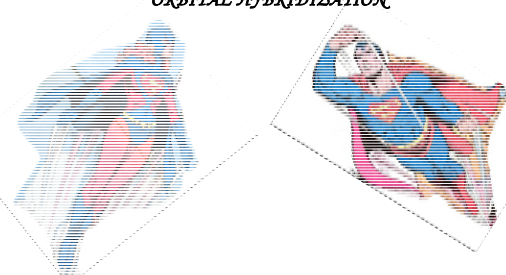


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Sessions 15-16

quantum mechanics to the rescue !!!!!

ORBITAL HYBRIDIZATION



7

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)

8

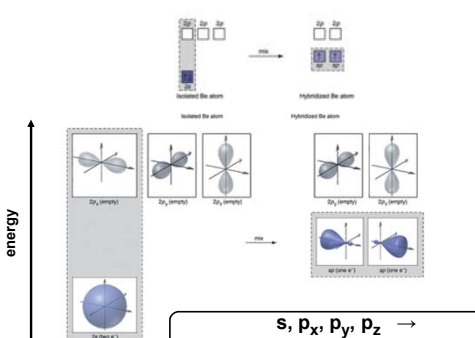
Different order of presentation than text

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)



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

sp hybridization (figure 14.16)



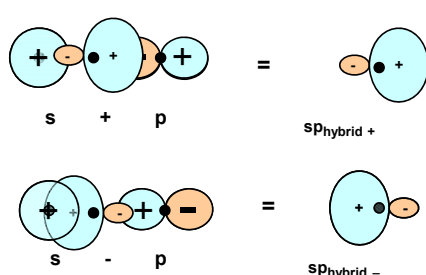
Orbitals in a free C atom

Orbitals in the sp hybridized C in CO₂

- 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)

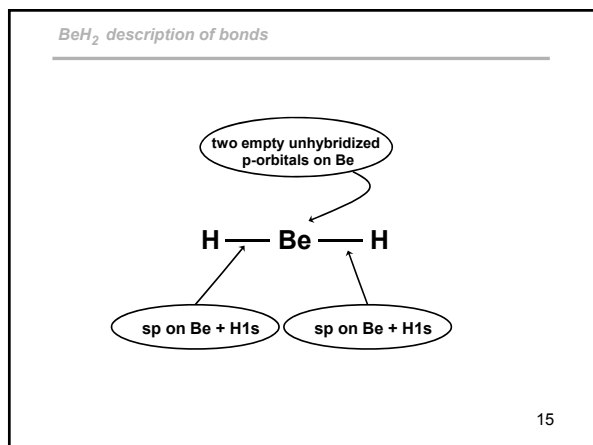
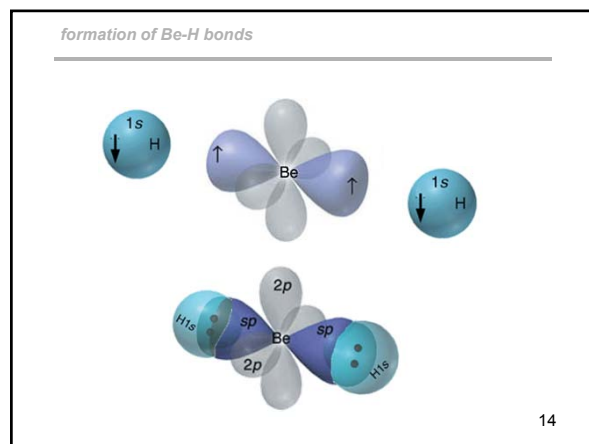
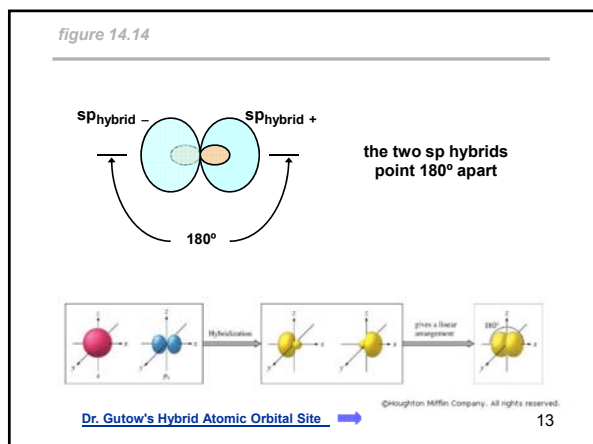


