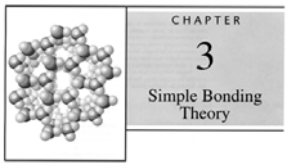
5. Molecular Orbitals



5.1 Formation of Molecular Orbitals (MO's) from Atomic Orbitals (AO's)

$$\Psi = c_a\Psi_a + c_b\Psi_b$$

Ψ = molecular wave function
Ψ_a and Ψ_b = atomic wave functions
c_a and c_b = adjustable coefficients

for H_2

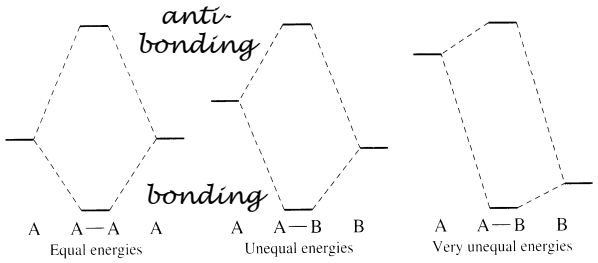
$H_a + H_b$ $\quad \Psi(\sigma) = N[c_a\Psi(1s_a) + c_b\Psi(1s_b)] = 1/\sqrt{2}\,[\Psi(1s_a) + \Psi(1s_b)]$

$H_a - H_b$ $\quad \Psi(\sigma^*) = N[c_a\Psi(1s_a) - c_b\Psi(1s_b)] = 1/\sqrt{2}\,[\Psi(1s_a) - \Psi(1s_b)]$

$c_a = c_b = 1$ and $N = 1/\sqrt{2}$ for σ and σ^*
Approximation! Remember, an anti-bonding MO is more anti-bonding then a bonding is bonding

5. Molecular Orbitals

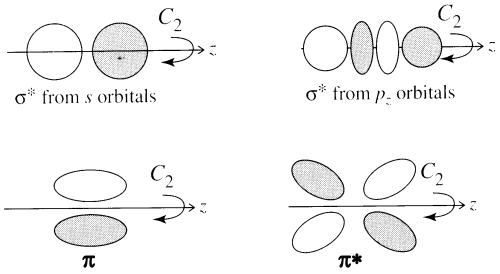
The significance of c_a and c_b in: $\Psi_{A-B} = c_a\Psi_a \pm c_b\Psi_b$



…there can be **non-bonding orbitals** as well!

5. Molecular Orbitals

The σ, π and σ, π* notation*

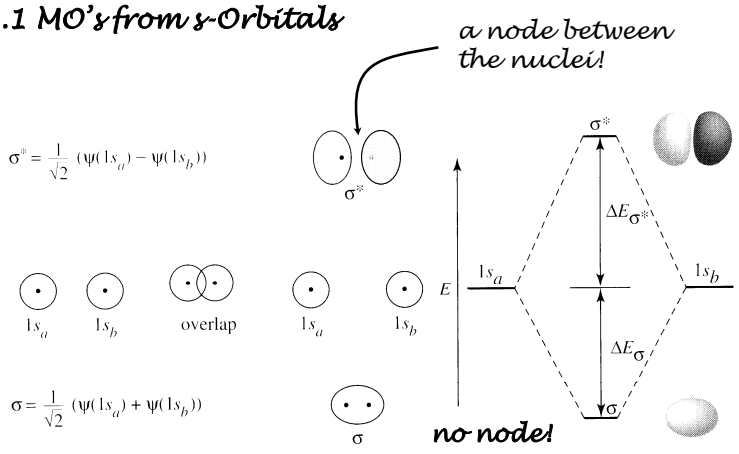


…don't forget about **δ and δ* orbitals!**

5. Molecular Orbitals

5.1.1 MO's from s-Orbitals

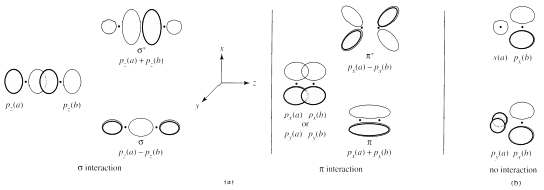
a node between the nuclei!

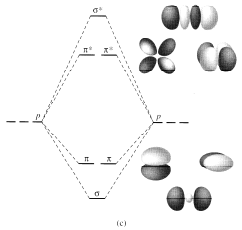


no node!

5. Molecular Orbitals

5.1.2 MO's from p-Orbitals





however, there can be nodes in bonding MO's from p- and d-orbitals!

