MOLECULAR ORBITAL THEORY- PART II

For the simple case of the one-electron bond in H_2^+ we have seen that using the LCAO principle together with the variational principle led to a recipe for computing some approximate orbitals for a system that would be very difficult to solve analytically. To generalize this to the more interesting case of many electrons, we take our direction from our experience with the independent particle model (IPM) applied to atoms and we build up antisymmetrized wavefunctions out of the molecular orbitals. This is the basic idea behind molecular orbital theory – there are many variations on the central theme, but the same steps are always applied. Rather than go step-by-step and deal with H_2 and then Li_2 and then LiH … we will instead begin by stating the general rules for applying MO theory to any system and then proceed to show some illustrations of how this works out in practice.

1) Define a basis of atomic orbitals

For H_2^+ our atomic orbital basis was simple: we used the 1s functions from both hydrogen atoms and wrote our molecular orbitals as linear combinations of our basis functions:

$$\psi = c_1 1s_A + c_2 1s_B$$

Note that the AO basis determines the **dimension** of our MO vector and also determines the quality of our result – if we had chosen the 3p orbitals instead of the 1s orbitals, our results for H_2^+ would have been very wrong!

For more complicated systems, we will require a more extensive AO basis. For example, in O_2 we might want to include all the 2s and 2p orbitals on both oxygens, in which case our MOs would take the form

$$\psi = c_1 2s_A + c_2 2p_{xA} + c_3 2p_{yA} + c_4 2p_{zA} + c_5 2s_B + c_6 2p_{xB} + c_7 2p_{yB} + c_8 2p_{zB}$$

Meanwhile, for methane we might want to include the 1s functions on all four hydrogens and the 2s and 2p functions on carbon:

$$\psi = c_1 1s_1 + c_2 1s_2 + c_3 1s_3 + c_4 1s_4 + c_5 2s + c_6 2p_x + c_7 2p_y + c_8 2p_z$$

In the general case, we will write:

$$\psi = \sum_{i=1}^{N} c_i \phi_i^{AO}$$

and represent our MOs by column vectors:

$$\vec{\psi} = \begin{pmatrix} c_1 \\ c_2 \\ \dots \\ c_N \end{pmatrix}$$

We note that for the sake of accuracy it is never a bad idea to include more AO functions than you might think necessary – more AO functions will always lead to more accurate results. The price is that the more accurate computations also tend to be more complicated and time consuming. To illustrate, note that we could have chosen to write the H_2^+ MOs as linear combinations of four functions – the 1s and 2s states on each atom:

$$\psi = c_1 1s_A + c_2 1s_B + c_3 2s_A + c_4 2s_B$$

Now, when we use the variational principle to get the coefficients of the lowest MO , $\mathbf{c_0}$, we are guaranteed that there is no set of coefficients that will give us a lower energy. This is the foundation of the variational method. Note that one possible set of coefficients is c_3=c_4=0, in which case our 4-function expansion reduces to the 2-function expansion above. Thus, *the variationally optimal 4-function MO will always have an energy less than or equal to the optimal 2-function MO*. As a result, the expansion with four functions allows the approximate MO to get closer to the ground state energy. This makes sense, as the four AO expansion has more flexibility than the constrained two AO expansion used previously. The reason we didn't use the four function expansion from the beginning is that all the algebra is twice as difficult when we use four functions as two: the vectors are twice as long, the matrices are twice as big…. At least for a first try, it is generally good to start with the smallest conceivable set of AOs for performing a calculation. If higher accuracy is required, a longer expansion can be tried.

2) Compute the relevant matrix representations

For H_2^+ we had to compute two matrices – the Hamiltonian and the overlap, which were both 2-by-2 by virtue of the two AO basis functions:

$$\mathbf{H} \equiv \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \equiv \begin{pmatrix} \int 1s_A \hat{H}_{el} 1s_A d\tau & \int 1s_A \hat{H}_{el} 1s_B d\tau \\ \int 1s_B \hat{H}_{el} 1s_A d\tau & \int 1s_B \hat{H}_{el} 1s_B d\tau \end{pmatrix}$$

$$\mathbf{S} \equiv \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix} \equiv \begin{pmatrix} \int 1s_A 1s_A d\tau & \int 1s_A 1s_B d\tau \\ \int 1s_B 1s_A d\tau & \int 1s_B 1s_B d\tau \end{pmatrix}$$

