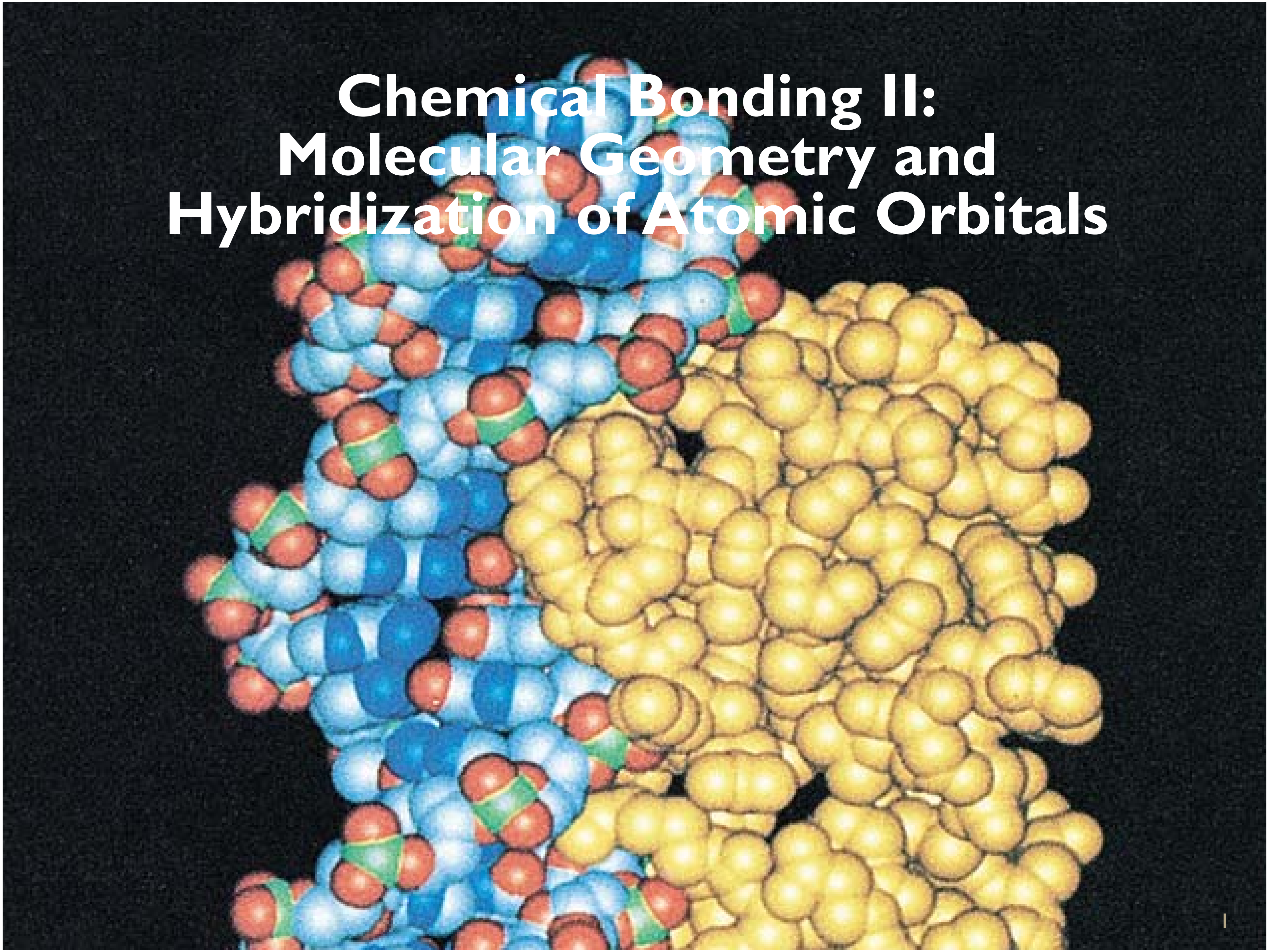
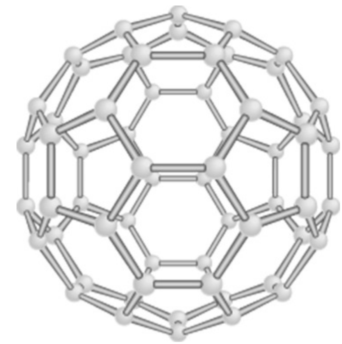
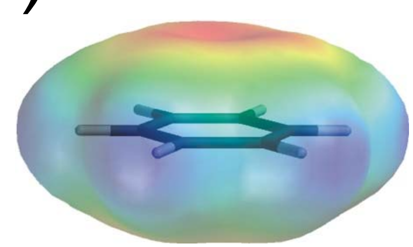
Chemical Bonding II: Molecular Geometry and Hybridization of Atomic Orbitals



Chemical Bonding II



- Molecular Geometry (10.1)
- Dipole Moments (10.2)
- Valence Bond Theory (10.3)
- Hybridization of Atomic Orbitals (10.4)
- Hybridization in Molecules Containing Double and Triple Bonds (10.5)
- Molecular Orbital Theory (10.6)



Chemical Bonding II

- Molecular Shape
  - Basic geometries
  - VSEPR
- Polarity
  - Electronegativity
  - Bond moments
  - Dipole moments
- Valence Bond Theory
  - Bond energy and bond length
  - Atomic orbitals
  - Hybridization
    - Sigma and pi overlap
- Molecular Orbital Theory
  - Atomic orbitals to molecular orbitals
  - Bonding and antibonding
  - Order of molecular orbitals
  - Stability of bonds
  - Bond order

10.1 Molecular Geometry

- Are molecules flat (2D)?
- If not, how do we determine the three dimensional shape of molecules?
- How do lone pairs figure into the shape of molecules?
- Does shape really matter?

Moving from bonding into structure

10.1 Molecular Geometry

- Consider the central atom (A):

What will affect the shape of the molecule?

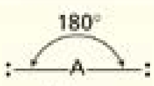
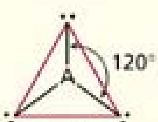
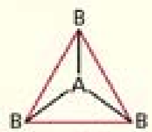
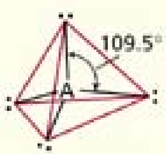
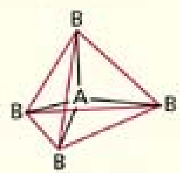
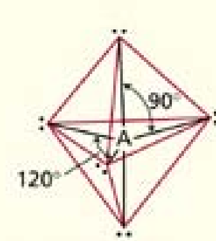
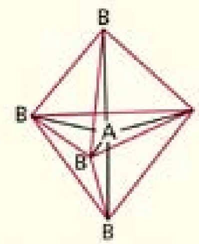
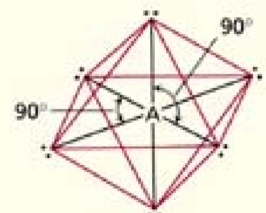
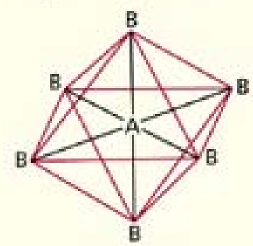
  - Number of bonded atoms (terminal atoms in simpler molecules) (B)
    - Regardless of multiple bonds
  - Number of lone pairs

- *We will first consider molecules with no lone pairs on the central atoms*

10.1 Molecular Geometry

All of the molecules have no lone pairs on the central atom.
Only the number of terminal atoms affects the shape.

TABLE 10.1 Arrangement of Electron Pairs About a Central Atom (A) in a Molecule and Geometry of Some Simple Molecules and Ions in Which the Central Atom Has No Lone Pairs

Number of Electron Pairs	Arrangement of Electron Pairs*	Molecular Geometry*	Examples
2	 Linear	B—A—B Linear	$BeCl_2$, $HgCl_2$
3	 Trigonal planar	 Trigonal planar	BF_3
4	 Tetrahedral	 Tetrahedral	CH_4, NH_4^+
5	 Trigonal bipyramidal	 Trigonal bipyramidal	PCl_5
6	 Octahedral	 Octahedral	SF_6

*The colored lines are used only to show the overall shapes; they do not represent bonds.

