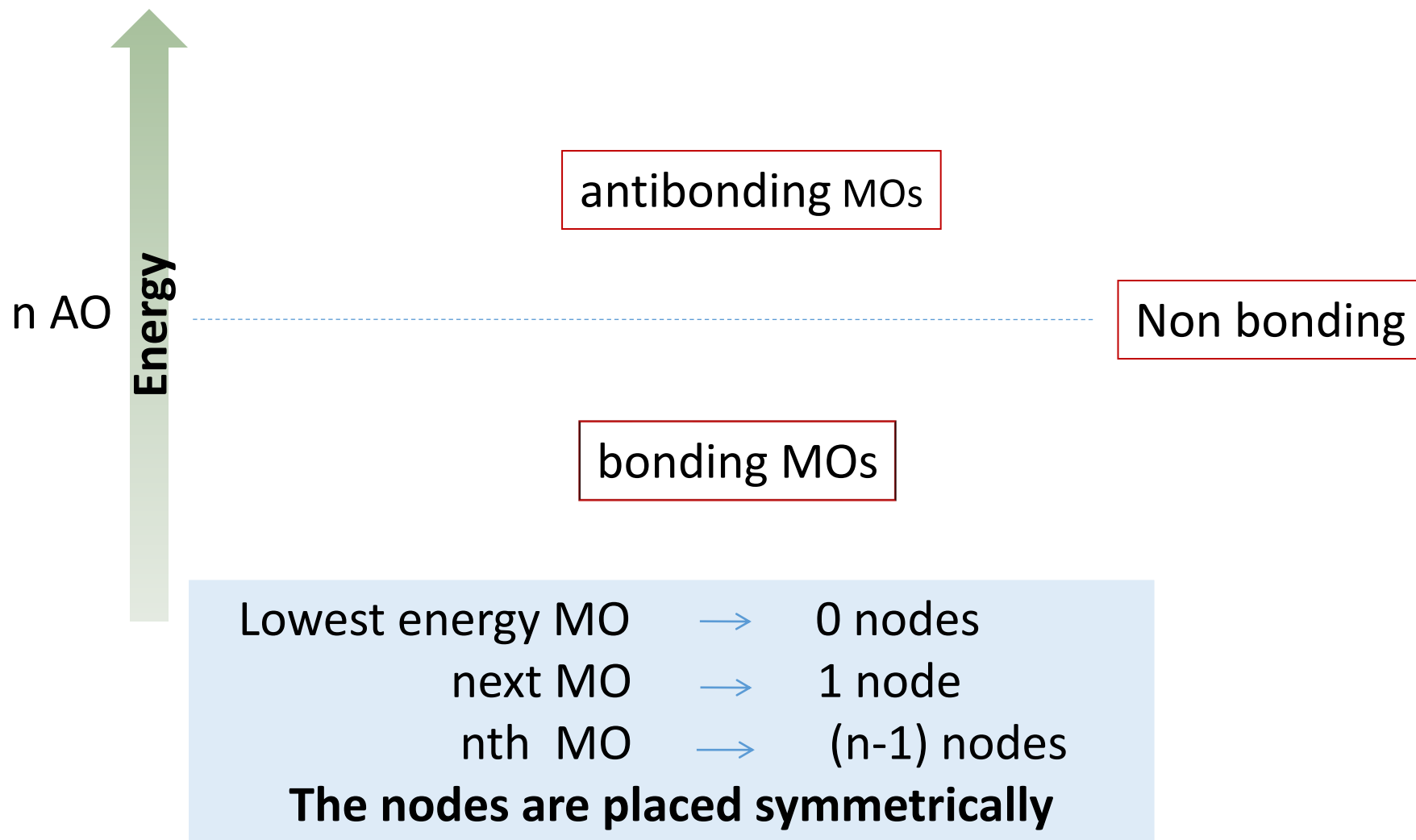


Recap - MO Construction Acyclic Conjugated Polyenes

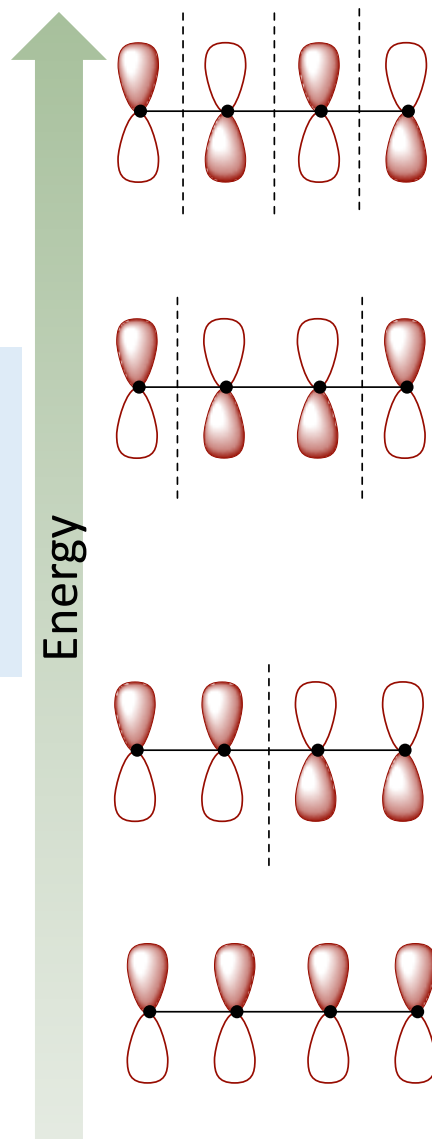


When n is even – $n/2$ bonding and $n/2$ antibonding MOs exist

When n is odd – $(n-1)/2$ bonding, 1 non-bonding and $(n-1)/2$ antibonding MOs exist

Butadiene MOs

The nodes are placed symmetrically



$$\text{---} \quad \Psi_4 = c_1\phi_1 - c_2\phi_2 + c_3\phi_3 - c_4\phi_4$$

$$\text{---} \quad \Psi_3 = c_1\phi_1 - c_2\phi_2 - c_3\phi_3 + c_4\phi_4$$

LUMO

$$\uparrow\downarrow \quad \Psi_2 = c_1\phi_1 + c_2\phi_2 - c_3\phi_3 - c_4\phi_4$$

HOMO

$$\uparrow\downarrow \quad \Psi_1 = c_1\phi_1 + c_2\phi_2 + c_3\phi_3 + c_4\phi_4$$

