Lecture 15
Molecular Orbitals for Diatomic Molecules

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.
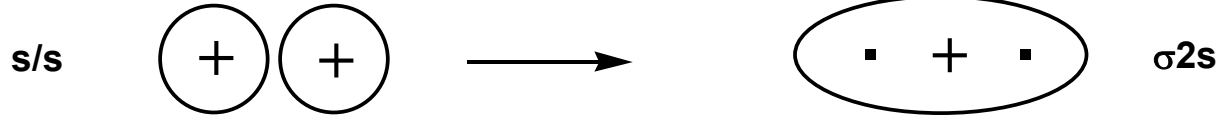
General rule:

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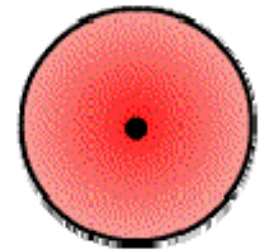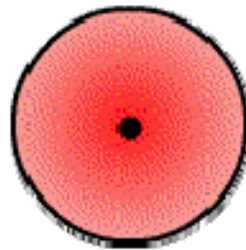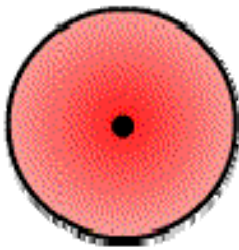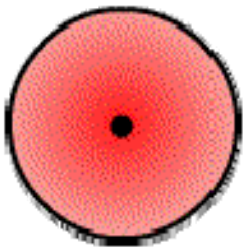
Consider the electron distribution in each of these:

s/s

σ2s

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

σ*2s

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

Bonding Interaction

$\Psi_b = 1s_A + 1s_B$

Anti-Bonding Interaction

$\Psi_a = 1s_A - 1s_B$

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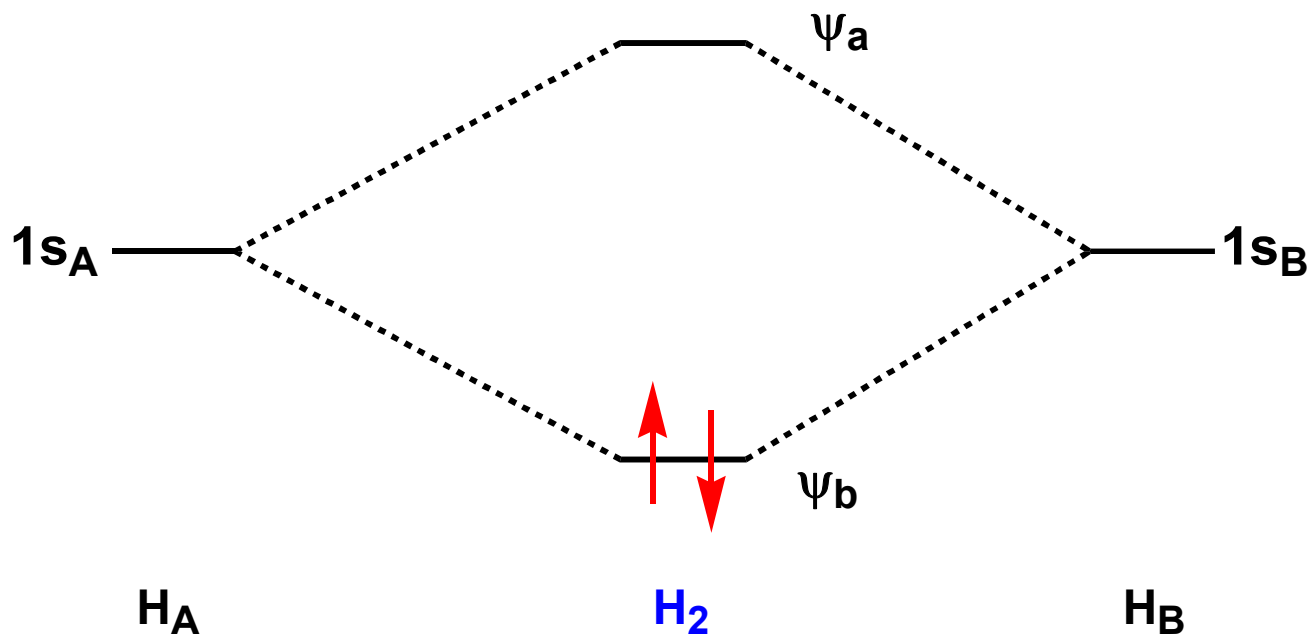
Probability of finding electron there is:

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

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.
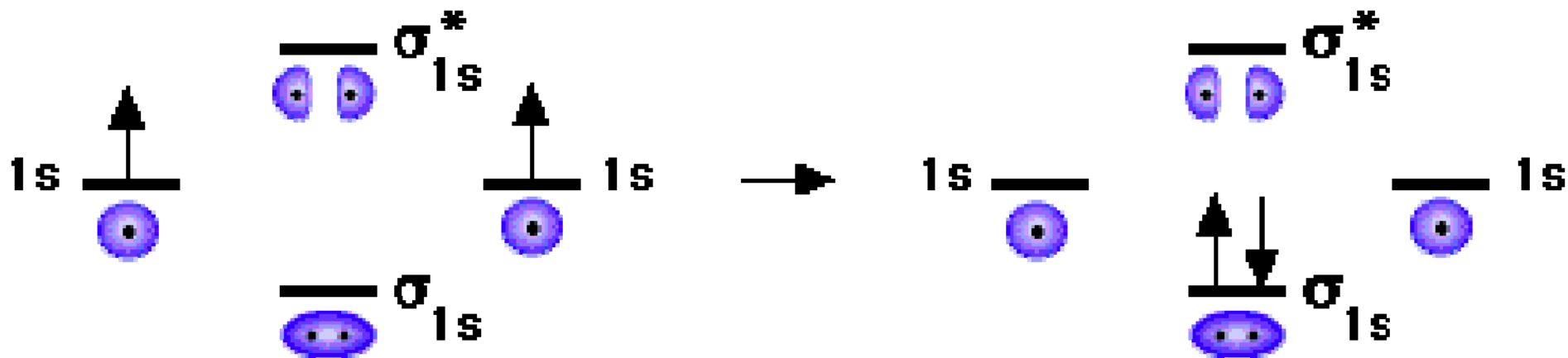
Thus an electron in ψ_b will hold the nuclei together, one in ψ_a will push them apart.

