Hybrid Molecular Orbitals

Last time you learned how to construct molecule orbital diagrams for simple molecules based on the symmetry of the atomic orbitals. Molecular orbitals extend over the entire molecule although there can be more electron density in particular regions. The bonding in a molecule predicted from this model corresponds well with the measurable physical and chemical properties.

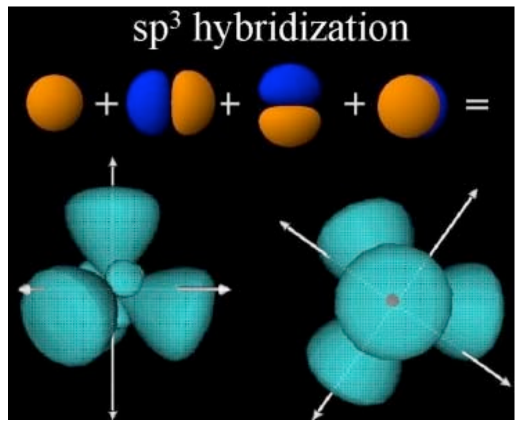
We could use the symmetry-based method to construct molecular orbital diagrams for larger molecules as well, but this can get complicated for larger structures.

In this section you'll see how to use a simplified, localized bonding approach to molecular orbitals. It is especially useful for organic molecules. Hybrid orbitals can be used to form sigma bonding and sigma antibonding molecular orbitals. Pi bonds are formed by the overlap of atomic p orbitals in the molecule.

Outline

- Sigma bonds with sp3 orbitals
- Sigma bonds with sp, sp2 orbitals
- Pi bonds
- Homework

The figure at right shows the 2s, $2p_x$, $2p_y$, and $2p_z$ orbitals combining into 4 $2sp^3$ orbitals.



Procedure for Constructing Molecular Orbital Diagrams Based on Hybrid Orbitals

1. Begin with the Lewis structure.

2. Decide how many orbitals each atom needs to make its sigma bonds and to hold its non-bonding electrons. Draw the atomic and hybrid orbitals on on side of the page.

3. For each sigma bond, take a hybrid (or atomic) orbital from each atom. Use these to generate a sigma bonding and a sigma antibonding molecular orbital. The average energy of the molecular orbitals must be the same as the average energy of the two orbitals you used to make them.

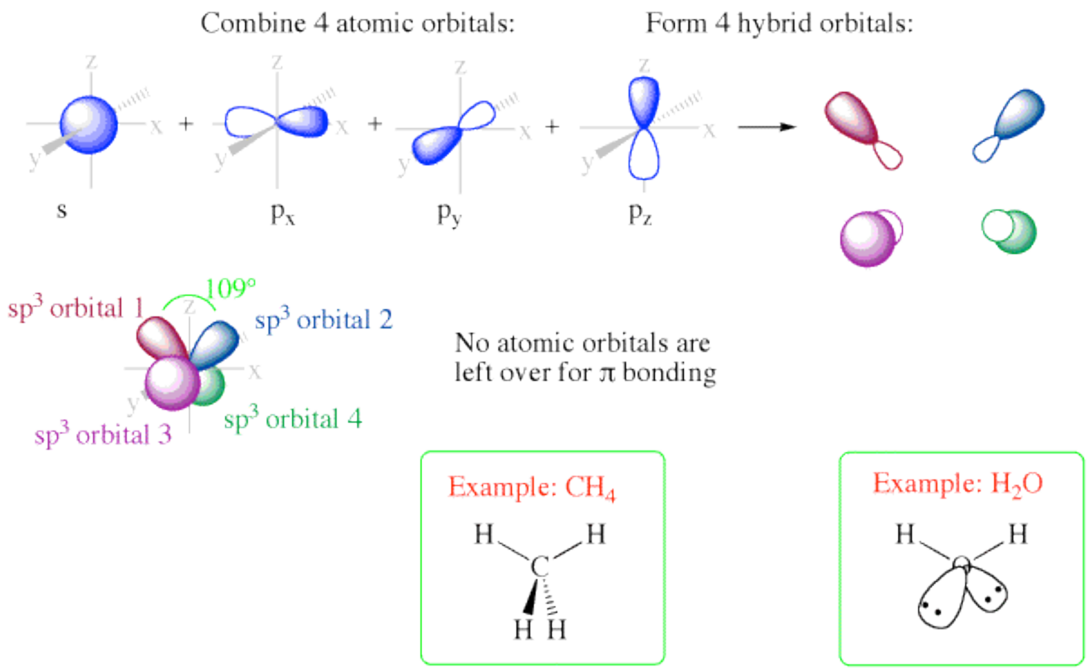
4. Use any hybrid orbitals left after after making the sigma orbitals for non-bonding molecular orbitals (without a change in energy).

5. Combine any parallel p orbitals on adjacent atoms into a set of pi molecular orbitals.

6. Total the valence electrons from all atoms and add these to the molecular orbital diagram, filling the lowest energy orbitals first.

Sigma Bonds with sp^3 Hybrid Orbitals

Atoms that have 4 bonds, 3 bonds and 1 lone pair, 2 bonds and 2 lone pairs, or 1 bond and 3 lone pairs need four hybrid orbitals 109 degrees apart. Combining an s orbital, a p_x orbital, a p_y orbital, and a p_z orbital makes four, sp^3 orbitals in a tetrahedral array.

