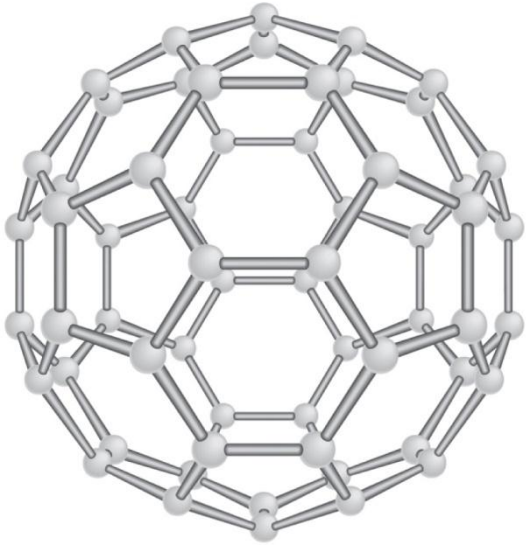
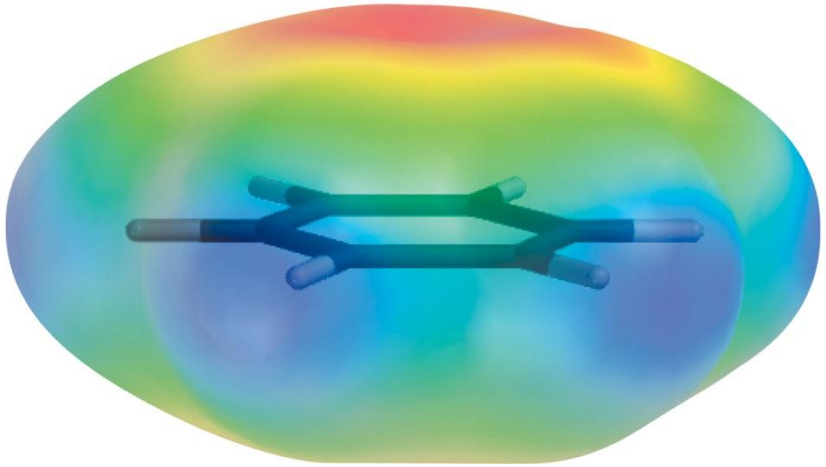


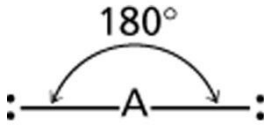
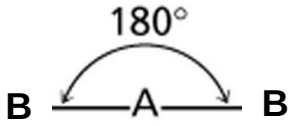


Chemical Bonding II: Molecular Geometry and Hybridization of Atomic Orbitals

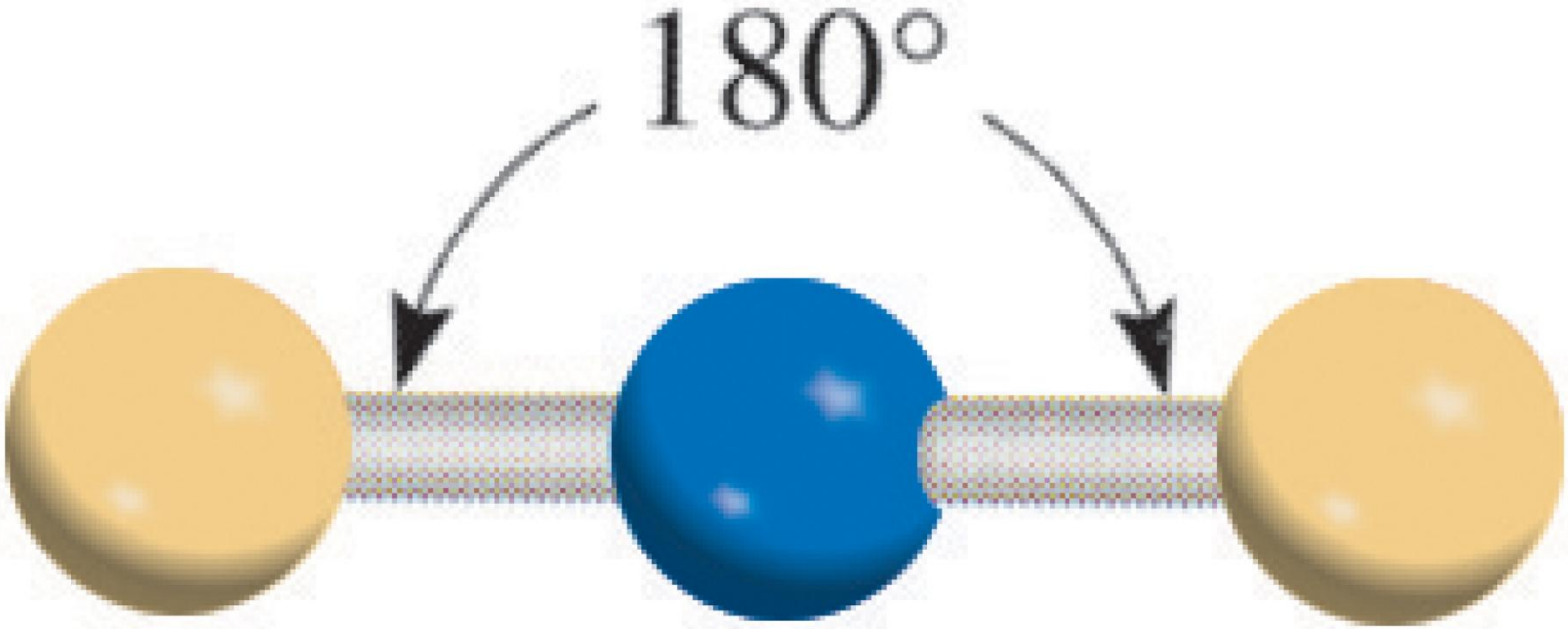
Chapter 10

Valence shell electron pair repulsion (VSEPR) model:

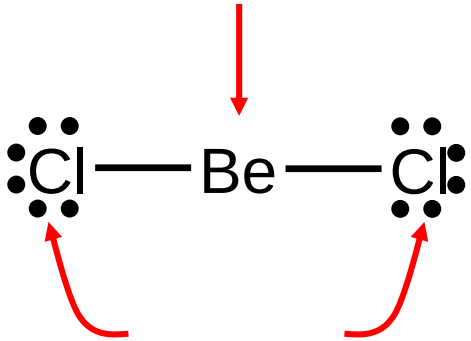
Predict the geometry of the molecule from the electrostatic repulsions between the electron (bonding and nonbonding) pairs.

