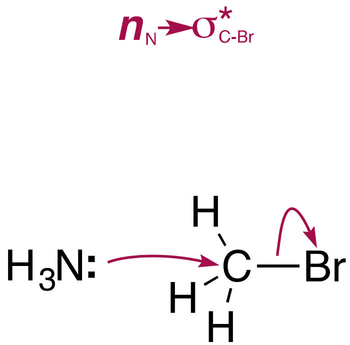
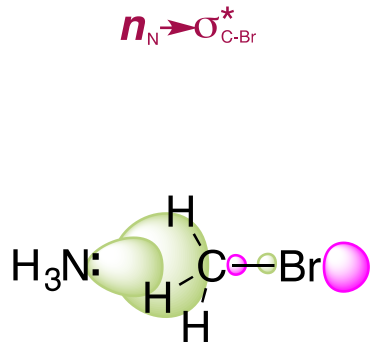
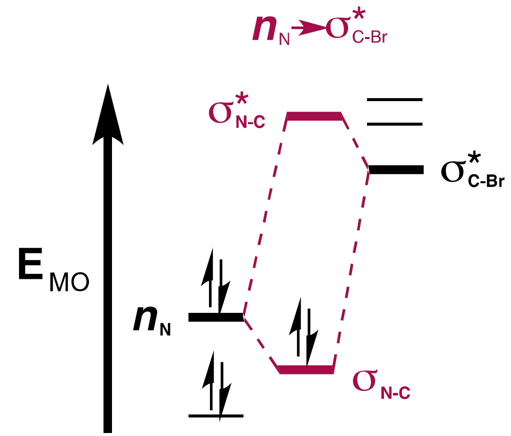
Topic 2: Molecular Orbital Theory





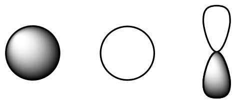


Reading: **Ch. 1 of your sophomore organic chemistry textbook**
I. Fleming *Molecular Orbitals and Organic Chemical Reactions*, **Ch. 2 & 3**

Bradley, J. D.; Gerrans, G. C.
"Frontier molecular orbitals. A link between kinetics and bonding theory."
J. Chem. Educ. **1973**, *50*, 463.

The Need For Orbitals

- Heisenberg said we can't specify the location of electrons
- We need orbitals to describe where the pairs of electrons want to be
- Orbital phases help us see how one electron avoids the other, even though they are in the same orbital



- There are three basic types of orbitals

  1. Atomic Orbitals
  2. Hybrid Atomic Orbitals
  3. Molecular Orbitals

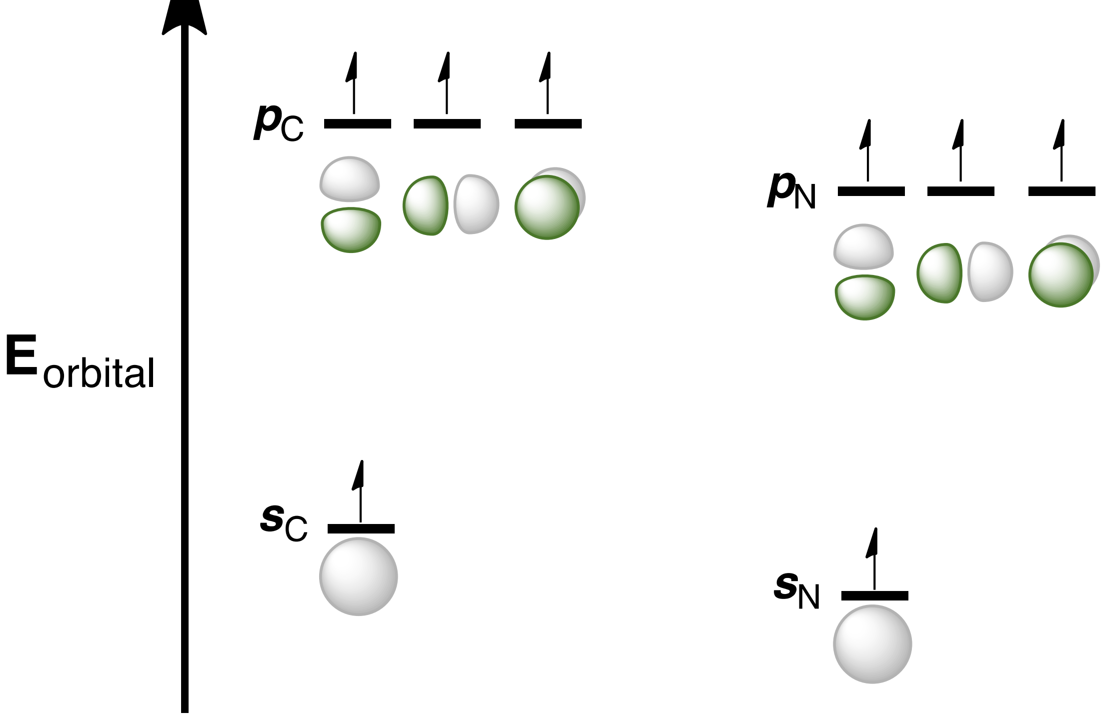
  Let's review them…

1. Atomic Orbitals - Review

- There are four types of **atomic orbitals**: ***s, p, d, f***
- We can rationalize <u>everything in this class</u> using combinations of ***s*** and ***p*** orbitals
- **p orbitals** are way higher in energy than s orbitals
- electronegativity decreases orbital energy

