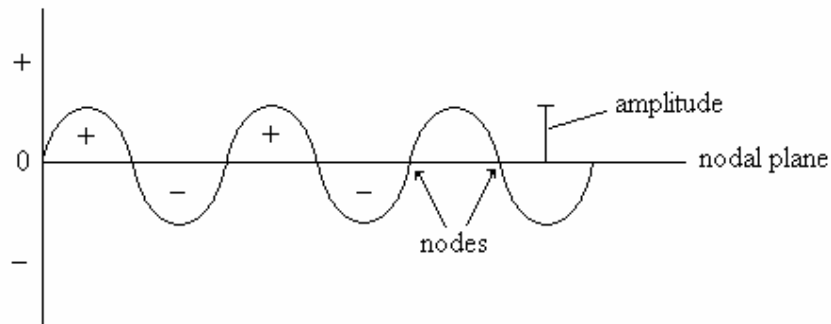# WAVE EQUATIONS, WAVE FUNCTIONS AND ORBITALS

According to the quantum mechanical concept, electrons in atoms and molecules are considered as 'standing waves' or 'stationery waves' (similar to vibrations in a stretched string, but in 3 dimensions).

Properties of a wave

Consider a standing wave in a stretched string. As we proceed horizontally along the string, the **vertical displacement** (or **amplitude**) of the wave increases in one direction, passes through a maximum, decreases to zero and then increases in the opposite direction. *The places where the amplitude is zero are called* **nodes**. The nodes lie on a plane called the **nodal plane** (which lies perpendicular to the plane of the paper along the x-axis in the above diagram). Upward displacement and downward displacement correspond to opposite **phases** of the wave. To distinguish between the two phases, one is given a '+' sign and the other a '−' sign. If two waves are superimposed exactly out-of-phase (crests of one overlapping with the troughs of the other), they would cancel each other (sum of their amplitudes will become zero).

The differential equation which describes the wave is called a **wave equation** (for an electron, this is the Schrödinger equation). Solution of this equation gives the amplitude 'Φ' (phi) as a function, *f(x)*, of the distance 'x' along the wave. Such a function is called the **wave function**.

Electron waves are described by a wave equation of the same general form as that of string waves. The wave functions that are acceptable solutions to this equation give the amplitude Φ as a function of three coordinates x, y and z necessary to describe motion in three dimensions. These electron wave functions are called **orbitals**. (Any wave equation has a set of solutions – actually an infinity of them – each corresponding to a different energy level. The 'quantum' thus comes naturally out of the mathematics).

The electron wave can also have nodes, where the amplitude is zero. On opposite sides of a node, the amplitude has opposite signs, or the wave is of opposite phases. Eg. between the two lobes of a p-orbital lies a nodal plane perpendicular to the axis of the orbital. Therefore the two lobes are of opposite phases. This is often indicated by '+' and '−' signs. Note that these symbols do not represent charges. The amplitude or wave function Φ is the orbital. But it is the square of the wave function (Φ^2) that has physical meaning. For electron waves, Φ^2 represents the

probability of finding the electron in any particular place. Irrespective of the sign of Φ, Φ^2 is always positive; this makes sense, since probability cannot be negative.
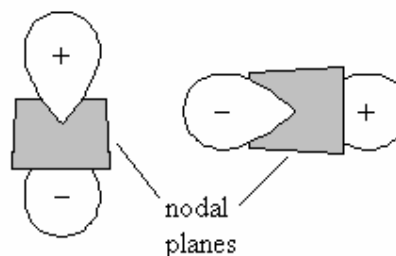
Molecular orbitals – LCAO method

According to molecular orbital theory (MOT), *electrons in molecules are in* **molecular orbitals**, just as electrons in atoms are in atomic orbitals. Electrons in molecules are filled in molecular orbitals in accordance with the 'aufbau' principle, Hund's rule of maximum multiplicity and Pauli's exclusion principle.

For simplicity, molecular orbitals are considered to be obtained by the combination of atomic orbitals of atoms in the molecule. This is analogous to the 'orbital overlap' concept. For a diatomic molecule AB, *the wave functions for molecular orbitals are obtained by either adding the wave functions of atomic orbitals in A and B, or by subtracting the wave function of one atom from the other, by following certain principles.* This is known as the **linear combination of atomic orbitals** (LCAO) method. For molecules having more than two atoms (poly atomic molecules), this process must take into account the atomic orbitals of all atoms in them.

If 'Ψ' (psi) represents the molecular orbital of AB, and Φ_A and Φ_B represents the atomic orbitals of A and B respectively, then

$$\Psi_+ = \Phi_A + \Phi_B \qquad \text{and} \qquad \Psi_- = \Phi_A - \Phi_B$$

When the electron is near atom A, Ψ resembles Φ_A; when it is near atom B, Ψ resembles Φ_B. Contribution of atomic orbital from the nearer atom increases while that from the farther atom decreases. For the combination to be 'effective', ie. for the molecular orbital to be more stable than the separate atomic orbitals, Φ_A and Φ_B must
(a) overlap to a considerable extent,
(b) be of comparable energy, and
(c) must have the same symmetry about the bond axis.
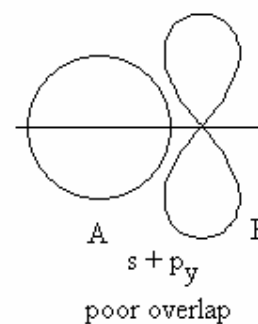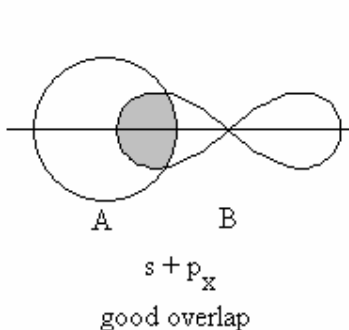
Symmetry of orbitals (meaning of statement 'c' above)
By 'symmetry of orbitals', we mean their direction in space, and the phases of the lobes. If the orbitals are not directed along the same axis, there cannot be appreciable overlap. For example, see figures:
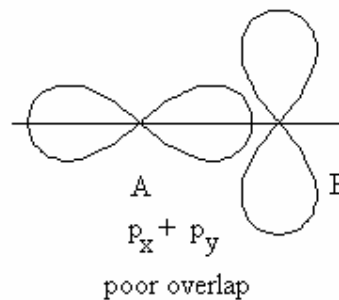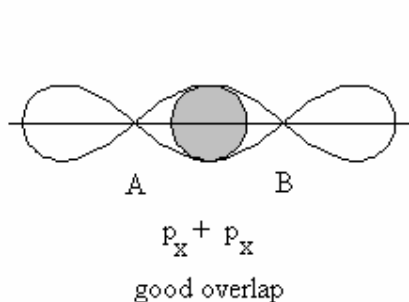
Apart from the direction of approach, the lobes which overlap must have the same sign for effective overlap. Waves of opposite signs will destroy each other.
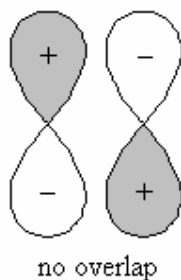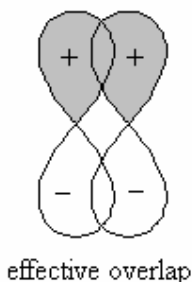

