Lecture 2: Bonding Theories

Note Title 9/1/2016

Announcements:

1) Problem Set 1 is posted on the course website. Due Thurs, 9/8 at the beginning of class.

2) Colloquium TOMORROW: Prof. Lars Gundlach, 4pm, 101 BRL

Today:

1) Qualitative Molecular Orbital Theory

2) Huckel Molecular Orbital Theory

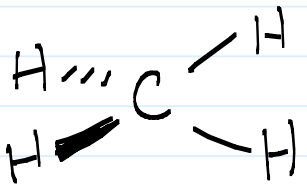
3) Frontier Molecular Orbital Theory

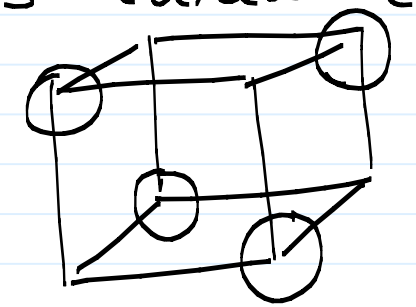
4) Arrow-Pushing Mechanisms (if we have time)

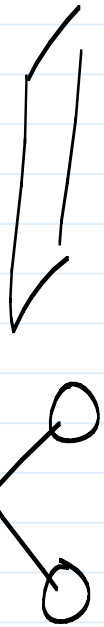
CH_4

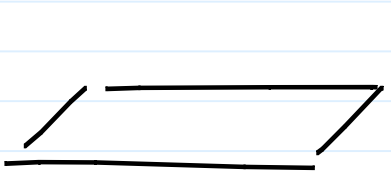
Qualitative Molecular Theory (QMOT)

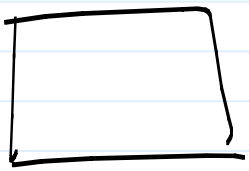
- consider valence AO's
- e^-s are delocalized
- LCAO's (Linear combination of atomic orbitals)





