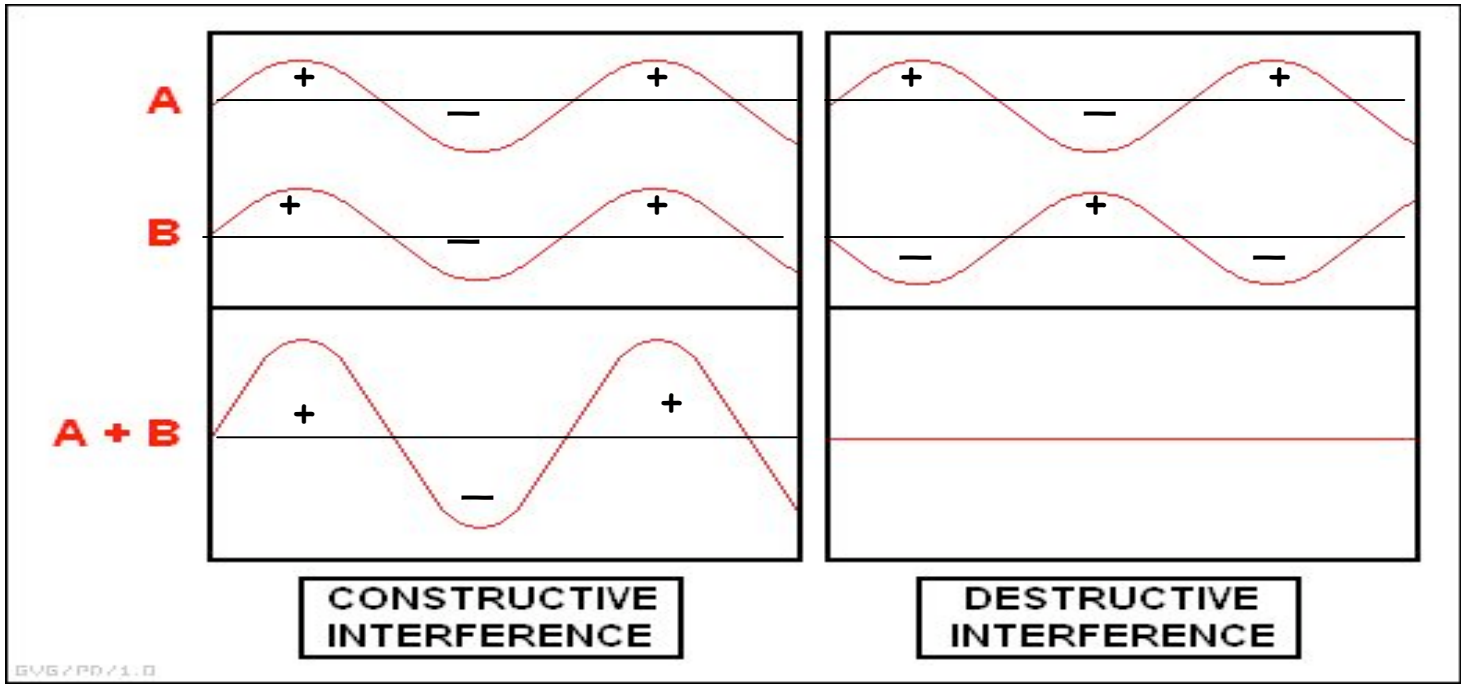
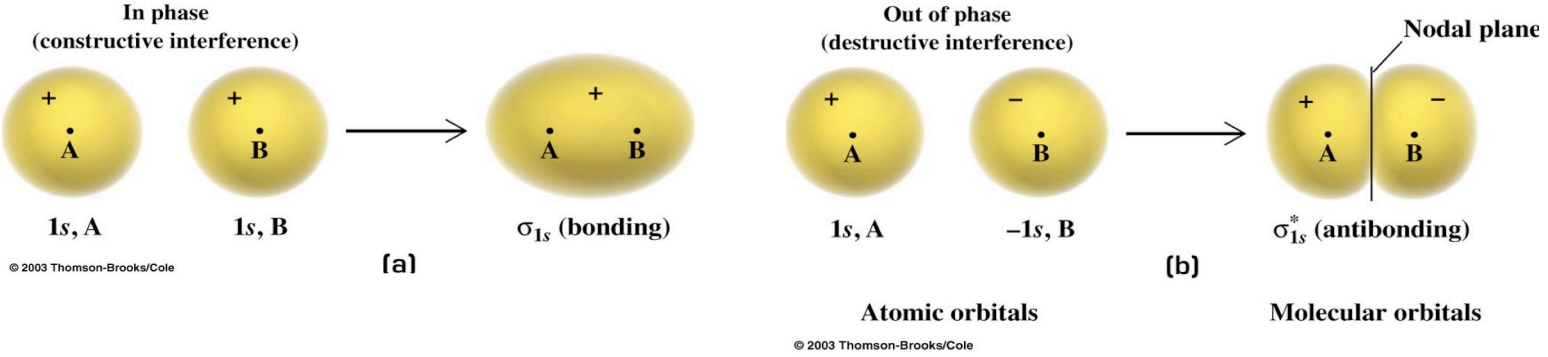
Lecture 16 C1403 October 31, 2005

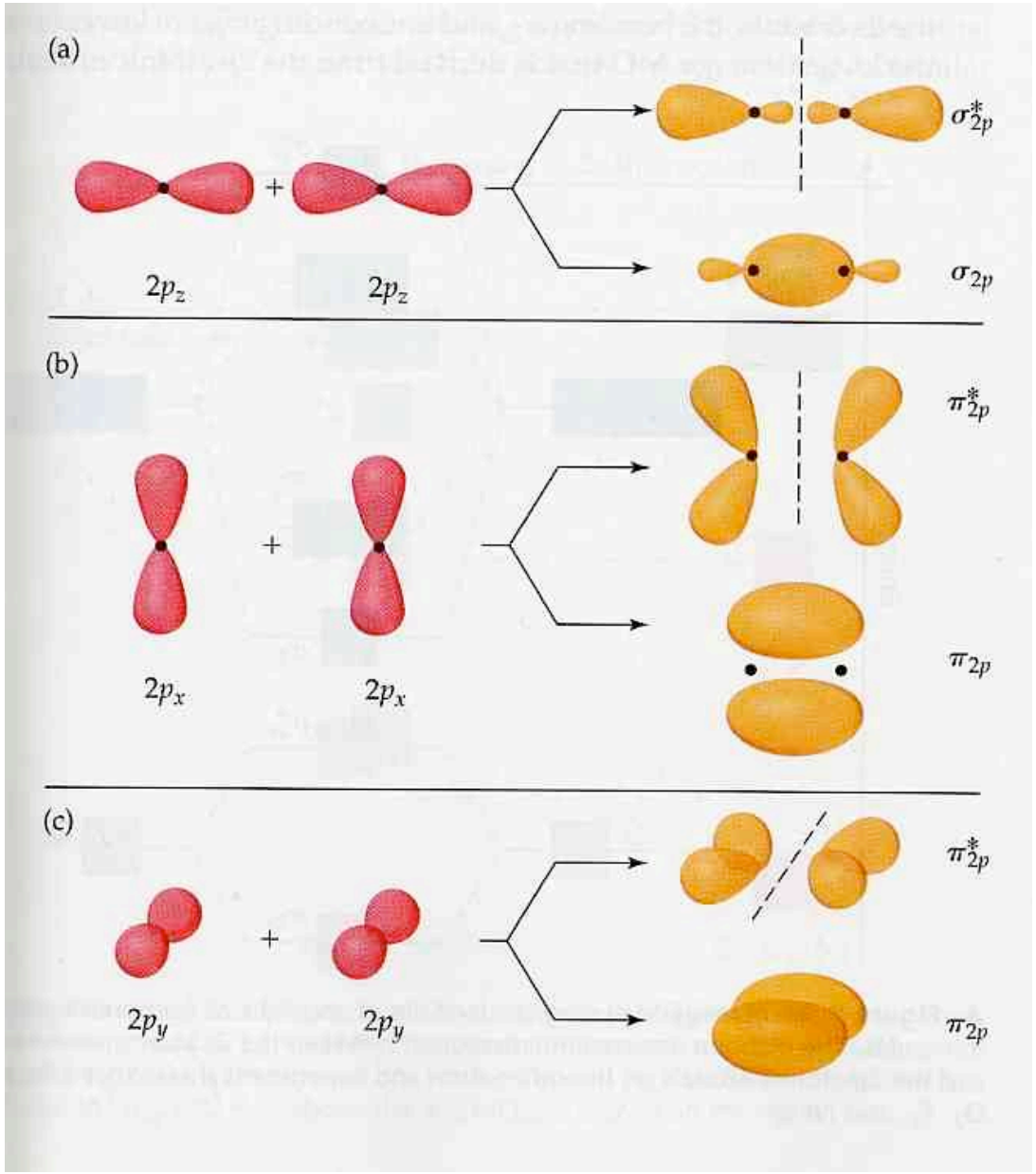
18.1 Molecular orbital theory: molecular orbitals and diatomic molecules

18.2 Valence bond theory: hybridized orbitals and polyatomic molecules

Bond order, bond lengths, connections of MO theory and VB theory with Lewis structures


A
B
A + B
CONSTRUCTIVE INTERFERENCE
DESTRUCTIVE INTERFERENCE


In phase
(constructive interference)
1s, A
1s, B
σ1s (bonding)
(a)
© 2003 Thomson-Brooks/Cole
Out of phase
(destructive interference)
1s, A
–1s, B
Nodal plane
σ*1s (antibonding)
(b)
Atomic orbitals
Molecular orbitals
© 2003 Thomson-Brooks/Cole



