1. Structure and Bonding

Organic Chemistry

- "Organic" – until mid 1800's referred to compounds from living sources (mineral sources were "inorganic")
- **Wöhler** in 1828 showed that urea, an organic compound, could be synthesized in the lab
- Today, **organic compounds** are those based on carbon structures and **organic chemistry** studies their structures and reactions

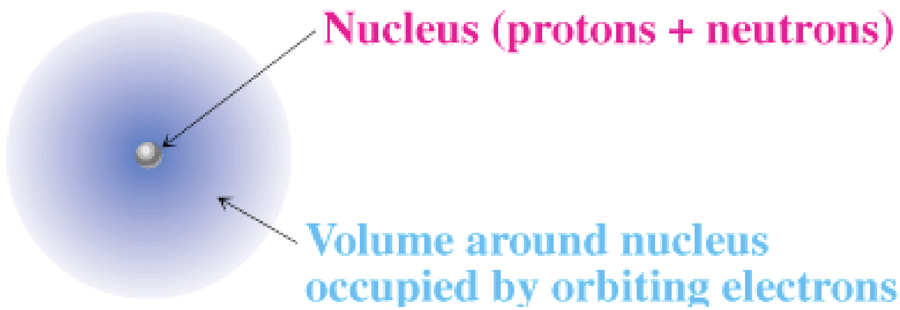
  - Includes biological molecules, drugs, solvents, dyes
  - Does not include metal salts and materials (inorganic)
  - Does not include materials of large repeating molecules without sequences (polymers)

Please read sections 1.1 – 1.2 for review.

1.1 Atomic Structure

Structure of an atom:

Positively charged *nucleus* (very dense, protons and neutrons) and smal (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

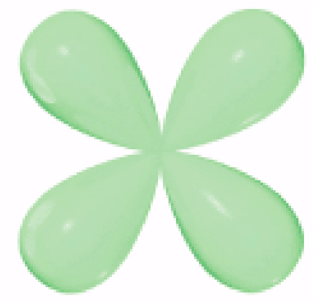
- **Quantum mechanics**: describes electron energies and locations by a *wave equation*
  - *Wave function* solution of wave equation
  - Each Wave function is an **orbital**, ψ
- A plot of ψ 2 describes where electron most likely to be
- Electron cloud has no specific boundary so we show most probable 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 chemistry
- *s* orbitals: spherical, nucleus at center
- *p* orbitals: dumbbell-shaped, nucleus at middle

An s orbital

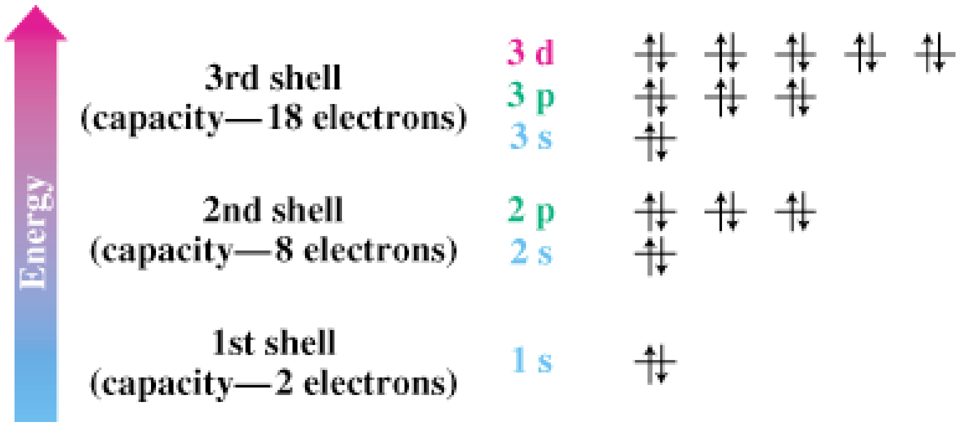
A p orbital



A d orbital

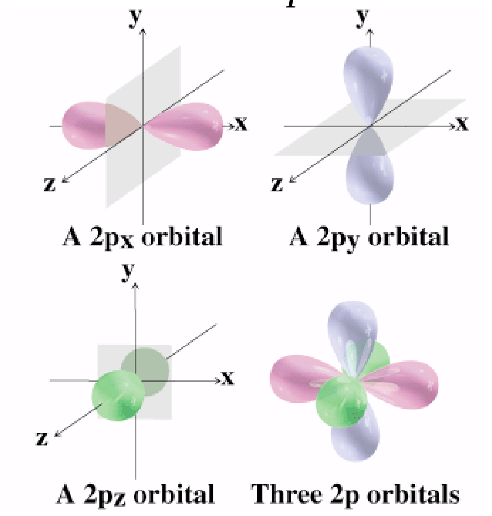
Orbitals and Shells

- 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
- 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**



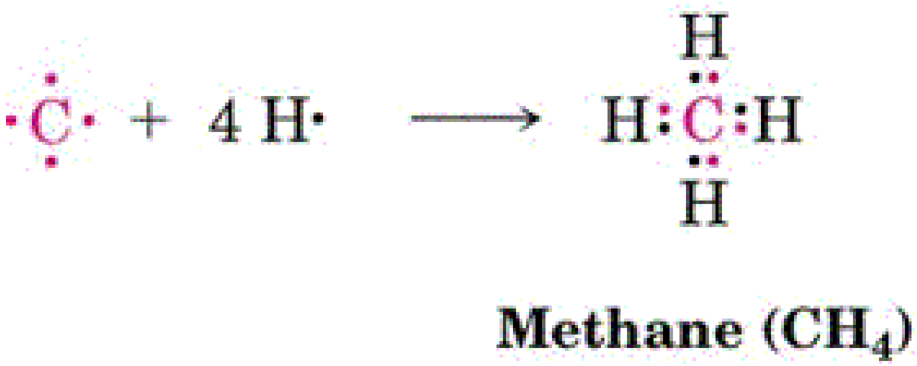
1.5 Covalent Bonds

Number of Covalent Bonds to an Atom

- 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

Valences of Carbon

- Carbon has four valence electrons ($2s^2\ 2p^2$), forming four bonds (CH_4)



- Oxygen has six valence electrons ($2s^2\ 2p^4$) but forms two bonds (H_2O)

Water (H_2O)

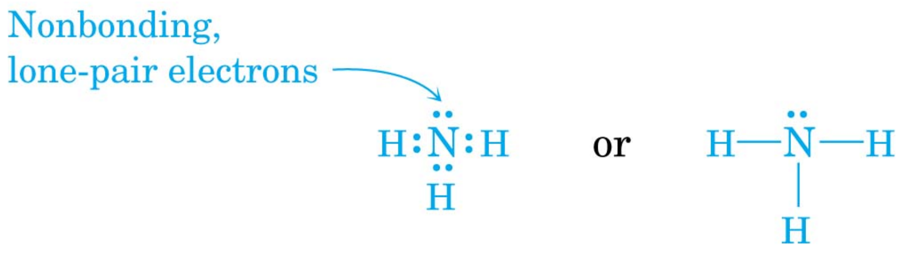
Methanol (CH_3OH)

- Nitrogen has five valence electrons (2*s*2 2*p*3) but forms only three bonds (NH3)

Ammonia (NH_3)

Non-bonding electrons

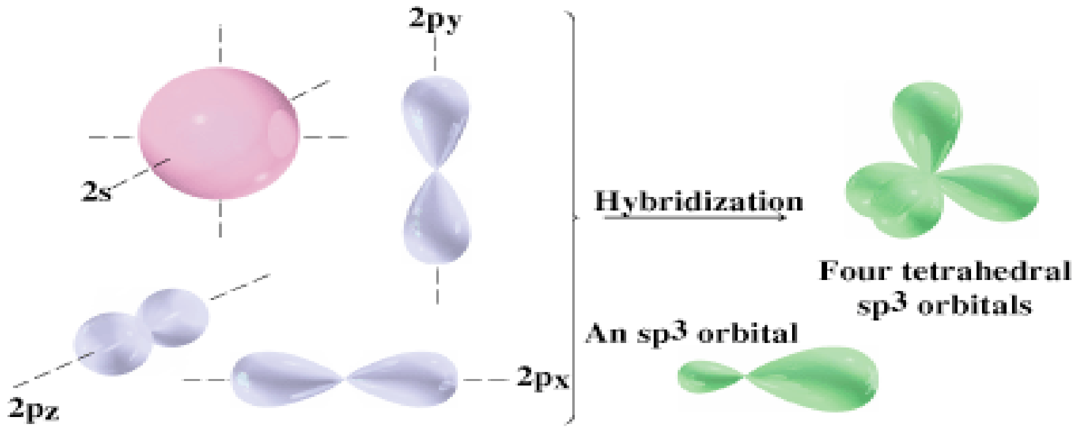
Valence electrons not used in bonding are called **nonbonding electrons**, or **lone-pair electrons**
Nitrogen atom in ammonia (NH3) shares six valence electrons in three covalent bonds and remaining two valence electrons are nonbonding lone pair



