# Molecular Orbital Tutorial

Atomic Orbitals

All molecular orbitals (MOs) are made by combining atomic orbitals (AOs). These AOs are the familiar s and p orbitals. As we move down the periodic table we will encounter d,f and g AOs but we will leave these orbitals to the inorganic chemists who love them and concentrate on the two orbitals of most relevance to organic chemistry, the s and p atomic orbitals.

Hydrogen

Most organic molecules include hydrogen. Hydrogen has only the 1s orbital to consider. The wavefunction for the s orbital is spherical in shape with the maximum value at the centre of the sphere and the value decays exponentially as distance from the centre increases.

In Figure 1 we see some representations of an s orbital. An s orbital can be represented graphically as a plot of the wavefunction (A), an electron density diagram (B), or a simple circle (C). We will use the simple circle because all we need to keep track of for our purposes is the shape (and relative size) of the orbitals.

*Figure 1.   Graphical representations of an s orbital*
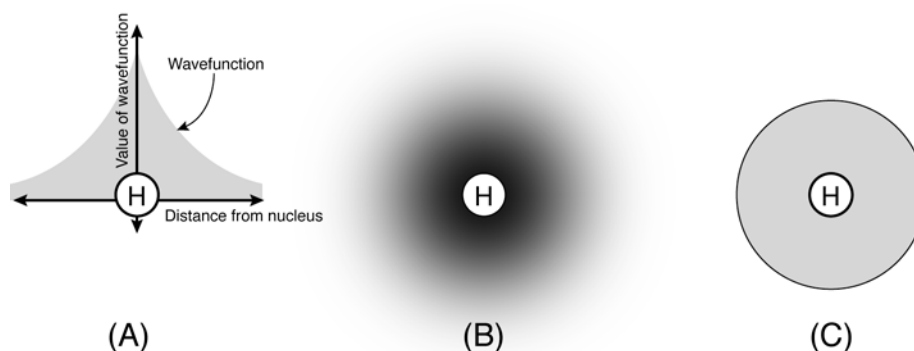
Carbon

All organic molecules include carbon. The valence shell of carbon has a 2s and three 2p orbitals. The 2s orbital is similar in size and identical in shape to the 1s orbital of hydrogen.

The p orbital is very different. The wave function is shaped somewhat like a sine wave. It changes sign and has a value of zero at the nucleus. The region of space where the wavefunction is zero describes a plane that intersects the nucleus.

In Figure 2 we see representations of a p orbital. A p orbital can be graphically represented by a plot of the wavefunction (A), an electron density diagram (B), or a graphical diagram (C). We will use the graphical diagram. Note the different colors in the lobes of the p orbital. These denote the change in sign as we cross the node (sign

changes on either side of a node). Dark is one sign and light is another (its doesn't matter which is positive or negative, what matters is that they are different).

Figure 2.   Graphical representations of a p orbital

(A)   (B)   (C)
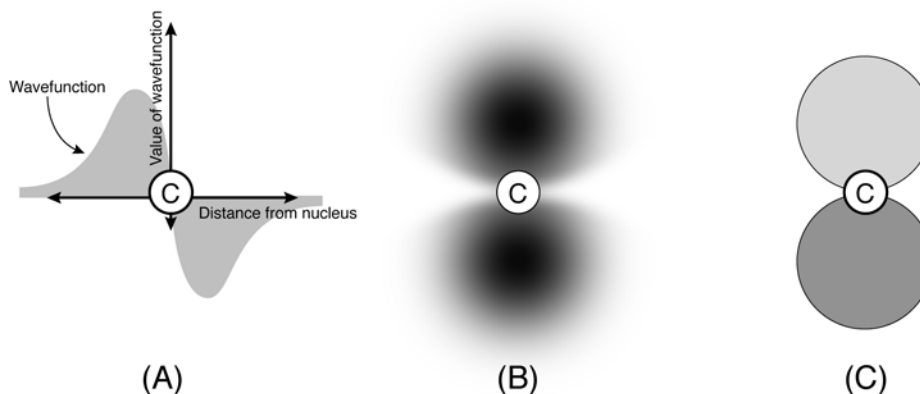
Simple Molecular Orbitals

When atoms combine to make molecules, atomic orbitals must combine to make molecular orbitals. The total number or orbitals does not change. 10 atomic orbitals will combine to give 10 molecular orbitals. When two atomic orbitals combine to make a bond, the result will be two molecular orbitals; one with lower energy (bonding orbital) and one with higher energy (antibonding orbital). The electrons in the bond will be in the lower energy bonding orbital and the system is lower in energy with a bond than without. This more stable combination of orbitals is the reason for the existence covalent bonds.

Let us consider the simplest case of a molecular orbital system, the single bond in a hydrogen molecule.

Rules for Orbital Combinations

To have atomic orbitals interact to create molecular orbitals we must be able to mathematically combine them. In order for the combination to be possible we must obey the following rules.

1. The orbitals must be physically close enough to interact. The magnitude of the combination is inversely proportional to the distance between the atoms.

2. The orbitals must combine along an axis of mutual symmetry. The magnitude of the combination will be proportional to the cosine of the angle between the orbitals if they are not perfectly aligned. Remember that $Cos(0º) = 1$ and $Cos(90º) = 0$.

3. The orbitals must be similar in size and energy. The magnitude of the combination is inversely proportional to the difference in size or energy.

Throughout this tutorial we will see how these three rules are applied.

The Hydrogen Molecule

When two hydrogen atoms are separated by a distance equal to a H-H bond we are certainly close enough for the two 1s orbitals to interact. These two orbitals are the basis set, the set of orbitals that we are combining. The two 1s orbitals in our basis set are identical in size and energy. They are spherical and so will always share a common axis of symmetry. So we expect a very large magnitude of combination.

Interaction Energy

What do we mean by a large magnitude of combination? I am referring to the interaction energy, ΔE. The interaction energy, ΔE, is the amount of energy that is released upon combination of the orbitals. It is how much lower in energy the bonding orbital is compared to the basis set orbitals. The antibonding orbital is higher in energy by an amount equal to the interaction energy. Since only the bonding orbital is filled, the H2 molecule is more stable than two neutral H atoms by energy equal to $2 \cdot \Delta E$ (2 electrons).

*Figure 3.   Energies of molecular orbitals of H_2.*
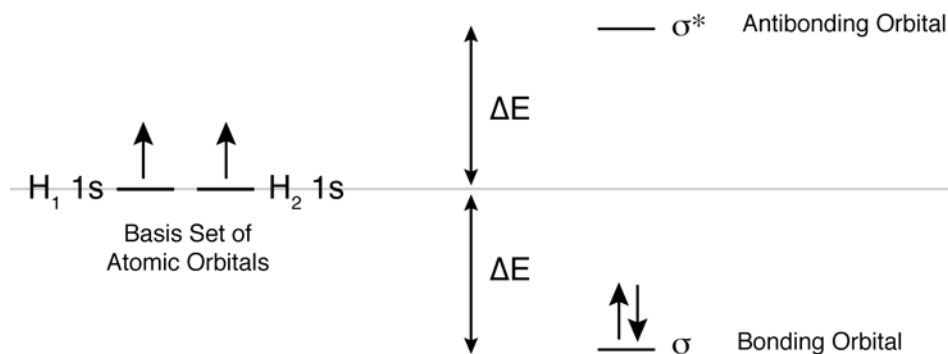
So we know the relative energies of the bonding and antibonding orbitals. These orbitals are for the σ-bond between the hydrogen atoms. The orbitals are designated σ and σ^* for the bonding and antibonding orbitals, respectively. What do these orbitals look like?

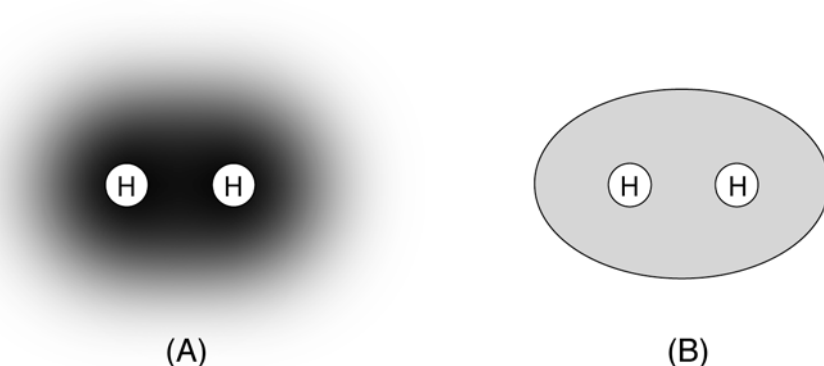**Shape of the Bonding Molecular Orbital**

There are only two ways to combine two things, we can add them together or we can subtract them from each other. The same is true for combining orbitals. Let us consider adding the 1s orbitals together. In Figure 4 we see the mathematical result of adding two 1s orbitals together.

Figure 4.   Adding two 1s orbitals together
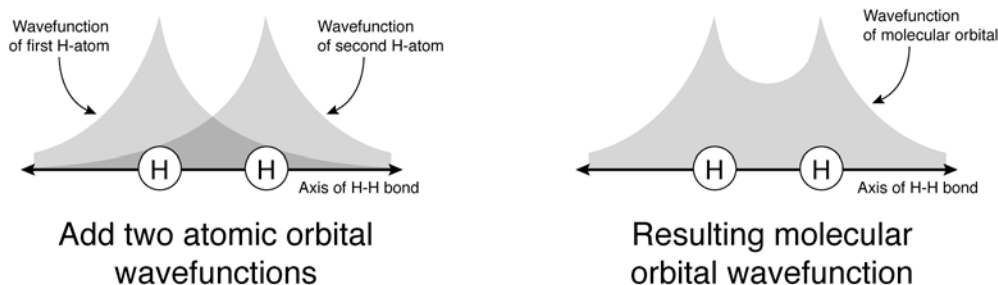
We can see that the two H atoms now share a molecular orbital that has electron density between the two atoms. This is the bond between the two atoms. Observe that the electron density also extend out past the hydrogen atoms in the H-H bond. This can be expressed graphically as shown in Figure 5 by an electron density diagram (A), or a graphical diagram (B).

Figure 5. Graphical representations of the H-H bonding molecular orbital.

(A)   (B)

**Shape of the Antibonding Molecular Orbital**

We have added the two atomic orbitals together (positive combination), now let us substract them (negative combination). In Figure 6 we see the mathematical result of subtracting two 1s orbitals.

Figure 6. Negative combination of two 1s atomic orbitals.

