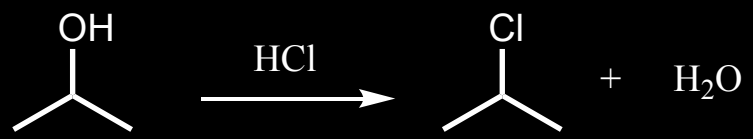
Kinetic versus thermodynamic control:

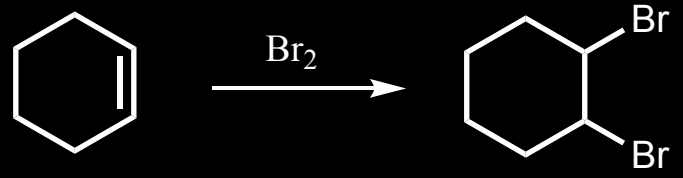
selected examples using MO theory (DAR, 1,3-butadiene addition, enolate alkylation, naphthalene sulfonation)

Types of organic reactions

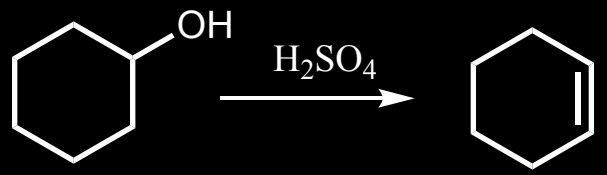
Substitution



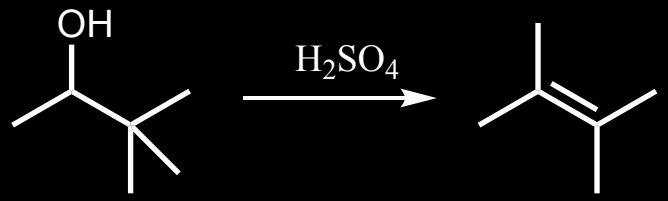
Addition



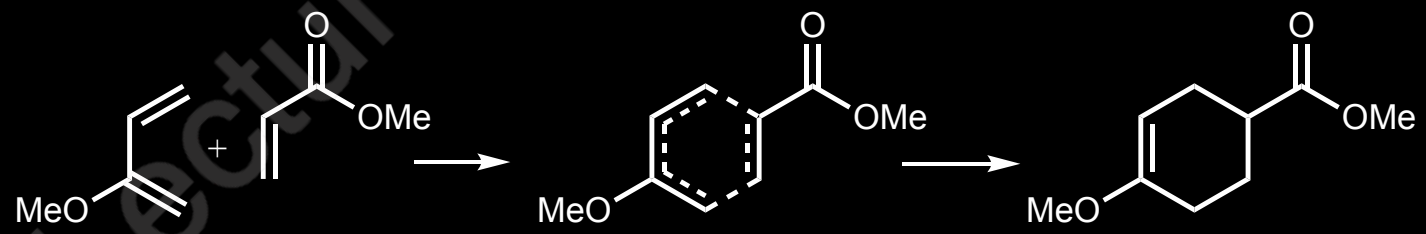
Elimination



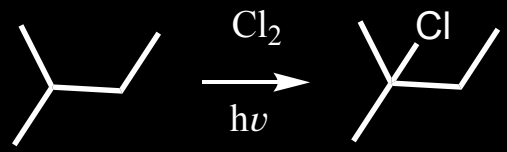
Rearrangement



Pericyclic Reaction



Radical Reaction

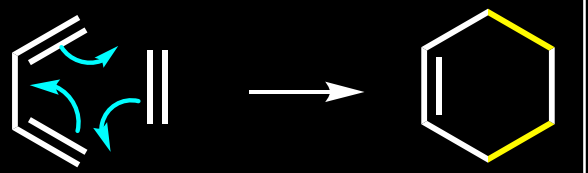


Pericyclic reactions

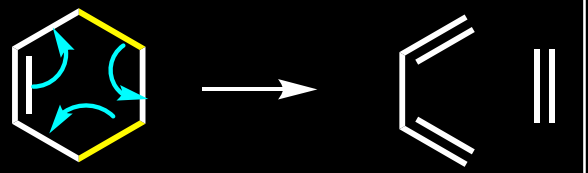
Pericyclic reactions, which do not involve ionic or radical intermediates, are a unique type of reaction involving π electrons.

There are 3 major classes of pericyclic reactions: cycloaddition reactions, electrocyclic reactions and sigmatropic rearrangements.

