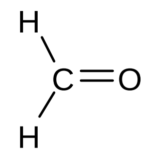
Chemistry 2331H Tuesday, September 20

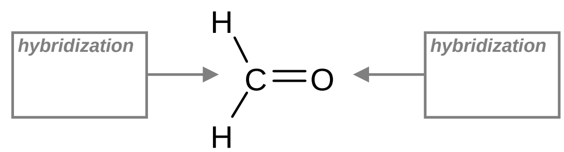
Workshop 7
Molecular Orbitals

In a molecule of formaldehyde, the four atoms contribute a total of 12 valence electrons to bonding and lone pairs in the molecule. (Oxygen has 6 valence electrons, carbon has 4, and each hydrogen has 1).

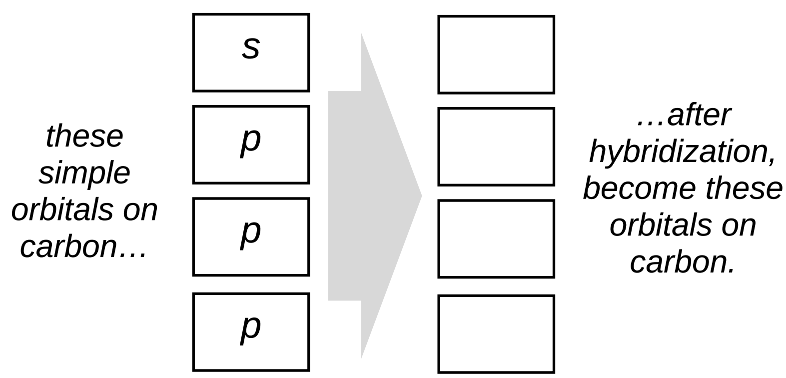


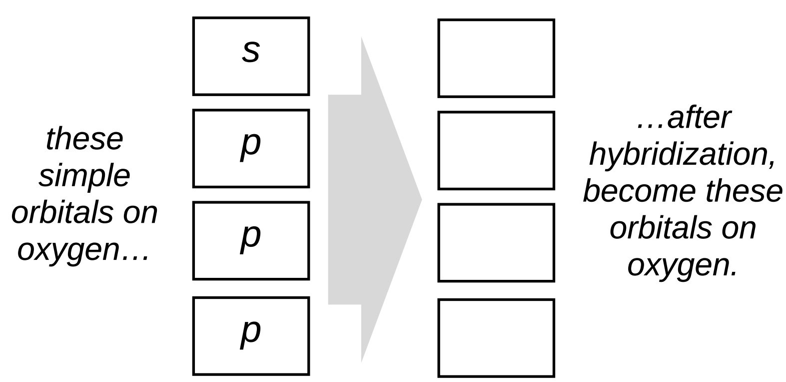
In the absence of bonding, these valence electrons would occupy H(1*s*), C(2*s*), C(2*p*), O(2*s*) and O(2*p*) orbitals. However, bonding causes these simple, valence-level atomic orbitals to hybridize into hybrid atomic orbitals, and then to mix to form molecular orbitals.

a) What is the hybridization on the C and O atoms in formaldehyde?



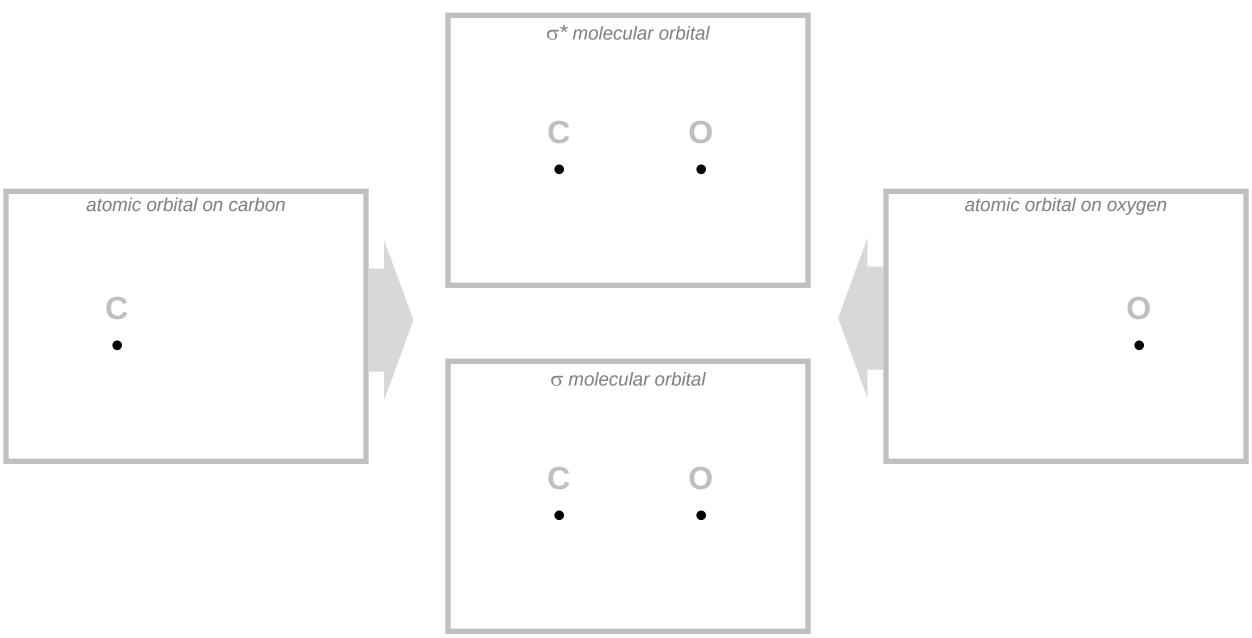
b) C and O each start with four simple, valence-level atomic orbitals: one *s* orbital, and three *p* orbitals. After hybridization, each atom must still have four orbitals. What are these four orbitals? Which are hybrid orbitals, and which are still simple (unhybridized)?