Orbital Energy Diagram

ignore *d* & *f* orbitals



	B	C	N	O	F

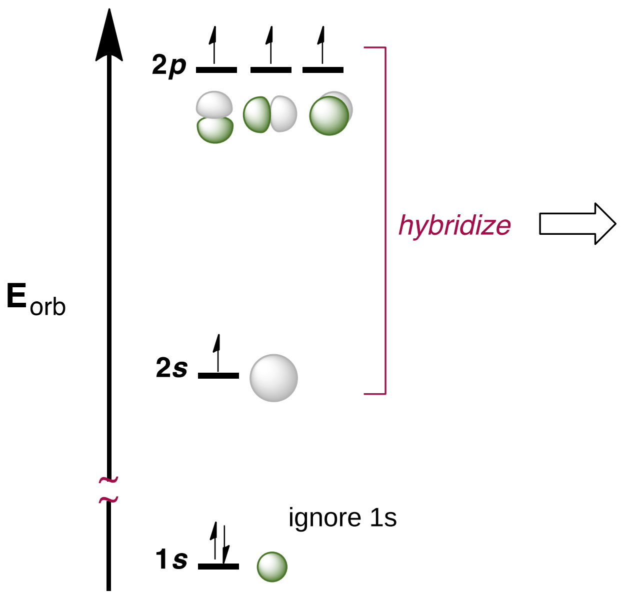
There's a spherical node inside the 2s orbital, but let's ignore it.

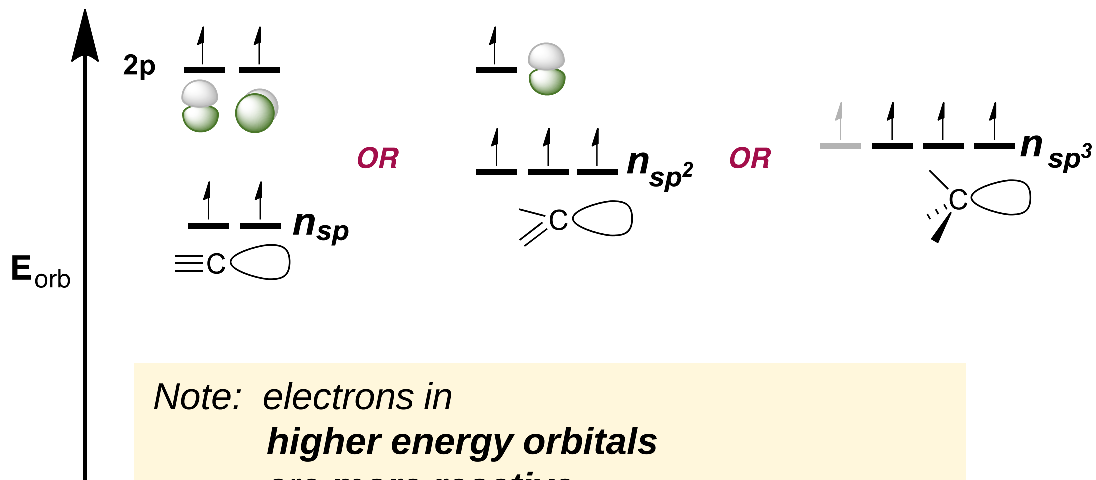
2. Hybrid Atomic Orbitals - Review

- **Mixing Rule**: **When you mix two orbitals, you get two orbitals**

The reason you get two orbitals is because there are always two arbitrary phasing combinations

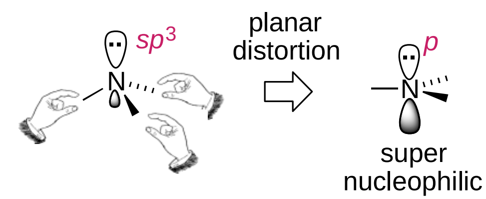
- Three ways to mix one 2**s** and three 2**p** orbitals of 2nd row atoms to give non-bonding orbitals, ***n***





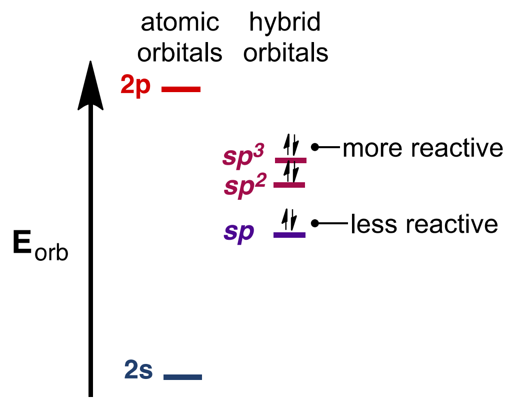
Note: electrons in
higher energy orbitals
are ***more reactive***

- Atom **geometry correlates with hybridization** (VSEPR theory). If you could force ammonia to be planar, the lone pair would end up in a *super high energy* p orbital.



