

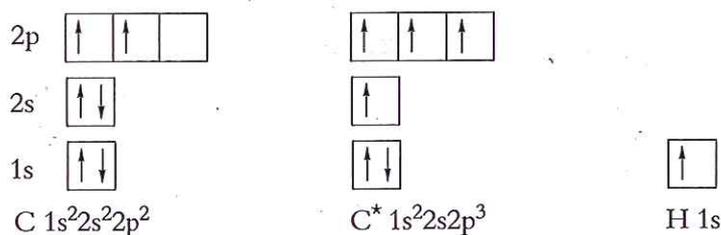
*5.3 SHAPES OF MOLECULES: A MOLECULAR ORBITAL TREATMENT

An alternative to the VSEPR treatment is the molecular orbital approach

The valence shell electron pair repulsion theory provides a simple treatment of the shapes of covalent molecules. A more precise treatment of the spatial distribution of covalent bonds about a central atom involves a consideration of the atomic orbitals used in bond formation. The shapes of atomic orbitals are described in § 2.4.2 and shown in Figures 2.4B to 2.4D. When **atomic orbitals** overlap, **molecular orbitals** are formed. The **molecular orbital approach** is illustrated in this section.

5.3.1 METHANE: sp^3 HYBRID ORBITALS

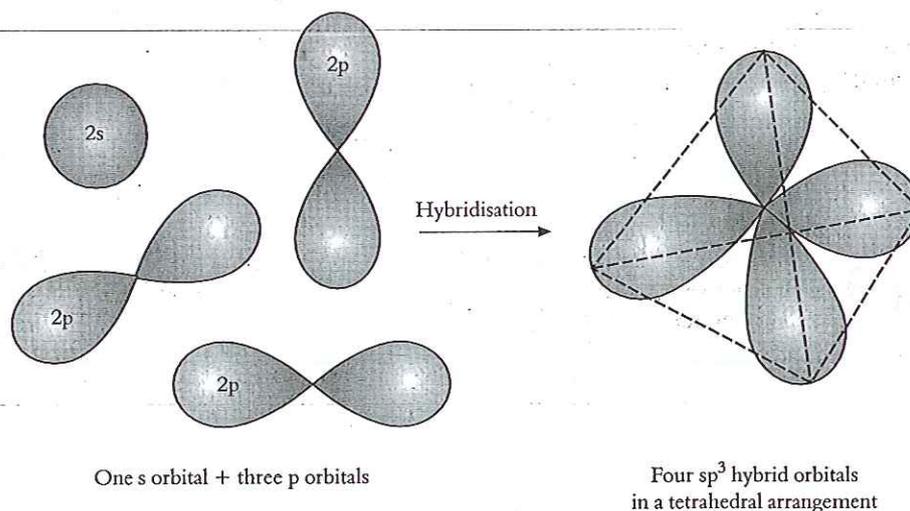
The electronic configuration of carbon in its normal, C, and excited, C^* , states and hydrogen, H, are shown below:



In carbon, an s electron is promoted to a p orbital

Each carbon atom, C, has two unpaired electrons, and one might expect carbon to form two bonds. It would not then attain a neon-like structure: it needs to share four electrons to do this. A sharing of four electrons can be achieved by promoting one of the 2s electrons into the 2p level. The excited carbon atom, C^* , might be expected to form two different kinds of bond, using one s orbital and three p orbitals. Actually, the electron density distributes itself evenly through four bonding orbitals, which are called sp^3 hybrid orbitals (Figure 5.3A).

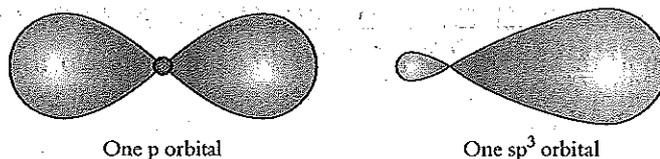
Figure 5.3A
The sp^3 hybrid orbitals of carbon



One s orbital and three p orbitals form four sp^3 hybrid orbitals.

The sp^3 atomic orbital is more concentrated in direction than a p orbital [see Figure 5.3B]. An sp^3 orbital is therefore able to overlap more extensively and form stronger bonds than a p orbital.

