

# *Molecular Orbital Approach to Bonding*

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The following slides were mainly a gift from Professor Martyn Poliakoff Of the Department of Chemistry in Nottingham, England. Tom Poliakoff also used these slides and prepared them, to my knowledge. You might also check The MIT open courseware lecture to refresh your memory of molecular orbitals.

## MIT Open Courseware lecture

<https://www.youtube.com/watch?v=llaa-iEYDLI>

HF

<https://www.youtube.com/watch?v=estiedAIXII>

$B_2H_6$

<https://www.youtube.com/watch?v=GD5CrjyAKx4>

CO

<http://www.chemtube3d.com/orbitalsCO.htm>

**Molecular Orbitals are constructed from overlap of atomic orbitals that match symmetry and in Energy**

**Table 1.8** Valence state ionization energies (electron volts)

Element	1s	2s	2p	3s	3p	4s	4p
H	13.6	—	—	—	—	—	—
He	24.6	—	—	—	—	—	—
Li	—	5.4	—	—	—	—	—
Be	—	9.3	—	—	—	—	—
B	—	14.0	8.3	—	—	—	—
C	—	19.4	10.6	—	—	—	—
N	—	25.6	13.2	—	—	—	—
O	—	32.3	15.8	—	—	—	—
F	—	40.2	18.6	—	—	—	—
Ne	—	48.5	21.6	—	—	—	—
Na	—	—	—	5.1	—	—	—
Mg	—	—	—	7.6	—	—	—
Al	—	—	—	11.3	5.9	—	—
Si	—	—	—	14.9	7.7	—	—
P	—	—	—	18.8	10.1	—	—
S	—	—	—	20.7	11.6	—	—
Cl	—	—	—	25.3	13.7	—	—
Ar	—	—	—	29.2	15.8	—	—
K	—	—	—	—	—	4.3	—
Ca	—	—	—	—	—	6.1	—
Zn	—	—	—	—	—	9.4	—
Ga	—	—	—	—	—	12.6	6.0
Ge	—	—	—	—	—	15.6	7.6
As	—	—	—	—	—	17.6	9.1
Se	—	—	—	—	—	20.8	10.8
Br	—	—	—	—	—	24.1	12.5
Kr	—	—	—	—	—	27.5	14.3

Source: DeKock, R. L.; Gray, H. B. *Chemical Structure and Bonding*; Benjamin/Cummings: Menlo Park, CA, 1980; p. 227.

## Valence Bond Approach: Localized Bonds, just like Lewis Structures and

**VSEPR**

Basis of VB approach: overlap orbitals in each bond separately. Each bond is **LOCALISED** between two atoms.

### MOLECULAR ORBITAL APPROACH

In molecular orbital (MO) approach - overlap orbitals for the whole molecule - bonding is therefore **DELOCALISED**. We will look first at **DIATOMIC MOLECULES** and only later move on to **POLYATOMIC MOLECULES**.

### MOLECULAR ORBITAL THEORY FOR DIATOMIC MOLECULES

In principle, set up Schrödinger wave equation for molecule and solve it.

Solution will involve **molecular orbitals** - similar to atomic orbitals - but **centred around all of the nuclei in molecule**. Each defined by sets of quantum numbers, with electron probability density determined by  $\psi^2$ , where  $\psi$  = molecular wave function.

**Approximate method:**

At any moment, electron near one nucleus - approximate behaviour like electron in atomic orbital for that atom. Over time - electron associated with other nuclei in molecule. Therefore construct molecular orbitals (m.o.'s) by forming:

**L**inear **C**ombination of **A**tomic  
**O**rbitals

It is this, **LCAO**, method which we will use to construct m.o.'s.

Simplest example -  $H_2$ : two H atoms  $H_A$  and  $H_B$

Only two a.o.'s ( $1s_A$ ,  $1s_B$ ) to form linear combinations.

General rule:

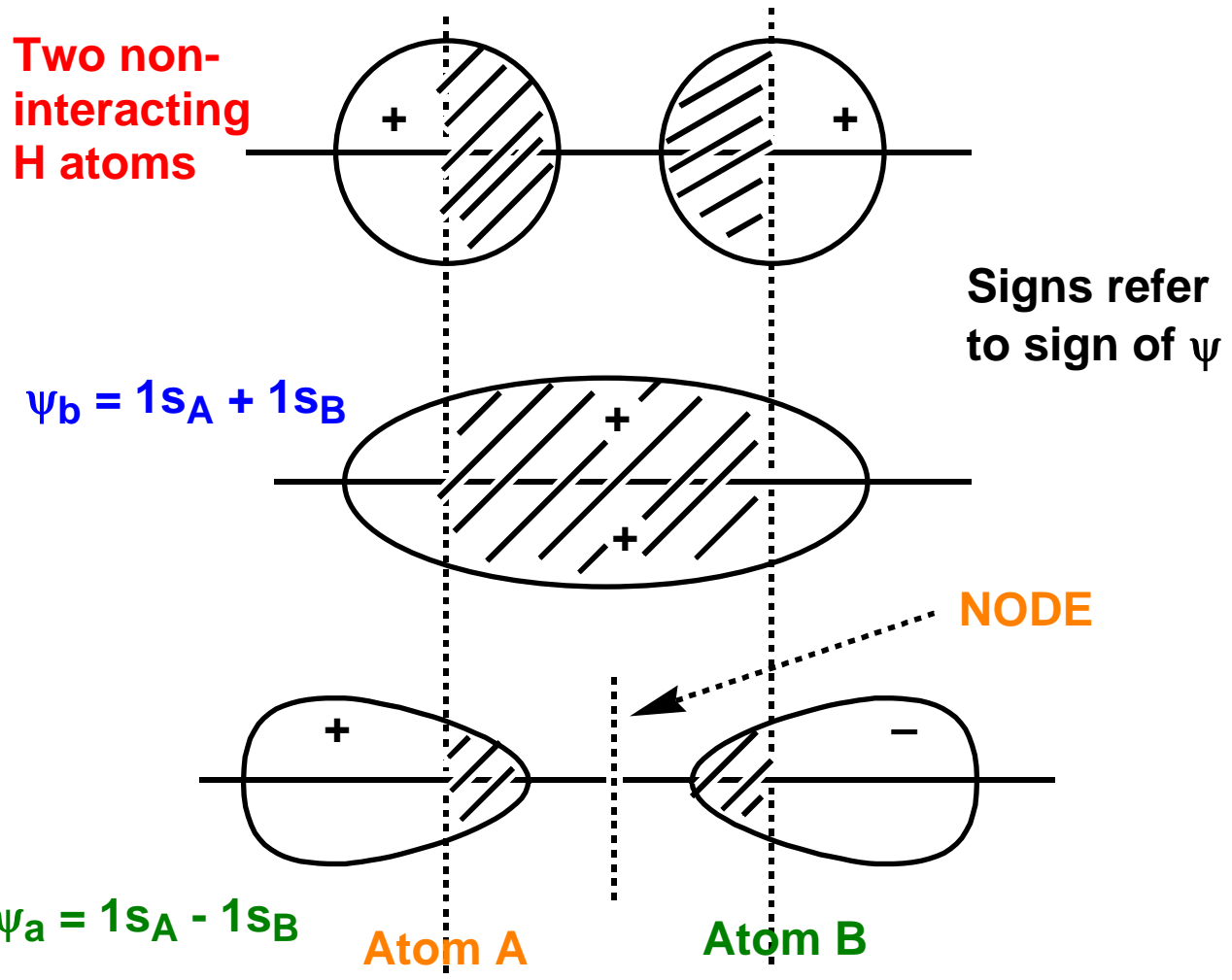
$n$  a.o.'s  $\longrightarrow$   $n$  m.o.'s

So we can only construct 2 m.o.'s for  $H_2$  - and these are:

$$\psi_b = 1s_A + 1s_B \quad \text{and} \quad \psi_a = 1s_A - 1s_B$$

i.e. the sum ( $\psi_b$ ) and the difference ( $\psi_a$ ) of the constituent a.o.'s.

Consider the electron distribution in each of these:



Consider in each case the **INTERNUCLEAR REGION**

Probability of finding electron there is:

$$\psi_b > 1s_A, 1s_B > \psi_a$$

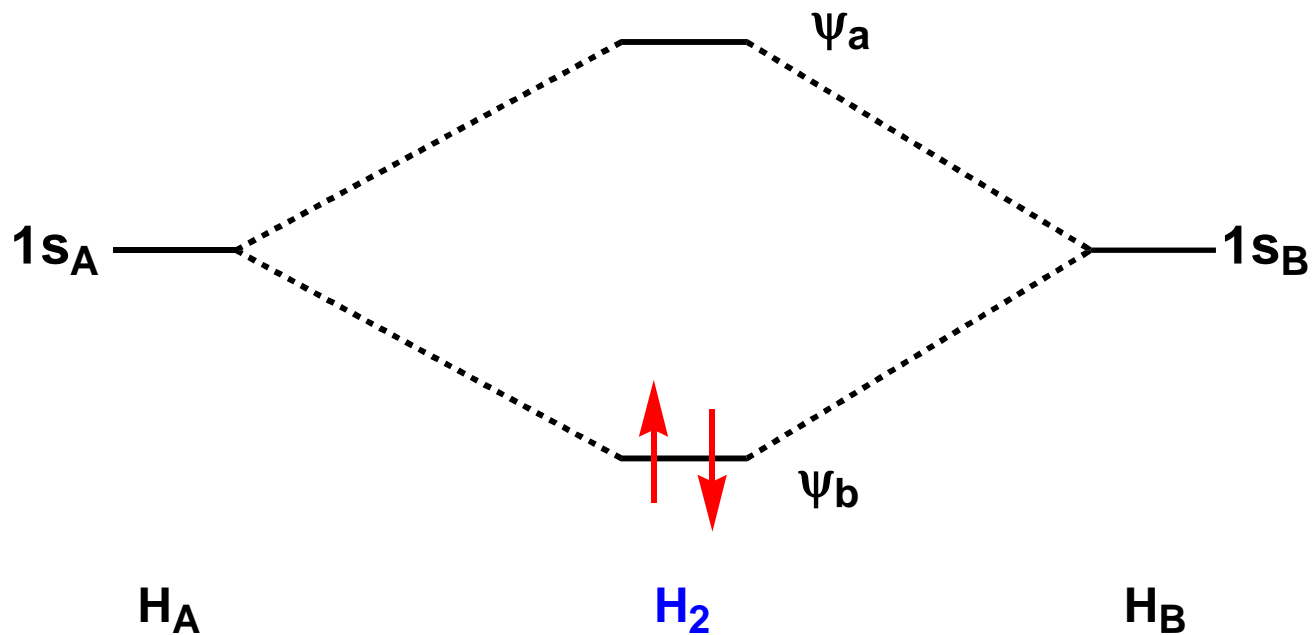
Electron in this region attracted to **BOTH** nuclei, therefore most favourable position. Hence, **electron in  $\psi_b$  will be at lower energy than in non-interacting a.o.'s, and electron in  $\psi_a$  will be at higher energy still.**