Quantum mechanics shows that linear combination of two wave functions (atomic orbitals) gives two combinations of molecular orbitals. These are called **bonding** molecular orbitals and **antibonding** molecular orbitals. (In other words, the number of molecular orbitals generated is equal to the total number of combining atomic orbitals. Half of these are bonding and the other half antibonding).

2

$$\Psi = \Phi_A + \Phi_B \qquad \text{(bonding orbital, stabilizes the molecule)}$$
$$\Psi^* = \Phi_A - \Phi_B \qquad \text{(antibonding molecular orbital, destabilizes the molecule)}$$

In the bonding orbitals, electrons are concentrated in the region between the atomic nuclei. This lowers the energy of the system. Antibonding orbitals have a nodal plane perpendicular to the inter nuclear axis and cutting between the two nuclei. Electrons in antibonding orbitals tend to force the atoms apart. The decrease in energy of the bonding orbital is equal to the increase in energy of the antibonding orbital.
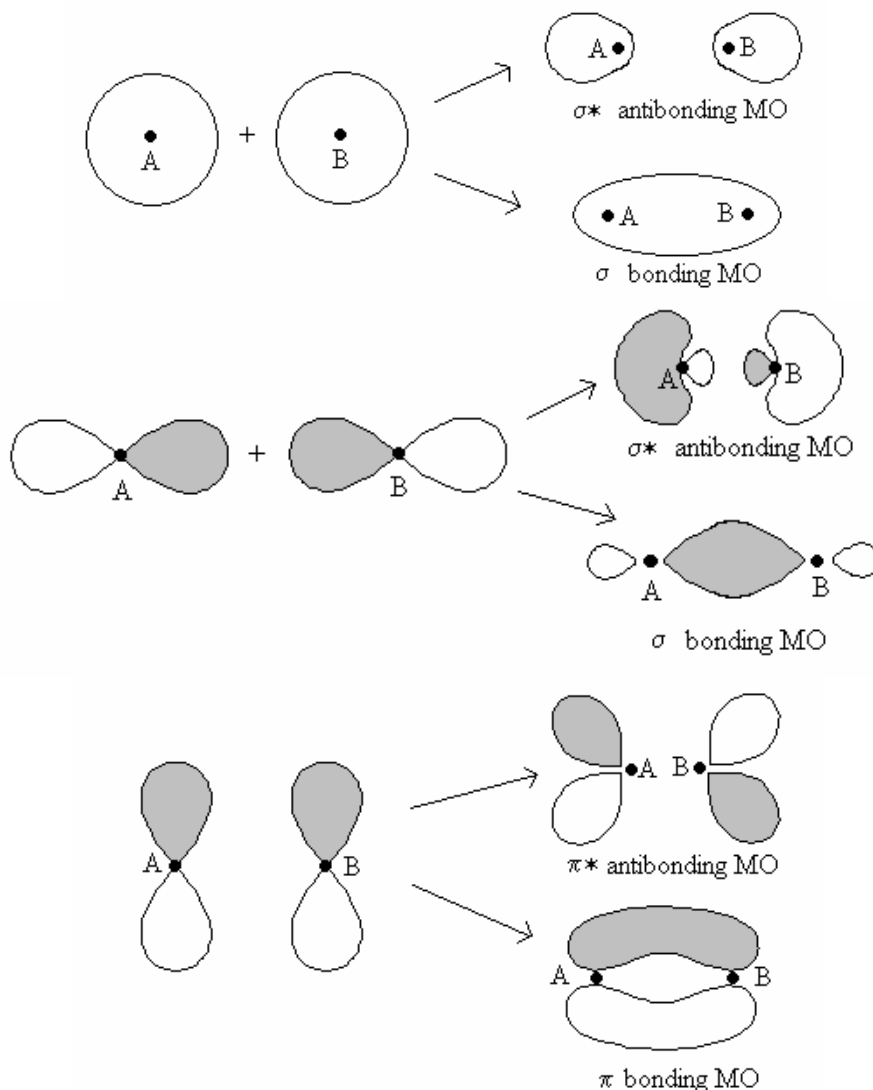
In addition to bonding and antibonding orbitals, there is a third kind called non-bonding orbitals. These hold unshared pairs of electrons. They neither increase nor decrease the energy of the system. [For a discussion on simple diatomic molecules, look up any +2 text book].
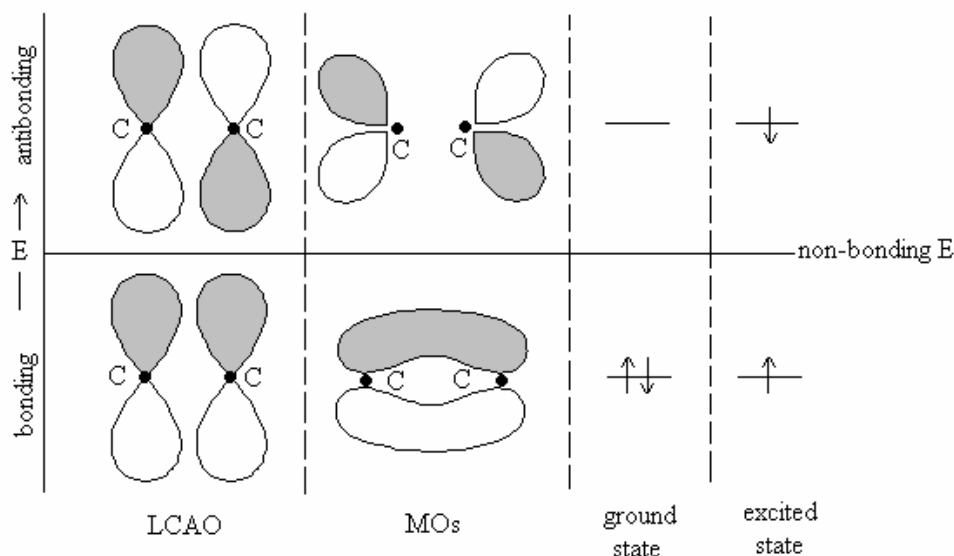
Hückel molecular orbital theory (HMO theory): Before computers enabled elaborate MO calculations to be performed routinely, it was necessary to apply greatly simplified approximations to molecules of interest to organic chemists. The most useful of these approximations were those of the Hückel molecular orbital theory for treatment of conjugated systems. HMO theory is based on the assumption that it is the π system that is of importance in determining the chemical and spectroscopic properties of conjugated polyenes and aromatic compounds, and that the π system can be treated independently of the σ framework in conjugated planar molecules. The basis for treating the σ and π systems independently of each other is their orthogonality. The σ orbital system

