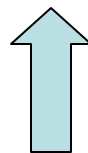


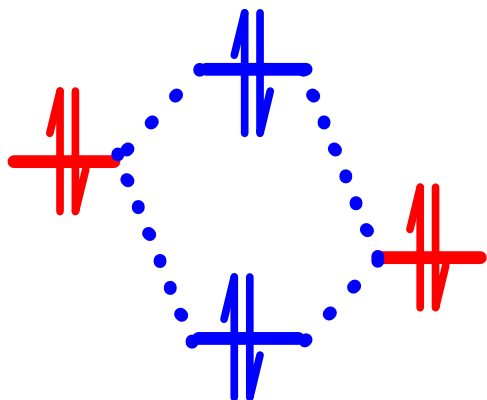
Frontier MO Theory of Rxn Rates & Selectivity

As Reactants Collide

- theory of reactant-reactant interactions
 - no solvent
 - no entropy
- Long-range
 - electrostatic
- Short-range
 - electrostatic + steric + ORBITAL

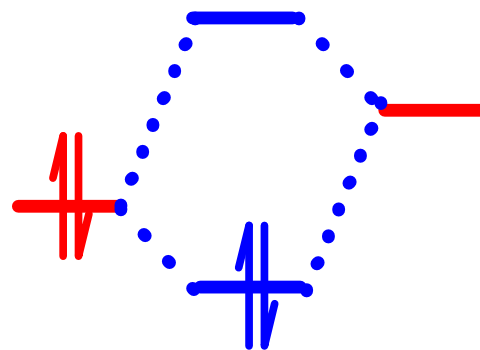


MO_{Rct 1}-MO_{Rct 2}



2 filled Rct MOs mix
make 2 filled TS MOs

net destabilization



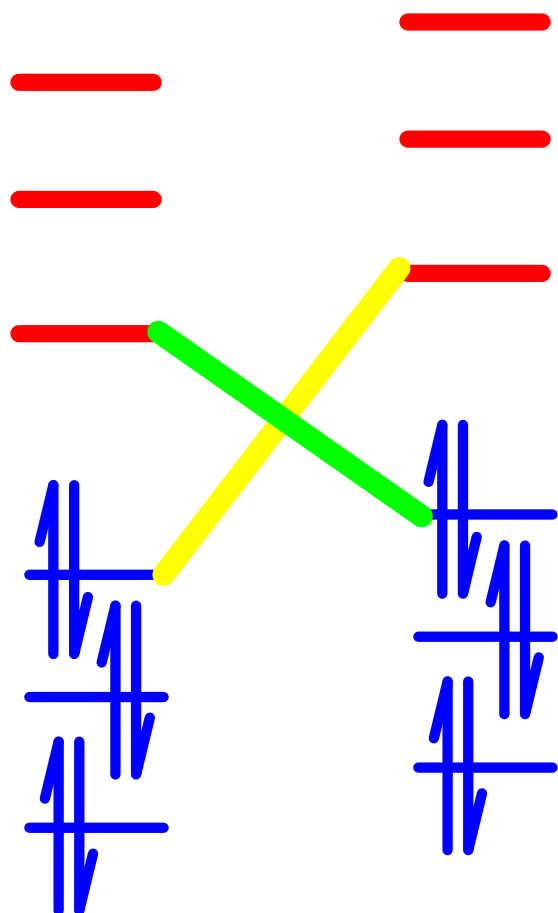
filled + empty Rct MOs mix
make filled + empty TS MOs

net stabilization

Fast Rxn if Large MO Stabilization

- Stabilization $E \approx (H_{12})^2 / (E_1 - E_2)$
 - Many possible pairings & stabilizations
- Which do we consider?
 - Largest stabilization from HOMO-LUMO
 - minimizes $E_1 - E_2$
 - Evaluate 2 HOMO-LUMO
 - “dominant” interaction minimizes $E_1 - E_2$

Gaps & Rxn Polarity



- e-rich molecule
 - high HOMO / LUMO
- e-poor molecule
 - low HOMO / LUMO
- dominant FMO =
 - $\text{HOMO}_{\text{rich}}$ & $\text{LUMO}_{\text{poor}}$
- polar rxns fast
 - small gap
 - delocalize electrons
 - $\text{HO} \rightarrow \text{HO} + \lambda \text{LU}$

