Chapter 1

The Basics
Bonding and Molecular Structure

Created by
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About The Authors

These Powerpoint Lecture Slides were created and prepared by Professor William Tam and his wife Dr. Phillis Chang.

Professor William Tam received his B.Sc. at the University of Hong Kong in 1990 and his Ph.D. at the University of Toronto (Canada) in 1995. He was an NSERC postdoctoral fellow at the Imperial College (UK) and at Harvard University (USA). He joined the Department of Chemistry at the University of Guelph (Ontario, Canada) in 1998 and is currently a Full Professor and Associate Chair in the department. Professor Tam has received several awards in research and teaching, and according to *Essential Science Indicators*, he is currently ranked as the Top 1% most cited Chemists worldwide. He has published four books and over 80 scientific papers in top international journals such as *J. Am. Chem. Soc., Angew. Chem., Org. Lett.,* and *J. Org. Chem.*

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1. Introduction

- The name Organic Chemistry came from the word organism
- Organic Chemistry is the study of carbon compounds. Carbon, atomic number 6, is a second-row element. Although carbon is the principal element in organic compounds, most also contain hydrogen, and many contain nitrogen, oxygen, phosphorus, sulfur, chlorine, or other elements

- Most of the compounds found in nature - those we rely on for food, medicine, clothing (cotton, wool, silk), and energy (natural gas, petroleum) - are organic as well
- Important organic compounds are not, however, limited to the ones we find in nature
- Chemists have learned to synthesize millions of organic compounds never found in nature, including synthetic fabrics, plastics, synthetic rubber, medicines, and even things like photographic film & Super glue

2. Atomic Structure

- Compounds
  - made up of elements combined in different proportions
- Elements
  - made up of atoms
- Atoms
  - positively charged nucleus containing protons and neutrons
  - with a surrounding cloud of negatively charged electrons

- Each element is distinguished by its atomic number (Z)

- Atomic number = number of protons in nucleus

PERIODIC TABLE OF THE ELEMENTS

Atomic number → 6
Symbol → C
Name (IUPAC) → Carbon
Atomic mass → 12.011

Chemical Abstracts Service group notation →

IA	IIA											IIIA	IVA	VA	VIA	VIIA	VIIIA
1 H Hydrogen 1.0079																	2 He Helium 4.0026
3 Li Lithium 6.941	4 Be Beryllium 9.0122											5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180
11 Na Sodium 22,990	12 Mg Magnesium 24.305											13 Al Aluminum 26.982	14 Si Silicon 28.086	15 P Phosphorus 30.974	16 S Sulfur 32.065	17 Cl Chlorine 35.453	18 Ar Argon 39.948
19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.867	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.409	31 Ga Gallium 69.723	32 Ge Germanium 72.64	33 As Arsenic 74.922	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.798
37 Rb Rubidium 85.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.94	43 Tc Technetium (98)	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.91	46 Pd Palladium 106.42	47 Ag Silver 107.87	48 Cd Cadmium 112.41	49 In Indium 114.82	50 Sn Tin 118.71	51 Sb Antimony 121.76	52 Te Tellurium 127.60	53 I Iodine 126.90	54 Xe Xenon 131.29
55 Cs Cesium 132.91	56 Ba Barium 137.33	57 La Lanthanum 138.91	72 Hf Hafnium 178.49	73 Ta Tantalum 180.95	74 W Tungsten 183.84	75 Re Rhenium 186.21	76 Os Osmium 190.23	77 Ir Iridium 192.22	78 Pt Platinum 195.08	79 Au Gold 196.97	80 Hg Mercury 200.59	81 Tl Thallium 204.38	82 Pb Lead 207.2	83 Bi Bismuth 208.98	84 Po Polonium (209)	85 At Astatine (210)	86 Rn Radon (222)
87 Fr Francium (223)	88 Ra Radium (226)	89 Ac Actinium (227)	104 Rf Rutherfordium (261)	105 Db Dubnium (262)	106 Sg Seaborgium (266)	107 Bh Bohrium (264)	108 Hs Hassium (277)	109 Mt Meitnerium (268)	110 Uun (281)	111 Uuu (272)	112 Uub (285)		114 Uuq (289)				

(Lanthanide series (58-71) and actinide series (90-103) elements not shown)

2A. Isotopes

- Although all the nuclei of all atoms of the same element will have the same number of protons, some atoms of the same element may have different masses because they have different numbers of neutrons. Such atoms are called isotopes

❖ Examples

(1)	^{12}C	^{13}C	^{14}C
	(6 protons 6 neutrons)	(6 protons 7 neutrons)	(6 protons 8 neutrons)
(2)	^{1}H	^{2}H	^{3}H
	Hydrogen (1 proton 0 neutrons)	Deuterium (1 proton 1 neutron)	Tritium (1 proton 2 neutrons)

2B. Valence Electrons

- Electrons that surround the nucleus exist in shells of increasing energy and at increasing distances from the nucleus. The most important **shell**, called the **valence shell**, is the outermost shell because the electrons of this shell are the ones that an atom uses in making chemical bonds with other atoms to form compounds
- The number of electrons in the valence shell (called **valence electrons**) is equal to the group number of the atom

- e.g. Carbon is in group IVA
  - Carbon has 4 valence electrons

- e.g. Nitrogen is in group VA
  - Nitrogen has 5 valence electrons

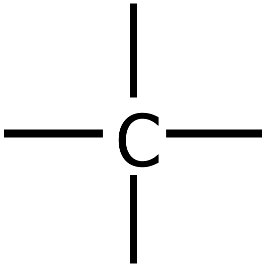
- e.g. Halogens are in group VIIA
  - F, Cl, Br, I all have 7 valence electrons

3. The Structural Theory of Organic Chemistry

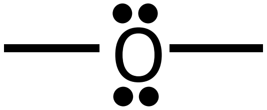
- Number of covalent bonds usually formed by some elements typically encountered in organic compounds

Element	# of covalent bonds	Element	# of covalent bonds
H	1	F	1
C	4	Cl	1
N	3 (or 4)	Br	1
O	2	I	1

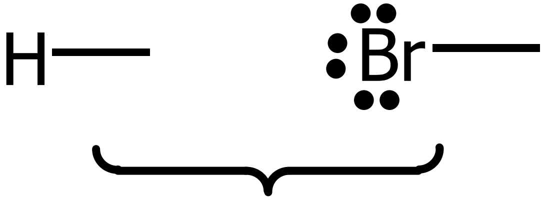
- Thus
  - C is *tetravalent*
  - O is *divalent*
  - H and halogens are *monovalent*



(tetravalent)

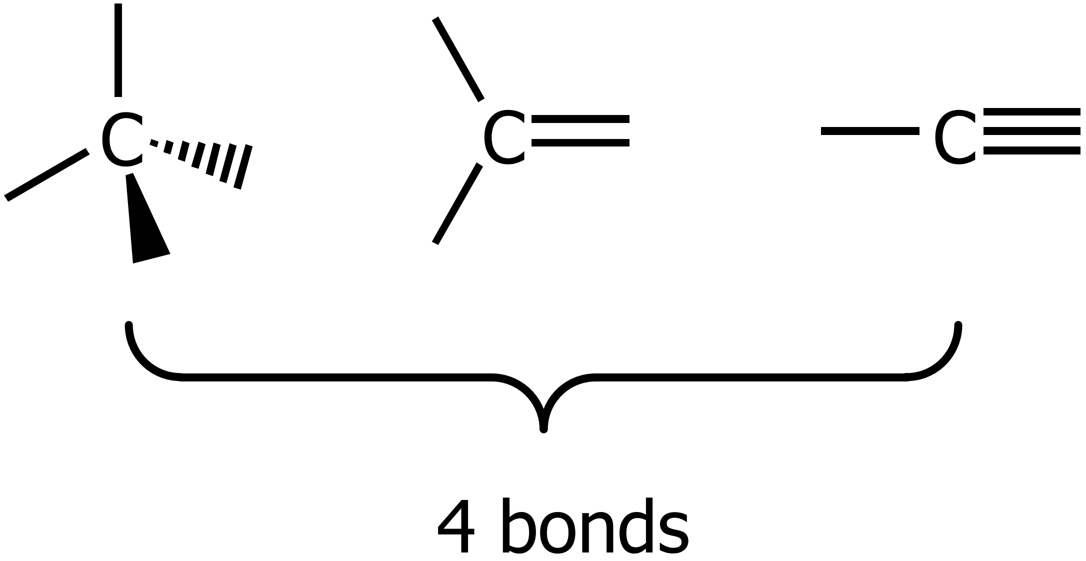


(divalent)

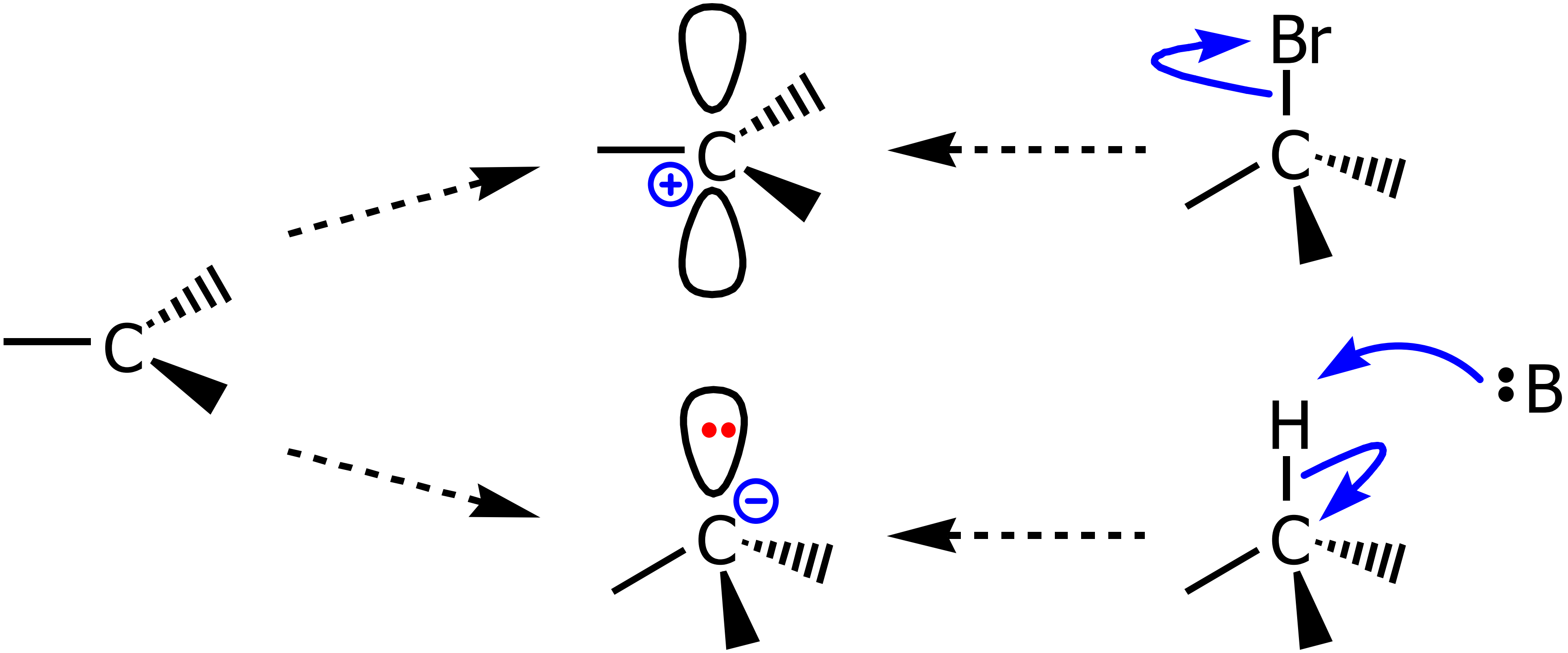


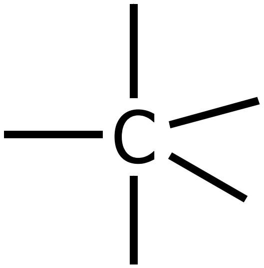
(monovalent)

- Important:
  - Do not draw any structure with more than 4 bonds on a carbon



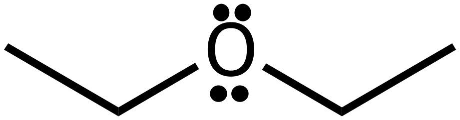
- 3 bonds on carbon ⇒ need a charge on carbon



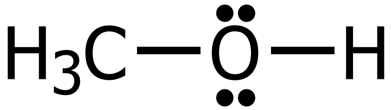


Never draw 5 (or more) bonds on carbon

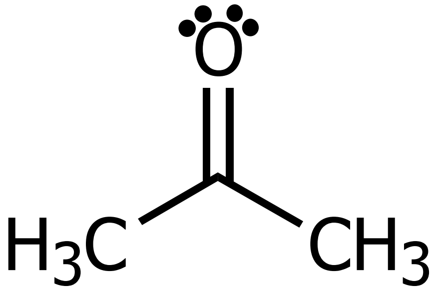
- Oxygen
  - Usually *divalent*



(diethyl ether)



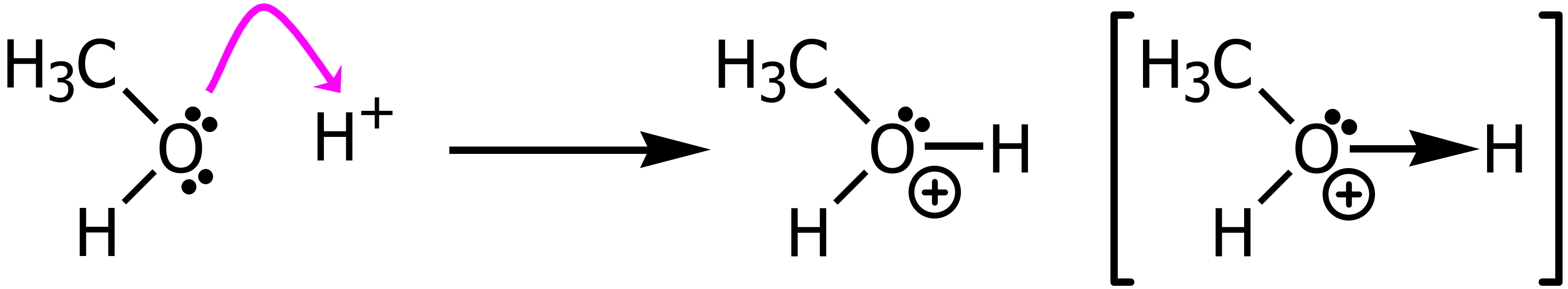
(methanol)



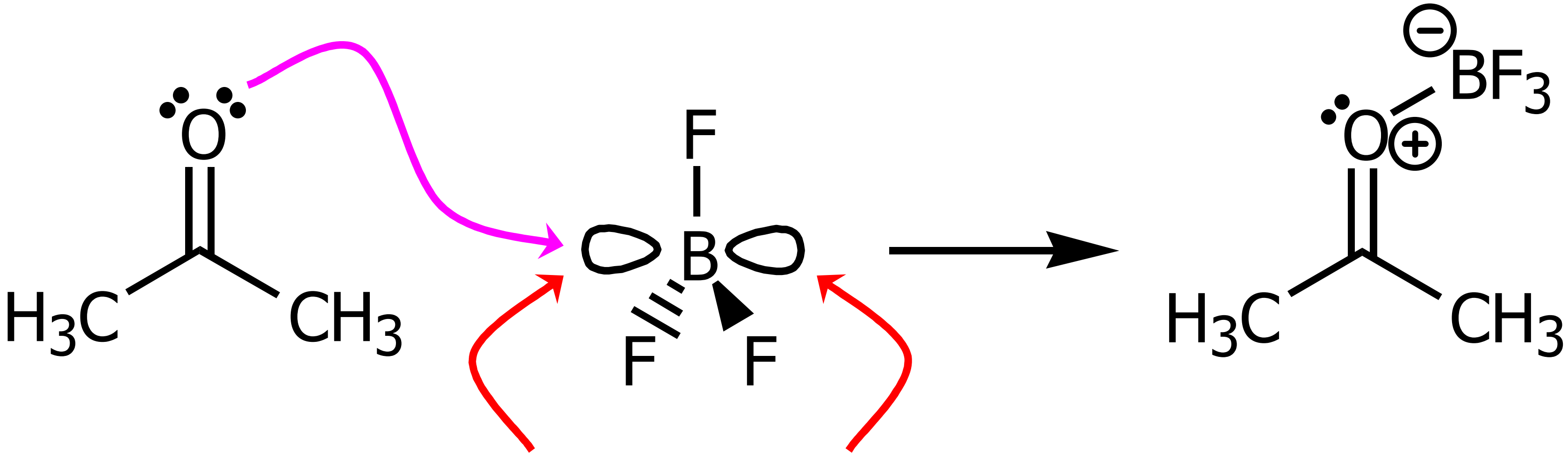
(acetone)

- Lone pair electrons on oxygen can donate electrons to a Lewis acid
  - 3 bonds on oxygen (with a positive charge on oxygen)

e.g.



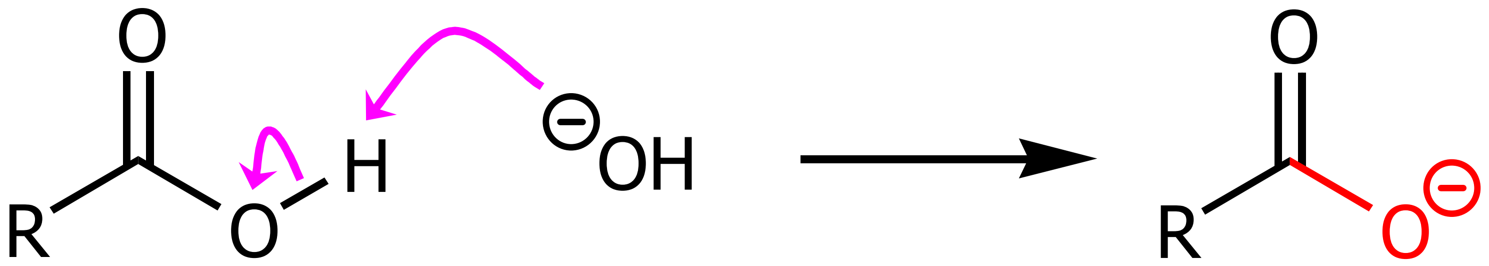
dative
covalent bond



empty p-orbitals

- ❖ One bond on oxygen
  - Usually need a negative charge on oxygen

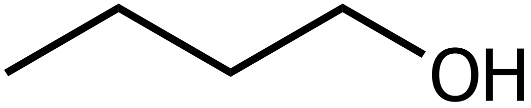
e.g.



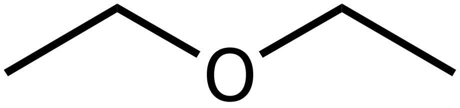
3A. Isomers: The Importance of Structural Formulas

- Different compounds that have the same molecular formula. Such compounds are called isomers

e.g.



1-Butanol

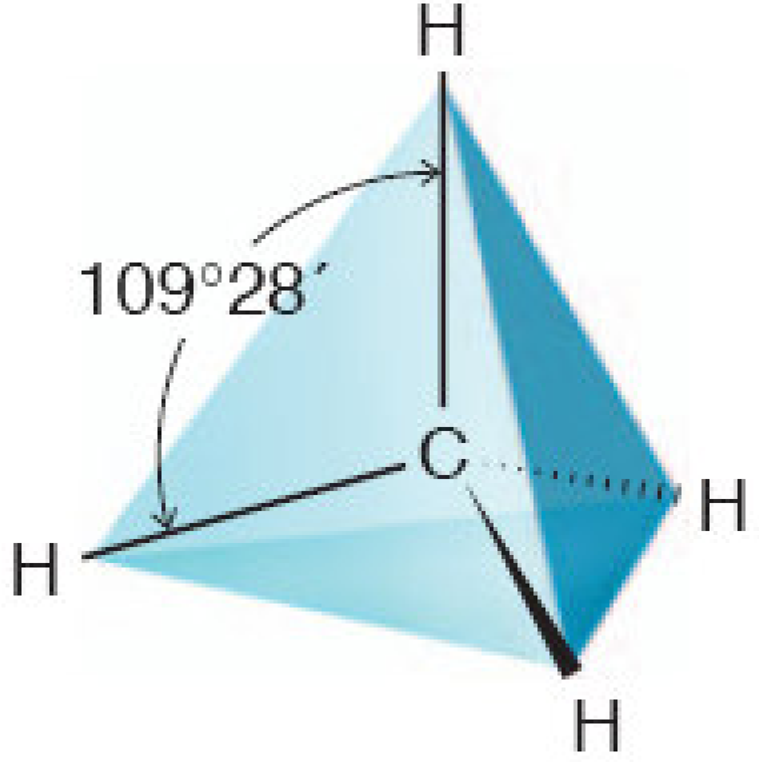


Diethyl ether

- Both have the molecular formula $C_4H_{10}O$
- They are constitutional isomers
- Constitutional isomers usually have different physical properties (e.g., melting point, boiling point, and density) and different chemical properties (reactivity)

3B. The Tetrahedral Shape of Methane

Methane



4. Chemical Bonds: The Octet Rule

- **Ionic** (or electrovalent) bonds are formed by the transfer of one or more electrons from one atom to another to create ions

- **Covalent** bonds result when atoms share electrons

- Octet Rule
  - In forming compounds, they gain, lose, or share electrons to give a stable electron configuration characterized by 8 valence electrons
  - When the octet rule is satisfied for C, N, O and F, they have an electron configuration analogous to the noble gas Ne

- Recall: electron configuration of noble (inert) gas

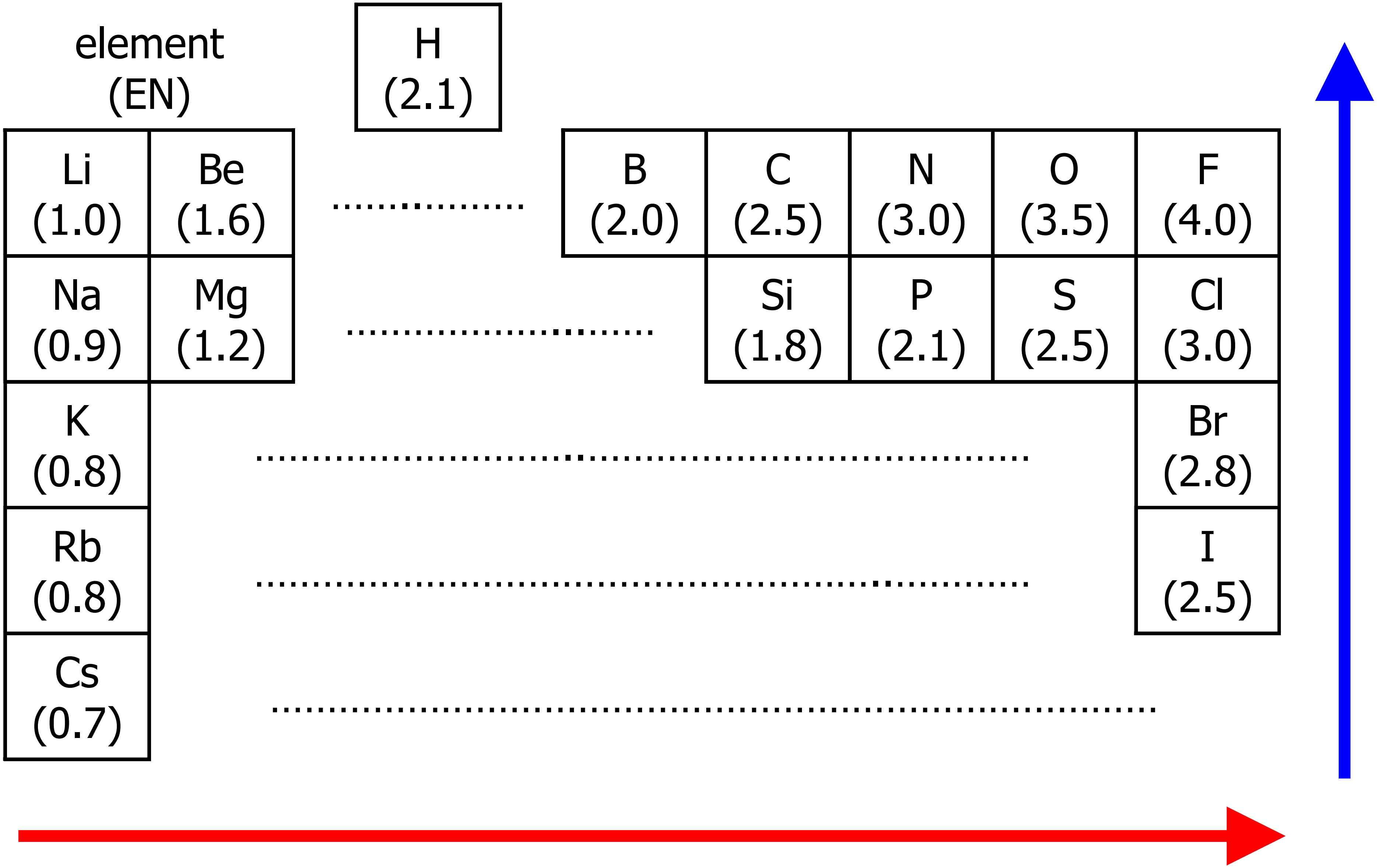
		# of e^-s in outer shell
H	$[1s^2]$	2
Ne	$1s^2[2s^22p^6]$	8
Ar	$1s^22s^22p^6[3s^23p^6]$	8