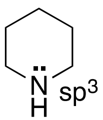
2. Hybrid Atomic Orbitals – Differences in Reactivity Based on p Character

n Assess p character in molecular orbitals corresponding to every bond and every lone pair because it predicts the reactivity of the electrons.



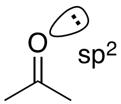
n **More p character = more basic and more nucleophilic**

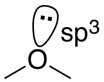
	lone pair	**%*p***	**p*K*a′**	**relative basicity**
C—N̈H$_2$	sp^3	75	+10	100000
C=N̈H	sp^2	67	~5	1
C≡N:	sp	50	-10	0.000000000000001



100,000x
more basic

n The magnitude of the effect is less pronounced for oxygen, which is less reactive overall than nitrogen.





1000x
more basic

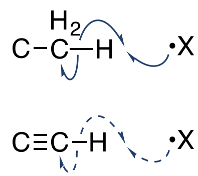
2. Quantitative Differences in Reactivity based on *p* Character

- More ***p*** character in C-H sigma bonds correlates with lower Bond Dissociation Energies. (Compare *only* C-H bonds)

BDE is **defined** as the energy required for homolysis in a hypothetical reaction:

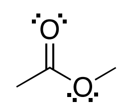
$$R{-}H \longrightarrow R\bullet + \bullet H$$

C-H bond	%*p*	%*s*	C-H *BDE*	relative homolytic reactivity
$C{-}CH_2{-}H$	75	25	98 kcal/mol	1
$C{=}CH{-}H$	67	33	110	10^{-9}
$C{\equiv}C{-}H$	50	50	131	10^{-24}

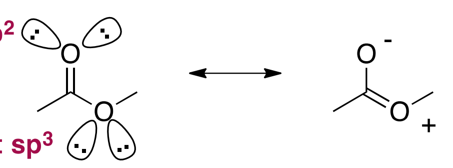


no way

- **BIG Caution**: assign hybridization AFTER considering resonance. If you don't consider resonance then you're not really thinking about molecular orbitals.

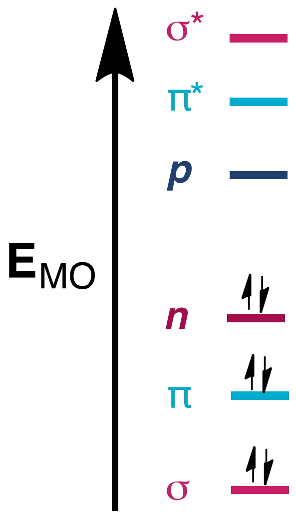


which atom is most basic?



3. Molecular Orbitals – **Six Types of "Frontier" Molecular Orbitals**

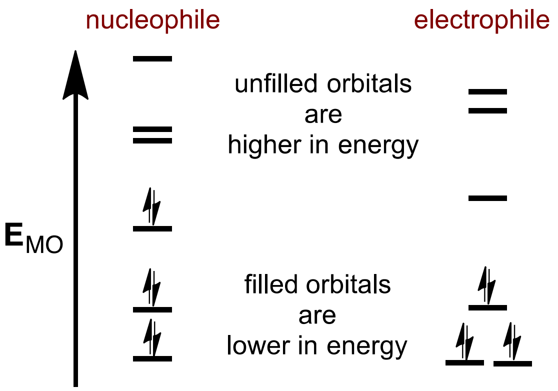
n Arrows start from filled orbitals and end on un-filled orbitals. There are **six canonical classes of frontier molecular orbitals** that are used for arrow pushing.



n Commit these canonical orbitals, and their relative energies to memory.

n Since there are only three types of filled FMOs and three types of unfilled FMOs, that means that **there are only 3x3= 9 types of *non-concerted* elementary chemical reactions**. We'll spend the rest of this quarter talking about these nine types of interactions between filled and un-filled orbitals.

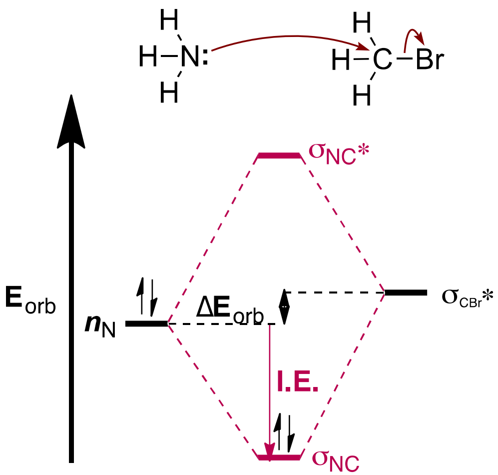
n Note that unfilled molecular orbitals are always higher in energy than filled molecular orbitals. (Aufbau principle).

