Molecular Orbitals and Huckel Theory For Conjugated Systems

In this topic we will discuss

- What are Molecular orbitals? How are they formed? HOMO and LUMO? Why MOT?
- About empty cups and FMO approach
- How to construct MO diagrams of conjugated polyenes?
- How to calculate the energy of MOs of polyenes?
- Huckel Theory for conjugated systems
- Stability of Benzene
- Aromaticity and its effect on properties
- How do we use MOs for rationalizing and predicting the course of organic reactions?

Wave nature of electrons

- **Dual nature : Particle (Charge, mass), wave (diffraction)**

- **Quantum mechanics invokes that in submicroscopic world, there is no real distinction between particles and waves.**

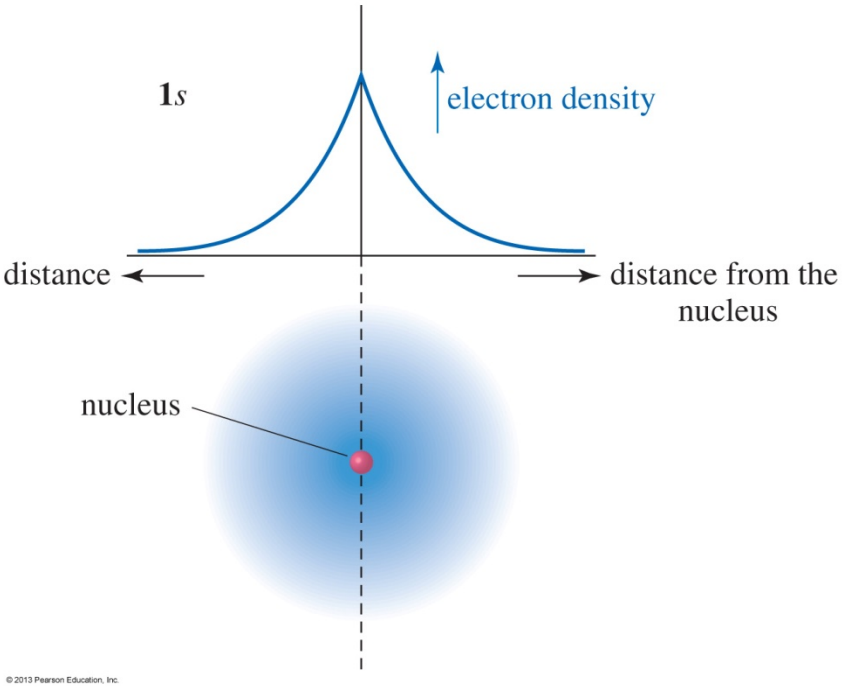
- ***Heisenberg's uncertainty principle***
  The exact position and momentum of the electron cannot be specified; only the probability of finding an electron in a certain region of space can be specified.

- **An atomic orbital is a three-dimensional region around the nucleus where there is a high probability of finding an electron. It is a description of wave properties of electron in an atom. It is described by a mathematical function called *a wave function* (ψ).**

Electronic Structure of the Atom

- **An atom has a dense, positively charged nucleus surrounded by a cloud of electrons.**

- **The electron density is highest at the nucleus and drops off exponentially with increasing distance from the nucleus in any direction.**



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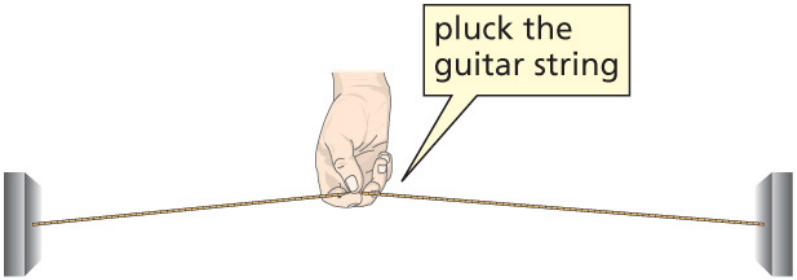
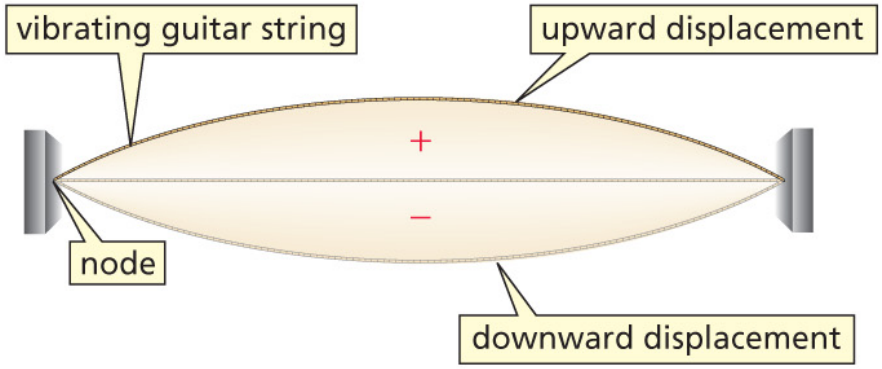
A Standing Wave



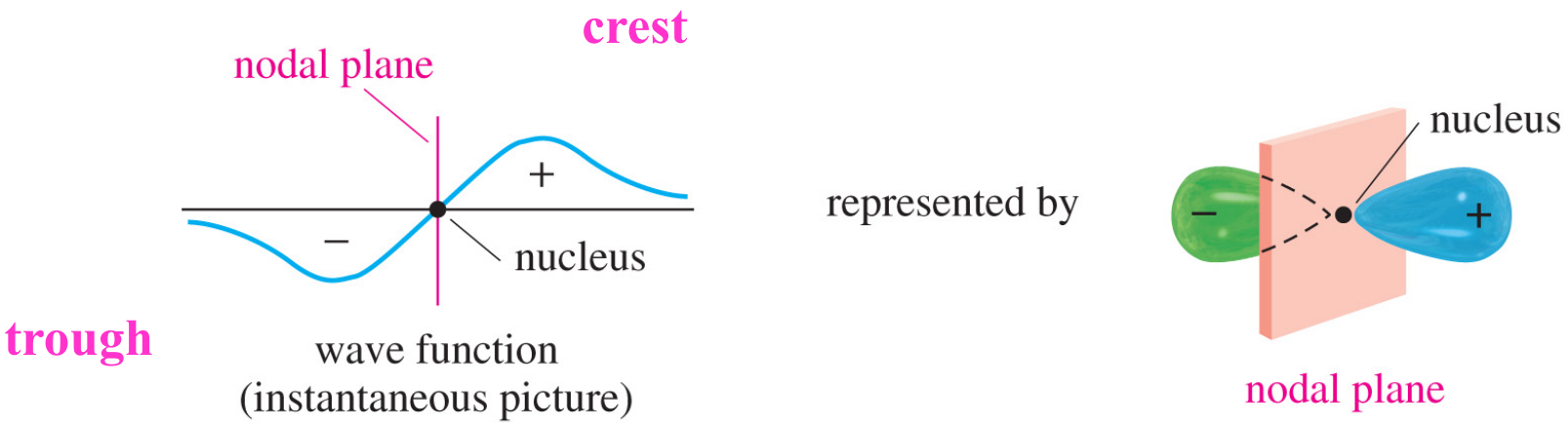
peak/ crest



trough

Electron behaves like a standing wave
But it is more like a 3 Dimensional surface

Wave Properties of Electrons/Orbitals



- **Standing wave vibrates in fixed location.**
- **Wave function, ψ, is a mathematical description of size, shape, and orientation.**
- **Amplitude may be positive or negative.**
- ***Node*: Amplitude is zero.**
- **(+) & (–) do not indicate charges but just the phase**
- **ψ^2 denotes the electron density probability.**

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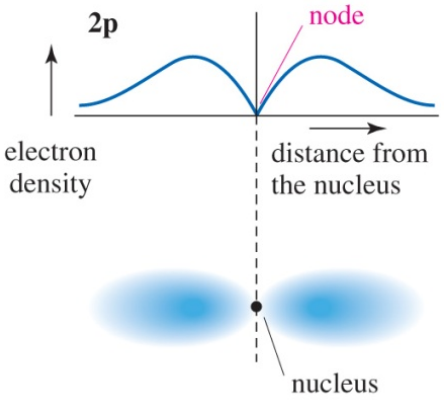
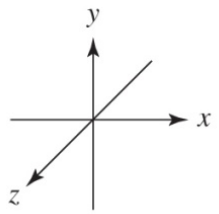
The 2*p* Orbitals

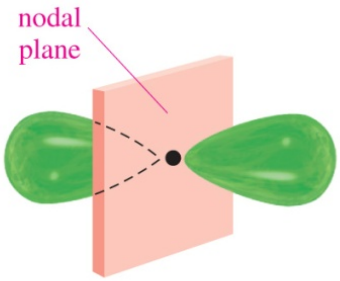
computer-generated 2*p* atomic orbital

- There are three 2*p* orbitals, oriented at right angles to each other.
- Each *p* orbital consists of two lobes.
- Each is labeled according to its orientation along the *x*, *y*, or *z* axis.

