4. Bonding in molecules: the molecular orbital (MO) method

There is more than one approach to the theory of the chemical bond. In my judgment, the most generally useful is the method of molecular orbitals. Within MO theory, there are a variety of different approaches, as well as a vast range of levels of approximation actually used by practicing theoreticians. We will not concern ourselves at all with these fine points, taking the results of the wavefunctions found by others. We will learn a few qualitative rules for the behaviour of wavefunctions under various conditions, but that is the extent of our sophistication.

A very important and useful feature of MO theory is that it lends itself directly to describing the bonding in solids, especially that of metals and semiconductors. With the increasing importance of high-technology materials to modern industrial society, it has become more important than ever that chemists have a good understanding of solids, and thus we will consider bonds in solids (other than the ionic bond, which we covered in detail in Chemistry 2810) later on in these lectures.

4.1 Essence of the MO method

Consider the simplest molecule, $\text{H}_2^+$. Here we have a species with three interacting particles, two protons and one electron. All three interact by electrostatic attraction, as shown at right:

What molecular orbital theory suggests is that the correct approach to this, and every other, molecule is to re-solve the Schrödinger equation for this three-body problem. We first simplify the problem by fixing the inter-nuclear distance at the average bond-length measured for the molecule. This assumption can always be altered later and the problem resolved for a different, fixed, inter-nuclear separation. Nonetheless, this is still a more difficult problem than that for the H-atom, since the potential field, $V$, is now cylindrical rather than spherical. Remember that the equation has the general form:

$$-\frac{\hbar^2}{2m} \left( \frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} \right) + V \Psi = E \Psi$$

Where the Hamiltonian operator at the left operates on the wavefunction $\Psi$ to give a set of solutions at different energies, which are called the Eigenvalues, and the wavefunctions are the Eigenfunctions of the system. If this mathematical system can be solved, it leads to the derivation of the exact molecular orbitals of the simplest molecule, $\text{H}_2^+$. For this molecule, the math has been solved, and the solutions derived as closed analytical functions. Mathematicians have apparently proven that closed-form solutions do not exist for this so-called three-body problem. In particular, just as for the atom, the problems start with the addition of the second electron. Thus even the simple molecule $\text{H}_2$ has not been treated by exact molecular orbital theory.

The hallmarks of the MO method are that each different molecule, and each different conformation of those molecules, leads to a unique pattern of wavefunctions delocalized over the whole molecule. As in the H-atom, each orbital can accommodate a maximum of two electrons, and those electrons must be spin paired. Again as in the atom, the two electrons in a given orbital must have their electrons paired up, so that the molecule must pay the spin-pairing energy to accept the second electron, etc. Again as in the atom, there is a molecular analogy to the Aufbau principle, so that the electrons fill into the new molecular orbitals in such a way as to achieve the lowest possible overall electron configuration (most stable in energy.)

4.1.1 Approximate MO theory

The difficulties in exact MO theory have largely been overcome by a wide variety of approximate methods. As a result, MO theory is actually a collection of competing and overlapping methodologies. If you ever have a look at the computational engine in programs such as HyperChem or Gaussian98, you will see that there a large list of "methods" to choose from, including the Extended Hückel, CINDO, MINDO, AM1, PPP and various ab initio methods. These all refer to different levels of approximation, with the last mentioned being the most exacting, and thus generally leading to a better approximation to the true molecular orbitals of the molecule.

We will develop a bonding model in lecture that is even more simplified than these computerized methods, although we will from time-to-time correct our bonding schemes by comparison to what is shown by high-level calculations, or even better, by experiment.

4.1.2 The LCAO method

One of the most common general approaches taken in MO theory, and one that fits in with the chemist's notion of bringing two atoms together to form a chemical bond, is to consider the molecular orbitals as being formed from constituent atomic orbitals. One motivation for this notion is the consideration that when an electron is close to the nucleus of an atom, its behaviour is very similar to that of equivalent electrons in free atoms of that type. This modeling of MO's in terms of contributing atomic orbitals is
called **linear combination of atomic orbitals**, or LCAO. A linear combination is a sum with varying contributions by the constituents, the extent of the contribution being indicated by **weighting coefficients**.

The LCAO method raises the issue of what the most appropriate atomic orbitals (AO's) should be used to construct the molecular orbitals. Each atom, after all, has an infinite number of solutions to Schrödinger's equation. However, for most chemical situations, the atom will be in its **ground state**. Just as there are ground and excited states for atoms, so there will be ground and excited states for molecules, and each state requires its own LCAO calculation, differing in which AO's are used, and with which weighting coefficients they appear in the LCAO equations. This leads to one of the most important principles in LCAO theory:

1. **Those orbitals which are closest to each other in energy will undergo the greatest amount of interaction.**

A second and related principle is:

2. **Only orbitals within a narrow range of energy have the right properties to undergo significant interaction.**

Such orbitals are called the **valence atomic orbitals**, and they are the most important contributors to the LCAO-MO’s that are important for bonding. The range of energies wherein chemical bonding can take place may be shown using a graphic we have already considered, but which I will repeat here with a band drawn in that designates the valence zone:

![Energy Level Diagram](image)

It is this energetic consideration that is behind the concept of a **valence shell**. Thus, whereas the \( n = 1 \) level is the valence level for the hydrogen, it becomes a **core** level for Li, and similarly the \( n = 2 \) level is the valence level for Li to F, but becomes a core level for sodium. The valence zone that I have drawn in is not fixed in stone, but corresponds approximately to the highest energy that can be attained by chemical ionization. In fact, the \( 2s \) levels of N and F are involved in covalent bonding, but we must remember that they are very deeply buried atomic orbitals.

Although both the atomic and molecular electronic structure is derived from quantum mechanics, it helps understanding greatly to remember the physical basis underlying atomic structure. For example, let us see if we can rationalize why the only important levels for bonding of two elements from the second period are the \( 2s \) and \( 2p \). At a typical chemical bonding distance, we find that **only the orbitals from the valence level are of appropriate size to allow for bonding.** Remember that the radial probability density functions we developed for the atom each have a variable radial scale depending on the size of the effective nuclear charge that the electrons in those orbitals experience. We can pictorially represent this by drawing spheres to represent the 90% probability density of \( 1s, 2s, \) and \( 3s \) levels:

![Spheres]

Here we see that the very low-energy \( 1s \) orbitals (a) are so tightly bound to the nucleus that they do not reach out to the other nucleus with appreciable electron density; the \( 2s \) valence level is optimally able to have significant overlap with high electron density. The \( 3s \) level beyond the valence shell, however, is much larger and hence much more diffuse. Although it extends well over the region involving both nuclei, any electrons in such an orbital would have such low electron density that they would be useless at doing chemical bonding. As the energy level diagram indicates, the \( 3s \) orbital **becomes a valence orbital** in the third period because it shrinks to the right size an energy as the nuclear charge increases.
Although the energy level diagram only shows the filled levels, it is easy to extrapolate the line of $2p$ levels back up to Be and Li, and see that in these two elements the empty $2p$ level is only slightly higher than the filled $2s$ level. This is significant, because it emphasizes an important third principle:

© Empty atomic levels close in energy to filled AO’s must be included as part of the basis set of atomic orbitals.

The basis set will thus include the most important atomic orbitals from which one constructs the new molecular orbitals of the molecule. It stands to reason, then, that if an excited state of a molecule is being calculated, more inclusion of higher-lying atomic orbitals will be required in the basis set. In our discussion we will focus entirely on ground state molecular electronic structure, and we will operate with a minimum basis set.

4.1.3 One-electron theory

The next approximation that we make is to assume that the MO’s we derive are unaltered by the presence of other electrons in the same or neighbouring levels. We can then construct the possible MO’s, and populate them with as many electrons as we need. This simplification is known as one electron theory, or as the complete neglect of differential overlap (CNDO). We will allow for the cost of the electron pairing energy, and will indicate this by simply adjusting the energy of doubly occupied molecular levels up a bit higher than if they were simply $\propto$ that of a singly occupied orbital. At the computational level, the most common improvement on such one-electron theory is to allow for differential overlap. This is usually done by either a variational or a perturbational approach that starts with the one-electron wavefunctions, then proceeds to modify them by considering first the most important inter-orbital cross-terms, and working out to towards the lesser important until the right degree of accuracy is achieved.

4.1.4 The first row diatomics as an example

We are now ready to consider the first-row diatomic molecules, i.e. those made up of H and/or He atoms. We recognize that the basis set will be the two $1s$ orbitals on the individual atoms. We can then see that these can be combined in an in-phase (leading to a bonding arrangement) and an out-of-phase manner (leading to an anti-bonding arrangement).

