基礎有機化學

(Organic Chemistry)

Textbook: “***Organic Chemistry***” Eighth Edition, Solomons & Fryhle

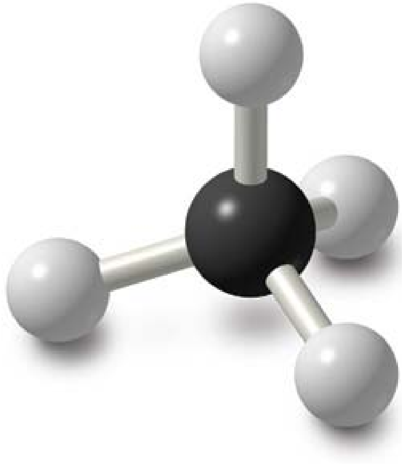
第1章 →第6章：有機化學中的基本概念
第7章 →第25章：各類有機化合物的性質

第1章 有機化學的概念和化學鍵 (Carbon Compounds and Chemical Bonds)

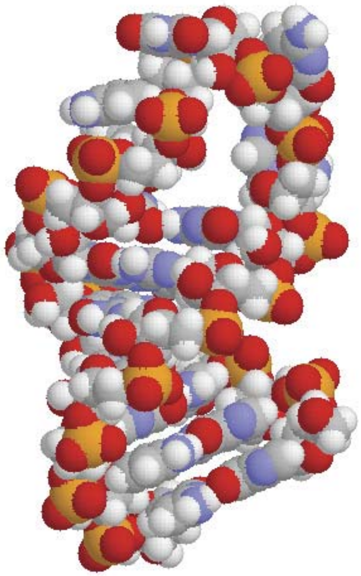
一）Introduction:

Organic Chemistry: “the chemistry of the compounds of carbon”

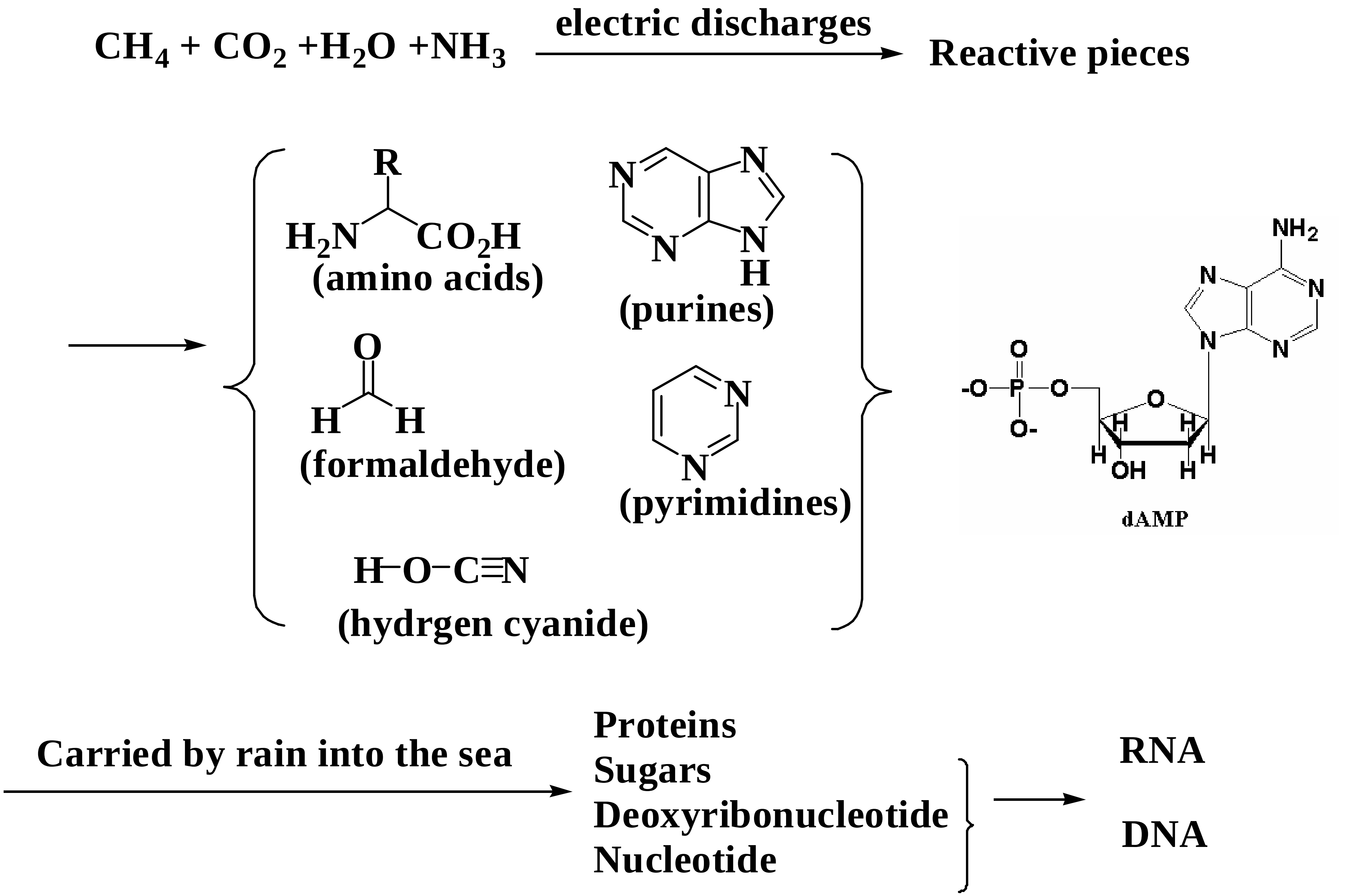
a) The human body is largely composed of organic compounds:



Methane



An RNA molecule



$$\mathrm{CH_4 + CO_2 + H_2O + NH_3} \xrightarrow{\text{electric discharges}} \text{Reactive pieces}$$

(amino acids)

(purines)

(formaldehyde)

(pyrimidines)

$\mathrm{H{-}O{-}C{\equiv}N}$

(hydrgen cyanide)

dAMP

Carried by rain into the sea →

Proteins
Sugars
Deoxyribonucleotide
Nucleotide

→

RNA

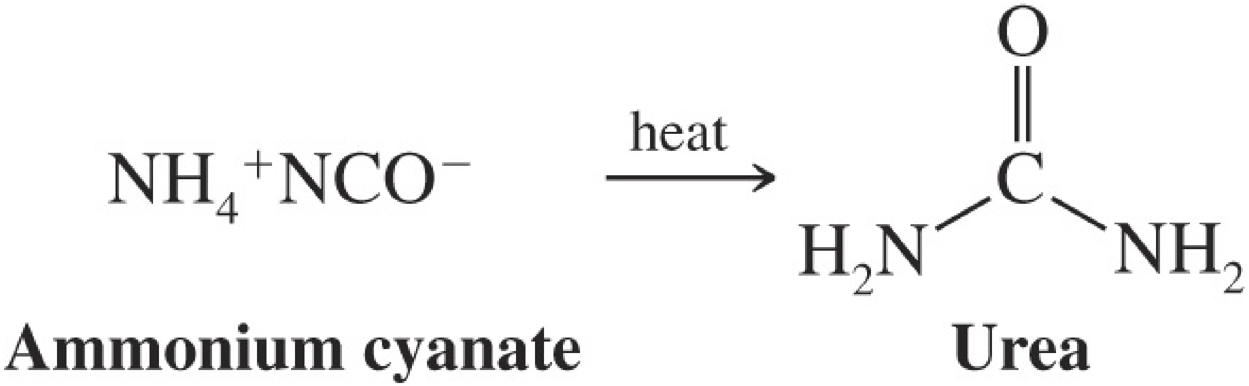
DNA

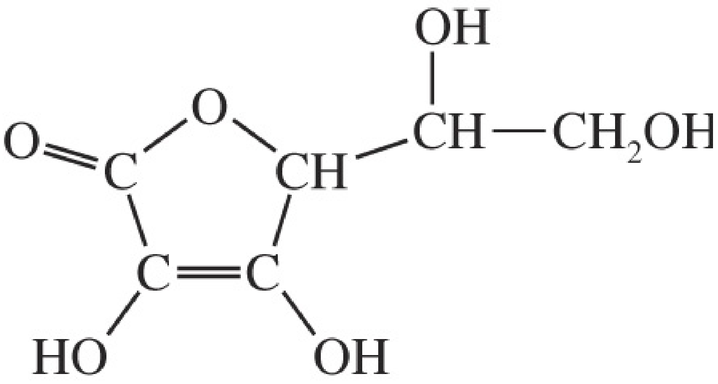
b) Organic chemistry plays a central role in medicine, bioengineering etc.
The concept of “*environment-friendly*”

二) The development of organic chemistry as a science: early nineteenth century

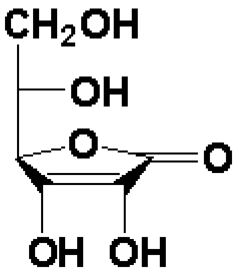
Vitalism

- ■ It was originally thought organic compounds could be made only by living things by intervention of a “vital force”
- ■ Fredrich Wöhler disproved vitalism in 1828 by making the organic compound urea from the inorganic salt ammonium cyanate by evaporation:

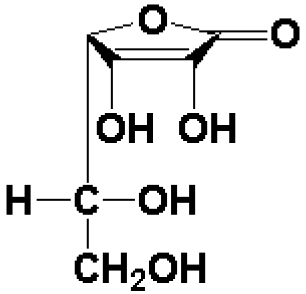




Vitamin C



L- ascorbic acid (natural)



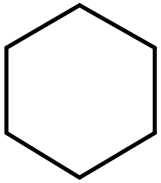
D- ascorbic acid

- **The concept of “*qualitative and quantitative analysis methods*”**
- **In 1874, Antoine Lavoisier showed that organic compound were composed primarily of C, H, O.**
- ***Empirical formulas and molecular formulas* (1860, Stanislao Cannizzaro)**

$H_2C{=}CH_2$

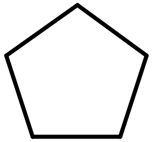
ethene

C_2H_4



cyclohexane

C_6H_{12}



cyclopetane

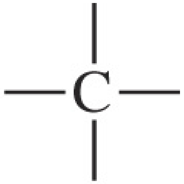
C_5H_{10}

empirical formulas: CH_2

三) The structural theory of organic chemistry

■Structural Theory (1858-1861)

Valence(價): atoms in organic compounds form a fixed number of bonds; the measure of this ability is called valence.



Carbon atoms are tetravalent

Oxygen atoms are divalent

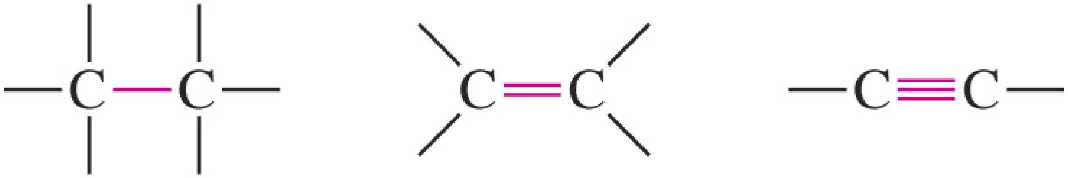
Hydrogen and halogen atoms are monovalent

(neutral)

(N: 3)

Carbon can form one or more bonds to other carbons:

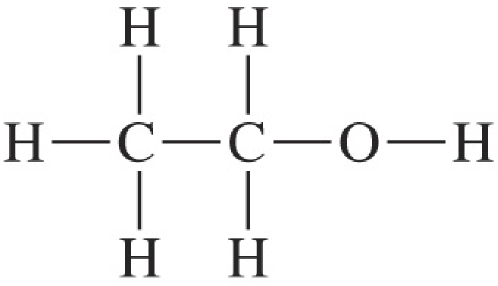
Carbon–carbon bonds



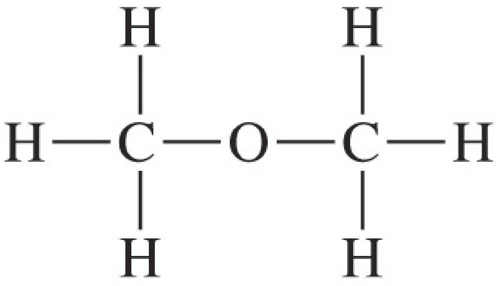
Single bond **Double bond** **Triple bond**

■ **Isomers (Isomerism, Isomeric):** are different molecules with the same molecular formula. Many types of isomers exist

Example:



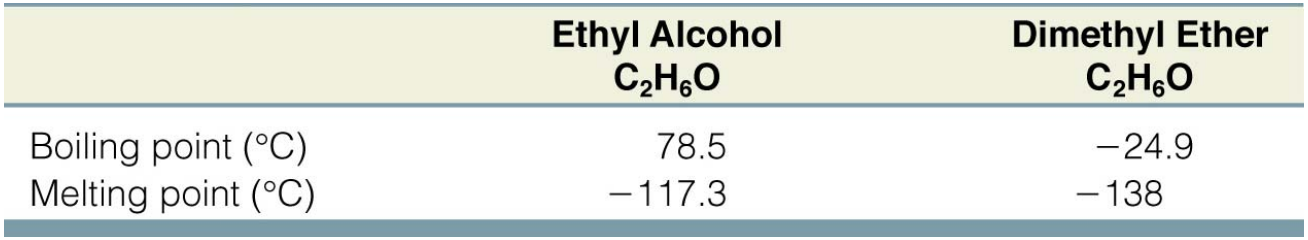
Ethyl alcohol



Dimethyl ether

Consider two compounds with molecular formula C2H6O:

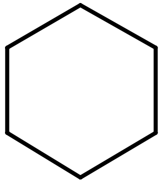
*These compounds cannot be distinguished based on molecular formula; however they have different **structural formulas** and different chemical and physical properties.



	Ethyl Alcohol C_2H_6O	Dimethyl Ether C_2H_6O
Boiling point (°C)	78.5	−24.9
Melting point (°C)	−117.3	−138

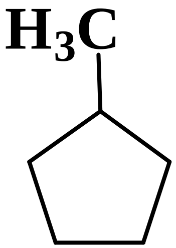
***The two compounds differ in the *connectivity* of their atoms (C-C-O and C-O-C).**

***Constitutional Isomers**: different compounds with the same molecular formulas but differ in the sequence in which their atoms are bonded together.



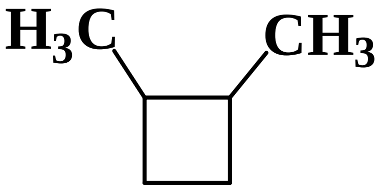
cyclohexane

C_6H_{12}



methyl-cyclopetane

C_6H_{12}

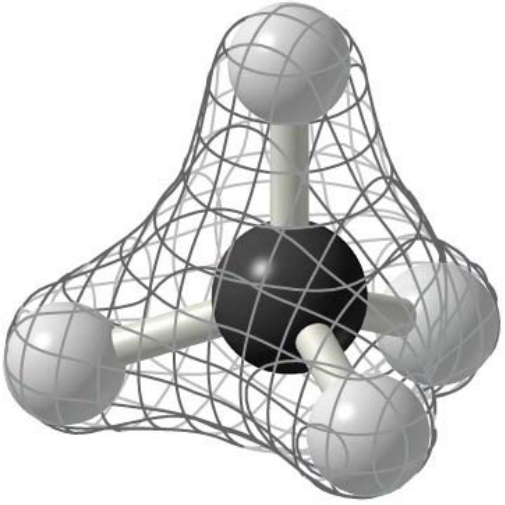


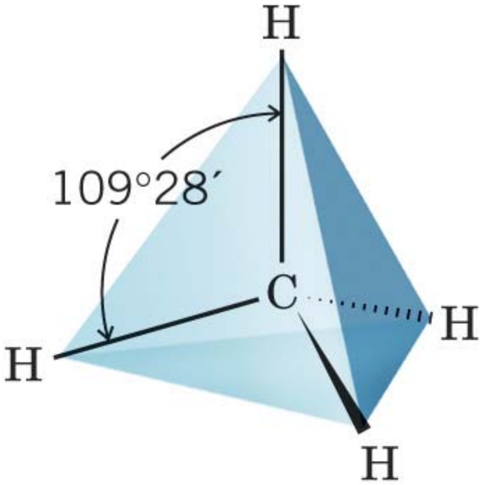
1,2-dimethyl-cyclobutane

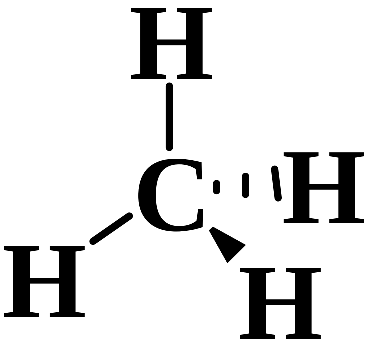
C_6H_{12}

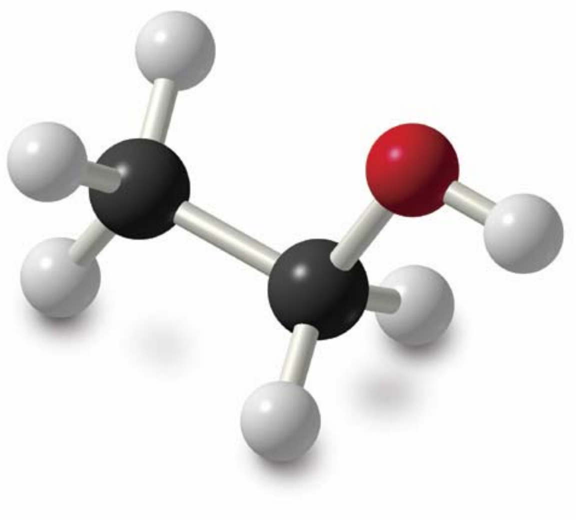
Considering C4H10, C3H8O?

■ The three-dimensional shape of organic molecules

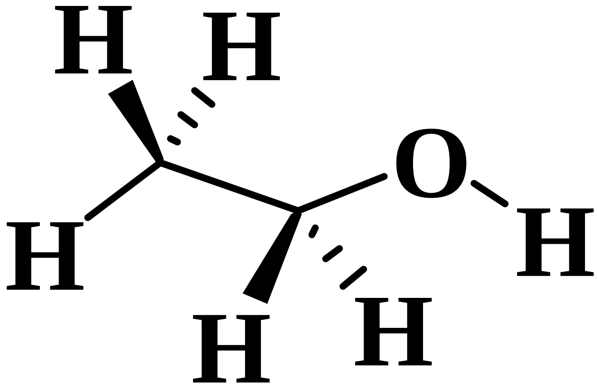








Ethyl alcohol



四) Chemical bonds: ionic bond and covalent bond

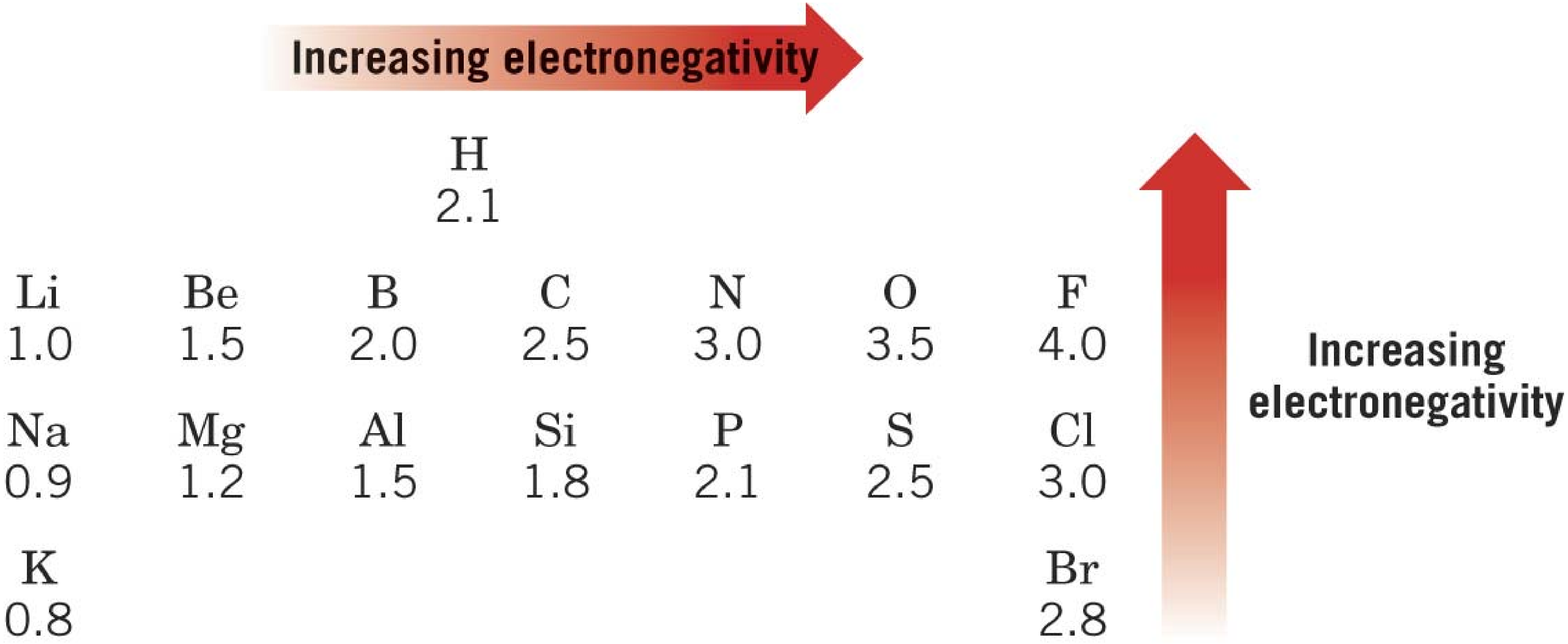
■ **Octet Rule** (Lewis):

*Atoms form bonds to produce the electron configuration of a noble gas (because the electronic configuration of noble gases is particularly stable).

