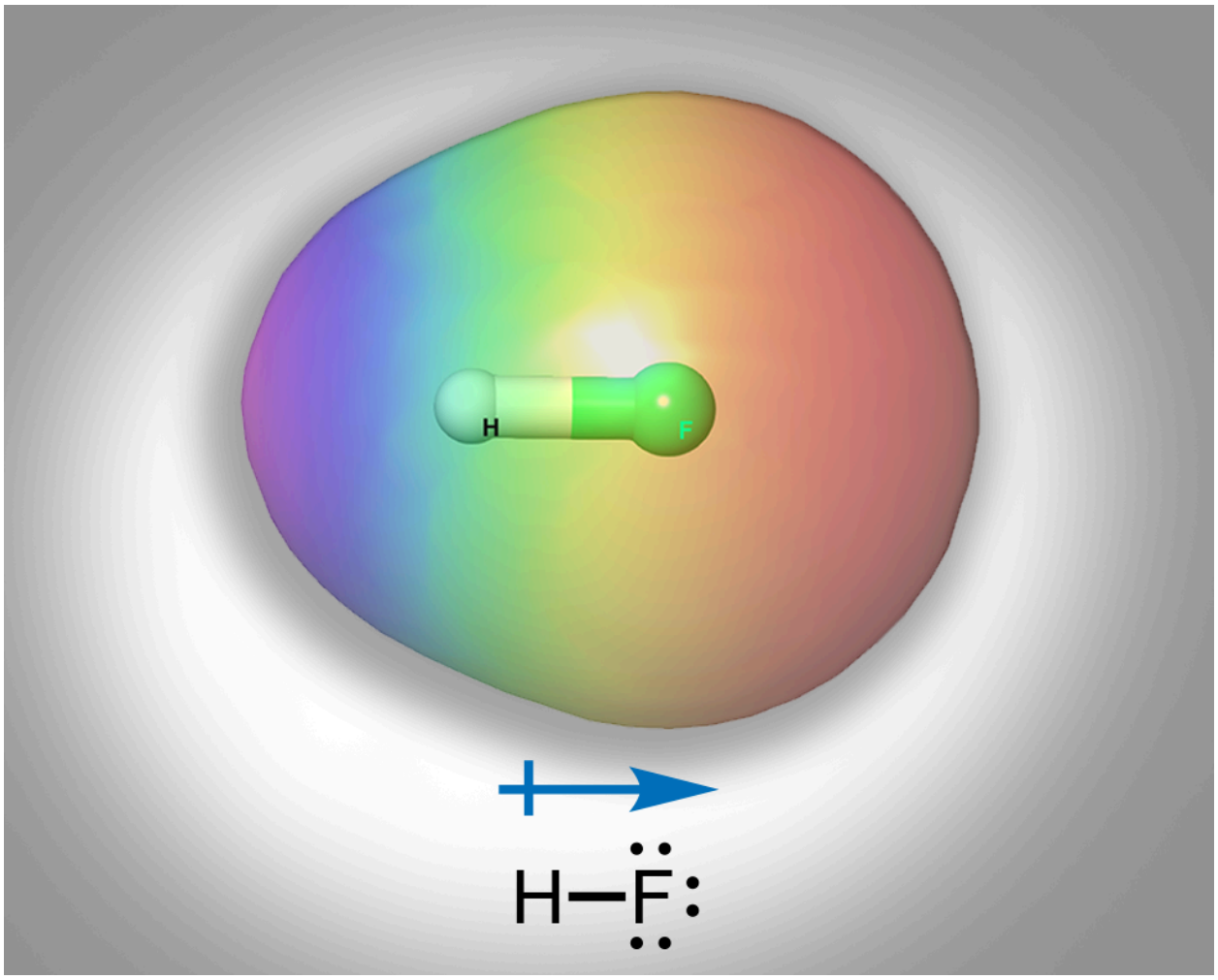
HOMO-LUMO Energy Gap



HOMO-LUMO Energy Gap

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:

- Explain Molecular Orbital (MO) theory and how it relates to HOMO-LUMO energy gap calculations
- 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

Lesson Contents:

Standards Alignment:

- *Connections to AP*
  - Properties of Substances and Mixtures (Unit 3)
- *IB Diploma Programme:*
  - Models of bonding and structure (Structure 2)
- *ACS Guidelines*
  - Electronic, steric, and orbital interactions in the behavior and properties of molecules (Conceptual Topics)
- *AAMC MCAT*
  - Electron Structure – Orbital structure (4E)

Assessments for Understanding:

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

Associated Documentation Pages: Jaguar Geometry Optimization: The Basics

Warm-Up Questions:

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?