MO’s for $\text{He}_2^*$

Using LCAO theory, this can be written mathematically as:

$$\Psi^b = \phi_{1s}(A) + \phi_{1s}(B) \quad \text{and} \quad \Psi^a = \phi_{1s}(A) - \phi_{1s}(B)$$

Pictorially this can be shown by sketches showing what happens when the orbitals are combined (both with the same size and distance separation), one case in phase, which leads to constructive interference, and hence an increase in amplitude of the wavefunction in the critical inter-nuclear region, and in the other case destructively, leading to a lowering of wavefunction amplitude in the inter-nuclear region. In MO's, as in AO’s, the square of the wavefunction is directly related to the electron density distribution, and hence the constructive interference leads to an orbital with a net increase in electron density between the nuclei, effectively gluing the two nuclei together by their mutual attraction to those electron(s). On the other hand, electrons in the destructively-interfering combination will be excluded from the inter-nuclear region, and population of this MO leads to the negation of the bond created by the constructive interference. We refer to these two situations, respectively, as bonding molecular orbitals and anti-bonding molecular orbitals. We often indicate the relative phases of the interacted wavefunctions by shading, here done in green and red.

We now consider the relative energy of the two types of interaction. Much as we rationalized atomic energy levels in the atom, we can think of what effect the electron experiences in the two combinations. We first adopt a simpler orbital labeling system, using molecular symmetry to do so. The symmetry of both LCAO’s is sigma, so we label the bonding and antibonding MO’s as $\sigma$ and $\sigma^*$, respectively. The electrons in $\sigma$ will be lowered in energy compared to an electron in a single H atom, because it spends more time being attracted to both nuclei in the inter-nuclear region. On the other hand, an electron in $\sigma^*$ will experience less nuclear attraction than in the free atom, because it is expelled from nearly half the volume of the free atom. Thus we diagram $\sigma$ as dropping below the energy of the free atom orbital, and $\sigma^*$ as rising above the energy of the free atom orbital. If we allow for the inherent inter-nuclear ($+ +$) repulsion, we can diagram $\sigma^*$ as rising more than $\sigma$ drops, as shown in the more accurate energy level diagram at the far right.
Generalization for first row diatomics

This simplistic scheme, first worked out in the early days of quantum mechanics by Heitler and London, accurately accounts for the bond energy and bond length of the simplest molecule, \( \text{H}_2^+ \), and is adequate to treat any combination of first-row diatomic. Thus if we take either two \( \text{H} 1s \) or two \( \text{He} 1s \) orbitals, and consider the total electron count involved in the four possible molecular combinations of diatomics, we discover what is diagrammed in the following figure:

\[
\begin{align*}
\text{H}_2^+ & \quad \text{H}_2 & \quad \text{He}_2^+ & \quad \text{He}_2 \\
272 & \quad 452 & \quad 301 & \quad 0 \\
1.06 & \quad 0.76 & \quad 0.5 & \quad 0 \\
0.5 & \quad \text{Bond Order} & \quad 1 & \quad 0.5 & \quad 0
\end{align*}
\]

The data below the molecules are taken from experiment, and include the bond dissociation energy (B.D.E.) in kJ mol\(^{-1}\), the bond distance in Å and the bond order (dimension-less). One of the neat advantages of MO theory is that we can postulate real bonds using a single electron, rather than the two-electron bond pairs of simple valence bond theory. In fact, \( \text{H}_2^+ \) is a very good little molecule, which can be studied accurately by electronic spectroscopy. Its bond energy is in fact greater than many two-electron bonds involving heavier atoms.

In order to correlate bonding in MO theory to the well-established valence-bond conventions, we define the concept of bond order in such a way that a bond populated by two electrons has a bond order of one. However, bond orders may be any order, unlike in VB theory:

\[
\text{bond order} = \frac{1}{2} \left[ \# \text{ of electrons in bonding MO's} - \# \text{ of electrons in anti-bonding MO's} \right]
\]

Empty orbitals and Spectroscopy

One important advantage of MO theory over the simpler VB method is the ease with which it can comprehend spectroscopic processes. This is done with the same simplicity as atomic line spectra, as being due to the promotion of an electron from a full to a higher-lying empty orbital, and/or the decay of an excited electron from such an excited state to the ground state. The energy of the photon, given by \( E = h \nu \), must match exactly the difference in energy between the two orbital levels.

For the dihydrogen molecule, \( \text{H}_2 \), there is an ultraviolet absorption band at 109 nm, corresponding to an energy difference of 11.4 eV between the bonding and antibonding levels. Most molecular absorption spectra of this type show broad lines rather than the sharp line spectra typical of atomic spectra. However, molecules, unlike atoms, are capable of undergoing rotational and vibrational motion. It is found that such motions for small molecules are also quantized. This results in coupling of the rotational and vibrational energy levels with the transitions due to the electron excitation. Some excitations lose a little energy to vibrational or rotational energy-level changes. Others gain energy from these sources. The net result is that we no longer have sharp lines, but multiplets in the spectrum, if it is measured in the gas phase. But in solution, multiple interactions between the molecules (they “bump” into each other) tend to collapse all these energy levels together. The net result is that UV-vis absorption spectra tend to be broad lumps of energy absorption rather than sharp lines. Nevertheless, the principle in terms of the basic quantum phenomenon of an electron being excited from a lower lying orbital to an empty higher orbital is identical to the atom and to the molecule.
4.2 The second row diatomic molecules

When we turn to the second row of the periodic table, the 1s orbitals drop way down in energy. This means that (i) the smaller orbitals overlap less, and hence the energy gap between bonding and antibonding orbitals decreases, and (ii) both $\sigma_{1s}$ and $\sigma^*_{1s}$ are occupied. The net effect is that these MOs no longer contribute to bonding effects between the atoms in the second row diatomics. This is a general phenomenon, so that we always ignore the core orbitals when considering a bonding scheme.

We call the important orbitals the valence MOs, and these logically enough are usually derived form the valence atomic orbitals of the constituent atoms. Theoreticians have also coined the term *frontier orbitals* to indicate those MOs which are most important to reactivity of the molecule, and these are usually the Highest Occupied Molecular Orbital, HOMO, and the Lowest Unoccupied Molecular Orbital, LUMO. However, sometimes orbitals slightly lower than the HOMO or higher than the LUMO are also frontier orbitals.

4.2.1 Generalized orbital overlap

From the shapes of the orbitals we can go directly to the important concept of orbital overlap: bonds between atoms will only occur if there is significant constructive interference between some of the waves on one atom and some on the other. This is called orbital overlap.

Symmetry classification of orbital interactions

When we combine more than one orbital on one atom with those on another, the geometry of the interaction results in *different symmetry classes of orbital overlap*. The important symmetry classes for the diatomic molecules, and by inference for any two-atom interaction (i.e. one bond in a longer molecule) are $\sigma$, $\pi$ and $\delta$. Delta bonds are extremely rare, being encountered only for certain heavy transition metals which can possess a quadruple bond. Pi bonds are normally part of double and triple bonds. These simplified bonding descriptions can be generalized by considering the following listing of different bond types.
Shown at the right are a fairly comprehensive sample of possible orbital interactions that lead to the three classes of overlap symmetry.

**Constructive, destructive and orthogonal overlap**

Not all combinations of overlap are possible. Those interactions that lead to no net constructive or destructive interference are said to be orthogonal. Orthogonal interactions lead to a third class of orbital, the non-bonding molecular orbital. Of course, the most common form of orthogonal interaction is among the orbitals of a single atom. Thus the ns, np, and nd orbitals within an atom all occupy the same region of space, but coexist because they are orthogonal. A common kind of orthogonal interaction in a molecule occurs when an atomic orbital on one atom is of a different symmetry class, and therefore cannot interact with any orbital on the other atom. Such an unhybridized AO is carried over into the MO scheme without alteration.

4.2.2 **"First order" MO diagrams for the diatomics**

We are now ready to construct at least a first attempt at the molecular orbital diagram for a second-row diatomic molecule. We use a fragment approach, as shown below, in which we bring the two atoms with their valence orbitals (the basis set) together, and indicate which interactions lead to more stable, and which to less stable, MO’s. The lines connecting the AO’s and MO’s in this diagram have no real significance, and are added mostly to guide the eye. The approximate orbital shapes that are produced by these interactions is shown in the sketches at the right hand side of the diagram.

**MO description of 2nd row homonuclear diatomic molecules**

Note that the total number of nodes are preserved between the incident atomic orbitals and the resulting MO’s. Also, it is often difficult to render the resultant MO’s accurately, unless you happen to be a good artist. For most purposes, topologically correct diagrams will suffice, i.e. just draw the overlapped AO’s in the position they hold in the molecule, but shade them as to
show the constructive and destructive overlap. Nonetheless it is very important to study the final forms of these MO's on the right, because that is closer to the actual electron distributions that our topologically correct diagrams represent. For an even better visualization, run an empirical MO calculation on a computer, and rotate the resulting wire-frame orbitals in space to appreciate their 3-dimensional nature better.

