MOLECULAR ORBITAL DIAGRAM

Magadh University, Bodh-Gaya

Dr. Partha Pratim Das
Assistant Professor
P.G. Department of Chemistry
Magadh University, Bodh-Gaya

❑**Basis of Valence bond approach: Overlap of orbitals in each bond separately. Each bond is LOCALISED between two atoms.**

❑**Basis of molecular orbital (MO) approach: Overlap of orbitals occurs for the whole molecule-bonding is therefore DELOCALISED.**

❖**Atomic orbitals:** Orbitals that are localized on single atoms.

❖**Molecular orbitals:** Orbitals that span two or more atoms. These are constructed by overlapping atomic orbitals (AOs) which match in symmetry and size.

In principle, To construct MO diagram of a any Molecule, first, set up Schrödinger wave equation for that molecule and then, solve it!!!

Solution will involve **Linear Combination of Atomic Orbitals** which are **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.**

Linear Combination of Atomic Orbitals

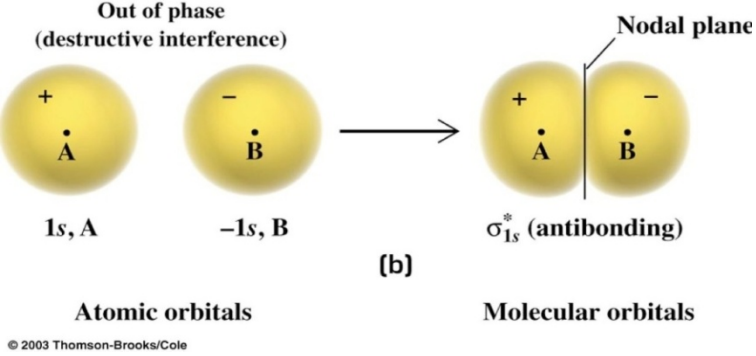
Simplest example - H_2: two H atoms H_A and H_B
Only two A.O.'s ($1s_A$, $1s_B$) to form linear combinations.

General rule: **n A.O.'s → n M.O.'s**

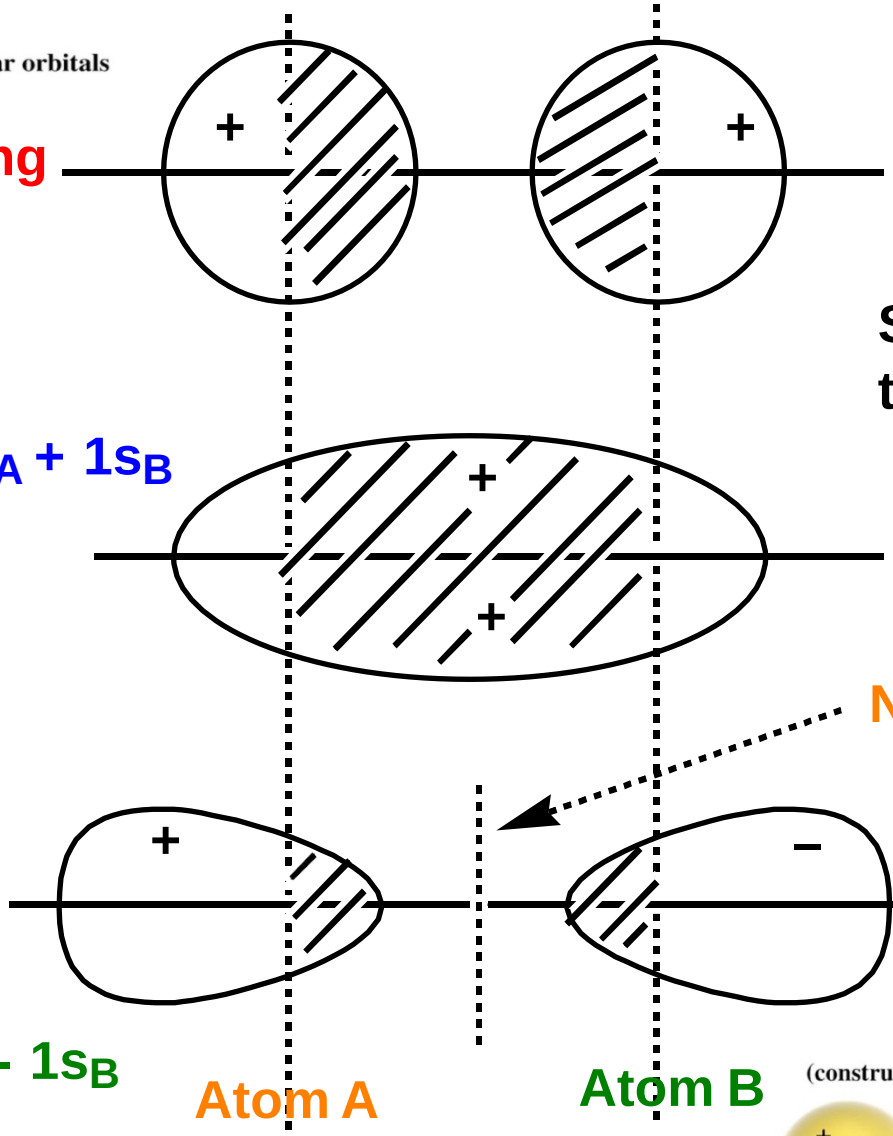
So we can only construct 2 m.o.'s for H_2 - and these are:

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

i.e. the sum (ψ_b) and the difference (ψ_a) of the constituent A.O.'s.



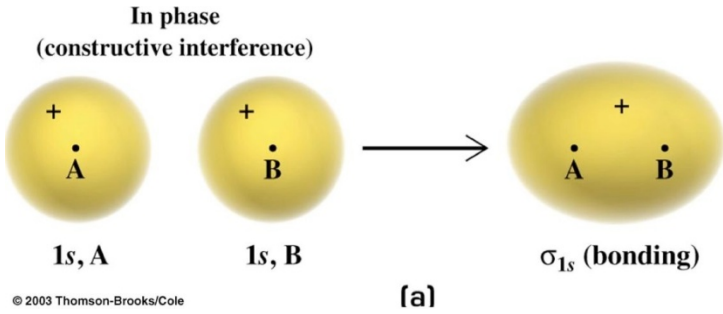
Two non-interacting H atoms



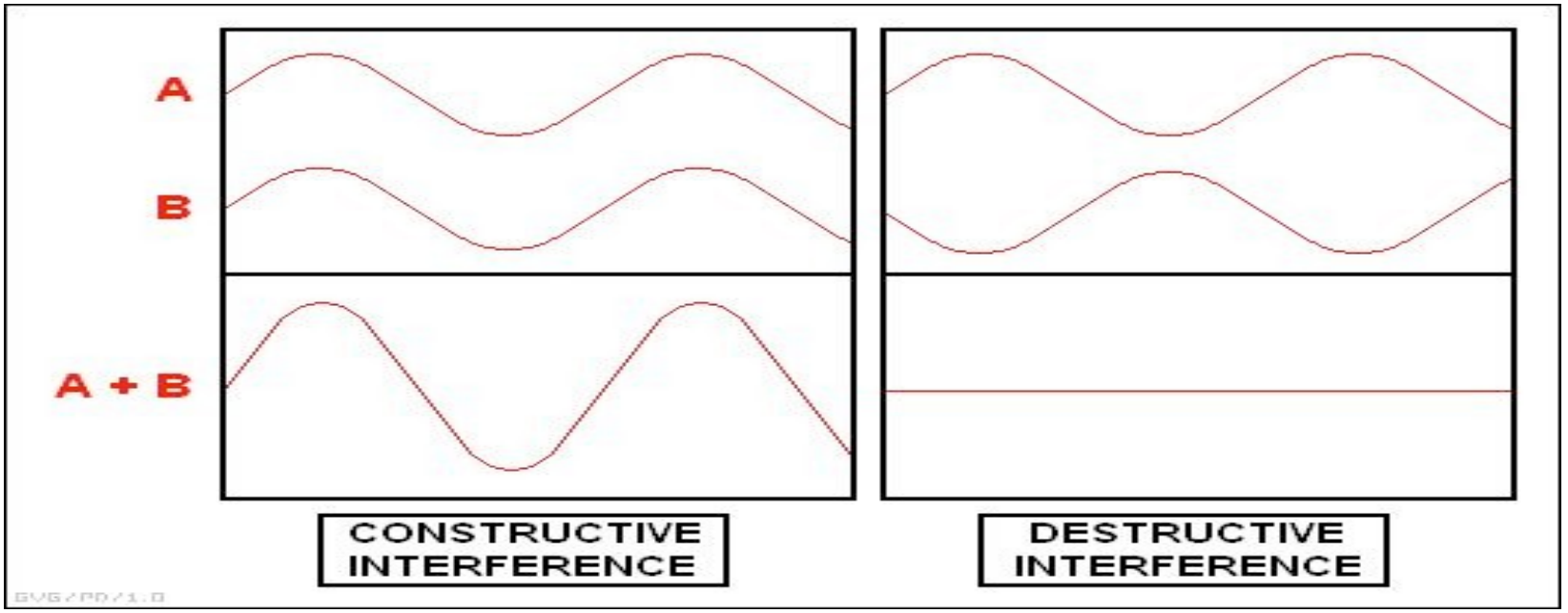
Signs refer to sign of ψ

$\psi_b = 1s_A + 1s_B$

$\psi_a = 1s_A - 1s_B$



Constructive and destructive interference of waves



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

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

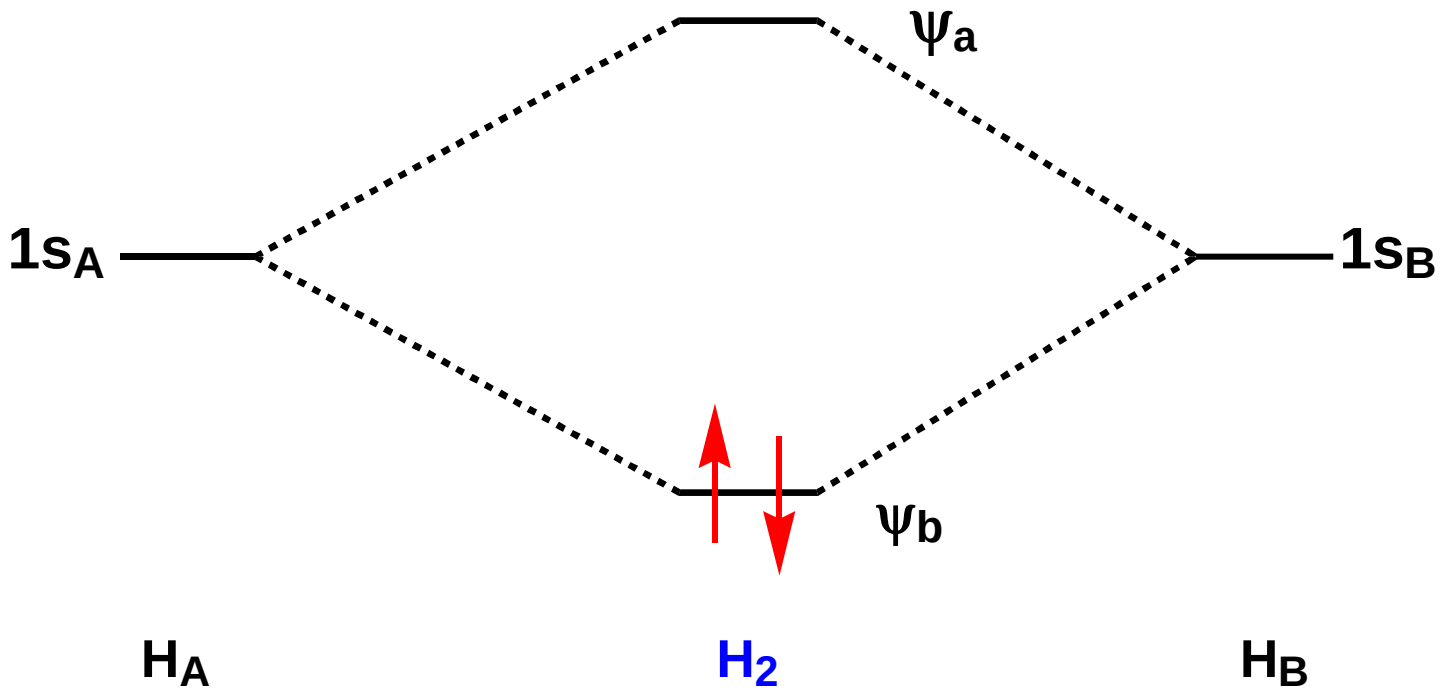
Electron in INTERNUCLER region is attracted by BOTH nuclei. Hence, electrons in ψ_b will be at lower energy than in non-interacting ψ_a A. O.'s, which will be at higher energy.

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

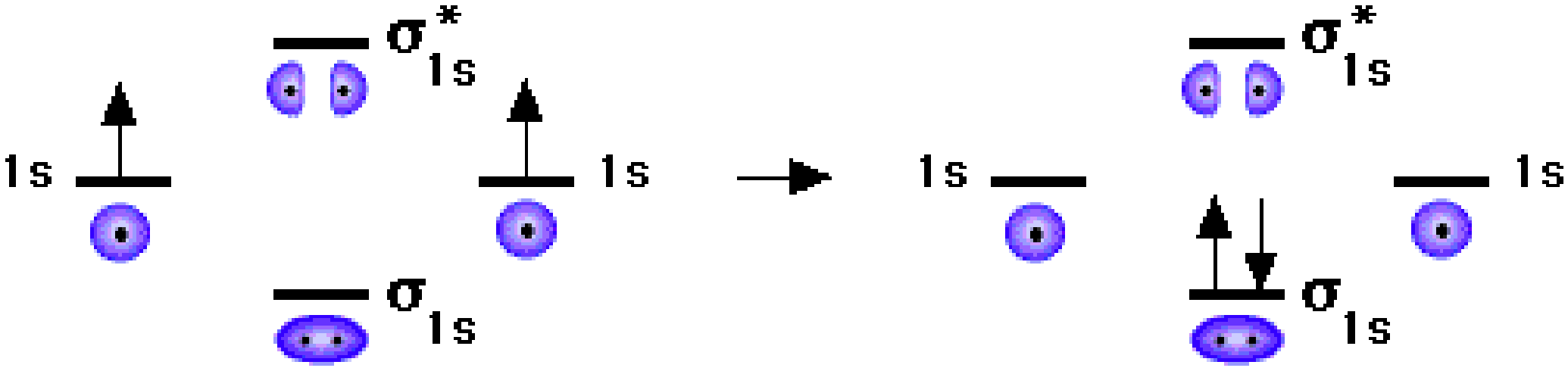
ψ_b is a BONDING M. O.

ψ_a is an ANTI-BONDING M. O.

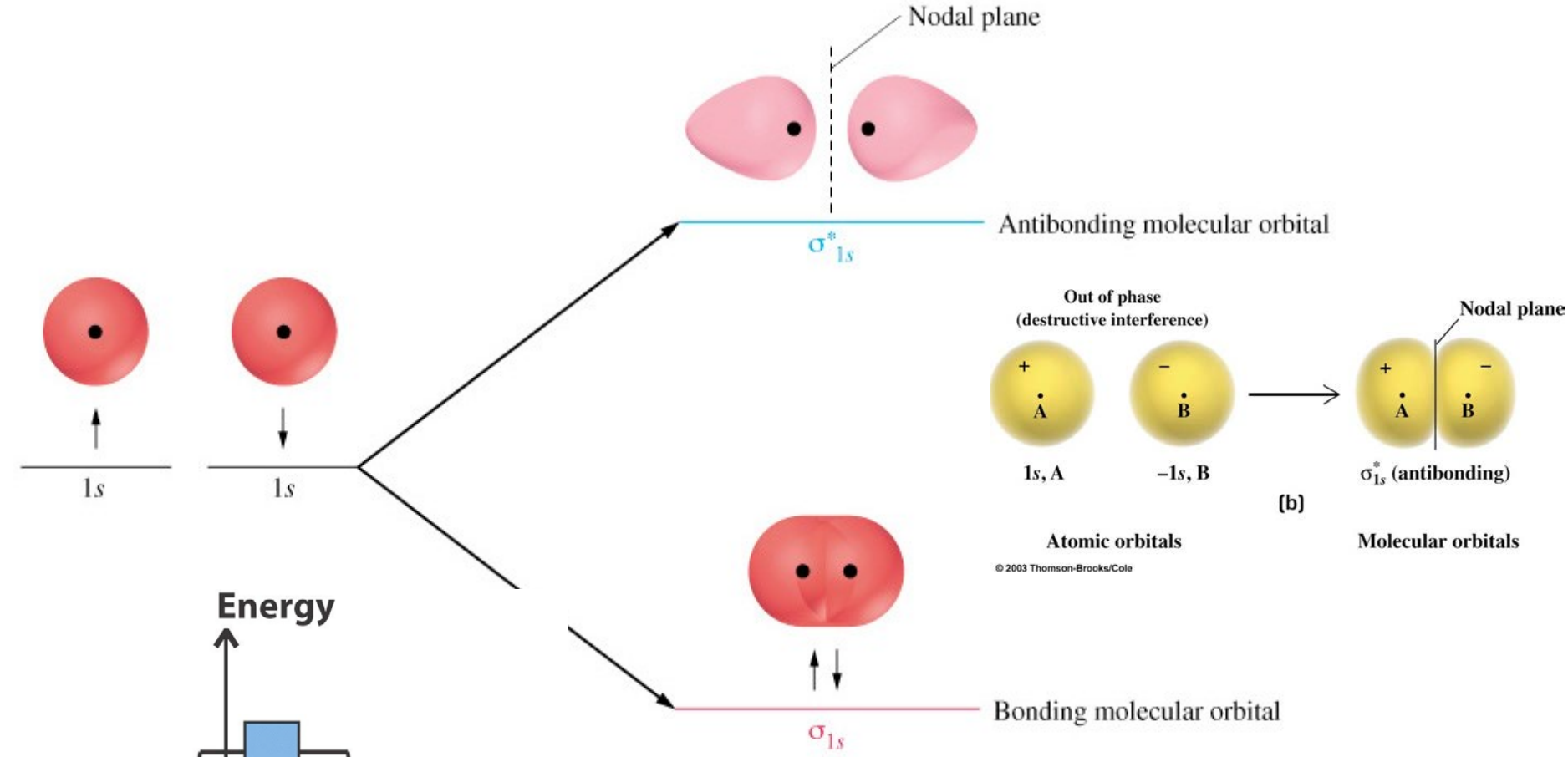
Thus we can draw Energy Level Diagram/ Correlation diagram for M.O.'s of H_2 :

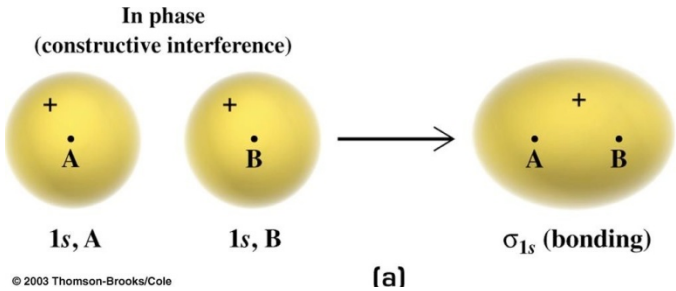


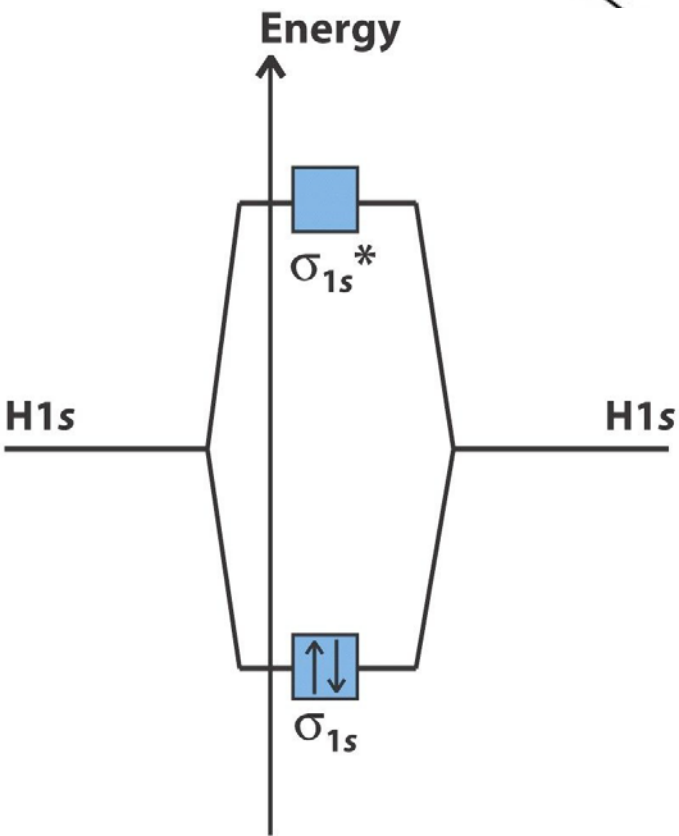
By Aufbau & Pauli principles - the 2 electrons go into ψ_b - with paired spins.



