Molecular Orbital Approach to Bonding

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The following slides were modified from 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=estiedAlXII

B_2H_6 https://www.youtube.com/watch?v=GD5CrjyAKx4

CO   http://www.chemtube3d.com/orbitalsCO.htm

Bond Dissociation Energies

Can you account for these trends? Yes, you can.

Average Bond Dissociation Energies, D (kJ/mol)[a]									
H—H	436[a]	C—H	410	N—H	390	O—H	460	F—F	159[a]
H—C	410	C—C	350	N—C	300	O—C	350	Cl—Cl	243[a]
H—F	570[a]	C—F	450	N—F	270	O—F	180	Br—Br	193[a]
H—Cl	432[a]	C—Cl	330	N—Cl	200	O—Cl	200	I—I	151[a]
H—Br	366[a]	C—Br	270	N—Br	240	O—Br	210	S—F	310
H—I	298[a]	C—I	240	N—I	—	O—I	220	S—Cl	250
H—N	390	C—N	300	N—N	240	O—N	200	S—Br	210
H—O	460	C—O	350	N—O	200	O—O	180	S—S	225
H—S	340	C—S	260	N—S	—	O—S	—		

Multiple covalent bonds

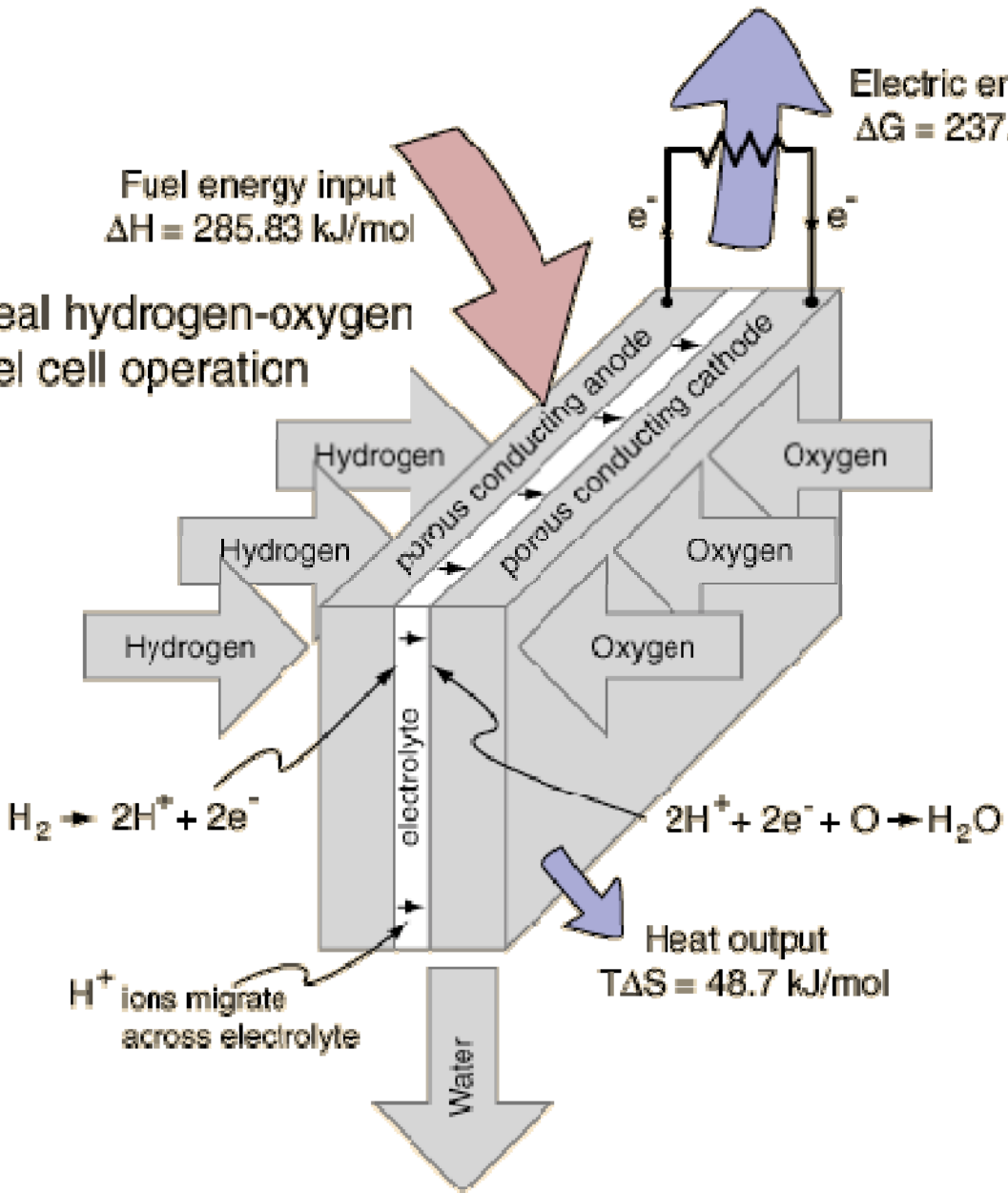|									
C=C	611	C≡C	835	C=O	732	O=O	498[a]	N≡N	945[a]