In the general case, the Hamiltonian and overlap become N-by-N matrices of the form:

$$\mathbf{H} \equiv \begin{pmatrix} H_{11} & H_{12} & \dots & H_{1N} \\ H_{21} & H_{22} & \dots & H_{2N} \\ \dots & \dots & \dots & \dots \\ H_{N1} & H_{N2} & \dots & H_{NN} \end{pmatrix} \equiv \begin{pmatrix} \int \phi_1^{AO} \hat{H} \phi_1^{AO} & \int \phi_1^{AO} \hat{H} \phi_2^{AO} & \int \phi_1^{AO} \hat{H} \phi_N^{AO} \\ \int \phi_2^{AO} \hat{H} \phi_1^{AO} & \int \phi_2^{AO} \hat{H} \phi_2^{AO} & \int \phi_2^{AO} \hat{H} \phi_N^{AO} \\ & & \\ \int \phi_N^{AO} \hat{H} \phi_1^{AO} & \int \phi_N^{AO} \hat{H} \phi_2^{AO} & \int \phi_N^{AO} \hat{H} \phi_N^{AO} \end{pmatrix}$$

$$\mathbf{S} \equiv \begin{pmatrix} S_{11} & S_{12} & \dots & S_{1N} \\ S_{21} & S_{22} & \dots & S_{2N} \\ \dots & \dots & \dots & \dots \\ S_{N1} & S_{N2} & \dots & S_{NN} \end{pmatrix} \equiv \begin{pmatrix} \int \phi_1^{AO} \phi_1^{AO} & \int \phi_1^{AO} \phi_2^{AO} & \int \phi_1^{AO} \phi_N^{AO} \\ \int \phi_2^{AO} \phi_1^{AO} & \int \phi_2^{AO} \phi_2^{AO} & \int \phi_2^{AO} \phi_N^{AO} \\ & & \\ \int \phi_N^{AO} \phi_1^{AO} & \int \phi_N^{AO} \phi_2^{AO} & \int \phi_N^{AO} \phi_N^{AO} \end{pmatrix}$$

This step is where much of the hard work is done in most MO calculations. Not only can the integrals between the different AO functions be very tricky to work out, there are a lot of them to be computed – N^2 of them, to be exact! This hard work is best done in an automated fashion by a computer, and in practice we will usually give you explicit values for the matrix elements for this step. However, it is important for you to realize what the matrix elements **mean**. The diagonal elements of $\mathbf{H}$ represent the average energies of putting electrons in each AO and the off-diagonal terms tell us how strongly coupled one AO is to another. The diagonal elements of S are normalization integrals and the off-diagonal terms tell us how much spatial overlap there is between the different AOs

3) Solve the generalized eigenvalue problem

For every MO problem, the central step is determining the MOs, which always involves solving the generalized eigenvalue problem:

$$\mathbf{H} \bullet \mathbf{c}^{\alpha} = E_{\alpha} \mathbf{S} \bullet \mathbf{c}^{\alpha}$$

The eigenvalues from this equation are the MO energies. The eigenvectors are the coefficients of the molecular orbitals, written as sums of AOs:

$$\psi^{\alpha}(\mathbf{r}) = \sum_{i=1}^{N} c_i^{\alpha} \phi_i^{AO}(\mathbf{r})$$

In general, we will obtain N molecular orbitals out of N atomic orbitals. This step is precisely the same as what we did for H_2^+, just generalized to the N-orbital case. We note that for anything larger than a 2-by-2, it

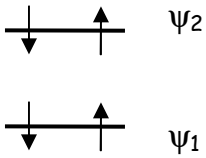
is usually best to ask a computer to solve the generalized eigenvalue problem for you.

4) Occupy the orbitals according to a stick diagram

At this point, we must depart from the H_2^+ model and begin to account for the fact that we have multiple electrons. To do so, we follow the prescription of the independent particle model and build a Slater determinant out of our orbitals. However, whereas for atoms we built the determinant out of atomic orbitals, for molecules we will build the determinant out of molecular orbitals:

$$\Psi \equiv \begin{vmatrix} \psi^{1\uparrow}(1) & \psi^{1\downarrow}(1) & \ldots & \psi^{N\downarrow}(1) \\ \psi^{1\uparrow}(2) & \psi^{1\downarrow}(2) & \ldots & \psi^{N\downarrow}(2) \\ \ldots & \ldots & \ldots & \ldots \\ \psi^{1\uparrow}(N) & \psi^{1\downarrow}(N) & \ldots & \psi^{N\downarrow}(N) \end{vmatrix}$$

As was the case for atoms, it is much easier to reason in terms of stick diagrams, rather than write out all of the orbitals in determinant form. So, for example, we would associate a stick diagram like this



with a determinant:

$$\Psi(1,2,3,4) \equiv \begin{vmatrix} \psi^{1\uparrow}(1) & \psi^{1\downarrow}(1) & \psi^{2\uparrow}(1) & \psi^{2\downarrow}(1) \\ \psi^{1\uparrow}(2) & \psi^{1\downarrow}(2) & \psi^{2\uparrow}(2) & \psi^{2\downarrow}(2) \\ \psi^{1\uparrow}(3) & \psi^{1\downarrow}(3) & \psi^{2\uparrow}(3) & \psi^{2\downarrow}(3) \\ \psi^{1\uparrow}(4) & \psi^{1\downarrow}(4) & \psi^{2\uparrow}(4) & \psi^{2\downarrow}(4) \end{vmatrix}$$

But all the information we would need is contained in the stick diagram and, of course, the MOs.

