1. Structure and Bonding

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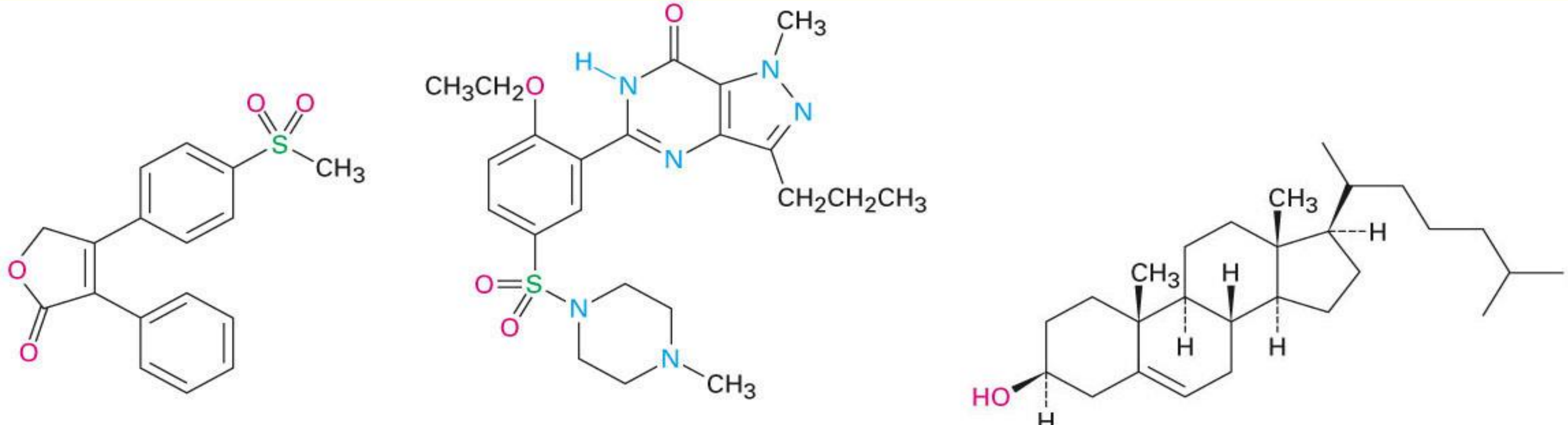
Based on McMurry's *Organic Chemistry*, 7th edition

What is Organic Chemistry?

- Living things are made of organic chemicals
- Proteins that make up hair
- DNA, controls genetic make-up
- Foods, medicines
- Examine structures below



Rofecoxib (Vioxx)

Sildenafil (Viagra)

Cholesterol

Organic Chemistry

The Chemistry of Carbon Compounds

Cell phones

Computers

DVDs

advanced technologies

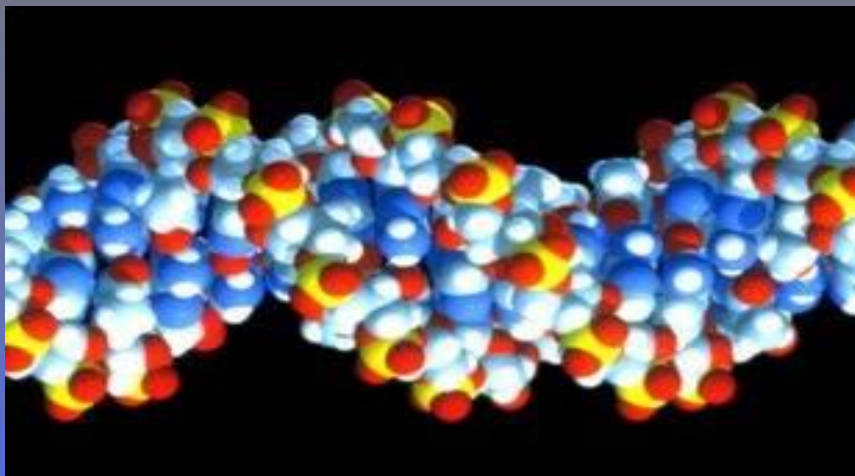
Organic Chemistry

The Chemistry of Carbon Compounds

all living systems

advanced technologies

Some organic chemicals

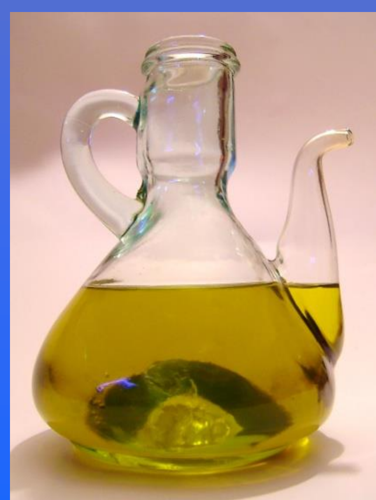


DNA

Medicines

- Active Pharmaceutical Ingredients
- Excipients

Materials



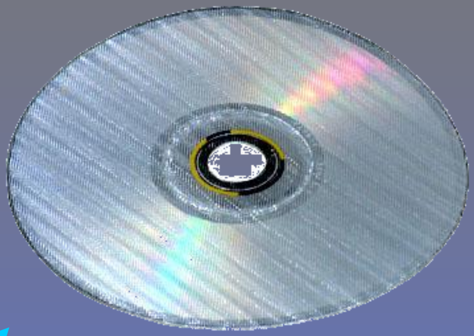
Essential oils

Fuels

Pigments

Liquid crystal display

Stuff

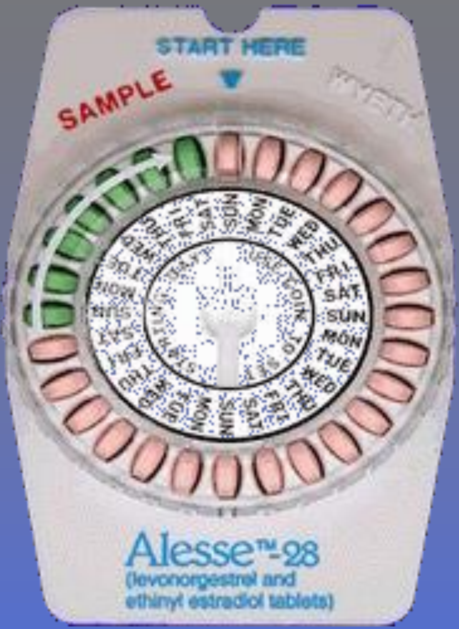


Electronics

Polymers

Drugs

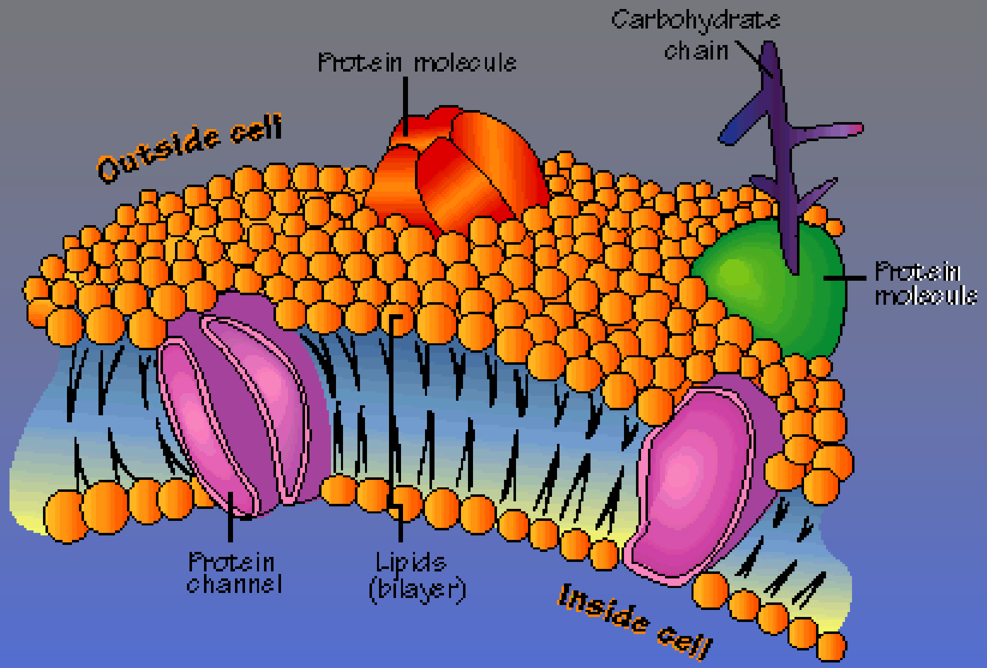

RITE AID
COATED FOR EASIER SWALLOWING
Ibuprofen
Tablets USP, 200 mg Each
Pain Reliever • Fever Reducer
100 Brown Coated Tablets


START HERE
SAMPLE
Alesse™-28
(levonorgestrel and
ethinyl estradiol tablets)