Class	# of atoms bonded to central atom	# lone pairs on central atom	Arrangement of electron pairs	Molecular Geometry
AB_2	2	0	linear 	linear 

Beryllium Chloride

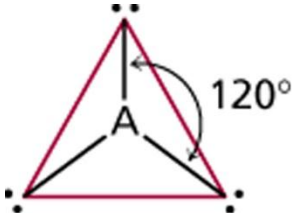
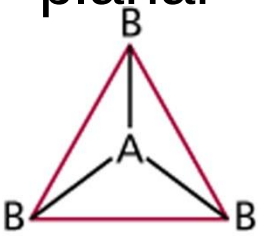


0 lone pairs on central atom

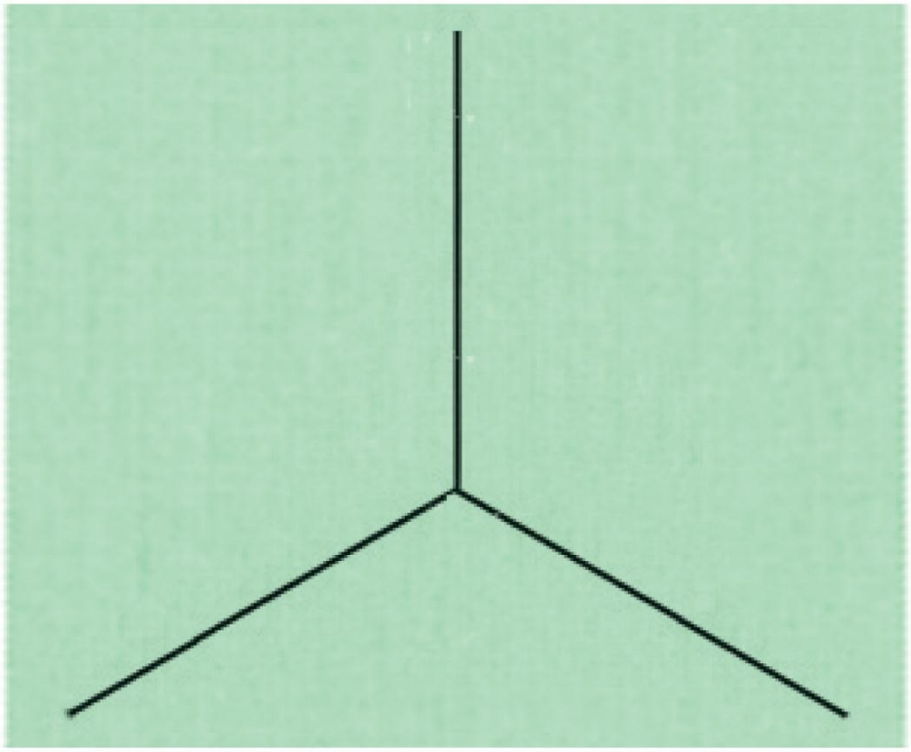


2 atoms bonded to central atom

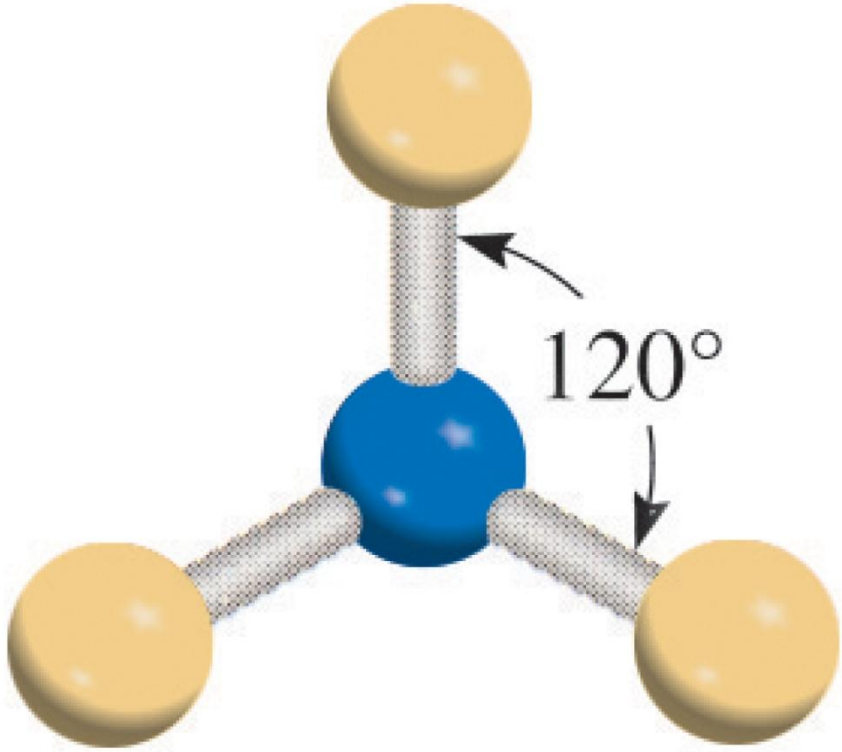
VSEPR

Class	# of atoms bonded to central atom	# lone pairs on central atom	Arrangement of electron pairs	Molecular Geometry
AB_2	2	0	linear	linear
AB_3	3	0	trigonal planar 	trigonal planar 

Boron Trifluoride

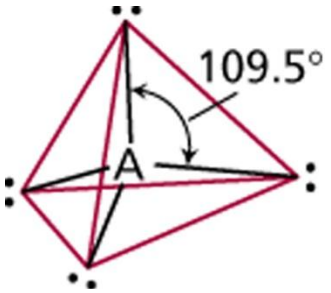


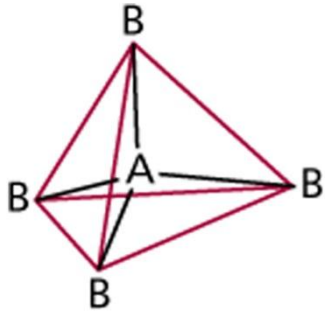
Planar



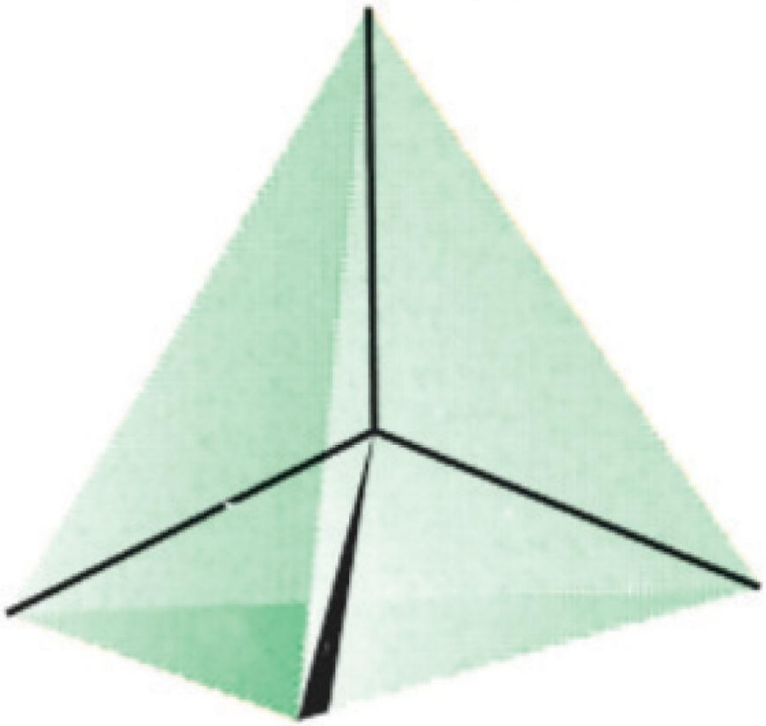
VSEPR

Class	# of atoms bonded to central atom	# lone pairs on central atom	Arrangement of electron pairs	Molecular Geometry
AB_2	2	0	linear	linear
AB_3	3	0	trigonal planar	trigonal planar
AB_4	4	0	tetrahedral	tetrahedral

