**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)

![Diels-Alder Reaction Diagram](image)

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 1s orbitals, but now we are imagining that they are p orbitals (we are looking down at them from above).
MOs and reactivity

- 3 nodes
- 2 nodes
- 1 node
- 0 nodes

Rotation 90°

E

y

z

x

z

HOMO

LUMO
Energies

See also Frost Circle for Cyclics
WHY?

Heat causes the transformation of one molecule into another. The reaction shows the interaction of dienes and dienophiles, leading to the formation of an adduct.

**HOMO of diene**

**LUMO of diene**

**LUMO of alkene**

**HOMO of alkene**

**moving up from the bottom**

**diene**

**dienophile**

**Adduct formation**

**Adduct**
WHY?

\[ \text{heat} \quad \text{no reaction} \]

\[ \text{light} \quad \text{square} \]
Photochemical Stimulation

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.
Yay!!