18.2

Bonding in Methane and Orbital Hybridization

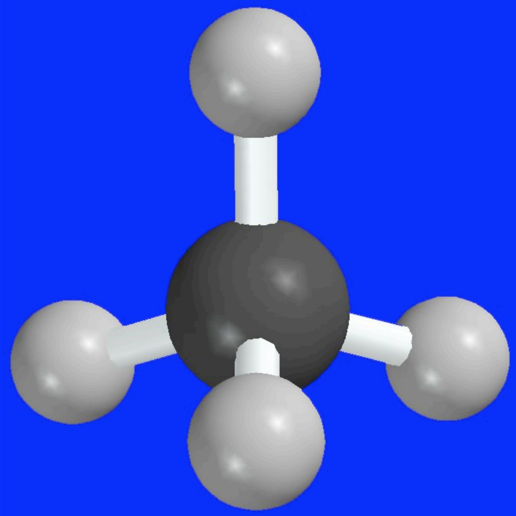
Structure of Methane

tetrahedral

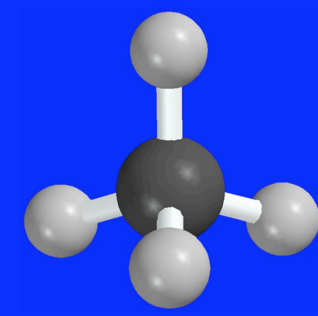
bond angles = 109.5°

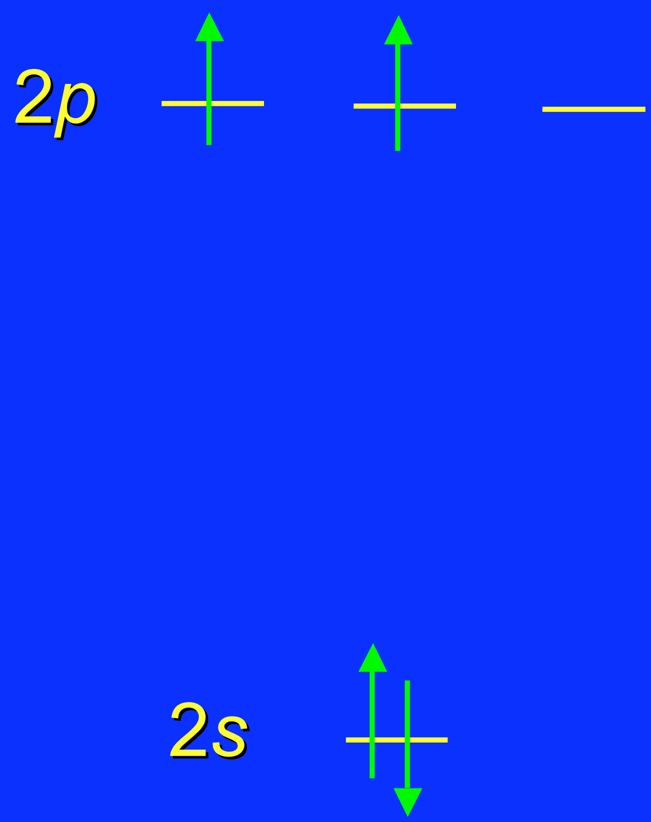
bond distances = 110 pm

but structure seems inconsistent with electron configuration of carbon



Electron configuration of carbon



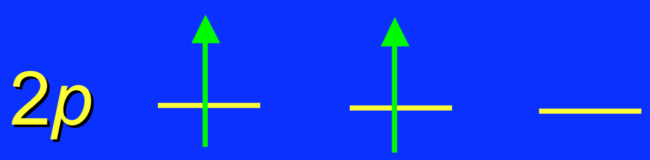


only two unpaired electrons

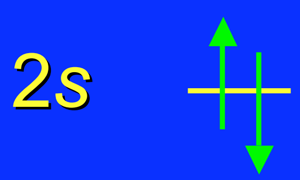
should form σ bonds to only two hydrogen atoms

bonds should be at right angles to one another

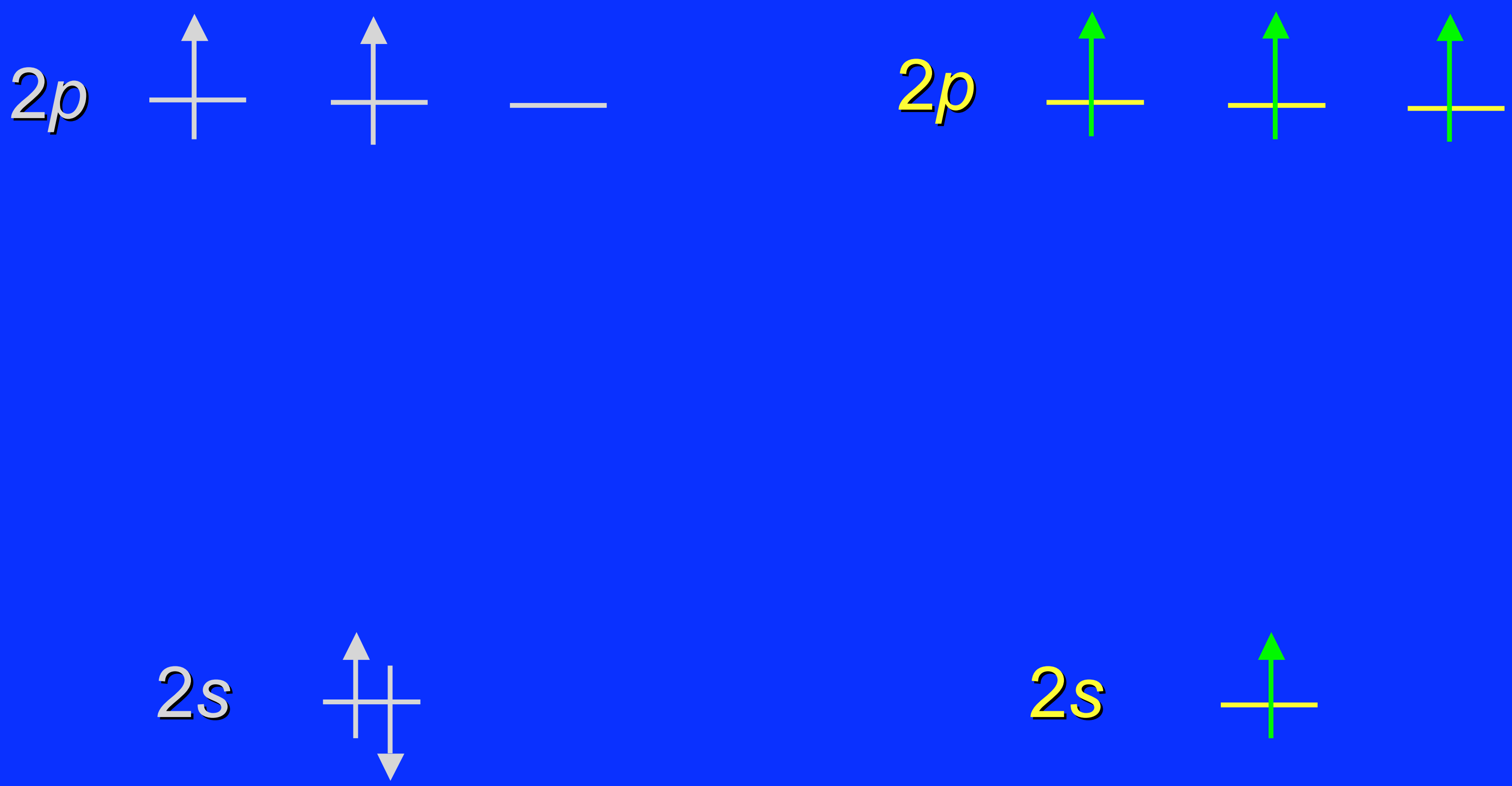
sp^3 *Orbital Hybridization*



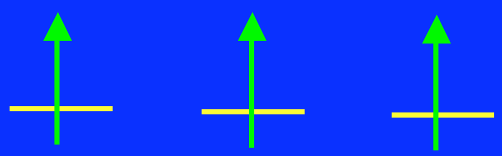
Promote an electron from the 2*s* to the 2*p* orbital



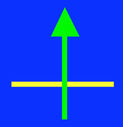
sp^3 Orbital Hybridization



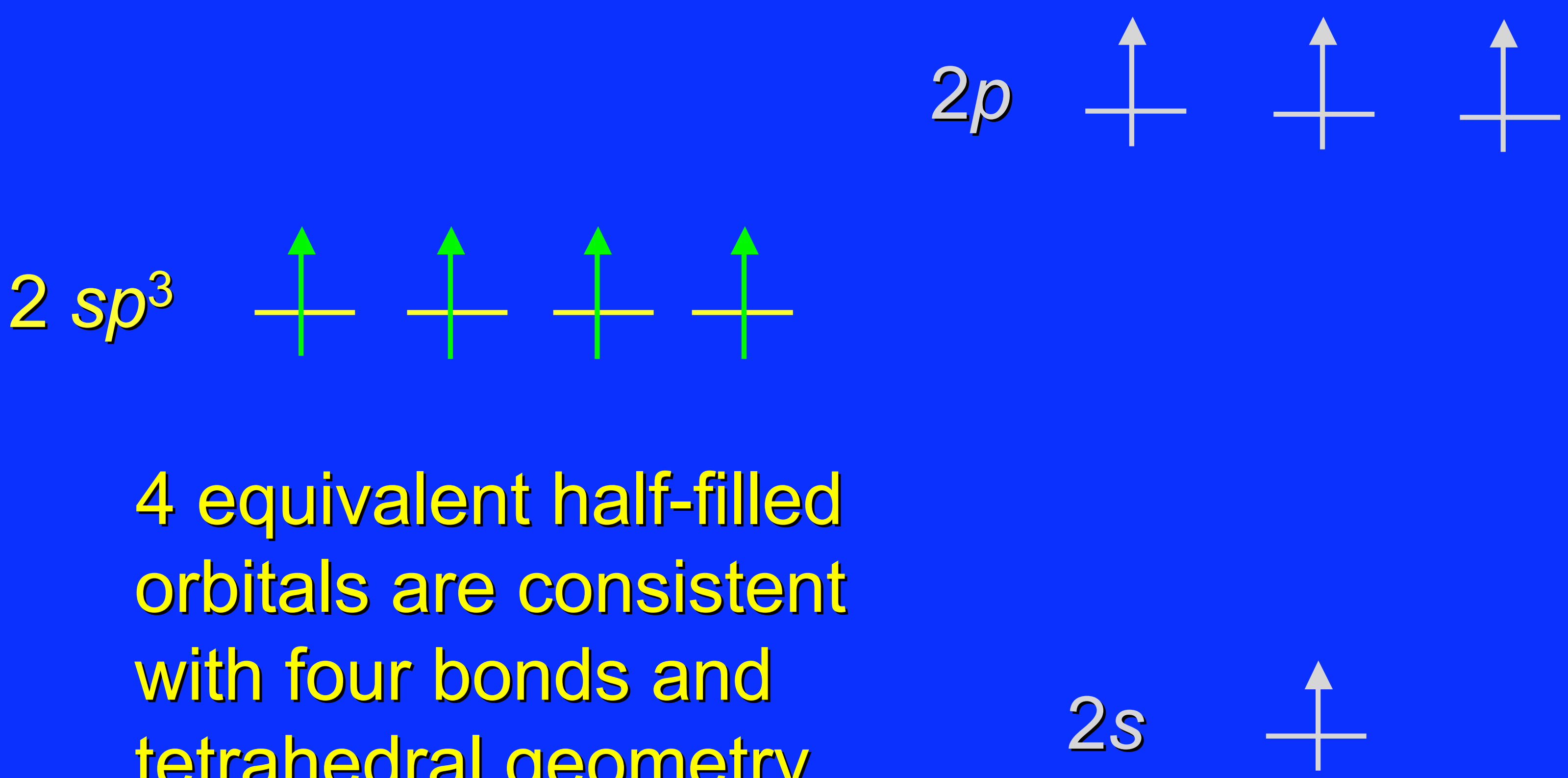
sp^3 *Orbital Hybridization*

2p 

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

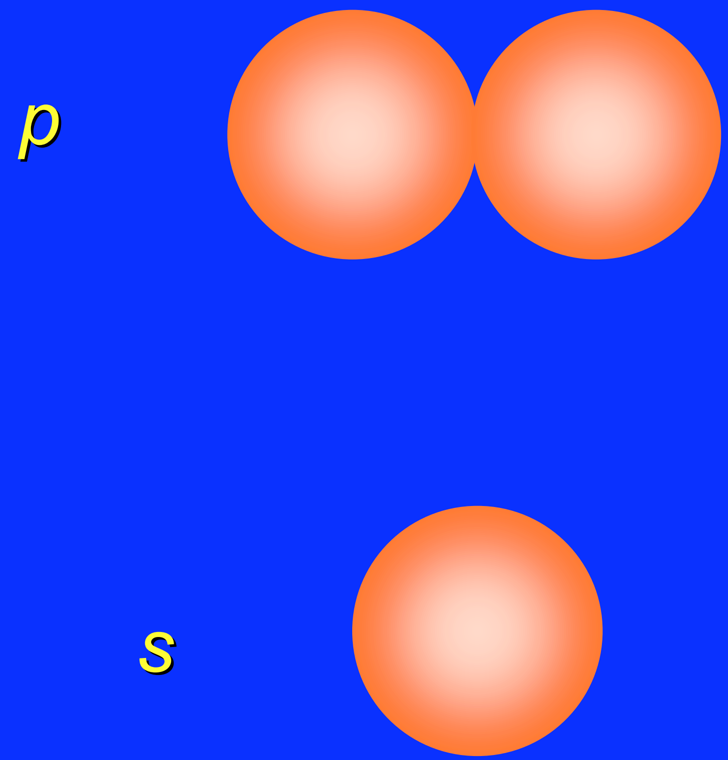
2s 

sp^3 Orbital Hybridization

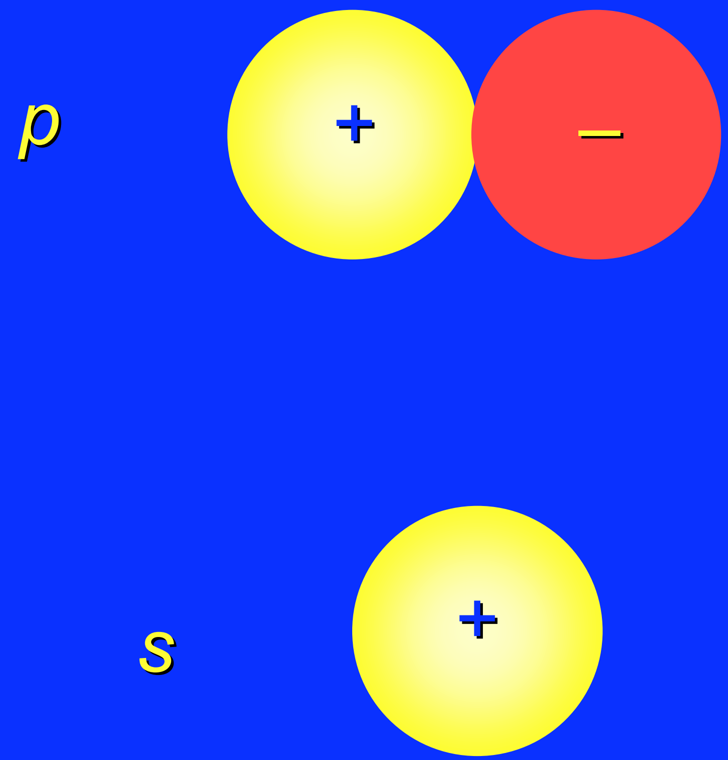


4 equivalent half-filled orbitals are consistent with four bonds and tetrahedral geometry

Shapes of orbitals

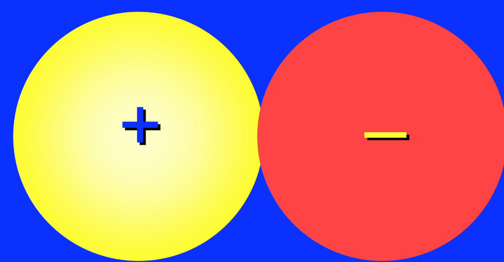


Nodal properties of orbitals



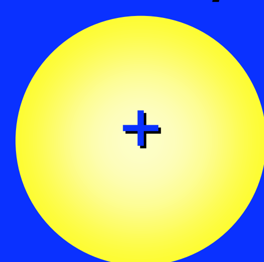
Shape of sp³ hybrid orbitals

p



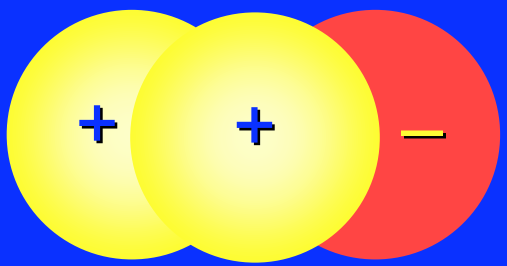
take the *s* orbital and place it on top of the *p* orbital

s



Shape of sp^3 hybrid orbitals

s + *p*

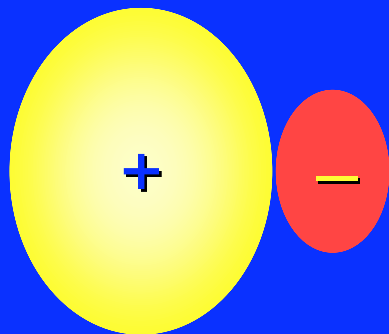


reinforcement of electron wave in regions where sign is the same

destructive interference in regions of opposite sign

Shape of sp^3 hybrid orbitals

sp hybrid



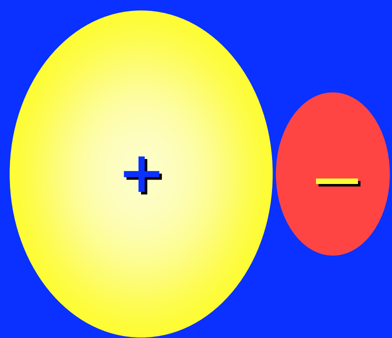
orbital shown is *sp* hybrid

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

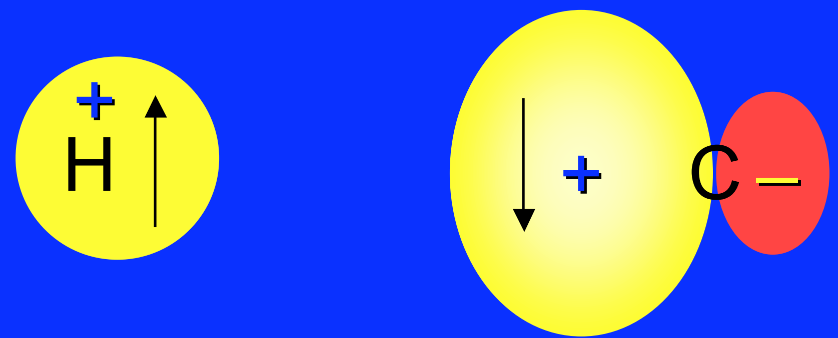
higher probability of finding an electron on one side of the nucleus than the other

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:

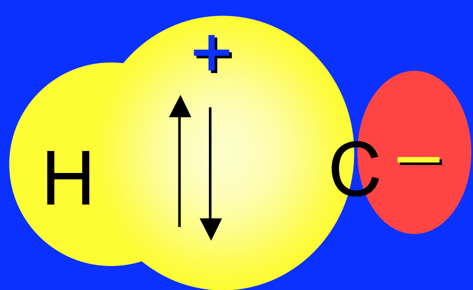
s



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

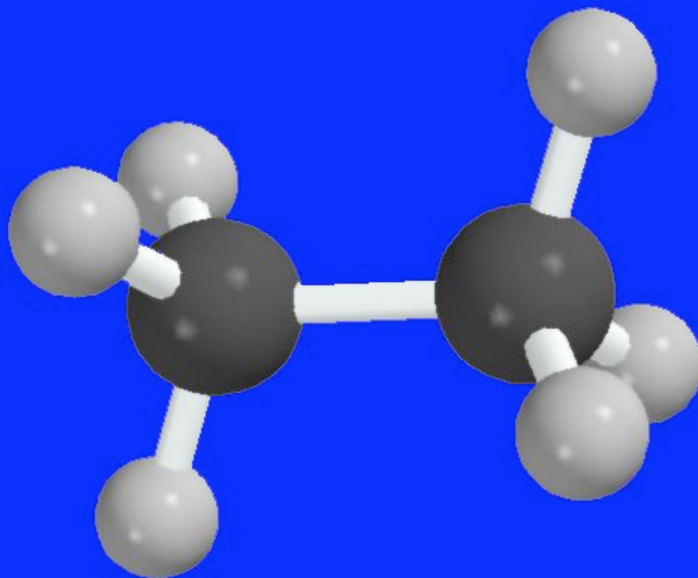
bonds involving sp^3 hybrid orbitals are stronger than those involving *s*-*s* overlap or *p*-*p* overlap

18,2
sp^3 Hybridization
and Bonding in Ethane

Structure of Ethane

C_2H_6

CH_3CH_3

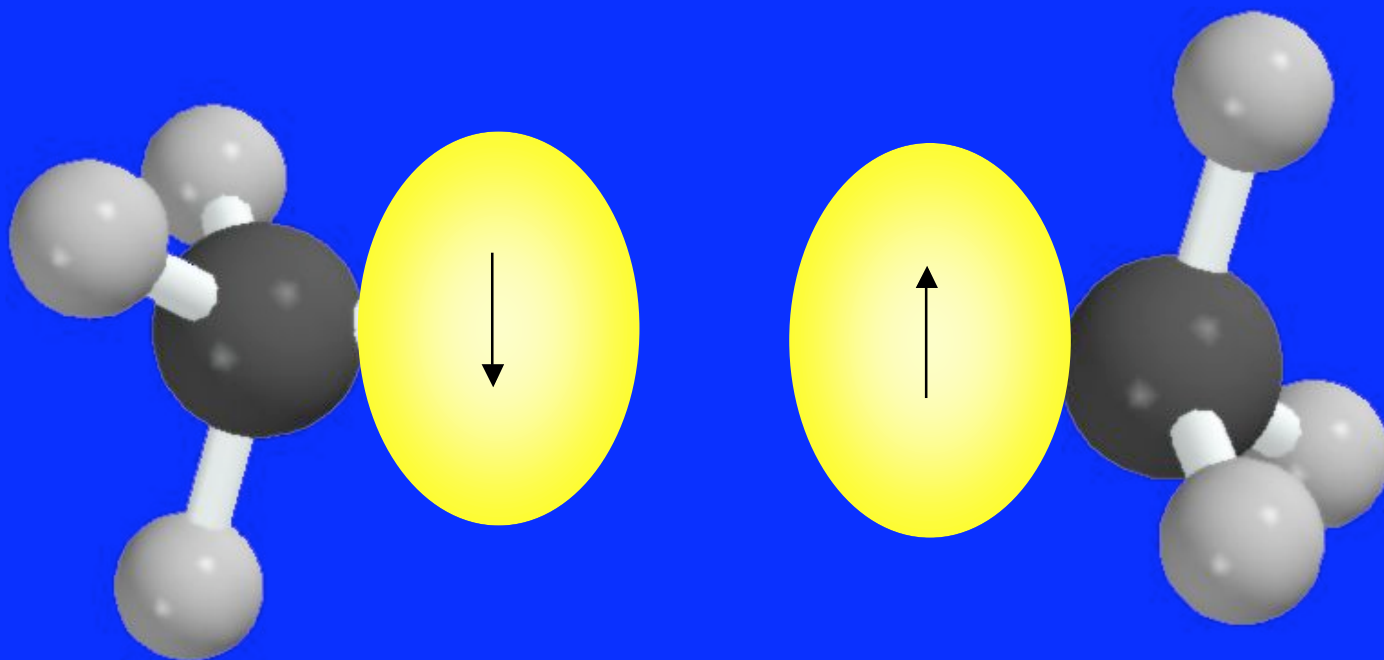


tetrahedral geometry at each carbon

C—H bond distance = 110 pm

C—C bond distance = 153 pm

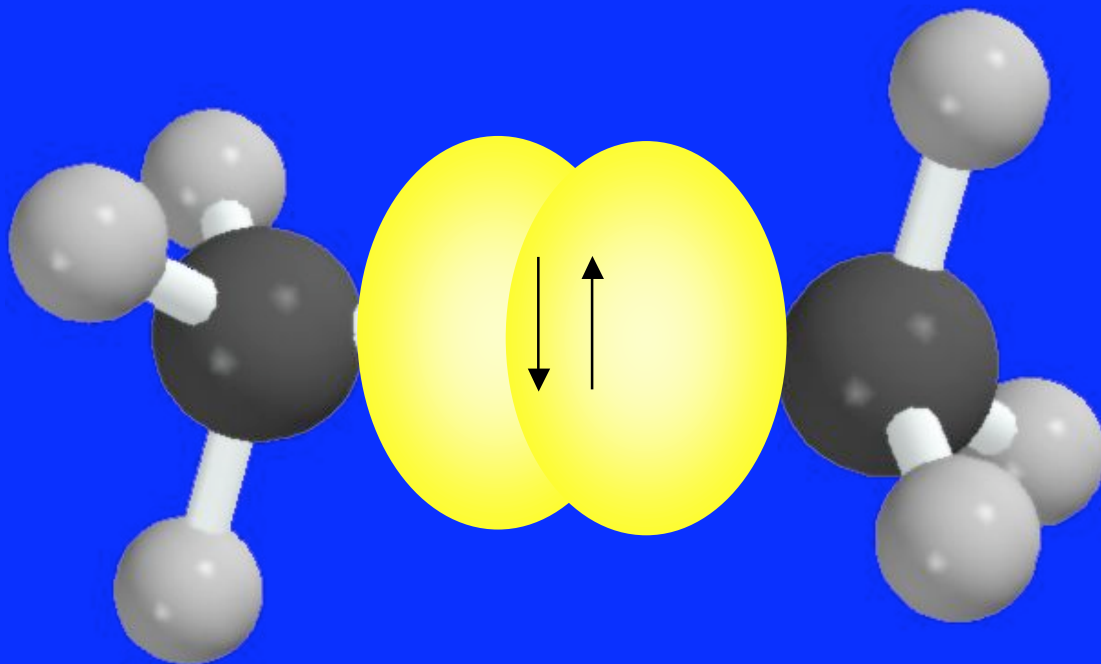
The C—C σ Bond in Ethane



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.

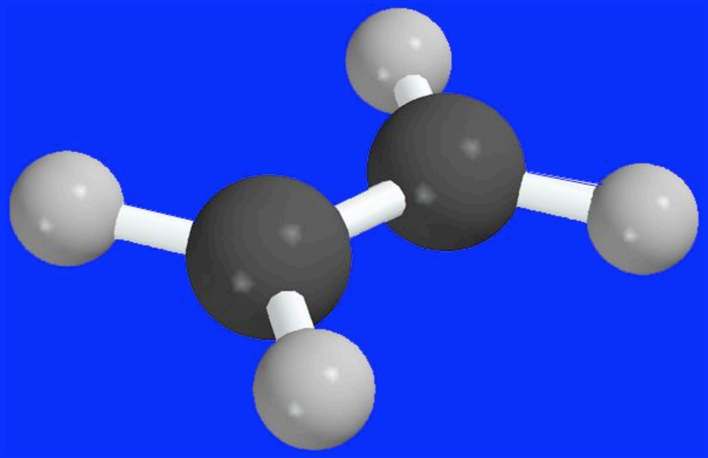
Overlap is along internuclear axis to give a σ bond.

18.2
sp^2 Hybridization
and Bonding in Ethylene

Structure of Ethylene

C_2H_4

$H_2C{=}CH_2$



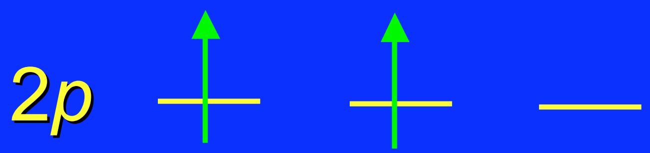
planar

bond angles: close to 120°

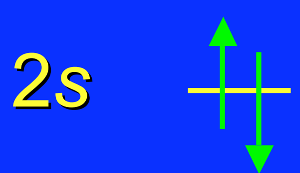
bond distances: C—H = 110 pm

C=C = 134 pm

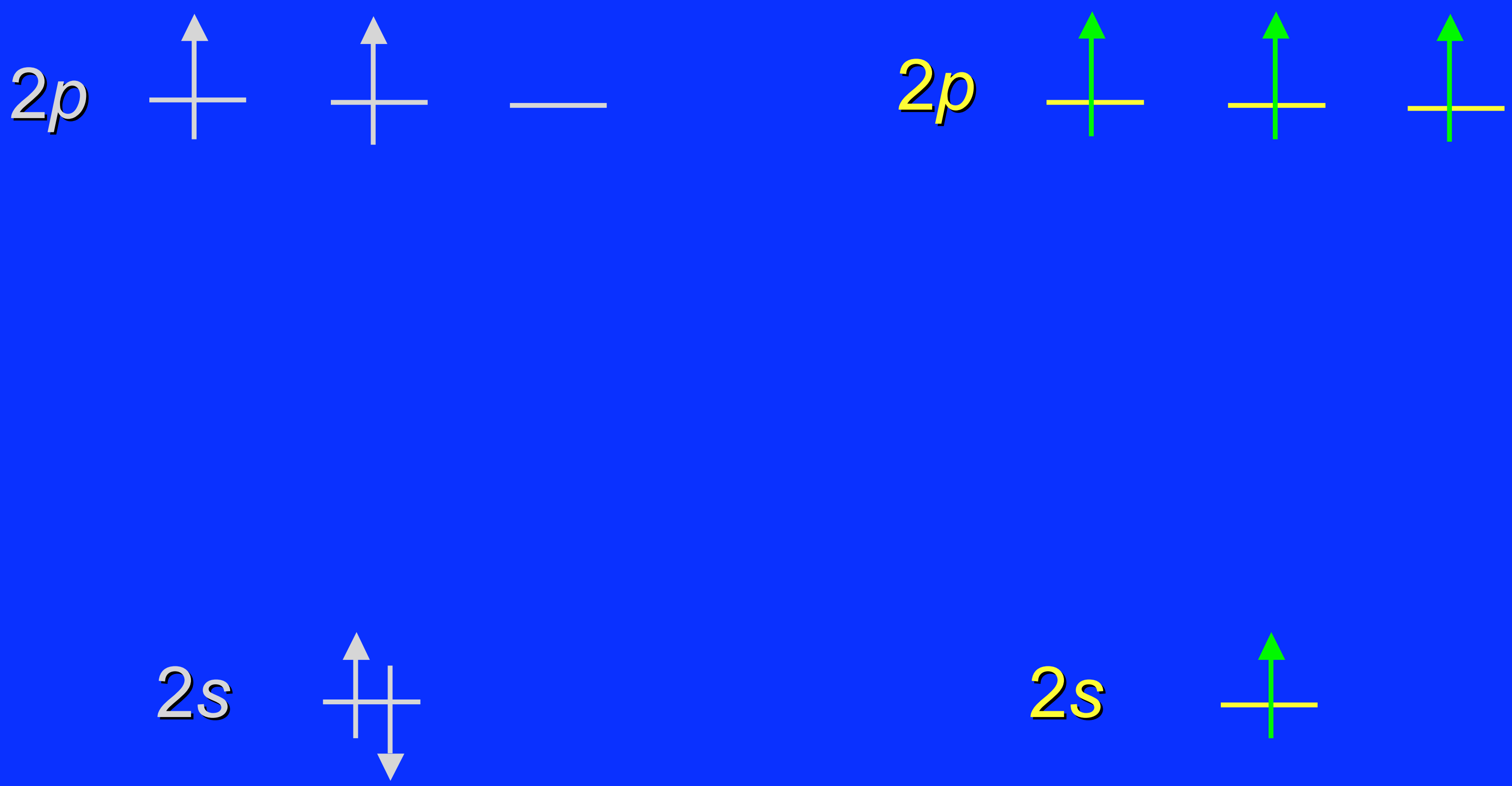
sp^2 *Orbital Hybridization*



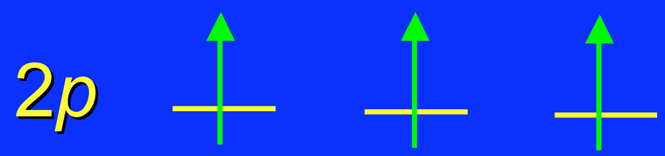
Promote an electron from the 2*s* to the 2*p* orbital



