Atomic Orbitals - Orbitals of Isolated Atoms

Electrons will tend to fill orbitals in order of increasing energy:

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s$$

The maximum number of electrons which can be accomodated in an orbital is 2, with spins paired (Pauli principle), and when orbitals of the same energy (*degenerate* orbitals) fill, electrons fill these one at a time with the electron spins unpaired until the orbitals are all half filled (one electron each) (Hund's rule).

Consider carbon:

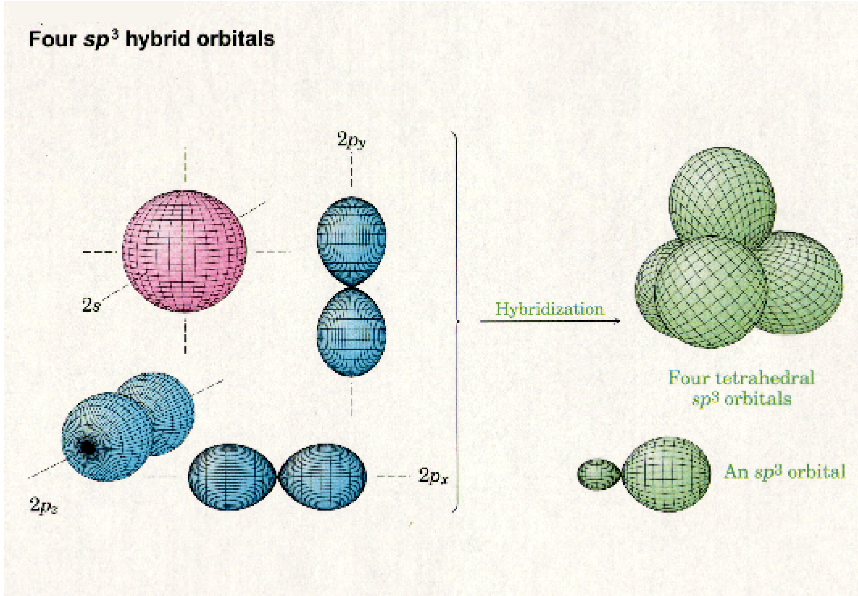
$$1s^2 < 2s^2 < 2p_x^{\ 1},\ 2p_y^{\ 1},\ 2p_z^{\ 0}$$

When the valence electrons in an isolated carbon are used to form covalent bonds with other atoms, they enter *molecular orbitals, MOs*, orbitals which extend over 2 or more atoms in a molecule. A relatively easy way for us to see how these MOs form is to transform the atomic orbitals (AOs) of the atom of interest, in our case carbon, to hybrid AOs which have the same orientation in space as the MOs they will become. [This requires some vector math *hocus pocus*, with which we shall not be concerned.] The core electrons, to a first approximation, remain in their AOs.

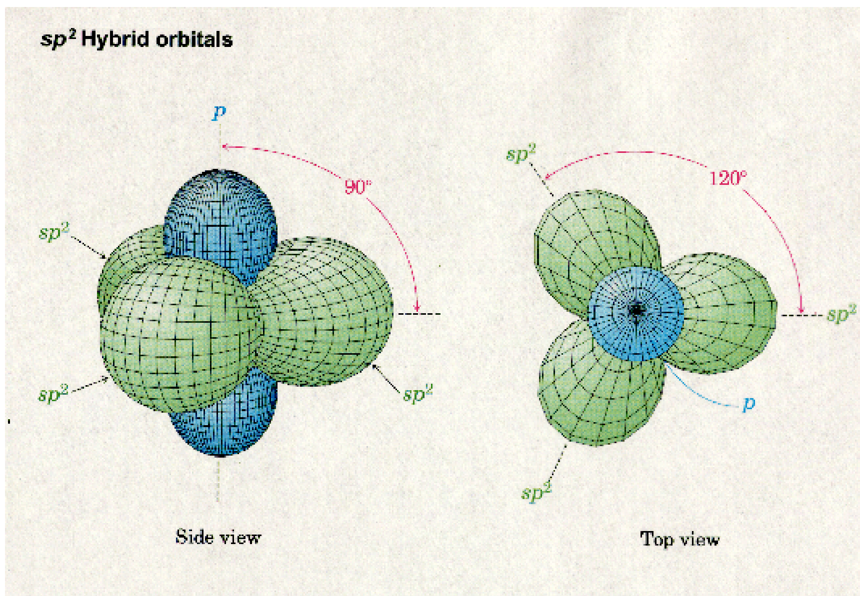
Let's see how this works.

