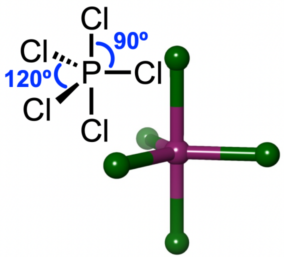
VSEPR Theory

Created with: Release 2021-3
Prerequisites: working knowledge of Maestro
Files Supplied: VSEPR_theory_worksheet, glycine.mae
Categories: high school, general chemistry 1

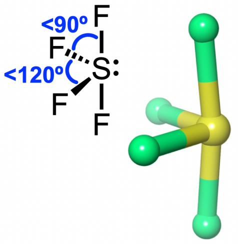
About this Lesson

In this lesson plan, students will examine the three-dimensional shapes and sizes of molecules through the VSEPR model by analyzing their bond angles and bond lengths. Starting with Lewis structures, students will identify the regions of electron density around a central atom and analyze the best fit molecular geometry.

Using Maestro, students will build and optimize molecular geometries with Jaguar and measure bond distances and angles to predict geometric arrangements. These calculations will help with visualizing how certain geometries better minimize electron repulsions than others.



Trigonal Bipyramidal



Sawhorse or seesaw

Learning Objectives

- Use Lewis structures and the valence shell electron-pair repulsion (VSEPR) model to create and predict shapes of molecules
- Perform quantum mechanical calculations to optimize molecular geometries and measure bond distances and angles of various small molecules

Standards

- *NY State Core Curriculum*
  - Explain properties of materials in terms of arrangement and properties of the atoms that compose them (Standard 4, Key Idea 3.1)
- *Connections to AP*
  - VSEPR and Bond Hybridization (SAP 6)
- *ACS Guidelines*
  - Understand molecular structure and bonding (Section 5.2)
- *ETS Chemistry GRE*
  - Inorganic Chemistry – General Chemistry on Molecular Substances (2.C)
- *AAMC MCAT*
  - Nature of molecules and intermolecular interactions (5B)

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 molecular geometries and Lewis structures
- Visual assessment of student-generated optimized geometries and measurements

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

Watch the Khan Academy videos on VSEPR theory.

1) Carbonate, CO_3^{-2}, is a common polyatomic ion found in various materials from eggshells to antacids. Draw the Lewis structure of CO_3^{-2} and assign formal charges.
2) What is its electron domain geometry?
3) What is its molecular geometry?

Lesson Outline

1. What you will need for this lesson

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 “VSEPR_Theory” and copy folder to Desktop
    - Here, you will find the lesson plan, worksheet, and any additional resources

Figure 1-1. Open Maestro

3. Open **Maestro**
    a. See Starting Maestro if you need help

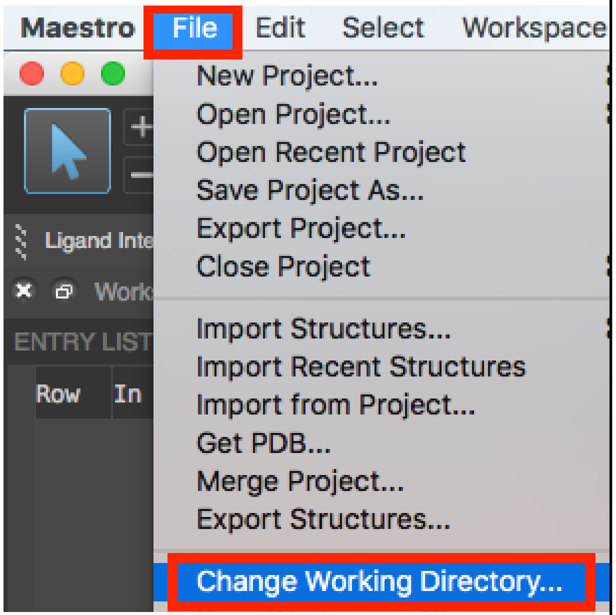


Figure 1-2. Change Working Directory option.

4. Go to **File > Change Working Directory**
5. Find your “VSEPR_Theory” folder that you duplicated to your Desktop, and click **Choose**

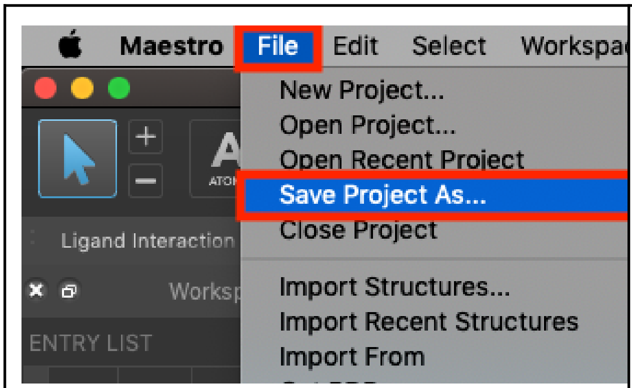
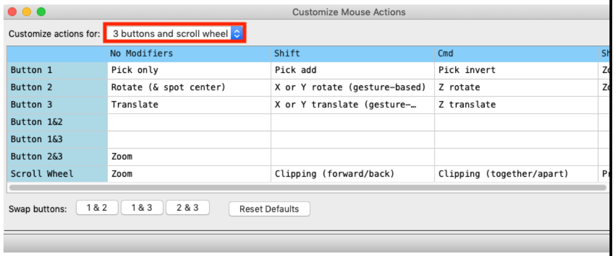


Figure 1-3. Save Project panel.