sp² Orbital Hybridization



sp^2 *Orbital Hybridization*

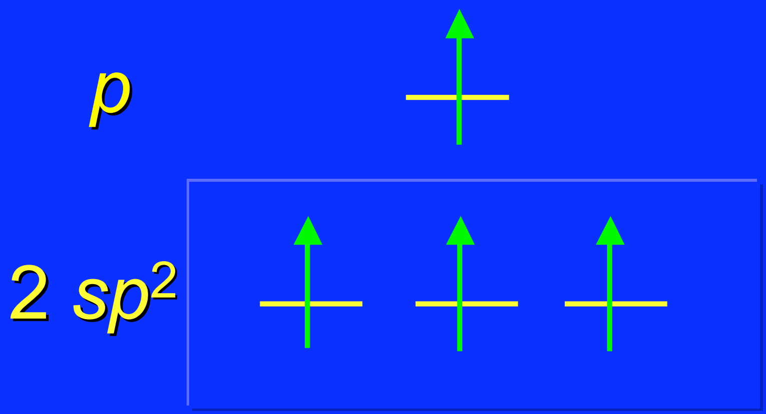


Mix together (hybridize) the 2*s* orbital and two of the three 2*p* orbitals

sp^2 *Orbital Hybridization*

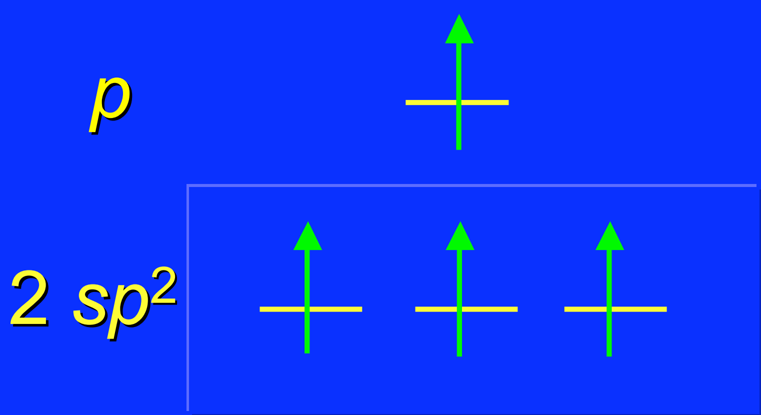
3 equivalent half-filled
sp^2 hybrid orbitals plus
1 p orbital left
unhybridized

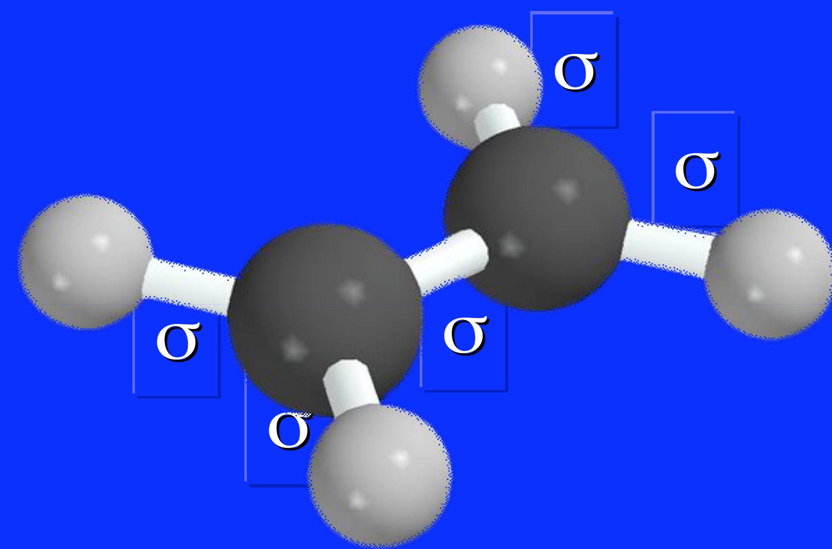
sp^2 *Orbital Hybridization*



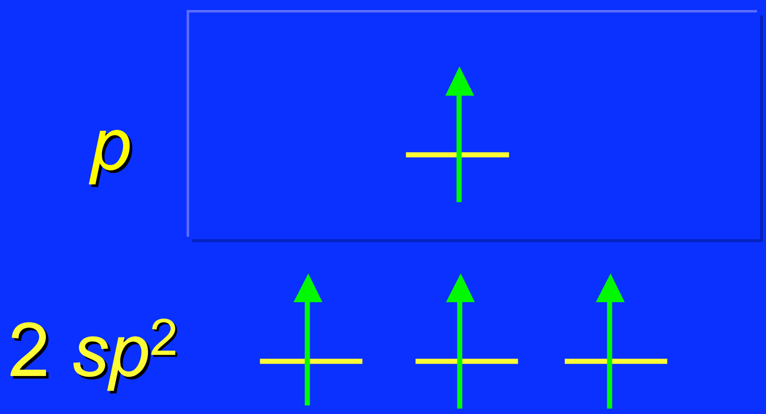
2 of the 3 sp^2 orbitals are involved in σ bonds to hydrogens; the other is involved in a σ bond to carbon

sp^2 Orbital Hybridization



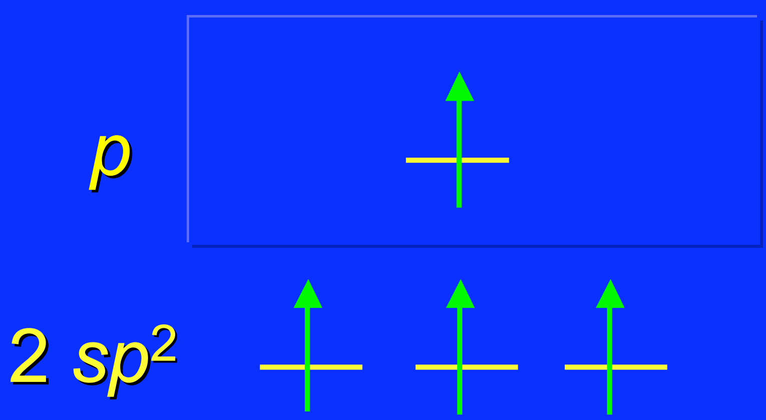


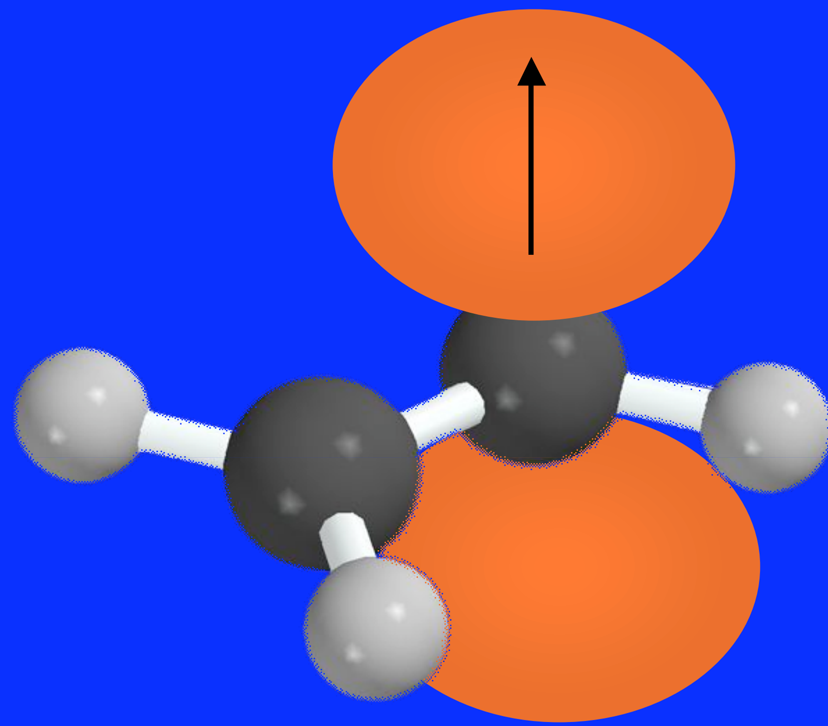
π Bonding in Ethylene



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

π Bonding in Ethylene

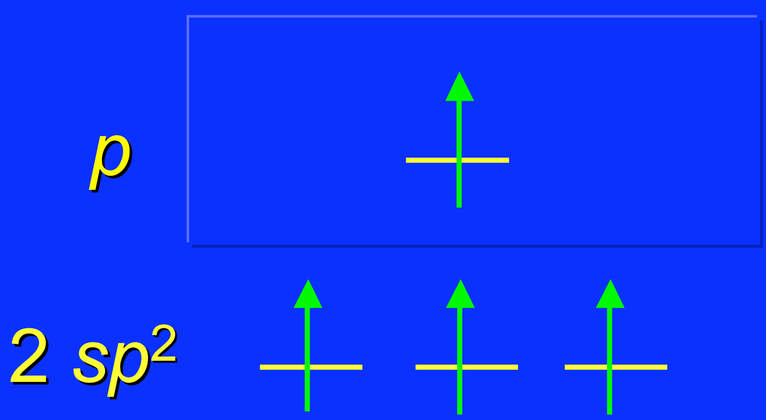


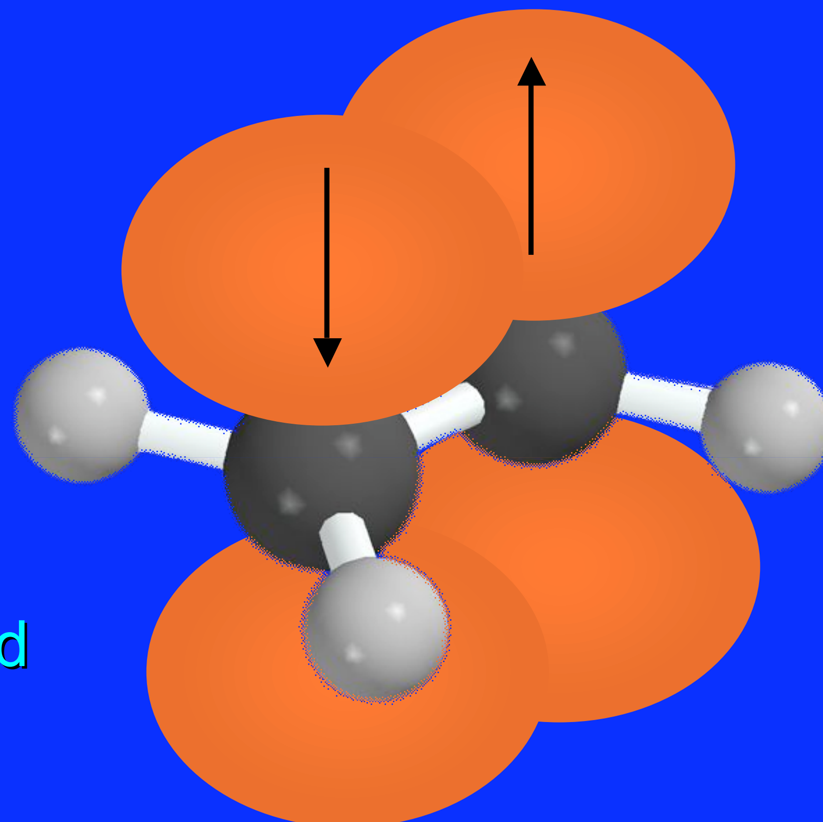


each carbon has an unhybridized 2*p* orbital

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

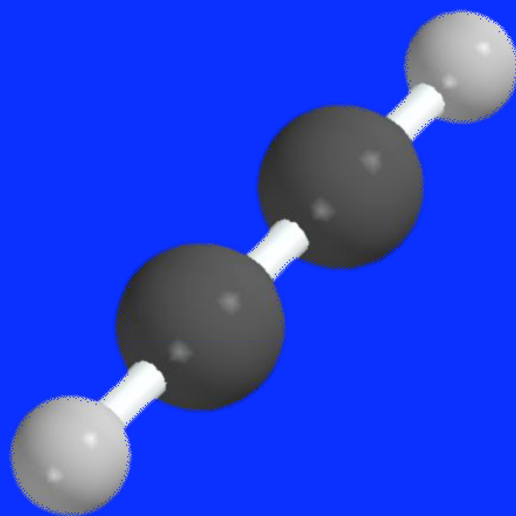
double bond in ethylene has a σ component and a π component

18.2
sp Hybridization
and Bonding in Acetylene

Structure of Acetylene

C_2H_2

HC≡CH



linear

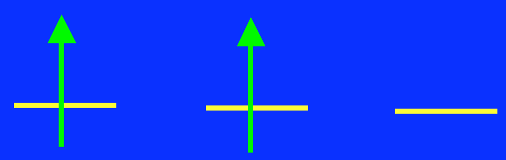
bond angles: 180°

bond distances: C—H = 106 pm

CC = 120 pm

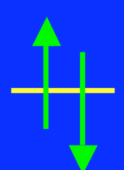
sp *Orbital Hybridization*

2p

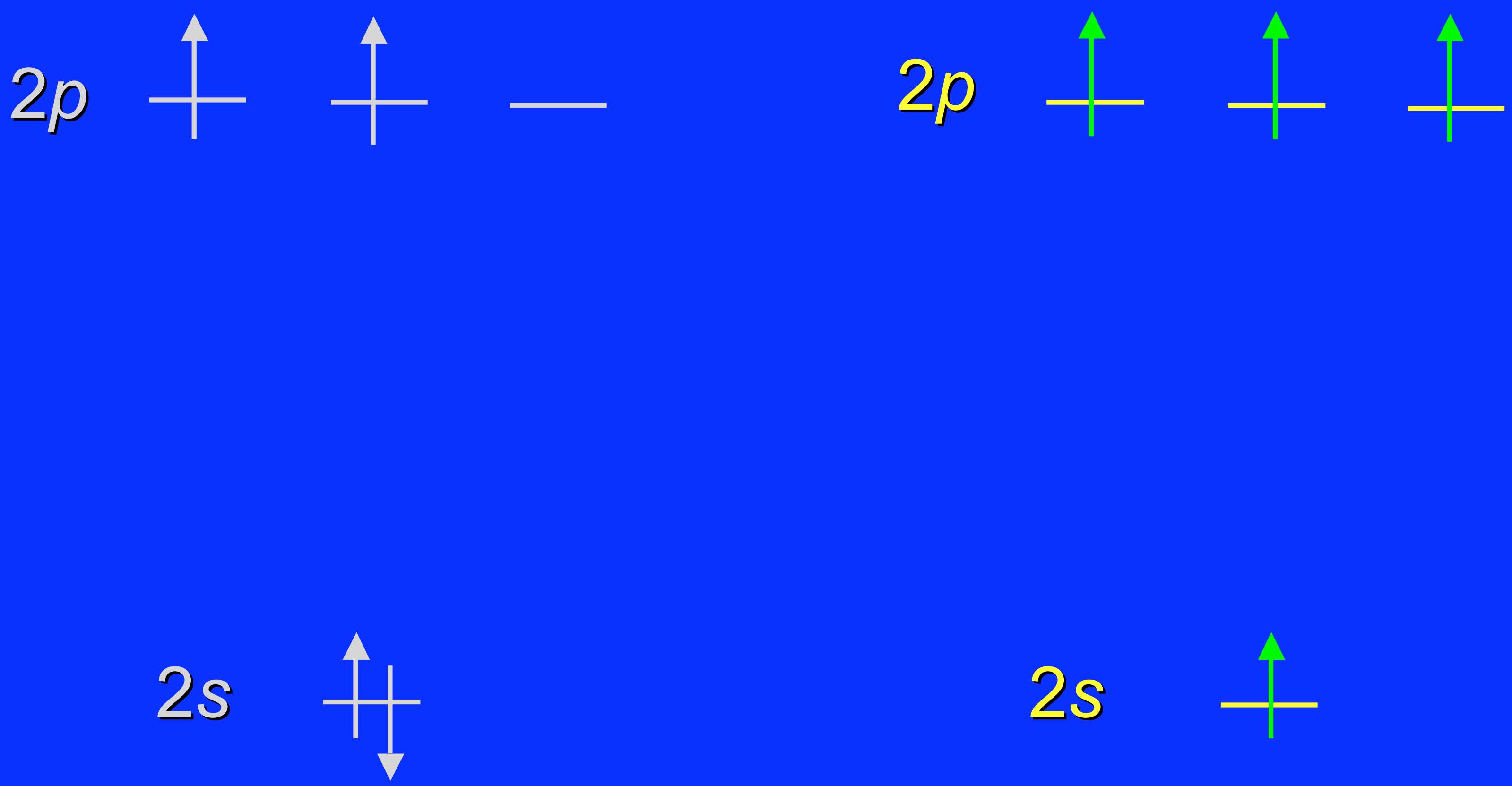


Promote an electron from the 2*s* to the 2*p* orbital

2s

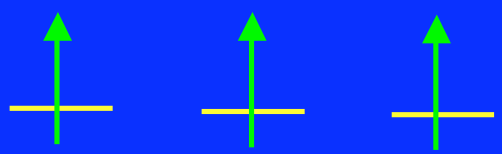


sp Orbital Hybridization



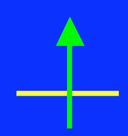
sp Orbital Hybridization

2p

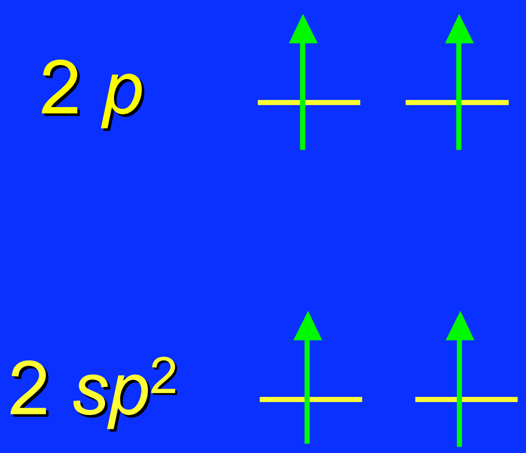


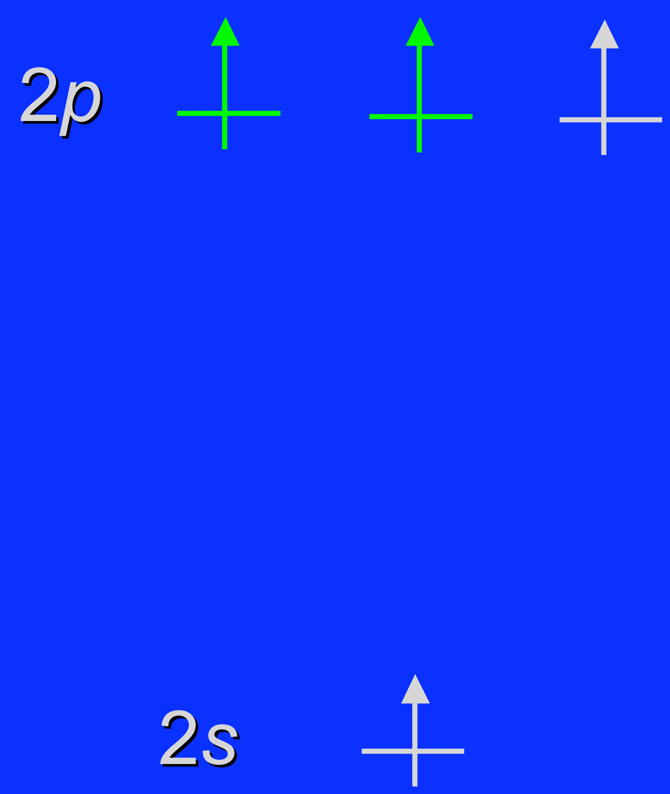
Mix together (hybridize) the 2*s* orbital and <u>one</u> of the three 2*p* orbitals

2s



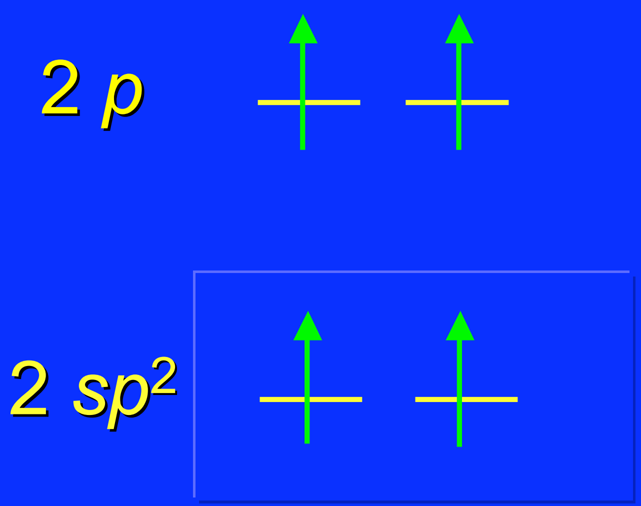
sp Orbital Hybridization





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

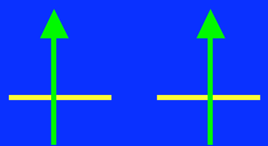
sp Orbital Hybridization



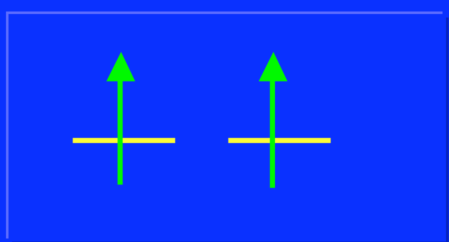
1 of the 2 *sp* orbitals is involved in a σ bond to hydrogen; the other is involved in a σ bond to carbon