Hybrid Atomic Orbitals

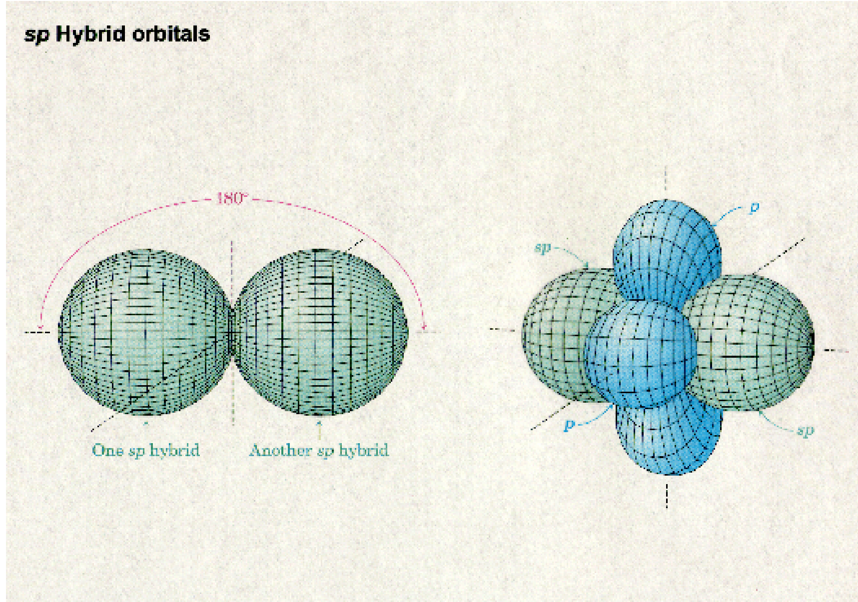
1. If the atom is tetrahedral in a compound, it is sp^3 hybridized. The 2s and the three 2p orbitals present in the uncombined atom have formed *four* sp^3 hybrid orbitals (pointing to the apexes of a tetrahedron), which may form *molecular orbitals* or may hold unshared pairs of electrons in the molecule.



2. If the atom is trigonal in a compound, it is sp^2 hybridized. The 2s and *two* of the three 2p orbitals present in the uncombined atom have formed *three* sp^2 hybrid orbitals (pointing to the apexes of an equilateral triangle), which may form *molecular orbitals* or may hold unshared pairs of electrons in the molecule. The 2p orbital which is not hybridized will usually form a *molecular orbital*.



3. If the atom is digonal (linear) in a compound, it is sp hybridized. The 2s and *one* of the three 2p orbitals present in the uncombined atom have formed *two* sp hybrid orbitals (collinear, pointing in opposite directions), which may form *molecular orbitals* or may hold unshared pairs of electrons in the molecule. The two 2p orbitals which are not hybridized will usually form *molecular orbitals*.



Molecular Orbitals

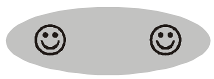
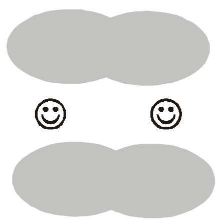
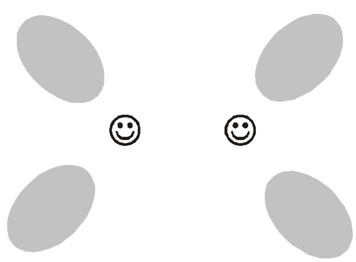
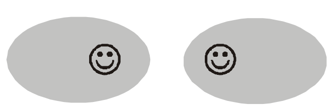
Orbital- Region of space around an atom or within a molecule which can accommodate one or two electrons (Pauli principle).

Orbitals associated with an atom: *atomic orbitals*.

