Chemistry 124   Second Examination Answers   **October 18, 2010**

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 :   **L**inear **C**ombination of **A**tomic **O**rbitals – **M**olecular **O**rbital

SCF :   **S**elf-**C**onsistent **F**ield

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

   The Self-Consistent Field procedure attempts to approximate the influence of
electron-electron repulsion by holding all electrons but one in a fixed cloud while the
orbital of that one electron is calculated. That electron is then held fixed in the
cloud, while another electron's orbital is adjusted. One thus cycles repeatedly
through all the electrons, one at a time, until the orbital shapes and energies stop
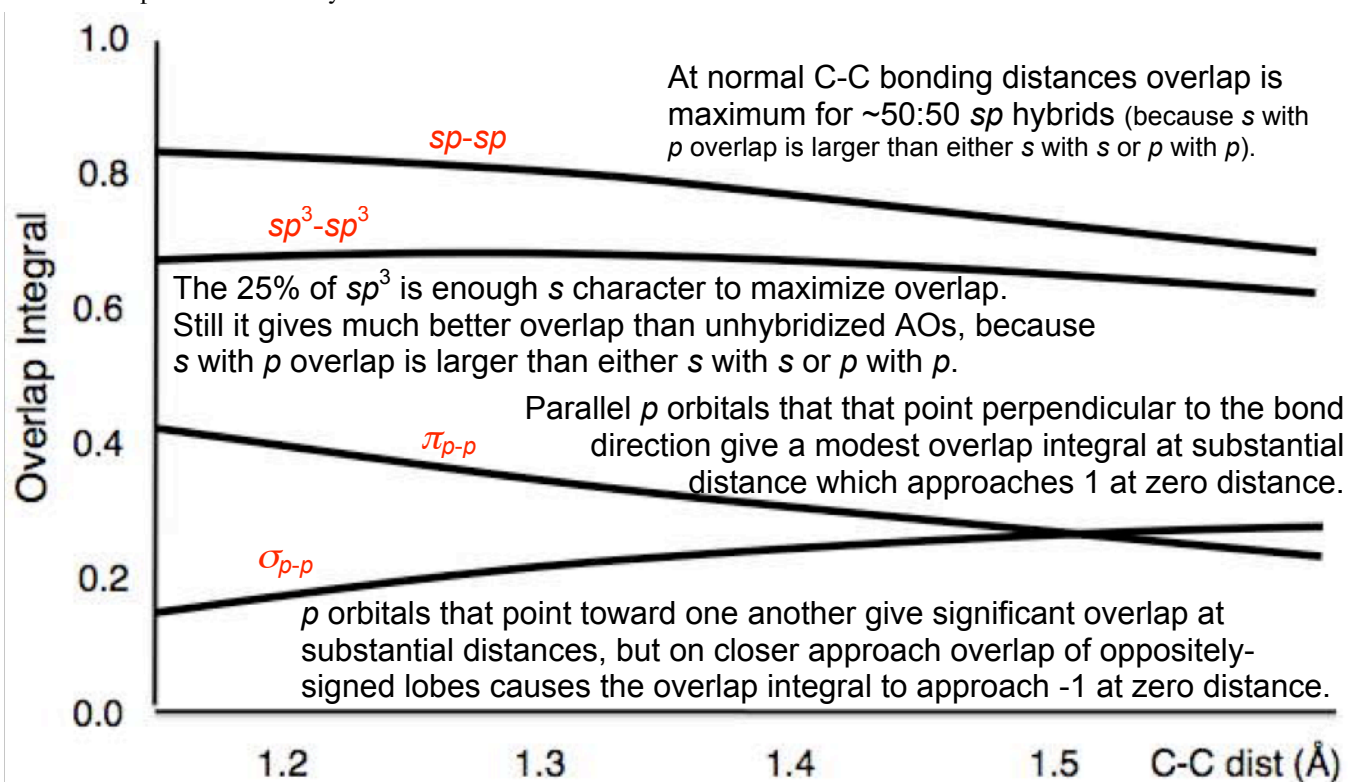changing significantly.

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?

   The residual error after an SCF calculation is called "correlation energy". It is
inevitable that the SCF procedure overestimate electron-electron repulsion, because it
treats the electrons as fixed clouds, when in fact the electrons can correlate their motion
with one another so as to avoid high repulsion, even while keeping the average one-
electron probability distribution constant.

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.

   Overlap is important because when one writes a molecular orbital as a linear
combination (sum) of atomic orbitals and then squares the MO to find the probability
distribution, there are cross-terms in the square, *i.e.* $(A+B)^2 = A^2 + B^2 + 2AB$. The
product AB is significant in the region between the nuclei where the two orbitals both
have significant amplitude, *i.e.* they overlap. Addition of this overlap term increases
the probability density above that expected from the sum the two independent AOs
$(A^2 + B^2)$.

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 *sp³* hybrids. Label each curve and explain the basis of your choices in a few words.

Graph: y-axis "Overlap Integral" from 0.0 to 1.0; x-axis "C-C dist (Å)" with marks 1.2, 1.3, 1.4, 1.5.

sp-sp

At normal C-C bonding distances overlap is maximum for ~50:50 *sp* hybrids (because *s* with *p* overlap is larger than either *s* with *s* or *p* with *p*).

sp³-sp³

The 25% of *sp³* is enough *s* character to maximize overlap. Still it gives much better overlap than unhybridized AOs, because *s* with *p* overlap is larger than either *s* with *s* or *p* with *p*.

π_{p-p}

Parallel *p* orbitals that that point perpendicular to the bond direction give a modest overlap integral at substantial distance which approaches 1 at zero distance.

σ_{p-p}

p orbitals that point toward one another give significant overlap at substantial distances, but on closer approach overlap of oppositely-signed lobes causes the overlap integral to approach -1 at zero distance.

3.   (4 min) **Explain** one energetic factor that would prefer NH_3 to be planar, **AND** another that favors a pyramidal geometry.

Maximizing overlap (and thus bond strength) for three bonds from an atom requires *sp²* hybridization and thus planar geometry (120° bond angles). However if all of the 2*s*-character of an atom is consumed by bonding, any remaining electrons (specifically the unshared pair of N) must be accommodated in a 2*p* orbital, whose energy is higher than the 2*s* orbital in a many-electron atom. That is, the unshared pair is lower in energy in a pyramidal structure.

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⁺ ion**.

Average Kinetic, Potential (Coulombic), and thus total energy of an electron in a particular H-like orbital all scale with Z^2. Thus the *1s* H atom (Z=1, *n*=1) and the *2s* He⁺ ion (Z=2, *n*=2) have the same energy since they have the same Z/*n* ratio.

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?

The valence orbitals of Mg are higher in energy than those of Zn and B, thus its σ bond to carbon is a much higher-energy HOMO, which is much more reactive. For some purposes this extra reactivity is a good thing, but when aiming to prepare a complex organic molecule with a variety of functional groups, it is good to have less reactive HOMO reagents that are more selective in choosing which LUMO to react with.

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

The examples we discussed in lecture are the dimers of BH_3 and CH_3-Li. Each of these contains two of the 3-center-2-electron "Y" bonds linking H and two B atoms in the first case, and CH_3 with two Li atoms in the second.

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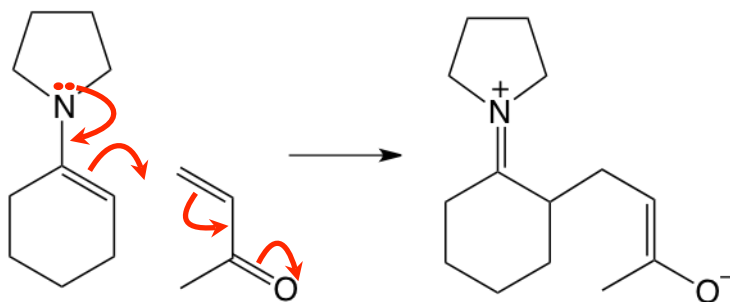
7. (3 min) Draw curved arrows denoting the electron-pair motions in this reaction.

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.

The unshared electron pair (*n*) of the nitrogen atom is an unusually high-energy occupied orbital because, although N has a larger nuclear charge than our "standard" C and H atoms, this atomic orbital has not been lowered in energy by mixing with an orbital of another atom (as are our standard $\sigma_{C\text{-}C}$ and $\sigma_{C\text{-}H}$ bonding orbitals).

The unusual pairwise orbitals are $\pi_{C=C}$ and $\pi*_{C=C}$. These orbitals are unusual because of their small splitting due to relatively weak π overlap of the parallel $2p_C$ orbitals. Thus $\pi*_{C=C}$ is unusually low in energy (compared to $\sigma*_{C\text{-}C}$), while $\pi_{C=C}$ is unusually high in energy (compared to $\sigma_{C\text{-}C}$). The $\pi*_{C=C}$ orbital is also low because the $2p_C$ orbitals from which it is constructed are slightly higher in energy that the standard sp^3 C hybrid AOs.

B) (3.5 min) Show how "RESONANCE" should influence enamine reactivity by changing the SHAPE and ENERGY of its HOMO.

The $2p_N$ unshared electron pair atomic orbital of the nitrogen atom has π overlap with the adjacent unusually low $\pi*_{C=C}$ vacant orbital. Thus these orbitals will mix and the electrons of the unshared pair will be lowered in energy as they shift into an orbital that is bonding between N and the central C, but remains antibonding between the two carbons.

(Actually there is also mixing between the N lone pair and $\pi_{C=C}$. Since both of these orbitals are doubly occupied, this mixing has little consequence for the total energy.   Later on we will discuss such "allylic" systems involving three successive p orbitals with π overlap.)

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.

In the enamine nitrogen's "unshared-pair" HOMO is lowered in energy (and made less reactive) by mixing with $\pi^*_{C=C}$ (see 8b above). In the case of the amide, it is more extensively mixed with the lower-energy $\pi^*_{C=O}$, thus the HOMO of the amide is even less reactive that that of the enamine for purposes of attacking the low LUMO of the unsaturated ketone.

Now consider the unsaturated ketone:
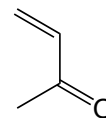
10. (5 min) **Draw and label** short horizontal lines on the following graph to show approximate energies for the following SEVEN *localized* orbitals of the unsaturated ketone compared to the horizontal dashed line, which denotes the energy of a **carbon sp³** hybrid orbital and the line denoting the energy of σ_{C-C} :

$$\mathbf{p_C} \qquad \mathbf{p_O} \qquad \mathbf{\sigma^*_{C-C}} \qquad \mathbf{\pi_{C=C}} \qquad \mathbf{\pi^*_{C=C}} \qquad \mathbf{\pi_{C=O}} \qquad \mathbf{\pi^*_{C=O}}$$

Also **draw lines to connect** bonding and antibonding orbitals to their AO components, as shown for σ_{C-C}.
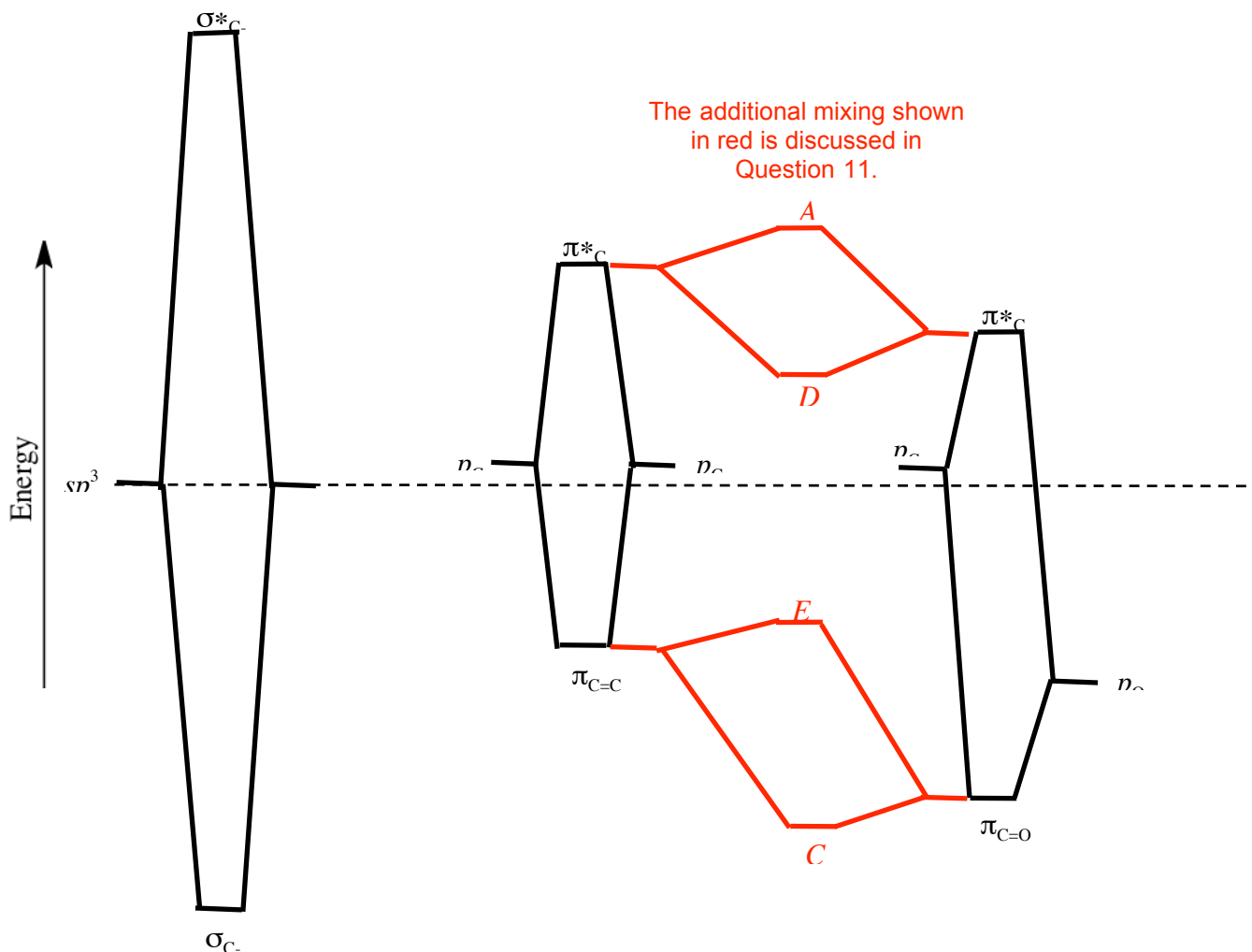
11. (4.5 min) Below are shown side and top views of five MOs of acrolein ($H_2C=CH-CH=O$), which is analogous to the unsaturated ketone reagent in the Stork enamine alkylation reaction. Classify each MO as sigma or pi and identify how it is derived from orbitals of Question 9.   (*The first two cases are worked as examples*.)
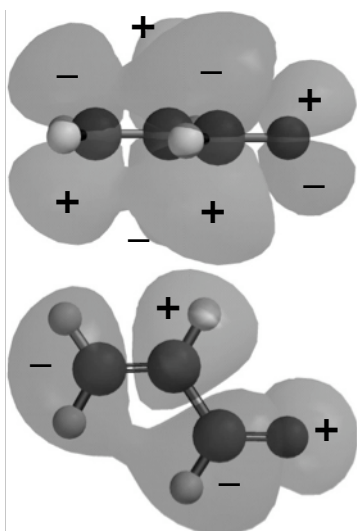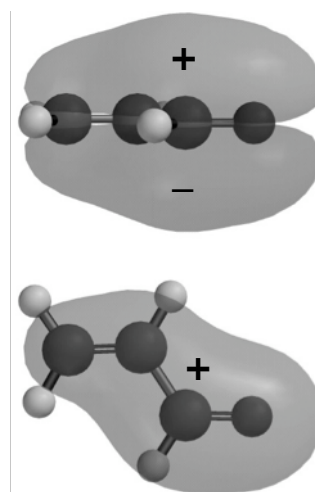

A is a π MO.
It is the C-C antibonding mixture of $\pi^*_{C=C}$ with $\pi^*_{C=O}$.
(note that the 2p orbital on the central rear carbon has the opposite phase from the 2p orbital on the central front carbon.)
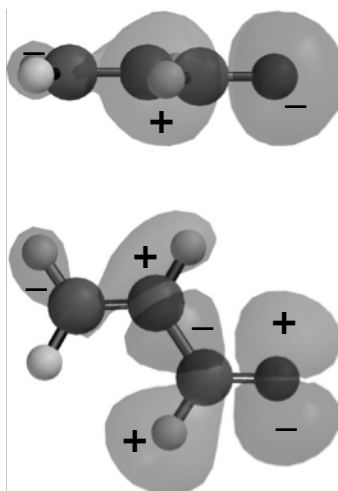
B is a σ MO.
It is the antibonding mixture of a p orbital on O with a number of σ_{C-C} and σ_{H-H} orbitals

C is a π MO (see the AO nodes in the top view).
It is the bonding mixture of the $\pi_{C=C}$ orbital with the $\pi_{C=O}$ orbital. Note in the top view that the lower-energy $\pi_{C=O}$ orbital is dominant in this lower-energy combination.
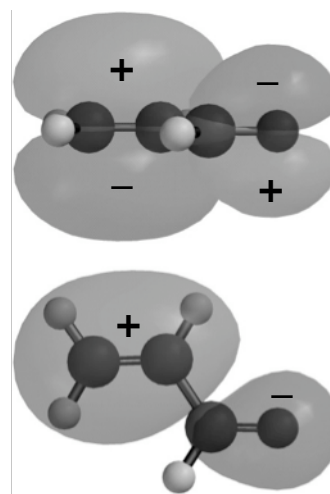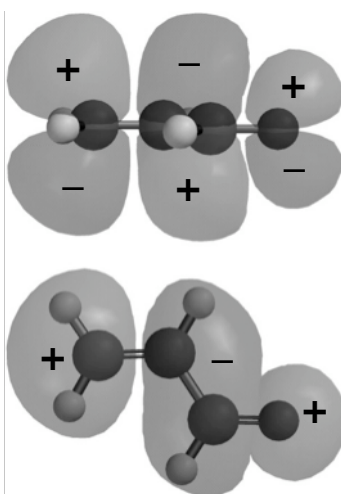
D is a π MO (see the AO nodes in the top view).
It is the bonding mixture of the $\pi_{*C=C}$ orbital with the $\pi_{*C=O}$ orbital. It seems surprising in the top view that the higher-energy $\pi_{C=C}$ orbital appears dominant in this lower-energy combination. Partly this is beause of the more condensed nature of the *2p* atomic orbital on O.

E is a π MO (see the AO nodes in the top view).
It is the antibonding mixture of the $\pi_{C=C}$ orbital with the $\pi_{C=O}$ orbital. Note in the top view that the higher-energy $\pi_{C=C}$ orbital is dominant in this higher-energy combination.