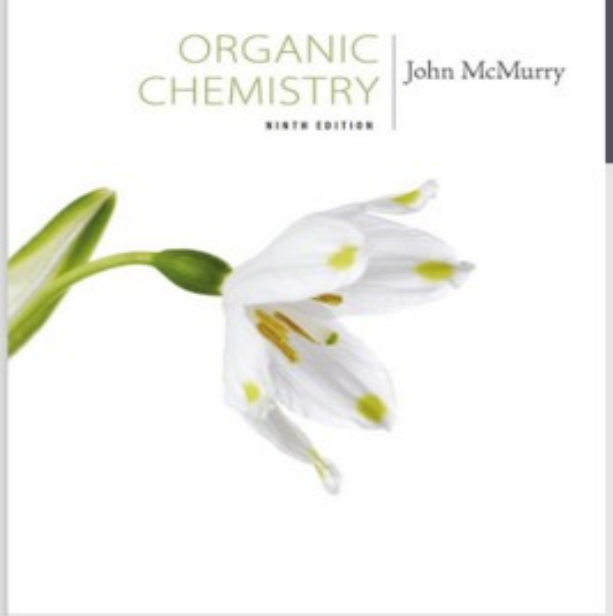


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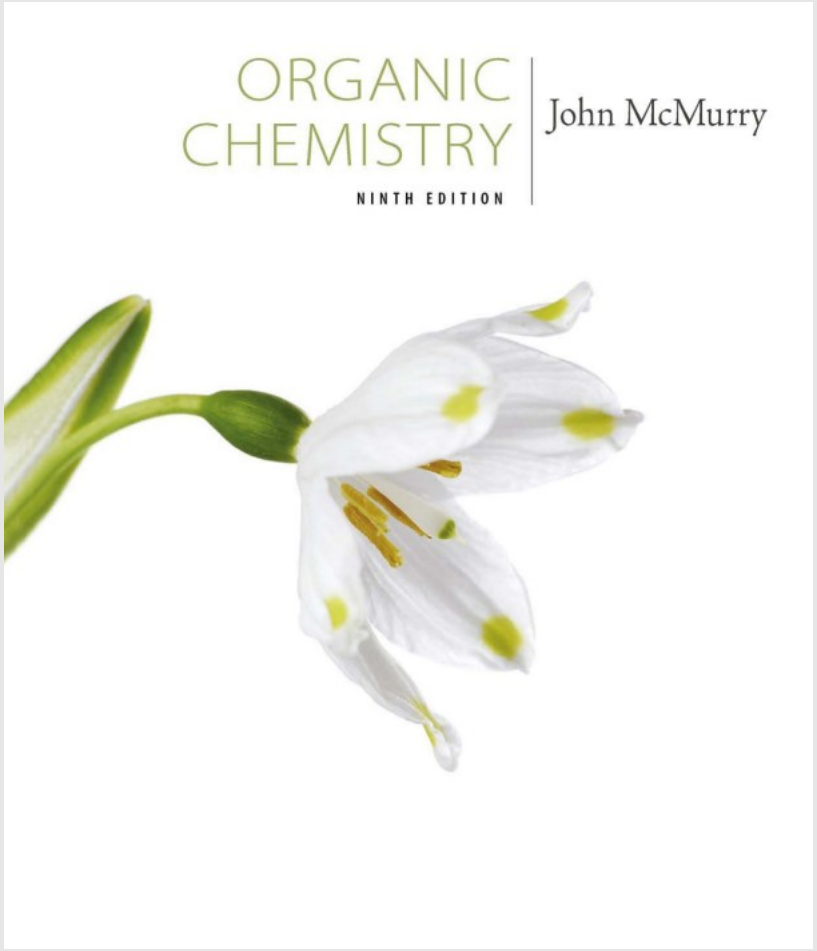
# Organic Chemistry 1
## 0825-202

**Dr. Hanan A. Althikrallah**

WhatsApp: +966135897502

halhekrallh@kfu.edu.sa

# References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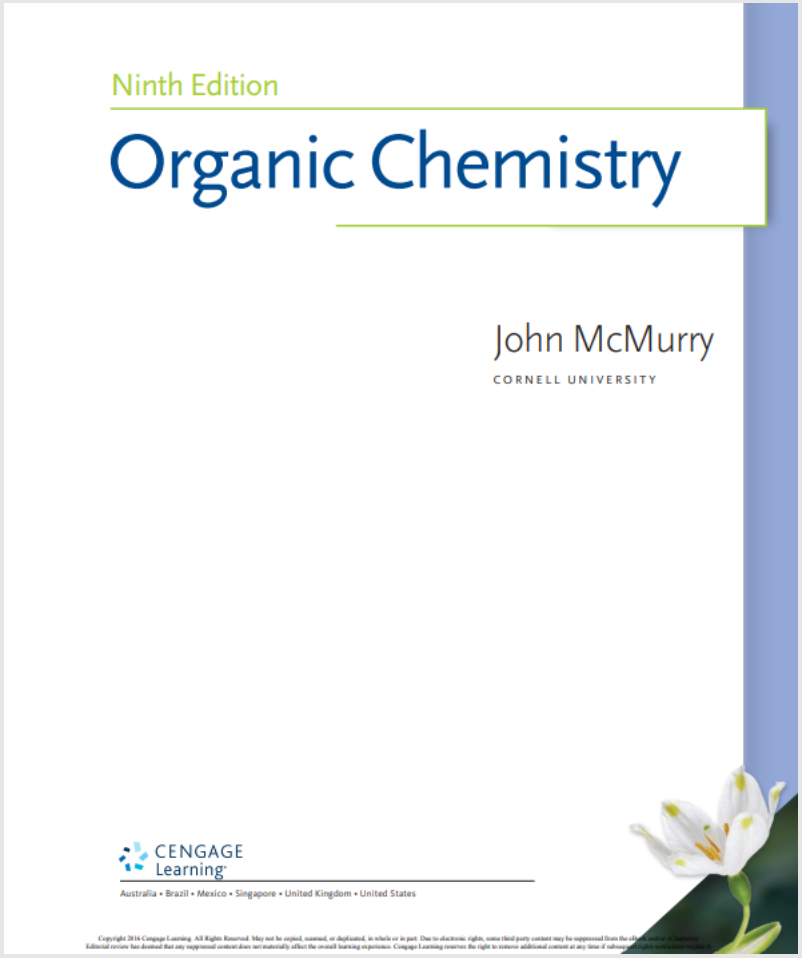
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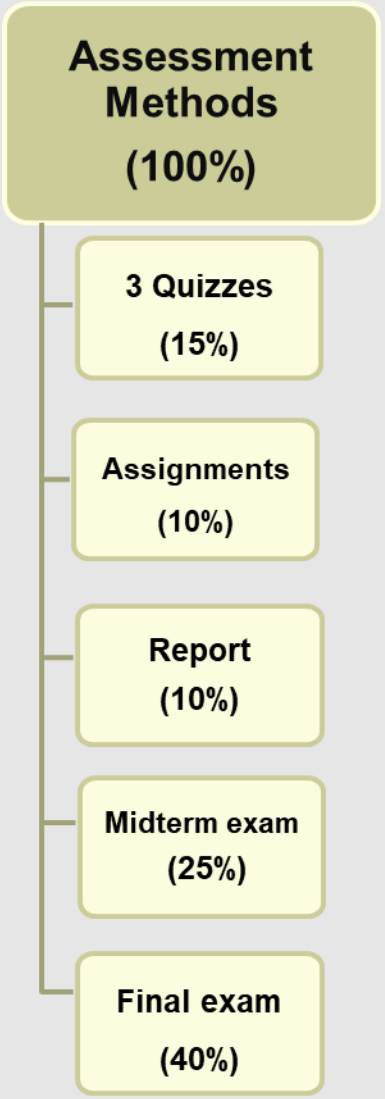
# Course Evaluation & Grading

- ❑ Assignments & Homework 10%
- ❑ Midterm Exam 25%
- ❑ Quizzes 15%
- ❑ Practice in class & Oral skills 10%
- ❑ Final Exam 40%

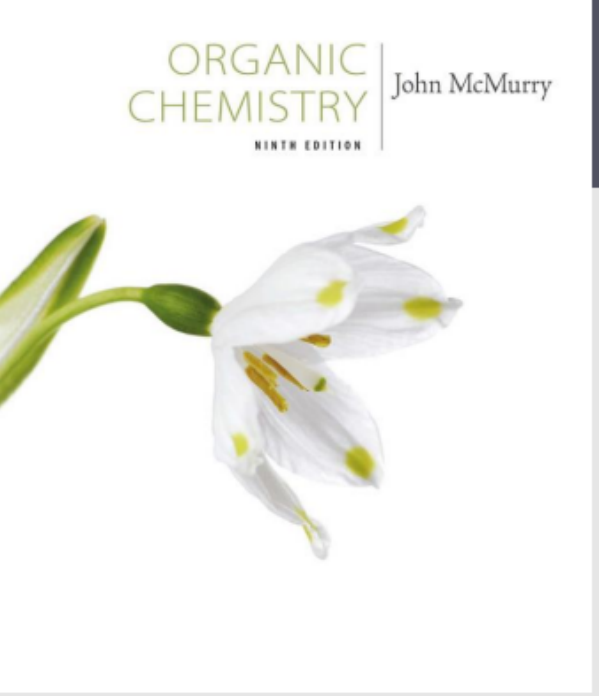


# Course Policy

- **No late homework, please.**
- **No late attendance, please**
- **All exams are closed-book.**
- **(1) quiz is closed book, and (2) others are open book.**
- **60% Marks are required to pass the course**
- **Absence is not allowed for exams and quizzes. Only for Emergency Cases after an administrative approval**.

