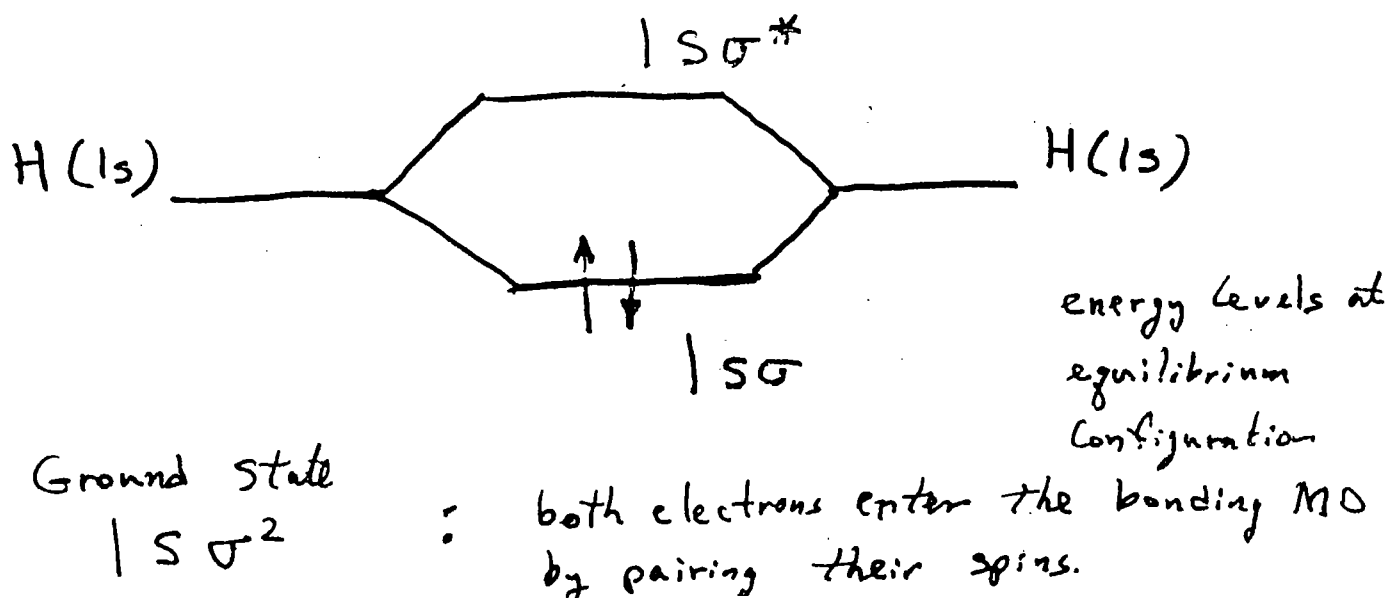


Extension to Diatomic Molecules LECTURE 20

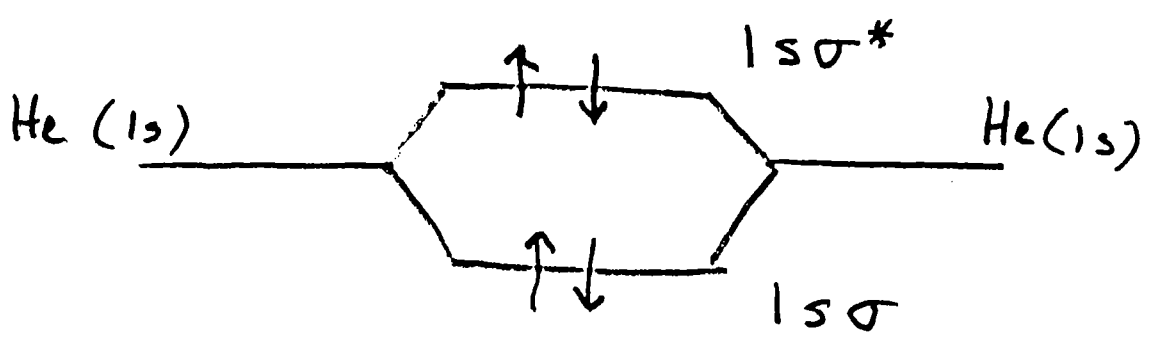
With more Electrons

- Use H_2^+ as a framework
- Construct MO's by linear combination of AO's
- add electrons to lowest available MO with Pauli exclusion principle
- If degenerate MO's - add electrons to each individual MO before doubly occupying
- apply Hund's rule - most parallel spins (unpaired) preferred

Consider H_2



Consider He_2



One-1s orbital from each atom

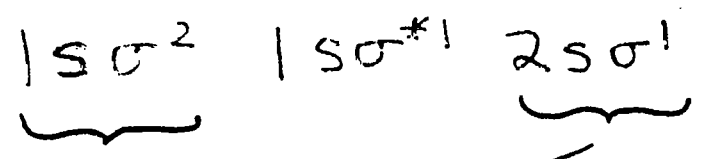
- Anti bond is slightly more antibonding than a bond is bonding.