[a] Exact value

Ideal hydrogen-oxygen fuel cell operation

Fuel energy input
$\Delta H = 285.83$ kJ/mol

Electric energy output
$\Delta G = 237.13$ kJ/mol

e^- e^-

porous conducting anode   porous conducting cathode

Hydrogen   Oxygen

Hydrogen   Oxygen

Hydrogen   Oxygen

electrolyte

$H_2 \rightarrow 2H^+ + 2e^-$ $2H^+ + 2e^- + O \rightarrow H_2O$

Heat output
$T\Delta S = 48.7$ kJ/mol

H^+ ions migrate across electrolyte

Water

More Bond Dissociation Energies

Silicon

Si—Si	327(10)
Si—Br	343(50)
Si—C	435(21)
Si—Cl	456(42)
Si—F	540(13)
Si—H	298.49(46)
Si—I	339(84)
Si—N	439(38)
Si—O	798(8)
Si—S	619(13)
Si—Se	531(25)
H_3Si—SiH_3	339(17)
$(CH_3)_3Si$—$Si(CH_3)_3$	339
$(Aryl)_3Si$—$Si(aryl)_3$	368(31)
Si—Te	506(38)

Video : Oxygen

http://www.periodicvideos.com/videos/008.htm

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.

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

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: De-Localized Orbitals and Electrons in them ➤   Energy Levels, Magnetism

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 ψ^2, where ψ = 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:

Linear Combination of Atomic Orbitals

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:

$$n \text{ a.o.'s} \longrightarrow n \text{ m.o.'s}$$

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 (ψ_b) and the difference (ψ_a) of the constituent a.o.'s.
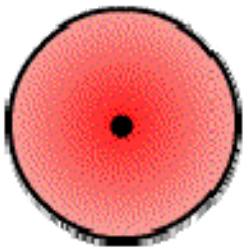
Consider the electron distribution in each of these:
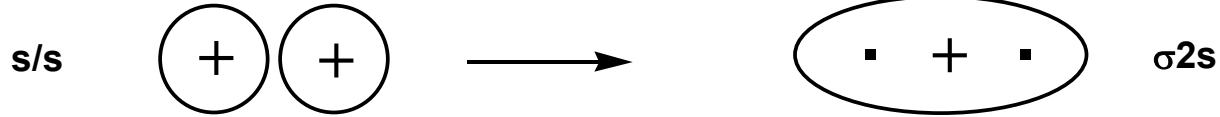
s/s

σ2s

s + s overlap everywhere positive→ BONDING M.O.

σ*2s

s – s overlap everywhere negative→ ANTI-BONDING M.O.

Bonding Interaction

Anti-Bonding Interaction
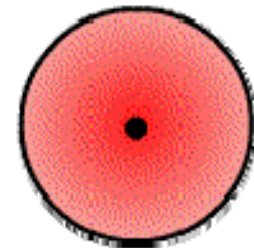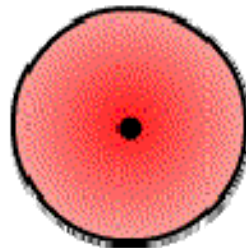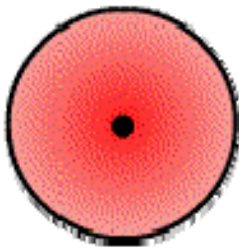
$\Psi_b = 1s_A + 1s_B$

