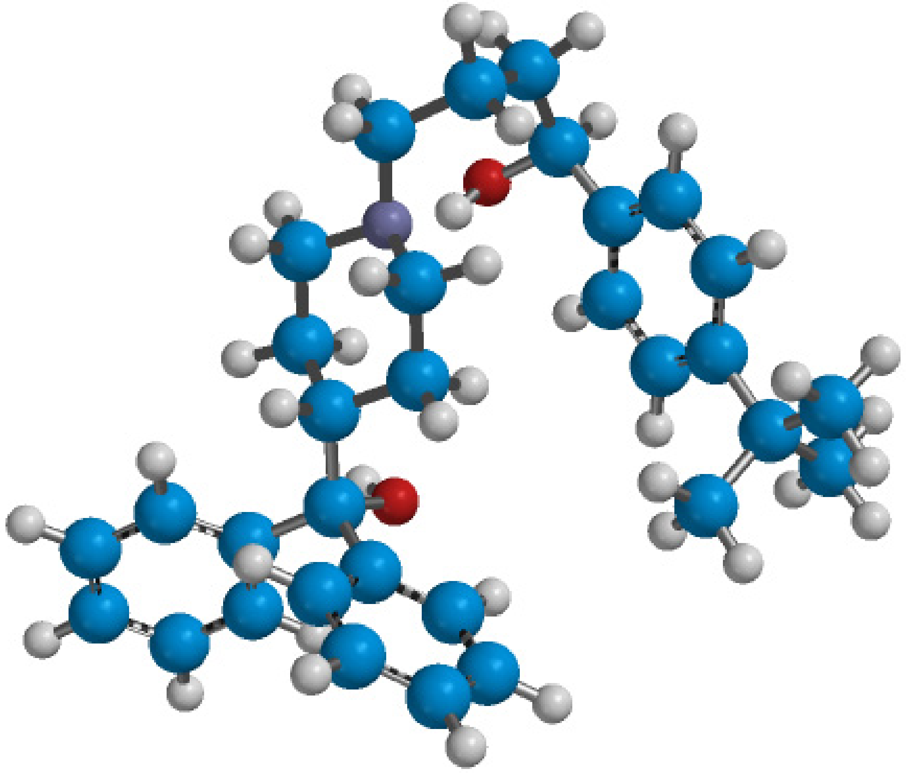
1

STRUCTURE AND BONDING IN ORGANIC COMPOUNDS



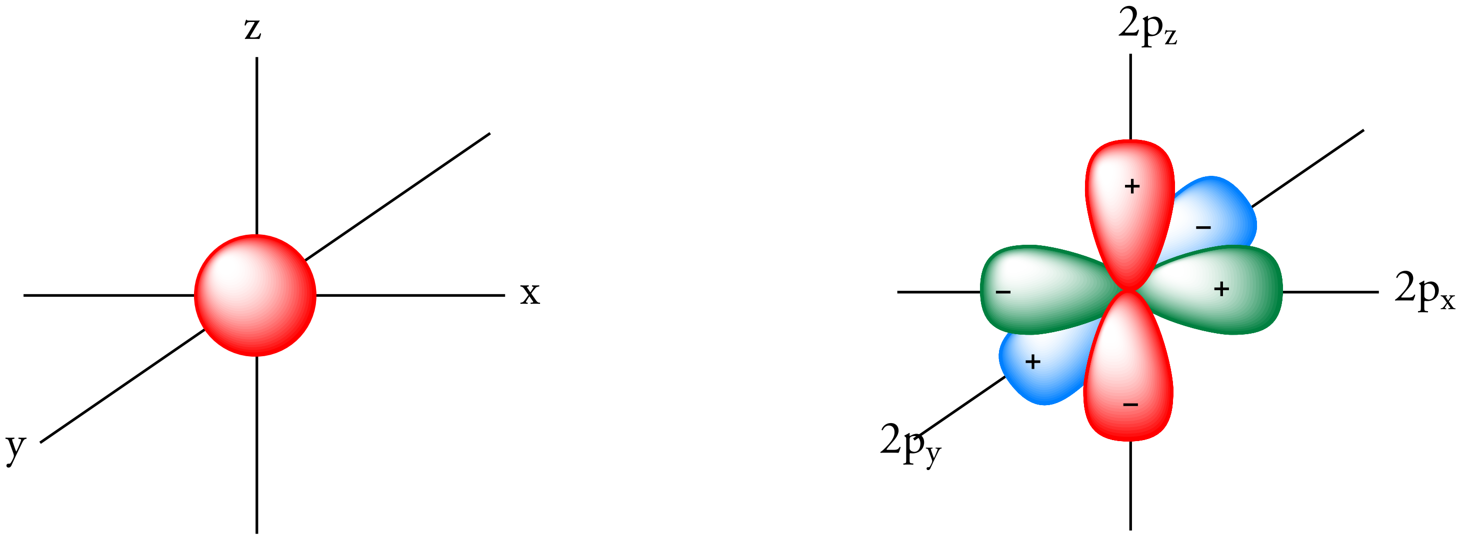
Terfenedine

1.1 BRIEF REVIEW OF ATOMIC STRUCTURE

Atomic Orbitals

Figure 1. 1 Shapes of 2s and 2p Oribtals

(a) An orbital is a boundary surface enclosing a volume where electrons can be located with 90% probability. An s orbital has a spherical boundary surface.(b) Boundary surfaces of the three mutually perpendicular 2p orbitals. Each orbital can hold a maximum of two electrons. The + and - signs on the orbitals refers to the phase of the orbital, *not* to the charge of the orbital.



s orbital
(a)

2p orbitals
(b)

1.1 BRIEF REVIEW OF ATOMIC STRUCTURE

Atomic Orbitals

Table 1.1 Electron Configurations of First and Second Period Elements

Element	**Atomic Number**	**1s**	**2s**	**$2p_x$**	**$2p_y$**	**$2p_z$**	**Electron Configuration**
H	1	1					$1s^1$
He	2	2					$1s^2$
Li	3	2	1				$1s^2 2s^1$
Be	4	2	2				$1s^2 2s^2$
B	5	2	2	1(↑)			$1s^2 2s^2 2p^1$
C	6	2	2	1 (↑)	1 (↑)		$1s^2 2s^2 2p^2$
N	7	2	2	1 (↑)	1 (↑)	1 (↑)	$1s^2 2s^2 2p^3$
O	8	2	2	2(↑↓)	1 (↑)	1 (↑)	$1s^2 2s^2 2p^4$
F	9	2	2	2 (↑↓)	2 (↑↓)	1 (↑)	$1s^2 2s^2 2p^5$
Ne	10	2	2	2 (↑↓)	2 (↑↓)	2 (↑↓)	$1s^2 2s^2 2p^6$

1.2 ATOMIC PROPERTIES

Atomic Radius

Figure 1.2
Atomic radii in picometers, pm (10^{-12} m)

H						
37						
Li	**Be**	**B**	**C**	**N**	**O**	**F**
152	111	88	77	70	66	64
Na	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**
186	160	143	117	110	104	99
						Br
						114
						I
						133

1.2 ATOMIC PROPERTIES

Electronegativity

Figure 1.3
Electronegativity

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
						Br 2.8
						I 2.5

1.3 IONIC AND COVALENT BONDS

Ionic Bonds

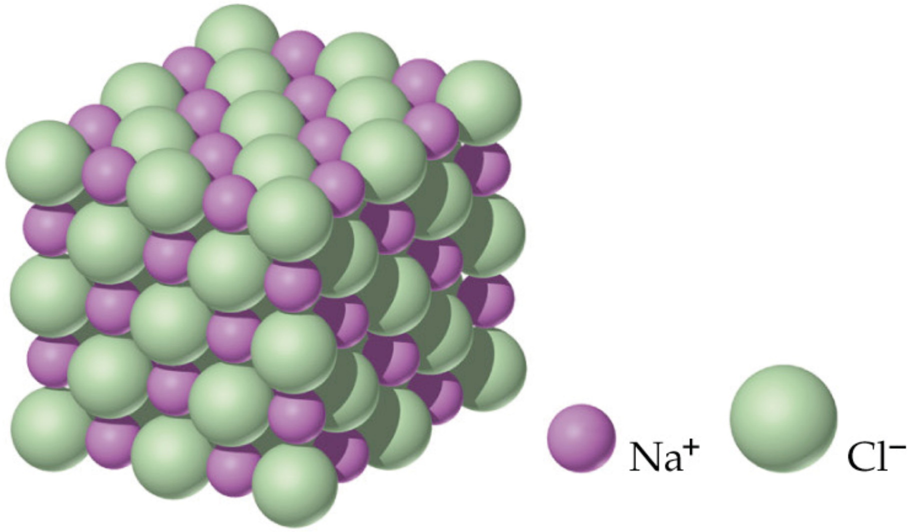


Figure 1.4 Sodium chloride Crystal

In the ionic solid, sodium chloride, each sodium ion is surrounded by 6 chloride ions and each chloride ion is surrounded by 6 sodium ions.

1.3 IONIC AND COVALENT BONDS

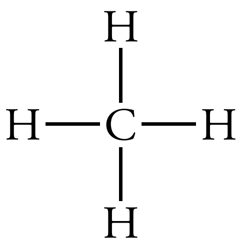
Covalent Bonds

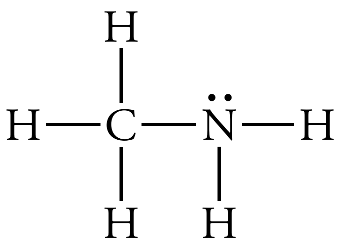
Table 1.2

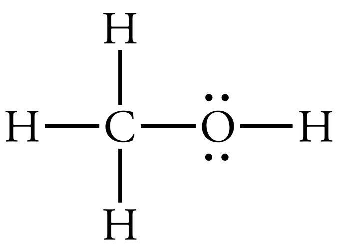
Valences of Common Elements*

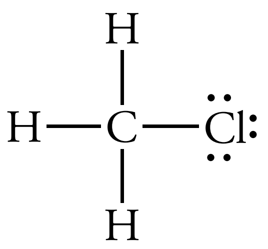
Atom	**Valence**
Hydrogen	1
Fluorine	1
Bromine	1
Chlorine	1
Iodine	1
Oxygen	2
Sulfur	2
Nitrogen	3
Carbon	4

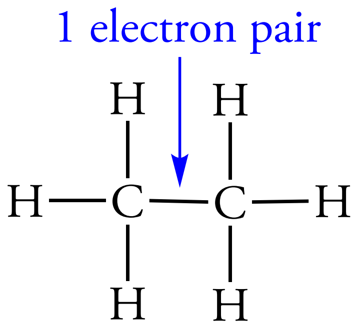
*The valence is the usual number of bonds formed by the atom in neutral compounds.


methane

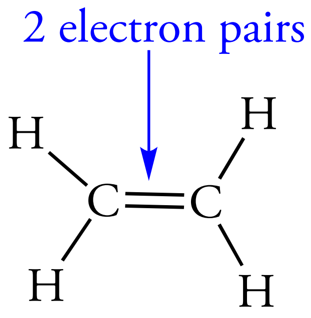

aminomethane


methanol

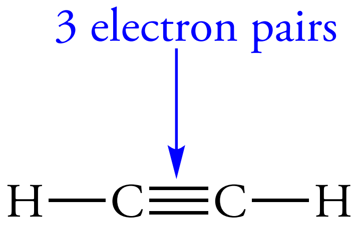

chloromethane



ethane



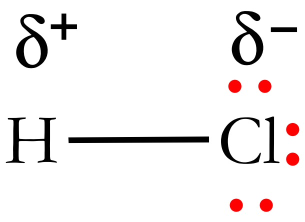
ethene

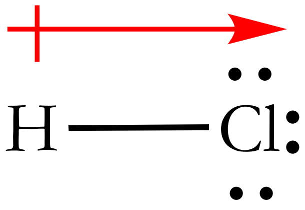


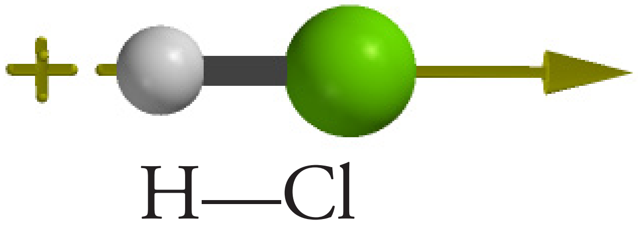
ethyne

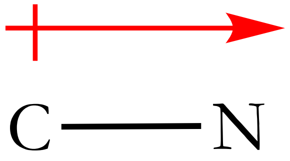
1.3 IONIC AND COVALENT BONDS

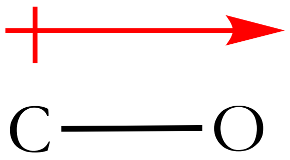
Polar Covalent Bonds

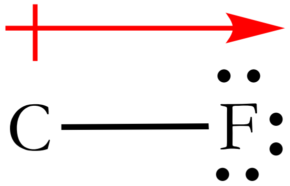


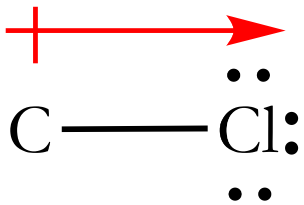


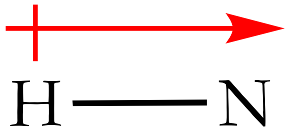


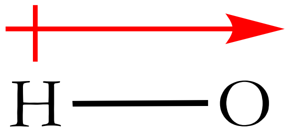




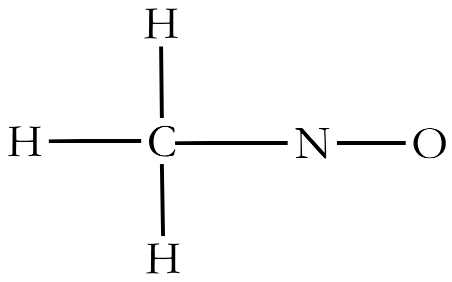




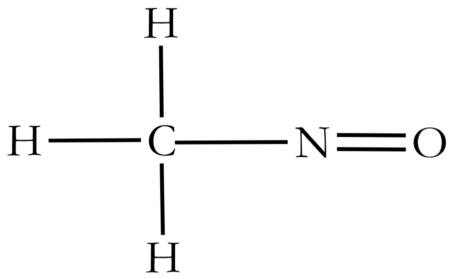




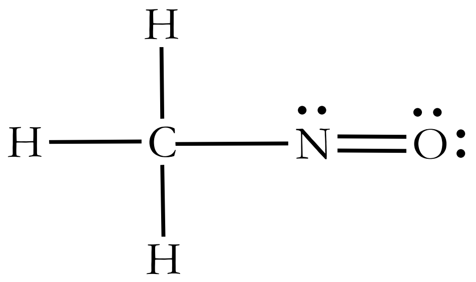
1.4 STRATEGIES FOR WRITING LEWIS STRUCTURES