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



Customize actions for: 3 buttons and scroll wheel

	No Modifiers	Shift	Cmd	Sh
Button 1	Pick only	Pick add	Pick invert	Zo
Button 2	Rotate (& spot center)	X or Y rotate (gesture-based)	Z rotate	Zo
Button 3	Translate	X or Y translate (gesture-…	Z translate	
Button 1&2				
Button 1&3				
Button 2&3	Zoom			
Scroll Wheel	Zoom	Clipping (forward/back)	Clipping (together/apart)	Pr

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

8. Finally, check your **Mouse Actions**
    a. PC : **Edit > Customize Mouse Actions**
    b. Mac : **Workspace > 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. Molecular Shapes and the VSEPR Model

The shape of a molecule is three-dimensional and its molecular bonds can be described in terms of their distances, angles, and relative arrangements in space. A **bond angle** is the angle between any two bonds that include a common atom, usually measured in degrees. A **bond distance** (or bond length) is the distance between the nuclei of two bonded atoms along the straight line joining the nuclei. Bond distances are measured in Ångstroms (1 Å = 10^{-10}m) or picometers (1 pm = 10^{-12}m, 100 pm = 1 Å).

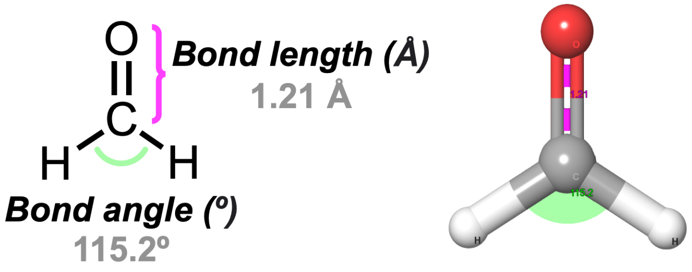


Figure 2-1. Bond distances (lengths) and angles are shown for the formaldehyde molecule, CH_2O.

Majority of the molecules you will be seeing have the general formula of "AB_n" where the central atom "A" is bonded to "*n*" number of "B" atoms. For example, the molecule carbon dioxide or CO_2 is an AB_2 molecule where carbon is the central atom "A" that is connected to 2 oxygen atoms, or "B_2". Another example is ammonia or NH_3 which is an AB_3 molecule. The number of shapes possible for AB_n molecules depends on the value of *n*. An AB_2 molecule can either be *linear* (bond angle = 180º) or *bent* (bond angle ≠ 180º). An AB_3 molecule also has two different shapes. If the A atom lies in the same plane as the B atoms, the shape is called *trigonal planar* (bond angles = 120º). However, if the A atom lies above the plane of the B atoms, the shape is called *trigonal pyramidal* (various bond angles).

3. The VSEPR Model

The valence shell electron-pair repulsion model (VSEPR) model allows us to predict the molecular structure, including approximate bond angles around a central atom, of a molecule simply by examining the number of bonds and lone pair of electrons in its Lewis structure. The VSEPR model assumes that electron pairs in the valence shell of a central atom will adopt an arrangement that minimizes repulsions between electron pairs by maximizing the distance between them.

Recall that a single covalent bond between two atoms is made up of a *bonding pair of electrons*, which is the region in which the electrons are most likely to be found. This region is called an **electron domain**. A *nonbonding pair of electrons*, also called a nonbonding lone pair, defines an electron domain that is located on one specific atom. Shown below is the Lewis structure of ammonia or NH_3 which consists of a total of four electron domains around the central nitrogen atom – three bonding pairs as shown by single bonds, and one nonbonding pair as represented by 2 dots.

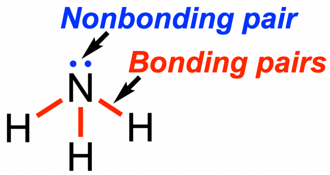


Figure 3-1. Lewis structure of NH_3

Each multiple bond (i.e. double bonds, triple bonds) constitutes a single electron domain. For example, carbon dioxide or CO_2 contains two electron domains around the central carbon atom – two bonding pairs as shown by each double bond.

