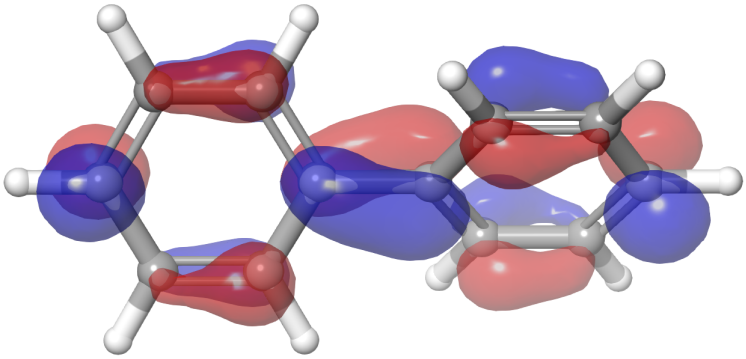
HOMO-LUMO Energy Gap

Created with: Release 2021-3
Prerequisites: working knowledge of Maestro
Files Supplied: HOMO_LUMO_worksheet
Categories: general chemistry, organic chemistry

About this Lesson

Using Maestro, students will use the 2D Sketcher to learn how to draw small molecules. Energy minimizations and geometry optimization calculations will be performed using Jaguar. Molecular orbital surfaces of the HOMO and LUMO will also be calculated and visualized. HOMO-LUMO energy gaps can be found in the project table.



Learning Objectives

- Build a molecule using the 2D sketcher
- Run a Jaguar optimization calculation to generate the molecular orbital surfaces
- Visualize the HOMO and LUMO of a molecule
- Calculate the HOMO–LUMO energy gap using results in the Project Table

Standards

- *ACS Guidelines*
  - Electronic, steric, and orbital interactions in the behavior and properties of molecules (Conceptual Topics)
- *ETS Chemistry GRE*
  - Organic Chemistry – Molecular orbital theory (3F)
- *AAMC MCAT*
  - Electron Structure – Orbital structure (4E)

Assessments

The following types of formative assessments are embedded in this lesson:

- Assessment of student understanding through discussion of warm-up questions and filling in any knowledge gaps about valence bond theory vs. molecular orbital theory
- Visual assessment of student-generated molecular orbitals and calculations of HOMO-LUMO energy gaps

Warm-Up Questions: To be done on their own or at the beginning of class

Watch the Khan Academy video on Molecular Orbital Theory and answer the following question for the molecule ethyne.

1) What is the molecular geometry of the central atom?
2) What types of bonds are in the molecule? What atomic and/or hybrid orbitals make up each bond?

Lesson Outline

1. What you will need for this lesson

<table>
<tr>
<td></td>
<td>
1. Go to the ‘Data’ folder and open your Class Folder found on the virtual cluster’s desktop.
2. Right-click on the folder called “HOMO-LUMO_gap” and copy folder to Desktop
Here, you will find the lesson plan
</td>
</tr>
<tr>
<td>


Figure 1-1. Open Maestro.
</td>
<td>
3. Open Maestro
a. See Starting Maestro if you need help
</td>
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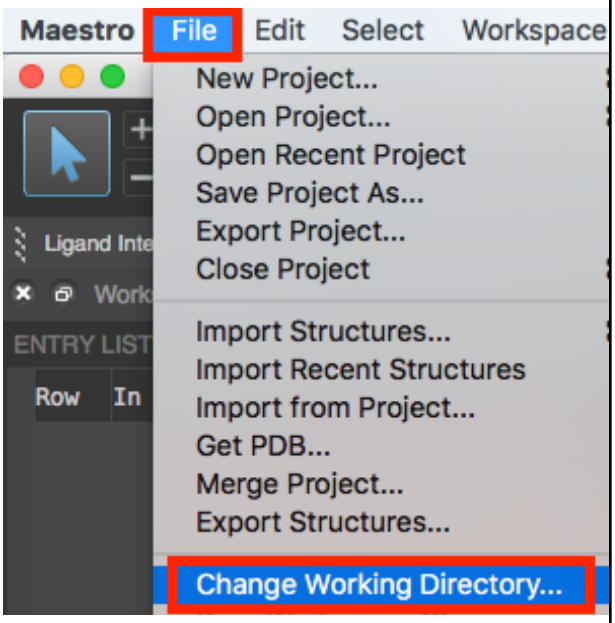
<td>


Figure 1-2. Change Working Directory option.
</td>
<td>
4. Go to File > Change Working Directory
5. Find your “HOMO-LUMO_gap” folder that you duplicated to your Desktop, and click Choose
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</tr>
</table>