*For most atoms of interest this means achieving a valence shell configuration of 8 electrons corresponding to that of the nearest noble gas.

*Atoms close to helium achieve a valence shell configuration of 2 electrons.

■ **Electronegativity(電負性)**: is a measure of the ability of an atom to attract electrons.



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						Br 2.8

■Atoms can form either ionic or covalent bonds to satisfy the octet rule

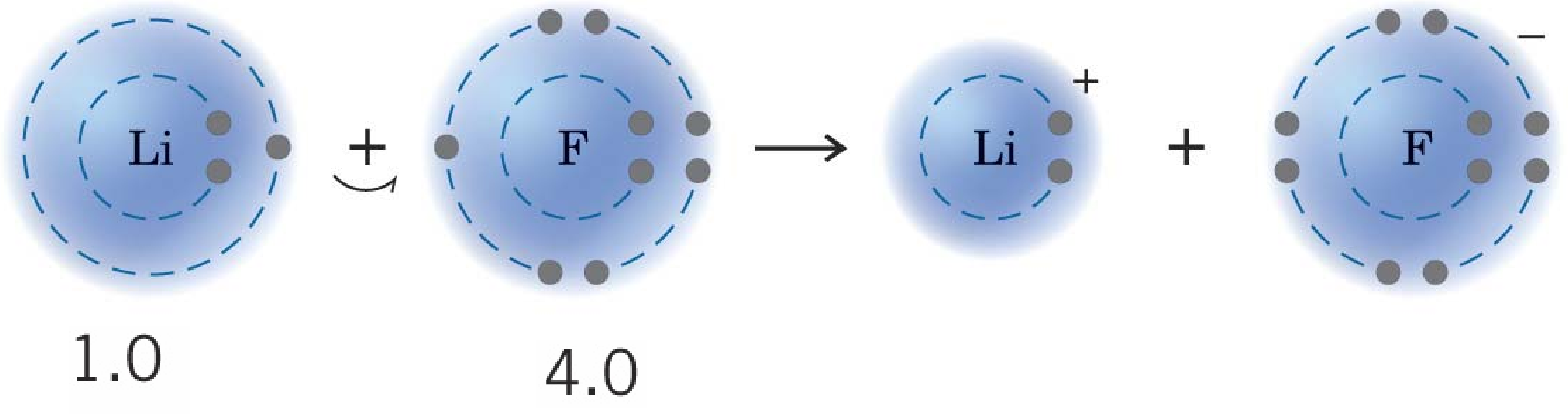
■ Ionic bond:

***When ionic bonds are formed atoms gain or lose electrons to achieve the electronic configuration of the nearest noble gas**

***In the process the atoms become ionic**

***The resulting oppositely charged ions attract and form ionic bonds**

***This generally happens between atoms of widely different electronegativities**



LiF: exist in crystalline state, often called as salt.

Considering MgBr2

■ Covalent bond:

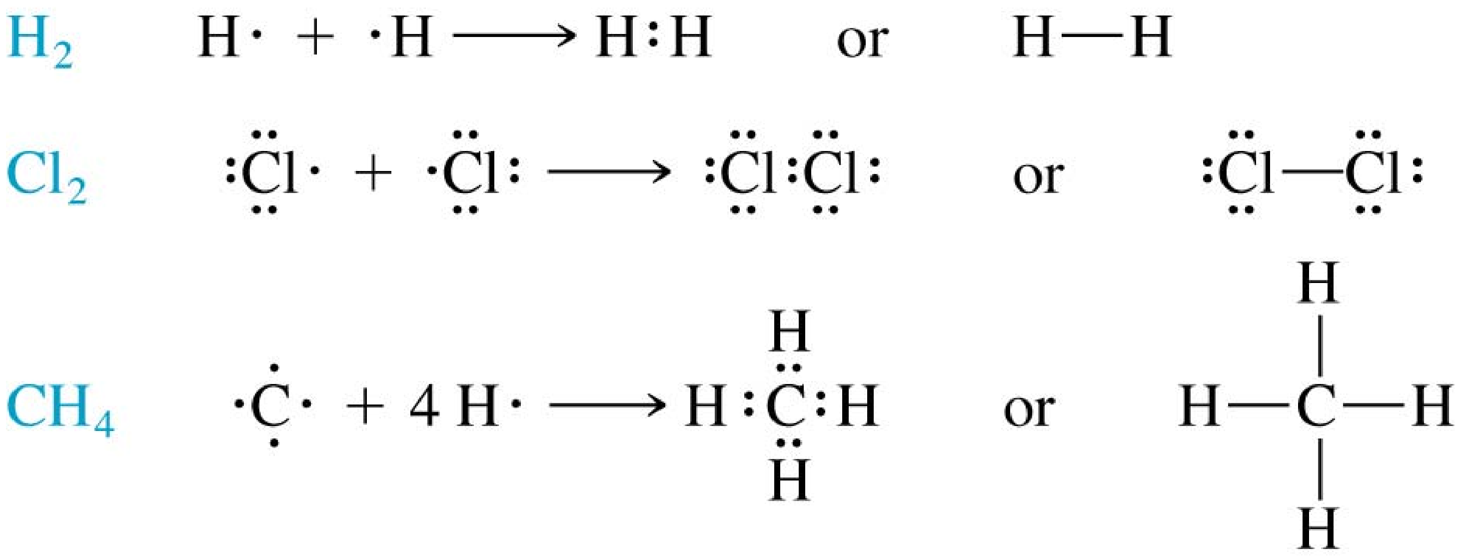
*Covalent bonds occur between atoms of similar electronegativity (close to each other in the periodic table)

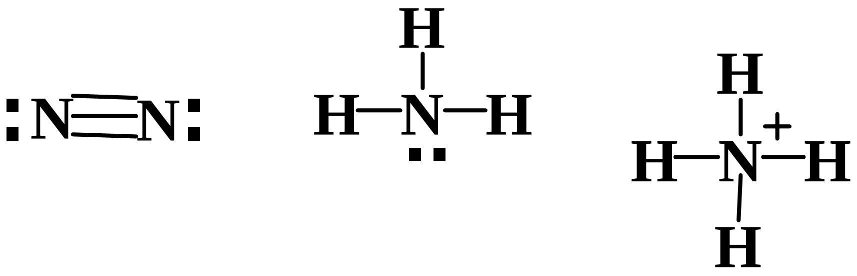
*Atoms achieve octets by *sharing* of valence electrons

*Molecules result from this covalent bonding

*Valence electrons can be indicated by dots (electron-dot formula or *Lewis structures) but this is time-consuming

*The usual way to indicate the a pair of electrons shared by two atoms is to use a line (dash formulas) (one line = two





Considering O2, (CH4)4C

- Lewis structures (shared electrons using dashs; unshared using dots) :

* Atoms bond by using their valence electrons

*The number of valence electrons is equal to the group number of the atom

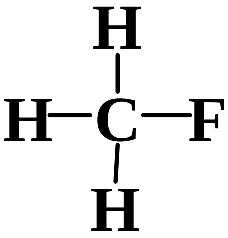
Carbon is in group 4A and has 4 valence electrons
Hydrogen is in group 1A and has 1 valence electron
Oxygen is in group 6A and has 6 valence electrons
Nitrogen is in group 5A and has 5 valence electrons

***To construct molecules, the atoms are assembled with the correct number of valence electrons**

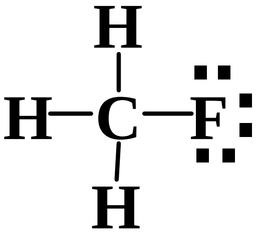
Example: write the Lewis structure of CF4

1) **The total number of valence electrons of all atoms are 4 + 3(1) + 7 = 14**

2) **Using pairs of electrons to form bonds between all atoms that are bonded to each other**



3) **According to the Octet Rule, adding the reminding non-donding electrons to the atoms (14 – 8 = 6)**

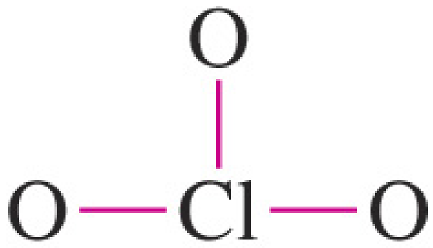


***If the molecule is an ion, electrons are added or subtracted to give it the proper charge. The structure is written to satisfy the octet rule for each atom and to give the correct charge**

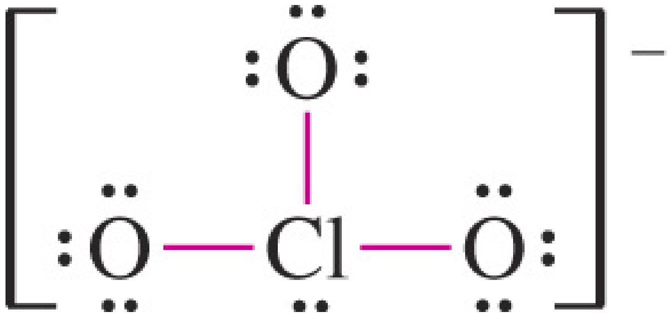
Example: **Write the Lewis structure for the chlorate ion (ClO_3^-)**

- **The total number of valence electrons including the electron for the negative charge is calculated**

$$\underset{\substack{\uparrow\\ \text{Cl}}}{7} + \underset{\substack{\uparrow\\ 3\ \text{O}}}{3(6)} + \underset{\substack{\uparrow\\ e^-}}{1} = 26$$

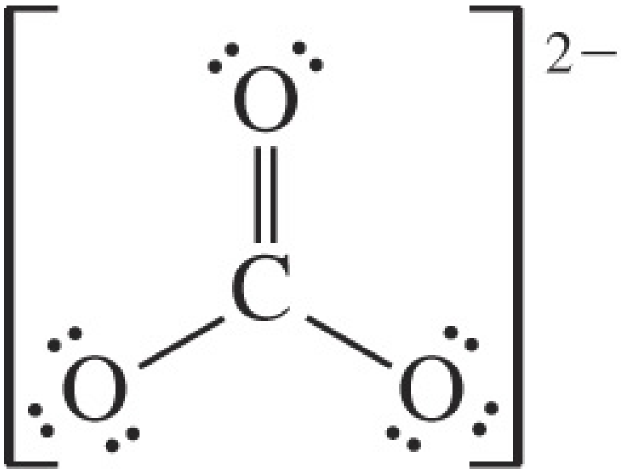


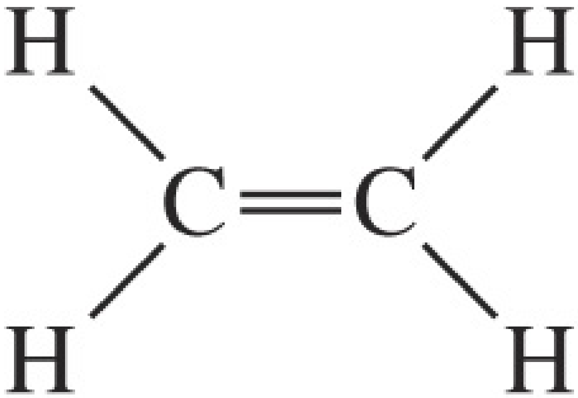
- **Three pairs of electrons are used to bond the chlorine to the oxygens**



Considering HF, CHF3

***If necessary, multiple bonds can be used to satisfy the octet rule for each atom**





and

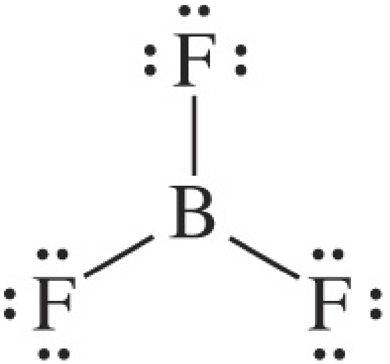
$$H-C\equiv C-H$$

Considering H2SO3, HCN, F2, HNO2, HCO3

*The octet rule applies usually to atoms in the second row of the periodic table (C, O, N, F) which are limited to valence electrons in the 2s and 2p orbitals.

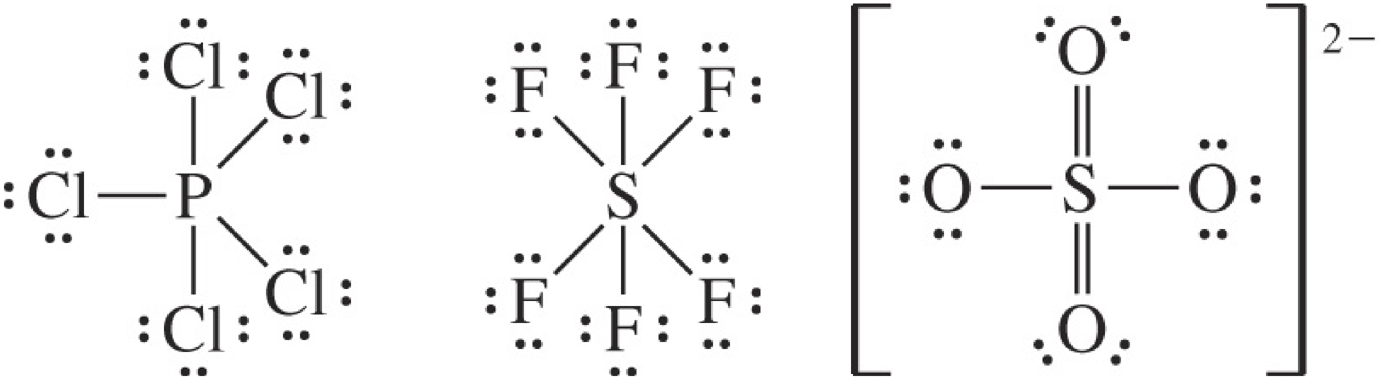
*In second row elements *fewer* electrons are possible

Example:



*In higher rows other orbitals are accessible and more than 8 electrons around an atom are possible

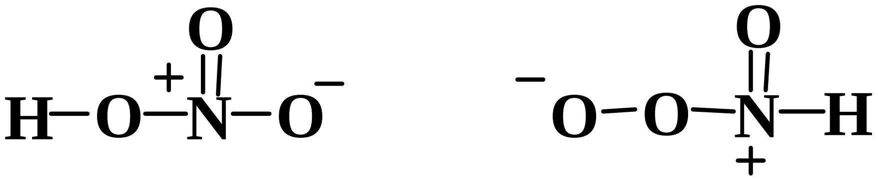
Example: PCl5 and SF6



Considering H2SO4, BH4^{-}

*Before writing Lewis structures, we must know how atoms are connected to each other.

Considering HNO3



$$\mathrm{H{-}\overset{+}{O}{-}\overset{\overset{\displaystyle O}{\|}}{N}{-}O^{-}} \qquad \mathrm{{}^{-}O{-}O{-}\underset{+}{\overset{\overset{\displaystyle O}{\|}}{N}}{-}H}$$

■Formal charge of Lewis Structure:A formal charge is a positive or negative charge on an individual atom

*The sum of formal charges on individual atoms is the total charge of the molecule or ion

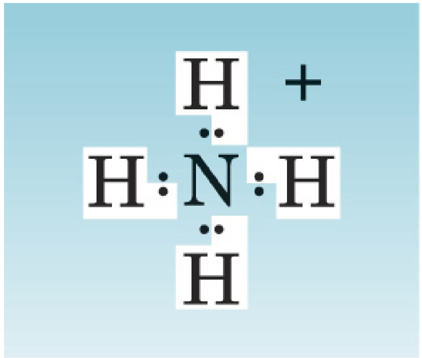
*The formal charge is calculated by subtracting the assigned electrons on the atom in the molecule from the electrons in the neutral atom

*Electrons in bonds are evenly split between the two atoms; one to each atom

*Lone pair electrons belong to the atom itself

Examples

- Ammonium ion $(NH_4)^+$

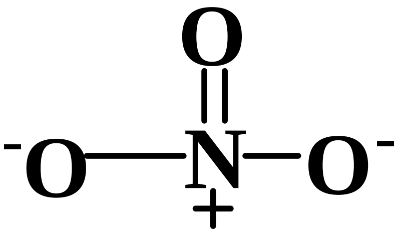


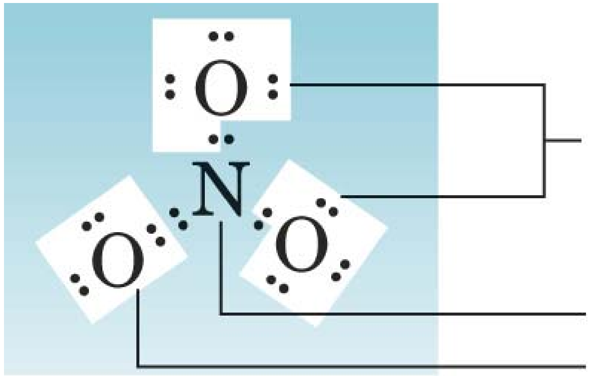
For hydrogen: valence electrons of free atom = 1
subtract assigned electrons = −1
Formal charge = 0

For nitrogen: valence electrons of free atom = 5
subtract assigned electrons = −4
Formal charge = +1

Charge on ion = 4(0) + 1 = +1

- Nitrate ion $(NO_3)^-$





Formal charge = 6 − 7 = −1

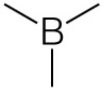
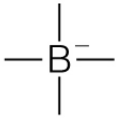
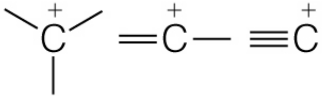
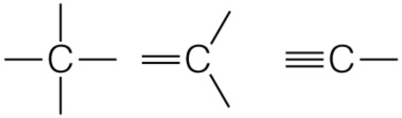
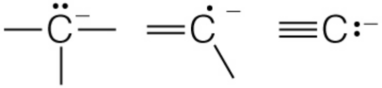
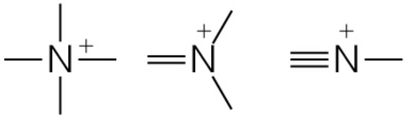
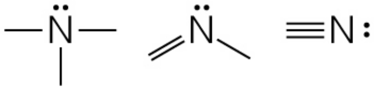
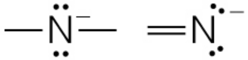
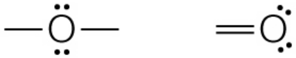
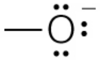
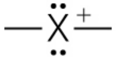
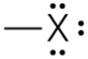
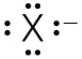
Formal charge = 5 − 4 = +1

Formal charge = 6 − 6 = 0

Charge on ion = 2(−1) + 1 + 0 = −1

Considering $NO2^-$, CN^-,$HCO3^-$, $NH2^-$, $HSO4^-$, $HC2^-$

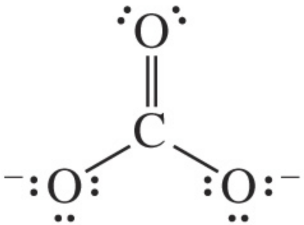
A Summary of Formal Charges

Group	Formal Charge of +1	Formal Charge of 0	Formal Charge of −1
3A			
4A			
5A			
6A			
7A		 (X = F, Cl, Br, or I)	