Subtract two atomic orbital wavefunctions

Resulting molecular orbital wavefunction
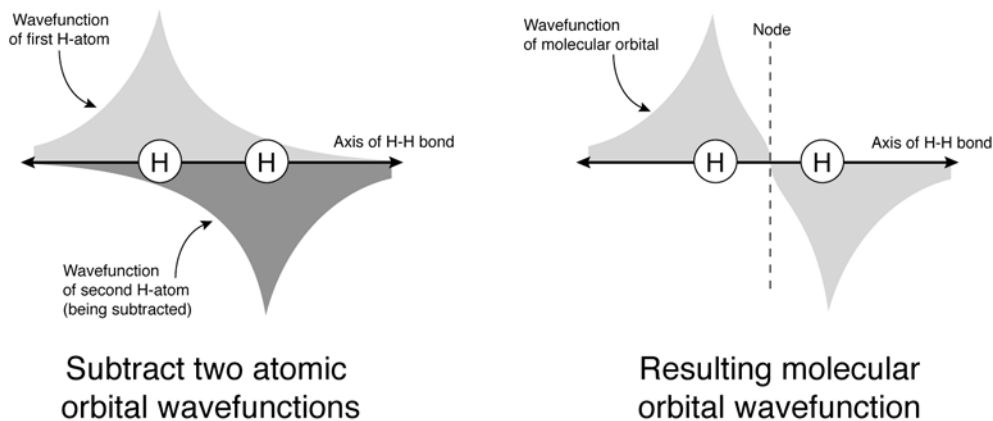
At a point halfway between the hydrogen atoms, the two identical atomic orbital wavefunctions cancel out completely. At this point, the wavefunction has a value of zero. This is a node, a region of zero electronic density. The sign of the wavefunction is different on either side of a node. The node is where the wavefunction crosses the axis of the wavefunction plot and changes sign. To go from +1 to –1, we must pass through zero. This same concept can be expressed graphically as shown in Figure 7 by an electron density diagram (A), or a graphical diagram (B).

Figure 7. *Graphical representations of the H-H antibonding molecular orbital.*

(A)   (B)
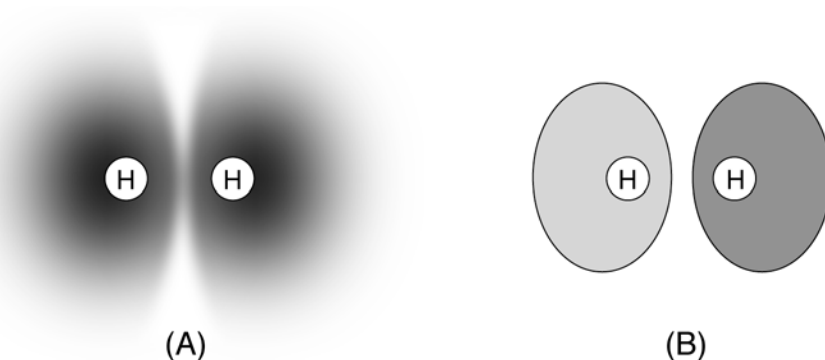
Relative Energies of Orbitals

So we now have an idea of the physical shapes for bonding and antibonding orbitals from the representations in Figure 5 and Figure 7. We can rank orbitals combined from identical atomic orbitals in energy by examining their shape. If the shape of two combined orbitals is identical (same number of nodes, same symmetry) then the energies will also be identical. If the shapes are not the same (different number of nodes), the orbital with more nodes is higher in energy.

Comparing the physical shapes for bonding and antibonding orbitals from the representations in Figure 5 and Figure 7 shows that the antibonding orbital has one node and the bonding orbital has none. The antibonding orbital will be the higher energy result of the two possible ways of combining orbitals. In the energy diagram in Figure 3, the antibonding orbital will be the σ* orbital and the bonding orbital will be the σ orbital.

Adding Circles – Graphical Orbital Combinations

As we move on to slightly more complex orbitals we will not be using mathematical combinations as shown in Figure 4 and Figure 6. We will use a very simple concept involving adding shapes together. In simple molecules, this is amazingly accurate for describing molecular orbitals and is still very informative for more complex systems.

For an example of this method, lets turn back to the hydrogen molecule.
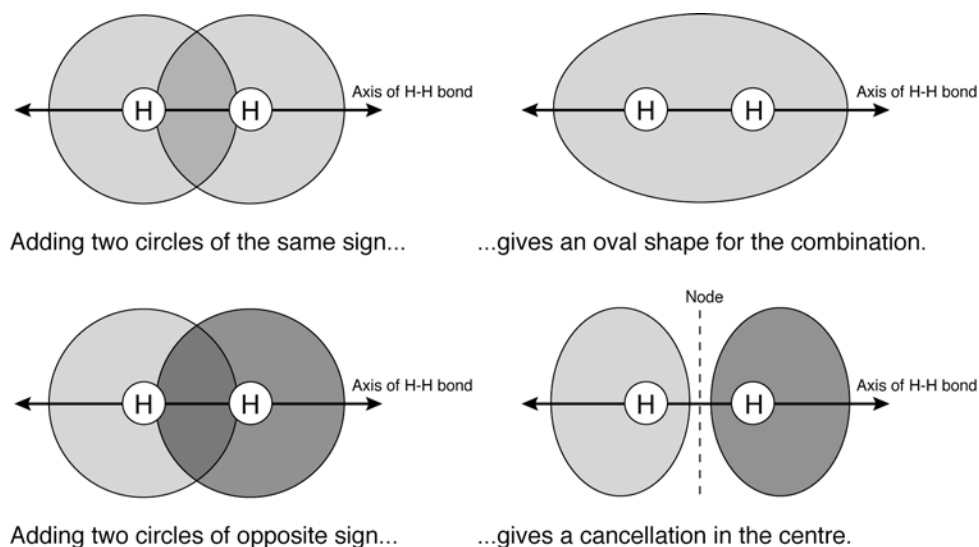
Graphical Molecular Orbitals in H_2.

We will first create a basis set of graphical orbitals by drawing two circular 1s orbitals around each hydrogen atom in an H_2 molecule. Draw the circles large enough to overlap since we know that the 1s orbitals interact.

Next, ask yourself what happens when you add two identical circles that overlap? What happens if you subtract one from the other? Perhaps the answer lies in Figure 8?

Adding two circles will give you an oval shape. Subtracting them will leave you with the parts of the circles that do not interact relatively unchanged and a region where they cancel each other out completely (a node).

From now on we will only be adding shapes together. That will be the extent of the math for this tutorial. So brush up on your kindergarten math notes and lets proceed.

Figure 8.   *Linear combination of hydrogen atomic orbitals.*

Adding two circles of the same sign...   ...gives an oval shape for the combination.

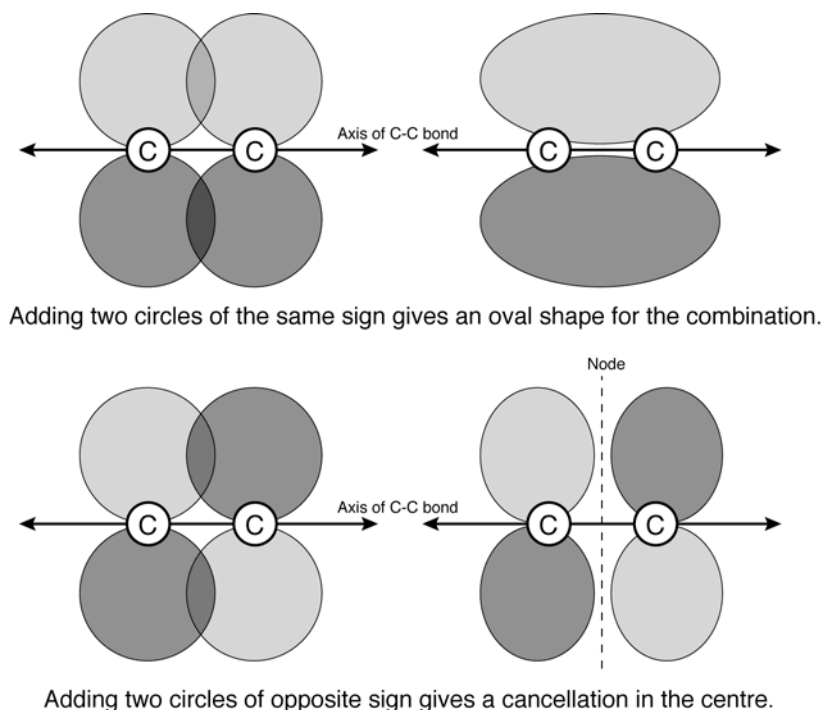Adding two circles of opposite sign...   ...gives a cancellation in the centre.

The easiest way to substract two orbitals is to invert the sign of one of them and add them together. Remember from elementary school when you learned that $1 - 1 = 1 + (-1)$. We use the same principle here.

Graphical Combination of p Orbitals.

We know that double bonds are the result of a σ-bond and a π-bond. The σ-bond can be understood by adding hybrid atomic orbitals of carbon together as in the case of hydrogen. (We will discuss hybrid orbitals and carbon atoms later.) The π-bond is the result of a linear combination of p orbitals.

Lets combine two p orbitals to give the bonding and antibonding molecular orbitals of a π-bond as shown in Figure 9.

Figure 9.   Linear combination of p orbitals

Adding two circles of the same sign gives an oval shape for the combination.

Adding two circles of opposite sign gives a cancellation in the centre.

Observe that we are combining the p orbitals along one of their axes of symmetry. Here we have lined them up along their mutual 2-fold axes of symmetry. Along this axis, a p orbital can be rotated 180 degrees and still have the same physical position. A half-turn does not alter the physical appearance of the orbital. If orbitals line up along a mutual axis of symmetry they will be able to have maximum interaction.

Both molecular orbitals have a node along the C-C bond axis. They will always have the same node as the two p orbitals that were combined. The negative combination of the orbitals gave an orbital with an additional node perpendicular to the C-C bond. Since this molecular orbital has two nodes, it is higher in energy that the other molecular orbital, which has only the one node.

Symmetries of Bonds

σ and π-bonds are named for their symmetries. σ-bonds have a circular axis of symmetry (looking down the axis of the bond, the orbital appears to be a circle; any small turn will not change the shape at all.) π-bonds have a two-fold axis of symmetry, just like the p orbitals that combined to create them.

Hybrid Atomic Orbitals

We have shown how to create the σ and π molecular orbital systems for covalent bonds via the combination of s and p orbitals, respectively. But using just s and p orbitals in our basis sets can result in a lot of math, as we will see. We can avoid this math by letting the long-haired physicists do the math in advance and using predefined combinations of s and p atomic orbitals in our basis sets. These predefined combinations are hybrid orbitals.

SP₃ Hybrid Atomic Orbitals

Often, the known geometry of a molecule does not align the bonds perfectly with the p orbitals. Let us consider the case of methane.

Methane is a carbon atom bonded to 4 hydrogen atoms. According to the VSEPR theory, these bonds will adopt a geometrical configuration around the carbon to maximize the distance between them. The best shape to accomplish this goal is a tetrahedron.

Figure 10.   Tetrahedral shape of methane.
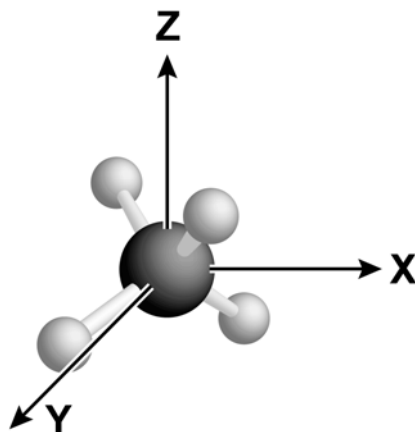
Note that in Figure 10, none of the C-H bonds aligns with an axis (x,y or z). Even if I chose to draw the diagram with one C-H bond lined up with the z-axis, for example, the other three would still be away from the other two axes. The angle between each pair of C-H bonds is 109°. This fits the definition of the tetrahedron.

