Chemistry 1B

Fall 2016

Sessions ~~Lectures~~ 15-16

Covalent Bonding and Geometry

in Polyatomic Molecules

- 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

- 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 B_2, C_2, N_2 diatomics)

bonding with H •

expected from
atomic configuration

[He] 2s Li • **Li-H**

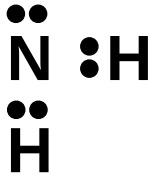
[He]2s^2 Be : **no bonds** **but BeH_2 exists**

[He]2s^{2}2p $\dot{\dot{B}}$ • **: B-H** **but also BH_3**

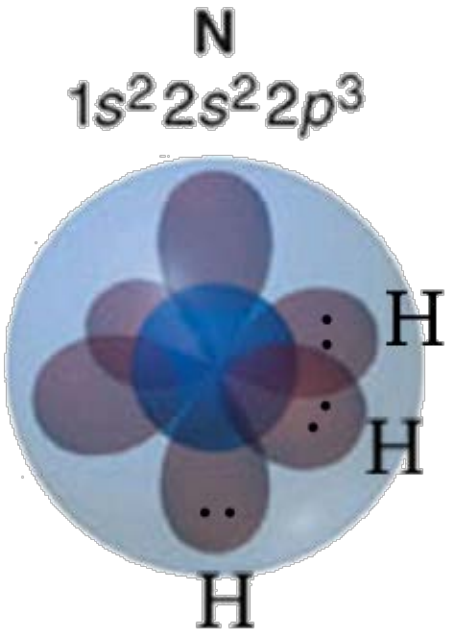
[He]2s^{2}2p^2 $\dot{\dot{C}}$ • **:CH_2** **but also CH_4**

[He]2s^{2}2p^3 •$\dot{\dot{N}}$ • **:NH_3**

also H_2O and HF

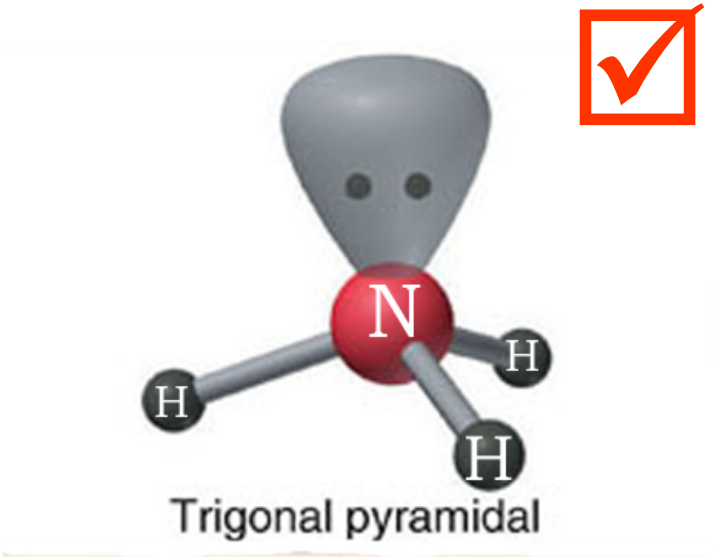
$[He]2s^2 2p^3$  

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



H-N-H angle = 90º

BUT



H-N-H angle = 107º

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

ORBITAL HYBRIDIZATION

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

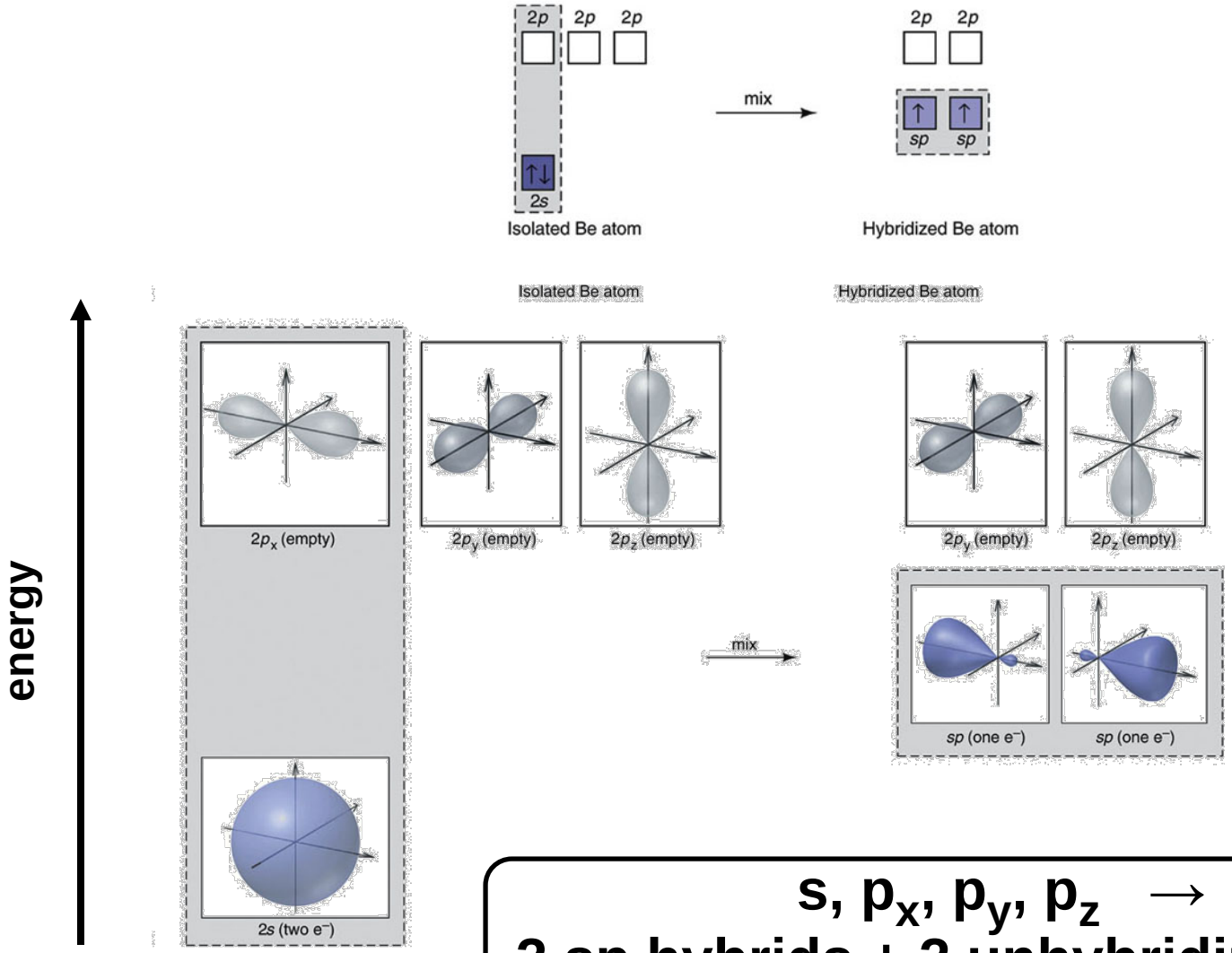
Energy gains (advantages of hybrid orbitals)

- 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)

Zumdahl: sp^3 ➔ sp^2 ➔ sp ☹

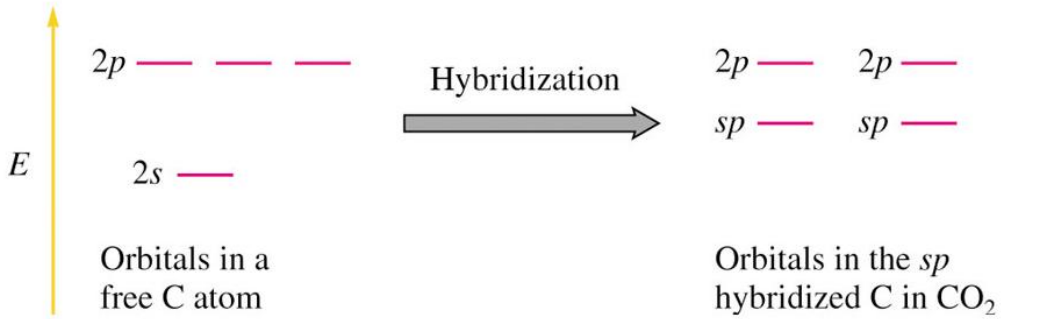
US: sp ➔ sp^2 ➔ sp^3 ☺

sp hybridization in BeH_2 (Silberberg fig 11.2)



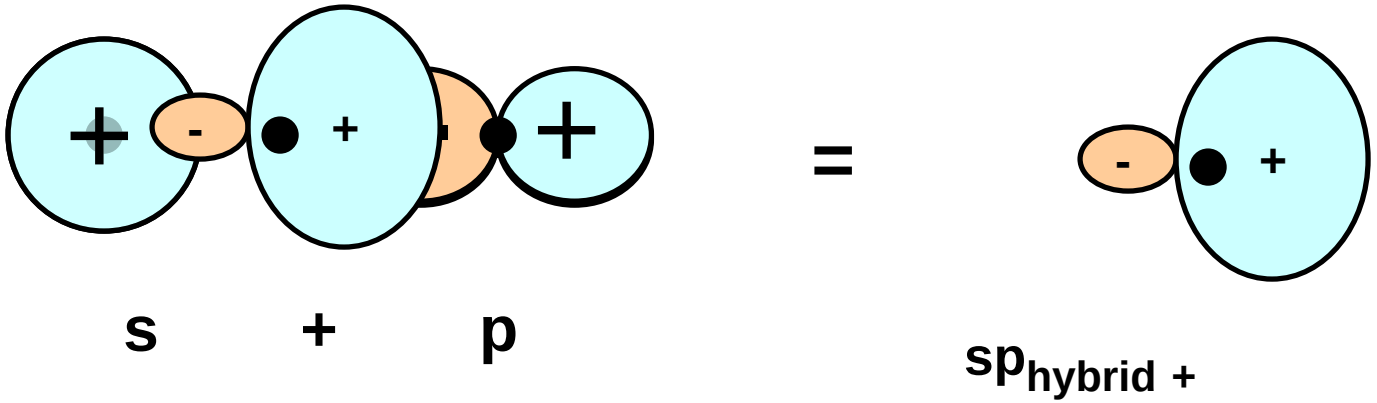
s, p_x, p_y, p_z → 2 sp hybrids + 2 unhybridized p ao's

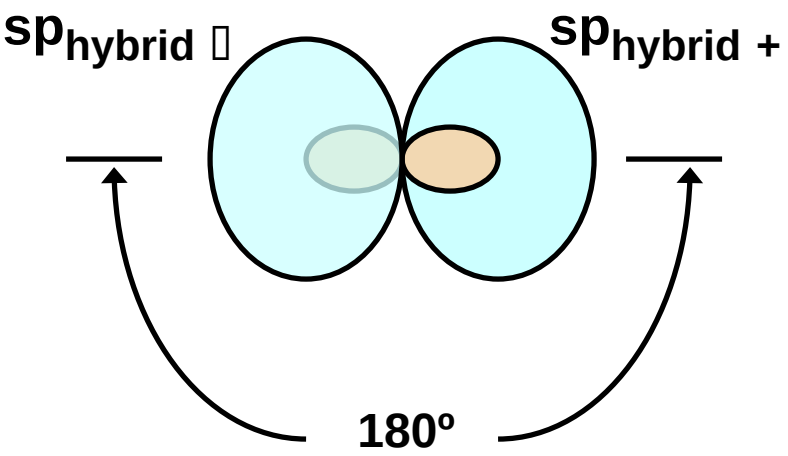
sp hybridization (figure 14.16)



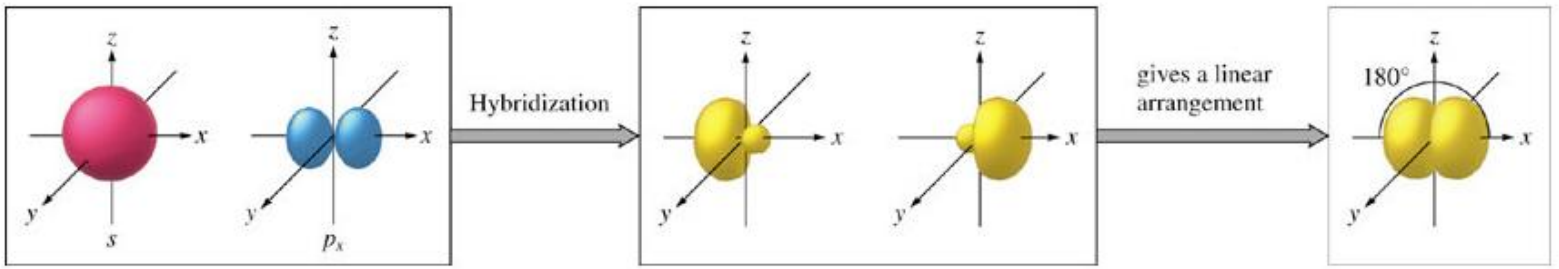
- **s, px, py, pz → 2 sp hybrids + 2 unhybridized p ao's**