**Thus an electron in  $\psi_b$  will hold the nuclei together, one in  $\psi_a$  will push them apart.**

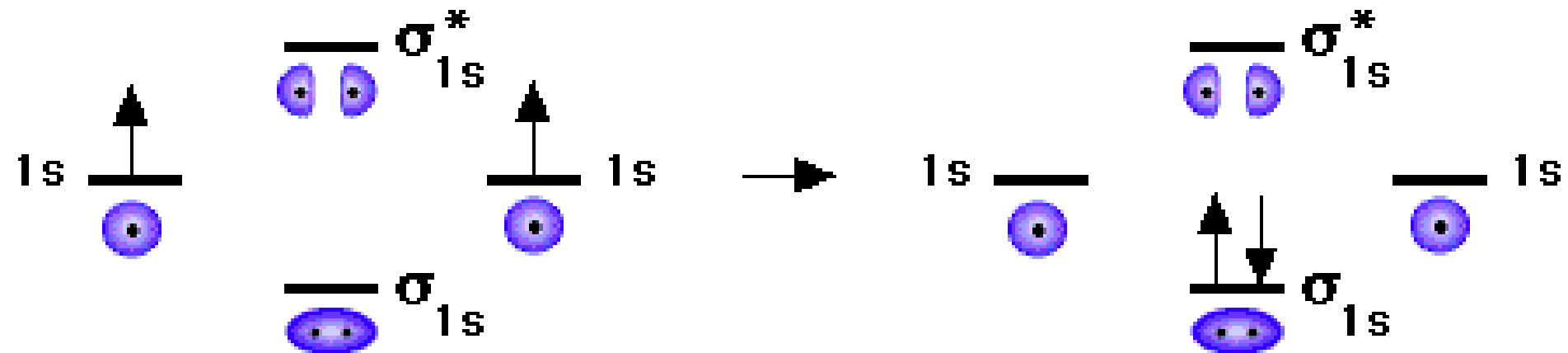
**$\psi_b$  is a BONDING m.o.,**

**$\psi_a$  is an ANTI-BONDING m.o.**

Thus we can draw **ENERGY LEVEL DIAGRAM** for m.o.'s of  $H_2$  :

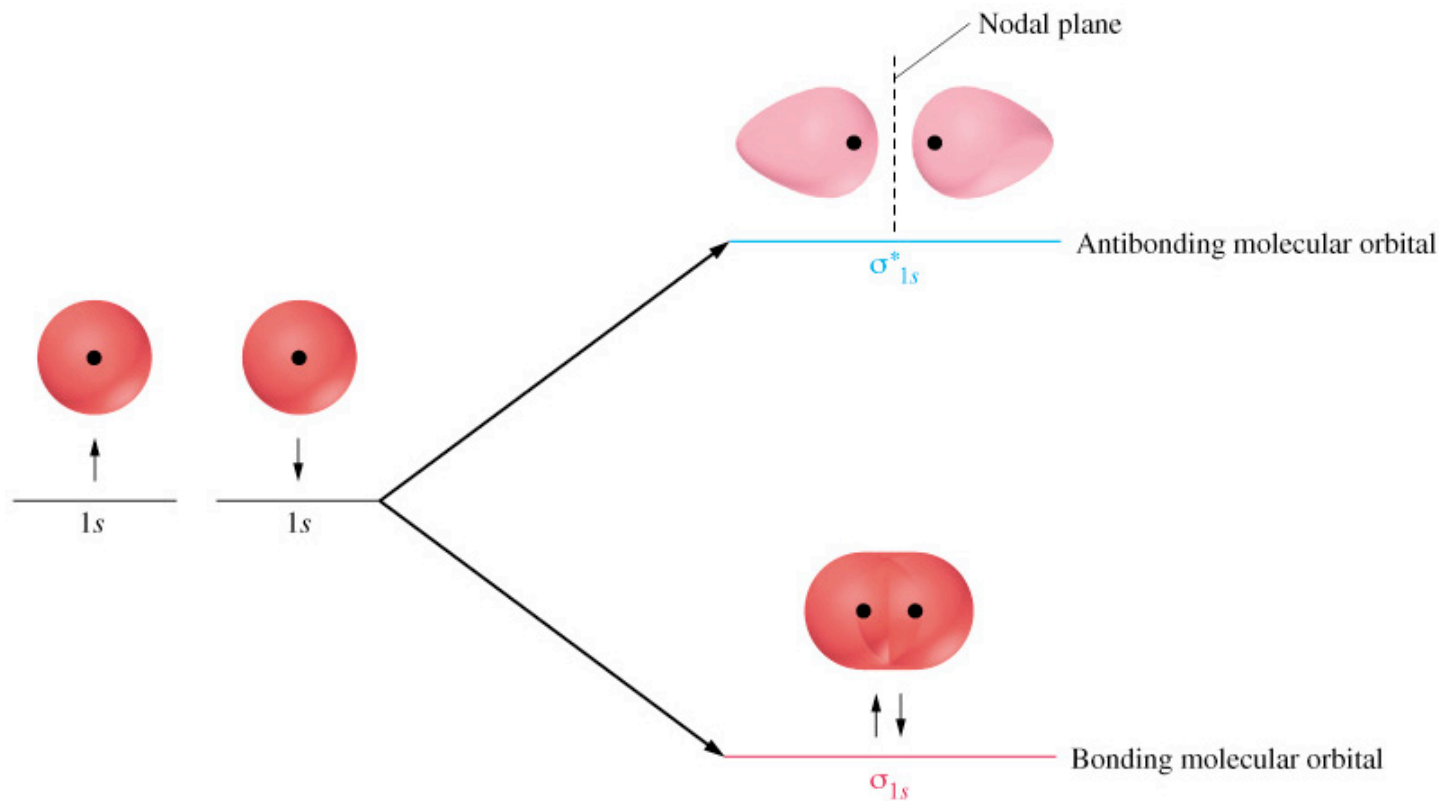


**By aufbau & Pauli principles - the 2 electrons go into  $\psi_b$  - with paired spins.**





# MO's for H<sub>2</sub> molecule



<http://www.chemtube3d.com/orbitalsCO.htm>

## BOND ORDER

By Lewis/V.B. theory - **one pair of electrons = one bond.**

To be consistent, in M.O. theory, define BOND ORDER as follows:

$$\text{Bond order} = \frac{[(\text{No. of electrons in bonding m.o.'s}) - (\text{No. of electrons in antibonding m.o.'s})]}{2}$$

Thus, for H<sub>2</sub>, bond order =  $(2 - 0)/2 = 1$  (i.e. a single bond - as expected)

### Magnetic Properties of Molecules

**All electrons paired** - repelled by magnetic field - **DIAMAGNETIC**

**One or more unpaired electrons** - attracted into magnetic field - **PARAMAGNETIC**

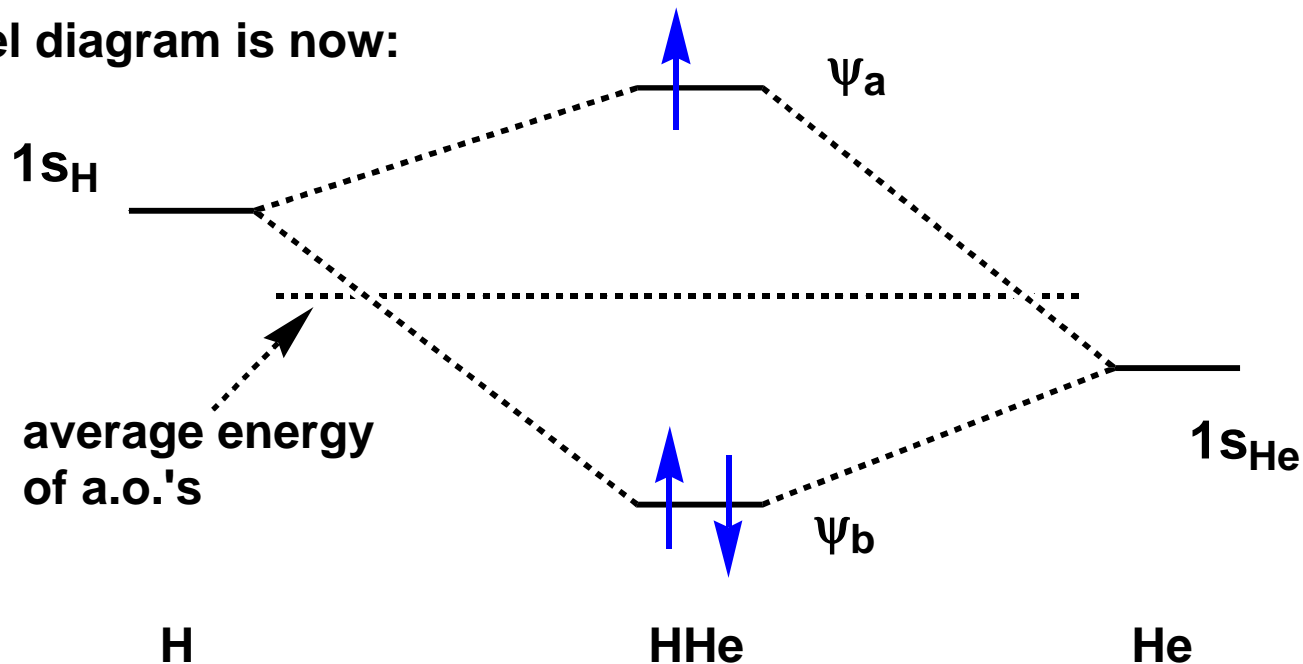
**H<sub>2</sub> is diamagnetic.**

# HETERONUCLEAR DIATOMIC MOLECULES

Simplest would be **HHe**. Differs from  $H_2$  in two ways:

- (1) A.O. energies for H, He different. He - greater nuclear charge, electrons more tightly bound.
- (2) Now three electrons to feed into m.o.'s.

Energy level diagram is now:



For heteronuclear diatomics, m.o.'s formed symmetrically above and below **AVERAGE** energy of constituent a.o.'s

For HHe, bond order =  $(2 - 1)/2 = 1/2$  i.e. v. wk. "1/2" bond - not formed under normal conditions - v. unstable.

Unpaired electron, **PARAMAGNETIC**.

Note for "He<sub>2</sub>" - extra electron in antibonding m.o. - therefore bond order = 0. Molecule does not exist - no force to hold atoms together.

He is monatomic gas.

## M.O.'s for homonuclear diatomics ( $A_2$ ) for elements of first row of the Periodic Table

For  $Li_2$ ,  $Be_2$ ,  $B_2$  etc., more complex than for  $H_2$ ,  $He_2$  - more available a.o.'s - 1s, 2s, 2p. Are there restrictions on overlap?

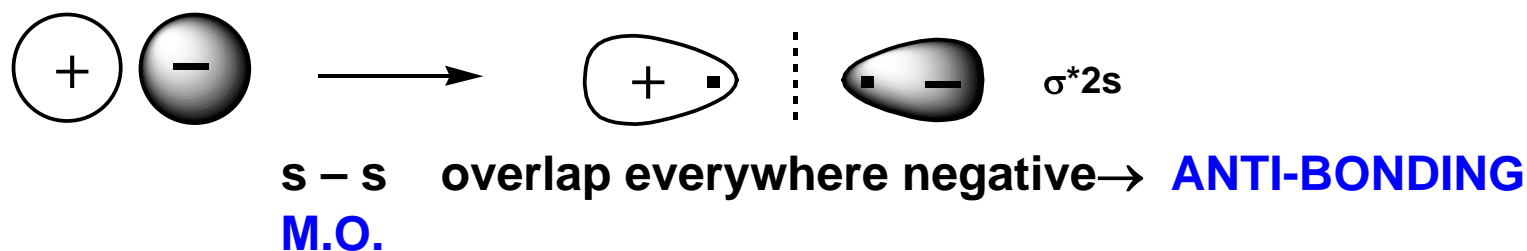
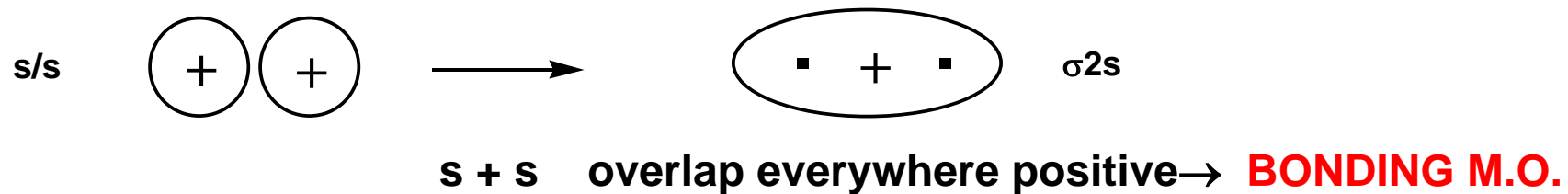
(1) **VALENCE** electrons only - core electrons too close to nucleus, too tightly bound

(2) **Most efficient overlap between orbitals of same energy**, i.e. for homonuclear diatomics this means 2s/2s, 2p/2p (for heteronuclear diatomics - see later)

(3) **SYMMETRY RESTRICTIONS**

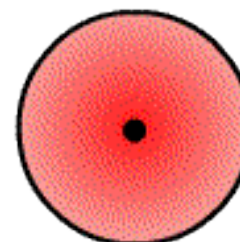
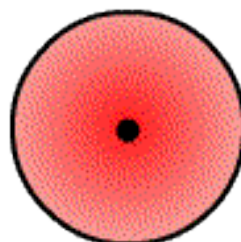
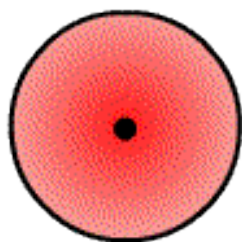
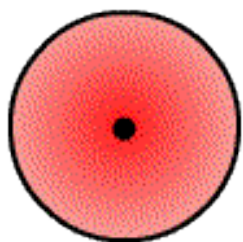
These are best shown pictorially

Let us see how this works for **2s and 2p orbitals**.



