2 , we can make molecular orbitals by adding 1s orbitals to 1s, but not 1s to 2p, because the energy difference is too high. However, when we make H_2O we have no choice but to add 1s from hydrogen and 2p from oxygen together, since they are the closest in energy (the higher nuclear charge of O lowers the energy of the 2p orbital until it is close enough to the hydrogen 1s energy.) We often find, though, that within a shell, orbitals from different subshells can be close enough in energy to combine. For example, while in O_2 the 2s orbitals combine to make a pair of molecular orbitals and the 2p orbitals combine to make six molecular orbitals, in N_2 , where the 2s and 2p electrons are closer in energy, the situation is more complicated. Here some of the orbitals have contributions from both s and p atomic orbitals.

4) Adding orbitals together (positive overlap) gives what is called a bonding molecular orbital.

5) Subtracting orbitals (negative overlap) gives an **antibonding molecular orbital**. (Note that this is a new feature of molecular orbital theory, since valence bond theory only included bonding orbitals)

6) A sigma bond is cylindrically symmetric about the intermolecular axis, the axis connecting the atoms.

- 7) A pi bond has a nodal plane that contains the bond axis.
- 8) Nonbonding Molecular Orbitals are unchanged atomic orbitals. (These only occur in heteronuclear molecules.)
- 9) Antibonding orbitals have a nodal plane perpendicular to the bond axis.

Let's do some examples and see how this works. For the hydrogen molecule, each H has an s orbital with an electron in it. We can either add or subtract them but we need to end up with two molecular orbitals, since we started out with two atomic orbitals. We get the first orbital by adding the two atomic orbitals in phase, and it looks like this.

The electron density is spread over the entire hydrogen molecule, but is concentrated between the two nuclei. **This orbital is called a σ bonding orbital.** The second orbital is obtained by subtracting the two 1s orbitals, which results in the electron density being higher on the outside of the two nuclei, so that there is a net positive charge between the two nuclei and they repel. This second kind of orbital is called an **antibonding orbital and is symbolized by σ^* .** Each orbital can hold up to two electrons. **Each electron in a bonding orbital increases the bond order by 1/2, while each electron in an antibonding orbital decreases the bond order by 1/2.** Electrons in nonbonding orbitals do not affect the bond order.

Remember that when we talked about filling atomic orbitals we used an energy level diagram to determine the order in which we put electrons into orbitals. Thus, for atoms, first we fill 1s orbitals, then 2s, 2p, 3s, 3p, etc, going from the lowest energy orbitals to the highest. If

we're going to put electrons into molecular orbitals we'll need to know which has the lower energy, a bonding or an antibonding orbital, and which has the higher energy. Remember that when we form a bond, we are increasing the stability of our atoms compared to when they are apart. Things that are more stable are at lower energies, so this tells us that a **bonding orbital has lower energy than the two atomic orbitals it is formed from**. Because the **antibonding orbital** causes the atoms to repel each other, it **will have a higher energy** than the two atomic orbitals it is formed from.

We represent this with an energy level diagram for molecular orbitals. To make sure we understand which atomic orbitals were used to generate the molecular orbitals, we include the original atomic orbitals in the diagram. First we draw lines for the energy of the two 1s orbitals, then between them and below we draw a line for the σ 1s bonding orbital, while between them and above we draw a line for the σ^* 1s antibonding orbital, each at the appropriate energy. We call this an orbital diagram. To figure out the bonding we merely put electrons into orbitals using the Pauli exclusion principle, and Hund's rule.

We can examine the way that the energies of these hydrogen molecular orbitals are related to the electron distribution in the orbitals by looking at this simulation of the formation of hydrogen bonding and antibonding orbitals as a function of distance between the atoms. <http://chalk.richmond.edu/CMoR/local/bonding/diatom/diatom.htm> On the right hand side of the simulation we have the 1s orbitals from which the bonding and antibonding molecular orbitals are formed. Notice that at the beginning, when the atoms are far apart, the orbitals have the exact same appearance as two independent hydrogen 1s orbitals, as we expect. If we now bring the hydrogen atoms a short distance closer together, we notice a small region developing in which the electron's orbitals overlap. For the bonding orbital, this results in an increase in electron density

between the two atoms, and a decrease in energy relative to the separated atoms. For the antibonding orbital, this results in a decrease in electron density between the two atoms and a subsequent increase in the energy of the orbital relative to the separated atoms. However, because the overlap is small, the effect is small. You can see that as we decrease the separation between the atoms, the overlap increases, and the energies of the molecular orbitals deviate more and more from the original atomic energy levels. The stabilization of the bonding molecular orbital and the destabilization of the antibonding molecular orbital reach a peak at the equilibrium bond length. Note also that the antibonding orbitals are destabilized to a greater extent than the bonding orbitals are stabilized, although the method of calculation used to generate this diagram greatly exaggerates this effect.