of a planar conjugated system lies in the nodal plane of the π system and does not interact with it. Because of its simplicity, HMO theory has been extremely valuable in the application of MO concepts to organic chemistry. It provides a good qualitative description of the π molecular orbitals in both cyclic and acyclic conjugated systems. In favourable cases such as aromatic ring systems, it provides a quite thorough analysis of the relative stability of the structures. This treatment is applied in the following discussions.

**Electronic configuration of an isolated double bond – the ethene molecule**
We shall discuss the MO for the π-bond only. Since there is a combination of two p-orbitals, one on each C-atom, there will be two molecular orbitals. These are the π and π* MOs.

In the ground state, the electron pair is in the lowest energy level, namely the π-bonding MO and stabilises the system. This is the $\pi^2$ configuration. Absorption of UV light promotes one electron to the π* MO, retaining its opposite spin (the first excited state). This is the $\pi^1\pi^{*1}$ configuration. This is less stable since the lowering of energy by the π electon is offset by the π* electron. In the next excited state, both electrons are in the π* MO, meaning that the bond is broken.

Extra stability of a conjugated diene system – the 1,3-butadiene molecule
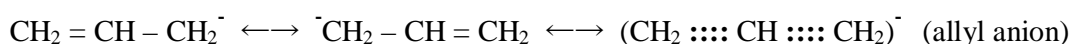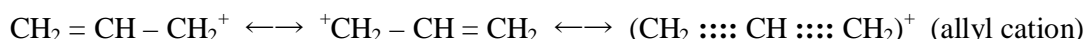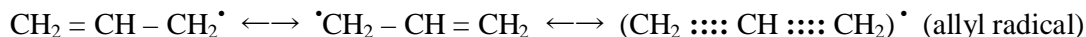
$CH_2 = CH – CH = CH_2$
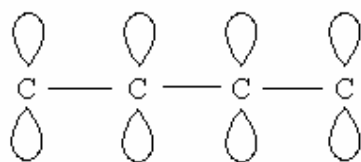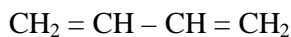
This molecule is more stable than a compound with two isolated double bonds. This is because the electrons are delocalized over the four carbon atoms. Four p-orbitals on adjacent C-atoms are involved, producing four MOs. These are ψ_1, ψ_2, ψ_3 and ψ_4. Of these, ψ_1 and ψ_2 are bonding π-MOs.
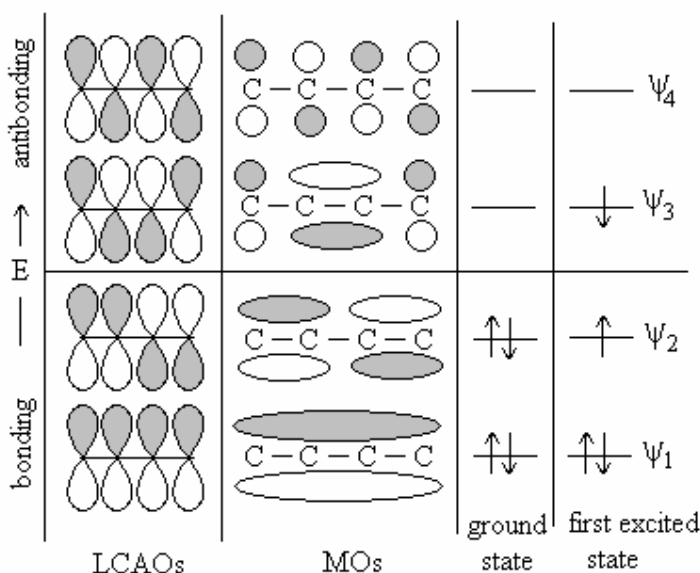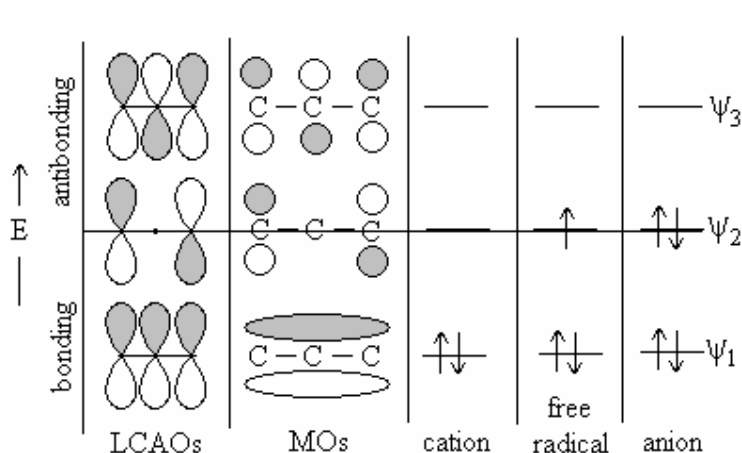
ψ_3 and ψ_4 are antibonding π^*-MOs. In the ground state, all four electrons are in the bonding orbitals (ψ_1 and ψ_2). This lowers the energy of the system considerably.

