

9.3: Molecular Orbital Theory

There are a number of ways to describe the electronic structure in diatomic molecules and the wavefunctions that are needed for the descriptions. **Molecular Orbital theory** provides one such example. There are many ways to describe molecular orbitals. One of the most commonly used is the method of using **linear combinations of atomic orbitals** (LCAO).

Linear Combinations of Atomic Orbitals (LCAO)

Consider a wavefunctions derived from the Schrödinger equation that can be expressed as linear combinations of the 1s orbitals centered on each atom. The wavefunction can then be written

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = c_1(1s_1) + c_2(1s_2)$$

In this expression, r_1 and r_2 are the coordinates (position vectors) for nuclei 1 and 2. $1s_1$ and $1s_2$ refer to the 1s orbitals centered on nuclei 1 and 2 respectively. Due to the symmetry of the molecule, the magnitudes of c_1 and c_2 must be the same.

$$c_1 = c_2 = c$$

In order to be normalized, the wave function must satisfy

$$\begin{aligned} 1 &= c^2 \int (1s_1 + 1s_2)(1s_1 + 1s_2) d\tau \\ &= c^2 \int 1s_1 1s_1 d\tau + 2c^2 \int 1s_1 1s_2 d\tau + c^2 \int 1s_2 1s_2 d\tau \end{aligned}$$

The first and the third integrals in this expression are unity due to the fact that the 1s orbitals are themselves normalized. This the expression becomes

$$\begin{aligned} 1 &= 2c^2 + 2c^2 \int 1s_1 1s_2 d\tau \\ &= 2c^2 (1 + \int 1s_1 1s_2 d\tau) \end{aligned}$$

The integral in this expression $\int 1s_1 1s_2 d\tau$ does not vanish due to orthogonality as we have seen in other examples, since the wavefunctions are centered in different locations. The magnitude of the integral, therefore, depends on the degree to which the two orbitals overlap one another. The **overlap integral** is commonly given the symbol S . The magnitude of the normalization constant for the molecular wavefunction will depend intimately on the magnitude of this overlap.

$$1 = 2c^2 (1 + S)$$

Solving for c , the following results

$$c = [2(1 + S)]^{\frac{1}{2}}$$

And the wavefunction can be written as

$$\psi(r_1, r_1) = \frac{1}{[2(1 + S)]^{1/2}} (1s_1 + 1s_2)$$

The value of the overlap integral S will depend on the size of the orbitals and also the internuclear separation. The above wavefunction is an example of a **bonding orbital** as the value of the overlap S will be positive. Positive overlap is a stabilizing condition and acts to hold a molecule together. But just as a linear combination can be constructed from the sum of the 1s orbitals on the two H atoms, one can also be constructed from the difference.

$$\psi(r_1, r_1) = c(1s_1 - 1s_2)$$

This wavefunction will have **negative overlap** and thus produce an **antibonding orbital** which, if populated, has the effect of destabilizing the molecule.

The Expectation Value for Energy

The energies of these bonding and antibonding orbitals can be calculated from the following expressions

$$\begin{aligned}\langle E \rangle &= \frac{\int \psi^* \hat{H} \psi \, d\tau}{\int \psi^* \psi \, d\tau} \\ &= \frac{\int (c_1 1s_1 + c_2 1s_2) \hat{H} (c_1 1s_1 + c_2 1s_2) \, d\tau}{\int (c_1 1s_1 + c_2 1s_2) (c_1 1s_1 + c_2 1s_2) \, d\tau} = \frac{c_1^2 H_{11} + 2c_1 c_2 H_{12} + c_2^2 H_{22}}{c_1^2 + 2c_1 c_2 S + c_2^2}\end{aligned}$$

In this expression, H_{11} and H_{22} are the **Coulomb integrals** defined by

$$H_{ii} = \int 1s_i \hat{H} 1s_i \, d\tau$$

It can be easily shown that $H_{11} = H_{22}$ by symmetry. The other type of integral (besides S, the overlap integral which has already been discussed) is H_{12} , called the **exchange integral**.

$$H_{ij} = \int 1s_i \hat{H} 1s_j \, d\tau$$

The energy of the wavefunction is minimized by use of the variational principle. Specifically, the coefficients c_1 and c_2 must be chosen so as to minimize the energy of the wavefunction. This is done by differentiating the energy expression and setting it equal to zero (since the derivative will be zero at the minimum.) For simplicity, the expression is rearranged so that implicit differentiation is easier to see.

$$E (c_1^2 + 2c_1 c_2 S + c_2^2) = c_1^2 H_{11} + 2c_1 c_2 H_{12} + c_2^2 H_{22}$$

