5 Electron Densities, Electrostatic Potentials, and Reactivity Indices (Spartan)

Exercise 1 Visualizing Different Bond Types

Build the H_2 molecule.
Choose Setup / Calculations. Equilibrium Geometry at Ground State with Semi-Empirical PM3.
Click Submit.
Save as dihydrogen.spartan in an appropriate folder.
Click "OK" to started message and "OK" to completed message.
Choose Setup / Surfaces and Click Add.
In the Add Surface Dialog box, choose Surface Density (bond), Property None, Resolution Intermediate, then Click "OK".
Click Add, choose Surface Density (bond), Property Potential, Resolution Intermediate, then click "OK".
Close the Surfaces window.
Click Setup / Submit.
Click "OK" to started message and "OK" to completed message.
Choose Display / Surfaces. Check the yellow box next to Density to observe the electron density surface. If needed, the Surfaces window may be moved to a convenient location.
View the electrostatic potential by checking the yellow box next to Density Potential. Uncheck the other box. Red indicates (-) and blue indicates (+) charge. Rotate the molecule.
Save and Close the file.

Click New File
Build the H-F molecule.
Choose Setup / Calculations. Equilibrium Geometry at Ground State with Semi-Empirical PM3.
Click Submit.
Save as hydfluor.spartan in an appropriate folder.
Click "OK" to started message and "OK" to completed message.
Choose Setup / Surfaces and Click Add.
In the Add Surface Dialog box, choose Surface Density (bond), Property None, Resolution Intermediate, then Click "OK".
Click Add, choose Surface Density (bond), Property Potential, Resolution Intermediate, then click "OK".
Close the Surfaces window.
Click Setup / Submit.
Click "OK" to started message and "OK" to completed message.
Choose Display / Surfaces. Check the yellow box next to Density to observe the electron density surface. If needed, the Surfaces window may be moved to a convenient location.
View the electrostatic potential by checking the yellow box next to Density Potential. Uncheck the other box. Red indicates (-) and blue indicates (+) charge. Rotate the molecule.
Save and Close the file.

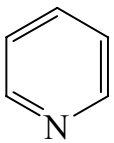
Click New File
Using the 'Expert" level, build Li-H using "s" atomic hybrids (1st row, 1st column underneath Periodic Table) with a single bond.
Choose Setup / Calculations. Equilibrium Geometry at Ground State with Semi-Empirical PM3.
Click Submit.
Save as lithhyd.spartan in an appropriate folder.
Click "OK" to started message and "OK" to completed message.
Choose Setup / Surfaces and Click Add.
In the Add Surface Dialog box, choose Surface Density (bond), Property None, Resolution Intermediate, then Click "OK".
Click Add, choose Surface Density (bond), Property Potential, Resolution Intermediate, then click "OK".
Close the Surfaces window.
Click Setup / Submit.
Click "OK" to started message and "OK" to completed message.
Choose Display / Surfaces. Check the yellow box next to Density to observe the electron density surface. The Surfaces window may be moved to a convenient location.
View the electrostatic potential by checking the yellow box next to Density Potential. Uncheck the other box. Red indicates (-) and blue indicates (+) charge. Rotate the molecule.
Save and Close the file.

View the various surfaces using the steps above. Does the shape of the electron density surface make sense in each case? _____
Do the colors of the electrostatic potential mapped onto the electron density make sense in each case? _____
Are these surfaces what you expected to see for H_2, HF and LiH?

Exercise 2 Charge Distribution in Aromatic Compounds

Click New File
Using the "Expert" level, build a molecule of benzene using sp^2-hybridized C.
To close the ring, go to Build / Make Bond and click on the empty valences of the adjacent C's.
Choose Setup / Calculations. Equilibrium Geometry at Ground State with Semi-Empirical PM3.
Click Submit.
Save as benzenepm3.spartan in an appropriate folder.
Click "OK" to started message and "OK" to completed message.
Calculate and View the Electron Density and Electrostatic Potential as described above for LiH.
Based on the electrostatic potential, draw a sketch of how you believe benzene molecules would stack together in the solid state.
Save and Close the file.

Click new File
Using the "Expert" level, build a molecule of pyridine using sp^2-hybridized C & N.
To close the ring, go to Build / Make Bond and click on the empty valences of adjacent atoms.

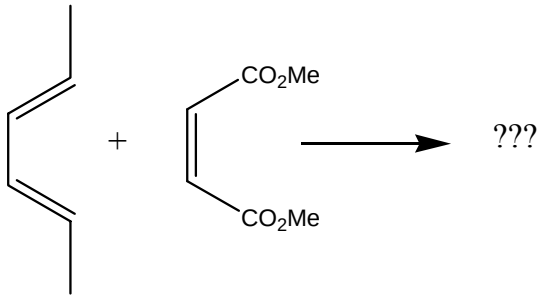


Choose Setup / Calculations. Equilibrium Geometry at Ground State with Semi-Empirical PM3.
Click Submit.
Save as pyridinepm3.spartan in an appropriate folder.
Click "OK" to started message and "OK" to completed message.
Calculate and View the Electron Density and Electrostatic Potential as described above for LiH.
Describe the differences between the benzene and pyridine charge distribution. What causes this difference?
Save and Close the file.

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 the *cycloaddition* reaction below, C-2 and C-5 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.

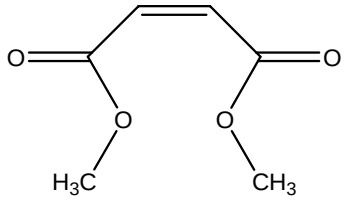
The frontier molecular orbital approach is a good way to understand this reaction. We will look at a simple Diels-Alder reaction involving 2,4-hexadiene and dimethyl maleate:



Using the "Entry" level builder, draw a molecule of 2,4-hexadiene. You will probably end up with the *transoid* form.
To turn this into the required *cisoid* form (shown above), click on the single C-C bond between carbons 3 & 4. A red "rotation" arrow should appear. Hold down the "Alt" key on the keyboard while you click and vertically drag the mouse somewhere away from the molecule until you have the cisoid form.
To make sure you have a planar molecule, click on the "Measure Dihedral" icon (13th across the top), then click on each of the four carbon atoms, in order (C2 – C5). The angle is displayed in the lower right corner. If the angle is not 0.00º, hold down the "Alt" key and click and vertically drag the mouse until the angle is 0.00º.
Click on the "Dihedral Constraint" icon (18th across the top) to lock this angle.
Click on the "Minimization" icon (10th across top). This does a simple MM minimization.
Choose Setup / Calculations. Choose Equilibrium Geometry at Ground State with Semi-Empirical PM3, Print Orbitals and Energies.
Click Submit. Save as hexadienepm3.spartan in an appropriate folder.
Click "OK" to started message and "OK" to completed message.
Choose Setup / Surfaces and Click Add.

In the Add Surface Dialog box, choose Surface HOMO, Resolution Medium, then Click "OK".
Click Add again, choose Surface LUMO, Resolution Medium, then click "OK".
Click Setup / Submit.
Click "OK" to started message and "OK" to completed message.
View the HOMO and LUMO by checking/unchecking the yellow box in the "Surfaces" window.
On which carbon atoms are the largest lobes of the HOMO located? _____
Choose Display / Properties.
Record the energy of the HOMO _____ eV and the LUMO _____ eV.
Save and Close the file.

Build a molecule of dimethyl maleate using appropriate hybridizations.
As above, rotate around the appropriate single bonds to achieve the structure shown below:



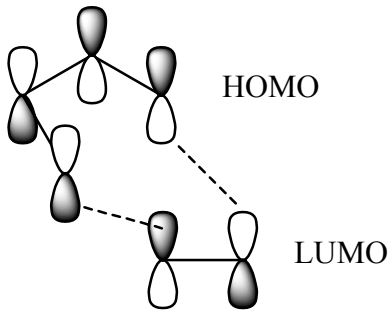
Click on the "Minimization" icon (10th across top). This does a simple MM minimization.
Choose Setup / Calculations. Choose Equilibrium Geometry at Ground State with Semi-Empirical PM3, Print Orbitals and Energies.
Click Submit. Save as dimethmalpm3.spartan in an appropriate folder.
Click "OK" to started message and "OK" to completed message.
Choose Setup / Surfaces and Click Add.
In the Add Surface Dialog box, choose Surface HOMO, Resolution Medium, then Click "OK".
Click Add again, choose Surface LUMO, Resolution Medium, then click "OK".
Click Setup / Submit.
Click "OK" to started message and "OK" to completed message.
View the HOMO and LUMO by checking/unchecking the yellow box in the "Surfaces" window.
On which carbon atoms are the largest lobes of the LUMO located? _____
Choose Display / Properties.
Record the energy of the HOMO _____ eV and the LUMO _____ eV.
Save and Close the file.

In the space below, plot the relative energies of the frontier orbitals of butadiene on the left, and malice anhydride on the right. (Recall that more negative energies Are more stable and are lower on the plot).

Orbital
Energy in eV

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

Choose File / Open.
Open the hexaadienepm3.spartan file. Choose Display / Surfaces / HOMO.
Open the dimethmalpm3.spartan file. Choose Display / Surfaces / LUMO.
Rotate each molecule into the simplified orientation shown below:



Each molecule can be independently rotated by clicking on it, then using left click/drag. Recall that frontier MO theory states that the largest lobes of the HOMO on one molecule will interact with the largest lobes of the LUMO on the other reactant.

In the space below, make a sketch of how the two molecules will approach one another to react. Also, draw the structure of the expected product.