Need help? Contact us at teaching@schrodinger.com

1. Setting Up the Maestro Session

At the start of the Maestro session, it is essential to 1) check your mouse actions, 2) change the file path to the Working Directory for this lesson, and 3) save your project file. The working directory indicated in this section contains the files necessary to complete this

lesson. If you do not set the appropriate working directory, you will be unable to run any calculations.

1. Launch the Virtual Cluster

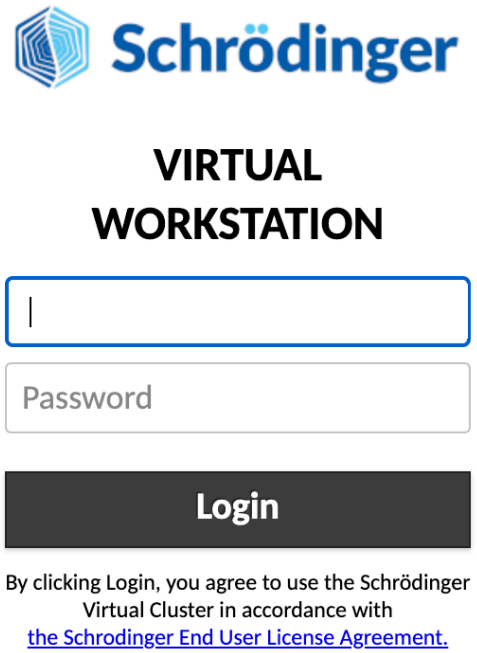


Figure 1-1. Virtual workstation login page.

2. Double-click the **course-data** folder on the desktop

Figure 1-2. Course-data folder on the desktop.

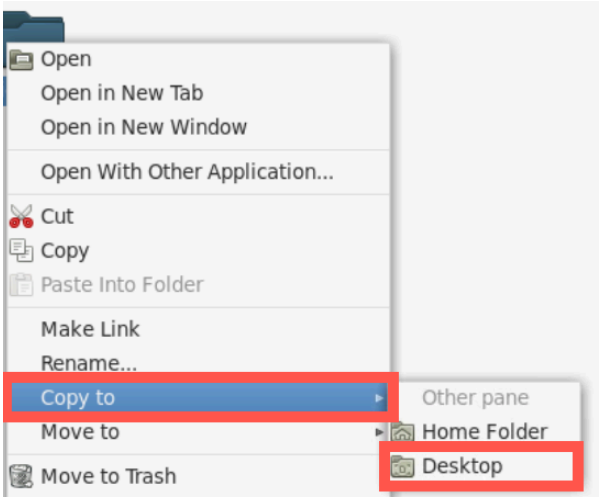


Figure 1-3. Copy the lesson folder to the Desktop.

3. Right-click the `Energy_Gap` folder and select **Copy to > Desktop**

4. Double-click the Maestro icon on the desktop

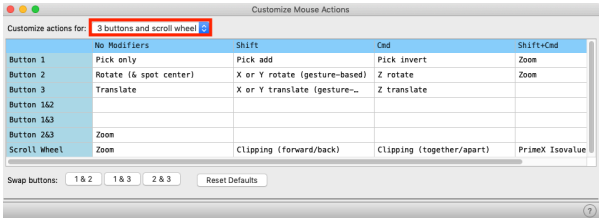


Figure 1-4. Change the mouse actions.