5) Compute the energy

There are a variety of ways to compute the energy once the MOs have been obtained. The simplest is to use the non-interacting particle picture we used for atoms. Here, the energy of N electrons is just given by the sum of the energies of the N orbitals that are occupied:

$$E = \sum_{i=1}^{N} E_i$$

A more accurate way is to use the independent particle model to add an average electron-electron repulsion to the energy:

$$E = \left\langle \hat{H} \right\rangle = \sum_{i=1}^{N} E_i + \sum_{i<j}^{N} \tilde{J}_{ij} - \tilde{K}_{ij}$$

Where now the Coulomb and exchange integrals use molecular orbitals rather than atomic orbitals:

$$\tilde{J}_{ij} \equiv \iint \psi_i^*(1)\psi_j^*(2)\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}\psi_i(1)\psi_j(2)d\mathbf{r}_1 d\mathbf{r}_2 d\sigma_1 d\sigma_2$$

$$\tilde{K}_{ij} \equiv \iint \psi_i^*(1)\psi_j^*(2)\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}\psi_i(2)\psi_j(1)d\mathbf{r}_1 d\mathbf{r}_2 d\sigma_1 d\sigma_2$$

In fact, as we will see later on, there are even more elaborate ways to obtain the energy from an MO calculation. When we work things out by hand, the non-interacting picture is easiest and we will usually work in that approximation when dealing with MOs.

Diatomic molecules

As a first application of MO theory, it is useful to consider first-row diatomic molecules (B_2, C_2, N_2,O_2, CO,CN, NO, etc.), which actually map rather nicely on to an MO picture. We'll go step-by step for the generic "AB" diatomic to show how this fits into the MO theory framework.

1) ***Define a basis of atomic orbitals***. To begin with, one would consider a set consisting of 10 atomic orbitals – 5 on A and 5 on B:

$$\psi = c_1 1s_A + c_2 1s_B + c_3 2s_A + c_4 2s_B + c_5 2p_{zA} + c_6 2p_{zB} + c_7 2p_{yA} + c_8 2p_{yB} + c_9 2p_{xA} + c_{10} 2p_{xB}$$

However, for all the diatomics above, the 1s orbitals on both atoms will be doubly occupied. Since we will primarily be interested in comparing the MO descriptions of different diatomics the eternally occupied 1s orbital will have no qualitative effect on our comparisons. It is therefore customary to remove the 1s orbitals from the expansion:

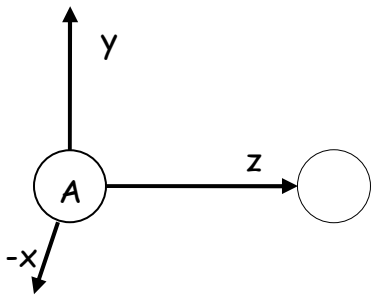
$$\psi = c_1 2s_A + c_2 2s_B + c_3 2p_{zA} + c_4 2p_{zB} + c_5 2p_{yA} + c_6 2p_{yB} + c_7 2p_{xA} + c_8 2p_{xB}$$

The latter approximation is referred to as the **valence electron** or **frozen core** approximation. The advantage is that it reduces the length of our vectors from 10 to 8.

2) ***Compute the Matrix Representations***. Here, we have the rather daunting task of computing two 8-by-8 matrices. As mentioned above, we won't be concerned in this class about filling in precise values for matrix elements here. However, we will be very interested in obtaining the proper shape of the matrix by determining which matrix elements are zero and which are not. The Hamiltonian takes the shape:

