

every bonding interaction, which means there are eight MOs altogether (which is correct since there were eight AOs to start with).

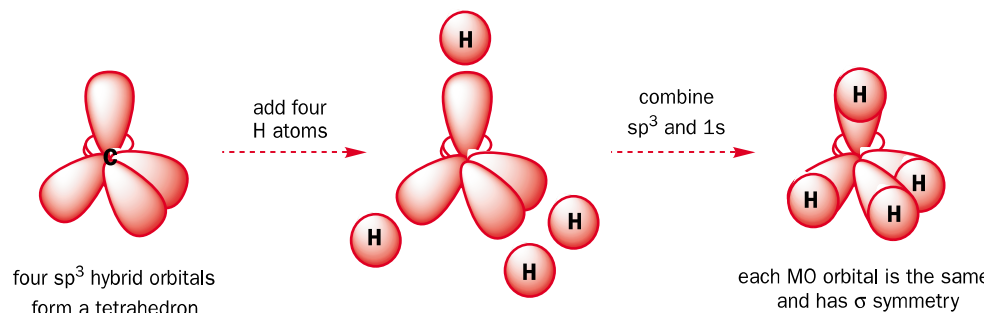
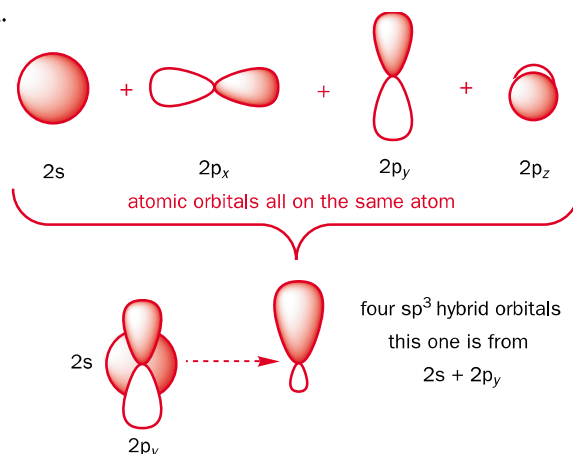
Organic chemists can just about understand this ‘correct’ MO picture of methane and theoretical chemists are able to construct correct MOs for very much more complex molecules than methane. There is experimental evidence too that these pictures are correct. Other experiments reveal that all four C–H bonds in methane are exactly the same and yet the MOs for methane are not all the same. *There is no contradiction here!* The molecular orbital approach tells us that there is one MO of one kind and three of another but the electrons in them are shared out over all five atoms. No one hydrogen atom has more or less electrons than any other—they are all equivalent. Techniques that tell us the structure of methane do not tell us where bonds are; they simply tell us where the atoms are located in space—we draw in bonds connecting atoms together. Certainly the *atoms* form a regular tetrahedron but exactly where the electrons are is a different matter entirely. The classical picture of two atoms held together by a pair of electrons is not necessarily correct—the five atoms in methane are held together by electrons but these are in molecular orbitals, which spread over all the atoms. We are going to need the classical picture when we draw mechanisms. Methane only has one carbon atom—imagine what it would be like with larger compounds that can contain hundreds of carbon atoms! Fortunately, there is another, simpler method we can use to describe bonding that preserves the important points from this theory.

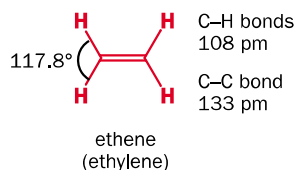
Hybridization of atomic orbitals

For most of organic chemistry, it is helpful to consider the molecule as being made up of atoms held together by bonds consisting of a pair of electrons. When working out the MOs for methane, we used the carbon 2s and all three of the 2p orbitals to combine with the hydrogen 1s orbitals. Each orbital combined with all the hydrogen orbitals equally. Another way to consider the bonding would be to combine the carbon 2s and 2p orbitals first to make four new orbitals. Each of these orbitals would be exactly the same and be composed of one-quarter of the 2s orbital and three-quarters of one of the p orbitals. The new orbitals are called sp^3 hybrid orbitals to show the proportions of the AOs in each. This process of mixing is called **hybridization**.

Combining four atomic orbitals on the same atom gives the same total number of hybrid orbitals. Each of these has one-quarter s character and three-quarters p character. The sp^3 orbital has a planar node through the nucleus like a p orbital but one lobe is larger than the other because of the extra contribution of the 2s orbital, which adds to one lobe but subtracts from the other.

