Learning Outcomes – Part 1

At the end of this module you should be able to….

- **Represent** 3D molecules using appropriate 2D representations

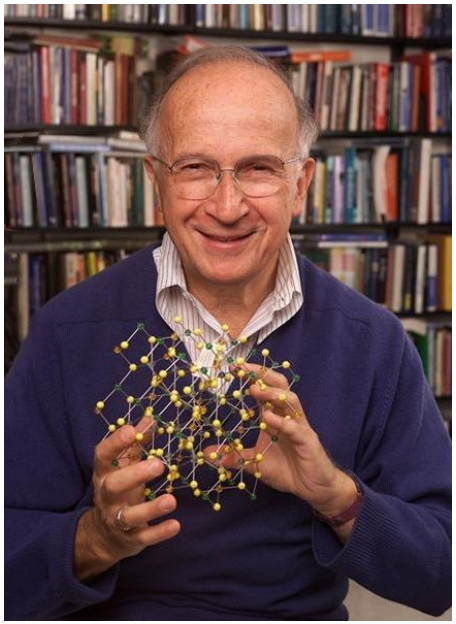
- **Determine** the energetically favourable conformation of butanes, cyclohexane derivatives, decalins.

- **Explain** the effect of conformational equilibrium on reactivity.

Reading assignment: Revision of CIP rules, R/S and E/Z descriptors.

Part 2: MO Theory Applications to Pericyclic Reactions and Photochemistry

Who are these chemists?
Hint – you will hear about them in the next few lectures.



Learning Outcomes – Part 2

At the end of this module you should be able to….

- **Construct** π–molecular orbitals for conjugated polyenes
- **Explain** the reactivity of molecules and reaction outcomes based on MO Theory
- **Predict** the stereochemical outcome of the pericyclic reaction under the given reaction condition