# Course Contents

- ❑ **Chapter 1: Introduction to Structure & Bonding**
- ❑ **Chapter 2: Polar Covalent Bonds; Acids and Bases**
- ❑ **Chapter 3: Structure and Stereochemistry of Alkanes & Cycloalkanes**
- ❑ **Chapter 4&5: Alkenes and Alkynes**
- ❑ **Chapter 6: Alkyl Halides**
- ❑ **Chapter 7: Alcohols, Ethers, Epoxides, and Thiols**
- ❑ **Chapter 8: Aldehydes & Ketones**
- ❑ **Chapter 9&10: Carboxylic Acids & their derivatives**
- ❑ **Chapter 11: Amines**

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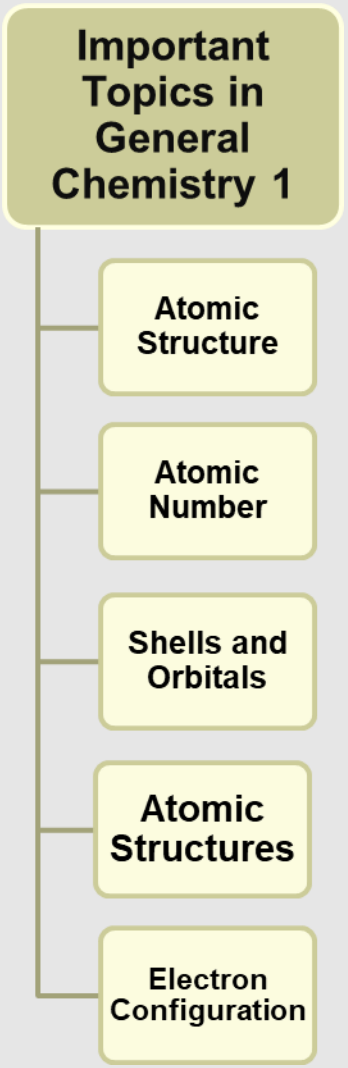
# Chapter 1
# Structure and Bonding

***Edited by:*** Dr. Ahmed Khalil
Department of Chemistry, College of Science
King Faisal University, Saudi Arabia
Email: akkhalil@kfu.edu.sa

# Important Topics in General Chemistry 1




Students should revise the following parts in General Chemistry 1 course:

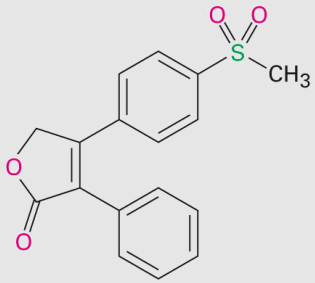
- Atomic Structure
- Atomic Number and Atomic Mass
- Shells, Subshells, and Orbitals
- Atomic Structures: Orbitals, Shapes
- Electron Configuration: **Aufbau Principle, Pauli exclusion principle, and Hund's rule**

# What is Organic Chemistry?

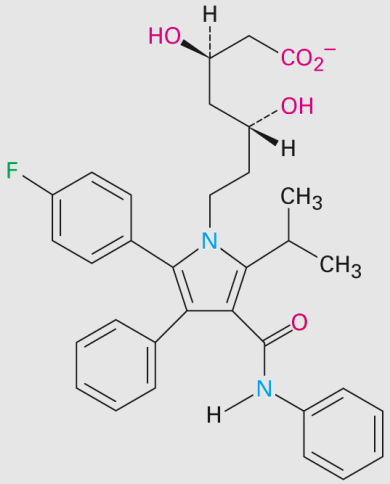
- Living things are made of organic chemicals (carbon-based compounds)
- Proteins that make up hair
- DNA, controls genetic make-up
- Foods, medicines

**Organic Chemistry**

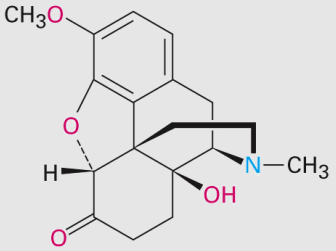
- importance
- Origins of Organic Chemistry
- Abundance of Organic Compounds



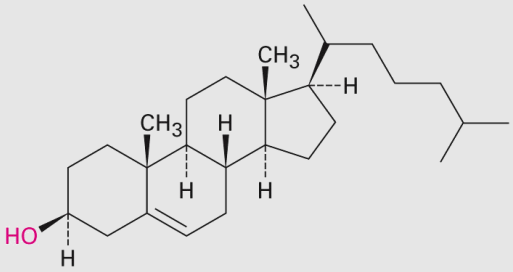
Rofecoxib (Vioxx)



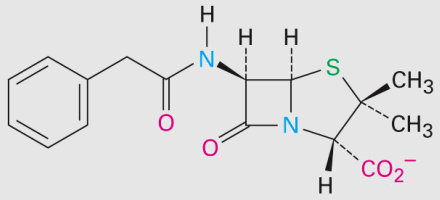
Atorvastatin (Lipitor)



Oxycodone (OxyContin)



Cholesterol



Benzylpenicillin

# Origins of Organic Chemistry

Foundations of organic chemistry from mid-1700's.

Compounds obtained from plants, animals hard to isolate, and purify.

Compounds also decomposed more easily.

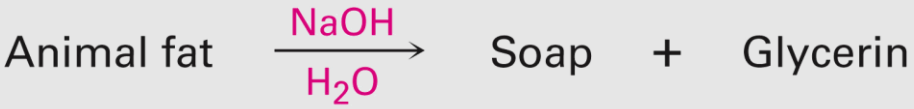
Torben Bergman (1770) first to make distinction between organic and inorganic chemistry.

It was thought that organic compounds must contain some "vital force" because they were from living sources.

# Origins of Organic Chemistry

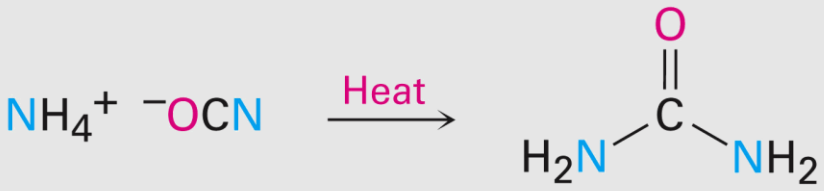
Because of “vital force”, it was thought that organic compounds could not be synthesized in laboratory like inorganic compounds.

1816, Chevreul showed that not to be the case, he could prepare soap from animal fat and an alkali and glycerol is a product





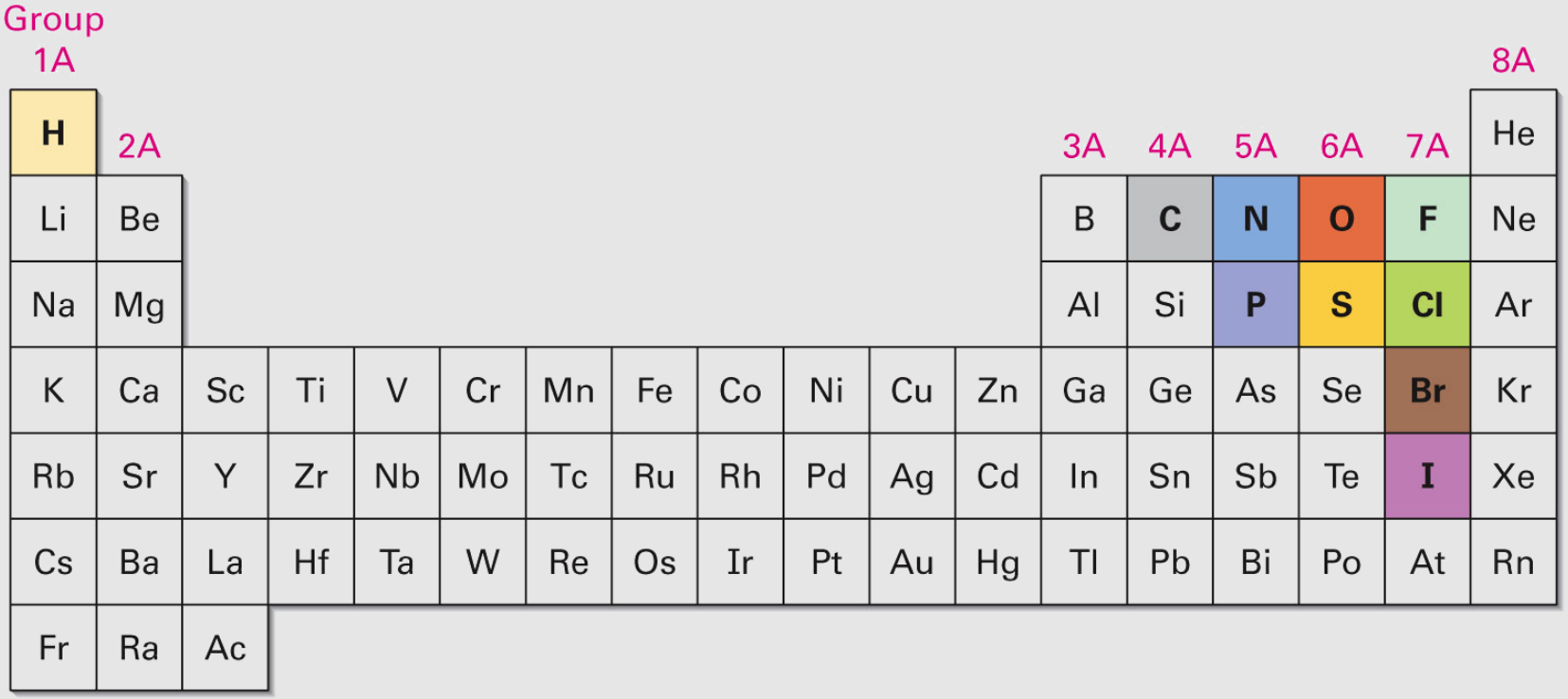
1828, Woehler showed that it was possible to convert inorganic salt ammonium cyanate into organic substance “urea”




**Ammonium cyanate** **Urea**

# Origins of Organic Chemistry

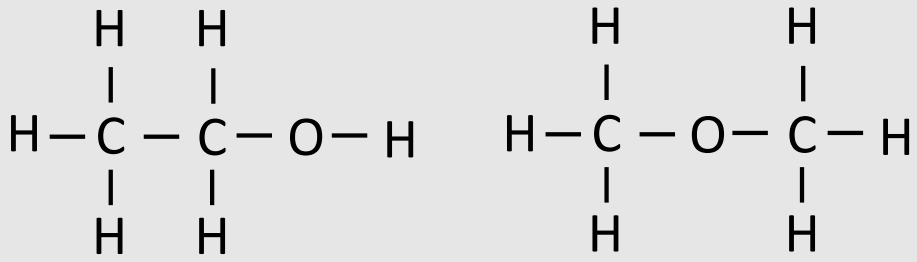
- Organic chemistry is study of carbon compounds.
- Why is it so special?
- 90% of more than 30 million chemical compounds contain carbon.
- Examination of carbon in periodic chart answers some of these questions.
- Carbon is group 4A element, it can share 4 valence electrons and form 4 covalent bonds.



