

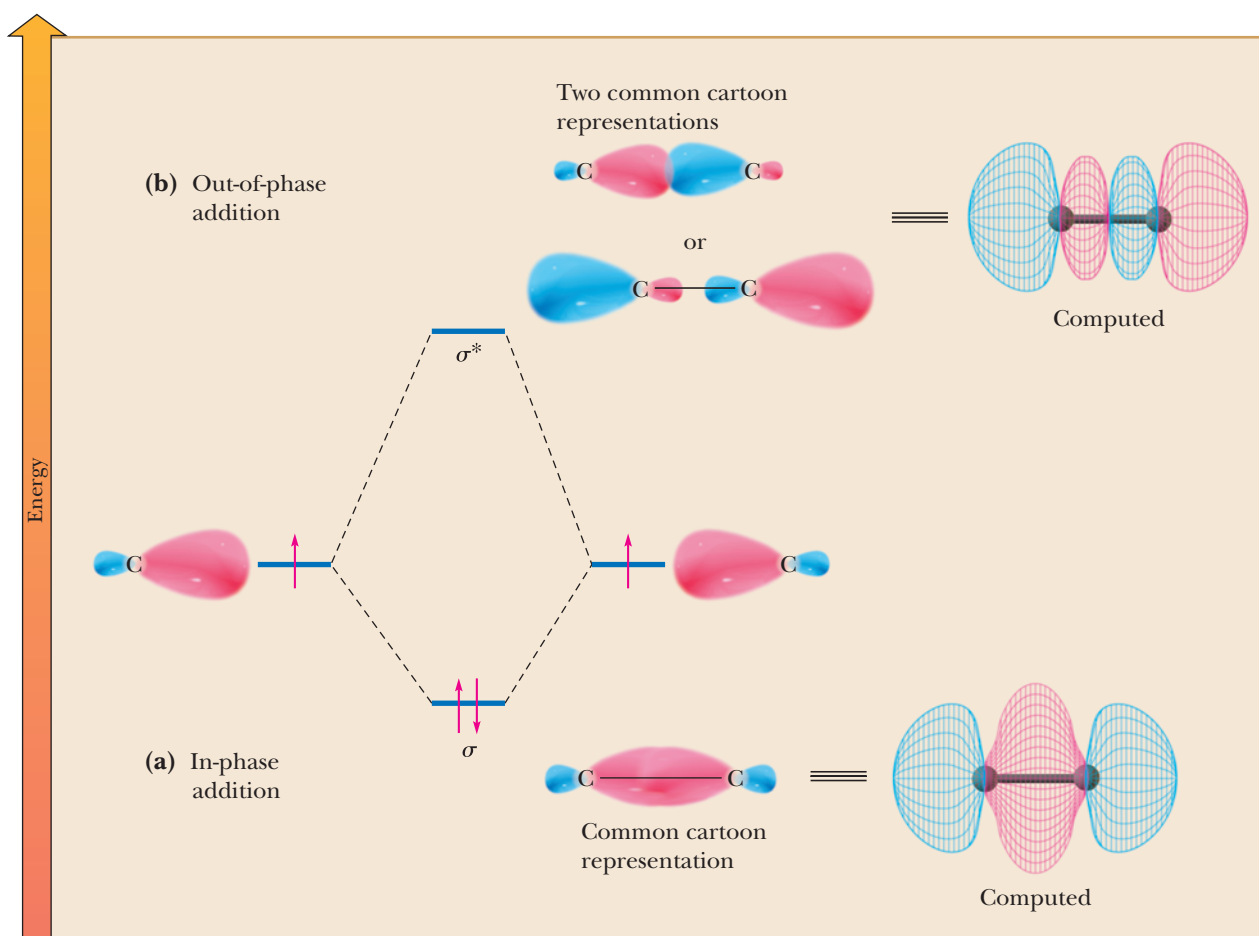
Figure 1.17

Molecular orbital mixing diagram for the creation of any C—H σ bond. (a) In-phase addition of a C hybrid orbital (albeit sp^3 , sp^2 , or sp) with a H $1s$ orbital forms a σ orbital that is lower in energy than the two starting orbitals. When the resulting orbital is populated with two electrons, a σ bond results. (b) Addition of the orbitals in an out-of-phase manner (meaning reversing the phasing of one of the starting orbitals) leads to an antibonding σ^* orbital.