■Resonance in organic chemistry (very important):

*Often a single Lewis structure does not accurately represent the true structure of a molecule

*The real carbonate ion is not represented by any of the structures 1,2 or 3



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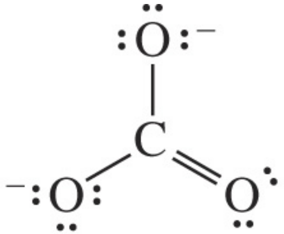
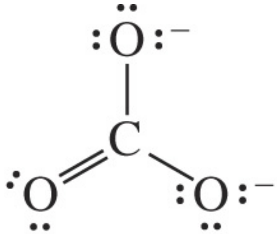
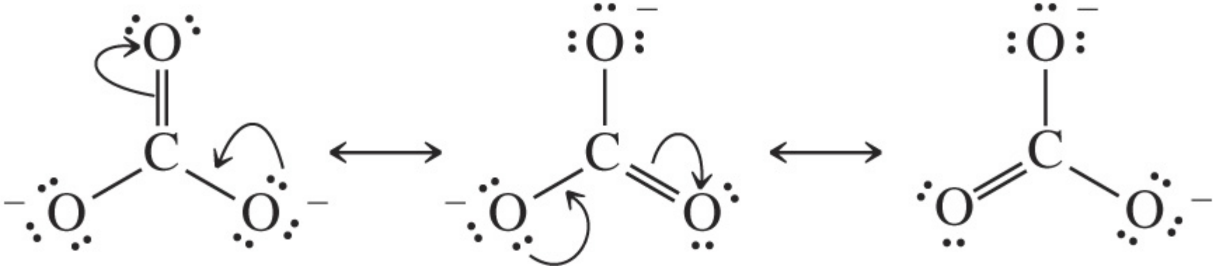


2



3

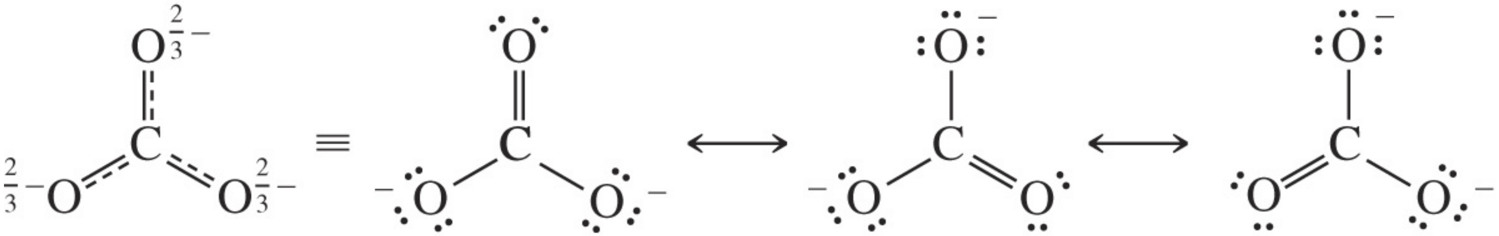
* Each atom has the noble gas configuration; we can convert one structure into another by changing the position of the electrons, without changing the relative positions of the atomic nuclei.



Curve arrow: movement of a electron pair

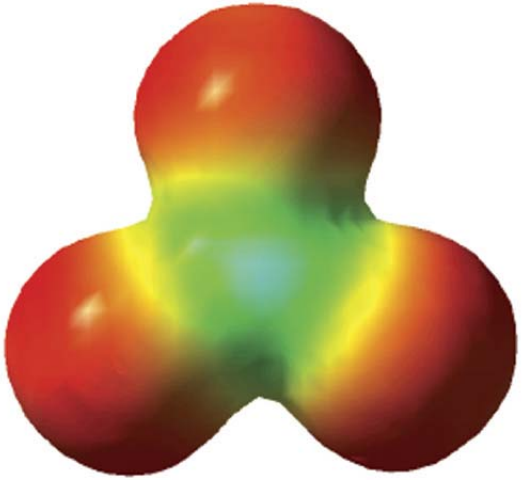
*X-ray studies showed that all of the carbon-oxygen bonds are of equal length, therefore none of three structures will be true representation for the molecule.

- The real structure is a resonance hybrid or mixture of all three Lewis structures
- Double headed arrows are used to show that the three Lewis structures are resonance contributors to the true structure



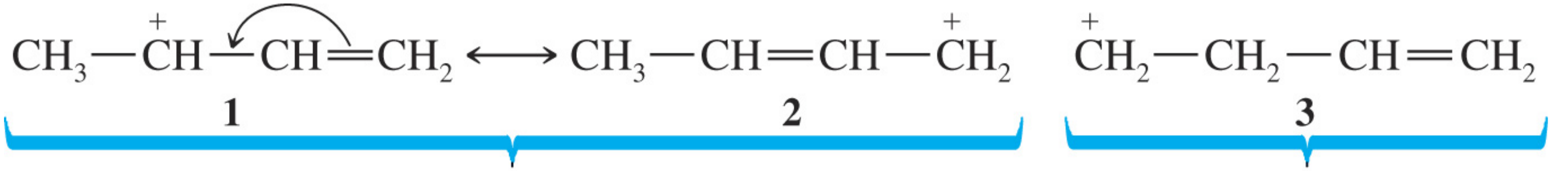
- The use of equilibrium arrows is incorrect since the three structures do not equilibrate; the true structure is a hybrid (average) of all three Lewis structures

*A calculated electrostatic potential map of carbonate clearly shows the electron density is spread equally among the three oxygen atoms.



*Summary of rules for resonance:

1) Resonance structure exist only on paper!!!
2) Wring resonance structure we are only to allow to move electrons

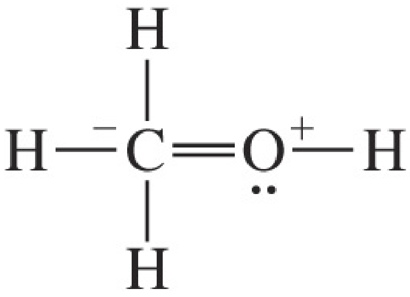


$$CH_3-\overset{+}{C}H-CH=CH_2 \longleftrightarrow CH_3-CH=CH-\overset{+}{C}H_2 \qquad \overset{+}{C}H_2-CH_2-CH=CH_2$$

These are resonance structures.

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

3) All structure must be proper Lewis structure

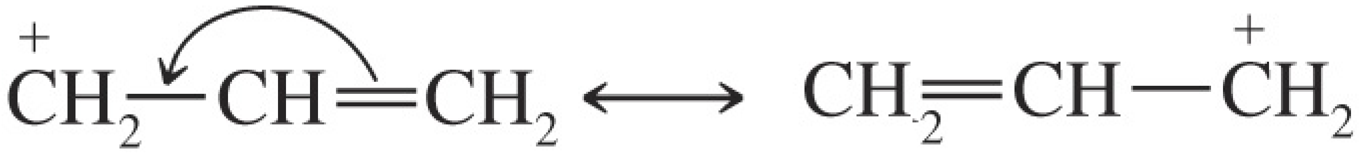


$$\mathrm{H{-}\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{-}{C}}}{=}\underset{\cdot\cdot}{\overset{+}{O}}{-}H}$$

This is not a proper resonance structure for methanol because carbon has five bonds. Elements of the first major row of the periodic table cannot have more than eight electrons in their valence shell.

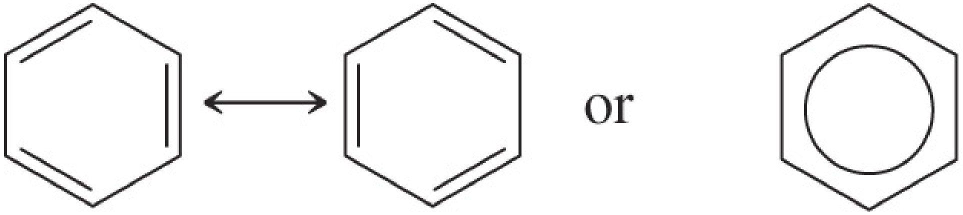
4) The energy of actual molecule is lower than the energy that might be estimated for any contributing structure.

5) Equivalent resonance forms make equal contributions to the structure of the real molecule. Structures with equivalent resonance forms tend to be greatly stabilized



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

1 **2**

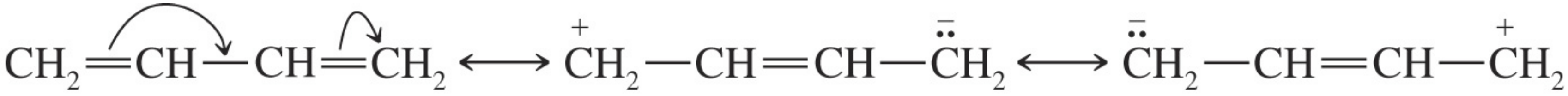


Resonance structures for benzene

Representation of hybrid

The two resonance forms of benzene contribute equally and greatly stabilize it

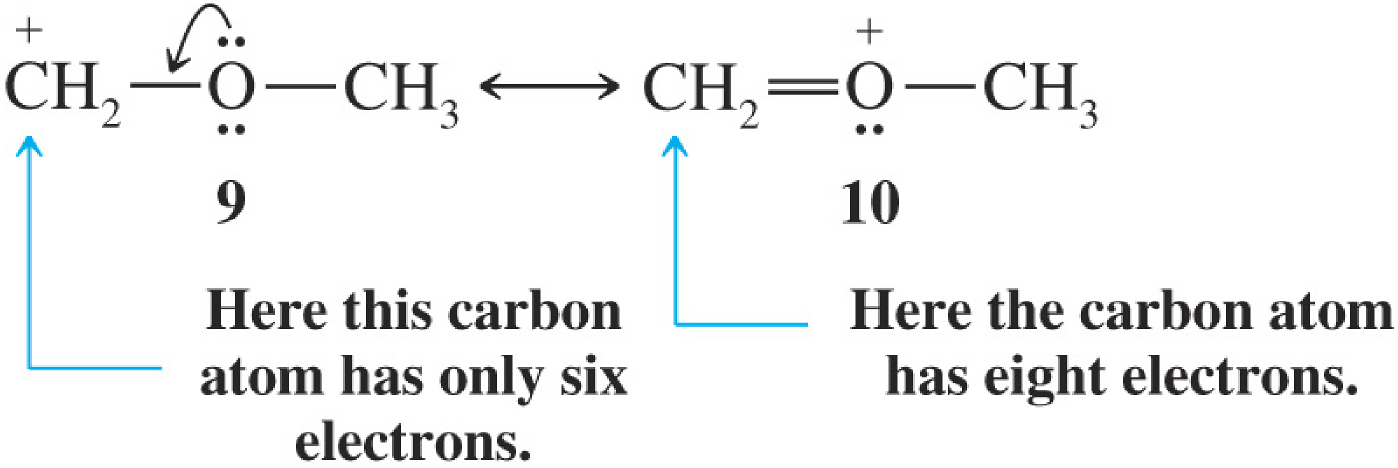
6) The more stable a structure is, the greater is its contribution to the hybrid:



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

6 **7** **8**

This structure is the most stable because it contains more covalent bonds.

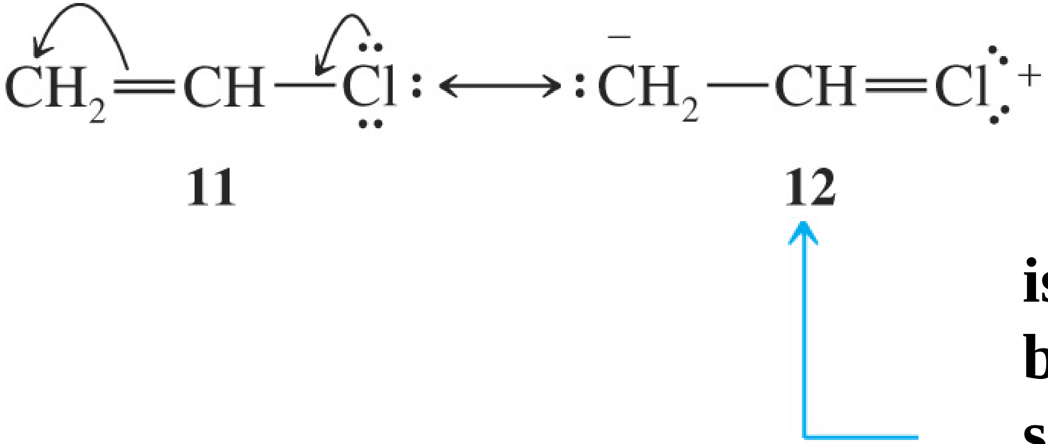


$$\overset{+}{C}H_2-\ddot{\underset{..}{O}}-CH_3 \longleftrightarrow CH_2=\overset{+}{\underset{..}{O}}-CH_3$$

9 **10**

Here this carbon atom has only six electrons.

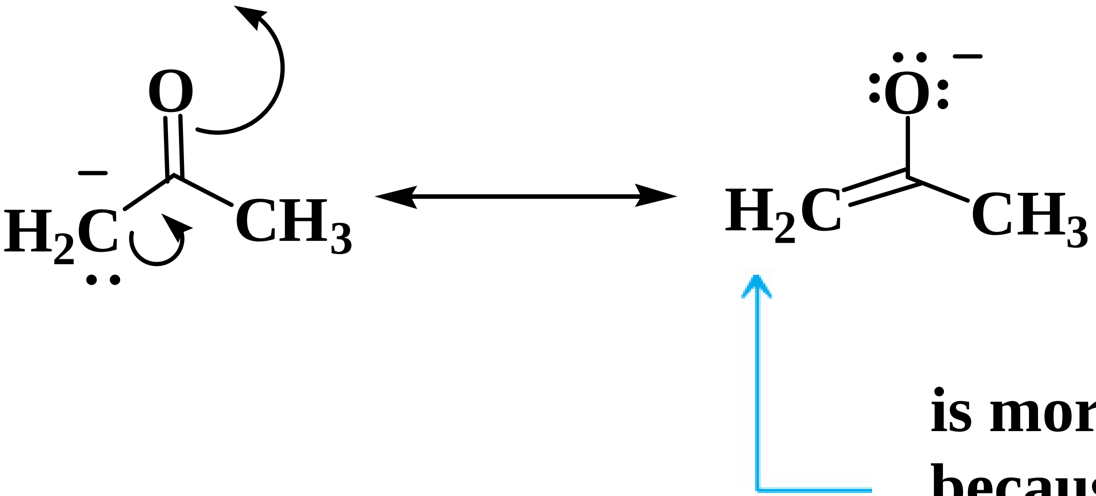
Here the carbon atom has eight electrons.



$$CH_2=CH-\ddot{\underset{..}{Cl}}: \longleftrightarrow :\overset{-}{C}H_2-CH=\overset{+}{Cl}:$$

11 **12**

is less important because it has charge separation

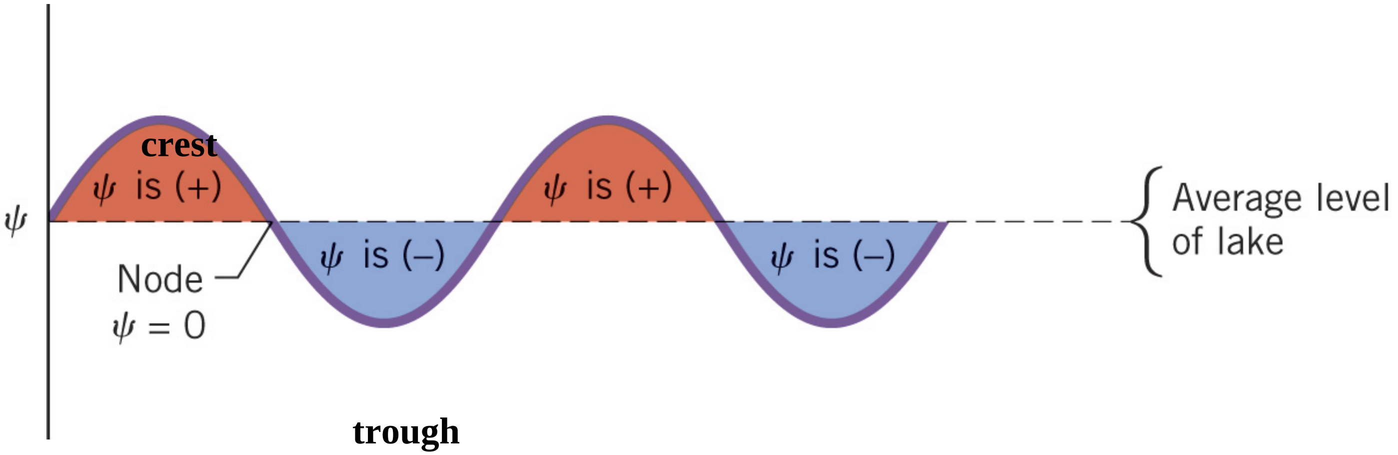


is more important because negative charge on higher electronegtive atom

五) Quantum mechanics, atomic orbitals and molecular orbitals

■ Wave function (ψ)

***By taking into account the wave nature of electrons, Schrödinger described a wave equation for a hydrogen atom.**
***Wave Equations are used to calculate: 1) The energy associated with the state of the electron 2) The probability of finding the electron in a particular state**
***A wave equation is solved to yield a series of wave functions for the atom.**
***The wave functions psi (ψ) describe a series of states with different energies for each electron:**



*** Wave equations can reinforce each other if they have the same phase sign or interfere with each other if they have different signs**

■ Atomic orbitals

* Born: The physical reality of Ψ is that when squared (Ψ^2) it gives the probability of finding an electron in a particular location in space (x, y, z).

*Plots of Ψ^2 in three dimensions generate the shape of *s*, *p*, *d* and *f* atomic orbitals (AOs)

*Only *s* and *p* orbitals are very important in organic chemistry

Orbital: a region in space where the probability of finding an electron is large.

*The typical representation of orbitals are those volumes which contain the electron 90-95% of the time

*The characters of *1s*, *2s* and *2p* orbitals:

1) 1*s* and 2*s* orbitals are spheres centered around the nucleus. Each orbital can accommodate 2 electrons

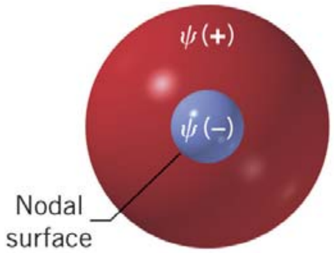
2) The 2*s* orbital is higher in energy and contains a nodal surface ($\Psi = 0$) in its center

3) Each 2*p* orbital has two nearly touching spheres (or lobes). One sphere has a positive phase sign and the other a negative phase sign; a nodal plane separates the spheres

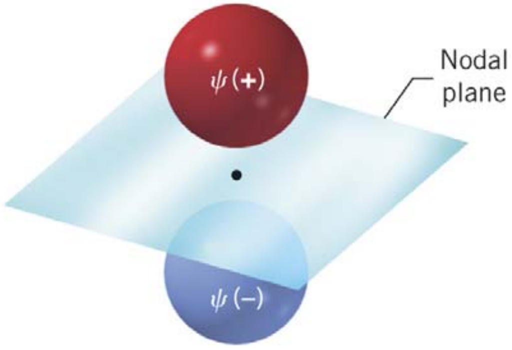
4 There are three 2*p* orbitals which are perpendicular (orthoganol) to each other

5)Each *p* orbital can accommodate 2 electrons for a total of 6 electrons, All three *p* orbitals are <u>degenerate (equal in energy)</u>, The 2*p* orbitals are higher in energy than the 1*s* or 2*s*

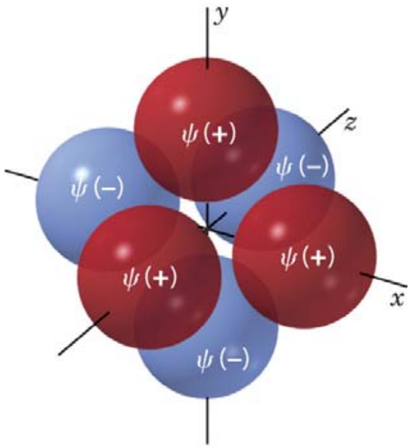
1s Orbital



2s Orbital



A pure 2*p* orbital
(unhybridized)



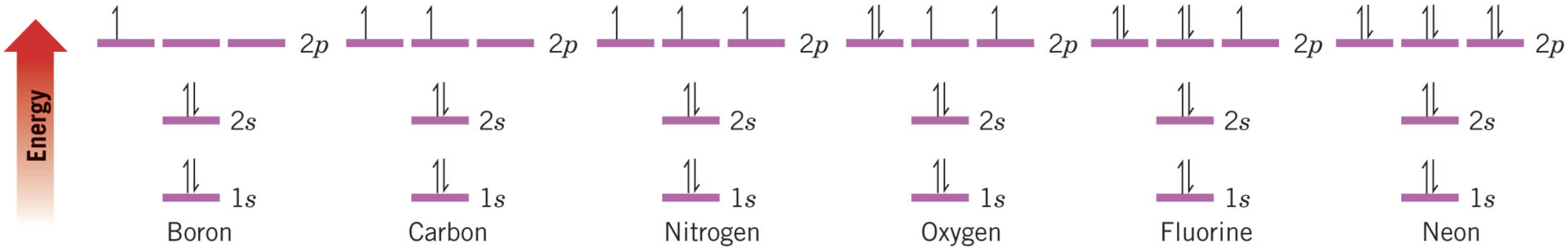
Three mutually perpendicular
(orthogonal) 2p orbitals
(unhybridized)

5) The sign of the wave function *does not* indicate a greater or lesser probability of finding an electron in that location

6) The greater the number of nodes in an orbital the higher its energy. 2*s* and 2*p* orbitals each have one node and are higher in energy than the 1*s* orbital which has no nodes

7) Atoms can be assigned electronic configuration using the following rules:
a) Aufbau Principle: The lowest energy orbitals are filled first
b) Pauli Exclusion Principle: A maximum of two spin paired electrons may be placed in each orbital
c) Hund's Rule: One electron is added to each degenerate (equal energy orbital) before a second electron is added

8) The greatest utility of atomic orbitals is in using them as models for understanding how atoms combine to form molecules.