Activity

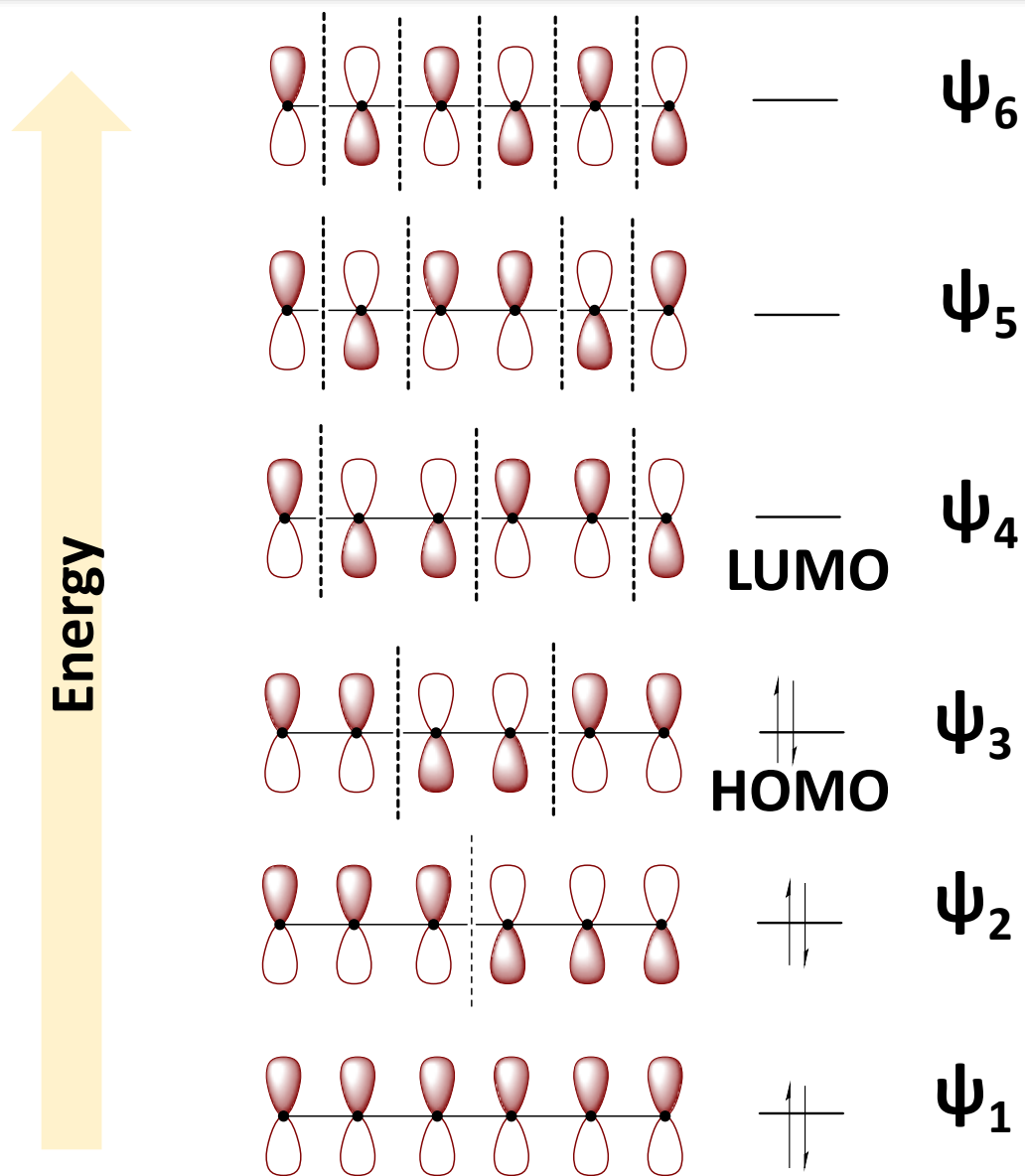
Draw the MOs for
hexatriene

A Small Activity

