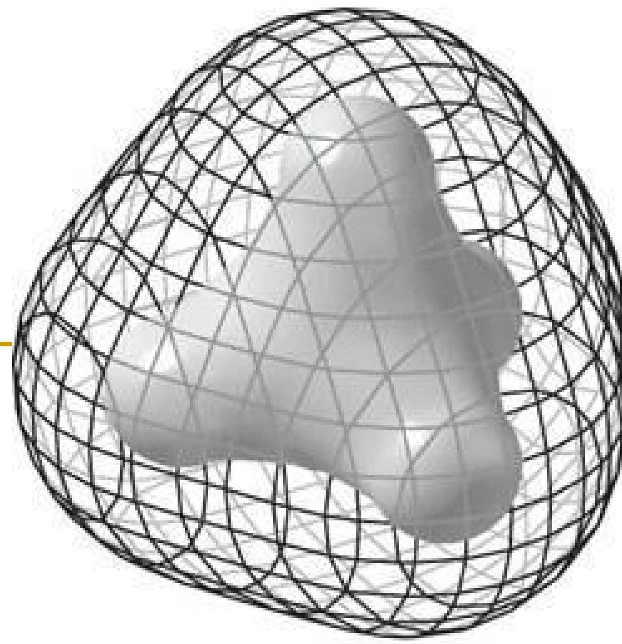
1.14 the orbital view of bonding:

The sigma bond



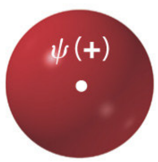
A limitation of Lewis Theory of Bonding

- It does not explain the three dimensional geometries of molecules!

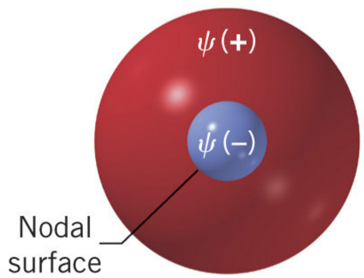
Molecular Orbital Theory (MO)

- 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

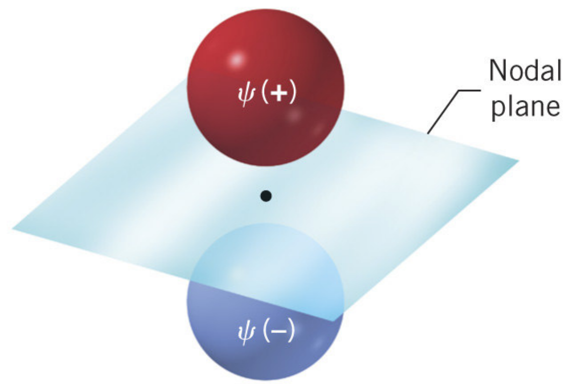
- 1*s* and 2*s* orbitals are spheres centered around the nucleus
  - Each orbital can accommodate 2 electrons
  - The 2*s* orbital is higher in energy and contains a nodal surface (probability of finding electrons = 0) in its center
- Each 2*p* orbital has two nearly touching spheres (or lobes)
  - One 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 (orthoganol) 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*



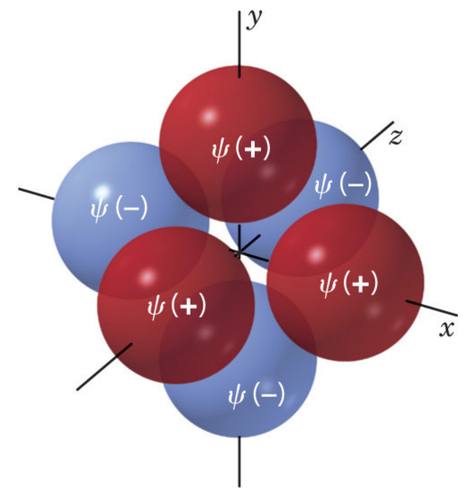
1s Orbital



2s Orbital

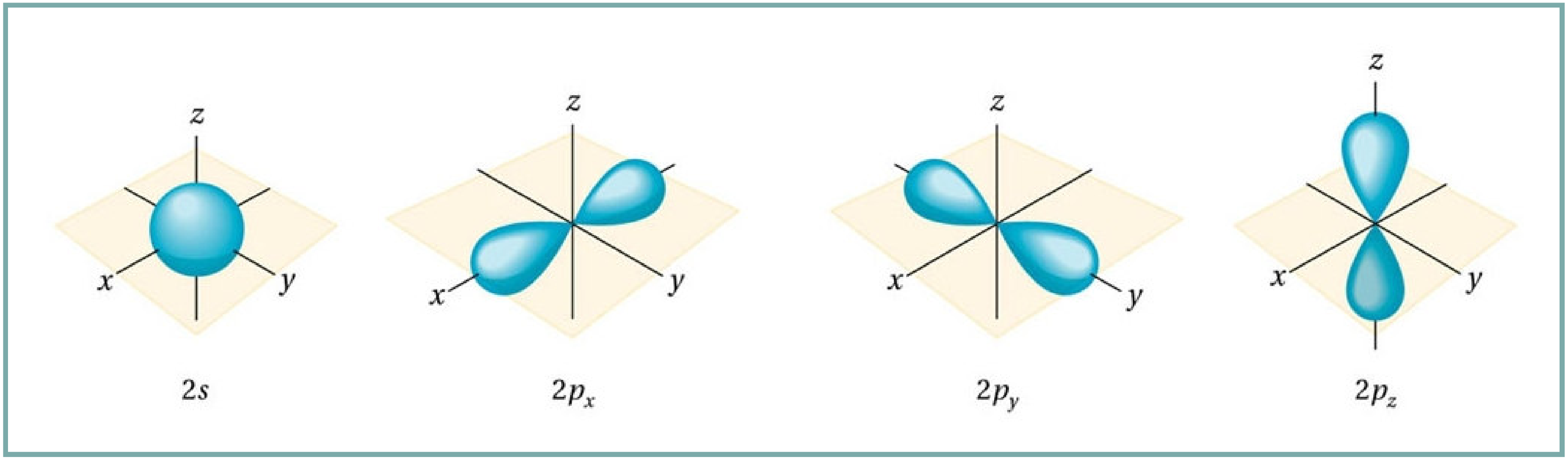


A pure 2p orbital (unhybridized)



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

Figure 1.2 Shapes of the *s* and *p* orbitals used by valence electrons of a carbon



- As two atoms approach each other their atomic orbitals (AOs) overlap to become molecular orbitals (MOs)
- The number of MOs that result must always equal the number of AOs used

- Example: H_2 molecule
  - As the hydrogen atoms approach each other their 1*s* orbitals begin to overlap
  - The MOs that form encompass both nuclei
  - The electrons are not restricted to the vicinity of one nucleus or another
  - Each MO has a maximum of 2 spin-paired electrons
- The two electrons between the nuclei serve to attract the nuclei towards each other (covalent bond)

The sigma bond

- A sigma (σ) orbital lies along the axis between two bonded atoms; a pair of electrons in a sigma orbital is called a sigma bond.

Figure 1.3 The molecular orbital representation of covalent bond formation

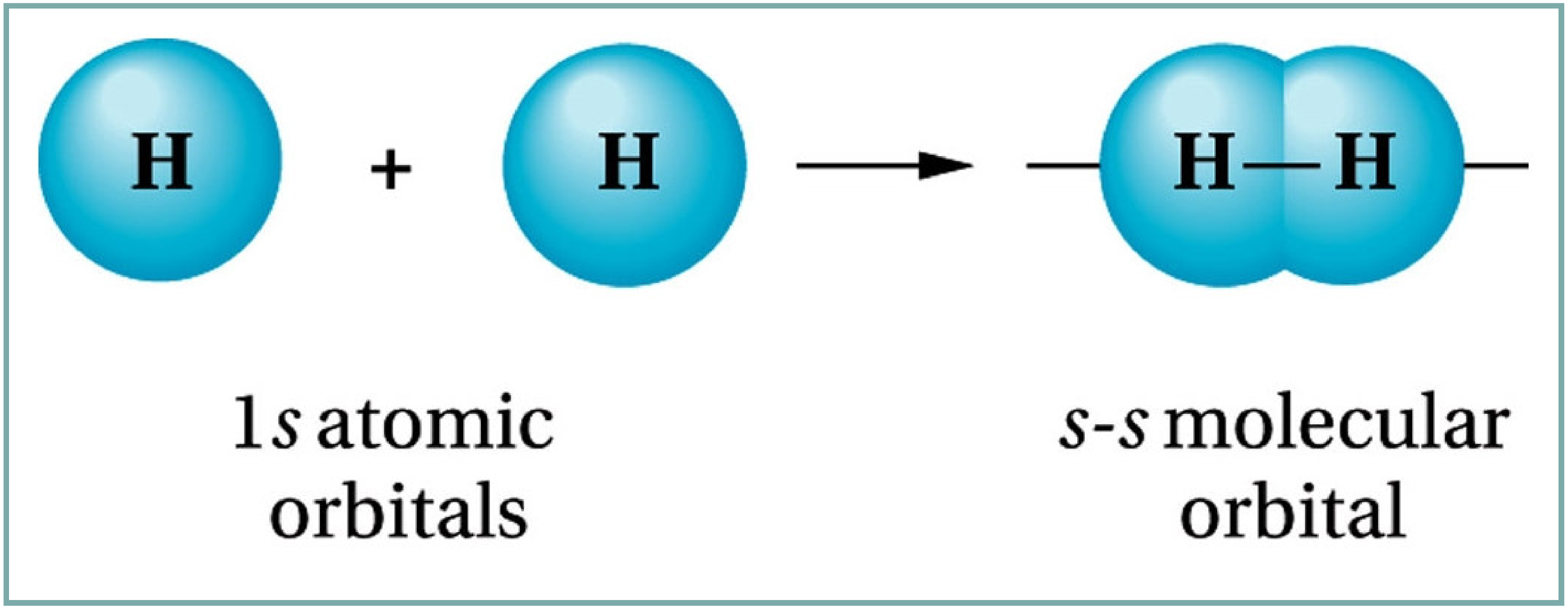
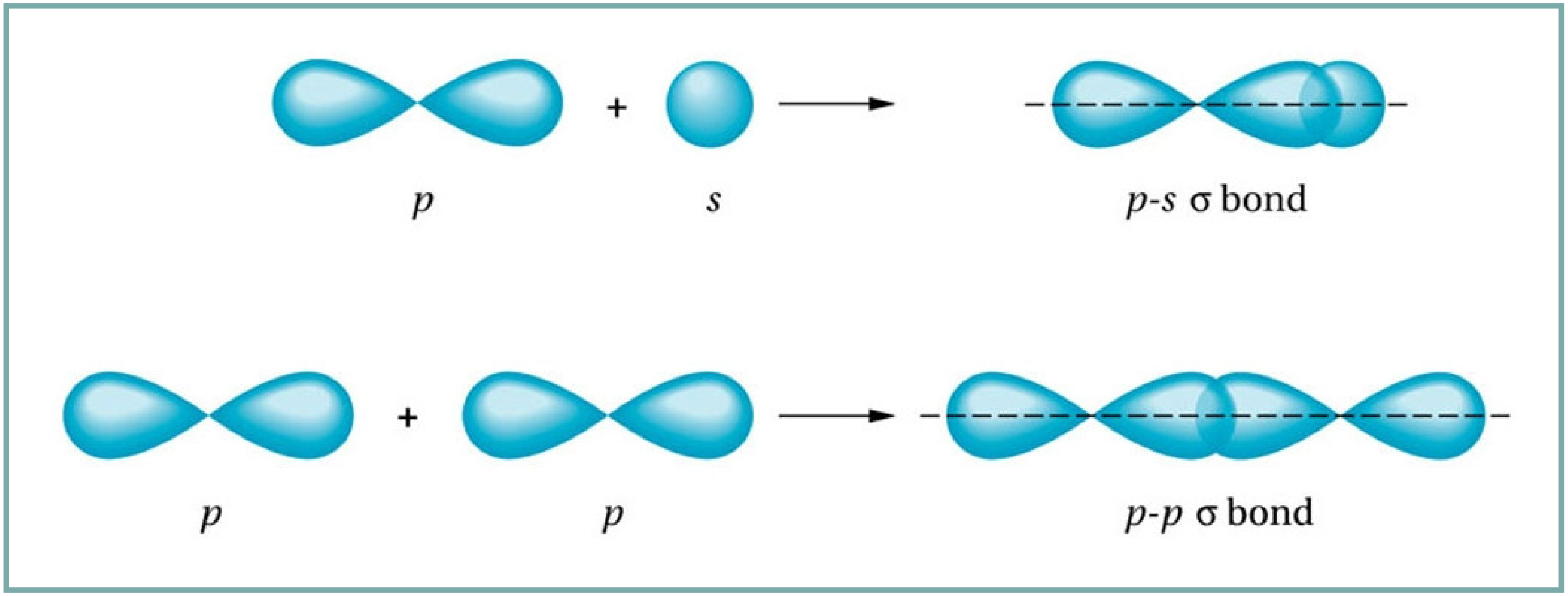
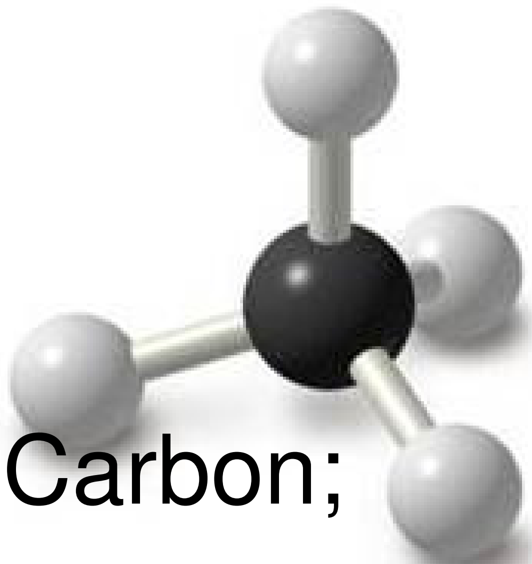


Figure 1.4 Orbital overlap to form σ bonds



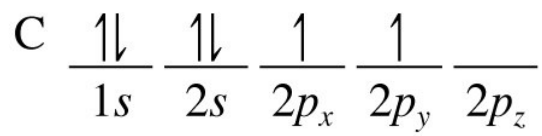
1.15 Carbon *sp*^{3} Hybrid Orbitals



1.16 Tetrahedral Carbon; the Bonding in Methane

The Structure of Methane and Ethane: sp^3 Hybridization

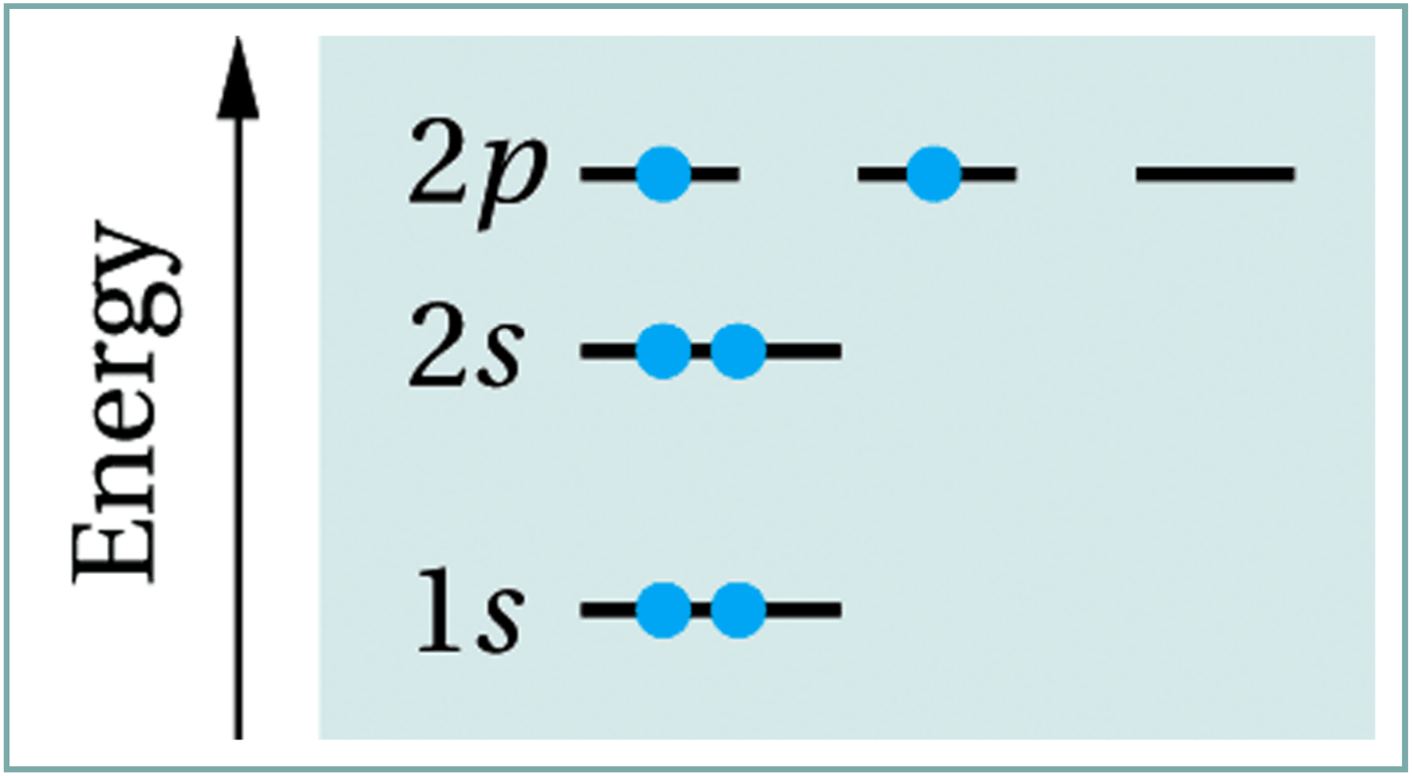
- The structure of methane with its four identical tetrahedral bonds cannot be adequately explained using the electronic configuration of carbon



Ground state of a carbon atom

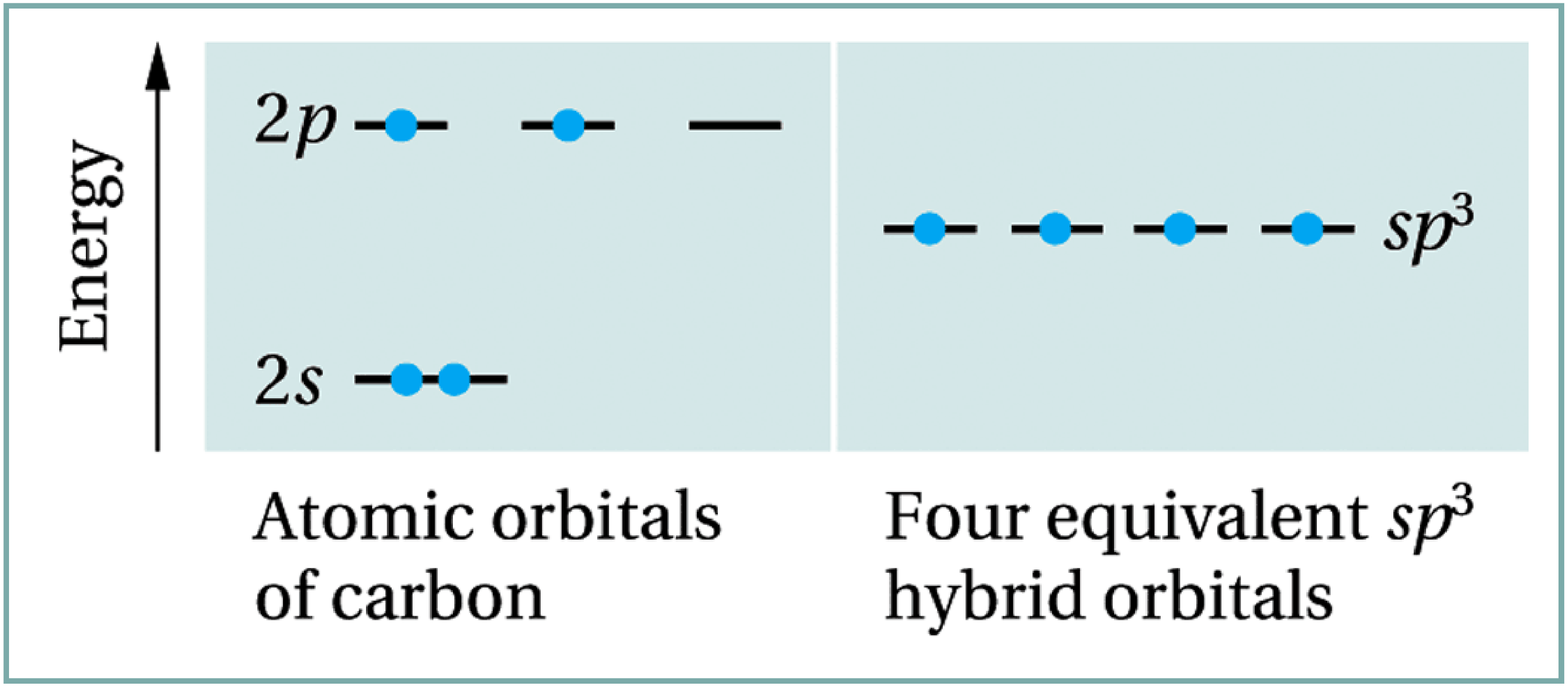
- Hybridization of the valence orbitals (2*s* and 2*p*) provides four new identical orbitals which can be used for the bonding in methane
- *Orbital hybridization* is a mathematical combination of the 2*s* and 2*p* wave functions to obtain wave functions for the new orbitals

Figure 1.5 Distribution of the six electrons in a carbon atom



- 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
- The four sp^3 orbitals are then combined with the 1*s* orbitals of four hydrogens to give the molecular orbitals of methane
- Each new molecular orbital can accommodate 2 electrons

Figure 1.6 Unhybridized vs *sp*^{3} hybridized orbitals on carbon



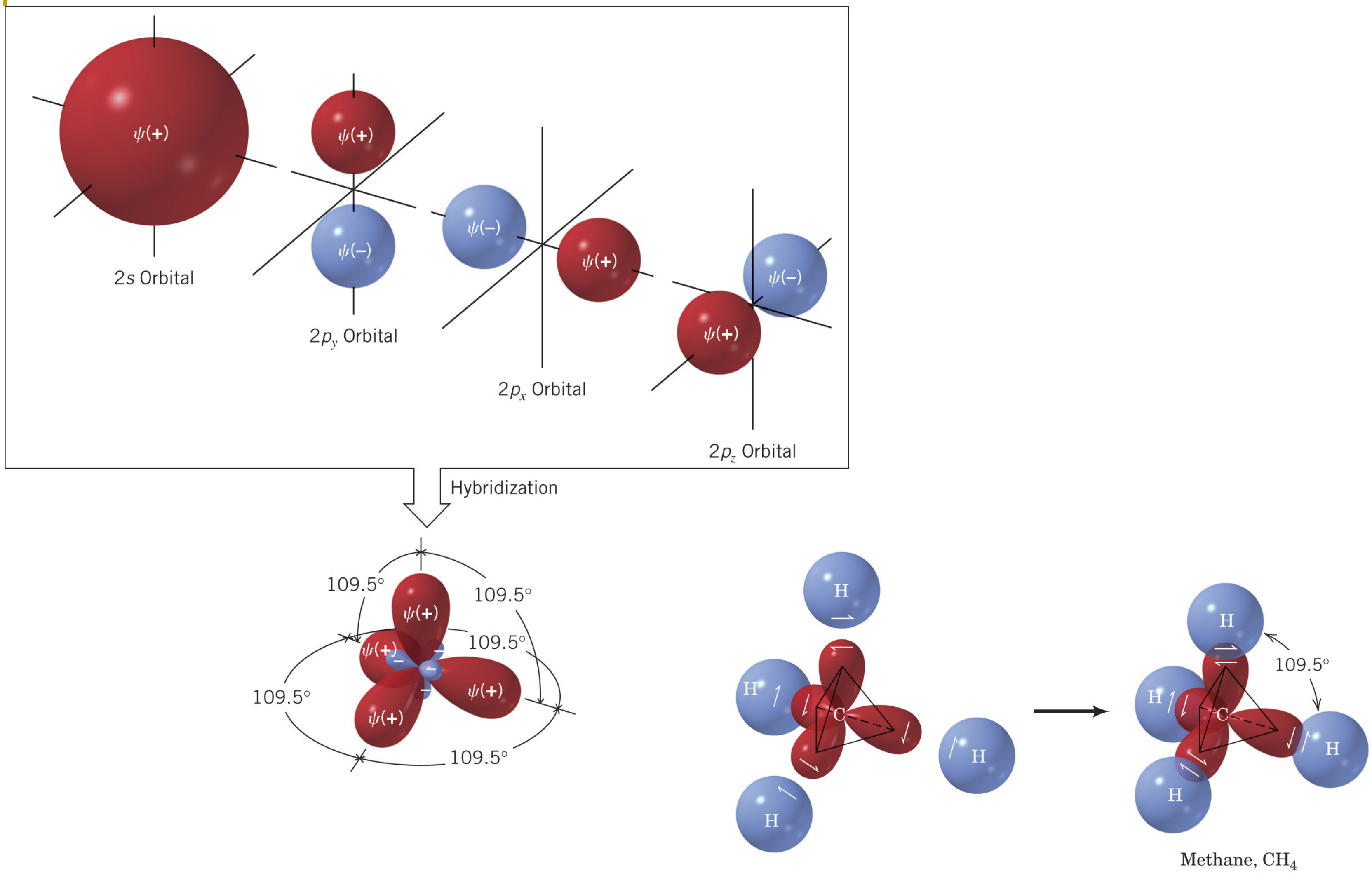
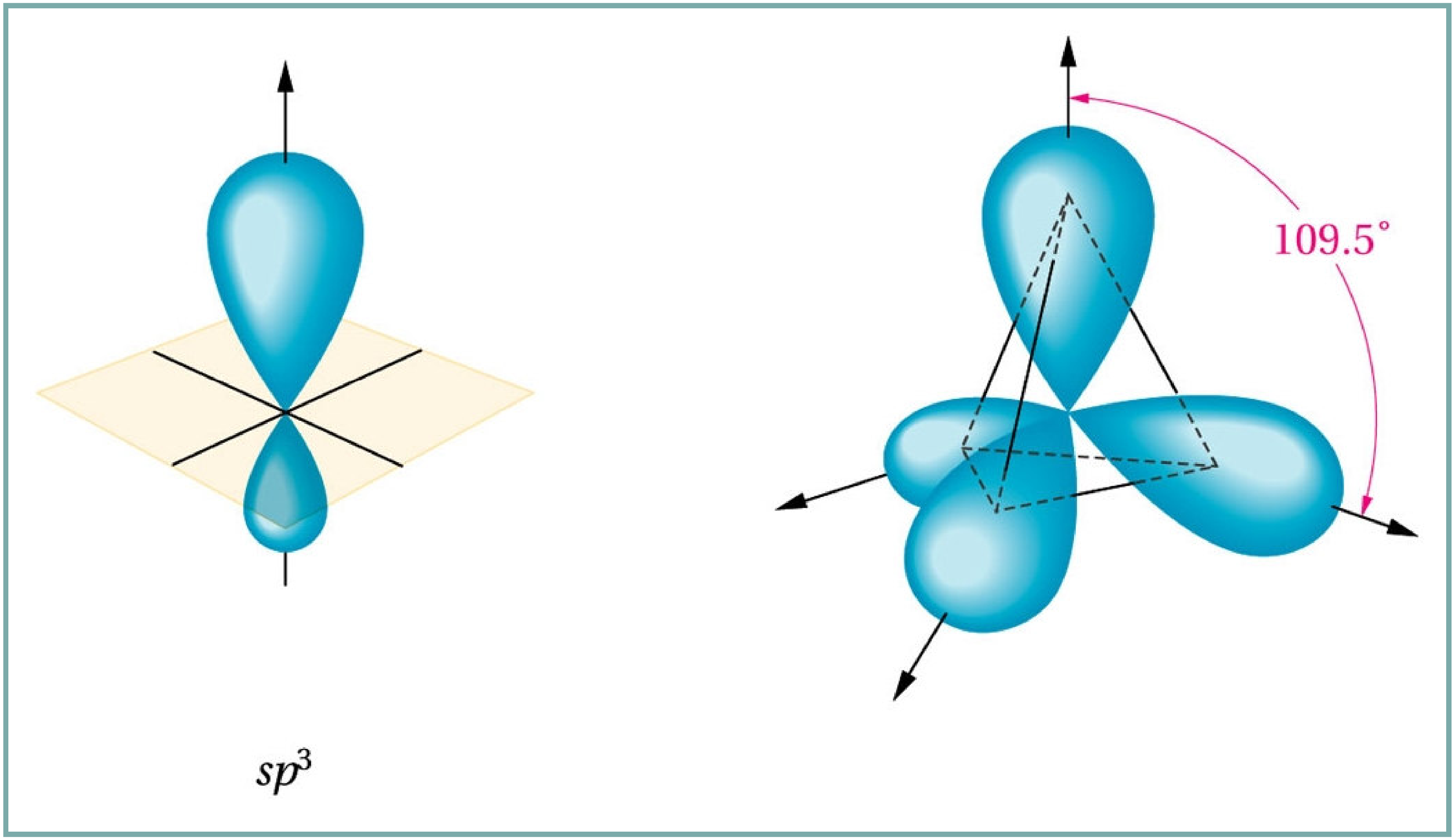
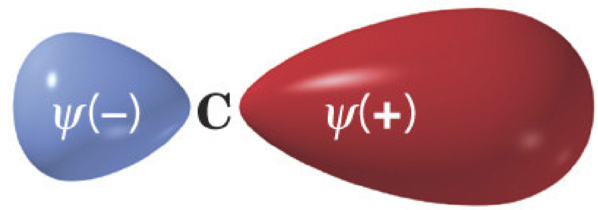

ψ(+)
2s Orbital
ψ(+)
ψ(−)
2p_y Orbital
ψ(−)
ψ(+)
2p_x Orbital
ψ(−)
ψ(+)
2p_z Orbital
Hybridization
109.5°
109.5°
109.5°
109.5°
109.5°
ψ(+)
ψ(+)
ψ(+)
ψ(+)
H
H
C
H
H
H
H
C
H
H
109.5°
Methane, CH_4

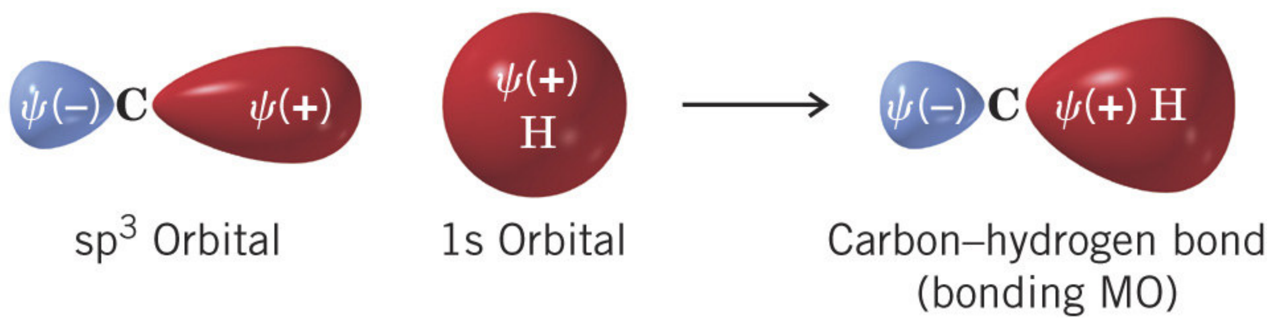
Figure 1.7 *sp*^{3} orbitals extending in one direction



- An sp^3 orbital looks like a *p* orbital with one lobe greatly extended
  - Often the small lobe is not drawn

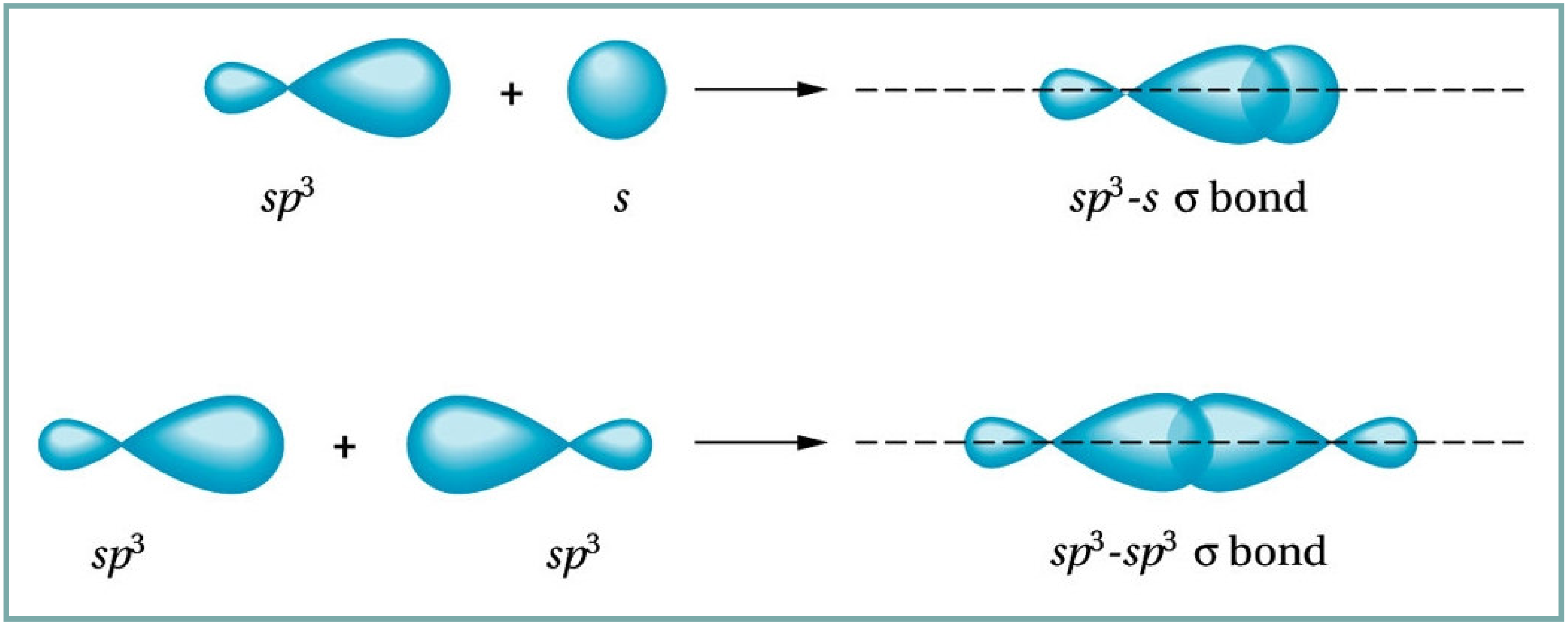


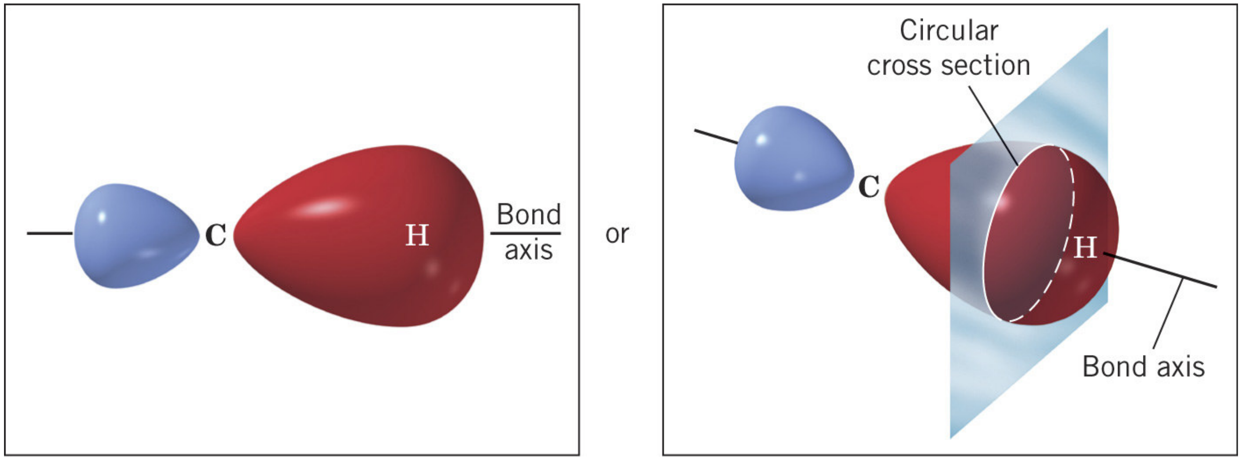
- The extended sp^3 lobe can then overlap well with the hydrogen 1*s* to form a strong bond



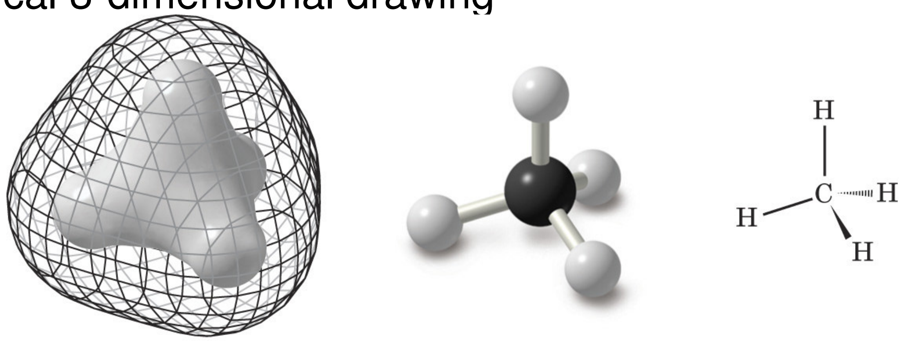
- The bond formed is called a sigma (σ) bond because it is circularly symmetrical in cross section when view along the bond axis

Figure 1.7 Examples of sigma bonds formed from *sp*^{3} hybrid orbitals





- A variety of representations of methane show its tetrahedral nature and electron distribution
- a. calculated electron density surface b. ball-and-stick model c. a typical 3-dimensional drawing



(a) (b) (c)

Figure 1.9 Methane

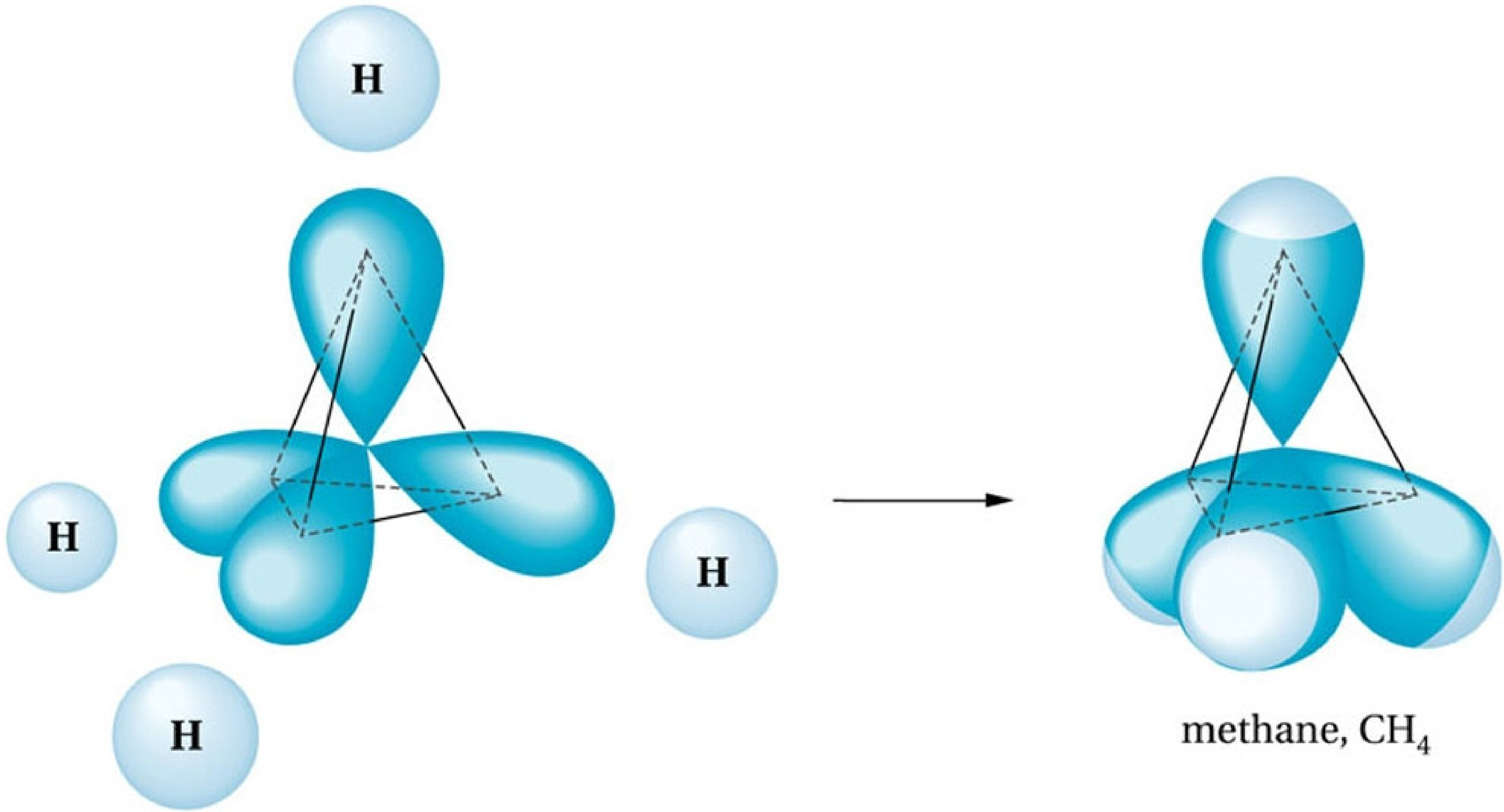
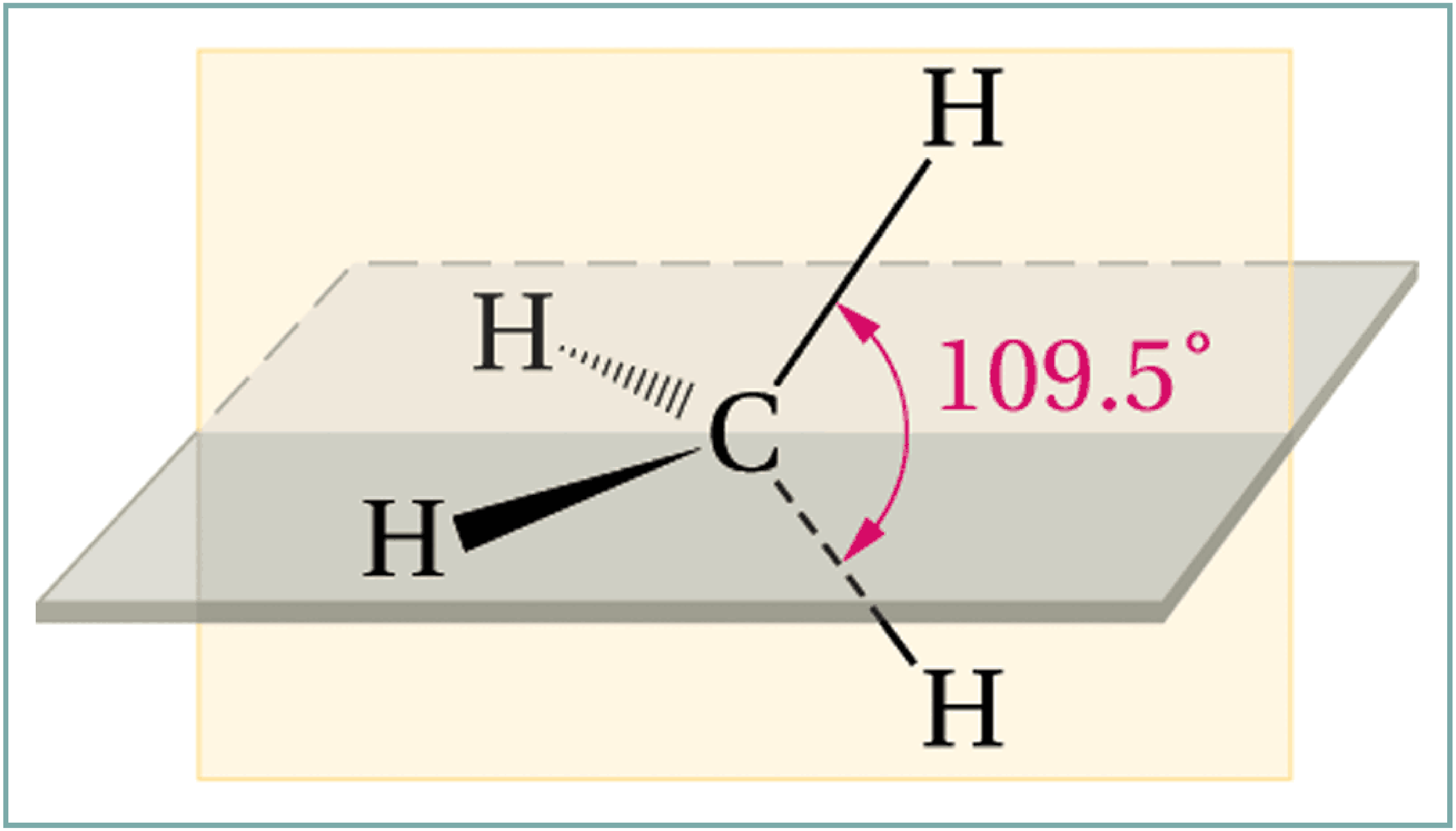
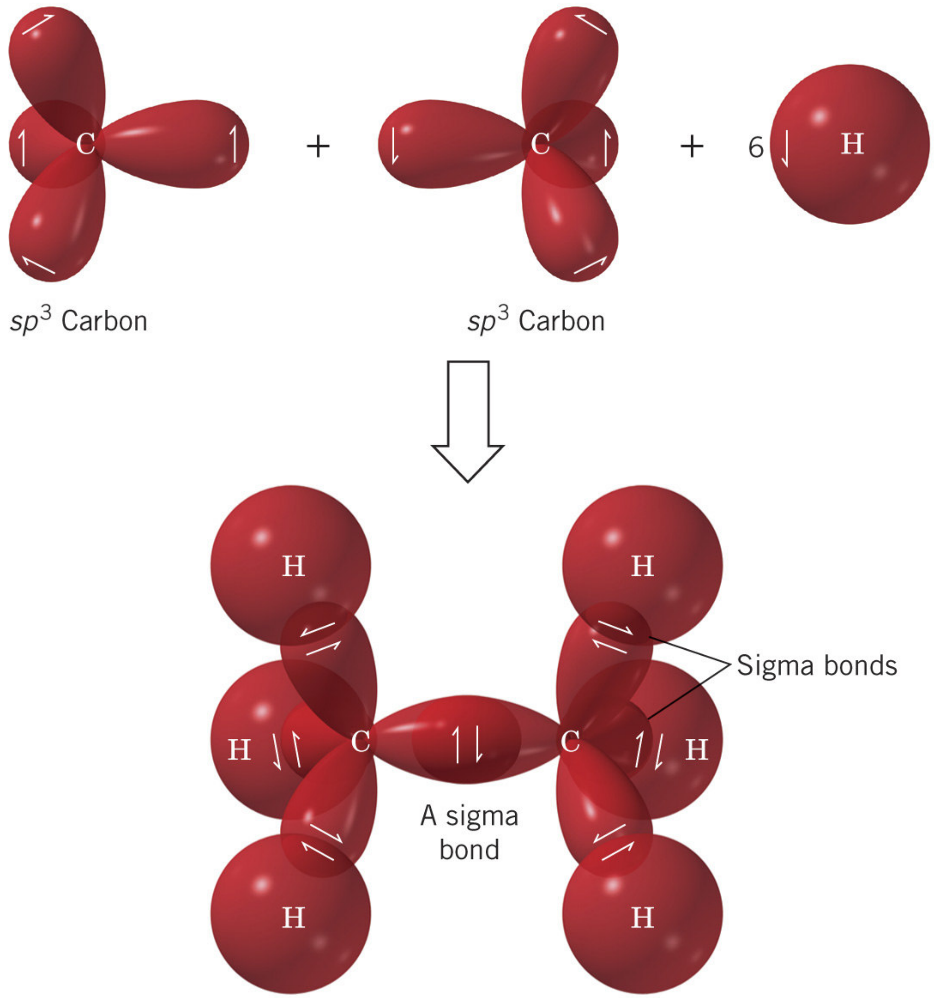


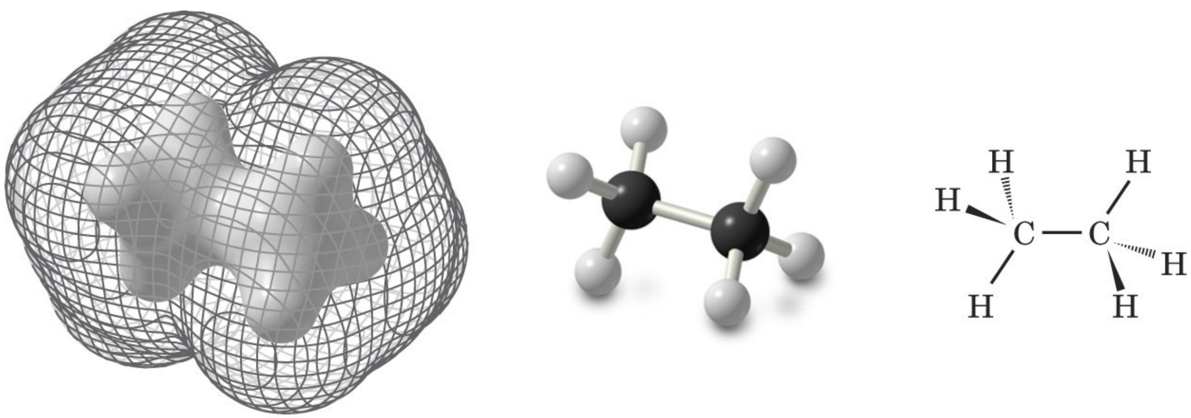
Figure 1.10 Planes in methane



- Ethane (C_2H_6)
  - The carbon-carbon bond is made from overlap of two *sp³* 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



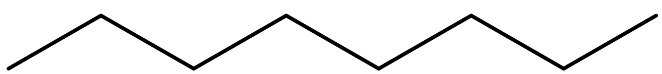
(*a*) (*b*) (*c*)

- 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

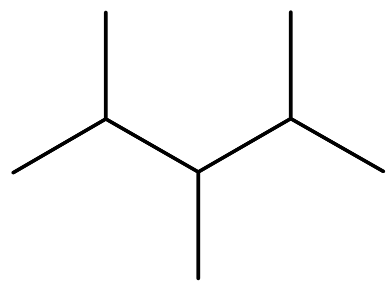
1.17 Classification According to Molecular Framework

1.17.a Acyclic Compounds

- Acyclic:
  - not cyclic
  - Have chains of carbon atoms but no rings
  - The chains may be unbranched or branched.

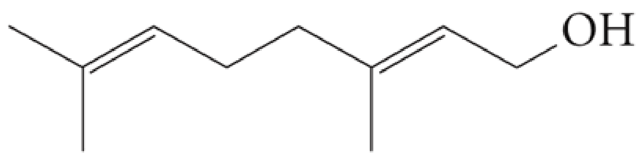


unbranched chain of eight carbons



branched chain of eight carbons

Figure 1.11 Examples of natural acyclic compounds



geraniol
(oil of roses)
bp 229–230°C

A branched chain compound used in perfumes

$CH_3(CH_2)_5CH_3$

heptane
(petroleum)
bp 98.4°C

A hydrocarbon present in petroleum, used as a standard in testing the octane rating of gasoline.

$$CH_3\overset{\overset{O}{\|}}{C}(CH_2)_4CH_3$$

2-heptanone
(oil of cloves)
bp 151.5°C

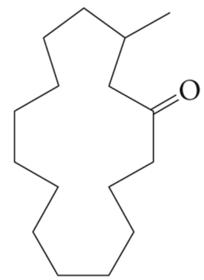
A colorless liquid with a fruity odor, in part responsible for the "peppery" odor of blue cheese

1.17.b Carbocyclic Compounds

- Carbocyclic: contain rings of carbon atoms
  - The smallest possible carbon ring has 3 carbon atoms.
  - Rings may have chains of carbon atoms attached to them
  - And may contain multiple bonds

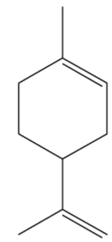
Figure 1.12 Examples of natural carbocyclic compunds with rings of various sizes and

shapes



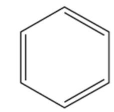
muscone
(musk deer)
bp 327–330°C

A 15-membered ring ketone, used in perfumes



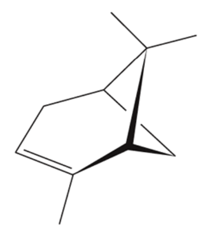
limonene
(citrus fruit oils)
bp 178°C

A ring with two side chains, one of which is branched



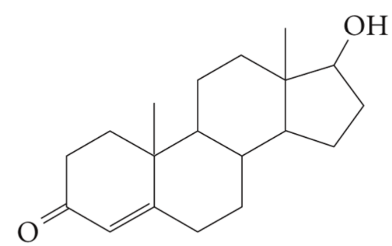
benzene
(petroleum)
mp 5.5°C, bp 80.1°C

A very common ring



α-pinene
(turpentine)
bp 156.2°C

A bicyclic molecule; one would have to break *two* bonds to make it acyclic



testosterone
(testes)
mp 155°C

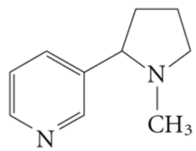
A male sex hormone in which several rings of common sizes are *fused* together; that is, they share two adjacent carbon atoms

1.17.c Heterocyclic Compounds

- Heterocyclic: at least 1 atom in the ring must be a heteroatom, an atom that is not carbon
  - The most common heteroatoms are, oxygen, nitrogen, and sulfur, but heterocyclics with other elements are also known
  - Heterocyclic rings come in many sizes, and may contain multiple bonds, may have carbon chains or rings attached to them
  - Found in many natural products

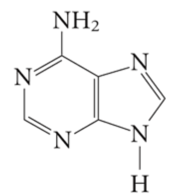
Figure 1.13

Examples of natural heterocyclic compounds



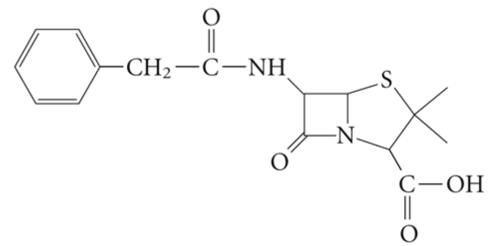
nicotine
bp 246°C

Present in tobacco, nicotine has two heterocyclic rings of different sizes, each containing one nitrogen.



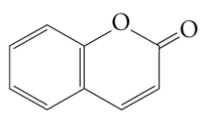
adenine
mp 360–365°C
(decomposes)

One of the four heterocyclic bases of DNA, adenine contains two fused heterocyclic rings, each of which contains two heteroatoms (nitrogen).



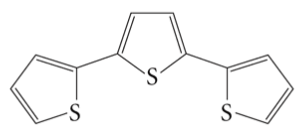
penicillin-G
(amorphous solid)

One of the most widely used antibiotics, penicillin has two heterocyclic rings, the smaller of which is crucial to biological activity.



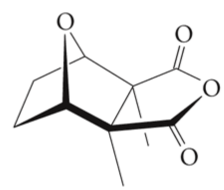
coumarin
mp 71°C

Found in clover and grasses, coumarin produces the pleasant odor of new-mown hay.



α-terthienyl
mp 92–93°C

This compound, with three linked sulfur-containing rings, is present in certain marigold species.



cantharidin
mp 218°C

This compound, an oxygen heterocycle, is the active principle in cantharis (also known as Spanish fly), a material isolated from certain dried beetles of the species *Cantharis vesicatoria* and incorrectly thought by some to increase sexual desire.

1.18 Classification According to Functional Groups

Functional Groups

- Are
  - Groups of atoms that have characteristic chemical properties regardless of the molecular framework to which they are attached

Table 1.6 The main functional groups

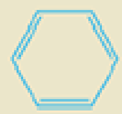
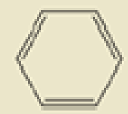
	Structure	Class of compound	Specific example	Common name of the specific example
A. Functional groups that are a part of the molecular framework	—C—C— (single bond)	alkane	$CH_3—CH_3$	ethane, a component of natural gas
	C=C	alkene	$CH_2=CH_2$	ethylene, used to make polyethylene
	—C≡C—	alkyne	HC≡CH	acetylene, used in welding
		arene		benzene, raw material for polystyrene and phenol
B. Functional groups containing oxygen				
1. With carbon–oxygen single bonds	—C—OH	alcohol	CH_3CH_2OH	ethyl alcohol, found in beer, wines, and liquors
	—C—O—C—	ether	$CH_3CH_2OCH_2CH_3$	diethyl ether, once a common anesthetic

Table 1.6 The main functional groups

	Structure	Class of compound	Specific example	Common name of the specific example
*2. With carbon–oxygen double bonds**	$-C(=O)-H$	aldehyde	$CH_2{=}O$	formaldehyde, used to preserve biological specimens
	$-\overset{\vert}{\underset{\vert}{C}}-C(=O)-\overset{\vert}{\underset{\vert}{C}}-$	ketone	$CH_3C(=O)CH_3$	acetone, a solvent for varnish and rubber cement
3. With single and double carbon–oxygen bonds	$-C(=O)-OH$	carboxylic acid	$CH_3C(=O)-OH$	acetic acid, a component of vinegar
	$-C(=O)-O-\overset{\vert}{\underset{\vert}{C}}-$	ester	$CH_3C(=O)-OCH_2CH_3$	ethyl acetate, a solvent for nail polish and model airplane glue
*C. Functional groups containing nitrogen***	$-\overset{\vert}{\underset{\vert}{C}}-NH_2$	primary amine	$CH_3CH_2NH_2$	ethylamine, smells like ammonia
	$-C{\equiv}N$	nitrile	$CH_2{=}CH-C{\equiv}N$	acrylonitrile, raw material for making Orlon
D. Functional group with oxygen and nitrogen	$-C(=O)-NH_2$	primary amide	$H-C(=O)-NH_2$	formamide, a softener for paper
E. Functional group with halogen	$-X$	alkyl or aryl halide	CH_3Cl	methyl chloride, refrigerant and local anesthetic

End of Chapter 1

Dr. Abdullah I. Saleh