Cycloadditions

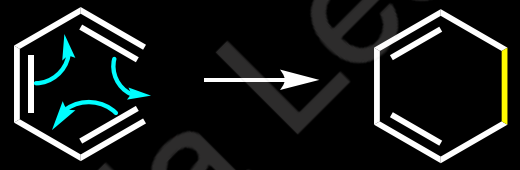


Two sigma bonds are formed

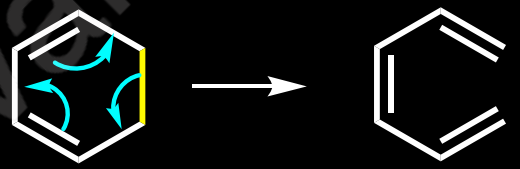


….or broken

Electrocyclic reactions

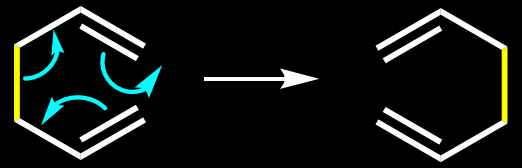


one sigma bonds is formed



….or broken

Sigmatropic Rearrangements

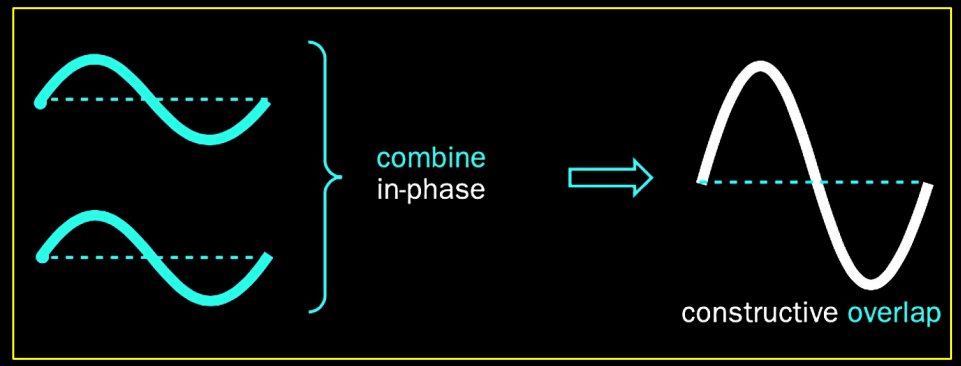


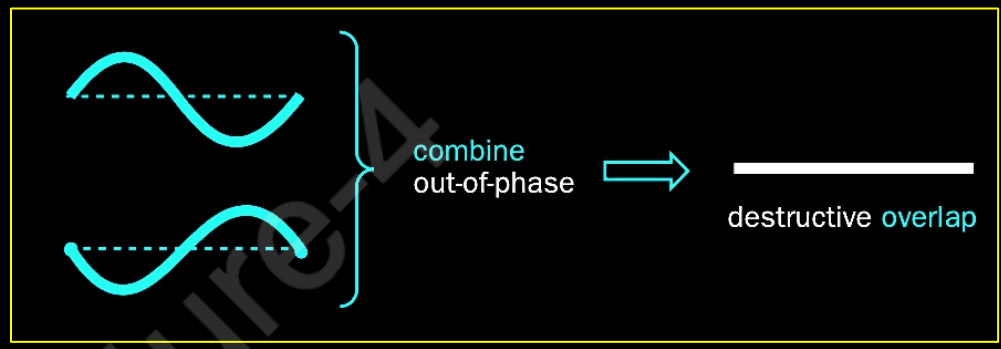
one sigma bonds is formed as another breaks

We can understand these reactions easily with the help of Molecular orbitals!

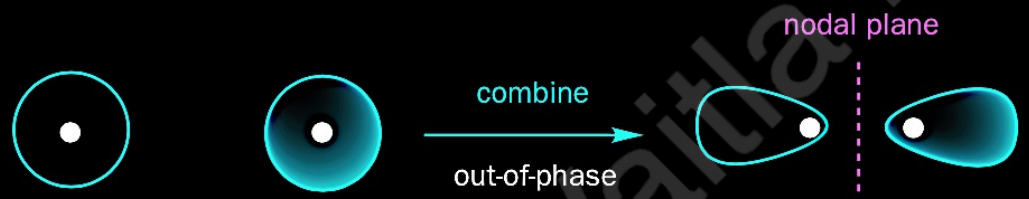
Molecular orbitals

Linear Combination of Atomic Orbitals (LCAO)