Stability of the allyl free radical, allyl cation and allyl anion
These are generally described as resonance stabilized. *When a molecular system can be represented by several structures, all having the same energy, without any change in the positions of its atoms, there is observed to be an increased stability due to lowering of energy. The various structures that can be so written are called **canonical forms**, and the actual structure is a **resonance hybrid** of all these forms. The decrease in energy caused by resonance is called **resonance stabilization energy** of the system.* The allyl system is a three-carbon system with a double bond, which is said to be stabilized by resonance.

$$CH_2 = CH - CH_2^{\bullet} \longleftrightarrow {}^{\bullet}CH_2 - CH = CH_2 \longleftrightarrow (CH_2 :::: CH :::: CH_2)^{\bullet} \text{ (allyl radical)}$$

$$CH_2 = CH - CH_2^{+} \longleftrightarrow {}^{+}CH_2 - CH = CH_2 \longleftrightarrow (CH_2 :::: CH :::: CH_2)^{+} \text{ (allyl cation)}$$

$$CH_2 = CH - CH_2^{-} \longleftrightarrow {}^{-}CH_2 - CH = CH_2 \longleftrightarrow (CH_2 :::: CH :::: CH_2)^{-} \text{ (allyl anion)}$$

According to the MO concept, there are three p-orbitals, one on each C-atom, and each contain a single electron. Therefore three molecular orbitals will be formed, ψ_1, ψ_2, and ψ_3. The three electrons are to be placed in these orbitals according to 'aufbau' principle. ψ_1 is the bonding MO, ψ_2 is a non-bonding orbital and ψ_3 is the antibonding MO. There is a node on the middle C-atom in ψ_2.

Thus in the allyl free radical, there are three p-electrons (one on each C-atom involved in the double bond and one on the radical). Of these, two electrons with opposite spins are placed in the bonding MO ψ_1 and one electron in the non-bonding MO ψ_2. The two electrons in the low energy ψ_1 stabilizes the system while the electron in ψ_2 has the original energy.

In the allyl cation, there are only two p-electrons, and they go into the bonding MO, ψ_1. In the allyl anion, there are four p-electrons. A pair of electrons each are placed in the ψ_1 and ψ_2 MOs. All the three systems are stable because there are no electrons in the π^* orbitals in any of them. Comparatively, the stabilities of the three systems are in the order:

$$\text{allyl cation} > \text{allyl free radical} > \text{allyl anion}$$

This is because the anion will have an electron in the π^* antibonding orbital in the first excited state. The free radical will have an electron in the π^* orbital only in the second excited state, and in the cation only in the third excited state. In the bonding MO, the electrons are delocalized over all three C-atoms.

Aromatic character – the Hückel 4n+2 rule
Cyclic systems other than benzene are also found to exhibit extra stability known as aromaticity. In 1931, Erich Hückel postulated the necessary conditions for aromaticity.
   (1) There should be a ring system.

(2) The molecule (ring) should be flat.
(3) There must be 4n+2 π-electrons in the system.

Aromaticity as explained by MO theory: [Ref: Wingrove AS and Caret AL. "Organic Chemistry." Harper & Row (1981). p 542-545; Carey F.A., Organic Chemistry 5th edn., Tata McGraw-Hill, (2003), p 451]

Why is the Hückel number (4n + 2) so important? The answer comes from MO theory. The MOs associated with the π-electron system of any simple aromatic compound can be generated (an ad-hoc simplified technique that correctly represents the results obtained by solving the wave equations) in the following manner (known as the **Frost circle** method):

(1) Draw the carbon ring system inscribed in a circle so that the vertex of one ring atom is pointed downwards towards the bottom of the page, and draw a horizontal through the centre dividing the circle into two halves.
(2) Each atom in the ring now represents a level associated with a molecular orbital. Those below the horizontal diameter represent bonding MOs and those above the horizontal diameter represent antibonding MOs.
(3) If the system is composed of an even number of atoms in the ring, the MOs obtained in this way are divided into equal number of bonding and antibonding orbitals. These are symmetrically distributed about a line drawn through the centre of the cyclic system.
(4) If the system contains an odd number of ring atoms, then there will be unequal numbers of bonding and antibonding orbitals.
(5) The circle may be omitted if only a qualitative treatment is required.

The scheme is illustrated below using cyclopropene, cyclopentadiene and benzene as examples.
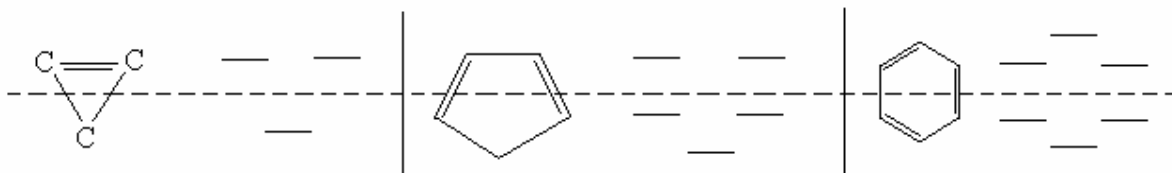

Stability of benzene – the concept of 'aromaticity'

Benzene is extremely stable for a molecule with three double bonds. The MO picture of benzene is as follows: There are six p-orbitals, one on each C-atom in the ring. These should lead to the formation of six MOs, three of them bonding and the remaining three antibonding. All the six electrons are accommodated in the three bonding MOs in pairs. The bonding orbitals are formed as shown in the figure:
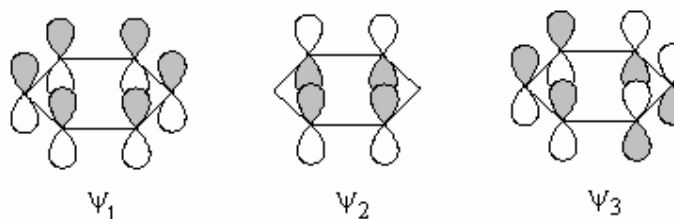

The lowest orbital ψ_1 encompasses all six C-atoms. Orbitals ψ_2 and ψ_3 are different in shape but have equal energy. Together, they also provide electron density over all C-atoms. The result is a highly symmetrical molecule with considerable delocalization of π-electrons. *There are no electrons in the antibonding orbitals. The bonding orbitals are all fully occupied.* This leads to a great lowering of energy of the system, which is usually called the resonance stabilization energy of the aromatic system. Benzene, with 6 π-electrons (n = 1) is the perfect example for an aromatic system.
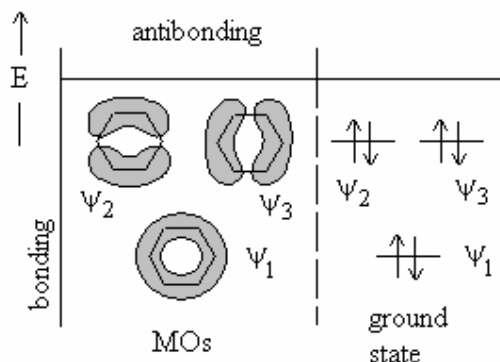
Thus, *a ring system having all the π-bonding orbitals completely filled, with no electrons in the antibonding orbitals will be highly stable. This is aromaticity according to MO theory. Such a system will contain 4n+2 π-electrons. This is the actual basis of Hückels rule*.

