CHEMISTRY 31

- Organic Chemistry Lecture I

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What is Organic Chemistry?

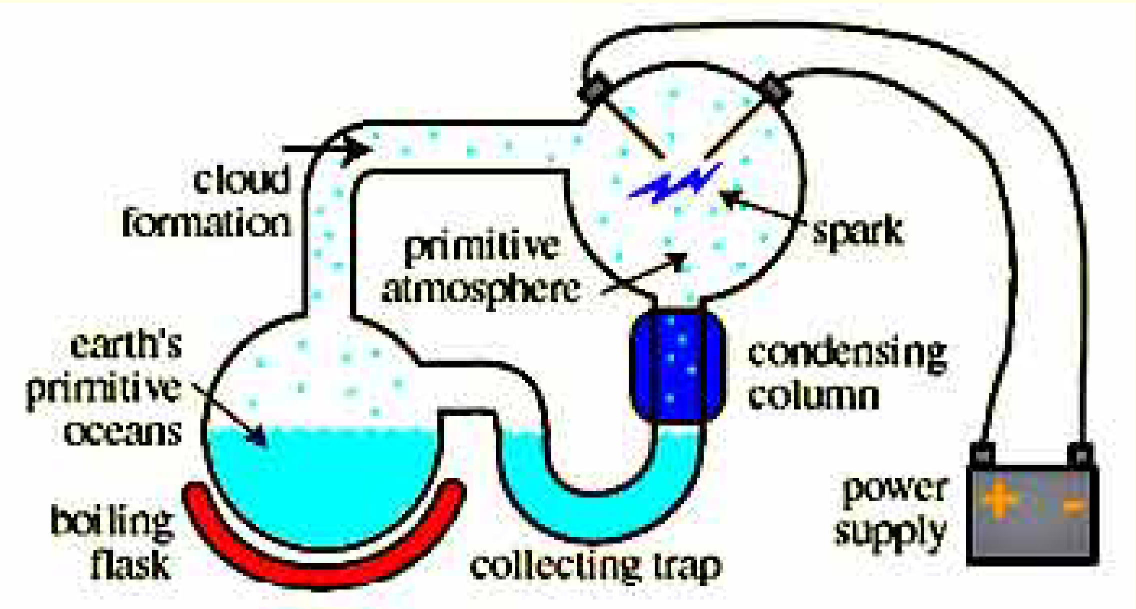
- 1780's
  Chemistry of compounds from living organisms

- Vitalism: 1750-1850
  Inorganic compounds – non-living source
  Organic compounds – living source

- August Kekule (1861)
  Organic chemistry = a study of the compounds of carbon

Origins of Life

- Stanley Miller 1950



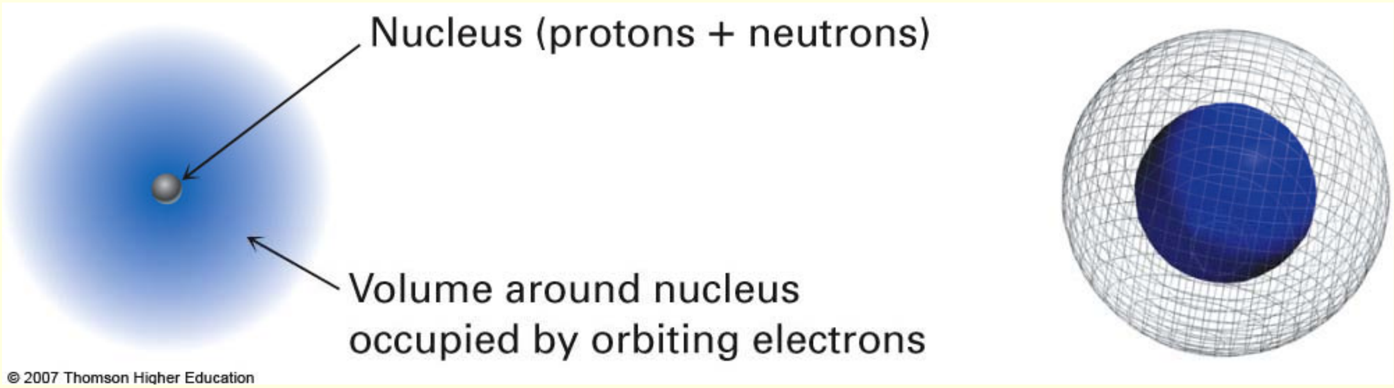
Synthesis of amino acids, formaldehyde, purines and pyrimidines from earth's primordial atmosphere (H_2, H_2O, O_2, NH_3, CO_2, CH_4) and static discharge

Organic Chemist's View of the Periodic Table of Elements

1 **H** 1.00794						*Organic Chemist's View of the Periodic Table of Elements*											6 **C** 12.011
3 **Li** 6.941	6 **C** 12.011											5 **B** 10.811	6 **C** 12.011	7 **N** 14.0067	8 **O** 15.9994	9 **F** 18.99840	6 **C** 12.011
11 **Na** 22.98977	12 **Mg** 24.305											13 **Al** 26.98154	14 **Si** 28.0855	15 **P** 30.97376	16 **S** 32.066	17 **Cl** 35.4527	6 **C** 12.011
19 **K** 39.0983	20 **Ca** 40.078	6 **C** 12.011	22 Ti 47.88	6 **C** 12.011	24 Cr 51.9961	25 Mn 54.9380	26 Fe 55.847	6 **C** 12.011	6 **C** 12.011	29 Cu 63.546	30 Zn 65.39	6 **C** 12.011	6 **C** 12.011	6 **C** 12.011	6 **C** 12.011	35 **Br** 79.904	6 **C** 12.011
6 **C** 12.011	6 **C** 12.011	6 **C** 12.011	6 **C** 12.011	6 **C** 12.011	6 **C** 12.011	6 **C** 12.011	6 **C** 12.011	6 **C** 12.011	46 Pd 106.42	6 **C** 12.011	6 **C** 12.011	6 **C** 12.011	6 **C** 12.011	6 **C** 12.011	6 **C** 12.011	53 **I** 126.9045	6 **C** 12.011
6 **C** 12.011	6 **C** 12.011	6 **C** 12.011	6 **C** 12.011	6 **C** 12.011	6 **C** 12.011	6 **C** 12.011	76 Os 190.2	6 **C** 12.011	6 **C** 12.011	6 **C** 12.011	80 Hg 200.59	6 **C** 12.011	6 **C** 12.011	6 **C** 12.011	6 **C** 12.011	6 **C** 12.011	6 **C** 12.011
6 **C** 12.011	6 **C** 12.011	6 **C** 12.011	6 **C** 12.011	6 **C** 12.011	6 **C** 12.011	6 **C** 12.011	6 **C** 12.011	6 **C** 12.011	**110** (269)	**111** (272)	**112** (277)		**114** (285)		**116** (289)		**118** (293)
*Lanthanide Series			6 **C** 12.011	6 **C** 12.011	6 **C** 12.011	6 **C** 12.011	6 **C** 12.011	6 **C** 12.011	6 **C** 12.011	6 **C** 12.011	6 **C** 12.011	6 **C** 12.011	6 **C** 12.011	6 **C** 12.011	6 **C** 12.011	6 **C** 12.011	
†Actinide Series			6 **C** 12.011	6 **C** 12.011	6 **C** 12.011	6 **C** 12.011	6 **C** 12.011	6 **C** 12.011	6 **C** 12.011	6 **C** 12.011	6 **C** 12.011	6 **C** 12.011	6 **C** 12.011	6 **C** 12.011	6 **C** 12.011	6 **C** 12.011	

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

6
C
12.011

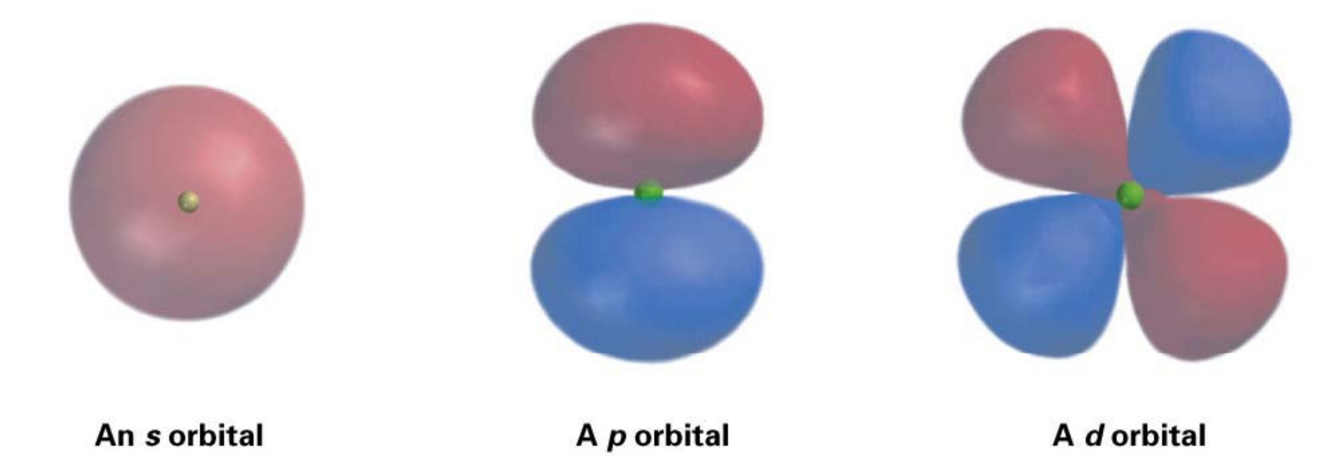
- The *atomic number* (*Z*) is the number of protons in the atom's nucleus (neutral atom then has same number of electrons)
- The *mass number* (*A*) is the number of protons plus neutrons
- All the atoms of a given element have the same atomic number
- **Isotopes** are atoms of the same element that have different numbers of neutrons and therefore different mass numbers (^{13}C, ^{2}H or D)
- 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