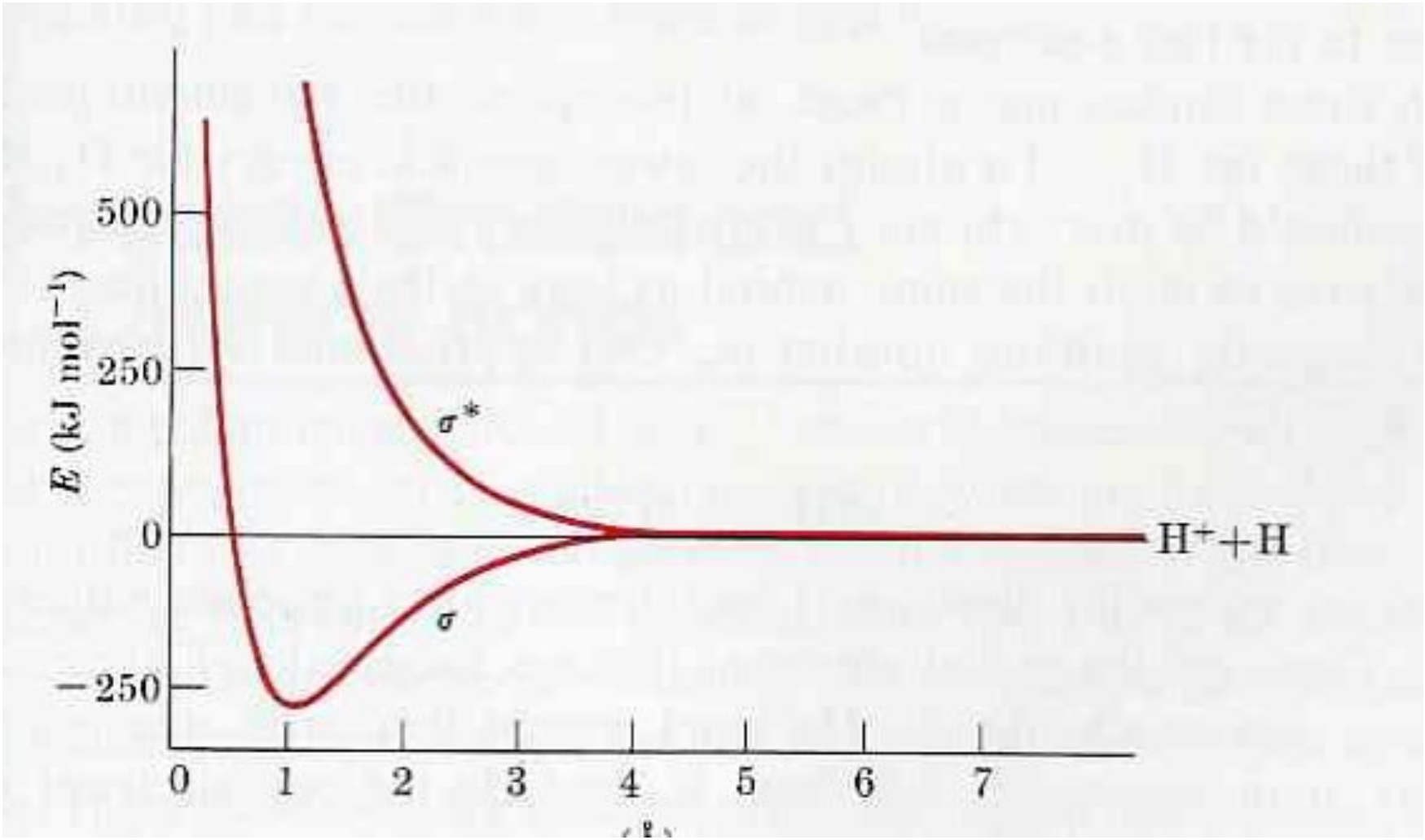
Making of a σ_z and σ_z^* orbital from overlap of two $2p_z$ orbitals

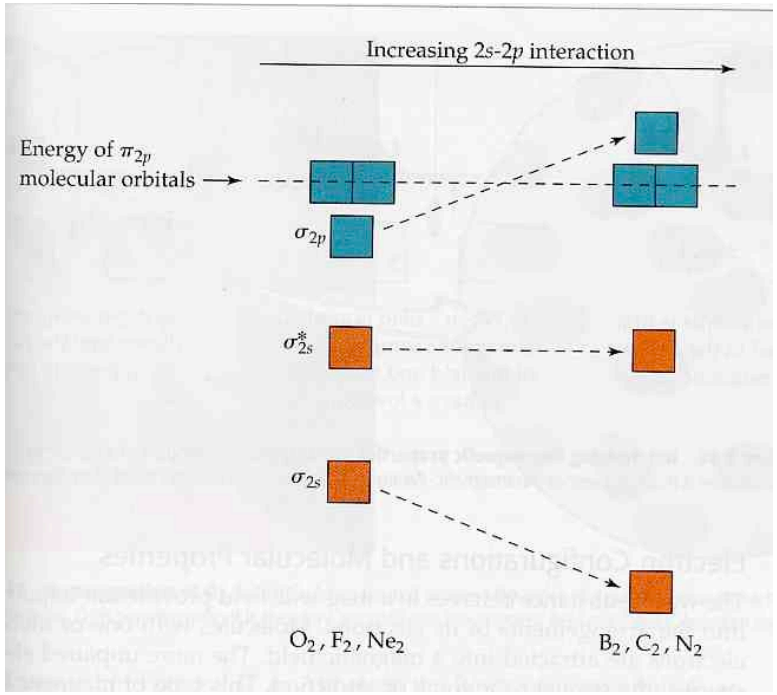
Making of a π_x and π_x^* orbital from overlap of two $2p_x$ orbitals

Making of a π_y and π_y^* orbital from overlap of two $2p_y$ orbitals

Potential energy curves for the σ and σ* orbitals of a diatomic molecule

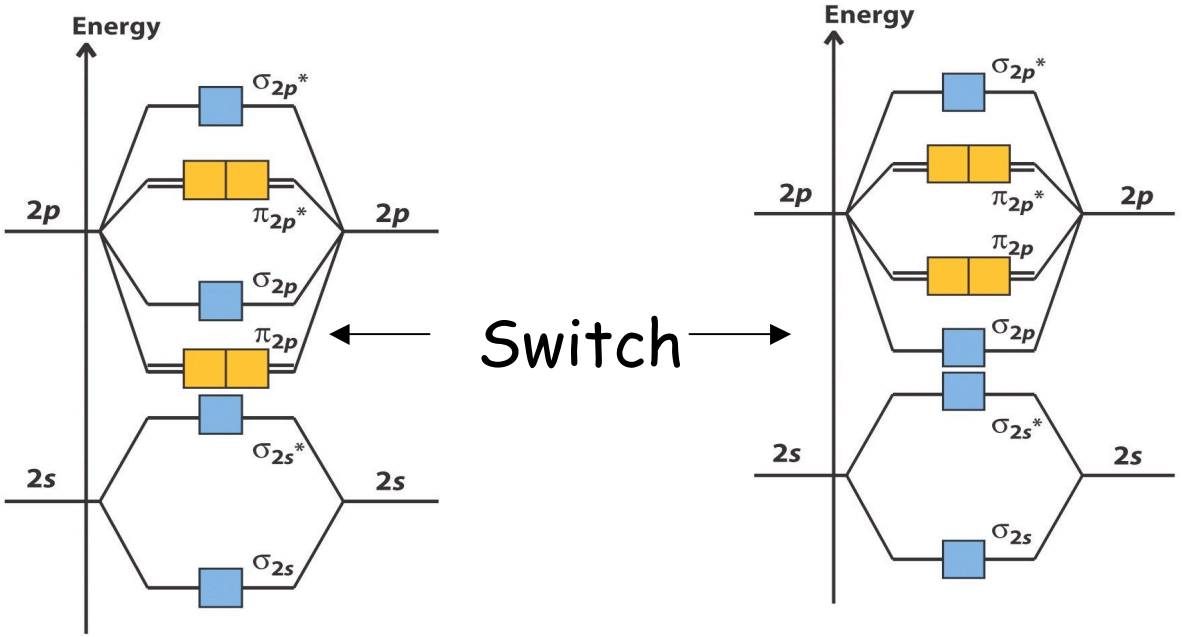
Distance dependence of the energy of a σ and σ* orbital





The reason for the "switch" in the s and p MOs

Larger gap between σ_{2s} and σ_{2p} with increasing Z



O_2 Bond length = 1.21Å

Bond order?

O_2^+ Bond length = 1.12 Å

O_2^- Bond length = 1.26 Å

O_2^{2-} Bond length = 1.49 Å

Compare the Lewis and MO structures of diatomic molecules

C_2

N_2

O_2

F_2

What is the bond order of NO in Lewis terms and MO theory?