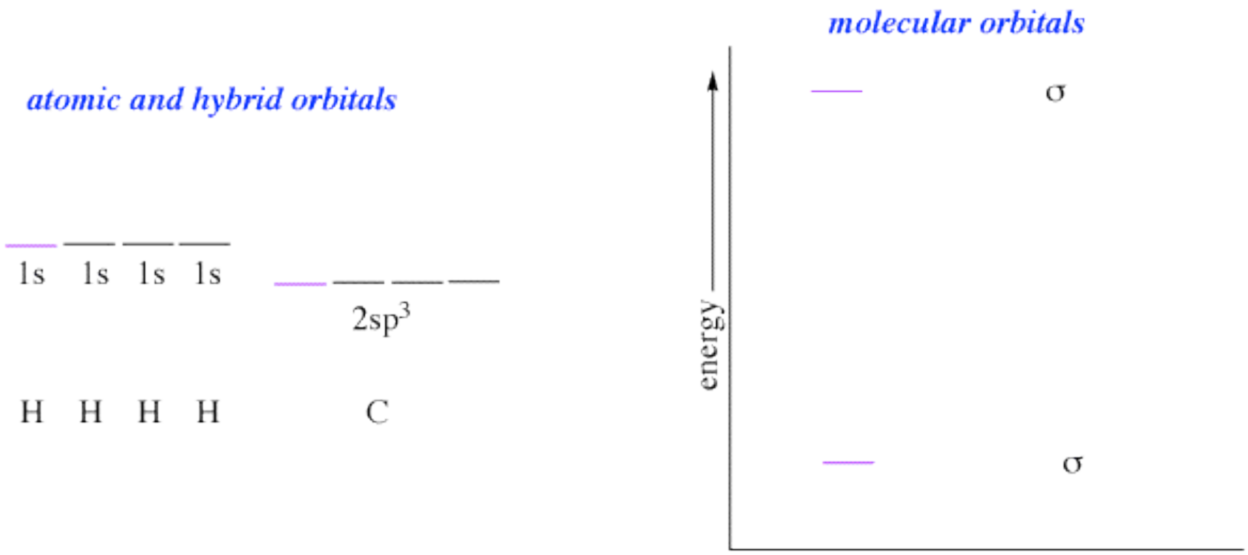


Molecular Orbital of Methane, CH_4

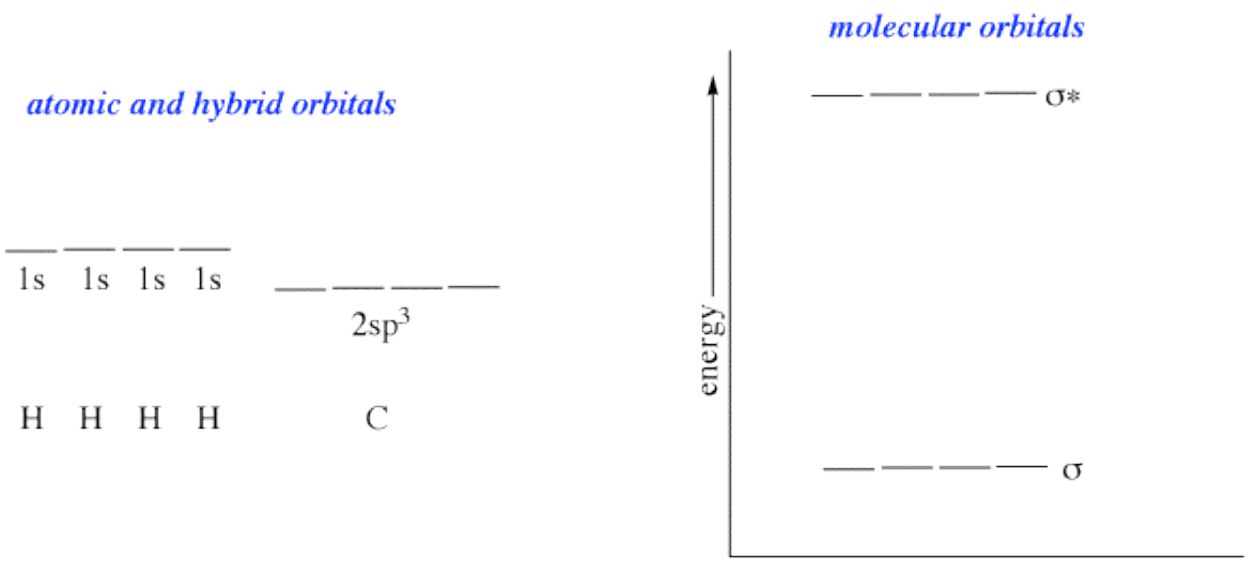
1. The Lewis structure shows us that the carbon atom makes 4 sigma bonds to hydrogen and has no non-bonding electron pairs.

2. The central carbon atom combines its 2s, $2p_x$, $2p_y$, and $2p_z$ valence orbitals to make four, $2sp^3$ hybrid orbitals.

3. Each one of these combines with a 1s atomic orbital from a hydrogen atom. These 2 atomic and hybrid orbitals form 2 molecular orbitals, a sigma bonding orbital and a sigma antibonding orbital.



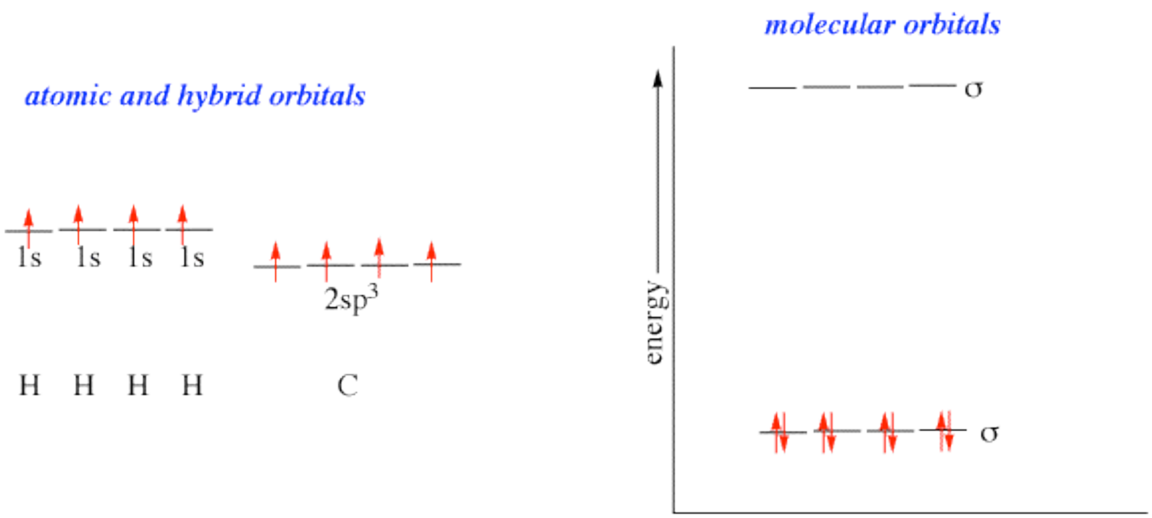
After we combine all 4 H(1s) orbitals with the 4 C($2sp^3$) orbitals, the diagram looks like this.