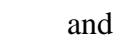

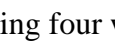

Now we want to generate an electronic configuration for the hydrogen molecule. For the hydrogen atoms, we have two electrons in our original 1s orbitals so we need to put two electrons into our molecular orbitals. Since we can put two electrons into each orbital both go into the σ 1s orbital, and hydrogen has a configuration we label $1s\sigma^2$. How do we calculate bond order when we use molecular orbitals? The answer is that the **bond order is the number of bonding electrons minus the number of antibonding electrons divided by two, i.e.**

$$b.o. = \frac{\text{bonding } e^- - \text{antibonding } e^-}{2}$$

Note that non-bonding electrons do not contribute to the bond order.

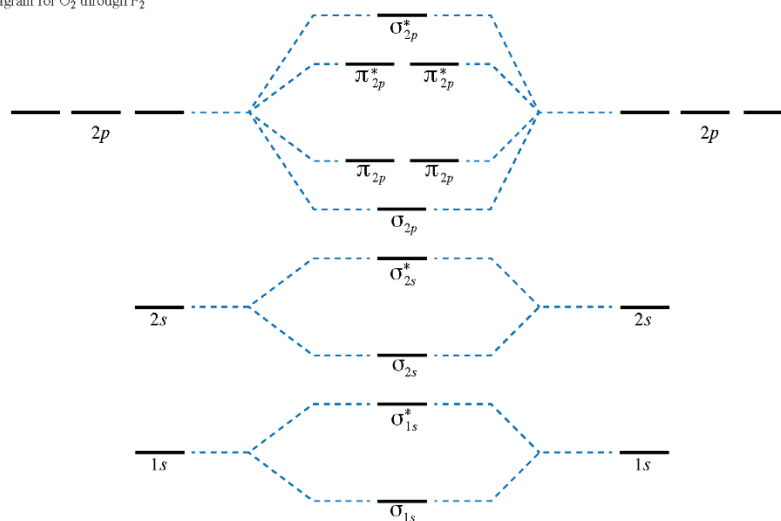
We can use this energy level diagram to see why we can't form the molecule He_2 . He has 2 electrons in a 1s orbital so we use 1s orbitals to create our molecular orbitals, and we get the same diagram as for hydrogen. But now we have 4 electrons to put into our orbitals. The first two

go into the σ 1s orbital, but the second two go into the antibonding orbital. Since we have two bonding and two antibonding electrons the bond order is zero, and no bond is formed.

The hydrogen molecular orbitals were formed from 1s atomic orbitals. We can form molecular orbitals from other atomic orbitals as well. Let's look at the simulation for this now. <http://chalk.richmond.edu/CMoR/local/bonding/diatom/diatom.htm> Imagine two atoms from the second period, with a 2s and 3 2p orbitals in addition to the 1s orbital. The two 2s orbitals will form a $2s\sigma$ bonding orbital and a $2s\sigma^*$ antibonding orbital. Now consider the 2p orbitals. Two will be pointing at each other. These two will form a pair of σ orbitals, called the $2p\sigma$ and $2p\sigma^*$ orbitals, which will look like  and . The remaining four will be side by side and will make two $2p\pi$ bonding orbitals and two $2p\pi^*$ antibonding orbitals, which look like  and . We call the π orbitals π_x and π_y to indicate that they are in different planes.