$\Psi_a = 1s_A - 1s_B$

Consider in each case the INTERNUCLEAR REGION
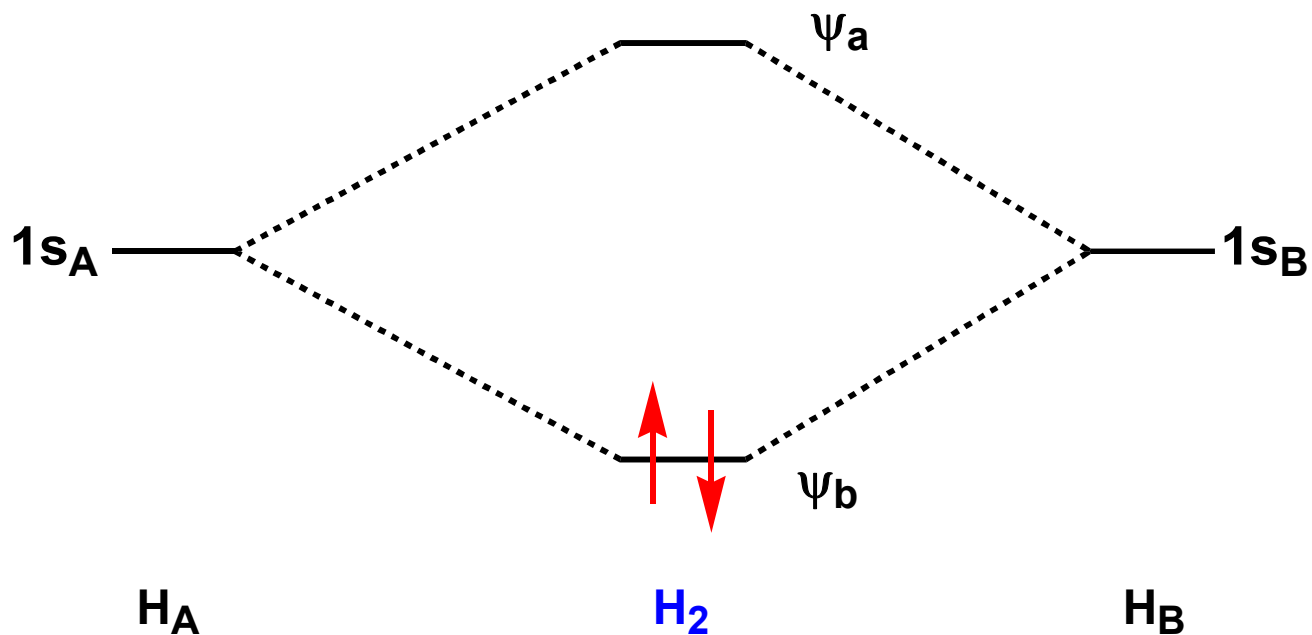
Probability of finding electron there is:

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

Electron in this region attracted to BOTH nuclei, therefore most favourable position. Hence, electron in ψ_b will be at lower energy than in non-interacting a.o.'s, and electron in ψ_a will be at higher energy still.
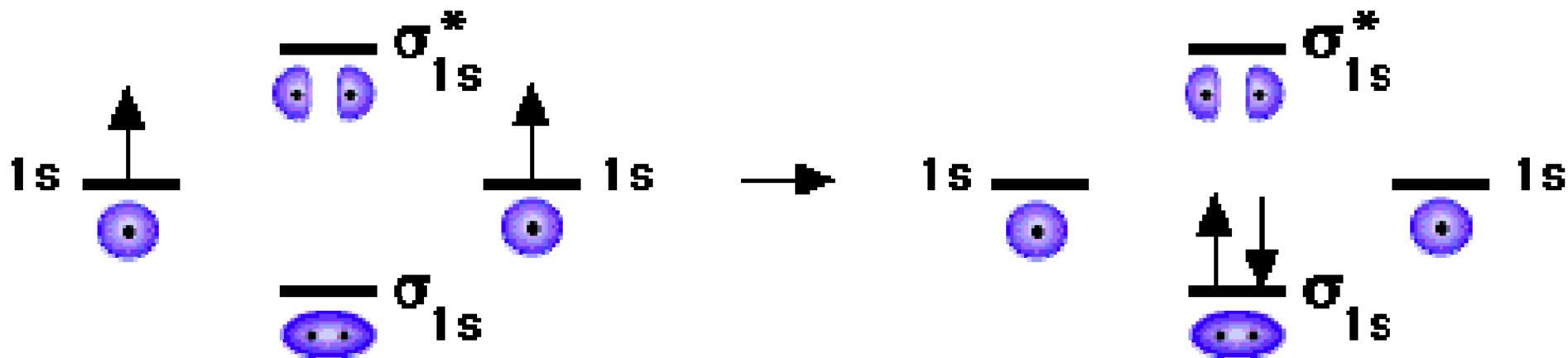
Thus an electron in ψ_b will hold the nuclei together, one in ψ_a will push them apart.

