

Chemistry 1B

Fall 2016

Sessions ~~Lectures~~ 15-16
Covalent Bonding and Geometry
in Polyatomic Molecules

1

LISTEN UP!!!

- WE WILL NOW BE COVERING THE FIRST PART OF CHAPTER 14 (pp 663-676) AND THEN (688-692)
- You will go **CRAZY** unless you concentrate on the material presented in lecture and homework

2

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Sessions 15-16

covalent bonding in polyatomic molecules

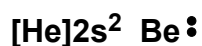
- similar to bonding in diatomic molecules in that ao's on one atom constructively interfere with on second atom to form bonds
- new twist is that the covalent bonds **can involve more than one ao on each atom** (we had a taste of this with the extra 2s-2p interactions in the B₂, C₂, N₂ diatomics)

3

what "bonds" would atoms in their ground atomic states form ?

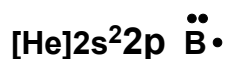
bonding with H •

expected from
atomic configuration



no bonds

but BeH₂ exists



• B-H

but also BH₃



•CH₂

but also CH₄



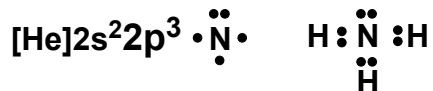
•NH₃

also H₂O and HF

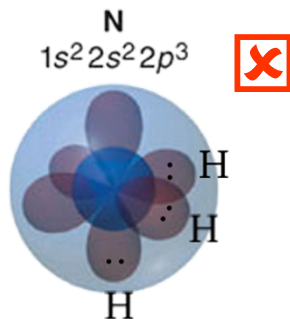
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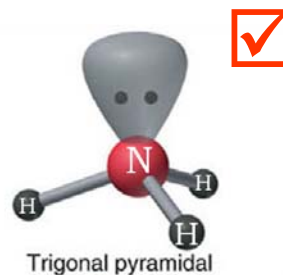
also what does qm have to say about bond angles



has the $2p^3$ electron in orbitals which are at 90°



BUT



H-N-H angle = 90°

H-N-H angle = 107°

5

so what's wrong with electrons in atomic configuration ???

Observed increased stability (lower energy) over 'atomic' ground state configuration via:

- **formation of additional covalent bonds**
- **arrangement of electron groups to minimize repulsion**

How does one account for:

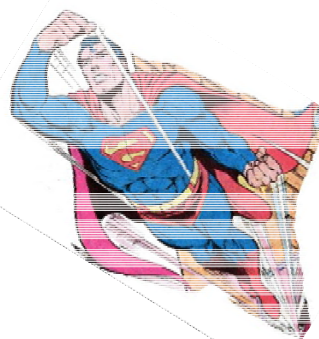
- formation of additional bonds over what would be expected from atomic electron configuration
- bond angles different than those between atomic [p]orbitals

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quantum mechanics to the rescue !!!!!

ORBITAL HYBRIDIZATION



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Hybridization (energy costs and gains)



In forming covalent bonds an atom may use higher energy ao's which are not occupied in the ground state of the isolated atom.

Energy costs (disadvantages of hybrid orbitals)

- uses 'higher' energy ao's

Energy gains (advantages of hybrid orbitals)

- form more covalent bonds than in atomic configuration
- gives geometry where electron groups minimize repulsion (a la VSEPR)
- gives better overlap (constructive interference between orbitals on two atoms forming a bond)

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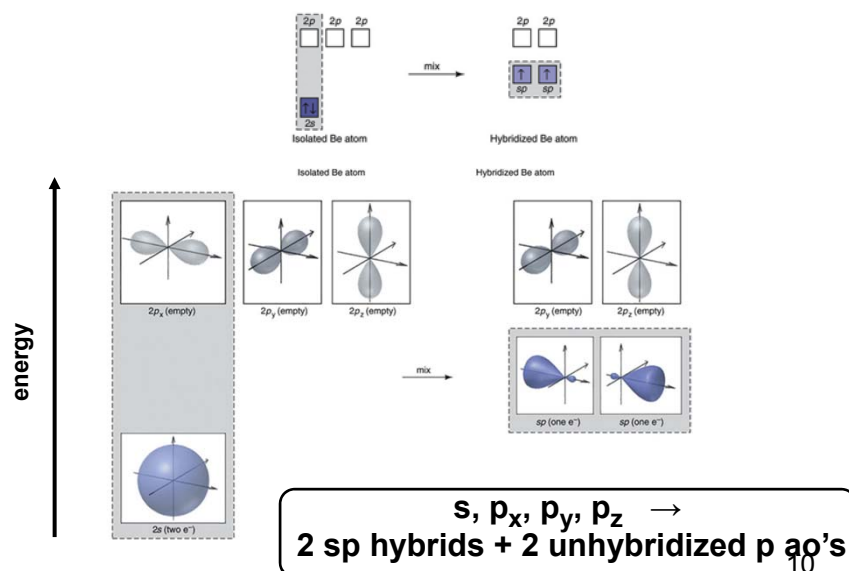
Different order of presentation than text

Zumdahl: $sp^3 \rightarrow sp^2 \rightarrow sp$ ☹️

US: $sp \rightarrow sp^2 \rightarrow sp^3$ 😊

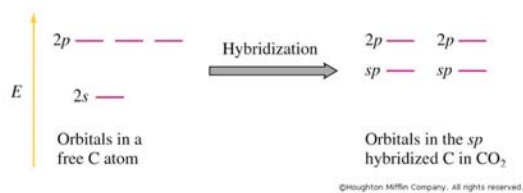
9

sp hybridization in BeH₂ (Silberberg fig 11.2)



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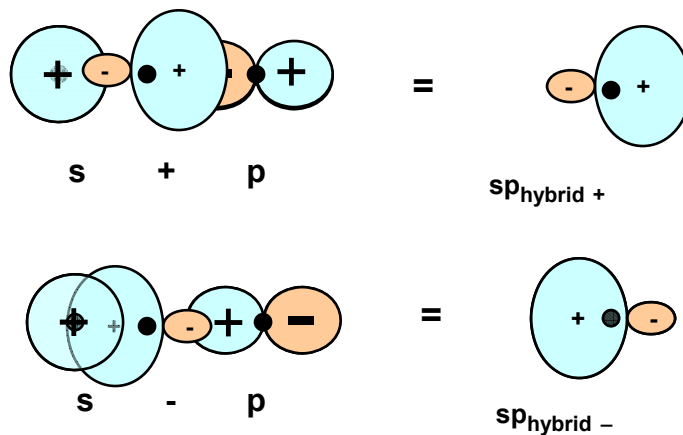
sp hybridization (figure 14.16)



- **s, p_x, p_y, p_z → 2 sp hybrids + 2 unhybridized p ao's**
- **angle between sp hybrids is 180° giving linear geometry**

11

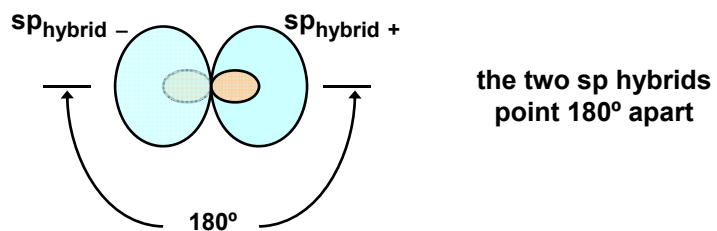
*nature of the sp hybrids (adding of ao's on **SAME** atom)*