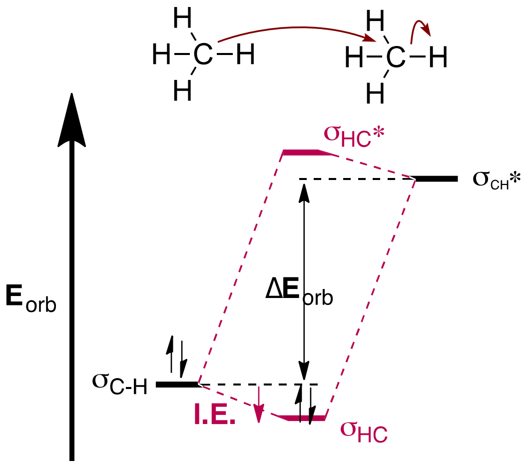


n Perturbation theory says that you get more orbital Interaction Energy, (I.E.) by mixing MOs that are closer in energy

$$\textbf{Orbital Interaction Energy} = \frac{\text{orbital overlap}}{\mathbf{E}_{\text{filled}}\text{-}\mathbf{E}_{\text{empty}}}$$

n **M.O. Interaction diagrams** are used to graphically depict the energetic consequences that result from perturbation of molecular orbitals through pair-wise mixing.

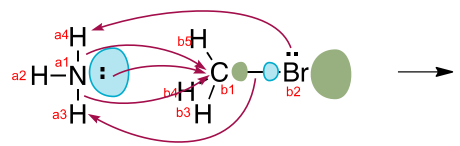




n If you could predict which filled orbitals are higher in energy and which unfilled orbitals are lower in energy, then you could predict which reactions would be fast and which reactions would be slow. You'll spend the rest of the quarter practicing those predictions.

3. Molecular Orbitals – **FRONTIER Molecular Orbitals**

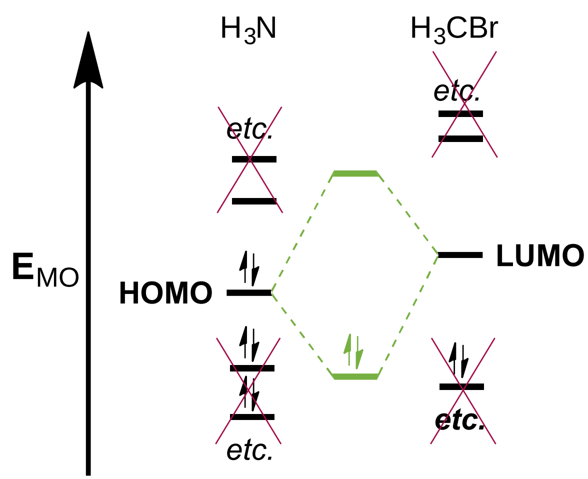
- When two reactants interact, every filled orbital in one reactant interacts with every filled orbital in the other reactant. We can quantify that with perturbation theory resulting in a mathematical equation with lots of terms.



abbreviated as...

$$\textbf{Orbital Interaction Energy} = \sum_{r}^{NH_3\ \text{occ.}} \sum_{s}^{CH_3Br\ \text{unocc.}} \frac{\sum_{ab} 2(c_{ra}c_{sb}\beta_{ab})^2}{(E_s - E_r)} + \sum_{r}^{CH_3Br\ \text{occ.}} \sum_{s}^{NH_3\ \text{unocc.}} \frac{\sum_{ab} 2(c_{ra}c_{sb}\beta_{ab})^2}{(E_s - E_r)} = \sum_{\text{all MOs}} \frac{\text{orbital overlap}}{\mathbf{E}_{\text{filled}} - \mathbf{E}_{\text{empty}}}$$

- When two reactants interact, most of the orbital interactions are not energetically favorable. The summed energy from orbital interactions usually comes from a single interaction: between the highest occupied molecular orbital (HOMO) in one reactant, and the lowest unoccupied molecular orbital (LUMO) in the other reactant. The HOMO and LUMO are the **frontier orbitals**.



A complex summation of orbital interactions...

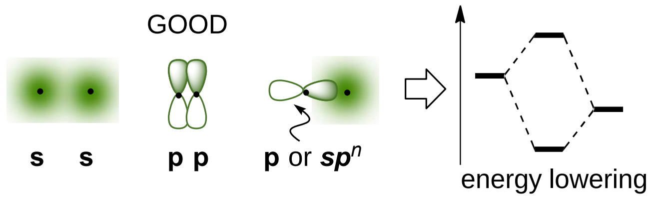
$$\sum_{\text{all MOs}} \frac{\text{orbital overlap}}{\mathbf{E}_{\text{filled}} - \mathbf{E}_{\text{empty}}}$$

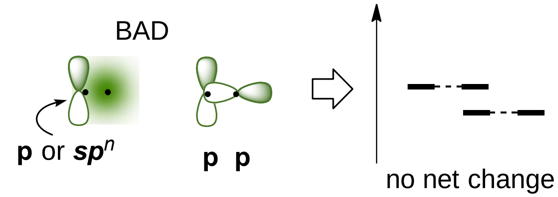
reduces to...

$$\propto \frac{\text{orbital overlap}}{\mathbf{E}_{\text{HOMO}} - \mathbf{E}_{\text{LUMO}}}$$

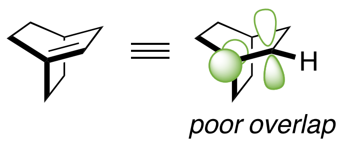
3. Molecular Orbitals - **The Importance of Orbital Overlap**

n **Correct symmetry** is required for effective overlap. Graphically, like phases lead to constructive interactions, but unlike phases lead to destructive interactions.