Table 10.1 p. 325

10.1 Molecular Geometry

Valence Shell Electron Pair Repulsion (VSEPR)

- Predicts the geometry of the molecule from the electrostatic repulsions between the electron (bonding and nonbonding) pairs

Lone pair – lone pair repulsion

>

Lone pair – bonded atom repulsion

>

Bonded atom – bonded atom repulsion

VSEPR

10.1 Molecular Geometry

- Must consider (on the central atom(A)):
  - The number of terminal atoms (B)
  - The number of lone pairs (E)

- The sum of these will give a similar (close) bond angle to the geometries of the number of electron groups from before

- For instance: O_3 will have the general formula of AB_2E (3 electron groups) and close to a bond angle (idealized) of 120°.

VSEPR

10.1 Molecular Geometry

Electron Groups	# of lone pairs	Shape	Example
2	0	Linear	CO_2
3	0	Trigonal planar	BH_3
4	0	Tetrahedral	CH_4
5	0	Trigonal bipyramidal	PCl_5
6	0	Octahedral	SF_6

VSEPR

10.1 Molecular Geometry

Electron Groups	# of lone pairs	Shape	Example
2	0	Linear	CO_2
3	0	Trigonal planar	BH_3
3	1	Bent	O_3
4	0	Tetrahedral	CH_4
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VSEPR

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2	0	Linear	CO_2
3	0	Trigonal planar	BH_3
3	1	Bent	O_3
4	0	Tetrahedral	CH_4
4	1	Pyramidal	NH_3
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6	0	Octahedral	SF_6

VSEPR

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3	0	Trigonal planar	BH_3
3	1	Bent	O_3
4	0	Tetrahedral	CH_4
4	1	Pyramidal	NH_3
4	2	Bent	H_2O
5	0	Trigonal bipyramidal	PCl_5
6	0	Octahedral	SF_6

VSEPR

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Electron Groups	# of lone pairs	Shape	Example
2	0	Linear	CO_2
3	0	Trigonal planar	BH_3
3	1	Bent	O_3
4	0	Tetrahedral	CH_4
4	1	Pyramidal	NH_3
4	2	Bent	H_2O
5	0	Trigonal bipyramidal	PCl_5
5	1	See-saw (distorted tetrahedron)	SF_4
6	0	Octahedral	SF_6

VSEPR

10.1 Molecular Geometry

Electron Groups	# of lone pairs	Shape	Example
2	0	Linear	CO_2
3	0	Trigonal planar	BH_3
3	1	Bent	O_3
4	0	Tetrahedral	CH_4
4	1	Pyramidal	NH_3
4	2	Bent	H_2O
5	0	Trigonal bipyramidal	PCl_5
5	1	See-saw (distorted tetrahedron)	SF_4
5	2	T-shaped	ICl_3
6	0	Octahedral	SF_6

VSEPR

10.1 Molecular Geometry

Electron Groups	# of lone pairs	Shape	Example
2	0	Linear	CO_2
3	0	Trigonal planar	BH_3
3	1	Bent	O_3
4	0	Tetrahedral	CH_4
4	1	Pyramidal	NH_3
4	2	Bent	H_2O
5	0	Trigonal bipyramidal	PCl_5
5	1	See-saw (distorted tetrahedron)	SF_4
5	2	T-shaped	ICl_3
5	3	Linear	I_3^-
6	0	Octahedral	SF_6

VSEPR

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Electron Groups	# of lone pairs	Shape	Example
2	0	Linear	CO_2
3	0	Trigonal planar	BH_3
3	1	Bent	O_3
4	0	Tetrahedral	CH_4
4	1	Pyramidal	NH_3
4	2	Bent	H_2O
5	0	Trigonal bipyramidal	PCl_5
5	1	See-saw (distorted tetrahedron)	SF_4
5	2	T-shaped	ICl_3
5	3	Linear	I_3^-
6	0	Octahedral	SF_6
6	1	Square pyramidal	BrF_5

VSEPR

10.1 Molecular Geometry

Electron Groups	# of lone pairs	Shape	Example
2	0	Linear	CO_2
3	0	Trigonal planar	BH_3
3	1	Bent	O_3
4	0	Tetrahedral	CH_4
4	1	Pyramidal	NH_3
4	2	Bent	H_2O
5	0	Trigonal bipyramidal	PCl_5
5	1	See-saw (distorted tetrahedron)	SF_4
5	2	T-shaped	ICl_3
5	3	Linear	I_3^-
6	0	Octahedral	SF_6
6	1	Square pyramidal	BrF_5
6	2	Square planar	XeF_4

VSEPR

Table 10.2	Geometry of Simple Molecules and Ions in Which the Central Atom Has One or More Lone Pairs					
Class of molecule	**Total number of electron pairs**	**Number of bonding pairs**	**Number of lone pairs**	**Arrangement of electron pairs***	**Geometry**	**Examples**
AB_2E	3	2	1	Trigonal planar	Bent	SO_2
AB_3E	4	3	1	Tetrahedral	Trigonal pyramidal	NH_3
AB_2E_2	4	2	2	Tetrahedral	Bent	H_2O
AB_4E	5	4	1	Trigonal bipyramidal	Distorted tetrahedron (or seesaw)	SF_4
AB_3E_2	5	3	2	Trigonal bipyramidal	T-shaped	ClF_3
AB_2E_3	5	2	3	Trigonal bipyramidal	Linear	I_3^-
AB_5E	6	5	1	Octahedral	Square pyramidal	BrF_5
AB_4E_2	6	4	2	Octahedral	Square planar	XeF_4

*The colored lines are used to show the overall shape, not bonds.

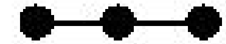
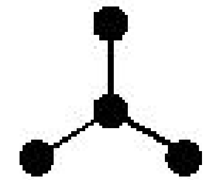
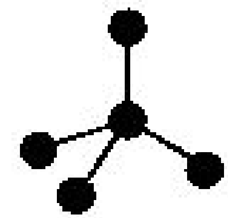
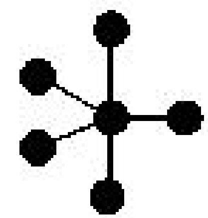
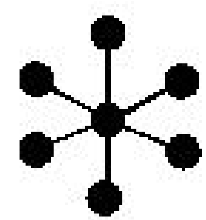
Idealized bond angle of 120°

Idealized bond angle of 109.5°

Idealized bond angles of 90° and 120°; linear molecule (with 3 lone pairs on the central atom has a bond angle of 180°)

Idealized bond angle of 90°

Table 10.2 p. 331

# electron groups	Bond angle	Base geometry	# lone pairs	Shape	
2	180°	Linear	0	Linear	
3	120°	Trigonal planar	0	Trigonal planar	
			1	Bent	
4	109.5°	Tetrahedral	0	Tetrahedral	
			1	Trigonal pyramidal	
			2	bent	
5	90°/120°	Trigonal bipyramidal	0	Trigonal bipyramidal	
			1	See-saw	
			2	t-shaped	
			3	Linear	
6	90°	Octahedral	0	Octahedral	
			1	Square pyramidal	
			2	Square planar	

