Frontier Molecular Orbitals – HOMO and LUMO

It makes sense that the HOMO and LUMO are the orbitals most likely to be involved in chemical reactivity.

- Chemical reactions involve the redistribution of electrons (creation and destruction of bonds, oxidation, reduction, …)

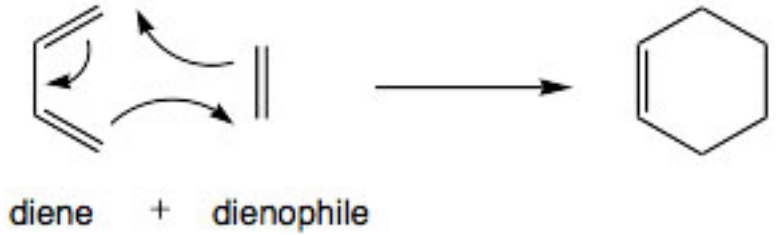
- The HOMO is the orbital of highest energy that is still occupied, so energetically it is the easiest to remove electrons from this orbital. This could be simply donating electron density to form a bond (act as a Lewis base) or it could be oxidation.

- The LUMO is the lowest lying orbital that is empty, so energetically it is the easiest to add more electrons into this orbital…Lewis acid; reduction.

- It isn't *always* the HOMO and/or LUMO involved in chemical reactivity. Symmetry plays a role, too. If the HOMO or LUMO isn't of the correct symmetry, it might be the HOMO-1 or the LUMO+1 that is involved in the reaction.

Organic Reactions: Diels-Alder Reactions

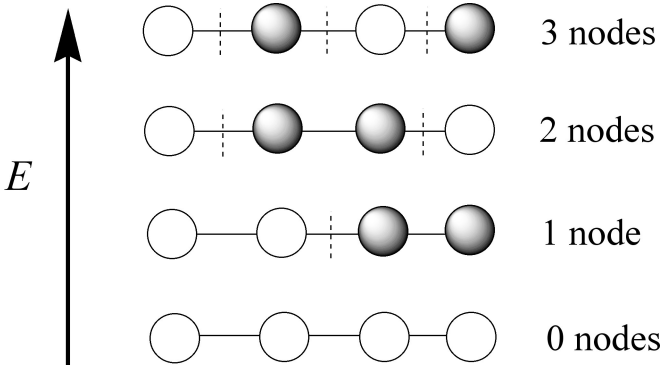
Recall: A Diels-Alder reaction is one in which a *diene* reacts with a *dienophile* to form a ring. (i.e., cycloaddition)

