

30 Total Possible Points:

0, 5, or 10 for completeness

0, 5, or 10 for #6a

0, 5, or 10 for #9

CHEM 633: Advanced Organic Chem: Physical

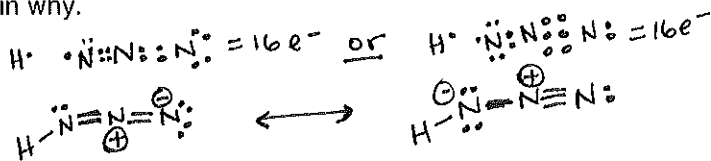
Problem Set 1 – Answer Key

Due on 9/8/09

1. Using the VSEPR model, draw Lewis dot structures for the following compounds. When appropriate, clearly indicate the geometry of the compound. When more than one structure is possible, indicate the best representation and explain why.

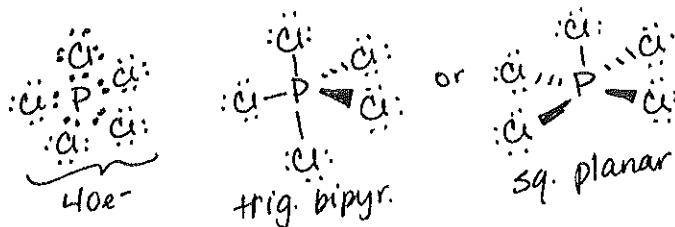
a. HN_3

$$\begin{aligned} \text{Total \# of } e^- \text{'s: } & 3 \cdot \ddot{\text{N}} \cdot = 3 \times 5 = 15 \\ & 1 \cdot \text{H} = 1 \times 1 = 1 \\ & \underline{16e^-} \end{aligned}$$



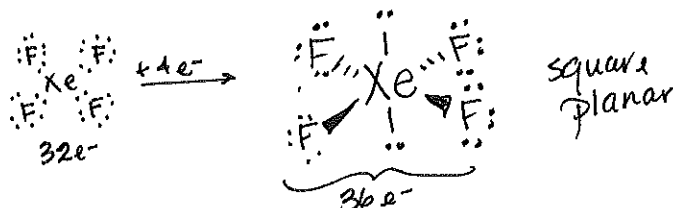
b. PCl_5

$$\begin{aligned} \text{total \# of } e^- \text{'s: } & 1 \cdot \ddot{\text{P}} \cdot = 5e^- \\ & 5 \times \ddot{\text{Cl}} \cdot = \frac{35e^-}{40e^-} \end{aligned}$$



c. XeF_4

$$\begin{aligned} \text{Total \# of } e^- \text{'s: } & 1 \times \ddot{\text{Xe}} \cdot = 8e^- \\ & 4 \times \ddot{\text{F}} \cdot = \frac{28e^-}{36e^-} \end{aligned}$$



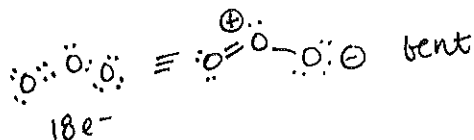
d. SF_4

$$\begin{aligned} \text{Total \# of } e^- \text{'s: } & 1 \times \ddot{\text{S}} \cdot = 6e^- \\ & 4 \times \ddot{\text{F}} \cdot = \frac{28e^-}{34e^-} \end{aligned}$$



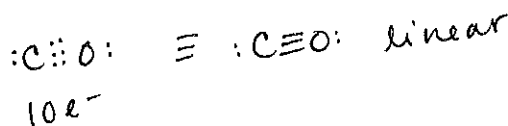
e. O_3

$$3 \times \ddot{\text{O}} \cdot = 18e^-$$



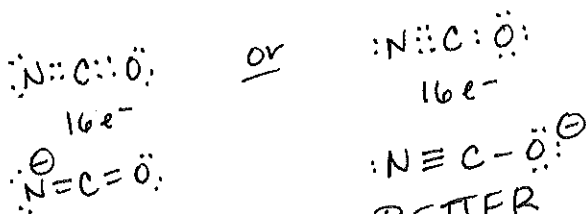
f. CO

$$\begin{aligned} 1 \times \ddot{\text{C}} \cdot & = 4e^- \\ 1 \times \ddot{\text{O}} \cdot & = \frac{6e^-}{10e^-} \end{aligned}$$



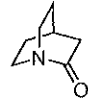
g. NCO^-

$$\begin{aligned} 1 \times \ddot{\text{N}} \cdot & = 5e^- \\ 1 \times \ddot{\text{C}} \cdot & = 4e^- \\ 1 \times \ddot{\text{O}} \cdot & = 6e^- \\ 1 \times \ominus & = \frac{1e^-}{16e^-} \end{aligned}$$

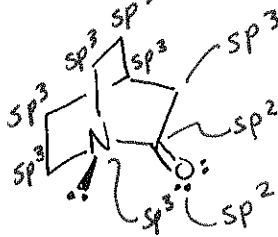


Oxygen is more electronegative than N.

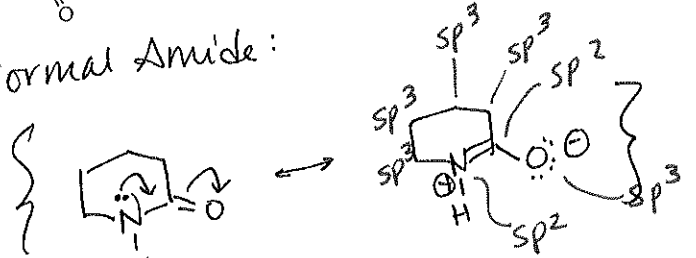
2. In the following molecules, label the hybridization of all the atoms. Please explain your reasoning for the hybridization of the nitrogen atoms.



"Special" Amide:



Normal Amide:



Consider orbitals:
⊥ orbitals ≠ overlap.