10.1 Molecular Geometry

VSEPR

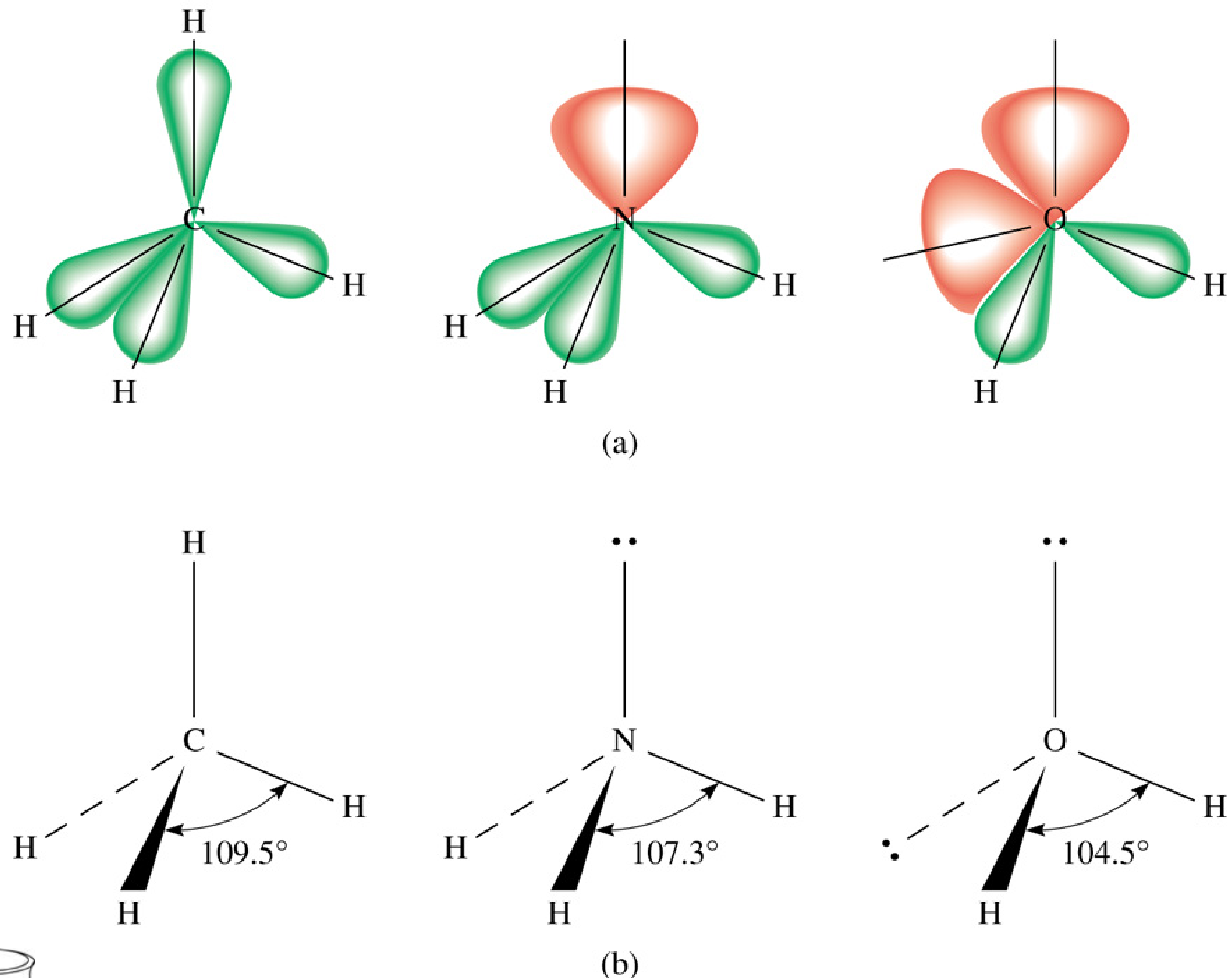


Figure 10.1 p. 329

10.2 Dipole Moments

- Already discuss polar versus nonpolar covalent bonds:
  - electronegativity

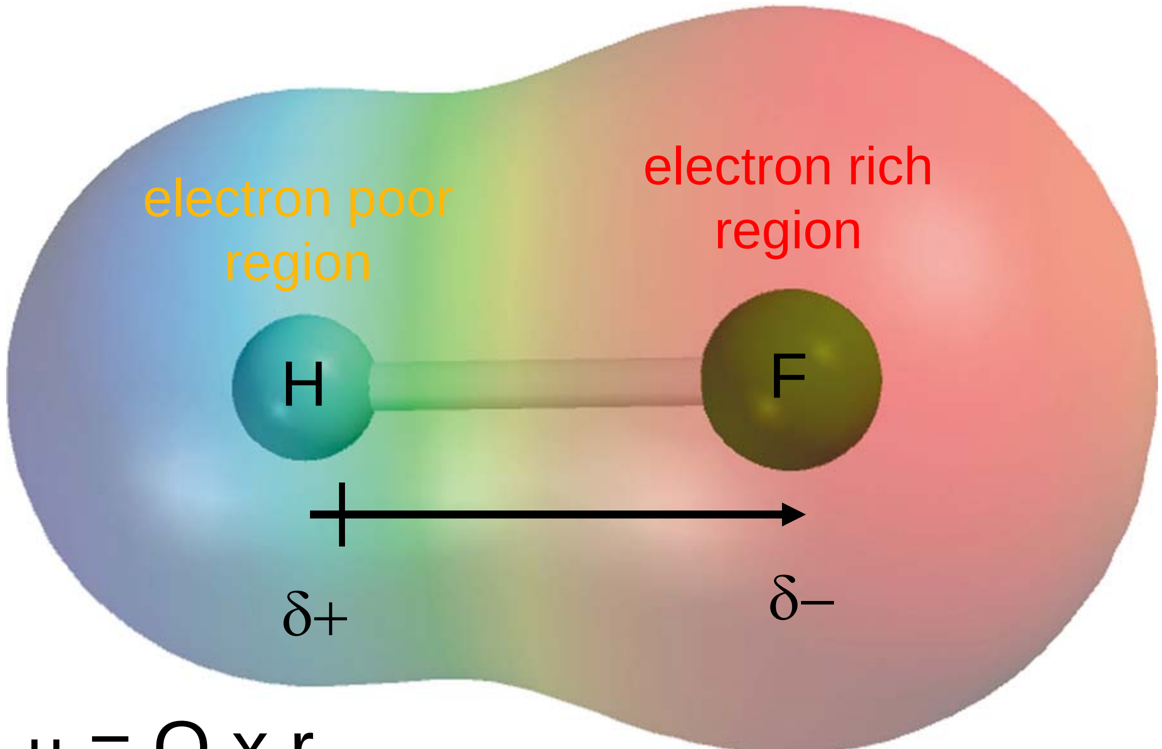
Increasing electronegativity

Increasing electronegativity

1A	2A	3B	4B	5B	6B	7B		8B		1B	2B	3A	4A	5A	6A	7A	8A
H 2.1																	
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.9	Ni 1.9	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr 3.0
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe 2.6
Cs 0.7	Ba 0.9	La-Lu 1.0-1.2	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.9	Bi 1.9	Po 2.0	At 2.2	
Fr 0.7	Ra 0.9																

Figure 9.5 p. 296

10.2 Dipole Moments



$\mu = Q \times r$

Q is the charge

r is the distance between charges

1 D (Debye) = 3.36×10^{-30} C m

Figure 9.4 p. 296

10.2 Dipole Moments

Table 10.3 Dipole Moments of Some Polar Molecules

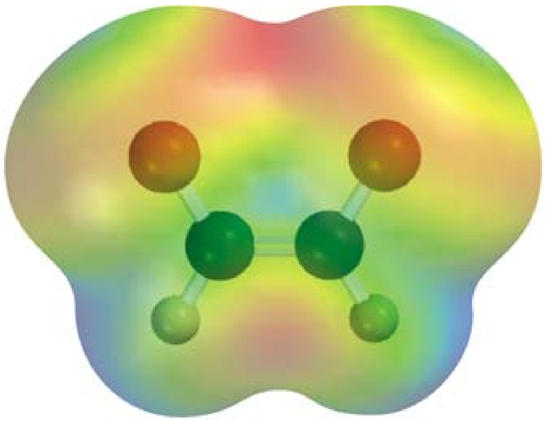
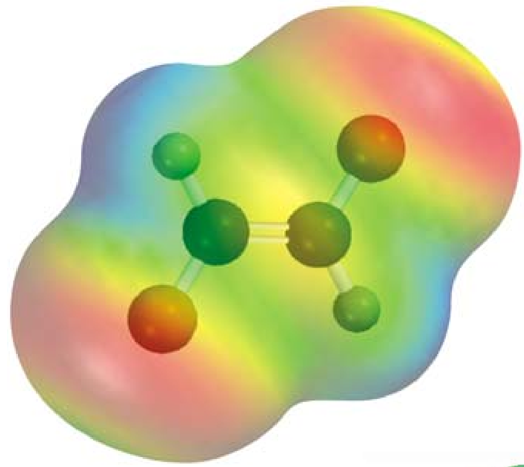
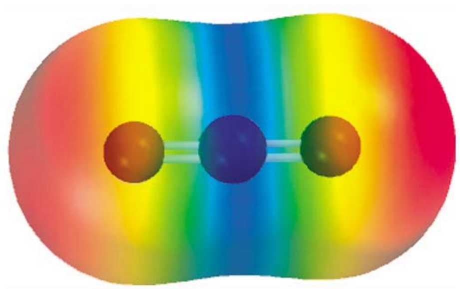
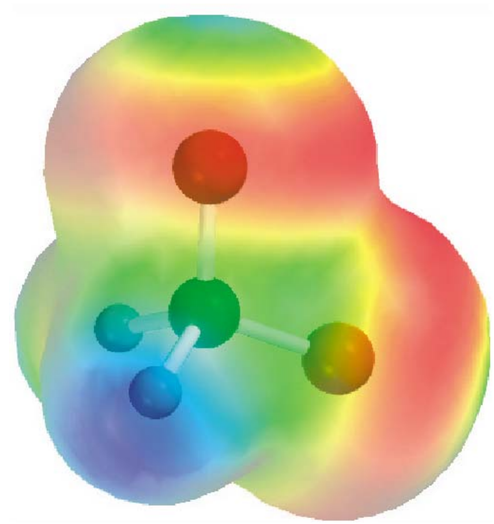
Molecule	Geometry	Dipole Moment (D)
HF	Linear	1.92
HCl	Linear	1.08
HBr	Linear	0.78
HI	Linear	0.38
H_2O	Bent	1.87
H_2S	Bent	1.10
NH_3	Trigonal pyramidal	1.46
SO_2	Bent	1.60