**σ versus π overlap**

A very important conclusion has been included on the diagram above, and that is that the end-on σ overlap of the 2p orbitals leads to greater bonding and antibonding interaction than the side-on π overlap. Why is this the case? This can better be appreciated by considering some scale diagrams of orbitals drawn at typical single and triple-bonding distances.

First of all, a single bond is longer than a double bond. This is because the optimal overlap is achieved in σ bonding when the nuclei are further apart than is optimal for π overlap. Indeed, at the distance shown in the diagram at the left, the sideways overlap of the same 3p orbital is negligible at best. Thus on forming a double bond, the bond distance gets shorter. A triple (σ + 2π) bond is even shorter, because there are two π bonds requiring a shorter distance for optimal overlap. What is important to realize, as shown on the next diagram, is that even at the shorter distance found in a multiple bond, the overlap efficiency of the σ interaction is still greater than that of the π interaction. This should be seen as strictly a consequence of geometry.

Since the σ overlap is greater, the electrons experience a stronger attraction to the nuclei (or repulsion in the antibonding case), and thus the energy of the σ orbitals drops lower than that of the π orbitals when equivalent np orbitals overlap in this fashion.

### 4.2.3 Orbital mixing and a "second order" treatment of the diatomics

An important reason to use symmetry labels in MO theory is that symmetry controls the types of interactions that are possible. This leads first to another of our basic rules of LCAO theory:

1. **Only orbitals of the same symmetry can interact constructively or destructively to form bonding and antibonding orbitals.**

But a second consequence of symmetry that is almost equally important is the so-called **non-crossing rule**. This states that:

2. **When two energy levels of the same symmetry class approach each other in energy, they will interact (mix) in such a way that the lower level will drop in energy and the higher level will rise in energy.**

In the diatomic molecules, this effect is most dramatic for the early molecules such as Li₂ and Be₂. We have already noted that in these elements, the atomic 2s and 2p levels are very close to one another. A consequence of this is that the energy of the resulting diatomic 1σ and 2σ orbitals come very close to one another. They therefore undergo extensive s-p mixing, with the result that the lower level gains p character, and is lowered in energy, while the higher level gains s character in order to become less strongly bonding. A consequence of this is that the strict division of the MO's to individual atomic parentage becomes less...
clear-cut, and from now on we will not be using this labeling method. Instead, we will simply number orbitals with the same symmetry labels from 1 to \(n\) up the MO diagram starting from the bottom. The non-crossing rule can be diagrammed as follows:

The "g" orbitals will end up being much closer to each other as a consequence of how the diagram is constructed, and it is clear from (a) in the figure that these two levels would have crossed if linear correlation had occurred. The situation for the "u" orbitals is less dramatic, but the effect is nonetheless the same, so that the two levels mix and thereby pull apart from one another as the nuclei are brought closer together. You may wonder as to how this mixing is accomplished, and this is best understood by considering the topological sketches of these two orbital types.

I have arbitrarily mixed in 30% of the same-symmetry orbital in each case: in fact the extent of mixing will change directly with the atomic \(s-p\) separation in energy. Further, it will not be usual that the degree of mixing of \(\sigma_g\) and \(\sigma_u\) will be by the same amount in a given molecule. But the principle of mixing operates this way in all cases. Note that the resulting MO's are no longer sublabeled "2\(\sigma\)" and "2\(p\)", because that strict distinction has been lost. In fact, from now on we will use symmetry labels directly created for the MO's, and not worry too much as to which AO's they originally came from. Note also that we have created orbitals of partial bonding and anti-bonding character! This will also complicate our calculations of bond order, which in most MO diagrams will not be completely cut and dried.

Consider carefully what has happened to the MO's resulting from the mixing: 1\(\sigma_g\) has gained increased electron density in the inter-nuclear region. We would expect it therefore to be lowered in energy. 1\(\sigma_u\) has decreased electron density in the inter-nuclear region as well, but this was anti-bonding electron density, so this orbital has become less anti-bonding than previously. Thus we would also expect this orbital to be lowered in energy. On the other hand, 2\(\sigma_g\) has lost electron density in the inter-nuclear region, which was bonding, and has become polarized to the left- and right-sides. It is well on its way to be a non-bonding MO, one that corresponds to the VB notion of a lone pair. However, note that in MO theory, such lone pairs are described as delocalized rather than as localized regions of electron density. Which is more accurate? We will look for evidence on this issue a little later in our discussion. For the moment, we recognize that this orbital will be raised in energy. In fact, it is the raising of the energy of 2\(\sigma_g\) which is the most noticeable effect of second-order mixing among the second-row diatomic molecules, because it is possible for this level to be raised so much that it ends up above the \(\pi\) level, thus causing a level-inversion in the MO diagrams of the second-row diatomics. Finally we recognize that 2\(\sigma_u\) "paid the penalty" of all this re-mixing by becoming a highly-unfavourable strongly anti-bonding orbital, and thus we expect this orbital to be raised in energy significantly where strong second-order mixing occurs.
We are now ready to see the effect of all these hybridizations on the energy level of the molecule. Note that the π levels are unaffected, because they have nothing that they can mix with in the homonuclear diatomics.

MO description of 2nd row homonuclear diatomic molecules

Energy levels in original diatomic construction

Now that the theory is in place, we are ready to apply it to the actual molecules, and the results of detailed calculations and measurements on all the second-row diatomics are shown in the following diagram:
To see how this picture fits with the experimental results on such molecules, consider the following table of data:

<table>
<thead>
<tr>
<th>Property</th>
<th>Li₂</th>
<th>Be₂</th>
<th>B₂</th>
<th>C₂</th>
<th>N₂</th>
<th>O₂</th>
<th>F₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond length (Å)</td>
<td>2.67</td>
<td>–</td>
<td>1.59</td>
<td>1.24</td>
<td>1.10</td>
<td>1.21</td>
<td>1.42</td>
</tr>
<tr>
<td>Bond energy (kJ mol⁻¹)</td>
<td>110</td>
<td>–</td>
<td>272</td>
<td>602</td>
<td>941</td>
<td>493</td>
<td>138</td>
</tr>
<tr>
<td>Bond order</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>2</td>
<td>1</td>
</tr>
</tbody>
</table>

There are some important features of these molecules that bear consideration, partly because of their intrinsic interest, and also because similar situations will crop up for many of the more complex molecules we will encounter later. Note first of all that 6 of the 8 possible second-row diatomic molecules can exist (though only N₂, O₂ and F₂ are the most stable forms of those elements).

Note that strong evidence for the orbital mixing we have been considering is provided by the magnetic properties of B₂ and C₂. Thus the former is paramagnetic (two unpaired electrons in π) and the later diamagnetic (all electrons paired), consistent with the diagram. If a level inversion did not exist, then the opposite should be true, i.e. B₂ diamagnetic and C₂ paramagnetic. The bonding in B₂ is also quite unique, with the net single bond being a π-bond, but without a σ bond to support it! Similarly C₂ has two π-bonds but no net σ bond!

Note that N₂ would be diamagnetic with or without a level inversion, and so we will need additional experimental evidence to support the order of the MO's in this molecule. Note that MO theory clearly predicts that O₂ will be paramagnetic with two unpaired electrons. This is not obvious from the Lewis structure of dioxygen, which has a double bond and 4 lone pairs. Note also that the "double bond" in this molecule is the net result of having a "triple bond" and a single anti-bond. This situation leads to weaker overall bonding than a bond order of 2 when there are no anti-bonds, e.g. compare O₂ with C₂. Similarly F₂ has a single bond that is the net of a "triple bond" and a "double anti-bond". Consequently F₂ has a very low bond energy. We are not surprised to learn that much of the chemistry of this diatomic molecule occurs via radical processes, in which the weak F–F bond is first broken to form two reactive F atoms. Finally note that bond distances go down from left to right across the PT for bonds of similar bond order. In part this reflects the reduction in size of the atoms themselves in the same direction.

4.2.4 Using CACAO and HyperChem

A quantum-chemistry computer program will calculate a "best" MO description of a molecule in one go, the degree of accuracy depending on the sophistication of the method being used. A well-known approximate MO method is the Extended Hückel method developed originally by Nobel laureate Roald Hoffman. This is a low-power MO method that uses the one-electron approximation in conjunction with experimentally derived atomic energy levels. It is therefore often called and "empirical MO method". The Extended Hückel method (EHMO) is incorporated into several popular software packages, of which two are ones you are likely to have a chance to use. The first program is CACAO, a wonderful implementation of Hoffman's original code into a Window's compatible software package that is provided free by an engaging pair of Italian inorganic chemists. Please consult your instructor if you wish to obtain your own copy of CACAO.