The 3 p orbitals of carbon are orthogonal to each other (they are perpendicular to each other). We cannot create 4 C-H bonds using the 3 perpendicular p orbitals and the s orbital of carbon separately. If we did so, at least three of the C-H bonds would be at 90° to each other. We observe 109° in nature, not 90°.

Making the Hybrid Orbitals

We have 4 C-H bonds. So, being minor-league mathematicians, we would prefer to have 4 simple orbitals that are at 109° from each other and line up perfectly with our future C-H bonds. We need 4 new atomic orbitals that fit our geometry.

We have 4 classic atomic orbitals in the valence shell of carbon: the 2s and the $2p_x$, $2p_y$ and $2p_z$ orbitals. The p orbitals are designated x,y and z because I have chosen (and it is only my choice) to imagine them aligned with the axes of the above diagram. The axes are at 90° to each other and that matches up with what I know about p orbitals. The s orbital is a sphere centered on the origin of the axes.

We have 4 orbitals and I need 4 new hybrid orbitals. I can mathematically combine the 4 atomic orbitals to get the 4 new hybrid orbitals. Whenever n orbitals are combined, the result is n new orbitals. This is true for molecular orbitals (2 orbitals combine to give a new bonding orbital and an antibonding orbital) and it is true for making hybrid orbitals.

When making hybrid orbitals from a basis set of atomic orbitals we only use positive combinations (we only add them together). Orbitals combine most strongly when their axes of mutual symmetry are aligned. If the axes are not aligned, the magnitude of the combination is proportional to the cosine of the angle between the axes of mutual symmetry. For hybrid orbitals we chose a vector (a line in space) that is aligned with a C-H bond (this is the axis of symmetry for the new hybrid orbital that corresponds to that C-H bond).

So for one of the C-H bonds, we will add all the orbitals together according to the following method…
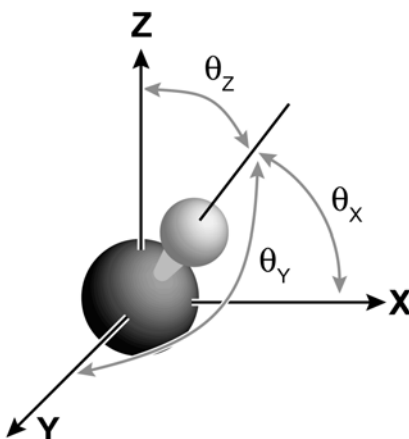
Equation 1

$$\phi_1 = A_1 \cdot \phi_S + B_1 \cdot \phi_{P_X} + C_1 \cdot \phi_{P_Y} + D_1 \cdot \phi_{P_Z}$$

Where ϕ represents an atomic orbital (ϕ_1 is the new hybrid orbital that we are creating mathematically) and A,B,C and D are coefficients that represent the magnitude of interaction with the target vector (or the fraction of each of the classic atomic orbitals that contribute to a hybrid atomic orbital that whose axis is along the target vector).

For the s orbital, the coefficient A represents the amount of it that is contributed to the new hybrid orbital. We will be mixing the s orbital into 4 new hybrid orbitals so we will be using 25% of the s orbital in each hybrid orbital. The B,C, and D coefficients are proportional to the cosine of the angle between out target vector along the desired C-H bond and the p_x, p_y and p_z orbitals. Observe the angles between the axes of the p orbitals and our target vector in Figure 11.

Figure 11.　*Target C-H bond and angles from C-H bond axis to axes of p orbitals. We will calculate an SP$_3$ orbital for carbon that has an axis aligned with this C-H bond.*

So we can rewrite Equation 1 to replace the coefficients A,B,C and D with their corresponding mathematical values…

Equation 2

$$\phi_1 = 0.25 \cdot \phi_S + \cos(\theta_X) \cdot \phi_{P_X} + \cos(\theta_Y) \cdot \phi_{P_Y} + \cos(\theta_Z) \cdot \phi_{P_Z}$$

We can write a similar equation for each of the 4 hybrid orbitals that align with each of the 4 C-H bonds. In every case we are just adding the atomic orbitals together in fractions according to their contribution to the desired hybrid orbital on the give C-H bond axis (or target vector). The complete set of 4 equations for the 4 hybrid orbitals is given below as Equation 3. The coefficients A, B, C and D follow the same scheme as in Equation 2. The s orbital coefficient, A, is 0.25 (the s orbital is shared evenly with the 4 bonds) and the p orbital coefficients, B, C, and D, are proportional to the cosine of the angle between the given C-H bond and the p orbitals. (Note: The coefficients are not exactly 0.25 and cos(θ). They are proportional to these values and the true values reflect more detailed calculations).

Equation 3

$$\phi_1 = A_1 \cdot \phi_S + B_1 \cdot \phi_{P_X} + C_1 \cdot \phi_{P_Y} + D_1 \cdot \phi_{P_Z}$$

$$\phi_2 = A_2 \cdot \phi_S + B_2 \cdot \phi_{P_X} + C_2 \cdot \phi_{P_Y} + D_2 \cdot \phi_{P_Z}$$

$$\phi_3 = A_3 \cdot \phi_S + B_3 \cdot \phi_{P_X} + C_3 \cdot \phi_{P_Y} + D_3 \cdot \phi_{P_Z}$$

$$\phi_4 = A_4 \cdot \phi_S + B_4 \cdot \phi_{P_X} + C_4 \cdot \phi_{P_Y} + D_4 \cdot \phi_{P_Z}$$

All the hybrid orbitals will be identical in shape and will differ only in the orientation of their axes of symmetry (along each C-H bond, see Figure 14). After adding up the fractions of atomic orbitals for the orbital described by Equation 2, we will have a new hybrid orbital. The basis set is shown graphically in Figure 12 and the resulting calculated hybrid atomic orbital is shown in Figure 13.

Figure 12.   *The basis set for combining classic atomic orbitals into a hybrid orbital. Their contribution to the new hybrid orbital aligned along the desired C-H bond*
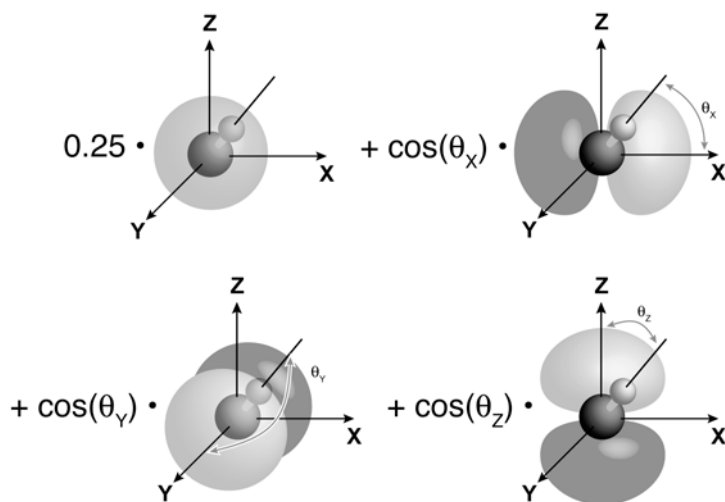
The shape of the new orbital is shown in Figure 13.

Figure 13. *The SP$_3$ atomic orbitals constructed from the S, P$_X$, P$_Y$ and P$_Z$ atomic orbitals in Figure 12 by adding them together in proportion to the coefficients.*

SP$_3$ Orbital (side view)

SP$_3$ Orbital
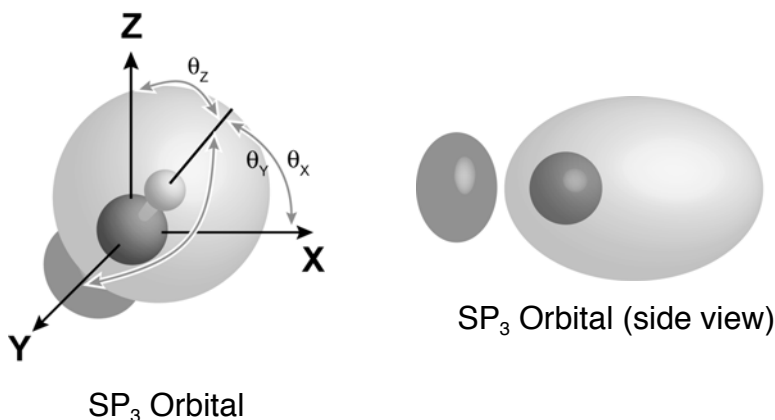
This orbital is designated as an SP$_3$ hybrid atomic orbital because it is made from the combination of as s atomic orbital and all 3 p atomic orbitals.

The orbital constructed by adding together the 4 atomic orbitals using coefficients for the C-H bond in Figure 11 is designated as ϕ_1. The other three hybrid atomic orbitals, ϕ_2, ϕ_3 and ϕ_4, are the result of using different θ_X, θ_Y and θ_Z angles corresponding to the other 3 C-H bonds. All 4 of the SP$_3$ orbitals are shown in Figure 14. Each was calculated in the same manner as the hybrid atomic orbital above.

Figure 14. *All 4 SP$_3$ orbitals for the carbon in methane. Each orbital corresponds to the axis of a C-H bond and they are all 109° away from each other.*

ϕ_1 ϕ_2 ϕ_3 ϕ_4
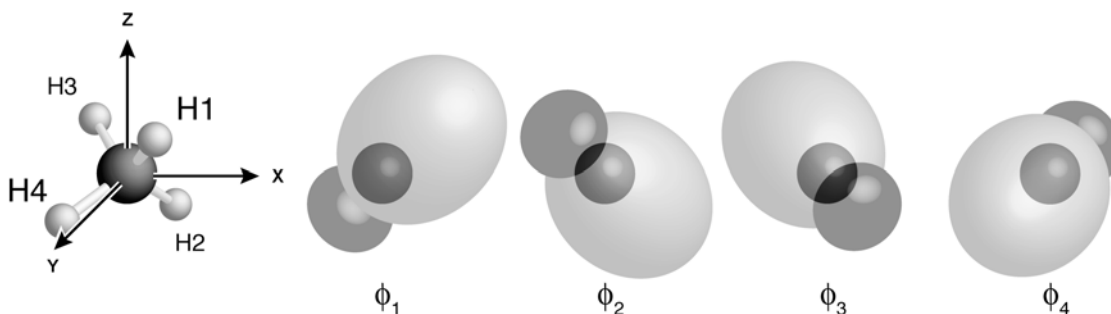
Remember, these hybrid atomic orbitals are only atomic orbitals. They are mathematical recombinations of the classical atomic orbitals so that we can have an orbital that lines up with the bond for which we wish to construct a molecular orbital. We will combine the SP$_3$ hybrid orbital of the carbon atom with the s orbital of the hydrogen atom to make a molecular orbital system for the C-H bond. More on that later…

SP$_2$ Hybrid Atomic Orbitals

Consider a system where there are only three groups around the carbon atom. In agrrement with VSEPR theory, these groups will space themselves in a plane at 120° apart. But p orbitals are at 90° to each other. We are again in a situation where we must

calculate in advance some combination of p and s atomic orbitals to create hybrid atomic orbitals that align with the bonds that we wish to create.