Ammonia

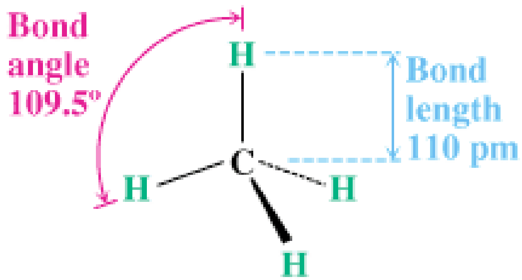
1.7 Hybridization: *sp*^{3} Orbitals and the Structure of Ethane

- 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 = sp3), Pauling (1931) (Number of hybrid orbitals after hybridization, equals number of unhybridized orbitals before hybridization).



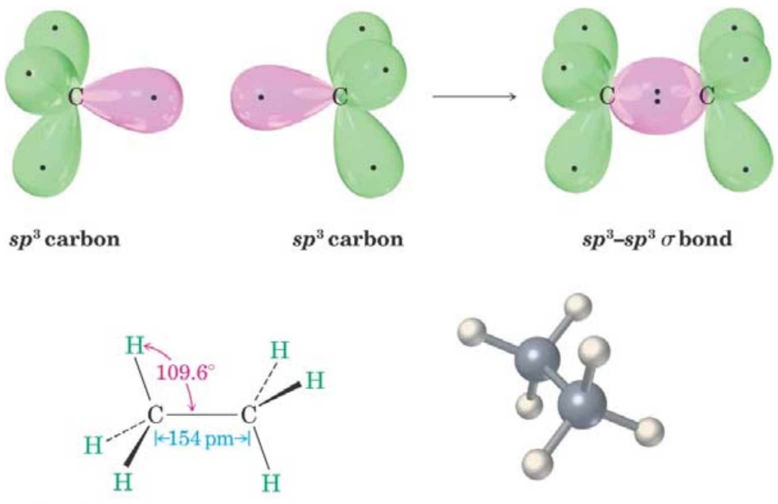
Tetrahedral Structure of Methane

- *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*.



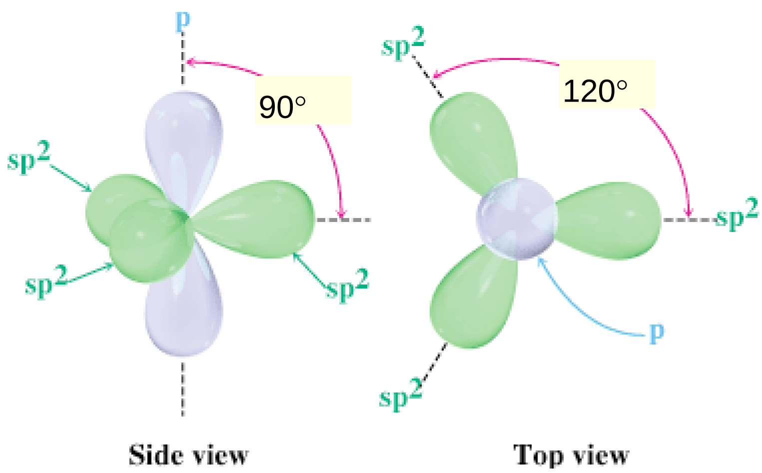
1.8 Hybridization: *sp3* Orbitals and the Structure of Ethane

- Two C’s bond to each other by s 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



1.9 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 = sp2)
- *sp*2 orbitals are in a plane with120° angles
- Remaining *p* orbital is perpendicular to the plane

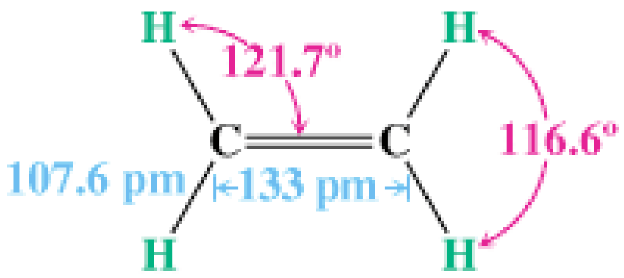


Bonds From sp2 Hybrid Orbitals

- 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 s 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