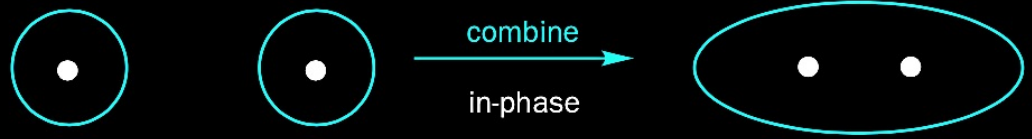




combination of two s orbitals

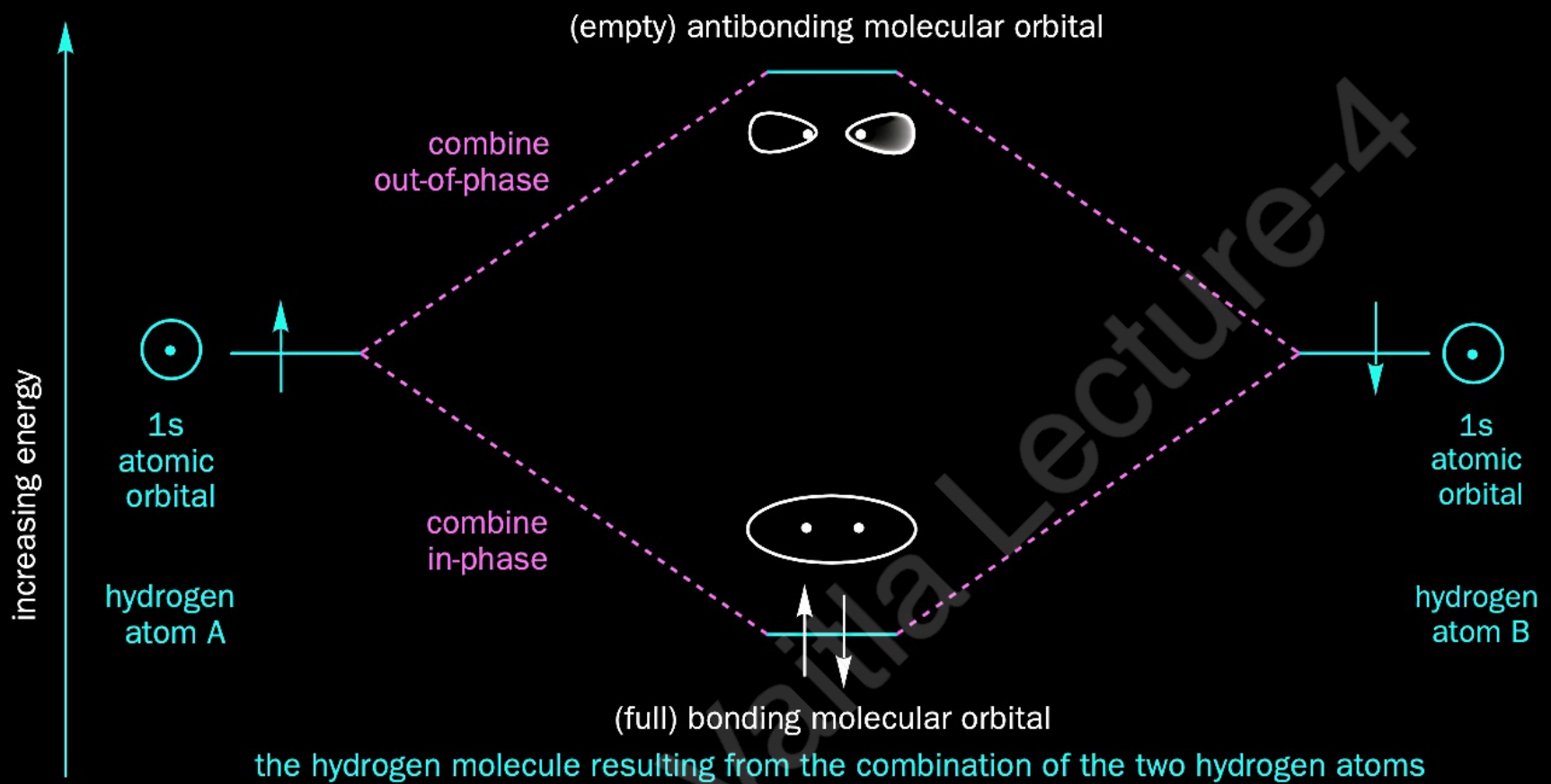


the two 1s orbitals combining out-of-phase to give an **antibonding orbital**



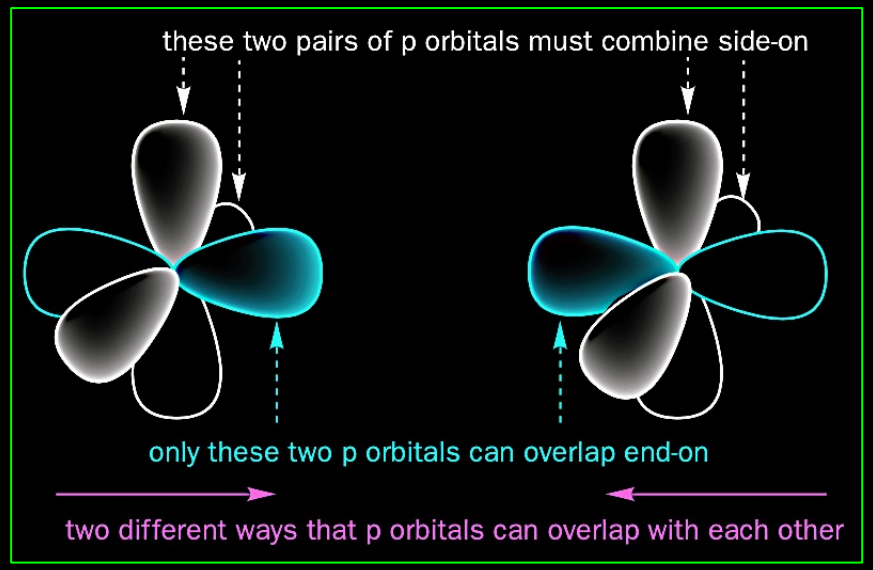
the two 1s orbitals combining in-phase to give a **bonding orbital**

energy level diagram

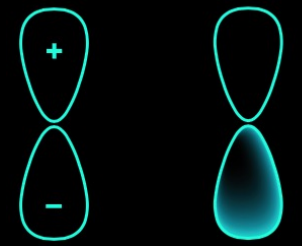


the hydrogen molecule resulting from the combination of the two hydrogen atoms

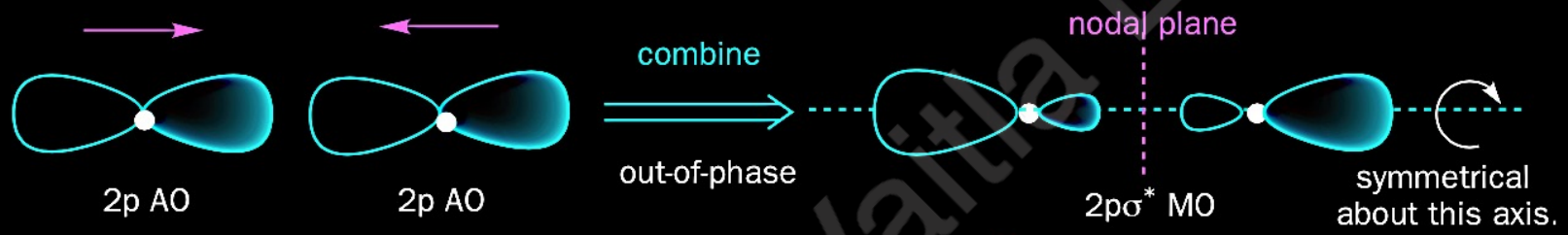
Molecular orbitals



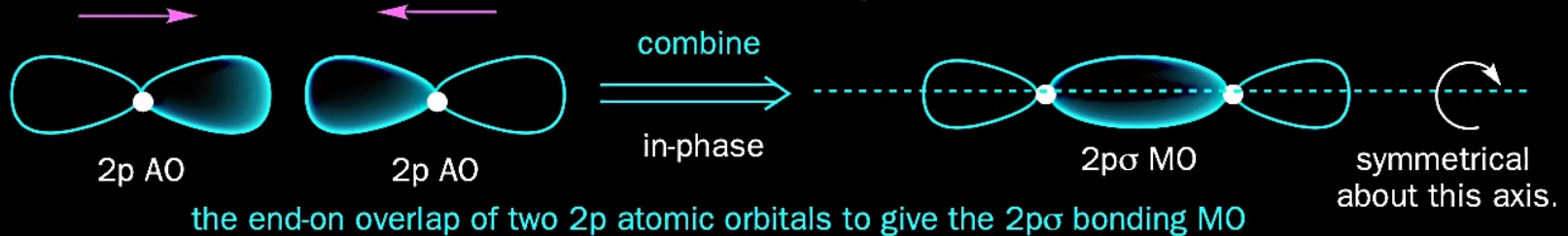
combination of two p orbitals



here the different phases of the p orbital are shown by shading one half and not the other



