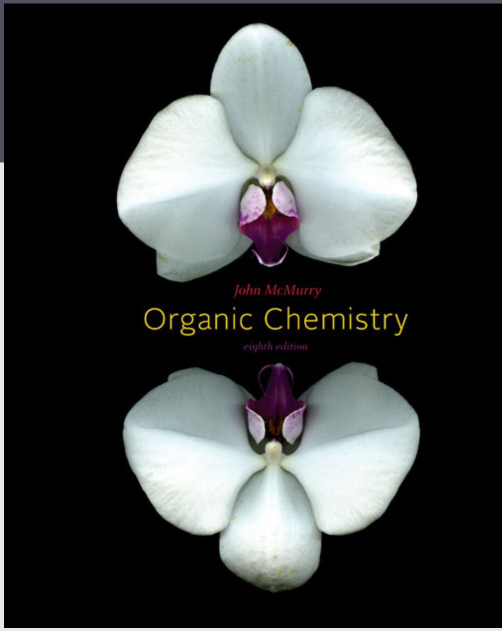


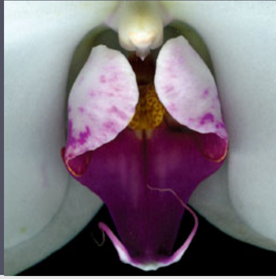
John E. McMurry

www.cengage.com/chemistry/mcmurry

Chapter 1
Structure and Bonding

Paul D. Adams • University of Arkansas

Origins of Organic Chemistry



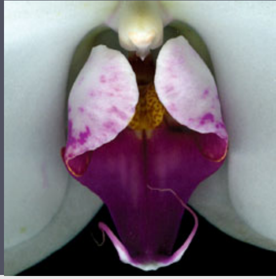
- Organic chemistry is study of carbon compounds.
- Why is it so special?
- 90% of more than 30 million chemical compounds contain carbon.
- Examination of carbon in periodic chart answers some of these questions.
- Carbon is group 4A element, it can share 4 valence electrons and form 4 covalent bonds.

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															

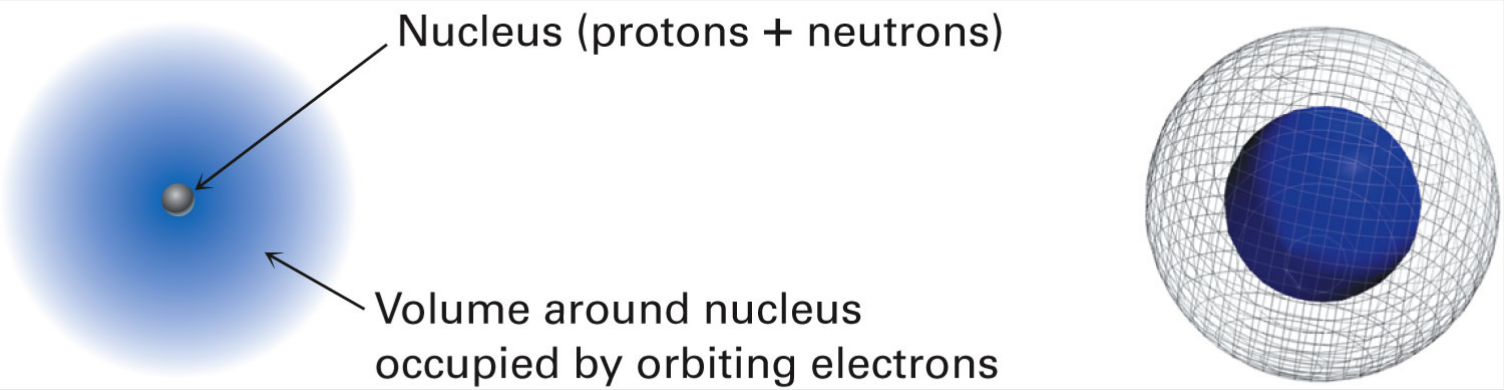
Why This Chapter?

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

1.1 Atomic Structure

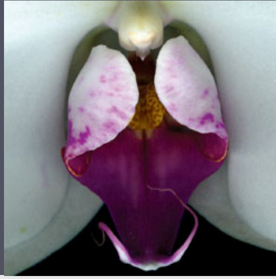


- Structure of an atom: small diameter (2×10^{-10} m = 200 pm)
  - *Nucleus* very dense
    - protons (positively charged)
    - neutrons (neutral)
    - small (10^{-15} m)
  - *Electrons*
    - negatively charged
    - located in space remindful of a cloud (10^{-10} m) around nucleus



[*ångström* (Å) is 10^{-10} m = 100 pm]

Atomic Number and Atomic Mass



- The *atomic number* (*Z*): number of protons in nucleus
- The *mass number* (*A*): number of protons plus neutrons
- All atoms of same element have the same *Z* value
- **Isotopes:** atoms of the same element with different numbers of neutrons and thus different *A*

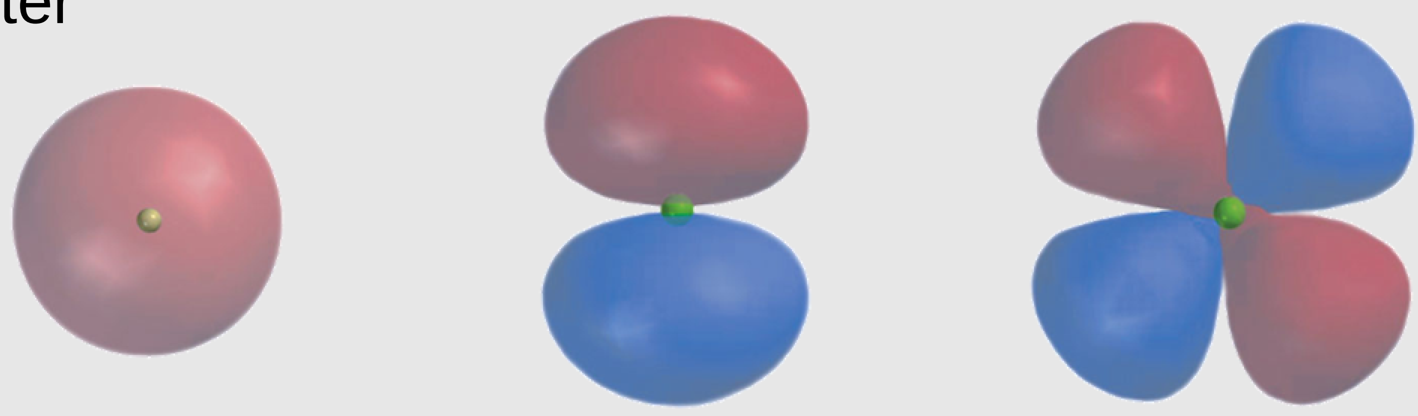
$$ {}^{A}_{Z}\mathrm{C} \quad {}^{12}_{6}\mathrm{C} \quad {}^{13}_{6}\mathrm{C} $$

- The **atomic mass** (*atomic weight*) of an element is weighted average mass in atomic mass units (amu) of an element’s naturally occurring isotopes.
- Carbon:

$$ \frac{(98.9 \times 12.000) + (1.1 \times 13.000)}{100} = 12.011 $$

Shapes of Atomic Orbitals for Electrons

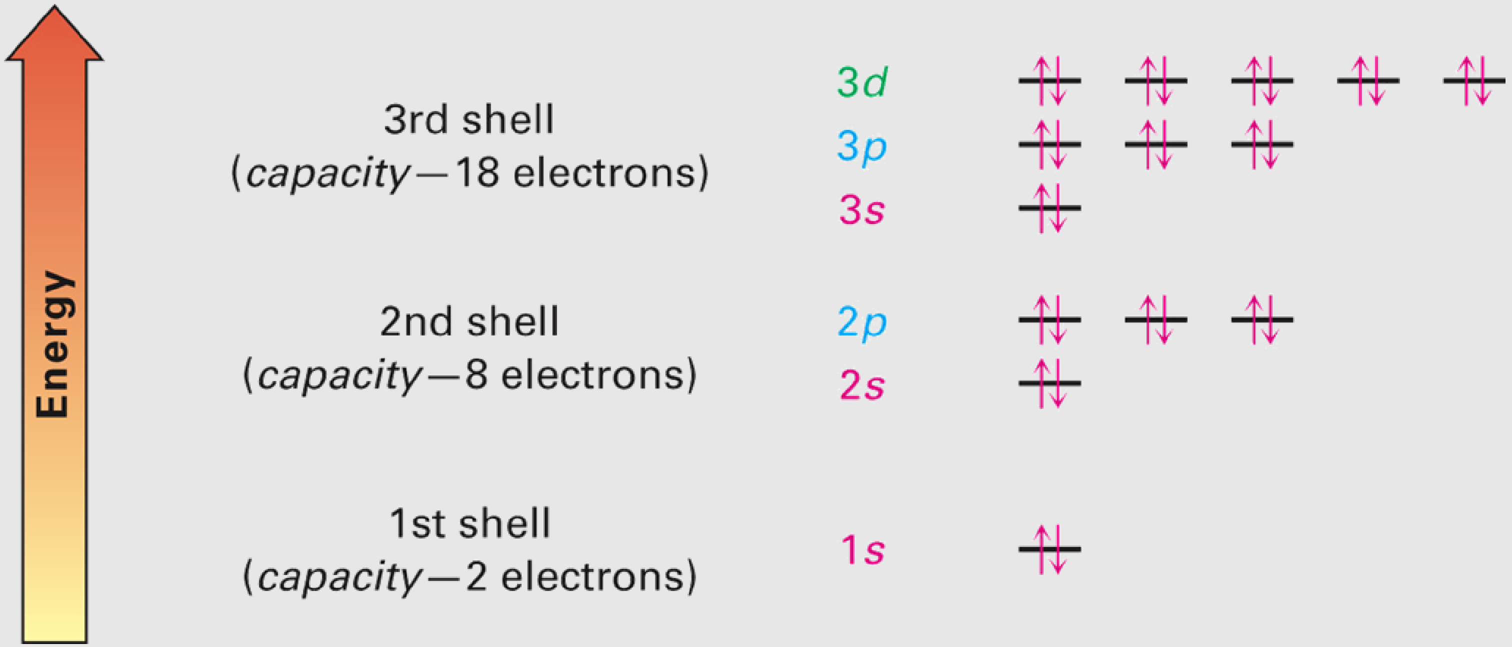
- Four different kinds of orbitals for electrons based on those derived for a hydrogen atom
- Denoted *s*, *p*, *d*, and *f*
- *s* and *p* orbitals most important in organic and biological chemistry
- *s* orbitals: spherical, nucleus at center
- *p* orbitals: dumbbell-shaped, nucleus at middle
- d orbitals: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



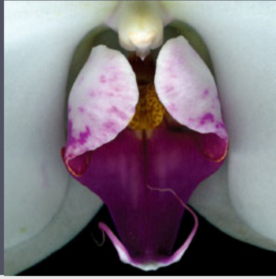
An *s* orbital | A *p* orbital | A *d* orbital

Orbitals and Shells (Continued)

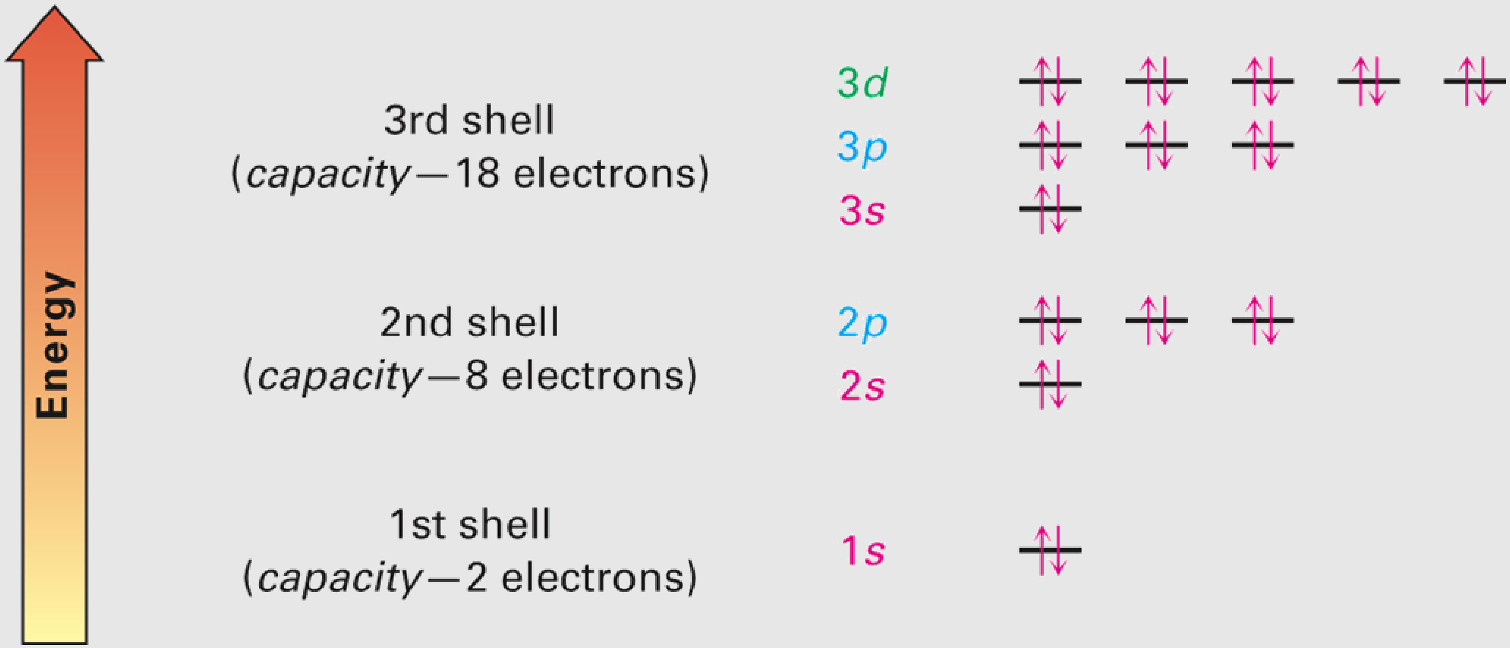
- Orbitals are grouped in **shells** of increasing size and energy
- Different shells contain different numbers and kinds of orbitals
- Each orbital can be occupied by two electrons

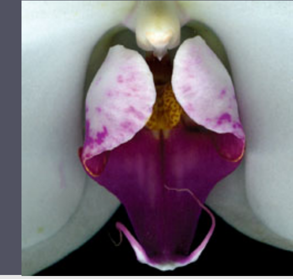


Orbitals and Shells (Continued)



- 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

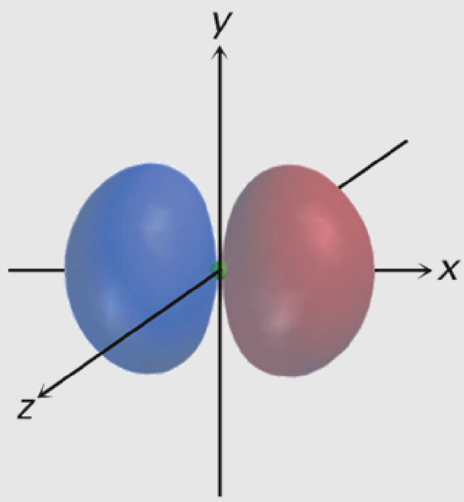




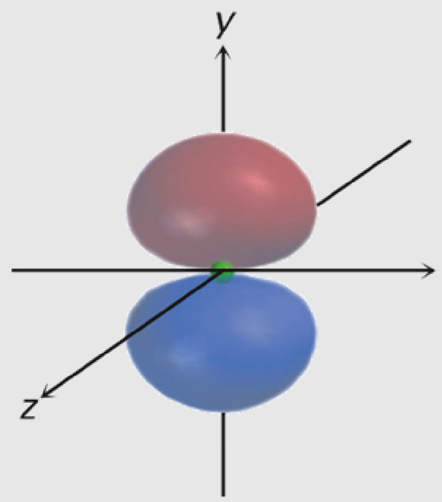
P-Orbitals

- In each shell there are three perpendicular *p* orbitals, p_x, p_y, and p_z, of equal energy

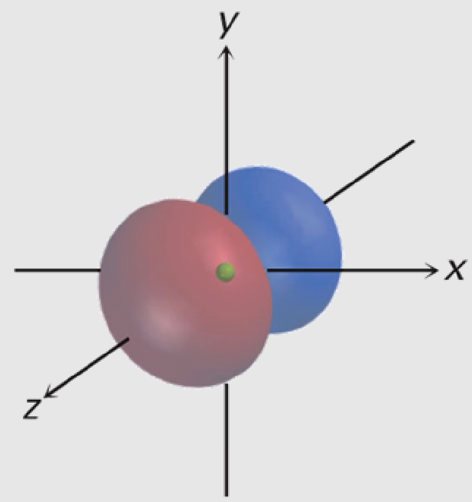
- Lobes of a *p* orbital are separated by region of zero electron density, a **node**



A $2p_x$ orbital



A $2p_y$ orbital



A $2p_z$ orbital

1.3 Atomic Structure: Electron Configurations

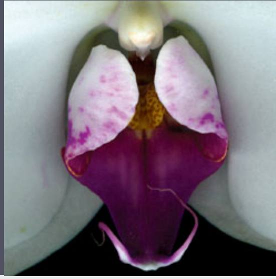
- **Ground-state electron configuration** (i.e., lowest energy arrangement) of atom
  - lists orbitals occupied by its electrons.
- Rules:
  - 1. Lowest-energy orbitals fill first: 1*s* $\rightarrow$ 2*s* $\rightarrow$ 2*p* $\rightarrow$ 3*s* $\rightarrow$ 3*p* $\rightarrow$ 4*s* $\rightarrow$ 3*d* (*Aufbau* (“build-up”) principle)

1.3 Atomic Structure: Electron Configurations

- **Ground-state electron configuration** (i.e., lowest energy arrangement) of atom
  - lists orbitals occupied by its electrons.
- Rules:
  - 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

1.3 Atomic Structure: Electron Configurations

- **Ground-state electron configuration** (i.e., lowest energy arrangement) of atom
  - lists orbitals occupied by its electrons.
- Rules:
  - 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***).
    - To the chalkboard (p-orbital filling as example)



1.4 Development of Chemical Bonding Theory

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

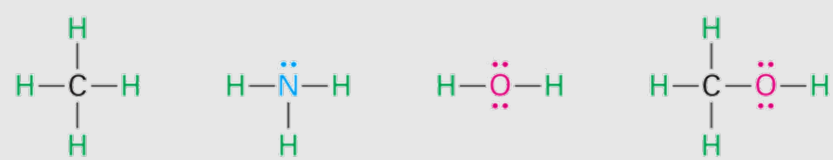
Development of Chemical Bonding Theory

- **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 ($2s^2$ $2p^2$) due to 4 e- in valence shell

Electron-dot structures (Lewis structures)

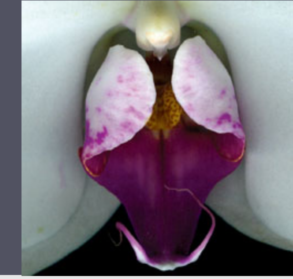
- **Kekulé structures** (line-bond structures) have a line drawn between two atoms indicating a 2 e- covalent bond.
- Stable molecule results at completed shell, octet (eight dots) **for main-group** atoms (two for hydrogen)

Line-bond structures (Kekulé structures)

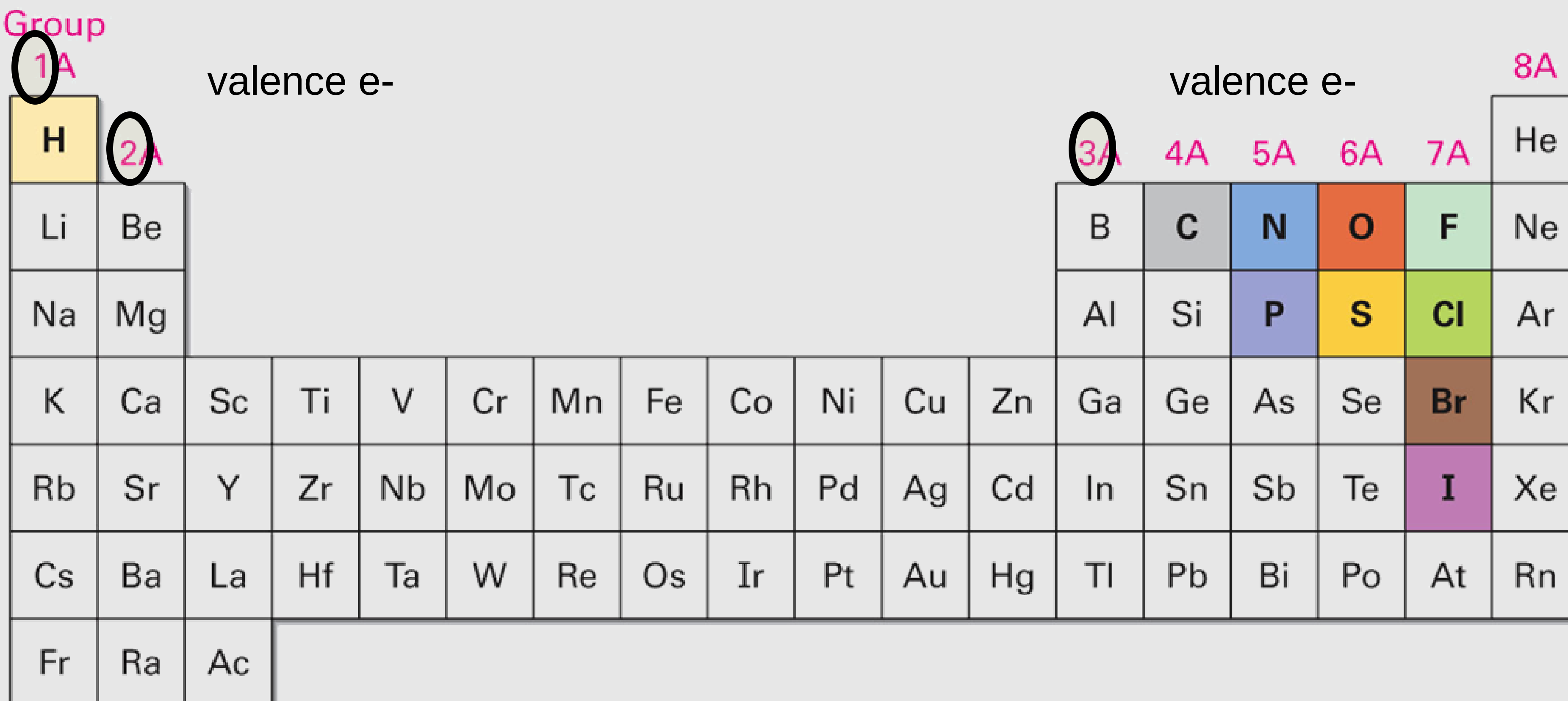


Methane (CH_4) | Ammonia (NH_3) | Water (H_2O) | Methanol (CH_3OH)