4A. Ionic Bonds

- Atoms may gain or lose electrons and form charged particles called **ions**
  - An **ionic bond** is an attractive force between oppositely charged ions

❖ Electronegativity (EN)

- The intrinsic ability of an atom to attract the shared electrons in a covalent bond
- Electronegativities are based on an arbitrary scale, with F the most electronegative (EN = 4.0) and Cs the least (EN = 0.7)



element (EN)		H (2.1)					
Li (1.0)	Be (1.6)		B (2.0)	C (2.5)	N (3.0)	O (3.5)	F (4.0)
Na (0.9)	Mg (1.2)			Si (1.8)	P (2.1)	S (2.5)	Cl (3.0)
K (0.8)							Br (2.8)
Rb (0.8)							I (2.5)
Cs (0.7)							

give 1 e^- to

Na

$1s^2\,2s^2\,2p^6\,3s^1$

(1 e^- in outermost shell)

Cl

$1s^2\,2s^2\,2p^6\,3s^2\,3p^5$

(7 e^- in outermost shell)

ionic bonding

Na^+

$$1s^2\,\underbrace{2s^2\,2p^6}_{8}$$

Cl^-

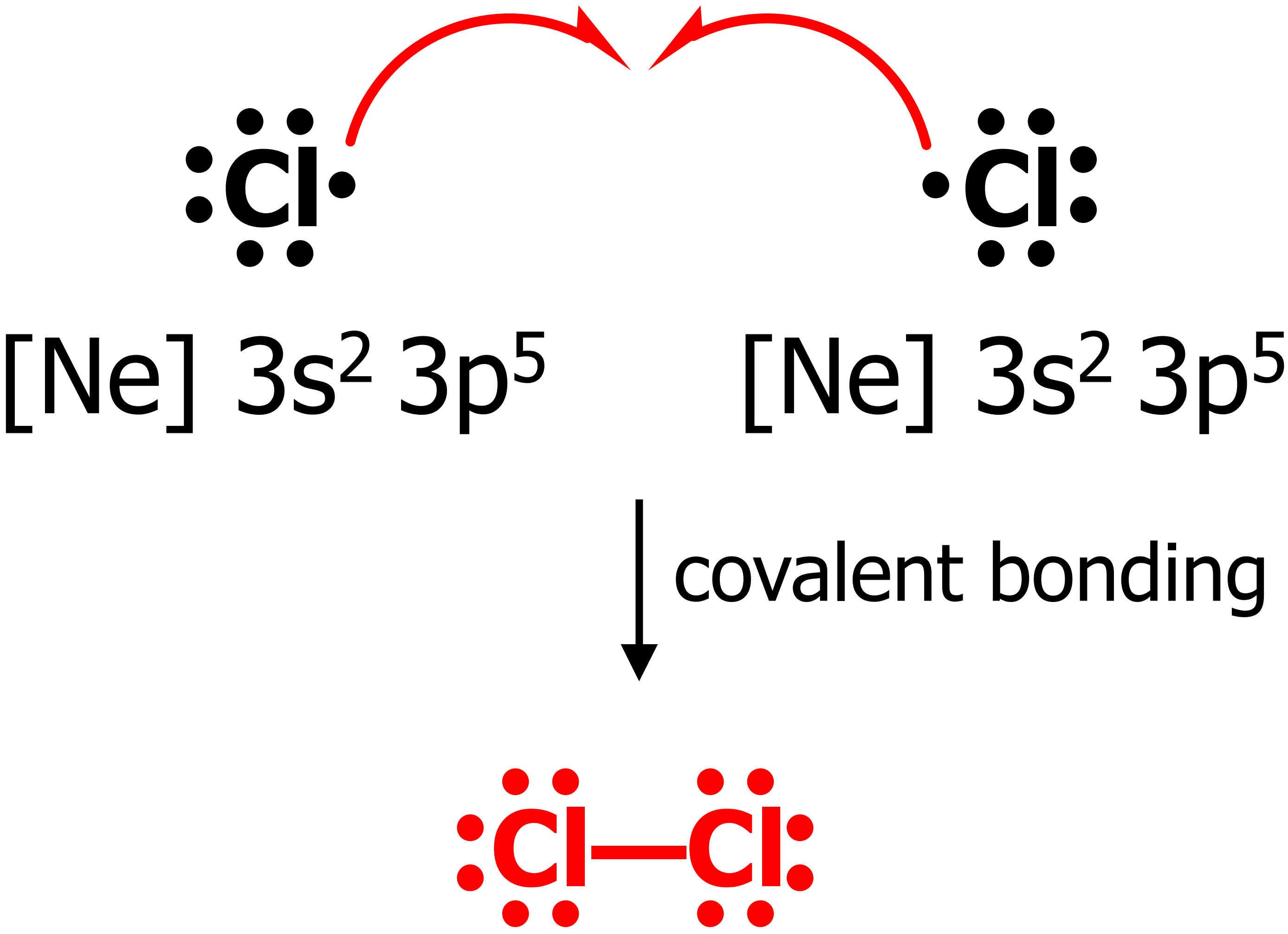
$$1s^2\,2s^2\,2p^6\,\underbrace{3s^2\,3p^6}_{8}$$

4B. Covalent Bonds & Lewis Structures

- **Covalent bonds** form by sharing of electrons between atoms of similar electronegativities to achieve the configuration of a noble gas

- **Molecules** are composed of atoms joined exclusively or predominantly by covalent bonds

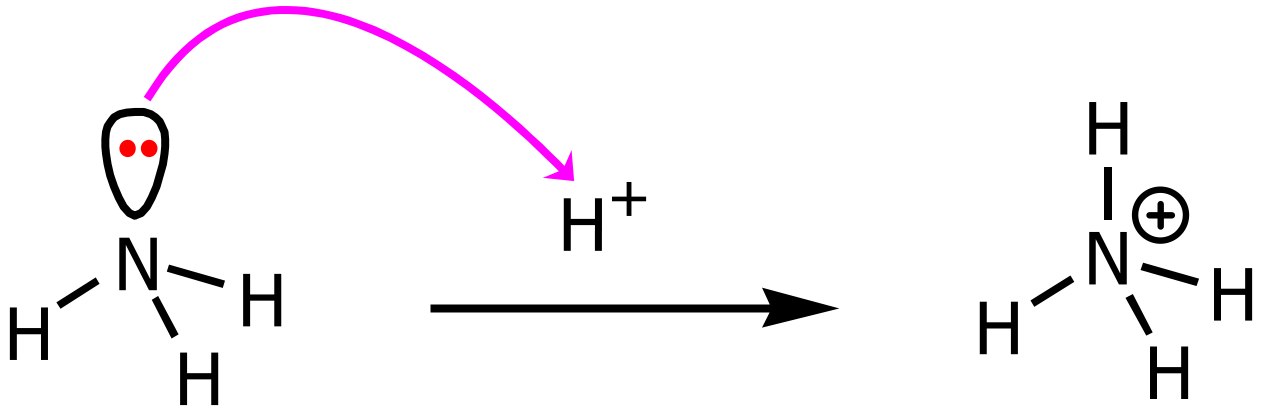
- Example



$[Ne]\ 3s^2\ 3p^5$ $[Ne]\ 3s^2\ 3p^5$

covalent bonding

- Ions, themselves, may contain covalent bonds. Consider, as an example, the ammonium ion



(ammonia)
(3 bonds on N)

(ammonium cation)
(4 bonds on N with
a positive charge on N)

5. How to Write Lewis Structures

- Lewis structures show the connections between atoms in a molecule or ion using only the valence electrons of the atoms involved
- For main group elements, the number of valence electrons a neutral atom brings to a Lewis structure is the same as its group number in the periodic table

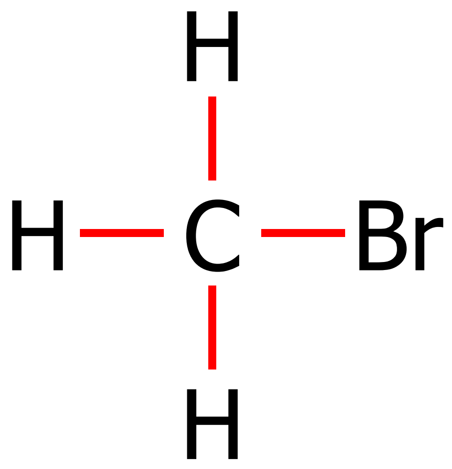
- If the structure we are drawing is a negative ion (an anion), we add one electron for each negative charge to the original count of valence electrons. If the structure is a positive ion (a cation), we subtract one electron for each positive charge
- In drawing Lewis structures we try to give each atom the electron configuration of a noble gas

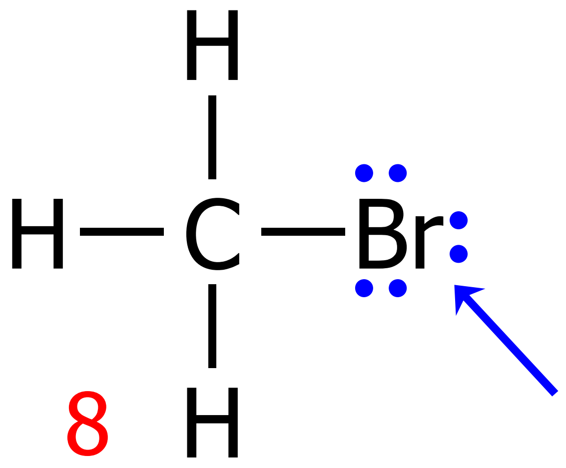
❖ Examples

(1) Lewis structure of CH_3Br

- Total number of all valence electrons:

$$\underset{4}{\overset{\text{C}}{\downarrow}} + \underset{1}{\overset{\text{H}}{\downarrow}} \text{ x } 3 + \underset{7}{\overset{\text{Br}}{\downarrow}} = 14$$

- 

- 

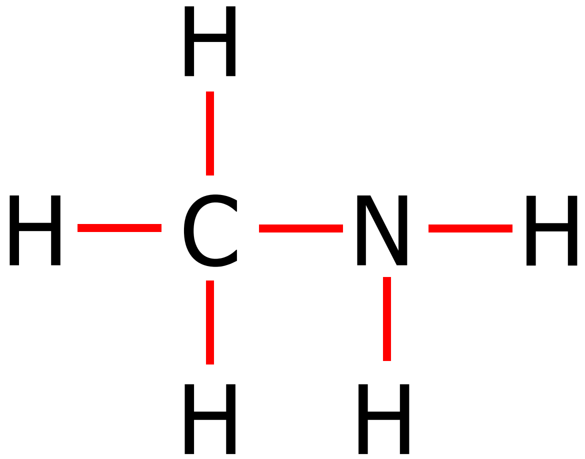
8 valence electrons

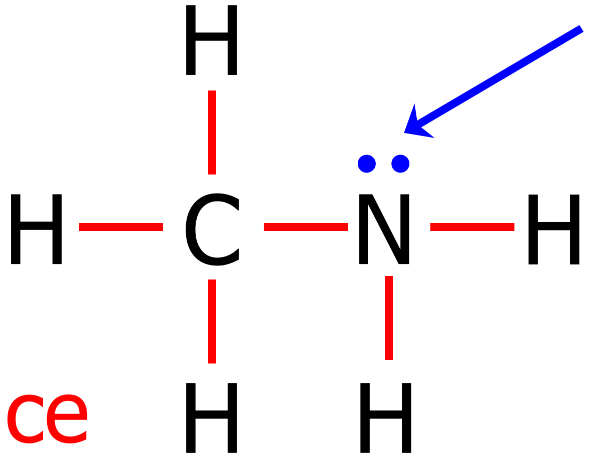
remaining 6 valence electrons

(2) Lewis structure of methylamine (CH_5N)

- Total number of all valence electrons:

$$\overset{\text{C}}{\overset{\downarrow}{4}} + \overset{\text{H}}{\overset{\downarrow}{1}} \text{ x } 5 + \overset{\text{N}}{\overset{\downarrow}{5}} = 14$$





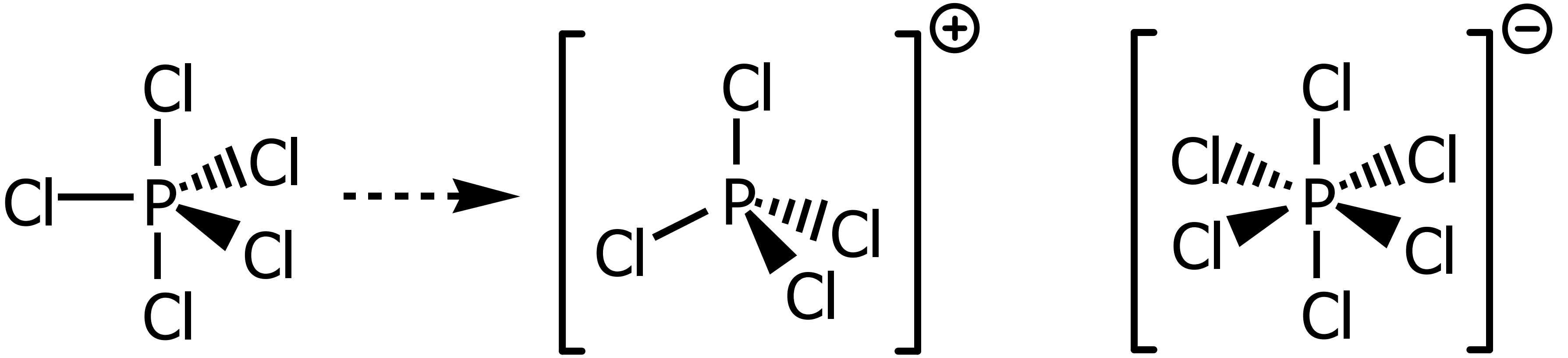
2 valence electrons left

12 valence electrons

6. Exceptions to the Octet Rule

- Elements in the 2^{nd} row in the periodic table usually obey the Octet Rule (Li, Be, B, C, N, O, F) since they have one 2s and three 2p orbitals available for bonding
- Elements in the 3^{rd} row in the periodic table have d orbitals that can be used for bonding and may not obey the Octet Rule

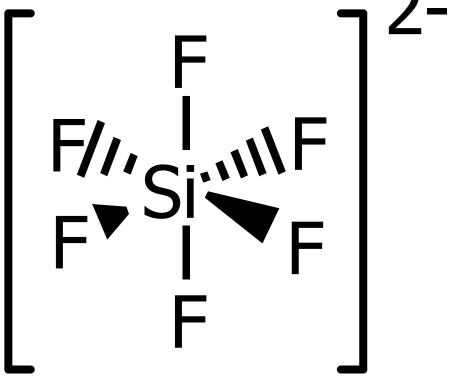
❖ Examples



(PCl$_5$)

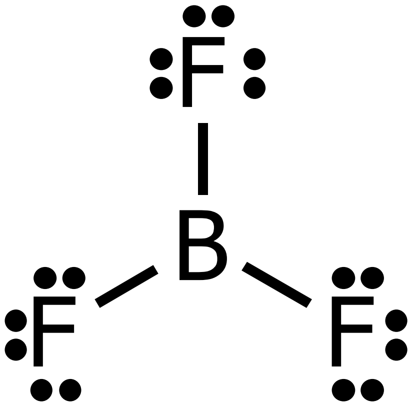
Phosphorus pentachloride

m.p. = 179^{o}C



(SiF$_6^{2-}$)

- Some highly reactive molecules or ions have atoms with fewer than eight electrons in their outer shell



7. Formal Charges and How to Calculate Them

- Formal charge number of valence electrons 1/2 number of shared electrons – number of unshared electrons

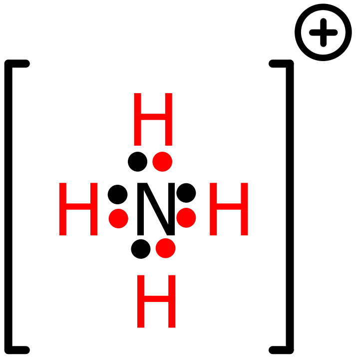
or

$$\boxed{F = Z - S/2 - U}$$

where *F* is the formal charge, *Z* is the group number of the element, *S* equals the number of shared electrons, and *U* is the number of unshared electrons

- Examples

(1) The Ammonium ion (NH_4^+)



Recall: $\boxed{F = Z - S/2 - U}$

Formal charge of H:

$$= 1 - 2/2 - 0 \;\; = \underline{\underline{0}}$$

group number of H

number of shared electrons

number of unshared electrons

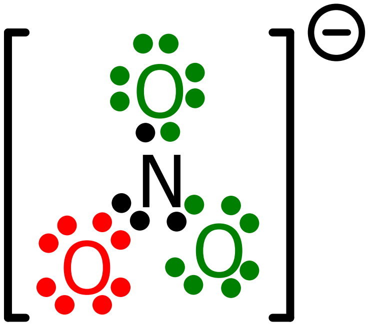
Formal charge of N:

$$= \underset{\substack{\uparrow\\\text{group}\\\text{number}\\\text{of N}}}{5} - \underset{\substack{\nwarrow\\\text{number}\\\text{of shared}\\\text{electrons}}}{8/2} - \underset{\substack{\nwarrow\\\text{number of}\\\text{unshared}\\\text{electrons}}}{0} = \underline{\underline{+1}}$$

Charge on ion = 4 x 0 +1 = +1

⇒ The arithmetic sum of all the formal charges in a molecule or ion will equal the overall charge on the molecule or ion

(2) The Nitrate ion (NO_3^-)



Recall: $\boxed{F = Z - S/2 - U}$

Formal charge of O:

$$= 6 - 2/2 - 6 = \underline{\underline{-1}}$$

group number of O

number of shared electrons

number of unshared electrons

Formal charge of O:

$$= 6 - 4/2 - 4 \;=\; \underline{\underline{0}}$$

group number of O	number of shared electrons	number of unshared electrons

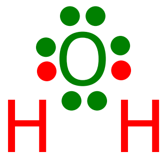
Formal charge of N:

$$= 5 - 8/2 - 0 \;=\; \underline{\underline{+1}}$$

group number of N	number of shared electrons	number of unshared electrons

Charge on ion = $2 \times (-1) + 0 + 1 = -1$

(3) Water (H_2O)
The sum of the formal charges on each atom making up a molecule must be zero



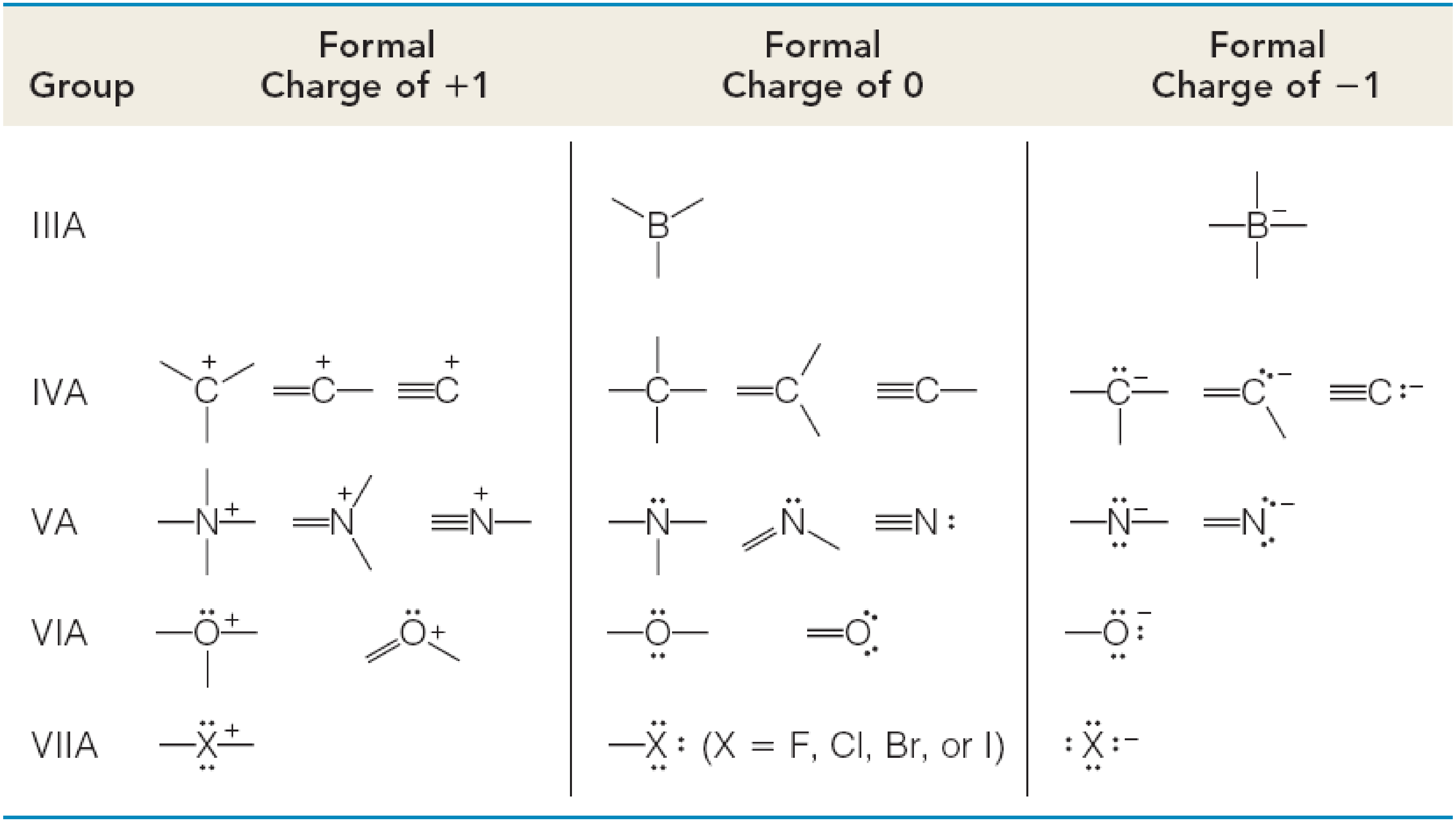
Formal charge of O $= 6 - 4/2 - 4 = \underline{\underline{\ 0\ }}$

Formal charge of H $= 1 - 2/2 - 0 = \underline{\underline{\ 0\ }}$

Charge on molecule $= 0 + 2 \times 0 = 0$

7A. A Summary of Formal Charges

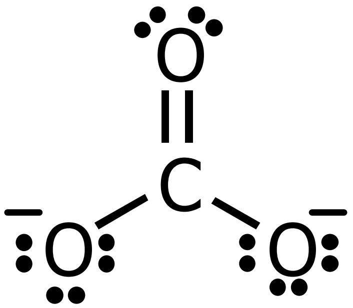
A Summary of Formal Charges



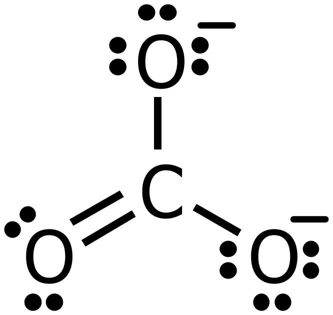
8. Resonance Theory

- In a Lewis structure, we draw a well-defined location for the electrons in a molecule. In many molecules and ions (especially those containing π bonds), more than one *equivalent* Lewis structure can be drawn which represent the same molecule

- We can write three *different* but *equivalent* structures, 1–3



1



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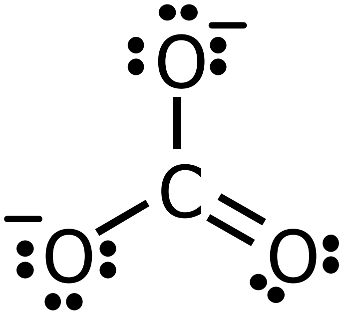

