

Molecular Orbitals of Common Functional Groups

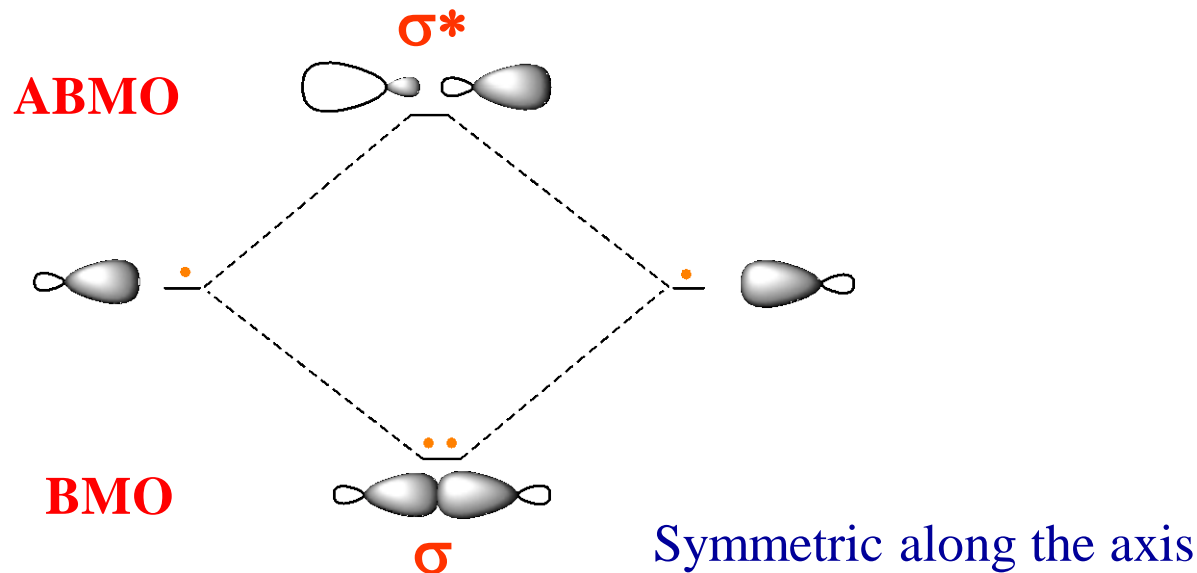
Introduction

In this module, a broad and qualitative overview of basic molecular orbital (MO) theory is provided. The simplified picture of MO for some standard functional groups are emphasized. The concept of node in the context of MO and its effect on the energy levels of these MOs are also given.

The objective of this module is to provide important molecular orbitals of conjugated olefins, which are typically used in the discussion of cycloaddition and other pericyclic reactions. Understanding of orbital symmetry rules demands a prior knowledge of molecular orbitals.

In addition, molecular orbitals are very useful toward understanding reaction mechanism, such as the direction of approach of the nucleophiles, stereochemistry of elimination reactions and many more situations. Conformational features, stability of reactive intermediates etc., can also be explained by using molecular orbital theory concepts.

Sigma Orbitals



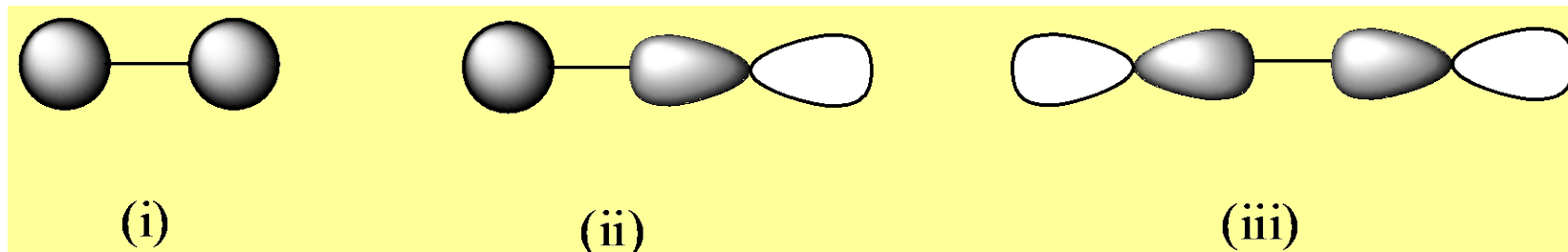
For any bonding molecular orbital (BMO) there should be a corresponding antibonding molecular orbital (ABMO)