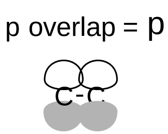


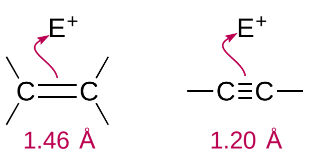


n **Bredt's Rule**: Bridgehead olefins are unstable

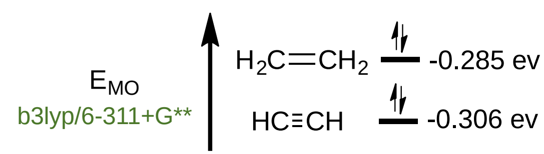


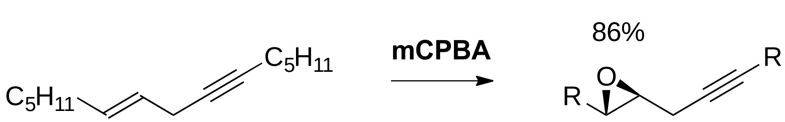
n ***p*** orbitals overlap more effectively when they are closer together.
Longer bonds are less stable and more nucleophilic





closer p orbitals
= better overlap
= more stable pi bond
= less reactive pi bond



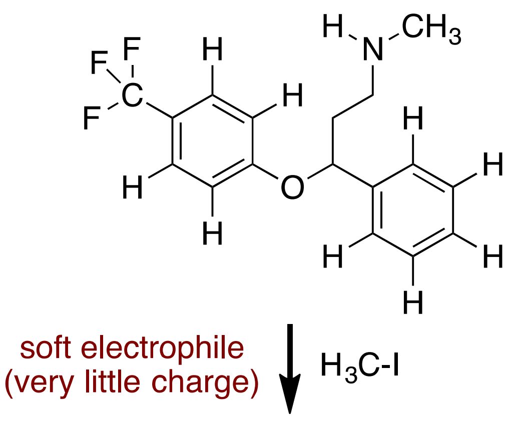


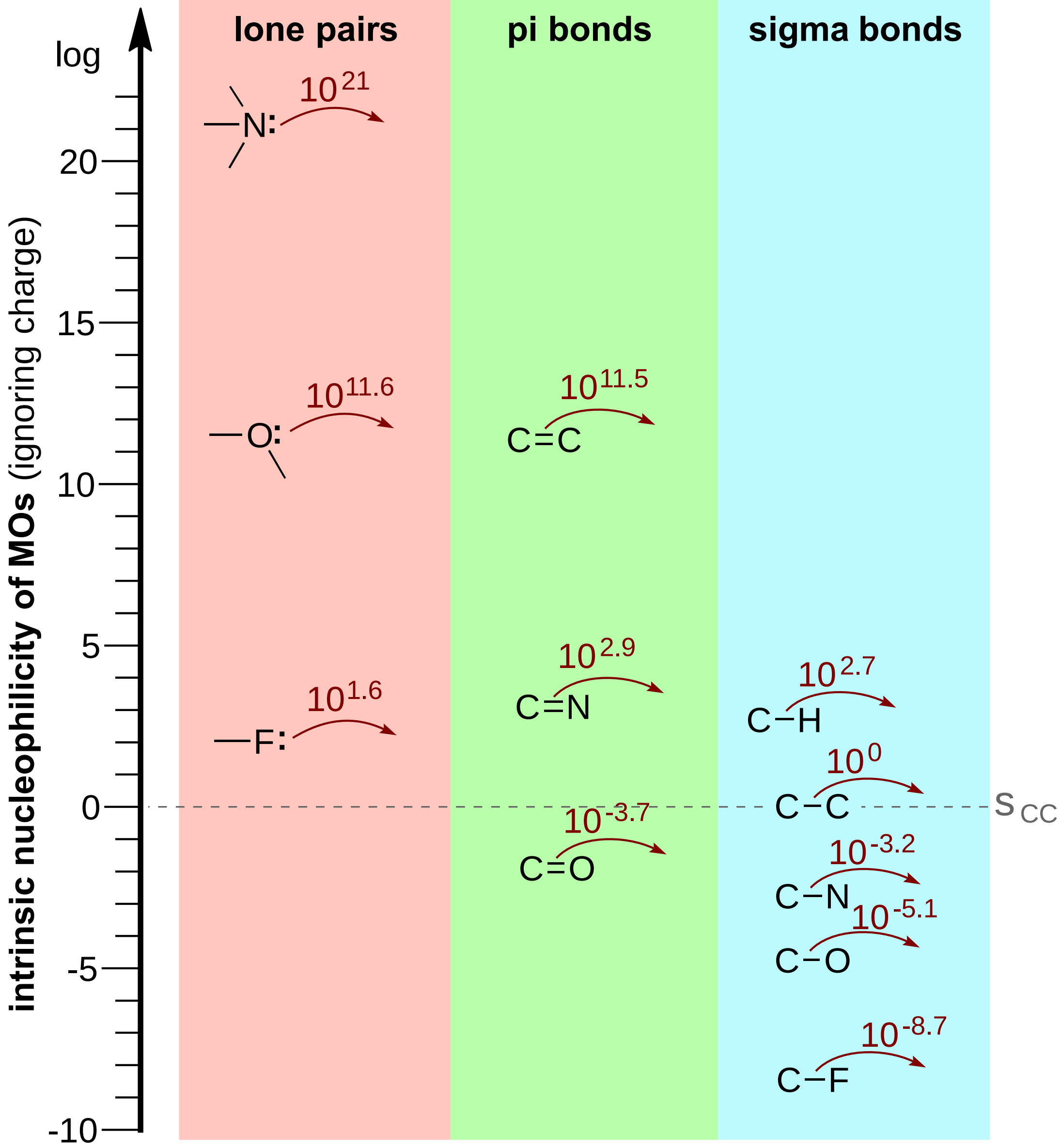
Capon, R. J.; Barrow, R. A. *J. Org. Chem.* **1998**, *63*, 75-83