18.2 Polyatomic molecules

Valence bond versus molecular orbital theory

Hybridization of atomic orbitals to form molecular orbitals

sp, sp^2 and sp^3 hybridized orbitals

Hybridized orbitals and Lewis structures and molecular geometries

Double bonds and triple bonds

18.2
Bonding in Methane and Orbital Hybridization

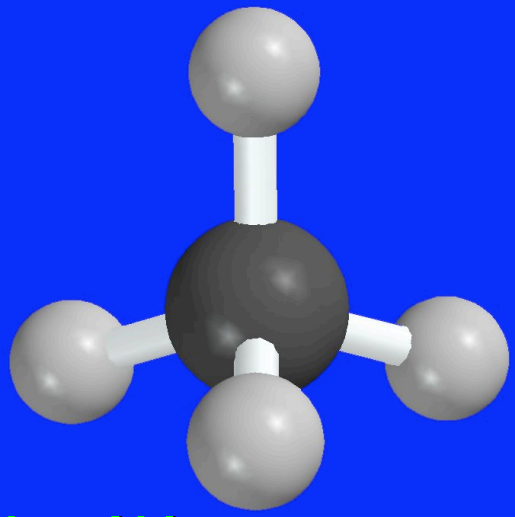
Structure of Methane

tetrahedral

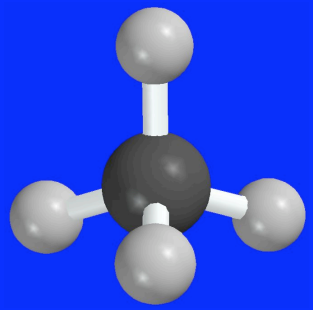
bond angles = 109.5°

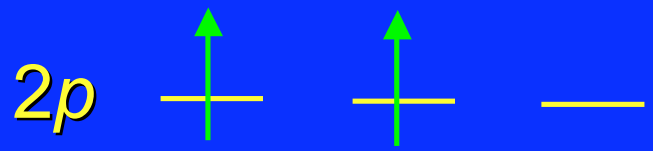
bond distances = 110 pm

but structure seems inconsistent with electron configuration of carbon



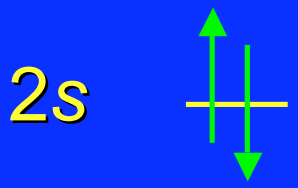
Electron configuration of carbon





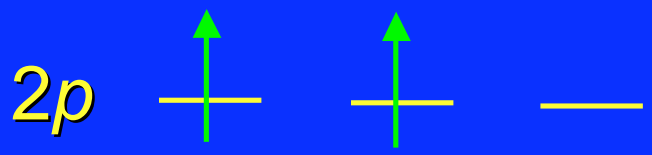
only two unpaired electrons

should form σ bonds to only two hydrogen atoms

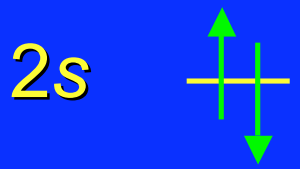


bonds should be at right angles to one another

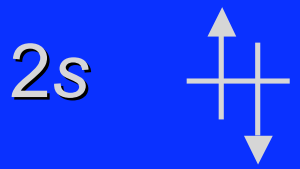
sp^3 Orbital Hybridization



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



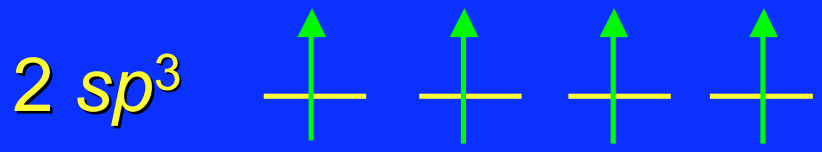
sp^3 Orbital Hybridization



sp^3 Orbital Hybridization

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

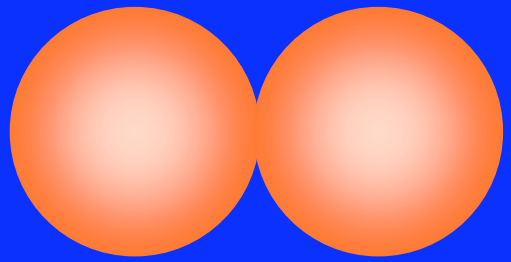
sp^3 Orbital Hybridization



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

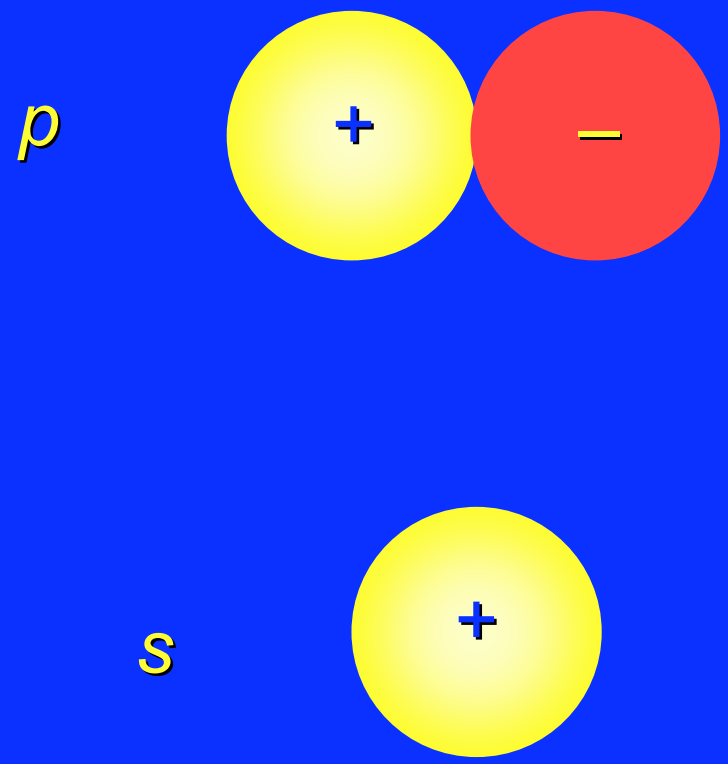
Shapes of orbitals

p



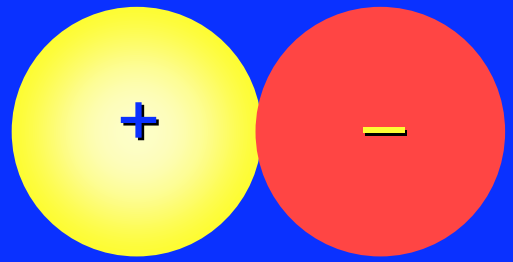
s

Nodal properties of orbitals



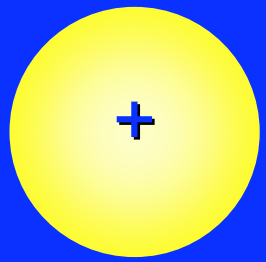
Shape of sp^3 hybrid orbitals

p



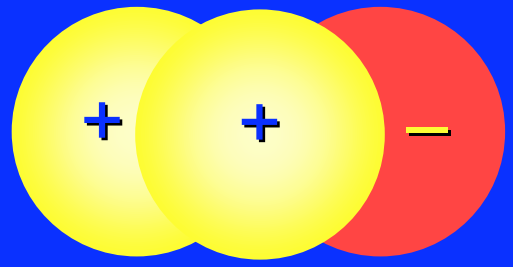
take the *s* orbital and place it on top of the *p* orbital

s



Shape of sp^3 hybrid orbitals

$s + p$

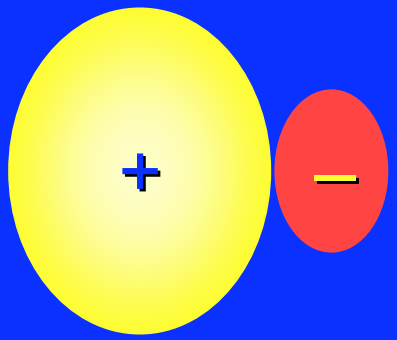


reinforcement of electron wave in regions where sign is the same

destructive interference in regions of opposite sign

Shape of sp^3 hybrid orbitals

sp hybrid



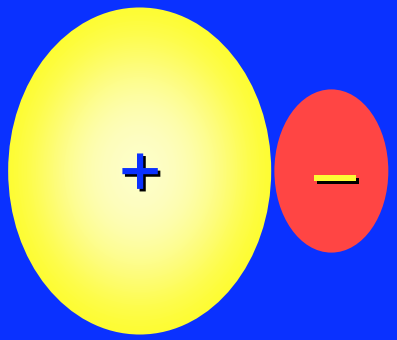
orbital shown is *sp* hybrid

analogous procedure using three *s* orbitals and one *p* orbital gives sp^3 hybrid

shape of sp^3 hybrid is similar

Shape of sp^3 hybrid orbitals

sp hybrid



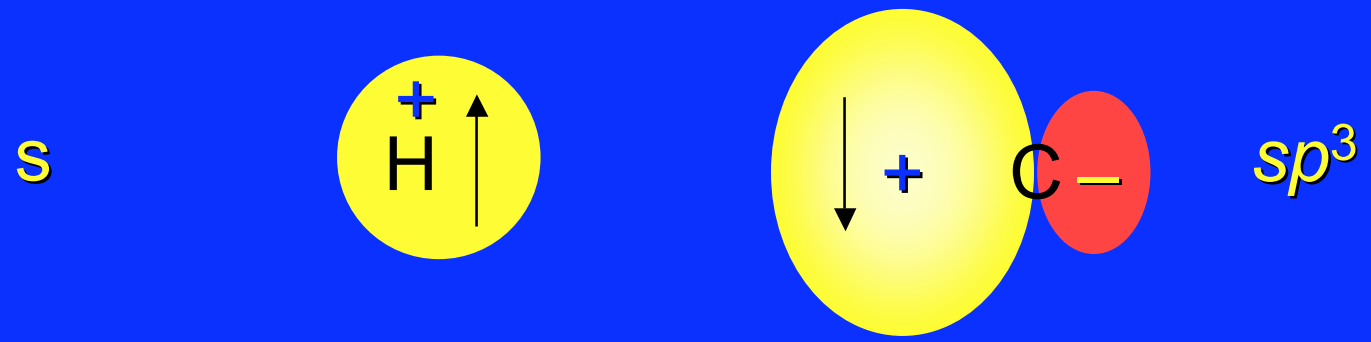
hybrid orbital is not symmetrical

higher probability of finding an electron on one side of the nucleus than the other

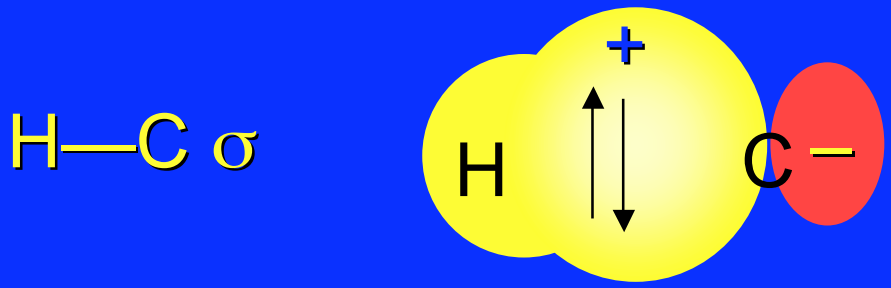
leads to stronger bonds

The C—H σ Bond in Methane

In-phase overlap of a half-filled 1*s* orbital of hydrogen with a half-filled sp^3 hybrid orbital of carbon:



gives a σ bond.



Justification for Orbital Hybridization

consistent with structure of methane

allows for formation of 4 bonds rather than 2

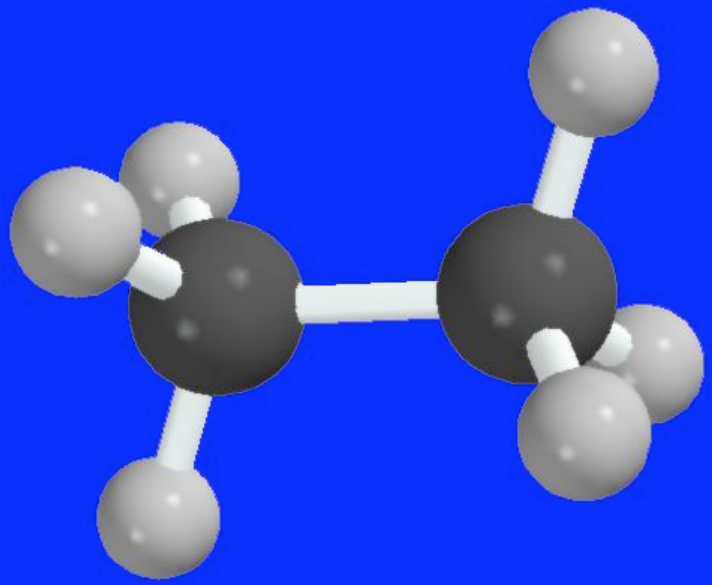
bonds involving sp^3 hybrid orbitals are stronger than those involving *s-s* overlap or *p-p* overlap