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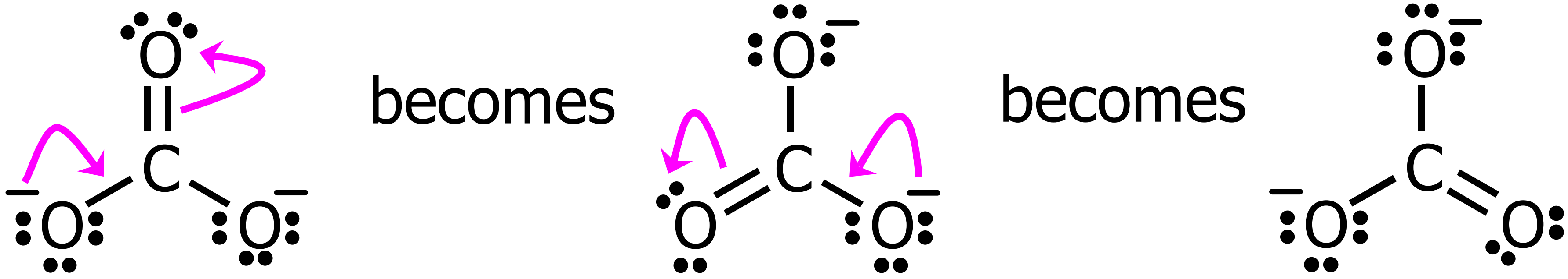
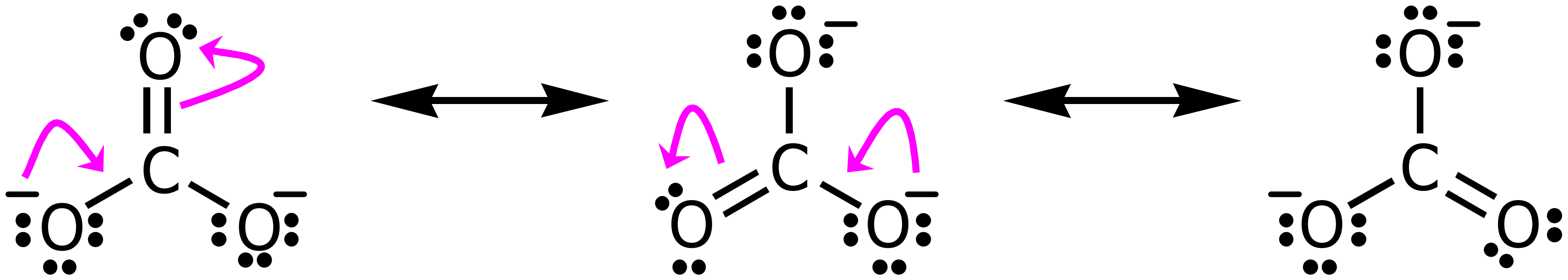


1 2 3

⇒ Structures 1–3, although not identical on paper, are equivalent; all of its carbon–oxygen bonds are of equal length

- Resonance theory states that whenever a molecule or ion can be represented by two or more Lewis structures *that differ only in the positions of the electrons*, two things will be true:
  - None of these structures, which we call resonance structures or resonance contributors, will be a realistic representation for the molecule or ion. None will be in complete accord with the physical or chemical properties of the substance
  - The actual molecule or ion will be better represented by a hybrid (average) of these structures

- Resonance structures, then, are not real structures for the actual molecule or ion; they exist only on paper



- It is also important to distinguish between resonance and an **equilibrium**

- In an equilibrium between two or more species, it is quite correct to think of different structures and moving (or fluctuating) atoms, but not in the case of resonance (as in the carbonate ion). Here the atoms do not move, and the "structures" exist only on paper. An equilibrium is indicated by $\rightleftharpoons$ and resonance by $\longleftrightarrow$

8A. How to Write Resonance Structures

- **Resonance structures exist only on paper**. Although they have no real existence of their own, **resonance structures** are useful because they allow us to describe molecules and ions for which a single Lewis structure is inadequate

- We write two or more Lewis structures, calling them resonance structures or resonance contributors. We connect these structures by double-headed arrows $\longleftrightarrow$, and we say that the real molecule or ion is a hybrid of all of them

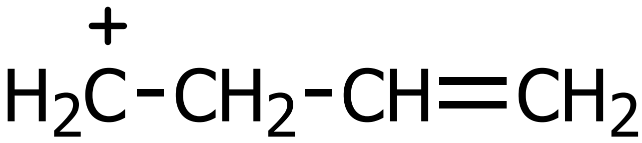
- We are only allowed to move electrons in writing resonance structures

$$H_3C-\overset{+}{C}H-CH=CH_2 \longleftrightarrow H_3C-\overset{+}{C}H-CH=CH_2$$

1

2

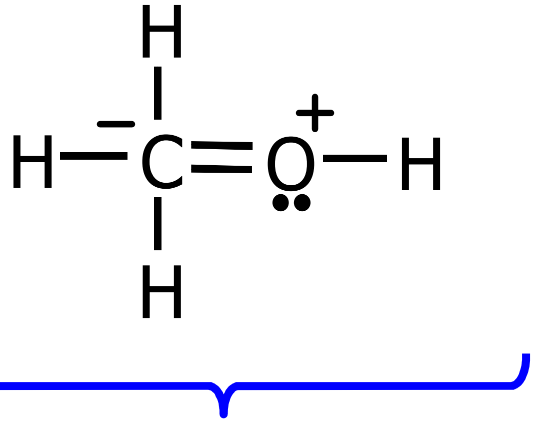
These are resonance structures



$$H_2\overset{+}{C}-CH_2-CH=CH_2$$

This is not a proper resonance structure of 1 and 2 because a hydrogen atom has been moved

- All of the structures must be proper Lewis structures



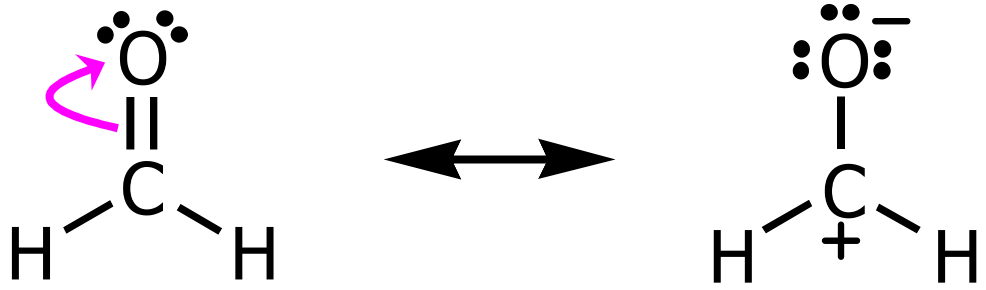
This is not a proper resonance structure of methanol

- The energy of the resonance hybrid is lower than the energy of any contributing structure. Resonance stabilizes a molecule or ion. This is especially true when the resonance structures are equivalent. Chemists call this stabilization resonance stabilization. If the resonance structures are equivalent, then the resonance stabilization is large

- The more stable a structure is (when taken by itself), the greater is its contribution to the hybrid
- The more covalent bonds a structure has, the more stable it is
- Charge separation decreases stability

Resonance structures for formaldehyde

Four covalent bonds



Three covalent bonds

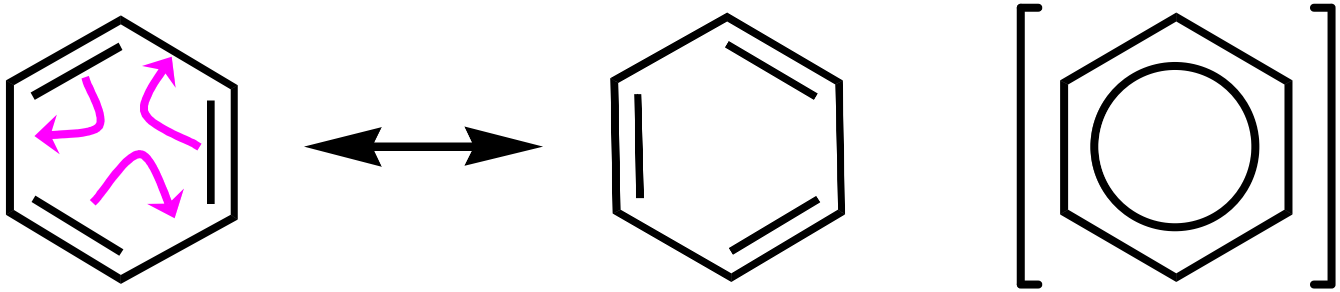
more stable

less stable

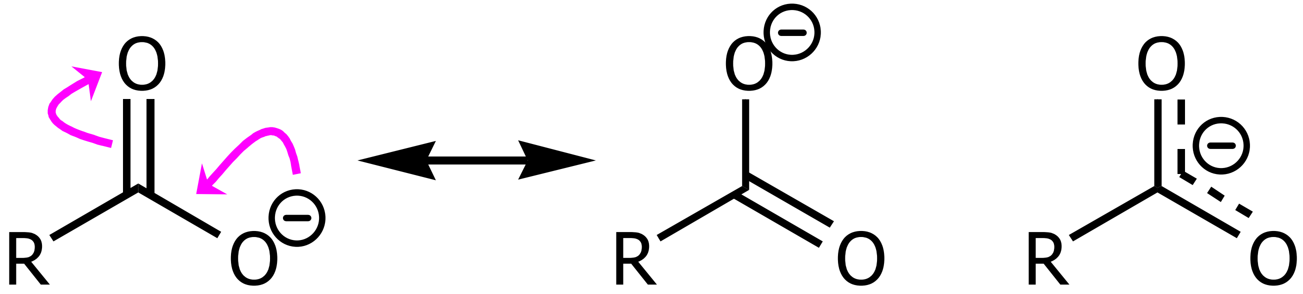
- Structures in which all the atoms have a complete valence shell of electrons (i.e., the noble gas structure) are more stable

❖ Examples

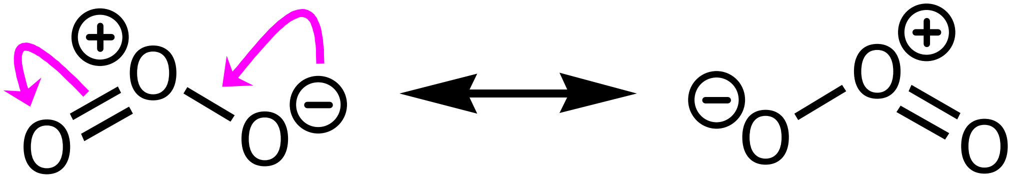
(1) Benzene



(2) Carboxylate ion (RCOO$^-$)



(3) Ozone (O_3)



9. Quantum Mechanics & Atomic Structure

❖ Wave mechanics & quantum mechanics

- Each wave function (ψ) corresponds to a different energy state for an electron

- Each energy state is a sublevel where one or two electrons can reside

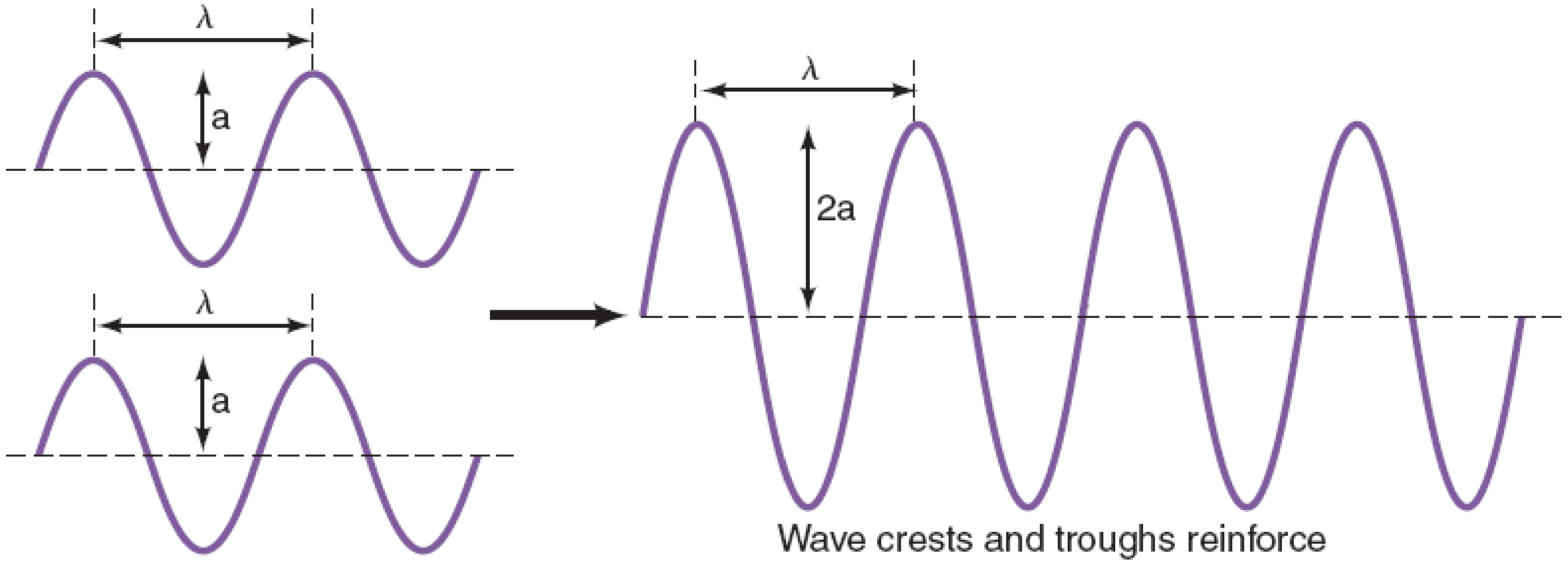
- Wave functions are tools for calculating two important properties
  - The energy associated with the state of the electron can be calculated
  - The relative probability of an electron residing at particular places in the sublevel can be determined

- The phase sign of a wave equation indicates whether the solution is positive or negative when calculated for a given point in space relative to the nucleus

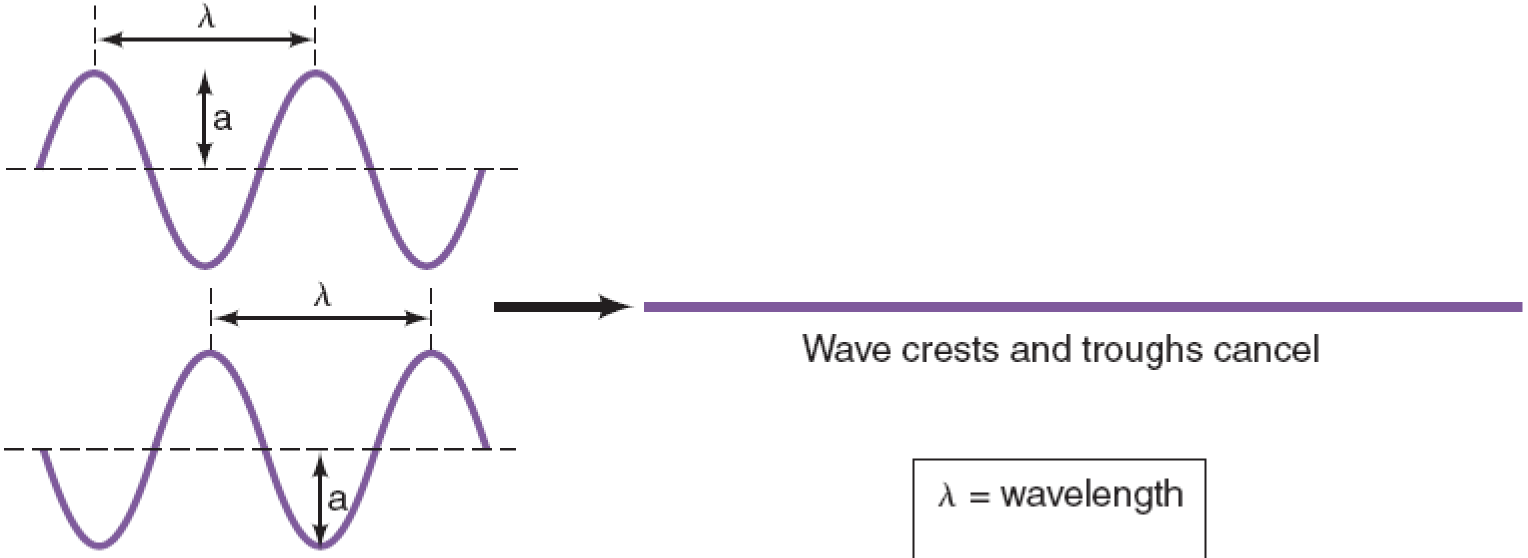
- Wave functions, whether they are for sound waves, lake waves, or the energy of an electron, have the possibility of constructive interference and destructive interference

- **Constructive interference** occurs when wave functions with the same phase sign interact. There is a *reinforcing effect* and the amplitude of the wave function increases
- **Destructive interference** occurs when wave functions with opposite phase signs interact. There is a *subtractive effect* and the amplitude of the wave function goes to zero or changes sign

Constructive interference of waves



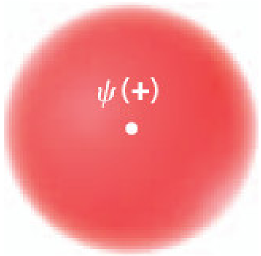
Destructive interference of waves



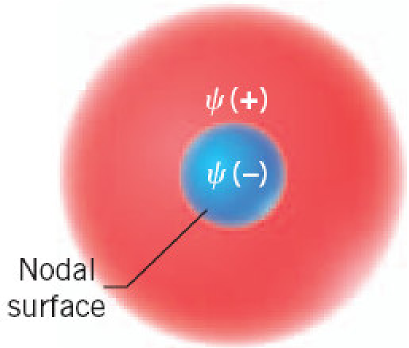
λ = wavelength

a = amplitude

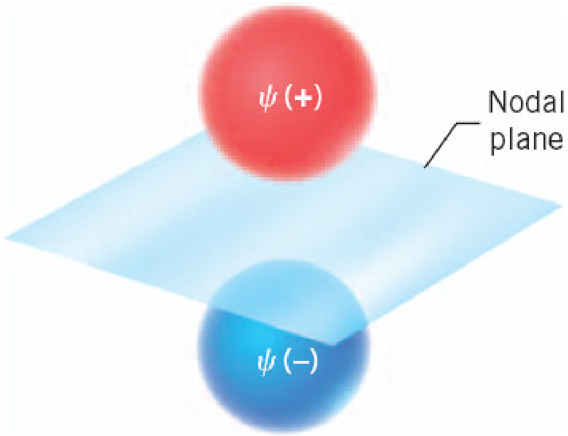
10. Atomic Orbitals and Electron Configuration



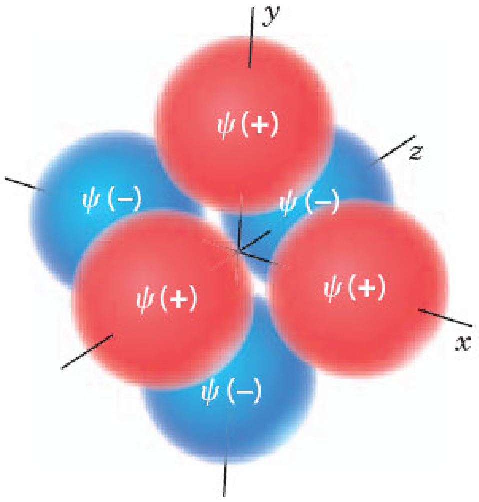
1*s* Orbital



2*s* Orbital



A pure (unhybridized) 2*p* orbital has two lobes.



There are three 2*p* orbitals, each with a (+) and (–) lobe, aligned symmetrically along the *x*, *y*, and *z* axes.

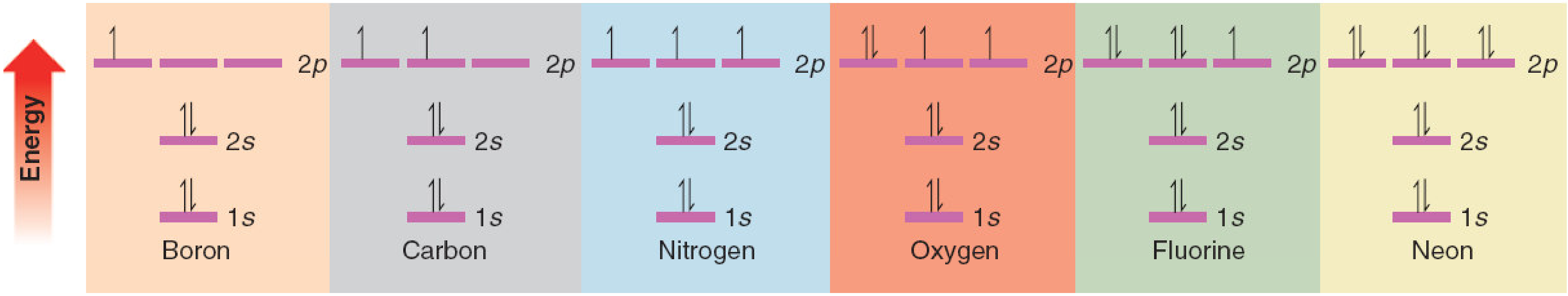
10A. Electron Configurations

- The relative energies of atomic orbitals in the 1st & 2nd principal shells are as follows:
  - Electrons in 1*s* orbitals have the lowest energy because they are closest to the positive nucleus
  - Electrons in 2*s* orbitals are next lowest in energy
  - Electrons of the three 2*p* orbitals have equal but higher energy than the 2*s* orbital
  - Orbitals of equal energy (such as the three 2*p* orbitals) are called **degenerate orbitals**

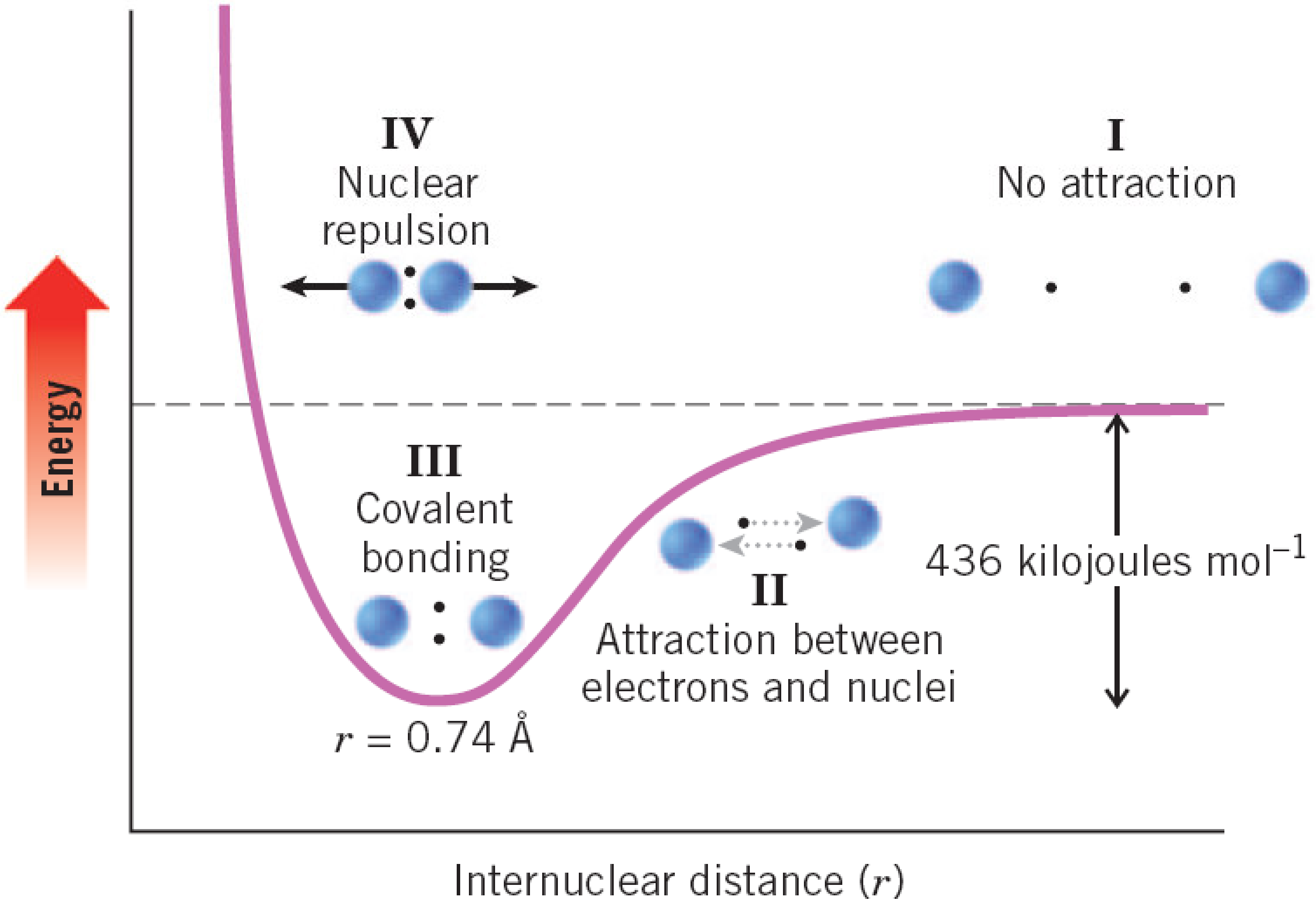
- **Aufbau principle**
  - Orbitals are filled so that those of lowest energy are filled first

- **Pauli exclusion principle**
  - A maximum of two electrons may be placed in each orbital *but only when the spins of the electrons are paired*

- **Hund’s rule**
  - When we come to orbitals of equal energy (degenerate orbitals) such as the three *p* orbitals, we add one electron to each *with their spins unpaired* until each of the degenerate orbitals contains one electron. (This allows the electrons, which repel each other, to be farther apart.) Then we begin adding a second electron to each degenerate orbital so that the spins are paired


Energy
2p
2s
1s
Boron
Carbon
Nitrogen
Oxygen
Fluorine
Neon

11. Molecular Orbitals

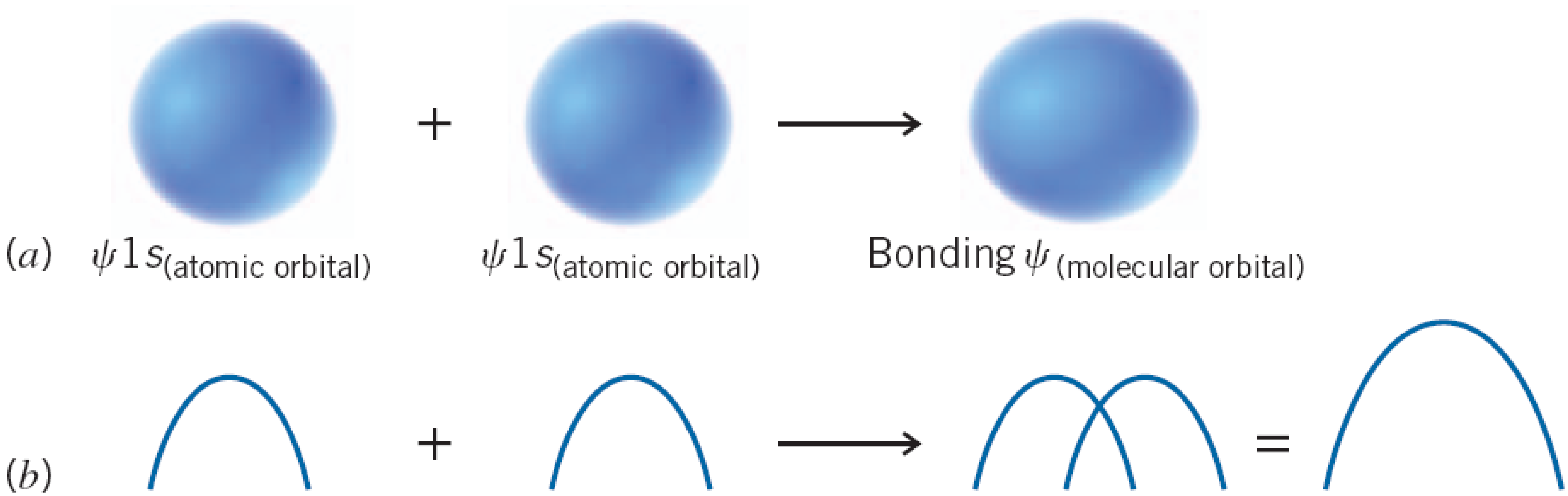


- We cannot simultaneously know the position and momentum of an electron
- An **atomic orbital** represents the region of space where one or two electrons of an isolated atom are likely to be found
- A **molecular orbital (MO)** represents the region of space where one or two electrons of a molecule are likely to be found

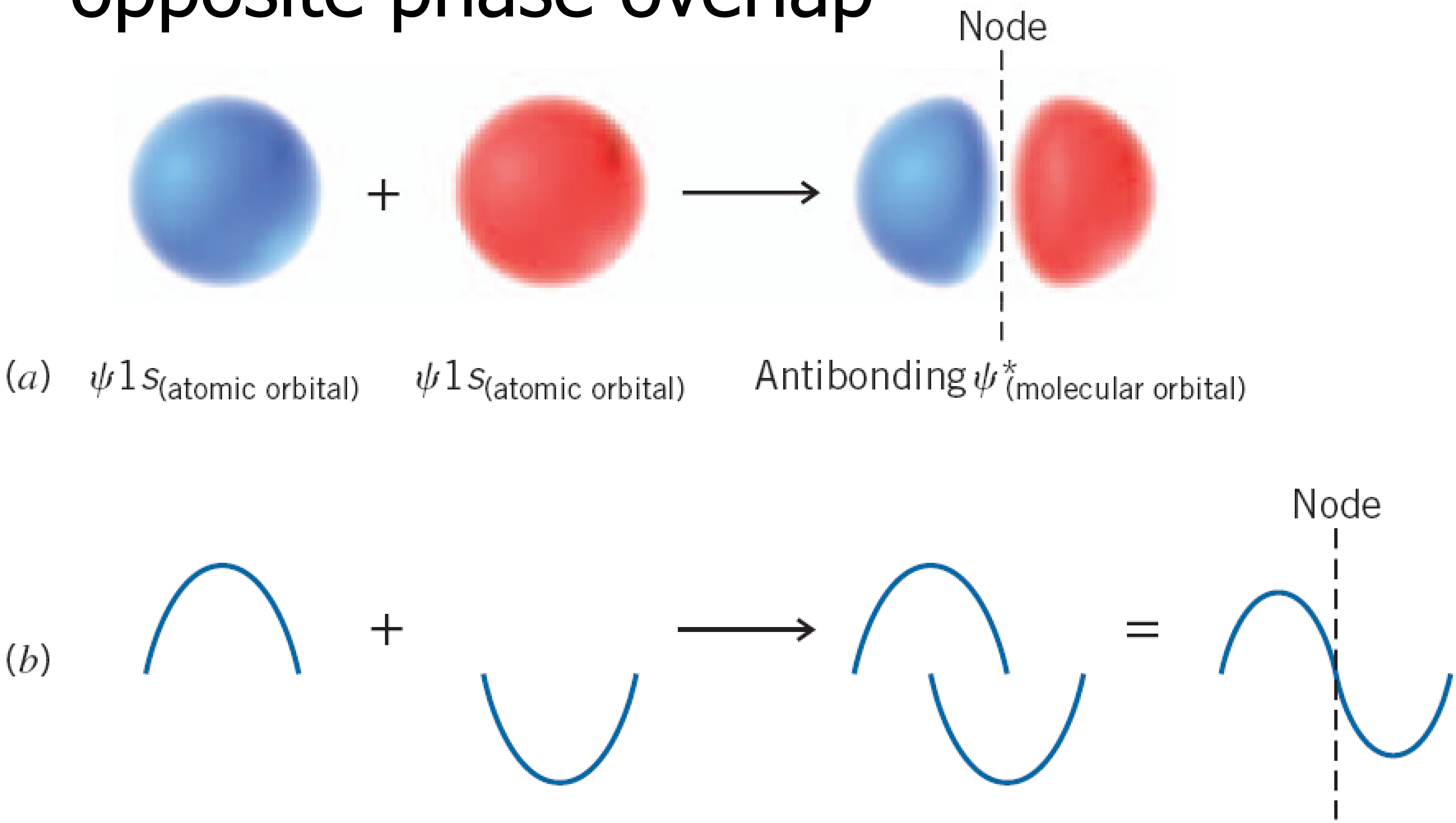
- An orbital (atomic or molecular) can contain a maximum of two spin-paired electrons (Pauli exclusion principle)

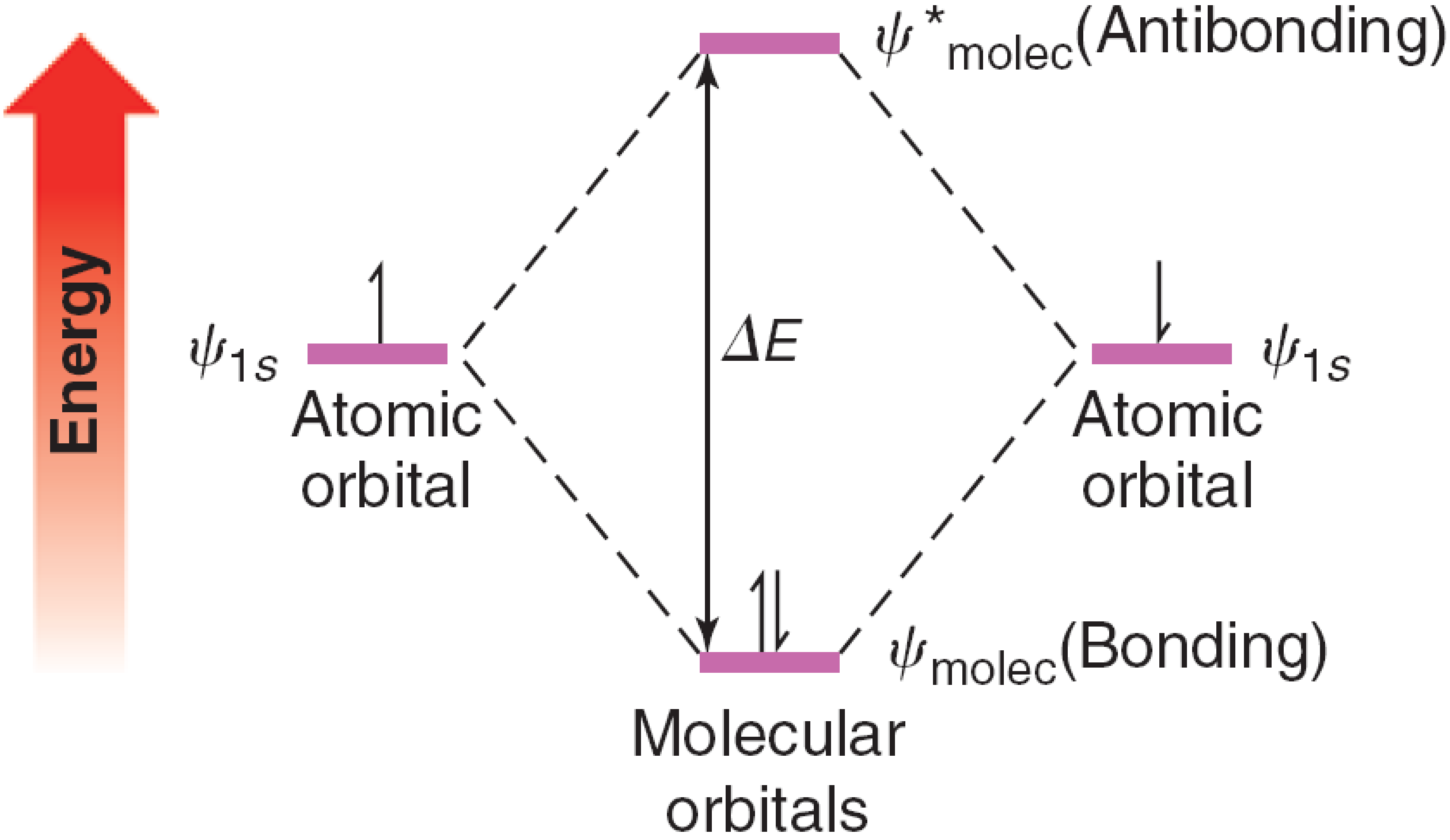
- When atomic orbitals combine to form molecular orbitals, the number of molecular orbitals that result always equals the number of atomic orbitals that combine

- A **bonding molecular orbital** (ψ_{molec}) results when two orbitals of the same phase overlap



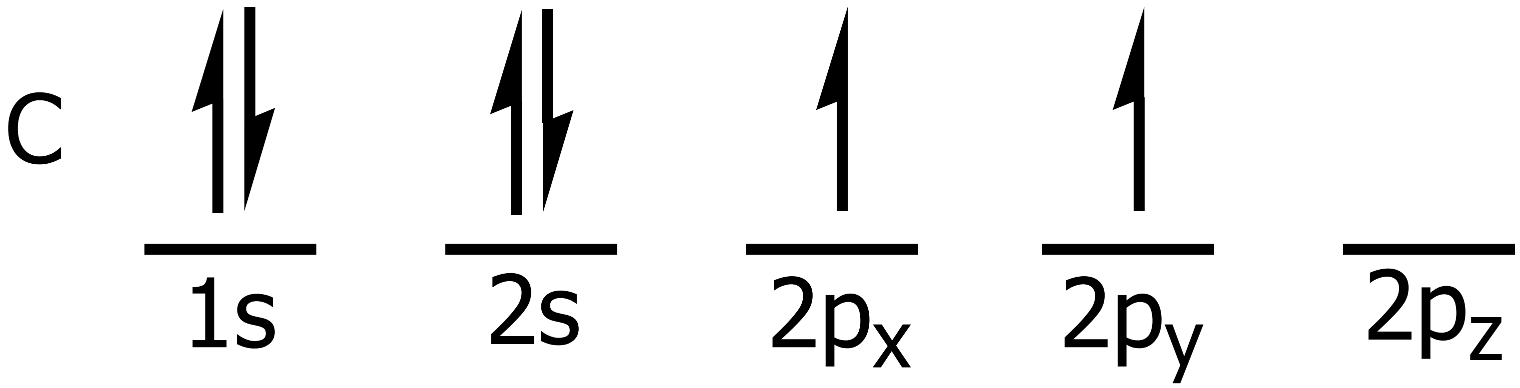
- An **antibonding molecular orbital** (ψ^*_{molec}) results when two orbitals of opposite phase overlap



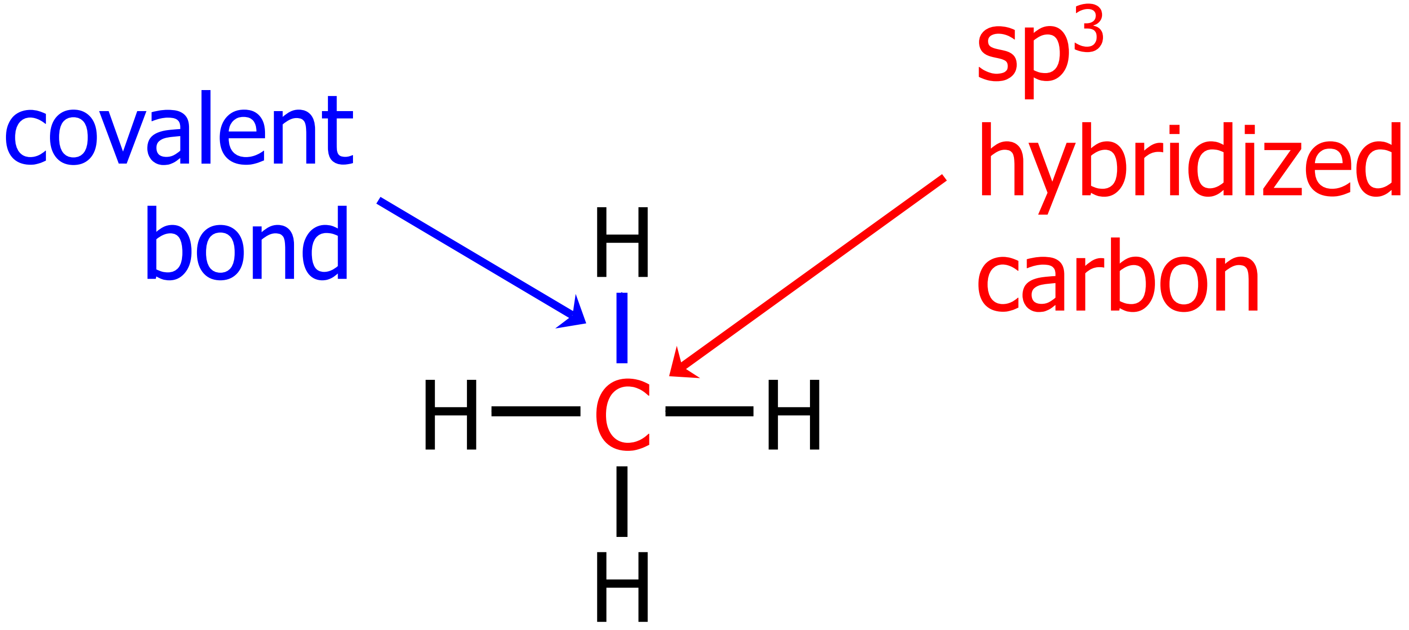

Energy
ψ^*_{molec}(Antibonding)
ψ_{1s}
Atomic orbital
ΔE
ψ_{1s}
Atomic orbital
ψ_{molec}(Bonding)
Molecular orbitals

12. The Structure of Methane and Ethane: sp^3 Hybridization

Ground state of a carbon atom



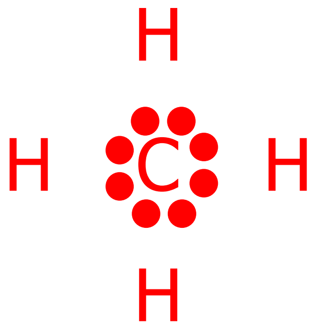
- Hybridization
  - sp^3



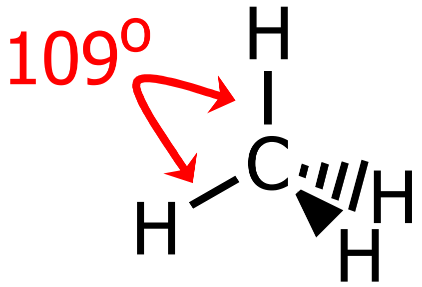
(line bond structure)

Hybridization

- sp^3



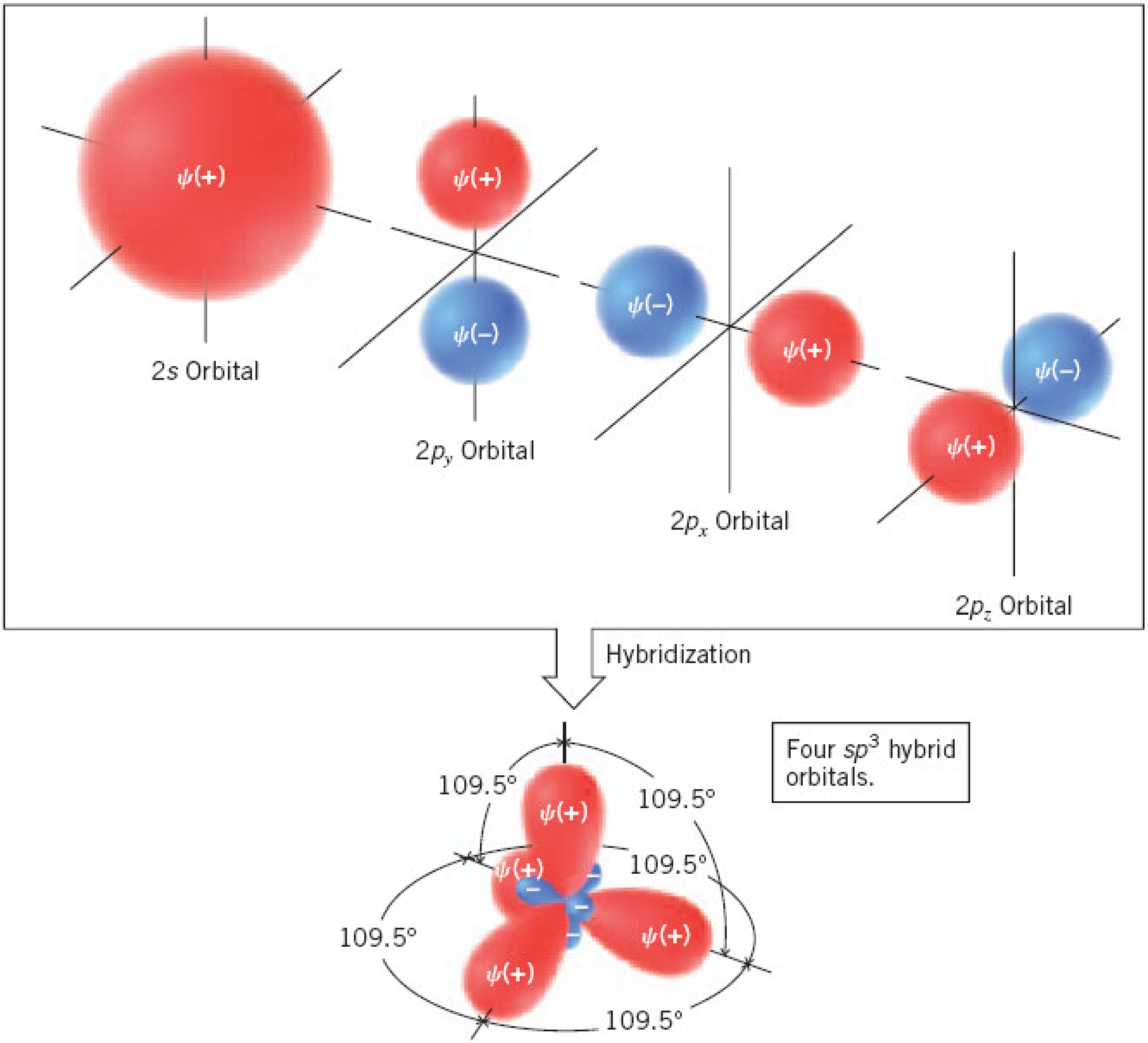
(Lewis structure)

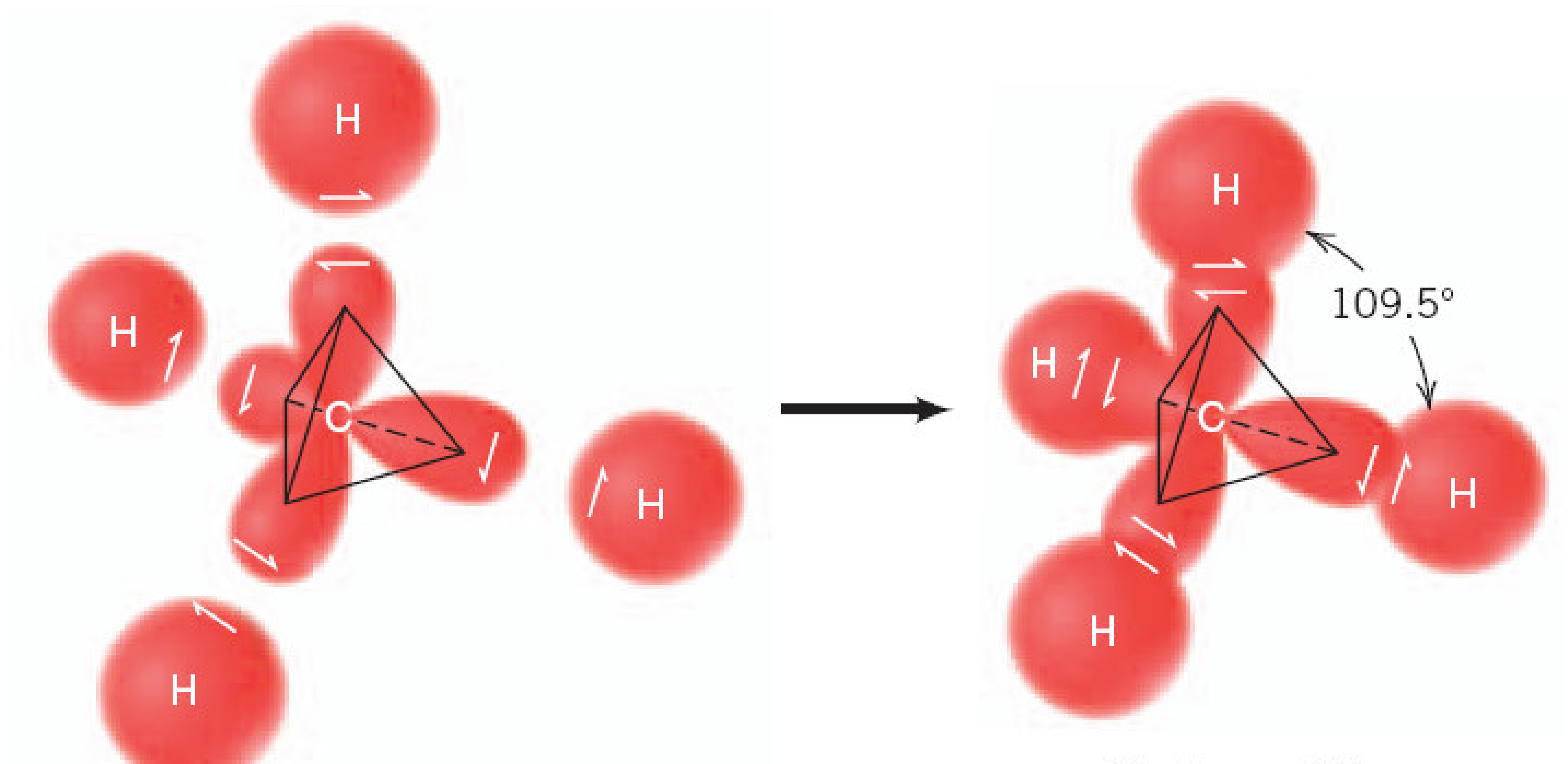


(3-D stucture)

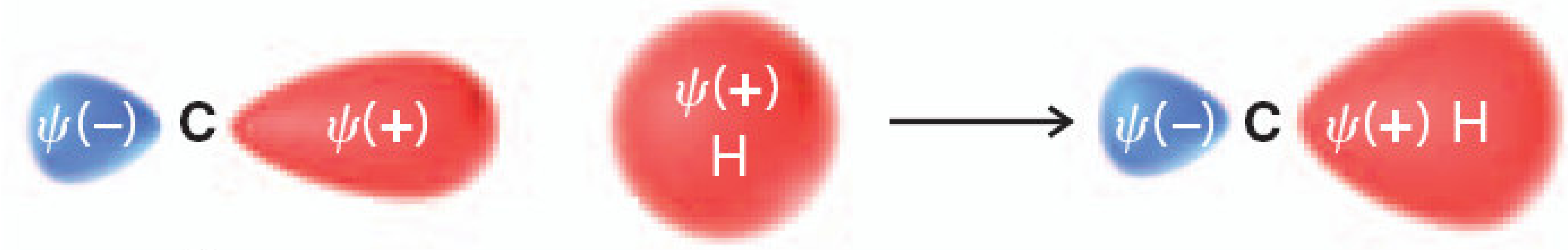
- Tetrahedral structure
- Carbon with 4 σ bonds