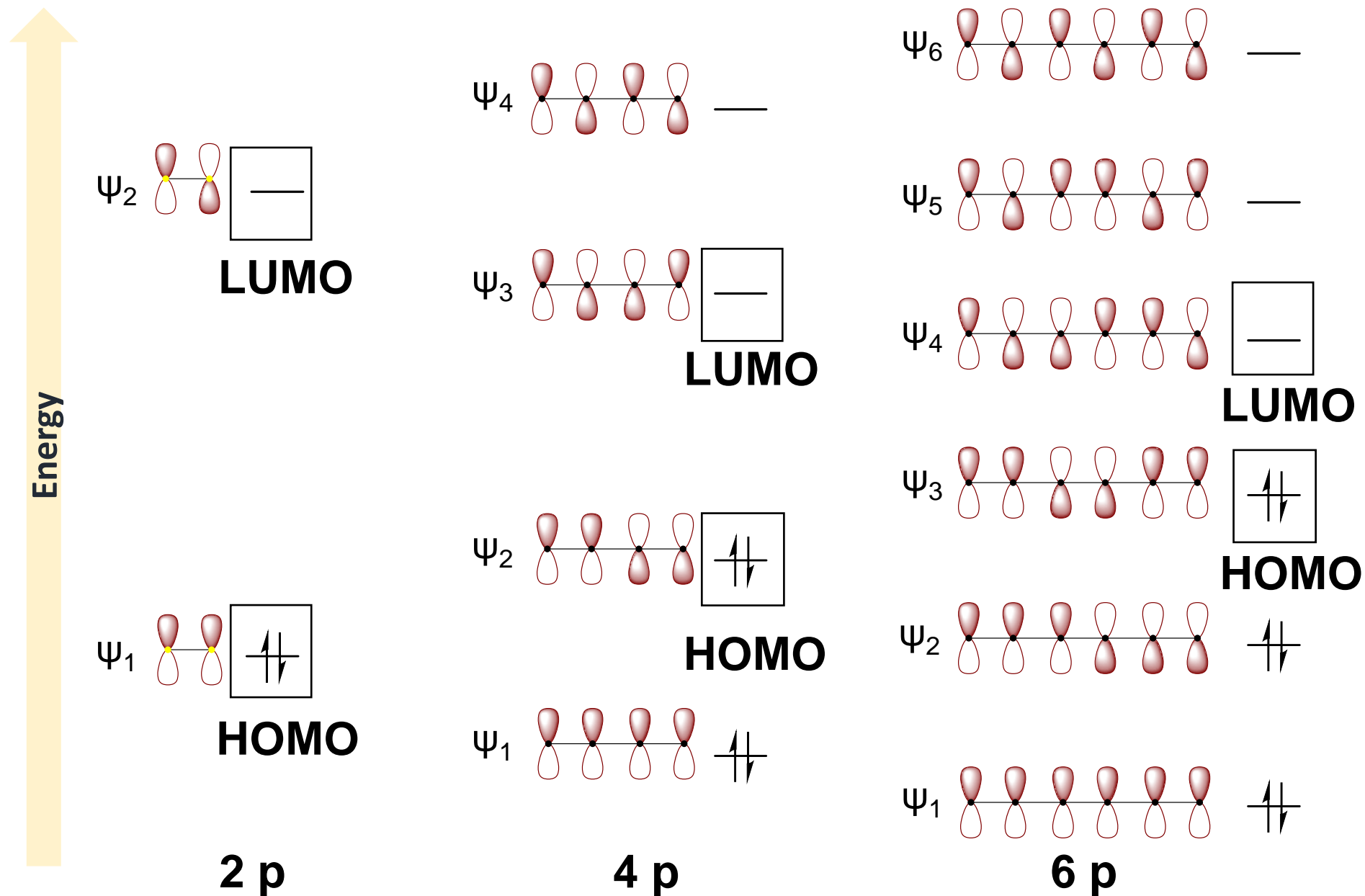
- Go to www.menti.com –
- Use code 2278 5484