- **angle between sp hybrids is 180° giving linear geometry**

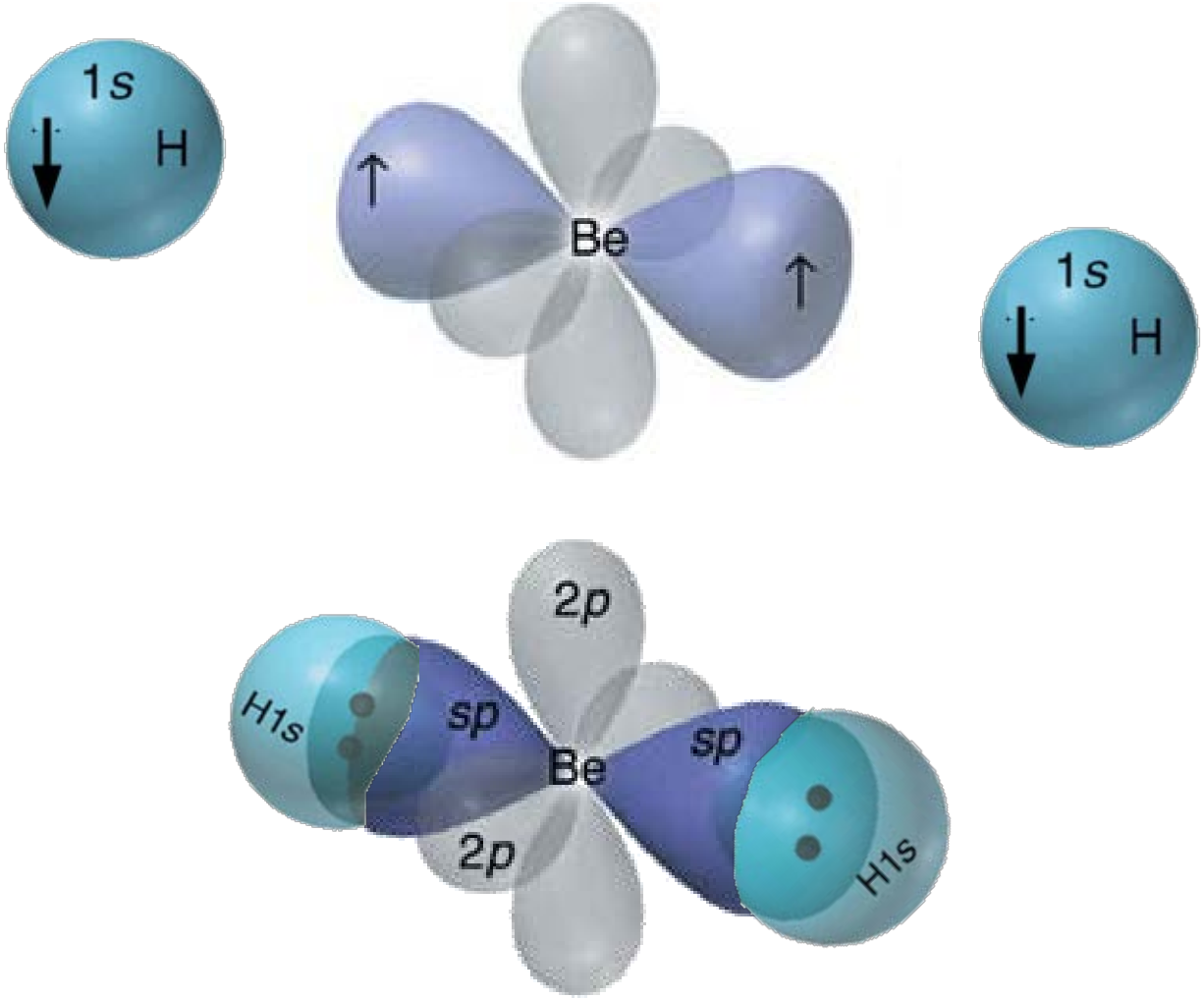

s + p
=
sp hybrid +
s - p
=
sp hybrid □



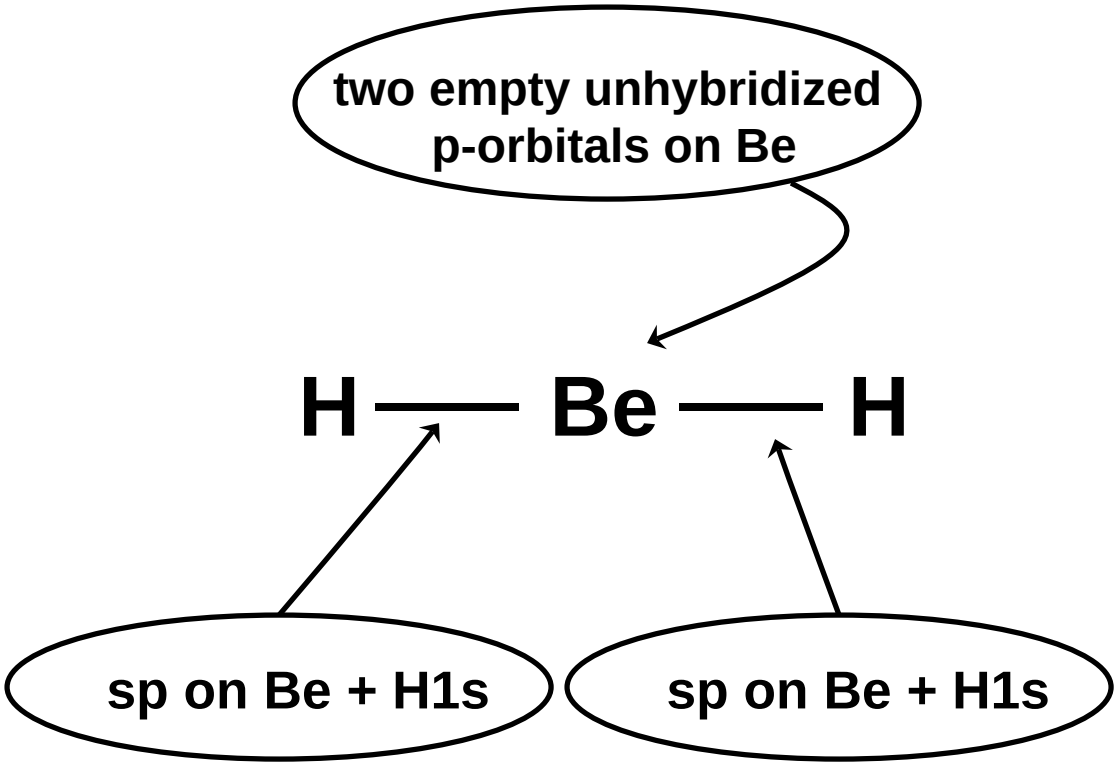
the two sp hybrids point 180° apart



Dr. Gutow's Hybrid Atomic Orbital Site


1s
H
Be
1s
H
2p
H1s
sp
Be
sp
2p
H1s

BeH_2 description of bonds

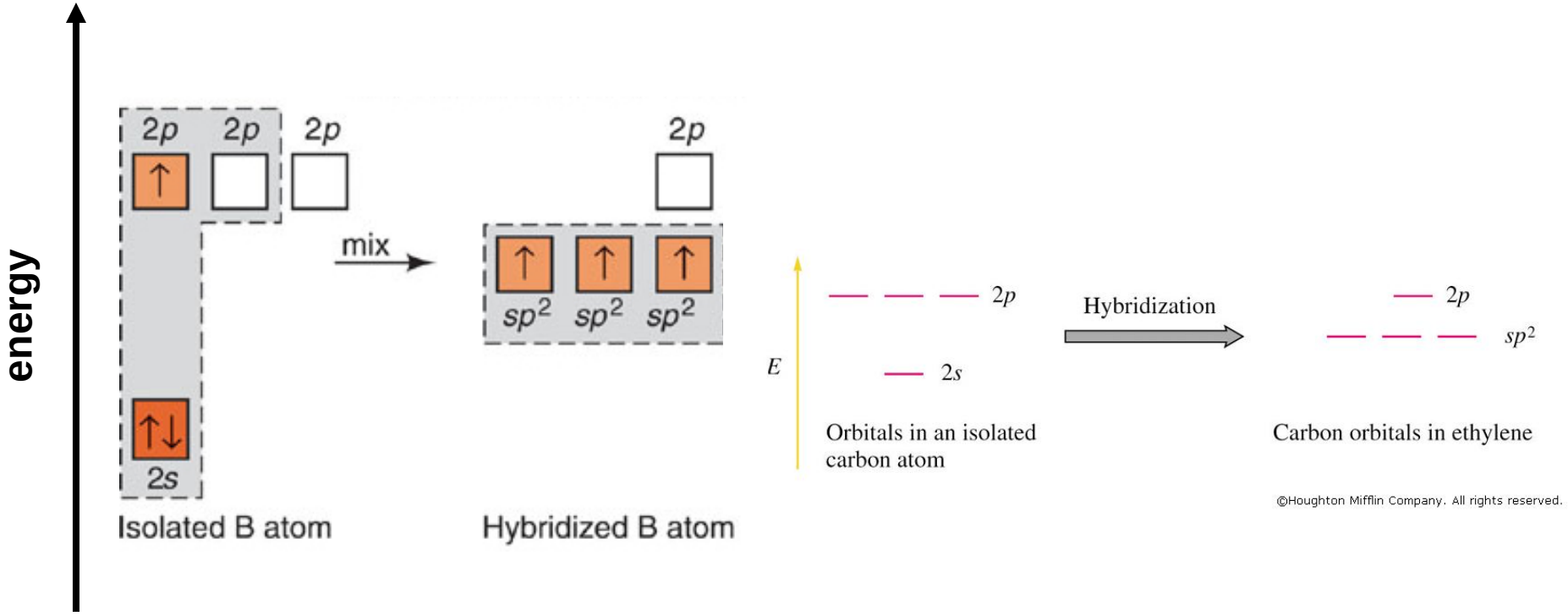


- The ‘first’ step of hybridization involves combining orbitals on **A SINGLE** atom. This may involve orbitals which do not have **NET** overlap (e.g. 2s and 2p) to get the hybrid orbitals (e.g. sp_+ and sp_-)

- 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 ½ (E_{2s}+E_{2p})]

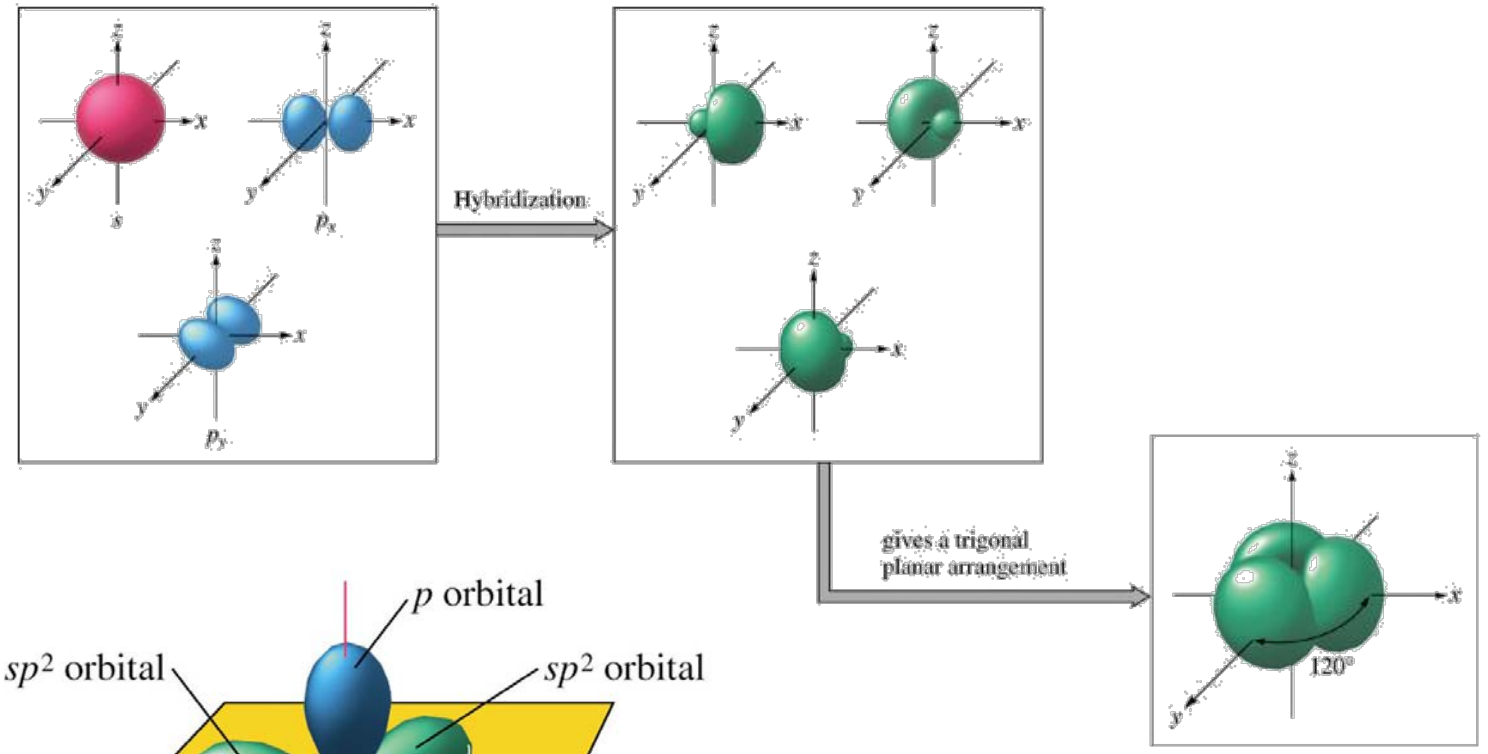
- Bonding occurs when the hybrids on **TWO** atoms constructively interfere to give a lower energy localized m.o. (a chemical bond)

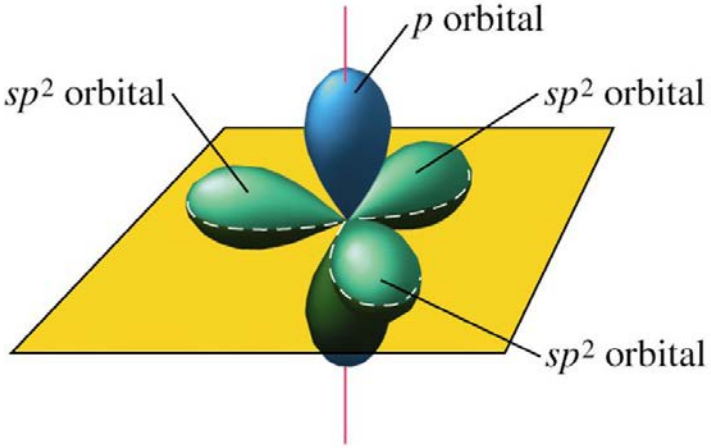
bonding in BH_3 ---- sp^2 hybrids (figure 14.9)



s, p_x, p_y, p_z →
3 sp^2 hybrids +
1 unhybridized p ao

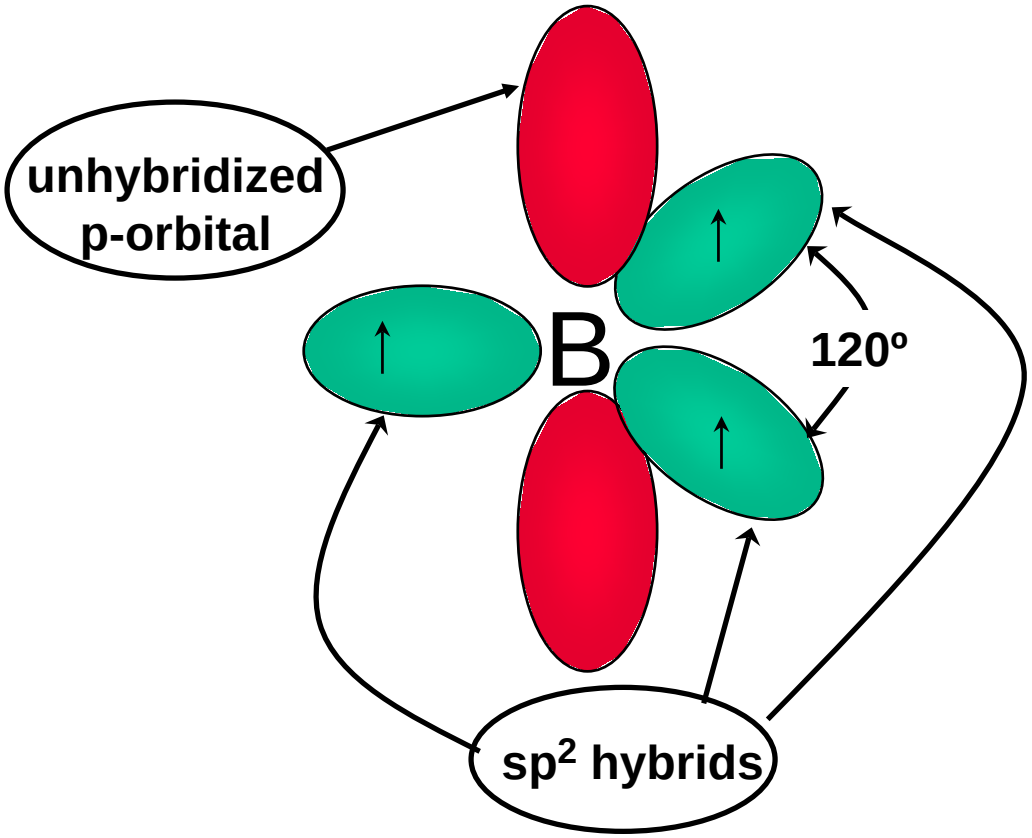
geometry of sp^2 hybrids (figure 14.8, 14.10)





