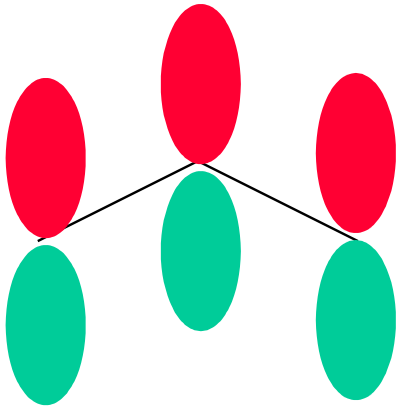
Sections 6.6 and 6.11

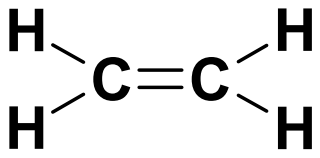
PI SYSTEMS

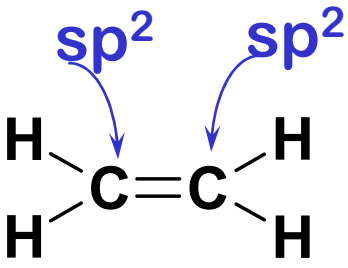
MOLECULAR ORBITAL DIAGRAMS



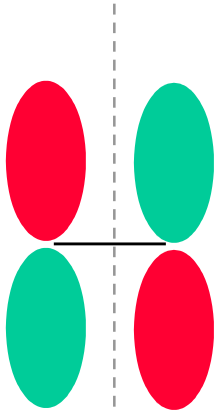
PI(π) MOLECULAR ORBITAL SYSTEMS

TWO 2p ORBITALS - ETHYLENE



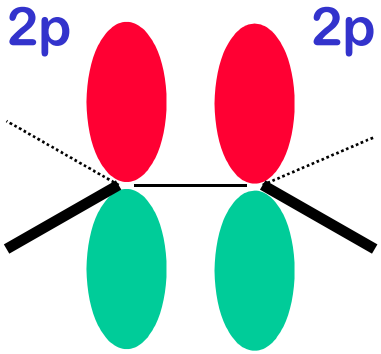


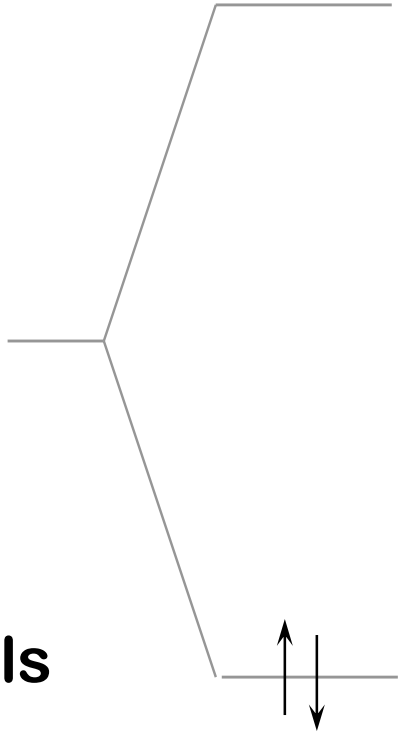
Higher energy = additional node

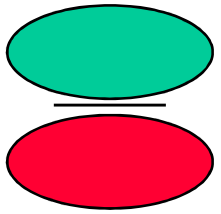


π^*

node





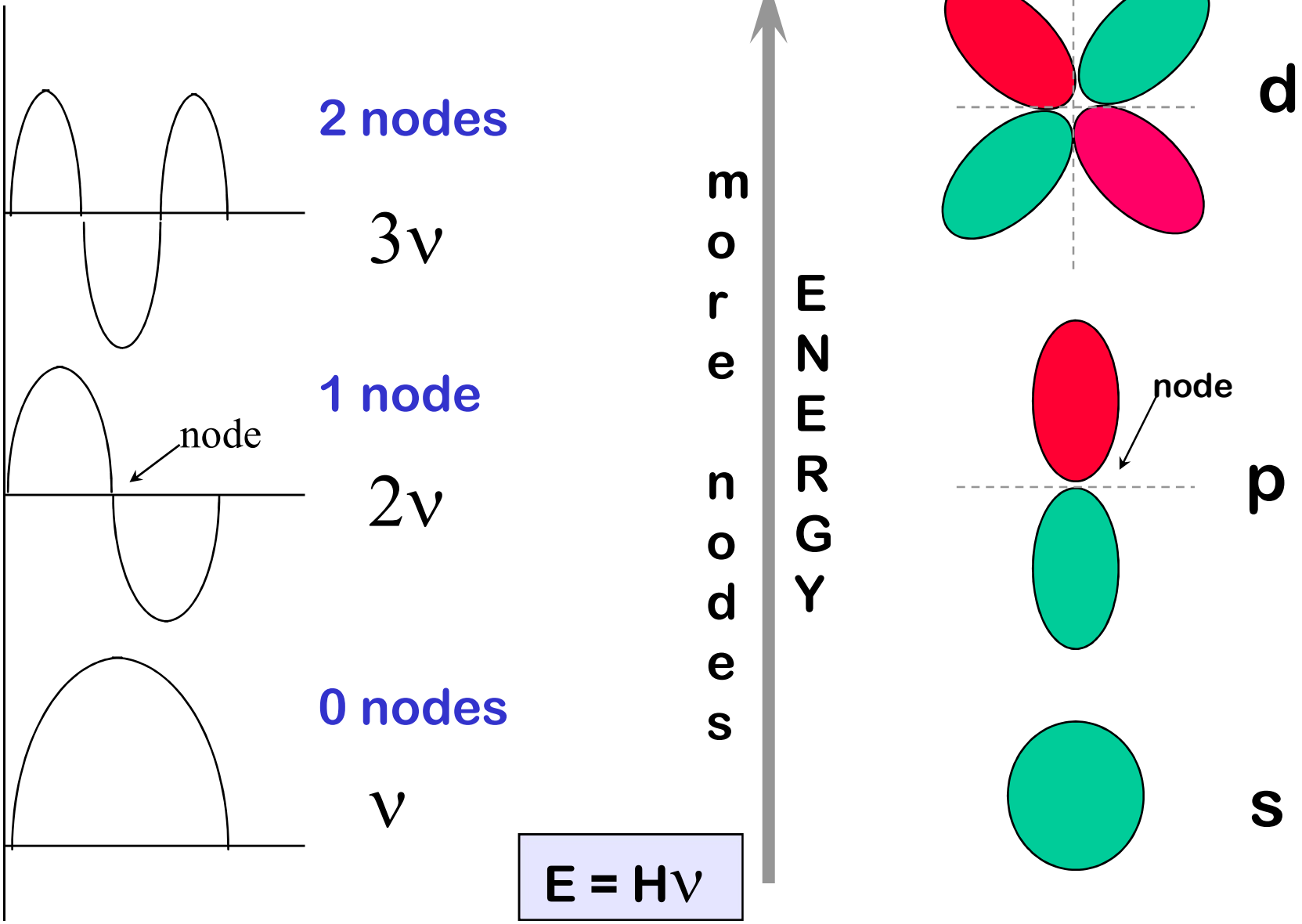


π

Two atomic 2p orbitals combine to make a pi system of two molecular orbitals.