Happy answering 😊

MOs of Hexatriene



MOs – See any patterns?



MOs of Larger Conjugated Polyenes

- The lowest energy orbital is always symmetric with respect to the principal mirror plane
- The energy of the MO increases as the no: of nodes increases

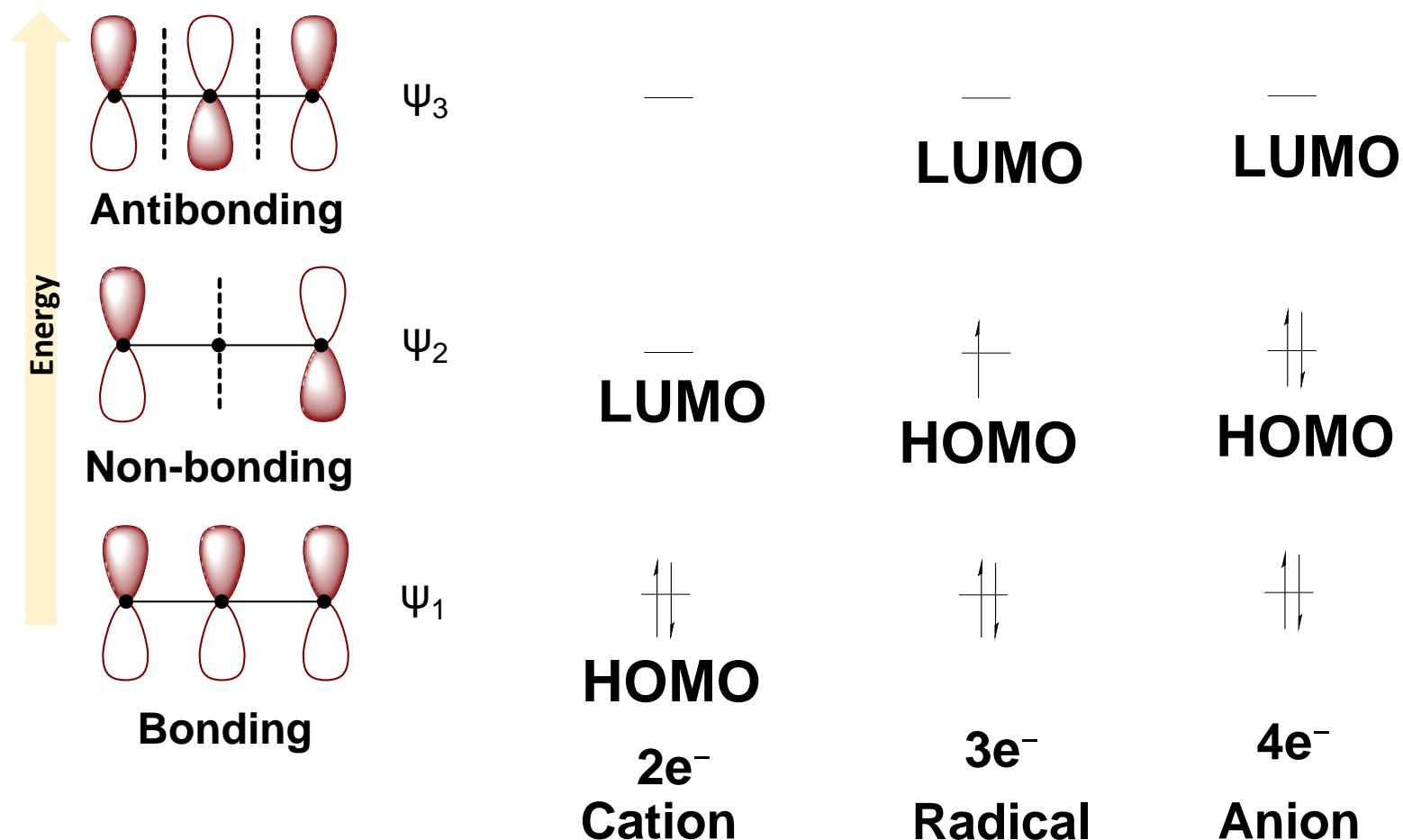
Eg. ψ_1 - 0 nodes
 ψ_2 - 1 node
 ψ_n - n-1 nodes