The shading of the above orbitals that are overlapping shows that they are 'in-phase' for bonding orbital formation

In the anti-bonding orbital out-of-phase combination of participating orbital occurs

Note: BMO is toward the internuclear direction while ABMO is away from the internuclear direction

More on sigma orbitals



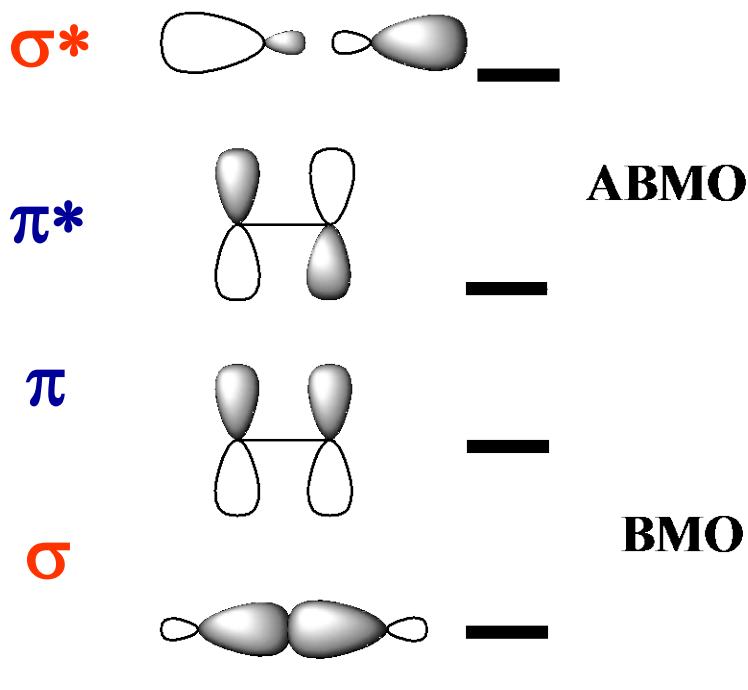
σ

σ -type overlaps contain **no nodes** along the **internuclear axis**.

Symmetric along the axis

Note that the word 'type' refers to the symmetry relation. For example, orbital as shown in (i) does not change its sign when it is rotated along the internuclear axis (horizontal axis passing through both the nuclei in this picture). Similarly, (ii) and (iii) also doesn't change the sign. Hence, there are orbitals are exhibit similar symmetry features as that of a pure sigma bonding molecular orbital. Hence, these are termed as sigma-type orbitals

Types of Orbitals: Ethylene

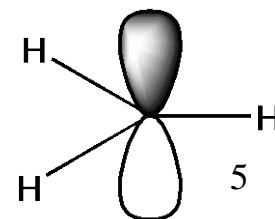


Note: π -orbitals are formed by the lateral overlap between p-orbitals centered on two adjacent atoms



Note: Nonbonding orbitals are orbitals centered on atoms, but it doesn't interact with other atomic orbitals. When a molecule is formed by the linear combination of atomic orbital (LCAO), the atomic orbitals that are left free are also called nonbonding molecular orbital. Term non-bonding is used simply because those orbitals are not bonding

Nonbonding orbital: e.g., p_z -orbital (AO) on BH_3



Types of Orbitals: BH_3

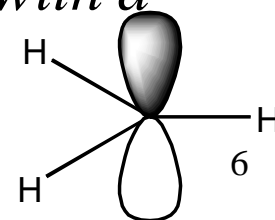
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It is important to notice that these are orbitals that appear in the frontier region (higher energy or leading (frontier) orbitals) of a molecule. Hence the influence of these orbitals on the properties/reactivities of these molecules are high.

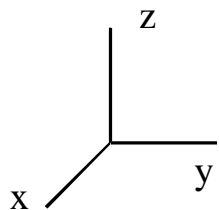
For instance, the nonbonding orbital on BH_3 renders Lewis acid features to the molecule.

Non-bonding Mos are denoted by small letter *n* usually with a subscript conveying on which atom it is located.

