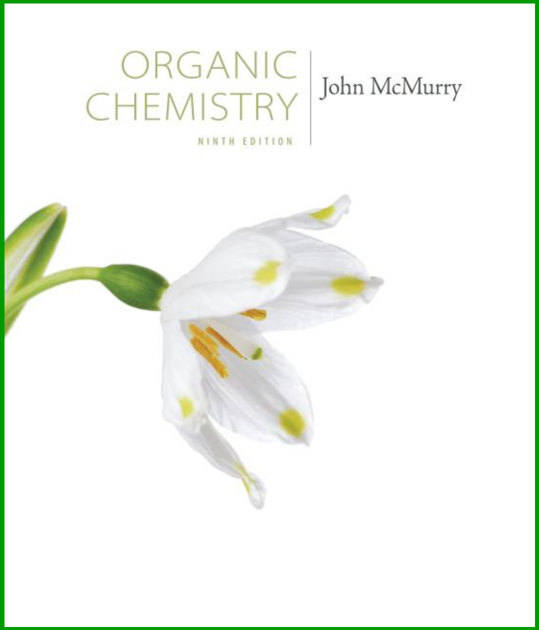


John E. McMurry

www.cengage.com/chemistry/mcmurry

Chapter 1
Structure and Bonding

Learning Objectives

(1.1)

- Atomic structure: The nucleus

(1.2)

- Atomic structure: Orbitals

(1.3)

- Atomic structure: Electron configurations

(1.4)

- Development of chemical bonding theory

Learning Objectives

(1.5)

- Describing chemical bonds: Valence bond theory

(1.6)

- sp^3 hybrid orbitals and the structure of methane

(1.7)

- sp^3 hybrid orbitals and the structure of ethane

(1.8)

- sp^2 hybrid orbitals and the structure of ethylene

Learning Objectives

(1.9)

- *sp* hybrid orbitals and the structure of acetylene

(1.10)

- Hybridization of nitrogen, oxygen, phosphorus, and sulfur

(1.11)

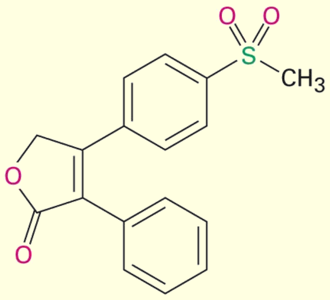
- Describing chemical bonds: Molecular orbital theory

(1.12)

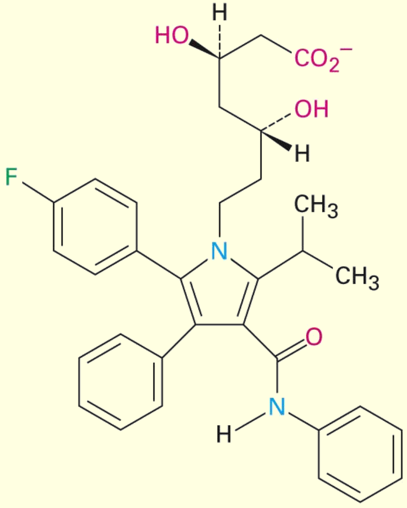
- Drawing chemical structures

What is Organic Chemistry?

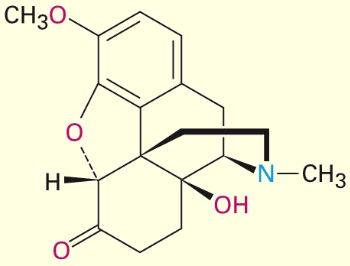
- Living things are made of organic chemicals
  - Proteins that make up hair
  - DNA
  - Foods and medicines



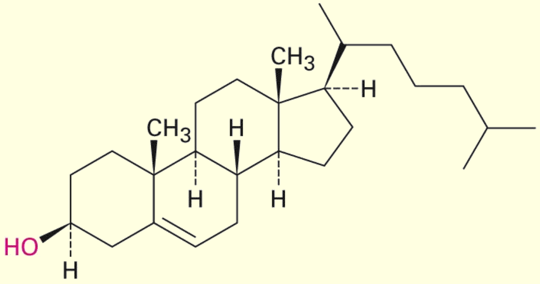
Rofecoxib
(Vioxx)



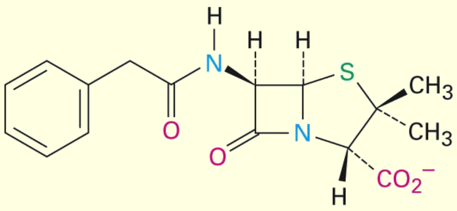
Atorvastatin
(Lipitor)



Oxycodone
(OxyContin)



Cholesterol



Benzylpenicillin

Origins of Organic Chemistry

- Foundations date from mid-1700’s
- Compounds obtained from plants and animals
  - Low-melting solids
  - Hard to isolate, purify, and work with
- Organic compounds were considered to have some vital force as they were from living sources
  - Thought that it could not be synthesized in laboratory

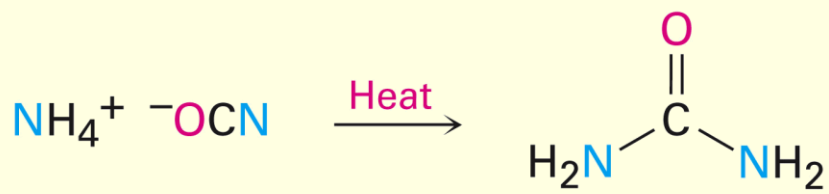
Origins of Organic Chemistry

- 1816, Chevreul found that soap can be separated into several organic compounds which he termed fatty acids

$$\text{Animal fat} \xrightarrow[H_2O]{NaOH} \text{Soap} + \text{Glycerin}$$

$$\text{Soap} \xrightarrow{H_3O^+} \text{“Fatty acids”}$$

- 1828, Wöhler showed that it was possible to convert inorganic salt ammonium cyanate into organic substance urea



Ammonium cyanate **Urea**

Organic Chemistry

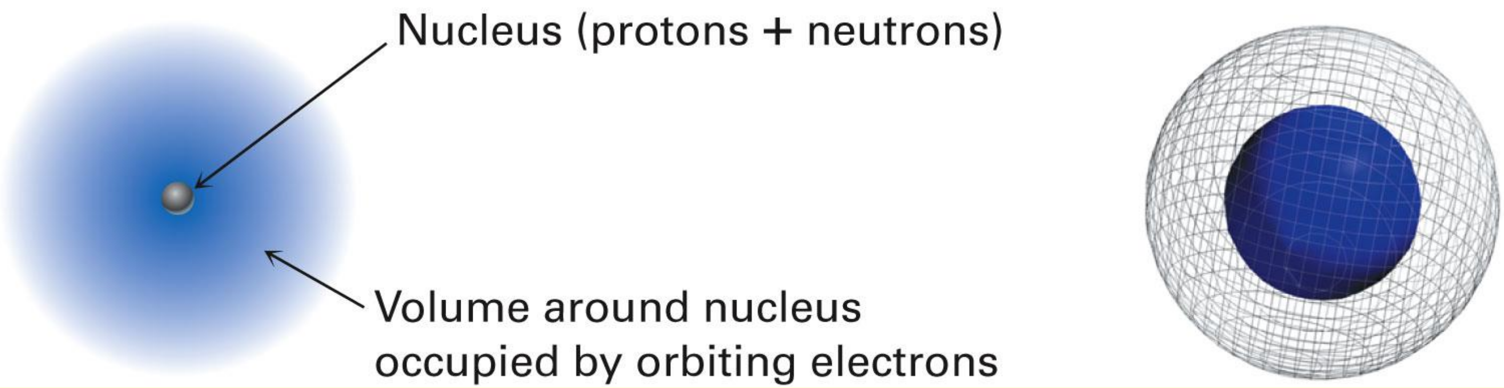
- Study of carbon compounds
- More than 50 million known chemical compounds contain carbon
- Carbon is a group 4A element
  - Can share 4 valence electrons and form 4 covalent bonds
  - Able to bond with one another to form long chains and rings
  - Only element that has the ability to form immense diversity of compounds

Figure 1.1 - The Position of Carbon in the Periodic Table

Group 1A	2A											3A	4A	5A	6A	7A	8A
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															

Atomic Structure - The Nucleus

- Positively charged
  - Surrounded by a cloud of negatively charged electrons (at a distance of 10^{-10} m)
- Consist of subatomic particles
  - Protons, positively charged
  - Neutrons, electrically neutral



Atomic Structure - The Nucleus

- Diameter of an atom is about 2×10^{-10} m
  - 200 picometers (pm) [the unit ångström (Å) is 10^{-10} m = 100 pm]

Atomic Number and Atomic Mass

- Atomic number (Z) - Number of protons in an atom's nucleus
- Mass number (A) - Number of protons plus neutrons
- Atoms of a given element have the same atomic number
- **Isotopes**: Atoms with the same atomic number but different mass numbers
- Atomic mass (atomic weight) - Weighted average mass in atomic mass units (amu) of an element’s naturally occurring isotopes

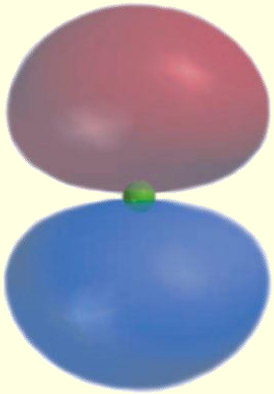
Atomic Structure - Orbitals

- Wave equation - Mathematical equation which describes the behavior of a specific electron in an atom
  - Wave function, or **orbital**, is the solution of wave equation
  - Denoted by the Greek letter psi (Ψ)
- Plot of ψ^2 describes where an electron is most likely to be
- An electron cloud has no specific boundary
  - Most probable area is considered

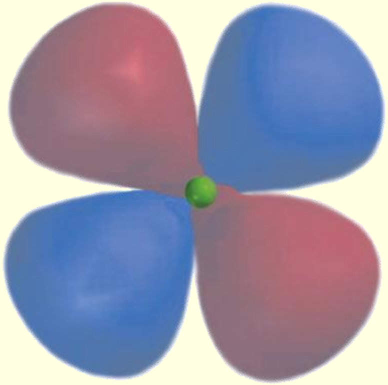
Atomic Structure - Orbitals

- *s*, *p*, *d*, and *f* are different kinds of orbitals
- *s* and *p* orbitals are common 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