The four sp^3 orbitals on one carbon atom point to the corners of a tetrahedron and methane can be formed by overlapping the large lobe of each sp^3 orbital with



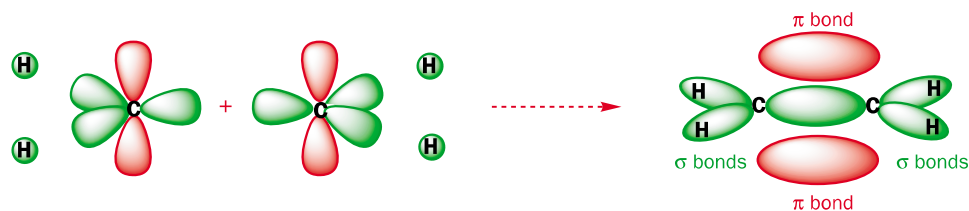
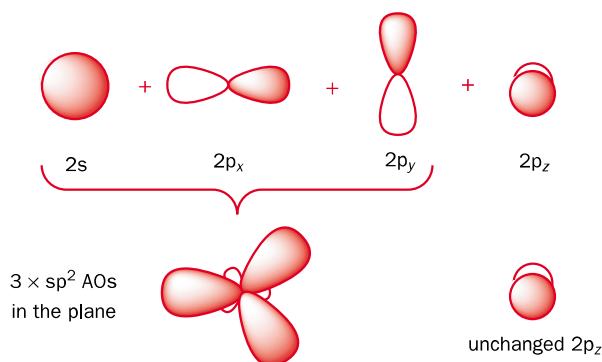


the 1s orbital of a hydrogen atom. Each overlap forms an MO ($2sp^3 + 1s$) and we can put two electrons in each to form a C-H σ bond. There will of course also be an antibonding MO, σ^* ($2sp^3 - 1s$) in each case, but these orbitals are empty.

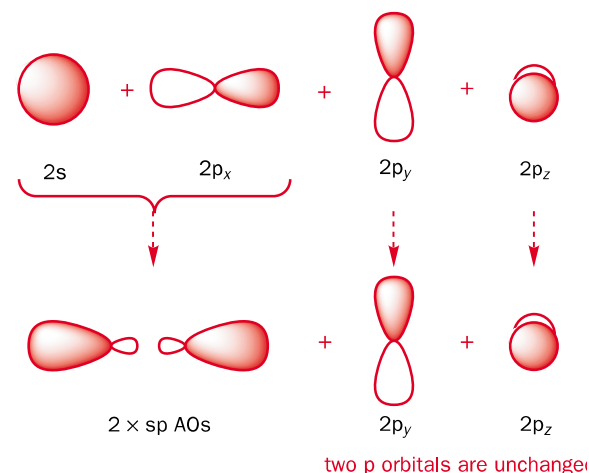
The great advantage of this method is that it can be used to build up structures of much larger molecules quickly and without having to imagine that the molecule is made up from isolated atoms. So it is easy to work out the structure of ethene (ethylene) the simplest alkene. Ethene is a planar molecule with bond angles close to 120° . Our approach will be to hybridize all the orbitals needed for the C-H framework and see what is left over. In this case we need three bonds from each carbon atom (one to make a C-C bond and two to make C-H bonds).

Therefore we need to combine the 2s orbital on each carbon atom with two p orbitals to make the three bonds. We could hybridize the 2s, $2p_x$, and $2p_y$ orbitals (that is, all the AOs in the plane) to form three equal sp^2 hybrid atomic orbitals, leaving the $2p_z$ orbital unchanged. These sp^2 hybrid orbitals will have one-third s character and only two-thirds p character.

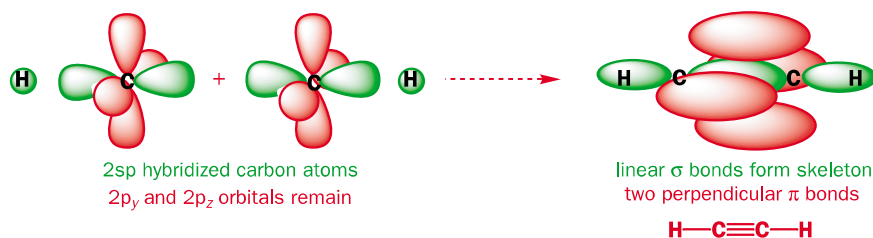
The three sp^2 hybrid atomic orbitals on each carbon atom can overlap with three other orbitals (two hydrogen 1s AOs and one sp^2 AO from the other carbon) to form three σ MOs. This leaves the two $2p_z$ orbitals, one on each carbon, which combine to form the π MO. The skeleton of the molecule has five σ bonds (one C-C and four C-H) in the plane and the central π bond is formed by two $2p_z$ orbitals above and below the plane.