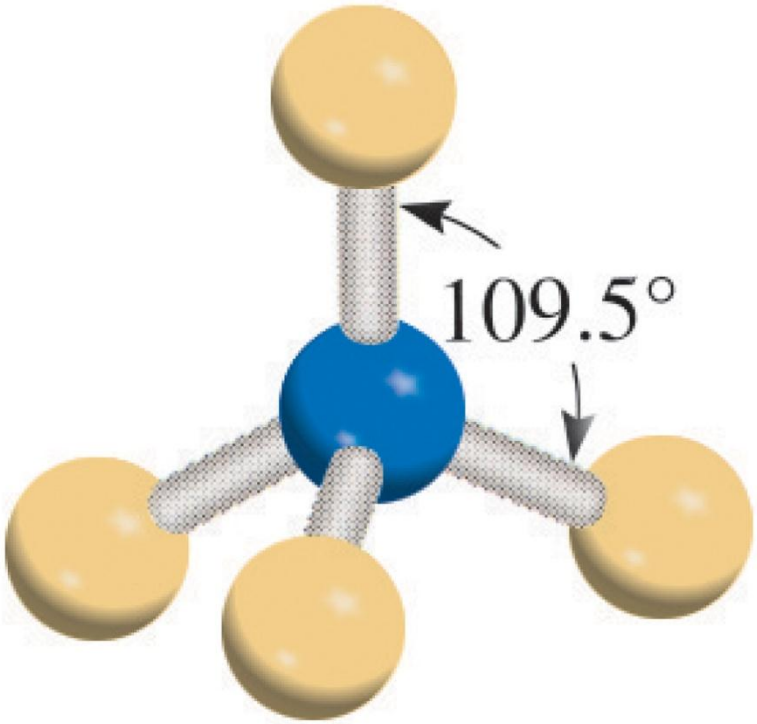




Methane

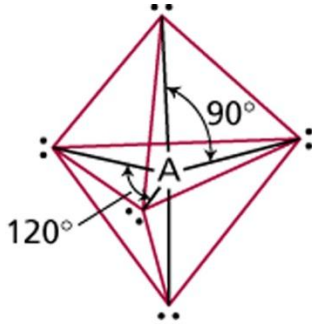


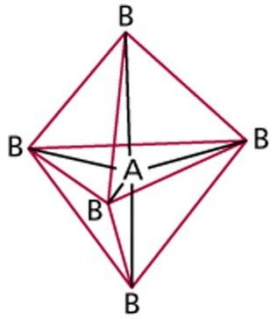
Tetrahedral



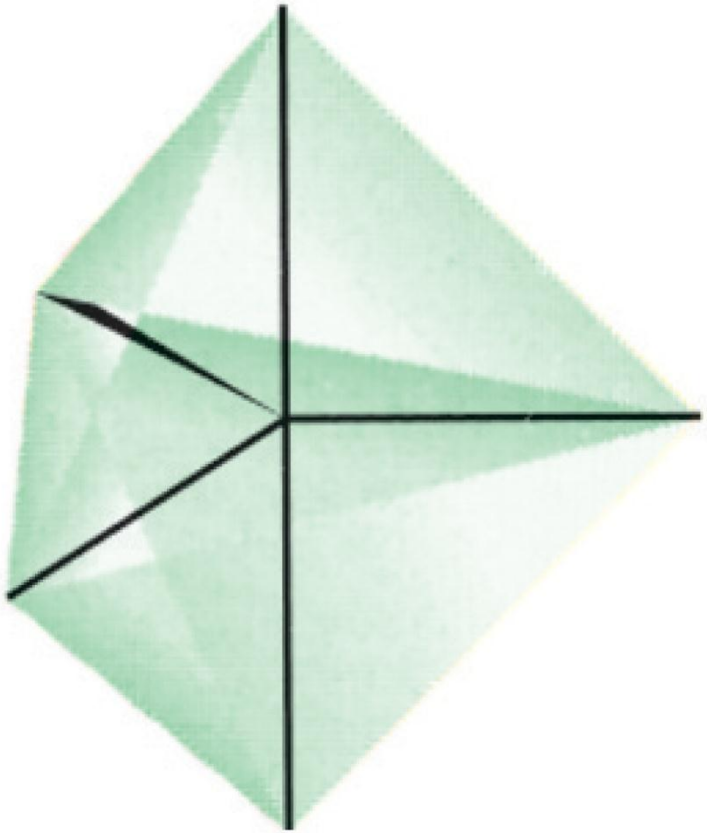
VSEPR

Class	# of atoms bonded to central atom	# lone pairs on central atom	Arrangement of electron pairs	Molecular Geometry
AB_2	2	0	linear	linear
AB_3	3	0	trigonal planar	trigonal planar
AB_4	4	0	tetrahedral	tetrahedral
AB_5	5	0	trigonal bipyramidal	trigonal bipyramidal