MO's for H_2 Molecule







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 i.e. the net number of bonds, allowing for the cancellation of bonds by anti-bonds

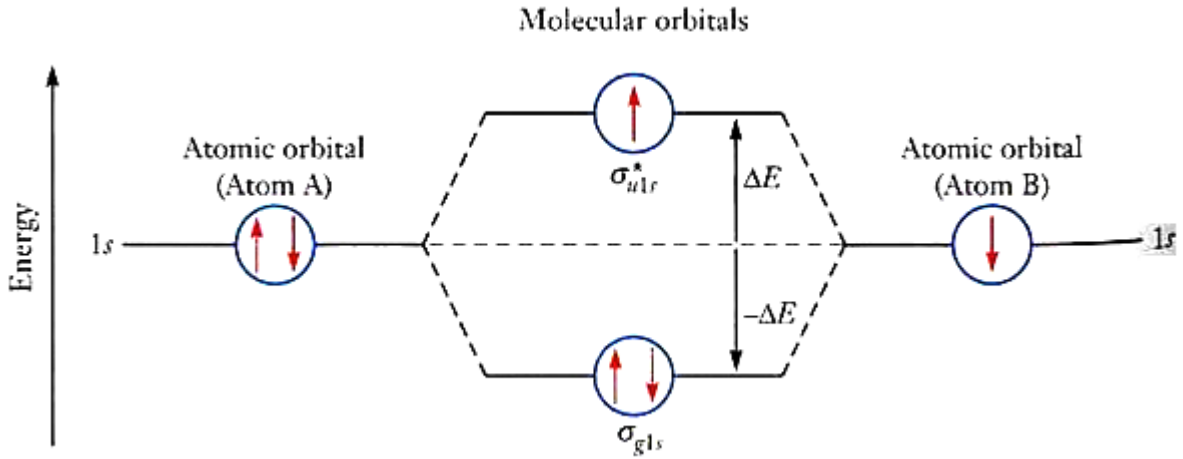
Thus, for H_2, bond order = (2 - 0)/2 = 1 (i.e. a single bond - as expected), Any diatomic molecule with B.O. > 0 is considered stable relative to the two dissociated atoms.

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.

The electronic configuration of a H_2 molecule is σ_{1s}^2
The subscript ($_{1s}$) tells which AOs are combined, the superscript (^{2}) tells how many electrons are in the MO
What is the bond order of the first electronically excited state of H_2? The electronic configuration of the first excited state of H_2 is $(\sigma_{1s})^1(\sigma^*_{1s})^1$. Bond order = 1/2(1 - 1) = 0. Photochemical excitation of H_2 makes it fly apart into 2 H atoms.

What hypothetical diatomic molecules might fit this electron configuration?



- Answer: Any diatomic with three electron Isoelectronic valence = $(\sigma_{1s})^2\ (\sigma_{1s}^*)^1$
- Plausible diatomics possessing only combinations of H or He atoms: H_2^-, He_2^+, HHe and the configuration $(\sigma_{1s})^2(\sigma_{1s}^*)^1$
  - A shared pair of electrons make a single covalent bond
  - Electrons in bonding orbitals enhance bonding, electrons in anti-bonding orbitals reduce bonding

TABLE Configurations and Bond Orders for First-Row Homonuclear Diatomic Molecules

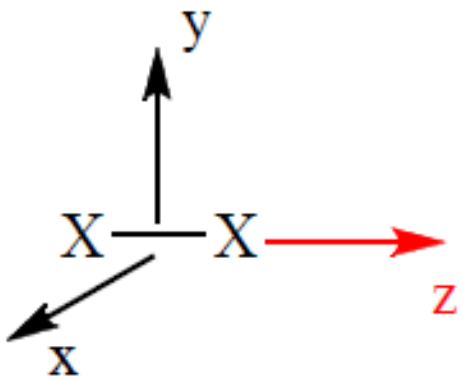
Species	Electron Configuration	Bond Order	Bond Enthalpy (kJ mol^{-1})	Bond Length (Å)
H_2^+	$(\sigma_{1s})^1$	$\frac{1}{2}$	255	1.06
H_2	$(\sigma_{1s})^2$	1	431	0.74
He_2^+	$(\sigma_{1s})^2(\sigma_{1s}^*)^1$	$\frac{1}{2}$	251	1.08
He_2	$(\sigma_{1s})^2(\sigma_{1s}^*)^2$	0	Not observed	

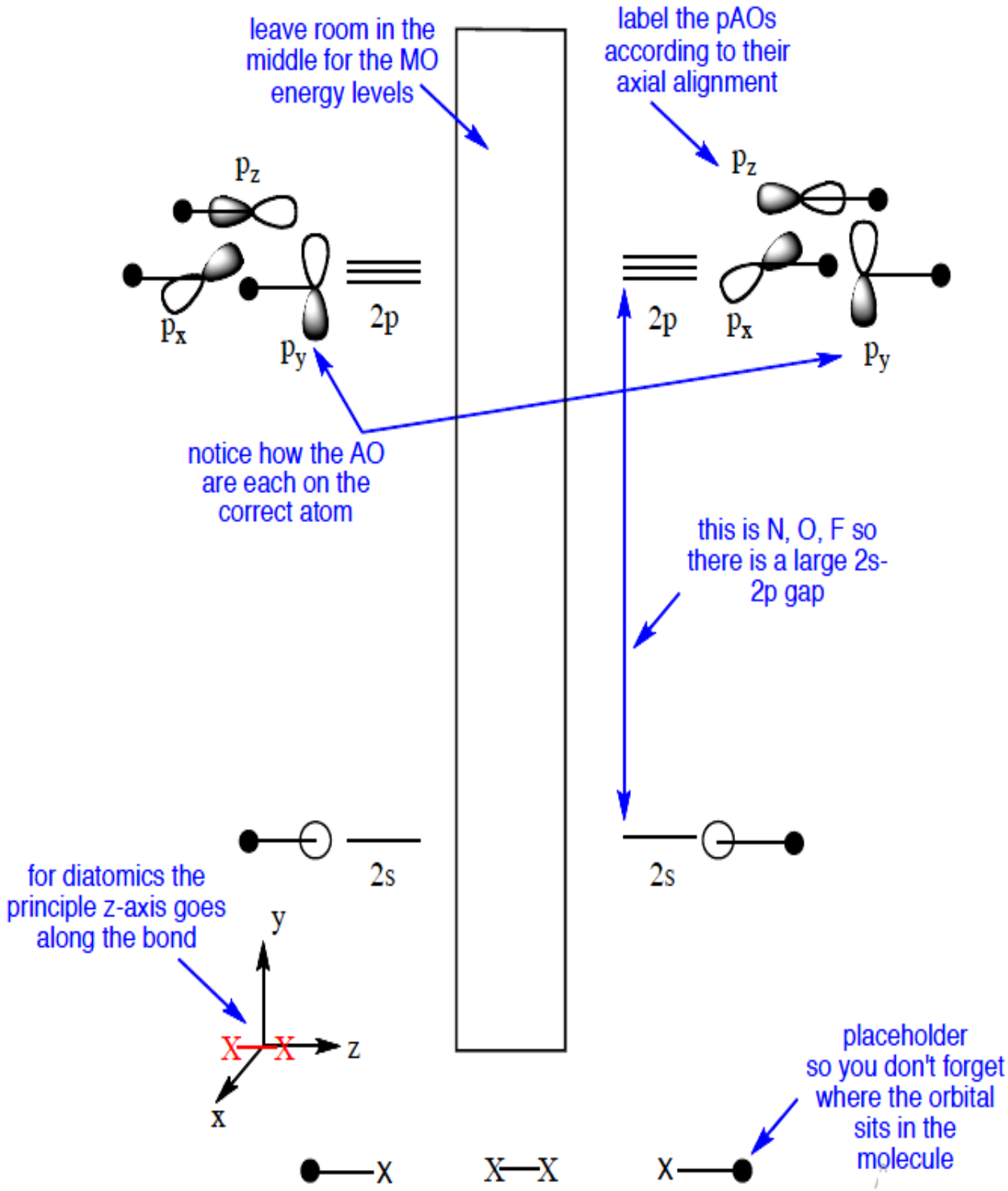
Setting up the diagram

❖Start by considering the axial definition: Always put the z-axis along the bond in diatomics.

❖Always add a diagram clearly showing how the axial system related to your molecule on your MO diagram then start the diagram itself, remember the vertical "axis" of the whole diagram is energy and the horizontal axis are the fragments, atoms in the case of a simple diatomic

❖Add the molecule in the centre at the bottom, and the individual atomic fragments either side, don't forget to add placeholders so that you know where the orbtials should ‘sit’.





Now you need the atomic orbitals,

- The 1s AOs are not shown, generally only the valence orbitals are shown in MO diagrams.
- For C the gap between the 2s and 2p orbitals is small, this is why C forms sp hybrids.
- However for all the other elements to the right of C such as N, O, F the sp gap is larger and gets increases long the periodic table, thus for F the gap is very large.
- Put the 2s and 2p AOs on the diagram taking note of the distance between the energy levels.

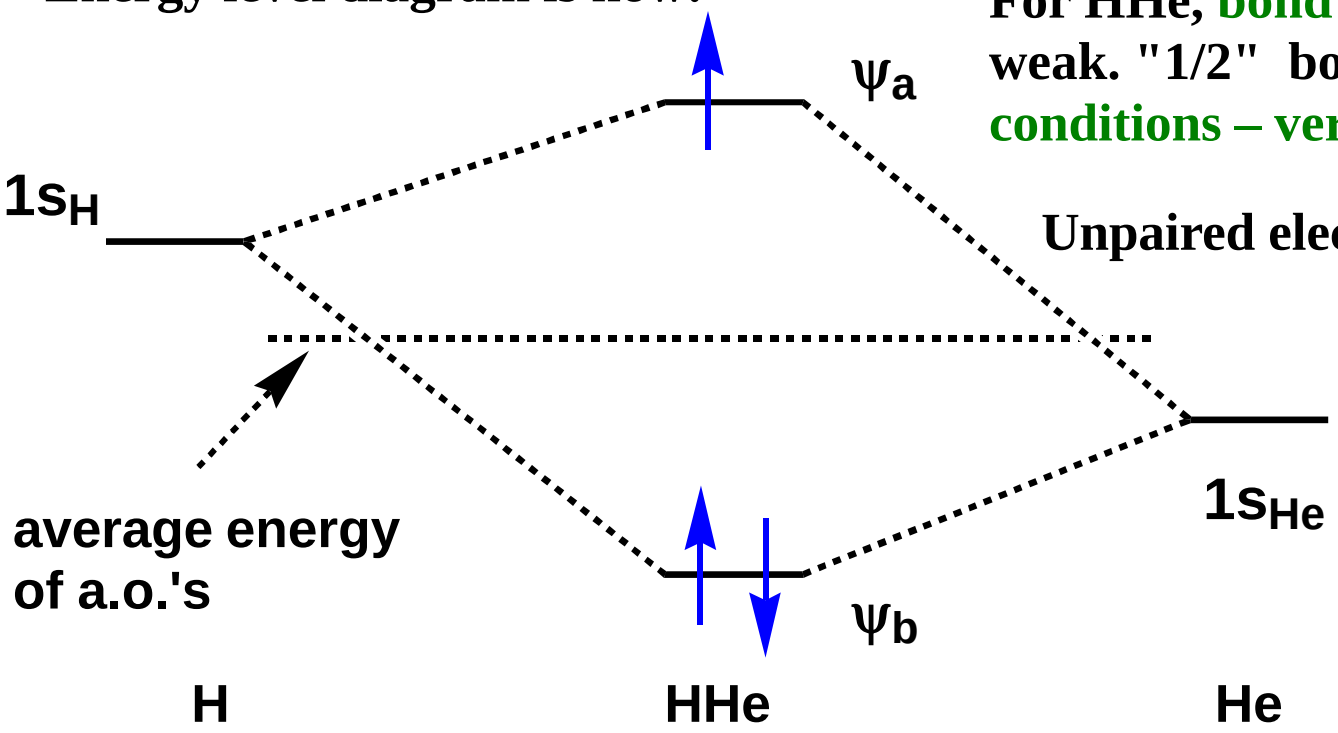
Heteronuclear diatomic molecules

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

(1) A.O. energies for H, He different. He has greater nuclear charge, electrons are more tightly bound.

(2) Now three electrons to feed into M.O.'s.

Energy level diagram is now:



For HHe, bond order = (2 - 1)/2 = 1/2 i.e. very weak. "1/2" bond- not formed under normal conditions – very 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.

For heteronuclear diatomics, M.O.'s formed symmetrically above and below AVERAGE energy of constituent A.O.'s

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

Li_2, Be_2, B_2 etc. are more complex than for H_2, HHe due to more available A.O.'s - 1s, 2s, 2p. Are there restrictions on overlap?

(1) VALENCE electrons are involved 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)

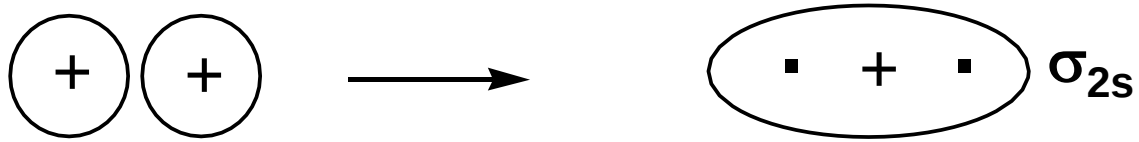
(3) SYMMETRY RESTRICTIONS These are best shown pictorially

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

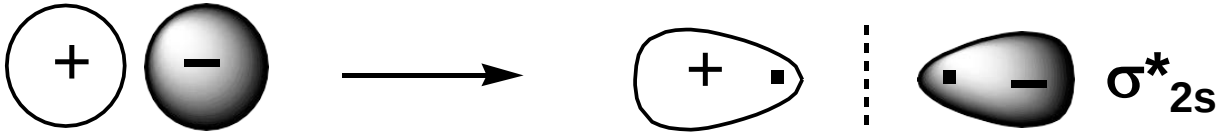
Building up the MOs of simple diatomic molecules

Mix atomic orbitals (AOs) of the same or similar energies to form molecular orbitals (MOs)

$2s + 2s$	$= \sigma_{2s} + \sigma_{2s}^*$	
$2p_z + 2p_z$	$= \pi_{2p} + \pi_{2p}^*$	Total of 8 MOs which can hold up to 16 electrons
$2p_x + 2p_x$	$= \pi_{2p} + \pi_{2p}^*$	
$2p_y + 2p_y$	$= \pi_{2p} + \pi_{2p}^*$	

s/s  σ_{2s}

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

 σ^*_{2s}

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

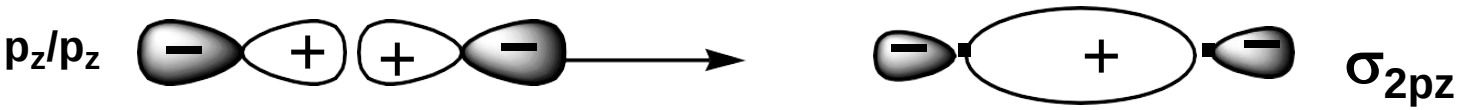
Bonding Interaction

$\psi_b = 1s_A + 1s_B$

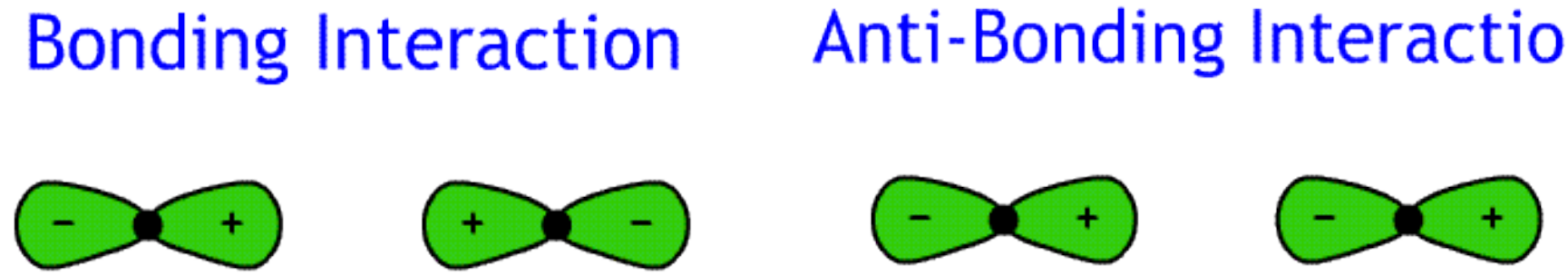
Anti-Bonding Interaction

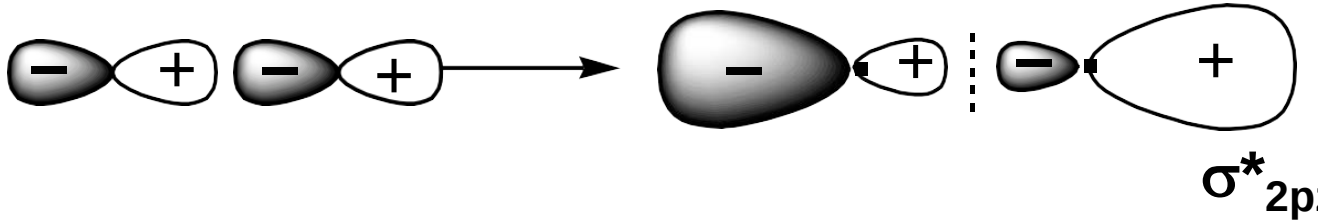
$\psi_a = 1s_A - 1s_B$

For p orbitals - three orbitals 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 → BONDING M.O.