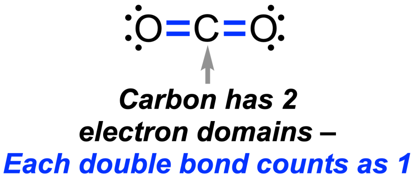


Figure 3-2. Lewis structure of CO_2

We can use the following steps of the VSEPR model to predict the shapes of molecules or ions:

1) Draw the Lewis structure of the molecule or ion and be sure to draw all nonbonding lone pairs of electrons if necessary.
2) Count the number of electron domains around the central atom. Remember that each nonbonding electron pair, single bond, double bond, and triple bond count as *one electron domain* each.
3) Identify the *electron domain geometry* based on the number of electron domains: linear, trigonal planar, tetrahedral, trigonal bipyramidal, or octahedral (Table X, first column).
4) Use the number of nonbonding lone pairs to determine the *molecular geometry*. If more than one arrangement of lone pairs and chemical bonds is possible, choose the one that will minimize electron repulsions. Remember that the magnitude of electron repulsion is greatest between nonbonding regions and decreases as follows:
   lone pair–lone pair > lone pair–bonding pair > bonding pair–bonding pair

The following table represents electron domain and molecular geometries for various domains around a central atom with examples for each.

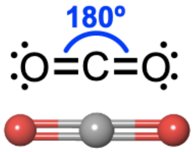
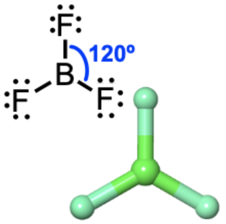
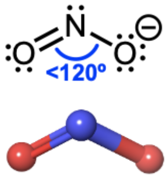
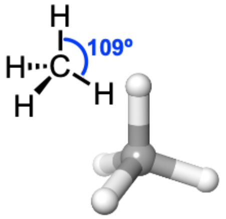
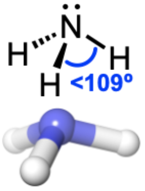
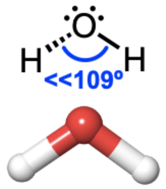
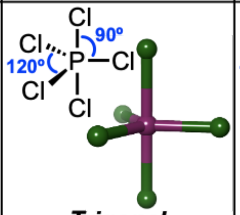
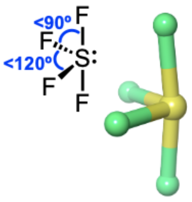
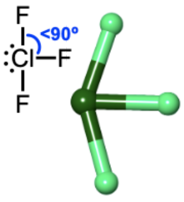
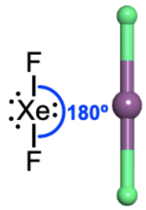
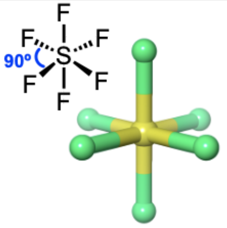
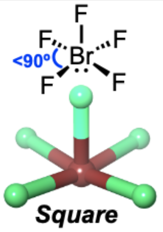
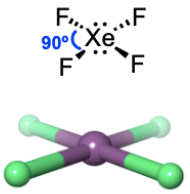
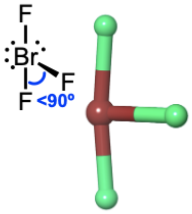
Number of Electron Domains	Electron Domain Geometry; 0 Nonbonding Lone Pairs	1 Nonbonding Lone Pair	2 Nonbonding Lone Pairs	3 Nonbonding Lone Pairs
2	 ***Linear***			
3	 ***Trigonal Planar***	 ***Bent or angular***		
4	 ***Tetrahedral***	 ***Trigonal pyramidal***	 ***Bent***	
5	 ***Trigonal Bipyramidal***	 ***Sawhorse or seesaw***	 ***T-shape***	 ***Linear***
6	 ***Octahedral***	 ***Square Pyramidal***	 ***Square Planar***	 ***T-shape***

Table 3-1. Electron Domain and Molecular Geometries using the VSEPR Model

Example #1. Draw the Lewis structure for $SeCl_2$. Then, determine the number of electron domains and predict the electron domain and molecular geometry of $SeCl_2$ using the VSEPR model. *Hint: Determine which atom is the central atom and don't forget about the octet rule!*

- Lewis structure:

- # of electron domains (including lone pairs):

- Electron domain geometry:

- Molecular geometry:

<u>Computational Exercise #1:</u> Geometry Optimization using Maestro

Although the Lewis structure of $SeCl_2$ looks relatively flat and two-dimensional, now we are going to build a three-dimensional structure of $SeCl_2$ and then optimize its geometry using Maestro. Visualizing the molecular structure can be done in three different ways: 1) Through the 2D Sketcher, 2) Through the 3D Builder, or 3) By importing pre-built molecules. We will be using the 3D Builder tool in Maestro.