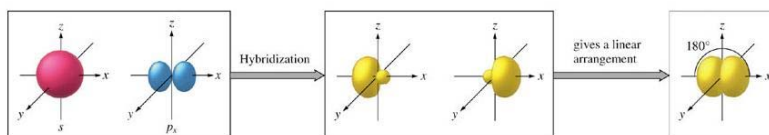
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figure 14.14



the two sp hybrids
point 180° apart

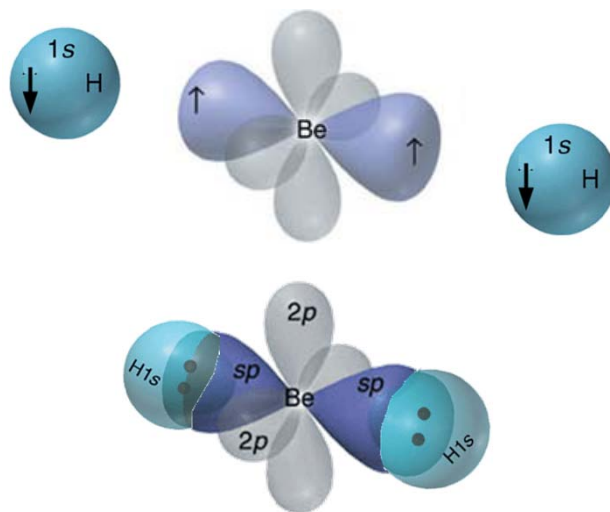


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[Dr. Gutow's Hybrid Atomic Orbital Site](#) →

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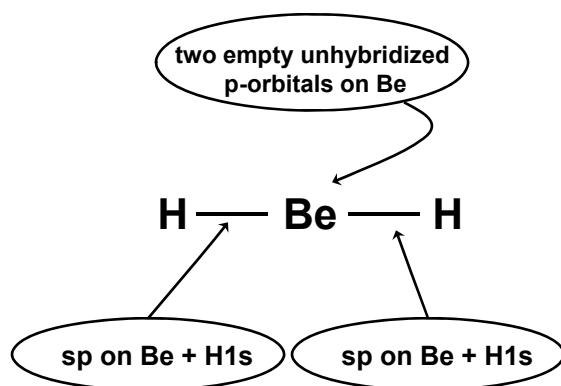
formation of Be-H bonds



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BeH₂ description of bonds



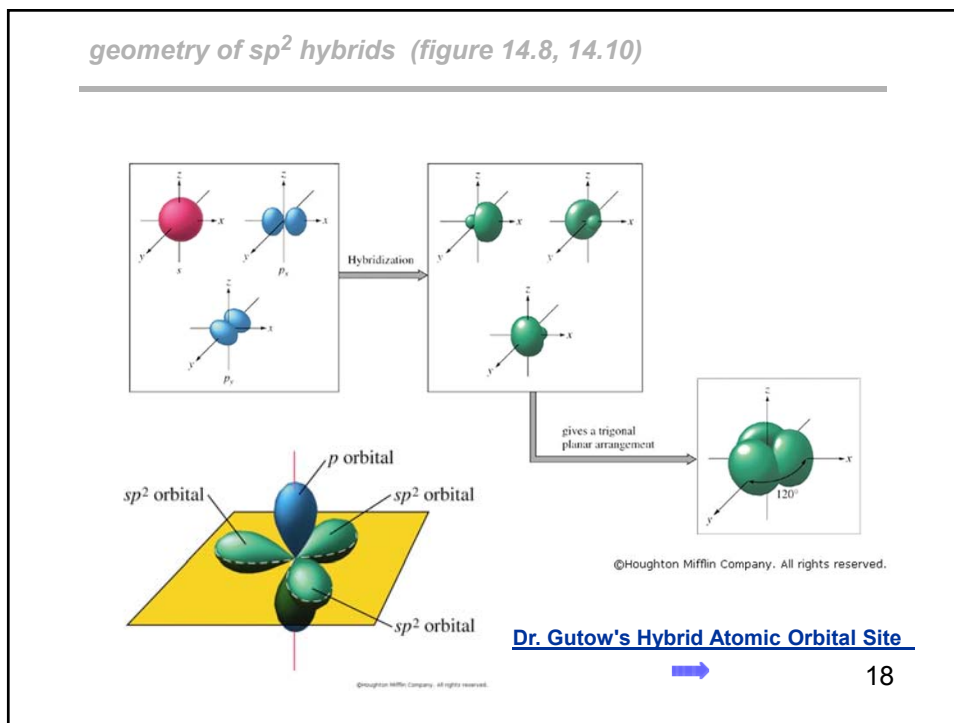
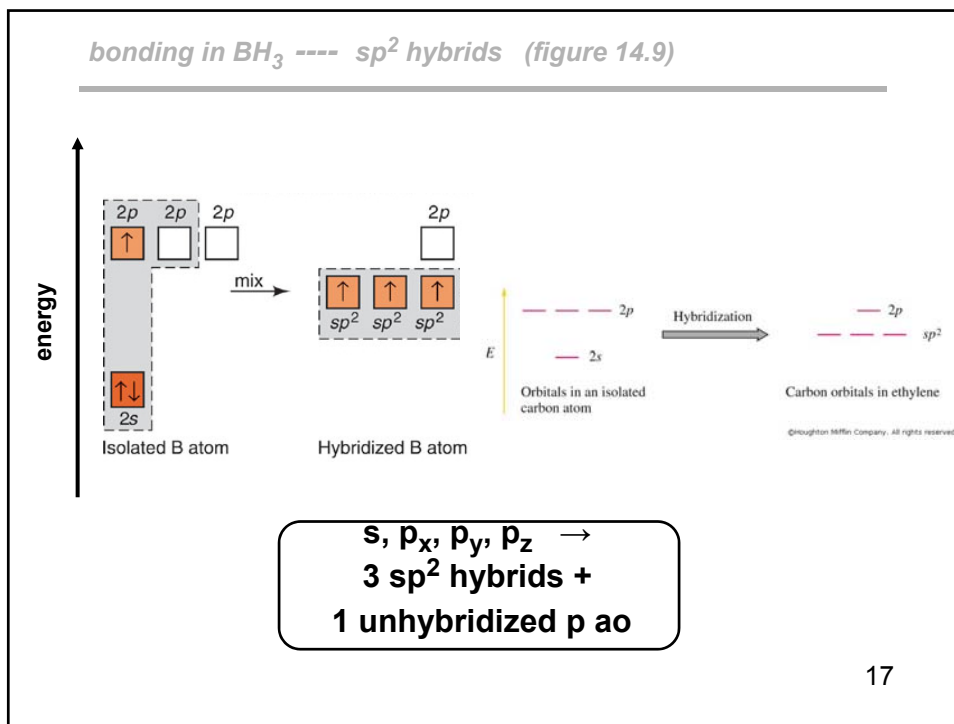
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hybridization vs bonding

