Lecture 29

When we solve the Schrödinger equation for the hydrogen molecule using these means we get a number of different **potential energy curves**, which we refer to as the **electronic states of the molecule**. In analogy to the case for atomic electronic states, we identify these states using **molecular term symbols**. The means for determining these molecular term symbols is somewhat more complicated than that for atomic term symbols, so we will limit ourselves to a description of the term symbol. **The term tells us the values of certain angular momenta just as before**. In this case the angular momenta are the **spin angular momentum, S**, and **the component of the orbital angular momentum L in the direction of the bond axis, the axial component**. **The axial component is given the symbol Λ**. We calculate Λ by adding up the axial components of the angular momentum for each one electron orbital and taking their absolute value, i.e.,

$$\Lambda = \left| \lambda_1 + \lambda_2 + \lambda_3 + \ldots \right|$$

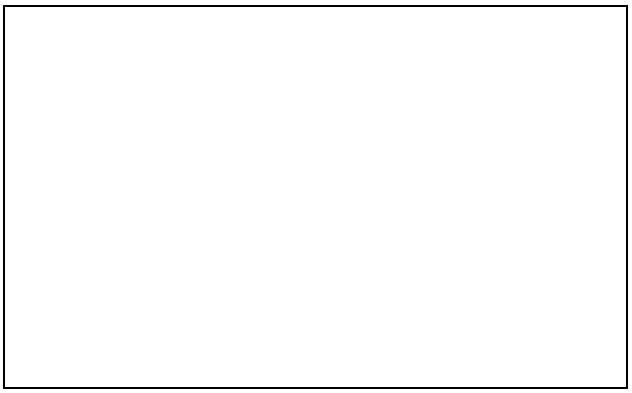
where $\lambda_1$, $\lambda_2$ and so on are the axial components of the orbital angular momentum of each electron. An electron in a σ orbital has $\lambda = 0$, while an electron in a π orbital has $\lambda = \pm 1$. When $\Lambda = 0$ we call the state a Σ state, when $\Lambda = 1$ we call it a Π state, when $\Lambda = 2$ we call it a Δ state and so on. The most basic form of the term symbol is ${}^{2S+1}\Lambda$.

For the ground state of the hydrogen molecule, all the angular momenta cancel to yield S = 0 and Λ = 0. Thus the ground state of hydrogen is a ${}^1\Sigma$ state. As before, when molecules have inversion symmetry, this state can also be labeled as g or u. **We determine whether a molecular electronic state is g or u by first finding the parity (g or u) of the orbitals that each of the electrons are in, and multiplying according to the rules g x g = u x u = g and g x u = u**. Thus if we had a configuration where two electrons were both in $1s\sigma_g$ orbitals, the overall parity would

be g x g = g. If on the other hand one electron was in a $1s\sigma_g$ orbital and the other in a $1s\sigma_u$ orbital the parity of the molecule would be g x u = u. Thus the ground state for $H_2$ is $^1\Sigma_g$.

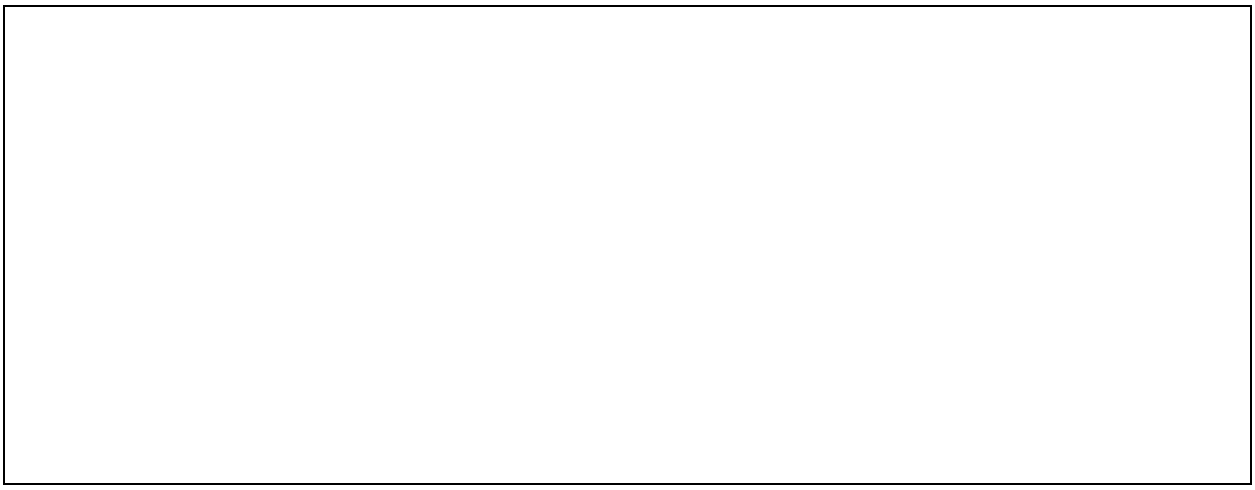
Let's look at the **molecular electronic configurations of several first row homonuclear diatomic molecules**. The easiest way to do this is to write our energy level diagrams, and on each side, where we have the original atomic orbitals, put the number of electrons in each atom. These will be the electrons that we use to fill our molecular orbitals. Let's start with the molecule $He_2^+$. $He_2^+$ has three electrons. The first two go into our lowest energy orbital, the $1s\sigma_g$ bonding orbital, while the third electron goes into our next orbital, the $1s\sigma_u$ antibonding orbital. **The molecule will have some stability if the number of electrons in bonding orbitals outnumbers the number of electrons in antibonding orbitals**. In this case we have two electrons in bonding orbitals and one in an antibonding orbital, so a bond forms. To characterize the strength of the bond we define a new term called the **bond order**. In molecular orbital theory, **the bond order is defined as one half (the number of bonding electrons - the number of antibonding electrons).** Thus if we have one net bonding electron, we have a bond order of ½. If we have two we have a bond order of one, which you usually refer to as a single bond. If we have four bonding electrons we have a bond order of two or a double bond and so on. Thus for $He_2^+$, our bond order is (2-1)/2 = 1/2. Any time our bond order is greater than zero a stable ground state molecule will form, although in the case of $He_2^+$, the bond is weak, with a $D_e$ = 2.5 eV. Because the molecule has a single unpaired electron, it will be a doublet, and because all of the electrons are in σ orbitals,

it will be a Σ state. To determine the parity, we take the product of the parities of the three electrons, g x g x u = u. So our molecular term symbol for the ground state of $He_2^+$ is $^2\Sigma_u$.