Bonding Interaction

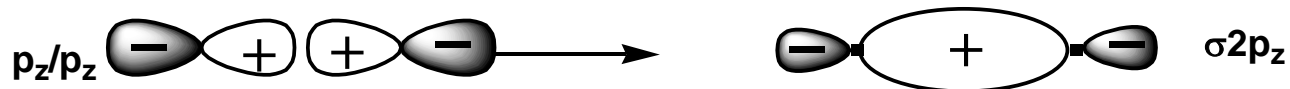
Anti-Bonding Interaction



$$\psi_b = 1s_A + 1s_B$$

$$\psi_a = 1s_A - 1s_B$$

For p orbitals - three per atom. Define z-axis as molecular axis. Hence  $p_z$  orbitals can overlap in same way as s orbitals.



$p_z + p_z$  overlap everywhere positive  $\rightarrow$  **BONDING M.O.**

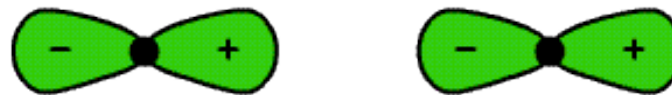
Bonding Interaction



$$\psi_b = p_z + p_z$$

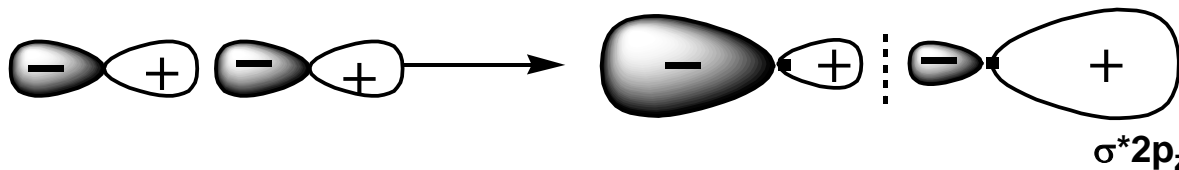
End-to-end overlap forms  $\sigma 2p_z$  MO

Anti-Bonding Interaction



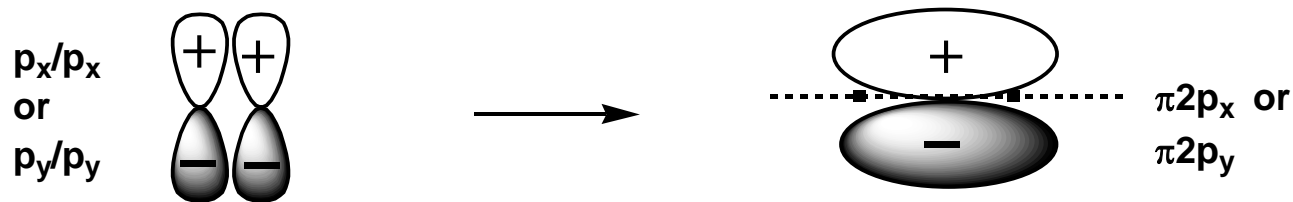
$$\psi_a = p_z - p_z$$

End-to-end overlap forms  $\sigma^* 2p_z$  MO



$p_z - p_z$  overlap everywhere negative  $\rightarrow$  **ANTI-BONDING M.O.**

$p_x$ ,  $p_y$  orbitals are perpendicular to axis, but can still interact



$p_x + p_x$  overlap everywhere positive  $\rightarrow$  **BONDING M.O.**

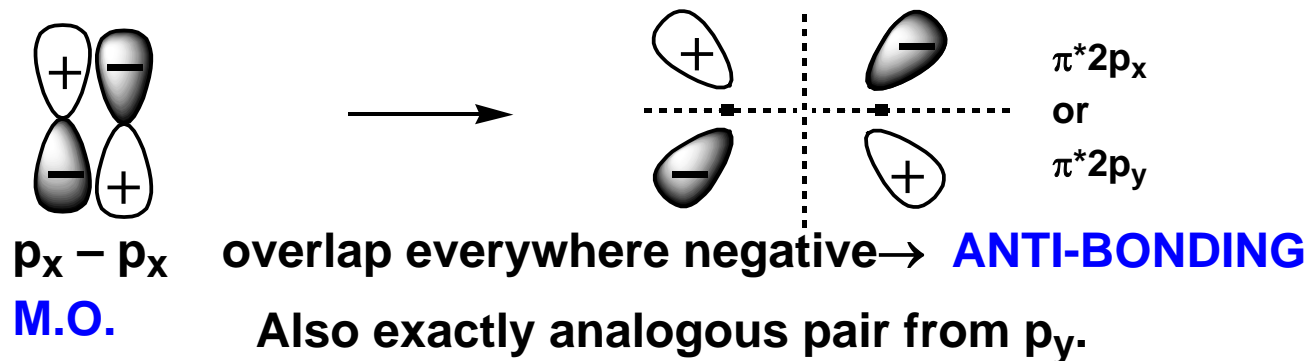
## Bonding Interaction



$$\psi_b = p_x + p_x \text{ or } \psi_b = p_y + p_y$$

Side-to-side overlap forms  $\pi 2p_x$  or  $\pi 2p_y$  MO





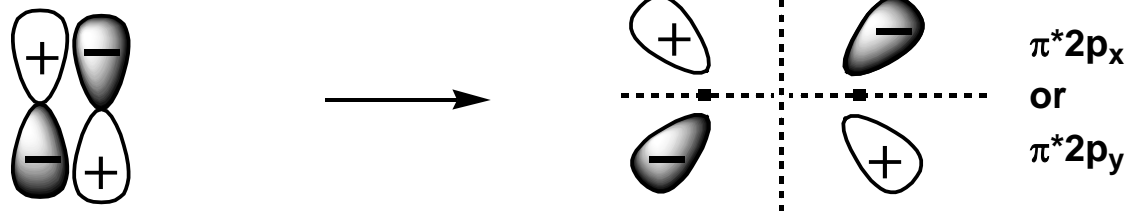
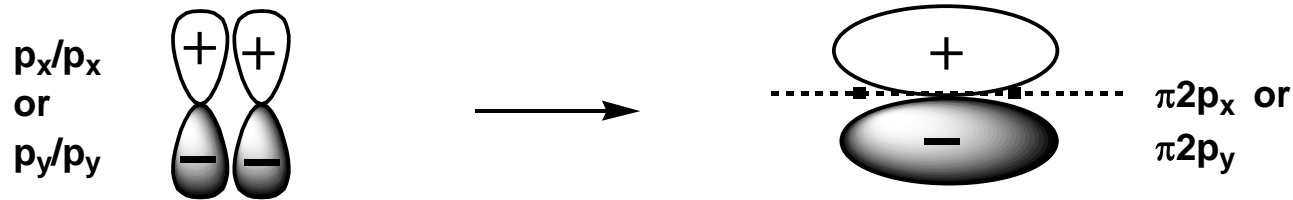
Need to consider all possibilities (could be needed for heteronuclear diatomics)

## Anti-Bonding Interaction



$$\psi_a = p_x - p_x \text{ or } \psi_b = p_y - p_y$$

Side-to-side overlap forms  $\pi^*2p_x$  or  $\pi^*2p_y$  MO



## Bonding Interaction



$$\psi_b = p_x + p_x \text{ or } \psi_b = p_y + p_y$$

Side-to-side overlap forms  $\pi 2p_x$  or  $\pi 2p_y$  MO

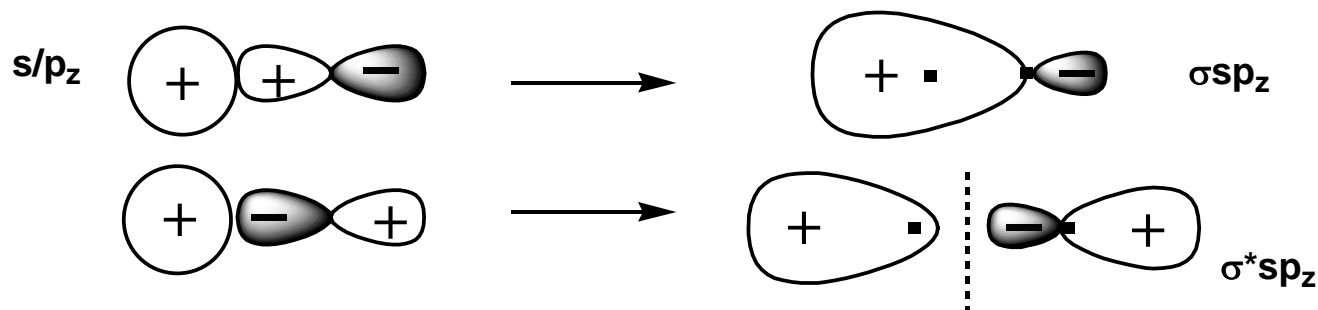
## Anti-Bonding Interaction



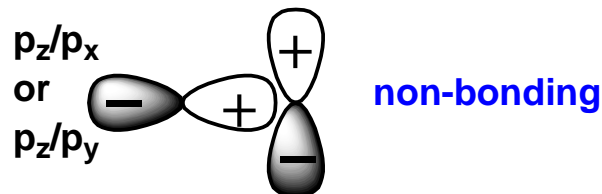
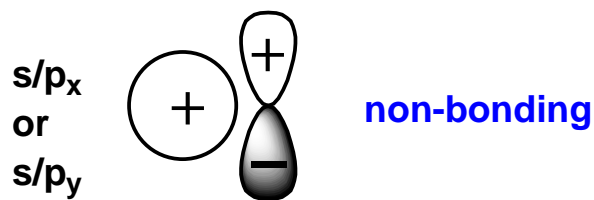
$$\psi_a = p_x - p_x \text{ or } \psi_b = p_y - p_y$$

Side-to-side overlap forms  $\pi^* 2p_x$  or  $\pi^* 2p_y$  MO

**s/p<sub>z</sub> gives bonding and anti-bonding pair.**



**s/p<sub>x</sub> or p<sub>y</sub> and p<sub>z</sub>/p<sub>x</sub> or p<sub>y</sub> all non-bonding (positive and negative overlaps cancel. No overlap at all for p<sub>x</sub>/p<sub>y</sub>).**



**Before moving on to show the energy level diagram for A<sub>2</sub> molecules - we need to be clear about the labels for m.o.'s**

## LABELS FOR M.O.'S

Two types of m.o. - in terms of **symmetry to rotation about molecular axis.**

$s/s$ ,  $p_z/p_z$ ,  $s/p_z$  - **completely symmetrical** to such rotation.