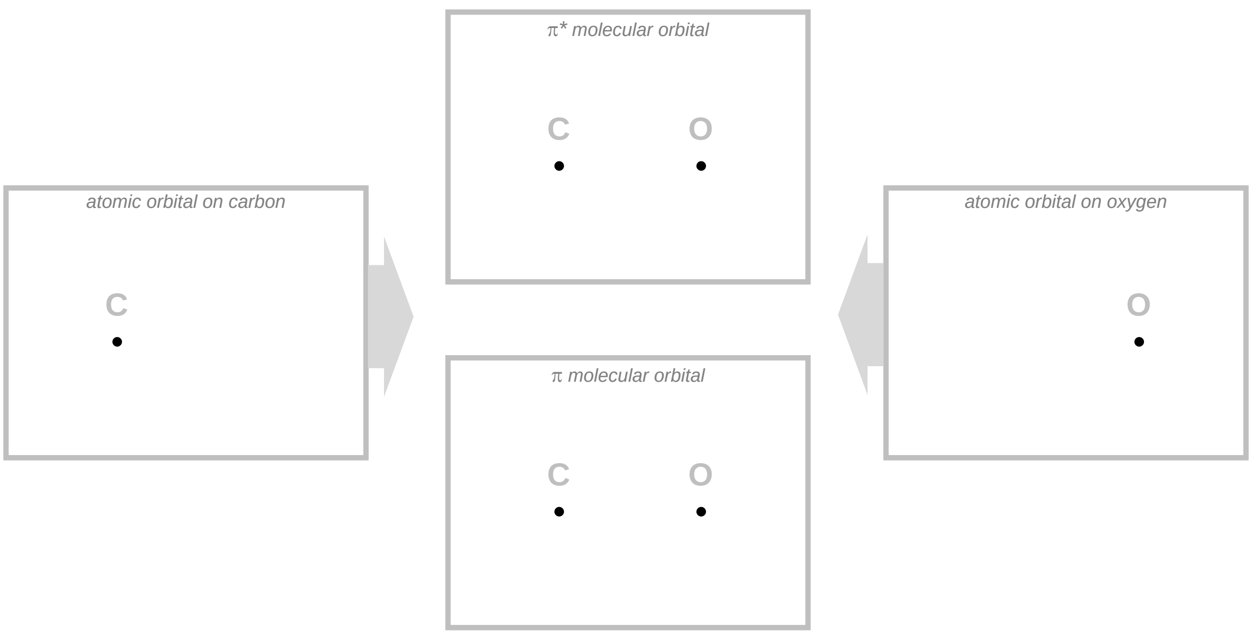
c) The C=O double bond really consists of two bonds: a σ bond, and a π bond. Let's first consider the σ bond. The σ bonding molecular orbital, as well as a σ* antibonding orbital, are formed by the mixing of one atomic orbital from carbon and one atomic orbital from oxygen. Which atomic orbitals? Draw an energy diagram that shows how the two starting orbitals mix to form two product orbitals. How do the energies of the product molecular orbitals relate to the starting orbitals?

d) In this part, you will draw the shapes of the orbitals that you drew energies for in part (c). What do the σ and σ* molecular orbitals look like? How do they relate to the shapes of the starting, atomic orbitals?



e) Now let's apply the same principles to the C-O π bond. Which atomic orbitals—one from carbon, one from oxygen—mix to form the π bonding and π^* antibonding orbitals? Draw an energy diagram that shows how the two starting orbitals mix to form two product orbitals. Again, how do the energies of the product molecular orbitals relate to the starting orbitals?