An *s* orbital



A *p* orbital

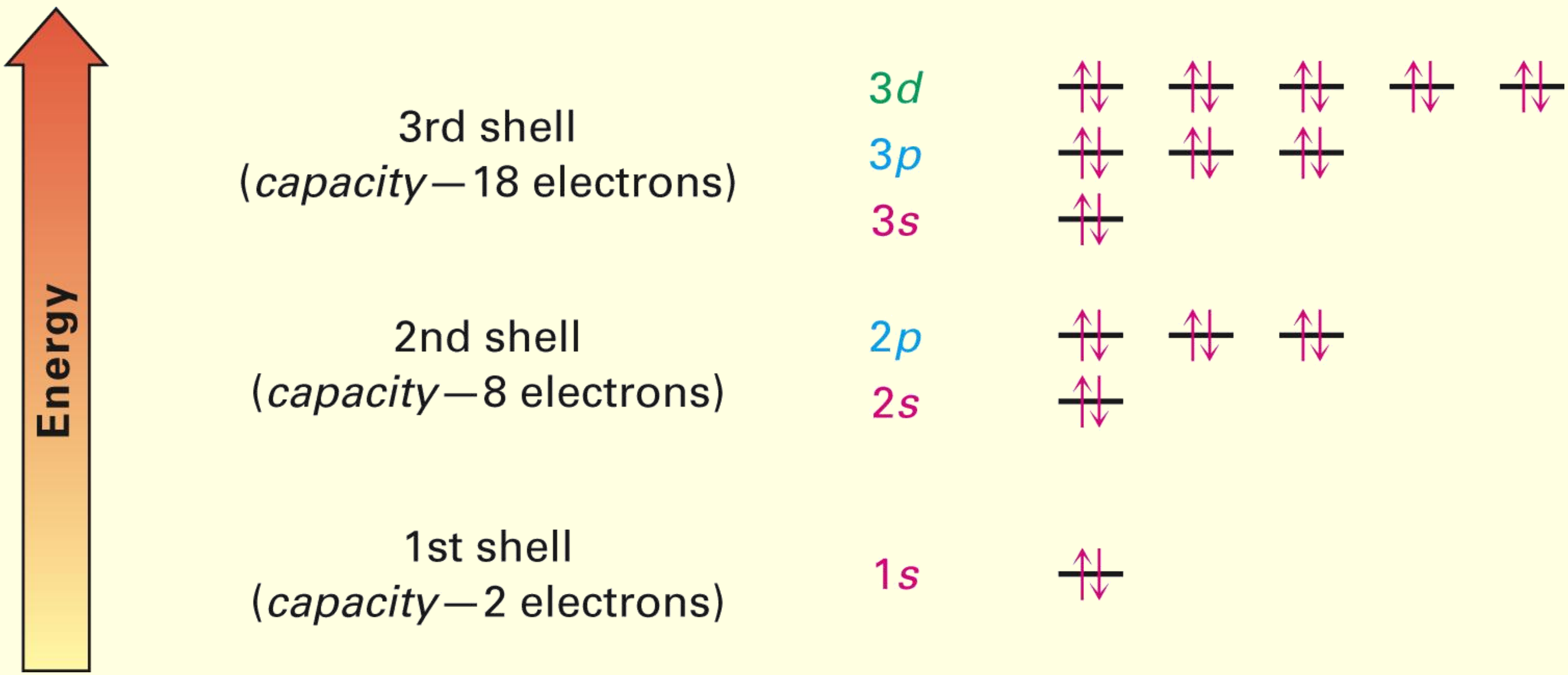


A *d* orbital

Atomic Structure - Orbitals

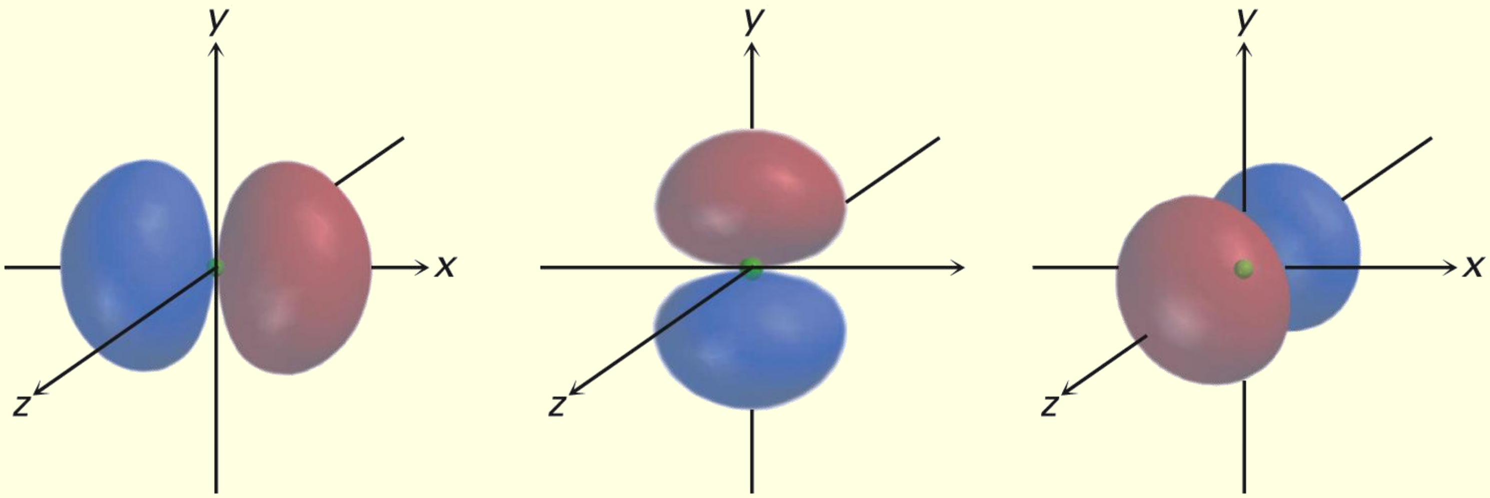
- Orbitals in an atom are organized into different **electron shells**
  - Centered around the nucleus in shells of increasing size and energy
- Different shells contain different numbers and kinds of orbitals
- Each orbital can be occupied by two electrons

Figure 1.4 - The Energy Levels of Electrons in an Atom

P-Orbitals

- Each shell consists of three mutually perpendicular *p* orbitals
  - Denoted p_x, p_y, and p_z
- **Node**: Region of zero electron density
  - Separates two lobes of each p orbital



A 2p_x orbital **A 2p_y orbital** **A 2p_z orbital**

Atomic Structure: Electron Configurations

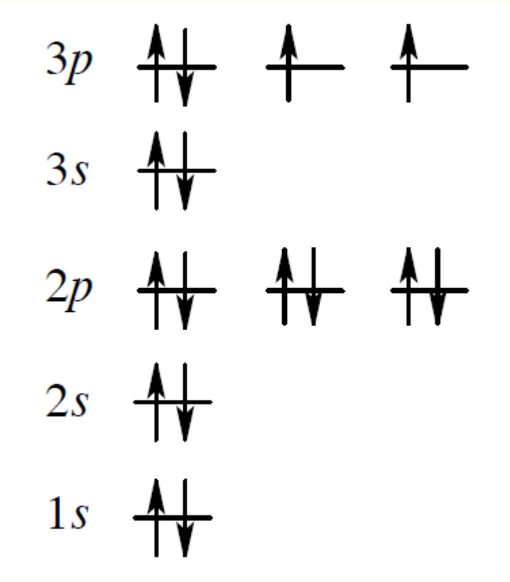
- **Ground-state electron configuration**: Listing of orbitals occupied by an atom's electrons
  - Called lowest-energy arrangement
- Rules
  - Lowest-energy orbitals fill first, in the order of $1s \rightarrow 2s \rightarrow 2p \rightarrow 3s \rightarrow 3p \rightarrow 4s \rightarrow 3d$
    - Aufbau principle

Atomic Structure: Electron Configurations

- Electrons act as if they were spinning around an axis
  - 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
- If two or more empty orbitals of equal energy are available, electrons occupy each with parallel spins until all orbitals have one electron
  - Hund's rule

Worked Example

- Give the ground-state electron configuration for sulfur
- Solution:
  - Atomic number of sulfur is 16
    - Number of electrons = 16



In a more concise way it can be written as

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$

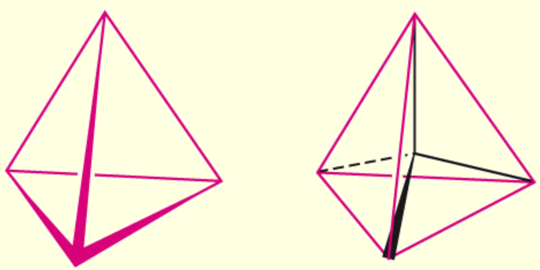
Worked Example

- How many electrons does magnesium have in its outermost electron shell?
- Solution:
  - Elements of the periodic table are organized into groups based on the number of outer-shell electrons each element has
  - Using the periodic table we locate the group of the element, magnesium
  - Magnesium - Group 2A
    - Has two electrons in its outermost shell

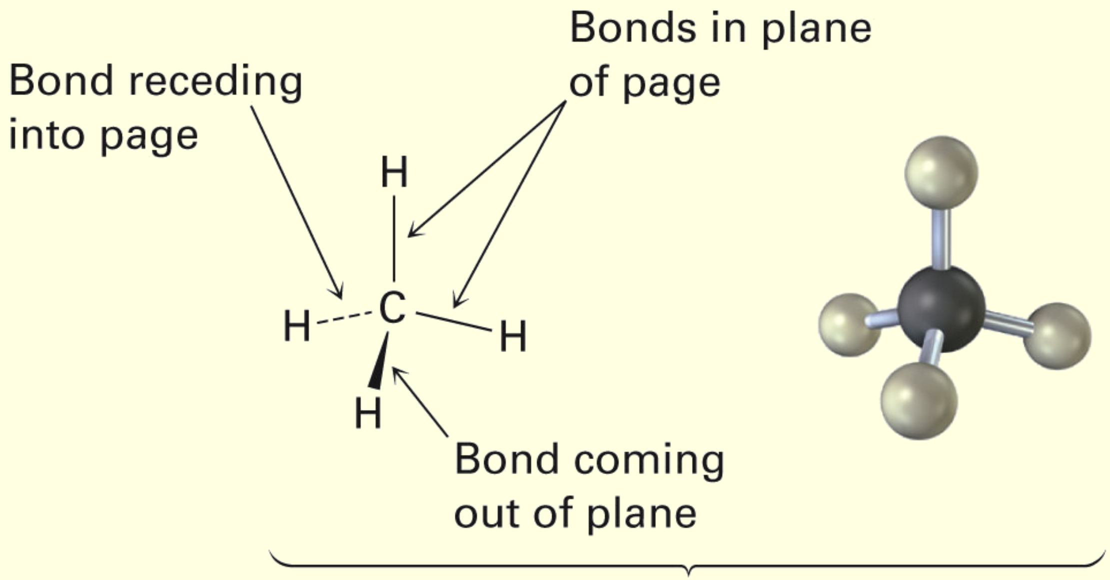
Development of Chemical Bonding Theory

- Kekulé and Couper independently observed that carbon is tetravalent
- Jacobus Van't Hoff and Le Bel proposed that the four bonds of carbon have specific spatial directions
  - Atoms surround carbon at corners of a regular tetrahedron