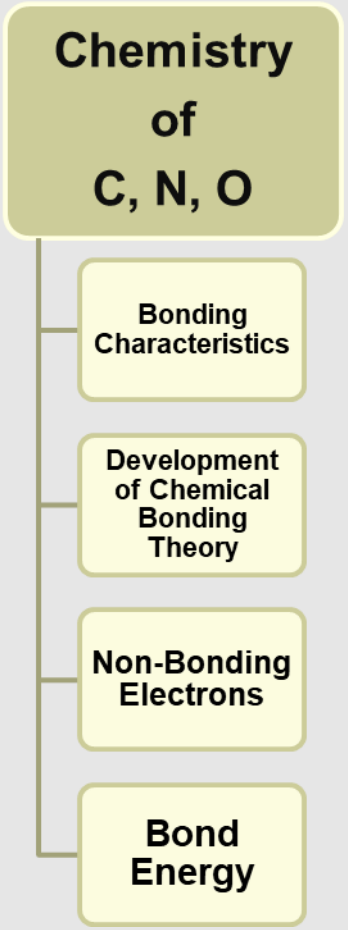
# Abundance of Organic Compounds

- ***Why are there so many more organic compounds than inorganic?***
- Carbon has unique bonding characteristics
  - Strong, covalent bonds with C and H
- Isomerism
  - Groups of carbon atoms can form more than one unique compound

Structural Isomers of $C_2H_6O$



# Development of Chemical Bonding Theory

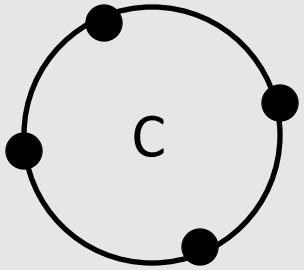


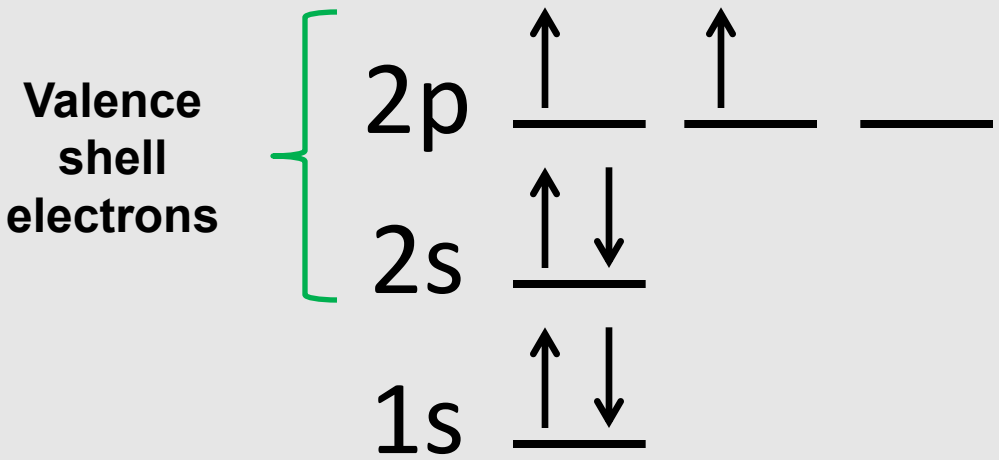

- Atoms with one, two, or three valence electrons form one, two, or three bonds.
- Atoms with four or more valence electrons form as many bonds as they need electrons to fill the *s* and *p* levels of their valence shells to reach a stable octet.
- Carbon has four valence electrons ($2s^2\ 2p^2$), forming four bonds ($CH_4$).

# Development of Chemical Bonding Theory

- Nitrogen has five valence electrons ($2s^2\ 2p^3$) but forms only three bonds ($NH_3$).
- Oxygen has six valence electrons ($2s^2\ 2p^4$) but forms two bonds ($H_2O$)

# Bonding Characteristics of Carbon

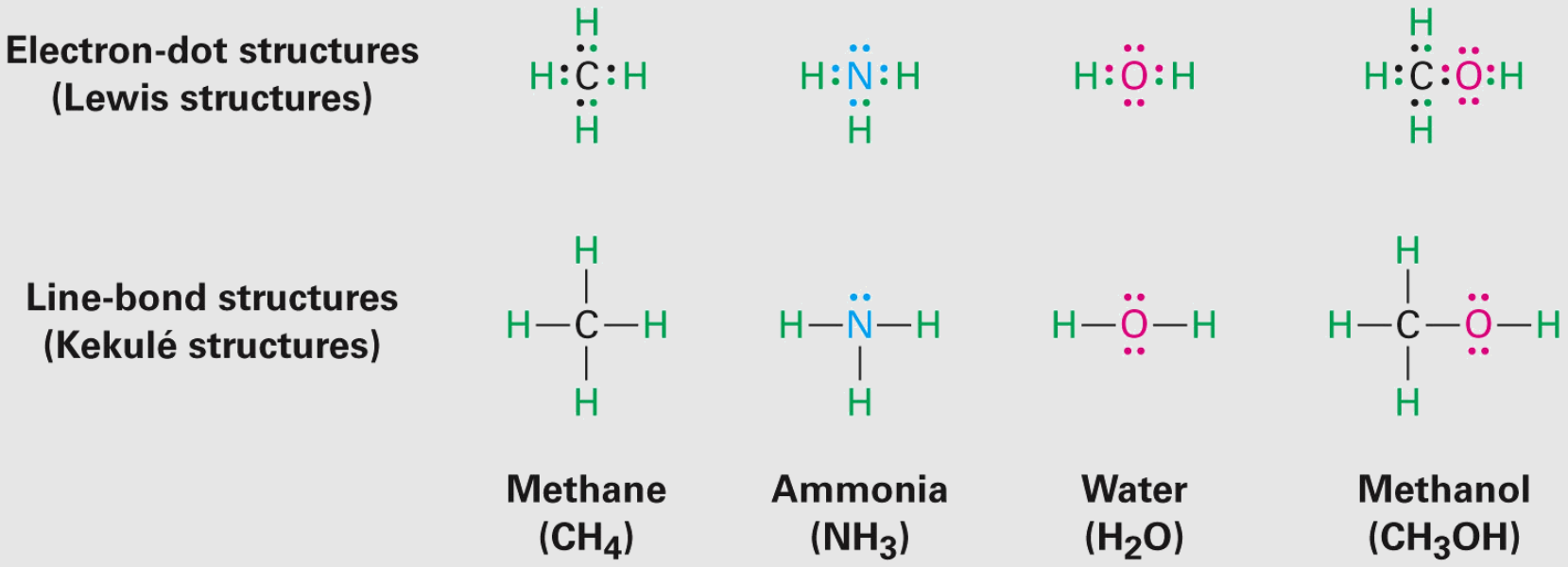



Q: If 2s electrons are already paired, with only 2 2p electrons unpaired, how does carbon form 4 covalent bonds?

# Development of Chemical Bonding Theory

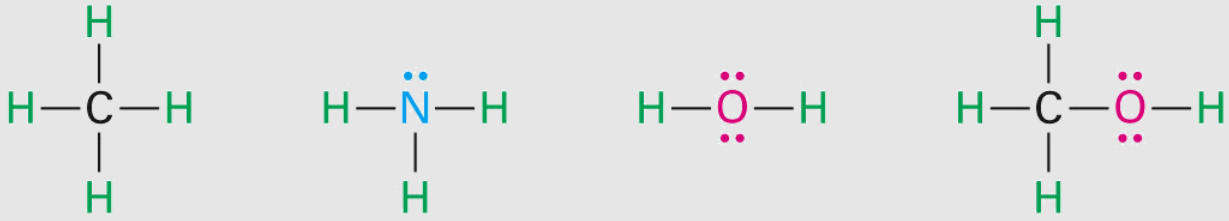
- **Lewis structures** (electron dot) show valence electrons of an atom as dots
  - Hydrogen has one dot, representing its 1*s* electron
  - Carbon has four dots ($2s^2\ 2p^2$)
- **Kekulé structures** (line-bond structures) have a line drawn between two atoms indicating a 2 electrons covalent bond.
- Stable molecule results at completed shell, octet (eight dots) for main-group atoms (two for hydrogen)



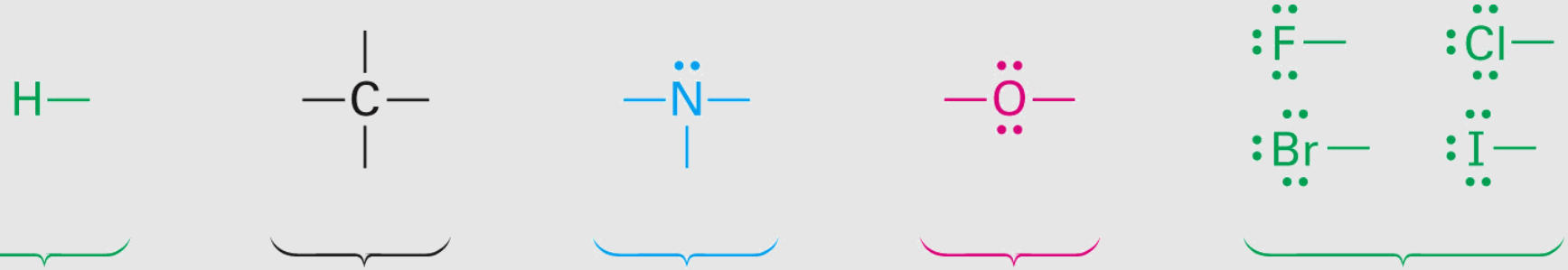
# Development of Chemical Bonding Theory

**Electron-dot structures (Lewis structures)**

**Line-bond structures (Kekulé structures)**



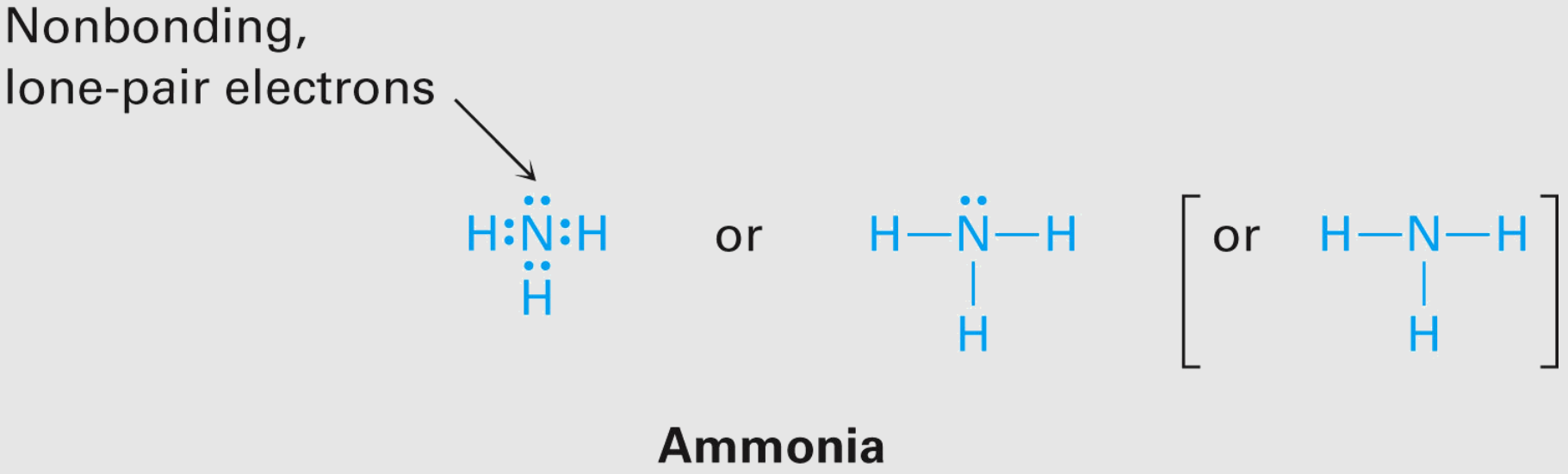
**Methane ($CH_4$)** **Ammonia ($NH_3$)** **Water ($H_2O$)** **Methanol ($CH_3OH$)**



**One bond** **Four bonds** **Three bonds** **Two bonds** **One bond**

# Non-Bonding Electrons

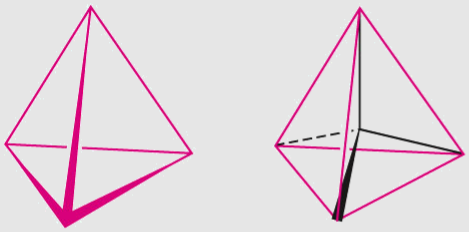
- Valence electrons not used in bonding are called **nonbonding electrons**, or **lone-pair electrons**
  - Nitrogen atom in ammonia ($NH_3$)
    - Shares six valence electrons in three covalent bonds and remaining two valence electrons are nonbonding lone pair



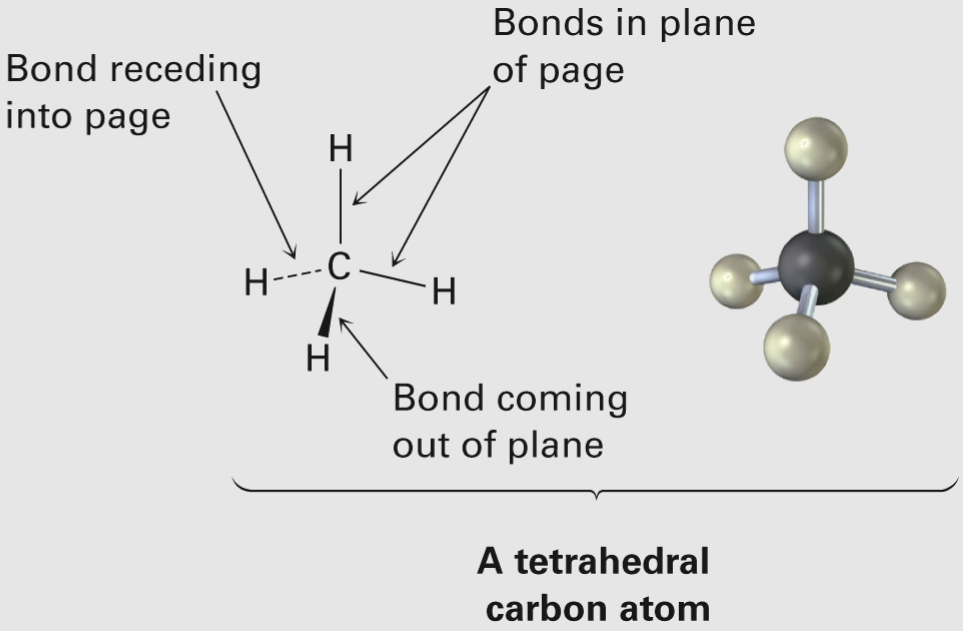

**Ammonia**

# Development of Chemical Bonding Theory

- Kekulé and Couper independently observed that carbon always has four bonds
- van't Hoff and Le Bel proposed that the four bonds of carbon have specific spatial directions
  - Atoms surround carbon as corners of a tetrahedron



**A regular tetrahedron**



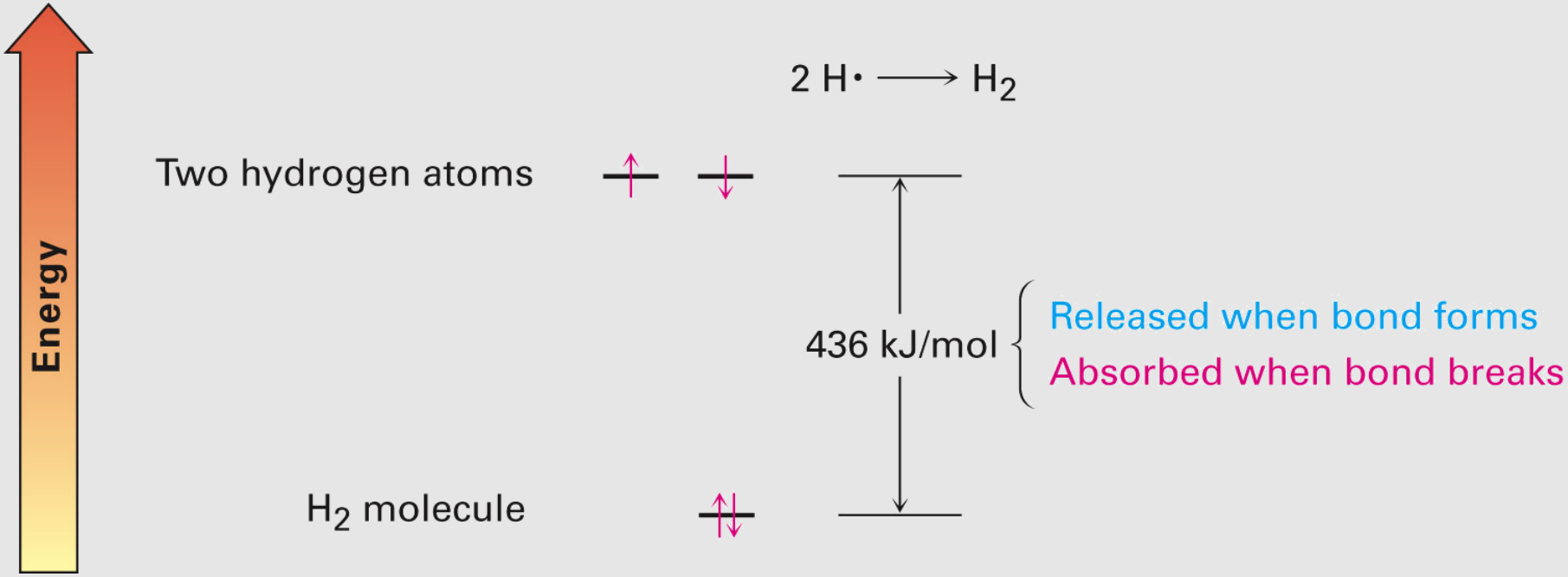

**A tetrahedral carbon atom**

# Development of Chemical Bonding Theory

- Atoms form bonds because the compound that results is more stable than the separate atoms
- Ionic bonds in salts form as a result of electron transfers
- Organic compounds have covalent bonds from sharing electrons (G. N. Lewis, 1916)

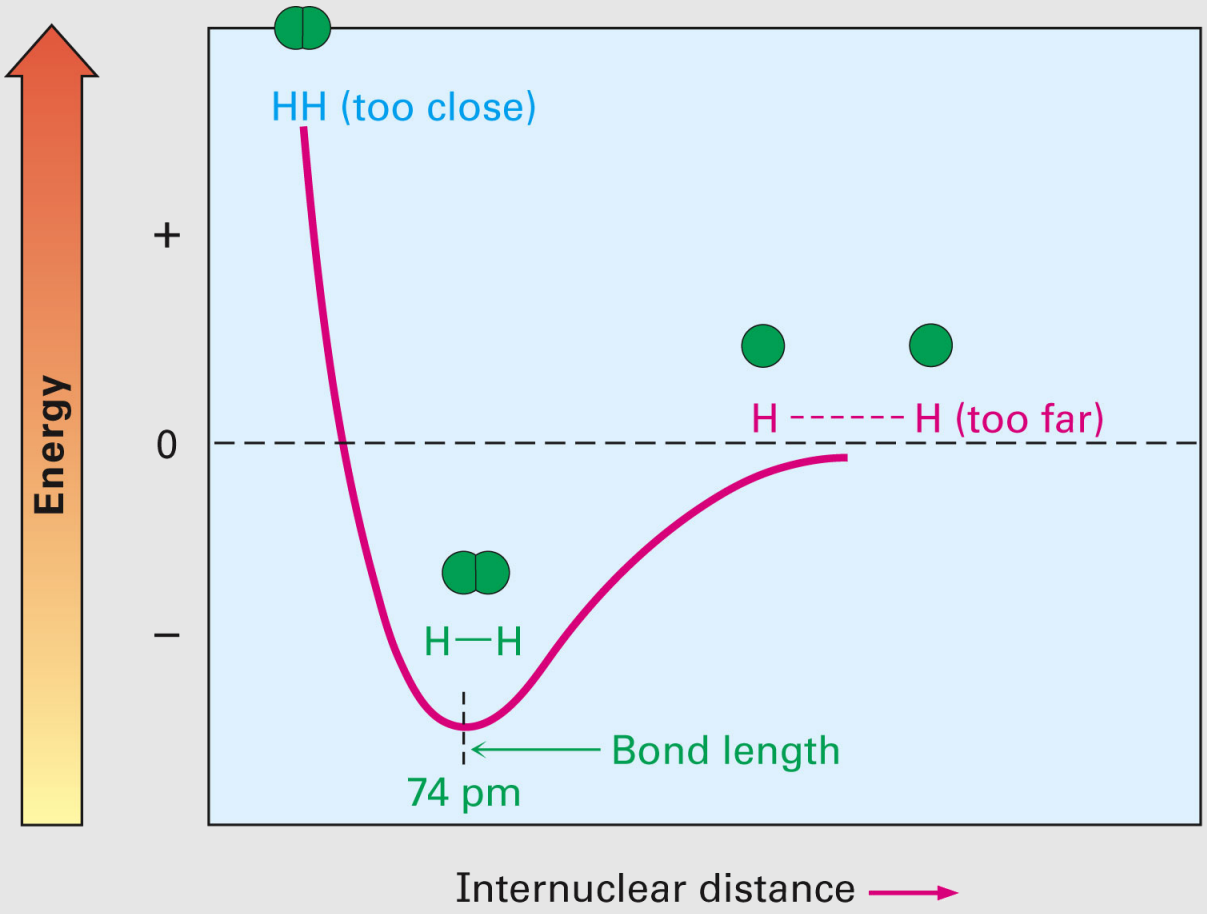
# Bond Energy

- Reaction 2 H· $\rightarrow$ $H_2$ releases 436 kJ/mol
- Product has 436 kJ/mol less energy than two atoms: H–H has **bond strength** of 436 kJ/mol. (1 kJ = 0.2390 kcal; 1 kcal = 4.184 kJ)

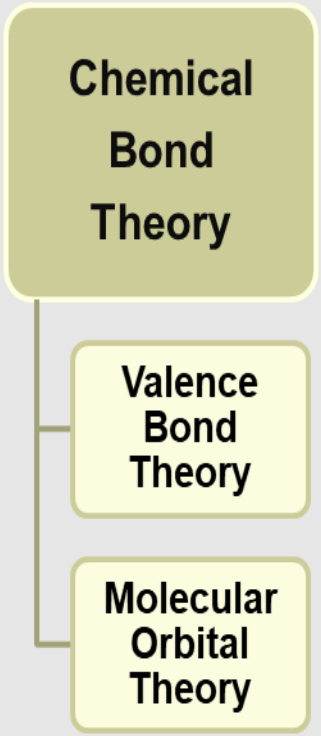


# Bond Energy

- Distance between nuclei that leads to maximum stability
- If too close, they repel because both are positively charged
- If too far apart, bonding is weak



# Describing Chemical Bonds: Valence Bond Theory

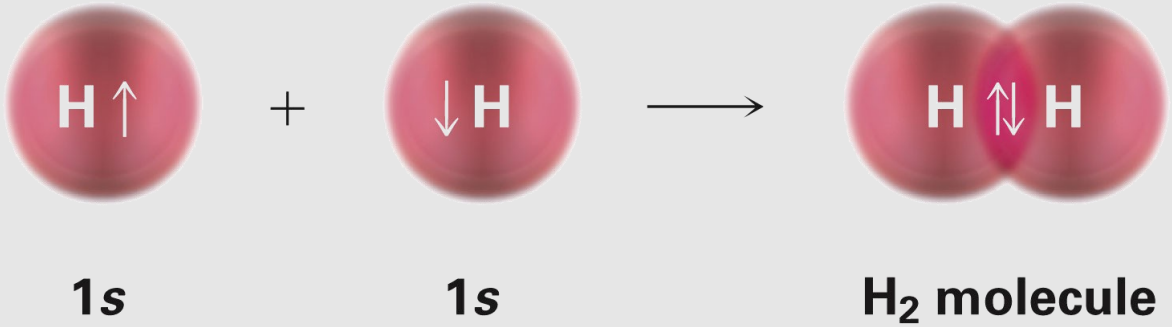



- Covalent bond forms when two atoms approach each other closely so that a singly occupied orbital on one atom *overlaps* a singly occupied orbital on the other atom
- Two models to describe covalent bonding.

Valence bond theory, Molecular orbital theory

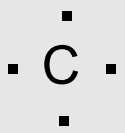
**Valence Bond Theory:**

- Electrons are paired in the overlapping orbitals and are attracted to nuclei of both atoms
  - H–H bond results from the overlap of two singly occupied hydrogen 1*s* orbitals
  - H-H bond is *cylindrically symmetrical*, **sigma (σ) bond**



# Hybridization of Atomic Orbitals

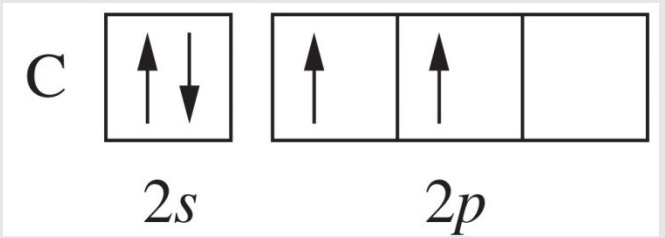
4 valence $e^{-1}$

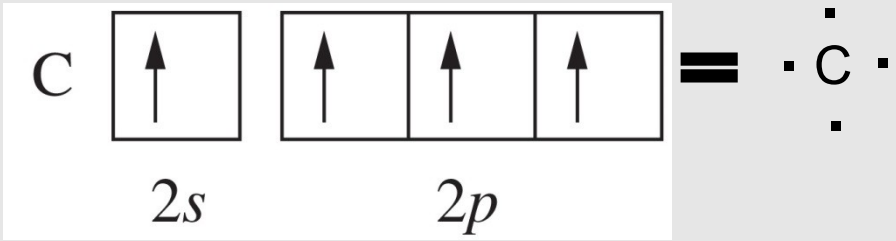



Lewis symbol

**Pure atomic orbitals**

**Hybrid orbitals**

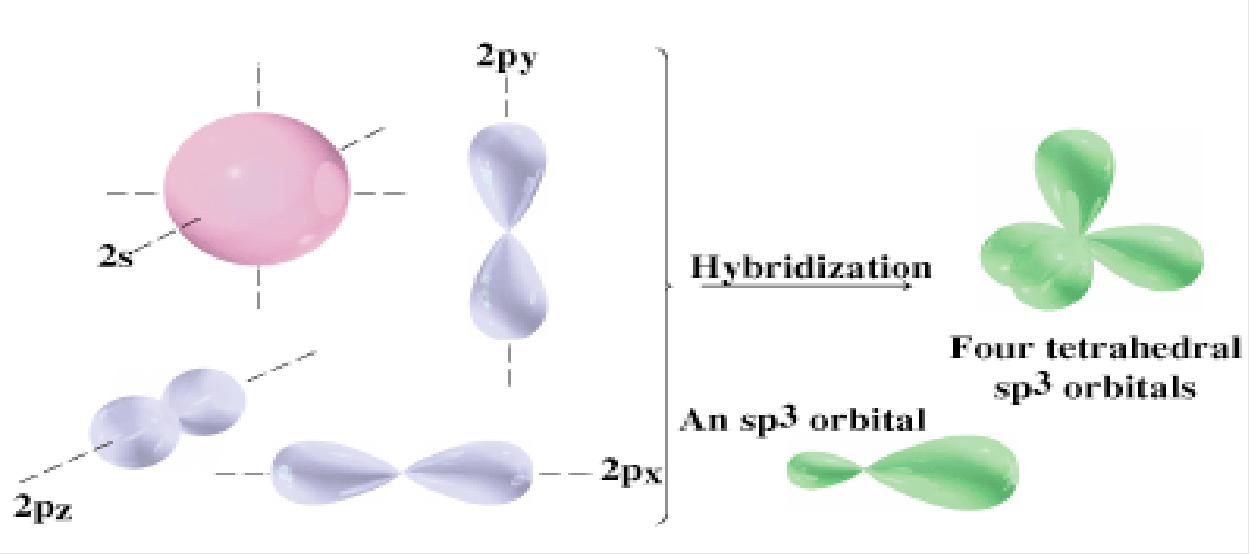



The mathematical process of replacing pure atomic orbitals with reformulated atomic orbitals for bonded atoms is called **hybridization**, and the new orbitals are called **hybrid orbitals**.

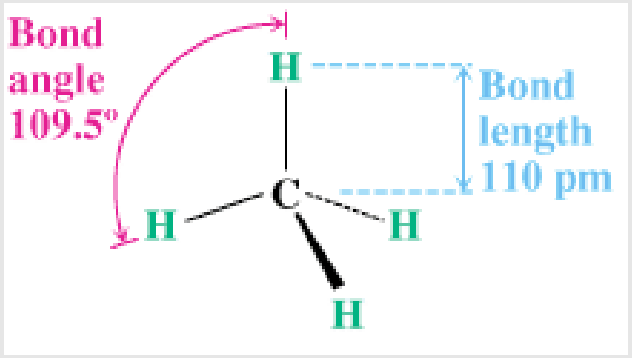
# Hybridization: $sp^3$ Orbitals and the Structure of Methane

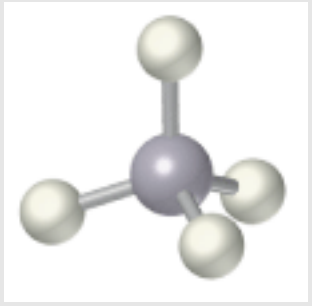
- Carbon has 4 valence electrons ($2s^2\ 2p^2$)
- In $CH_4$, all C–H bonds are identical (tetrahedral)
- ***sp*³ hybrid orbitals**: *s* orbital and three *p* orbitals combine to form four equivalent, unsymmetrical, tetrahedral orbitals (sppp = $sp^3$), Pauling (1931)

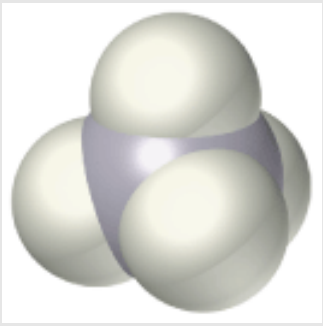


# Tetrahedral Structure of Methane

- $sp^3$ orbitals on C overlap with 1*s* orbitals on 4 H atom to form four identical C-H bonds
- Each C–H bond has a strength of 438 kJ/mol and length of 110 pm
- **Bond angle**: each H–C–H is 109.5˚ , the *tetrahedral angle*.

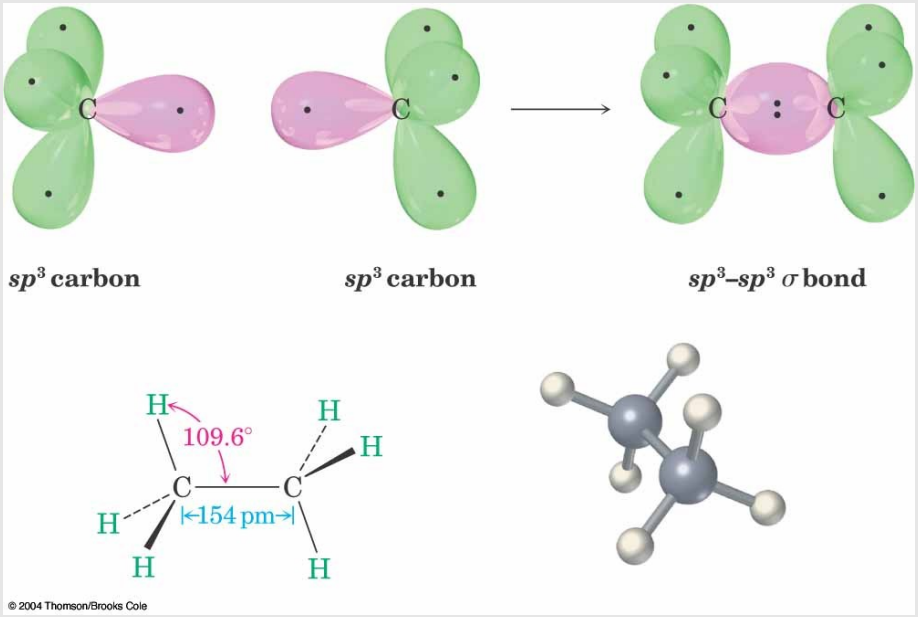




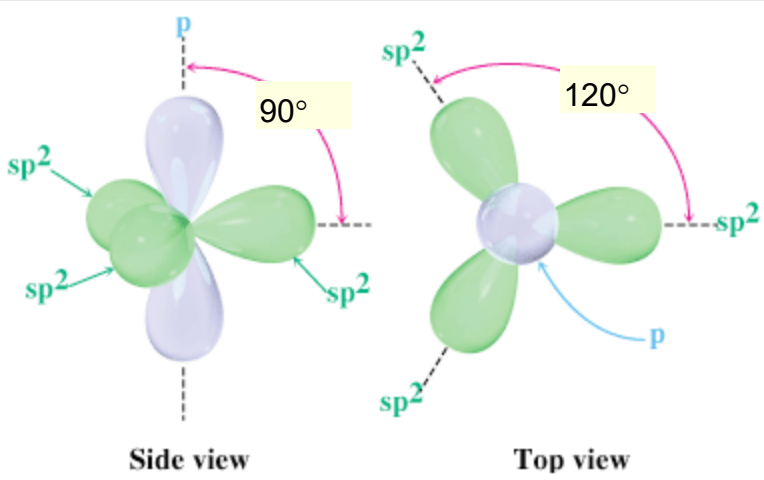
# Hybridization: $sp^3$ Orbitals and the Structure of Ethane

- Two C's bond to each other by $\sigma$ overlap of an $sp^3$ orbital from each
- Three $sp^3$ orbitals on each C overlap with H 1*s* orbitals to form six C–H bonds
- C–H bond strength in ethane 420 kJ/mol
- C–C bond is 154 pm long and strength is 376 kJ/mol
- All bond angles of ethane are tetrahedral



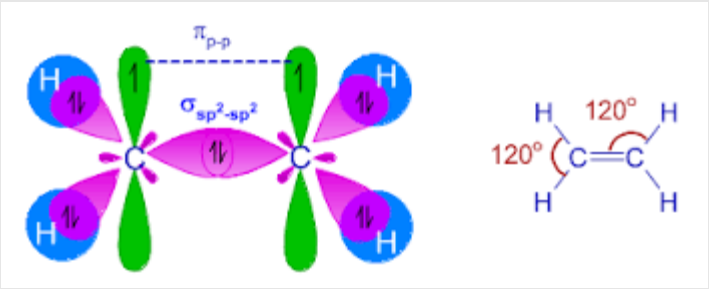
# Hybridization: $sp^2$ Orbitals and the Structure of Ethylene

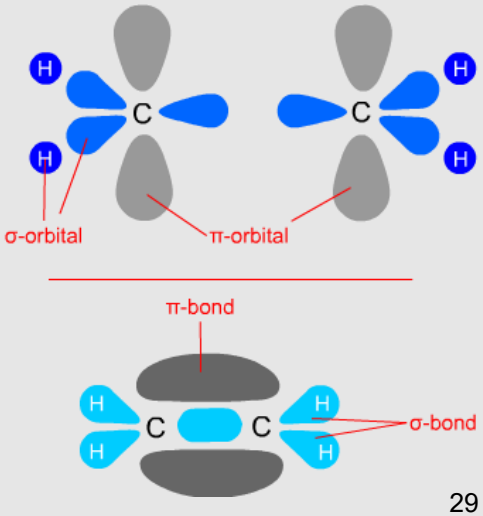
- **$sp^2$ hybrid orbitals:** 2*s* orbital combines with *two* 2*p* orbitals, giving 3 orbitals (spp = $sp^2$)
- $sp^2$ orbitals are in a plane with120˚ angles
- Remaining *p* orbital is perpendicular to the plane



# Bonds From $sp^2$ Hybrid Orbitals

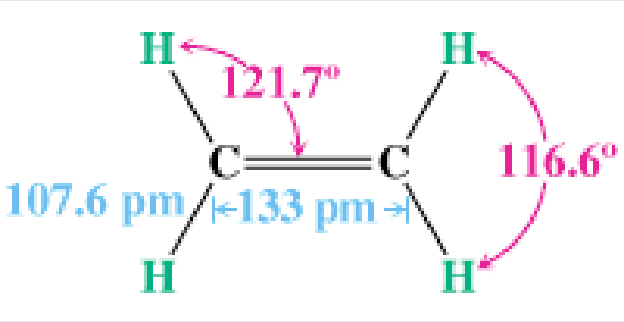
- Two $sp^2$-hybridized orbitals overlap to form a $\sigma$ bond
- *p* orbitals overlap *side-to-side* to formation a **pi ($\pi$) bond**
- $sp^2$–$sp^2$ $\sigma$ bond and 2*p*–2*p* $\pi$ bond result in sharing four electrons and formation of C-C double bond
- Electrons in the $\sigma$ bond are centered between nuclei
- Electrons in the $\pi$ bond occupy regions are on either side of a line between nuclei

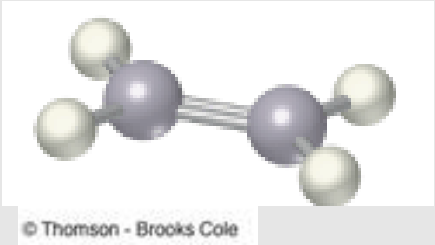


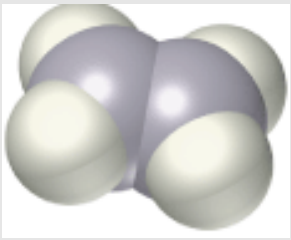



# Structure of Ethylene

- H atoms form σ bonds with four $sp^2$ orbitals
- H–C–H and H–C–C bond angles of about 120°
- C–C double bond in ethylene shorter and stronger than single bond in ethane
- Ethylene C=C bond length 133 pm (C–C 154 pm)

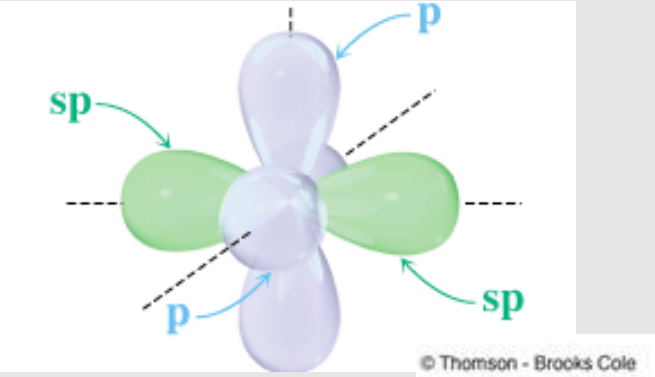


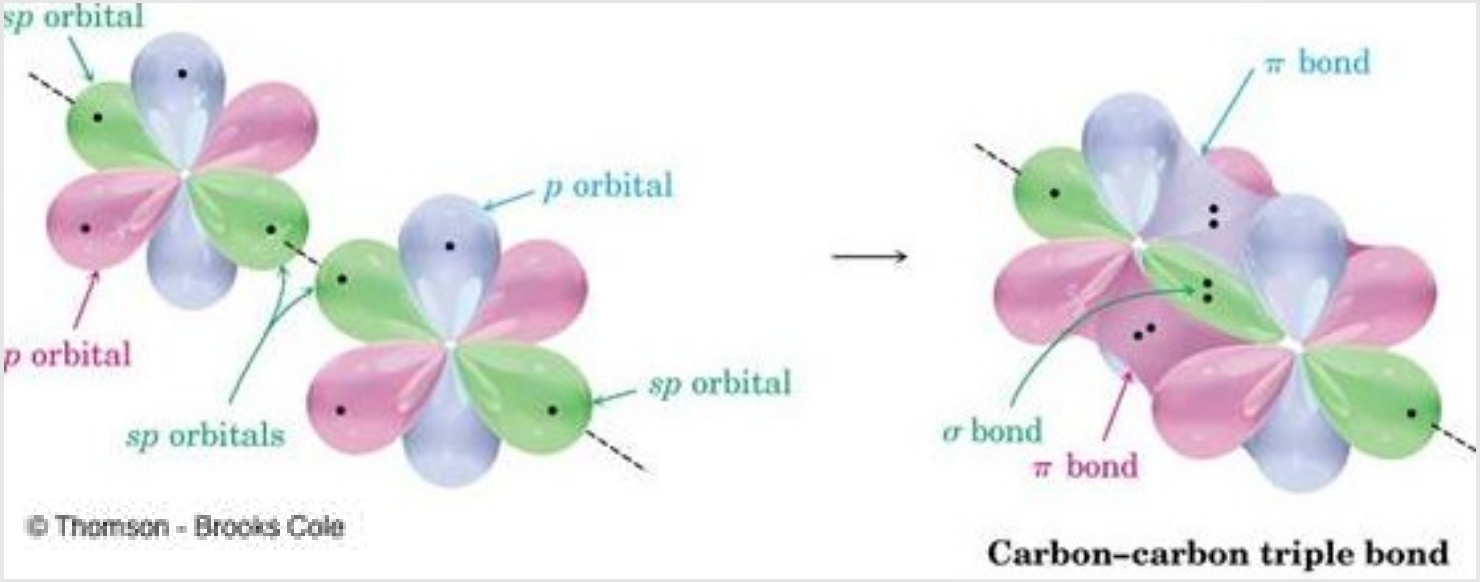
# Hybridization: *sp* Orbitals and the Structure of Acetylene

- C-C a *triple* bond sharing six electrons
- Carbon 2*s* orbital hybridizes with a single *p* orbital giving two *sp* hybrids
  - two *p* orbitals remain unchanged
- *sp* orbitals are linear, 180° apart on *x*-axis
- Two *p* orbitals are perpendicular on the *y*-axis and the *z*-axis



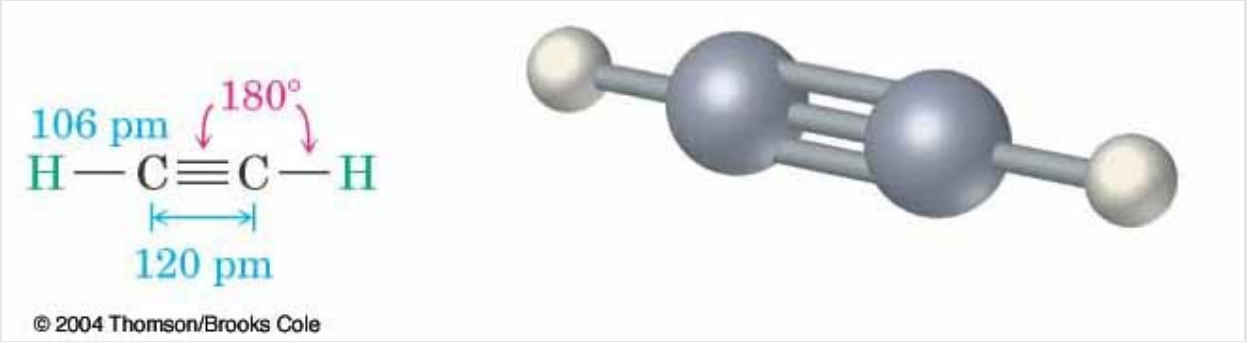
# Orbitals of Acetylene

- Two *sp* hybrid orbitals from each C form *sp*–*sp* $\sigma$ bond
- *pz* orbitals from each C form a $p_z$–$p_z$ $\pi$ bond by sideways overlap and $p_y$ orbitals overlap similarly



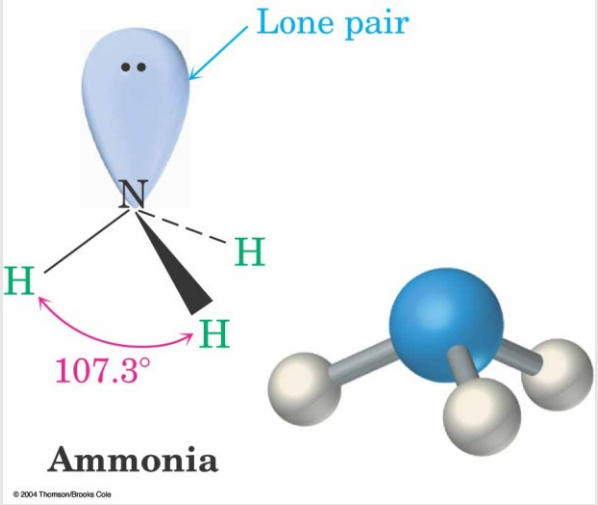
# Bonding in Acetylene

- Sharing of six electrons forms C≡C
- Two *sp* orbitals form σ bonds with hydrogens



# Hybridization of Nitrogen and Oxygen

- Elements other than C can have hybridized orbitals
- H–N–H bond angle in ammonia ($NH_3$) 107.3°
- N's orbitals (sppp) hybridize to form four $sp^3$ orbitals
- One $sp^3$ orbital is occupied by two nonbonding electrons, and three $sp^3$ orbitals have one electron each, forming bonds to H



# Hybridization of Oxygen in Water

- The oxygen atom is $sp^3$-hybridized
- Oxygen has six valence-shell electrons but forms only two covalent bonds, leaving two lone pairs
- The H–O–H bond angle is 104.5°

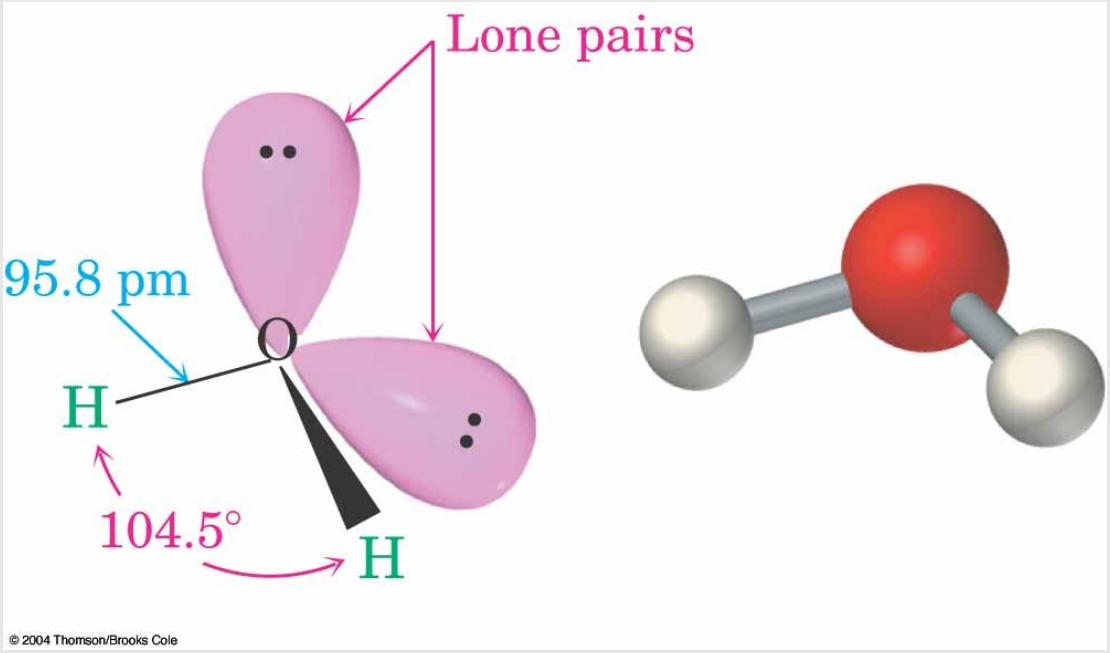
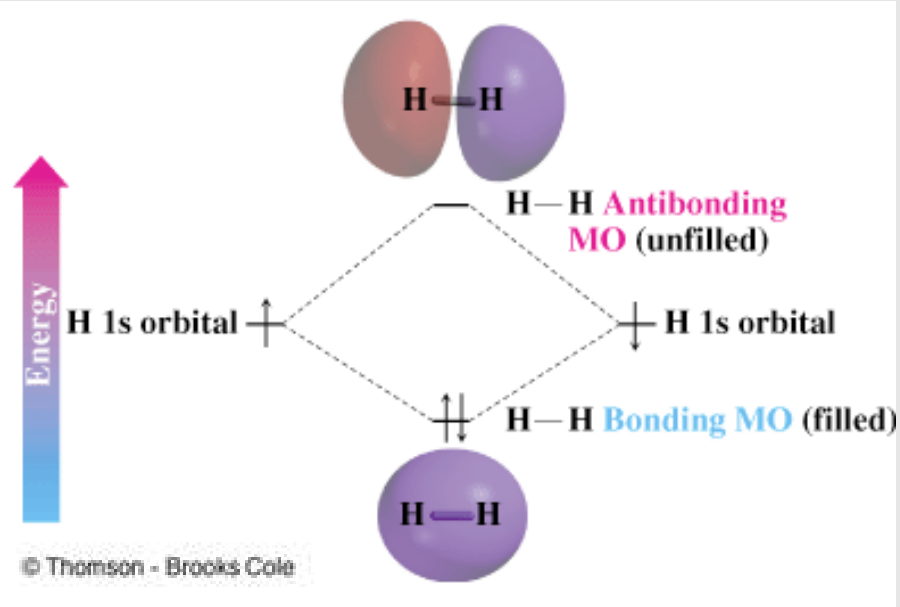