All such given Greek symbol :  $\sigma$  ("sigma")

$p_x/p_x$ ,  $p_y/p_y$  - **change sign every  $180^\circ$  rotation** - these are

given symbol :  $\pi$  ("pi")

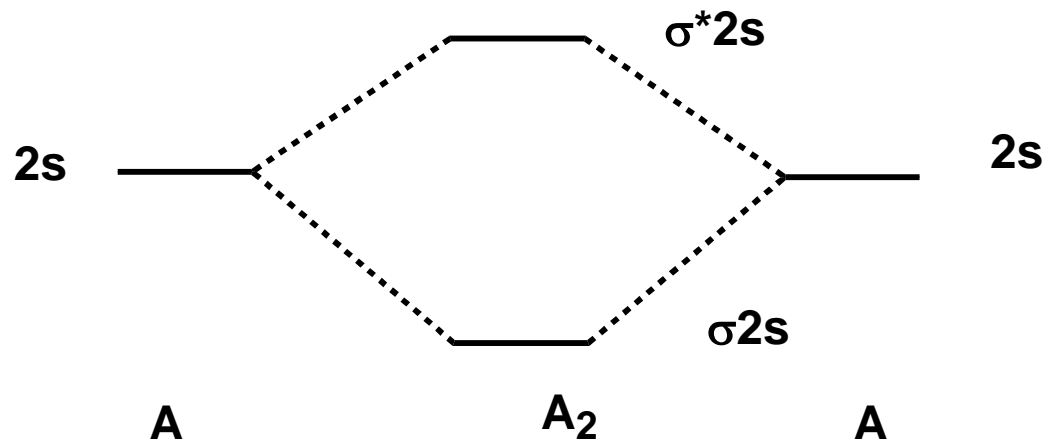
Note - same symbols as for valence bonds (above)

Bonding and antibonding orbitals of each type - differentiated by **asterisk ("star") on the antibonding ones.**

What is the m.o. energy level for these  $A_2$  molecules?

## M.O. Energy Level Diagram for $A_2$ (A = Li, Be)

Remember: 1s orbitals effectively non-bonding,



Use Aufbau, Pauli, Hund - just as in filling atomic orbitals

**Li<sub>2</sub>**

Only two valence electrons, i.e.  $\sigma_s^2 \sigma_s^{*0}$ . **Bond order = 1. Diamagnetic**

Li<sub>2</sub> exists in gas phase over metallic lithium.

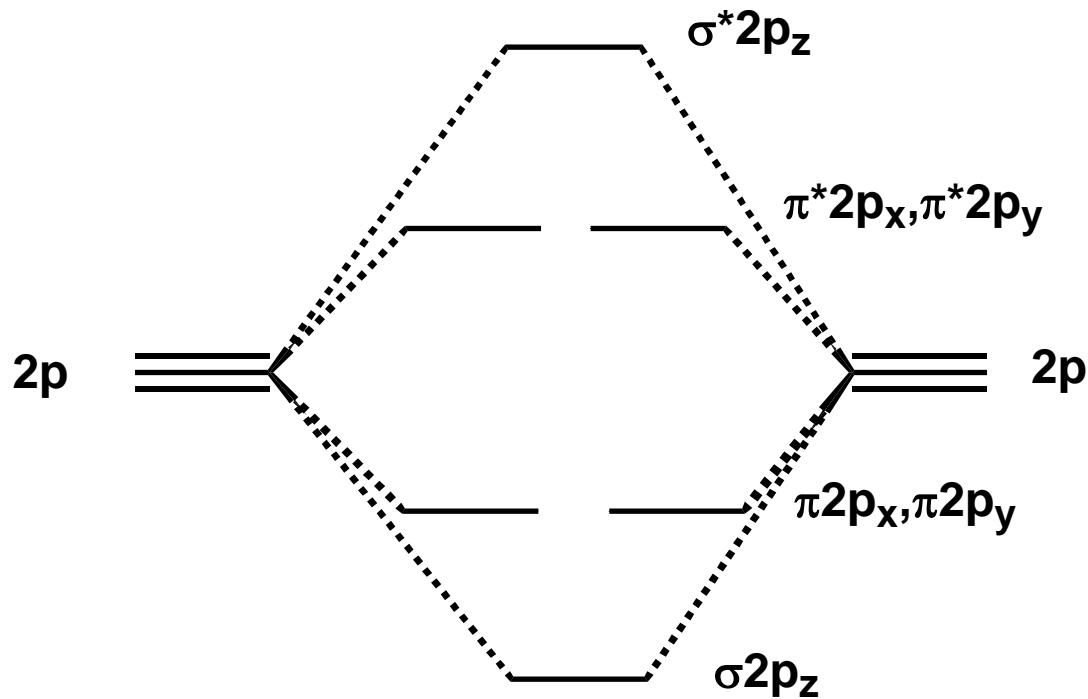
**"Be<sub>2</sub>"**

$\sigma_s^2 \sigma_s^{*2}$

**Bond order = 0 - no net bonding energy, so molecule does not exist.**

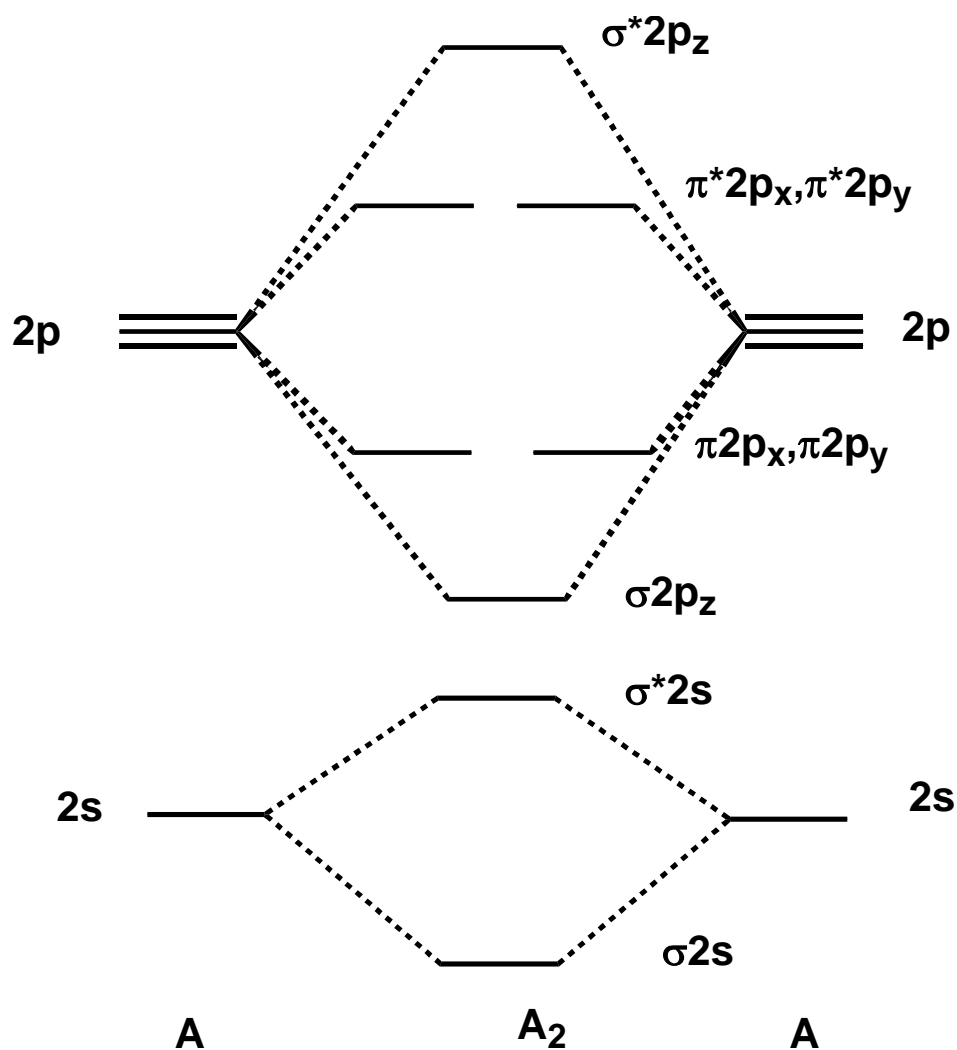
Beryllium in gas phase is monatomic.

## m.o.'s derived from 2p a.o.'s:



1.  $p_x, p_y$  alike in all respects except orientation, so m.o.'s derived from them must be degenerate.
2. sideways ( $\pi$ ) overlap is less efficient than end-on ( $\sigma$ ), so  $\pi$  m.o.'s less bonding than  $\sigma$

**M.O. Energy Level Diagram for  $A_2$   
( $A = O$ )**



$O_2$

Electronic configuration:  $\sigma_s^2 \sigma_s^* 2 \sigma_{pz}^2 \pi_{px}^2 \pi_{py}^2 \pi_{px}^* 1 \pi_{py}^* 1$

Note Hund's rule again! **Bond order =  $(8 - 4)/2 = 2$**   
**(double bond) and PARAMAGNETIC.**

V.B. theory could not explain paramagnetism.



$O_2$  is paramagnetic

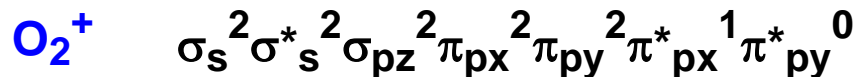




## O<sub>2</sub> is only one of a series of diatomic oxygen species:

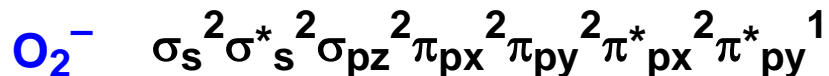
O<sub>2</sub><sup>+</sup> - "oxidation of oxygen" in O<sub>2</sub><sup>+</sup>PtF<sub>6</sub><sup>-</sup>; O<sub>2</sub> - normal form of oxygen  
O<sub>2</sub><sup>-</sup> - superoxide ion, e.g. K<sup>+</sup>O<sub>2</sub><sup>-</sup>; O<sub>2</sub><sup>2-</sup> - peroxide ion, e.g. Na<sub>2</sub><sup>2+</sup>O<sub>2</sub><sup>2-</sup>

### Electron configurations:



electron lost from anti-bonding m.o. - stronger bond than O<sub>2</sub>. **Bond order = 2.5**

