5 Electron Densities, Electrostatic Potentials, and Reactivity Indices

Exercise 1 Visualizing Different Bond Types.

Build a molecule of dihydrogen using the Hydrogen Terminal fragment. Clean the
structure.
Run a PM3 optimization. Save the files as dihydrogen.chk and dihydrogen.cjf.
Click Results / Surfaces. Click Cube Actions / New Cube, choose Total Density, and click
OK. Click Cube Actions / New Cube, choose ESP.
With Electron Density is the Cube Available choice, choose Surface Actions / New
Mapped Surface and click OK to display Electron Density mapped on
Electrostatic Potential.
The molecule and surface may be resized by right clicking and dragging and rotated by
left clicking and dragging. To see the molecule within the surface, click View /
Display Format and choose Surface / Transparent.
Record your observations.
Close everything except the main Control Panel.

Build a molecule of hydrogen fluoride using the Fluorine Terminal fragment and run a
PM3 optimization. Save the files as hydrogenfluoride.chk and
hydrogenfluoride.cjf.
Click Results / Surfaces and repeat the above steps to observe the molecule and surface.
Record your observations.
Close everything except the main Control Panel.

Build a molecule of lithium fluoride using the Fluorine Terminal fragment and the
Lithium atom fragment replacing the H atom. Run a PM3 optimization. Save
the files as lithiumfluoride.chk and lithiumfluoride.cjf.
Click Results / Surfaces and repeat the above steps to observe the molecule and surface.
Record your observations.
Close everything except the main Control Panel.

Build a molecule of lithium hydride using the Lithium Terminal fragment and run a
PM3 optimization. Save the files as hydrogenfluoride.chk and
hydrogenfluoride.cjf.
Click Results / Surfaces. Observe only the Total Density surface and molelcule.
Record your observations.
Close everything except the main Control Panel.

Compare/contrast the various surfaces for H_2, HF, LiF, and LiH. Are they what you
expected?

Exercise 2 Charge Distribution in Aromatic Compounds.

Build a molecule of benzene by clicking the Ring Fragment icon and choosing the
    benzene fragment. Click in the View workspace.
Minimize at the PM3 level. Save the files as benzene.chk and benzene.cjf.
Click Results / Surfaces. Click Cube Actions / New Cube / Total Density / OK and Cube
    Actions / New Cube / ESP / OK. Be sure Electron Density appears in the Cubes
    Available window.
Click Surface Actions / New Mapped Surface to display the Electron Density on ESP
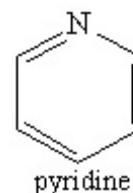   surface.
Record your observations.
Close everything except the main Control Panel.

Either open the file PYRIDINEPM3.chk or construct the pyridine molecule
    using the pyridine Ring Fragment.
Run a PM3 minimization if needed.
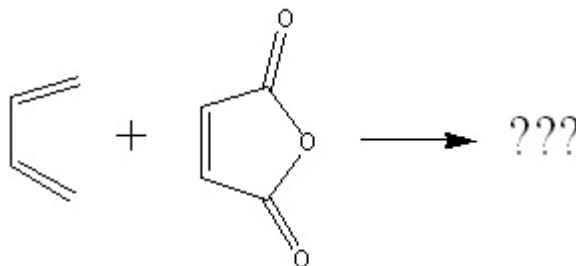Display the Electron Density on ESP surface as above and record your
    observations.

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

Exercise 3 The Diels-Alder Reaction

α,β-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 4π electrons (diene) and 2π 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. Use the Carbon Trivalent fragment four times in the View
workspace. After clicking the Clean icon, the structure probably will be the
transoid form.

Click the Modify Dihedral icon and click the four C atoms to open the Semichem
SmartSlide dialog box. Use the slider to adjust the dihedral angle to ~0 °. Click
the Clean icon.

Run a PM3 optimization. Save the files as cisC4H6.chk and cisC4H6.cjf.

Click the Molecular Orbital Editor icon (2nd row, 6th across) to open the MOs window.
Click the Visualize tab, choose HOMO,LUMO for the Add Type, and click
Update. These orbitals may be observed by clicking each gray square in the
orbital listing window at the right.

View the HOMO and LUMO surfaces. Does the shape of each orbital 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: _____, _____
Eh. Leave the HOMO displayed on the screen.

Click the New icon (1st row, 12th across).

Build a molecule of maleic anhydride. Start with the tetrahydrofuran fragment (4th row,
1st across). Use the Delete Atom icon (1st row, 11th across) to delete one H atom
from each of the four C atoms. Next click the Oxygen Trivalent fragment on
each of the remaining H atoms attached to the C atoms. Add the C=C double
bond by clicking the Modify Bond icon (1st row, 6th across) and clicking the two C
atoms to open the Semichem SmartSlide dialog box. Click the radio button next
to the double bond and click OK. Form each of the C=O double bonds in the
same way.

Run a PM3 optimization. Save the files as maleic.chk and maleic.cjf.

View the HOMO and LUMO surfaces as above. 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:
_____, _____ Eh. 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. 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.