Covalent Bonding and Molecular Orbitals

Chemistry 35

Fall 2000

From Atoms to Molecules: The Covalent Bond

- So, what happens to e^- in *atomic orbitals* when two atoms approach and form a *covalent bond?*

Mathematically:

-let's look at the formation of a **hydrogen molecule**:

-*we start with:* 1 e^-/each in 1s atomic orbitals

-*we'll end up with:* **2 e^- in *molecular obital(s)***

HOW? Make linear combinations of the 1s orbital wavefunctions:

$$\psi_{mol} = \psi_{1s}(A) \pm \psi_{1s}(B)$$

Then, solve via the SWE!

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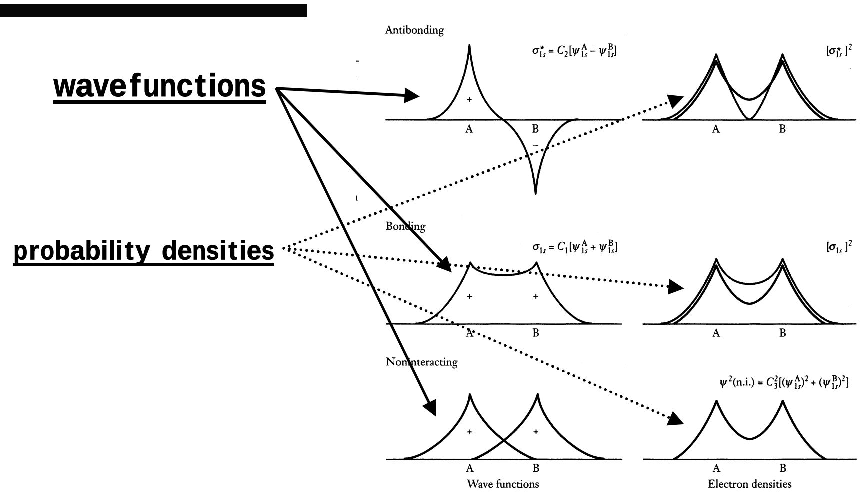
Hydrogen Wavefunctions



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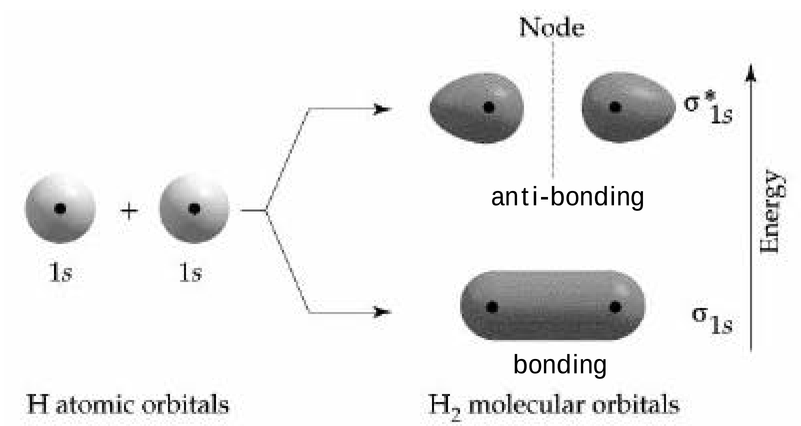
Hydrogen Molecular Orbitals



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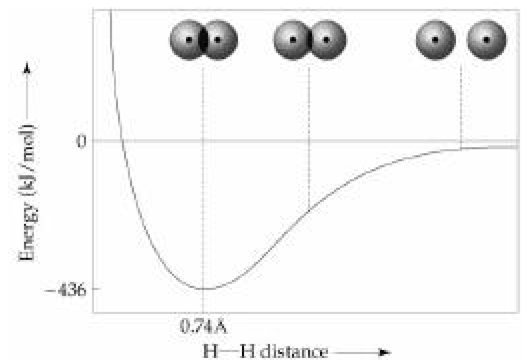
Hydrogen MO Formation: Internuclear Separation

- SWE solved with nuclei *at a specific separation distance* . . . How does the **energy** of the new MO vary with **internuclear separation**?



movie

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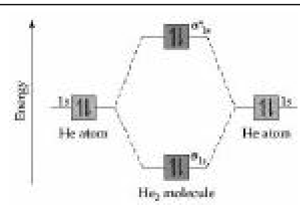
MO Theory: Homonuclear Diatomic Molecules

- Let's look at the *s-bonding* properties of some homonuclear diatomic molecules:

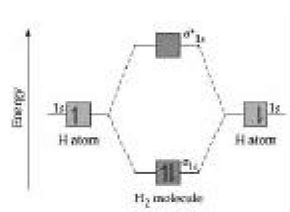
Bond order =

½(bonding e$^-$ - anti-bonding e$^-$)



For He$_2$: B.O. = 1 - 1 = ***0***

(no bond)



For H$_2$: B.O. = 1 - 0 = ***1***

(single bond)

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Configurations and Bond Orders: 1st Period Diatomics

Species	Config.	B.O.	Energy	Length
H_2^+	$(\sigma_{1s})^1$	½	255 kJ/mol	1.06 Å
H_2	$(\sigma_{1s})^2$	1	431 kJ/mol	0.74 Å
He_2^+	$(\sigma_{1s})^2(\sigma^*_{1s})^1$	½	251 kJ/mol	1.08 Å
He_2	$(\sigma_{1s})^2(\sigma^*_{1s})^2$	0	~0	LARGE

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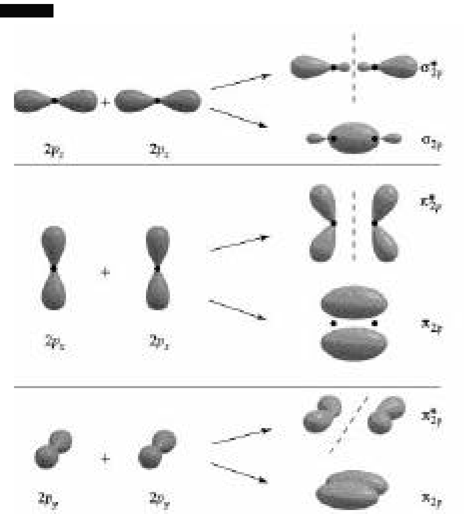
Combining p-orbitals: σ and π MO's

end-on overlap

side-on overlap



antibonding

bonding

antibonding

bonding

antibonding

bonding

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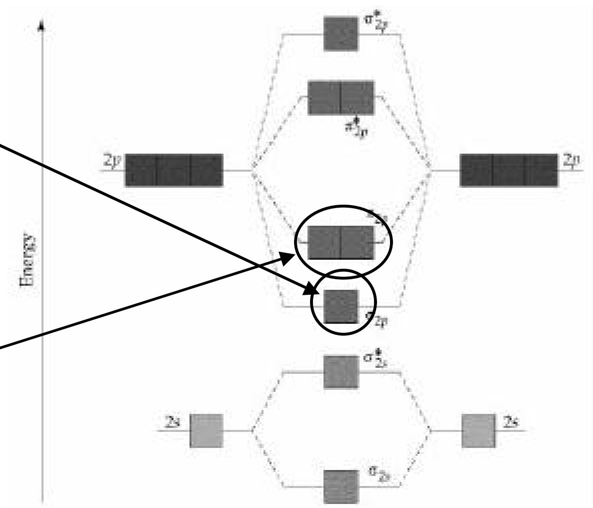
2nd Period MO Energies

σ_{2p} has lowest energy due to better overlap (end-on) of $2p_z$ orbitals

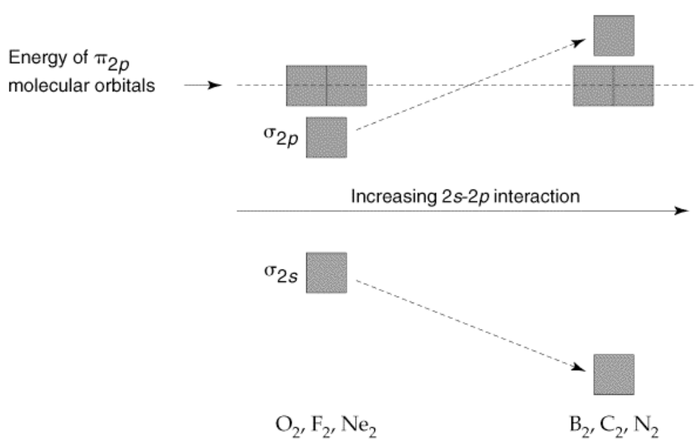
π_{2p} orbitals are *degenerate* and at higher energy than the σ_{2p}



2nd Period MO Energies: Shift!

For Z <8:

2s and 2p orbitals can interact enough to change energies of the resulting σ_{2s} and σ_{2p} MOs.



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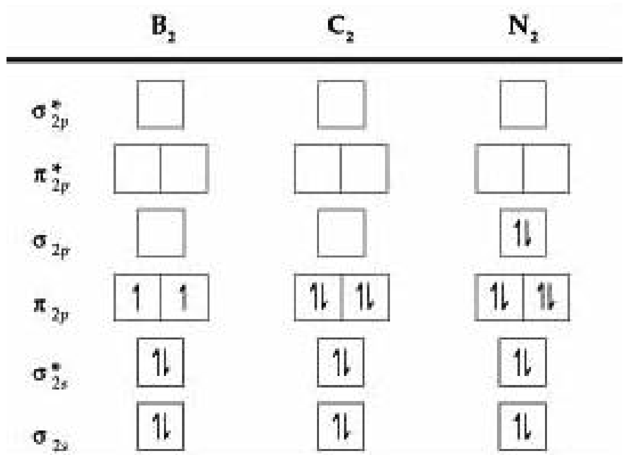
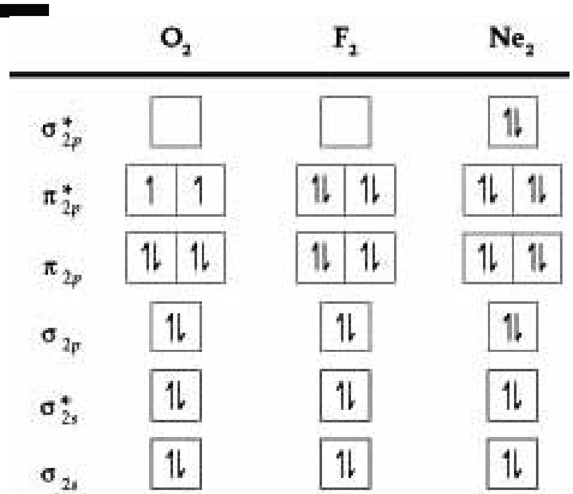
2nd Period Diatomics: π first

Note that B_2 has *unpaired electrons* so it must be <u>**paramagnetic**</u>



2nd Period Diatomics: σ first

O_2 *also* has <u>unpaired electrons</u> so it must be ***paramagnetic***



Configurations and Bond Orders: 2nd Period Diatomics

Species	Config.	B.O.	Energy	Length
Li_2	$(\sigma_{2s})^2$	1	105 kJ/mol	2.67 Å
Be_2	$(\sigma_{2s})^2(\sigma^*_{2s})^2$	0	9 kJ/mol	2.45 Å
B_2	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2p})^2$	1	289 kJ/mol	1.59 Å
C_2	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2p})^4$	2	599 kJ/mol	1.24 Å
N_2	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2p})^4(\sigma_{2p})^2$	3	942 kJ/mol	1.10 Å
O_2	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p})^2(\pi_{2p})^4(\pi^*_{2p})^2$	2	494 kJ/mol	1.21 Å
F_2	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p})^2(\pi_{2p})^4(\pi^*_{2p})^4$	1	154 kJ/mol	1.41 Å

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Heteronuclear Diatomics

- Different atoms = different *atomic orbital* energies
  - So, when combining *atomic* orbitals, we don't always combine *like* orbitals
  - And, if we do combine *like* orbitals (e.g., 1s and 1s), they are not necessarily at the same energy, so they combine *unequally*
  - RESULT: ***asymmetry***
    - *Unequal* distribution of electron density between the two atoms
    - Resulting *molecular orbitals* are not symmetrical
    - Bond is *polar* and has a *dipole moment* (μ)

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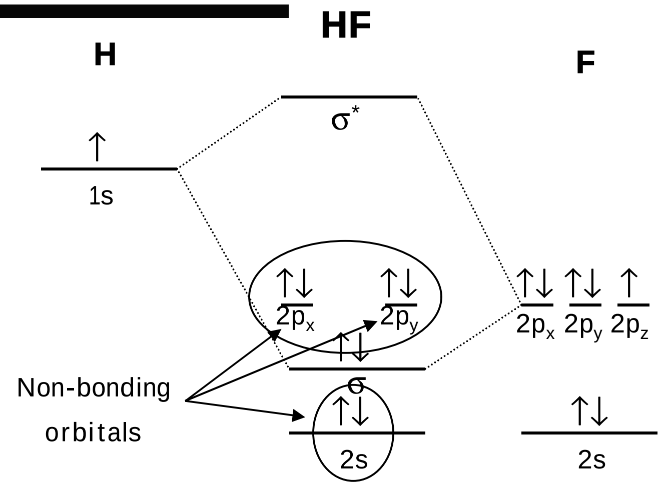
Example: HF



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Orbital Mixing

- Mixing of orbitals depends on *symmetry* and on *energy* matches
- The extent to which an atomic orbital contributes to the molecular orbital wavefunction is represented in the mixing equation:

$$\psi_{mol} = \sigma = C_H\psi_{1s}(H) + C_F\,\psi_{2p}(F)$$

- The magnitudes of C_H and C_F will reflect the degree to which these *atomic orbitals* contribute to the resulting *molecular orbital* wavefunction

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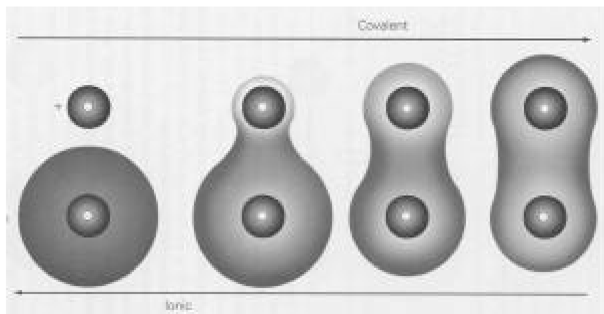
Polar Covalent Continuum

- Replacing **H** with ***Na*** pushes its *s-orbital* to higher energy, <u>decreasing the mixing with the p_z-orbital on F</u>
- $C_{Na} < C_H$ so resulting MO will have more electron density on **F** (more polar)



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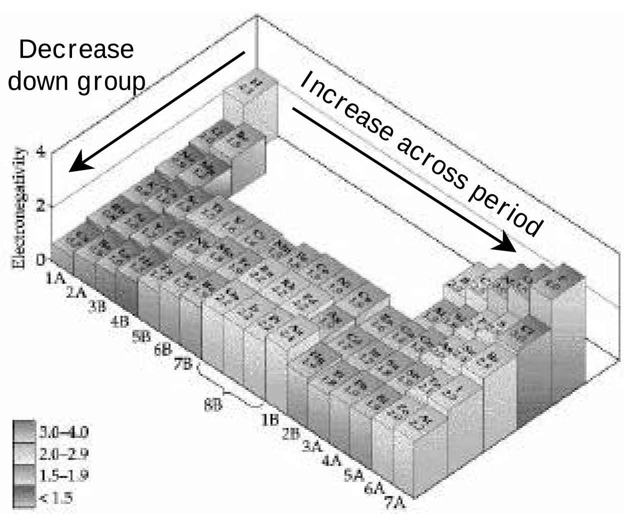
Electronegativity: Periodic Trends



Determining %-Ionic Character

- If we know a molecule's *dipole moment* and **bond length**, then we can assess the degree of charge separation (ionic character) across the bond:

% - Ionic character = δ x 100, where:

$$\delta = \mu / (e \times d)$$

μ - dipole moment
e - charge on an electron
d - bond length

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%-Ionic Character Examples

- So, for **HCl:** μ = 1.08 D d = 1.27 Å

$$\delta = \frac{1.08\ \text{D}}{(1.602 \times 10^{-19}\ \text{C})(1.27 \times 10^{-10}\ \text{m})} \times \frac{3.336 \times 10^{-30}\ \text{C-m}}{\text{D}}$$

δ = **0.177086** $\Rightarrow$ *17.7 % ionic character*

- For **NaCl**: μ = 9.001 D d = 2.36 Å

δ = **0.794223** $\Rightarrow$ *79.4 % ionic character*

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Dipole Moments and Bond Properties

- Trends in the *Hydrogen Halides:*

Compound	d (Å)	μ (D)	%-δ	ΔEN
HF	0.92	1.82	41.2	1.9
HCl	1.27	1.08	17.7	0.9
HBr	1.41	0.82	12.1	0.7
HI	1.61	0.44	5.7	0.4

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Questions?

- How can we relate this *molecular orbital* model to the bonding and molecular geometries of some real molecules?

Example: **CH_4**

-tetrahedral structure (109.5^o bond angles)
-all four C-H bonds identical
-all nicely predicted using VSEPR model

***BUT:** how do we combine the 2p orbitals of Carbon with the 1s orbitals of Hydrogen to obtain this structure?

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Hybrid Orbitals

- We can combine *atomic orbital wavefunctions* to make a **new** set of ***hybrid orbitals*** that better represent the bonding properties observed
- For carbon, in CH_4, we need ***four equivalent orbitals*** which are oriented towards the corners of a tetrahedron:

$$\psi_{hybrid} = C_s\psi_{2s} + C_p\,\psi_{2p}$$

NOTE: it's really more complicated than this (as we are combining FOUR orbitals: 2s plus the three 2p orbitals of carbon).

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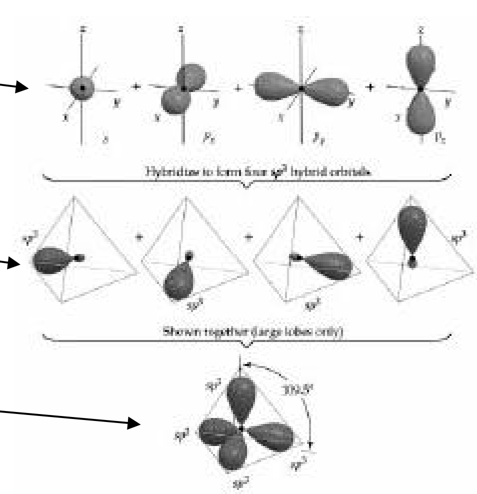
sp^3 hybrid orbitals

C: $1s^2 2s^2\ 2p^2$

4 sp^3 *hybrid* orbitals formed

$\uparrow$ $\uparrow$ $\uparrow$ $\uparrow$

4 e^- in sp^3 orbitals



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*__BUT:__ how do we combine the 2p orbitals of Carbon with the 1s orbitals of Hydrogen to obtain this structure?

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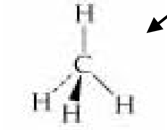
More Questions!

- Look at the structures of some simple hydrocarbons:

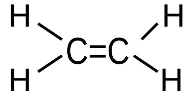
CH_4, C_2H_4, C_2H_2

Methane



tetrahedral

Ethylene



trigonal planar

Acetylene

H-C ≡C-H

linear

How can this be done with carbon's $2s^2 2p^2$ config?

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Hybrid Orbitals

- We can combine *atomic orbital wavefunctions* to make a **new** set of ***hybrid orbitals*** that better represent the bonding properties observed

- For carbon, in CH_4, we need ***four equivalent orbitals*** which are oriented towards the corners of a tetrahedron:

$$\psi_{hybrid} = C_s \psi_{2s} + C_p \psi_{2p}$$

NOTE: it's really more complicated than this (as we are combining FOUR orbitals: 2s plus the three 2p orbitals of carbon).

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Example

- Let's look first at a simpler example: **BeF_2**

Be: $1s^2 2s^2$ ← filled orbitals, ***no e^- to share***

F: $1s^2 2s^2 2p^5$ ← has e^- in a 2p orbital to share

Solution: put the 2 Be valence e^- in *new* orbitals (unpaired)

How? First, promote 1 e^- to a 2p orbital:

$$2s^2 \rightarrow 2s^1 2p^1$$

Then, *mix and combine* the 2s and 2p orbitals, to make ***two NEW equivalent orbitals:***

$$2s^1 2p^1 \rightarrow \underline{\uparrow}\ \underline{\uparrow}$$

sp *hybrid* orbitals

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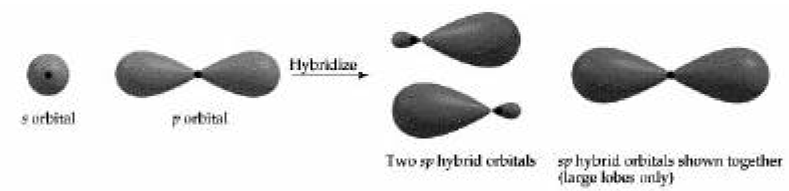
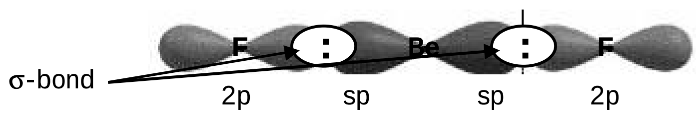
sp Hybrid Orbitals

- This is what they look like:



Now, Be has unpaired electrons to share with F:



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sp^2 Hybrid Orbitals

- If we need *three* equivalent orbitals, we can mix the s-orbital with *two* p-orbitals:

Example:

BF_3

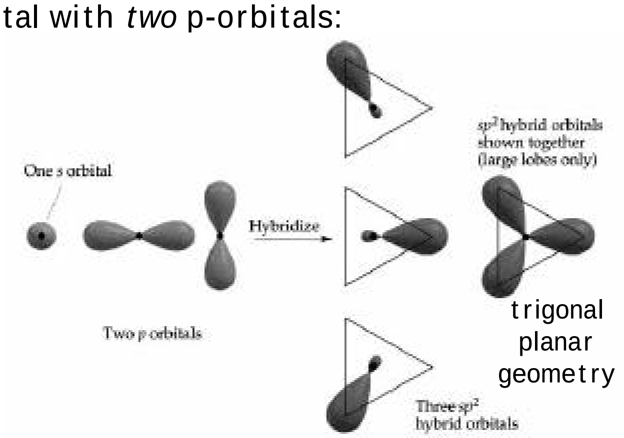
B: $1s^2 2s^2 2p^1$

promote ↓

$1s^2 2s^1 2p^2$

hybridize ↓

$1s^2 (sp^2)^3$



sp^3 Hybrid Orbitals

- If we need *four* equivalent orbitals, we can mix the s-orbital with *all three* p-orbitals:

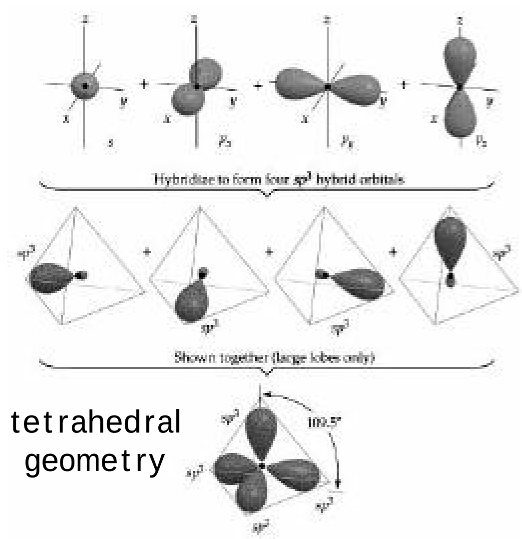
Example:

CH_4

C: $1s^2 2s^2 2p^2$

↓ *hybridize*

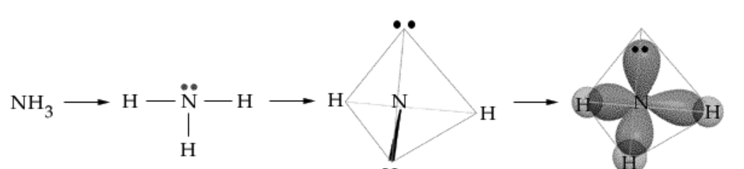
$1s^2(sp^3)^4$



tetrahedral geometry

How do we know which hybrid orbitals to use?

- **Three step process:**
  1. Draw the *Lewis structure*
  2. Determine the *electron-domain geometry* (VSEPR)
  3. Select the *hybrid orbitals* needed to obtain the determined geometry



Lewis structure

tetrahedral

sp^3

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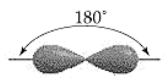
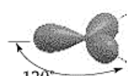
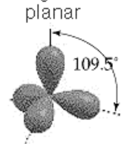
Hybrid Orbitals and Electron-Domain Geometry

Geometrical Arrangements Characteristic of Hybrid Orbital Sets

Atomic Orbital Set	Hybrid Orbital Set	Geometry	Examples
sp	Two *sp*	 180° Linear	BeF_2, $HgCl_2$
spp	Three sp^2	 120° Trigonal planar	BF_3, SO_3
sppp	Four sp^3	 109.5° Tetrahedral	CH_4, NH_3, H_2O, NH_4^+

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What about "Expanded Octets"?

- Need to include some of the *d-orbitals* in our hybridization scheme:

s + ppp + d = *FIVE* **sp³d** hybrid orbitals in a **trigonal bipyramidal** orientation

s + ppp + dd = *SIX* **sp³d²** hybrid orbitals in an **octahedral** orientation

So *that's* why P and S can accommodate "expanded octets" but N and O cannot . . . there are no "2d" orbitals!

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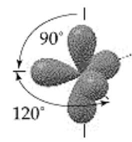
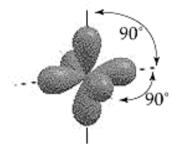
More Hybrid Orbitals and Electron-Domain Geometry

Geometrical Arrangements Characteristic of Hybrid Orbital Sets

Atomic Orbital Set	Hybrid Orbital Set	Geometry	Examples
spppd	Five sp^3d	 Trigonal bipyramidal	PF_5, SF_4, BrF_3, $SbCl_5^{2-}$
spppd, d	Six sp^3d^2		SF_6, ClF_5, XeF_4, PF_6^-

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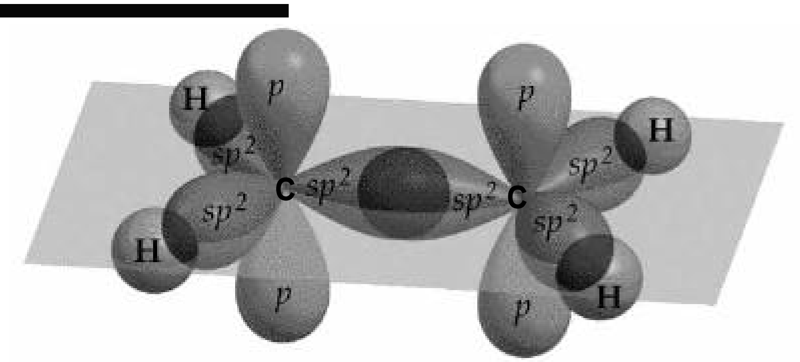
Ethylene (C_2H_4) Orbitals



Carbon: sp^2 hybridized (trigonal planar)

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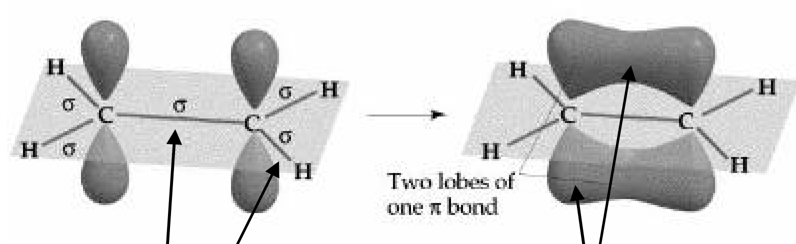
Ethylene (C_2H_4) Bonding



σ - bonds:

from sp²- s overlap

from sp² - sp² overlap

π - bond:

From $2p_z$ - $2p_z$ overlap

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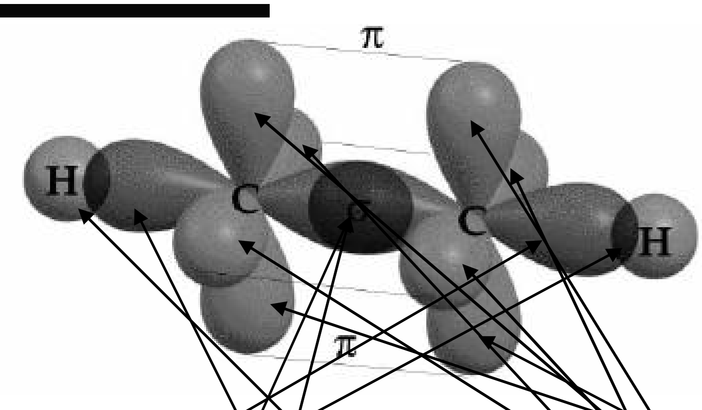
C_2H_2 (Acetylene) Bonding



σ - bonds: C-H (sp - 1s)

C-C (sp - sp)

π - bonds: C-C (p_z - p_z)

C-C (p_y - p_y)

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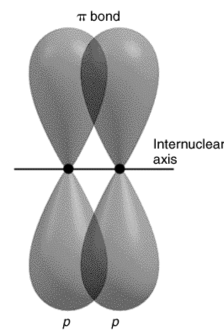
Multiple Bonds

- **Single Bonds**
  - *End-on* orbital overlap: **σ-bond**
- **Double Bonds**
  - **σ-bond** *plus* a **π-bond**
- **Triple Bonds**
  - **σ-bond** *plus* ***TWO*** **π-bonds**



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Delocalized Bonding

- How can we better understand the bonding represented by Lewis *resonance structures?*

Example: **NO_3^-**

-three Lewis resonance structures

-1 N=O bond and 2 N-O bonds: 3 possible combinations

-trigonal planar geometry:

-**N:** 3 e^- in sp^2 hybrid orbitals
1 e^- in p_z orbital

-**O:** 2 unpaired e^- in p_z and p_y orbitals

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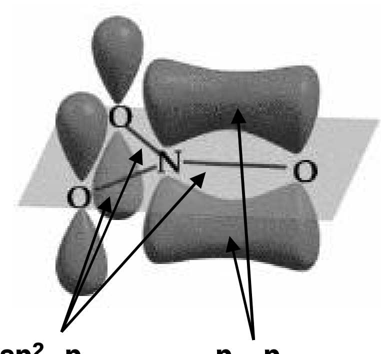
Bond Delocalization in NO_3^-

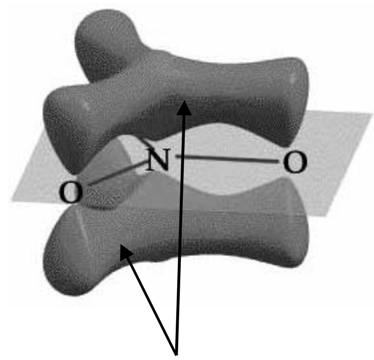


sp^2 - p_y

σ - bonds

p_z - p_z

π - bond



Delocalized **π - bond**

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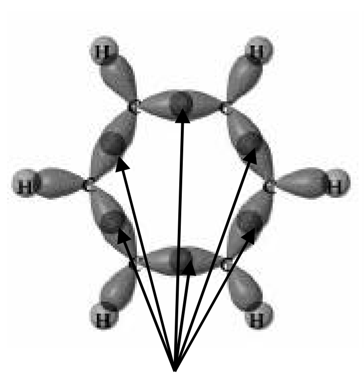
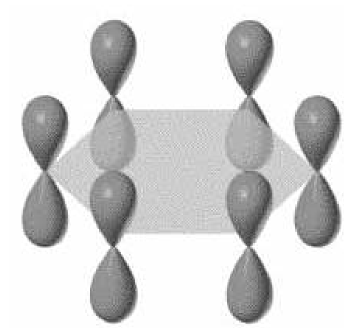
Benzene (C_6H_6)



σ - bonds: sp^2 - sp^2 (C-C)



Carbon p_z - orbitals

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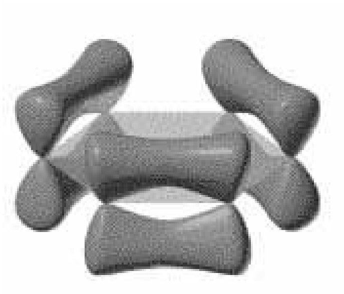
Benzene: Delocalized π-orbitals



Localized **π-bonds**

(two structures possible)

***De*localized** **π-bonding**

(***one*** structure only)

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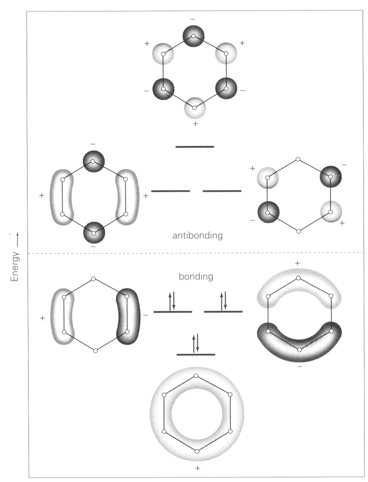
Delocalized Orbital Energies

- Delocalized e^- fill a *new* set of **molecular orbitals** formed by linear combinations of the six carbon p_z-orbitals:



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