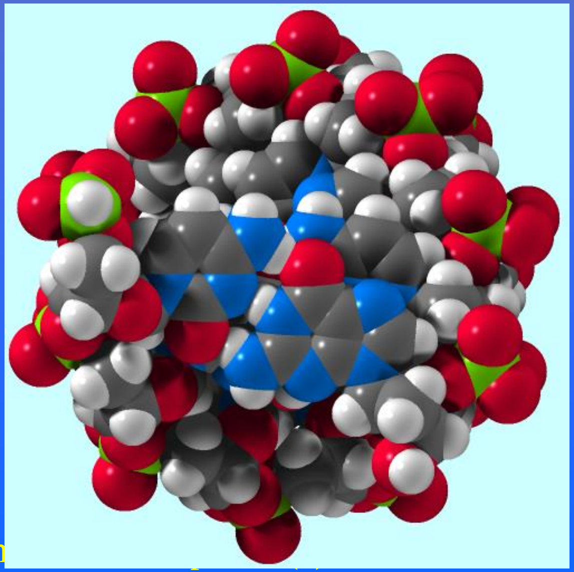

Pfizer


Heineken

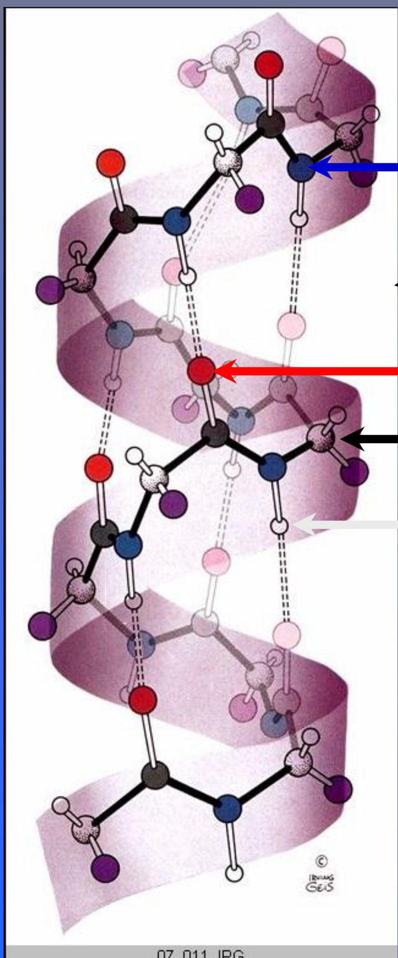
Life



Carbohydrate chain
Protein molecule
Outside cell
Protein molecule
Protein channel
Lipids (bilayer)
Inside cell



Hierarchical organization of biological structures

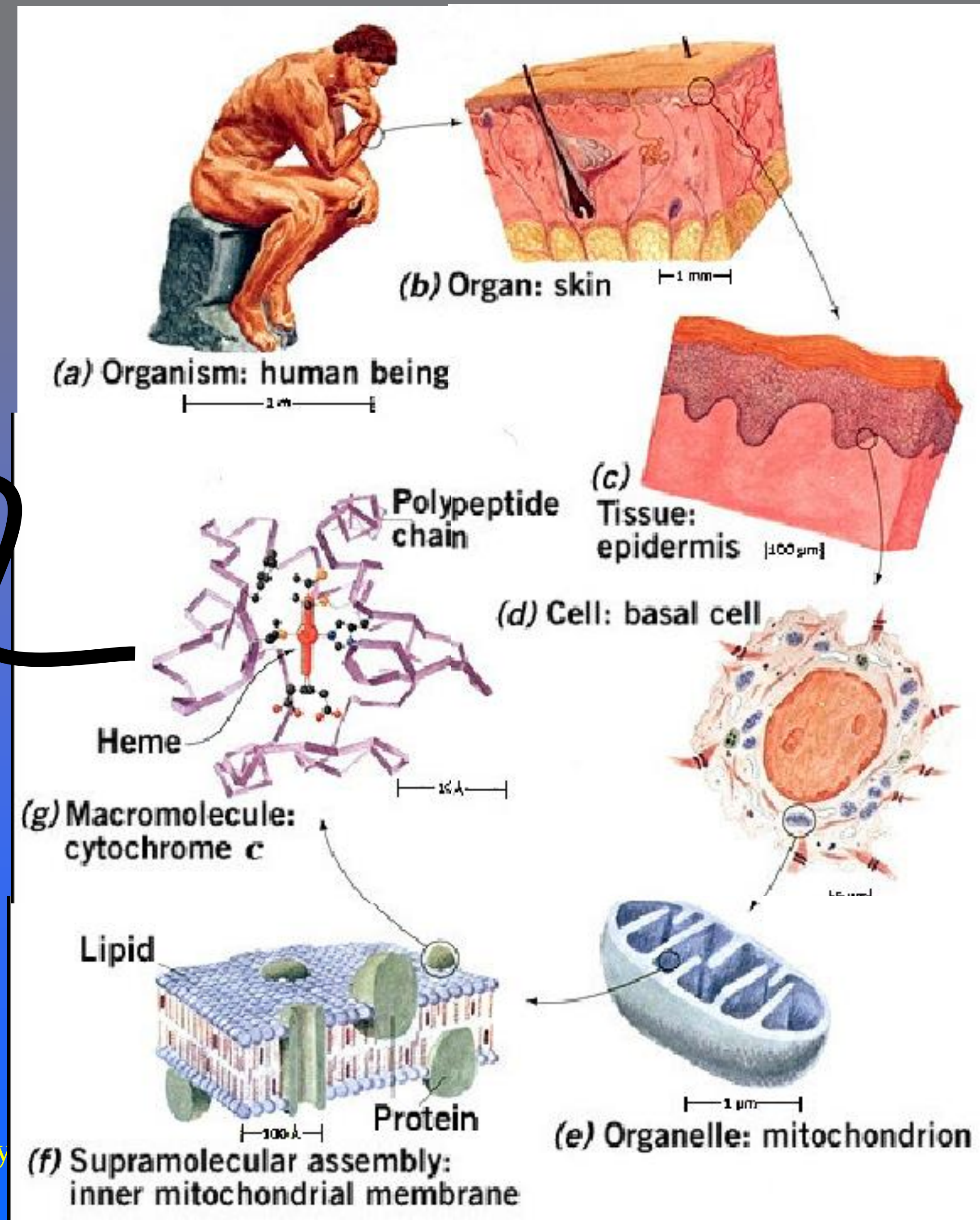


nitrogen

oxygen

carbon

hydrogen



McMurry

millions of organic molecules

nitrogen

oxygen

carbon

hydrogen

ca adrenaline

millions of organic molecules

Understanding life requires an understanding of the organic molecules of life.

millions of organic molecules

The goals of organic chemistry are to develop tools and their application to understand the structure and reactivity of organic molecules.

Origins of Organic Chemistry

Foundations of organic chemistry from mid-1700's.

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

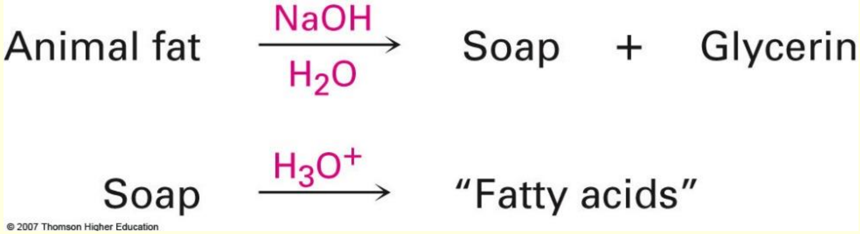
Compounds also decomposed more easily.

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

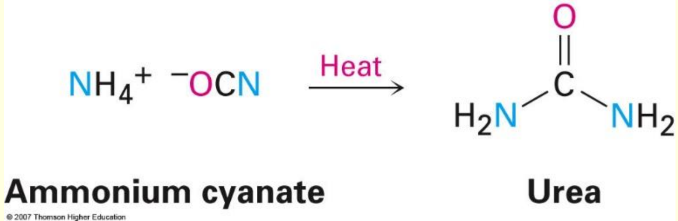
It was thought that organic compounds must contain some "vital force" because they were from living sources.

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



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



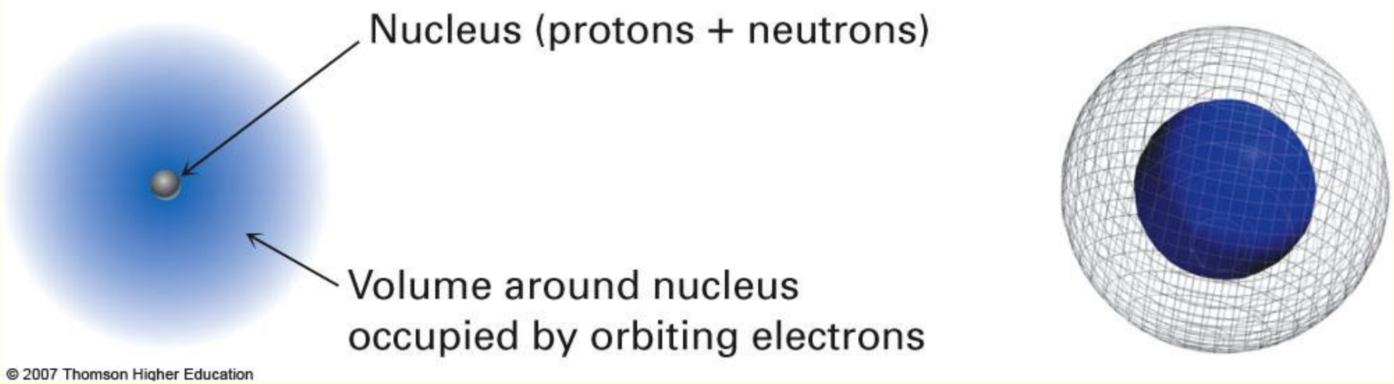
- Organic chemistry is study of carbon compounds.
- Why is it so special?
  - 90% of more than 30 million chemical compounds contain carbon.
  - Examination of carbon in periodic chart answers some of these questions.
  - Carbon is group 4A element, it can share 4 valence electrons and form 4 covalent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

Why this chapter?