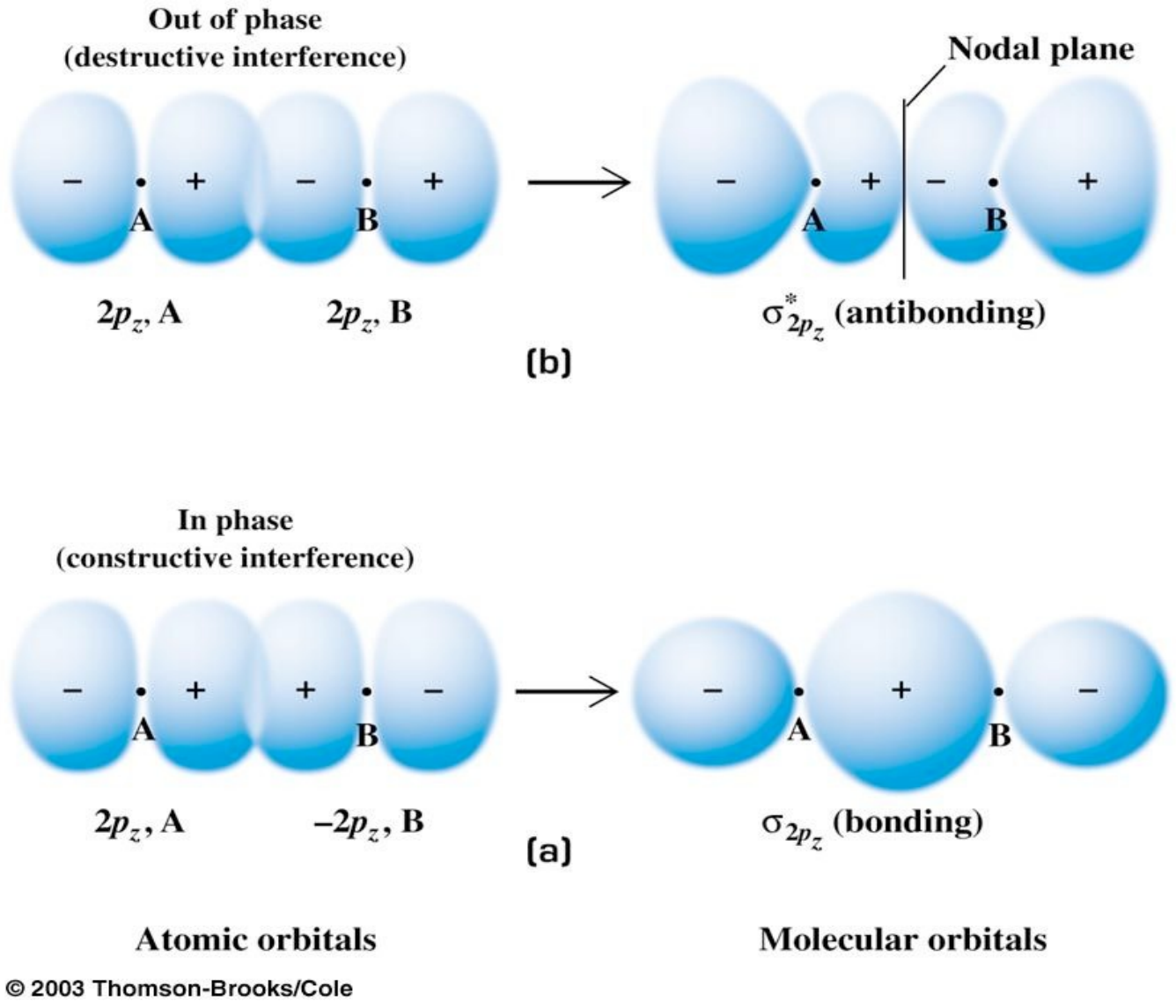


$p_z - p_z$ overlap everywhere negative → ANTI-BONDING M.O.

Constructive and destructive overlap of 2p orbitals to form σ and σ* orbitals

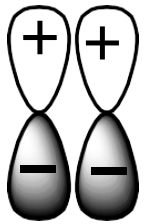
(a) Bonding σ orbital; (b) Antibonding σ* orbital

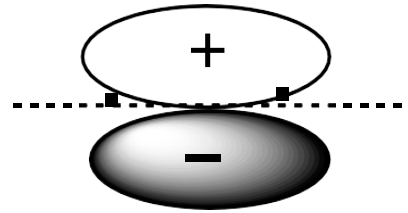
Overlap along the internuclear axis is termed σ overlap. The resulting orbitals are called σ and σ* orbitals



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

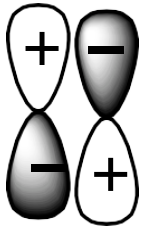
p_x/p_x or p_y/p_y

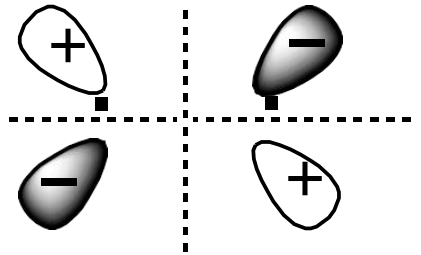




$\pi 2p_x$ or $\pi 2p_y$

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





$\pi^* 2p_x$ or $\pi^* 2p_y$

$p_x - p_x$ overlap everywhere negative → ANTI-BONDING M. O. Also exactly analogous pair from p_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

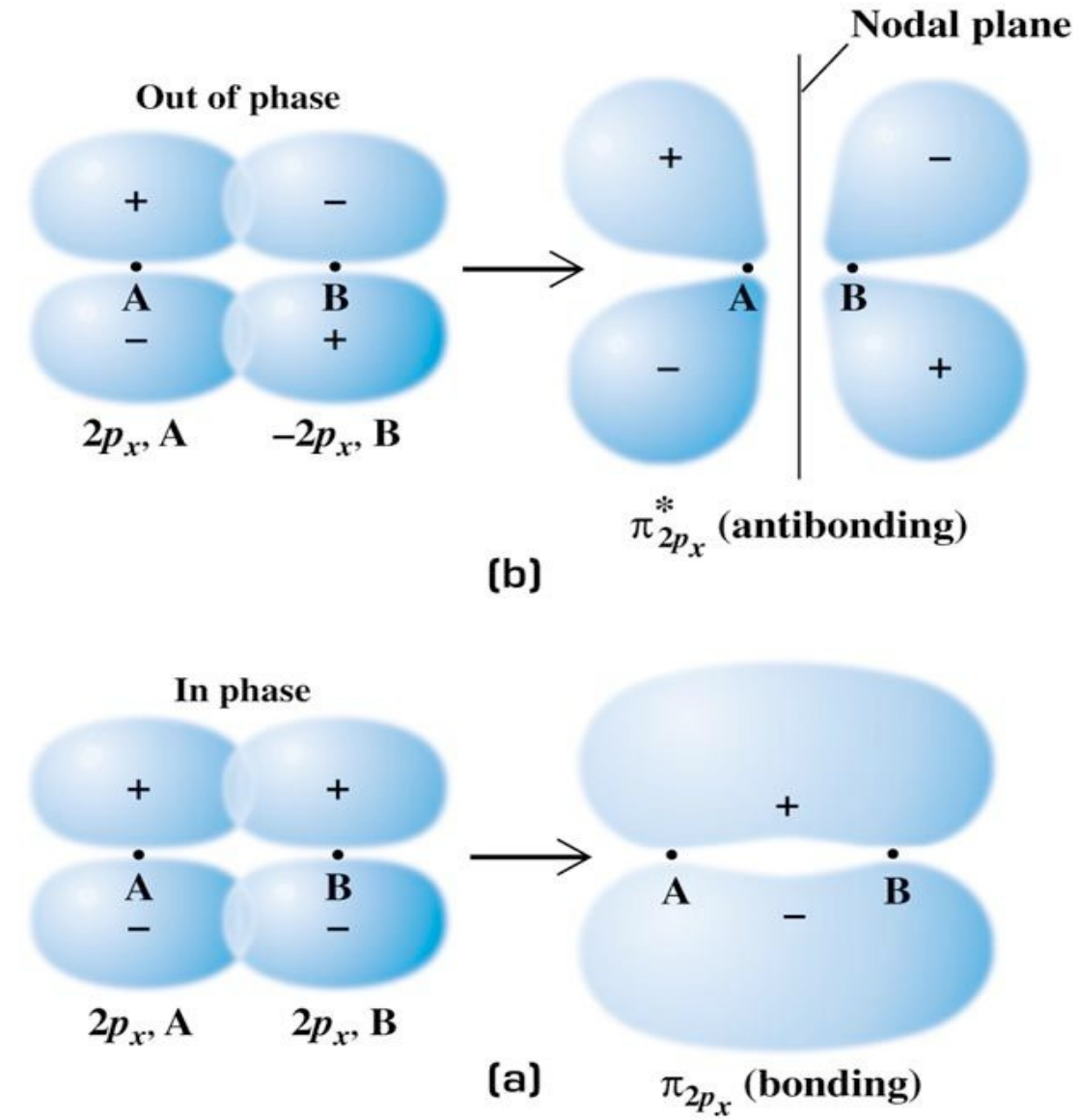
$\psi_a = p_x - p_x$ or $\psi_b = p_y - p_y$

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

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

Constructive and destructive overlap of 2 p orbitals to form π and π^* orbitals

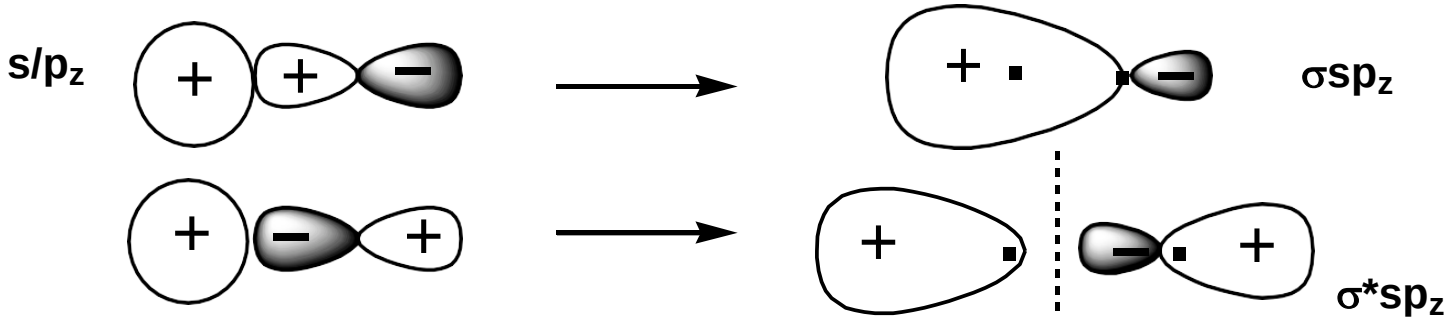
(a) Bonding π orbital; (b) Antibonding π^* orbital



Overlap perpendicular to the internuclear axis is termed p overlap. A nodal plane that contains the bond axis. The resulting orbitals are called π and π^* orbitals

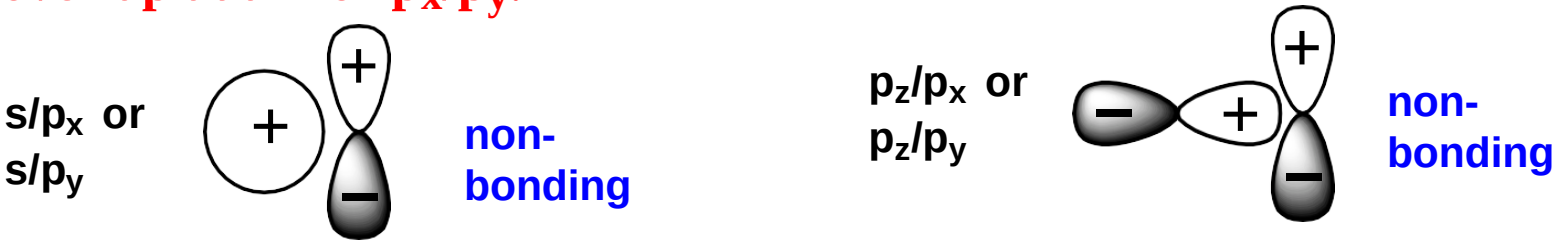
Remember: + and - refer to mathematical symbols, not charge

s/p_z gives bonding and anti-bonding pair.



s/p_x or p_y and p_z/p_x or p_y gives all non-bonding (positive and negative overlaps cancel).

No overlap at all for p_x/p_y.



Before moving on to show the energy level diagram for A_2 molecules - we need to be clear about the 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 : σ ("sigma")

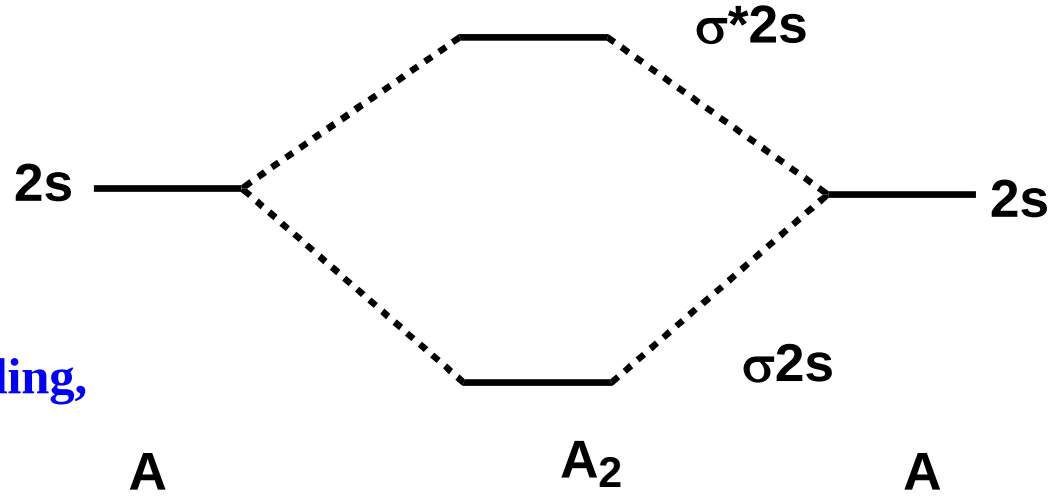
p_x/p_x, p_y/p_y - change sign every 180^o rotation - these are given symbol : π ("pi")

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

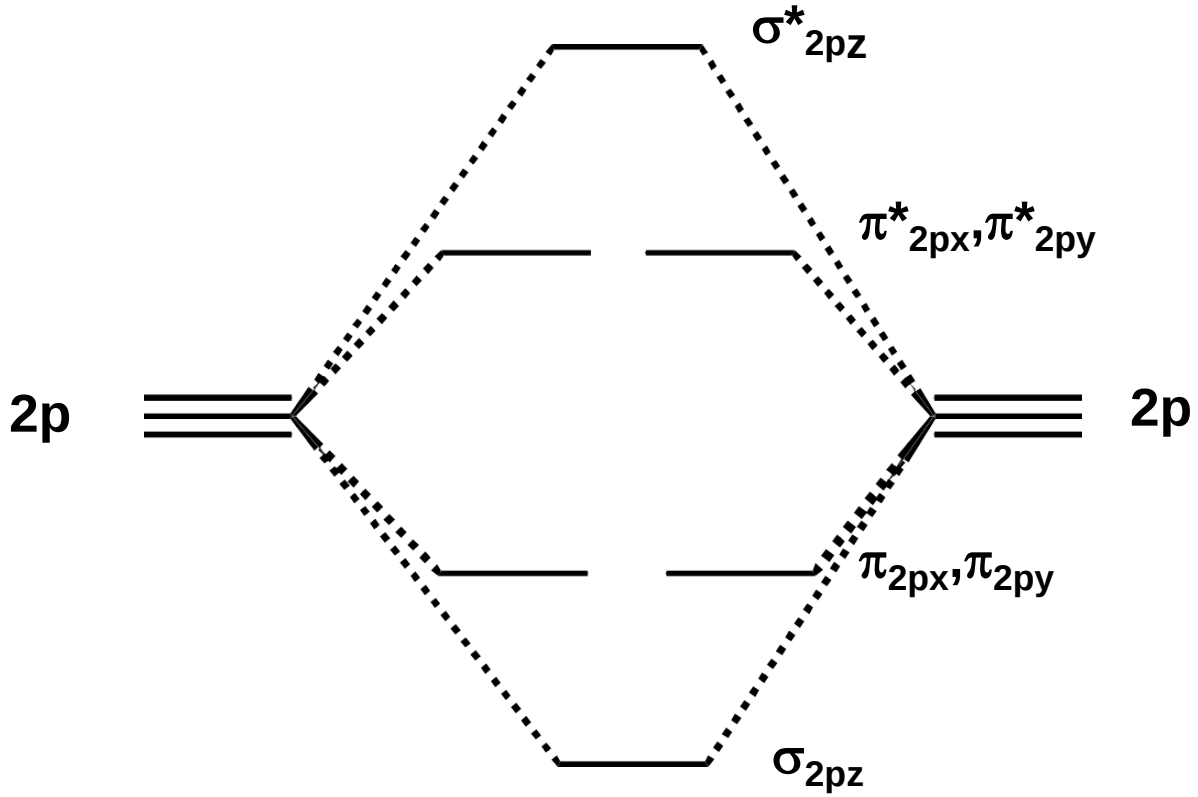
Li_2 Only two valence electrons, i.e. $\sigma_s^2\ \sigma^*_s{}^0$. Bond order = 1. Diamagnetic

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.

M.O.'s derived from 2p A.O.'s:



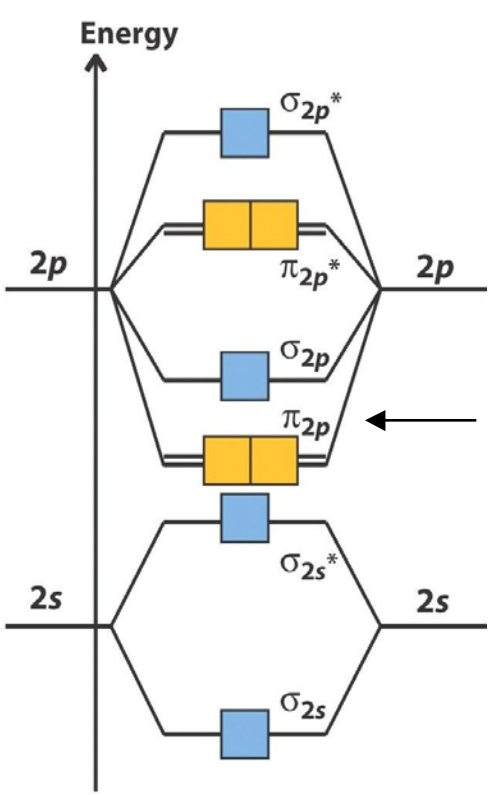
❖ p_x, p_y alike in all respects except orientation, so M. O.'s derived from them must be degenerate.

❖ Sideways (π) overlap is less efficient than end-on (σ), so π M. O.'s less bonding than σ

Now we have the orbitals, what are their relative energies?