**TABLE 1-2** Comparison of C–C and C–H Bonds in Methane, Ethane, Ethylene, and Acetylene

| Molecule | Bond | Bond strength (kJ/mol) | Bond strength (kcal/mol) | Bond length (pm) |
|---|---|---|---|---|
| Methane, $CH_4$ | ($sp^3$) C—H | 439 | 105 | 109 |
| Ethane, $CH_3CH_3$ | ($sp^3$) C—C ($sp^3$) | 377 | 90 | 154 |
| | ($sp^3$) C—H | 421 | 101 | 109 |
| Ethylene, $H_2C{=}CH_2$ | ($sp^2$) C=C ($sp^2$) | 728 | 174 | 134 |
| | ($sp^2$) C—H | 464 | 111 | 109 |
| Acetylene, HC≡CH | ($sp$) C≡C ($sp$) | 965 | 231 | 120 |
| | ($sp$) C—H | 558 | 133 | 106 |

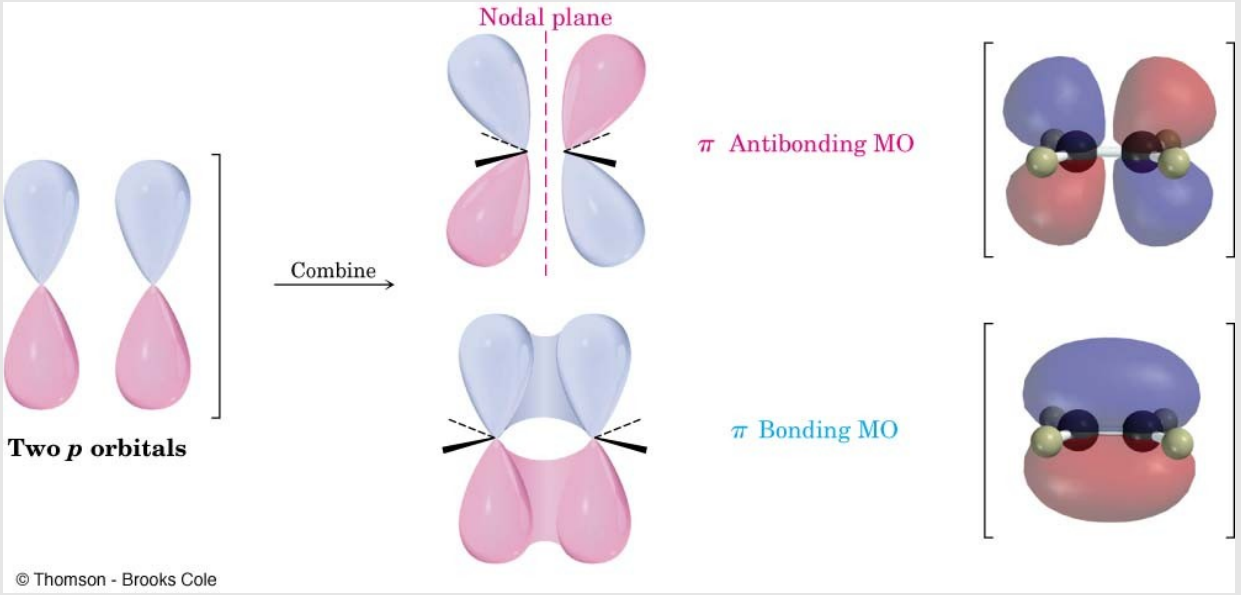
# Molecular Orbital Theory

- A *molecular* orbital (MO): where electrons are most likely to be found (specific energy and general shape) in a *molecule*
- Additive combination (bonding) MO is lower in energy
- Subtractive combination (antibonding) forms MO is higher



# Molecular Orbitals in Ethylene

- The $\pi$ bonding MO is from combining *p* orbital lobes with the same algebraic sign
- The $\pi$ antibonding MO is from combining lobes with opposite signs
- Only bonding MO is occupied



# Representing Organic Compounds

- Compounds can be represented in many different ways.
- Some representations provide information about the structure, while others do not.
- **Molecular Formula**: Number of atoms of each element in one molecule of a compound (no structural information).
  - Ex. $C_6H_{14}$
- **Empirical Formula**: Relative ratio's of elements present.
  - Ex. $CH_2O$ could be $CH_2O$ or $C_2H_4O_2$.
- **Line bond (Kekule) Structures**: Show all atoms and bonds.
- **Condensed Structures**: Show all atoms, but only show bonds when necessary.
- **Skeletal Structures**: Show C-C bonds and all atoms that are not C or H.

Even simpler than condensed structures are **skeletal structures** such as those shown in TABLE 1-3. The rules for drawing skeletal structures are straightforward.

### RULE 1

Carbon atoms aren't usually shown. Instead, a carbon atom is assumed to be at each intersection of two lines (bonds) and at the end of each line. Occasionally, a carbon atom might be indicated for emphasis or clarity.

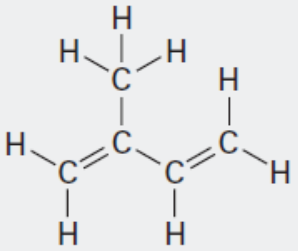
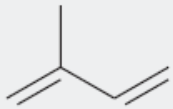
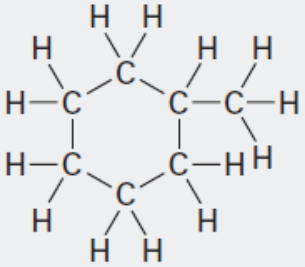
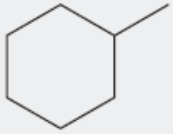
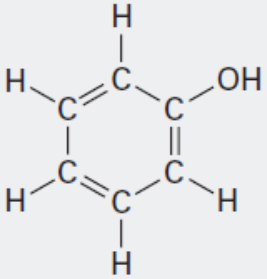
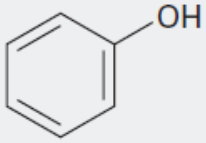
### RULE 2

Hydrogen atoms bonded to carbon aren't shown. Because carbon always has a valence of 4, we mentally supply the correct number of hydrogen atoms for each carbon.

### RULE 3

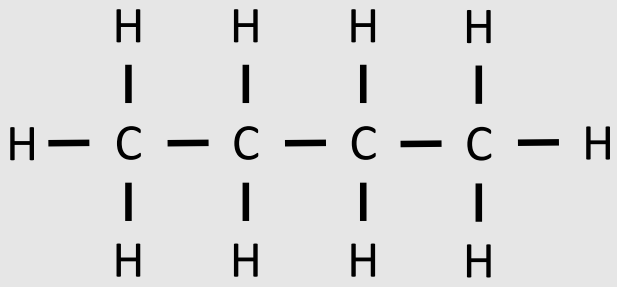
Atoms other than carbon and hydrogen *are* shown.

**TABLE 1-3 Kekulé and Skeletal Structures for Some Compounds**

| Compound | Kekulé structure | Skeletal structure |
|---|---|---|
| Isoprene, $C_5H_8$ |  |  |
| Methylcyclohexane, $C_7H_{14}$ |  |  |
| Phenol, $C_6H_6O$ |  |  |

# Representing Organic Compounds

Structural Formula



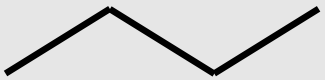
***Also called Line-bond or Kekule structures.***

Condensed Structural Formula

$CH_3CH_2CH_2CH_3$

$CH_3(CH_2)_2CH_3$

Skeletal Structure



***Learn this quickly, it will save you much time.***

Molecular Formula

$C_4H_{10}$

# Summary

- **Organic chemistry** – chemistry of carbon compounds
- **Covalent bonds** - electron pair is shared between atoms
- **Valence bond theory -** electron sharing occurs by overlap of two atomic orbitals
- **Molecular orbital (MO) theory**, - bonds result from combination of atomic orbitals to give molecular orbitals, which belong to the entire molecule
- **Sigma (σ) bonds** - Circular cross-section and are formed by head-on interaction
- **Pi (π) bonds** – "dumbbell" shape from sideways interaction of *p* orbitals
- Carbon uses hybrid orbitals to form bonds in organic molecules.
  - In single bonds with tetrahedral geometry, carbon has four ***sp*$^3$ hybrid orbitals**
  - In double bonds with planar geometry, carbon uses three equivalent ***sp*$^2$ hybrid orbitals** and one unhybridized *p* orbital
  - Carbon uses two equivalent ***sp* hybrid orbitals** to form a triple bond with linear geometry, with two unhybridized *p* orbitals
- Atoms such as nitrogen and oxygen hybridize to form strong, oriented bonds
  - The nitrogen atom in ammonia and the oxygen atom in water are *sp*$^3$-hybridized