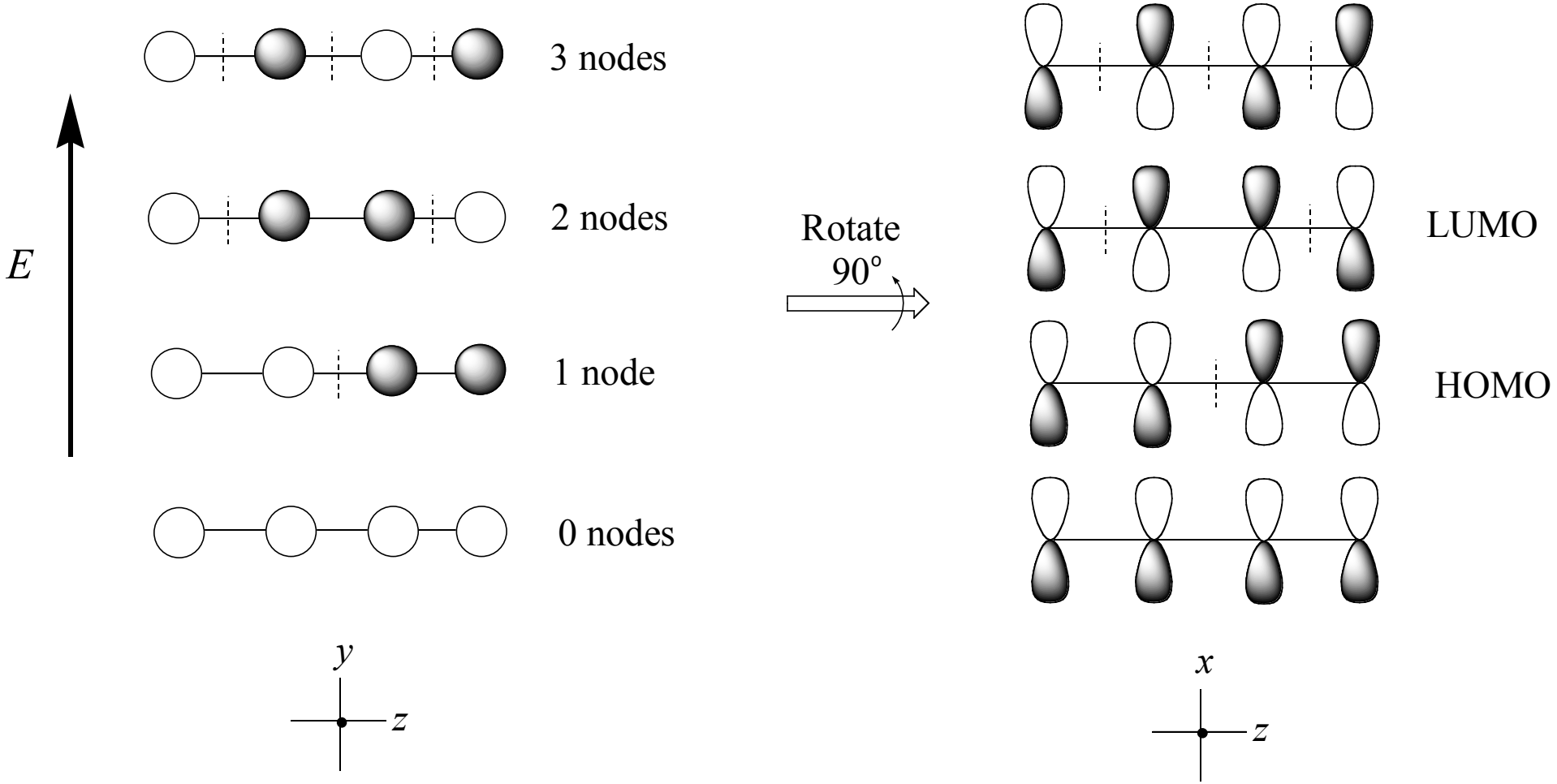


In order to understand the Diels-Alder reaction using MO theory, we need to identify the FRONTIER MOLECULAR ORBITALS of the reagents.

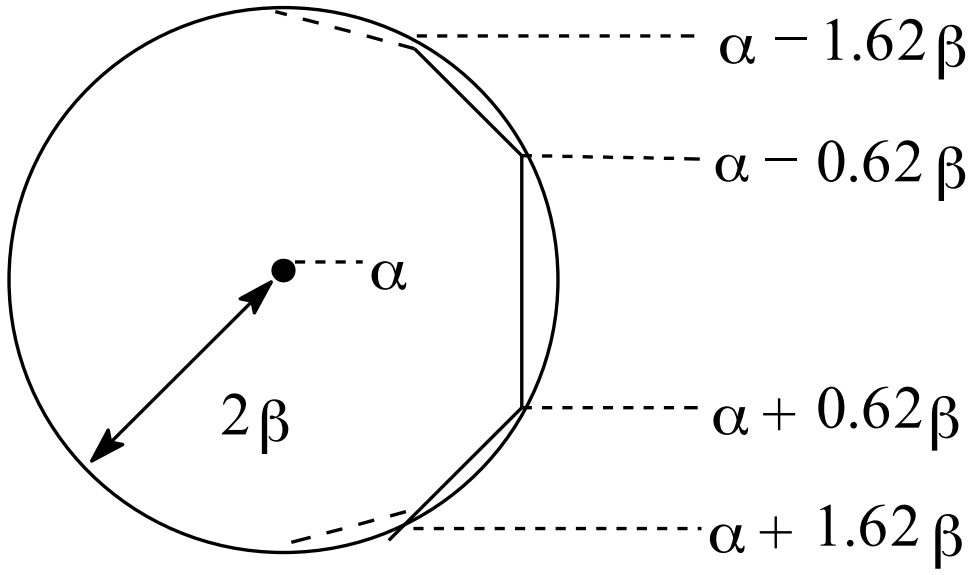
The diene and the dienophile have π frontier molecular orbitals.

Start by looking at the MOs of linear 4-membered conjugated chains. We can use the same drawings as for 1*s* orbitals, but now we are imagining that they are *p* orbitals (we are looking down at them from above).