## Non-benzenoid aromatic systems

Cyclopropenyl cation
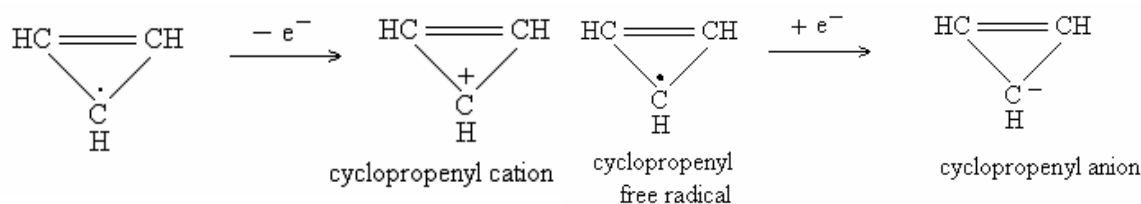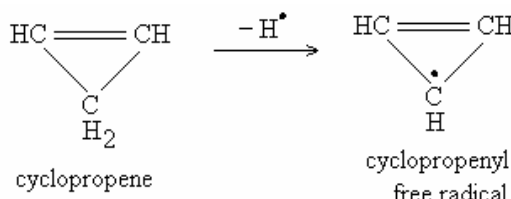
Resonance structures can be drawn for all these systems:
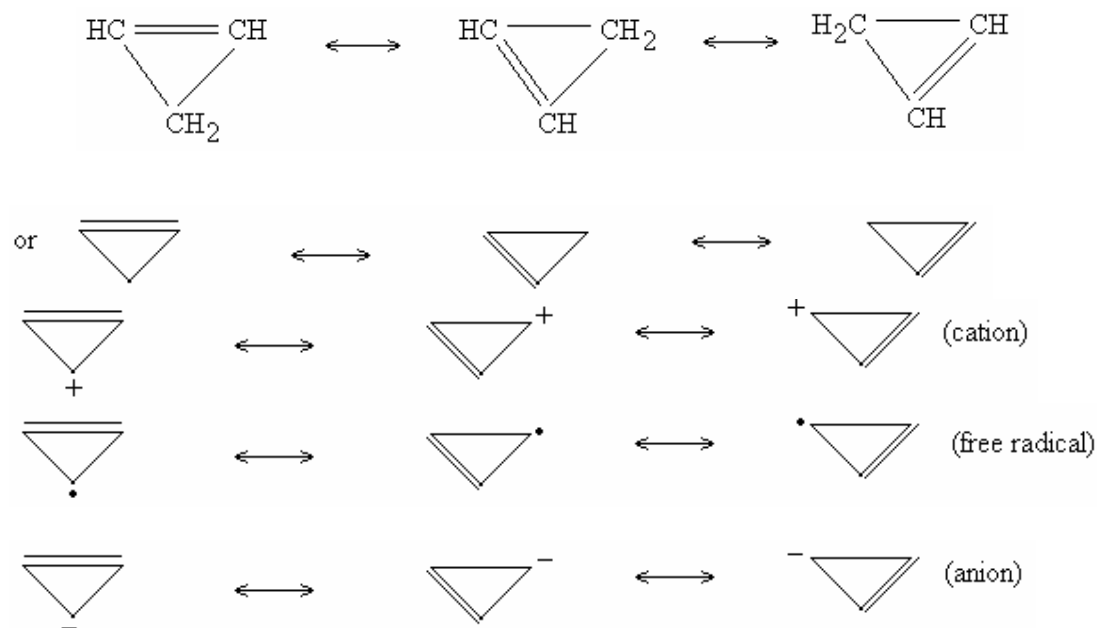
Yet, only the cation behaves as a stable aromatic system. The cyclopropenyl free radical and anion are not stabilized; in fact the anion is an exceptionally unstable system. *Therefore resonance alone cannot explain aromatic stability*. According to Hückel rules, the stability can be attributed to the two π-electrons present in the cation (n = 0). But the free radical with three π-electrons and the anion with four π-electrons cannot be aromatic.

7

A better understanding of the principles underlying the Hückel rules is provided by MO theory. Linear combination of three p-orbitals gives rise to a set of three MOs, out of which one is a bonding MO. The remaining two are **degenerate** (having the same energy) antibonding orbitals.
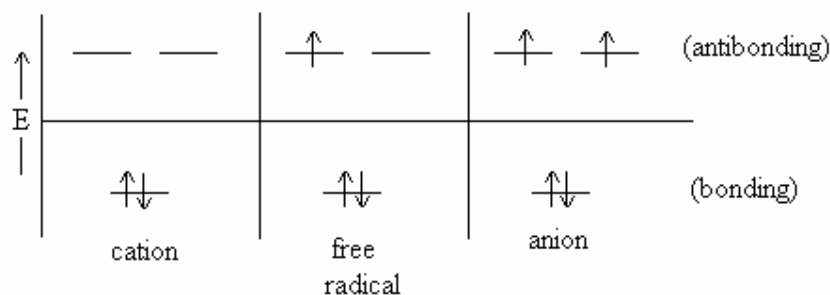
In the cation, there are only two π-electrons which go into the bonding MO. There are no electrons in the antibonding orbitals. The lowering of energy due to the electron pair in the bonding MO provides the stability or aromaticity. In the free radical, there is one additional electron in the antibonding orbital, tending to destabilize the system. In the cyclopropenyl anion, there are two electrons in the antibonding MO, which completely cancels the stabilizing effect of the electron pair in the bonding MO. Note that in the allyl system, the third and fourth electrons go into a **non-bonding** orbital, whereas in the cyclic system they go into **antibonding** orbitals. Thus the cyclopropenyl free radical and anion are much more unstable than their allyl counterparts.