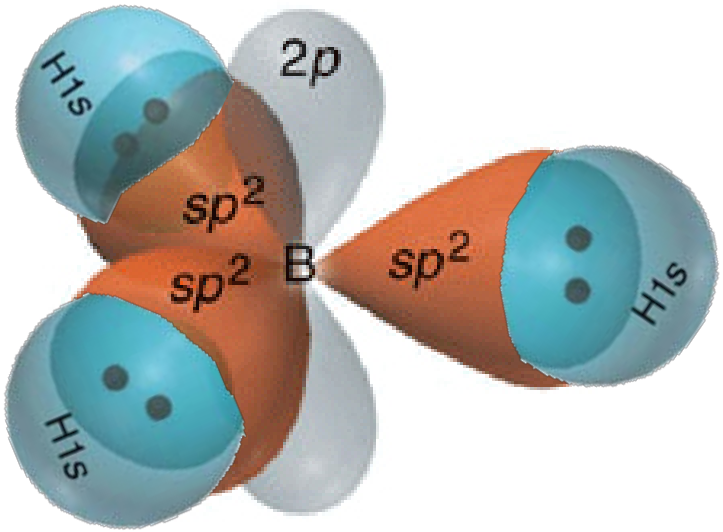
[Dr. Gutow's Hybrid Atomic Orbital Site]

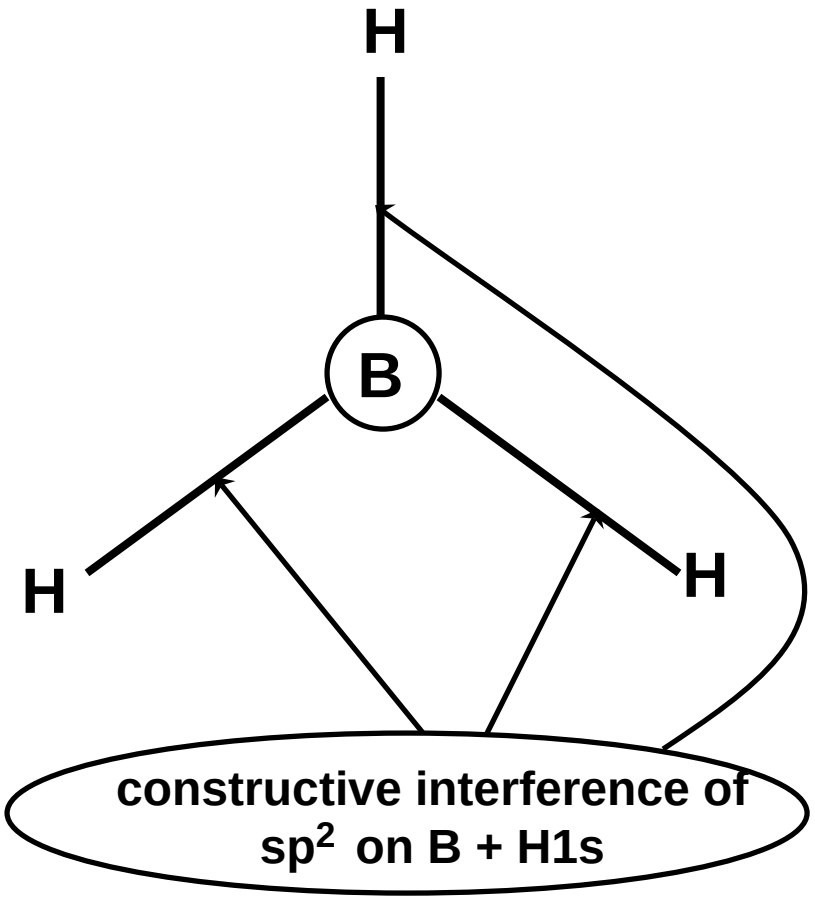
geometry of sp^2 hybrids



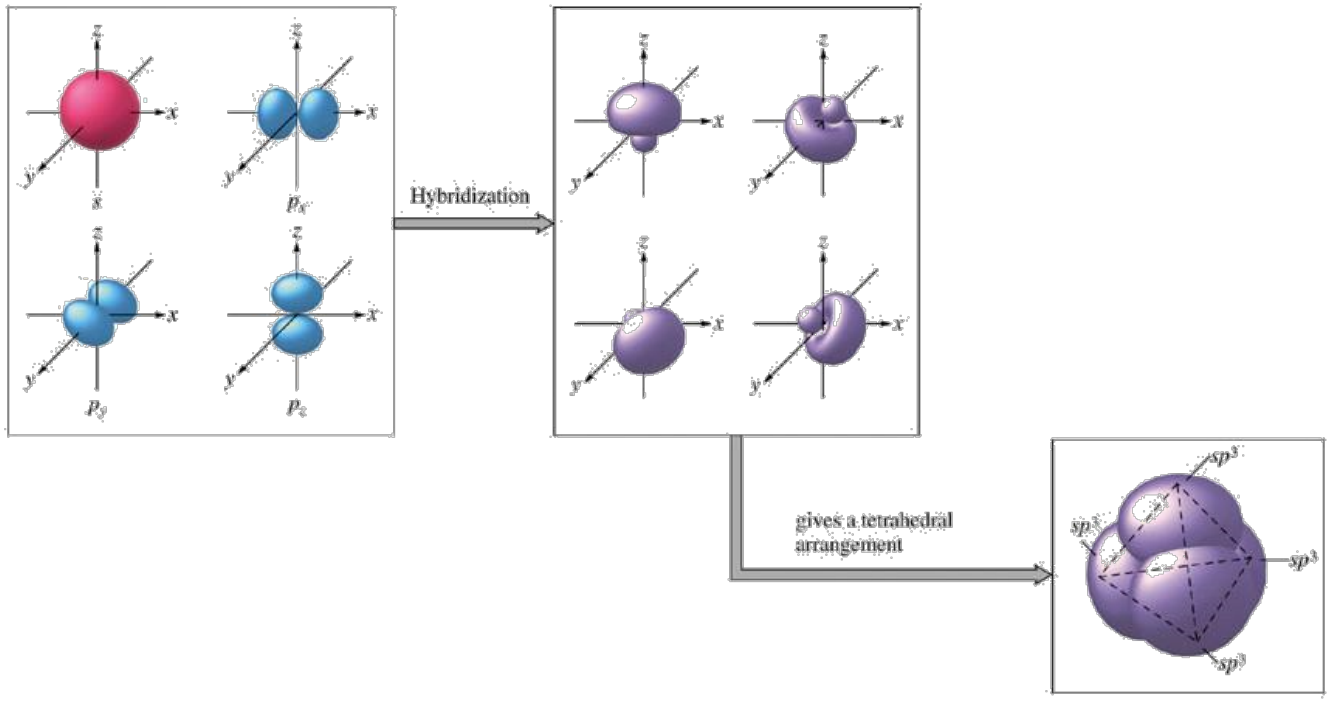
- **the 3 sp^2 hybrids are in a plane with 120º angles between them**
- **this results in trigonal planar geometry for the bonds formed by the hybrids**
- **the unhybridized p is perpendicular to the plane**

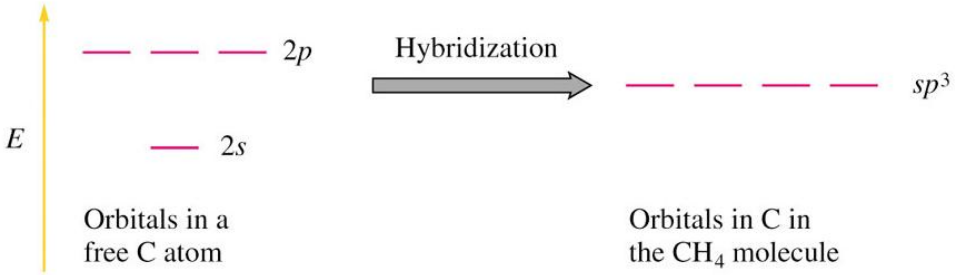
bonding in BH_3 : trigonal planar geometry





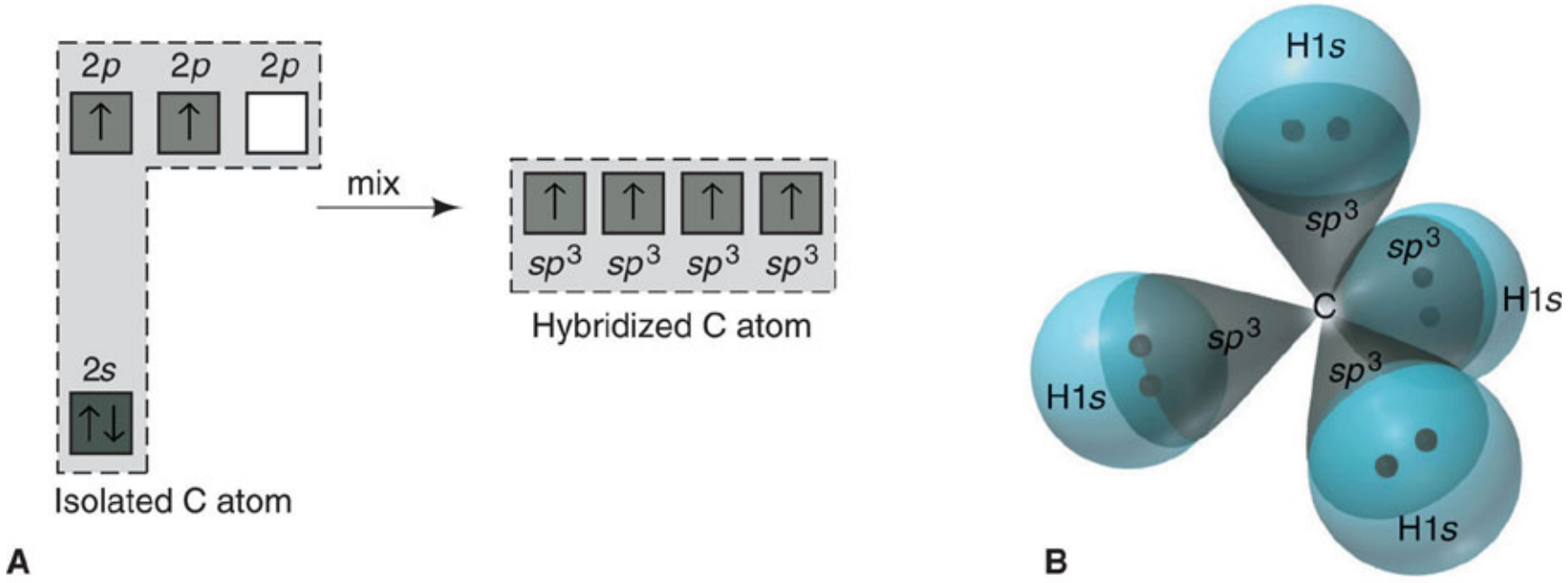
CH_4: sp^3 hybridization (figures 14.3 and 14.5)





[Dr. Gutow's Hybrid Atomic Orbital Site]

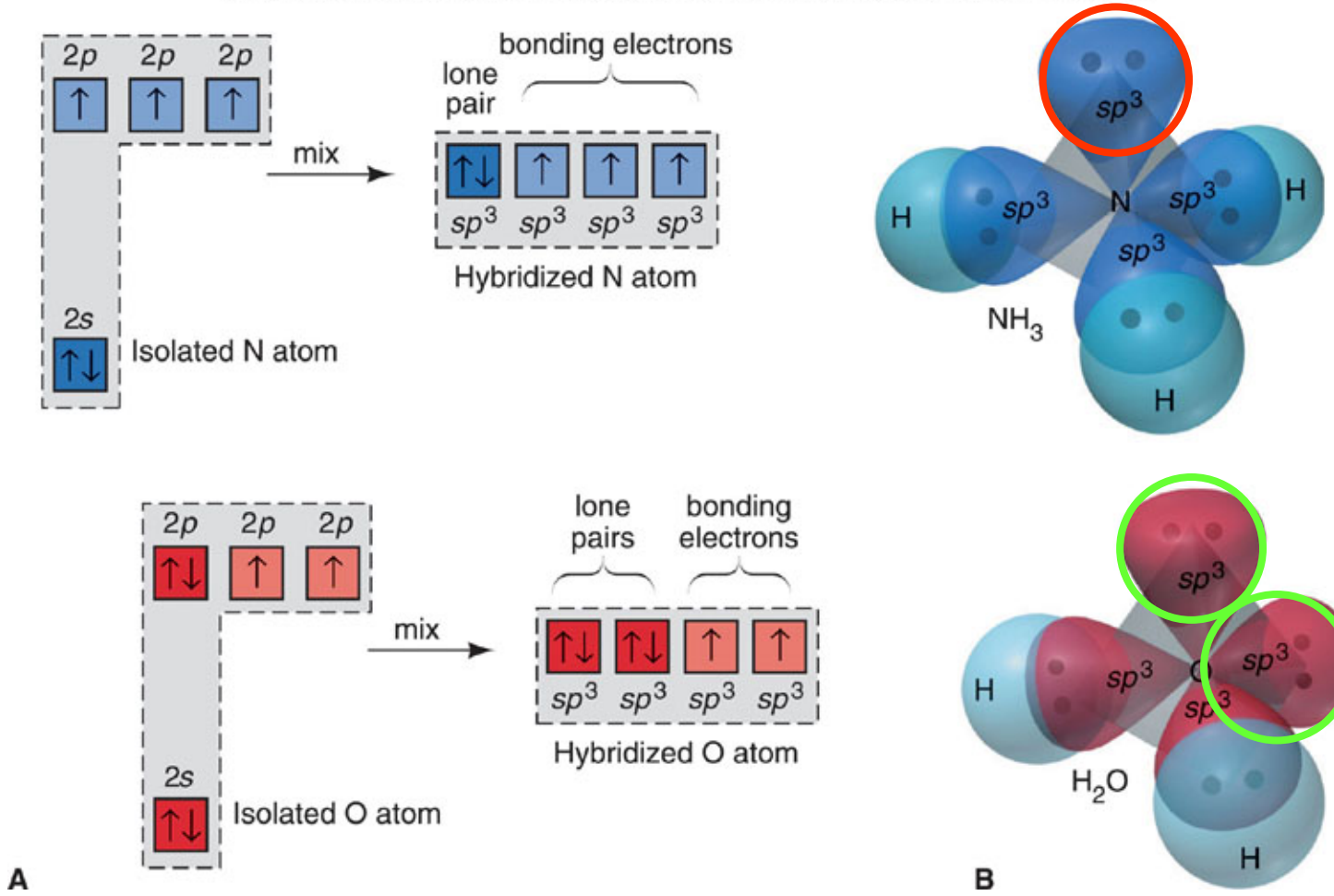
CH_4: sp^3 hybridization



s, p_x, p_y, p_z → 4 sp^3 hybrids (no unhybridized p ao's)