As a simple example of a system where SP₂ hybrid atomic orbitals will be helpful we will use a carbon atom with three protons. This system is a cation and has only three electron pairs (in the C-H bonds) around the carbon atom. So these bonds will space themselves to attain maximum distance between them. The angles between the bonds are 120°.

Figure 15. *An example of a system where we use SP₂ hybrid atomic orbitals for carbon. Here we have a methylene cation.*
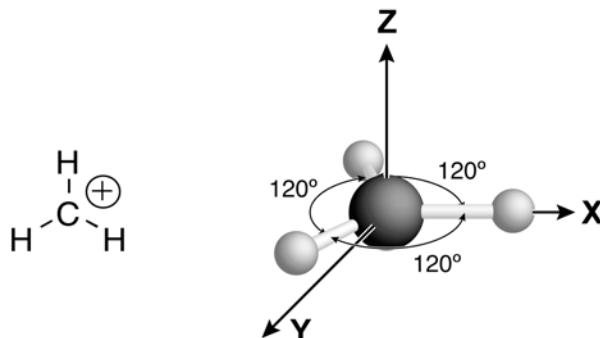
We will construct the hybrid orbitals in exactly the same way as above. We will select one of the 3 C-H bonds and calculate the angles between the bond axis and the p-orbitals, θ. The coefficients for the contributions of each p orbital are proportional to cos(θ).

Observe that the p_z orbital (the p orbital aligned with the z-axis) will be at an angle of 90° to all three C-H bonds. Cos(90°) = 0. So the coefficient for contribution of the p_z orbital to a hybrid atomic orbital aligned with one of the above C-H bonds is zero. The p_z orbital does not contribute to any hybrid atomic orbitals that correspond to the axes of the three C-H bonds. The p_z orbital is not involved at all in the SP₂ hybrid orbital system. It will not be included in our calculations.

The basis set of orbital that we will combine to make a set of SP₂ orbitals will include the s orbital and the p_x and p_y orbitals. These three orbitals will be combined to make the three hybrid atomic orbitals. There are three hybrid orbitals to which the s orbital will contribute and so will will use a coefficient of 0.33 for the s orbital.

The three hybrid atomic orbitals can be describes as in Equation 4
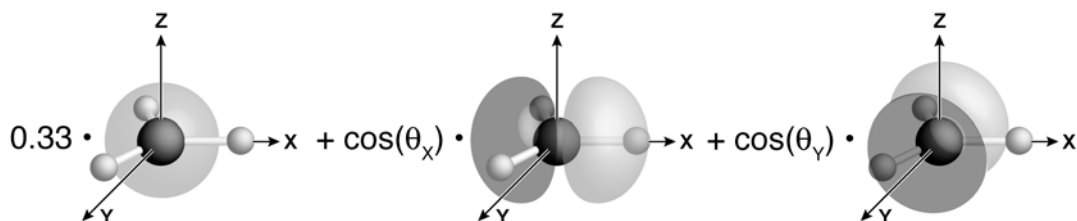
Equation 4

$$\phi_1 = 0.33 \cdot \phi_S + \cos\left(\theta_{X_1}\right) \cdot \phi_{P_X} + \cos\left(\theta_{Y_1}\right) \cdot \phi_{P_Y}$$

$$\phi_2 = 0.33 \cdot \phi_S + \cos\left(\theta_{X_2}\right) \cdot \phi_{P_X} + \cos\left(\theta_{Y_2}\right) \cdot \phi_{P_Y}$$

$$\phi_3 = 0.33 \cdot \phi_S + \cos\left(\theta_{X_3}\right) \cdot \phi_{P_X} + \cos\left(\theta_{Y_3}\right) \cdot \phi_{P_Y}$$

The basis set of orbitals used is shown in Figure 16.

Figure 16. *Basis set of orbitals combined for SP₂ system. The s, pₓ and p_y orbitals are combined to make the three hybrid atomic orbitals shown in Figure 17.*

$$0.33 \cdot \quad + \cos(\theta_X) \cdot \quad + \cos(\theta_Y) \cdot$$

Mathematical combination of the wavefunctions with respect to the axis of the desired CH bonds results in the following SP_2 hybrid atomic orbitals.

Figure 17. *Basis set of atomic orbitals for the carbon atom in the CH_3 cation. The ϕ_1, ϕ_2 and ϕ_3 are the SP_2 hybrid atomic orbitals calculated from the basis set in Figure 16. The p_z orbital remains unchanged.*

$$\phi_1 \qquad \phi_2 \qquad \phi_3$$

P_z
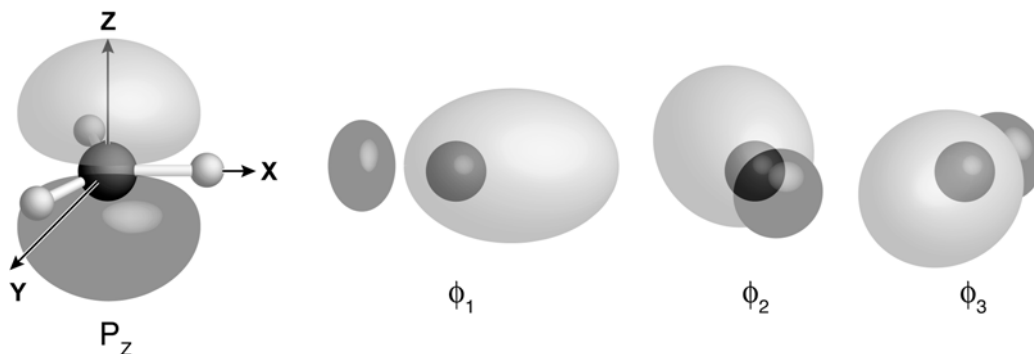
Observe that SP_2 orbitals look very, very similar to SP_3 orbitals. The major difference in the shape of the orbital is the fact that there is slightly more s orbital in each SP_2 orbital compared to SP_3 orbitals. We will use these hybrid atomic orbitals to make covalent bonds shortly. Remember that the p_z orbital has not been involved at all in the hybrid orbitals. It is still a separate p orbital. This carbon atom can be imagined to have 4 atomic orbitals, the three hybrid orbitals and the p_z orbital.

SP Atomic Hybrid Orbitals

We have considered hybrid atomic orbitals for carbon that can be used in a basis set for a tetrahedral arrangement (the SP_3 orbital set) and a trigonal planar arrangement (the SP_2 orbital set). Now let us consider a linear system. We will use a carbon atom in acetylene as an example.

Figure 18. *Acetylene is a linear molecule. We will consider constructing hybrid atomic orbitals for a carbon atom that align with its two bonds.*

$$H-C\equiv C-H$$
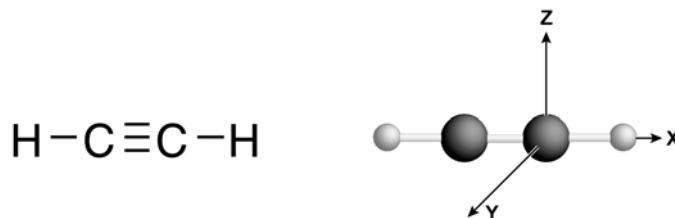
The two bonds are aligned with the x-axis in our scheme. We have also chosen to align the p orbitals along the x, y and z axes. This means that the p_y and p_z orbitals are at 90° to the axis of the desired hybrid orbitals. The cosine of 90° is zero so these orbitals do not contribute to the desired hybrid orbitals. Only the s orbital and p_x orbital will be contributing to the two SP orbitals.

The s orbital is being shared between two hybrid orbitals so we will use a coefficient of 0.5 for its contribution to each. The contribution of the p_x orbital will be proportional to the cosine of the angle between the p_x orbital axis and the two bond axes. In a linear system, these angles are 0° and 180° so the coefficients will be 1 and –1, respectively.

The hybrid atomic orbitals for a linear system at a carbon atom are given in Equation 5.

Equation 5

$$\phi_1 = 0.5 \cdot \phi_S + \cos(0°) \cdot \phi_{P_X} = 0.5 \cdot \phi_S + \phi_{P_X}$$
$$\phi_2 = 0.5 \cdot \phi_S + \cos(180°) \cdot \phi_{P_X} = 0.5 \cdot \phi_S - \phi_{P_X}$$

We observe from Equation 5 that we can construct two hybrid SP atomic orbitals from the s orbital and the p_x orbital simply by adding them together or subtracting them. The basis set of orbitals used in shown in Figure 19.

Figure 19. *Basis set for constructing SP hybrid atomic orbitals for a carbon atom in acetylene.*
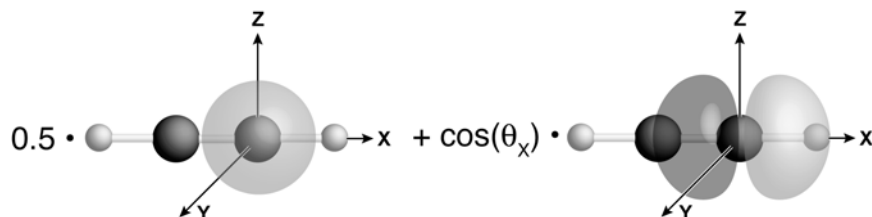

Since this is the simplest case, we can do a simple graphical combination of the orbitals according to Equation 5.

Figure 20. *Graphical combination of the basis set atomic orbitals to give the two SP hybrid atomic orbitals.*
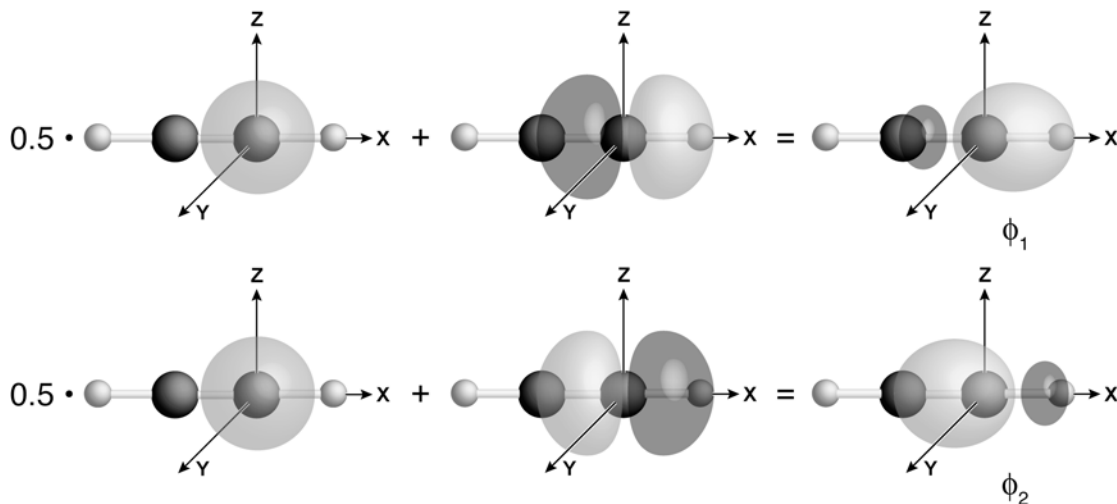
So by combining the atomic orbitals in our basis set (see Figure 19) we get the two SP hybrid orbitals that are used to account for bonds in a linear carbon system (see Figure 20). Along with these two SP hybrid atomic orbitals there are the p_z and p_y orbitals that were not used. So the basis set of atomic orbitals used in a linear carbon system would be the 4 orbitals shown in Figure 21.