ψ_b is a BONDING m.o.,

ψ_a is an ANTI-BONDING m.o.

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

ψ_a

$1s_A$ — — — $1s_B$

ψ_b

H_A **H_2** H_B

By aufbau & Pauli principles - the 2 electrons go into ψ_b - with paired spins.

σ^*_{1s}

$1s$ $1s$ → $1s$ $1s$

σ_{1s}

σ^*_{1s}

σ_{1s}

MO's for H$_2$ molecule

http://www.chemtube3d.com/orbitalsCO.htm
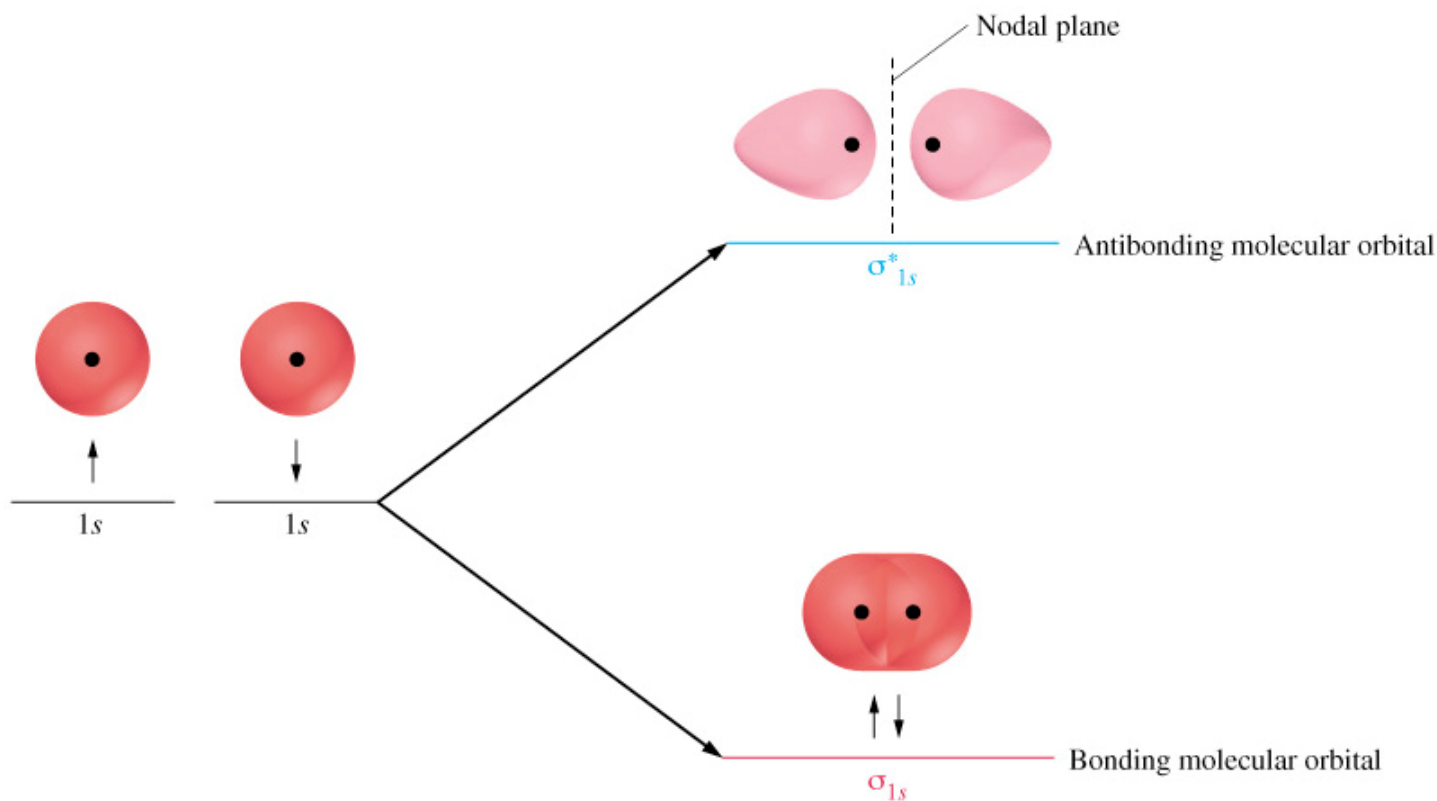
M.O.'s for homonuclear diatomics (A_2) for elements of first row of the Periodic Table

For Li_2, Be_2, B_2 etc., more complex than for H_2, HHe - 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**.