- Review ideas from general chemistry: atoms, bonds, molecular geometry

1.1 Atomic Structure

- Structure of an atom
  - Positively charged *nucleus* (very dense, protons and neutrons) and small (10^{-15} m)
  - Negatively charged electrons are in a cloud (10^{-10} m) around nucleus
- Diameter is about 2×10^{-10} m (200 *picometers* (pm)) [the unit *angstrom* (Å) is 10^{-10} m = 100 pm]



Atomic Number and Atomic Mass

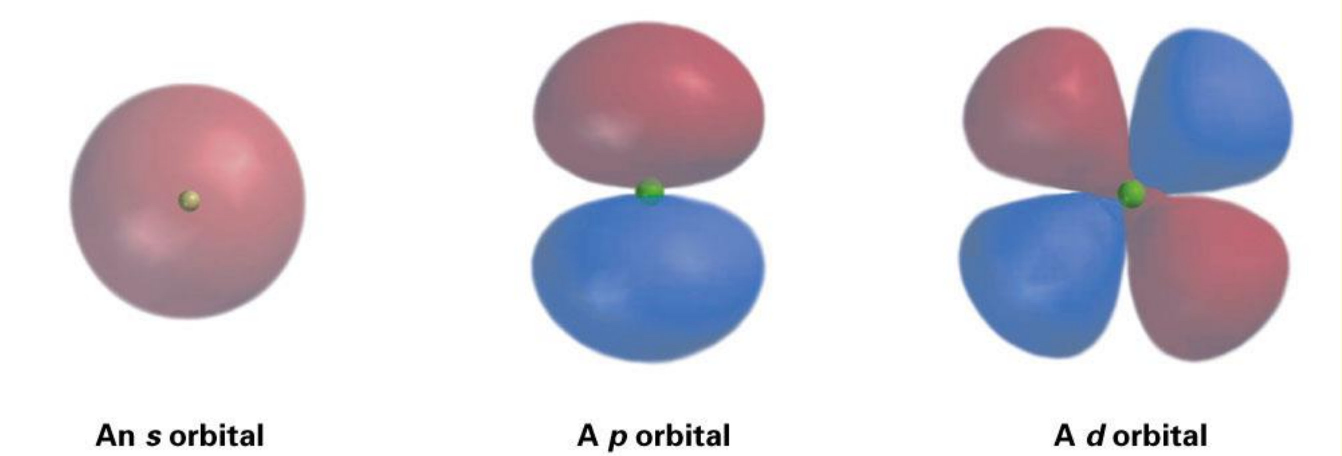
- The *atomic number* (*Z*) is the number of protons in the atom's nucleus
- The *mass number* (*A*) is the number of protons plus neutrons
- All the atoms of a given element have the same atomic number
- **Isotopes** are atoms of the same element that have different numbers of neutrons and therefore different mass numbers
- The **atomic mass** (*atomic weight*) of an element is the weighted average mass in atomic mass units (amu) of an element’s naturally occurring isotopes

1.2 Atomic Structure: Orbitals

- **Quantum mechanics**: describes electron energies and locations by a *wave equation*
  - *Wave function* solution of wave equation
  - Each wave function is an **orbital**, ψ
- A plot of ψ^2 describes where electron most likely to be
- Electron cloud has no specific boundary so we show most probable area

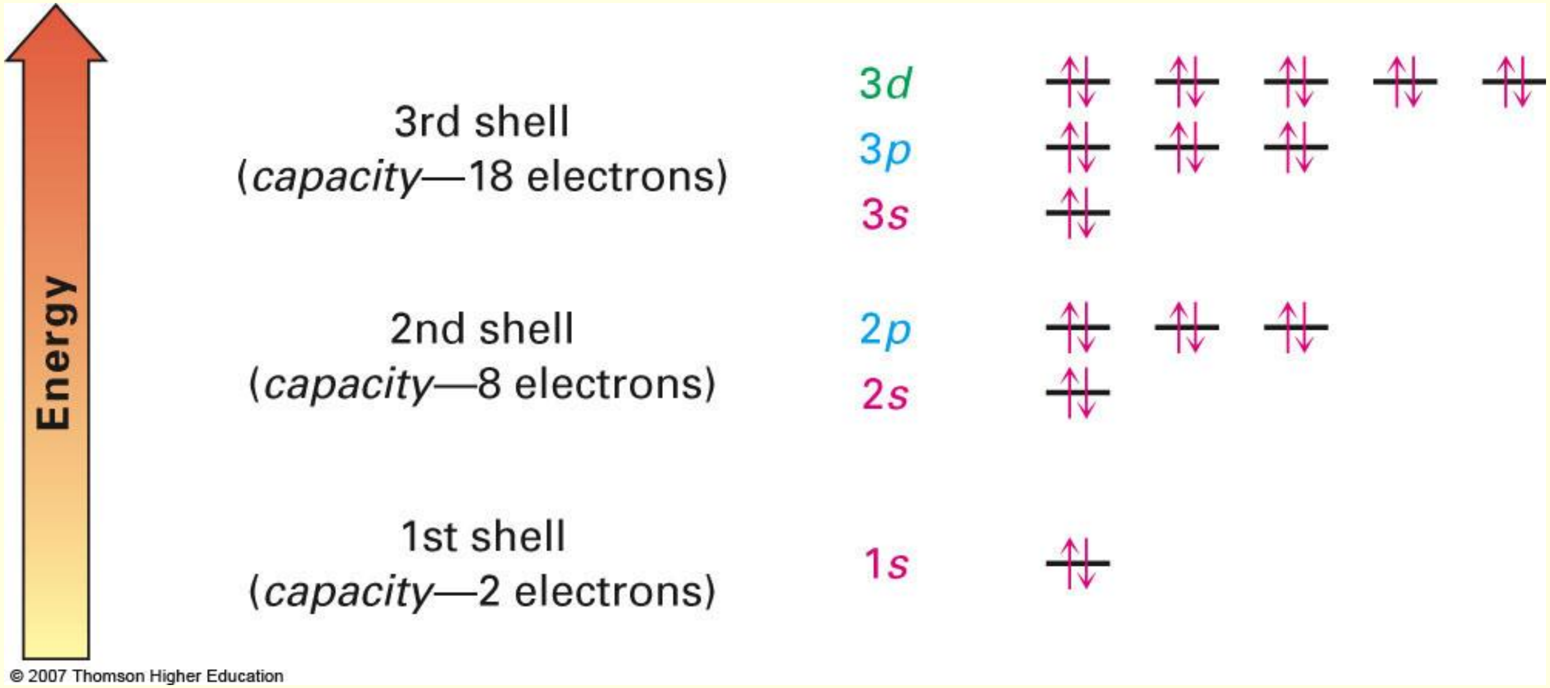
Shapes of Atomic Orbitals for Electrons

- Four different kinds of orbitals for electrons based on those derived for a hydrogen atom
- Denoted *s*, *p*, *d*, and *f*
- *s* and *p* orbitals most important in organic and biological chemistry
- *s* orbitals: spherical, nucleus at center
- *p* orbitals: dumbbell-shaped, nucleus at middle
- d orbitals: elongated dumbbell-shaped, nucleus at center



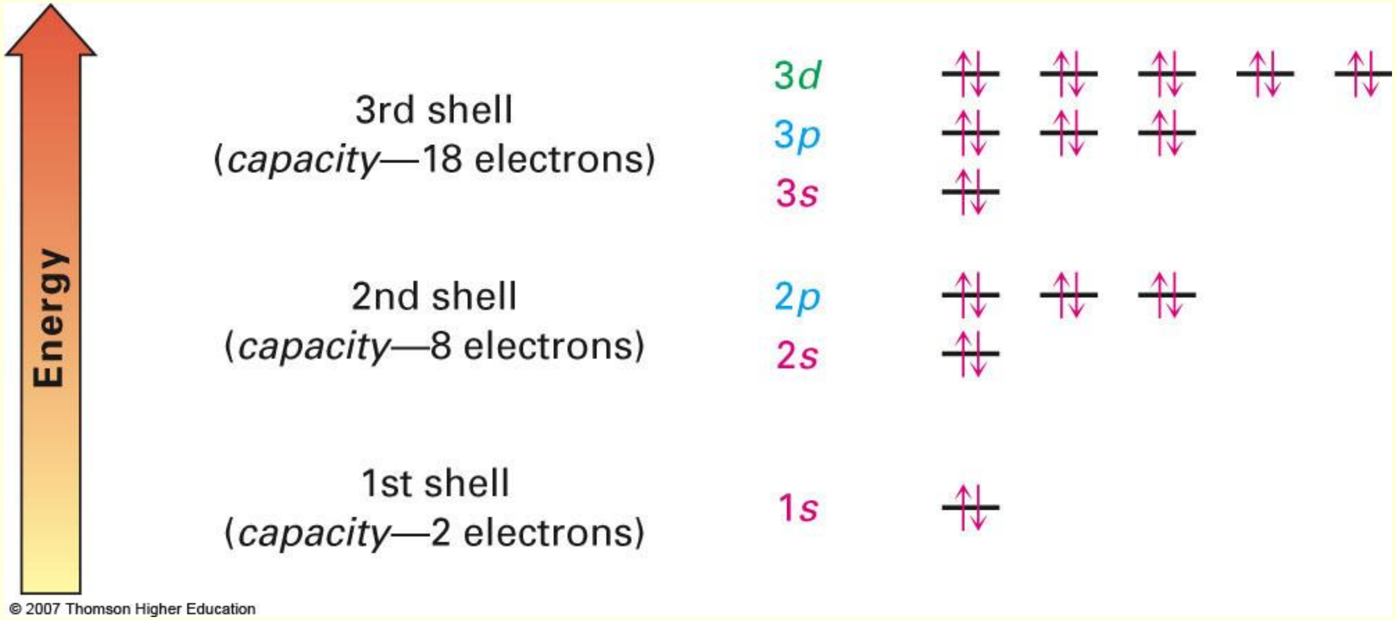
Orbitals and Shells part 1

- Orbitals are grouped in **shells** of increasing size and energy
- Different shells contain different numbers and kinds of orbitals
- Each orbital can be occupied by two electrons