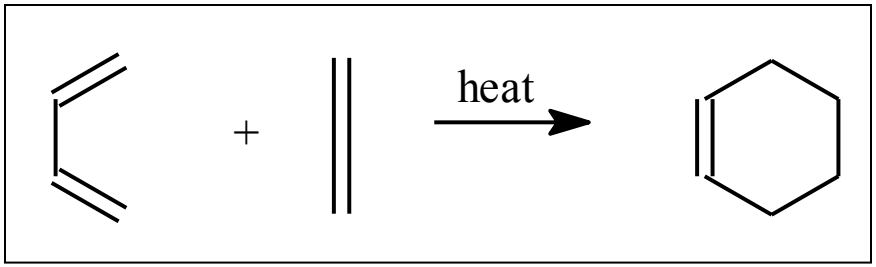

3 nodes
2 nodes
1 node
0 nodes
E
Rotate
90°
LUMO
HOMO
y
z
x
z

Energies

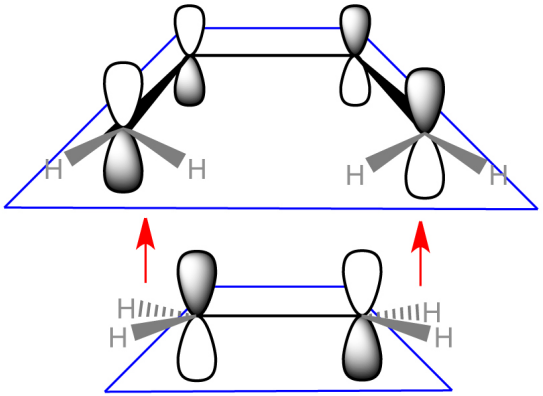


See also Frost Circle for Cyclics

WHY?



