Hybridization of Orbitals

Structure & Properties of Matter

Atomic Orbitals and Bonding

- Previously:
  - –Electron configurations
  - –Lewis structures
  - –Bonding
  - –Shapes of molecules
- Now:
  - –How do atoms form covalent bonds?
  - –Which orbitals are involved?

- Which electrons are involved in bonding?

  Valence electrons

- Where are valence electrons?

  In atomic orbitals

- Bonds are formed by the combination of atomic orbitals

- Linear combination of atomic orbitals (LCAO)

A. Valence Bond Model

- Hybridization
  - –Atomic orbitals of the *same* atom interact
  - –Hybrid orbitals formed
  - –Bonds formed between hybrid orbitals of two atoms

Let's consider carbon…

- How many valence electrons?

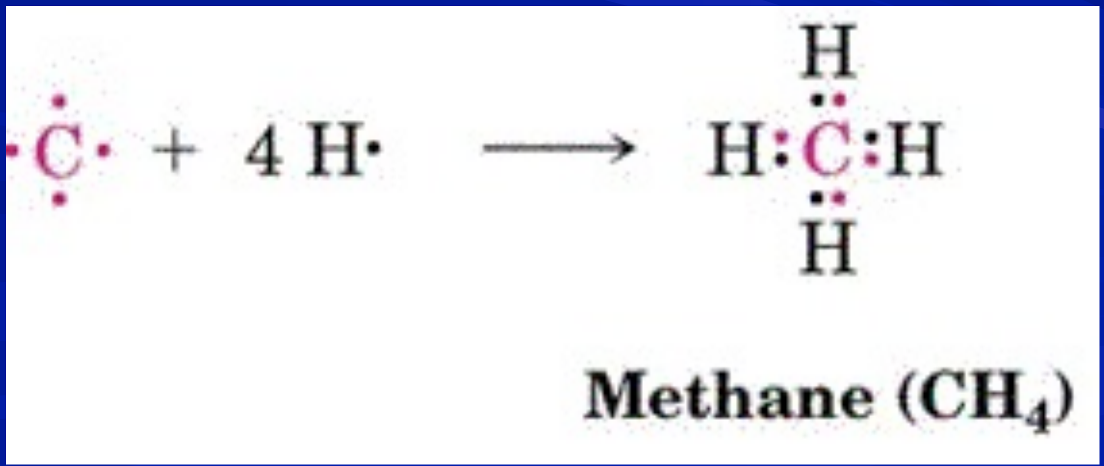
  4

- In which orbitals?

  $2s^2 2p^2$

- So, both the 2*s* and 2*p* orbitals are used to form bonds
- How many bonds does carbon form?
  – 4!!!!!!!!!!!!!!! You better know that...
- All four C-H bonds are the same
  – i.e. there are not two types of bonds from the two different orbitals
- How do we explain this?

  Hybridization



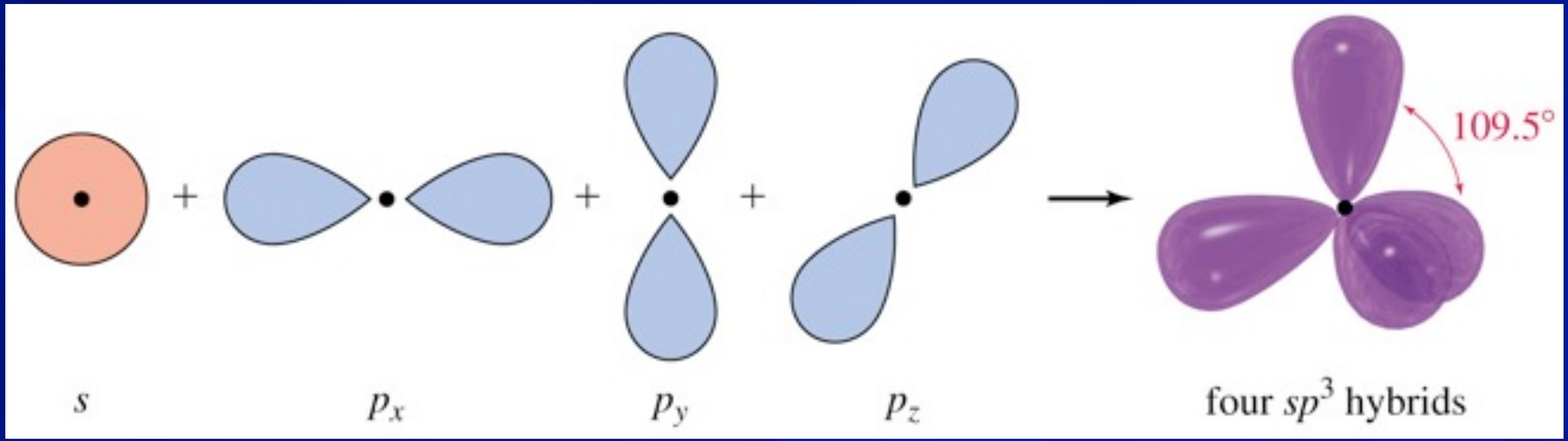
B. Hybrid Orbitals

- The *s* and *p* orbitals of the C atom combine with each other to form hybrid orbitals *before* they combine with orbitals of another atom to form a covalent bond

sp^3 hybridization

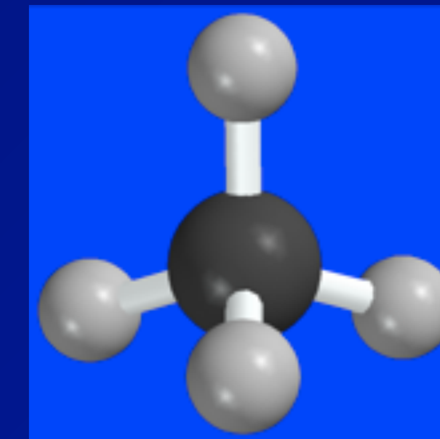
4 atomic orbitals → 4 equivalent hybrid orbitals

$s + p_x + p_y + p_z \rightarrow 4\ sppp = 4\ sp^3$



- Orbitals have two lobes (unsymmetrical)
- Orbitals arrange in space with larger lobes away from one another (tetrahedral shape)
- Each hybrid orbital holds $2e^-$

Electron configuration of carbon

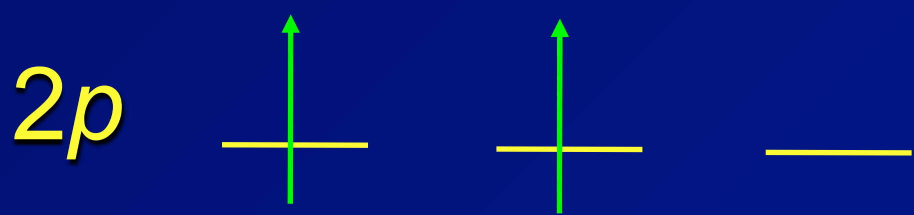


only two unpaired electrons

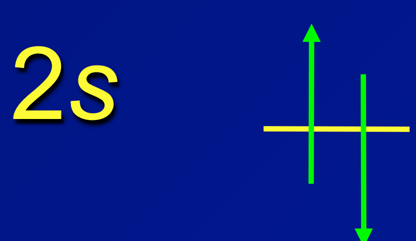
should form σ bonds to only two hydrogen atoms