12A. The Structure of Methane





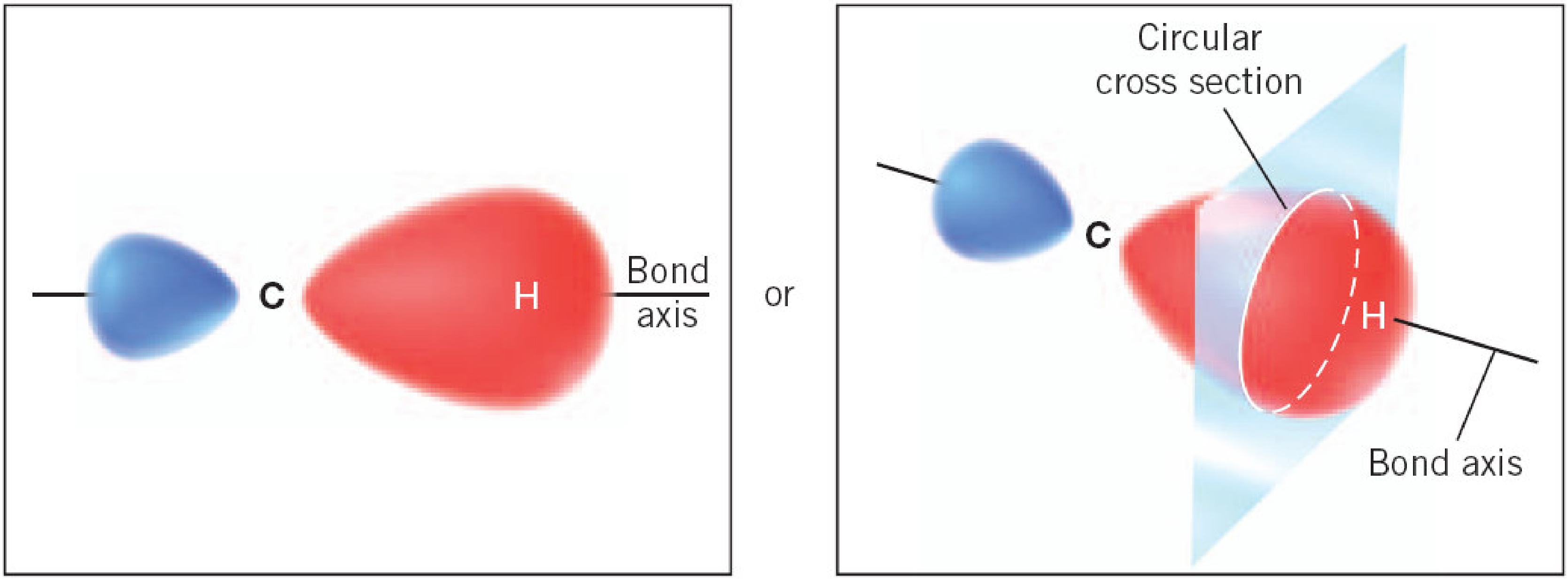
Methane, CH_4

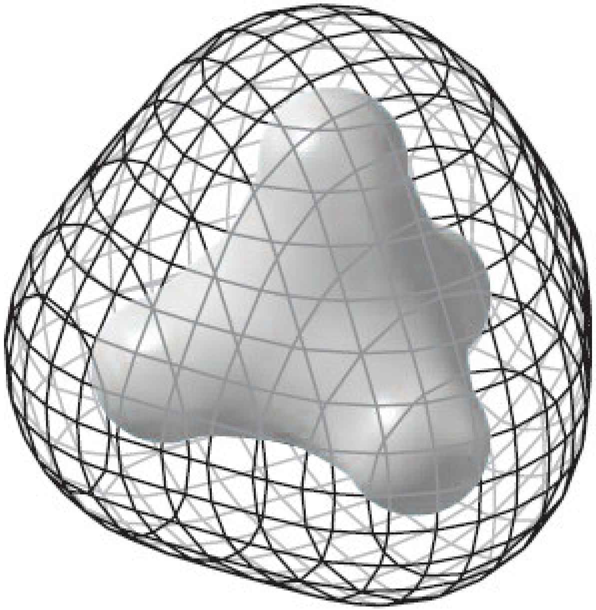


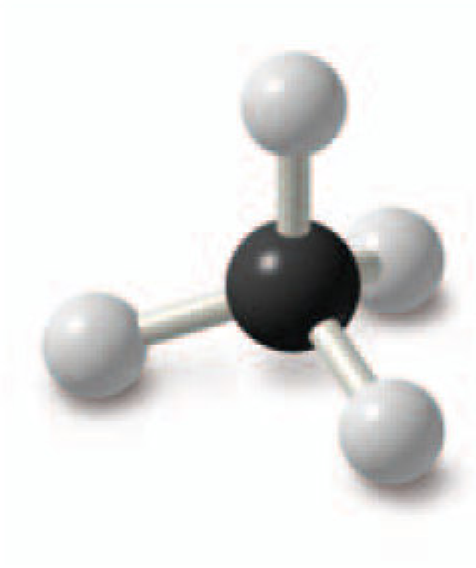
sp^3 Orbital

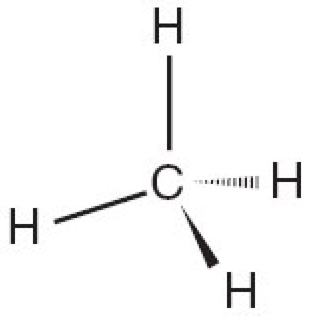
1s Orbital

Carbon–hydrogen bond
(bonding MO)

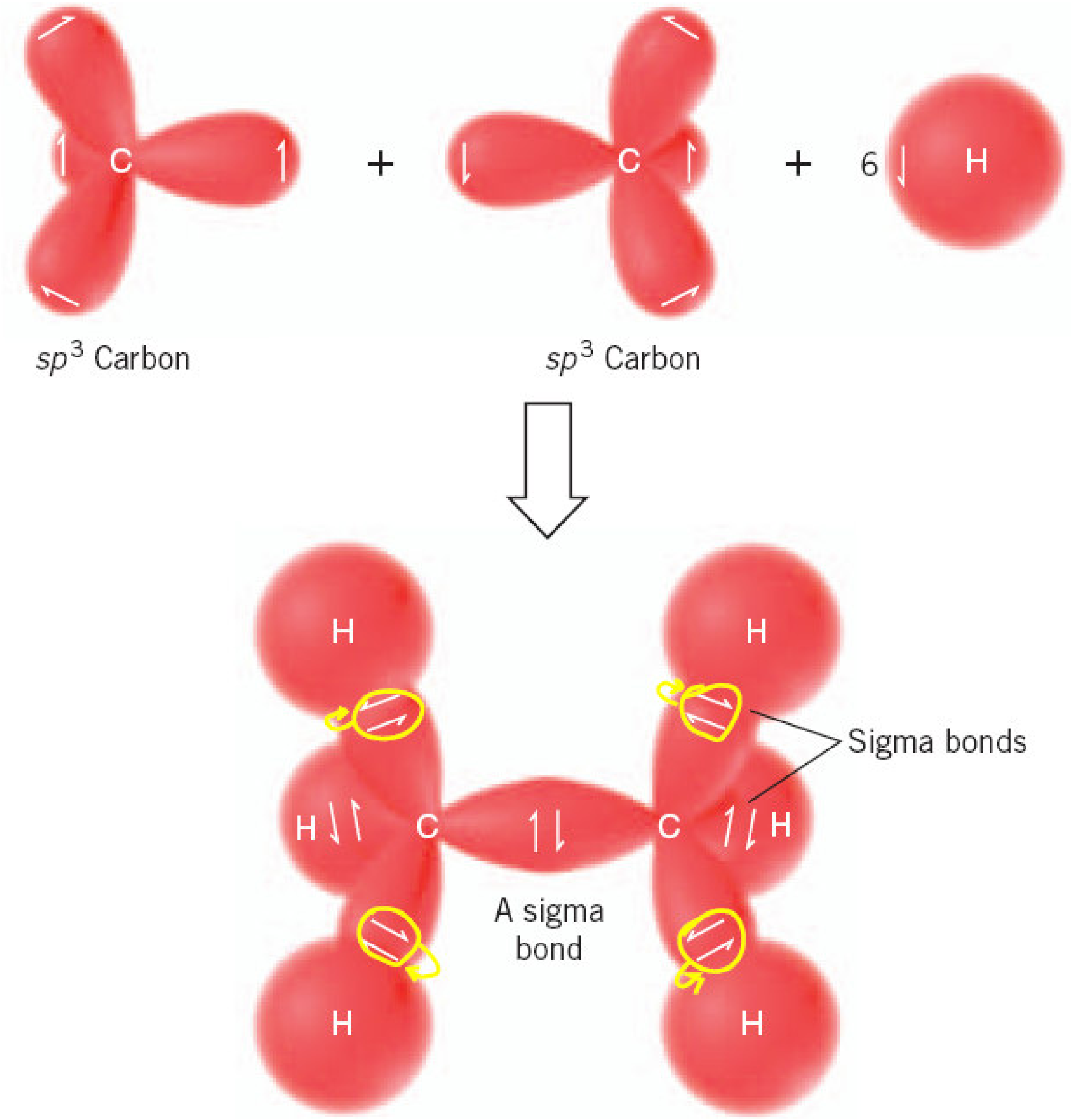

C
H
Bond axis
or
Circular cross section
C
H
Bond axis

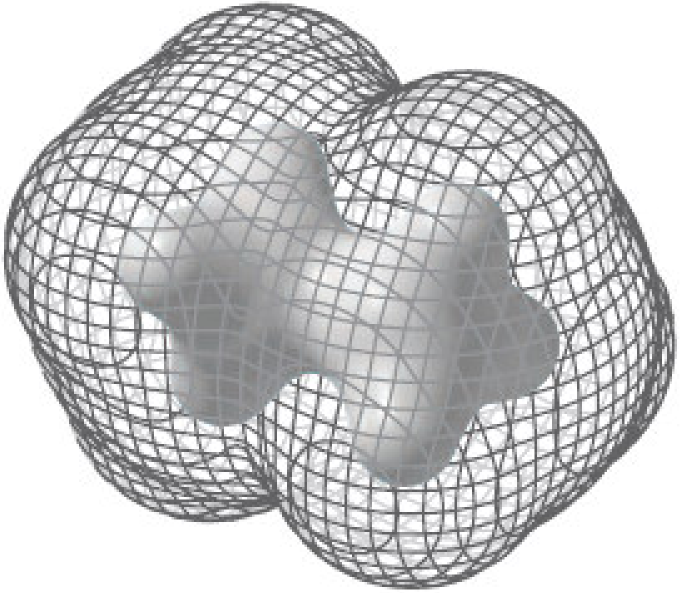


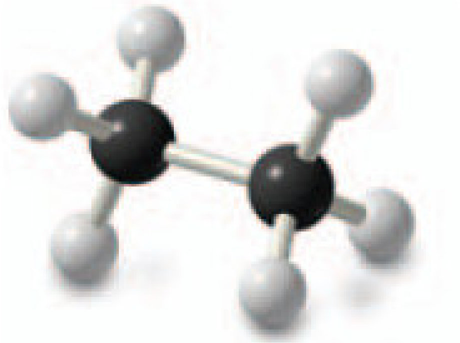


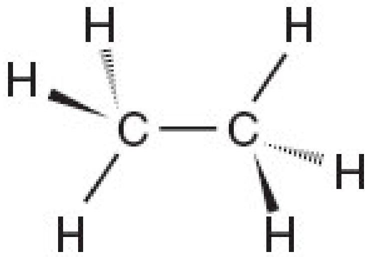

H
C
H
H
H

12B. The Structure of Ethane



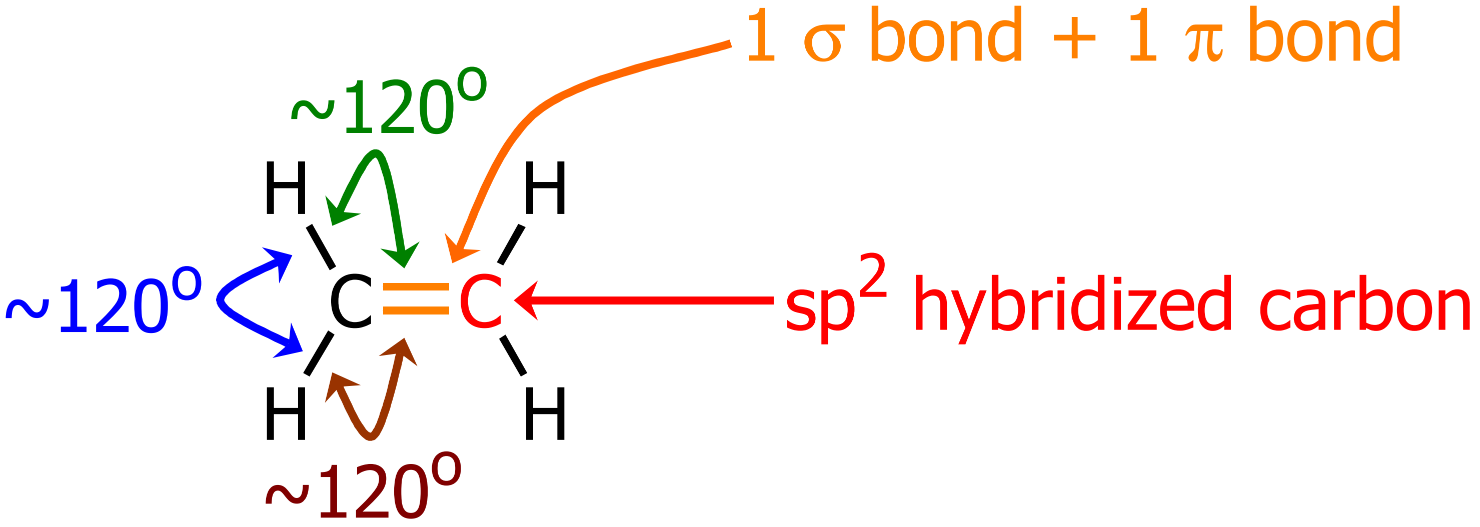





H
H
H
C
C
H
H
H
H

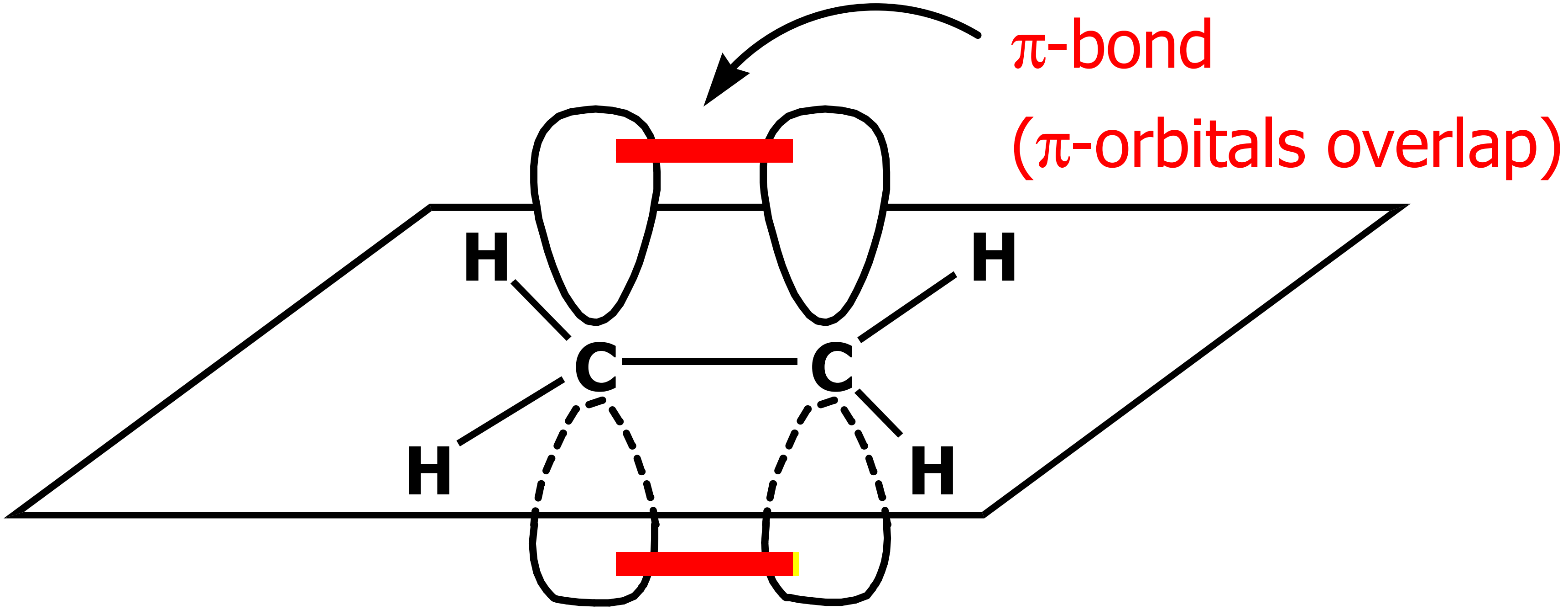
13. The Structure of Ethene (Ethylene): sp^2 Hybridization