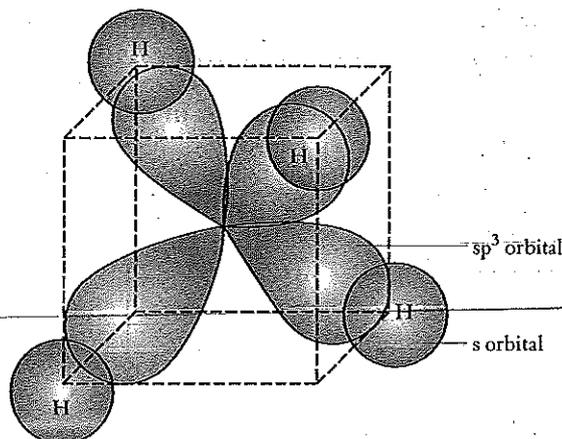
Figure 5.3B
Comparison of atomic orbitals



The overlapping of the four sp^3 orbitals of carbon and four s orbitals of hydrogen in methane is shown in Figure 5.3C. Experimental evidence for the tetrahedral arrangement is gained from X ray diffraction studies of diamond. The angle between the bonds is shown to be 109.5° [see Figure 6.6A, § 6.6].

Figure 5.3C
Overlapping of atomic orbitals in methane

In methane, four sp^3 hybrid orbitals of C overlap with four s orbitals of four H atoms



5.3.2 DOUBLE BONDS

A double bond is less than twice as strong as a single bond ...

... and a triple bond has less than three times the strength of a single bond

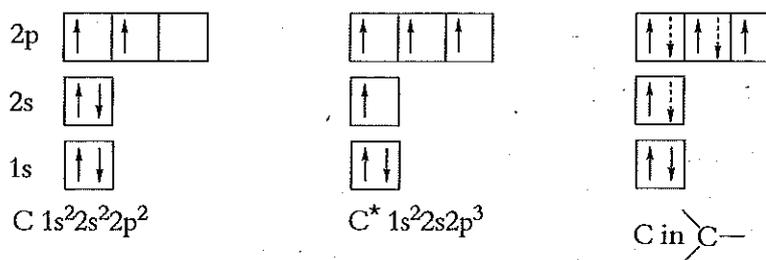
Carbon forms double bonds in compounds such as carbon dioxide, $O=C=O$, and ethene, $H_2C=CH_2$. The double bond is not simply two single bonds. The amount of energy required to break a certain bond in a mole of molecules is called the **standard bond enthalpy** [§ 10.11]. Standard bond enthalpies of carbon-carbon bonds are

$C-C$	346 kJ mol^{-1}
$C=C$	610 kJ mol^{-1}
$C\equiv C$	837 kJ mol^{-1}

The $C=C$ bond is less than twice as strong as a $C-C$ bond, and the $C\equiv C$ bond is less than three times as strong as a $C-C$ bond.

Two p orbitals and one s orbital can hybridise to form three coplanar sp^2 hybrid orbitals

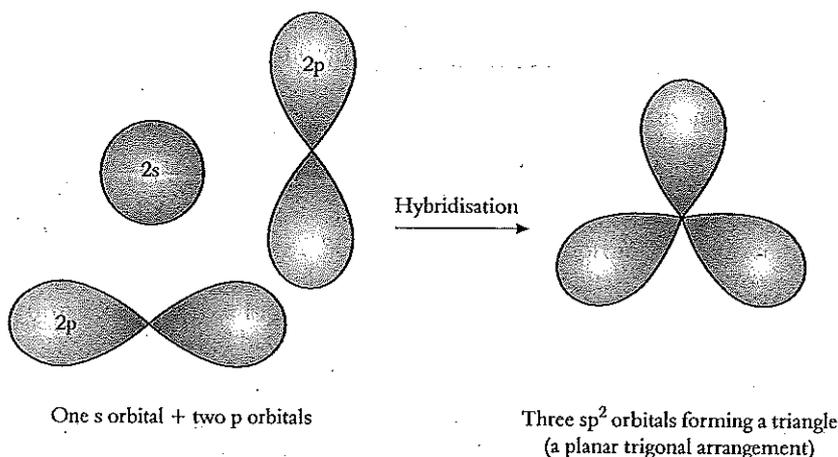
In a molecule of ethene, each carbon atom uses a 2s orbital and two of the three 2p orbitals to form three sp^2 hybrid bonds [see Figure 5.3F]. The electronic configurations of carbon are shown below:



The three sp^2 hybrid orbitals are coplanar with an angle of 120° between them.