Intrinsic Reactivity of Canonical MOs Used for Arrow-Pushing: l.p., pi bonds, sigma bonds

- Generally the reactivity of nucleophilic groups used for arrow pushing follows the order: l.p. > pi > sigma.
- Electronegativity plays an important role in determining nucleophilicity.
- You usually won't have a problem identifying the most reactive pair of electrons in a molecule.

fluoxetine
Prozac®





Based on MO energies calculated with B3LYP/6-31++G(d,p) versus the LUMO for $H_3CCH=O$. Assumes equal orbital overlap.

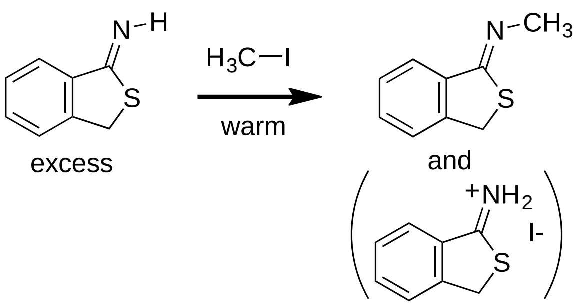
Intrinsic Reactivity of Canonical MOs Used for Arrow-Pushing

n How accurate are the intrinsic reactivitivities of the canonical MOs? **Maybe ±10^5 ????**

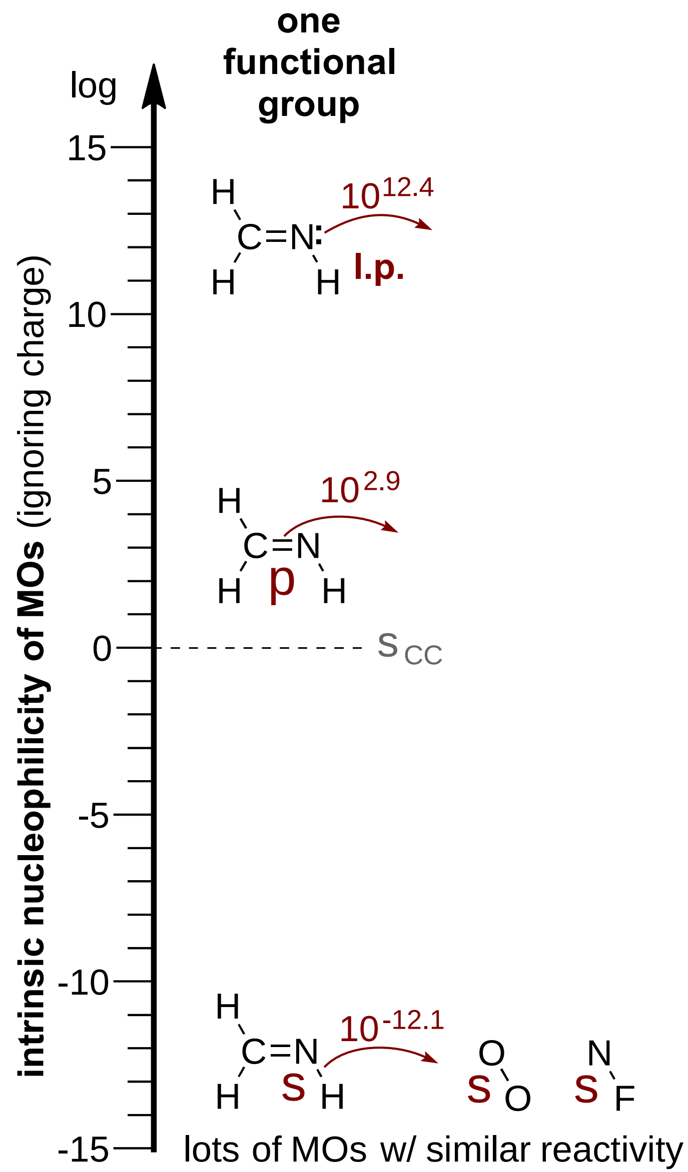
n Lot's of the lower energy FMOs will have similar reactivity, but usually, it won't be difficult to identify the most reactive frontier orbital.

n Remember that generally: l.p. > pi > sigma

Suggest a plausible arrow-pushing mechanism:



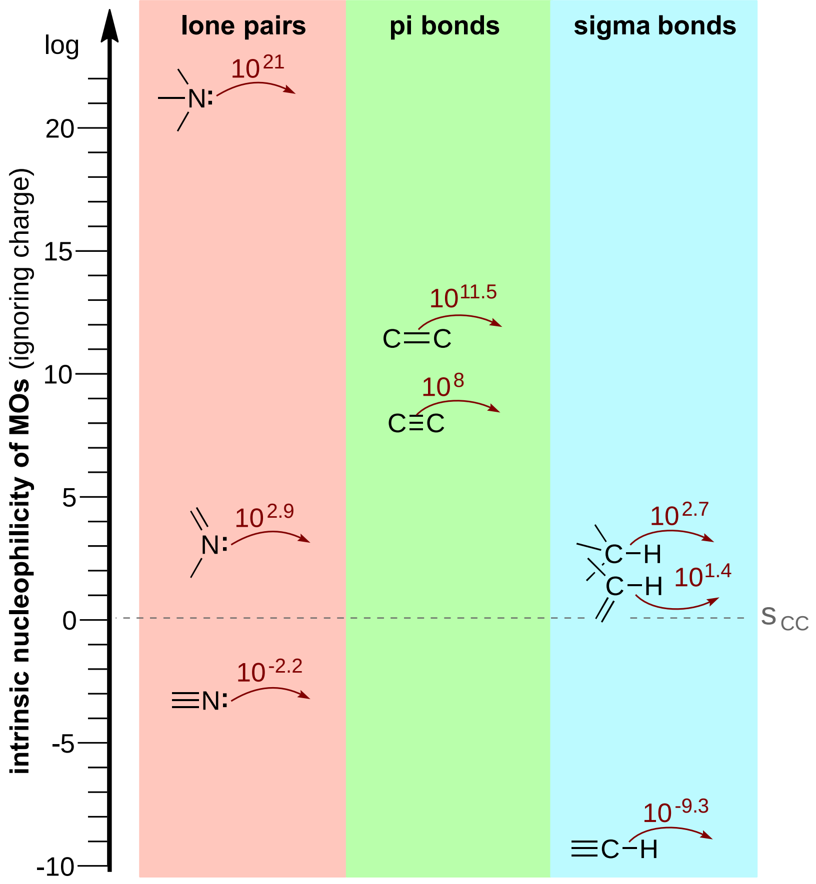
Gabriel, et al.
Chem. Ber. **1890**, 2478



The Importance of Hybridization and p Character

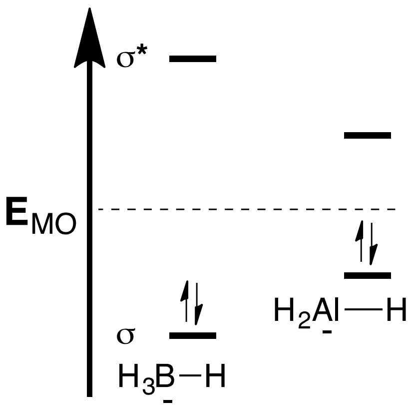
- More p character = more nucleophilic
- Less p character = less nucleophilic

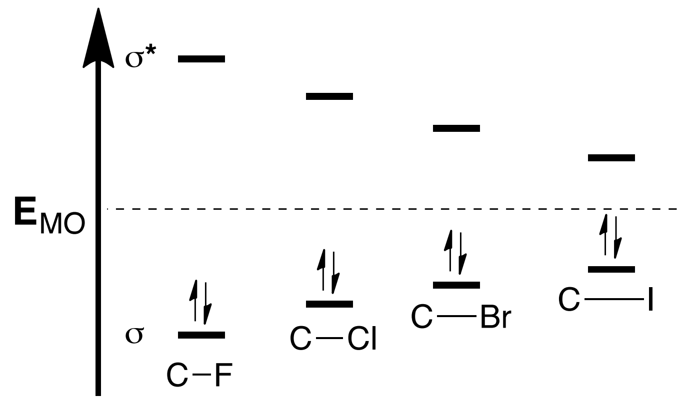
- ***p*** orbitals overlap more effectively when they are closer together.
  Longer bonds are less stable and more nucleophilic



Effect of Bond Length on the Energy of Frontier Orbitals

- Longer bonds are more nucleophilic.
- Longer bonds are easier to break.

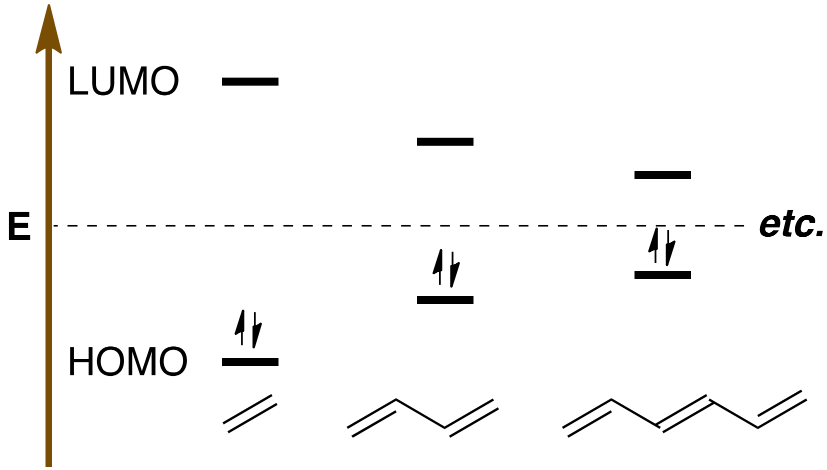




- *That is why*: AlH_4^- is more nucleophilic than BH_4^-
- *That is why*: S_N2 reactions with R—I are faster than S_N2 reactions with R-Cl