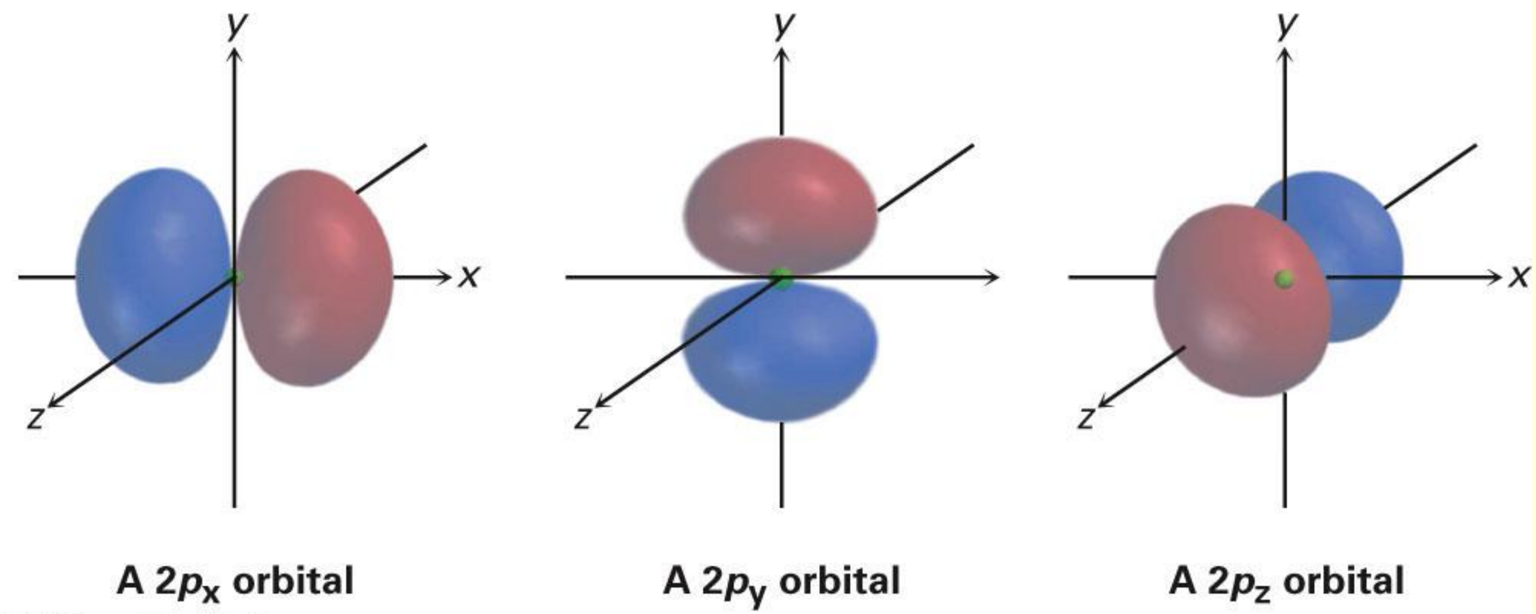
Orbitals and Shells part 2

- First shell contains one *s* orbital, denoted 1*s*, holds only two electrons
- Second shell contains one *s* orbital (2*s*) and three *p* orbitals (2*p*), eight electrons
- Third shell contains an *s* orbital (3*s*), three *p* orbitals (3*p*), and five *d* orbitals (3*d*), 18 electrons

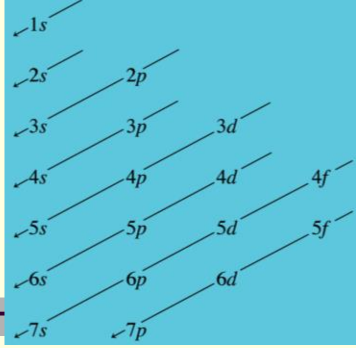


p-Orbitals

- In each shell there are three perpendicular *p* orbitals, p_x, p_y, and p_z, of equal energy
- Lobes of a *p* orbital are separated by region of zero electron density, a **node**



1.3 Atomic Structure: Electron Configurations



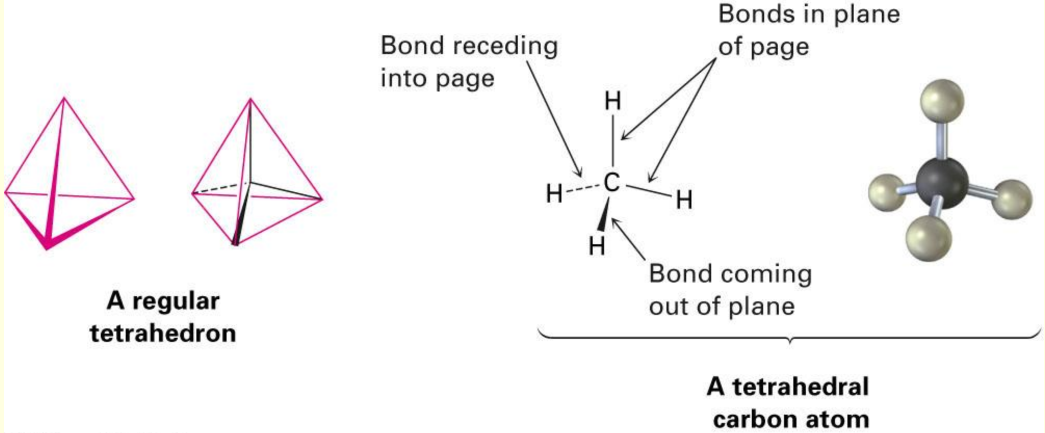
- **Ground-state electron configuration** (lowest energy arrangement) of an atom lists orbitals occupied by its electrons. Rules:
- 1. Lowest-energy orbitals fill first: 1*s* → 2*s* → 2*p* → 3*s* → 3*p* → 4*s* → 3*d* (*Aufbau* (“build-up”) principle)
- 2. Electrons act as if they were spinning around an axis. Electron spin can have only two orientations, up ↑ and down ↓. Only two electrons can occupy an orbital, and they must be of opposite spin (*Pauli exclusion principle*) to have unique wave equations
- 3. If two or more empty orbitals of equal energy are available, electrons occupy each with spins parallel until all orbitals have one electron (*Hund's rule*).

1.4 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



- 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)

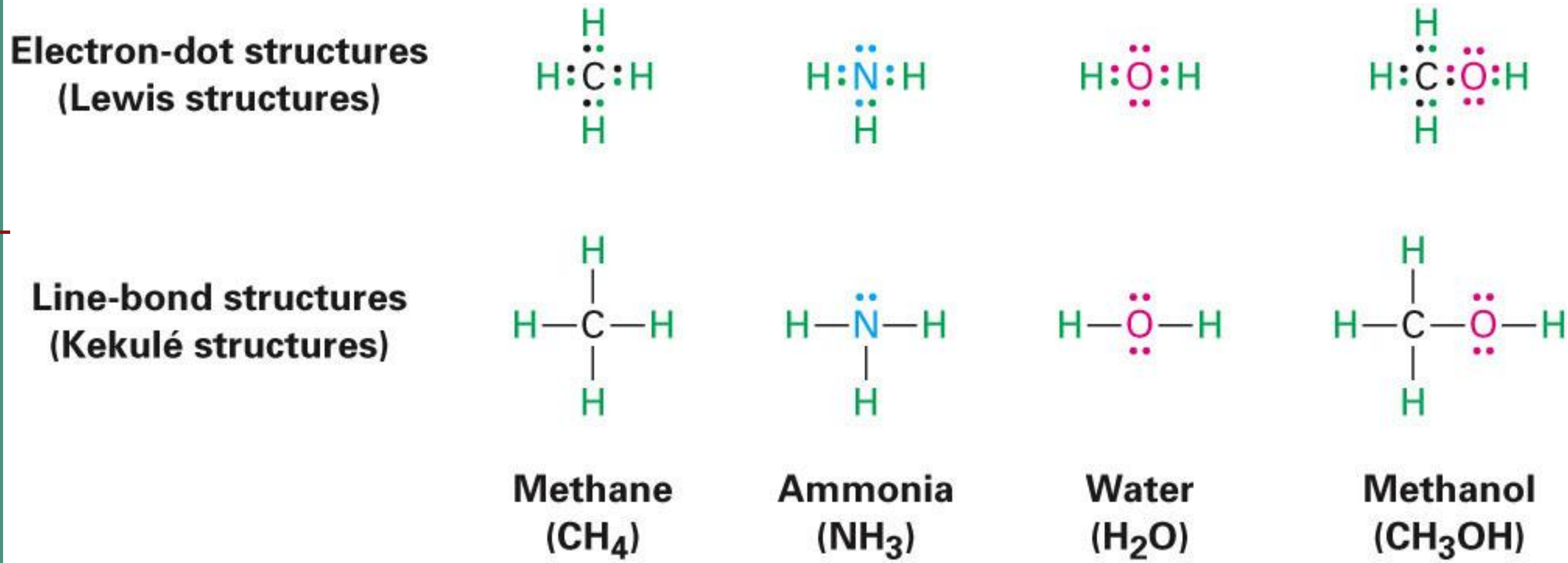
- **Lewis structures** (electron dot) show valence electrons of an atom as dots
  - Hydrogen has one dot, representing its 1*s* electron
  - Carbon has four dots ($2s^2\ 2p^2$)
- **Kekule structures** (line-bond structures) have a line drawn between two atoms indicating a 2 electron covalent bond.
-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

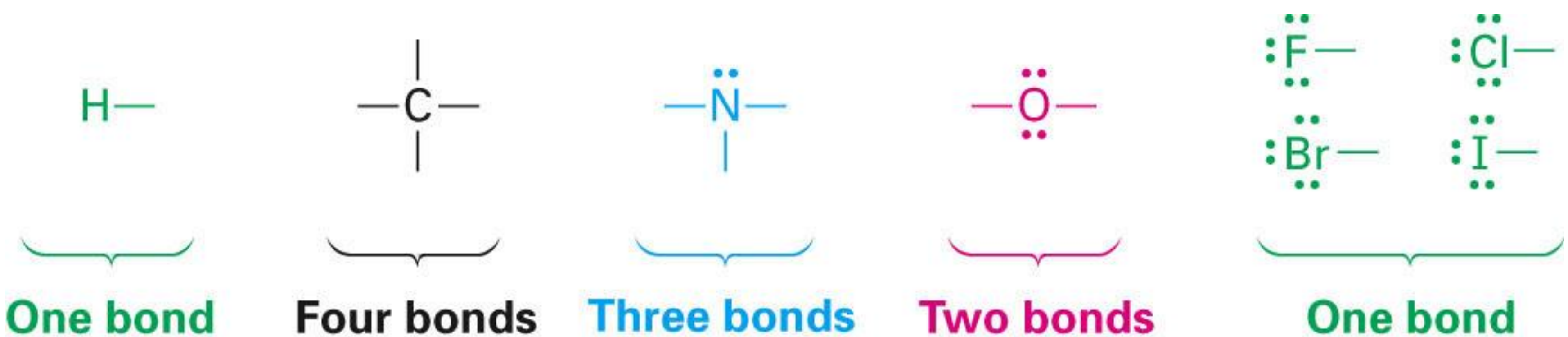
- Atoms with one, two, or three valence electrons form one, two, or three bonds.

- 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).