This computational exercise consists of 3 parts:

1) Build $SeCl_2$ using the 3D Builder
2) Optimize the Geometry using Quantum Mechanic DFT Calculations
3) Measure the Bond Lengths and Angles in $SeCl_2$

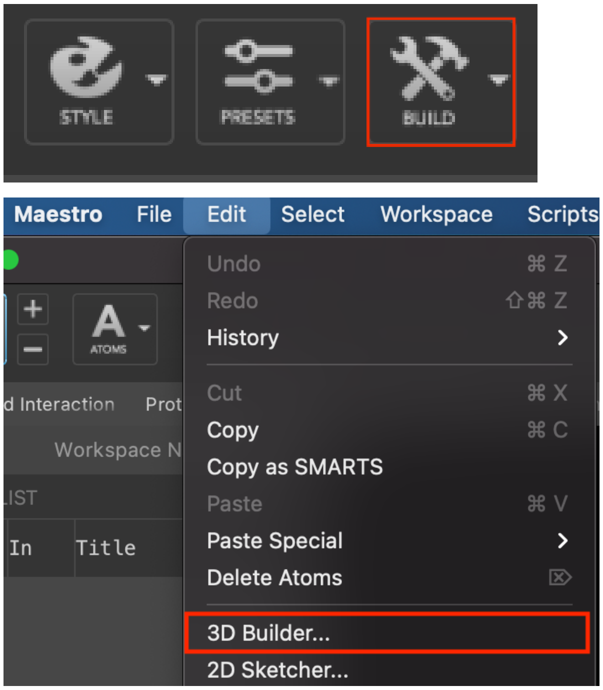


Figure 3-3. Open 3D Builder.

Part 1. Build $SeCl_2$ using the 3D Builder

Before optimizing any molecular geometry, you will need a starting molecule in your workspace. Let's draw the structure of $SeCl_2$ using the 3D Builder

1. Click the **Build** button, or Go to **Edit** > **3D Builder**

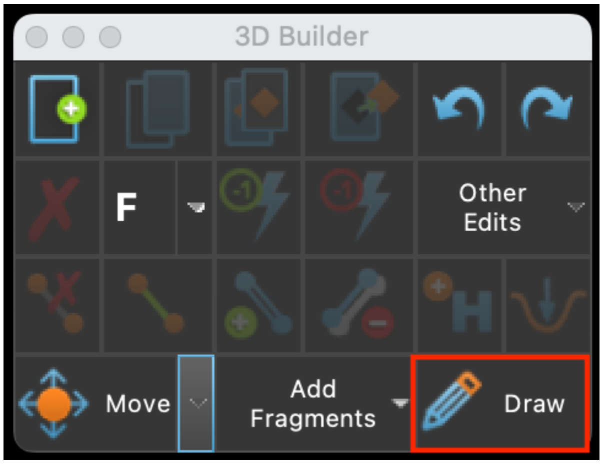
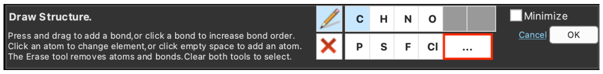


Figure 3-4. 3D Builder window appears.



Draw Structure.

Press and drag to add a bond,or click a bond to increase bond order.
Click an atom to change element,or click empty space to add an atom.
The Erase tool removes atoms and bonds.Clear both tools to select.

Figure 3-5. Drawing banner opens.

2. Click **Draw** in the 3D Builder panel
    - A selection window will open
    - Click the 3 dots to open a periodic table of elements
    - Click Se for Selenium and place an Se atom anywhere in the workspace
3. Notice that SeH_2 was placed in the workspace. Go back to the periodic table of elements, click Cl for chlorine and then replace each H atom with Cl by clicking on them

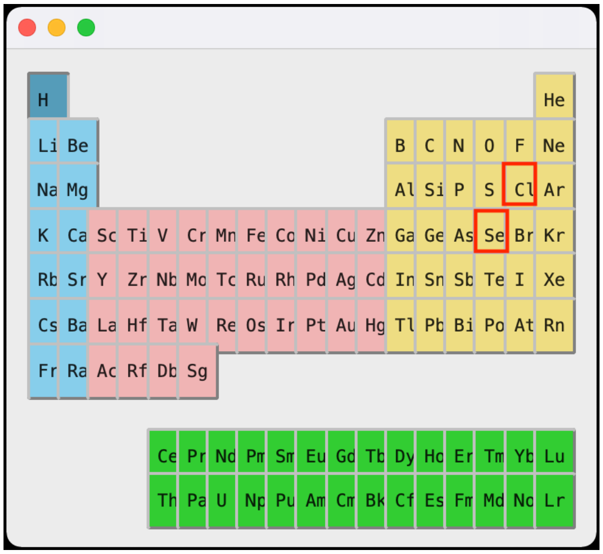


Figure 3-6. Periodic table of elements opens.