Figure 21.   Basis set orbitals for a linear carbon system. They are the p_y, p_z and 2 SP orbitals.
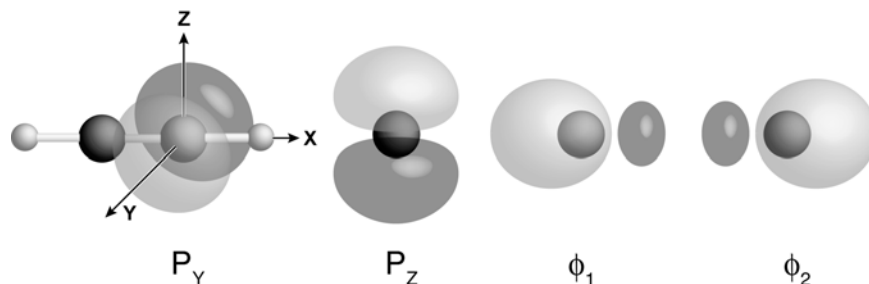
Summary (All that you really need to know about hybrid orbitals)

In this section we have seen the origin of hybrid atomic orbitals. It is important to realize that hybrid orbitals are not real; they are mathematical combinations of existing s and p orbitals. By constructing hybrid orbitals we are doing all of the complicated math in advance to get atomic orbitals that can be easily combined graphically with atomic orbitals of other atoms to make molecular orbitals.

Depending on where we want the bonds to be, we will…

   i.   combine all 4 atomic orbitals to make hybrid atomic orbitals that can be used for tetrahedral systems (SP_3, see Figure 14)

   ii.   combine 3 atomic orbitals orbitals to make hybrid atomic orbitals that can be used for trigonal planar systems (SP_2, see Figure 17)

   iii.   combine 2 atomic orbitals orbitals to make hybrid atomic orbitals that can be used for linear systems (SP, see Figure 21)

A hybrid orbital system is a basis set of atomic orbitals that fit the geometry of the groups around carbon atom. This basis set has been calculated from the existing atomic orbitals according to the contributions of each atomic orbital to a molecular orbital along a particular bond. Changing the hybridization of a carbon atom (e.g. when a tetrahedral carbon is converted to a trigonal planar carbon after departure of a leaving group) is NOT a change in electronic configuration of the carbon. It always has an s orbital and 3 p orbitals. Changing hybridization is when we choose to use a different basis set of precalculated hybrid atomic orbitals due to the geometry change. Hybrid orbitals are a mathematical creation in order to simplify our molecular orbital calculations.

How do we know when to use a given set of hybrid atomic orbitals? We will use the set that corresponds to the geometry around our carbon atom.

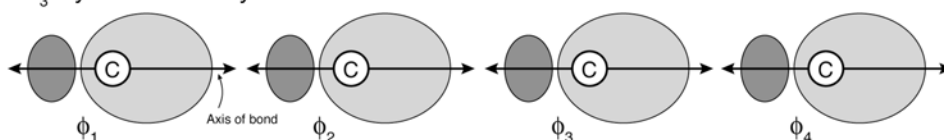## *Molecular Orbital Systems of Organic Molecules*

We have seen how to graphically combine s orbitals to make the molecular orbital system in a hydrogen molecule. In that system our basis set consisted of an s atomic orbital from each hydrogen atom. When we have carbon atoms (or other second row elements) in the system we will find ourselves using basis sets of SP, SP_2 or SP_3 hybrid atomic orbitals.

Basis sets for the 3 hybrid orbital systems are summarized in Figure 22. For the SP_3 system we have the 4 SP_3 hybrid orbitals, for the SP_2 system we have the 3 hybrid SP_2 orbitals and the p orbital, and the SP system we have the 2 hybrid SP orbitals and the 2 p orbitals. Observe that all the SP_x orbitals are very similar in shape. The only difference between the types of SP_x orbitals is the different contribution ratios between s orbitals and p orbitals.

In Figure 22 the orbitals are all shown in relation to the axis of a bond. The SP_x orbitals are, by definition aligned with a bond (that is why we created them). The p orbitals are perpendicular to the bonds (that is why they were not included in the SP_x hybrid orbitals).

Figure 22.   *Basis sets for SP_3, SP_2 and SP hybrid atomic orbital systems. The orbitals are shown in relation to a bond axis. Their 3-D relationship of the atomic orbitals to each other is shown in Figure 14, Figure 17 and Figure 21.*
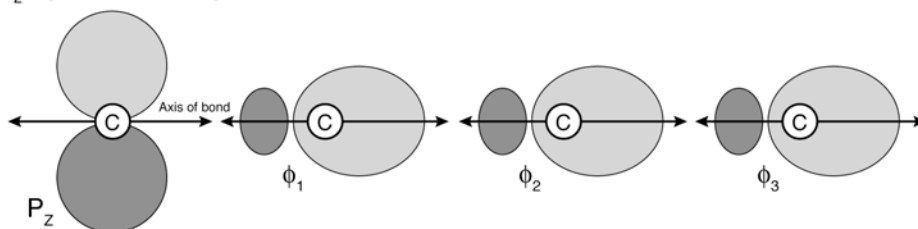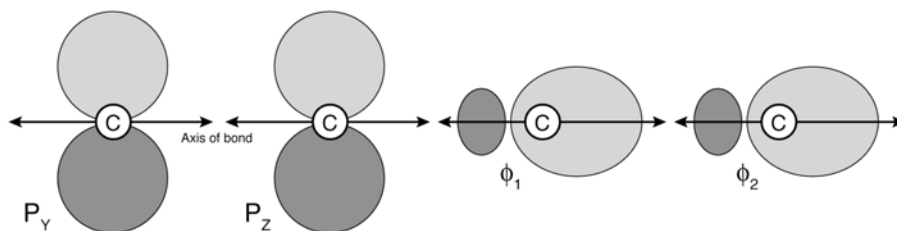

We will combine these basis sets with other basis sets to create molecular orbitals in organic molecules.
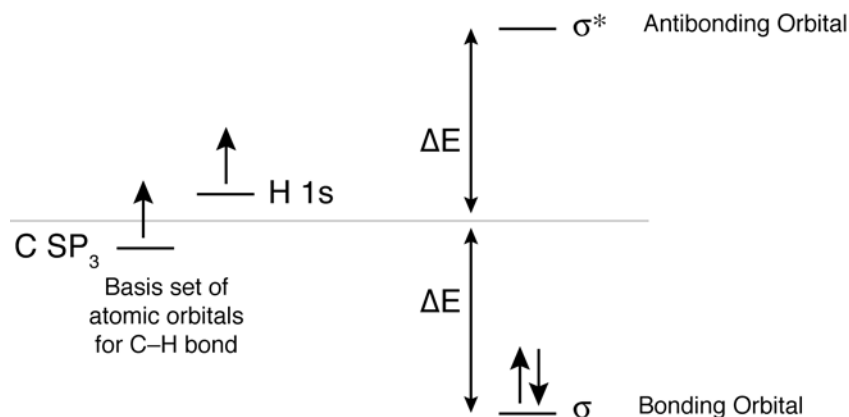
Molecular Orbitals of Methane

Methane has a molecular formula of CH_4. It is known that the hydrogen atoms form a tetrahedral arrangement around the carbon. Each C-H bond can be made by combining an s orbital from a hydrogen atom and an SP_3 orbital from the carbon atom. We spare ourselves the effort of calculating the separate contributions of the carbon s, p_x, p_y and p_z atomic orbitals (based on their angles to the s orbital of the hydrogen in the C-H bond) by using the SP_3 hybrid atomic orbitals as the basis set for the carbon atom. All these calculations were done in advance when we calculated the SP_3 hybrid atomic orbital basis set from the classic atomic orbital basis set.

Energies of the Molecular Orbitals for the C–H Covalent Bond

Let us consider combining an SP_3 hybrid atomic orbital of the carbon atom and an s orbital of a hydrogen atom to create a C–H covalent bond. We will be combining the two atomic orbitals and the new pair of molecular orbitals will split by the interaction energy. One orbital will be lowered in energy (the bonding orbital) and the other will be raised in energy (the antibonding orbital).

Note that the two orbitals that I am using as a basis set for this bond are not equal in energy. Only atomic orbitals of identical atoms are likely to be identical in energy. here I show the carbon orbital as being lower that the hydrogen orbital. Generally, the more electronegative atom has the lower energy orbitals (not always true) because electrons are lower in energy where they are better stabilized (more electronegative atoms can hold a greater electronic density). The closer in energy the two combining atomic orbitals are, the greater the interaction energy, ΔE. Identical atoms will have the biggest split in energy on combining to create molecular orbitals.
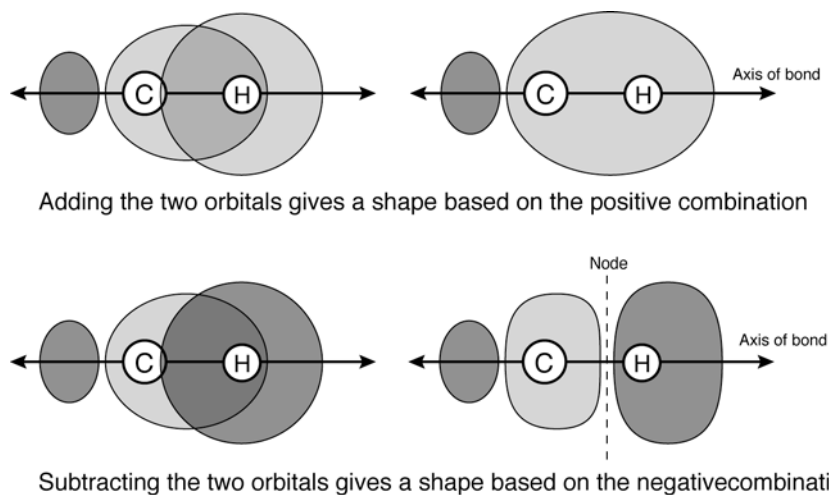
Figure 23.   Energies of molecular orbitals in a C-H bond

Shapes of the Molecular Orbitals for the C–H Covalent Bond

The shapes of the molecular orbitals derived from the combination of the two orbitals in the basis set for a C-H covalent bond in methane can be obtained by a graphical combination of the two orbitals. We can combine them positively (add them together) or we can combine them negatively (subtract them from each other).

Figure 24.   *Linear combination of atomic orbitals for a C–H covalent bond*

Adding the two orbitals gives a shape based on the positive combination

Subtracting the two orbitals gives a shape based on the negativecombination

The higher energy molecular orbital will be the one with the most nodes. The lower orbital system in Figure 24 has 3 nodes and the upper has 2 nodes. The lower is the antibonding orbital (observe a point of zero electron density in the bond) and the upper is the bonding orbital (observe electron density covering the entire bond).

All the Molecular Orbitals

The molecular orbital system for each C-H bond will be composed of separate pairs of SP_3 and s orbitals. Each system will be identical to the C–H bond discussed above.