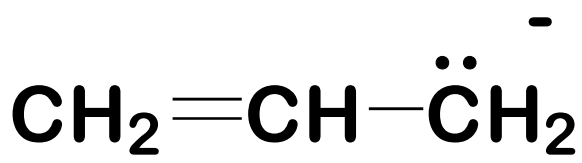
ORBITAL ENERGY AND NODES

RELATIONSHIP BETWEEN NODES AND ENERGY



PI MOLECULAR ORBITAL SYSTEMS

THREE 2p ORBITALS - ALLYL ANION



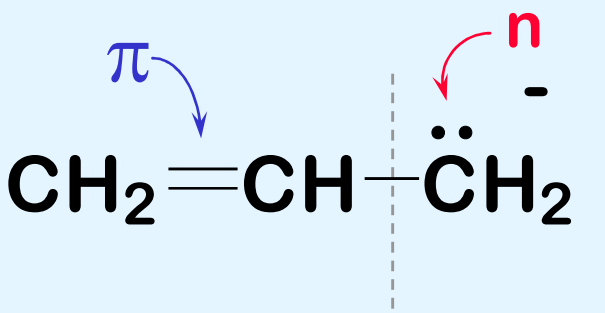
Systems that have resonance form:

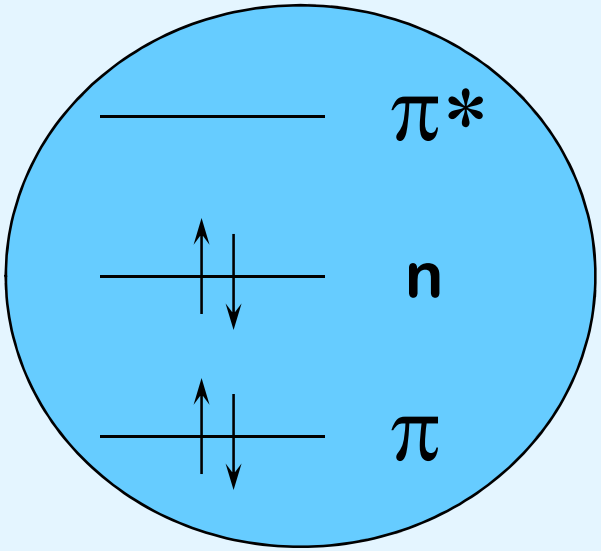
pi molecular orbital systems.

The interacting π bonds and unshared pairs rehybridize to form new system of orbitals.