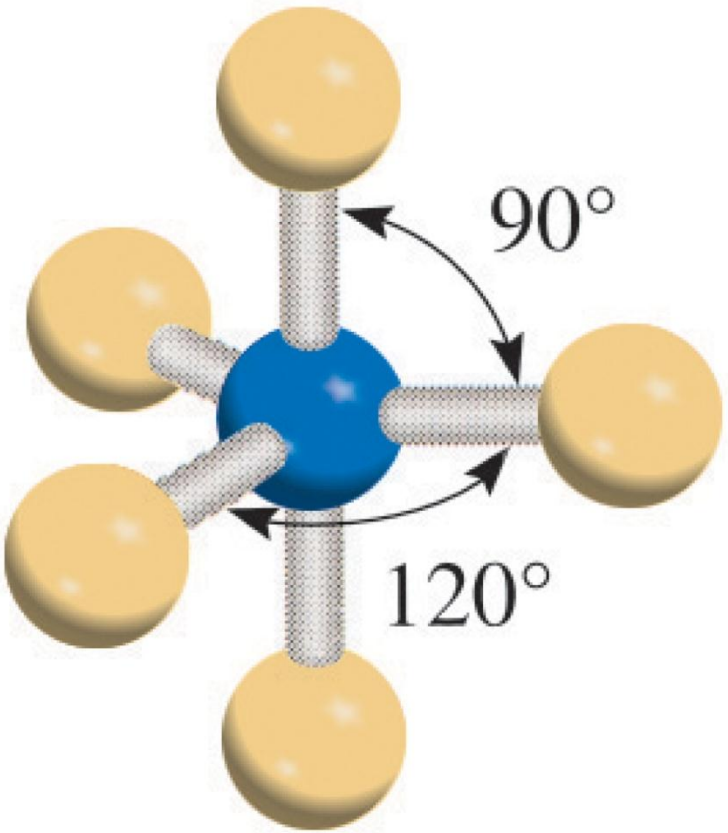




Phosphorus Pentachloride

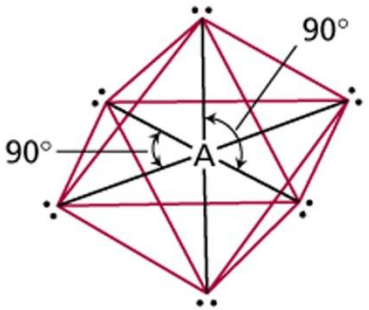


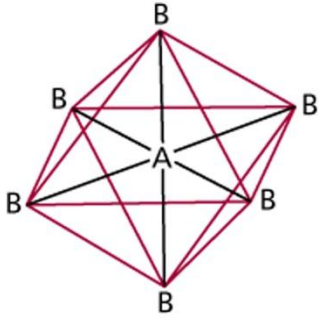
Trigonal bipyramidal



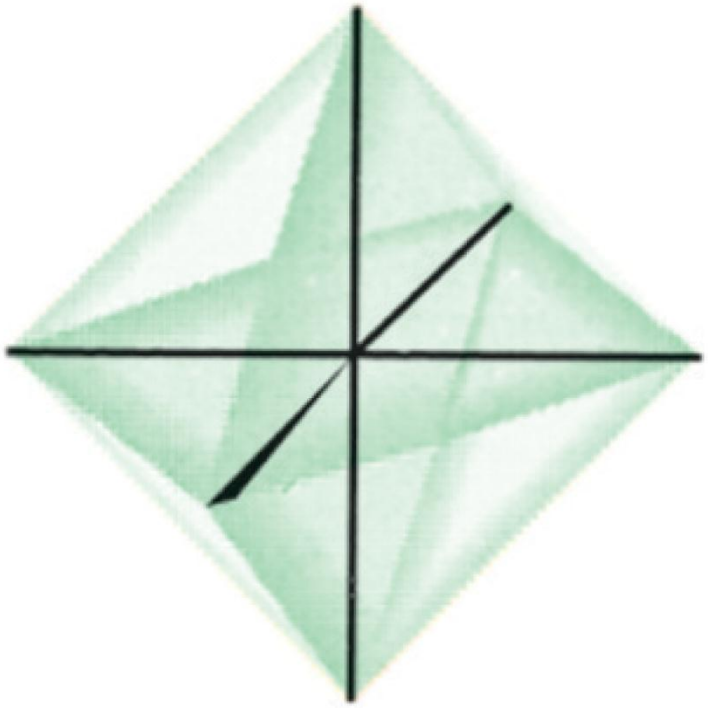
VSEPR

Class	# of atoms bonded to central atom	# lone pairs on central atom	Arrangement of electron pairs	Molecular Geometry
AB_2	2	0	linear	linear
AB_3	3	0	trigonal planar	trigonal planar
AB_4	4	0	tetrahedral	tetrahedral
AB_5	5	0	trigonal bipyramidal	trigonal bipyramidal
AB_6	6	0	octahedral	octahedral





Sulfur Hexafluoride



Octahedral

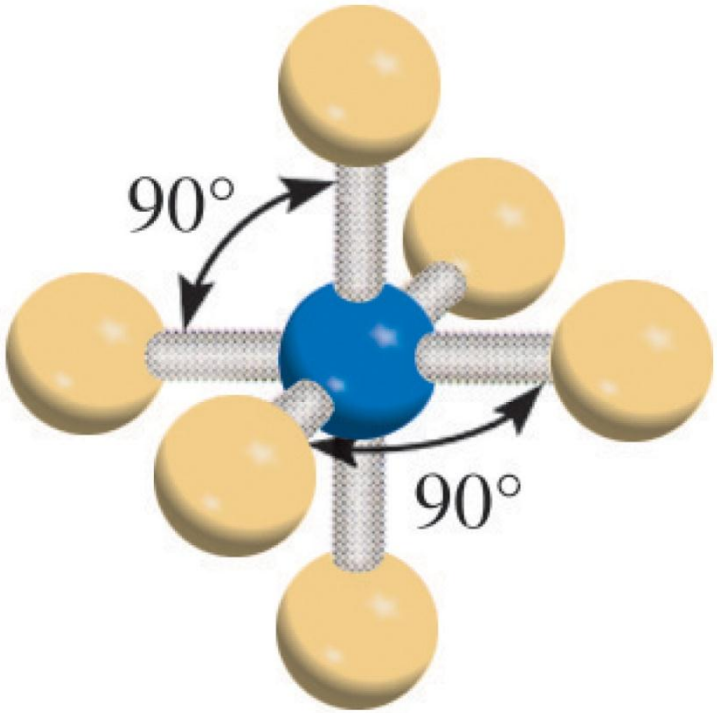
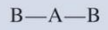
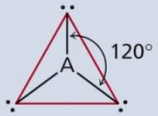
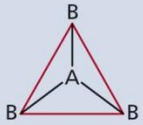
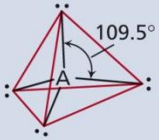
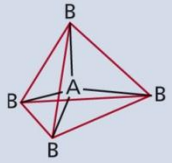
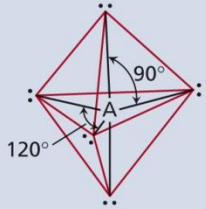
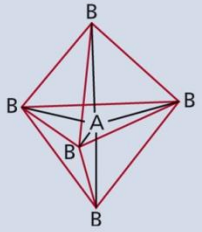
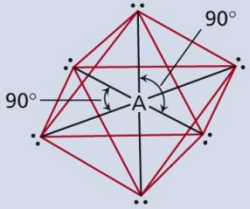
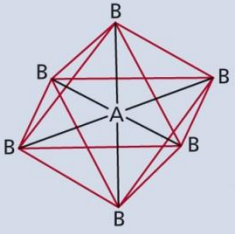
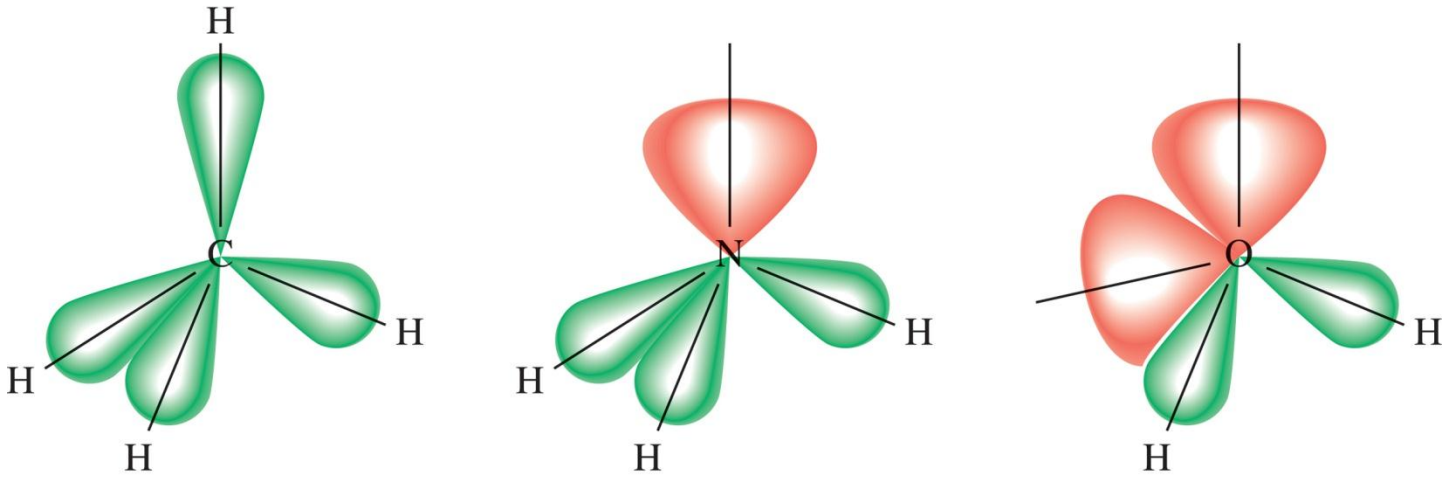