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}

$1s$ $1s$ → $1s$

σ_{1s}

σ^*_{1s}

$1s$

σ_{1s}

MO's for H$_2$ molecule

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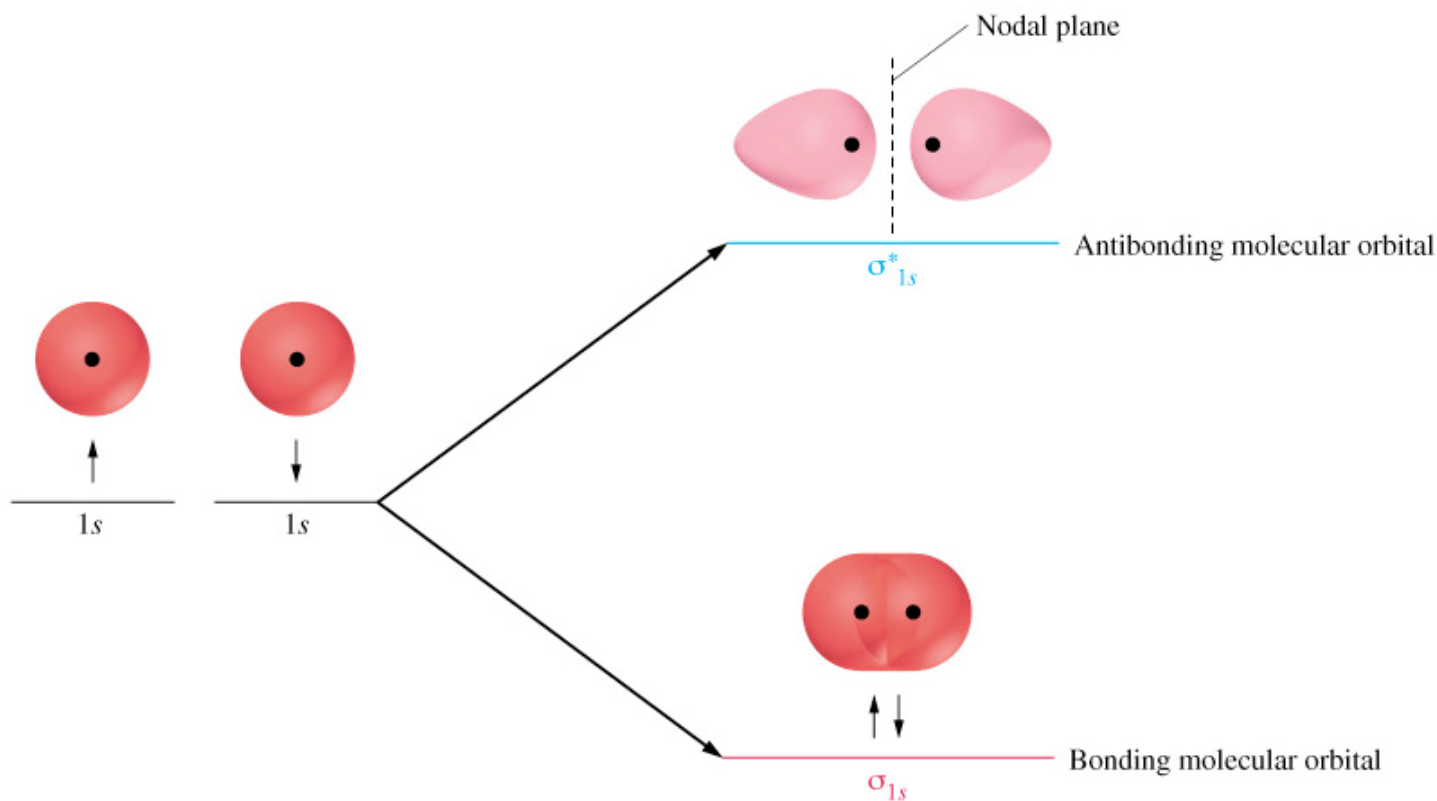
M.O.'s for homonuclear diatomics (A_2) for elements of first row of the Periodic Table

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

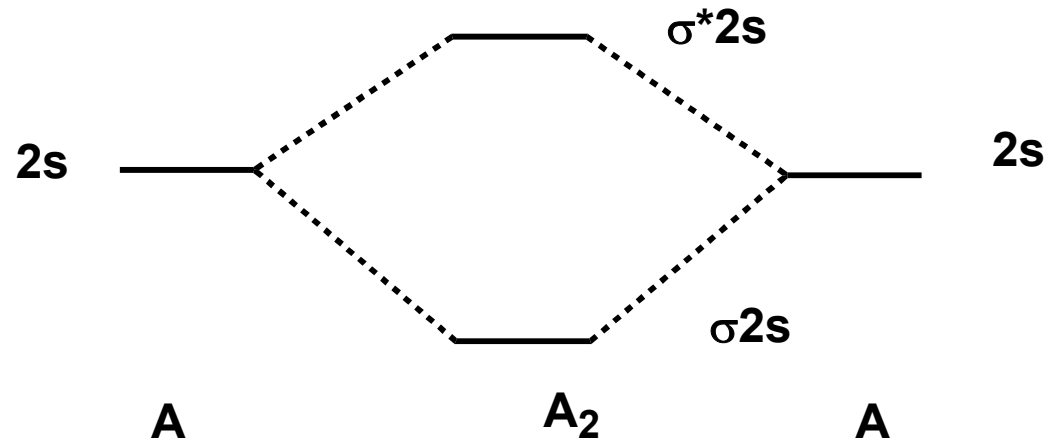**Thus, for H_2, bond order = (2 - 0)/2 = 1   (i.e. a single bond - as expected)**