***Electronic Configurations of Some Second Row Elements**

■ Molecular Orbitals (MOs) of H_2

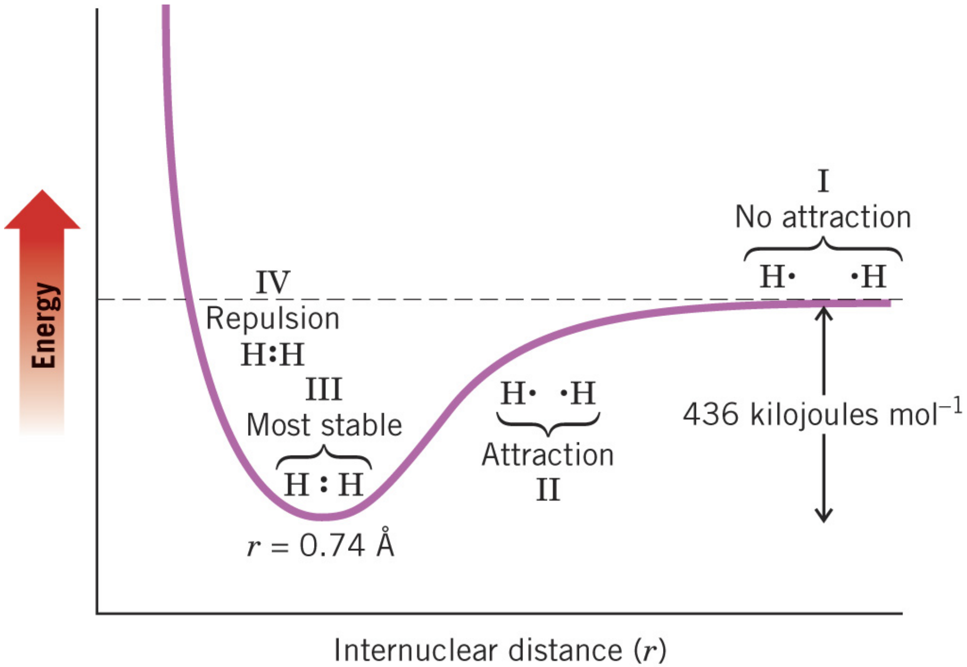
1) A simple model of bonding is illustrated by forming molecular H_2 from H atoms and varying distance:

Region I: The total energy of two isolated atoms

Region II: The nucleus of one atom starts attracting the electrons of the other; the energy of the system is lowered. The attraction more than compensates for the repulsive force between the two nuclei.

Region III: at 0.74 Å the attraction of electrons and nuclei exactly balances repulsion of the two nuclei; this is the bond length of H_2

Region IV: energy of system rises as the repulsion of the two nuclei predominates



The problems associated with this model:

a) **This simple model of bonding does not take into account the fact that electrons are not stationary but constantly moving around.**

b) **It violates the Heisenberg uncertainty principle which states, the position and momentum of an electron cannot simultaneously be known.**

2) Quantum mechanics solves this problem by talking about the <u>probability</u> (Ψ^2) of finding an electron at a certain location in space instead of where the electron is precisely.

As two atoms approach each other their atomic orbitals (AOs) overlap to become molecular orbitals (MOs) .The wave functions of the AOs are combined to yield the new wave functions of the MOs. <u>The number of MOs that result must always equal the number of AOs used.</u>

3) Binding MO (Ψ_{molec}) and Anti-bonding molecular orbital (Ψ^*_{molec}): of H2:

*As the hydrogen atoms approach each other their 1*s* orbitals (Ψ_{1s}) begin to overlap

*The MOs that form encompass both nuclei

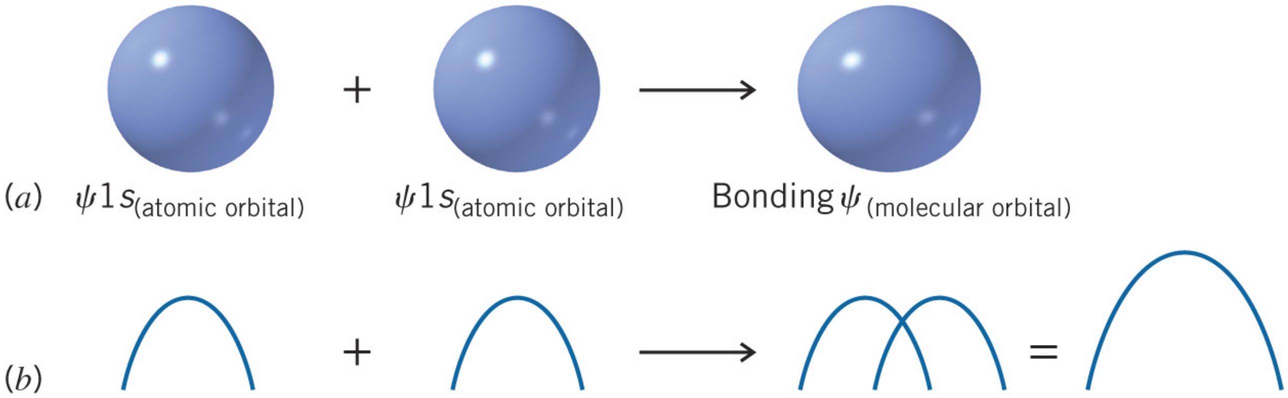
*The electrons are not restricted to the vicinity of one nucleus or another

*Each MO has a maximum of 2 spin-paired electrons

*Addition of wave functions of the two atoms leads to a ***bonding molecular orbital***

*Subtraction of wave functions of the two atoms leads to an ***anti-bonding molecular orbital***

*The mathematic operation by which wave functions are added or subtracted is called the linear combination of atomic orbitals (LCAO)



*AOs combine by addition (the AOs of the same phase sign overlap)

*The wave functions reinforce

*The value of Ψ increases between the two nuclei

*The value of Ψ^2 (electron probability density) in the region between the two nuclei increases

*The two electrons between the nuclei serve to attract the nuclei towards each other

*This is the ground state (lowest energy state) of the MO

Anti-bonding molecular orbital (Ψ^*_{molec}):

*Formed by interaction of AOs with opposite phase signs

*Wave functions interfere and a node is produced ($\Psi = 0$)

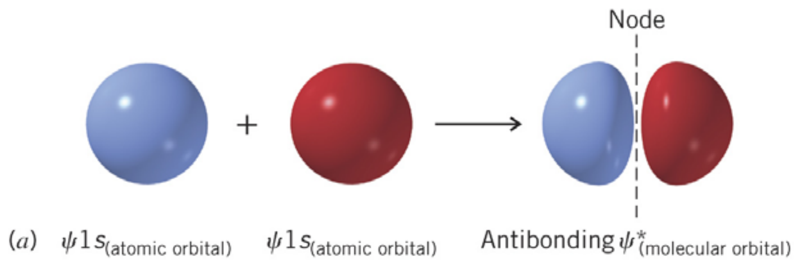
*In the region between the two nuclei, a node is produced

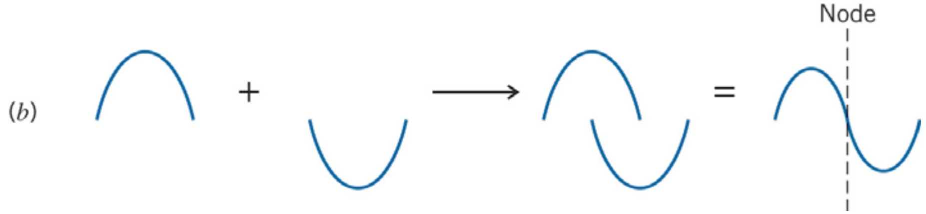
*On either side of the node Ψ is small

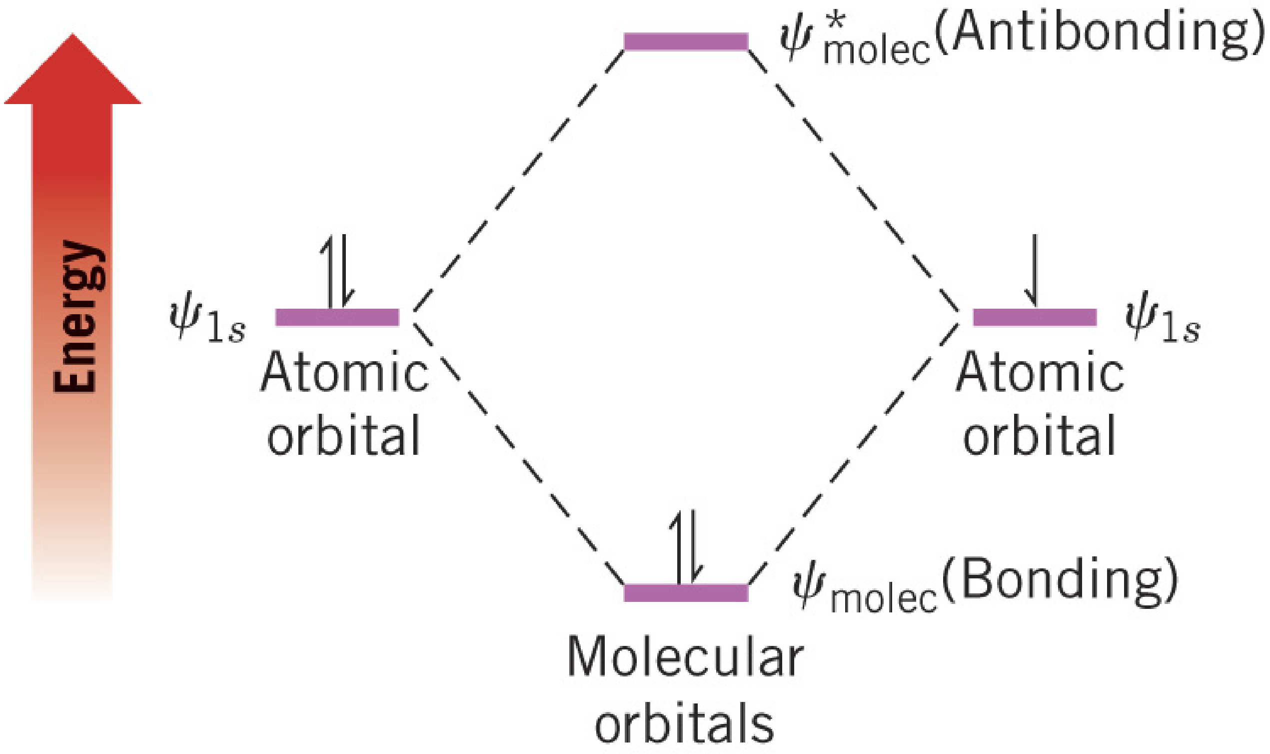
*Ψ^2 (electron probability density) is small

*Electrons in the anti-bonding orbital avoid the region between the two nuclei

*Repulsive forces between the nuclei predominate and electrons in anti-bonding orbitals make nuclei fly apart


Node
(a)
$\psi 1s_{\text{(atomic orbital)}}$
+
$\psi 1s_{\text{(atomic orbital)}}$
Antibonding $\psi^*_{\text{(molecular orbital)}}$

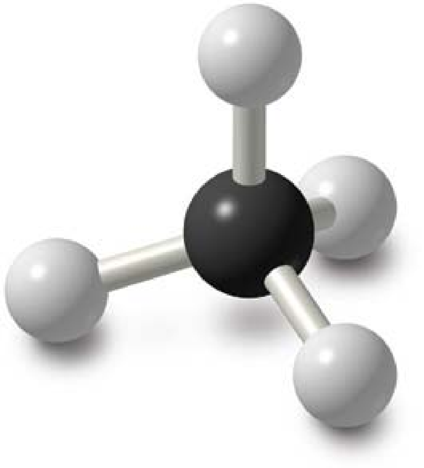

Node
(b)
+
=


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

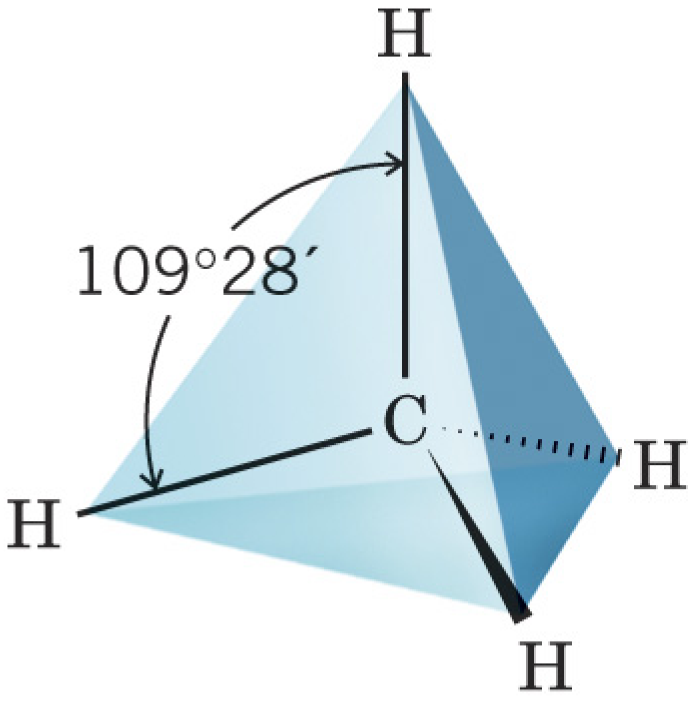
*** The energy of electrons in the bonding orbitals is substantially less than the energy of electrons in the individual atoms, the energy of electrons in the anti-bonding orbitals is substantially more.**

***In the ground state of the hydrogen molecule electrons occupy the lower energy bonding orbital only**

■ *sp*^{3} Hybridization



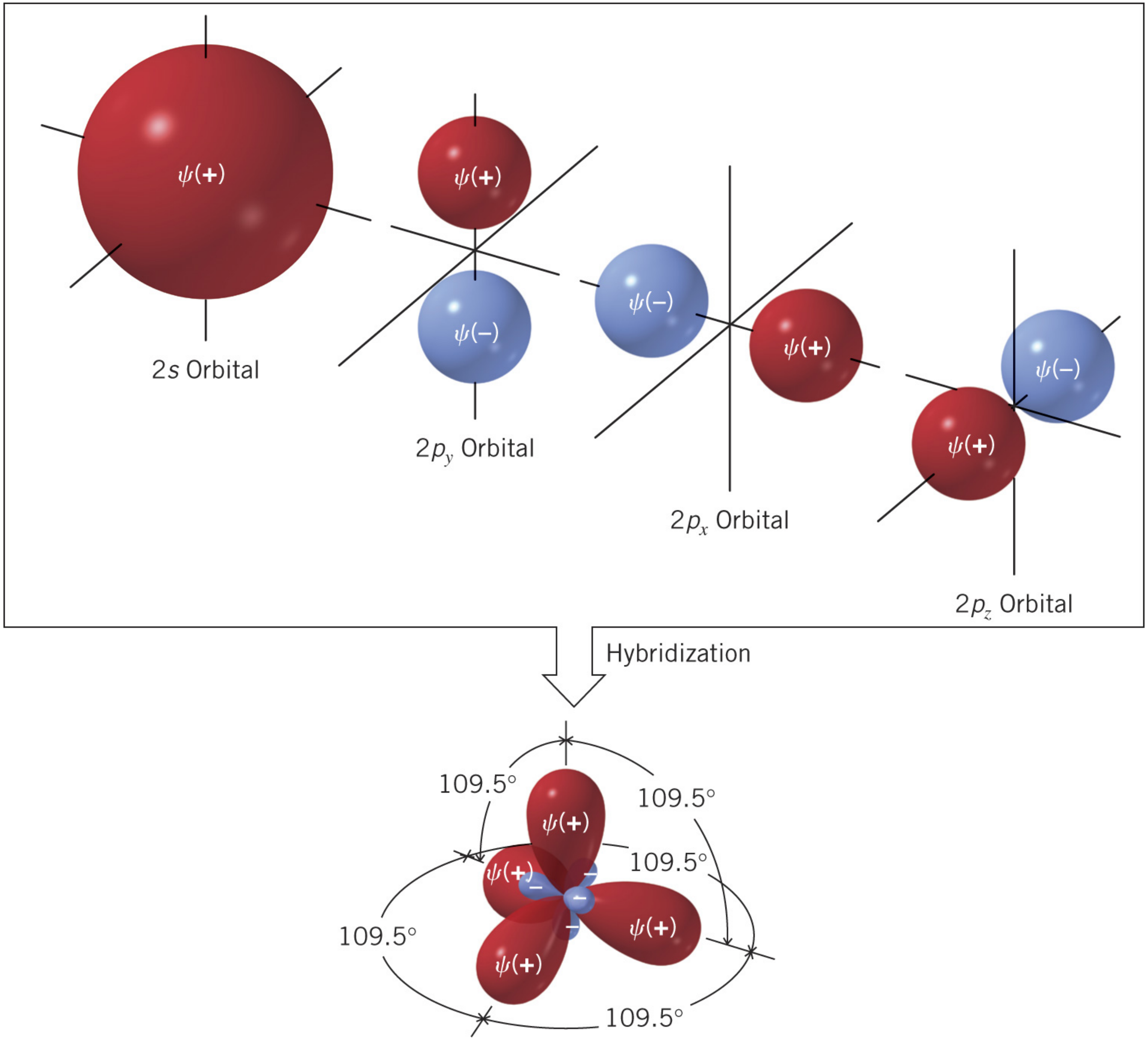
Methane



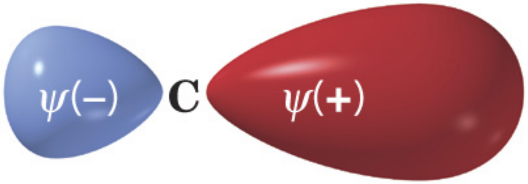
Tetrahedral

***When taken alone, the simple s and p orbital do not provide a satisfactory model for the tetravelent-tetrahedral carbon of methane.**