bonds should be at right angles to one another

sp^3 *Orbital Hybridization*



Promote an electron from the 2*s* to the 2*p* orbital

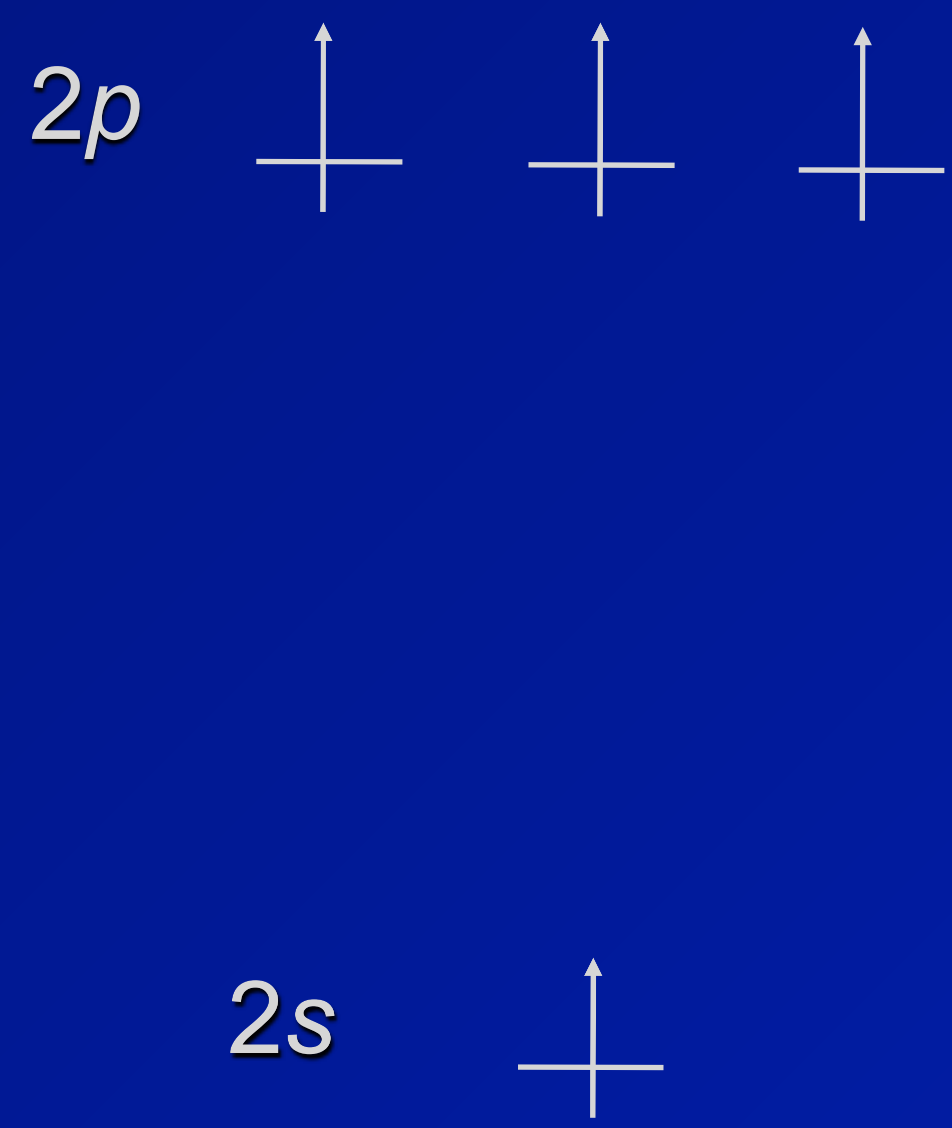


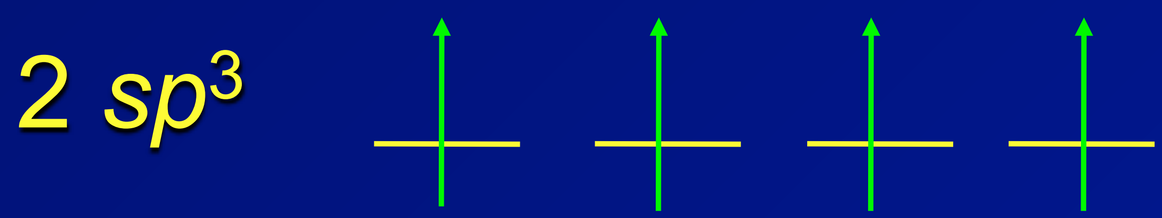
sp^3 Orbital Hybridization

sp^3 *Orbital Hybridization*

Mix together (hybridize) the 2*s* orbital and the three 2*p* orbitals

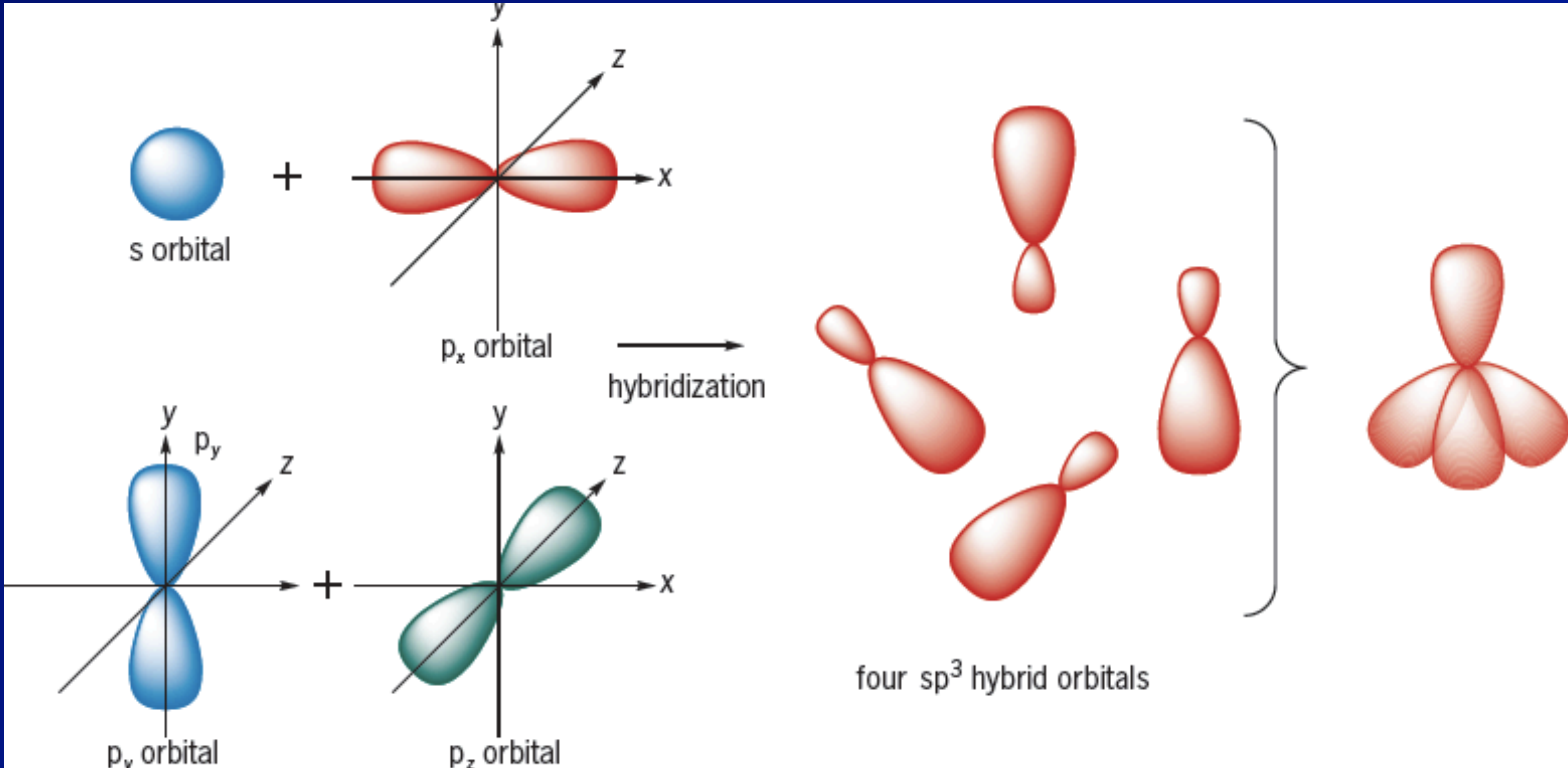
sp^3 Orbital Hybridization





4 equivalent half-filled orbitals are consistent with four bonds and tetrahedral geometry