Gaps & Rates

- Normal Diels-Alder
 - e-rich diene (high HOMO)
 - e-poor dienophile (low LUMO)
- Dienophile LUMO
 - bonding interaction w/ pi system of X stabilizes LUMO

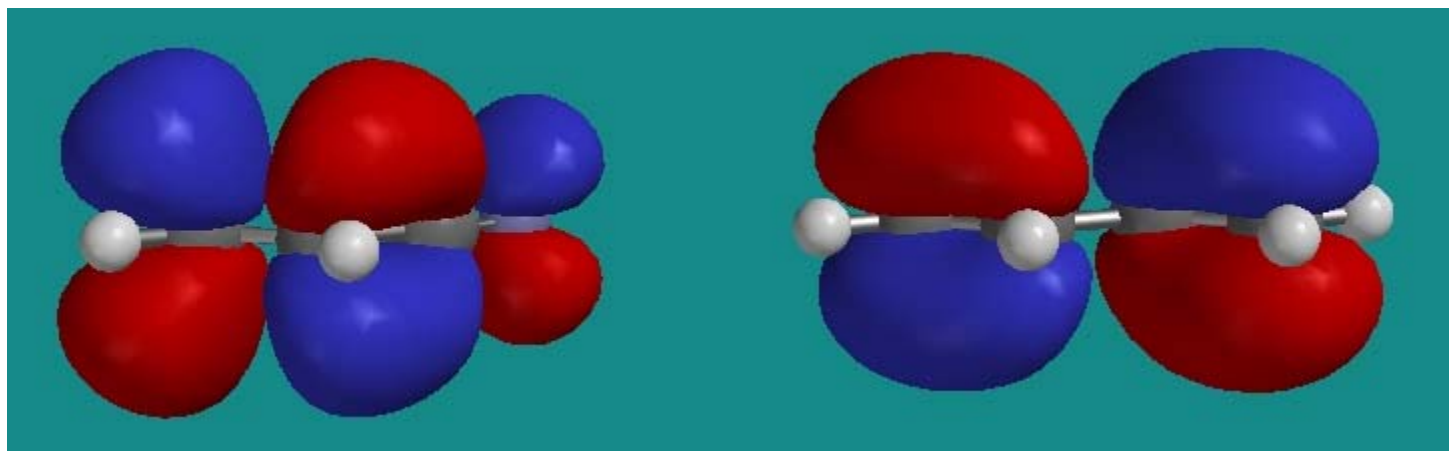
CH ₂ =CHX	LUMO (eV)
OCH ₃	5.7
CH ₂ CH ₃	5.2
H	5.1
SCH ₃	4.3
CF ₃	3.6
CH=CH ₂	3.6
SO ₂ CH ₃	3.1
C≡N	2.8
CH=O	2.6
NO ₂	1.3

Gaps & Rates

- Inverse Electron Demand Diels-Alder
 - e-poor diene (low LUMO)
 - e-rich dienophile (high HOMO)
- Dienophile HOMO
 - antibonding interaction w/ pi system of X destabilizes HOMO

CH ₂ =CHX	HOMO (eV)
SCH ₃	-8.8
CH=CH ₂	-8.8
OCH ₃	-9.3
CH ₂ CH ₃	-9.8
H	-10.3
CH=O	-10.7
C≡N	-10.8
SO ₂ CH ₃	-11.5
CF ₃	-11.6
NO ₂	-12.0 (HO-1)