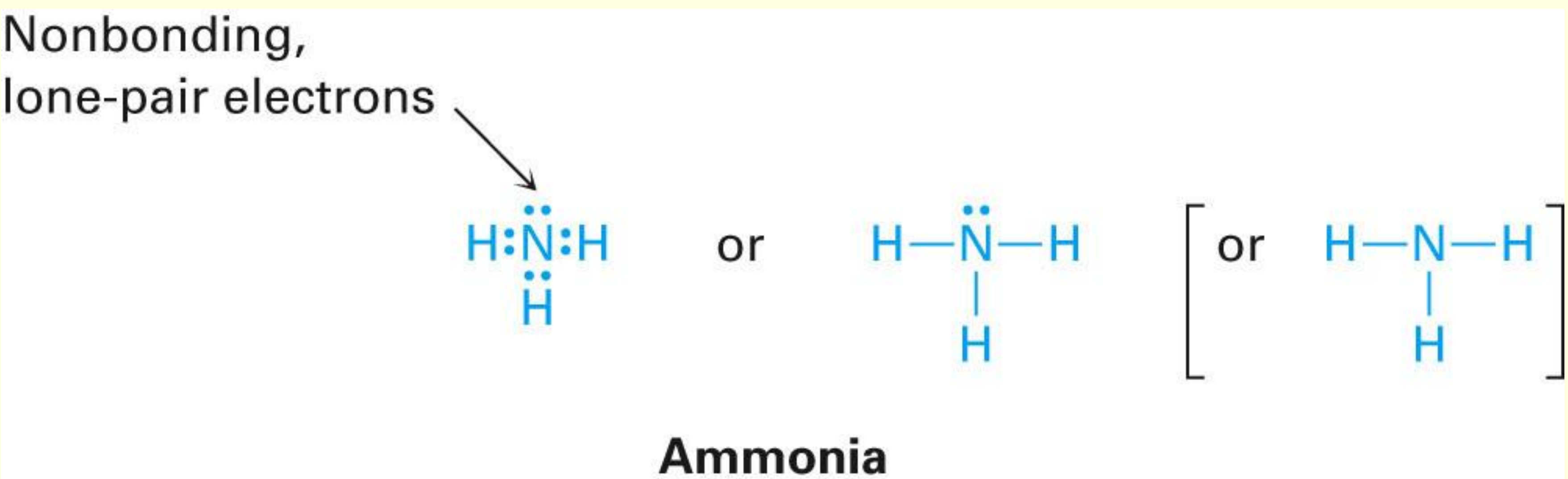
- Nitrogen has five valence electrons ($2s^2$ $2p^3$) but forms only three bonds (NH_3).
- Oxygen has six valence electrons ($2s^2$ $2p^4$) but forms two bonds (H_2O)


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

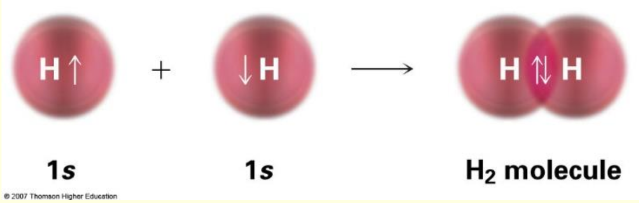
- Valence electrons not used in bonding are called **nonbonding electrons**, or **lone-pair electrons**
  - Nitrogen atom in ammonia (NH_3)
    - Shares six valence electrons in three covalent bonds and remaining two valence electrons are nonbonding lone pair



1.5 The Nature of 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

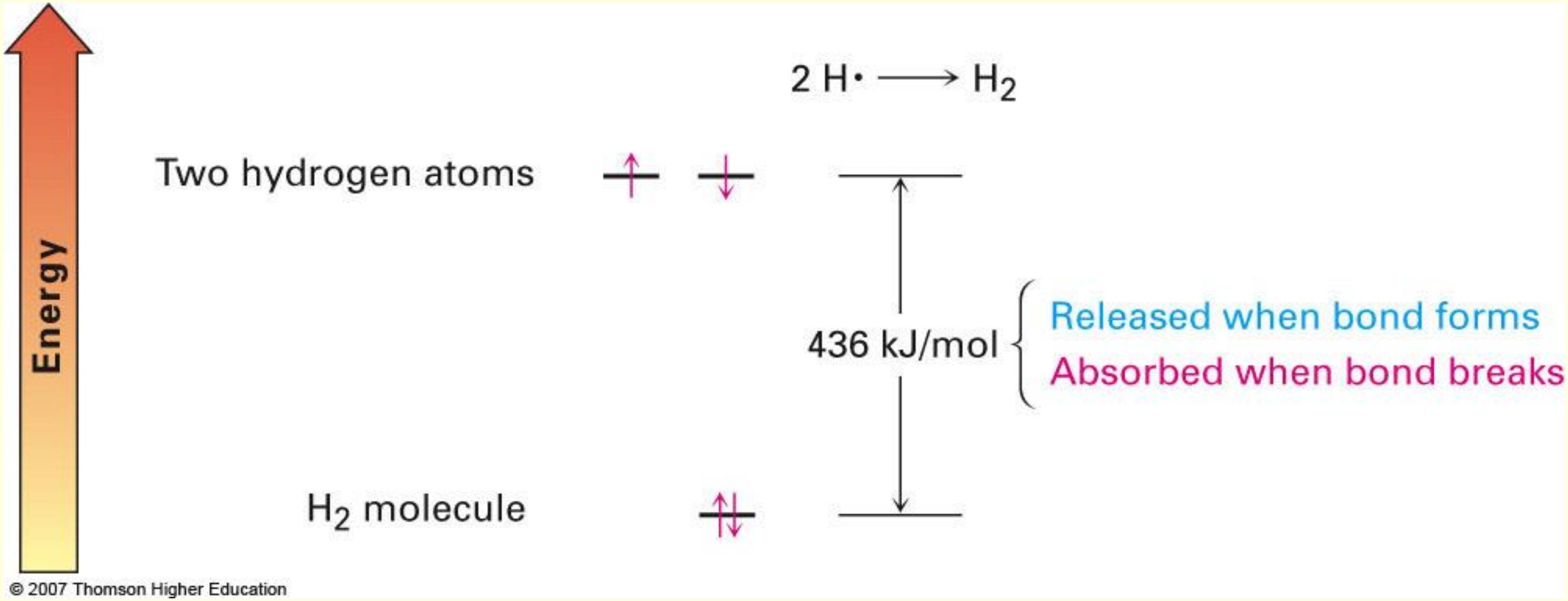


Valence Bond Theory:

- 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**

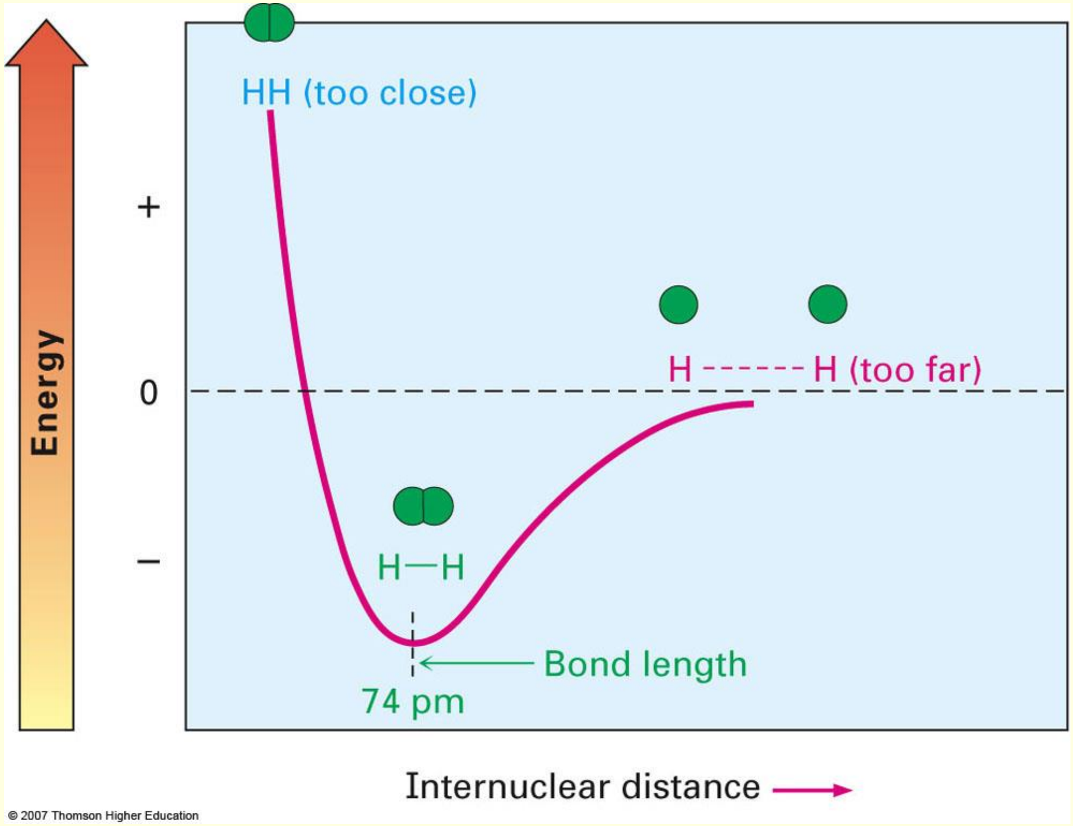
Bond Energy

- Reaction 2 H· → 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)