HyperChem is a commercial product, and is quite expensive. If you wish to own a copy of this program, an inexpensive version called HyperChem Lite, which incorporates the EHMO method, is available for about US$50 by downloading off the internet. The URL of the company is www.hypercube.com. The full versions of HyperChem also contain more sophisticated "semi-empirical" and "ab initio" molecular orbital methods. The interface in HyperChem is entirely interactive on the computer screen, and uses a mouse to create and manipulate the structure. CACAO, by contrast, is a command-driven Fortran computer program that was developed from code first written in the 1960's. However, despite the antiquated interface, the program does incorporate some nifty features that directly reflect Hoffman's insightful approach to MO theory. In particular, the fragment orbital analysis used by the program most directly resembles the approach taken in these lecture notes. I would therefore recommend that you invest the time required to become an adequate CACAO user. Here follow some extracts of the input code and the output from CACAO for dinitrogen.

Input file for N₂:

```
TITL  nitrogen
PAR  0 DIST
KEYW EL WF CM OV OP RO NC
ORIG  DU
INT N -1 1 0.564 180 0
INT N -1 2 0.564 0 0
FMO
FRAG 2 1
END
```

(consult the manual for explanation of the arcane command language!)

Here is the energy level diagram:
Here are the plots of the MO's in wire-frame representation:
4.2.5 Ultra-violet photoelectron spectroscopy

Although ultraviolet absorption spectra have proved very useful for the analysis of the electronic structure of diatomic molecules more complex than \( \text{H}_2 \), a more direct portrayal of the molecular orbital energy levels can often be achieved by using ultraviolet photoelectron spectroscopy (UV-PES) in which electrons are ejected from the orbitals they occupy in molecules. In this technique, a sample is irradiated with 'hard' (high frequency) ultraviolet radiation (typically the He(l) line of 21.22 eV radiation from excited He atoms, or the He(ll) line at 40.8 eV) and the kinetic energies of the photoelectrons - the ejected electrons - are measured. Because a photon of frequency \( \nu \) has energy \( h\nu \), if it expels an electron with ionization energy \( \text{IE} \) from the molecule, the kinetic energy \( E_k \) of the photoelectron will be:

\[
E_k = h\nu - \text{IE}
\]

The lower in energy the electron lies initially (that is, the more tightly it is bound in the molecule), the greater its ionization energy and hence the lower its kinetic energy after it is ejected. The instrument used to measure UV-PES shares many components with a mass spectrometer. A schematic of the device is shown at right. Since all electrons have the same mass, instead of selecting out the mass in the magnetic analyzer (as done in a mass spectrometer), the kinetic energy can be measured. The detector circuitry subtracts the kinetic energy from the known source energy, and thus we get a readout of intensity (y axis) against IE - a photoelectron spectrum.

Because the peaks in a photoelectron spectrum correspond to the various kinetic energies of photoelectrons ejected from different energy levels of the molecule, the spectrum gives a vivid portrayal of the molecular orbital energy levels of a molecule. To analyze a photoelectron spectrum we use the simplifying assumption called Koopman's theorem:

\[
\text{IE} = -E_{\text{orbital}}
\]

In other words, we assume that the ionization energies are the exact inverse of the orbital energies of the M.O.s in the molecule. Thus UV-PES gives us a literal "snapshot" of the M.O.s of a molecule! Though an approximation, it holds remarkably well for small molecules. A typical UV-PES of a small molecule is shown in schematic form below, keyed to the vibrational changes that occur in the molecule during ionization.
In the un-ionized molecule, most of the molecules will be in the ground vibrational state, and have the average inter-nuclear separation that chemists call the "bond length". If ionization results in a 1+ molecule with very similar bond strength to the original, the vibrational levels of the produced ion will be very similar to that of the neutral molecule, and most of the ions will be in the ground vibrational state. In this case, the ionization will result in a single peak corresponding to the transition from the ground vibrational state of the molecule to the ground vibrational state of the ion. There will be a few small daughter peaks resulting from that fraction of both molecule and ion that populate higher vibrational states, but these will be minimal.

On the other hand, if the ionization causes a significant change in bond-strength, either by removal of an anti-bonding electron (bond strengthening), or removal of a bonding electron (bond weakening), the bond length will alter significantly. My sketch shows the case of bond weakening, with the average inter-nuclear separation increasing. Vertical ionization will then automatically push the ion into a large number of vibrational excited states, and the result is an envelope of evenly spaced peaks instead of a single peak. This is shown in the spectrum by the middle band, which has lots of vibrational fine structure, whereas the 1st and 3rd peaks are sharp.

The interpretation of this in terms of molecular orbitals is that the 1st and 3rd peaks are from orbitals that are mostly or completely non-bonding, whereas the 2nd peak is from an orbital that is either strongly bonding or strongly anti-bonding. The way I have drawn the potential wells, in this case it is from a strongly bonding orbital (though this choice is not obvious from the spectrum alone.) To summarize our discussion:

- The smallest IE represents electrons from the HOMO
- If the MO is strongly bonding or anti-bonding, the ionization will have a vibrational fine structure. This can actually be used in small molecules such as N₂ to measure the N–N stretching frequency, which does not show up in the IR spectrum.
- If the peak is sharp, the MO is essentially non-bonding.
- For larger molecules, the lower orbitals tend to be closely spaced in energy, so that a virtually continuous ionization band is usually seen at higher energies for larger molecules.
- Ionizations requiring >21.22 eV require the use of He-II photons, and such ionizations are always broad, so that little can be said about bonding/anti-bonding vs. non-bonding for such high-energy processes. Often only He-I data is reported, so that as a general rule, only the higher-lying MO's in an MO diagram will be interpreted by UV-PES.

Let us now apply our ideas to a real-life example: dinitrogen. This vitally important diatomic molecular element has been studied by UV-PES. In the diagram below, the UV-PES spectrum has been turned on its side, and the ionization energies keyed to the energy levels in the MO diagram. Topologically correct sketches of the orbitals are also provided.

Here are some of the important features to pay attention to:
• The first IE has little bonding character, consistent with ionization of electrons from the $2\sigma_g$ level, which through second-order mixing has lost most of its bonding character, and become non-bonding.
• The second IE is an envelope of peaks due to a lot of vibrational fine structure. This is fully consistent with ionization out of the strongly bonding $\pi_u$ MO.
• The third IE is again from a non-bonding level, and this is consistent with ionization out of the $1\sigma_u$ level in this molecule.
• Note that the labelling of the UV-PES, taken from the textbook, is different, because they have included the $\sigma_g$ and $\sigma_u$ formally derived from the $1s$ level in their count. We will not do this in our own diagrams, although it is never wrong to do so - just unnecessary.
• We cannot see the fourth IE from the $1\sigma_g$ level using He-I radiation. However, it has been measured with the He-II source, and is found as a broad lump at about 40 eV!
• The UV-PES data therefore provide experimental evidence for the level inversion shown in the previous diagram of all the second-row diatomics. In the case of N$_2$, both alternative electron arrangements lead to diamagnetic structures, so that we need this additional evidence to prove the structure.
• Note also that in comparison to the Lewis structure of N$_2$, :\text{N}\equiv\text{N}:; the MO description has similarities and differences. The bond order is indeed 3 by both descriptions (6 electrons in the bonding MO's $1\sigma_g$ and $\pi_u$). There are two lone-pair type orbitals, $1\sigma_u$ and $2\sigma_g$. However, the lone pairs are not equivalent, as the Lewis structure would suggest. One is the HOMO, and will be used as the donor atom when N$_2$ acts as a (weak) Lewis base, the other is deeply buried and will not be involved in reactivity (its not a frontier orbital).
4.3 Heteronuclear diatomics

4.3.1 Heteronuclear MO interactions

In the general bonding situation, the atoms bonded will not be of the same type. If atom A and atom B are bonded to one another, and for point of argument, A is the more electronegative element, then the bonding interaction will look as follows:

There are several significant differences here from the homonuclear case. The energy of the in-phase combination of orbitals is closer to that of the A atomic orbital. Also it has a greater coefficient $c_A$, that is that the MO has more A character than B character. The reverse is true for the out-of-phase interaction. Here the MO is of course the anti-bonding analogue. However, the energy of this interaction is indeed closer to that of the B atomic orbital, and the MO has a larger $c'_B$ coefficient. In colloquial parlance, we say that $\sigma$ is polarized towards A, while $\sigma^*$ is polarized towards B.

The extent to which the energy level diagram is asymmetric, and the consequent extent of the polarization of the resulting MO’s, depends entirely upon how close the energies of the constituent AO’s are. A first guess as to how separate they are is given by the Pauling electronegativity. A large $\Delta \chi$ results in a very asymmetric interaction, while a small $\Delta \chi$ will lead to a weakly asymmetric interaction. Of course, when AO’s differ greatly in energy, their ability to overlap is greatly compromised. In the limit, we should get an ionic description of the bonding (that is, the bonding MO is entirely localized on A, which accepts the electron to become $A^-$, while B becomes $B^+$, and its valence orbital is empty.)