the end-on overlap of two 2p atomic orbitals to give the 2pσ* antibonding MO

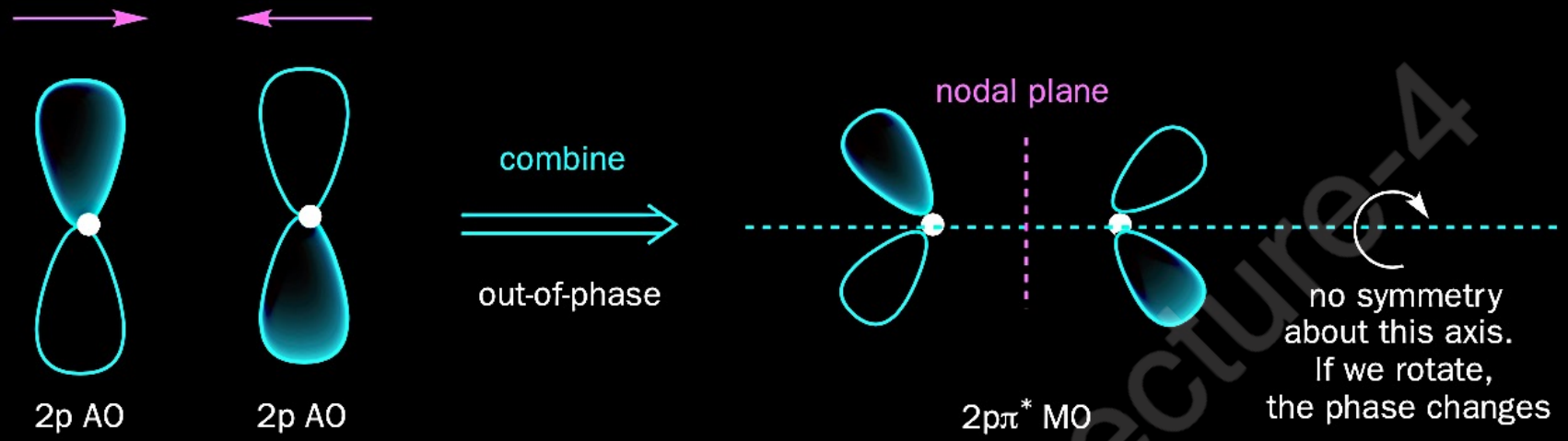


the end-on overlap of two 2p atomic orbitals to give the 2pσ bonding MO

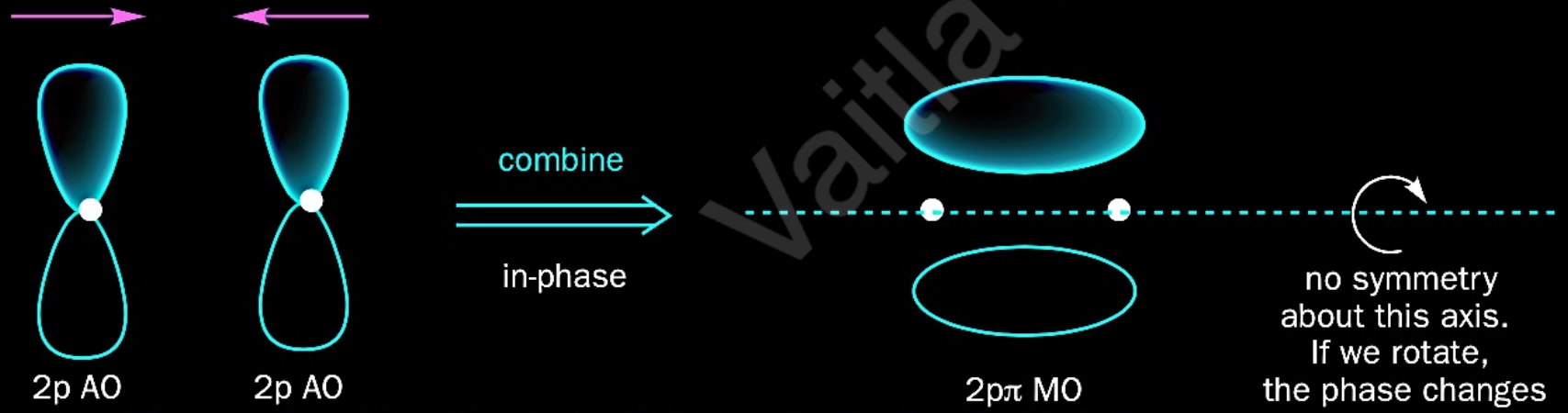
The end-on overlap

Molecular orbitals

The side-on overlap



the side-on overlap of two 2p atomic orbitals to give the 2pπ* antibonding MO

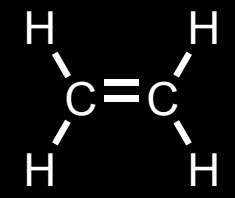


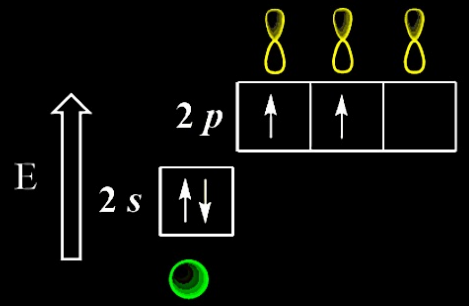
the side-on overlap of two 2p atomic orbitals to give the 2pπ bonding MO