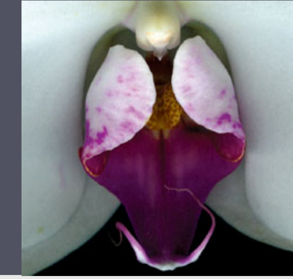
Development of Chemical Bonding Theory



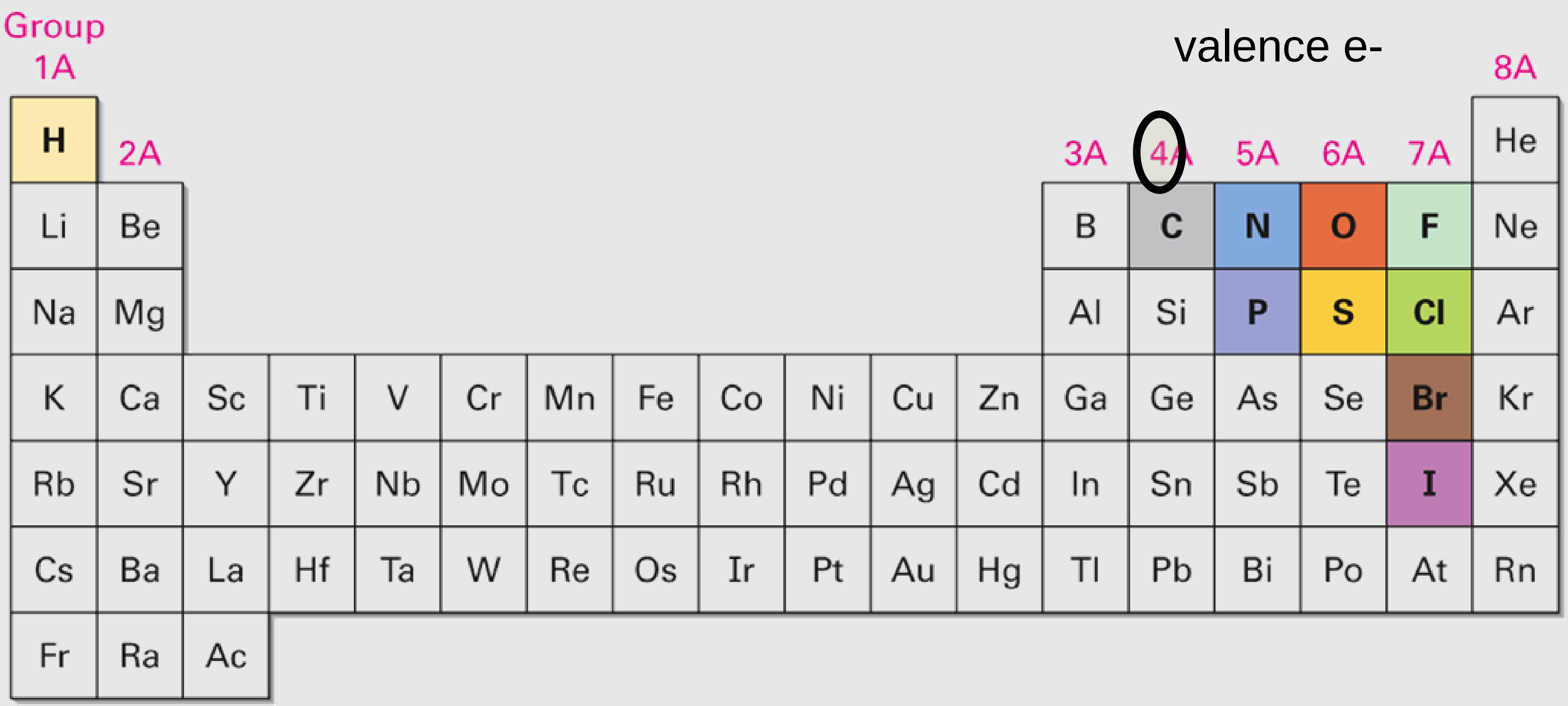
- Atoms with one, two, or three valence electrons form one, two, or three bonds.



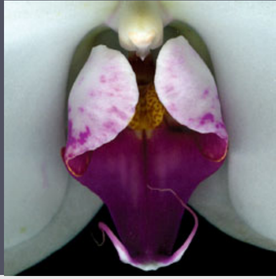
Development of Chemical Bonding Theory



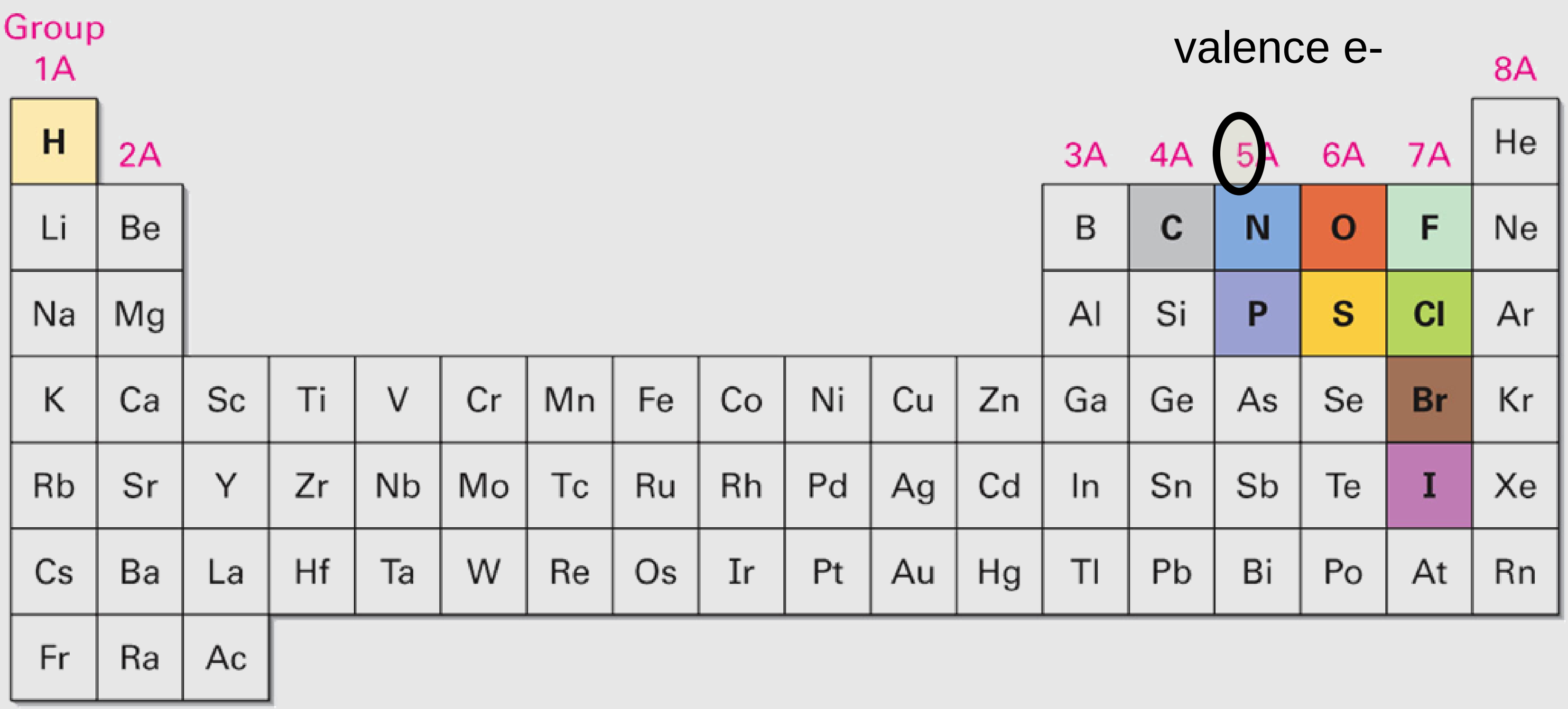
- Atoms with four or more valence electrons form as many bonds as electrons needed to fill the *s* and *p* levels of their valence shells to reach a stable octet.
- Carbon has four valence electrons ($2s^2\ 2p^2$), forming four bonds (CH_4).



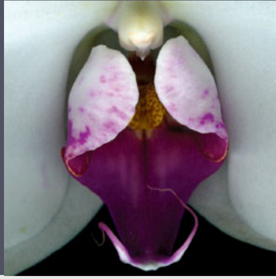
Development of Chemical Bonding Theory



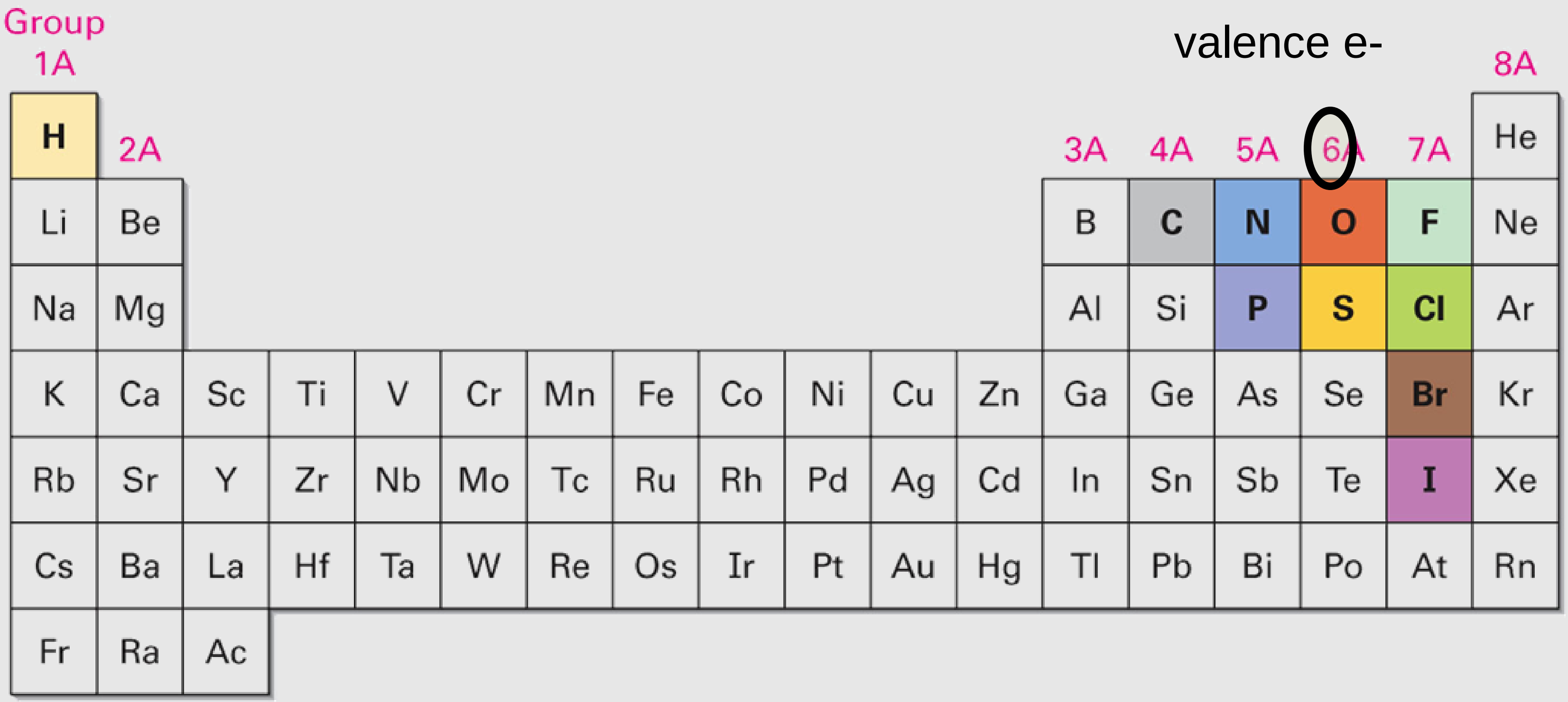
- Nitrogen has five valence electrons ($2s^2\ 2p^3$) but forms only three bonds (NH_3).



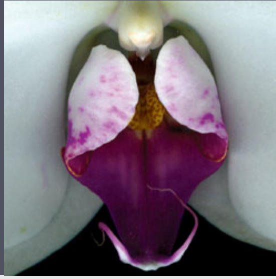
Development of Chemical Bonding Theory

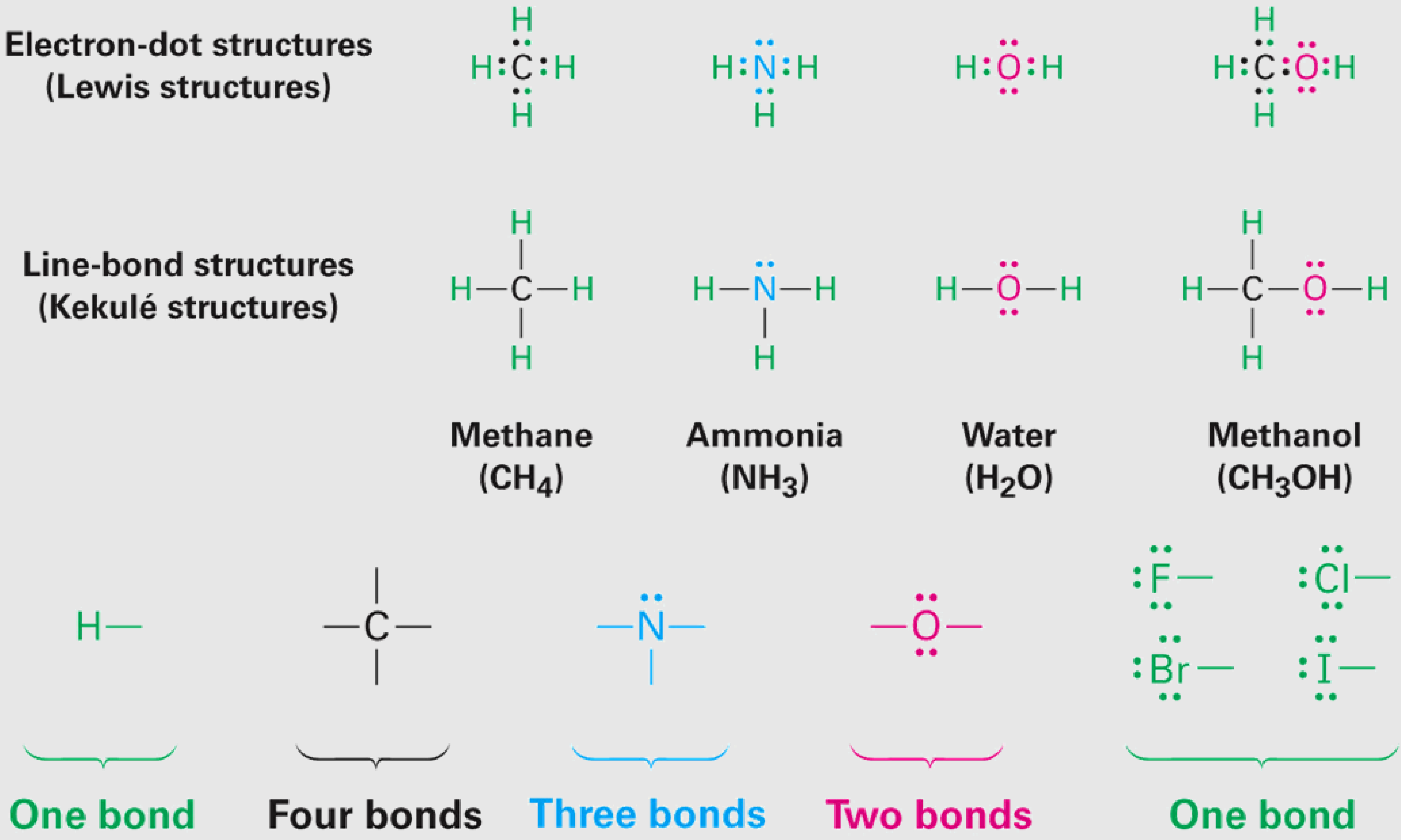


- Oxygen has six valence electrons ($2s^2\ 2p^4$) but forms two bonds (H_2O)



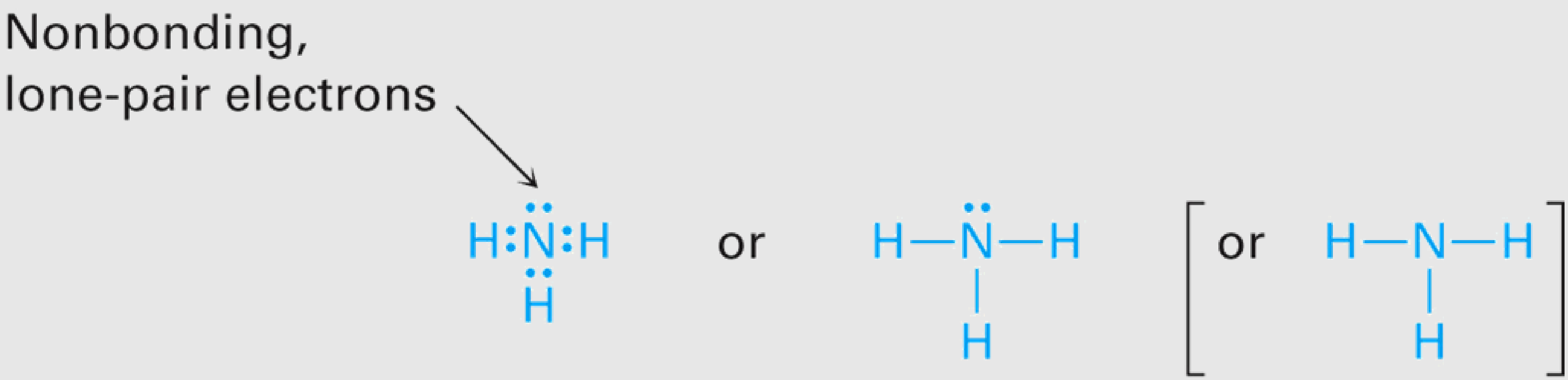
Development of Chemical Bonding Theory





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

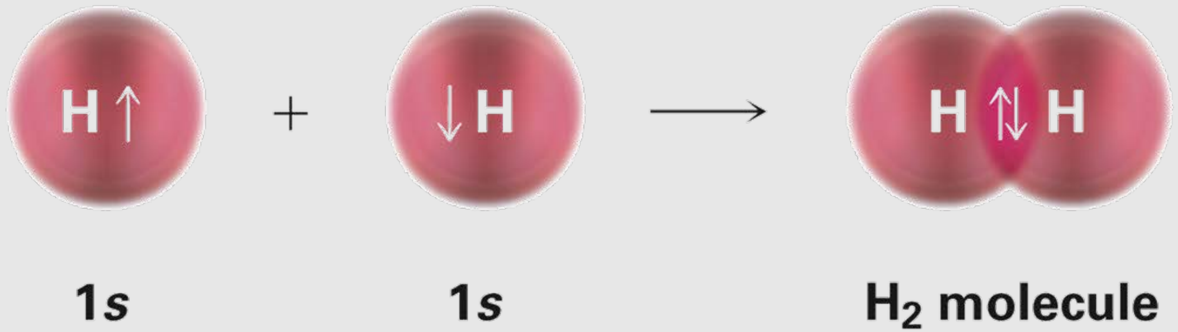


Ammonia

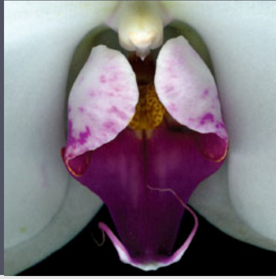
1.5 Describing Chemical Bonds: Valence Bond Theory

- **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

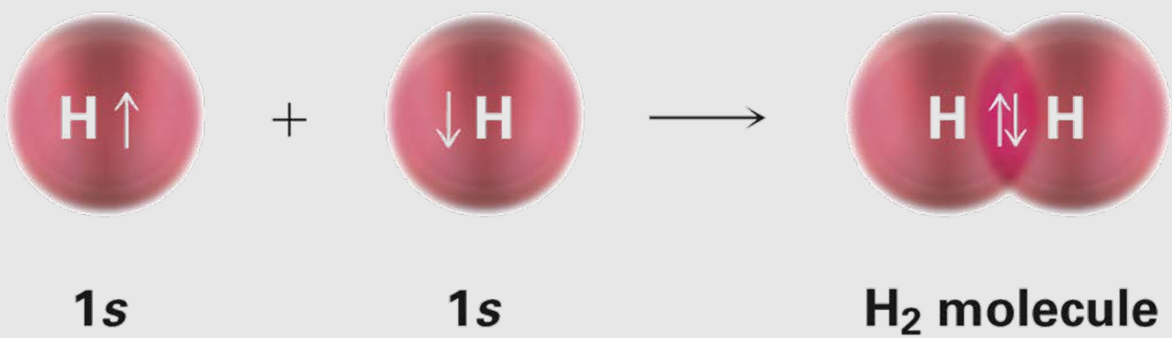


1.5 Describing Chemical Bonds: Valence Bond Theory

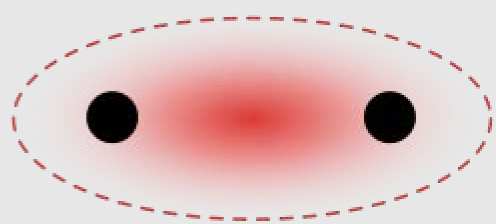


Valence Bond Theory:

- 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**

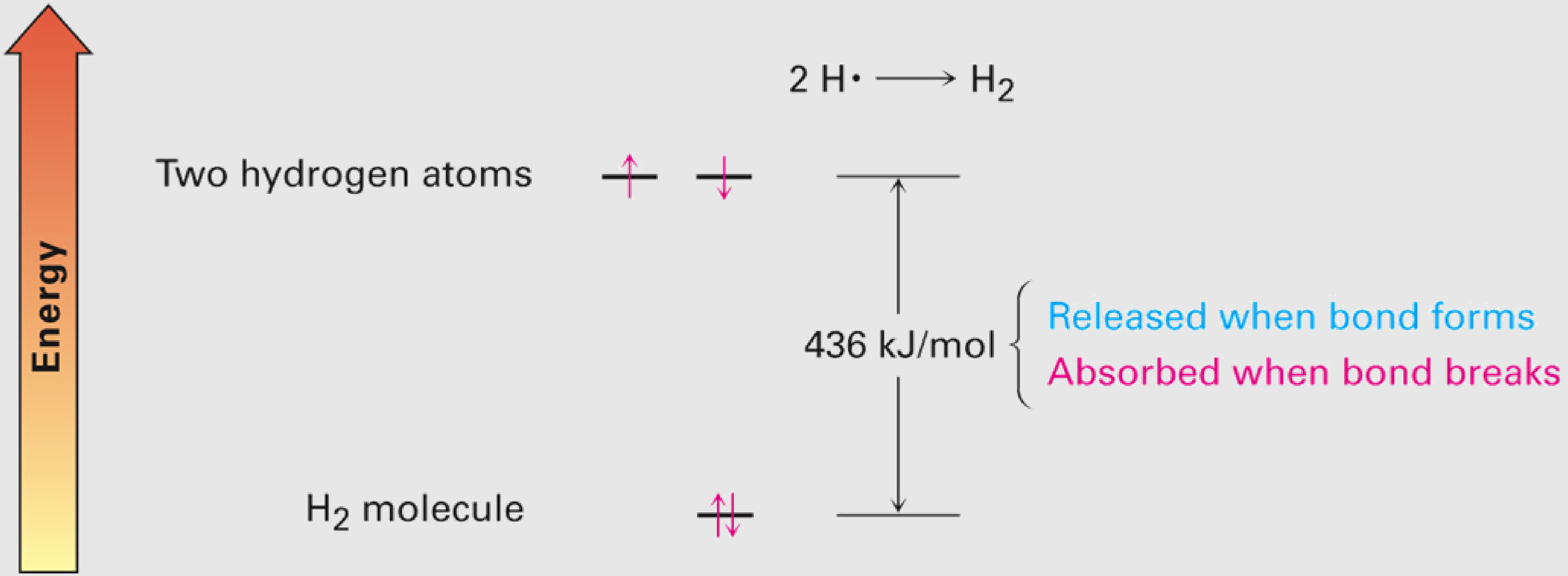


cylindrically symmetrical



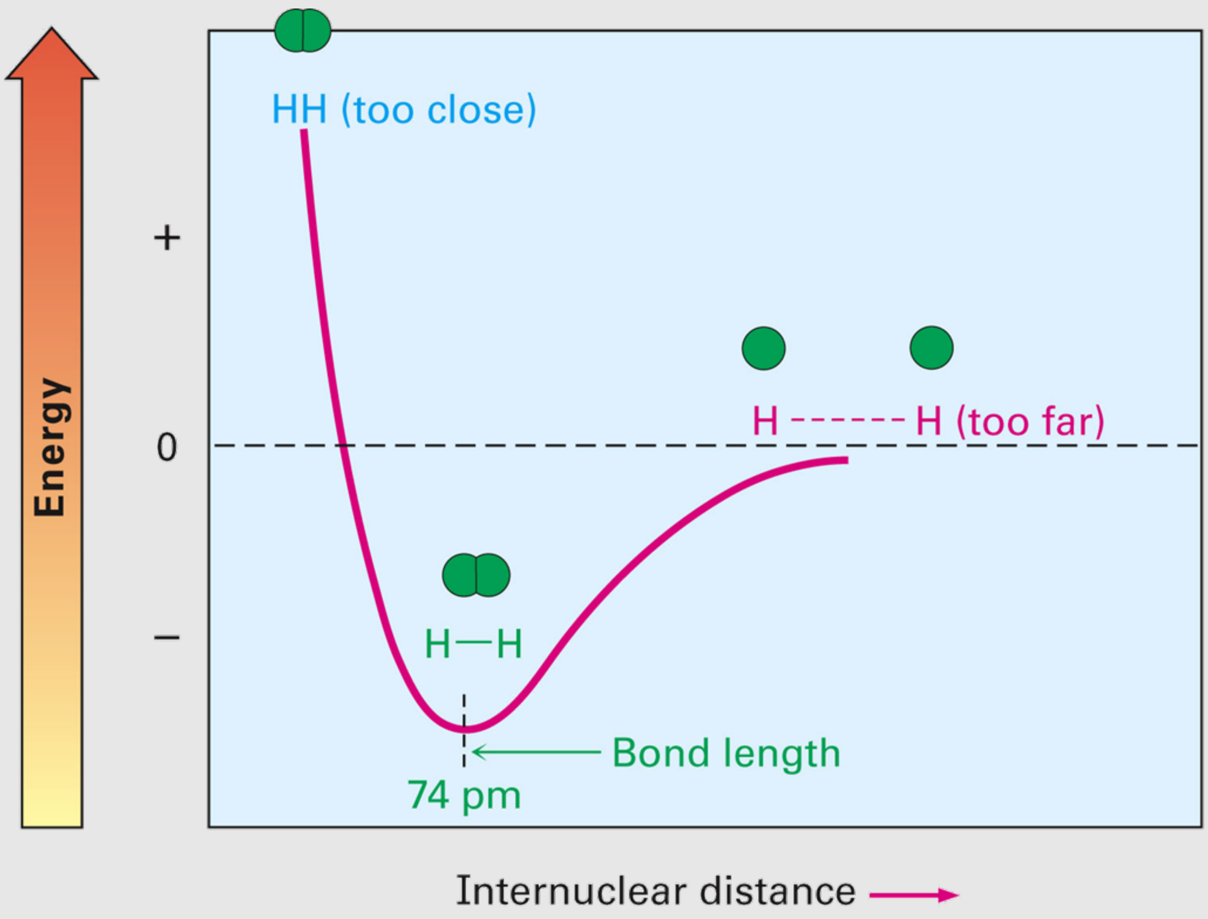
Bond Energy

- Reaction 2 H· → H_2 releases 436 kJ/mol
  - i.e., product has 436 kJ/mol less energy than two atoms: H–H has **bond strength** of 436 kJ/mol



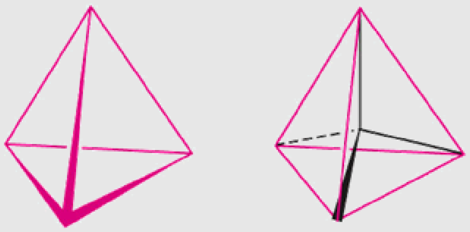
Bond Energy

- 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

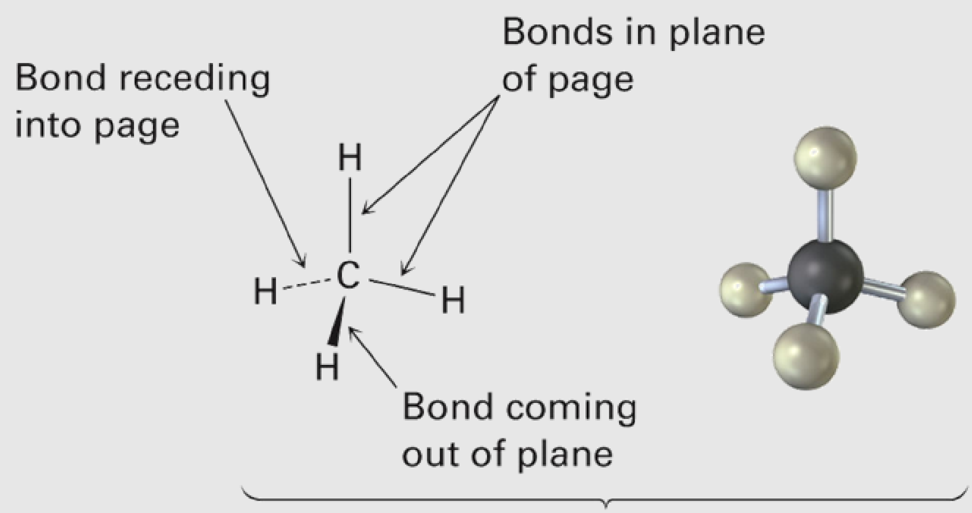


Describing Chemical Bonding Theory

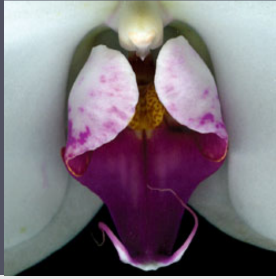
- Kekulé and Couper independently observed that carbon always has four bonds
- van't Hoff and Le Bel proposed that the four bonds of carbon have specific spatial directions
  - Atoms surround carbon as corners of a tetrahedron



A regular tetrahedron

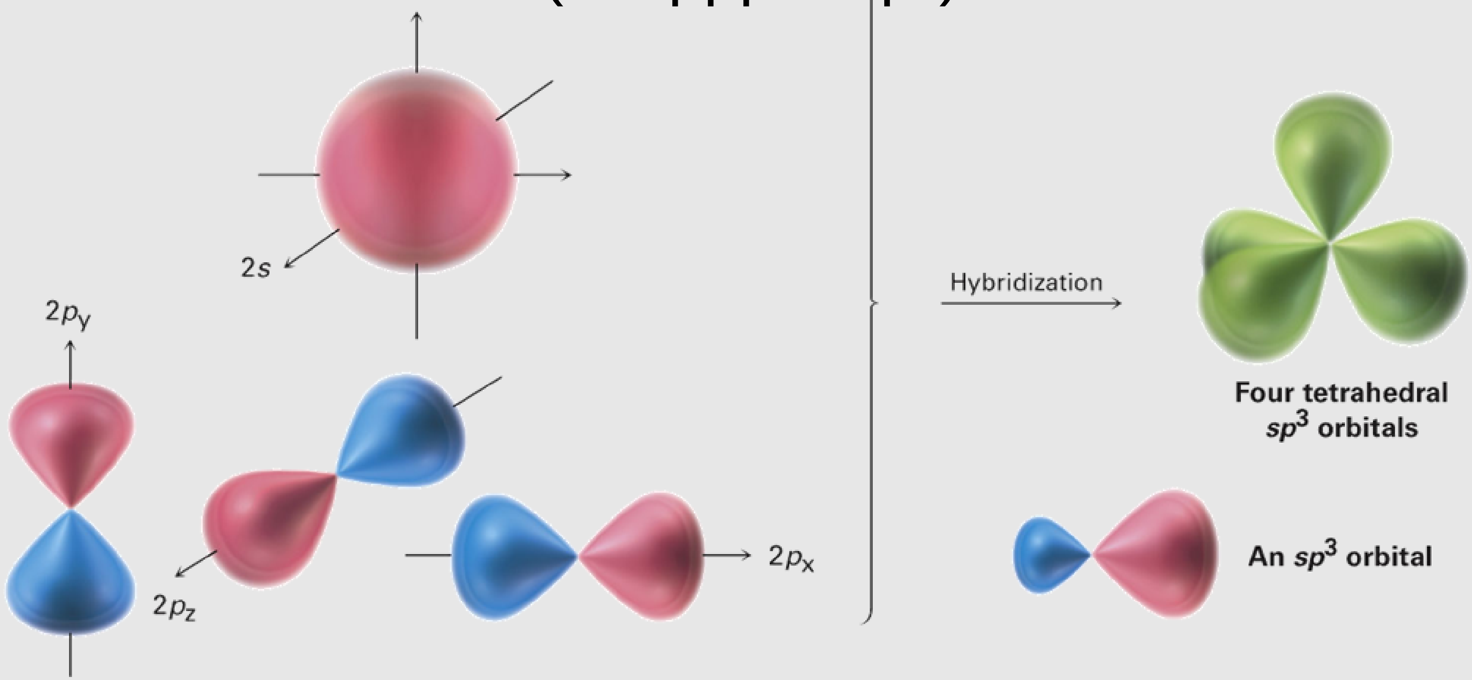


A tetrahedral carbon atom

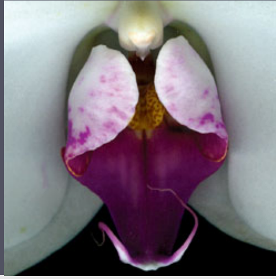


1.6 *sp*^{3} Orbitals and the Structure of Methane

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

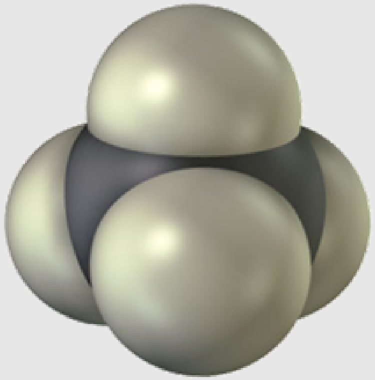


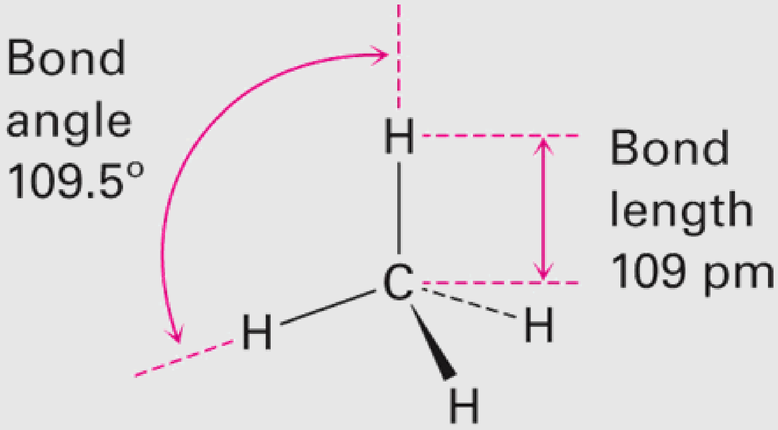
Linus Pauling (1931): his picture near men's bathroom across from elevators

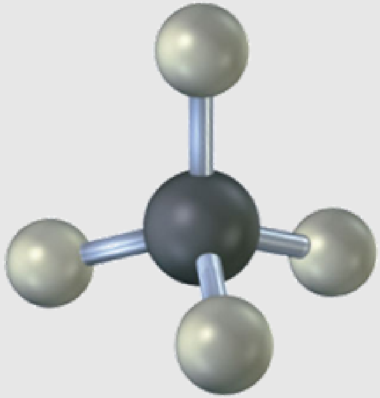


The Structure of Methane

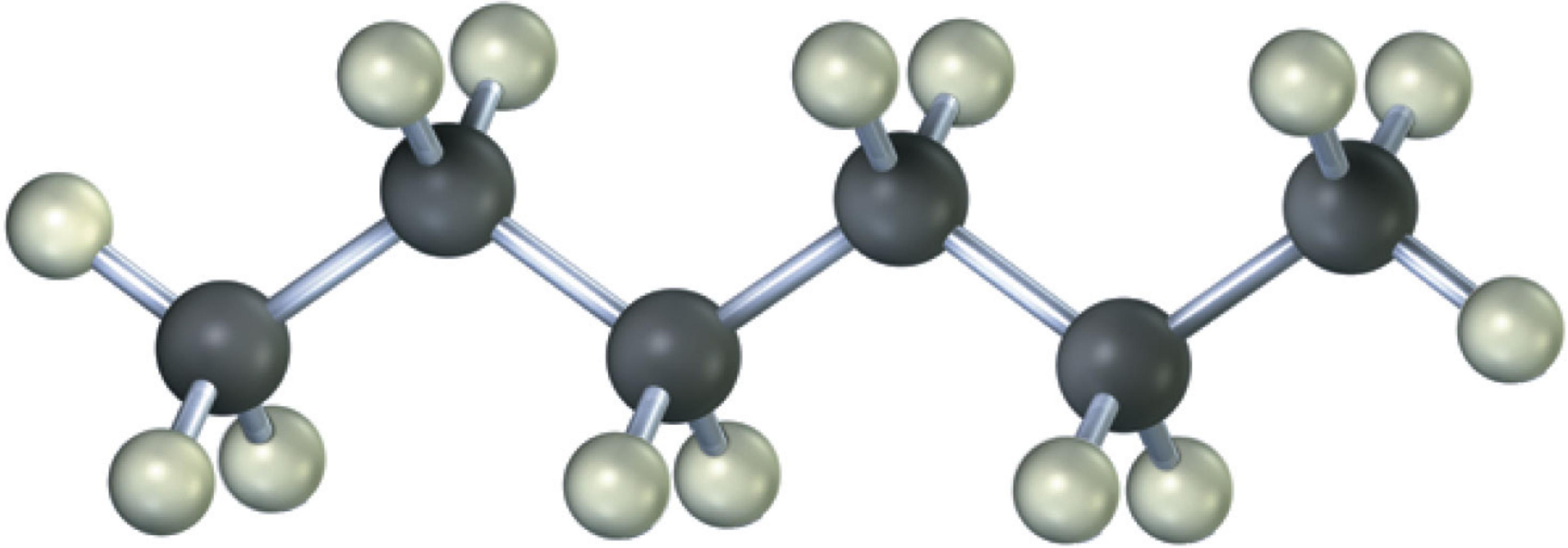
- *sp*^{3} orbitals on C overlap with 1*s* orbitals on 4 H atoms to form four identical C-H bonds
- Each C–H bond has a strength of 439 kJ/mol and length of 109 pm
- **Bond angle**: each H–C–H is 109.5° : the *tetrahedral angle*.







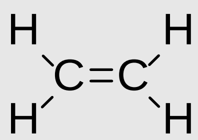
1.7 *sp*^{3} Orbital-based Structure of Hexane



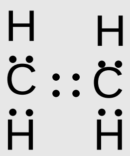
Hexane

1.8 *sp*^{2} Orbitals and the Structure of Ethylene

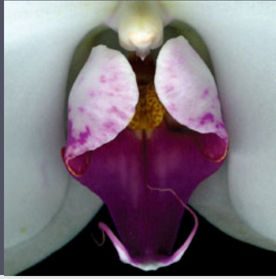
- Some Representations of Ethylene are given
  - To explain planar geometry and trigonal shape about C's in ethylene



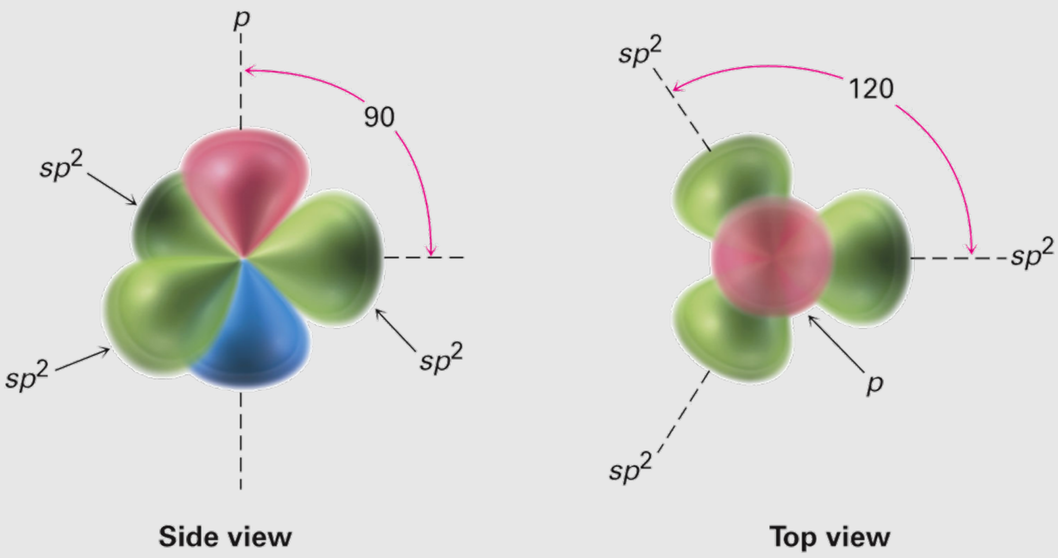
$H_2C{=}CH_2$



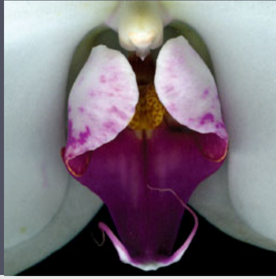
1.8 *sp*^{2} Orbitals and the Structure of Ethylene



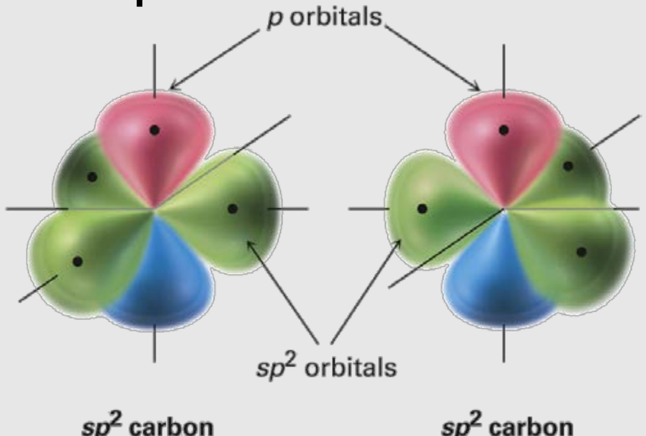
- ***sp*^{2} hybrid orbitals:** 2*s* orbital combines with *two* 2*p* orbitals, giving 3 orbitals (s + pp = sp^2). This results in a double bond.
- *sp*^{2} orbitals are in a plane with120° angles
- Remaining *p* orbital is perpendicular to the plane



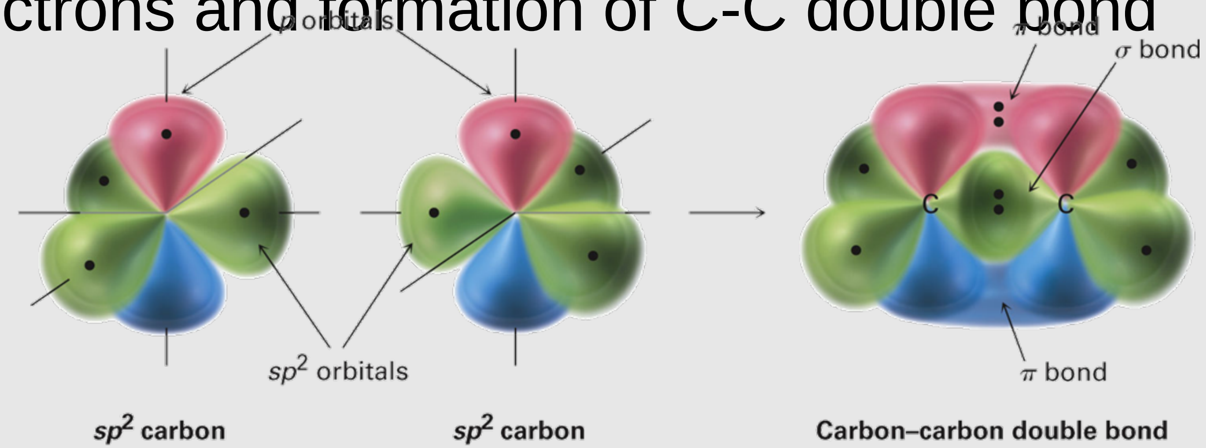
Bonds From sp^2 Hybrid Orbitals



- Two sp^2-hybridized orbitals overlap to form a σ bond
- *p* orbitals overlap *side-to-side* to formation a **pi (π) bond**

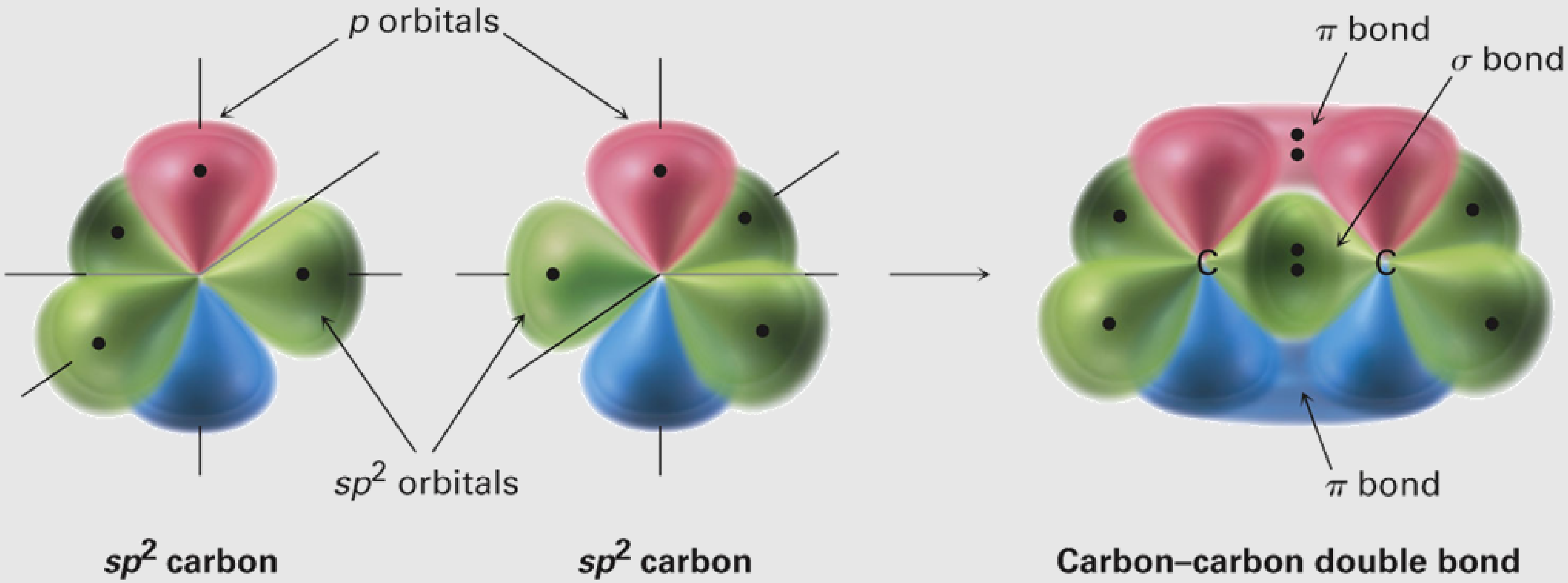


- sp^2–sp^2 σ bond and 2*p*–2*p* π bond result in sharing four electrons and formation of C-C double bond

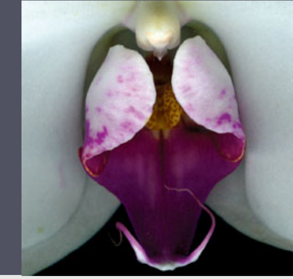


Bonds From sp^2 Hybrid Orbitals

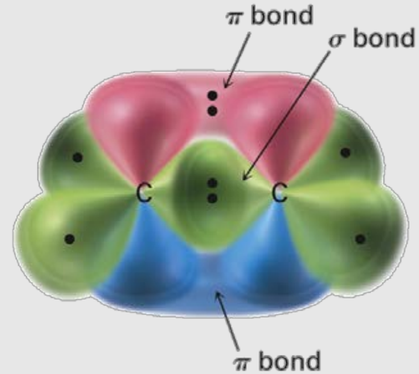
- Electrons in the σ bond are centered between nuclei
- Electrons in the π bond occupy regions are on either side of a line between nuclei

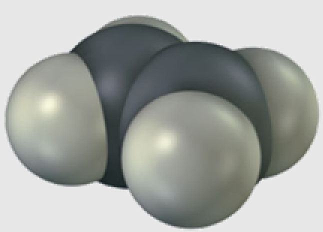


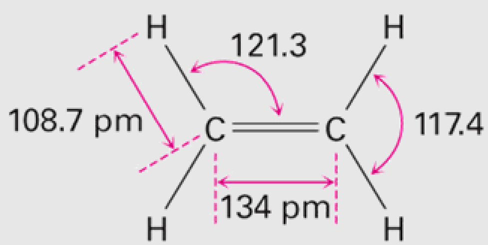
Structure of Ethylene

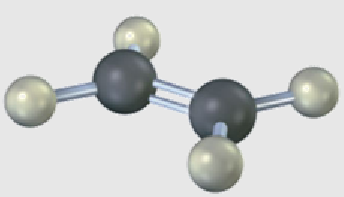


- H atoms form σ bonds with four sp^2 orbitals
- H–C–H and H–C–C bond angles of about 120°
- C–C double bond in ethylene shorter and stronger than single bond in ethane
- Ethylene C=C bond length 134 pm (C–C 154 pm)