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:

Bond order = [(No. of electrons in bonding m.o.'s) – (No. of electrons in antibonding m.o.'s)]/2

Thus, for H_2, bond order = (2 - 0)/2 = 1   (i.e. a single bond - as expected)
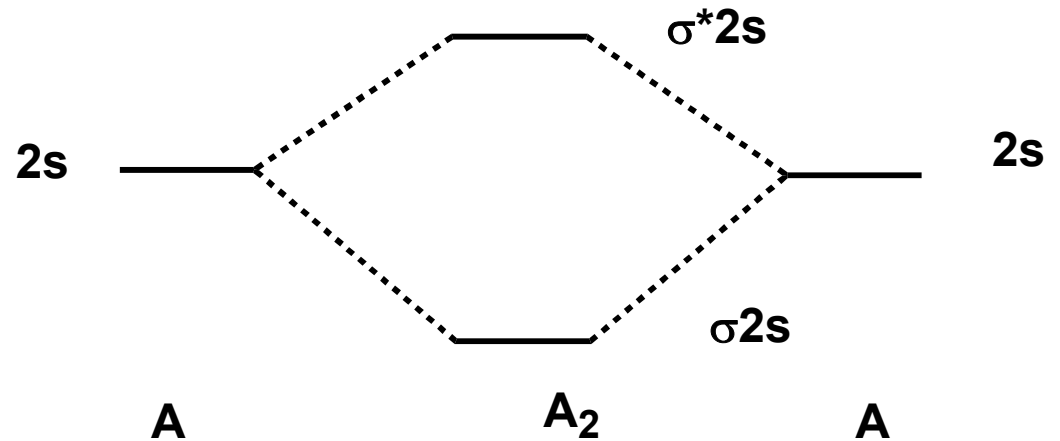
Magnetic Properties of Molecules

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

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

H_2 is diamagnetic.

M.O.Energy Level Diagram for A$_2$ (A = Li, Be)

σ*2s

2s ——————   —————— 2s

σ2s

A   A$_2$ A

Remember: **1s orbitals effectively non-bonding,**

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

Li$_2$ | Only two valence electrons, i.e. $\sigma_s^2 \sigma^*_s^0$. **Bond order = 1.   Diamagnetic**
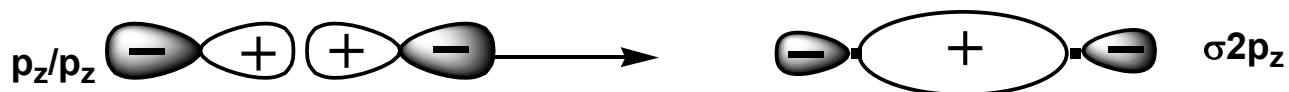Li$_2$ exists in gas phase over metallic lithium.

"Be$_2$" | $\sigma_s^2 \sigma^*_s^2$ **Bond order = 0 - no net bonding energy, so molecule does not exist.**
Beryllium in gas phase is monatomic.

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 $\sigma 2p_z$

$p_z + p_z$ overlap everywhere positive→ BONDING M.O.

Bonding Interaction   **Anti-Bonding Interaction**

$\Psi_b = p_z + p_z$

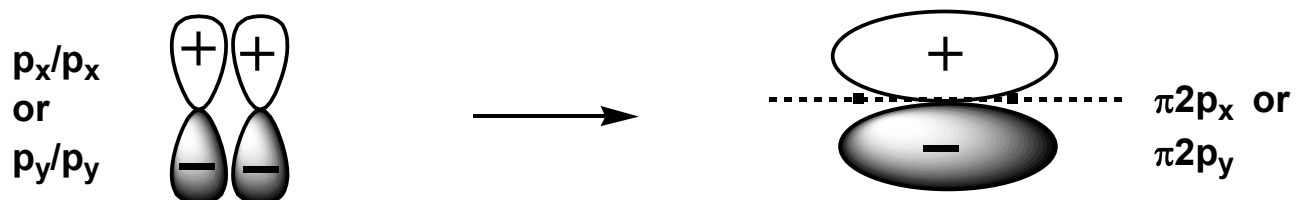End-to-end overlap forms $\sigma 2p_z$ MO

$\Psi_a = p_z - p_z$

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

 $\sigma^* 2p_z$
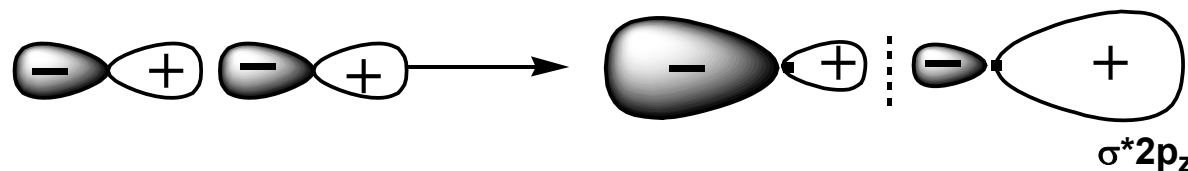
$p_z - p_z$ overlap everywhere negative→ ANTI-BONDING M.O.