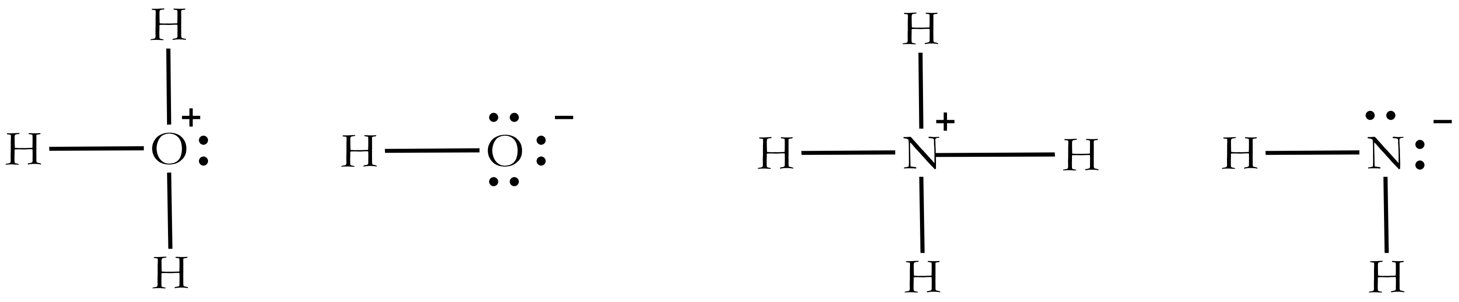
Atom	*Electrons present*	*Electrons needed*
hydrogen	2 for each one	0
carbon	4 x 2= 8	0
nitrogen	2 x 2= 4	4
oxygen	2	6



Atom	*Electrons present*	*Electrons needed*
hydrogen	2 for each one	0
carbon	4 x 2= 8	0
nitrogen	2 + 4= 6	2
oxygen	4	4

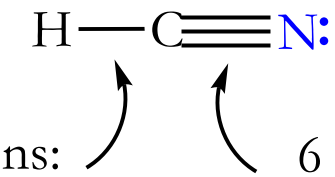


1.5 FORMAL CHARGE



$$\text{formal charge} = \left(\begin{array}{l}\text{number of valence}\\ \text{electrons in free atom}\end{array}\right) - \left(\begin{array}{l}\text{number of valence}\\ \text{electrons in bonded atom}\end{array}\right)$$

$$\text{formal charge} = \left(\begin{array}{l}\text{number of valence}\\ \text{electrons in free atom}\end{array}\right) - \left(\begin{array}{l}\text{number of valence}\\ \text{electrons in bonded atom}\end{array}\right) - 1/2\left(\text{number of bonded electrons}\right)$$



lone pair electrons: assign both to nitrogen

two bonding electrons:
assign 1 to hydrogen
assign 1 to carbon

6 bonding electrons:
assign 3 to carbon
assign 3 to nitrogen

formal charge of hydrogen = 1 – 0 – 1/2(2) = 0
formal charge of carbon = 4 – 0 – 1/2(8) = 0
formal charge of nitrogen = 5 – 2 – 1/2(6) = 0

1.6 MOLECULAR GEOMETRY

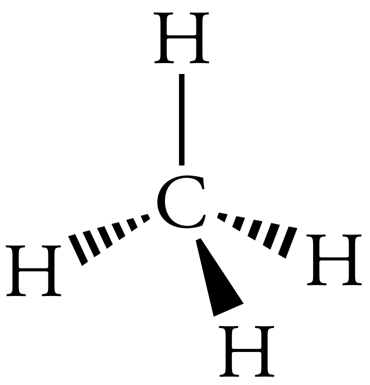
Bond Lengths

Table 1.3

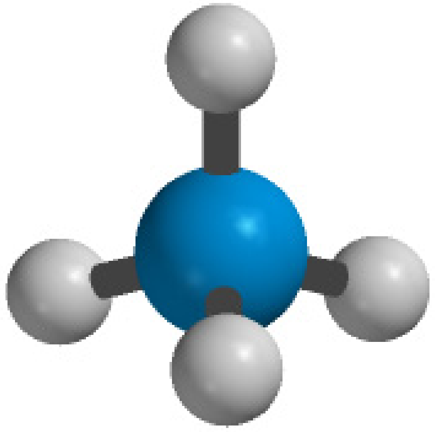
Average Bond Lengths

Structural Unit	Bond length (pm)
H—C	110
H—N	98
H—O	94
H—F	92
H—S	132
H—Cl	127
H—Br	142
H—I	161
C—C	154
C—N	147
C—O	143
C—F	141
C—Cl	176
C—Br	191
C—I	210
C=C	134
C=O	122
alkyne C≡C	121
cyano (C≡N)	115

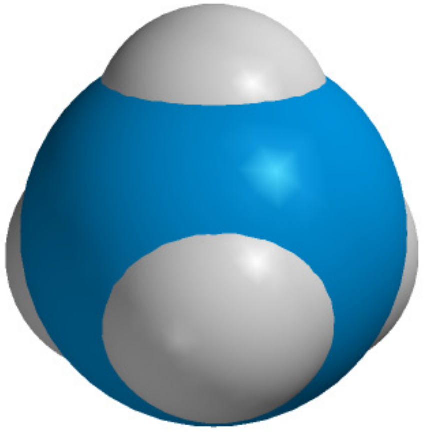
Figure 1.5 Structural Formulas and Molecular Models



(a) Perspective Structure

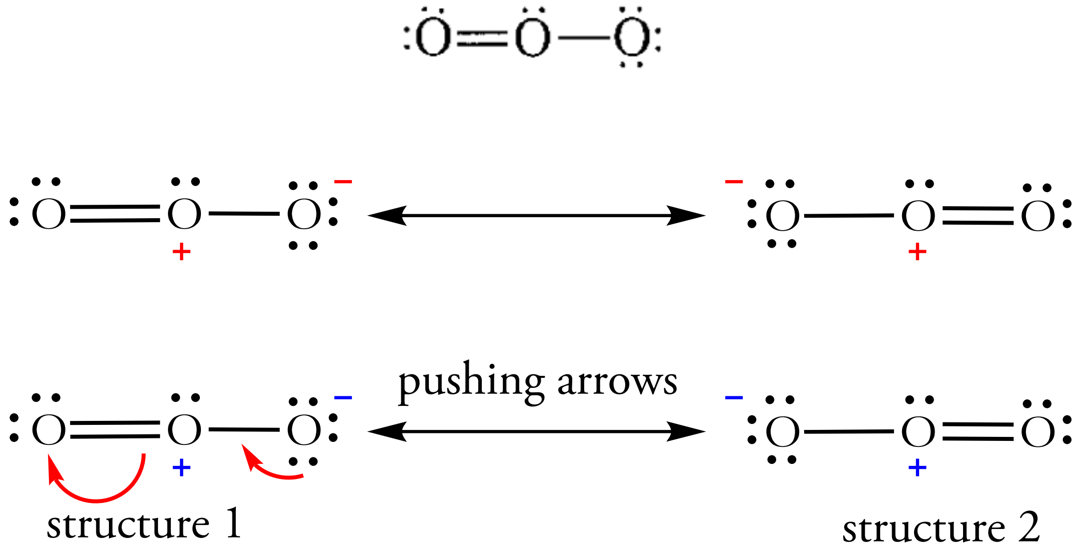


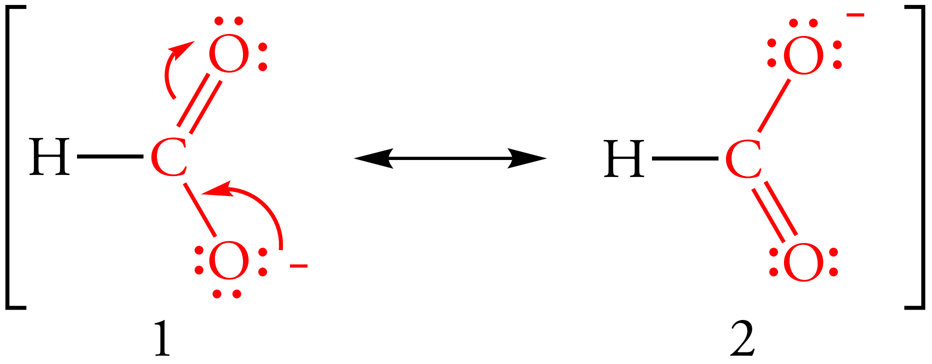
(b) Ball-and-stick Model



(c) Space-filling Model

1.7 RESONANCE STRUCTURES

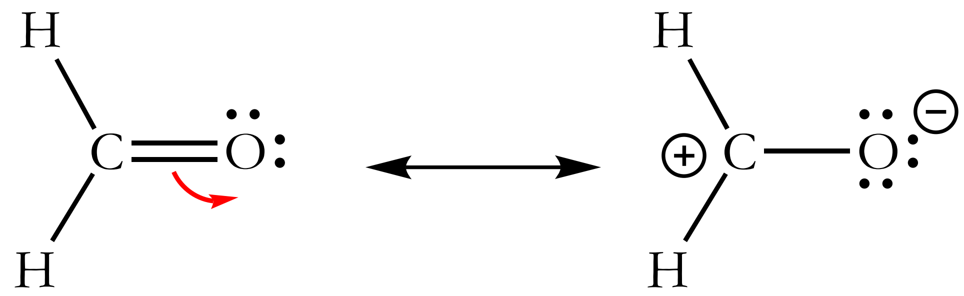




Resonance structures of carboxylate ion

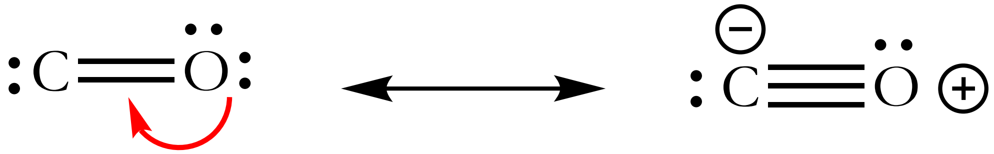
1.7 RESONANCE STRUCTURES

Nonequivalent Resonance Structures



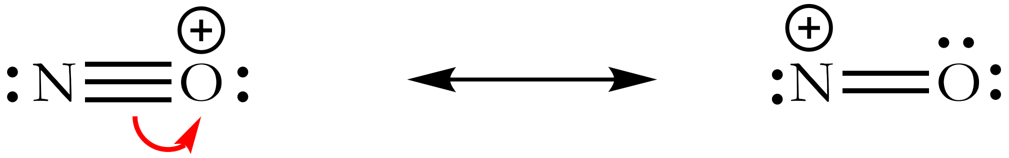
major contributor 1

minor contributor 2



minor contributor 1

major contributor 2

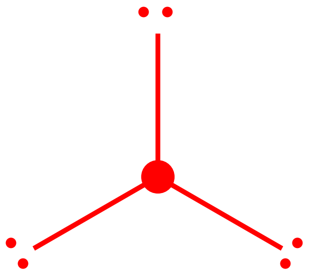


major contributor 1

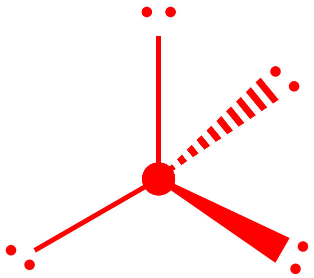
minor contributor 2

1.8 VALENCE SHELL ELECTRON PAIR REPULSION THEORY

two electron pairs

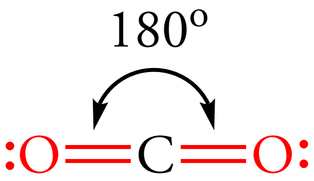


three electron pairs

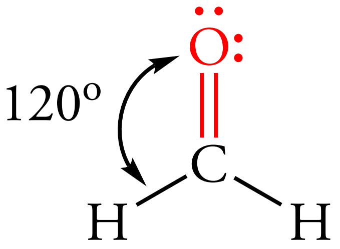


four electron pairs

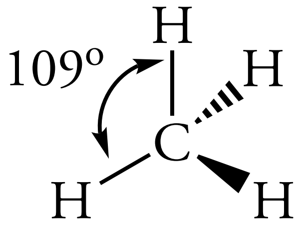
molecular geometry:



linear



trigonal planar

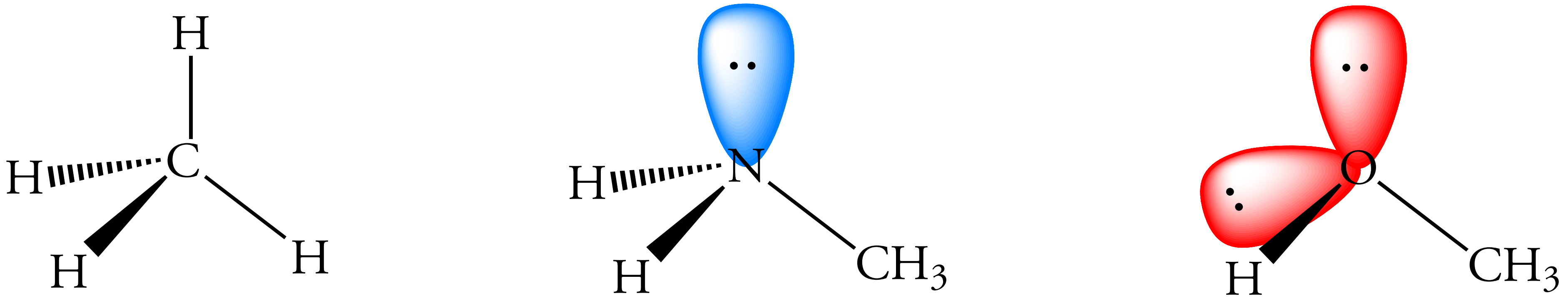


tetrahedral

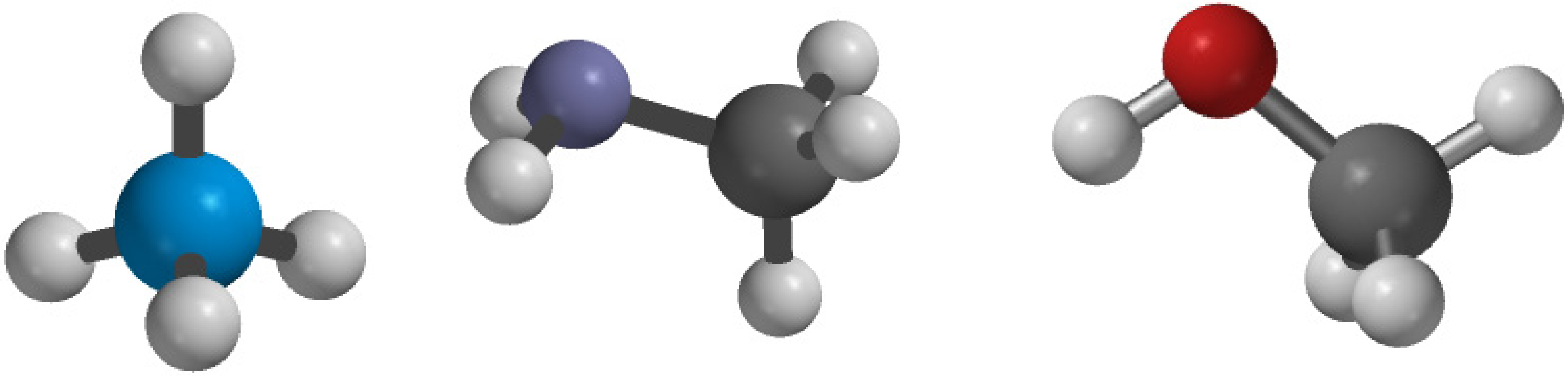
1.8 VALENCE SHELL ELECTRON PAIR REPULSION THEORY

Figure 1.6 VSEPR Model Predicts Geometry Around a Central Atom

All electron pairs in methane, aminomethane, and methanol are directed to the corners of a tetrahedron. However, the geometry around the nitrogen atom in aminomethane is described as trigonal pyramidal; the geometry around the oxygen atom in methanol molecule is angular.



methane aminomethane methanol



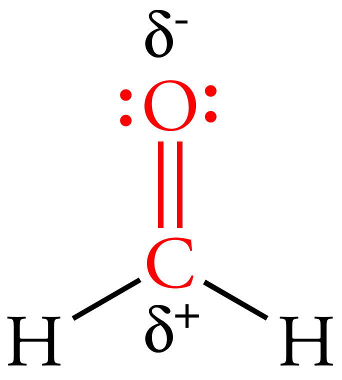
methane aminomethane methanol

1.9 DIPOLE MOMENTS

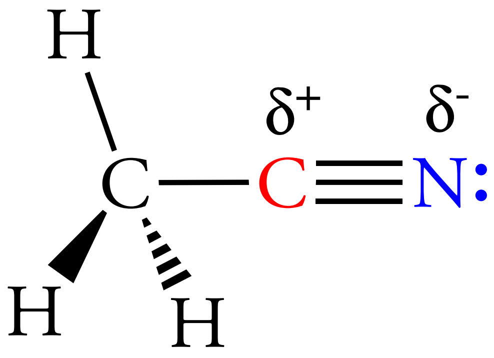
Determining Charge Separation

=lqlr

$$\frac{0.85 \times 10^{-10}\ \text{esu}}{4.8 \times 10^{-10}\ \text{esu/electron}} = 0.18\ \text{electron}$$



methanal



cyanomethane

1.9 DIPOLE MOMENTS

Table 1.4

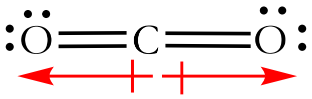
Average Dipole Moments (D)

Structural Unit[1]	Bond Moments (D)
H—C	0.4
H—N	1.3
H—O	1.5
H—F	1.7
H—S	0.7
H—Cl	1.1
H—Br	0.8
H—I	0.4
C—C	0.0
C—N	0.2
C—O	0.7
C—F	1.4
C—Cl	1.5
C—Br	1.4
C—I	1.2
C=O	2.3
C≡N	3.5

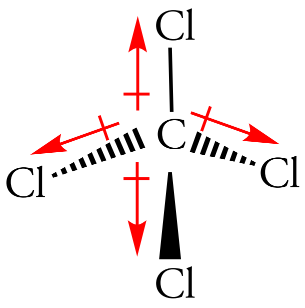
[1] The more electronegative atom in the bond is on the right.

1.9 DIPOLE MOMENTS

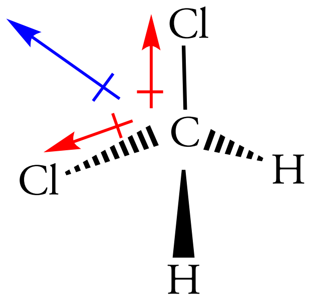
Bond Polarity and Molecular Geometry



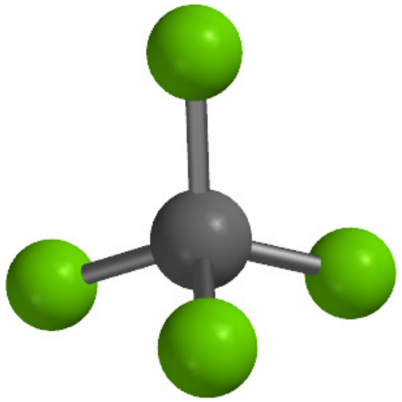
Blue arrow: direction of net dipole moment.



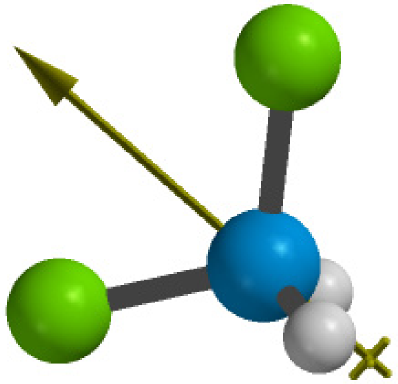
The bond moments cancel
and there is no net polarity.



The bond moments do not cancel
and there is a net polarity.



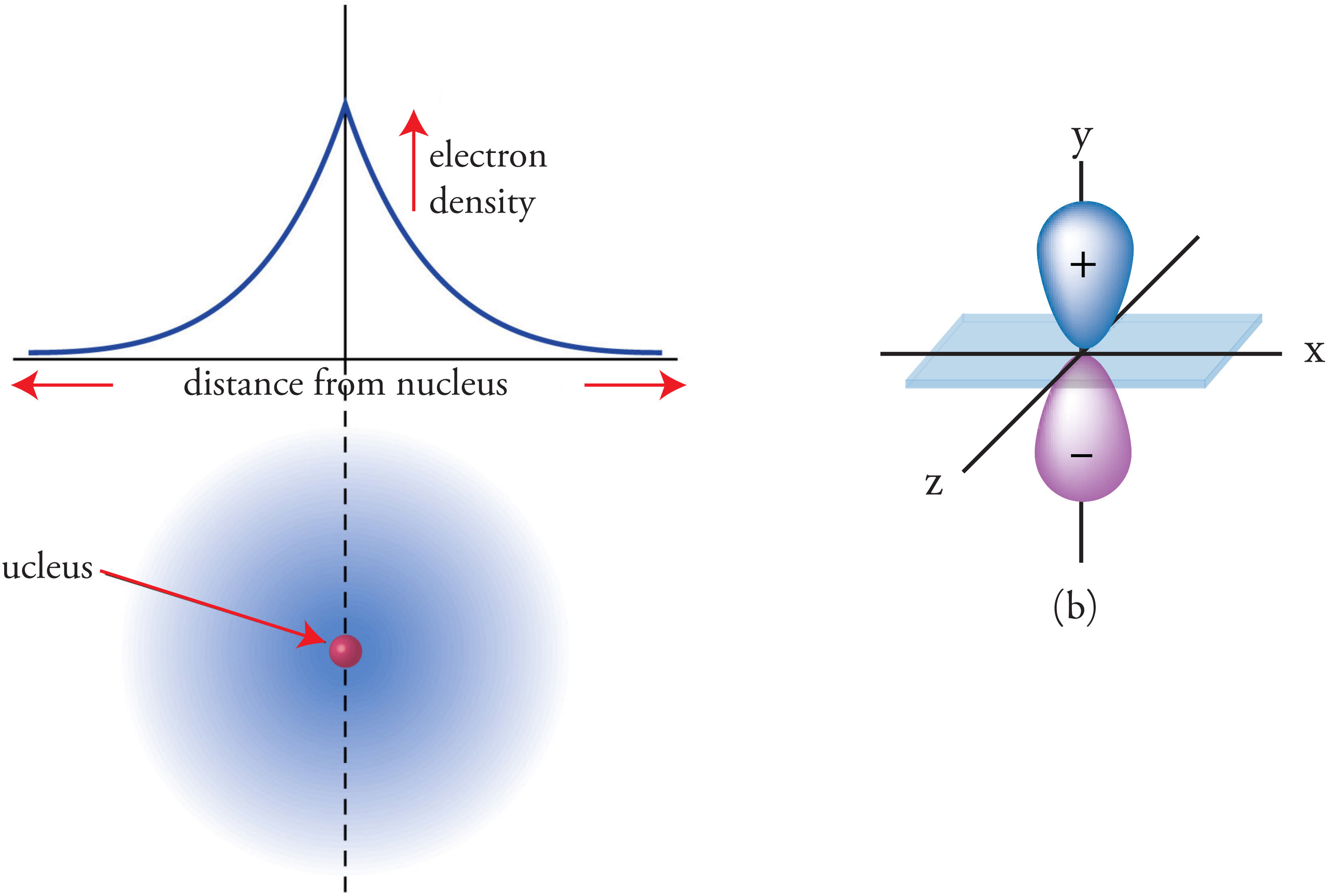
Tetrachloromethane



Dichloromethane

1.10 MOLECULAR ORBITAL THEORY

Atomic Orbitals



(a) 1s orbital

(b)

Figure 1.7 Atomic Orbitals

(a) The wave function of an s orbital is spherically symmetrical. The sign of the wave function does not change within the orbital. There is a 90% probability of finding a 1s electron within the shaded area.

(b) The sign of the wave function for a $2p_y$ orbital is positive above the x-z plane and negative below the x-z plane. A node exists at a point between the lobes of the orbital, and the entire x-z plane is a nodal plane. There is a 0% probability of finding a $2p_y$ electron in the x-z plane.

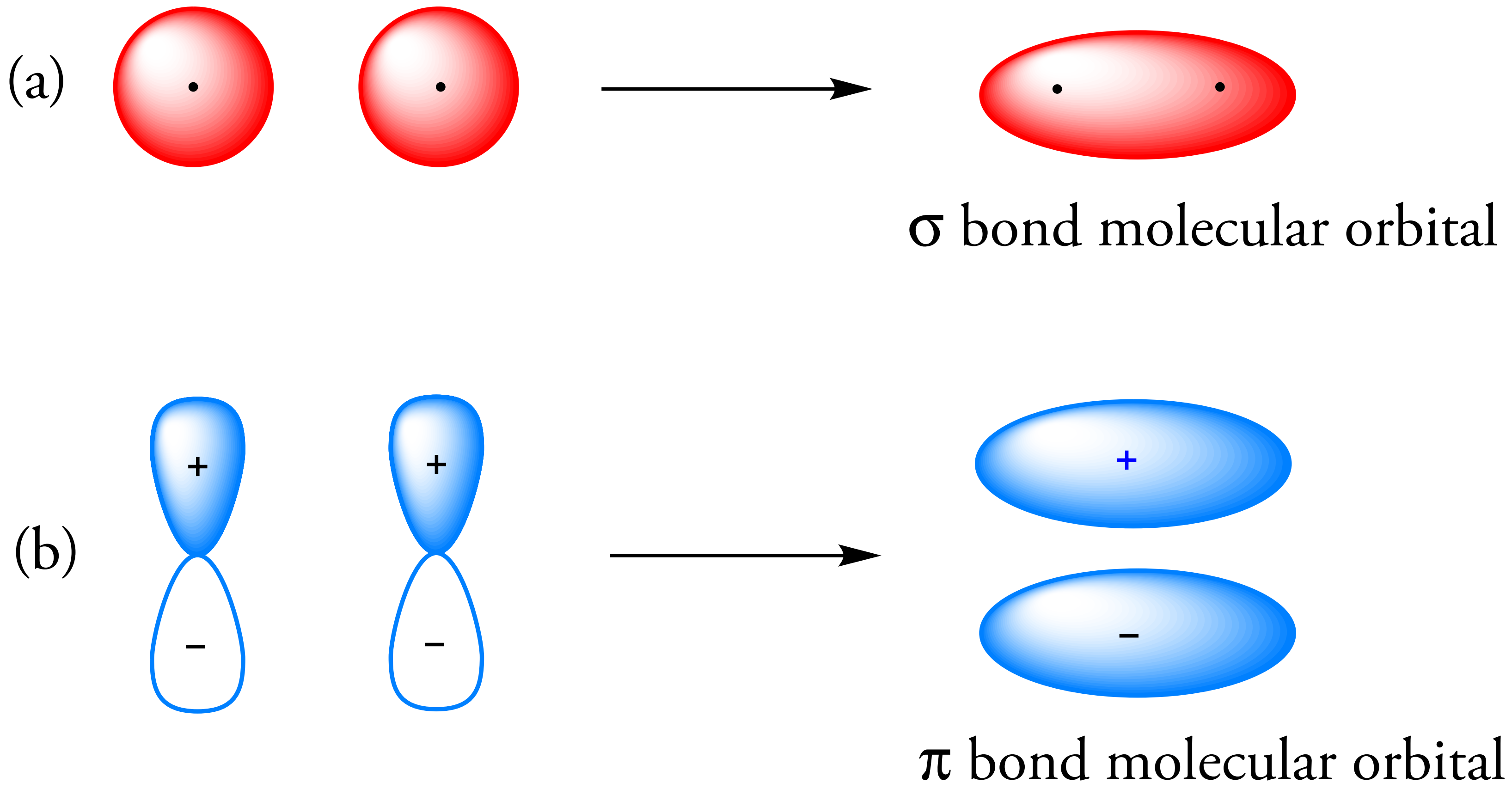
1.10 MOLECULAR ORBITAL THEORY

Molecular Orbitals

Figure 1.8 Linear Combinations of Atomic Orbitals

(a) When the is atomic orbitals of hydrogen atoms overlap, they may do so with reinforcement of the wave functions. The constructive interaction—that is, the addition of wave functions—gives a sigma (σ) molecular orbital. The electron density between two nuclei is located in this cylindrically symmetrical region.

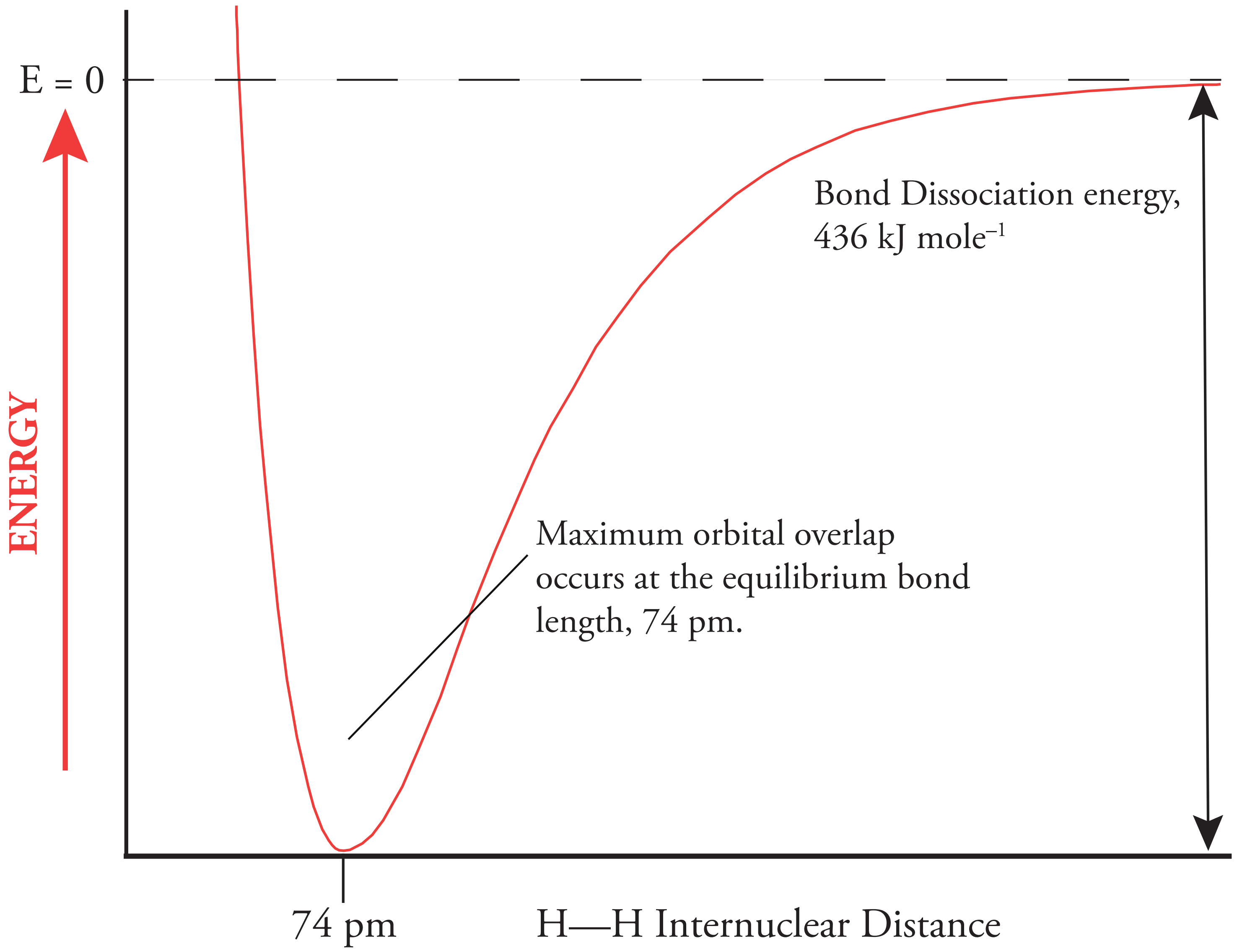
(b) When two 2p orbitals overlap side-by-side, they may do so with reinforcement of the wave functions. The constructive interaction—that is, the addition of wave functions—results in a pi (π) molecular orbital.



1.11 THE HYDROGEN MOLECULE

Figure 1.9 Plot of Energy vs. Internuclear Separation for the Hydrogen Molecule

An energy minimum for the interaction of two hydrogen atoms occurs when they are 74 pm apart. This minimum corresponds to bond formation between the two atoms. If the nuclei move closer, the energy rapidly increases because the two positively charged nuclei repel each other more.

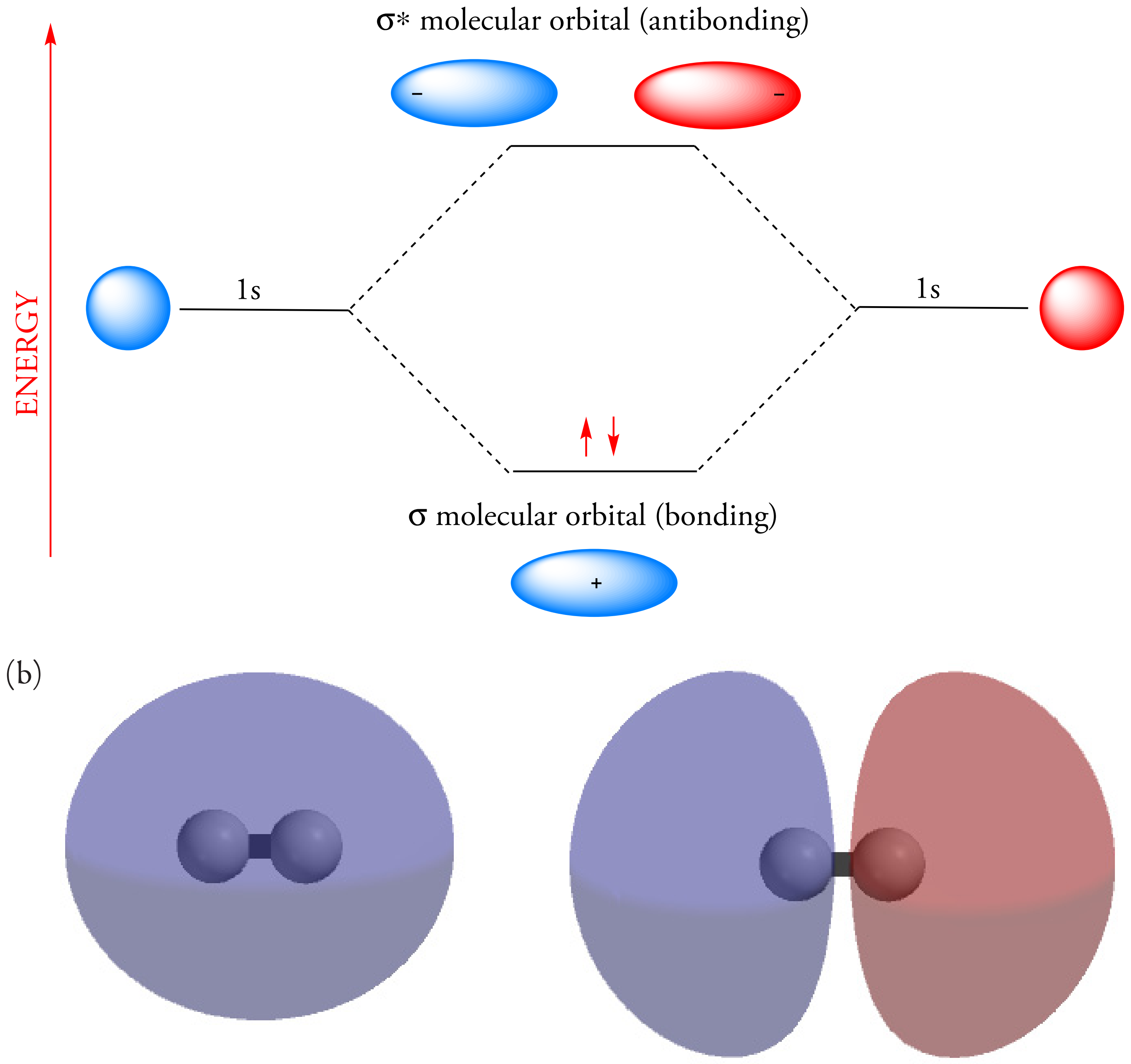


1.11 THE HYDROGEN MOLECULE

Figure 1.10 Energy of Bonding and Antibonding Molecular Orbitals

(a) Two molecular orbitals are formed by combining two 1s hydrogen orbitals. The bonding molecular orbital, σ, is lower in energy that the antibonding molecular orbital, σ^*. There is no electron density between the two nuclei in the antibonding orbital.

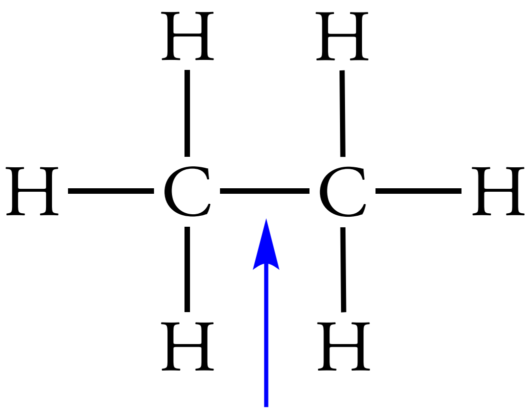
(b) Molecular orbital view of hydrogen bonding and antibonding orbitals.