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



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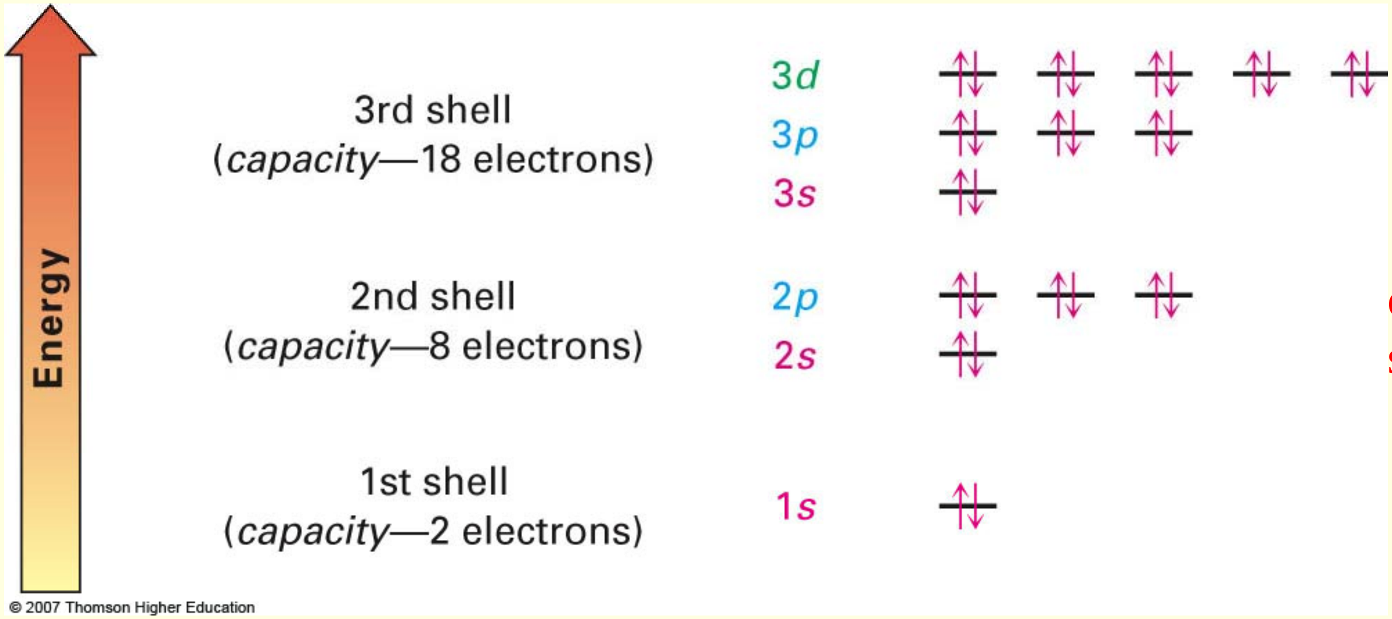
Orbitals and Shells

- 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



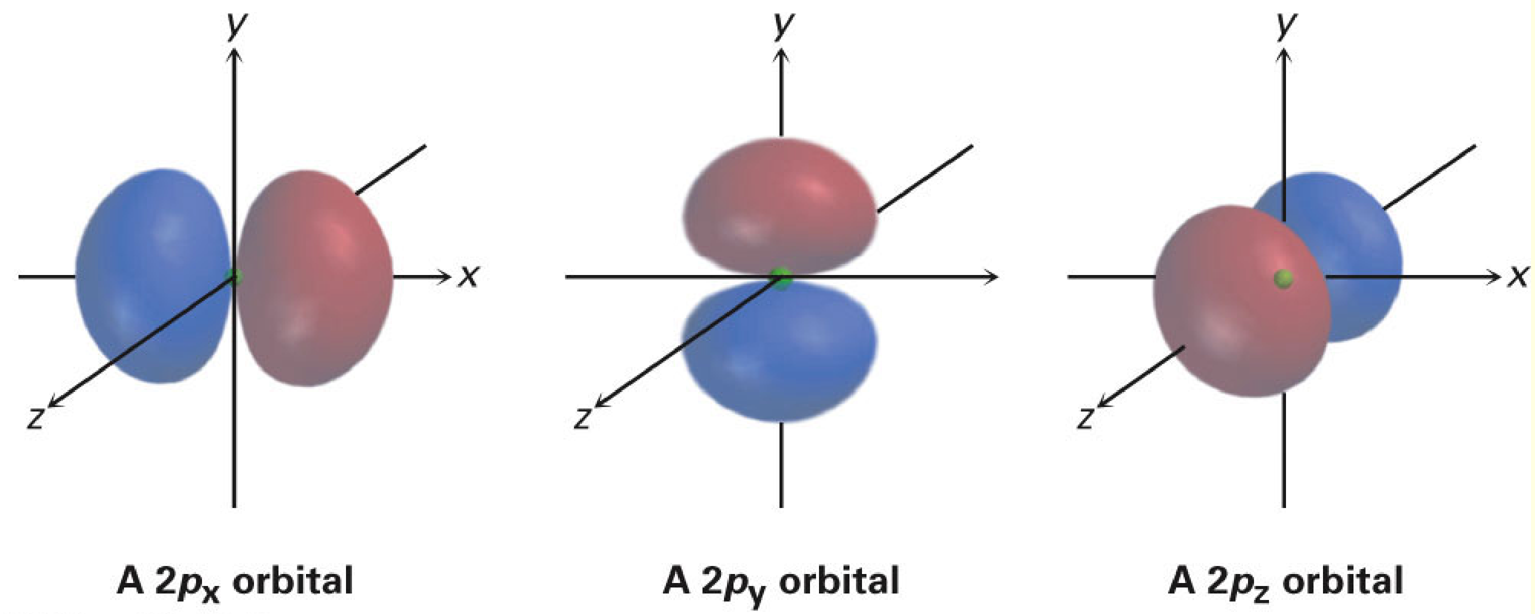
valence shell

octet for second row

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**



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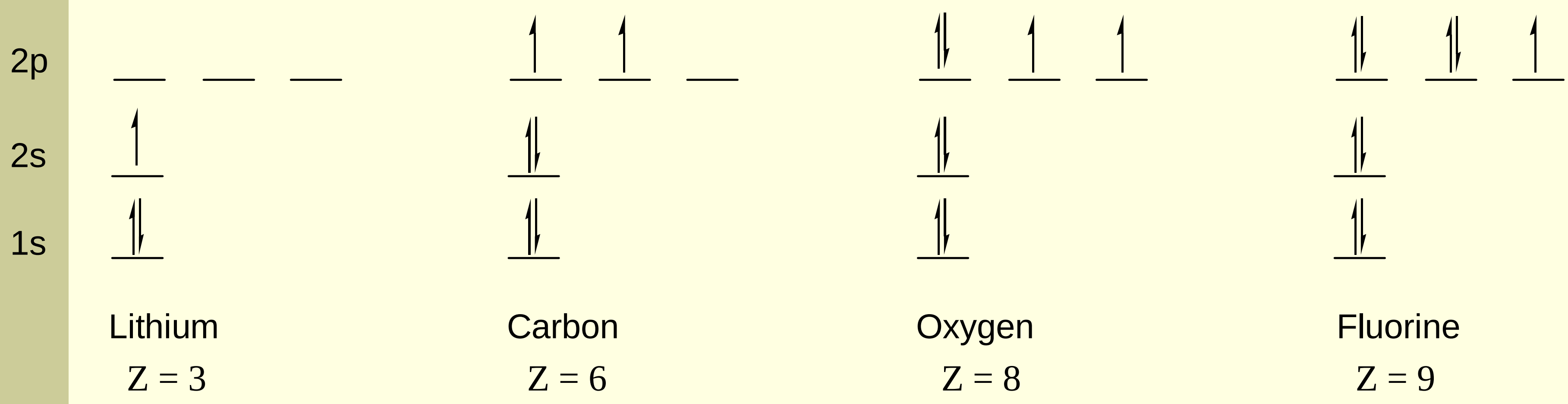
Atomic Structure: Electron Configurations

- **Ground-state electron configuration** 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. 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*).