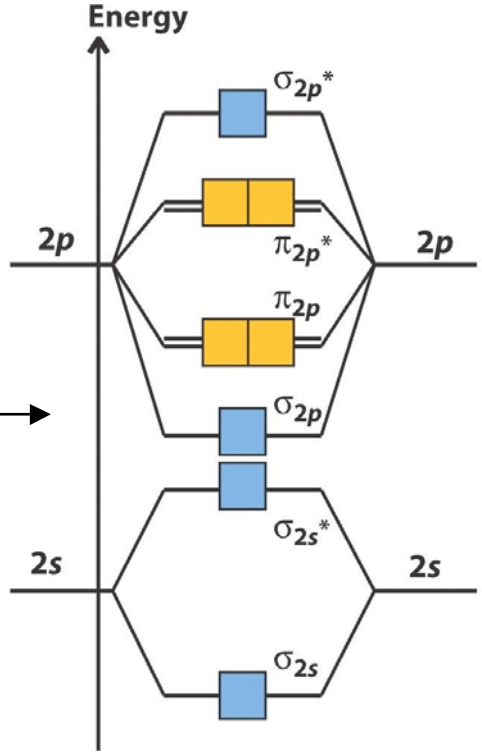
Orbital energies for the ^{3}Li-^{10}Ne

Note: (1) The energy of the σ_{2p} and π_{2p} orbitals switch energy places between N and O;
(2) The electron configuration for any isoelectronic valences is the same.



Li, Be, B, C, N

Switch



O, F, Ne

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	Δ
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

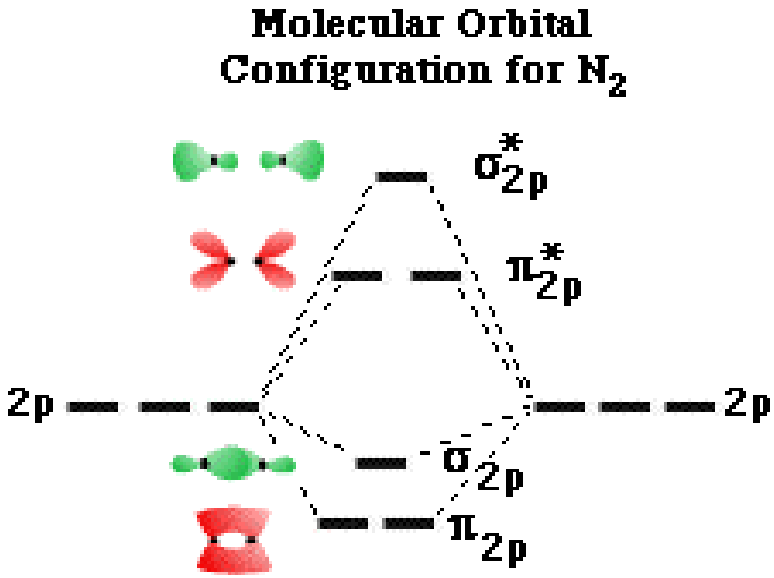
This leads to a different ordering of the M.O's for so-called "s-p mixing".

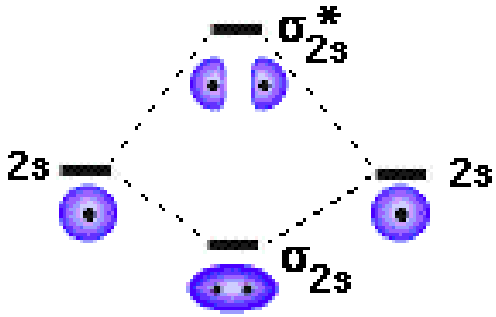
What about B, C and N??

N_2 **This is of major importance:**

$$(\sigma_{2s})^2(\sigma^*_{2s})^2\ (\pi_{2p})^4(\sigma_{2p})^2$$

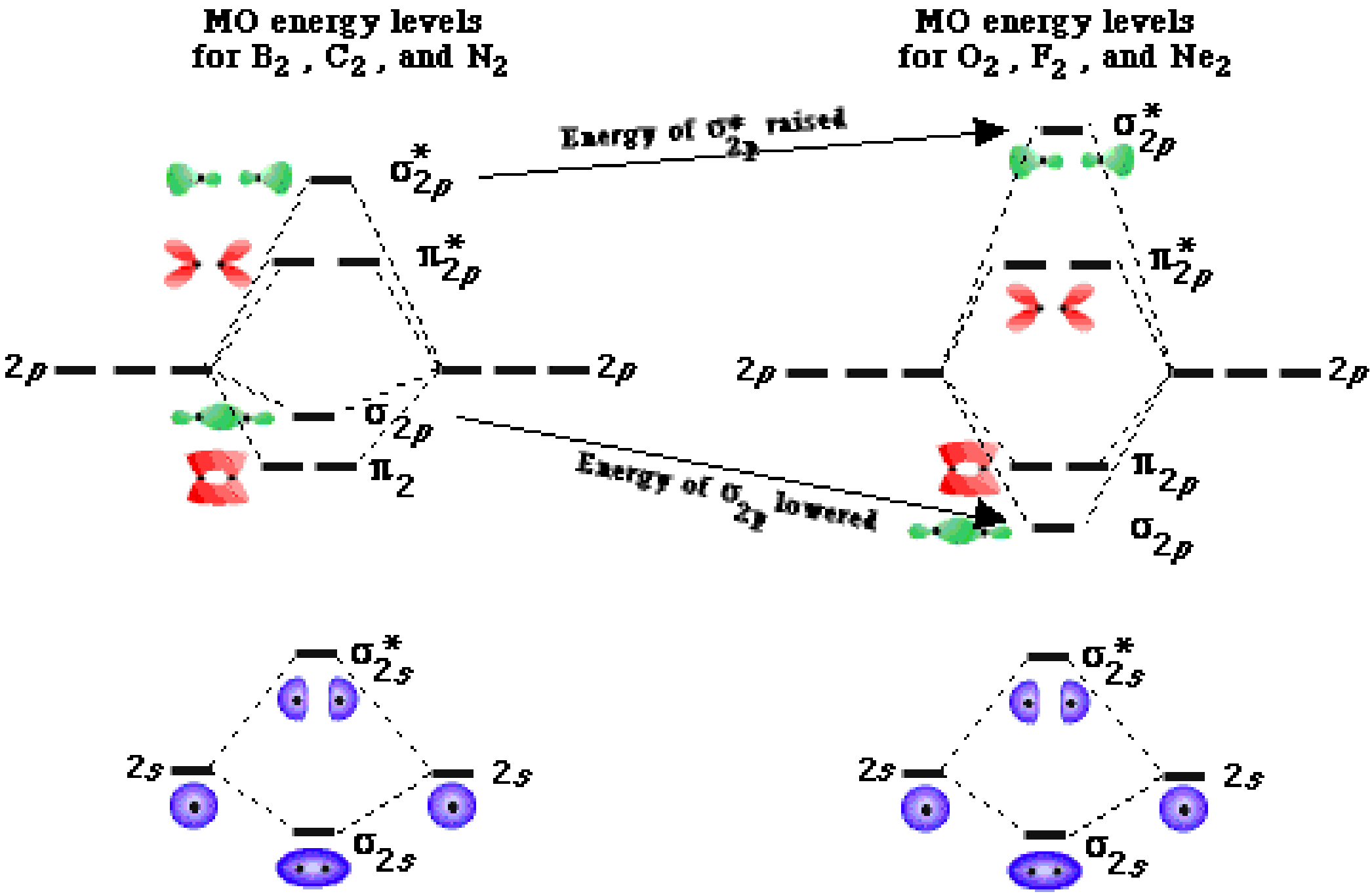
Bond order = (8 - 2)/2 = 3
i.e. triple bond, very strong, stable molecule.
Diamagnetic.
(Note the different order of s/p orbitals)





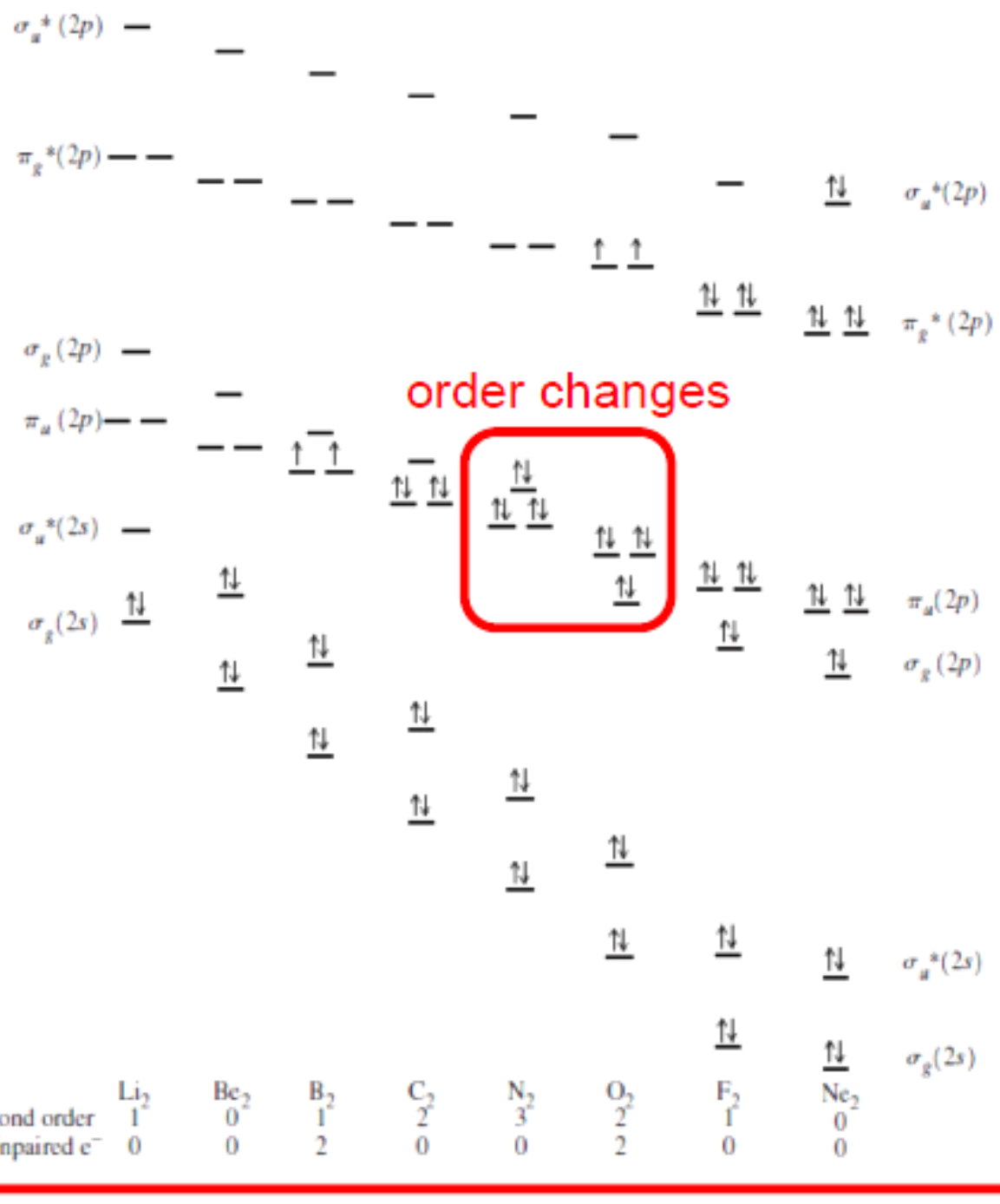
B_2 and C_2

C_2 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
Energy of σ^*_{2p} raised
Energy of σ_{2p} lowered
σ^*_{2p}
π^*_{2p}
$2p$
$2p$
σ_{2p}
π_2
π_{2p}
σ_{2p}
σ^*_{2s}
$2s$
$2s$
σ_{2s}

Orbital Mixing

The size of the effect depends on the 2s-2p energy difference.



small Z_{eff} = small energy difference = large *sp* mixing

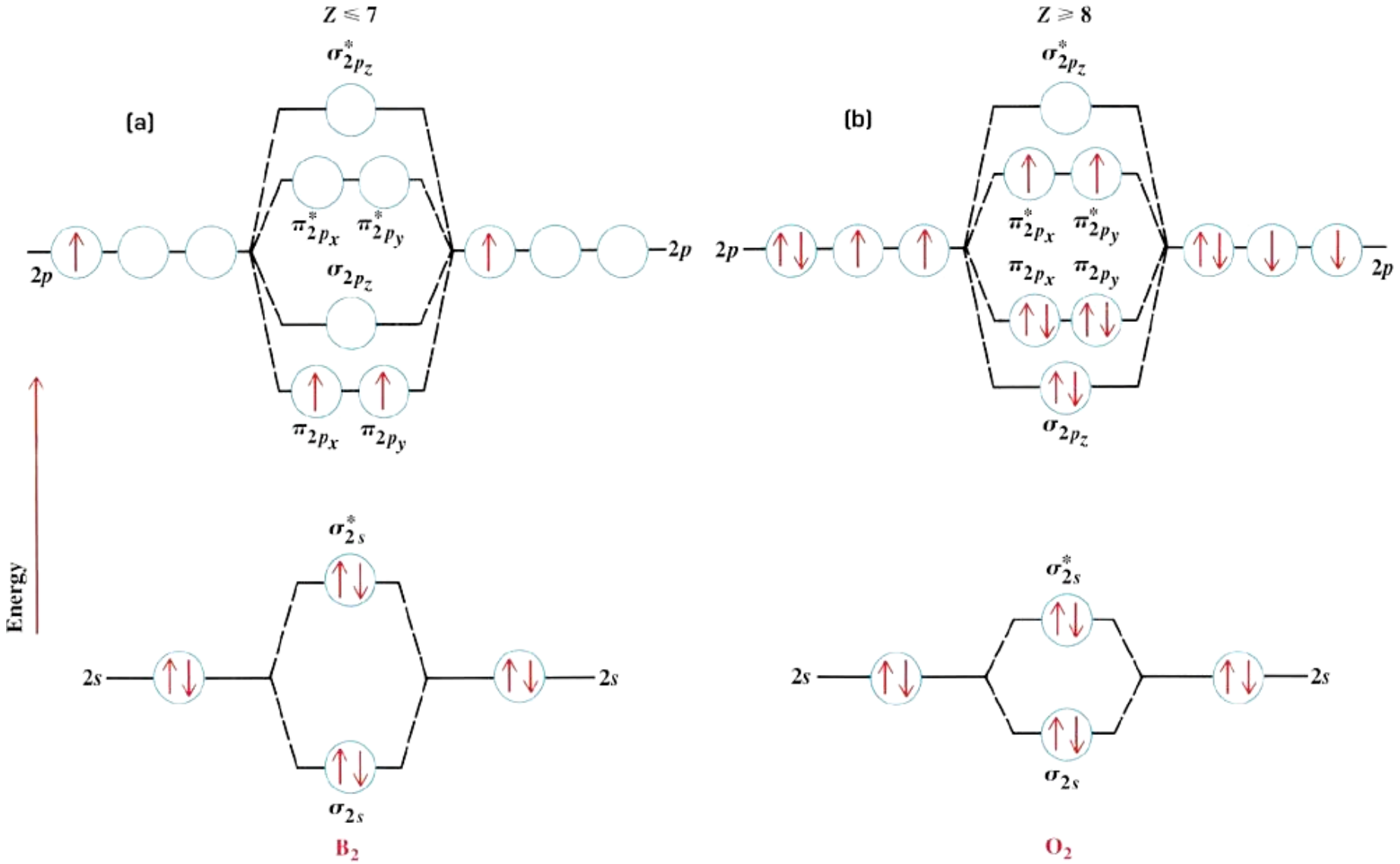
large Z_{eff} = large energy difference = small *sp* mixing

Correlation diagrams for B_2 (left) and O_2 (right)

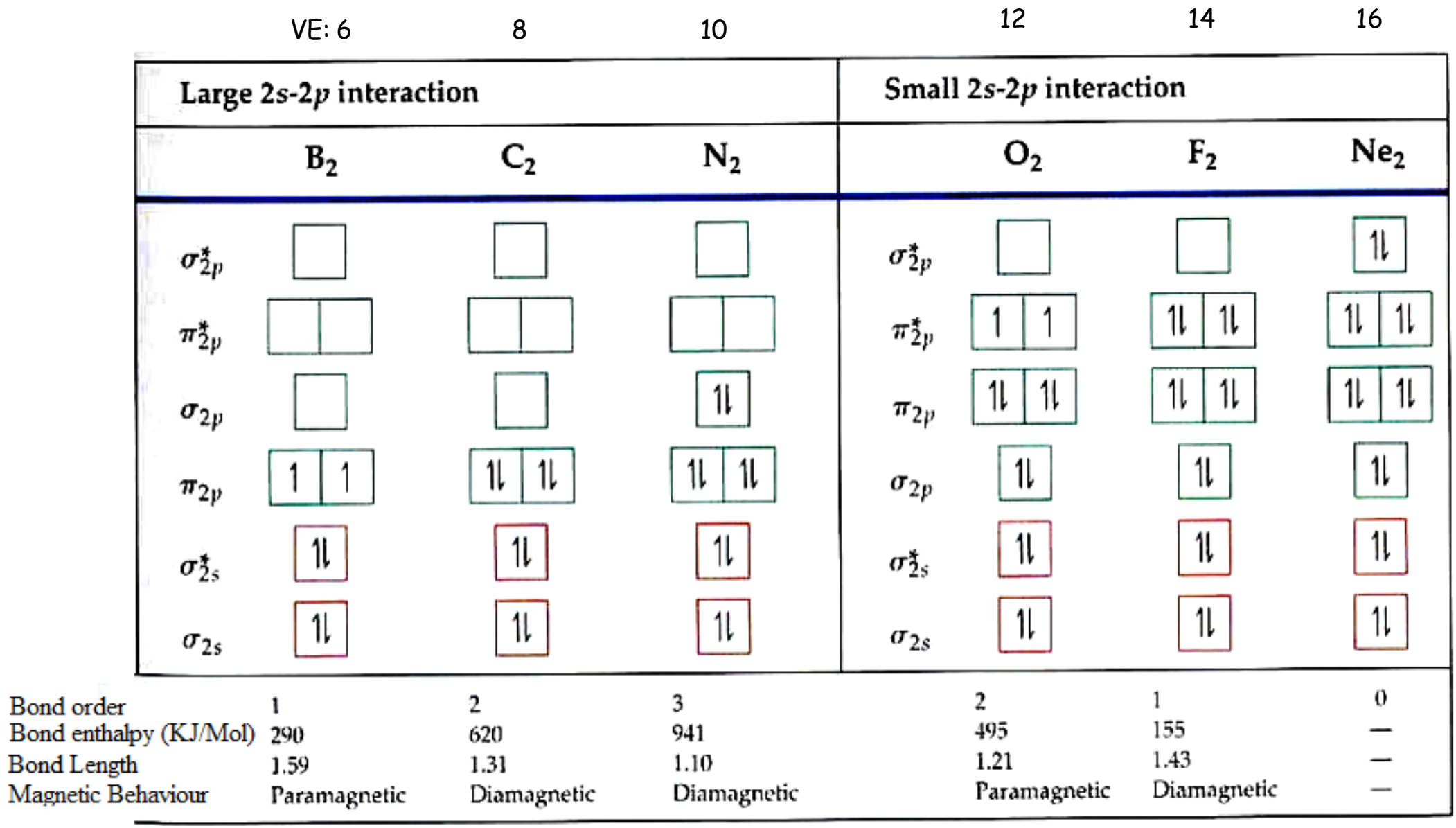
6 VE: $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p}\uparrow\uparrow)^2(\pi_{2p}^*)^0(\sigma_{2p}^*)^0$

12 VE: $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*\uparrow\uparrow)^2(\sigma_{2p}^*)^0$

What are the bond orders? What are the magnetic properties?



