Faculty of Pharmacy

ORGANIC CHEMISTRY

NEU Organic Chemistry
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*Organic Chemistry, 7th Ed.
Graham Solomons and Craig Fryhle

Chapter 1

Introduction to Organic Chemistry

1.1 Introduction

- **Organic Chemistry**

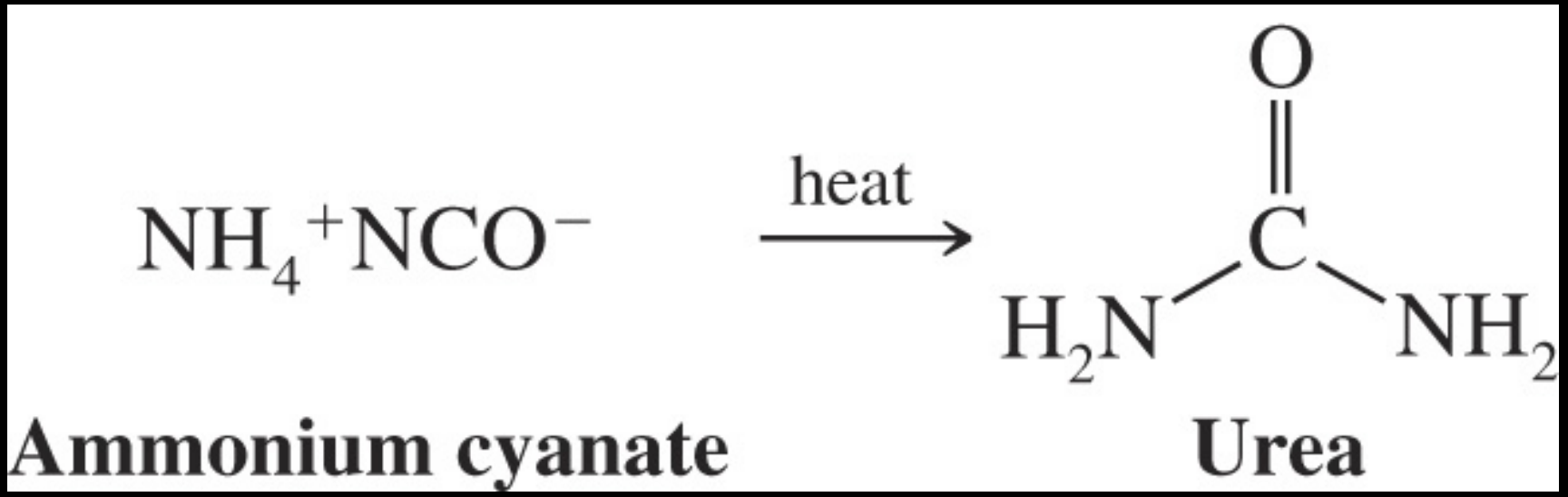
  - ➔ **The chemistry of the compounds of carbon**

  - ➔ **The human body is largely composed of organic compounds**

  - ➔ **Organic chemistry plays a central role in medicine, bioengineering etc.**

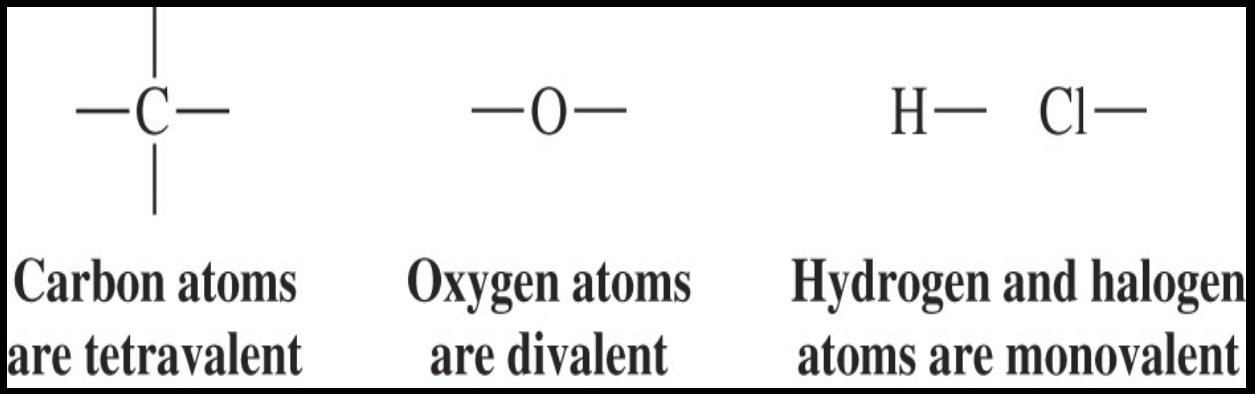
Vitalism

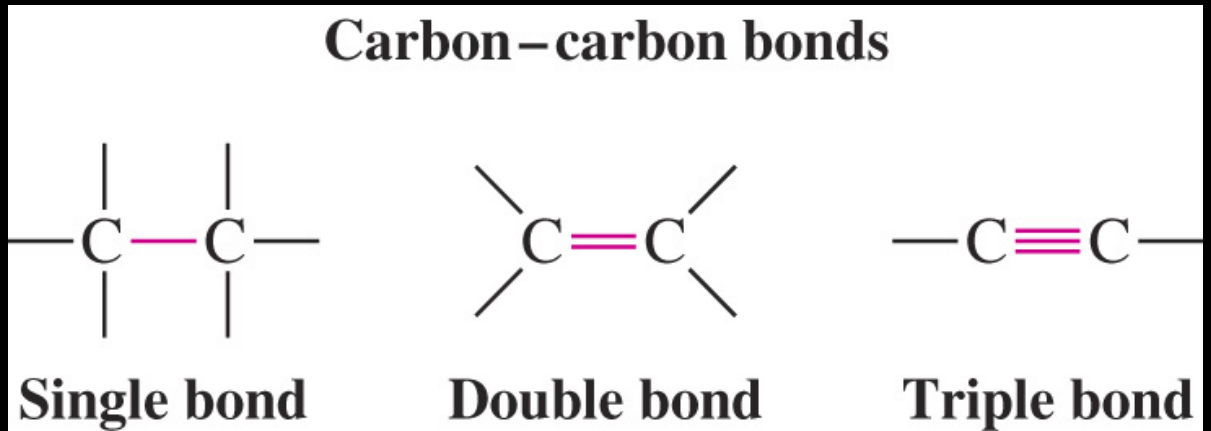
- It was originally thought organic compounds could be made only by living things by intervention of a "vital force"
- Fredrich Wöhler disproved vitalism in 1828 by making the organic compound urea from the inorganic salt ammonium cyanate by evaporation:



1.3 Structural Theory

- **Central Premises**
  1. **Valency**: atoms in organic compounds form a fixed number of bonds
  2. Carbon can form one or more bonds to other carbons





1.3A Isomers

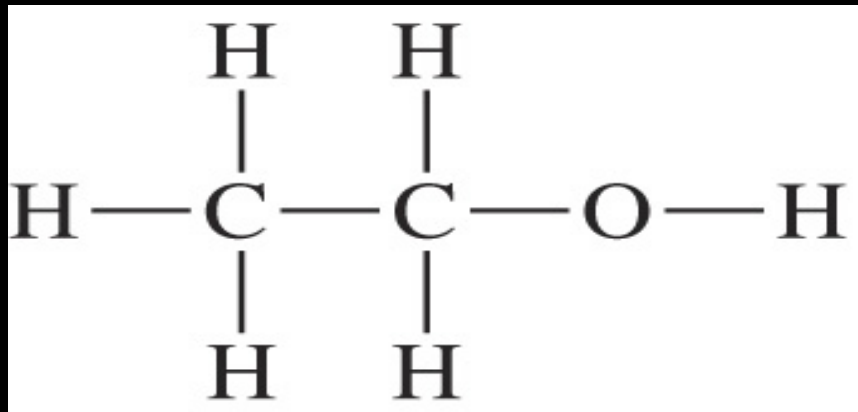
➔ Isomers are different molecules with the same molecular formula

➔ Many types of isomers exist

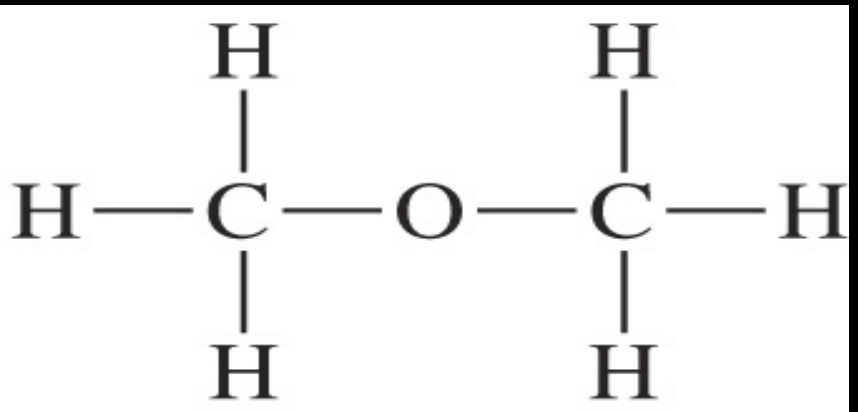
Example

- Consider two compounds with molecular formula e.g. C_2H_6O
- These compounds cannot be distinguished based on molecular formula; however they have different structures
- The two compounds differ in the ***connectivity*** of their atoms

C_2H_6O



Ethyl alcohol



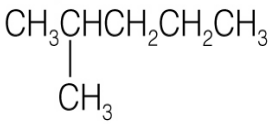
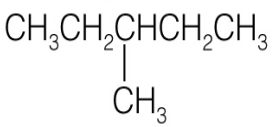
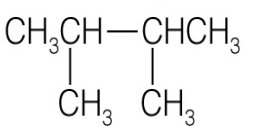
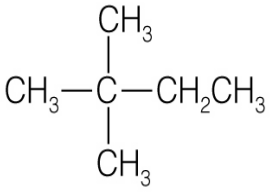
Dimethyl ether

Constitutional Isomers

- Constitutional isomers are one type of isomer
- They are different compounds that have the same molecular formula but different connectivity of atoms
- They often differ in physical properties (e.g. boiling point, melting point, density) and chemical properties

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

Example for Constitutional Isomers

Molecular Formula	Structural Formula	mp (°C)	bp (°C)[a] (1 atm)	Density[b] (g mL^{-1})	Index of Refraction[c] (n_D 20°C)
C_6H_{14}	$CH_3CH_2CH_2CH_2CH_2CH_3$	−95	68.7	0.6594^{20}	1.3748
C_6H_{14}		−153.7	60.3	0.6532^{20}	1.3714
C_6H_{14}		−118	63.3	0.6643^{20}	1.3765
C_6H_{14}		−128.8	58	0.6616^{20}	1.3750
C_6H_{14}		−98	49.7	0.6492^{20}	1.3688

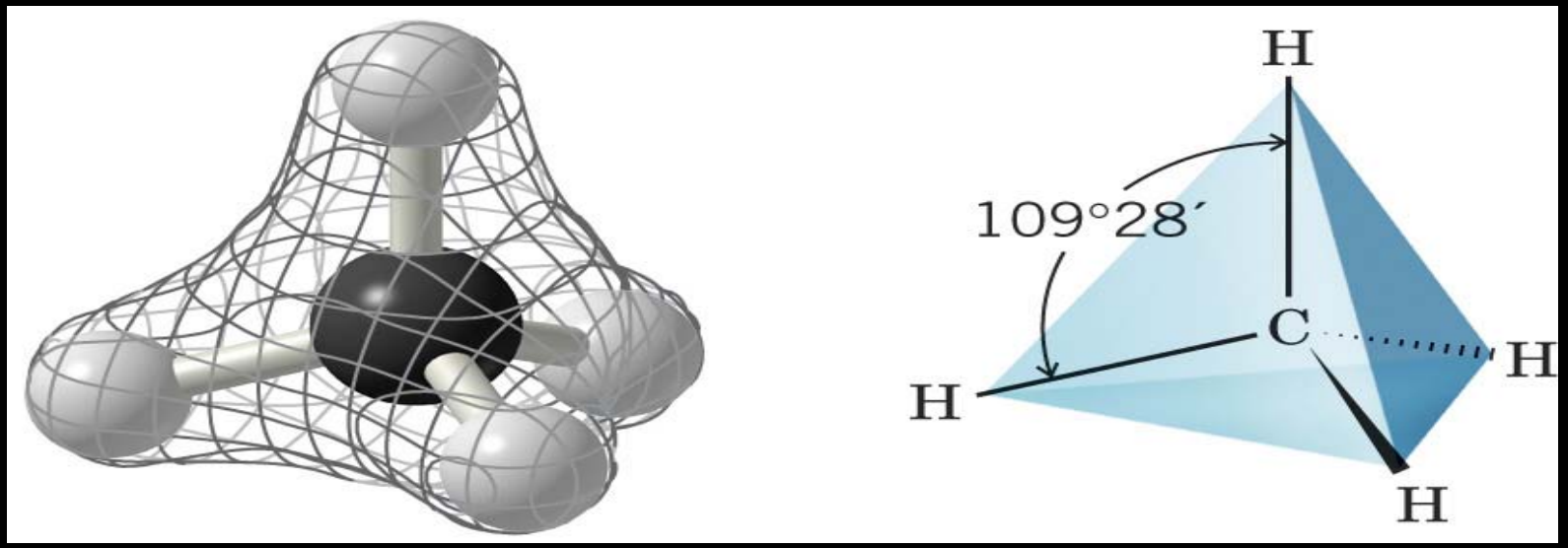
[a] Unless otherwise indicated, all boiling points given in this book are at 1 atm or 760 torr.

[b] The superscript indicates the temperature at which the density was measured.

[c] The index of refraction is a measure of the ability of the alkane to bend (refract) light rays. The values reported are for light of the D line of the sodium spectrum (n_D).

Three Dimensional Shape of Molecules

- It was proposed in 1874 by van't Hoff and le Bel that the four bonds around carbon where not all in a plane but rather in a tetrahedral arrangement *i.e.* the four C-H bonds point towards the corners of a regular tetrahedron



Chemical Bonds

- **Ionic Bonds**
  Formed by transfer of one or more electrons from one atom to another to create ions

- **Covalent Bonds**
  A bond that results when atoms share electrons

1.4. Chemical Bonds: The Octet Rule

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

Ionic Bonds

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

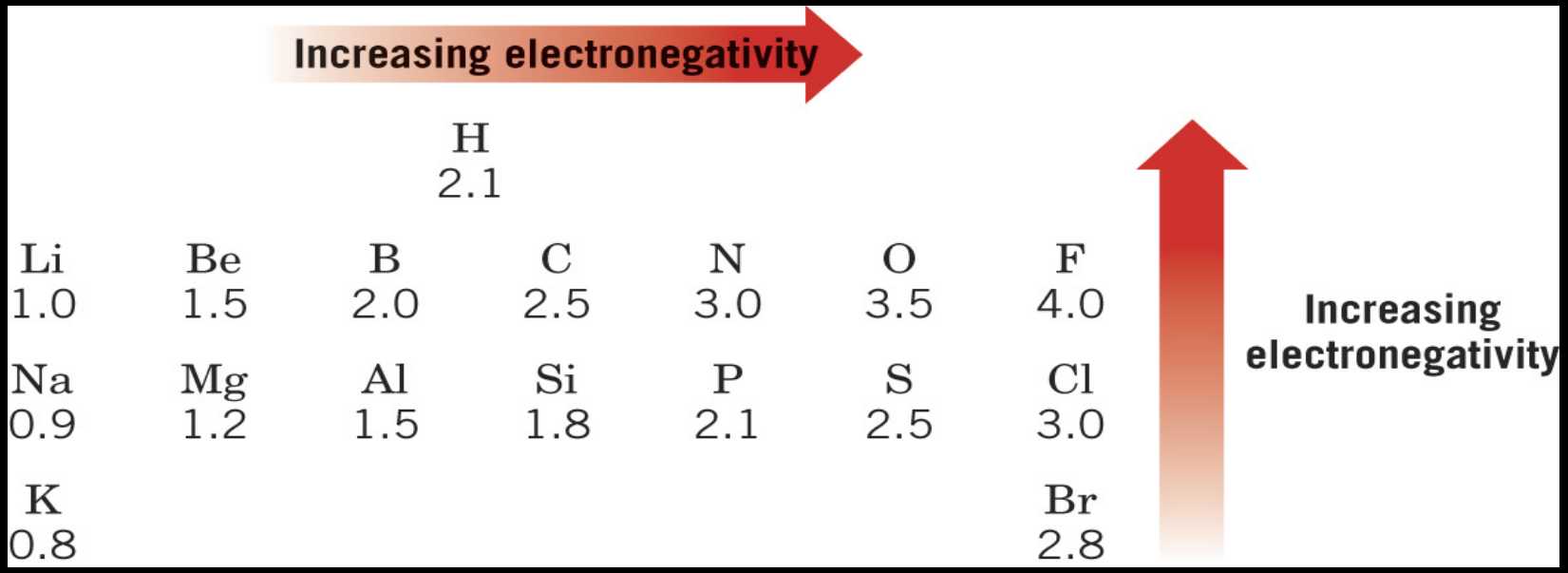
  In the process the atoms become ionic

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

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

Electronegativity

- Electronegativity is the ability of an atom to attract electrons
- It increases from left to right and from bottom to top in the periodic table (noble gases excluded)
  - *Fluorine is the most electronegative atom and can stabilize excess electron density the best