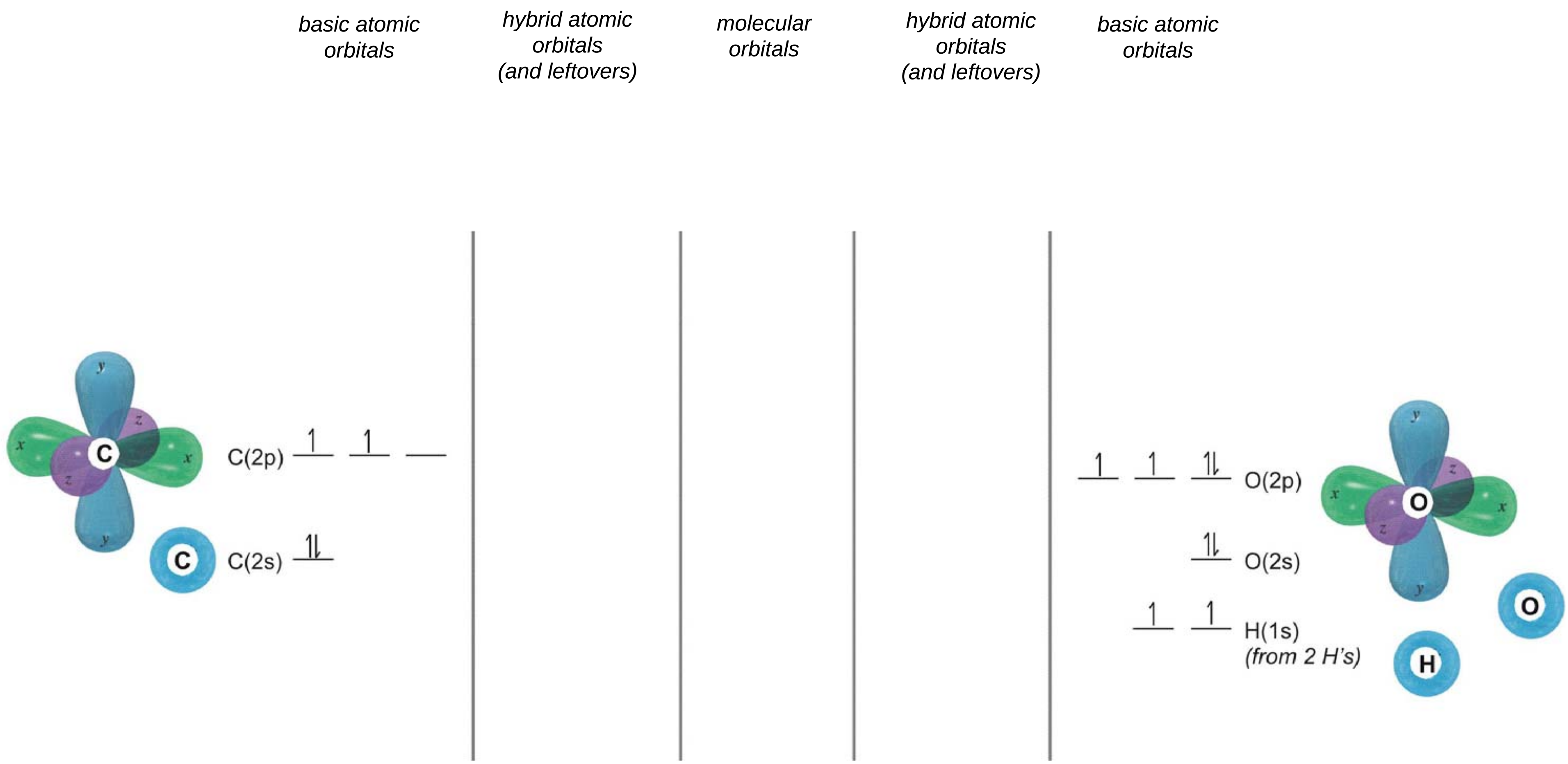
f) In this part, you will draw the shapes of the orbitals that you drew energies for in part (e). What do the π and π^* molecular orbitals look like? How do they relate to the shapes of the starting, atomic orbitals?



g) On the previous two pages, we used up two of the four hybridized atomic orbitals on carbon, and two of the four hybridized atomic orbitals on oxygen. What happens to the other two orbitals on each atom? Do they mix with orbitals on other atoms? Do they remain unmixed, non-bonding orbitals containing non-bonding (lone-pair) electrons?

h) On the next page, there is a valence orbital energy diagram for the entire formaldehyde molecule, including all atoms and all valence orbitals. Replicate any mixing you did in parts (b), (c) and (e) on this diagram. Then, illustrate any mixing (or non-mixing) that we didn't already do.

i) Finally, fill these molecular orbitals with the 12 valence electrons. Does everything in the diagram make sense. Are all the bonding orbitals filled, and the antibonding orbitals empty? Do lone-pair orbitals contain lone-pair electrons?


basic atomic orbitals
hybrid atomic orbitals (and leftovers)
molecular orbitals
hybrid atomic orbitals (and leftovers)
basic atomic orbitals
C(2p)
C(2s)
C
O(2p)
O(2s)
H(1s)
(from 2 H's)
O
H