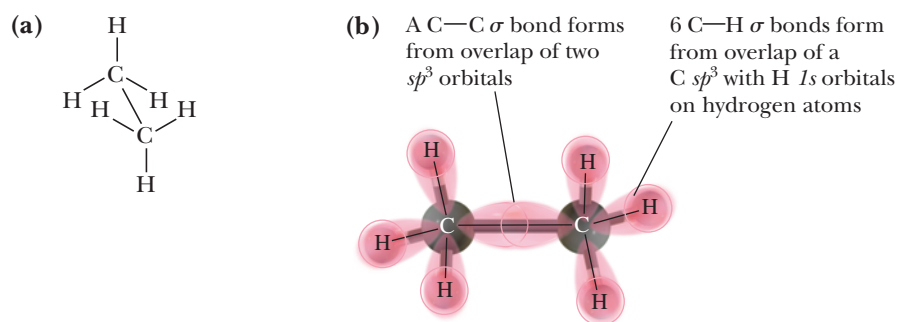
molecular orbital is higher in energy than the two atomic orbitals and is antibonding. Only the lower-energy orbital is populated with electrons in methane. Population of the σ bonding orbital results in what we call a σ bond between the C and the H. Each of the four C—H bonds in methane is created in the manner discussed here. Also, although we created this picture for the C—H bonds in methane, we will view all C—H bonds in other organic structures in the same way. In other words, even with sp^2 and sp hybridized carbons, we think of their C—H bonds as looking similar to those in Figure 1.17.

It is important to note in Figures 1.17 and 1.10, as well as in the orbital mixing diagrams (Figures 1.18, 1.21, and 1.25), that the energy of the antibonding orbital goes up further than the drop experienced by the bonding orbital. This is the reason that population of the antibonding orbital with electrons leads to cleavage of the bond. Early, less accurate theoretical methods for modeling bonding found the increase and decrease in energy of these respective orbitals to be identical, but the bonding approach described here correctly predicts the relative energies.

An identical approach used to create C—H σ bonds is used to create C—C σ bonds. For example, whenever a C—C bond exists in an organic structure we consider the overlap of hybrid orbitals on the two carbons. As shown in Figure 1.18, the overlap of two sp^3 hybrid orbitals on the individual carbons creates σ bonding and antibonding molecular orbitals. Only the bonding orbital is populated with electrons, thereby creating a carbon-carbon σ bond. We consider all C—C σ bonds to consist of orbitals similar to those given in Figure 1.18.

**Figure 1.18**

Molecular orbital mixing diagram for the creation of any C—C σ bond. (a) In-phase addition of two C hybrid orbitals (albeit sp^3 , sp^2 , or sp orbital) forms a σ orbital that is lower in energy than the two starting orbitals. When the resulting orbital is populated with two electrons, a σ bond results. (b) Addition of the orbitals in an out-of-phase manner (meaning reversing the phasing of one of the starting orbitals) leads to an antibonding σ^* orbital.