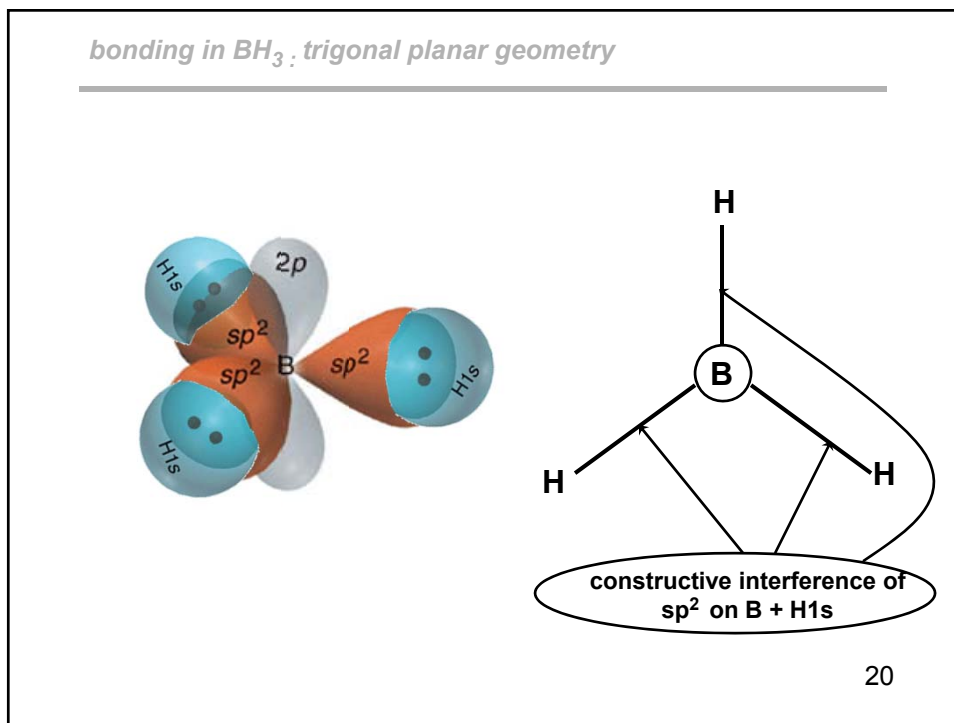
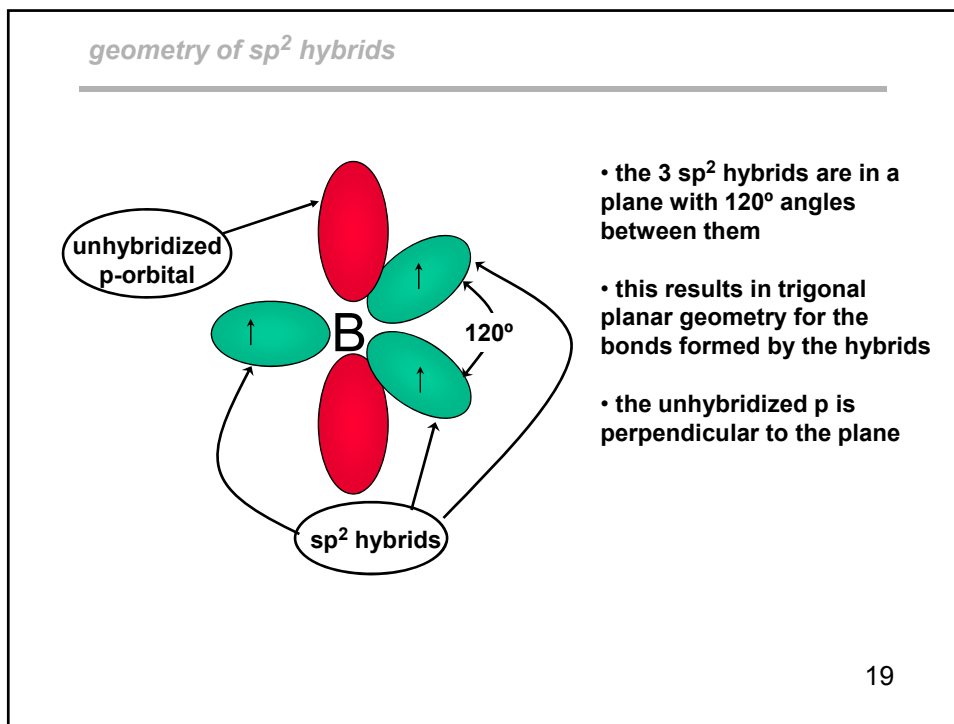
- The 'first' step of hybridization involves combining orbitals on **A SINGLE** atom. This may involve orbitals which do not have **NET** overlap (e.g. 2s and 2p) to get the hybrid orbitals (e.g. sp_+ and sp_-)
- Since there is no net interference, this step involves **NO** change of energy from that of the average of the a.o. energies [i.e. sp hybrids have average energy of $\frac{1}{2}(E_{2s} + E_{2p})$]
- Bonding occurs when the **hybrids on TWO** atoms constructively interfere to give a lower energy localized m.o. (a chemical bond)

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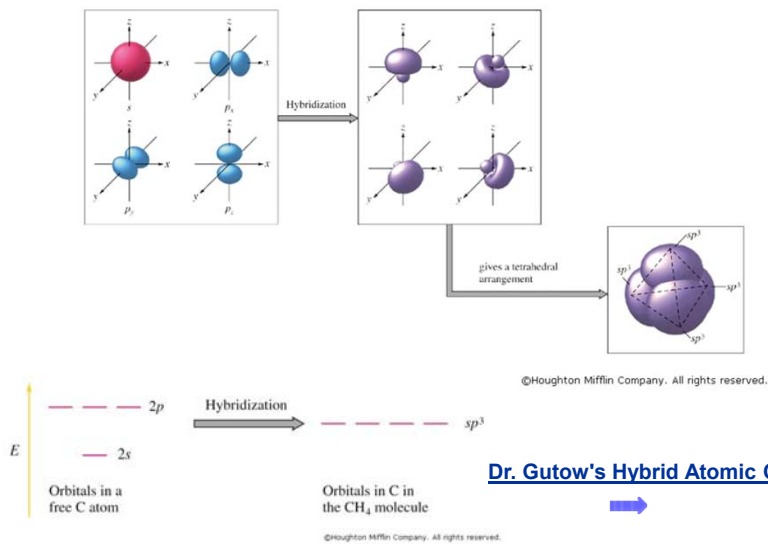


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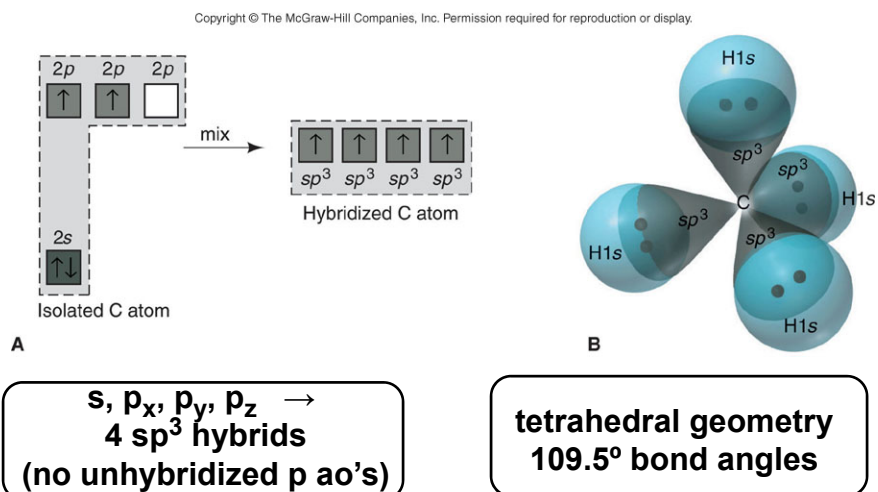


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CH₄: sp³ hybridization (figures 14.3 and 14.5)



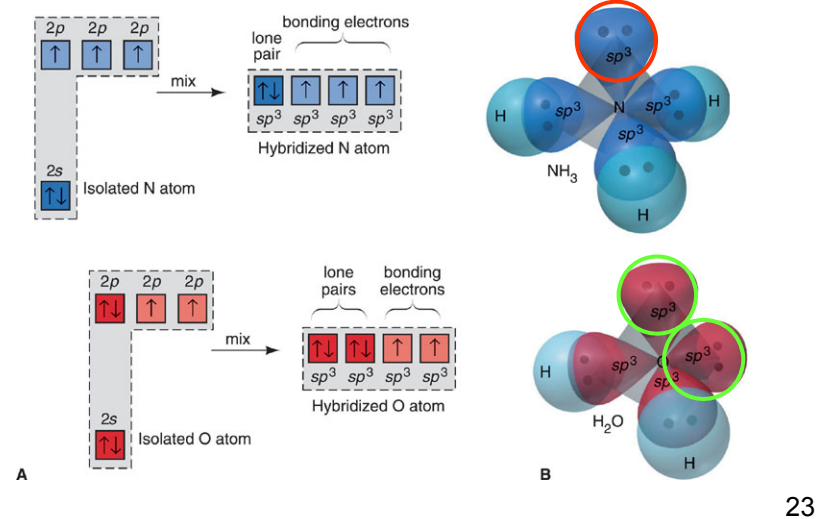
CH₄: sp³ hybridization



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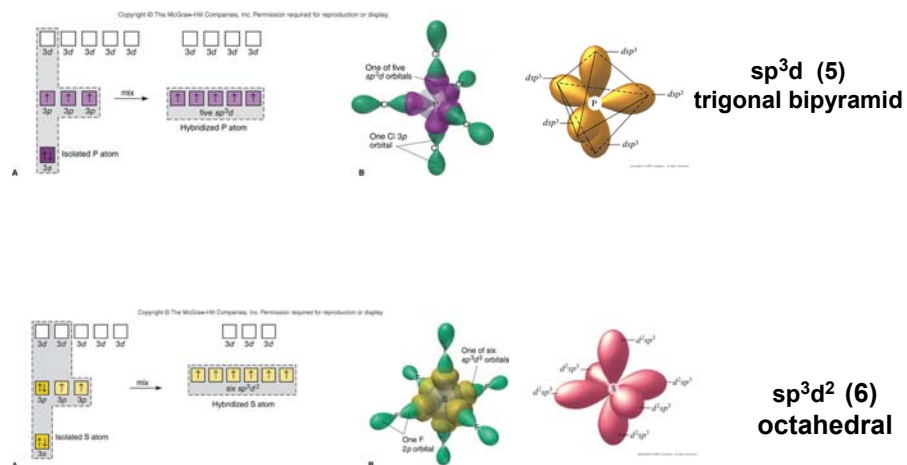
lone pairs can occupy hybrid orbitals (fig. 11.5)

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other hybridizations (pp. 668-670)

DON'T FRET



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summary (figure 14.24)

Number of Effective Pairs	Arrangement of Pairs	Hybridization Required
2	Linear	sp
3	Trigonal planar	sp^2
4	Tetrahedral	sp^3
5	Trigonal bipyramidal	d^1sp^3
6	Octahedral	d^2sp^3

know that these exist

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**HYBRIDIZATION:
multiple bonds,
geometric isomers.**

pp. 668-671

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Sessions 15-16

have covered worksheet 10-9, sections I-V

Chemistry 1B-O2, Fall 2016, Study Guide and Worksheet IX

Learning Objectives and Worksheet IX

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Sections I-V Bonding in Polyatomic Molecules:

RETURNING TO THE FIRST PART OF CHAPTER 14 (pp. 433-476), to cover covalent bonding in polyatomic molecules, and then onto molecular dipoles (pp. 488-493).

In the previous class sections we have investigated how covalent bonds are formed by the constructive interference of atomic orbitals on two atoms in a diatomic molecule. Now we are prepared to extend these concepts to polyatomic molecules.

I. Ground state atomic configurations do not predict molecular structures

1. In the H_2 molecule we saw how atomic orbitals containing an unpaired electron on each H atom interact to form a bonding molecular orbital that accommodated the electron pair. For the atoms below, indicate the formulas of the hydrides that would be formed by an H atom combining with unpaired electrons in the atom's ground state to form QH bonds.

I. Li
 II. Be
 III. B
 IV. C
 V. N

2. In the ground state of atomic nitrogen, $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^0$, 3 H atoms could interact with the unpaired electrons in the $2p$ orbitals to form the stable acet structure NH_3 . From your knowledge of the geometry of the $2s$, $2p_x$, $2p_y$, and $2p_z$ atomic orbitals the predicted H-N-H bond angle would be _____°.

II. General principles of hybridization

1. In forming covalent bonds in polyatomic molecules hybrid orbitals may be utilized. A hybrid orbital consists of _____ that may include both occupied and unoccupied in the atom's ground state configuration.

2. In forming hybrids what are the "costs" in terms of energetics (i.e. higher energy relative to atomic _____) would be a cost of forming hybrids. This is why isolated atoms do not "naturally" go to a hybridized state.

1

Chemistry 1B-O2, Fall 2016, Study Guide and Worksheet IX

3. There are several energetic advantages accrued (lowering of energy) when an atom utilizes hybrids to form covalent bonds in a polyatomic molecule. These include:

I. _____
 II. _____
 III. _____

4. We will see that whether a molecular structure involves primarily atomic or hybrid orbitals depends on the "winner" of the energy costs vs energy gains. In describing the m.a. of diatomic molecules we focused on combinations of unhybridized atomic orbitals. However $s-p$ mixing or sp hybridization was invoked for the energy ordering for B_2 , C_2 , N_2 , but not O_2 or F_2 . In terms of energy costs vs gains, why would $s-p$ mixing occur for the lower atomic number 2nd row atoms but not for 2nd or 3rd?

5. A bonding orbital between a hybrid orbital on boron atom and a $1s$ atom is formed by _____ between the hybrid orbital and a $1s$ a.o. on the H atom.

III. sp hybridization

1. In sp hybridization the $2s$, $2p_x$, $2p_y$, and $2p_z$ a.o. form _____ sp hybrids leaving _____ unhybridized $2p$ orbitals.

2. The sp hybrids are directed _____ apart and the unhybridized $2p$ a.o.'s are _____ to the direction of the sp hybrids.

3. If H atoms bond with unpaired electrons in the sp hybrids the resulting molecular geometry is _____.

Bonding in acetylene C_2H_2 applet (helps with HW#7, 51):
<http://www.chem.tamu.edu/teaching/med/3dmodels/bonding/html/moBonding.html>

IV. sp^2 hybridization

1. In sp^2 hybridization the $2s$, $2p_x$, $2p_y$, and $2p_z$ a.o. form _____ sp^2 hybrids leaving _____ unhybridized $2p$ orbitals.

2. The sp^2 hybrids are directed _____ apart and the unhybridized $2p$ a.o. is _____ to the plane of the sp^2 hybrids.

3. If H atoms bond with unpaired electrons in the sp^2 hybrids the resulting molecular geometry is _____.

2

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this video: worksheet 10-9 sections VI-VII

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V. sp^3 hybridization

1. In sp^3 hybridization the $2s$, $2p_x$, $2p_y$, and $2p_z$ a.o. form _____ sp^3 hybrids leaving _____ unhybridized $2p$ orbitals.