Table 10.3 p. 336

10.2 Dipole Moments

- Already discuss polar versus nonpolar covalent bonds:
  - electronegativity
- How do these bonds overall contribute to molecular polarity?
- Why does it matter if a molecule is polar or nonpolar?

10.2 Dipole Moments

Margin figures p. 335 and 337

10.3 Valence Bond Theory

- How are single, double, and triple bonds represented in Lewis dot structures?
- Are all single bonds represented the same?
- Are all single bonds the same?
  - same length
  - same energy

10.3 Valence Bond Theory

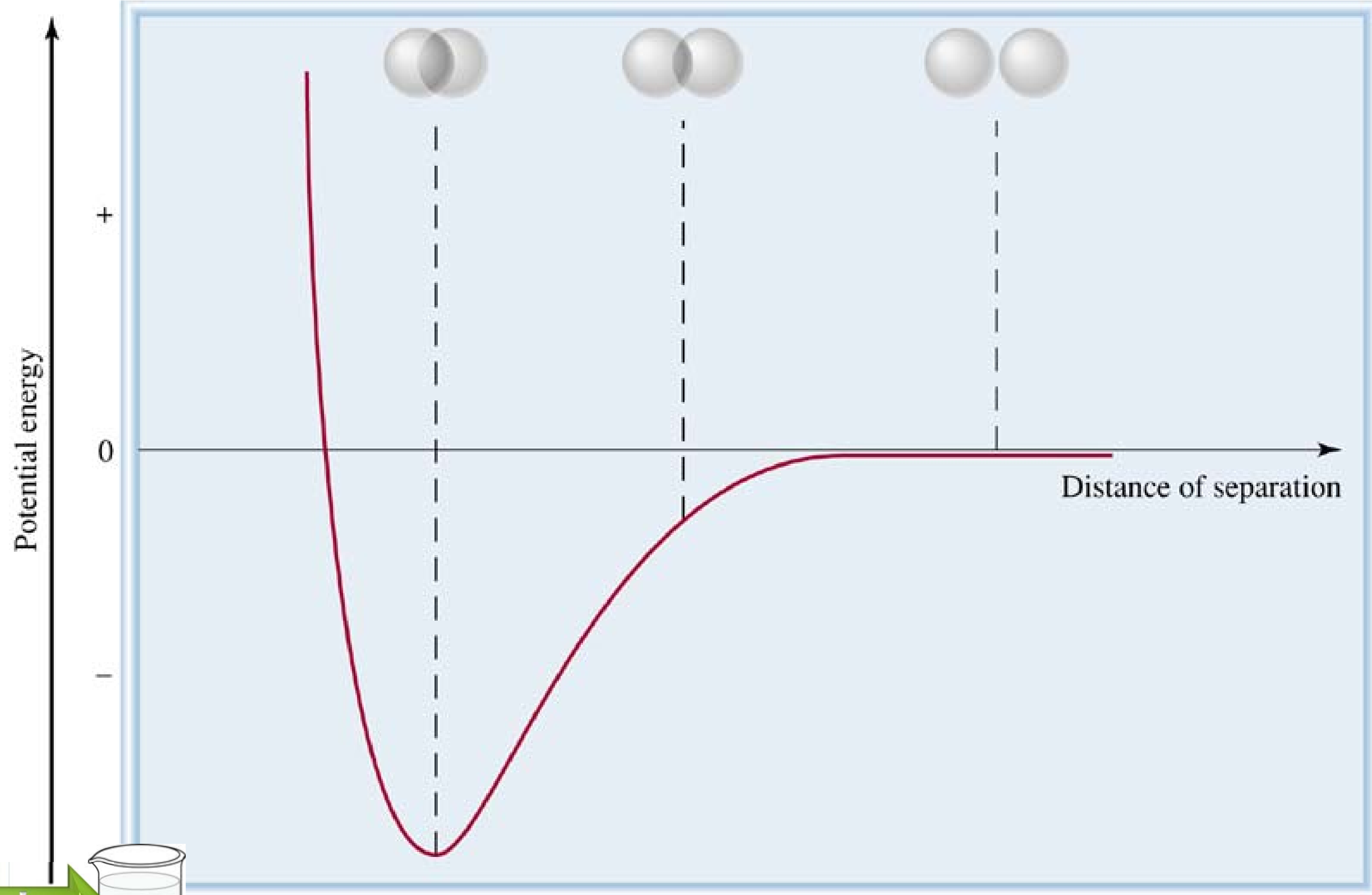


Figure 10.4 p. 338

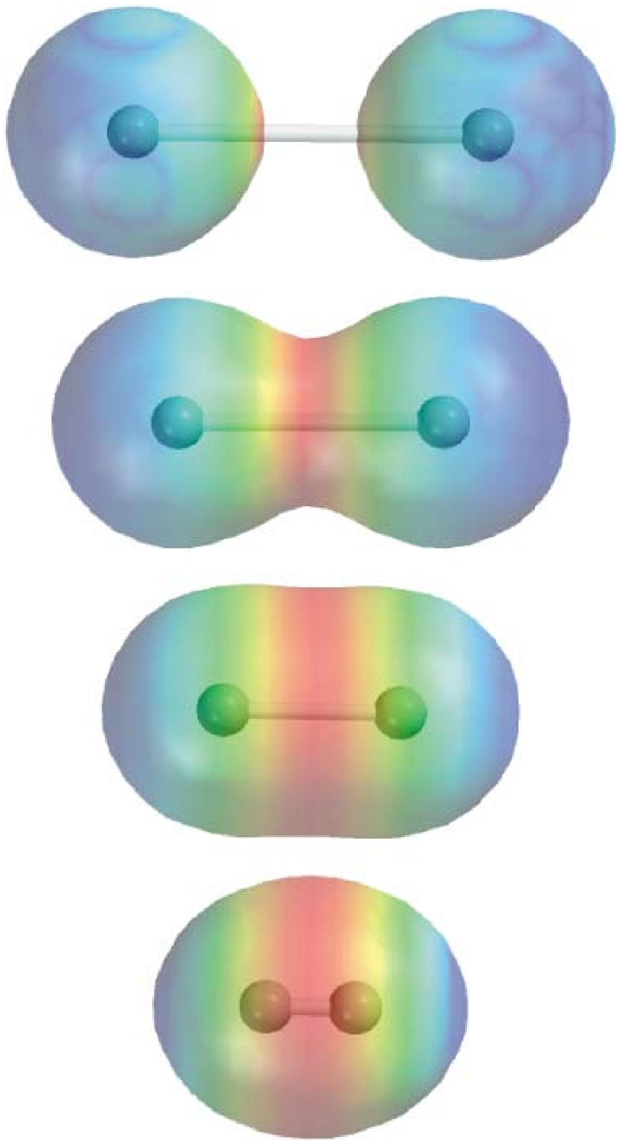
10.3 Valence Bond Theory

How do we model the bonds in H_2 and F_2?

	Bond Dissociation Energy	Bond Length	Overlap Of
H_2	436.4 kJ/mole	74 pm	1s atomic orbitals
F_2	150.6 kJ/mole	142 pm	2p atomic orbitals

Valence bond theory – bonds are formed by sharing of e^- from overlapping **atomic** orbitals.

