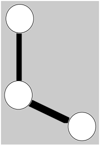
> *"The carbon atom has four valence electrons. The spectrum shows that one of the electrons is different from the other three, and yet the four bonds of the carbon atom seem to be identical with one another....I had the idea that the electrons might occupy four equivalent tetrahedral orbitals....I worked at my desk all night, so full of excitement that I could hardly write."*
>
> *Linus Pauling*

The Structure of Molecules
& VSEPR (Review)

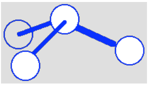
So far, you have mostly dealt with two-dimensional or "connectivity" representations of molecules and ions. This approach has been very useful in constructing Lewis structures and in considering covalent bonds. Compounds such as water, H_2O, ammonia, NH_3, and buckminsterfullerene, C_{60} are molecular compounds whose atoms are held together with covalent bonds. It is very important to perceive their three-dimensional structures. Three-dimensional structures have a different kind of importance than do two-dimensional representations. Three-dimensional representations inform us about the interactions between different molecules and interactions between different parts of the same molecule in space.

Examples of 3-dimensional molecular structures follow.

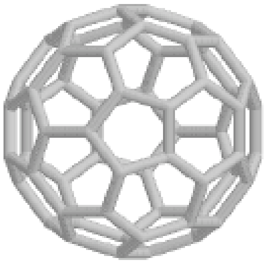
Water:



Ammonia:



Buckminsterfullerene:



There are several models used in chemistry to predict the shapes of molecular structures. An important intorductory model is the Valence Shell Electron Pair Repulsion model, or VSEPR. The VSEPR model is a useful starting point to approximate three-dimensional structures of molecules. You will also be introduced to other more rigorous models, which have mathematical and empirical foundations. One model includes the concept of orbital hybridization, as mentioned by Professor Pauling in the opening quote. Other approaches consider molecular orbitals, their respective energies and their effects on molecular geometry.

The Valence Shell Electron Pair Repulsion Model

SEE: *http://chemconnections.org/general/movies/VSEPR.MOV*

The VSEPR model considers the interaction among the electrons within a molecule or ion as the determining factor of structure. You will use the two-dimensional Lewis diagram as the basis for the three-dimensional molecular structure.

To understand the VSEPR model, consider each "group" of electrons as an arm of electron density projecting from the central atom. Each arm repels all the other arms, so each individual arm tries to get as far away from the others as possible. In this context, consider a "group" of electrons to be one of the following:

a)	a single bond	(2 shared electrons)
b)	a double bond	(4 shared electrons)
c)	a triple bond	(6 shared electrons)
d)	an unshared pair	(a lone pair or "non-bonded" pair)

The electron-pair geometry, or arrangement of electron groups around a central atom, is based on the number of groups around that atom. Each geometry has a name which chemists use to describe the shape:

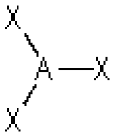
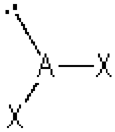
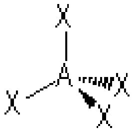
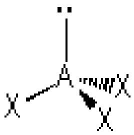
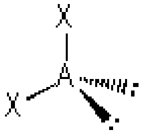
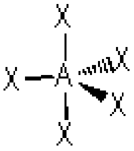
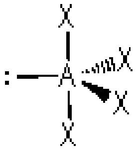
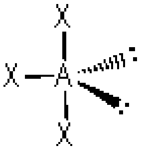
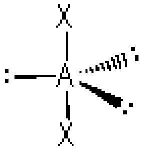
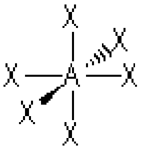
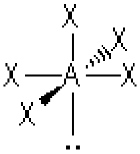
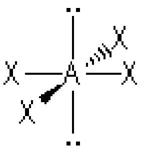
Number of Electron Groups Around the Central Atom	**Electron-Pair Geometry**
2	Linear
3	Trigonal Planar
4	Tetrahedral
5	Trigonal bipyramidal
6	Octahedral

The molecular geometry is determined by the number of atoms bonded to the electron groups around the central atom. Be mindful that there are other geometries other than those listed, and the terminology that refers to molecular geometry can vary.
See: *http://chemconnections.org/VSEPR-jmol/*

Number of Electron Groups Around the Central Atom	**Number of Groups of Electrons Bonded to an Atom**	**Molecular Geometry**
2	2	Linear
3	3	Trigonal Planar
3	2	Angular
4	4	Tetrahedral
4	3	Trigonal pyramidal
4	2	Bent
5	5	Trigonal bipyramidal
5	4	See-saw
5	3	T-shaped
6	6	Octahedral
6	5	Square pyramidal
6	4	Square planar

Covalent Bond Types
(Common Neutral Atoms in Organic Molecules)

Symbol	*Valence electrons*	*Number of Bonds*	*Types*	*Shape*
C	4	4 4 4	4 single or 2 single + 1 double or 1 single + 1 triple	Tetrahedral Trigonal Planar Linear
H	1	1	1 single	
O	6	2 2	1 double or 2 single	Linear Bent
N	5	3 3 3	3 single or 1 single + 1 double or 1 triple	Trigonal Pyramidal Bent Linear