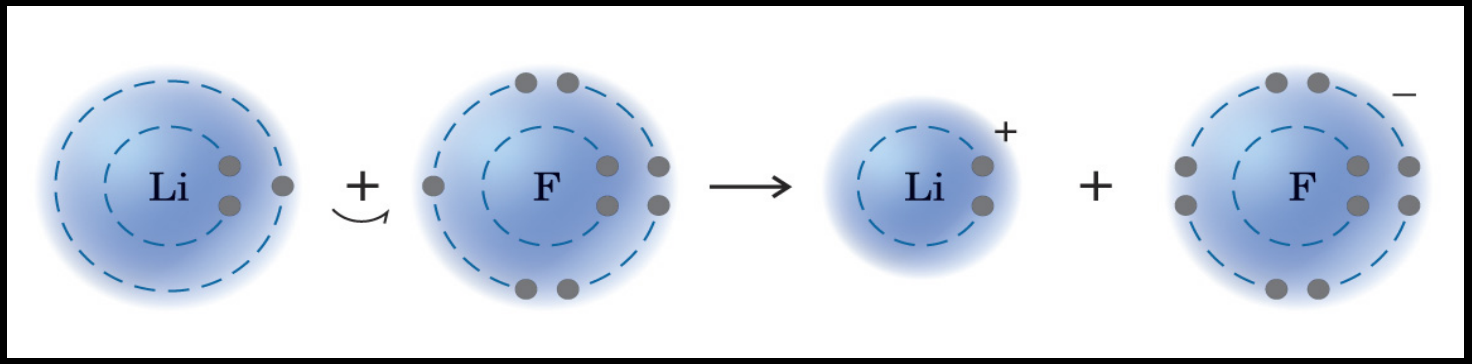


Example of an Ionic Bond

- **Lithium loses an electron (to have the configuration of helium) and becomes positively charged**

- **Fluoride gains an electron (to have the configuration of neon) and becomes negatively charged**

- **The positively charged lithium and the negatively charged fluoride form a strong ionic bond (actually in a crystalline lattice)**



Covalent Bonds

- **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 two electrons in a bond is to use a line (one line = two electrons)**

1.5 Writing Lewis Structures

➔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

Lewis Structures continued

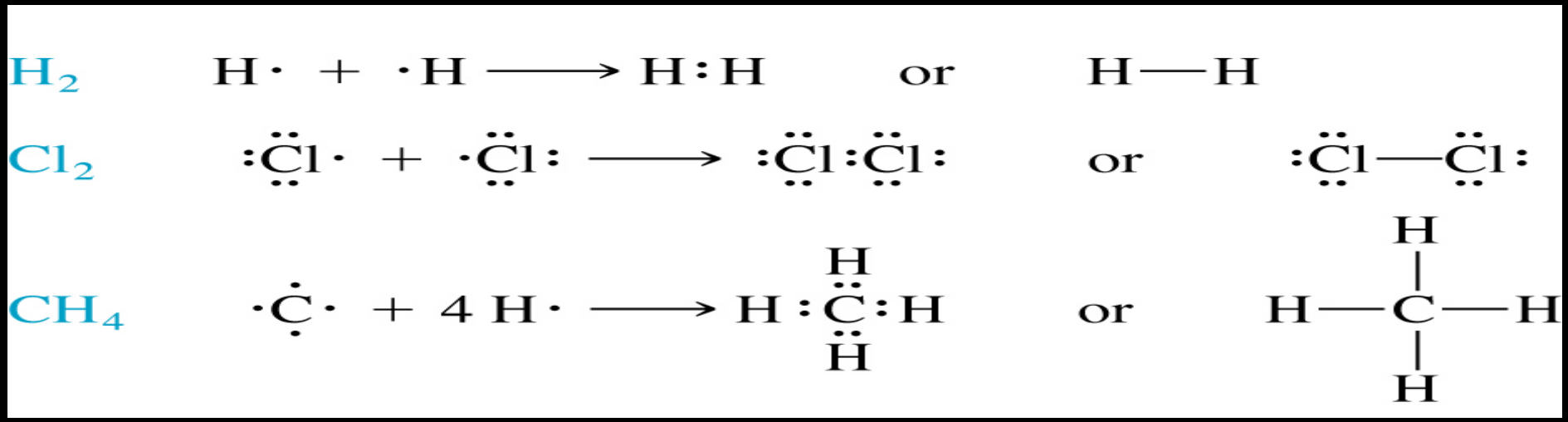
➔To construct molecules the atoms are assembled with the correct number of valence electrons

➔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

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

Examples of Covalent Bonding



Example

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

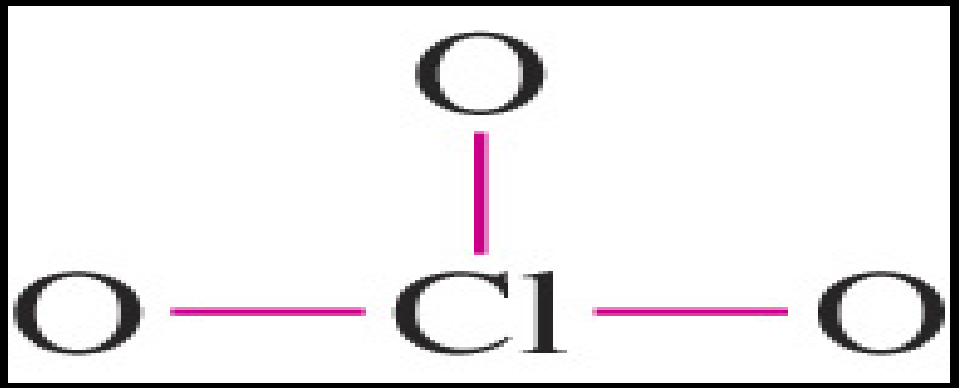
- **The total number of valence electrons including the electron for the negative charge is calculated**

$$7 + 3(6) + 1 = 26$$

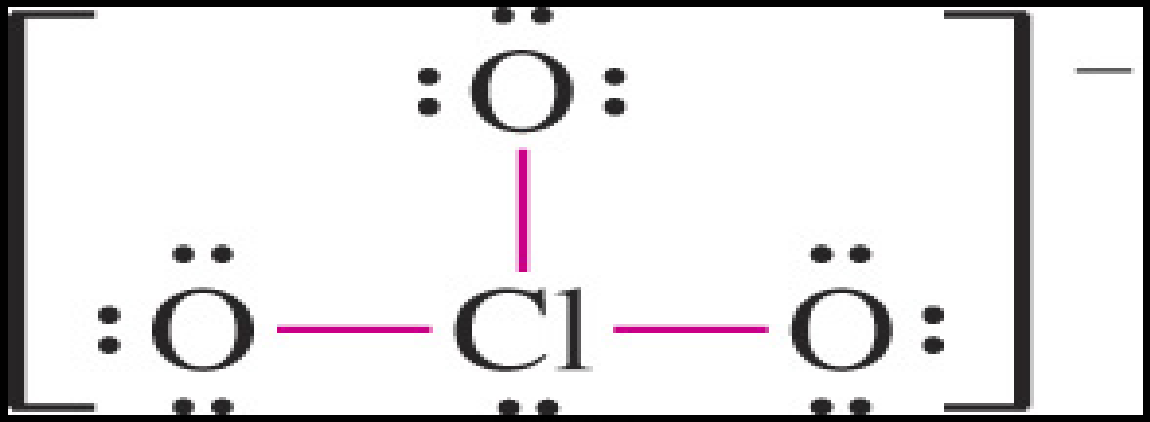
↑ ↑ ↑

Cl 3 O e^-

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



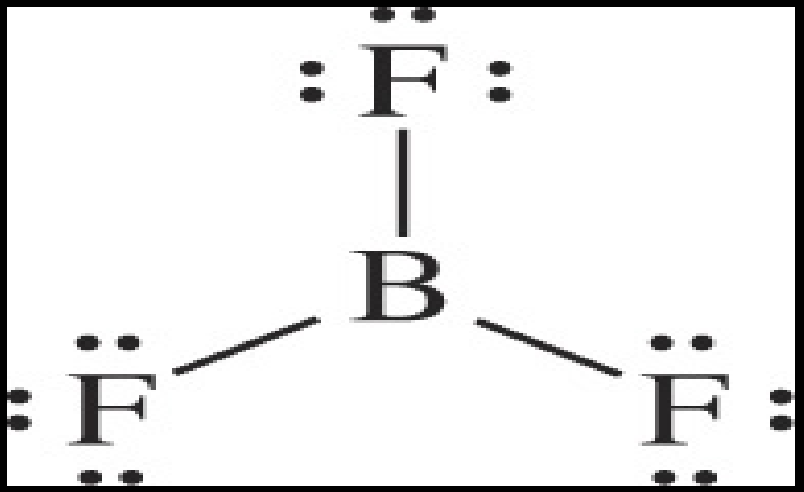
- **The remaining 20 electrons are added to give each atom an octet**



1.6 Exceptions to the Octet Rule

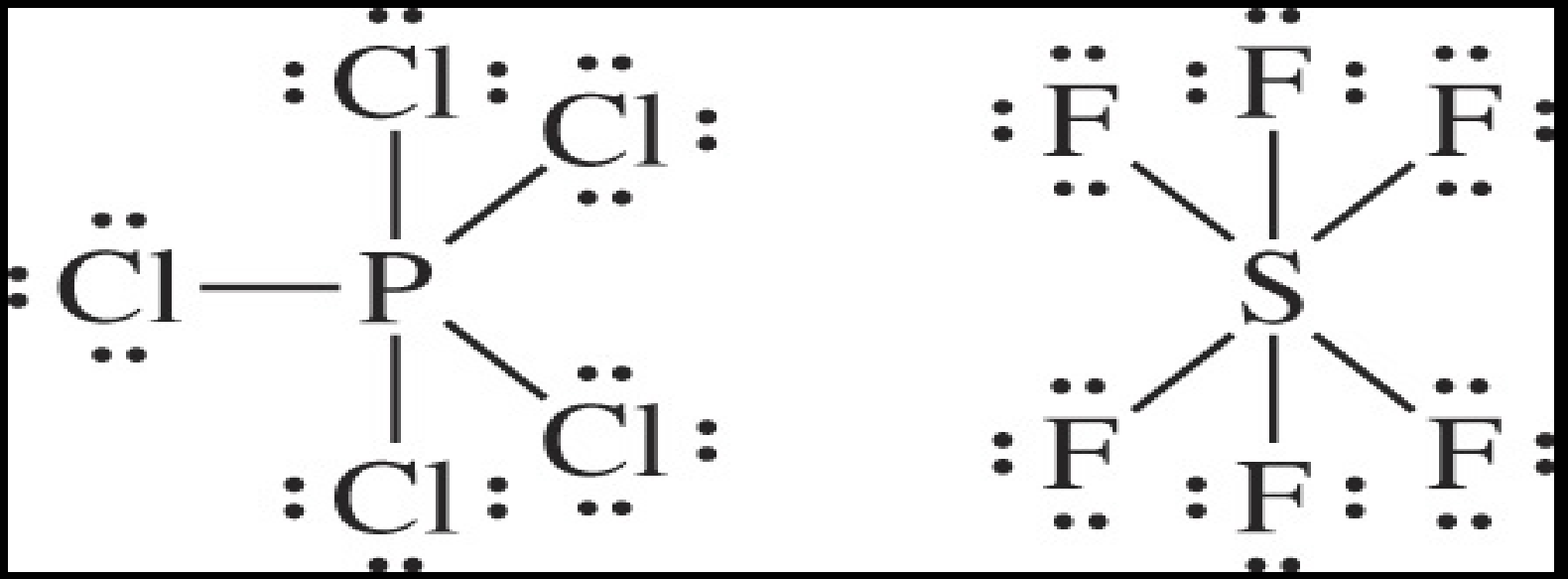
- **The octet rule applies only to atoms in the second row of the periodic table (C, O, N, F) which are limited to valence electrons in the 2s and 2p orbitals**
- **In second row elements *fewer* electrons are possible**

➔Example: BF_3



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

Example: PCl_5 and SF_6



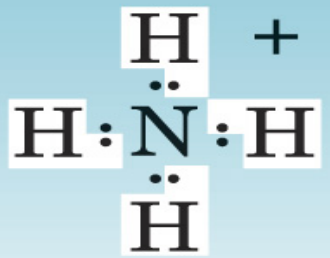
1.7 Formal Charge

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 (NH_4NO_3)

- **Ammonium ion $(NH_4)^+$**

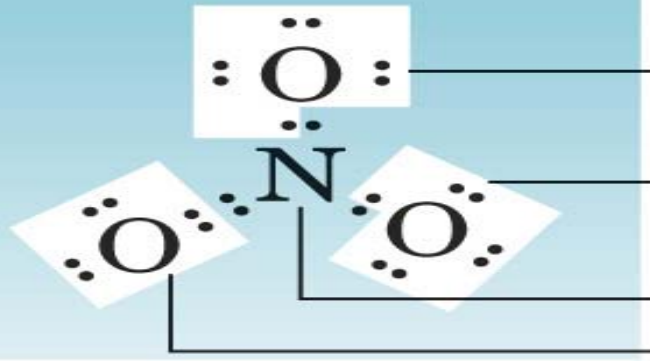


For hydrogen: valence electrons of free atom = 1
subtract assigned electrons = −1
Formal charge = 0

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

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

- **Nitrate ion $(NO_3)^-$**



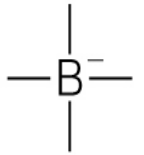
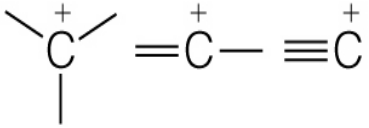
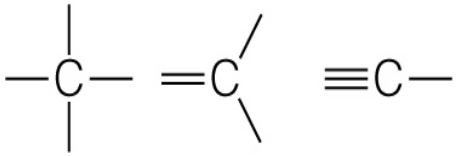
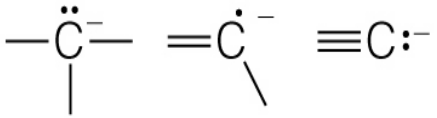
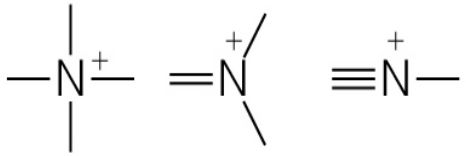
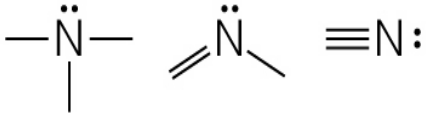
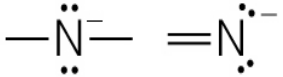
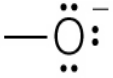
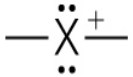
Formal charge = 6 − 7 = −1

Formal charge = 5 − 4 = +1

Formal charge = 6 − 6 = 0

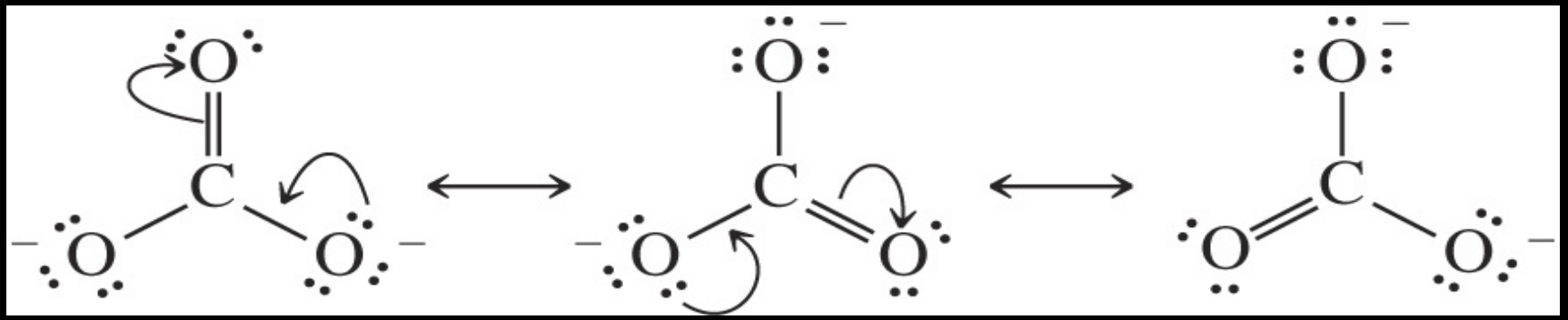
Charge on ion = 2(−1) + 1 + 0 = −1

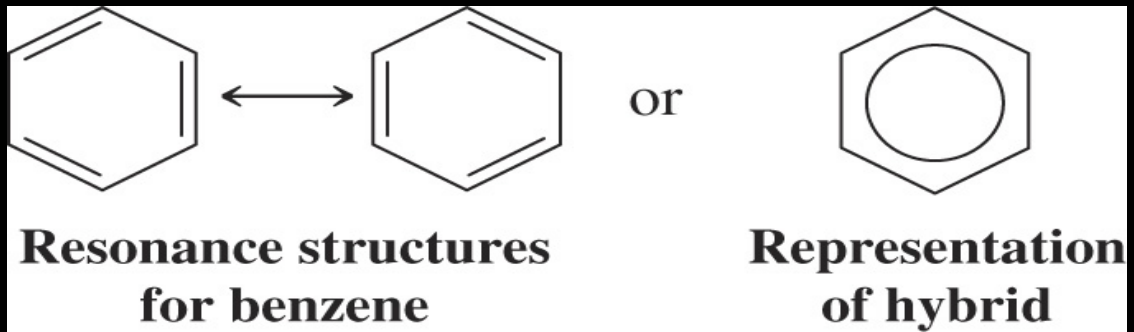
A Summary of Formal Charges

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

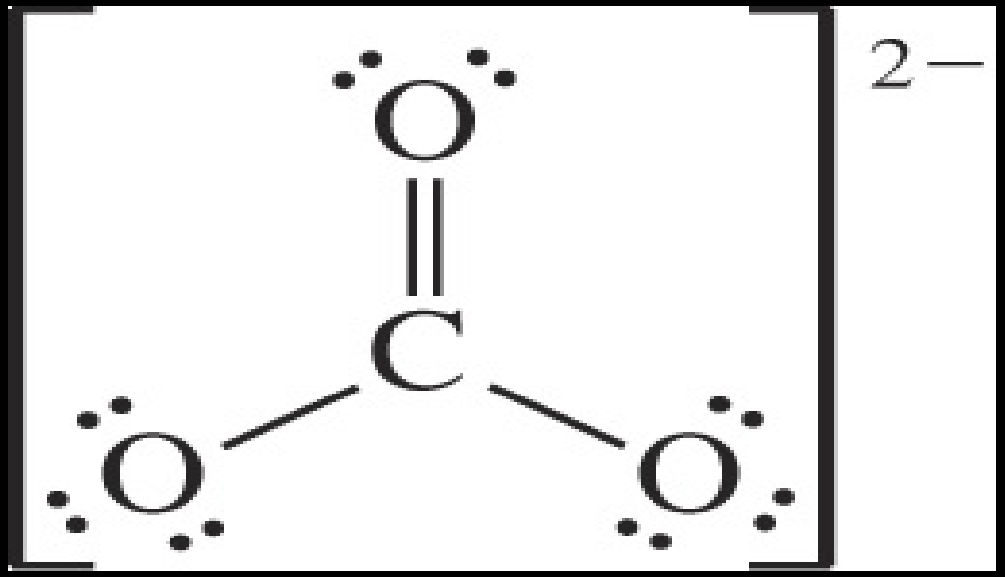
1.8 Resonance

- **Theory used to represent and model certain types of non-classical molecular structures**
  - **➔Often a single Lewis structure does not accurately represent the true structure of a molecule**
  - **➔The true carbonate structure is a hybrid (average) of all three Lewis structures**