FIGURE 5-2 Interactions of *p* Orbitals. (a) Formation of molecular orbitals. (b) Orbitals that do not form molecular orbitals. (c) Energy level diagram.

5. Molecular Orbitals

5.1.3 MO's from d-Orbitals

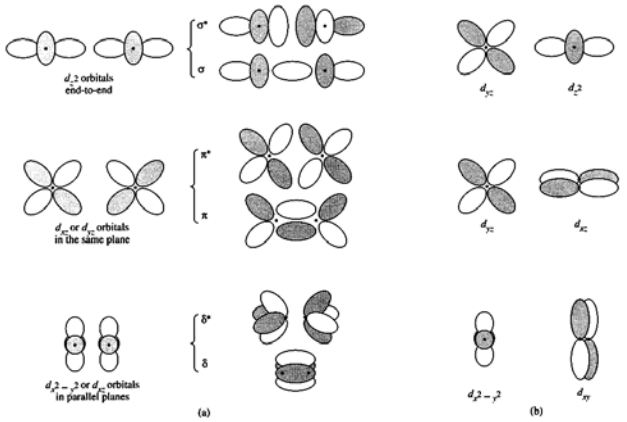
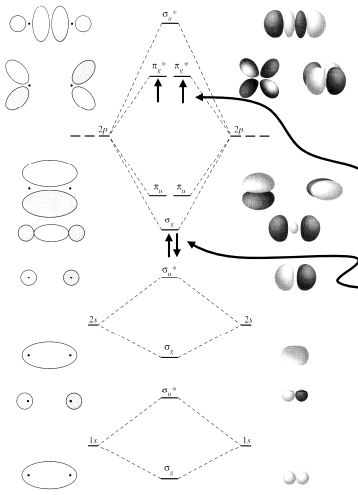


FIGURE 5-3 Interactions of *d* Orbitals. (a) Formation of molecular orbitals. (b) Orbitals that do not form molecular orbitals.

5.2 Homonuclear Diatomic Molecules



$$\text{Bond order} = \frac{1}{2}\left[\begin{pmatrix}\text{number of electrons}\\ \text{in bonding orbitals}\end{pmatrix} - \begin{pmatrix}\text{number of electrons}\\ \text{in antibonding orbitals}\end{pmatrix}\right]$$

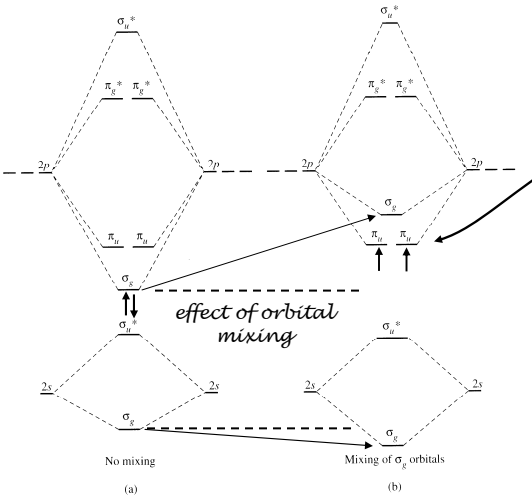
MO-Diagram for the first 10 elements:

Works great for O_2 -> explains O_2's paramagnetism

But predicts B_2 to be diamagnetic

-> Orbital Mixing!

5.2 Homonuclear Diatomic Molecules



degenerate orbitals

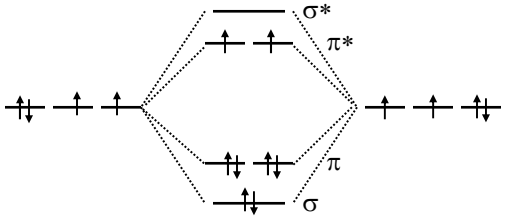
- Aufbau principle
- Hund's Rule
- Pauli's Principle:

B_2 is paramagnetic!
BO = 1, no σ-bond!

C2 is diamagnetic
BO = 2, two π-bonds

C—C Distance (pm)	
C=C (gas phase)	132
H—C≡C—H	120.5
CaC_2	119.1

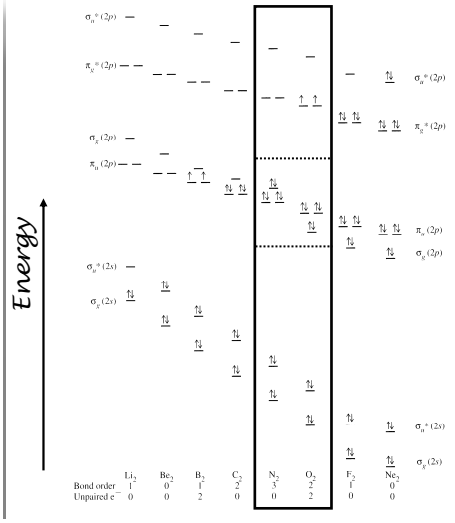
5.2 Homonuclear Diatomic Molecules



	Bond Order	*Internuclear Distance (pm)*
O_2^+ (dioxygenyl)[7]	2.5	112.3
O_2 (dioxygen)[8]	2.0	120.07
O_2^- (superoxide)[9]	1.5	128
O_2^{2-} (peroxide)[8]	1.0	149

NOTE: Oxygen-oxygen distances in O_2^- and O_2^{2-} are influenced by the cation. This influence is especially strong in the case of O_2^{2-} and is one factor in its unusually long bond distance.

5.2 Homonuclear Diatomic Molecules

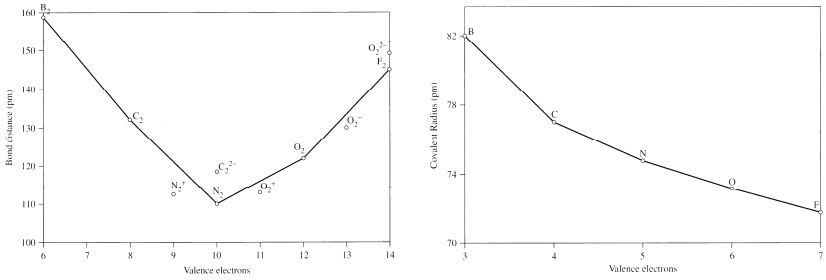


Energy of all orbitals decreases as increased nuclear charge attracts the electrons more strongly

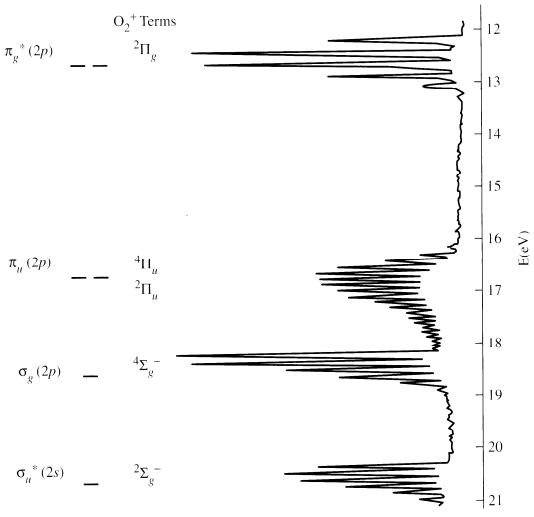
Effect is larger for s-orbitals!

5.2 Homonuclear Diatomic Molecules

Bond Distances & Orders, Atomic Number & Radii



5.2 Homonuclear Diatomic Molecules



Photoelectron Spectroscopy:

$O_2 + h\nu \rightarrow O_2^+ + e^-$

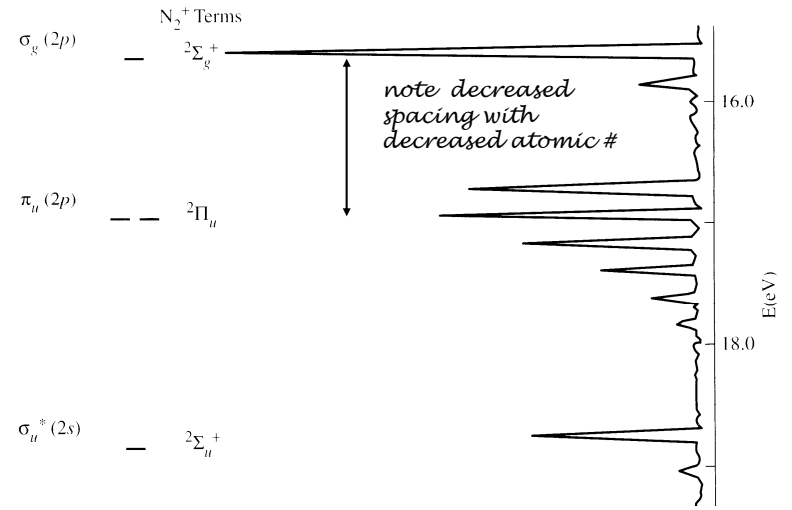
Ionization Energy (**binding energy**) =

$h\nu$ – kinetic energy of expelled e^-

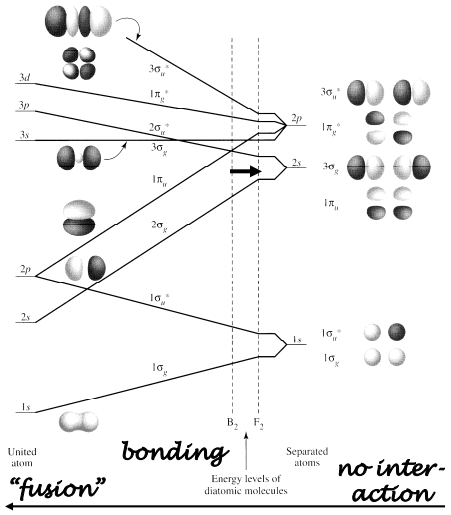
Remember

- Morse-Potential
- Vibrational Fine Structure

5.2 Homonuclear Diatomic Molecules



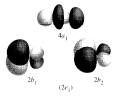
5.2 Homonuclear Diatomic Molecules

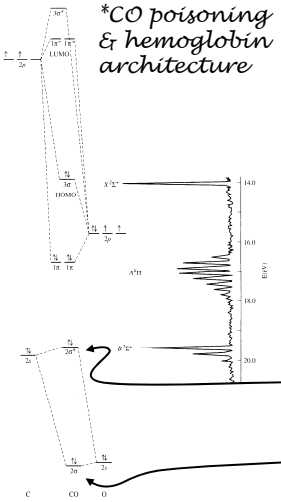


A Correlation Diagram for Diatomic Molecules

5.3 Heteronuclear Diatomic Molecules

very important* empty anti-bonding MO's





*CO poisoning & hemoglobin architecture

Electronegativity
2.54 3.61

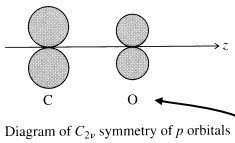
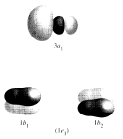


Diagram of C_{2v} symmetry of p orbitals

very important* filled bonding MO

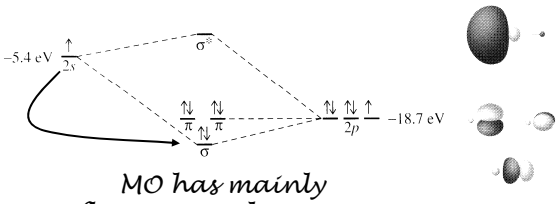


greater nuclear charge, lower energy AO's more contracted orbitals

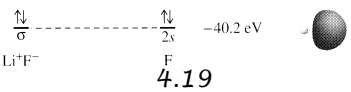
MO has mainly carbon character

MO has mainly oxygen character

5.3 Ionic Compounds & Molecular Orbitals



MO has mainly fluorine p_z-character
-> Li^+ and F^- (p^6)



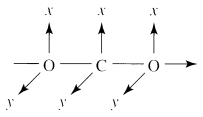
Li F
0.91 4.19
Electronegativity

5.4 Molecular Orbitals for Larger Molecules

5.4.2 Carbon Dioxide's Molecular Orbital Diagram

O=C=O

$D_{\infty h}$ -> D_{2h}



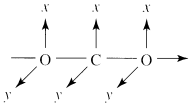
D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$		
A_g	1	1	1	1	1	1	1	1		x^2, y^2, z^2
B_{1g}	1	1	−1	−1	1	1	−1	−1	R_z	xy
B_{2g}	1	−1	1	−1	1	−1	1	−1	R_y	xz
B_{3g}	1	−1	−1	1	1	−1	−1	1	R_x	yz
A_u	1	1	1	1	−1	−1	−1	−1		
B_{1u}	1	1	−1	−1	−1	−1	1	1	z	
B_{2u}	1	−1	1	−1	−1	1	−1	1	y	
B_{3u}	1	−1	−1	1	−1	1	1	−1	x	

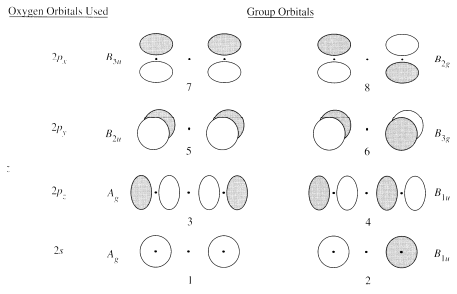
5.4 Molecular Orbitals for Larger Molecules

5.4.2 Carbon Dioxide's Molecular Orbital Diagram

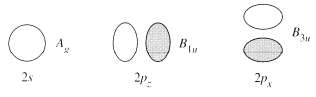
O=C=O

$D_{\infty h}$ -> D_{2h}



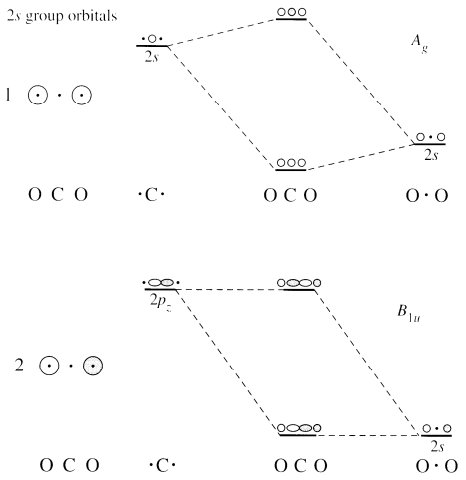


Oxygen Group Theory

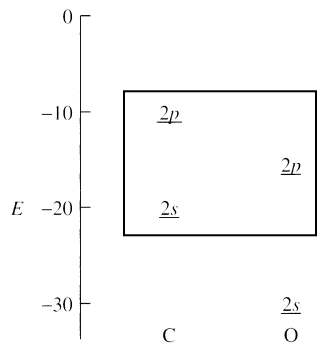


Carbon Group Theory

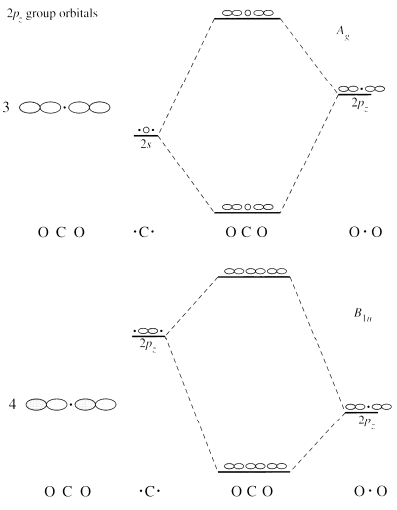
5.4 Molecular Orbitals for Larger Molecules



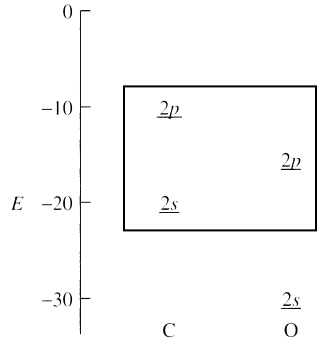
Orbital	2s	2p
Carbon	−19.4 eV	−10.7 eV
Oxygen	−32.4 eV	−15.9 eV



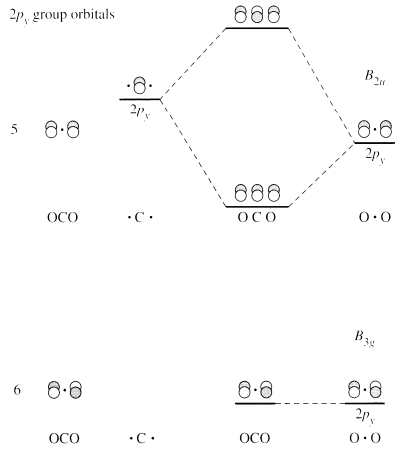
5.4 Molecular Orbitals for Larger Molecules



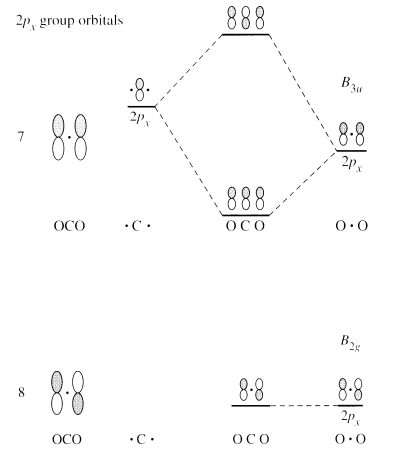
Orbital	2s	2p
Carbon	−19.4 eV	−10.7 eV
Oxygen	−32.4 eV	−15.9 eV



5.4 Molecular Orbitals for Larger Molecules

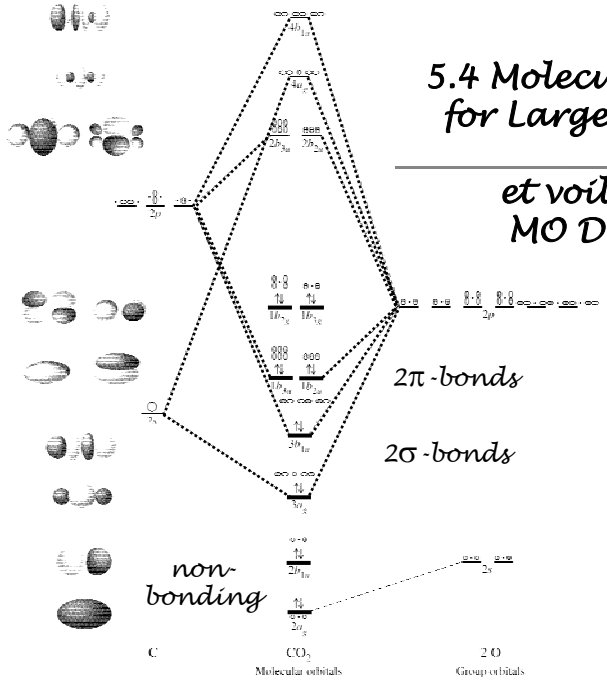


5.4 Molecular Orbitals for Larger Molecules



5.4 Molecular Orbitals for Larger Molecules

et voila... CO_2 MO Diagram



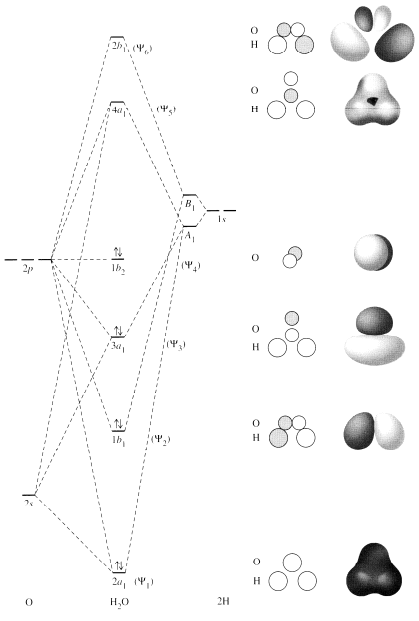
2π -bonds

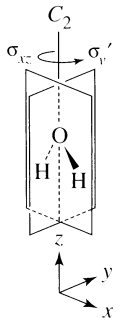
2σ -bonds

$:O=C=O:$

5.4 Molecular Orbitals for Larger Molecules

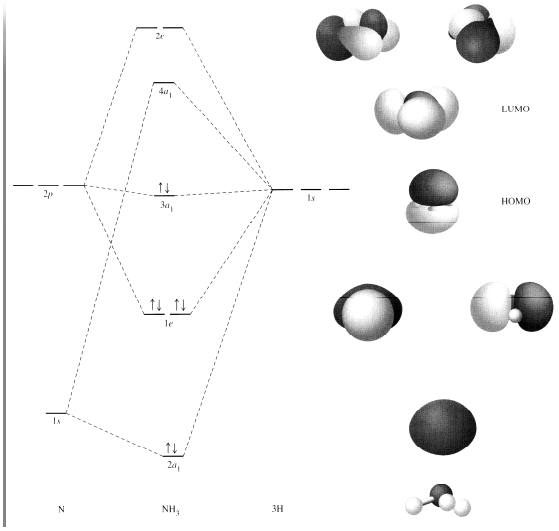
e.g. Water





5.4 Molecular Orbitals for Larger Molecules

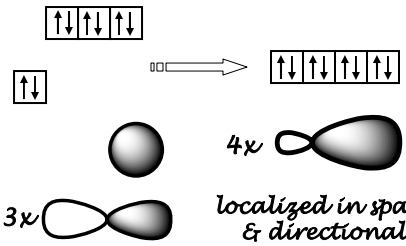
e.g. Ammonia



5.4 Molecular Shapes & Hybrid Orbitals

Combination of Atomic Orbitals to form **Hybrid Orbitals**

Old but very useful concept!



localized in space & directional

Try this for NH_3, H_2O, *and* CO_2