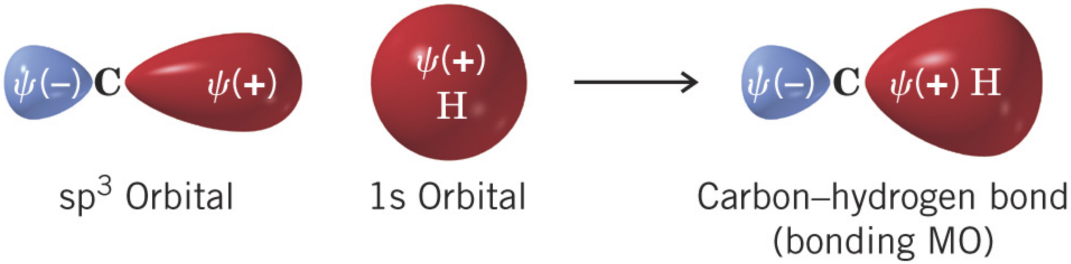
***Orbital hybridization**: the combination of individual wave function for s and p orbitals to obtained wave function of new orbitals (*sp*^{3}, *sp*^{2}, *sp* hybrid atomic orbitals).**



*** In addition to accounting properly for the shape of methane, the hybridization model also explain the very strong bonds that are formed between carbon and hydrogen.**

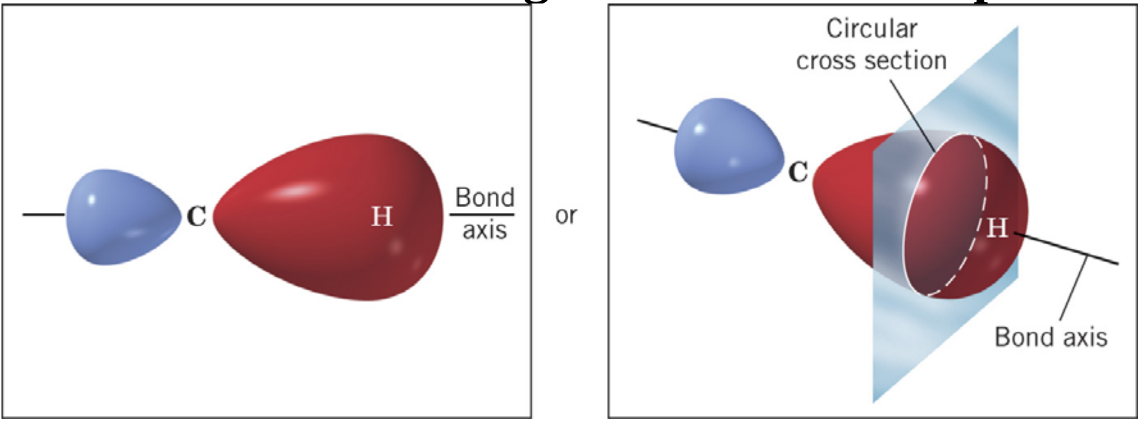


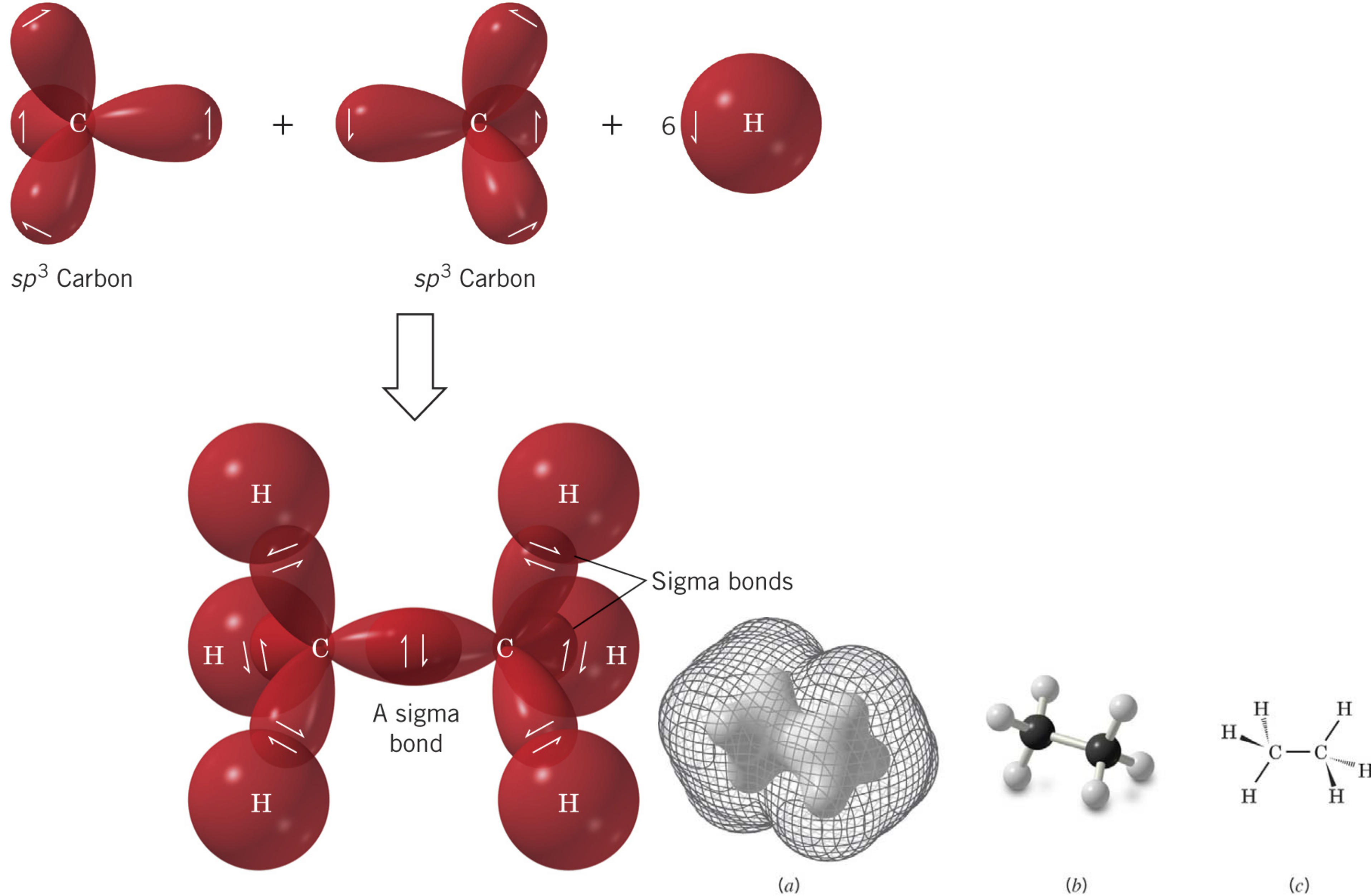
The positive lobe of sp3 orbital is large and is extended into space



The overlap between it and 1s orbital o hydrogen is also large

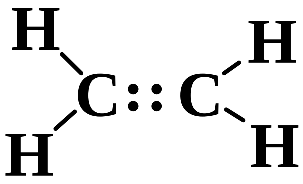
***sigma bond (δ): the bond formed by orbitals overlapping in circularly symmetrical in cross section when viewed along the bond axis. All pure single bonds are sigma bonds.**




C
+
C
+
6
H
sp^3 Carbon
sp^3 Carbon
H
H
Sigma bonds
H
C
C
H
A sigma bond
H
H
H
H
H
C
C
H
H
H

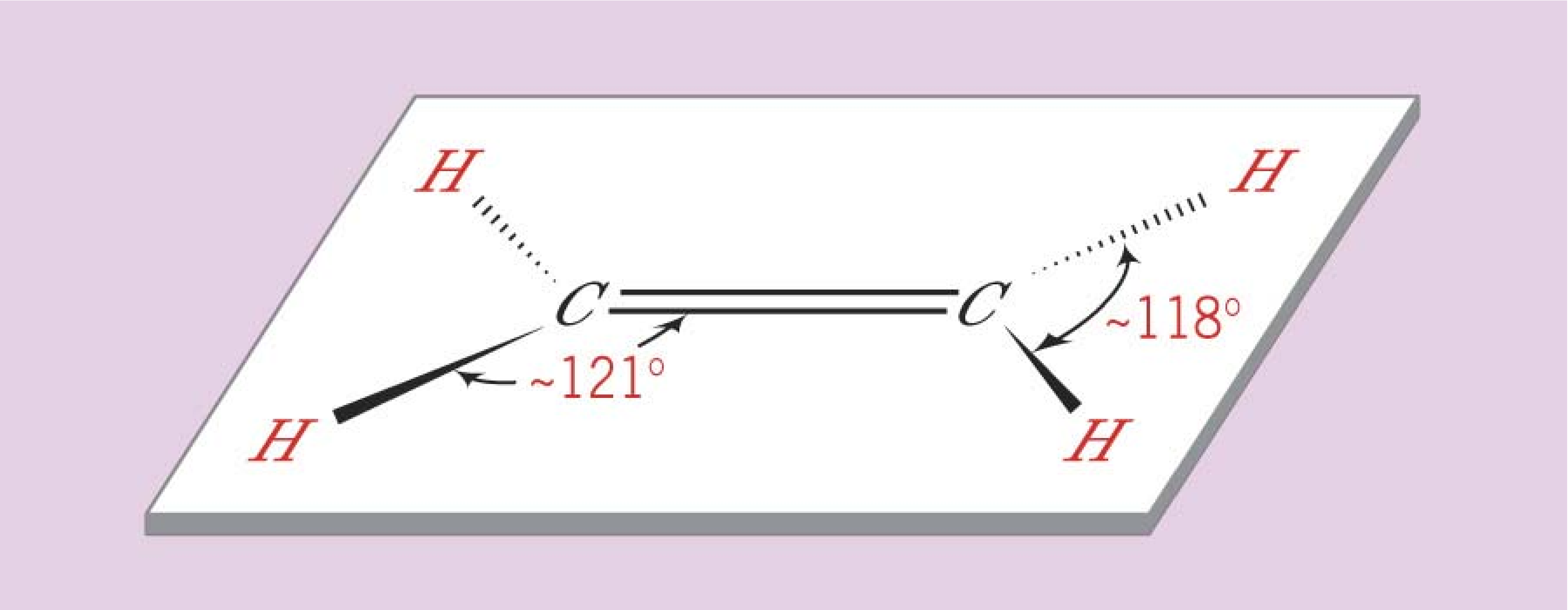
(*a*) (*b*) (*c*)

■*sp*^{2} Hybridization, *pi* (π) bond:



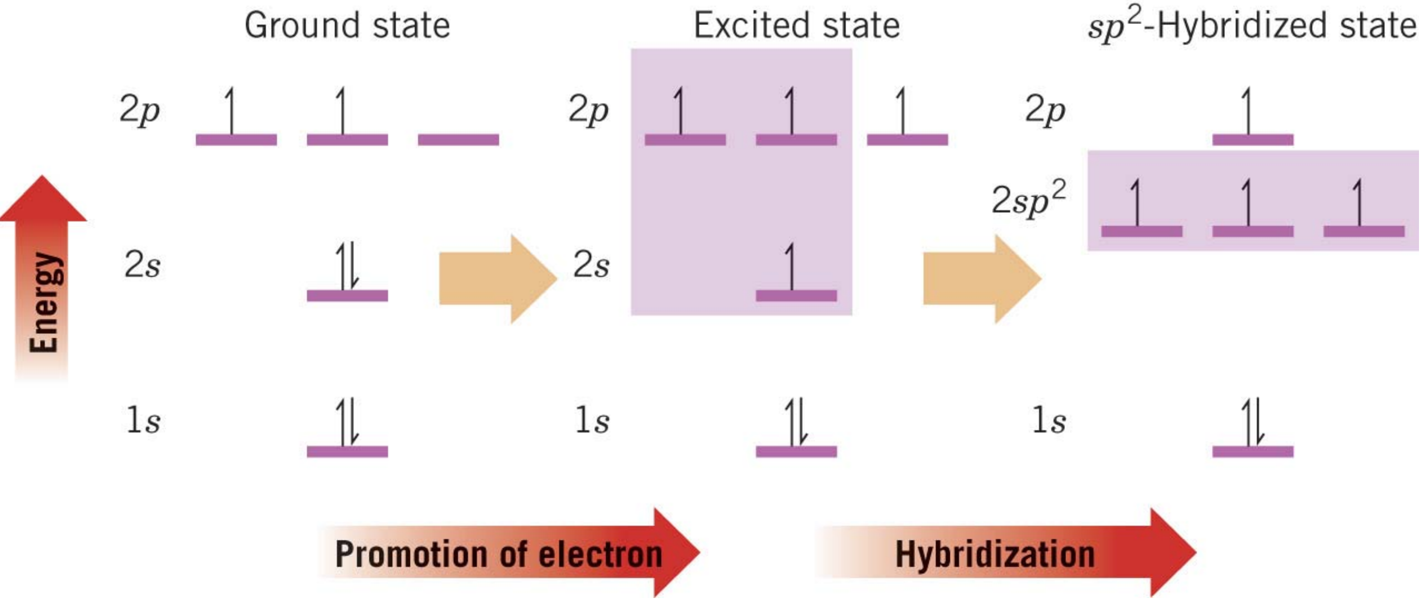
$H_2C{=}CH_2$

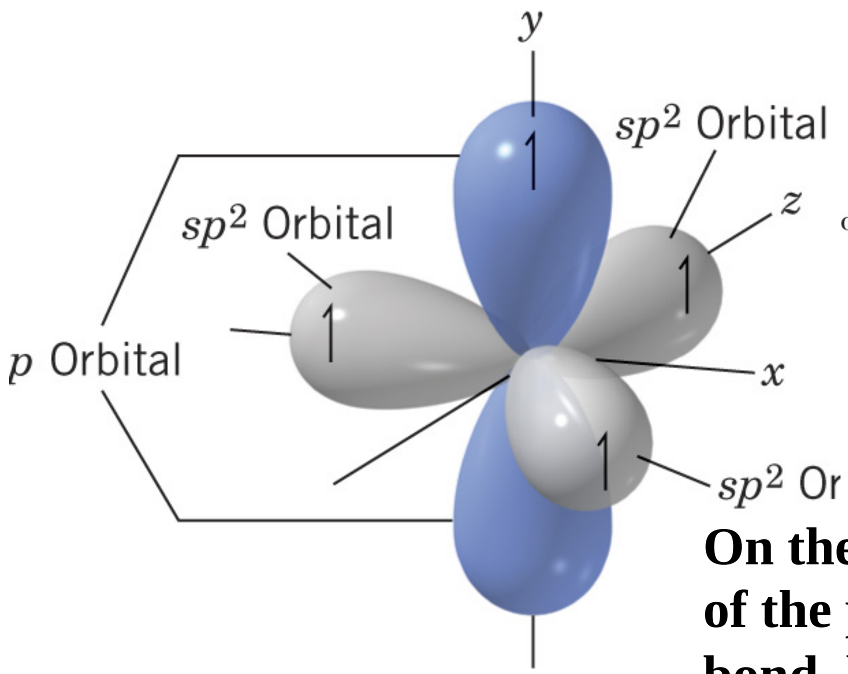
ethene

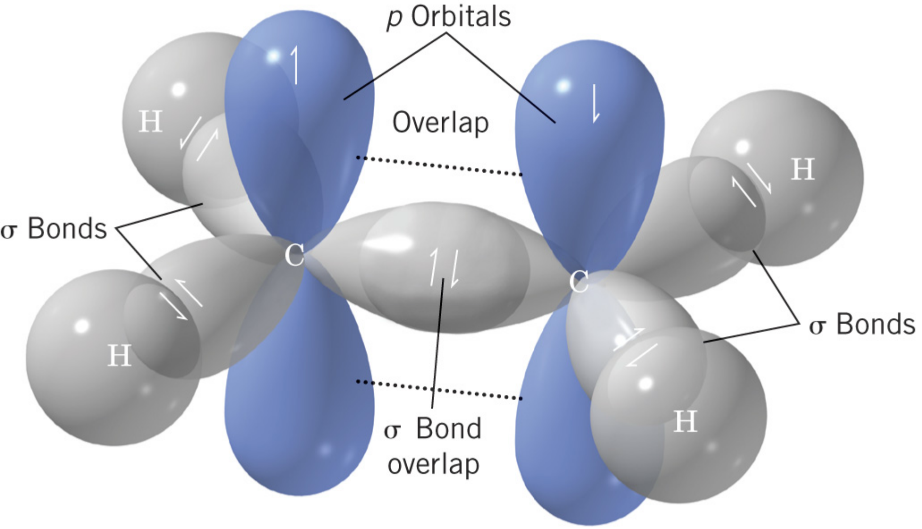


Trigonal planar

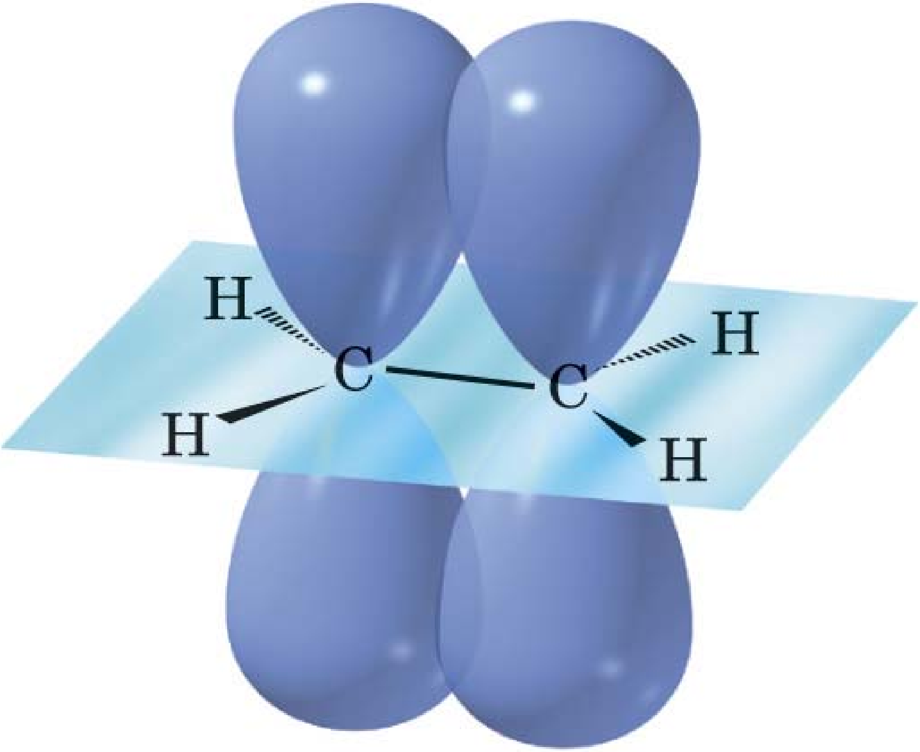
sp^2 Hybridization:





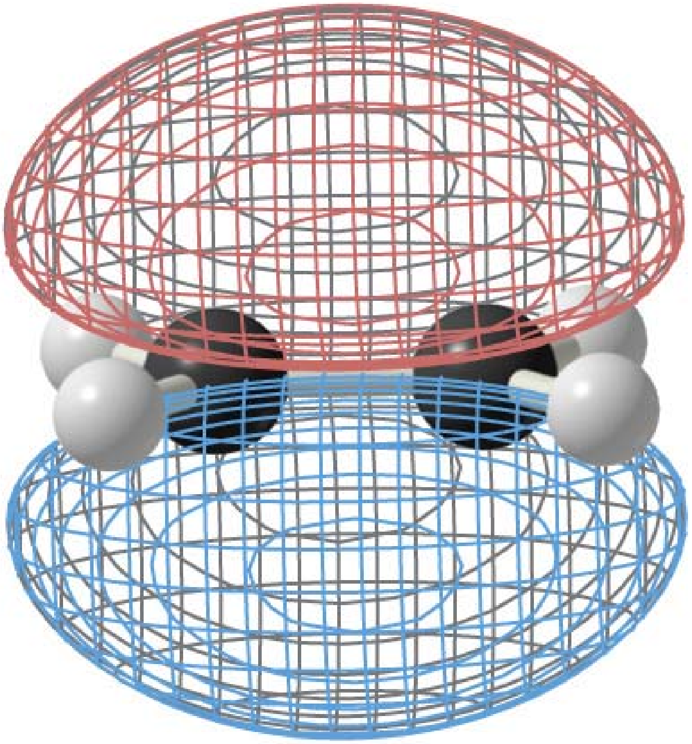


On the δ-bond framework, the sideways overlap of the p orbitals results in a new type of covalent bond, known as a <u>pi (π) bond</u>