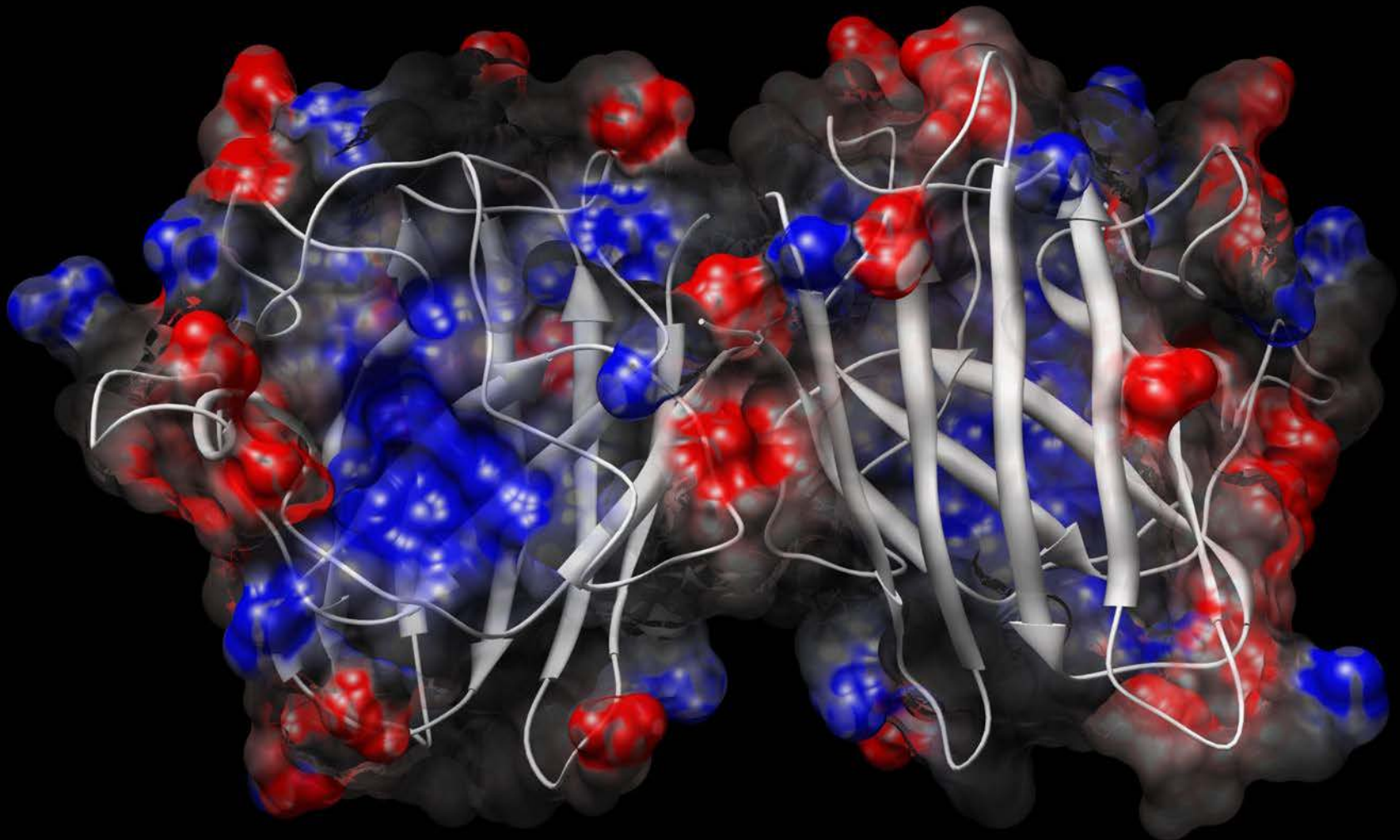
**Paramagnetic** - but less so than O<sub>2</sub> - only one unpaired electron.

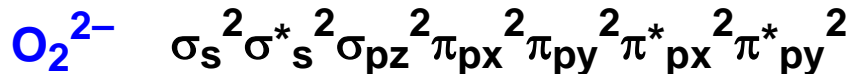


electron gained in anti-bonding m.o. - weaker bond than O<sub>2</sub>. **Bond order = 1.5**

**Paramagnetic** (one unpaired electron).

# ***Superoxide Dismutase (SOD)***





**Bond order = 1. Diamagnetic**

Note bond lengths

$\text{O}_2^+$  - 112 pm

$\text{O}_2$  - 120 pm

$\text{O}_2^-$  - 126 pm

$\text{O}_2^{2-}$  - 149 pm

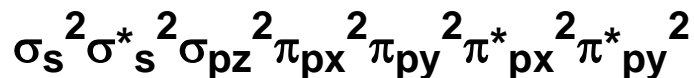


**Weaker bonds, therefore longer bonds**

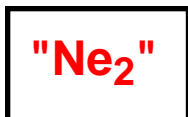


**Isoelectronic with  $\text{O}_2^{2-}$**

**Electronic configuration:**



**Bond order = 1. Diamagnetic**



**Bond order = 0**

**Therefore does not exist. Neon is a monatomic gas**

TABLE 9.5

## Bond Energies (in kJ/mol)\*

		Single Bonds									
		H	C	N	O	S	F	Cl	Br	I	
H	432										
C	411	346									
N	386	305	167								
O	459	358	201	142							
S	363	272	—	—	226						
F	565	485	283	190	284	155					
Cl	428	327	313	218	255	249	240				
Br	362	285	—	201	217	249	216	190			
I	295	213	—	201	—	278	208	175	149		
		Multiple Bonds									
C=C	602	C=N	615	C=O	745 (799 in CO <sub>2</sub> )						
C≡C	835	C≡N	887	C=O	1072						
N=N	418	N=O	607	S=O (in SO <sub>2</sub> )	532						
N≡N	942	O=O	494	S=O (in SO <sub>3</sub> )	469						

## Bond Dissociation Energies

O-O	498.36	kJ/mol	Cl -O	267.47
N-O	631.32		Br -O	235.4
C-O	1076.38		I -O	240
S-O	517.90			
P-O	598			
Si-O	799.6			

Source : CRC Handbook of Chemistry and Physics  
87th ed. , "Bond Dissociation Energies" (Y.-L.  
Ruo and J.A. Kerr) , pp. 9-54 to 9-59 (2006)

## What about B, C and N??

*Energy difference between s and p orbitals is not so great as in O and F. Therefore there is significant interaction of sigma molecular orbitals  
Derived from 2s and 2p.*

Valence State Ionization Energies (eV)

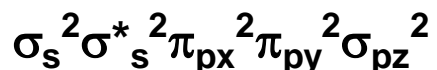
	2s	2p	$\Delta$
B	14.0	8.3	5.7
C	19.4	10.6	8.8
N	25.6	13.2	12.4
O	32.3	15.8	16.5
F	40.2	21.6	18.6

***This leads to a different ordering of the mo 's. The so-called "s-p mixing". It's not difficult – look it up in an advanced book, if you are interested***

# What about B, C and N??

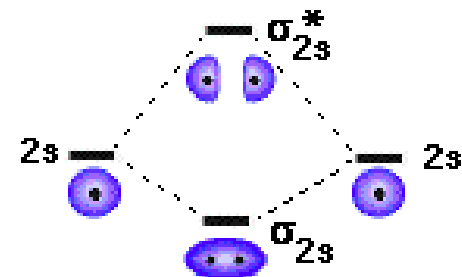
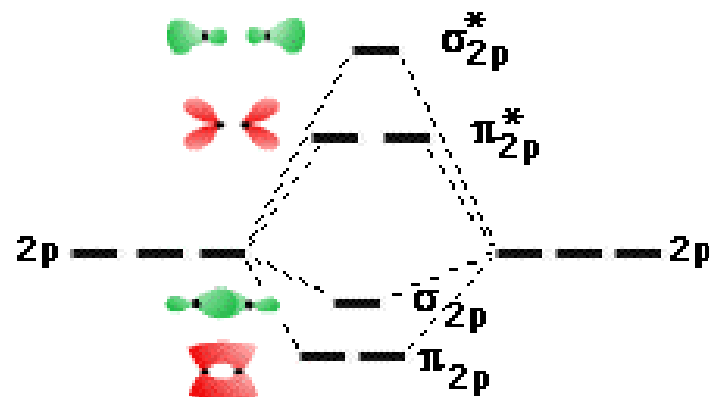
**N<sub>2</sub>**

This is of major importance:



Bond order =  $(8 - 2)/2 = 3$   
 i.e. triple bond, very strong, stable molecule.  
 Diamagnetic.  
 (Note the different order of s/p orbitals)

Molecular Orbital Configuration for N<sub>2</sub>

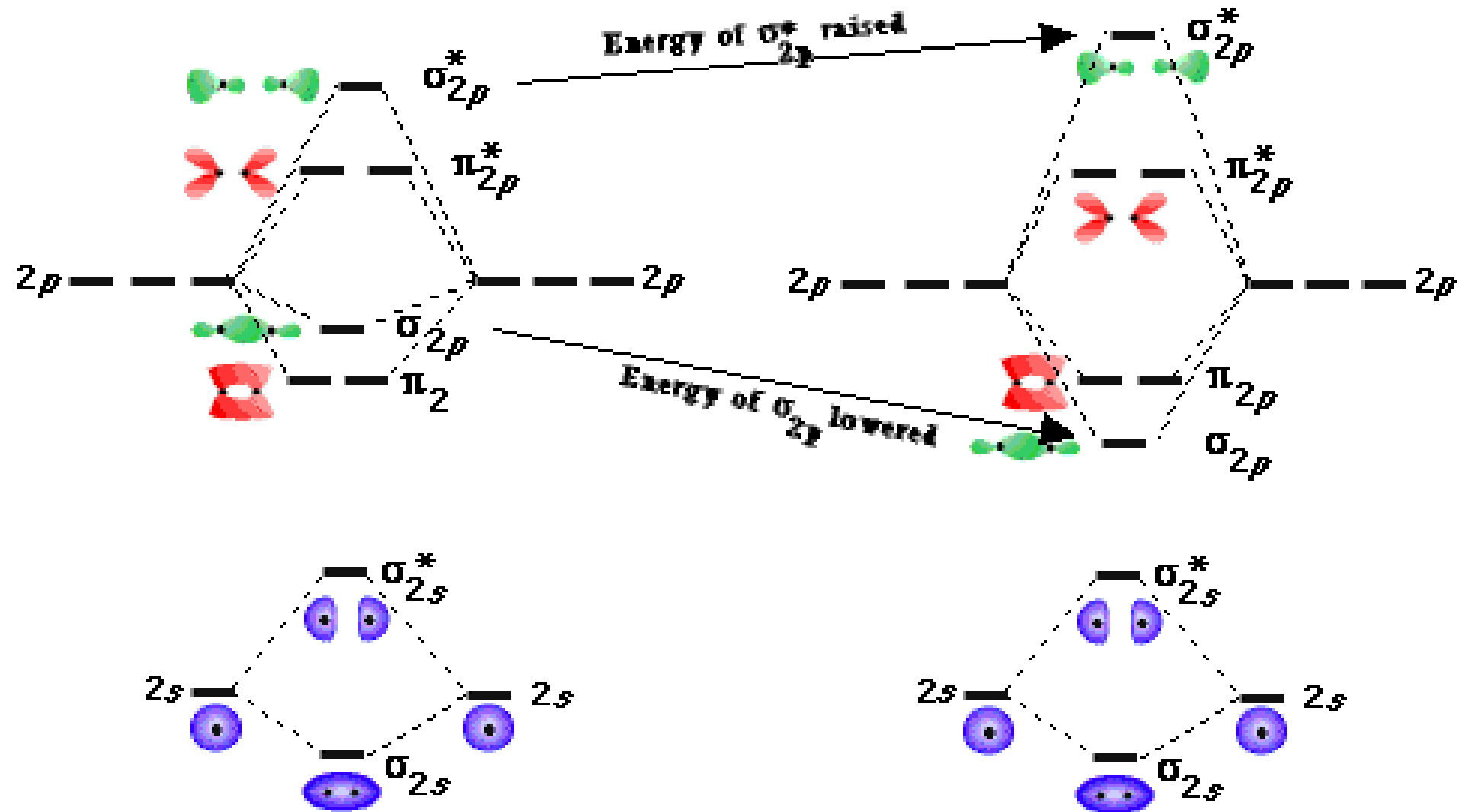


**B<sub>2</sub> and C<sub>2</sub>**

C<sub>2</sub> is important in flames and comets, interstellar space

MO energy levels  
for  $B_2$ ,  $C_2$ , and  $N_2$

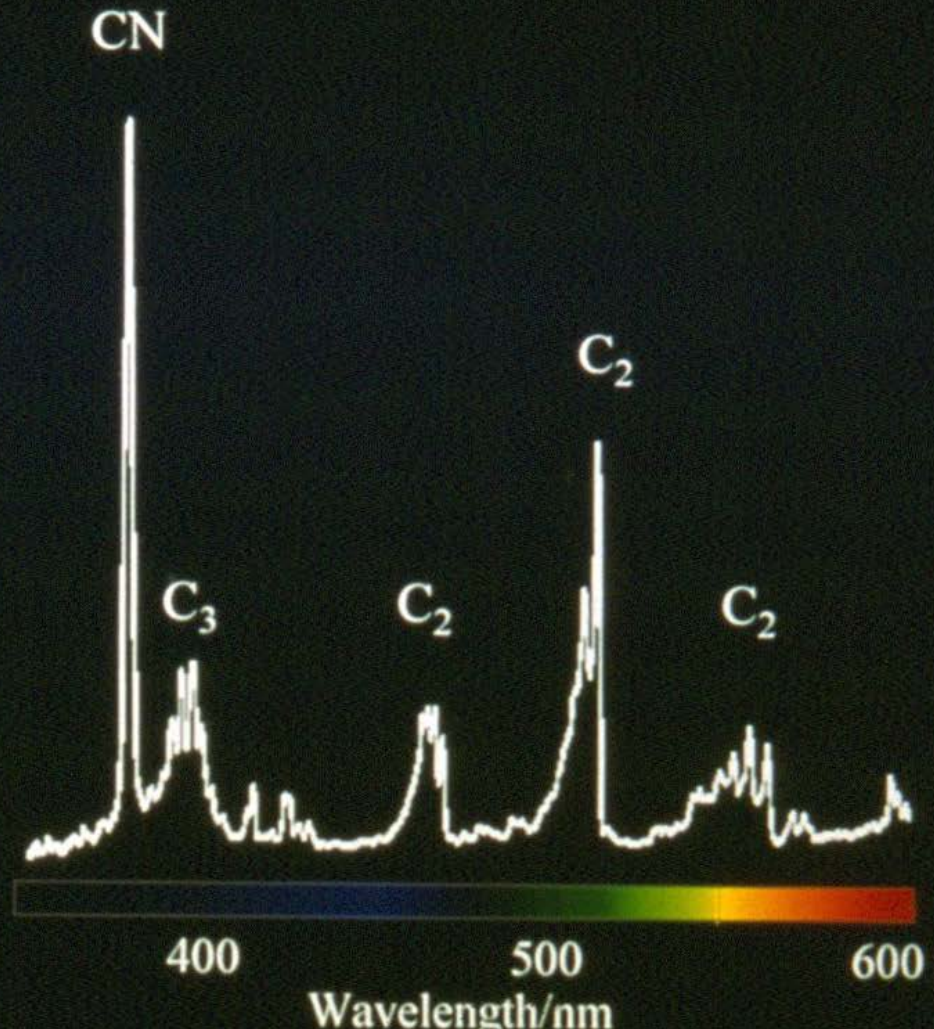
MO energy levels  
for  $O_2$ ,  $F_2$ , and  $Ne_2$





# Light Emission from Comets

- ◆ Light from the Sun is absorbed by cometary molecules
- ◆ The absorbed energy is re-emitted at specific wavelengths (colours)
- ◆ The light is detected with a spectrometer on a large telescope



## Heteronuclear Diatomic Molecules (AB) Involving First Row Elements

Remember two basic principles:

(1) A.o. energies decrease as nuclear charge increases.

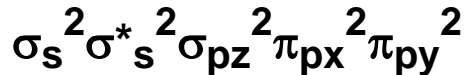
(2) Bonding/antibonding m.o.'s formed symmetrically below/above average of a.o. energies, respectively.

M.o. energy level diagram based on that for  $A_2$ :

# Molecular Orbital Energy Level Diagram for a Heteronuclear Diatomic

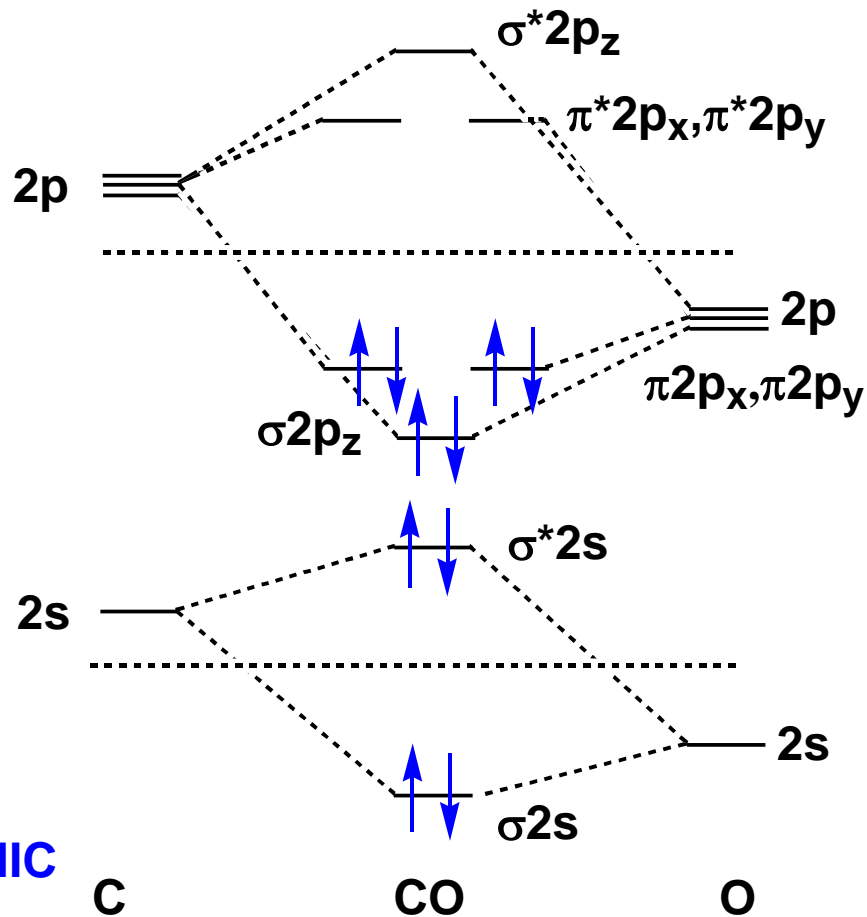
e.g. for CO - similar to N<sub>2</sub>  
 - but with different a.o.  
 energies for C and O,  
 i.e. O > C.

Electronic configuration:



Bond order =  $(8 - 2)/2 = 3$

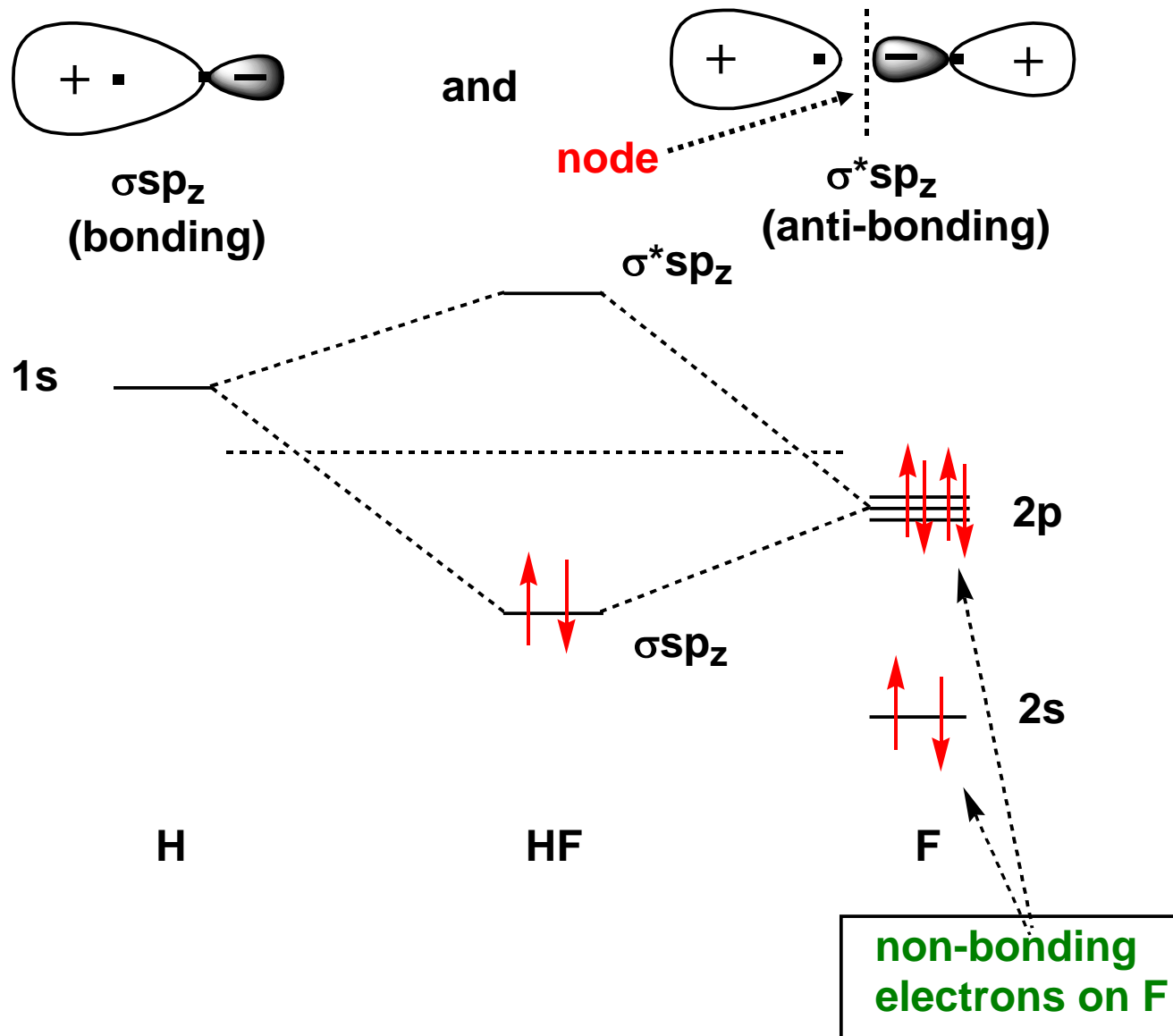
Just like N<sub>2</sub> : ISOELECTRONIC  
 (i.e. same no. of electrons).  
 DIAMAGNETIC.



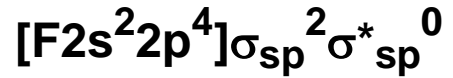
A different type of heteronuclear diatomic:

**HF**

H  $1s^1$  F  $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$  **Overlap between H1s and F2p<sub>z</sub> giving:**



**Electronic configuration:**



**Diamagnetic. Bond order = 1**

**F2s non-bonding - too low in energy**

**F2p<sub>x</sub>, 2p<sub>y</sub> non-bonding because of wrong symmetry**

# Molecular Orbitals in Polyatomic Molecules

In the vast majority of cases, bonds can be described as **LOCALISED** between pairs of nuclei - therefore can use VB approach.

At this stage we only need to use molecular orbitals (m.o.'s) when **DELOCALISATION** of electrons occurs - i.e. when several Lewis structures have to be drawn.

Even in these cases we can use the **VB approach for the  $\sigma$ -framework**, and construct m.o.'s only for the  **$\pi$ -bonds**.

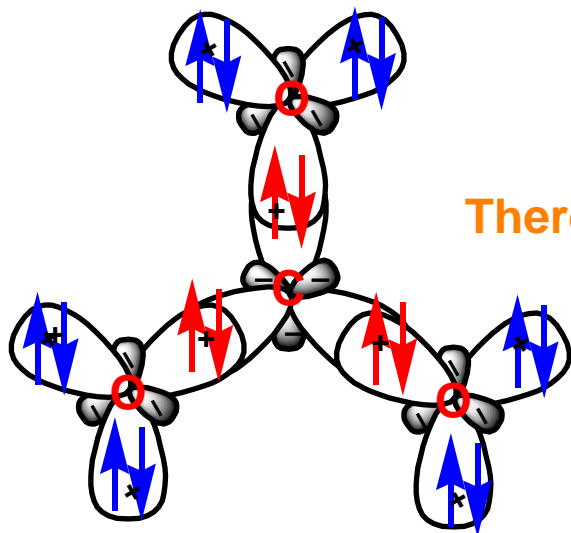
Just look at TWO examples - one inorganic ( $\text{CO}_3^{2-}$ ), one organic (benzene,  $\text{C}_6\text{H}_6$ ).

**Carbonate ion,  $\text{CO}_3^{2-}$ .**

Regular trigonal planar, equal bonds, all angles  $120^\circ$ .

