

Chem 260 Laboratory 10

This lab continues the exploration of bond formation. The linear combination of atomic orbitals is demonstrated in the carbene (CH_2) molecular fragment, and then two fragments are combined to investigate the molecular orbitals of ethene.

LINEAR COMBINATION OF ATOMIC ORBITALS

1. Start HyperChem and draw the diatomic molecule CH. Optimize the structure. Open a log file (EHT print level 1) and do a single point calculation with multiplicity set to 2.
2. Close the log file and read it with Notepad or Word. Switch back and forth with the HyperChem Orbitals display, or display both windows on the screen at the same time. [The orbitals are best displayed if you shift the molecule to the edge of the HyperChem screen before selecting orbitals. That way you can select different energy levels and Plot orbitals without having to close the Orbitals window.]
3. There are 5 molecular orbitals, made up from the H $1s$ atomic orbital and the C $2s$ and $2p$ orbitals. [Recall that the Extended Hückel method ignores the “core” electrons in the C $1s$ orbital.] Notice how molecular orbital **1** is essentially made from H $1s$ and C $2s$. M.O. **2** is a combination of H $1s$ and the C $2s2p_x$ hybrid orbital. See how there is a node through the C (because of the symmetry of p_x) but clearly bonding between the atoms. M.O. **5** is the antibonding orbital formed from H $1s$ and the C sp_x hybrid. M.O.'s **3** and **4** are combinations of the C p_y and p_z orbitals, both of which are perpendicular to the C-H axis – rotate CH out of plane to see the p orbitals when looking along the C-H axis.
4. Now perform a similar analysis of the molecular orbitals of CH_2 . Start by drawing the ethene molecule. Use Model Build. The resulting structure should have the C=C bond vertical on the page. Save this file for later use. Delete the lower CH_2 so that the remaining structure has a V shape. [This is just so that everyone uses the same axis definitions.] Open a log file, perform the EHT calculation and view the orbitals. Cut and paste the orbital plots into a lab report. [Remember to setup image as a metafile, not bitmap, and paste special as a picture.]

ASK FOR A PRINTOUT OF THE MOLECULAR ORBITALS AT THIS STAGE

5. Label each orbital with one of the following combinations (the order has been scrambled so that it is not a complete give-away):

$x\text{-H-H}, s\text{+H+H}, x\text{+H+H}, s\text{+y-H-H}, s\text{+y+H+H}, z$

[This labeling is meant as an *indication* of the component atomic orbitals only. The letters x, y, z and s are shorthand for the carbon $2s$ and $2p$ orbitals.]

BONDING ORBITALS IN ETHENE

6. Return to the ethene structure you saved earlier. Do the usual EHT calculation, including a log file. There are 12 molecular orbitals, twice as many as in CH_2 . By comparing the orbital shapes and the LCAO coefficients try to match each CH_2 orbital with a pair of ethene orbitals.

7. Classify the ethene orbitals as C-C σ , C-C σ^* , C-C π , C-C π^* , C-H and C-H*. List them in a table with highest energy at the top. The table should have columns showing orbital number, energy and your classification.
8. Now explore what happens when you distort ethene by twisting about the C-C bond. To do this, select H-C-C-H and Edit/Set Bond Torsion. Try dihedral angles of 135° and 90° . Look at the log files to see how the orbital mixing varies with angle. Some orbitals (those which are primarily concerned with C-H bonds) do not change. What about the C-C σ and C-C π orbitals? Notice how “pseudo” π orbitals are formed when the H-C-H fragment is aligned with a p orbital on the other carbon.