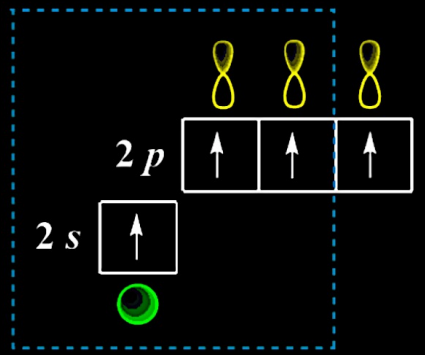
Molecular orbitals

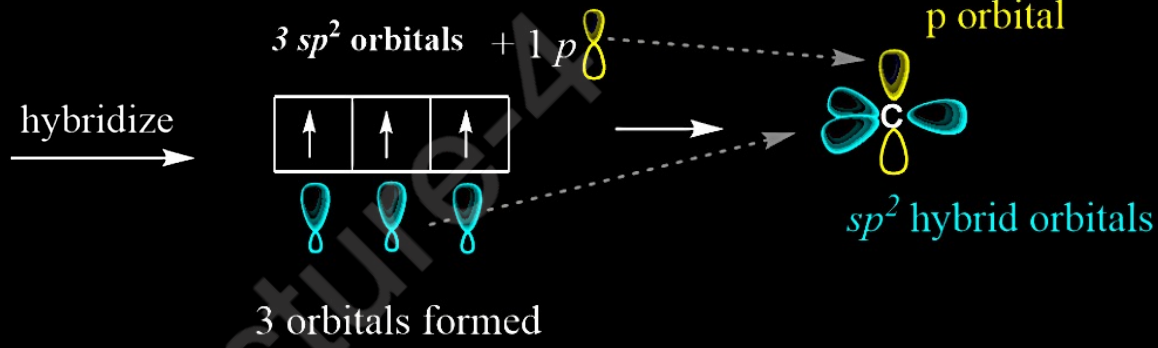
C – $1s^2 2s^2 2p^2$

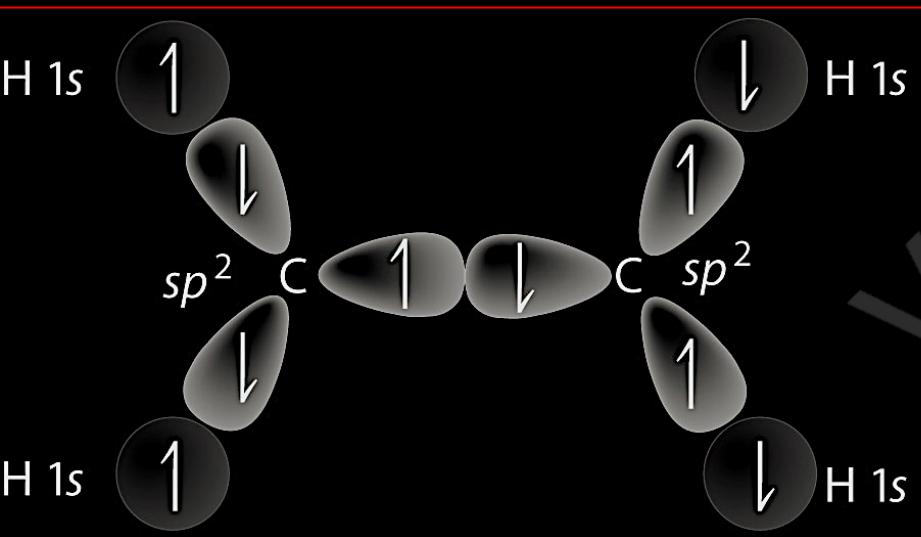
Bonding in Ethelene



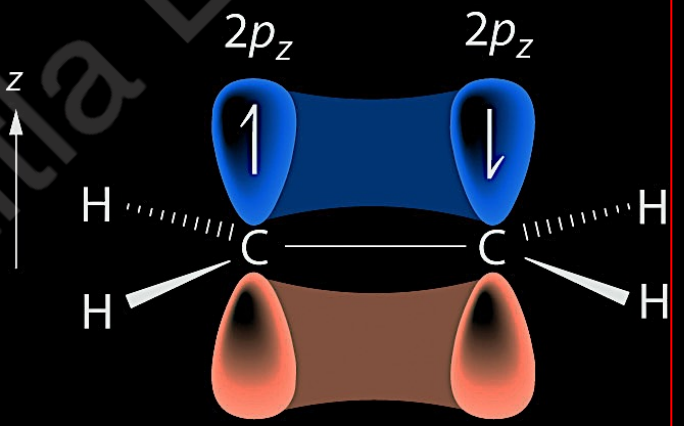








(a) C_2H_4 σ-bonded framework



(b) C_2H_4 π bonding

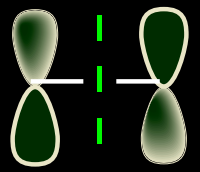
Molecular orbitals

HOMO = Highest Occupied Molecular Orbital

LUMO = Lowest Unoccupied Molecular Orbital

Destructive overlap

Antibonding

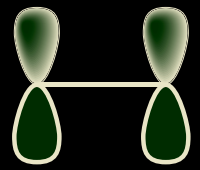


π_2^*

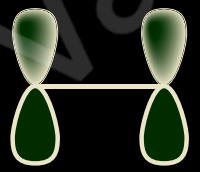
LUMO

node

E



Bonding



π_1

HOMO

Constructive overlap

Summary of MOT

The atomic orbitals combine to form a new orbital known as **molecular orbital**

Constructive overlap results **Bonding Molecular orbital (B.M.O)** and
destructive overlap results **Antibonding Molecular Orbital (A.B.M.O)**

The, B.M.O has lower energy and hence greater stability
than the corresponding A.M.O.

Electrons of the molecule are filled just like in case of atomic orbitals –
Follow Aufbau, Pauli exclusion, and Hund'e rule.

….First BMO then ABMO

Summary of MOT

Destructive overlap results Nodal Plane- possibility of finding electrons are minimum.

BMO are represented as σ, π and ABMO are represented as σ^*, π^*

HOMO - *'Highest Occupied Molecular Orbital'*,

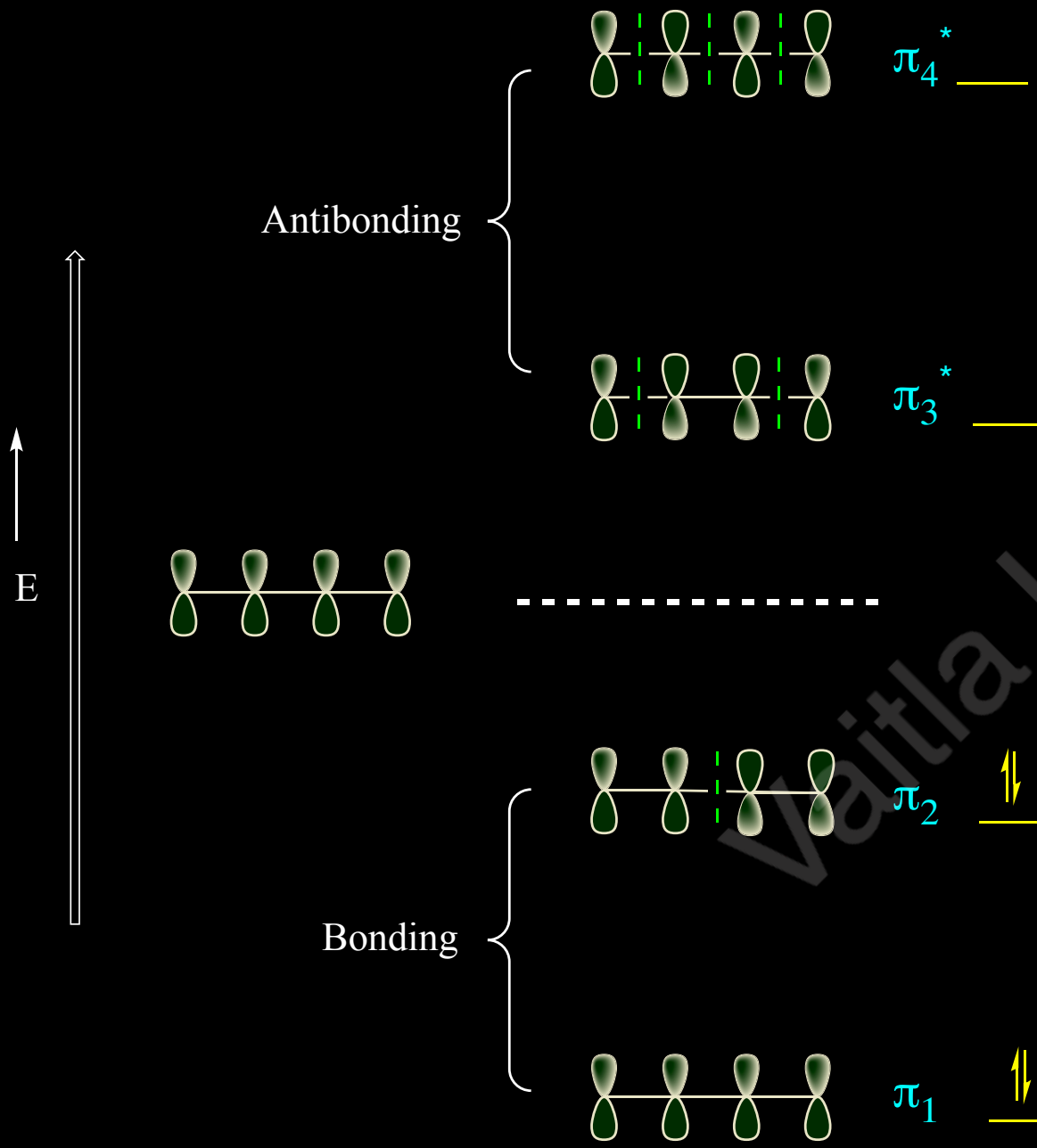
LUMO - *'Lowest Unoccupied Molecular Orbital'*.

