

Molecular Shapes Laboratory

Introduction to VSEPR Theory

This laboratory introduces the concept of Valence Shell Electron Pair Repulsion (VSEPR) theory and the molecular geometry and bonding that it describes. In this exercise, we use VSEPR theory to predict the shapes of various molecules. This process is critical to a proper understanding of general chemistry. The VSEPR theory's description of bonding is also essential to a detailed comprehension of chemical properties and reactions.

VSEPR theory deals with covalent bonding in molecules (bonding that shares pairs of electrons between two or more atoms). By assigning electrons to bonding and non-bonding pairs and distributing these pairs of electrons around an atom, it is possible to predict the preferred spatial arrangement of bonds by simply spacing the electrons as far apart from each other as possible. To determine this arrangement, you must first sketch a **Lewis structure** of the molecule. Next, use the Lewis structure to find the **steric number** of the central atom or atoms. The steric number determines the **electron group geometry** and **hybridization**. The **ligand number** is the number of atoms which are bonded to the central atom. The **molecular shape** is determined by the electron group geometry and the ligand number.

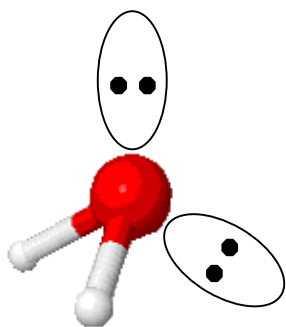


Figure 1: Steric number = 4, tetrahedral electron group geometry of H_2O



Figure 2: Ligand number = 2, bent molecular shape of H_2O

Figures 1 and 2 illustrate the difference between electron group geometry and molecular shape. On the next page, Table 1 lists the possible molecular shapes and how they are derived from steric numbers, electron group geometries, and ligand numbers.

Steric #	Electron Group Geometry	Ligand #	Molecular Shape	Bond Angles
2	Linear	2	Linear	180
3	Trigonal plane	3	Trigonal plane	120
		2	Bent	<120
4	Tetrahedron	4	Tetrahedron	109.5
		3	Trigonal pyramid	<109.5
		2	Bent	<109.5
5	Trigonal bipyramid	5	Trigonal bipyramid	120, 90
		4	See-saw	<120, <90
		3	Tee	<90
		2	Linear	180
6	Octahedron	6	Octahedron	90
		5	Square pyramid	<90
		4	Square planar	90

Table 1: Molecular Shapes

We will be using computer models to verify the VSEPR predictions we make. These models have been validated by experiment, so we will not need to experimentally measure any molecules. In later chemistry courses, you will have the opportunity to learn some of the methods that are used to test computational models.

Orbital Overlap Sketches

The best way to visualize the electron pair repulsion described by the VSEPR theory is to draw a geometric representation of each model that we will call an **orbital overlap sketch**. The sketch will display each atom, represented by a letter or two of text, surrounded with lone pair and bonding pair electrons. Covalent bonding pairs of electrons can come in two varieties: sigma (σ) and pi (π) bonds. Each of these will be represented by a different geometry that is clearly visible in the orbital overlap sketch. An orbital overlap sketch for ethene (also known as ethylene, C_2H_4) is shown in Figure 3.

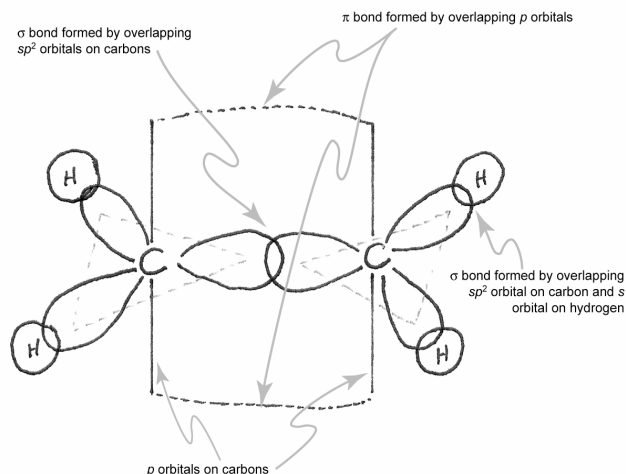


Figure 3. Orbital overlap sketch of ethene.

