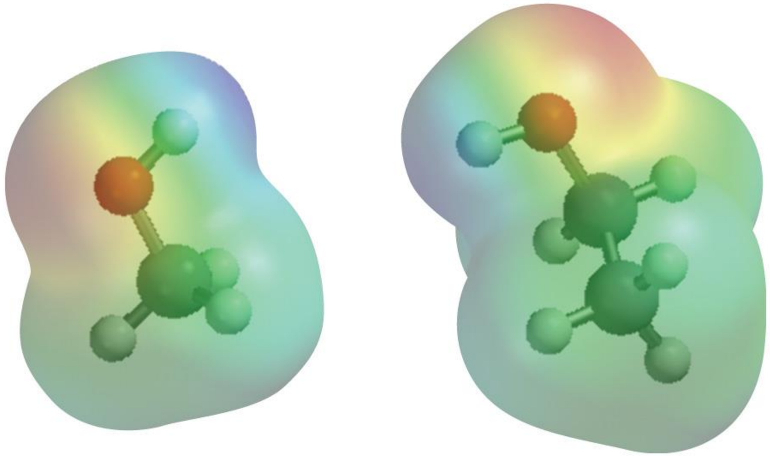
Petrucci • Harwood • Herring • Madura

Ninth Edition

GENERAL CHEMISTRY

Principles and Modern Applications



Chapter 10: Chemical Bonding I: Basic Concepts

Philip Dutton
University of Windsor, Canada
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Contents

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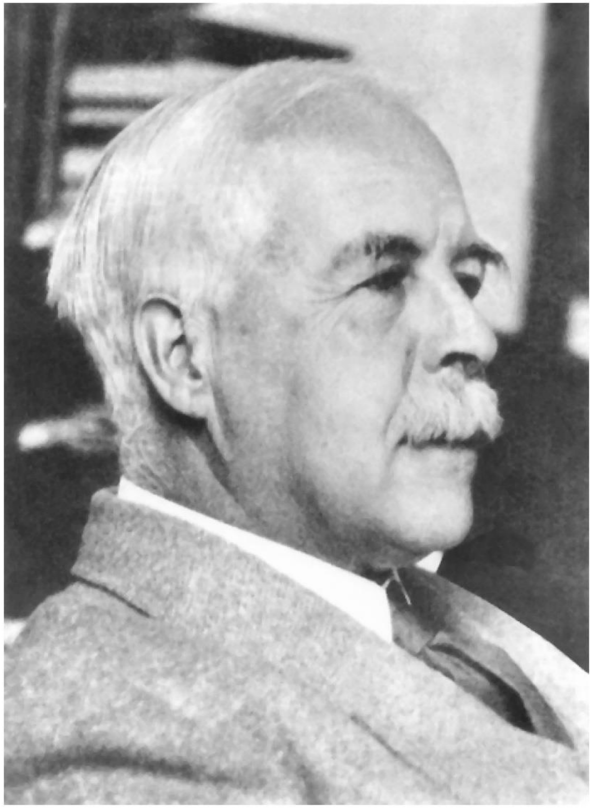
10-1 Lewis Theory: An Overview

- Valence *e*$^-$ play a fundamental role in chemical bonding.
- *e*$^-$ transfer leads to *ionic bonds.*
- Sharing of *e*$^-$ leads to *covalent bonds.*
- *e*$^-$ are transferred of shared to give each atom a noble gas configuration
  - *the octet.*



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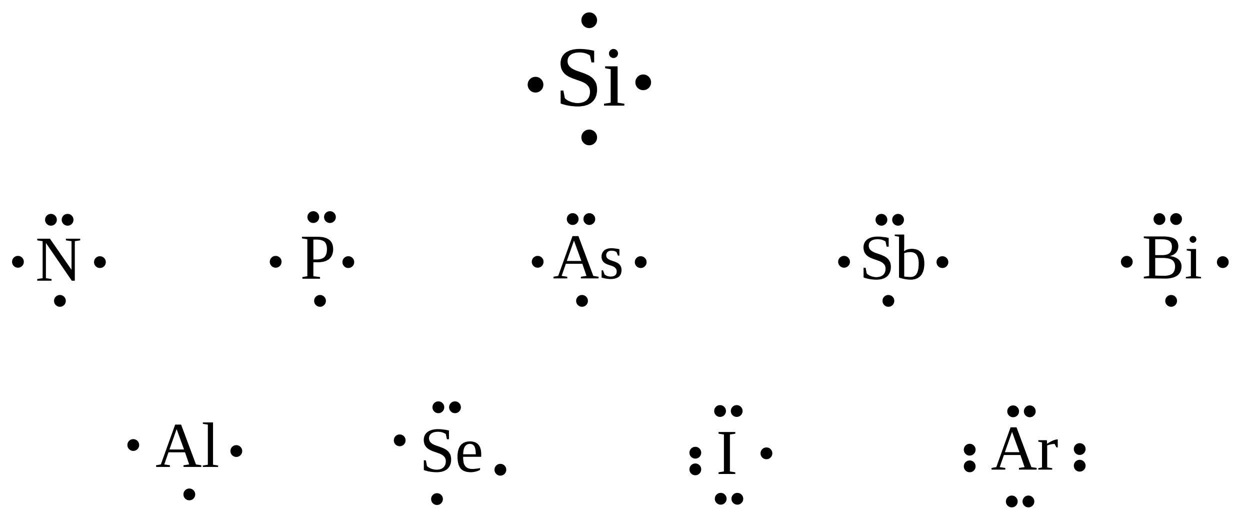
Lewis Symbols

- A chemical symbol represents the nucleus and the *core e*$^-$.
- Dots around the symbol represent *valence e*$^-$.



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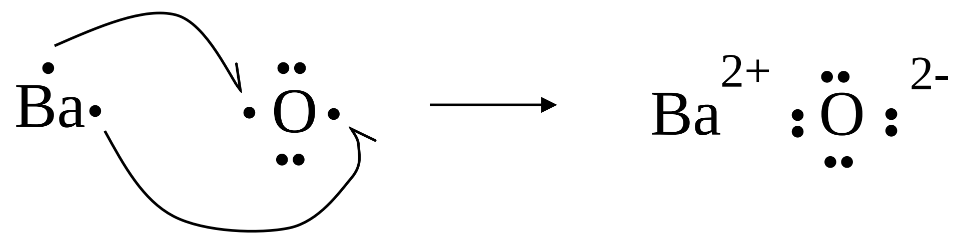
EXAMPLE 10-2

Writing Lewis Structures of Ionic Compounds. Write Lewis structures for the following compounds: (a) BaO; (b) $MgCl_2$; (c) aluminum oxide.

BaO



Note the use of the "fishhook" arrow to denote a single electron movement. A "double headed" arrow means that two electrons move.

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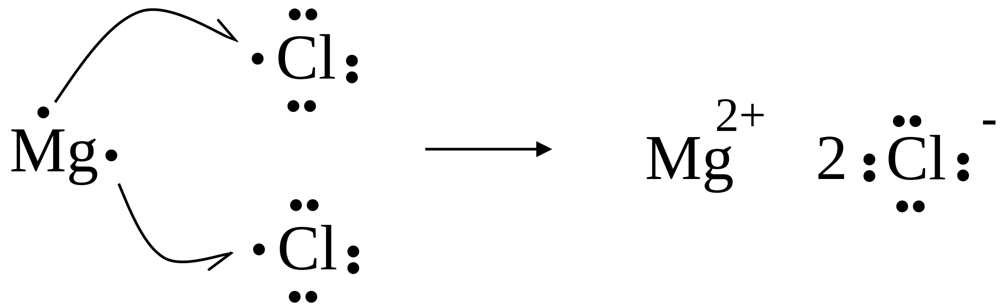
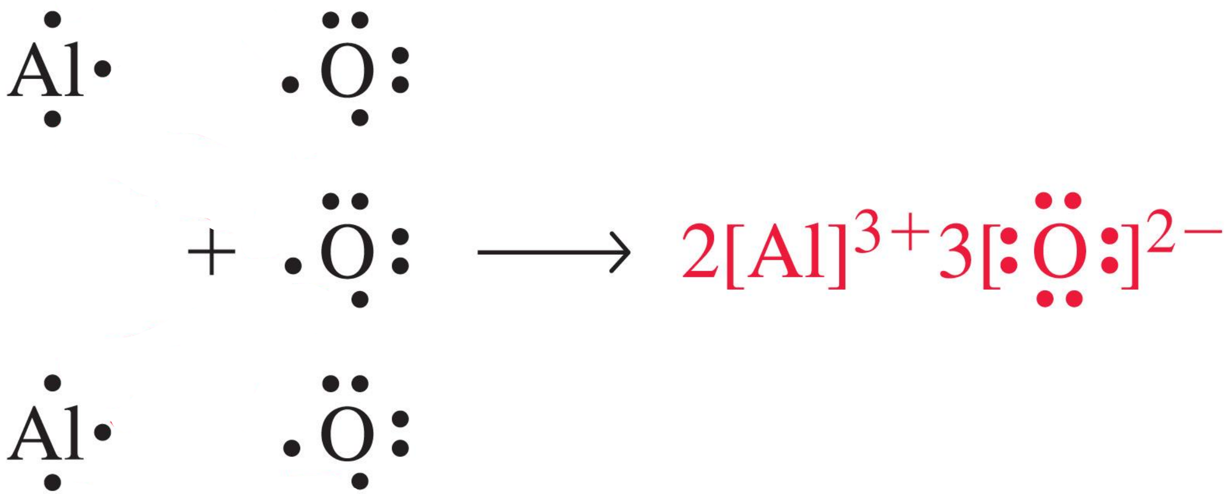
EXAMPLE 10-2

$MgCl_2$





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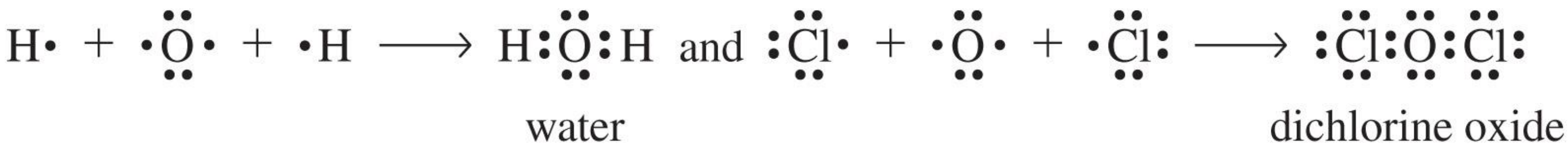
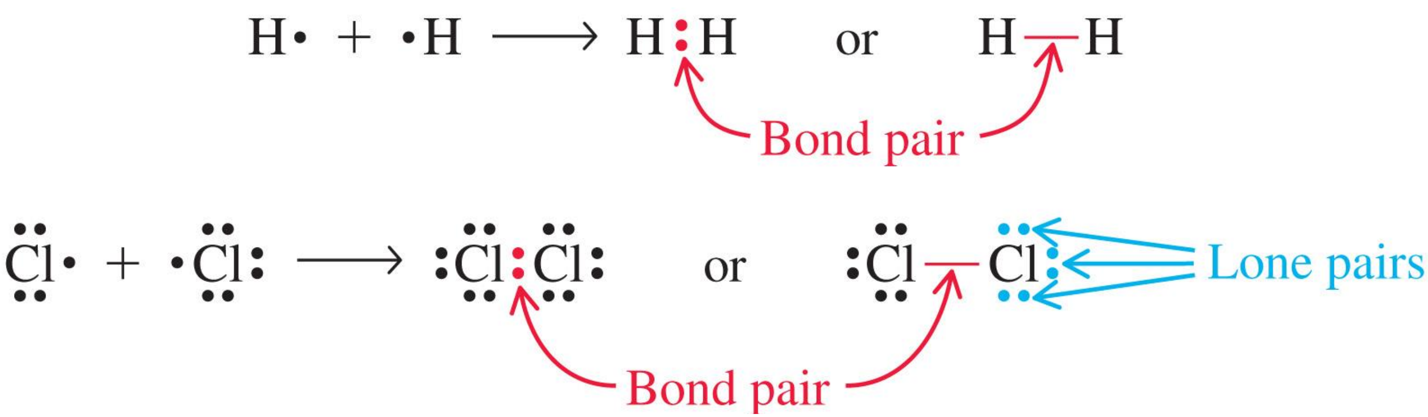
10-2 Covalent Bonding: An Introduction





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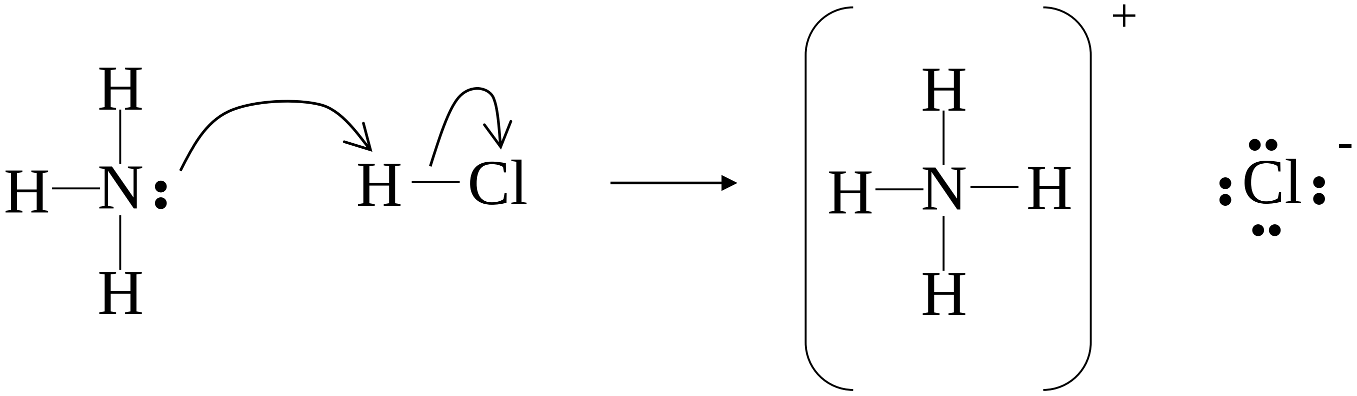
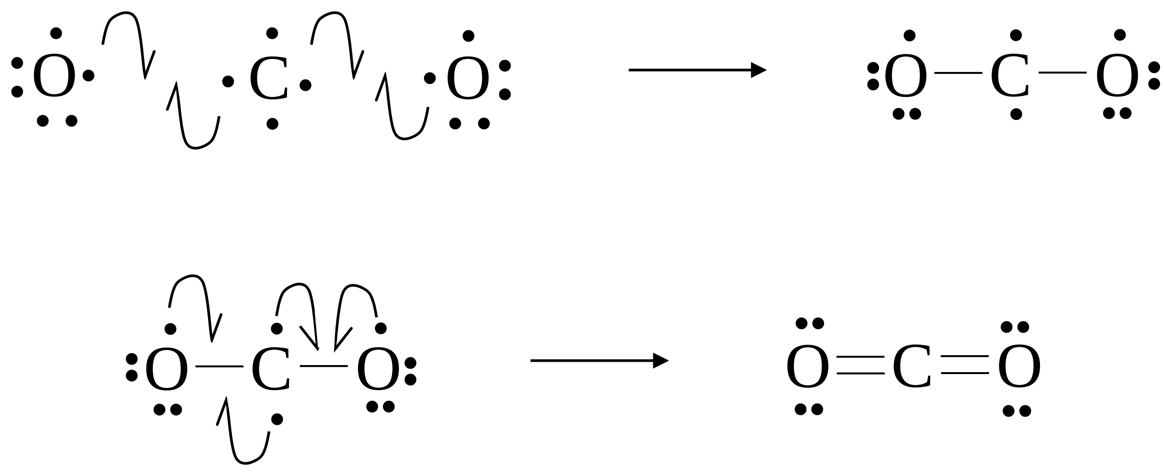
Coordinate Covalent Bonds

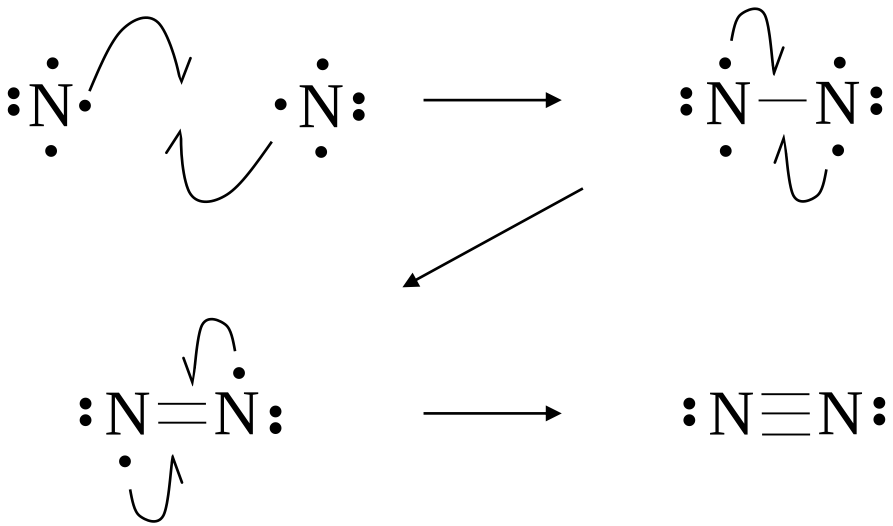


Note the "double headed" arrow
showing that two electrons move.

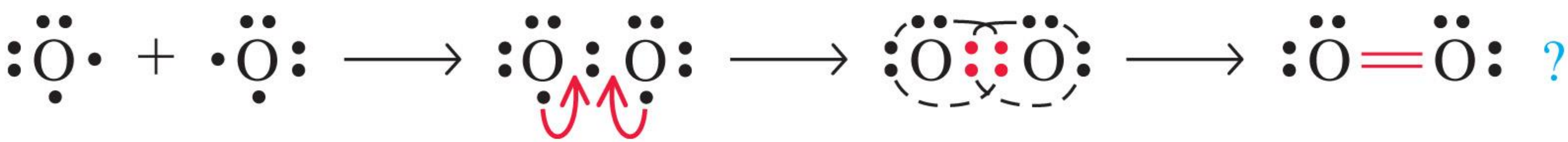
Multiple Covalent Bonds



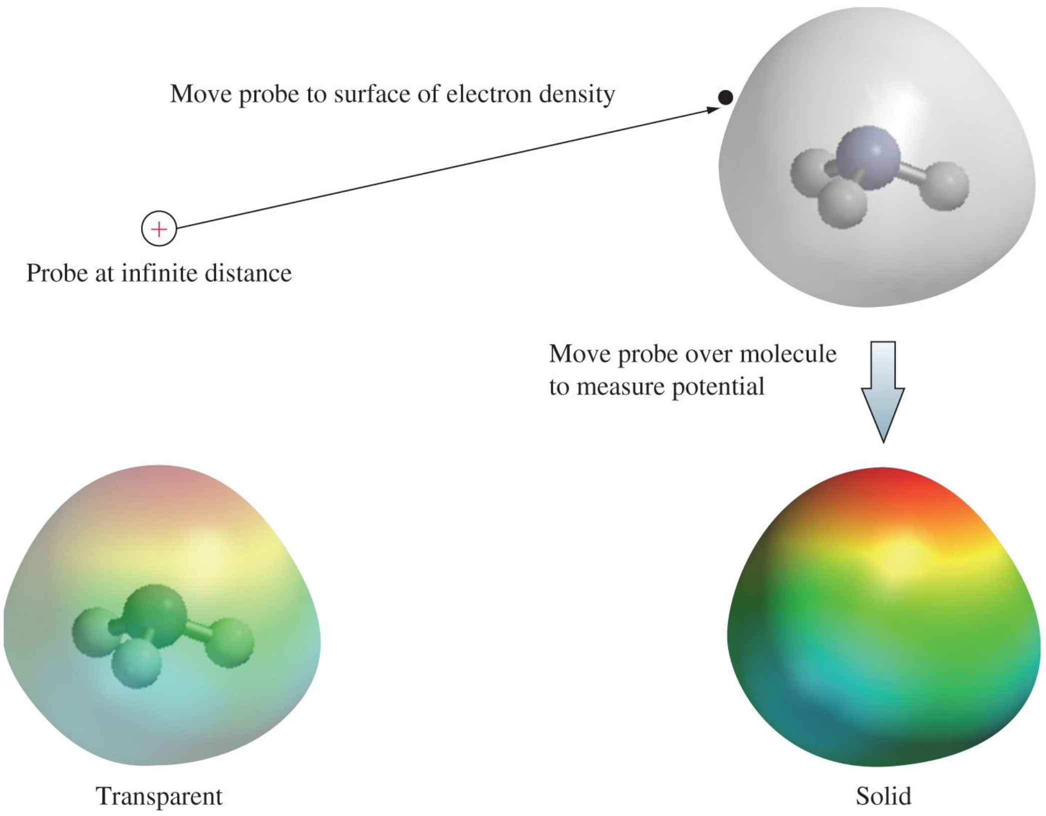
Multiple Covalent Bonds



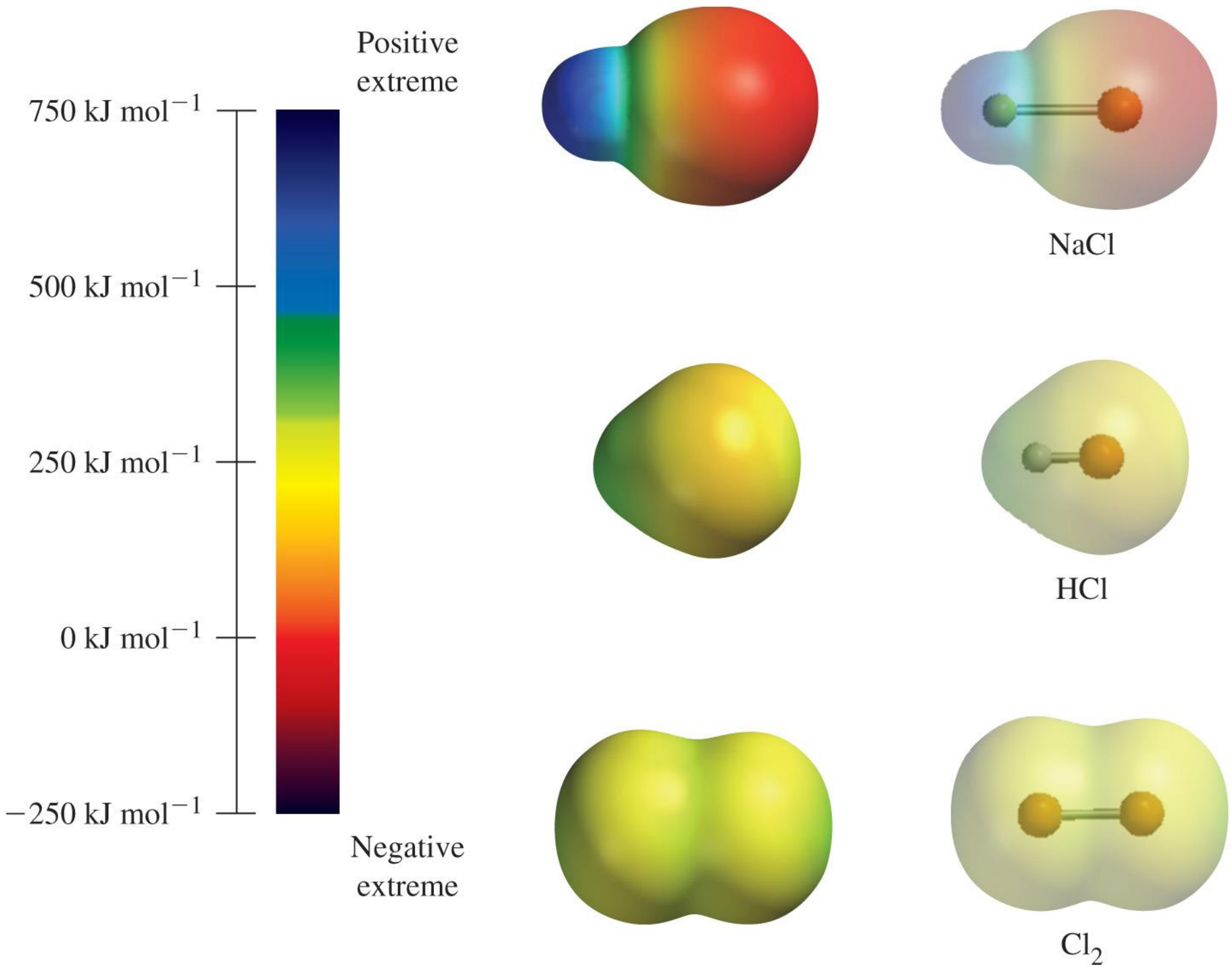
Paramagnetism of Oxygen



10-3 Polar Covalent Bonds and Electrostatic Potential Maps



Polar Molecules



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Electronegativity

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
H 2.1																
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5
Cs 0.8	Ba 0.9	La* 1.1	Hf 1.3	Ta 1.5	W 2.4	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2
Fr 0.7	Ra 0.9	Ac† 1.1														

- below 1.0
- 1.0–1.4
- 1.5–1.9
- 2.0–2.4
- 2.5–2.9
- 3.0–4.0

*Lanthanides: 1.1–1.3
†Actinides: 1.3–1.5

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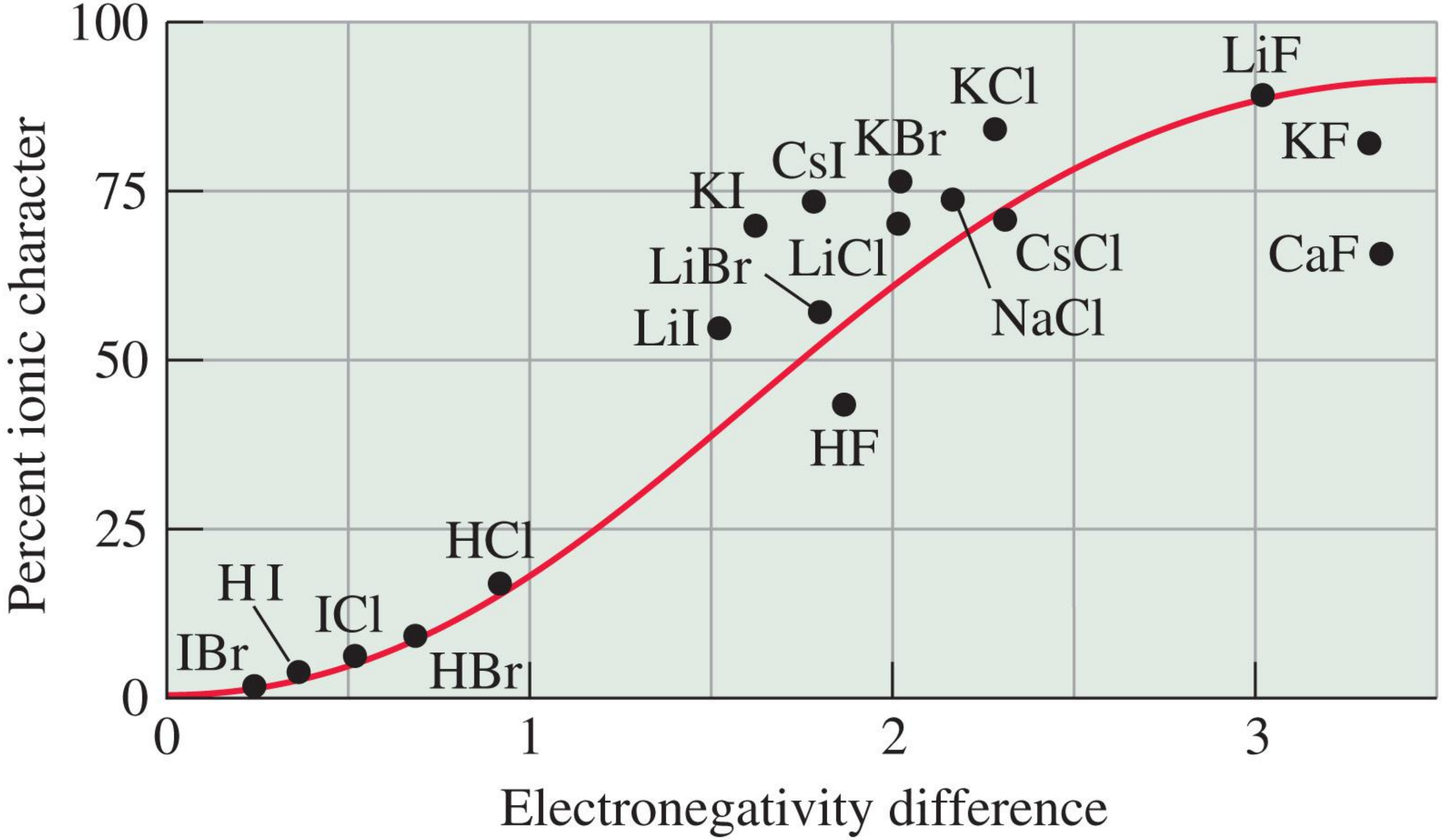
Percent Ionic Character



10-4 Writing Lewis Structures

- *All* the valence e^- of atoms must appear.
- *Usually*, the e^- are paired.
- *Usually*, each atom requires an octet.
  - H only requires 2 e^-.
- Multiple bonds may be needed.
  - Readily formed by C, N, O, S, and P.

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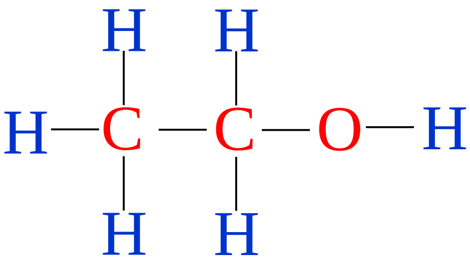
Skeletal Structure

- Identify central and terminal atoms.



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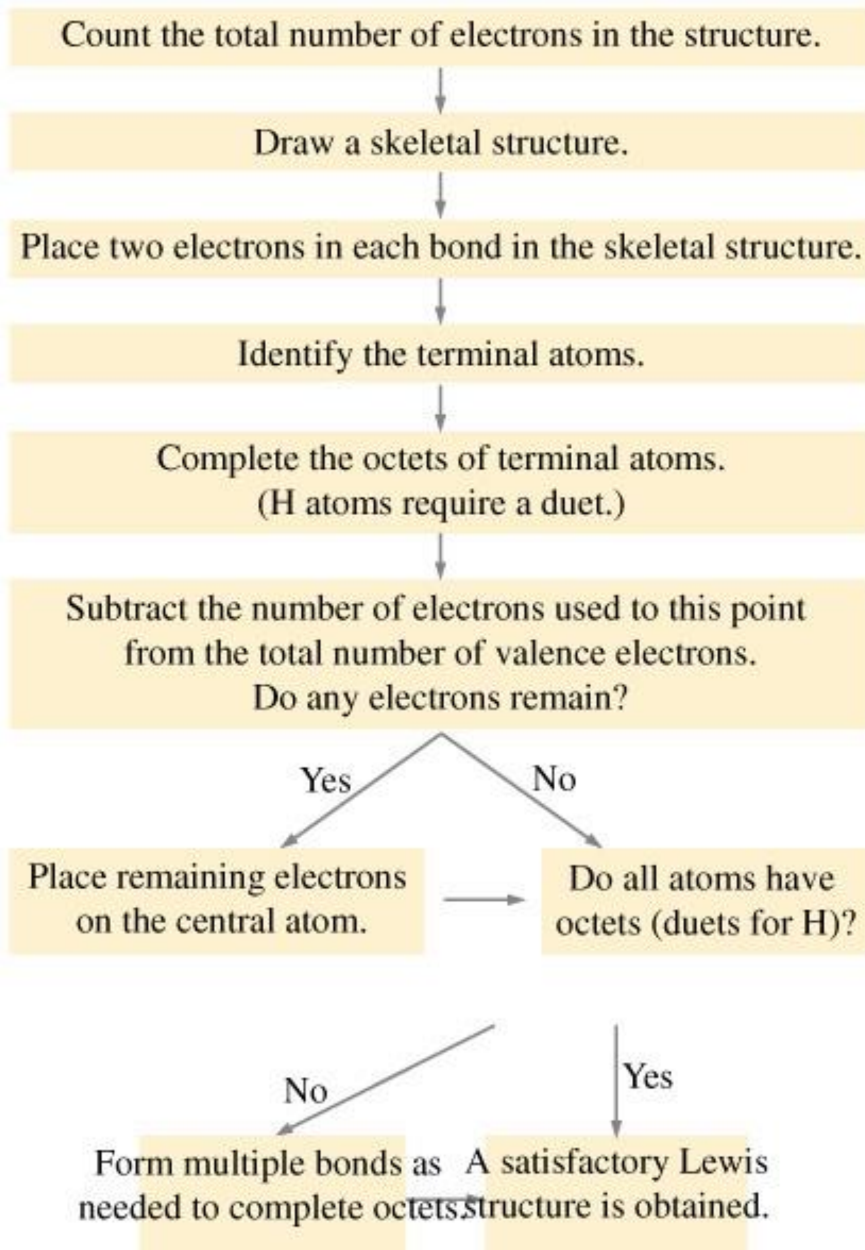
Skeletal Structure

- *Hydrogen atoms are always terminal atoms.*
- *Central atoms are generally those with the lowest electronegativity.*
- *Carbon atoms are always central atoms.*
- *Generally structures are compact and symmetrical.*

Strategy for Writing Lewis Structures



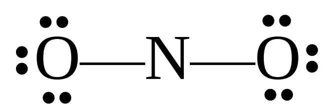
EXAMPLE10-7

Writing a Lewis Structure for a Polyatomic Ion. Write the Lewis structure for the nitronium ion, NO_2^+.

Step 1: Total valence e^- = 5 + 6 + 6 – 1 = 16 e^-

Step 2: Identify the central and terminal atoms

Step 3: Plausible structure: O—N—O

Step 4: Add e^- to terminal atoms: 

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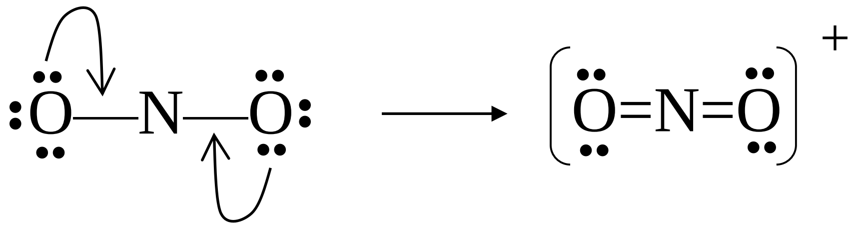
EXAMPLE 10-7

Step 5: Determine e^- left over: $16 - 4 - 12 = 0$

Step 6: Use multiple bonds to satisfy octets.



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Formal Charge

$$FC = \#_{\text{valence } e\text{-}} - \#_{\text{lone pair } e\text{-}} - \frac{1}{2}\#_{\text{bond pair } e\text{-}}$$

$$\overset{\bullet\bullet}{\underset{\bullet\bullet}{O}}=\overset{+}{N}=\overset{\bullet\bullet}{\underset{\bullet\bullet}{O}}$$

$$FC(O) = 6 - 4 - \frac{1}{2}(4) = 0$$

$$FC(N) = 5 - 0 - \frac{1}{2}(8) = +1$$

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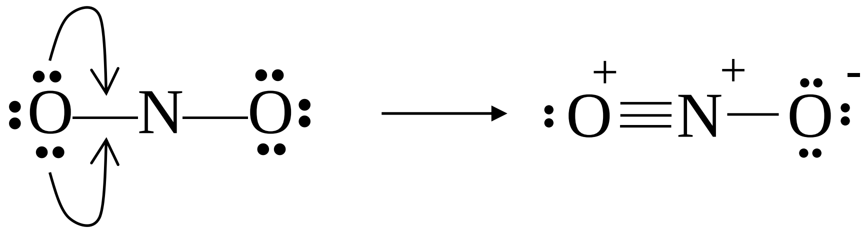
Alternative Lewis Structure



$$FC(O\equiv) = 6 - 2 - \frac{1}{2}(6) = +1$$

$$FC(N) = 5 - 0 - \frac{1}{2}(8) = +1$$

$$FC(O—) = 6 - 6 - \frac{1}{2}(2) = -1$$

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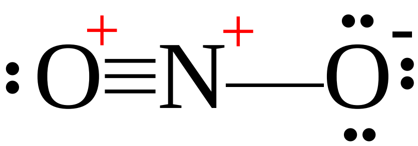
Alternative Lewis Structures

- Sum of FC is the overall charge.
- FC should be as small as possible.
- Negative FC usually on most electronegative elements.
- FC of same sign on adjacent atoms is unlikely.



EXAMPLE 10-7

Using the Formal Charge in Writing Lewis Structures. Write the most plausible Lewis structure of nitrosyl chloride, NOCl, one of the oxidizing agents present in *aqua regia*.

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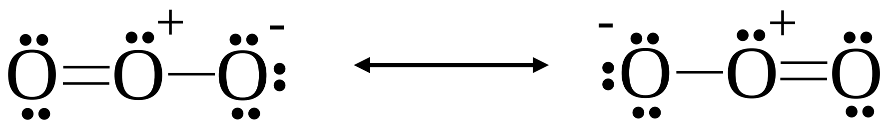
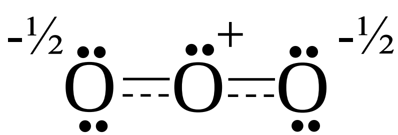
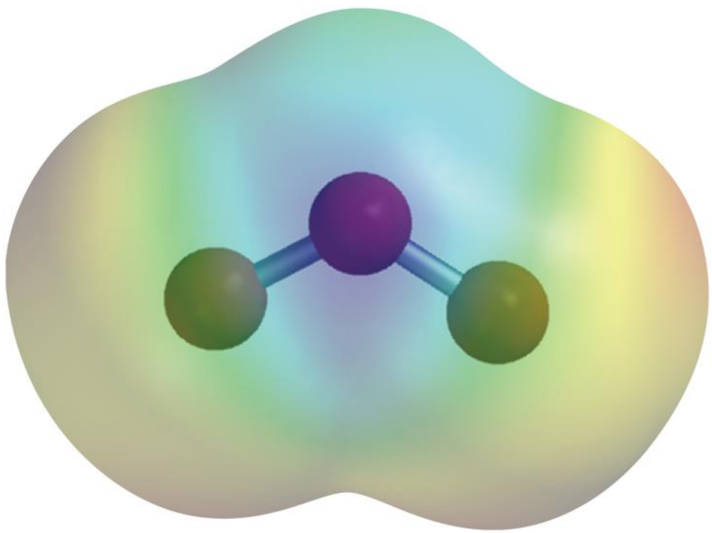
10-5 Resonance







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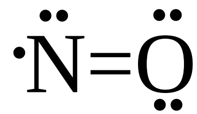
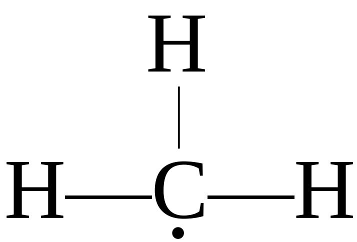
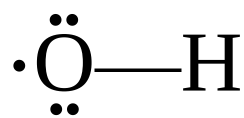
10-6 Exceptions to the Octet Rule

- Odd e^- species.

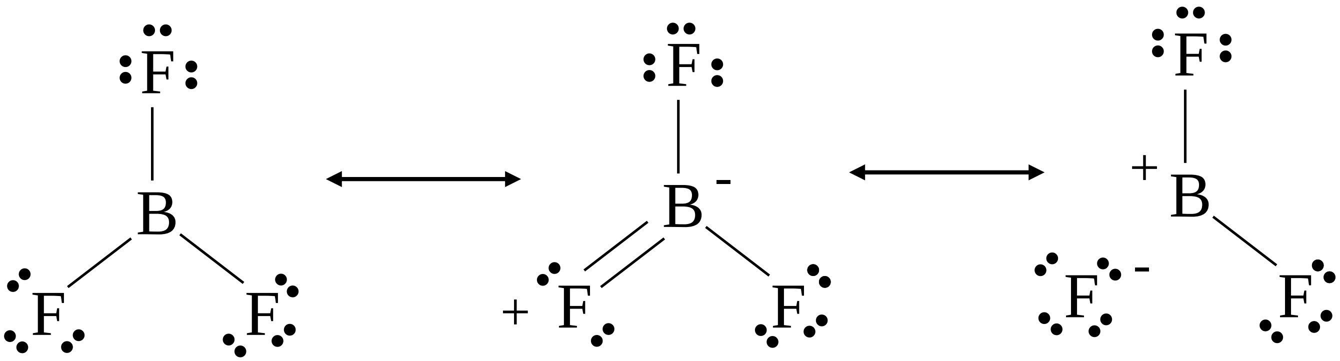






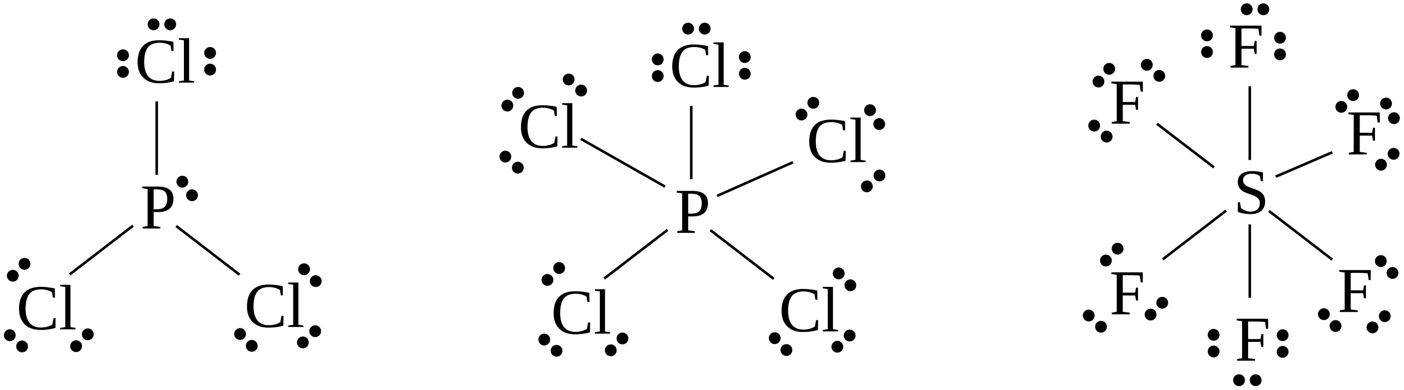
Exceptions to the Octet Rule

- Incomplete octets.



Exceptions to the Octet Rule

- Expanded octets.



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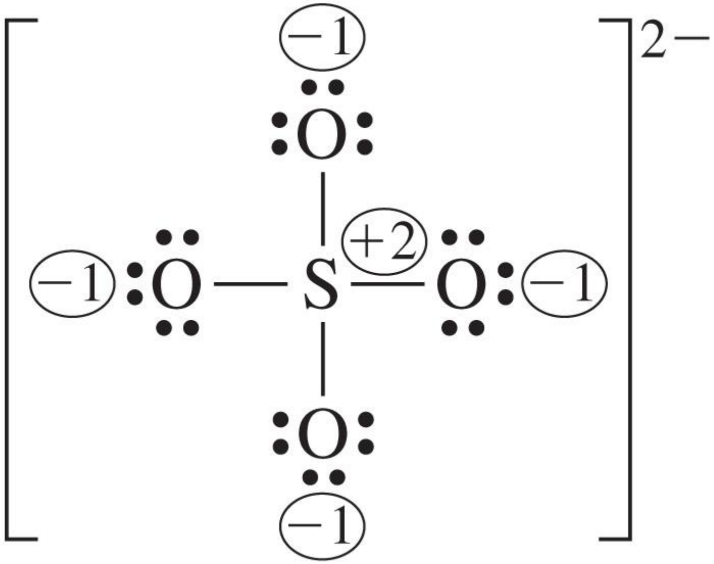
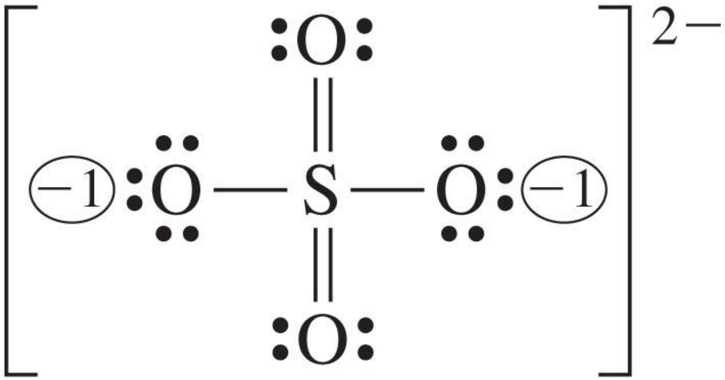
Expanded Valence Shell

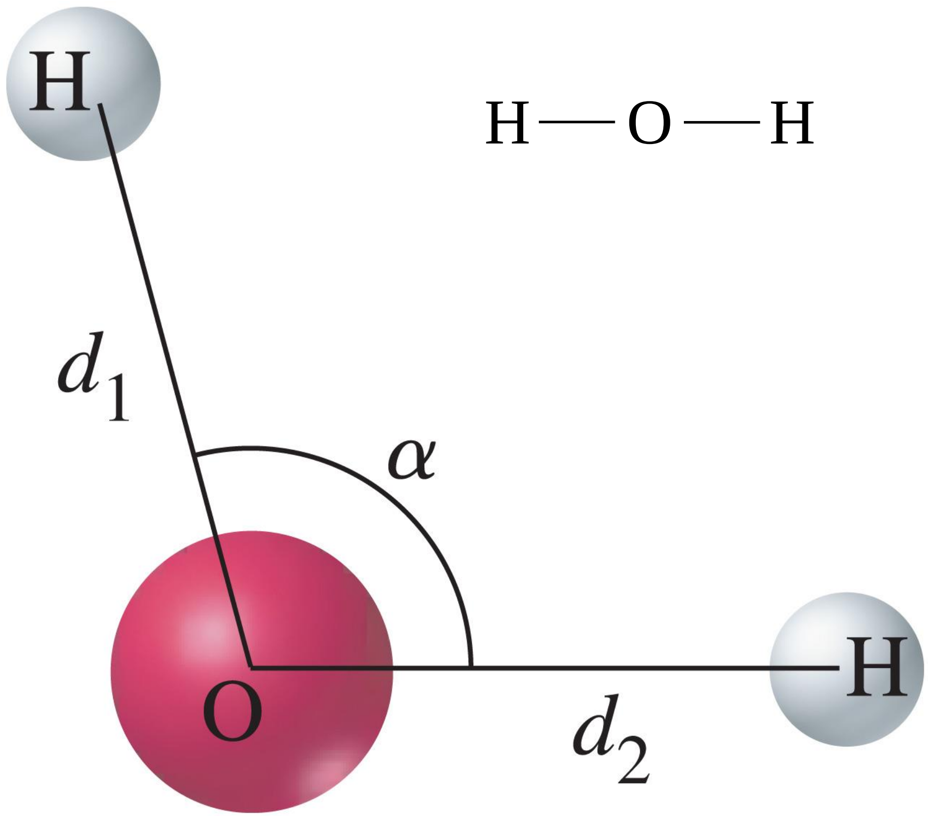


Normal octet



Expanded valence shell

10-7 The Shapes of Molecules



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Terminology

- Bond length – distance between nuclei.
- Bond angle – angle between adjacent bonds.
- VSEPR Theory
  - Electron pairs repel each other whether they are in chemical bonds (bond pairs) or unshared (lone pairs). Electron pairs assume orientations about an atom to minimize repulsions.
- Electron group geometry – distribution of e^- pairs.
- Molecular geometry – distribution of nuclei.

Balloon Analogy

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Methane, Ammonia and Water

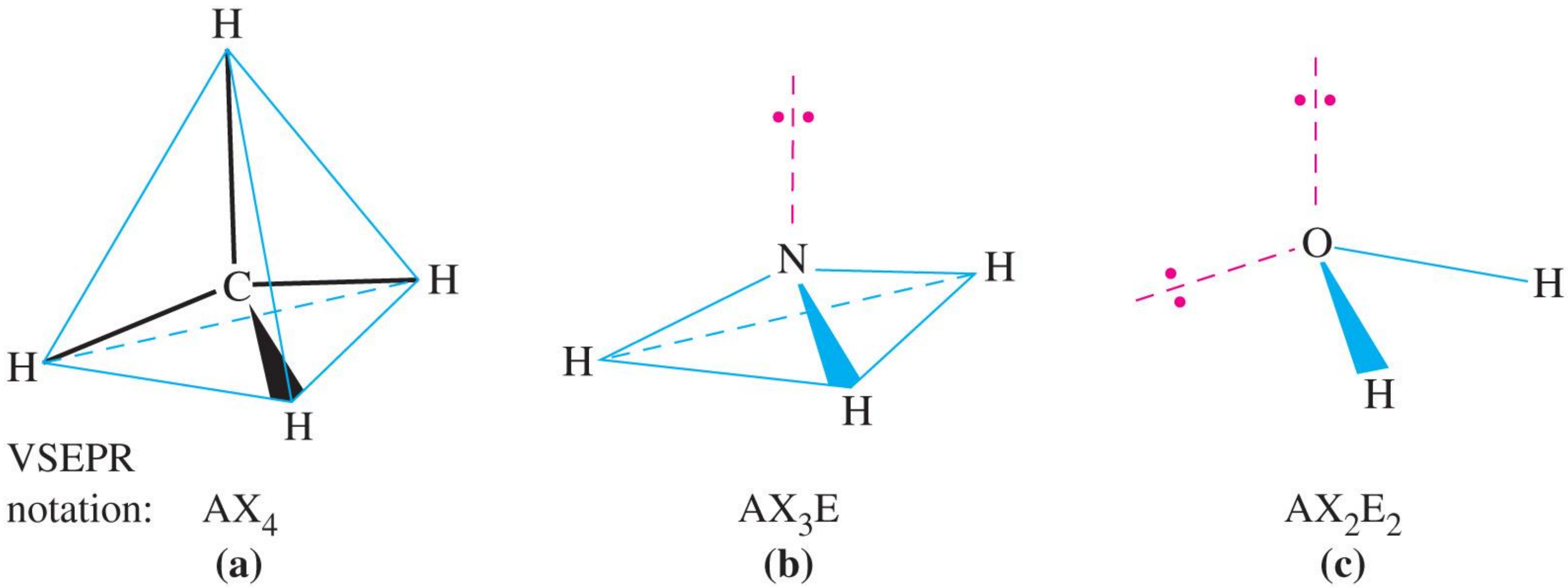

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Table 10.1 Molecular Geometry as a Function of Electron Group Geometry

Number of Electron Groups	Electron-Group Geometry	Number of Lone Pairs	VSEPR Notation	Molecular Geometry	Ideal Bond Angles	Example	*VSEPR Basic Molecular Configurations models*
2	linear	0	AX_2	 (linear)	180°	$BeC1_2$	

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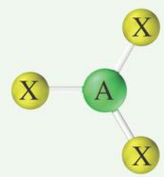
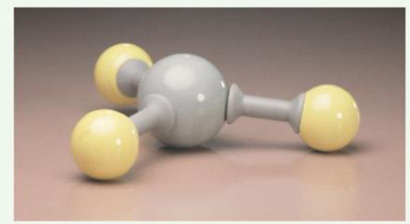
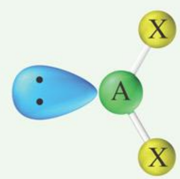
TABLE 10.1 (Continued)

Number of Electron Groups	Electron-Group Geometry	Number of Lone Pairs	VSEPR Notation	Molecular Geometry	Ideal Bond Angles	Example	
3	trigonal-planar	0	AX_3	 (trigonal planar)	120°	BF_3	
	trigonal-planar	1	AX_2E	 (bent)	120°	SO_2[a]	

[a]For a discussion of the structure of SO_2, see page 402.
[b]For a discussion of the placement of the lone-pair electrons in this structure, see page 401.

TABLE 10.1 (Continued)

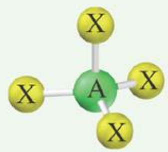
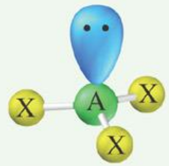
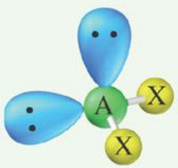
Number of Electron Groups	Electron-Group Geometry	Number of Lone Pairs	VSEPR Notation	Molecular Geometry	Ideal Bond Angles	Example
4	tetrahedral	0	AX_4	 (tetrahedral)	109.5°	CH_4
	tetrahedral	1	AX_3E	 (trigonal-pyramidal)	109.5°	NH_3
	tetrahedral	2	AX_2E_2	 (bent)	109.5°	OH_2

TABLE 10.1 (Continued)

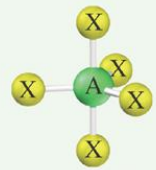
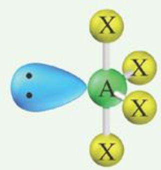
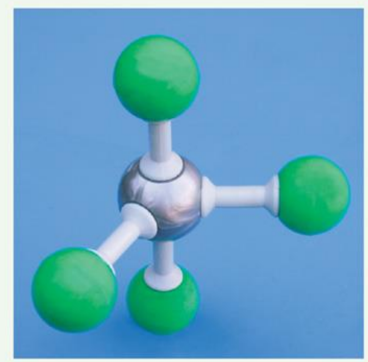
Number of Electron Groups	Electron-Group Geometry	Number of Lone Pairs	VSEPR Notation	Molecular Geometry	Ideal Bond Angles	Example	
5	trigonal-bipyramidal	0	AX_5	 (trigonal-bipyramidal)	90°, 120°	$PC1_5$	
	trigonal-bipyramidal	1	AX_4E^b	 (seesaw)	90°, 120°	SF_4	

TABLE 10.1 (Continued)

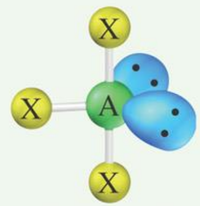
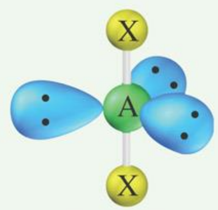
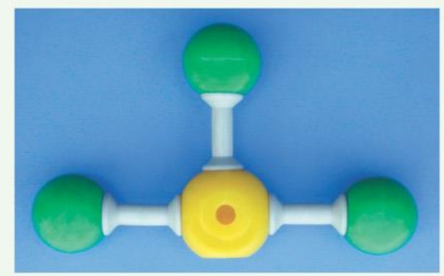
Number of Electron Groups	Electron-Group Geometry	Number of Lone Pairs	VSEPR Notation	Molecular Geometry	Ideal Bond Angles	Example
	trigonal-bipyramidal	2	AX_3E_2	 (T-shaped)	90°	$C1F_3$
	trigonal-bipyramidal	3	AX_2E_3	 (linear)	180°	XeF_2 

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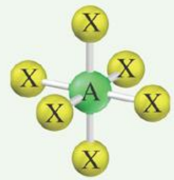
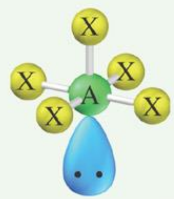
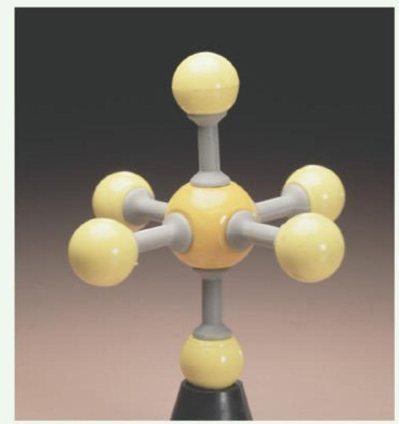
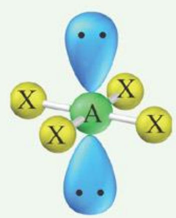
TABLE 10.1 (Continued)

Number of Electron Groups	Electron-Group Geometry	Number of Lone Pairs	VSEPR Notation	Molecular Geometry	Ideal Bond Angles	Example	
6	octahedral	0	AX_6	 (octahedral)	90°	SF_6	
	octahedral	1	AX_5E	 (square-pyramidal))	90°	BrF_5	
	octahedral	2	AX_4E_2	 (square-planar)	90°	XeF_4	

Applying VSEPR Theory

- Draw a plausible Lewis structure.
- Determine the number of e^- groups and identify them as *bond* or *lone* pairs.
- Establish the e^- group geometry.
- Determine the molecular geometry.
- Multiple bonds count as one group of electrons.
- More than one central atom can be handled individually.

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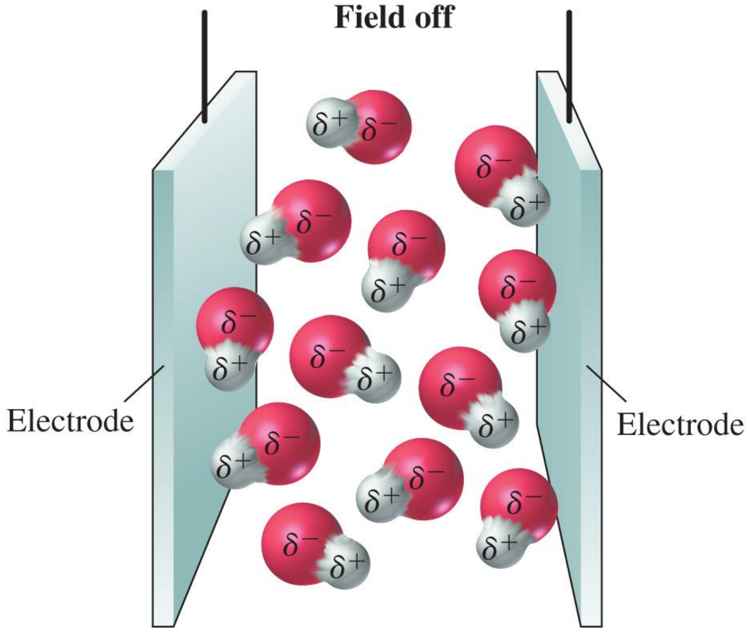
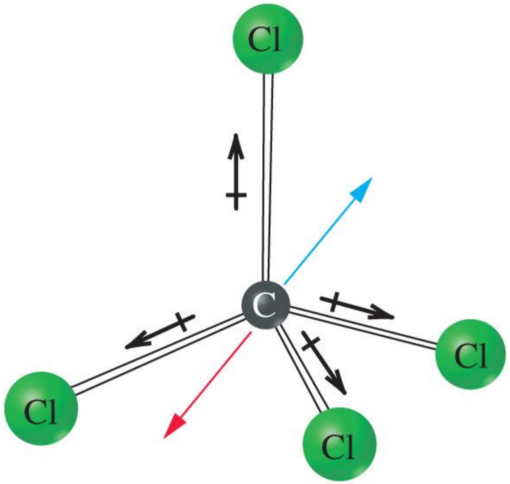
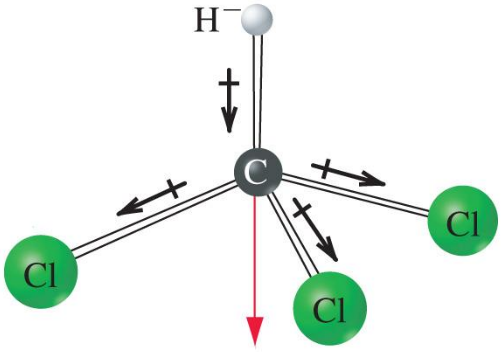
Dipole Moments