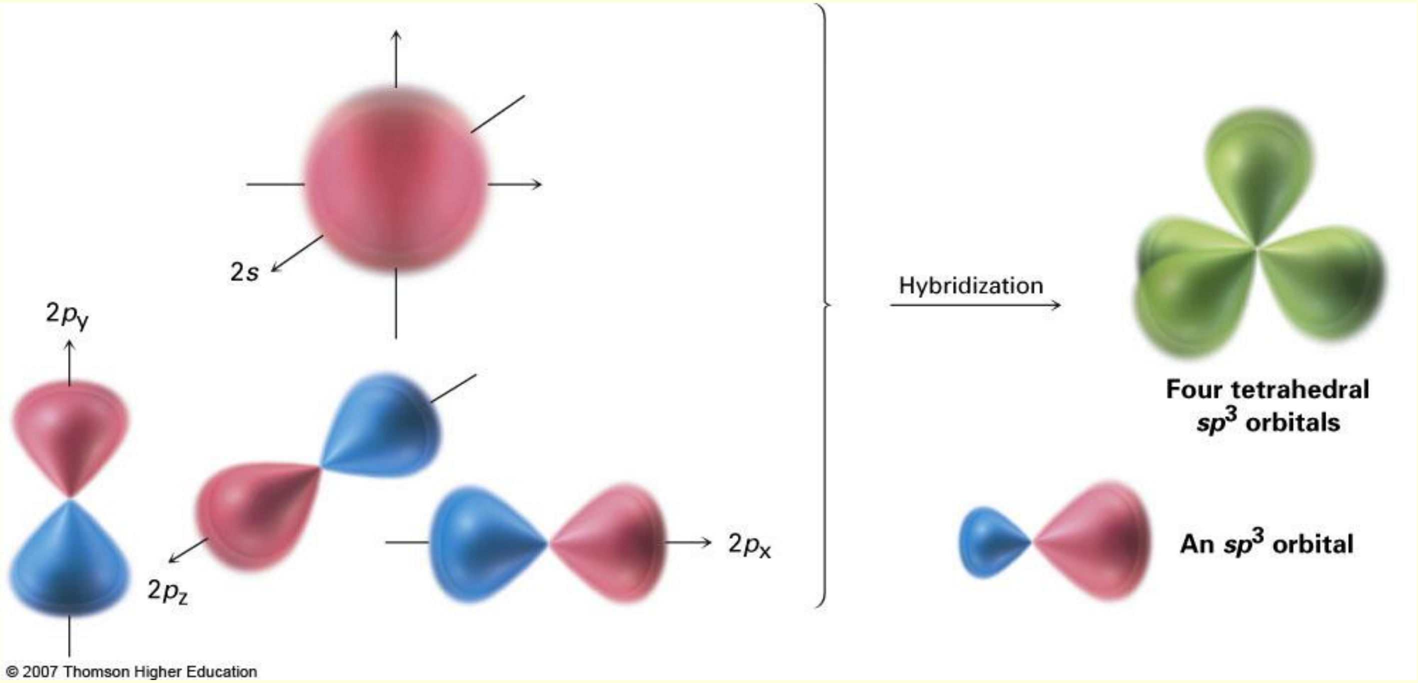
Bond Length

- 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



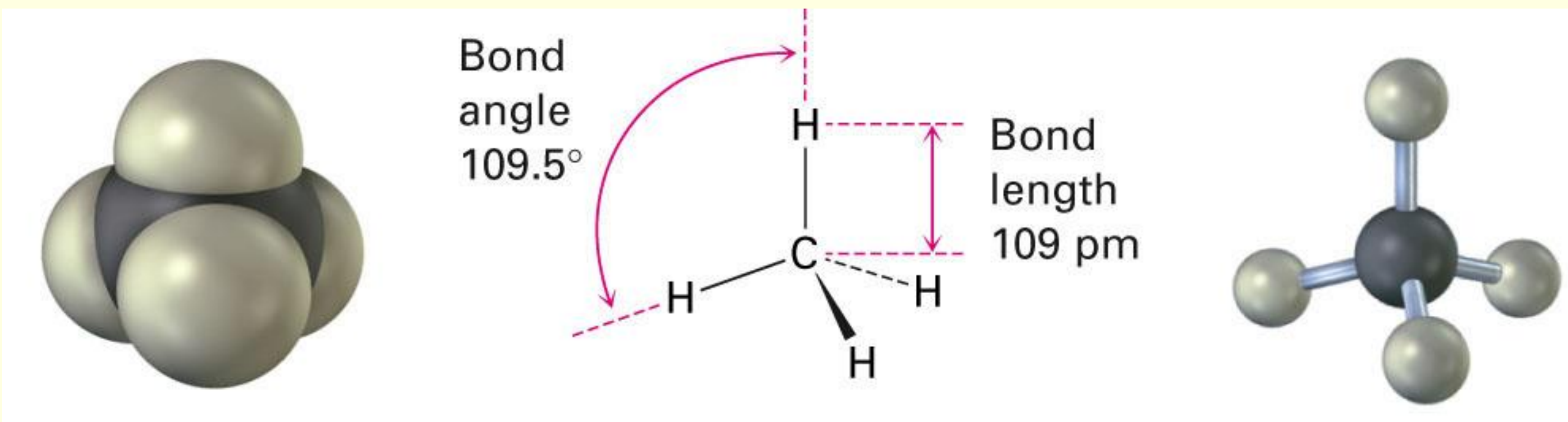
1.6 *sp*^{3} Orbitals and the Structure of Methane

- 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)



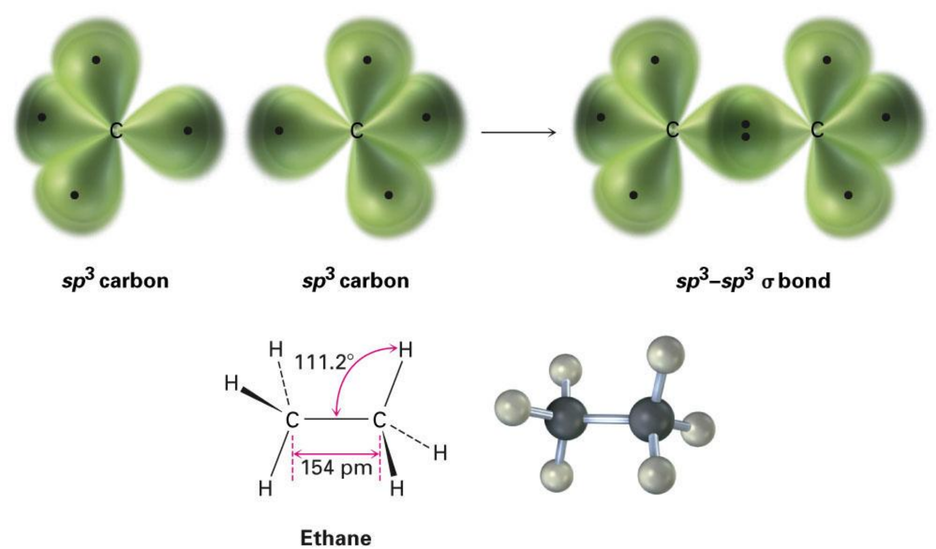
The Structure of Methane

- *sp*3 orbitals on C overlap with 1*s* orbitals on 4 H atoms to form four identical C-H bonds
- Each C–H bond has a strength of 436 (438) kJ/mol and length of 109 pm
- **Bond angle**: each H–C–H is 109.5°, the *tetrahedral angle*.



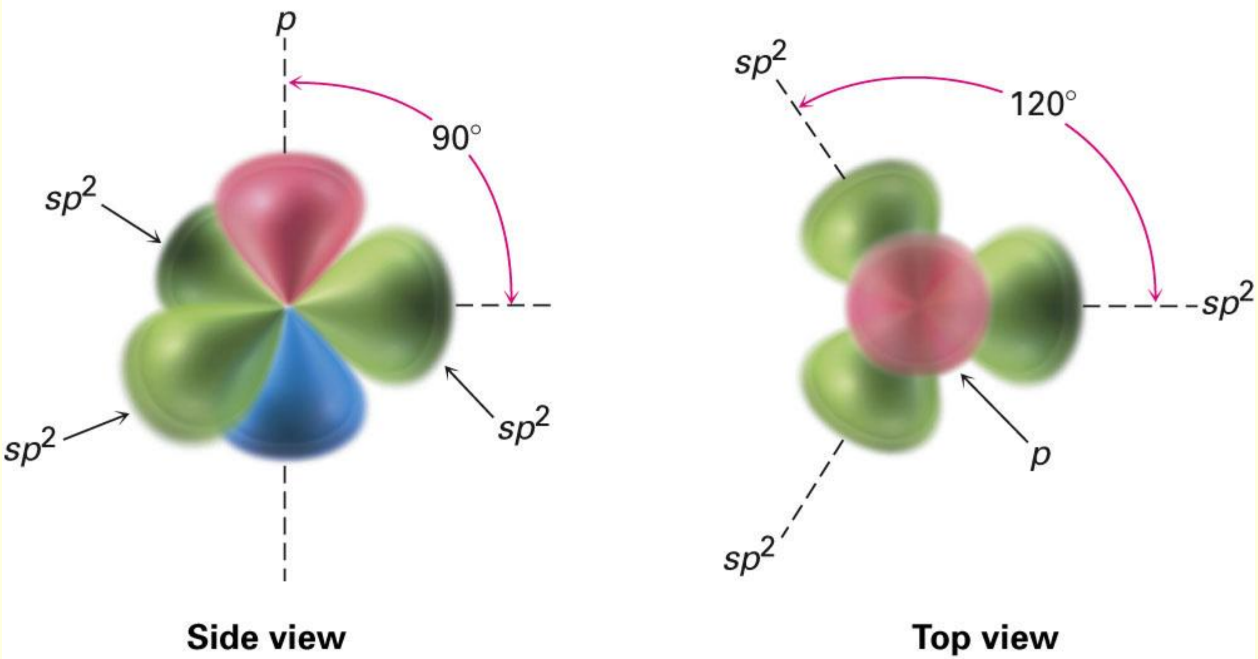
1.7 sp^3 Orbitals and the Structure of Ethane

- Two C's bond to each other by σ 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 423 kJ/mol
- C–C bond is 154 pm long and strength is 376 kJ/mol
- All bond angles of ethane are tetrahedral



1.8 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). This results in a double bond.
- *sp^2* orbitals are in a plane with120° angles
- Remaining *p* orbital is perpendicular to the plane