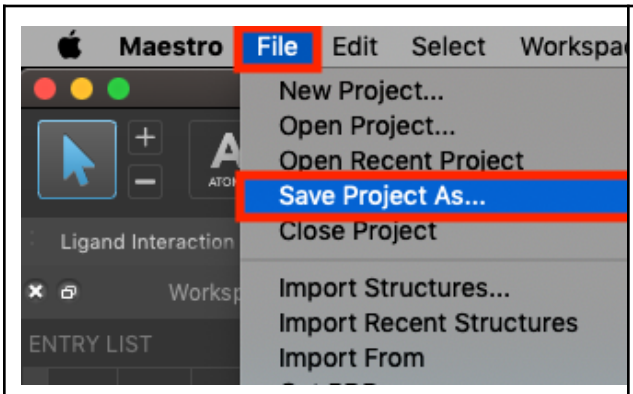


Figure 1-3. Save Project panel.

6. Next, go to **File > Save Project As**
7. Type “HOMO-LUMO_gap” and click **Save**
    - The project will be titled HOMO-LUMO_gap.prj

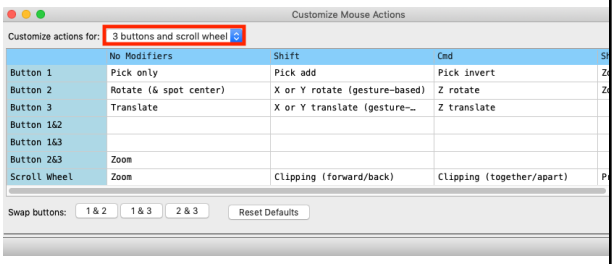


Figure 1-4. Choose the best mouse option for your set up.

8. Finally, check your **Mouse Actions**
    - **Edit > Customize Mouse Actions**

9. Make sure you have **the best option chosen for your set up**. This lesson was written with a three-button mouse with a scroll wheel, meaning the scroll wheel is a button as well as a wheel. If you do not have a mouse, choose **Trackpad**.

2. Introduction to Molecular Orbital Theory

Molecular orbital (MO) theory describes electrons in a bond that are delocalized between two specific atoms. MO theory uses a mathematical method called the **linear combination of atomic orbitals (LCAO)** to combine atomic orbitals to make molecular orbitals. An atomic orbital is a region of space associated with an individual atom, while a molecular orbital is associated with an entire molecule. For instance, a molecule is considered to be a single entity held together by many electron clouds. MO theory gives rise to bonding and antibonding orbitals. To help explain this, let's look at an MO energy diagram for the molecule H_2 in **Figure 1** below.

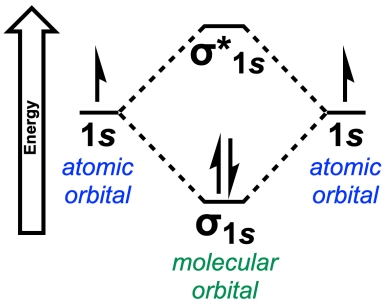


Figure 1. Molecular orbital diagram for H_2.

In an MO energy diagram, atomic orbitals are represented on the right- and left-hand sides, with each atomic orbital for H_2 having one electron. These atomic orbitals are combined mathematically using LCAO to produce two molecular orbitals: a bonding 1*s* sigma (σ), and an antibonding 1*s* sigma star (σ*). When each of the electrons from the atomic orbitals combine, they fill the lower energy MO bonding orbital first. These two electrons in the bonding orbital are what make the covalent bond, or σ bond in the molecule H_2.

For every molecule, two of its molecular orbitals are of particular interest. One is the **highest occupied molecular orbital (HOMO)** which is the highest energy MO that has any electrons in it. And the second is the **lowest unoccupied molecular orbital (LUMO)** which is the lowest energy place to put or excite an electron. These two orbitals are closest in energy out of all of the orbitals in a molecule; therefore, it is the most important energy gap to consider. The energy difference between the HOMO and LUMO, otherwise known as the **HOMO-LUMO energy gap**, is generally the lowest energy electronic excitation that is possible in a molecule. The energy of the HOMO-LUMO gap can tell us about what wavelengths the compound can absorb. In other words, measuring the wavelengths a compound absorbs in the lab using instrumentation called UV-Vis spectroscopy, or a spectrophotometer, can be used to measure the HOMO-LUMO gap. One can also calculate the HOMO-LUMO energy gap using density functional theory (DFT) methods. We will discuss ways to compute this energy value using Schrödinger's Maestro.

3. HOMO–LUMO Energy Gaps in H_2 and C_2H_2

If H_2 is exposed to light of a wavelength with energy equal to ΔE, or the HOMO-LUMO energy gap, this wavelength will be absorbed and the energy will be used to bump one of the electrons from the HOMO to the LUMO, as shown in **Figure 2**. In other words, an electron will go from the σ to the σ* orbital. This is referred to as a **σ-σ* transition**. The energy, ΔE, for this electronic transition is 258 kcal/mol, corresponding to light with a wavelength of 111 nm.