Antiaromaticity

Calculations show that in the cyclopropenyl anion, the expected stabilization due to delocalization of electrons does not occur (ie. there is no resonance energy). It is in fact even less stable than unconjugated cyclopropene. Such *cyclic molecules in which delocalization of electrons lead to destabilization are called **antiaromatic systems***. More refined calculations predict that *monocyclic compounds that have **4n** π-electrons are antiaromatic* (less stable than the non-cyclic analogues). They are called "antiaromatic" because of their high degree of instability. The delocalization of electrons in antiaromatic systems result in an increase in energy and thus in a decrease in stability over the localized electronic configuration. Antiaromatic compounds have either unfilled bonding orbitals, or electrons in antibonding orbitals.

Cyclopropenyl anion (4 π-electrons), cyclobutadiene (4 π-electrons), cyclopentadienyl cation (4 π-electrons), cycloheptatrienyl anion (8 π-electrons), cyclooctatetraene (8 π-electrons) etc. are a few other examples for antiaromatic systems.

Other aromatic systems

These are ring systems similar to the cyclopropenyl cation, in which the anion or cation are more stabilized by resonance compared to the neutral molecule. Examples are the cyclopentadienyl anion, cycloheptatrienyl cation (also known as tropylium ion) and cyclooctatetraenyl dianion.

cyclopentadienyl anion
6 π-electrons (n = 1)

cycloheptatrienyl cation
(tropylium ion)
6 π-electrons (n = 1)

cyclooctatetraenyl dianion
10 π-electrons (n = 2)
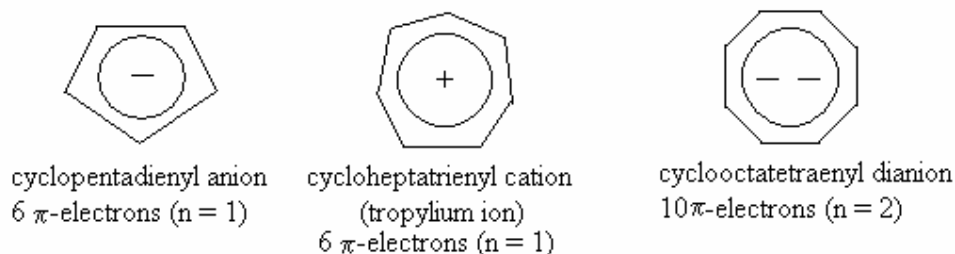
In the cyclopentadienyl system, linear combination of five p-orbitals give five MOs, three of which are bonding and the remaining two, antibonding.
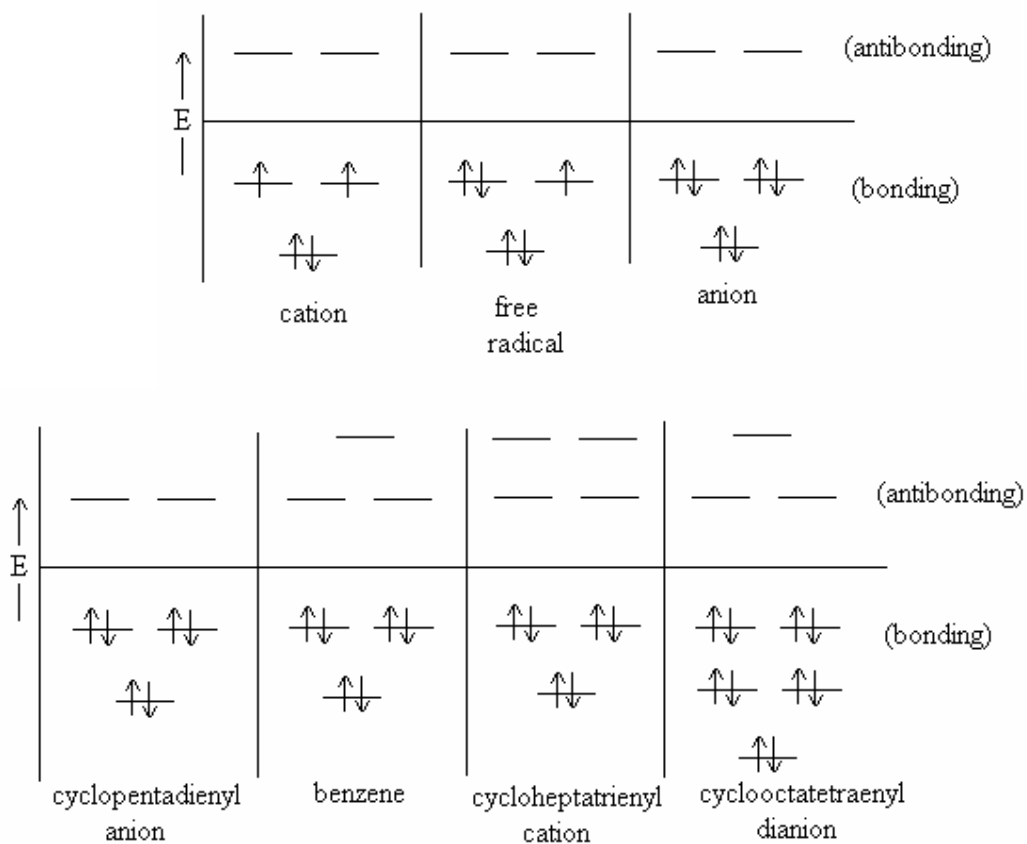

The cyclopentadienyl free radical has 5 π-electrons. Two of these go into the lowest bonding MO, and the remaining three occupy a pair of degenerate bonding MOs of slightly higher energy. There are no electrons in the antibonding MOs. Therefore the system is stable. The cation has only four π-electrons, all of which go into bonding MOs. In the cyclopentadienyl anion, there are six π-electrons, making the bonding MOs fully filled. When the bonding MOs are fully filled, there will be 4n+2 π-electrons. Thus the principle underlying Hückel's rule is to have a complete set of bonding MOs in a system with flat rings. Such an electronic configuration is compared to the inert gas electronic configuration in atoms.

All the ring systems discussed above have a single bonding MO at the lowest level, and a series of degenerate pairs above this. Those with full bonding MOs are aromatic.