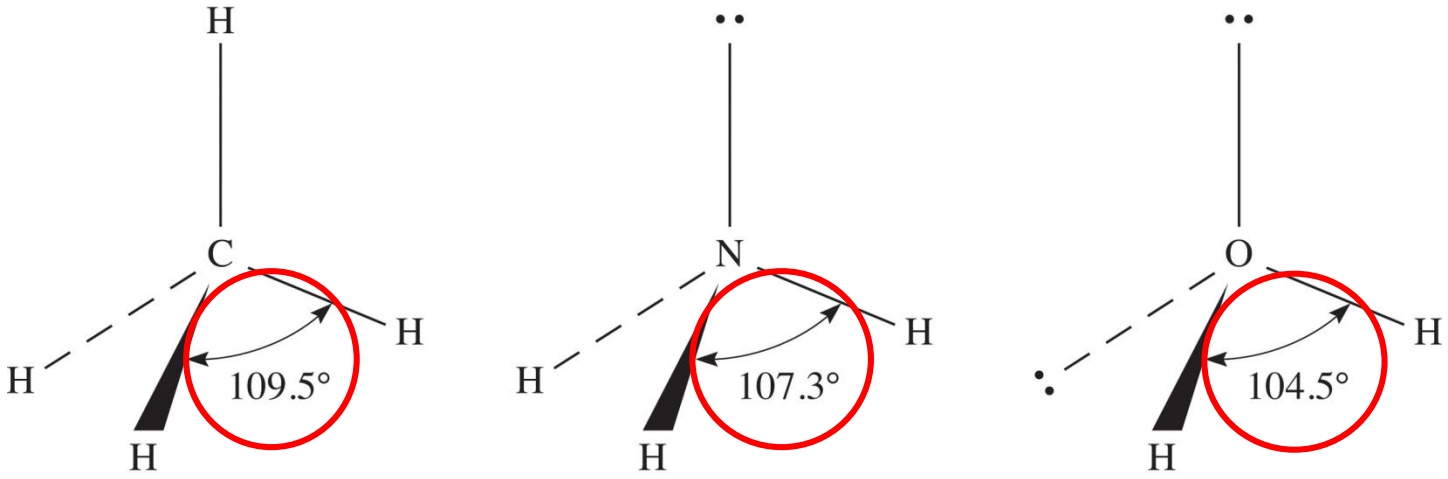
Table 10.1 Arrangement of Electron Pairs About a Central Atom (A) in a Molecule and Geometry of Some Simple Molecules and Ions in Which the Central Atom Has No Lone Pairs

Number of Electron Pairs	Arrangement of Electron Pairs*	Molecular Geometry*	Examples
2	 Linear	 Linear	$BeCl_2$, $HgCl_2$
3	 Trigonal planar	 Trigonal planar	BF_3
4	 Tetrahedral	 Tetrahedral	CH_4, NH_4^+
5	 Trigonal bipyramidal	 Trigonal bipyramidal	PCl_5
6	 Octahedral	 Octahedral	SF_6

*The colored lines are used only to show the overall shapes; they do not represent bonds.



(a)

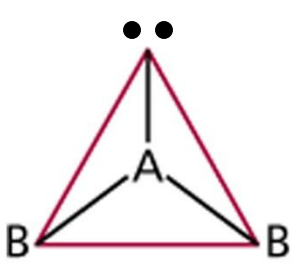


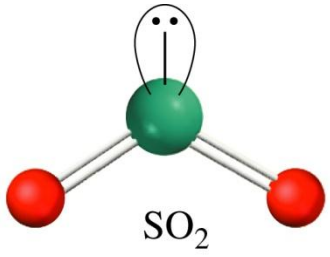
(b)

lone-pair vs. lone-pair repulsion > lone-pair vs. bonding-pair repulsion > bonding-pair vs. bonding-pair repulsion

VSEPR

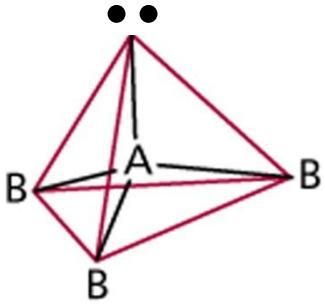
Class	# of atoms bonded to central atom	# lone pairs on central atom	Arrangement of electron pairs	Molecular Geometry
AB_3	3	0	trigonal planar	trigonal planar
AB_2E	2	1	trigonal planar	bent

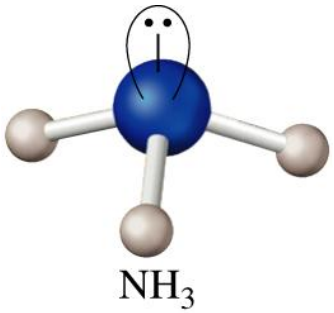




VSEPR

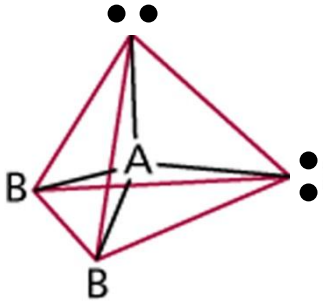
Class	# of atoms bonded to central atom	# lone pairs on central atom	Arrangement of electron pairs	Molecular Geometry
AB_4	4	0	tetrahedral	tetrahedral
AB_3E	3	1	tetrahedral	trigonal pyramidal





VSEPR

Class	# of atoms bonded to central atom	# lone pairs on central atom	Arrangement of electron pairs	Molecular Geometry
AB_4	4	0	tetrahedral	tetrahedral
AB_3E	3	1	tetrahedral	trigonal pyramidal
AB_2E_2	2	2	tetrahedral	bent



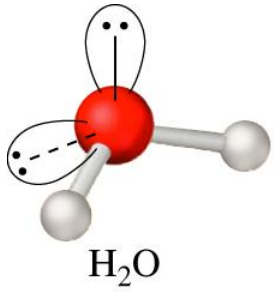
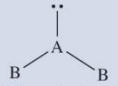
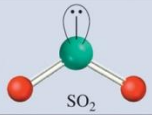
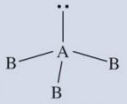
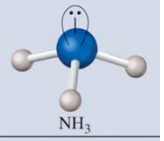
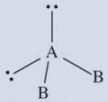
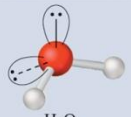
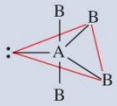
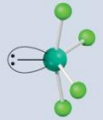
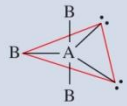
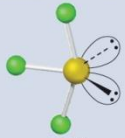
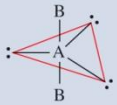
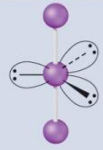
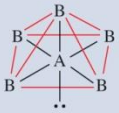
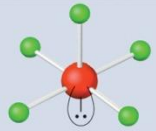
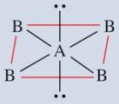
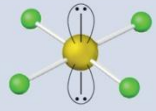


Table 10.2 Geometry of Simple Molecules and Ions in Which the Central Atom Has One or More Lone Pairs

Class of Molecule	Total Number of Electron Pairs	Number of Bonding Pairs	Number of Lone Pairs	Arrangement of Electron Pairs*	Geometry of Molecule or Ion	Examples
AB_2E	3	2	1	 Trigonal planar	Bent	 SO_2
AB_3E	4	3	1	 Tetrahedral	Trigonal pyramidal	 NH_3
AB_2E_2	4	2	2	 Tetrahedral	Bent	 H_2O
AB_4E	5	4	1	 Trigonal bipyramidal	Distorted tetrahedron (or seesaw)	 SF_4
AB_3E_2	5	3	2	 Trigonal bipyramidal	T-shaped	 ClF_3
AB_2E_3	5	2	3	 Trigonal bipyramidal	Linear	 I_3^-
AB_5E	6	5	1	 Octahedral	Square pyramidal	 BrF_5
AB_4E_2	6	4	2	 Octahedral	Square planar	 XeF_4

*The colored lines are used to show the overall shape, not bonds.