The strongest covalent overlap is always between orbitals which are close in energy and similar in size. The latter controls the diffuseness of the wave function. If electronegativity is an insufficient guide, we can once again employ the SCF energies of the atomic orbitals that we introduced earlier:
Let us now apply these principles to some examples.

### 4.3.2 Heteronuclear diatomics: HF as the first example

HF differs from the previously considered molecules in two important ways: (1) first the energy of the constituent AO are different for H and F, and (2) second, the molecule belongs to a different point group. It is $C_{\infty v}$. We start by orienting the AO’s on the page, as shown below, and can then apply the principle that, in general, the strongest overlap will be between orbitals of the same symmetry that are closest to each other in energy:

![Molecular orbital diagram](image)

This leads to a “first order” attempt to sketch the MO’s of the HF molecule. Given the much higher energy of the H 1s level, it is obvious that we would expect a stronger interaction with the F $p_z$ orbital than with the F $s$ orbital. However, this conclusion is not completely warranted for the following reason: the resulting MO $2\sigma$ will end up being close to the energy of the unhybridized F $2s$ orbital which in the molecule has the formal symmetry label $1\sigma$. Now in the $C_{\infty v}$ point group $1\sigma$ and $2\sigma$ have the same symmetry character, since the distinction between “$g$” and “$u$” does not exist in this point group. Therefore we expect significant second-order mixing of these to orbitals. This results in $1\sigma$ being lowered in energy and gaining H 1s character (hence becoming bonding) while $2\sigma$ loses bonding character, rising in energy and become more lone-pair like.

To check the validity of our thinking we can (1) consult the UV-PES, and (2) try a semi-empirical MO calculation, in this case using the AM1 method.

1. **UV-PES of HF**

The PES is not that easy to interpret. We note that the first ionization comes from a non-bonding type of orbital, and this is consistent with $\pi_1$ as the HOMO.

But for $\sigma_1$ and $\sigma_2$ the evidence is rather indistinct. Both are rather broad and indistinct, but broadness generally hides unresolved vibrational fine structure, so both orbitals probably have at least partial bond character.
Perhaps the best way to use the results of this PES is to compare the orbital energies to that of an AM1 calculation. Below is the result of the AM1 calculation. The calculated energies are \(-14\), \(-17\) and \(-50\) eV, in reasonable agreement with the \(-16\), \(-19\) and \(-40\) eV from the experiment. The results are shown below. Note that \(\pi\) is a molecular orbital that contains only the unhybridized fluorine \(p_x\) and \(p_y\) orbitals. These lone-pair type MO’s are the HOMO of the molecule. Both bonding MO’s are strongly polarized towards the fluorine atom, in full agreement with the very large dipole moment on HF, which tends towards the description \(\text{H}^+ - \text{F}^-\).

4.3.3 Heteronuclear diatomics: CO as a second example

Carbon monoxide is significant both from an electronic structure point of view and as in view great chemical importance. Thus CO is the chief reagent operating in a conventional blast furnace. It is used in the water gas conversion and methane to hydrogen and hydrocarbons, is also a significant toxin. This toxicity is a result great tendency to complex to transition metals, making it one of the most important ligands for series of elements. We start our analysis by that CO is actually isoelectronic to dinitrogen. Its description starts from the realization that carbon is \textit{less} and oxygen is \textit{more} electronegative. The differences are significant, the \(\Delta \chi\) is smaller than for HF – the bonding will less ionic character.

A UV-PES of CO is presented at right to us check the validity of the MO calculation. The bands are provided with blown-up display for of viewing.

A key feature of this MO diagram is that the energy of the C 2s AO is very nearly equally between the oxygen \(s\) and \(p_z\) levels. This will tell you right away that the overlap will involve extensive mixing. It is very hard in such a situation to guess using pen
and paper where the energies of the resulting MO’s will fall. As in the case of \( \text{N}_2 \), the mixing results in \( 2\sigma \) and \( 3\sigma \) having very little residual bonding character. They are in fact the “lone pairs” seen in the Lewis structure \( :\text{C}=:\text{O} \).

Now the PES confirms the relative energy levels of the calculation shown below. Thus the HOMO is a non-bonding orbital (\( 3\sigma \)), the next orbital is strongly bonding or antibonding (\( 1\pi \)), and the third is again non-bonding (\( 2\sigma \)). Note that this PES does not show the most deeply bound orbital – it was obtained only using the He I light source which has a maximum energy of about 22 eV. Finally, note that the complete Lewis structure of CO puts a formal negative charge on C and a formal positive charge on O (against the expected polarity from the element electronegativities). The MO calculation explains this counter-intuitive result: the negative charge on C corresponds to the HOMO \( 3\sigma \) orbital being strongly polarized towards the C. Thus in this molecule, unlike \( \text{N}_2 \), one of the lone pairs is very much more localized on one atom – C, and the other (\( 2\sigma \)) on another atom – O.

### 4.3.4 Summary of the approximate LCAO method

Let’s remember the key points of our qualitative "back-of-the-envelope" approach to building molecular orbital bonding descriptions:

- it is remarkably reliable - although we understand MO theory in terms of qualitative arguments, we will wherever it is critical use MO diagrams substantiated by high-level calculations or experimental evidence like PES
- atomic orbitals can and will interact with orbitals on other nuclei which have the same symmetry
- the resulting MO’s can further interact with other MO’s of the same symmetry (orbital mixing)
- the strongest interactions occur between those orbitals which are closest in energy
- for heteronuclear bonds, the relative order of the atomic orbitals can be deduced by the electronegativities of the bonded elements
- for heteronuclear bonds, the resulting MO’s are polarized such that the more bonding orbital is dominated by contribution from the more electronegative element, whereas the more antibonding orbital is dominated by contribution from the less electronegative element
- to be useful, an MO treatment for a molecule should have both an energy level diagram and topologically correct sketches of the resulting MO’s
- ultra-violet PES is an experimental "snapshot" of the inverse of a MO diagram; sharp peaks emanate from orbitals which are essentially non-bonding; peaks with lots of fine-structure emanate from strongly bonding or anti-bonding MO’s
- PES of molecules with degenerate orbitals containing unpaired electrons often show two peaks for ionizations from those orbitals, corresponding to ionizations with and without spin-pairing
the bond order for a molecule is defined as:

\[ \frac{1}{2} \times (\text{number of electrons in bonding orbitals} - \text{number of electrons in antibonding orbitals}) \]

ignore non-bonding orbitals in this count! Bond order harmonizes MO theory to the popular Lewis dot structures; partial bond-orders are permissible in MO theory

### 4.3.5 Using HyperChem as a tool in determining MO bonding descriptions

We are fortunate to be able to use quantitative MO calculation programs to enhance our treatment of bonding. The following factors should be taken into account when using HyperChem to perform MO calculations.

- **In this course, we will only use Semi-Empirical methods, and in particular we use AM1 for simple 1st and 2nd period elements, and PM3 for other molecules. PM3 is has been parameterized for a considerable greater number of elements than has AM1. Note that a feature of all semi-empirical methods is that only the valence orbitals are used in calculations. The effect of the core orbitals is accounted for by parameterization.**

- **This affects orbital numbering. If you select an *ab initio* method, there will be more MO’s since in this methodology the core orbitals are included, and are used effectively to calculate the nuclear charges experienced by the valence orbitals for each given molecule and structure.**

- **Be sure to invoke the Model Build or Add Hydrogens and Model Build feature before performing a semi-empirical calculation. Indeed, unless you have good reason not to, you should usually perform a geometry minimization within the method of calculation you are using (e.g. AM1 or PM3). There will, however, be exceptions, and in those cases remember that a quantum calculation can always be performed for any given ensemble of atoms, whether or not they are realistic chemical species.**

- **Before performing the calculation, it is often advantageous to use the Edit – Align Molecules feature, and here align both the Major and Minor axes to Cartesian coordinates of your choosing. This step will ensure that your orbitals are aligned orthogonal to the axes of the screen. Note that it is often useful to move the molecule to some slight angle for better viewing. This does not affect the alignment procedure, and the aligned orbital will now move with the molecule and do not require re-calculation.**

- **Always check that the Setup – SemiEmpirical – Options have been set correctly for your molecule or ion. The Total Charge ge is either an integer for a positive charge, 0 for a neutral molecule, or –1, -2, -3 etc. for anions. Directly associated with this setting is that of Spin Multiplicity. A multiplicity of 1 indicates zero unpaired electrons; 2 means 1 u.p.e., 3 is 2 u.p.e., etc. This MUST be set correctly and re-set between calculations.**

- **Under the Compute menu, you have the choice of a Single Point Calculation or a Geometry Optimization. While in general the latter is to be preferred, there will be important occasions where you will choose to perform Single Point calculations. For example, some models can only be created by the Model Builder, but cannot be geometry optimized at all. Others will only be optimized by molecular mechanics (MM+). Thus you could carry out a single point MO calculation on a geometry generated by an MM+ geometry optimization.**

- **Once either of this type of calculation have been performed, other options become available on the Compute menu, including the calculation of the vibrations, transition states, orbitals, etc. Once vibrations are calculated, it becomes possible to view the Vibrational Spectrum of a given molecule.**

- **Under the Orbitals menu, an energy level diagram is presented which provides orbital energies in electron volts, orbital labels using symmetry derived from the point group, and the ability to Plot individual wave functions. Under the Options menu you can set a large number of plotting options, such as the Isosurface rendering method, the isosurface grid mesh size, the orbital contour value, and several others.**

- **After selecting your options, you have the choice of plotting any one of the MO’s on the remainder of the screen (possibly you will have to reduce the size of your molecule, or move if off-centre to see it fully), or else you can hit the OK button. Once this has been done, you are left with the model and the isosurface grid, which can be re-oriented as much or as little as you want. This is how you get to truly understand the shape of any given calculated molecular orbital.**
4.3.6 Bond properties

The diatomic molecules are a good place to review common descriptions of bond properties that we first saw in General Chemistry. Consider the following correlation between the bond energy, bond length and bond order for element-element bonds among 2nd-period elements. For diatomics, the bond energies are exact. For polyatomics, the method of average bond enthalpies has been applied.