5. Check your mouse actions.
    - Go to **Workspace > Customize Mouse Actions**
    - *Note:* This lesson was made with a three-button mouse with a scroll wheel, but a trackpad can still be used
    - ***Trackpad keys:***
        - **Up/Down trackpad** = Zoom In/Out
        - **Option** = Rotate
        - **Control** = Translate

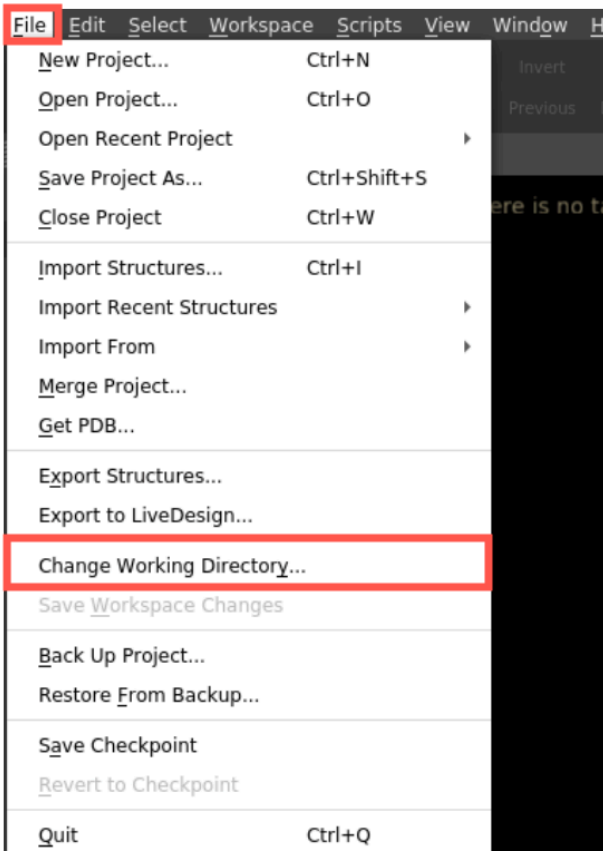


Figure 1-5. Change Working Directory option.

6. Go to File > Change Working Directory

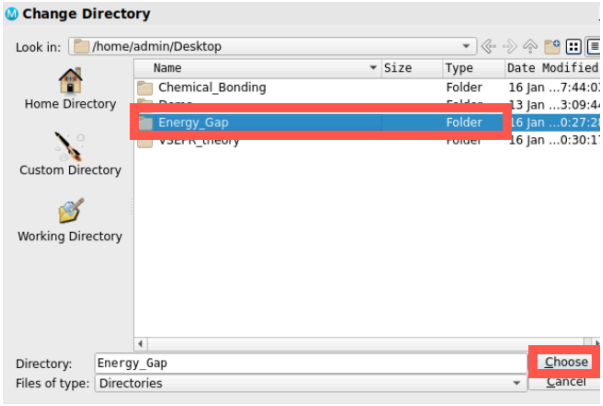


Figure 1-6. Change Working Directory panel.

7. Navigate to Desktop > `Energy_Gap` folder and click **Choose**

Pre-generated input and results files are included for running jobs or examining output

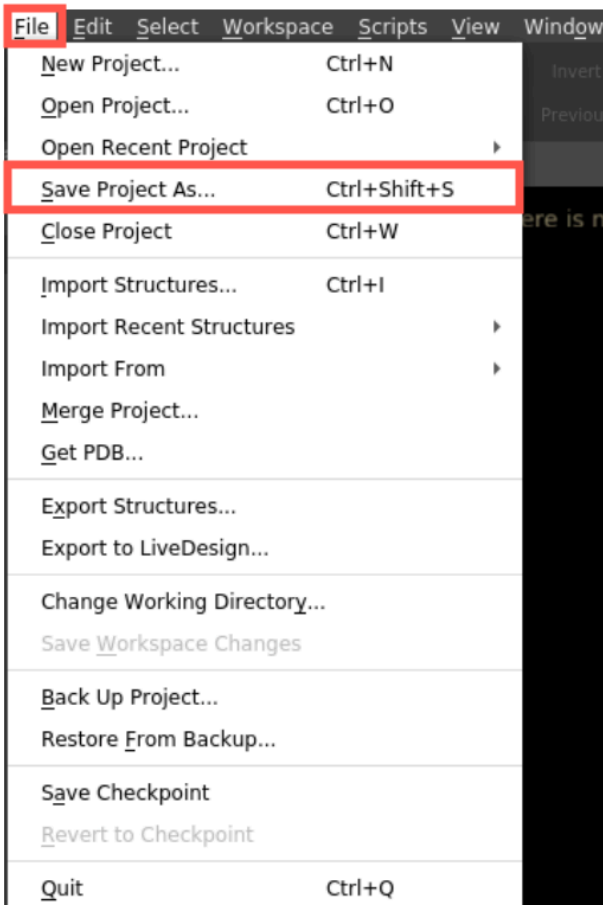


Figure 1-7. Save Project option.