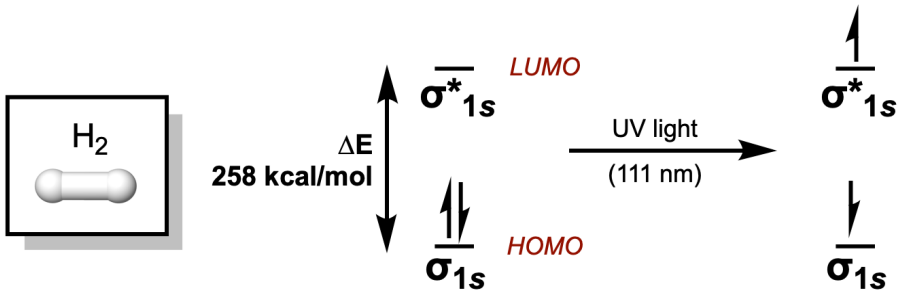


Figure 2. Excitation of H_2 to depict a σ-σ* transition.

When a double-bonded molecule, such as ethylene, absorbs light, it undergoes a **π-π* transition** as shown in **Figure 3**. Since π-π* energy gaps are narrower than σ-σ* gaps, ethylene absorbs light at 165 nm which is a longer wavelength than H_2. Although the energy for ethylene's HOMO-LUMO gap has been measured, chemists generally do not look at the UV-Vis spectrum below 200 nm. The UV-Vis measurable range is generally 200-800 nm range total. As such, ethene would be said to be UV inactive, since most instrumentation would not pick up the pi to pi-star transition in this system.

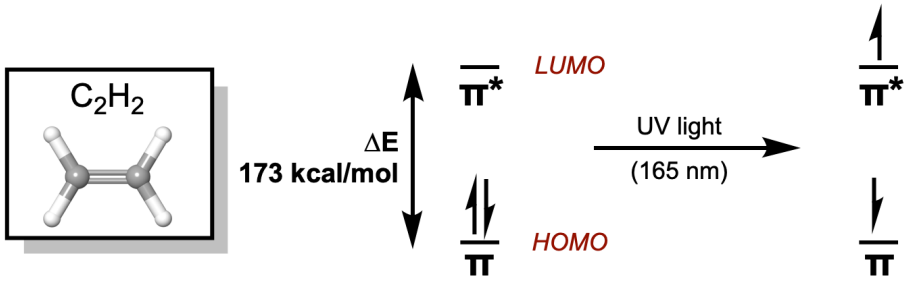


Figure 3. Excitation of ethylene to depict a π-π* transition.

Example #1: A molecule absorbs light of λ = 490 nm. What do you predict is the HOMO-LUMO gap of that molecule in units of eV? Use Planck's equation (E = *hc*/λ) to solve the problem.

4. Calculating a HOMO–LUMO Energy Gap

Computational Exercise: Calculating Molecular Orbitals in Maestro

This exercise involves 4 parts:

- **Part 1:** Build the molecule using 2D sketcher
- **Part 2:** Run a Jaguar optimization job and calculate molecular orbitals
- **Part 3:** Visualize the HOMO and LUMO
- **Part 4:** View the HOMO–LUMO energy gap in the Project Table

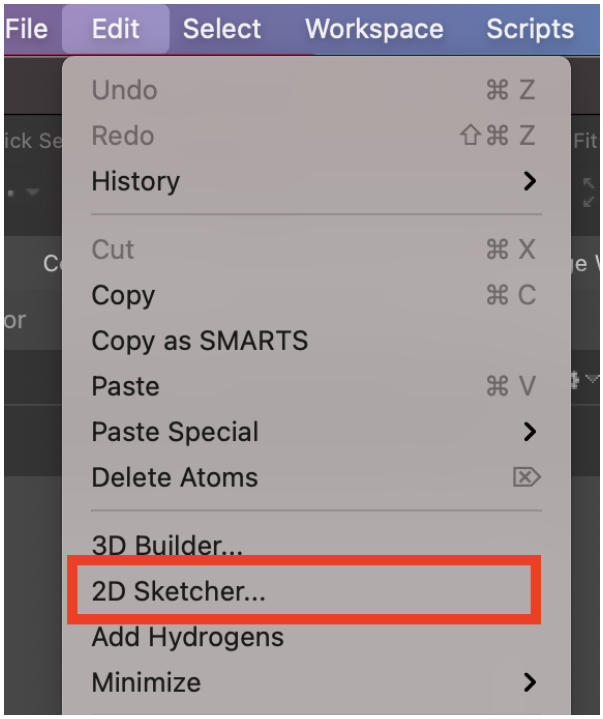


Figure 2-1. Opening 2D Sketcher

Part 1. Build biphenyl using 2D Sketcher

Let's draw the structure of biphenyl using the 2D sketcher.