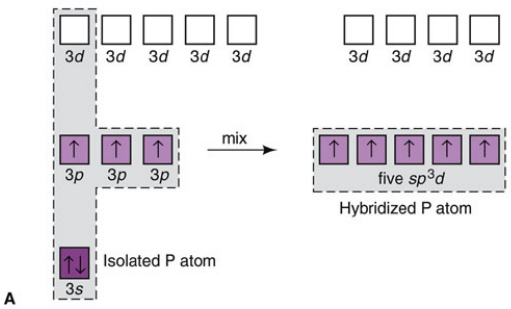
tetrahedral geometry 109.5° bond angles

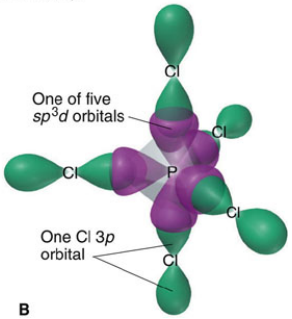
lone pairs can occupy hybrid orbitals (fig. 11.5)

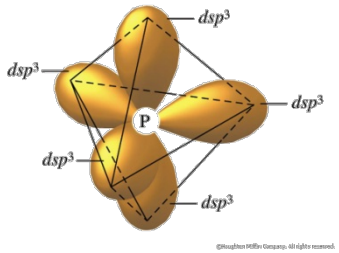


other hybridizations (pp. 668-670)

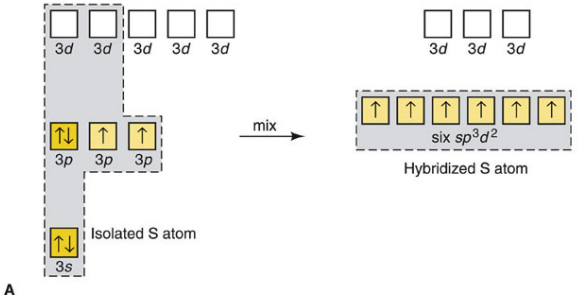
DON'T FRET

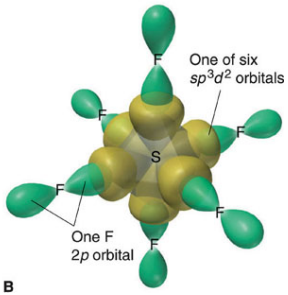


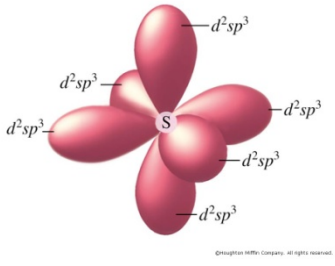




sp^3d (5)
trigonal bipyramid

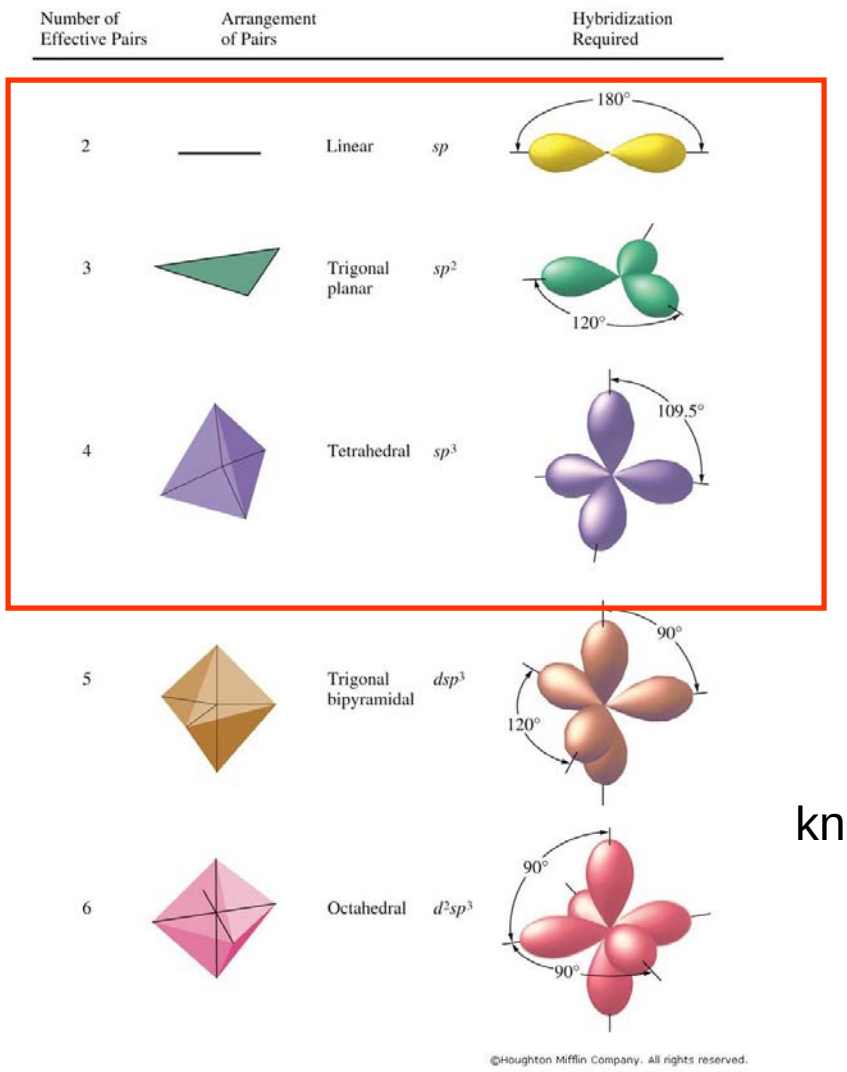






sp^3d^2 (6)
octahedral

summary (figure 14.24)



know that these exist

HYBRIDIZATION:

multiple bonds,

geometric isomers.

pp. 668-671

have covered worksheet ~~10~~ 9, sections I-V

Learning Objectives and Worksheet IX

Chemistry 1B-AL Fall 2016

Sessions Lectures (15-16) Bonding in Polyatomic Molecules:

RETURNING TO THE FIRST PART OF CHAPTER 14 (pp. 633-676), to cover covalent bonding in polyatomic molecules, and then onto molecular dipoles (pp 688-692).

In the previous class sessions 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 X– H bonds.
   i. Li
   ii. Be
   iii. B
   iv. C
   v. N

2. In the ground state of atomic nitrogen, $1s^2 2s^2 2p_x 2p_y 2p_z$ ↑ ↑ ↑ , 3 H· atoms could interact with the unpaired electrons in the 2p orbitals to form the stable octet structure NH_3. From your knowledge of the geometry of the $2p_x$, $2p_y$, 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 atom): _____ would be a cost of forming hybrids. This is why isolated atoms do not "naturally" go to a hybridized state.

HW#7: S14

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.o. 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 Z=8 or 9 ?

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

HW#7: 51

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://switkes.chemistry.ucsc.edu/teaching/Jmol/AcetyleneBonding/AcetyleneBonding.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 orbital.
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 _____.

this video: worksheet ~~10~~ 9 sections VI-VII

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 sp3 hybrids:
http://www.uwosh.edu/faculty_staff/gutow/Orbitals/N/sp3%20hybrid.shtml

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_2CHCH_3
   - 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 _____.

HW#7: 51,54, S15

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?

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

V. sp³ hybridization
1. In sp³ hybridization the 2s, 2p_x, 2p_y, and 2p_z a.o. form _____ sp³ hybrids leaving _____ unhybridized 2p orbitals.
2. The sp³ hybrids are directed _____° apart.
3. If H- atoms bond with unpaired electrons **in the sp³ hybrids** the resulting molecular geometry is _____.

Excellent website to visualize sp3 hybrids:
http://www.uwosh.edu/faculty_staff/gutow/Orbitals/N/sp3%20hybrid.shtml

VI. Bonding in molecules with more than one 2nd row atom
1. In the molecule n-propane $CH_3CH_2CH_3$
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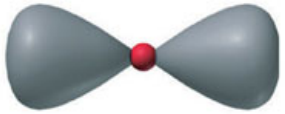
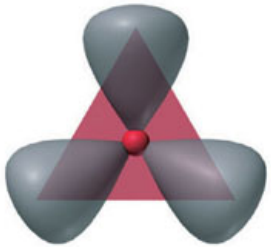
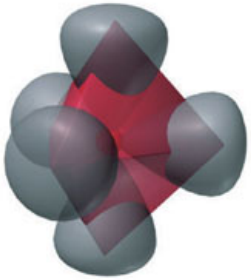
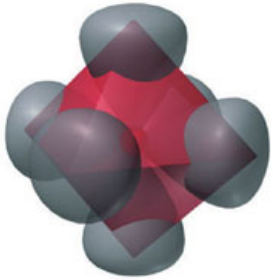
HW#7: 51,54, S15

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?

clicker questions worksheet ~~10~~ 9, sections I-VII

Monday, 14 November

Table 11.1 Composition and Orientation of Hybrid Orbitals

	Linear	Trigonal Planar	Tetrahedral	Trigonal Bipyramidal	Octahedral
Atomic orbitals mixed	one *s* one *p*	one *s* two *p*	one *s* three *p*	one *s* three *p* one *d*	one *s* three *p* two *d*
Hybrid orbitals formed	two *sp*	three sp^2	four sp^3	five sp^3d	six sp^3d^2
Unhybridized orbitals remaining	two *p*	one *p*	none	four *d*	three *d*
Orientation					

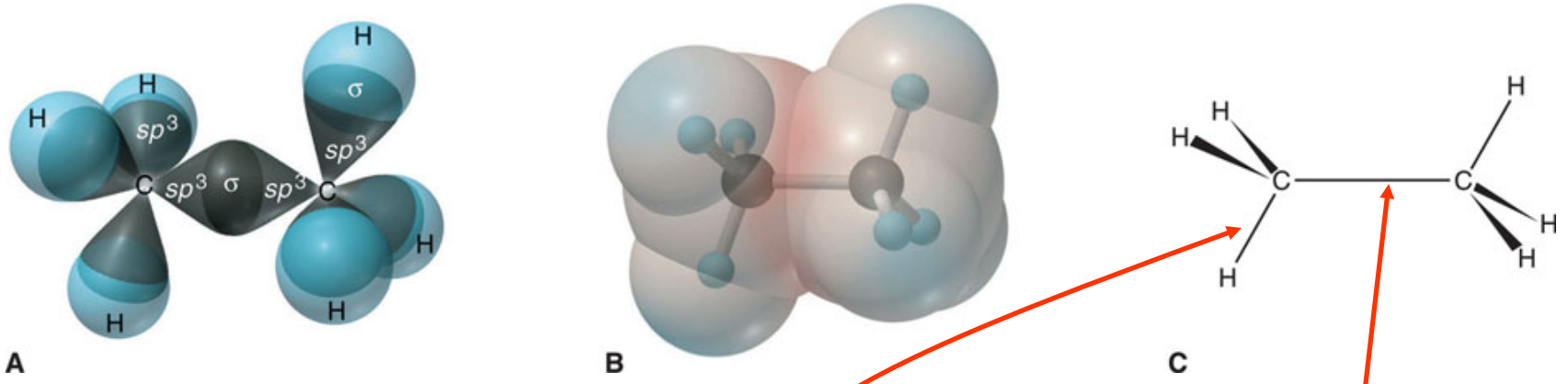
know that these exist

movie:
good summary of hybridization

from Silberberg supplemental material

"valence bond theory"≡"localized bond theory"

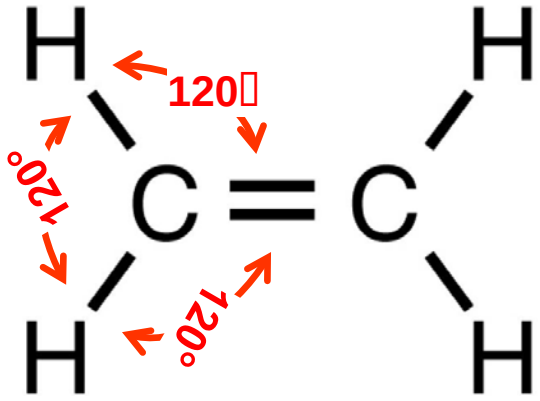
bonding in molecules with several 2nd row atoms



C_2H_6 ➡

sp^3 on C + H1s

sp^3 on C + sp^3 on C

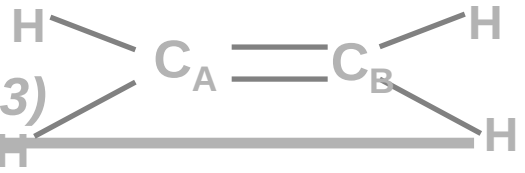


from VSEPR

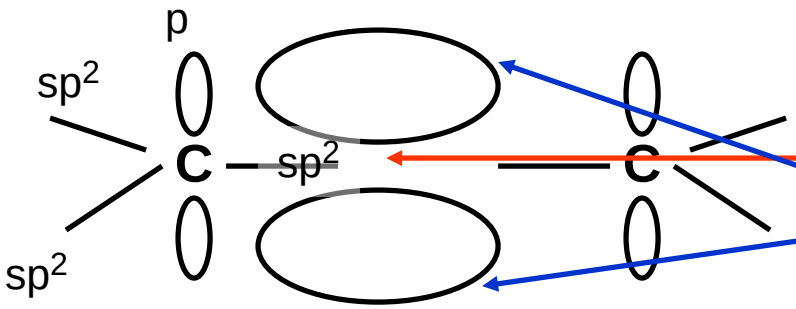
- SN=3
- trigonal planar

- sp^2

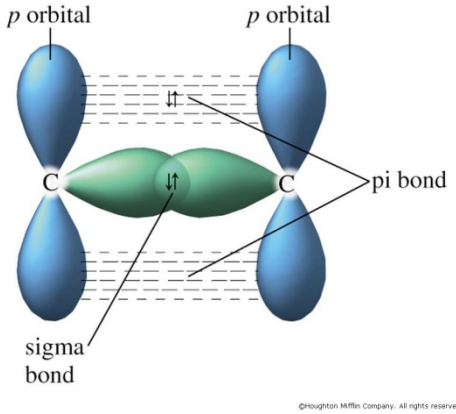
double bond – sp^2 hybridization (figs 14.12, 14.13)