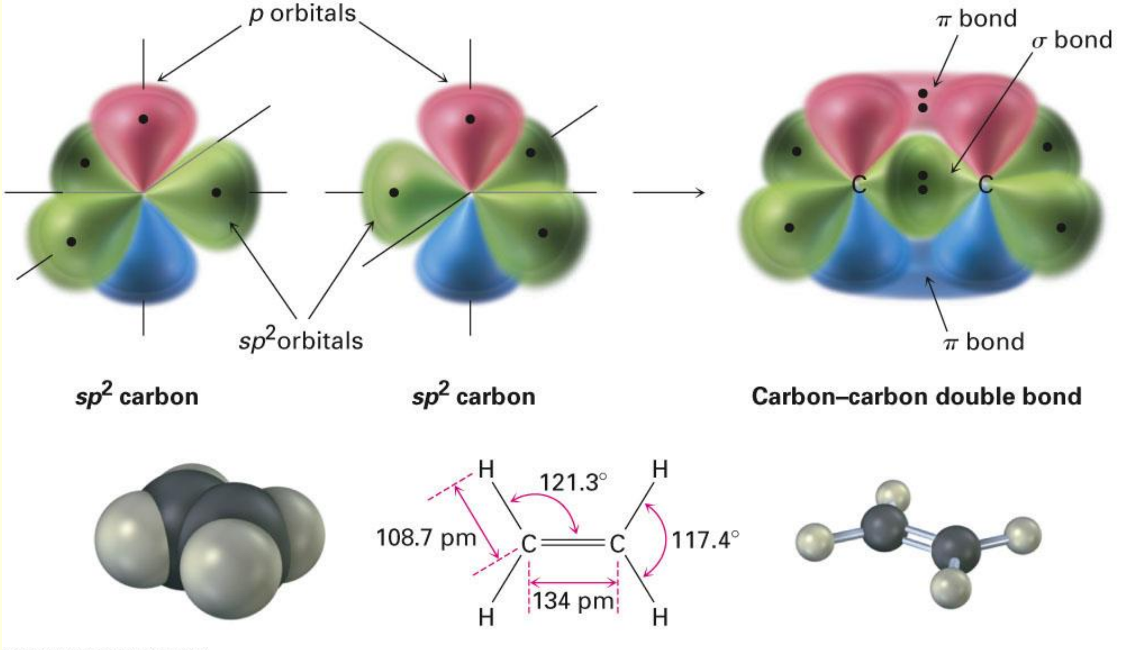


Bonds From sp^2 Hybrid Orbitals

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

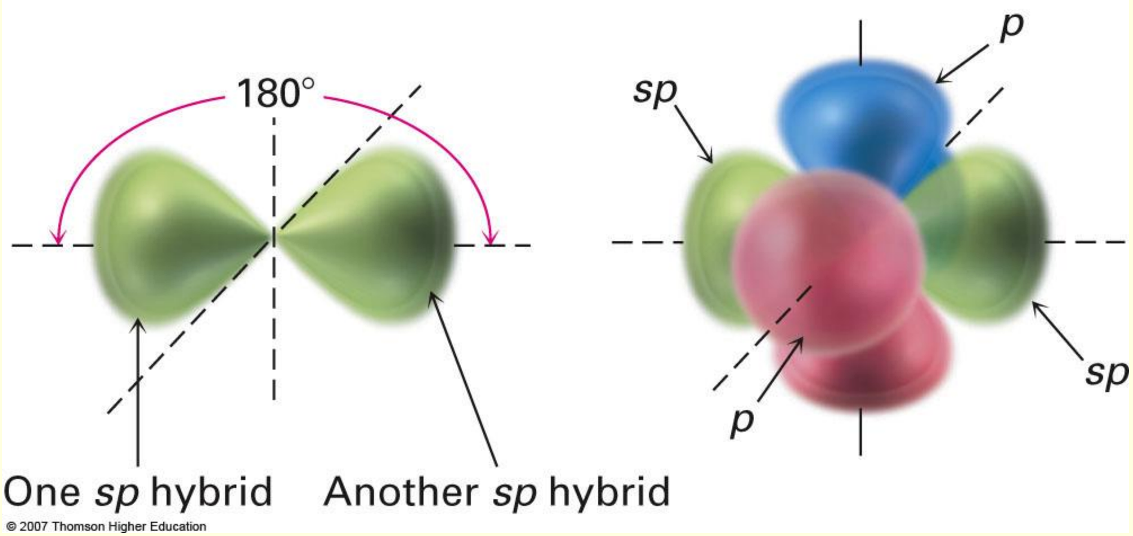
Structure of Ethylene

- 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 134 pm (C–C 154 pm)



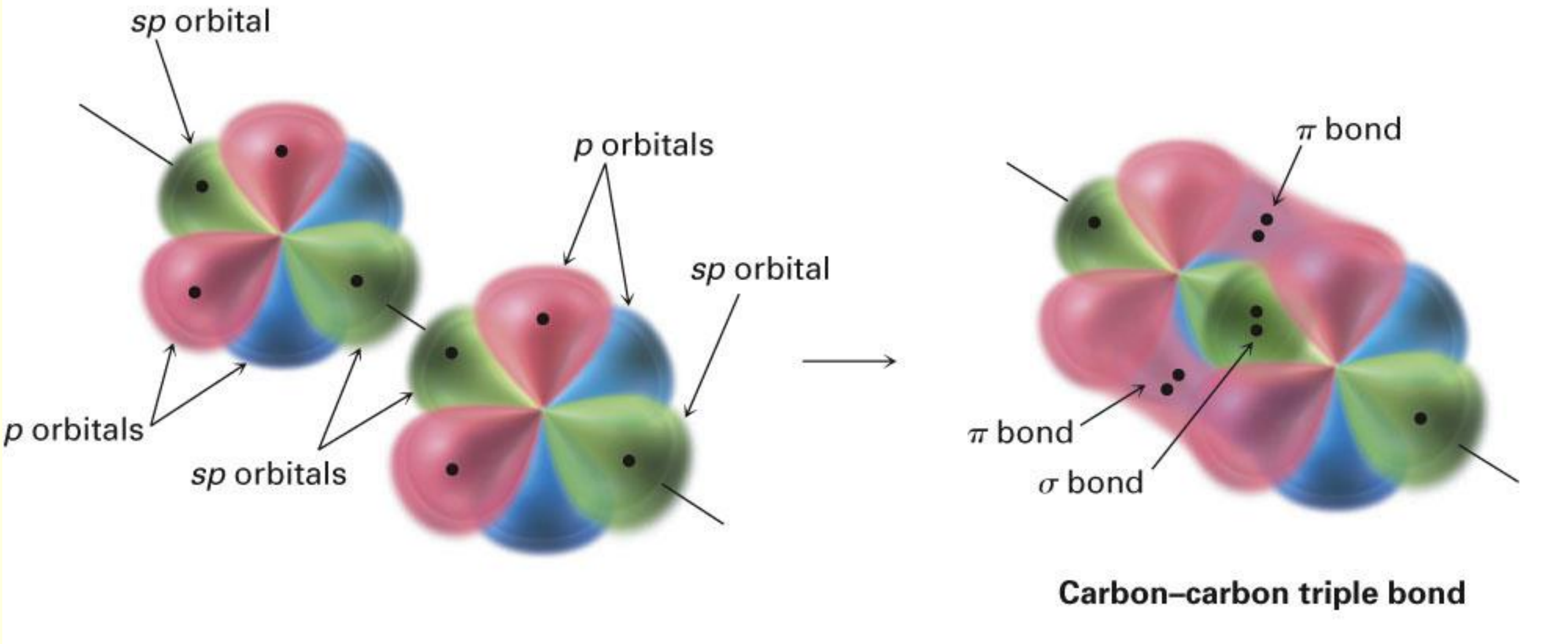
1.9 *sp* Orbitals and the Structure of Acetylene

- 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* σ bond
- p_z orbitals from each C form a p_z–p_z π 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

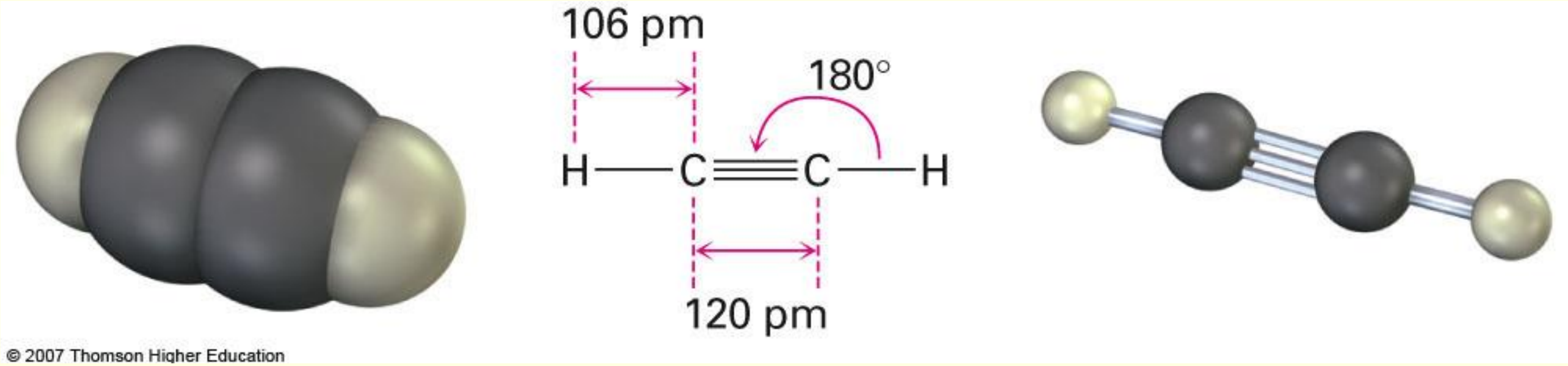
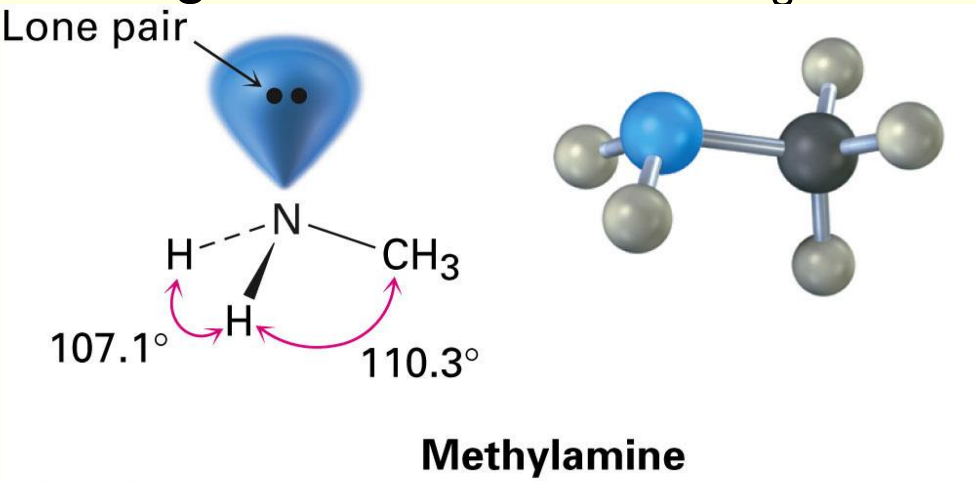