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)

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
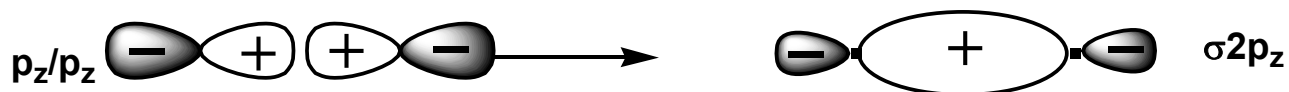 Li_2 exists in gas phase over metallic lithium.

"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

$\Psi_b = p_z + p_z$ $\Psi_a = p_z - p_z$

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

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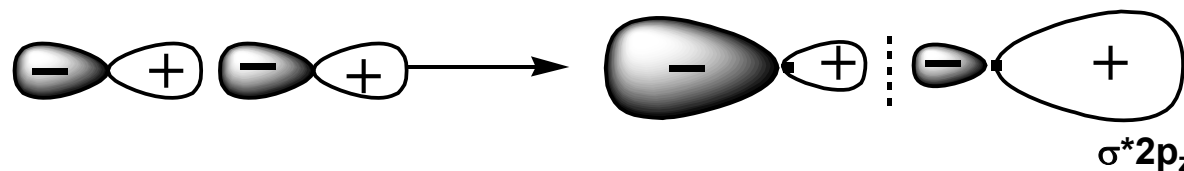
$p_z - p_z$ overlap everywhere negative→ ANTI-BONDING M.O.

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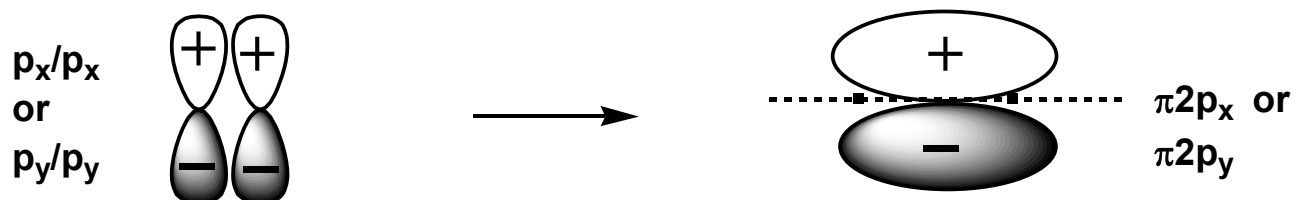
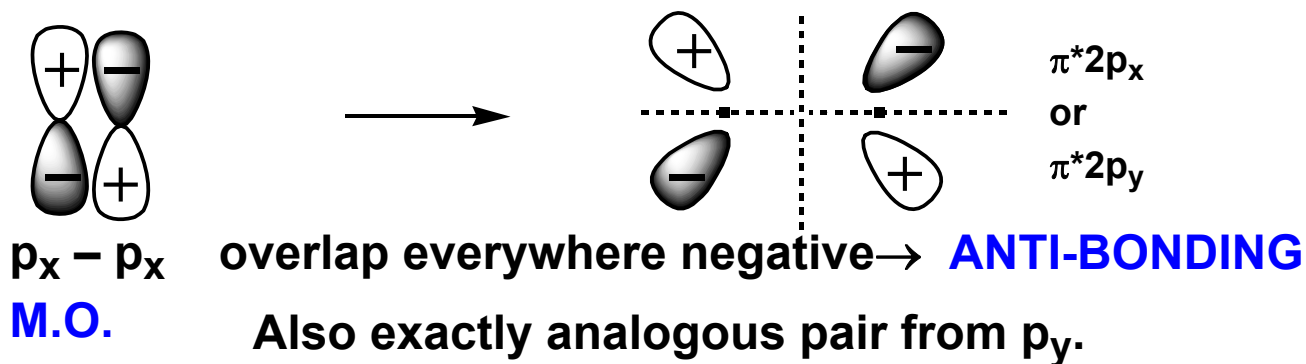p_x/p_x
or
p_y/p_y

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

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

Bonding Interaction

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

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

$p_x - p_x$ overlap everywhere negative→ **ANTI-BONDING**

π^*2p_x
or
π^*2p_y

M.O.

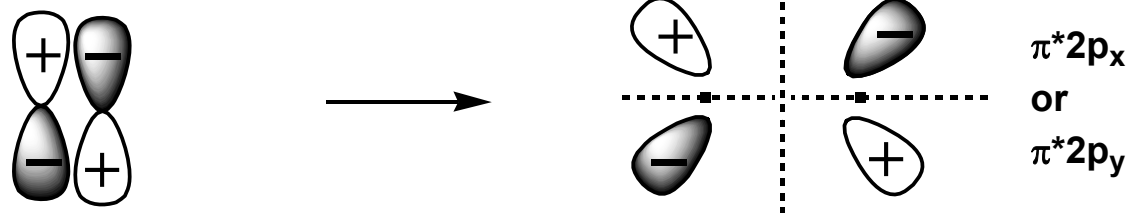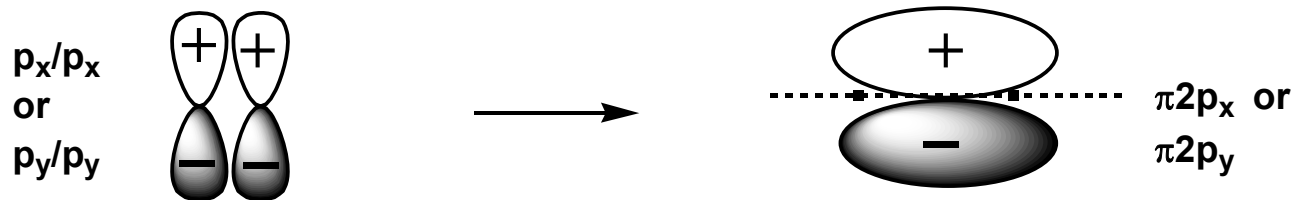**Also exactly analogous pair from p_y.**