- sp^2

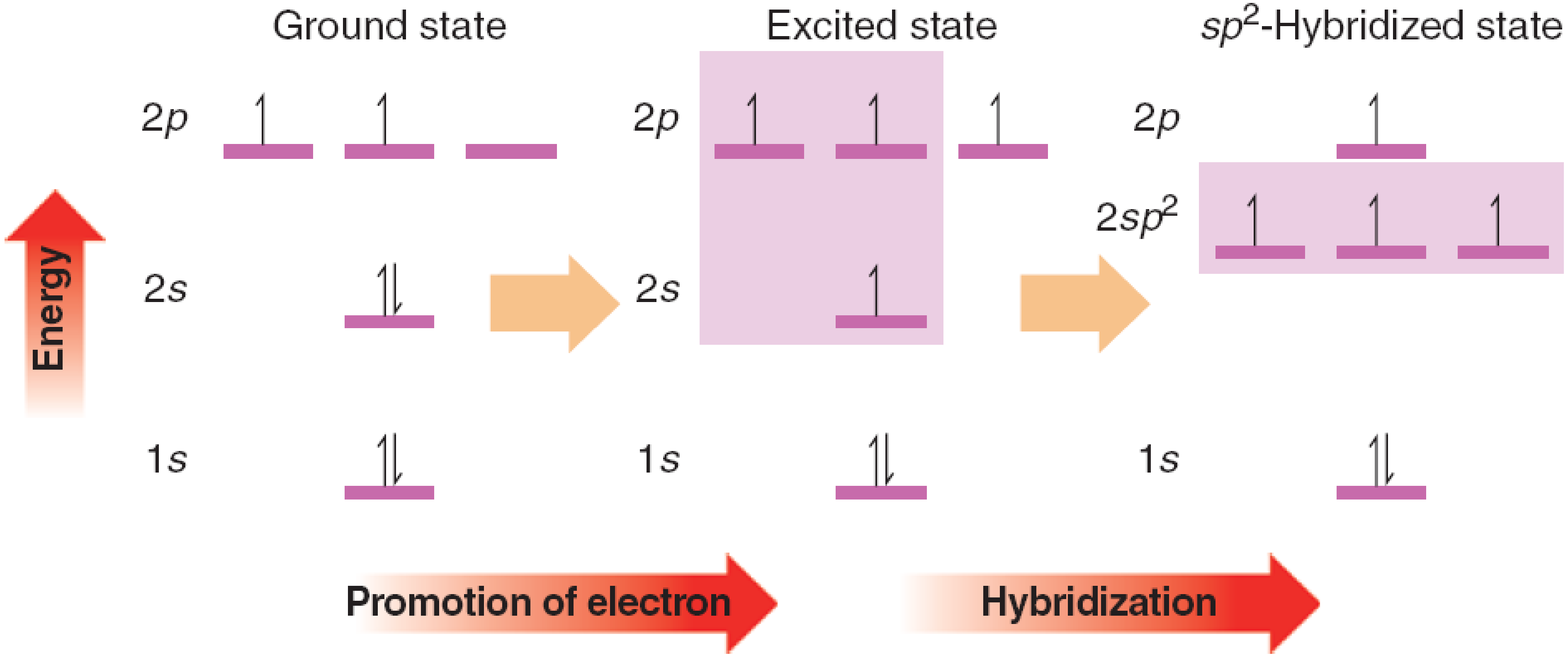


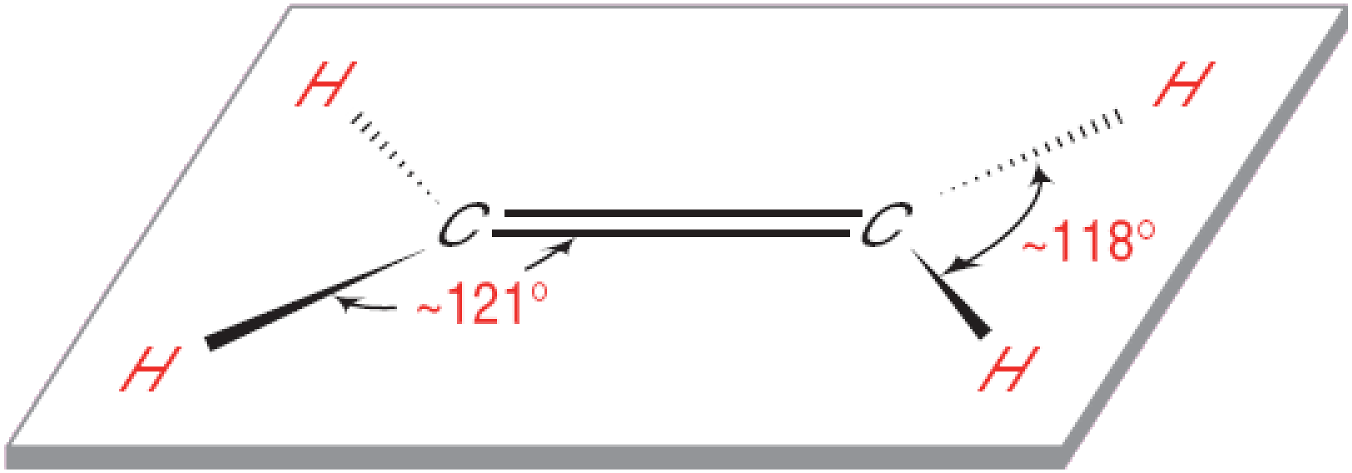
❖ sp^2

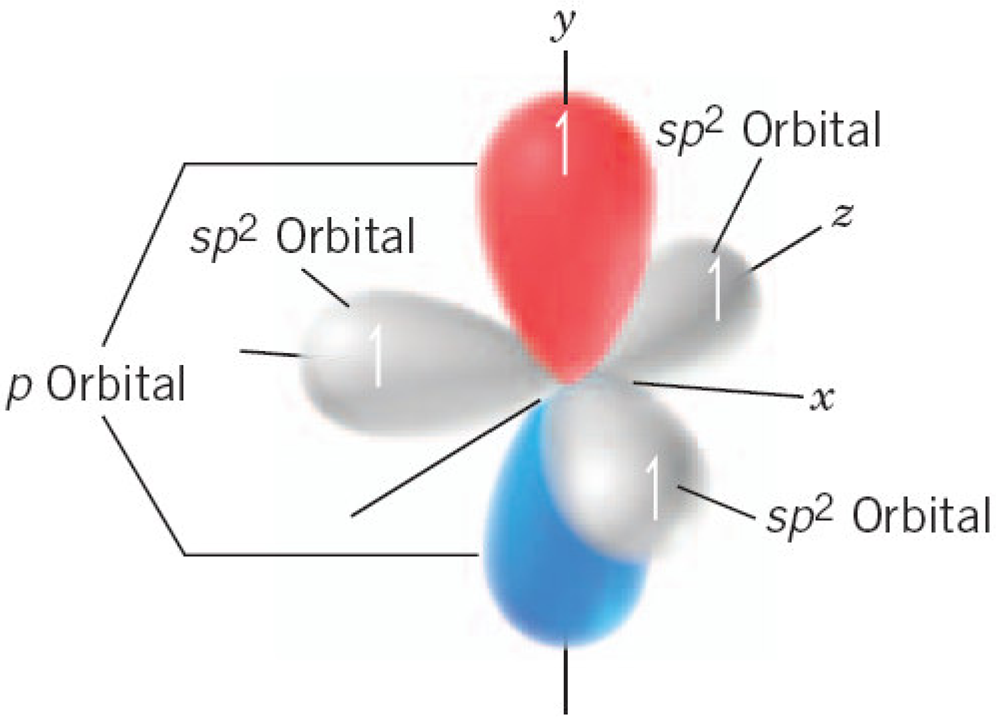
3-Dimensional View

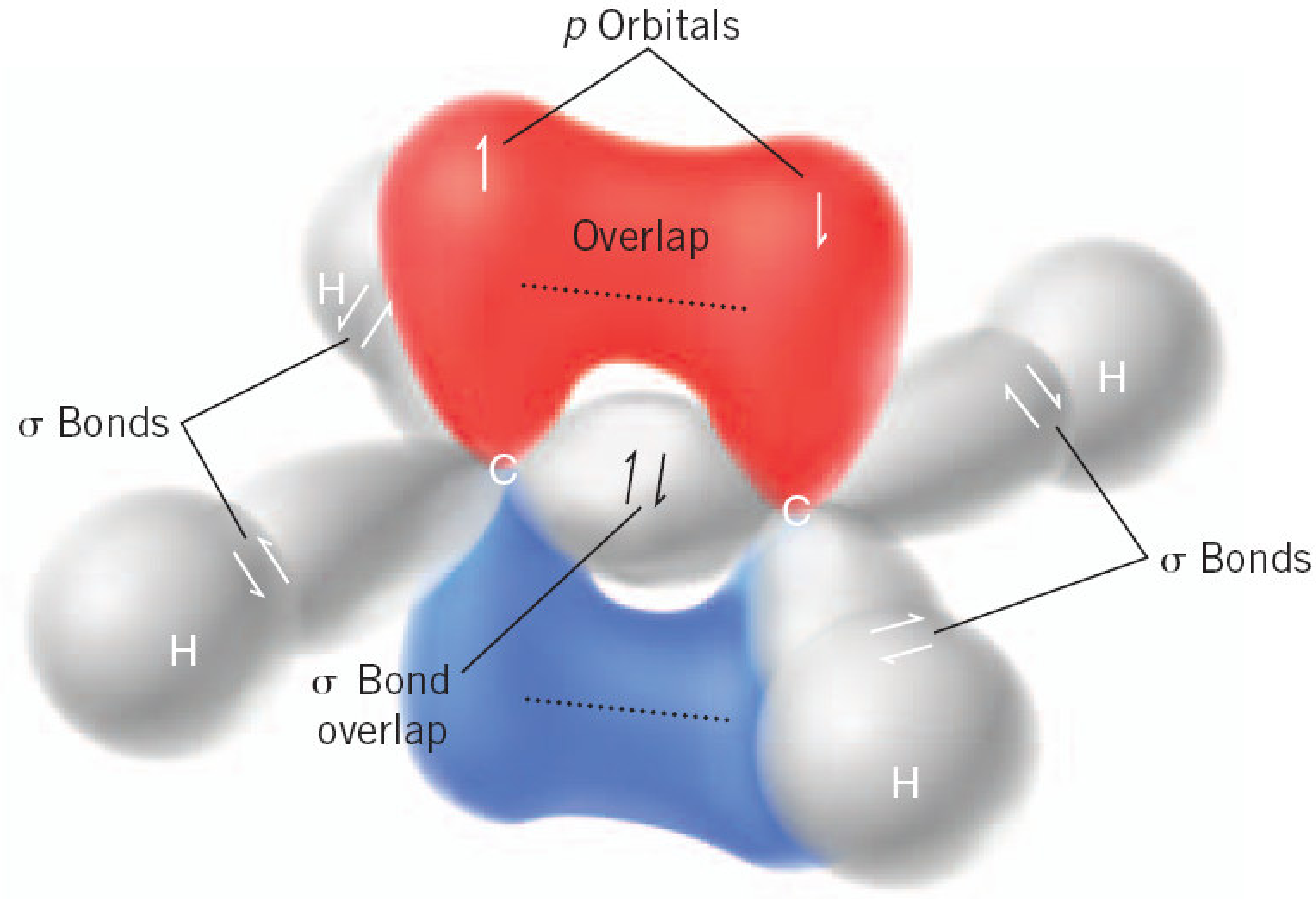


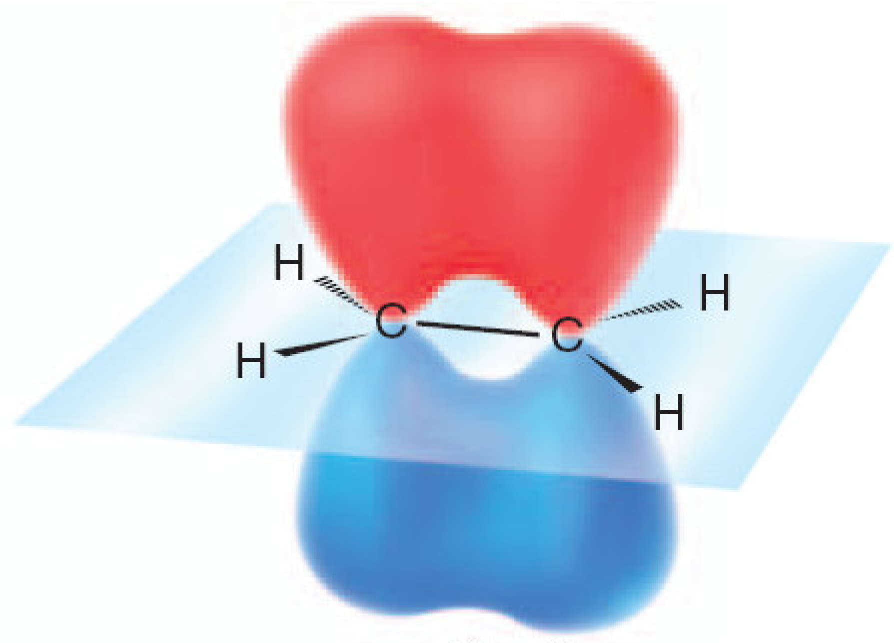
- Planar structure
- Carbon with (3σ + 1π) bonds


Ground state
Excited state
sp^2-Hybridized state
Energy
2p
2s
1s
2p
2s
1s
2p
$2sp^2$
1s
Promotion of electron
Hybridization

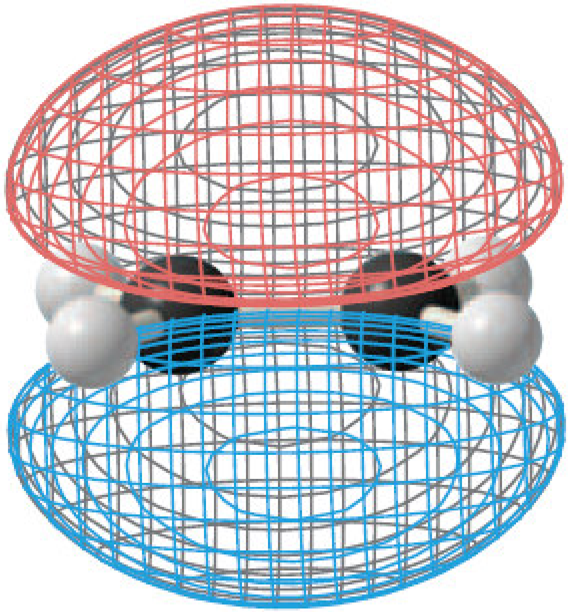

H
H
C
C
~121°
~118°
H
H

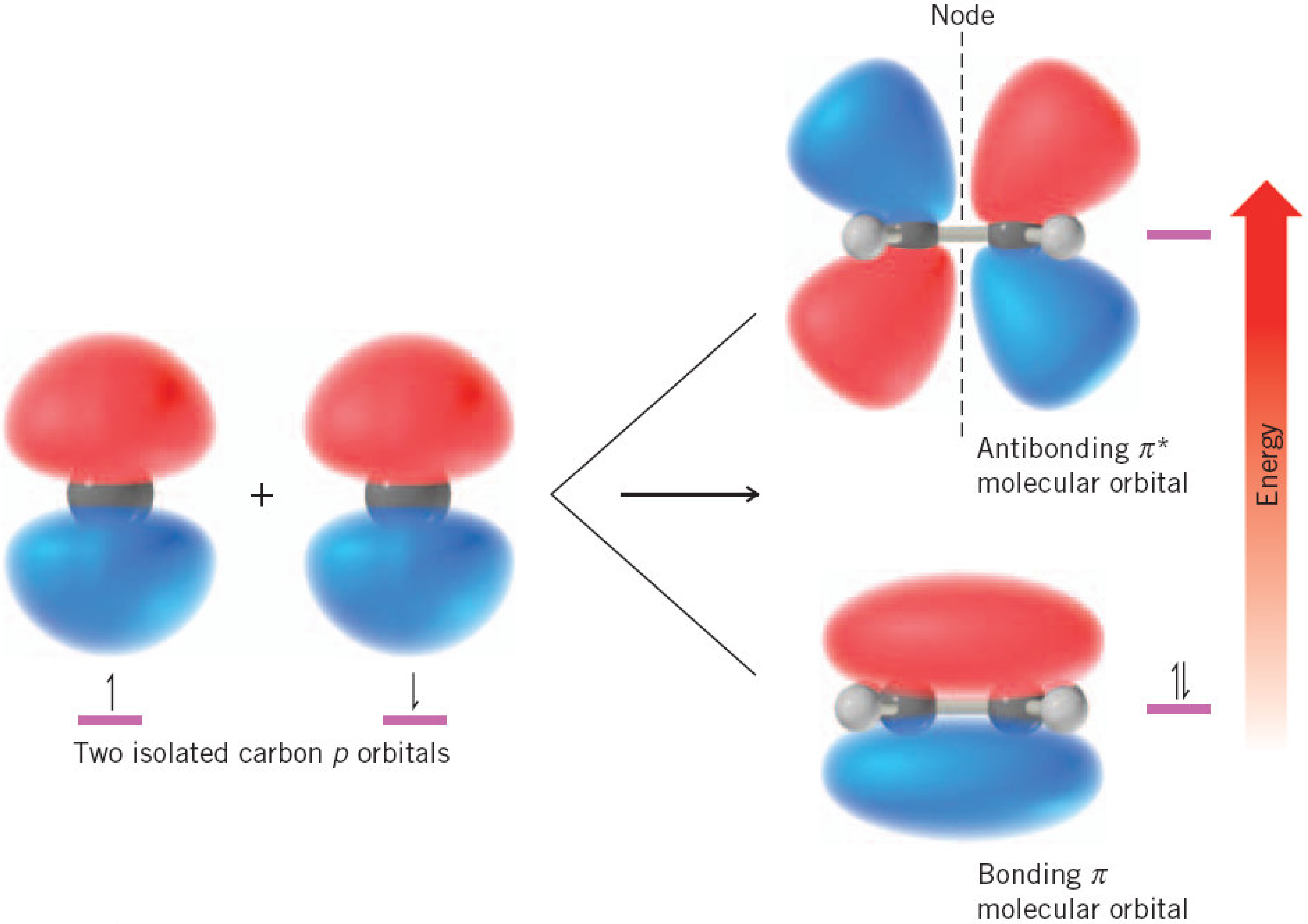

y
sp2 Orbital
z
sp2 Orbital
p Orbital
x
sp2 Orbital
1
1
1
1


p Orbitals
Overlap
H
σ Bonds
C
C
H
σ Bonds
H
σ Bond overlap
H



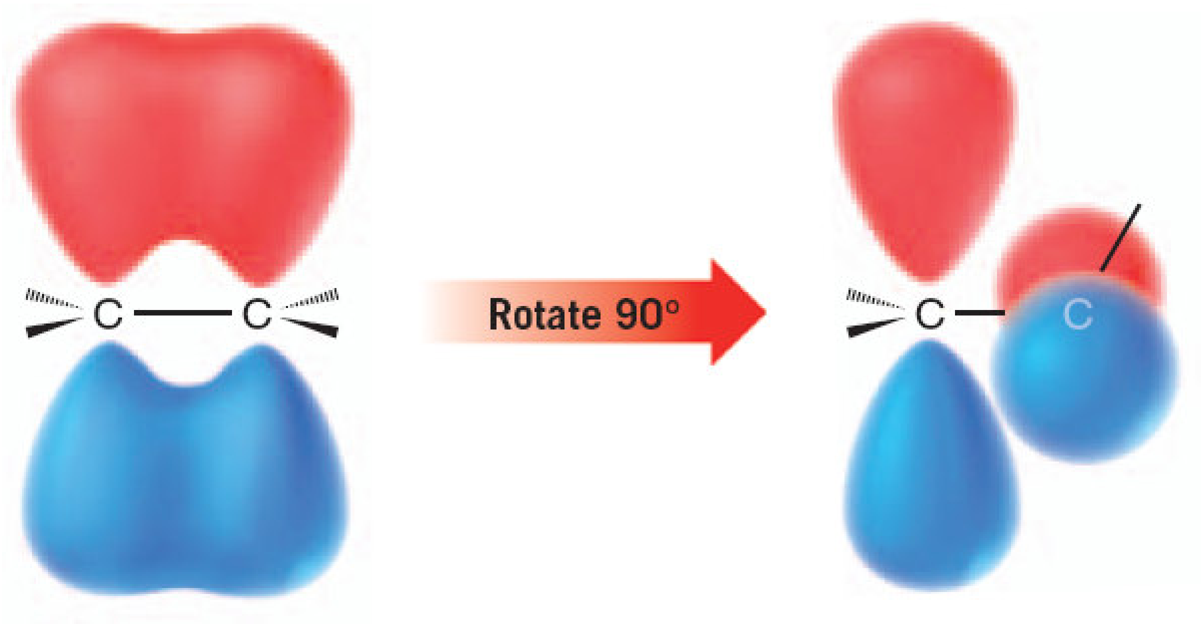
π Bond




Node
Antibonding π^* molecular orbital
Energy
Two isolated carbon p orbitals
Bonding π molecular orbital

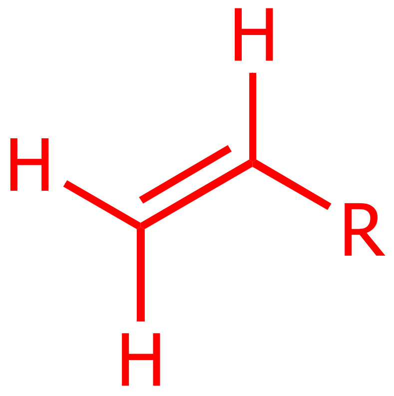
13A. Restricted Rotation and the Double Bond

- There is a large energy barrier to rotation associated with groups joined by a double bond
  - ~264 $kJmol^{-1}$ (strength of the π bond)
  - To compare: rotation of groups joined by C-C single bonds ~13-26 $kJmol^{-1}$

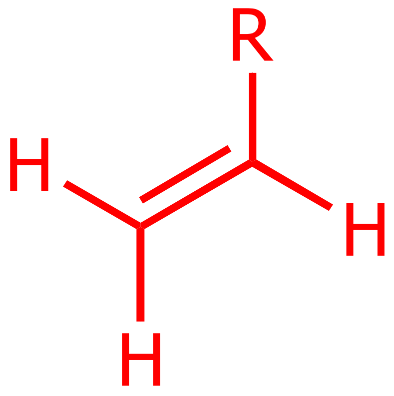

C
C
Rotate 90°
C
C

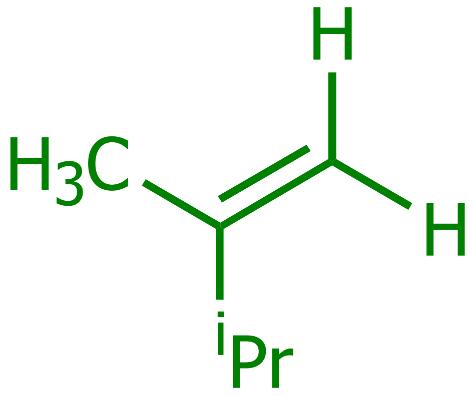
13B. Cis–Trans Isomerism

- Stereochemistry of double bonds

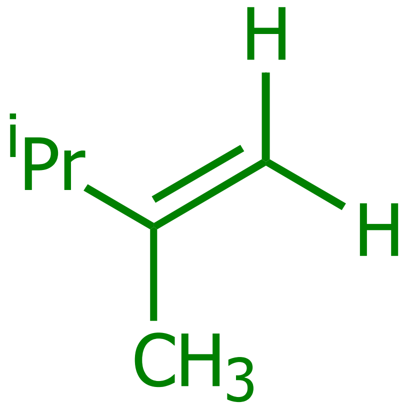


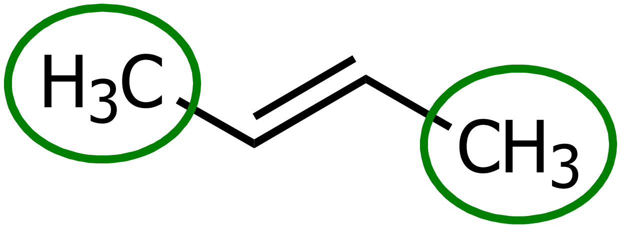
identical to





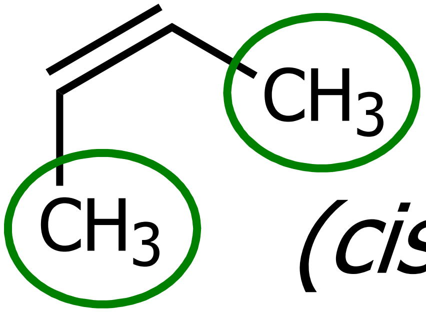
identical to





(trans)

different from



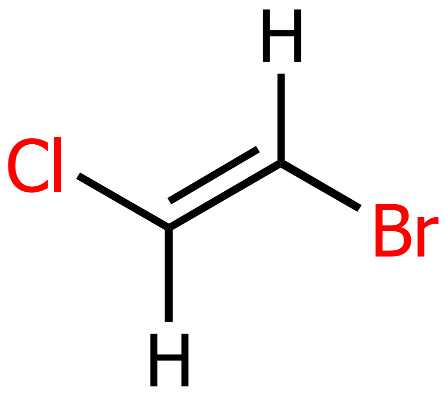
(cis)

- Restricted rotation of C=C

- *Cis*-*Trans* System
  - ♦ Useful for 1,2 disubstituted alkenes

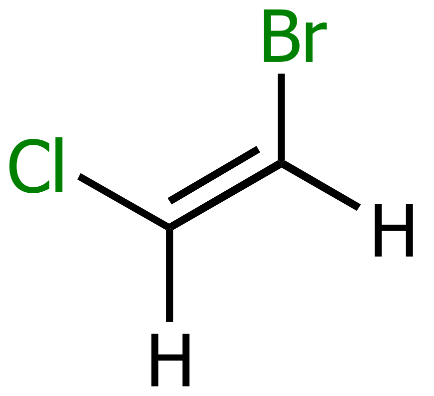
e.g.

(1)



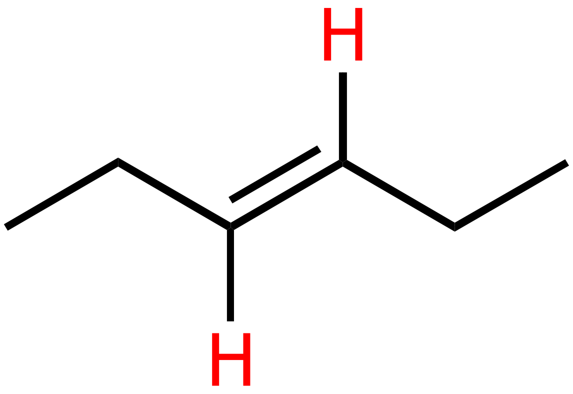
trans -1-Bromo-
2-chloroethane

vs.



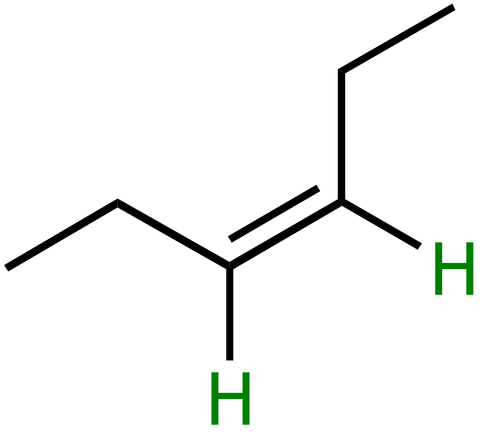
cis-1-Bromo-
2-chloroethane

(2)



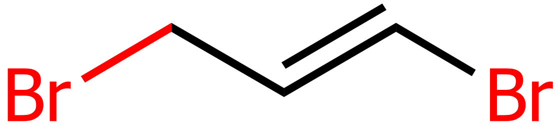
trans -3-Hexene

vs.



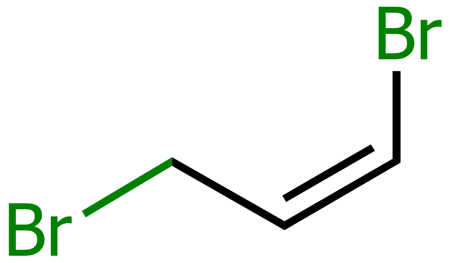
cis -3-Hexene

(3)



trans -1,3-
Dibromopropene

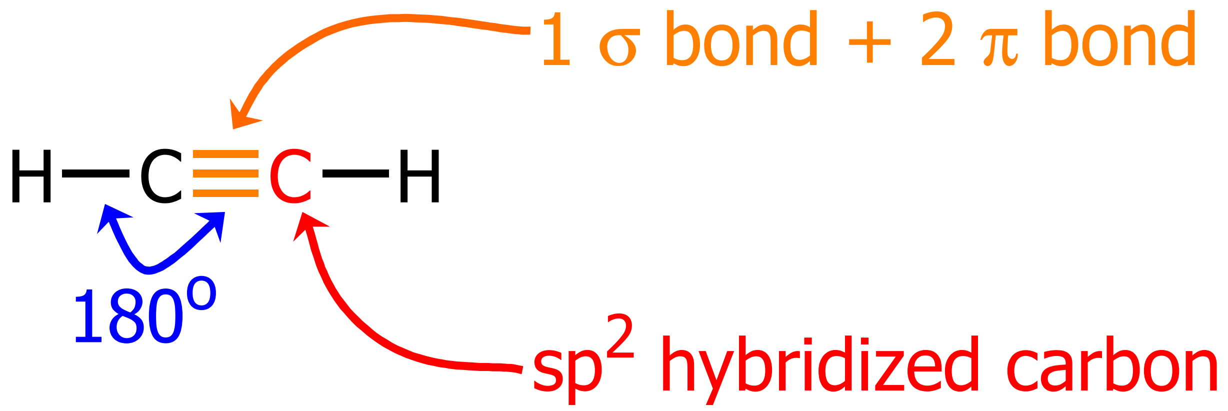
vs.



