"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 (Valence Shell Electron Pair Replusion)

patial arrangements of atoms in covalently bonded molecules and polyatomic ions do not have only two-dimensions as are typically drawn in many of their representations. This "flat" approach is quick for constructing Lewis structures and in considering covalent bonds. However, it is only a first step. It is most important to perceive and understand the basis for three-dimensional structures. Three-dimensional structures have a different kind of importance than do two-dimensional representations. Three-dimensional representations inform us of the interactions between different molecules and interactions between different parts of the same molecule in space. They explain many physical and molecular properties such as boiling point, the mode of action and effectiveness of drugs, the toxicity of poisons, and the properties of plastics and polymers.

Consider the three-dimensional molecular structures of water, H₂O, ammonia, NH₃, and buckminsterfullerene, C₆₀ which follow.

Water:



Ammonia:



Buckminsterfullerene:



There are several models used in chemistry to predict the respective shapes of molecular structures. An important simple model is the Valence Shell Electron Pair Repulsion model, or VSEPR. The VSEPR model is a useful starting point to approximate threedimensional structures of many molecules. Be aware that there are other much more rigorous models, which have mathematical and empirical foundations. One model includes the concept of orbital hybridization, as mentioned in Linus Pauling's opening quote. Other modeling approaches consider molecular orbitals, their respective energies and their effects on molecular geometry, and semi-empirical data to represent three dimensional molecular structures. These models use complex algorithms and experimental data in software programs that a few decades ago were only available to a handful of scientists, who had access to large main-frame computers. Today there are many computational programs available that run on desktop computers; some of these are freely available such as MOPAC through WebMO.

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. The two-dimensional Lewis diagram is 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: <u>http://chemconnections.org/VSEPR-jmol/</u>

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
С	4	4	4 single or	Tetrahedral
		4	$\frac{2 \text{ single } +}{0 \text{ or }}$	Trigonal Planar
		4	<u>1 triple</u>	Linear
Н	1	1	1 single	
0	6	2	<u>1 double</u> or	Linear
		2	<u>2 single</u>	Bent
Ν	5	3	3 single or	Trigonal Pyramidal
		3	1 single + <u>1 double</u>	Bent
		3	or <u>1 triple</u>	Linear

http://www.ucalgary.ca/~ntaucoin/VSEPRtable.pdf

Table of VSEPR shapes

Number of groups in the arrangement	Nur	Hybridization of central atom			
2	2	X—A—X linear		sp	
3	3 X A—X	2	2		
	χ΄ trigonal plana	r b	χ [′] bent/V-shaped		
4	4 X J	3	2 X	sp ³	
	X X X	X X X	X A Straight		
	tetrahedral	trigonal pyramidal	bent/V-shaped		
5	5 4 X	х 3 Х Х	2 X	sp ³ d	
		Å, ∰X X − Å, ≪			
	trigonal bipyramidal see-	-saw	ed linear		
6	6 X	5 X	4 X	sp ³ d ²	
	X A X	x A X	X A X		
	octahedral	square pyramidal	quare square planar ramidal		

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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 CO₂ and H₂O, 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 CO₂, 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.

Self Test Questions/ Lewis Structure Review

Me	ethar	ne (C	H ₄):		C	loro	form		Free	on 1	1			
	н					Cl				Cl				
н	С	н			н	С	C1		Cl	С	H	7		
	Η					Cl				C.	1			
Me	ethyl	isoth	iocy	anate:	Eť	hylei	ne:		Tri	chlo	oroe	ethyl	ene:	
	Н				Н		Н		Cl			Cl		
Н	С	Ν	С	S	C		C		I	С	С			
	Н				н		Н		Cl			Н		
Me	than	ol:			Eth	nanal	l (Ace	etaldehy	/de):	Fo	rmi	ic aci	id:	
	Н					Н	0				0			
Н	С	0	Н		Н	С	С	Н		Н	С	0	Н	
	Н					Н								
Eth	iyl a	mine			Fo	orma	mide	:		Me	thy	l niti	rosan	nine:
	н	Η				0					Н	н		
н	С	С	И	Н	Н	С	И	Н		н	С	И	И	0
	н	н	н				Н				н			

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

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) CH4	c) PCl5
b) NO3-	d) SO4 ²⁻

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

