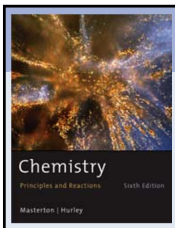

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Chapter 7
Covalent Bonding

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Outline

1. Lewis Structures; the Octet Rule
2. Molecular Geometry
3. Molecular Polarity
4. Atomic Orbitals; Hybridization

Covalent Bonding Introduction, 1

- Recall that electrons in atoms are placed into atomic orbitals according to the Aufbau principle and Hund's Rule
- In this section of the course, we will look at the location of electrons in molecules containing covalent bonds

Covalent Bonding Introduction, 2

- **Electron density**
  - Electrons are located between nuclei
    - Electrostatic energy of the system is lowered
    - When two hydrogen atoms come together, electron density is spread over the entire molecule
  - Study of the covalent bond as it exists in molecules and polyatomic ions

Figure 7.1 – The Hydrogen Molecule

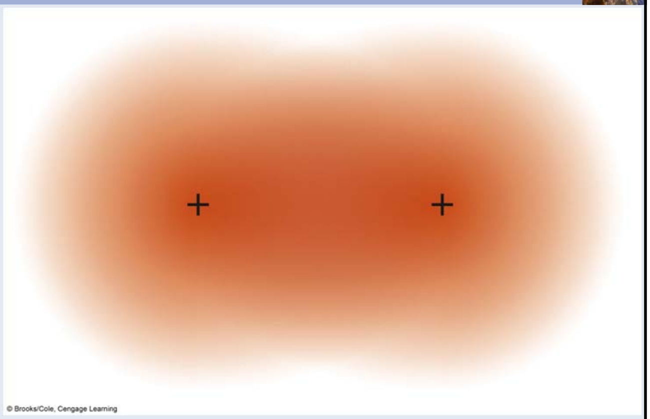
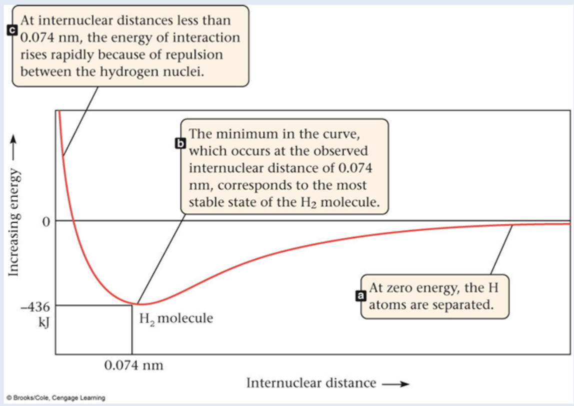


Figure 7.2



Lewis Structures

- Recall that atoms may form ions that are isoelectronic with the nearest noble gas
  - Na forms Na^+ $1s^2 2s^2 2p^6 3s^1 \rightarrow 1s^2 2s^2 2p^6$
  - F forms F^- $1s^2 2s^2 2p^5 \rightarrow 1s^2 2s^2 2p^6$
- Some atoms share electrons rather than ionize
  - Sharing results in atoms becoming isoelectronic with the nearest noble gas, as they do in forming ions

Table 1.1

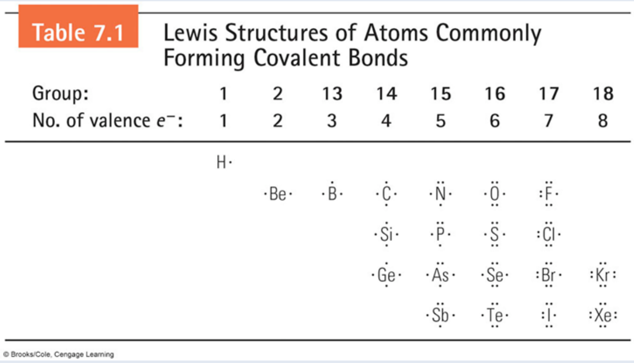


Table 7.1 Lewis Structures of Atoms Commonly Forming Covalent Bonds

Group:	1	2	13	14	15	16	17	18
No. of valence e^-:	1	2	3	4	5	6	7	8
	H							
		Be	B	C	N	O	F	
				Si	P	S	Cl	
				Ge	As	Se	Br	Kr
					Sb	Te	I	Xe