2. The sp^3 hybrids are directed _____ apart.

3. If H atoms bond with unpaired electrons in the sp^3 hybrids the resulting molecular geometry is _____.

Excellent website to visualize sp^3 hybrids:
http://www.uconn.edu/faculty_staff/afrow/Orbitals/Use%20Hybrid%20.html

VI. Bonding in molecules with more than one 2nd row atom

1. In the molecule n-propane $CH_3CH_2CH_3$

I. the geometry around the central carbon would be _____
 II. the C-C bonds would be the result of constructive interference between _____
 III. the C-H bonds would be the result of constructive interference between _____

2. In the molecule propene $CH_3CH=CH_2$

I. the geometry around the central carbon would be _____
 II. the C-C bond(s) would be the result of constructive interference between _____
 a. _____ and _____ (for one component of double bond)
 b. _____ and _____ (for the second component)
 III. the C-C single bond would be the result of constructive interference between _____

VII. When might an atomic bond with unhybridized a.o.'s?

1. The geometry of some molecules with third row central atoms indicates that the atom is forming bonds with predominantly unhybridized a.o.'s. Why might this be so in terms of the costs and advantages of hybridization?

3

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V. sp^3 hybridization

1. In sp^3 hybridization the $2s$, $2p_x$, $2p_y$, and $2p_z$ a.o. form _____ sp^3 hybrids leaving _____ unhybridized $2p$ orbitals.

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3

clicker questions worksheet 10-9, sections I-VII

Monday, 14 November

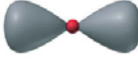



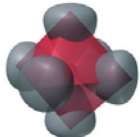
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summary

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Table 11.1 Composition and Orientation of Hybrid Orbitals

	Linear	Trigonal Planar	Tetrahedral	Trigonal Bipyramidal	Octahedral
Atomic orbitals mixed	one <i>s</i> one <i>p</i>	one <i>s</i> two <i>p</i>	one <i>s</i> three <i>p</i>	one <i>s</i> three <i>p</i> one <i>d</i>	one <i>s</i> three <i>p</i> two <i>d</i>
Hybrid orbitals formed	two <u><i>sp</i></u>	three <u><i>sp</i>²</u>	four <u><i>sp</i>³</u>	five <i>sp</i> ³ <i>d</i>	six <i>sp</i> ³ <i>d</i> ²
Unhybridized orbitals remaining	two <i>p</i>	one <i>p</i>	none	four <i>d</i>	three <i>d</i>
Orientation					

know that these exist



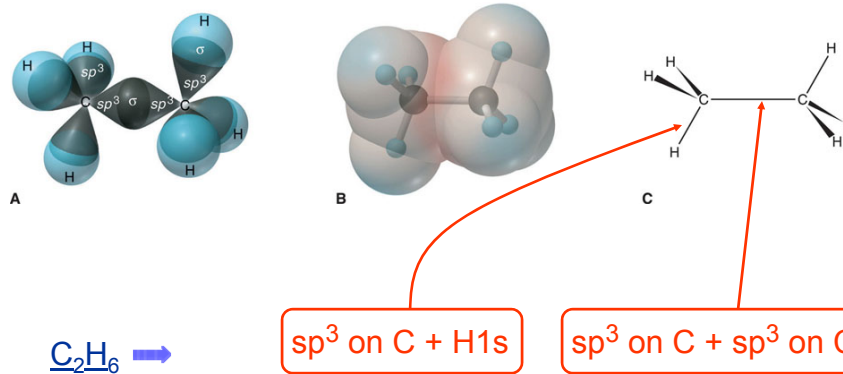
movie:
good summary of hybridization →
from Silberberg supplemental material

"valence bond theory" = "localized bond theory"

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bonding in molecules with several 2nd row atoms

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ethylene (ethane)

from VSEPR

- SN=3
- trigonal planar

↓

- sp^2

31

double bond – sp^2 hybridization (figs 14.12, 14.13)

3 sp^2 hybrids
+ unhybridized
p-orbital

double bond:
 $\sigma: sp^2 + sp^2$
 $\pi: p_\pi + p_\pi$

sigma bond

pi bond

(a)

(b)

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14.12 Ethylene (ethane) is a planar molecule. The carbon-carbon double bond is formed by the overlap of two sp^2 hybrid orbitals, one from each carbon, to form a σ bond. The remaining two unhybridized p orbitals on each carbon overlap to form a π bond. The π bond is formed by the overlap of p orbitals, which are oriented perpendicular to the plane of the σ bond. The resulting double bond is stronger than a single bond, and the molecule is rigid.

[Dr. Gutow's Hybrid Atomic Orbital Site](#)

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acetylene (ethyne)

$\text{H} - \text{C} \equiv \text{C} - \text{H}$

from VSEPR

- SN=2
- linear

↓

- sp

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triple bond (sp hybridization) H-C≡C-H (figure 22.10)

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$\text{H} - \text{C} \equiv \text{C} - \text{H}$

$\sigma: sp + sp$
 $\pi_y: p_{\pi y} + p_{\pi y}$
 $\pi_z: p_{\pi z} + p_{\pi z}$

sp on C + H1s

C_2H_2 →

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to hybridize or not to hybridize

to hybridize or not to hybridize



that is the question?

35

molecules with 3rd and 4th row atoms

Bond angles : H₂O (105°) vs H₂S (92.2°)
NH₃ (107°) vs PH₃ (93.4°) →

- As the central atom becomes larger the bond angles reflect unhybridized p orbital axes.
- These are cases where hybridization would be driven by reduction of electron group repulsion and increased bonding overlap (same number of bonds if unhybridized or hybridized).
- As the central atom gets larger, the repulsion between electron groups (e.g. lone pairs) decreases and thus the atom is more likely to remain unhybridized.

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terminal atoms: to hybridize or not to hybridize

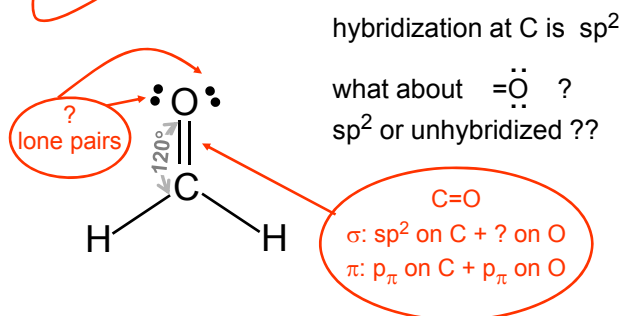
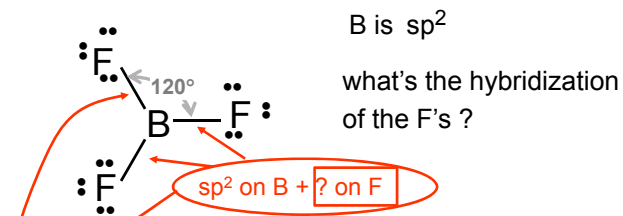
to hybridize or not to hybridize



that is still the question?