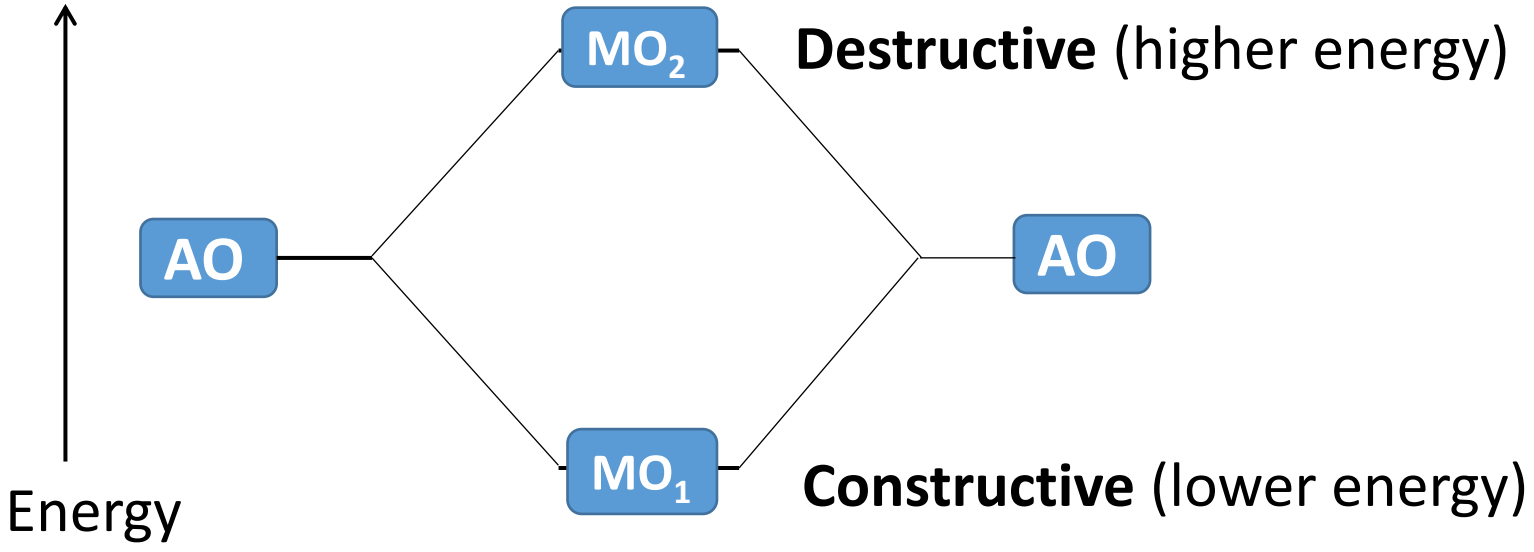
Molecular Orbital Theory

Molecular Bonds – formed when two atoms are brought from infinity close to each other

Molecular orbitals - obtained by combining the atomic orbitals (AO) on the atoms

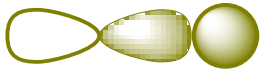
How do the AOs combine?