Predicting Molecular Geometry

1. Draw Lewis structure for molecule.
2. Count number of lone pairs on the central atom and number of atoms bonded to the central atom.
3. Use VSEPR to predict the geometry of the molecule.

Example 10.1

Use the VSEPR model to predict the geometry of the following molecules and ions:

(a) AsH_3

(b) OF_2

(c) $AlCl_4^-$

(d) I_3^-

(e) C_2H_4

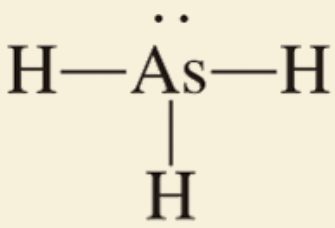
Example 10.1

Strategy The sequence of steps in determining molecular geometry is as follows:

draw Lewis structure ⟶ find arrangement of electron pairs ⟶ find arrangement of bonding pairs ⟶ determine geometry based on bonding pairs

Solution

(a) The Lewis structure of AsH_3 is

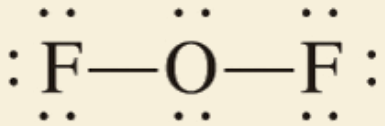


There are four electron pairs around the central atom; therefore, the electron pair arrangement is tetrahedral (see Table 10.1).

Example 10.1

Recall that the geometry of a molecule is determined only by the arrangement of atoms (in this case the As and H atoms). Thus, removing the lone pair leaves us with three bonding pairs and a trigonal pyramidal geometry, like NH_3. We cannot predict the HAsH angle accurately, but we know that it is less than 109.5° because the repulsion of the bonding electron pairs in the As—H bonds by the lone pair on As is greater than the repulsion between the bonding pairs.

(b) The Lewis structure of OF_2 is

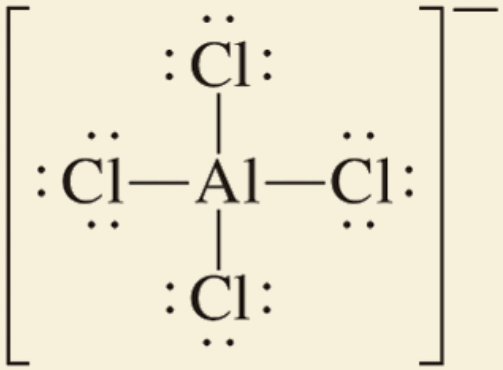


There are four electron pairs around the central atom; therefore, the electron pair arrangement is tetrahedral.

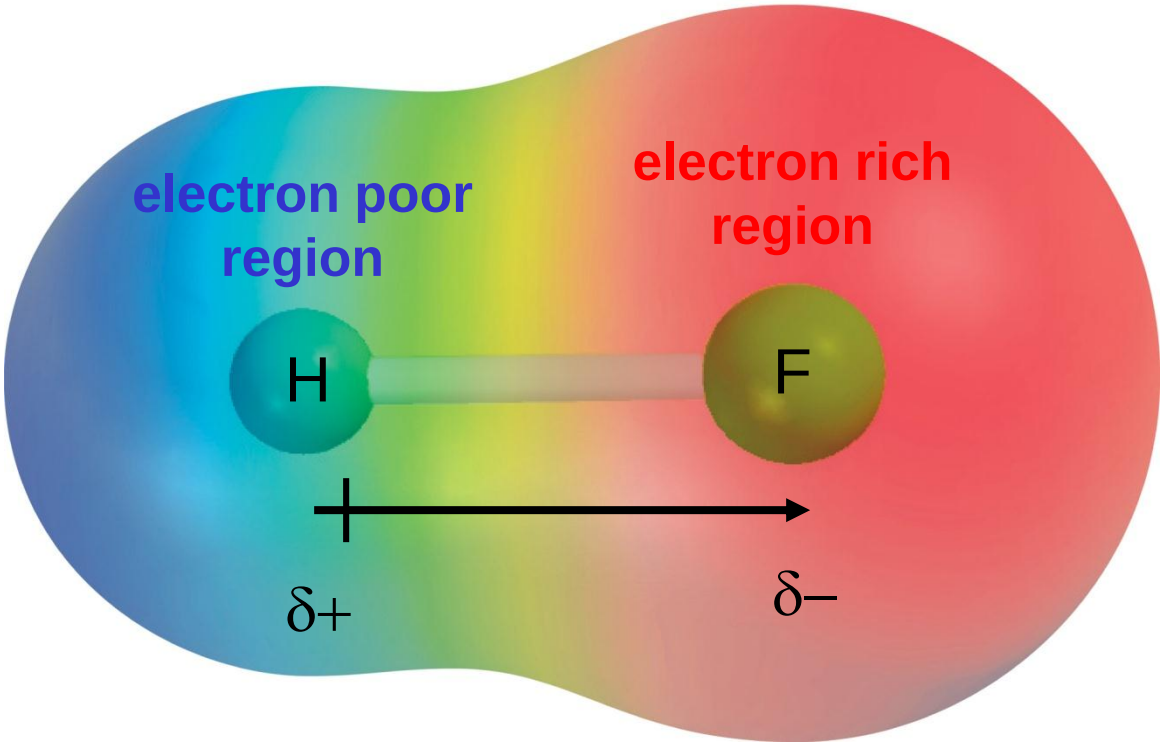
Example 10.1

Recall that the geometry of a molecule is determined only by the arrangement of atoms (in this case the O and F atoms). Thus, removing the two lone pairs leaves us with two bonding pairs and a bent geometry, like H_2O. We cannot predict the FOF angle accurately, but we know that it must be less than 109.5° because the repulsion of the bonding electron pairs in the O−F bonds by the lone pairs on O is greater than the repulsion between the bonding pairs.