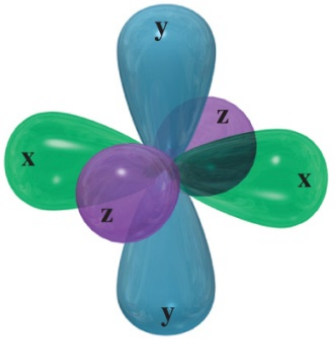




directions of axes
(*z* comes out toward us)



the $2p_x$ orbital



the $2p_x$, $2p_y$, and $2p_z$ orbitals superimposed at 90° angles

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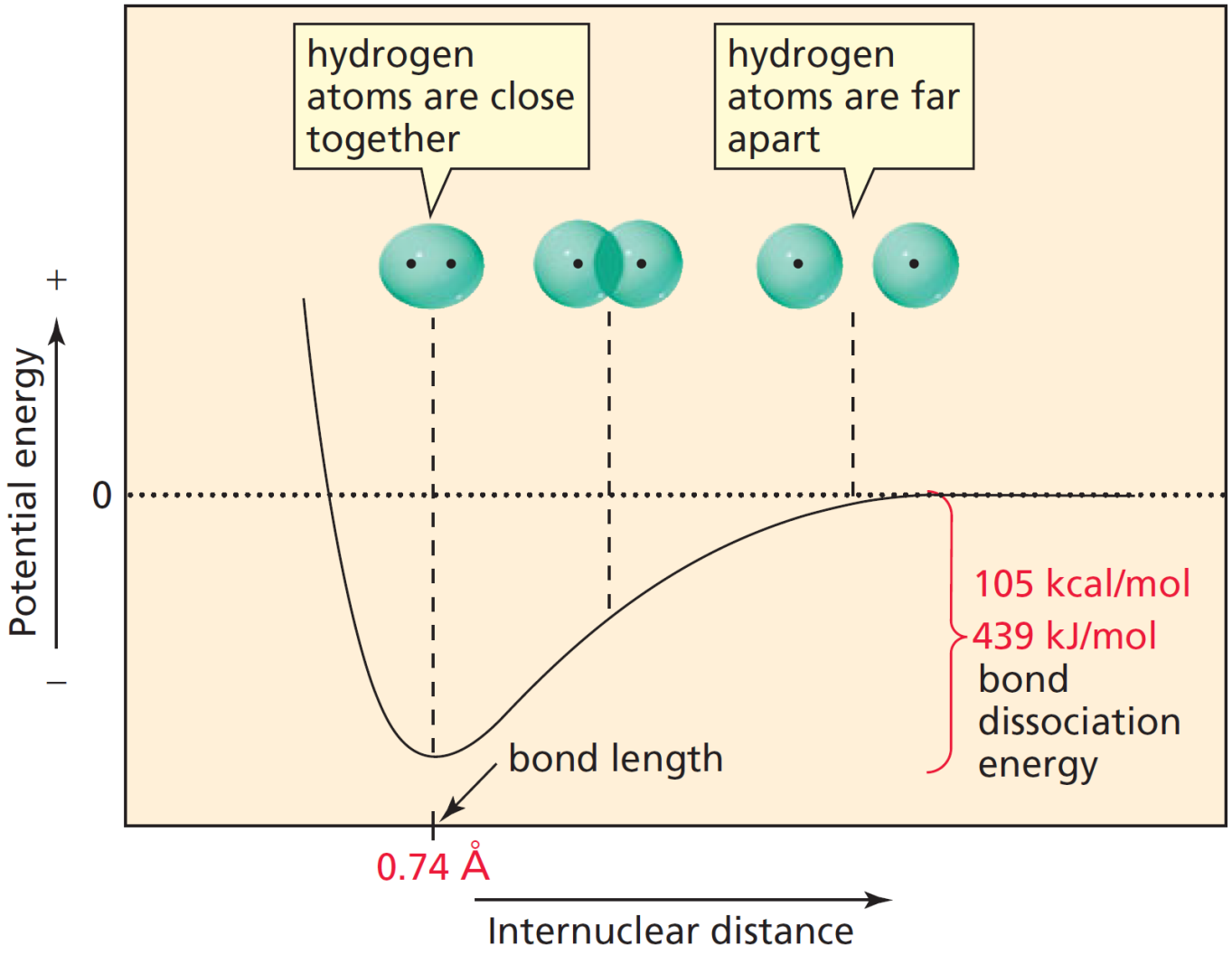
Molecular Orbital Theory

- How a covalent bond is formed?
- The Lewis model treats electrons like particles and not like waves
- MOT combines their wave like properties and the tendency to complete the octet by sharing electrons – complete picture
- Covalent bonds form when AOs combine to form MOs