$\sigma$ -framework: use  $sp^2$  hybrids on both C and O's.

2 electrons in each bond + lone pairs in remaining  $sp^2$  hybrids on O's = 18 electrons

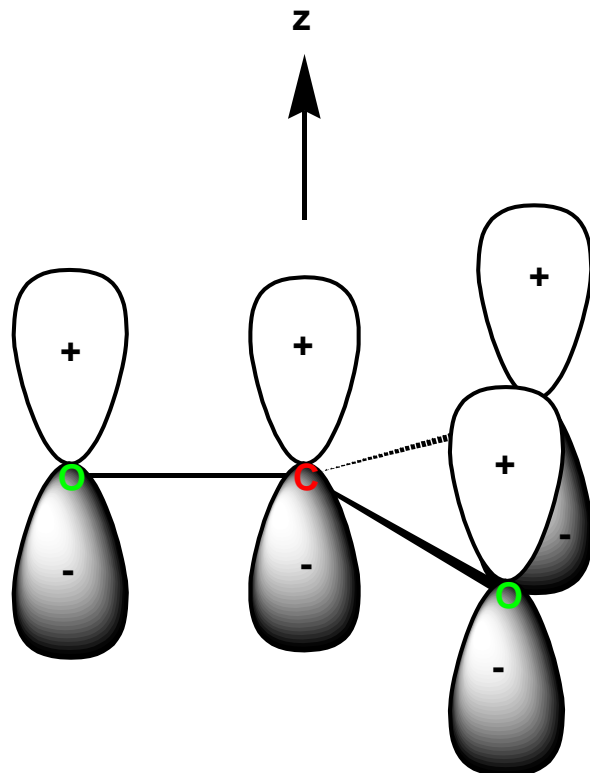


Total number of valence electrons = 4 (C) + 18 (3 O's) + 2 (negative charges) = 24

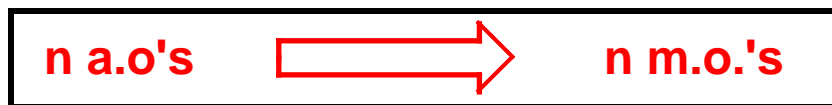
Therefore have 6 electrons to put into  $\pi$ -type orbitals

Which orbitals are available for  $\pi$ -bonding?

On each atom,  $sp^2$  hybrid formation uses  $p_x$  and  $p_y$  orbitals. Therefore one  $p_z$  orbital on each atom is available for  $\pi$ -bonding - 4 orbitals in total.



Remember general rule:

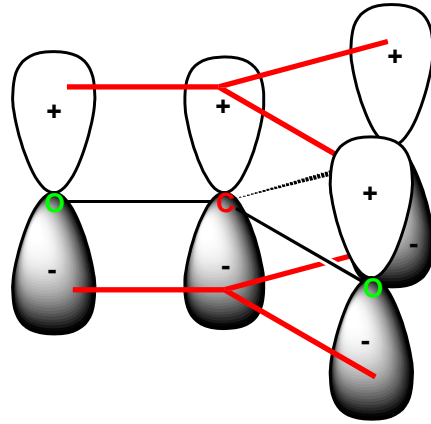


Therefore we will form **4 m.o.'s**

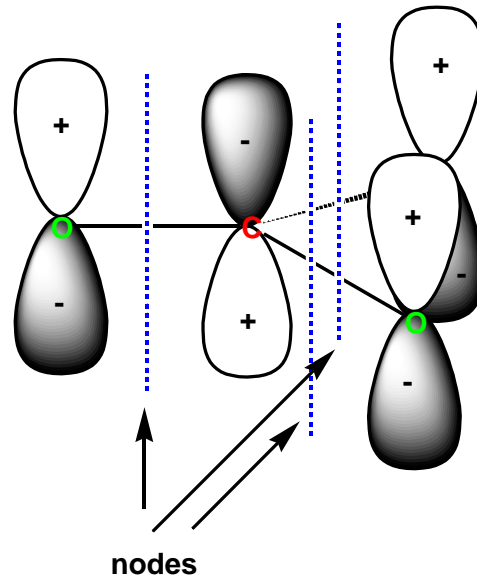
Details of how to calculate what these look like left until later.



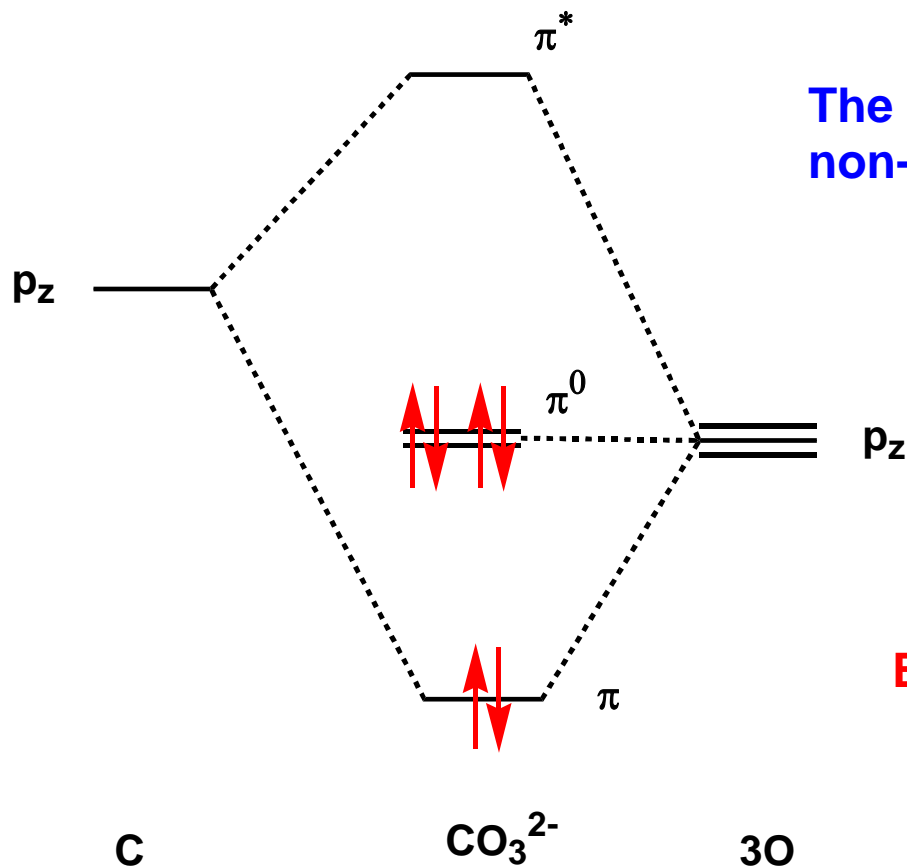
By analogy with diatomic m.o.'s - most strongly bonding m.o. will be the one which increases electron density in all of the bonds:



The most antibonding m.o. will have **NODES** on all of the bonds:



The remaining two turn out to be non-bonding, giving the energy level for the  $\pi$ -bonding in  $\text{CO}_3^{2-}$  as follows:



The 6 electrons just fill the bonding and non-bonding m.o.'s.

One  $\pi$ -bond shared out equally in a delocalised m.o.

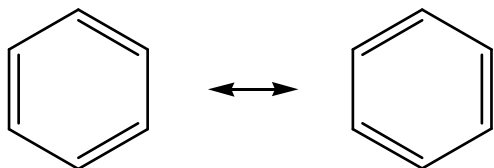
Each bond therefore  $1\sigma + 1/3\pi$

All electrons paired - therefore **DIAMAGNETIC**



## Benzene, C<sub>6</sub>H<sub>6</sub>

Remember that there are two equivalent Lewis structures for benzene:



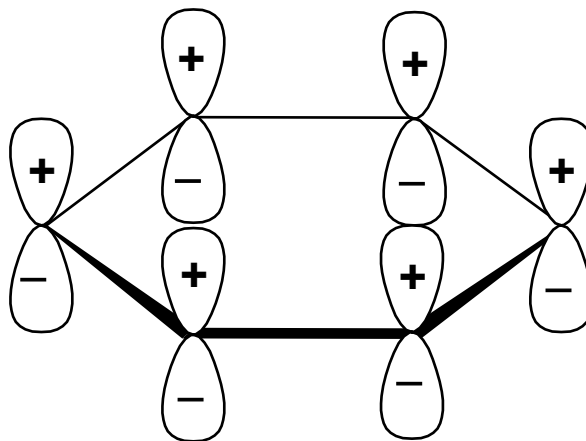
Simplified drawing - CH at each corner.

Benzene is in fact a **regular hexagon** - all **C-C bonds equal**, and with a **length intermediate between C-C and C=C**.

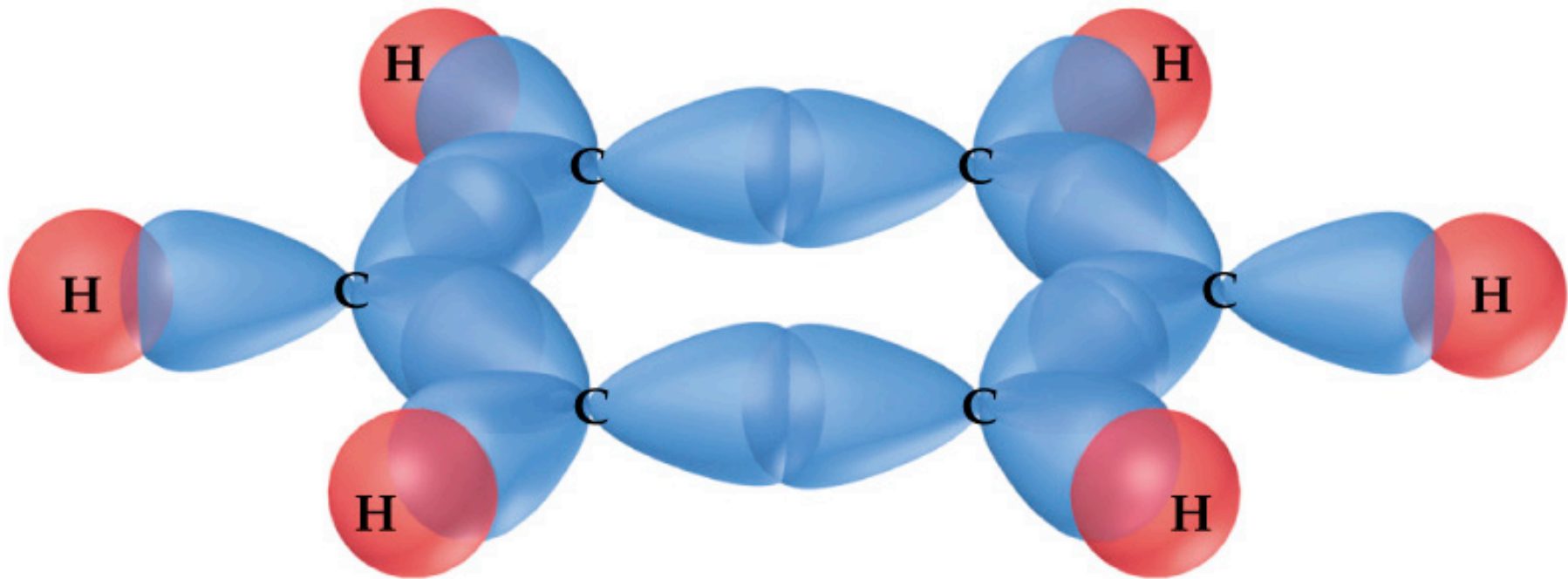
**$\sigma$ -framework** -  $sp^2$  hybridisation at each C, forming a  $\sigma$ -bond to H and two adjacent C atoms