Orbitals which result from the interaction of two or more atomic orbitals on different atoms: *molecular orbitals*.

Just as different atomic orbitals (1s, 2p, and 3d, for example) have different shapes, so do different molecular orbitals. The shapes of the four principal types of molecular orbitals are shown on the following page.

Types of Molecular Orbitals

Name	Shape	Other Characteristics
σ		☞ Formed by head-on approach of two AOs on different atoms. Bonding orbital. The covalent bond which results is σ-bond. Single bonds are σ-bonds . One of the bonds in a multiple bond is a σ bond.
π		☞ Formed by parallel approach of two (or more) p orbitals on different atoms. Bonding orbital. The covalent bond which results is a π–bond. Multiple bonds consist of one σ and one or two π bonds.
π*		☞ Each time a two atom π-orbital is formed, one of these is formed also. Antibonding. Higher in energy than π or σ.
σ*		☞ Each time a σ orbital is formed, one of these is formed also. Antibonding. Higher in energy than π*.

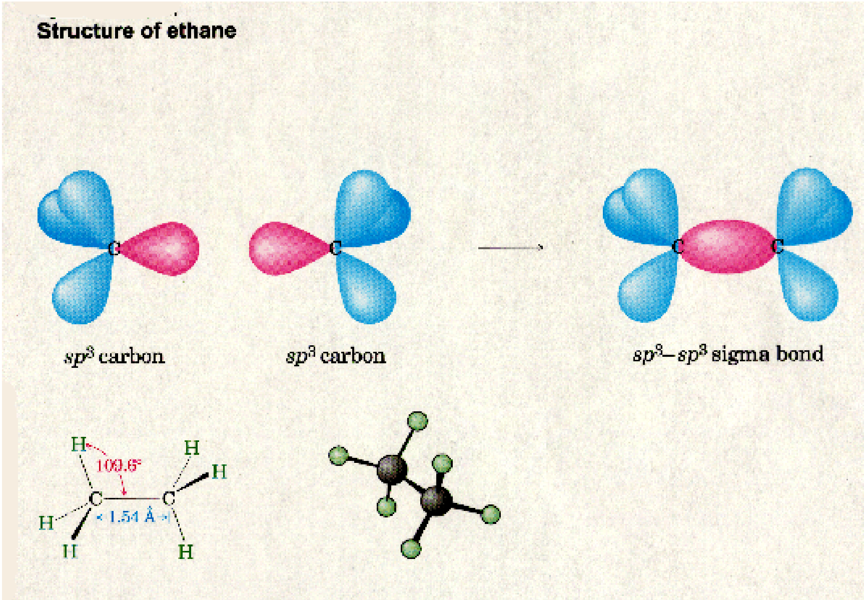
Note: Nuclei are shown greatly enlarged.

Bonding orbitals are usually occupied by electrons; antibonding orbitals usually are not.

<u>Combining Atomic Orbitals into Molecular Orbitals to Form Compounds</u>

Ethane is an example of a compound in which the four sp^3 hybrid atomic orbitals on each of the carbons form σ molecular orbitals.

One sp^3 orbital on each carbon gets together with one sp^3 orbital on the other carbon to form a σ and a σ* molecular orbital. The σ molecular orbital takes two electrons and the σ* orbital is unoccupied.