18.2
sp^3 Hybridization and Bonding in Ethane

Structure of Ethane

C_2H_6

CH_3CH_3

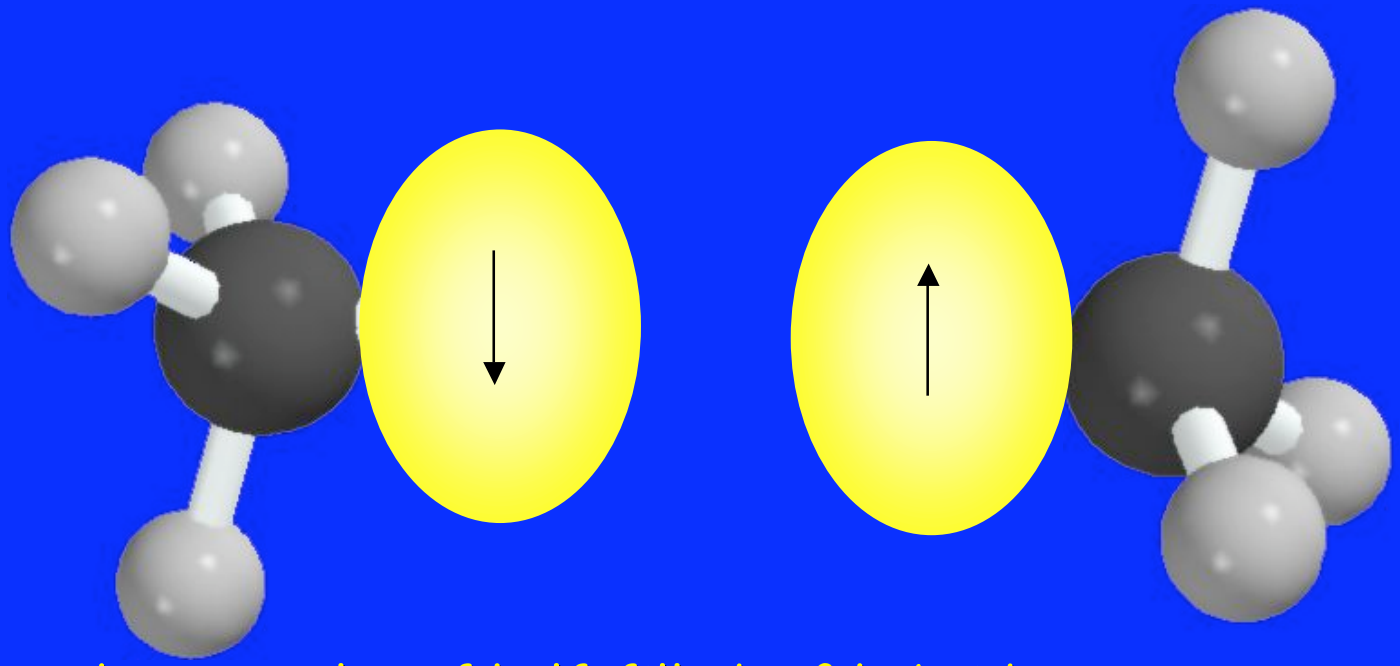


tetrahedral geometry at each carbon

C—H bond distance = 110 pm

C—C bond distance = 153 pm

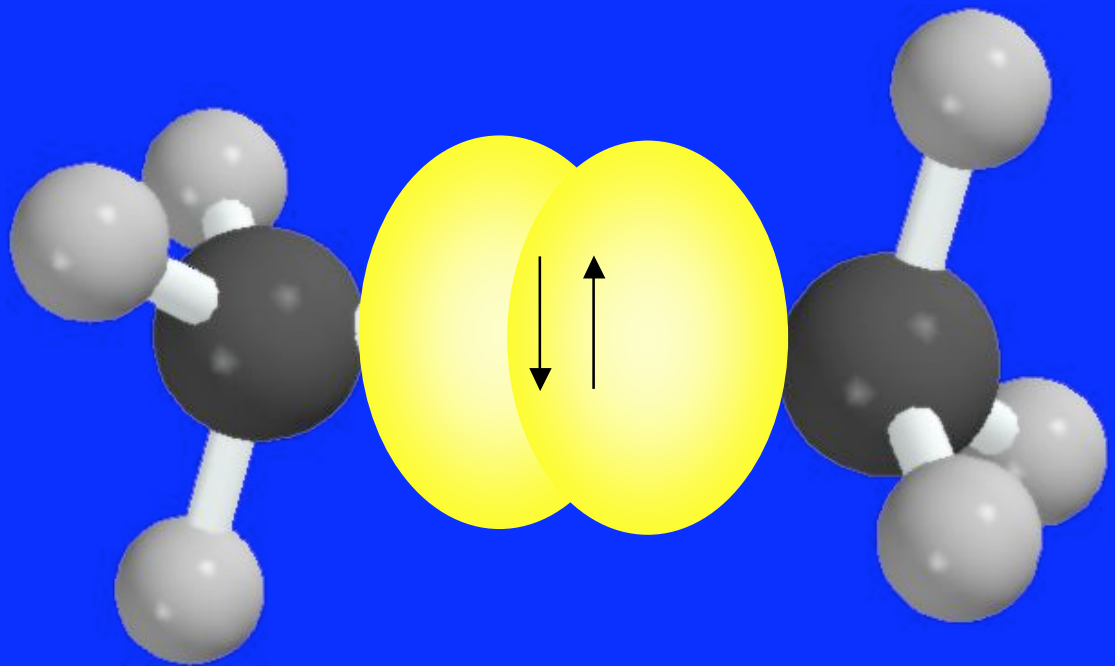
The C—C σ Bond in Ethane



In-phase overlap of half-filled sp^3 hybrid orbital of one carbon with half-filled sp^3 hybrid orbital of another.

Overlap is along internuclear axis to give a σ bond.

The C—C σ Bond in Ethane



In-phase overlap of half-filled sp^3 hybrid orbital of one carbon with half-filled sp^3 hybrid orbital of another.

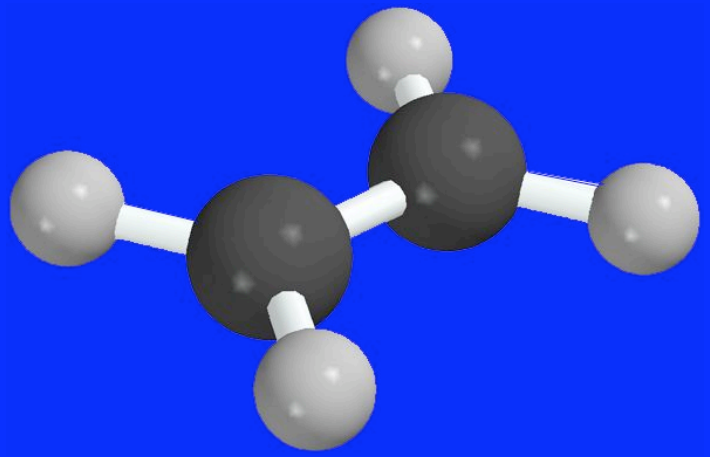
Overlap is along internuclear axis to give a σ bond.