**$\pi$ -bonding** - a  $p_z$  orbital on each C, i.e. 6 a.o.'s, therefore **6 m.o.'s will be formed**.

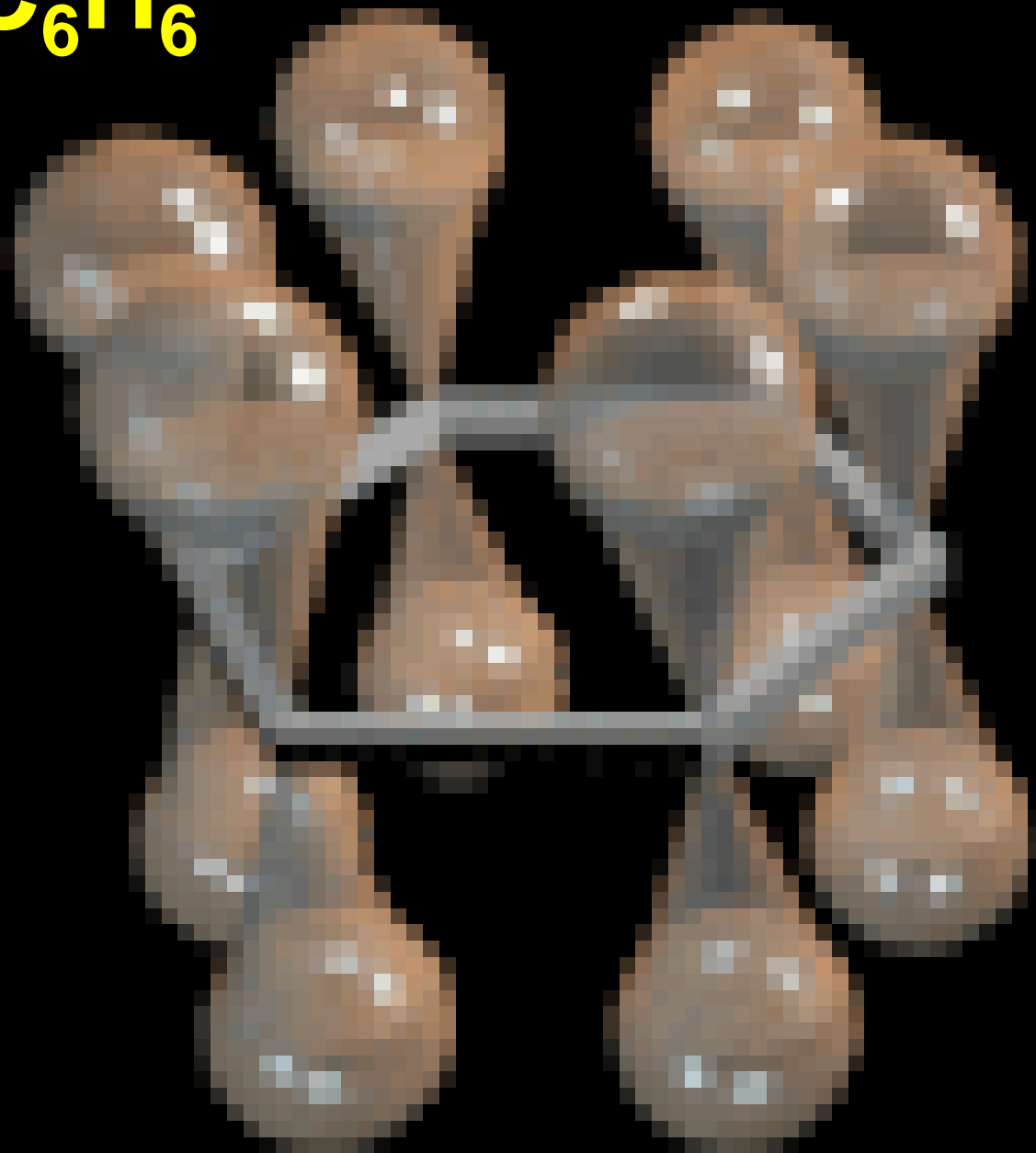
A.o.'s for  $\pi$ -bonding:



# sigma bonds in Benzene



# Pi-bonds $C_6H_6$

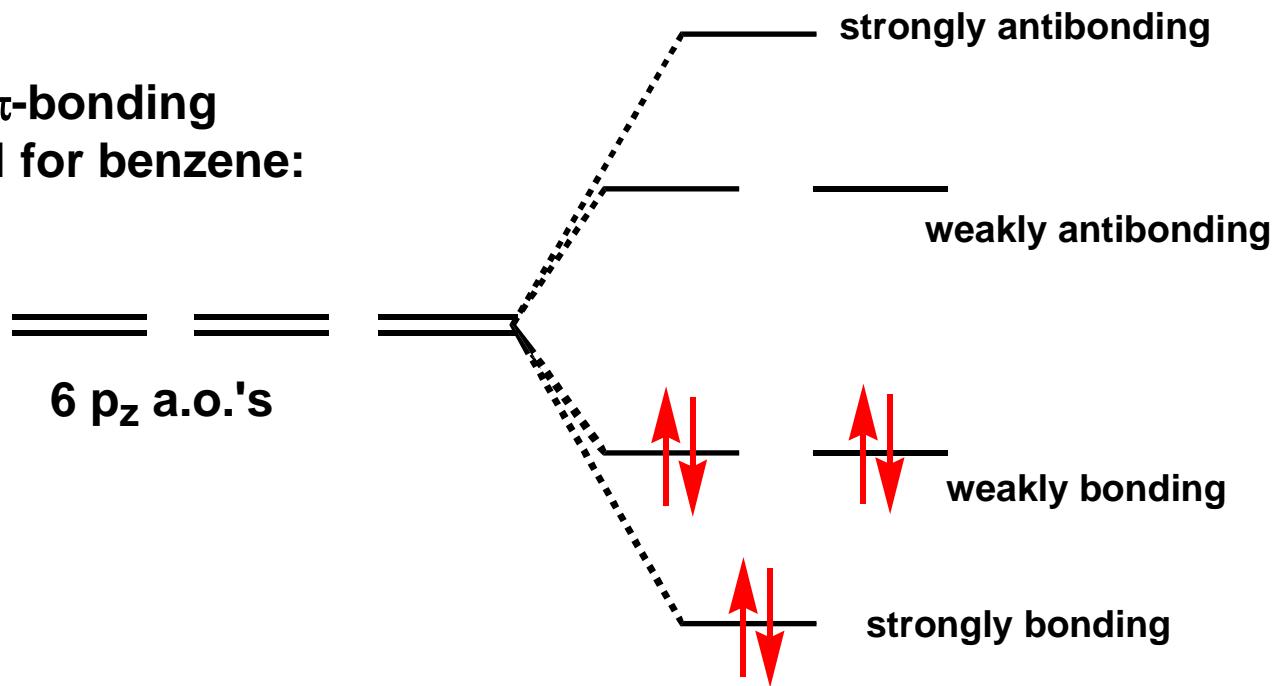


By analogy with carbonate - **most strongly bonding m.o.** formed by adding all of these a.o.'s together (incr. electron density in each bond).

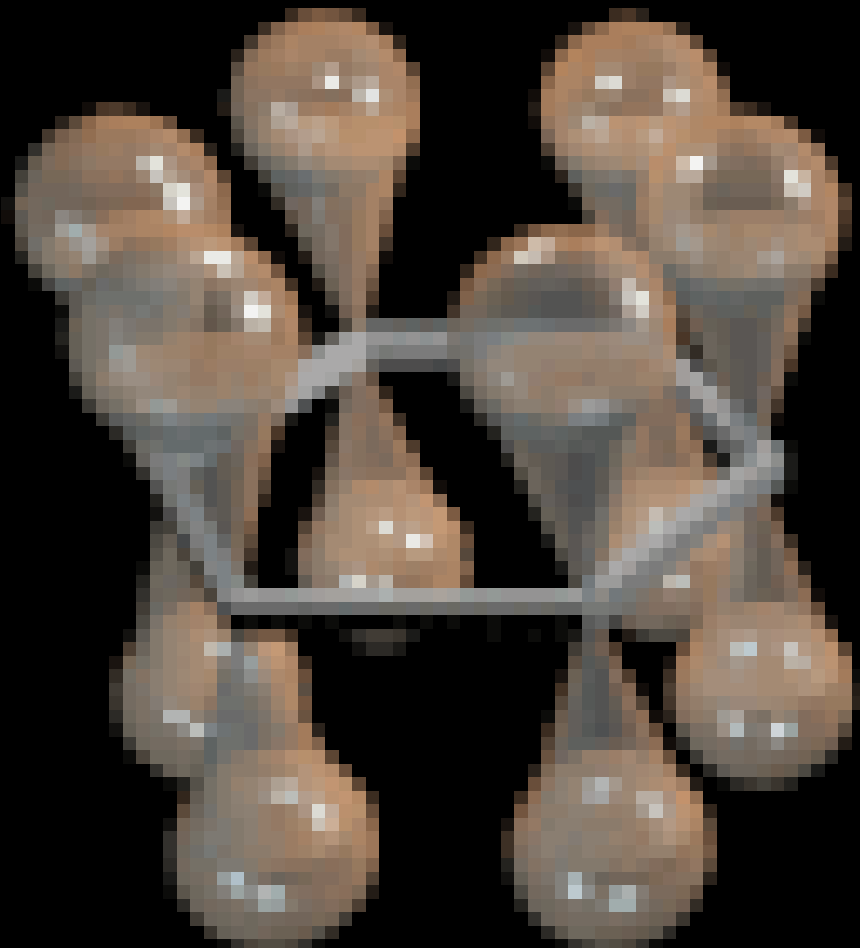
Also by analogy with carbonate - **most strongly antibonding m.o.** formed by combining all of these a.o.'s together to give NODES between each pair of C atoms

In addition, the remaining 4 m.o.'s will comprise two **WEAKLY BONDING** and two **WEAKLY ANTIBONDING** combinations

Thus we have a  $\pi$ -bonding m.o. energy level for benzene:



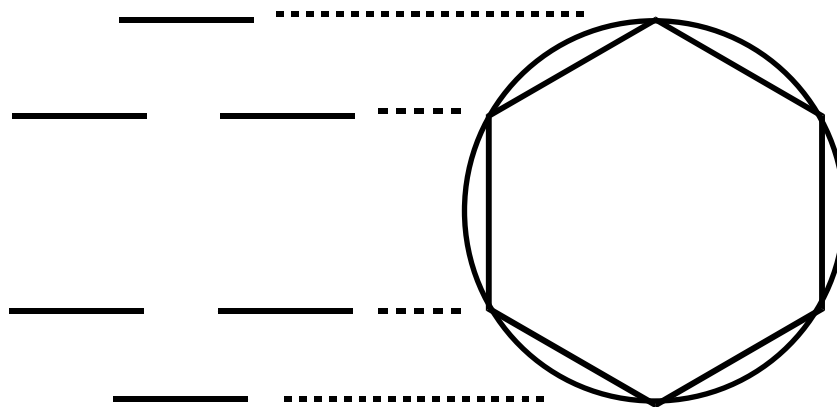
# Pi-bonds $C_6H_6$





There are 6 electrons (one per C atom) - and these fill the strongly and weakly antibonding m.o.'s. These orbitals are **DELOCALISED**, and explain the observed properties of benzene. Note stability as all bonding m.o.'s are full, and all electrons paired.

Note - there is a **simple pictorial method for obtaining the relative energies of the  $\pi$ -m.o.'s of benzene and any other cyclic  $C_nH_n$  compound**. Draw a circle round the shape of the molecule with one corner at the lowest part of the circle - and the corners just touching the circle. This gives the m.o. energies!



Any molecule where  $\pi$ -electrons are *delocalised* is said to show **CONJUGATION** - and the properties of such molecules are different from those with localised multiple bonds -lots of examples in Organic Chemistry.

In particular, cyclic compounds like benzene (with a **FULL SHELL** of  $\pi$ -m.o's) are described as being **AROMATIC**. Aromaticity confers specific properties on such compounds. In particular they are more stable (**lower energy**) than would have been predicted on the basis of localised double bond formation.