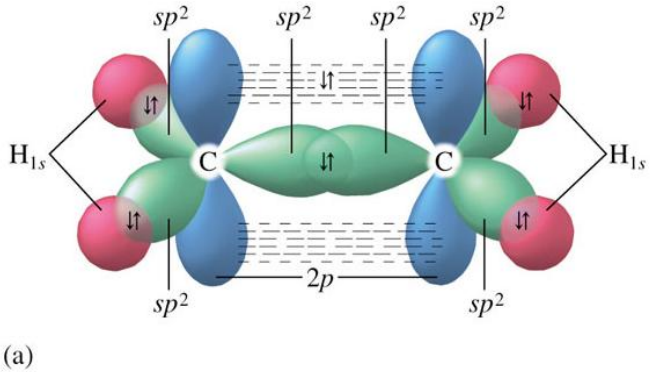


3 sp^2 hybrids
+ unhybridized
p-orbital

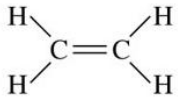


double bond:
σ: sp^2 + sp^2
π: p_π + p_π



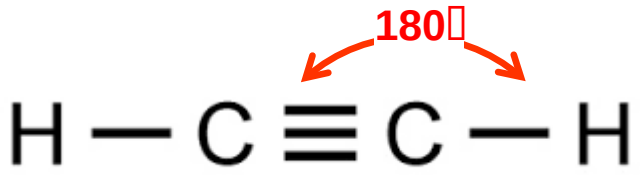


(a)



(b)

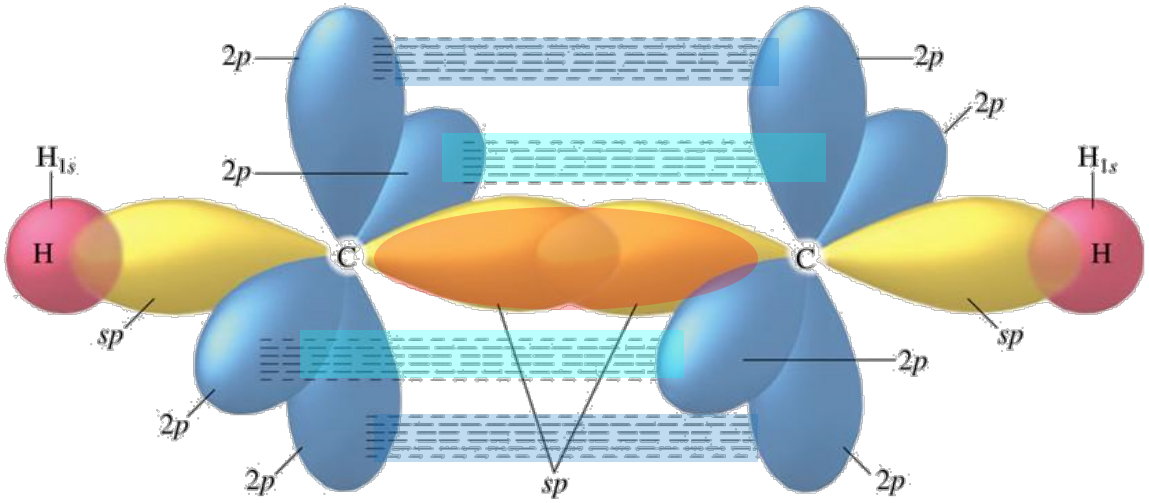
Dr. Gutow's Hybrid Atomic Orbital Site

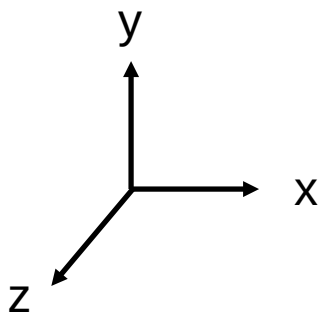


from VSEPR

- SN=2
- linear

- sp





H□ C□C□ H

σ: sp + sp

π_y: $p_{\pi y}$ + $p_{\pi y}$

π_z: $p_{\pi z}$ + $p_{\pi z}$

sp on C + H1s

C_2H_2

to hybridize or not to hybridize

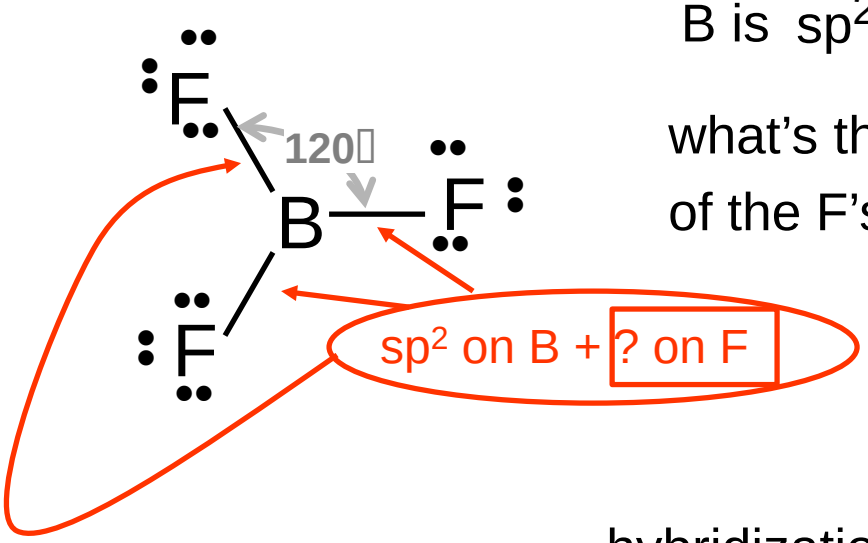
that is the question?

Bond angles : H_2O (105º) vs H_2S (92.2º)
NH_3 (107º) vs PH_3 (93.4º)

- As the central atom becomes larger the bond angles reflect unhybridized p oribital aos.
- 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.

to hybridize or not to hybridize

that is still the question?



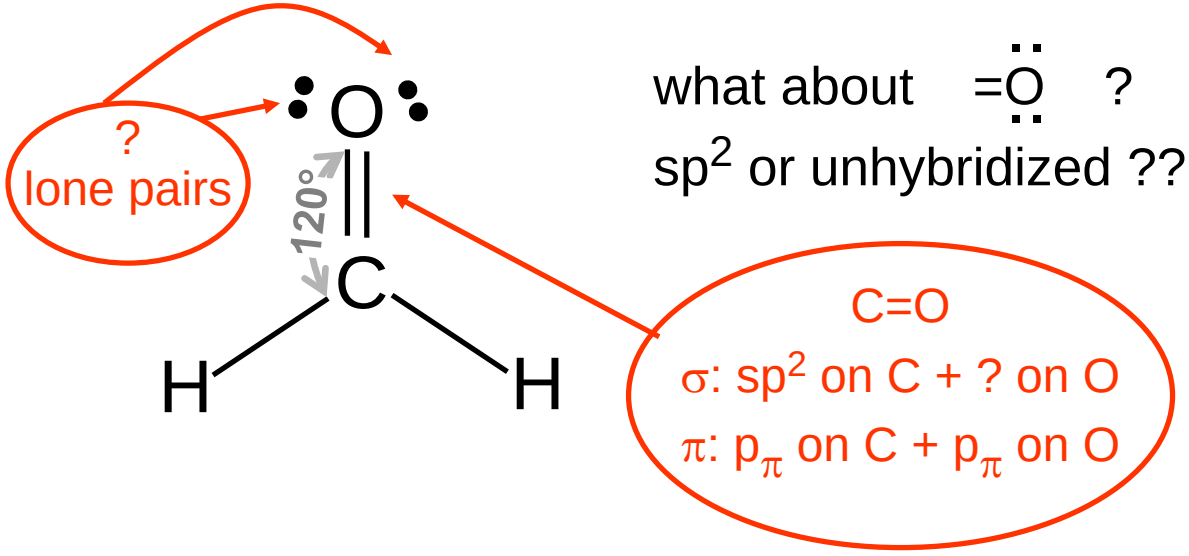
B is sp^2

what's the hybridization of the F's ?

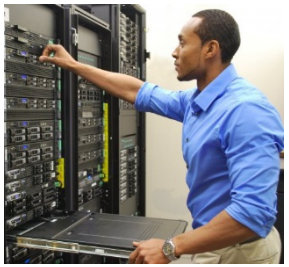
hybridization at C is sp^2

what about =O ?

sp^2 or unhybridized ??



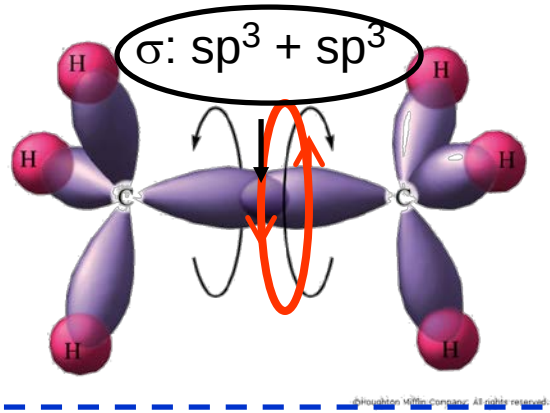
when there is no experimental structural evidence, the state of hybridization state in terminal atoms is often obtained from quantum mechanical calculations



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

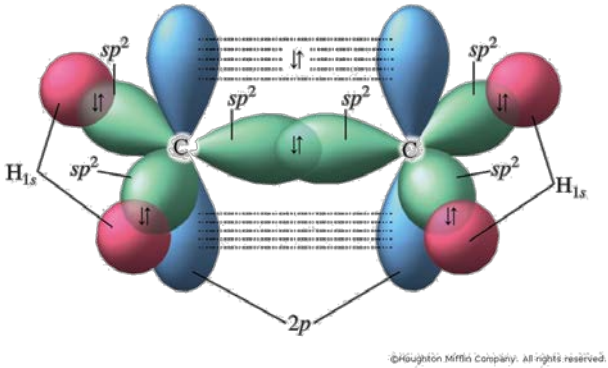
[no] rotation around double bond (figs 21.7 and 21.8)