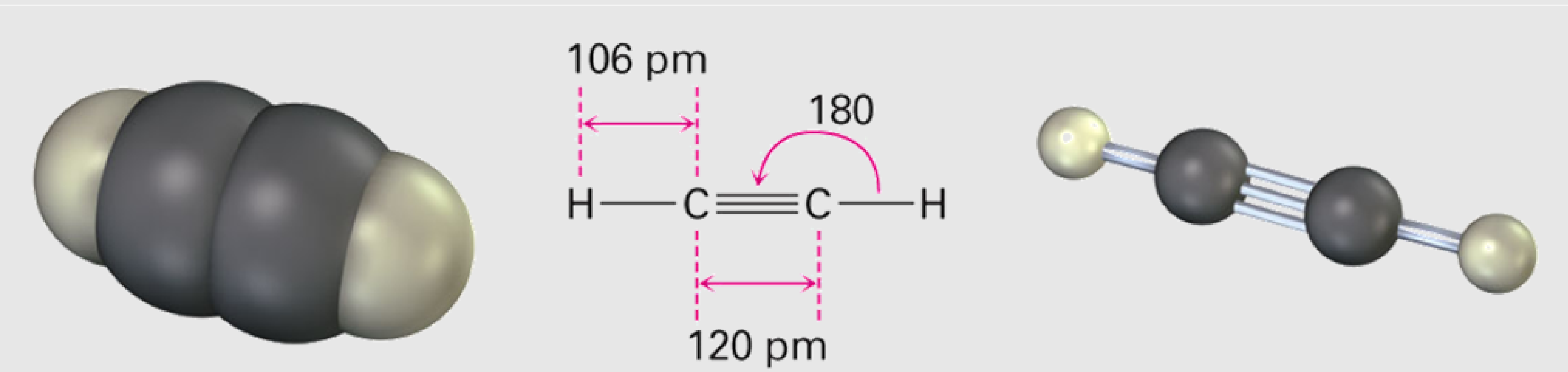






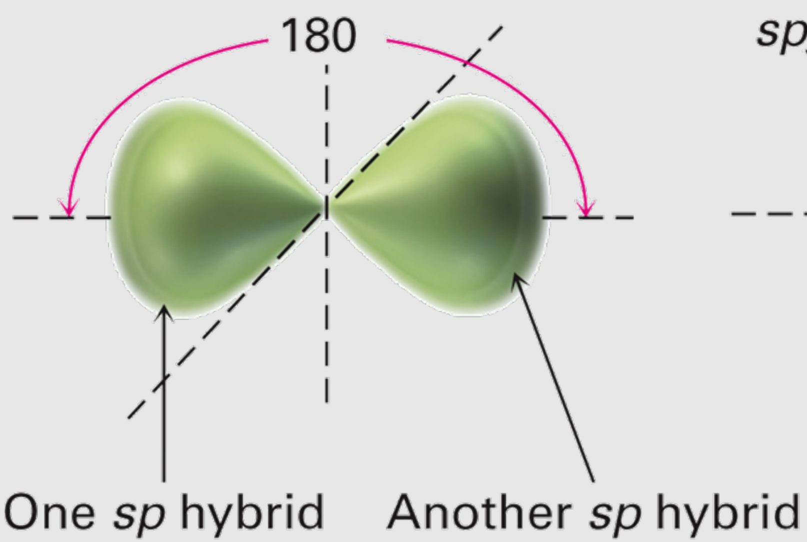
1.9 *sp* Orbitals and the Structure of Acetylene

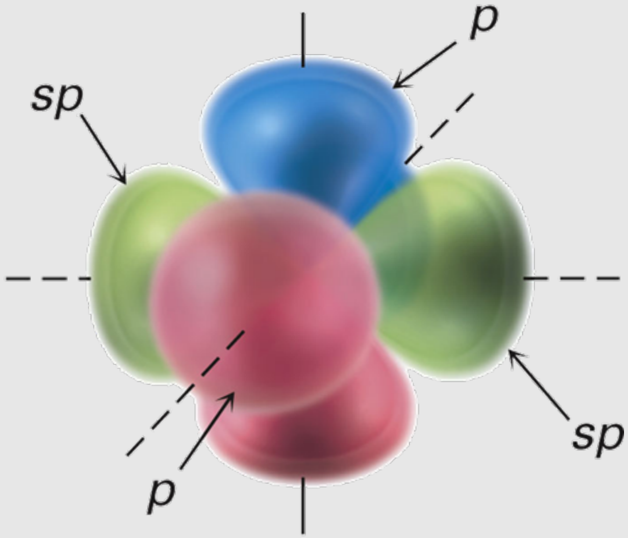
- Sharing of six electrons forms C ≡C
- Two *sp* orbitals form σ bonds with hydrogens



sp Orbitals and the Structure of Acetylene

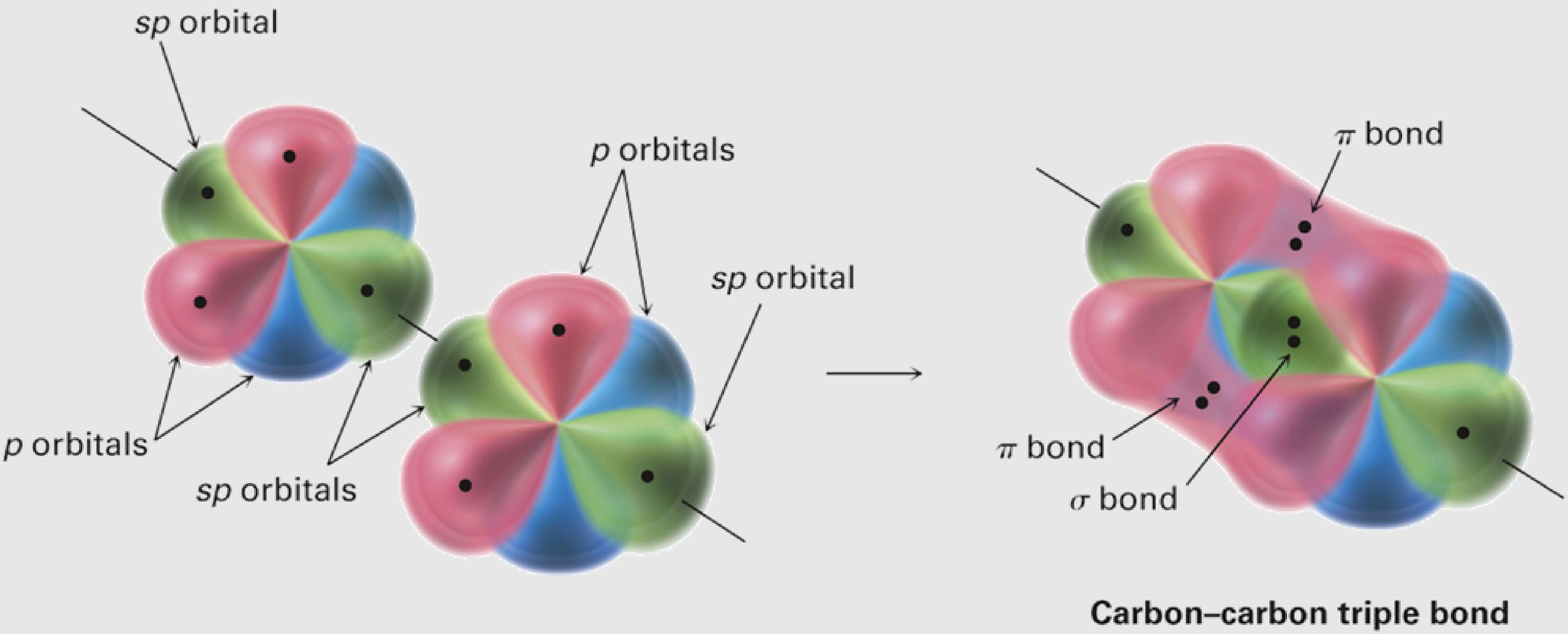
- C-C a *triple* bond sharing six electrons
- Carbon 2*s* orbital hybridizes with a single *p* orbital giving two *sp* hybrids
  - two *p* orbitals remain unchanged
- *sp* orbitals are linear, 180° apart on *x*-axis
- Two *p* orbitals are perpendicular on the *y*-axis and the *z*-axis





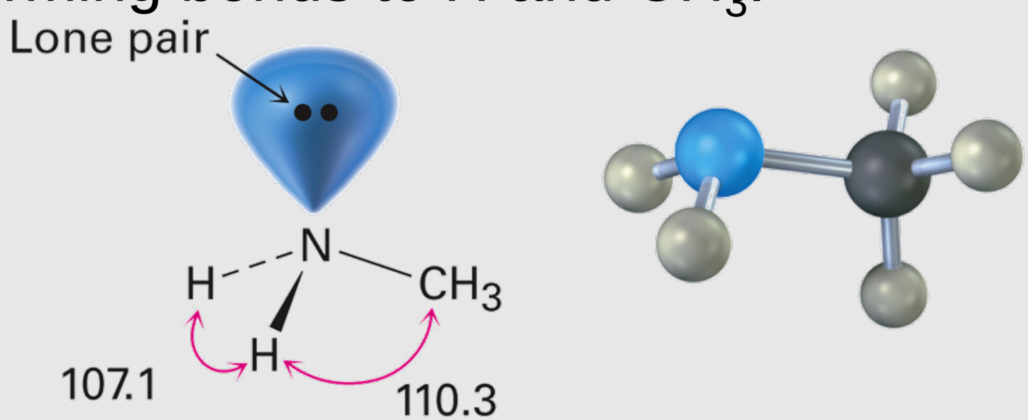
Orbitals of Acetylene

- 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



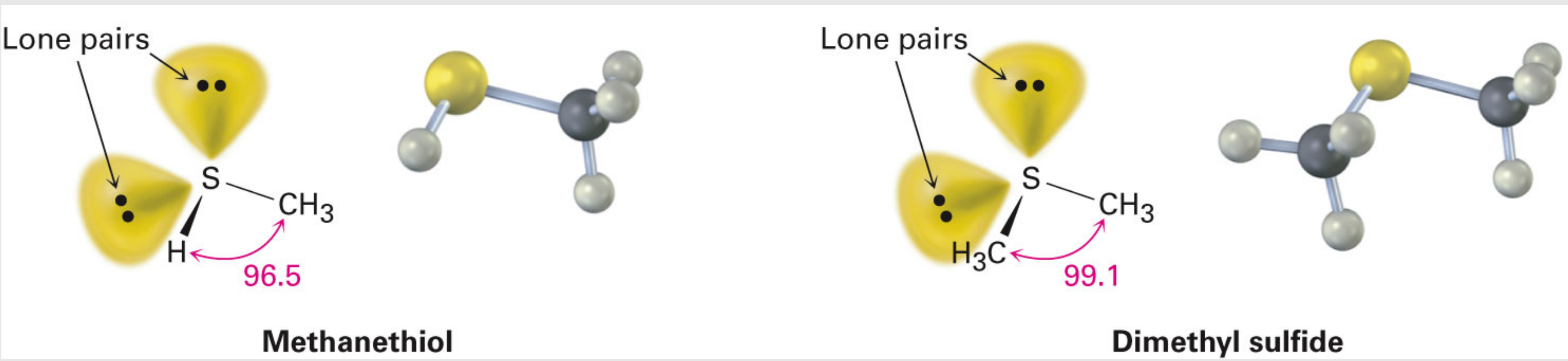
1.10 Hybridization of Nitrogen and Oxygen

- 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.