18.2
sp^2 Hybridization and Bonding in Ethylene

Structure of Ethylene

C_2H_4

$H_2C{=}CH_2$



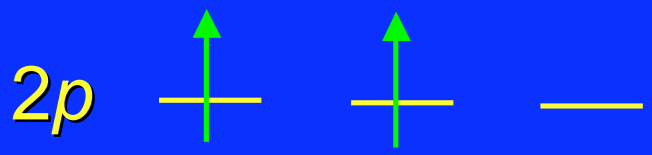
planar

bond angles: close to 120°

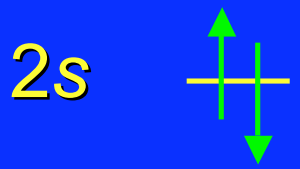
bond distances: C—H = 110 pm

C=C = 134 pm

sp^2 Orbital Hybridization

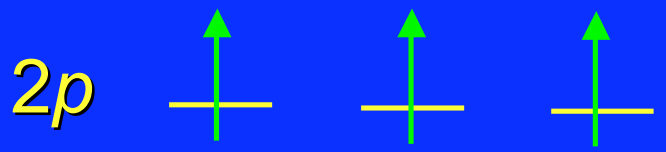


Promote an electron from the 2*s* to the 2*p* orbital

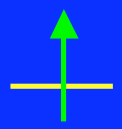


sp^2 Orbital Hybridization

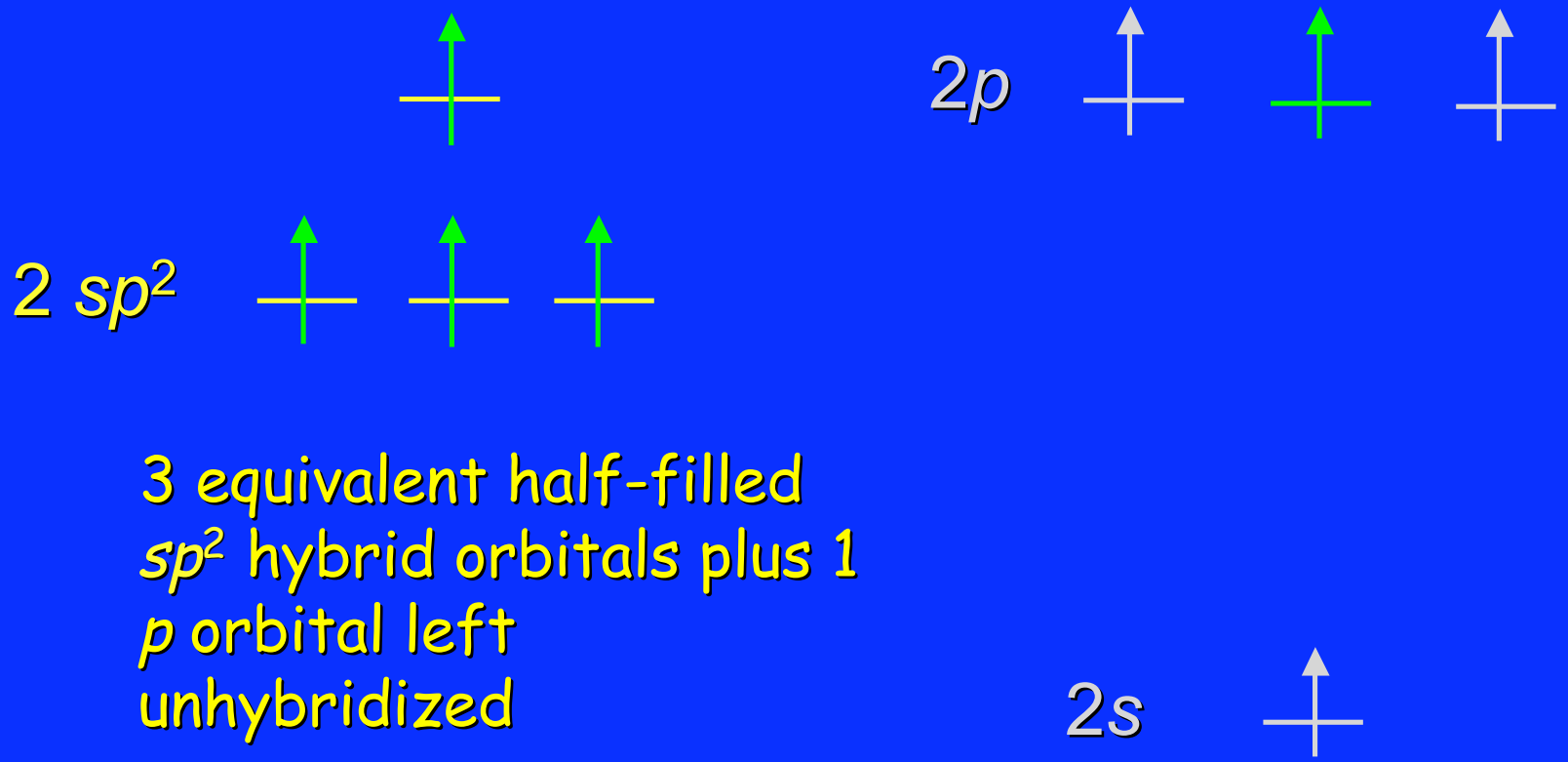
sp^2 Orbital Hybridization



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

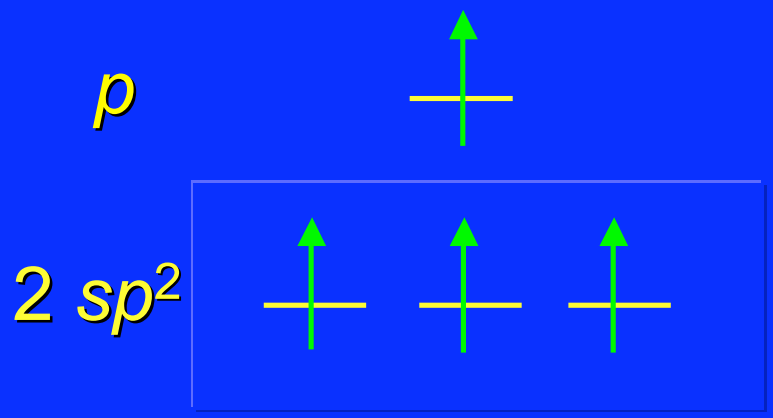


sp^2 Orbital Hybridization



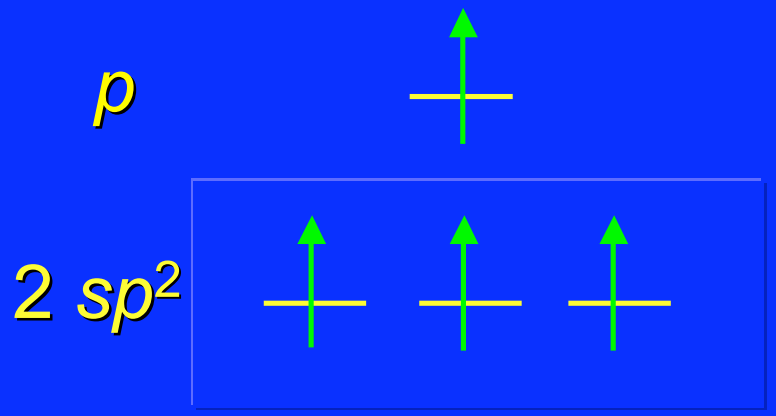
3 equivalent half-filled sp^2 hybrid orbitals plus 1 *p* orbital left unhybridized

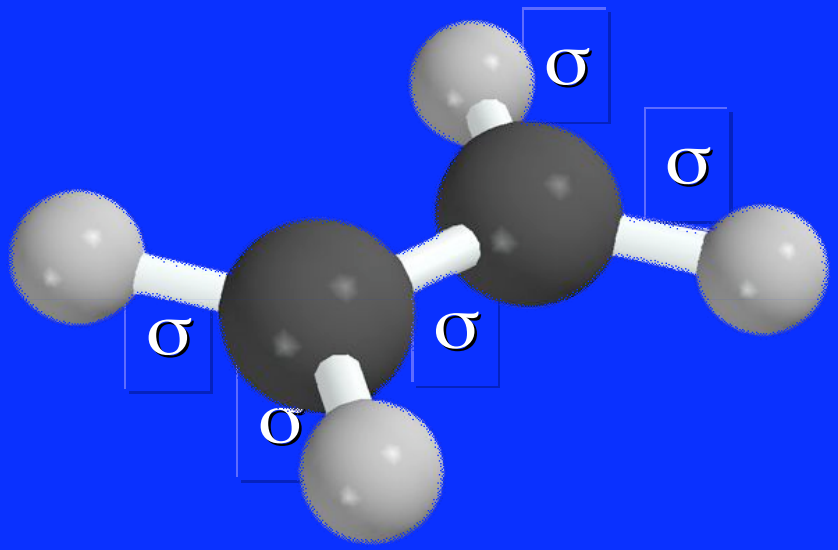
sp^2 Orbital Hybridization



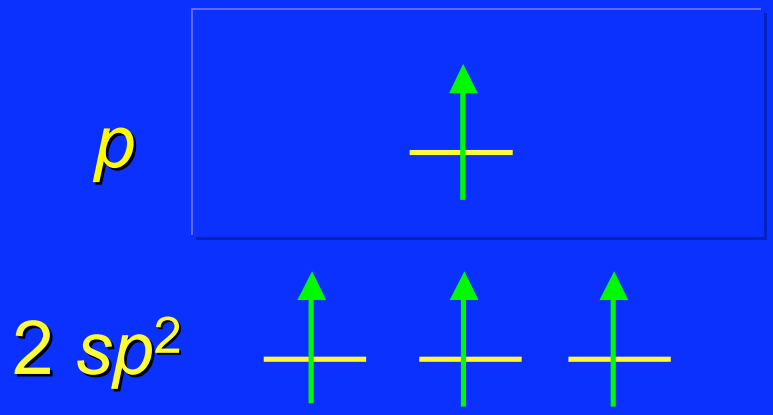
2 of the 3 sp^2 orbitals are involved in σ bonds to hydrogens; the other is involved in a σ bond to carbon

sp^2 Orbital Hybridization



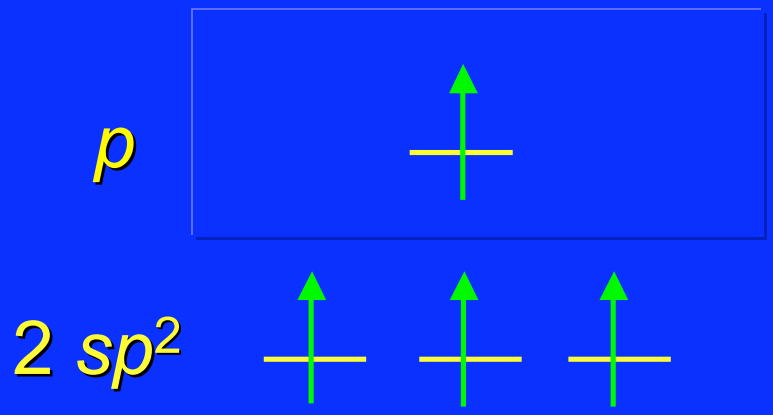


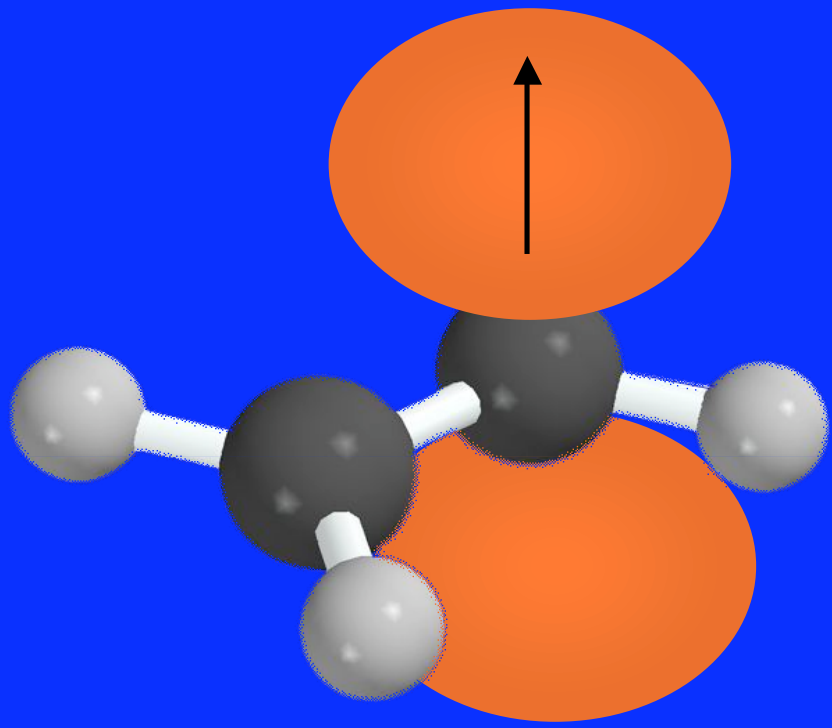
π Bonding in Ethylene



the unhybridized *p* orbital of carbon is involved in π bonding to the other carbon