Dipole Moments



(a) CCl_4: a nonpolar molecule



(b) $CHCl_3$: a polar molecule

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Bond Order and Bond Length

- Bond Order
  - Single bond, order = 1
  - Double bond, order = 2
- Bond Length
  - Distance between two nuclei
- Higher bond order
  - Shorter bond
  - Stronger bond

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TABLE 10.2 Some Average Bond Lengths[a]

Bond	Bond Length, pm	Bond	Bond Length, pm	Bond	Bond Length, pm
H—H	74.14	C—C	154	N—N	145
H—C	110	C=C	134	N=N	123
H—N	100	C≡C	120	N≡N	109.8
H—O	97	C—N	147	N—O	136
H—S	132	C=N	128	N=O	120
H—F	91.7	C≡N	116	O—O	145
H—C1	127.4	C—O	143	O=O	121
H—Br	141.4	C=O	120	F—F	143
H—I	160.9	C—C1	178	C1—C1	199
				Br—Br	228
				I—I	266

[a]Most values (C—H, N—H, C—H, and so on) are averaged over a number of species containing the indicated bond and may vary by a few picometers. Where a diatomic molecule exists, the value given is the actual bond length in that molecule (H_2, N_2, HF, and so on) and is known more precisely.

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Bond Energies

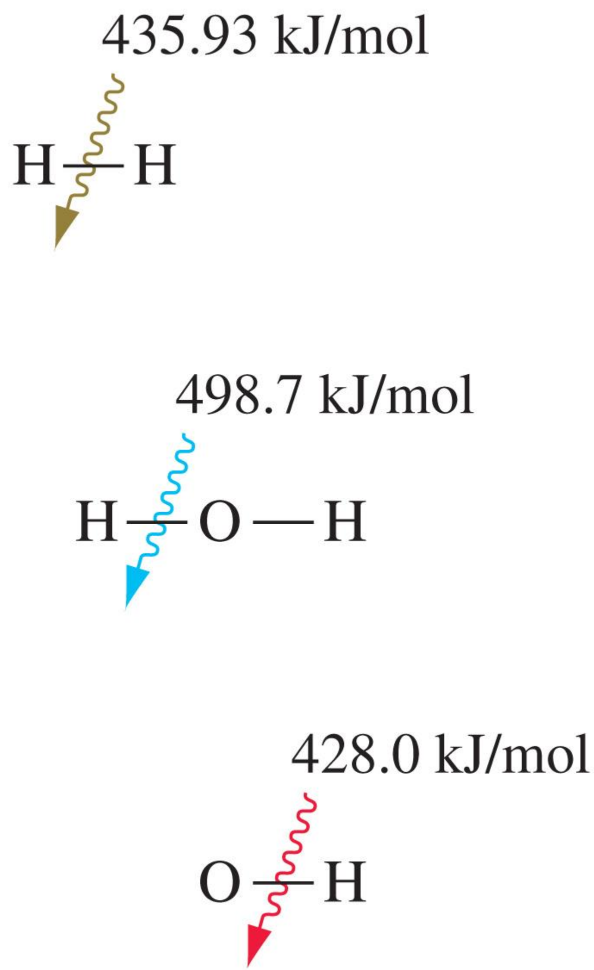


TABLE 10.3 Some Average Bond Energies[a]

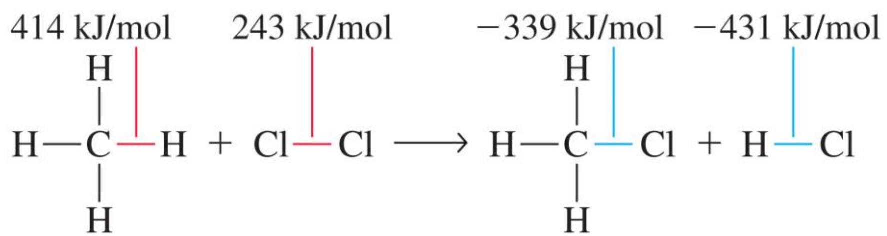
Bond	Bond Energy, kJ/mol	Bond	Bond Energy kJ/mol	Bond	Bond Energy kJ/mol
H—H	436	C—C	347	N—N	163
H—C	414	C=C	611	N=N	418
H—N	389	C≡C	837	N≡N	946
H—O	464	C—N	305	N—O	222
H—S	368	C=N	615	N=O	590
H—F	565	C≡N	891	O—O	142
H—C1	431	C—O	360	O=O	498
H—Br	364	C=O	736[b]	F—F	159
H—I	297	C—C1	339	C1—C1	243
				Br—Br	193
				I—I	151

[a] Although all data are listed with about the same precision (three significant figures), some values are actually known more precisely. Specifically, the values for the diatomic molecules H_2, HF, HCl, HBr, HI, N_2 (N≡N), O_2 (O=O), F_2, Cl_2, Br_2, and I_2 are actually bond-dissociation energies, rather than average bond energies.

[b] The value for the C=O bonds in CO_2 is 799 kJ/mol.

EXAMPLE 10-15

Calculating an Enthalpy of Reaction from Bond Energies. The reaction of methane (CH_4) and chlorine produces a mixture of products called chloromethanes. One of these is monochloromethane, CH_3Cl, used in the preparation of silicones. Calculate ΔH for the reaction.



$$\Delta H_{rxn} = \Sigma\, \Delta H(\text{product bonds}) - \Sigma \Delta H(\text{reactant bonds})$$

$$= \Sigma\, \Delta H \text{ bonds formed} - \Sigma\, \Delta H \text{ bonds broken}$$

$$= -770 \text{ kJ/mol} - (657 \text{ kJ/mol}) = -113 \text{ kJ/mol}$$

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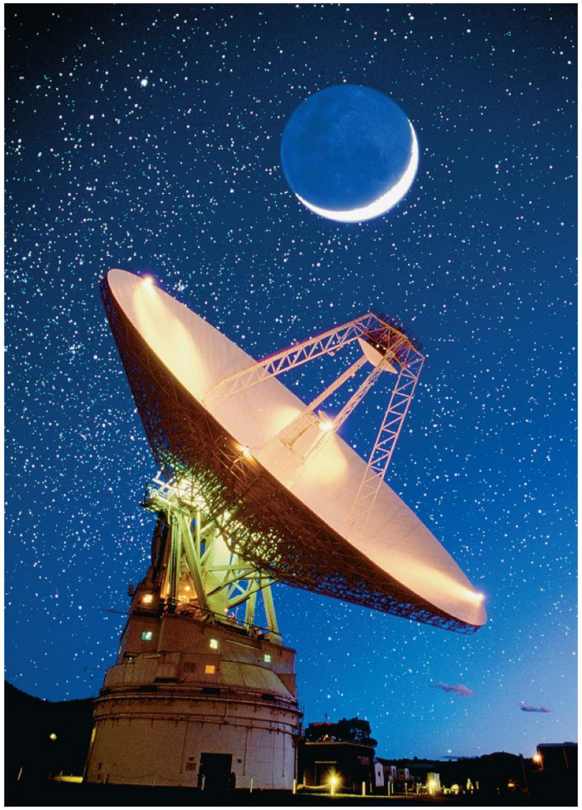
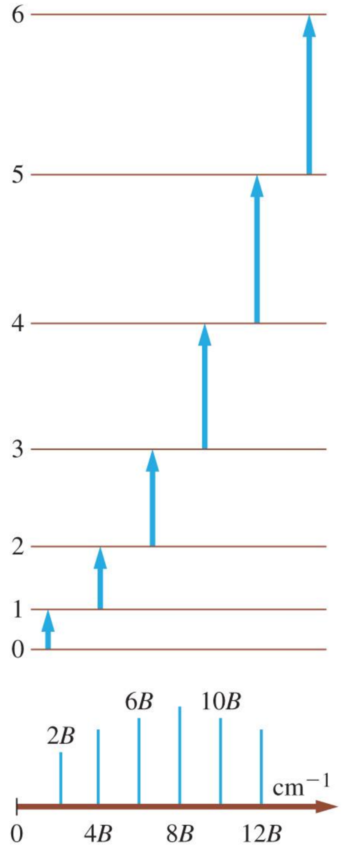
Focus on Molecules in Space: Measuring Bond Lengths





End of Chapter Questions

- Testing your decisions:
  - If you get an error or a nonsense result, then climb back to an intersection where you KNOW you were correct, and take another route.