Think of the wave nature of electrons

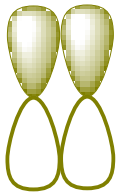


Types of Orbital Mixing

σ



σ



π

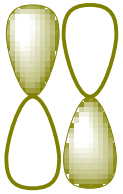
σ*

σ*

Rows A & B

Axial overlap

σ MO



π*

Row C

Lateral overlap

π MO

Column A

Constructive

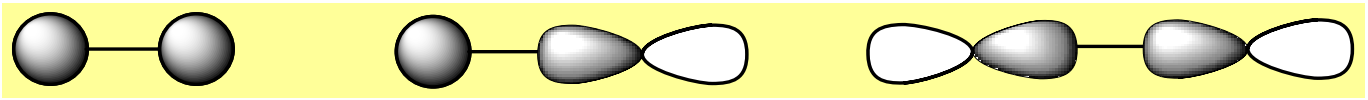
Bonding MO

Column B

Destructive

Antibonding MO

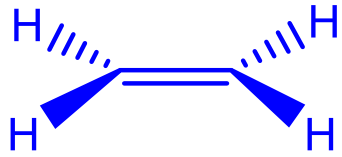
More on σ Orbitals

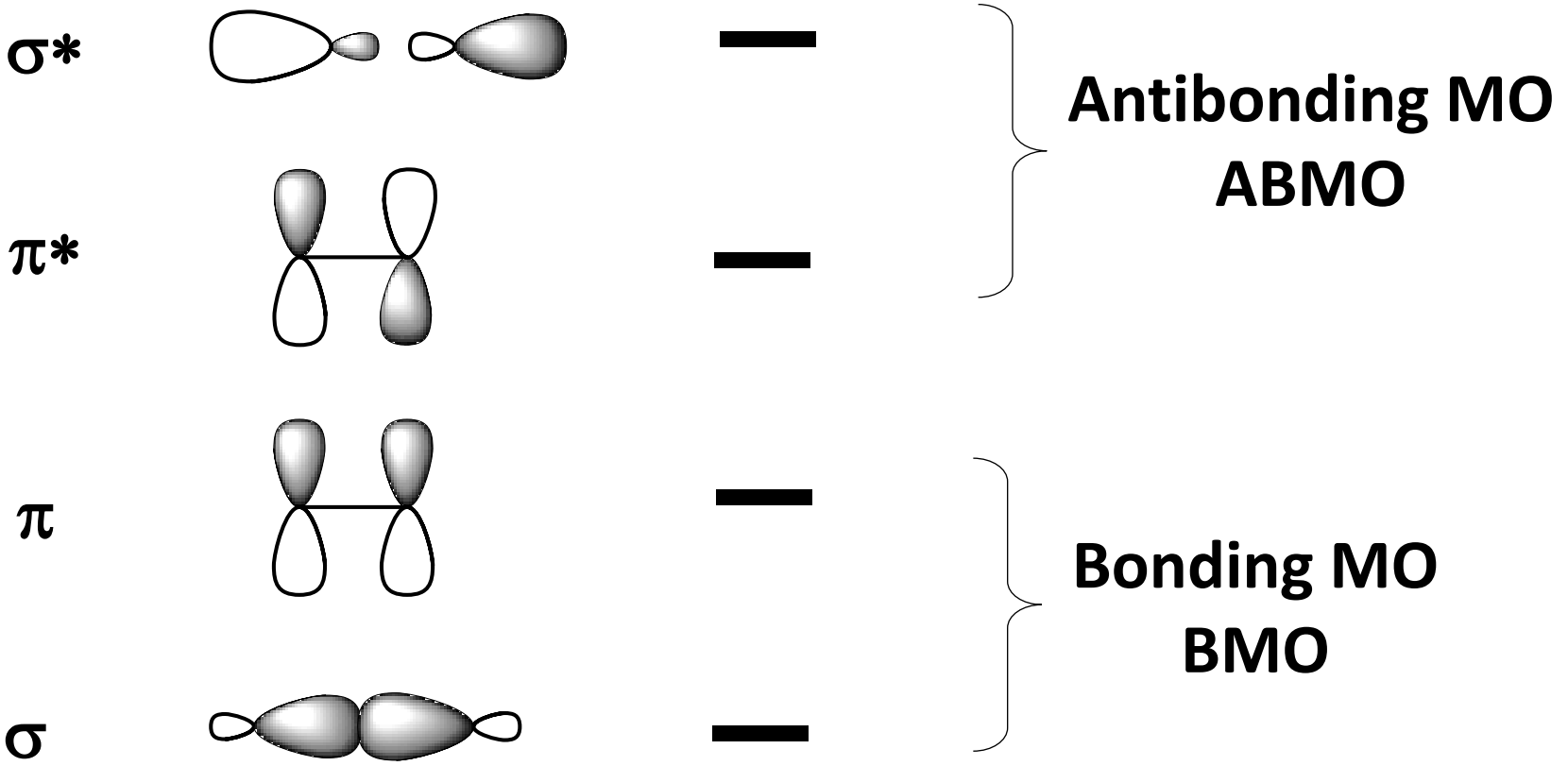


σ

- No nodes along the internuclear axis (Ignore AO nodes e.g. of p orbital)
- Symmetric along the axis

Types of Orbitals – Ethylene (C=C)