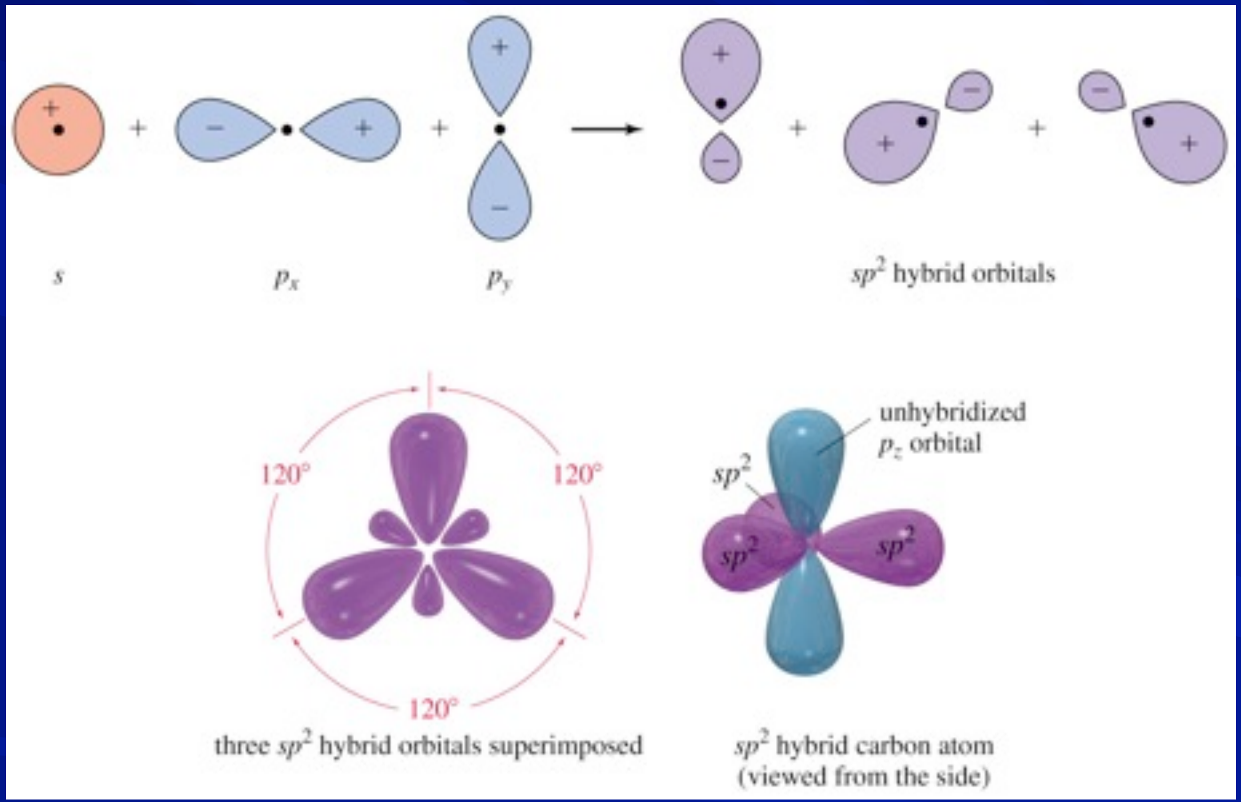
Shape of sp^3 hybrid orbitals



sp^2 hybridization

4 atomic orbitals → 3 equivalent hybrid orbitals +
1 unhybridized *p* orbital

$$s + p_x + p_y + p_z \rightarrow 3\ spp + 1\ p = 3\ sp^2 + 1\ p$$



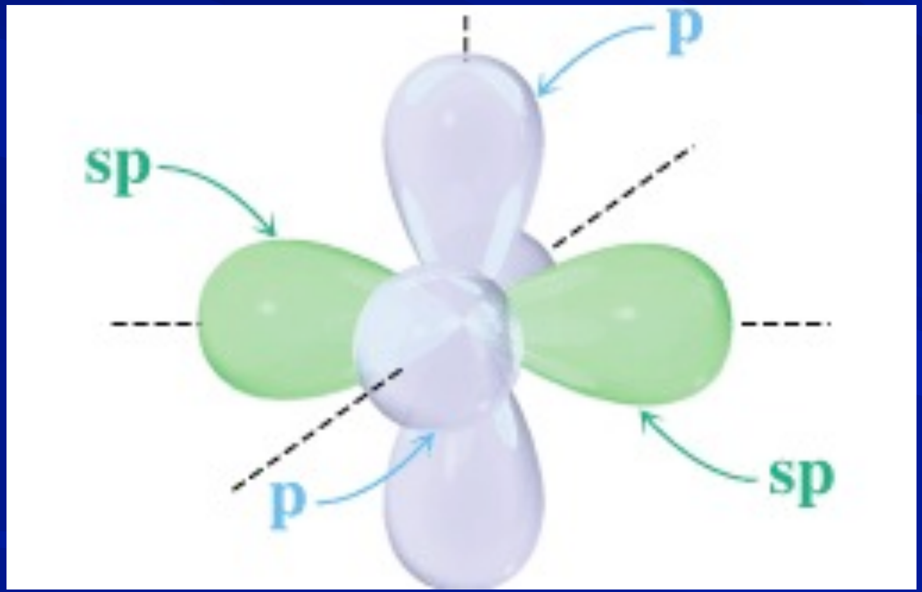
- Geometry = trigonal planar (bond angle = 120º)
- Remaining *p* orbital is perpendicular to the plane

sp hybridization

4 atomic orbitals → 2 equivalent hybrid orbitals +

2 unhybridized *p* orbital

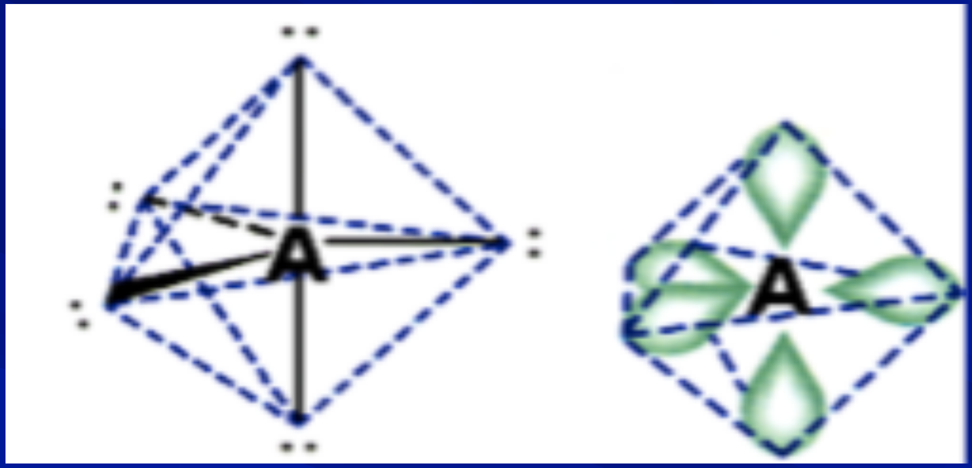
$$s + p_x + p_y + p_z \rightarrow 2\ sp + 2\ p$$



