AN INTRODUCTION TO SPARTAN

OBJECTIVE

This tutorial introduces a number of basic operations in Spartan Student required for molecule manipulation, property query and spectra and graphics display. Specifically it shows how to: a) open molecules, b) view different models and manipulate molecules on screen, c) measure bond distances, angles and dihedral angles, d) display energies, dipole moments, and atomic charges and e) display graphical surfaces and property maps. Finally, these tools will be utilized to illustrate the use of Spartan’s model kits as well as the steps involved in examining and querying different molecular model styles and in carrying out a quantum chemical calculation.

REPORT INSTRUCTIONS

Take notes while completing the procedures for this tutorial and then complete the appropriate Sapling assignment. No work needs to be done in your ELN for this assignment.

INTRODUCTION

“The best arrangement of a given number of electron pairs (or bonds) is the one that minimizes the repulsions among them.” This simple idea is the basis of the valence-shell electron-pair repulsions (VSEPR) model. As shown below, the model dictates that two electron pairs are arranged linearly, three pairs are arranged in a trigonal planar fashion, four are arranged tetrahedrally, five are arranged as a trigonal bipyramid, and six are arranged octahedrally. These symmetrical molecules have “ideal” bond angles and no molecular dipoles.

When lone pairs of electrons are present or more than one type of atom is bound, bond angles and dipoles are effected.
Organic molecules are made up of a relatively few elements and generally obey conventional valence rules. They may be easily built using the organic model kit. Alternatively, the inorganic model kit is necessary for molecules that incorporate other elements or do not conform to normal valence rules. Both model kits can be used to demonstrate the molecular geometries of various structures.

**PROCEDURE**

**Part A: Basic Spartan Operations**

a. Click on the *Tutorials Folder* link (next to this document on the lab manual webpage). A Google Drive will open with many files. Go to the File menu and choose Download. An icon will appear in the bottom left of the web browsers frame: ![Tutorials (.zip) icon](image). Click on the ▼ on the right side of the icon and choose Open. Drag the folder onto the desktop and open it. Alternatively, you can find the Tutorial Folder by going to the Program Files of your PC: ProgramFiles(x86)/Wavefunction/Spartan Student v5/Tutorials or to the Applications Folder of your Mac (the Tutorials folder is present as a separate icon). (The folder actually downloads with the program.)

b. Open the file named basic operations. A single file containing *ethane, acetic acid dimer, propene, ammonia, hydrogen peroxide, acetic acid, water, cyclohexanone, ethylene, benzene, aniline* and *cyclohexenone* will be opened. A ball-and-spoke model for the first molecule (*ethane*) will be displayed, and its name appears at the bottom of the screen.

c. Practice rotating, translating (dragging), and zooming ethane:

i. Rotating:
   - **PC:** *move* the mouse while holding down the left mouse button. Hold the shift & mouse button down and the model will rotate around an internal center point.
   - **Mac:** *move* the mouse while holding down the mouse button. Hold the shift & mouse button down and the model will rotate around an internal center point.
ii. Translating:
   **PC:** move the mouse while holding down the right button.
   **Mac:** move the mouse while holding down the mouse button and the ⌘ button.

iii. Zooming:
   **PC:** use the center mouse wheel (scroll wheel) if available, or hold down the Shift key in addition to the right button while dragging the mouse up (zoom in) or down (zoom out).
   **Mac:** if using a Magic Mouse, just run finger up and down mouse.

*Click on Model from the menu bar. One after another, select Wire, Ball and Wire, Tube and finally Ball and Spoke from the Model menu. All four models for ethane show roughly the same information. The wire model looks the most like a conventional line formula. It uses color to distinguish different atoms, and one, two and three lines between atoms to indicate single, double and triple bonds, respectively.*

The ball-and-wire model is identical to the wire model, except that atom positions are represented by small spheres, making it easy to identify atom locations. The tube model is identical to the wire model, except that bonds are represented by solid cylinders. The tube model is better than the wire model in conveying three-dimensional shape. The ball-and-spoke model is a variation on the tube model; atom positions are represented by colored spheres, making it easy to see atom locations.

Select **Space Filling** from the Model menu.
The space-filling model is different from the other models in that bonds are not shown. Rather, each atom is displayed as a colored sphere that represents its size. Thus, the space-filling model for a molecule provides a measure of its size. While lines between atoms are not drawn, the existence (or absence) of bonds can be inferred from the extent to which spheres on neighboring atoms overlap. If two spheres substantially overlap, then the atoms are almost certainly bonded, and conversely, if two spheres barely overlap, then the atoms are not bonded. Intermediate overlaps suggest weak bonding, for example, hydrogen bonding.

3. Click once on the right arrow key at the bottom left of the screen. This will move to the next molecule in the document, acetic acid dimer. Its name will appear at the bottom of the screen. If you make a mistake, use the backward or forward step keys to get to acetic acid dimer in the document. Switch to a space-filling model and look for overlap between the (OH) hydrogen on one acetic acid molecule and the (carbonyl) oxygen on the other. Return to a ball-and-spoke model and select Hydrogen Bonds from the Model menu. The two hydrogen bonds, that are responsible for holding the acetic acid molecules together, will be drawn.

Ball-and-Spoke model for acetic acid dimer with hydrogen bonds displayed

4. Distances, angles, and dihedral angles can easily be measured with Spartan Student using Measure Distance, Measure Angle, and Measure Dihedral, respectively, from the Geometry menu.

a) Measure Distance: This measures the distance between two atoms. Click once on to move to the next molecule, propene, and then select Measure Distance from the Geometry menu. Click on a bond or on two atoms (the atoms do not need to be bonded). The distance
Ångstroms) will be displayed at the bottom of the screen. Repeat the process for several atoms. When you are finished, select View from the Build menu (or click on the icon at the top of the screen).

b) **Measure Angle**: This measures the angle around a central atom. Click once on \( \text{H} \) to move to the next molecule, ammonia, and then select Measure Angle from the Geometry menu. Click first on H, then on N, then on another H. Alternatively, click on two NH bonds. The HNH angle (in degrees) will be displayed at the bottom of the screen. Click on when you are finished.

c) **Measure Dihedral**: This measures the angle formed by two intersecting planes, one containing the first three atoms selected and the other containing the last three atoms selected. Click once on \( \text{H} \) to move to the next molecule, hydrogen peroxide, then select Measure Dihedral from the Geometry menu and then click in turn on the four atoms (HOOH) that make up hydrogen peroxide. The HOOH dihedral angle will be displayed at the bottom of the screen. Click on when you are finished.

5. Energies, dipole moments and atomic charges among other calculated properties, are available from Properties under the Display menu.

a) **Energy**: Click once on \( \text{H} \) to move to the next molecule, acetic acid, and then select Properties from the Display menu. The Molecule Properties dialog appears.

This provides the energy for acetic acid in atomic units (Energy in au). Also provided is an estimate of the energy in water (Energy(aq) in au).
b) **Dipole Moment:** The magnitude of the dipole moment (**Dipole Moment** in debyes) is also provided in the **Molecule Properties** dialog. A large dipole moment indicates large separation of charge. You can attach the dipole moment vector, where the + side refers to the positive end of the dipole, to the model on the screen, by **checking** the box to the left of **Display Dipole Vector** near the bottom of the dialog.

c) **Atomic Charges:** To display the charge on an atom, **click** on the atom with the **Molecule Properties** dialog on the screen. The **Atom Properties** dialog replaces the **Molecule Properties** dialog.

**Electrostatic** atomic charges are given in units of electrons. A positive charge indicates a deficiency of electrons on an atom and a negative charge, an excess of electrons. Repeat for other atoms. Confirm that the positively-charged atom(s) lie at the positive end of the dipole moment vector. When you are finished, close the dialog. Select **Close** from the **File** menu (or **click** on ) to close the file.

**Part B: VSEPR Bond Geometries**

1. **Linear: Carbon Dioxide (CO₂)**

1. **Click** with the left mouse button on **File** from the menu bar. Then **click** on **New Build** from the menu that appears (or **click** on the icon at the top of the screen), then **clicking** on the **Inorganic** tab at the top of the Model Kit on the right hand side of the screen.

The inorganic model kit contains an atom bar (**clicking** on it will
bring up the Periodic Table) followed by a selection of atomic hybrids, then bond types, and finally Rings, Groups, Ligands, More and Clipboard menus (all except for Ligands are the same as found in the organic model kit).

Note: Spartan Student’s model kits connect atomic fragments (as well as groups, rings and ligands) through free valences. Any free valences that remain upon exiting a model kit are automatically converted to hydrogen atoms; it is not necessary to explicitly add hydrogens to open valences.

2. Click on the atom bar to bring up the Periodic Table.

   Select C in the Periodic Table and the two coordinate linear structure \( \text{---} \) from the list of atomic hybrids. Click on the green screen, a linear carbon will appear.

3. Click on the atom bar, select O in the Periodic Table and the one-coordinate entry \( \text{---} \) from the list of atomic hybrids. One after the other, click on the free valence positions of carbon. Red balls will appear bonded to carbon, indicating the presence of two oxygen atoms.

4. Select the double bond \( \text{——} \) and double click on the two bonds between carbon and oxygen.

5. Select Minimize from the Build menu.

6. Select View from the Build menu (or click on the \( \text{建} \) icon at the top of the screen). The model kit disappears, leaving only a ball-and-spoke model of carbon dioxide on screen. Practice rotating, translating (dragging), and zooming carbon dioxide using the directions given in Part A.
7. From the **Model** menu select **Configure** and under **Atom** select **Mass Number** and click **Apply**, then click **OK**.

Mass numbers will appear next to the individual atoms. Remove the atom labels by clicking to deselect **Labels** from the **Model** menu.

8. Select **Calculations...** from the **Setup** menu, and perform the following operations in the **Calculations** dialog which appears.

Select **Equilibrium Geometry** from the leftmost menu to the right of **Calculate**. This specifies optimization of equilibrium geometry. Select **Hartree-Fock** and then **3-21G** from the middle and right menus to the right of **Calculate**. This specifies a Hartree-Fock calculation using the 3-21G split-valence basis set. This method generally provides a reliable account of geometries. When you finish, **click** on **Submit** to start the calculation.

9. The **Save As** window appears. Enter a name for the file (carbondioxide, for example) and choose the folder you want the file saved in. (It’s a good idea to set up a folder for just Spartan files on your Desktop and save everything there.) **Click** on **Save**.

You will be notified that the calculation has been submitted.
Spartan Tutorial

10. You will be notified when the calculation has completed.

Click on OK to remove the message from the screen. Select Output from the Display menu. A window containing text output for the job appears.

You can scan the output from the Hartree-Fock calculation by using the scroll bar at the right of the window or by clicking (left button) on or inside the output window and using the scroll wheel on your mouse. The information at the top of the dialog includes the task, basis set, charge and multiplicity, as well as further details of the calculation.

Eventually, a series of lines appear, under the heading “Optimization”. These tell the history of the optimization process. Each line (or “Step”) provides results for a particular geometry. Ideally, the energy will approach a minimum value for an optimized (best) geometry. If the geometry was not optimized satisfactorily an error message, such as: “Optimization has exceeded N steps – Stop”, will be displayed following the last optimization cycle. If this were the case, you would have been notified that the job had failed, rather than seeing the
“completed” message dialog. Resubmit the calculation in this case.

*Click* on at the top of the output dialog to close it.

You may examine the total energy and dipole moment among other calculated properties without having to go through the output. Select **Properties** from the **Display** menu to bring up the **Molecule Properties** dialog.

![Molecule Properties dialog](image)

*Click* on an atom. The **(Molecule Properties)** dialog will be replaced by the **Atom Properties** dialog.

![Atom Properties dialog](image)

Among other things, this provides atomic charges. To obtain the charge on another atom, simply *click* on it. Inspect all the atomic charges on carbon dioxide (by *clicking* on the appropriate atoms). When you are finished, *click* on at the top of the **Atom Properties**
dialog to close it.

11. Select **Measure Angle** from the **Geometry** menu. Select the three atoms of the molecule. Note down the O-C-O angle that appears at the bottom of the screen.

12. Select **Surfaces** from either the **Setup** or **Display** menu. **Click** on **Add...** (at the bottom of the **Surfaces** dialog that results). Select **Electrostatic Potential Map**. (This is surface represents the electron richness (or poorness) of different areas of a molecule by using a rainbow of colors). If you have chosen the wrong surface, **click** on its description in the surface window and then **click** on **Delete** at the bottom of the window.

13. The graphics calculation should run automatically following your request. (However, if the **Status** indicates that it is **Pending**, go to the **Set Up** menu and chose **Submit**.) When it has completed, select **Electrostatic Potential Map** by **clicking** in the selection box (under O/I) in the **Surfaces** dialog. (If the rainbow colored surface does not appear go to the **Set Up** menu and chose **Submit**.) The surface itself corresponds to the electron density and provides a measure of the overall size and shape of carbon dioxide. The colors indicate values of the electrostatic potential on this surface; by convention, colors toward red correspond to negative potential (stabilizing interaction between the molecule and a positive charge), while colors toward blue correspond to positive potential. **Click** on the surface and a **Style** field will appear in the bottom right corner of the program window. **Change** the **Style** to **Transparent** and note which atom(s) are in the reddest areas and bluest areas.

14. Select **Close** from the **File** menu (or **click** on ) to remove carbon dioxide from the screen. Also, close any open dialogs.

**II. Trigonal Planar: Boron Trifluoride (BF₃)**

1. Bring up the inorganic model kit. **Click** on the atom bar to bring up the **Periodic Table**. Select (**click** on **B** in the **Periodic Table** and the three coordinate) from the list of atomic hybrids. **Click** on the screen.

3. Add fluorines to the open valence positions of boron. (This can be done in the inorganic
model kit, but it is easier to go to the organic model kit and choose –F.)

4. Select **Minimize** from the **Build** menu. Click on the model kit to remove the model kit.

5. Select **Calculations...** from the **Setup** menu. Specify calculation of **Equilibrium Geometry** using the **Hartree-Fock 3-21G** model. Submit the calculation.

6. Determine the final energy of boron trifluoride.

7. Determine the F-B-F bond angle and note it down.

8. Finally, calculate the electrostatic potential map and view the surface.

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**III. Tetrahedral: Chloroform (CCl₄)**

1. Bring up the organic model kit.

2. Select the tetrahedral carbon atom. Click on the screen.

3. Add chlorines to the open valence positions of carbon.

4. Select **Minimize** from the **Build** menu. Click on the model kit to remove the model kit.

5. Select **Calculations...** from the **Setup** menu. Specify calculation of **Equilibrium Geometry** using the **Hartree-Fock 3-21G** model. Submit the calculation.

6. Determine the final energy of chloroform.

7. Record the Cl-C-Cl bond angles.

8. Finally, calculate the electrostatic potential map and view the surface.

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**IV. Trigonal Bipyramidal: Phosphorus Pentachloride (PCl₅)**

1. Bring up the inorganic model kit.

2. Click on the atom bar to bring up the **Periodic Table**. Select (click on) P in the **Periodic Table** and the five coordinate from the list of atomic hybrids. Click on the screen.

3. Add chlorines to the open valence positions of phosphorus.

4. Select **Minimize** from the **Build** menu. Click on the model kit to remove the model kit.

5. Select **Calculations...** from the **Setup** menu. Specify calculation of **Equilibrium Geometry** using the **Hartree-Fock 3-21G** model. Submit the calculation.

6. Determine the final energy of boron trifluoride.

7. Record the Cl-P-Cl bond angles (something is a bit different about this molecule).

8. Finally, calculate the electrostatic potential map and view the surface.
V. Octahedral: Sulfur Hexafluoride (SF$_6$)

1. Bring up the inorganic model kit.
2. Click on the atom bar to bring up the Periodic Table. Select (click on) S in the Periodic Table and the six coordinate from the list of atomic hybrids. Click on the screen.
3. Add fluorines to the open valence positions of sulfur.
4. Select Minimize from the Build menu. Click on to remove the model kit.
5. Select Calculations... from the Setup menu. Specify calculation of Equilibrium Geometry using the Hartree-Fock 3-21G model. Submit the calculation.
6. Determine the final energy of sulfur hexafluoride.
7. Record the F-S-F bond angle.
8. Finally, calculate the electrostatic potential map and view the surface.

VI. Other Molecules

Use what you have learned to build NH$_3$, CHCl$_3$, and SeF$_4$. (Note: For SeF$_4$ you will need to delete one or more of the open valences (the yellow sticks), go to the Build menu and choose Delete then click on the open valence.) Make sure you use VSEPR rules and create molecules with the correct molecular geometry. Record bond angles and energies. Create and inspect the electrostatic potential map.

Remember to log onto Sapling and complete the assignment.