

## 5 Electron Densities, Electrostatic Potentials, and Reactivity Indices

### Exercise 1 Visualizing Different Bond Types.

Build a molecule of dihydrogen using “s-line” hybridized H atoms. Clean up the structure by selecting Beautify / Comprehensive.

Save as dihydrogen.csf in the CACheUser\cachetmp directory. Calculate the electron density by selecting Experiment / New and selecting chemical sample electron density using PM3 geometry with PM3 wavefunction.

Calculate the electrostatic isopotential by selecting Experiment / New and selecting electrostatic isopotential using PM3 geometry with PM3 wavefunction.

View the electrostatic isopotential mapped onto the electron density by selecting Analyze / Show Surfaces and click on dihydrogen.csf.EonD, then click “OK”.

Investigate the different viewing parameters by selecting Analyze / Surface Attributes and click on “Wireframe” or “Dotted”, etc., to see the various display modes.

View the electrostatic isopotential alone by selecting Analyze / Show Surfaces and click on dihydrogen.csf.Elec. To avoid the display of multiple surfaces, make sure the dihydrogen.csf.EonD file does not have a check next to it.

Build a molecule of hydrogen fluoride using “s-line” hybridized H and  $sp^3$  hybridized F. Clean up the structure by selecting Beautify / Comprehensive.

Save as hydrogenfluoride.csf in the CACheUser\cachetmp directory. Calculate the electron density by selecting Experiment / New and selecting chemical sample electron density using PM3 geometry with PM3 wavefunction.

Calculate the electrostatic isopotential by selecting Experiment / New and selecting electrostatic isopotential using PM3 geometry with PM3 wavefunction.

View the electrostatic isopotential mapped onto the electron density by selecting Analyze / Show Surfaces and click on hydrogenfluoride.csf.EonD, then click “OK”. To understand what the colors mean, click once on the displayed surface so that it is “solid”. Select Analyze / Surface Legend. Study the legend. Do the colors make sense? \_\_\_\_\_

View the electrostatic isopotential alone by selecting Analyze / Show Surfaces and click on hydrogenfluoride.csf.Elec. To avoid the display of multiple surfaces, make sure the hydrogenfluoride.csf.EonD file does not have a check next to it.

(NOTE: Red = (+) and Blue = (-).

Build a molecule of lithium hydride using “s-line” hybridized Li and “s-line” hybridized H. Clean up the structure by selecting Beautify / Comprehensive.

Save as lithiumhydride.csf in the CACheUser\cachetmp directory. Calculate the electron density by selecting Experiment / New and selecting chemical sample electron density using PM3 geometry with PM3 wavefunction.

Calculate the electrostatic isopotential by selecting Experiment / New and selecting electrostatic isopotential using PM3 geometry with PM3 wavefunction.  
View the various surfaces using the steps above. Does the potential map make sense?

\_\_\_\_\_

Do the colors of the electrostatic isopotential on the electron density make sense?

\_\_\_\_\_

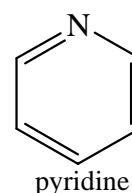
Compare/contrast the various surfaces for H<sub>2</sub>, HF and LiH. Are they what you expected?

### **Exercise 2 Charge Distribution in Aromatic Compounds.**

Build a molecule of benzene using sp<sup>2</sup> hybridized C. Be sure to alternate the double bonds. Clean up the structure by selecting Beautify / Comprehensive.  
Save as benzene.csf in the CACheUser\cachetmp directory. Calculate the electron density by selecting Experiment / New and selecting chemical sample electron density using PM3 geometry with PM3 wavefunction.  
Calculate the electrostatic isopotential by selecting Experiment / New and selecting electrostatic isopotential using PM3 geometry with PM3 wavefunction.  
View these surfaces as described on the previous page.

Based on the electrostatic isopotential, draw a sketch of how you believe benzene molecules would stack together in the solid state.

Build a molecule of pyridine using sp<sup>2</sup> hybridized C and N. Clean up the structure by selecting Beautify / Comprehensive.  
Save as pyridine.csf in the CACheUser\cachetmp directory. Calculate the electron density by selecting Experiment / New and selecting chemical sample electron density using PM3 geometry with PM3 wavefunction.