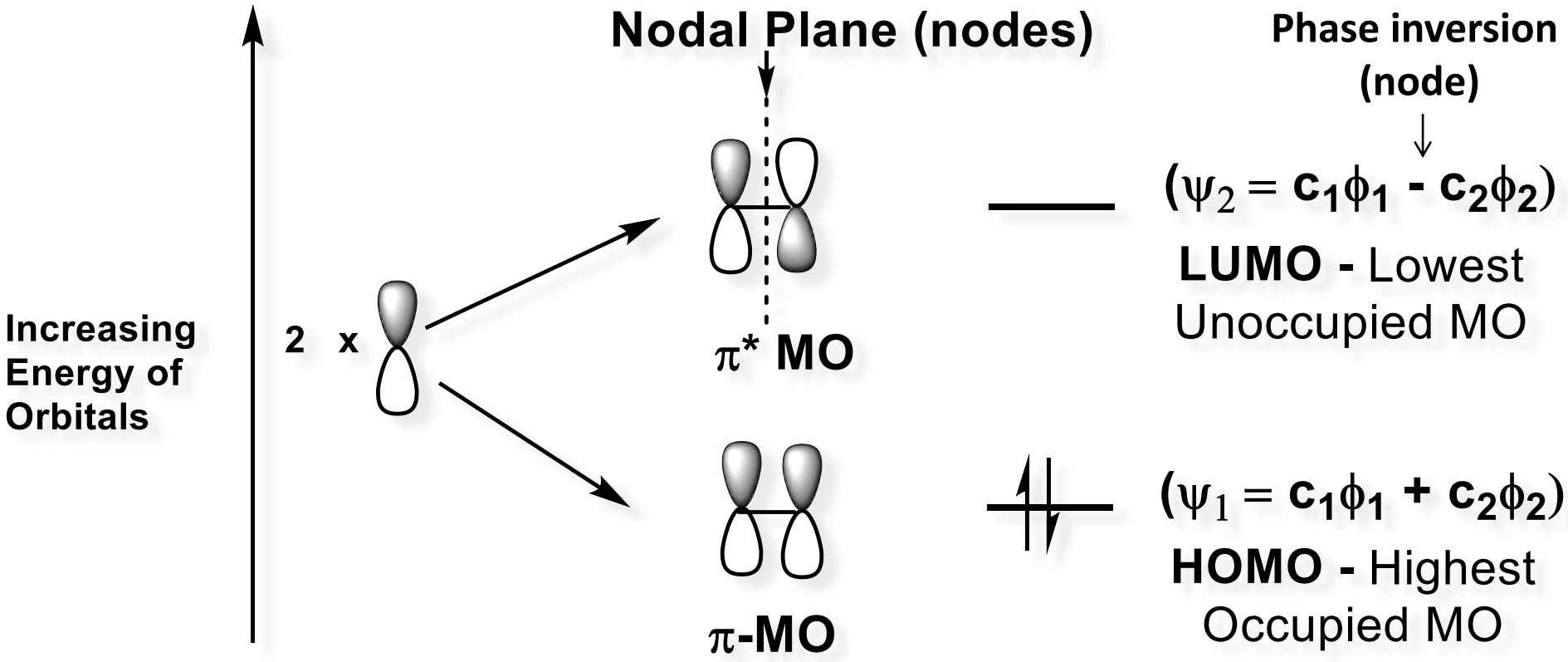




Huckel – The sigma framework can be neglected!!