Number of groups in the arrangement	Number of bonding groups? SHAPE				Hybridization of central atom
2	2  linear				sp
3	3  trigonal planar	2  bent/V-shaped			sp^2
4	4  tetrahedral	3  trigonal pyramidal	2  bent/V-shaped		sp^3
5	5  trigonal bipyramidal	4  see-saw	3  T-shaped	2  linear	sp^3d
6	6  octahedral	5  square pyramidal	4  square planar		sp^3d^2

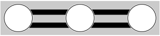
Refinement of the VSEPR Model

Lone electron pairs, which are not confined between nuclei, use more space than do bonding pairs, which are restricted to the narrow space between their two nuclei. The "fat" lone pairs distort the ideal electron-pair geometries predicted by VSEPR theory. Consider the ammonia molecule as an example. It has four electron pairs, and thus VSEPR predicts a tetrahedral geometry with 109.5° bond angles. However, one of the four is a lone pair, taking up more space, and so the three bonding electron pairs are squeezed together slightly. The experimentally measured H–N–H bond angle in ammonia is, in fact, 107.3°.

Dipole Moment

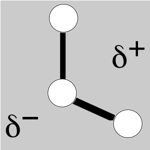
A polar molecule is also known as a dipole. The distribution of charge is asymmetric in a dipole, resulting in positive and negative poles. In other words, there is a little more negative charge on one end of the molecule than on the other. The amount of "uneven-ness" in charge distribution varies among different molecules. To illustrate this concept, let's consider CO_2 and H_2O, which are both three-atom molecules.

Carbon dioxide has two electron groups, both bonded, so its molecular geometry is linear. Oxygen is more electronegative than carbon, so if we considered the C=O bond alone, the bonding electrons would be asymmetrically distributed toward the oxygen atom. But the bond is not alone; there are two C=O bonds in CO_2, opposite one another:



The pull toward the oxygen atom on the left exactly balances the pull toward the oxygen atom on the right. The polar bonds cancel one another. The molecule itself is nonpolar.

Water has four electron groups, with two bonded, so it has a bent molecular geometry. Oxygen is more electronegative than hydrogen, so an isolated O–H bond has its bonding electrons distributed toward the oxygen atom. Now let's consider the overall molecule:



The pull toward the oxygen atom is not balanced by a pull in the opposite direction. In fact, both pairs of bonding electrons will be distributed toward the oxygen atom, creating a significant build-up of electrons on that end of the molecule. We indicate this with a δ^-, which is used to symbolize a partial negative charge. The opposite end of the water molecule will be electron deficient, and therefore possess a partial positive charge, indicated by the symbol δ^+.

A polar molecule, such as water, is said to have a dipole moment. The dipole moment of molecules can be quantitatively measured, and it is usually expressed in a unit called a debye, symbol D. The unit is named after Peter Debye, who made many important contributions to our understanding of molecular polarity, but who recently has been discredited for his support of the Nazis during WW II.

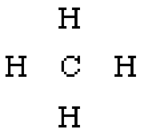
For the purpose of this discussion, we will limit our use of quantitative dipole moments to express the relative polarity of molecules. The more polar a molecule, the greater the value of its dipole moment. Nonpolar molecules have a zero dipole moment.

Water, with a dipole moment of 1.85 D, has one of the largest dipole moments of any molecule. This property of water molecules leads to significant effects on the macroscopic behavior of water. For example, water is able to dissolve ionic compounds because of its large dipole moment. The anomalously high boiling point of water is also a consequence of its extreme polarity.

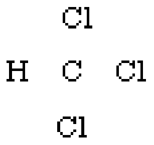
Review / Self Test

1. Complete the Lewis structures for the following compounds showing **all** electrons:

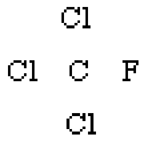
Methane (CH_4):



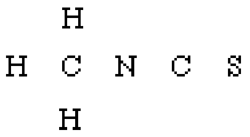
Chloroform:



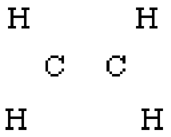
Freon_{11}:



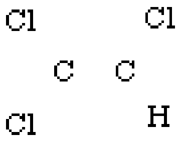
Methylisothiocyanate:



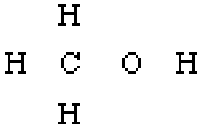
Ethylene:



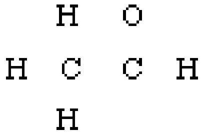
Trichloroethylene:



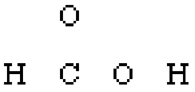
Methanol:



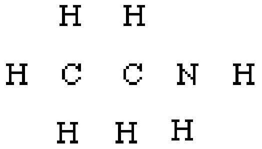
Ethanal (Acetaldehyde):



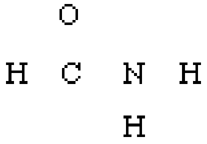
Formic acid:



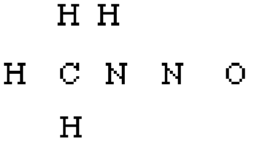
Ethyl amine:



Formamide:



Methyl nitrosamine:



2. For each of the following, (i) draw a Lewis diagram, (ii) count the number of electron groups around the central atom and the number of bonded electron groups, (iii) draw a three-dimensional representation of the molecule, (iv) give the values of the ideal bond angles, and (v) give the name of the electron-pair and molecular geometries.

a) CH_4	c) PCl_5
b) NO_3^-	d) SO_4^{2-}

3. Calculate the formal charge for each oxygen atom in the following molecules and clearly indicate their respective charge.