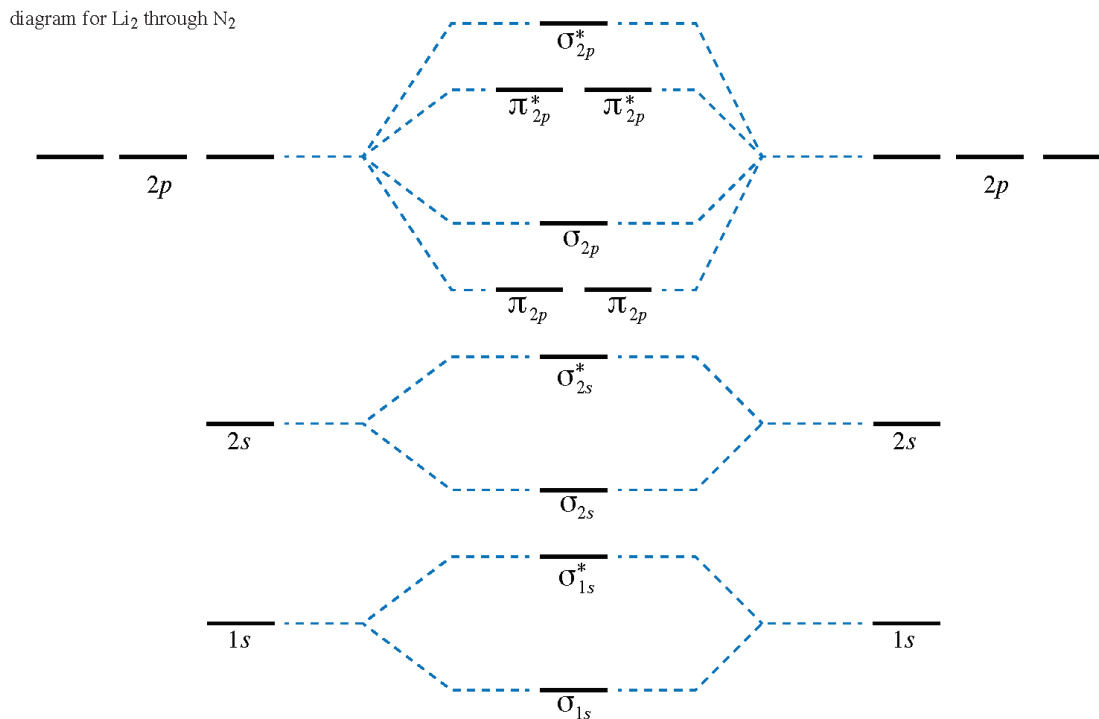
We now need to know the relative energies of all of these orbitals. The molecular orbitals from the 1s will be lowest in energy, followed by the orbitals formed from the 2s. However, the order of the rest of the $n = 2$ molecular orbitals depends on whether the atoms are heavier or lighter than N. For O_2 , and F_2 the energy diagram is

diagram for O_2 through F_2



O_2 , and level

while for Li_2 , Be_2 , B_2 , C_2 , and N_2 the energy level diagram is



Let's use these to figure out the bonding for N_2 and O_2 . For N_2 we use our second diagram. N_2 has 14 electrons so we start filling from the bottom. Two go into the $1s\sigma$, two into the $1s\sigma^*$, two into $2s\sigma$, two into $2s\sigma^*$, two into the $2\pi_x$, two into the $2\pi_y$ and the last two into the $2p\sigma$ orbital. Altogether we have 10 electrons in bonding orbitals and 4 in antibonding electrons for a bond order of 3. Experiments show that N_2 is triple bonded so our theory gives the correct prediction.

For O_2 , we use the other energy level diagram. The oxygens have 8 electrons each so we need to find room for 16 electrons. The first eight go into the $1s\sigma$, $1s\sigma^*$, $2s\sigma$, and $2s\sigma^*$ orbitals. Then we put two each into the $2p\sigma$, π_x , and π_y orbitals. This leaves two for the π^*_x and π^*_y orbitals. According to Hund's rule, which also holds for molecular orbitals, the two electrons will each go into a different π^* orbital, with the same spin. Altogether, O_2 has 16 electrons, 10 of which are in

bonding orbitals, and 6 of which are in antibonding orbitals, so it has a bond order of 2, which is confirmed by experiment. However, molecular orbital theory predicts what neither Lewis dot structures nor Valence bond theory can predict. Oxygen has two unpaired electrons and is therefore paramagnetic. This has been amply confirmed by theory, and is a confirmation of the power of the MO theory.

The cases we have considered so far are for molecules where both atoms are the same, homonuclear diatomic molecules. Let's look at HF, a molecule where the two atoms are different, a heteronuclear diatomic molecule. If we put our hydrogen 1s orbital on one side of an energy diagram and the fluorine orbitals on the other side, we notice that the fluorine orbital with the energy closest to that of the hydrogen 1s orbital is the fluorine 2p orbital, so this is the orbital with which the σ and σ^* orbitals are formed. Since none of the other orbitals combine with orbitals from another atom, their energies stay the same and they are called non-bonding orbitals. The overall orbital diagram for HF is

and we see that on filling the orbitals of HF with electrons, that HF has two electrons in σ orbitals and 8 in nonbonding orbitals for an overall bond order of 1.

In developing our molecular orbitals we have ignored hybridization. Why? Because with orbitals of diatomic molecules we do not have to invoke hybridization. The normal atomic

orbitals are sufficient unto the cause of the day. How do we do a molecular orbital diagram for molecules that need hybridization in the valence bond theory? It turns out that in the molecular orbital picture hybridization is completely unnecessary. To explain this, note that all hybridization is saying is that combination of simple atomic orbitals is not sufficient to describe the bonding of some molecules. Hybridization is the solution to this problem. However this mixing of several atomic orbitals occurs as a matter of course in molecular orbital theory. Remember that we said earlier that different orbitals within the same atom often combine in making molecular orbitals. In fact this has the same effect as hybridization, but instead of having to be imposed as an external constraint, it comes about as a natural consequence of molecular orbital theory.