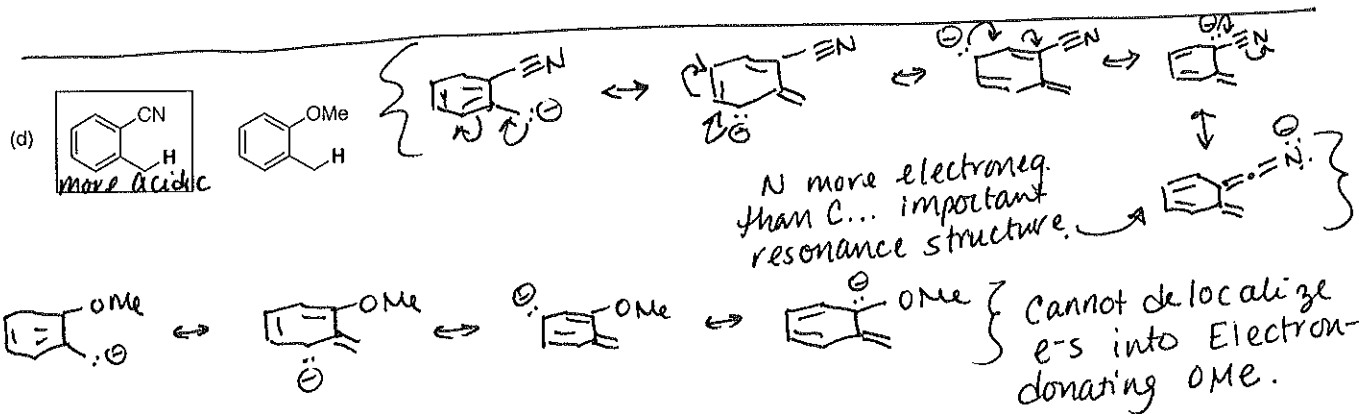
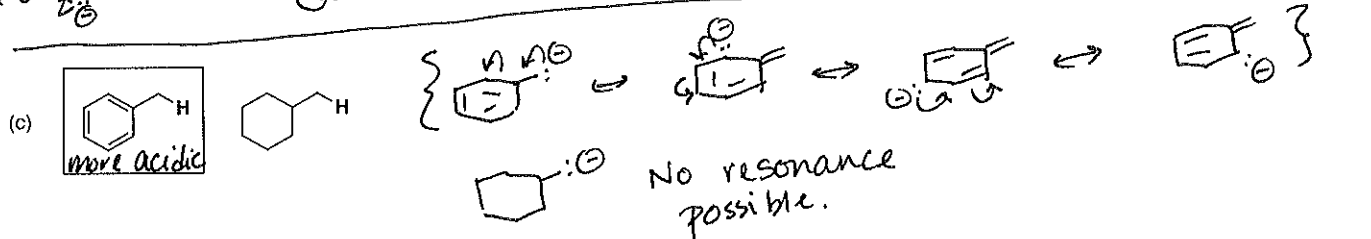
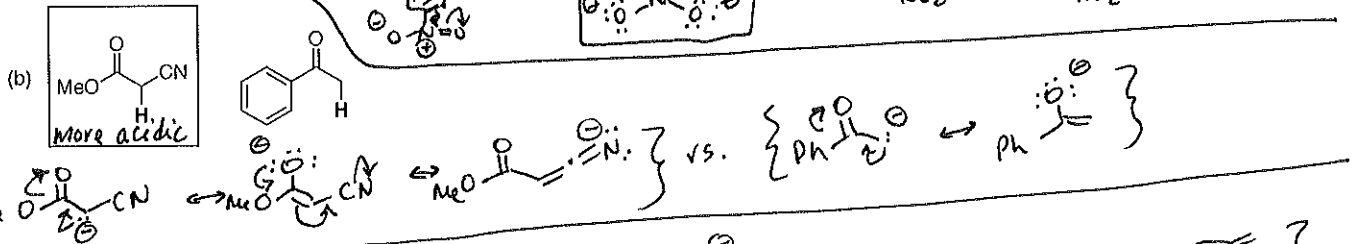
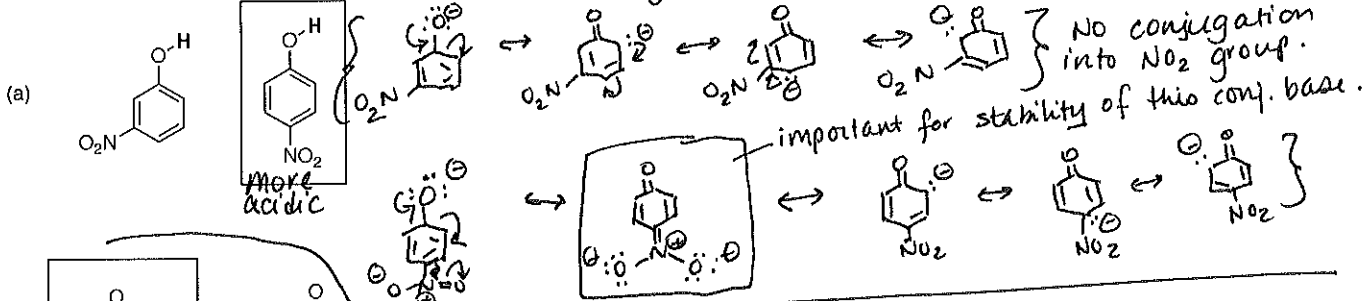


Ref: Tani, K.; Stoltz, B.M. Nature 2006, 441, 731.

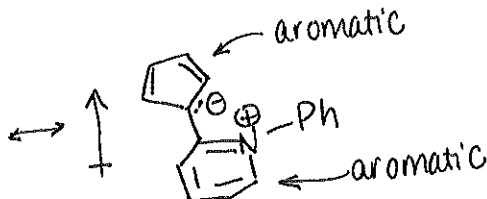
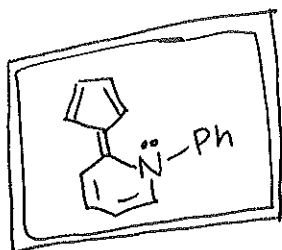
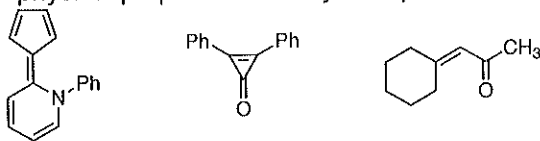
3. Predict and explain which of the emboldened protons (H) in each pair of molecules will be more acidic.

More delocalization
↓
More stable.

To predict acidity, compare stability of conjugate bases:



4. What physical properties, such as absorption spectra, bond lengths, dipole moments, etc., could be examined to obtain evidence of resonance interactions in the following molecules? What deviations from "normal" physical properties would you expect to find?

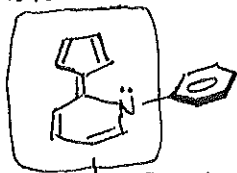


Ref: Ammon, H.L.;
Wheeler, G.L. J. Am. Chem. Soc. 1975,
97, 2326.

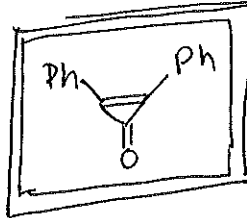
- dipole moment
- twisting of Cp-Ar bond.
- longer C=C bond between rings.

Experimental Data
→ X-ray structure reveals longer C=C bond
→ Cp twisted by 18.6°

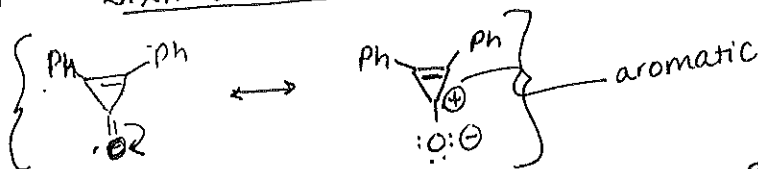
Note:



If this system is fully conjugated, it would be **ANTIAROMATIC** (12e⁻s = 4n e⁻s).