single

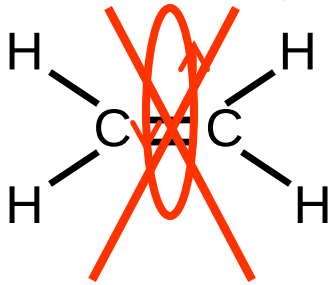


‘free’ rotation about single bond

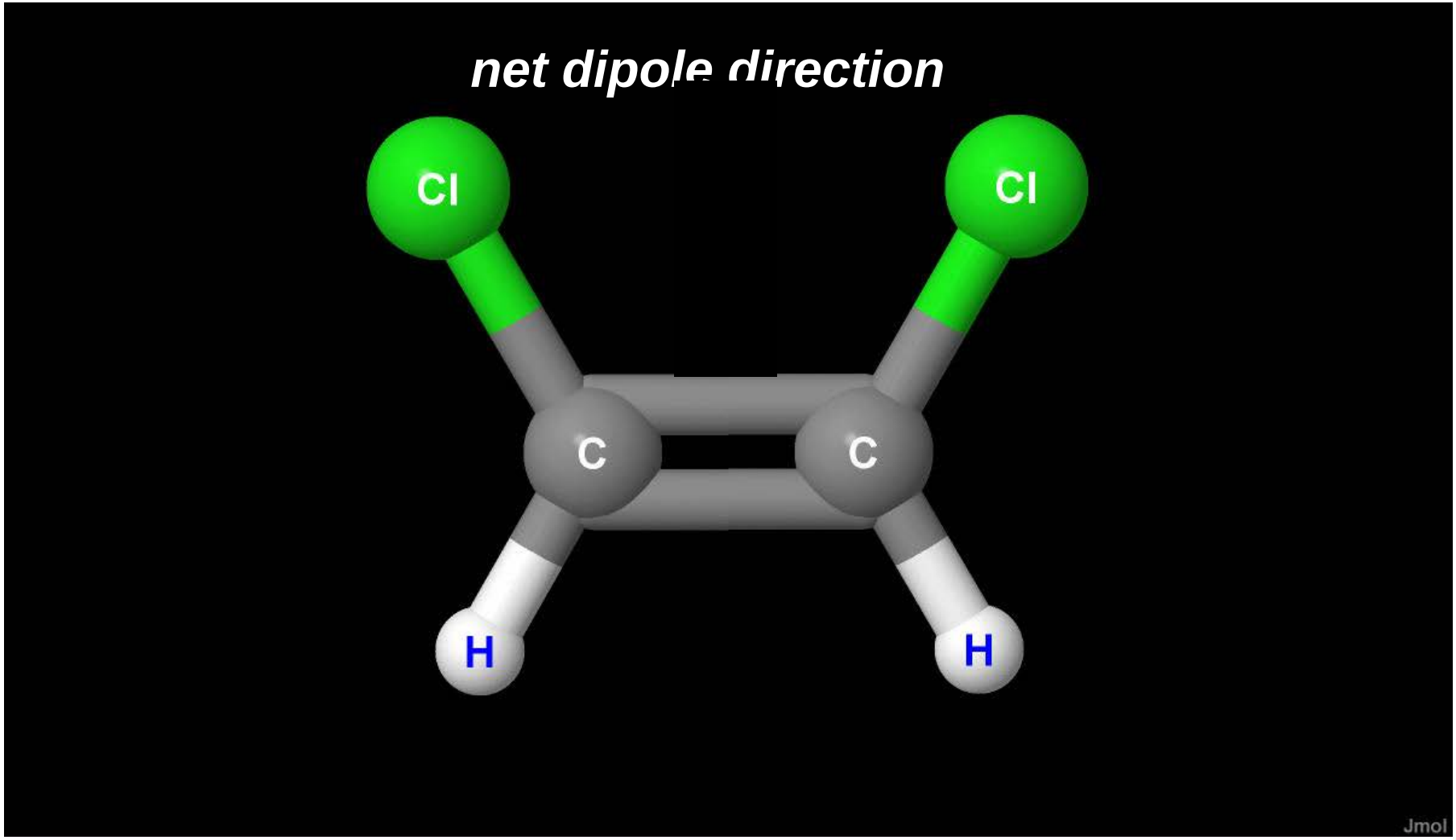
double



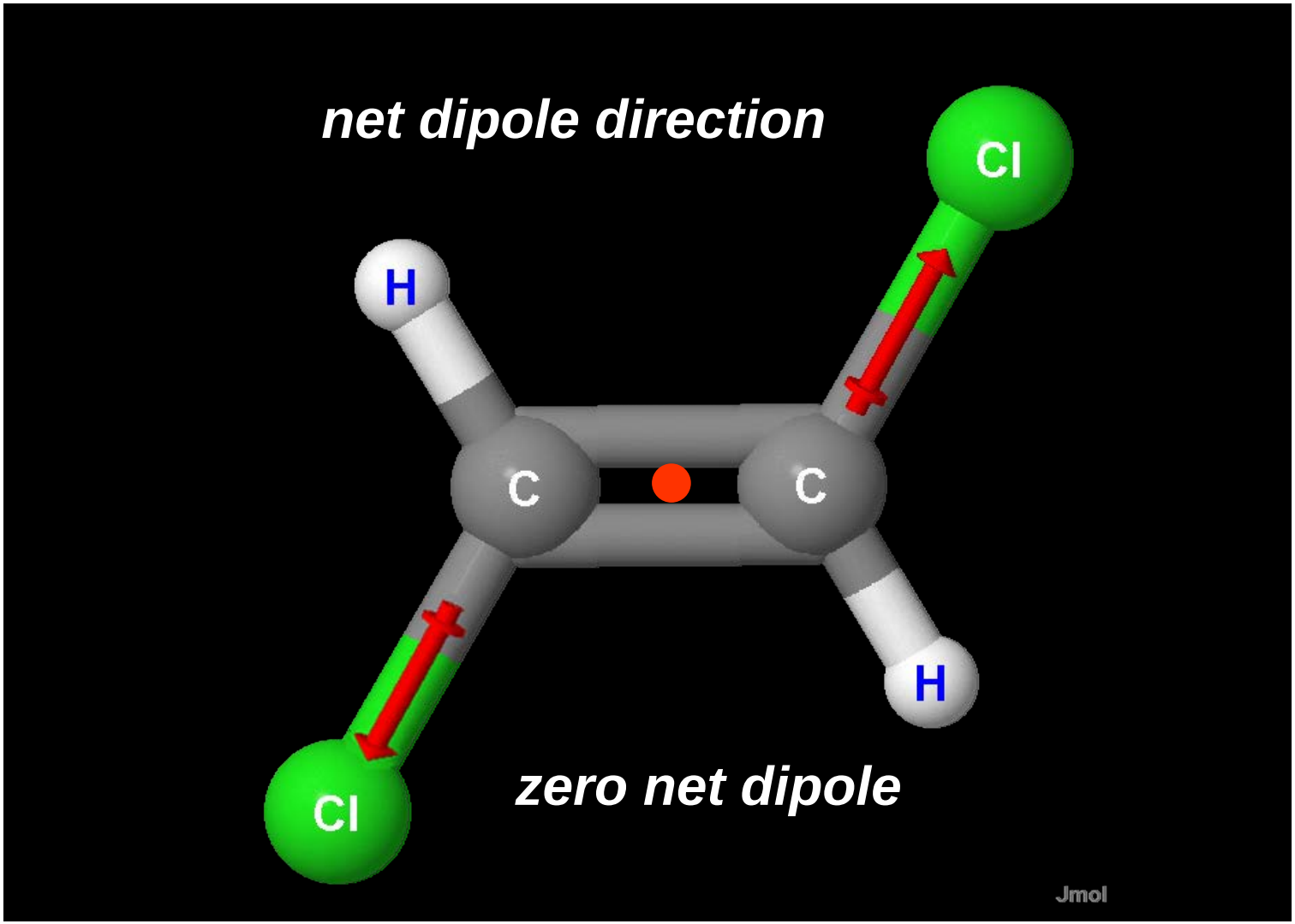
Note that the extra, overlapping pi-bond prevents free rotation around the double bond. One would have to break the pi-bond to be able to rotate around the sigma bond.



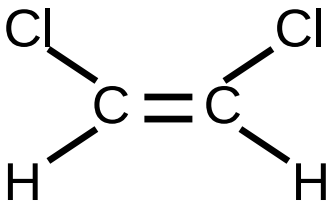
no rotation around double bond



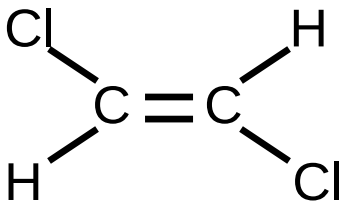
cis 1,2 dichloroethylene ➡



trans 1,2 dichloroethylene ➡



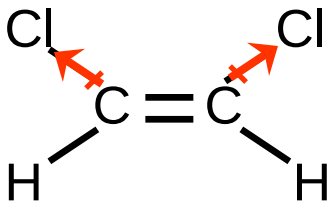
vs



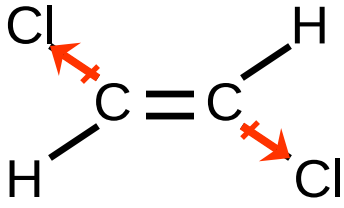
cis 1,2 dichloroethylene

trans 1,2 dichloroethylene

will not interconvert under ‘normal’ conditions



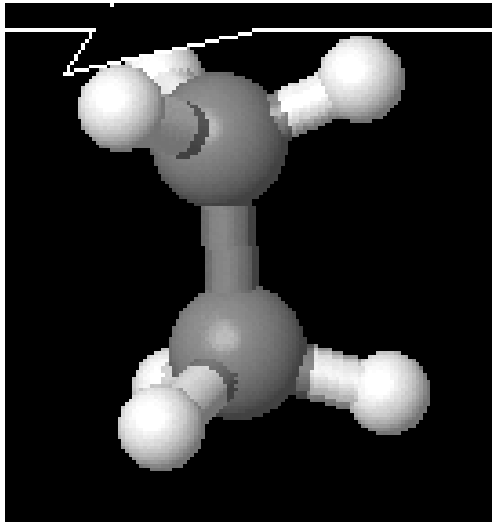
net dipole ↕

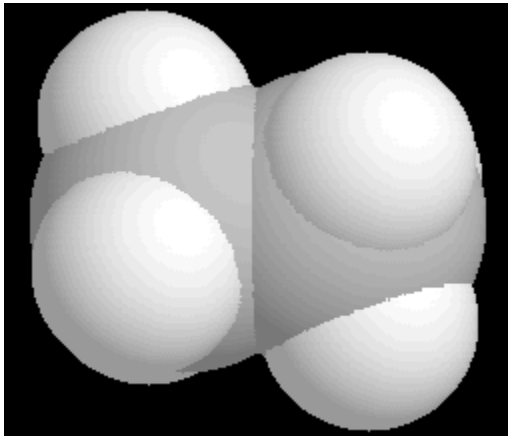


no net dipole •

Finis

and

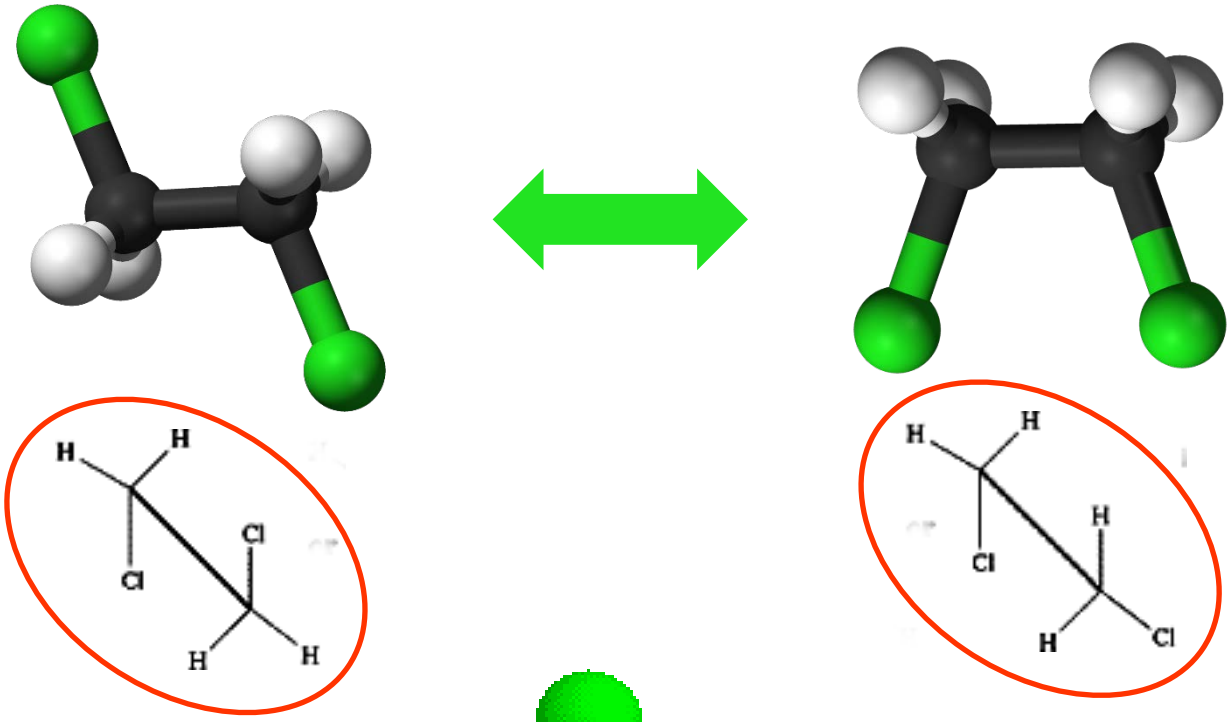


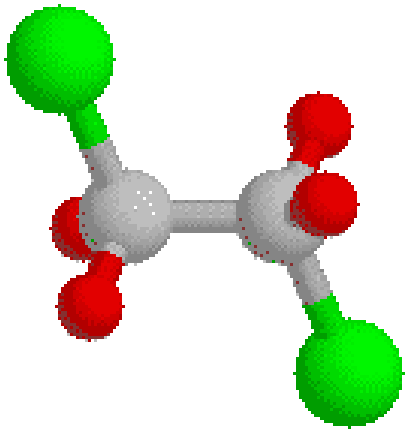


'free' rotation around single bond of ethane

maybe not so free !!
pair-share exercise

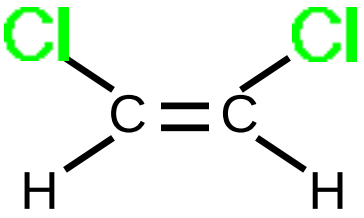
no *geometric isomers normal conditions (1,2 dichloroethane)*

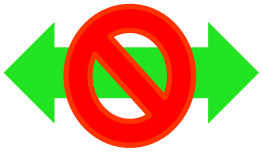


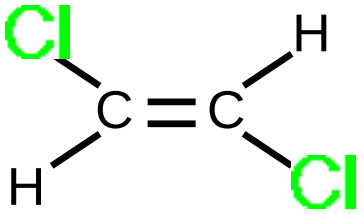


no geometric isomers

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





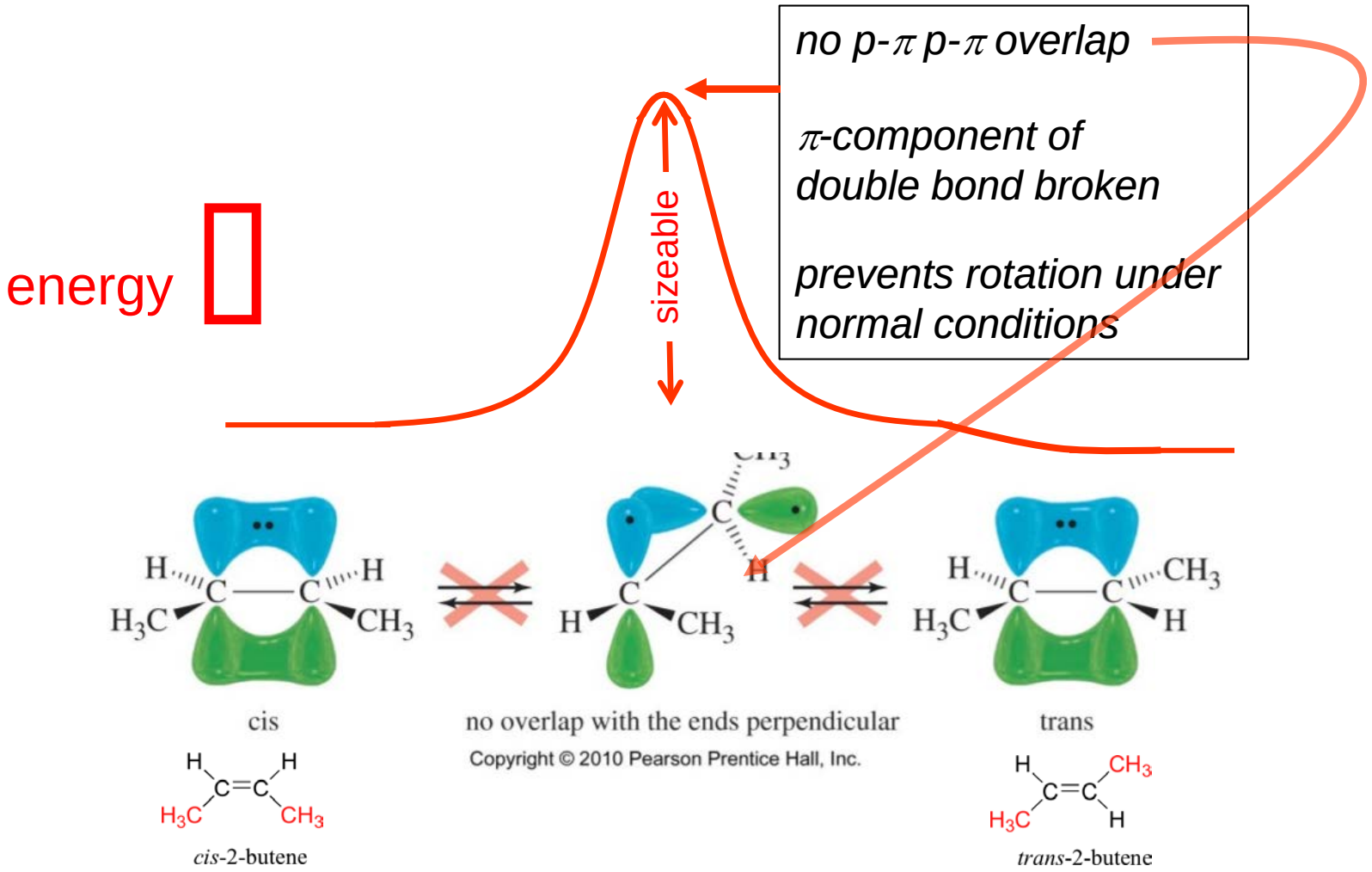


cis 1,2 dichloroethylene

trans 1,2 dichloroethylene

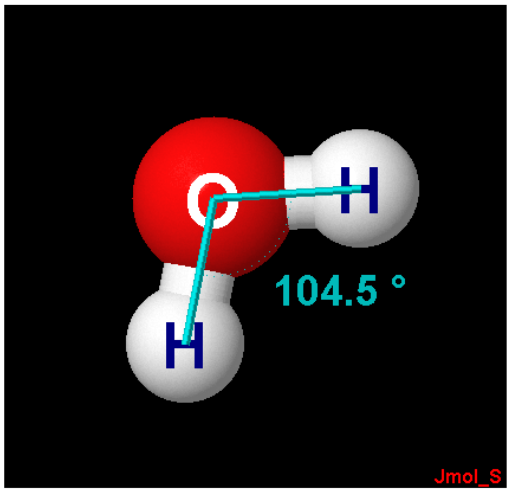
will not interconvert under 'normal' conditions

[no] rotation around double bond

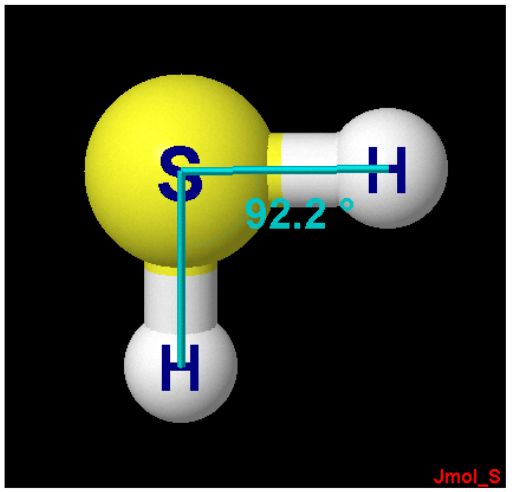


but does “no” mean “never” ?