Since the cyclopentadienyl anion is aromatic, cyclopentadiene exhibits a strong tendency to lose a proton and become the anion. *Thus cyclopentadiene is a fairly strong acid compared to other hydrocarbons or alkenes* (pKa = 15 for cyclopentadiene compared to 45 for cycloheptatriene) and can be deprotonated using potassium t-butoxide anion.
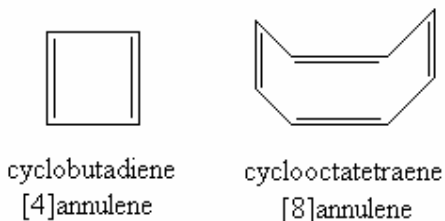
Mesoionic compounds
The cycloheptatrienyl cation (tropylium ion) is so stable as to form ionic halides, which is unusual for organic compounds. These compounds are known as mesoionic compounds. Eg. Tropylium bromide, C_7H_7Br, melts only above 200°C, is soluble in water but insoluble in non-polar organic solvents and gives an immediate precipitate with silver nitrate solution. All these indicate that it is a strongly ionic compound similar to NaCl or NaBr.
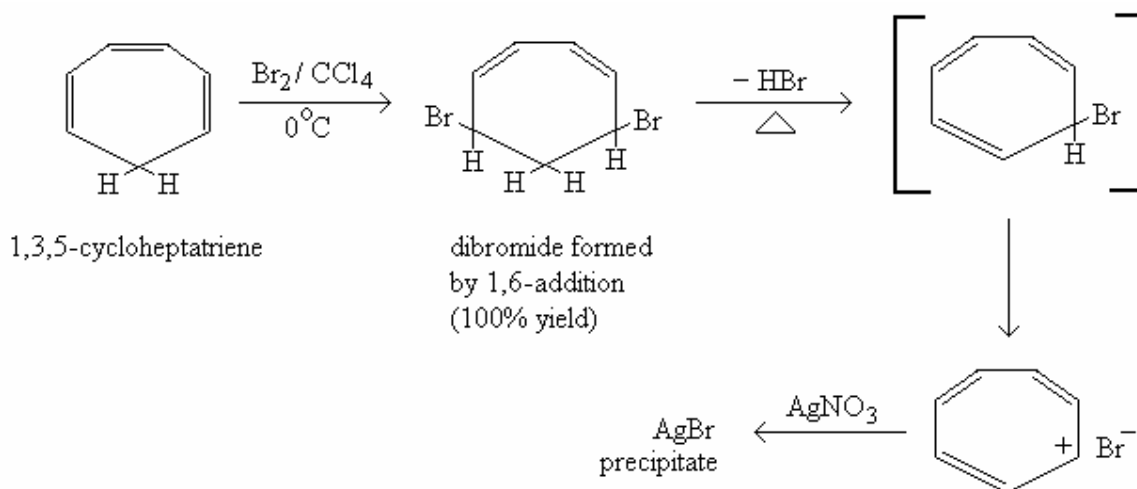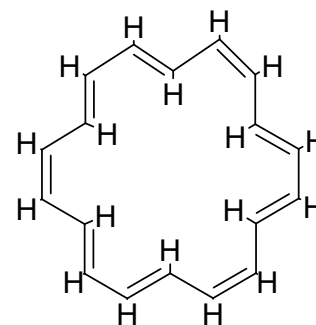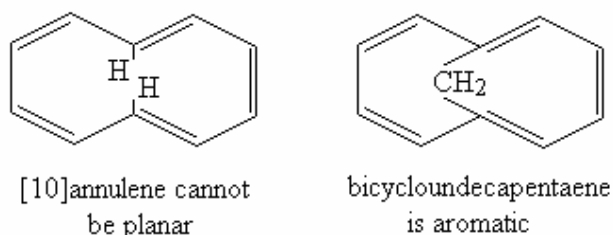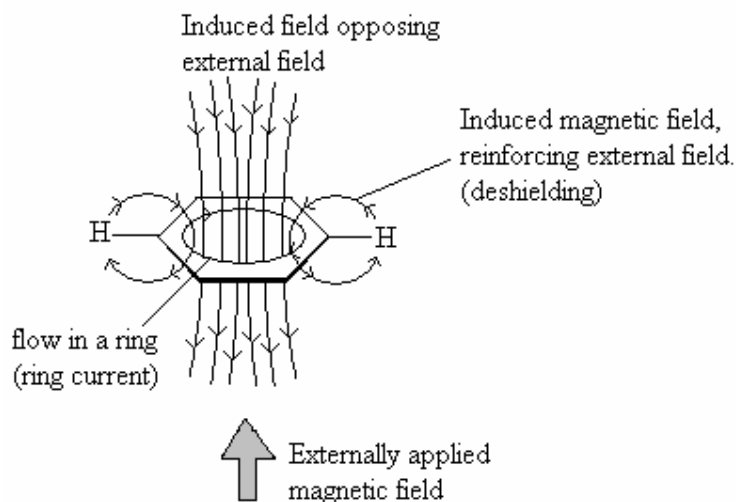
Aromaticity of annulenes

A good number of non-benzenoid large ring compounds having conjugate system of double bonds were synthesized and examined to test for aromatic character. These compounds are called annulenes. They are named according to the number of carbon atoms present in them, for example [10]annulene, [16]annulene, [18]annulene etc. **Cyclobutadiene** or [4]annulene has never been isolated, but has been detected by IR studies when it is generated at very low temperatures of about 4 K. Since it has only 4 π-electrons, it is expected to be antiaromatic and therefore unstable. **Benzene** is [6]annulene according to this system. **Cyclooctatetraene** or [8]annulene is non-planar (tub-shaped) and hence conjugation is not possible. A planar regular octagon must have a bond angle of 135°. In contrast, the dianion of cyclooctatetraene is planar and shows aromatic character. For example, cyclooctatetraene has two different bond lengths of 135 pm and 150 pm. But in the dianion, all bond lengths are equal, 141 pm.

cyclobutadiene [4]annulene   cyclooctatetraene [8]annulene

Larger rings with cis-double bonds cannot be planar because the bond angles required will be greater than 135°. However, trans double bonds are possible which may put H-atoms inside the ring, where they interfere with each other and prevent planarity unless the rings are sufficiently large. For example, although **[10]annulene** has 4n+2 π-electrons, it cannot be planar due to the steric repulsion between the two H-atoms inside the ring, and is therefore not aromatic. On the other hand, **bicyclo undecapentaene** with a similar structure, but with the steric hindrance removed, is found to be aromatic (10 π-electrons). **Only for rings consisting of 18 or more C-atoms is this steric hindrance removed**. None of these larger ring compounds have the stability of benzene, although some of them have the properties associated with aromaticity, such as resonance energy.