In this sketch, each carbon atom is represented by a C and each hydrogen atom by an H, and they are spaced apart to make the best possible two-dimensional representation of a three-dimensional molecule. On each H atom is a spherical $1s$ shell of electron density that is used in bonding, and on each C atom are three oval sp^2 orbitals that construct a σ bond between each C and H and between the two carbons. There is a shared pair of electrons in each of these σ bonds. There is also a π bond in ethene, shown as the “goalposts” above and below the plane of the rest of the C_2H_4 molecule. A dashed line above and below the central σ bond represents the single π bond in this molecule.

It is possible to have two π bonds and one σ bond between a pair of atoms, as shown in ethyne (also known as acetylene, C_2H_2) in Figure 4.

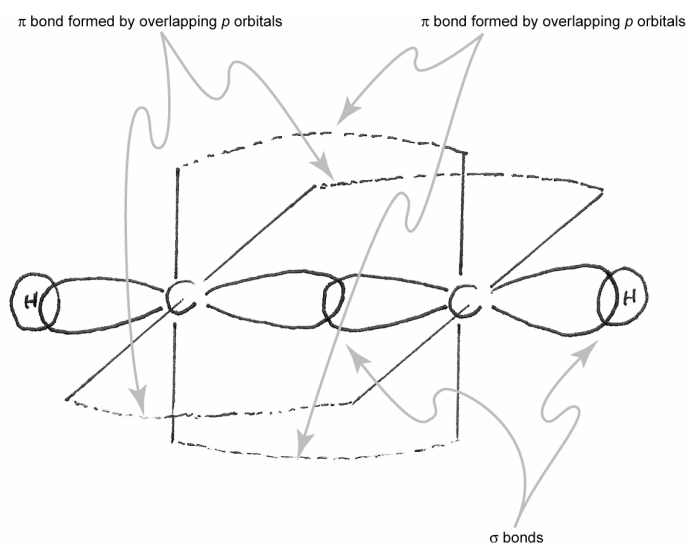


Figure 4. Orbital overlap sketch of ethyne.

In this case the orbital overlap sketch clearly shows the space in front and behind, as well as above and below the central σ bond as being occupied by shared pairs of electrons in each of two π bonds.

As the molecules get more complicated, so does the molecular geometry and the corresponding orbital overlap sketch. When there are many atoms in a molecule, there will be an associated molecular geometry of electron pairs around each atom (except for hydrogen). A typical orbital overlap sketch is shown for acetic acid in Figure 5.

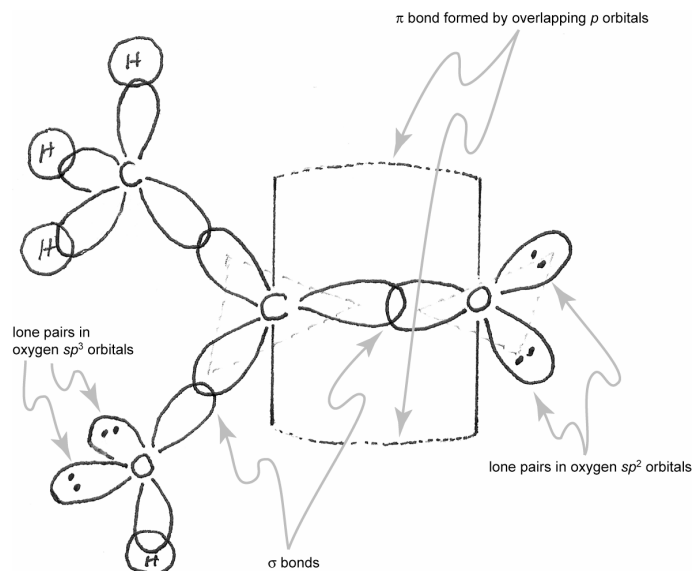


Figure 5. Orbital overlap sketch of acetic acid.

Note that with a correct sketch, it is possible to look at acetic acid and decide instantly that there must be seven σ bonds, one π bond, and four pairs of non-bonding electrons (indicated by the orbitals around each oxygen atom that have a pair of dots in them). It is also possible to see that the electron group geometry around the outer carbon atom is tetrahedral, while the electron group geometry around the central carbon atom is trigonal planar. This demonstrates some of the power of a clear orbital overlap sketch. By indicating the lone-pair electrons as orbitals with dots in them, it is possible to visualize the electron group geometry and realize that the carbon-oxygen-hydrogen bond angle is not linear in this molecule. Because of repulsion from the two lone pairs of electrons about the oxygen atom, this bond angle is “bent” in shape.