10.3 Valence Bond Theory



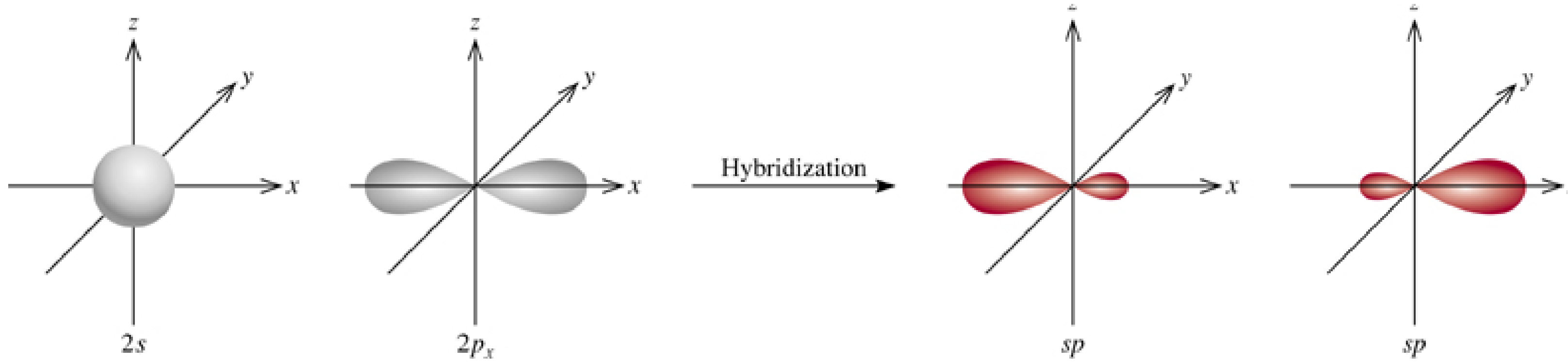
Change in electron density as two hydrogen atoms approach each other.

Figure 10.5 p. 339

10.4 Hybridization of Atomic Orbitals

- In terms of atomic orbitals, how do bonds form?
- How are these represented using atomic orbitals?
- What are sigma bonds?
- What is hybridization?
  - Mixing of atomic orbitals in an atom (usually a central atom) to generate a set of hybrid orbitals
- How are hybrid atomic orbitals more conducive to molecular shapes that are observed?

10.4 Hybridization of Atomic Orbitals



sp

Figures 10.9 and 10.10 p. 342

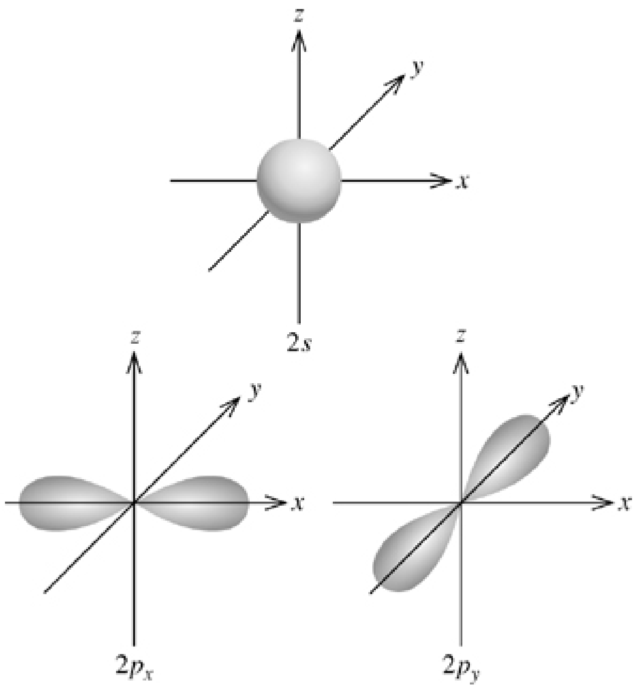
10.4 Hybridization of Atomic Orbitals

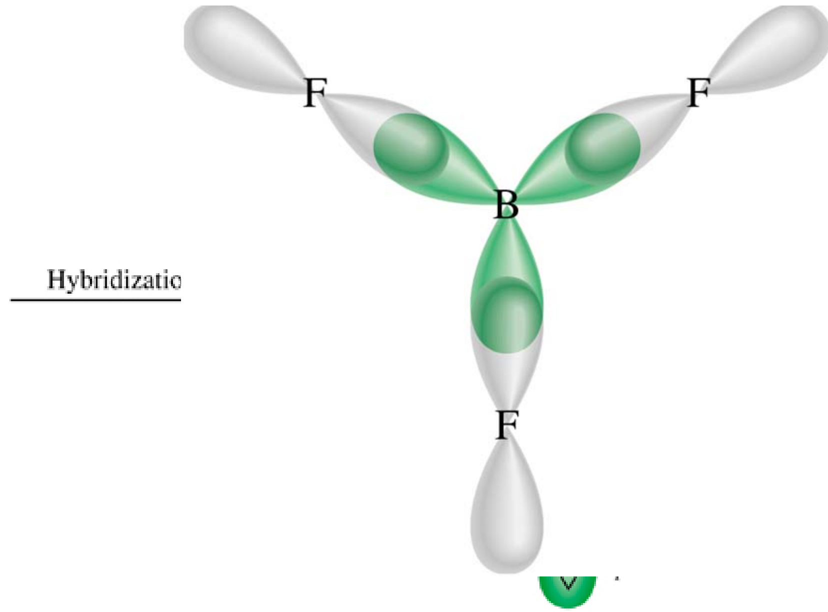
- In terms of atomic orbitals, how do bonds form?
- How are these represented using atomic orbitals?
- What are sigma bonds?
- What is hybridization?
  - Mixing of atomic orbitals in an atom (usually a central atom) to generate a set of hybrid orbitals
- How are hybrid atomic orbitals more conducive to molecular shapes that are observed?

10.4 Hybridization of Atomic Orbitals

1. Mix at least 2 nonequivalent atomic orbitals (e.g. s and p). Hybrid orbitals have very different shape from original atomic orbitals.
2. Number of hybrid orbitals is equal to number of pure atomic orbitals used in the hybridization process.
3. Covalent bonds are formed by:
   a. Overlap of atomic orbitals with other atomic orbitals (bonds in H_2)
   b. Overlap of hybrid orbitals with atomic orbitals
   c. Overlap of hybrid orbitals with other hybrid orbitals