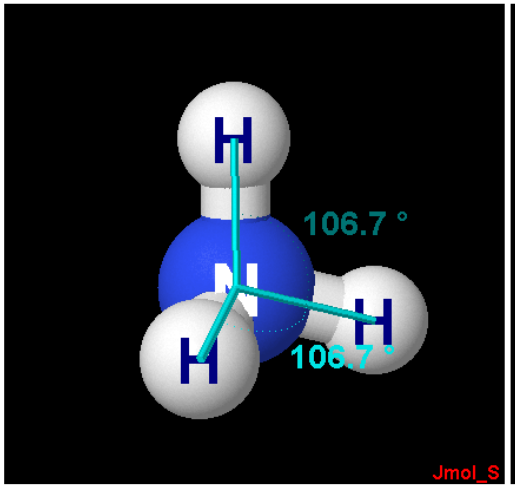
hybridization or not: 2nd row vs 2rd row



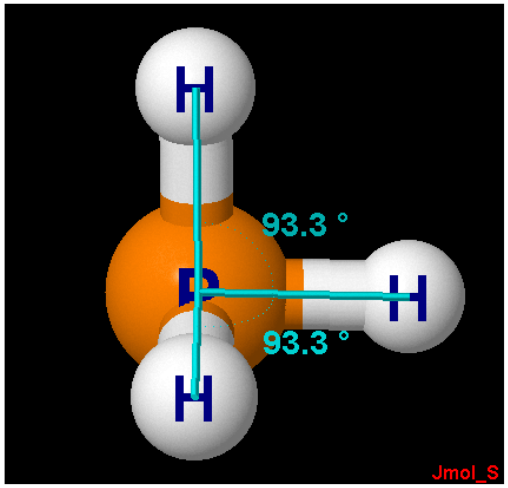
H_2O



H_2S



NH_3



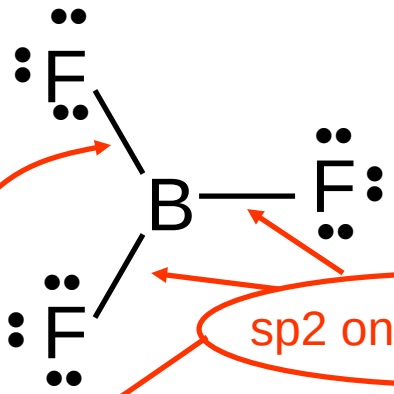
PH_3

to hybridize or not to hybridize

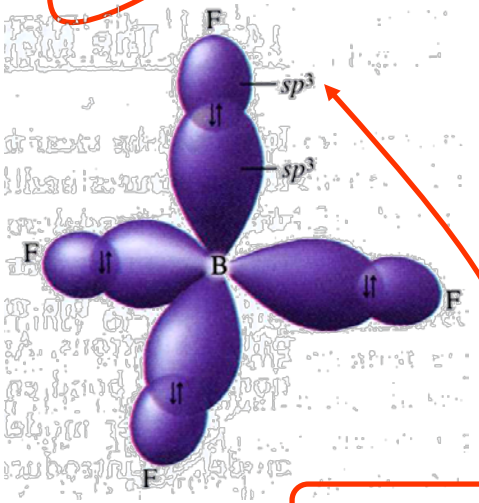
that is still the question?

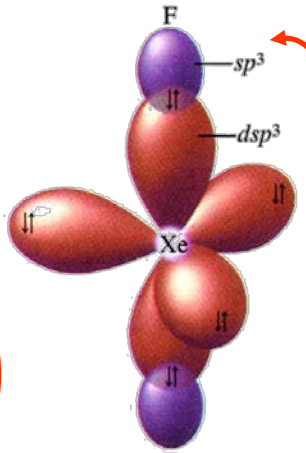
B is sp^2

what's the hybridization of the F's ?

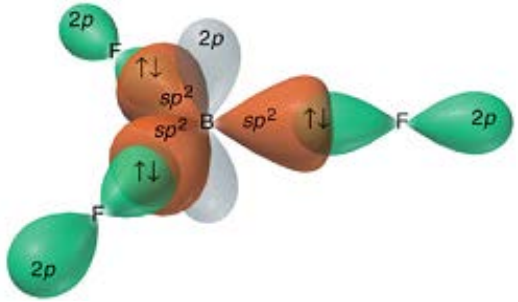


sp2 on B + sp^3 on F

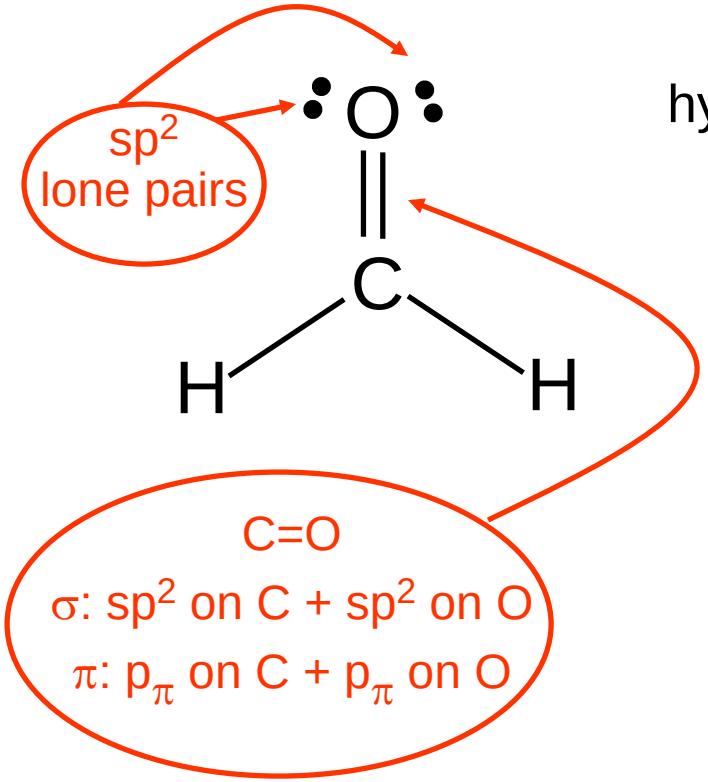




Zumdahl: F is sp^3



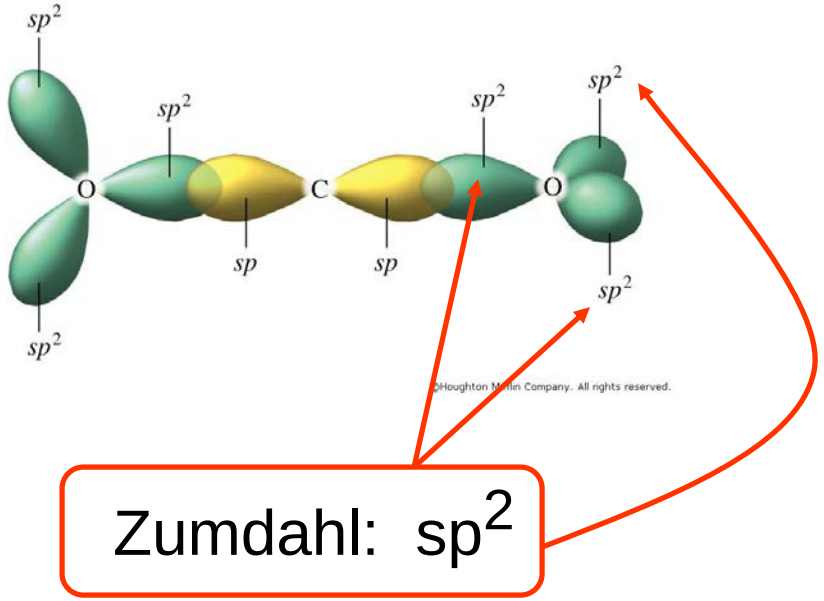
Other texts:
F remains unhybridized

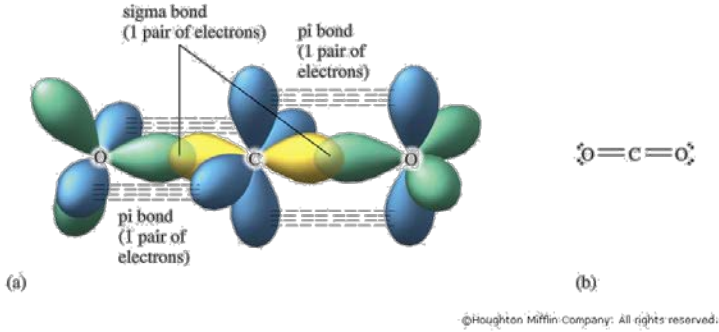


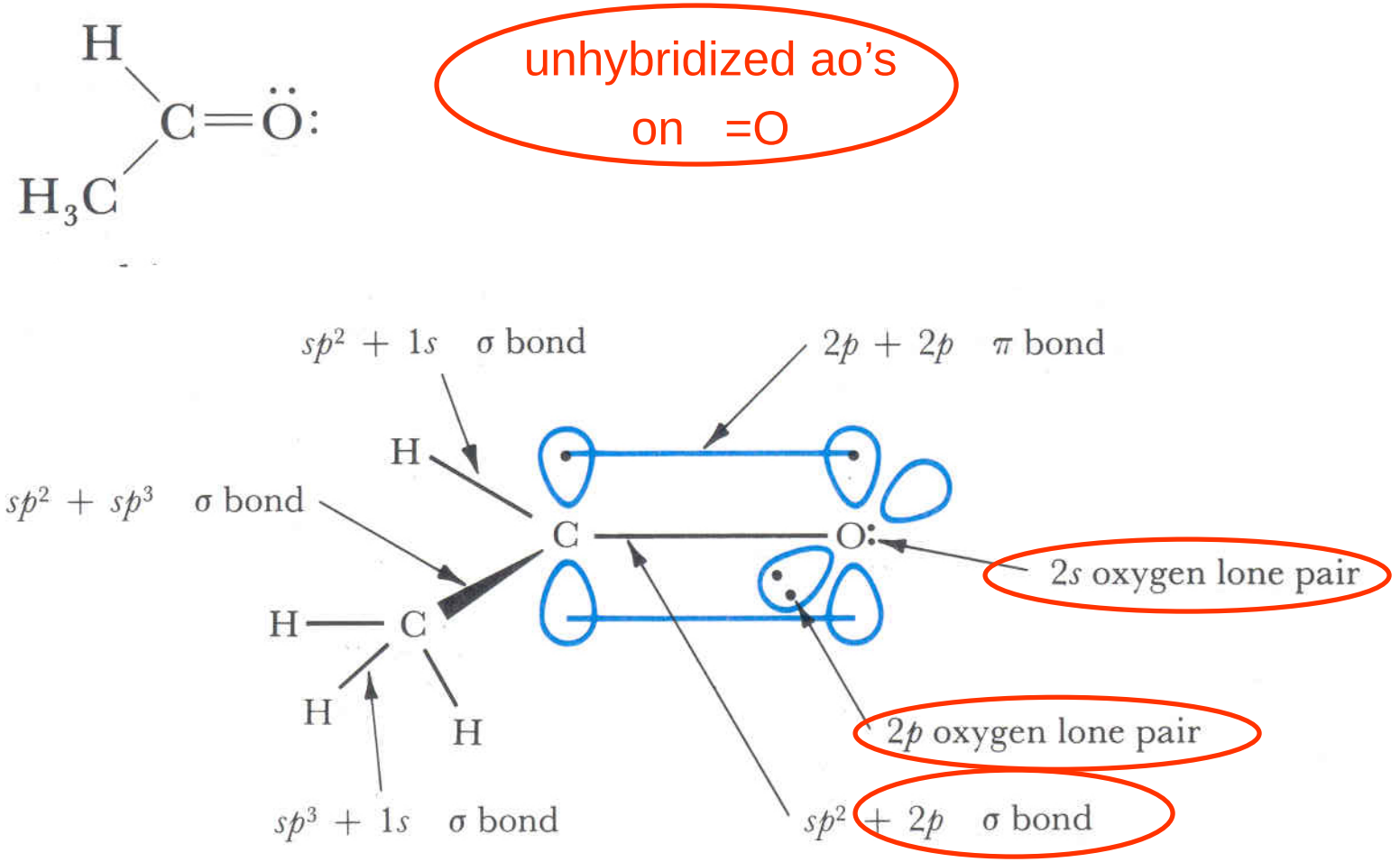
hybridization at C is sp^2

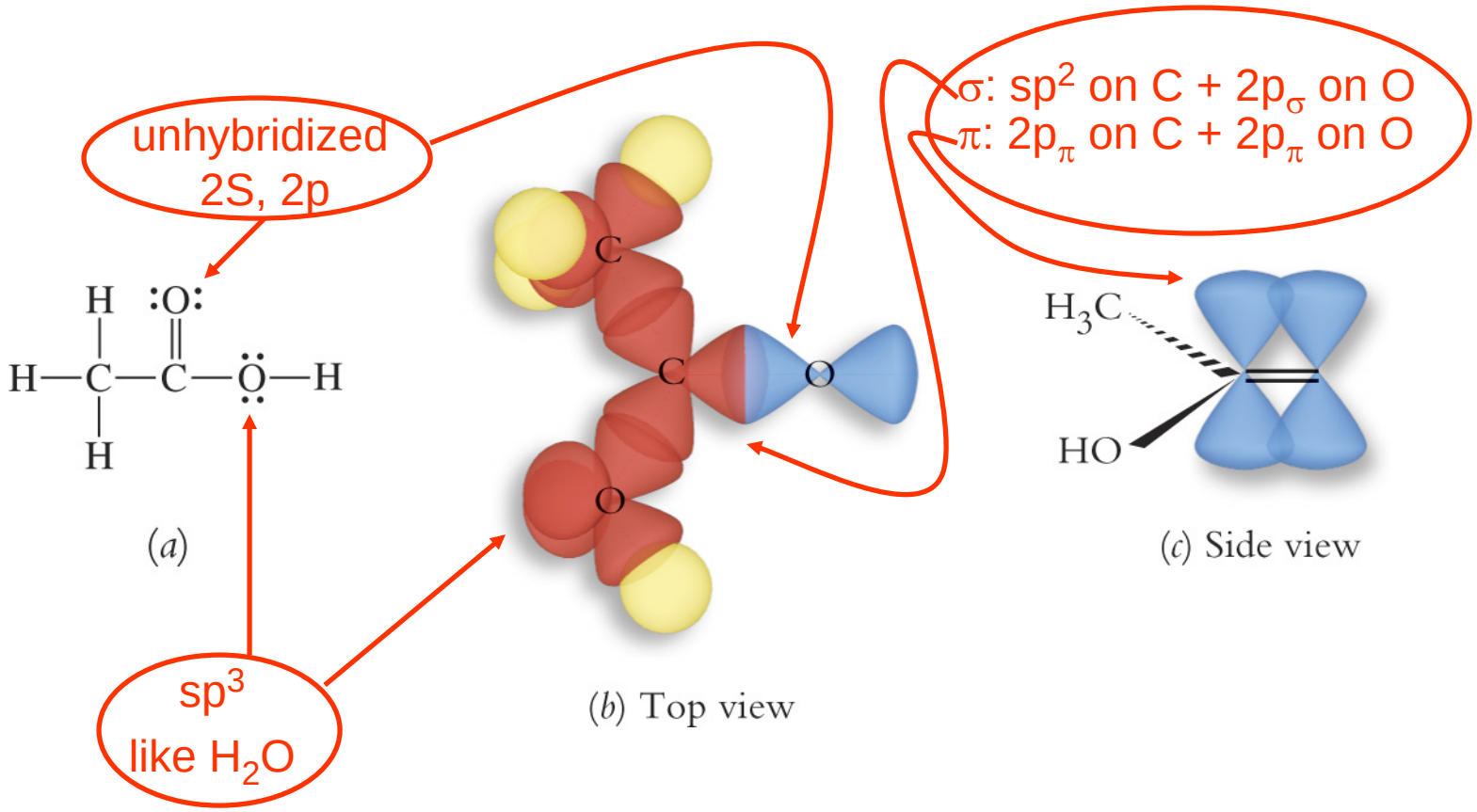
what about =Ö: ?