- Helium dimer is less stable than separated atoms $\therefore \text{He}_2$ does not form

Consider one $\text{He}(1s) \rightarrow (2s)$

$2s\sigma \equiv$ MO formed from overlap of 2s-orbital

Then



the bonding exceeds the antibonding

Excited dimers \equiv eximers do form.

Homonuclear Diatomic Molecules

$\sigma + \pi$ MO's

Assumptions

- Core orbitals of the inner closed shells of the atoms are too compact for much overlap and can be ignored
- higher virtual orbitals assumed too high in energy to be important
- The MO's can be constructed using only valence orbitals

Consider the 2nd row atoms

As for the previous 1s case:
 the bonding of the two atoms gives \Rightarrow

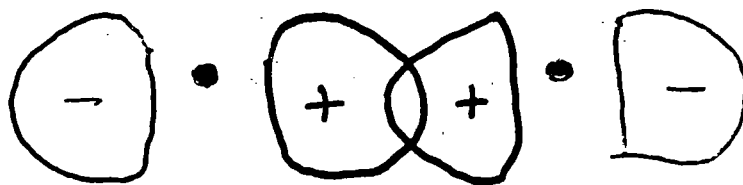
$2s\sigma$	bonding
$2s\sigma^*$	antibonding

Consider Situation Where p-orbitals on the two atoms are available for bonding

I The internuclear axis defines the z-axis of the coordinate system.

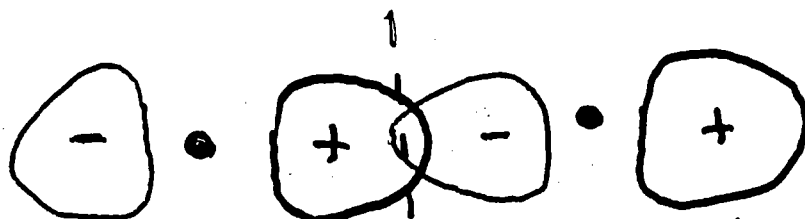
Consider the overlap of the two $2p_z$ - orbitals directed along the internuclear axis.

$2p\sigma$



Constructive interference \equiv bonding

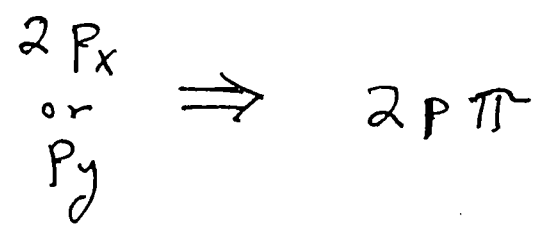
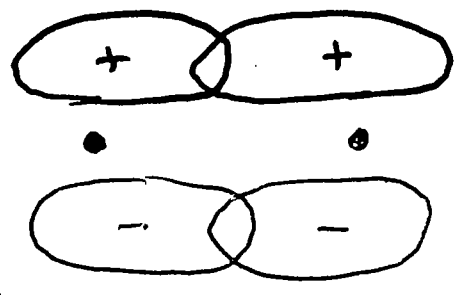
$2p\sigma^*$



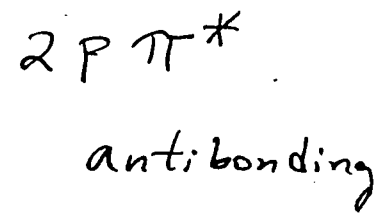
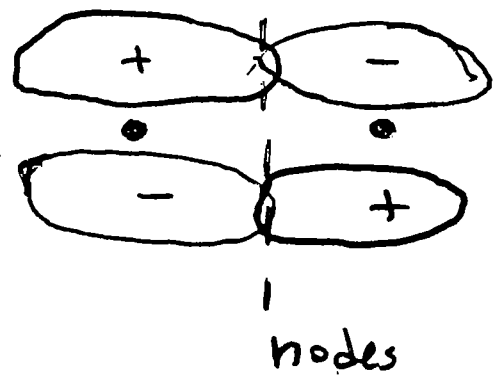
destructive \equiv antibonding
node

II

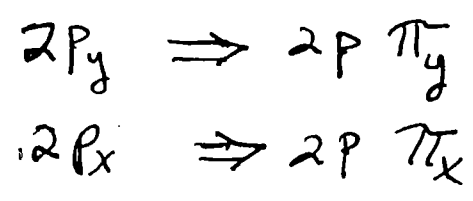
Consider broad-side-on interaction of $2p_x$ and $2p_y$