4. There are no remaining hybrid orbitals.

5. There are no p orbitals.

6. The total number of electrons is 8, 4 from carbon and 1 from each hydrogen atom

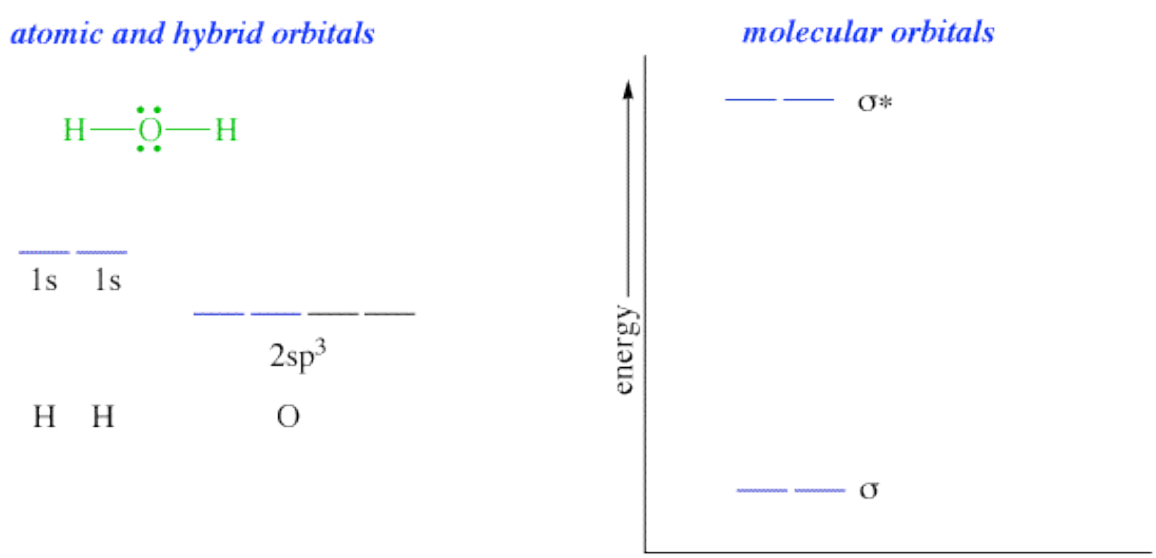


Molecular Orbital of Water, H_2O

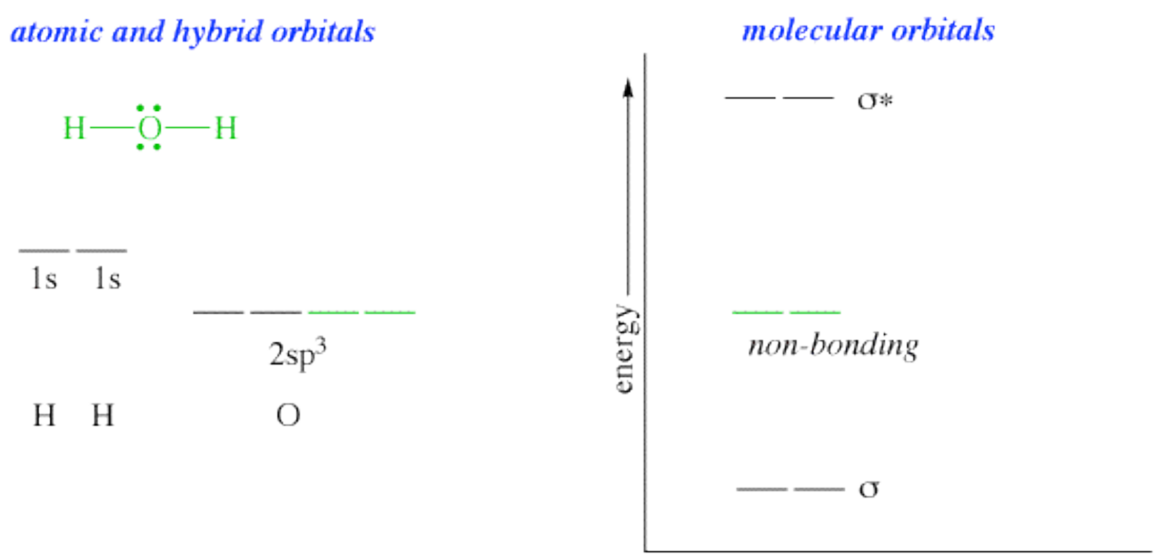
1. The Lewis structure shows that the oxygen in water has two bonding pairs and two lone pairs of electrons around it.

2. Oxygen makes four $2sp^3$ hybrid orbitals from its valence orbitals. Each hydrogen atom has a 1s orbital.

3. Two of the O(2sp3) hybrid orbitals and 2 of the H(1s) orbitals combine to make 2 sigma bonding and 2 sigma antibonding molecular orbitals.

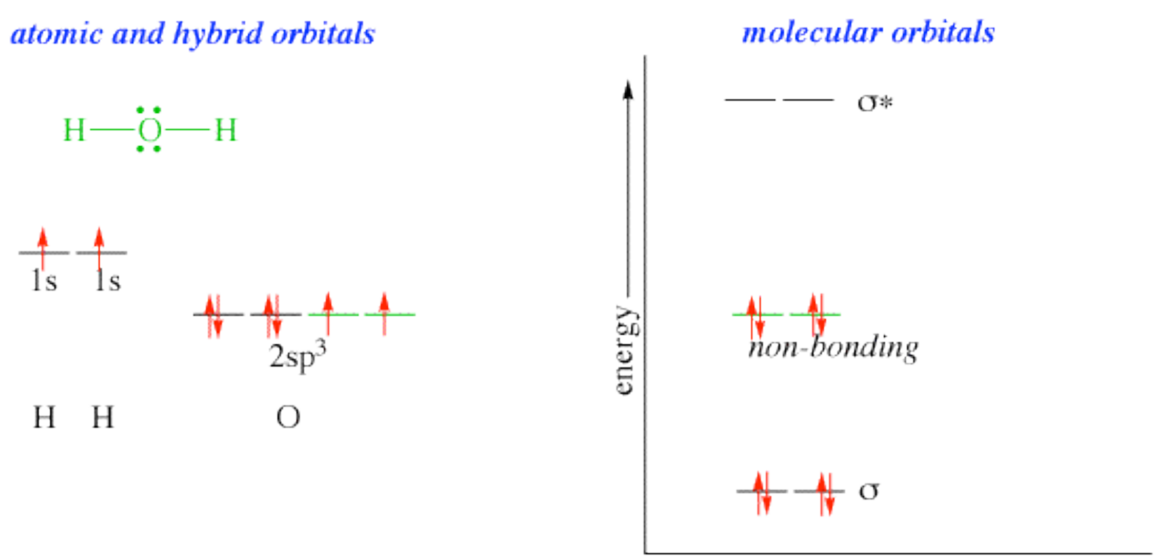


4. The remaining 2 O(2sp3) hybrid orbitals become non-bonding molecular orbitals.



5. There are no p orbitals. All orbitals have been used to make the sigma and non-bonding molecular orbitals.

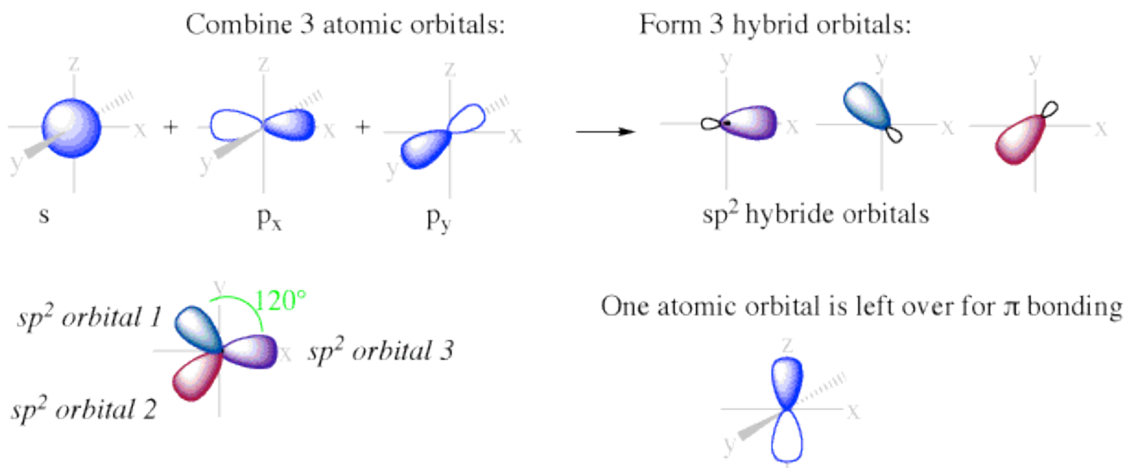
6. The molecule has a total of 8 electrons, 6 from oxygen and 1 from each hydrogen atom.