8. Go to File > Save Project As

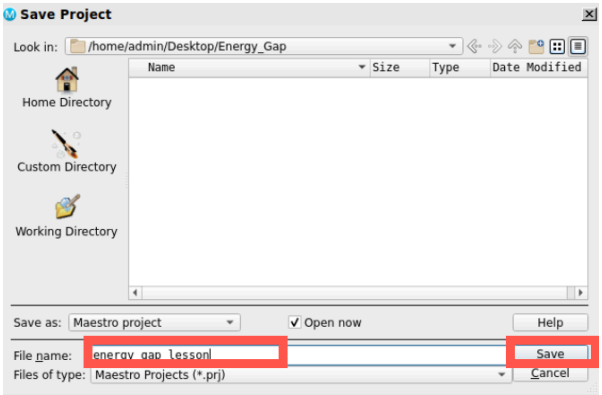


Figure 1-8. Save Project panel.

9. Change the *File name* to `energy_gap_lesson`, click Save
    - The project is now named energy_gap_lesson.prj

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 H2 in **Figure 1** below.

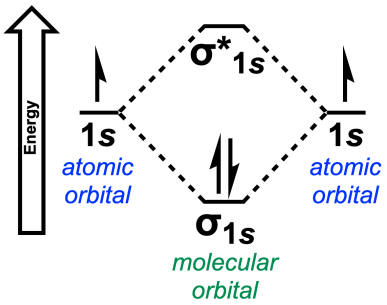


Figure 2.1. Molecular orbital diagram for H2.

In an MO energy diagram, atomic orbitals are represented on the right- and left-hand sides, with each atomic orbital for H2 having one electron. These atomic orbitals are combined mathematically using LCAO to produce two molecular orbitals: a bonding 1s sigma (σ), and an antibonding 1s 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 H2.

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.

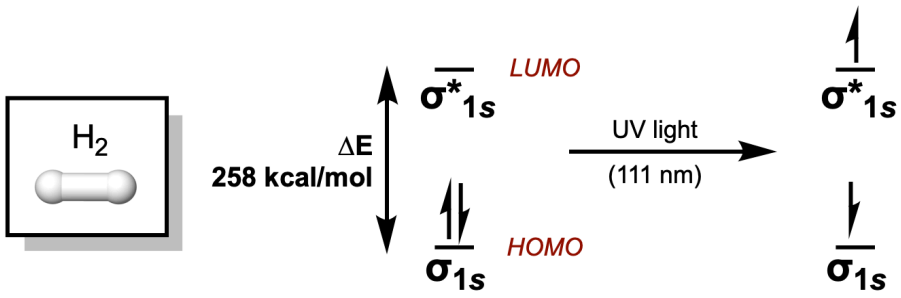


Figure 3.1. Excitation of H_2 to depict a σ-σ* transition.

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.

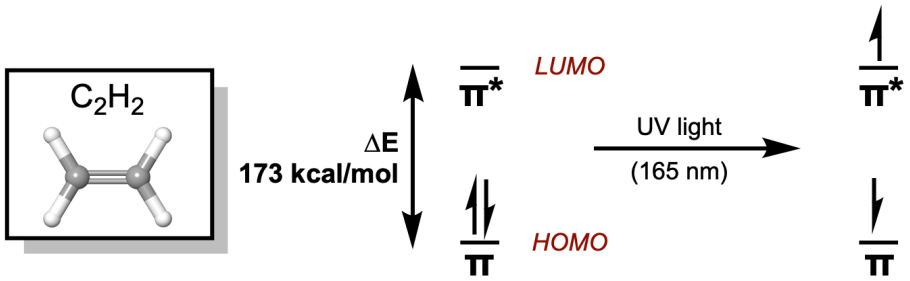


Figure 3.2. Excitation of ethylene to depict a π-π* transition.