A basis set of 4 SP_3 hybrid atomic orbitals of carbon combined with a basis set of 4 s orbitals from hydrogen will combine give a set of molecular orbitals that accounts for all the covalent bonds in a methane molecule. We place the hydrogen atoms in a tetrahedral arrangement around the carbon atom and set them at a distance equal to the known C–H bond distances. We place our set of 4 SP_3 orbitals to align with the 4 hydrogen atoms. With this physical arrangement we will get the combinations outlined in Figure 25.

Figure 25. *The molecular orbital system of methane. A basis set of atomic orbitals combines according to their mutual spatial relationships to give a set of molecular orbitals.*
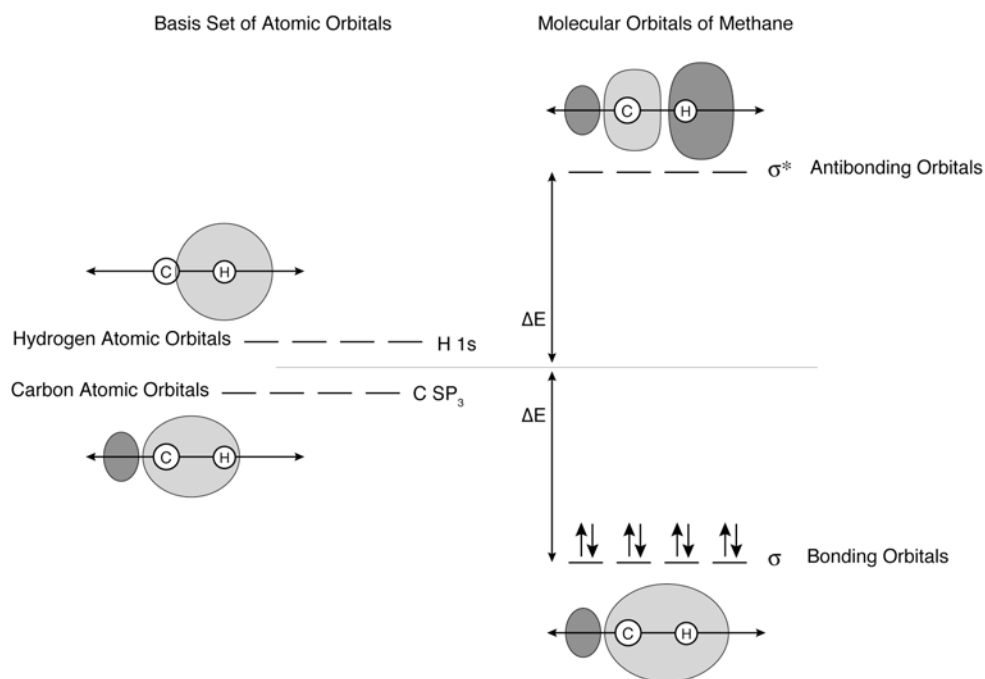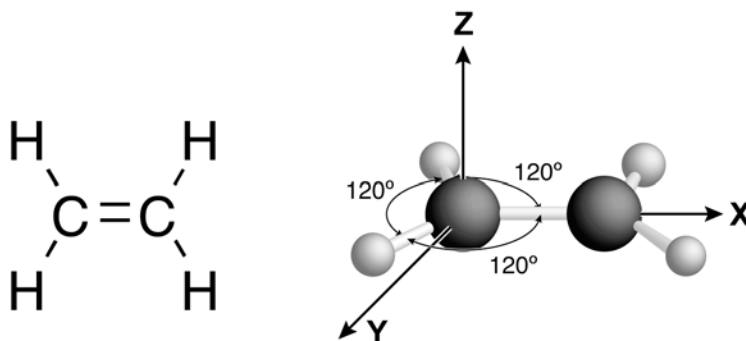
Molecular Orbitals of Acetylene

Acetylene has an empirical formula of C_2H_4. It is known to be a planar molecule with all bond angles being 120°. We will use the SP_2 hybrid atomic orbitals as the basis sets for the two carbon atoms.

There are 2 C–H bonds and they are treated exactly as in the case of methane C-H bonds. There is a C–C bond that will require the combination of 2 SP_2 orbitals. There are 2 p orbitals that will combine to give a π bond system.

Figure 26. *The ethylene molecule*
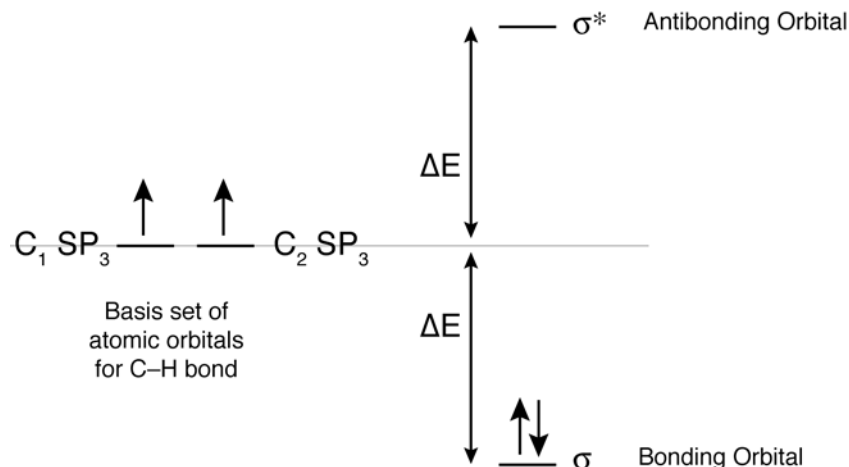

Energies of the Molecular Orbitals of the C–C σ bond

The C–C σ bond is created by a combination of an SP_2 orbital from each of the 2 carbon atoms. These 2 atoms are identical so the SP_2 orbitals are identical in energy. The

interaction energy, ΔE, is greatest for orbitals of identical energy. The result is that the bonding orbital will be lower in energy for a C–C bond than a C–H bond and the antibonding orbital will be higher in energy.
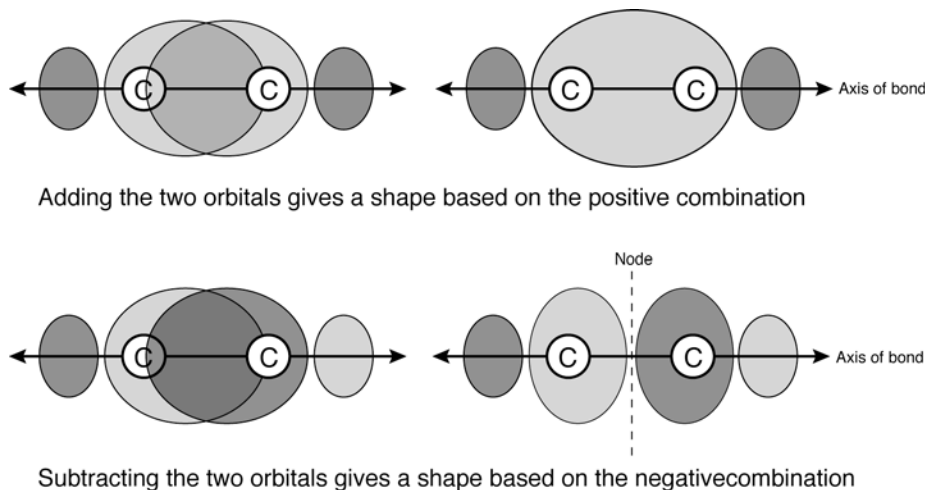
Figure 27.   Energies of molecular orbitals for a C–C σ bond

Shapes of the Molecular Orbitals of the C–C σ bond

A graphical combination of the SP_2 orbitals involved in the C– C σ bond will give a good representation of the shape of the molecular orbitals for the σ bond.

Figure 28.   Linear combination of atomic orbitals for a C–C σ bond

Adding the two orbitals gives a shape based on the positive combination

Subtracting the two orbitals gives a shape based on the negativecombination

The orbital with 2 nodes is the lower energy bonding orbital and the orbital with 3 nodes is the higher energy antibonding orbital.

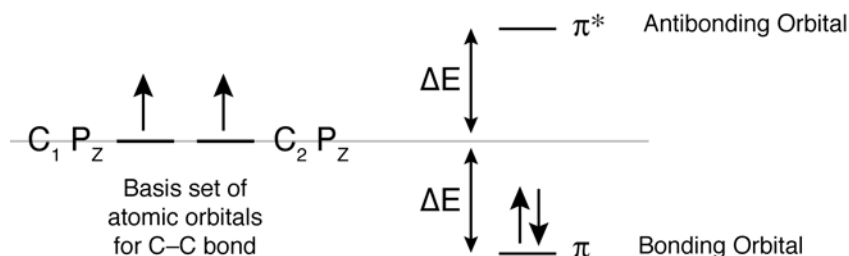**Energies of the Molecular Orbitals of the C–C π bond**

We have combined all the SP_2 orbitals in the system. 4 SP_2 orbitals were combined with 4 s orbitals to make the C–H bonds. The 2 remaining SP_2 orbitals were combined to make the C–C σ bond. There are 2 p orbitals remaining, the p_z orbitals on each carbon atom.

To combine these orbitals, which are perpendicular to the SP$_2$ orbitals of each carbon atom, we must place all SP$_2$ orbitals in the same plane. This is why ethylene is planar, to allow for combination of the p orbitals (this is why all double bonds are planar and cannot rotate).

Now both p$_z$ orbitals are aligned in a parallel manner along their mutual 2-fold axis of symmetry. The angle between them is 0° so interaction is at the highest magnitude $(\cos(0) = 1)$. Orbitals combined along a 2-fold axis of symmetry do not have as large an interaction energy, ΔE, as orbitals combined along a circular axis of symmetry. So the splitting of the molecular orbitals is not as great as in the case of a CC or CH σ bond.
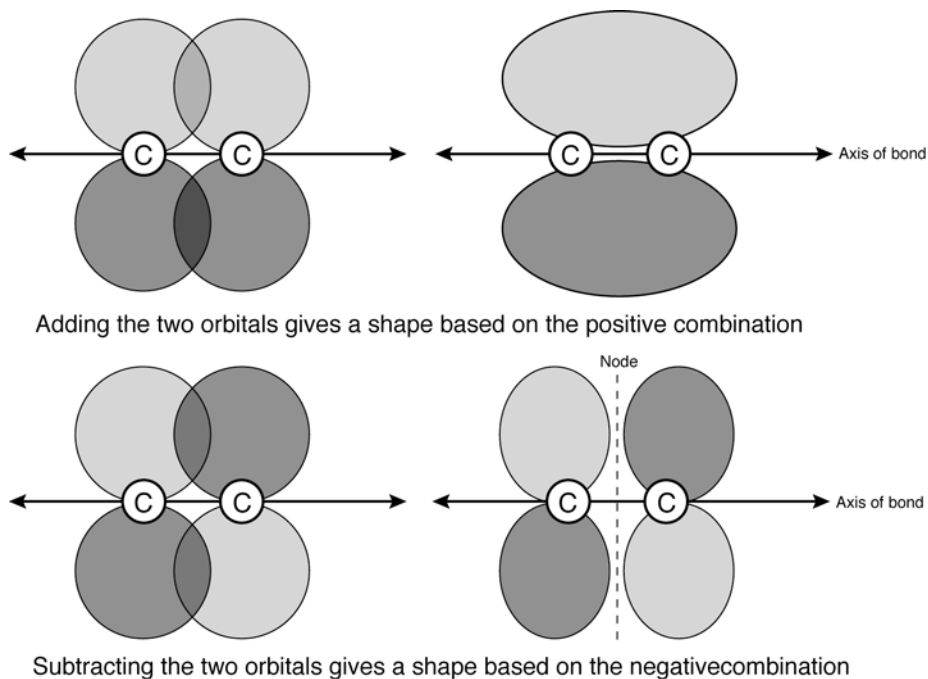
Figure 29.   *Energies of molecular orbitals for a C–C π bond*

Shapes of the Molecular Orbitals of the C–C π bond

The shapes of the π orbitals are obtained by graphical combination of the two p$_z$ orbitals. Using the method described in Figure 9, we combine the two p$_z$ orbitals to make 2 new molecular orbitals. The top orbital has one node (the plane of the molecule) and is the bonding orbital. The lower molecular orbital has 2 nodes and is the antibonding orbital.