Valence

- Outermost electrons are called valence electrons
  - Consider F
    - $1s^2 2s^2 2p^5$
    - 1s are *core* electrons
    - 2s and 2p are *valence* electrons
  - Consider HF
    - Hydrogen contributes a 1s electron to form a covalent bond
    - F contributes seven electrons and shares one more
    - Total of eight valence electrons
    - F in HF now has a total of eight valence electrons; H has two

Electron Ownership

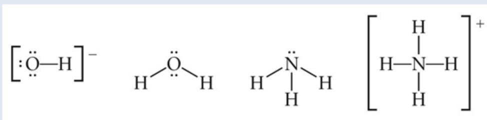
- An atom owns
  - All lone electrons
    - Shown as lone pairs
  - Half the number of bonding electrons
    - A bond pair is shown as a line
    - Multiple bonds are possible
      - Double bonds are two pairs
      - Triple bonds are three pairs

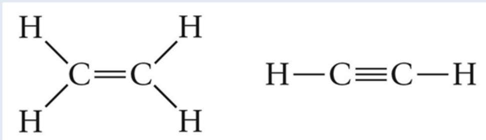
Tools

- Lewis structures
  - Distribute electron pairs in a molecule such that each atom achieves an octed (hydrogen a duet)
- Molecular geometry
  - Location of both shared and unshared electron pairs leads to VSEPR geometry

Examples of Lewis Structures

- OH^-, H_2O, NH_3, NH_4^+, C_2H_4, C_2H_2





ethylene, C_2H_4 acetylene, C_2H_2

The Octet Rule

- Main group elements seek to attain an octet of electrons
  - Recall that an s^2p^6 configuration is isoelectronic with a noble gas
  - Closed electron shells
  - Exception: H
    - The duet rule

Writing Lewis Structures*

1. Count the number of valence electrons
2. Draw a skeleton structure for the species, joining the atoms by single bonds
3. Determine the number of valence electrons still available for distribution
4. Determine the number of valence electrons required to fill out an octet for each atom (except H) in the structure

*see p. 169 of the text

1. Counting the Valence Electrons

- Total the valence electrons for each atom present in the molecule or ion.
  - For an anion, add one electron for each unit of negative charge
  - For a cation, subtract one electron for each unit of positive charge

2. Drawing the Skeleton Structure

- One atom must be central
  - This is usually the first one written in the formula
  - Less electronegative elements are usually central
  - Atoms that are usually terminal, not central
    - Hydrogen (must be terminal)
    - Halogens
    - Oxygen

3. Determining the Number of Valence Electrons Left

- Each bond represents a pair of electrons

4. Completing the Octets

- Distribute the remaining electrons to complete the octet for each element
  - In some cases, multiple bonds are required
    - Some elements never participate in multiple bonds: hydrogen and halogens

Example 7.1

Example 7.1 Draw Lewis structures of

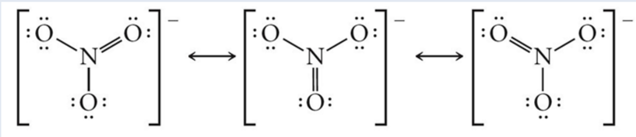
(a) the hypochlorite ion, OCl^- (b) ethane, C_2H_6

Strategy Follow the steps described above. For the OCl^- ion, only one skeleton is possible. For ethane keep in mind that the carbon atom ordinarily forms four bonds. Hydrogen must be a terminal atom because it forms only one bond.

SOLUTION

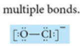
(a) (1) The number of valence electrons is 6 (from O) + 7 (from Cl) + 1 (from the −1 charge) = 14.
(2) The skeleton structure is $[O—Cl]^-$.
(3) The number of electrons available for distribution is 14 (originally) − 2 (used in skeleton) = 12.
(4) The number of electrons required to give each atom an octet is 6 (for O) + 6 (for Cl) = 12.