Constructive interference
bonding orbital



When viewed along the axis of the molecule, a π orbital looks like a p-orbital

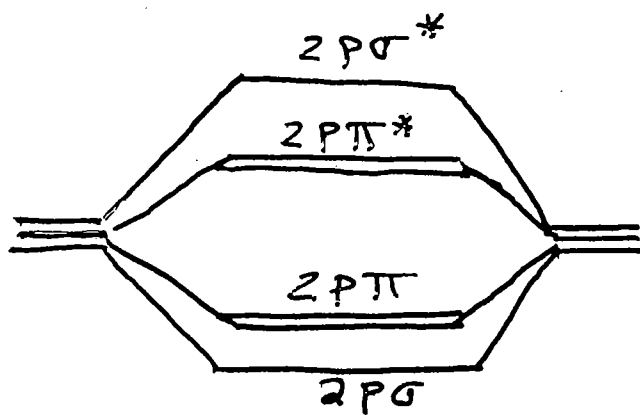


The two $2p\pi$ are degenerate

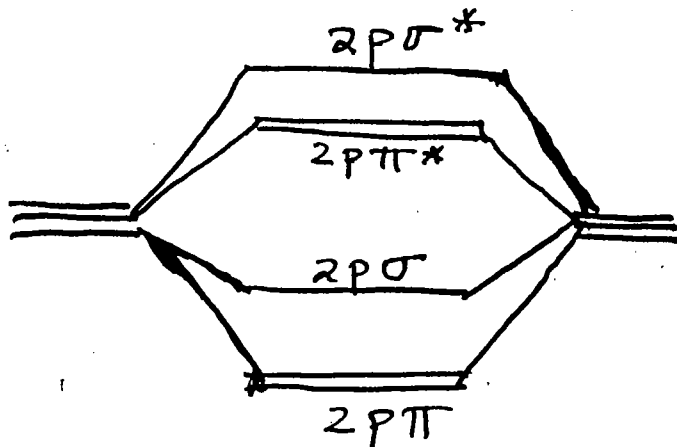
Expectations for bonding due to σ and π MO's

- Since the overlap occurs off-axis and away from the optimum bonding region, π orbitals are expected to be less strongly bonding than σ -orbitals
- But, the above is not always true, in fact often not the case!

Expected



More
Usual
Case



Can also have S-p overlap

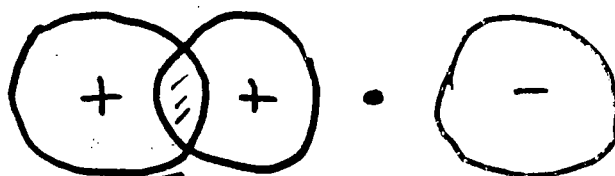
7

(strong bonds usually arise from the overlap of atomic orbitals having similar energies)

But - possibility of S-p overlap depends on the symmetry of the arrangement.

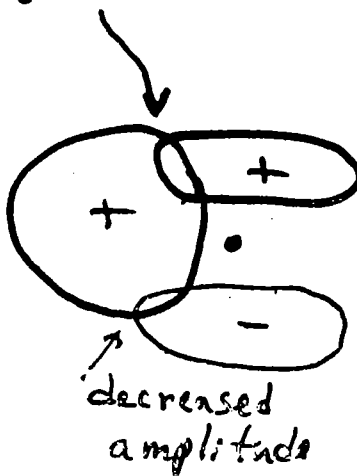
I End-on overlap leads to formation of an axially symmetric σ -bond

2S - 2P_z
overlap



enhanced amplitude

2S - 2P_x
overlap
no contribution
to bonding



broad side
overlap
gives no
net
accumulation
of electron
density

Measurement of the Extent of the overlap of two orbitals

Overlap integral :

