Chemistry 124   Second Examination Answer Key   **October 19, 2009**

1. (5 min) Explain why the bonding combination of two orbitals is more favorable energetically than the antibonding combination. Discuss **both potential and kinetic energies**.

Potential Energy: Through the "2AB" overlap term the bonding combination increases electron density between the bonded nuclei at the expense of density at a similar distance on the "far side" of each nucleus. Proximity to a second nucleus lowers the potential energy.

Kinetic Energy: The combination with fewer nodes (the one where the overlapping waves reinforce) has less curvature toward the baseline and thus less kinetic energy.

[Troublemakers will note that this contravenes the "Virial Theorem", which we have not discussed, but which requires that changes in kinetic energy be half as large as those in potential energy and of *opposite* sign. In fact the lowered curvature mentioned in the answer above reduces the kinetic energy "pressure" for spreading the wave function. This allows contraction of the atomic orbitals toward the nuclei in a "second stage", lowering the potential energy still further and increasing the kinetic energy, as required by the Virial Theorem.]

2. (5 min) **Sketch** the most important **orbital interactions** involved in dimerization of two BH_3 molecules, and comment on the **energies** of the orbitals that interact.

Each BH_3 has an unusually low LUMO (the vacant *2p* orbital of the B atom that is low in energy compared to a CH σ* orbital, despite the low nuclear charge of B, because it has not mixed with the orthogonal *1s* orbitals of the H atoms).

Each BH_3 also has an unusually high HOMO (a B-H σ bonding orbital, large on H, that is unusually high because the component sp^2 hybrid of B is higher than the corresponding carbon orbital would be. This is because the B nucleus has one fewer protons than the C nucleus.)
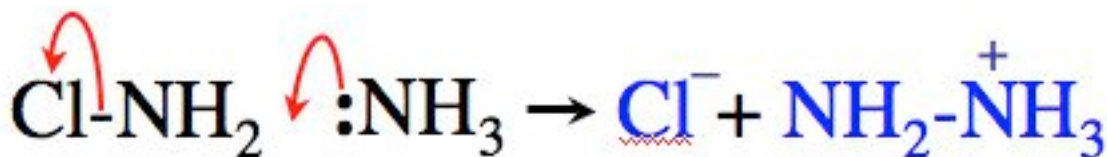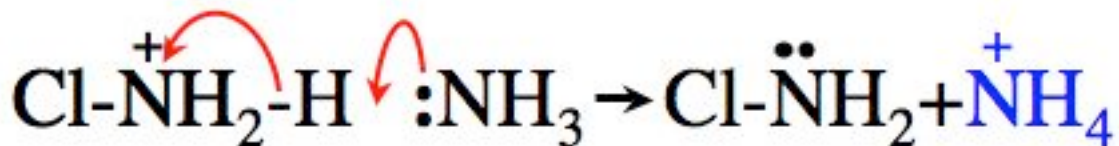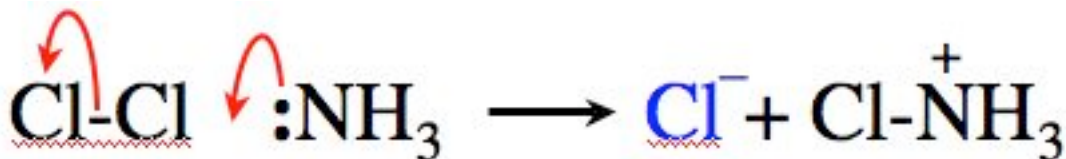
There is thus significant HOMO-LUMO mixing in both directions.
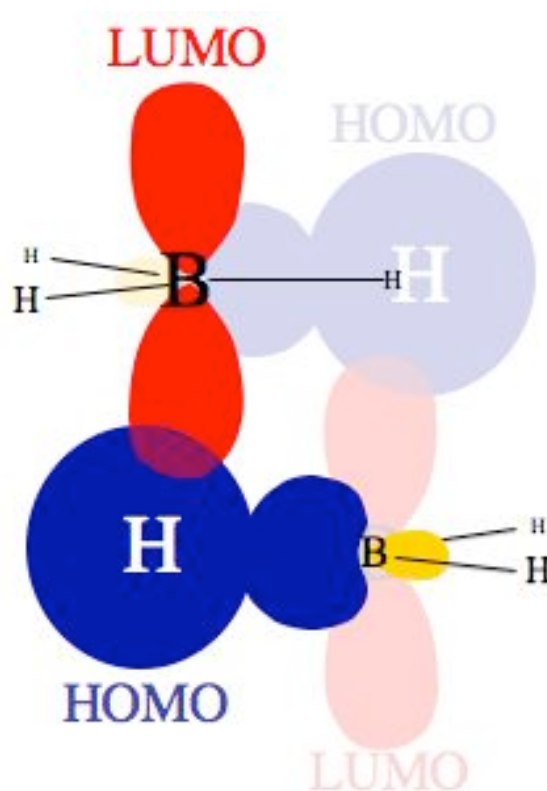
3.   (5 min) Rationalize the observed geometry of the **CF₃** radical in terms of the factors that determine orbital **hybridization**.
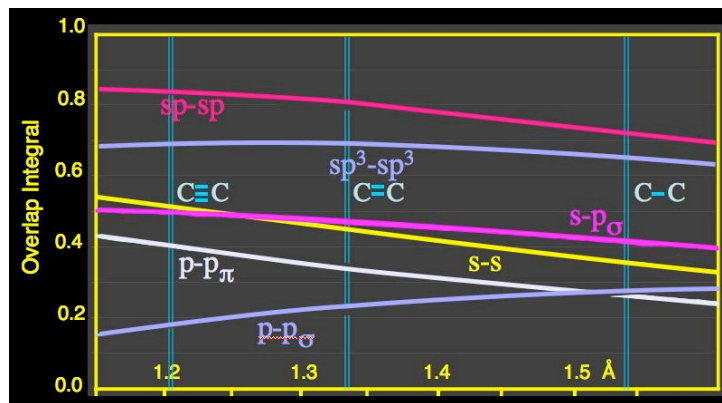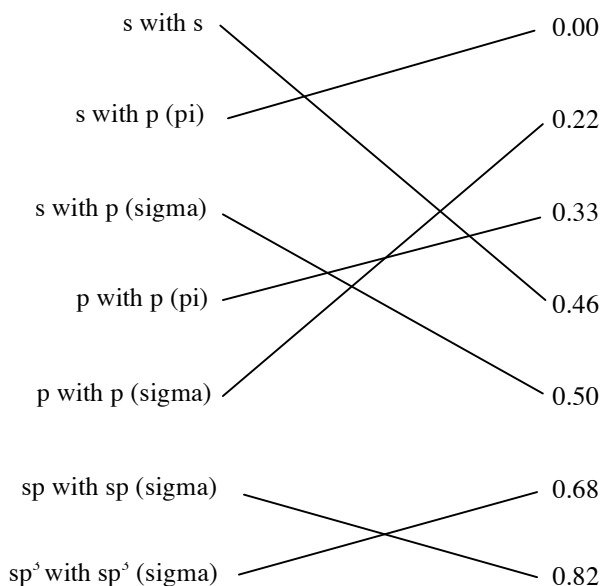(You do NOT need to describe the ESR experiment or its interpretation.)

A carbon atoms that uses 3 sp^2 bonding hybrids is planar. Increased p-character in the bonding hybrids makes the geometry pyramidal. In CF_3 the strongest bonds would use sp^2 hybrids on the C atom (because they give the best total overlap), but this would leave a high-energy p orbital for the odd electron on C. This electron is only on C, while the bonding pairs spend most of their time on F (with its higher nuclear charge). Thus the C atom would gain overall electron stabilization by devoting some of its s-character to its lone electron at the expense of the three σ_{C-F} bonding pairs that are mostly on F. This requires $sp^{>2}$ carbon hybridization in the bonding orbitals and thus pyramidal geometry.

4.   (6 min) Draw the three reactions involved in oxidation of NH_3 by Cl_2 to give hydrazinium hydrochloride (NH_2NH_3Cl). Draw **curved arrows** carefully, AND very briefly explain how the three reactions are **analogous** in HOMO/LUMO terms.

$$Cl\text{-}Cl \quad :NH_3 \longrightarrow Cl^- + Cl\text{-}\overset{+}{N}H_3$$

$$Cl\text{-}\overset{+}{N}H_2\text{-}H \quad :NH_3 \rightarrow Cl\text{-}\ddot{N}H_2 + \overset{+}{N}H_4$$

$$Cl\text{-}NH_2 \quad :NH_3 \rightarrow Cl^- + NH_2\text{-}\overset{+}{N}H_3$$

In each of the three reactions the HOMO (lone pair on N of NH_3) overlaps with a σ^* LUMO to form a new bond with the atom attacked while breaking the bond between the attacked atom and its former partner. The atoms attacked are Cl, H, and N, respectively.

5. (4 minutes) Draw lines to match each of the following mixings of **valence orbitals of two adjacent carbon atoms** with the appropriate overlap integral at the **normal distance of a C=C double bond**. [No explanations required]

s with s	0.00
s with p (pi)	0.22
s with p (sigma)	0.33
p with p (pi)	0.46
p with p (sigma)	0.50
sp with sp (sigma)	0.68
sp³ with sp³ (sigma)	0.82

6. (6 min) Describe "**correlation energy**" touching briefly on the following points: **(a)** how it relates to the energy of **self-consistent-field orbitals**; **(b)** the **direction** of its influence on electronic energy; and **(c)** the extent to which it might be **negligible**.

   (a) *Correlation energy* is the name given to the difference between the self-consistent field energy (where electron-electron repulsion is treated as the coulombic interaction between fixed clouds) and the true energy obtained from experiment or from a high-level calculation that accounts for the ability of electrons instantaneously to stay out of each other's way by correlating their motion.

   (b) Since electrons reduce their average repulsion by correlating their motion, correction for correlation always lowers the energy from what is calculated by self-consistent-field methods.

   (c) Correlation energy for typical organic molecules is about as large as a bond energy, but it could be neglected in calculating the *difference* between different arrangements of the same atoms, if their correlation energies were identical. In fact *changes* in correlation energy can be roughly 10-20% of bond energy. So for the qualitative purposes of understanding how bonds work it can be neglected, but for quantitative purposes (*e.g.* calculating rates or equilibrium constants), it must usually be taken into account.

7.   An article in the November 2009 issue of *Clinical Infectious Diseases* suggests that some fatalities during the 1918-19 influenza pandemic were caused by overprescription of the first artifical "wonder drug", asprin (acetylsalicylic acid). Bayer had lost patent protection in February 1917. Many other manufacturers had jumped in to manufacture and market the drug that was being prescribed in what are now know to be toxic doses.

(a) (2 min) How does salicylic acid relate to the "Doctrine of Sympathies" of Paracelsus?

> The *Doctrine of Sympathies* held that the remedy for a malady was to be found in nature near the malady's source. Malaria was prevalent in swampy areas, where the willow (salix) grows. An extract of willow bark contains salicylic acid, which was found to lower the fever that came with malaria.

Salicylic acid was (and is) cheap to make using the "Kolbe" synthesis, which had been developed in 1860. It involves treating phenol (hydroxybenzene) with NaOH and CO_2.

(b) (4 min) **Name** the HOMO and the LUMO involved in reaction shown below between phenol and hydroxide. Say **what factors** (if any) make them *unusually* high or low. [Save resonance for Part c.]

HOMO: The unshared pair on the hydroxide anion is unusually high both because it is not involved in bonding O to another atom (which lowers the energy of our reference σ_{C-C} electrons) and because of the negative charge (extra electron-electron repulsion).

LUMO: σ^*_{O-H} is unusually low in energy for a vacant orbital because of bad E-match due to the low energy of its constituent atomic orbital of the oxygen atom (due to its nucleus having two more protons than than C does).

(c) (6 min) Consider "resonance" involving **only the closest double bond** of the benzene ring (*i.e.* treat phenol as an enol) **both** in phenol and in the "phenoxide" anion product. **DRAW** the resonance structures below each structure **AND EXPLAIN** in terms of "HOMO/LUMO" mixing of localized orbitals whether this resonance should favor or disfavor formation of phenoxide as shown.
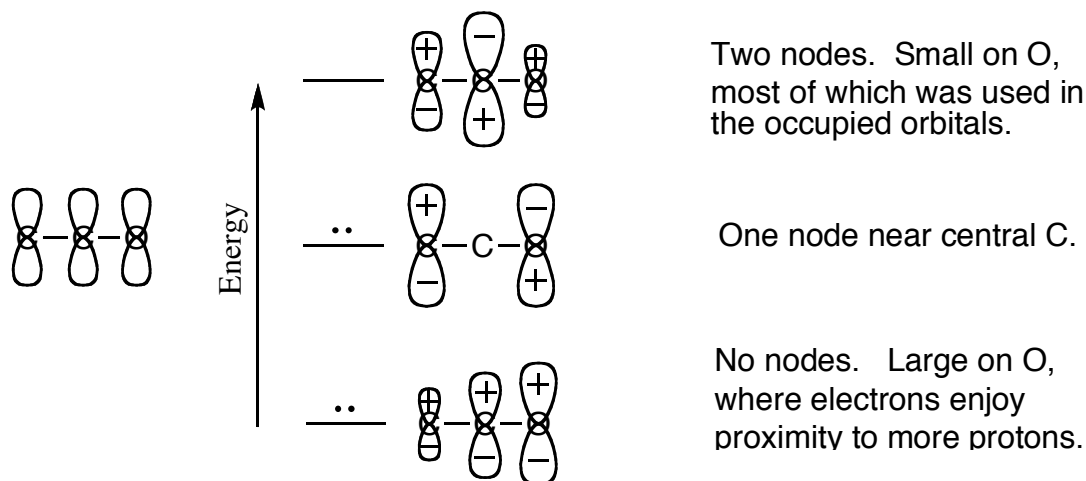
> In both cases an unshared pair of electrons on the oxygen atoms is stabilized by mixing with the adjacent $\pi^*_{C=C}$. Stabilization of the anion by this mixing is larger, because its unshared pair is higher in energy due to the negative charge of the anion.
>
> Thus resonance favors the reaction as written.

> [In the language of resonance stabilization of Lewis structures, stabilization of phenoxide is greater because it does not require "charge separation", but the question specifically requested using HOMO/LUMO language. Many students erred by drawing wrong charges on the resonance structures or failing to notice that the negative carbon is bonded to H as well as to two other carbon atoms. Such problems will fade quickly with experience. Remember that trivalent O is positive, because in forming the third bond (like the 4th of N) the O atom loses half-interest in an unshared pair.]
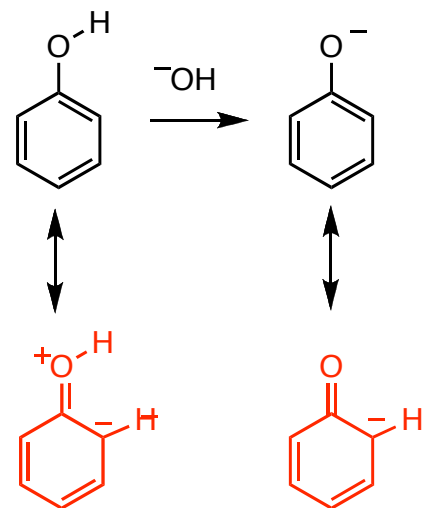
(d) (6 min) The pi orbitals of the enolate anion are made from the parallel atomic *2p* orbitals of the C, C, and O atoms shown below left. Over the letters on the right **sketch the three MOs** a computer would make from these three AOs with appropriate relative sizes and signs for the AOs in each MO. [A few words of explanation might help]

Two nodes. Small on O, most of which was used in the occupied orbitals.

One node near central C.

No nodes.   Large on O, where electrons enjoy proximity to more protons.

(e) (1 min; **note the small credit**, don't waste time on this challenging question unless you have answered the others as well as possible and become bored)

Draw structures with **curved arrows** to complete the Kolbe reaction, and explain **why** it is favorable to proceed from the phenolate to the salicylate.
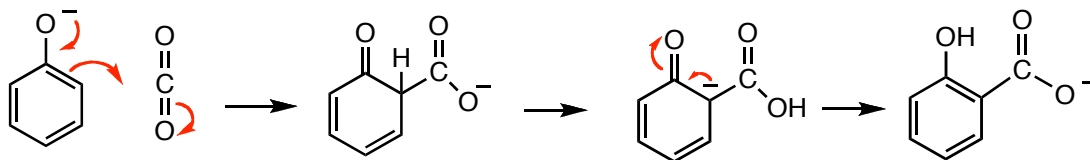
[Note that I did **not** expect answers to this question, and certainly not sophisticated answers. We'll see a lot more of this kind of thing later on. There are two key processes: (1) forming the new C-C bond and (2) moving the H attached to a ring C atom to the O atom, which may seem more challenging. The new C-C bond is formed by using the "enolate anion resonance structure" of part (c), *i.e.* the enolate HOMO of part (d), to attack $\pi^*_{C=O}$ (first three curved arrows). The H motion probably occurs in several steps, removal from the C to generate a second "enolate anion", and addition to its O⁻ resonance structure (pair of curved arrows) to form the new OH group. I formulated the third structure with a protonated carboxylate (the carboxylate of one molecule could take the proton from another) in order to avoid creating an unfavorable dianion *en route* to the most stable carboxylate anion.]

Phenol ("carbolic acid") has a pK_a of 10. The pK_a of salicylic acid is 3. Thus the carboxylate form of the anion should be preferred by a factor of 10^7. The charge on the carboxylate anion is stabilized by two O nuclei, while there is only one O in the phenolate.

[There is also the consideration that a C-H bond and the second bond of a C=O are lost, while an O-H bond and a C-C bond are formed, but this is getting even more involved. We'll talk about such things later.]