FORMATION OF A PI MOLECULAR ORBITAL SYSTEM

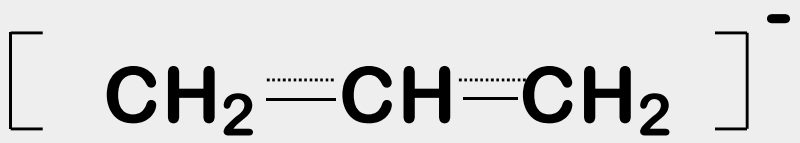
no resonance

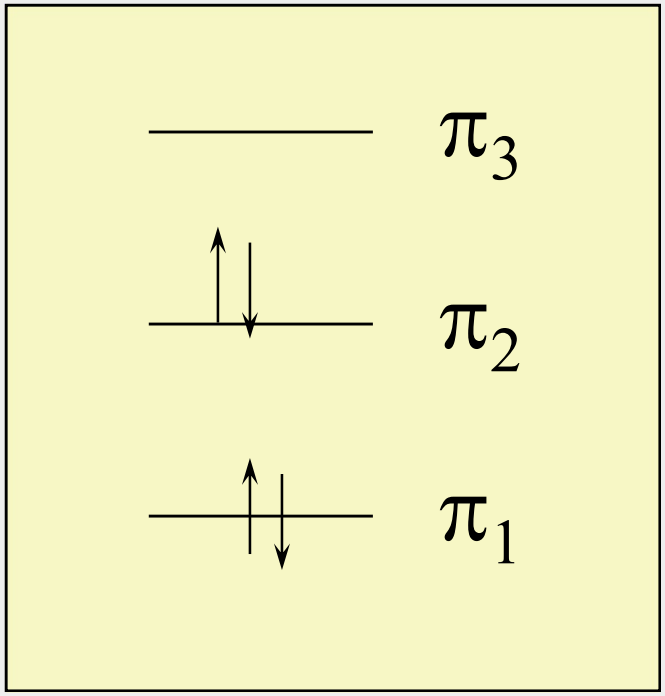




pi bond + empty 2p

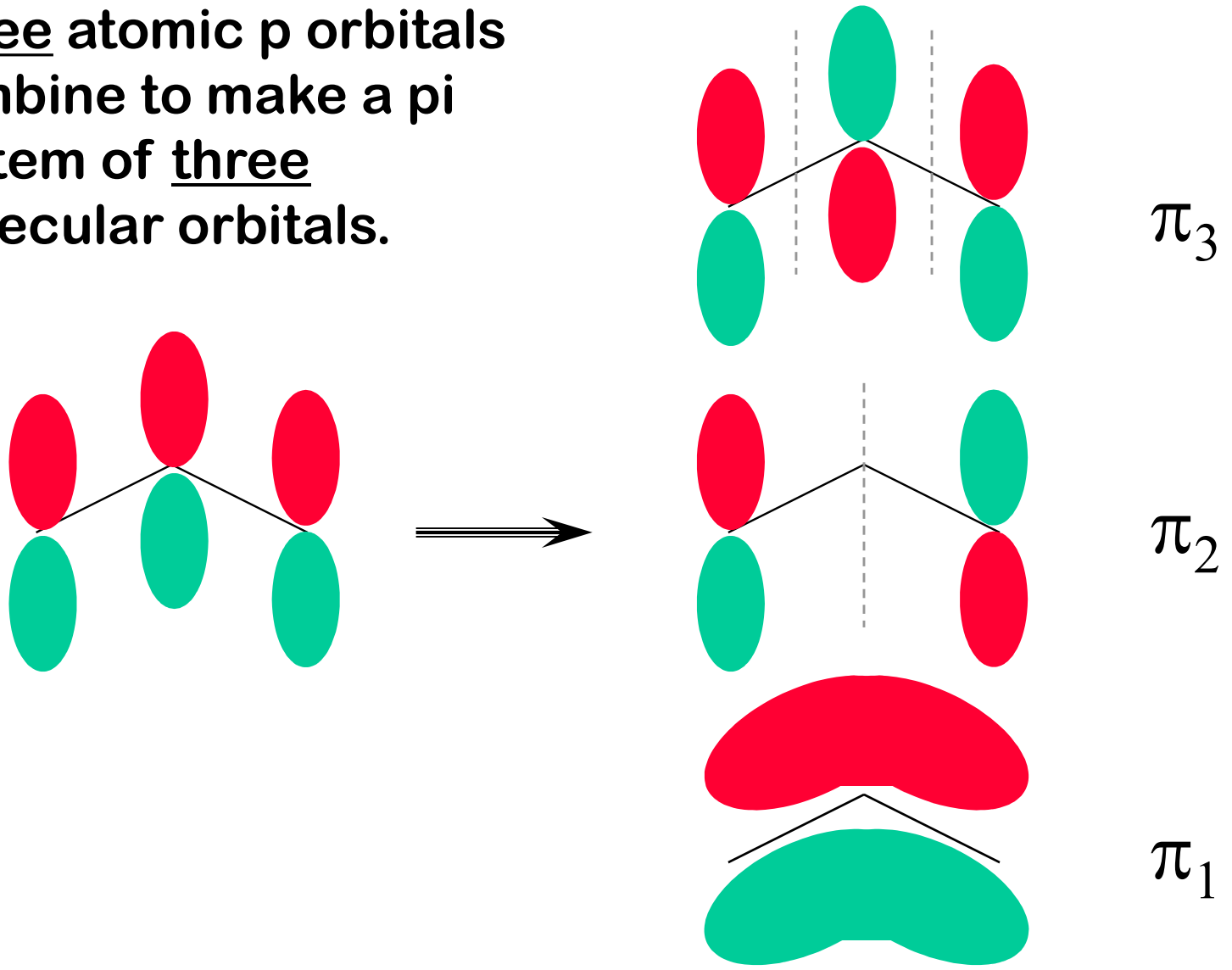
resonance





pi molecular orbital system

Three atomic p orbitals combine to make a pi system of three molecular orbitals.



GENERAL PRINCIPLE

When the number of p orbitals forming a resonance system = n

….. they will "hybridize" …..

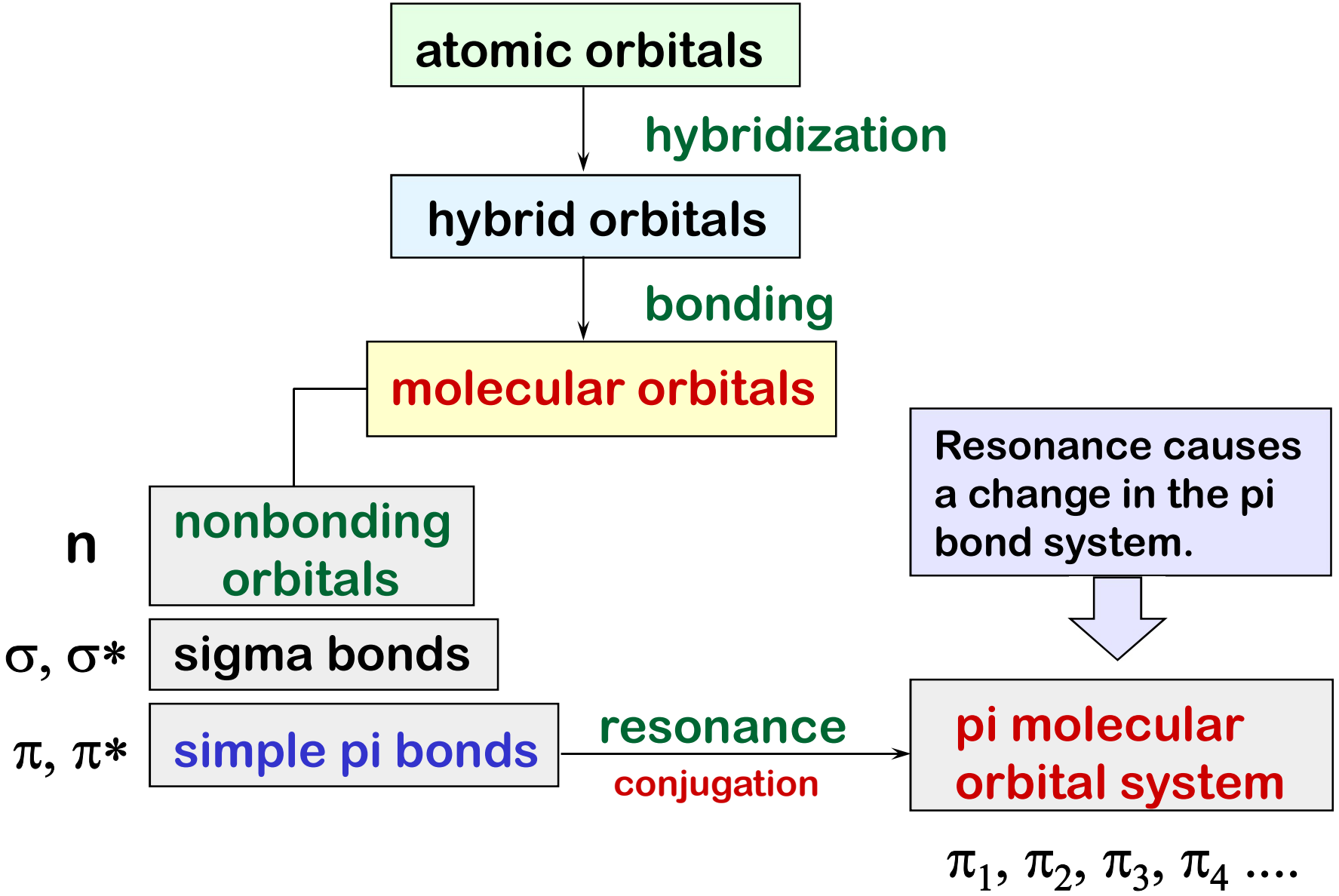
to form the same number (n) of pi molecular orbitals.

four 2p….. give …. four molecular orbitals

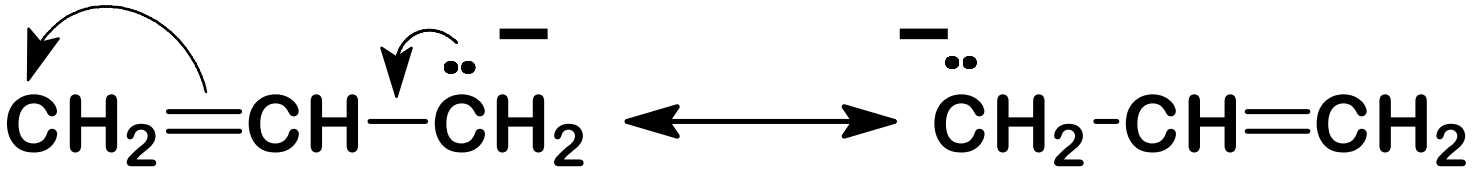
(p+p+p+p …. $\longrightarrow$ $\pi_1 + \pi_2 + \pi_3 + \pi_4$ **)**