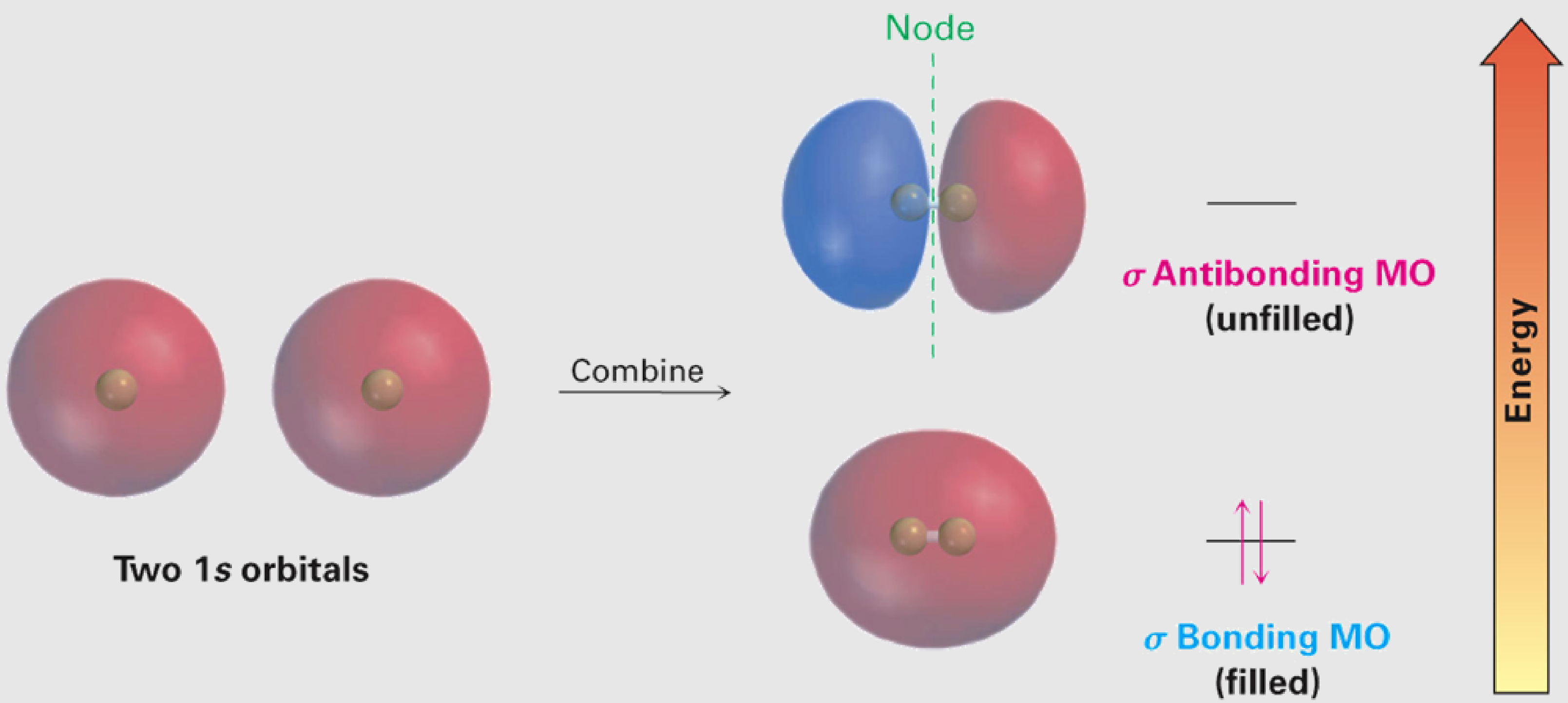
Methylamine

1.10 Hybridization of Sulfur



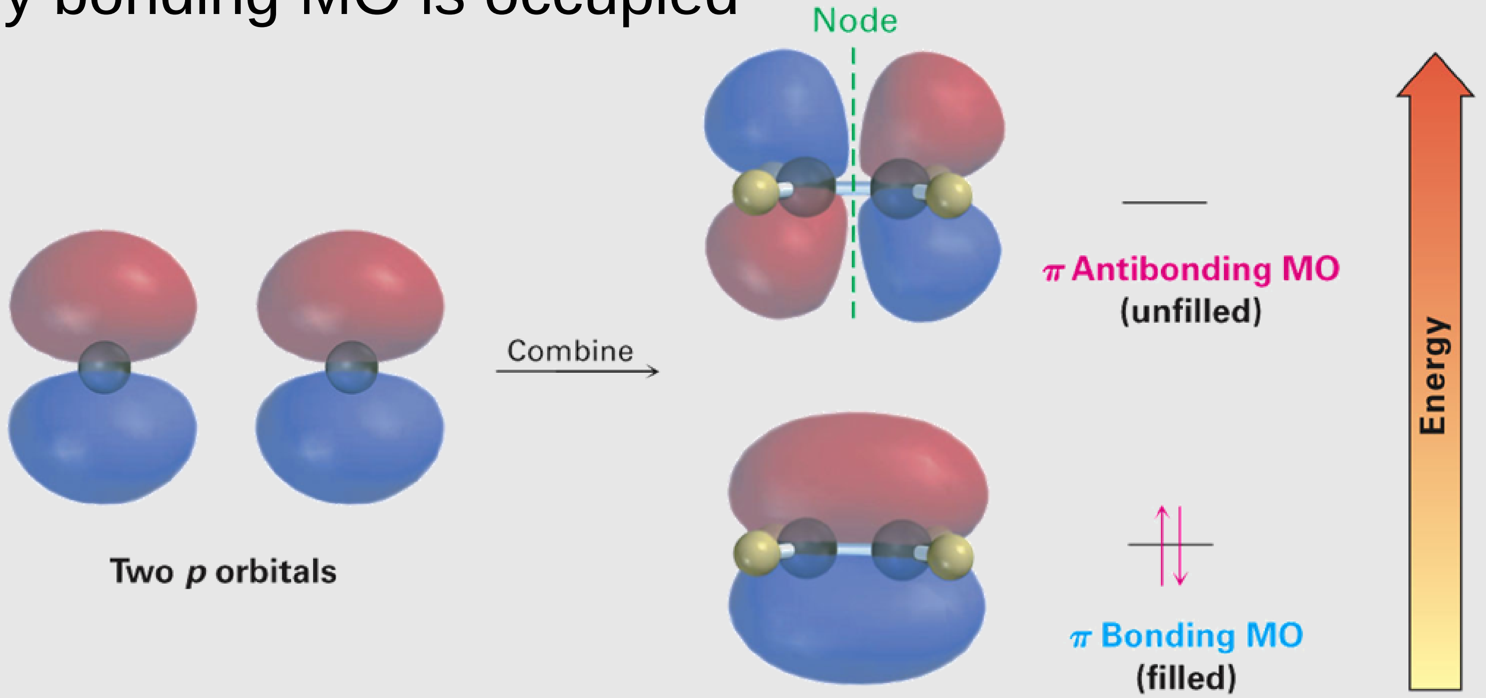
1.11 Describing Chemical Bonds: Molecular Orbital Theory

- 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

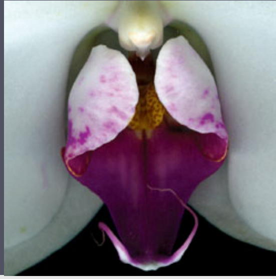


Molecular Orbitals in Ethylene

- 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

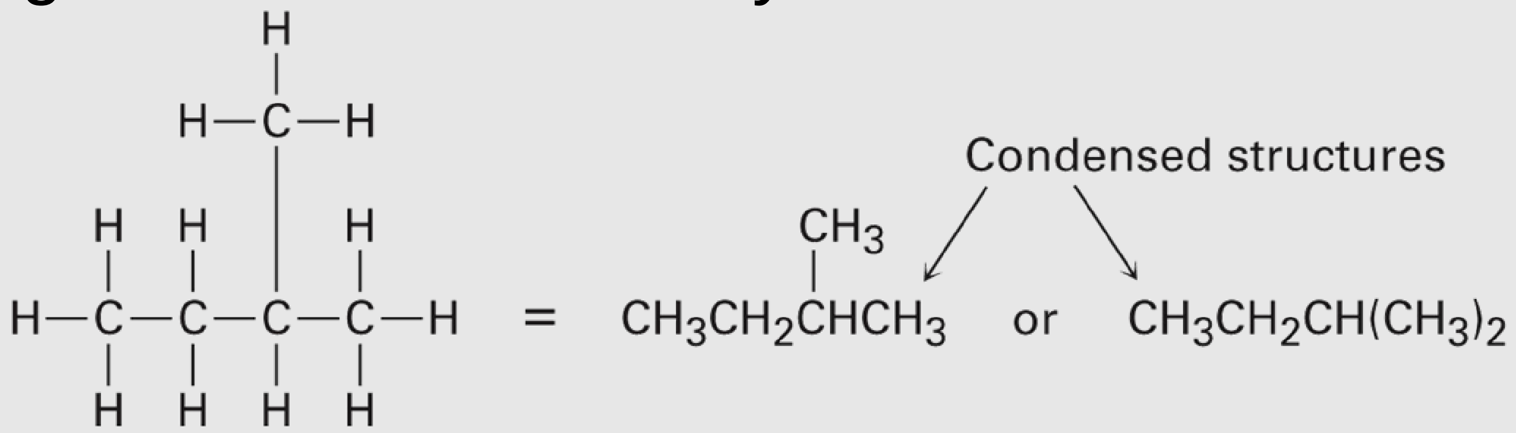


1.12 Drawing Structures (Avoided in this Class)



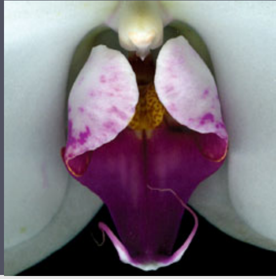
- Drawing every bond in organic molecule can become tedious.
- Several shorthand methods have been developed to write structures.
- Condensed structures don't have C-H or C-C single bonds shown. They are understood.

e.g.



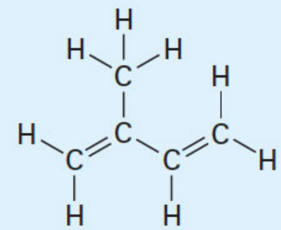
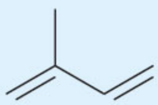
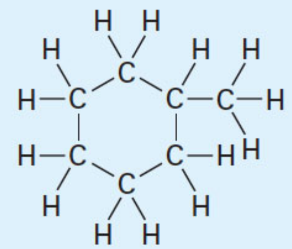
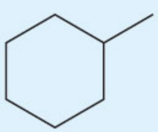
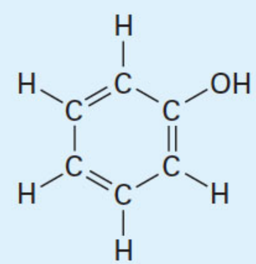
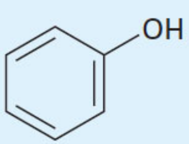
2-Methylbutane

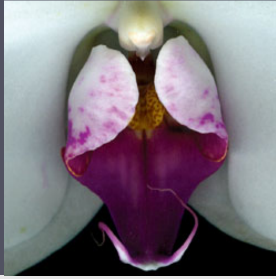
Drawing Skeletal Structures (Commonly Used)



General Rules:

1) Carbon atoms aren't usually shown

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

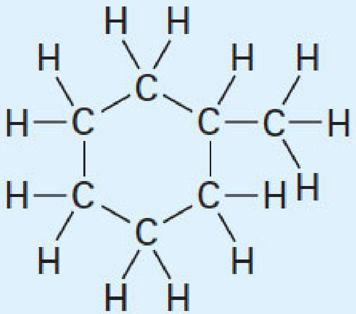


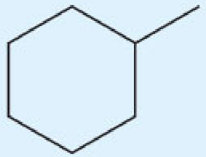
Drawing Skeletal Structures (Commonly Used)

General Rules:

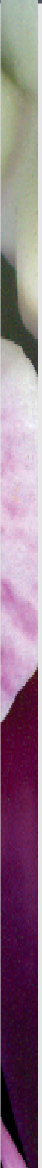
2) Instead a carbon atom is assumed to be at each intersection of two lines (bonds) and at the end of each line.

Methylcyclohexane, C_7H_{14}





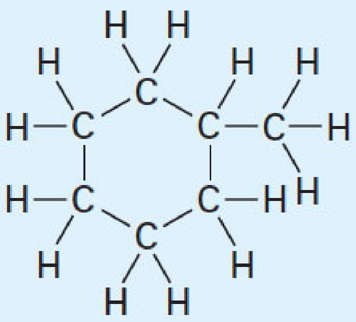
Drawing Skeletal Structures (Commonly Used)

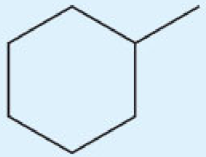


General Rules:

3) Hydrogen atoms bonded to carbon aren't shown.

Methylcyclohexane, C_7H_{14}



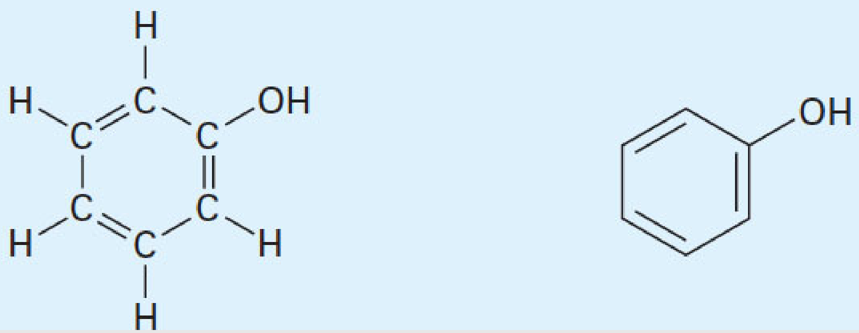


Drawing Skeletal Structures (Commonly Used)

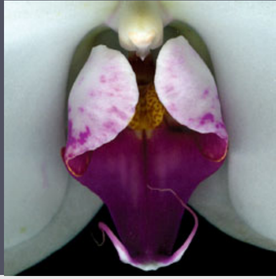
General Rules:

4) Atoms other than carbon and hydrogen ARE shown

Phenol, C_6H_6O

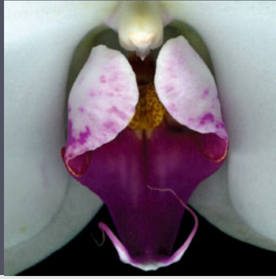


Summary



- **Organic chemistry** – chemistry of carbon compounds
- **Atom**: charged nucleus containing positively charged protons and netrually charged neutrons 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 (Continued)



- **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

Let’s Work a Problem

Draw an electron-dot structure for acetonitrile, C_2H_3N, which contains a carbon-nitrogen triple bond. How many electrons does the nitrogen atom have in its outer shell ? How many are bonding, and how many are non-bonding?

Answer

To address this question, we must realize that the nitrogen will contain 8 electrons in its outer shell. Six will be used in the C-N triple bond (shaded box), and two are non-bonding