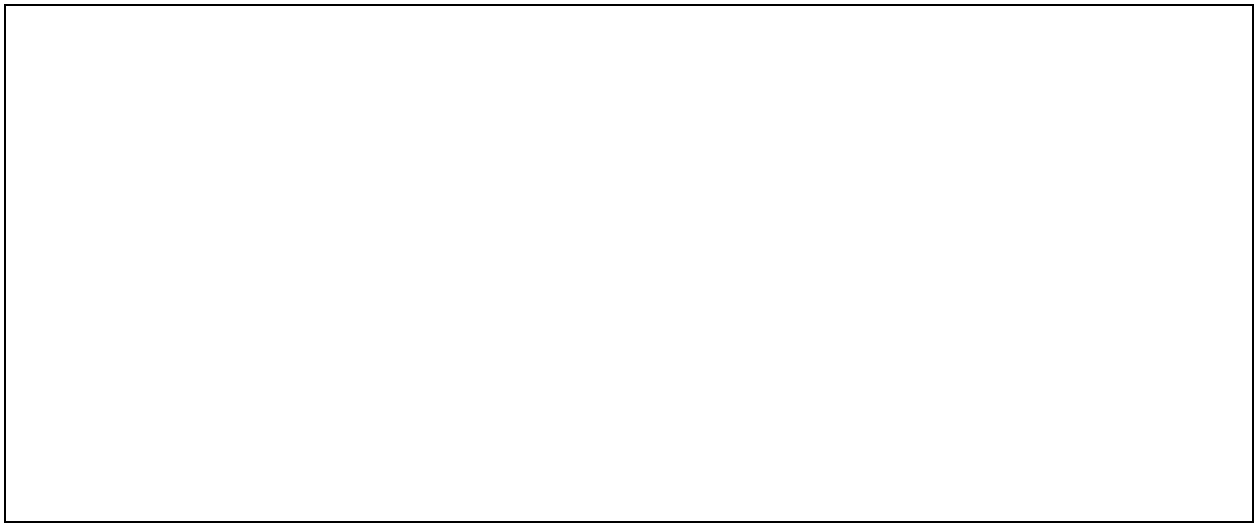
For $He_2$, we have four electrons available for bonding, two from each He. The first two go into our lowest orbital, the $1s\sigma_g$ bonding orbital, and the other two go into our $1s\sigma_u$ antibonding orbital. The number of bonding electrons is equal to the number of antibonding electrons so the bond order is zero and no bond forms. The $He_2$ molecule is not stable in the ground state, although it can be observed if one of its electrons is in an excited state. You can see how this works, because the next available orbital will be a 2sσg bonding orbital, so the HOMO-LUMO transition takes an electron from an antibonding orbital to a bonding orbital, increasing the bond order to $\frac{3\,bonding - 1\,antibonding}{2}$ for a bond order of one. A species which is stable only in the excited state is called an excimer or an exciplex. They are called excimers (a shortened version of EXCIted state diMER) when both of the species held together are the same, and exciplexes (short for EXCIted state comPLEXES) when the two species are different. Excimers are the lasing medium for some of our most powerful lasers, in particular the type of laser most typically used for Lasik eye surgery, called a (wait for it) Excimer Laser.

Next, we consider the bonding of $Li_2$, and $Be_2$. Lithium has 3 electrons, so we must place 6 electrons in our molecular orbitals. The first four go to fill the $1s\sigma$ bonding and antibonding



orbitals, and the final two go into the $2s\sigma_g$ bonding molecular orbital. There are four bonding electrons and 2 antibonding electrons, so the bond order is (4-2)/2 = 1. The bonding energy of $Li_2$ is only 1.14 eV however. LET'S THINK ABOUT WHY THIS MIGHT BE THE CASE. Since all the electrons are paired this will be a singlet state. As in the case of $He^{2+}$, all the electrons are in $\sigma$ orbitals, so the molecule will be in a $\Sigma$ state. Finally, the parity will be g, so the molecular term symbol for $Li_2$ is $^1\Sigma_g$.

For $Be_2$, we have 8 electrons to put in our molecular orbitals. The first six go in the same orbitals as $Li_2$, $1s\sigma_g$, $1s\sigma_u$ and $2s\sigma_g$. The final two go in the next highest orbital, the antibonding $2s\sigma_u$ orbital. Thus for $Be_2$ we have four bonding electrons and 4 antibonding electrons for a bond order of 0, and no bond forms. LET'S LOOK AT THE EFFECT OF CREATING A CATION OF $BE_2$, AN ANION, AND A HOMO-LUMO EXCITED STATE ON THE BOND ORDER OF $BE_2$.



Next we turn to $B_2$ and $C_2$. Since both of these will clearly have filled $1s\sigma$ orbitals, we will exclude the $1s\sigma$ orbitals from our diagrams. For $B_2$ we have 10 electrons. Four are taken up by the $1s\sigma_g$ and $1s\sigma_u$ orbitals. Four more are taken up by the $2s\sigma_g$ and $2s\sigma_u$ orbitals. The remaining two will have to go into molecular orbitals made up from the 2p atomic orbitals. The next energy level consists of two degenerate $2p\pi_u$ bonding orbitals. According to Hund's rule we put one electron in each of the two orbitals with the spins aligned in the same direction. Thus $B_2$ has a bond order of 1, since there are six bonding and four antibonding electrons, and the $D_e$ is 3.0 eV. Since the two electrons have spins aligned in the same direction we have a triplet state, and the molecular term symbol is $^3\Sigma_g$. $C_2$ has two more electrons than $B_2$, and fills the $2p\pi_u$ bonding orbitals. The bond order is two since there are 8 bonding and 4 antibonding electrons. The bond energy is approximately twice that of the single bonded $B_2$ at 6.36 eV. The molecular term symbol is $^1\Sigma_g$. $N_2$ has two more valence electrons than $C_2$. Since both the $2p\pi_u$ orbitals are

filled, we move up to the next level, the $2p\sigma_g$ bonding orbital, and put both electrons in this level. Thus nitrogen has 10 bonding electrons and 4 antibonding electrons, and is triple bonded. The bond energy is a little less than three times that of boron, and is 8.86 eV. To do the structure of $O_2$, we need to change to the energy level order for $Z \geq 8$. The first eight electrons go into the $1s\sigma$ and $2s\sigma$ orbitals and result in a bond order of 0. Next we fill the $2p\sigma_g$, and both the $2p\pi_u$ bonding orbitals. The next level is the doubly degenerate $2p\pi_g$ antibonding level. Since there are two degenerate levels, each gets one electron with the spins aligned. The bond order of oxygen is 2, since there are 10 bonding and six antibonding electrons, and the bond energy is 6.77 eV. An important observation is that this ground state is a triplet, with term symbol $^3\Sigma$. This implies that oxygen is a paramagnetic molecule in its ground state. The explanation of oxygen's triplet ground state was one of the early triumphs of the molecular orbital theory.