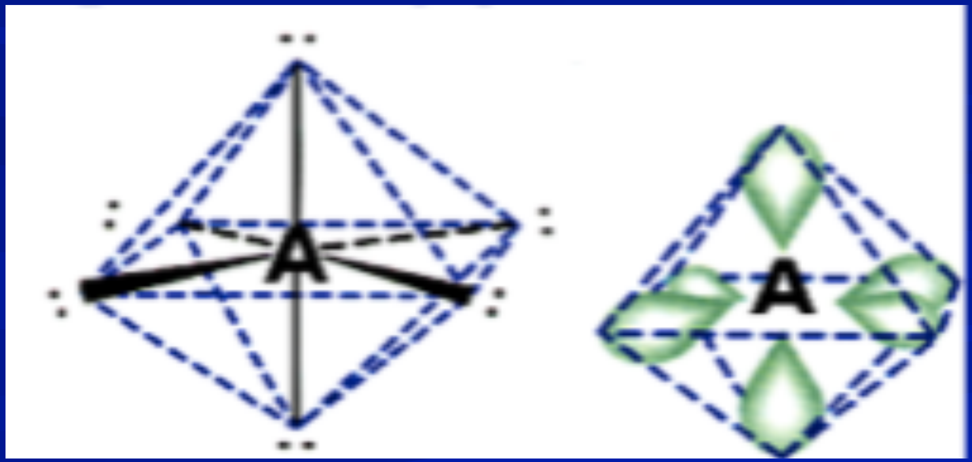
- Geometry = linear (bond angle = 180º)
- Remaining *p* orbitals are perpendicular on y-axis and z-axis

With *d* orbitals…

- $s + p + p + p + d \rightarrow 5\ sp^3d$
- Geometry = trigonal bipyramidal

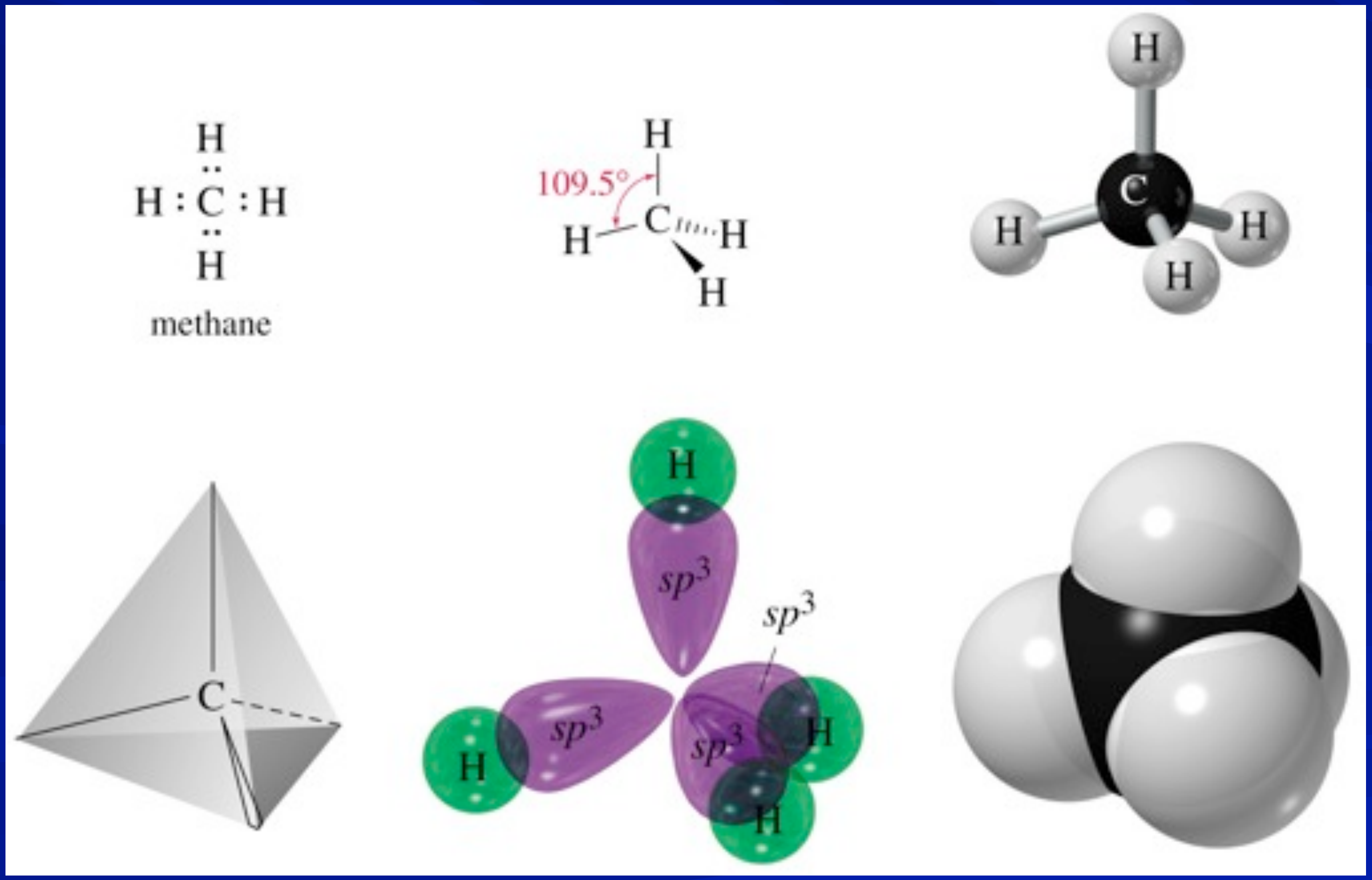


- $s + p + p + p + d + d \rightarrow 6\ sp^3d^2$
- Geometry = Octahedral



C. Bond Formation

- Ex: Methane (CH_4)
- The *sp*^{3} hybrid orbitals on C overlap with 1*s* orbitals on 4 H atoms to form four identical C-H bonds
- Each C–H bond has the same bond length and strength
- **Bond angle**: each H–C–H is 109.5°, the *tetrahedral angle*.

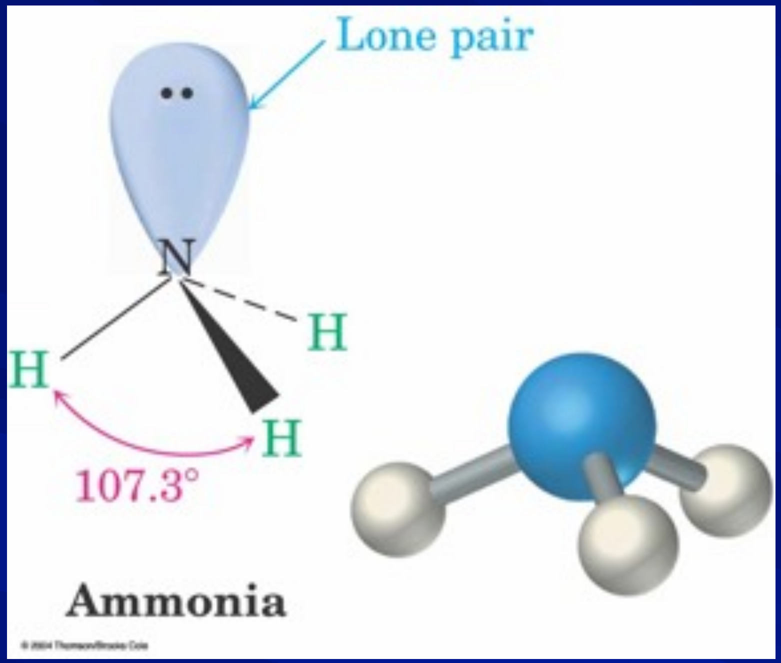


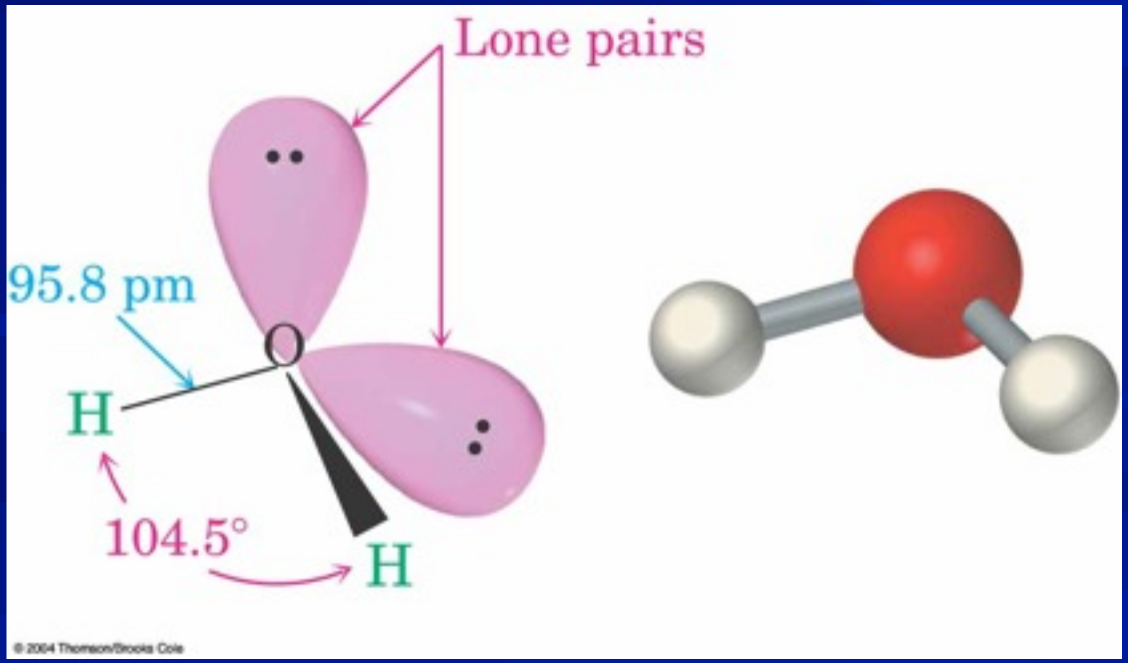
Motivation for hybridization?

- Better orbital overlap with larger lobe of sp^3 hybrid orbital then with unhybridized *p* orbital
- Stronger bond

- Electron pairs farther apart in hybrid orbitals
- Lower energy

Atoms with Lone Pairs

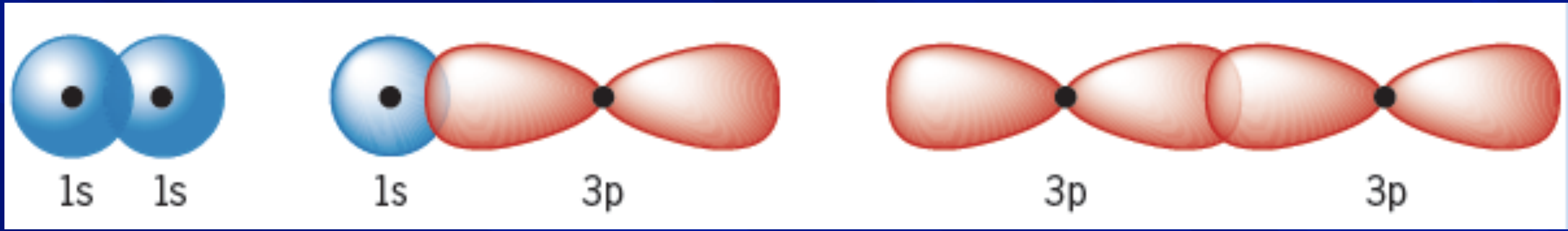




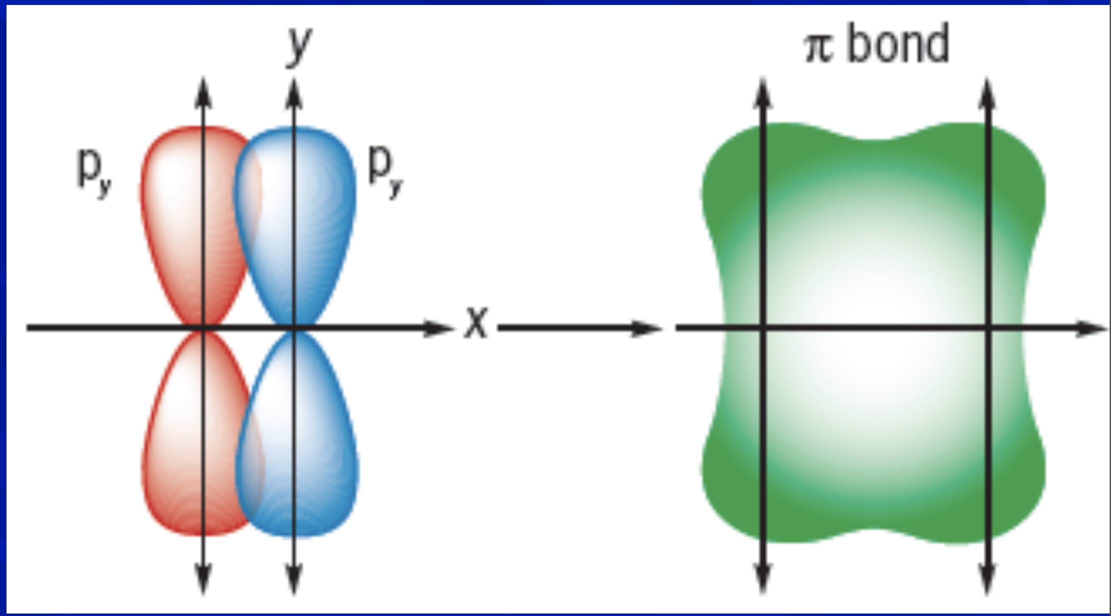
- Same theory
- Look at number of e$^-$ groups to determine hybridization
- Lone pairs will occupy hybrid orbital
- Ammonia:
  - N's orbitals (sppp) hybridize to form four *sp*^{3} orbitals
  - One *sp*^{3} orbital is occupied by two nonbonding electrons, and three *sp*^{3} orbitals have one electron each, forming bonds to H
  - H–N–H bond angle is 107.3°
- Water
  - The oxygen atom is *sp*^{3}-hybridized
  - The H–O–H bond angle is 104.5°

Types of Bonds

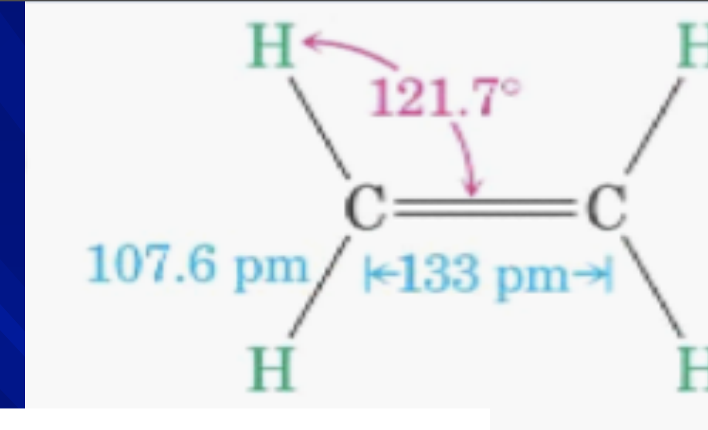
- Methane, ammonia, water have only single bonds
- 1. Sigma (σ) bonds
  - – Electron density centered between nuclei
  - – Most common type of bond