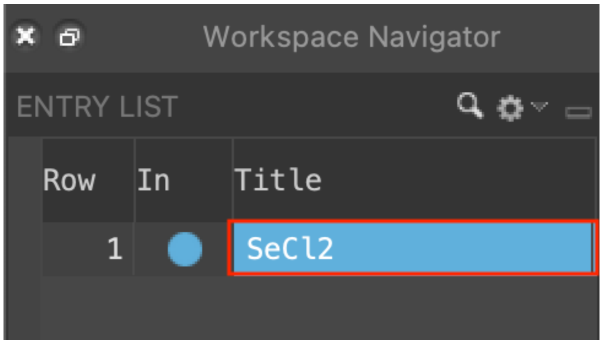


Figure 3-7. Changing the entry name to $SeCl_2$.

4. Change the name in the Entry List to SeCl2 by double clicking on the structure name.

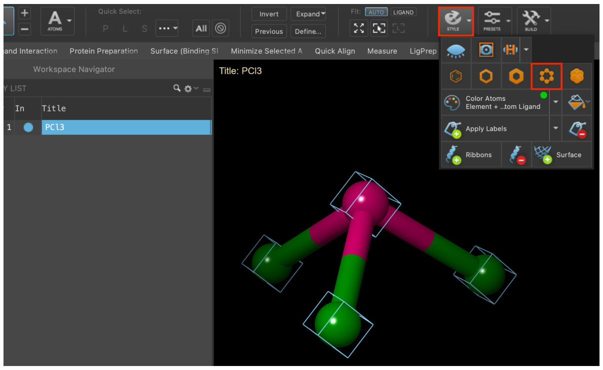
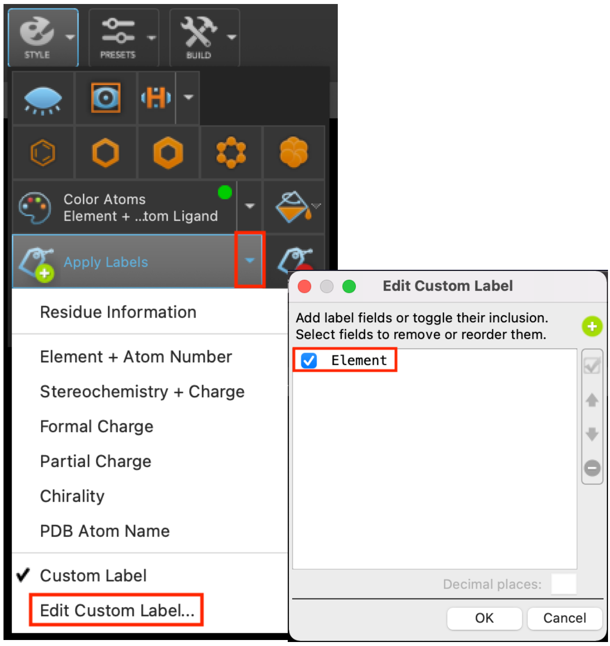


Figure 3-8. Viewing and styling $SeCl_2$.

6. Close the 3D Builder panel
    - ○ The $SeCl_2$ molecule is <u>selected</u> in the entry list and <u>included</u> in the <u>workspace</u>
7. Change the representation to ball-and-stick by clicking on the **Style** menu and choosing **Apply ball-and-stick representation**
8. Change the color of the atoms by clicking on the **Style > Color Atoms > Element + Custom Ligand**



Add label fields or toggle their inclusion.
Select fields to remove or reorder them.

Figure 3-9. Labeling atoms.

Figure 3.10. Toggling labels on.

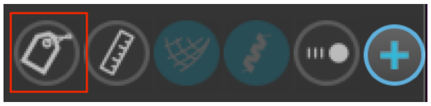


Figure 3.11. Toggling labels off.

9. To display atom labels, click **Style > Apply Labels** then click the drop down arrow on the right side
10. Click **Edit Custom Labeling**
11. Checkbox **Element** and press **OK**
12. 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

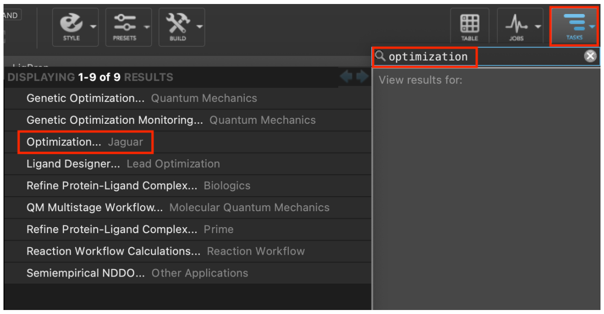
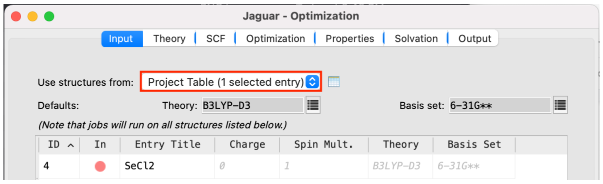


Figure 3.12. Opening the Jaguar Optimization panel.