Differentiation of this expression with respect to c_1 and c_2 yields two expressions which can be used to find the two unknowns, c_1 and c_2 .

$$\begin{aligned}E (2c_1 + 2c_2 S) + \frac{\partial E}{\partial c_1} (c_1^2 + 2c_1 c_2 S + c_2^2) &= 2c_1 H_{11} + 2c_2 H_{12} \\ E (2c_2 + 2c_1 S) + \frac{\partial E}{\partial c_2} (c_1^2 + 2c_1 c_2 S + c_2^2) &= 2c_2 H_{22} + 2c_1 H_{12}\end{aligned}$$

Since $\frac{\partial E}{\partial c_1} = 0$ at the minimum, the second terms on the left sides of the above equations vanish. (How nice of them!)

$$\begin{aligned}E (2c_1 + 2c_2 S) &= 2c_1 H_{11} + 2c_2 H_{12} \\ E (2c_2 + 2c_1 S) &= 2c_2 H_{22} + 2c_1 H_{12}\end{aligned}$$

These expressions can be rearranged.

$$\begin{aligned}c_1 (E - H_{11}) + c_2 (SE - H_{12}) &= 0 \\ c_1 (H_{12} - SE) + c_2 (E - H_{22}) &= 0\end{aligned}$$

So long as the Coulomb, Exchange and Overlap integrals can be determined, the coefficients can be as well. The non-trivial solution for c_1 and c_2 can be found from the determinant of the matrix shown below being set to zero.

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

It can be shown (although it will not be shown here) that

$$H_{ii} = E(1s) + J$$

where $E(1s)$ is the energy of a 1s orbital in hydrogen and J is an expression that depends on internuclear distance (r), given by

$$J = e^{-2r} \left(1 + \frac{1}{r} \right)$$

Similarly, H_{ij} can be determined from

$$H_{ij} = E(1s)S + K$$

where K is given by

$$K = \frac{S}{r} - e^{-r}(1+r)$$

Notice that the expressions for both J and K vanish as r approaches ∞ . Given these substitutions, the determinant equation becomes

$$\begin{vmatrix} E_{1s} + J + E & E_{1s} + K - SE \\ E_{1s}S + K - SE & E_{1s} + J + E \end{vmatrix} = 0$$

Or

$$(E_{1s} + J + E)^2 - (E_{1s} + K - SE)^2 = 0$$

Being quadratic in E , this expression yields two solutions for the energy. One will give the energy of the bonding orbital and the other will be the energy of the antibonding orbital. (Now how much would you pay?) These energies are given by the expressions

$$E_{\text{bonding}} = E_{1s} + \frac{J + K}{1 + S}$$

and

$$E_{\text{antibonding}} = E_{1s} + \frac{J - K}{1 - S}$$

The following diagrams show the radial wavefunctions (across the z-axis of the molecule) for both the bonding and antibonding combinations of 1s orbitals. The graph on the left shows the value of the wavefunction, while the one on the right shows the square of the wavefunction. Note the node in the middle of the molecule in the antibonding orbital!

The following figures show the axial wavefunction for the

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

bonding and the

$$\psi = 1s_A - 1s_B$$

antibonding orbitals (on the left) and the corresponding squared axial wavefunctions on the right.

Bonding:

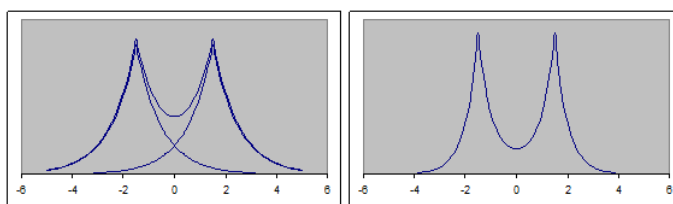


Figure 9.3.1

Antibonding:

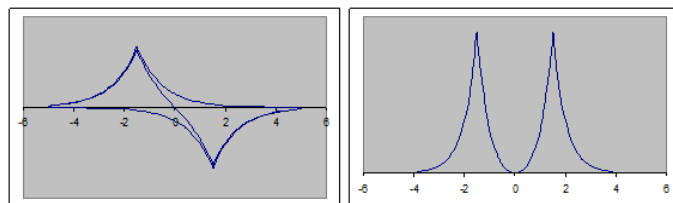


Figure 9.3.2

These orbitals are easy to visualize and understand based on a pictorial approach of linear combinations of orbitals as well. In the pictorial approach, the emphasis is on the sign of the function in the overlap region.