Figure 5.3D

The sp^2 hybrid orbitals of carbon



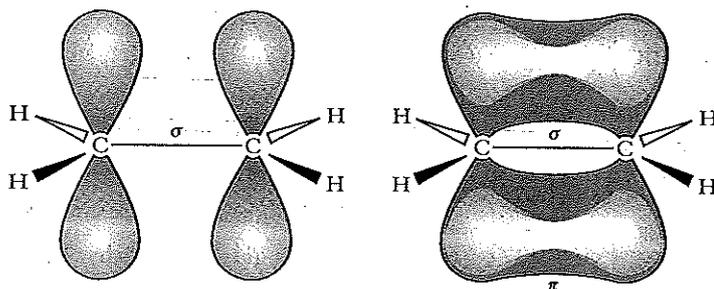
Each C has an unhybridised p orbital ...

The carbon-carbon bond formed when the sp^2 orbitals of neighbouring carbon atoms overlap is called a σ , **sigma**, bond. In σ bonds, e.g. any single bond, overlap of atomic orbitals occurs along the line joining the two bonded atoms. There is an unhybridised p orbital at right angles to the plane of the three sp^2 orbitals, and the p orbitals on adjacent carbon atoms are close enough to overlap. The overlapping occurs at the sides of the orbitals [see Figure 5.3E].

Figure 5.3E

The ethene molecule

Overlapping of atomic orbitals along the line joining the two bonded atoms is a σ (sigma) bond



(a) The C atoms have unhybridised p orbitals.

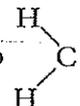
(b) Sideways overlap between the two parallel p orbitals produces one π orbital.

... Sideways overlap between p orbitals is called a π (pi) bond ...

This type of bond, produced by sideways overlapping of p orbitals above and below the plane of the sp^2 bonds, is called a π , **pi**, bond. It is not as strong as a σ bond since there is less overlapping of orbitals [see Figure 5.3F]. This is why the $C=C$ bond is less than twice as strong as a $C-C$ bond.

Since overlapping of p orbitals on adjacent carbon atoms can occur only when

... π bonds are less strong than σ bonds

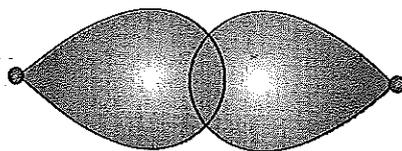
the p orbitals are parallel, the two  structures must be coplanar, i.e., lie

For π bonds to be formed the atoms in $H_2C=CH_2$ must be coplanar

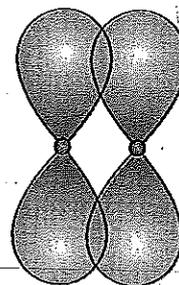
in the same plane. If one CH_2 group twists with respect to the other, the amount of overlapping of p orbitals will decrease and the π bond will be partially broken. Since it requires energy to break a bond, the most stable arrangement of the molecules is the one in which all six atoms lie in the same plane [see Figure 27.5B(a), § 27.5.3].

Figure 5.3F

The difference between σ and π bonds



(a) σ bonding.
The orbitals point towards each other.



(b) π bonding.
The orbitals are parallel and overlap sideways.

π bond formation is restricted to small atoms

The formation of strong π bonds is restricted to members of the second period: carbon, nitrogen and oxygen. In larger atoms, strong π bonds are not formed because, being removed from the line between the centres of the atoms, the π bond becomes rapidly weaker as the size of the atom increases.

CHECKPOINT 5.3: BONDING

- Deduce the shapes of the following species:
 AsH_3 , PH_4^+ , H_3O^+ , CS_2 , $\text{CH}_2=\text{C}=\text{CH}_2$, $\text{HC}\equiv\text{N}$.
- What is the arrangement of bonds around the central atom in each of the following species:
 CH_4 , BF_3 , NF_3 , ICl_4^- , BrO_3^- , ClO_4^- , CHCl_3 ?
- Write structures which show the arrangement of electrons in the bonding orbitals of:
 O_2 , CO_2 , NO_3^- and GN^-
(e.g., $\text{O}::\text{O}$)
- What can you deduce from the fact that, whereas water has a dipole moment, carbon dioxide has none?
- Write electron structures for: PH_3 , NH_3 , NH_4Cl , H_2O , H_2O_2 , SiH_4 , HOCl
(e.g., $\text{H}:\ddot{\text{P}}:\text{H}$)
 H
- The ammonium ion and methane are said to be *isoelectronic*. What does this mean? Why do the compounds have different chemical properties?
- (a) Sketch the arrangement of bonds in $\text{CF}_2=\text{CF}_2$.
(b) Explain why there are two isomers with the formula $\text{CFCl}=\text{CFCl}$.