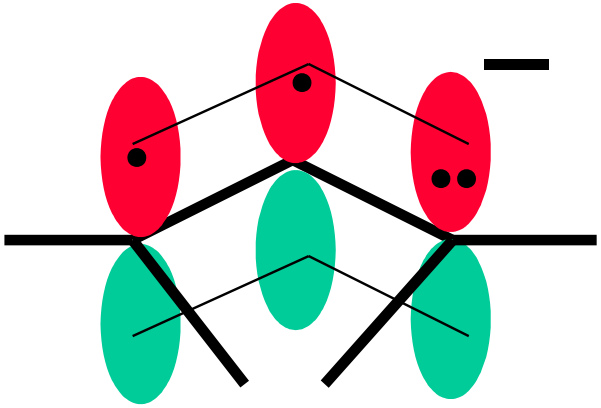
n 2p….. gives …. n molecular orbitals

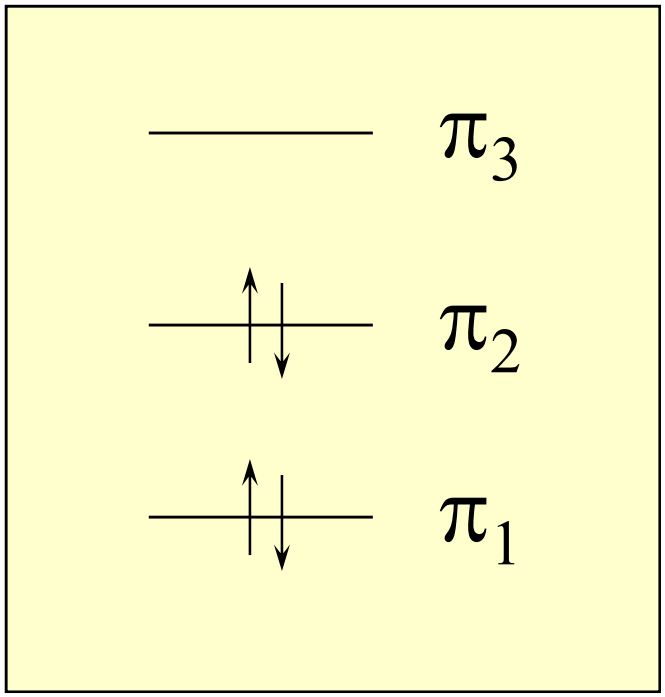
BONDING IN A MOLECULE WITH A CONJUGATED PI SYSTEM