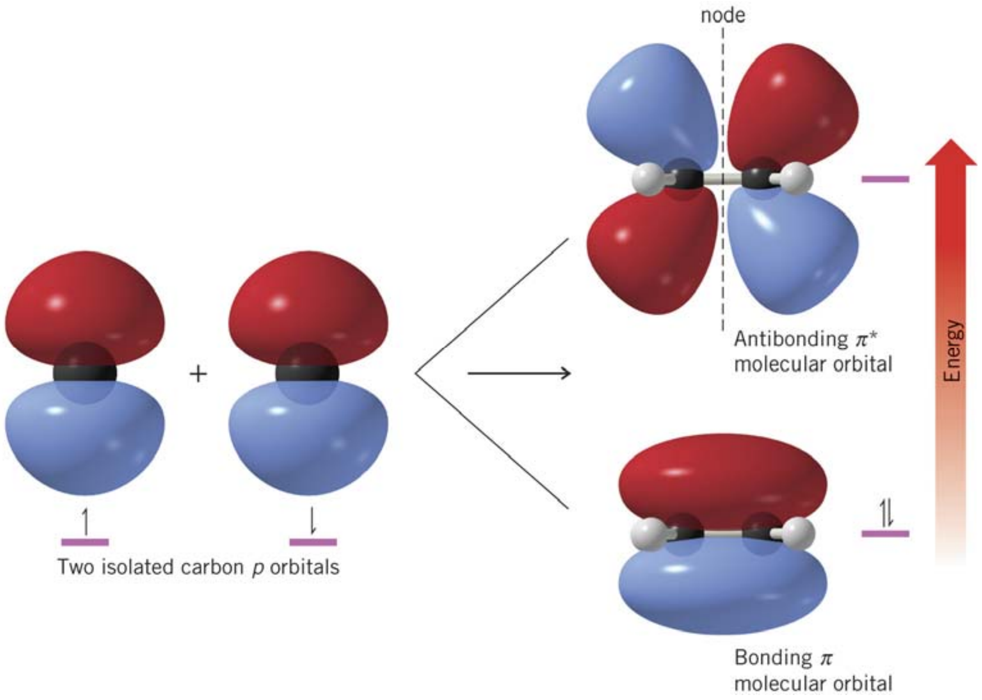


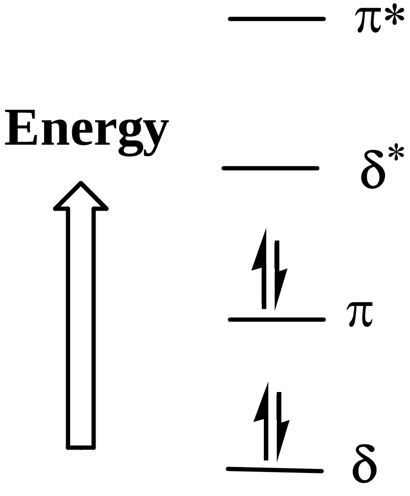
π Bond

(*a*)

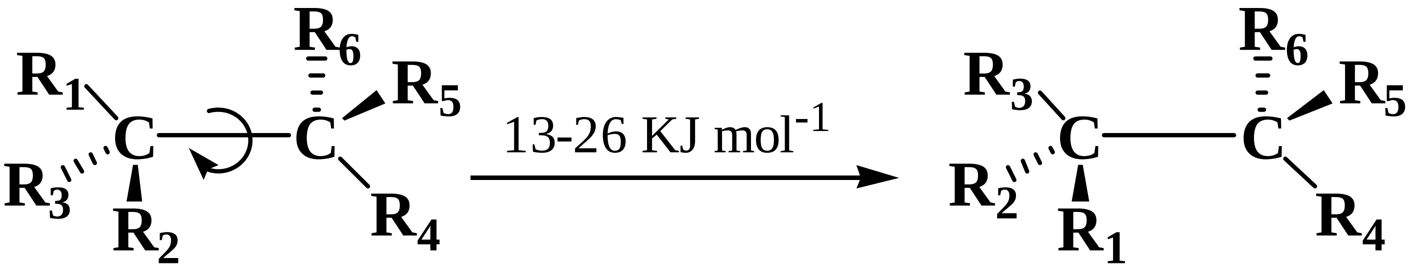


(*b*)

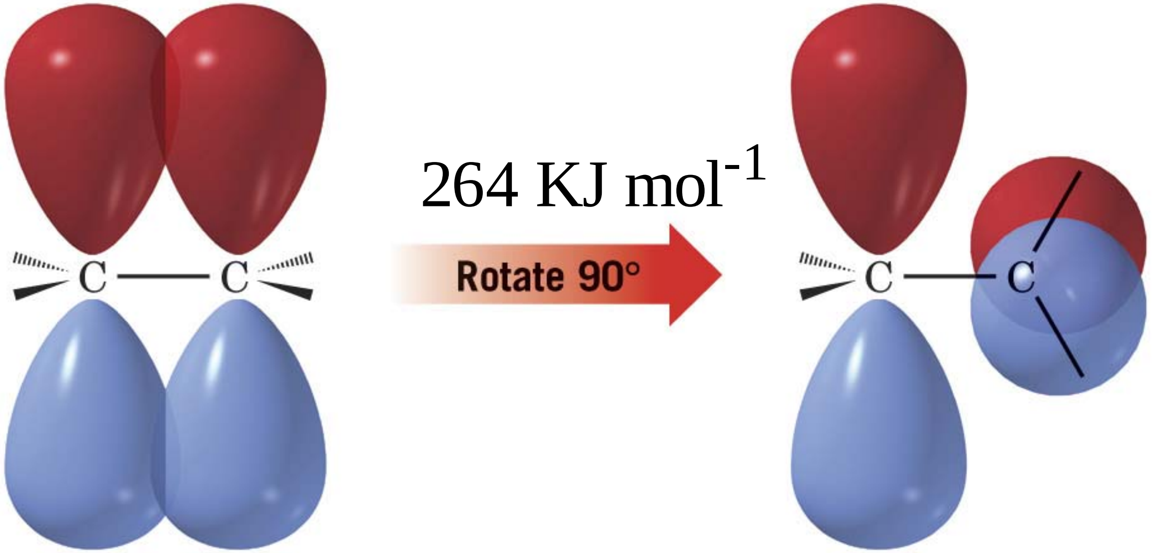

node
+
Two isolated carbon p orbitals
Antibonding π^* molecular orbital
Energy
Bonding π molecular orbital


π*
Energy
δ*
π
δ

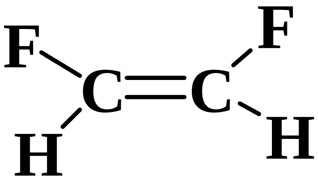
Cis and Trans Isomers (Stereoisomers):



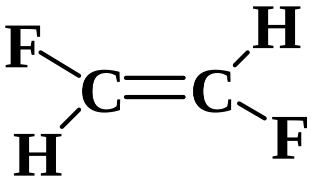
13-26 KJ mol^{-1}



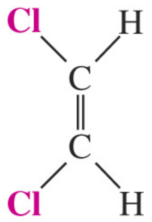
264 KJ mol^{-1}



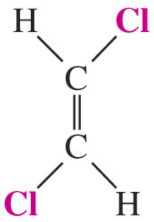
Cis



Trans

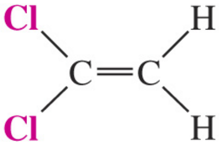


cis-1,2-Dichloroethene

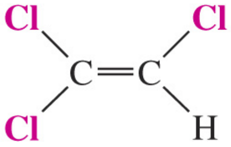


trans-1,2-Dichloroethene

The two isomers are not superposable to each other (stereoisomers)



1,1-Dichloroethene
(no cis–trans isomerism)



1,1,2-Trichloroethene
(no cis–trans isomerism)

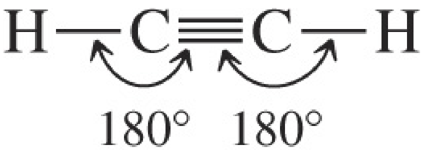
Cis-trans **isomerism is not possible if one carbon of the double bond has two identical groups**

Exercise: which of the following alkenes can exist as cis-trans isomer?

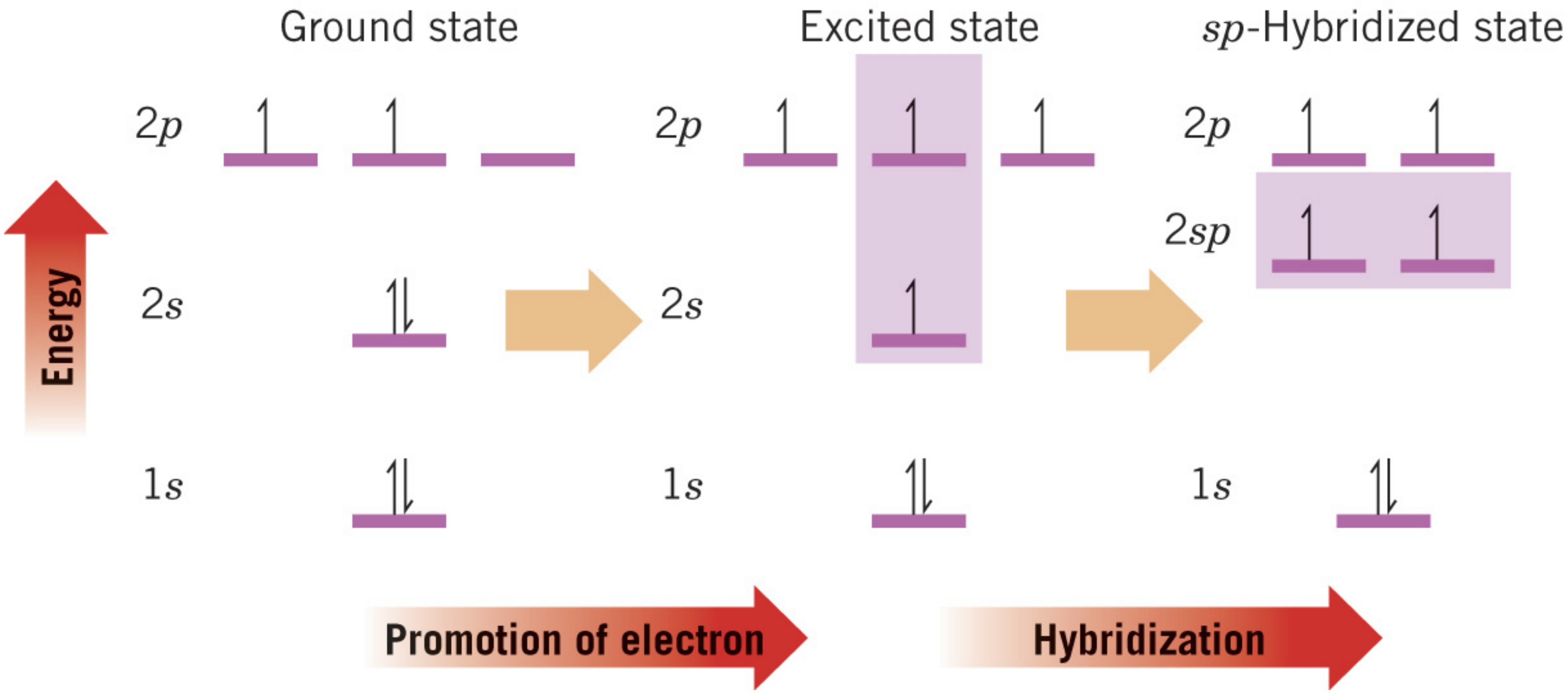
$H_2C{=}CHCH_2CH_3$ $H_2C{=}C(CH_3)_2$

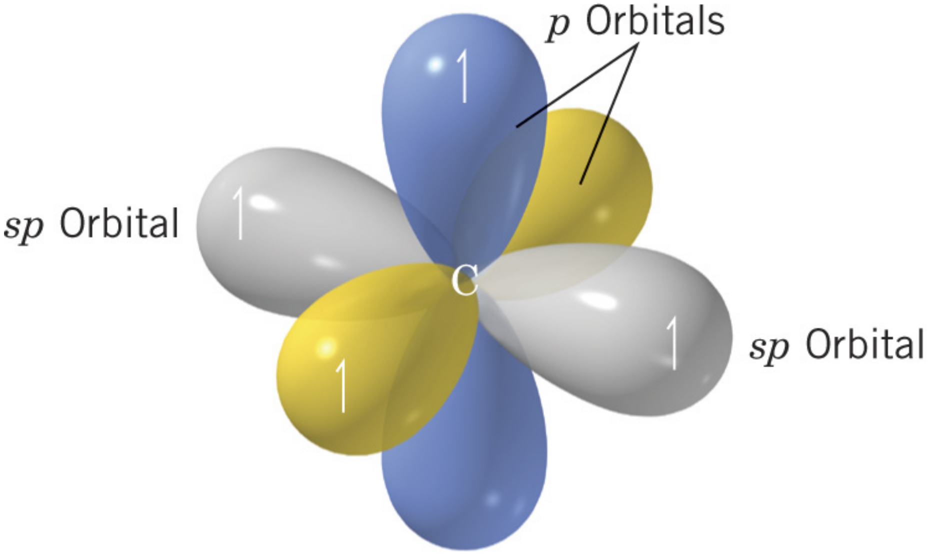
$H_3CHC{=}CHCH_3$ $H_3CH_2CHC{=}CHCl$

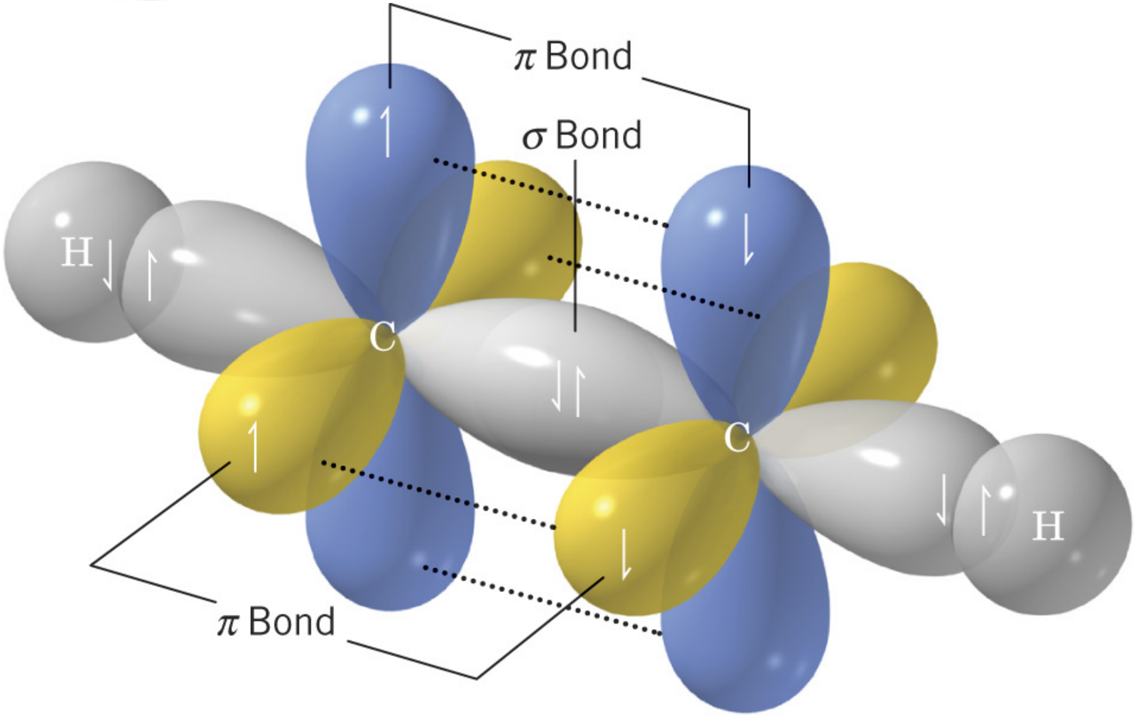
■*sp* Hybridization:



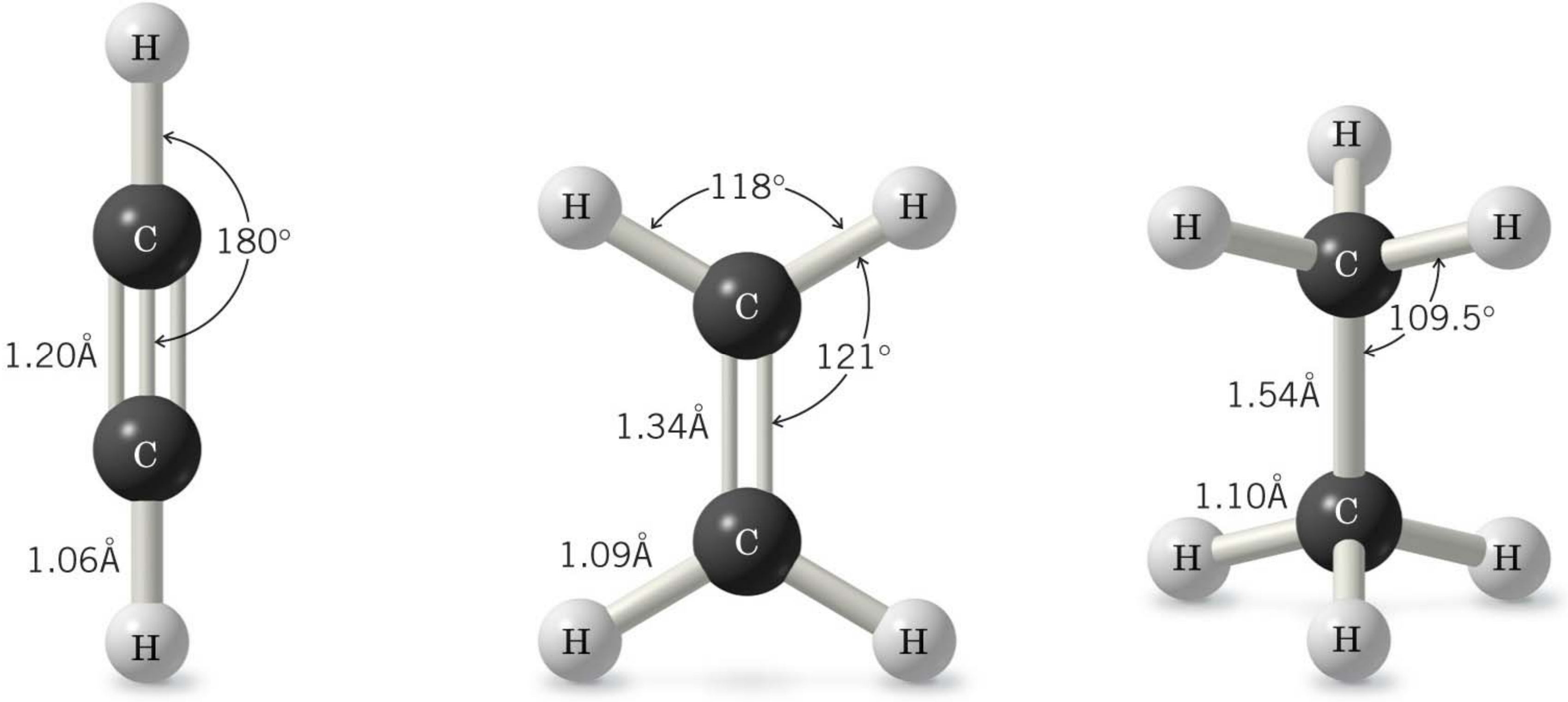
Linear




p Orbitals
sp Orbital
C
sp Orbital


π Bond
σ Bond
H
C
C
H
π Bond

■ Bond lengths of ethyne, ethene and ethane



The shortest C-H bonds are associated with those carbon orbitals with the greatest *s* character.