σ bonding molecular orbital

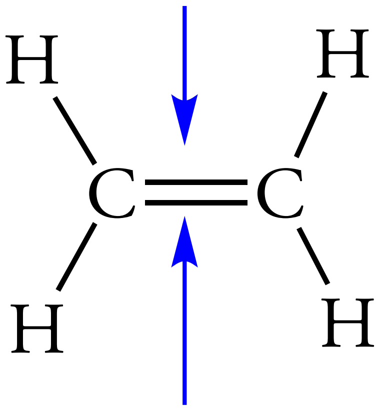
σ* antibonding molecular orbital

1.12 BONDING IN CARBON COMPOUNDS



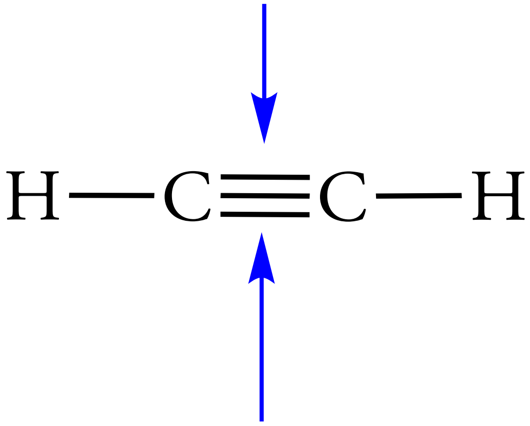
one σ bond

one π bond



one σ bond

two π bonds

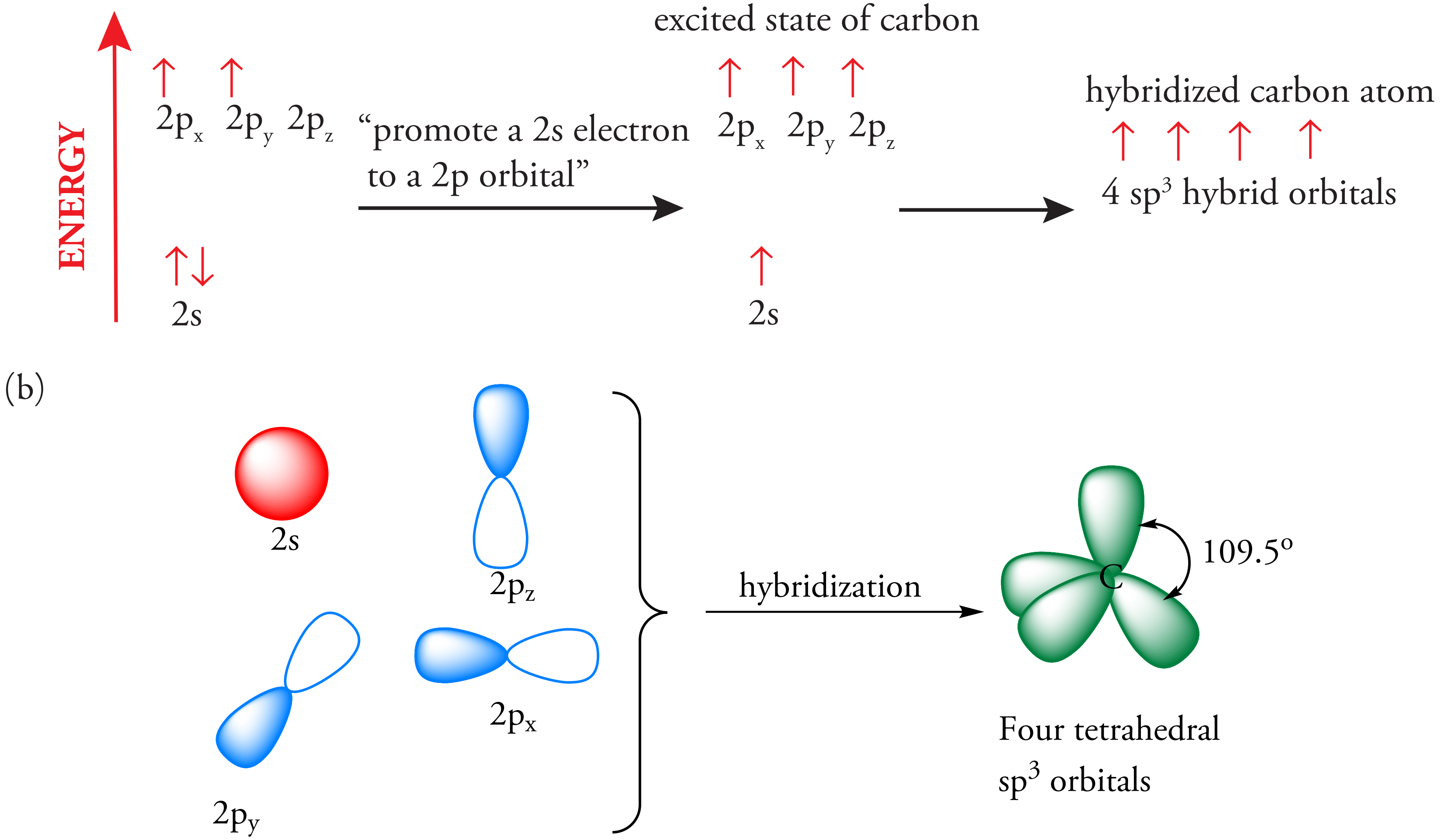


one σ bond

1.13 sp^3 HYBRIDIZATION OF CARBON IN METHANE

Figure 1.11
sp^3-Hybridized Carbon Atom

(a) The original set of four atomic orbitals on carbon are mixed, or hybridized to give four new sp^3-hybridized atomic orbitals.
(b) We have represented the new hybrid orbitals with a new color to emphasize the notion that the hybrid orbitals replace the original unhybridized orbitals.



ENERGY

$2p_x$ $2p_y$ $2p_z$

$2s$

"promote a 2s electron to a 2p orbital"

excited state of carbon

$2p_x$ $2p_y$ $2p_z$

$2s$

hybridized carbon atom

4 sp^3 hybrid orbitals

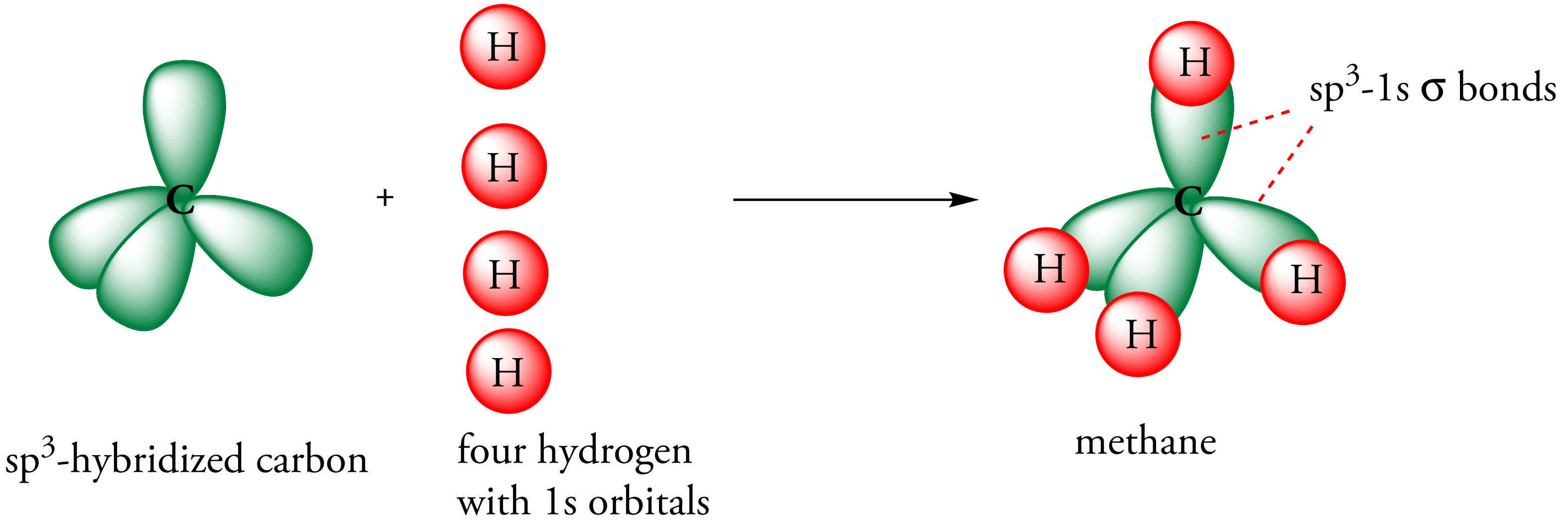
(b)

Four tetrahedral sp^3 orbitals

1.13 sp^3 HYBRIDIZATION OF CARBON IN METHANE

Figure 1.12 sp^3 Hybridized Carbon in Methane

The shapes of the sp^3 hybrid atomic orbital in methane. The outer boundary encloses a region of space with a 90% probability of finding an electron. The four identical sp^3 hybrid orbitals point at the corners of a regular tetrahedron.



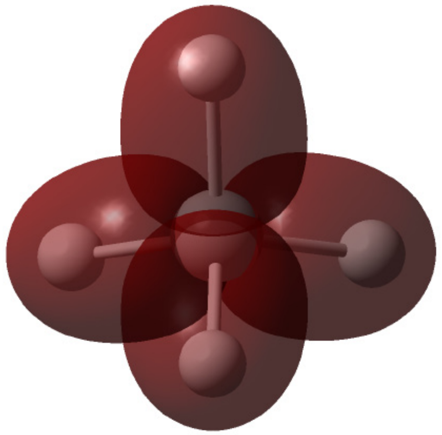
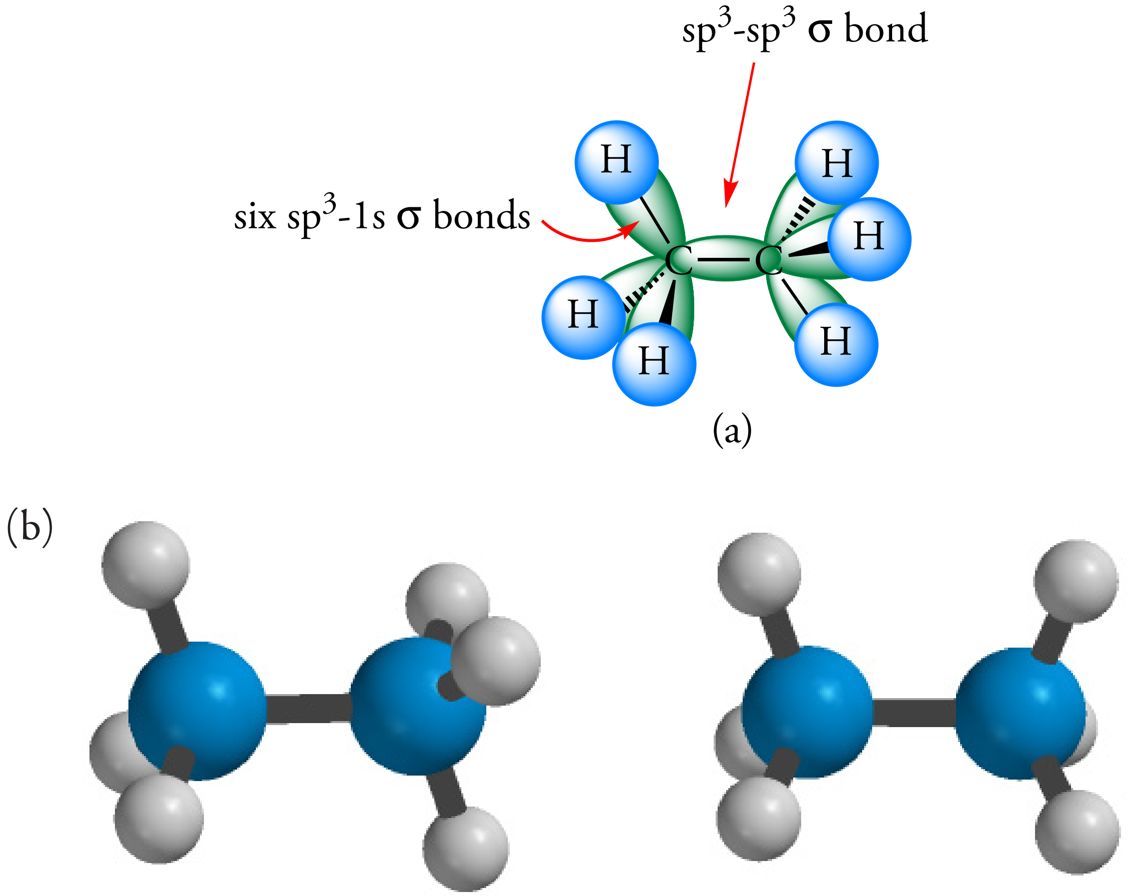


Figure 1.13 Bonding and Structure of Ethane and Conformations of Ethane

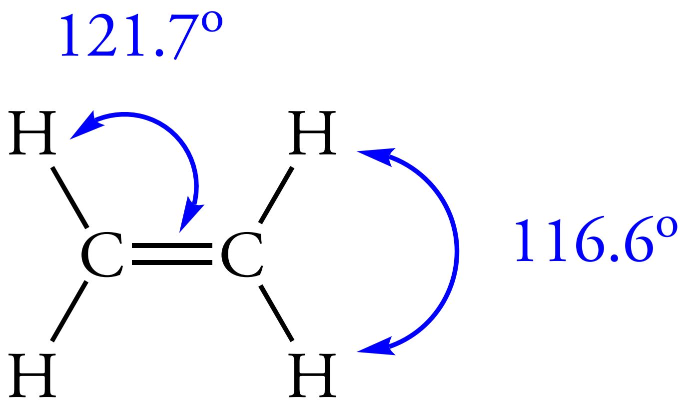
(a) The bonding molecular orbital of the C—C bond in ethane is cylindrically symmetrical.

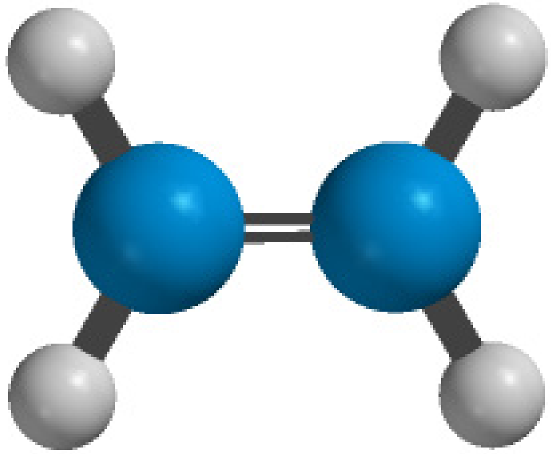
(b) Rotation of the two methyl groups about the C—C bond axis maintains the bond, but changes the relative positions of the C—H bonds.



Two conformations of ethane

1.15 sp^2 HYBRIDIZATION OF CARBON IN ETHENE

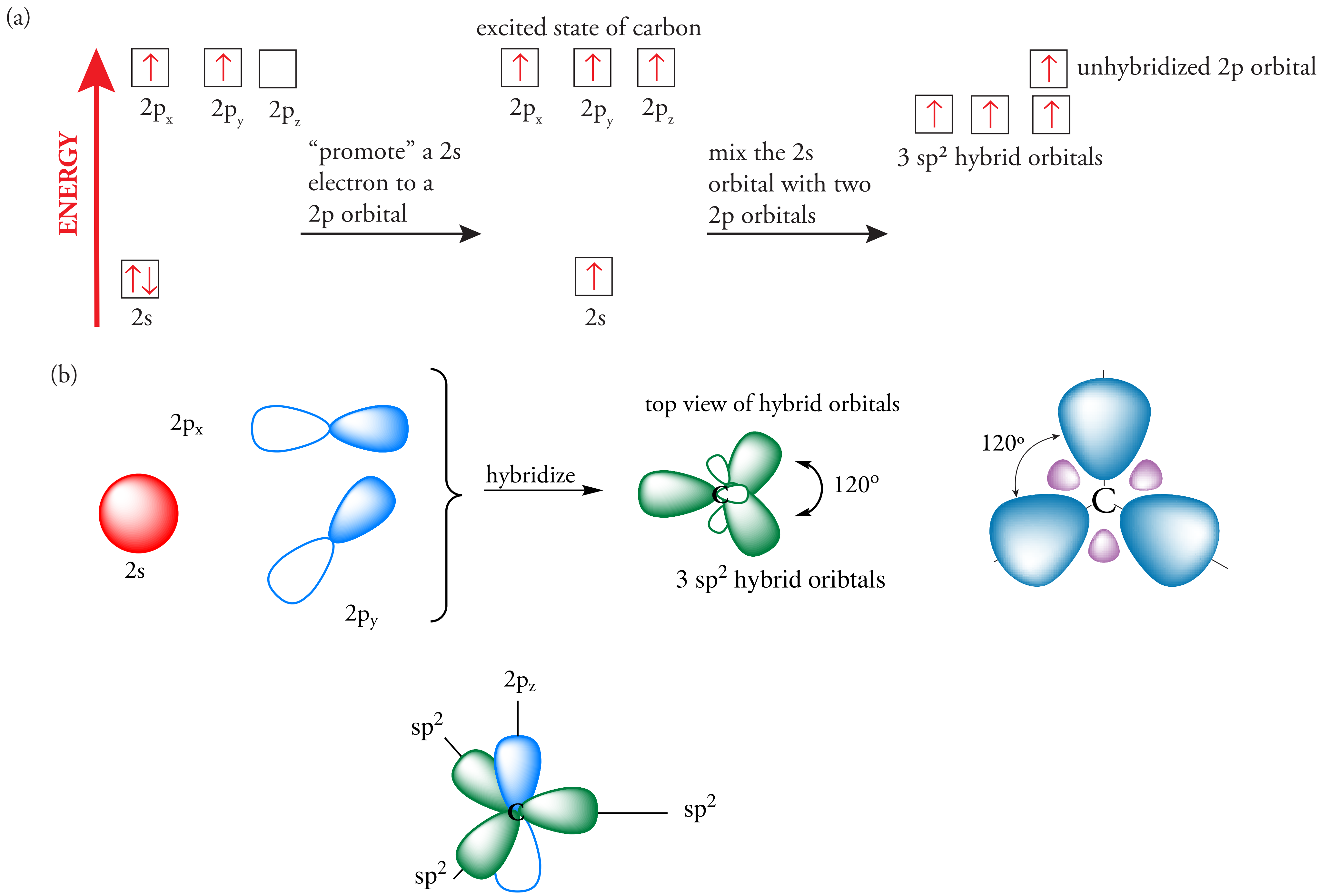




1.15 sp^2 HYBRIDIZATION OF CARBON IN ETHENE

Figure 1.14 sp^2 Hybrid Orbitals

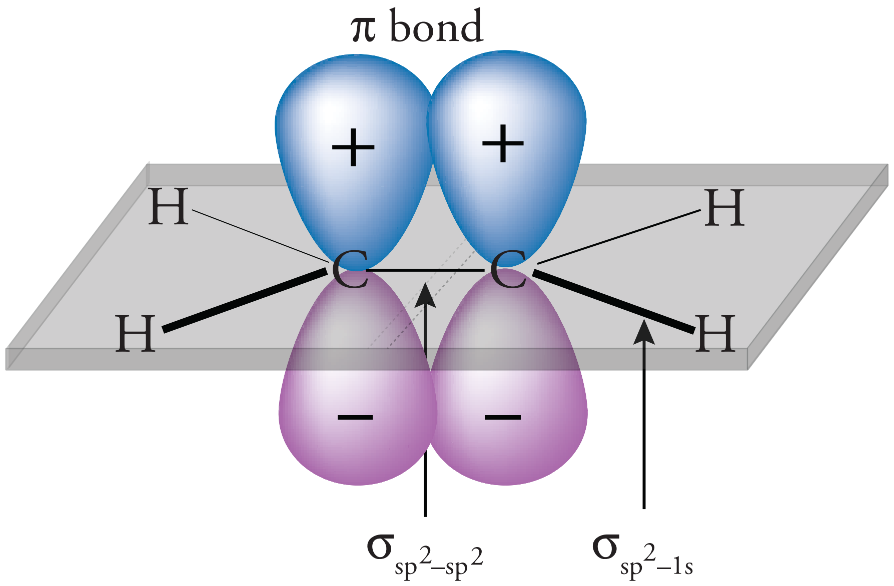
(a) Schematic diagram of orbital hybridization. (b) Shapes of sp^2 hybrid orbitals. The shape of an sp^2 hybrid atomic orbital in ethene. The outer boundary encloses a region of space with a 90% probability of finding an electron. The three identical sp^2 hybrid orbitals point at the corners of a triangle.



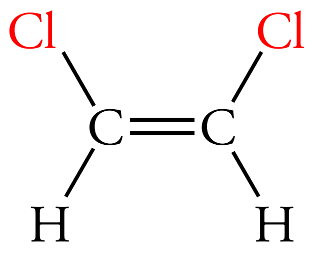
side view: three sp^2 hybrid orbitals and 2p orbital

1.15 sp^2 HYBRIDIZATION OF CARBON IN ETHENE

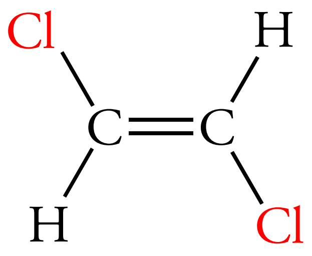
Figure 1.15 Bonding and Structure in Ethene



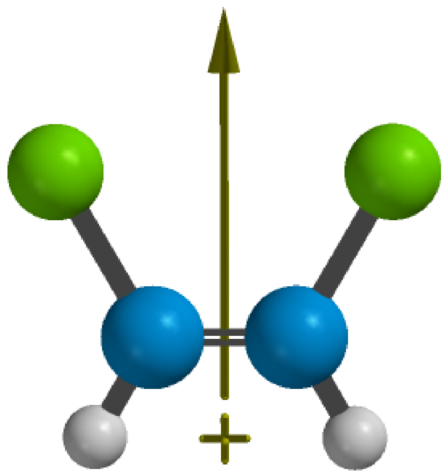
1.15 sp^2 HYBRIDIZATION OF CARBON IN ETHENE



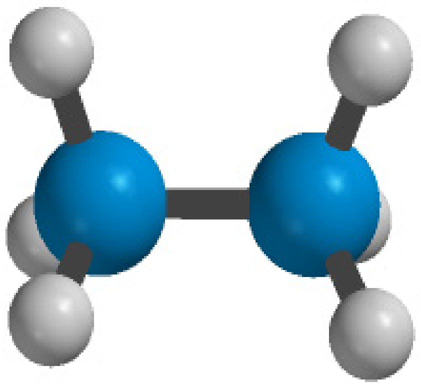
cis-1,2-dichloroethene



trans-1,2-dichloroethene



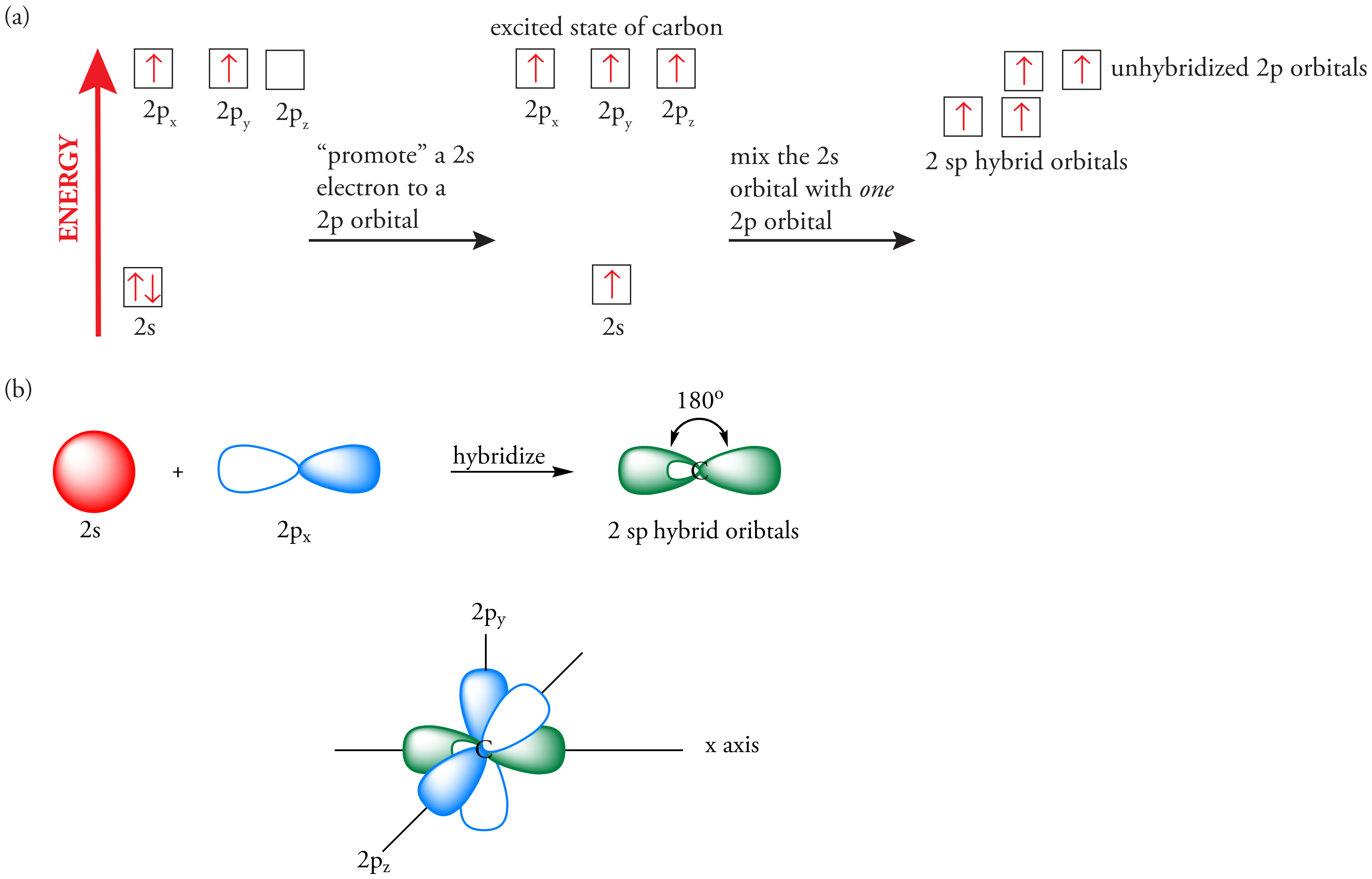
μ = 1.9 D



μ = 0 D

1.16 sp HYBRIDIZATION OF CARBON IN ETHYNE

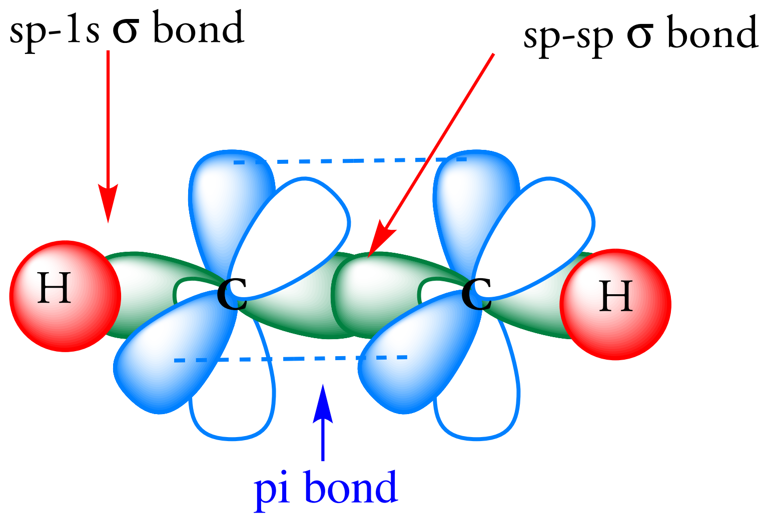
Figure 1.16
sp-Hybridized Carbon Atom



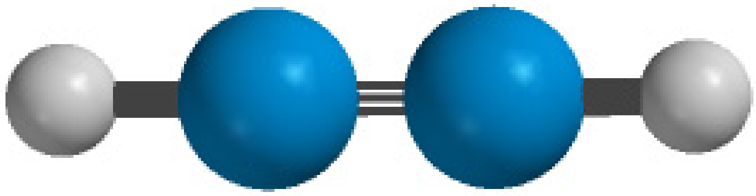
side view: two sp hybrid orbitals and two 2p orbitals

1.16 sp HYBRIDIZATION OF CARBON IN ETHYNE

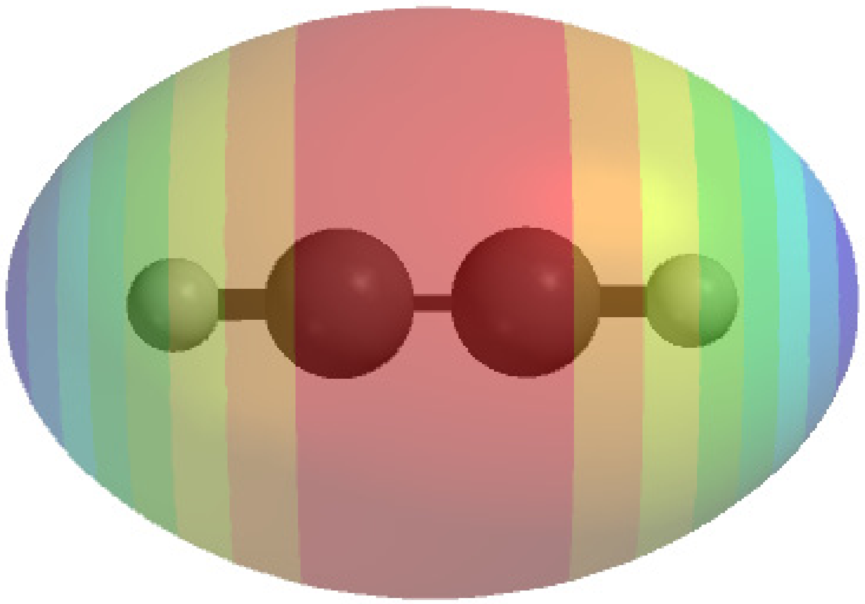
Figure 1.17 Structure and Bonding in Ethyne



Bonding in ethyne: the σ bonds are colinear; the π bonds lie above and below, and in front and behind the carbon-carbon sigma bond.



Ball-and-stick model of ethyne



Electron density map of ethyne. Although the molecule is nonpolar overall, each C—H bond is polar. The carbon has a small partial positive charge (shaded red), and the hydrogen has an equal and opposite partial negative charge (shaded blue).

1.17 EFFECT OF HYBRIDIZATION ON BOND LENGTH AND BOND STRENGTH

Table 1.5
Average Bond Energies in Ethane, Ethene and Ethyne

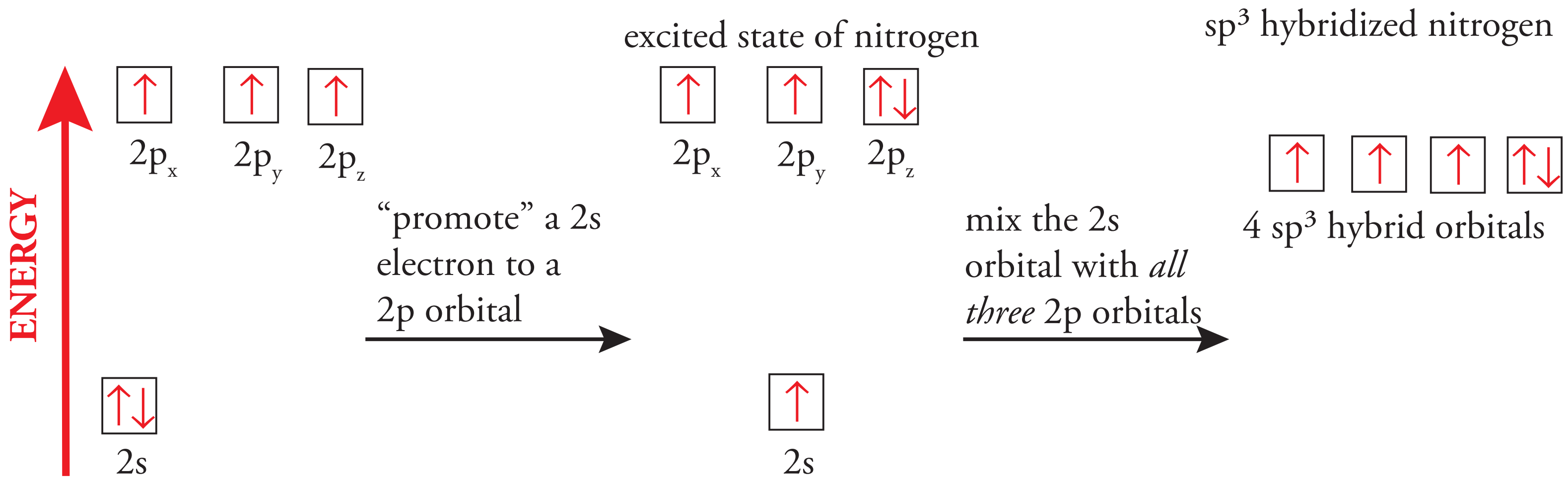
Bond Type	Bond Energy (kJ mole^{-1})
H—C (sp^3)	410
H—C (sp^2)	422
H—C (sp)	523
C—C (sp^3)	347
C=C (sp^2)	610
C≡C (sp)	837

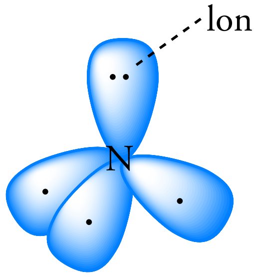
Table 1.6
Average Bond Lengths (pm)

H—C (sp^3)	109
H—C (sp^2)	107
H—C (sp)	105
C—C (sp^3)	154
C=C (sp^2)	133
C≡C (sp)	120

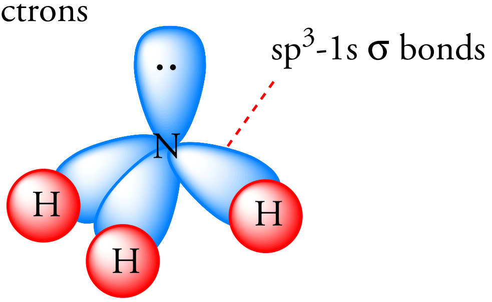
1.18 HYBRIDIZATION OF NITROGEN

Figure 1.18 sp³-Hybridized Nitrogen Atom

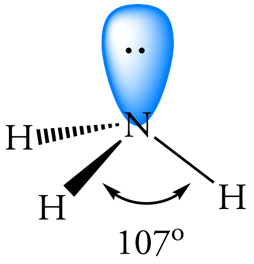


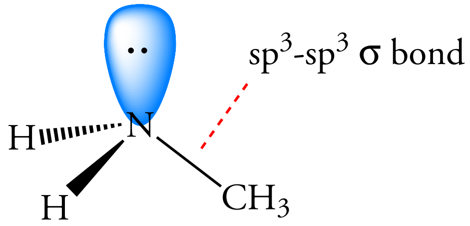


sp^3-hybridized nitrogen



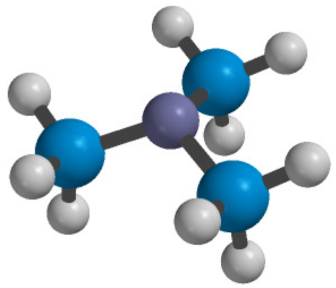
ammonia





aminomethane

Ball-and-Stick Structure of Ammonia Showing Its Dipole.
Since nitrogen is more electronegative than hydrogen, the positive end of the dipole is on nitrogen and the negative end of the dipole is directed to the lone the lone pair, which is not shown in the ball-and-stick diagram.

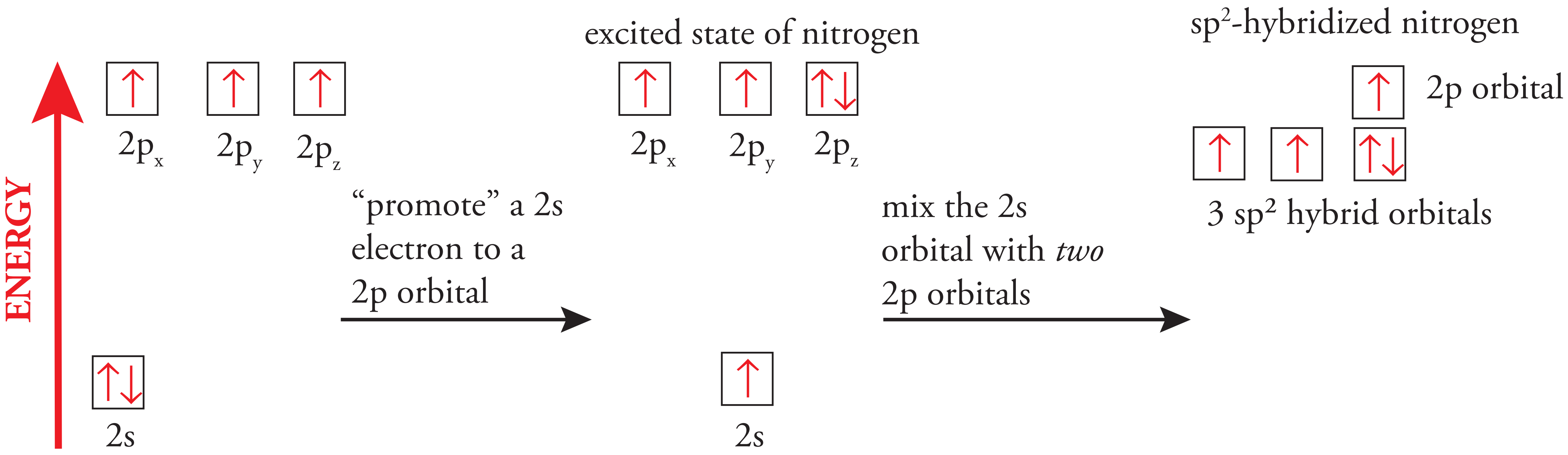


trimethylamine

Ball-and-Stick Structure of Triethylamine.
All three hydrogen atoms of ammonia have been replaced with alkyl groups.

1.18 HYBRIDIZATION OF NITROGEN

Figure 1.19 sp^2-Hybridized Nitrogen Atom



ENERGY

$2p_x$ $2p_y$ $2p_z$

2s

“promote” a 2s electron to a 2p orbital

excited state of nitrogen

$2p_x$ $2p_y$ $2p_z$

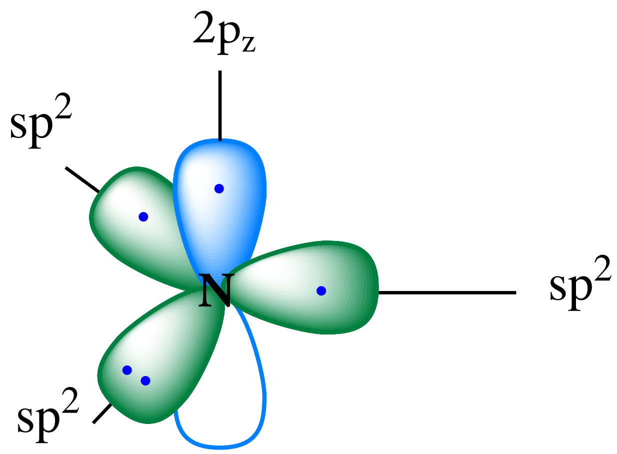
2s

mix the 2s orbital with *two* 2p orbitals

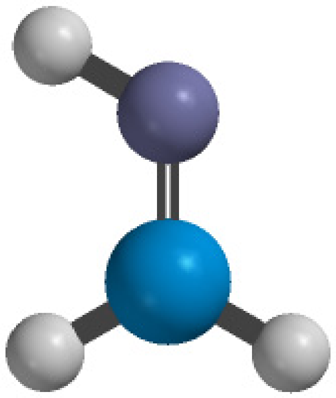
sp^2-hybridized nitrogen

2p orbital

3 sp^2 hybrid orbitals



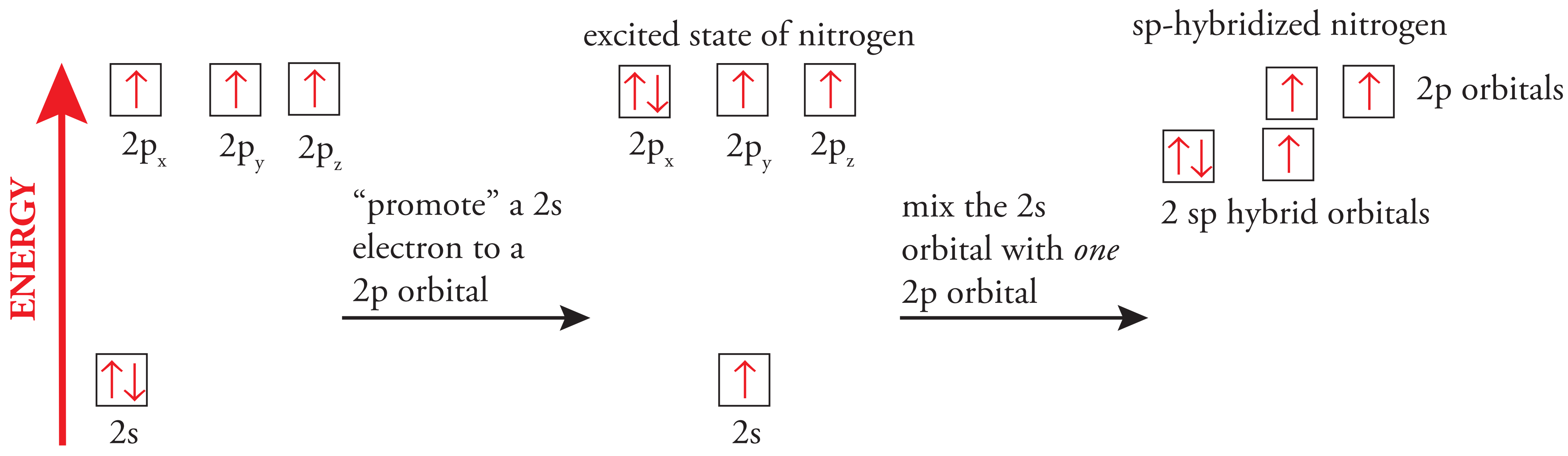
side view: three sp^2 hybrid orbitals and 2p orbital on nitrogen



Ball-and-Stick Structure of formaldimine, the nitrogen analog of ethene. The nitrogen and carbon atoms are both sp^2-hybridized.

1.18 HYBRIDIZATION OF NITROGEN

Figure 1.20 sp-Hybridized Nitrogen Atom


ENERGY

$2p_x$ $2p_y$ $2p_z$

2s

"promote" a 2s electron to a 2p orbital

excited state of nitrogen

$2p_x$ $2p_y$ $2p_z$

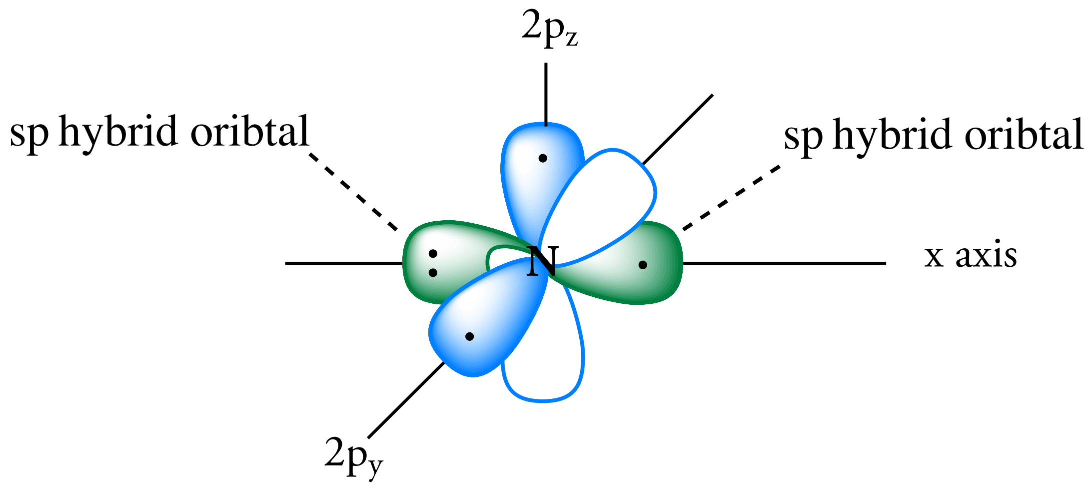
2s

mix the 2s orbital with *one* 2p orbital

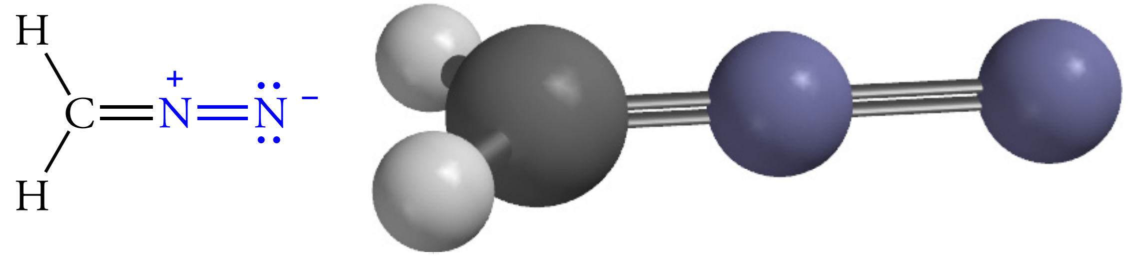
sp-hybridized nitrogen

2p orbitals

2 sp hybrid orbitals



side view: two sp hybrid orbitals and two 2p orbitals

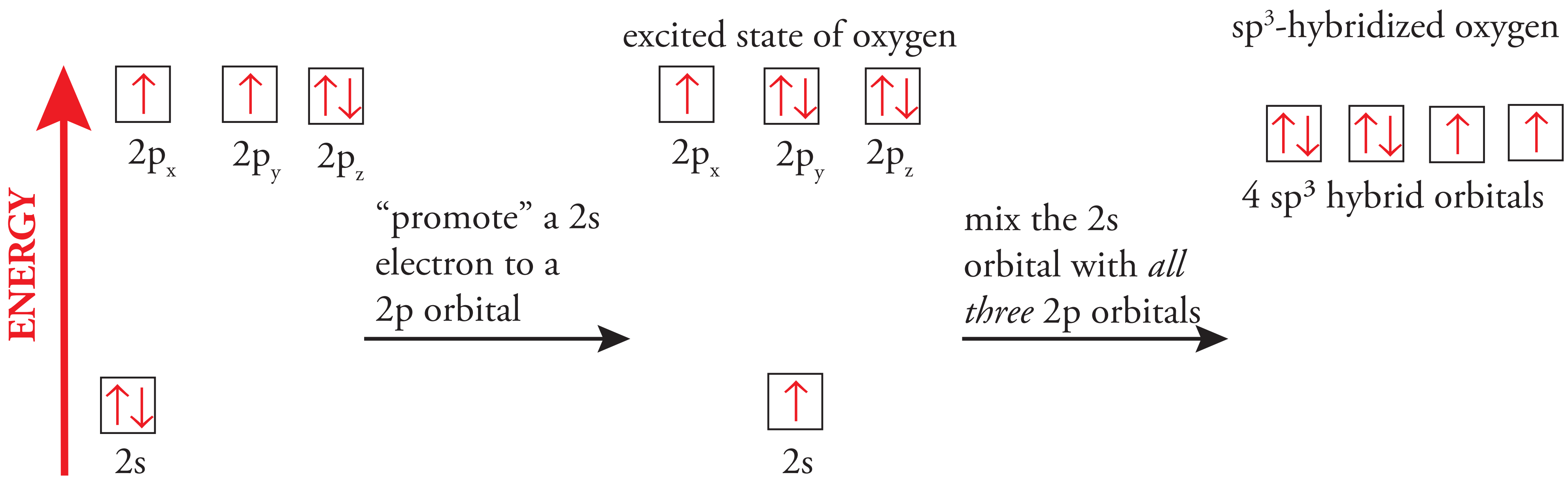


Bond-Line Structures and Ball-and-Stick Structure of Dizaomethane.

The central nitrogen is sp-hybridized and the terminal nitrogen and carbon atoms are sp^2-hybridized. The terminal nitrogen has two nonbonded electron pairs, and it has a negative charge. Diazomethane is a highly explosive yellow gas.

1.19 HYBRIDIZATION OF OXYGEN

Figure 1.21
sp^3-Hybridized Oxygen Atom



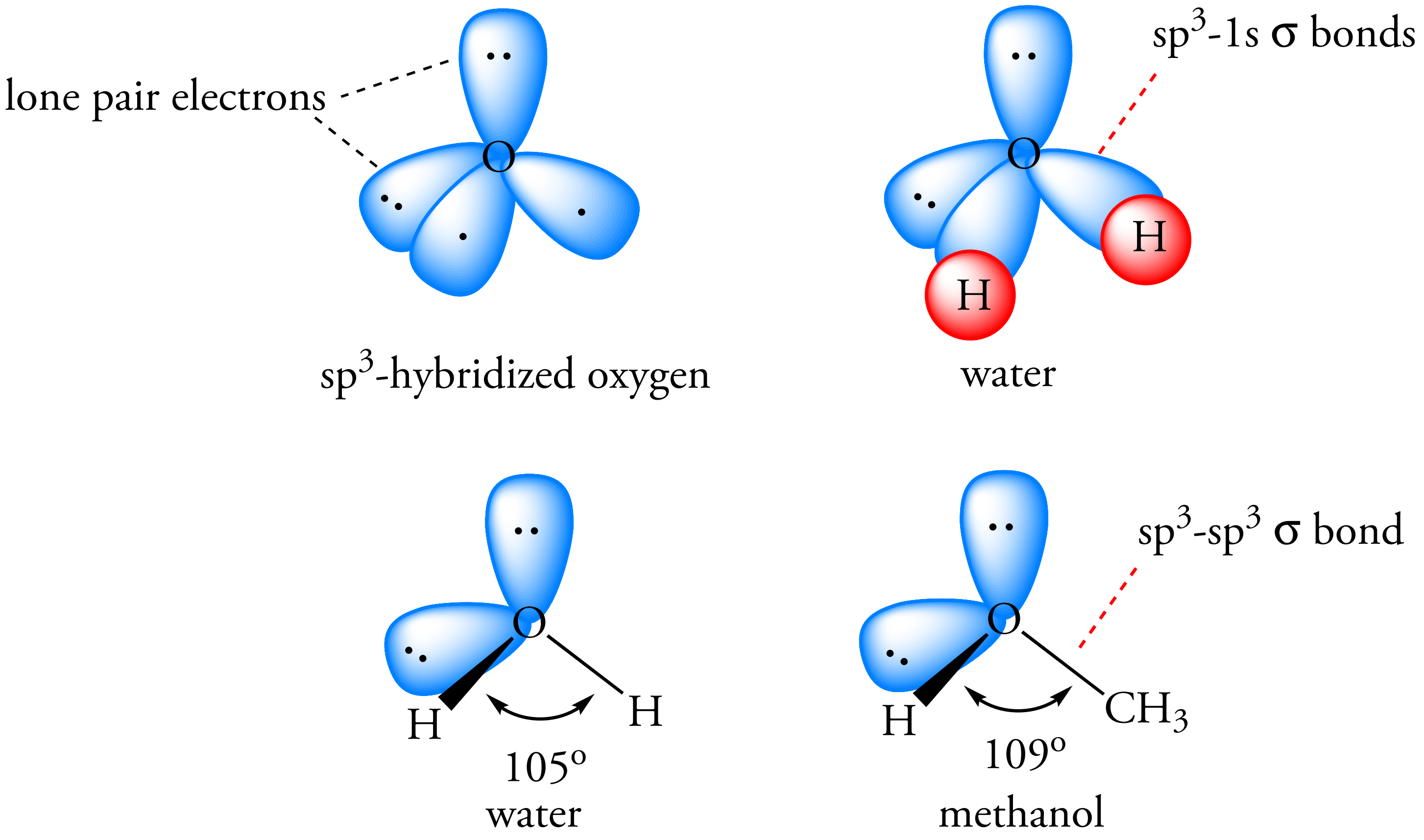
excited state of oxygen

sp^3-hybridized oxygen

"promote" a 2s electron to a 2p orbital

mix the 2s orbital with *all three* 2p orbitals

4 sp^3 hybrid orbitals



lone pair electrons

sp^3-1s σ bonds

sp^3-hybridized oxygen

water

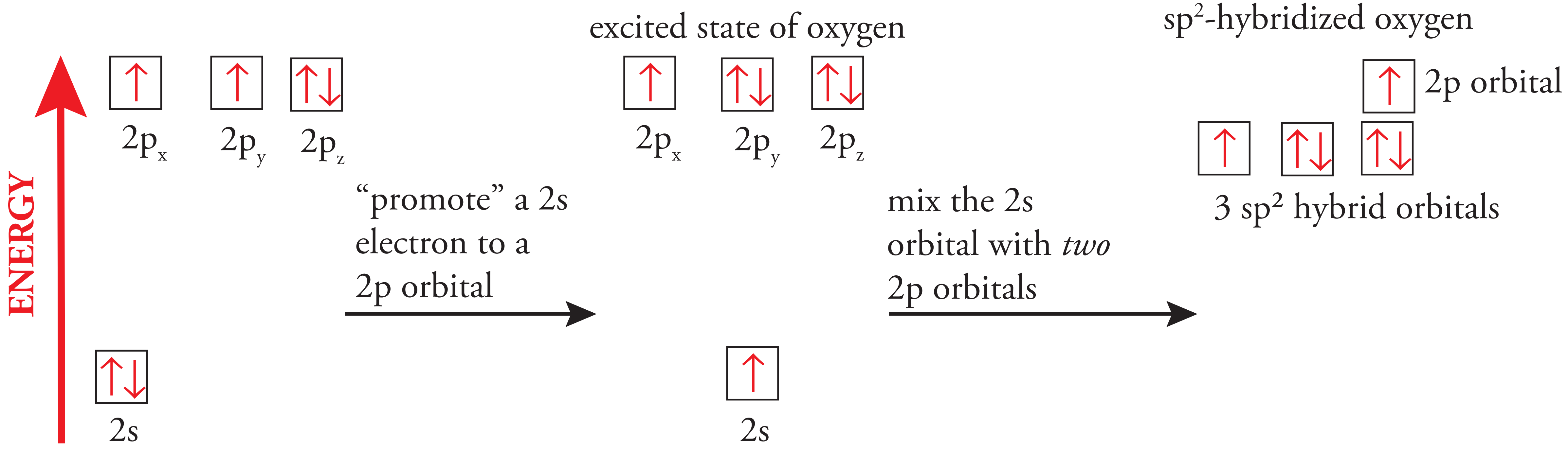
sp^3-sp^3 σ bond

105°
water

109°
methanol

1.19 HYBRIDIZATION OF OXYGEN

Figure 1.23 sp^2-Hybridized Oxygen Atom



ENERGY

$2p_x$ $2p_y$ $2p_z$

$2s$

“promote” a 2s electron to a 2p orbital

excited state of oxygen

$2p_x$ $2p_y$ $2p_z$

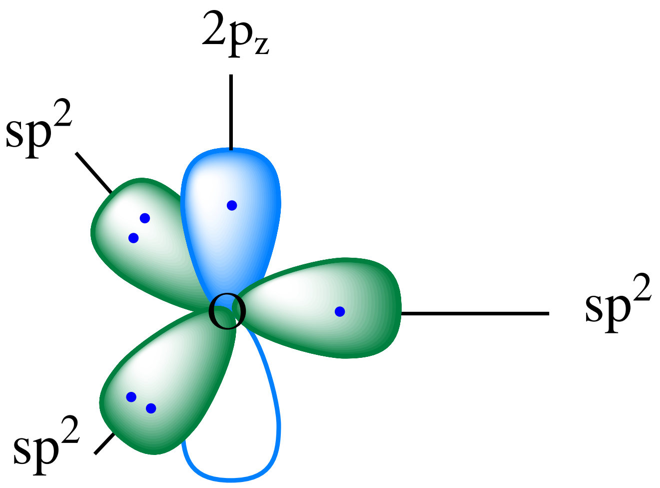
$2s$

mix the 2s orbital with *two* 2p orbitals

sp^2-hybridized oxygen

2p orbital

3 sp^2 hybrid orbitals



side view: three sp^2 hybrid orbitals and 2p orbital on oxygen

Summary of Orbital Hybridization and Its Relation to VSEPR Theory

Table 1. 7 Hybridization, Electron Pair Geometry, and Molecular, Geometry

Hybridization	Electron Pair Geometry	Molecular Geometry	Nonbonded Electrons	σ bonds	π bonds	Example
sp	Linear	Linear	2 unpaired (e.g. $2p_y^1$, $2p_z^1$ on adjacent atoms)	2	2	Ethyne
sp^2	Trigonal planar	Trigonal Planar	1 (e.g. $2p_z^1$, $2p_z^1$ on adjacent atoms)	3	1	Ethene
sp^3	Tetrahedral	Tetrahedral	0	4	0	Methane
sp^3	Tetrahedral	Pyramidal	2	3	0	Ammonia
sp^3	Tetrahedral	Angular	4 (two pairs)	2	0	Water
Reactive Intermediates						
sp^2	Trigonal Planar	Trigonal Planar	none	3	0	Carbocation
sp^2	Trigonal Planar	Trigonal Planar	1	3	0	Carbon Radical
sp^3	Tetrahedral	Pyramidal	2	3	0	Carbanion