ALLYL ANION

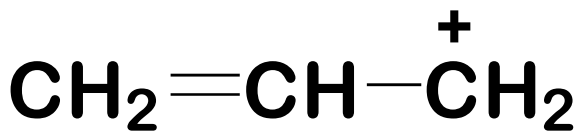




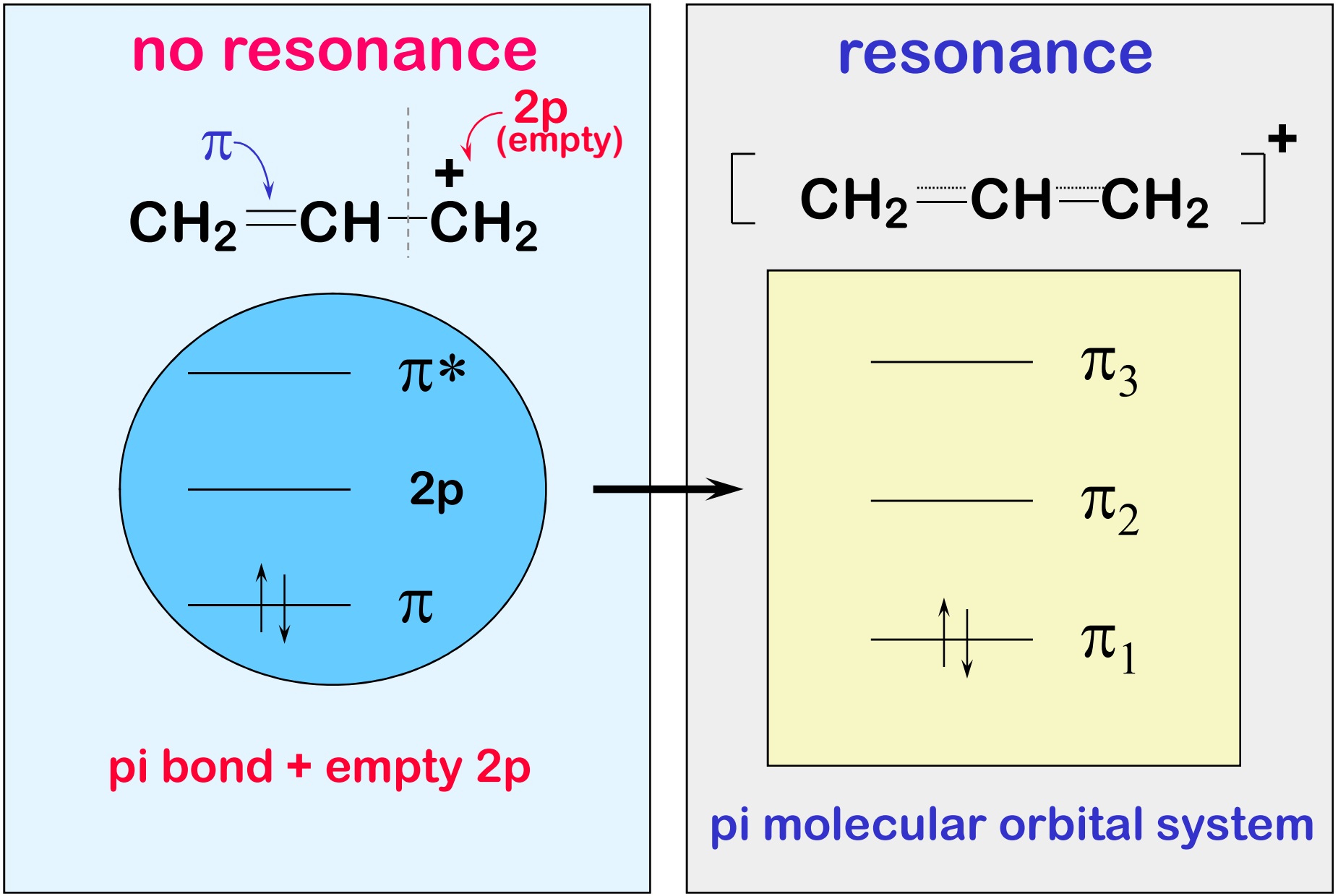


PI MOLECULAR ORBITAL SYSTEMS

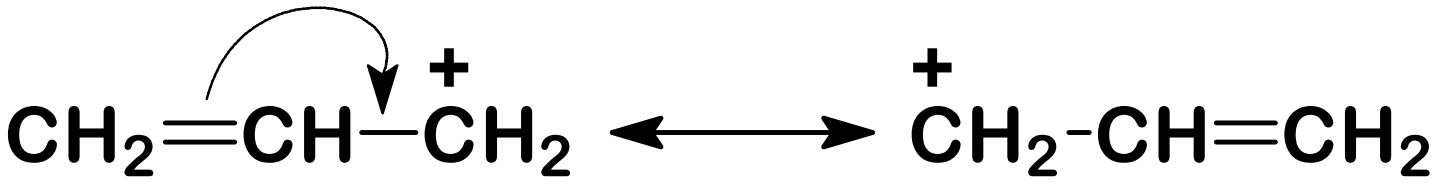
THREE 2p ORBITALS - ALLYL CATION

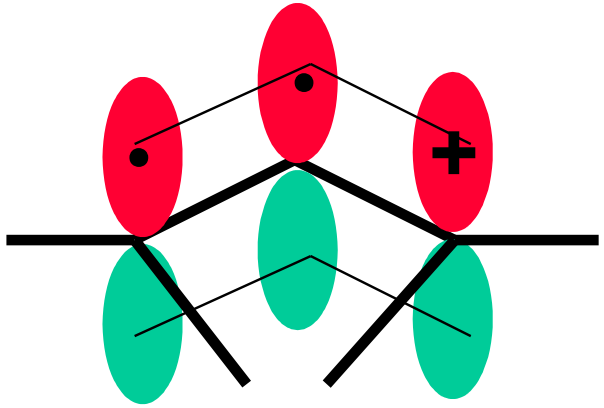


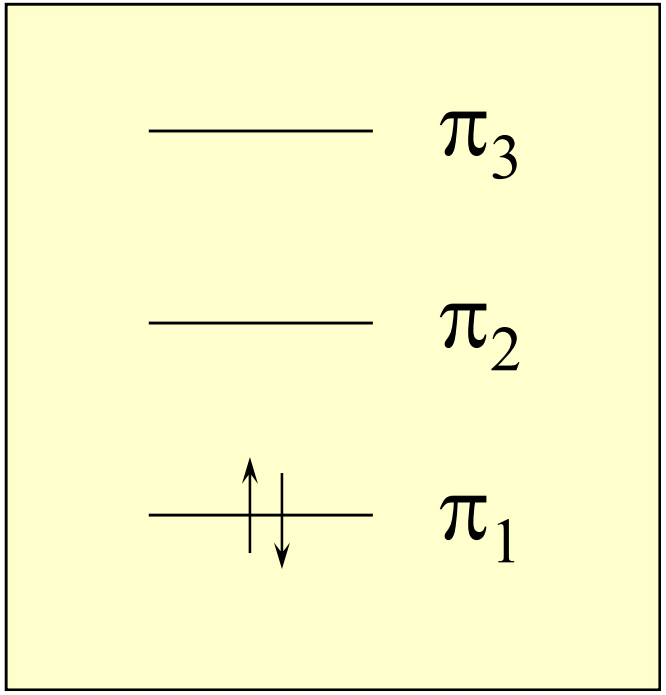
FORMATION OF A PI MOLECULAR ORBITAL SYSTEM