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

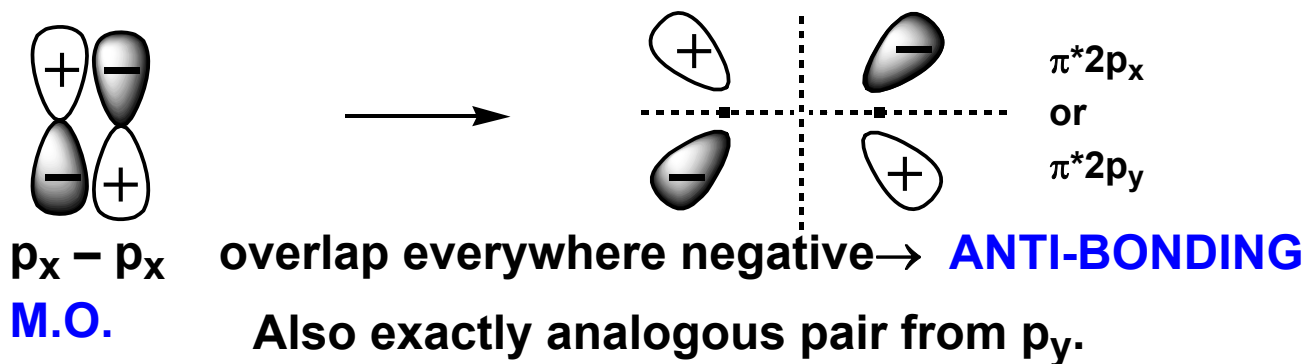p_x/p_x
or
p_y/p_y

$p_x + p_x$ overlap everywhere positive→ **BONDING M.O.**

$\pi 2p_x$ or
$\pi 2p_y$

Bonding Interaction

$\Psi_b = p_x + p_x$ or $\Psi_b = p_y + p_y$

Side-to-side overlap forms $\Pi 2p_{x \text{ or } y}$ MO

$p_x - p_x$ overlap everywhere negative→ **ANTI-BONDING**
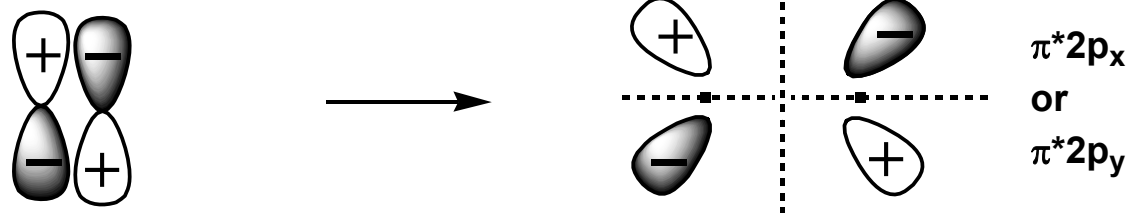
M.O.

Also exactly analogous pair from p_y.