Figure 30.   *Linear combination of atomic orbitals for a C–C π bond.*

Adding the two orbitals gives a shape based on the positive combination

Subtracting the two orbitals gives a shape based on the negativecombination

All the Molecular Orbitals

As we have learned above, we have the following sets of molecular orbitals from the combination of the basis set of atomic orbitals:

i. A pair of molecular orbitals for each C–H bond resulting from the combination of an SP_2 orbital and an s orbital. This will be 4 identical pairs of orbitals, one pair for each identical C–H bond.

ii. A pair of molecular orbitals for the C–C bond resulting from the combination of 2 SP_2 orbitals. This pair is split the widest in terms of energy and will be the highest and lowest energy molecular orbitals.

iii. A pair of molecular orbitals for the C–C π bond resulting from the combination of 2 P_z orbitals. This pair is split the least and will be in the middle the other pairs of orbitals.

The complete molecular orbital diagram is given in Figure 31.

*Figure 31.   Molecular orbital diagram for ethylene.*
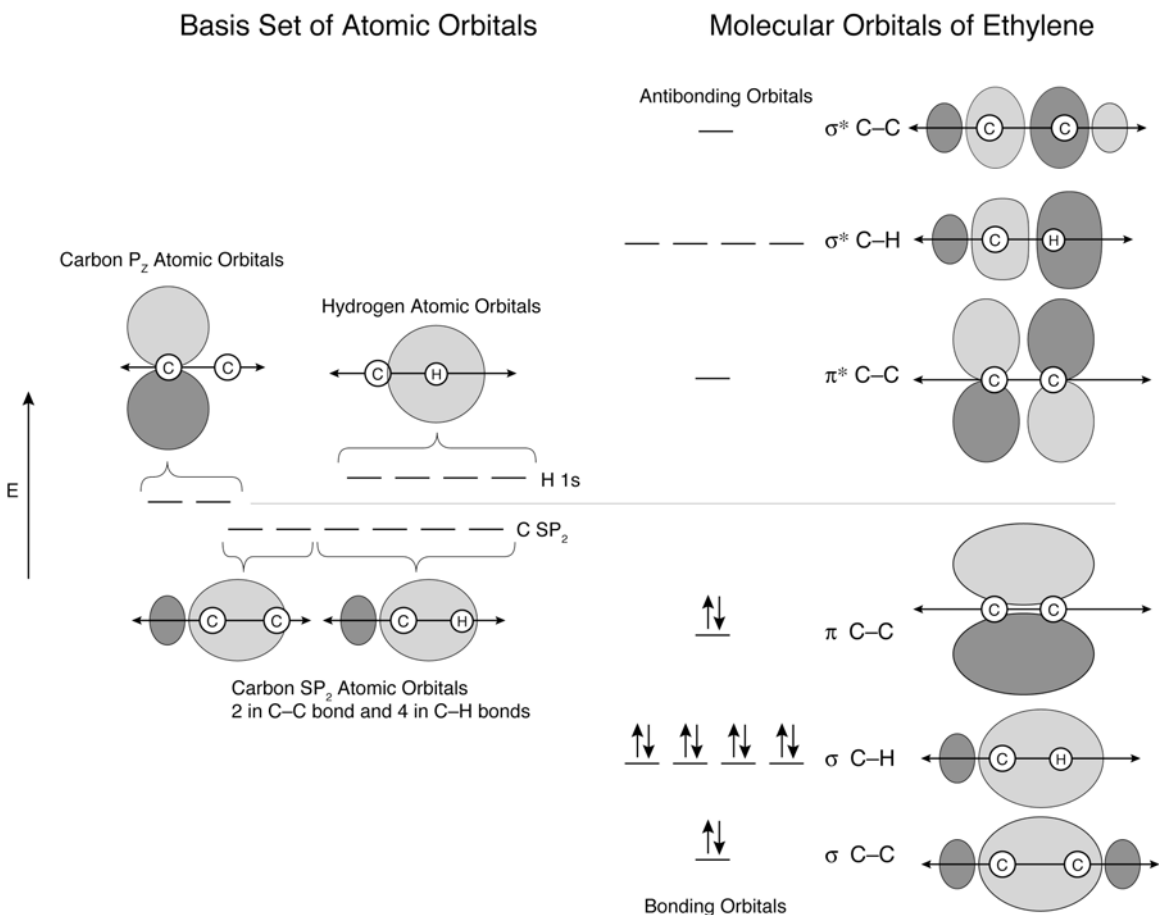
The chemistry of ethylene is seen in its orbitals. If a pair of electrons from ethylene were to be donated to an electrophile, they would most likely come from the highest energy electron pair. The highest energy orbital that is occupied is called the "highest occupied molecular orbital" or HOMO. The HOMO is where electrons will come from if ethylene

is acting as a nucleophile. If ethylene is acting as an electrophile and is receiving a pair of electrons, they will most likely combine with the "lowest unoccupied molecular orbital" or LUMO. Both the HOMO and LUMO are involved with the π system. That is why the functional group in ethylene is the double bond.

Molecular Orbitals of Cyanide Ion

Cyanide anion is a nucleophile (and a base). But what electron pair is the most likely to act as a nucleophile? Will the nucleophile be the π-system, the lone pair of the nitrogen or the lone pair of the carbon? Examining the Lewis structure in Figure 32 will give us a good idea but the final answer lies with a molecular orbital diagram.

Figure 32.   Structure of cyanide anion.
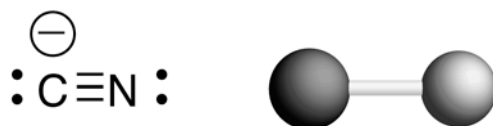
In the Lewis structure, the formal negative charge lies on the carbon atom. This hints that the carbon atom will be the nucleophile using the lone pair of the π-system as the electron pair that makes the new bond. But nitrogen is more electronegative than carbon and will hold more of the electron density in the bond. So maybe nitrogen will be the nucleophile. Let us consider the orbitals to achieve clarity and serenity.

In this system we have a linear system for each atom (one lone pair and one atom bonded to each atom) so we will use the SP basis set of hybrid atomic orbitals for each atom.

Since nitrogen is more electronegative than carbon, the atomic orbitals will be lower in energy. More electronegative atoms are better able to stabilize electrons so electrons in the orbitals of that atom are lower in energy relative to a less electronegative atom.

The basis sets of carbon and nitrogen will combine according to orbital symmetries (p-orbitals combine with p-orbitals and SP with SP). We observe that there are two pairs of P orbitals on each atom in the bond. If we align the p_y orbitals, they can interact along their mutual two-fold axis of symmetry. The p_z orbitals will do the same. This will result in two equivalent π-orbital systems. The two π systems do not interact with each other because they are at 90° to each other. There is an SP orbital on carbon and one on nitrogen that point toward each other. We will combine these two SP orbitals to make the α-bond molecular orbital system. The other two SP orbitals point away from each other. This increases the distance between their regions with greatest magnitude. The result is that they will interact weakly with each other and we will assume that they do not interact at all.

The results of our graphical combinations and energy estimations are seen in Figure 33. The combination of two SP orbitals produces the largest split in energy and the combination of p orbitals produces a relatively smaller split. The lone pair molecular orbitals are unchanged in shape and energy, as they were not combined with any other orbitals.

Because the carbon atomic orbitals were placed higher in energy than the nitrogen atomic orbitals, we see the lone pair of carbon is the HOMO for this system. Cyanide will likely

act as a nucleophile using the lone pair on carbon as the nucleophilic electron pair. There we have it; a simple graphical analysis explains the nucleophilic behaviour of cyanide ion.

Figure 33. Molecular orbitals of cyanide anion. Note the molecular orbitals for the lone pairs are uncombined, leftover SP orbitals.
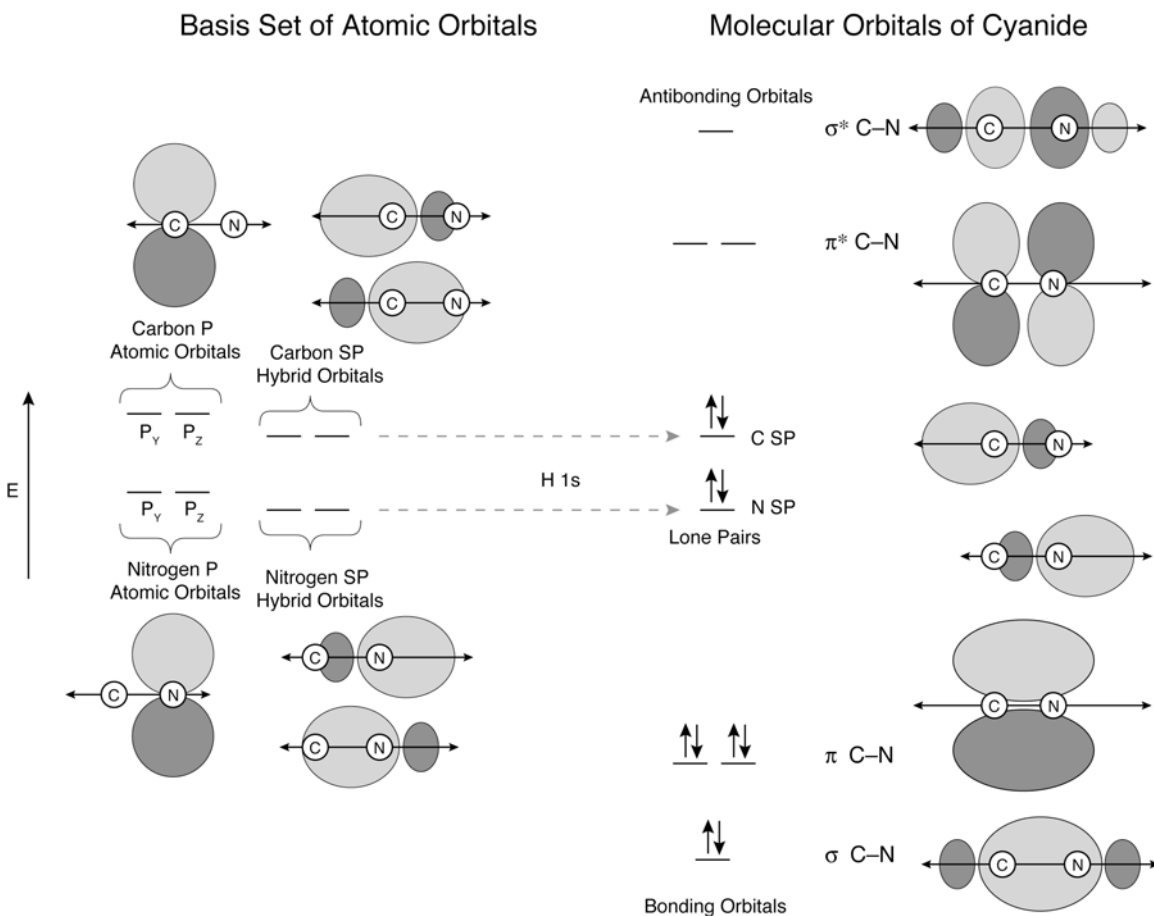
For more complex systems we can often ignore large parts of the molecule that are not involved in the chemistry in which we are interested. For example, the σ-bonding molecular orbitals are often of little interest as we focus on the HOMO and LUMO for interpreting chemistry of functional groups.

