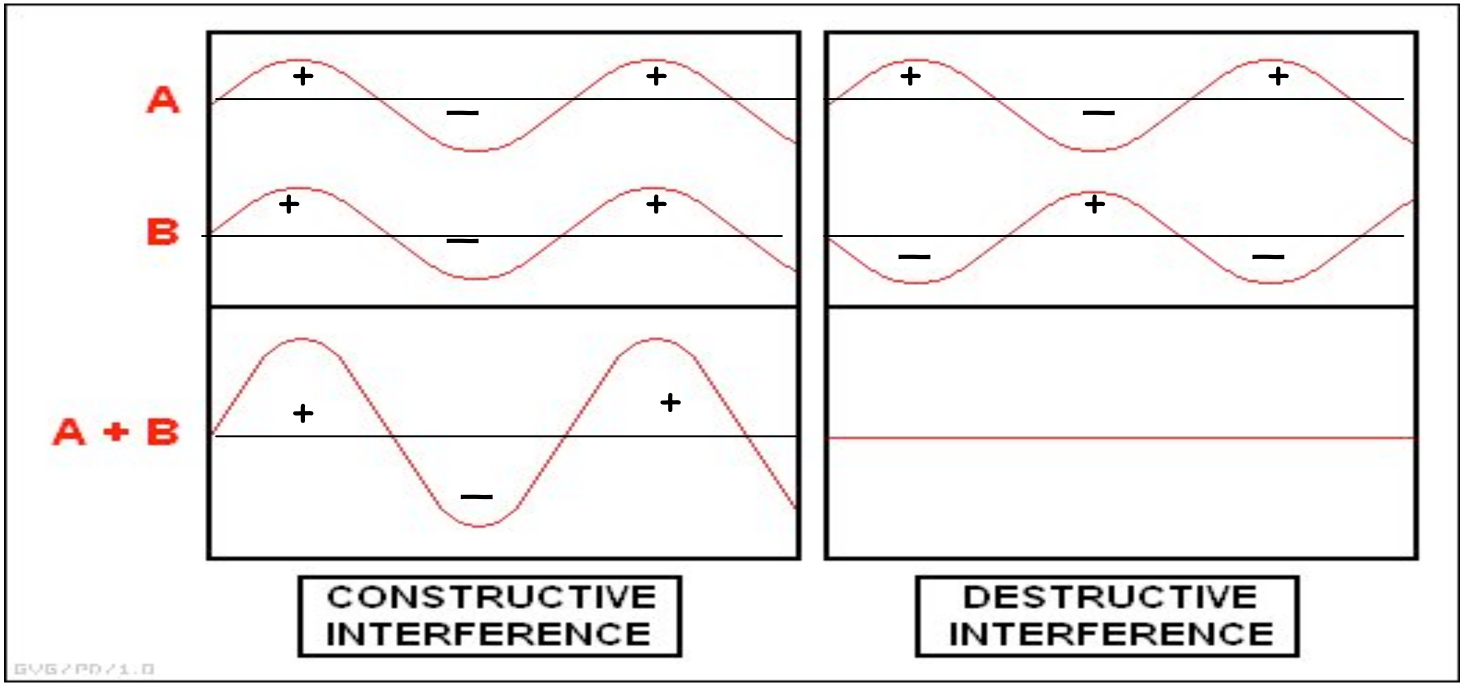
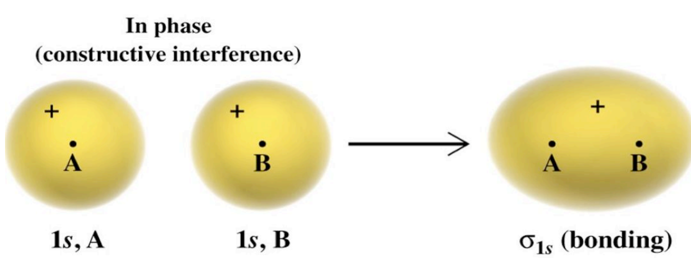
Lecture 16 C1403 October 31, 2005

18.1 Molecular orbital theory: molecular orbitals and diatomic molecules

18.2 Valence bond theory: hybridized orbitals and polyatomic molecules. From steric number to hybridization of atoms

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





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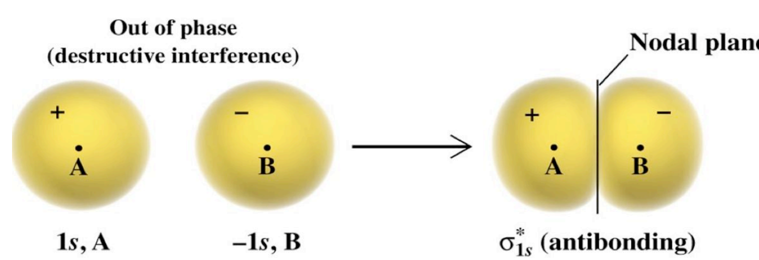


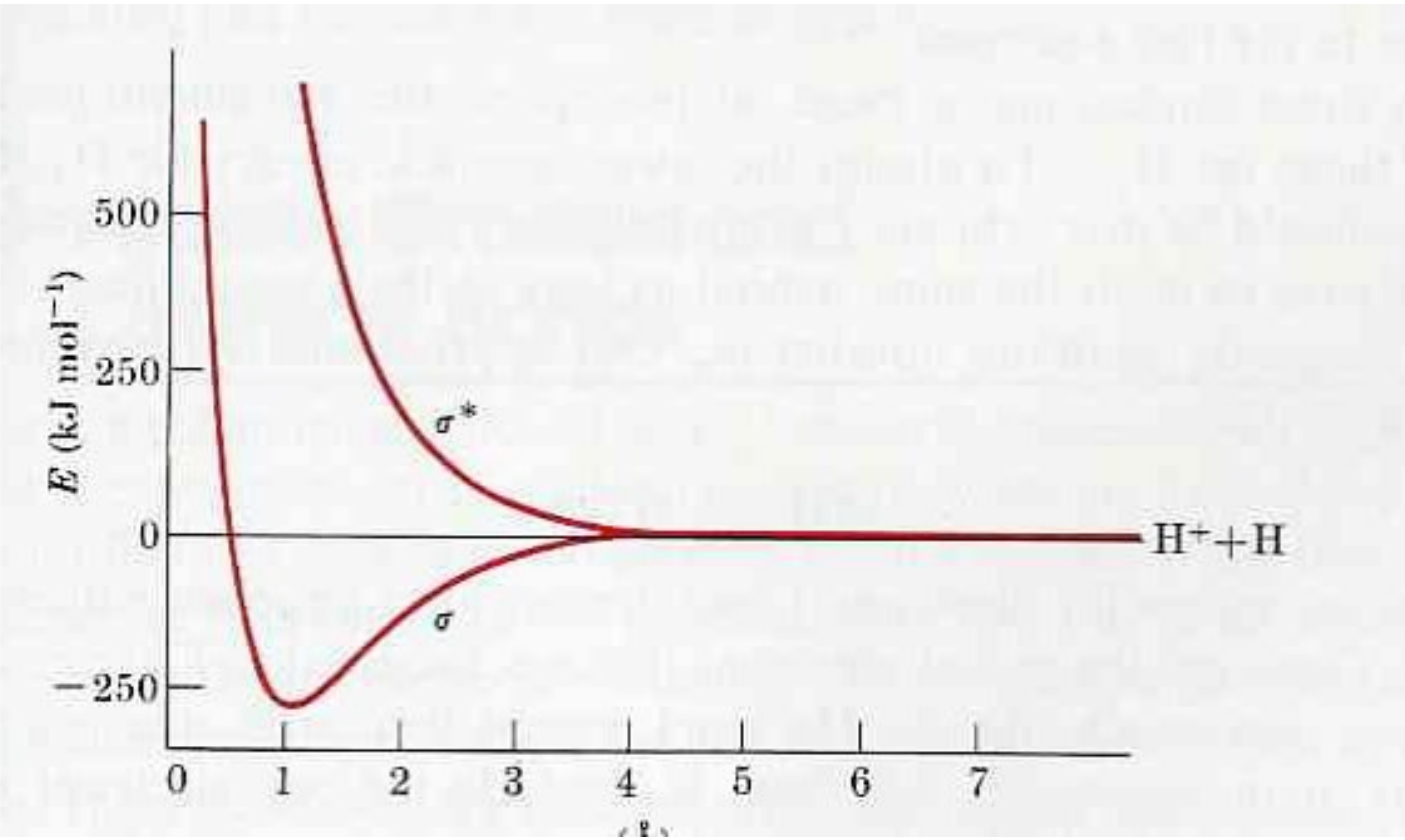
(b)

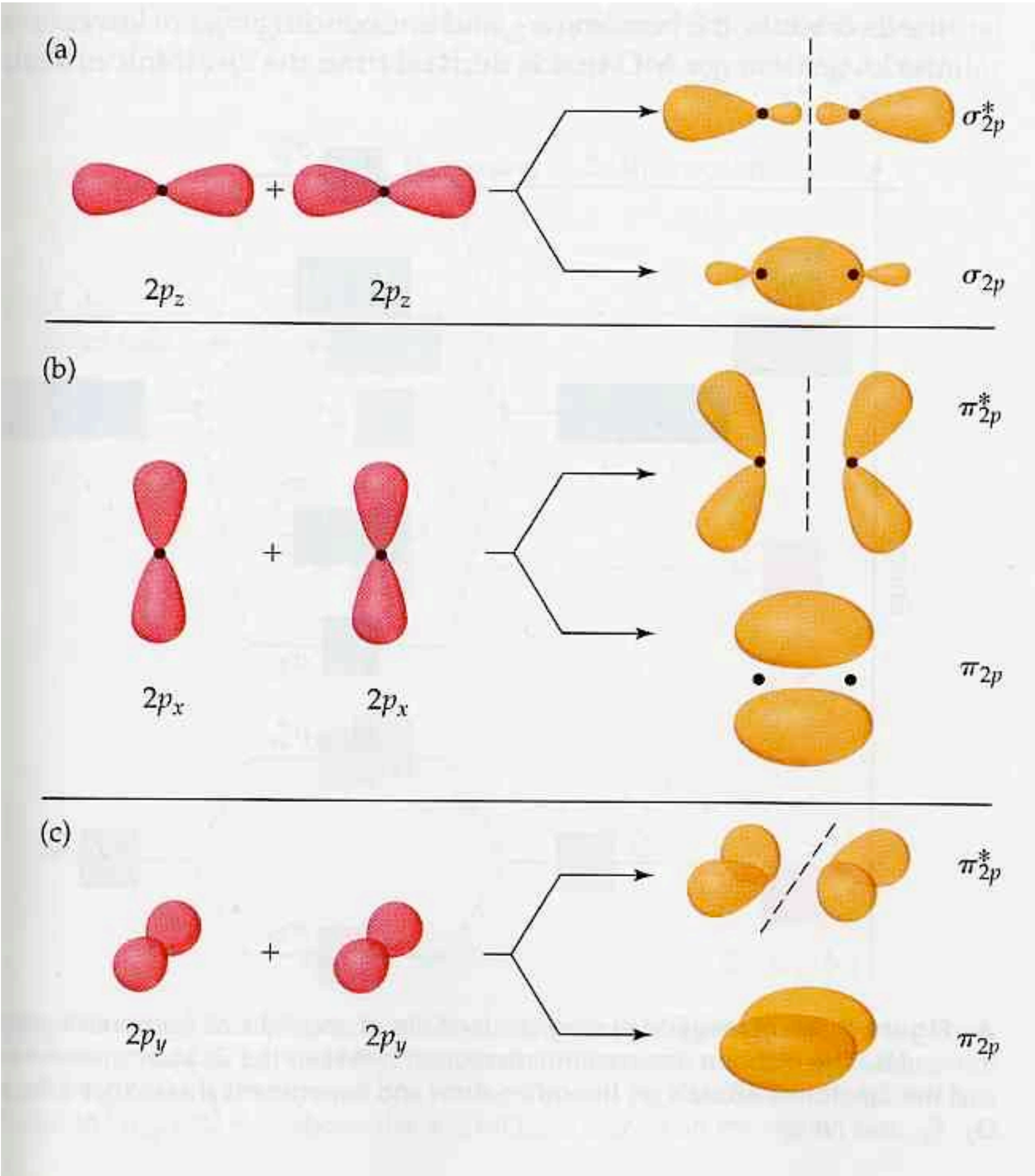
Atomic orbitals

Molecular 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

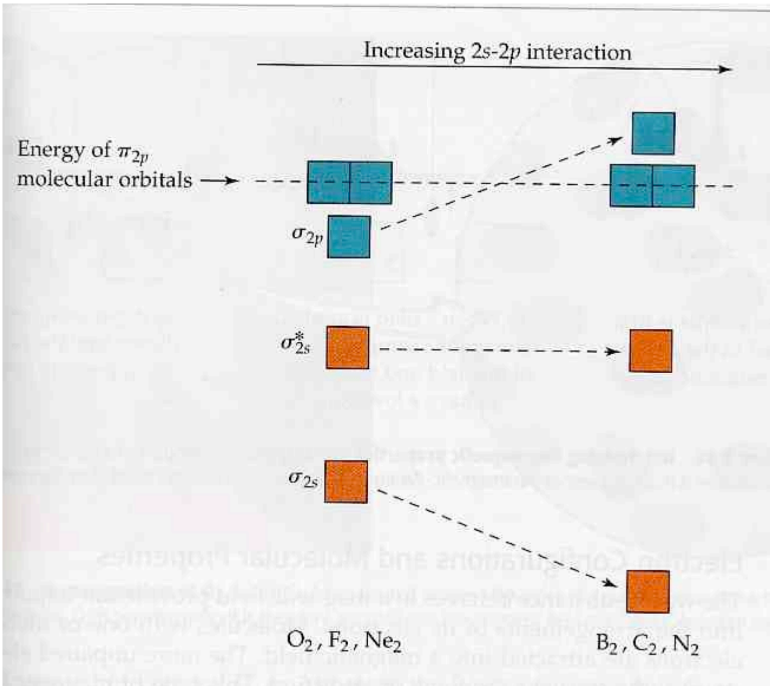




Making of a σ_z and σ_z* orbital from overlap of two $2p_z$ orbitals

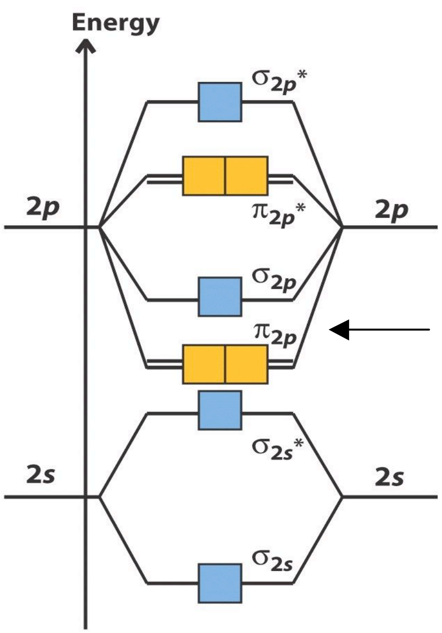
Making of a π_x and π_x* orbital from overlap of two $2p_x$ orbitals

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

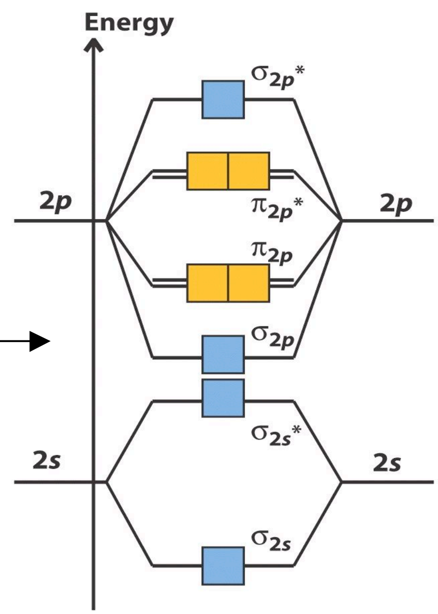


The reason for the "switch" in the s and p MOs

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



Switch



Bond order: connection to bond energy and bond length

Bond enthalpy = bond energy = energy required to break the bonds between two atoms

Bond length = distance between two nuclei in a bond

TABLE 18–1 Configurations and Bond Orders for First-Row Homonuclear Diatomic Molecules

Species	Electron Configuration	Bond Order	Bond Enthalpy (kJ mol^{-1})	Bond Length (Å)
H_2^+	$(\sigma_{1s})^1$	$\frac{1}{2}$	255	1.06
H_2	$(\sigma_{1s})^2$	1	431	0.74
He_2^+	$(\sigma_{1s})^2(\sigma_{1s}^*)^1$	$\frac{1}{2}$	251	1.08
He_2	$(\sigma_{1s})^2(\sigma_{1s}^*)^2$	0	Not observed	

Some examples of configurations, bond lengths, bond strength and bond order

O_2 = $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^2$

O_2^+ = $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^1$

O_2^{1-} = $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^3$

O_2^{2-} = $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^4$

O_2 Bond length = 1.21Å Bond order = 2

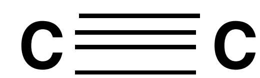
O_2^+ Bond length = 1.12 Å Bond order = 5/2

O_2^- Bond length = 1.26 Å Bond order = 3/2

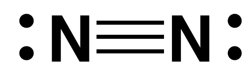
O_2^{2-} Bond length = 1.49 Å Bond order = 1

Compare the Lewis and MO structures of diatomic molecules

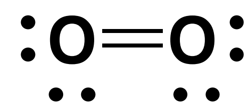
C_2 $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^0(\pi_{2p}^*)^0(\sigma_{2p}^*)^0$



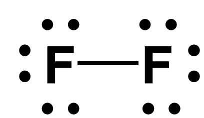
N_2 $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^2(\pi_{2p}^*)^0(\sigma_{2p}^*)^0$



O_2 $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^2(\sigma_{2p}^*)^0$



F_2 $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^4(\sigma_{2p}^*)^0$



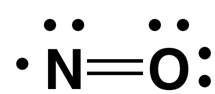
What is the bond order of NO in Lewis terms and MO theory?

Valence electrons = 11

NO: $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^1(\sigma_{2p}^*)^0$

BO = 1/2(8 - 3) = 5/2

Lewis structure: BO = 2?



Odd electron is in an antibonding orbital

18.2 Polyatomic molecules

Valence bond versus molecular orbital theory

Hybridization of atomic orbitals to form molecular orbitals

From steric numbers to sp, sp^2 and sp^3 hybridized orbitals

Hybridized orbitals and Lewis structures and molecular geometries

Double bonds and triple bonds

Hybridization is a theory that starts with geometry of molecules and then decides on the hybridization of the atoms based on steric number of the atoms

Steric number happens to be the same as the number of hybrid orbitals

TABLE 3.2 Hybridization and Molecular Shape*

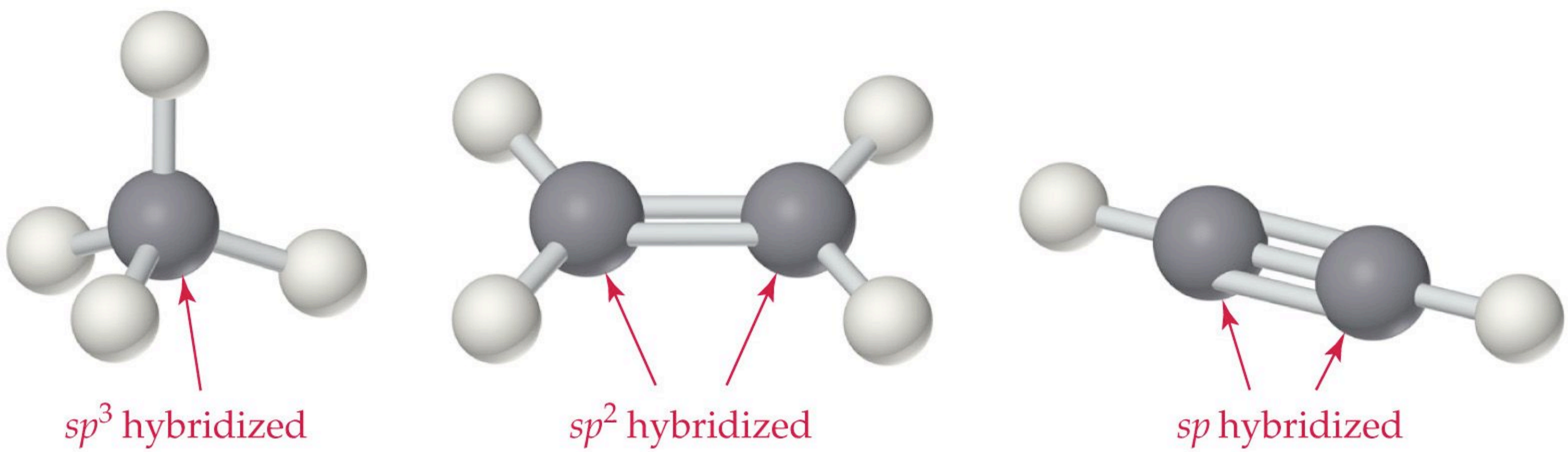
Electron arrangement	Number of atomic orbitals	Hybridization of the central atom	Number of hybrid orbitals
linear	2	sp	2
trigonal planar	3	sp^2	3
tetrahedral	4	sp^3	4
trigonal bipyramidal	5	sp^3d	5
octahedral	6	sp^3d^2	6

*Other combinations of *s*-, *p*-, and *d*-orbitals can give rise to the same or different shapes, but these combinations are the most common.

Hybridization

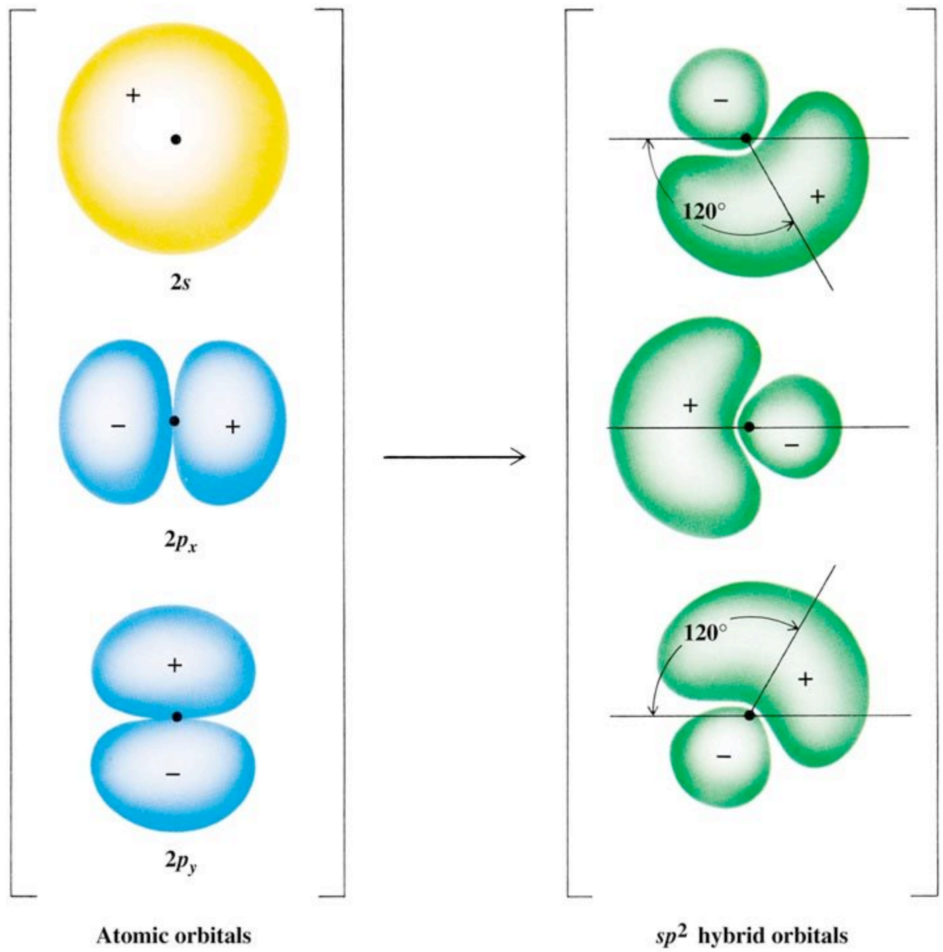
If more than two atoms are involved in a molecule, the shapes of the orbitals must match the shape of the bonds that are needed (trigonal, tetrahedral, etc.). The atomic orbitals do not have these shapes, and must be mixed (hybridized) to achieve the needed shapes

Three exemplar organic molecules



The hybridization of a s orbital and two p orbitals to produce three sp^2 orbitals

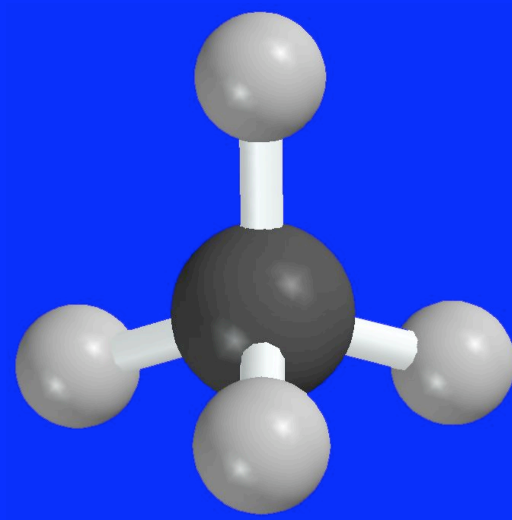
Three Atomic orbitals Aos
2s + two 2p



Three hybrid Orbitals HAOs
sp^2

18.2
Bonding in Methane and Orbital Hybridization

Structure of Methane



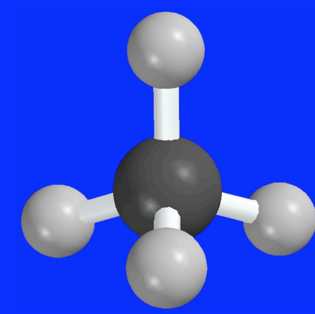
tetrahedral

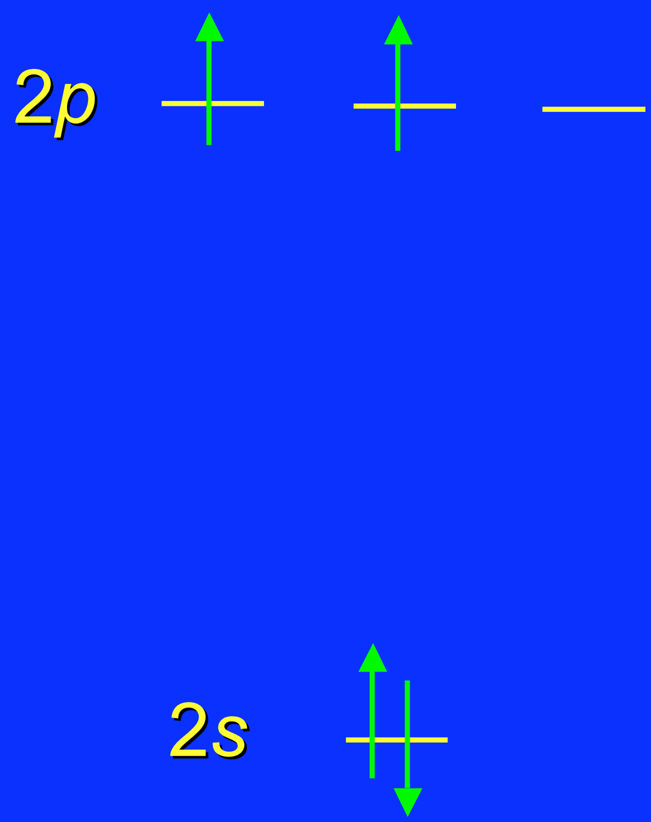
bond angles = 109.5°

bond distances = 110 pm

but structure seems inconsistent with electron configuration of carbon

Electron configuration of carbon



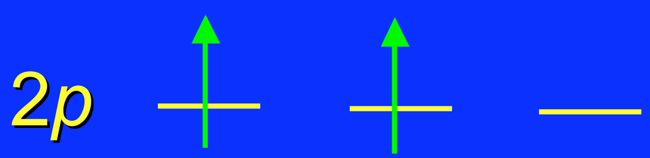


only two unpaired electrons

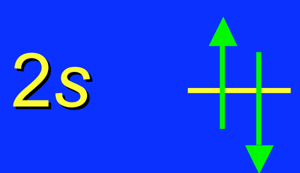
should form σ bonds to only two hydrogen atoms

bonds should be at right angles to one another

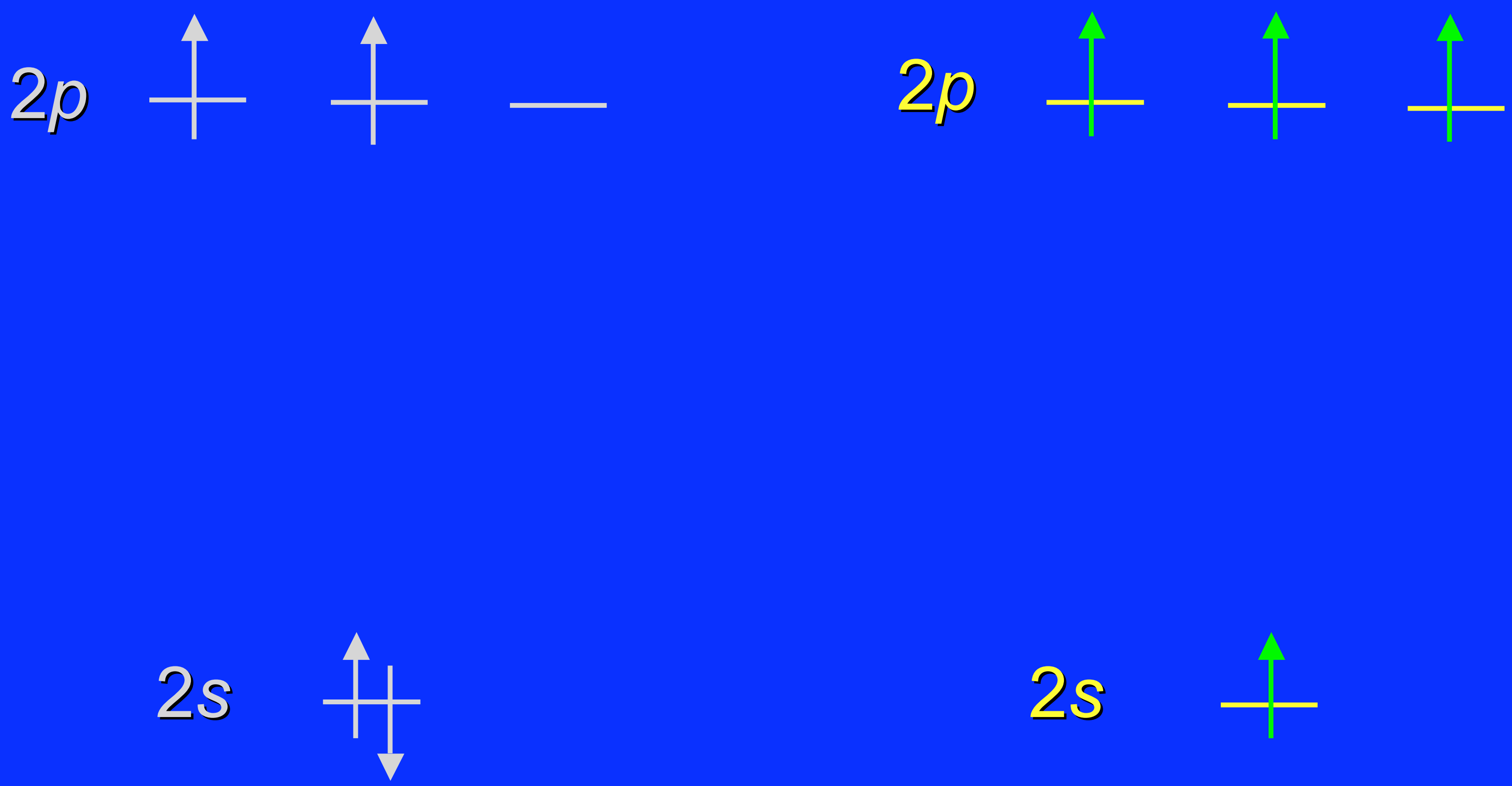
sp^3 Orbital Hybridization



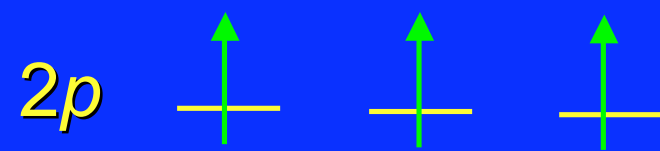
Promote an electron from the 2*s* to the 2*p* orbital



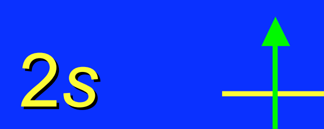
sp^3 Orbital Hybridization



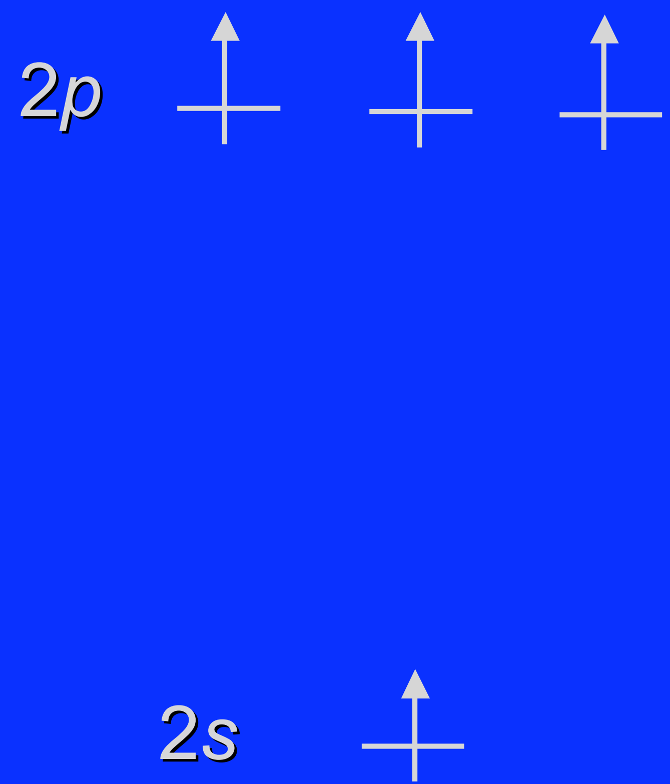
sp^3 Orbital Hybridization

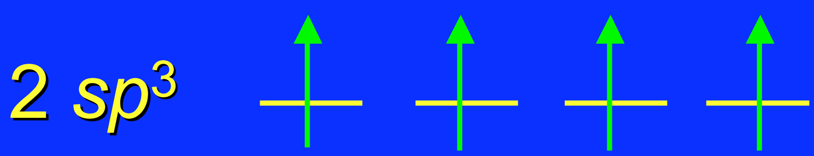


Mix together (hybridize) the 2*s* orbital and the three 2*p* orbitals



sp^3 Orbital Hybridization



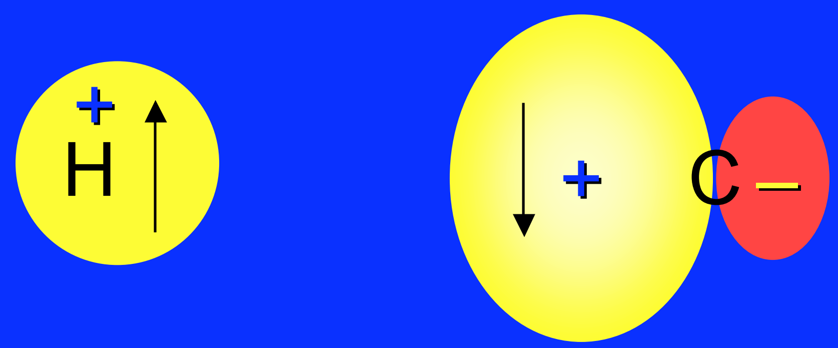


4 equivalent half-filled orbitals are consistent with four bonds and tetrahedral geometry

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:

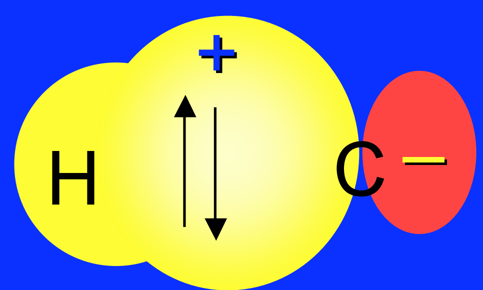
s



sp^3

gives a σ bond.

H—C σ



Justification for Orbital Hybridization

consistent with structure of methane

allows for formation of 4 bonds rather than 2

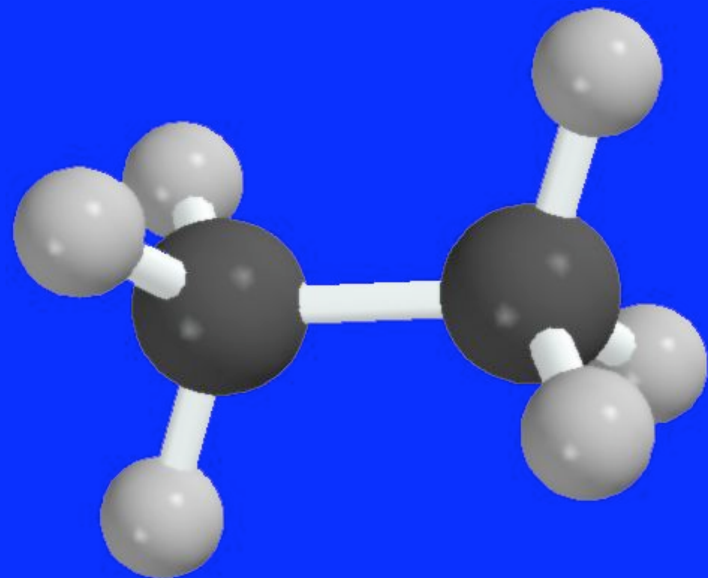
bonds involving sp^3 hybrid orbitals are stronger than those involving *s*-*s* overlap or *p*-*p* overlap

18.2
sp^3 Hybridization and Bonding in Ethane

Structure of Ethane

C_2H_6

CH_3CH_3

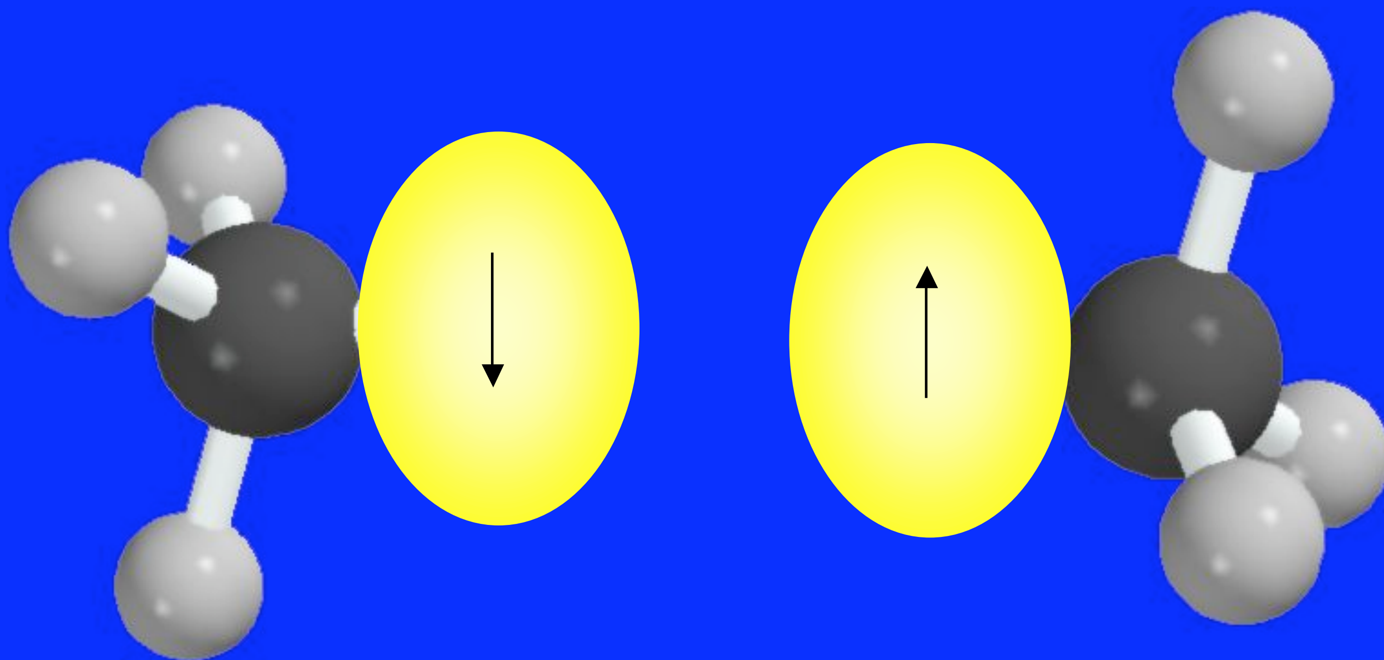


tetrahedral geometry at each carbon

C—H bond distance = 110 pm

C—C bond distance = 153 pm

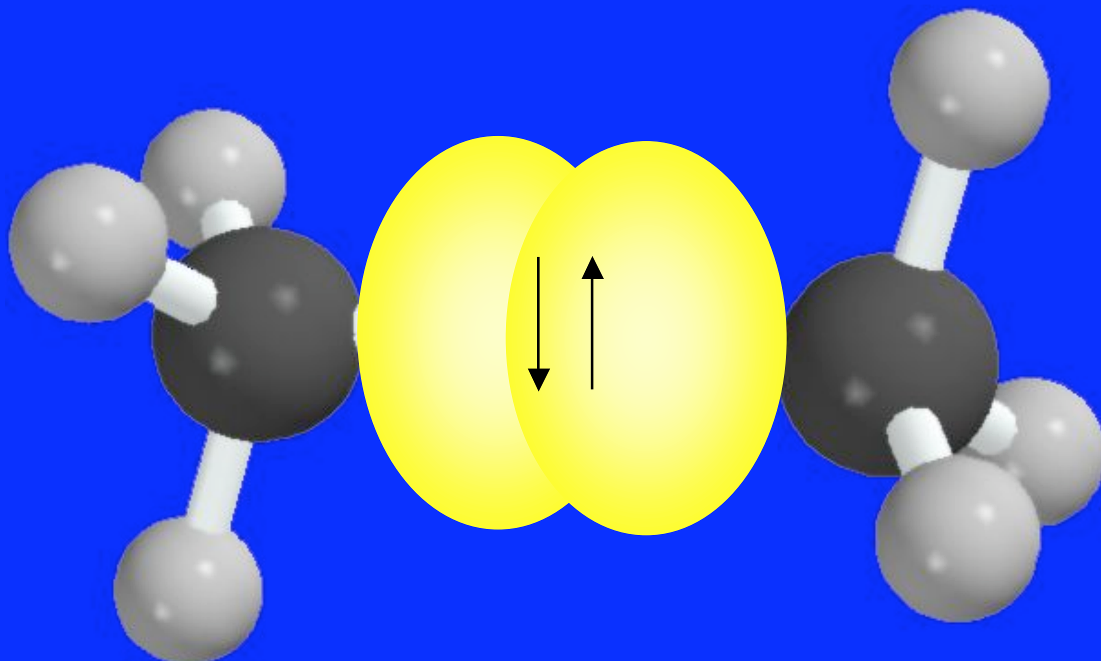
The C—C σ Bond in Ethane



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



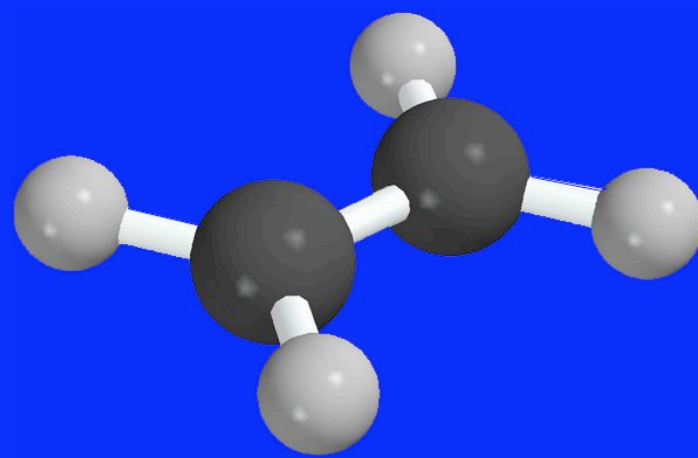
In-phase overlap of half-filled sp^3 hybrid orbital of one carbon with half-filled sp^3 hybrid orbital of another.

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



$H_2C{=}CH_2$

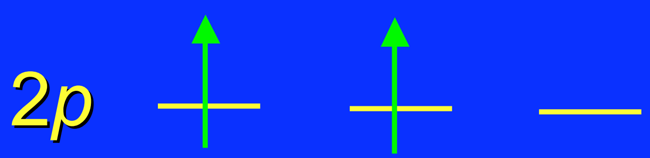
planar

bond angles: close to 120°

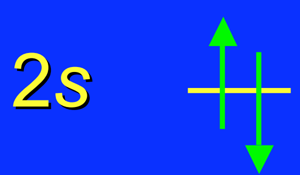
bond distances: C—H = 110 pm

C=C = 134 pm

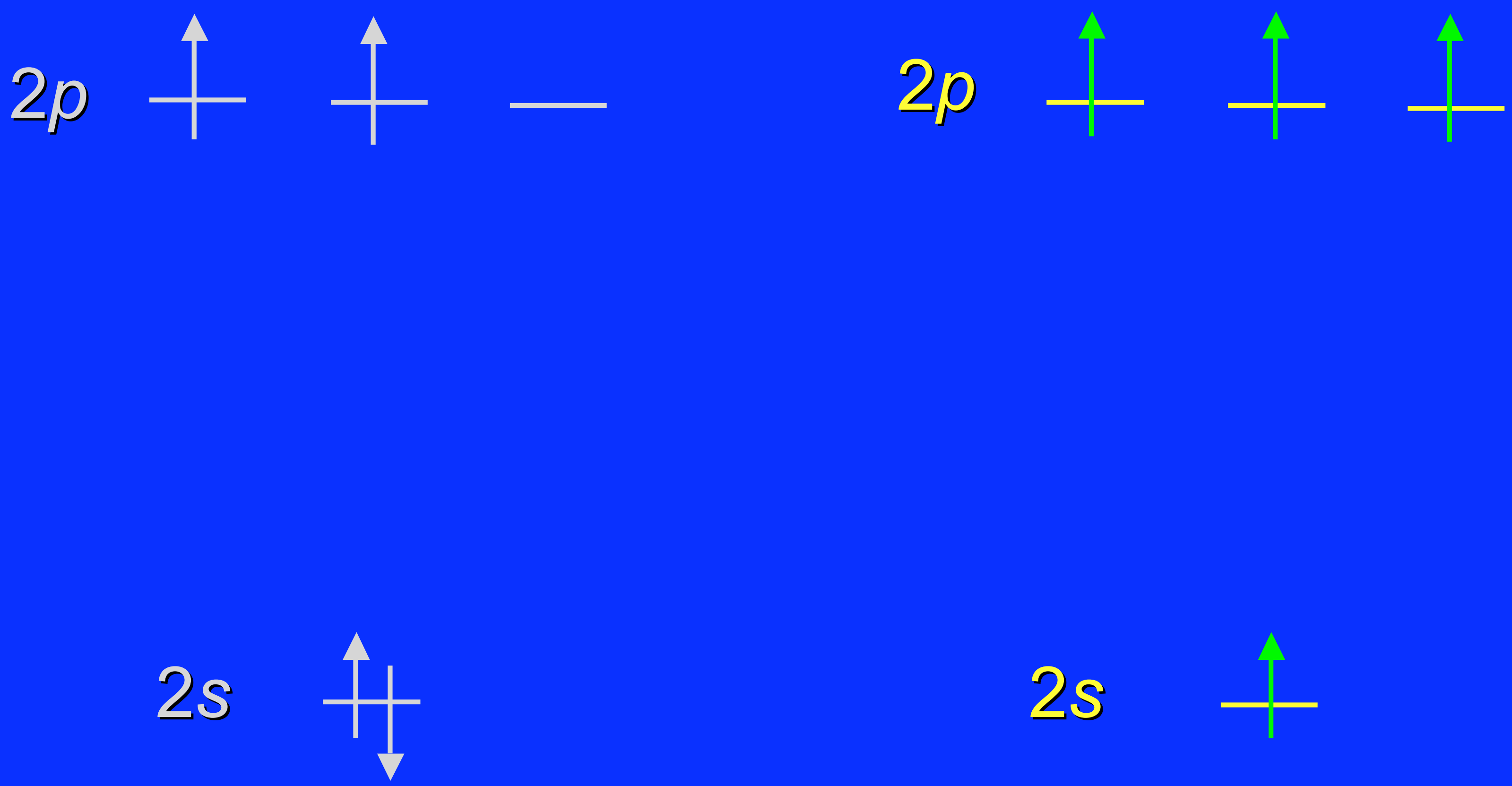
sp^2 Orbital Hybridization



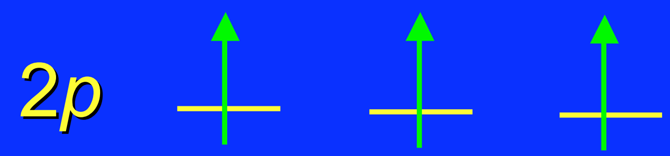
Promote an electron from the 2*s* to the 2*p* orbital



sp^2 Orbital Hybridization

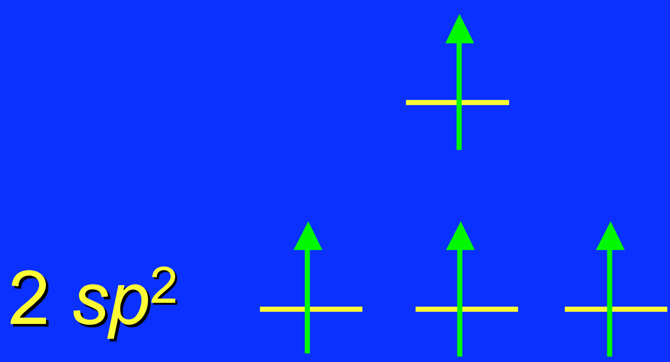


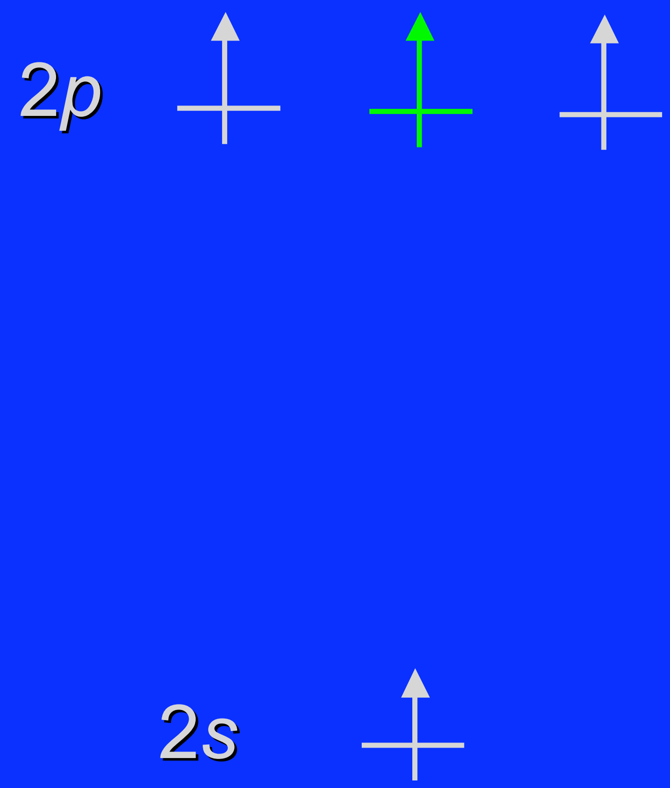
sp^2 Orbital Hybridization



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

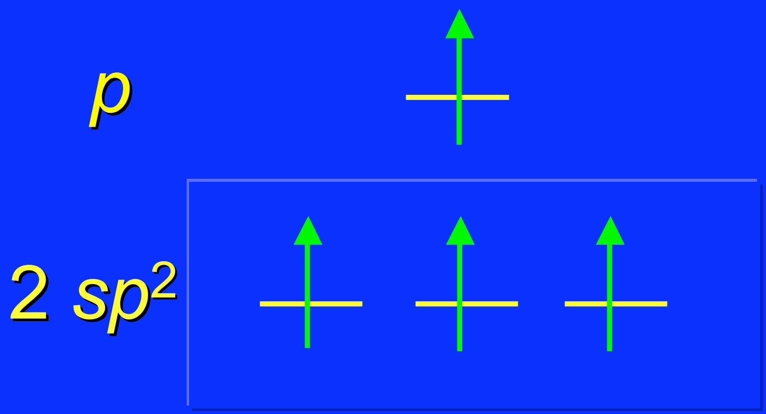
sp^2 Orbital Hybridization





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

sp^2 Orbital Hybridization



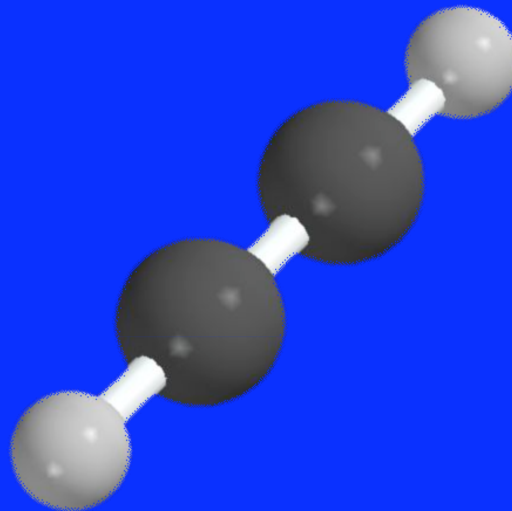
2 of the 3 sp^2 orbitals are involved in σ bonds to hydrogens; the other is involved in a σ bond to carbon

1.18
sp Hybridization and Bonding in Acetylene

Structure of Acetylene

C_2H_2

$HC \equiv CH$



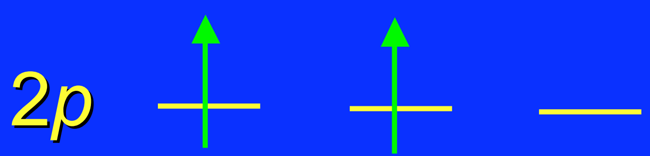
linear

bond angles: 180°

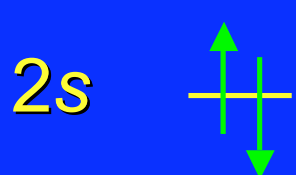
bond distances: C—H = 106 pm

CC = 120 pm

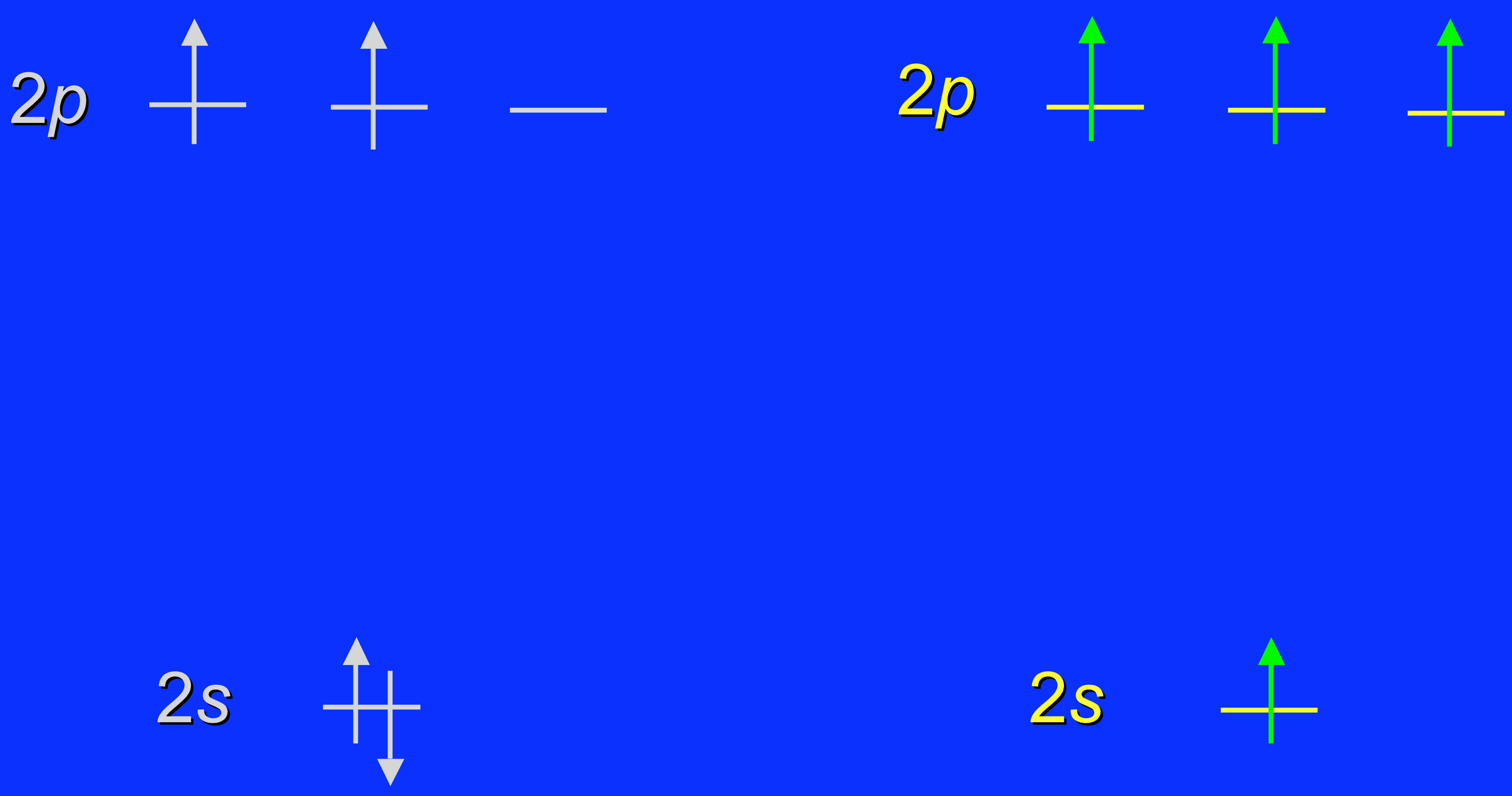
sp Orbital Hybridization



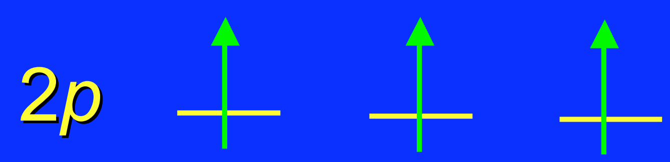
Promote an electron from the 2*s* to the 2*p* orbital



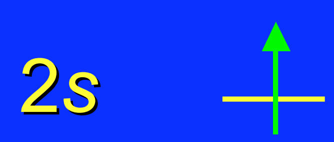
sp Orbital Hybridization



sp Orbital Hybridization



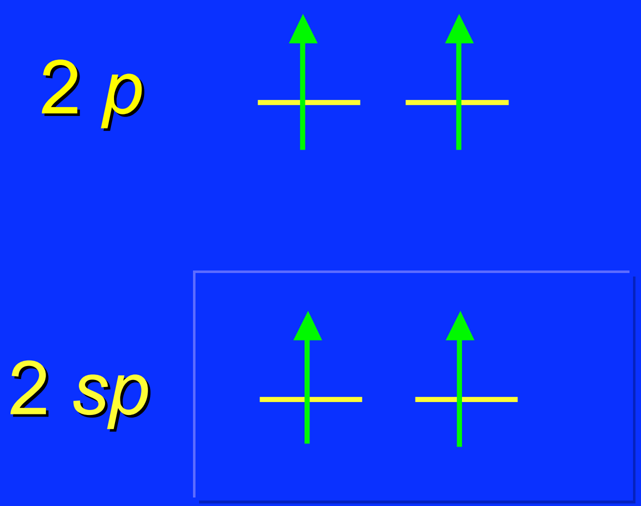
Mix together (hybridize) the 2*s*
orbital and <u>one</u> of the three 2*p* orbitals



sp Orbital Hybridization

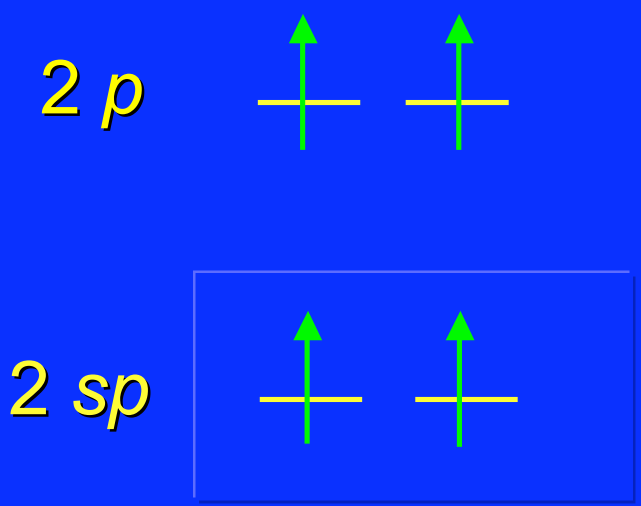
2 equivalent half-filled *sp* hybrid orbitals plus 2 *p* orbitals left unhybridized