10.4 Hybridization of Atomic Orbitals



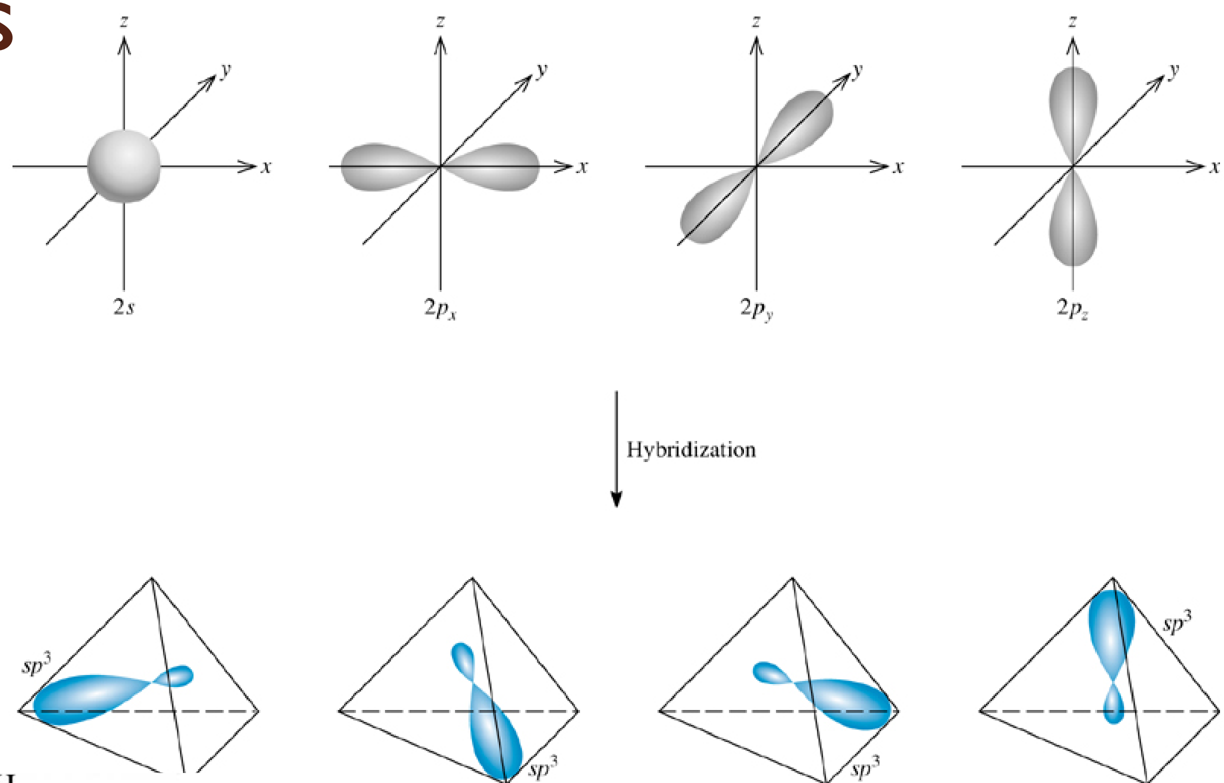


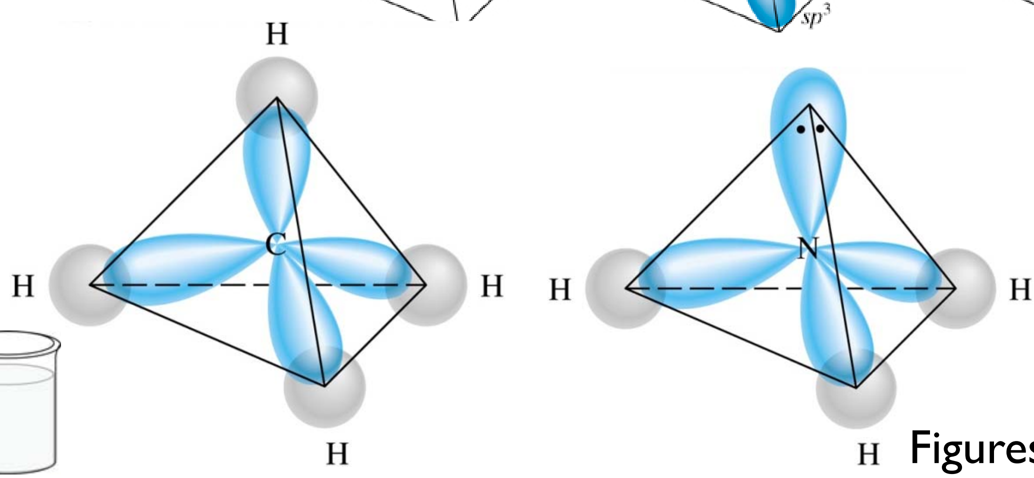
sp^2

Figures 10.11 and 10.12 p. 343

10.4 Hybridization of Atomic Orbitals

sp^3





Figures 10.6 -10.8 p. 340-341

10.5 Hybridization in molecules containing double and triple bonds

- What are double and triple bonds?
- What are pi bonds?
- How do pi bonds fit into the model of using hybridized atomic orbitals for sigma bonding?
- Does this fit with the bond energies and lengths we have?

10.5 Hybridization in molecules containing double and triple bonds

C_2H_4

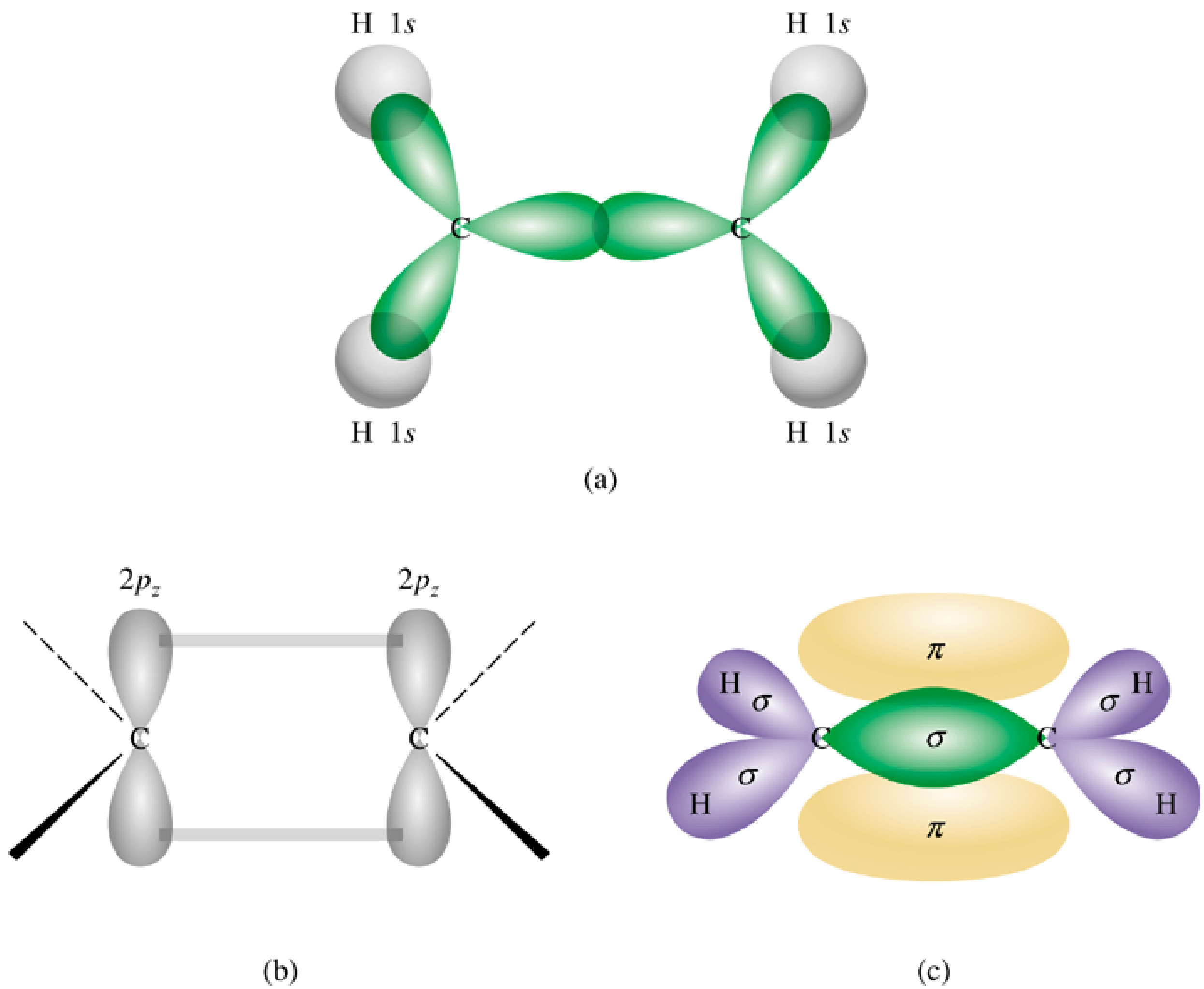
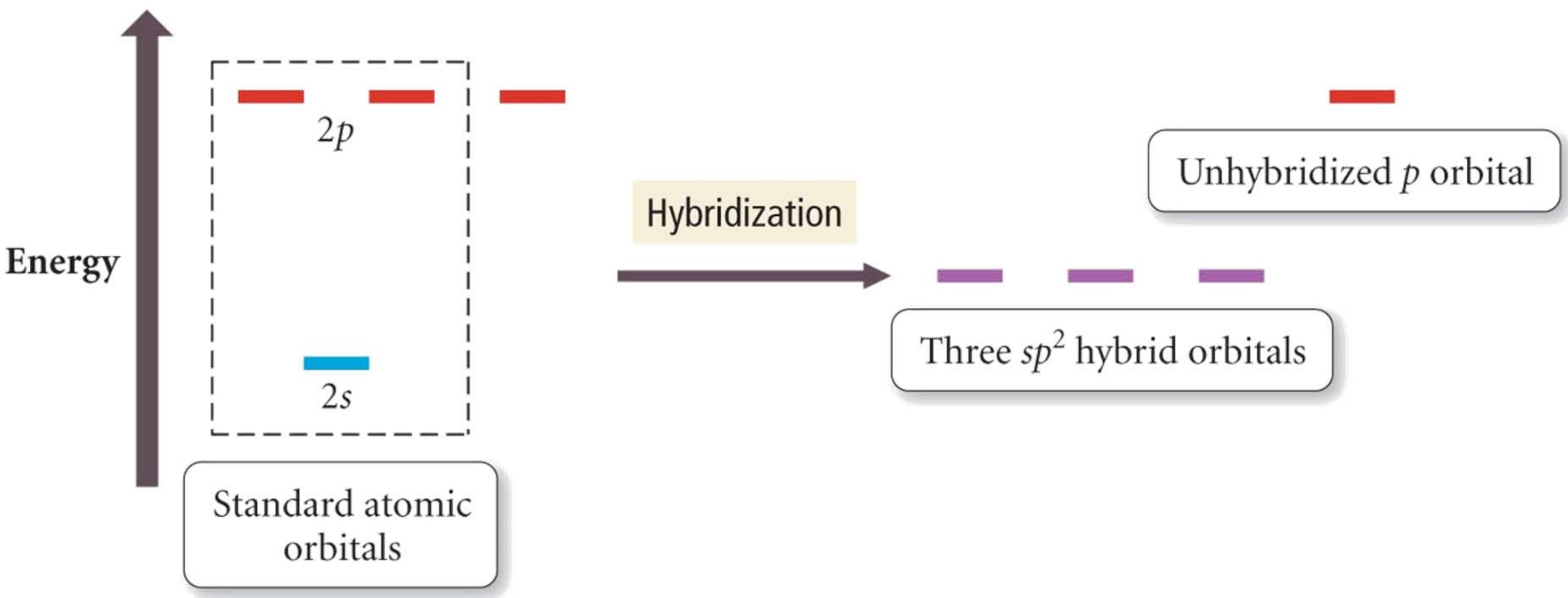