π Bonding in Ethylene

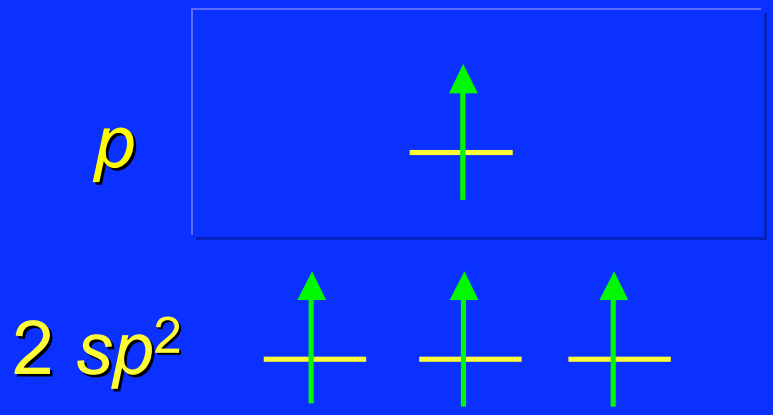


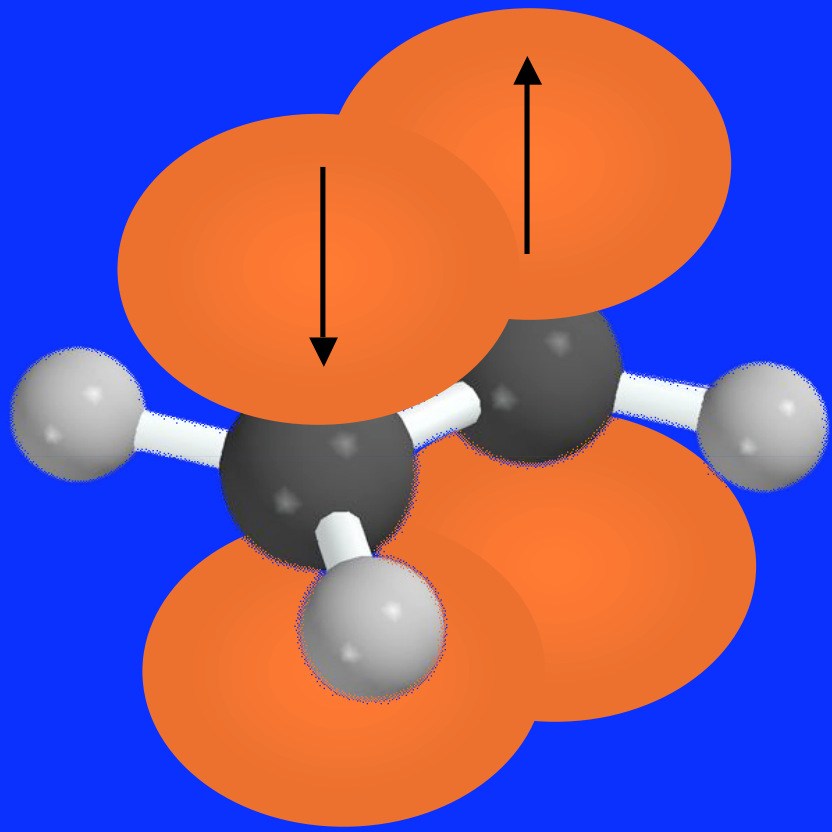


each carbon has an unhybridized 2*p* orbital

axis of orbital is perpendicular to the plane of the σ bonds

π Bonding in Ethylene

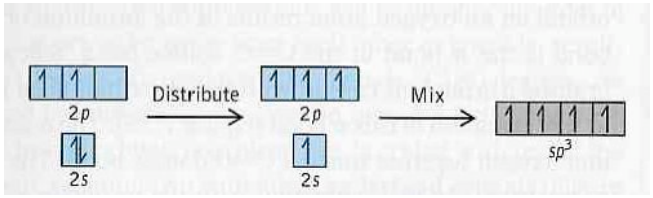


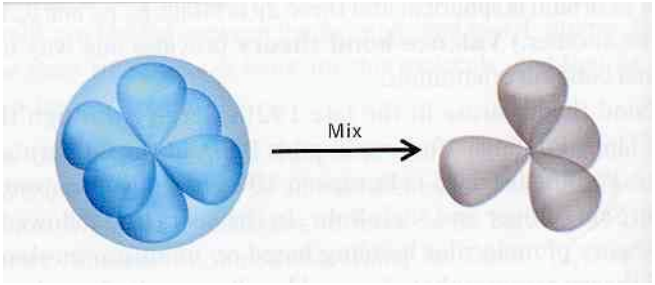


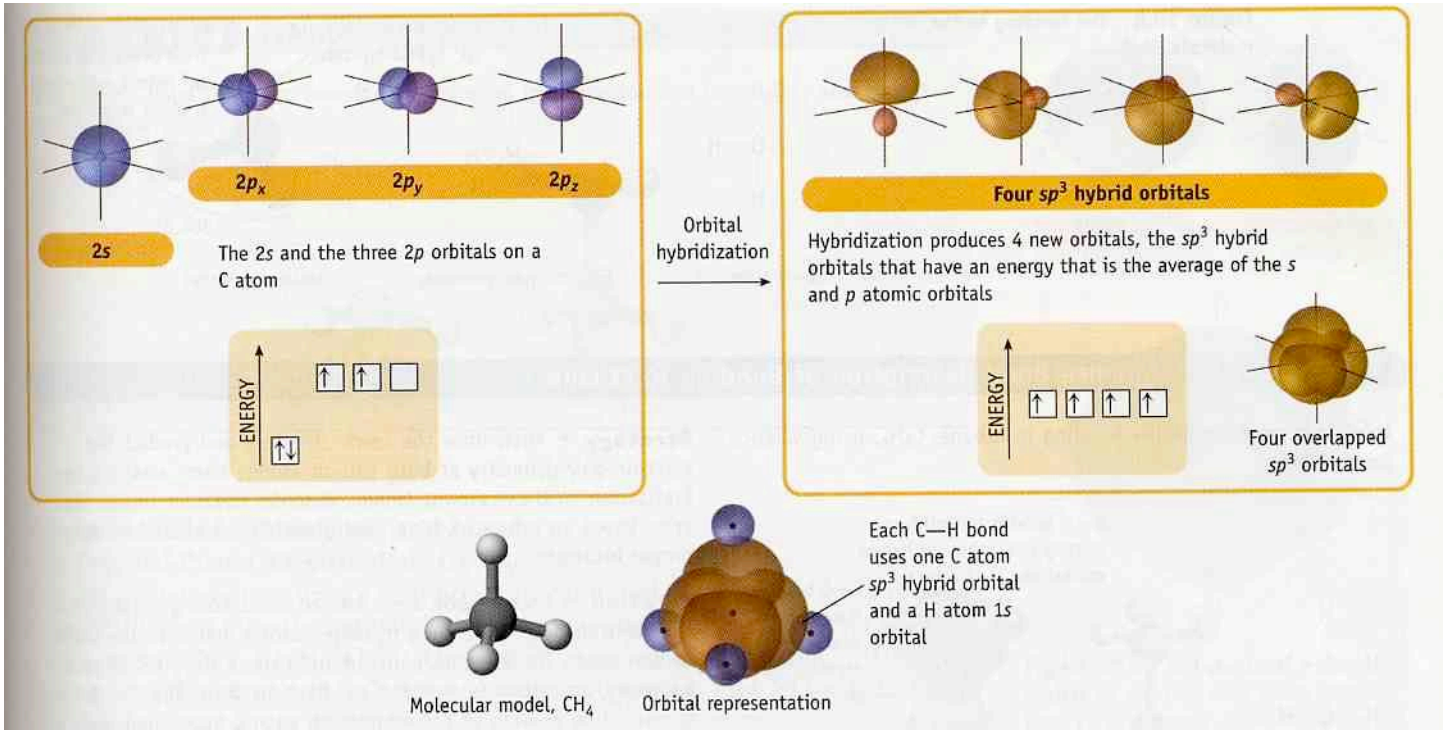
side-by-side overlap of half-filled *p* orbitals gives a π bond