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*"terminal" atoms bonded to only one other atom
(no clues from molecular geometry, i.e. molecular shape)*



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hybridization state of terminal atoms

when there is no experimental structural evidence, the state of hybridization state in terminal atoms is often obtained from quantum mechanical calculations



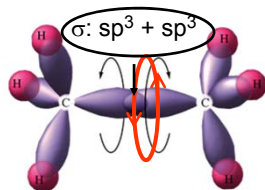
in our next class session, we will look at some examples and come to an "agreement" on what are appropriate specifications for the state of hybridization for various bonding situations



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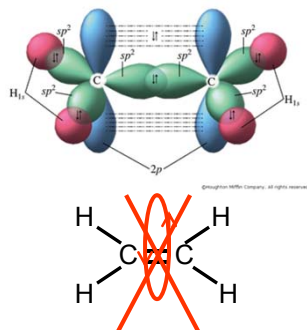
[no] rotation around double bond (figs 21.7 and 21.8)

single



'free' rotation about single bond ↓

double



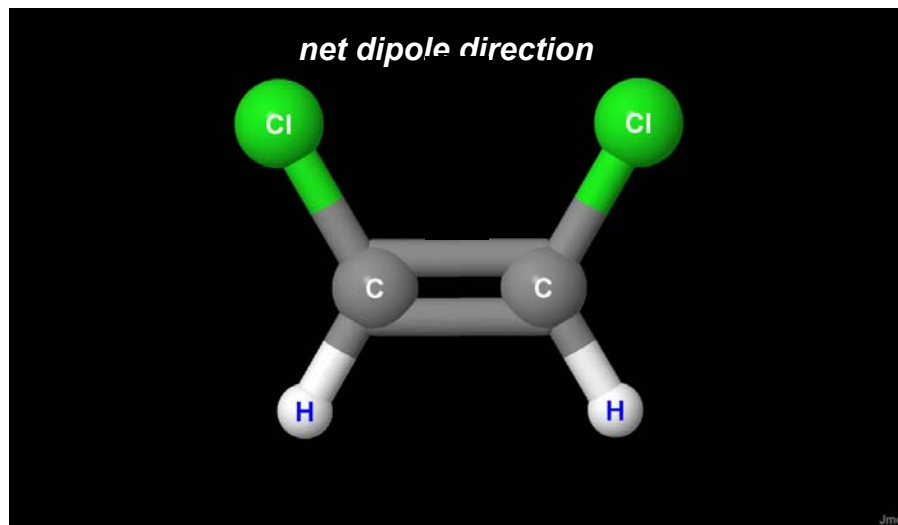
Note that the extra, overlapping pi-bond prevents free rotation around the double bond. One would have to break the pi-bond to be able to rotate around the sigma bond.

no rotation around double bond

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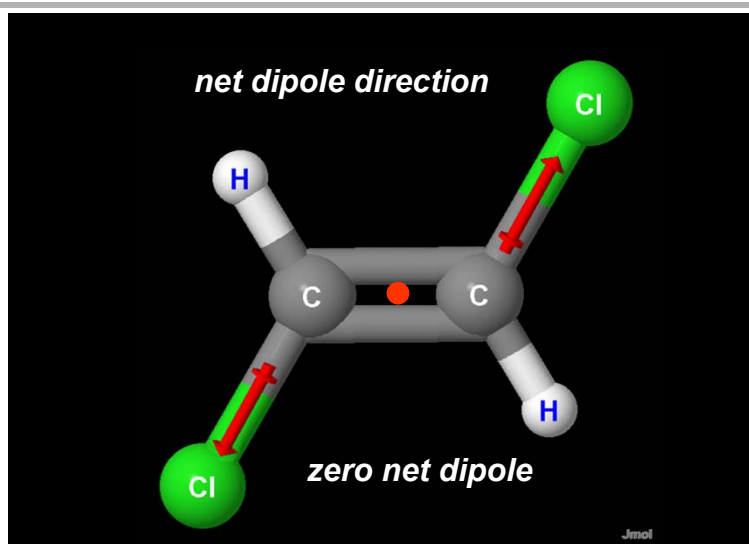
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dipole moments of geometric isomers (cis 1,2 dichloroethylene [cis 1,2 dichloroethene])



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dipole moments of geometric isomers (trans 1,2 dichloroethylene [trans 1,2 dichloroethene])

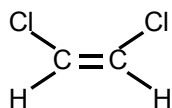


trans 1,2 dichloroethylene →

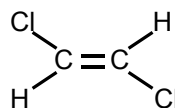
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double bonds and geometric isomers



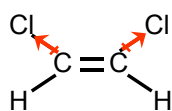
vs



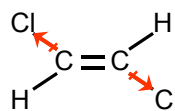
cis 1,2 dichloroethene

trans 1,2 dichloroethene

will not interconvert under 'normal' conditions



net dipole \updownarrow



no net dipole •

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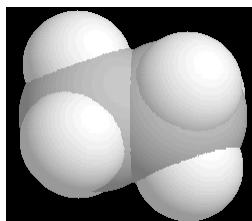
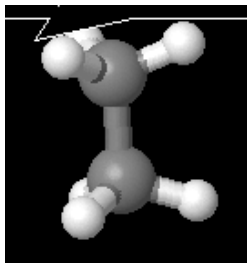
Finis
and



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'free' rotation around a single bond



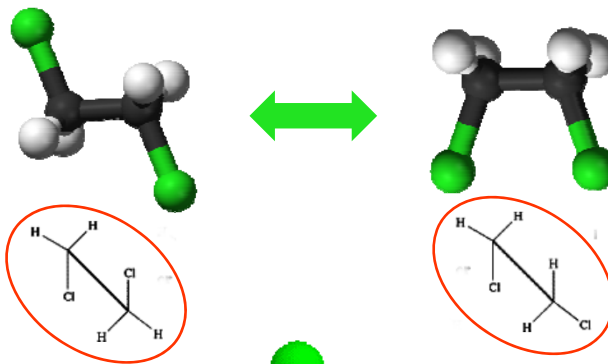
'free' rotation around single bond of ethane

maybe not so free !!
pair-share exercise

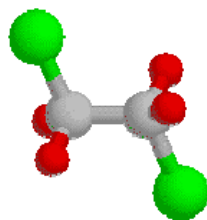


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no geometric isomers normal conditions (1,2 dichloroethane)



no geometric isomers

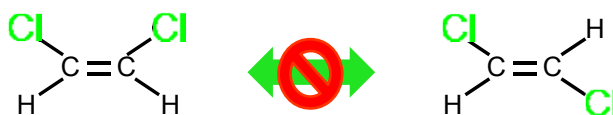


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double bonds and geometric isomers

geometric isomers: two or more compounds which contain the same number and types of atoms, and bonds (i.e., the connectivity between atoms is the same), but which have different spatial arrangements of the interatomic distances between atoms and thus have differing physical and chemical properties



cis 1,2 dichloroethylene

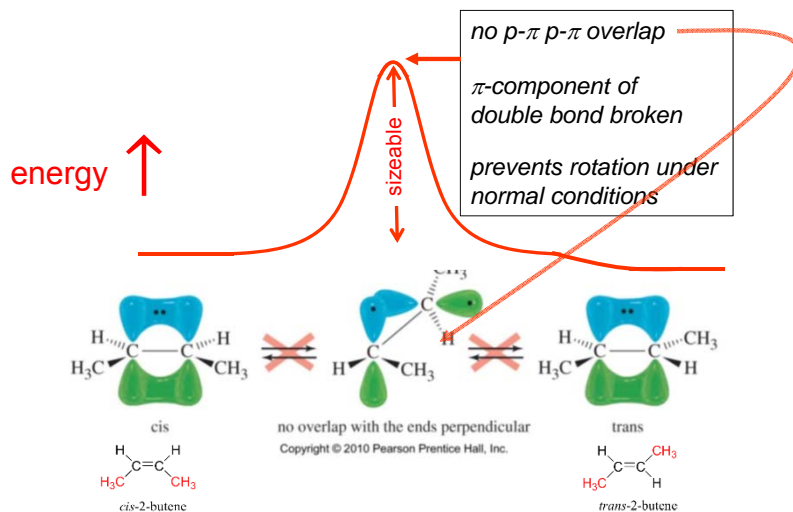
trans 1,2 dichloroethylene

will not interconvert under 'normal' conditions



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[no] rotation around double bond