Ethylene – Simplified MO picture

The σ – framework neglected as it is in the nodal plane of the p atomic orbitals



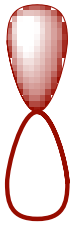
Qualitative Picture – Hückel's MO

Applying to Larger Conjugated Systems

Molecular Orbital Picture

Let us look at the π-bonding interactions closely

The σ – framework neglected as it is in the nodal plane

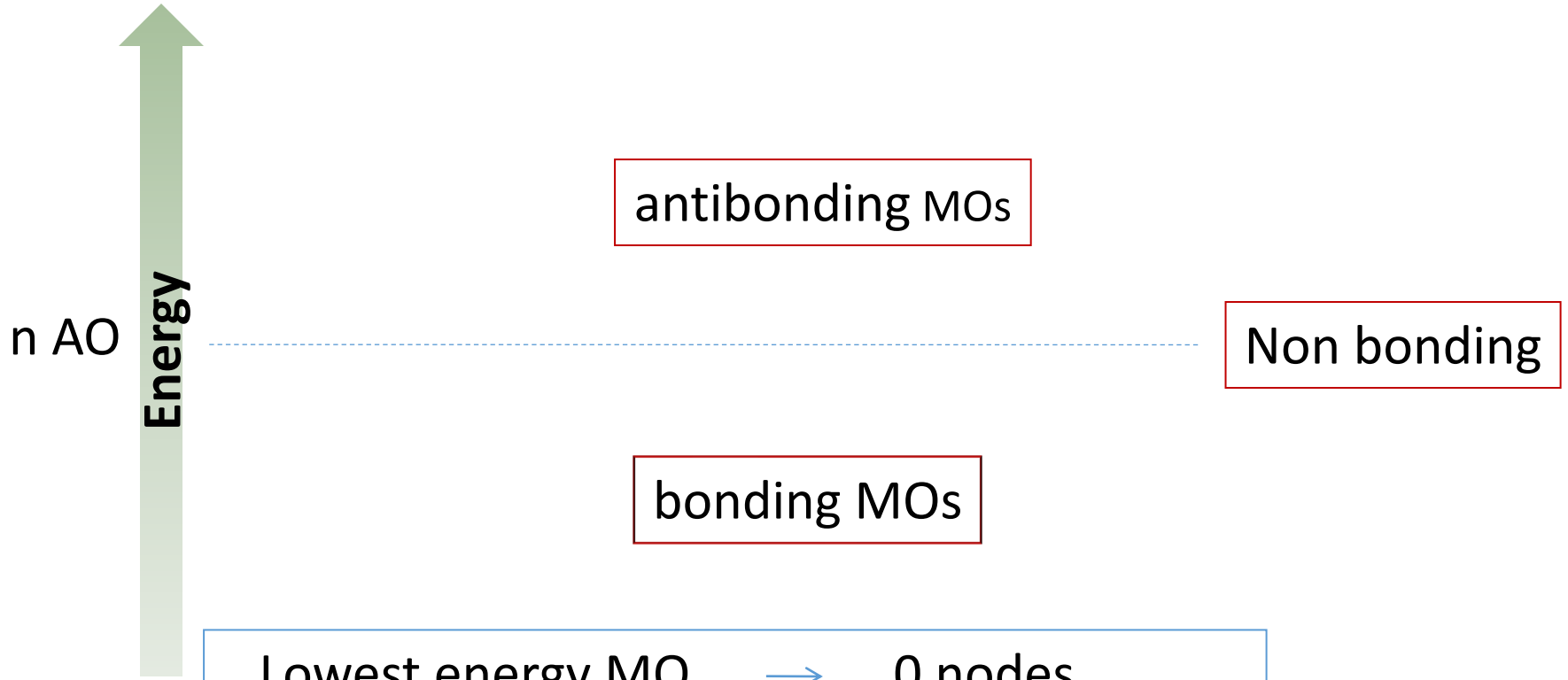


n → **interact** → **π/ψ MOs**

n

Qualitative Picture – Hückel's MO

MO Construction Acyclic Conjugated Polyenes



Lowest energy MO → 0 nodes

next MO → 1 node

nth MO → (n-1) nodes

The nodes are placed symmetrically

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

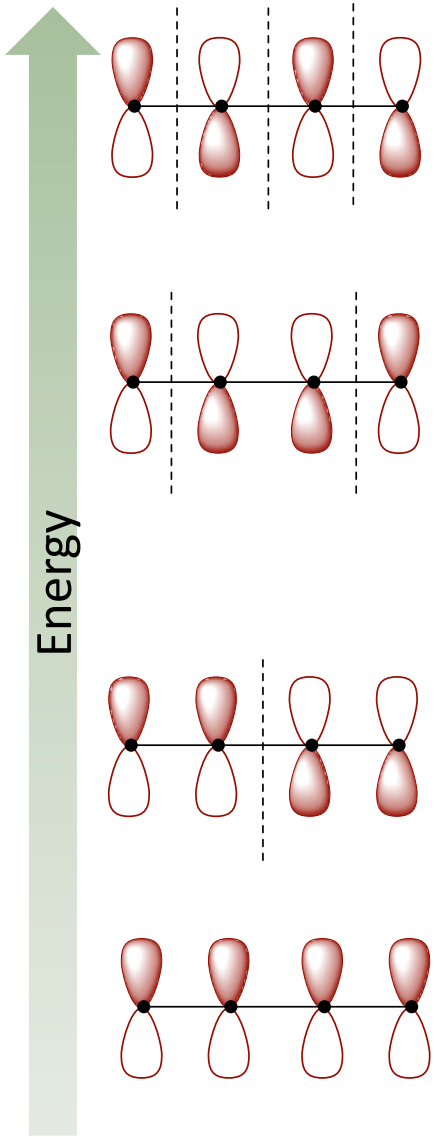
When n is odd – (n-1)/2 bonding, 1 non-bonding and (n-1)/2 antibonding MOs exist

Activity

Draw the MOs for butadiene

Butadiene MOs

Write the wave equation for each MO



$\Psi_4 = c_1\varphi_1 - c_2\varphi_2 + c_3\varphi_3 - c_4\varphi_4$

$\Psi_3 = c_1\varphi_1 - c_2\varphi_2 - c_3\varphi_3 + c_4\varphi_4$

LUMO

$\Psi_2 = c_1\varphi_1 + c_2\varphi_2 - c_3\varphi_3 - c_4\varphi_4$

HOMO

$\Psi_1 = c_1\varphi_1 + c_2\varphi_2 + c_3\varphi_3 + c_4\varphi_4$

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