➔ **The carbonate ion (CO_3^{2-}) with 24 valence electrons and two negative charges must incorporate a double bond to satisfy the octet rule for every atom**



1.9 Quantum Mechanics

- A mathematical description of bonding that takes into account the **wave nature of electrons**
- 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 are used to calculate:
  - The energy associated with the state of the electron
  - The **probability of finding the electron** in a particular state

1.10 Atomic Orbitals (AOs)

- 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**
- Plots of Ψ^2 in three dimensions generate the shape of ***s*, *p*, *d* and *f* orbitals**
- 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**

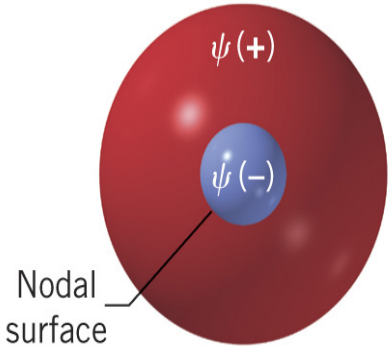
- **1s and 2s orbitals are spheres centered around the nucleus**
  - **Each orbital can accommodate 2 electrons**
  - **The 2s orbital is higher in energy and contains a nodal surface ($\Psi = 0$) in its center**

- **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**

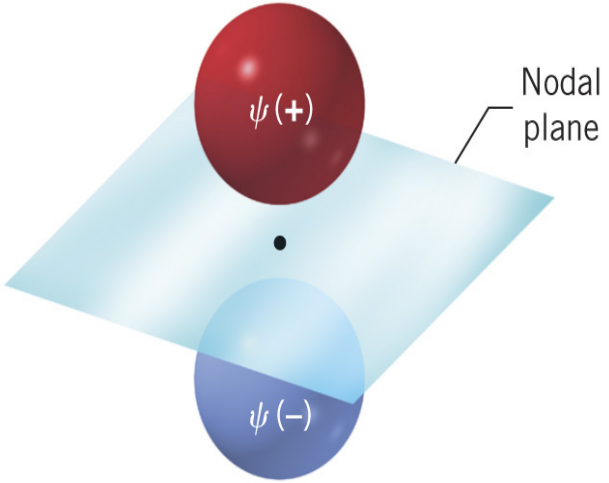
➢ **There are three 2*p* orbitals which are perpendicular (orthogonal) to each other**

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

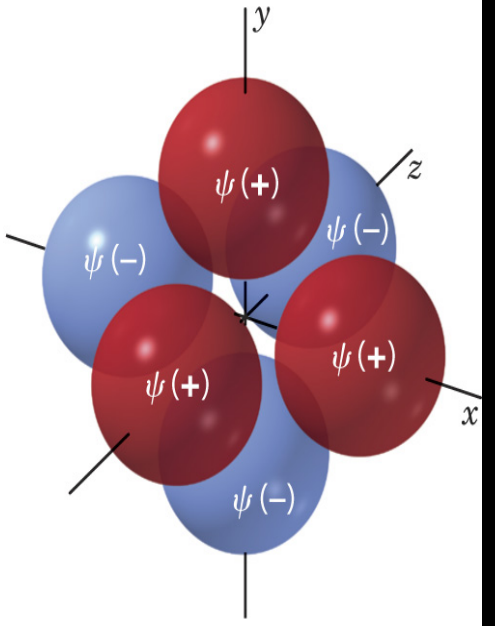
1*s* Orbital



2*s* Orbital



A pure 2*p* orbital
(unhybridized)



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

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

- **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**

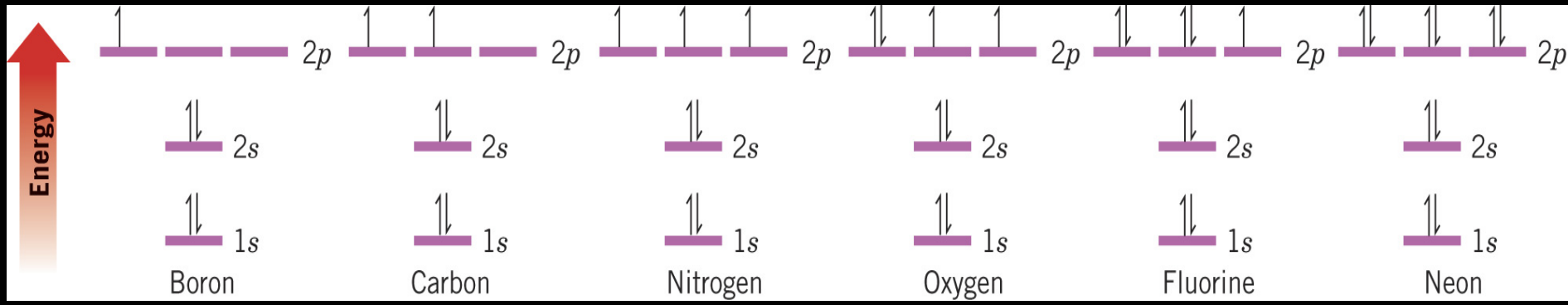
Atoms can be assigned electronic configuration using the following rules:

- **Aufbau Principle**: The lowest energy orbitals are filled first

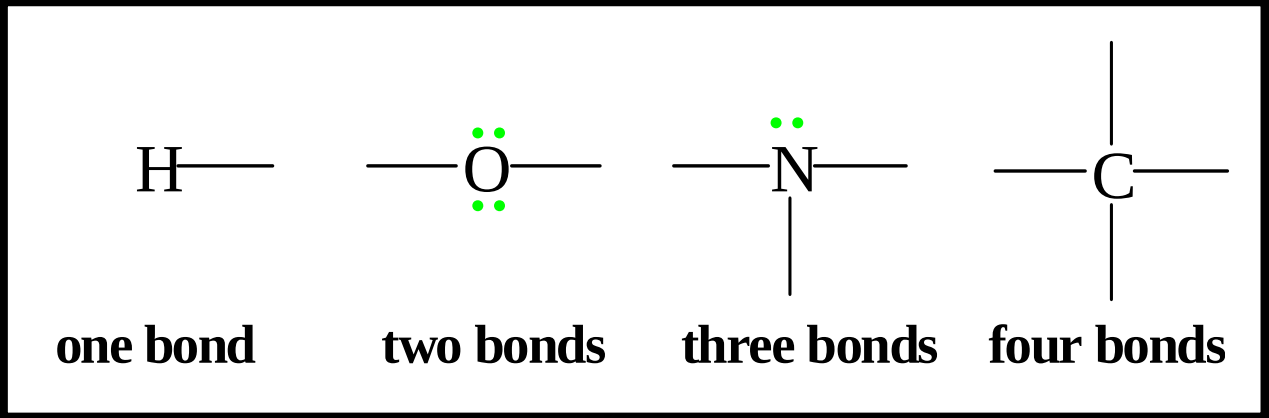
- **Pauli Exclusion Principle**: A maximum of two spin paired electrons may be placed in each orbital

- **Hund's Rule**: One electron is added to each degenerate (equal energy orbital) before a second electron is added

Electronic Configurations of Some Second Row Elements



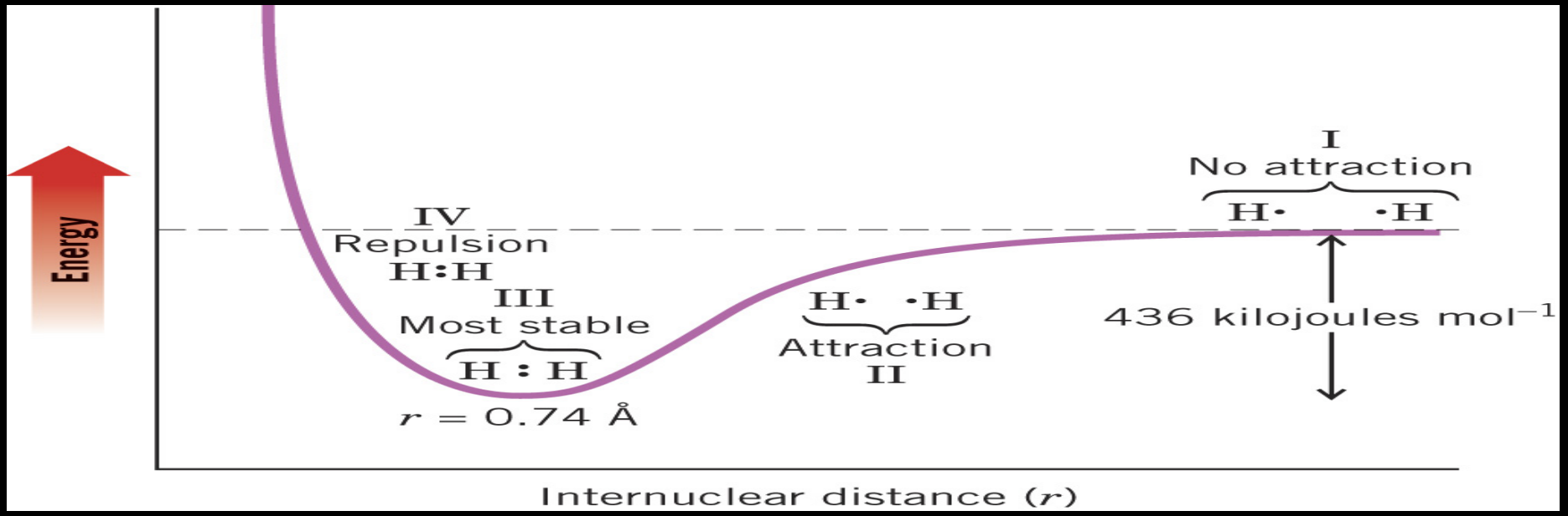
Number of Covalent Bonds



1.11 Molecular Orbitals (MOs)

➔ 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
- 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


Energy
I
No attraction
H· ·H
IV
Repulsion
H:H
III
Most stable
H : H
r = 0.74 Å
H· ·H
Attraction
II
436 kilojoules mol⁻¹
Internuclear distance (r)

- 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

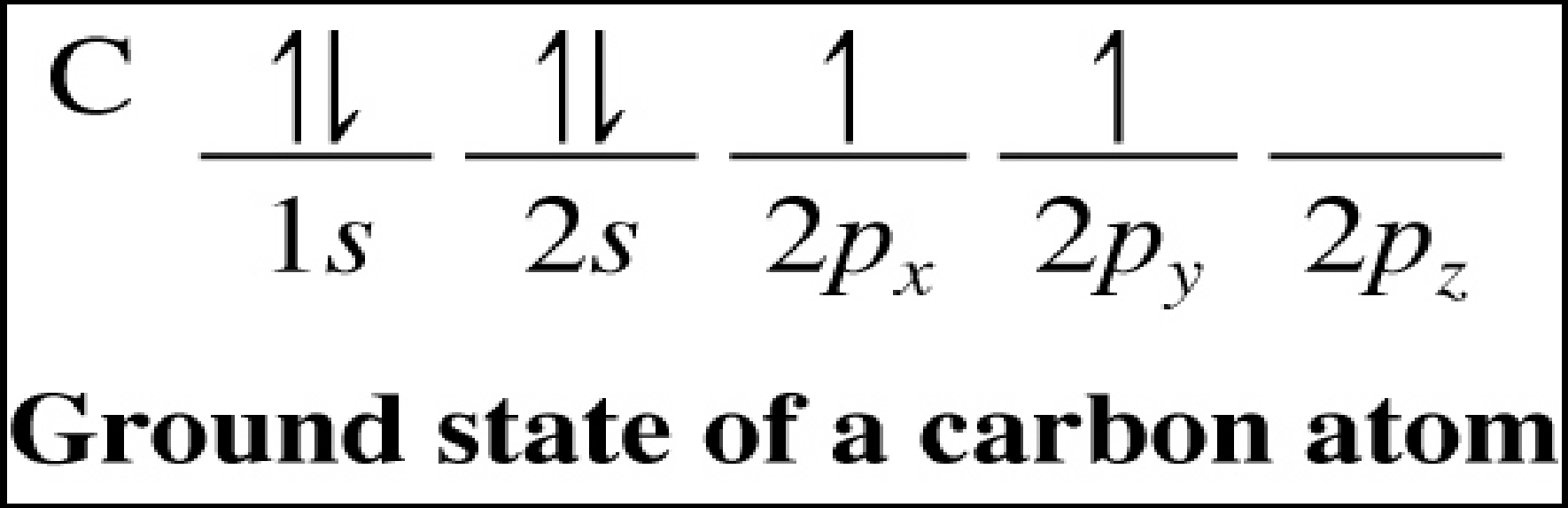
- The number of MOs that result must always equal the number of AOs used

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

- **Geometry of the molecule is determined by the number of sets of electrons by using geometrical principles**

1.12 The Structure of Methane (CH_4) and Ethane (CH_3CH_3): sp^3 Hybridization

➔**The structure of methane with its four identical tetrahedral bonds cannot be adequately explained using the electronic configuration of carbon**



Ground state of a carbon atom

- The attached groups in CH_4 (i.e. Hydrogen atoms) are **not at the angles of the p orbitals** and their atomic orbitals would not have maximum overlap to form strong bonds

- **Hybridization** of the valence orbitals (2*s* and 2*p*) provides **four new identical orbitals** which match the bond angles of the attached groups. There is one sp^3 hybridized carbon and three hydrogen atoms in methane

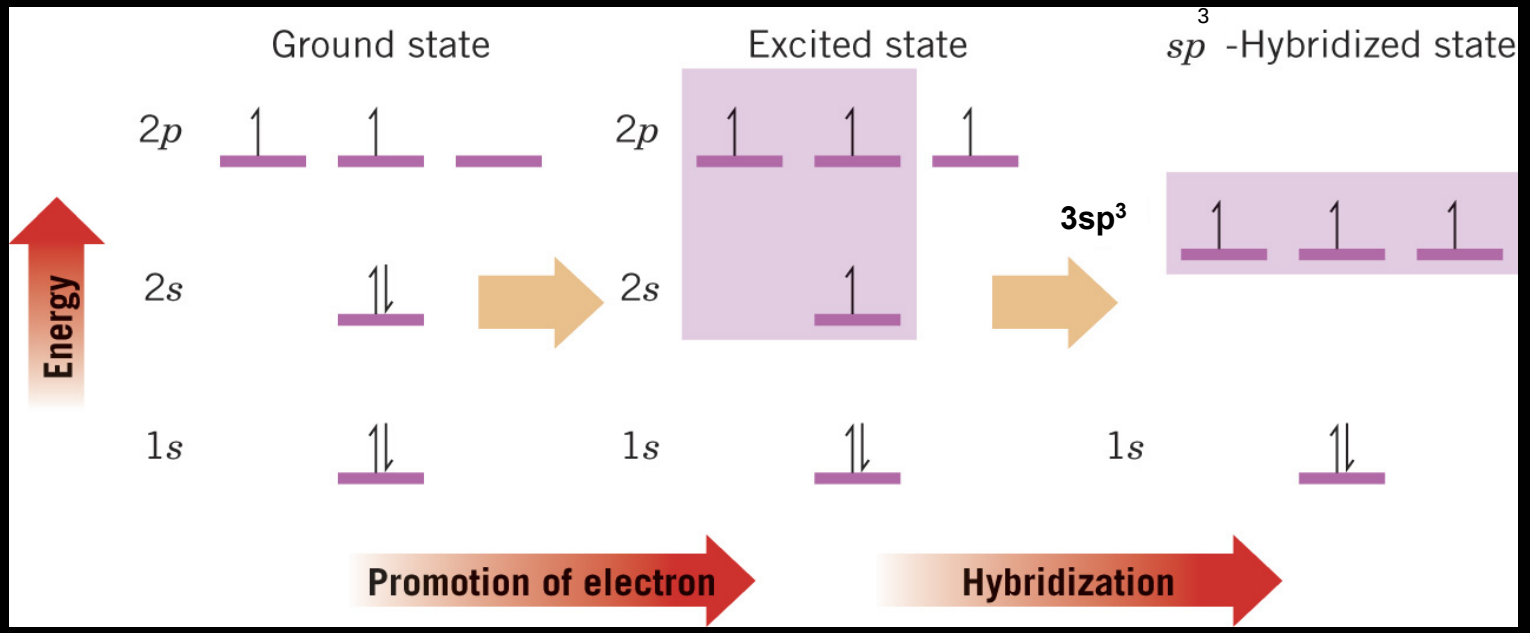
- *Orbital hybridization* is a mathematical combination of the 2*s* and 2*p* wave functions to obtain wave functions for the new orbitals