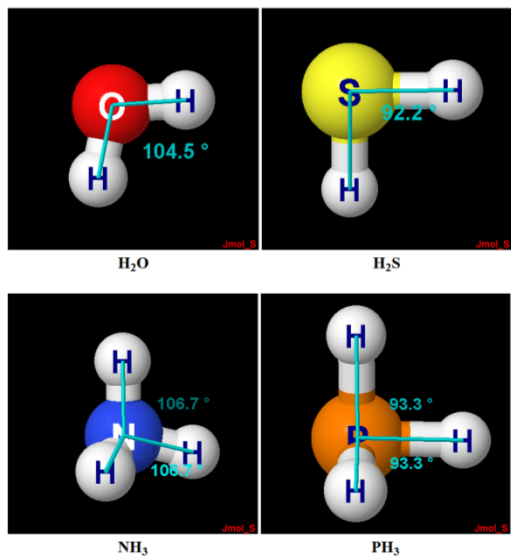
but does “no” mean “never” ?



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hybridization or not: 2nd row vs 2rd row



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terminal atoms: to hybridize or not to hybridize

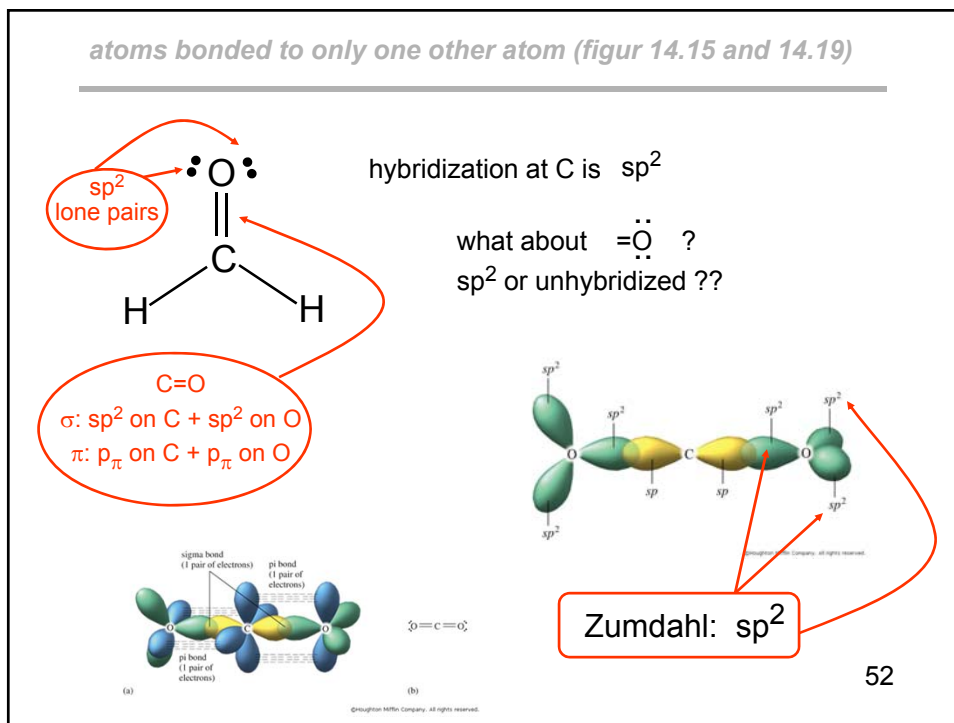
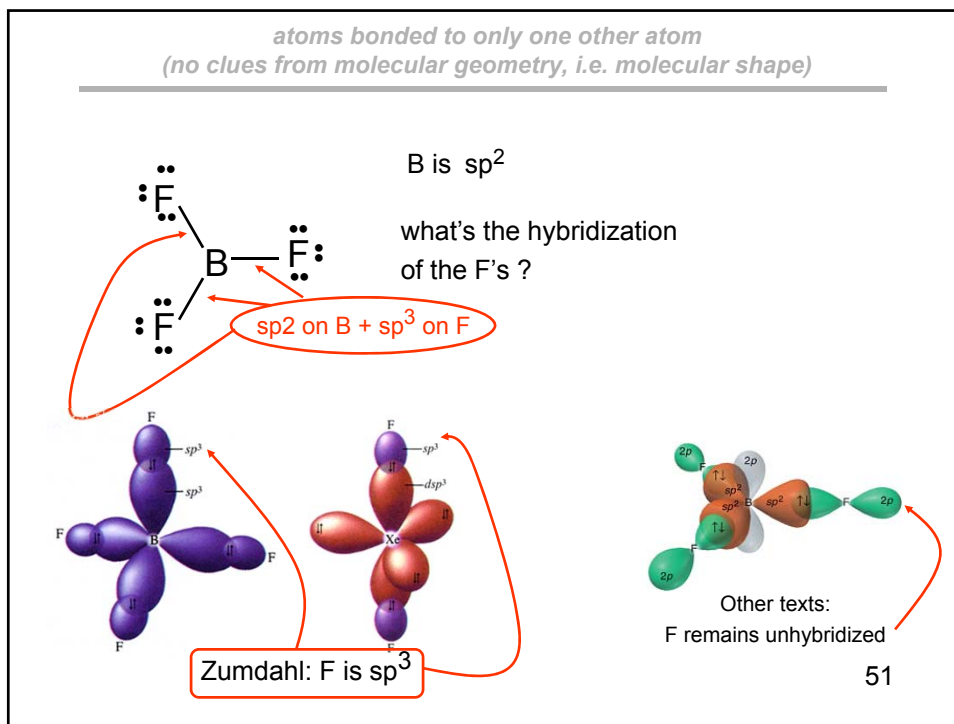
to hybridize or not to hybridize



that is still the question?

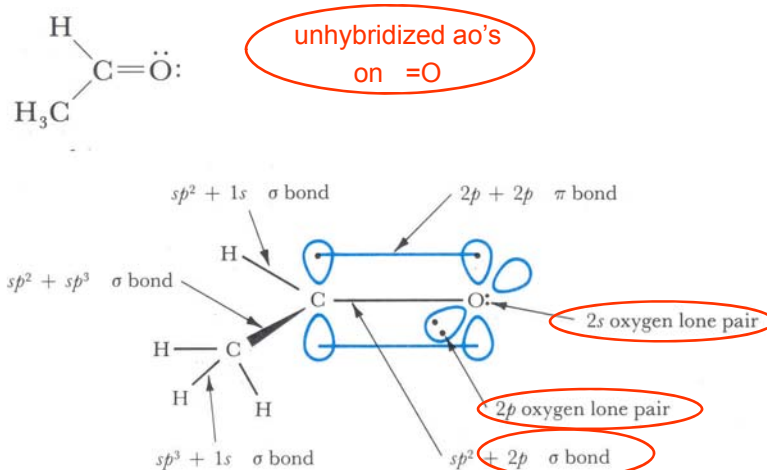
50

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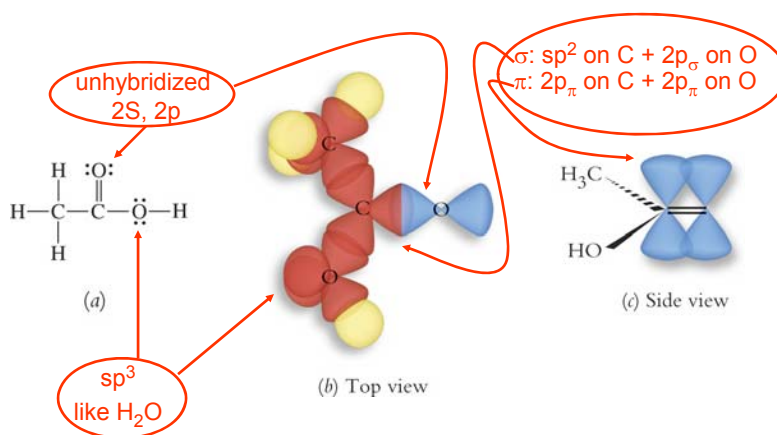
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more on oxygen (DGH)



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even more on oxygen: (Olmstead; previous chem 1B book)



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the "word" from quantum mechanical calculation

Reprinted from THE JOURNAL OF CHEMICAL PHYSICS, Vol. 53, No. 7, 2645-2657, 1 October 1970
 Printed in U. S. A.