Nitrate Ion

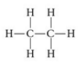


Example 7.1 (cont'd)

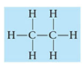
The number of available electrons is the same as the number required. This skeleton structure is correct; there are no multiple bonds. The Lewis structure is



(b) (1) the number of valence electrons is 8 (from the two carbon atoms) + 6 (from the six hydrogen atoms) for a total of 14.
(2) Because carbon forms four bonds and hydrogen must be a terminal atom, the only reasonable skeleton is



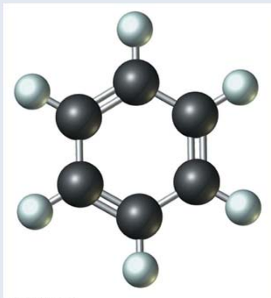
(3) The skeleton contains seven single bonds, using up $7 \times 2e^- = 14e^-$. This is exactly the number available, as shown in (1). It follows that the skeleton is also the Lewis structure:

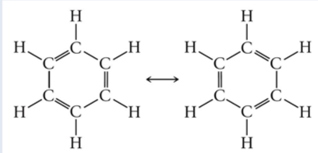


There are no unshared electron pairs.

Reality Check Whenever you write a Lewis structure, check to see if it follows the octet rule. The structures written for OCl^- and C_2H_6 do just that; each atom except H is surrounded by eight electrons.

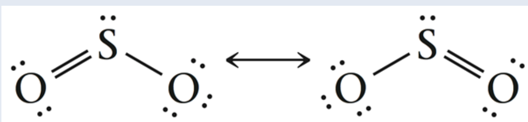
Benzene





Resonance Forms

- In certain cases, Lewis structures do not represent chemical or physical reality
  - Consider SO_2
  - Both S-O bonds are equal in length, yet the Lewis structure indicates one double and one single bond



Notes on Resonance Structures

1. Resonance forms are not different molecules, nor are they representations of electron shifting
2. Resonance structures arise when two Lewis structures are equally plausible
3. Only ***electrons*** can be shifted in resonance structures. Atoms ***cannot*** be moved.

Example 7.3

Example 7.3 Write two resonance structures for the NO_2^- ion.

Strategy Write a Lewis structure for the NO_2^- ion, following the usual steps. Then write the other resonance form by changing the position of the multiple bond. Do *not* change the skeleton structure.

SOLUTION The Lewis structures of the two resonance forms are

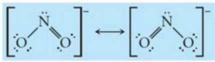
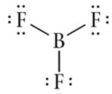


Table 7.2 BeF_2 and BF_3

Table 7.2 Possible Structures for BeF_2 and BF_3

Structure I	C_f	Structure II	C_f
:F̈=Be=F̈:	Be = −2 F = +1	:F̈—Be—F̈:	Be = 0 F = 0
	B = −1 F = +1,0,0		B = 0 F = 0

Formal Charges

- Formal charges are analogous to oxidations numbers:
  - They are not actual charges
  - They keep track of electron ownership

Rules Governing Formal Charge

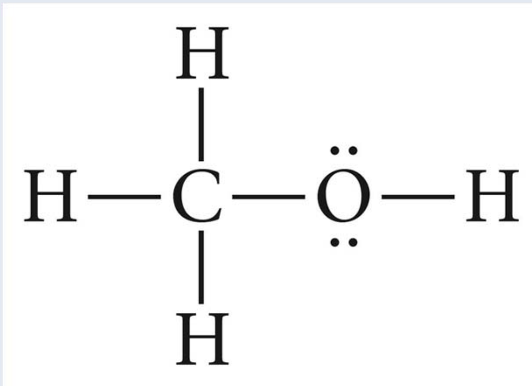
- The quality of a Lewis structure can be determined by the distribution of formal charge
  - Minimize charges
    - Best to have no C_f or small C_f
  - Watch electronegativity
    - The most electronegative atoms should have the most negative formal charge
  - Minimize separation of charge

Formal Charges

- Formal charges are determined by totaling the number of valence electrons (X), and then subtracting the total of the number of lone electrons (Y) plus half the number of bonding electrons (Z/2)

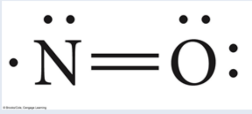
$$C_f = X - \left(Y + \frac{Z}{2}\right)$$