double bond in ethylene has a σ component and a π component

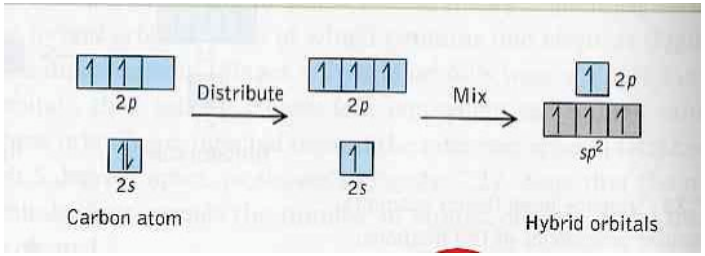
Hybridization and methane: CH_4

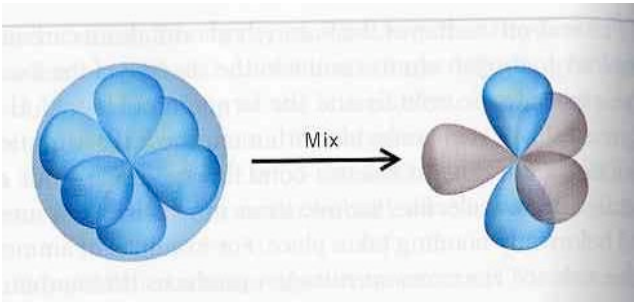


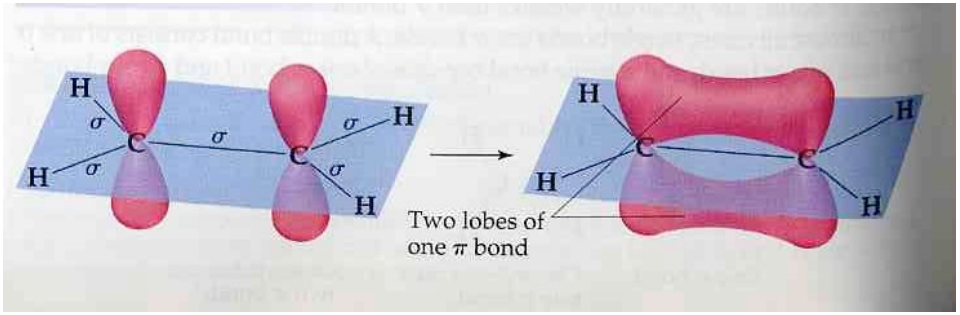


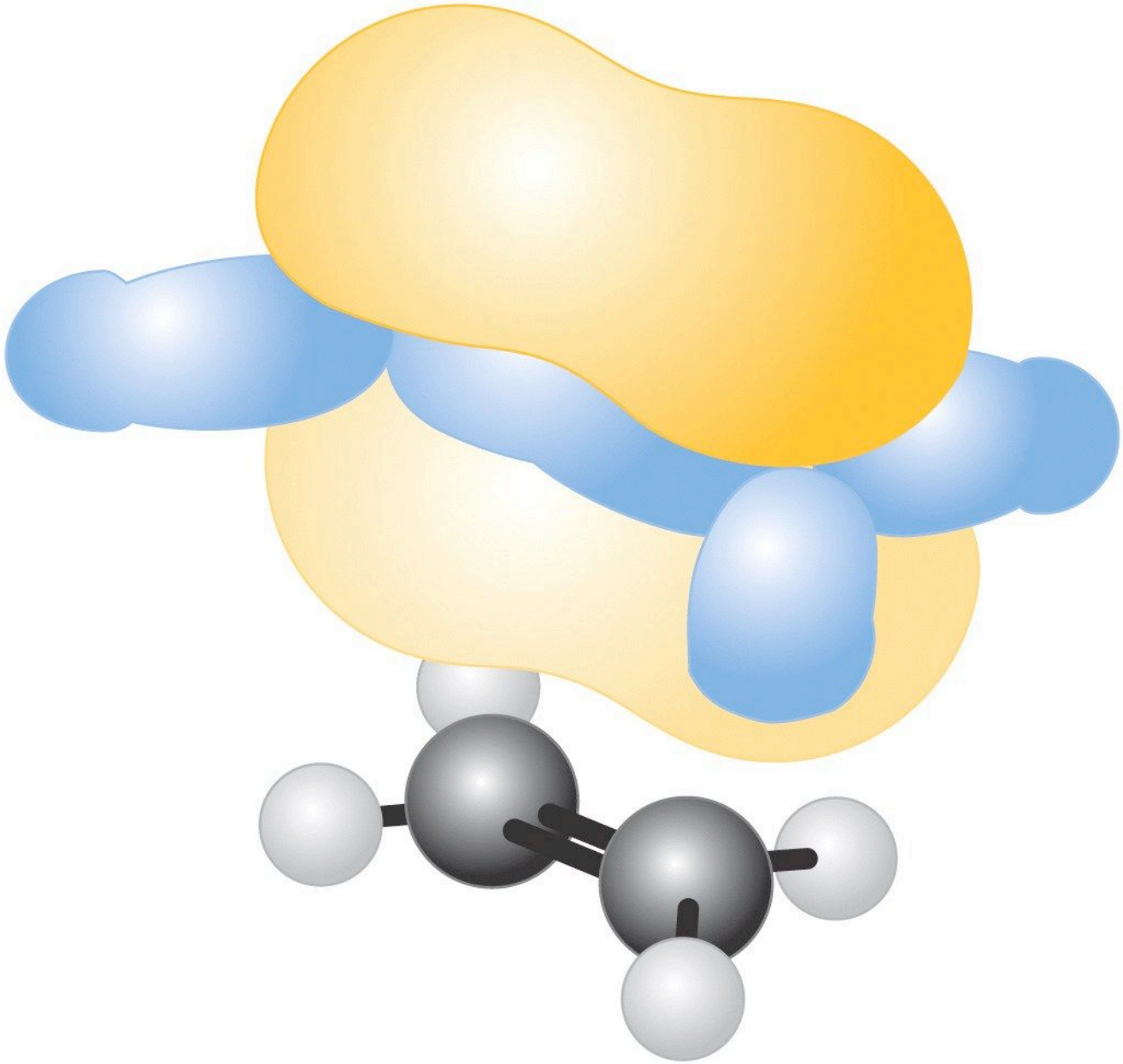


sp^3 hybridization and ethylene: $H_2C=CH_2$



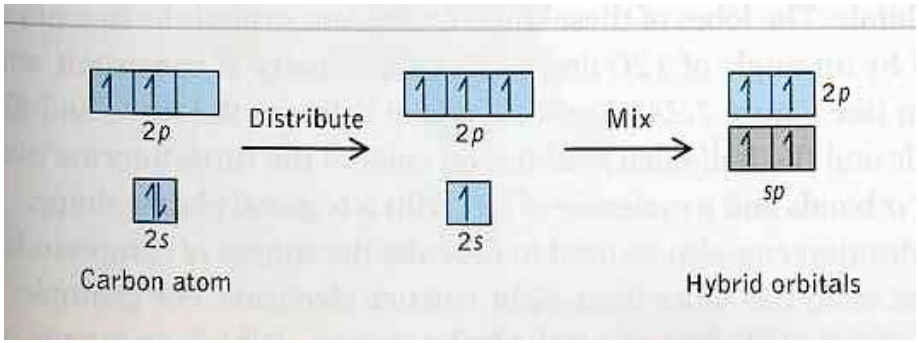


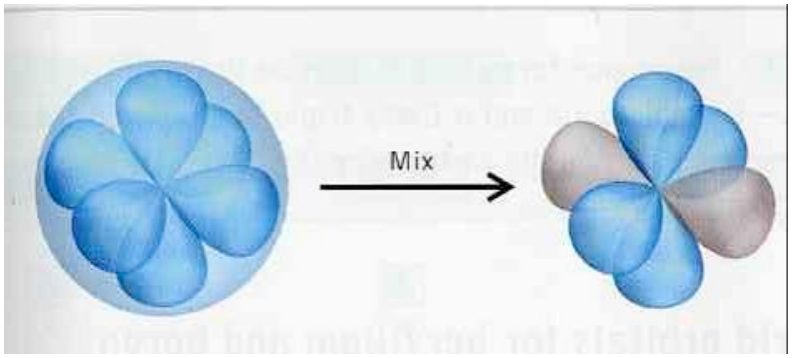


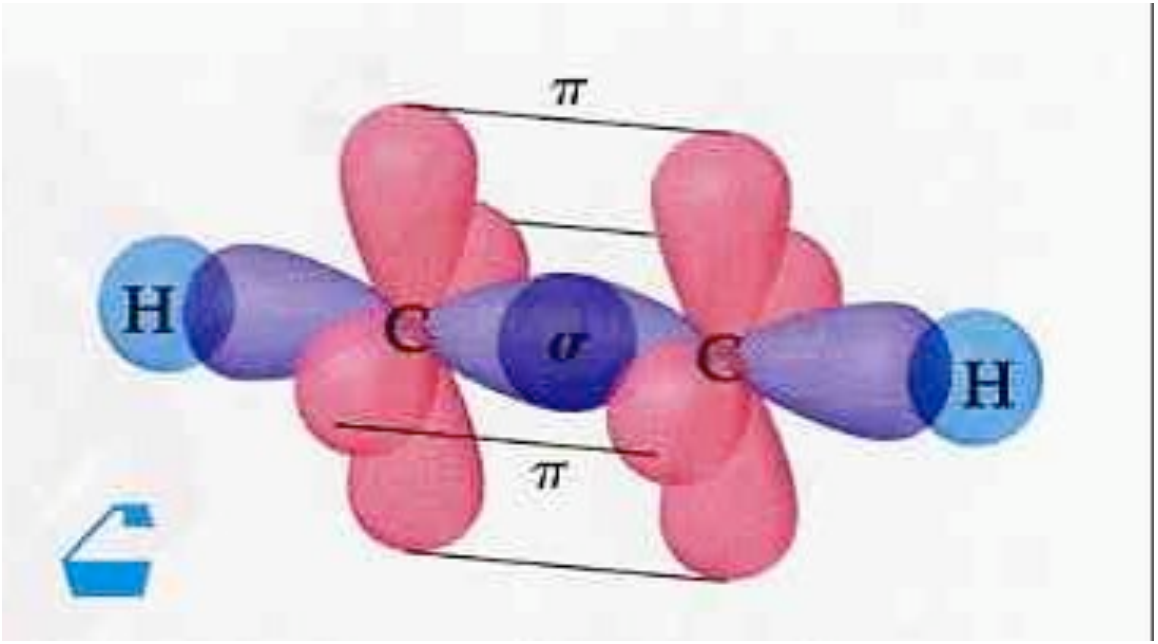


Ground state > excite one electron > mix orbitals:

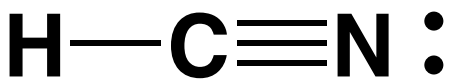
one s orbital and one p orbital = two sp orbitals

