



Molecular Geometry

Lewis structures are good for figuring out how atoms are bonded to each other within a molecule and where any lone pairs of electrons are. They're quite flexible in terms of how the atoms can be arranged on the page: bond length and angles between bonds don't necessarily have to match reality. On the other hand, the information you write down in a Lewis structure is useful for figuring out what the real shape of a molecule is.

Even within a molecule, the rules about opposite charges attracting and like charges repelling each other still apply. Electrons all have the same charge, so even when they're bonded, they'll try to get as far away from each other as possible. Because of this mutual repulsion, the orbitals for a single atom change into new shapes to separate them as much as possible. What shape they form depends on how many electrons pairs there are around an atom. We count these pairs as **electron domains (E.D.)**. In terms of changing shape, only lone pairs of electrons and primary bonds between atoms are included. The "extra" bonds of double and triple bonds don't count. The number of electron domains is the primary factor in determining the shape of a molecule. This starts by figuring out the **electron domain geometry**.

The table below lists the electron domain geometries for different numbers of domains. Each geometry has a bond angle associated with it; this is the angle that the bonds are away from each other. (Hybridization will be discussed later in this handout.)

# domains	E.D. geometry	Bond angle	Hybridization
2	linear 	180°	sp
3	trigonal planar 	120°	sp ²
4	tetrahedral 	~109.5°	sp ³
5	trigonal bipyramidal 	120° at "equator" 90° from axial to equatorial	sp ³ d
6	octahedral 	90°	sp ³ d ²

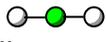
In all these cases, the darker sphere is the central atom. The linear and trigonal planar geometries are flat (planar). The white spheres in the tetrahedral geometry sit at the corners of a pyramid with a triangular base so that the sides of the pyramid are the same size and shape as the base. Both the trigonal bipyramidal and octahedral geometries have one atom bonded straight up and one straight down (called **axial bonds**), and the rest form a flat shape around their "equators" (called **equatorial bonds**); the flat shapes they form are an equilateral triangle and a square, respectively.



Each geometry corresponds to a **hybridization** of atomic orbitals, meaning that several orbitals of different energy levels “average out” to the same energy level to facilitate bonding with other atoms. The worksheet on Hybrid Orbitals will help you to see how hybridization works.

It is important to remember that for *electron domain* geometries, the white spheres don't necessarily represent atoms. They can also be lone pairs of electrons. The presence of lone pairs of electrons will mean two things. First, the charge of the electrons will not be balanced by a positive charge in the nucleus of another atom, as it would be in a bond. Second, the electrons will stay closer to the nucleus of the central atom. The end result is that a lone pair of electrons will reduce the bond angles slightly, pushing the bonds away from the location of the lone pair.

The **molecular geometry** around a central atom is the shape of the actual bonds to other atoms. To determine the molecular geometry for a particular atom, you need to know what electron domain geometry it has and the number of lone pairs around the central atom. The table below shows the progression of changes to the geometry when atoms are replaced by lone pairs:

# lone pairs	2 - linear	3 - trigonal planar	4 - tetrahedral	5 - trigonal bipyramidal	6 - octahedral
0	 linear	 trigonal planar	 tetrahedral	 trigonal bipyramidal	 octahedral
1		 bent ($<120^\circ$)	 trigonal pyramidal ($<109.5^\circ$)	 seesaw ($<120^\circ, <90^\circ$)	 square pyramidal
2			 bent ($<109.5^\circ$)	 T-shaped ($<90^\circ$)	 square planar
3				 linear	 T-shaped
4					 linear

The “bond” that gets replaced at each step will be the one that gives the new lone pair the most room. In the columns 2–4 of the table, it doesn't matter which one that is because they're symmetrical in every possible direction. In column 5, the equatorial bonds are replaced first because they are farther from each other than the axial bonds are from the equatorial ones. In column 6, it doesn't matter which bond is replaced first,

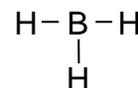


since all bond angles are 90°

Example 1: Determine the molecular geometry of: (a) BH_3 (b) CH_2O (c) NH_3 (d) BrF_5 .

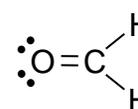
Solution: First, we draw the Lewis diagram for each structure, then we determine the electron domain geometry, and from there, the molecular geometry.