The diagram shown at the right gives the final correlation, that between bond energy and bond length. The colour coding here is the same as that used above (nitrogen, red oxygen, etc.). Such plots are extremely useful because the bond length is commonly measured by experimental methods as IR spectroscopy or single-X-ray diffraction studies. Note that to interpret this empirical curve is required. The lines are not straight.

We conclude that, in general,

1. Bond enthalpy for a given pair of bonds increases as bond order increases.
2. Bond length decreases as bond order increases.
3. For a given pair of elements, the bond enthalpy increases as bond length decreases.

However, the relative energy of single, double and triple bonds is not the same for all element combinations. For C–C bonds, a single bond is more than half as strong as a double bond. But for nitrogen, N–N at 163 kJ mol⁻¹ is much weaker than half a double bond (N=N at 409 kJ mol⁻¹). Indeed the N≡N triple bond at 945 kJ mol⁻¹ is by far the most stable form of nitrogen in terms of kJ mol⁻¹ per bond order! Yet for phosphorus in the same group, the trend more resembles that of C. The energies of P–P, P=P and P≡P bonds are approximately 200, 310 and 490 kJ mol⁻¹. Such factors will be extremely important to our discussion of the chemical properties of the main group elements, and in particular we will discover that the 2nd-period elements in general are exceptions in the periodic table, and that the normative behaviour occurs for the 3rd and higher periods.
4.4 Polyatomic molecules A: the hypothetical polyhydrogen molecules

Our approach to the molecular orbital description of the bonding in polyatomic molecules will start by considering a simple-minded extension of the arguments we introduced originally to produce an LCAO one-electron theory for the H$_2^+$ molecule. Just as we used that model to describe the bonding in real species such as H$_2$, we will take the resulting one electron orbitals and add electrons and make arguments about which bonding situations are more or less likely. In this fashion we will be able to describe potentially real molecules such as the H$_3^+$ ion.

4.4.1 Constructing molecular orbitals: H$_3$ as a paradigm.

Here for the first time we have to worry about shape. The two logical limiting structures for trihydrogen are linear and equilateral triangular. This does not mean that some intermediate shape might not be adopted, and an exhaustive search of possible geometries would be required in a full-scale theoretical study. For our purposes, these two high symmetry situations will suffice. In general, we are going to be using symmetry as an aid in our discussion of bonding. Whenever the true shape of a molecule is lower than the expected symmetry, we will note that as an exception.

Linear H$_3$

We have three 1s orbitals spaced along a line. The LCAO approach generates the following three MO’s in $D_∞h$. First there is

$$\Psi_1 = 1σ_g = c_{1,1s}(A) + c_{1,1s}(B) + c_{1,1s}(C)$$

Next comes:

$$\Psi_2 = 2σ_u = c_{2,1s}(A) - c_{2,1s}(C)$$

Then:

$$\Psi_3 = 3σ_g = c_{3,1s}(A) - c_{3,1s}(C)$$

The topology of these orbitals is shown in the figure at right. The coefficients $c_{11}$, $c_{12}$, $c_{13}$, $c_{22}$, $c_{23}$, $c_{31}$, $c_{32}$, $c_{33}$ are called normalization coefficients. These take care of the total amount of any given atomic orbital that is available for mixing. Note that the middle orbital cannot have a non-zero contribution from $φ_{1s}(B)$. All attempts to insert this atomic orbital into the mix results in an orthogonal interaction (what is gained at left is lost at right, etc.) The coefficients accommodate this by assigning a relatively larger proportion to $φ_{1s}(B)$ in $1σ$ and $2σ$ than to either $φ_{1s}(A)$ or $φ_{1s}(C)$.

Our paper efforts at determining MO bonding schemes will largely ignore such scaling factors, but the semi-empirical calculations take these factors into account. Note that the form of the normalization coefficients naturally describe a $3 \times 3$ matrix, and all computerized MO calculation methods heavily use matrix algebra to perform the calculations.

Triangular H$_3$

Another reasonable hypothesis for the shape of H$_3$ is an equilateral triangle. We could construct the orbital topologies first by just bending the linear ones over. However, we are now no longer in the linear point group, but in $D_{3h}$. Here we run into a common problem in polyatomic MO theory: degenerate orbitals, and how to represent them. It turns out by rigorous calculation as well as from group theory that the two orbitals derived from bending $2σ_g$ and $3σ_g$ become exactly degenerate in the triangular geometry. The labels we now use for the orbitals are those taken from the $D_{3h}$ character table. It is not possible to discuss the two components of $e'$ separately, and the relative sizes of the orbitals is meant to suggest the fact that these MO’s are normalized. Thus:

$$\Psi_1 = a_1 = c_{1,1s}(A) + c_{1,1s}(B) + c_{1,1s}(C)$$

and

$$e' = \begin{cases} 
\Psi_2 = c_{2,1s}(A) - c_{2,1s}(C) \\
\Psi_3 = c_{3,1s}(A) - c_{3,1s}(C)
\end{cases}$$

and

$$e' = \begin{cases} 
\Psi_2 = c_{2,1s}(A) - c_{2,1s}(C) \\
\Psi_3 = c_{3,1s}(A) - c_{3,1s}(C)
\end{cases}$$
The orbitals are labeled using the Mulliken representations, which describe how the given MO transforms within the indicated point group. These labels are found in the right-hand column of the table. These labels are also used for other symmetry-related properties. Thus for example the possible normal modes of vibration for a molecule with this point symmetry are thus labeled. The \( a_1 \) orbital is easily identified as the fully symmetrical case, for which all the entries in the character table are +1. This wave function possesses the full symmetry of the molecule (or higher). The origin of the \( e' \) label from the character table is not easy to explain without delving rather deeply into Group Theory. Suffice it to say at this point that the set of two wave functions together account for the characters in the table. When you need such labels, they will be provided (see below for the normal source of such information.)

<table>
<thead>
<tr>
<th>( D_{rb} ) (6m2)</th>
<th>( E )</th>
<th>( 2C_3 )</th>
<th>( 3C_2 )</th>
<th>( \sigma_h )</th>
<th>( 2S_3 )</th>
<th>( 3\sigma_v )</th>
<th>( h = 12 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A'_1 )</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>( x^2 + y^2 + z^2 )</td>
</tr>
<tr>
<td>( A'_2 )</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>( R_z )</td>
</tr>
<tr>
<td>( E' )</td>
<td>2</td>
<td>-1</td>
<td>0</td>
<td>2</td>
<td>-1</td>
<td>0</td>
<td>( (x, y) )</td>
</tr>
<tr>
<td>( A''_1 )</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>( z )</td>
</tr>
<tr>
<td>( A''_2 )</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>( (R_x, R_y) )</td>
</tr>
<tr>
<td>( E'' )</td>
<td>2</td>
<td>-1</td>
<td>0</td>
<td>-2</td>
<td>1</td>
<td>0</td>
<td>( (x, yz) )</td>
</tr>
</tbody>
</table>

The shapes of these three wave functions are shown in the following graphic. Note once again how the normalization coefficients are used to distribute the contribution of each AO evenly between the MO's:

4.4.2 Walsh diagrams

Now we could well ask ourselves: Which is the more likely structure for \( \text{H}_3^+ \)? The answer is that it depends on the number of electrons in our molecule! This question has been answered in a general fashion by Walsh, who constructed diagrams such as the one shown at right for this purpose. This is a correlation diagram that has been created for the orbitals of \( \text{H}_3 \). In practice, the calculation is performed as several angles between the extremes of linear and triangular, and smooth curves are drawn through the resulting points. This produces the following scale. The best shape is that which gives the lowest overall energy.