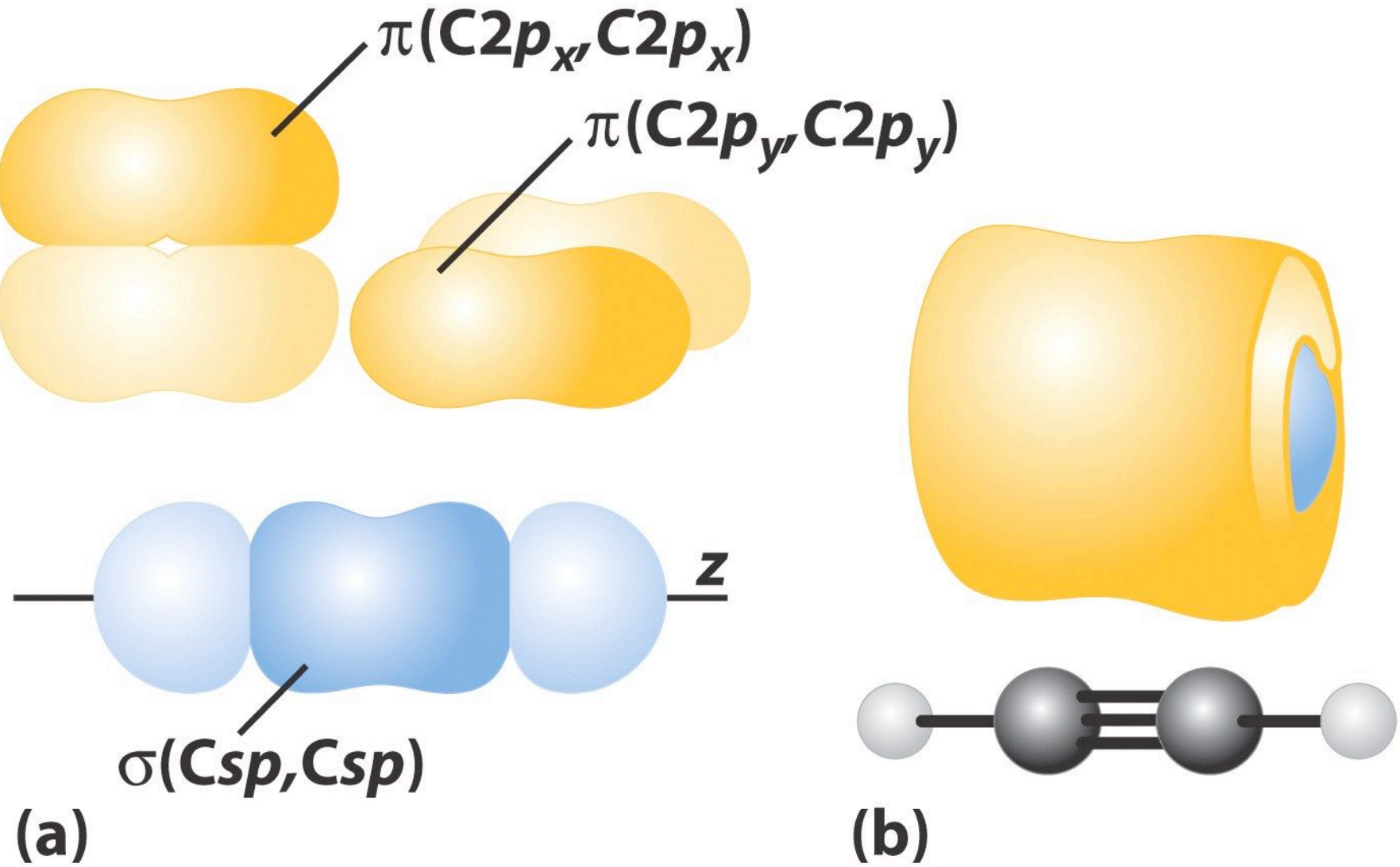






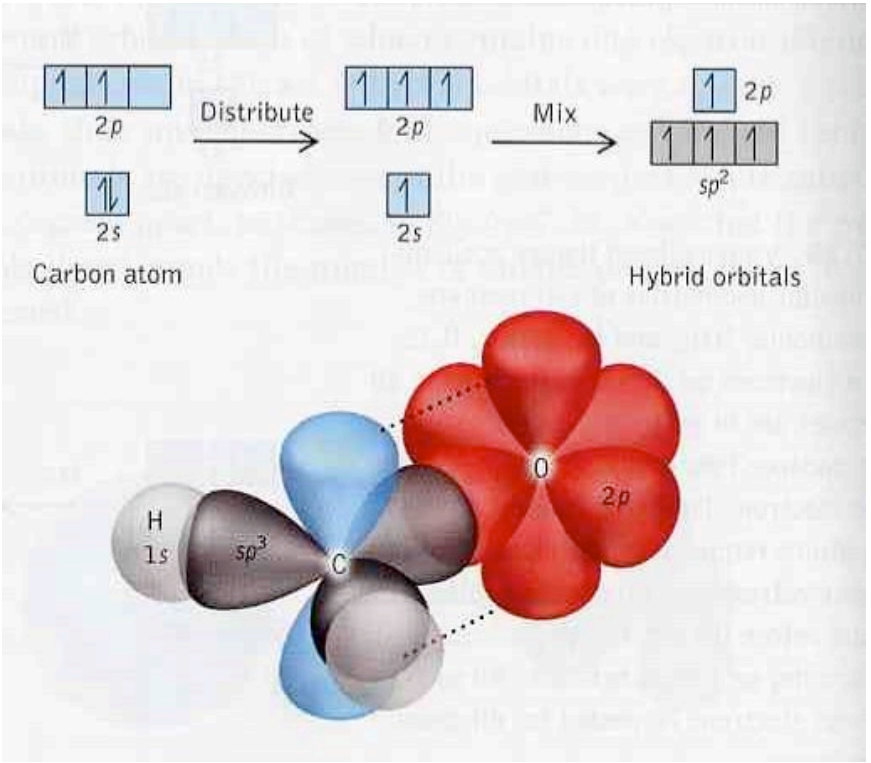
Acetylene



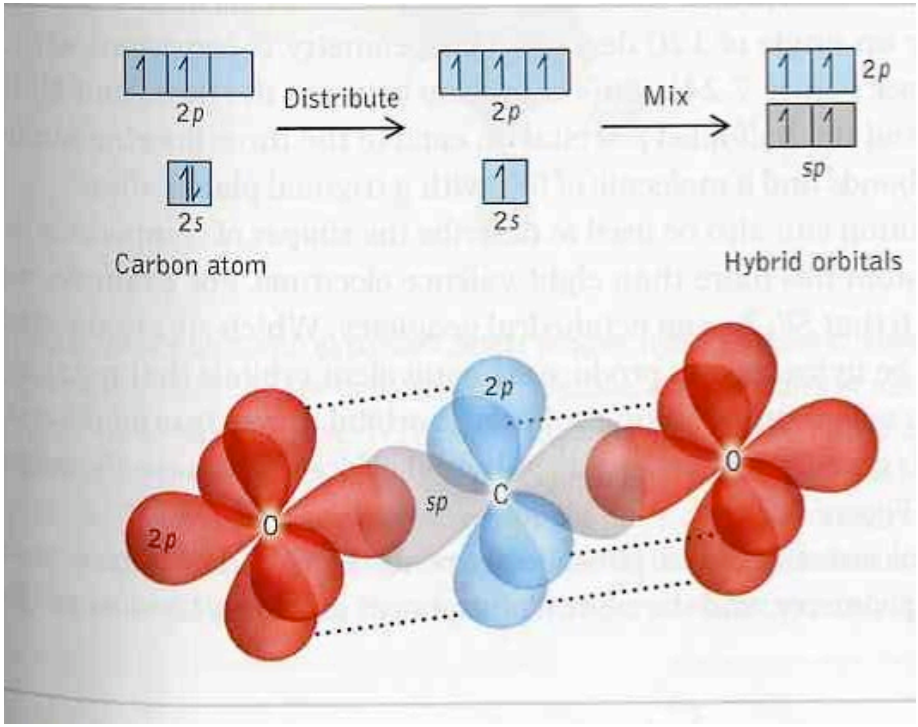

π(C2p$_x$,C2p$_x$)
π(C2p$_y$,C2p$_y$)
z
σ(Csp,Csp)
(a)
(b)

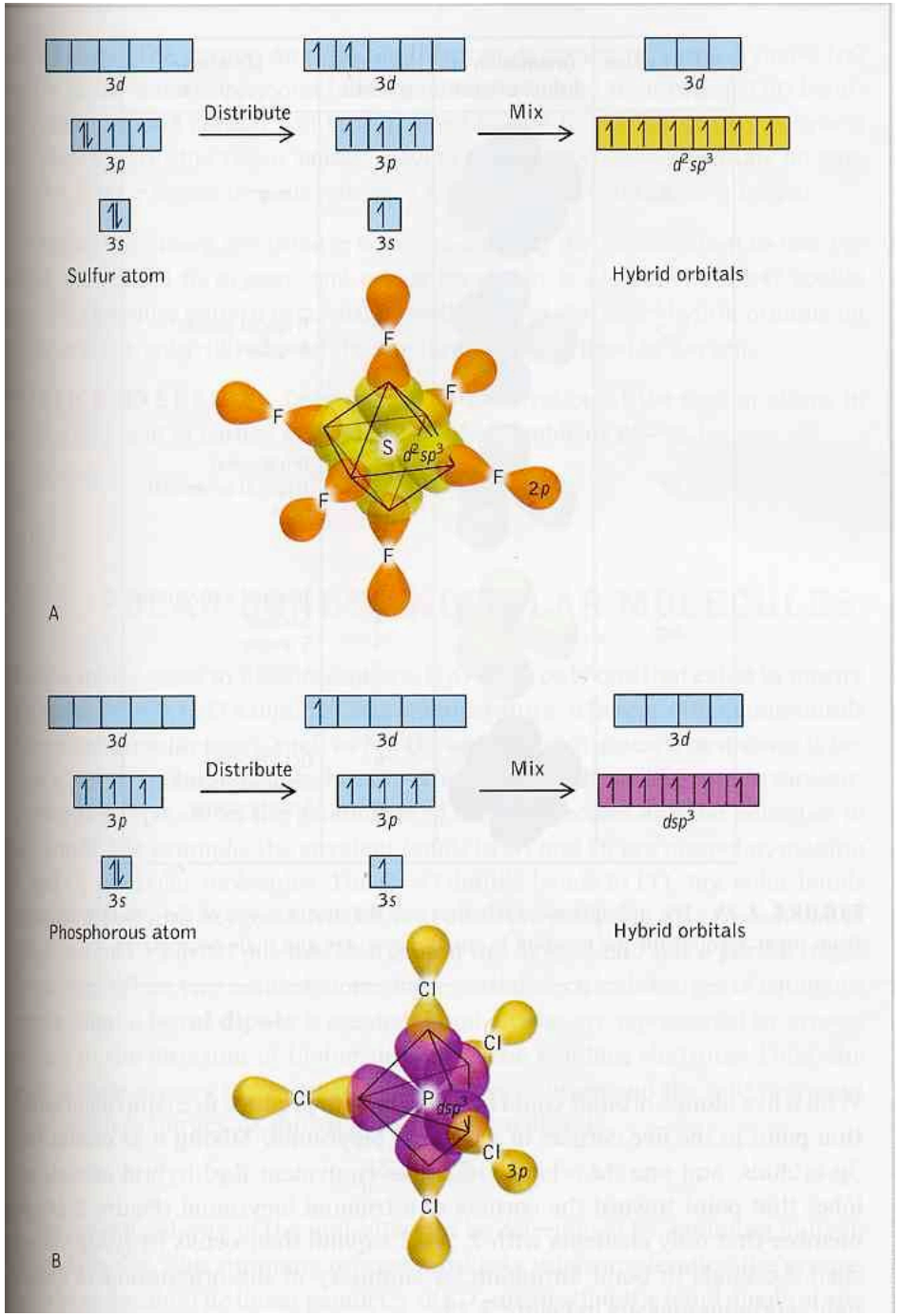
Other examples of sp^2 and sp hybridized carbon

Formaldehyde: $H_2C{=}O$



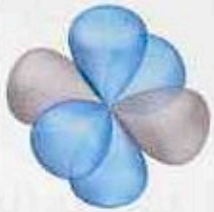
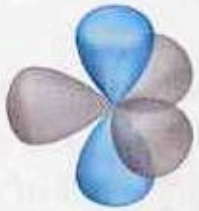
Carbon dioxide: $O{=}C{=}O$





d^2sp^3 hybridization

dsp^3 hybridization

Hybridization	Orientation of hybrid orbitals	Number of σ bonds	Molecular geometrics
sp		2	Linear
sp^2		3 2	Trigonal planar Angular
sp^3		4 3 2	Tetrahedral Trigonal pyramidal Bent
dsp^3		5 4 3 2	Trigonal bipyramidal Seesaw T shape Linear
d^2sp^3		6 5 4	Octahedral Square pyramidal Square planar

SN = 2

SN = 3

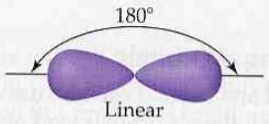
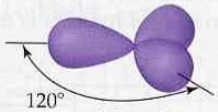
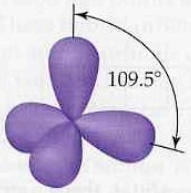
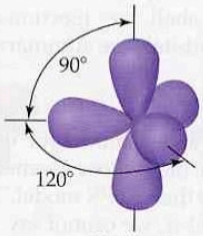
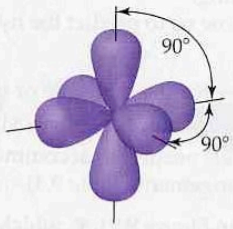
SN = 4

SN = 5

SN = 6

Hybrid orbitals are constructed on an atom to reproduce the electronic arrangement characteristics that will yield the experimental shape of a molecule

TABLE 9.4 Geometric Arrangements Characteristic of Hybrid Orbital Sets

Atomic Orbital Set	Hybrid Orbital Set	Geometry	Examples
s,p	Two *sp*	 Linear	BeF_2, $HgCl_2$
s,p,p	Three sp^2	 Trigonal planar	BF_3, SO_3
s,p,p,p	Four sp^3	 Tetrahedral	CH_4, NH_3, H_2O, N
s,p,p,p,d	Five sp^3d	 Trigonal bipyramidal	PF_5, SF_4, BrF_3
s,p,p,p,d,d	Six sp^3d^2	 Octahedral	SF_6, ClF_5, XeF_4, $PF_$

BeF_2: SN = 2 = sp

BF_3: SN = 3 = sp^2

CH_4: SN = 4 = sp^3

PF_5: SN = 5 = sp^3d

SF_6: SN = 6 = sp^3d^2

Describe the bonding for ethane, ethene and acetylene in terms of overlap of hybridized orbitals

Ethane:

Ethylene:

Acetylene: