

### Homework 9/23/2010

Let us consider molecules consisting of three Carbon atoms. With three carbon atoms, we can form a chain, which is schematically given by



The molecule is called allyl and the chemical formula is  $C_3H_5$ . We can also make a “triangle”, schematically given by



The molecule is called cyclopropenyl and its chemical formula is  $C_3H_3$  (the Carbon atoms in cyclopropenyl form  $sp^2$  hybrids. The  $60^\circ$  angles cause a significant bondstrain, which we neglect here.)

1a. The allyl molecule consist of planar  $sp^2$  hybrids. Draw the structure of the allyl molecule (show the positions of the Carbon and Hydrogen atoms with respect to each other).

1b. Using that Carbon is  $2s^2 2p^2$  (we can leave the strongly bound C 1s orbitals out of our consideration), show that both molecules have three electrons in the  $\pi$  states formed by the out-of-plane  $p_z$  orbitals.

1c. Set up the matrix for the Carbon  $p_z$  orbitals for allyl. Include only a nearest neighbor matrix element  $T < 0$ . Calculate the eigenenergies.

1d. In Cyclopropenyl, all the Carbon atoms are equivalent and we can apply periodic boundary conditions. What are the possible  $k$  values? By making a Fourier transform of the kinetic energy term, we find that the energies are given by  $E_k = 2T \cos ka$ . What are the eigenenergies of cyclopropenyl?

1e. We can set up a matrix for cyclopropenyl in the same way as for allyl. Show (by inspection) that the eigenenergies obtained in 1d satisfy the secular equation.

1f. What is the stablest molecule: cyclopropenyl  $C_3H_3$ , its cation  $(C_3H_3)^+$ , or its anion  $(C_3H_3)^-$  (draw a diagram of the energy levels).