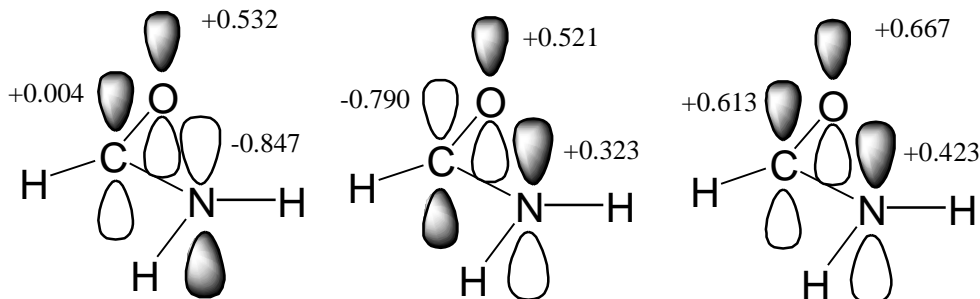


QUIZ #2 (100 points)

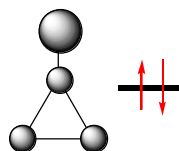
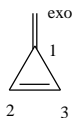
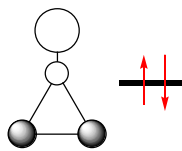
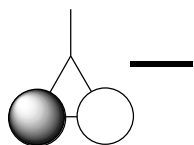
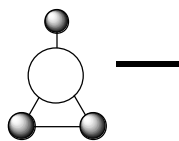
Answer all questions as completely as you can. Clearly show your work and reasoning.

1. The AM1-RHF π -molecular orbitals for formamide are shown below, with no particular ordering. (60 pts)

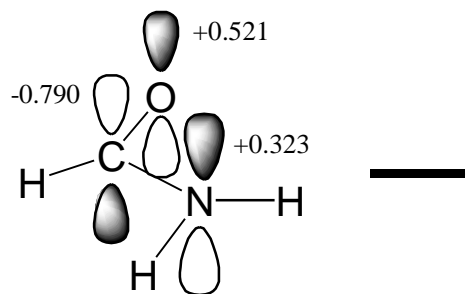


- Draw a qualitative energy diagram that shows the orbitals with the correct energy ordering – be sure to label your energy axis.
- Put the correct number of electrons in each orbital for your diagram. Show alpha and beta spin properly.
- Use your MO diagram to predict which π -bond in formamide is the *strongest*. Justify using the numbers/diagram as you give it.

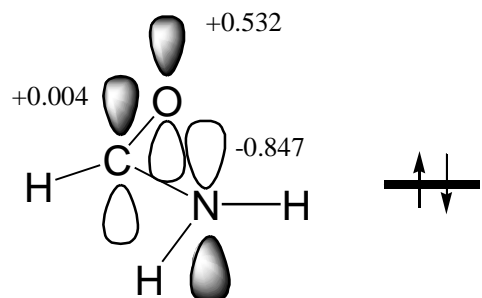
2. The π -molecular orbitals for methylenecyclopropene are shown below in correct energetic order. *Place the correct number of electrons in the diagram for the neutral molecule*, and answer the following question – which molecule has the strongest C2-C3 bond, the neutral species, the radical cation, or the radical anion? *Briefly explain your answer.* (40 pts)



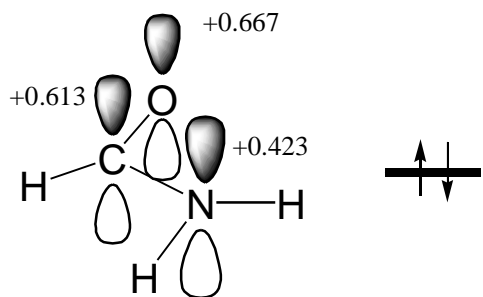
There are four pi-electrons to put in the MOs, from two pi-bonds. If we add one electron to make a radical anion, we put it into a LUMO that has a very large π -antibonding interaction between C2-C3 and so will weaken the bond. If we remove one electron to make a radical cation, we remove it from a HOMO that has a bonding interaction between C2-C3 and so will weaken the bond. Therefore, the neutral species has the strongest C2-C3 bond.



The ordering of the π -MOs is as shown to the left. The lowest energy orbital has all bonding interactions. The HOMO has a near-zero coefficient on its central carbon atom, and is essentially a NBMO (nonbonding π -MO). The LUMO has all antibonding interactions. (Note how these orbitals qualitatively resemble the orbitals for allyl, with some perturbation by the fact that we do not have a symmetrical π -system in this case.) You need to remember the rules of valence to know that N gives two electrons from its p-orbital, while C and O each give one in this case.



Four electrons go into the orbitals as shown (carbon and oxygen each contribute one electron, nitrogen contributes two based on valence rules).



The occupied MOs control bond orders and populations. In this case the C-N bond is worth $[(2 e^-)(+0.423)(+0.613) + (2e^-)(-0.847)(+0.004)] = 0.512$; the C-O bond is worth $[(2 e^-)(+0.667)(+0.613) + (2e^-)(-0.532)(+0.004)] = 0.813$. Therefore, the C=O bond is indeed somewhat stronger than the C-N bond, as expected.

(Notice that this MO picture does not fit the oft-given resonance picture for an amide, in which a formal (+)-charge is placed on the nitrogen for one resonance structure. In reality, as the MO picture shows, carbon is electron deficient while oxygen and nitrogen are electron rich. This makes sense, because nucleophiles should attack the carbon, not the nitrogen or oxygen. It also makes sense to have the electropositive carbon between two electronegative elements, O and N)

