

Chemistry 124 Second Examination  
October 18, 2010

Name \_\_\_\_\_

The exam budgets 50 minutes, but you may have 60 minutes to finish it. Good answers can fit in the space provided. Question values correspond to allotted time. Don't waste too much time on cheap questions.

**Read each question carefully to see what it asks for (bold face is used to help highlight questions).  
Make sure you are answering the question, not just saying something vaguely relevant to its topic.**

- 1.** To describe the distribution and energy of electrons in a molecule, chemists often use LCAO-MOs whose shapes are adjusted by the SCF procedure.

**A.** (1 min) Write out the words abbreviated by LCAO-MO and SCF.

LCAO-MO :

SCF :

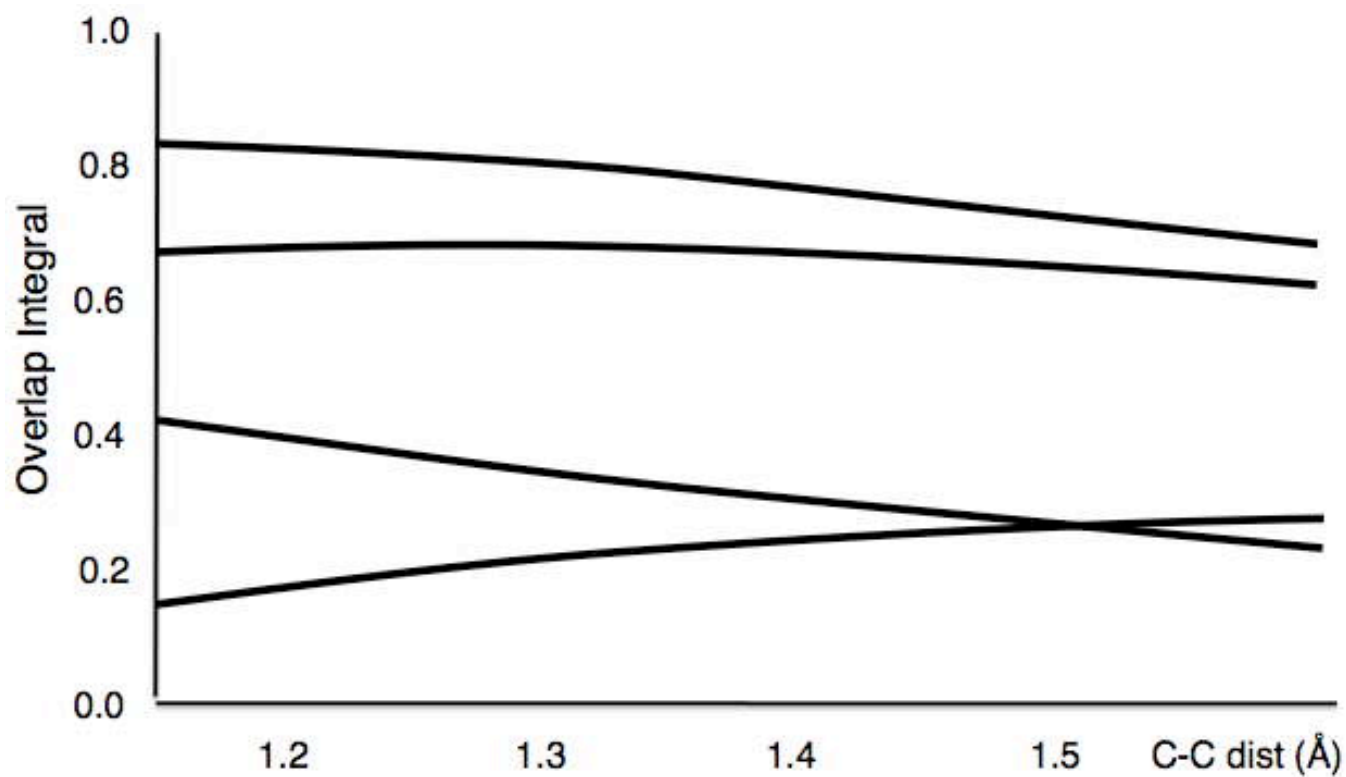
**B.** (3 min) State what problem the SCF procedure is intended to address, and describe VERY briefly how it works.

**C.** (2 min) What is the **name** for the error that is inherent in the SCF approach? Why is this error inevitable in an SCF scheme?

## 1. (cont.)

- D. (3 min) When describing bonding by a pair of atoms in terms of LCAO, a term involving “overlap” arises mathematically. Write a **mathematical expression** to show where overlap arises **AND** how it influences the electron distribution in a bond.

2. (4 min) This graph plots sigma and pi overlap integrals between  $2p$  orbitals of two carbon atoms as a function of the distance between them. It also plots the sigma overlap for two  $sp$  hybrids and for two  $sp^3$  hybrids. Label each curve and explain the basis of your choices in a few words.

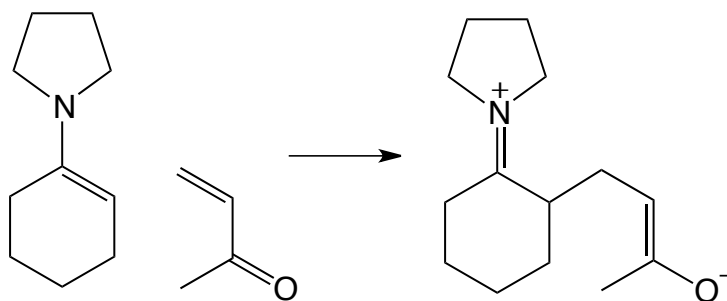


- 3.** (4 min) **Explain** one energetic factor that would prefer  $\text{NH}_3$  to be planar, **AND** another that favors a pyramidal geometry.
- 4.** (3 min) We saw that the (negative) total energy of an “H-like” one-electron atom is proportional to  $1/n^2$ , where  $n$  is the principal quantum number. Combine this information with the scaling of energy with nuclear charge ( $Z$ ) to decide **which energy is higher:** the  $1s$  orbital of the **H atom** or the  $2s$  orbital of the **He<sup>+</sup> ion**.
- 5.** (3 min) If Victor Grignard had already earned a Nobel Prize almost 100 years ago for the used of R-Mg bonds in synthesis, why was it sensible in 2010 for Negishi and Suzuki to share the prize for somewhat analogous use of the analogous organo-metal bond R-Zn and R-B?

6. (3 min) Draw the structure of a *specific* example of a 3-center 2-electron bond.

### STORK ENAMINE ALKYLATION

The remainder of the exam has as a theme the following key step of the “Stork enamine alkylation”, which is named after its inventor, Columbia University’s Prof. Gilbert Stork. It involves bond formation between an “enamine” (the first reagent below - the name derives from its being both an alkene and an amine) and an “unsaturated ketone” (the second reagent).



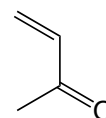
7. (3 min) Draw curved arrows denoting the electron-pair motions in this reaction.

Consider the enamine functional group.

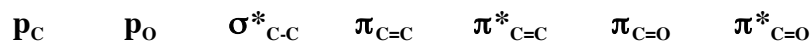
8. Use words and diagrams showing the **shape AND the energy** of orbitals to answer the following series of questions, and thus to describe what makes the enamine capable of this reaction:
- A) (3 min) Give the **names** the *localized* (ATOMIC or PAIRWISE) orbitals of the enamine molecule that have **unusual** energy, and say why each of these localized orbitals would *individually* be expected to be reactive.
- B) (3.5 min) Show how “RESONANCE” should influence enamine reactivity by changing the SHAPE and ENERGY of its HOMO.

9. (5 min) Which should be more reactive in attacking an unsaturated ketone (as in the Stork enamine alkylation), an **enamine** or an **amide**? That is, compare the enamine functional group shown of Question 8 with the amide functional group in terms of analogous localized orbitals and “delocalized” orbitals they give by mixing.

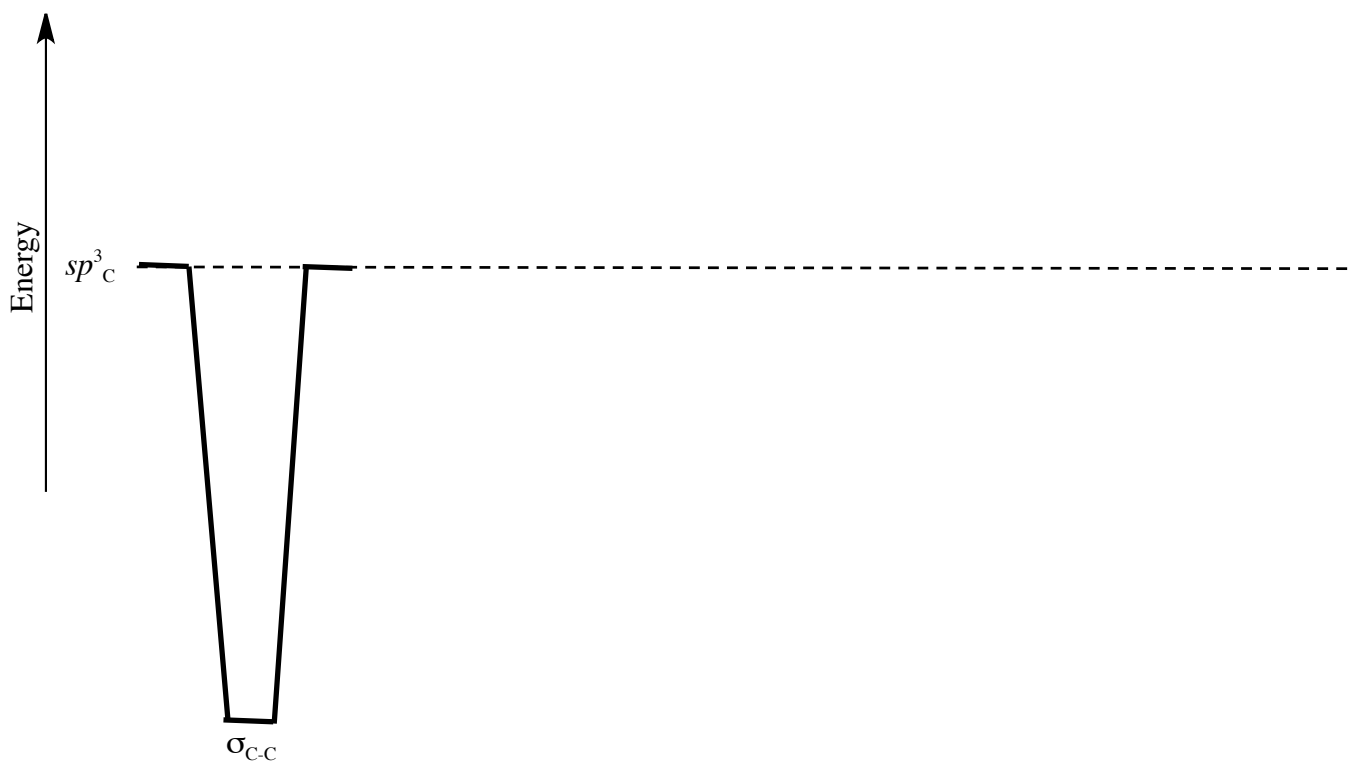
Now consider the unsaturated ketone:



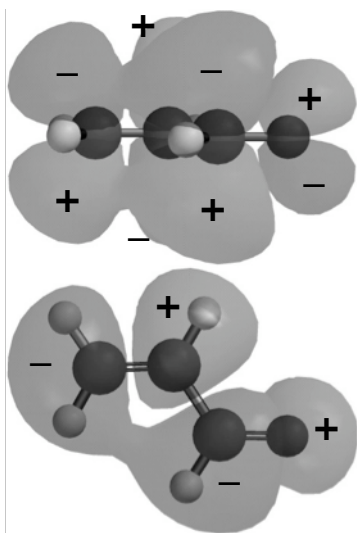
10. (5 min) **Draw and label** short horizontal lines on the following graph to show approximate energies for the following SEVEN *localized* orbitals of the unsaturated ketone compared to the horizontal dashed line, which denotes the energy of a **carbon  $sp^3$**  hybrid orbital and the line denoting the energy of  $\sigma_{C-C}$  :



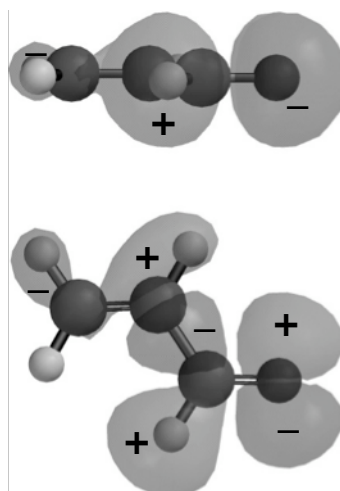
Also **draw lines to connect** bonding and antibonding orbitals to their AO components, as shown for  $\sigma_{C-C}$ .



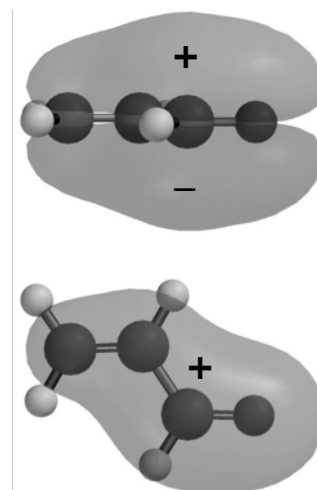
- 11.** (4.5 min) Below are shown side and top views of five MOs of acrolein ( $\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{O}$ ), which is analogous to the unsaturated ketone reagent in the Stork enamine alkylation reaction. Classify each MO as sigma or pi and identify how it is derived from orbitals of Question 9. (*The first two cases are worked as examples.*)



**A** is a  $\pi$  MO.  
It is the C-C antibonding mixture of  $\pi^*_{\text{C}=\text{C}}$  with  $\pi^*_{\text{C}=\text{O}}$ .  
(note that the 2p orbital on the central rear carbon has the opposite phase from the 2p orbital on the central front carbon.)

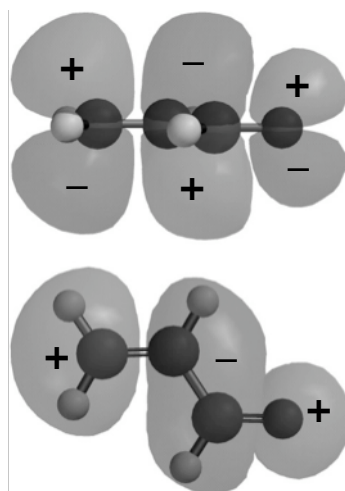


**B** is a  $\sigma$  MO.  
It is the antibonding mixture of a p orbital on O with a number of  $\sigma_{\text{C}-\text{C}}$  and  $\sigma_{\text{H}-\text{H}}$  orbitals



**C** is

**D** is



**E** is