**Figure 1.19**

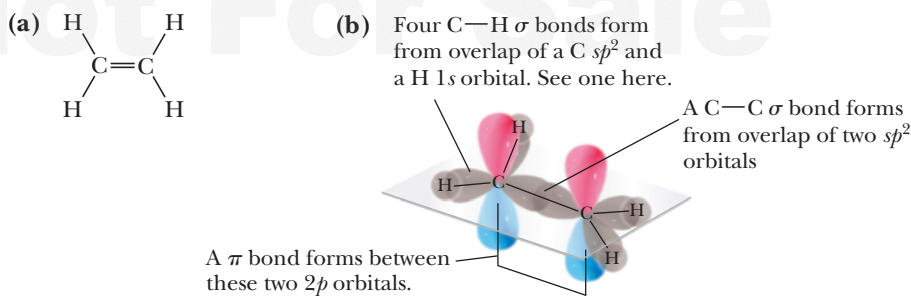
(a) Lewis structure for ethane (CH_3CH_3). (b) Overlap of sp^3 hybrid orbitals on adjacent carbons forms a C—C σ bond (see Figure 1.18), and overlap of carbon sp^3 hybrid orbitals with hydrogen $1s$ orbitals gives C—H σ bonds (see Figure 1.17).

For example, the simplest two-carbon compound ethane (CH_3CH_3) contains one C—C σ bond and six C—H σ bonds. As shown in Figure 1.19, we consider these bonds to arise from overlap of H $1s$ and C sp^3 orbitals, while the actual bonding orbitals appear as shown in Figures 1.17 and 1.18.

Let's now examine compounds with a double bond. Anytime there is a double bond, sp^2 hybridization should be considered for the atoms involved. For example, second-period elements use a combination of an sp^2 hybrid orbital and the unhybridized $2p$ atomic orbital to form double bonds. Consider ethylene, C_2H_4 , whose Lewis structure is shown in Figure 1.20(a). A σ bond between the carbons in ethylene is formed by overlapping sp^2 hybrid orbitals along a common axis as

Figure 1.20

Covalent bond formation in ethylene (CH_2CH_2). (a) Lewis structure. (b) Overlap of sp^2 hybrid orbitals on adjacent carbons forms a C—C σ bond (see Figure 1.18), and overlap of carbon sp^2 hybrid orbitals on carbons with $1s$ orbitals on hydrogens gives C—H σ bonds (see Figure 1.17). Further, overlap of parallel $2p$ orbitals on the adjacent carbons gives a π bond (see Figure 1.21).



Pi (π) molecular orbital

A molecular orbital with a nodal plane that cuts through both atomic nuclei, with electron density concentrated above and below the nodal plane.

seen in Figure 1.18(b). Each carbon also forms σ bonds with two hydrogens (as in Figure 1.17).

The combination of parallel $2p$ atomic orbitals by in phase and out of phase addition of their wave functions to give a **pi (π) bonding molecular orbital** and a pi antibonding molecular orbital (π^*) is shown in Figure 1.21. A π bonding molecular orbital has a nodal plane that cuts through both atomic nuclei, with electron density above and below the nodal plane concentrated between the nuclei. We picture all isolated π bonds between carbons to have orbitals such as those of Figure 1.21.

Lastly, let's examine triple bonds. Anytime there is a triple bond, sp hybridization is appropriate for the atoms involved. Figure 1.22 shows an orbital overlap diagram for acetylene, C_2H_2 . A carbon-carbon triple bond consists of one σ bond formed by overlapping sp hybrid orbitals and two π bonds. Overlapping a pair of parallel $2p$ atomic orbitals gives one π bond. Overlapping the other pair of parallel $2p$ atomic orbitals (perpendicular to the first pair) gives the second π bond.

The relationship among the number of atoms bonded to carbon, orbital hybridization, and types of bonds involved is summarized in Table 1.10.

Figure 1.21

Molecular orbital mixing diagram for the creation of any C—C π bond. (a) Addition of two p atomic orbitals in phase leads to a π orbital that is lower in energy than the two separate starting orbitals. When populated with two electrons the π orbital gives a π bond. (b) Addition of the p orbitals in an out-of-phase manner (meaning a reversal of phasing in one of the starting orbitals) leads to a π^* orbital. Population of this orbital with one or two electrons leads to weakening or cleavage of the π bond respectively.

