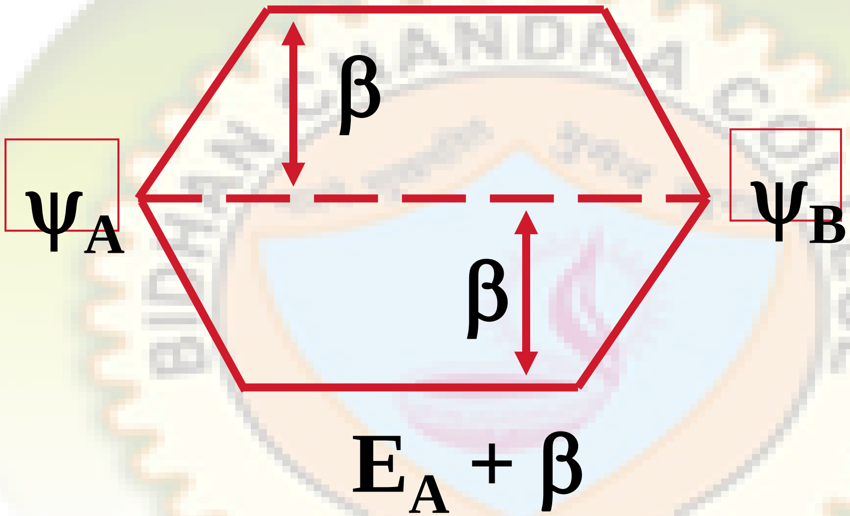
Introduction to Molecular Orbital Theory:



Dr. Sujit Kumar Bera

Department of Chemistry

Molecular Orbital Theory: Introduction

- In the molecular orbital model, orbitals on individual atoms interact to produce new orbitals, called molecular orbitals, which are now identified with the whole molecule.

- THROW OUT THE IDEA OF LOCALIZED BONDING

Why Do Atoms Form Molecules?

The Aufbau principle tells us to put electrons into the lowest energy configuration in atoms. Similarly, molecules form when the total energy of the electrons is lower in the molecule than in individual atoms.

Basic questions??

1. Molecular Orbitals   What are the *shapes* of the waves?
Where are the lobes and nodes?
What is the electron density distribution?

2. Allowed Energies.   How do the allowed energies change when bonds form?

Diatomic Molecular Orbital Theory

- In the case of diatomic molecules, the interactions are easy to see and may be thought of as arising from the constructive interference of the electron waves (orbitals) on two different atoms, producing a bonding molecular orbital, and the destructive interference of the electron waves, producing an antibonding molecular orbital

- **This Approach is called LCAO-MO**

(Linear Combination of Atomic Orbitals to Produce Molecular Orbitals)

A Little Math is need to understand

Only a Little I promise!

Linear combination of atomic orbitals

Rules for linear combination

1. Atomic orbitals must be roughly of the same energy.

2. The orbital must overlap one another as much as possible- atoms must be close enough for effective overlap.

3. In order to produce bonding and antibonding MOs, either the symmetry of two atomic orbital must remain unchanged when rotated about the internuclear line or both atomic orbitals must change symmetry in identical manner.

Rules for the use of MOs

- **When *two* AOs mix, *two* MOs will be produced**

- **Each orbital can have a total of *two* electrons (Pauli principle)**

- **Lowest energy orbitals are filled first (Aufbau principle)**

- **Unpaired electrons have parallel spin (Hund's rule)**

Bond order = ½ (bonding electrons – antibonding electrons)

Linear Combination of Atomic Orbitals (LCAO)

The wave function for the molecular orbitals can be approximated by taking linear combinations of atomic orbitals.

$$\psi_{AB} = N(c_A \psi_A + c_B \psi_B)$$

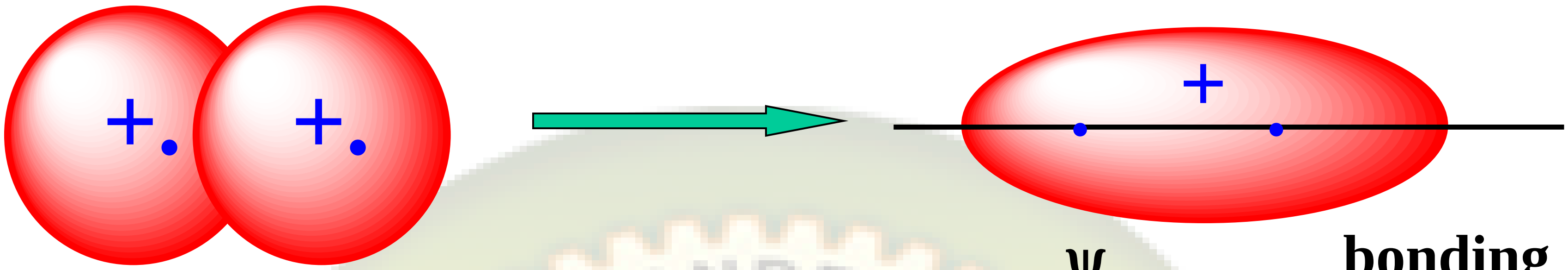
c – extent to which each AO contributes to the MO

$$\psi^2_{AB} = (c_A^2 \psi_A^2 + 2c_A c_B \psi_A \psi_B + c_B^2 \psi_B^2)$$

Probability density

Overlap integral

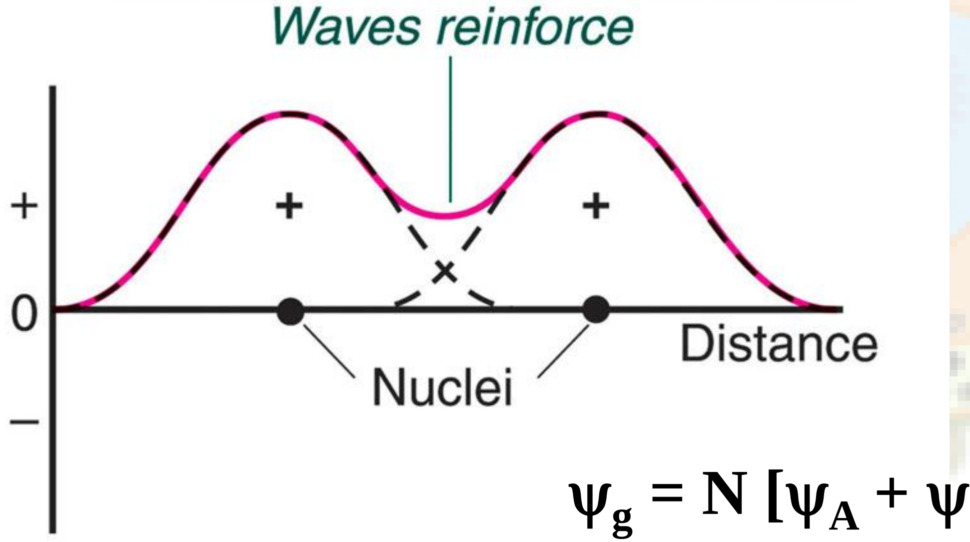
Constructive interference

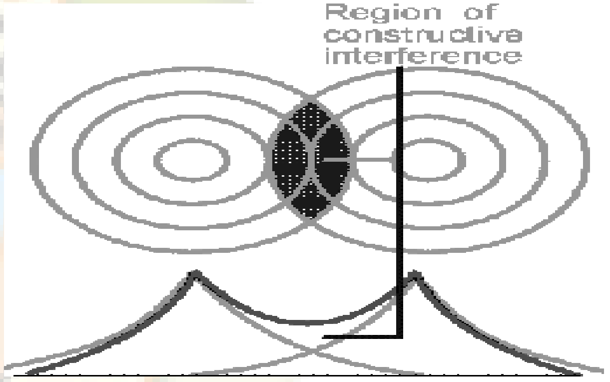


ψ_g

bonding

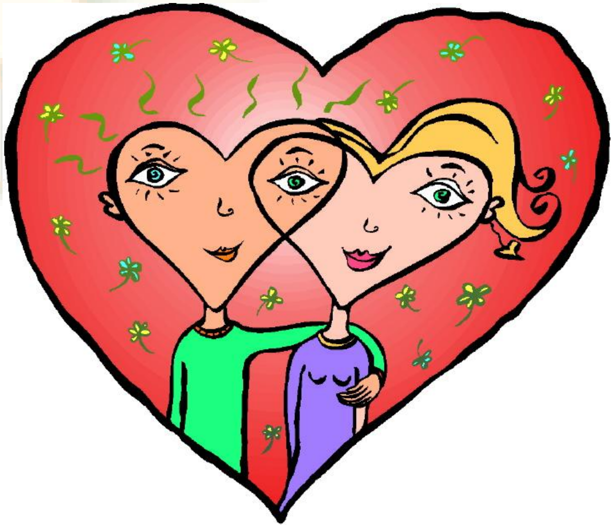
$c_A = c_B = 1$





$$\psi_g = N\,[\psi_A + \psi_B]$$

Amplitudes of wave functions added



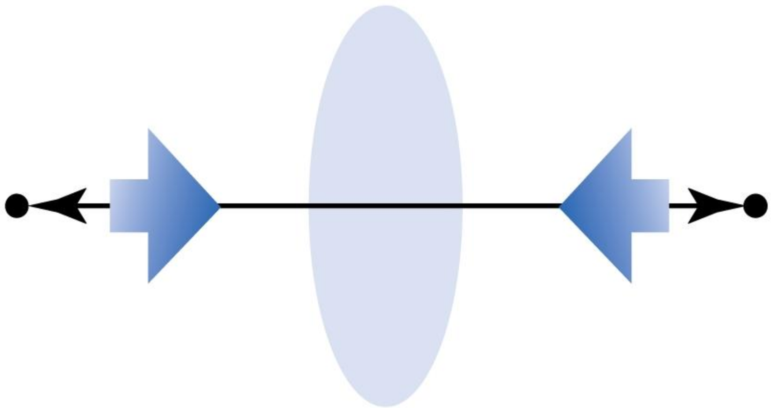
What holds the molecule together?

- There is nothing magic about the molecule being bonded
  - Electrons preferentially spend time between the two nuclei. They act as electrostatic “glue”

$$\psi^2_{AB} = (c_A^2\,\psi_A^2 + 2c_Ac_B\,\psi_A\,\psi_B + c_B^2\,\psi_B^2)$$

density between atoms

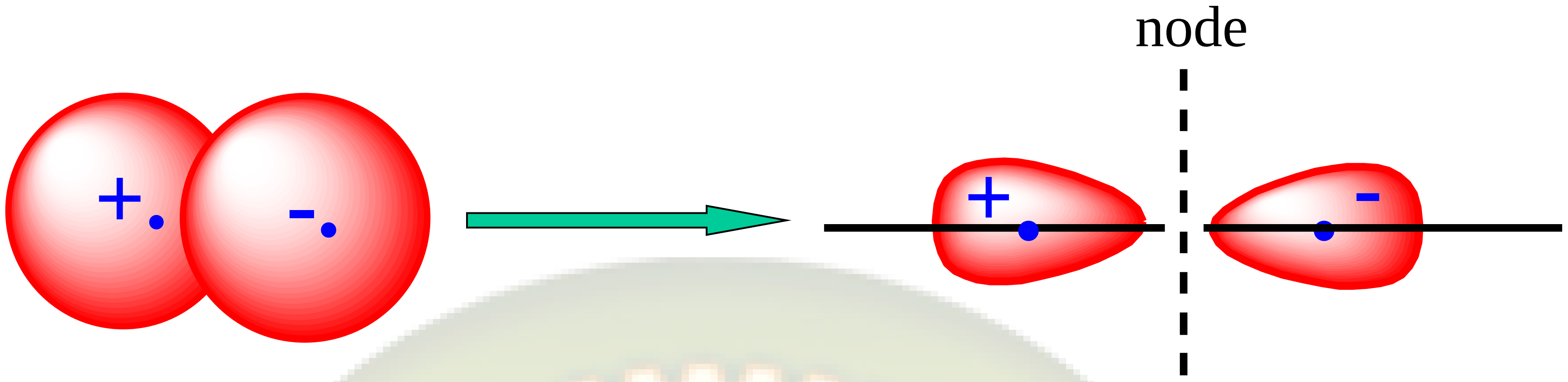
electron density on original atoms,



The accumulation of electron density between the nuclei put the electron in a position where it interacts strongly with both nuclei.

Nuclei are shielded from each other

The energy of the molecule is lower

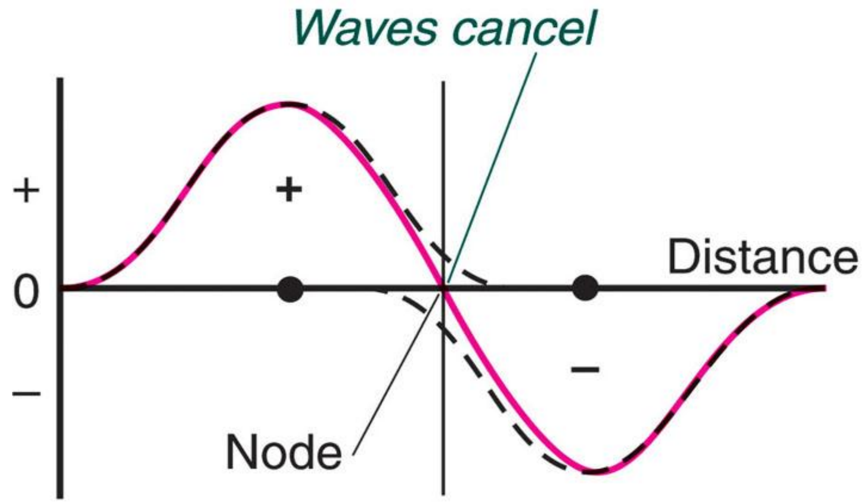


$c_A = +1, c_B = -1$

ψ_u

antibonding

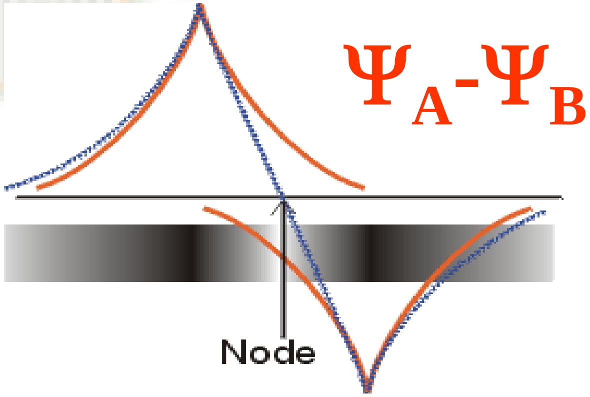
$\psi_u = N [\psi_A - \psi_B]$

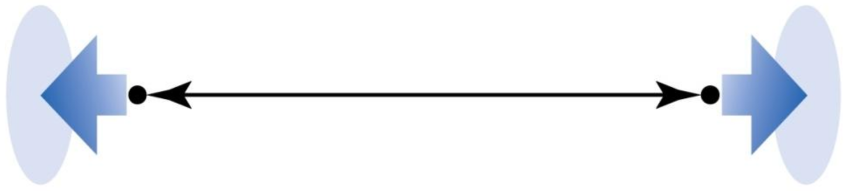


Amplitudes of wave functions subtracted.

Destructive interference

Nodal plane perpendicular to the H-H bond axis (en density = 0) Energy of the en in this orbital is higher.





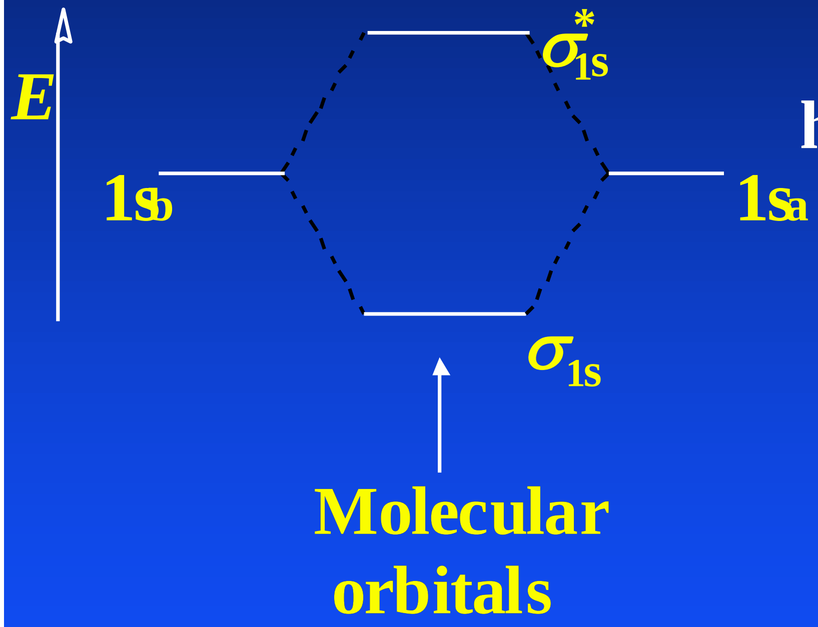
(b)

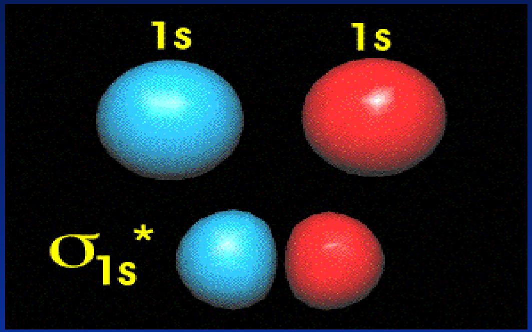
- The electron is excluded from internuclear region → destabilizing

Antibonding

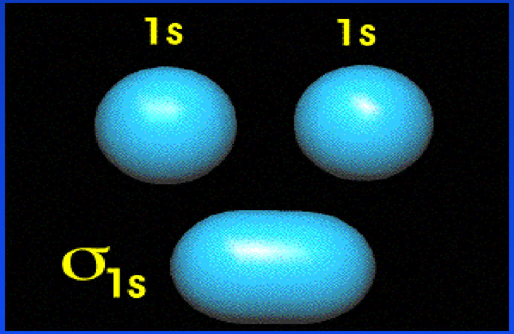
When 2 atomic orbitals combine there are 2 resultant orbitals.

Eg. s orbitals

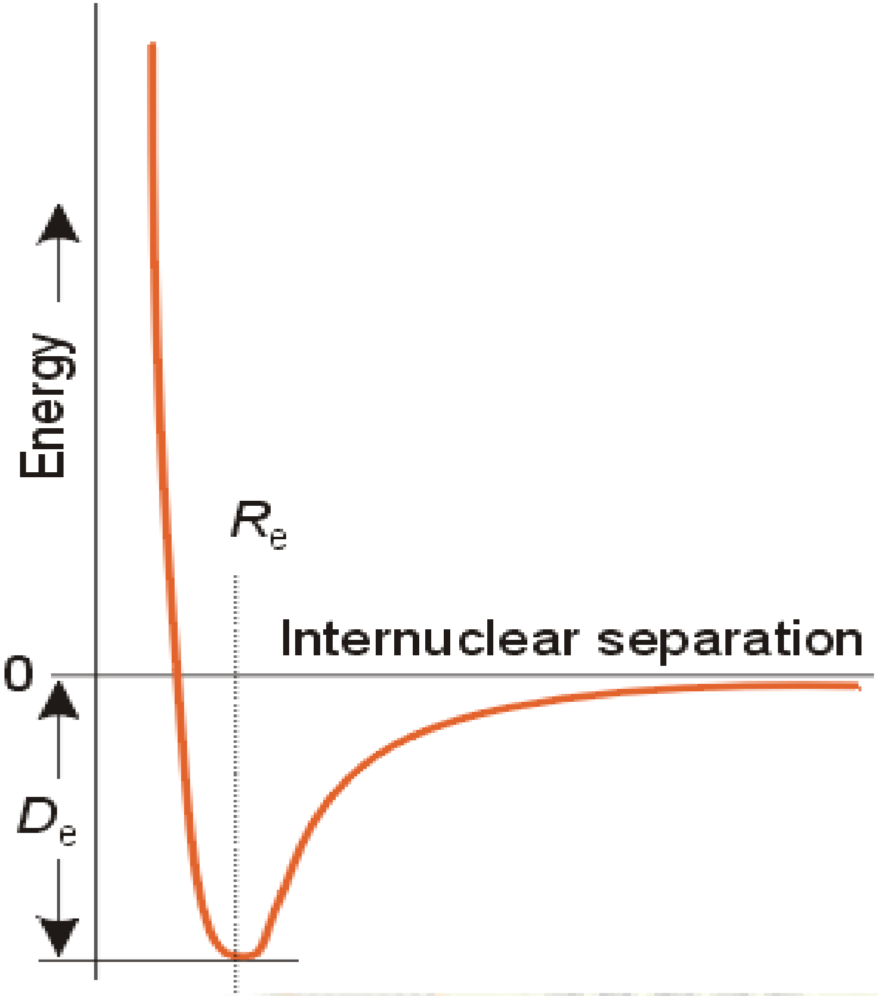


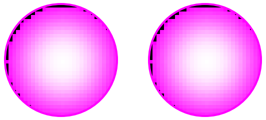


high energy antibonding orbital



low energy bonding orbital

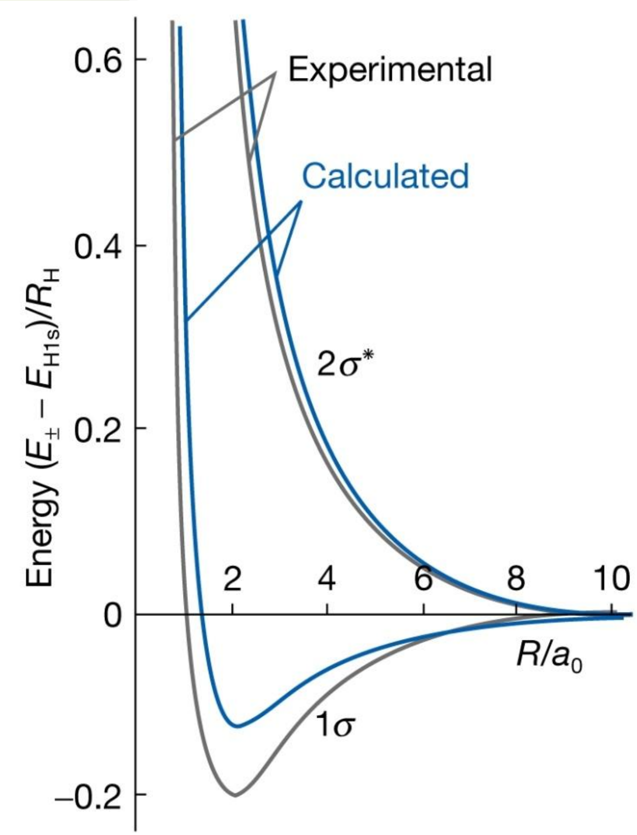


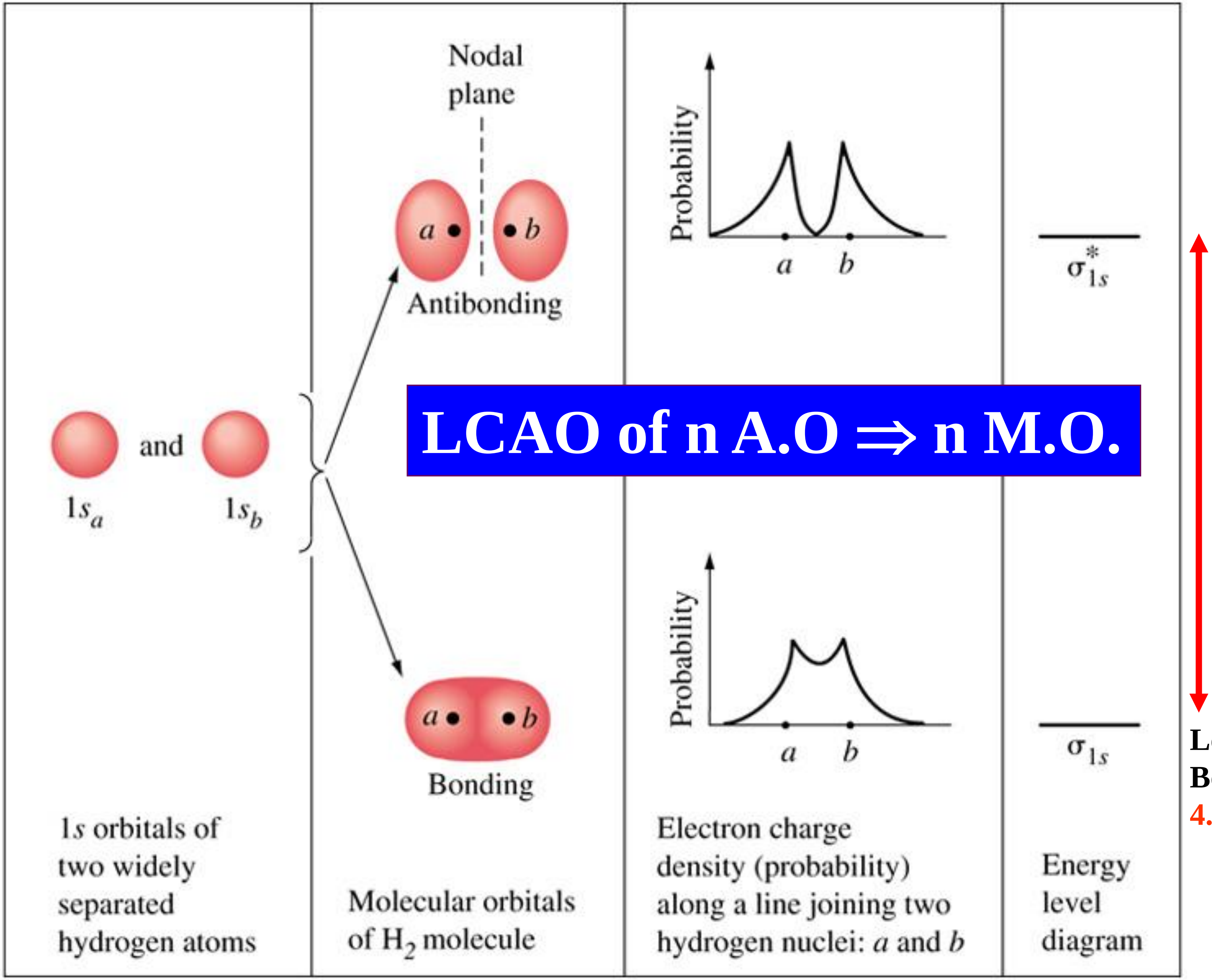


Molecular potential energy curve shows the variation of the molecular energy with internuclear separation.

Looking at the Energy Profile

- Bonding orbital
- called *1s orbital*
- *s electron*
- The energy of 1s orbital decreases as R decreases
- However at small separation, repulsion becomes large
- There is a minimum in potential energy curve





LCAO of n A.O ⇒ n M.O.

H_2

11.4 eV

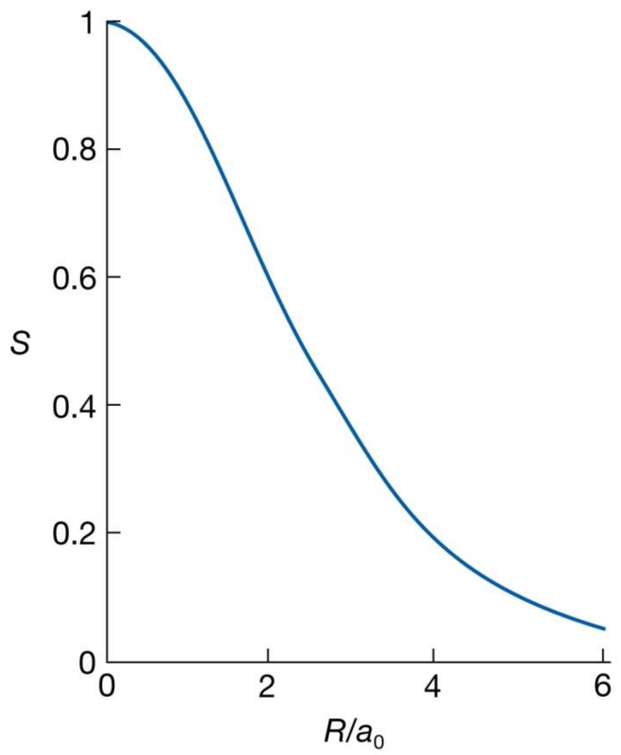
109 nm

Location of
Bonding orbital
4.5 eV

The overlap integral

- **The extent to which two atomic orbitals on different atom overlaps : the overlap integral**

$$S = \int \psi_A{}^* \psi_B \, d\tau$$



- The extent to which orbitals overlap can be evaluated using an overlap integral S.
  - S = 0 indicates that the orbitals do not overlap/interact with one another
  - S depends on the symmetry of the orbital

S > 0 Bonding

S < 0 anti

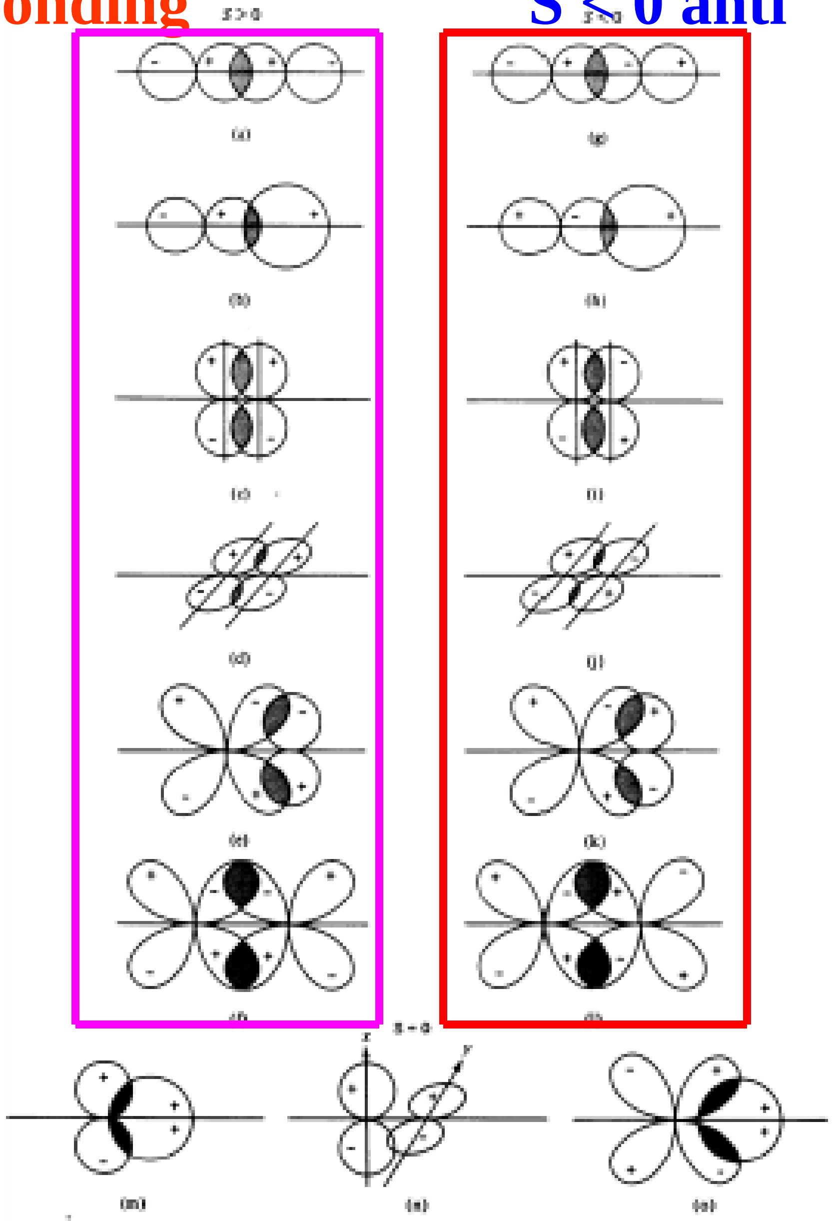


Fig. 5.8 Arrangement of atomic orbitals resulting in positive (a–f), negative (g–l), and zero (m–o) overlap.

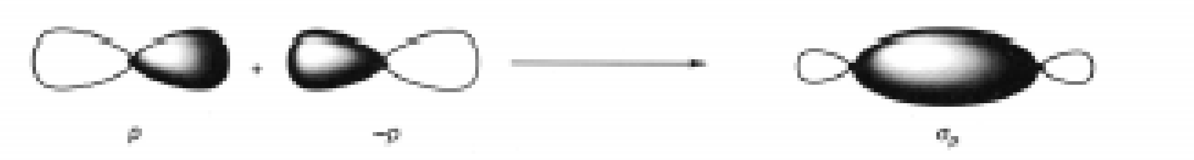
S = 0 nonbonding

Bond strength depends on the degree of overlap

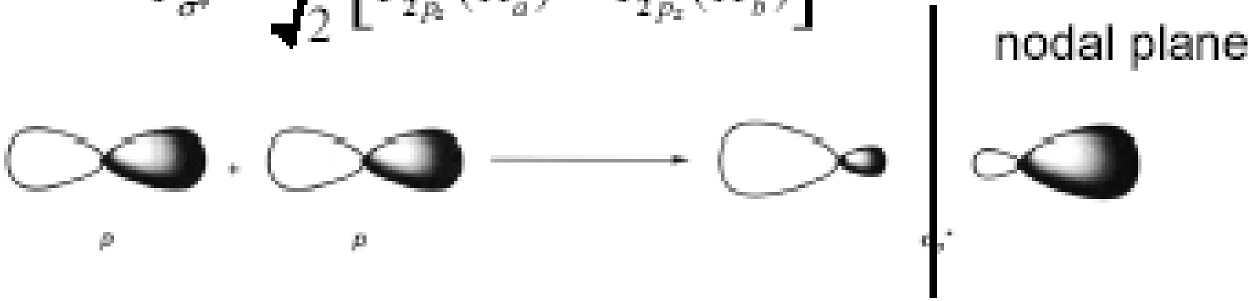
Linear combinations of p_z orbitals

- Addition of two p_z AOs results a bonding σ_p MO, subtraction will give an *antibonding* σ_p* MO with a nodal plane perpendicular to the bond axis

$$\Psi_\sigma = \frac{1}{\sqrt{2}}\left[\Psi_{2p_z}(H_a)+\Psi_{2p_z}(H_b)\right]$$

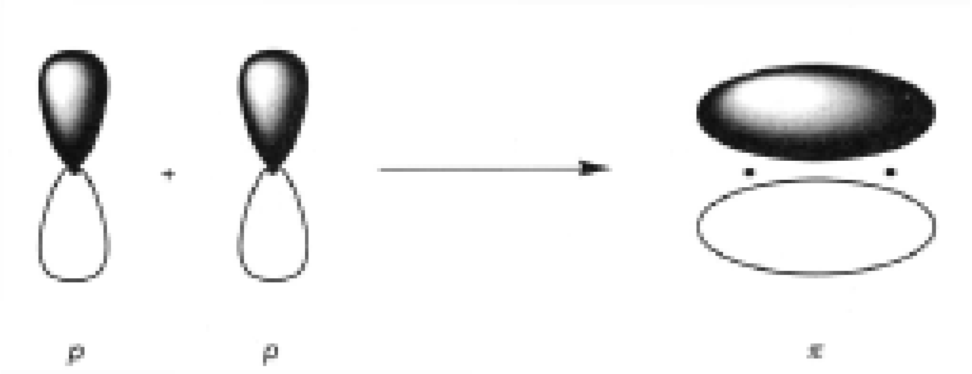


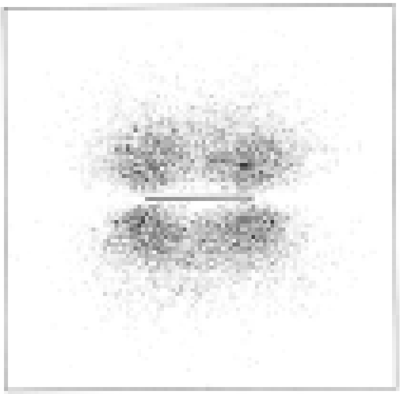
$$\Psi_{\sigma*} = \frac{1}{\sqrt{2}}\left[\Psi_{2p_z}(H_a)-\Psi_{2p_z}(H_b)\right]$$



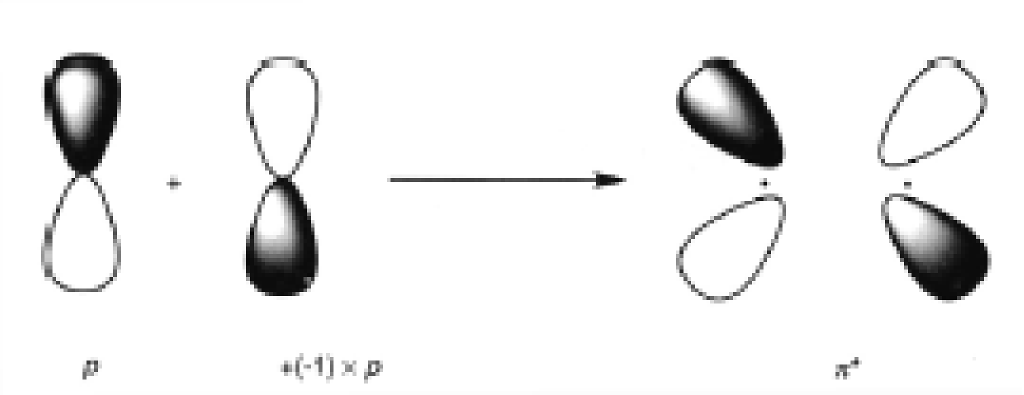
Linear combinations of p_x and p_y orbitals

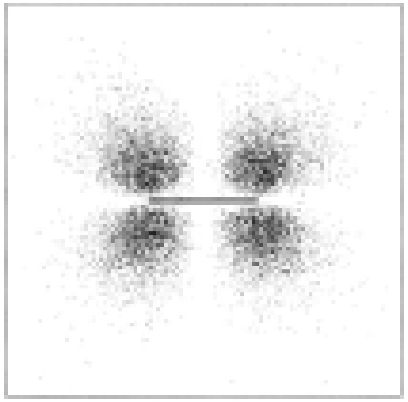
- Addition of two p_x (or p_y) AOs results a bonding π_p MO containing a nodal plane along the bond axis:

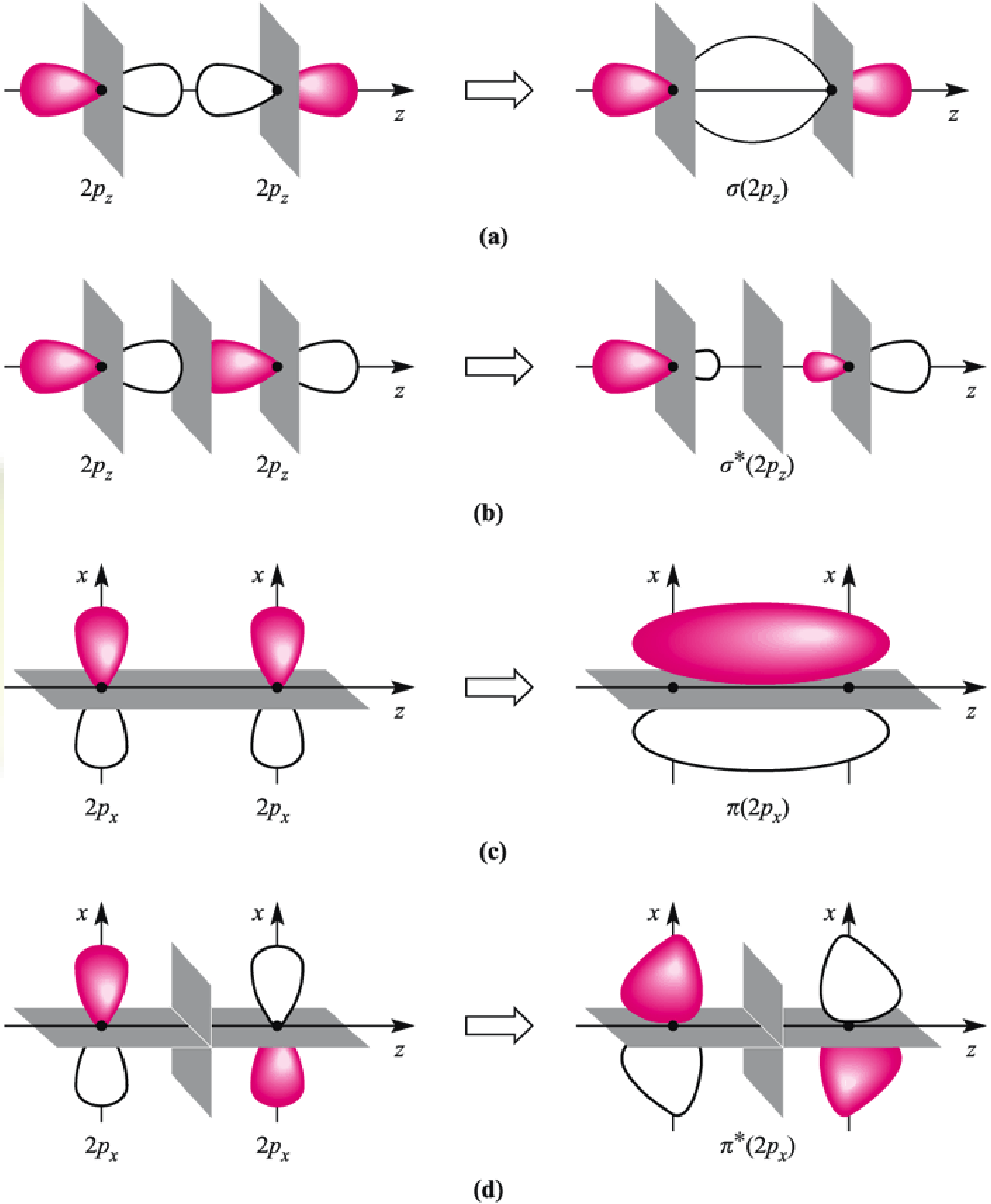




- Subtraction results an *antibonding* π_p* MO with *two* nodal planes: one plane *perpendicular* and one *parallel* to the bond axis






z
$2p_z$
$2p_z$
$\sigma(2p_z)$
(a)
z
$2p_z$
$2p_z$
$\sigma^*(2p_z)$
(b)
x
z
$2p_x$
$2p_x$
$\pi(2p_x)$
(c)
x
z
$2p_x$
$2p_x$
$\pi^*(2p_x)$
(d)

Homonuclear Diatomics

- **MOs may be classified according to:**

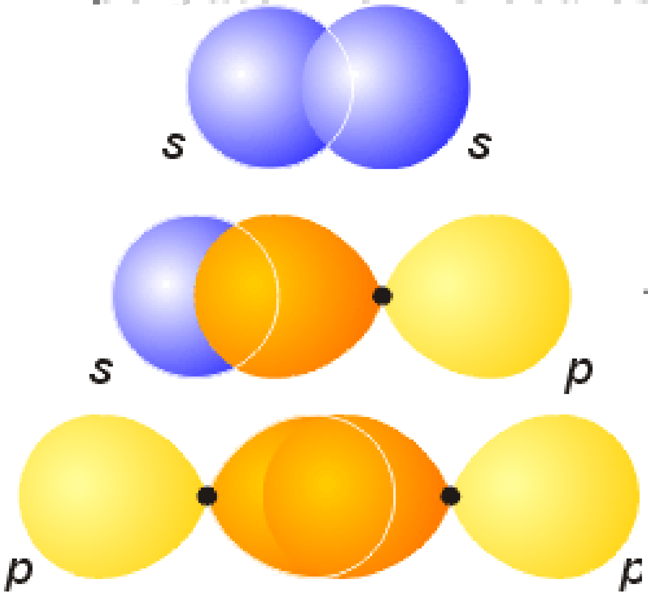
(i) Their symmetry around the molecular axis.

(ii) Their bonding and antibonding character.

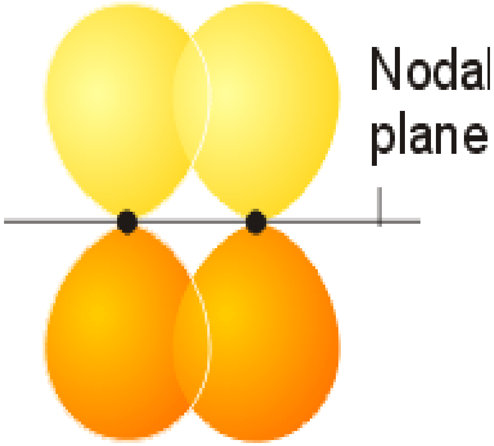
- $\sigma_{1s} < \sigma_{1s}^* < \sigma_{2s} < \sigma_{2s}^* < \sigma_{2p} < \pi_y(2p) = \pi_z(2p) < \pi_y^*(2p) = \pi_z^*(2p) < \sigma_{2p}^*$.

Classifying orbitals by symmetry

- Orbitals in diatomics can be classified according to their rotational symmetry characteristics as σ, π or δ. These classifications are strictly only valid for diatomics, but we also use them to describe bonds between pairs of atoms in polyatomic molecules.

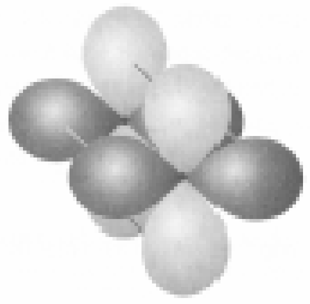


σ orbitals



π orbitals

$dx^2\text{-}dy^2$ and d_{xy}



3.19 The formation of δ orbitals from *d*-orbital overlap. The orbital has two mutually perpendicular nodal planes that intersect along the internuclear axis.