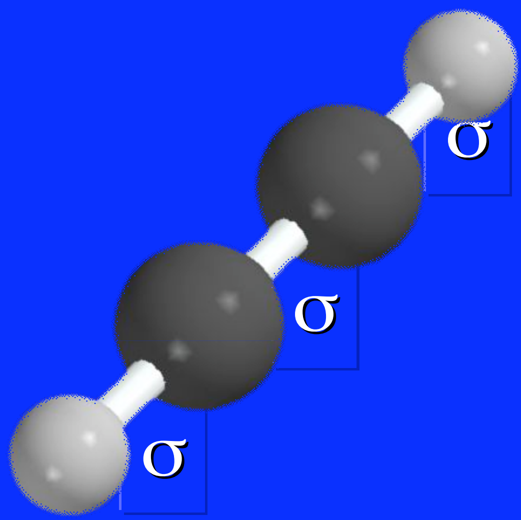
sp Orbital Hybridization



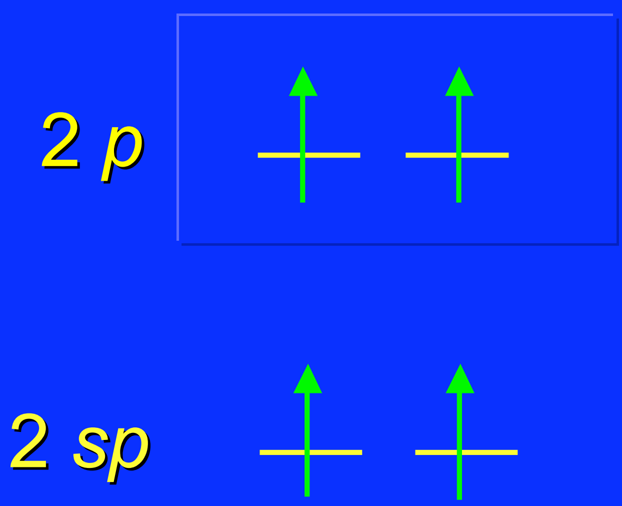
1 of the 2 *sp* orbitals is involved in a σ bond to hydrogen; the other is involved in a σ bond to carbon

sp Orbital Hybridization



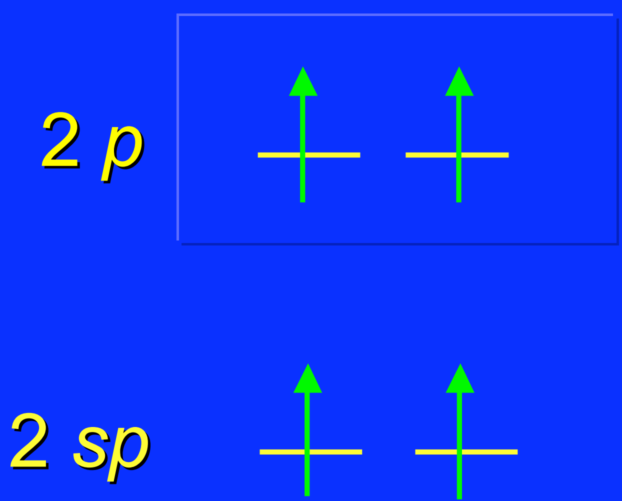


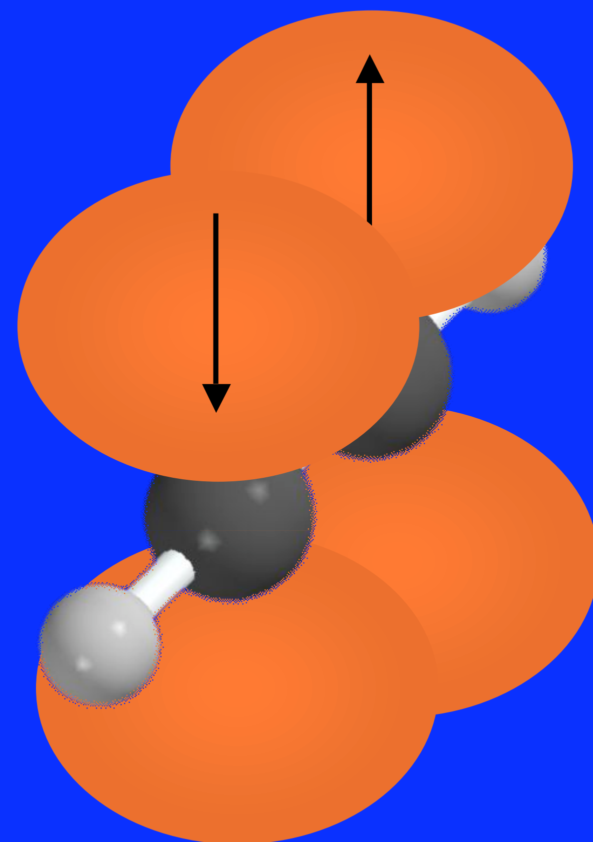
π Bonding in Acetylene



the unhybridized *p* orbitals of carbon are involved in separate π bonds to the other carbon

π Bonding in Acetylene





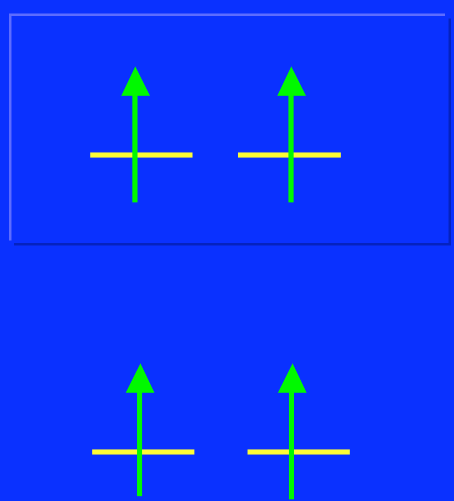
one π bond involves one of the p orbitals on each carbon

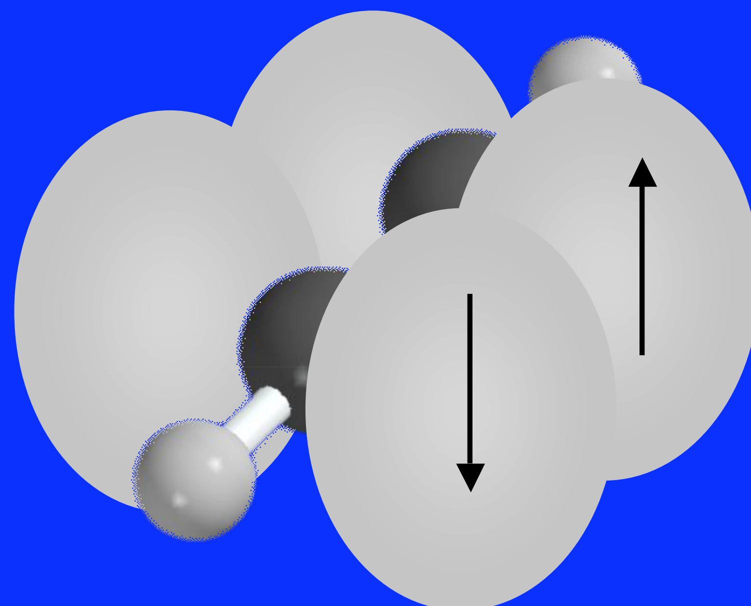
there is a second π bond perpendicular to this one

π Bonding in Acetylene

2 p

2 sp

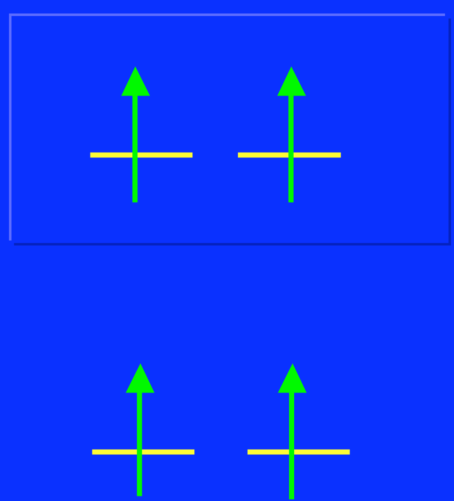


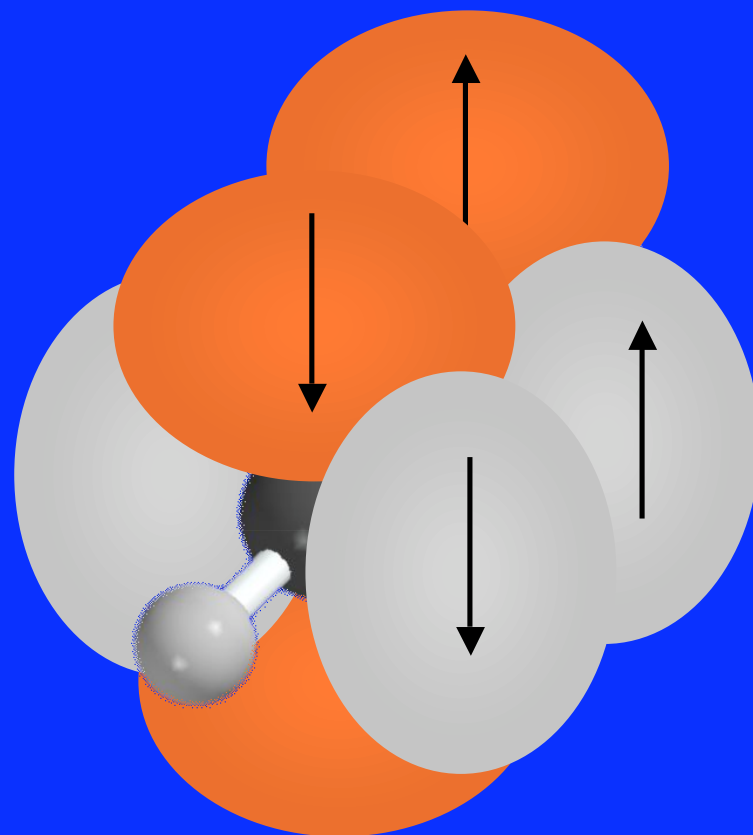


π Bonding in Acetylene

2 p

2 sp





How to determine the hybridization of an atom in a polyatomic molecule

Draw a Lewis structure of the molecule

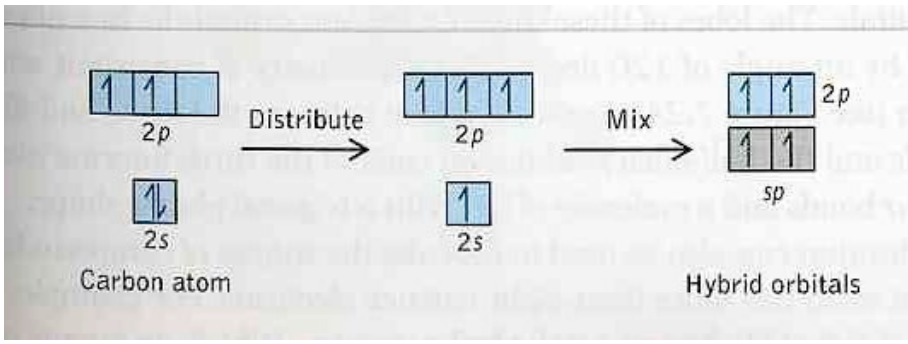
Determine the steric number of the atoms of the molecule

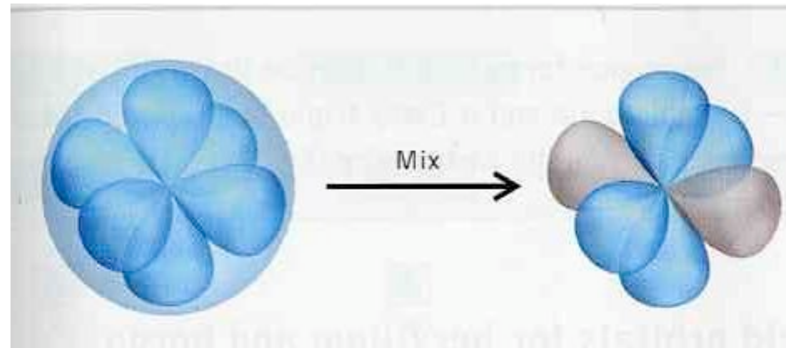
From the steric number assign hybridization as follows:

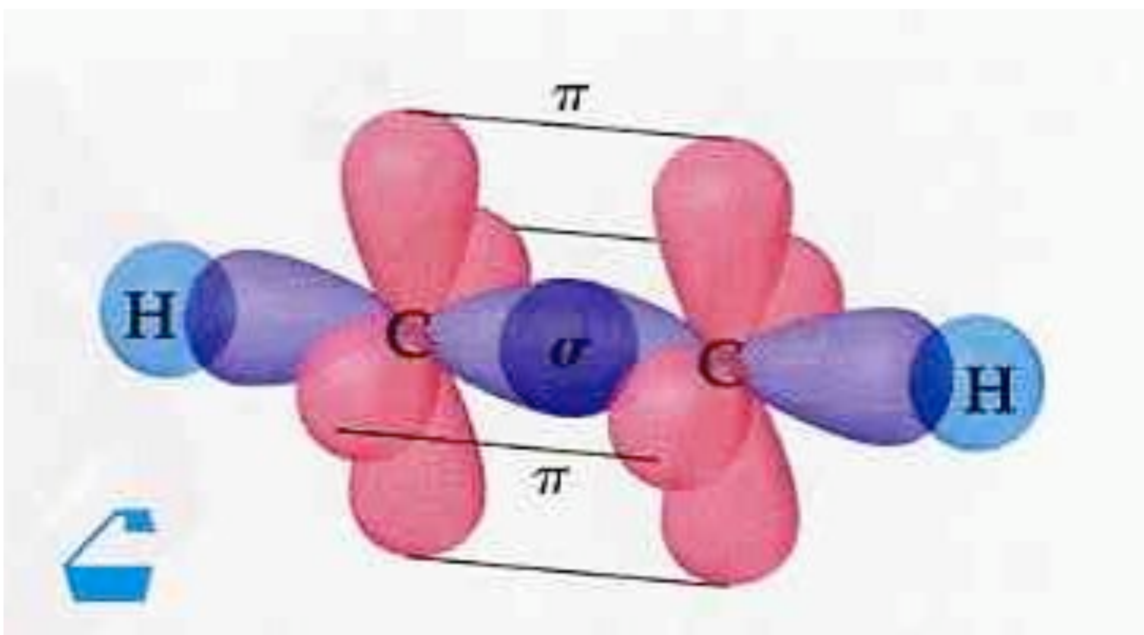
Steric number	Hybridization	Example
2	sp	$HC\equiv CH$
3	sp^2	$H_2C=CH_2$
4	sp^3	H_3C-CH_3

sp hybridization and acetylene: H—C≡C—H

one s orbital and one p orbital = two sp orbitals







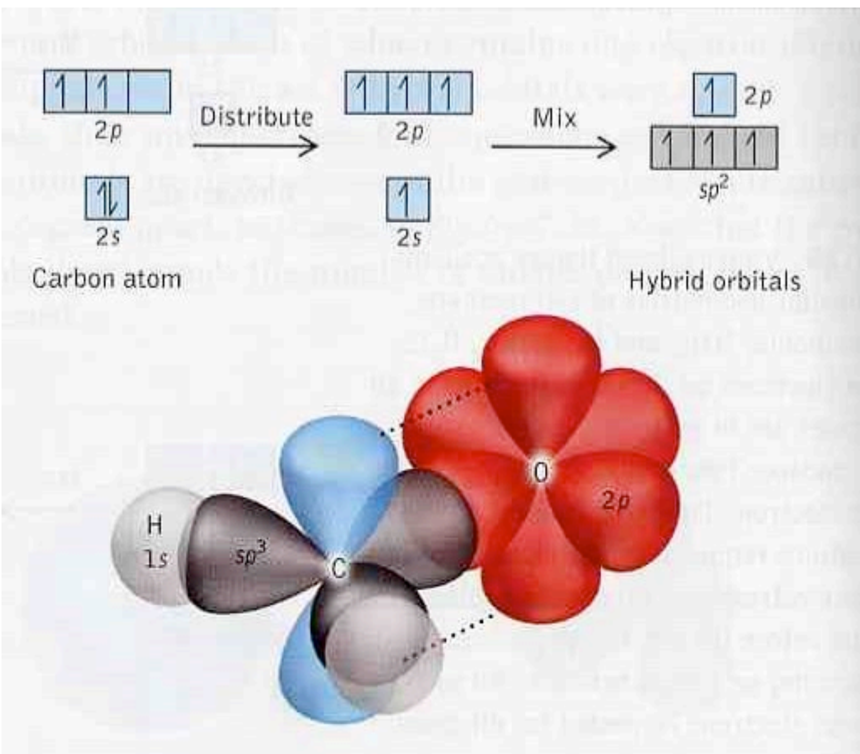
An isoelectroic molecule

H—C≡N :

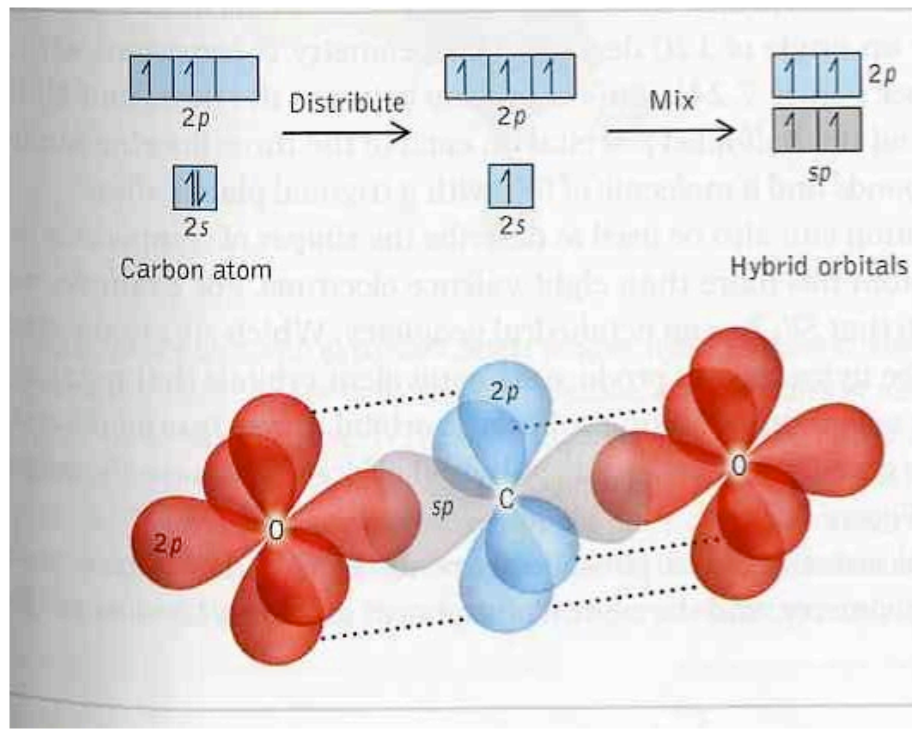
Other examples of sp^2 and sp hybridized carbon

Formaldehyde: $H_2C{=}O$

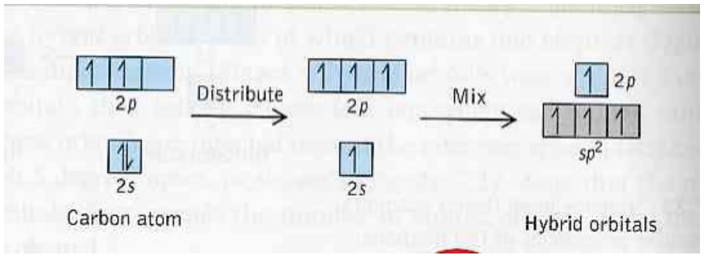
Typo: CH bond in figure below should be labeled sp^2

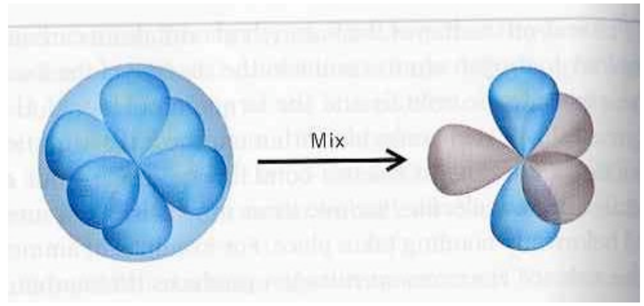


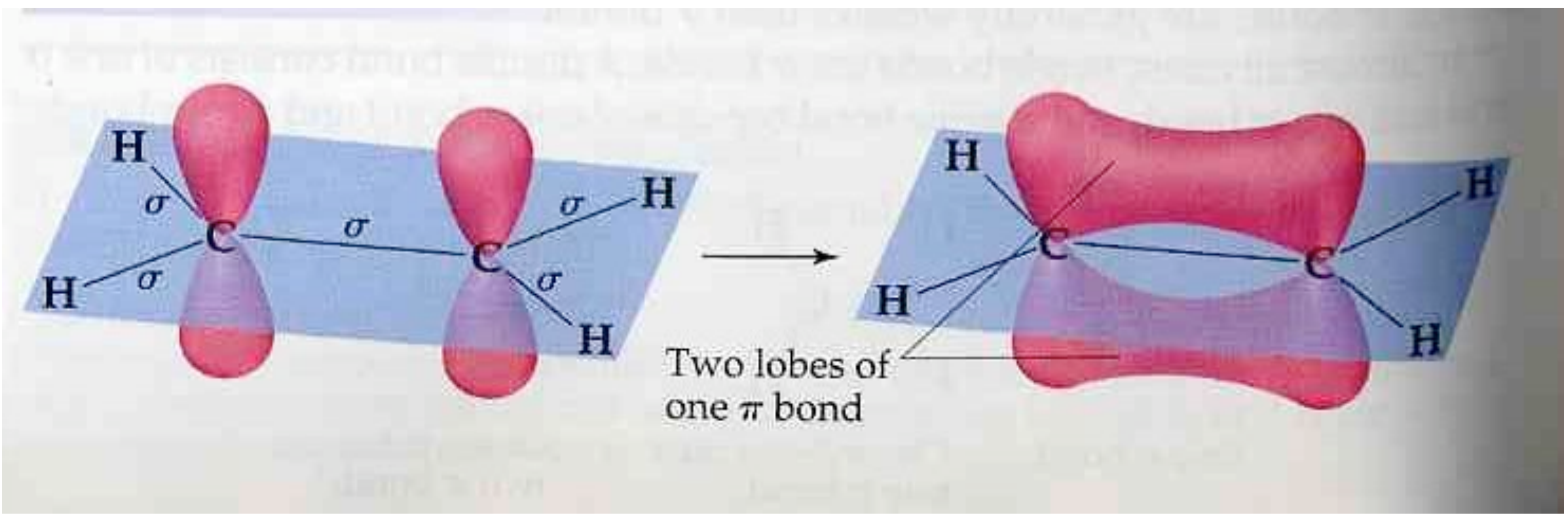
Carbon dioxide: O=C=O



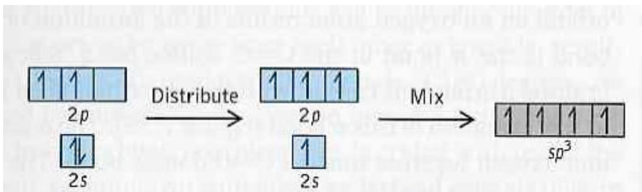
sp^2 hybridization and ethylene: $H_2C{=}CH_2$