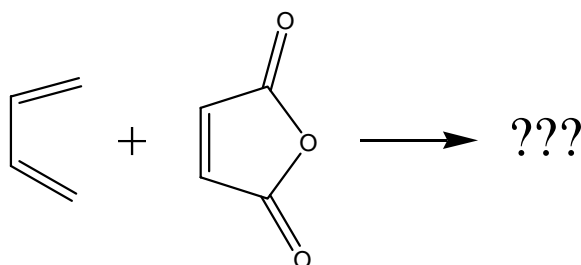
Calculate the electrostatic isopotential by selecting Experiment / New and selecting electrostatic isopotential using PM3 geometry with PM3 wavefunction.  
View these surfaces as described above.

Describe the differences between the benzene and pyridine charge distribution. What causes this difference?

### Exercise 3 The Diels-Alder Reaction

$\alpha,\beta$ -unsaturated carbonyl compounds undergo an exceedingly useful reaction with conjugated dienes known as the Diels-Alder reaction. In this *cycloaddition* reaction, C-1 and C-4 of the conjugated diene become attached to the doubly-bonded carbons of the unsaturated carbonyl compound to form a six-membered ring. The reaction involves systems with  $4\pi$  electrons (diene) and  $2\pi$  electrons (dienophile), and is therefore a  $[4+2]$  cycloaddition.

The frontier molecular orbital approach is a good way to understand this reaction. We will look at a simple Diels-Alder reaction involving butadiene and maleic anhydride:



Draw *cisoid*-butadiene (as pictured on the previous page), and do a Beautify / Comprehensive. Your butadiene has turned into the *transoid* form, as this form is more stable.

To lock the geometry into the *cisoid* form, use the select tool and click on a terminal carbon. Hold down the shift key and click on the remaining carbon atoms, in order (1-4).

Choose Adjust / Dihedral angle and use the small down arrow key to adjust the angle to  $0^\circ$ .

Click on the Define Geometry box, and also click on the Lock Geometry box. Click OK. You should now have the correct form of butadiene. Save the file as butadieneDFT.csf.

Calculate the HOMO and LUMO by choosing Experiment / New; Property of Chemical Sample; Property HOMO & LUMO; Using DFT geometry with B88-LYP wave function.

View the HOMO and LUMO by choosing Analyze / Show Surfaces. Note the HOMO is green/blue, while the LUMO is red/yellow. Does the shape of these two orbitals make sense? \_\_\_\_ What type of orbital is the HOMO, the LUMO? \_\_\_\_ On which atoms are the largest lobes of the HOMO located? \_\_\_\_ Record the energies of both the HOMO and LUMO. **Leave the HOMO displayed on the screen.**

Choose File / New and build a molecule of maleic anhydride using appropriate hybridizations.

Do a Beautify / Comprehensive and save the file a malanhydDFT.csf.

Calculate the HOMO and LUMO as above. What sort of orbital does the HOMO appear to be? \_\_\_\_\_ On what atoms do the largest lobes of the LUMO lie? \_\_\_\_\_ Record the energies of both the HOMO and LUMO. \_\_\_\_\_ **Leave the LUMO displayed on the screen.**

In the space below, sketch the relative energies of the HOMO and LUMO of butadiene on the left and the HOMO and LUMO of maleic anhydride on the right. (Recall that more negative energies are more stable and are lower on the plot.

The HOMO on one molecule nearest in energy to the LUMO of the other molecule are the ones that will be involved in the reaction. What two orbitals will interact on these molecules? \_\_\_\_\_

You should now have two windows open, one which displays the HOMO of butadiene, and the other of which shows the LUMO of maleic anhydride. If other windows are also open, go ahead and close them now.

Choose Window / Tile. Separately click on the select tool in each window, click somewhere in that window away from the molecule, then type "Control F". This centers and fits the molecule into the new window.

Assuming that the blue lobe of the HOMO and the red lobe of the LUMO are both (+) in sign, make a sketch in the space below of how these two molecules will approach one another to react. Recall that the largest lobe of the HOMO will overlap with the largest lobe of the LUMO. Also draw the structure of the resulting product.