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

Anti-Bonding Interaction

$$\Psi_a = p_x - p_x \text{ or } \Psi_b = p_y - p_y$$

Side-to-side overlap forms $\Pi^*2p_{x \text{ or } y}$ 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 $\psi_b = p_y + p_y$
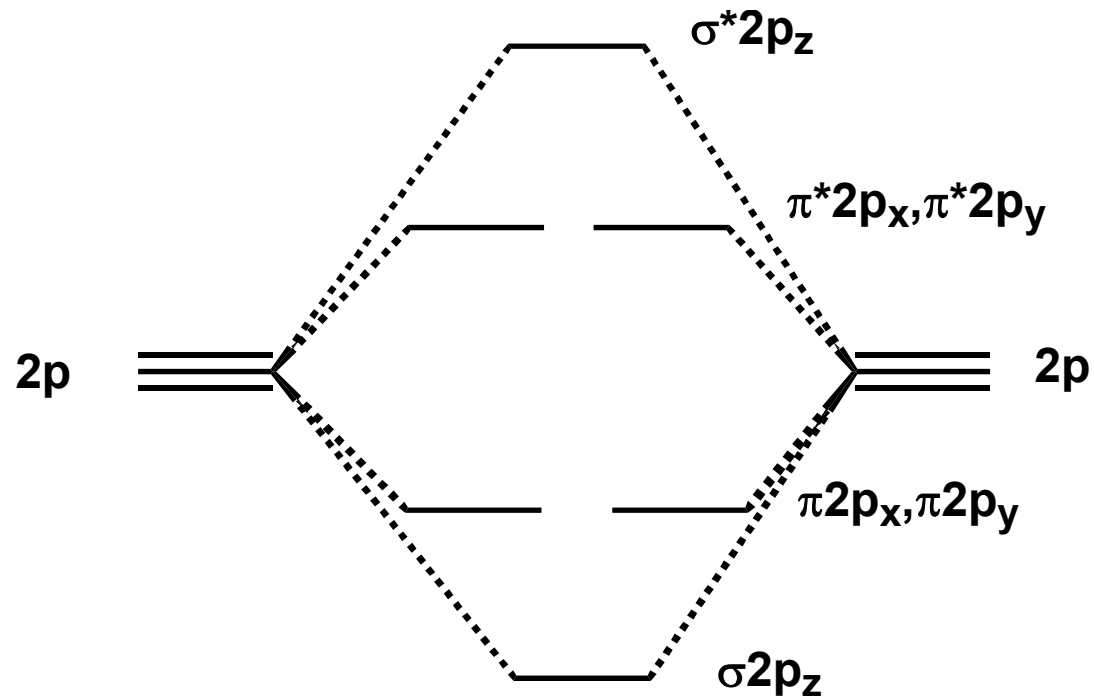
Side-to-side overlap forms $\pi 2p_{x \text{ or } y}$ MO