Figure 10.15, p. 346

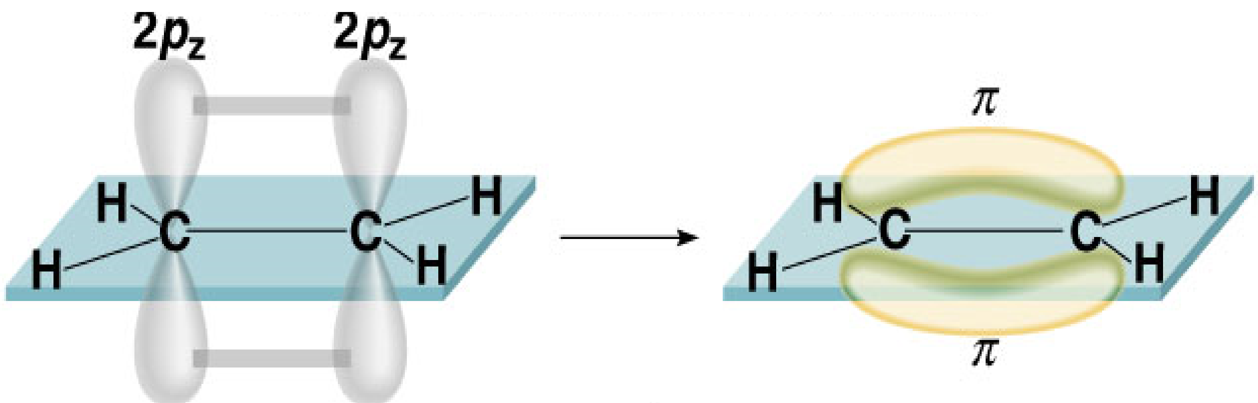
10.5 Hybridization in molecules containing double and triple bonds

C_2H_4

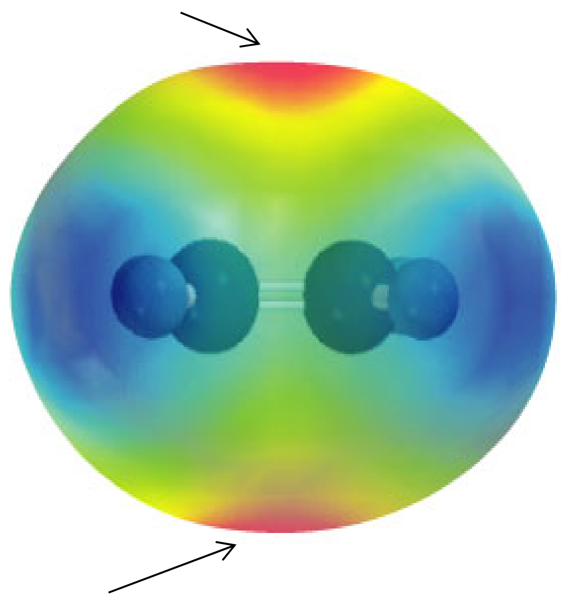


C_2H_4

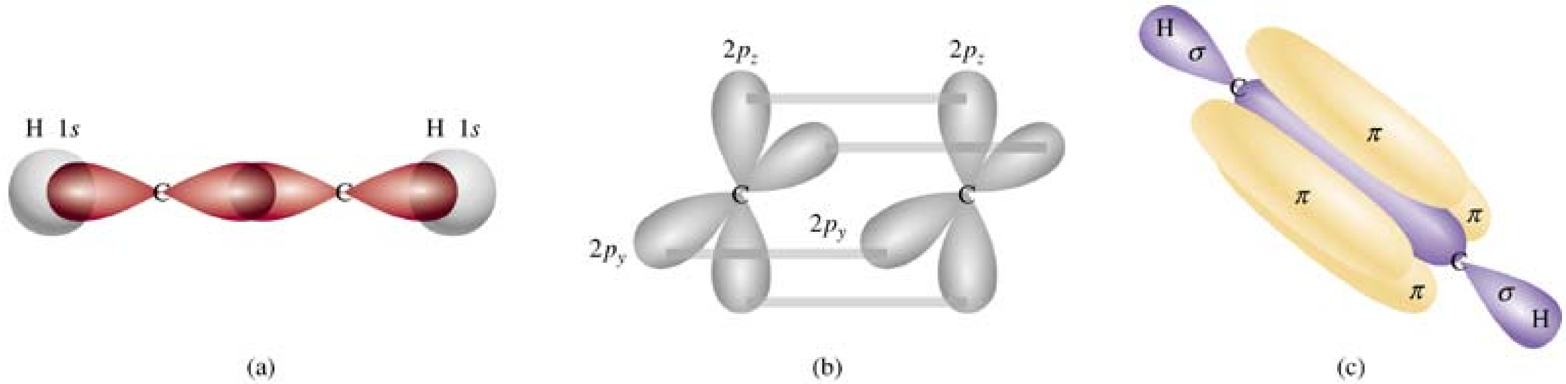
10.5 Hybridization in molecules containing double and triple bonds



(a)