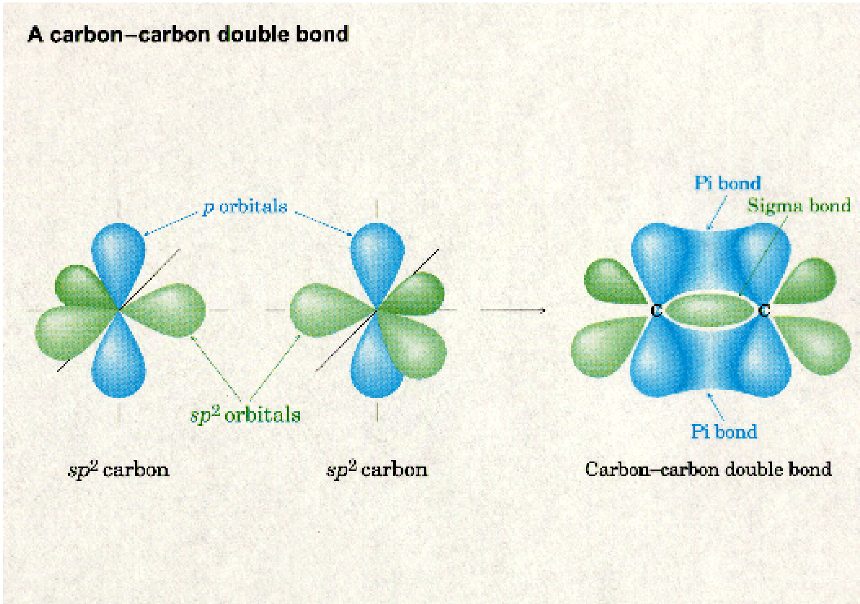


The remaining three sp^3 orbitals on each carbon join with 1s orbitals from hydrogen atoms to form σ and σ* molecular orbitals. The σ orbitals are each occupied by two electrons and the σ* orbitals are vacant.

Since the σ* orbitals are vacant we often ignore them unless there is some reason to take them into account.

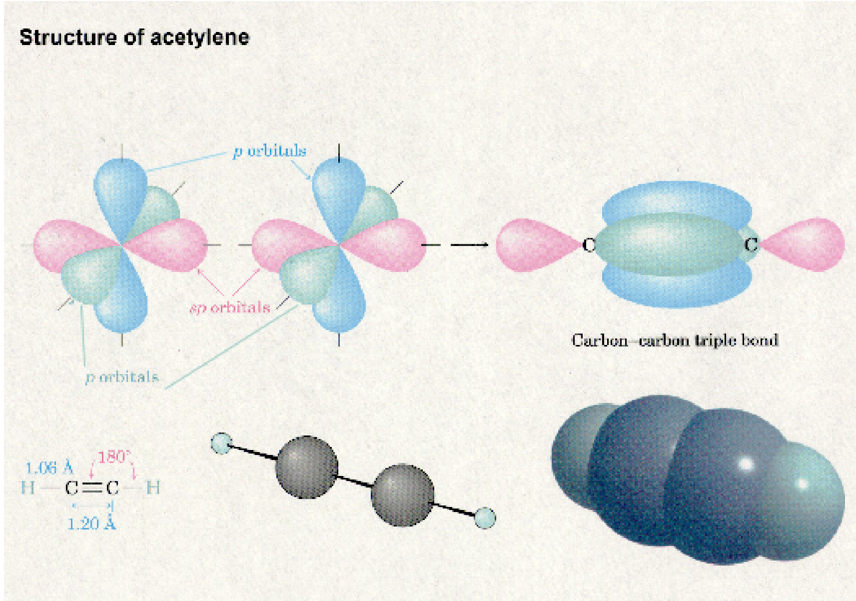
Ethylene is an example of a compound formed between two sp^2 hybridized carbons. One of the sp^2 orbitals on one carbon joins head-on with one of the sp^2 orbitals on the other carbon to form a σ orbital, occupied by two electrons, and an unoccupied σ* orbital.

The unhybridized p orbital on one carbon joins with the p orbital on the other carbon to form a π orbital, occupied by two electrons, and a π* orbital that is unoccupied.



Finally, the two remaining sp^2 hybrid orbitals on each carbon form σ and σ* orbitals with the 1s orbitals of hydrogen atoms. The σ orbitals are each occupied by two electrons; the σ* orbitals are unoccupied.

Acetylene is an example of a compound formed between two sp hybridized carbon atoms. One of the sp orbitals on one carbon joins head-on with one of the sp orbitals on the other carbon to form a



σ orbital, occupied by two electrons, and an unoccupied σ* orbital.

One unhybridized p orbital on one carbon joins with one p orbital on the other carbon to form a π orbital, occupied by two electrons, and a π* orbital that is unoccupied. The remaining p orbitals on each carbon also join together to form a second π orbital, occupied by two electrons, and a π* orbital that is unoccupied.

The remaining sp orbital on each carbon joins with a 1s orbital from hydrogen to form an occupied σ orbital and an unoccupied σ* orbital.