All You Really Need To Know About Molecular Orbitals

We have seen how to graphically combine atomic orbitals to get an approximation of their shape. We have learned that identical atomic orbitals split the resulting molecular orbitals the widest in terms of energy and that p orbitals split the least when combined. Using this information we can produce a fairly good approximation of the molecular orbitals in most small organic molecules.

Atomic orbitals that represent lone pairs in a molecule will have no second atomic orbital to combine with and will not change in energy or shape.

The most important thing to know is that the above points are all incorrect but are still very useful. They involve enormous simplifications of a complex phenomenon. The biggest assumption is that two orbitals in a bond interact with only each other. This is not the case. All orbitals aligned along mutual axes of symmetry at any angle other than 90° will interact to some extent. The two orbitals that we use to make the bond are the biggest contributor to the new molecular orbitals (and we assume they are the only contributors) but other nearby orbitals can contribute.

Advanced Topics

Have I excited you about molecular orbitals? Do you want to learn more? The following material is no more difficult to understand that what has come before but the topics apply more to subjects covered in more advanced organic chemistry courses.

Molecular Orbitals of Polar Bonds

Carbon and hydrogen atoms are similar in electronegativity. But oxygen, nitrogen and halogens are among the atoms that are much more electronegative than carbon. Bonds between carbon and these elements will be polar. The orbital system of cyanide described above ignores this fact. Including this concept would not alter the conclusions but it can be informative.

Uneven combinations

In graphical terms, the molecular orbital will be most similar to the atomic orbital to which it is closest in energy. As we have seen, two atomic orbitals combine to give pair of molecular orbitals. If these two orbitals are similar in energy, they each give equal contributions to the bonding and antibonding orbitals. If the orbitals are different in energy, they will contribute unevenly to the two molecular orbitals. The higher energy atomic orbital will be closest in energy to the antibonding molecular orbital and will contribute more to that orbital than the lower energy atomic orbital. The lower energy atomic orbital will be closest in energy to the bonding molecular orbital and will contribute more to that orbital than the higher energy atomic orbital.

According to Equation 6, the contribution of each orbital to the molecular orbital is governed by the coefficients, A and B. These coefficients are related to the cosine of the angle between the axes of mutual symmetry ($\cos(0°) = 1$) and the difference in size and energy between the orbitals. We have maximum combination due to angle but the contributions are not equal due to the difference in energy.
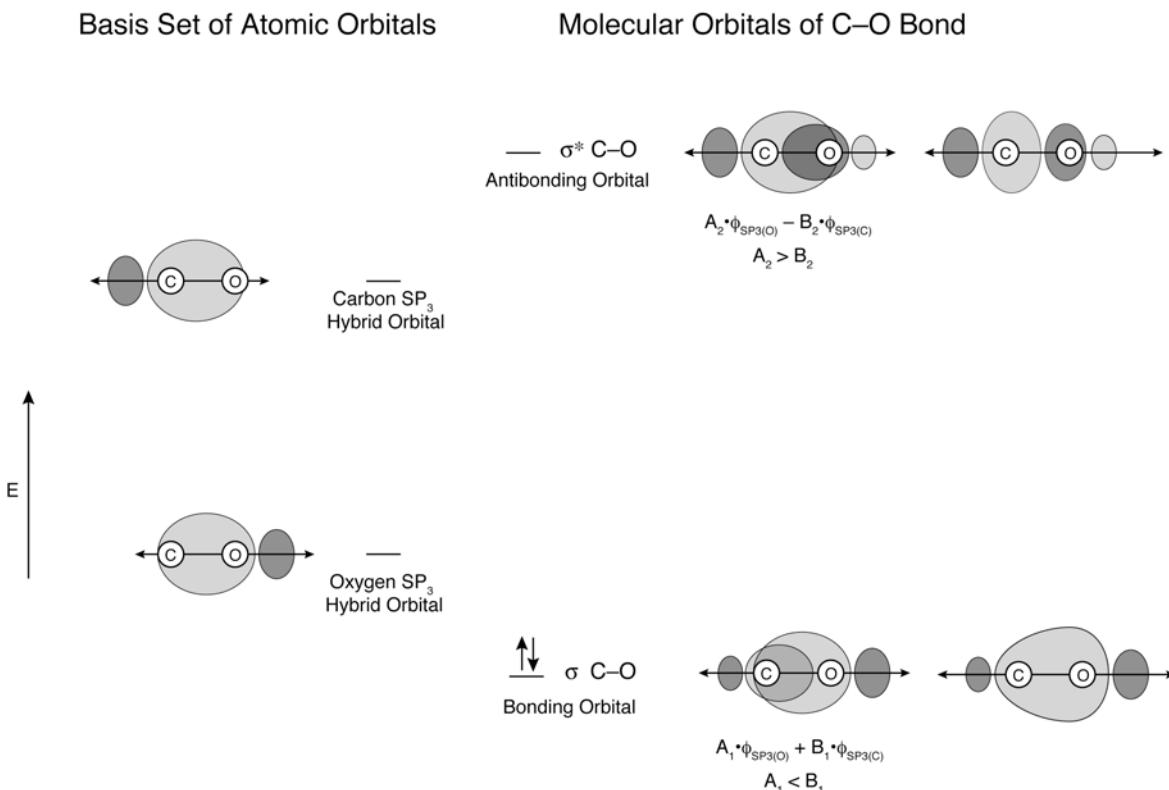
Equation 6

$$\varphi_1 = A_1 \cdot \phi_{SP_3(O)} + B_1 \cdot \phi_{SP_3(C)}$$

$$\varphi_2 = A_2 \cdot \phi_{SP_3(O)} + B_2 \cdot \phi_{SP_3(C)}$$

The concept is illustrated by Figure 34 where the molecular orbitals of a C–O σ-bond are calculated from the SP_3 atomic orbitals of the carbon and oxygen atoms.

Figure 34. Uneven contributions of SP3 atomic orbitals in the C–O σ-bond.

Basis Set of Atomic Orbitals   Molecular Orbitals of C–O Bond

σ* C–O
Antibonding Orbital

$$A_2 \cdot \phi_{SP3(O)} - B_2 \cdot \phi_{SP3(C)}$$
$$A_2 > B_2$$

Carbon SP$_3$
Hybrid Orbital

Oxygen SP$_3$
Hybrid Orbital

σ C–O
Bonding Orbital

$$A_1 \cdot \phi_{SP3(O)} + B_1 \cdot \phi_{SP3(C)}$$
$$A_1 < B_1$$

In Figure 34, we see the molecular orbitals shown as combinations of atomic orbitals and as the shapes derived from those combinations. Observe the shapes of the molecular orbitals. The bonding orbital has a greater magnitude at the oxygen atom (it is closest in energy to the oxygen atom atomic orbital). This reflects the greater electronic density at oxygen in the polar C–O bond. The antibonding orbital has a greater magnitude at the carbon atom (it is closest in energy to the carbon atom atomic orbital). This reflects that the carbon atom is where the filled orbital of an incoming nucleophile will attack.

Consequences of the Shapes of the Molecular Orbitals

Regiospecific Nucleophilic Attack

Molecular Orbitals of Conjugated π-Systems

Figure 35. Molecular Orbitals of Butadiene.

Standing Waves   Graphical Molecular Orbitals   Calculated Molecular Orbitals
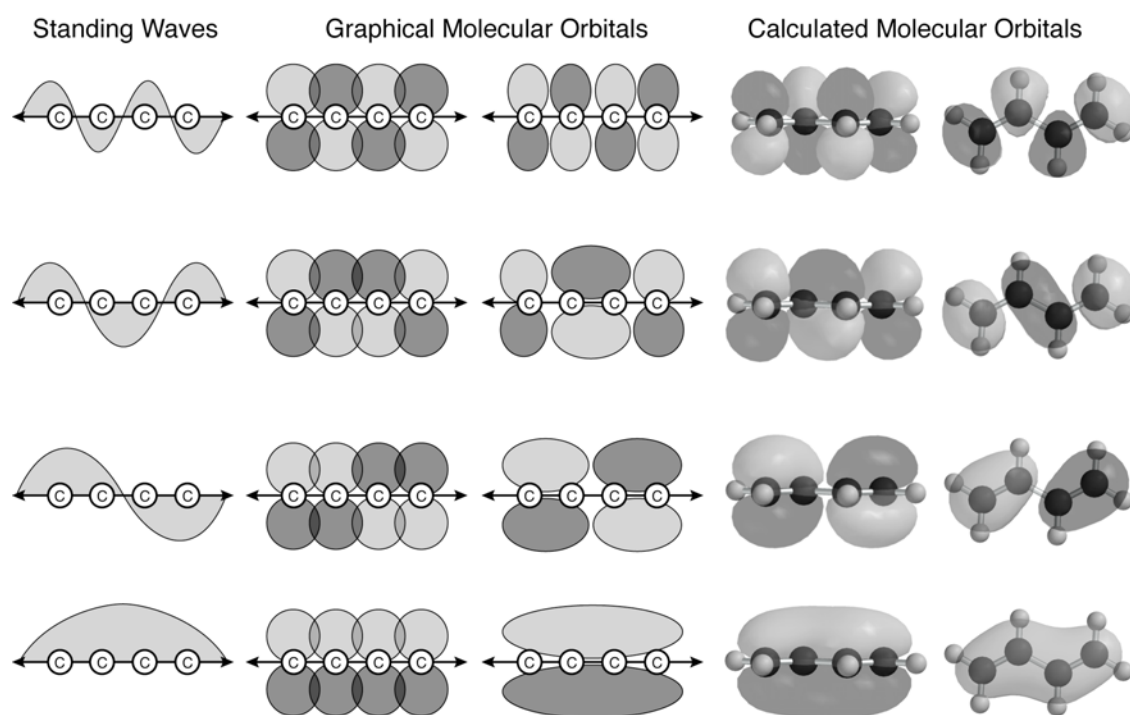
Glossary

Basis set

Atomic Orbital (AO)

Molecular Orbital (MO)

Hybrid Atomic Orbital

Linear Combination of Atomic Orbitals (LCAO)

Tetrahedral

Trigonal Planar

Linear

Graphical combination