In the following exercises, you are asked to construct a Lewis dot diagram of each molecule and determine the electron group geometry and molecular shape. You must then use this information to construct a correct orbital overlap sketch for each molecule. You will then get to check your prediction against the computer model for each structure, and learn the value of orbital overlap sketches.

WebMO

WebMO is a computational chemistry interface that allows you to access intensive computational programs. These programs can, among other things, optimize molecular geometries, construct molecular orbitals, and determine vibrational frequencies. The following instructions are a basic outline for building a molecule and performing a calculation on it.

1. To access WebMO, open a web browser and go to <http://curie.chem.hope.edu>. Click the WebMO button on the left side of the page. On the next page, choose

the General Chemistry link. Login to WebMO with the user name and password provided by your instructor. You will be taken to the WebMO Job Manager. From this page you can create new jobs and view completed jobs.

2. Create a new job by clicking the New Job tab. Click “Open Editor.” The screen that comes up will look like the figure on the next page.

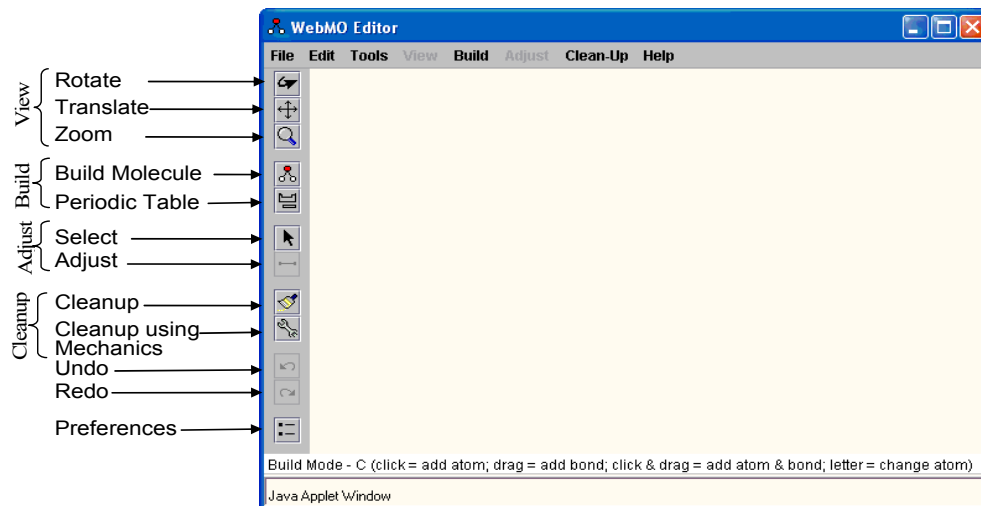











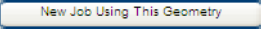


Figure 6: WebMO Editor

The following is a brief description of the editor’s capabilities. Use this as a reference when constructing your own molecules.

- a. View mode – Rotate , translate , and zoom  allow you to manipulate your view of the structure.
 - b. Build mode – The build molecule button  allows you to add atoms and bonds to your molecule. Use the periodic table  to select the atom you wish to add.
 - c. Adjust mode – The select arrow  allows you to determine characteristics of an atom or groups of atoms. If just one atom is selected, its charge and hybridization will be shown at the bottom of the screen. To adjust either of these, right click on the atom. To select additional atoms, hold the Shift key while clicking. If two atoms are selected, the distance between them is displayed. If three or four are selected, the display will show the magnitude of a bond angle or dihedral angle. If multiple atoms are selected, the bond length, angle, or dihedral angle can be manually changed with the adjust button.
 - d. Clean-up – The comprehensive cleanup  adds hydrogens to all unfilled valencies, gives each atom the correct hybridization, and idealizes all the bond angles and bond lengths. A comprehensive cleanup with mechanics  does all this and then tries to put the molecule in its most stable conformation. If you do not want to do everything a comprehensive clean-up does, you can choose options individually from the Clean-Up menu.
3. To begin building a molecule, choose the atom you want from the periodic table. Click the screen to add it. To create a new atom bonded to this one, click the atom and drag to an empty area. Bonds can also be drawn between two existing atoms.

When you are finished building the molecule, perform any necessary clean-up steps. To continue, close the editor and click .

4. At the Choose Computational Engine page, select the desired engine. Click  to move to the Job Options page. Here you must give your job a unique name beginning with your initials, specify the type of calculation (always perform a geometry optimization as your first job with any molecule), provide the charge and multiplicity, and fill any other fields required by the engine. Click  once again to submit the job and return to the Job Manager.
5. When the Job Manager first loads, your job's status will be "queued." If you click the Refresh tab, it will most likely either be "running" or "completed." If you do not click the tab, the page will refresh itself after several seconds. Calculations in this exercise should not take more than one or two minutes.
6. You can view your results by clicking on the job name. In addition to looking at the tables on the View Job page, you can measure the geometry by using the select arrow, just as you could in the editor. If you wish to do any further analysis, simply click . You will be taken back to the Build Molecule page, with your optimized molecule already built.

Pre-Lab Exercise

Consider the molecule H₂O and perform each of the following tasks in your laboratory notebook.

1. Sketch the Lewis structure for H₂O.
2. Determine the steric number of the oxygen atom.
3. What is the electron group geometry?
4. What is the hybridization of the oxygen atom?
5. How many lone pairs are around the oxygen atom?
6. What is the ligand number of the oxygen atom?
7. What is the molecular shape?
8. Draw an orbital overlap sketch of the molecule.

You should bring your Olmsted and Williams textbook to this laboratory as it contains many useful references for the Lewis structures, hybridization, and orbital overlap sketches that you will be asked to perform.

Procedure

This week you will be analyzing a variety of molecules through the use of physical and computational models. As you study these models, you will record information about them in your notebook. Your report will consist of information from your notebook as well as the pre-lab and post-lab questions. For each molecule you work with, you must do the following:

1. Sketch a Lewis structure for the compound.
2. Determine the steric number for the central atom.

3. Use the steric number to determine the electron group geometry and hybridization.
4. Determine the molecular shape, taking ligand number into account.
5. Draw an orbital overlap sketch of the compound.
6. Build a model of the compound using the modeling kit.
7. Use WebMO to build and compute the optimized geometry.
8. Compare your VSEPR molecular shape and your optimized WebMO structure.
9. Answer any detailed questions that require additional analysis. Any such questions will appear in the instructions for that molecule.

Part I: Instructor-led calculation – NH₃

In Part I of this experiment, you will follow along with the instructor as he or she performs a VSEPR analysis of a molecule and then uses WebMO to analyze it computationally. Before you begin, you will want to create a folder to allow you to easily find your jobs. On the left side of the Job Manager page, click the “Manage folders” link. Click “New Folder” and use your initials to give it a name. Now click “Return to Job Manager.” Every time you finish a calculation, you should put the results in this folder by checking the box next to the job name and selecting your folder under the Move To tab.

You are now ready to begin your first job with WebMO. Your instructor will lead you through the construction and optimization of ammonia, NH₃. Follow the above procedure, recording each step in your notebook. After your calculation is finished, open your results and click the magnifying glass next to “Dipole Moment.” Indicate the direction of the dipole moment on your Lewis structure and record its magnitude.


Part II: Group Calculation – NO₃⁻


Work in groups of two or three to analyze NO₃⁻. Begin by completing steps 1-6 of the procedure. Build NO₃⁻ in the WebMO editor. Instead of doing a comprehensive clean-up, select “Hybridization” and “Geometry” from the Clean-Up menu. (We do not want to add any hydrogen atoms to the oxygen atoms.) At the Choose Computational Engine page, select the Mopac engine. Perform a geometry optimization on your structure using the default theory and multiplicity. Verify that the charge is -1. When it is finished, move it to your folder. Open your results and click [New Job Using This Geometry](#). Use the Mopac engine to do a molecular orbital calculation. In your notebook, compare your results (especially the bond order table) to your VSEPR structure. Which representation of NO₃⁻ best shows the effect of resonance?

Part III: Detailed Analysis

In Part III, your group will be assigned a molecule to study in more detail. Begin by completing steps 1-6 in the procedure. Each group should then perform a geometry optimization, which is described in step A. There may then be an additional step requiring a second calculation. The final step of each problem contains the questions you need to answer in your notebook and share in your presentation. You do not need to

record the results of other groups. Once you have finished your analysis, read the directions and begin preparing for Part IV.