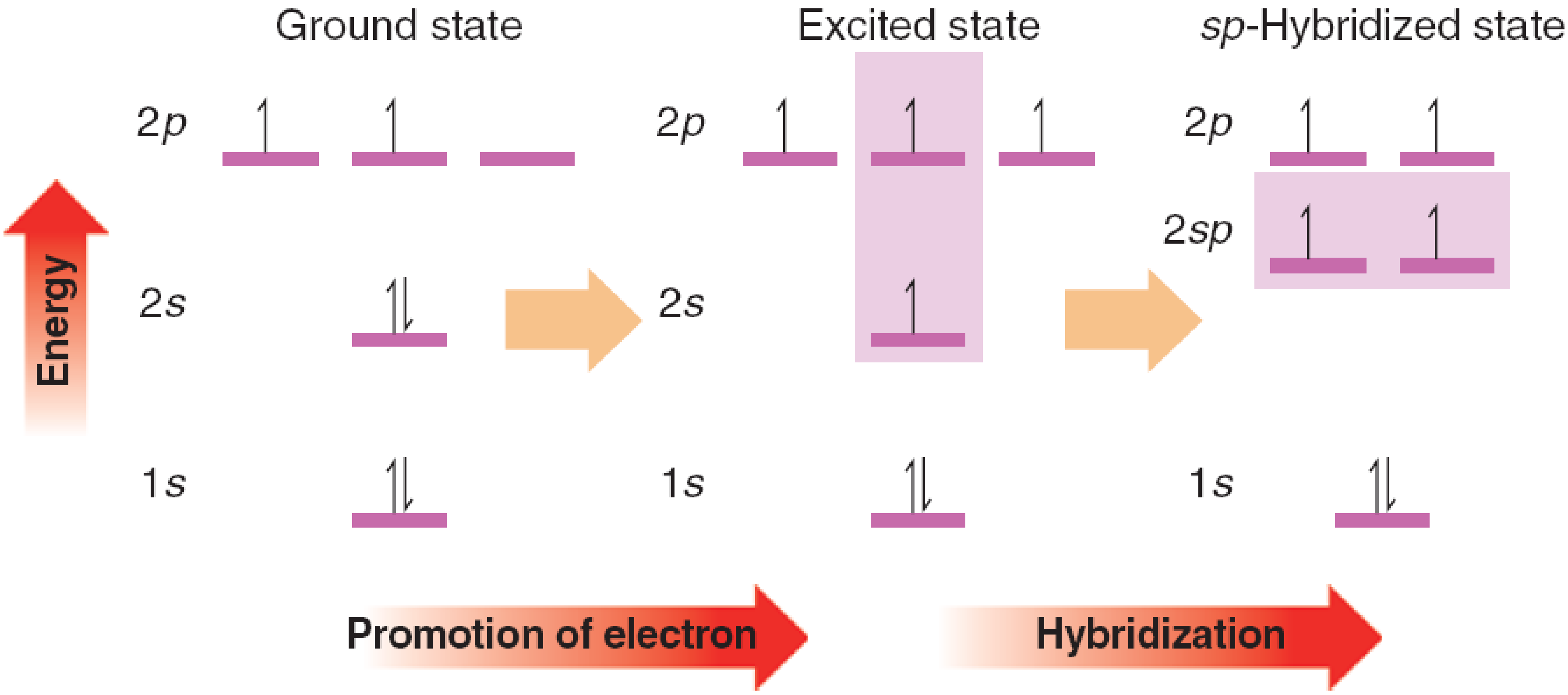
cis -1,3-
Dibromopropene

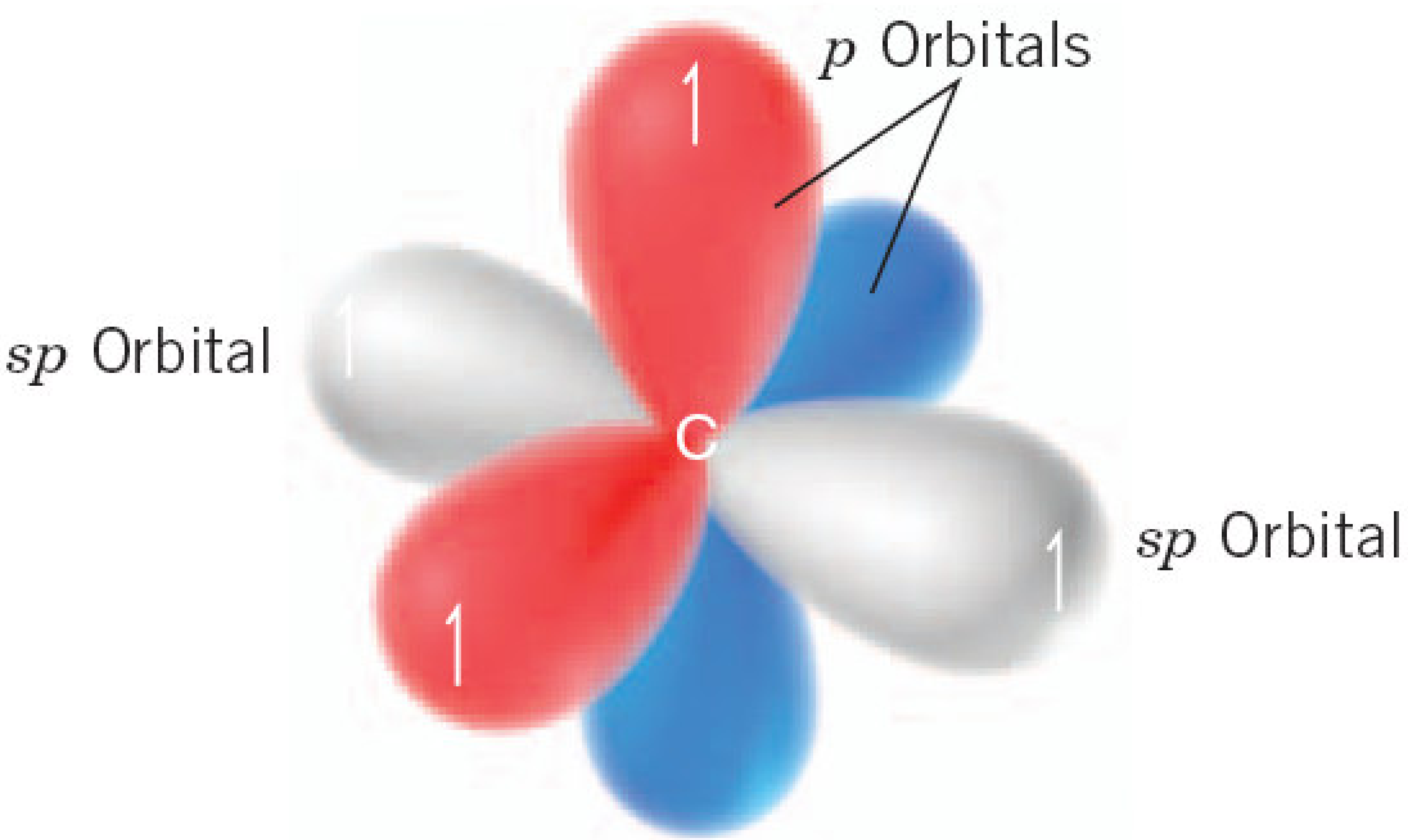
14. The Structure of Ethyne (Acetylene): sp Hybridization

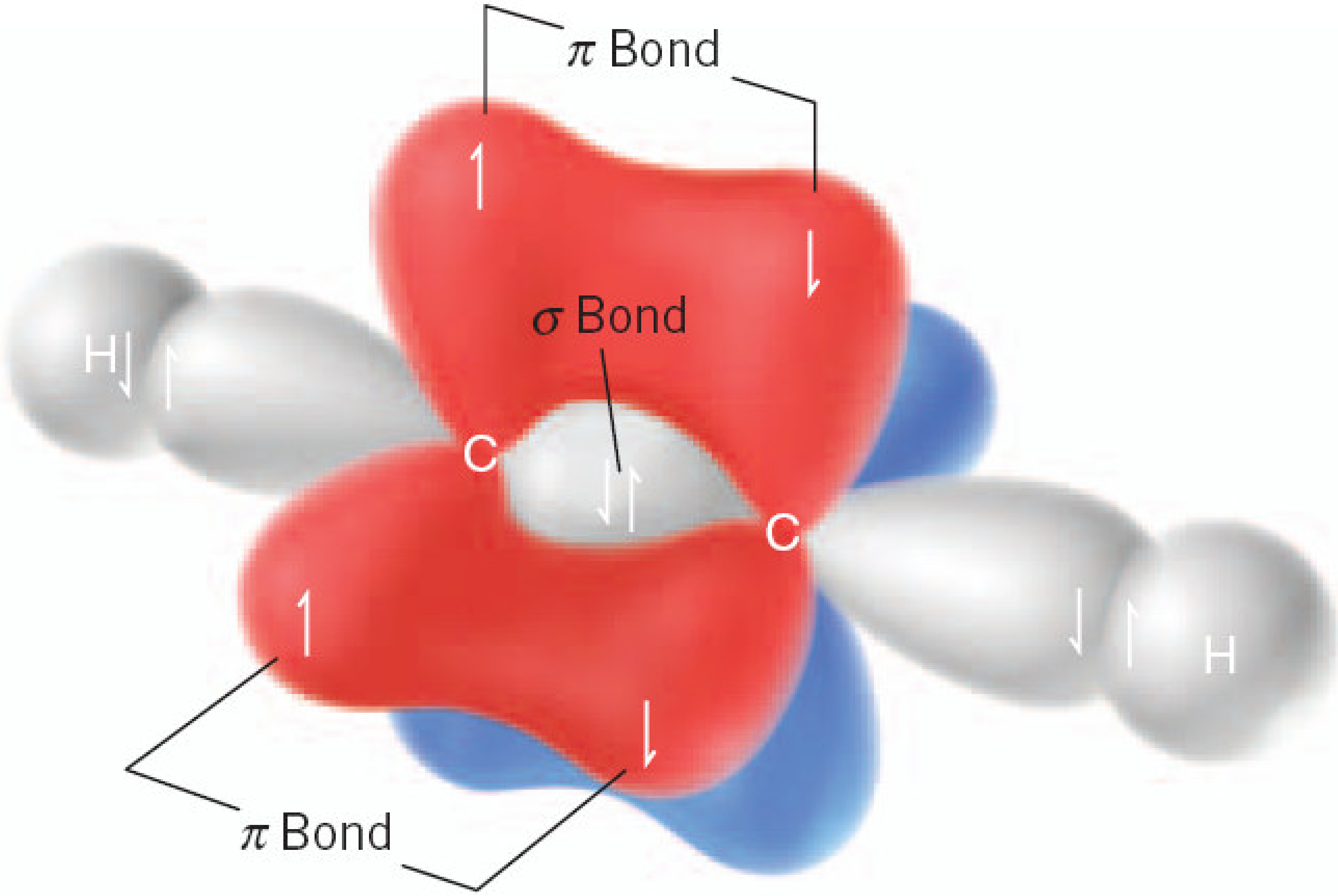
- ❖ sp



- Linear structure
- Carbon with (2 σ + 2 π) bonds


Ground state
Excited state
sp-Hybridized state
Energy
2*p*
2*s*
1*s*
2*p*
2*s*
1*s*
2*p*
2*sp*
1*s*
Promotion of electron
Hybridization

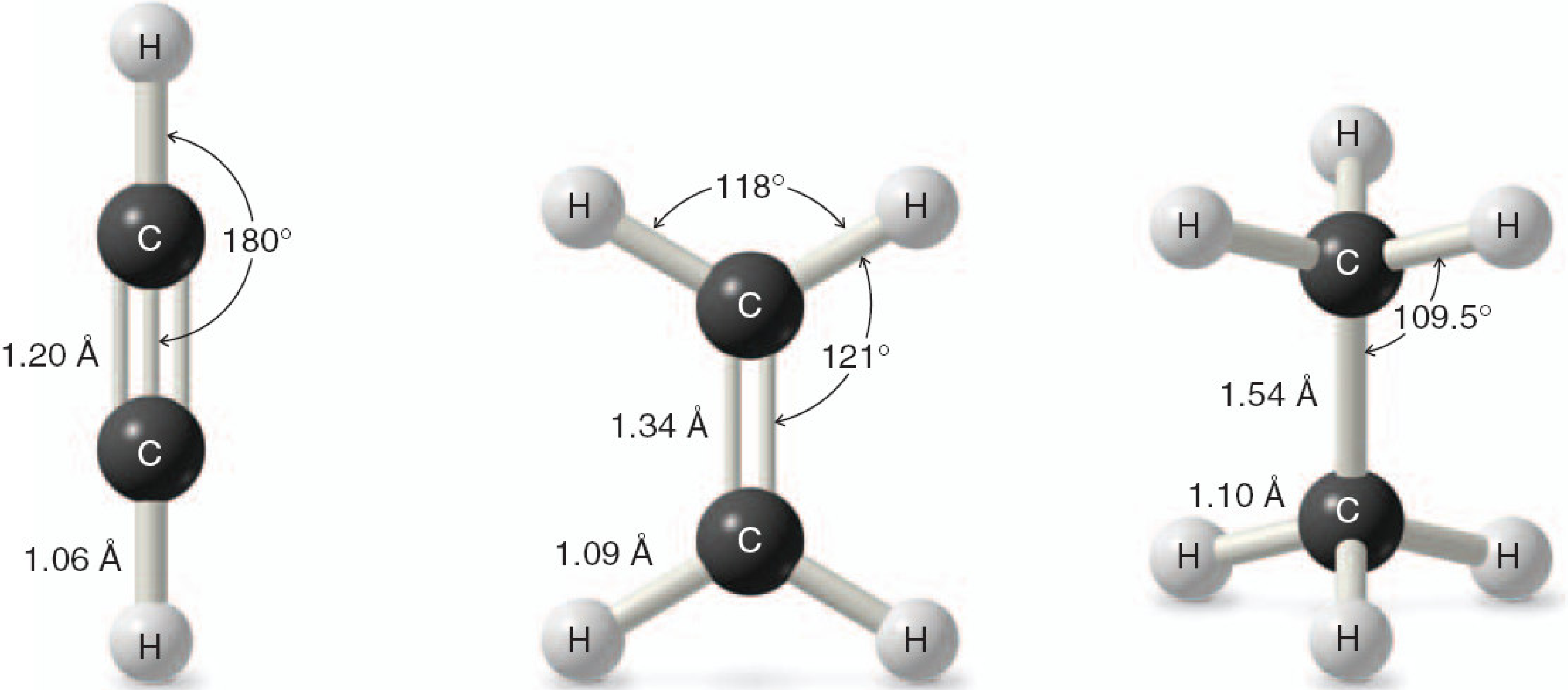

p Orbitals
sp Orbital
sp Orbital
C
1
1
1
1
1
1


π Bond
σ Bond
H
C
C
H
π Bond

- sp orbital
  - 50% *s* character, 50% *p* character

- sp^2 orbital
  - 33% *s* character, 66% *p* character

- sp^3 orbital
  - 25% *s* character, 75% *p* character


H
C
180°
1.20 Å
C
1.06 Å
H
H
118°
H
C
121°
1.34 Å
C
1.09 Å
H
H
H
H
H
C
109.5°
1.54 Å
1.10 Å
C
H
H
H

15. A Summary of Important Concepts That Come from Quantum Mechanics

1) An **atomic orbital (AO)** corresponds to a region of space about the nucleus of a single atom where there is a high probability of finding an electron. *s* orbitals are spherical, *p* orbitals are like two almost-tangent spheres. Orbitals can hold a maximum of two electrons when their spins are paired

2) When atomic orbitals overlap, they combine to form **molecular orbitals (MOs)**

3) When atomic orbitals with the same phase sign interact, they combine to form a **bonding molecular orbital**

4) An **antibonding molecular orbital** forms when orbitals of opposite phase sign overlap

5) The **energy of electrons** in a bonding molecular orbital is less than the energy of the electrons in their separate atomic orbitals

6) The **number of molecular orbitals** always equals the number of atomic orbitals from which they are formed

7) **Hybrid atomic orbitals** are obtained by mixing (hybridizing) the wave functions for orbitals of different types (i.e., *s* and *p* orbitals) but from the same atom

8) Hybridizing three *p* orbitals with one *s* orbital yields four ***sp***

9) Hybridizing two *p* orbitals with one *s* orbital yields three **sp^2 orbitals** and they are trigonal planar

10) Hybridizing one *p* orbital with one *s* orbital yields two ***sp* orbitals**, a linear molecule

11) A **sigma** (σ) **bond** (a type of single bond) is one in which the electron density has circular symmetry when viewed along the bond axis

12) A **pi** (π) **bond**, part of double and triple carbon–carbon bonds, is one in which the electron densities of two adjacent parallel *p* orbitals overlap sideways to form a bonding pi molecular orbital

16. Molecular Geometry: The Valence Shell Electron Pair Repulsion Model

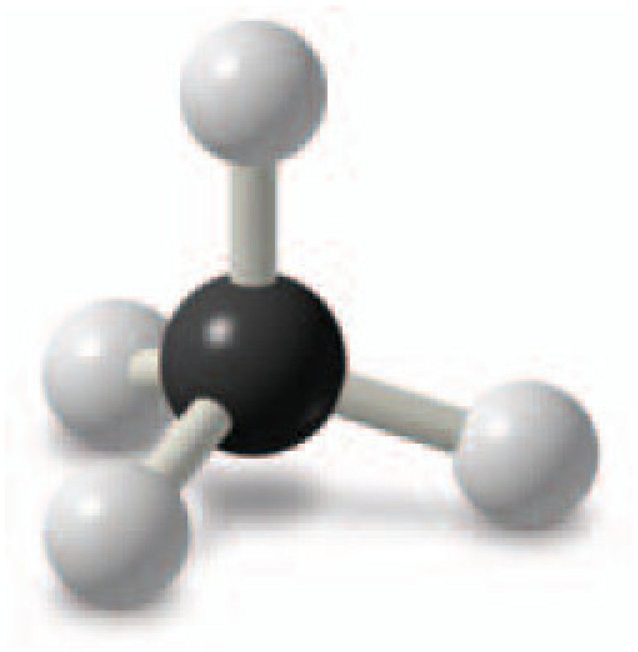
- Valence shell electron pair repulsion (VSEPR) model:
  1) We consider molecules (or ions) in which the central atom is covalently bonded to two or more atoms or groups

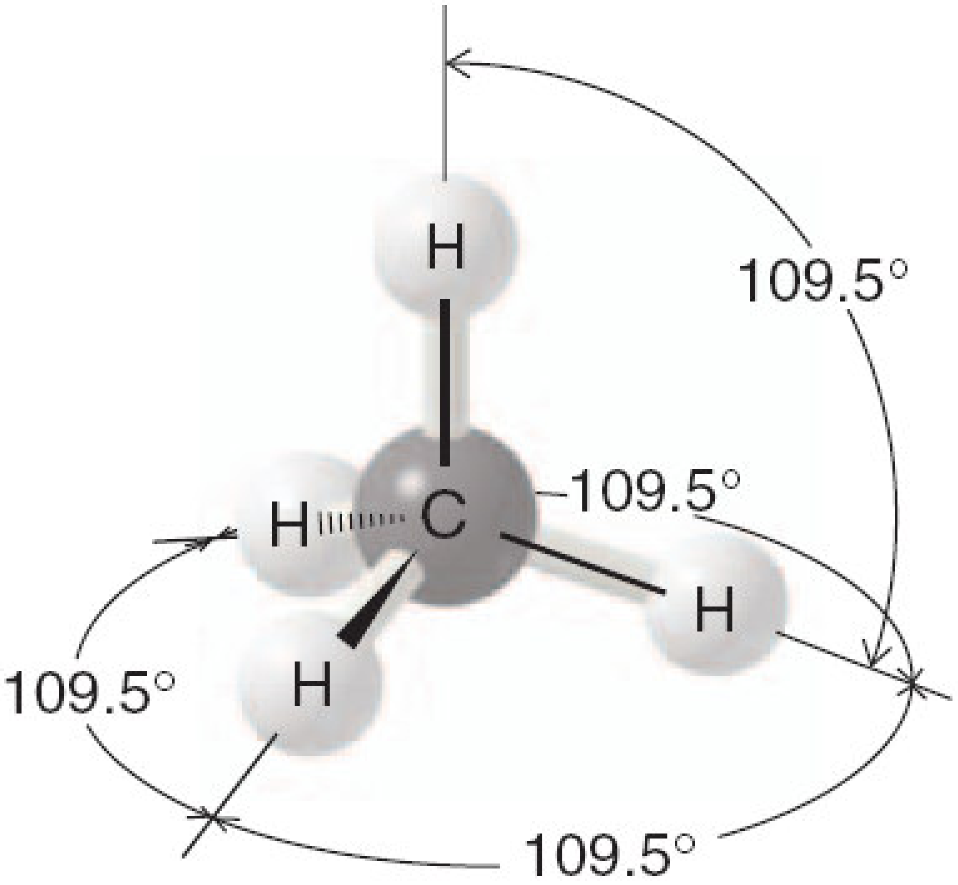
2) We consider all of the valence electron pairs of the central atom—both those that are shared in covalent bonds, called bonding pairs, and those that are unshared, called nonbonding pairs or unshared pairs or lone pairs

3) Because electron pairs repel each other, the electron pairs of the valence shell tend to stay as far apart as possible. The repulsion between nonbonding pairs is generally greater than that between bonding pairs

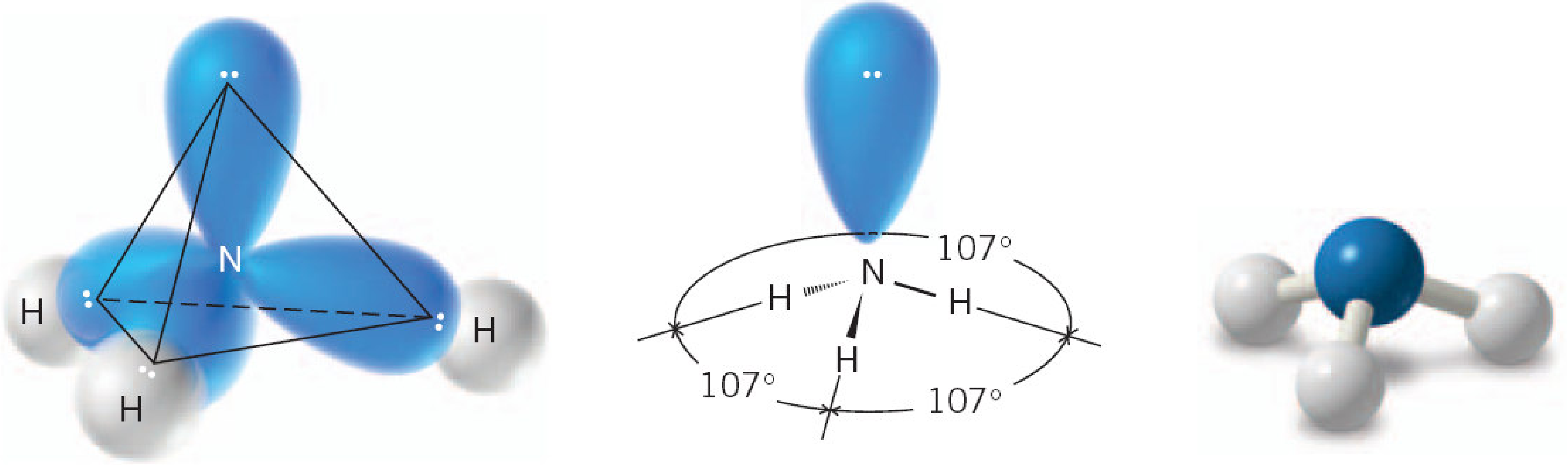
4) We arrive at the geometry of the molecule by considering all of the electron pairs, bonding and nonbonding, but we describe the shape of the molecule or ion by referring to the positions of the nuclei (or atoms) and not by the positions of the electron pairs

16A. Methane



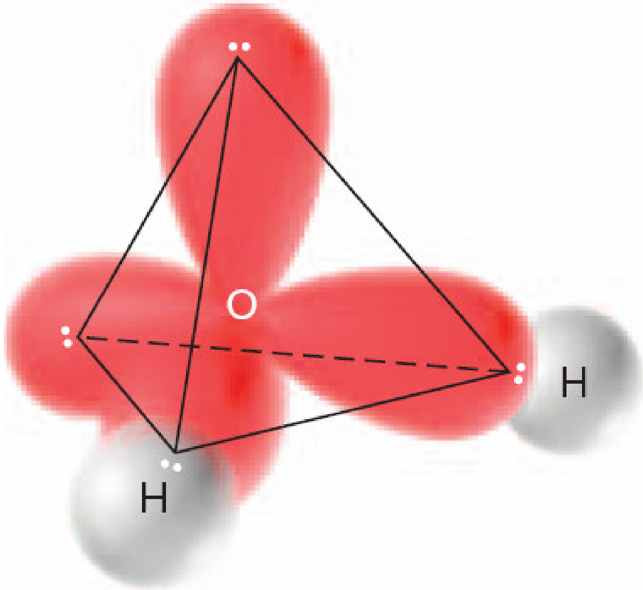


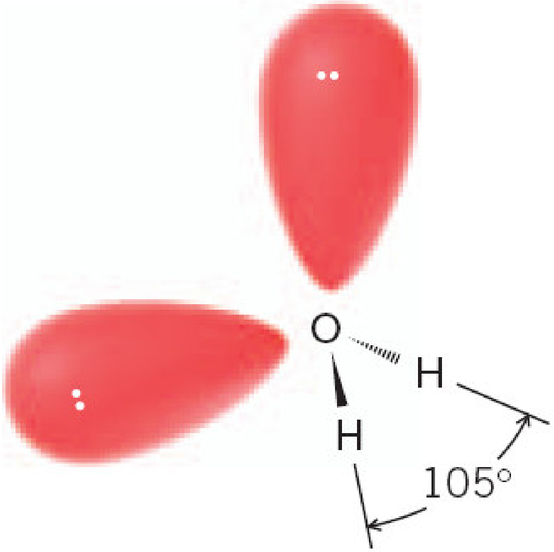
16B. Ammonia

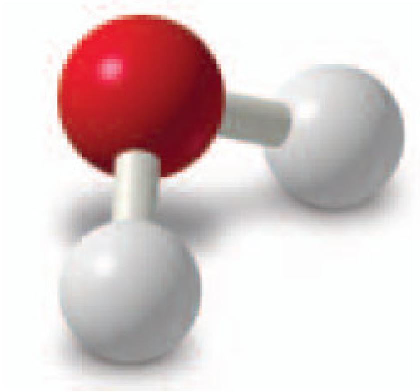


- A *tetrahedral arrangement* of the electron pairs explains the *trigonal pyramidal* arrangement of the four atoms. The bond angles are 107° (not 109.5°) because the nonbonding pair occupies more space than the bonding pairs