[10]annulene cannot be planar

bicycloundecapentaene is aromatic

10

Induced field opposing external field

Induced magnetic field, reinforcing external field. (deshielding)

flow in a ring (ring current)

Externally applied magnetic field

Aromaticity and NMR

A modern criterion of aromaticity for an unsaturated cyclic compound is the detection of a ring current by NMR spectroscopy. Benzene shows deshielding of the H-atoms which are pointing outwards from the ring. If there are H-atoms pointing towards the inside of the aromatic ring system (there are no such hydrogens in benzene), they are expected to be shielded. *The presence of a ring current evidenced by the shielding and deshielding of H-atoms based on their position inside or outside the ring indicates aromaticity.*

Cyclo octadecanonaene or [18]annulene, contains 18 π-electrons (4n+2, where n = 4). NMR spectrum of this molecule shows two kinds of H-atoms. 12 protons lie outside the ring. These are deshielded and absorb downfield. Because of the flat geometry, six H-atoms lie inside the ring and are shielded. These absorb upfield. Hence this molecule is aromatic. The 2:1 ratio of outside/inside protons make it easy to assign the NMR signals. The outside protons have a chemical shift δ of 9.3 ppm, which makes them even less shielded than those of benzene. On the other hand, the six inside protons have a *negative* chemical shift ($\delta = -3.0$), meaning that they appear to the *right* of the TMS peak. Thus the inside protons of [18]annulene are more than 12 ppm more shielded than the outside protons.


External Field
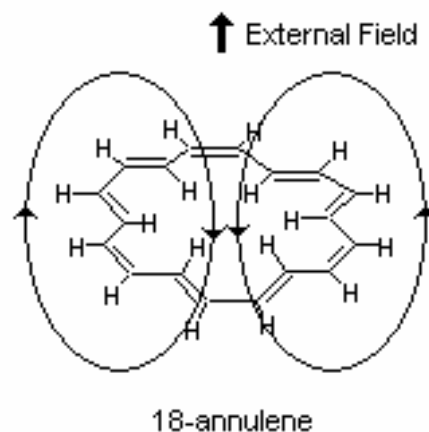
18-annulene

Cyclo hexadecanonaene or [16]annulene, contains 16 π-electrons (4n, where n = 4). Therefore it is antiaromatic. The ring current in this compound is in such a way that the outside H atoms are shielded and the inside H atoms are deshielded (opposite to that of aromatic compounds, indicating antiaromaticity). The 12 outside protons have a chemical shift δ of 5.3 ppm,

and the 4 inside protons have a chemical shift δ of 10.6 ppm,

Azulene, an isomer of naphthalene, is another example of a non-benzenoid aromatic compound. [Ref: 4].
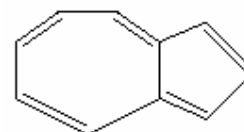
azulene
(aromatic)

**Homoaromaticity**: *This is a term used to describe systems in which a*
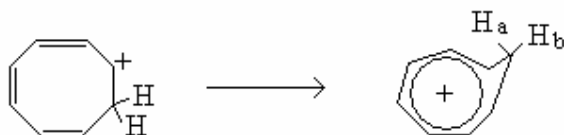
stabilized cyclic conjugated system is formed by bypassing one saturated atom. The properties of several such cationic species suggest that aromatic stabilization exists in them. The cyclooctatrienyl cation is an example.

11

A significant feature of the NMR spectrum of this cation is that the protons 'a' and 'b' exhibit sharply different chemical shifts. Proton 'a' is 5.8 ppm upfield of 'b', indicating the existence of an aromatic ring current. MO calculations also indicate that the homoconjugated structure is a good description of the cation and that there is a strong aromatic ring current.
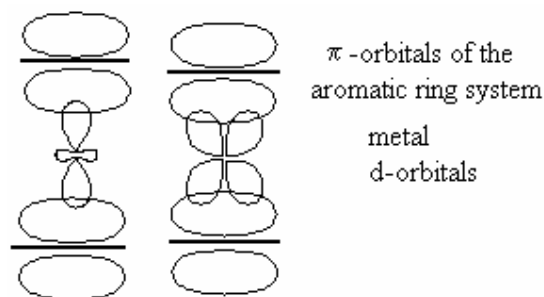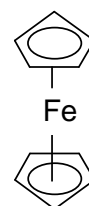
Pseudoaromaticity : Pseudoaromaticity is the aromaticity shown by non-benzenoid ring systems such as cyclopropenyl cation, cyclopentadienyl anion etc.

Metallocenes - Ferrocene

Cyclopentadienyl anion is so stable that cyclopentadiene is a comparatively strong acid (compared with other hydrocarbons; not with carboxylic acids or phenols).

(for cycloheptatriene, $K_a = 10^{-45}$)
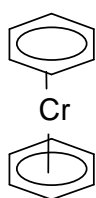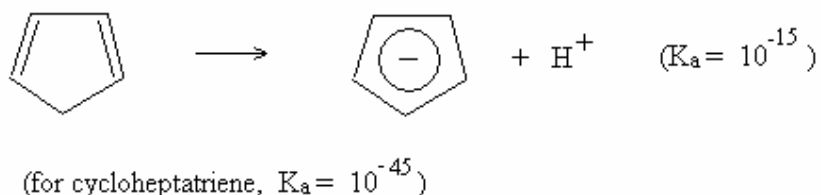
Iron salt of cyclopentadienyl anion, called **ferrocene** or **dicyclopentadienyl iron**, is a stable "sandwich" compound, with the Fe^{2+} ion between two cyclopentadienyl rings. Ferrocene undergoes two typically aromatic reactions, namely sulfonation and Friedel & Craft's reaction. In this compound, **the d-orbitals of the iron atom overlap with the π-bond system of cyclopentadiene**. Such compounds are therefore called π-complexes. Another example is dibenzyl chromium.

π -orbitals of the aromatic ring system

metal d-orbitals

Bonding in metallocenes