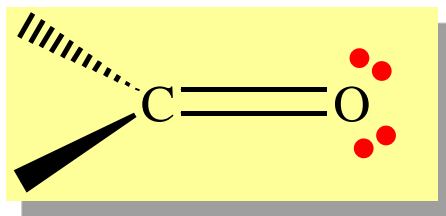
Nonbonding orbital: n_{B} on BH_3



Types of Orbitals: Formaldehyde



In xy-plane

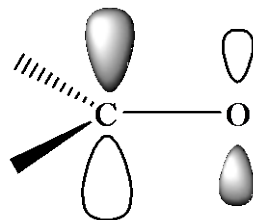


Frontier MOs

Nonbonding MOs

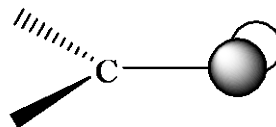
Hold the lone-pair
electrons

π_{CO}^*

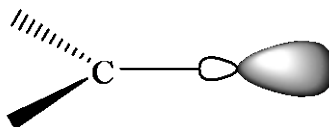


Empty levels

n_O

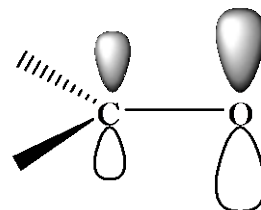


n'_O



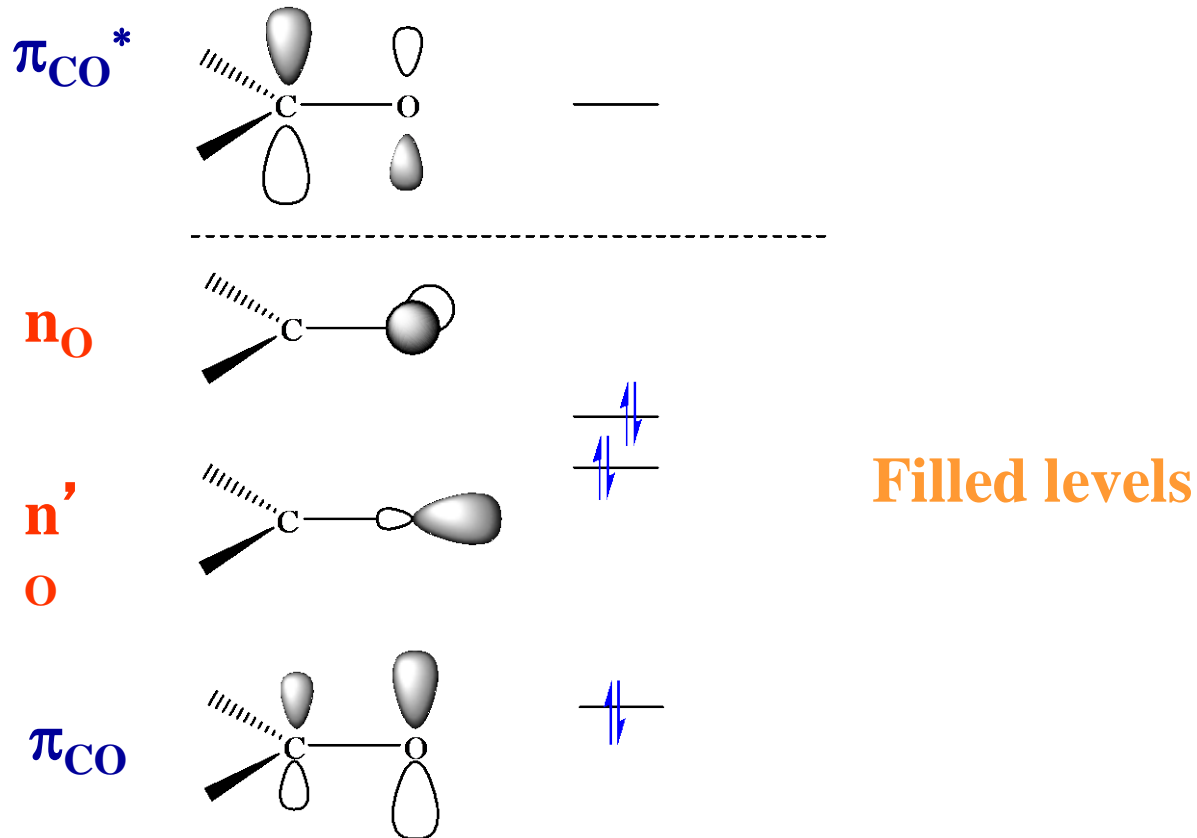