$$\mathbf{H} \equiv \begin{pmatrix}
\int s_A \hat{H} s_A & \int s_A \hat{H} s_B & \int s_A \hat{H} p_{zA} & \int s_A \hat{H} p_{zB} & \int s_A \hat{H} p_{yA} & \int s_A \hat{H} p_{yB} & \int s_A \hat{H} p_{xA} & \int s_A \hat{H} p_{xB} \\
\int s_B \hat{H} s_A & \int s_B \hat{H} s_B & \int s_B \hat{H} p_{zA} & \int s_B \hat{H} p_{zB} & \int s_B \hat{H} p_{yA} & \int s_B \hat{H} p_{yB} & \int s_B \hat{H} p_{xA} & \int s_B \hat{H} p_{xB} \\
\int p_{zA} \hat{H} s_A & \int p_{zA} \hat{H} s_B & \int p_{zA} \hat{H} p_{zA} & \int p_{zA} \hat{H} p_{zB} & \int p_{zA} \hat{H} p_{yA} & \int p_{zA} \hat{H} p_{yB} & \int p_{zA} \hat{H} p_{xA} & \int p_{zA} \hat{H} p_{xB} \\
\int p_{zB} \hat{H} s_A & \int p_{zB} \hat{H} s_B & \int p_{zB} \hat{H} p_{zA} & \int p_{zB} \hat{H} p_{zB} & \int p_{zB} \hat{H} p_{yA} & \int p_{zB} \hat{H} p_{yB} & \int p_{zB} \hat{H} p_{xA} & \int p_{zB} \hat{H} p_{xB} \\
\int p_{yA} \hat{H} s_A & \int p_{yA} \hat{H} s_B & \int p_{yA} \hat{H} p_{zA} & \int p_{yA} \hat{H} p_{zB} & \int p_{yA} \hat{H} p_{yA} & \int p_{yA} \hat{H} p_{yB} & \int p_{yA} \hat{H} p_{xA} & \int p_{yA} \hat{H} p_{xB} \\
\int p_{yB} \hat{H} s_A & \int p_{yB} \hat{H} s_B & \int p_{yB} \hat{H} p_{zA} & \int p_{yB} \hat{H} p_{zB} & \int p_{yB} \hat{H} p_{yA} & \int p_{yB} \hat{H} p_{yB} & \int p_{yB} \hat{H} p_{xA} & \int p_{yB} \hat{H} p_{xB} \\
\int p_{xA} \hat{H} s_A & \int p_{xA} \hat{H} s_B & \int p_{xA} \hat{H} p_{zA} & \int p_{xA} \hat{H} p_{zB} & \int p_{xA} \hat{H} p_{yA} & \int p_{xA} \hat{H} p_{yB} & \int p_{xA} \hat{H} p_{xA} & \int p_{xA} \hat{H} p_{xB} \\
\int p_{xB} \hat{H} s_A & \int p_{xB} \hat{H} s_B & \int p_{xB} \hat{H} p_{zA} & \int p_{xB} \hat{H} p_{zB} & \int p_{xB} \hat{H} p_{yA} & \int p_{xB} \hat{H} p_{yB} & \int p_{xB} \hat{H} p_{xA} & \int p_{xB} \hat{H} p_{xB}
\end{pmatrix}$$

We assume, for simplicity, that the AB-bond lies along the z-axis. Then it is relatively easy to see that the molecule is symmetric upon reflection around the x and y axes. As a result, the Hamiltonian for AB is also symmetric (even) with respect to reflection about x and y. Similarly, the s and p orbitals all have definite reflection symmetries:



	X Reflection	Y Reflection
Hamiltonian	+	+
s	+	+
p_z	+	+
p_y	+	-
p_x	-	+

Further, we note that if we perform an integral, if the integrand is odd with respect to reflection about either x or y the integrand will be zero.

This knocks out a bunch of integrals for us. For example, looking at reflection about x:

$$\int s_{A/B}\hat{H}p_{xA/B} = (+)(+)(-) = - \quad \Rightarrow \quad 0$$

$$\int p_{zA/B}\hat{H}p_{xA/B} = (+)(+)(-) = - \quad \Rightarrow \quad 0$$

$$\int p_{yA/B}\hat{H}p_{xA/B} = (+)(+)(-) = - \quad \Rightarrow \quad 0$$

$$\int p_{xA/B}\hat{H}p_{xA/B} = (-)(+)(-) = + \quad \Rightarrow \quad \neq 0$$

We have analogous expressions for reflection about y zero several more integrals. The result is that the Hamiltonian simplifies to

$$\mathbf{H} \equiv \begin{pmatrix} \int s_A\hat{H}s_A & \int s_A\hat{H}s_B & \int s_A\hat{H}p_{zA} & \int s_A\hat{H}p_{zB} & 0 & 0 & 0 & 0 \\ \int s_B\hat{H}s_A & \int s_B\hat{H}s_B & \int s_B\hat{H}p_{zA} & \int s_B\hat{H}p_{zB} & 0 & 0 & 0 & 0 \\ \int p_{zA}\hat{H}s_A & \int p_{zA}\hat{H}s_B & \int p_{zA}\hat{H}p_{zA} & \int p_{zA}\hat{H}p_{zB} & 0 & 0 & 0 & 0 \\ \int p_{zB}\hat{H}s_A & \int p_{zB}\hat{H}s_B & \int p_{zB}\hat{H}p_{zA} & \int p_{zB}\hat{H}p_{zB} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \int p_{yA}\hat{H}p_{yA} & \int p_{yA}\hat{H}p_{yB} & 0 & 0 \\ 0 & 0 & 0 & 0 & \int p_{yB}\hat{H}p_{yA} & \int p_{yB}\hat{H}p_{yB} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \int p_{xA}\hat{H}p_{xA} & \int p_{xA}\hat{H}p_{xB} \\ 0 & 0 & 0 & 0 & 0 & 0 & \int p_{xB}\hat{H}p_{xA} & \int p_{xB}\hat{H}p_{xB} \end{pmatrix}$$

which we write:

$$\mathbf{H} \equiv \begin{pmatrix} H_{11} & H_{12} & H_{13} & H_{14} & 0 & 0 & 0 & 0 \\ H_{21} & H_{22} & H_{23} & H_{24} & 0 & 0 & 0 & 0 \\ H_{31} & H_{32} & H_{33} & H_{34} & 0 & 0 & 0 & 0 \\ H_{41} & H_{42} & H_{43} & H_{44} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & H_{55} & H_{56} & 0 & 0 \\ 0 & 0 & 0 & 0 & H_{65} & H_{66} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & H_{77} & H_{78} \\ 0 & 0 & 0 & 0 & 0 & 0 & H_{87} & H_{88} \end{pmatrix}$$