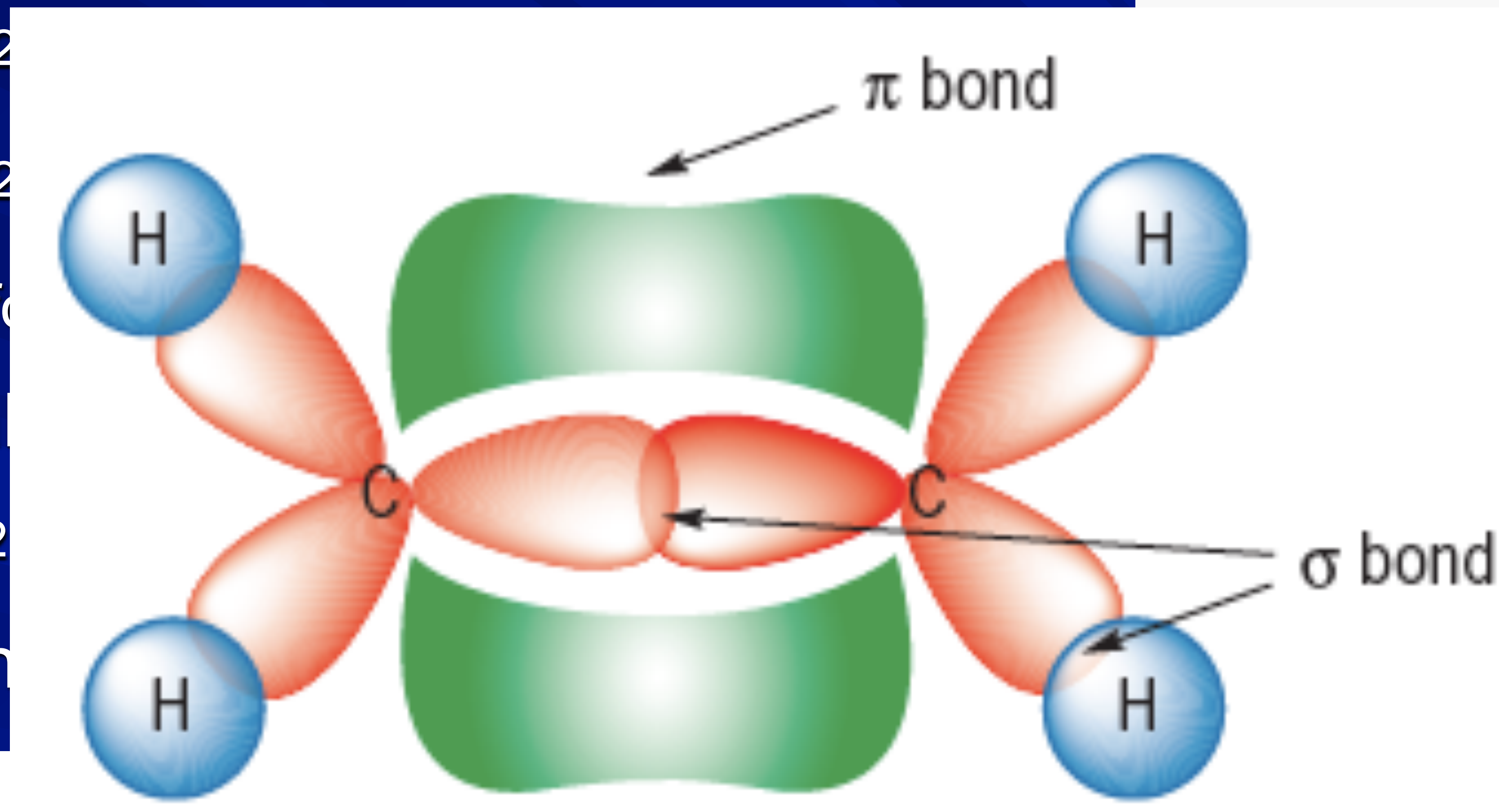
- 2. Pi (π) bonds
  - – Electron density above and below nuclei
  - – Associated with multiple bonds
  - – Overlap between two *p* orbitals
  - – Atoms are sp^2 or *sp* hybridized

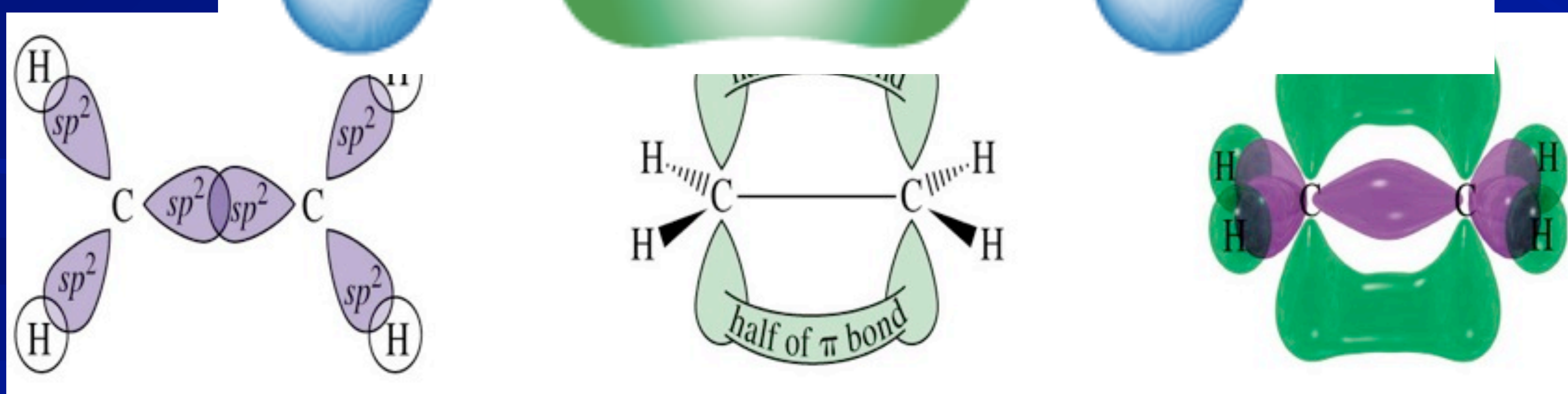


Formation of C_2H_4



- Two sp^2
- Two sp^2
  - Form f
- *p* orbital
- sp^2–sp^2 … ur
  electron





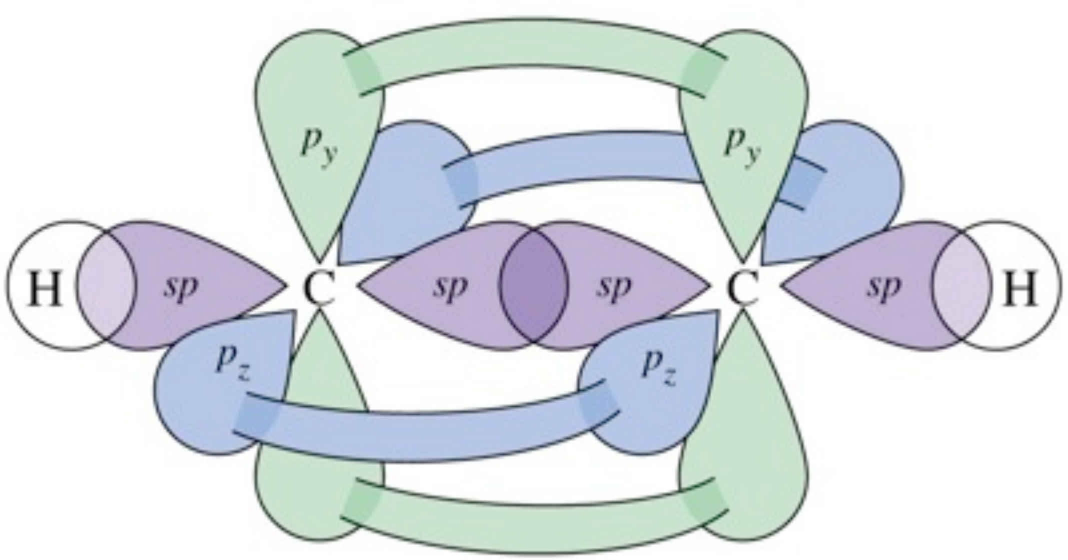
σ bond framework
(viewed from above the plane)