Practice #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 #1: 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

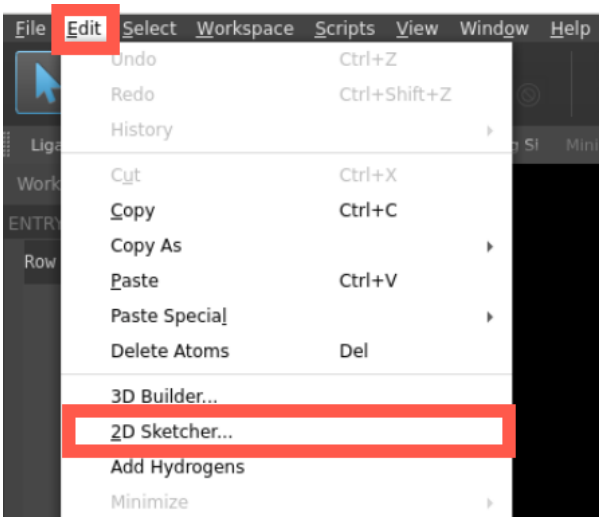


Figure 4-1. Opening 2D Sketcher.

Part 1. Build biphenyl using 2D Sketcher

Before optimizing any molecular geometry, you will need a starting molecule in your workspace. Let's draw the structure of biphenyl using the 2D sketcher.

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

The 2D sketcher functions like many standard 2D molecular drawing tools. For a complete overview of using the sketcher panel, see the 2D Sketcher Panel documentation.

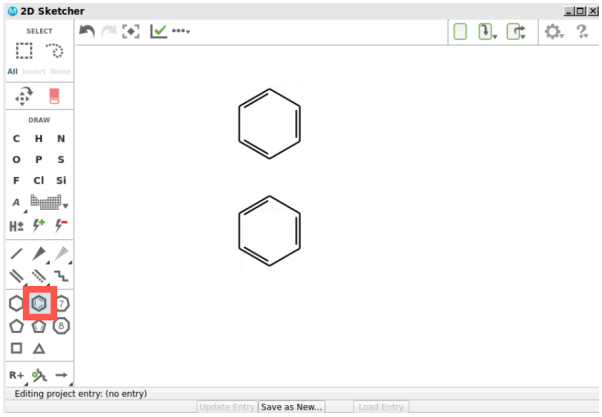


Figure 4-2. Drawing 2 benzene rings.

2. Draw **biphenyl** by first selecting the **benzene ring icon**
3. Place 2 benzene rings stacked on top of one another in the workspace

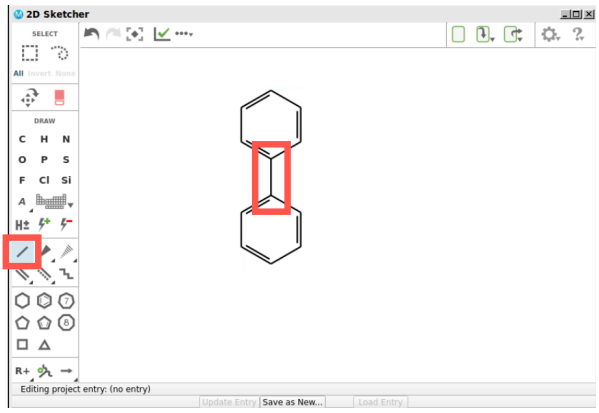


Figure 4-3. Connecting the 2 rings with 1 single bond.

4. Select the **single bond button**
5. **Connect the 2 rings** together with 1 single bond, as shown in **Figure 4-3**

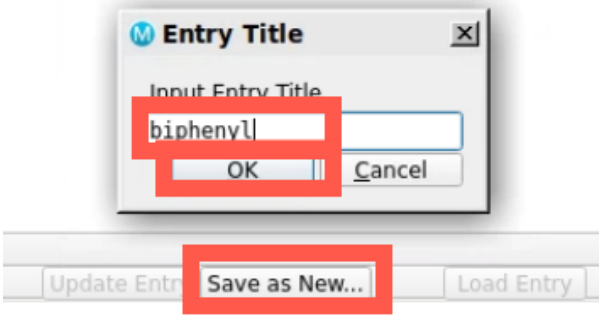


Figure 4-4. Save the entry title for biphenyl.