Ref: Breslow, R.; Eicher, T; Krebs, A; Peterson, R.A.; Posner, J.
J. Am. Chem. Soc. 1965, 87, 1320.



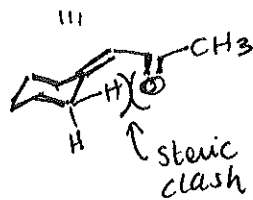
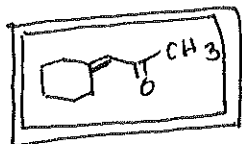
Expect:
↳ longer C=O bond

Experiment:

IR data:
C=C 1850 cm⁻¹
C=O 1640 cm⁻¹

↑
Less than "normal"
C=O (1715 cm⁻¹)
Note C-O ~ 1200 cm⁻¹

4 - continued:

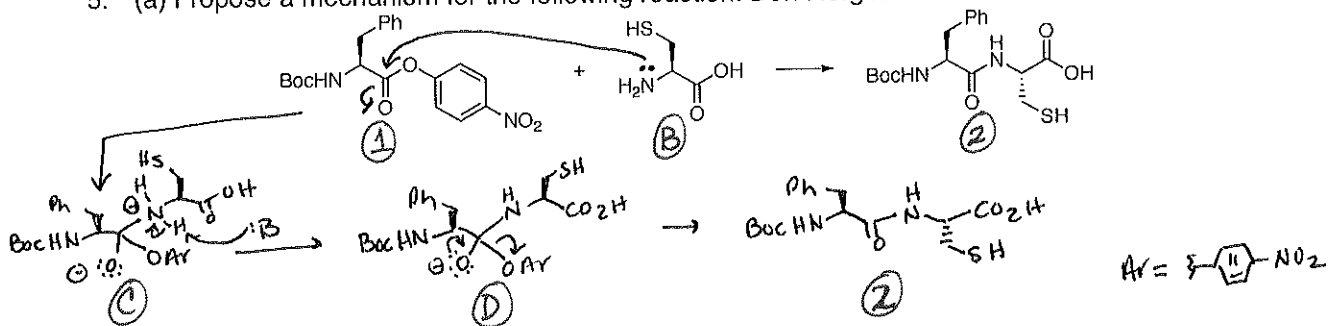


- Effect on absorption spectrum correlated w/ substitution on double bond.

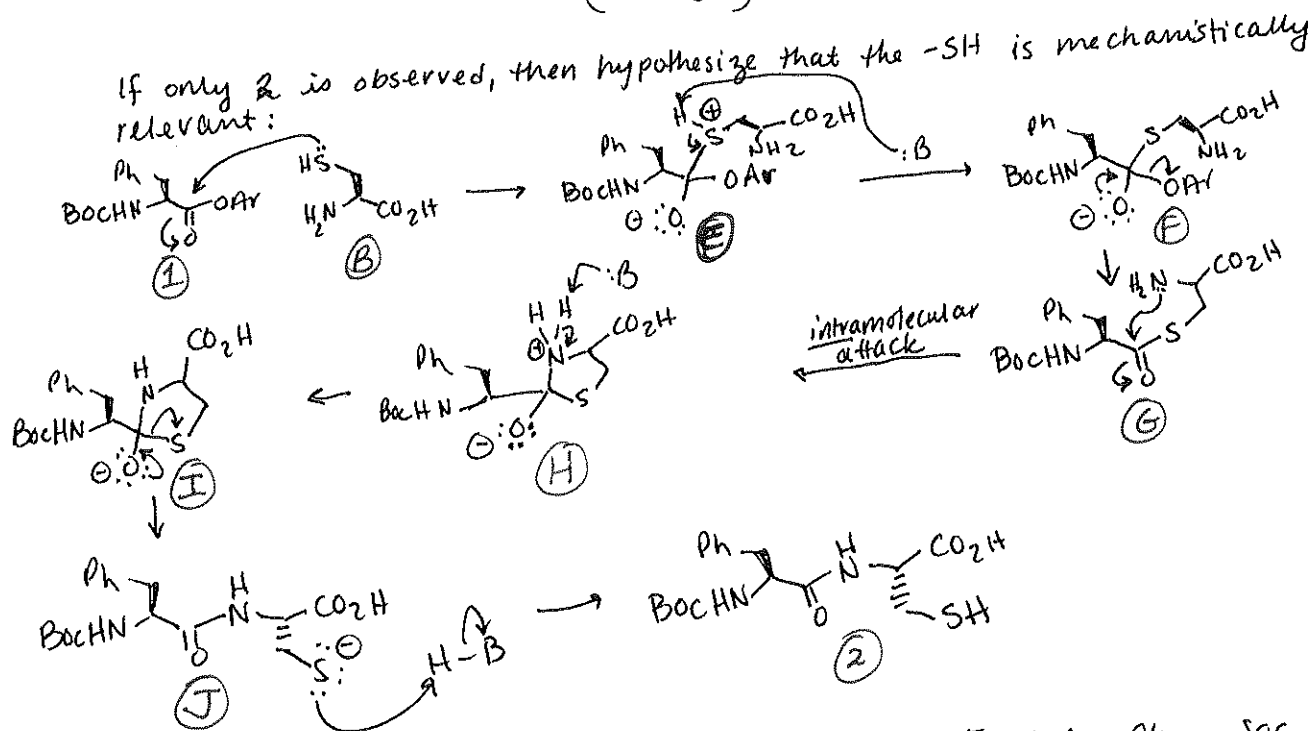
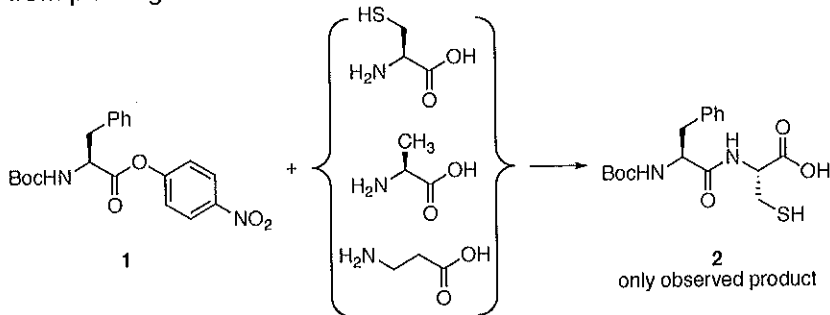
- Replacement of H on dbl bond w/ CH₃ (more e⁻ releasing) ⇒ shift λ_{max} to the red.