ALLYL CATION

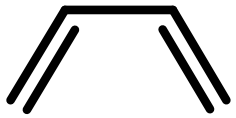




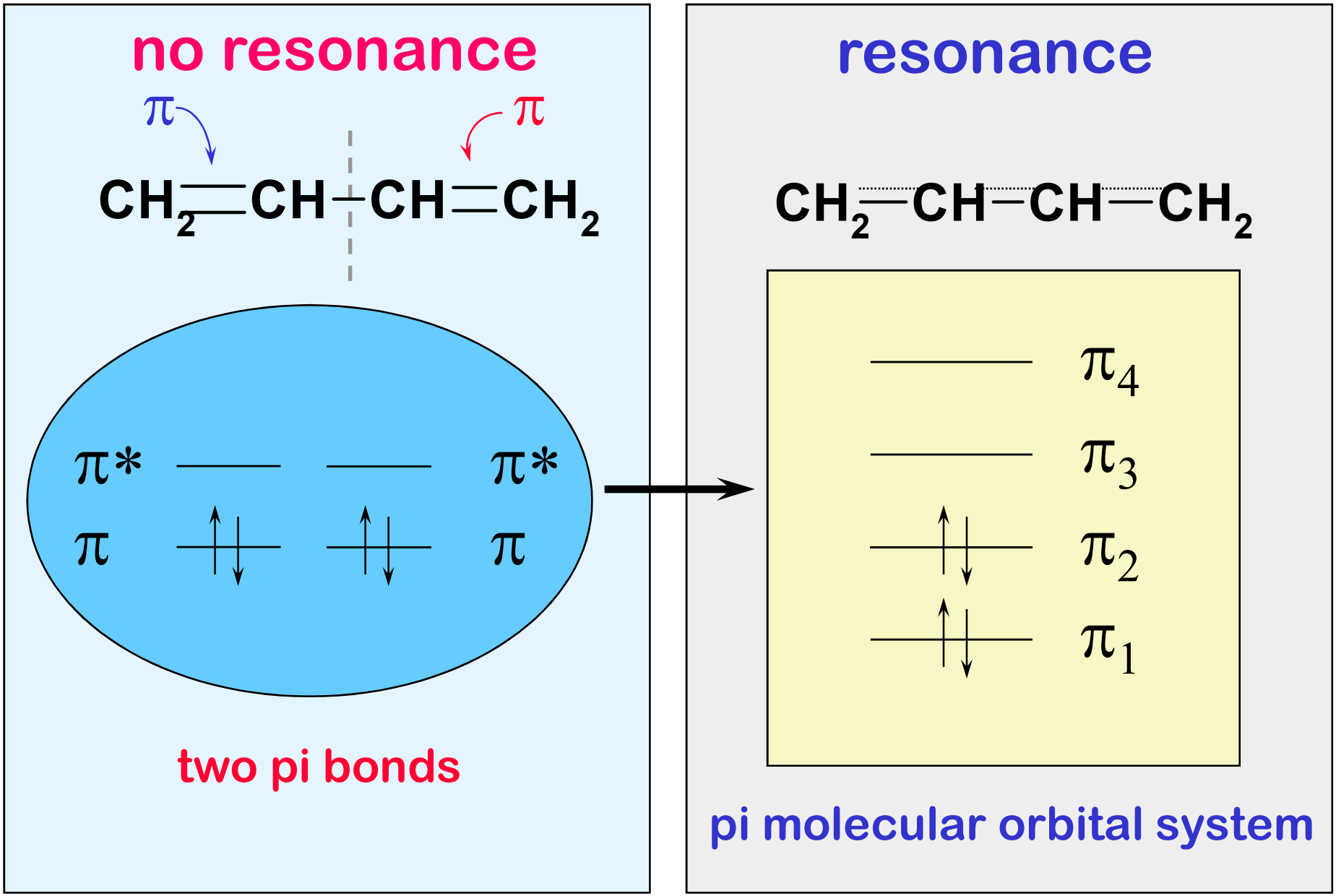


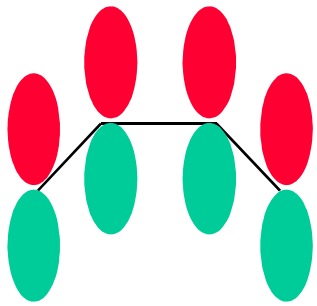
PI MOLECULAR ORBITAL SYSTEMS

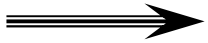
FOUR 2p ORBITALS - BUTADIENE

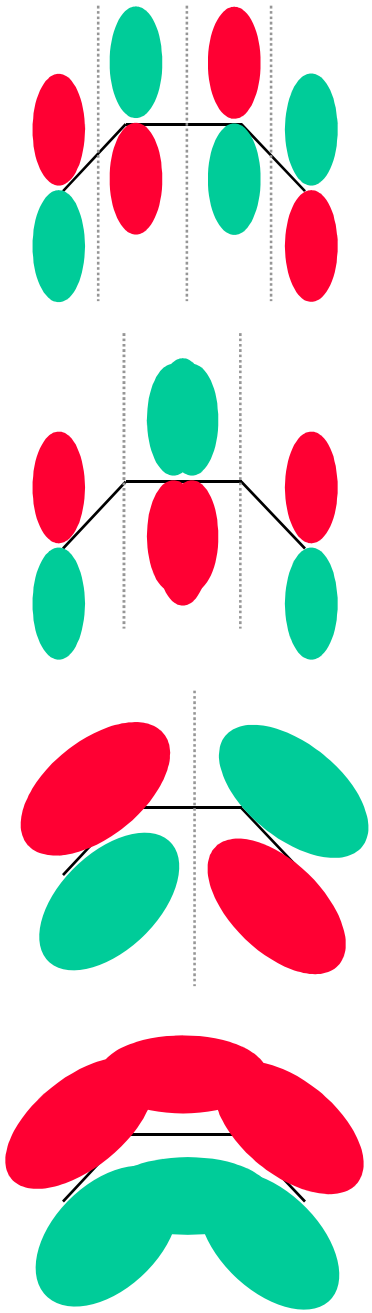


FORMATION OF A PI MOLECULAR ORBITAL SYSTEM









π_4

π_3

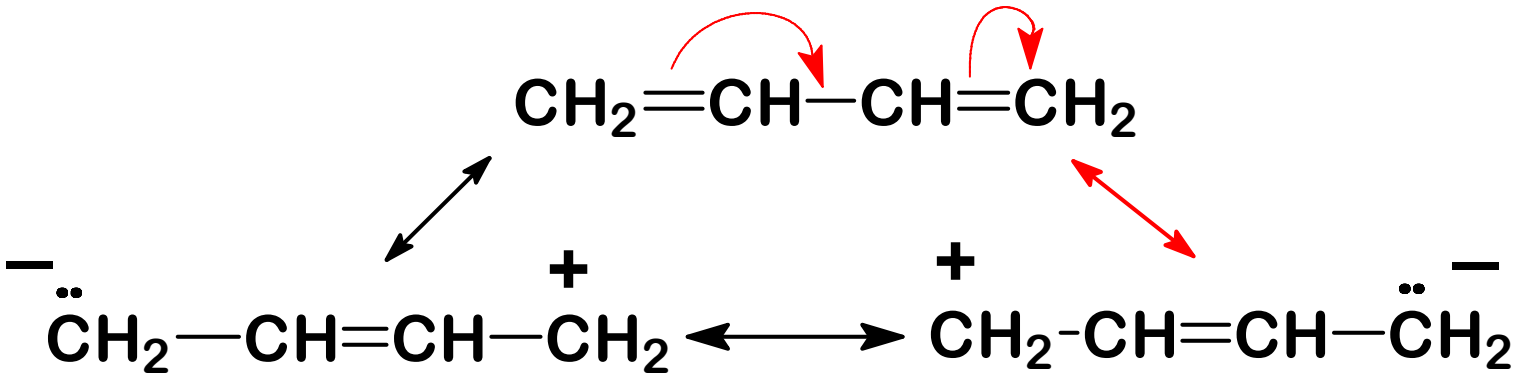
π_2

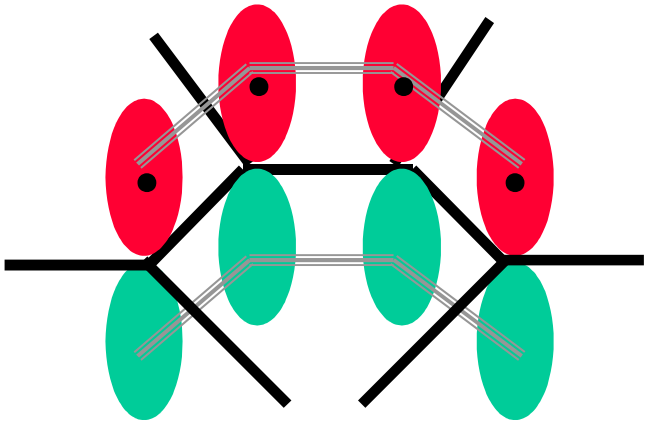
π_1

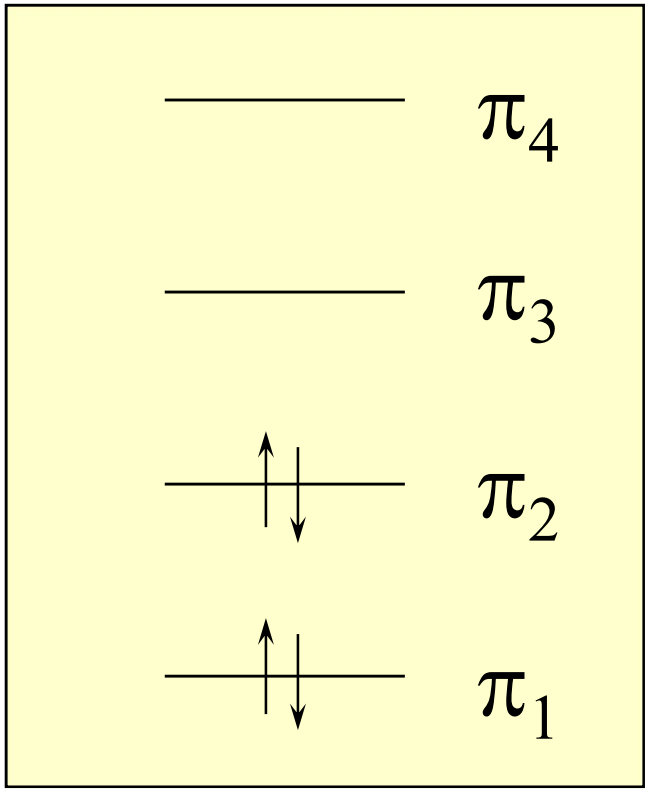
four p orbitals combine to make a system of four pi molecular orbitals