Figure 1.6 - A Representation of a Tetrahedral Carbon Atom



A regular tetrahedron



A tetrahedral carbon atom

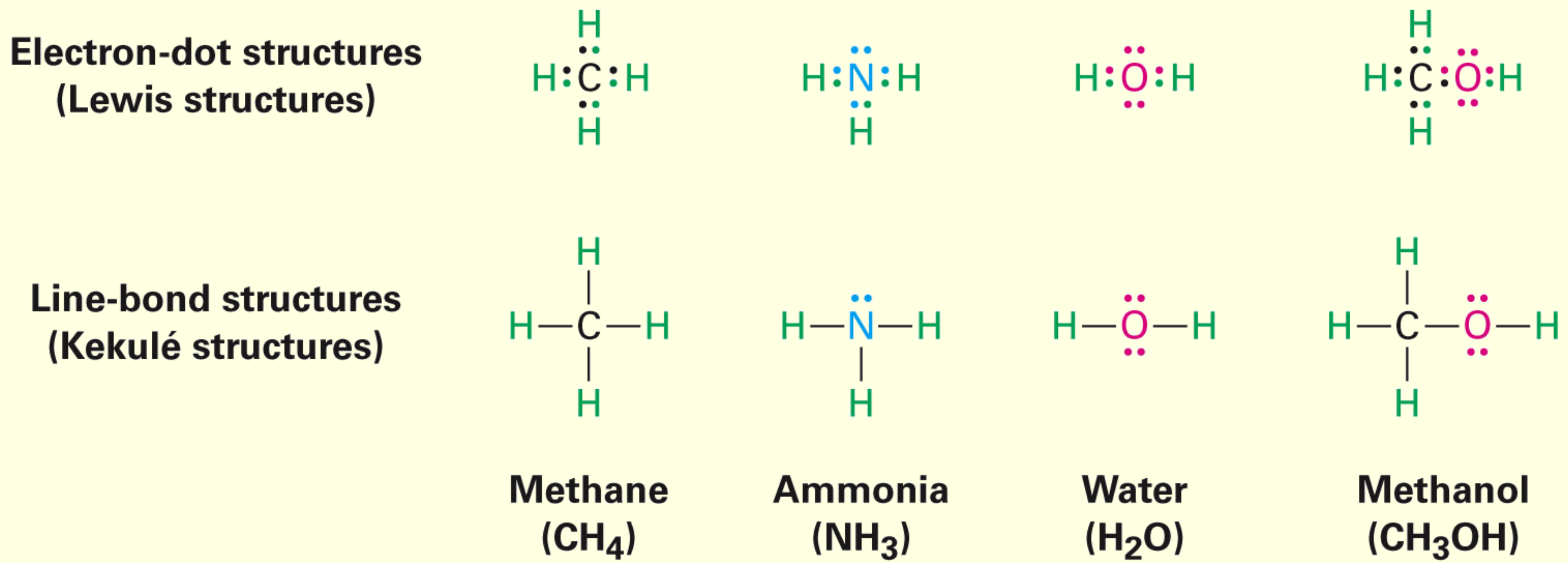
Development of Chemical Bonding Theory

- Atoms form bonds because the resulting compound is more stable than the separate atoms
- **Valence shell**: Atom's outermost shell
  - Impart special stability to the noble gas elements
- Ionic bonds - Ions held together by a electrostatic attraction
  - Formed as a result of electron transfers
- **Covalent bond**: Formed by sharing of electrons
  - Organic compounds have covalent bonds from sharing electrons

Development of Chemical Bonding Theory

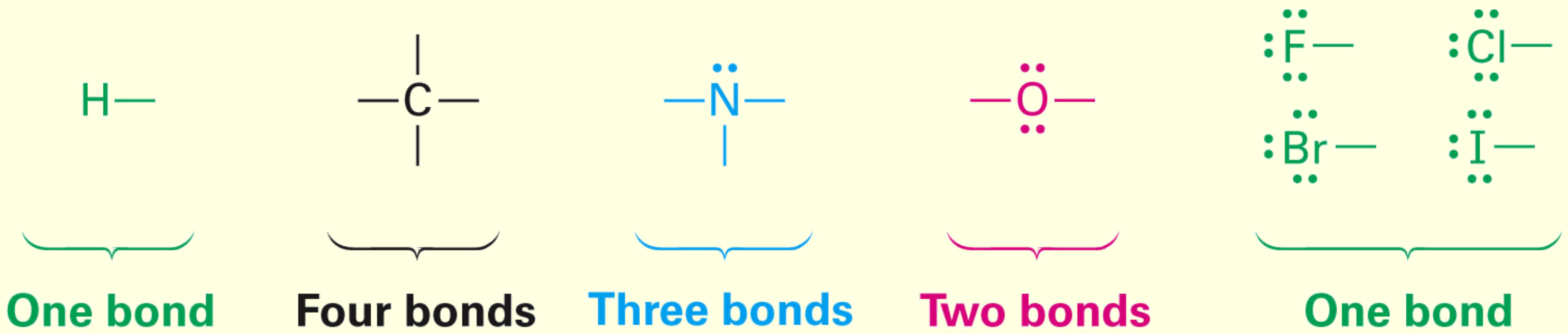
- **Molecule**: Neutral collection of atoms held together by covalent bonds
- **Electron-dot structures**: Represents valence shell electrons of an atom as dots
  - Called Lewis structures
- **Line-bond structures**: Indicates two-electron covalent bond as a line drawn between atoms
  - Called Kekulé structures

Development of Chemical Bonding Theory



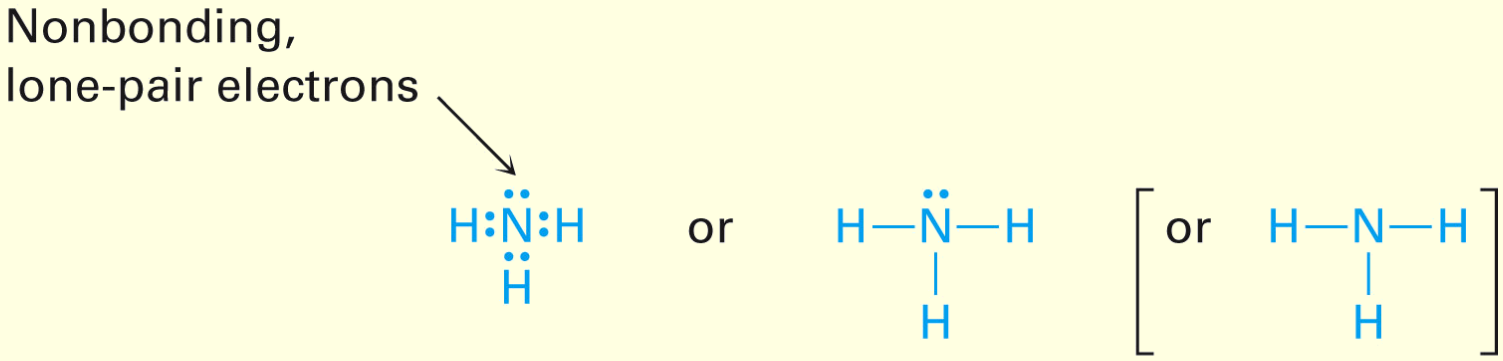
Development of Chemical Bonding Theory

- Number of covalent bonds an atom forms depends on the number of additional valence electrons it needs to reach a stable octet
- Carbon has four valence electrons ($2s^2\ 2p^2$), forming four bonds
- Nitrogen has five valence electrons ($2s^2\ 2p^3$), forming three bonds



Non-Bonding Electrons

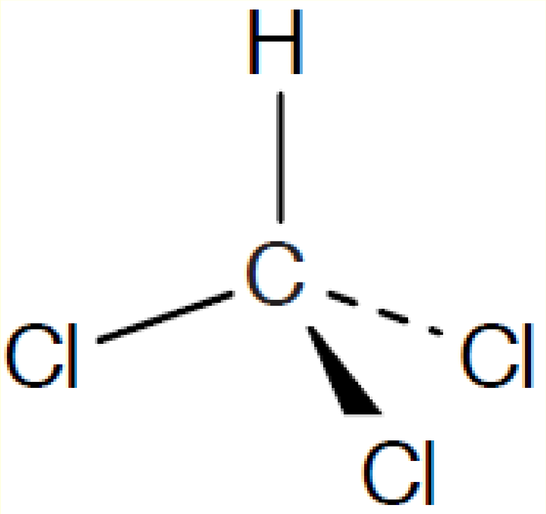
- Lone pair - Valence electrons not used in bonding
- Example
  - Nitrogen atom in ammonia (NH_3)
    - Shares six valence electrons in three covalent bonds
    - Two valence electrons are nonbonding lone pair



Ammonia

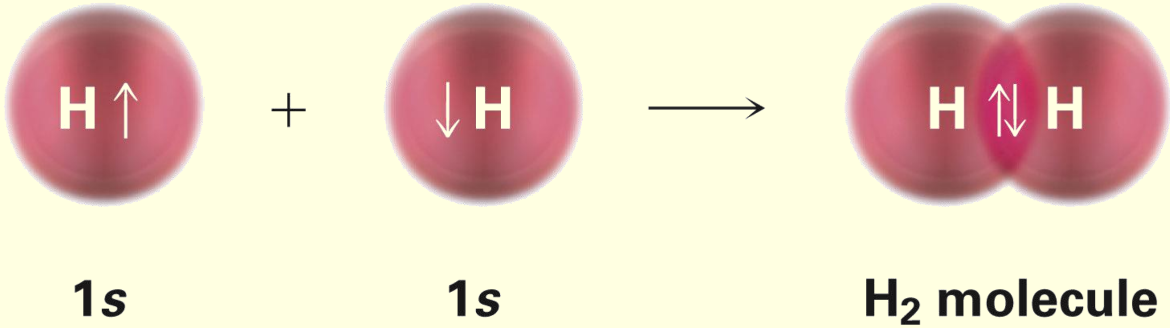
Worked Example

- Draw a molecule of chloroform, $CHCl_3$, using solid, wedged, and dashed lines to show its tetrahedral geometry
- Solution:



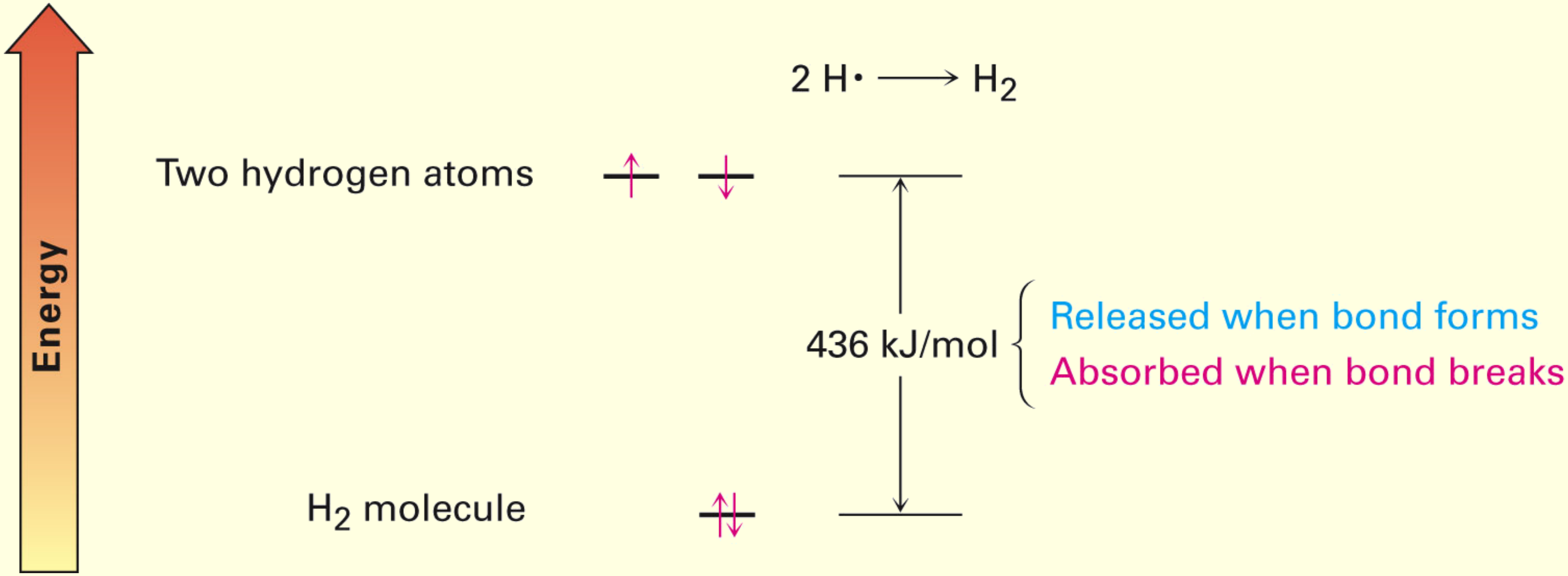
Valence Bond Theory

- 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
  - H–H bond results from the overlap of two singly occupied hydrogen 1s orbitals
  - H–H bond is cylindrically symmetrical, **sigma (σ) bond**



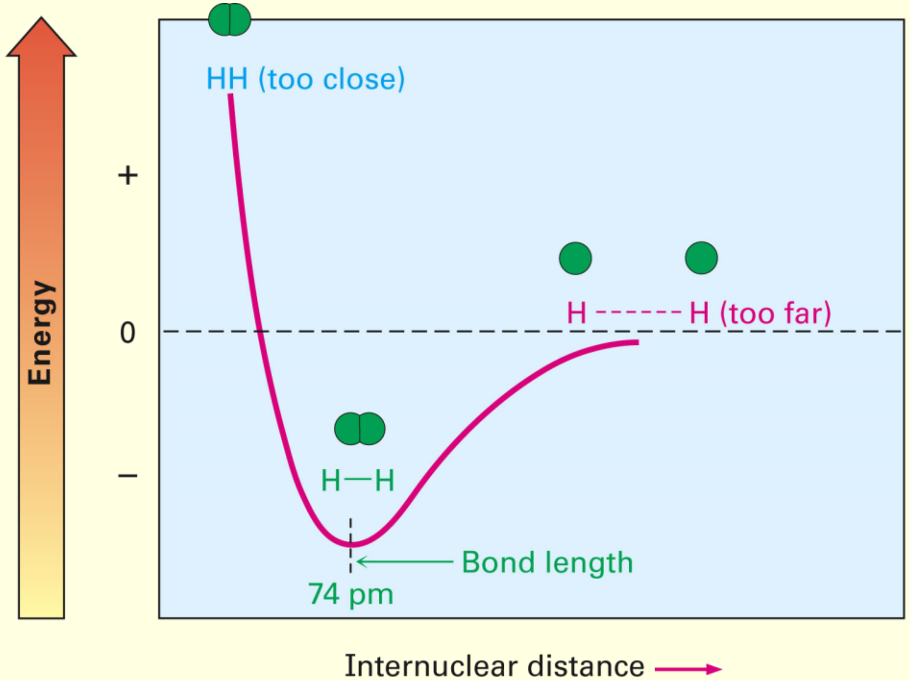
Valence Bond Theory

- Reaction 2 H· → H_2 releases 436 kJ/mol
- H–H has a **bond strength** of 436 kJ/mol (1 kJ = 0.2390 kcal; 1 kcal = 4.184 kJ)



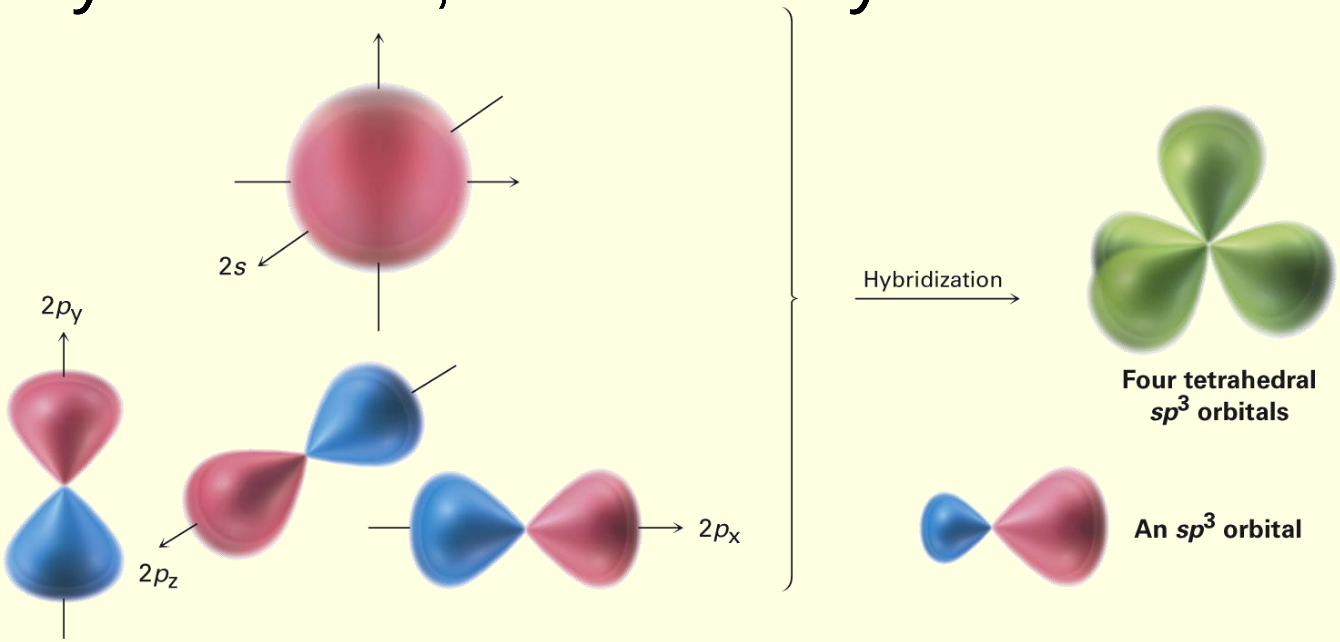
Valence Bond Theory

- **Bond length**: Ideal distance between nuclei that leads to maximum stability
  - If too close, they repel
  - If too far apart, bonding is weak



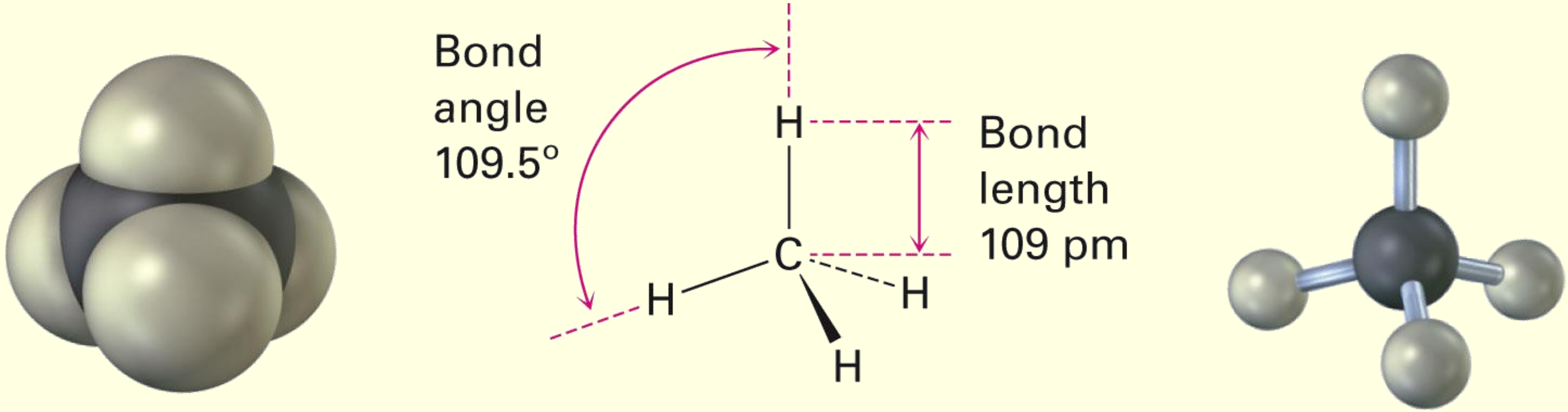
sp^3 Orbitals and the Structure of Methane

- 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, tetrahedrally oriented orbitals



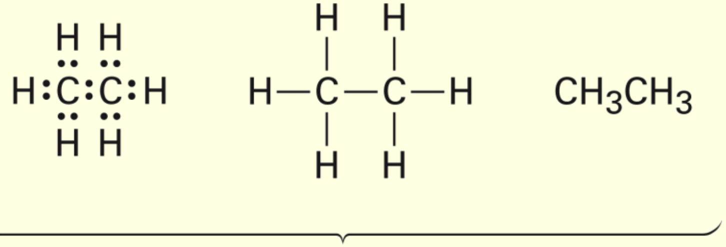
sp^3 Orbitals and the Structure of Methane

- sp^3 orbitals in a C atom overlap with 1*s* orbitals of an H atom to form four identical C–H bonds
- Each C–H bond has a strength of 439 kJ/mol and a length of 109 pm
- **Bond angle**: Formed between two adjacent bonds



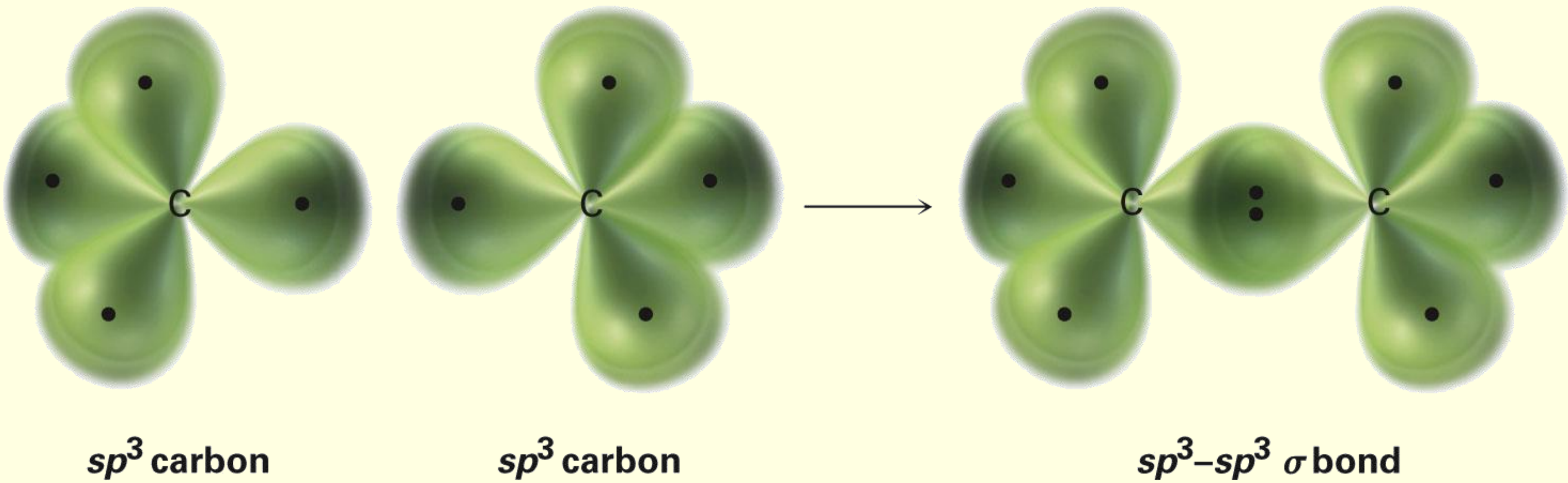
sp^3 Orbitals and the Structure of Ethane

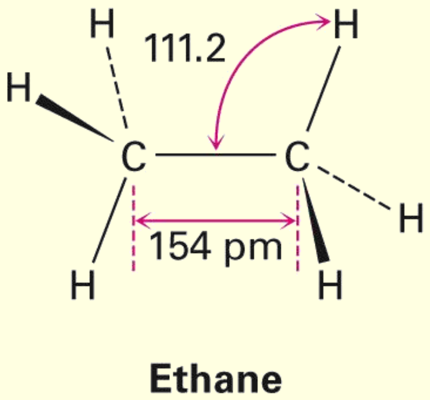
- Two C's bond to each other by σ overlap of an sp^3 orbital from each
- Three sp^3 orbitals on each C overlap with H 1*s* orbitals to form six C–H bonds
  - C–H bond strength in ethane is 421 kJ/mol
  - C–C bond is 154 pm long and strength is 377 kJ/mol
- Bond angles of ethane are tetrahedral

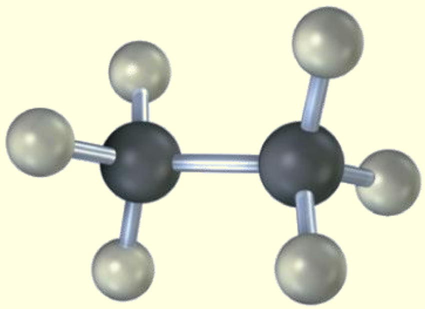


Some representations of ethane

Figure 1.12 - The Structure of Ethane

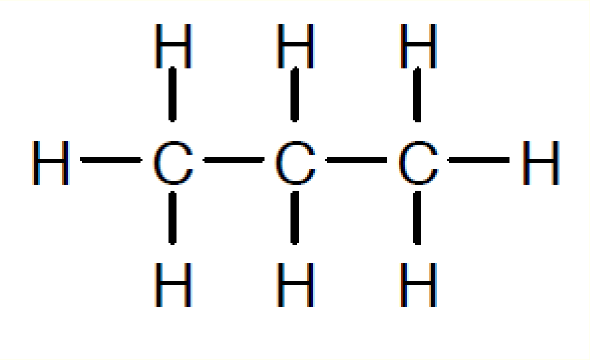


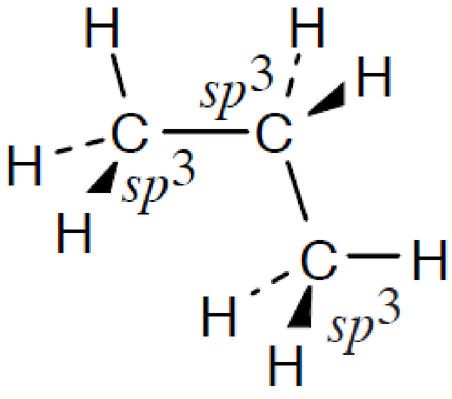




Worked Example

- Draw a line-bond structure for propane, $CH_3CH_2CH_3$
  - Predict the value of each bond angle, and indicate the overall shape of the molecule
- Solution:

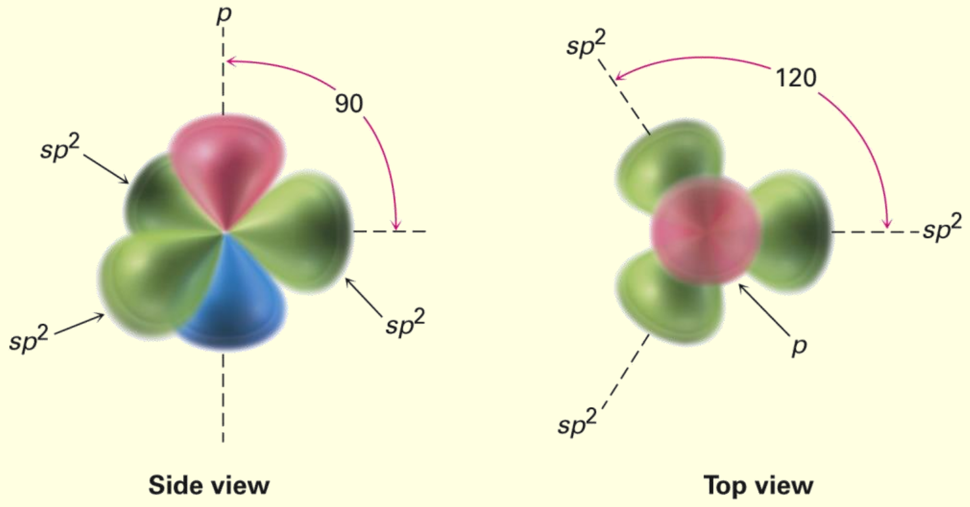




- Geometry - Tetrahedral
- Bond angles - 109° (approximately)

sp^2 Orbitals and the Structure of Ethylene

- **sp^2 hybrid orbitals**: Derived by combination of an *s* atomic orbital with two *p* atomic orbitals
- sp^2 orbitals are in a plane with an angle of 120° from each other
- Remaining *p* orbital is perpendicular to the plane

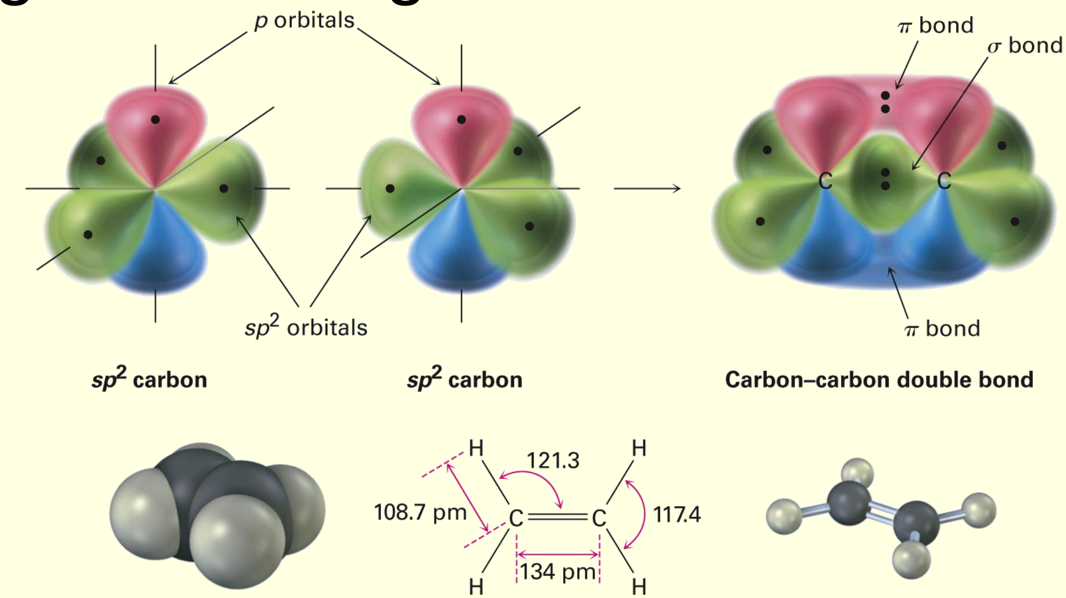


sp^2 Orbitals and the Structure of Ethylene

- Two *sp*^{2} hybridized orbitals overlap to form a σ bond
- *p* orbitals interact by sideways overlap to form a **pi (π) bond**
- *sp*^{2}–*sp*^{2} σ bond and 2*p*–2*p* 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 on either side of a line between nuclei

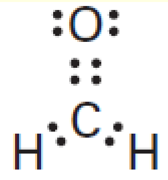
Structure of Ethylene

- H atoms form *s* bonds with four sp^2 orbitals
- H–C–H and H–C–C form bond angles of about 120°
- C–C double bond in ethylene is shorter and stronger than single bond in ethane

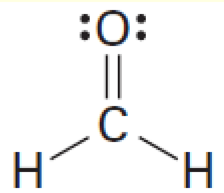


Worked Example

- Draw electron-dot and line-bond structures of formaldehyde
  - Indicate the hybridization of the carbon orbitals
- Solution:
  - Two hydrogens, one carbon, and one oxygen can combine in one way



Electron-dot structure



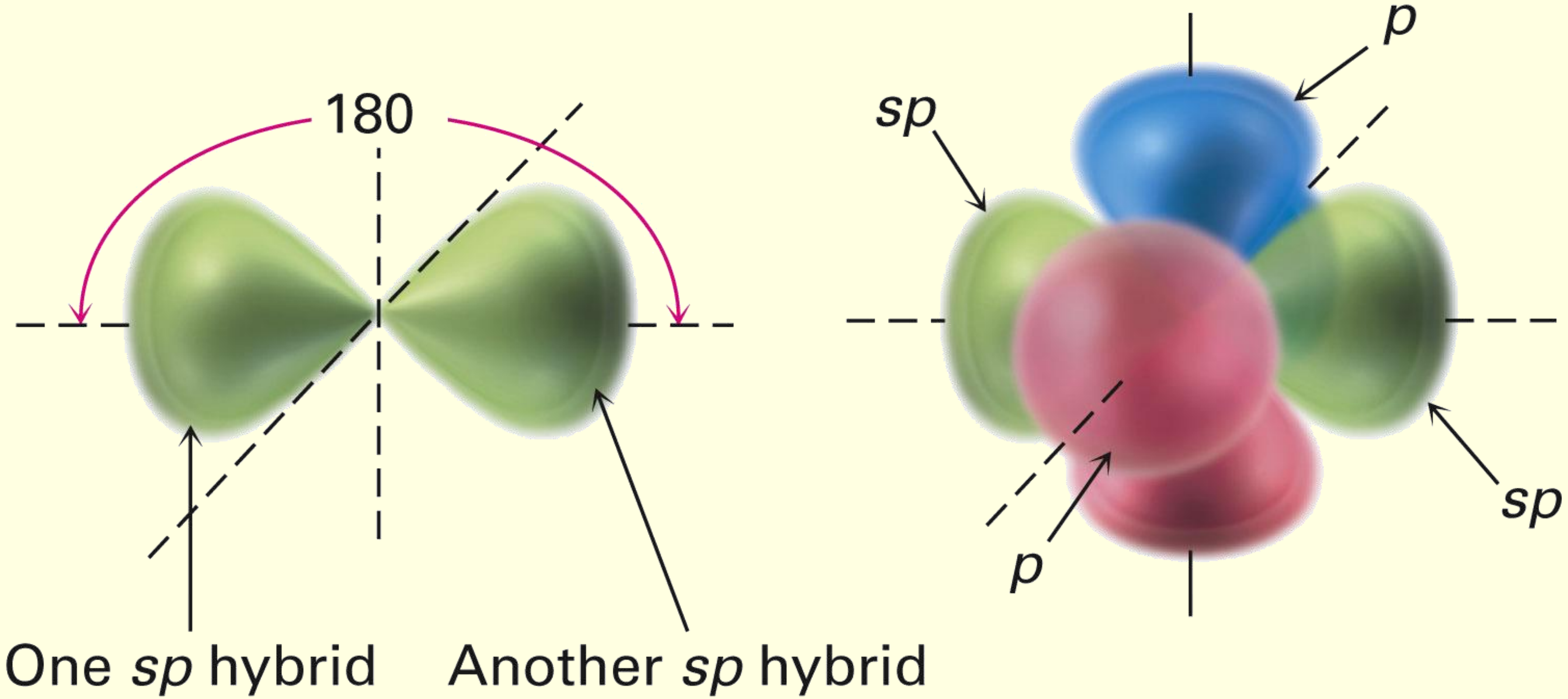
Line-bond structure

  - The orbitals are *sp*^{2}-hybridized

sp Orbitals and the Structure of Acetylene

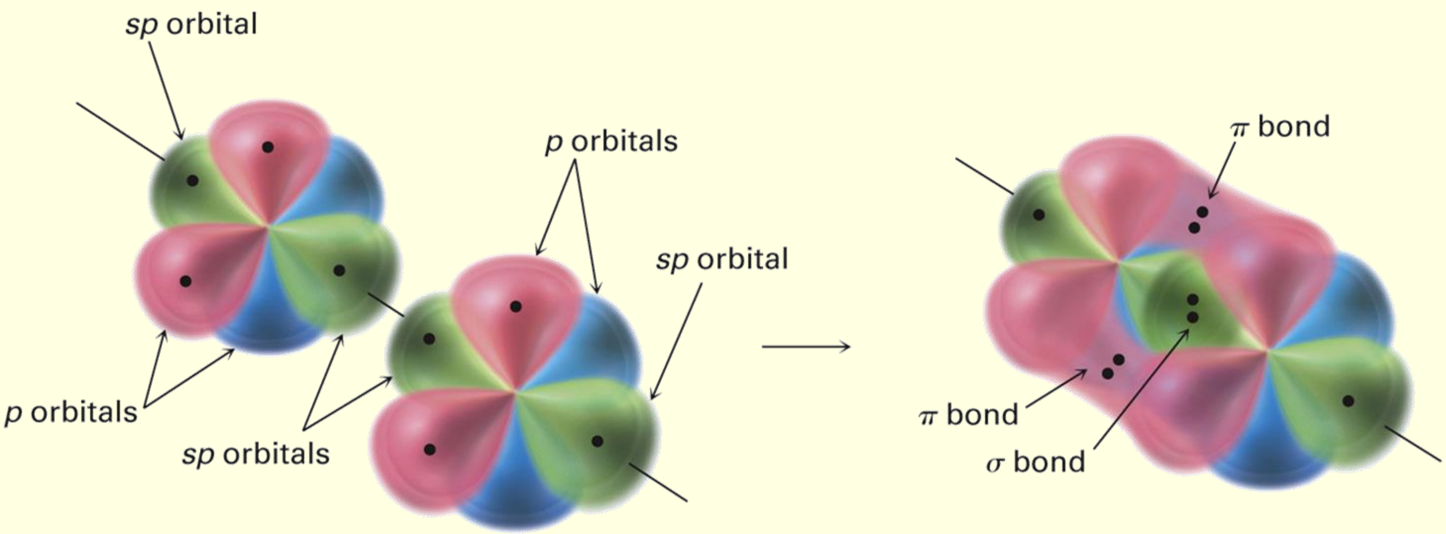
- Carbon can form a triple bond sharing six electrons
- Carbon 2s orbital hybridizes with a single *p* orbital giving two ***sp* hybrids**
  - Two p orbitals remain unchanged
- *sp* orbitals are linear, 180° apart on x-axis
- Two *p* orbitals are perpendicular on the y-axis and the z-axis

Figure 1.15 - *sp* Hybridization



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
  - p_y orbitals overlap to form p_y–p_y π bond



Carbon–carbon triple bond

Bonding in Acetylene

- Sharing of six electrons forms C≡C
- Two *sp* orbitals form σ bonds with hydrogens
- Shortest and strongest carbon–carbon bond

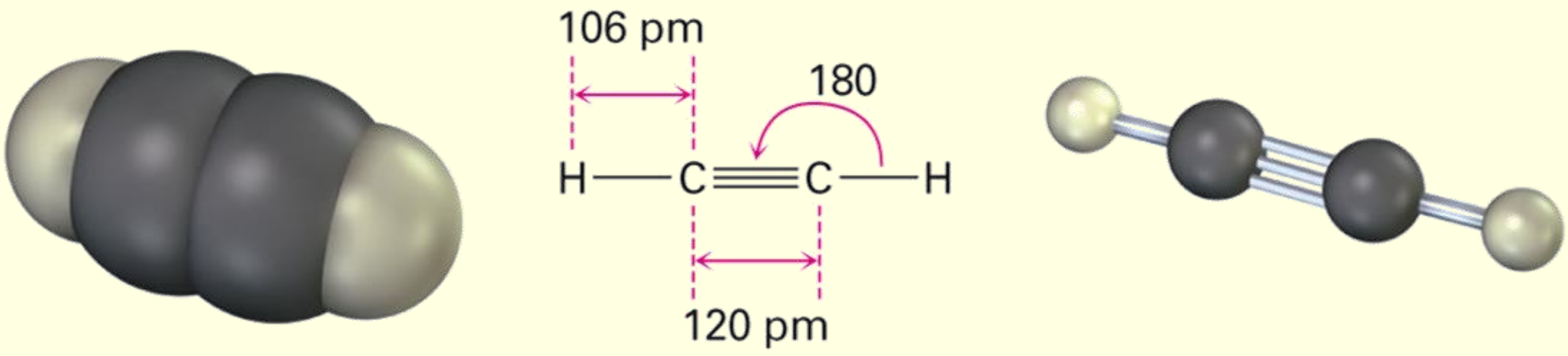
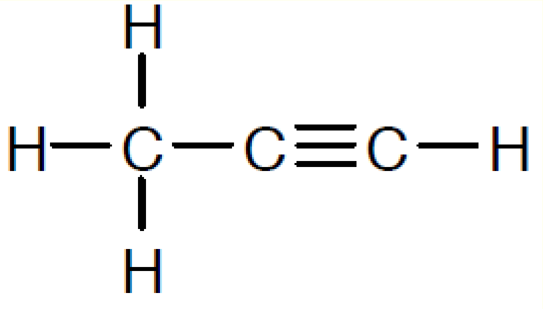


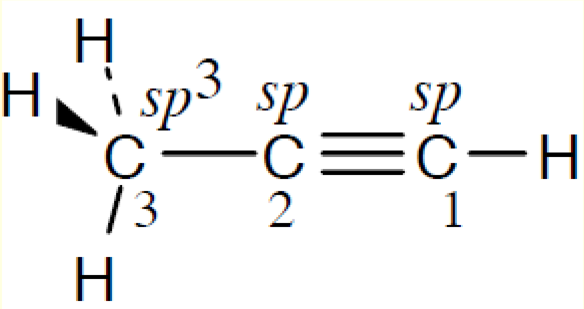
Table 1.2 - Comparison of C–C and C–H Bonds in Methane, Ethane, Ethylene, and Acetylene

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, $HC{\equiv}CH$	(sp) C≡C (sp)	965	231	120
	(sp) C—H	558	133	106

Worked Example

- Draw a line-bond structure for propyne, $CH_3C{\equiv}CH$
  - Indicate the hybridization of the orbitals on each carbon
  - Predict a value for each bond angle
- Solution:





Worked Example

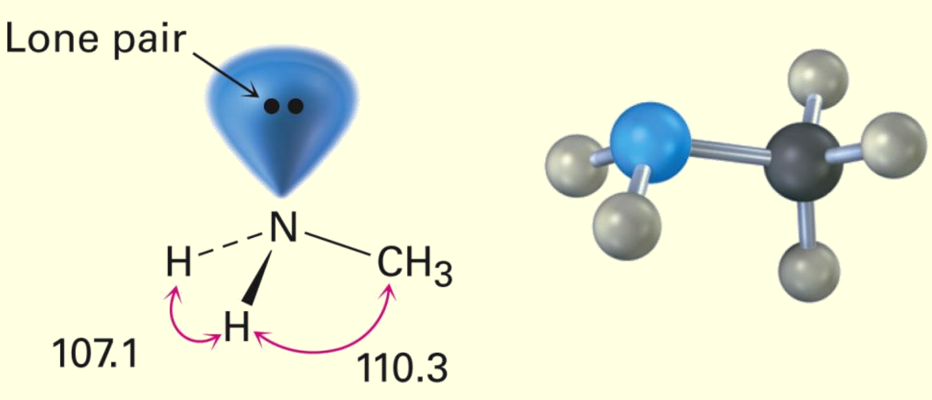
- C3-H bonds are σ bonds
  - Overlap of an *sp*^{3} orbital of carbon
  - 3 with *s* orbital of hydrogen
- C1-H bond is a σ bond
  - Overlap of an *sp* orbital of carbon
  - 1 with an *s* orbital of hydrogen
- C2-C3 bond is a σ bond
  - Overlap of an *sp* orbital of carbon
  - 2 with an *sp*^{3} orbital of carbon 3
- Three C1-C2 bonds

Worked Example

- Bond angle
  - Between three carbon atoms is 180˚
  - H–C1≡C2 is 180˚
  - Between hydrogen and the sp^3-hybridized carbon is 109˚

Hybridization of Nitrogen, Oxygen, Phosphorus, and Sulfur

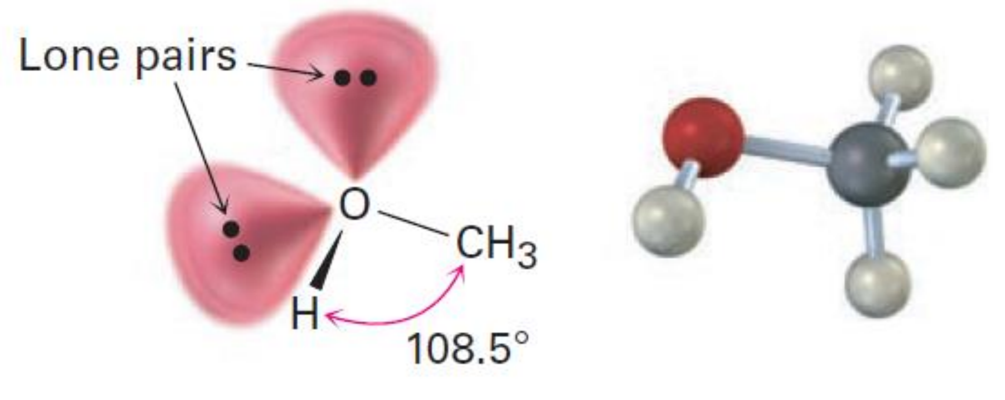
- H–N–H bond angle in methylamine 107.1°
- C–N–H bond angle is 110.3°
- N's orbitals hybridize to form four sp^3 orbitals
- One sp^3 orbital is occupied by two nonbonding electrons, and three sp^3 orbitals have one electron each



Methylamine

Hybridization of Nitrogen, Oxygen, Phosphorus, and Sulfur

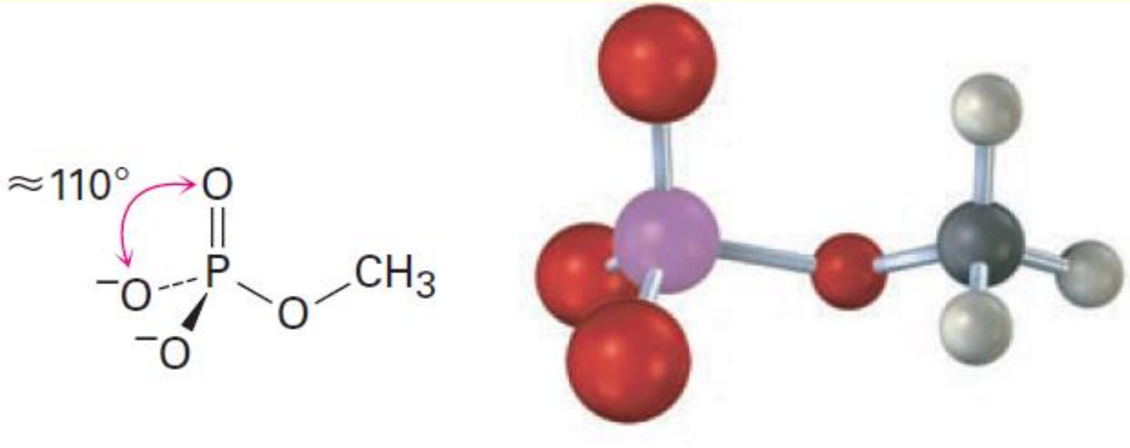
- Oxygen atom in methanol can be described as *sp*^{3}-hybridized
- C–O–H bond angle in methanol is 108.5
- Two *sp*^{3} hybrid orbitals on oxygen are occupied by nonbonding electron lone pairs



Methanol (methyl alcohol)

Hybridization of Nitrogen, Oxygen, Phosphorus, and Sulfur

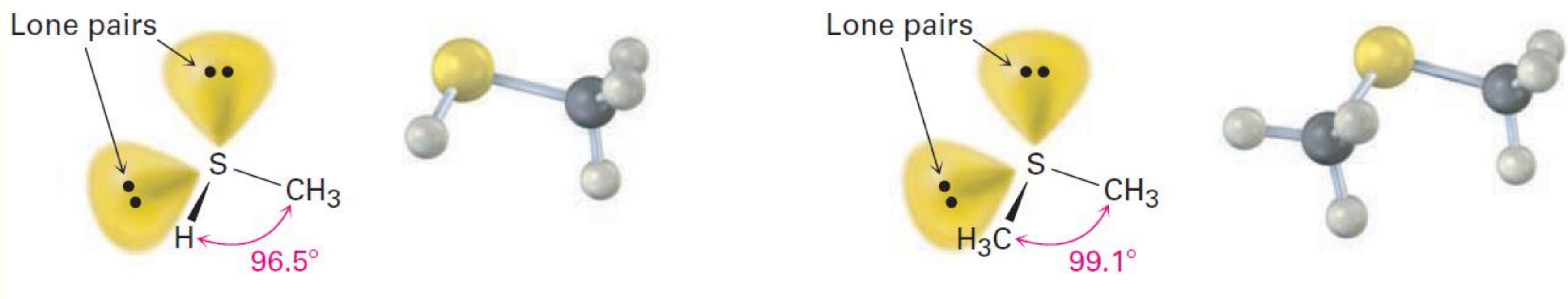
- Methyl phosphate, $CH_3OPO_3^{2-}$
- O–P–O bond angle is approximately 110 ° to 112°
  - Implies *sp*^{3} hybridization in the phosphorus orbitals



Methyl phosphate (an organophosphate)

Hybridization of Nitrogen, Oxygen, Phosphorus, and Sulfur

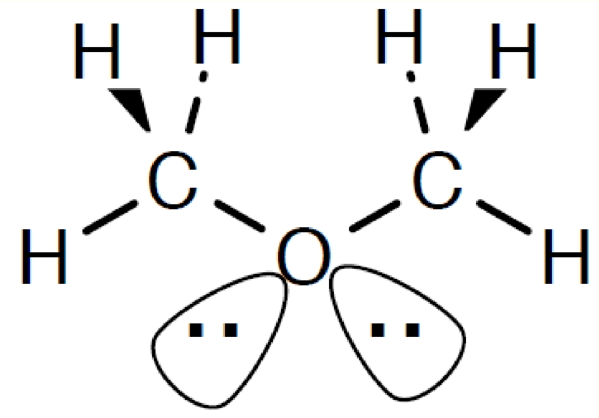
- Dimethyl sulfide [$(CH_3)_2S$] is the simplest example of a sulfide
- Described by approximate *sp*^{3} hybridization around sulfur
- Have significant deviation from the tetrahedral angle



Methanethiol   Dimethyl sulfide

Worked Example

- Identify all nonbonding lone pairs of electrons in the oxygen atom in dimethyl ether, $CH_3–O–CH_3$
  - What is its expected geometry
- Solution:

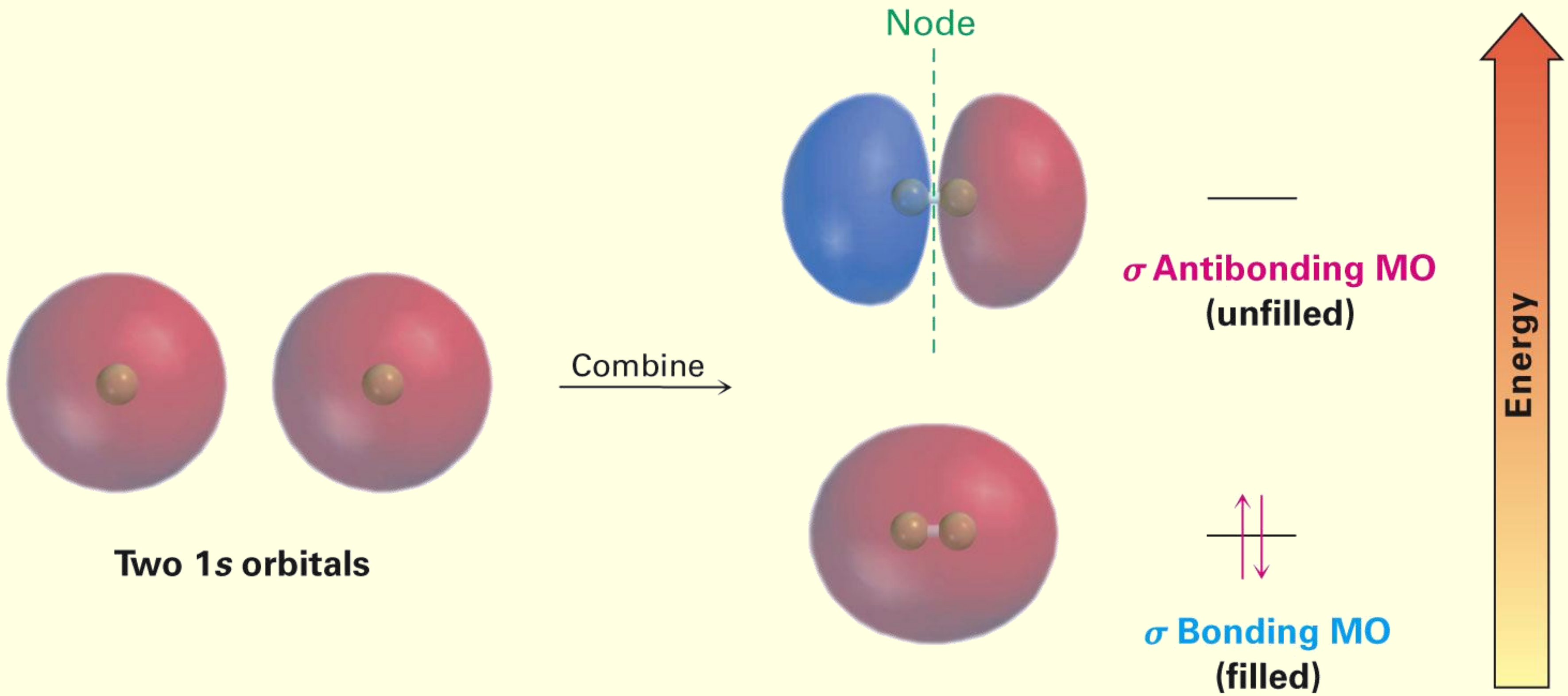


- The sp^3-hybridized oxygen atom has tetrahedral geometry

Molecular Orbital (MO) Theory

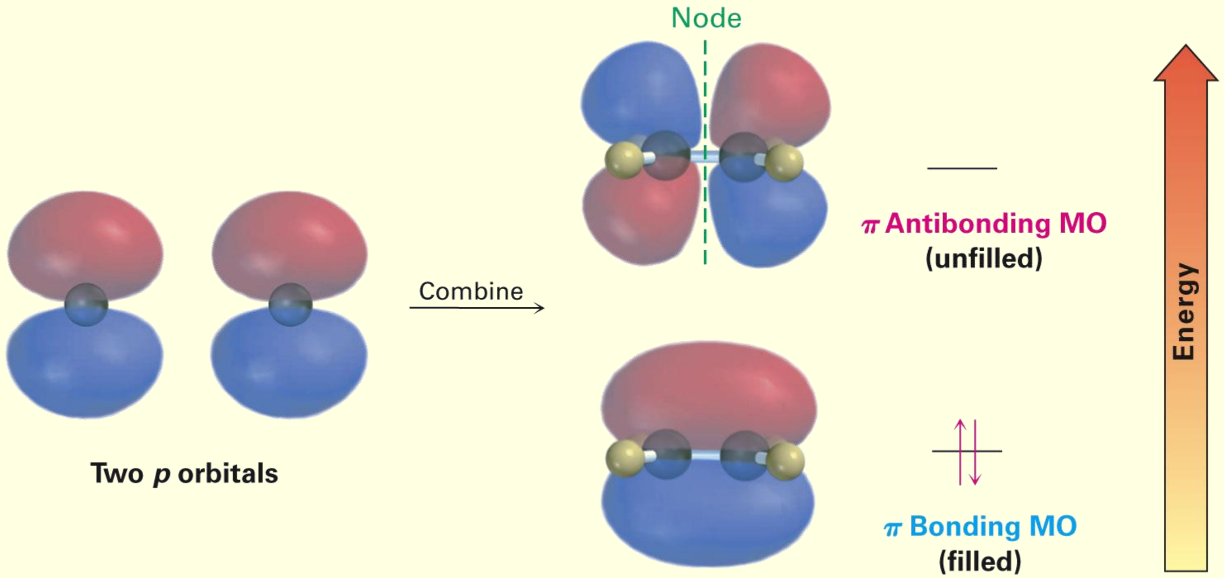
- Description of covalent bond formation as resulting from a mathematical combination of atomic orbitals to form molecular orbitals
- **Bonding MO**: Molecular orbital that is lower in energy than the atomic orbitals from which it is formed
- **Antibonding MO**: Molecular orbital that is higher in energy than the atomic orbitals from which it is formed

Figure 1.17 - Molecular Orbitals of H_2



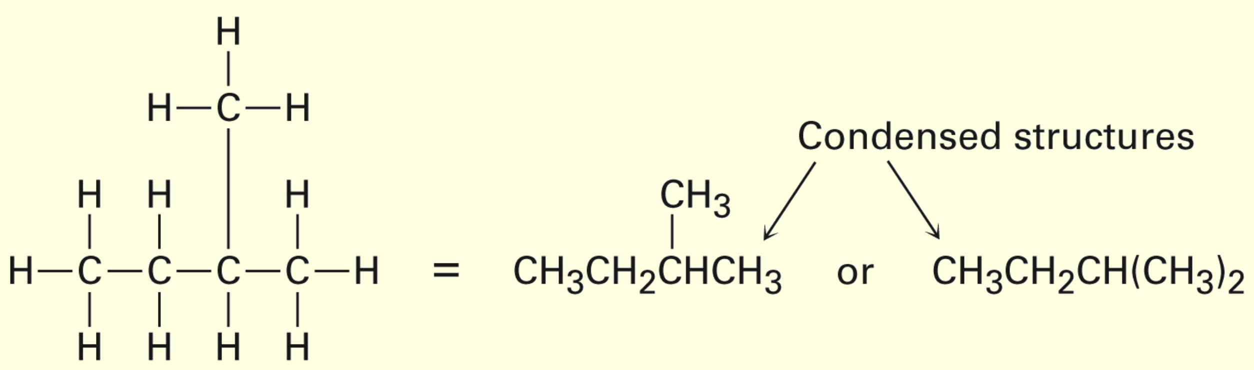
Molecular Orbital Theory

- 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



Drawing Chemical Structures

- Several shorthand methods have been developed to write structures
- **Condensed structures**: C-H or C-C single bonds are not shown, they are understood
- Example

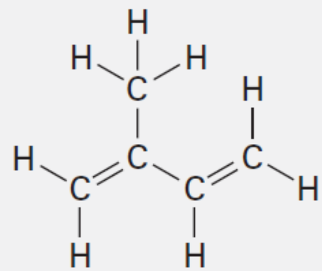
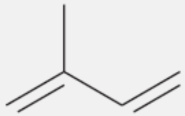
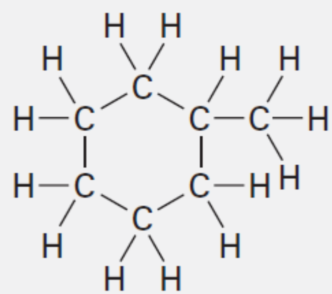
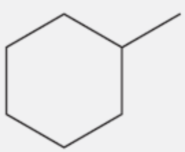
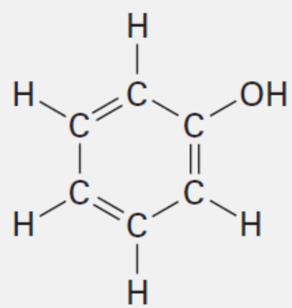
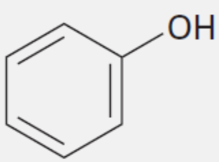


2-Methylbutane

Rules for Drawing Skeletal Structures

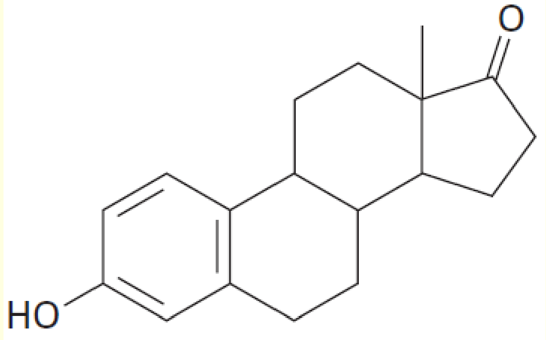
- Carbon atoms aren't usually shown
- Carbon atom is assumed to be at each intersection of two lines (bonds) and at the end of each line
- Hydrogen atoms bonded to carbon aren't shown
- Atoms other than carbon and hydrogen are shown

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		

Worked Example

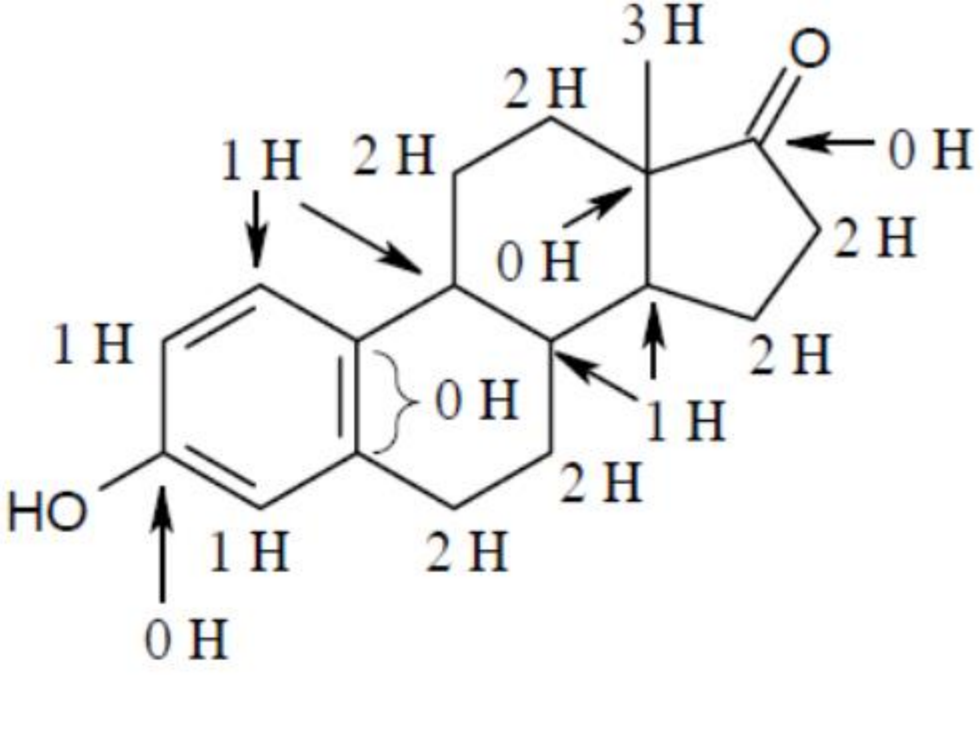
- How many hydrogens are bonded to each carbon in the following compound
  - Give the molecular formula of each substance



Estrone (a hormone)

Worked Example

- Solution:



Estrone – $C_{18}H_{22}O_2$

Summary

- Organic chemistry - Study of carbon compounds
- Atom: Charged nucleus containing positively charged protons and neutrally charged neutrons surrounded by negatively charged electrons
- Electronic structure of an atom is described by wave equation
  - Different orbitals have different energy levels and different shapes
    - *s* orbitals are spherical, *p* orbitals are dumbbell-shaped

Summary

- Covalent bonds - Electron pair is shared between atoms
- Valence bond theory - Electron sharing occurs by the overlapping 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

- Sigma (σ) bonds - Circular cross-section and are formed by head-on interaction
- Pi (π) bonds - Formed by 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

Summary

- 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
    - Nitrogen atom in ammonia and the oxygen atom in water are *sp*^{3}-hybridized
- Structures in which carbon–carbon and carbon–hydrogen bonds aren’t shown are called condensed structures