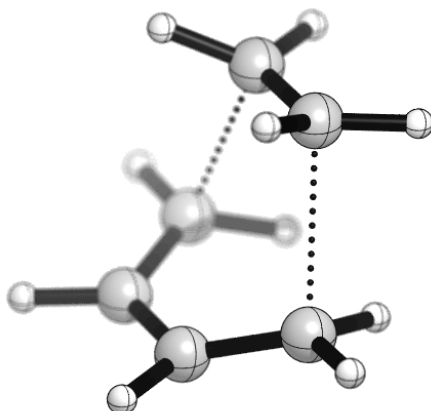# Molecular Properties

Objectives: rendering nice pictures, molecular orbitals, electrostatic potentials, point charges

In This Exercise: we will learn how to render nice pictures of molecular structures. We will also learn how to make pictures of molecular orbitals (MOs) and electrostatic potentials (ESPs). We can also use the MOs and ESPs to determine atomic charges.

Setup: Install CYLview (http://www.cylview.org/Download.html), a program for rendering molecular structures in three dimensions. There are different versions for Mac and PC. If you are using a Mac, you will need to have X11 (XQuartz) installed. You can download a DMG installer at https://www.xquartz.org/. It is quite possible you already have this program installed, so I would suggest trying to run CYLview on its own first.

Files: The calculations in this exercise are relatively easy, but you will need the checkpoint files that are generated when the jobs are run. These files are provided in the repository in the `population/chk/` folder.

Run Calculations:

Locate the Diels–Alder transition states for:

- butadiene + ethylene
- butadiene + acrolein (endo)
- butadiene + acrolein (endo) + BF_3 (bound trans)

Use B3LYP-D3BJ/6-31G* in the gas phase and save checkpoints:

```
%chk=g09.chk
%nprocshared=4
%mem=3GB
#p b3lyp/6-31g* empiricaldispersion=gd3bj opt freq=noraman pop=(chelpg,npa)
```

Also, locate the isolated ground states:
```
acrolein_BF3_isolated.gjf     acrolein_isolated.gjf    butadiene_acrolein_ts.gjf
butadiene_ethylene_ts.gjf     butadiene_isolated.gjf   ethylene_isolated.gjf
```

You can use the same trick as in Exercise 5: freeze the structures and look for the imaginary frequency instead of doing a bond scan.

CYLview: We will now render a three-dimensional picture of one of the transition states.

1. Open CYLview. Click on the DIR button and switch to the directory containing `butadiene_ethylene_ts.out`. (If you are using a mouse, it is possible the scroll wheel will not work properly.) Click DIR again and select the filename.

2. Click on the INTER button to add atom dotted bonds between the appropriate atoms.

3. Click on the Style button and select Houkmol. (You can also choose your own style.)

4. In the bottom right of the window, click on Set Focal Point and then click on an atom. The "camera" will place this atom in focus. The focal scale can be displayed by selecting "Show Focus scale on screen." You can adjust the focal depth in picture by selecting between Weak and Strong. "Focus follow selected atom" will maintain your choice if you rotate the molecule.

5. Similarly, you can gray out atoms that are in the back by selecting "Set Fog Depth."

6. Click on Preview (also in the bottom right) to render the image on screen.

7. To generate a PNG file in the current directory (which will automatically have the same name), click on Generate. Click on the Config button in the upper right to choose the size of this image. By default, the "generated" image will be twice the size of the image on screen.

8. Click on the Atoms button and click on Hide C–H. This option is useful for structures that have a lot of hydrogens. Render this image as well. If you need to display a particular C–H, then you will need to determine the atom number of the hydrogen, select it from the list, and click on Reset. Reset All will display every atom again.

Make a Movie: Three-dimensional structures with a lot of atoms in them can be hard to understand, particularly in presentations. One strategy that can be helpful is making a movie.

1. Click on Poses in the upper right. Orient the molecule as you would like for the start of the movie. Click on "Add." This creates a pose called "default."

2. Click on 640x480. This will be the resolution of your movie. I don't recommend making it any bigger because this task is very computationally intensive.

3. Click on Anim in the upper right. Click on Start pose and select "default."

4. Under Rotation Animation Options, click + until the Angle span is 360. Select a duration of 5 s and press Add. This will give you a linear rotation of 360 degrees that takes 5 seconds.

5. Click on Play Animation to get a preview. You may want to adjust the fog/focusing for the movie.

6. Click on Render animation to make an MPG file. This process could take a while, particularly if your computer is slow. Unfortunately, it can also make CYLview crash.

Plotting Molecular Orbitals: In this section, we will learn how to make pictures of the HOMO and LUMO.
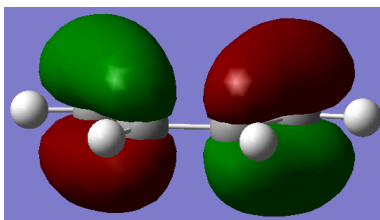
1. We will need a "formatted checkpoint file," which is the human-readable version of the `.chk` file. On Odyssey, locate the checkpoint for isolated butadiene:

```
[ekwan@rclogin04 chk]$ formchk butadiene_isolated.chk
 Read checkpoint file butadiene_isolated.chk
 Write formatted file butadiene_isolated.fchk
 FChkPn:  Coordinates translated and rotated.
 FChkPn:  Coordinates match /B/ after translation and rotation.
```

This generates an `fchk` file:

```
[ekwan@rclogin04 chk]$ head butadiene_isolated.fchk
Title Card Required
Freq       RB3LYP                                                 6-31G(d)
Number of atoms                            I               10
Info1-9                                     I    N=          9
        21          19        1002           0           0         100
         6          18        -502
Charge                                      I               0
Multiplicity                                I               1
Number of electrons                         I              30
Number of alpha electrons                   I              15
```

A lot of other information follows. If you look further down in the file, you will see the MO coefficients are printed along with the basis set functions.

2. To generate the MO surface, you will need to generate a "cube" file:

[ekwan@rclogin04 chk]$ cubegen 0 mo=homo butadiene_isolated.fchk butadiene_HOMO.cube 40 h

```
 There are a total of        63855 grid points.
 ElSum from          orbitals=         0.4994721984
```

(To display the LUMO, use `mo=lumo`. Other orbitals can be drawn by specifying their number.)

Transfer the new cube file to your computer and open it in GaussView. You will need to select "cube" as the file type in the open dialog.

3. Go to Results…Surfaces and click on Surface Actions. Click on New Surface.

4. The displayed surface is the HOMO at a given wavefunction density. If you change the MO = … field you can pull the surface in or out depending on your needs.

5. You can screenshot the result or use File…Save Image File to export the result for a publication. If you dislike the blue color in the background, you can change in GaussView…Preferences.

Plotting Electrostatic Potentials: The electrostatic potential at a given point is the force exerted on a test charge (a proton) by the electrons and nuclei in the molecule. The ESP is typically visualized by mappings its values on a surface of constant electron density.

1. Generate two new cubes (one for the electron density and one for the ESP):

```
[ekwan@rclogin04 chk]$ cubegen 0 density=scf butadiene_isolated.fchk
butadiene_isolated_density.cube 40 h

 There are a total of        63855 grid points.
 ElSum from          density=      22.0540710769

[ekwan@rclogin04 chk]$ cubegen 0 potential=scf butadiene_isolated.fchk
butadiene_isolated_potential.cube 40 h

 There are a total of        63855 grid points.
 ElSum from          density=      31.2907539106
```

2. Transfer these files to your computer and open the density cube file in GaussView. In Results…Surfaces, open the density cube file.

3. Click on the density cube file and select a density value of 0.01. Click on Surface Actions and select New Surface. This generates a surface of the electron density.

4. Go to Cube Actions in the Results…Surfaces dialog and press Load Cube. Load the ESP cube file.

5. Click on Surface Actions…New Mapped Surface and use the electrostatic potential (the only option). The displayed surface now shows the electrostatic potential mapped onto the density isosurface.

6. In the top part of the window, you can change what charges the different colors represent. For example, try -4E-2 for red and +4E-2 for blue.

7. You can make the surface transparent by clicking on View…Display Format…Surface…Format: Transparent. Drag the slider to select different transparency levels. You can also play with the "Z-clip" slider to "cut away" part of the view.

Population Analysis: The ESP describes the charge distribution of a molecule anywhere in space, but what about at particular atoms? In this section, we will examine an orbital-based method of assigning point charges (natural population analysis, NPA) and an ESP-based method (CHELPG). In general, orbital-based methods are useful for examining trends in charge distribution among related structures. However, the charges generally have basis-set convergence issues and do not reproduce the overall multipole moments well. In fact, orbital-based methods are poorly behaved with large basis sets, and in particular with diffuse functions, because the orbitals have significant population on atoms they are not centered on. ESP-based methods do not suffer from these problems, but do not reflect the charges of buried atoms very well. This is because the ESP charges are fit to the portion of the ESP that is near the van der Waals surface of the molecule. For thorough discussions of these issues, please see the chapters in the excellent books by Cramer or Jensen.

1. Let's examine the point charges on the carbons and oxygen of acrolein in the butadiene + acrolein transition state. Open `butadiene_acrolein_ts.out` in vi.

2. Population analysis will be performed for the last geometry (this was requested by the `pop=(chelpg,npa)` keywords). Go to the end of the file (`:$`) and scroll up to the phrase "`Population analysis using the SCF density.`"

3. The first section is a listing of all the occupied and unoccupied (virtual) orbitals. If you wanted to determine the number of an MO other than the HOMO or LUMO for the preceding section, you would count the orbitals in this section. The eigenvalues are the orbital energies in atomic units.

4. Scrolling down further will reveal the Mulliken charges. These are orbital-based charges and are very unstable with respect to basis set. They can even be less than zero or greater than 2! I generally don't recommend using them for analysis.

5. The next section is called `Electrostatic Properties Using The SCF Density`. The CHELPG charges are found in this section. (You can also view the charges in GaussView by going to Results...Charge Distribution. Be sure to have the last geometry selected and choose the correct kind of charges to view.)

6. Scrolling down further in the file will reveal the Natural Bond Orbital (NBO) analysis section. Locate the section that says "`Summary of Natural Population Analysis`". The charges are in the "`Natural Charge`" column. NBO charges are more resistant to basis set effects than other orbital-based charges, but tend to give much larger charges than any other method (orbital or otherwise). (Some people think that this is unphysical.) However, it should be safe to analyze NBO charges within a related set of structures at the same level of theory.

7. Here are the acrolein heavy atom charges for the various files:

Acrolein Atom	CHELPG charges		NBO charges	
	Isolated	Acrolein + BF_3	Isolated	Acrolein + BF_3
Beta Carbon	–0.268	–0.200	–0.349	–0.289
Alpha Carbon	–0.158	–0.171	–0.330	–0.338
Carbonyl Carbon	+0.483	+0.475	+0.366	+0.411
Carbonyl Oxygen	–0.445	–0.343	–0.515	–0.525

As expected, on binding the beta carbon becomes more positive and the alpha carbon becomes more negative. However, both methods predict that in isolated acrolein, the beta carbon is more negatively charged than the alpha carbon (in contrast to what one would draw in the resonance structure). This is most likely because there are two electropositive hydrogens adjacent to the beta carbon, but only one adjacent to the alpha carbon.

In the NBO picture, the carbonyl also becomes more polarized when it is bound. However, the polarization *decreases* in the CHELPG picture. It is possible this is because the presence of the BF_3 hides some of the change in charge from the vdW surface. It is also possible that the polarization decreases when a bond is formed between the oxygen and boron.

8. What happens to the charges in the various transition states?

Atom	CHELPG charges			NBO charges		
	butadiene + ethylene TS	butadiene + acrolein TS	Butadiene + acrolein-BF$_3$	butadiene + ethylene TS	butadiene + acrolein TS	Butadiene + acrolein-BF$_3$
Beta Carbon	−0.137	−0.069	+0.050	−0.463	−0.435	−0.406
Alpha Carbon	−0.137	−0.144	−0.291	−0.463	−0.343	−0.322
Carbonyl Carbon		+0.381	+0.400		+0.355	+0.323
Carbonyl Oxygen		−0.476	−0.397		−0.561	−0.608

Once again, the acrolein becomes more polarized with increasing coordination. Interestingly, the methods differ substantially on the charge for the beta carbon.

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