Part 2. Optimize the Geometry using Quantum Mechanic DFT Calculations

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

13. With the $SeCl_2$ entry selected and included, go to **Tasks > Optimization** using Jaguar



Use structures from: Project Table (1 selected entry)

Defaults: Theory: B3LYP-D3 Basis set: 6-31G**

(Note that jobs will run on all structures listed below.)

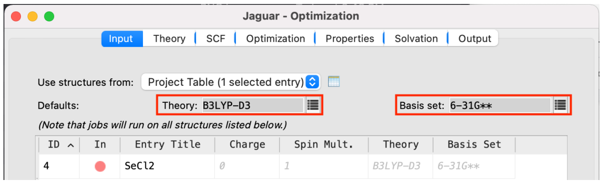
ID	In	Entry Title	Charge	Spin Mult.	Theory	Basis Set
4	●	SeCl2	0	1	B3LYP-D3	6-31G**

Figure 3.13. Setting the Jaguar Optimization panel to optimization.

- ○ The Jaguar Optimization panel opens

14. Use structures from **Project Table (1 selected entry)**

Note: We are optimizing one molecule, $SeCl_2$. By selecting many molecules in the entry list, we can optimize as many molecules as we would like concurrently with the same QM settings.



Use structures from: Project Table (1 selected entry)

Defaults: Theory: B3LYP-D3 Basis set: 6-31G**

(Note that jobs will run on all structures listed below.)

ID	In	Entry Title	Charge	Spin Mult.	Theory	Basis Set
4	●	SeCl2	0	1	B3LYP-D3	6-31G**

Figure 3.14. Setting the QM parameters for optimization.

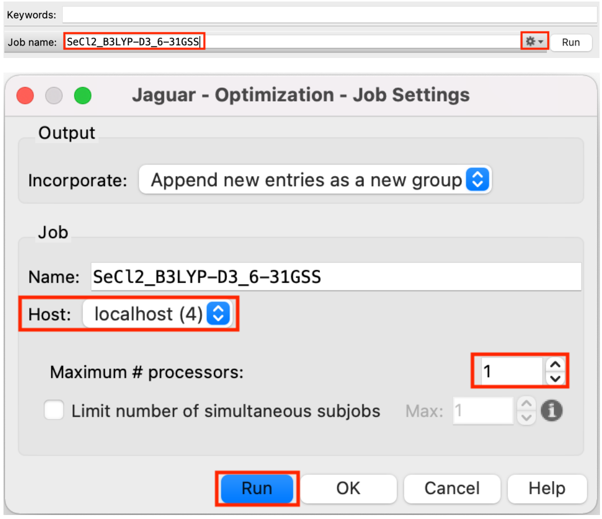
Various settings can be altered depending on the specific use case. We will only adjust the *Input* tab for this example.

15. For *Theory*, select B3LYP-D3
16. 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, $SeCl_2$ 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


Keywords:
Job name: SeCl2_B3LYP-D3_6-31GSS

Jaguar - Optimization - Job Settings

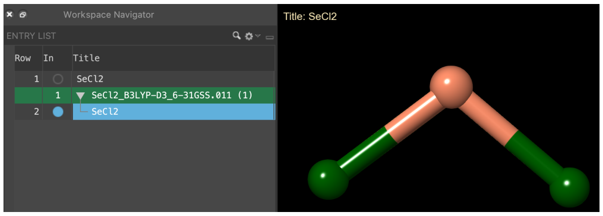
Output
Incorporate: Append new entries as a new group

Job
Name: SeCl2_B3LYP-D3_6-31GSS
Host: localhost (4)
Maximum # processors: 1
☐ Limit number of simultaneous subjobs Max: 1

Figure 3-15. Naming and running the job.

17. Change the *Job name* to **SeCl2_B3LYP-D3_6-31GSS**
    - Usually we incorporate stars (*) and pluses (+) into file names with S and P, respectively
18. Adjust the job settings (⚙▾) as needed
    - This job requires a CPU host and should complete in under 5 minutes
19. Click **Run**

Note: It is advised to also add in a *Vibrational frequencies* calculation (from the *Properties* tab). This involves a bit more computational expense, but is a useful way to be sure that your output is a minimum (as opposed to a maximum) on the Potential Energy Surface (PES). For more detail, see the Locating Transition States tutorial.