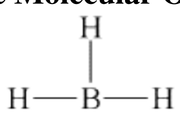
Sigma Bonds from sp and sp^2 Hybrid Orbitals

sp^2 Hybrid Orbitals in Borane

Atoms that have 3 bonds, 2 bonds and 1 lone pair, or 1 bond and 2 lone pairs need 3 orbitals that are 120 degrees apart. Consider the plane of these three orbitals to be the xy plane. Combining an s orbital with a p_x orbital and a p_y orbital makes three sp^2 hybrid orbitals.

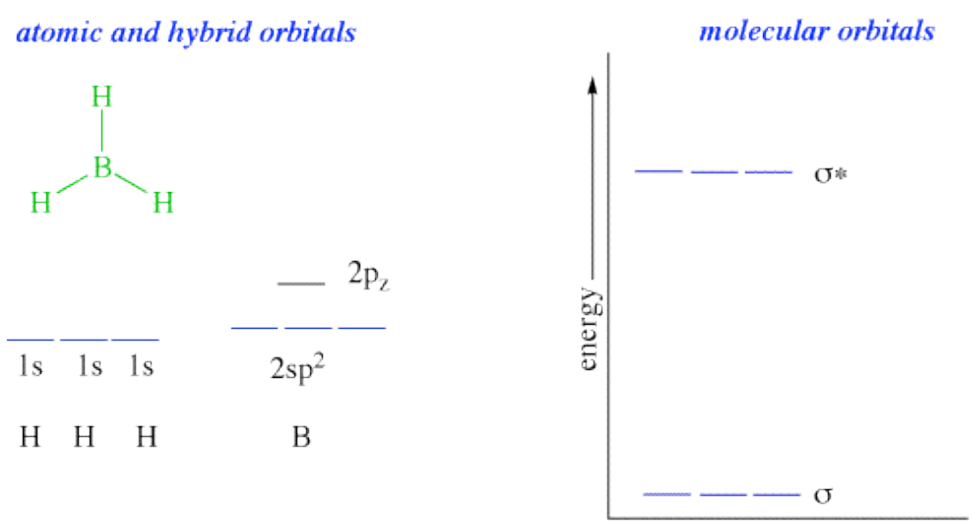


Borane Molecular Orbitals

1. 
2. The boron atom make three bonds to hydrogen and has no lone pairs of electrons. The molecule is trigonal planar.

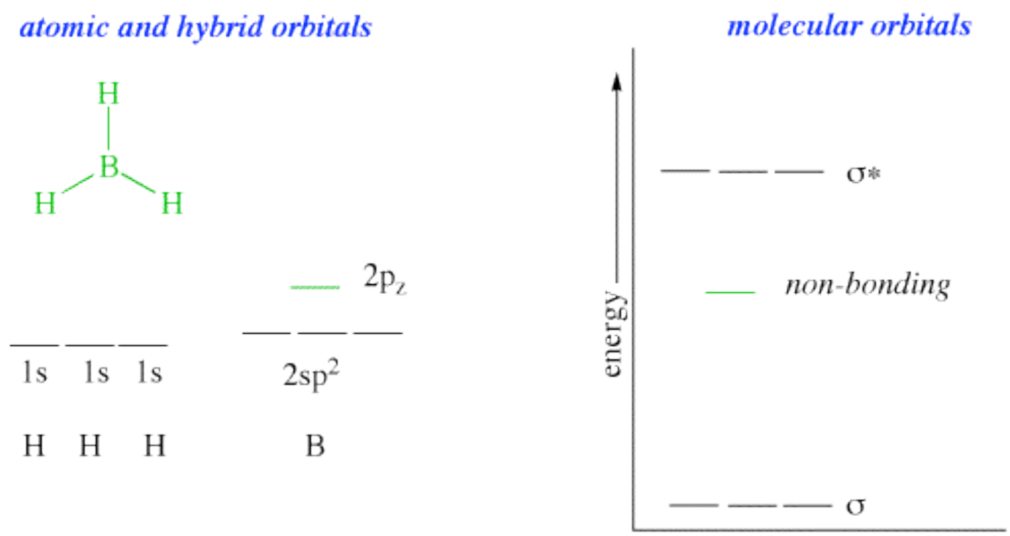
3. Molecules that have 3 bonds, 2 bonds and 1 lone pair, or 1 bond and 2 lone pairs need 3 orbitals that are 120 degrees apart. Consider the plane of these three orbitals to be the xy plane. Combining an s orbital with a p_x orbital and a p_y orbital makes three sp^2 hybrid orbitals. Hydrogen uses its 1s orbital to make bonds.

4. Combine each of the H(1s) orbitals with one of the $B(2sp^2)$ orbitals to make a sigma bonding and a sigma antibonding molecular orbital.

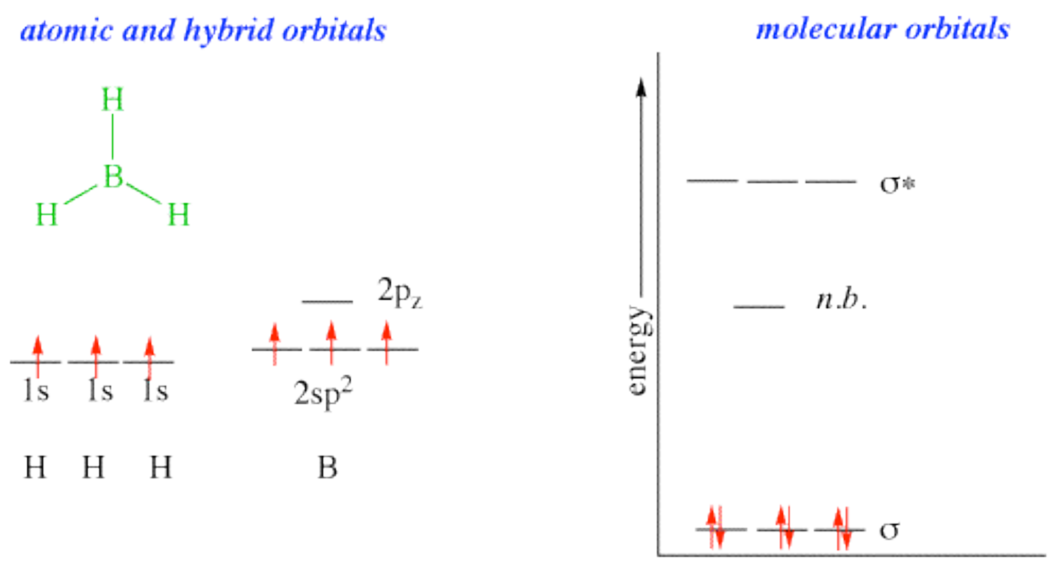


5. There are no remaining hybrid orbitals.

6. There is one p orbital on boron but there is no adjacent atom with another p orbital. Add it to the molecular orbital diagram as a non-bonding molecular orbital.