Table 1.2 Comparison of C—C and C—H Bonds in Methane, Ethane, Ethylene, and Acetylene

Molecule	Bond	Bond strength (kJ/mol)	Bond strength (kcal/mol)	Bond length (pm)
Methane, CH_4	(sp^3) C—H	436	104	109
Ethane, CH_3CH_3	(sp^3) C—C (sp^3)	376	90	154
	(sp^3) C—H	423	101	109
Ethylene, $H_2C{=}CH_2$	(sp^2) C—C (sp^2)	728	174	134
	(sp^2) C—H	465	111	109
Acetylene, $HC{\equiv}CH$	(sp) C≡C (sp)	965	231	120
	(sp) C—H	556	133	106

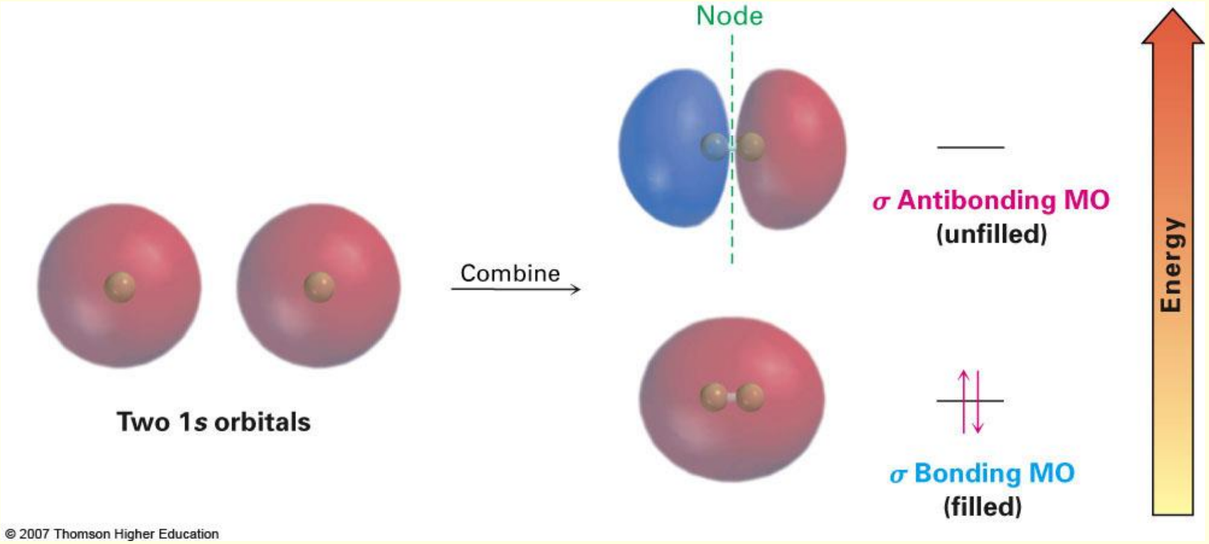
1.10 Hybridization of Nitrogen and Oxygen

- Elements other than C can have hybridized orbitals
- H–N–H bond angle in ammonia (NH_3) 107.3°
- C-N-H bond angle is 110.3 °
- 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 and CH_3.



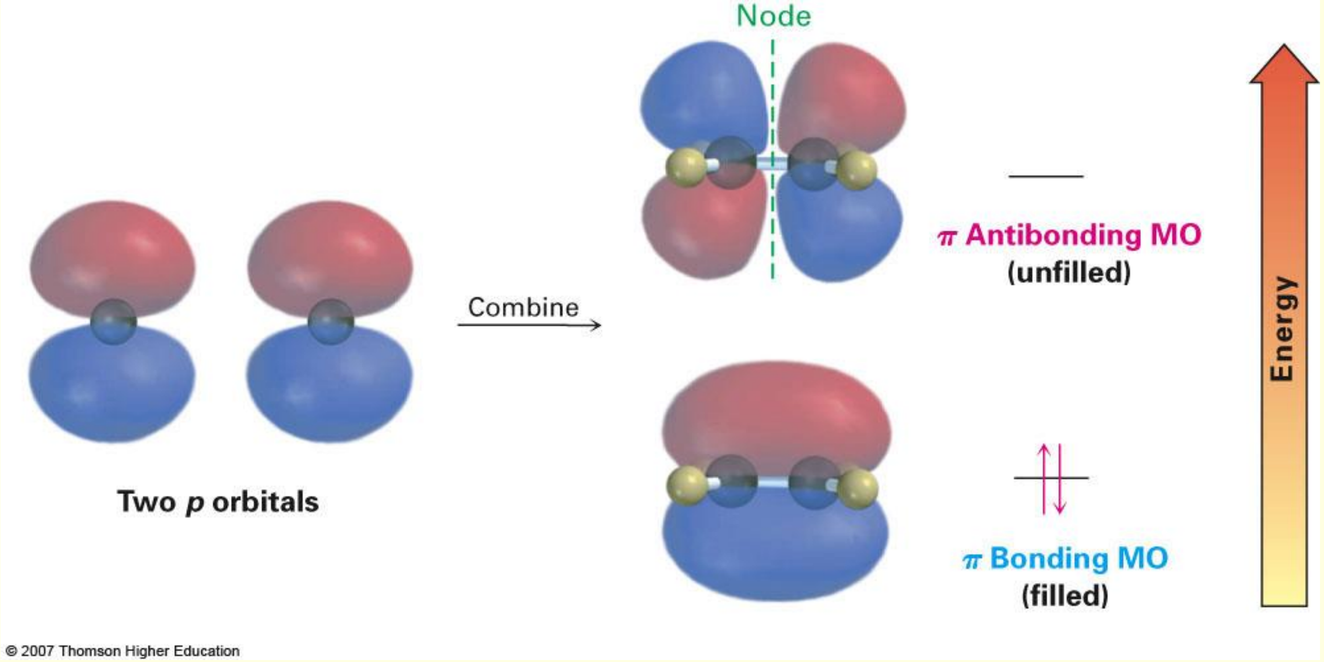
1.11 Molecular Orbital Theory

- 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) MO is higher energy



Molecular Orbitals in Ethylene

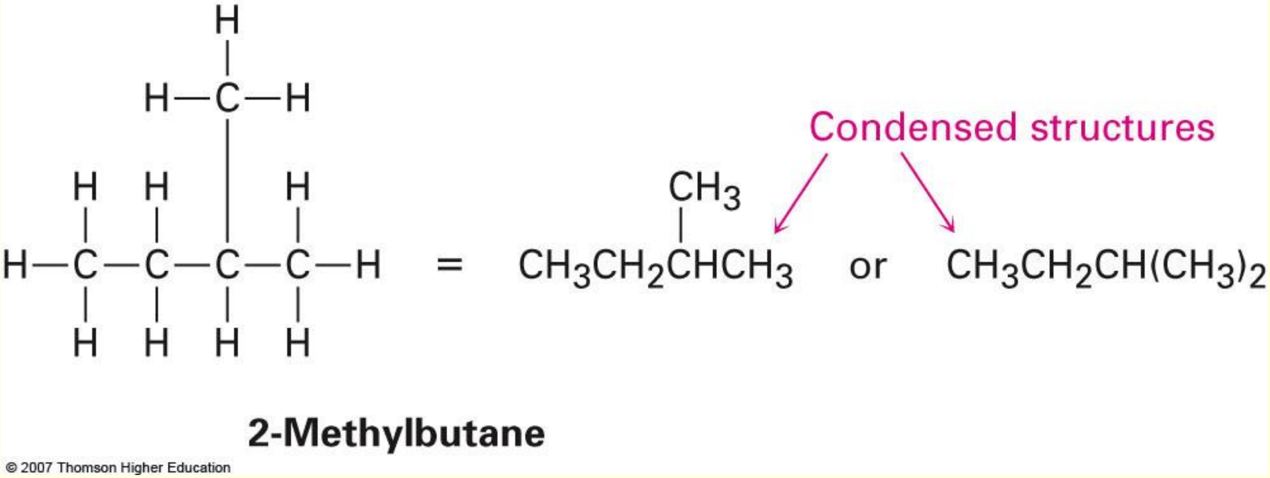
- The π bonding MO is from combining *p* orbital lobes with the same algebraic sign
- The π antibonding MO is from combining lobes with opposite signs
- Only bonding MO is occupied



1.12 Drawing Structures

- Drawing every bond in organic molecule can become tedious.
- Several shorthand methods have been developed to write structures.
- Condensed structures don't have C-H or C-C single bonds shown. They are understood.

e.g.



3 General Rules:

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.

2) Hydrogen atoms bonded to carbon aren’t shown.

3) Atoms other than carbon and hydrogen are shown (See table 1.3).

Summary

- **Organic chemistry** – chemistry of carbon compounds
- **Atom**: positively charged nucleus surrounded by negatively charged electrons
- Electronic structure of an atom described by wave equation
  - Electrons occupy **orbitals** around the nucleus.
  - Different orbitals have different energy levels and different shapes
    - *s* orbitals are spherical, *p* orbitals are dumbbell-shaped
- **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

Summary (cont'd)

- **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*** 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