- If the molecular charge is +1, there are two electrons in total. The lowest energy is then triangular (\( a' \) occupied, \( e' \) empty). (This is a real species.)
- If the molecular charge is –1, there are four electrons in total. Now it becomes energetically advantageous to occupy 1\( \sigma \) and 2\( \sigma \) and leave 3\( \sigma \) empty. The molecule is better off in the linear form. (This ion is unknown.)
- The most difficult case is neutral \( \text{H}_3 \). This would have an odd number of electrons (a radical) and thus not a stable configuration. Here it becomes a matter of calculation to see which combination of occupied orbitals leads to the lowest energy configuration.
4.4.3 The general polyhydrogen molecules

What is true of $H_3$ can be generalized to longer chains and rings of $H$ atoms. The assignment related to the current topic asks you to work out the orbital shapes and energies for linear and cyclic polyhydrogen up to $H_6$. Note that with HyperChem it is possible to generate all of these examples using the model builder. Do not try to geometry optimize the structures. Instead, perform AM1 calculations on the structures generated by the Model Builder. Be sure to adjust your calculations for the correct orbital occupancy for each species (and pay attention to the spin multiplicity!)

Note that what you end up doing is creating the symmetry-adapted group orbitals that we will later use when the given pattern of $H$ orbitals are placed around a suitable central atom. This does bring up the point that other geometries become possible once $H_4$ is achieved. Thus while we are now used to the linear and planar case, there is also the possibility of a tetrahedron. Which is actually likely to be the most stable geometry? On paper such questions are hard to answer, but with a program such as HyperChem they become remarkably easy to investigate.

These orbital patterns and their associated symmetry labels are also closely related to the kinds of delocalized orbitals that occur in aromatic $\pi$-systems and in various kinds of cluster molecules, of which there are many kinds across the periodic table. Thus far from being hypothetical exercises, these musings about the MO descriptions of the polyhydrogen molecules turn out to be essential foundational concepts for bonding theory in inorganic chemistry. Just as the H-atom wave functions formed our theoretical basis for deducing the orbitals of the rest of the elements with 100 or more valence electrons, so the polyhydrogen molecules are paradigms that can be used effectively to introduce many key bonding concepts adopted by the molecules of the heavier elements.

4.4.4 A general approach to molecular orbital theory

Mathematically, the LCAO approach can be summarized by the following equation:

$$\Psi_n = \sum_i c_i \phi_i$$

Here $\Psi_n$ represents any generalized wave function of a molecule which can be described as a sum of each of the constituent atomic orbitals times some coefficient, reflecting the degree of overlap. In this form, the sign of the coefficient determines whether constructive or destructive (or null) overlap occurs for any given atom orbital $\phi$. Here are some summary principles which are just as true of the simple polyhydrogen molecules as they are for any complex molecule:

1. There will always be a direct correspondence to the number of constituent atomic orbitals and the number of resulting MO's.
2. The greater the number of nodes in an MO the greater the antibonding character and higher the energy of that orbital.
3. Interaction between non-nearest neighbour atoms is the same as for nearest neighbours, but the effect is greatly diminished.
4. Molecular orbital energy is determined by both the energy of the basis atomic orbitals and the degree of overlap. In general, orbitals formed from $ns$ AO's lie at lower energy than those from the $np$ orbitals for the same value of $n$.

4.5 Polyatomic molecules B: the general central atom molecule

Many of the key molecules in both organic and main-group inorganic chemistry can be described using the central atom model (this is of course exactly where the VSEPR theory works well.) In the simplest case, the terminal atoms will all be of one type. So long as all the bonds in such a molecule are single bonds, the bonding in virtually any case can be approximated by replacing the terminal atoms by hydrogen. For other terminal atoms (e.g. the halogens), it is usually possible to find some pseudospherical orbital which forms bonds exactly the way that hydrogen does. The central atom then becomes some other kind of element (e.g. the organic example methane, which has a central carbon atom and four equivalent hydrogen atoms at the corner of a regular tetrahedron). An inorganic example might be the octahedral molecule $SF_6$, where sulfur is the central atom. The six fluorine terminal atoms can use cylindrical orbital (e.g. a valence $p$ orbital pointing towards $S$, or a suitable hybrid orbital such as an $sp$ hybrid) and we find that the bonding is formally analogous to that of the (non-existent) $SH_6$. 
4.5.1 A delocalized MO bonding description of water

As a simple inorganic model system, we will consider the water molecule H₂O, which has a central oxygen atom and two terminal hydrogen atoms. For this important paradigmatic system, we will actually derive symmetry-adapted group orbitals (SAO’s) and then show how these can be combined with the oxygen valence atomic orbitals. Later we will use pre-determined SAO’s to quickly build complex molecules.

Consider two H 1s orbitals placed where the hydrogen atoms of water are located but without the presence of the oxygen atom. However, the shape of water will be imposed, so that we must work in the point group C₂v. The question then becomes one of: How do the hydrogen atoms of water transform under C₂v symmetry? Note that two possibilities can exist, that in which the phase of the two AO’s is the same, and that in which their phases are opposite.

Note that the definition of the SAO’s depends on a choice of orientation of the molecule; here we place it in the yz plane. The highest-order rotation axis, in this case C₂ must be aligned along the z axis. If we perform the indicated symmetry operations on the in-phase set of hydrogen orbitals, we find that each leaves the set indistinguishable from the original. This is indicated by the entry +1 in the character table. Comparison to the complete C₂v table indicates that the correct Mulliken label for this set of character is a₁. If we now perform the same operations on the out-of-phase set, we find that the operations E and σ_yz leave the orbitals unchanged, but the other two operations switch the phases. Such a switch is said to be antisymmetric, and this is indicated by a –1 character. Comparison of this set of characters identifies this as the Mulliken label b₂.

We now consider how the orbitals of the central oxygen atom transform in the same point group.
Again, we compare these results with the $C_{2v}$ point group, and assign the corresponding Mulliken labels to the four atomic orbitals. Note that an easy short-cut to this process exists. Look on the character table below along each of the Mulliken labels that we generated above, and correlate them to the AO’s. Thus the $s$ and $p_z$ orbital are both $a_1$.

<table>
<thead>
<tr>
<th>$C_{2v}$ (2mm)</th>
<th>$E$</th>
<th>$C_2$</th>
<th>$a_r(xz)$</th>
<th>$a'_r(yz)$</th>
<th>$h = 4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>$x^2, y^2, z^2$</td>
</tr>
<tr>
<td>$A_2$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>$R_z, xy$</td>
</tr>
<tr>
<td>$B_1$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>$x, R_y, z$</td>
</tr>
<tr>
<td>$B_2$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>$y, R_x, yz$</td>
</tr>
</tbody>
</table>

Note that in the functions column of the point group, the functions $z$ and $x^2, y^2, z^2$ are found in the $A_1$ row. This tells us that for any central atom in point group $C_{2v}$, any atomic $s$ wave function will always transform as $A_1$, and any $p_z$ orbital will also transform as $A_1$.

Similarly, any $p_x$ function will always transform as $B_1$ because of the $x$ entry in that row. Any $p_y$ function transforms as $B_2$ because of the $y$ in that row. Thus in general we do not need to go through this laborious set of transformations in order to be able to assign the symmetry properties of the central atom AO’s. Rather we just read them off the respective character tables. The only thing that can go wrong is that the orientation of the molecule w.r.t. the axes needs to match correctly to that of the point group (and the matching SAO’s are used.) This we will mention as we use them.

The reason that we have gone through this exercise is the general MO principle learned earlier, that is that only orbitals of the same symmetry classification can interact with each other. Thus we have pre-assembled the orbitals belonging to the water molecule in such a way that they can be easily combined into the appropriate MO’s. It is also useful to recognize that the process of forming the SAO’s as done above moves these AO’s to a distance that they have within the molecule. They are thus aware of each other’s presence, i.e. they are weakly bonding and anti-bonding interactions. In effect we can order the SAO’s according to the number of nodes they possess.

We can now construct a first stab at creating the MO diagram for water. It is worthwhile analyzing the collection of bits on either side of the diagram. First of all, there is no equivalent on the hydrogen side to the oxygen AO with the $b_2$ label. This orbital must therefore remain unhybridized in the molecule, and its energy is transferred directly from the AO to the MO. It remains in the molecule as an oxygen $p_x$ orbital, and will be de-facto non-bonding. Secondly, we search for any symmetry species for which only one example can be found at either side of the diagram. This is true for $b_1$. We apply a simple heteronuclear MO interaction between these two atomic functions (see section 2.3.1), and recognize that $1b_1$ will have greater oxygen character, while $2b_2$ will have greater hydrogen character.