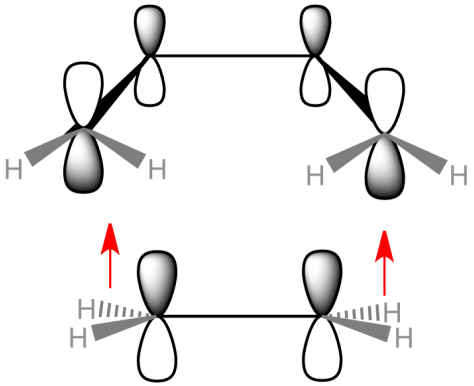
HOMO of diene



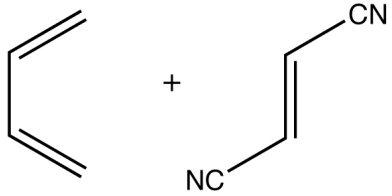
LUMO of alkene

moving up from the bottom

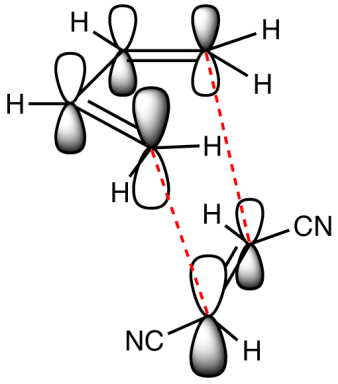
LUMO of diene



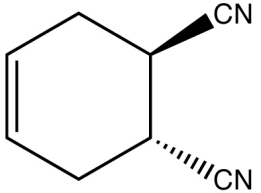
HOMO of alkene



diene dienophile

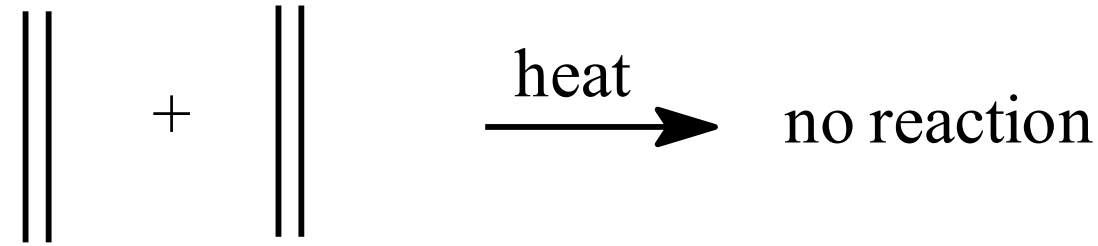


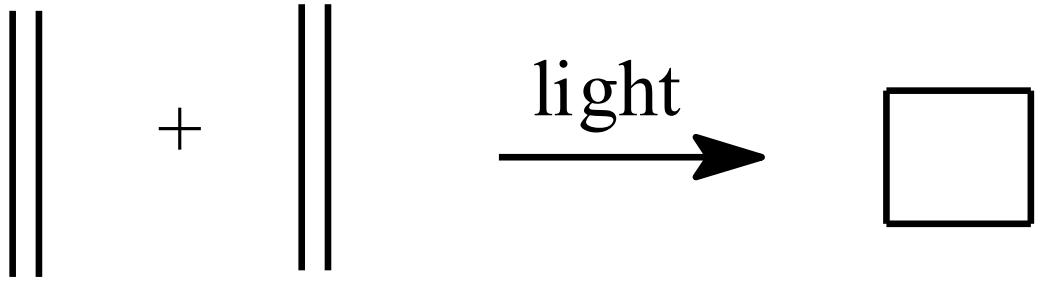
Adduct formation



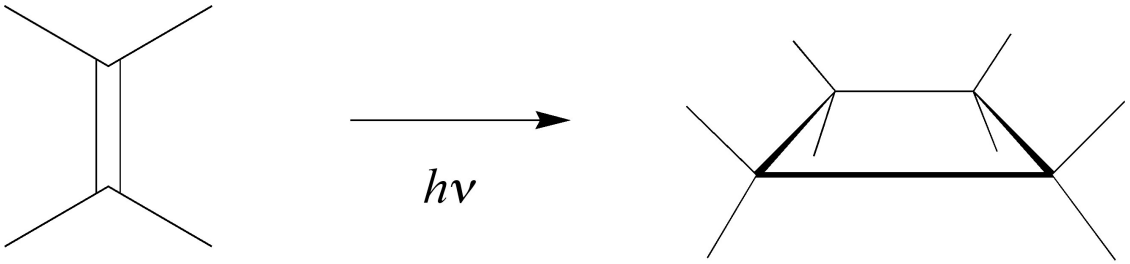
Adduct

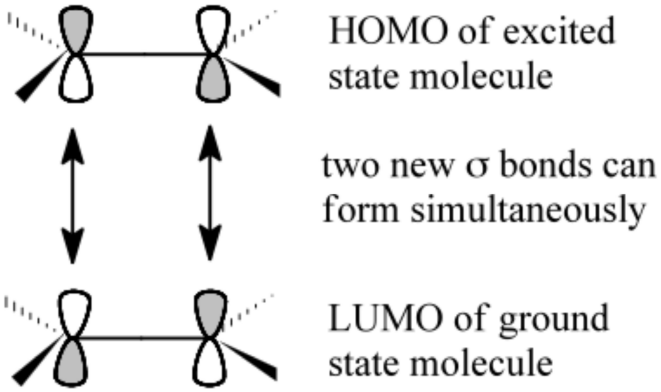
WHY?





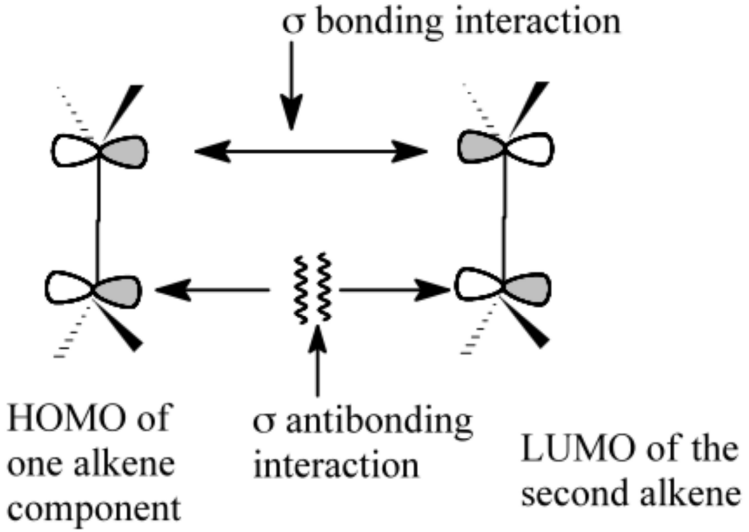
Photochemical Stimulation





LIGHT - reaction

Irradiation EXCITES an electron
from the HOMO to the LUMO!
So, the excited state HOMO is now
the same symmetry as the ground state LUMO.



HEAT - no reaction

Yay!!