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

Anti-Bonding Interaction

$\Psi_a = p_x - p_x$ or $\Psi_b = p_y - p_y$

Side-to-side overlap forms $\Pi^*2p_{x\ or\ y}$ MO

p_x/p_x
or
p_y/p_y

$\pi 2p_x$ or
$\pi 2p_y$

π^*2p_x
or
π^*2p_y
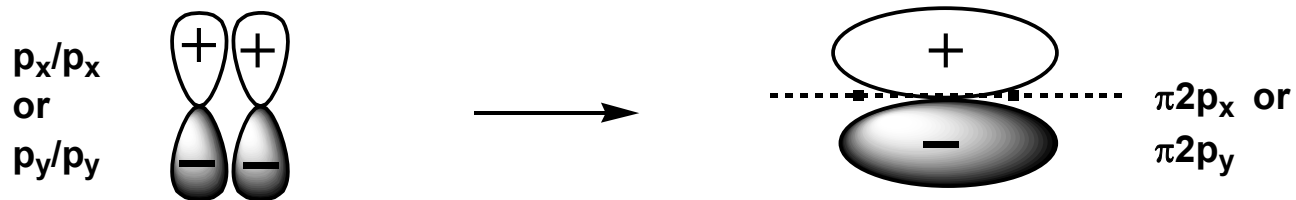
Bonding Interaction

$\Psi_b = p_x + p_x$ **or** $\Psi_b = p_y + p_y$

Side-to-side overlap forms $\pi 2p_{x\ or\ y}$ MO

Anti-Bonding Interaction

$\Psi_a = p_x - p_x$ **or** $\Psi_b = p_y - p_y$

Side-to-side overlap forms $\pi^*2p_{x\ or\ y}$ MO

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

σ^*2p_z

π^*2p_x, π^*2p_y

2p

2p

$\pi 2p_x, \pi 2p_y$

$\sigma 2p_z$
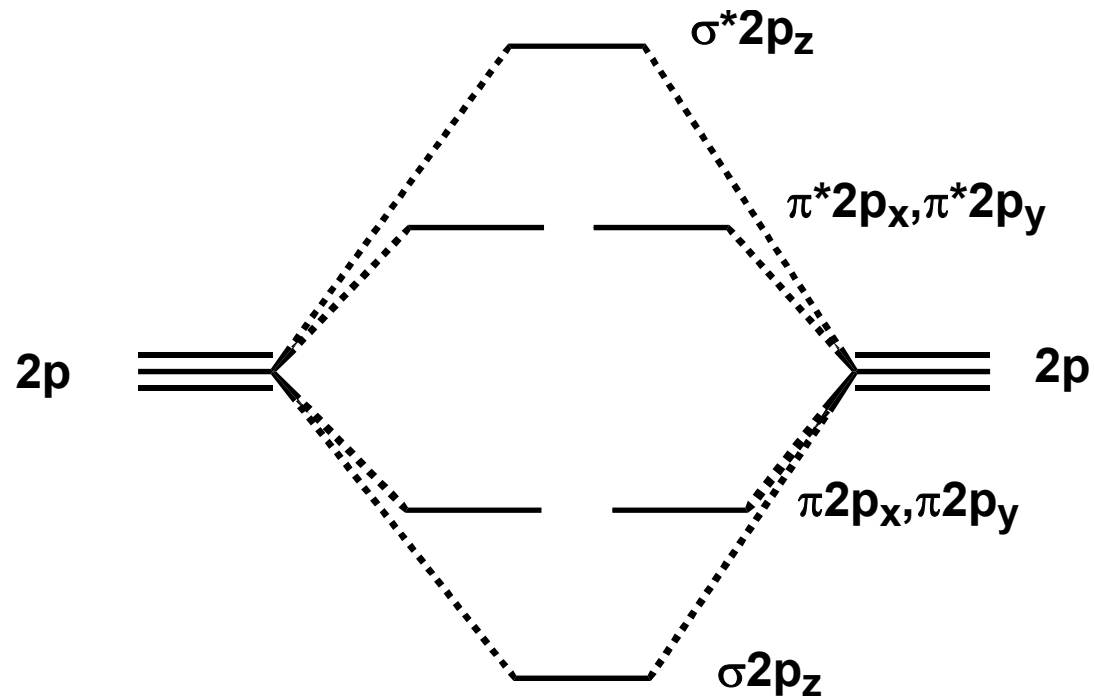
1. p_x, p_y alike in all respects except orientation, so m.o.'s derived from them must be degenerate.

2. sideways (π) overlap is less efficient than end-on (σ), so π m.o.'s less bonding than σ

M.O. Energy Level Diagram for A$_2$ (A = O)

σ^*2p_z

π^*2p_x, π^*2p_y

2p   2p

$\pi 2p_x, \pi 2p_y$

$\sigma 2p_z$

"No mixing of 2s and 2p"

σ^*2s

2s   2s

$\sigma 2s$

A   A$_2$ A

O$_2$
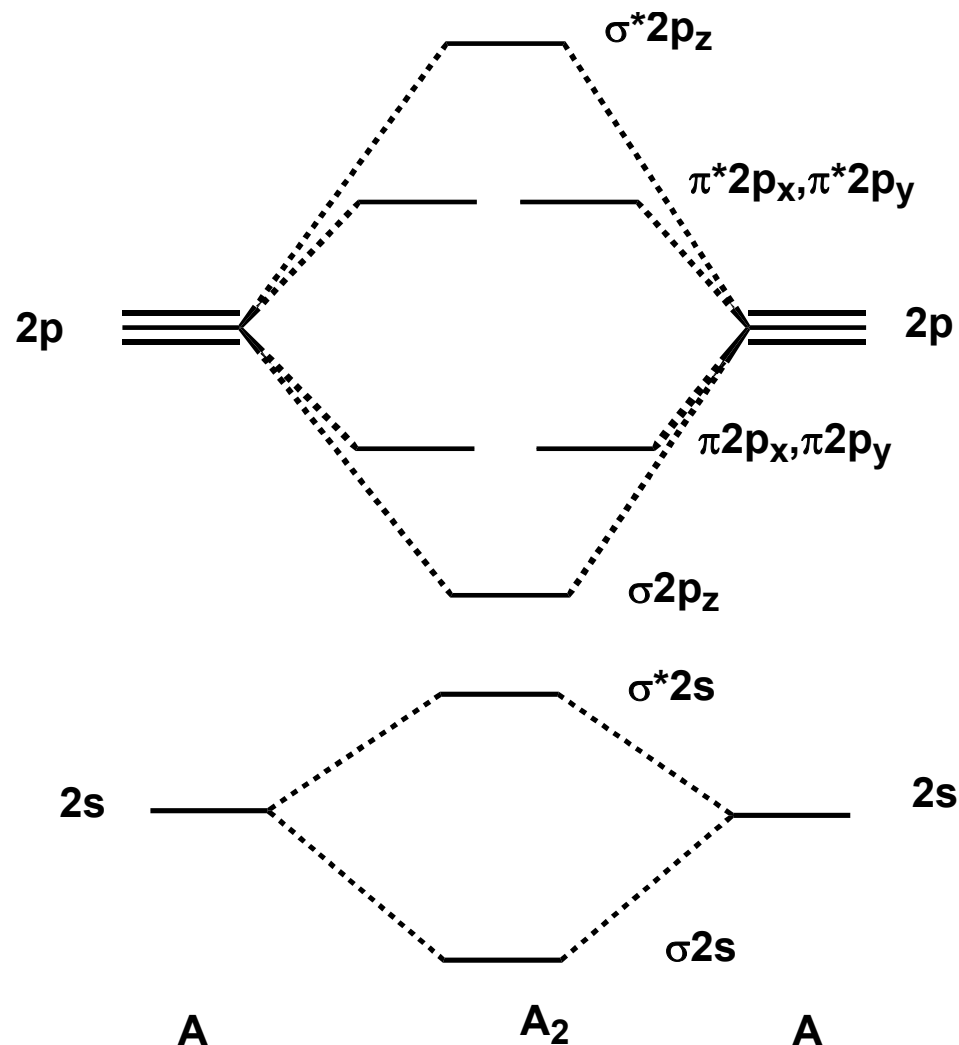
Electronic configuration: $\sigma_s^{\ 2}\sigma^*_s^{\ 2}\sigma_{pz}^{\ 2}\pi_{px}^{\ 2}\pi_{py}^{\ 2}\pi^*_{px}^{\ 1}\pi^*_{py}^{\ 1}$

Note Hund's rule again!   **Bond order = (8 - 4)/2 = 2
(double bond) and PARAMAGNETIC.
V.B. theory could not explain paramagnetism.**

MFT graphics
Chapter 5

Homonuclear Diatomics
No mixing vs. **mixing**
 of sigma orbitals
Derived from 2s and $2p_z$

No mixing　　　**mixing**

σ_u^*　　　　　　σ_u^*

π_g^* π_g^*　　　π_g^* π_g^*

$2p$　　　　　$2p$　　　$2p$　　　　$2p$

σ_g

π_u π_u　　　π_u π_u

σ_g

σ_u^*　　　　　　σ_u^*

$2s$　　　　　$2s$　　　$2s$　　　　$2s$

σ_g　　　　　　σ_g

No mixing　　　Mixing of σ_g orbitals

(a)　　　　　　(b)

$\sigma_u^*(2p)$ —

$\pi_g^*(2p)$ — —

$\sigma_g(2p)$ —

$\pi_u(2p)$ — —

$\sigma_u^*(2s)$ —

$\sigma_g(2s)$ ⇅

$\sigma_u^*(2p)$

$\pi_g^*(2p)$

$\pi_u(2p)$

$\sigma_g(2p)$

$\sigma_u^*(2s)$

$\sigma_g(2s)$

	Li$_2$	Be$_2$	B$_2$	C$_2$	N$_2$	O$_2$	F$_2$	Ne$_2$
Bond order	1	0	1	2	3	2	1	0
Unpaired e$^-$	0	0	2	0	0	2	0	0