**Exploring H2A Molecular Geometry with Spartan: MOs and Walsh Diagrams**

This worksheet will guide you through using Spartan to calculate the molecular orbital diagrams for bent H-A-H molecules (with A = Oxygen and Sulfur) and their cationic forms, using the Hartree-Fock method with the 6-31G\* basis set. You will systematically vary the H-A-H bond angle to create Walsh diagrams illustrating how orbital energies shift with molecular geometry. You will also explore how bond length affects the MO energy levels and investigate how changing the number of electrons in the MO affects the molecule’s total energy and preferred bond angle.

**Introduction to Computational Chemistry Methods**

Computational chemistry uses computer simulations to model and predict the behavior of molecules. These methods are broadly categorized into:

1. **Molecular Mechanics (MM):** These methods use classical physics (Newton’s laws) to describe molecules as balls (atoms) connected by springs (bonds). They are very fast and can handle very large systems (like proteins, DNA, RNA, etc.) but they do not account for electrons explicitly and thus cannot describe chemical reactions or electronic properties.
2. **Quantum Mechanics (QM):** These methods are based on solving the Schrodinger equation for a molecule. They are more computationally intensive but provide a more accurate description of electronic structure, bonding, and reactivity. QM methods are further divided into:
	* **Ab Initio Methods:** These methods are derived directly from first principles, with no experimental data used in their formulation. They aim to solve the Schrodinger equation as accurately as possible.
		+ **Density Functional Theory (DFT):** A powerful *ab initio* method that focuses on the electron density rather than the complex many-electron wavefunction. It has become very popular due to its good balance of accuracy and computational cost.
	* **Semi Empirical Methods:** These methods use some experimental data to simplify the calculations, making them faster but can be less accurate.

More information on these methods can be found on the [Spartan Documentation | wavefunction](https://www.wavefun.com/spartan-documentation) website by clicking on [Molecular Mechanics and Quantum Chemical Calculations](https://downloads.wavefun.com/FAQ/AGuidetoMM.pdf). For this activity we will use the Hartree Fock (HF) method. The HF method is a suitable choice for studying the H2O molecule because it offers a balance between computational efficiency and accuracy for small molecules like water. Below is some very basic information on the HF method; more detailed information can be found in the previous links.

**Hartree Fock (HF)** is a fundamental *ab initio* method. It approximates the many electron wavefunction as a single Slater determinant, meaning it treats electrons as moving independently in an average field created by all other electrons and the nuclei. This approximation simplifies the Schrodinger equation into a set of one-electron equations (the Hartree-Fock equations).

**Key aspects of Hartree Fock:**

**Self Consistent Field (SCF):** The HF method is iterative, meaning it starts with an initial guess for the electron distribution, calculates the average field, then uses this field to refine the electron distribution, repeating until the electron distribution and field are self-consistent (i.e. they don’t change significantly between iterations). The SCF total energy is a comprehensive measure of a molecules energy. It includes contributions from the kinetic energy of electrons, the attractive interactions between electrons and nuclei, the repulsive forces among electrons, and the repulsion between nuclei themselves.

In computational methods like Hartree-Fock, a basis set is a collection of mathematical functions used to describe the shapes of atomic orbitals. These functions serve as the building blocks for constructing the wavefunction of a molecule.

The 6-31G\* basis set is a moderate-size split-valence basis set, often used in computational chemistry for HF methods. It offers a good balance between accuracy and computational efficiency.

Structure of 6-31G\*

* 6-31G: This is the core of the basis set.
* The “6” represents a contraction of six Gaussian functions for core electrons.
* The “3” and “1” describe the electrons, split into a three-function inner component and a one-function outer component.
* The asterisk (\*) signifies polarization functions added to heavy atoms.

For deeper dives into the computational methods, you can refer to the provided links as well as other external resources. However, for the purposes of this course, a detailed understanding of those specifics is not required. You can now proceed directly with the Spartan activity.

**Spartan Activity**

*You will complete the following steps for both H2O and H2S. Once finished, you’ll compare your results and discuss the differences between the two molecules.*

**Part 1: Building H2A and Setting up the Calculation**

1. Launch Spartan: Open the Spartan software.
2. Build a New Molecule:
	* Go to File $\rightarrow $ New Build.
	* To the right, under “Model Kit” and “Organic”, select O (sp3) or S (sp3)
	* Click in the build window to place the oxygen atom. The hydrogen atoms will automatically be generated for the H2A molecule once the calculation begins.
3. **Set up Calculation:**
	* Go to Setup $\rightarrow $ Calculations...
	* In the Calculate section (see below), select “Equilibrium Geometry” at “Ground” state in “Gas”, with “Hartree-Fock”.
	* In the “Basis Set” dropdown menu, select 6-31G\*.



Click Submit. You will be asked to save the Spartan program. Once the program is saved, the calculation will begin.

**Part 2: Analyzing the Molecular Orbitals and Bond Angle**

1. **View Output:**
	* Once the calculation is complete (Spartan will notify you), go to Display $\rightarrow $ Output.
	* Scroll through the output window. Look for the section labeled “Molecular Orbital Energies”.
	* You will find a list of MOs with their corresponding energies (eV) as well as their representative symmetry labels. Identify the occupied and unoccupied orbitals and relate them to the previous MO diagram that you generated from the H2O class exercise. Write down the energies for the relevant orbitals. Also note down the total energy. You can find the total energy above the Molecular Orbital Energies table. The energy units are in Hartree’s. You can copy and paste the MO energy table into word by going to the right upper corner of the table and selecting “copy table to Clipboard”
2. **Visualize Molecular Orbitals:**
	* Go to Display $\rightarrow $ Orbital Energies.
	* Select the orbitals you are interested in (e.g., HOMO, LUMO). The molecular orbitals will show on the water molecule. You can rotate the water molecule / MO around by clicking and dragging your mouse pointer.
	* Take a screenshot of each MO and compare the MO’s to the MO’s you qualitatively drew in class on the whiteboard. Do they match?
3. **Determining the Bond Angle:**
	* Go to Geometry $\rightarrow $ Measure Angle…
	* Using your cursor, select / click one of the hydrogens, followed by oxygen, then the second hydrogen. All atoms should be heighted. In the right corner of the Spartan window, the angle is reported. Record this angle.
	* ****Ensure that the point group is C2v by checking the label in the bottom right corner of the Spartan

**Part 3: Manipulating Bond Angle and Deriving the Walsh Diagram**

A Walsh diagram plots the energy of molecular orbitals as a function of molecular geometry (in this case, the H-A-H bond angle).

1. **Setting the bond angle:**
	* Fix the bond lengths of the H2A. Go to “Geometry” $\rightarrow $ “Constrain Distance”. Next click one of the hydrogen atoms and the A atom. In the bottom right corner of the window, you will see a lock. Click the lock and this will set the bond distance. Repeat this with the other bond.
	* Go to Setup $\rightarrow $ Calculations...
	* In the Calculate section, change “Equilibrium Geometry” to “Energy”.
	* Keep “Hartree-Fock” and Basis Set as “ 6-31G\* ”. In the Start From section, change to “Current Geometry”



* + Click “Submit” and the calculation will start.
	+ Check to ensure the H-A-H bond angle has not changed.
	+ Next, adjust the angle to 100.0 degrees. To do this, click on the angle value reported in the lower right corner of the Spartan window. A dialog will appear. Set the angle to 100.0 degrees and click ENTER.
	+ Go back to Setup $\rightarrow $ Calculations and with the same calculation setup as before re-submit the job by clicking Submit.
	+ Once the calculation is complete, following Part 2 procedure, analyze the MO energy levels and copy/paste the table representing the MO energies and symmetry labels into the same word file. Be sure to label each table in the word file with the respective bond angle.
	+ Repeat with the following bond angles: 80, 85, 90, 95, 100, equilibrium angle, 110, 120, 130, 150, 170, 175, and 179 degrees.
1. **Constructing the Walsh Diagram:**
	* Using the data you collected, plot the energy of each molecular orbital (y-axis) against the H-A-H bond angle (x-axis). You can use whatever graphing software you like (Excel, Google Sheets, Origin, Egor Pro, etc). Connect the points for each orbital to show its energy trend.
	* Observe how the energies of the orbitals change as the molecule goes from a linear (180°) to a bent (80°) geometry.
2. **H-A-H bond angle versus total energy:**
	* Plot the H-A-H bond angle versus the total energy. Note the energy units are in Hartree’s.

**Part 4: Bond distance versus MO energy levels:**

* + Remove the bond length constraints and re-run the “Equilibrium Geometry” calculation using “Hartree-Fock” and Basis Set as “ 6-31G\* ”. Ensue that the bond angle and bond distances were the same as before.
	+ Fix the bond angle. Go to the “Geometry” tab and select “Constrain Angle”. Click all three atoms and in the bottom right corner of the screen click on the lock again to fix the bond angle.
	+ Next adjust the bond lengths. Ensure that both bond lengths are the same with both bonds. Adjust the bond lengths by ± 0.1 angstrom intervals up to ± 0.3 angstroms. Ensure that the point group remains C2v with each change/calculation. When performing the calculation, ensure that you have calculate “Energy” using “Hartree-Fock” and Basis Set as “ 6-31G\* ” and start from “Current Geometry”. For each bond change, record the total energy as well as the MO energies, including the antibonding orbitals. Make a bond length versus total energy and MO energy level plots.

**Questions:**

1. Based on your Walsh diagram, which orbitals stabilize or destabilize as the bond angle decreases from 180° to 80°?
2. Water has an experimental bond angle of ~105°. Does your Walsh diagram predict a bent or linear geometry for H2O? Explain your reasoning based on the total energy and the trends of individual orbitals.
3. How do the shapes of the molecular orbitals change as the bond angle changes? (Refer back to the orbital visualization in Part 2).
4. Based on the principles of Walsh diagrams, explain why BeH2 is linear while BH2 is bent. Consider the number of valence electrons and how they occupy the molecular orbitals. Next, calculate the BH2 bond angle with Spartan using the same computational setup you used for H2O (Equilibrium Geometry). Answer the following questions:
	* What is the reported point group?
	* What is the bond angle?
	* How does the bond angle compare to the bond angle of H2O? Does this conceptually make sense based on the Walsh diagram and considering the number of valence electrons and how they occupy the molecular orbitals?
5. Open your H2O Spartan file and recalculate the bond angle using the same computational setup as before (Equilibrium Geometry). For H2O+, how might the bond angle change? First, make your prediction based on the concepts of the Walsh diagram. Next, in the Calculations window, change the Total Charge to “Cation (1)” and change the Unpaired Electrons to “1”. Select Submit.

Did your bond angle change as predicted? Explain.

1. In Part 3, you plotted the H-A-H bond angle against the total energy. At what angle is the energy minimized, and does this correspond to the equilibrium geometry obtained from your Hartree-Fock calculation? Compare the equilibrium bond angles for H2O and H2S and discuss how differences in their molecular structures may account for any discrepancies. Additionally, if you sum up the energies of the occupied molecular orbitals and convert that total from electron volts to Hartrees, does it match the total energy? Explain why these two values are or aren’t equivalent.
2. When comparing the Walsh diagrams for H2O and H2S, can you qualitatively explain why the bond angle in H2S is smaller than in H2O? Do any MO energy levels in the H2O Walsh diagram show more or less substantial changes as the bond angle increases from 80° to 180°? Explain.
3. In Part 4 you made a H-A bond length versus MO energy level plot for the bonding and antibonding MO’s. Explain the trends with regards to what happens with the MO energy levels as the H-A bond length increases. Do the antibonding MO states have a different trend compared to the bonding MO states? How does increasing/decreasing the bond lengths affect the total energy? Explain.
4. Design a quick Spartan exercise that differs from those previously completed in this activity, but still relates to the topic covered here involving an AH2 molecule. Develop a question, make a prediction, test your prediction using Spartan, and provide an explanation.
5. Using your understanding of symmetry and character tables from the last class exercise where you qualitatively derived the molecular orbital (MO) energy levels of H2O, explain in general terms how Spartan performs this same setup/calculation. What aspects of the method are similar to your approach, and what parts are different?