10.5 Hybridization in molecules containing double and triple bonds

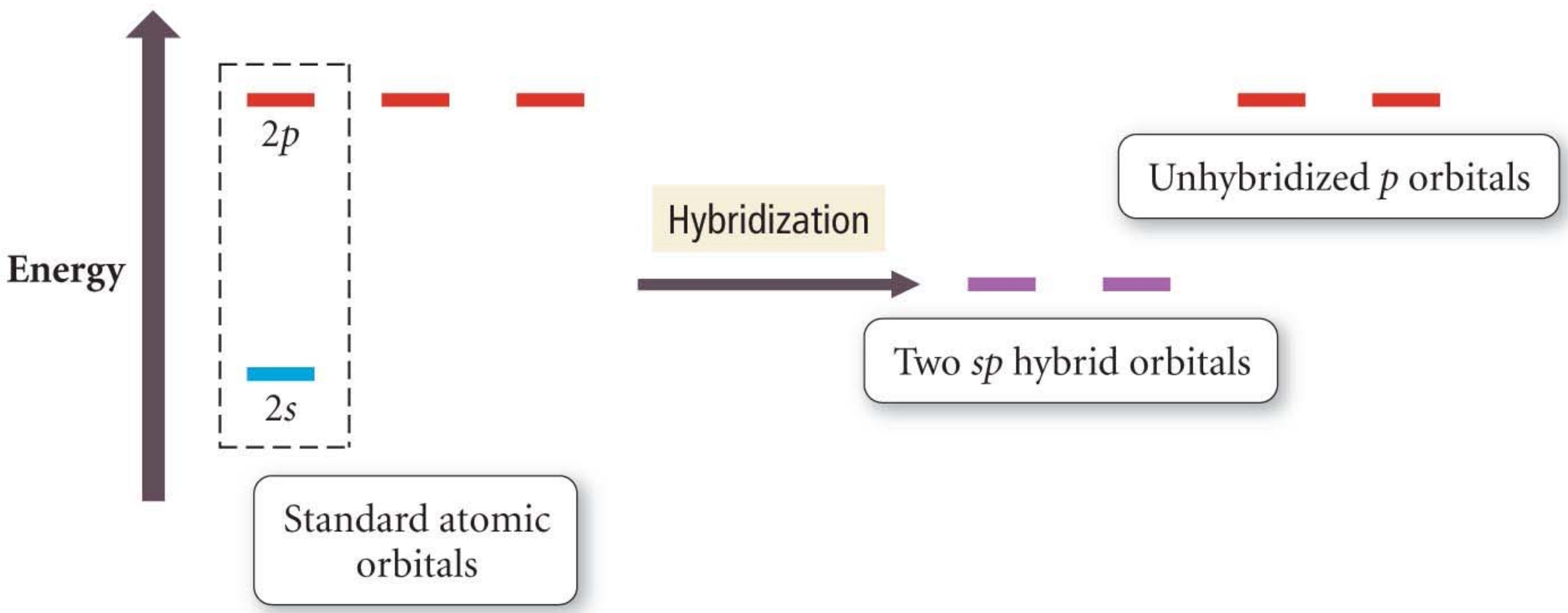


C_2H_2

Figure 10.18 p. 347

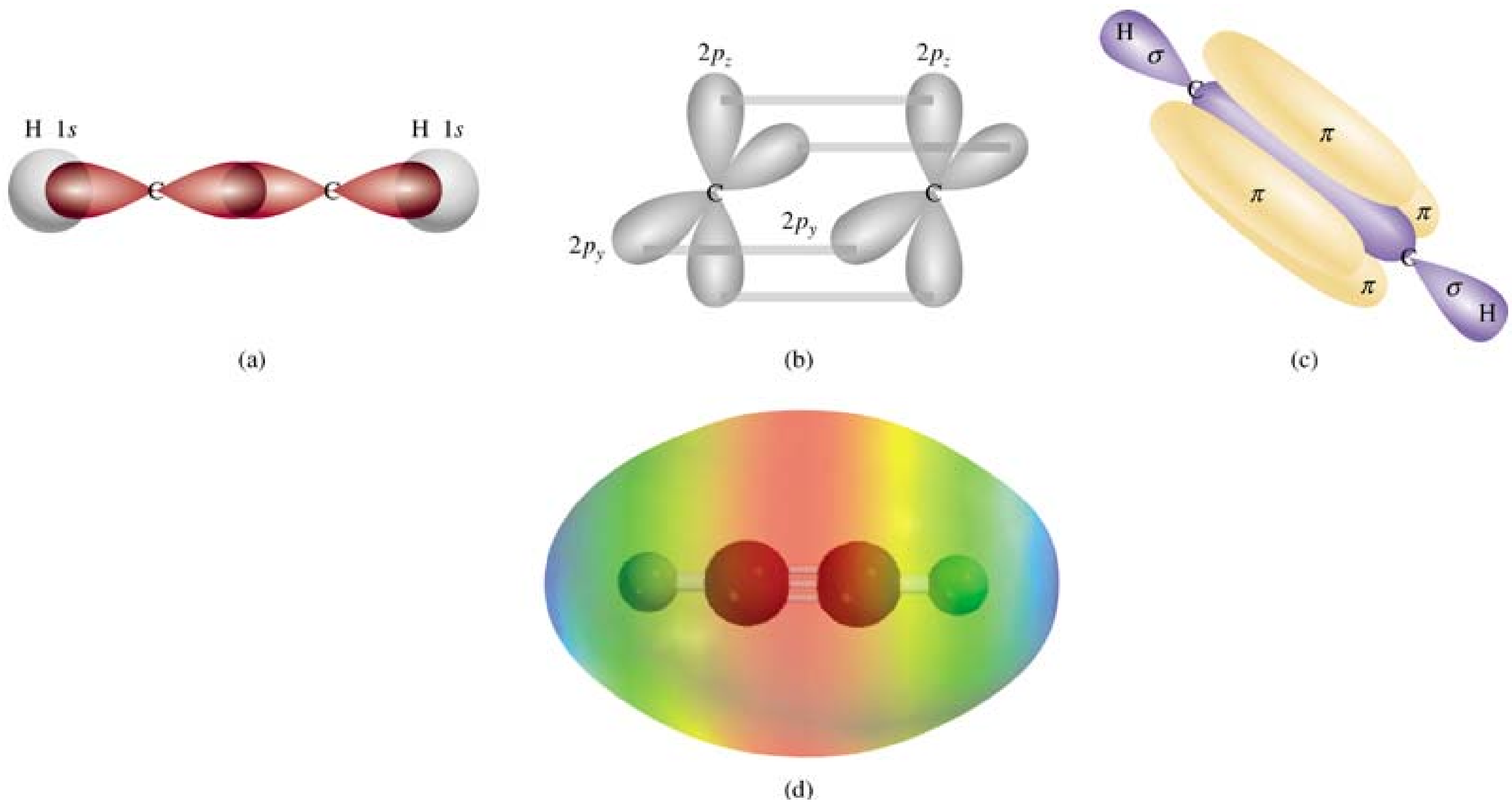
C_2H_2

10.5 Hybridization in molecules containing double and triple bonds



C_2H_2

10.5 Hybridization in molecules containing double and triple bonds



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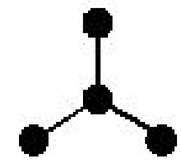
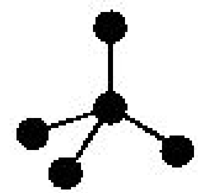
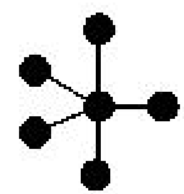
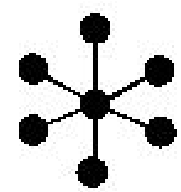
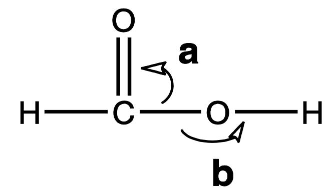
# electron groups	Bond angle	Base geometry	# lone pairs	Shape		Hybridization
2	180°	Linear	0	Linear		sp
3	120°	Trigonal planar	0	Trigonal planar		sp^2
			1	Bent		
4	109.5°	Tetrahedral	0	Tetrahedral		sp^3
			1	Trigonal pyramidal		
			2	bent		
5	90°/120°	Trigonal bipyramidal	0	Trigonal bipyramidal		sp^3d
			1	See-saw		
			2	t-shaped		
			3	Linear		
6	90°	Octahedral	0	Octahedral		sp^3d^2
			1	Square pyramidal		
			2	Square planar		

Chapter 10 – Practice

What are the marked bond angles in formic acid (shown)?

	a	b		a	b
A.	90°	180°	**B.**	120°	180°
C.	90°	109.5°	**D.**	120°	109.5°



What is the Lewis dot structure for bromine pentafluoride?

What is the formal charge on bromine?

What are the oxidation states on: Br F

What is the bond angle in this molecule?

What is the geometry of this molecule?

This molecule contains POLAR / NONPOLAR bonds. (Circle one)

This molecule is POLAR / NONPOLAR. (Circle one)

Chapter 10 – Practice

Which molecule contains polar bonds but is nonpolar?

(A) CH_4 **(B)** CH_2F_2 **(C)** HF **(D)** H_2

What is the hybridization of carbon when it makes 4 single bonds?

(A) *sp* **(B)** sp^2 **(C)** sp^3 **(D)** sp^3d