The most complex interaction will be when there is more than one orbital with the same symmetry label on either side of the diagram. This is true for the $a_1$ species, for which there are two on oxygen. Just as in the case of HF, we find that the H atomic
orbitals lie higher in energy than even the $2p$ orbitals of oxygen. As a first approximation, we might therefore assume that the only interaction of the $a_1$ SAO will be with the oxygen $p_z$ orbital. This will be a strong interaction, and lead to the bonding $2a_1$ and antibonding $3a_1$ orbitals. However, exactly as occurred in the HF example, this leads to two orbitals of the exact same symmetry label being located very close to each other in energy. We expect re-hybridization to occur, with $1a_1$ gaining bonding character (it is non-bonding as shown), while $2a_1$ will become less bonding. The difficulty is in knowing just how far this process is to progress. Thus what will the final orbital sequence be? Without further evidence, it is impossible to know what the correct answer is. We turn to the usual sources for this information.

(1) UV-PES for the water molecule:

This shows conclusively that the HOMO will be non-bonding (sharp peak at 12.5 eV). This can only mean that the HOMO remains the $b_1$ orbital of our MO diagram! The next three orbitals all have fine structure (or are broadened due to unresolved fine structure). They are found at about 15, 18 and 32 eV. The energy gaps are certainly not consistent with our simple MO diagram. We certainly expect $1b_2$ to be considerably lower in energy than $b_1$, since the latter is entirely non-bonding. This suggests that $1b_2$ is the orbital at 18 eV. This can only mean that the $2a_1$ orbital has moved above the energy of $1b_2$, to be the orbital found just below the HOMO. Correspondingly, $1a_1$ has become extremely stabilized at 32 eV. Thus the UV-PES can allow us to greatly improve our simple MO diagram, and allow us to assign the final position of the problematic $1a_1$ and $2a_1$ orbitals.

(2) An AM1 calculation is strongly in agreement with the PES, with orbital energies of –12.5, –15, –18 and –36 eV. Sketches of the MO topologies are shown below on a corrected “2nd order” MO diagram for the water molecule.

Note that in this MO description of water, there are not two equivalent lone pairs on oxygen. The truly non-bonding orbital is a perpendicular $p$ orbital, and the oxygen more closely approximates $sp^2$ than $sp^3$ hybridization. The PES supports this view!
4.5.2 The shape of EH₂ molecules

Our MO analysis of the bonding in H₂O is significantly different than the Lewis/VSEPR model, with its suggestion of sp³ hybridization and two equivalent lone pairs. However, the basic idea that water should be a bend molecule is retained. We now wish to probe this point a little deeper and try to understand why water is bent using MO reasoning. We also want to see if there will be cases in which an EH₂ molecule might be linear. Finally, we want to ask questions about the bond angle. The angle of 104° degrees was rationalized in the VSEPR method as a small departure from the ideal tetrahedral angle. But if the hybridization is not what that method suggests, then that was probably a specious factor. Indeed, this becomes an extremely germane topic for main group chemistry. For example, the bond angle in H₂S is 92.1°. Thus we want to consider all possible bond angles for this bonding system, and this is exactly what Walsh has done, considering angles ranging all the way from 90° to 180°. Note that when the model is forced to be exactly linear, the point group will change from C₂v to D₅h, and the symmetry labels of the orbitals will change. However, from the orbital topologies it is easy to assign the appropriate set of labels to the two classifications (the same orbitals will in general have different symmetry labels under different point groups).

A complete Walsh diagram graphs both the energies of the orbitals as a function of bond angle, and topological sketches of the MO’s as the bond angles change. Only limiting topologies are presented, but intermediate pictures can also be drawn. Now we are ready to ask ourselves why water has a bond angle of 104°. Indeed, the geometry that occurs when the electron configuration is \((1a_1^2)(1b_1^2)(2a_1^2)(1b_2^2)\) is somewhere in the middle of the diagram. On the other hand, we might expect that in H₂S the electron configuration changes to \((1a_1^2)(2a_1^2)(1b_1^2)(1b_2^2)\). This is in fact not born out by MO calculations, but the separation between \(2a_1\) and \(1b_1\) is indeed much larger in H₂S than in H₂O. This can be traced to the greater similarity of the AO energies of hydrogen and sulfur than hydrogen and oxygen, which affects the extent of orbital mixing significantly.

We can also ask ourselves: for what molecules is a linear geometry predicted? The answer is that linear is preferred whenever \(\pi_u\) is unoccupied, since then the destabilization that occurs to \(1\sigma_u\) on bending will not happen. This destabilization (i.e. poorer overlap of the \(p_y\) orbital) only occurs when it is compensated for by the greater stabilization of \(\pi_u\) as it is transformed to an ever more stable \(2a_1\) upon greater bending. The neutral molecule which meets this criterion is BeH₂.

An intermediate case, which might be expected to be mildly bent, is CH₂, i.e. the highly reactive singlet carbene molecule, which can be generated and studied in the gas phase at very low pressures. Carbene is indeed found to be mildly angular with a bond angle of 136°.
4.5.3 A delocalized MO bonding description of ammonia

In order to reinforce the method we have just learned, let us apply it to one more example. Although somewhat harder to visualize and to sketch, we choose an example that is not flat so that we can achieve a fully general bonding methodology. We choose to consider pyramidal NH$_3$. It belongs to the point group $C_3v$. We will take the nitrogen AO symmetry labels from the character table. Thus the N $p_z$ and $s$ orbitals will transform as $a_1$, and the $p_x$ and $p_y$ will transform as a set as $E$.

The hydrogen symmetry adapted group orbitals turn out to be the same as those for the triangular H$_3$ molecule (except that the H–H separation will be about twice as large in ammonia). However, the symmetry labels will not be the same as they were in the planar case, which was $D_{3h}$. The new labels are $a_1$ and $e$.

<table>
<thead>
<tr>
<th>$C_3v$</th>
<th>$E$</th>
<th>$2C_3$</th>
<th>$3a_v$</th>
<th>$h = 6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>$x$</td>
</tr>
<tr>
<td>$A_2$</td>
<td>1</td>
<td>1</td>
<td>$-1$</td>
<td>$R_z$</td>
</tr>
<tr>
<td>$E$</td>
<td>2</td>
<td>$-1$</td>
<td>0</td>
<td>$(x, y) \ (R_x, R_y) \ (x^2 - y^2, xy) \ (2x, y^2)$</td>
</tr>
</tbody>
</table>

Our MO diagram is built up by pre-ordering the SAO’s according to the number of nodes, and this means that the $a_1$ set will be lower in energy than the $e$ set. The easiest interactions are between $e$ on the left and the right, leading to two degenerate sets of MO’s, 1$e$, bonding, and 2$e$, antibonding. Once again, we are faced with a dilemma with respect to the two $a_1$ orbitals on the central nitrogen atom, and a single $a_1$ terminal atom set. This leads to three MO’s, 1$a_1$ strongly bonding, 2$a_1$ partly bonding or non-bonding, and 3$a_1$ which will be strongly antibonding. For further details, we once again turn to the UV-PES and AM1 calculations. There are indeed no entirely non-bonding orbitals in ammonia. Even the 2$a_1$ orbital, formally equivalent to the lone pair in the Lewis diagram of :NH$_3$ has partial bonding character. However, the extensive vibrational fine structure of this band (11 eV) can be explained by recognizing that removal of a nitrogen lone pair electron will lead to extensive flattening of the molecule. This will greatly change the bending and wagging modes of vibration. We thus must exercise caution in the application of interpretative principles for PES spectra developed for linear diatomic molecules. In non-linear molecules, we must consider any photoionization that can change at least one normal mode of vibration in the molecule.

Note that the PES does not include any peaks from the deeply bound 1$a_1$ orbital, because it uses only the He-I source limited to 22 eV.
4.6 The MO description of Lewis Acid-Base Complex Formation

Now that we have a firm grasp of molecular orbital theory as applied to small molecules, particularly the element hydrides, we can re-consider a well-known idea – that of Lewis acid-base interaction to form complexes – from an MO point of view. In general, the Lewis acid will have an accessible empty orbital, and this will usually be the LUMO of the acid. The Lewis base will have a filled orbital, and this is usually the HOMO of the acid. A complex forms when the two “fragment” orbitals combine to form a bonding and an antibonding combination, and the two electrons flow into the bonding MO of the new complex. This can be illustrated in a totally generally form by the following diagram:

Now the efficacy of LA-LB reactions has to do with the compatibility of the acid LUMO and the base HOMO. Compatibility means: (A) correct symmetry of orbitals; (B) best match in energy; (C) best match in “shape” by which is meant mostly the density of the MO – a hard acid will have a dense, contracted LUMO and a hard base will have a dense, contracted HOMO; a soft acid will have a diffuse, polarizable LUMO and a soft base will have a diffuse, polarizable HOMO. When these are well matched, a stronger interaction will take place.

There are in general three categories of interaction possible: [1] the acid LUMO is higher in energy than the base HOMO (the most common situation); [2] the acid LUMO and base HOMO are nearly equal in energy (rare, but leads to strong interactions) and [3] the acid LUMO is lower in energy than the base HOMO (rare, but it happens).