Again: Remember to ignore the nodes of the AO

- When you draw MOs place the nodes symmetrically

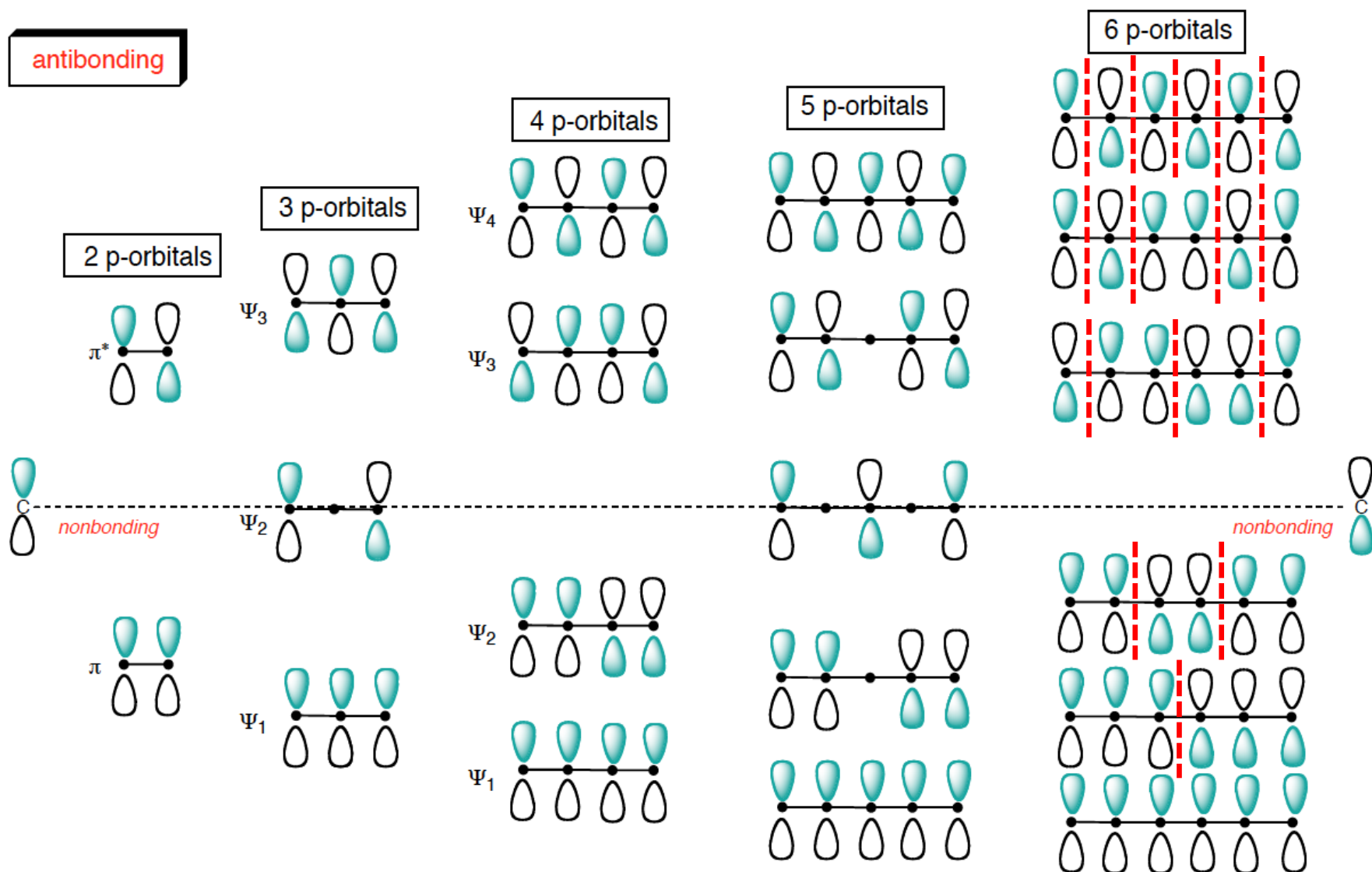
Draw the MOs of Allyl Cation

MOs of Allyl System



The nodes are placed symmetrically

Summary: Acyclic Conjugated Systems

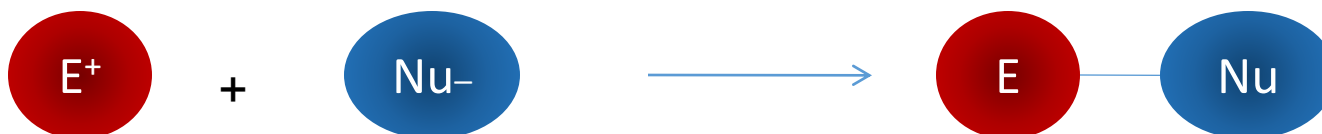


bonding

There are no nodal planes in the most stable bonding MO. With each higher MO, one additional nodal plane is added. The more nodes, the higher the orbital energy.

Broad Classification: Organic Reactions

- **Polar Mechanism**



- **Radical Mechanism**



- **Concerted Reactions**

All the bonding changes occur at the same time and in a single step – No intermediates involved !

Significance of Orbital Energies

A process that takes one stable molecular configuration (or set of nuclei and occupied and unoccupied orbitals) to another stable molecular configuration *via* unstable configurations

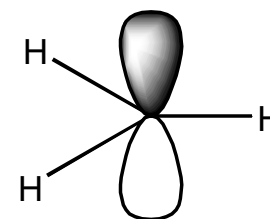
Transfer - electron rich to electron poor

Nucleophiles - Higher energy filled orbitals (Ready to donate electrons to suitable electrophiles)

e.g., NH_3 lone pair of electrons responsible for its nucleophilic nature is its nonbonding MO

Electrophiles- lower energy unfilled orbitals

e.g., empty nonbonding MO in BF_3 or CH_3^+



Common HOMO-LUMO Combinations

HOMO possibilities

Filled

σ

π

n (non-bonding)