1. Go to **Edit** > **2D Sketcher**

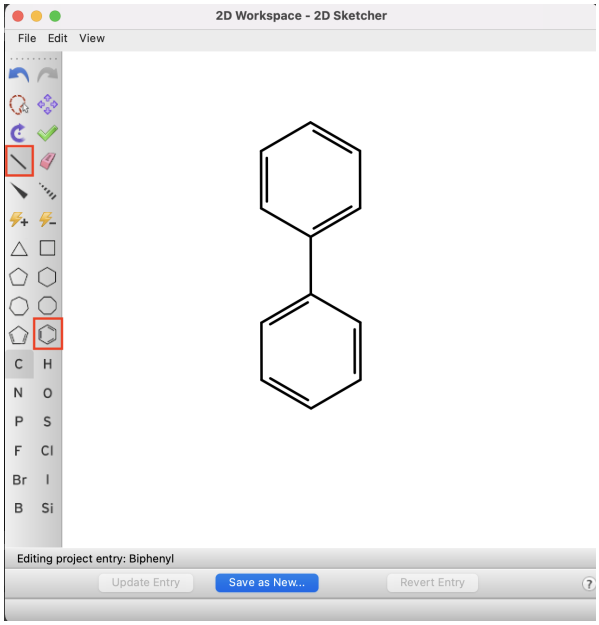


Figure 2-2. Drawing biphenyl.

2. **Draw** biphenyl exactly how it is shown in Figure 2-2.
    - Go to the selection bar on the left
    - Select the benzene ring in the selection bar then click in the blank white workspace to place a ring
    - Then select the single carbon bond button
    - Click and drag to add a carbon single bond at the bottom of the first benzene ring
    - Then click on the benzene ring button again
    - Click the end of the carbon single bond to place a second ring in the workspace
    - Try to replicate the sketch shown in the figure as closely

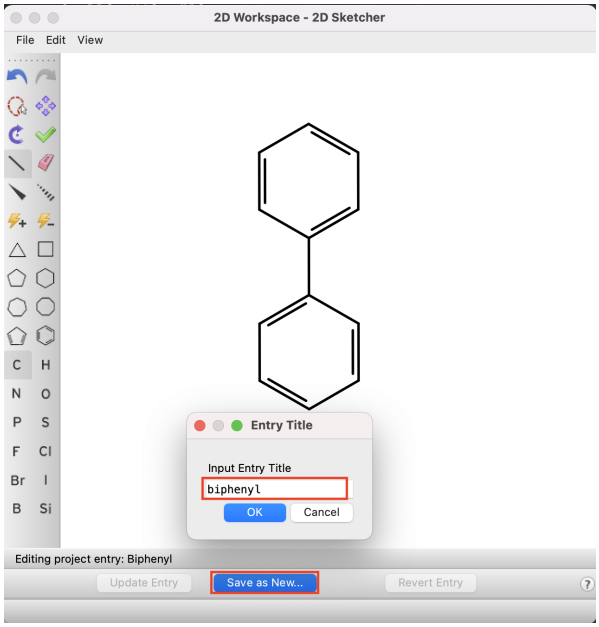


Figure 2-3. Saving 1-bromo-1-chloroethane.

as possible

3. Click on **Save as New** and for *Input Entry Title* write **biphenyl**. Click **OK**.

Figure 2-4. Clicking the Tasks button in the upper righthand corner.

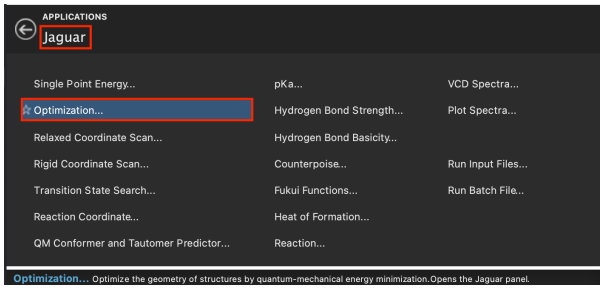


Figure 2-5. Opening the Jaguar Optimization panel.

Part 2. Optimize the Geometry using Quantum Mechanic DFT

Now let's optimize the molecule at the quantum mechanical level.

4. With the biphenyl entry selected and included, go to **Tasks > Optimization** using Jaguar
    - The Jaguar Optimization panel opens
5. Use structures from **Project Table (1 selected entry)**

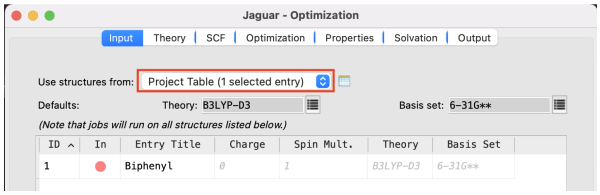


Figure 2-6. Setting the Jaguar Optimization panel to optimization.

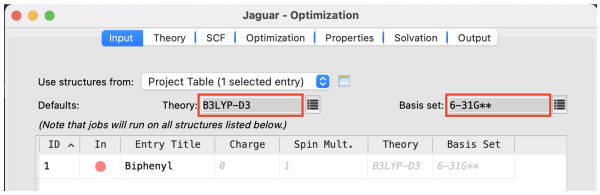


Figure 2-7. Setting the QM parameters for optimization.

Various settings can be altered depending on the specific use case. We will only adjust the *Input* tab for this example.

6. For *Theory*, select B3LYP-D3
7. For *Basis set*, select 6-31G**

A few additional comments about preparing for an optimization calculation:

- If you hover the mouse over the basis set in the table, you can see the number of basis functions associated with the basis set. This is useful to know since the quality of the basis set *usually* improves as the number of functions increases, noting again the trade-off between quality and computational expense
- Always make sure the charge and the spin multiplicity are correct (in this case, biphenyl is a neutral, singlet, so charge = 0 and spin multiplicity = 1). Multiplicity is defined as 2S + 1, where S is the total orbital spin of the molecule. For instance, a system with one unpaired electron is a doublet (multiplicity = 2), since the total orbital spin S = ½.
- Use the *Atom-Level Settings* button to define per-atom basis sets
- Constraints can be defined on the *Optimization* tab
- Properties, such as atomic charges, vibrational frequencies, surfaces and more can be requested on the *Properties* tab
- Solvent can be defined via several implicit solvation models on the *Solvation* tab. Note that this example is a gas-phase geometry optimization
- Read more about geometry optimization with Jaguar here

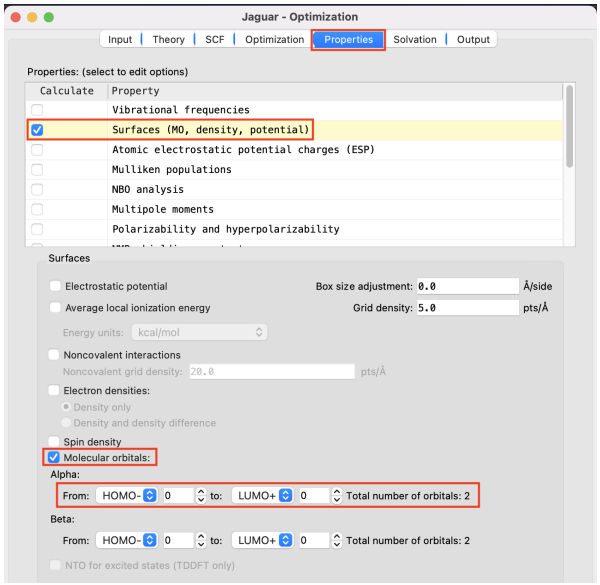


Figure 2-8. Selecting MO Surfaces in the Properties Tab.

8. Go to the Properties Tab
9. Select *Surfaces (MO, density, potential)*
10. Check mark *Molecular orbitals*
11. Leave HOMO-0 and LUMO+0 for this exercise. If you would like to visualize more molecular orbitals, you may increase these values as necessary

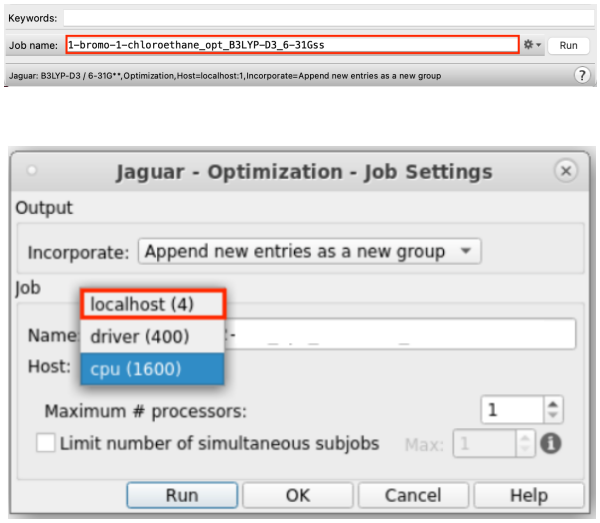


Figure 2-9. Naming and running the job.

12. Change the *Job name* to **Biphenyl_MOs_B3LYP-D3_6-31Gss**
    - Usually we incorporate stars (*) and pluses (+) into file names with S and P, respectively
13. Adjust the job settings ( ) by clicking the gear button to the right of the Job name
    - Choose localhost as your host with 1 processor
14. Click **Run**

Figure 2-10. Banner that shows the job is finished – Result has been incorporated.