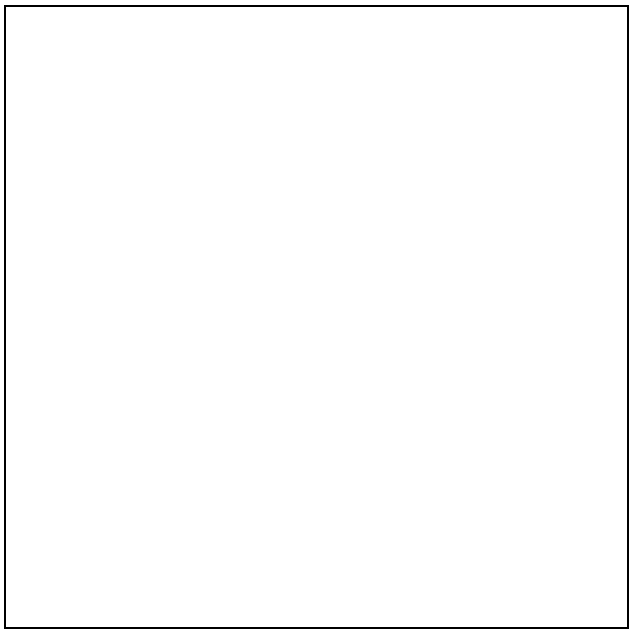
How do we use molecular orbitals to treat **the bonding of heteronuclear diatomic molecules?** The general idea is the same as that for the homonuclear diatomic molecules - we create molecular orbitals by taking linear combinations of atomic orbitals on the two atoms. The linear combinations will result in one bonding and one antibonding orbital for each pair of atomic orbitals. The only question is **which orbitals will combine**? The answer can be obtained by looking at which orbitals combine in homonuclear diatomic molecules. For example, a 1s orbital combines with a 1s orbital, a 2s orbital combines with a 2s orbital, and a 2p orbital combines with

a 2p orbital. The observation is that **the orbitals that combine are the ones that are closest in energy.** In fact this is exactly what we will find for the heteronuclear diatomic molecules. The orbitals that combine will be those that are closest in energy. **The closer in energy they are the stronger the stabilization of the bonding orbitals will be, and the stronger the bond.**

A logical question to ask is how we can tell which orbitals on different atoms are closest in energy. We can use spectroscopic methods to probe this, but the best tool is our old friend, photoelectron spectroscopy. It turns out that photoelectron spectroscopy can be applied to atoms and molecules as well as metal surfaces. In the case of atoms, the photoelectron equation can be written as $h\nu = \Phi_n + \frac{1}{2}mv^2$, where replacing $\Phi$ by $\Phi_n$ indicates that for an atom, there are several different work functions. For an atom these work functions are the binding energies of the occupied atomic orbitals. The experiment involves using a tuned laser to determine the photon frequencies at which electrons are ejected with zero kinetic energy. These frequencies can be used to determine the various binding energies. For the purposes of molecular orbital theory, the orbitals which overlap most strongly will be the ones for which the experimentally determined binding energies are the closest.

For example, in HF, the H 1s orbital is closest in energy to the F 2p orbital. Thus the orbital diagram is as follows. The lowest energy orbital is the F 1s, followed by the F 2s. Next are the F 2p and H 1s, which are approximately equal in energy. The H 1s and the F $2p_z$ (remember that by definition the bond axis is the z axis) combine to form a bonding and an antibonding orbital. The F $2p_x$ and $2p_y$ orbitals are unaffected. All of the unaffected orbitals, the F 1s, 2s, $2p_x$ and $2p_y$ orbitals, are called **nonbonding orbitals**. Thus, in heteronuclear molecules there will be three types of molecular orbitals an electron can reside in: bonding orbitals, nonbonding orbitals and

antibonding orbitals. Bonding orbitals will have lower energies than the atomic orbitals they were formed from. Nonbonding orbitals are unchanged atomic orbitals, and therefore have no energy change. Antibonding orbitals will have higher energies than the atomic orbitals they were formed from.



As before we fill the orbitals from lowest energy to highest. The bond order for these molecules will still be one half the difference between the number of bonding electrons and antibonding electrons. The nonbonding electrons do not contribute to the bond order. For the case of HF we have ten electrons. Two go into the F 1s nonbonding orbital, two go into the F 2s nonbonding orbital, the next two into the $\sigma_g$ bonding orbital and the final four in the F $2p_x$ and F $2p_y$ nonbonding orbitals. Thus for HF we have 8 nonbonding electrons and 2 bonding electrons for a bond order of 1.

For polyatomic molecules, we can follow the same general procedure, but it gets very complicated very rapidly. When we calculate the potential energy function for $H_2$ or HF, we have only one nuclear coordinate to worry about, the distance between the two nuclei, so the Born-Oppenheimer approximation is relatively easy to apply. However, when we consider even a small polyatomic molecule like vinyl iodide, $C_2H_3I$, the number of variables we have to adjust is much larger. To apply the Born-Oppenheimer approximation to this molecule, we need to fix 9 nuclear coordinates, five of which are bond lengths, and four of which are bond angles. This is not

impossible, but requires a significant amount of computer time at any level of theory above the HF level. In general, for all but the largest molecules (think nucleic acids or proteins), these calculations can be carried out to sufficient accuracy to determine the geometries and thermodynamics of the molecules to good accuracy. It is now, because of advances in computer technology and in the algorithms used in computational chemistry, also possible for calculations to be sufficiently accurate to provide useful predictive information about chemical kinetics. These calculations have to be at a higher level because an error even as low as ±1 kJ/mol can result in a significant error in rate constants. It also used to be the case that it was difficult to calculate vibrational frequencies accurately and quickly, but an application of computational quantum mechanics called Density Functional Theory gives good results (within 3%) for vibrational frequencies. In the case of these DFT calculations, the biggest error does not lie in the calculation of the potential from which the vibrational frequencies are generated, but rather in the assumption that the potential for these frequency calculations is harmonic. Recently Gerber et al have developed codes that allow anharmonic vibrational frequencies to be calculated from quantum chemical calculations, and combining this development with DFT can reduce the errors to the order of 0.1%.

Lecture 30

There is another model of chemical bonding, called the **valence bond** or Heitler-London model, which in its crudest forms is inferior to molecular orbital theory, but nonetheless easily gives qualitative insight into the bonding of a huge number of polyatomic molecules. **The valence bond model assumes that a bond forms when there is a significant overlap between two atomic valence orbitals.** For example, when we bring two hydrogen atoms together, the bond forms because the two hydrogen 1s orbitals physically overlap and electron density is increased between the two atoms to create a bond. For hydrogen this probably doesn't seem all that different than the molecular orbital model, except that in the valence bond model we haven't talked about antibonding orbitals, just bonding orbitals. The most important difference would be for a molecule like $Li_2$. The valence bond model would say that the single bond forms due only to the interaction between the valence 2s electrons, and that the four core 1s electrons are unchanged, and therefore are non-bonding. This is incorrect and is shown to be so by **photoelectron spectroscopy**. Photoelectron spectra show that atomic core orbitals are changed by the formation of molecules, just as the valence orbitals are and therefore confirm the molecular orbital picture.

Nonetheless, the valence bond model does a good job of predicting molecular geometries and bond orders, is easier to apply to qualitative treatments of larger molecules and tends to give better results when predicting properties of molecules near the dissociation limit, when interaction between core orbitals is naturally minimized. It is especially useful when it is combined with the idea of **hybrid orbitals**. **Hybrid orbitals are linear combinations of atomic orbitals from a single atom to make new atomic orbitals of a different symmetry**, which then combine with either unhybridized orbitals or hybrid orbitals on other atoms to make bonds. The hybrid orbitals on an atom, as you know from general chemistry, have fixed angles relative to each other. They

arise physically because the approach of nuclei to each other in the course of forming a molecule changes the symmetry of the interatomic potential, and therefore the Hamiltonian. Therefore, new atomic orbitals with reduced symmetry are formed. It is a convenient feature of these 'hybrid" orbitals that their angular distributions can be described as simple linear combinations of hydrogen angular functions. The physical origin of these hybrid orbitals lies in the fact that molecules, unlike atoms, don't have a spherically symmetric potential energy function. The hydrogenic orbitals are based on the surface of a sphere because the potential is symmetric. Similarly molecules will have valence orbitals whose shapes mirror the symmetry of the potential, which in turn mirrors the symmetry of the molecular geometry.

We'll illustrate the use of these orbitals by showing how they are applied to $BeH_2$, $BH_3$, $CH_4$, $NH_3$, and $H_2O$. $BeH_2$ is a linear molecule, with an angle of 180° between BeH bonds. The ground state electron configuration of Be is $1s^2\ 2s^2$. The first problem that we have to deal with is that in a $2s^2$ configuration Be has a filled valence subshell. Since the valence bond model most typically describes a bond as being either due to the overlap between two half-filled valence orbitals or due to the overlap between a filled and an unfilled valence orbital, this configuration doesn't allow Be to bond with hydrogen. However, if we promote one of the 2s electrons to a 2p orbital, we now have two half-filled orbitals with which to make BeH bonds. It is true that it takes energy to promote this electron, but the energy invested is more than returned when the two BeH bonds are formed. However, this is still not quite right. The first problem is that if we make one bond between a hydrogen 1s orbital and a Be 2s orbital, and one bond between a hydrogen 1s orbital and a Be 2p orbital, the electron densities of the bonds will be different, and the bonds will have different bond energies, bond lengths and dipole moments. Experiment shows that the two

bonds are completely identical. The second problem is that making one bond with a Be 2s orbital and the other with a Be 2p orbital doesn't yield a linear geometry, the experimental geometry of $BeH_2$.

We can resolve this problem if we **make two orbitals by taking the linear combination of the Be 2s and 2p orbitals**. We call these new orbitals sp orbitals and they are given by

$$\psi_{sp(i)} = \frac{1}{\sqrt{2}}(2s + 2p_x)$$

and

$$\psi_{sp(ii)} = \frac{1}{\sqrt{2}}(2s - 2p_x).$$

**The resulting orbitals are identical in every way except that they are oriented in opposite directions**. They look essentially like p orbitals with one lobe enlarged and the other shrunk. Note that it is completely arbitrary which of the 2p orbitals we used in making this hybrid sp orbital. Any of the orbitals COULD be used, but by convention we say that the orbital is the $p_z$ orbital, since the z axis is the bond axis by definition.

To make our BeH bonds we create two bonding orbitals from the H 1s orbitals and the Be sp orbitals. They are given by

$$\psi = c_1 1s_A + c_2 \psi_{sp(i)}$$

and

$$\psi' = c_1 1s_B + c_2 \psi_{sp(ii)}.$$

Since the two bonds are identical except in direction the constants $c_1$ and $c_2$ are the same in both wavefunctions. Once again notice that in this model the core Be 1s orbitals are completely uninvolved in the bonding.

For $BH_3$, experiment shows that there are three equivalent B-H bonds. We follow the same general procedure. B has the electron configuration $1s^2\ 2s^2\ 2p$. We take the three lowest available

orbitals, 2s, $2p_x$ and $2p_z$, and combine them to get three hybrid $sp^2$ orbitals. The three orbitals are given by

$$\psi_{sp^2(i)} = \frac{1}{\sqrt{3}}2s + \sqrt{\frac{2}{3}}2p_z$$

$$\psi_{sp^2(ii)} = \frac{1}{\sqrt{3}}2s - \frac{1}{\sqrt{6}}2p_z + \frac{1}{\sqrt{2}}2p_x$$

$$\psi_{sp^2(iii)} = \frac{1}{\sqrt{3}}2s - \frac{1}{\sqrt{6}}2p_z - \frac{1}{\sqrt{2}}2p_x$$

Note that all three of these orbitals will have probability densities that are 2/3 p and 1/3 s. They are all equivalent and differ only in that they point in different directions. They all lie within a plane and are at an angle of 120° from each other. As was the case with the $BeH_2$, we make our bonds by overlapping B $sp^2$ orbitals with H 1s orbitals.

A similar procedure is followed for $CH_4$, except here we need four equivalent orbitals. We get these by mixing the 2s and all three 2p orbitals of C to get four $sp^3$ orbitals. The four $sp^3$ orbitals are:

$$\psi_{sp^3(i)} = \frac{1}{\sqrt{4}}(2s + 2p_x + 2p_y + 2p_z)$$

$$\psi_{sp^3(ii)} = \frac{1}{\sqrt{4}}(2s - 2p_x - 2p_y + 2p_z)$$

$$\psi_{sp^3(iii)} = \frac{1}{\sqrt{4}}(2s + 2p_x - 2p_y - 2p_z)$$

$$\psi_{sp^3(iv)} = \frac{1}{\sqrt{4}}(2s - 2p_x + 2p_y - 2p_z)$$

These orbitals as you know, form a tetrahedron, with a separation of 109.5°.

In the molecules $NH_3$, $H_2O$ and HCl, the central atoms all have $sp^3$ hybridization. In each of these molecules, the $sp^3$ orbital either forms a bond by overlap with a hydrogen 1s orbital or contains a pair of electrons that are not involved in bonding and are called **lone pair electrons**. Experiment has shown that $sp^3$ molecules which contain lone pair electrons do not show bond angles of 109.5° as expected from the valence bond method, but have slightly smaller bond angles. In $NH_3$, which has one lone pair, the bond angle is 107°, while in $H_2O$ with two lone pairs, the bond angle is 104°.

**How do we decide what hybridization to use for an atom?** As a general rule, **we need enough hybrid orbitals to make room for all the bonding electrons and lone pairs which go around the atom**. $BeH_2$ had two bonds, so we needed two hybrid orbitals, which means we need sp hybridization. $NH_3$ has three bonds and a lone pair so we need four hybrid orbitals, and $sp^3$ hybridization.

What do we do if we want to create a molecule like $NF_3$? The fluorines could either be unhybridized or have $sp^3$ hybridization and still yield the same geometry. In addition, experiment won't help us distinguish between these two cases, since experiment will show that both give incorrect orbital energies. So what do we do? Since the physical explanation for hybridization is the change in the potential that the electrons feel when atoms come together to make a molecule, we would have to assume that F is hybridized as well. After all, the F electrons are subject to an anisotropic potential just as the N atoms are.

The valence bond method also can handle simple multiple bonded systems. Consider

ethylene. The formula is $H_2C=CH_2$. Experiment shows that each of the bonds in ethylene is 120° apart. This must mean that the orbitals on the carbon atoms are $sp^2$ orbitals. Two of the $sp^2$ orbitals that are formed on the two carbons are used to make σ bonds with the hydrogen atoms. The third $sp^2$ orbital is used to make the carbon-carbon sigma bond. This leaves a single unused electron in a p orbital on each carbon. The carbon 2p orbitals containing these unpaired electrons overlap to form a new bond that has a nodal surface where the C-C single bond is. In other words, each C atom forms two single σ bonds with H of the form

$$\psi_{CH\sigma} = c_1 1s_A + c_2 2sp^2$$

The 2 C atoms also form a σ bond with each other of the form -

$$\psi_{CC\sigma} = c_3(2sp^2 + 2sp^2)$$

Finally the 2 C atoms form the π bond with the two remaining p electrons:

$$\psi_{CC\pi} = c_4(2p_{zA} + 2p_{zB}).$$

Lecture 31

Unfortunately, the valence bond method does more poorly with extended π systems like benzene or conjugated polyenes. A still simple, but slightly more sophisticated theory of bonding is called **Hückel Molecular Orbital Theory**. In this method, **we use valence bond theory to generate the sigma-bonded skeleton of our molecules, and then use a simplified version of the molecular orbital theory to account for the bonding due to the extended π system**. Qualitatively we observe that the extended π bonds in conjugated systems are the result of a network of bonds that form between a series of half occupied p orbitals. Thus we expect that the molecular orbitals which describe the π bonding of these molecules will be a series of different linear combinations of these p orbitals. Let's look at the Hückel treatment of the π system for ethylene, 1,3 butadiene, and benzene to see how this method works.

For ethylene, two p orbitals are involved in our π bond, so a reasonable trial function will be

$$\psi = c_1\phi_1 + c_2\phi_2,$$

where $\phi_1$ and $\phi_2$ are $2p_z$ orbitals. Calculating the variational energy of this trial function leads to the secular determinantal equation,

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} = 0$$

where, as before, the integral $H_{ij}$ is given by

$$H_{ij} = \int \varphi_i^* \hat{H} \varphi_j d\tau$$

and the overlap integral $S_{ij}$ is given by

$$S_{ij} = \int \varphi_i^* \varphi_j d\tau$$

So far this is a normal molecular orbital treatment, albeit restricted to the π bonds. The Hückel molecular orbital method adds the following approximations which simplify the secular equation.

1) The overlap integrals $S_{ij}$ are set equal to zero unless i = j, when $S_{ii} = 1$. This has the effect of changing all the terms on the diagonal of the matrix to $H_{ii}$ - E and changing all of the terms that are not on the diagonal of the matrix to $H_{ij}$. Thus, the first approximation changes our determinantal equation to

$$\begin{vmatrix} H_{11} - E & H_{12} \\ H_{21} & H_{22} - E \end{vmatrix} = 0$$

Essentially this approximation amounts to assuming that the overlap integrals $S_{ij}$ are small enough that we can ignore them.

2) All of the diagonal elements $H_{ii}$ - E are assumed to be have the same value and are given the new symbol α. This is a reasonable approximation since all the orbitals we are putting into our matrix are $p_z$ orbitals. It is an approximation because it assumes that the energy of a p orbital at the end of a molecule will be the same as the energy of the p orbital in the middle of the molecule, even though the environments are different. It also assumes that the p orbital will have the same energy no matter which other atoms are bonded to the carbon atom.

3) The resonance integrals, $H_{ij}$ are set to zero, except for between neighboring atoms. The resonance integrals between these neighboring atoms have the form $H_{ij}$, where $j = i \pm 1$. Examples are $H_{32}$, $H_{23}$, $H_{12}$, $H_{43}$. The resonance integrals between neighboring atoms are assumed to be equal and are all given the symbol β. It is the values of the integral β which give us the extent of stabilization of our bonding orbitals and destabilization of our antibonding orbitals. Thus, **this approximation essentially says that the bonding occurs mainly through the interaction**

**between adjacent p orbitals**, and that the interactions between the p orbitals on the first and third carbons of a long molecule, for example, are negligible.

The secular equation now becomes

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = 0$$

The next feature of Hückel theory is that the values of the integrals $\alpha$ and $\beta$ are not determined theoretically, but by fitting the basic results of the theory to experimental results. Thus, the Hückel method is what is known as a **semiempirical theory**. Since the integrals $\alpha$ and $\beta$ are determined from experiments, we do not need to know the exact form of the Hamiltonian for the problem, a tremendous simplification.

If we expand out our determinant, the equation that results is

$$(\alpha\text{-}E)^2 + \beta^2 = 0,$$

which yields two different orbital energies, $E = \alpha + \beta$, and $E = \alpha - \beta$. When we evaluate the coulomb integral, **$\beta$, we find that it always has a negative value**, so the lowest of these two levels has energy $E = \alpha + \beta$. In interpreting these energies, it is useful to realize that **$\alpha$ is the energy of an electron in a nonbonding Hückel MO**, so the orbital with energy $\alpha + \beta$ is a bonding orbital, while the orbital with energy $\alpha - \beta$ is an antibonding orbital. **Each of these orbitals can accept up to two electrons, in keeping with the Pauli exclusion principle**. Since there are two electrons which are available in ethylene, both go in the orbital with energy $\alpha + \beta$, and the total $\pi$ electron energy is $2\alpha + 2\beta$.