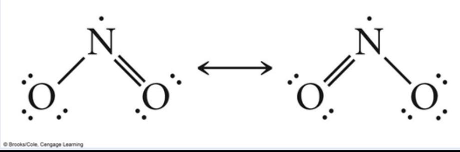
Example



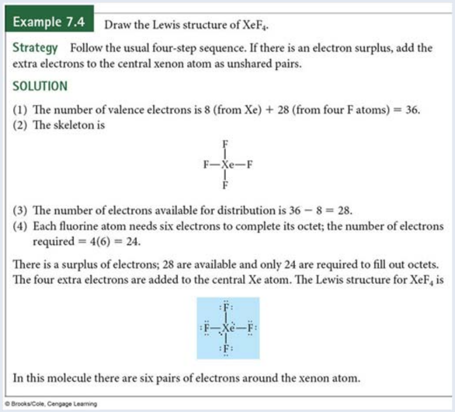
Exceptions to the Octet Rule, 1

- Electron deficient molecules
  - Odd electron species (free radicals)
  - Paramagnetic
  - Examples: NO, NO_2





Example 7.4 – Expanded Octets



Example 7.4 Draw the Lewis structure of XeF_4.

Strategy Follow the usual four-step sequence. If there is an electron surplus, add the extra electrons to the central xenon atom as unshared pairs.

SOLUTION

(1) The number of valence electrons is 8 (from Xe) + 28 (from four F atoms) = 36.
(2) The skeleton is

F
|
F—Xe—F
|
F

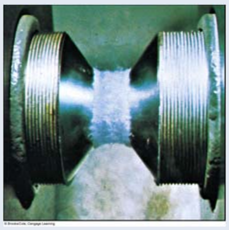
(3) The number of electrons available for distribution is 36 − 8 = 28.
(4) Each fluorine atom needs six electrons to complete its octet; the number of electrons required = 4(6) = 24.

There is a surplus of electrons; 28 are available and only 24 are required to fill out octets. The four extra electrons are added to the central Xe atom. The Lewis structure for XeF_4 is

In this molecule there are six pairs of electrons around the xenon atom.

Exceptions to the Octet Rule, 2

- Molecular oxygen, O_2
- Molecular oxygen is paramagnetic
- Although it has an even number of electrons, it exists as a *diradical (two unpaired electrons)*
- Lewis structure for O_2 is difficult to draw



Molecular Geometry

- Diatomic molecules are the easiest to visualize in three dimensions
  - HCl
  - Cl_2
- Diatomic molecules are ***linear***

Expanded Octets, 1

- Some elements are capable of surrounding themselves with more than four pairs of electrons
  - Expanded octets
  - PCl_5, SF_6

Period	Grp 15	Grp 16	Grp 17	Grp 18
3	P	S	Cl	
4	As	Se	Br	Kr
5	Sb	Te	I	Xe

Figure 7.4 – Ideal Geometries

- There is a fundamental geometry that corresponds to the total number of electron pairs around the central atom: 2, 3, 4, 5 and 6

linear | trigonal planar | tetrahedral | trigonal bipyramidal | octahedral

Valence Shell Electron Pair Repulsion Theory

- The ideal geometry of a molecule is determined by the way the electron pairs orient themselves in space
  - The orientation of electron pairs arises from electron repulsions
  - The electron pairs spread out so as to minimize repulsion

Two electron pairs

- ***Linear***
- Bond angles
  - The bond angle in a linear molecule is always 180°

Three electron pairs

- ***Trigonal planar***
- The electron pairs form an equilateral triangle around the central atom
- Bond angles are 120°

Four Electron Pairs

- ***Tetrahedral***
- Bond angles are 109.5°

Five Electron Pairs

- ***Trigonal bipyramid***
- Bond angles vary
  - In the trigonal plane, 120°
  - Between the plane and apexes, 90°
  - Between the central atom and both apexes, 180°

Six Electron Pairs

- ***Octahedron***
- The octahedron is a ***square bipyramid***
- Bond angles vary
  - 90° in and out of plane
  - 180° between diametrically opposite atoms and the central atom

Figure 7.5 - Molecular Geometry Summarized - 1

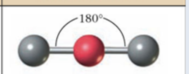
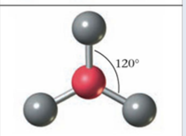
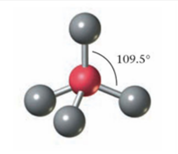
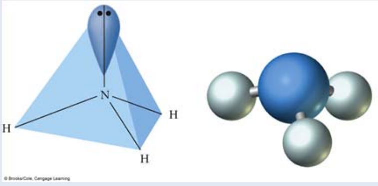
Species type	Orientation of electron pairs	Predicted bond angles	Example	Ball and stick model
AX_2	Linear	180°	BeF_2	
AX_3	Trigonal planar	120°	BF_3	
AX_4	Tetrahedron	109.5°	CH_4	

Figure 7.6-7.7 - Ammonia and Water



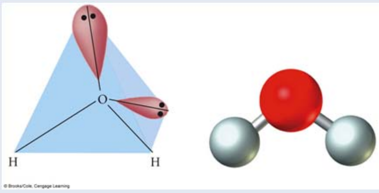
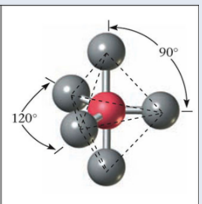
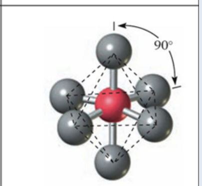


Figure 7.5 - Molecular Geometry Summarized, 2

AX_5	Trigonal bipyramid	90° 120° 180°	PF_5	
AX_6	Octahedron	90° 180°	SF_6	

Bond Angles and Lone Pairs

- Ammonia and water show smaller bond angles than predicted from the ideal geometry
  - The lone pair is larger in volume than a bond pair
  - There is a nucleus at only one end of the bond so the electrons are free to spread out over a larger area of space

Unshared Pairs and Geometry

- Electron pair geometry
  - Consider the ***terminal atoms*** and the ***lone pairs*** around the central atom
- Molecular geometry
  - Consider only the ***terminal atoms*** around the central atom

The A-X-E Notation

- A denotes a central atom
- X denotes a terminal atom
- E denotes a lone pair
- Example
  - Water
    - H_2O
    - O is central
      - Two lone pairs
      - Two hydrogens
    - AX_2E_2

Table 7.3 - Molecular Geometry Summary with Lone Pairs Included

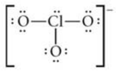
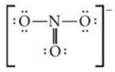
Table 7.3 Geometries with Two, Three, or Four Electron Pairs Around a Central Atom

No. of Terminal Atoms (X) + Unshared Pairs (E)	Species Type	Ideal Bond Angles*	Molecular Geometry	Examples
2	AX_2	180°	Linear	BeF_2, CO_2
3	AX_3	120°	Trigonal planar	BF_3, SO_3
	AX_2E	120°*	Bent	GeF_2, SO_2
4	AX_4	109.5°	Tetrahedron	CH_4
	AX_3E	109.5°*	Trigonal pyramid	NH_3
	AX_2E_2	109.5°*	Bent	H_2O

*In these species, the observed bond angle is ordinarily somewhat less than the ideal value.

Example 7.6

Example 7.6 Predict the geometries of the ClO_3^- ion, the NO_3^- ion, and the N_2O molecule, which have the Lewis structures

(a)  (b)  (c) :N̈=N=Ö:

Strategy Classify each species as AX_mE_n and use Table 7.3.

Example 7.5

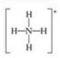
Example 7.5 Predict the geometry of

(a) NH_4^+ (b) GeF_2 (c) PF_3

Strategy Draw the Lewis structure as a first step. Then decide what type (AX_2, AX_3, and so on) the molecule is, focusing on the central atom. Remember, X represents a terminal atom, E an unshared pair of electrons.

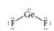
SOLUTION

(a) The Lewis structure for the ammonium ion is



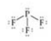
This is an AX_4 species. It is tetrahedral with 109.5° bond angles.

(b) The Lewis structure of GeF_2 (18 valence e^-) is



The central germanium atom has one unshared pair and two bonds.
This is a "bent" AX_2E species. The bond angle is expected to be a little less than 120°.

(c) The Lewis structure of PF_3 is



The central phosphorus atom has one unshared pair and three bonded atoms. The molecule is of type AX_3E; it should be a trigonal pyramid (like NH_3) with a bond angle somewhat less than 109.5° (actually, 104°).

Reality Check NH_4^+ is like CH_4, GeF_2 like SO_2, and PF_3 like NH_3.

Example 7.6 (cont'd)

SOLUTION

(a) The central atom, chlorine, is bonded to three oxygen atoms; it has one unshared pair. The ClO_3^- ion is of the type AX_3E. It is a trigonal pyramid; ideal bond angle is 109.5°.

(b) The central atom, nitrogen, is bonded to three oxygen atoms; it has no unshared pairs. The NO_3^- ion is of the type AX_3. It has the geometry of an equilateral triangle, with the nitrogen atom at the center; the bond angle is 120°. The ion is trigonal planar.

(c) The central nitrogen atom is bonded to two other atoms with no unshared pairs. The molecule, type AX_2, is linear, with a bond angle of 180°.

Multiple Bonds

- For molecular geometry purposes, multiple bonds behave the same as single bonds
  - All of the electron pairs are located in the same place (between the nuclei)
  - The geometry of the molecule is determined by the number of terminal atoms, which is not affected by the presence of a double or triple bond

Figure 7.8 - Molecular Geometry Summary 1

5 ELECTRON PAIRS

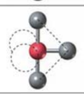
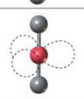
Species type	Structure	Description	Example	Bond angles
AX_5		Trigonal bipyramidal	PF_5	90°, 120°, 180°
AX_4E		See-saw	SF_4	90°, 120°, 180°
AX_3E_2		T-shaped	ClF_3	90°, 180°
AX_2E_3		Linear	XeF_2	180°

Figure 7.8 - Molecular Geometry Summary 2

6 ELECTRON PAIRS

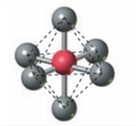
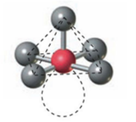
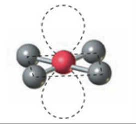
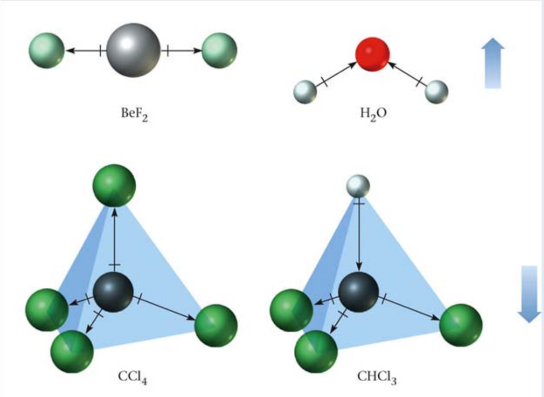
AX_6		Octahedral	SF_6	90°, 180°
AX_5E		Square pyramidal	ClF_5	90°, 180°
AX_4E_2		Square planar	XeF_4	90°, 180°

Figure 7.11 - Polarity of Molecules



Polarity - Bonds

- Recall that a polar bond has an asymmetric distribution of electrons
  - X-X is nonpolar
  - X-Y is polar
- Polarity of a bond increases with increasing difference in electronegativity between the two atoms
- Bond is a dipole
  - One end is (δ^+), while the other is (δ^-)

Example 7.7

Example 7.7 Determine whether each of the following is polar or nonpolar:

(a) SO_2 (b) BF_3 (c) CO_2

Strategy Write the Lewis structure of the molecule and classify it as AX_mE_n. Using Table 7.3 or Figure 7.5, decide on the geometry of the molecule. Then decide whether the dipoles cancel, in which case it is nonpolar.

Polarity - Molecules

- Molecules may also possess polarity
  - Positive and negative poles
  - Molecule is called a dipole
- Consider HF
  - H is δ^+ while F is δ^-
- Consider BeF_2
  - Be-F bond is polar
  - BeF_2 is nonpolar

Example 7.7 (cont'd)

SOLUTION

(a) The Lewis structure of SO_2 is shown on page 169; it is of the type AX_2E. The molecule is bent, so the dipoles do not cancel. The SO_2 molecule is polar.
(b) The Lewis structure of BF_3 is shown on page 173; it is of the type AX_3. The molecule is an equilateral triangle with the boron atom at the center. The three polar bonds cancel one another; BF_3 is nonpolar.
(c) The Lewis structure of CO_2 is shown on page 180; it is of the type AX_2. The molecule is linear, so the two C$\longrightarrow$O dipoles cancel each other; CO_2 is nonpolar.

Atomic Orbitals and Hybridization

- Valence Bond Model
  - Linus Pauling
    - Nobel Prize, 1954
  - Orbital diagrams
    - Isolated F atom (↑↓) (↑↓) (↑↓)(↑↓)(↑)
      1s 2s 2p
    - F atom in HF (↑↓) (↑↓) (↑↓)(↑↓)(↑↓)
      1s 2s 2p

Table 7.4 - Hybrid Orbitals and Geometry

Table 7.4 Hybrid Orbitals and Their Geometries

Number of Electron Pairs	Atomic Orbitals	Hybrid Orbitals	Orientation	Examples
2	s, p	sp	Linear	BeF_2, CO_2
3	s, two p	sp^2	Trigonal planar	BF_3, SO_3
4	s, three p	sp^3	Tetrahedron	CH_4, NH_3, H_2O
5	s, three p, d	sp^3d	Trigonal bipyramid	PCl_5, SF_4, ClF_3
6	s, three p, two d	sp^3d^2	Octahedron	SF_6, ClF_5, XeF_4

Valence Bond Theory

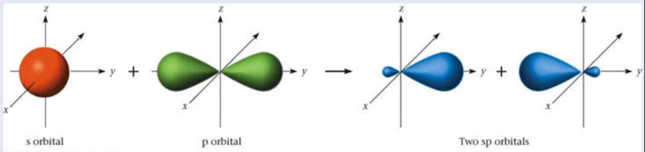
- Unpaired electrons from one atom pair with unpaired electrons from another atom and give rise to chemical bonds
- Simple extension of orbital diagrams

Hybrid Orbitals and Electron Occupancy

- Same rules we have seen before
  - In an atom, an orbital holds two electrons
  - In a molecule, an orbital also holds two electrons
- What electrons go into hybrid orbitals?
  - Lone pairs
  - One pair per bond
    - Even for a double bond, only one pair goes into the hybrid orbital

Figure 7.12 - Atomic Orbital Mathematics

- Two atomic orbitals produce two hybrid orbitals
  - One s + one p → two sp



Example 7.9

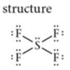
Example 7.9 Give the hybridization of

(a) carbon in CH_3Cl (b) phosphorus in PH_3 (c) sulfur in SF_4

Strategy Draw the Lewis structure for the molecule and determine the number of electron pairs (single bonds or unshared pairs) around the central atom. The possible hybridizations are sp (two pairs), sp^2 (three pairs), sp^3 (four pairs), sp^3d (five pairs), and sp^3d^2 (six pairs).

SOLUTION

(a) The hybridization is similar to that of CH_4; sp^3
(b) The hybridization is similar to that of NH_3; sp^3
(c) Sulfur tetrafluoride has the Lewis structure



There are five electron pairs around sulfur: four bonds and one unshared pair. The hybridization is sp^3d.

Reality Check If you are asked to predict the hybridization, as you are here, the geometry as in Example 7.6, or the polarity as in Example 7.7, you have to start with Lewis structures; that is why they are so important.

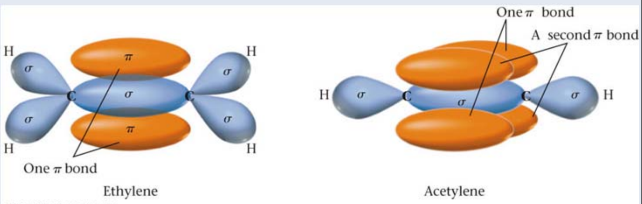
Multiple bonds

- Sigma (σ) bonds
  - Electron density is located between the nuclei
  - One pair of each bond is called a sigma pair
- Pi bonds (π)
  - Electron density is located above and below or in front of and in back of the nuclei
    - One pair of a double bond is called pi (π)
    - Two pairs of a triple bond are called pi (π)

Key Concepts

1. Draw Lewis structures for molecules and polyatomic ions.
2. Write resonance forms.
3. Use VSEPR theory to predict molecular geometry.
4. From the geometry of a species, predict whether it will be polar or not.
5. State the hybridization of a species.
6. State the number of sigma and pi bonds in a species.

Figure 7.13 - Ethylene and Acetylene



Example 7.11

Example 7.11 Give the number of pi and sigma bonds in

(a) NH_3 (b) NO_2^- (c) N_2

Strategy Refer back to Example 7.10 for the Lewis structures and apply the rules just cited.

SOLUTION

(a) 3 sigma bonds
(b) 2 sigma bonds, 1 pi bond
(c) 1 sigma bond, 2 pi bonds

Reality Check There are two pi bonds in a triple bond, one in a double bond, and none in a single bond.