Ethyne (acetylene) has a C-C triple bond. Each carbon bonds to only two other atoms to form a linear CH skeleton. Only the carbon 2s and $2p_x$ have the right symmetry to bind to only two atoms at once so we can hybridize these to form two sp hybrids on each carbon atom leaving the $2p_y$ and $2p_z$ to form π MOs with the 2p orbitals on the other carbon atom. These sp hybrids have 50% each s and p character and form a linear carbon skeleton.

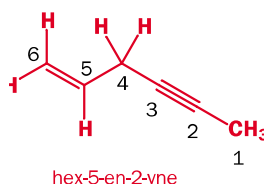


We could then form the MOs as shown below. Each sp hybrid AO overlaps with either a hydrogen 1s AO or with the sp orbital from the other carbon. The two sets of p orbitals combine to give two mutually perpendicular π MOs.

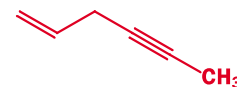


Hydrocarbon skeletons are built up from tetrahedral (sp^3), trigonal planar (sp^2), or linear (sp) hybridized carbon atoms. It is not necessary for you to go through the hybridization process each time you want to work out the shape of a skeleton. In real life molecules are not made from their constituent atoms but from other molecules and it doesn't matter how complicated a molecule might be or where it comes from; it will have an easily predictable shape. All you have to do is count up the single bonds at each carbon atom. If there are two, that carbon atom is linear (sp hybridized), if there are three, that carbon atom is trigonal (sp^2 hybridized), and, if there are four, that carbon atom is tetrahedral (sp^3 hybridized).

This hydrocarbon (hex-5-en-2-yne) has two linear sp carbon atoms (C2 and C3), two trigonal sp^2 carbon atoms (C5 and C6), a tetrahedral sp^3 CH_2 group in the middle of the chain (C4), and a tetrahedral sp^3 methyl group (C1) at the end of the chain. We had no need to look at any AOs to deduce this—we needed only to count the bonds.



Notice that atoms 1–4 are drawn in a straight line. Alkynes are linear—draw them like that!



If you had drawn the molecule more professionally as shown in the margin, you would have to check that you counted up to four bonds at each carbon. Of course, if you just look at the double and triple bonds, you will get the right answer without counting single bonds at all. Carbon atoms with no π bonds are tetrahedral (sp^3 hybridized), those with one π bond are trigonal (sp^2 hybridized), and those with two π bonds are linear (sp hybridized). This is essentially the VSEPR approach with a bit more logic behind it.

- All normal compounds of carbon have eight electrons in the outer shell ($n = 2$) of the carbon atom, all shared in bonds. It doesn't matter where these electrons come from; just fit them into the right MOs on sp , sp^2 , or sp^3 atoms.

We can hybridize any atoms

Hybridization is a property of AOs rather than specifically of carbon and, since all atoms have AOs, we can hybridize any atom. A tetrahedral arrangement of atoms about any central atom can be rationalized by describing the central atom as sp^3 hybridized. The three molecules shown here all have a tetrahedral structure and in each case the central atom can be considered to be sp^3 hybridized.

Each of these three molecules has four equivalent σ bonds from the central tetrahedral sp^3 atom, whether this is B, C, or N, and the same total number of bonding electrons—the molecules are said to be **isoelectronic**. These three elements come one after the other in the periodic table so each nucleus has one more proton than the last: B has 5, C has 6, and N has 7. This is why the charge on the central atom varies.

Compounds of the same three elements with only three bonds are more complicated. Borane, BH_3 , has only three pairs of bonding electrons. The central boron atom bonds to only three other atoms. We can therefore describe it as being sp^2 hybridized with an empty p orbital.

Each of the B–H bonds results from the overlap of an sp^2 orbital with the hydrogen 1s orbital. The