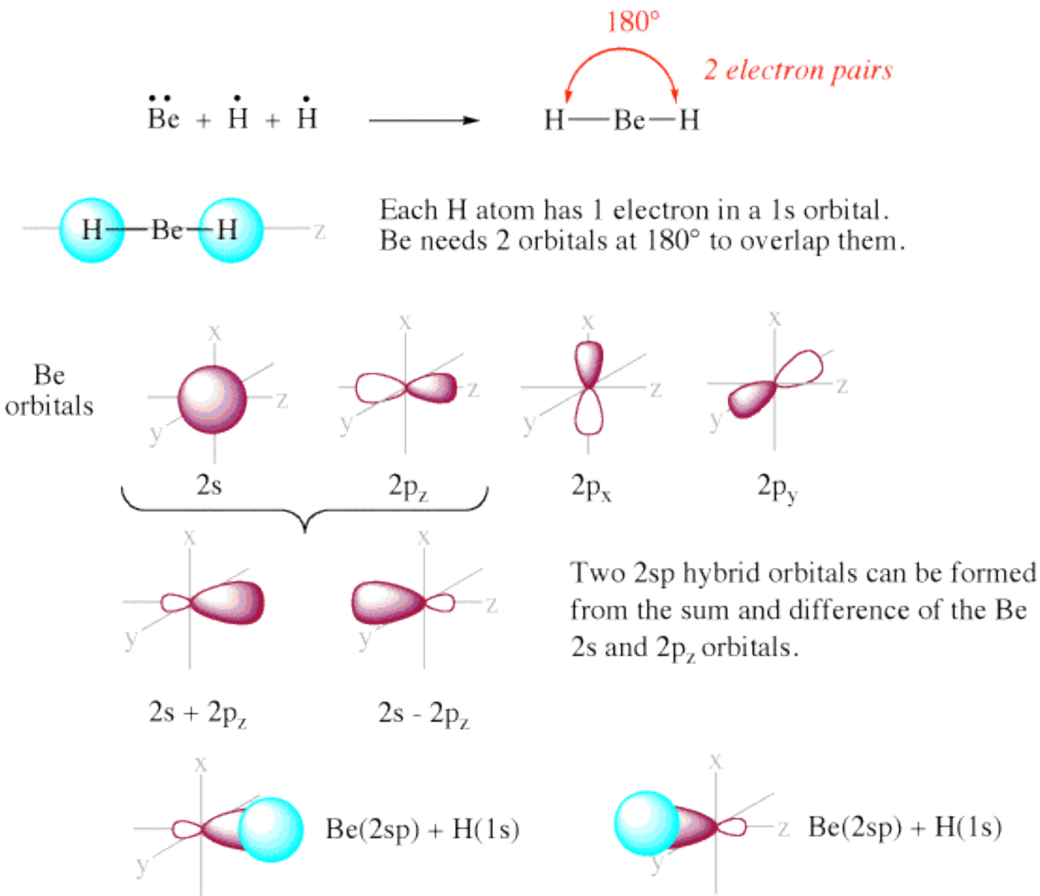
7. There are a total of 6 electrons to add to the molecular orbital diagram, 3 from boron and 1 from each hydrogen atom.



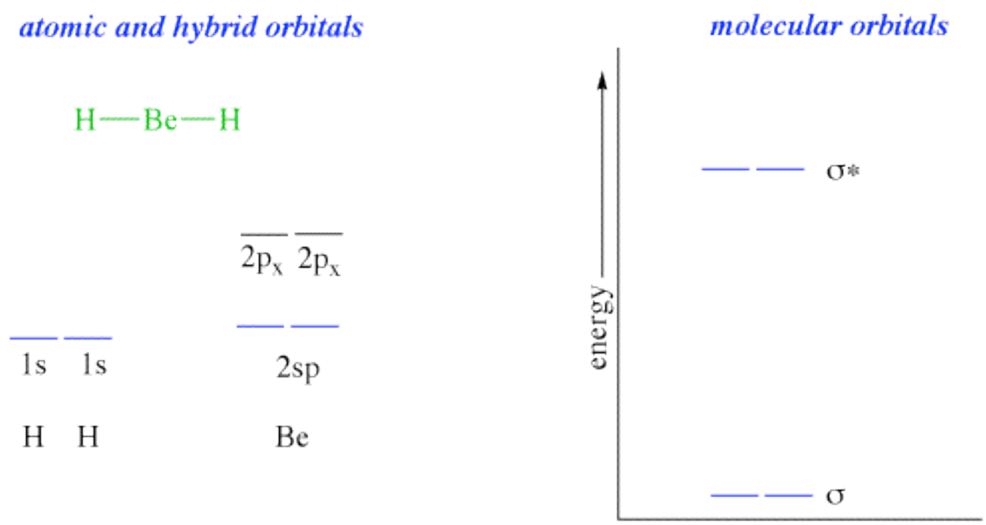
sp Hybrid Orbitals in BeH_2

1. The Lewis structure shows that the beryllium in BeH_2 makes 2 bonds and has no lone pairs. It is a linear molecule.

2. The beryllium atom needs 2 orbitals to form sigma bonds that can overlap with the two hydrogen 1s orbitals. If we consider the bond to be along the z axis, the beryllium atom will combine its 2s and $2p_z$ orbitals to make 2 hybrid orbitals. Each one points towards one of the hydrogen orbitals along the z axis.

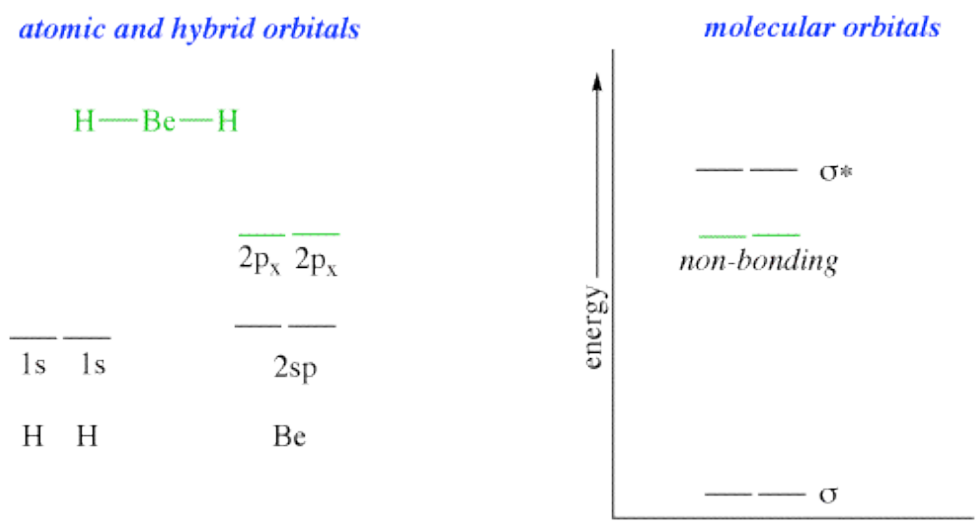


3. Combine each of the H(1s) orbitals with one of the Be(2sp) orbitals to make a sigma bonding and a sigma antibonding molecular orbital.