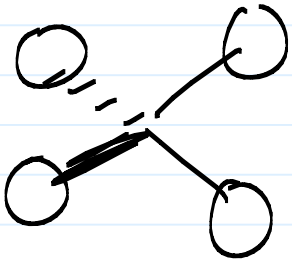


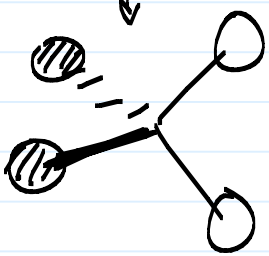


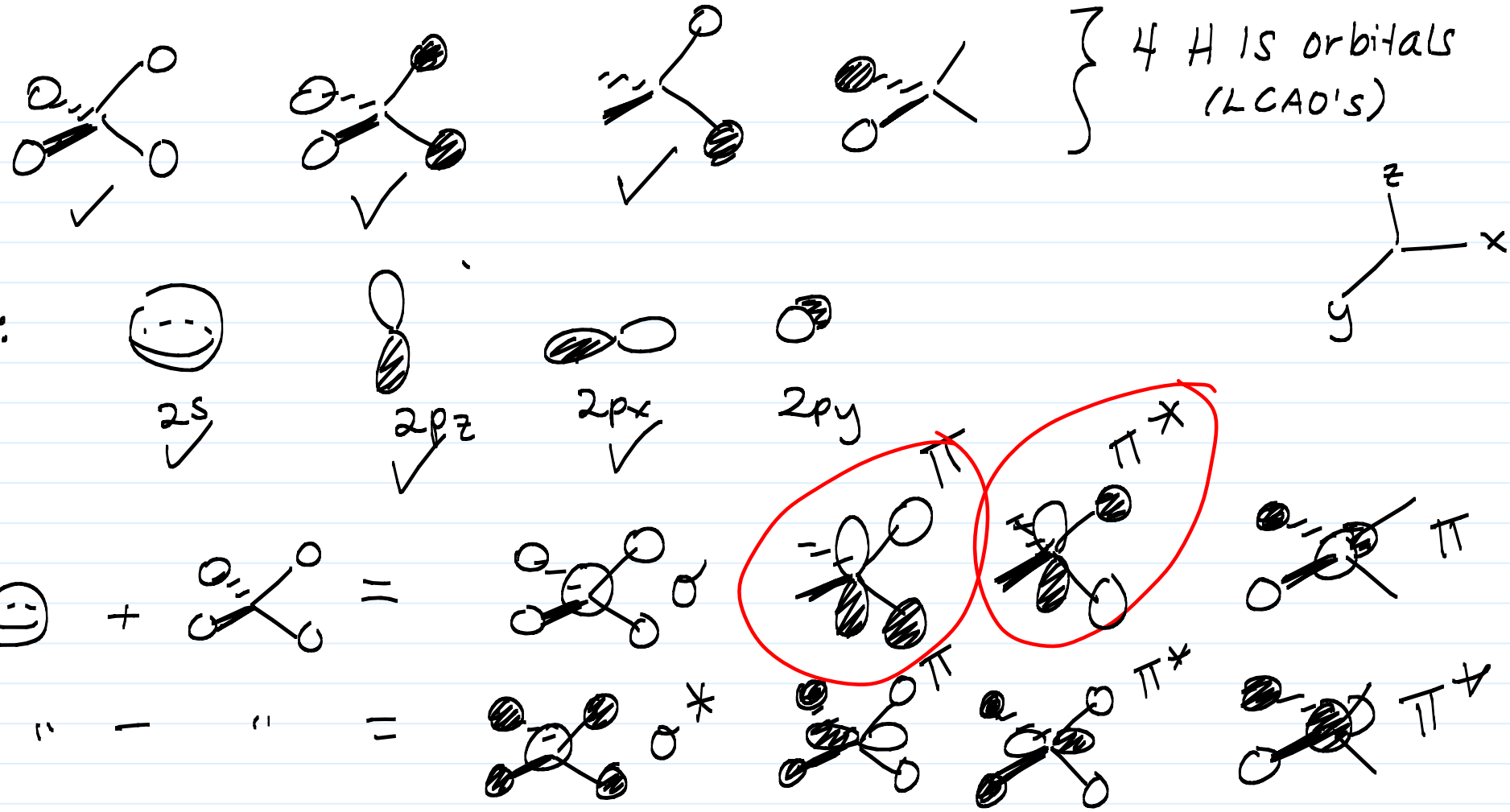


4 H 1s orbitals

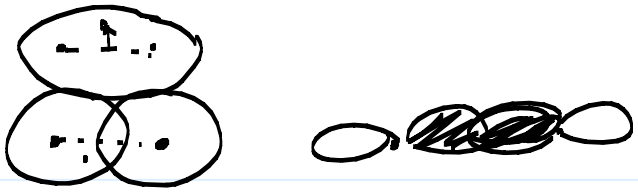
(LCAO)






4 H 1s orbitals
(LCAO's)
z
x
y
C:
2s
2pz
2px
2py
π
π*
σ
σ*

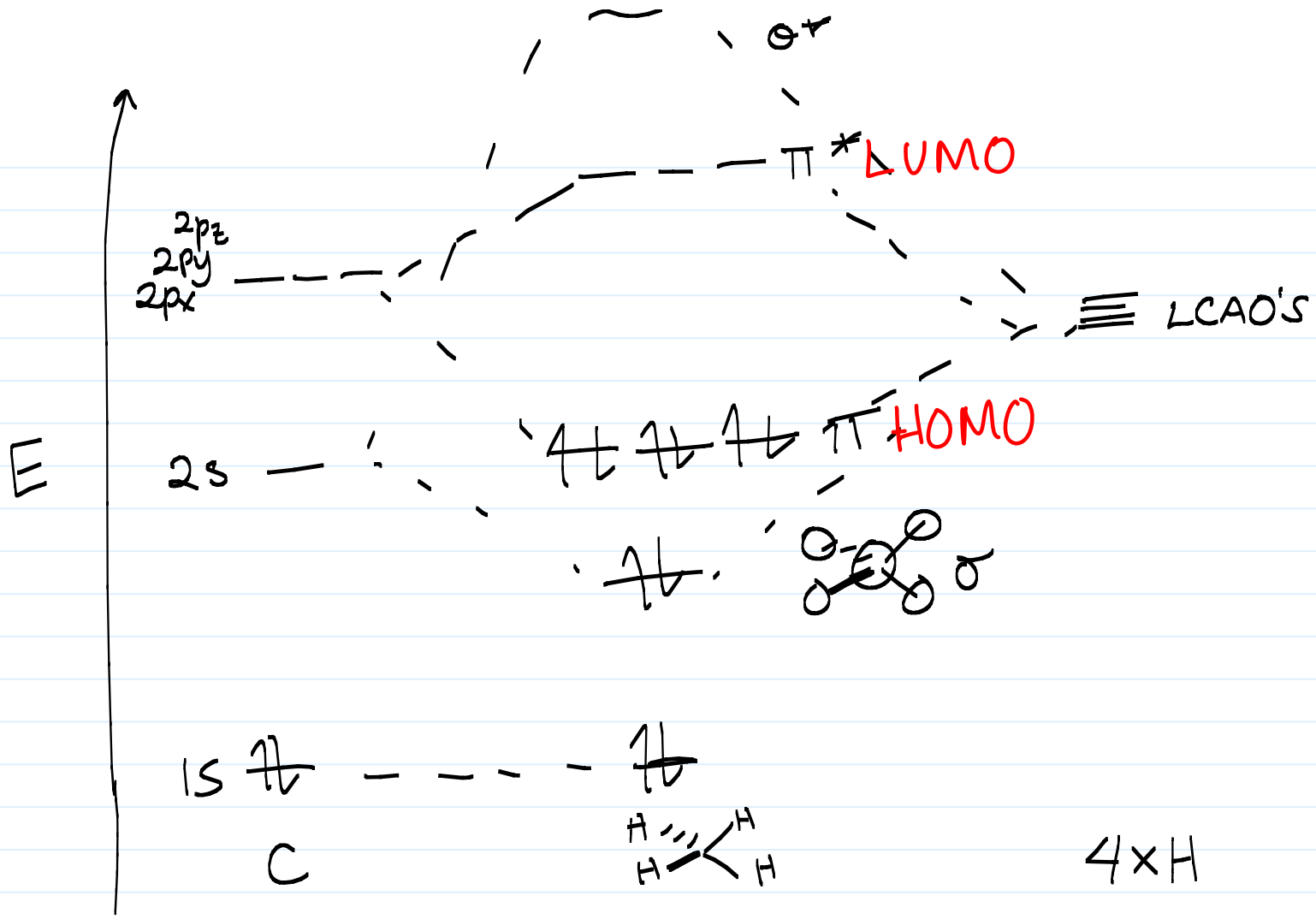
σ-bond:



e⁻ probability is symmetric about bond axis

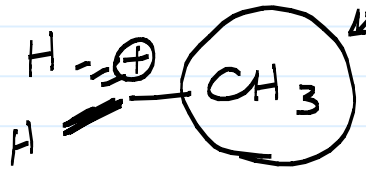
π-bond:

e⁻ probability is asymmetric about bond axis


π*
LUMO
2pz
2py
2px
LCAO's
E
2s
π
HOMO
σ
1s
C
4×H

Why do CH_3 groups stabilize carbocations?

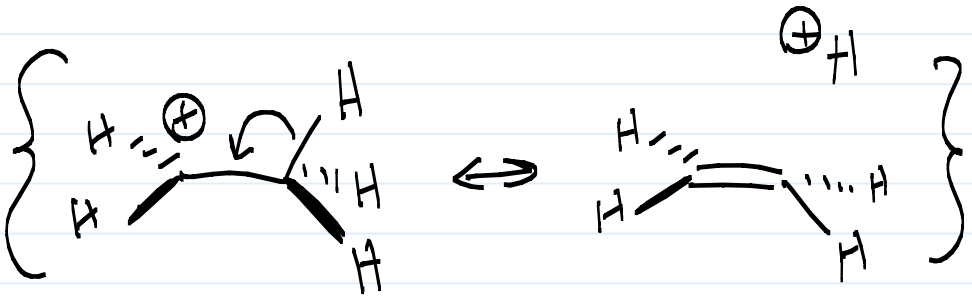
We will build a MO diagram for CH_3 to answer this question.