Anti-Bonding Interaction

$\psi_a = p_x - p_x$ or $\psi_b = p_y - p_y$

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

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

σ^*2p_z

π^*2p_x, π^*2p_y

2p

2p

$\pi 2p_x, \pi 2p_y$

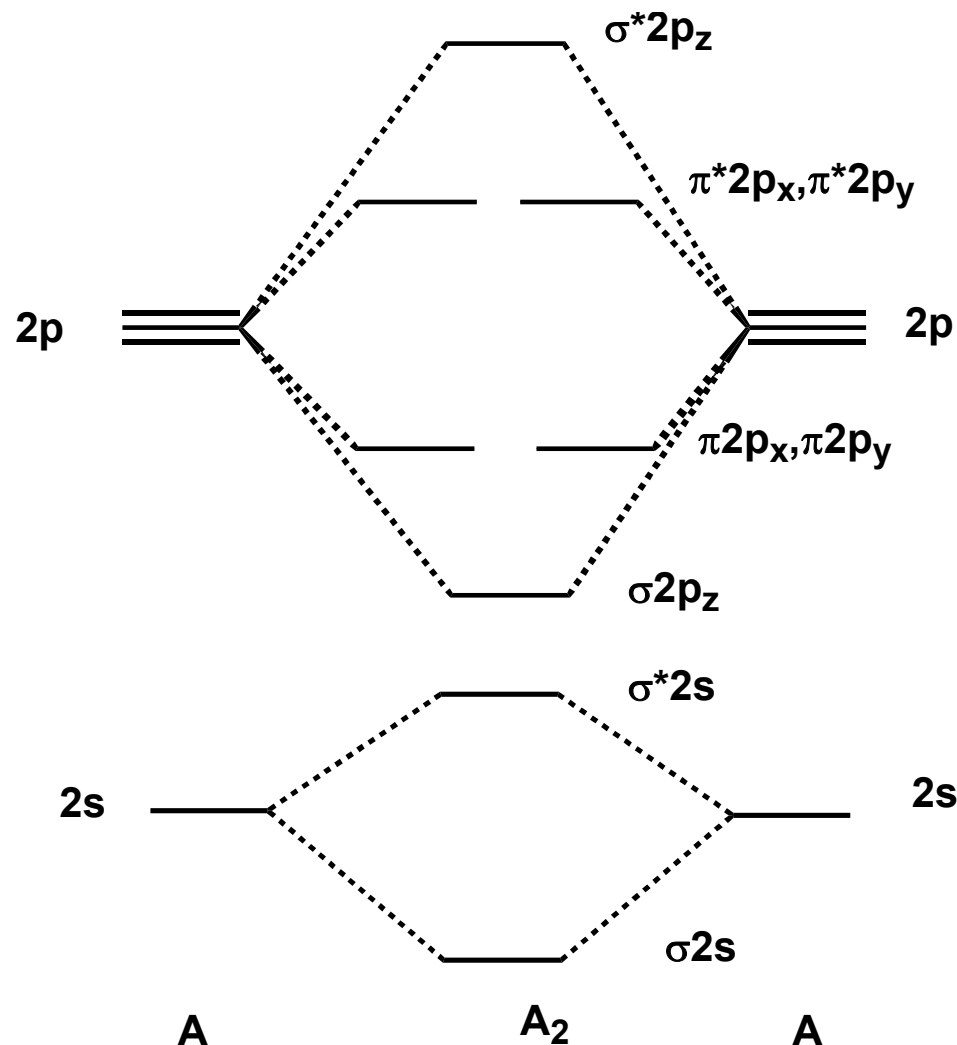$\sigma 2p_z$

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)

"No mixing of 2s and 2p"