Electron Configuration and Bonding



How do atoms fill octet? BONDING

Ionic = bonds from exchanging electrons

Covalent = bonds from sharing electrons

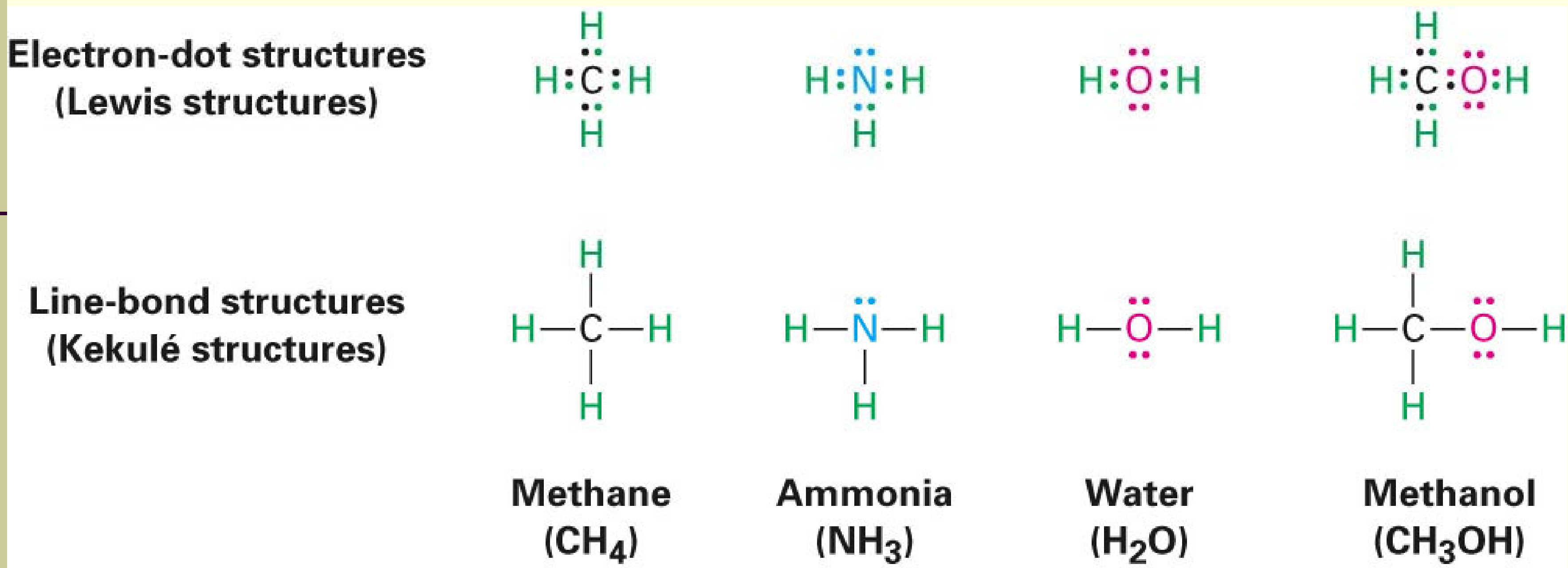
Valency = number of covalent bonds needed to fill valence octet

C = tetravalent N = trivalent O = divalent H = monovalent

Drawing Structures and Bonds

- **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)

  (third row atoms can expand beyond octet)



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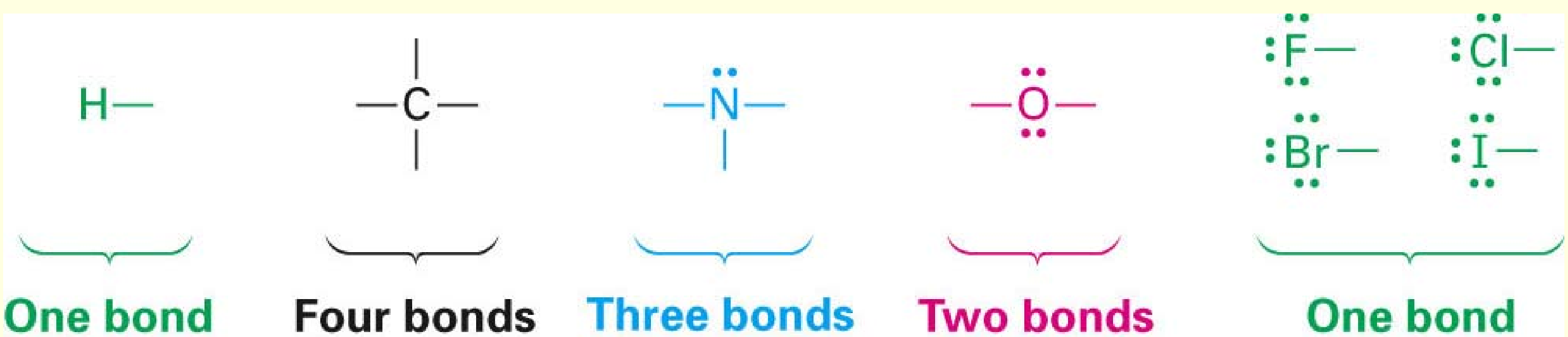

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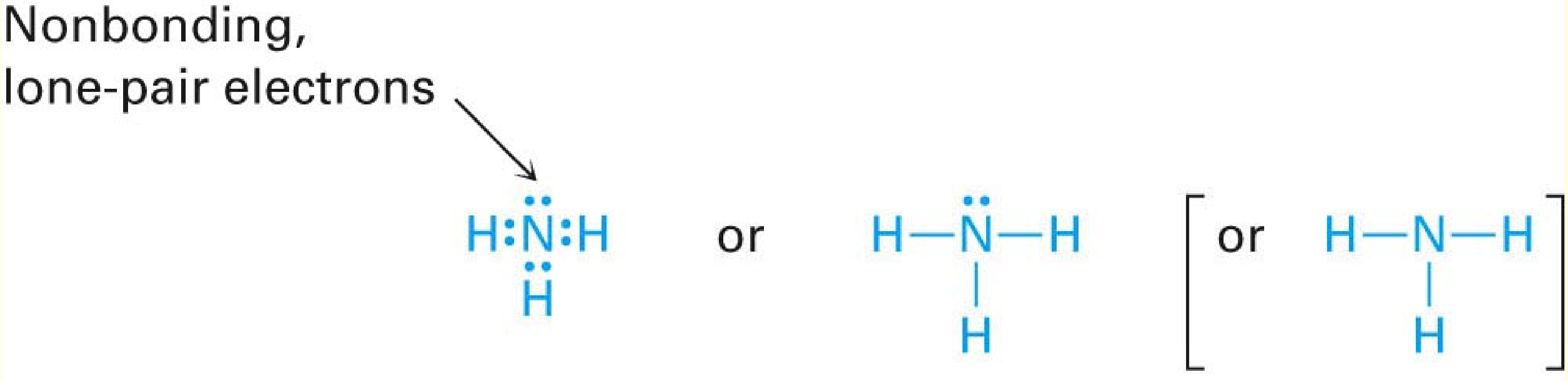
- Valence electrons not used in bonding are called **nonbonding electrons**, or **lone-pair electrons**
  - Nitrogen atom in ammonia (NH_3)
    - Shares six valence electrons in three covalent bonds and remaining two valence electrons are nonbonding lone pair



Ammonia

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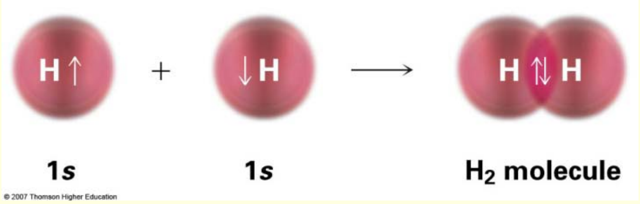
Bonding Model #1: Valence Bond Theory

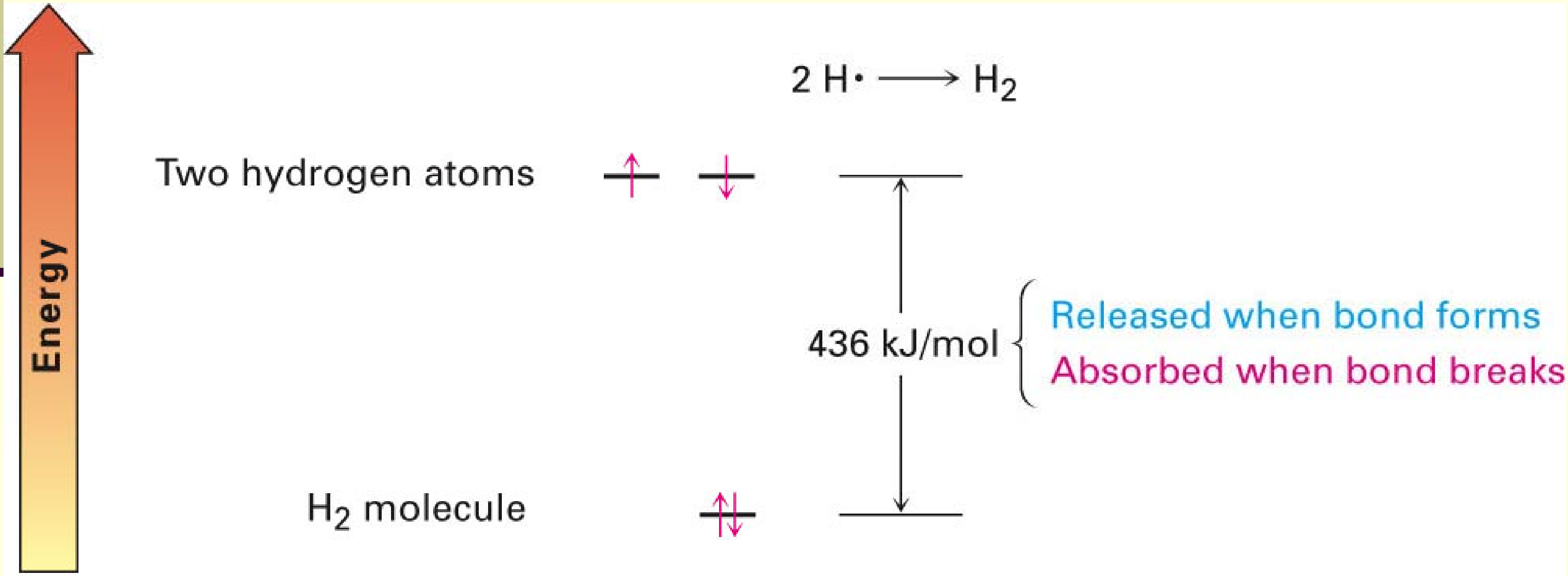
- Singly occupied orbital on one atom *overlaps* a singly occupied orbital on the other atom
- Electrons are paired and localized in the overlapping orbitals and are attracted to nuclei of both atoms
  - H–H bond results from the overlap of two singly occupied hydrogen 1*s* orbitals
  - Certain optimal distance
  - Smaller, more directional orbitals make stronger bonds due to better orbital overlap



pingpong ball - pingpong ball
pingpong ball - basketball
pingpong ball - watermelon

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)



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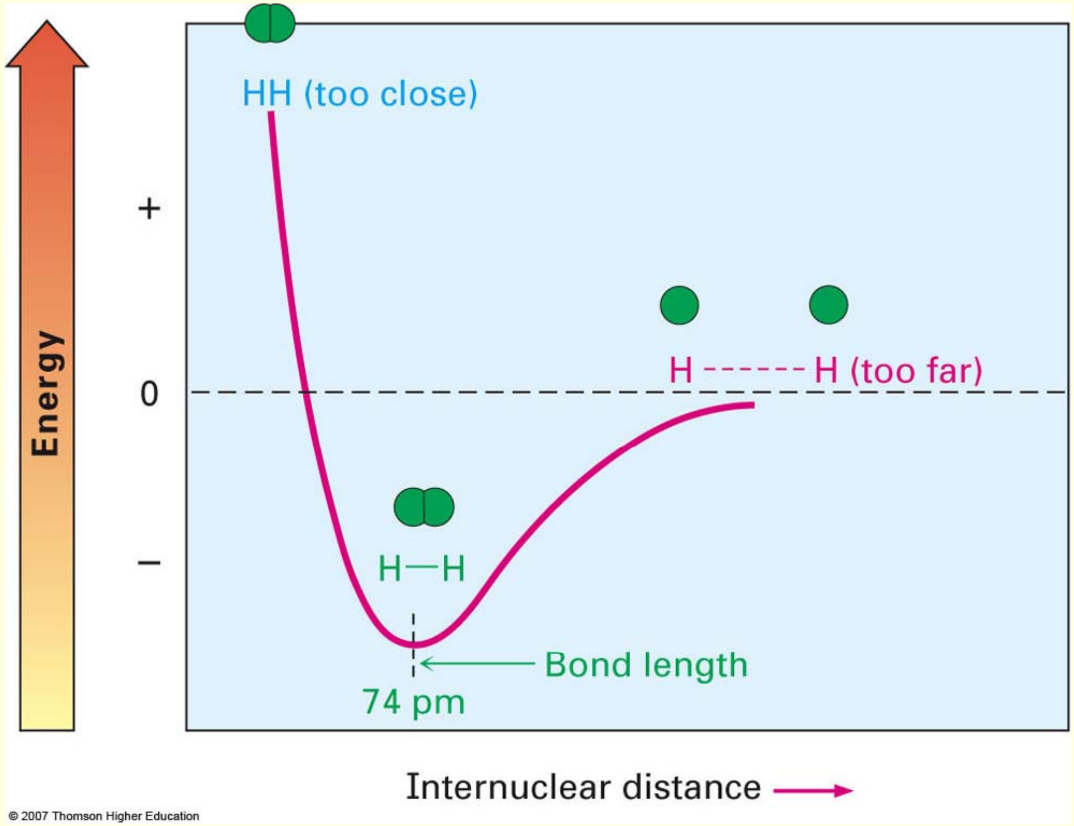
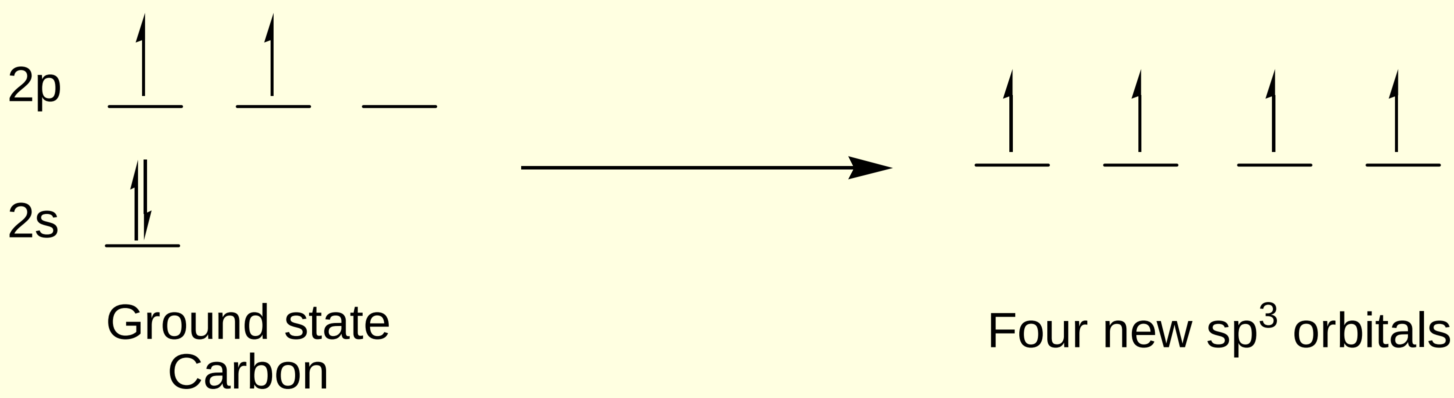
Bond Length