Electron configurations for the diatomic molecules: B_2, C_2, N_2, O_2, F_2, Ne_2



The molecular orbital electronic configuration of $^{7}N_2$

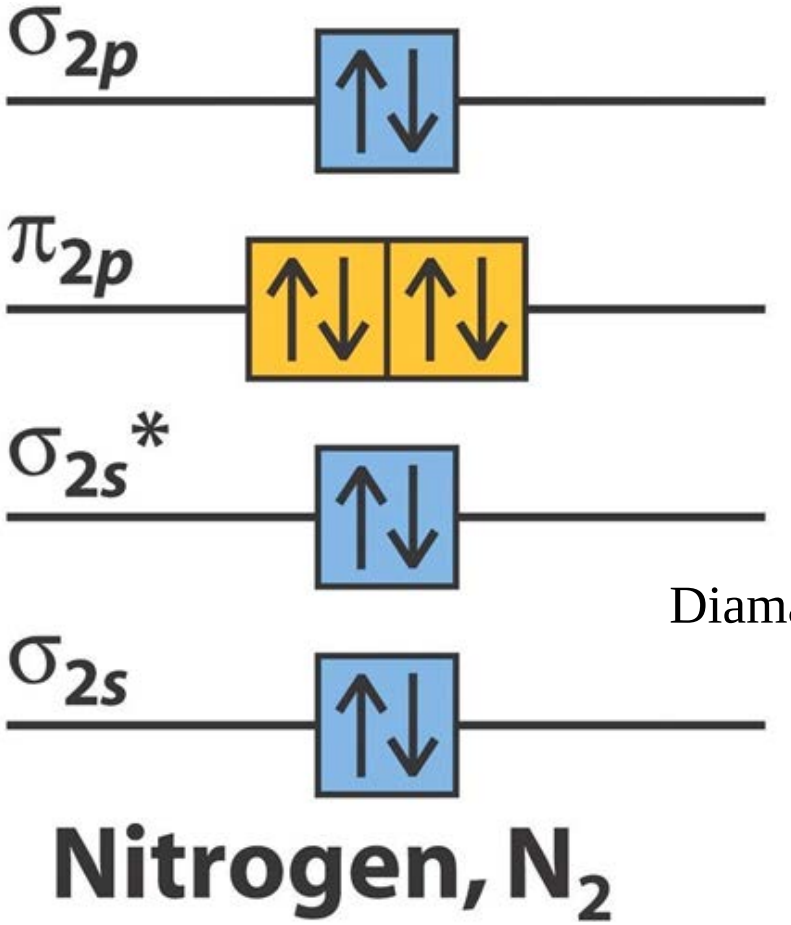
Group V: Valence electrons = 10. Ignore core electrons

What is the bond order of N_2?

BO = 1/2(N - N*) N = 8, N* = 2, N - N* = 6

BO = 1/2(6) = 3

How does the Lewis structure compare to the MO structure?



Lewis structure

:N≡N:

Diamagnetic: N_2: $(\sigma_{2s})^2(\sigma^*_{2s})^2\ (\pi_{2p})^4(\sigma_{2p})^2$

The molecular orbital electronic configuration of $^{9}F_2$

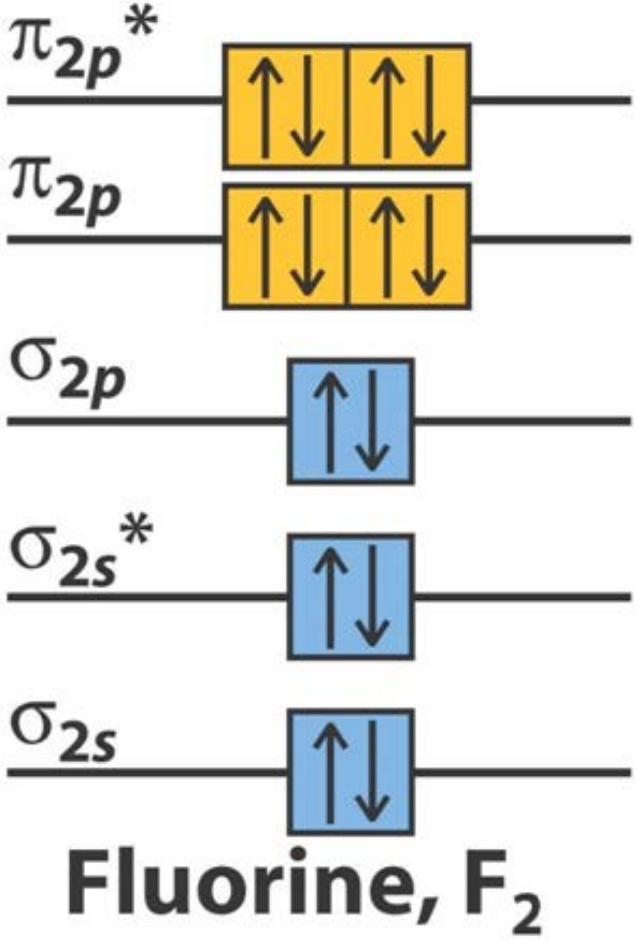
Group VII: Valence electrons = 14

What is the valence electronic configuration of F_2?

$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p})^2(\pi_{2p})^4(\pi^*_{2p})^4$

What is the bond order of F_2? BO = 1/2(8-6) = 1

F_2 possesses a net single bond



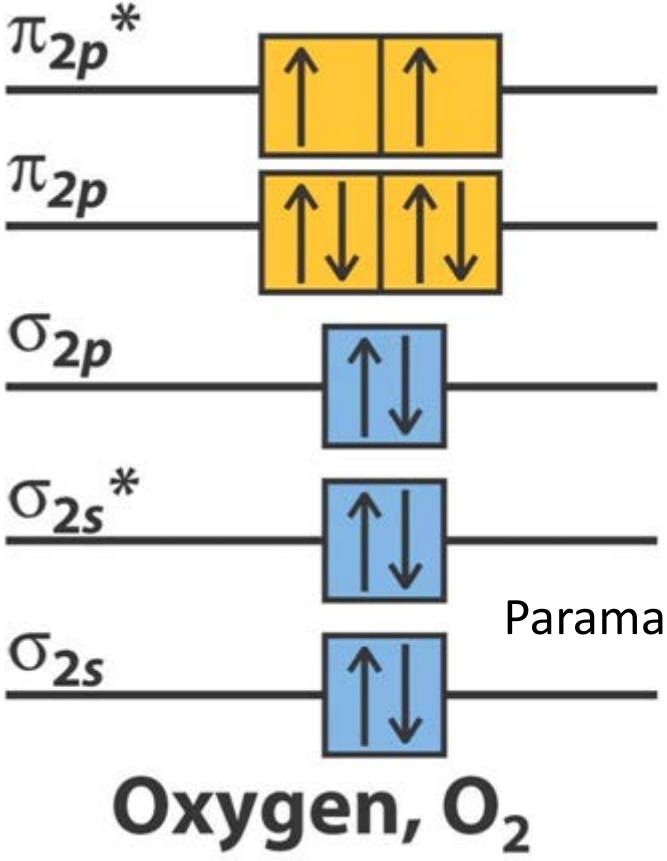
The molecular orbital electronic configuration of $^{8}O_2$

Group VI: Valence electrons = 12. Ignore core electrons

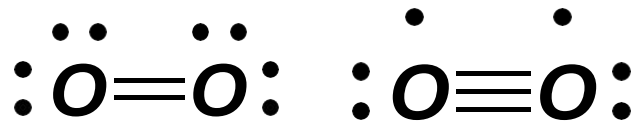
What is the electronic configuration of O_2? $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*\uparrow\uparrow)^2(\sigma_{2p}^*)^0$

What is the bond order of O_2? Bond order = 1/2(N - N*) 1/2(8 - 4) = 2

O_2 possesses a net double bond and is paramagnetic

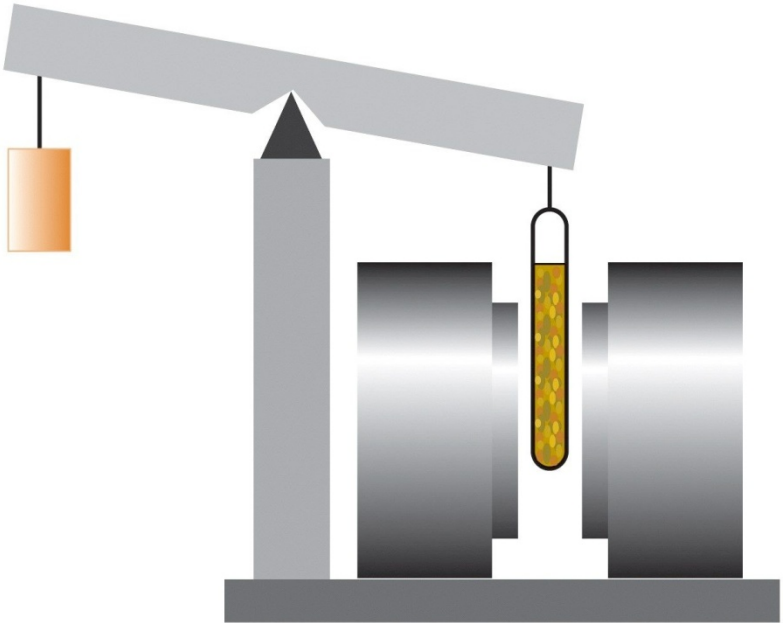


Lewis structures

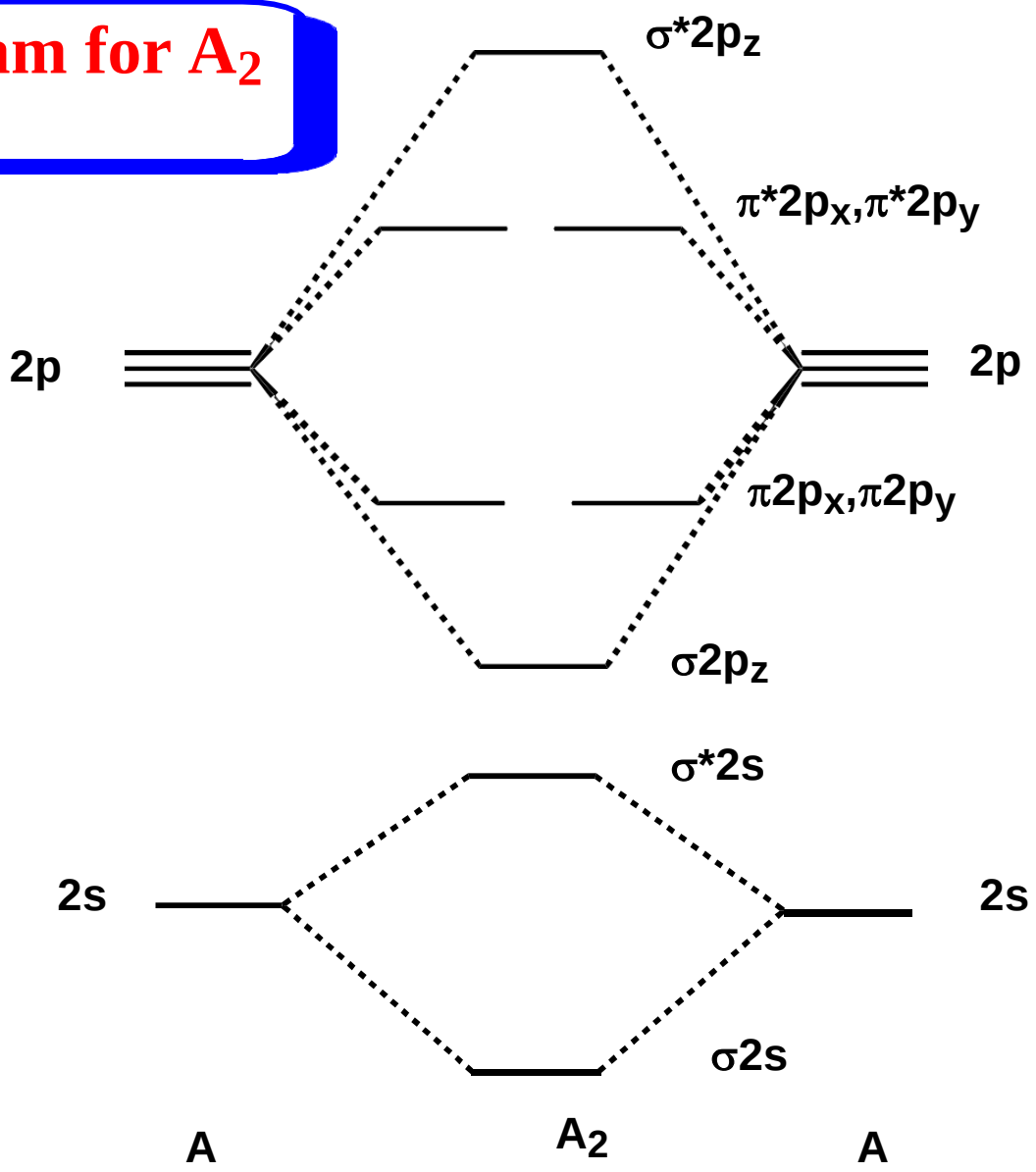


Paramagnetic: O_2: $(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p})^2(\pi_{2p})^4(\pi^*_{2p})^2$

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



O_2 is paramagnetic



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 only one of a series of diatomic oxygen species:

O_2^+ - "oxidation of oxygen" in $O_2^+PtF_6^-$; O_2 - normal form of oxygen

O_2^- - superoxide ion, e.g. $K^+O_2^-$; O_2^{2-} - peroxide ion, e.g. $Na_2^{2+}O_2^{2-}$

Electron configurations:

O_2^+ $\sigma_s^2\ \sigma^*_s{}^2\ \sigma_{pz}^2\ \pi_{px}^2\ \pi_{py}^2\ \pi^*_{px}{}^1\ \pi^*_{py}{}^0$

electron lost from anti-bonding m.o. - stronger bond than O_2. Bond order = 2.5

Paramagnetic - but less so than O_2 - only one unpaired electron.

O_2^- $\sigma_s^2\sigma^*_s{}^2\ \sigma_{pz}^2\ \pi_{px}^2\ \pi_{py}^2\ \pi^*_{px}{}^2\ \pi^*_{py}{}^1$

electron gained in anti-bonding m.o. - weaker bond than O_2. Bond order = 1.5

Paramagnetic (one unpaired electron).

O_2^{2-} $\sigma_s^2\ \sigma^*_s{}^2\ \sigma_{pz}^2\ \pi_{px}^2\ \pi_{py}^2\ \pi^*_{px}{}^2\ \pi^*_{py}{}^2$ Bond order = 1. Diamagnetic

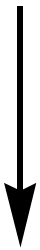
Note bond lengths

O_2^+ - 112 pm

O_2 - 120 pm

O_2^- - 126 pm

O_2^{2-} - 149 pm



Weaker bonds, therefore longer bonds

Molecular orbital configurations of homonuclear diatomics

Bond orders, bond lengths and bond energies

Molecular Orbitals of Homonuclear Diatomic Molecules

Species	Number of Valence Electrons	Ground-State Valence-Electron Configuration	Bond Order	Bond Length (Å)	Bond Enthalpy (kJ mol^{-1})
H_2	2	$(\sigma_{2s})^2$	1	0.746	436
He_2	4	$(\sigma_{1s})^2(\sigma_{1s}^*)^2$	0	Not observed	
Li_2	2	$(\sigma_{2s})^2$	1	2.67	106
Be_2	4	$(\sigma_{2s})^2(\sigma_{2s}^*)^2$	0	2.45	9
B_2	6	$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^2$	1	1.59	297
C_2	8	$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4$	2	1.24	607
N_2	10	$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p_z})^2$	3	1.10	945
O_2	12	$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p_z})^2(\pi_{2p})^4(\pi_{2p}^*)^2$	2	1.21	498
F_2	14	$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p_z})^2(\pi_{2p})^4(\pi_{2p}^*)^4$	1	1.41	158
Ne_2	16	$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p_z})^2(\pi_{2p})^4(\pi_{2p}^*)^4(\sigma_{2p_z}^*)^2$	0	Not observed	

The bond orders from MO theory agree with their Lewis structure

Heteronuclear Diatomic Molecules (AB) Involving First Row Elements

Remember two basic principles:

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

(2) Bonding/anti-bonding M. O.'s formed symmetrically below/above average of A. O. energies, respectively.

M. O. energy level diagram based on that for A_2:

e.g. for CO - similar to N_2 - but with different A. O. energies for C and O, i.e. O > C.

Electronic configuration:

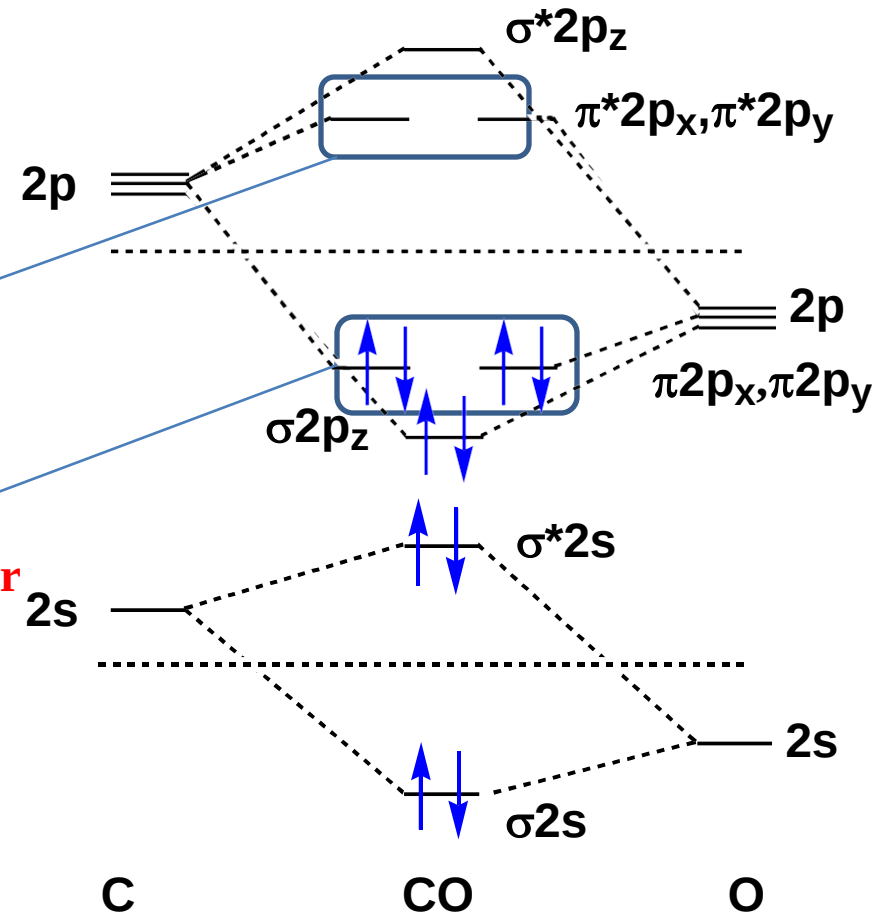
$\sigma_s^2\sigma^*{}_s^2\sigma_{pz}^2\pi_{px}^2\pi_{py}^2$

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

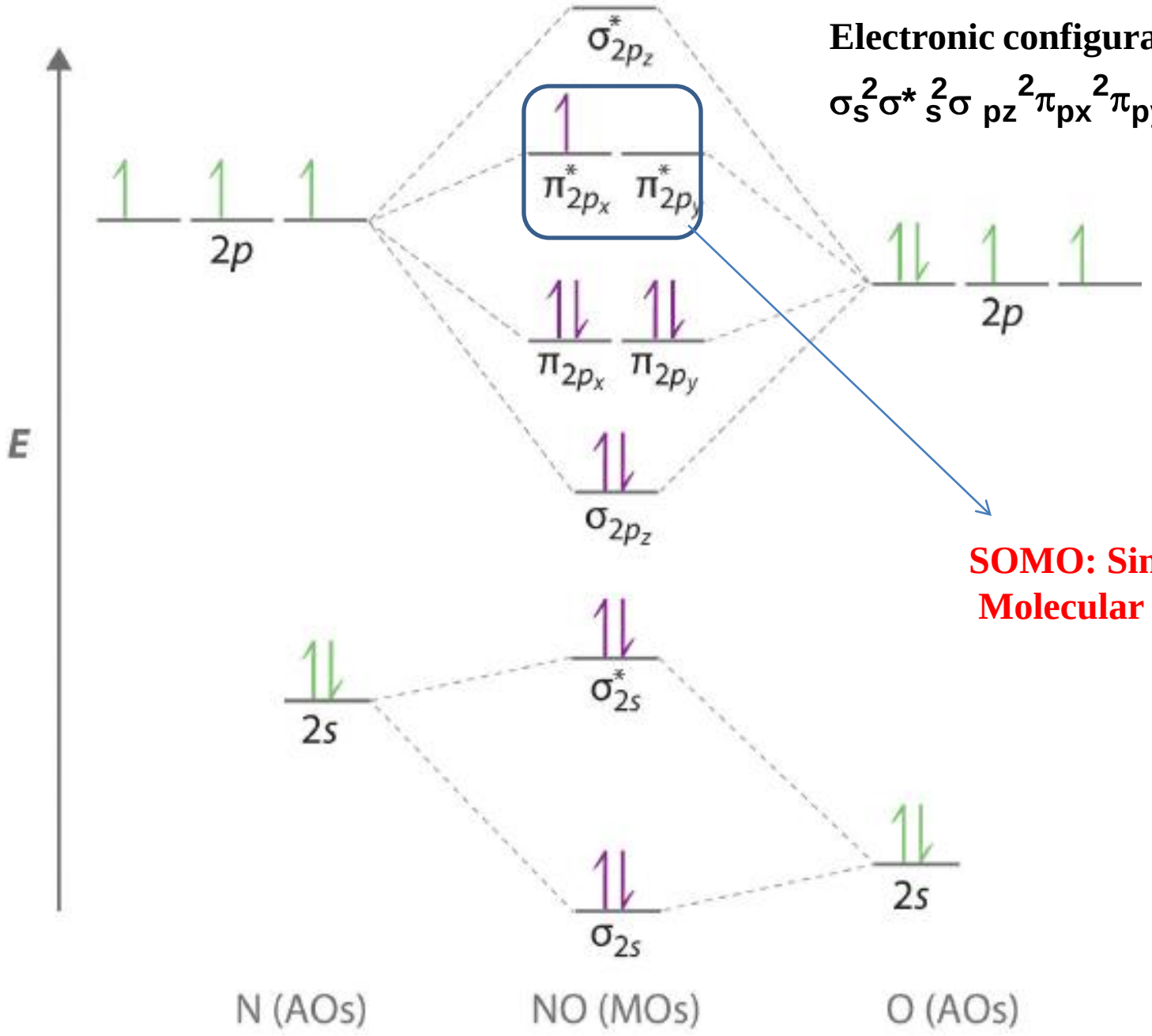
Just like N_2 : ISOELECTRONIC (i.e. same no. of electrons). DIAMAGNETIC.

LUMO: Lowest Unoccupied Molecular Orbital

HOMO: Highest Occupied Molecular Orbital



M. O. energy level diagram of NO



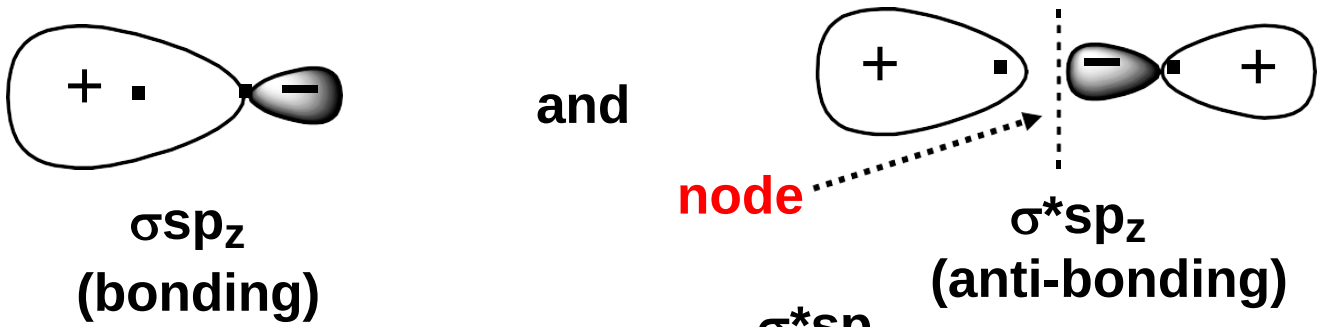
Electronic configuration:

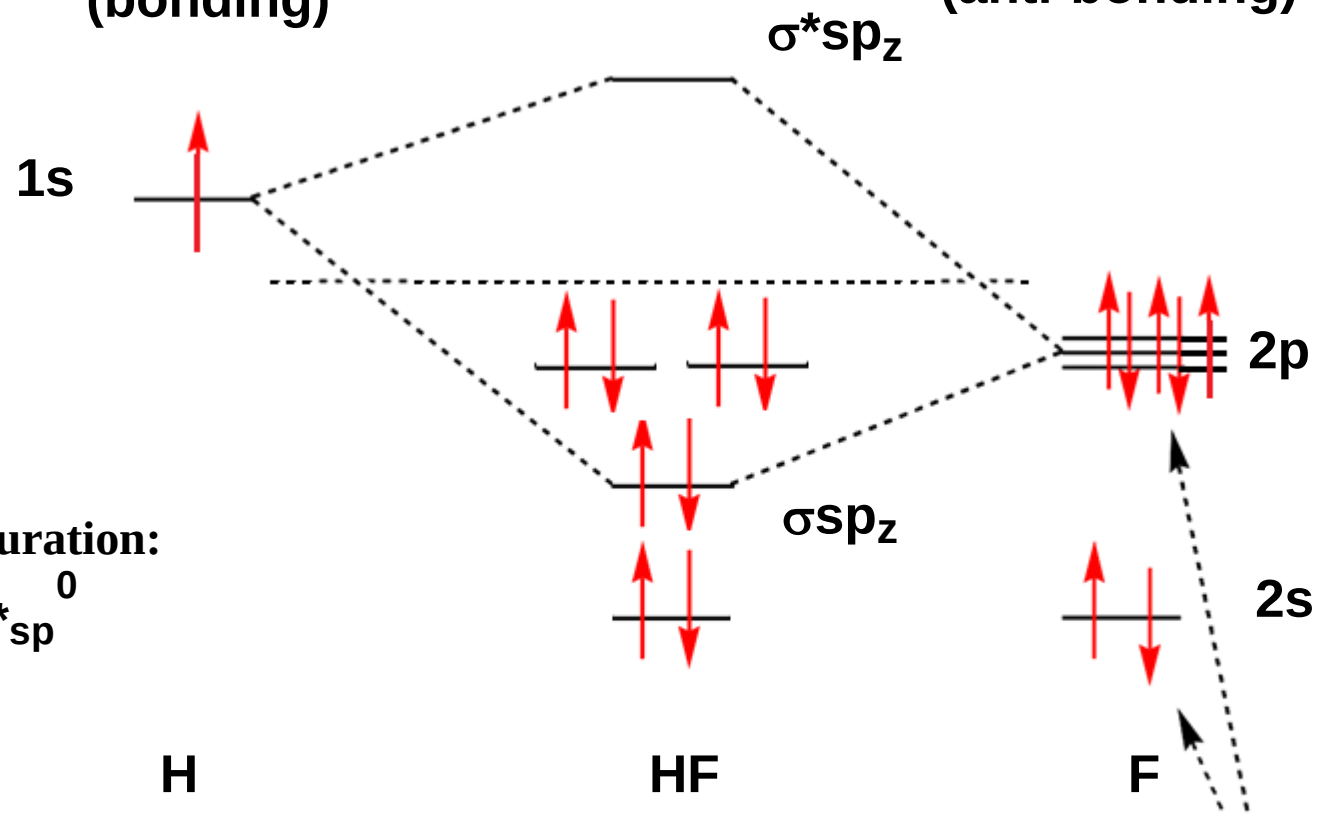
$\sigma_s^2 \sigma^*{}_s^2 \sigma_{pz}{}^2 \pi_{px}{}^2 \pi_{py}{}^2 \pi_{px}{}^* 1$

SOMO: Singly Occupied Molecular Orbital

A different type of heteronuclear diatomic MO

HF H $1s^1$ F $1s^2 2s^2 2p_x{}^2 2p_y{}^2 2p_z{}^1$ **Overlap between H1s and F2p_z giving:**





Electronic configuration:

$[F2s^2 2p^4]\sigma_{sp}{}^2 \sigma^*_{sp}{}^0$

Diamagnetic. **Bond order = 1**

F2s non-bonding - too low in energy

F2p_x,2p_y non-bonding because of wrong symmetry

non-bonding electrons on F

Molecular Orbitals for Triatomic Molecules

1. Determine point group of molecule (if linear, use D_{2h} and C_{2v} instead of $D_{\infty h}$ or $C_{\infty v}$)

2. Assign x, y, z coordinates (z-axis is principal axis; if non-linear, y axes of outer atoms point to central atom)

3. Find the characters of the reducible representation for the combination of valence orbitals on the outer atoms.

4. Find the irreducible representations (they correspond to the symmetry of **Ligand Group Orbitals (LGO)**, also called **Symmetry Adapted Linear Combinations, SALCs** of the orbitals)

5. Find AOs on central atom with the same symmetry

6. Combine AOs from central atom with those **Ligand Group Orbitals (LGO)** of same symmetry and similar energy to make the MO diagram

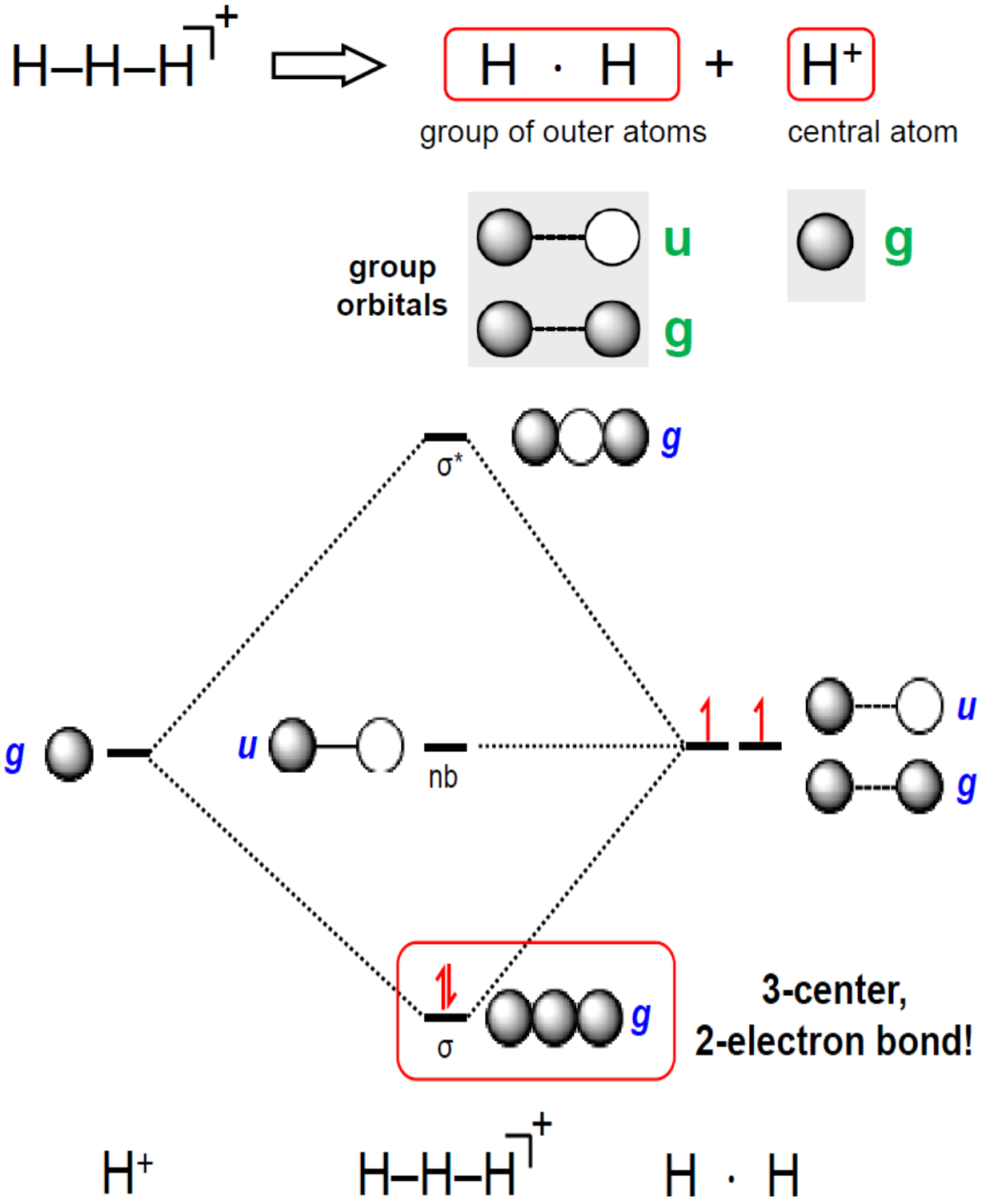
Linear H^{3+}

Among the easiest multi-atom molecules to build is linear H^{3+}.

General procedure for simple molecules that contain a central atom: build Ligand Group Orbitals using the outer atoms, then interact the Ligand Group Orbitals with the central atom orbitals to make the MOs.

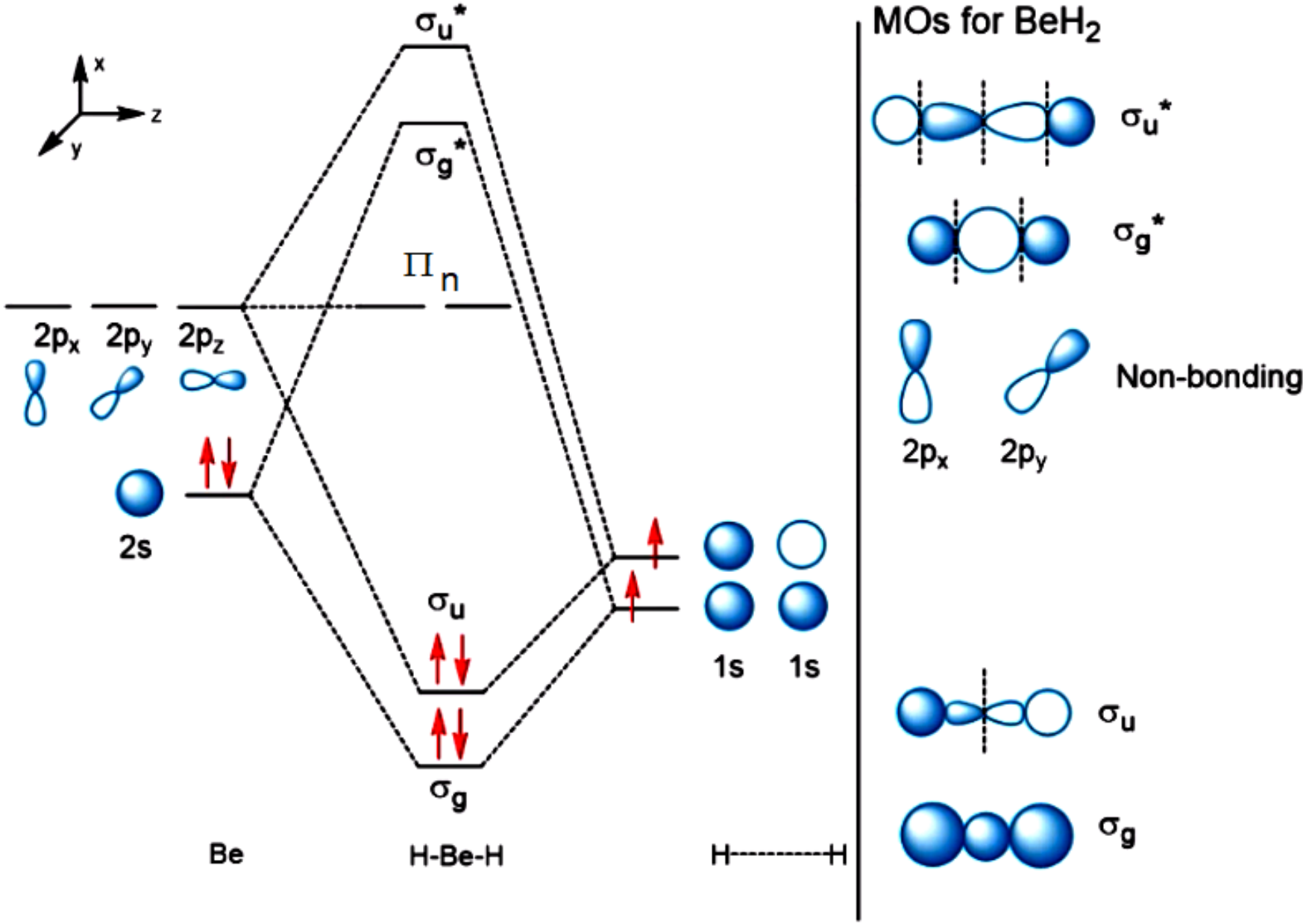
Only Ligand Group Orbitals and central atom orbitals with the same symmetry and similar energy will interact.

g orbitals interact, while u orbital is nonbonding.