The **HOMO** is the highest energy MO that has any electrons in it.

The **LUMO** is the next highest energy orbital (it will be empty).

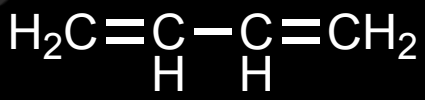
The **LUMO** is the lowest energy place to put or excite an electron.

Frontier molecular orbital theory



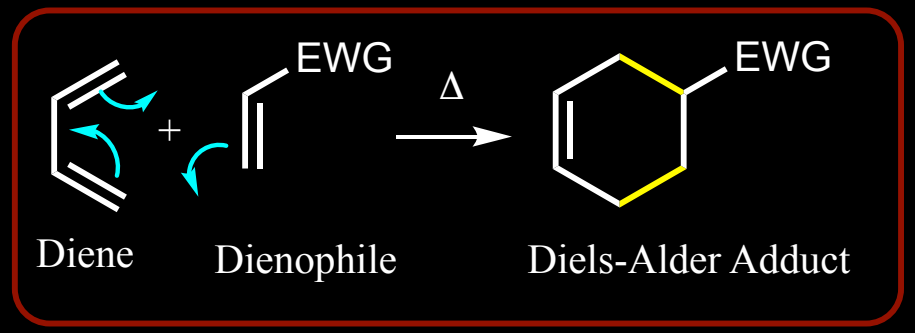
MOT of alkenes fails to explain

1) Unusual stability of conjugated dienes
2) Why do alkenes absorb UV light
3) Why some pericyclic reactions occur but others do not!

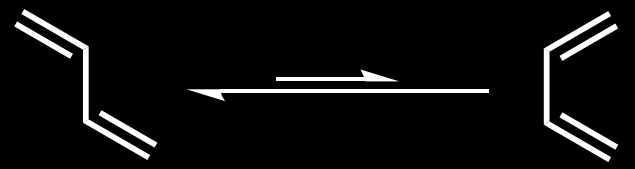


Diels-Alder reaction [4+2] Cycloaddition

Diels-Alder reaction

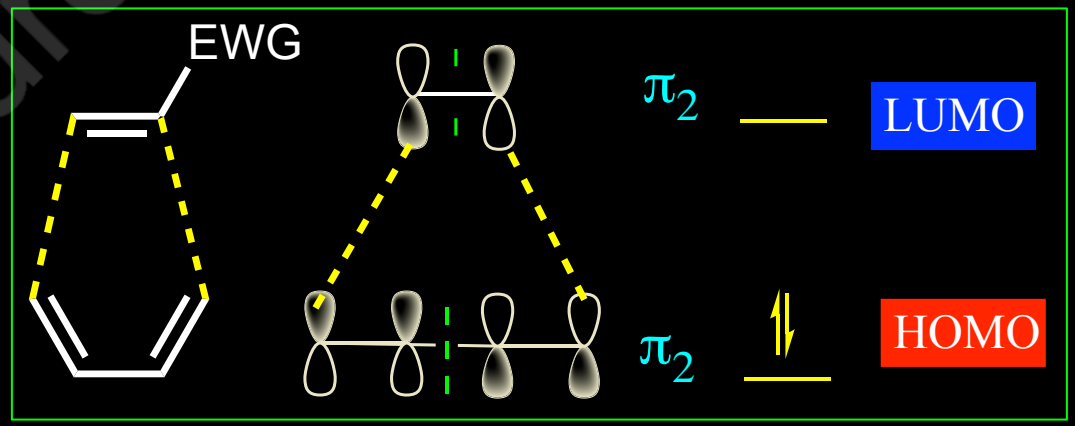


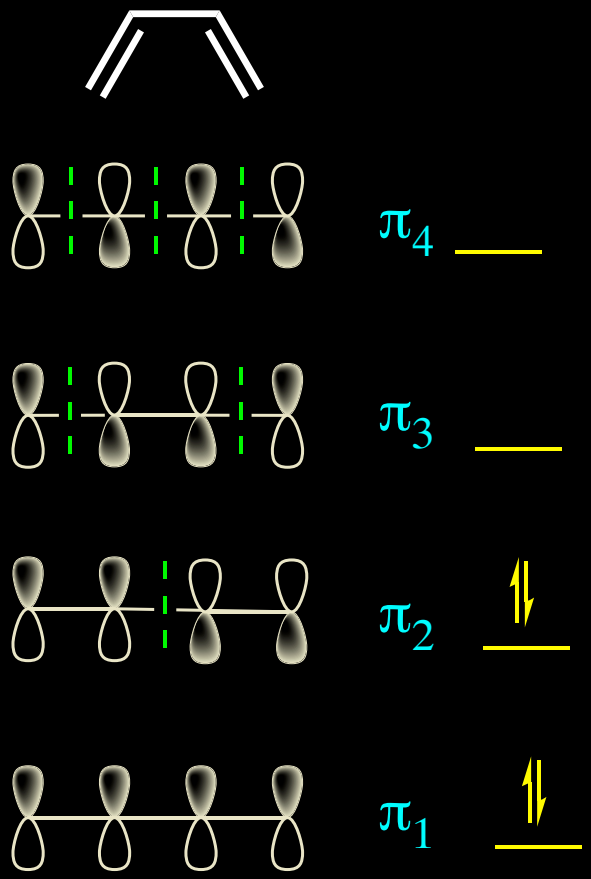
1,3-Butadiene

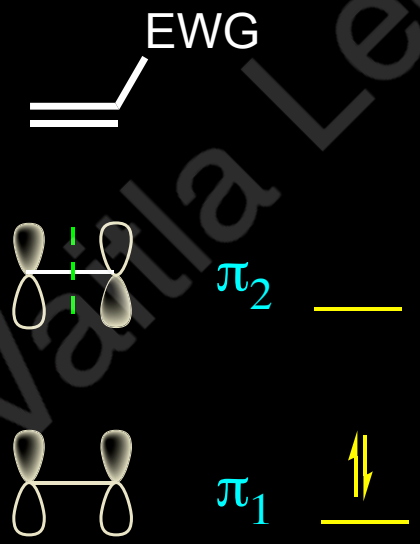


s-Trans — Do not undergo DAR

s-Cis — Undergoes DAR



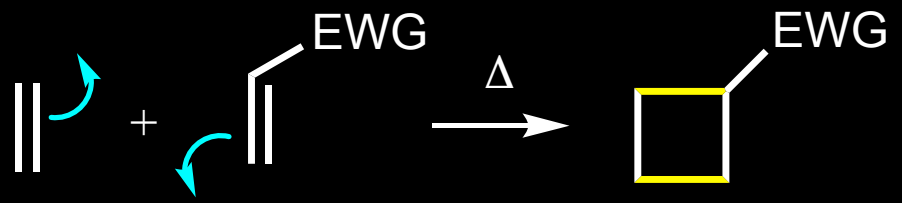


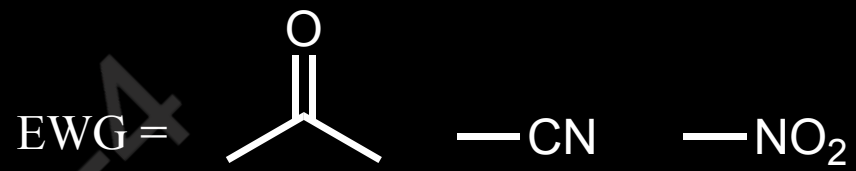


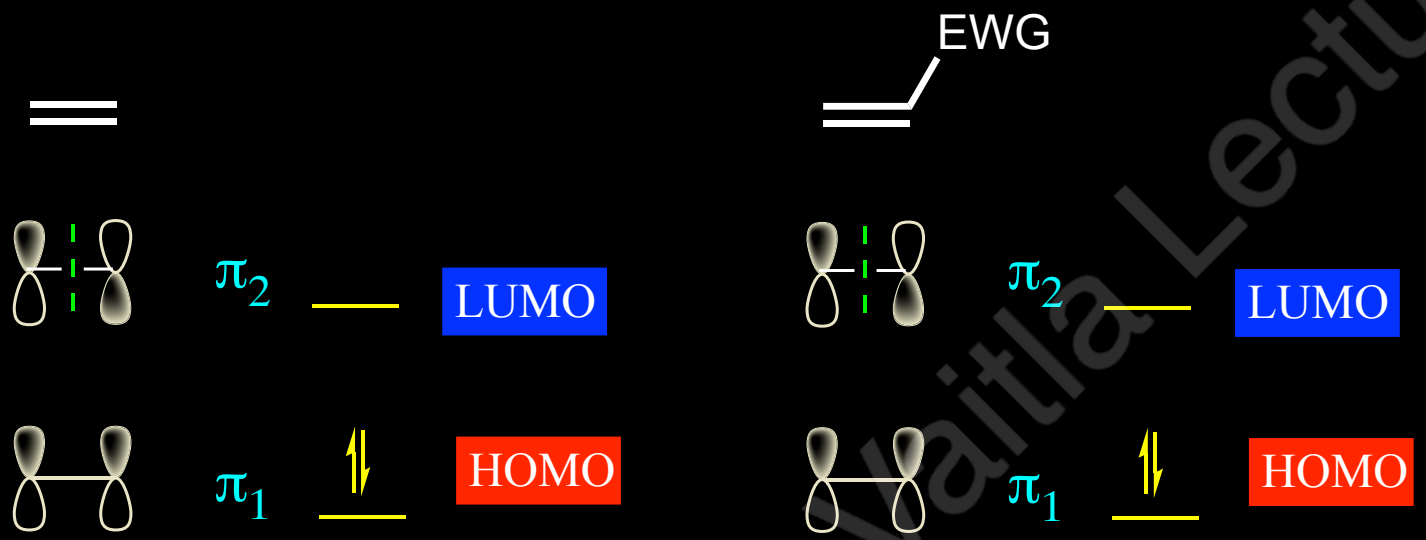
[4+2] Cycloaddition Reaction allowed under heating conditions