s + p = sp_{hybrid} +

s - p = sp_{hybrid} -

12

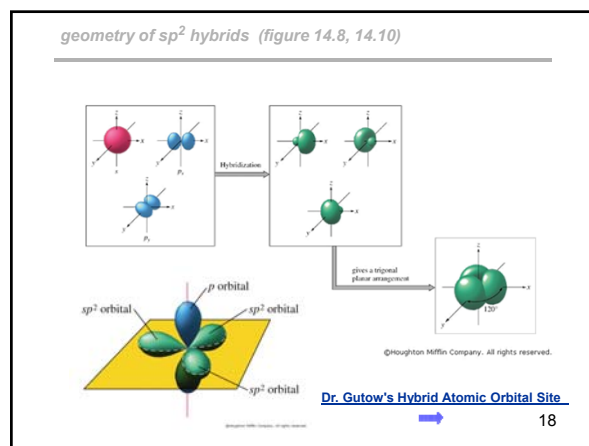
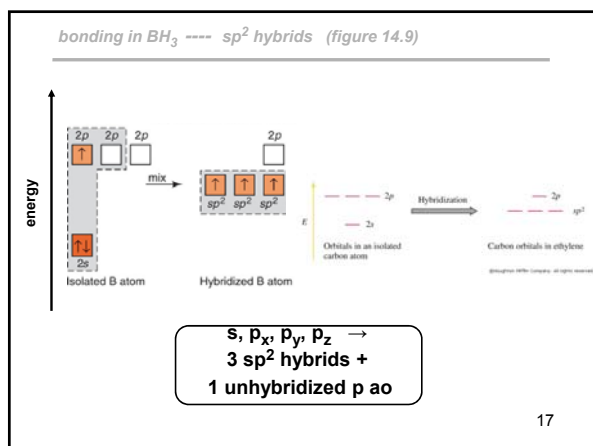
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hybridization vs bonding

- 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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geometry of sp^2 hybrids

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

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bonding in BH_3 , trigonal planar geometry

20

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

21

CH_4 : sp^3 hybridization

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Isolated C atom

Hybridized C atom

A

B

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

tetrahedral geometry
 109.5° bond angles

22

lone pairs can occupy hybrid orbitals (fig. 11.5)

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Isolated N atom

Hybridized N atom

A

B

23

other hybridizations (pp. 668-670)

DON'T FRET

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Isolated P atom

Hybridized P atom

A

B

C

D

24

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ethylene (ethene)

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:
 σ : $sp^2 + sp^2$
 π : $p_\pi + p_\pi$

Dr. Gutow's Hybrid Atomic Orbital Site

32

acetylene (ethyne)

from VSEPR

- SN=2
- linear

↓

- sp

33

triple bond (sp hybridization) $H-C\equiv C-H$ (figure 22.10)

σ : $sp + sp$
 π_y : $p_{xy} + p_{xy}$
 π_z : $p_{xz} + p_{xz}$

sp on C + H1s

C_2H_2 →

34

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 : H_2O (105°) vs H_2S (92.2°) →
 NH_3 (107°) vs PH_3 (93.4°)

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


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terminal atoms: to hybridize or not to hybridize

to hybridize or not to hybridize



that is still the question?

37

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

B is sp^2
what's the hybridization of the F's ?

sp^2 on B + ? on F


hybridization at C is sp^2
what about \ddot{O} ?
 sp^2 or unhybridized ??

$C=O$
 σ : sp^2 on C + ? on O
 π : p_π on C + p_π on O


38

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



39

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

single

σ : $sp^3 + sp^3$

'free' rotation about single bond ↓

double

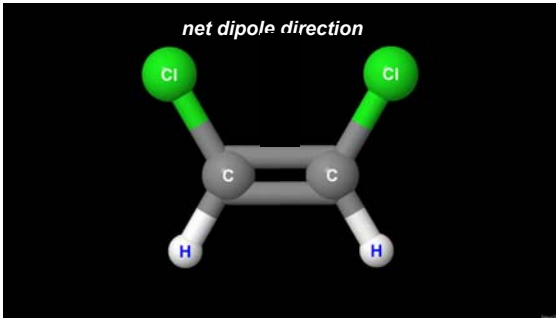
Note that the extra, overlapping pi-bond prevents free rotation around the double bond. One would have to break the pi-bond to be able to rotate around the sigma bond.

no rotation around double bond

40

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

net dipole direction

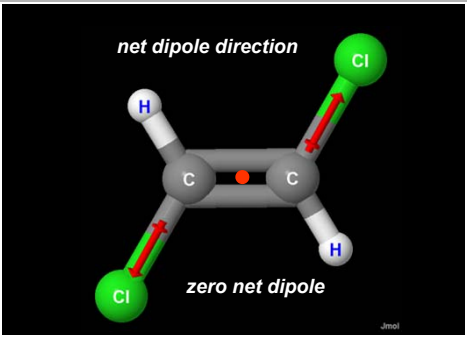


cis 1,2 dichloroethylene →

41

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

net dipole direction



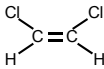
zero net dipole

trans 1,2 dichloroethylene →

42

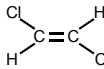
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double bonds and geometric isomers