σ^*2p_z

π^*2p_x, π^*2p_y

2p

2p

$\pi 2p_x, \pi 2p_y$

$\sigma 2p_z$

σ^*2s

2s

2s

$\sigma 2s$

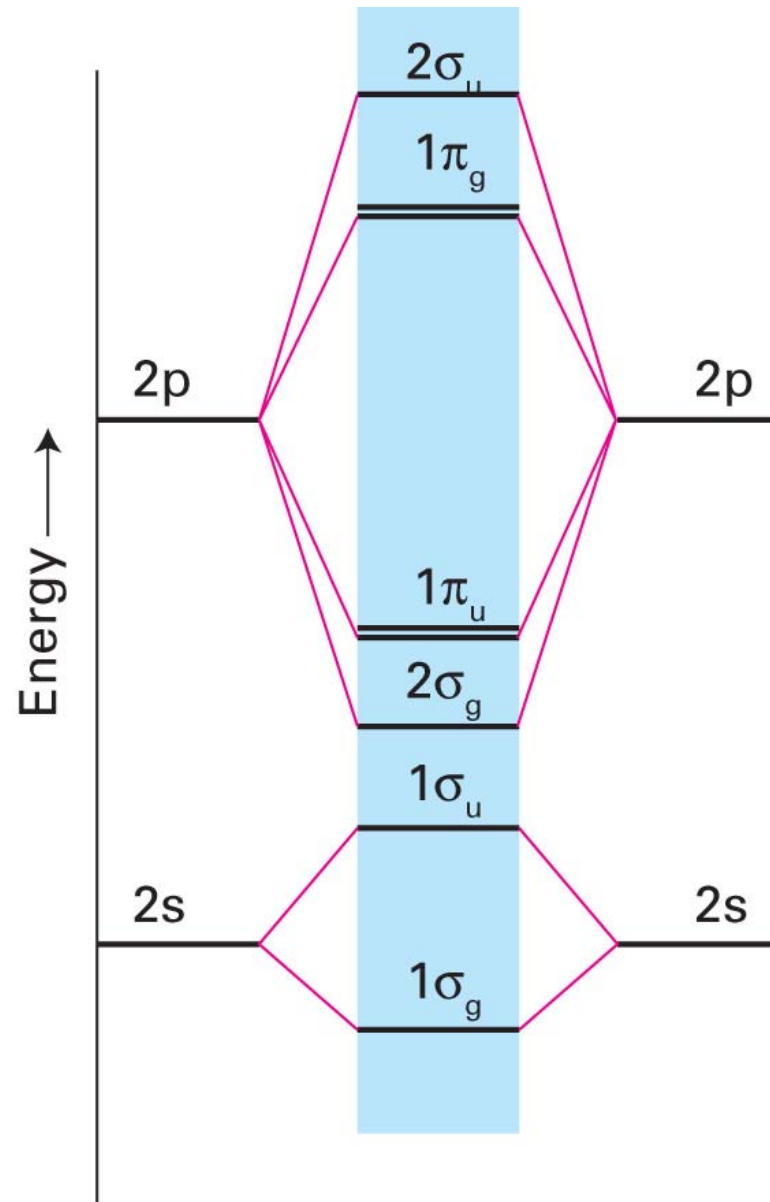A   A$_2$ A

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
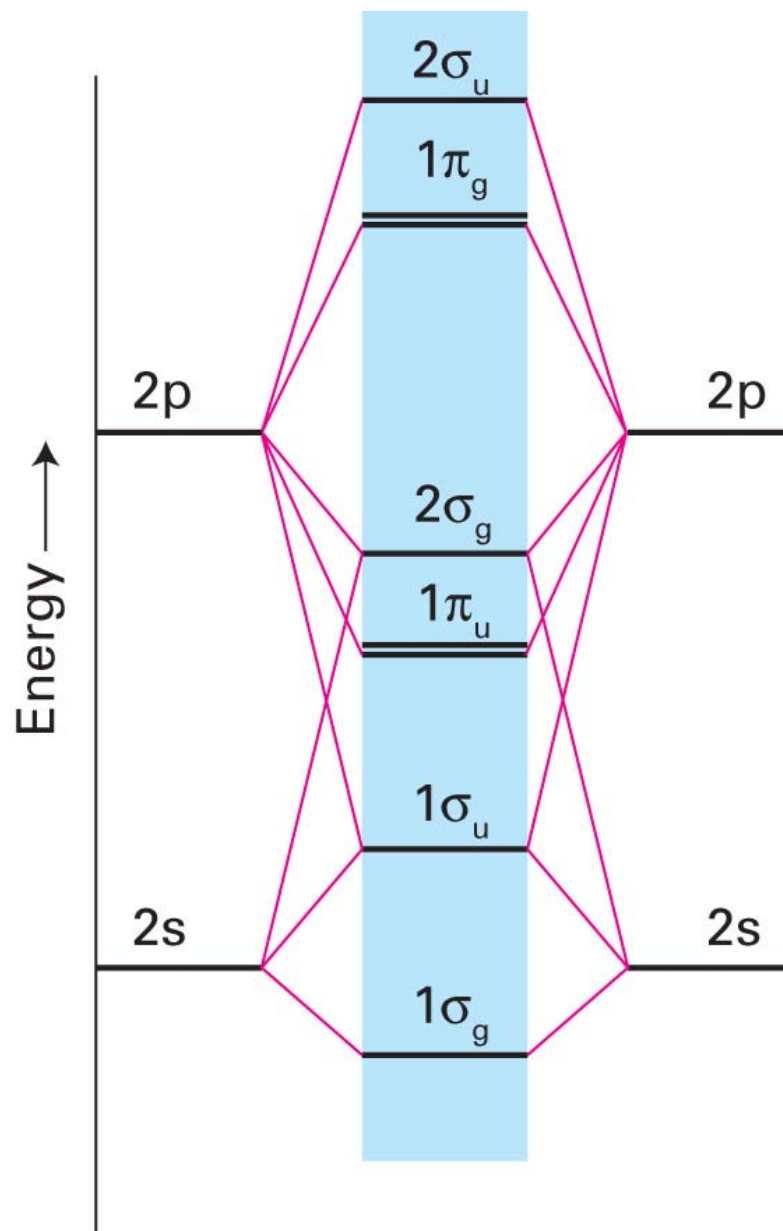(double bond) and PARAMAGNETIC.
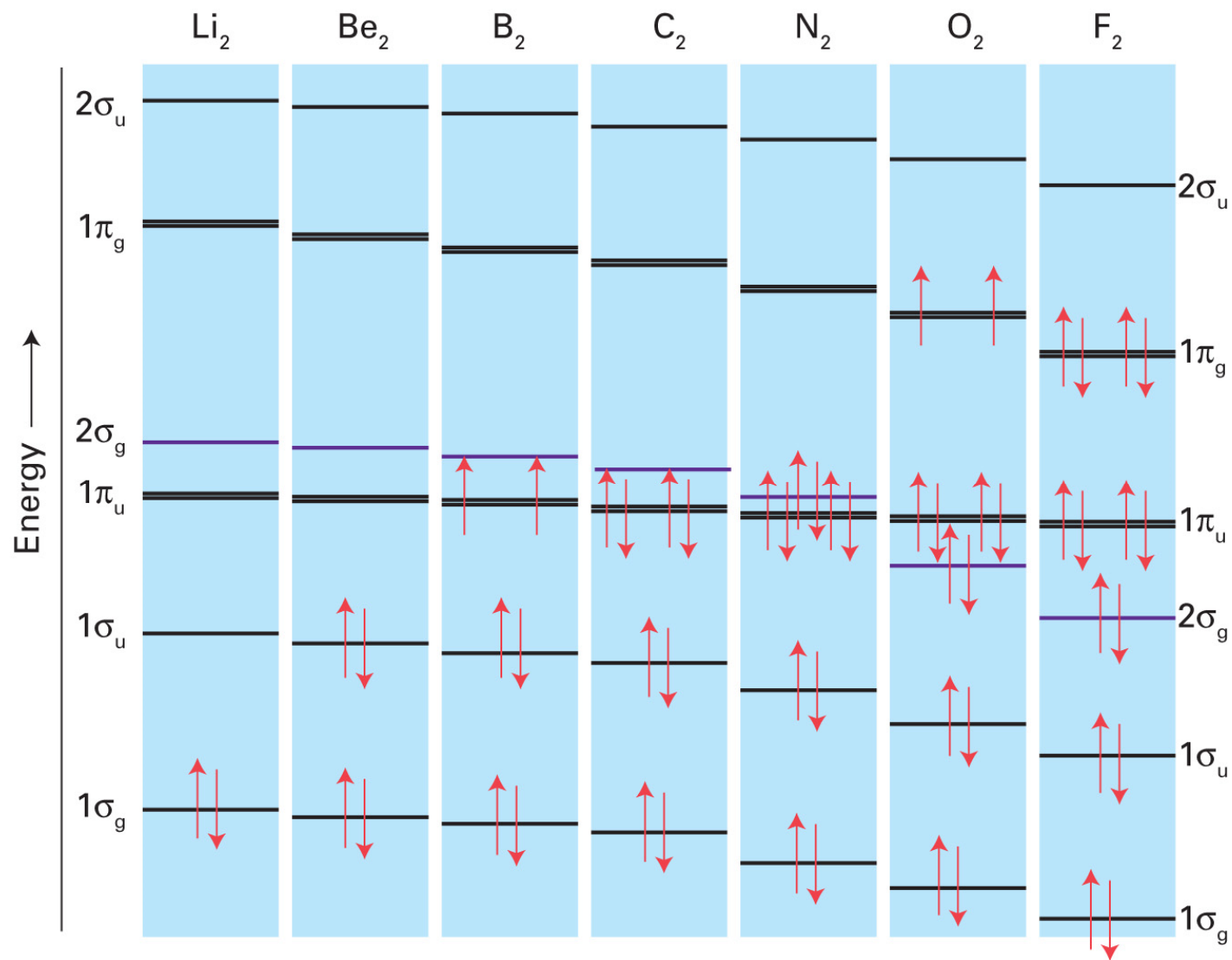V.B. theory could not explain paramagnetism.