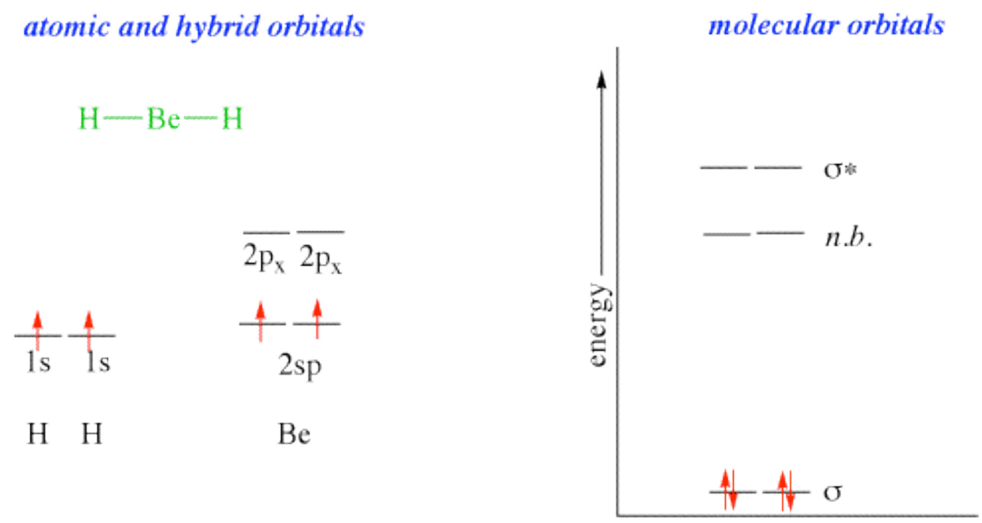


4. There are no remaining hybrid orbitals.

5. There are 2 remaining p orbitals on beryllium but there are no adjacent atoms with another p orbital. Add them to the molecular orbital diagram as non-bonding molecular orbitals.



6. There are a total of 4 electrons to add to the molecular orbital diagram, 2 from beryllium and 1 from each hydrogen atom.



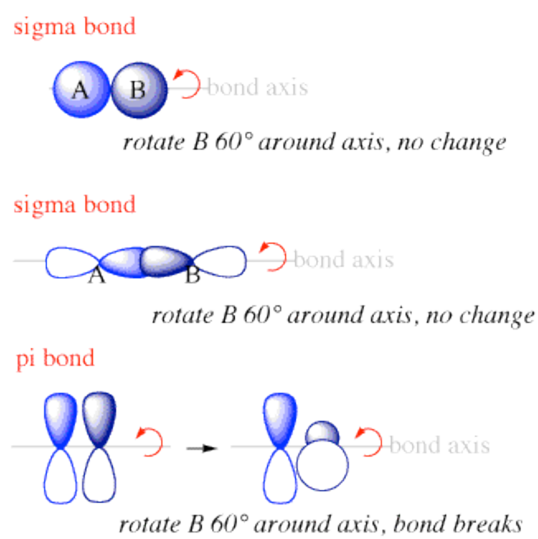
Pi Bonds

Hybrid orbitals are constructed from valence atomic orbitals and used to make **sigma bonds** between atoms.

Sigma bonds are formed by the overlap of orbitals that are pointing directly towards one another. If two atoms are connected by a sigma bond, rotating one of the atoms around the bond axis doesn't break the bond.

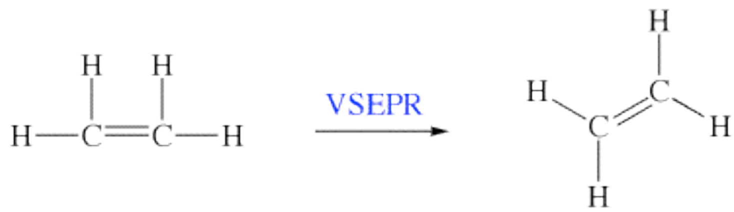
If a bond between two atoms is broken when one atom is rotated around the bond axis, that bond is called a **pi bond**.

Pi bonds are formed from the overlap of parallel p orbitals on adjacent atoms. They are not formed from hybrid orbitals.



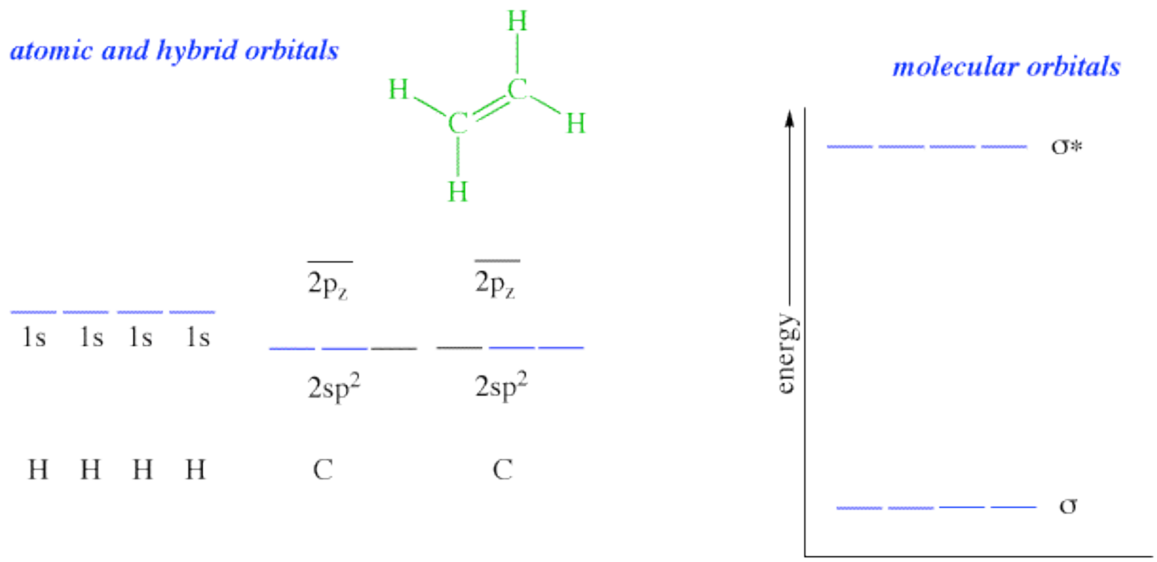
Ethene, sp2 hybridization with a pi bond

1. The Lewis structure of the molecule CH_2CH_2 is below. Each carbon forms 3 sigma bonds and has no lone pairs.

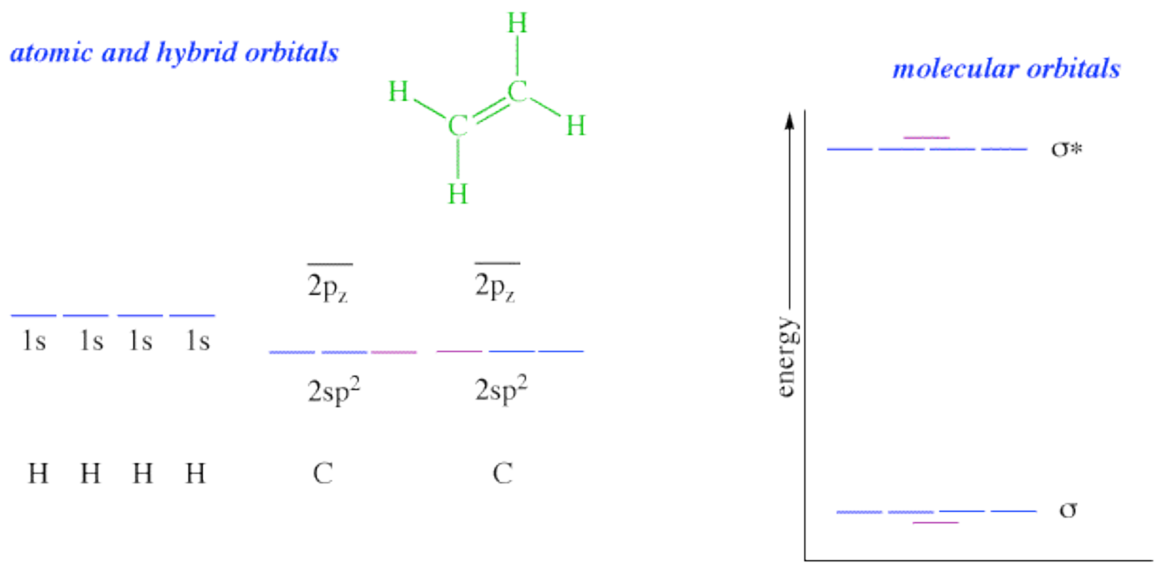


2. As with borane, make $2sp^2$ hybrid orbitals on each carbon from the 2s, $2p_x$, and $2p_y$ atomic orbitals. A $2p_z$ orbital remains on each carbon.

3. Combine each H(1s) orbital with a C($2sp^2$) orbital to make a sigma bonding and a sigma antibonding molecular orbital. (C-H bonds)

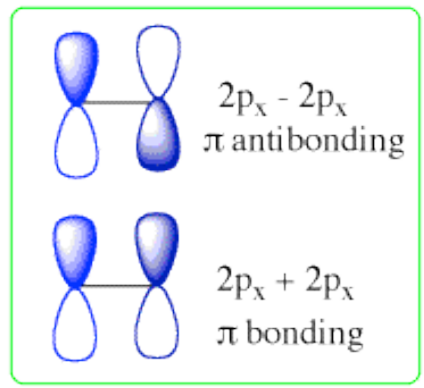


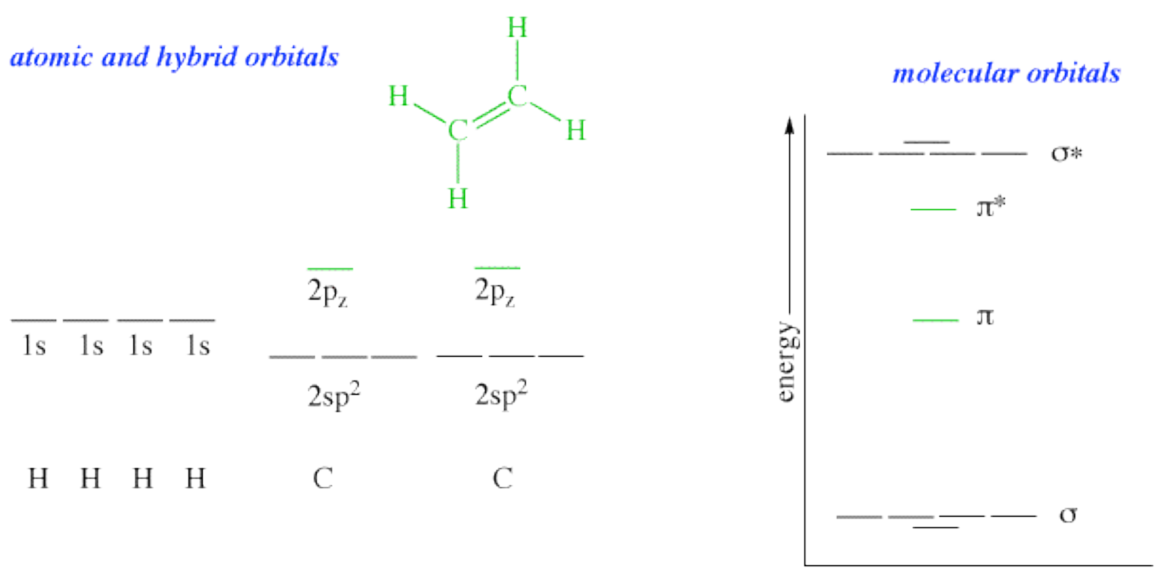
Combine the 2 C($2sp^2$) orbitals to make a sigma bonding and a sigma antibonding molecular orbital. (C-C bond)



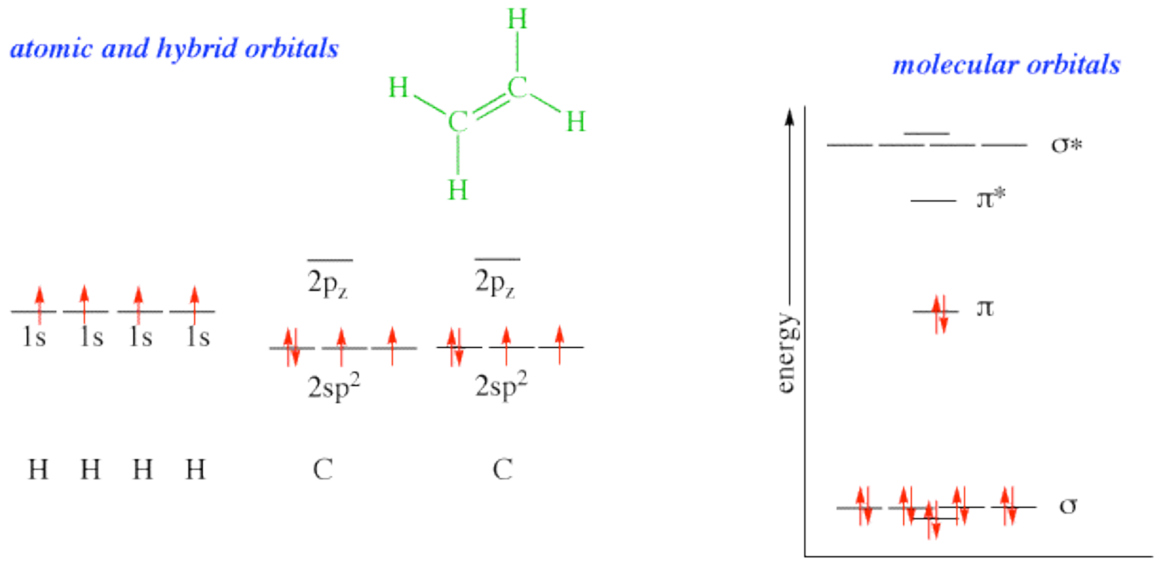
4. There are no remaining hybrid orbitals.

5. There remains a 2p orbital on each carbon. These can combine to make a pi bonding and a pi antibonding molecular orbital. The stabilization (decrease in energy) in going from the p orbital to pi bonding orbital equals the destabilization (increase in energy) in going from the p orbital to the pi antibonding orbital. The stabilization and destabilization in forming a pi bond are much less than for a sigma bond.





6. Finally, add the valence electrons to the molecular orbital diagram. Each carbon has 4 and each hydrogen 1 for a total of 12 electrons.

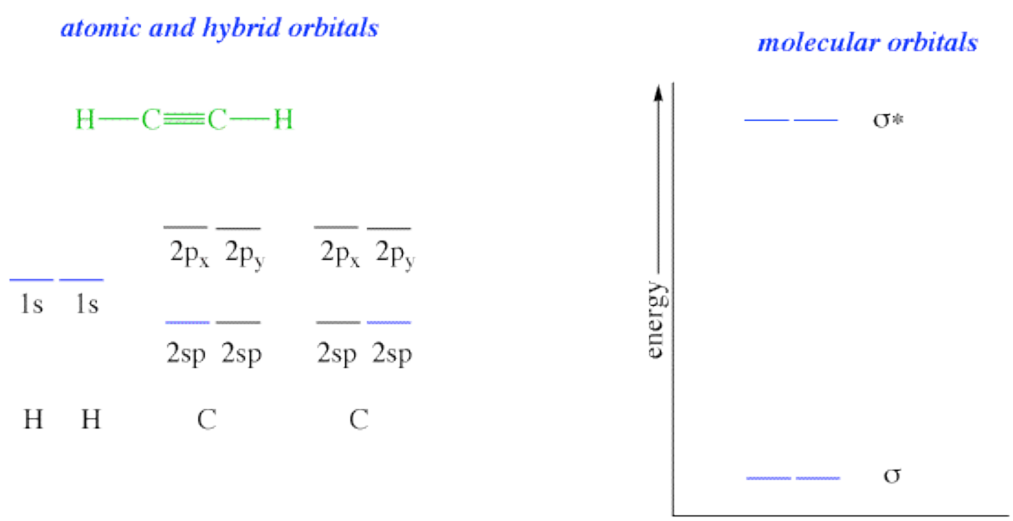


Ethyne, sp hybridization with two pi bonds

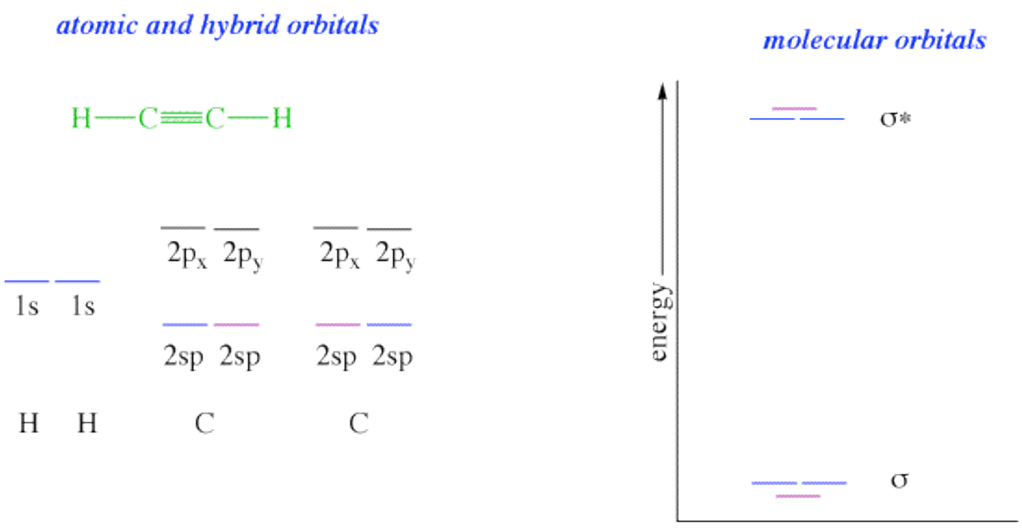
1. H—C≡C—H
2. Ethyne, HCCH, is a linear molecule. Each carbon atom makes 2 sigma bonds and has no lone pairs of electrons.

3. The carbon atoms in ethyne use 2sp hybrid orbitals to make their sigma bonds. After hybridization, a $2p_x$ and a $2p_y$ orbital remain on each carbon atom.

4. Combine each H(1s) orbital with a C(2sp) orbital to make a sigma bonding and a sigma antibonding molecular orbital. (C-H bonds)

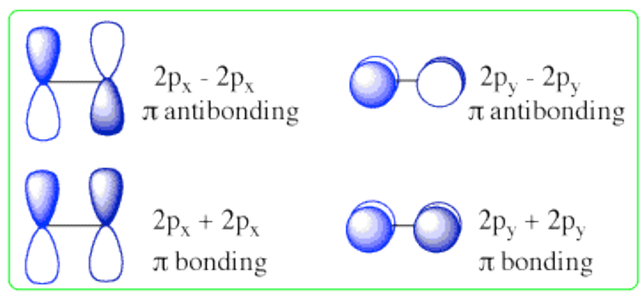


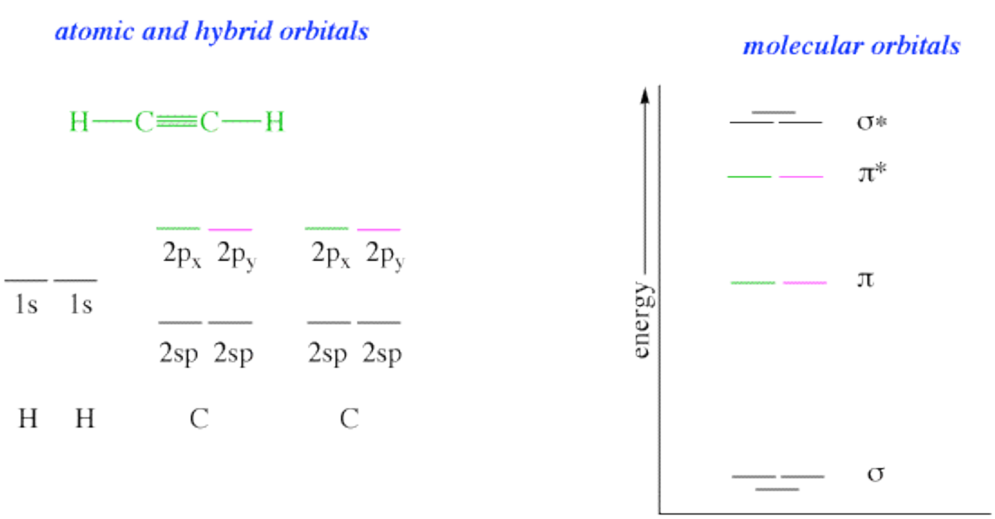
Combine the other 2 C(2sp) orbitals to make a sigma bonding and a sigma antibonding molecular orbital. (C-C bond)



5. There are no remaining hybrid orbitals.

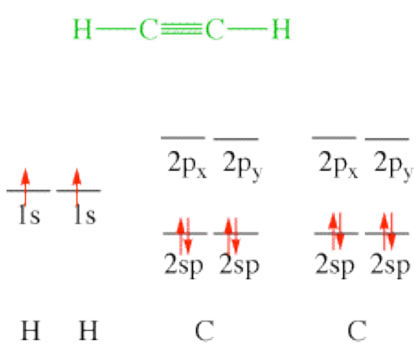
6. The $2p_x$ orbitals on each atom combine to make 2 pi symmetry orbitals. The $2p_y$ orbitals on each carbon combine to make another 2 pi symmetry orbitals, 90 degrees from the first set.





7. Add the valence electrons to the molecular orbital diagram. Each carbon has 4 and each hydrogen 1 for a total of 10 electrons.

atomic and hybrid orbitals



molecular orbitals