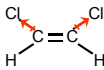
cis 1,2 dichloroethylene

vs

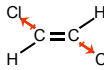


trans 1,2 dichloroethylene

will not interconvert under 'normal' conditions



net dipole \uparrow



no net dipole •

43

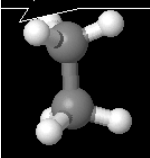

Finis

and




44

'free' rotation around a single bond

'free' rotation around single bond of ethane

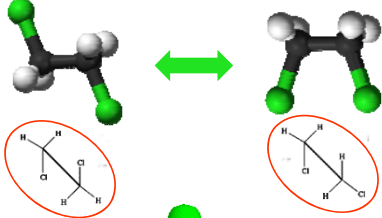
*maybe not so free !!
pair-share exercise*



↓

45

no geometric isomers normal conditions (1,2 dichloroethane)



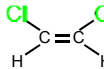
no geometric isomers

↑


46

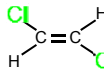
double bonds and geometric isomers

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





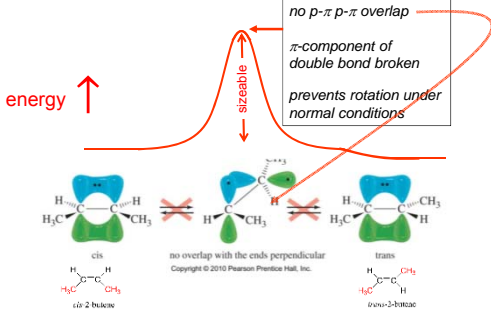
trans 1,2 dichloroethylene

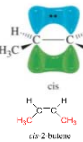
will not interconvert under 'normal' conditions

↓

47

[no] rotation around double bond

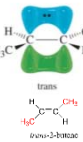




cis
cis-2-butene


no overlap with the ends perpendicular

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trans
trans-2-butene

but does "no" mean "never" ?



↑

48

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hybridization or not: 2nd row vs 2rd row

H2O

H2S

NH3

PH3

49

terminal atoms: to hybridize or not to hybridize

to hybridize or not to hybridize

that is still the question?

50

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

B is sp^2
what's the hybridization of the F's?
sp² on B + sp³ on F

Zumdahl: F is sp^3

Other texts:
F remains unhybridized

51

atoms bonded to only one other atom (fig 14.15 and 14.19)

hybridization at C is sp^2
what about =O ?
 sp^2 or unhybridized ??

sp² lone pairs

C=O
 σ : sp^2 on C + sp^2 on O
 π : p_x on C + p_x on O

Zumdahl: sp^2

52

more on oxygen (DGH)

unhybridized ao's on =O

2s oxygen lone pair
2p oxygen lone pair
sp³ + 2p sigma bond

53

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

unhybridized 2s, 2p
sp³ like H2O

sigma: sp² on C + 2p_z on O
pi: 2p_x on C + 2p_x on O

(a) Top view
(b) Side view

54

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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***

MAURITZ D. NIXON† good guy
Chemistry Department, Cornell University, Ithaca, New York 14853

m'er do well ROSSA SIMONE‡ WILLIAM M. LINDSEY§ Nobel Prize 1976
Cable Chemical Laboratory, Harvard University, Cambridge, Massachusetts 02138
(Received 26 February 1970)

calculation gives UNHYBRIDIZED

$\text{=}\ddot{\text{O}}\text{:}$

55

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

$\begin{array}{c} \text{X} \\ \diagdown \\ \text{O} \\ \diagup \\ \text{X} \end{array}$

definitely sp^3

$\text{X}=\ddot{\text{O}}\text{:}$

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

56

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)

57

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

58

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.

59

figures 14.48, 14.49 and 14.50

sigma bond framework

6 electrons shared by all six carbons in delocalized molecular orbitals

60

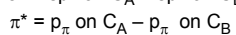
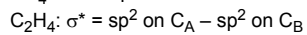
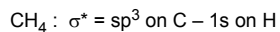
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excited-state orbitals in polyatomic molecules

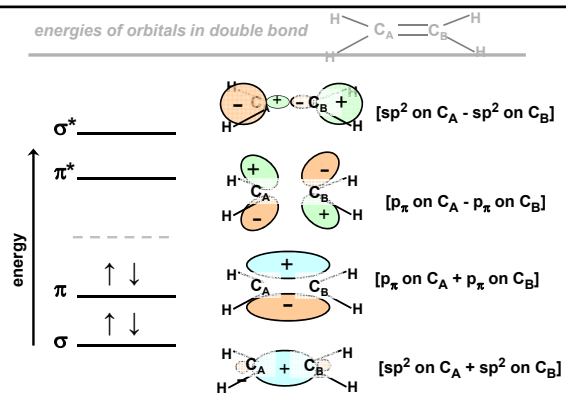
- destructive interference leads to antibonding orbitals which are not usually occupied in the ground state of molecules but which may become occupied upon excitation of electrons by light

- types of antibonding orbitals:



61

energies of orbitals in double bond



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END of SESSIONS
15-16

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