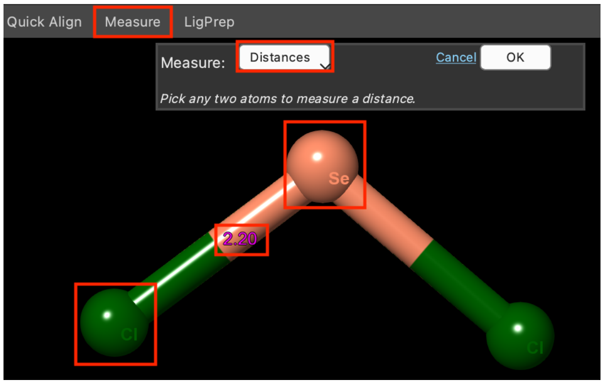


1 SeCl2
1 SeCl2_B3LYP-D3_6-31GSS.011 (1)
2 SeCl2

Figure 3-16. The output molecule of $SeCl_2$.

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

20. A new entry group is added to the entry list titled SeCl2_B3LYP-D3_6-31GSS.011 (1). Select and include the molecule titled SeCl2 in this sub-group. This is your optimized structure.

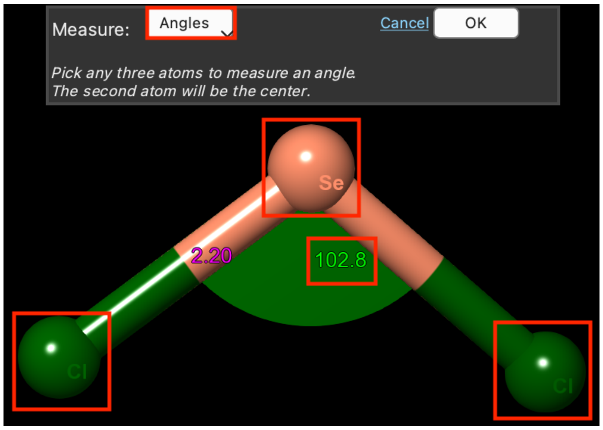


Pick any two atoms to measure a distance.

Figure 3-17. Measure the Se–Cl distance.

Part 3. Measure the Bond Lengths and Angles in $SeCl_2$

21. Go to **Workspace > Measure** (or click **Measure** in the Favorites toolbar)
    - A banner appears at the top of the workspace for defining measurements
22. With **Distances** selected for *Measure*, select one Cl atom and the Se atom.
    - The Se–Cl distance is labeled



Pick any three atoms to measure an angle.
The second atom will be the center.

Figure 3-18. Measure the Cl–Se–Cl angle.

23. Switch the *Measure* option to **Angles** and select one chlorine, then the phosphorus, and then another chlorine
    - The Cl–Se–Cl angle is labeled
24. Click **OK** to close the measurement banner

We can see that after $SeCl_2$ was optimized, the Se–Cl bond length is equal to 2.20Å and a Cl–Se–Cl bond angle of 102.8º.

VSEPR Model Analysis of $SeCl_2$:

Lewis Structure with predicted bond angles of $SeCl_2$ using the VSEPR Model:	**Optimized geometry of $SeCl_2$ using Maestro:**

Number of electron domains in $SeCl_2$:
Electron domain geometry:
Molecular geometry:
Predicted Cl–Se–Cl bond angle:
Calculated Cl–Se–Cl bond angle:

4. Effects of Nonbonding Electrons and Multiple Bonds on Bond Angles

Electron domains for nonbonding electron pairs exert greater repulsive forces on adjacent electron domains and tend to compress bond angles. VSEPR theory predicts these distortions by establishing an order of repulsions and an order of the amount of space occupied by different kinds of electron pairs. The order of electron-pair repulsions from greatest to least repulsion is:

lone pair-lone pair > lone pair-bonding pair > bonding pair-bonding pair

This order of repulsions determines the amount of space occupied by different regions of elections. A nonbonding lone pair of electrons occupies a larger region of space than a triple bond; in turn, electrons in a triple bond occupy more space than those in a double bond, and so on. The order of sizes from largest to smallest is:

lone pair > triple bond > double bond > single bond

Let’s see this taken into effect in the following examples.

Example #2. For each molecule below, (i) draw the Lewis structure with nonbonding electrons, (ii) determine the number of nonbonding lone pairs and bonding pairs on the central carbon atom, and (iii) predict the electron domain and molecular geometries using the VSEPR model.

	Lewis Structure	# of Nonbonding Lone Pairs on Carbon(s)	# of Bonding Pairs on Carbon(s)	Electron Domain Geometry	Predicted Molecular Geometry
HCN					
C_2H_4					
CH_3F					

Computational Exercise #2. For each molecule from Example #2, optimize each of their geometries using the DFT methods listed below. Then, determine all of the bond lengths and angles in each molecule. Check if your calculated measurements match the predicted values from your proposed molecular geometries based on the VSEPR method.

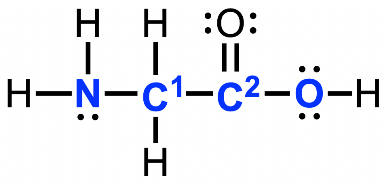
- **Theory:** B3LYP-D3
- **Basis set:** 6-31G** (6-31GSS)

	Optimized Geometry using Maestro	Bond Angles	Bond Distances	Predicted Molecular Geometry
HCN				
C_2H_4				
CH_3F				

5. Molecular Structure in Multicenter Molecules

So far, the majority of the molecules we have looked at only have one central atom. When a molecule or polyatomic ion has only one central atom, the molecular structure completely describes the shape of the molecule. Larger molecules, however, do not have a single central atom, but rather are connected by a chain of interior atoms that each possess a “local” geometry. The way these local structures are oriented with respect to one another also influences the molecular shape. For the scope of an introductory or general chemistry course, we will only focus on determining the local structures.

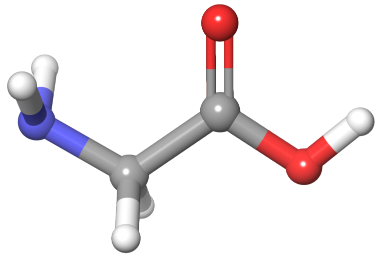
Example #3. The Lewis structure for the simplest amino acid, glycine, or $H_2NCH_2CO_2H$, is shown below. Predict the local geometry for the nitrogen atom, the two carbon atoms (labeled as C1 and C2), and the oxygen atom with a hydrogen atom attached. These atoms are also bolded in blue.



	# of Nonbonding Lone Pairs	# of Bonding Pairs	Electron Domain Geometry	Predicted Molecular Geometry
N				
C^1				
C^2				

O				

Computational Exercise #3. Go to File > Import Structures > Open Glycine.mae into your project file. Using the optimized structure of glycine, determine the following bond angles and see if your molecular geometry predictions from the VSEPR model match the calculated structure.



	Bond Angle	Predicted Molecular Geometry
N	H–N–H angle:	
C^1	N–C–C angle: N–C–H angle:	
C^2	O–C–O angle:	
O	H–O–C angle:	

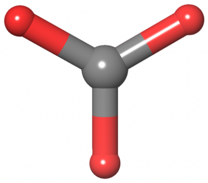
Analysis:

6. Individual Exercises

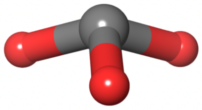
Part A: For each molecule below, (i) draw the Lewis structure with nonbonding electrons, (ii) determine the number of nonbonding lone pairs and bonding pairs on the central atom highlighted in blue, and (iii) predict the electron domain and molecular geometries using the VSEPR model.

	Lewis Structure	# of Nonbonding Lone Pairs on Central Atom	# of Bonding Pairs on Central Atom	Electron Domain Geometry	Predicted Molecular Geometry
H_3CNH_2					
BH_3					
ClF_3					

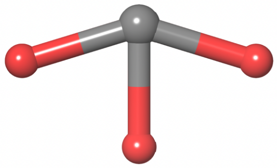
Part B: Shown below are ball-and-stick representations of three different AB_3 molecules where all “A” atoms are grey and all “B” atoms are red. Match the three molecules from Part A to the closest ball-and-stick representation and explain your reasoning. Remember to focus on the geometries around the *central atom*.



Molecule A



Molecule B



Molecule C

- Molecule A is ___________ because…

- Molecule B is ___________ because…

- Molecule C is ___________ because…

Part C: For each molecule from Part A, optimize each of their geometries using the DFT methods listed below. Then, determine all of the bond lengths and angles in each molecule. Check if your calculated measurements match the predicted values from your proposed molecular geometries based on the VSEPR method.

- **Theory:** B3LYP-D3
- **Basis set:** 6-31G** (6-31GSS)

	Optimized Geometry using Maestro	**Bond Angles**	**Bond Distances**	**Predicted Molecular Geometry**
H_3CNH_2				
BH_3				
ClF_3				

7. Summary, Additional Resources, and References

In this lesson, you learned about the VSEPR model and how it predicts the three-dimensional arrangement of atoms in a molecule. It states that valence electrons will assume an electron-pair geometry that minimizes repulsions between areas of high electron density (bonds and/or lone pairs). Molecular structure, which refers only to the placement of atoms in a molecule and not the electrons, is equivalent to electron-pair geometry only when there are no nonbonding lone pairs around the central atom.

Using Maestro, a simple geometry optimization using Jaguar can be performed to not only visualize a molecule's structure but also analyze bond lengths and angles. Calculated molecular geometries can be used to ensure one's VSEPR prediction is correct.

For further learning:

- 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

8. 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