(a π system)

BUTADIENE







CYCLIC RESONANCE SYSTEMS

CYCLIC PI MOLECULAR ORBITAL SYSTEMS
HAVE DEGENERATE ORBITALS

DEGENERATE ORBITALS

In cyclic systems, or other systems with high symmetry, there will be degenerate molecular orbitals.

degenerate = same energy

For instance, the set of 2p orbitals in an atom is degenerate

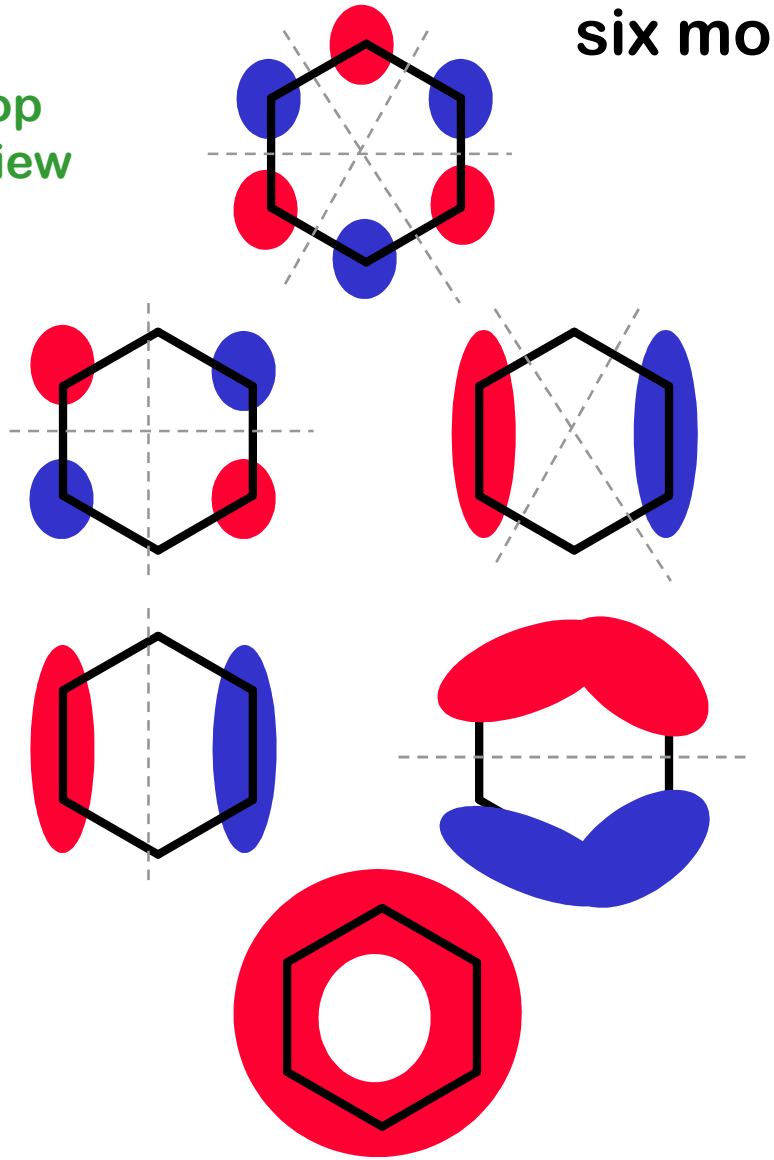
2px 2py 2pz

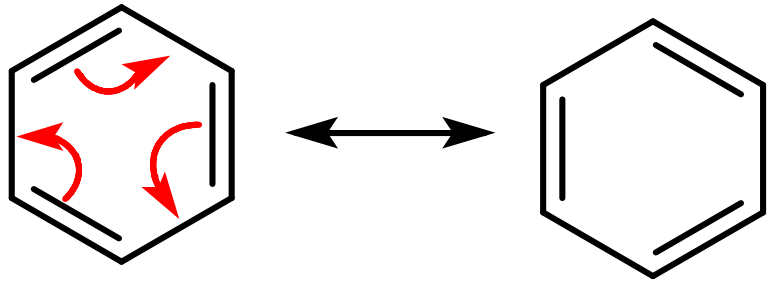
and they fill singly before pairing electrons (Hund Rule)