6. Click on **Save as New**
7. For *Input Entry Title*, write **biphenyl**.
8. Click **OK**.

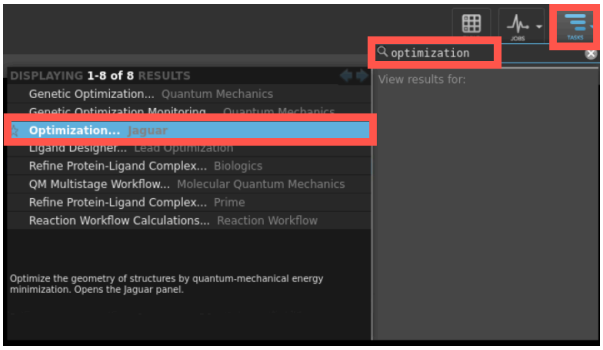


Figure 4-5. Opening up Jaguar from the Tasks bar.

Part 2. Optimize the Geometry using Quantum Mechanic DFT

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

1. Go to **Tasks > Optimization** using Jaguar
    a. The Jaguar Optimization panel opens

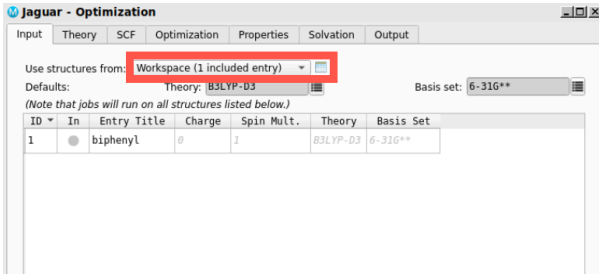


Figure 4-6. Setting the Jaguar Optimization panel to optimization.

2. Use structures from **Workspace (1 selected entry)**

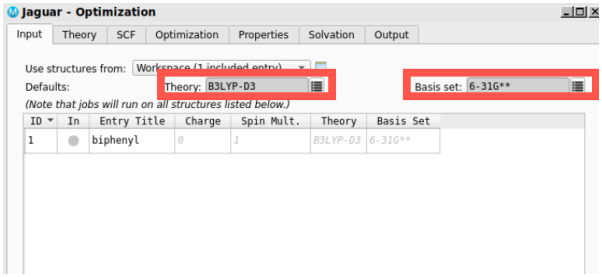


Figure 4-7. Setting the QM parameters for optimization.

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

3. For Theory, select **B3LYP-D3**
4. 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, PCl_3 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 and learn more about using the QM Multistage Workflow panel in the Introduction to Multistage Quantum Mechanical Workflows tutorial

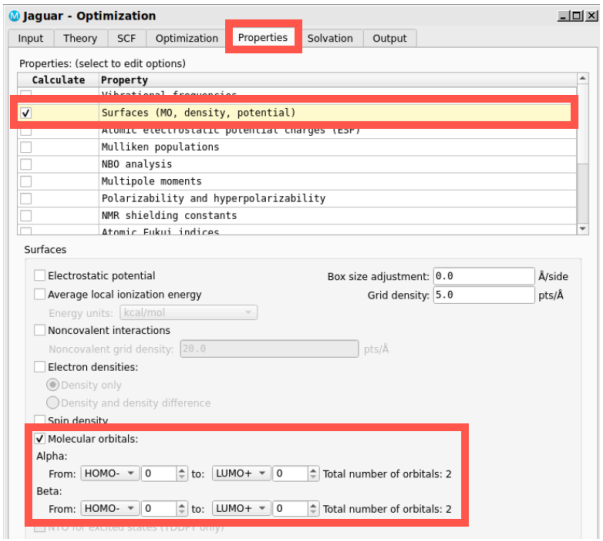


Figure 4-8. Selecting MO Surfaces in the Properties Tab.

5. Go to the **Properties Tab**
6. Select **Surfaces (MO, density, potential)**
7. Under the Surfaces section, check mark **Molecular orbitals**
8. 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

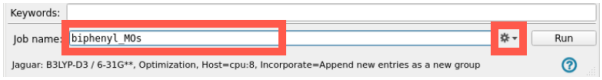


Figure 4-9. Naming the job.