Ref: Woodward, R. B. J. Am. Chem. Soc. 1941, 63, 1123.

5. (a) Propose a mechanism for the following reaction. Don't forget Ockham's Razor!



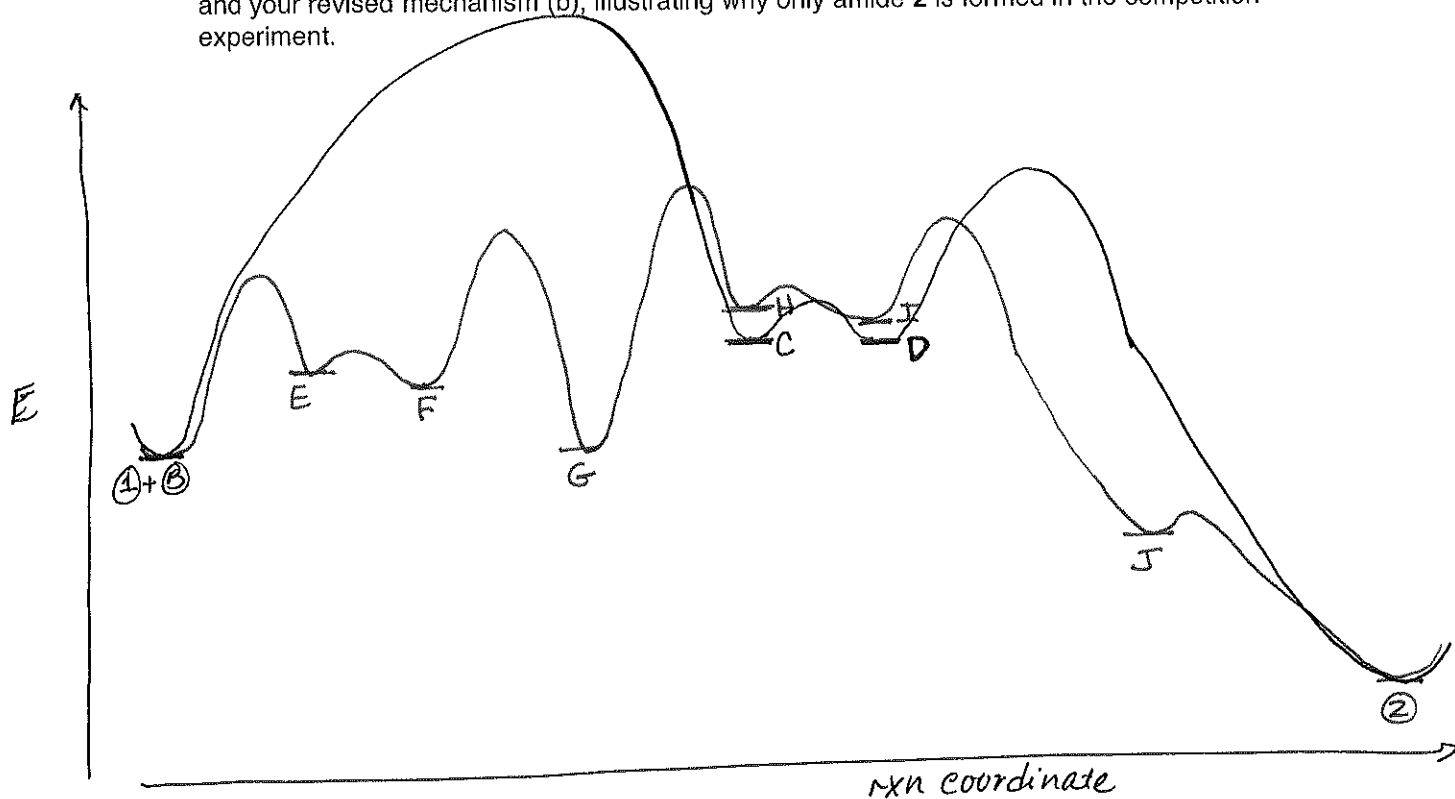
(b) When ester 1 is combined with three amino acids, only product 2 is observed. Please revise your mechanism from part A given these new results.



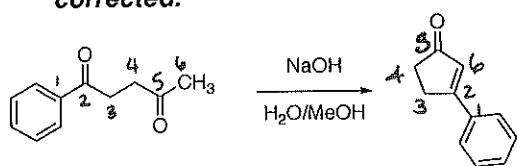
Ref: Wan, Q.; Chen, J.; Yuan, Y.; Danishefsky, S. J. *J. Am. Chem. Soc.* 2008, 130, 15814.

This reaction is Native Chemical Ligation, used for solid-phase peptide synthesis.

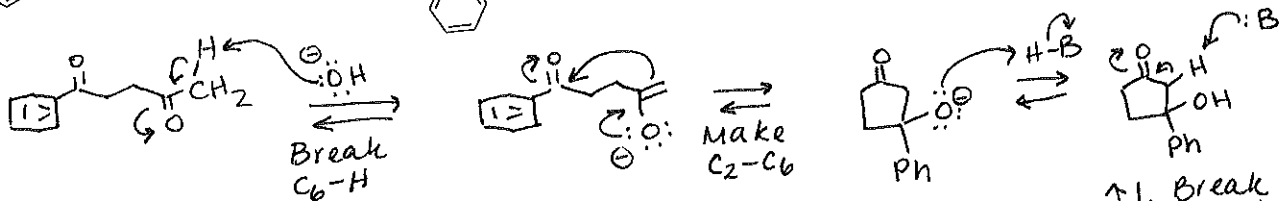
- (c) Please draw a reaction coordinate diagram that shows your originally proposed mechanism (a) and your revised mechanism (b), illustrating why only amide 2 is formed in the competition experiment.



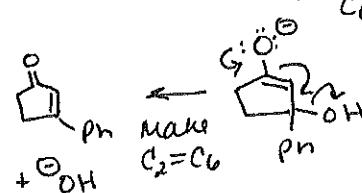
6. Please provide complete, detailed mechanisms for the following reactions. Watch formal charges and show flow of electrons for every step! **Please note that the fourth reaction has been corrected.**



Break / Make
 $\text{C}_2=\text{O}$ $\text{C}_2=\text{C}_6$
 $\text{C}_6-\text{H} \times 2$

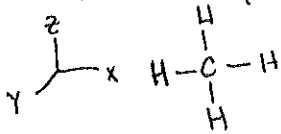


This is an Aldol condensation.