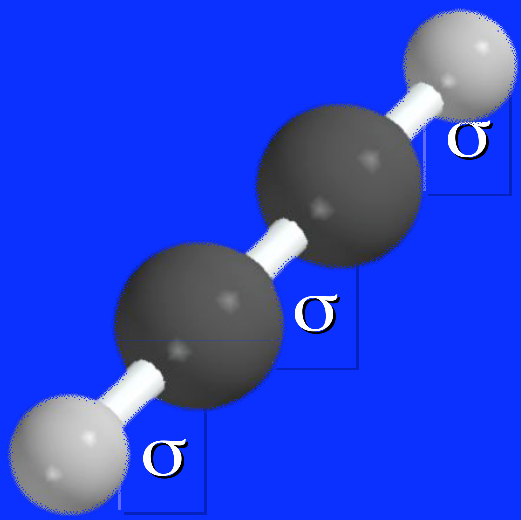
sp Orbital Hybridization

2 *p*

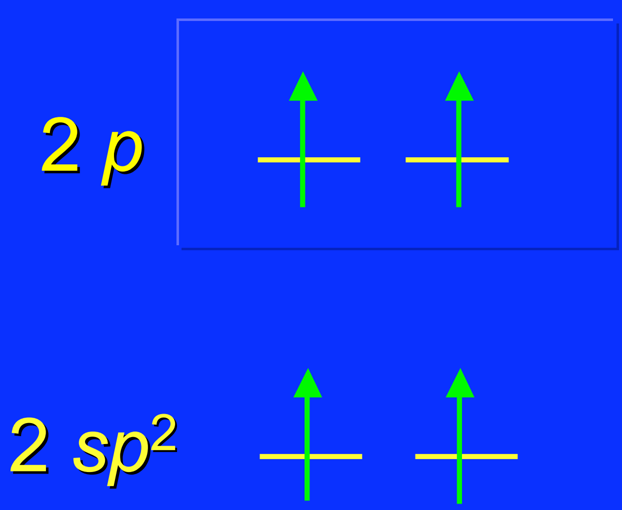


2 *sp*^{2}



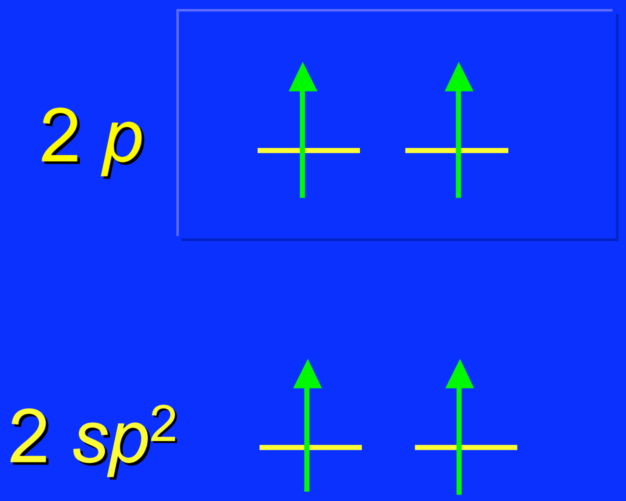


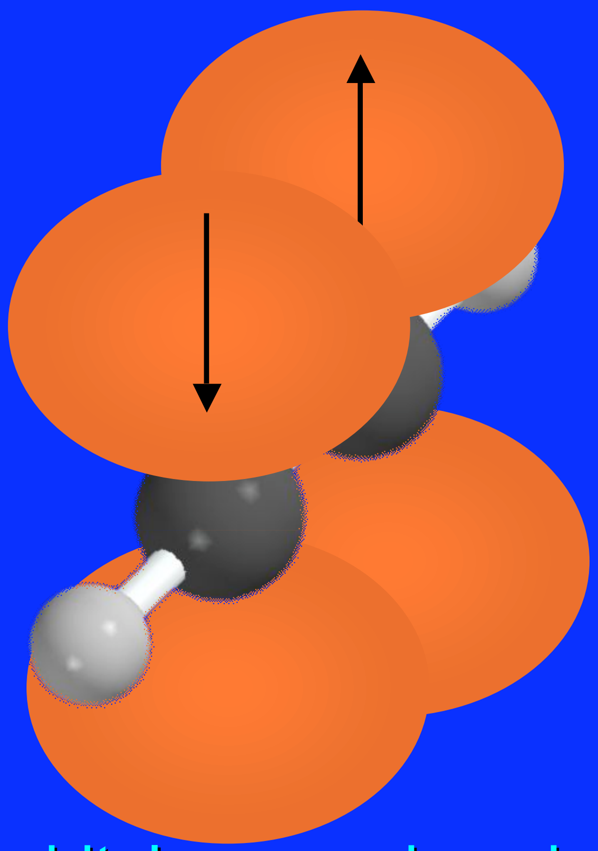
π Bonding in Acetylene



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

π Bonding in Acetylene





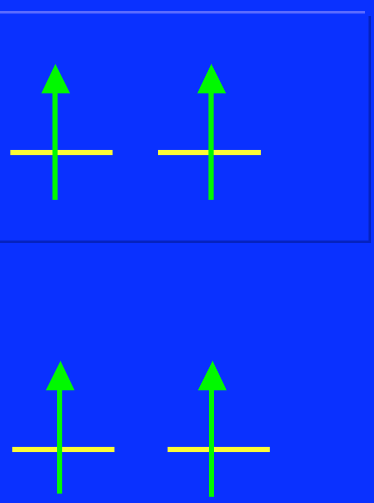
one π bond involves one of the p orbitals on each carbon

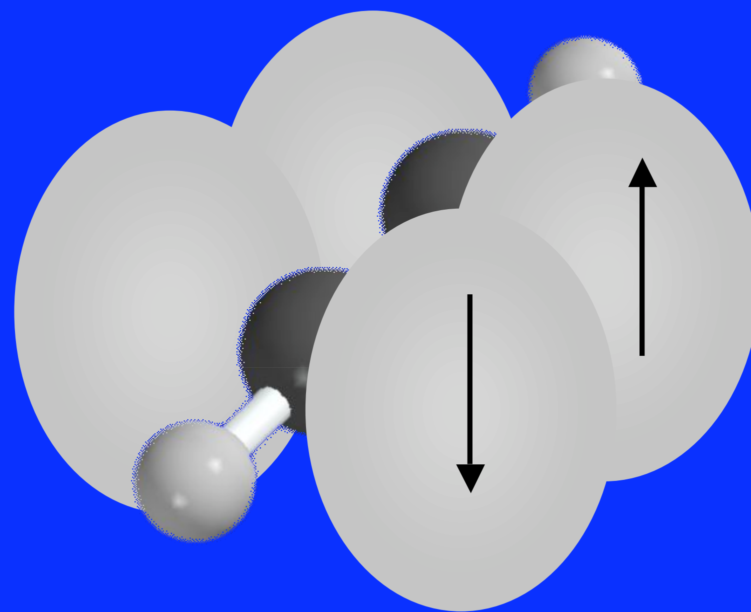
there is a second π bond perpendicular to this one

π Bonding in Acetylene

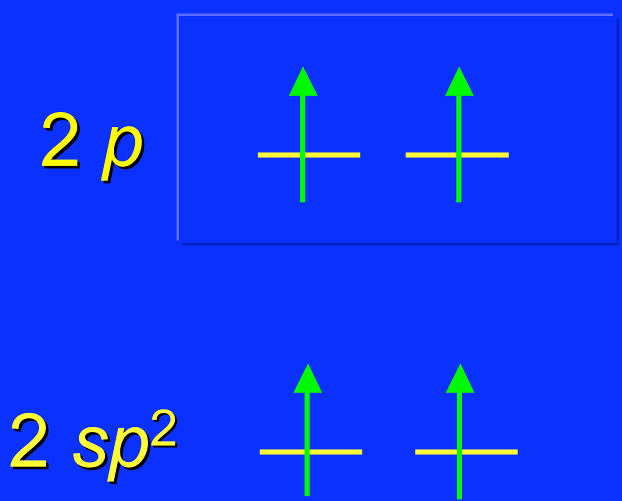
$2\ p$

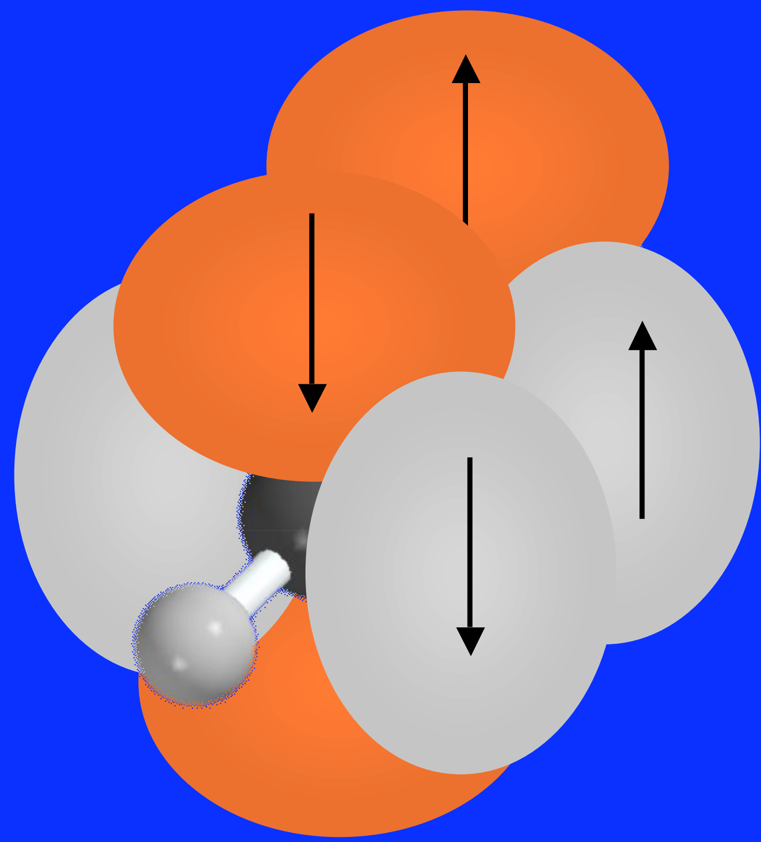
$2\ sp^2$





π Bonding in Acetylene





1.19
Which Theory of Chemical Bonding is Best?

Three Models

Lewis

- most familiar—easiest to apply

Valence-Bond (Orbital Hybridization)

- provides more insight than Lewis model
- ability to connect structure and reactivity to hybridization develops with practice

Molecular Orbital

- potentially the most powerful method
- but is the most abstract
- requires the most experience to use effectively