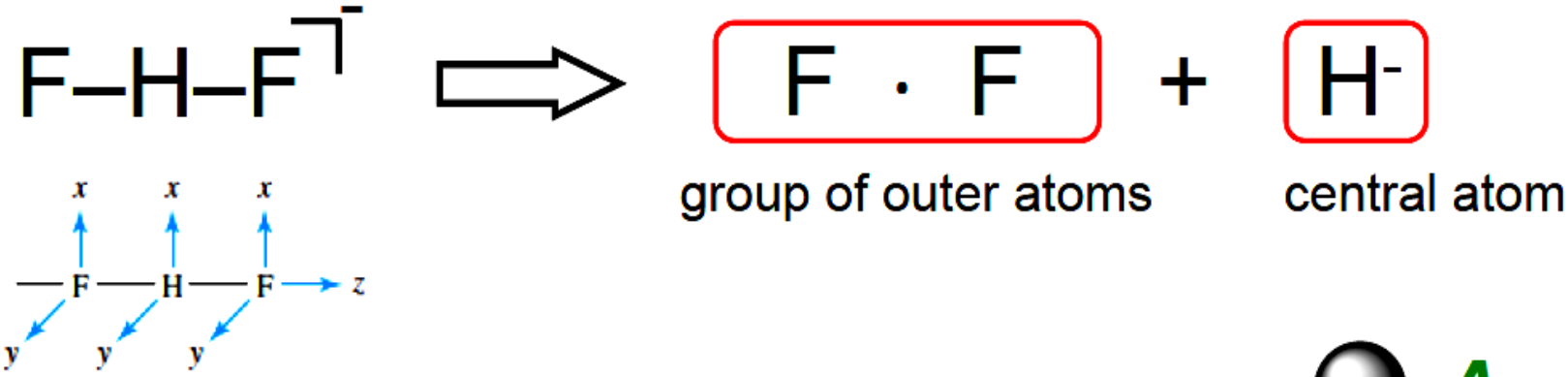
Linear BeH_2

The electronegativity of hydrogen is greater than that of beryllium so the hydrogen orbital are lower in energy. BeH_2 is strongly (Lewis) acidic as a result of its electron deficiency



Linear FHF^-

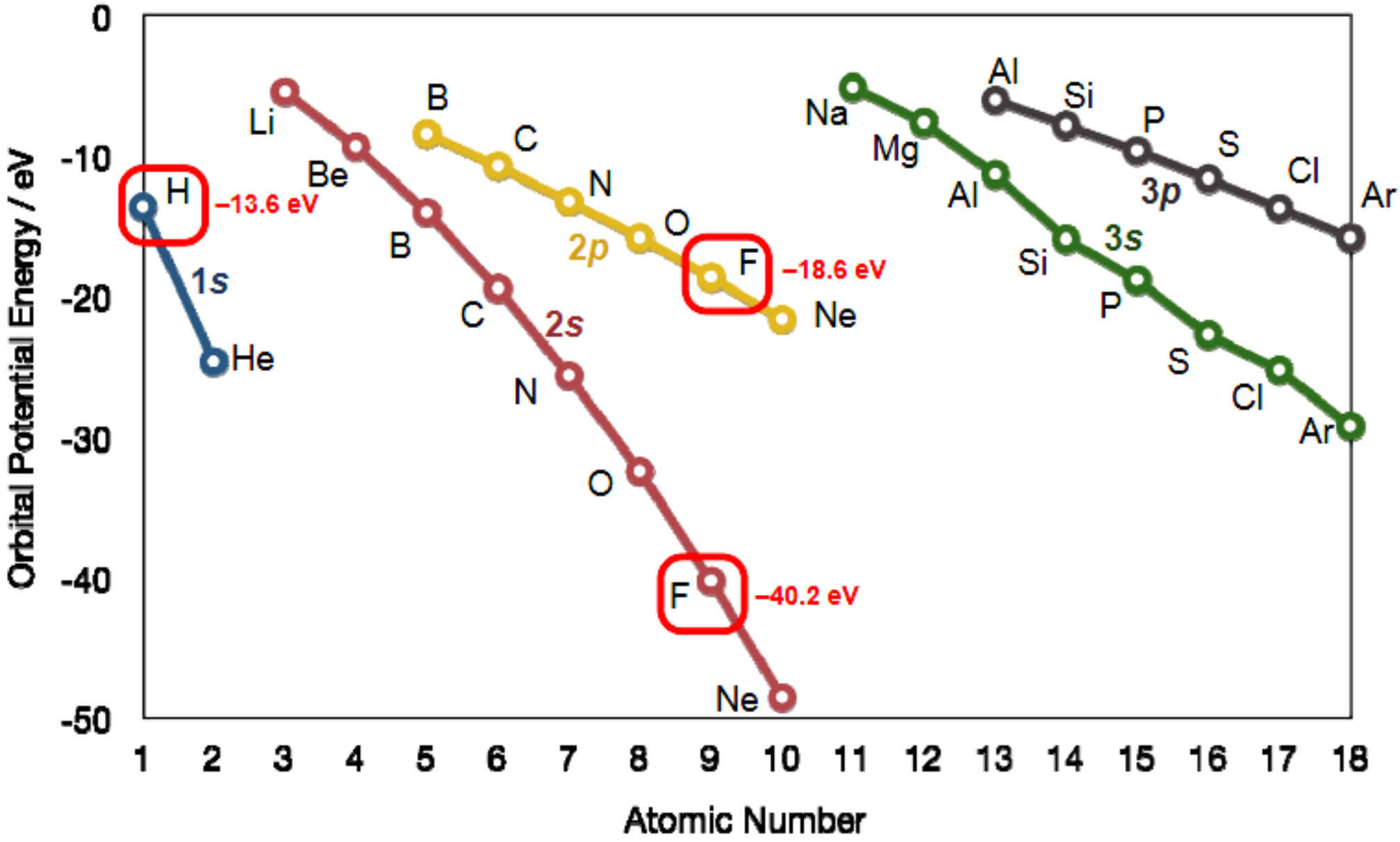
In building the group orbitals for FHF^-, we must consider the 2*s and 2p* orbitals of the two fluorines (8 AOs in total). Use point group D_{2h}.



The central atom has proper symmetry to interact only with group orbitals 1 and 3.

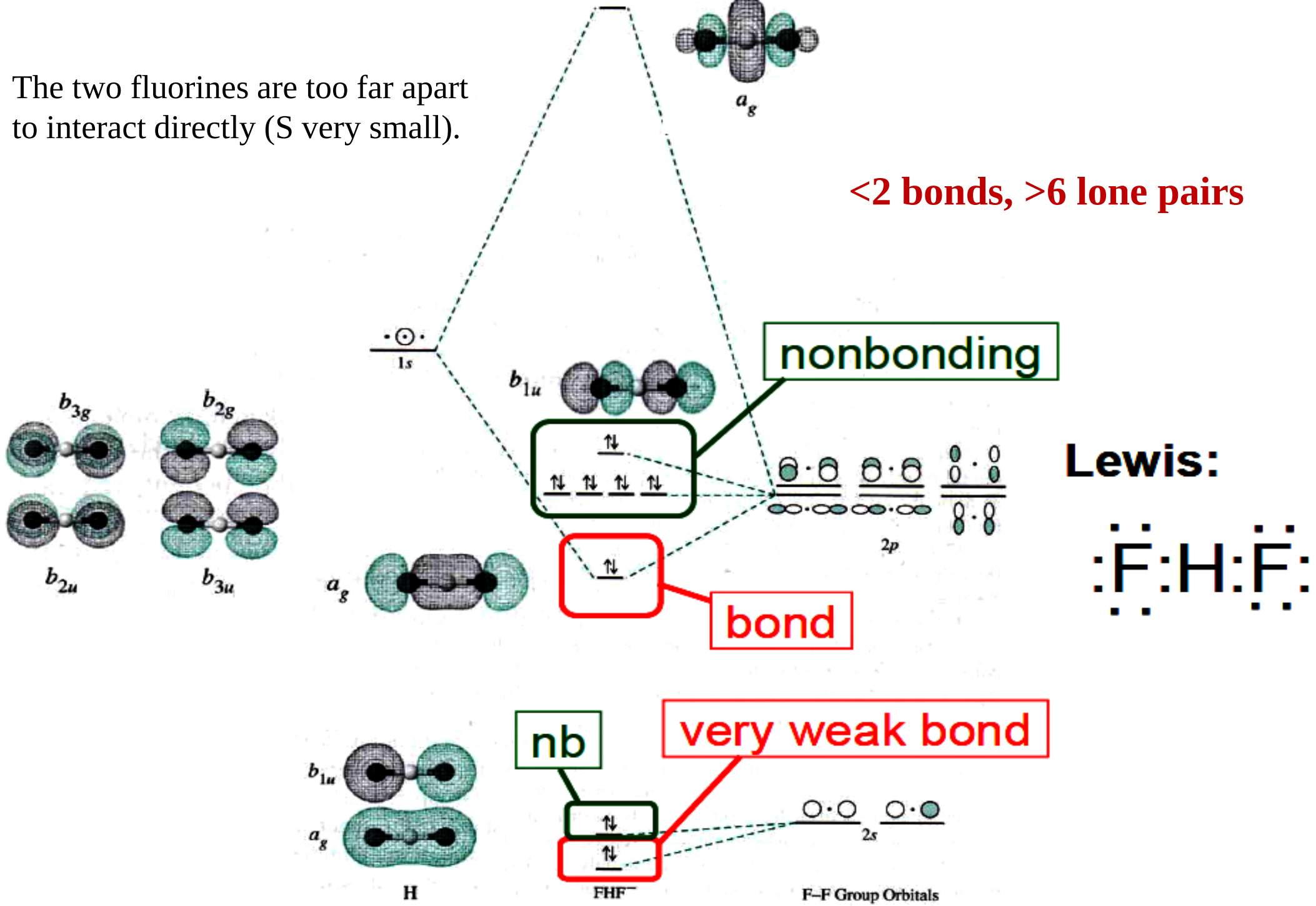
Relative AO Energies for MO Diagrams

F 2s orbital is very deep in energy and will be essentially nonbonding.



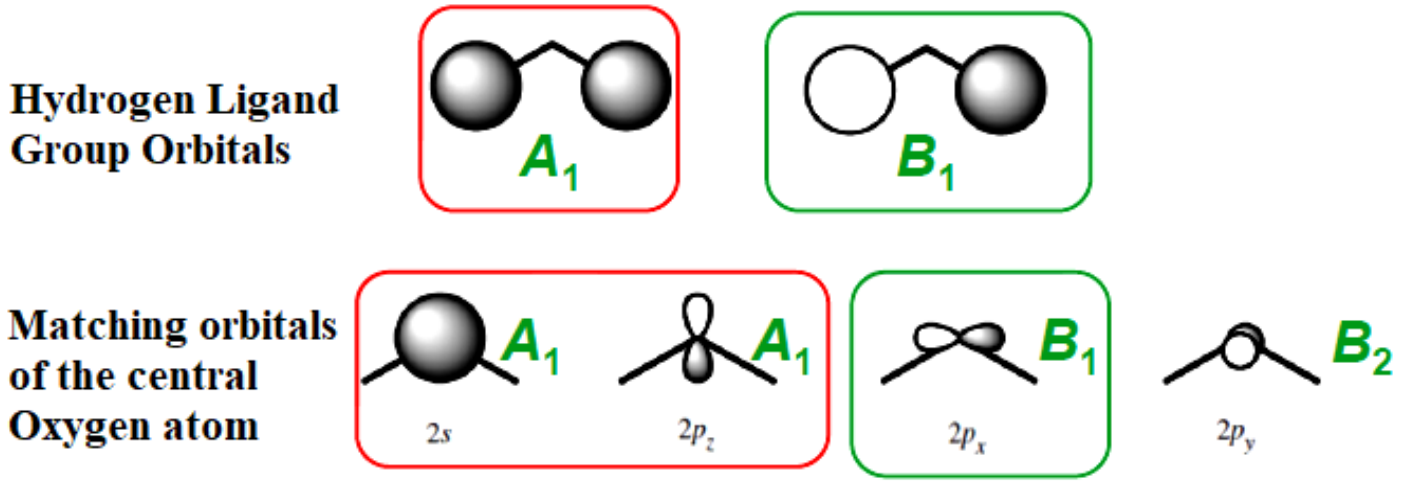
The two fluorines are too far apart to interact directly (S very small).

<2 bonds, >6 lone pairs

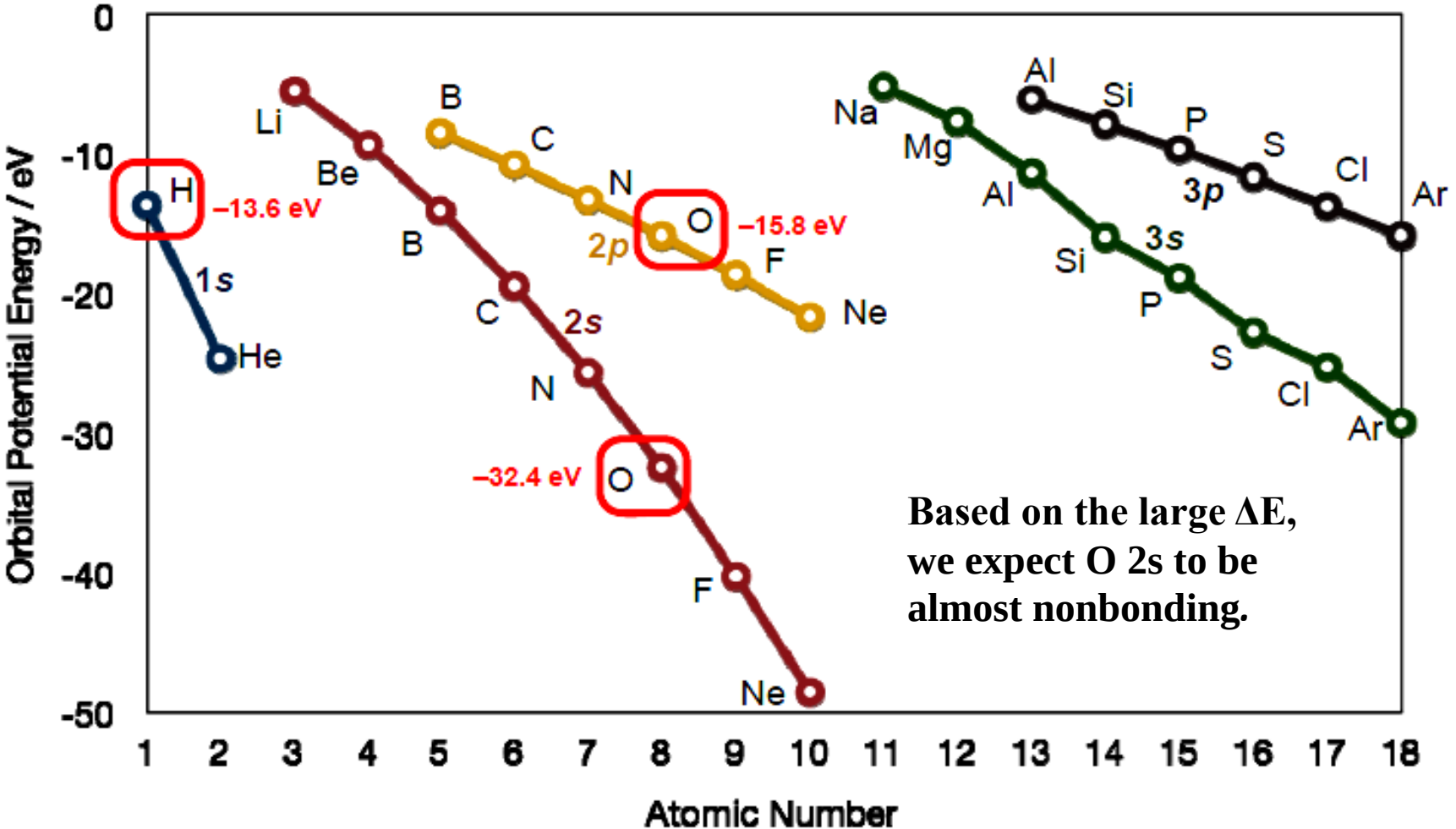


F 2s orbitals are too deep in energy to interact, leaving an interaction (σ) only with group orbital 3. Some sp-mixing occurs between a_g and b_{1u} MOs.

Water

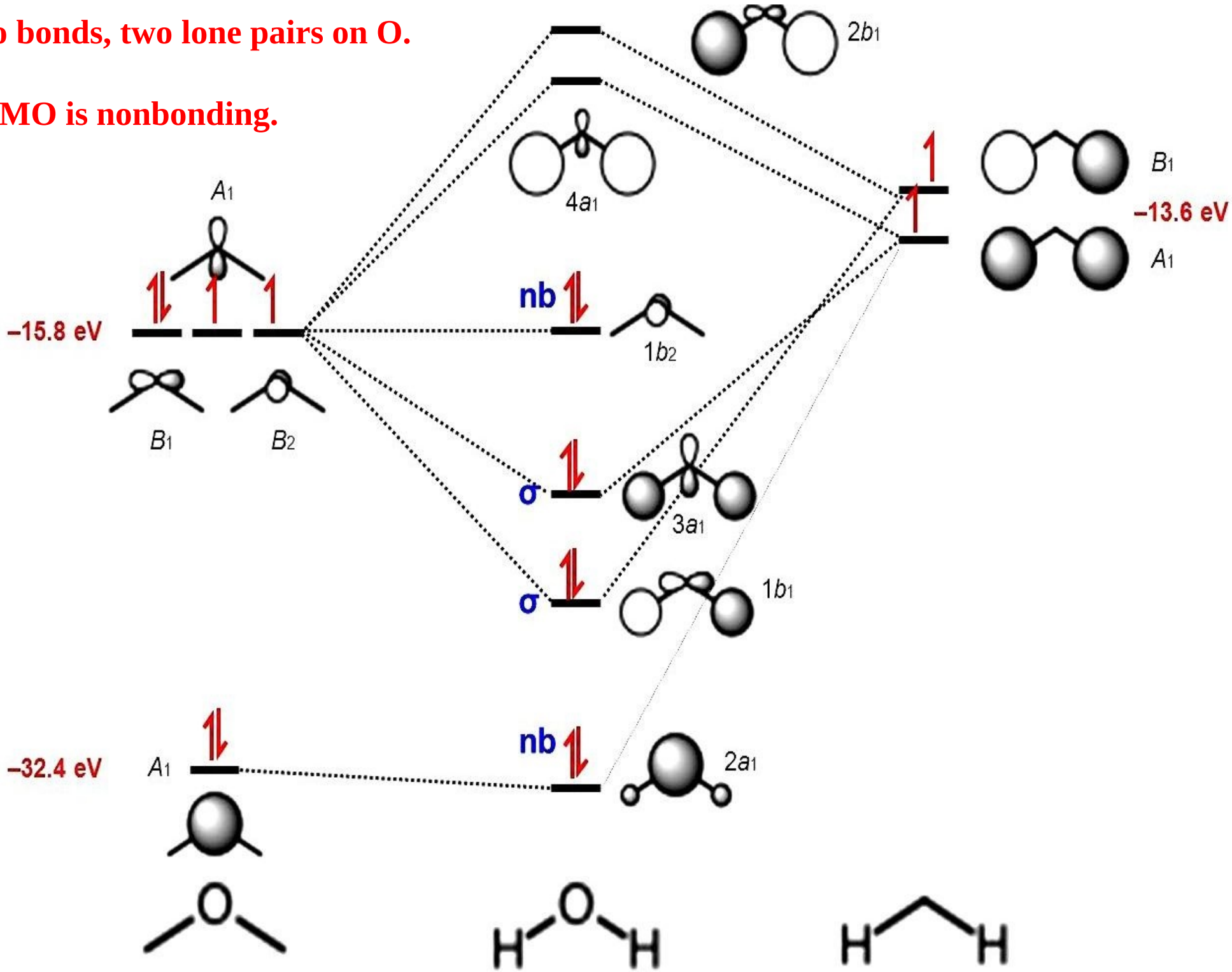


Hence, We can expect 6 MOs with O $2p_y$ totally non-bonding



Two bonds, two lone pairs on O.

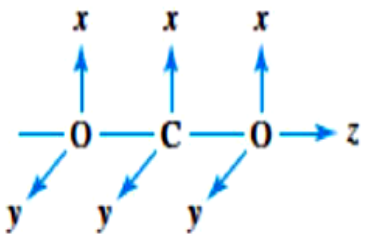
HOMO is nonbonding.

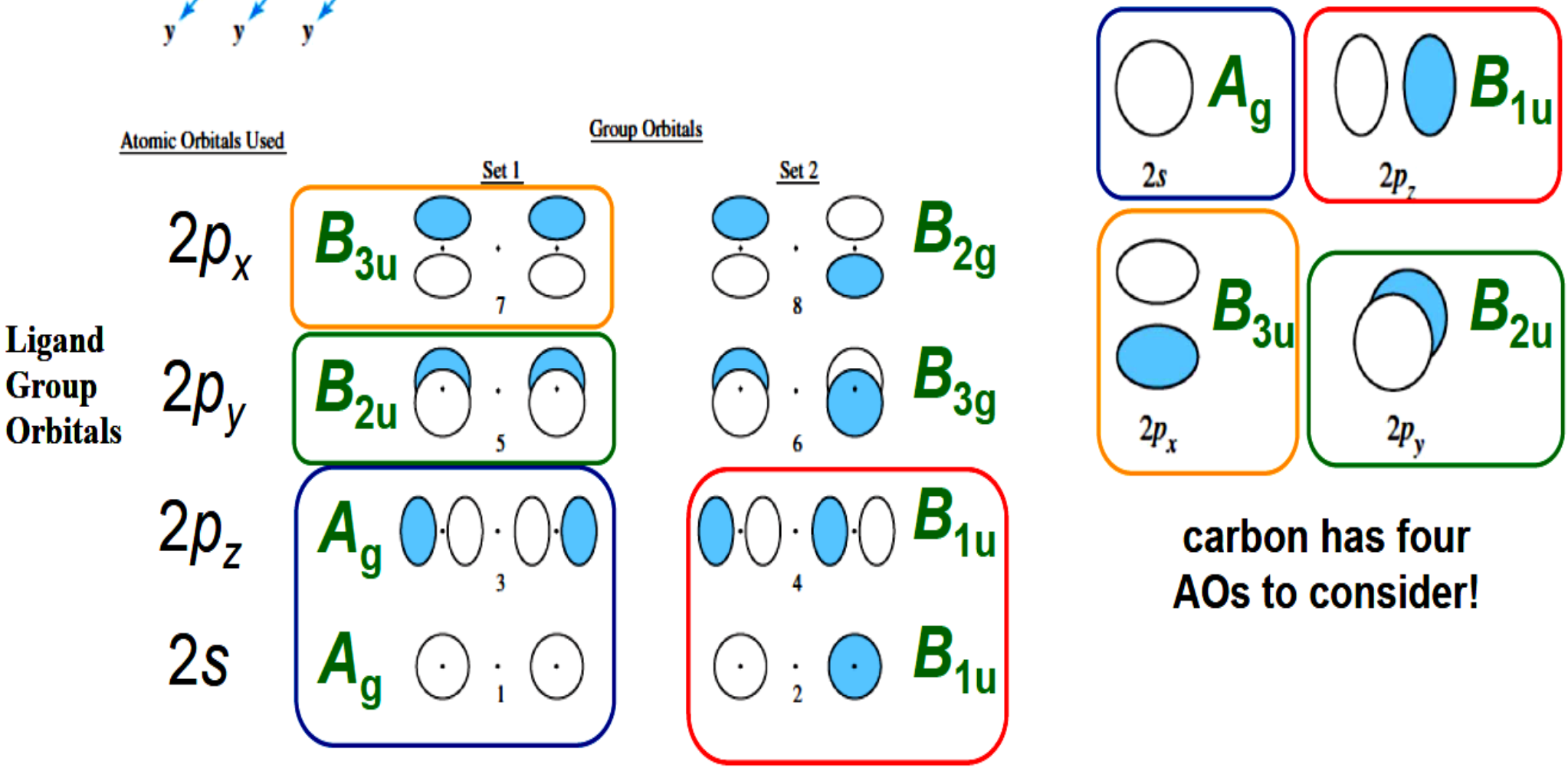


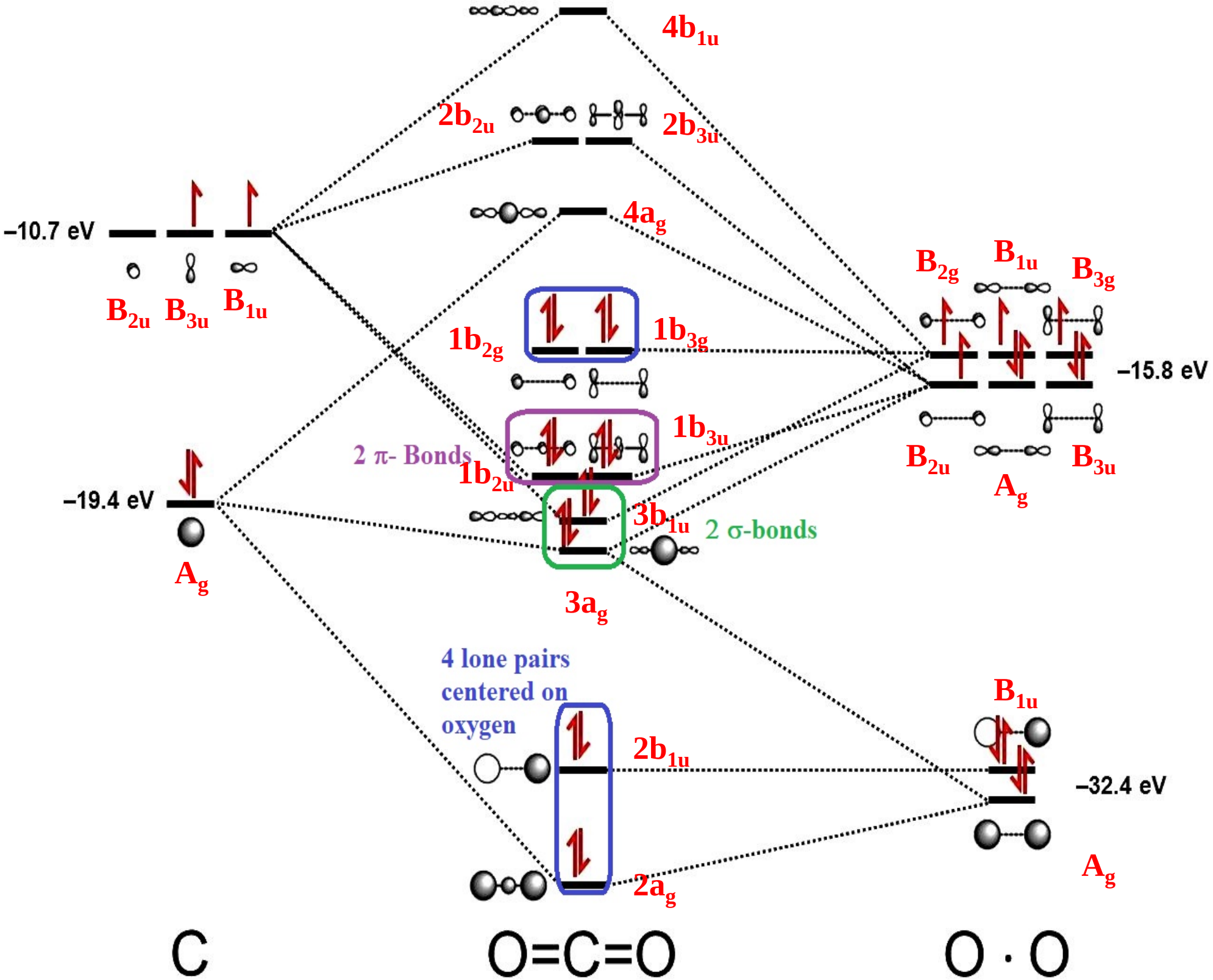
Carbon Dioxide: CO_2

O=C=O ⇨ O · O + C

group of outer atoms — central atom

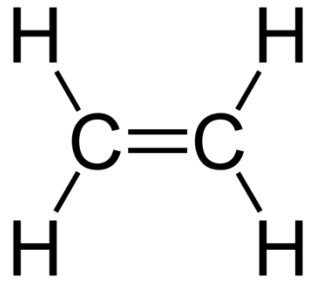





4b1u
2b2u
2b3u
4ag
−10.7 eV
B2u B3u B1u
1b2g
1b3g
B2g B1u B3g
−15.8 eV
1b3u
2 π- Bonds
1b2u
B2u Ag B3u
−19.4 eV
3b1u
2 σ-bonds
Ag
3ag
4 lone pairs centered on oxygen
B1u
2b1u
−32.4 eV
2ag
Ag
C
O=C=O
O · O

Molecular Orbitals for Multiatomic Molecules

Ethene



What we know and don't know from VSEPR

❖ From VSEPR theory, we know that there should be a trigonal planar arrangement around each carbon atom.

❖ For each carbon atom, the s, p_x and p_y orbitals are available to form bonds. These are needed to form the two bonds to the hydrogen atoms, and the carbon-carbon bond.

❖ There would therefore be one p orbital left over on each carbon, the p_z, oriented perpendicular to the trigonal plane.

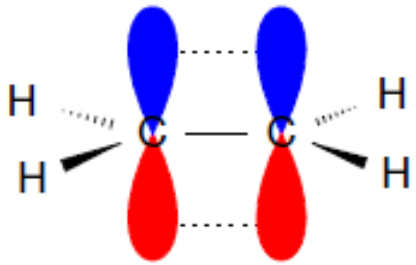
❖ The p_z orbital on one carbon atom can only combine with the p_z orbital on the other, forming a bond, if they are oriented identically, i.e. only if the molecule is flat.

MO Treatment

❖ The two pz orbitals combine to give one bonding and one anti-bonding orbital.

❖ There are two electrons which therefore occupy the bonding orbital, giving a bond order of 1 and an overall carbon-carbon bond order of 2.

❖ LCAO construction of bonding orbital:



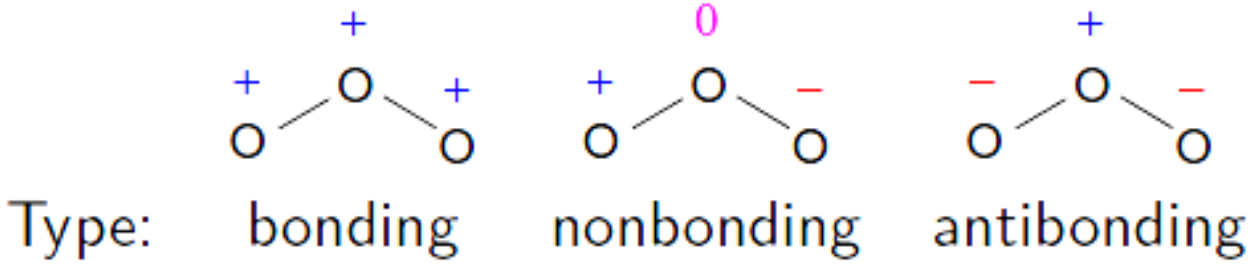
❖ Note that the bond enforces planarity since twisting about the bond axis would destroy the overlap between the p orbitals.

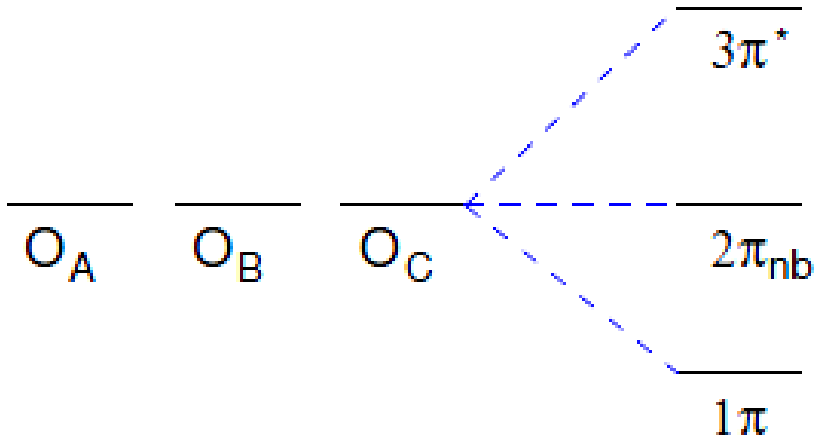
Ozone

❖ Ozone is planar, so there will be one p orbital from each oxygen atom perpendicular to the plane of the molecule.

❖ With three p orbitals, we can make three MOs.

❖ Possible arrangements:

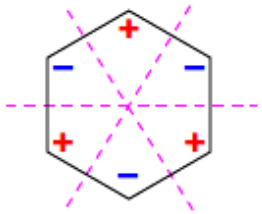


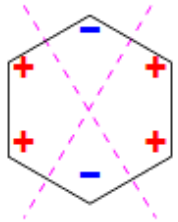


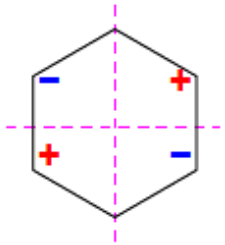
Benzene

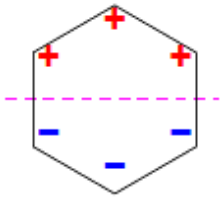
- There is one p orbital available for bonding per carbon atom, so six orbitals.
- There are six electrons in these orbitals.

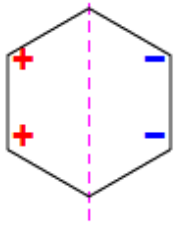
Highest energy

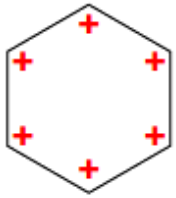




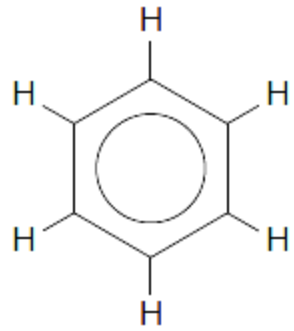


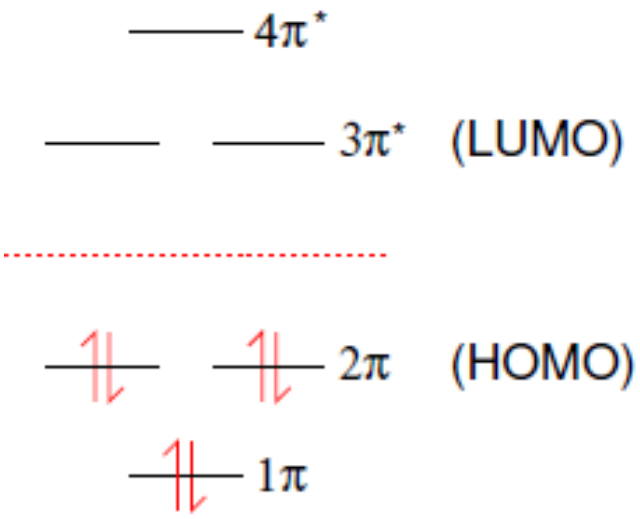






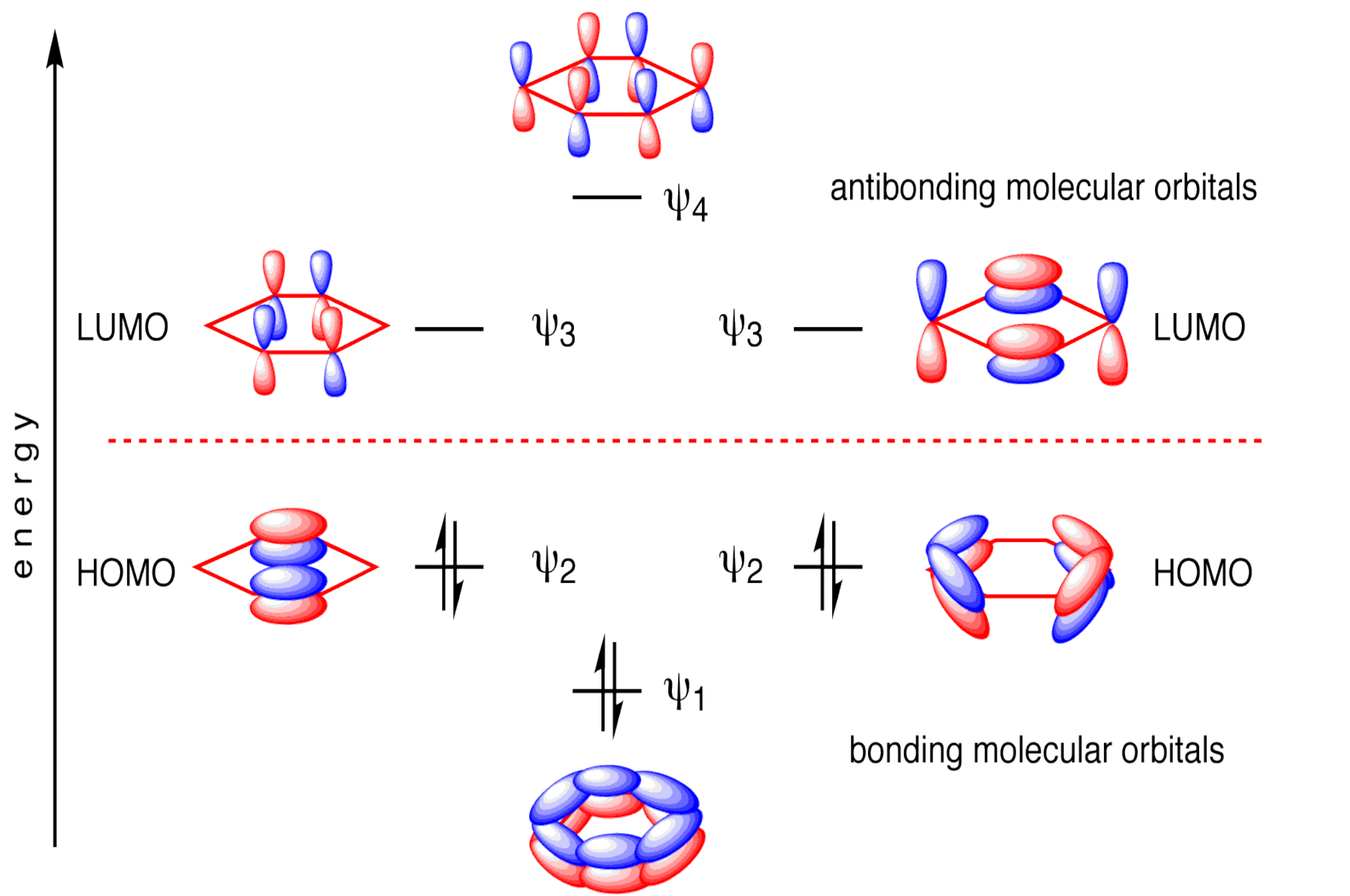
Lowest energy





The bottom three are bonding orbitals.
The top three are antibonding.

Orbital occupancy in benzene: $(1\pi)^2(2\pi)^4$



the π molecular orbitals for benzene. The dashed line represents the energy of an isolated p orbital – all orbitals below this line are bonding, all above it are antibonding. Benzene has six electrons in its π system so all the bonding MOs are fully occupied


Thank
you