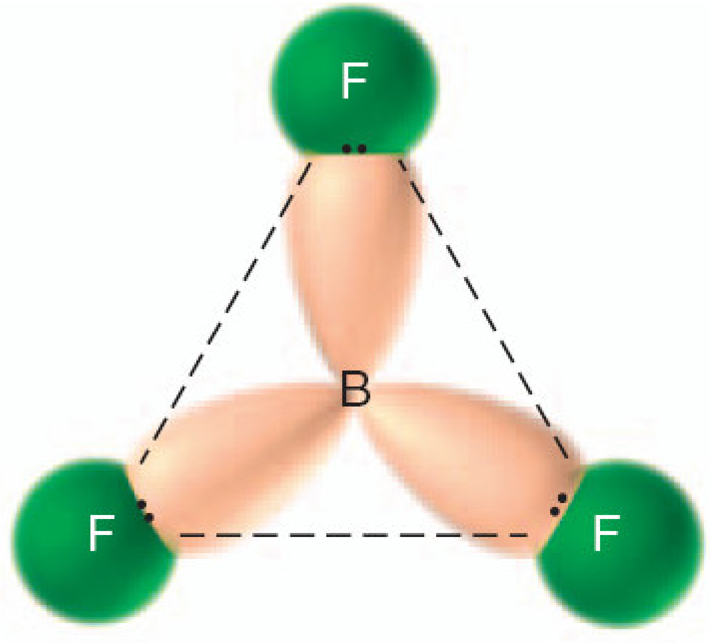
16C. Water

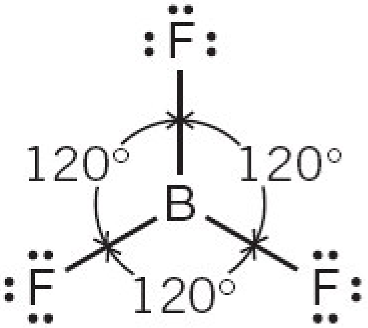


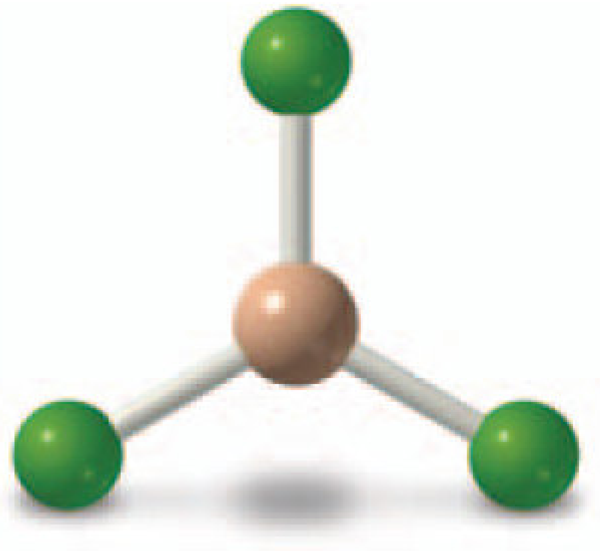




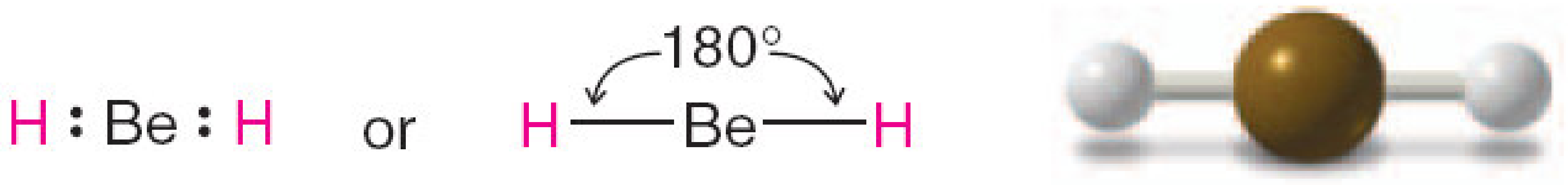
16D. Boron Trifluoride





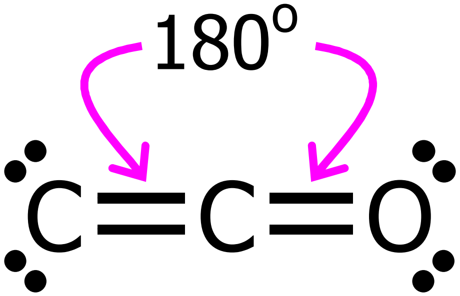


16E. Beryllium Hydride

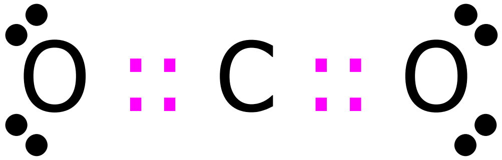


Linear geometry of BeH_2

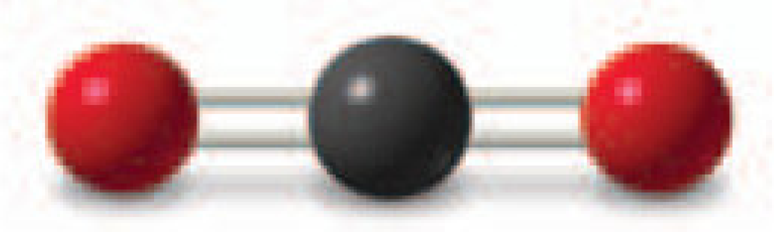
16F. Carbon Dioxide



or



The four electrons of each double bond act as a single unit and are maximally separated from each other.

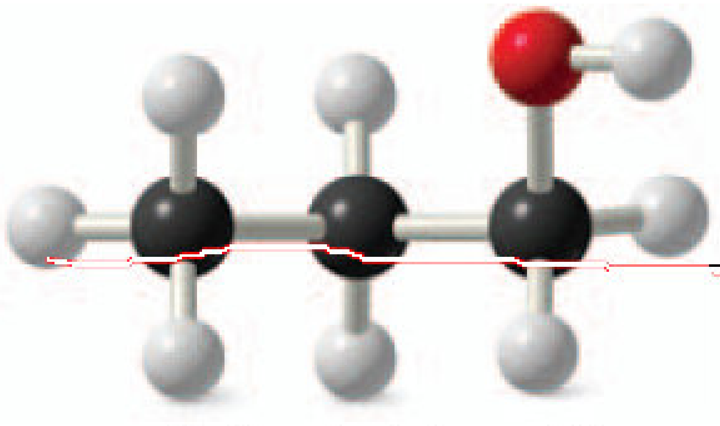


Shapes of Molecules and Ions from VSEPR Theory

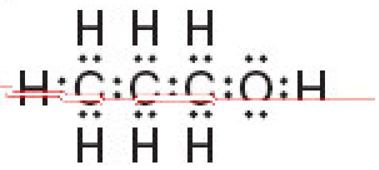
Number of Electron Pairs at Central Atom			Hybridization State of Central Atom	Shape of Molecule or Ion[a]	Examples
Bonding	Nonbonding	Total			
2	0	2	*sp*	Linear	BeH_2
3	0	3	sp^2	Trigonal planar	BF_3, CH_3^+
4	0	4	sp^3	Tetrahedral	CH_4, NH_4^+
3	1	4	$\sim sp^3$	Trigonal pyramidal	NH_3, CH_3^-
2	2	4	$\sim sp^3$	Angular	H_2O

[a] Referring to positions of atoms and excluding nonbonding pairs.

17. How to Interpret and Write Structural Formulas

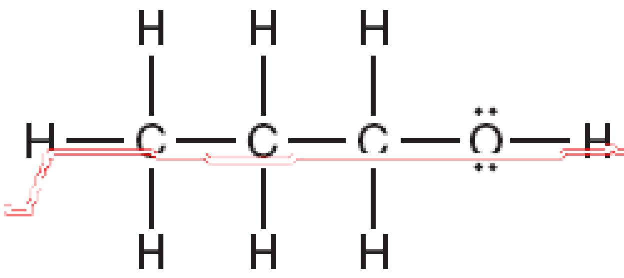


Ball-and-stick model
(*a*)



$H:\underset{H}{\overset{H}{C}}:\underset{H}{\overset{H}{C}}:\underset{H}{\overset{H}{C}}:\ddot{\underset{..}{O}}:H$

Dot formula
(*b*)

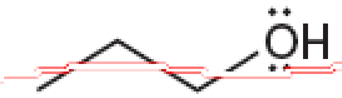


$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\ddot{\underset{..}{O}}-H$

Dash formula
(*c*)

$CH_3CH_2CH_2\ddot{\underset{..}{O}}H$

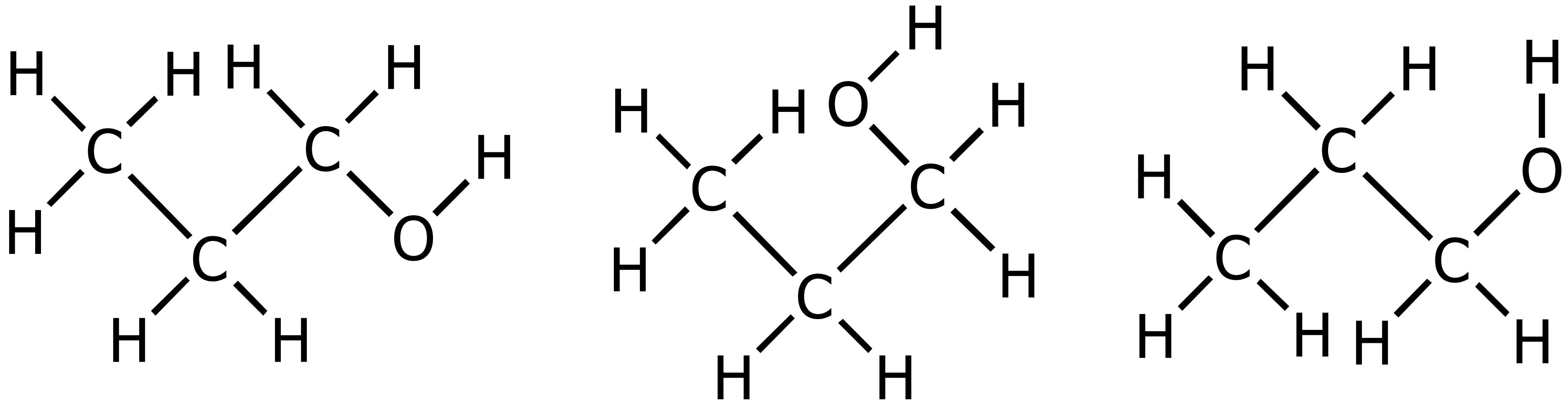
Condensed formula
(*d*)



Bond-line formula
(*e*)

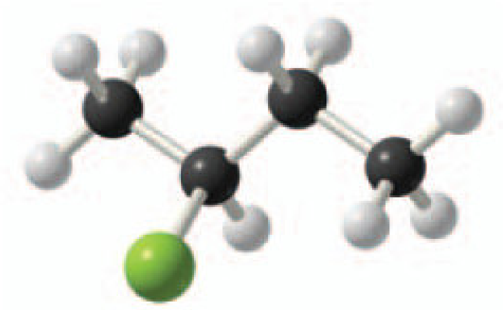
17A. Dash Structural Formulas

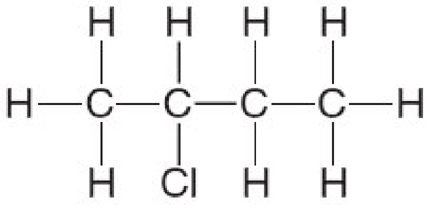
- Atoms joined by single bonds can rotate relatively freely with respect to one another



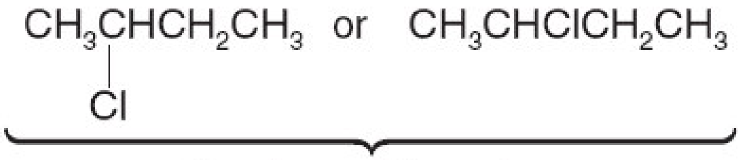
Equivalent dash formulas for propyl alcohol

17B. Condensed Structural Formulas



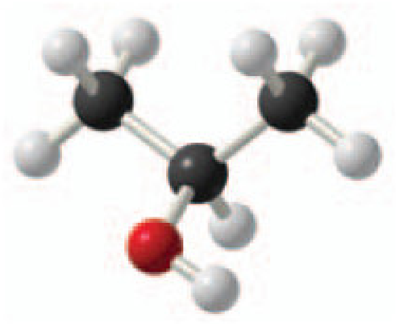


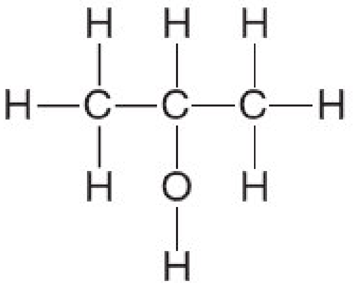
Dash formula



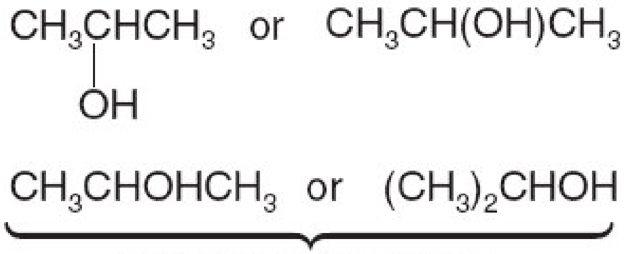
$CH_3\underset{\displaystyle Cl}{\underset{|}{C}}HCH_2CH_3$ or $CH_3CHClCH_2CH_3$

Condensed formulas





Dash formula



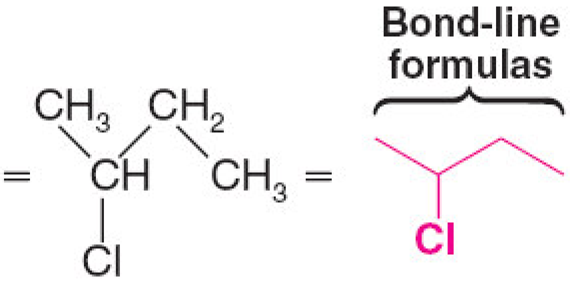
$CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCH_3$ or $CH_3CH(OH)CH_3$

$CH_3CHOHCH_3$ or $(CH_3)_2CHOH$

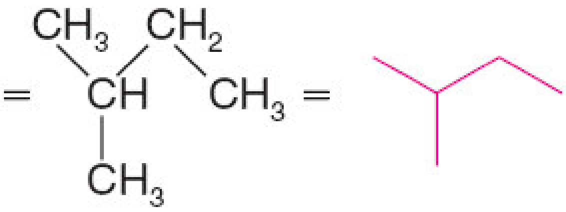
Condensed formulas

17C. Bond-Line Formulas

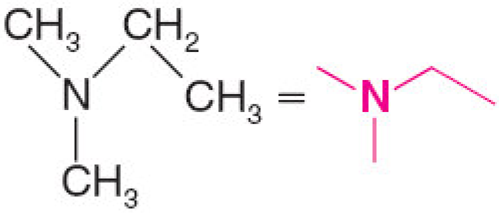
$CH_3CHClCH_2CH_3$ =

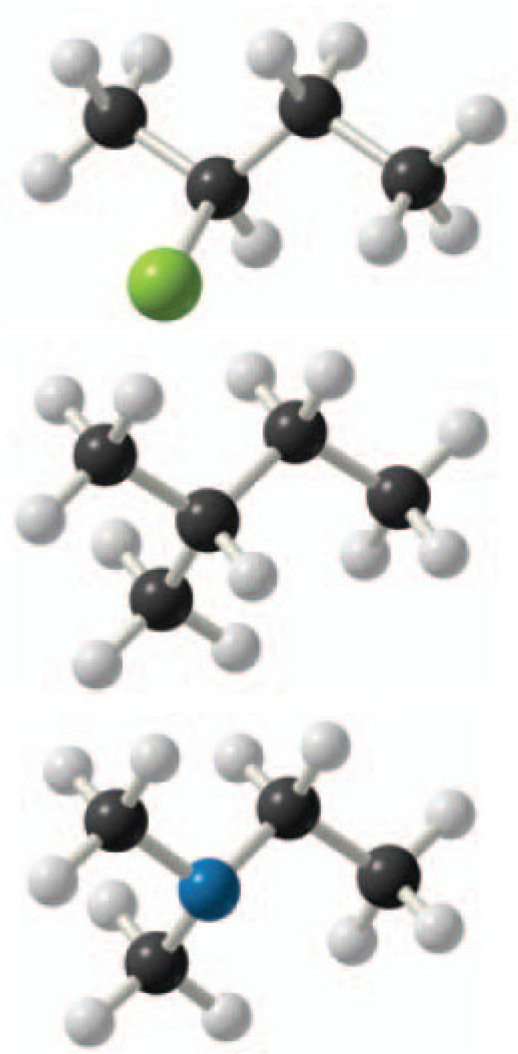


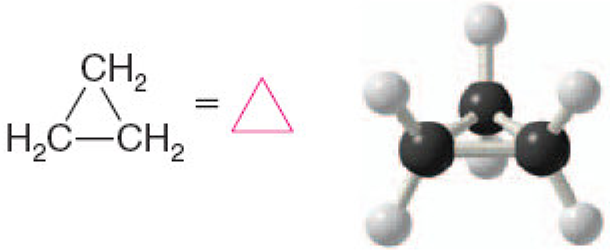
$CH_3CH(CH_3)CH_2CH_3$ =



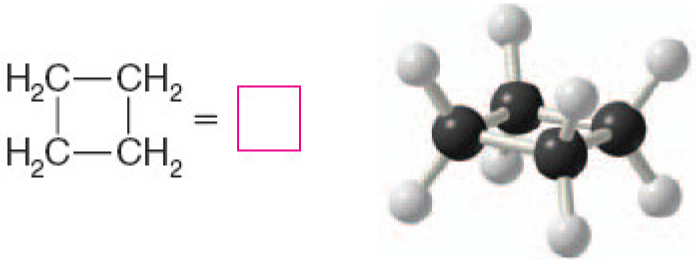
$(CH_3)_2NCH_2CH_3$ =

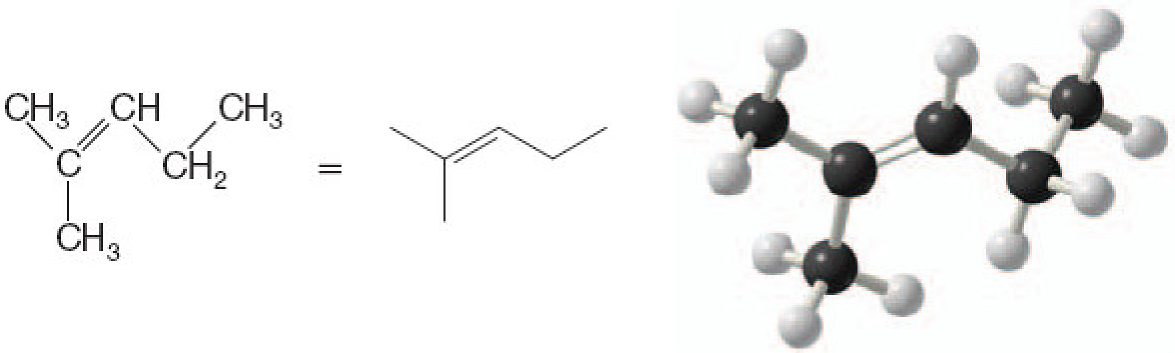




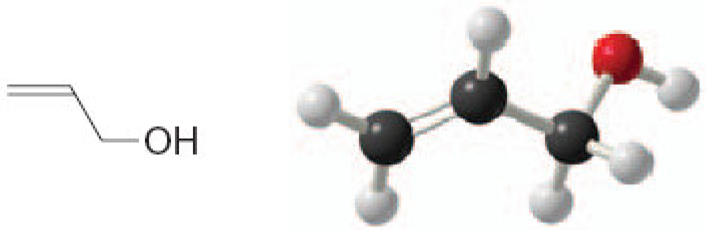


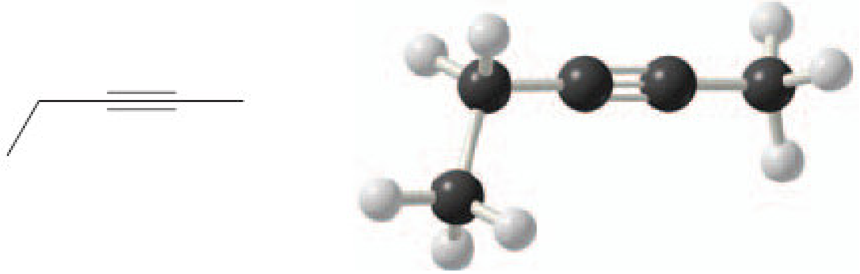
and



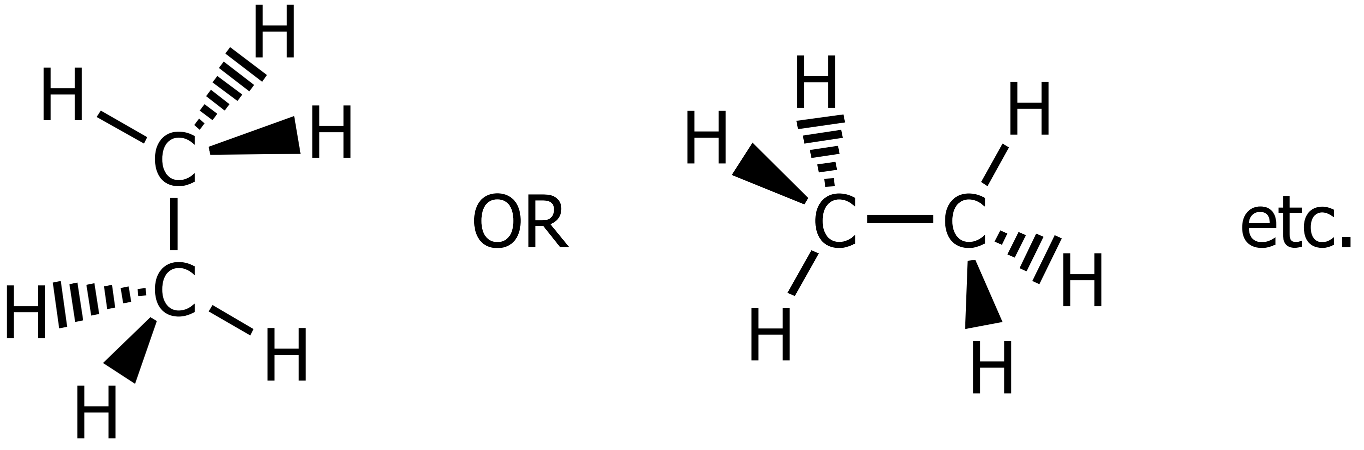


$CH_2{=}CHCH_2OH$ =

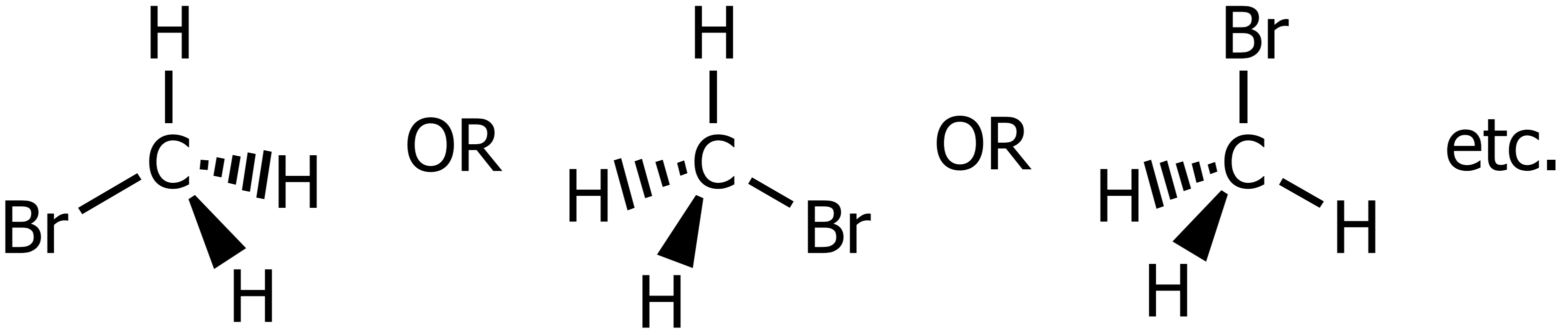




17D. Three-Dimensional Formulas

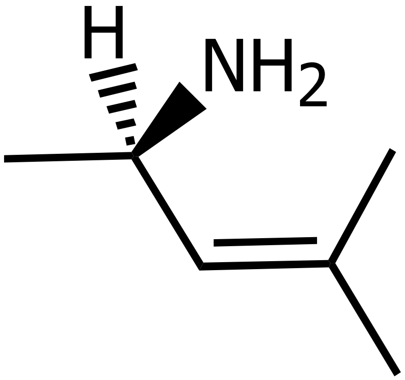


Ethane

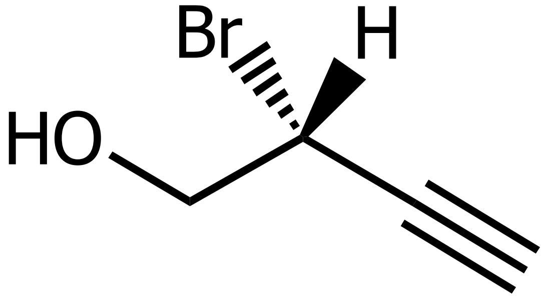


Bromomethane

Examples of bond-line formulas that include three-dimensional representations



An example involving trigonal planar geometry



An example involving linear geometry

🔔 END OF CHAPTER 1 🔔