It is easy to show that the overlap matrix has the same overall shape

$$\mathbf{S} \equiv \begin{pmatrix} S_{11} & S_{12} & S_{13} & S_{14} & 0 & 0 & 0 & 0 \\ S_{21} & S_{22} & S_{23} & S_{24} & 0 & 0 & 0 & 0 \\ S_{31} & S_{32} & S_{33} & S_{34} & 0 & 0 & 0 & 0 \\ S_{41} & S_{42} & S_{43} & S_{44} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & S_{55} & S_{56} & 0 & 0 \\ 0 & 0 & 0 & 0 & S_{65} & S_{66} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & S_{77} & S_{78} \\ 0 & 0 & 0 & 0 & 0 & 0 & S_{87} & S_{88} \end{pmatrix}$$

There are some additional symmetries in these matrices but the reflection symmetry properties are the most important.

3) ***Solve the generalized eigenvalue problem***. This part would be impossible if we hadn't simplified our matrices above. However, with the simplifications, it is clear that our matrices are **block diagonal**. For example:

$$\mathbf{H} \equiv \begin{array}{c} \begin{array}{cccccccc} s_A & s_B & p_{zA} & p_{zB} & p_{yA} & p_{yB} & p_{xA} & p_{xB} \end{array} \\ \begin{pmatrix} H_{11} & H_{12} & H_{13} & H_{14} & 0 & 0 & 0 & 0 \\ H_{21} & H_{22} & H_{23} & H_{24} & 0 & 0 & 0 & 0 \\ H_{31} & H_{32} & H_{33} & H_{34} & 0 & 0 & 0 & 0 \\ H_{41} & H_{42} & H_{43} & H_{44} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & H_{55} & H_{56} & 0 & 0 \\ 0 & 0 & 0 & 0 & H_{65} & H_{66} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & H_{77} & H_{78} \\ 0 & 0 & 0 & 0 & 0 & 0 & H_{87} & H_{88} \end{pmatrix} \end{array} \begin{array}{c} s_A \\ s_B \\ p_{zA} \\ p_{zB} \\ p_{yA} \\ p_{yB} \\ p_{xA} \\ p_{xB} \end{array}$$

And similarly for the overlap matrix. The nice thing about block diagonal matrices is you can reduce a large eigenvalue to several smaller ones. In this case, our matrices break down into a 4-by-4 block (s_A, s_B, p_{zA}, p_{zB}) a 2-by-2 block (p_{yA},p_{yB}) and another 2-by-2 block (p_{xA},p_{xB}). All the rest of the matrix is zero. As a result, we can decompose the above 8-by-8 into three separate eigenvalue problems:

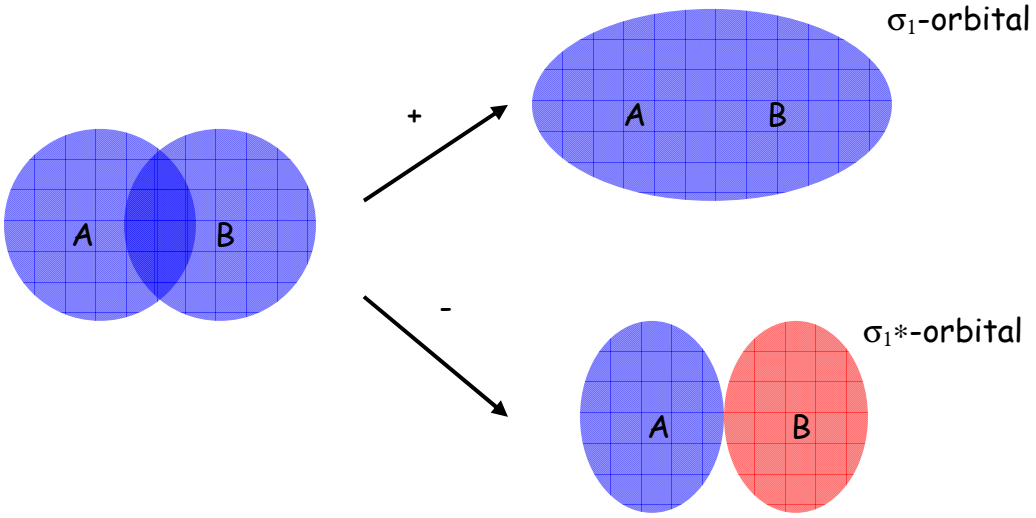
A) The first eigenvalue problem to be solved is a 4-by-4:

$$\begin{pmatrix} H_{11} & H_{12} & H_{13} & H_{14} \\ H_{21} & H_{22} & H_{23} & H_{24} \\ H_{31} & H_{32} & H_{33} & H_{34} \\ H_{41} & H_{42} & H_{43} & H_{44} \end{pmatrix} \begin{pmatrix} c_1^{\alpha} \\ c_2^{\alpha} \\ c_3^{\alpha} \\ c_4^{\alpha} \end{pmatrix} = E^{\alpha} \begin{pmatrix} S_{11} & S_{12} & S_{13} & S_{14} \\ S_{21} & S_{22} & S_{23} & S_{24} \\ S_{31} & S_{32} & S_{33} & S_{34} \\ S_{41} & S_{42} & S_{43} & S_{44} \end{pmatrix} \begin{pmatrix} c_1^{\alpha} \\ c_2^{\alpha} \\ c_3^{\alpha} \\ c_4^{\alpha} \end{pmatrix}$$

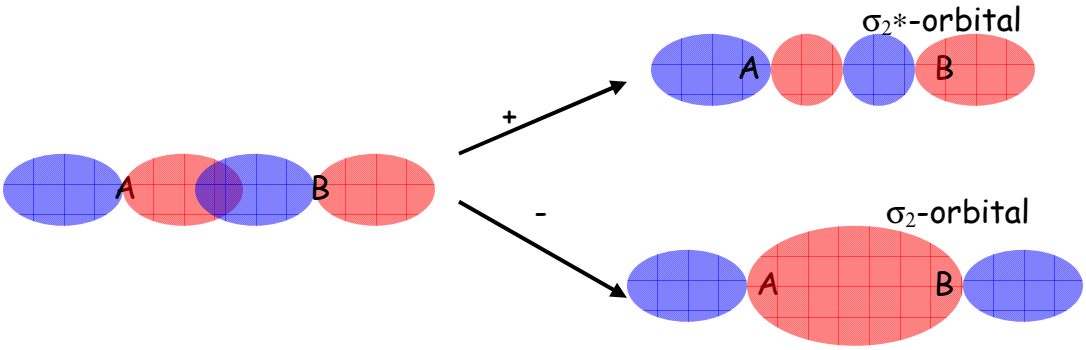
which will give us four molecular orbitals that can be written as linear combinations of the first four AOs (s_A, s_B, p_{zA}, p_{zB})

$$\psi^{\alpha} = c_1^{\alpha} 2s_A + c_2^{\alpha} 2s_B + c_3^{\alpha} 2p_{zA} + c_4^{\alpha} 2p_{zB}$$

Because these orbitals are symmetric with respect to reflection about both x and y, they will look something like the H_2^+ bonding and antibonding orbitals, and so they are referred to as σ-orbitals. For example, we can make the +/- combinations of the 2s orbitals to obtain one bonding orbital and one antibonding:

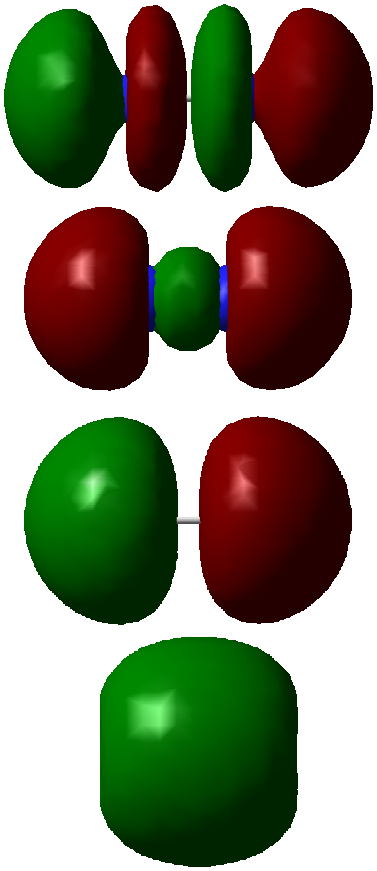


we can make the similar linear combinations of the 2pz orbitals to obtain:



where we label the upper orbital σ* because of the nodes between the nuclei, whereas the σ orbital has no nodes between the nuclei. Note

that these +/- combinations are just to illustrate what the orbitals will look like; in order to get the actual molecular orbitals we would need to diagonalize the 4-by-4 and get the eigenvectors. However, if we do that for a molecule like N2 we actually get orbitals that look strikingly similar to the ones above:



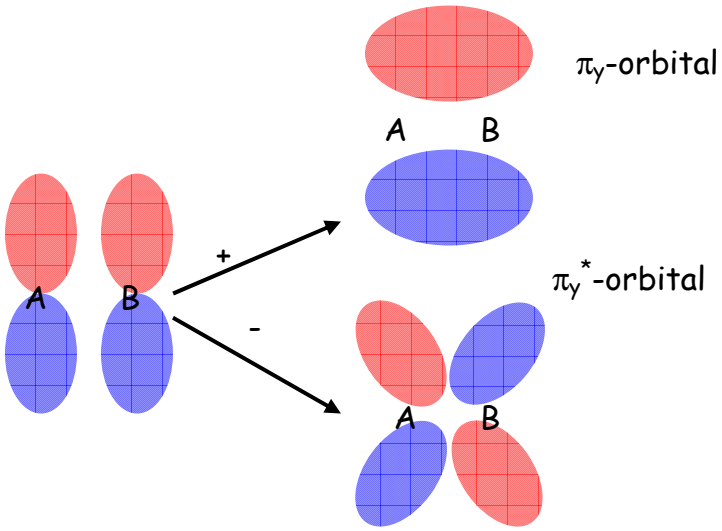
B) The second eigenvalue problem to be solved is a 2-by-2:

$$\begin{pmatrix} H_{55} & H_{56} \\ H_{65} & H_{66} \end{pmatrix}\begin{pmatrix} c_5{}^{\alpha} \\ c_6{}^{\alpha} \end{pmatrix} = E^{\alpha}\begin{pmatrix} S_{55} & S_{56} \\ S_{65} & S_{66} \end{pmatrix}\begin{pmatrix} c_5{}^{\alpha} \\ c_6{}^{\alpha} \end{pmatrix}$$

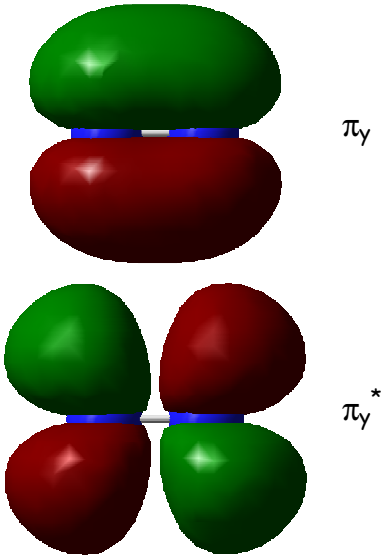
which will give us two molecular orbitals that can be written as linear combinations of the next two AOs (p_{yA},p_{yB}):

$$\psi^{\alpha} = c_5{}^{\alpha} 2p_{yA} + c_6{}^{\alpha} 2p_{yB}$$

These orbitals get "-" signs upon reflection about y, so we designate them π_y orbitals. We can again make the +/- combinations to get an idea what these orbitals look like:



Here again, the use of +/- combinations is only for illustration purposes. Unless we have a homonuclear diatomic, the coefficients will not be ±1. However, for a molecule like N_2, the orbitals look strikingly similar again:



C) The last eigenvalue problem is also 2-by-2:

$$\begin{pmatrix} H_{77} & H_{78} \\ H_{87} & H_{88} \end{pmatrix}\begin{pmatrix} c_7{}^{\alpha} \\ c_8{}^{\alpha} \end{pmatrix} = E^{\alpha}\begin{pmatrix} S_{77} & S_{78} \\ S_{87} & S_{88} \end{pmatrix}\begin{pmatrix} c_7{}^{\alpha} \\ c_8{}^{\alpha} \end{pmatrix}$$

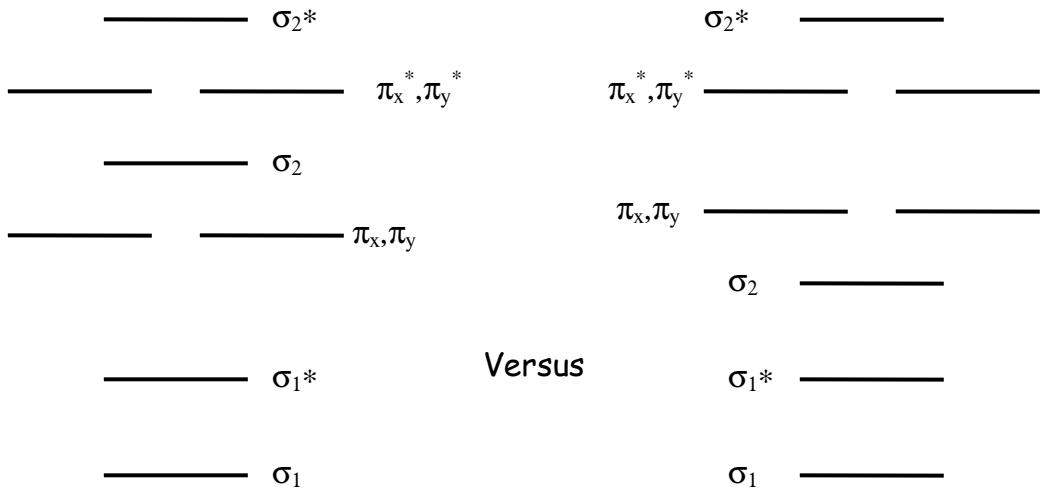
which will give us two molecular orbitals that can be written as linear combinations of the last two AOs (p_{xA},p_{xB}):