π bond
(viewed from alongside the plane)

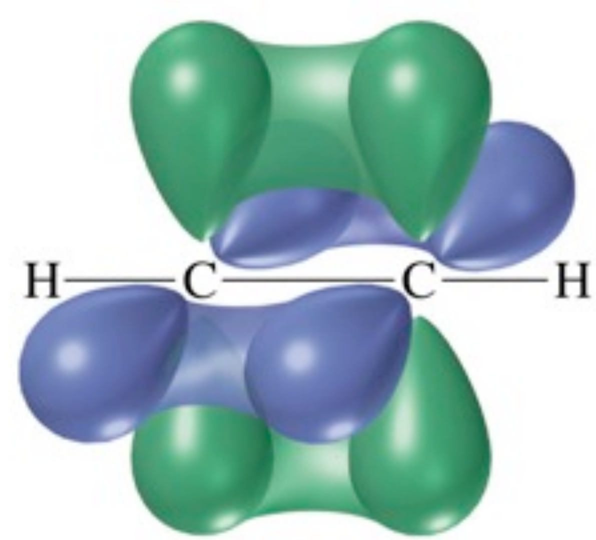
ethylene

Formation of acetylene (C_2H_2)

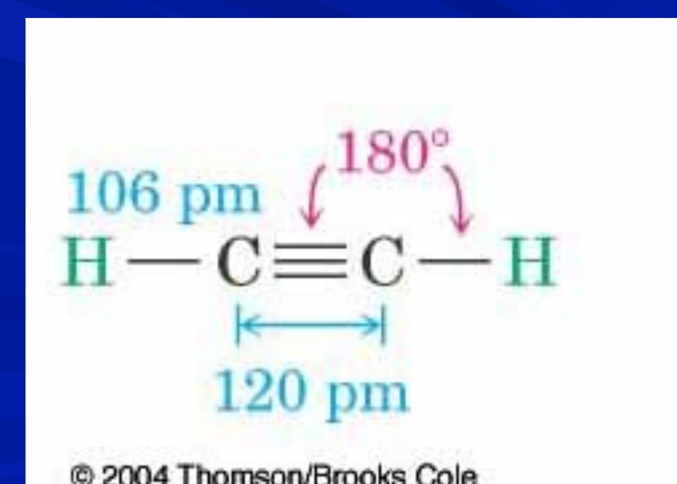
- Two *sp*-hybridized orbitals overlap to form a σ bond
- One *sp* orbital on each C overlap with H 1*s* orbitals
  - Form two C–H bonds
- *p* orbitals overlap *side-to-side* to form two π bonds
- *sp*–*sp* σ bond and two *p*–*p* π bonds result in sharing six electrons and formation of C-C triple bond
  - Shorter and stronger than double bond in ethylene