Dienophile FMO



LUMO $\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$

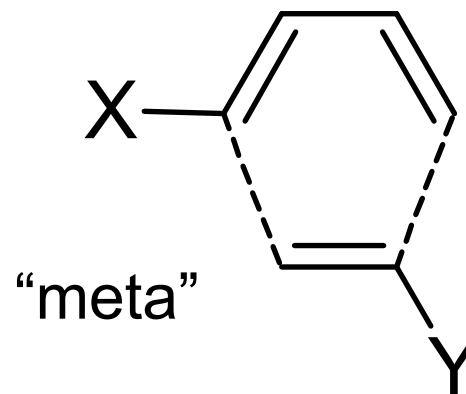
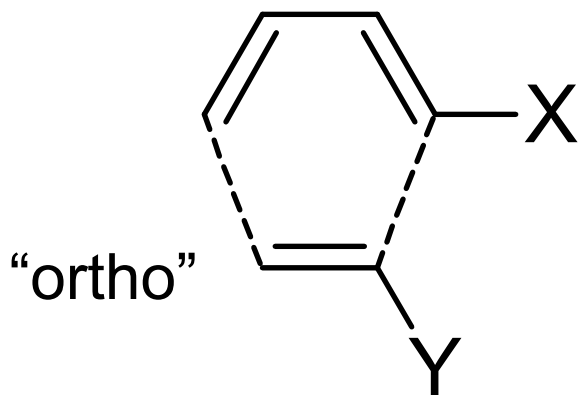
bonding btw empty pi systems \rightarrow lo LUMO

HOMO $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$

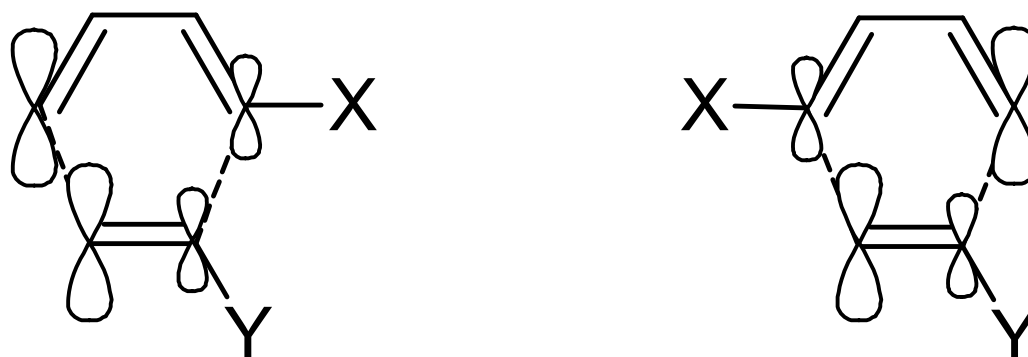
hi HOMO \leftarrow antibonding btw filled pi systems

Overlap & Regioselectivity

- Dominant FMO interaction
- Stabilization $E \approx (H_{12})^2/(E_1 - E_2)$
 - H_{12} proportional to $-S_{12}$ (overlap)
- Estimate overlap for 2 transition states
 - Largest stabilization from best overlap



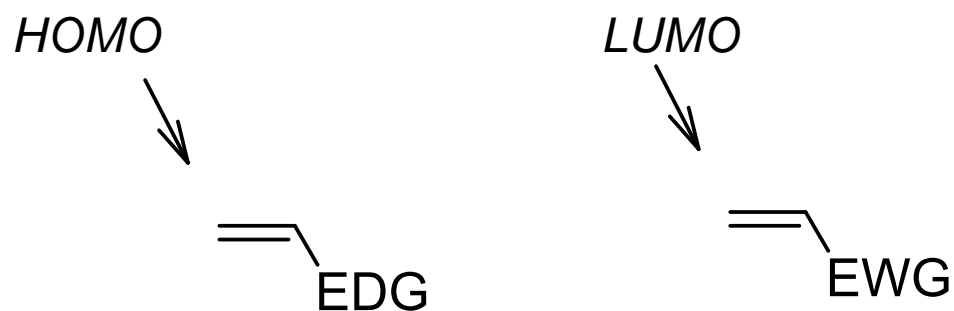
Overlap Simplified



- FMO sweeps over several atoms
 - look at overlap only where reactants approach
 - forming bonds (+ others?)
- Magnitude of FMO varies atom by atom
 - identify atom with “largest” magnitude
 - geometry with best overlap matches “largest” part of HOMO_1 with “largest” part of LUMO_2
 - example in drawing, ortho overlap > meta overlap

FMO Shapes

- Pencil & Paper
 - Do “mini” MO calculation (QM required)



- Computer
 - MO surface ☹ vs. MO coefficients ☺