(c) The Lewis structure of $AlCl_4^-$ is



Dipole Moments and Polar Molecules



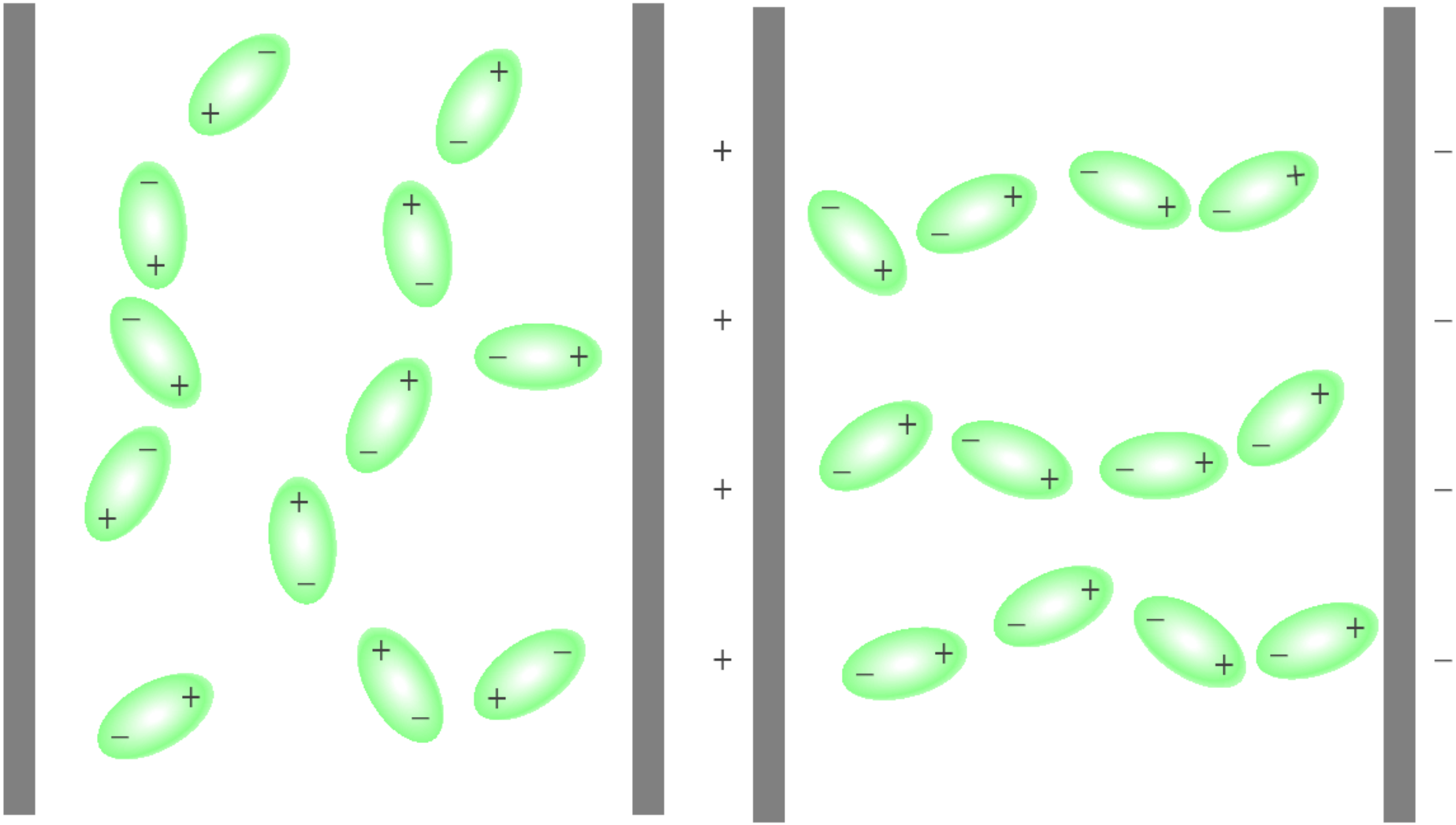
$\mu = Q \times r$

Q is the charge

r is the distance between charges

1 D = 3.36 x 10^{-30} C m

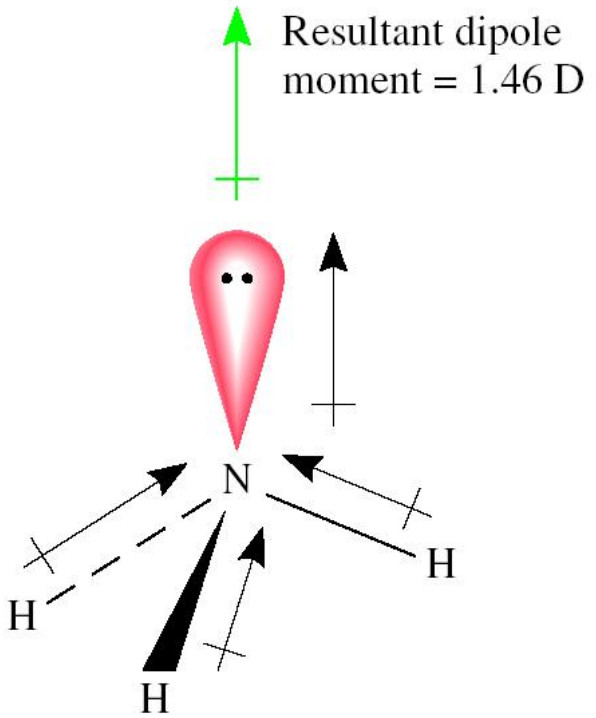
Behavior of Polar Molecules

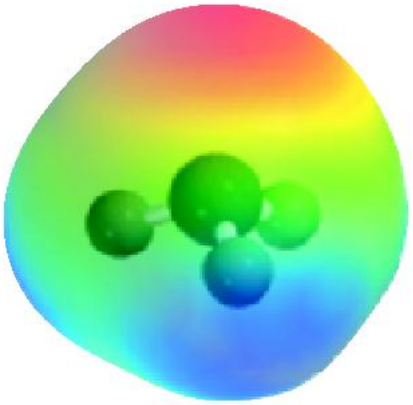


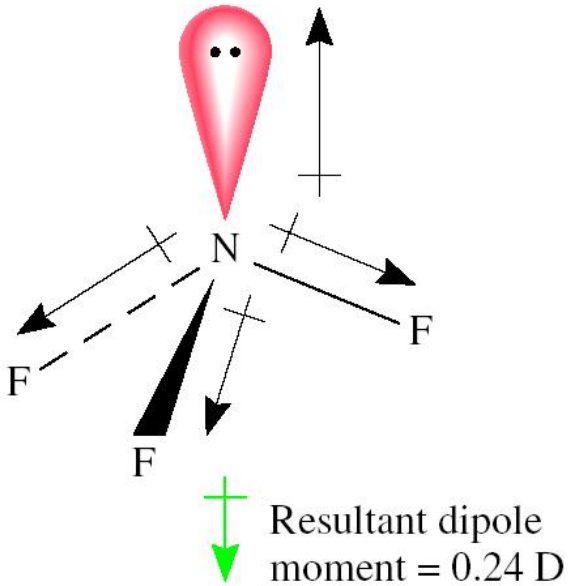
field off

field on

Bond moments and resultant dipole moments in NH_3 and NF_3.







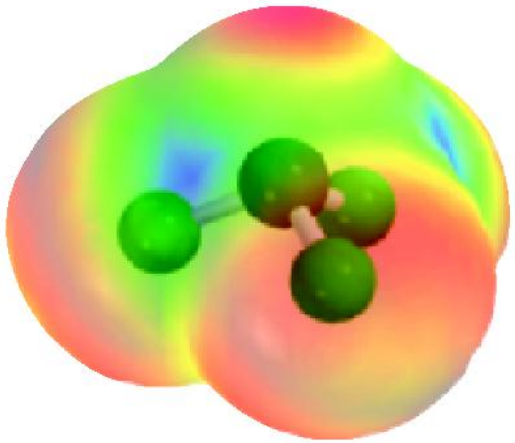


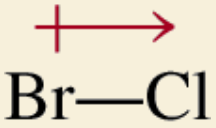
Table 10.3 Dipole Moments of Some Polar Molecules