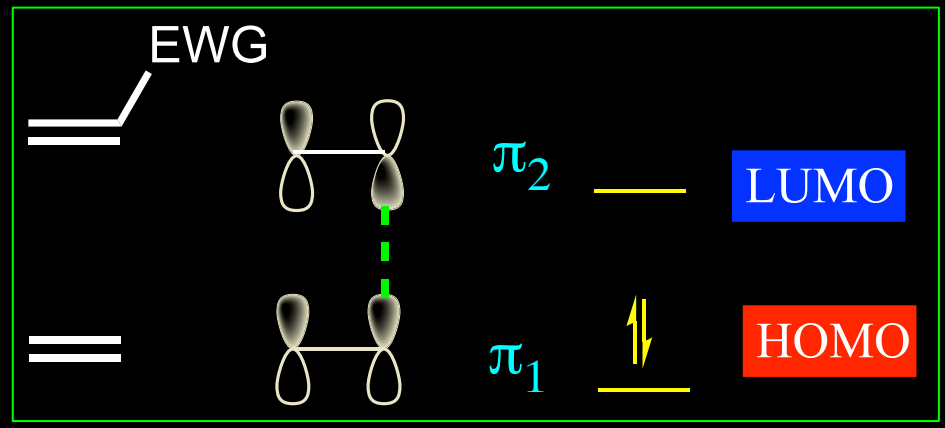
[2+2]-Cycloaddition

[2+2] Cycloaddition





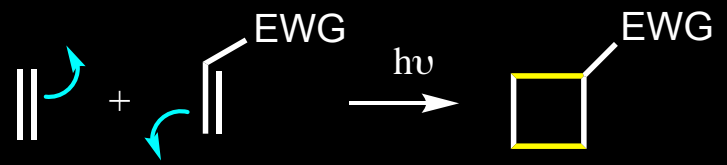


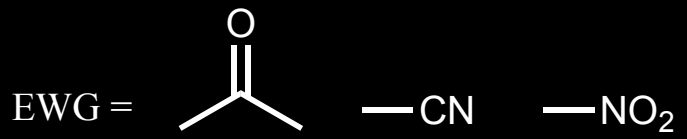


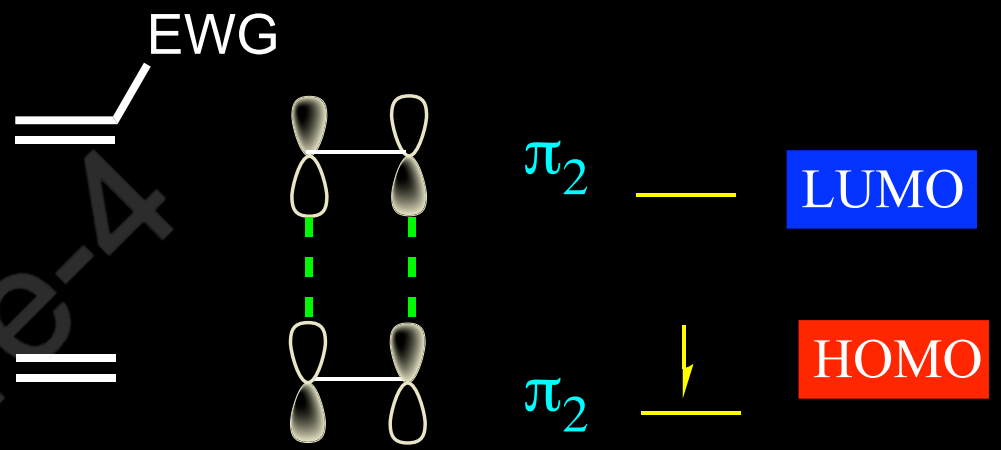
[2+2] Cycloaddition Reaction is Forbidden under heating conditions

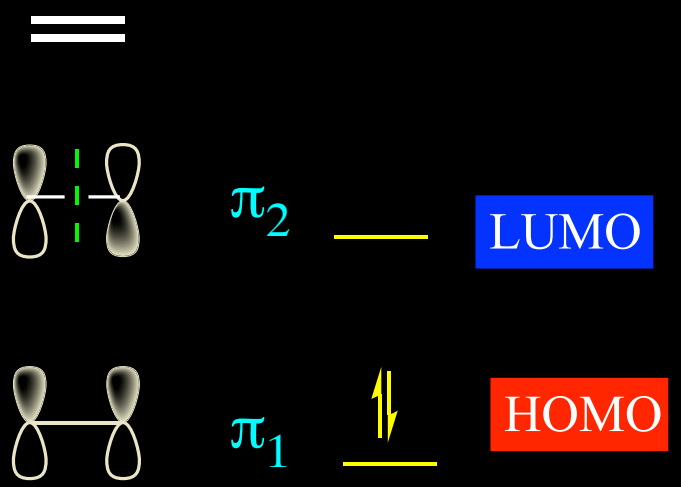
[2+2]-Cycloaddition

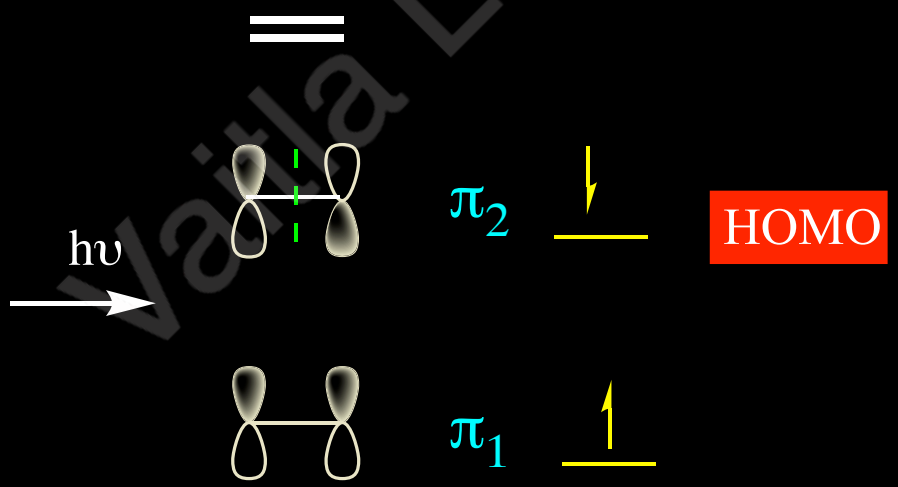
[2+2] Cycloaddition

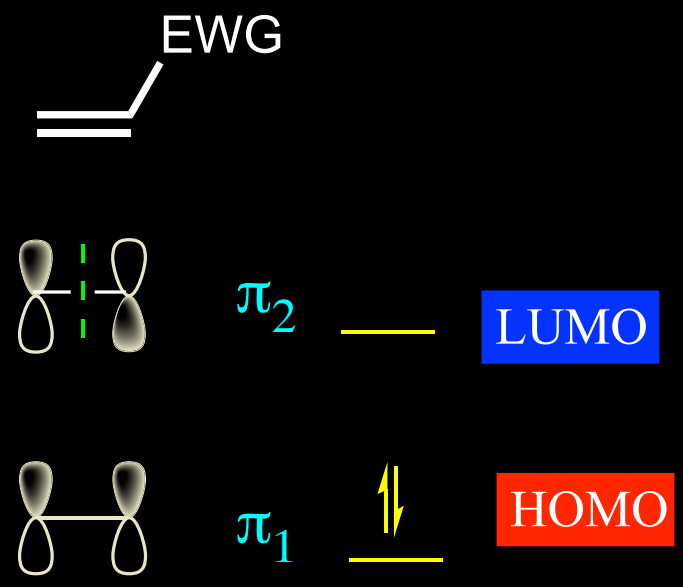












[2+2] Cycloaddition Reaction allowed under photochemical conditions