六）VSEPR theory (Valence shell electron pair repulsion)

*** This is a simple theory to predict the geometry of molecules**

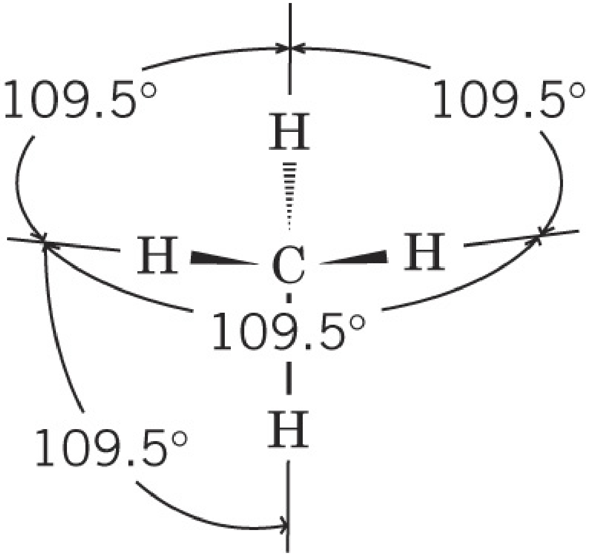
***All sets of valence electrons are considered including:**

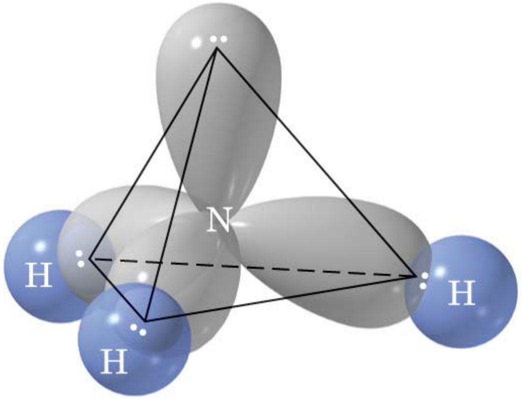
1) Bonding pairs involved in single or multiple bonds
2) Non-bonding pairs which are unshared

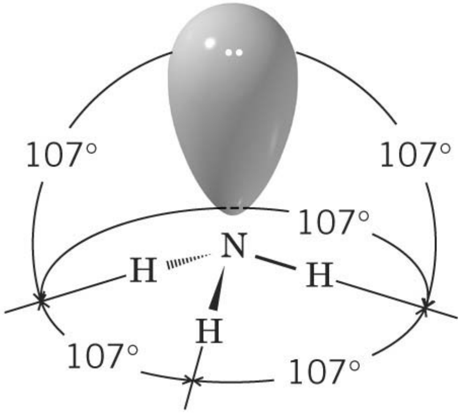
***Electron pairs repel each other and tend to be as far apart as possible from each other**

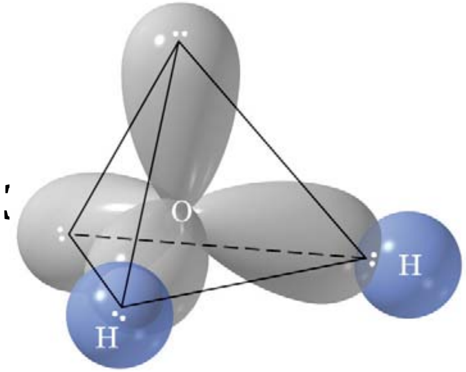
***Non-bonding electron pairs tend to repel other electrons more than bonding pairs do (*i.e.* they are "larger")**

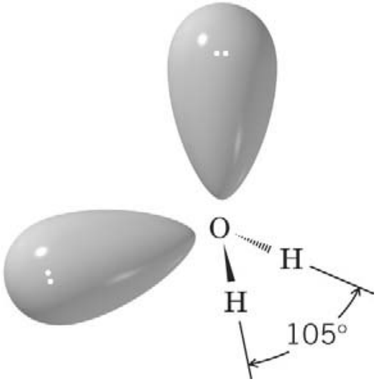
***The geometry of the molecule is determined by the number of sets of electrons by using geometrical principles**

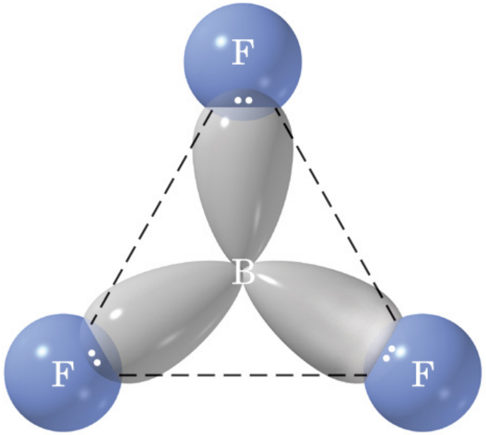


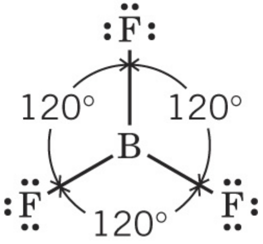




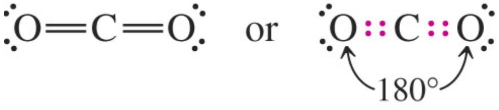








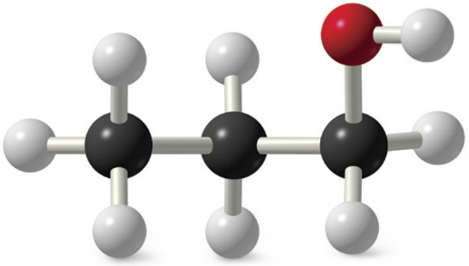
Linear geometry of BeH_2



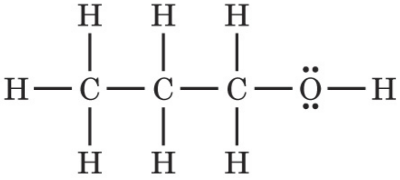
The four electrons of each double bond act as a single unit and are maximally separated from each other.

Exercise: Predict the geometry of following molecules: **BH4$^-$, NH4$^+$, BH3, SiF, BeF2, H2S, CF4, :CCl3$^-$**

七）Representation of Structural Formulas



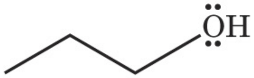
Ball-and-stick model
(*a*)



Dash formula
(*b*)

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

Condensed formula
(*c*)



Bond-line formula
(*d*)

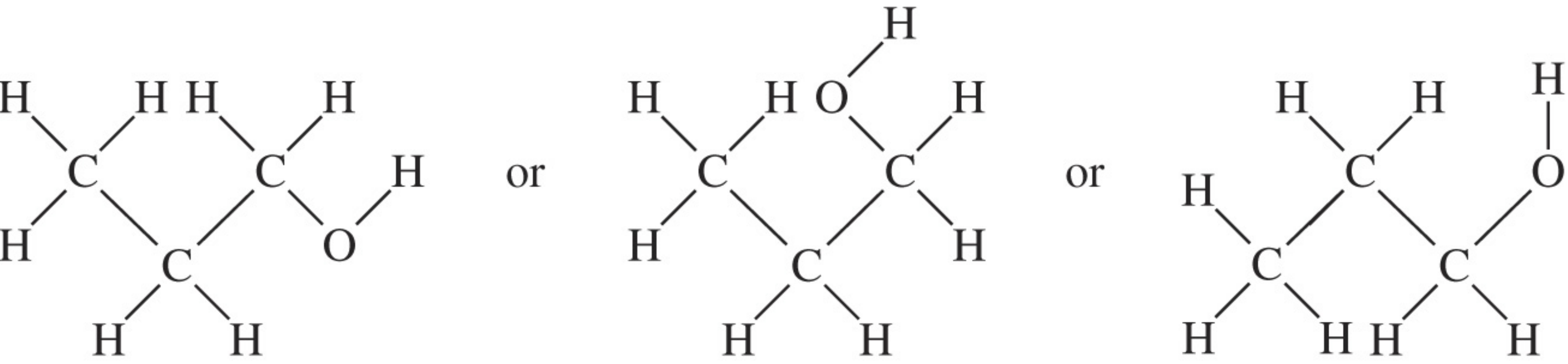
1) Dash formulas

*Each dash represents a pair of electrons

*This type of representation is meant to emphasize connectivity and does not represent the 3-dimensional nature of the molecule

* The dash formulas of propyl alcohol appear to have 90^{o} angles for carbons which actually have tetrahedral bond angles (109.5^{o})

* There is relatively free rotation around single bonds so the dash structures below are all equivalent



Equivalent dash formulas for propyl alcohol

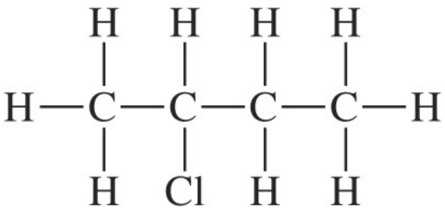
2) Condensed Structural Formulas

***In these representations, some or all of the dash lines are omitted**

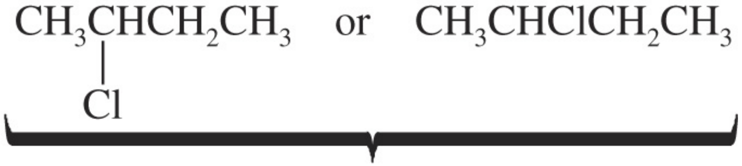
***In <u>partially condensed structures</u> all hydrogens attached to an atom are simply written after it but some or all of the other bonds are explicitly shown**

***In <u>fully condensed structure</u> all bonds are omitted and atoms attached to carbon are written immediately after it**

***For emphasis, branching groups are often written using vertical lines to connect them to the main chain**

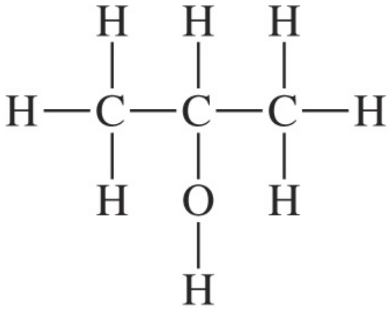


Dash formula

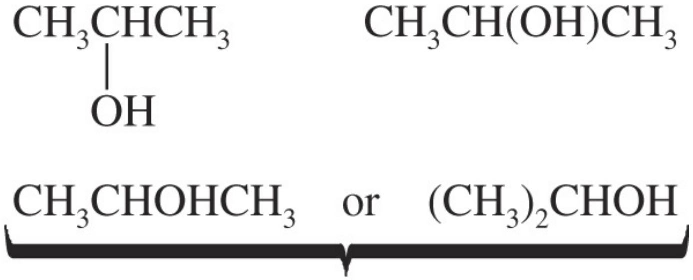


$CH_3\underset{|\atop Cl}{C}HCH_2CH_3$ or $CH_3CHClCH_2CH_3$

Condensed formulas



Dash formula



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

$CH_3CHOHCH_3$ or $(CH_3)_2CHOH$

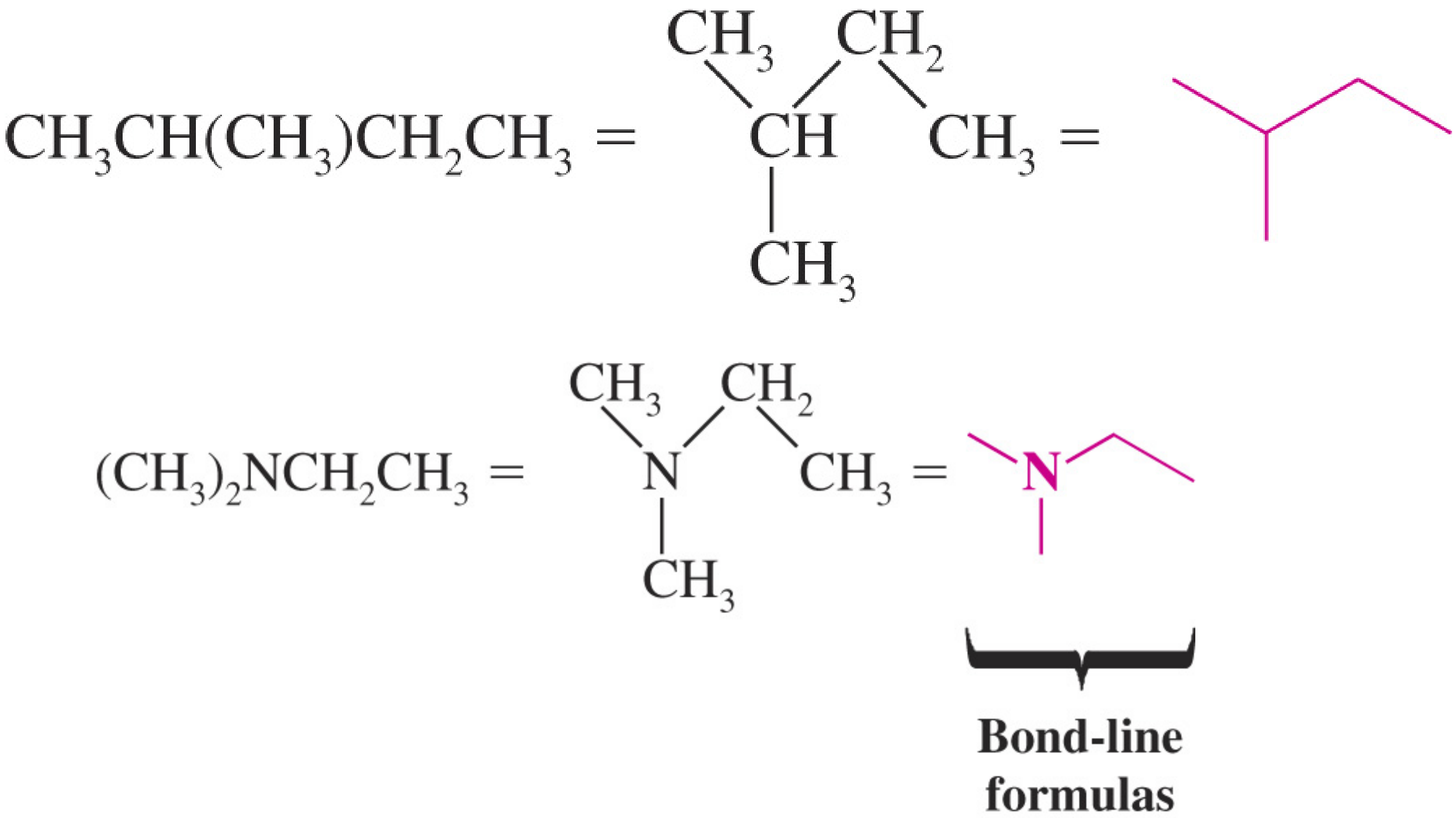
Condensed formulas

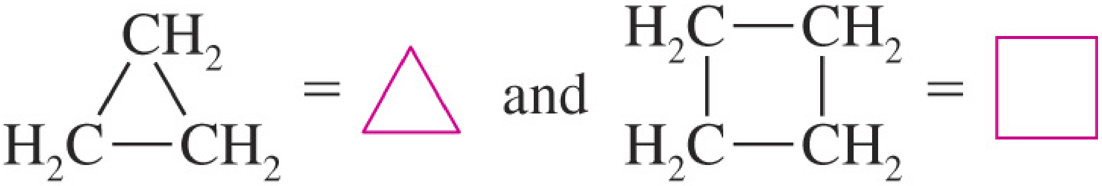
3) Bond-Line Formulas

***A further simplification of drawing organic molecules is to completely omit all carbons and hydrogens and only show heteroatoms (*e.g*. O, Cl, N) explicitly**

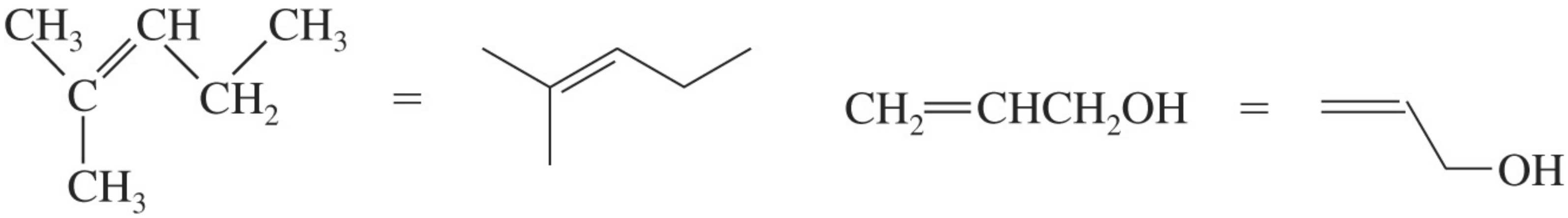
***Each intersection or end of line in a <u>zig-zag</u> represents a carbon with the appropriate amount of hydrogens**

***Heteroatoms with attached hydrogens must be drawn in explicitly**



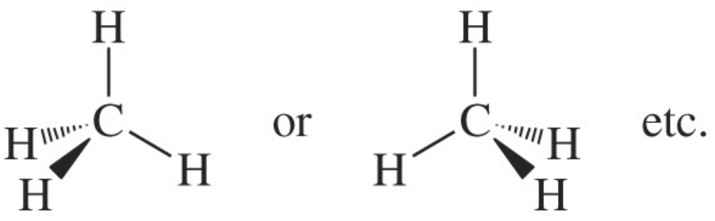


Cyclic compounds are condensed using a drawing of the corresponding polygon

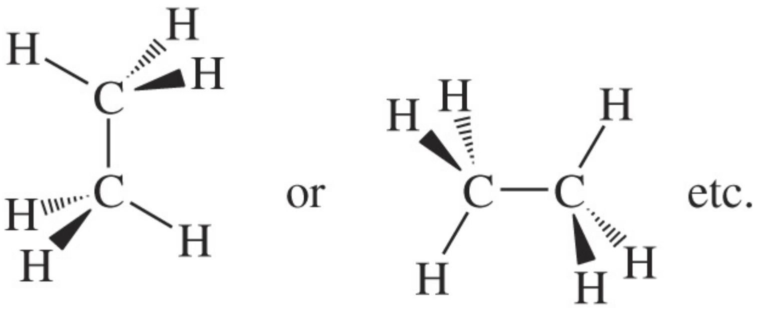


Multiple bonds are indicated by using the appropriate number of lines connecting the atoms

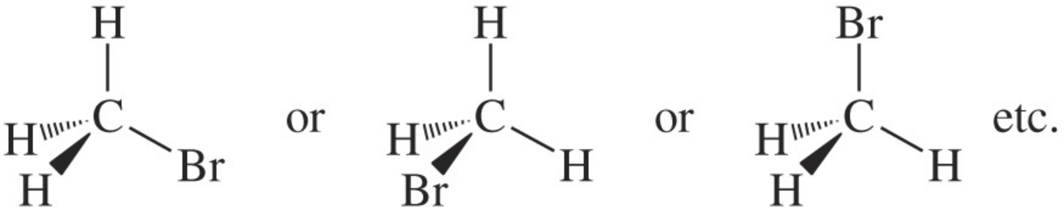
4) Three-Dimensional Formulas



Methane



Ethane



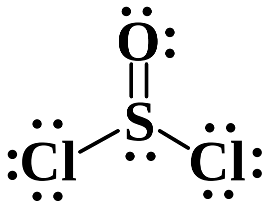
Bromomethane

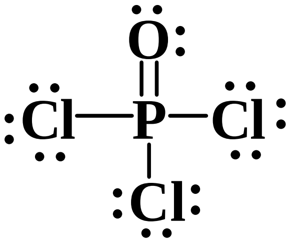
***Two of the bonds are drawn in the plane of the paper about 109^{o} apart**
*** The other two bonds are drawn in the opposite direction to the in- plane bonds but right next to each other**

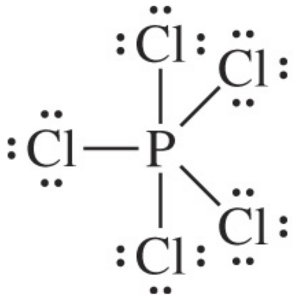
Exercise (Page 48):

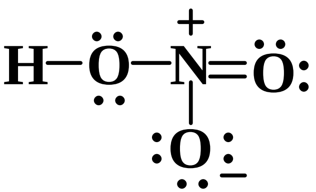
1.17 Which of the following ions possess the electrton configuration of a noble gas:
Na^+, Ca^{2+}, O^{2-}, Cl^-, H^-, S^{2-}

1.18 Write the Lewis structures:

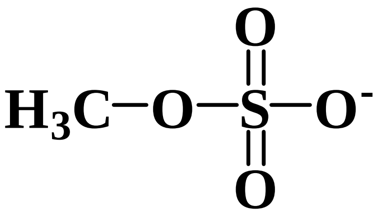


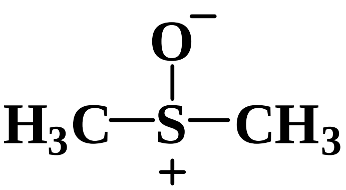


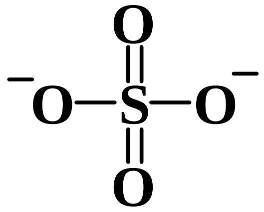


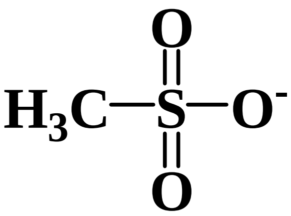


1.19 Give the formal charge on each of the following:



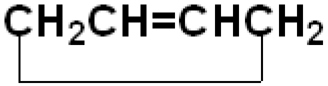






1.20 Write the condensed structural formula for each compound given here:

$(CH_3)_2CHCH_2OH$, $(CH_3)_2CHCOCH(CH_3)_2$,

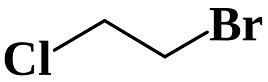


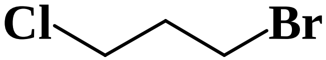
$(CH_3)_2CHCH_2CH_2OH$

1.21 What is the molecular formula for each of the compound given in problem 1.20? (omitted)

1.22:

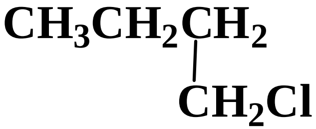
a)





Different compounds that are not isomeric

b)

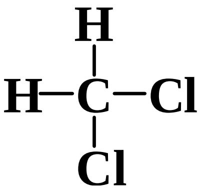


$$\begin{array}{l} CH_3CH_2CH_2 \\ \qquad\quad | \\ \qquad\quad CH_2Cl \end{array}$$

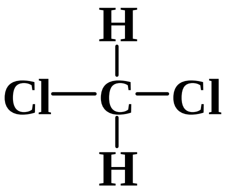
$ClCH_2CH(CH_3)_2$

Different compounds that are constitutional isomers

c)



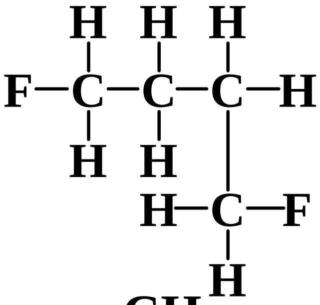
$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ H & - & C & - & Cl \\ & & | & & \\ & & Cl & & \end{array}$$



$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ Cl & - & C & - & Cl \\ & & | & & \\ & & H & & \end{array}$$

Same compounds

d)

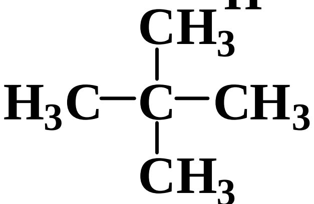


$$\begin{array}{ccccccccc} & & H & & H & & H & & \\ & & | & & | & & | & & \\ F & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & \\ & & H & & H & & | & & \\ & & & & H & - & C & - & F \\ & & & & & & | & & \\ & & & & & & H & & \end{array}$$

$CH_2FCH_2CH_2CH_2F$

Same compounds

e)



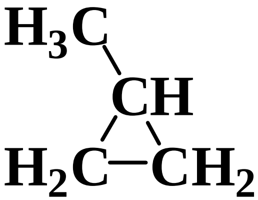
$$\begin{array}{ccccc} & & CH_3 & & \\ & & | & & \\ H_3C & - & C & - & CH_3 \\ & & | & & \\ & & CH_3 & & \end{array}$$

$(H_3C)_3C-CH_3$

Same compounds

f)

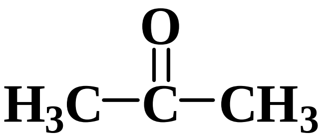
$H_2C{=}CHCH_2CH_3$



Different compounds that are constitutional isomers

g)

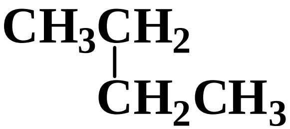
$CH_3OCH_2CH_3$



$H_3C{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3$

Different compounds that are not isomeric

h)

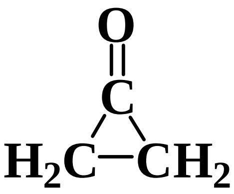


$CH_3CH_2{-}CH_2CH_3$

$CH_3CH_2CH_2CH_3$

Same compounds

i) $CH_3OCH_2CH_3$



Different compounds that are not isomeric

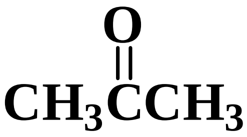
j) $CH_2ClCHClCH_3$ $CH_3CHClCH_2Cl$

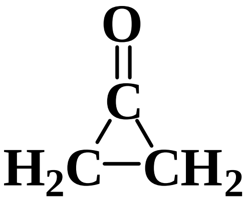
Same compounds

k) $CH_2ClCHClCH_3$ $CH_3CHClCH_2Cl$

Same compounds

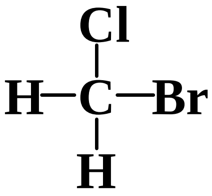
l)

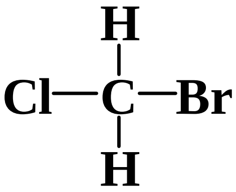

$$\begin{array}{c}\mathrm{O}\\ \|\\ \mathrm{CH_3CCH_3}\end{array}$$



Different compounds that are not isomeric

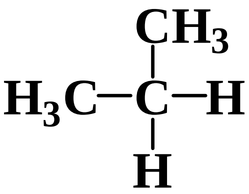
m)

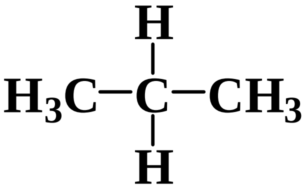

$$\begin{array}{c}\mathrm{Cl}\\ |\\ \mathrm{H-C-Br}\\ |\\ \mathrm{H}\end{array}$$


$$\begin{array}{c}\mathrm{H}\\ |\\ \mathrm{Cl-C-Br}\\ |\\ \mathrm{H}\end{array}$$

Same compounds

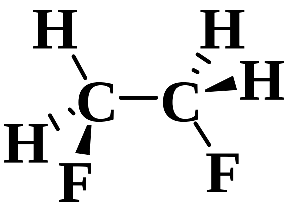
n)

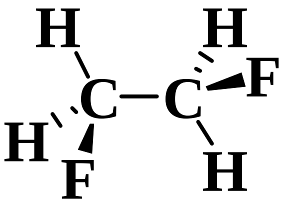

$$\begin{array}{c}\mathrm{CH_3}\\ |\\ \mathrm{H_3C-C-H}\\ |\\ \mathrm{H}\end{array}$$


$$\begin{array}{c}\mathrm{H}\\ |\\ \mathrm{H_3C-C-CH_3}\\ |\\ \mathrm{H}\end{array}$$

Same compounds

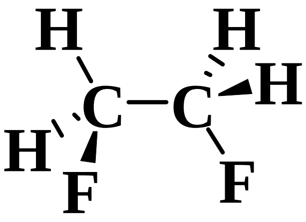
o)

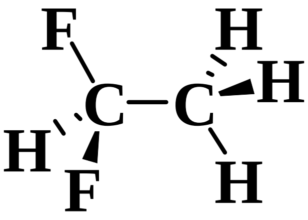




Same compounds

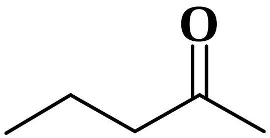
p)



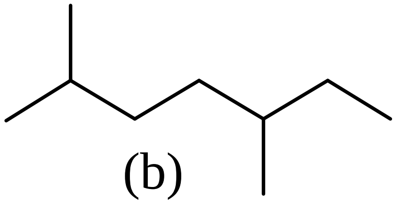


Different compounds that are not isomeric

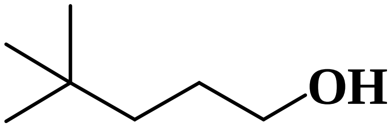
1.23 Rewrite each of the following using bond-line formulas:



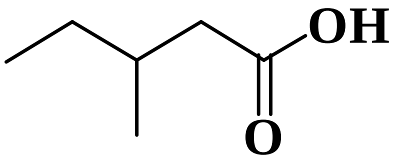
(a)



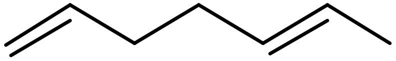
(b)



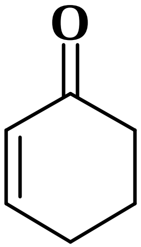
(c)



(d)

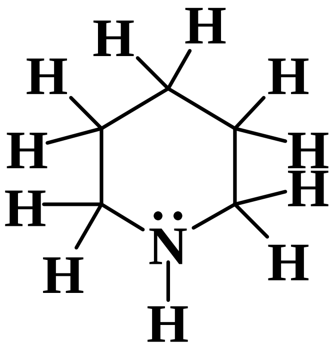


(e)

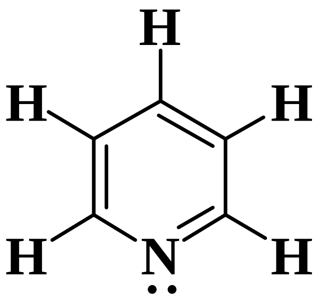


(f)

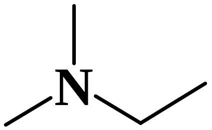
1.24 Write a dash formula for each of the following showing any unshared electron pairs:



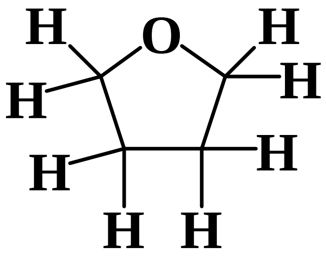
(a)



(b)

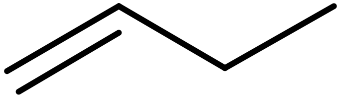


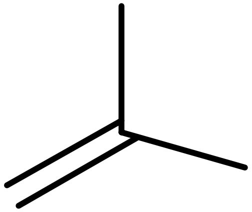
(c)

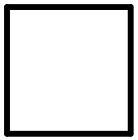


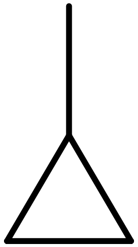
(d)

1.25 Write structural formulas of your choice for all of the constitutional isomers with the molecular formula C4H8.

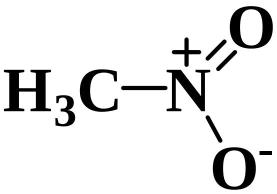






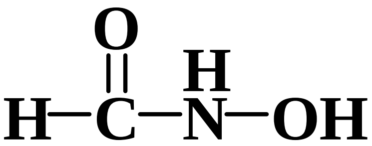


1.26 Write structural formulas for at least 3 three constitutional isomers (CH3NO2):



$H_3C-\overset{+}{N}(=O)-O^-$

$HO-CH_2-N=O$



$H-\overset{\overset{O}{\|}}{C}-\overset{H}{N}-OH$

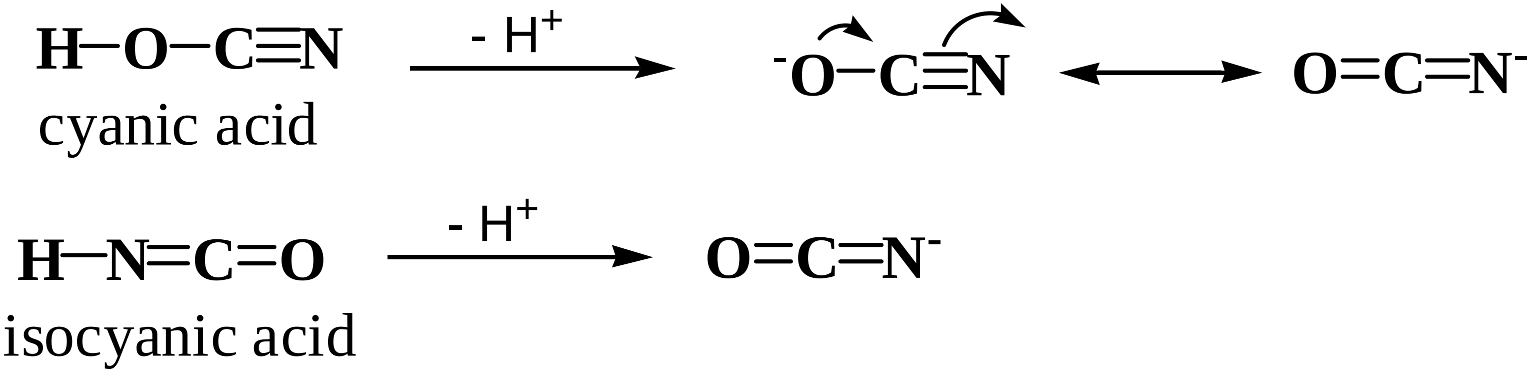
1.27

a) $H-O-C\equiv N$ $H-N=C=O$

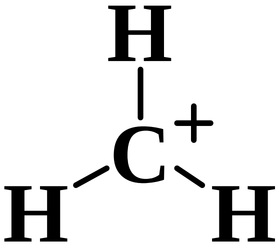
cyanic acid isocyanic acid

They are not resonance structures to each other because of the change of the position of atoms.

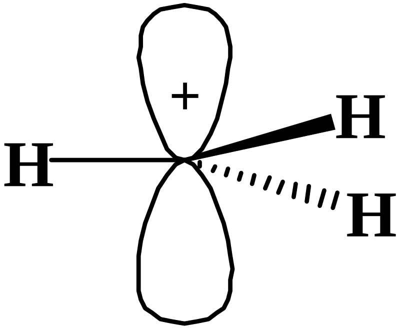
b)



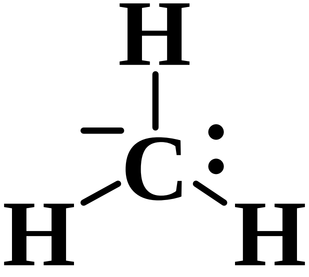
1.28 a)

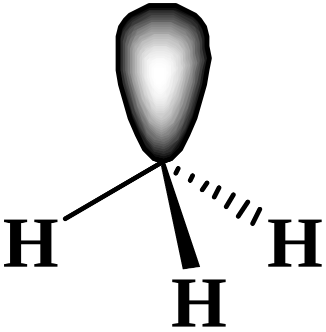


b) $(CH_3)^+$ c) triangle d) *sp^2*



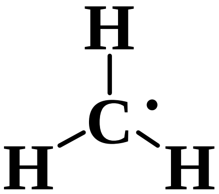
1.29 a)





b) $(CH_3)^-$ c) Tetrahedral d) *sp3*

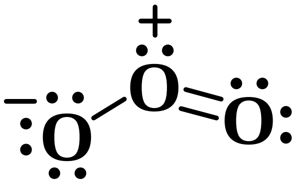
1.30 a)



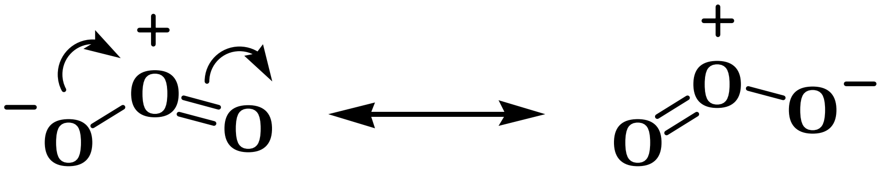
b) $(CH_3)^{\cdot}$

c) Given that the shape of this species is trigonal planar, the hybridization state of the carbon atom is *sp*^{2}.

1.31 a)



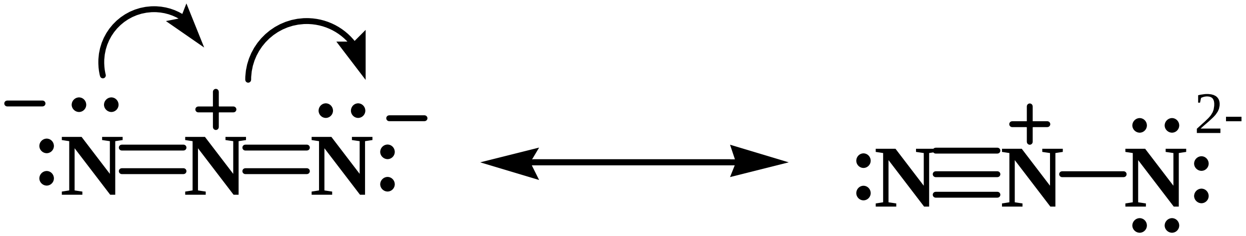
b)



c) The relative lengths of two O-O bonds are same due to the resonance.

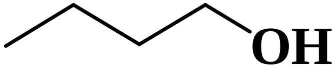
d) The angular shape is consistent with VSEPR theory, because the lone pair electrons in the middle oxygen repulse the electrons on the side oxygens.

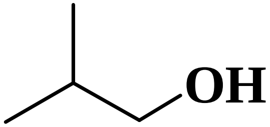
1.32 a)

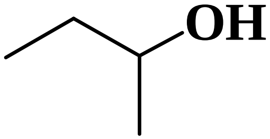


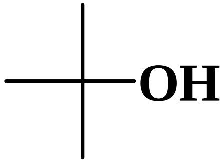
Linear

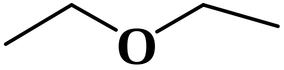
1.33 (a)

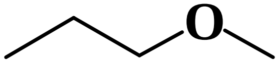


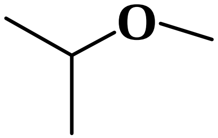












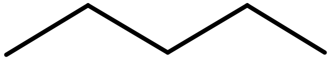
(b) $CH_3CH_2NH_2$

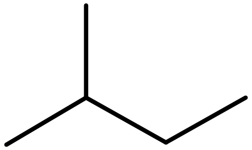
CH_3NHCH_3

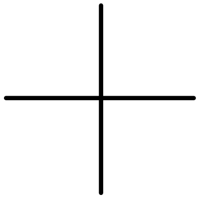
(c) $CH_3CH_2CH_2NH_2$ $(CH_3)_2CHNH_2$ $CH_3N(CH_3)_2$

$CH_3CH_2NHCH_3$

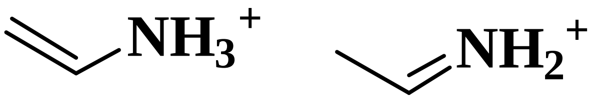
(d)



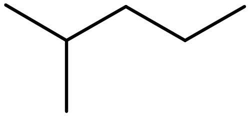




1.34 What is the relationship between the members of the following pairs?

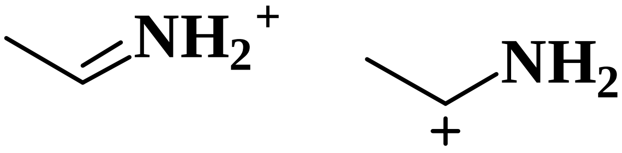
a) 

Constitutional isomers

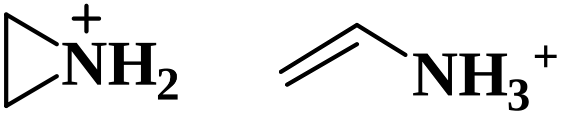
b) 

$CH_3CH_2CH_2CH(CH_3)_2$

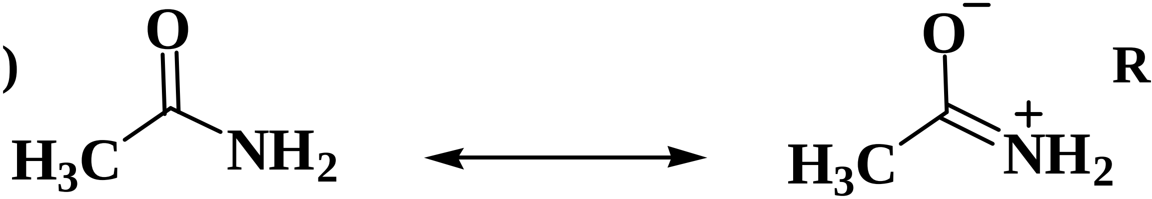
Same compounds

c) 

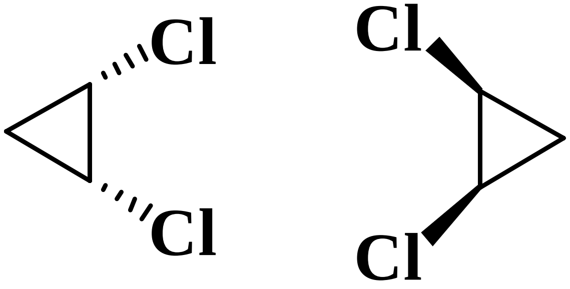
Resonance structures

d) 

Constitutional isomers

e) 

Resonance structures

f) 

Same compounds