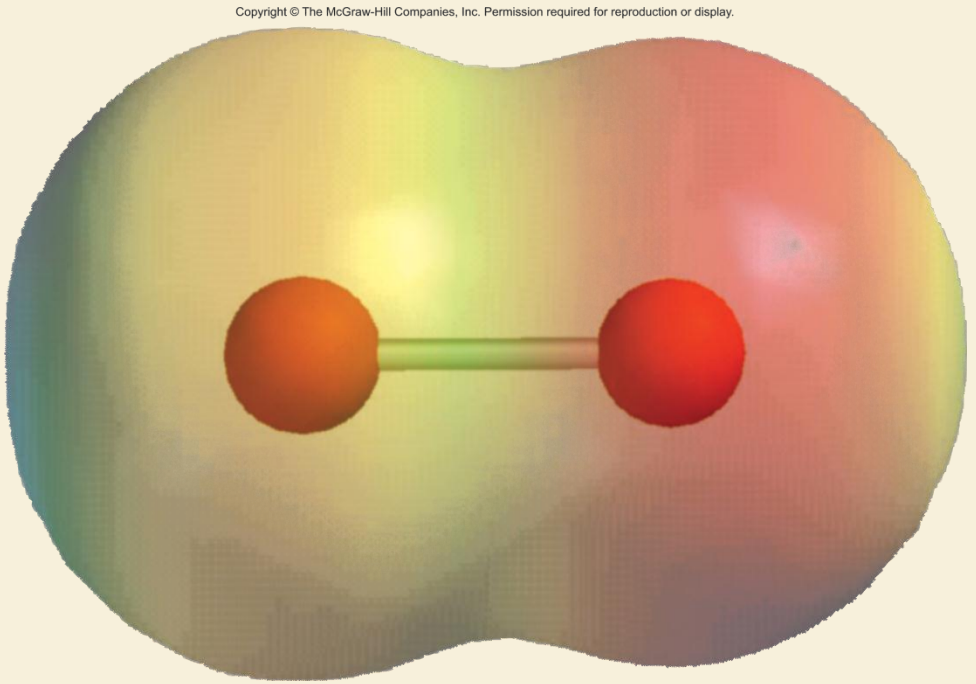
Molecule	Geometry	Dipole Moment (D)
HF	Linear	1.92
HCl	Linear	1.08
HBr	Linear	0.78
HI	Linear	0.38
H_2O	Bent	1.87
H_2S	Bent	1.10
NH_3	Trigonal pyramidal	1.46
SO_2	Bent	1.60

Example 10.2

Solution

(a) Because bromine chloride is diatomic, it has a linear geometry. Chlorine is more electronegative than bromine (see Figure 9.5), so BrCl is polar with chlorine at the negative end

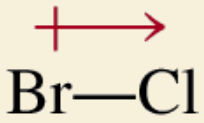


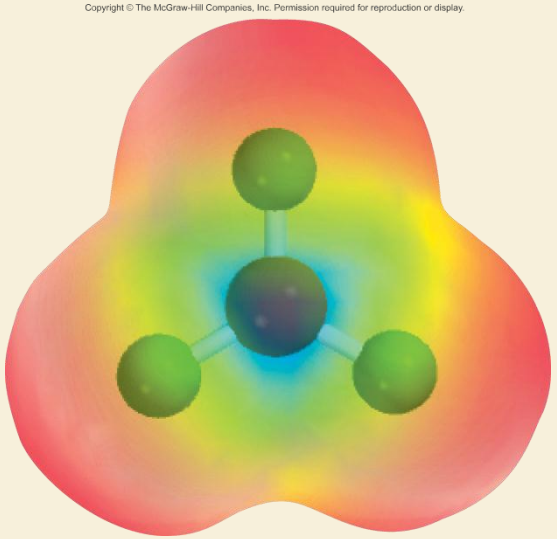


Thus, the molecule does have a dipole moment. In fact, all diatomic molecules containing different elements possess a dipole moment.

Example 10.2

(b) Because fluorine is more electronegative than boron, each B−F bond in BF_3 (boron trifluoride) is polar and the three bond moments are equal. However, the symmetry of a trigonal planar shape means that the three bond moments exactly cancel one another:

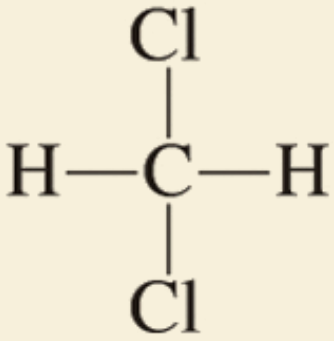




An analogy is an object that is pulled in the directions shown by the three bond moments. If the forces are equal, the object will not move. Consequently, BF_3 has no dipole moment; it is a nonpolar molecule.

Example 10.2

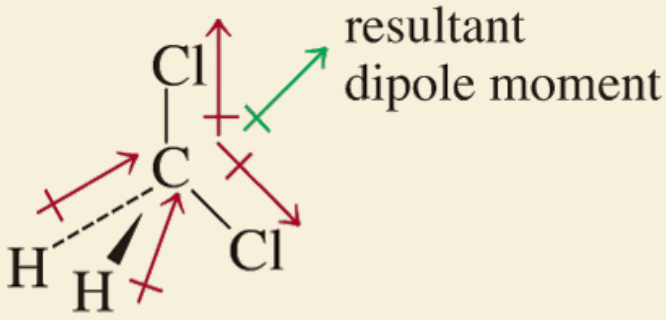
(c) The Lewis structure of CH_2Cl_2 (methylene chloride) is

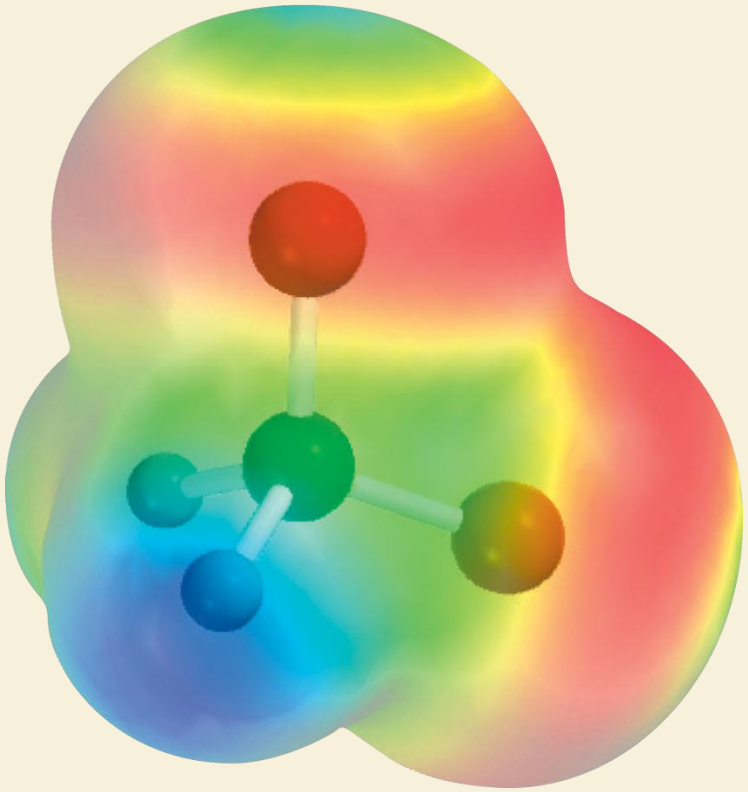


This molecule is similar to CH_4 in that it has an overall tetrahedral shape. However, because not all the bonds are identical, there are three different bond angles: HCH, HCCl, and ClCCl. These bond angles are close to, but not equal to, 109.5°.

Example 10.2

Because chlorine is more electronegative than carbon, which is more electronegative than hydrogen, the bond moments do not cancel and the molecule possesses a dipole moment:





Thus, CH_2Cl_2 is a polar molecule.