LUMO possibilities

Unfilled

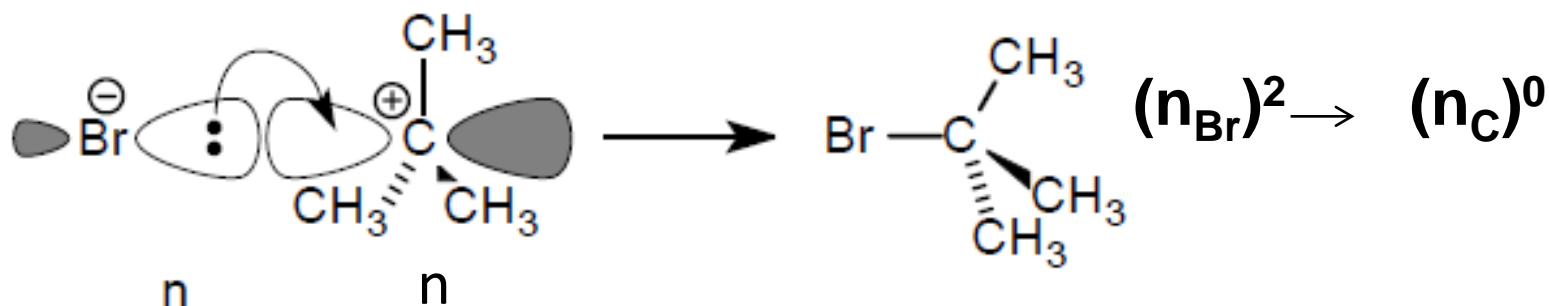
σ^*

π^*

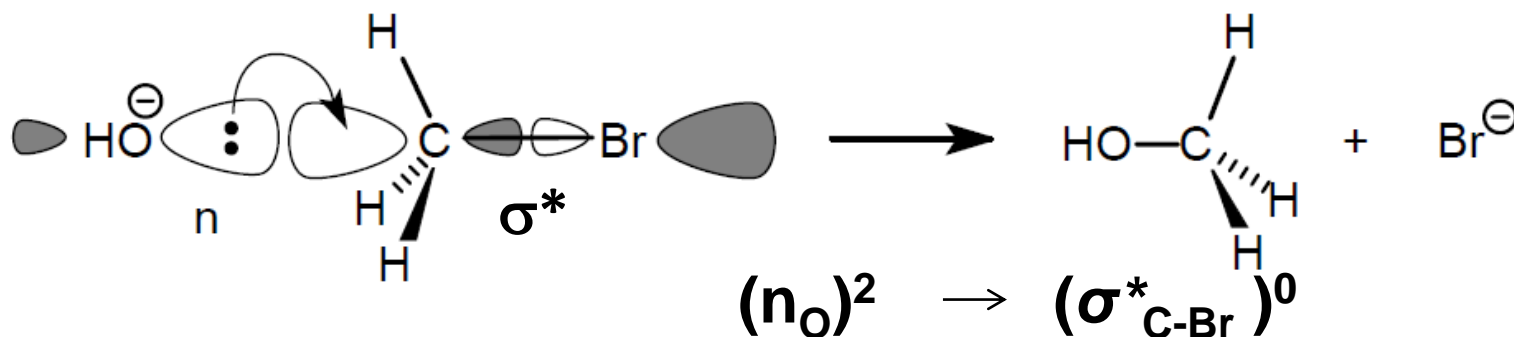
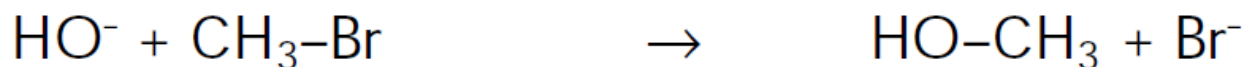
n (nonbonding)

Explanation of Reactions Through Molecular Orbitals

S_N1 Reaction – Attack from both sides of carbocation ok



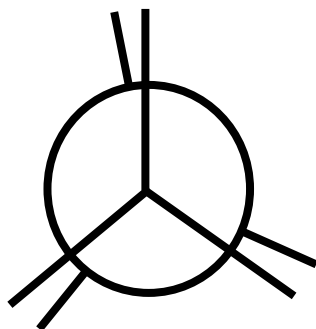
S_N2 Reaction – backside attack only possible



Rotational Barrier in Ethane

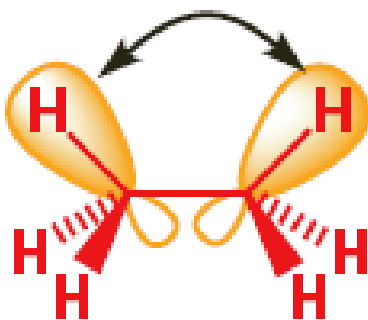
Barrier of 3 kcal mol⁻¹ due to steric and electronic effects

Transition state
is **eclipsed**

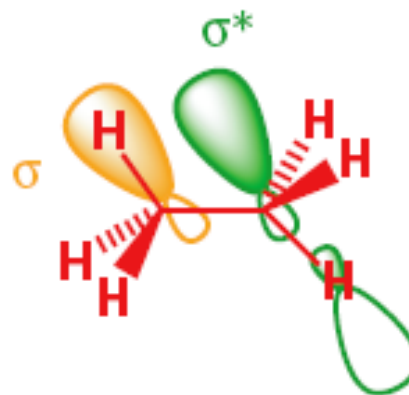
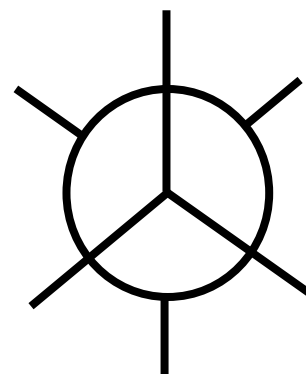


eclipsed:

filled orbitals repel



Most stable rotamer
is **staggered**



and empty C-H σ^*
antibonding orbital