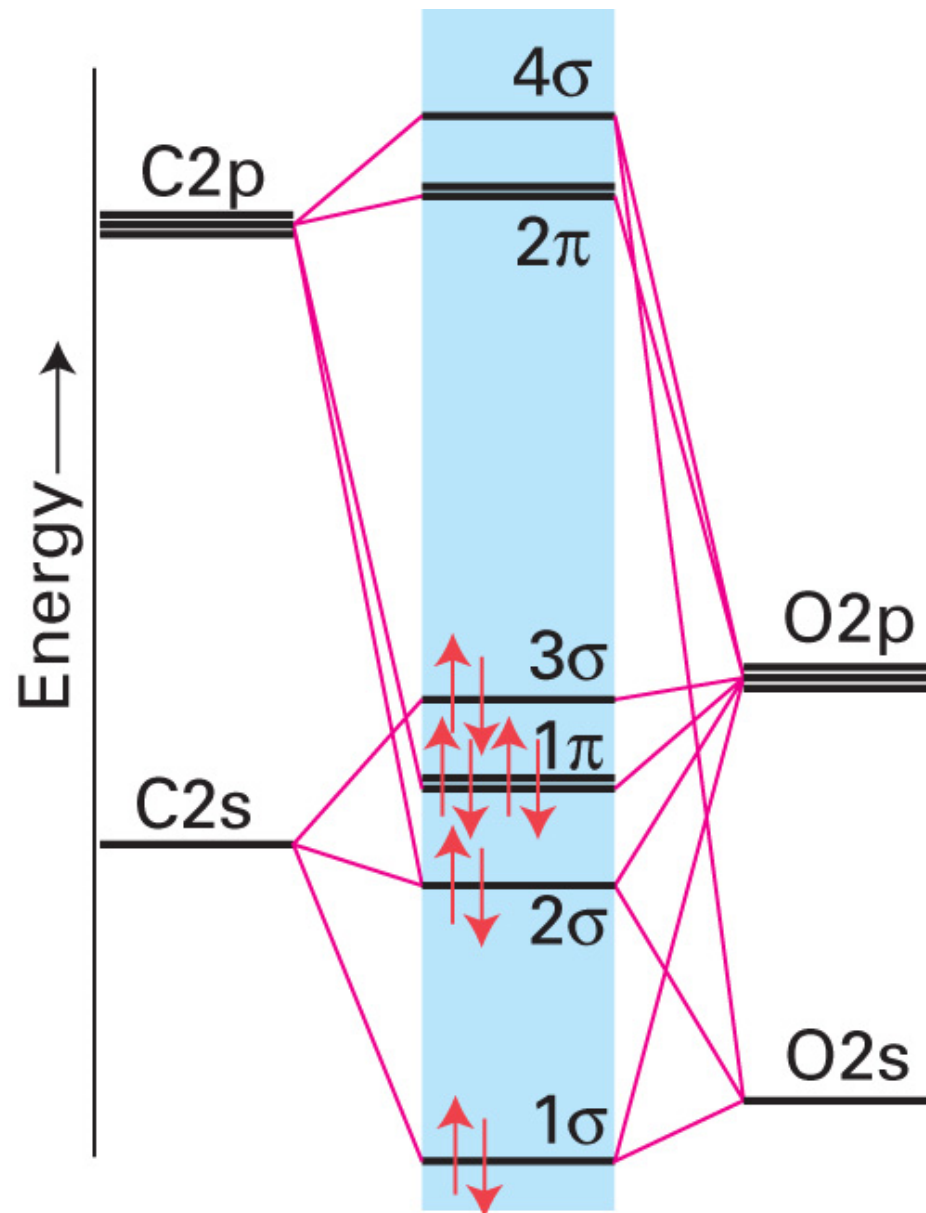Lecture 16 begins here

MO energy level diagram for O_2 and F_2

MO energy level diagram for Li$_2$ through N$_2$
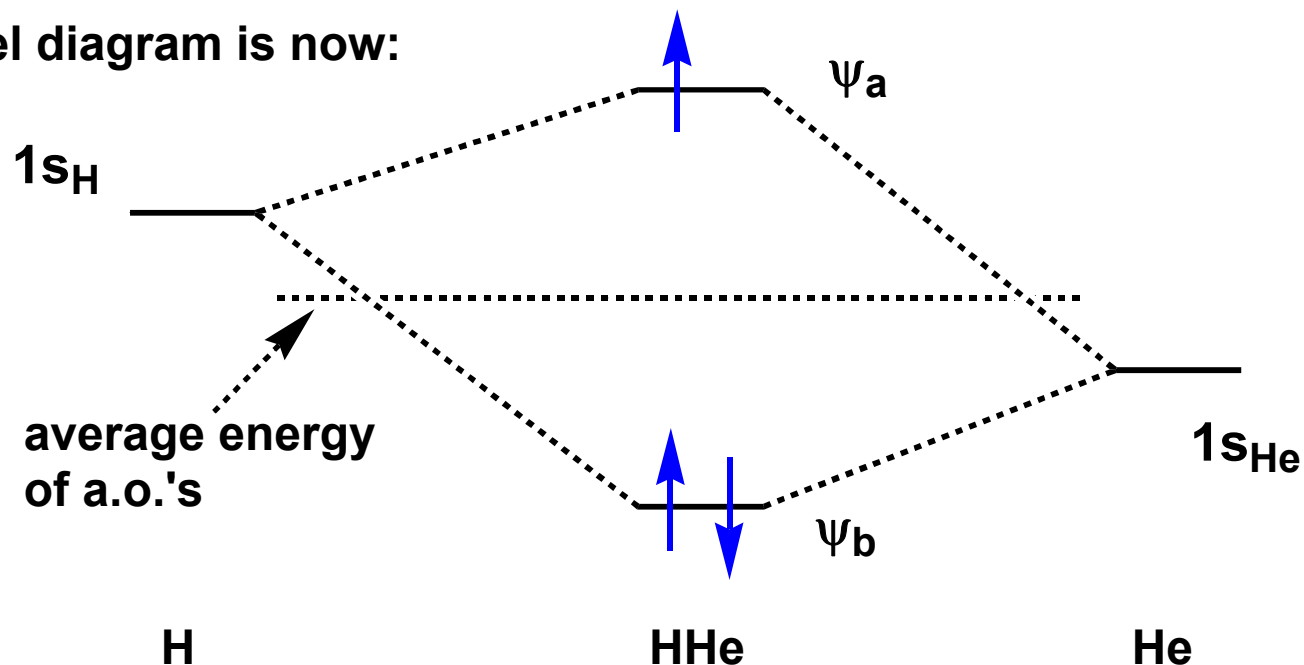
MO energy level diagram for CO

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.

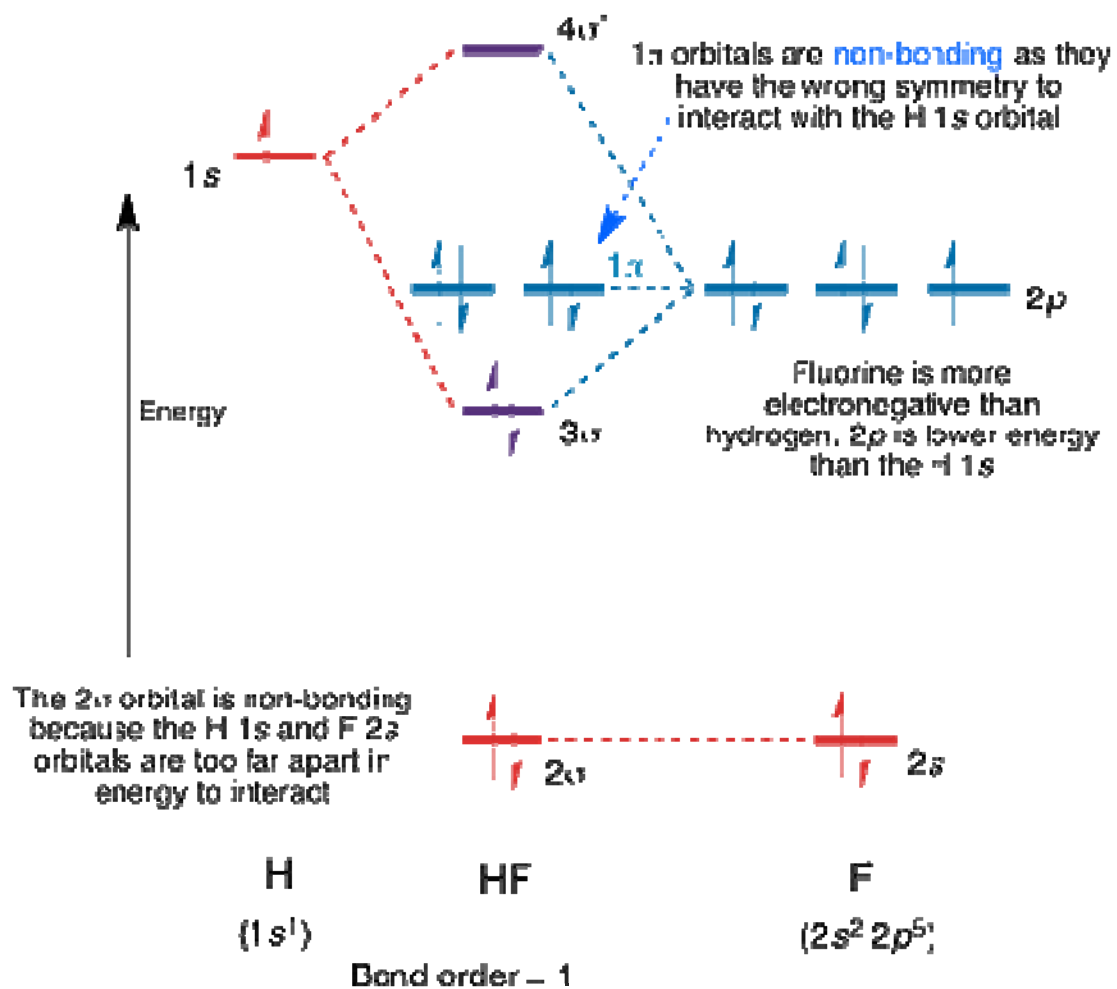**Energy level diagram is now:**

$1s_H$

ψ_a

average energy of a.o.'s

$1s_{He}$

ψ_b

H   HHe   He

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_2" - extra electron in antibonding m.o. - therefore bond order = 0. Molecule does not exist - no force to hold atoms together.
He is monatomic gas.

MO for Heteronuclear Diatomics: HF

$4\sigma^*$

$1s$

1π

$2p$

3σ

Energy

1π orbitals are non-bonding as they have the wrong symmetry to interact with the H $1s$ orbital

Fluorine is more electronegative than hydrogen. $2p$ is lower energy than the H $1s$

The 2σ orbital is non-bonding because the H $1s$ and F $2s$ orbitals are too far apart in energy to interact

2σ

$2s$

H

HF

F

$(1s^1)$

$(2s^2\,2p^5)$

Bond order = 1

MO's for CO: the contour plots and significance for Metal Carbonyls