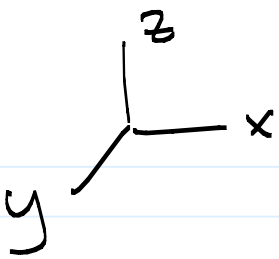


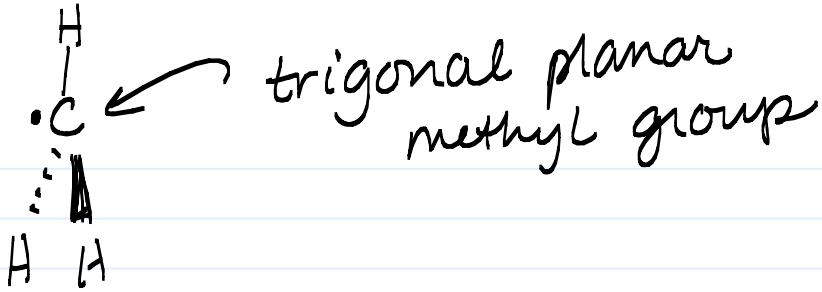
more stable

less stable

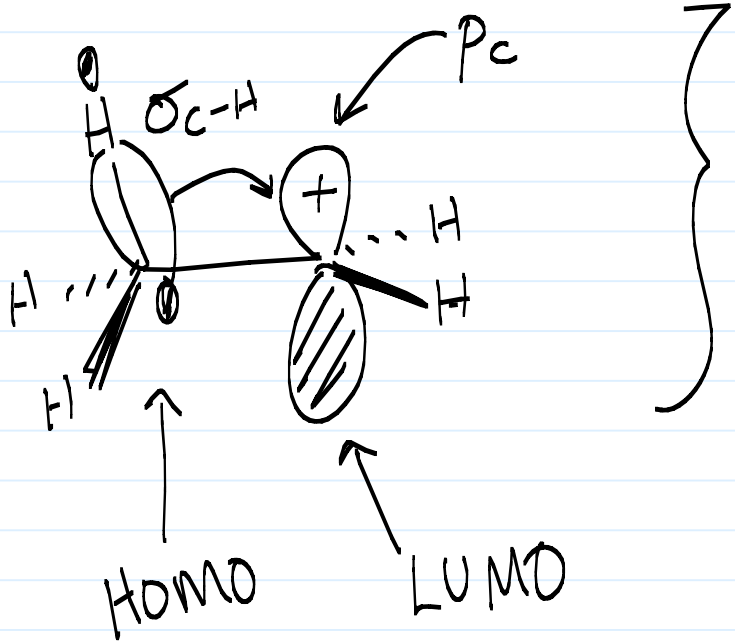
hyperconjugation







trigonal planar methyl group

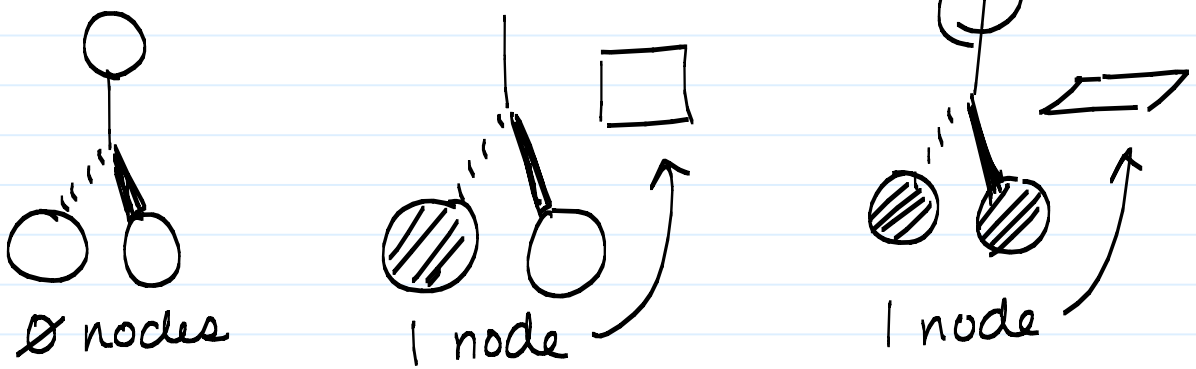


Frontier Molecular Orbital Picture (FMO)

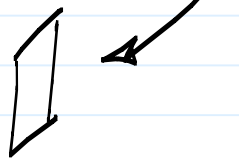
Building MO's for $^{\bullet}CH_3$ → trigonal planar to start.

← you can rotate 90° if that helps (but rotate back to bind w/ other carbon)

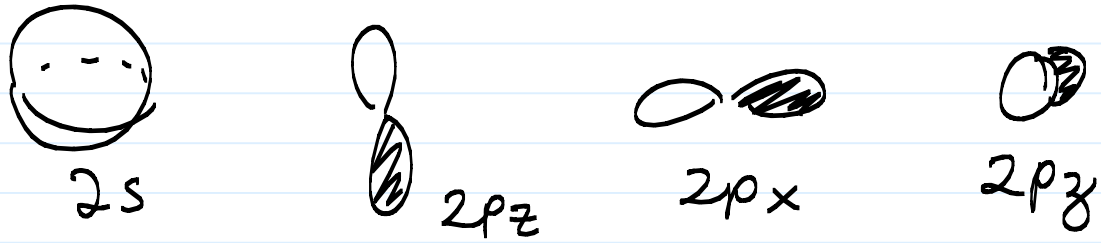
1) LCAO's of 3 H 1s orbitals



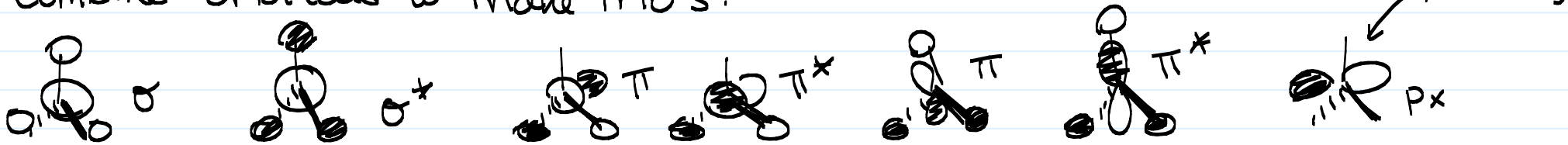
Note: 3rd possible node eliminates all lobes.



2) Carbon valence AO's:



3) Combine orbitals to make MO's:



4) Arrange by energy: