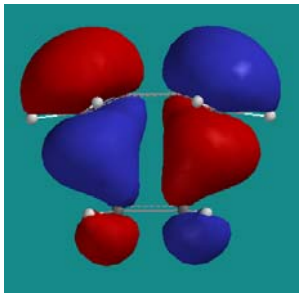
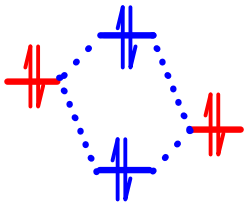
MO Compost

- Functional group → atomic orbitals
- Molecule w/ extended π system →
  functional group orbitals
- Bimolecular ‡ →
  molecular orbitals



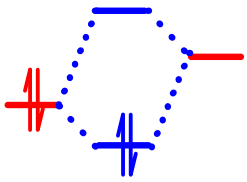
butadiene + ethylene HO-1

Key MO Combinations in Transition State



2 filled Rct MOs mix
make 2 filled TS MOs

net destabilization



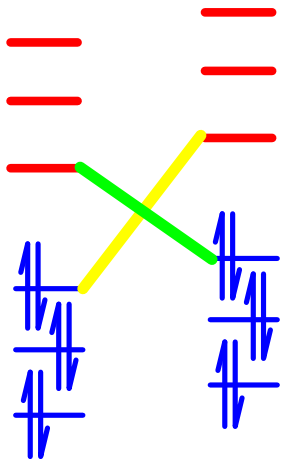
filled + empty Rct MOs mix
make filled + empty TS MOs

net stabilization

Frontier MO

- Lower E(‡) due to stabilizing MO interactions
- Stabilization E ≈ $\mu = (H_{AB})^2/(E_B - E_A)$
  - Many possible pairings & stabilizations
- Which do we consider?
  - Largest stabilization from HOMO-LUMO
    - minimizes $E_B - E_A$
  - Evaluate 2 HOMO-LUMO
    - "dominant" interaction minimizes $E_B - E_A$

Gaps & Rxn Polarity



- e-rich molecule
  - high HOMO / LUMO
- e-poor molecule
  - low HOMO / LUMO
- dominant FMO =
  - $HOMO_{rich}$ & $LUMO_{poor}$
- polar rxns fast
  - small gap
  - delocalize electrons
  - $HO_{‡} \approx HO_{rich} + \lambda\ LU_{poor}$

Gaps & Rates

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

CH_2=CHX	LUMO (eV)
OCH_3	5.7
CH_2CH_3	5.2
H	5.1
SCH_3	4.3
CF_3	3.6
$CH=CH_2$	3.6
SO_2CH_3	3.1
C≡N	2.8
CH=O	2.6
NO_2	1.3

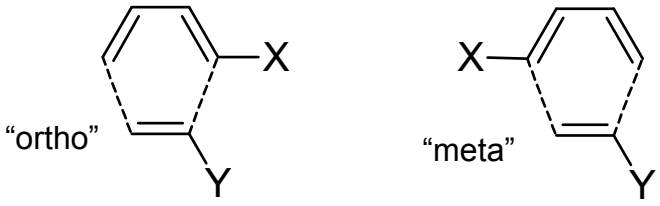
Gaps & Rates

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

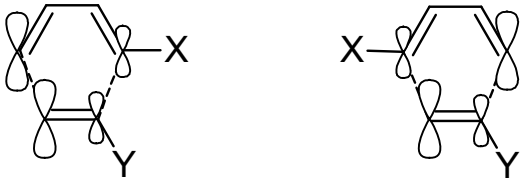
CH_2=CHX	HOMO (eV)
SCH_3	-8.8
$CH=CH_2$	-8.8
OCH_3	-9.3
CH_2CH_3	-9.8
H	-10.3
CH=O	-10.7
C≡N	-10.8
SO_2CH_3	-11.5
CF_3	-11.6
NO_2	-12.0 (HO-1)

Overlap & Regioselectivity

- Identify dominant FMO interaction
  - Same $E_B - E_A$ for both transition states
- Estimate overlap for 2 transition states
  - Largest stabilization from best FMO overlap



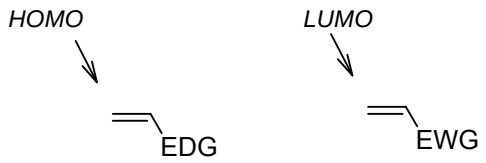
Overlap Simplified



- FMO sweep over several atoms
  - look at overlap only where reactants approach
- Total overlap ≈ sum of "pair overlaps"
  - best total overlap matches "largest" part of $HOMO_B$ with "largest" part of $LUMO_A$
    - example in drawing, ortho overlap > meta overlap

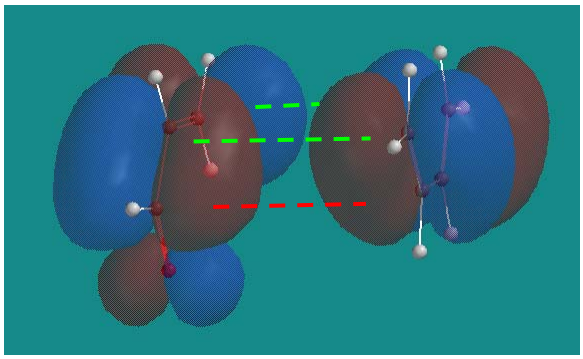
FMO Shapes

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



- Computer
  - MO surface ☹ vs. MO coefficients ☺

Endo Rule – Secondary MO Interactions?



additional “pair overlap” enhances H_{AB}
and stabilizes ‡