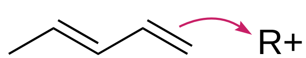
The Effect of Conjugation on the Energy of Filled and Unfilled Frontier Orbitals

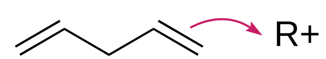
- Pi conjugation raises the HOMO and lowers the LUMO

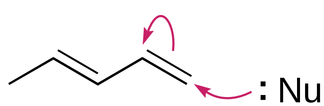


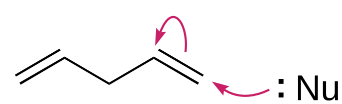
- *That is why*:

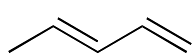
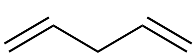
conjugated | **non-conjugated**



faster than




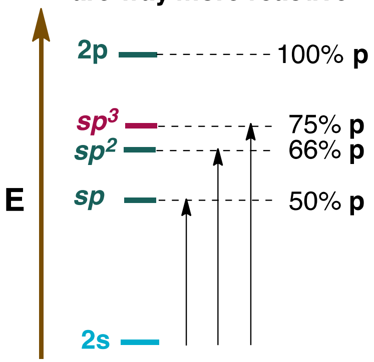
faster than


even though

more stable than


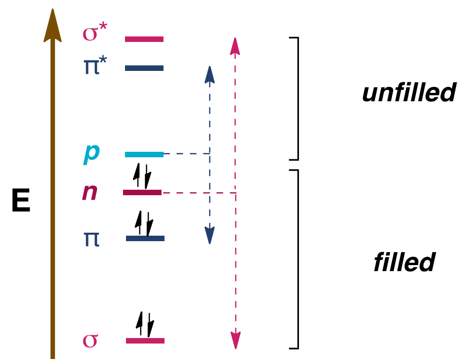
Summary of FMO Trends

$$\text{Rate} \propto \text{Coulombic} + \text{sterics} + \frac{\text{overlap}}{\Delta E_{MO}}$$

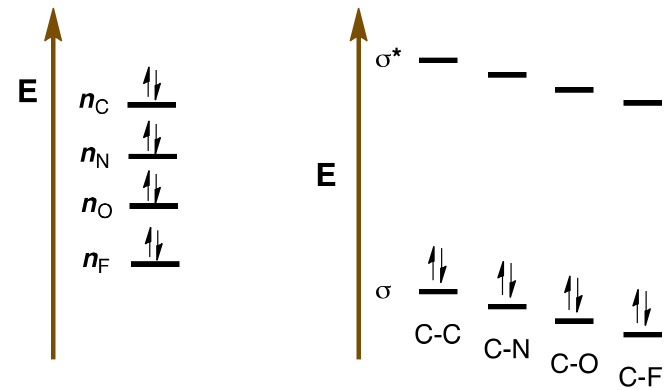
electrons in orbitals with
more p character
are way more reactive



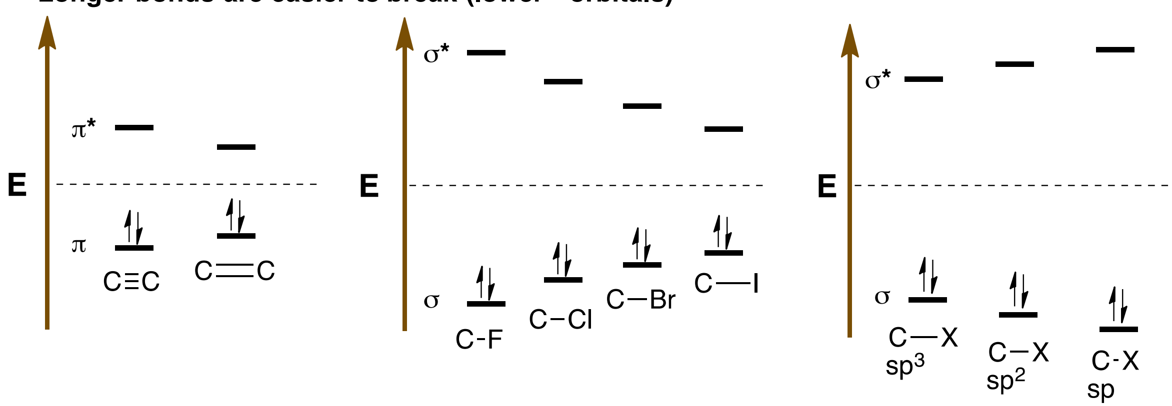
six types of canonical frontier orbitals



electronegativity correlates with lower orbital energies



Longer bonds are more nucleophilic
Longer bonds are easier to break (lower * orbitals)



Conjugation raises HOMO
Conjugation lowers LUMO