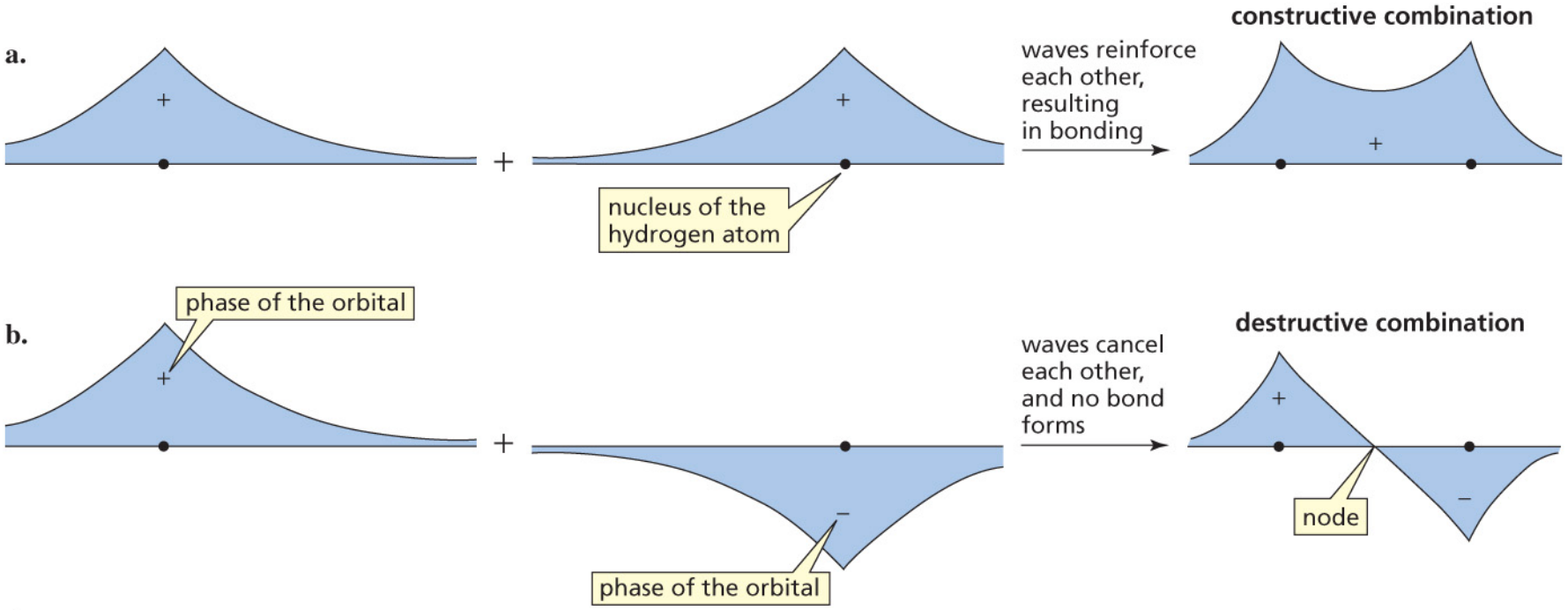
Linear Combination of Atomic Orbitals

- **Combining orbitals on the same atom is *hybridization*.**
- **Combining orbitals between two different atoms is *bond formation*. – M. O. Theory**
- **Molecular orbitals are formed by LCAO**
- **MOs belong to the whole molecule**
- **MOs have specific sizes, shapes & energy**
- **Conservation of orbitals – 2 AOs give 2 MOs**
- **Waves that are in phase add together. Amplitude increases.**
- **Waves that are out of phase cancel out.**

MO Theory : H_2 molecule

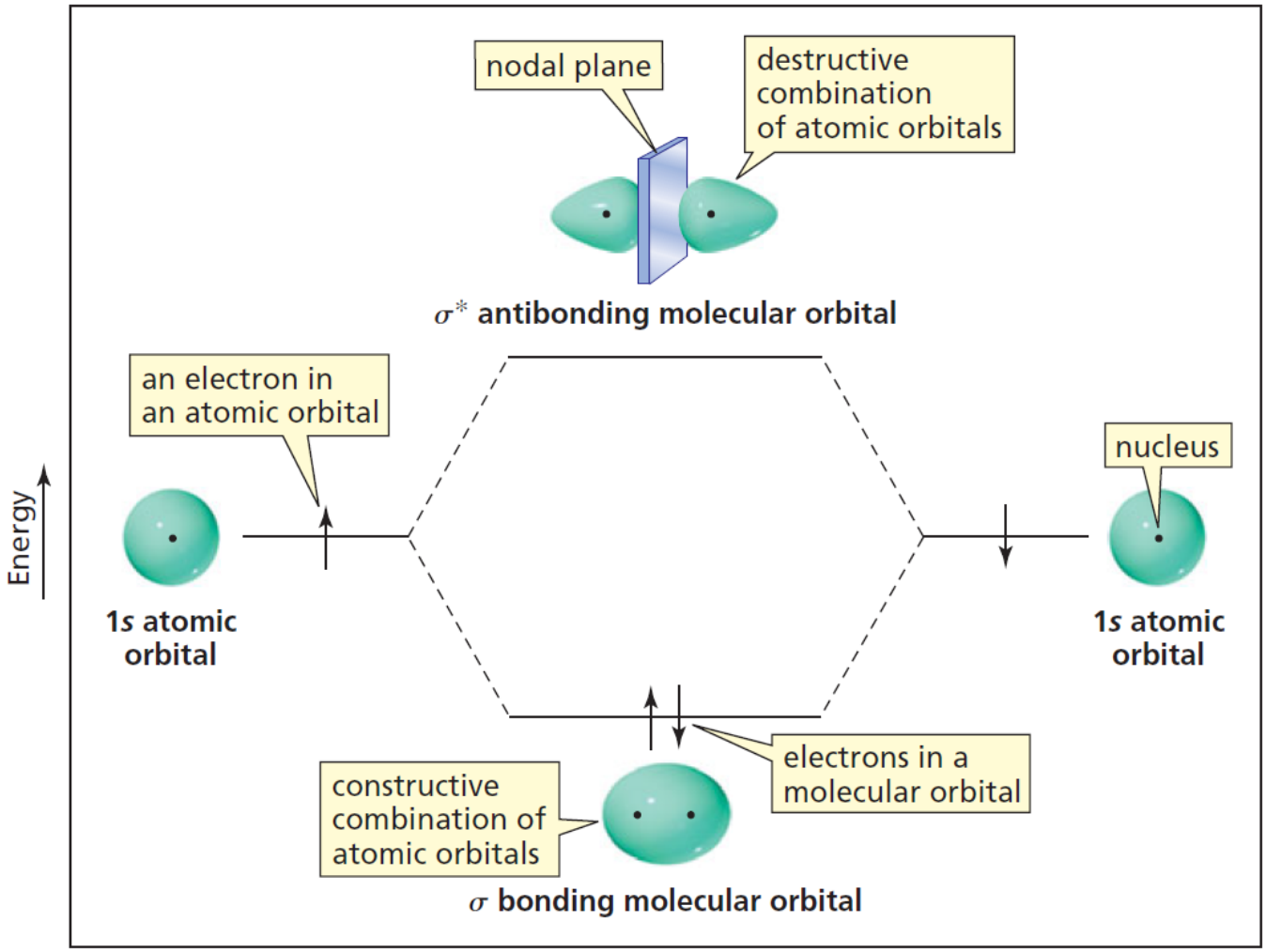


Waves Can Reinforce Each Other; Waves Can Cancel Each Other



Constructive combination = bonding
Destructive combination = antibonding

Molecular orbitals of H_2



Electrons are assigned based on aufbau principle, Pauli exclusion principle and Hund's rule. Lowest energy first and no more than two electrons per MO

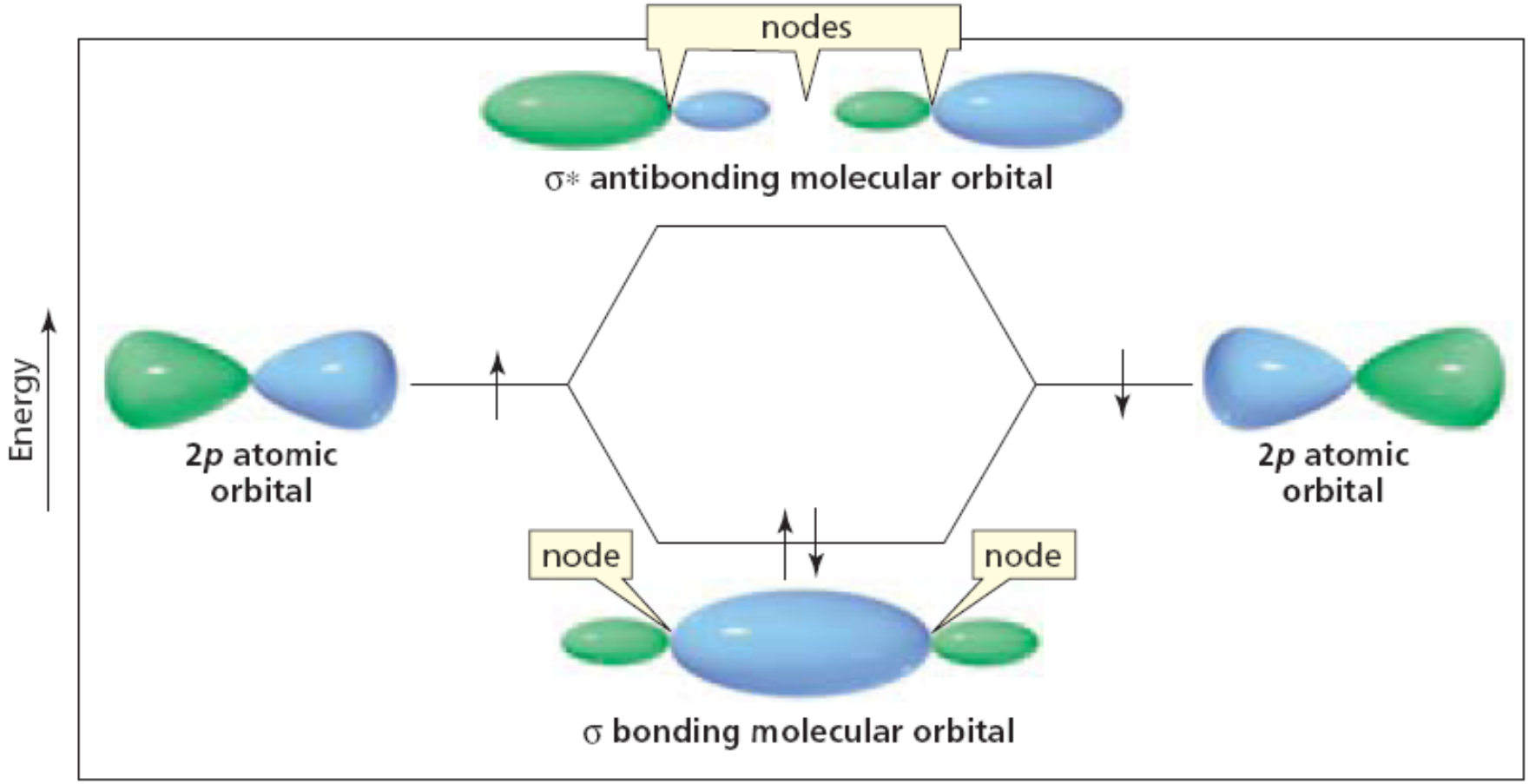
Bonding and antibonding orbitals

Electrons in a Bonding MO assist in bonding – Bond formation

Electrons in an antibonding MO detract from bonding – Bond breaking

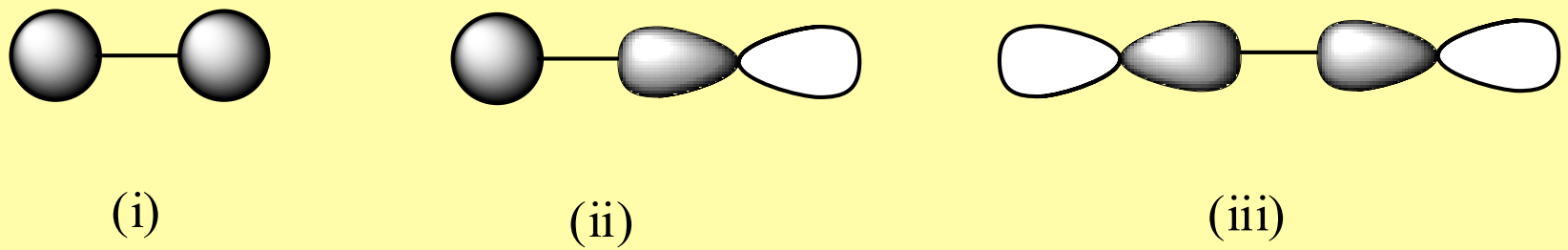
Covalent Bond strength increases as the atomic overlap increases

End on overlap of two p AOs



Sigma bonding MO are cylindrically symmetrical i.e. along inter-nuclear axis

More on sigma orbitals

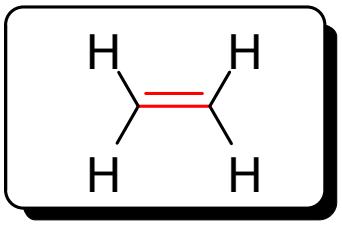


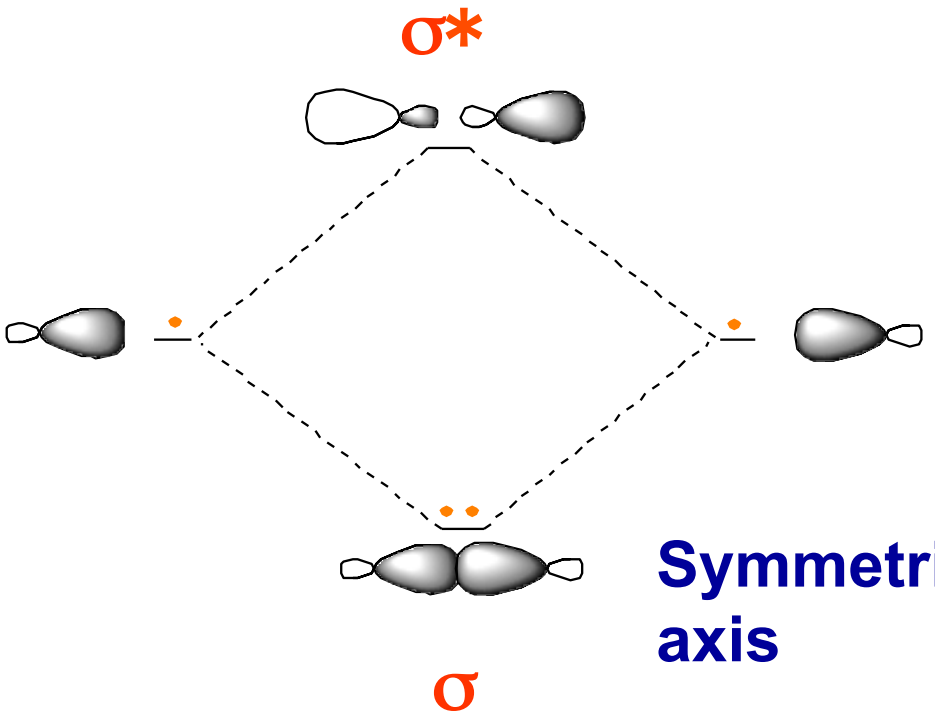
σ

sigma-type overlaps contain no nodes along the internuclear region/axis.

Symmetric along the axis

Orbital Symmetry in ethylene





Symmetric along the axis

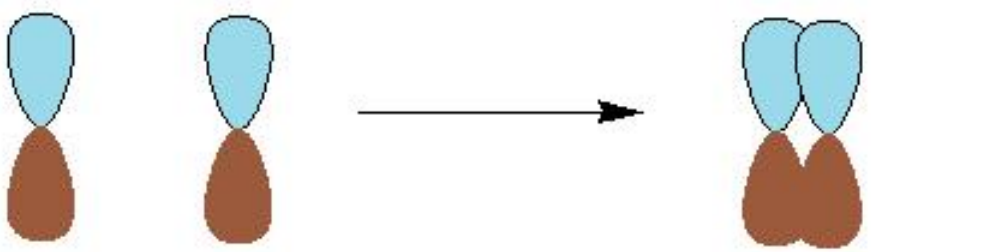
For any bonding molecular orbital (BMO) there should be a corresponding antibonding molecular orbital (ABMO)

Because the π-bonding portion of a molecule is perpendicular to the σ-bond framework, the π-bonds can be treated independently.

Types of overlap between orbitals

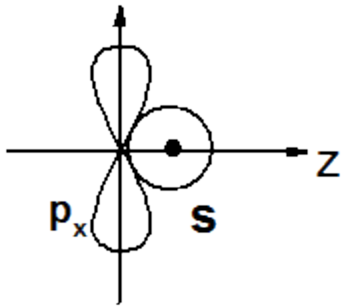
lateral overlap of atomic orbitals

(iv)

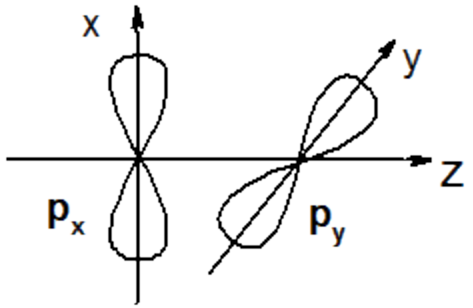


p-p orbitaloverlapping

Sideways overlapping of p orbitals produces a pi covalent bond



No overlap between s and P_x



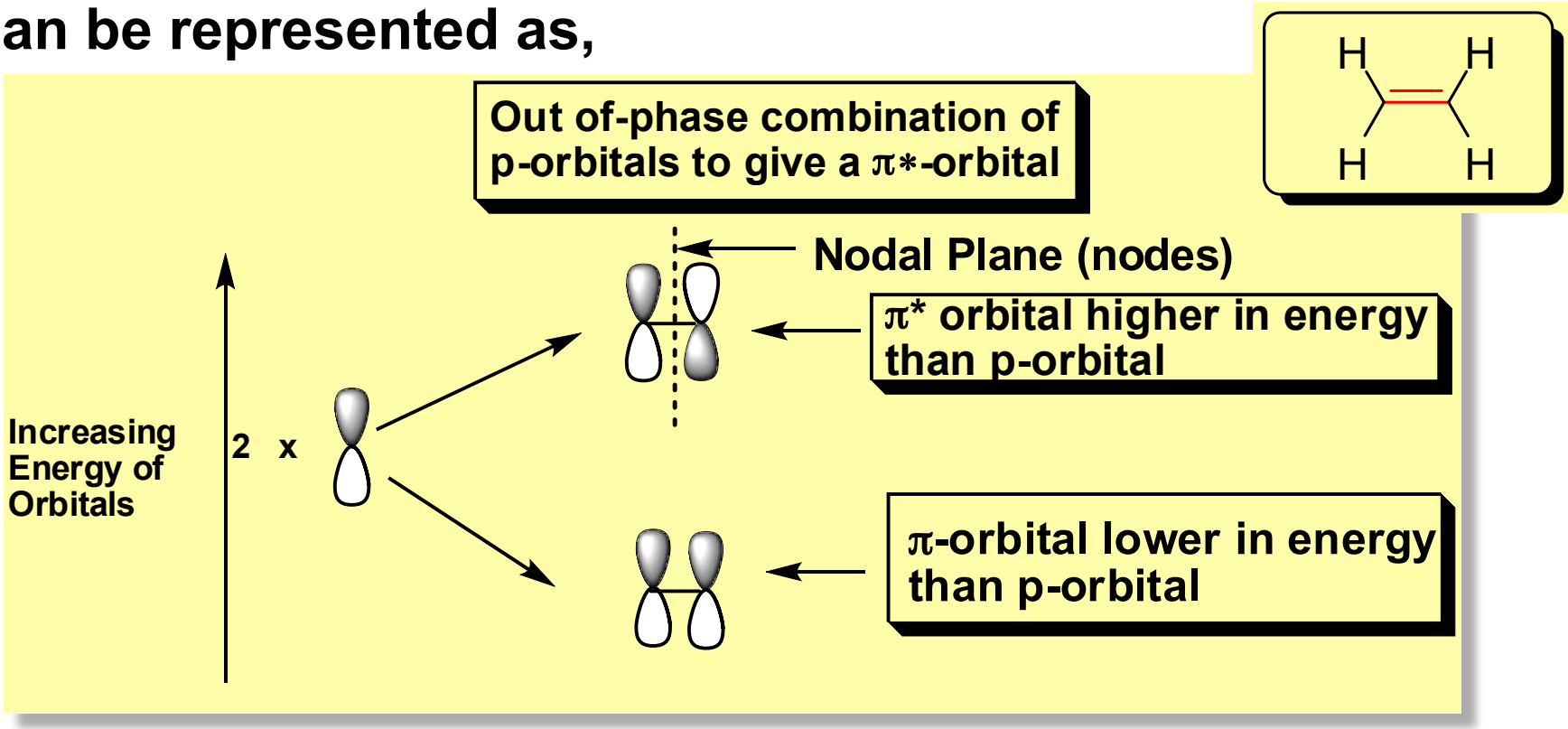
No overlap between P_x and P_y

Ethylene MOs

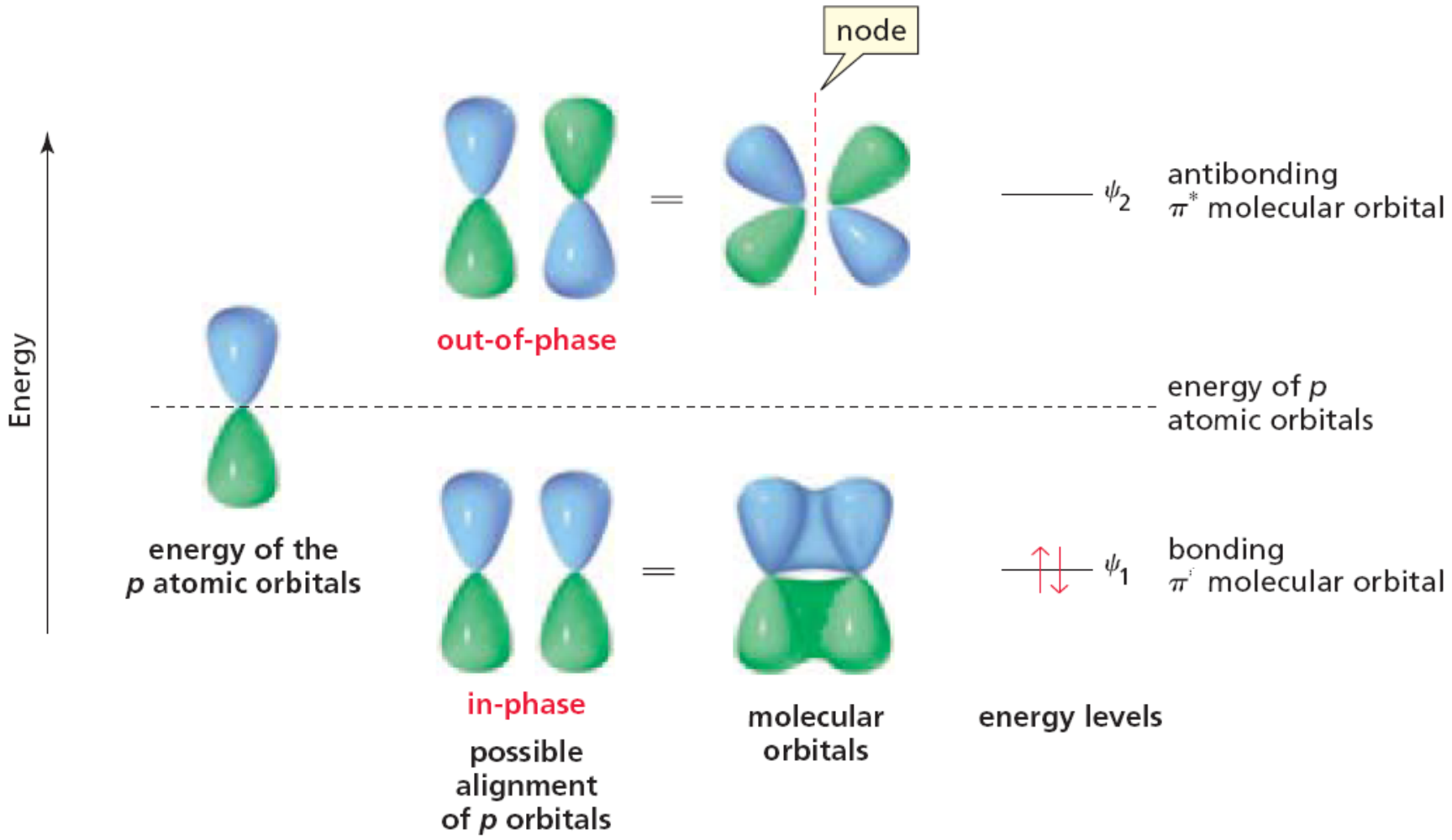
Ethylene shows interesting properties due to the presence of a π-bond

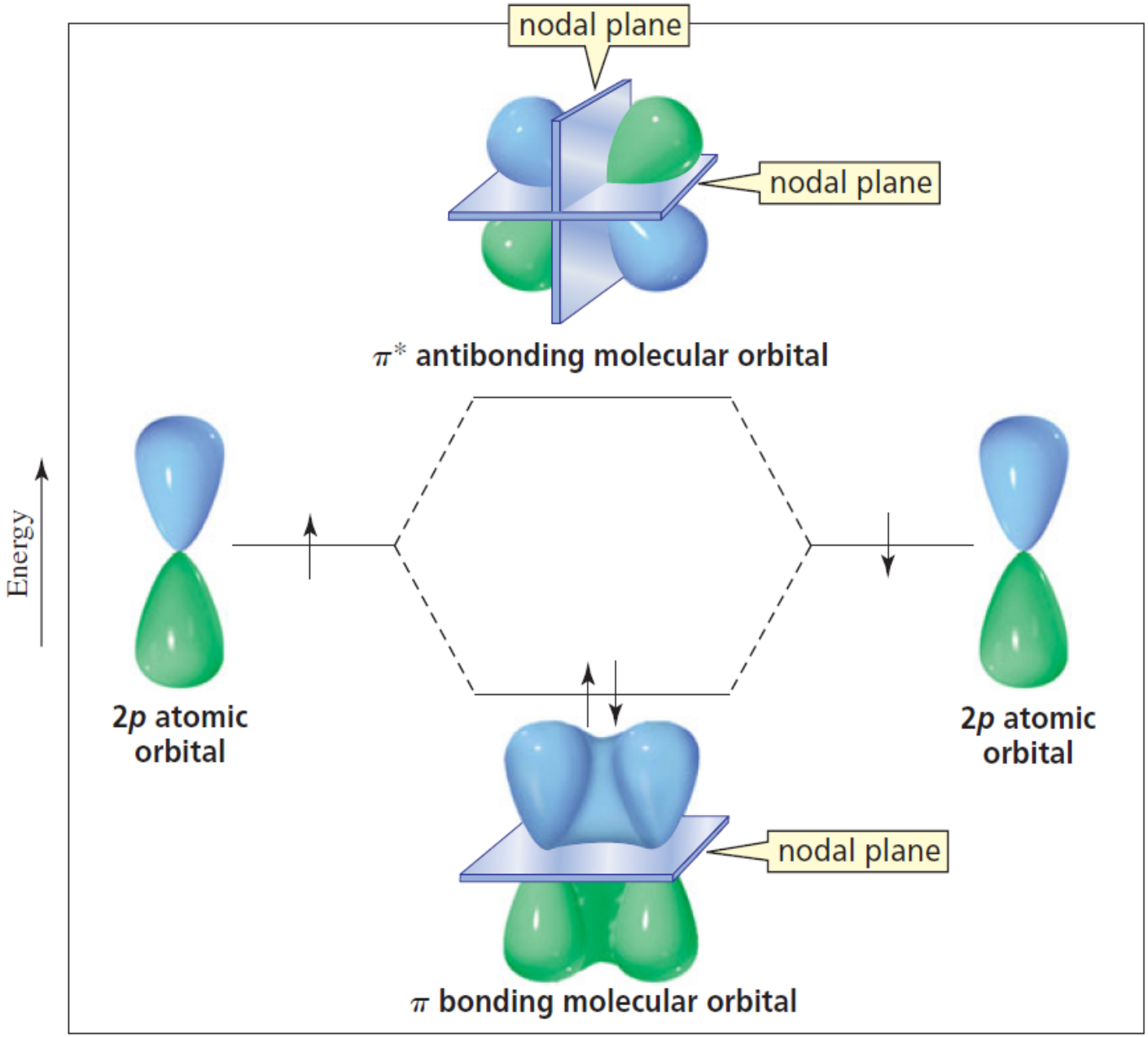
The C-C π-orbital is the Highest Occupied Molecular Orbital (HOMO) of the alkene

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



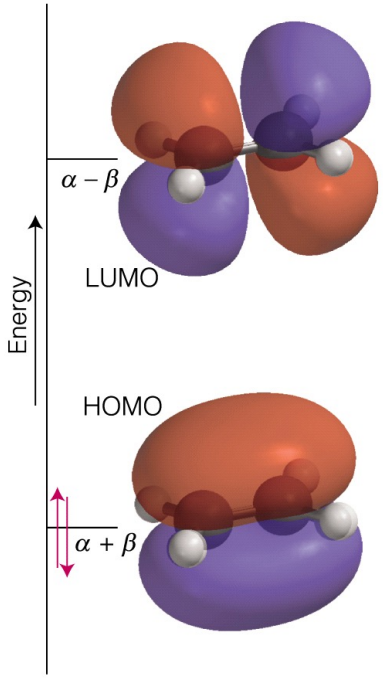
Side-to-side overlap of two p AOs




nodal plane
nodal plane
π* antibonding molecular orbital
Energy
2p atomic orbital
2p atomic orbital
nodal plane
π bonding molecular orbital

Ethylene MOs

Increasing Energy of Orbitals

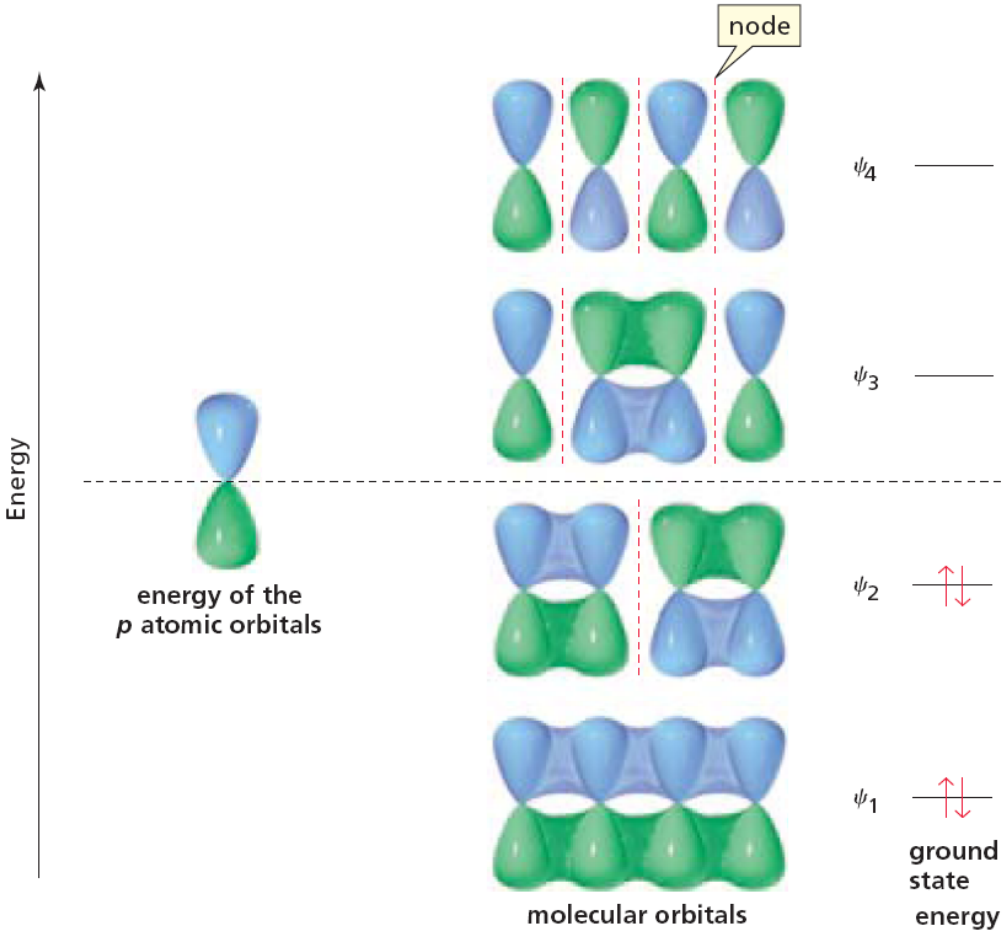


π* (Antibonding molecular orbital)

π (Bonding molecular orbital)

Total Number of π-electrons = 2
Total Number of π-orbitals = 2
Both electrons will occupy the lowest energy MO, i.e., BMO

Butadiene MOs



Although MOs have different energies, they all coexist

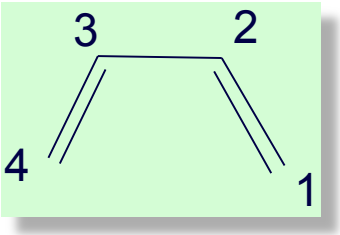
No. of bonding interactions > no. of nodes = bonding MO

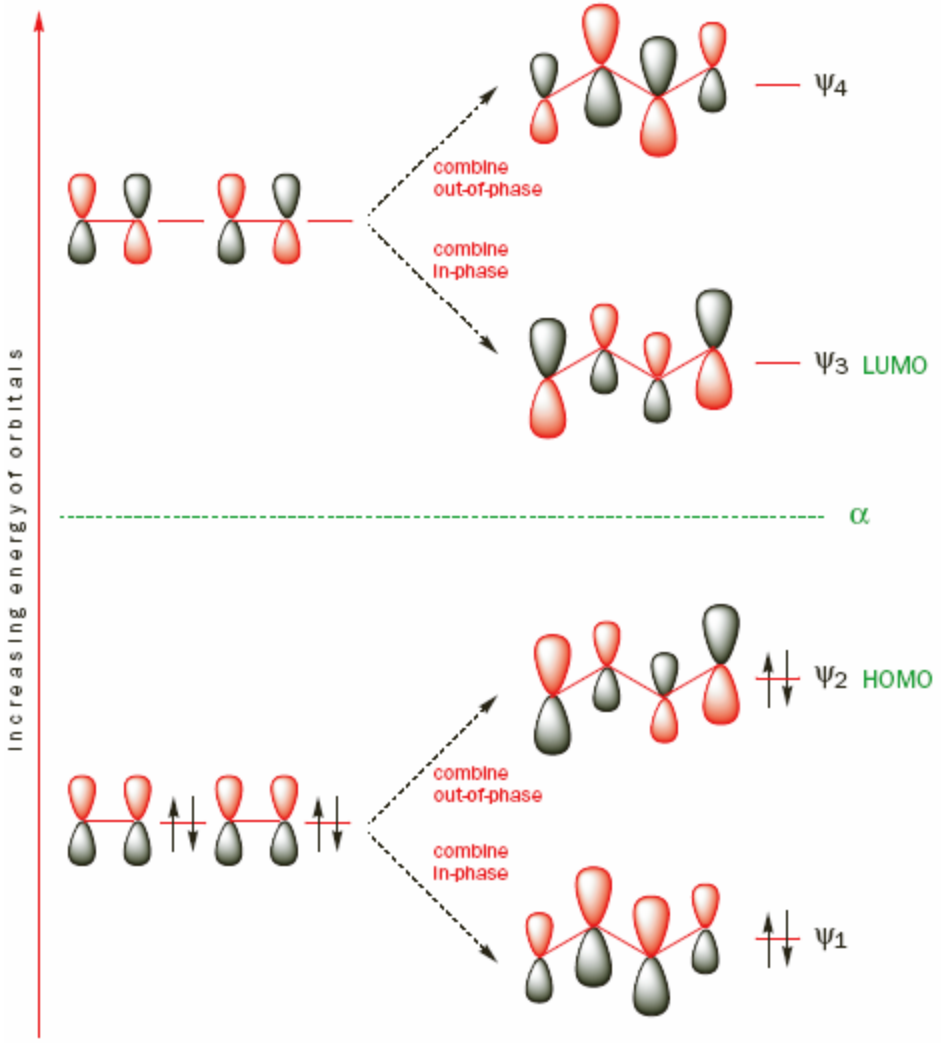
No. of bonding interactions < no. of nodes = anti-bonding MO

Butadiene MOs

Total number of pπ-orbitals = 4

Total number of π-electrons = 4





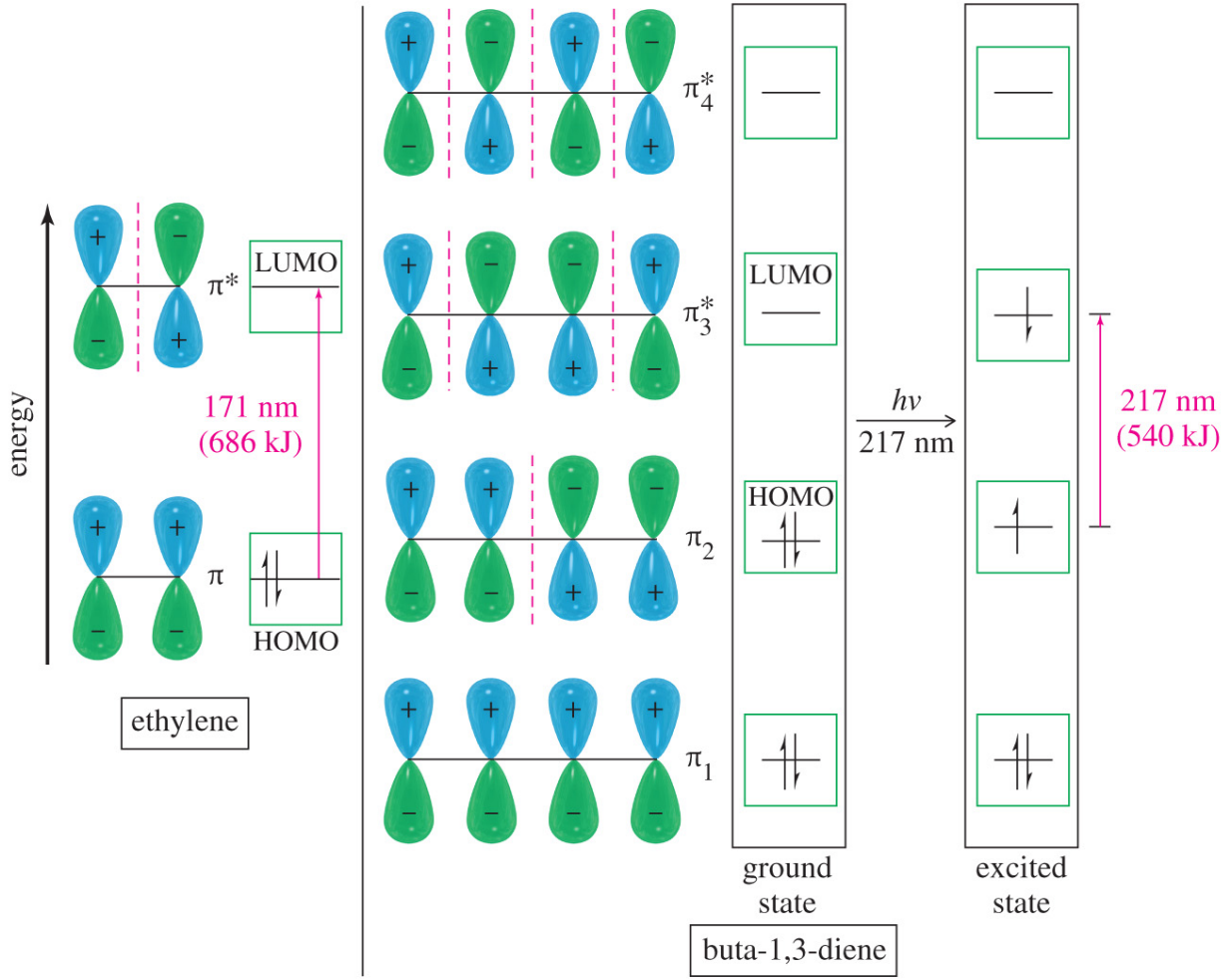
LUMO is lower in energy than the LUMO of ethylene

Butadiene is more reactive than ethylene

HOMO is higher in energy than the HOMO of ethylene

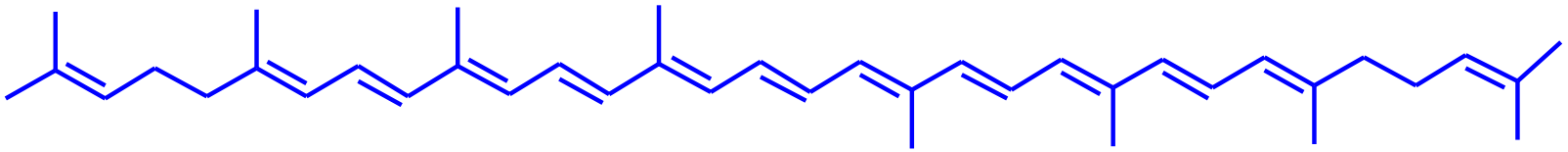
HOMO-LUMO Gap

$\pi \rightarrow \pi^*$ for Ethylene and Butadiene

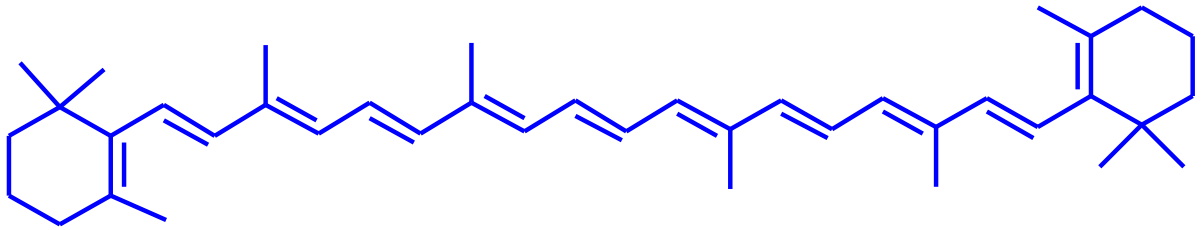


Extended Conjugation and Colour (E.g. 1)

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



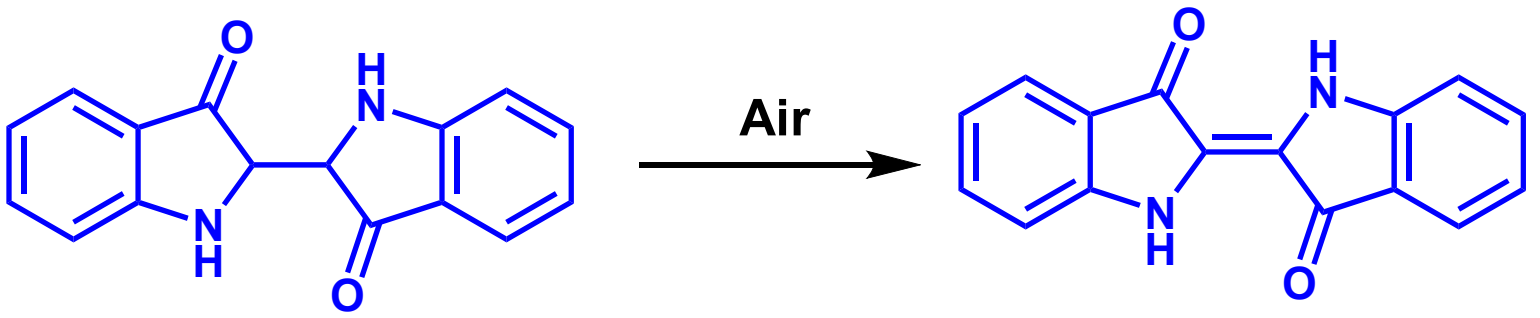
Lycopene, the red pigment present in tomatoes and other berries



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

Extended Conjugation and Color (E.g. 2)

The colour of the blue jeans come from the pigment indigo



Colourless Indigo precursor

Indigo

Jeans are generally dyed by immersion in a vat of reduced indigo, which is colourless since there is no conjugation.

When the cloth is hung up to dry, the oxygen in the air oxidizes the pigment to indigo and the jeans turn blue.

Generalizations for Acylic Polyenes

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

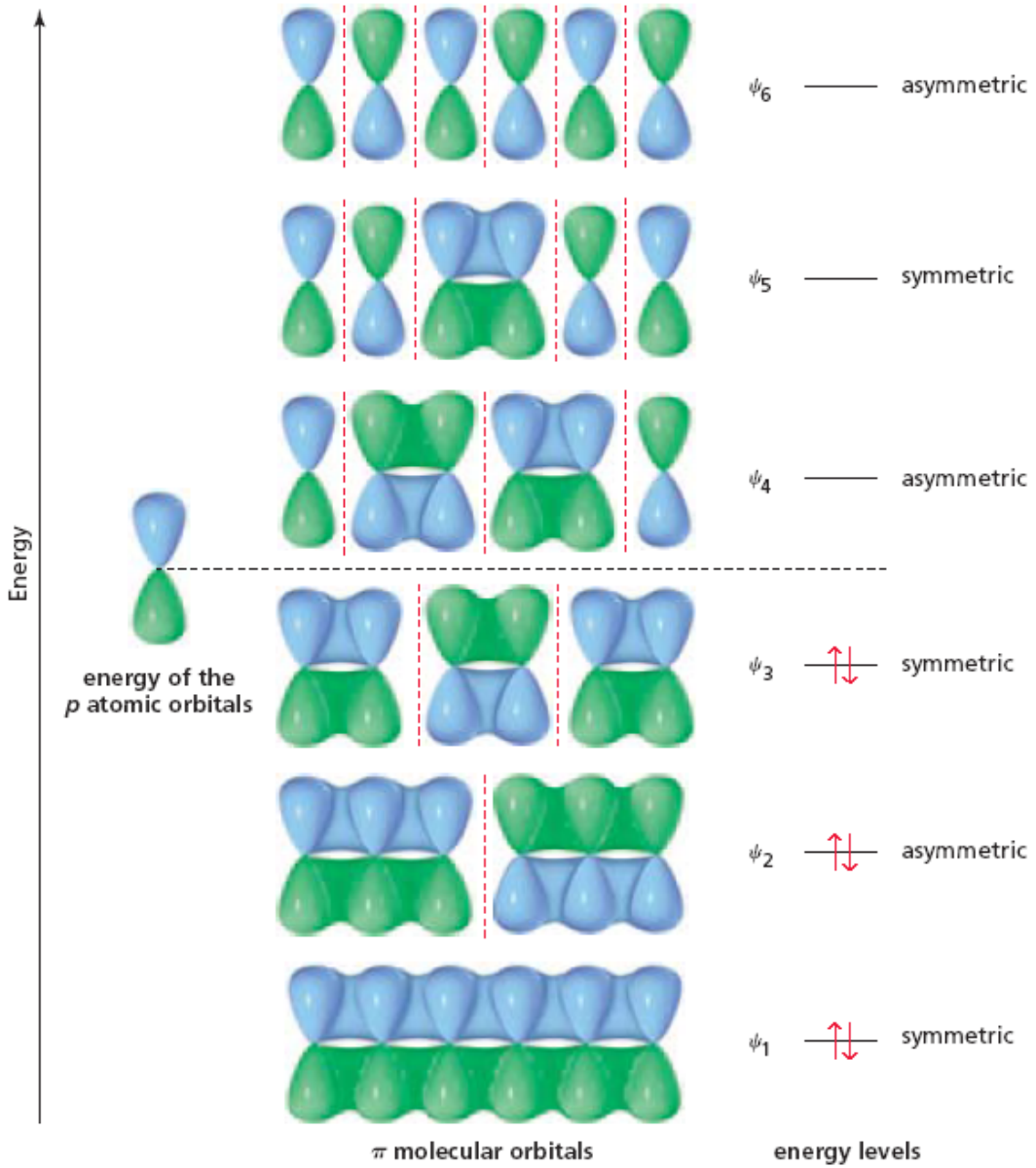
The number of nodes increases by ONE on going from one orbital to the next higher energy orbital

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

In systems with an odd number of atoms, the levels can have node/nodes at the carbon atoms. (homework: penta dienyl cation)

MOs alternate from symmetric to asymmetric as the MOs increase in energy (check it in 1,3,5-hexatriene)

MOs of 1,3,5-hexatriene



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