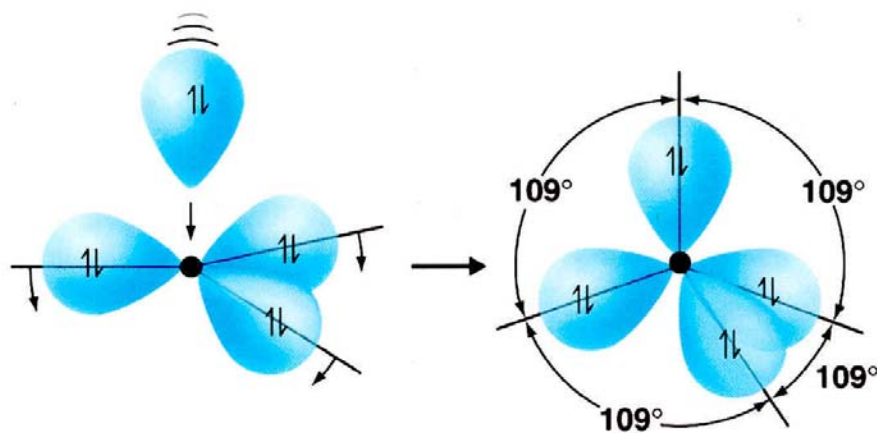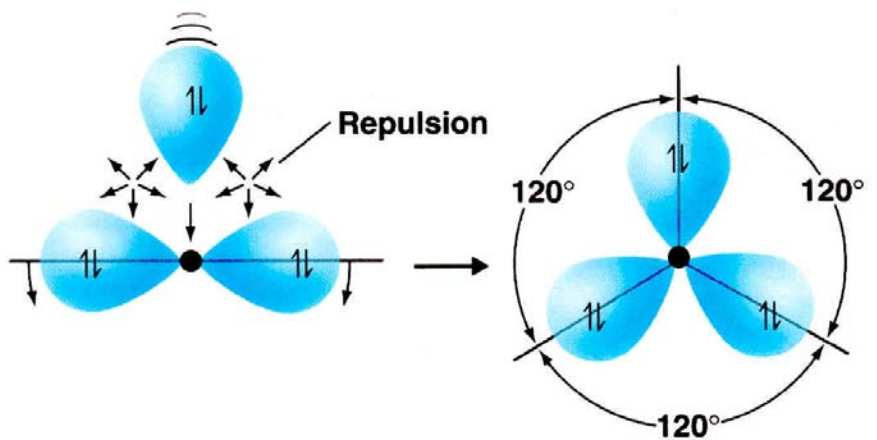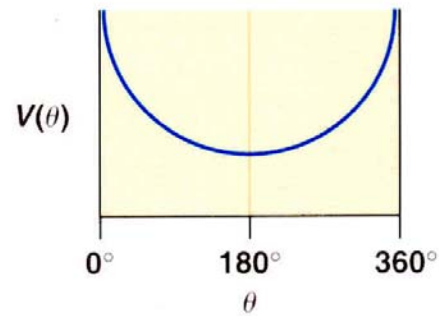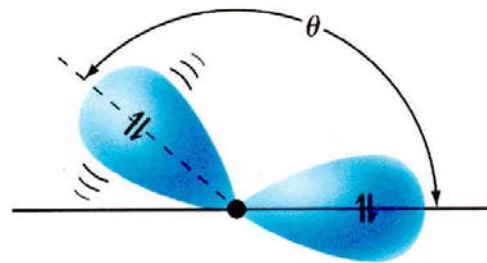# Topic 2E - The VSEPR Model

Potential energy minimization in the VSEPR model. The potential curve $V(\theta)$, called a *bending potential*, dictates the equilibrium angle θ.
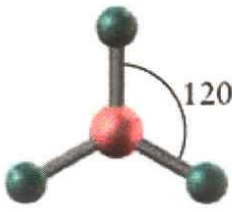
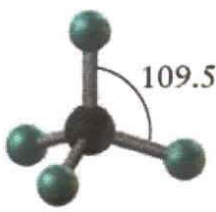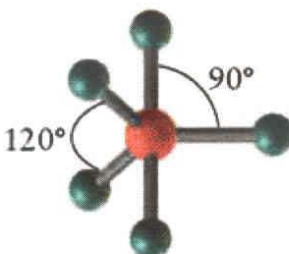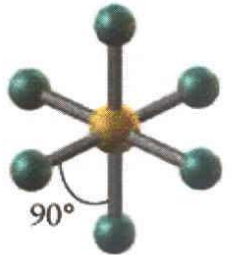# Valence-Shell Electron Pair Repulsion (VSEPR) Model

The following "rules" are helpful in using the VSEPR model to predict molecular structure:

- Determine the Lewis structure(s) for the molecule.

- For molecules having resonance structures, any of the structures can be used to predict the molecular structure.

- Sum the number of electron pairs around the central atom.

- When counting electron pairs, count each multiple bond as a *single* effective pair. (⇒ Steric Number, S.N.)

  S.N. = (# of atoms bonded to central atom) + (# of lone pairs on central atom)

- Determine the arrangement of the electron pairs that minimizes repulsions among them.

- Lone (non-bonding) electron pairs require more space than bonding pairs. Choose an arrangement that gives lone pairs as much room as possible. An angle of 120° or more between lone pairs provides enough space. Lone pairs at angles less than 120° may produce distortions from the idealized structure.

- Name the molecular structure based on the positions of the *atoms* in the structure, *not* the positions of the electron pairs.

T A B L E 3.8   Molecular Shapes Predicted by the Valence
Shell Electron-Pair Repulsion Theory

Molecule	Steric Number	Predicted Geometry		Example
AX_2	2	Linear	180°	CO_2
AX_3	3	Trigonal planar	120°	BF_3
AX_4	4	Tetrahedral	109.5°	CF_4
AX_5	5	Trigonal bipyramidal	120° 90°	PF_5
AX_6	6	Octahedral	90°	SF_6

Idealized Geometries for 2 and 3 VSEPR Electron Pairs

Molecular Class	Ideal Geometry	Example
AX_2	Linear (a)	$BeCl_2$
AX_3	Trigonal planar	BF_3
AX_2E	Bent (b)	SO_2
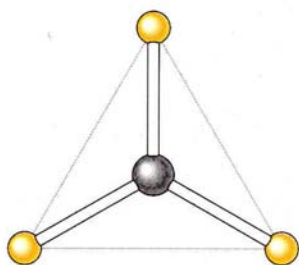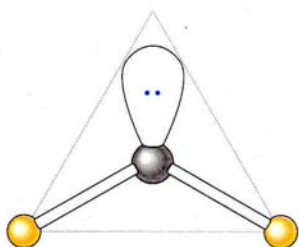
Idealized Geometries for 4 VSEPR Electron Pairs

Molecular Class	Ideal Geometry	Example
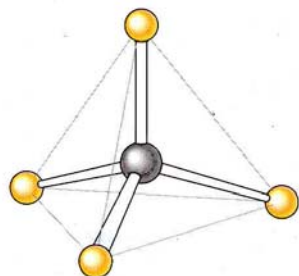
AX_4 **Tetrahedral** CH_4
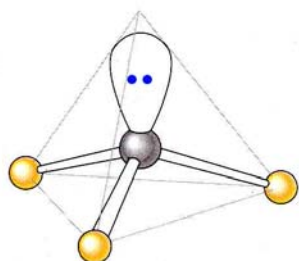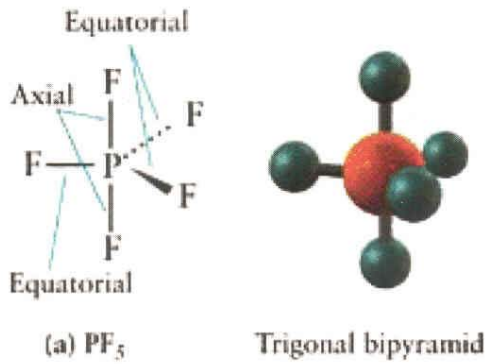
AX_3E **Trigonal pyramidal** NH_3
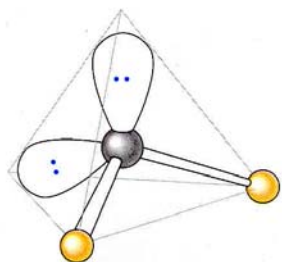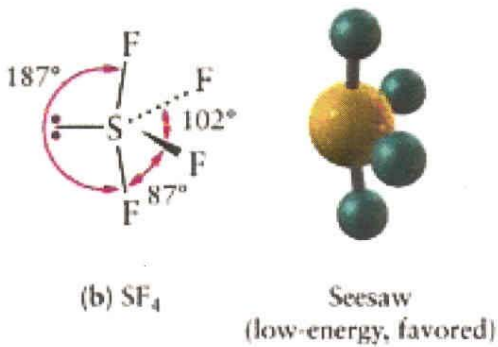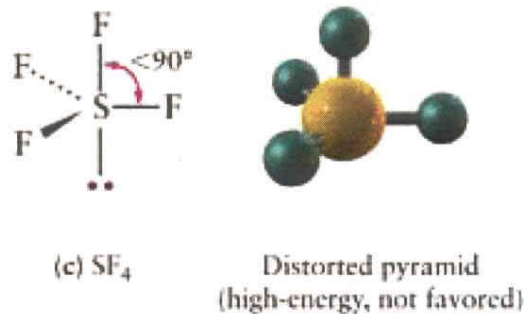
AX_2E_2 **Bent** H_2O

For PF_5, the axial P-F bond length is 1.58 Å, while the equatorial P-F bond length is 1.53 Å.
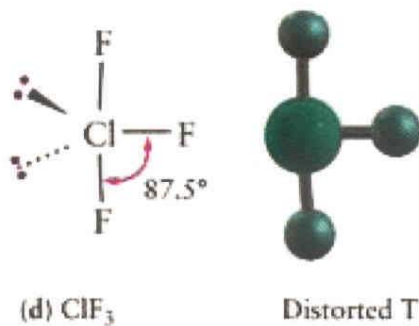
**For PCl_5, the axial P-Cl bond length is 2.19 Å, while the equatorial P-Cl bond length is 2.05 Å.**

(a) PF_5 Trigonal bipyramid

The single lone pair has _two_ 90° repulsions with bonding pairs and two 120° repulsions.

(b) SF_4 Seesaw (low-energy, favored)

The single lone pair has _three_ 90° repulsions with bonding pairs.

(c) SF_4 Distorted pyramid (high-energy, not favored)

Both lone pairs occupy equatorial positions to minimize 90° repulsions with bonding pairs.

(d) ClF_3 Distorted T
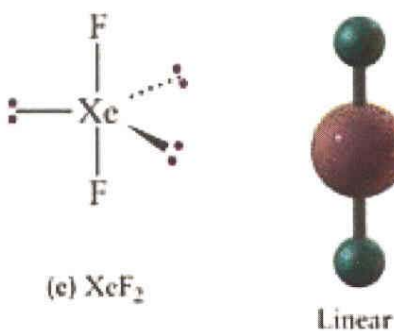
All three lone pairs occupy equatorial positions.

(e) XeF_2 Linear

Idealized Geometries for 6 VSEPR Electron Pairs

Molecular Class	Ideal Geometry	Example

AX_6 Octahedral SF_6

AX_5E Square pyramidal BrF_5

AX_4E_2 Square planar XeF_4

(a)

(b)
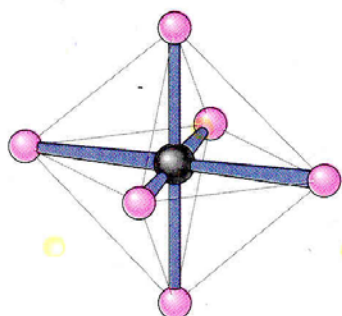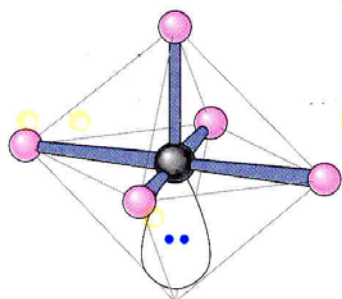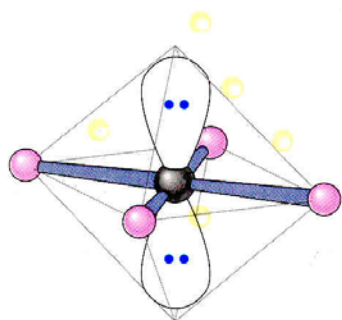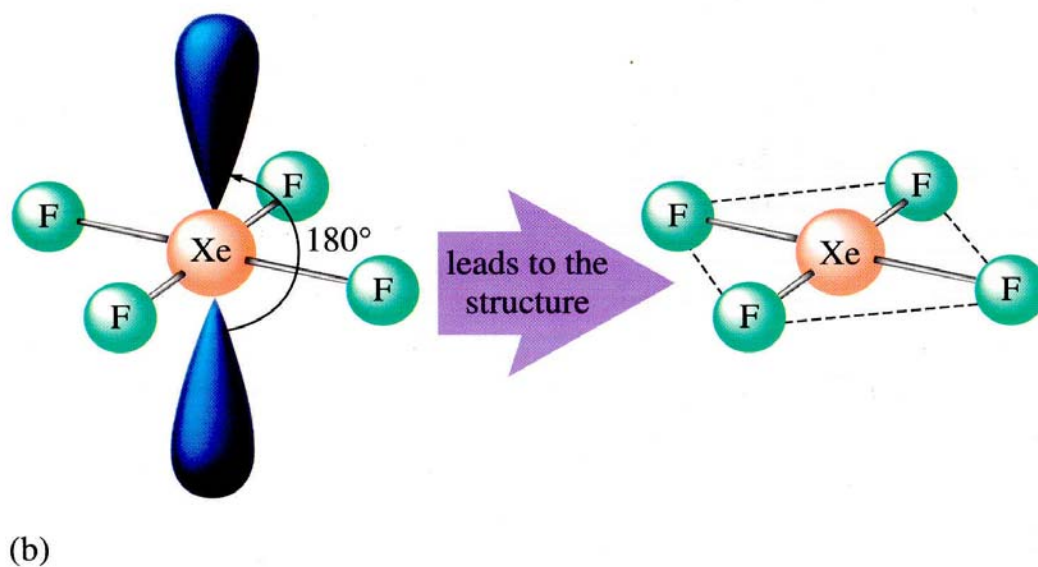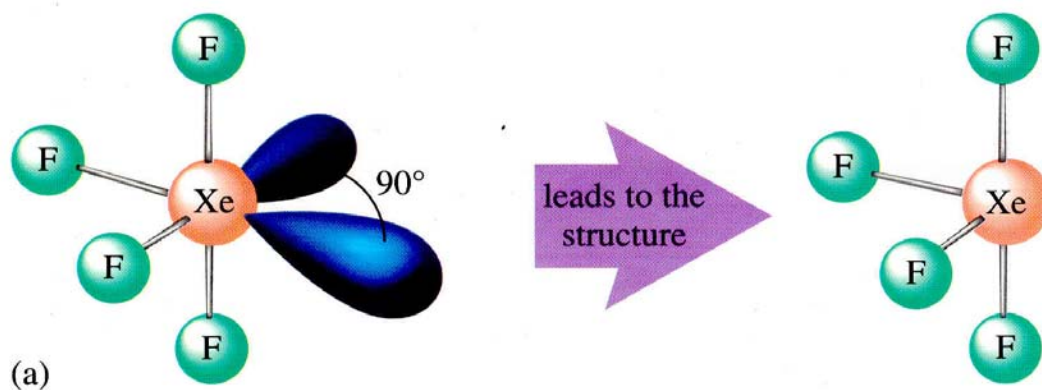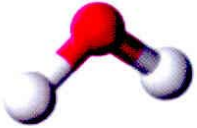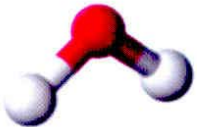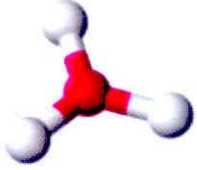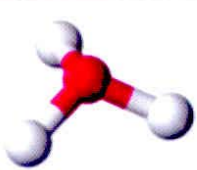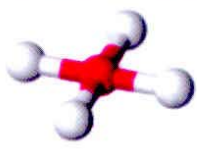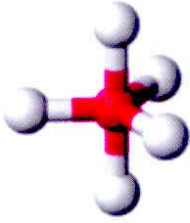
Figure 8.19
Possible structures for XeF$_4$

Typical Bonding Characteristics of Second-Row Elements in <u>Neutral</u> Compounds

Element	Bonding Pairs	Lone Pairs
Lithium	1	0
Beryllium	2	0
Boron	3	0
Carbon	4	0
Nitrogen	3	1
Oxygen	2	2
Fluorine	1	3
Neon	0	4

Examples of Molecular Structures:

Molecule Type	Shape	Electron arrangement†	Geometry‡	Examples
AX_2E_0	Linear			$BeCl_2$, $HgCl_2$, CO_2
AX_2E_1	Bent			NO_2^-, SO_2, O_3, CCl_2
AX_2E_2	Bent			H_2O, OF_2
AX_2E_3	Linear			XeF_2, I_3^-, $XeCl_2$
AX_3E_0	Trigonal planar			BF_3, CO_3^{2-}, NO_3^-, SO_3
AX_3E_1	Trigonal pyramidal			NH_3, PCl_3
AX_3E_2	T-shaped			ClF_3, BrF_3
AX_4E_0	Tetrahedral			CH_4, PO_4^{3-}, SO_4^{2-}, ClO_4^-, $TiCl_4$, XeO_4
AX_4E_1	Seesaw			SF_4
AX_4E_2	Square planar			XeF_4

AX_5E_0	Trigonal bipyramidal			PCl_5
AX_5E_1	Square pyramidal			ClF_5, BrF_5, $XeOF_4$
AX_5E_2	Pentagonal planar			XeF_5^-
AX_6E_0	Octahedral			SF_6, WCl_6
AX_6E_1	Pentagonal pyramidal			$XeOF_5^-$, IOF_5^{2-} [7]
AX_7E_0	Pentagonal bipyramidal			IF_7
AX_8E_0	Square antiprismatic			IF_8^-, ZrF_8^{4-}, ReF_8^-
AX_9E_0	Tricapped trigonal prismatic OR capped square antiprismatic			ReH_9^{2-}

† *Electron arrangement including lone pairs, shown in pale yellow*

‡ *Observed geometry (excluding lone pairs)*
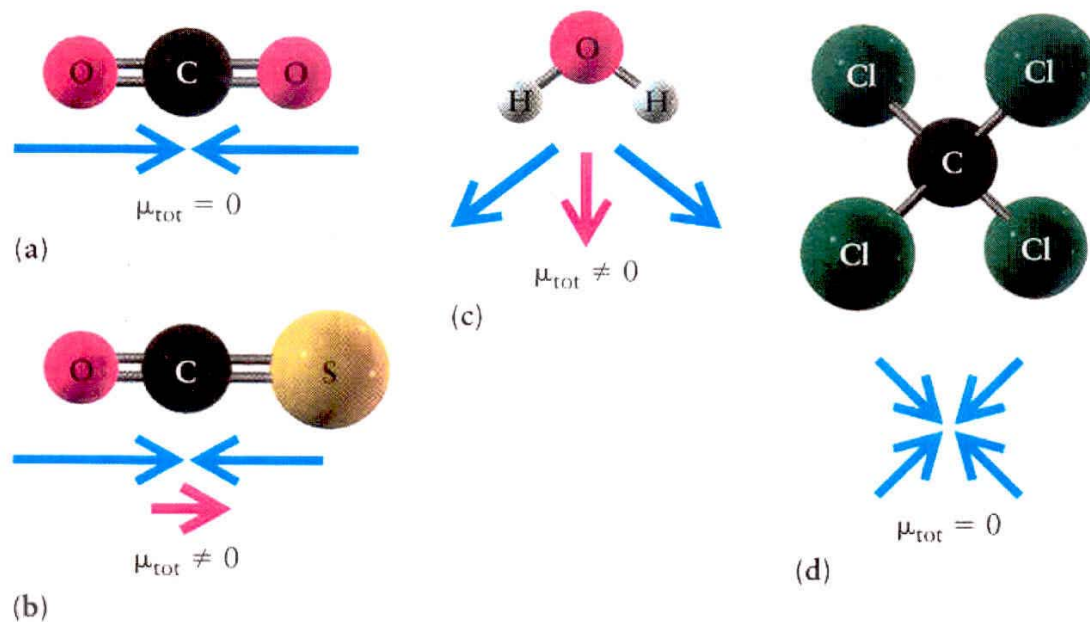
FIGURE 3.25 The total dipole moment of a molecule is obtained by vector addition of its bond dipoles. This operation is performed by adding the arrows when they lie pointing in the same direction, and subtracting the arrows if they lie pointing in different directions. (a) CO_2. (b) OCS. (c) H_2O. (d) CCl_4.

VSEPR type	Nonpolar	Polar	VSEPR type	Nonpolar	Polar
AX_2	CO_2	N_2O	AX_4	CH_4	CH_3Cl
AX_2E		SO_2, O	AX_4E		SF_4
AX_2E_2		H_2O	AX_4E_2	XeF_4	
AX_2E_3	XeF_2, I_3^-	$BrIF^-$	AX_5	PCl_5	PCl_4F
AX_2E_4	None known	None known	AX_5E		IF_5
AX_3	BrF_3	$COCl_2$	AX_6	SF_6	
AX_3E		NH_3			
AX_3E_2		ClF_3			
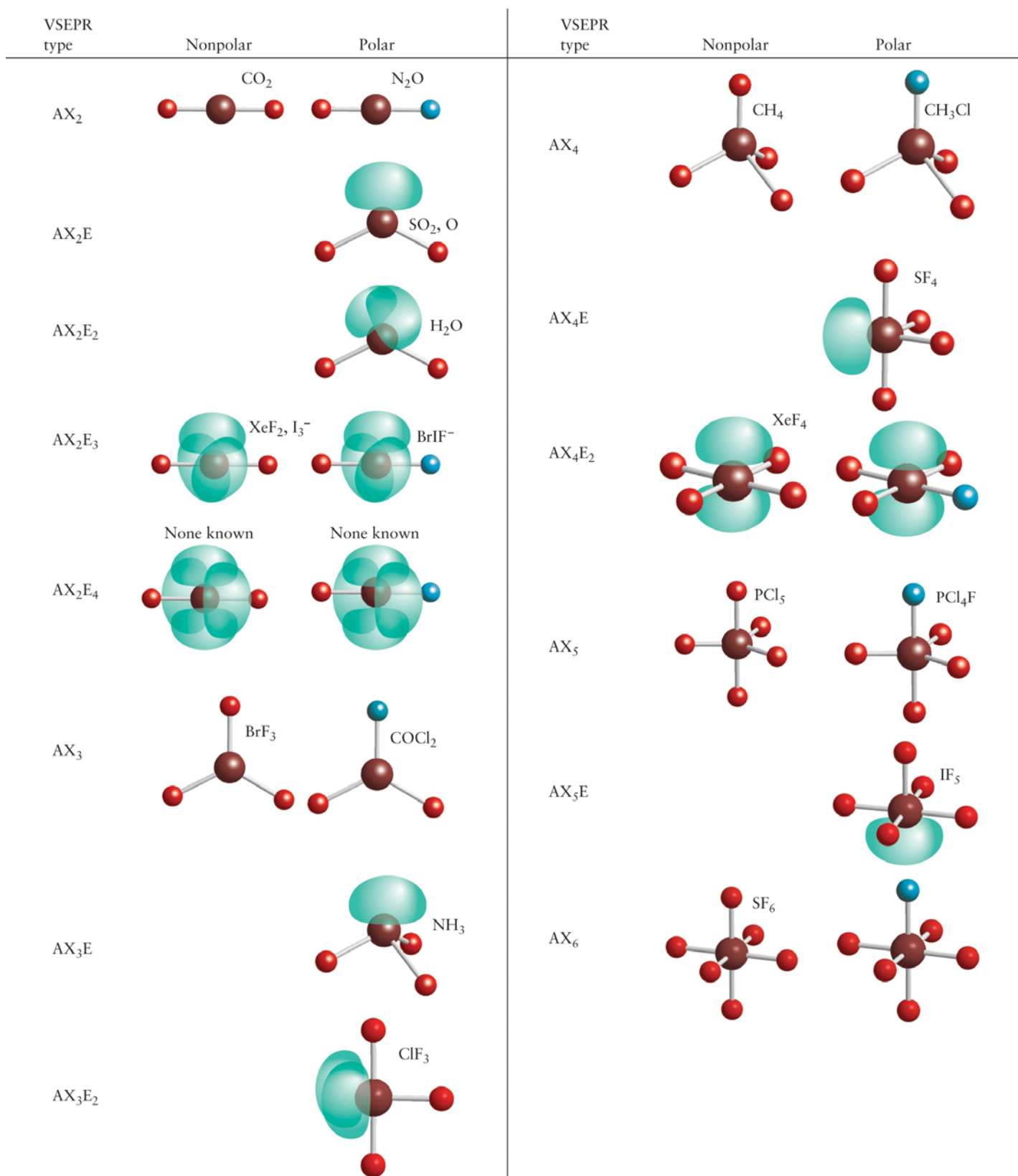
FIGURE 4.7 Arrangements of atoms that give rise to polar and nonpolar molecules. In the VSEPR formulas, A stands for a central atom, X for an attached atom, and E for a lone pair. Identical atoms are the same color; attached atoms colored differently belong to different elements. The green lobes represent lone pairs of electrons.

Molecular Electrostatic Potential Maps

LiH
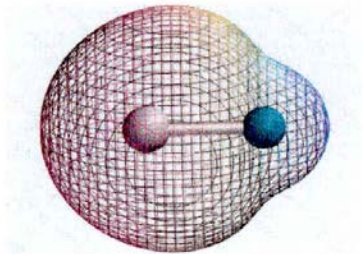
HF
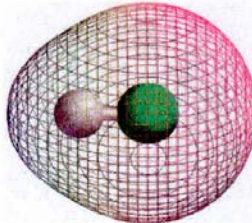
BeH$_2$
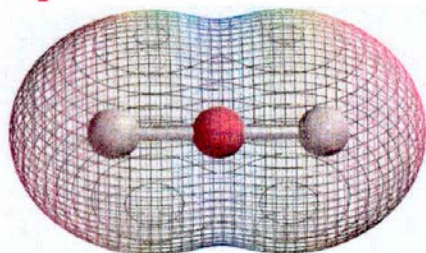
H$_2$O
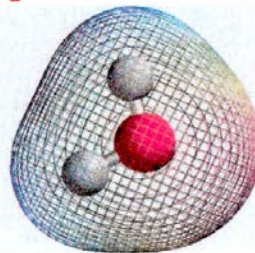
BH$_3$
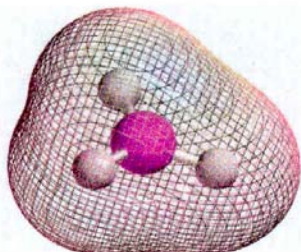
NH$_3$
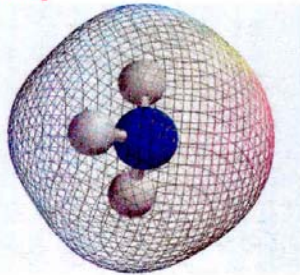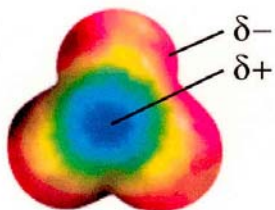
16 Nitrate ion

27 Carbon dioxide, CO$_2$

28 Water, H$_2$O
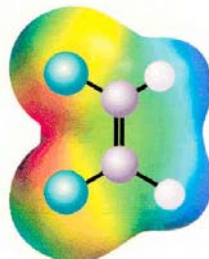
29 *cis*-Dichloroethene, C$_2$H$_2$Cl$_2$

***trans*-Dichloroethene, C$_2$H$_2$Cl$_2$**
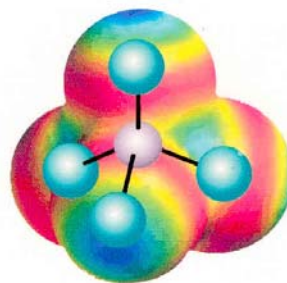
31 Tetrachloromethane, CCl$_4$
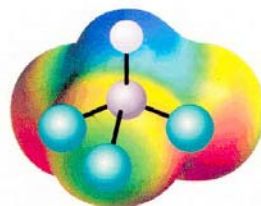
32 Trichloromethane, CHCl$_3$

TABLE 6.1

Selected molecular bond lengths r_e (Å) and dipole moments μ (D)

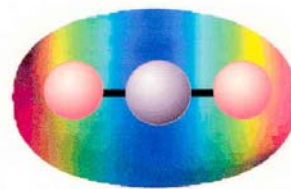| Diatomic molecules			Polyatomic molecules		
Molecule	r_e	μ	Molecule	r_e	μ
H_2	0.741	0	BeH_2	1.19	0
HF	0.917	1.82	H_2O	0.96	1.85
HCl	1.27	1.08	H_2S	1.35 (92°)*	0.97
HBr	1.41	0.82	HCN	1.06(C—H); 1.16(C≡N)	2.98
HI	1.60	0.44	CO_2	1.16	0
CO	1.13	0.11	NO_2	1.20 (134°)*	0.32
CS	1.53	1.98	N_2O	1.13(N≡N); 1.19(N—O)	0.17
N_2	1.10	0	SO_2	1.43	1.63
NO	1.15	0.15	O_3	1.28	0.53
O_2	1.21	0	CS_2	1.56	0
F_2	1.42	0	COS	1.19(C=O); 1.58(C=S)	0.71
SO	1.48	1.55	OF_2	1.42	0.30
ClF	1.63	0.88	ONF	1.13(N=O); 1.52(N—F)	1.81
Cl_2	1.99	0	HgI_2	2.77	0
Br_2	2.29	0	BF_3	1.44	0
I_2	2.66	0	NH_3	1.00	1.49
LiH	1.60	5.88	PH_3	1.43	0.58
LiF	1.56	6.33	SO_3	1.74	0
LiCl	2.02	7.13	PCl_3	2.10	0.78
LiBr	2.17	7.27	$SOCl_2$	1.56(S=O); 2.03(S—Cl)	1.45
LiI	2.39	7.43	NHF_2	1.00(N—H); 1.34(N—F)	1.92
NaF	1.93	8.16	CH_4	0.98	0
NaCl	2.36	9.00	CH_3F	1.41(C—F)	1.81
KF	2.17	8.60	CH_3Cl	1.76(C—Cl)	1.87
KCl	2.67	10.27	CH_2Cl_2		1.58
KBr	2.82	10.41	$CHCl_3$		1.01
RbF	2.27	8.55	CCl_4		0
CsF	2.35	7.88	CH_3I	2.10(C—I)	1.91
CsCl	2.57	10.42	SiF_4	1.81	0
SrO	1.92	8.90	SF_4	1.68	0.63
			PCl_5	2.05, 2.19	0
			IF_5	1.97	2.18
			SF_6	1.66	0
			C_2H_4	1.34(C=C); 0.99(C—H)	0
			N_2H_4	1.40(N—N); 1.00(N—H)	1.75
			H_2O_2	1.32(O—O); 0.96(O—H)	2.2

*Anomalous bond angle.