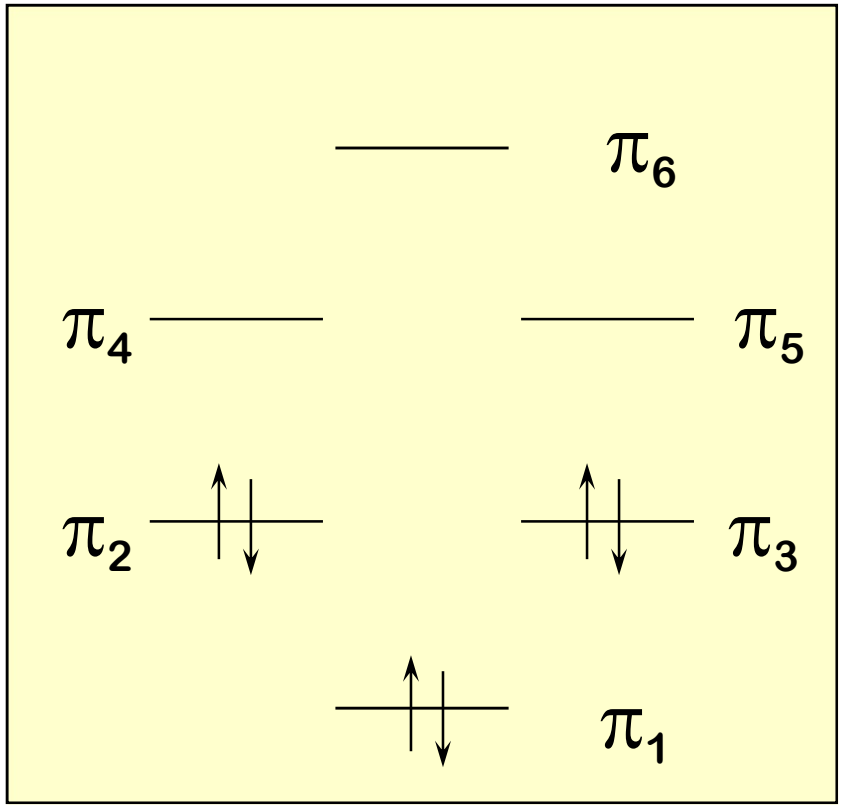
BENZENE PI MOLECULAR ORBITALS

six p's
six mo's

top
view



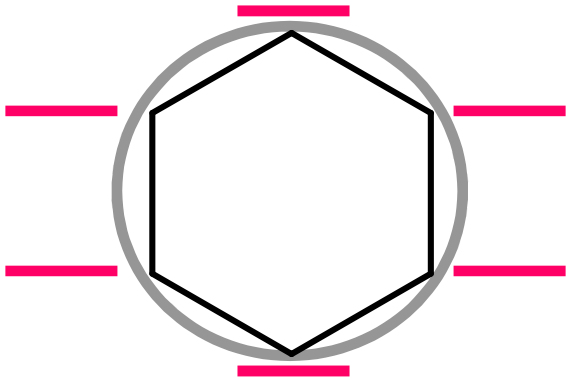




HÜCKEL PREDICTOR

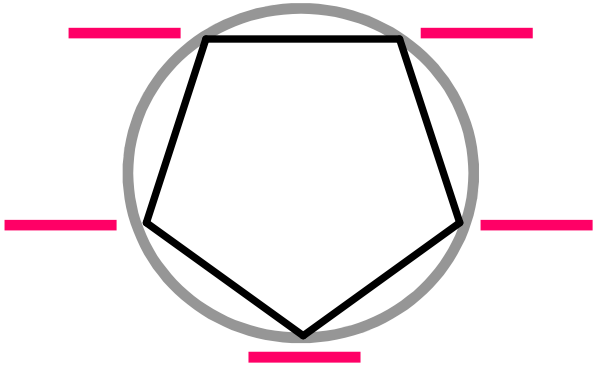
HÜCKEL PREDICTOR

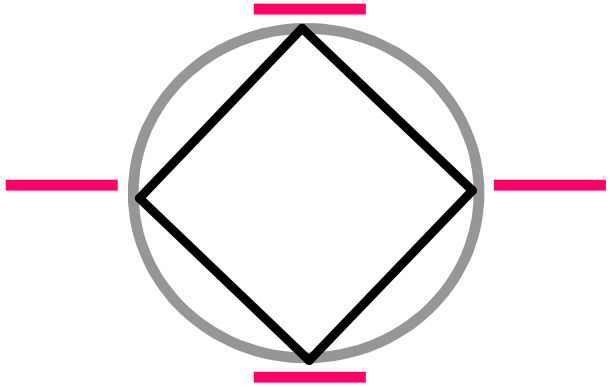
for cyclic conjugated systems



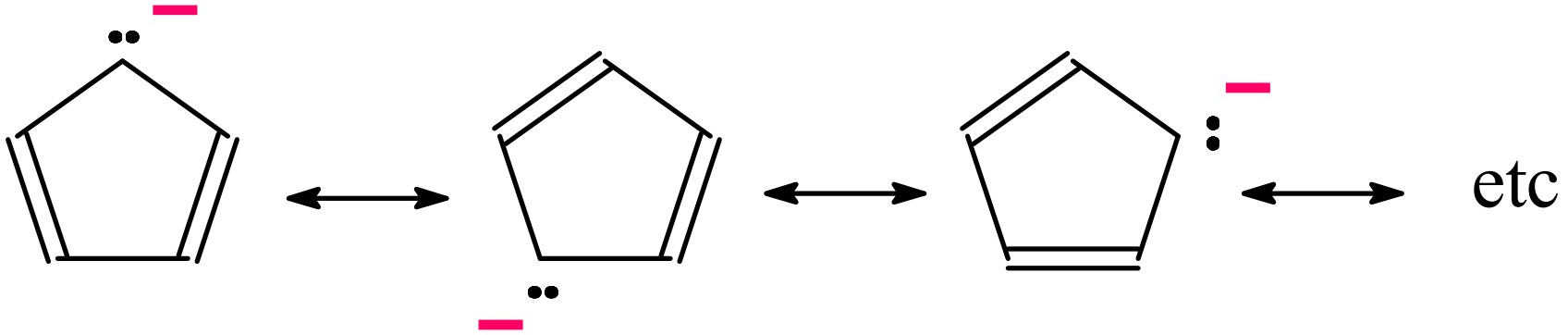
Inscribe the polygon which represents the cyclic system point down in a circle.

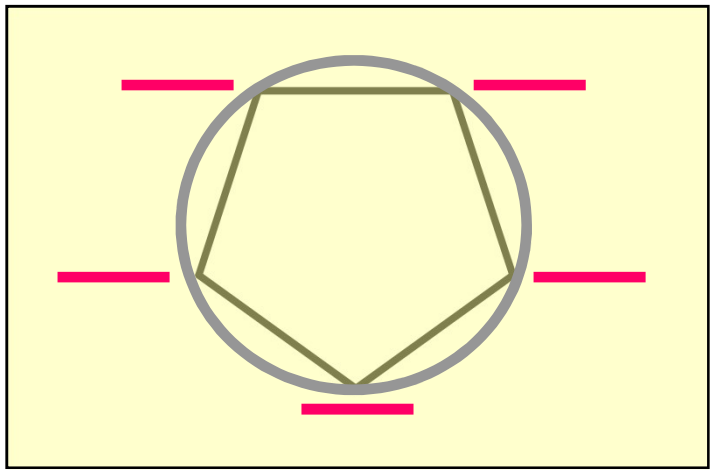
Places where the vertices of the polygon touch the circle define the pattern of energy levels (red lines).

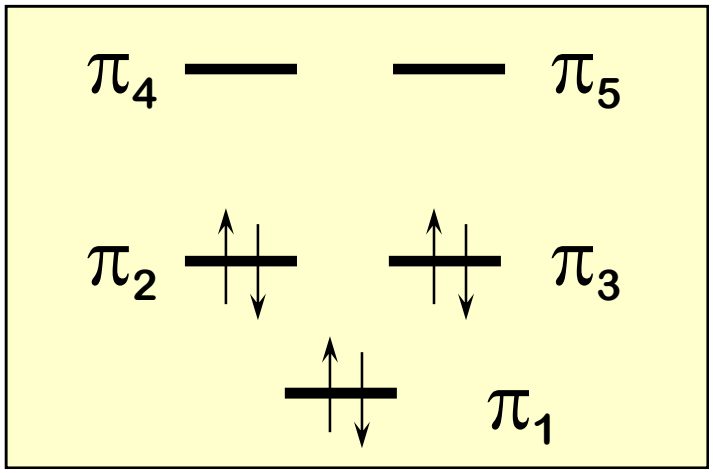




CYCLOPENTADIENYL ANION







CYCLOPENTADIENYL ANION