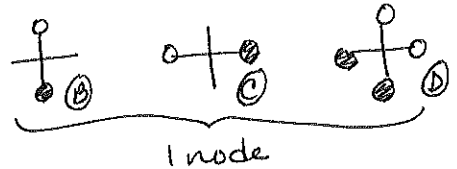
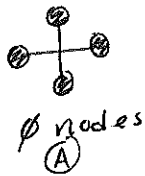


7. Use LCAO-MO Theory to explain why methane has a tetrahedral geometry instead of a square planar geometry.

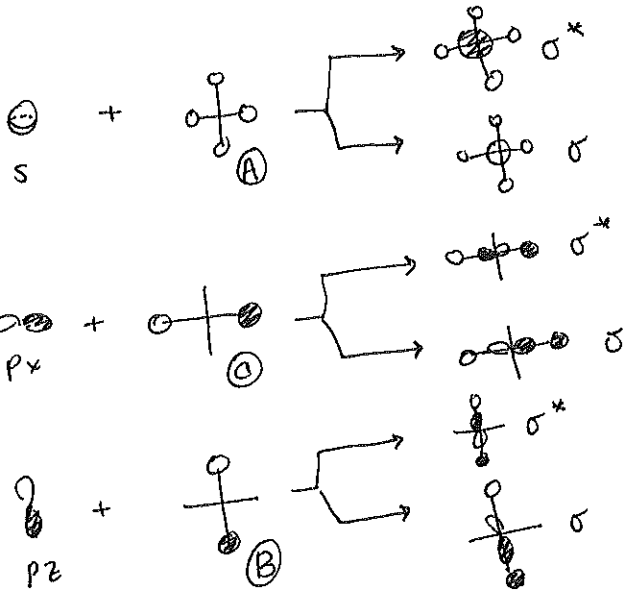
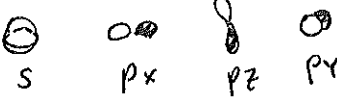
Consider square planar geometry:



LCAO's of 4 H 1s orbitals:



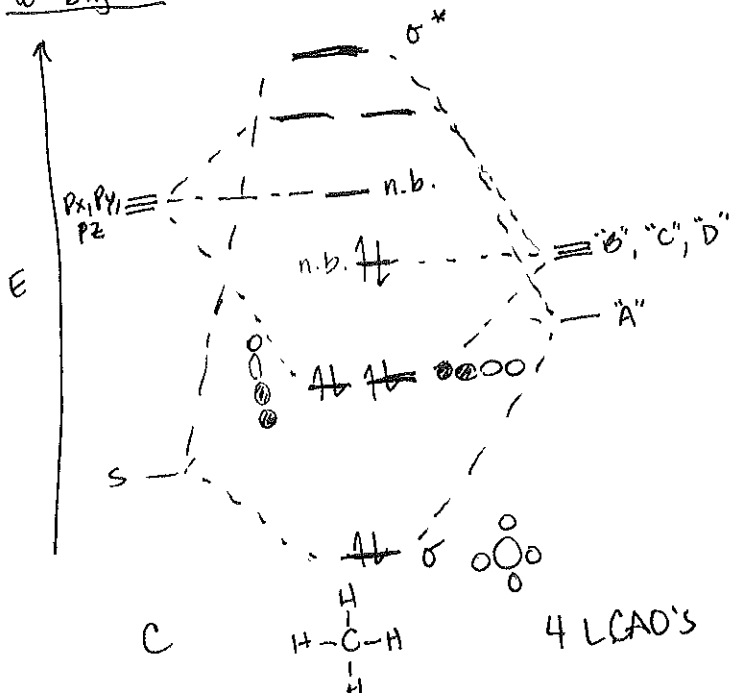
Combine w/ C orbitals:



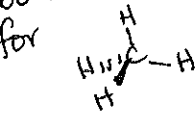
← Wrong symmetry for overlap w/ any C orbital.

← In the node of (B), (C), & (D). Symmetry is wrong to overlap w/ (A).

MO Diagram:



Expect lower C-H bonding (smaller bond order) than for



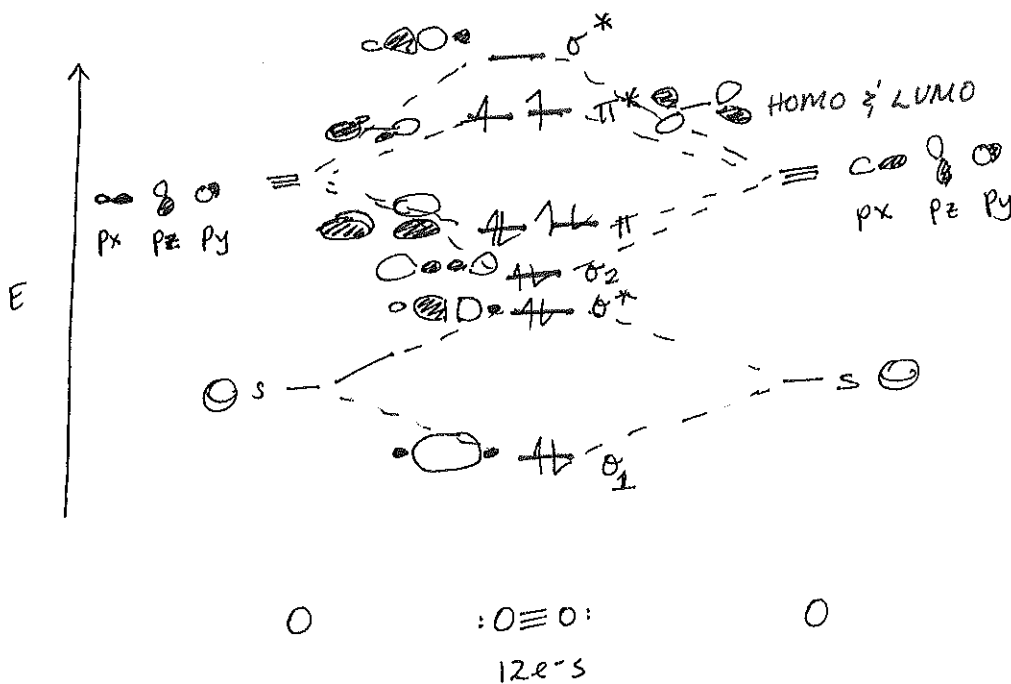
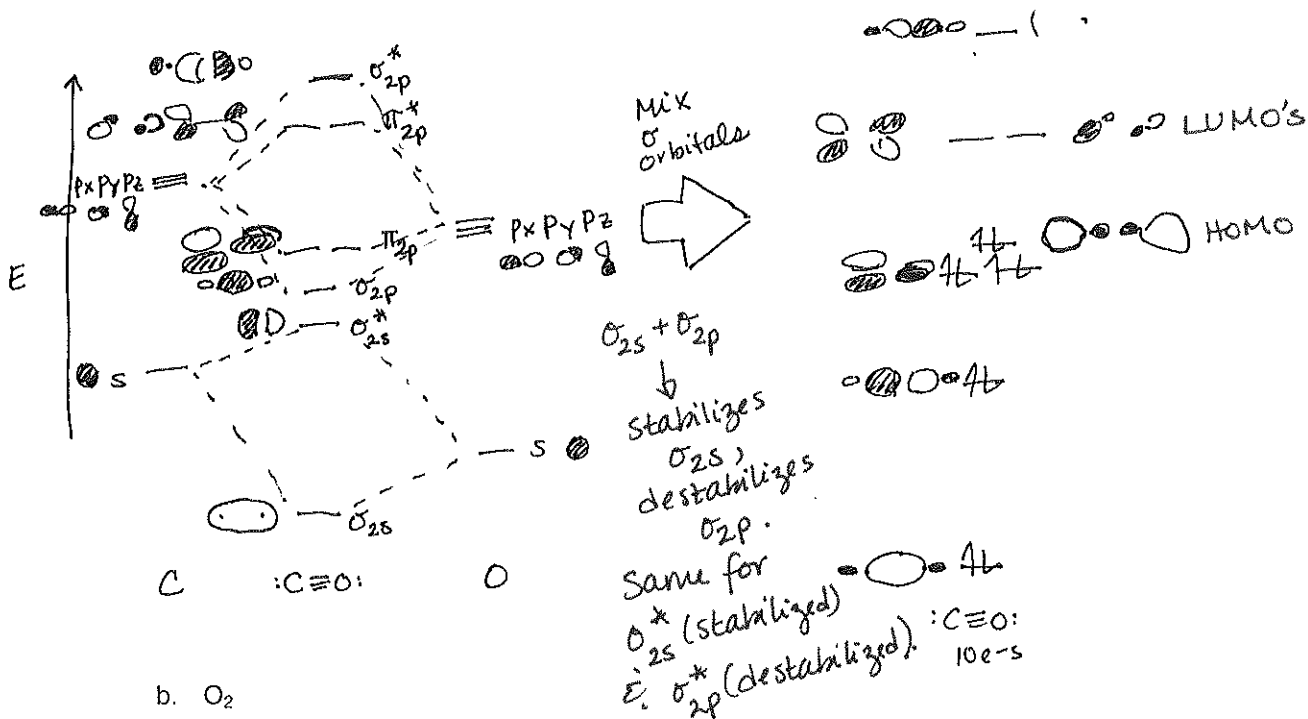
(See tetrahedral CH₄ M.O. in the lecture notes.)

n.b. = nonbonding.

Please note: For a great resource on constructing MO diagrams, see Orbital Interactions in Chemistry by Albright, Burdett & Whangbo.

8. Construct a MO diagram for the following molecules. Please explain explicitly any assumptions that you made. Please draw the shapes of the frontier molecular orbitals (both HOMO & LUMO).

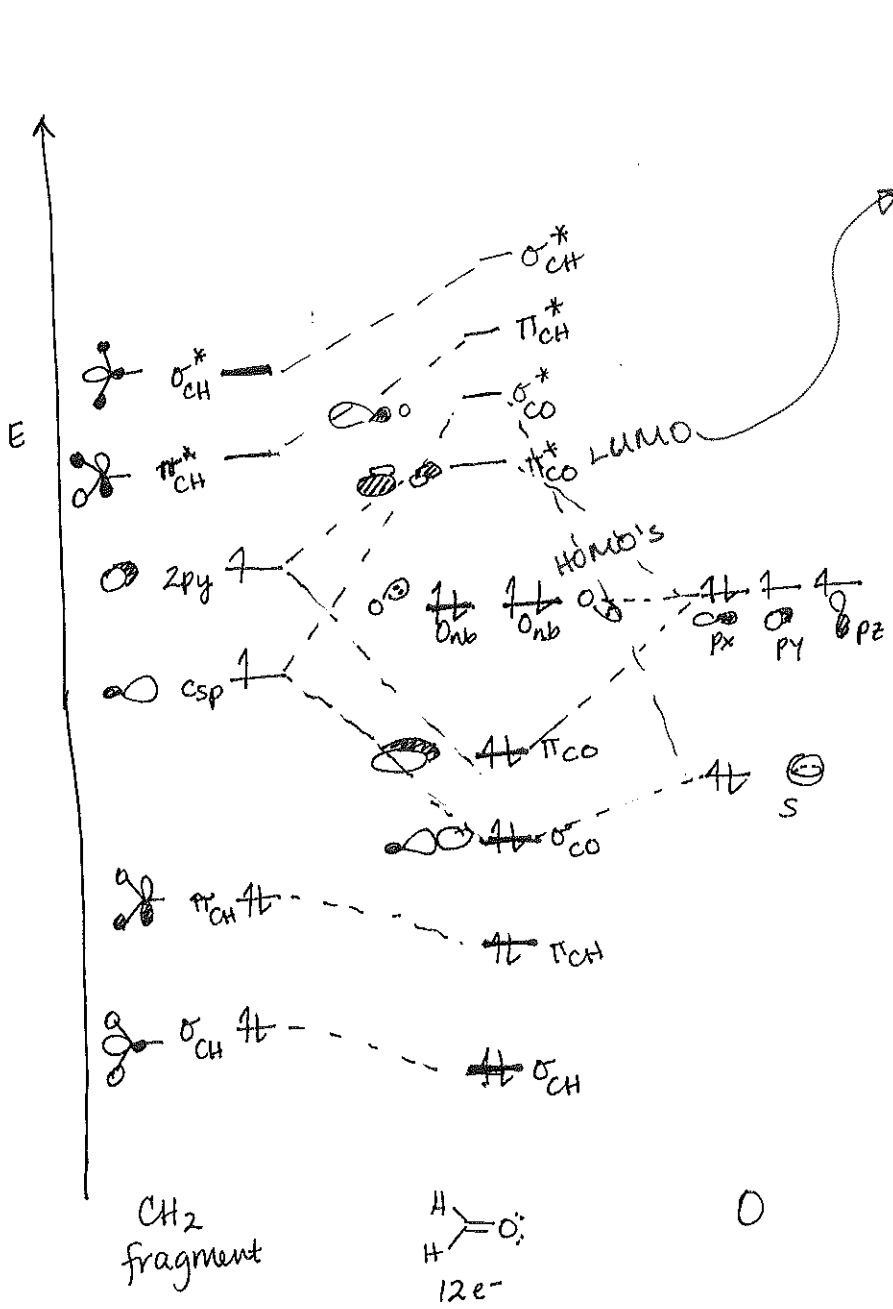
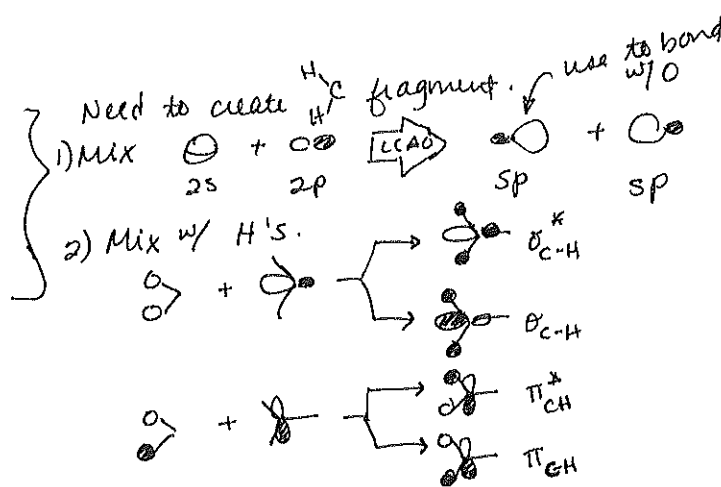
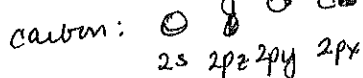
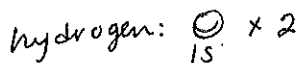
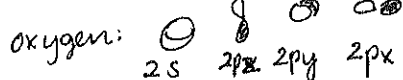
a. CO Note: AO's of oxygen are lower in energy than carbon's, because oxygen is more electronegative.



As w/ CO,
 the $\sigma_{2s} + \sigma_{2p}$
 $\& \sigma_{2s}^* + \sigma_{2p}^*$
 have the same
 symmetry &
 will mix.
 In this case, it
 does not destabilize
 σ_2 enough to
 reorder the orbitals.

c. $H_2C=O$

Basis set:



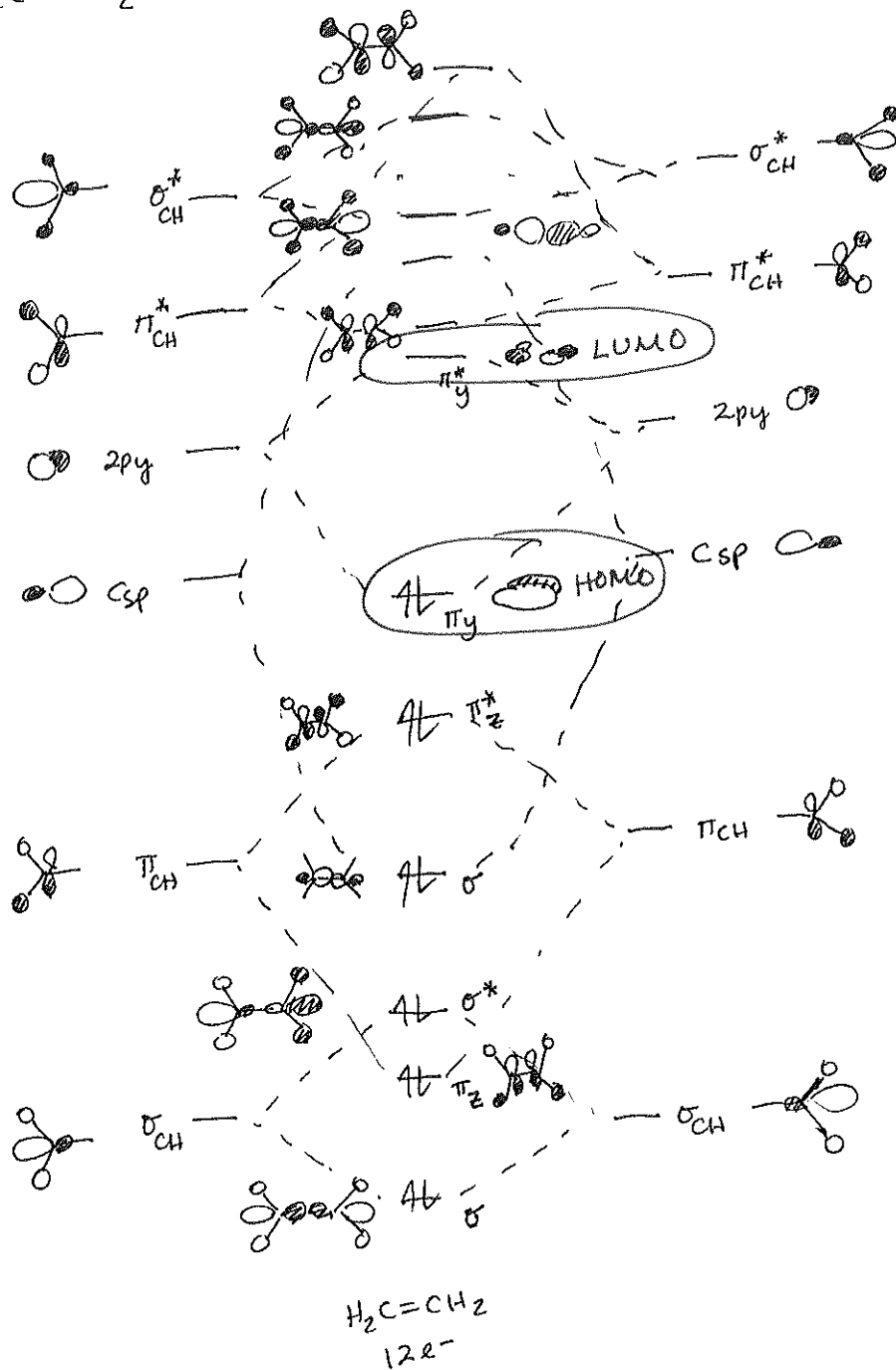
Rotating by 90°
Makes orbitals easier
to see:



C-H orbitals are
stabilized or destabilized
by interaction w/
O AO's.

Oxygen px and pz orbitals will mix with orbitals of CH2 fragment, but the coefficients will be larger on oxygen, so I drew these orbitals as nonbonding lone pairs.

d. $H_2C=CH_2$



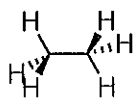
Use CH_2 fragments from part (c).

Assumption:
Reserve σ_{CH} for C-C bond.

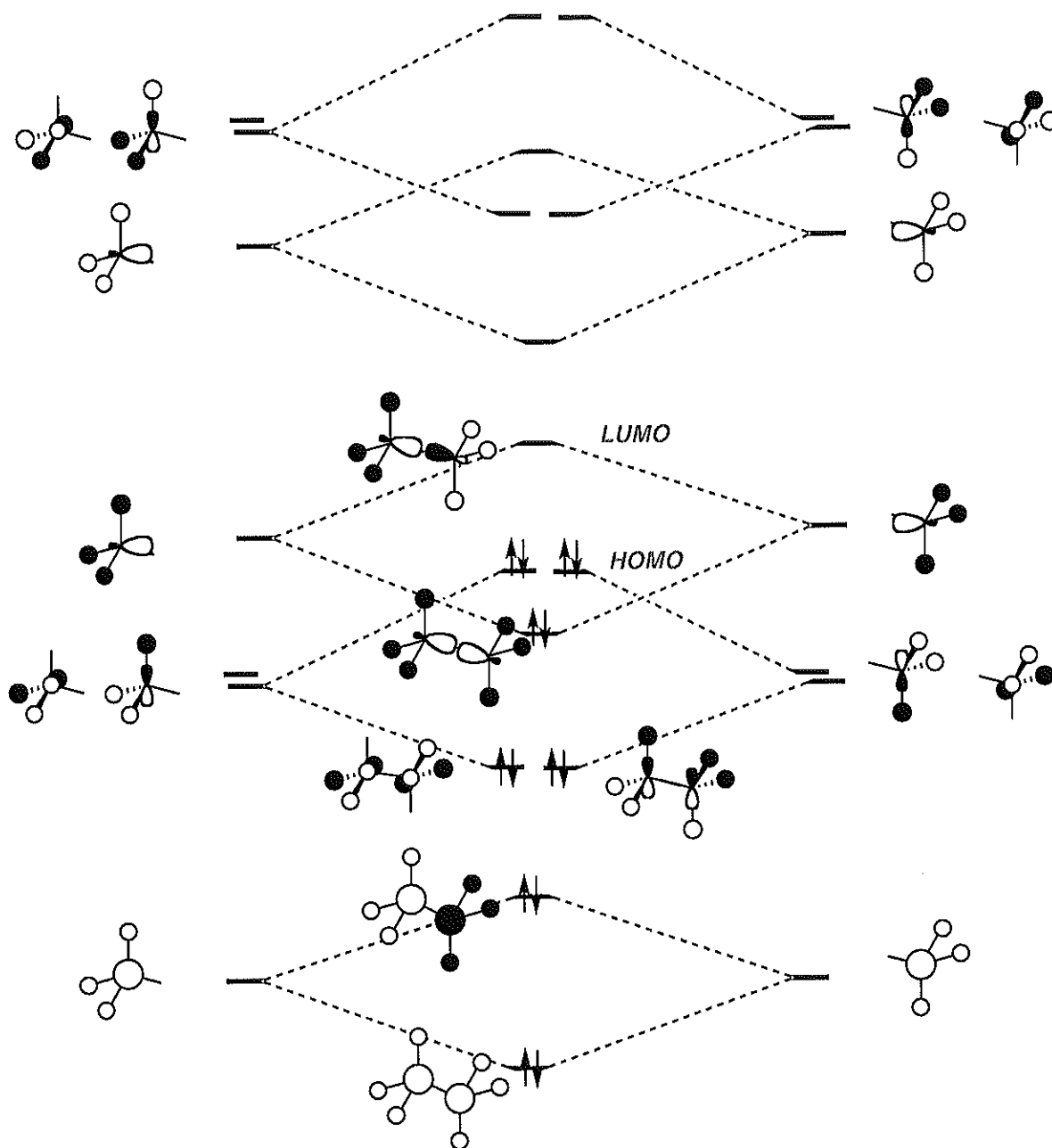
What determines the position of the energy levels?

- # of nodes
- bonding vs. antibonding
- how severe the destabilizing interactions are.

ex. H_3CCH_3



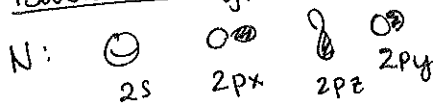
Staggered conformation is more stable.



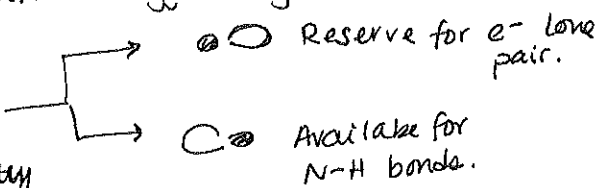
9. How many peaks would you expect in the X-ray photoelectron spectrum of ammonia? Please rationalize your answer by showing a MO diagram.

$\text{NH}_3 \equiv$ trigonal pyramidal / based on tetrahedral geometry.

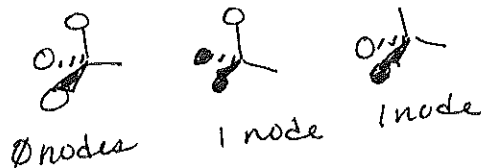
Basis Set: $\begin{matrix} z \\ y \end{matrix} \begin{matrix} x \\ z \\ y \end{matrix}$



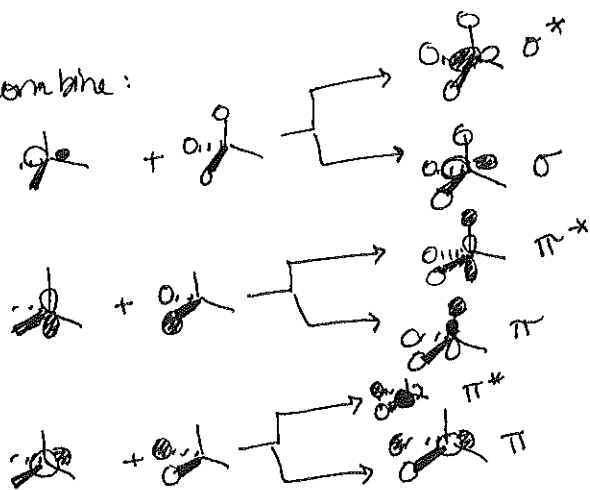
2s + 2p
Can combine
(same symmetry
abt x axis)



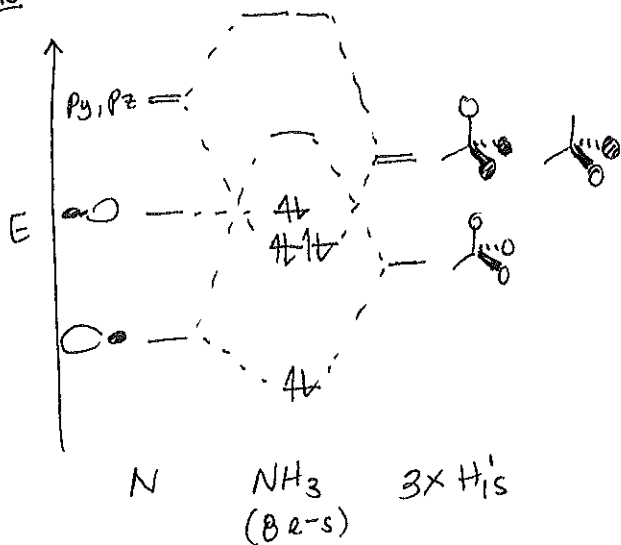
H: $3 \times \text{H}_{1s} \text{ (s)} \Rightarrow 3 \text{ LCAO's}$



Combine:



MO:



Photoelectron Spectrum:
3 energy levels for valence electrons
1 energy level for core electrons on N (1s)

4 peaks