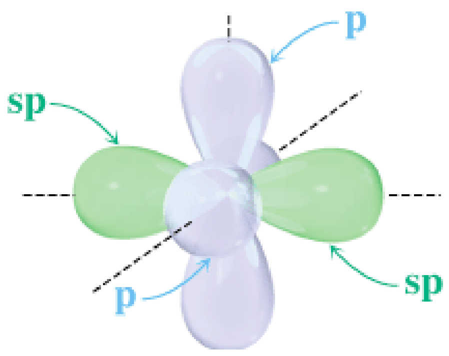
Structure of Ethylene

- H atoms form s bonds with four *sp*2 orbitals
- H–C–H and H–C–C 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)



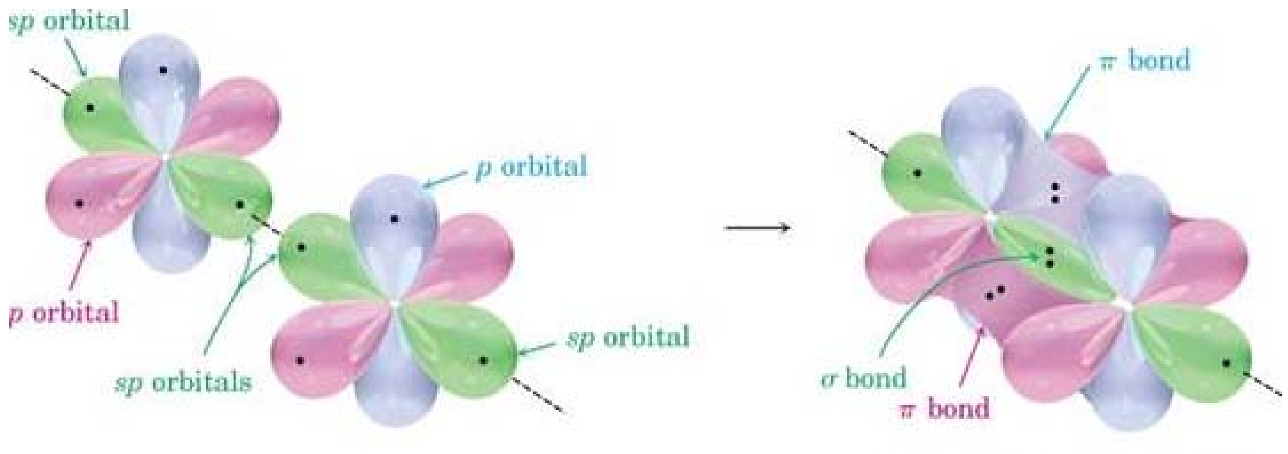
1.10 Hybridization: *sp* Orbitals and the Structure of Acetylene

- 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

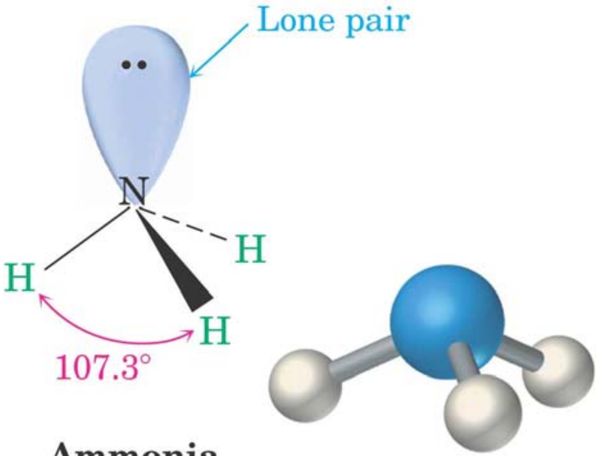
- Two *sp* hybrid orbitals from each C form *sp*–*sp* s bond
- *pz* orbitals from each C form a *pz*–*pz* π bond by sideways overlap and *py* orbitals overlap similarly



Carbon–carbon triple bond

1.11 Hybridization of Nitrogen and Oxygen

- Elements other than C can have hybridized orbitals
- H–N–H bond angle in ammonia (NH3) 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



Ammonia

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°