(a) BH_3 There are 3 valence electrons in boron, and 1 each in hydrogen, so there are 6 electrons total. We use all of them up in drawing the bonds for the molecule. The Lewis structure is at the right.



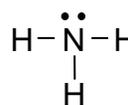
There are three electron domains, one for each bond. This means the electron domain geometry is trigonal planar. There are no lone pairs, so this is also the molecular geometry.

(b) CH_2O There are 4 valence electrons in carbon, 1 each in hydrogen and 6 in oxygen, so there are 12 electrons total. After bonding carbon to the other atoms, there are 6 left. The oxygen atom needs 6 more to get its octet, but that leave the central atom short, so we create a double bond between oxygen and carbon. The Lewis structure is at the right.



There are three electron domains here, not four. (The extra bond in the double bond isn't an electron domain.) The e.d. geometry is trigonal planar, and because there are no lone pairs, the molecular geometry is also trigonal planar.

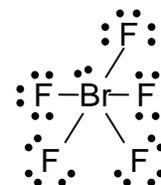
(c) NH_3 There are 5 valence electrons in nitrogen and 1 each in hydrogen, so there are 8 electrons total. The bonds for the molecule use up 6 of them, and the remaining 2 become a lone pair on the central atom. The Lewis structure is at right.



There are four electron domains here (the lone pair is one as well), so the e.d. geometry is tetrahedral. Because there is a lone pair, we go down one cell in the molecular geometry table, and the molecular geometry is trigonal pyramidal.

Notice that although this Lewis structure looks somewhat similar the one in (a), the two geometries for those answers are completely different because of the presence of the lone pair.

(d) BrF_5 All six of these atoms have 7 valence electrons, so there are 42 electrons total. After bonding, we have 32 left. Each of the fluorine atoms get 6 more to complete their octets, which leaves 2 left, which are a lone pair on the bromine. The Lewis structure is at right.



There are 6 electron domains (5 bonds plus 1 lone pair) and therefore the e.d. geometry is octahedral. Because there is a lone pair, we go down one cell in the molecular geometry table, and the molecular geometry is square pyramidal.

NOTE

For bond angles that have been reduced due to the presence of lone pairs, the precise angle is not predictable. It's enough to say that it's less than the normal bond angle.



EXERCISES

A. For each of the following compounds, determine (a) the number of electron domains (b) the electron domain geometry, (c) the molecular geometry, and (d) the bond angle or bond angles.

- | | |
|----------------------------------|--|
| 1) CH ₄ | 9) XeF ₄ |
| 2) BI ₃ | 10) HClO [<i>Hint: Oxygen is central.</i>] |
| 3) CO ₂ | 11) IO ₃ ⁻ |
| 4) TeF ₆ | 12) SO ₂ |
| 5) H ₂ O | 13) ClF ₃ |
| 6) NCl ₃ | 14) KrF ₂ |
| 7) PO ₄ ³⁻ | 15) N ₂ O [<i>Hint: Nitrogen is central.</i>] |
| 8) SeF ₄ | 16) XeO ₄ |

SOLUTIONS

- A. 1)(a) 4 (b) tetrahedral (c) tetrahedral (d) 109.5°
2)(a) 3 (b) trigonal planar (c) trigonal planar (d) 120°
3)(a) 2 (b) linear (c) linear (d) 180°
4)(a) 6 (b) octahedral (c) octahedral (d) 90°
5)(a) 4 (b) tetrahedral (c) bent (d) <109.5°
6)(a) 4 (b) tetrahedral (c) trigonal pyramidal (d) <109.5°
7)(a) 4 (b) tetrahedral (c) tetrahedral (d) 109.5°
8)(a) 5 (b) trigonal bipyramidal (c) seesaw (d) <90° and <120°
9)(a) 6 (b) octahedral (c) square planar (d) 90°
10)(a) 4 (b) tetrahedral (c) bent (d) <109.5°
11)(a) 4 (b) tetrahedral (c) trigonal pyramidal (d) <109.5°
12)(a) 3 (b) trigonal planar (c) bent (d) <120°
13)(a) 5 (b) trigonal bipyramidal (c) T-shaped (d) <90°
14)(a) 5 (b) trigonal bipyramidal (c) linear (d) 180°
15)(a) 2 (b) linear (c) linear (d) 180°
16)(a) 4 (b) tetrahedral (c) tetrahedral (d) 109.5°