- 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



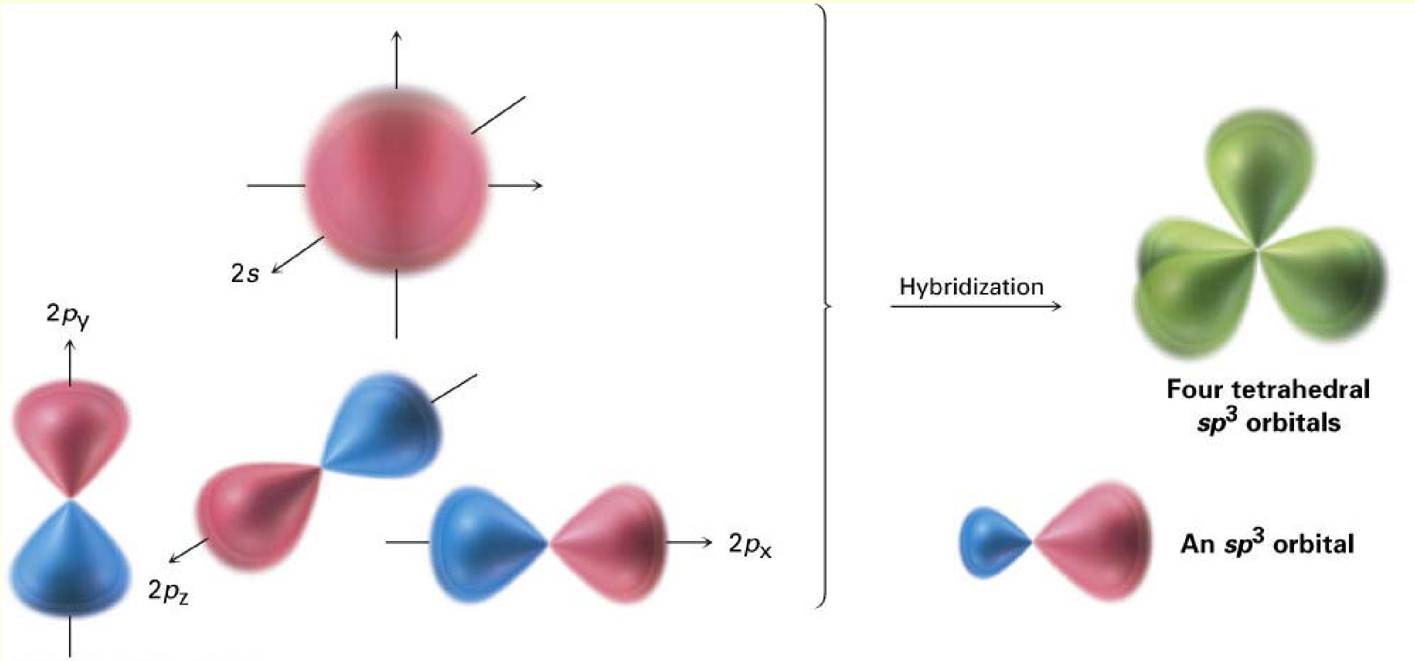
Hybridization for the Carbon Atom



- Why Hybridize?
  1. can now form 4 bonds instead of two to fill octet
  2. more directional orbital (increased s-character) gives stronger bond from better overlap of orbital
  3. maximize separation of electrons (VSEPR)

sp^3 Orbitals

- ***sp*³ hybrid orbitals**: *s* orbital and three *p* orbitals combine to form four equivalent, unsymmetrical, tetrahedral orbitals (sppp = sp^3), Pauling (1931)



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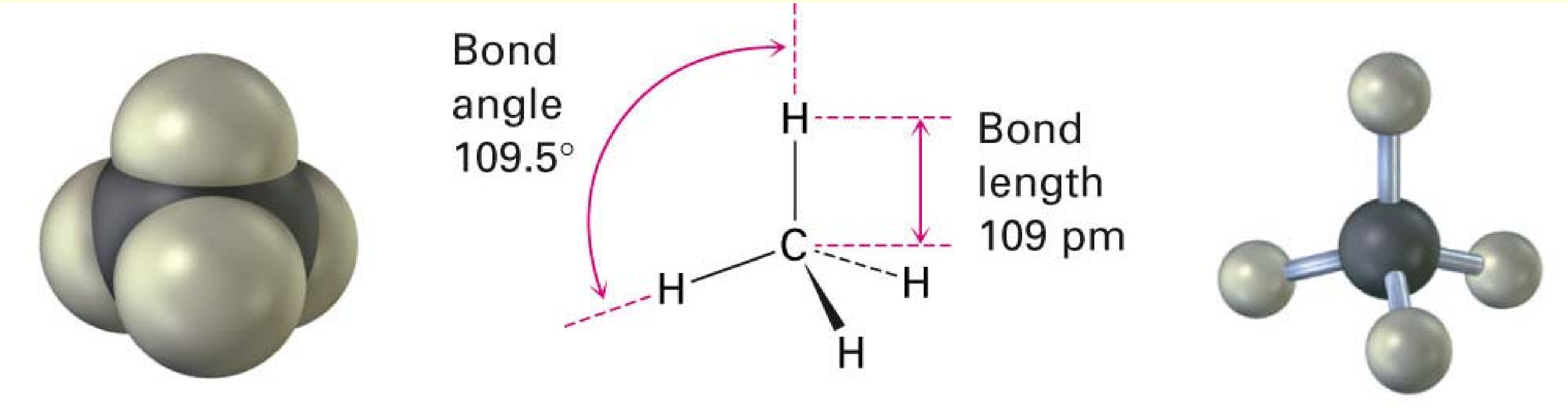
The Structure of Methane

- *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 438 kJ/mol and length of 109 pm
- **Bond angle**: each H–C–H is 109.5°, the *tetrahedral angle*.



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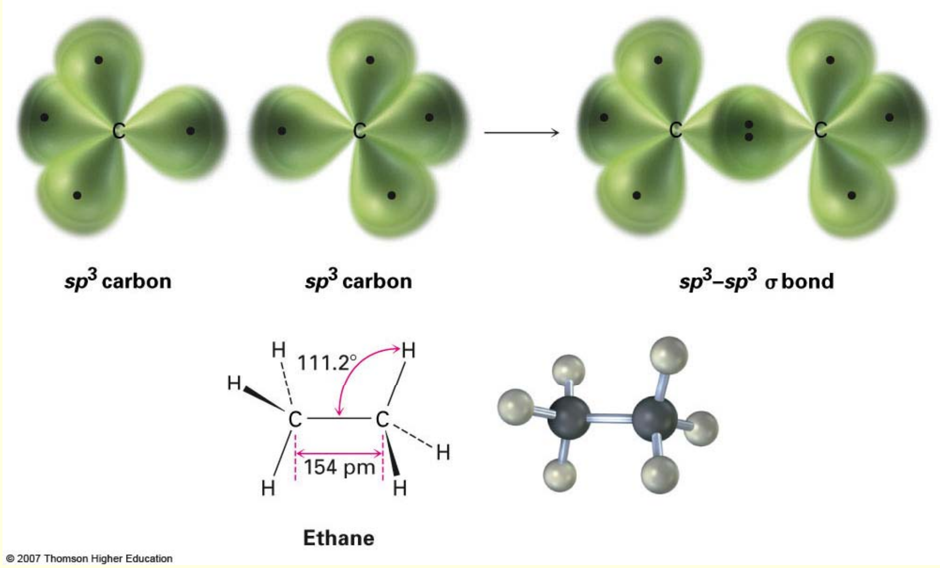
Hybridization: *sp³* Orbitals and the Structure of Ethane

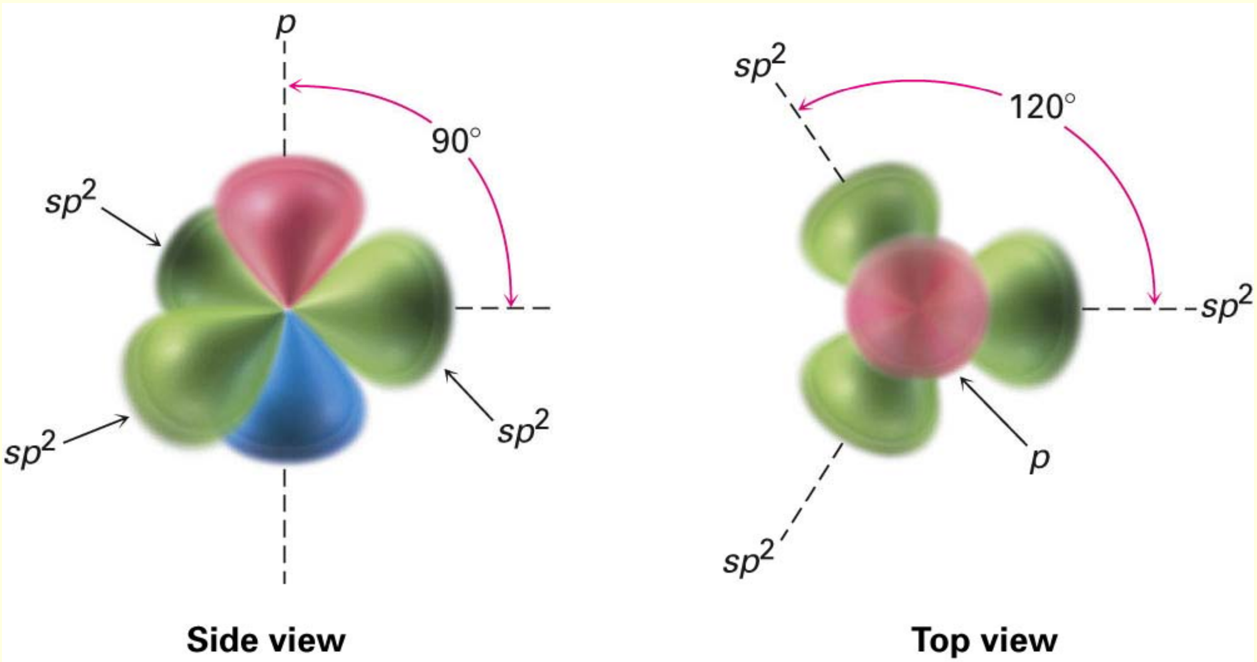
- Two C's bond to each other by σ overlap of an sp^3 orbital from each
- Three sp^3 orbitals on each C overlap with H 1*s* orbitals to form six C–H bonds
- C–H bond strength in ethane 423 kJ/mol
- C–C bond is 154 pm long and strength is 376 kJ/mol
- All bond angles of ethane are tetrahedral



one Csp^3-Csp^3 σ bond
6 Csp^3-H1s σ bonds

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 = 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



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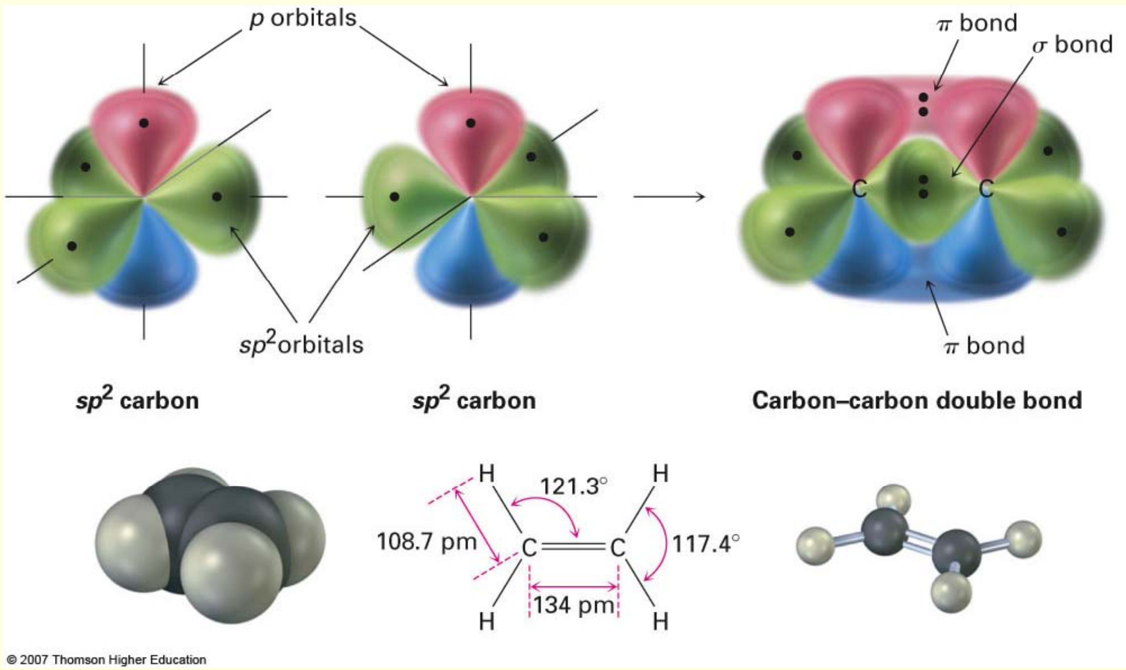
Double Bonds From sp^2 Hybrid Orbitals

- 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
- Electrons in the σ bond are centered between nuclei
- Electrons in the π bond occupy regions of space above and below plane of sigma bond
- As a result of weaker orbital overlap, pi bonds are weaker than sigma bonds

Structure of Ethylene

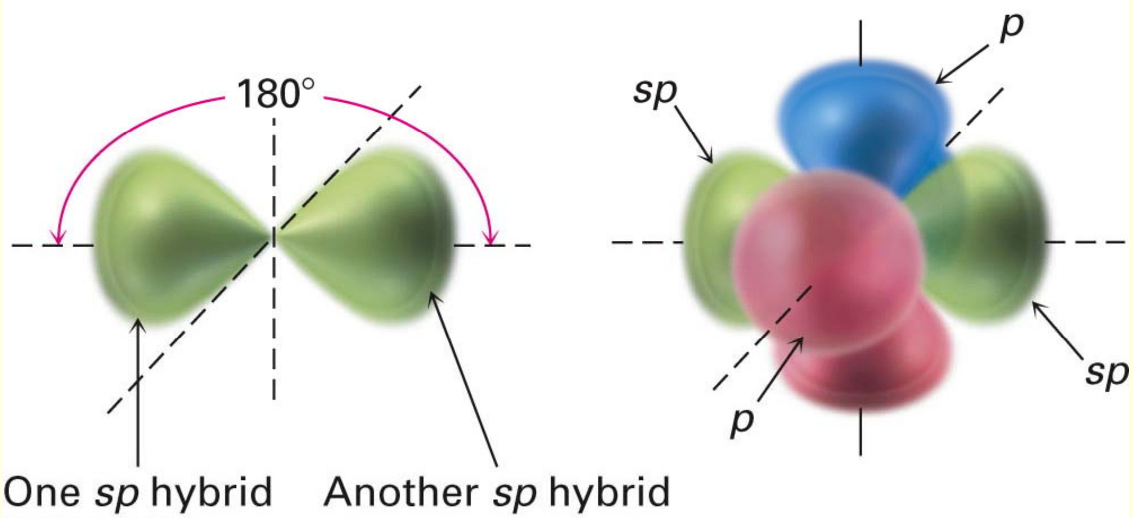
- H atoms form σ bonds with four *sp*^{2} orbitals
- H–C–H and H–C–C bond angles of about 120°
- C–C double bond in ethylene shorter and stronger than single bond in ethane (not twice as strong!)
- Ethylene C=C bond length 133 pm (C–C 154 pm)



one Csp^2-Csp^2 σ bond
one Cp-Cp π bond
4 Csp^2-H1s σ bonds

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



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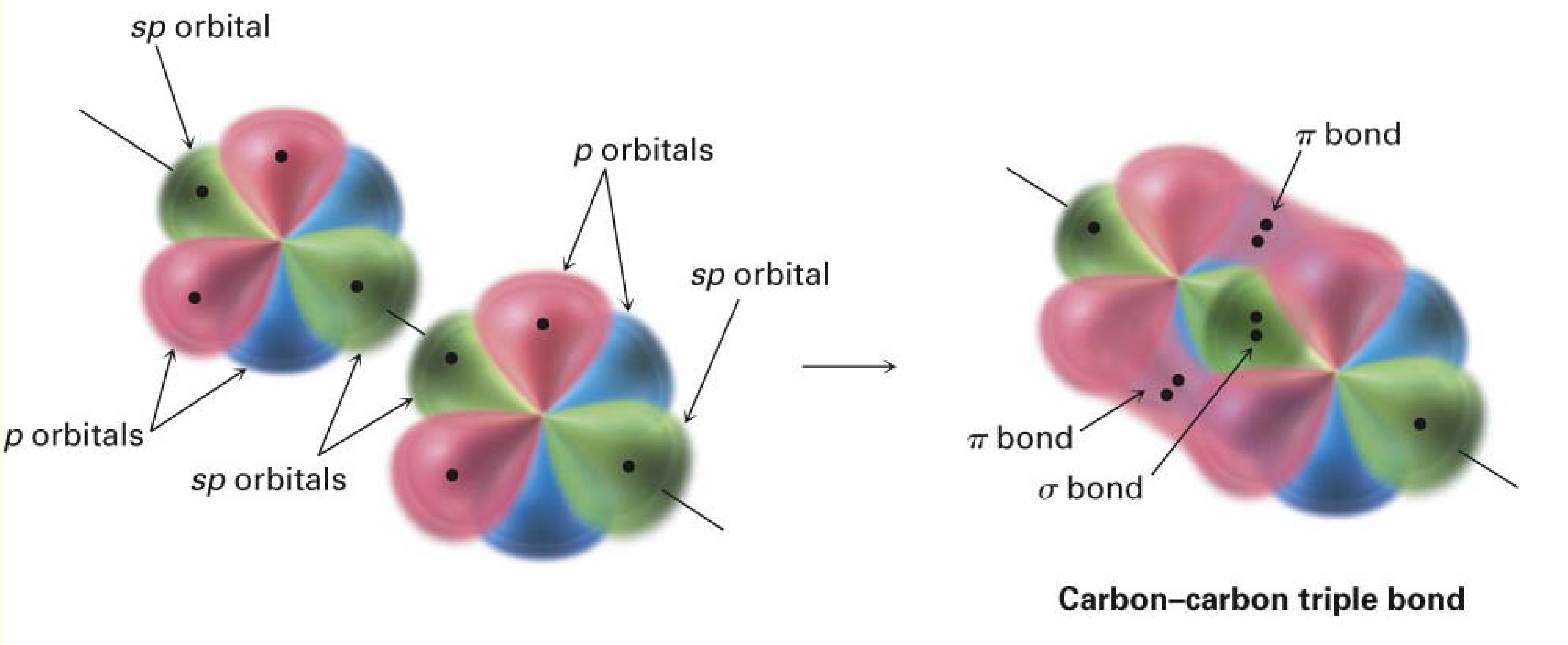
Orbitals of Acetylene

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



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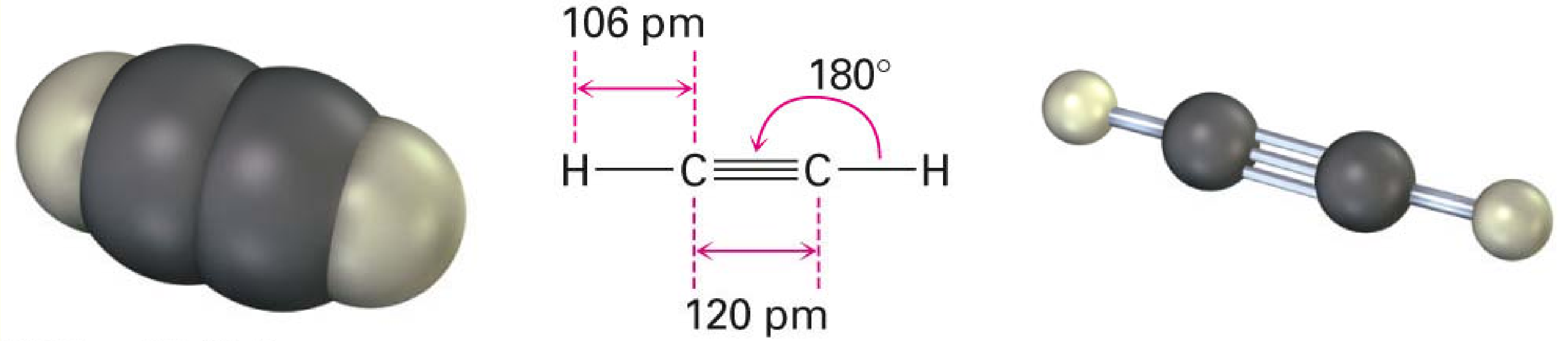
Bonding in Acetylene

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



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one Csp-Csp σ bond
two Cp-Cp π bonds
2 Csp-H1s σ bonds

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 1s	436	104	109
Ethane, CH_3CH_3	(sp^3) C—C (sp^3)	376	90	154
	(sp^3) C—H 1s	423	101	109
Ethylene, $H_2C{=}CH_2$	(sp^2) C=C (sp^2)	728	174	134
	(sp^2) C—H 1s	465	111	109
Acetylene, $HC{\equiv}CH$	(sp) C≡C (sp)	965	231	120
	(sp) C—H 1s	556	133	106

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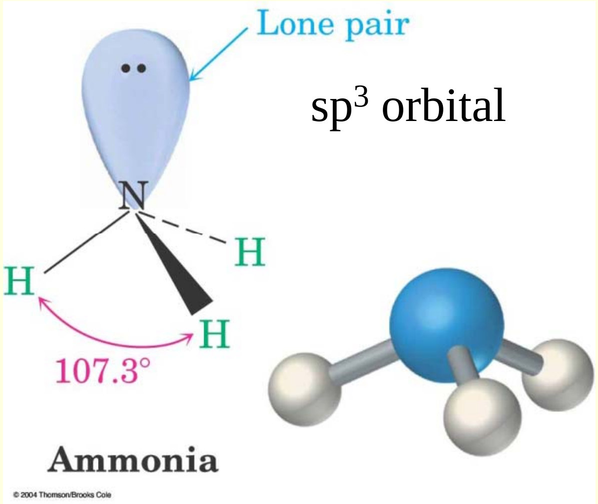
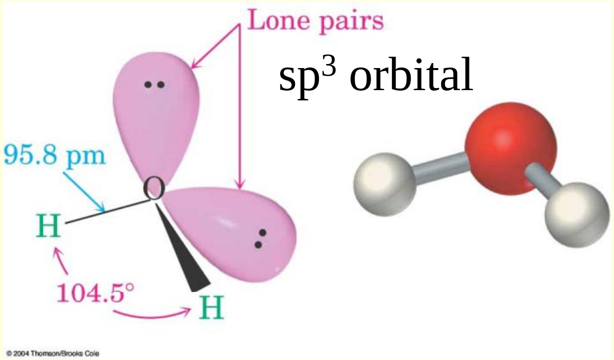
Note double and triple bonds described as combination of sigma and pi bonds

You should be able to explain trends in bond strength and length

Hybridization of Nitrogen and Oxygen

- Elements other than C can have hybridized orbitals
- H–N–H bond angle in ammonia (NH_3) 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

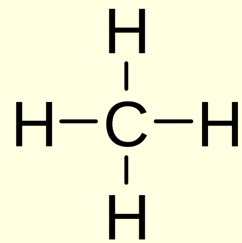




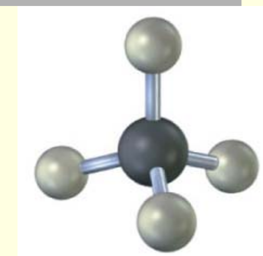
Summary for Hybridization of Carbon

(remember, neutral carbon always has four bonds)

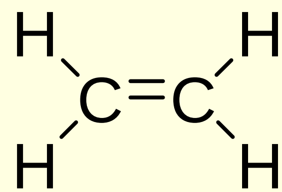
- 4 electron groups = sp^3
  (four σ bonds)



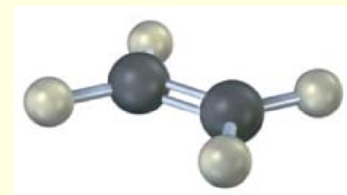
Tetrahedral
109.5°



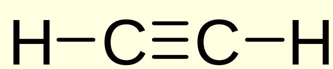
- 3 electron groups = sp^2
  (three σ bonds)
  (one π bond)



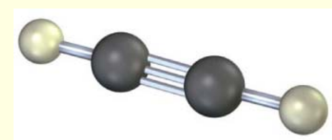
Trigonal
planar
120°



- 2 electron groups = sp
  (two σ bonds)
  (two π bonds)



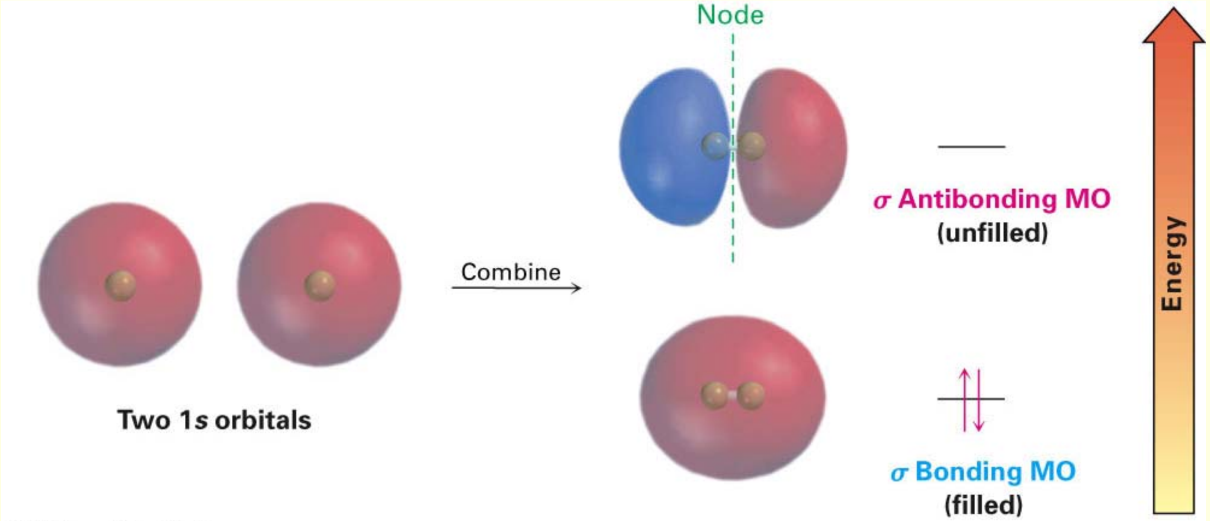
Linear
180°



- What do you predict for
  CH_3^+, CH_3^-, $:CH_2$

Bonding Model # 2: Molecular Orbital Theory

- A *molecular* orbital (MO): where electrons are most likely to be found in a *molecule* (delocalized over the entire molecule not just between atoms like valence bond)
- Combine n atomic orbitals to give n molecular orbitals
- Additive combination (bonding) MO is lower in energy
- Subtractive combination (antibonding) forms MO is higher



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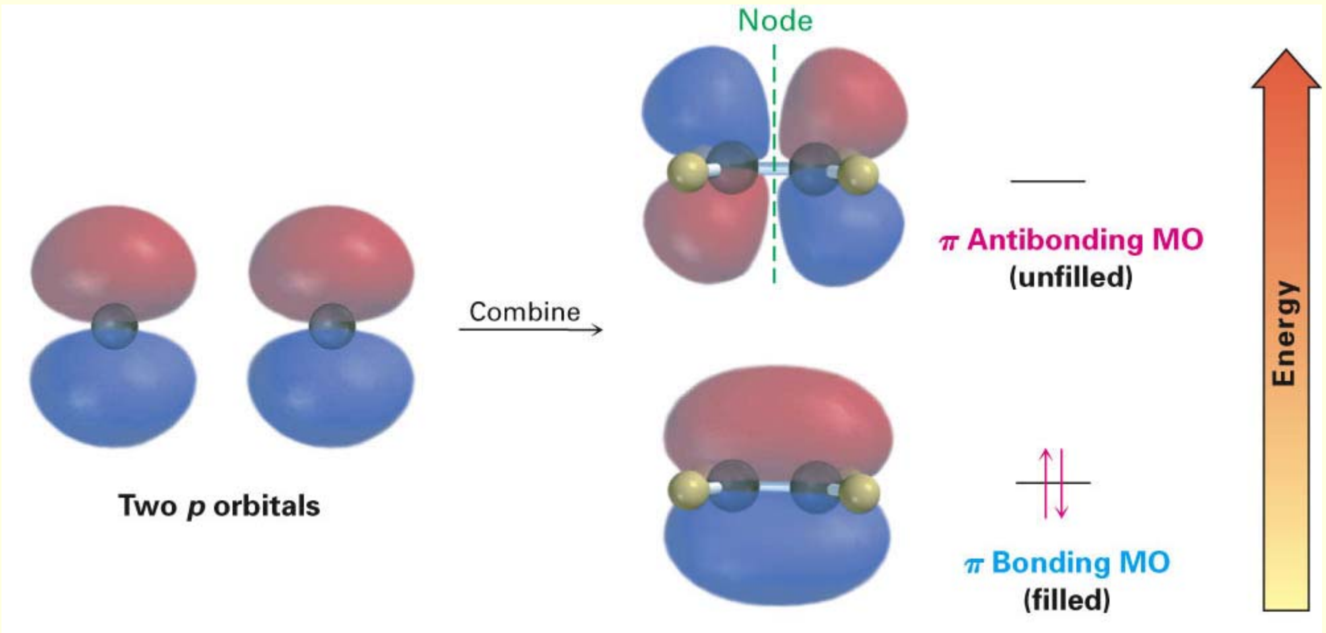
π-Molecular Orbitals in Ethylene

- 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



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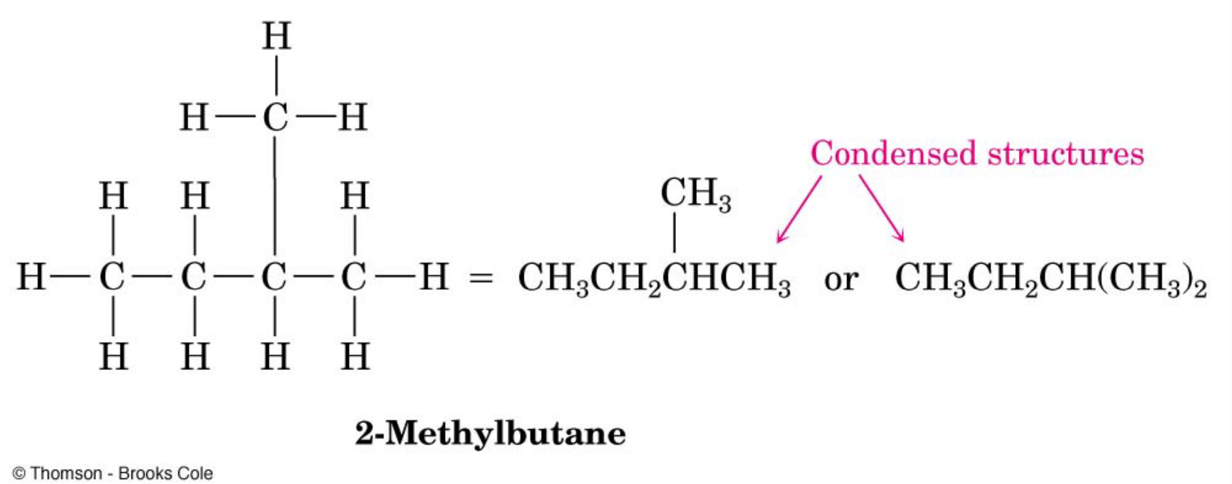
Drawing Chemical Structures

- Chemists use shorthand ways for writing structures
- **Condensed structures:** C-H and C-C single bonds aren't shown but understood
  - If C has 3 H's bonded to it, write CH3
  - If C has 2 H's bonded to it, write CH2; and so on. The compound called 2-methylbutane, for example, is written as follows:
- Horizontal bonds between carbons aren't shown in condensed structures—the CH3, CH2, and CH units are simply written next to each other but vertical bonds are added for clarity



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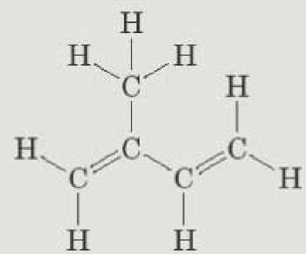
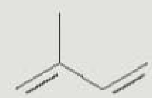
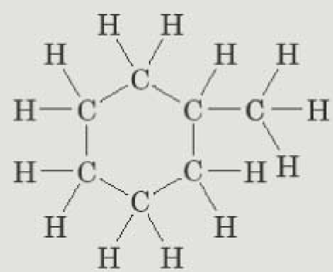
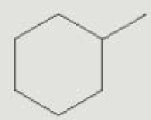
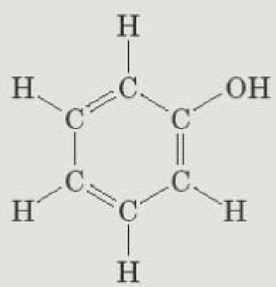
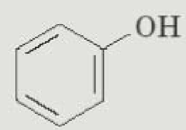
Skeletal Structures

- Minimum amount of information but unambiguous
- C’s not shown, assumed to be at each intersection of two lines (bonds) and at end of each line
- H’s bonded to C’s aren't shown – whatever number is needed will be there (each neutral carbon will have four total bonds). H's on non-carbon atoms are shown.
- All atoms other than C and H *are* shown
- Non-bonding electrons not typically shown (assumed enough to satisfy charge - see Ch 2)
- Charges must be explicitly shown

Examples

TABLE 2.4 Kekulé and Skeletal Structures for Some Compounds

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

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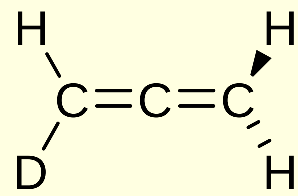
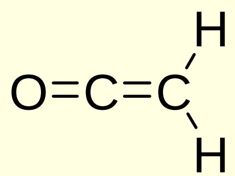
In-Class Practice Problems

1. Explain why the hydrogens atoms in the following compound are not all in the same plane.

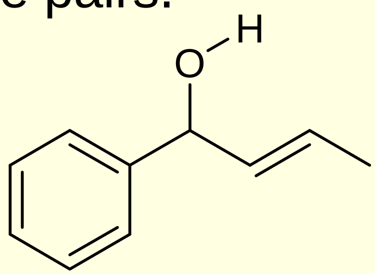


2. Predict the hybridization for each of the following central atoms.

BH_3 $\qquad$ PH_3

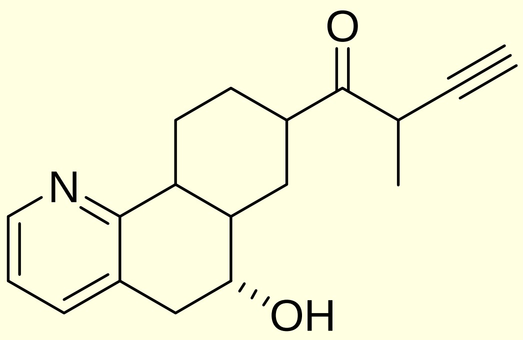


3. Convert the following skeletal drawing into a Kekule drawing with all hydrogens and lone pairs.



In-Class Practice Problems

For the following compound provide the following:



- hybridization of atoms
- bond angles (assume ideal values)
- geometry around atom (electronic, atomic)
- describe bond overlap, orbital location of lone pairs
- provide number of pi-bonds, sigma bonds
- provide missing hydrogens (also in 3-D), lone pairs

Will not be asked specific bond length, strength values but you should be able to qualitatively compare bond lengths and strengths (predict which is stronger, shorter, etc and explain)

May be asked to draw and label orbitals involved in bonding