The wavefunctions of the ethylene $\pi$ molecular orbitals are

$$\psi_1 = \frac{1}{\sqrt{2}}(2p_{zA} + 2p_{zB})$$

and $$\psi_2 = \frac{1}{\sqrt{2}}(2p_{zA} - 2p_{zB}).$$

$\psi_1$ has the same shape probability distribution as the $p\pi_u$ bonding orbital that we calculated for $H_2^+$, and $\psi_2$ has the same shape probability distribution as the $p\pi_g$ antibonding orbital of $H_2^+$, although in both cases the distributions of intensity along the z axis are different.

Let's look at the Hückel results for two other molecules of chemical interest. The first is butadiene, which is the smallest conjugated molecule. Butadiene exists in two configurations, cis and trans, but we will simplify by treating it as if it were a simple linear molecule. As before we use the valence bond treatment to obtain the σ bonded skeleton, just as you learned in general chemistry and organic chemistry. In this case, we have four p orbitals that contribute to the π bonds, so we will obtain four different π molecular orbitals with four different energies.

We begin by constructing our secular determinant. **When we have n atoms involved we will have an n x n secular determinant**. For this case where we have four atoms involved in the bonding we will have a four by four determinant. The four diagonal elements are all the same, α - E. The elements below and to the side of each of the diagonal elements are β. Thus our determinant for π molecular orbitals of butadiene is

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{vmatrix} = 0$$

We can simplify the solution of this secular equation by dividing the matrix through by β, and then

making the substitution $x = (\alpha - E)/\beta$. This results in the matrix

$$\begin{vmatrix} x & 1 & & \\ 1 & x & 1 & \\ & 1 & x & 1 \\ & & 1 & x \end{vmatrix} = 0$$

If we multiply this out we get

$$x^4 - 3x^2 + 1 = 0.$$

Although this is a quartic equation, it can be solved relatively easily by a second substitution, $y = x^2$, which changes the equation to

$$y^2 - 3y + 1 = 0,$$

which can be solved by the quadratic formula to yield the roots

$$y = x^2 = \frac{3 \pm \sqrt{5}}{2}$$

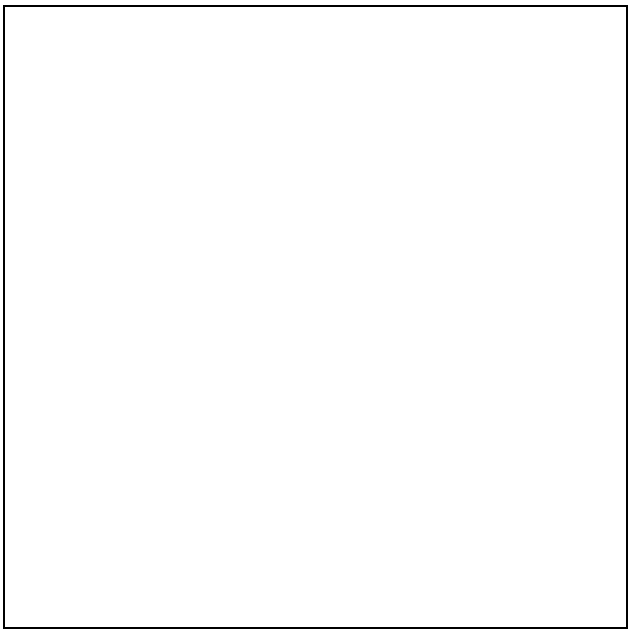
This in turn yields four roots for x,

$$x = \pm 1.61084$$

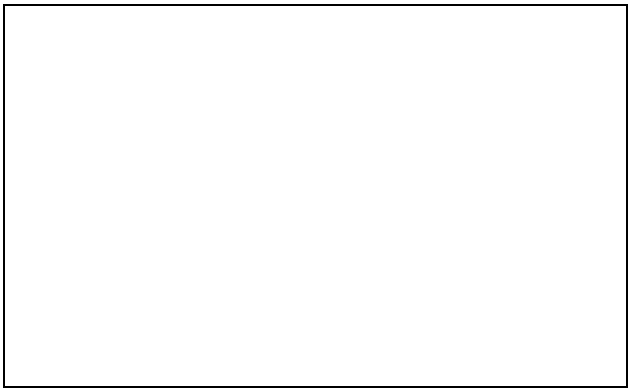
and $$x = \pm 0.6184.$$

Since $x = (\alpha - E)/\beta$, this means that in order of increasing energy, our four molecular orbitals have energies, $\alpha + 1.6108\beta$, $\alpha + .618\beta$, $\alpha - .618\beta$, and $\alpha - 1.6108\ \beta$. The first two of these levels are bonding orbitals and the final two are antibonding orbitals.

The molecular orbitals that correspond to these energies have the following appearance. The lowest energy molecular orbital is spread over all four carbon atoms, with the density above and below the plane containing the nuclei. The next molecular orbital has a node between the second and third carbons, but has its electron density spread between the first and second and third and fourth carbons. The next orbital has two nodes, and the highest orbital has three.



If we put two electrons into the first orbital, that means we are essentially creating 1/3 of a bond between each of the adjacent carbon pairs. Putting two electrons in the second molecular orbital creates 1/2 of a bond between the first and second carbons, and 1/2 of a bond between the third and fourth carbons. If we add these bonds together, and include the sigma bond from the valence bond skeleton, we get a bond order of 1 5/6 between $C_1$ and $C_2$, a bond order of 1 1/3 between $C_2$ and $C_3$, and a bond order of 1 5/6 between $C_3$ and $C_4$. This picture differs substantially from the standard picture of butadiene, where the bond order between $C_1$ and $C_2$ is 2, between $C_2$ and $C_3$ is 1 and between $C_3$ and $C_4$ is 2. Because the $\pi$ electron density is



spread over the whole molecule we say that the bonding is delocalized.

This delocalization has an effect on the π electron energy of butadiene as well. We can estimate the effect of this delocalization on the π electron energy by comparing the butadiene π energy with that of the simpler picture of butadiene π-bonding, which is simply twice the π electron energy of ethylene. To calculate the π electron energy of butadiene we note that our four π electrons go into the two bonding orbitals, which means that the total π electron energy of butadiene is $2 \times (\alpha + 1.618\beta) + 2 \times (\alpha + .618\ \beta) = 4\alpha + 4.472\ \beta$. Twice the π electron energy of ethylene is $4\alpha + 4\beta$, so our delocalization energy, $E_{butadiene} - 2\ E_{ethylene} = .472\ \beta$, which for butadiene is -35 kJ $mol^{-1}$. Again, this extra stability is due to the delocalization of the electrons across the entire length of the molecule.