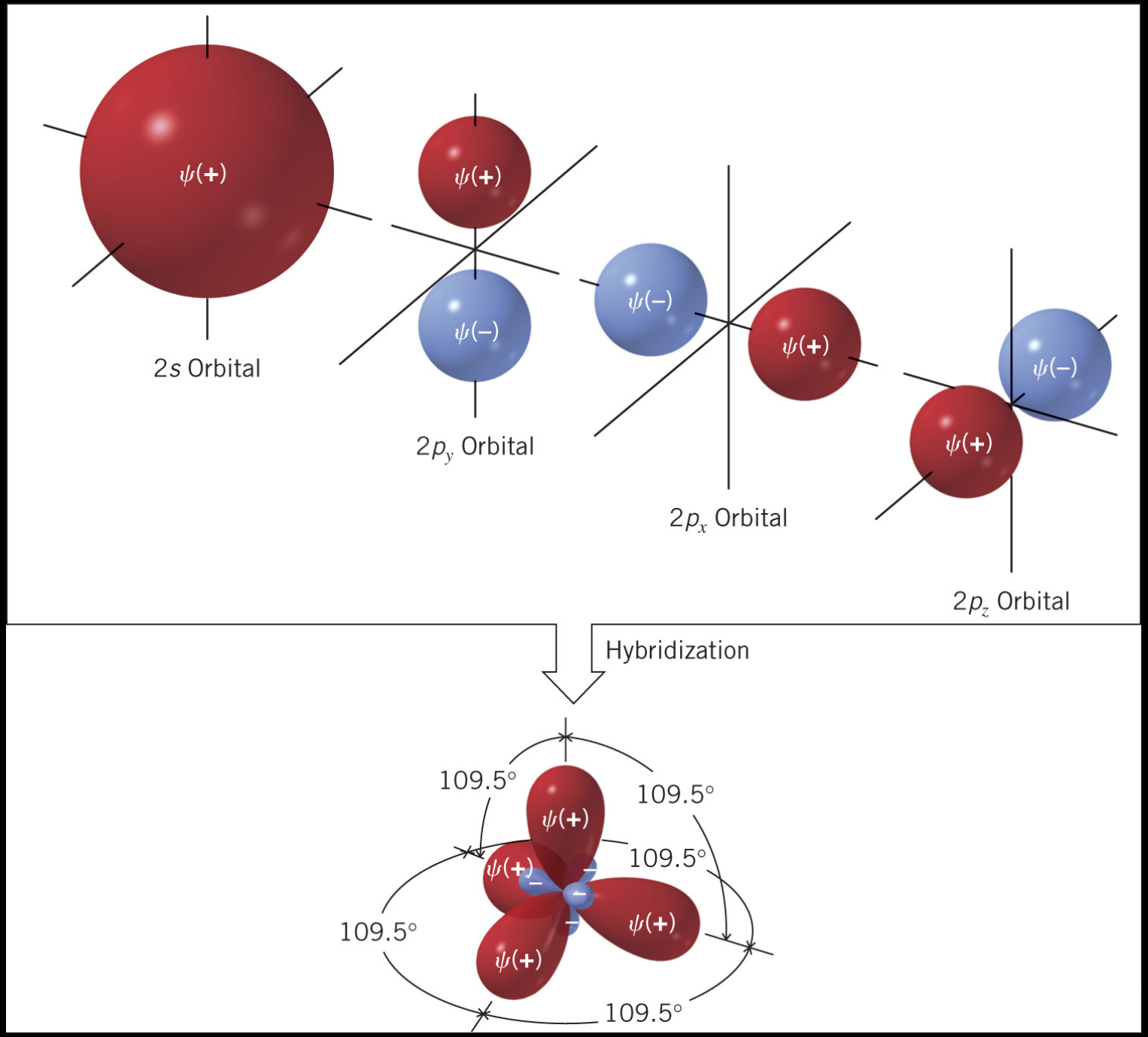
- **When one 2*s* orbital and three 2*p* orbitals are hybridized four new and identical sp^3 orbitals are obtained**

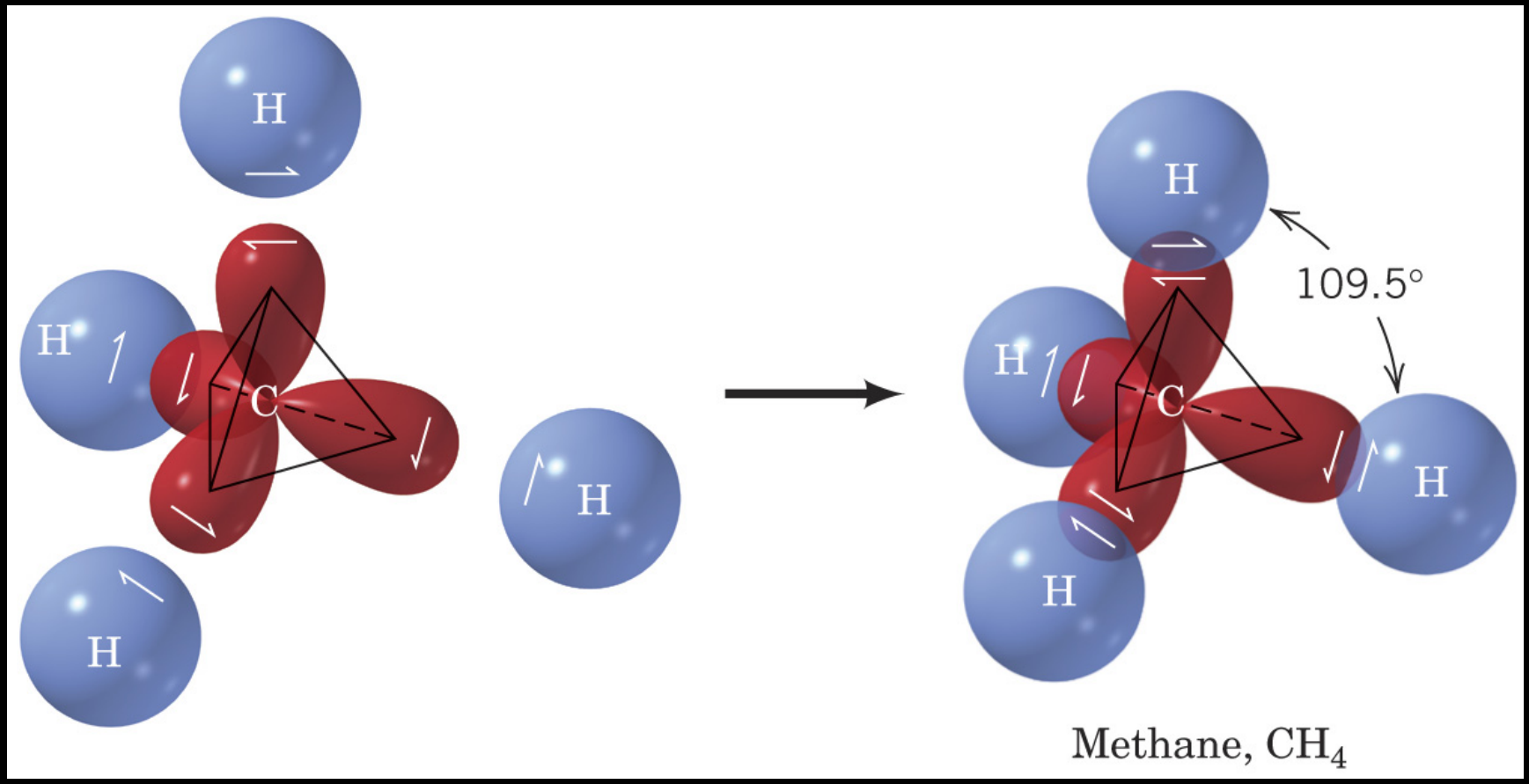
  - **When four orbitals are hybridized, four orbitals must result**
  - **Each new orbital has one part *s* character and 3 parts *p* character**
  - **The four identical orbitals are oriented in a tetrahedral arrangements (109.5° bond angle)**
  - **The resulting four C-H bonds are equivalent**

- The four sp^3 orbitals are then combined with the 1s orbitals of four hydrogens to give the molecular orbitals of methane

- Each new molecular orbital can accommodate 2 electrons

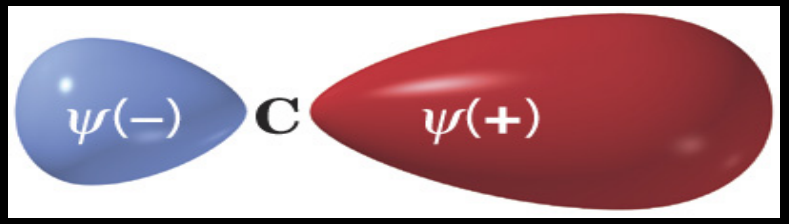



ψ(+)
2s Orbital
ψ(+)
ψ(−)
2p_y Orbital
ψ(−)
ψ(+)
2p_x Orbital
ψ(−)
ψ(+)
2p_z Orbital
Hybridization
109.5°
109.5°
109.5°
109.5°
109.5°
ψ(+)
ψ(+)
ψ(+)
ψ(+)

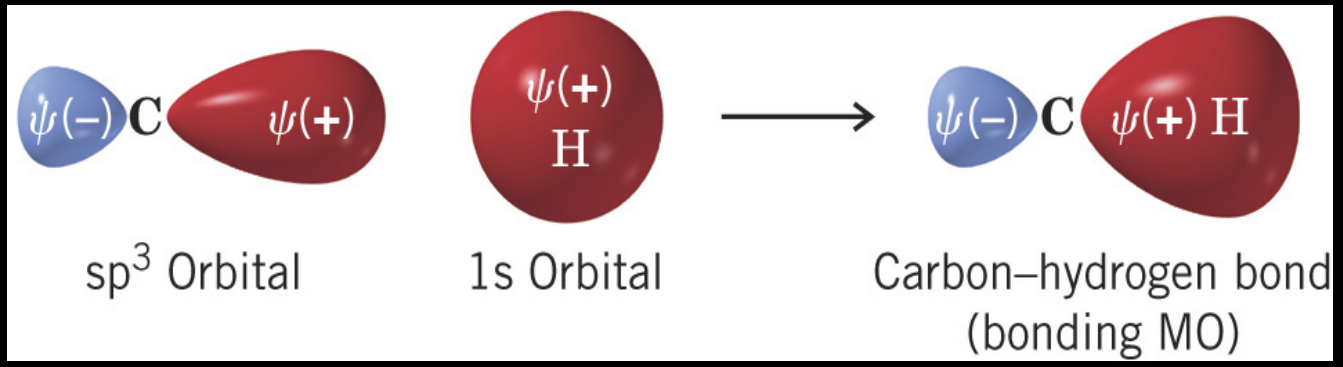


Methane, CH_4

➔An *sp*³ orbital looks like a *p* orbital with one lobe greatly extended

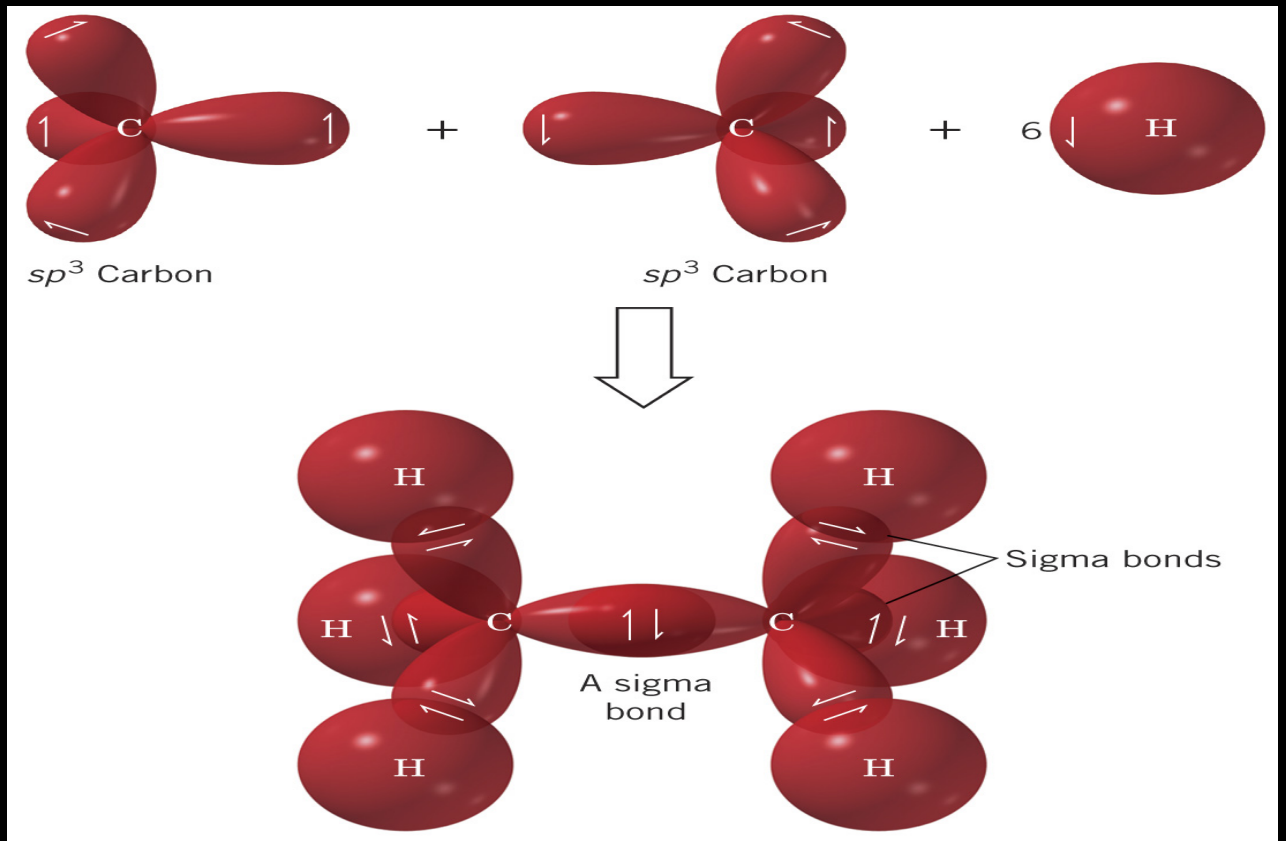


➔The extended *sp*³ lobe can then overlap well with the hydrogen 1*s* to form a strong bond



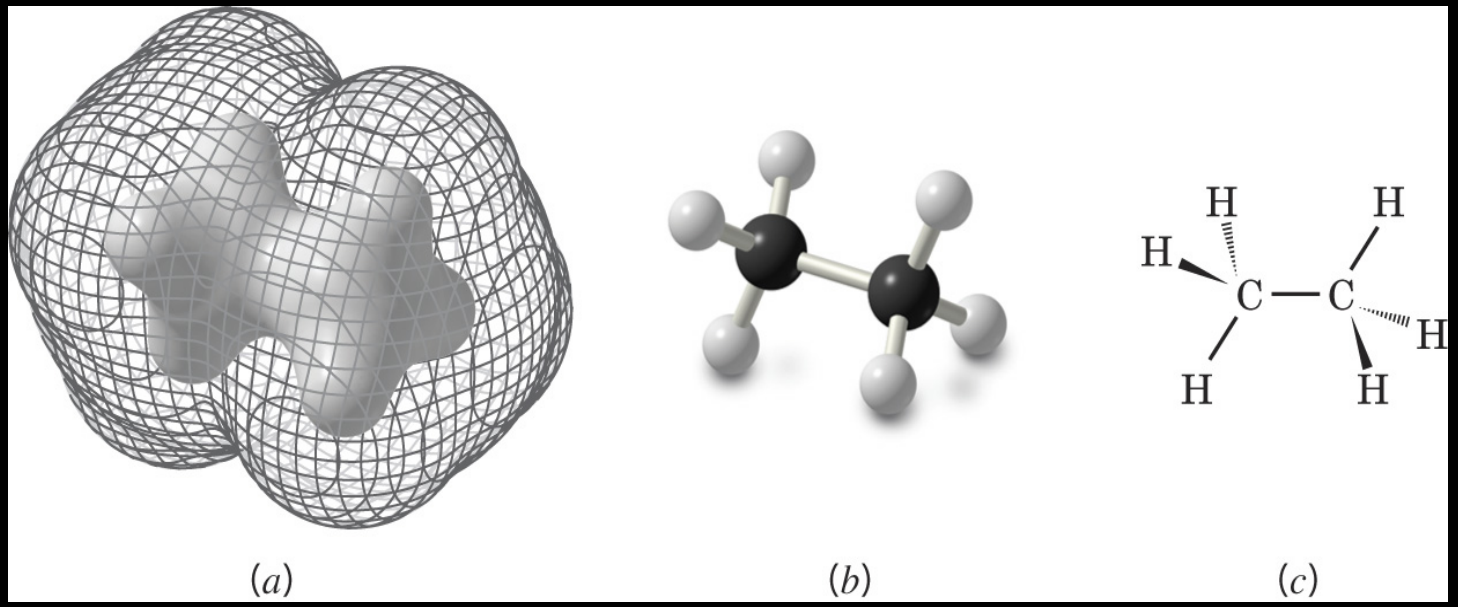
➔The bond formed is called a **sigma (σ)** bond because it is circularly symmetrical in cross section when view along the bond axis

- **Ethane (C_2H_6)**
  - ➔**The carbon-carbon bond is made from overlap of two *sp*³ orbitals to form a σ bond**
  - ➔**The molecule is approximately tetrahedral around each carbon**



➔**The representations of ethane show the tetrahedral arrangement around each carbon**

a. calculated electron density surface **b.** ball-and-stick model **c.** typical 3-dimensional drawing

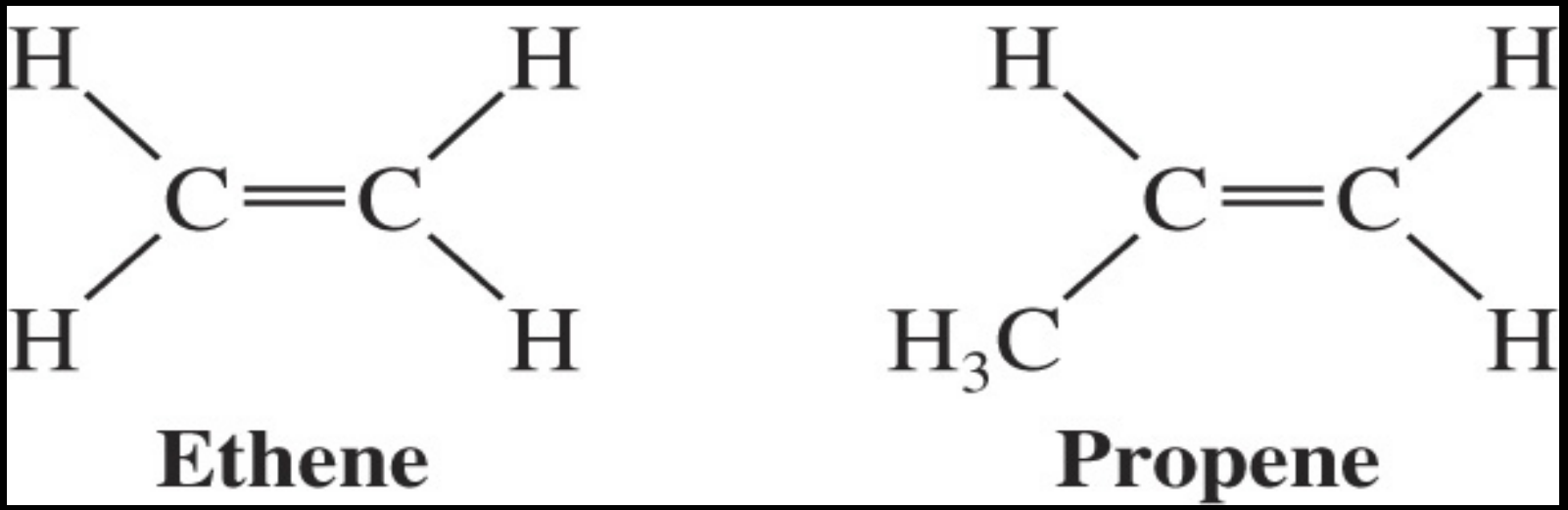


➔**Generally there is relatively free rotation about σ bonds. Very little energy (13-26 kcal/mol) is required to rotate around the carbon-carbon bond of ethane**

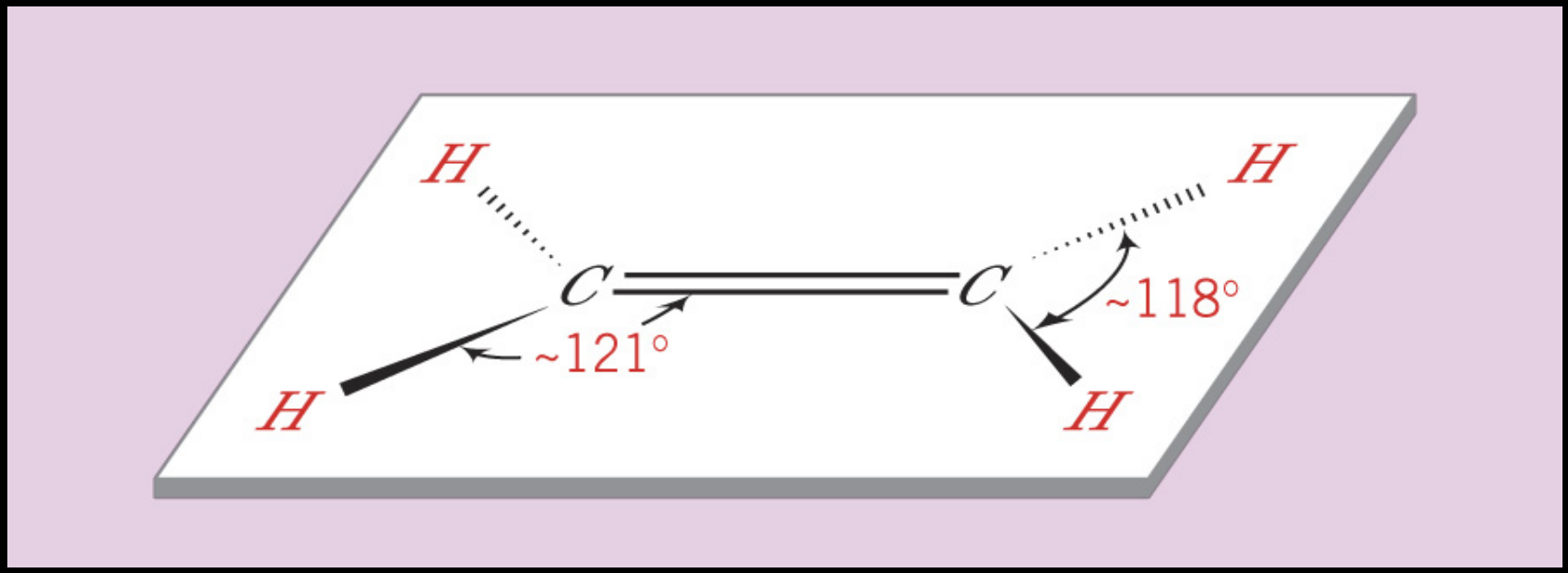
1.13 The Structure of Ethene (Ethylene) : sp^2 Hybridization

→ **Ethene (C_2H_2) contains a carbon-carbon double bond and is in the class of organic compounds called *alkenes***

- **Another example of the alkenes is propene**



- **The geometry around each carbon is called *trigonal planar***
- **All atoms directly connected to each carbon are in a plane**
- **The bonds point towards the corners of a regular triangle**
- **The bond angle are approximately 120°**



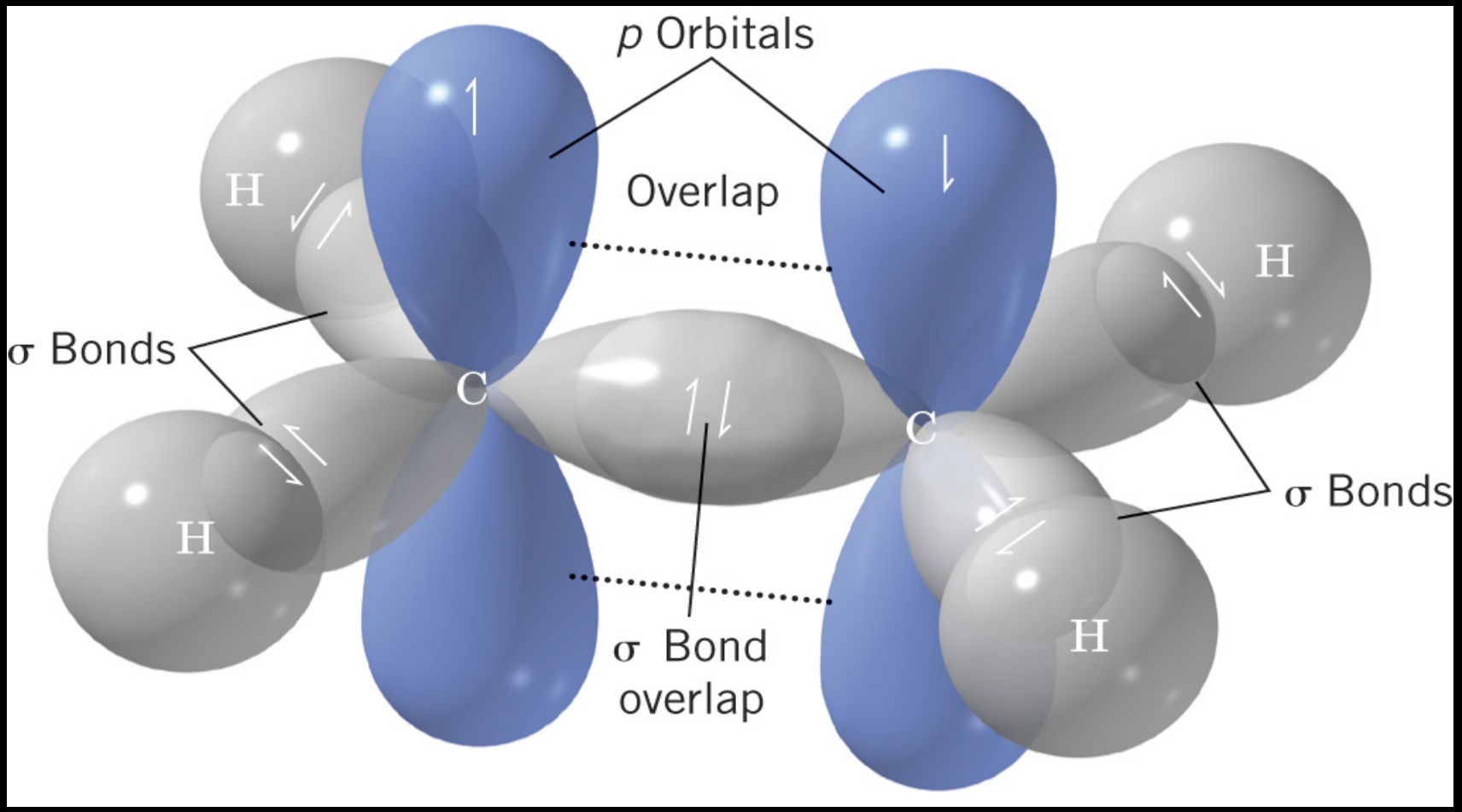
➔Overlap of *sp²* orbitals in ethylene results in formation of a s framework

- One *sp²* orbital on each carbon overlaps to form a carbon-carbon σ bond; the remaining sp^2 orbitals form bonds to hydrogen

➔The leftover *p* orbitals on each carbon overlap to form a bonding π bond between the two carbons

➔A π bond results from overlap of *p* orbitals above and below the plane of the σ bond

- It has a nodal plane passing through the two bonded nuclei and between the two lobes of the p molecular orbital


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

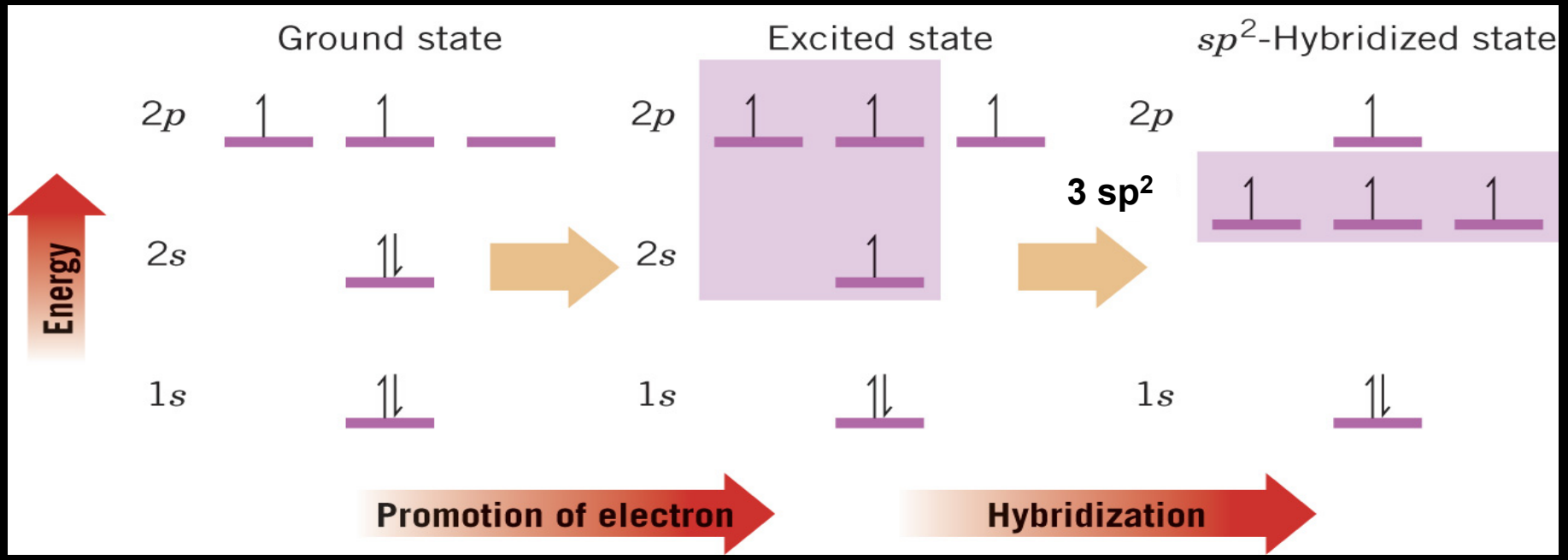
➔**There are three σ bonds around each carbon of ethene and these are formed by using sp^2 hybridized orbitals**

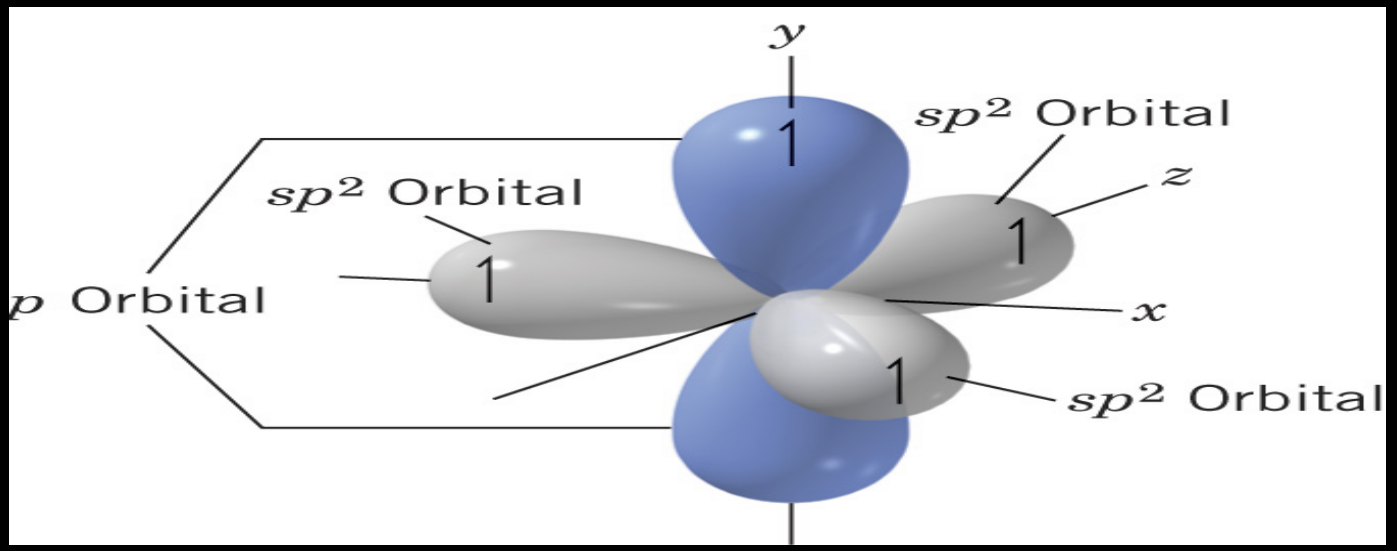
➔**The three sp^2 hybridized orbitals come from mixing one *s* and two *p* orbitals**

- **One *p* orbital is left unhybridized**

➔**The sp^2 orbitals are arranged in a trigonal planar arrangement**

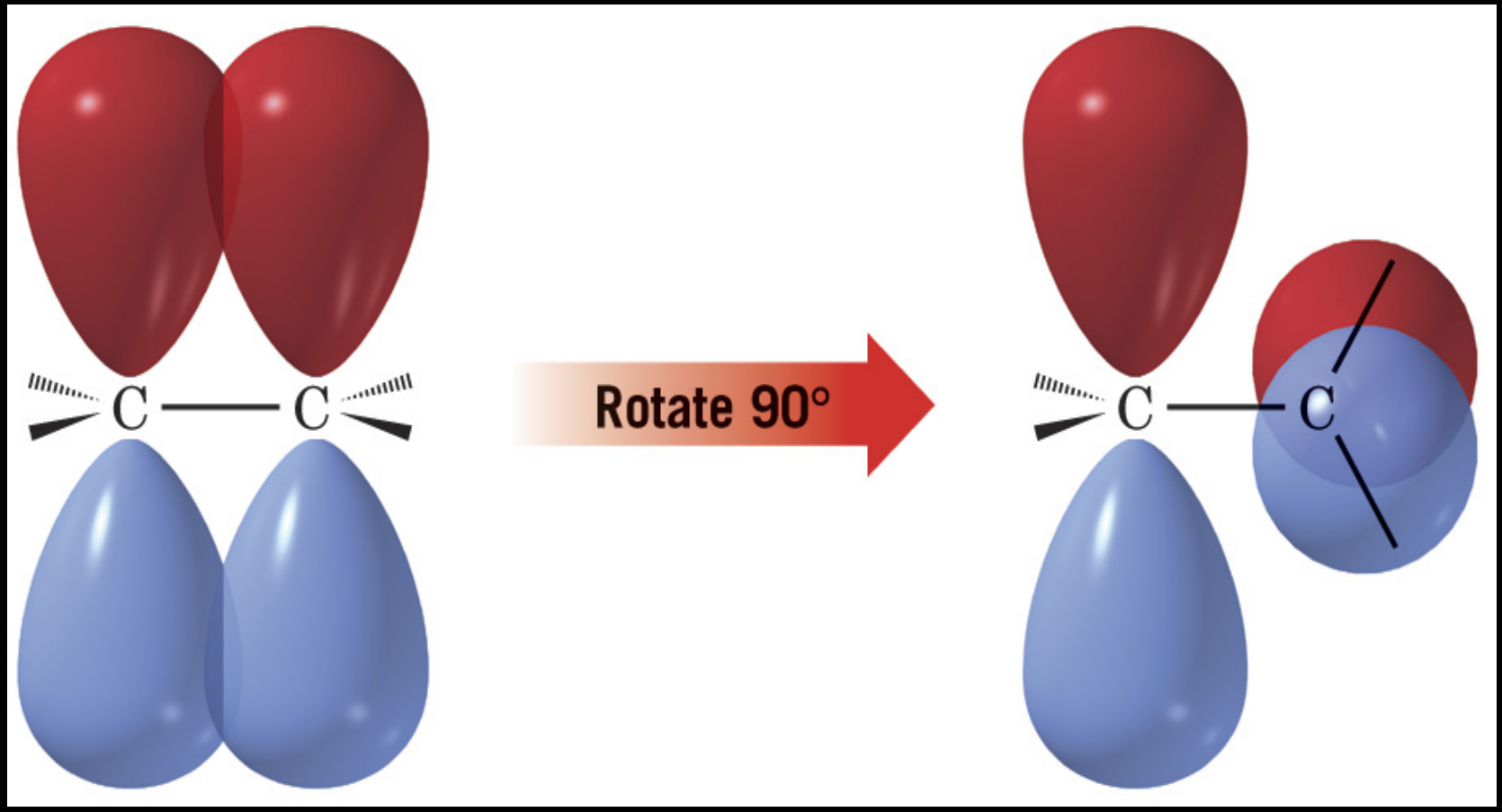
- **The *p* orbital is perpendicular (orthogonal) to the plane**


Ground state
Excited state
sp^2-Hybridized state
2p
2s
1s
Energy
3 sp²
Promotion of electron
Hybridization


y
sp² Orbital
z
sp² Orbital
p Orbital
x
sp² Orbital

Restricted Rotation and the Double Bond

- ➔There is a large energy barrier to rotation (about 264 kJ/mol) around the double bond
  - This corresponds to the strength of a π bond
  - The rotational barrier of a carbon-carbon single bond is 13-26 kJ/mol
- ➔This rotational barrier results because the *p* orbitals must be well aligned for maximum overlap and formation of the π bond
- ➔Rotation of the *p* orbitals 90^{o} totally breaks the π bond


C
C
Rotate 90°
C
C

Cis-trans isomers

➔**Cis-trans isomers are the result of restricted rotation about double bonds**

➔**These isomers have the same connectivity of atoms and differ only in the arrangement of atoms in space**

- **This puts them in the broader class of stereoisomers**

➔**The molecules below do not *superpose* on each other**

- One molecule is designated **cis** (**groups on same side**) and the other is **trans** (**groups on opposite side**)

cis-1,2-Dichloroethene

trans-1,2-Dichloroethene

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

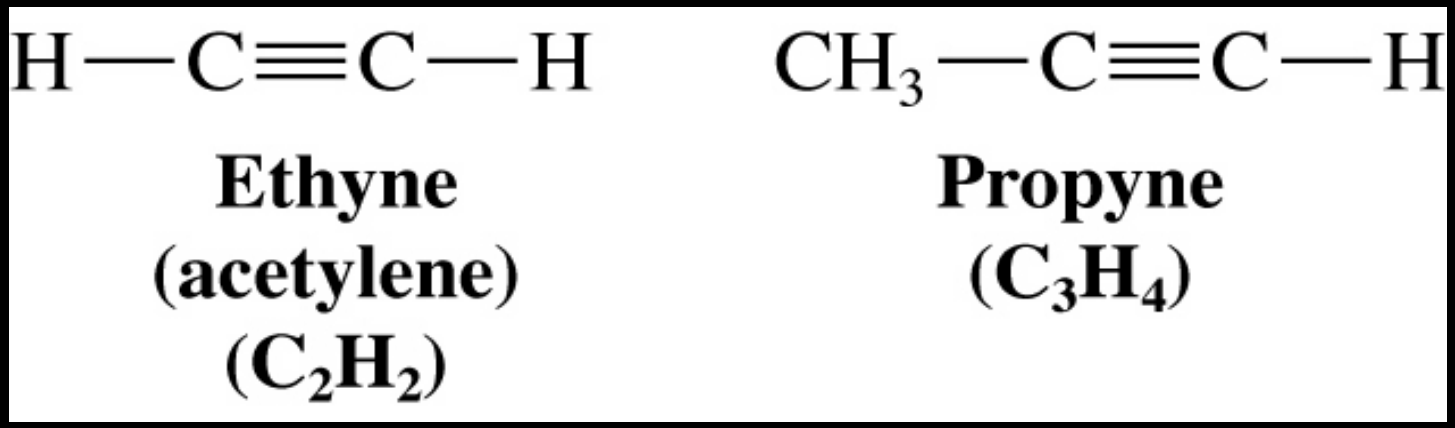
1,1-Dichloroethene
(no cis–trans isomerism)

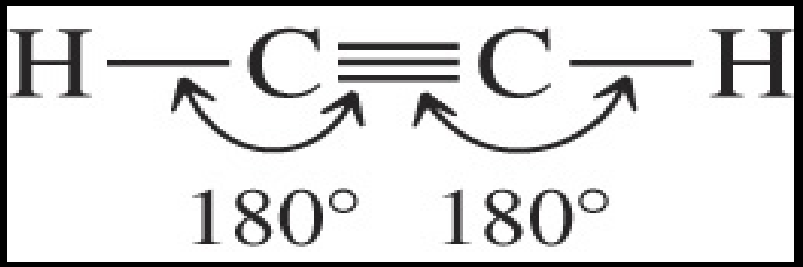
1,1,2-Trichloroethene
(no cis–trans isomerism)

1.14 The Structure of Ethyne (Acetylene): *sp* Hybridization

➔Ethyne (acetylene) is a member of a group of compounds called alkynes which all have carbon-carbon triple bonds

- Propyne is another typical alkyne

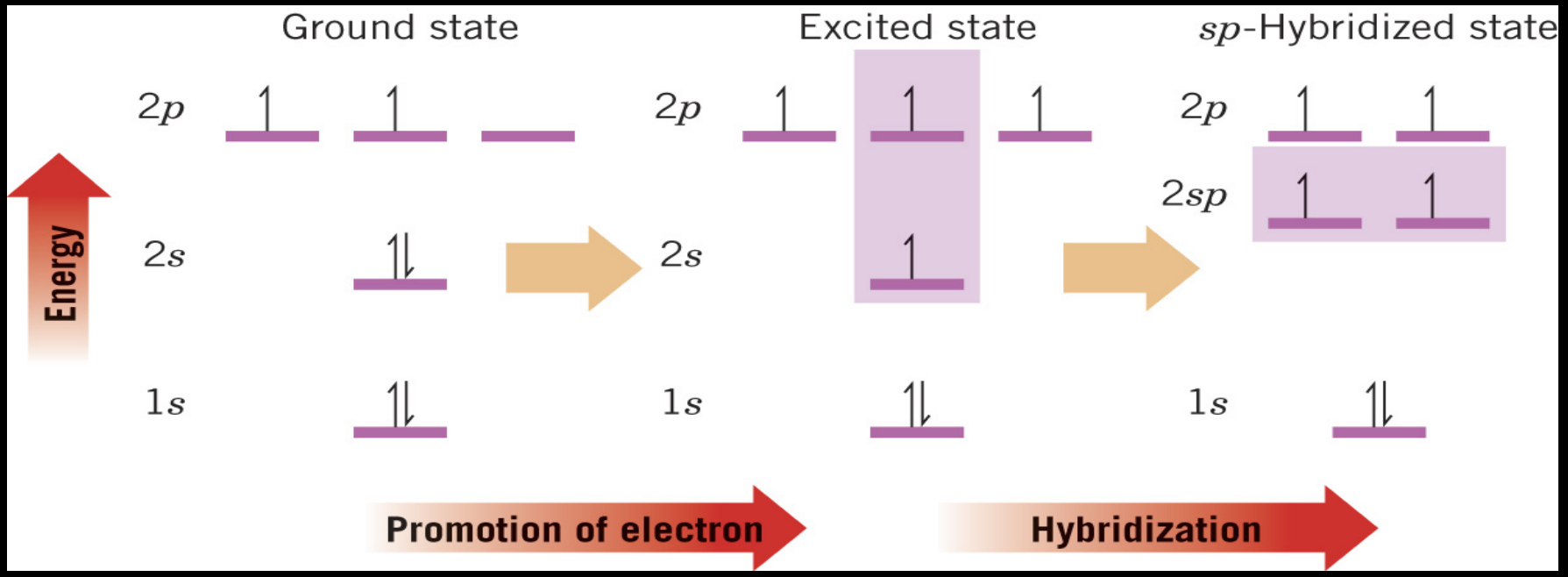




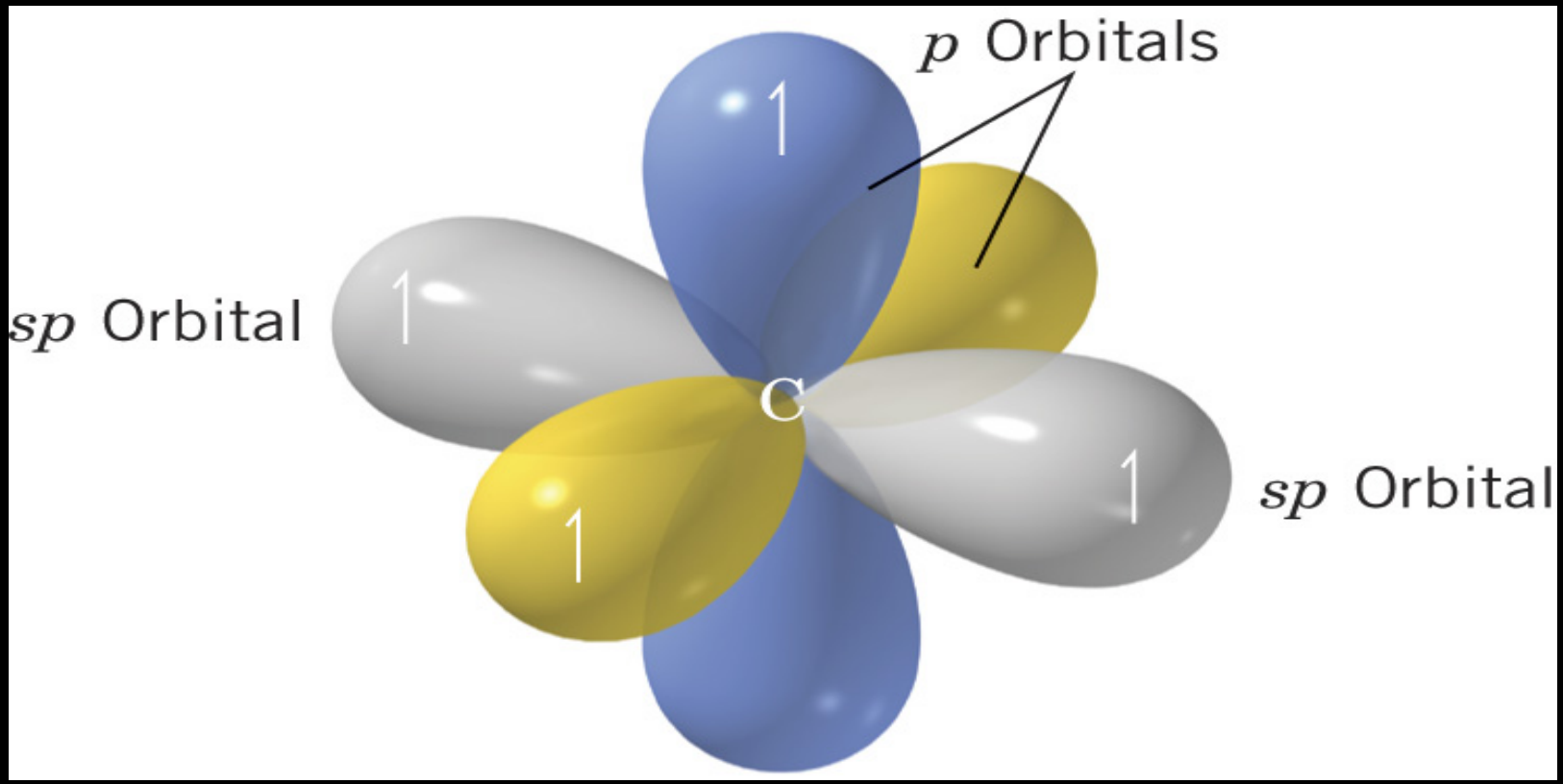
➔The arrangement of atoms around each carbon is linear with bond angles 180°

➔**The carbon in ethyne is *sp* hybridized**

- **One *s* and one *p* orbital are mixed to form two *sp* orbitals**
- **Two *p* orbitals are left unhybridized**



- **The two *sp* orbitals are oriented 180° relative to each other around the carbon nucleus**
- **The two *p* orbitals are perpendicular to the axis that passes through the center of the *sp* orbitals**

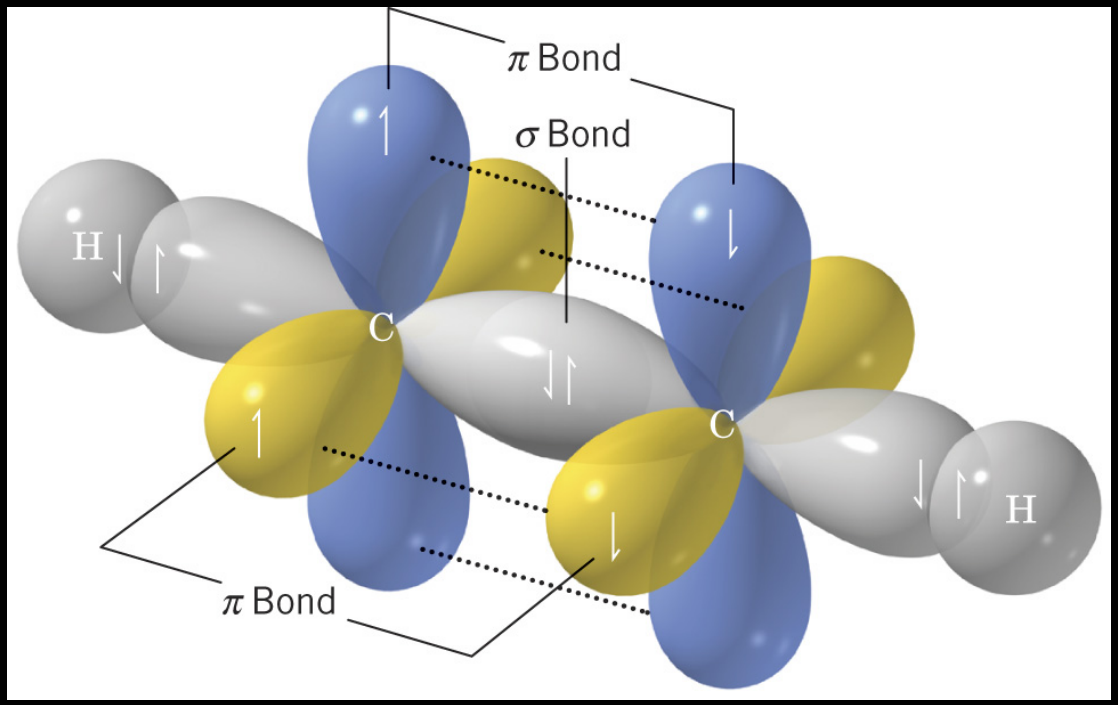


➔In ethyne the *sp* orbitals on the two carbons overlap to form a σ bond

- The remaining *sp* orbitals overlap with hydrogen 1s orbitals

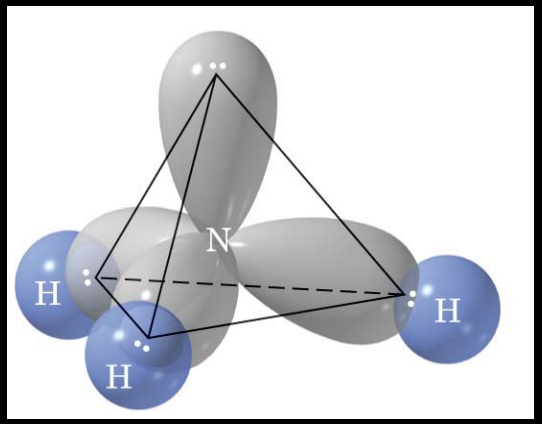
➔The *p* orbitals on each carbon overlap to form **two** π bonds

➔The **triple** bond consists of **one** σ **and two** π bonds



Examples of Hybridization in Non-Carbon Compounds

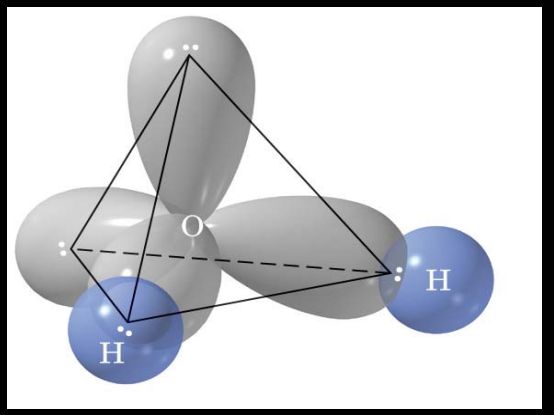
Ammonia



N is sp^3 in NH_3

There are four sets of electrons: 3 bonding pairs and 1 non-bonding pair

Water

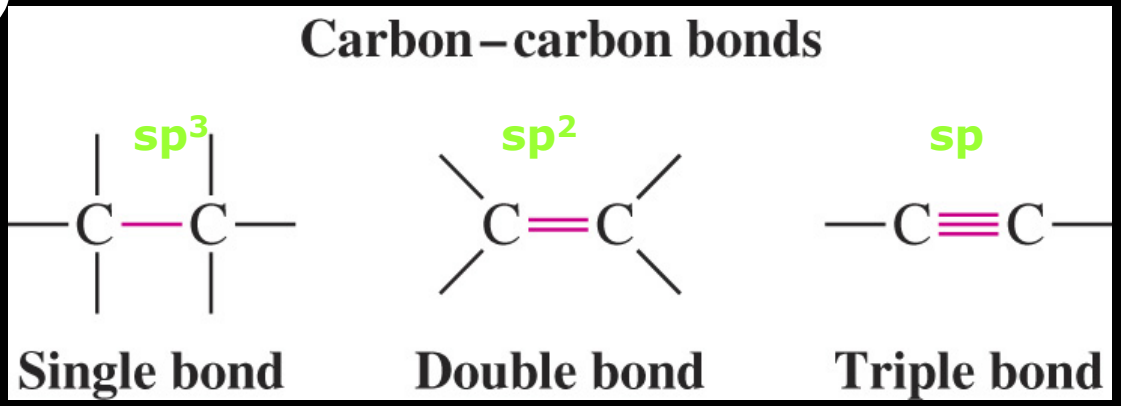


O is sp^3 in H_2O

There are four sets of Electrons: 2 bonding and 2 non-bonding pairs

Carbon-Carbon Covalent Bonds

- Sigma bonds are the most common bonds in organic chemistry
- All single bonds are sigma bonds
- A double bond always consists of a σ bond (using hybrid orbitals) and one π bond (using p orbitals)

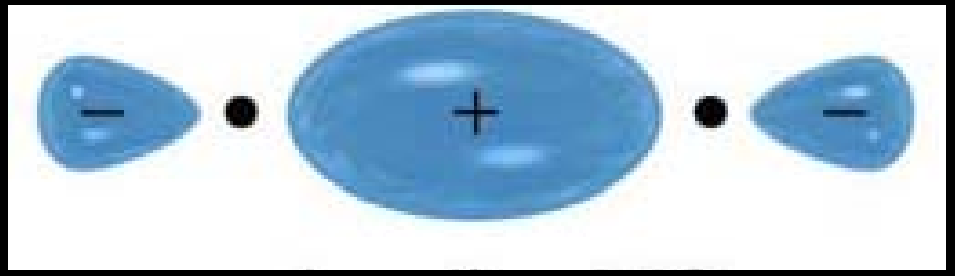


- Carbon-carbon σ bond is stronger, due to better overlap, less accessible bonding electrons
- Carbon-carbon π bond weaker thus reactive, more accessible electrons

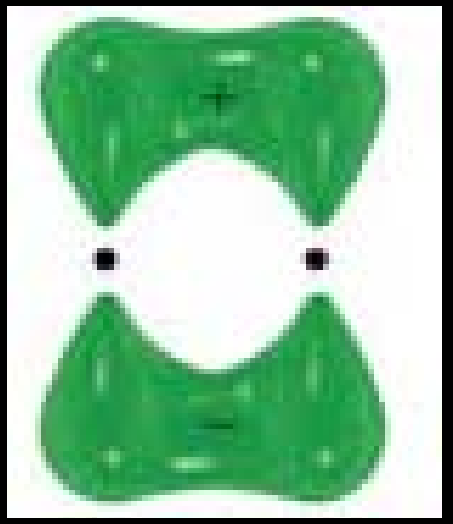
- π bonds are usually weaker than sigma bonds because their (negatively charged) electron density is farther from the positive charge of the atomic nucleus, which requires more energy

- From the perspective of quantum mechanics, this bond's weakness is explained by significantly less overlap between the component **p-orbitals** due to their parallel orientation

σ bond

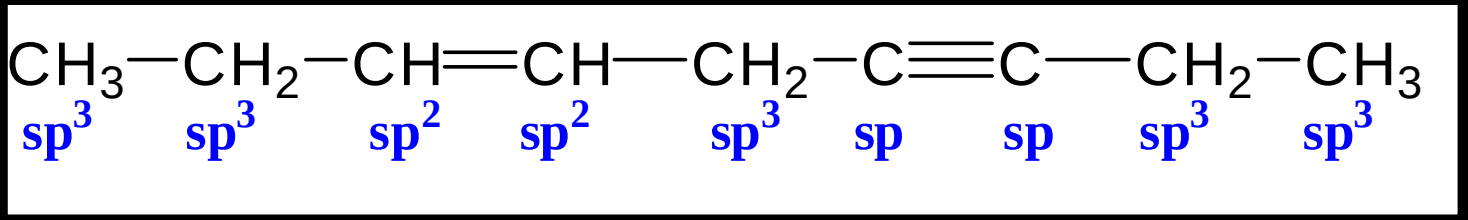


π bond



Summary of Hybridization for Carbon

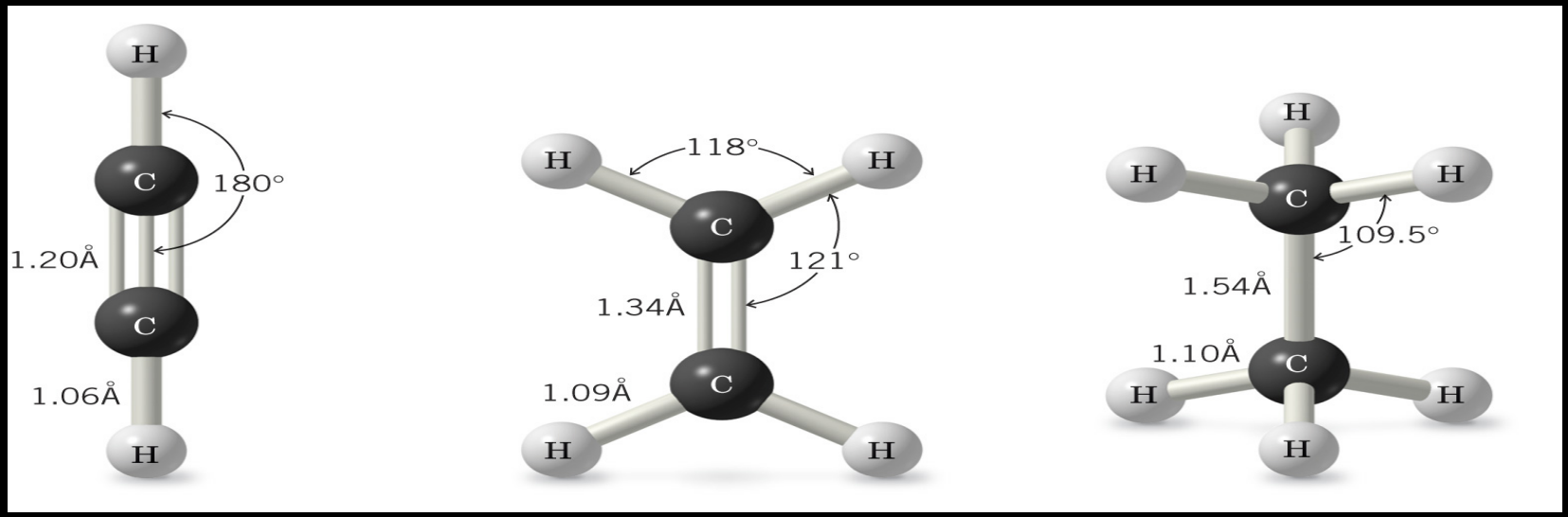
Type of Hybrid	sp^3	sp^2	sp
Atomic orbitals used	s, p, p, p	s, p, p	s, p
Number of hybrid orbitals formed	4	3	2
Number of atoms bonded to the C	4	3	2
Number of sigma bonds	4	3	2
Number of left over p orbitals	0	1	2
Number of pi bonds	0	1	2
Bonding pattern	| - C - |	\ C = /	= C = or - C º



Bond Lengths of Ethyne, Ethene and Ethane

- **The carbon-carbon bond length is shorter as more bonds hold the carbons together**
  - **With more electron density between the carbons, there is more "glue" to hold the nuclei of the carbons together**
- **The carbon-hydrogen bond lengths also get shorter with more *s* character of the bond**
  - **2*s* orbitals are held more closely to the nucleus than 2*p* orbitals**
  - **A hybridized orbital with more percent *s* character is held more closely to the nucleus than an orbital with less *s* character**

- **The *sp* orbital of ethyne has 50% *s* character and its C-H bond is shorter**
- **The sp^3 orbital of ethane has only 25% *s* character and its C-H bond is longer**



1.16 Molecular Geometry: The Valence Shell Electron Pair Repulsion (VSEPR) Model

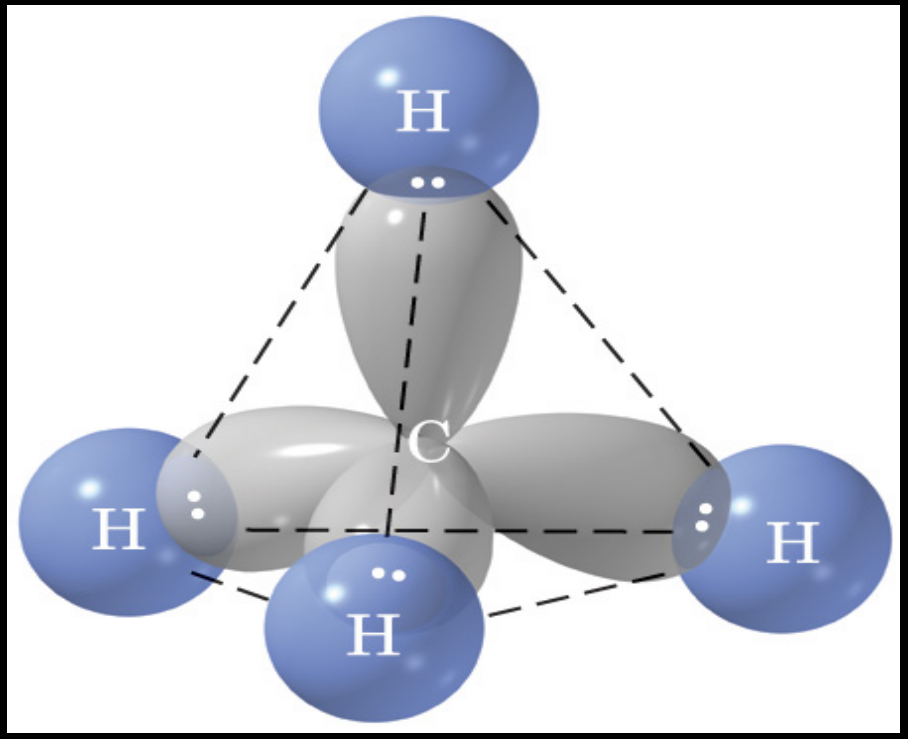
- This is a simple theory to predict the geometry of molecules

- All sets of valence electrons are considered including:
  - Bonding pairs involved in single or multiple bonds
  - Non-bonding pairs which are unshared

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

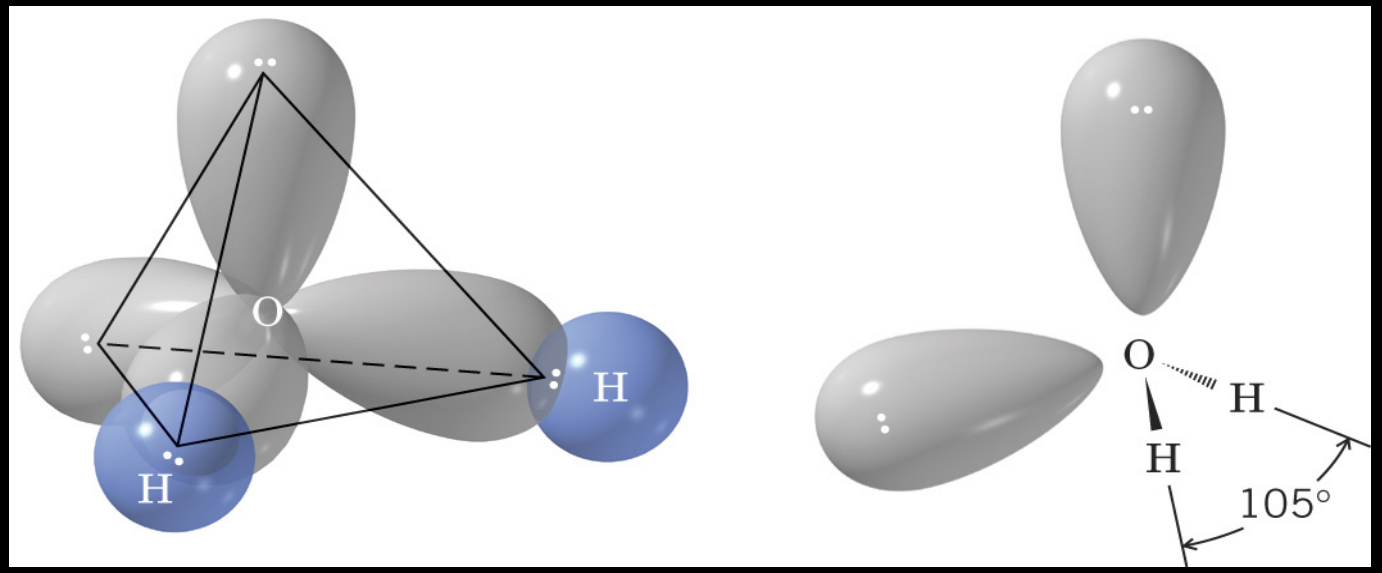
Structure of Methane

- The valence shell of methane contains four pairs or sets of electrons
- To be as far apart from each other as possible they adopt a tetrahedral arrangement (bond angle 109.5°)



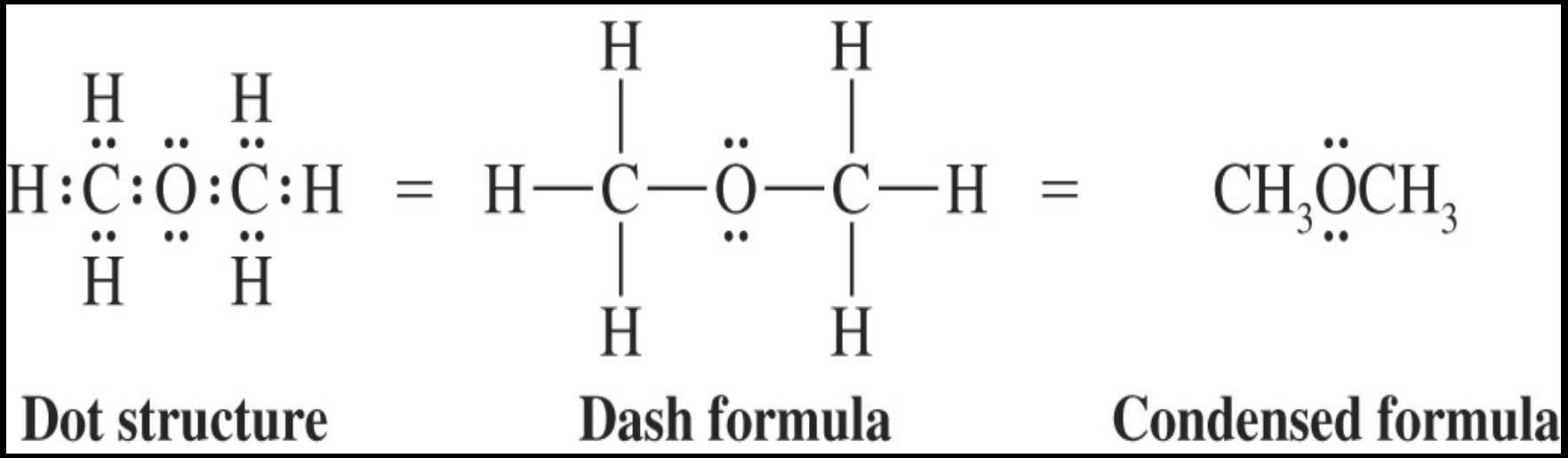
Structure of Water

- There are four sets of electrons including 2 bonding pairs and 2 non-bonding pairs
- Again the geometry is essentially tetrahedral but the actual shape of the atoms is considered to be an angular arrangement
- The bond angle is about 105° because the two "larger" nonbonding pairs compress the electrons in the oxygen-hydrogen bonds



1.17 Representations of Structural Formulas

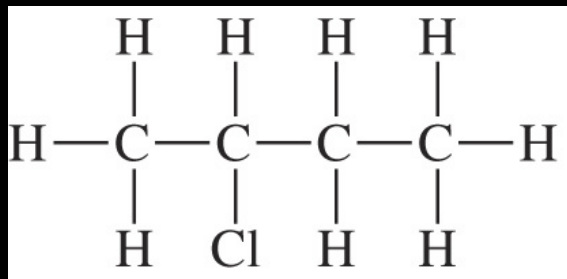
- Dot formulas are more cumbersome to draw than dash formulas and condensed formulas
- Lone-pair electrons are often (but not always) drawn in, especially when they are crucial to the chemistry being discussed



Condensed Structural Formulas

- In these representations, some or all of the dash lines are omitted
- In partially condensed structures all hydrogens attached to an atom are simply written after it but some or all of the other bonds are explicitly shown
- In fully condensed structure 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

Examples for Condensed Structural Formulas

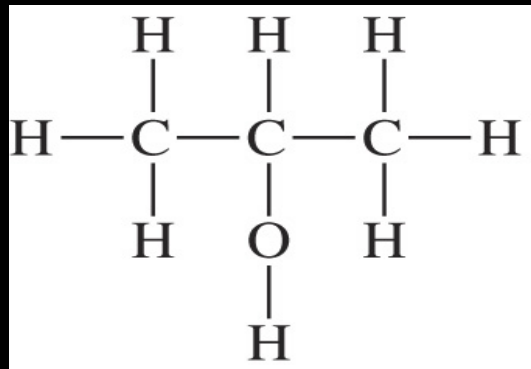


Dash formula

$CH_3CHCH_2CH_3$ or $CH_3CHClCH_2CH_3$

Cl

Condensed formulas



Dash formula

CH_3CHCH_3 $CH_3CH(OH)CH_3$

OH

$CH_3CHOHCH_3$ or $(CH_3)_2CHOH$

Condensed formulas

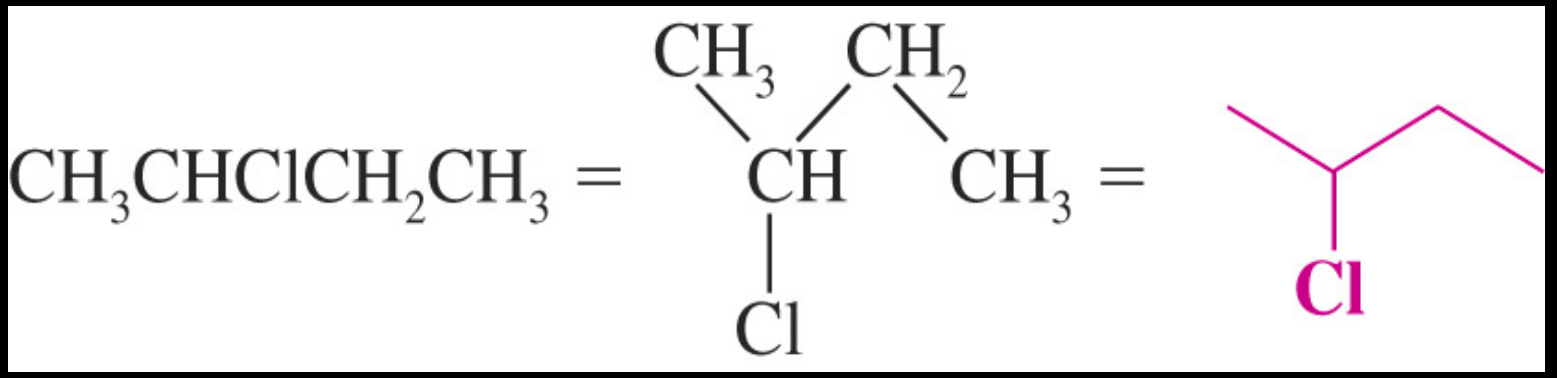
Bond-Line Formulas

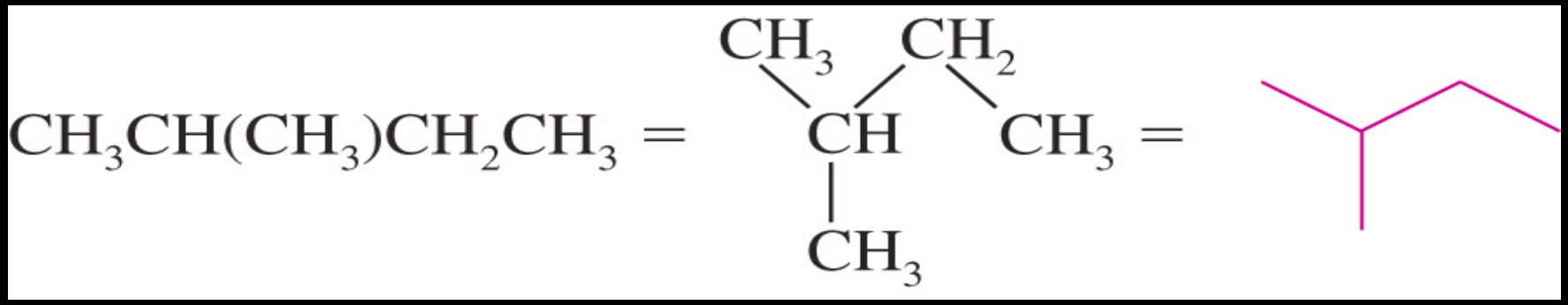
➔A further simplification of drawing organic molecules is to completely omit all carbons and hydrogens and only show heteroatoms (*e.g.* O, Cl, N) explicitly

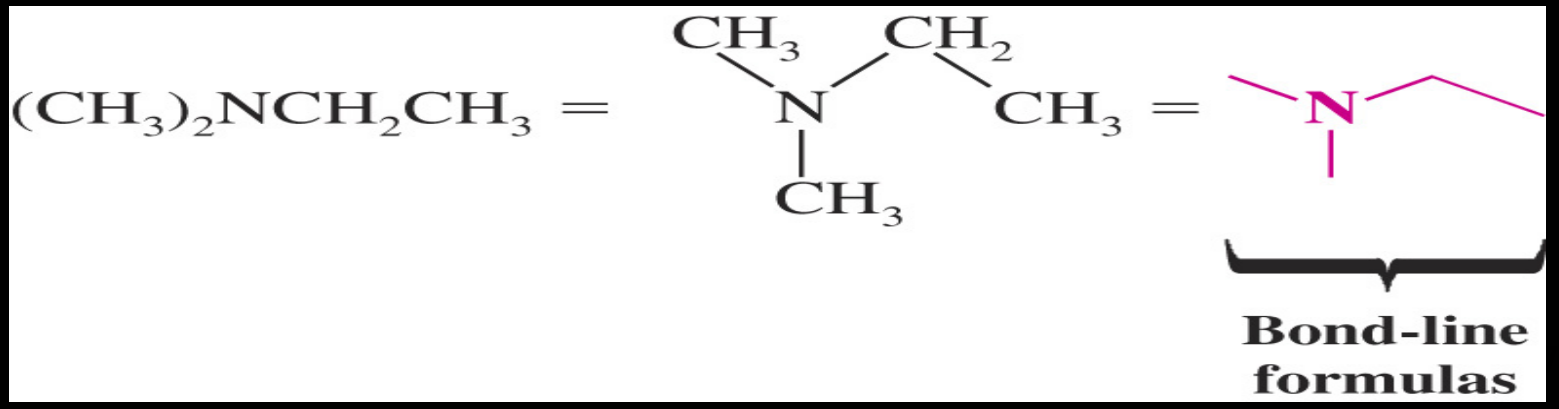
➔Each intersection or end of line in a zig-zag represents a carbon with the appropriate amount of hydrogens

- Heteroatoms with attached hydrogens must be drawn in explicitly

Example for Bond-Line Formulas

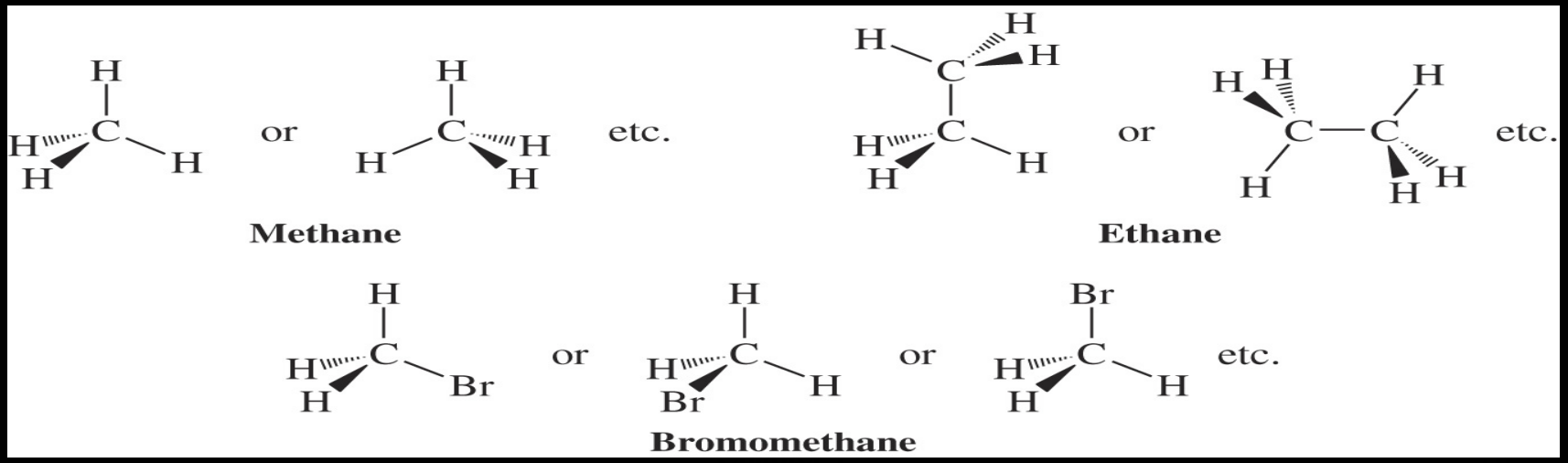






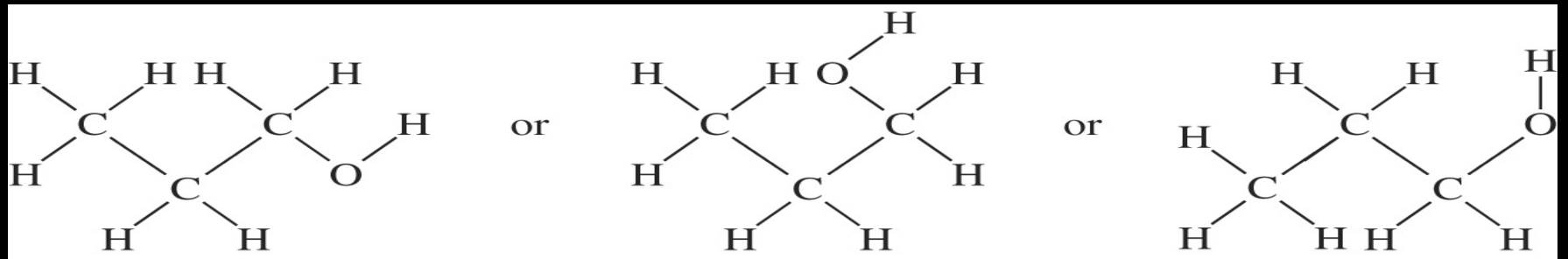
Three-Dimensional Formulas

- Since virtually all organic molecules have a 3-dimensional shape it is often important to be able to convey their shape
- The conventions for this are:
  - Bonds that lie in the plane of the paper are indicated by a simple line
  - Bonds that come forward out of the plane of the paper are indicated by a solid wedge
  - Bonds that go back out of the plane of the paper are indicated by a dashed wedge



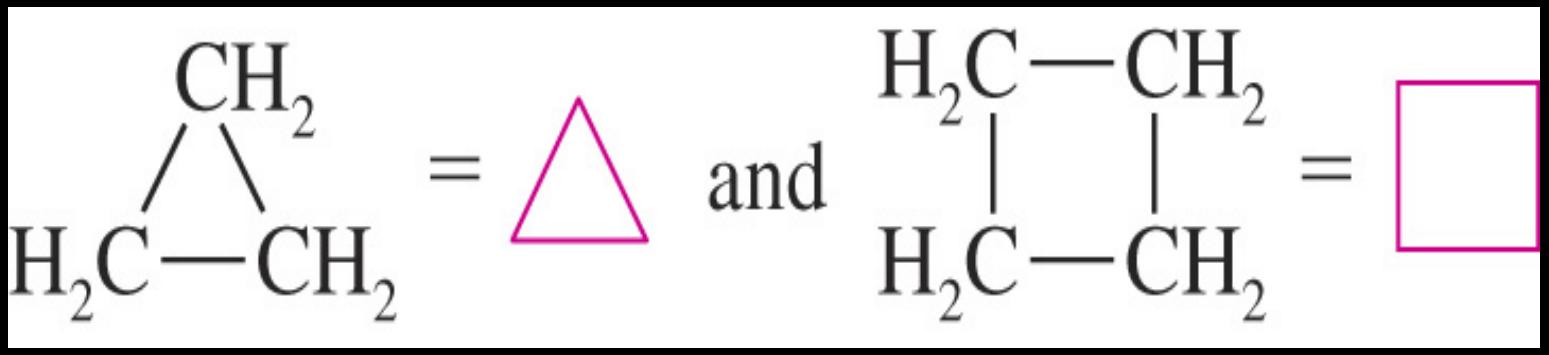
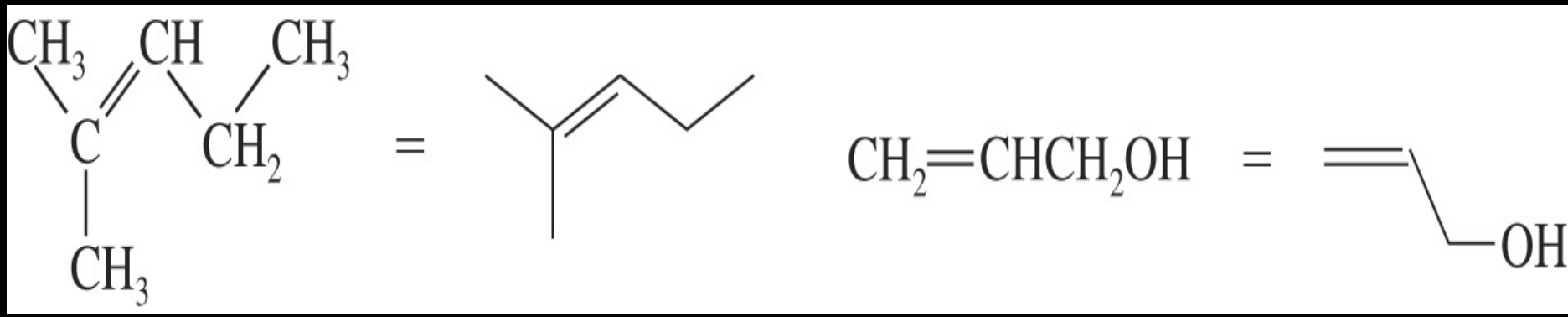
Dash Formulas

- 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° angles for carbons which actually have tetrahedral bond angles (109.5°)
- There is relatively free rotation around single bonds so the dash structures below are all equivalent



Equivalent dash formulas for propyl alcohol

➔**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**