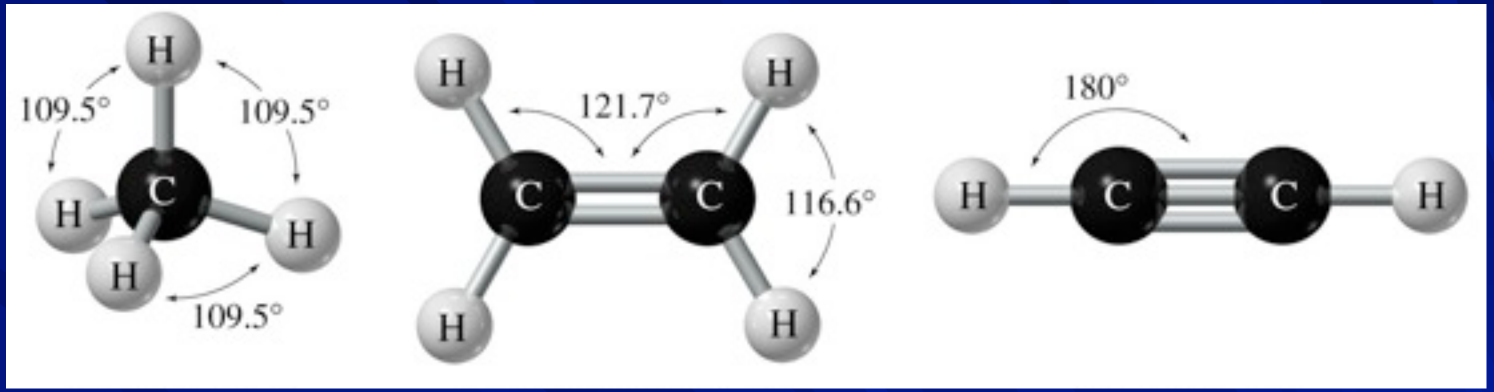
acetylene



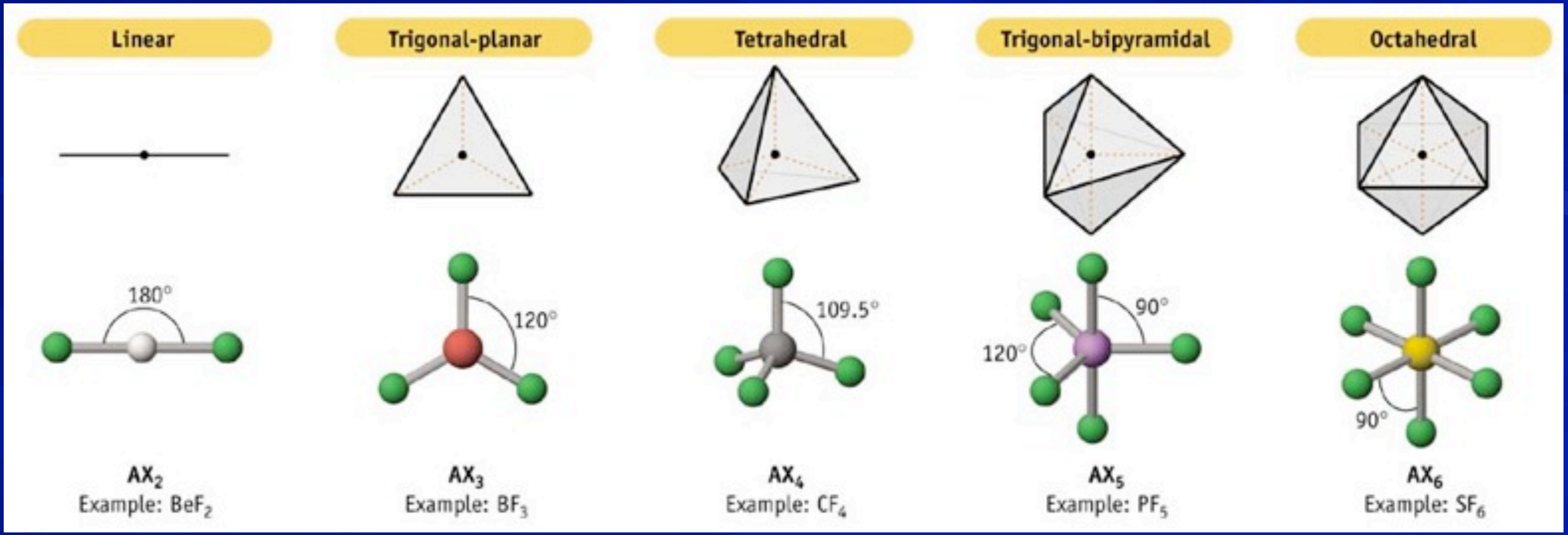
acetylene



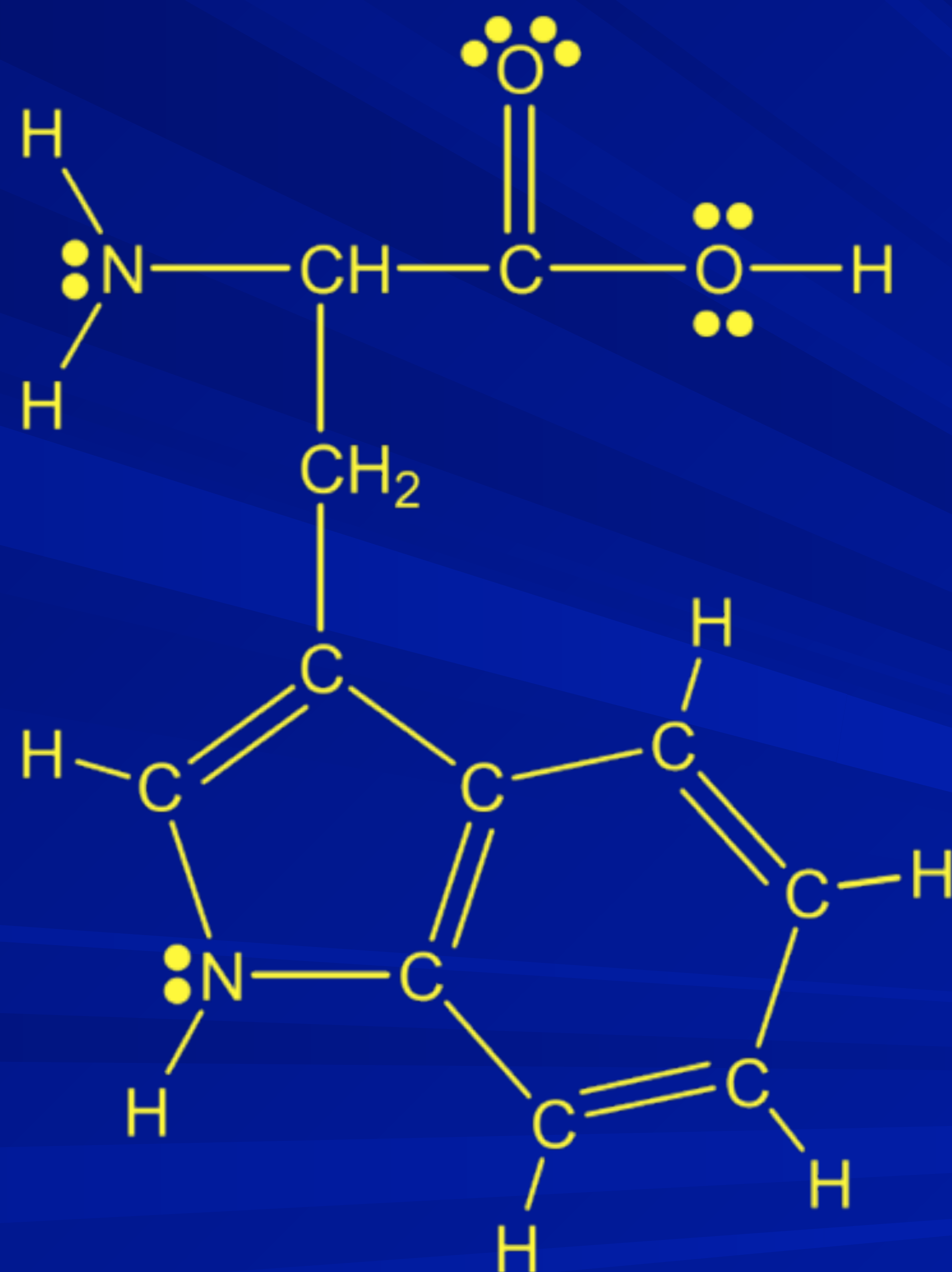
Summary of Hybridization



Hybridization of atom	sp^3d^2	sp^3d	sp^3	sp^2	sp
Example	SF_6	PCl_5	CH_4	C_2H_4, SO_3	C_2H_2, BeF_2
# Groups bonded to atom	6	5	4	3	2
Electronic geometry	Octahedral	Trigonal Bipyramidal	Tetrahedral	Trigonal planar	Linear
Bond angles	90°	90 °, 120 °	109.5 °	~120 °	~180 °



Predict hybridization, shape, and bond angles for the amino acid tryptophan



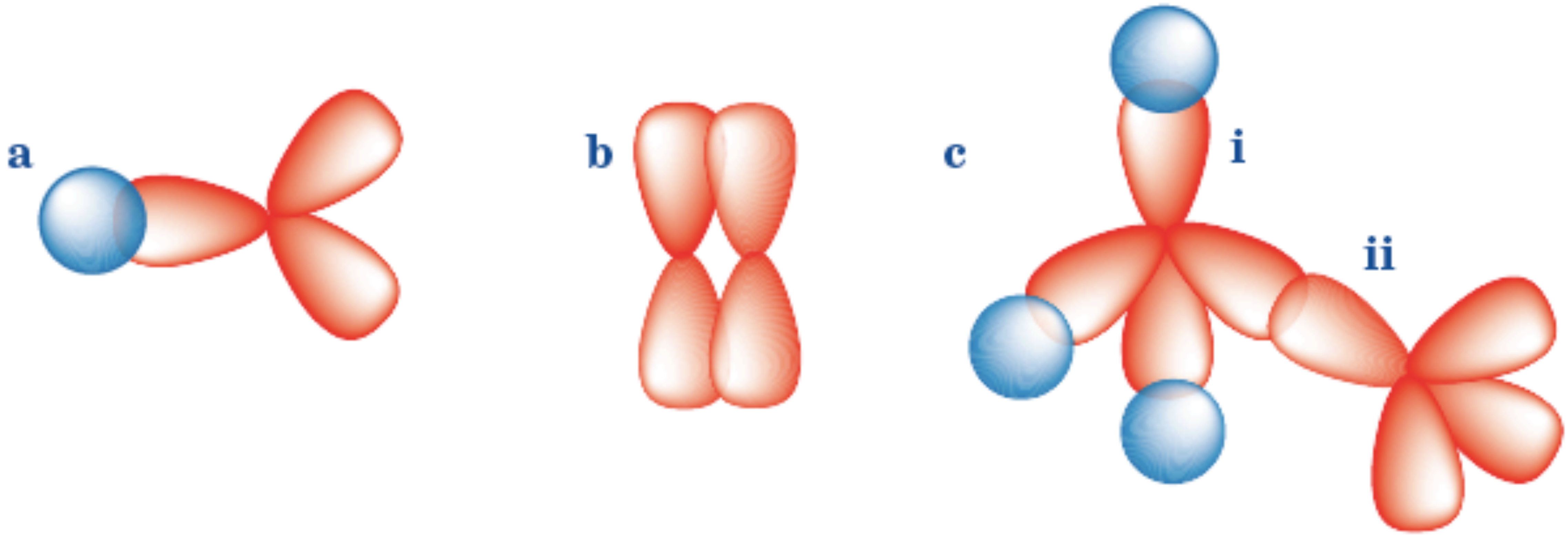
Try it!

1 Both σ (sigma) and π (pi) bonds involve the overlapping of orbitals. Draw a diagram to show the difference between the overlapping that constitutes a σ bond and the overlapping to make a π bond.

2 Copy and complete the following table to give an example and to indicate what type of bond could occur between the orbitals or hybrid orbitals listed.

Orbital 1	Orbital 2	Example of molecule in which the bond occurs	σ bond? (yes/no)	π bond? (yes/no)
s orbital	s orbital	H_2		
s orbital	sp hybrid orbital			
p orbital	p orbital			
sp^3 hybrid orbital	sp^2 hybrid orbital			

3 Consider the following diagrams and state whether they are illustrating a σ bond or a π bond.



4 Use the concepts of σ and π bonding to explain why a carbon–carbon double bond is not twice as strong as a carbon–carbon single bond.

5 State the type of hybridization that would be occurring in order for the following geometry to occur around the central atom.

a trigonal planar

b linear

c tetrahedral