We can do a similar treatment of benzene. In this case six p orbitals with six electrons are involved in the π system. The secular determinant is a six by six determinant. [What will the elements of the secular determinant be?] Expansion of this determinant leads to a sixth degree polynomial. The solutions of this polynomial are

$$E_1 = \alpha + 2\beta$$

$$E_2 = E_3 = \alpha + \beta$$

$$E_4 = E_5 = \alpha - \beta$$

$$E_6 = \alpha - 2\beta.$$

The π electrons will go only into molecular orbitals 1, 2, and 3. Molecular orbital one is completely delocalized over the six C atoms, while molecular orbitals 2 and 3 taken together are also delocalized over all six atoms. The net effect is to have a bond order of 1.5 for all bonds in benzene. The π electron energy of benzene is $6\alpha + 8\beta$, and using the same type of arguments we used for

calculating the delocalization energy of butadiene, we find that the delocalization energy of benzene is 2β or -150 k/mol.

Lecture 32

We've now completed our formal treatment of chemical bonding. However, there are three final topics that are important to treat before we finally leave the subject. These are electronegativity, ionic bonding, and hydrogen bonding. **Electronegativity** is a useful subject for a couple of reasons. Our discussion of chemical bonding thus far has been limited to covalent bonding, in which bonding occurs as a result of two or more atoms sharing electrons. However, we know that in many bonds, electrons are not shared between two atoms. In these cases, an electron is transferred from one atom to the other, creating an anion and a cation, which then form a bond as a result of their coulomb attraction. This is called an **ionic bond**. It is useful to know when a bond is going to be ionic and when it will be covalent. One of the useful properties of the electronegativity is that it allows us to estimate when a bond will be ionic and when it will be covalent.

Another reason that electronegativity is a useful concept is that it also allows us to estimate how evenly the electrons in a bond are shared between the two atoms. Our initial molecular orbital treatment was for homonuclear diatomic molecules where both atoms equally share the electrons. The case is more complex for heteronuclear diatomic molecules. We know from general chemistry that most often these electrons are not equally shared but that one of the atoms has a larger share of the electron density. The distribution of electron density between the two atoms is correctly determined by a full molecular orbital treatment, but as we've already mentioned, for molecules with large numbers of electrons or several nuclei, this can take a prohibitive amount of time. The electronegativity is a quick and semiquantitative means of determining whether the electrons in the bond will be shared equally, yielding a nonpolar molecule, or unequally, yielding a polar molecule.

**What is electronegativity?** It is simply a measure of the ability of an atom within a molecule to attract electrons to itself. It is to be carefully distinguished from the **electron affinity**, which is the energy released when an electron is added to an isolated atom, and is most clearly defined as the negative of the electron attachment energy. On a qualitative basis, the more similar the electronegativities of two atoms in a bond are, the less polar the bond will be. The more different the electronegativities, the more polar the bond will be. If the difference is large enough, the electron will actually transfer and we will have an ionic compound.

There are two important procedures for calculating electronegativity. The concept and first definition are due to Linus Pauling, who won a Nobel Prize for his contribution to the understanding of chemical bonding. Pauling observed that **the bond energy of a molecule A-B, E(A-B), is greater than the average of the bond energies of A with itself, E(A-A), and B with itself, E(B-B) when the molecule A-B is polar.** In other words for a polar molecule,

$$E(A\text{-}B) > 1/2\,(E(A\text{-}A) + E(B\text{-}B)).$$

Pauling based his electronegativity scale on this energy difference. He defined the difference in electronegativies of two atoms as

$$\Delta\text{electronegativity} = .050\left(\frac{\Delta_{AB}}{kJ/mol}\right)^{1/2},$$

where $\Delta_{AB}$ is the energy difference

$$\Delta_{AB} = E(A\text{-}B) - 1/2\,(E(A\text{-}A) + E(B\text{-}B)).$$

Since this formula only allows us to calculate differences between the electronegativities of two compounds, it is necessary to establish some standard atom as a basis of comparison. Hydrogen is a logical choice, since it can attain a noble gas configuration by gaining a single electron or by losing a single electron. As such, Pauling chose it as his standard and assigned it an

electronegativity of 2.1. Again, the larger the electronegativity, the greater the tendency the atom has to attract electrons to itself within a bond.

Remember that Pauling was the main proponent in this country of valence bond theory, while Robert Mulliken was the main proponent of molecular orbital theory. They were great rivals. As such it is not surprising that once the idea of electronegativity began to gain currency, Mulliken, in a typical scientific spirit of "anything you can do I can do better", proposed his own electronegativity scale. Mulliken reasoned that since electronegativity is the tendency of an atom in a molecule to attract electrons to itself, that it would be well represented by the average between the ionization energy, which is the energy necessary to remove an electron, and the electron affinity, which is the energy released when an electron is attached to an atom, i.e.,

$$\textbf{electronegativity} = 1/2\,(E_i + E_{ea}).$$

If these energies are expressed in electron volts, the Mulliken scale can be converted to the Pauling scale by dividing by 3.1. It turns out that while the two scales are not identical, they are very close.

**Electronegativities follow periodic trends**. The atom with the highest electronegativity is F, with a Pauling electronegativity of 3.98. The atom with the smallest electronegativity is Fr, with an electronegativity of .7. The electronegativity increases as we go diagonally from the lower left of the periodic table to the upper right. It is, however, not defined for the noble gases. We can understand these periodic trends if we consider the groups and periods separately.

**Electronegativities decrease as we go down a group**. We can understand this because the effective nuclear charge that the valence electrons feel is approximately the same as we go down a group, but the distance between the electrons and the nucleus increases. Thus the coulomb attraction decreases as we go down the group, and the tendency to attract electrons decreases.

Electronegativities increase as we go across a period. Here, the effective nuclear charge

increases as we move across the periodic table, and the size of the atom decreases. Taken together these mean a significant increase in the coulomb attraction, and therefore in the attraction of electrons by nuclei as we move across the period.

As I said, **we can use differences in electronegativity to discuss the distribution of electrons in a bond**. The observations should be familiar. In a given bond, the atom with a larger electronegativity will have a larger share of the electron density, and will be partially negative, while the atom with lower electronegativity will have a small positive charge, resulting in a dipole moment for the bond. We can also use the electronegativity to crudely describe the nature of the bonding as covalent or ionic. The general rule of thumb is that if the difference in electronegativities is > 1.7 that the bonding is more than 50% ionic, while if the difference of electronegativities is < 1.7 that the bonding is more than 50% covalent.

As we said earlier, if the difference in electronegativities is large enough then an ionic bond is formed. The attractive force in an ionic bond is the very strong coulomb attraction between the two ions, given by

$$E(R) = \frac{Q_1 Q_2}{4\pi\varepsilon_0 R}.$$

However, this can't be the only force involved in ionic bonding, or the two atoms would collapse into each other. The other force is a coulomb repulsion that becomes very strong when the electron clouds of the two ions get close enough to touch. At this point the repulsion energy increases very rapidly. The bond length $r_e$ of the ionic bond is the point at which the attraction and repulsion are exactly balanced.