When the job finishes, a banner will appear indicating that the result has been incorporated. At this time, the molecule with the optimized geometry is now shown in the workspace

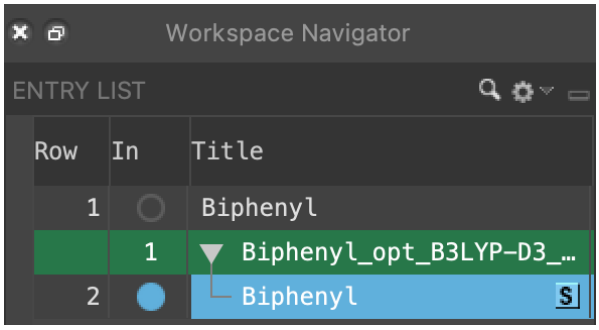


Figure 2-11. The output molecule of biphenyl.

15. A new entry group is added to the entry list. Select and include the molecule titled Biphenyl in this subgroup. This is your optimized structure.

Figure 2-12. Toggling the surfaces on.

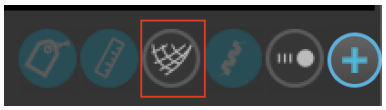


Figure 2-13. Toggling the surfaces off.

16. You can toggle on and off the molecular orbital surfaces at the bottom right-hand corner. Let's turn it off for now.
17. Change the representation to ball-and-stick by clicking on the **Style** menu and choosing **Apply ball-and-stick representation**

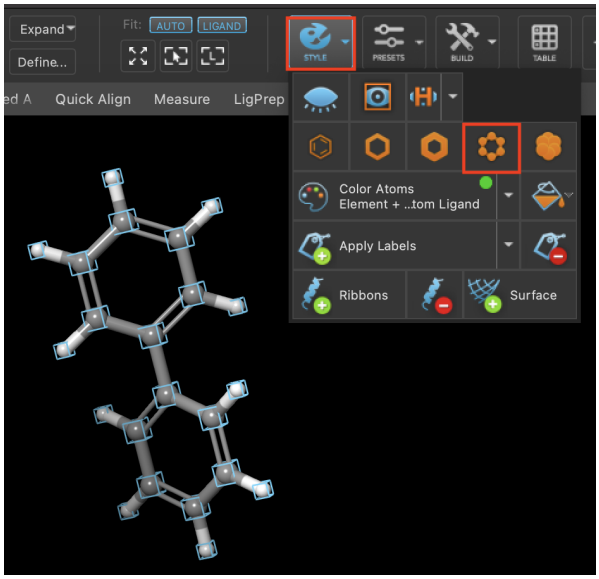


Figure 2-14. Viewing and styling biphenyl.

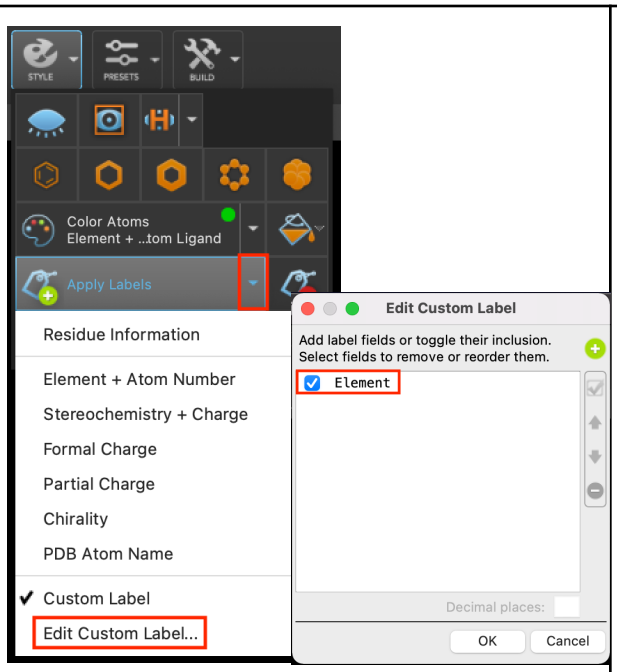


Figure 2-15. Labeling atoms.

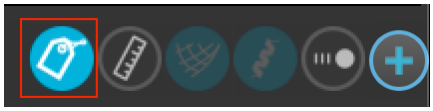


Figure 2-16. Toggling labels on.

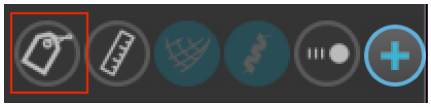
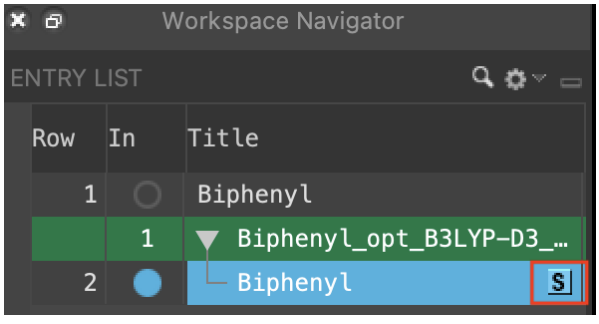


Figure 2-17. Toggling labels off.

18. To display atom labels, click **Style > Apply Labels** then click the drop down arrow on the right side
19. Click **Edit Custom Labeling**
20. Checkbox **Element** and press **OK**
21. Go back to **Style > Apply Labels > Custom Label** and now each atom in your workspace should be labeled

Note: You can toggle the atom labels on and off by clicking Annotations label button in the Workspace toggle on the bottom right corner



Part 3. Visualize the HOMO and LUMO

Now that we optimized the geometry of biphenyl, let's visualize the molecular orbitals.

22. Click the **S** button in the Entry List to the right of Biphenyl
23. Select either the HOMO or the LUMO to visualize
24. If you do not see any surfaces appear onto the molecule, remember to Toggle On the surfaces button in the bottom right-hand corner

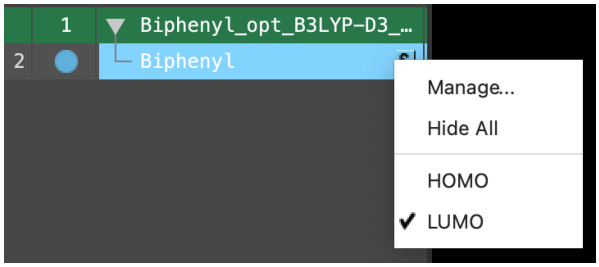


Figure 2-18. Selecting the Surface 'S' button in the Entry List

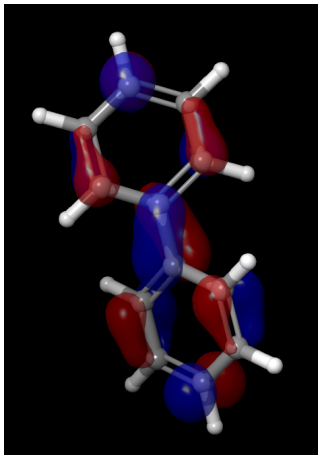


Figure 2-19. Visualizing molecular orbital surfaces

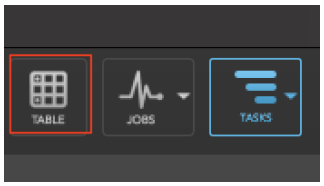


Figure 2-20. Selecting the Project Table

Part 4. View the HOMO–LUMO energy gap in the Project Table

25. Select the **Table** button in the upper right-hand corner
26. The Project Table window will open – here you will find a summary of data from the calculations you run
27. Select **Tree**
28. In the search bar, type **HOMO** and check mark the box for **HOMO**
29. In the search bar, type **LUMO** and check mark the box for **LUMO**
30. Close the Property Tree window

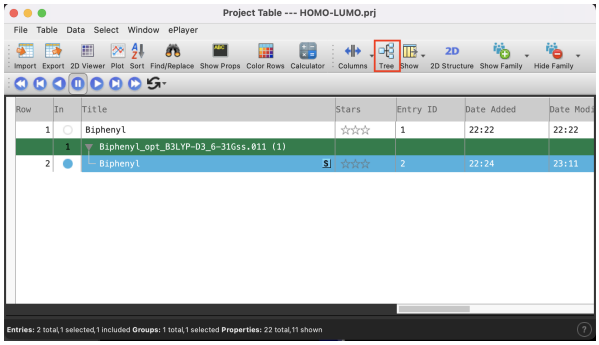


Figure 2-21. Opening the Project Table

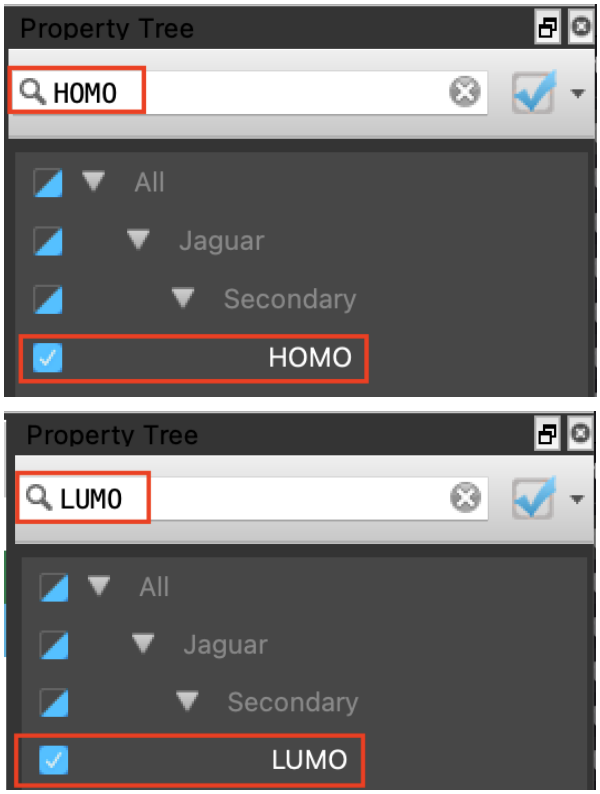


Figure 2-22. Using the Property Tree to add the HOMO and LUMO energy values to the Project Table

31. Go back to the Project Table and scroll until you see the energy values of the **HOMO** and **LUMO**; You may have to increase the column sizes to see the energy values
    - Note that these values are in units of Hartrees – Use this converter to change its units to either eV or kcal/mol
32. Take the absolute value of the HOMO energy value minus the LUMO energy value to obtain the HOMO–LUMO energy gap

Example #2: Take screenshots of biphenyl's HOMO and LUMO and include their energy values in units of Hartrees and eV. Determine the HOMO-LUMO energy gap in units of eV.

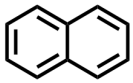
	in Hartrees	in eV
HOMO		
LUMO		
HOMO-LUMO Energy Gap		

Example #3: Using the HOMO-LUMO energy gap you calculated in eV, what wavelength of electromagnetic radiation do you expect it to absorb in units of nm?

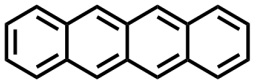
5. Individual Exercise

Part A: For each aromatic molecule, do the following:

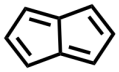
1) Calculate the HOMO and LUMO using Maestro and take screenshots of each HOMO and LUMO
2) List the HOMO and LUMO values in units of Hartrees and eV
3) Determine the HOMO-LUMO energy gap in units of Hartrees and eV



A



B



C

Molecule A:

HOMO screenshot:	**LUMO screenshot:**

	in Hartrees	**in eV**
HOMO		
LUMO		
HOMO-LUMO Energy Gap		

Molecule B:

HOMO screenshot:	LUMO screenshot:

	in Hartrees	in eV
HOMO		
LUMO		
HOMO-LUMO Energy Gap		

Molecule C:

HOMO screenshot:	LUMO screenshot:

	in Hartrees	in eV
HOMO		
LUMO		
HOMO-LUMO Energy Gap		

Part B: Rank all 3 molecules from highest to lowest HOMO-LUMO energy gap. Explain in a few sentences any trends that you see, taking note of conjugation within each aromatic system.

6. Summary, Additional Resources, and References

The overarching objective of this lesson was to introduce molecular orbital visualization. By using Maestro's computational tools, we learned to use the 2D Sketcher to conveniently build our molecules in 3D and how to optimize a structure's geometry using quantum mechanical DFT. Additionally, we changed the style of our molecules and applied labels to them. We also visualized both the HOMO and LUMO of a molecule and calculated the HOMO–LUMO energy gap.

For some related practice, proceed to explore other relevant tutorials:

- Introduction to Geometry Optimizations, Functionals, and Basis Sets

For further reading:

- Introduction to Computational Chemistry, 3rd Edition
- Essentials of Computational Chemistry: Theories and Models, 2nd Edition
- Molecular Modelling: Principles and Applications, 2nd Edition
- See the Jaguar help documentation

Glossary of Terms:

Entry List - a simplified view of the Project Table that allows you to perform basic operations such as selection and inclusion

Included - the entry is represented in the Workspace, the circle in the In column is blue

Project Table - displays the contents of a project and is also an interface for performing operations on selected entries, viewing properties, and organizing structures and data

Recent actions - This is a list of your recent actions, which you can use to reopen a panel, displayed below the Browse row. (Right-click to delete.)

Scratch Project - a temporary project in which work is not saved. Closing a scratch project removes all current work and begins a new scratch project

Selected - (1) the atoms are chosen in the Workspace. These atoms are referred to as "the selection" or "the atom selection". Workspace operations are performed on the selected atoms. (2) The entry is chosen in the Entry List (and Project Table) and the row for the entry is highlighted. Project operations are performed on all selected entries

Working Directory - the location that files are saved

Workspace - the 3D display area in the center of the main window, where molecular structures are displayed

2D Workspace - the 2D panel that opens from the “edit” dropdown that allows for the construction of molecules using a 2D sketcher

Tile - if multiple entries are included, included entries are displayed side by side in individual boxes rather than being overlaid in the same space