Bonding and Antibonding Orbitals Constructed from s Orbitals

The combination of 1s orbitals can be visualized in the following diagram

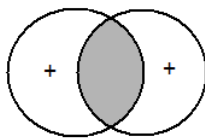


Figure 9.3.3

In this diagram, depicting the symmetric overlap to two 1s orbitals, it can be seen that the region of overlap will have a positive value (as it is given by the product of two positive numbers). This is an example of a s orbital since it is cylindrically symmetric about the internuclear axis.

Just as the symmetric combination can be depicted, the antisymmetric combination is also easy to generate.

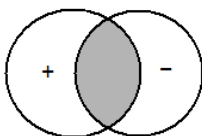


Figure 9.3.4

In this depiction, it should be clear that the region of overlap has a negative value. Another way to think about this is that the wavefunction must change sign as it crosses from left to right. This implies a node between the nuclei!

As stated before, the positive overlap depicted in the first orbital is a stabilizing condition, and the negative overlap in the second is destabilizing. This can be depicted in an orbital diagram.

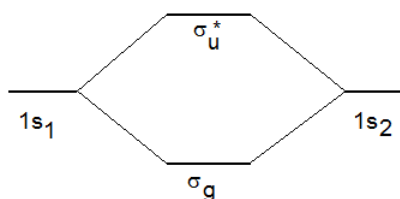


Figure 9.3.5

In this diagram, the atomic orbitals on the separated atoms are shown on the far right and left, and the orbitals in the middle column are the molecular orbitals that arise from the linear combination of the atomic orbitals. σ_g indicates the bonding orbital and σ_u^* indicates the antibonding orbital resulting from the symmetric and antisymmetric combinations of the 1s orbitals. The subscripts g and u state for **gerade** and **ungerade** respectively. Gerade is a German word meaning even, which ungerade means odd. Specifically, these terms (and subscripts) are used to indicate the symmetry of a function with respect to inversion. The g/u symmetry can be determined by drawing an arrow through the middle of a picture of a molecular orbital. If the arrow ends in a point with the opposite sign, the wavefunction is ungerade. However, it must be noted that this symmetry applies only to homonuclear diatomic molecules (and other molecules that possess an inversion center symmetry elements.) More will be discussed about molecular symmetry in later chapters.

Bonding and Antibonding Orbitals constructed from p Orbitals

Bonding and antibonding σ orbitals can be constructed from p-orbitals that are aligned on axis. In the diagram below, the upper picture indicates an antibonding orbital while the lower image is a bonding orbital.

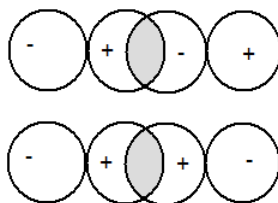


Figure 9.3.6

In addition to σ orbitals, π orbitals can also be constructed.

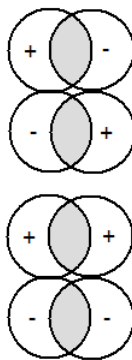


Figure 9.3.7

Clearly the π -bonding orbital is ungerade, while the π -antibonding orbital is gerade (if an inversion center exists within the molecule. It is also important to note that π -type overlap is smaller than σ -overlap, due to the need to get two nuclei so close together for strong overlap of the p orbitals in a π orientation. As such, the π orbitals are less stabilizing or destabilizing relative to the atomic orbital energies.

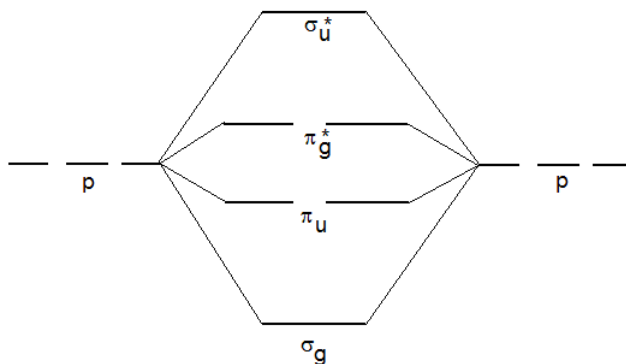


Figure 9.3.8

The σ bonding and antibonding orbitals will be formed by the symmetric and antisymmetric combinations of the p_z orbitals on the separated atoms, whereas the π orbitals will be formed from the p_x and p_y orbitals from the separated atoms.

Electronic Configurations

Electronic configurations can be written for molecules just as they can be for atoms. Instead of being numbered by the principle quantum number, however, molecular orbitals are numbered sequentially from the lowest energy orbital of a certain symmetry. Consider the following list of electronic configurations for homonuclear diatomic molecules formed using the first ten elements.