9. Change the Job name to **biphenyl_MOs**

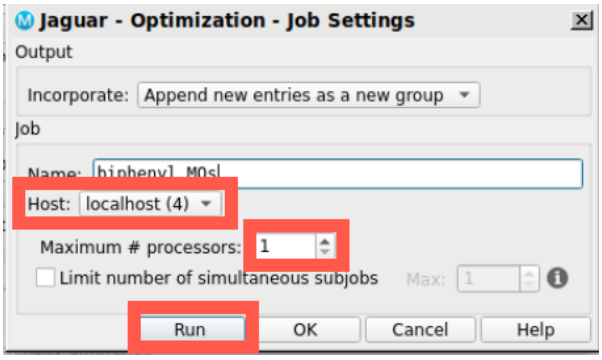


Figure 4-10. Running the job.

10. Adjust the job settings ( )
    a. This job requires 1 CPU host and should complete in under 2 minutes
11. Click **Run**

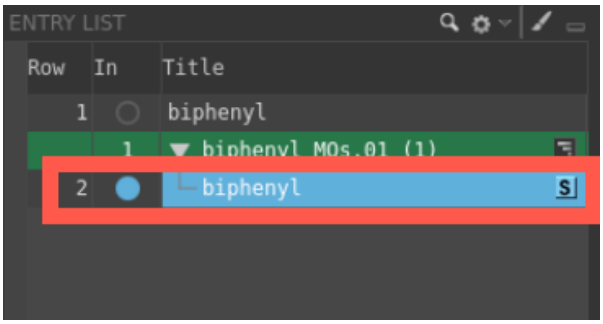


Figure 4-11. The output molecule of biphenyl.

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.

12. A new entry group is added to the entry list titled biphenyl_MOs.01 (1). Select and include the molecule titled biphenyl in this sub-group. This is your optimized structure

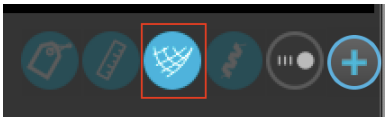
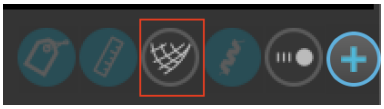


Figure 4-12. Toggling the surfaces on.



13. You can toggle on and off the molecular orbital surfaces at the bottom right-hand corner. Let's turn it off for now.

Figure 4-13. Toggling the surfaces off.

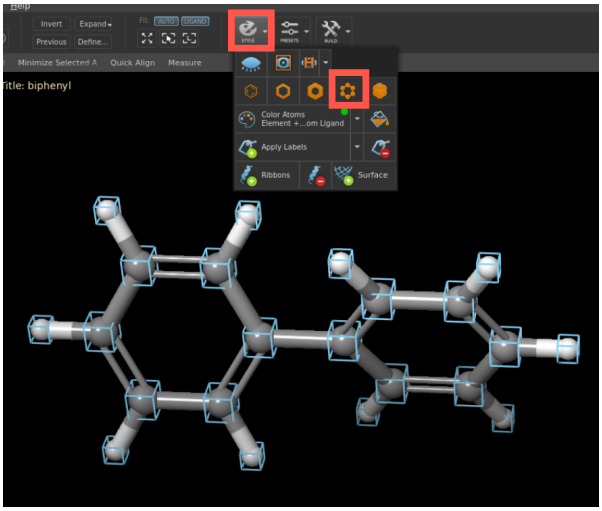


Figure 4-13. Viewing and styling biphenyl.

14. Change the representation to ball-and-stick by clicking on the **Style** menu and choosing **Apply ball-and-stick representation**

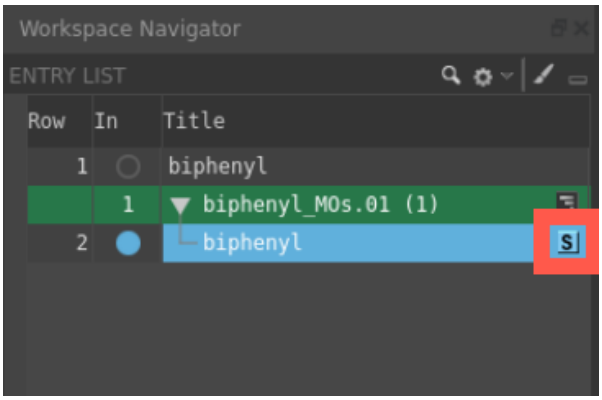


Figure 4-14. Selecting the Surface 'S' button in the Entry List.