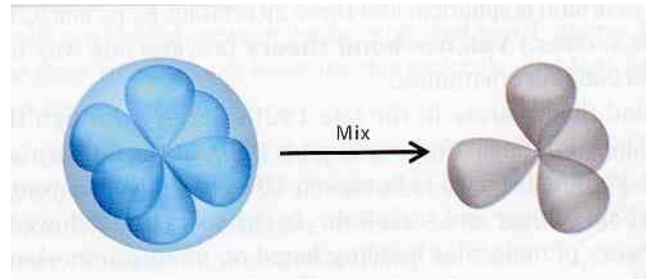


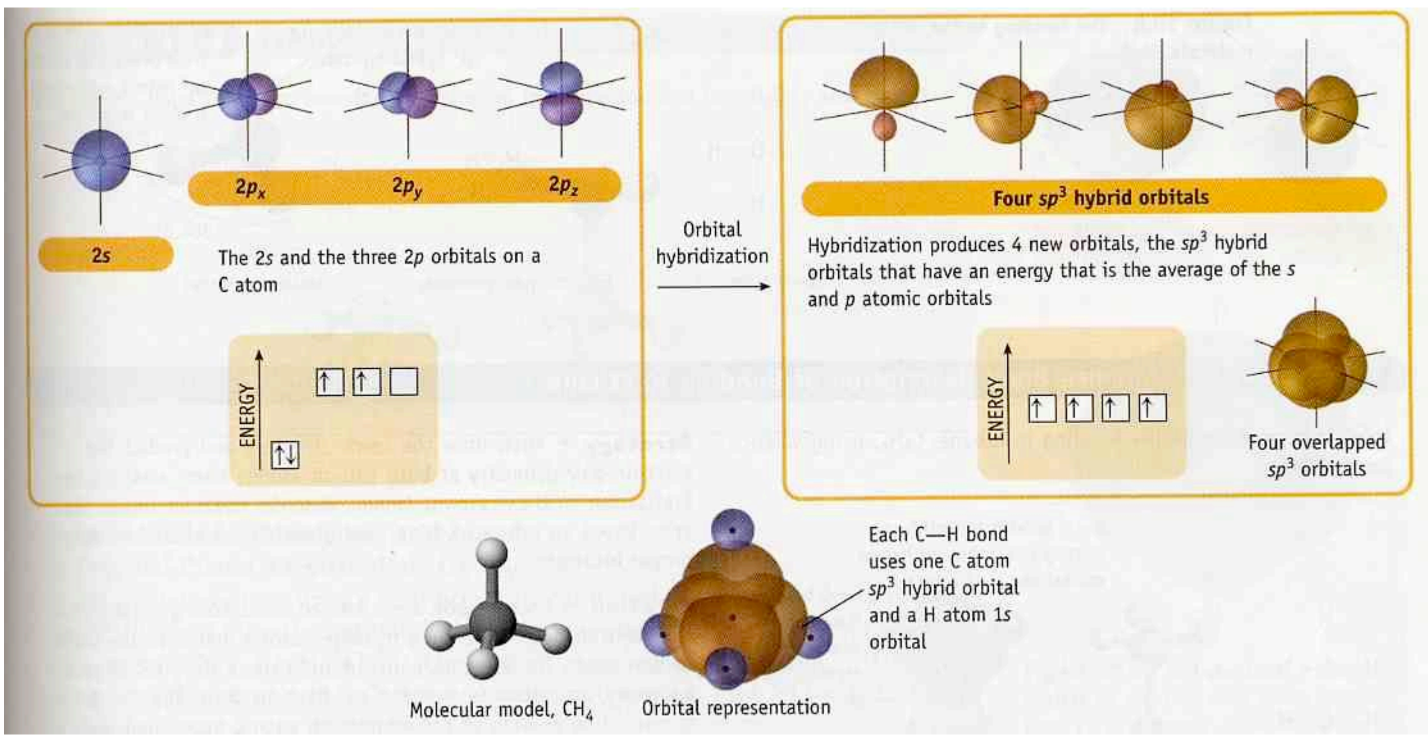


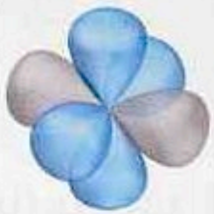
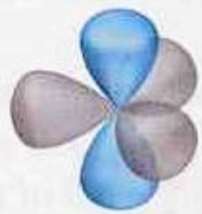


Hybridization and methane: CH_4







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^2*sp*^{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

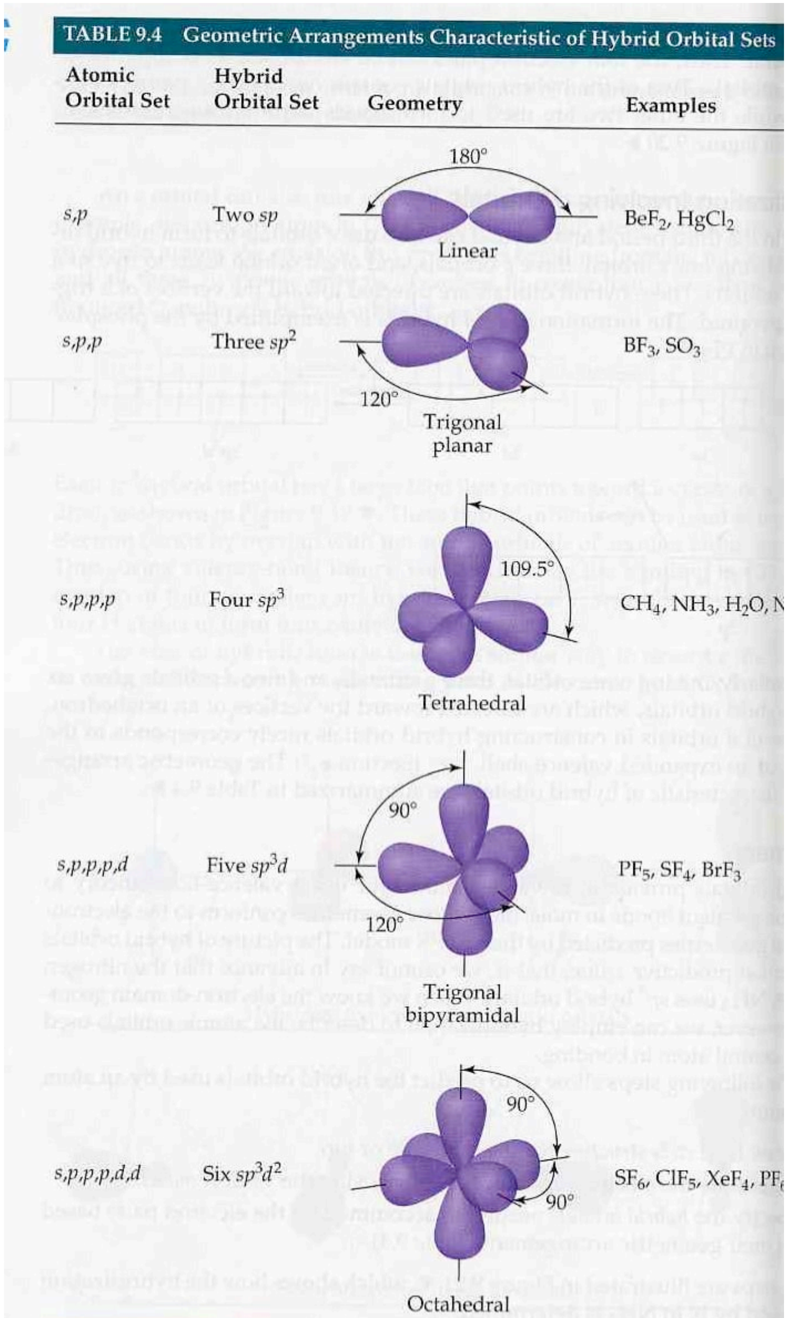


TABLE 9.4 Geometric Arrangements Characteristic of Hybrid Orbital Sets

Atomic Orbital Set	Hybrid Orbital Set	Geometry	Examples
s,p	Two sp	180° Linear	BeF_2, $HgCl_2$
s,p,p	Three sp^2	120° Trigonal planar	BF_3, SO_3
s,p,p,p	Four sp^3	109.5° Tetrahedral	CH_4, NH_3, H_2O, N
s,p,p,p,d	Five sp^3d	90°, 120° Trigonal bipyramidal	PF_5, SF_4, BrF_3
s,p,p,p,d,d	Six sp^3d^2	90°, 90° Octahedral	SF_6, ClF_5, XeF_4, PF

Examples

BeF_2: SN = 2 = sp

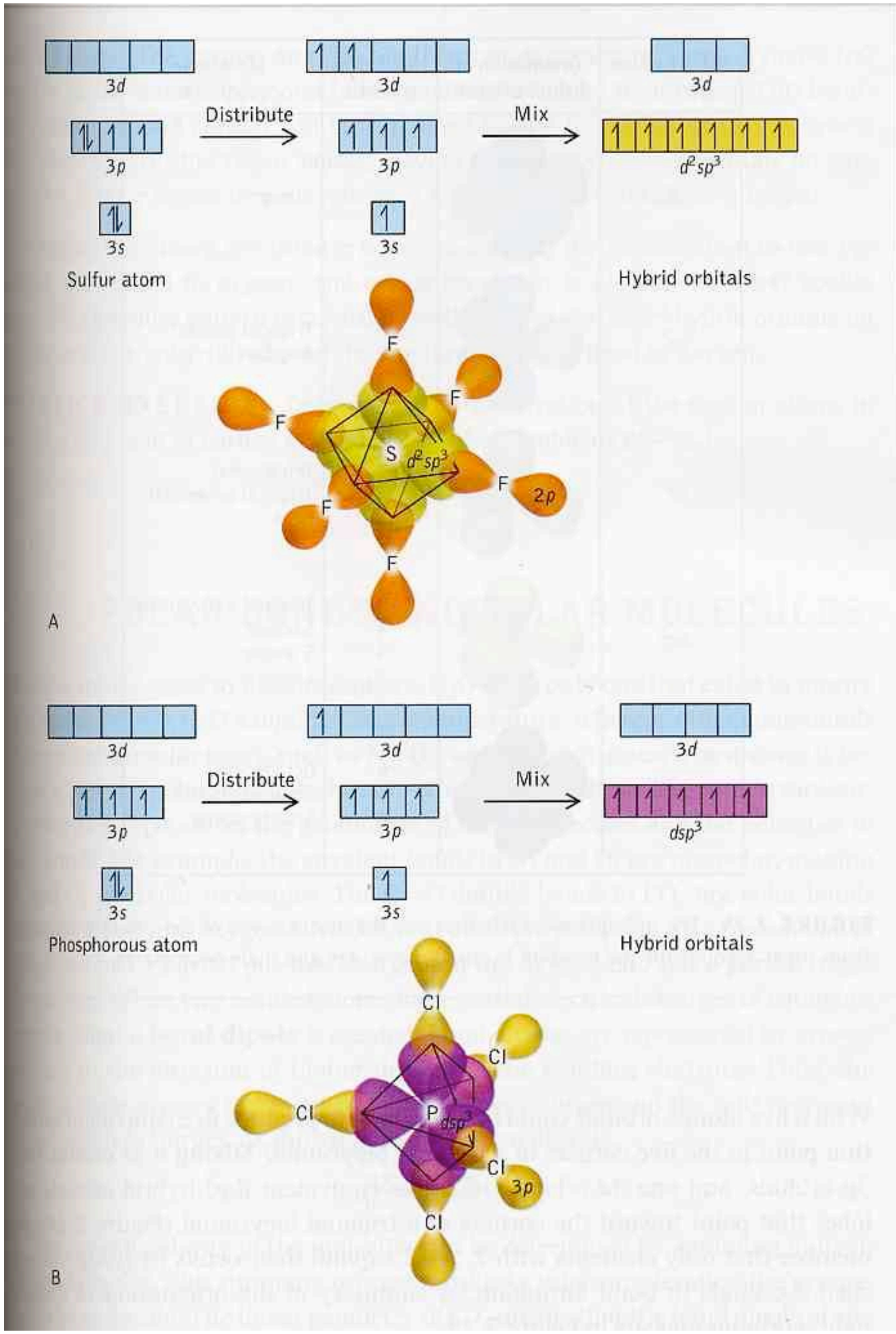
BF_3: SN = 3 = sp^2

CH_4: SN = 4 = sp^3

PF_5: SN = 5 = sp^3d

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

Extension to mixing of d orbitals



d^2sp^3 hybridization
six orbitals mixed = octahedral

dsp^3 hybridization
Five orbitals mixed = trigonal bipyramidal