Filled levels

π_{CO}



Description of Orbitals

Nonbonding MOs
Holds the lone-pair
electrons



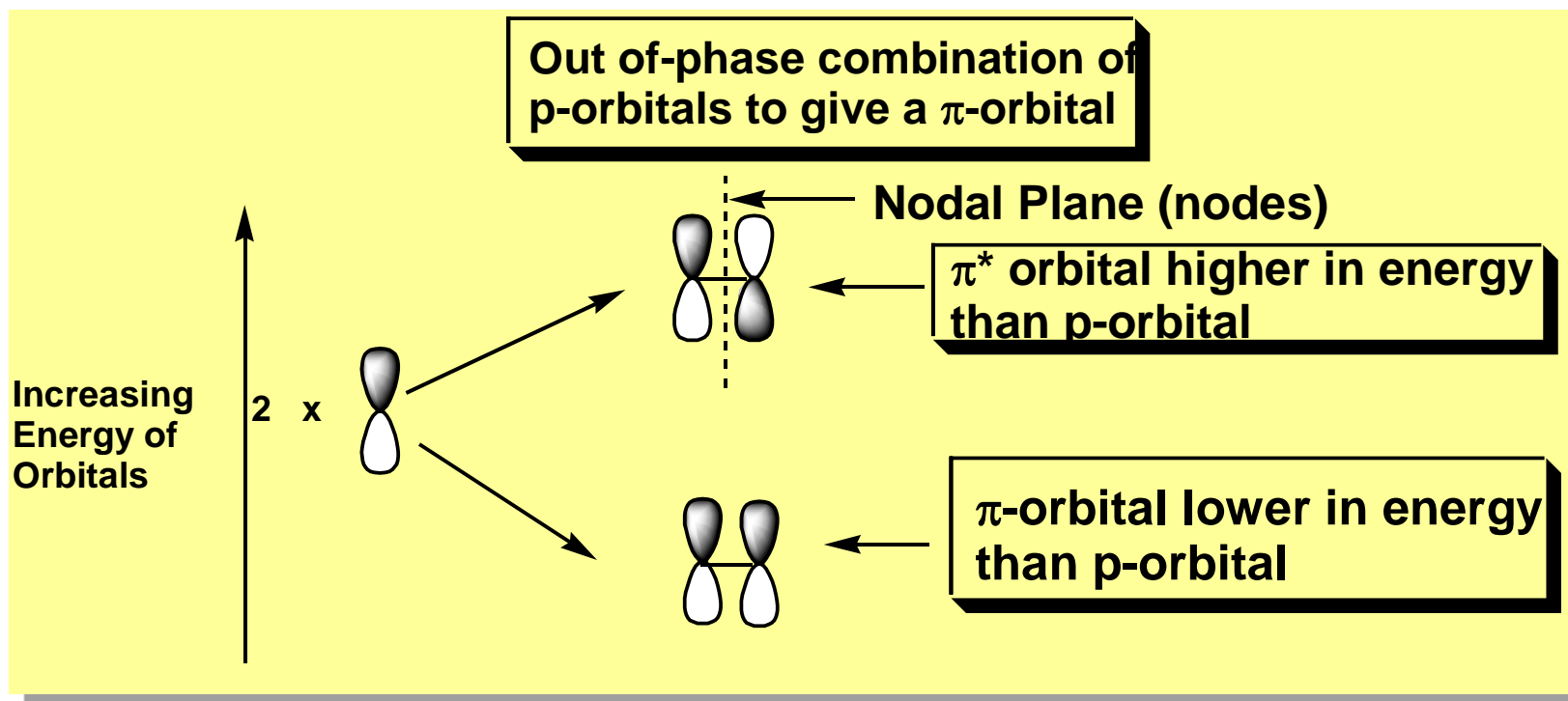
Here, both n_O and n'_O are non-bonding MOs. Careful examination would reveal that the lower lying NBMO is aligned along the C-O bond while the higher lying is perpendicular, but in the plane of the molecule. These NBMOs are therefore not of same energy (non-degenerate).

Ethylene MOs

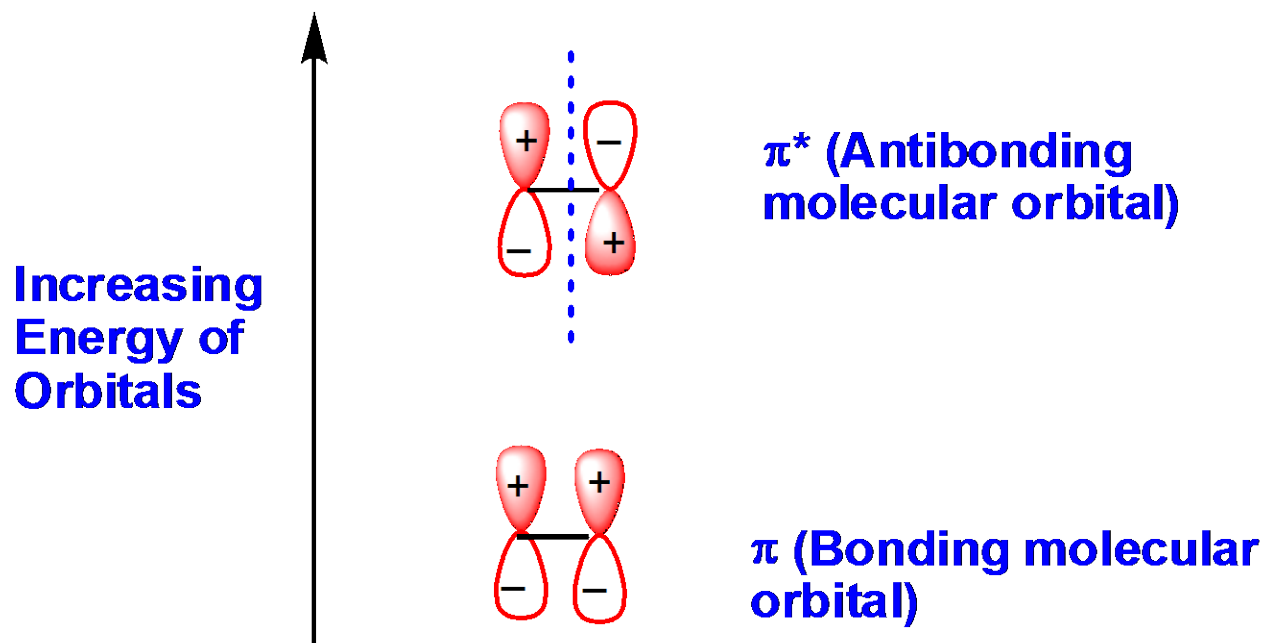
Ethylene shows interesting properties due to the presence of a π -bond

The C-C π -orbital is the **Highest Occupied Molecular Orbital (HOMO)** of the alkene

Linear Combination of p -orbitals, leading to C-C π -orbital can be represented as,



Ethylene MOs



Total Number of π -electrons = 2

Total Number of π -orbitals = 2

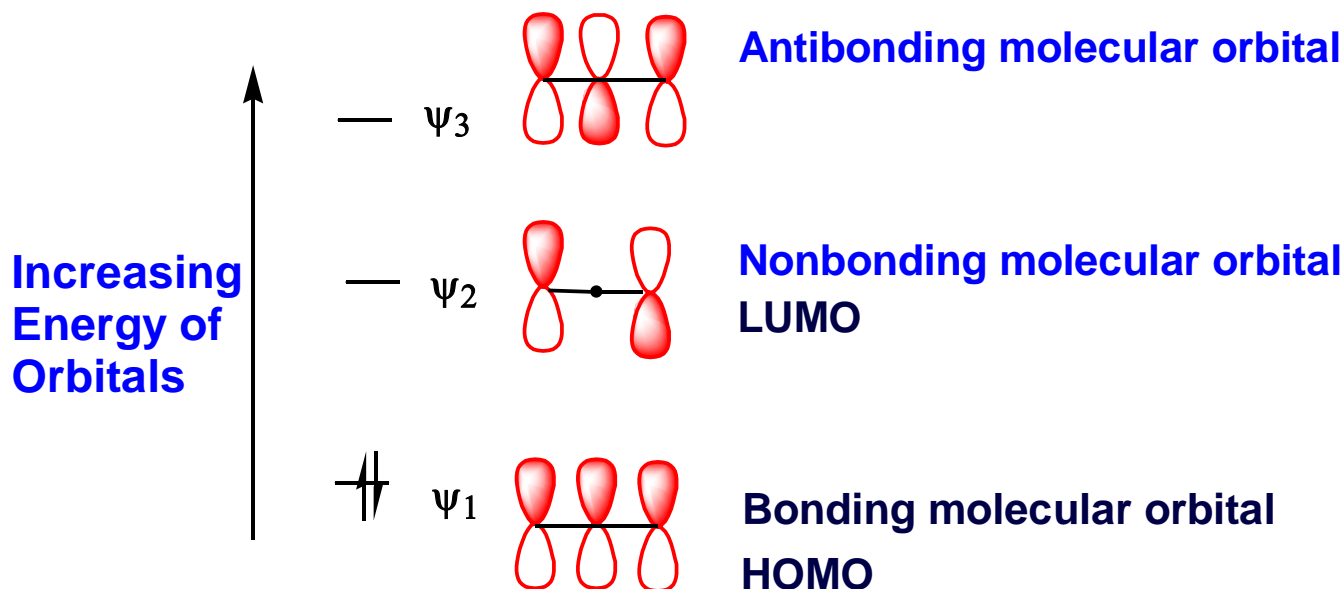
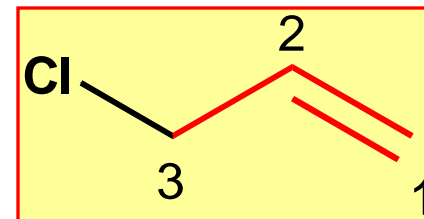
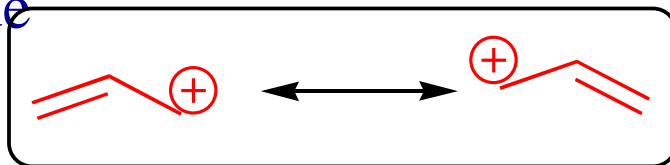
Both electrons will occupy the lowest energy MO, i.e., BMO

The blue dotted-line shown in ABMO is a nodal plane. Presence of a node in a MO will increase the energy of the corresponding MO. [The concept of node is comparable to the meeting point of a crest and a trough, used in the representation of a wave]

How about MOs for allyl system?

Allyl (three carbon conjugated system)

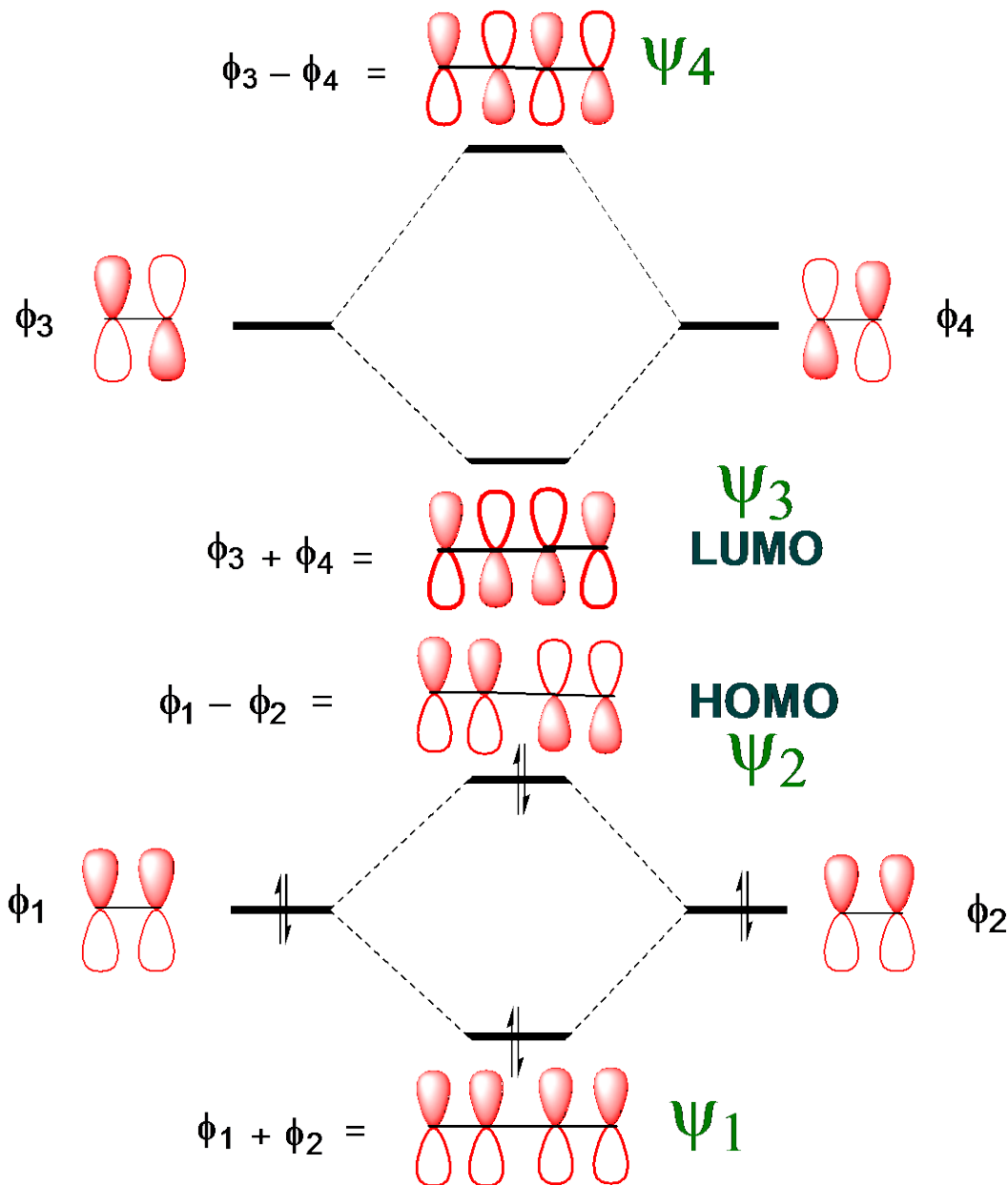
E.g., Allyl chloride



Note that the LUMO of this molecule has a node passing through the second carbon atom. The number nodes increase by one in the MOs of a linear conjugated system. There is no alternative way of placing a node other than having no contribution from the second carbon

Can we construct butadiene MOs?

The molecular orbitals of butadiene is a good example to shown that the energy of the MO increases with the number of nodes



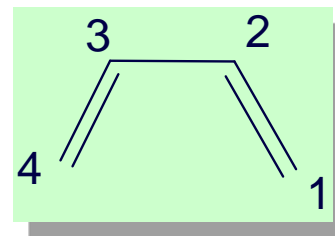
LUMO is lower in energy than the LUMO of ethylene

HOMO is higher in energy than the HOMO of ethylene

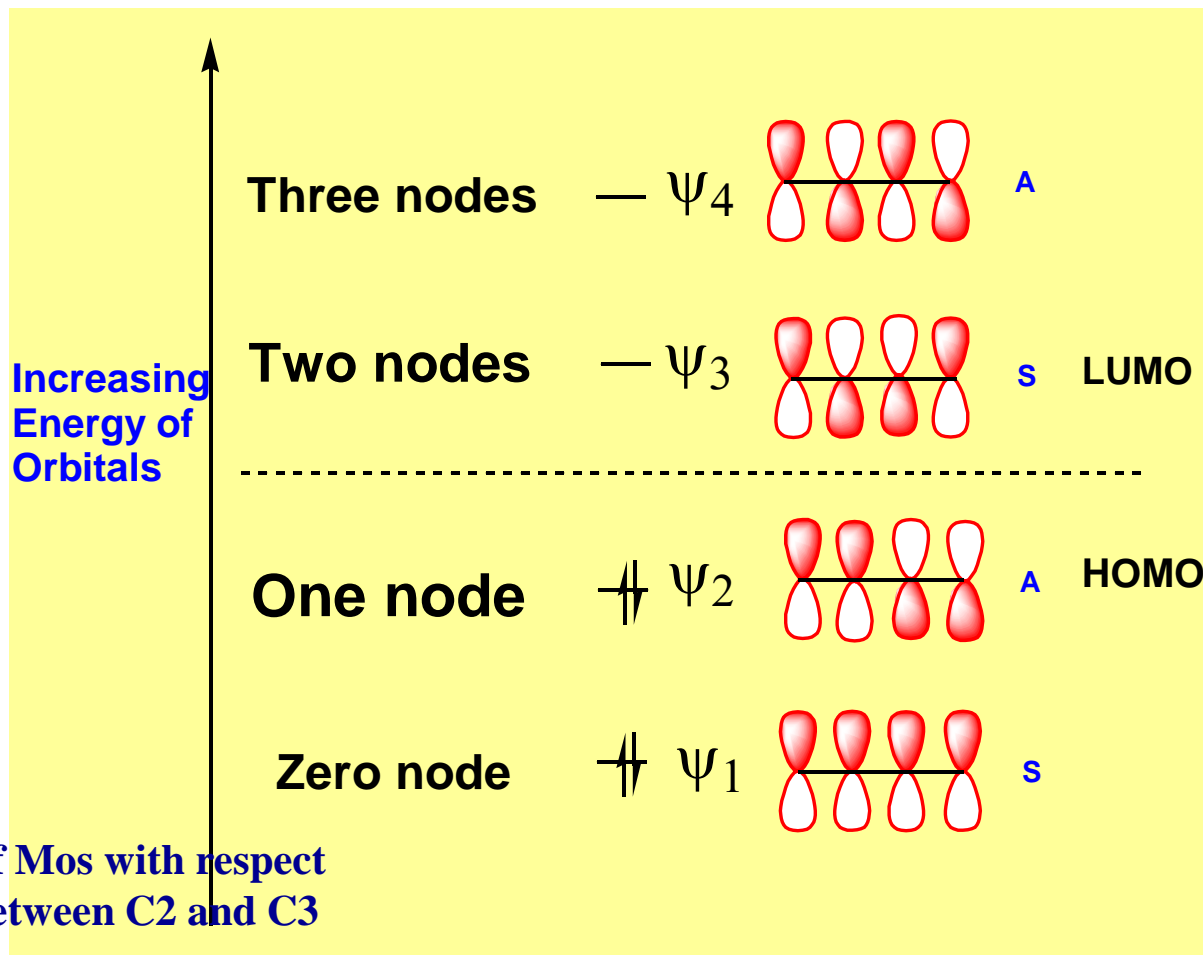
Butadiene MOs

Total number of π -orbitals = 4

Total number of π -electrons = 4



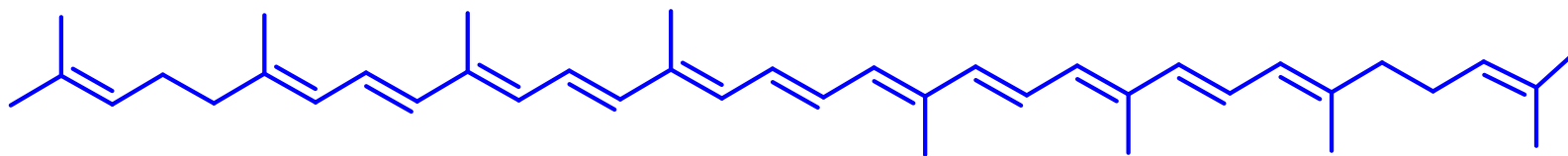
Butadiene is more reactive than ethylene



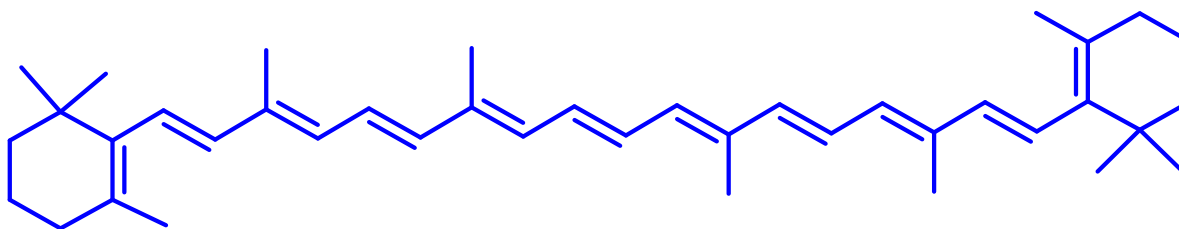
A and S are symmetry properties of MOs with respect to the plane of symmetry present between C2 and C3 carbon in s-cis geometry

Extended Conjugation and Colour (E.g. 1)

If the conjugation is extended further, the gap between HOMO and LUMO will decrease to allow the compound to absorb visible light and hence would become COLOURED.



Lycopene, the red pigment present in tomatoes and other berries



β -carotene, the red pigment present in carrots and other vegetables

Generalizations for acyclic polyenes

The lowest energy orbital is always symmetric with respect to the principal mirror plane

The number of nodes increases by ONE on going from one orbital to the next higher energy orbital

Nodes must be symmetrically located with respect to the central mirror plane

In systems with an odd number of atoms, the antisymmetric levels always have a node at the central carbon atom.

π Molecular Orbitals of Benzene