$$S = \int \psi_A^* \psi_B d\tau$$

- this value is small if ψ_A (or ψ_B) is small when the other is large

- when $S = 0$ \equiv termed Orthogonal wave functions

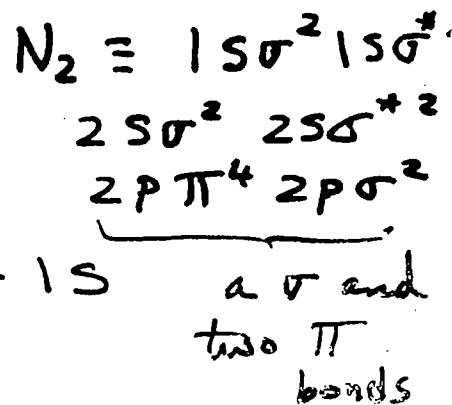
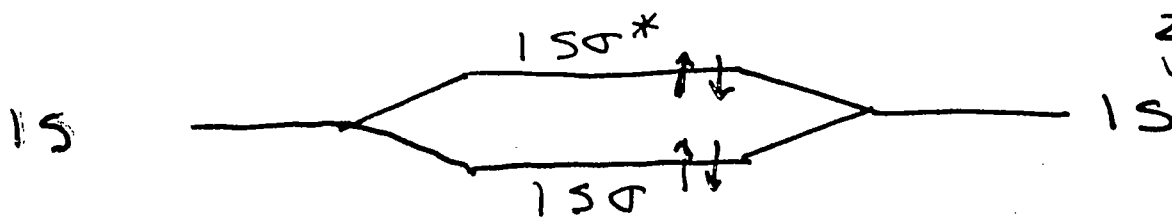
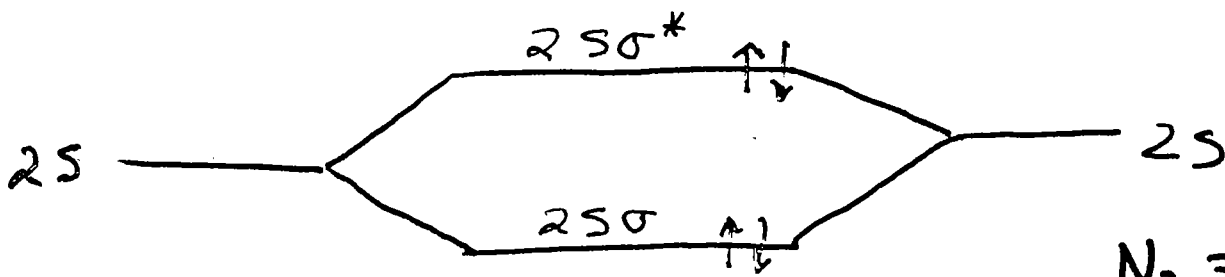
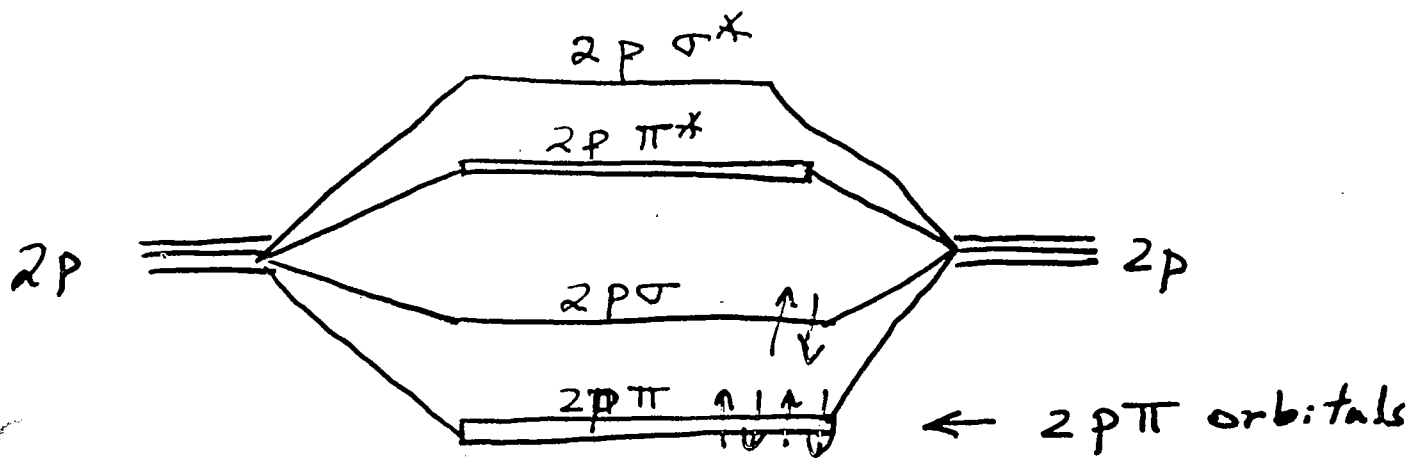
$S = 1$ the two are identical

Homonuclear Diatomic

Example : N_2

$2Z = 14$

\therefore 14 electrons to be accommodated



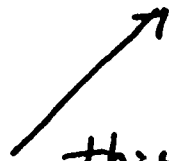
Bond order = bonds - antibonds = $5 - 2 = 3$ Triple Bond

Consider O_2

$$2Z = 2(8) = 16$$

Similar to N_2 , but 2 electrons

go into $2p\pi^*$



this offsets one π bond

\therefore Bond order = 2

\equiv double bond

1 σ and one π bond

From Aufbau & Hund : the two added

electrons for O_2 go into :

$2p\pi_x^*$

and

$2p\pi_y^*$

with parallel
spins

net spin angular momentum = $2S+1 = 2(1)+1 = 3$
 \therefore triplet

Unpaired spins - O_2 is paramagnetic - moves into
a magnetic field