1. H_2O_2
 - A. Use Mopac with default settings for your geometry optimization.
 - B. Examine the H-O-O angle. The H-O-H angle in water is found to be 107.7° when using this same computational method. Compare this angle with the H-O-O angle in H_2O_2 . Explain why they differ.
2. SO_4^{2-}
 - A. Use the Gaussian engine to perform a geometry optimization. Choose the 6-31G(d) basis set. The other default options do not need to be changed.
 - B. Examine each of the S-O bond lengths and O-S-O bond angles. How do they compare with each other? Compare this with your Lewis structure and explain.
3. O_3
 - A. Use Mopac to perform a geometry optimization. The default values on the Job Options page do not need to be changed.
 - B. Use the optimized geometry to perform a molecular orbital calculation with Mopac.
 - C. **Examine orbitals 6, 9, and 10 and compare them to Figure 10-37 in the text.** (To view an orbital, click on the magnifying glass next to its listing in the Molecular Orbital table.) Where do the calculation results and the text agree and disagree? What do MOs 6 and 7 say about the bonding in ozone? The bond order table may help you answer this.
4. NO_2
 - A. Use the Mopac engine to perform a geometry optimization. You will need to change the charge to 0 and the multiplicity to doublet on the Job Options page.
 - B. Use the optimized geometry to perform a molecular orbital calculation with Mopac.
 - C. Examine the orbital occupation. (To view an orbital, click on the magnifying glass next to its listing in the Molecular Orbital table.) Which orbital contains just one electron? Where in the molecule is this electron located? Does this single electron contribute to the bonding? Hint: Compare the MOs with the bond order table.
5. SF_4
 - A. Use Gaussian to perform a geometry optimization. Use the 3-21G basis set.
 - B. Perform a vibrational frequency calculation.
 - C. Examine each of the modes by clicking the  icon next to different vibrations in the Vibrational Modes table. Do all modes move all atoms? Pick two particularly interesting modes and sketch them in your notebook.
6. PCl_5
 - A. Use Gaussian to perform a geometry optimization. Use the 3-21G basis set.
 - B. Perform a vibrational frequency calculation.

- C. Examine each of the modes by clicking the  icon next to different vibrations in the Vibrational Modes table. Do all modes move all atoms? Pick two of the modes that you find particularly interesting and sketch them in your notebook.
7. ClF_3
- Use Gaussian to perform a geometry optimization. Select the 6-31G(d) basis set.
 - Use the optimized geometry to perform a molecular orbital calculation, still using the 6-31G(d) basis set.
 - Examine the partial charges on each atom. Explain why the partial charge of the axial fluorine atoms differs from that of the equatorial fluorine. Use the electrostatic potential map to help you explain the magnitude of the ClF_3 dipole moment when compared to the NH_3 dipole moment. To view the map, click the magnifying glass next to “Electrostatic Potential” in the Molecular Orbitals table. (Red portions of the map correspond to high electron density, while blue portions correspond to low electron density. The intermediate colors fill in the spectrum red > orange > yellow > green > blue.)
8. CO_2
- Use Mopac to perform a geometry optimization. You do not need to change any other fields on the Job Options page.
 - Use your optimized geometry to perform a molecular orbital calculation.
 - Use the electrostatic potential map to help you explain the magnitude of the CO_2 dipole moment compared to the NH_3 dipole moment. To view the map, click the magnifying glass next to “Electrostatic Potential” in the Molecular Orbitals table. (Red portions of the map correspond to high electron density, while blue portions correspond to low electron density. The intermediate colors fill in the spectrum red > orange > yellow > green > blue.)
9. IF_5
- Use Gaussian to optimize your geometry. Use the default options on the Job Options page.
 - Measure all of the F-I-F angles. How do they compare? Comment on the magnitude of the IF_5 dipole moment compared to the NH_3 dipole moment.
10. SF_6
- Use Gaussian to optimize your geometry. Use the default options on the Job Options page.
 - Measure all of the F-S-F angles. How do they compare with each other? Look at the dipole moment for SF_6 . How does it compare to that of NH_3 ? Why?

Part IV: Presentations

Each group must now prepare a five-minute presentation of their results. This presentation should include the electron group geometry and molecular shape of the

molecule as well as the results of the detailed analysis. You should show the results of your computations as part of the presentation.

Part V: Post-Lab Questions

The following questions are to be answered in your laboratory notebook.