Localized Bonds in SCF Wavefunctions for Polyatomic Molecules. III C-H and C-C Bonds*

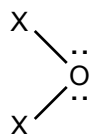
MARSHALL D. NEWTON, good guy
 Chemistry Department, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213
 AND
 n'er do well EUGENE SWITKES AND WILLIAM N. LIPSCOMB, Nobel Prize 1976
 Gibbs Chemical Laboratory, Harvard University, Cambridge, Massachusetts 02138
 (Received 26 February 1970)

calculation gives UNHYBRIDIZED



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so for CHEM 1B ('an agreement'):



definitely sp^3



either sp^2 with lone pairs in sp^2 's
 or unhybridized O with lone pairs in 2s and 2p

F, Cl, O^- , etc

sp^3 hybridized (a la Z.)

or unhybridized with p-bonding, lone pair in s and p

diatomic molecules

unhybridized ao's

(complex scheme for B_2 , C_2 , N_2 implies some sp hybridization)

$X-C \equiv N$:

N is sp hybridized with lone pair in sp hybrid



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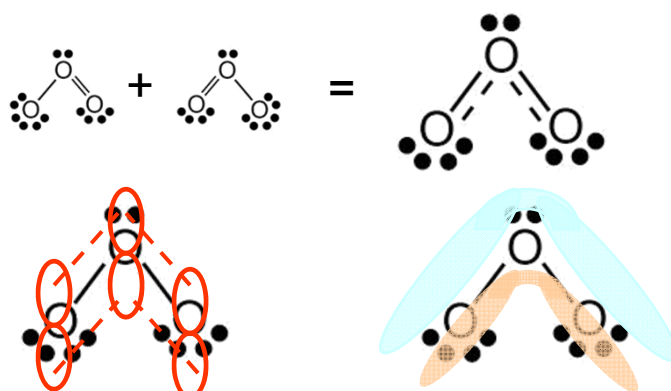
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delocalized bonding (pp. 688-690)

- electrons shared by more than two nuclei
- often associated with Lewis resonance structures
- most often involves p_{π} atomic orbitals interacting throughout a region of the molecule (called a conjugated or delocalized π -system)

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Ozone (see figures 14.47 and 14.51)



σ framework
 sp^2 hybridized O's
unhybridized p_{π} ao's

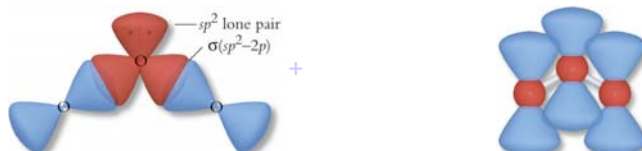
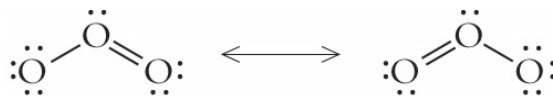
14 e's in σ -framework
4 e's in π -system
two, filled, delocalized, π mo's

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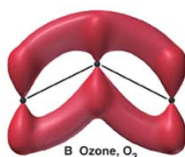
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from Olmstead (uses unhybridized O's on ends)

Ozone



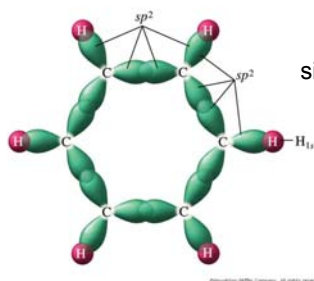
Delocalized π orbitals: An orbital in which electron density is distributed over more than two atoms.



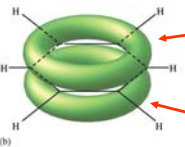
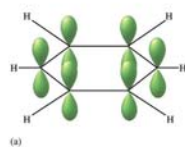
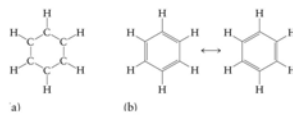
B Ozone, O_3

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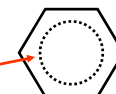
figures 14.48, 14.49 and 14.50



sigma bond framework



6 electrons shared by all six carbons in delocalized molecular orbitals



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excited-state orbitals in polyatomic molecules

- destructive interference leads to antibonding orbitals which are not usually occupied in the ground state of molecules but which may become occupied upon excitation of electrons by light
- types of antibonding orbitals:

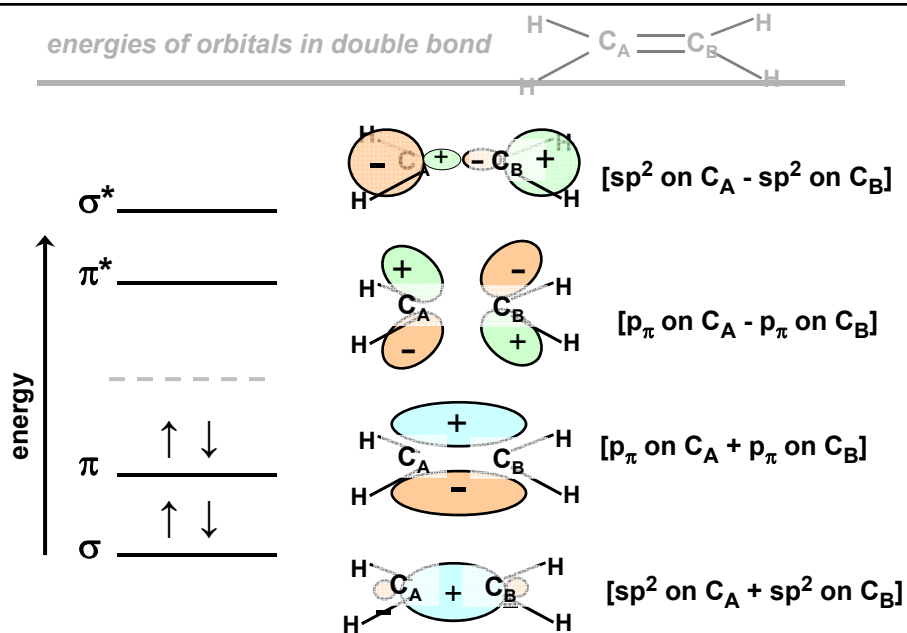
CH_4 : $\sigma^* = \text{sp}^3$ on C - 1s on H

C_2H_4 : $\sigma^* = \text{sp}^2$ on C_A - sp^2 on C_B

$\pi^* = \text{p}_\pi$ on C_A - p_π on C_B

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energies of orbitals in double bond



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END of SESSIONS
15-16

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