sp^2 or unhybridized ??






H
C=Ö:
H3C
unhybridized ao's
on =O
sp2 + 1s σ bond
2p + 2p π bond
sp2 + sp3 σ bond
H
C
O:
2s oxygen lone pair
H
C
H
H
2p oxygen lone pair
sp3 + 1s σ bond
sp2 + 2p σ bond


unhybridized
2S, 2p
σ: sp2 on C + 2pσ on O
π: 2pπ on C + 2pπ on O
sp3
like H2O
(a)
(b) Top view
(c) Side view
H3C
HO

the “word” from quantum mechanical calculation

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

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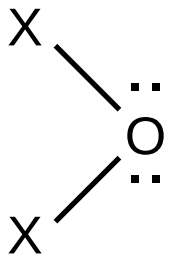
AND

n’er do well EUGENE SWITKES AND WILLIAM N. LIPSCOMB Nobel Prize 1976

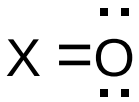
Gibbs Chemical Laboratory, Harvard University, Cambridge, Massachusetts 02138

(Received 26 February

calculation gives UNHYBRIDIZED



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

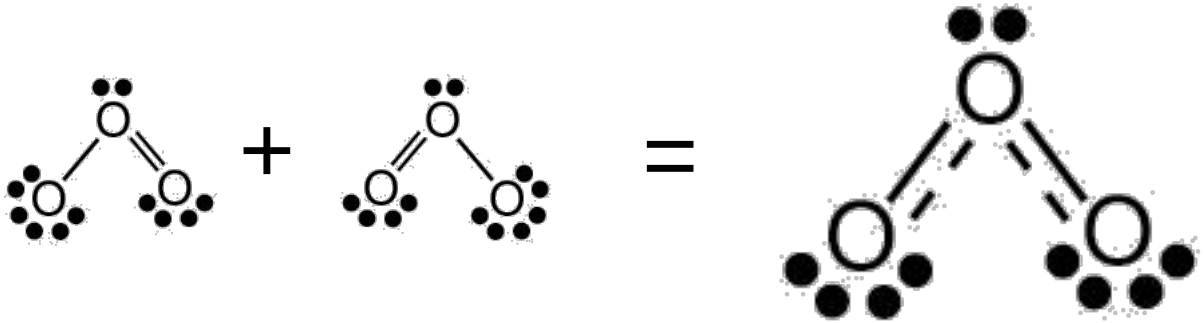
('complex' scheme for B_2, C_2, N_2 implies some sp hybridization)

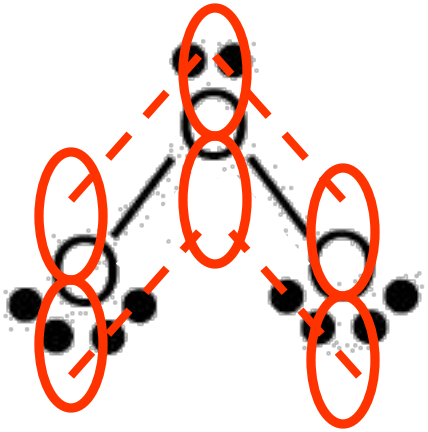
X-C≡N:

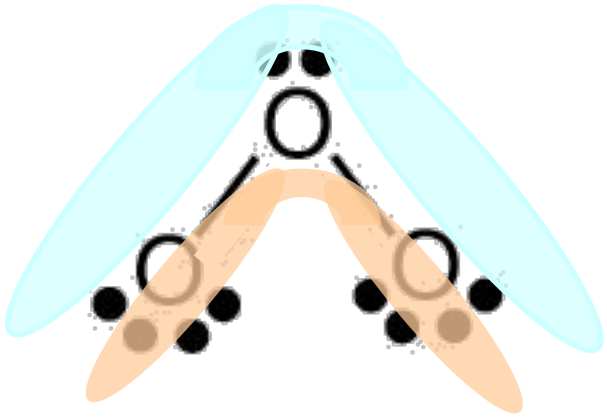
N is sp hybridized with lone pair in sp hybrid

- 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)

Ozone (see figures 14.47 and 14.51)







σ framework
sp^2 hybridized O's

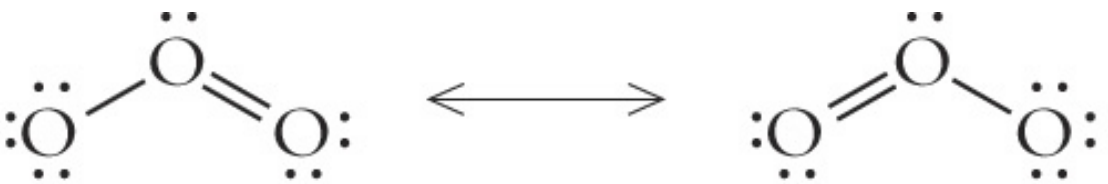
unhybridized p_π ao's

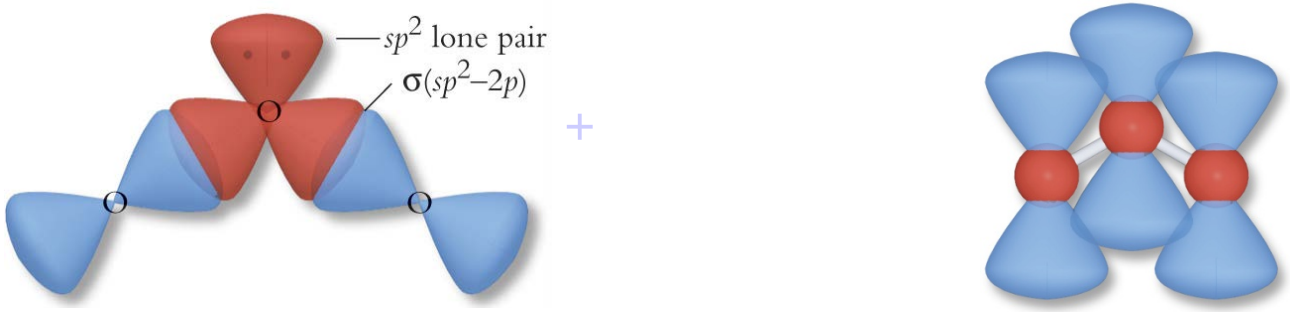
14 e's in σ-framework

4 e's in π-system

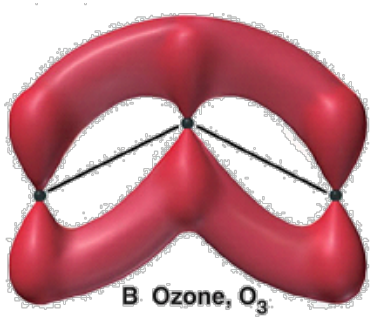
two, filled, delocalized, π mo's

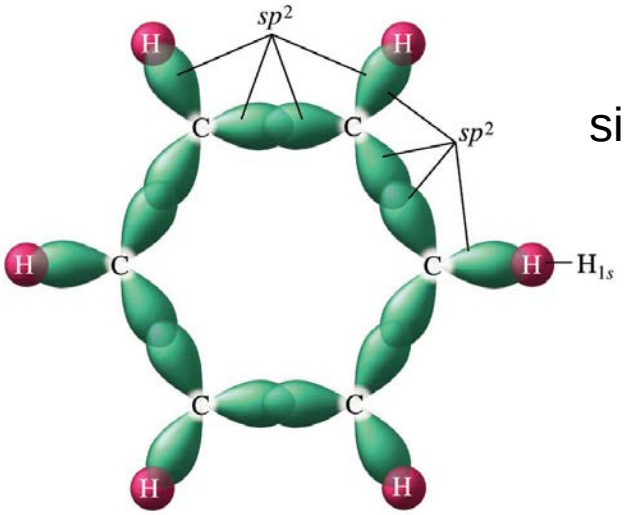
Ozone



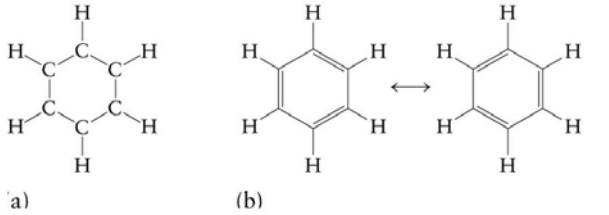


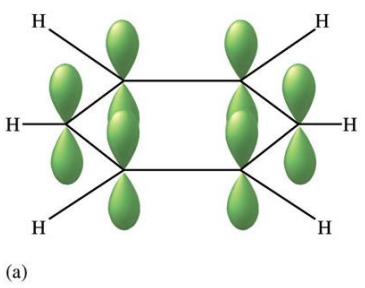
Delocalized π orbitals: An orbital in which electron density is distributed over more than two atoms.

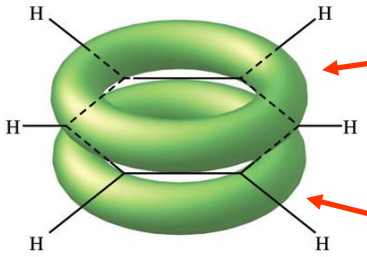




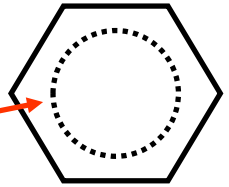
sigma bond framework







6 electrons shared by all six carbons in delocalized molecular orbitals



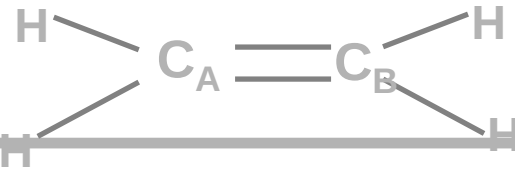
- destructive interference leads to antibonding orbitals which are not usually occupied in the ground state of molecules but which may become occupied upon excitation of electrons by light

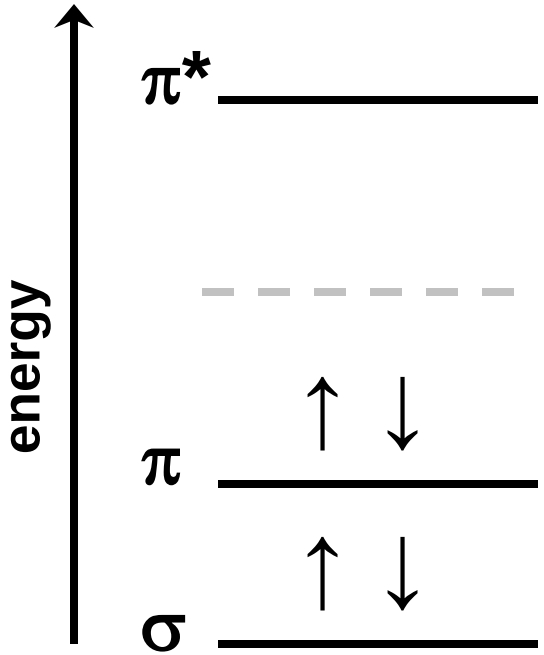
- types of antibonding orbitals:

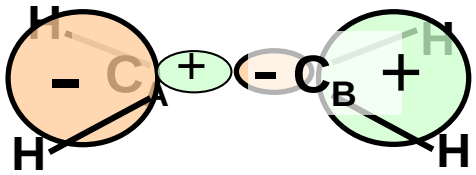
CH_4 : $\sigma^* = sp^3$ on C – 1s on H

C_2H_4: $\sigma^* = sp^2$ on C_A – sp^2 on C_B

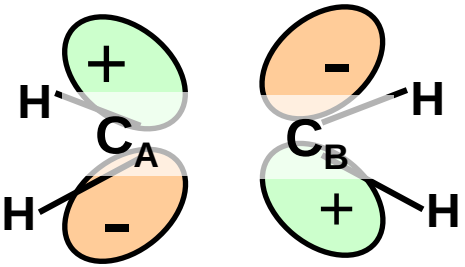
$\pi^* = p_\pi$ on C_A – p_π on C_B



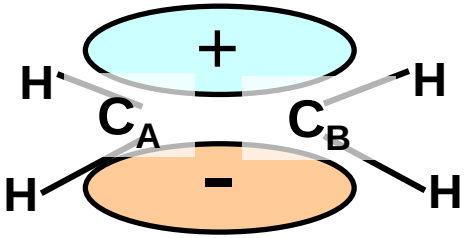




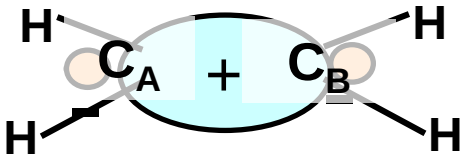
[sp^2 on C_A - sp^2 on C_B]



[p_π on C_A - p_π on C_B]



[p_π on C_A + p_π on C_B]



[sp^2 on C_A + sp^2 on C_B]

END of SESSIONS

15-16