At this point, the stabilization of the molecule relative to the separated ions is fairly well described by the coulomb energy alone, i.e., the energy of the reaction

$$M^+ + X^- \rightarrow MX$$

is given by

$$E(R) = \frac{Q_1 Q_2}{4\pi\varepsilon_0 R_e}.$$

However this energy is not the bond energy. The bond energy is the energy which is released from the reaction

$$M + X \rightarrow MX.$$

The difference between the dissociation to ions and the dissociation to neutral atoms is the pair of reactions,

$$M \rightarrow M^+ + e^-,$$

the ionization of M, and

$$X + e^- \rightarrow X^-,$$

the attachment of an electron to X. The energy of this first process is $E_i$, the ionization energy and energy of the second is $E_{ea}$, the electron affinity. Thus the bond energy is given by

$$E(R) - E_i(M) + E_{ea}(X).$$

For NaCl this gives a value of $D_o$ within 5% of the best experimental value. Note however, that this $D_0$ is for a diatomic molecule with ionic bonding. Ionic compounds typically are not found as diatomic molecules, but as arrangements of ions in extended 3 dimensional lattices. The energy of formation of such an ionic crystal is not simply the sum of the diatomic bonding energies for the atoms that form it, but represents more complex ionic interactions. However, the detailed consideration of ionic solids is outside of the subject matter for this class.

In addition to predicting ionic bonding, **electronegativity tells us when covalent bonds will be polar**. The consequences of polar bonds are hydrogen bonding and other types of

intermolecular forces. We consider H-bonding separately because it is intermediate in strength between a bond and other intermolecular forces like dipole-dipole forces, and because unlike other intermolecular forces, cannot be explained as a purely electrostatic phenomenon. H-bonding is ubiquitous - it is implicated in phenomena as varied as the three dimensional structure of proteins, the high boiling point of water and the presence of gas phase molecular complexes. **Substances that have hydrogen atoms bonded to small strongly electronegative atoms are capable of forming hydrogen bonds**. Examples of classic hydrogen bonding molecules are water, all alcohols, and HCl. The hydrogen bond forms because the bond polarity of these types of molecules results in a small excess of charge on the electronegative atom, and a small deficiency of charge on the H atom. The negative charge on the electronegative atom of one molecule is attracted to the positive H on the other. The strength of the hydrogen bond is due in part to the large polarity of the bond, but also due in part to the smallness of the H atom and the electronegative atom, which allows a closer approach of the partially charged species, and thus a stronger coulomb interaction.

One way to view hydrogen bonding is to look at it as a type of Lewis acid-base chemistry with a partial bond formed. Remember that a Lewis base is defined as an electron donor, while a Lewis acid is an electron acceptor. While H bonding species are usually species with full octets, the bond polarity results in an electron deficiency on the H atom which results in a capability to accept a small amount of electron density, while some of the excess electron density necessary for the electronegative atom to act as a Lewis base is also a result of the bond polarity. Thus we can view hydrogen-bonded complexes as weak Lewis acid-base adducts.

**H bonding is just the strongest of the intermolecular forces between neutral molecules.** These intermolecular forces result in an attraction between molecules, and yield equilibrium geometries with a dissociation energy $D_o$ and an equilibrium bond length $r_e$. However,

because hydrogen bonding interactions are weak, the bond lengths are typically long, greater than 3 or 4 angstroms, and the dissociation energies are typically weaker than the average energy of a molecule at room temperature, E = 3/2RT = 3.7 kJ/mol. These intermolecular forces have an attractive and a repulsive component.

There are three main types of attractive forces between neutral molecules. These are dipole-dipole forces, dipole-induced dipole forces and van der Waals (dispersion) forces. The potential energy function for two dipolar molecules averaged over all possible relative orientations is given by

$$< V(R) >_{dd} = -\frac{2}{3kT}\left(\frac{\mu_A \mu_B}{4\pi\varepsilon_0}\right)^2 \frac{1}{R^6}$$

where k is Boltzmann's constant, $\mu_A$ and $\mu_B$ are the dipole moments of the two species and R is the separation between the two molecules. For non-hydrogen-bonding neutral molecules, this is the strongest type of intermolecular force.

The next strongest force is the **dipole - induced dipole force**, which is generated when the electric field of a polar molecule either attracts or repels the electrons in another molecule, thereby distorting the electron distribution and inducing a dipole moment. The magnitude of the dipole-induced dipole force depends on a property of molecules called the **polarizability, $\alpha$**, which represents the response of the molecule's charge distribution to an external electric field and is always less than 1. The induced dipole moment for a molecule A in the presence of a dipole B is given by $\alpha_A \mu_B$, and the potential energy for the dipole induced dipole interaction is

$$< V(R) >_{id} = -\frac{\alpha_B \mu_A^2 + \alpha_A \mu_B^2}{(4\pi\varepsilon_0)^2 R^6}$$

Once again, this term is substantially weaker than the dipole dipole interaction.

The weakest of the three forces is variously called the **van der Waals force, the London force or the dispersion force**. This weakest of attractive forces has made itself known even in the entertainment industry where it was immortalized by the Clash's hit CD, "London Calling". It is the interaction between two induced dipoles, and is a result of the fact that molecular electron distributions are in a continuous state of flux and are only uniform on average. This force has an extremely complicated potential function, but like the other two forces, is proportional to $1/R^6$.

It is important to realize that **a pair of interacting dipoles will experience all three of these forces**. **A dipolar molecule interacting with a nonpolar molecule will experience only the dipole-induced dipole, and London forces**, and **two nonpolar molecules will experience only the London force.**

The repulsive part of the intermolecular forces comes from the contact between the electron clouds of the interacting molecules, and is much more complicated to treat than the attractive forces. However, an important experimental observation is that when the distance between the molecules is shorter than the experimental bond length, the potential energy of repulsion increases very rapidly.

The observations regarding attractive forces and repulsive forces were combined to create an approximate intermolecular potential called the **Lennard-Jones 6-12 potential**. The form of this potential energy function is

$$V = 4\varepsilon[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^{6}]$$

Here ε is the energy necessary to separate the two molecules, while σ is the separation of the molecules at which the attraction and repulsion yield the equilibrium bond length. The term raised to the sixth power represents the attractive forces, while the term raised to the 12th power

represents the repulsive force. Note that the attractive term was chosen to match the observed r dependence of attractive interactions, while the repulsive term satisfies the requirement of a rapid rise at short r. $\sigma$ and $\varepsilon$ are always experimentally determined. $\varepsilon$ is typically small, on the order of <3 kJ/mol, while $\sigma$ is usually long compared to covalent or ionic bonds.