Molecule	Electronic Configuration	Bond Order	Electronic State
H_2	$(1\sigma_g)^2$	1	$^1\Sigma_g^+$
He_2	$(1\sigma_g)^2(1\sigma_u^*)^2$	0	unbound

Molecule	Electronic Configuration	Bond Order	Electronic State
Li_2	$KK(2\sigma_g)^2$	1	$1\Sigma_g^+$
Be_2	$KK(2\sigma_g)^2(2\sigma_u^*)^2$	0	unbound
B_2	$KK(2\sigma_g)^2(2\sigma_u^*)^2(3\sigma_g)^2$	1	$1\Sigma_g^+$
C_2	$KK(2\sigma_g)^2(2\sigma_u^*)^2(3\sigma_g)^2(1\pi_u)^2$	2	$3\Sigma_g^-$
N_2	$KK(2\sigma_g)^2(2\sigma_u^*)^2(3\sigma_g)^2(1\pi_u)^4$	3	$1\Sigma_g^+$
O_2	$KK(2\sigma_g)^2(2\sigma_u^*)^2(3\sigma_g)^2(1\pi_u)^4(1\pi_g^*)^2$	2	$3\Sigma_g^-$
F_2	$KK(2\sigma_g)^2(2\sigma_u^*)^2(3\sigma_g)^2(1\pi_u)^4(1\pi_g^*)^4$	1	$1\Sigma_g^+$
Ne_2	$KK(2\sigma_g)^2(2\sigma_u^*)^2(3\sigma_g)^2(1\pi_u)^4(1\pi_g^*)^4(3\sigma_u^*)^2$	0	unbound

In this table, the older shell notation is used to indicate a filling of the inner shell electrons, $(1\sigma_g)^2(1\sigma_u^*)^2$. These are given the symbol KK.

Bond Order

The bond order of a molecule is determined by adding the number of electrons in bonding orbitals, subtracting the number of electrons in antibonding orbitals and dividing the result by 2 (since there are two electrons per orbital.)

$$\text{Bond Order} = \frac{\# \text{bonding} - \# \text{antibonding}}{2}$$

The larger the bond order, the stronger a chemical bond is predicted to be. Also, since strong bonds are short bonds, the larger the bond order, the shorter a bond is predicted to be.

Ionization of a molecule may have a profound affect on the bond order, and therefore the bond length. Consider the molecule c_2 that has an electronic configuration given by

$$c_2 : KK(2\sigma_g)^2(2\sigma_u^*)^2(3\sigma_g)^2(1\pi_u)^2$$

The addition of an electron to for c_2^- will require the electron to go into the $1\pi_u$ bonding subshell. This will have the effect of strengthening the bond (since it increases the bond order.) Removal of an electron to form c_2^+ would weaken the bond since it involves the removal of a bonding electron.

Paramagnetism

While the bond order of oxygen (O_2) is correctly predicted by a Lewis Structure, the Lewis structure fails to predict that the molecule will be **paramagnetic**. Paramagnetism is a property of a molecule or atom that occurs when the system has unpaired electrons. These electrons each have a small magnetic moment which can align with an external magnetic field, lowering the energy of the atom or molecule. As such, the atom or molecule will be attracted to a magnetic field.



Photograph showing liquid oxygen being trapped in a magnetic field due to its paramagnetic nature.

Figure 9.3.9

Oxygen, which has an electronic configuration given by

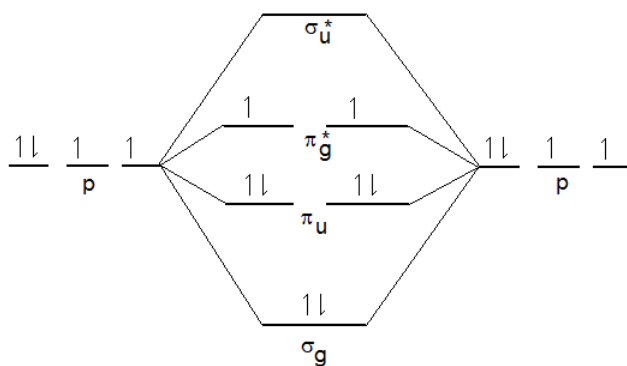
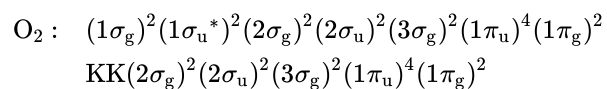


Figure 9.3.10

It is clear that there are two unpaired electrons. This is a property that cannot be predicted based on the Lewis Structure!

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