Part 3. Visualize the HOMO and LUMO

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

1. Click the **S button** in the **Entry List** to the right of Biphenyl

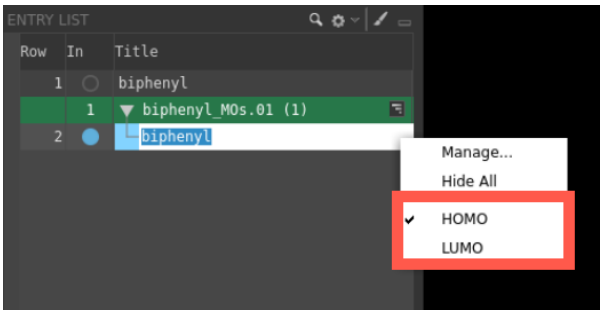


Figure 4-15. Selecting the either the HOMO or LUMO surface.

2. Select either the **HOMO** or the **LUMO** to visualize
    - **Note:** If you click on both the HOMO and the LUMO, both surfaces will appear. Only select one or the other

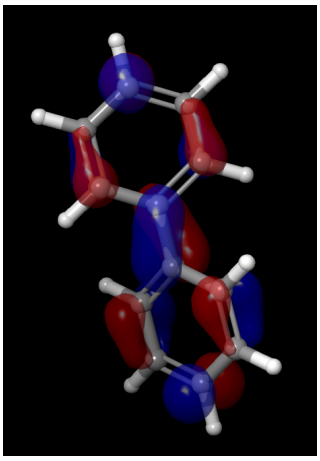


Figure 4-16. Visualizing molecular orbital surfaces.

3. If you do not see any surfaces appear onto the molecule, remember to **Toggle On** the surfaces button in the bottom right-hand corner

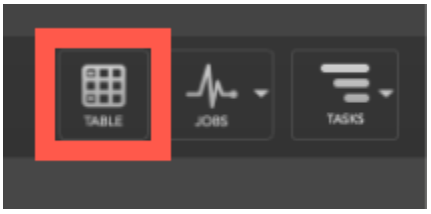


Figure 4-17. Selecting the Project Table.

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

1. Select the **Table** button in the upper right-hand corner
2. The **Project Table** window will open – here you will find a summary of data from the calculations you ran

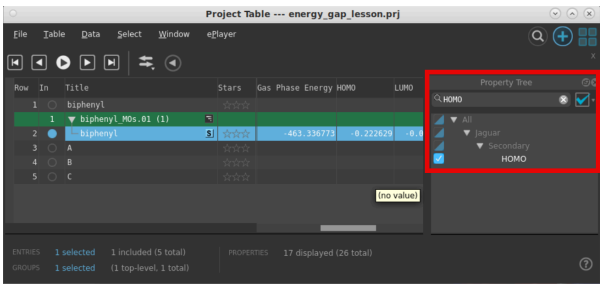


Figure 4-18. Using the Property Tree to add the HOMO and LUMO energy values to the Project Table.

3. In the Property Tree search bar, type **HOMO** and check mark the box for **HOMO**
4. Repeat step 3 for **LUMO**

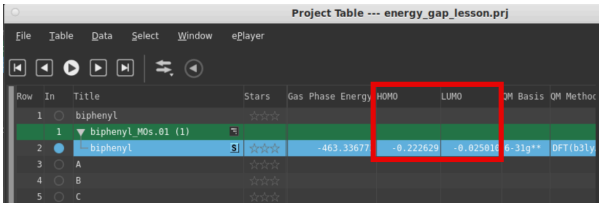


Figure 4-19. Using the HOMO and LUMO energy values to calculate their energy gap.

5. 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
6. Note that these values are in units of Hartrees – Use this converter to change its units to either eV or kcal/mol
7. Take the absolute value of the HOMO energy value minus the LUMO energy value to obtain the HOMO–LUMO energy gap

Pause & Think #1: 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.

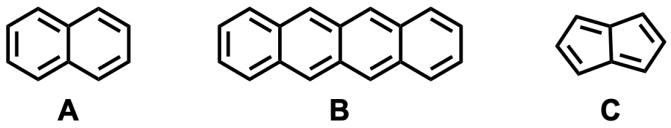
	in Hartrees	in eV
HOMO		
LUMO		
HOMO-LUMO Energy Gap		

Pause & Think #2: 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



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 further learning:

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

7. 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