1. Draw a Lewis structure for Br_3^- . Determine its molecular shape and draw an orbital overlap sketch.
2. The shape of PCl_5 was examined in this lab, and it was determined to be trigonal bipyramidal. Determine the geometry of PCl_3 and compare it to PCl_5 . Explain why they differ.
3. Do you expect NCl_3 to have a structure similar to PCl_3 ? Explain.
4. The compound NCl_5 does not exist. Why not?
5. Two NO_2 molecules can combine to form dinitrogen tetroxide, N_2O_4 . Draw the Lewis structure(s) for N_2O_4 .
6. One class of materials that have been proposed to selectively adsorb CO_2 from industrial emissions are zeolites. Figure 7 shows experimental data for one common type of zeolite, called silicalite, which selectively adsorbs CO_2 (solid line) relative to N_2 (dotted line). The structure of silicalite, which is composed of interconnected SiO_2 units, is shown in Figure 8, **and also in a video clip that is available online**. First, in 3 sentences or less, describe the structure of silicalite (viewing the video clip should inform your description). Second, use what you learned about CO_2 during the lab to suggest why silicalite preferentially adsorbs CO_2 compared to N_2 . Note that in silicalite the formal charge of Si is +4 and that the formal charge of O is -2.

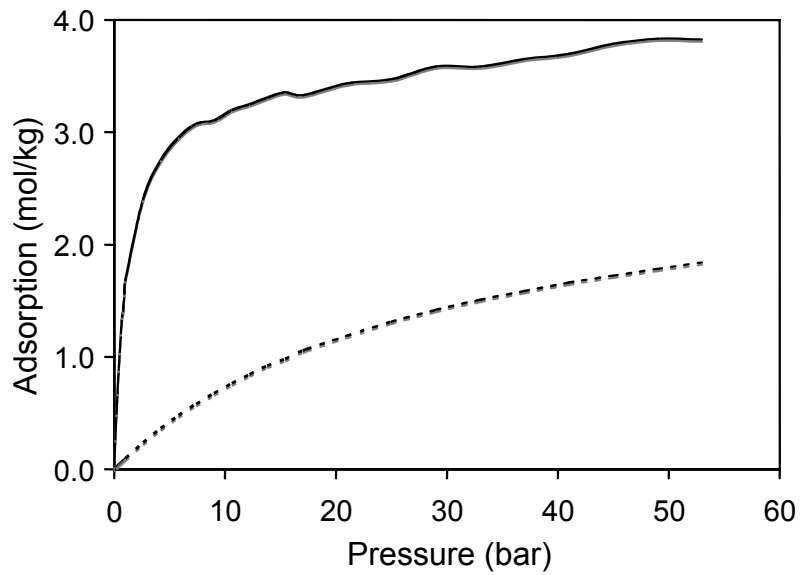


Figure 7. Relative adsorption of CO₂ (solid line) and N₂ (dashed line) onto silicalite. The units of the y-axis are moles of gas per kg of silicalite.

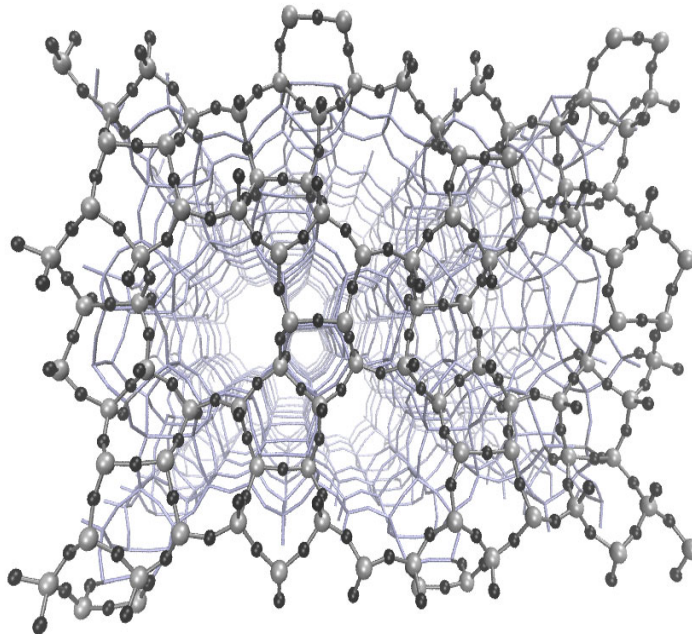


Figure 8. The molecular structure of silicalite, showing the combination of large and small voids that characterize a zeolite. The first 'layer' of atoms are shown as balls and sticks. Si atoms are light gray and O atoms are dark gray. The rest of the molecular structure is shown with lines connecting the bonds.