$$\psi^{\alpha} = c_5{}^{\alpha} 2p_{xA} + c_6{}^{\alpha} 2p_{xB}$$

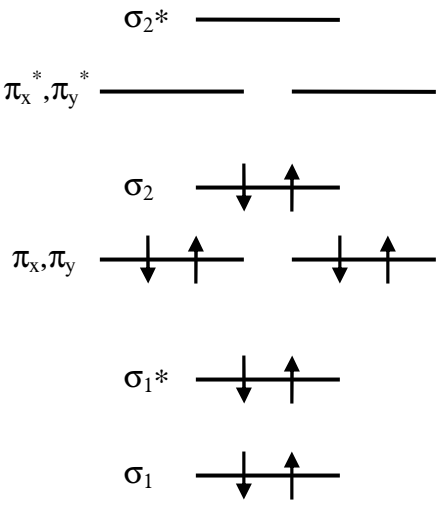
These orbitals get "-" signs upon reflection about x, so we designate them π_x orbitals. The qualitative picture of the π_x orbitals is the same

as for the π_y orbitals above, expect that the π_x orbitals come out of the page.

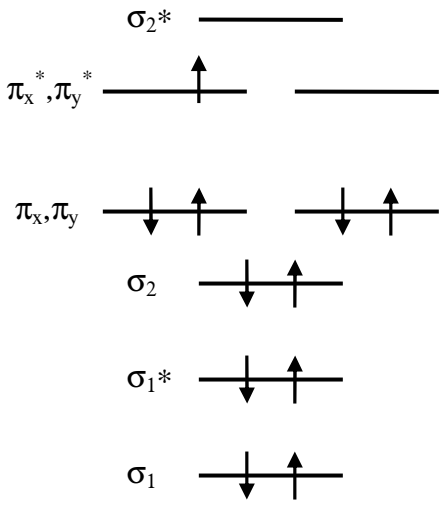
4) ***Occupy the orbitals based on a stick diagram***. The most important thing here is to know the energetic ordering of the orbitals. This would come out of actually evaluating the non-zero matrix elements in matrices above and then solving the generalized eigenvalue problem, which is tedious to do by hand. As a general rule however, there are only two commonly found MO diagrams for diatomics:



Hence, the only question is whether the second σ-bonding orbital is above or below the π-bonding orbitals. In practice, the σ-orbital (which has significant p_z character) is stabilized as you move from left to right along the periodic table, with the σ-orbital being less stable for atoms to the left of and including nitrogen and more stable for atoms to the right of N. Once we have the orbital energy diagram in hand, we can assign the electrons based on stick diagrams. For example, for CO we have 10 valence electrons and we predict a stick diagram for the ground state like the one at left below .Meanwhile for NO, which has 11 valence electrons, we have the stick diagram shown on the right.



CO MO diagram



NO MO diagram

We note one important feature we get directly out of the stick diagrams: the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). For example, in CO the HOMO is a π-bonding orbital, whereas the LUMO is a π* antibonding orbital. Meanwhile, for NO the HOMO and LUMO are both π* orbitals. These orbitals determine reactivity in a crude fashion, as when electrons are taken out of the molecule, they are removed from the HOMO, and when electrons are added, they are added to the LUMO.

5) ***Compute the energy***. Here we can say very little about diatomics, because we don't even know the orbital energies exactly, making it difficult to predict the energies of the whole molecule. If we knew the orbital energies, the total energy for CO, for example, would be:

$$E_{CO}=2E_{\sigma 1}+2E_{\sigma 1*}+2E_{\pi x}+2E_{\pi y}+2E_{\sigma 2}$$

As we don't know these orbital energies, we cannot evaluate the accuracy of this independent electron model for diatomics. However, the bond order is a useful descriptor that correlates very well with the MO energy. For a diatomic, the bond order is simply:

((# Bonding Electrons)-(# Antibonding Electrons))/2

The factor of two reflects the requirement of two electrons for forming a bond. A higher bond order implies a stronger bond and a lower bond order a weaker bond. Thus, MO theory predicts CO will have a stronger bond (bond order 3) than NO (bond order 2.5), which

is experimentally verifiable: the bond energy in NO is 6.5 eV, while the bond energy in CO is 11.1 eV.

There are a number of other successful predictions of MO theory for diatomics: O_2 is correctly predicted to be a spin triplet ground state, CO is correctly predicted to be slightly more stable than N_2, the highest occupied molecular orbital for C_2 is predicted to be degenerate …. Overall, given its basis on the independent particle model, MO theory predicts a surprisingly large array of chemical features correctly.