δ orbitals

$$\left[\mathbf{Cl_4Re}\substack{=\\=}\mathbf{ReCl_4}\right]^{2-}$$

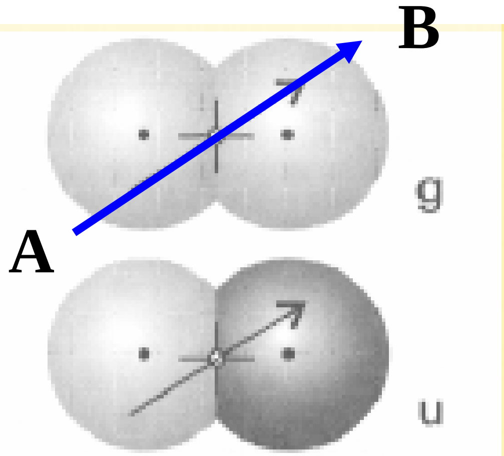
Found in quadruply bonded species such as $[Re_2Cl_8]^{2-}$

Ungerade or gerade ?

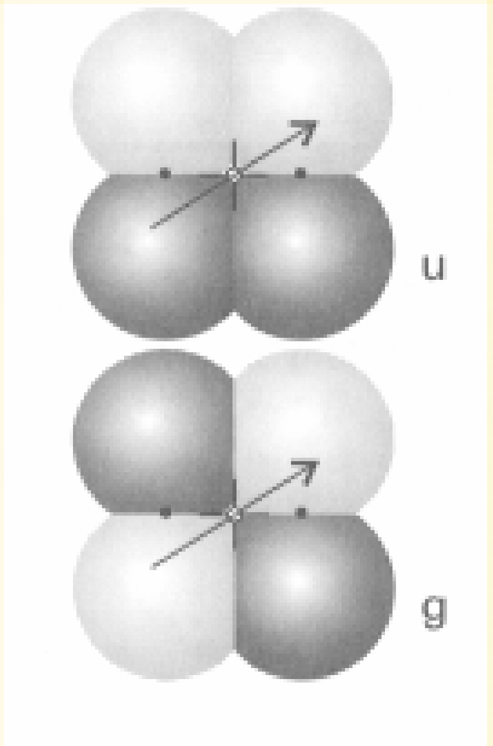
- MOs in molecules that are centrosymmetric can be classified as (g) or (u)
  - Useful for predicting spectroscopic transitions etc.
  - (g) implies that the wavefunction does not change sign on inversion through the center of the molecule. (u) means that it does change sign

g- identical under inversion

u- not identical

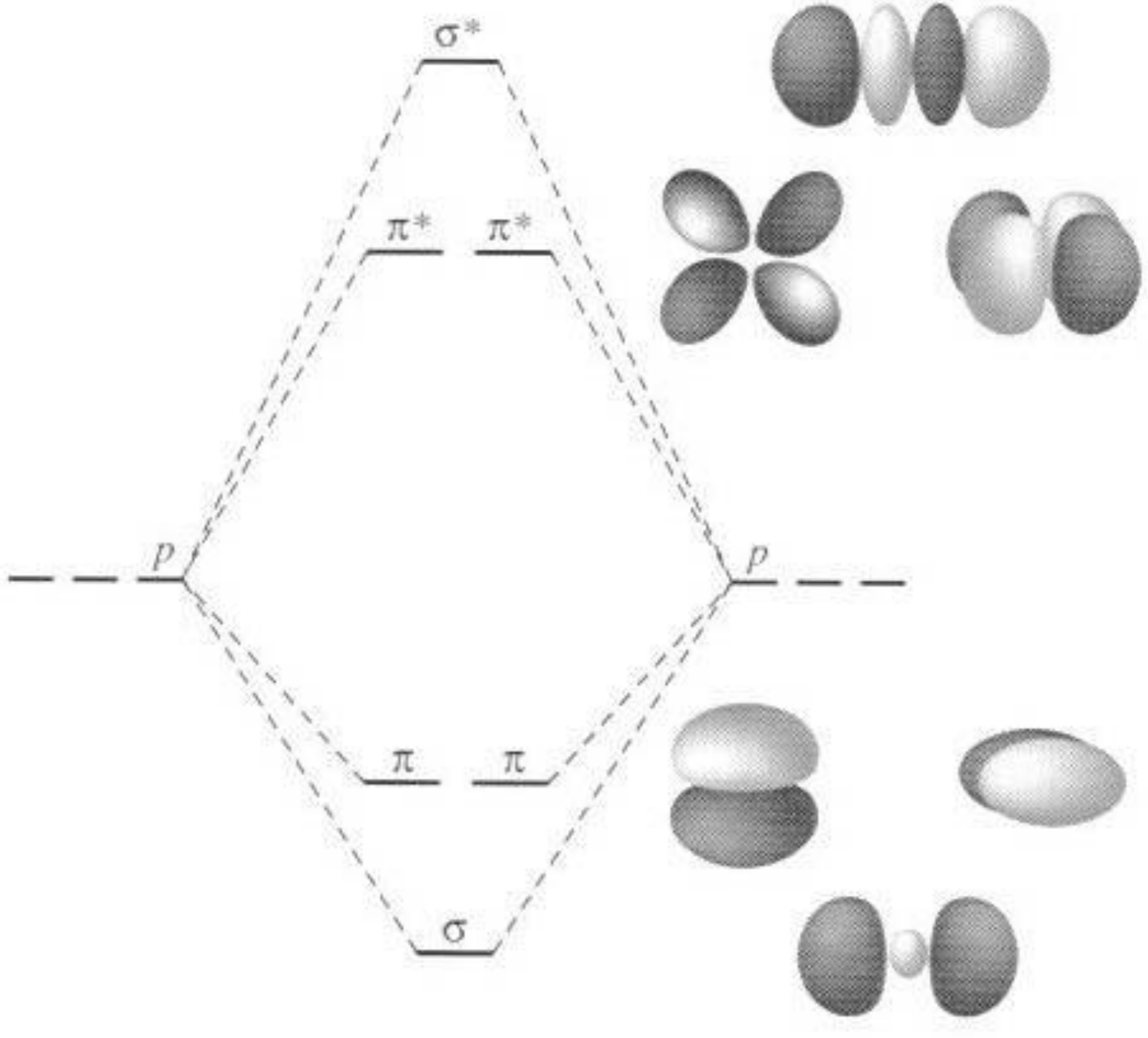


20 σ_g and σ_u orbitals



21 π_g and π_u orbitals

Place labels *g* or *u* in this diagram



(c)

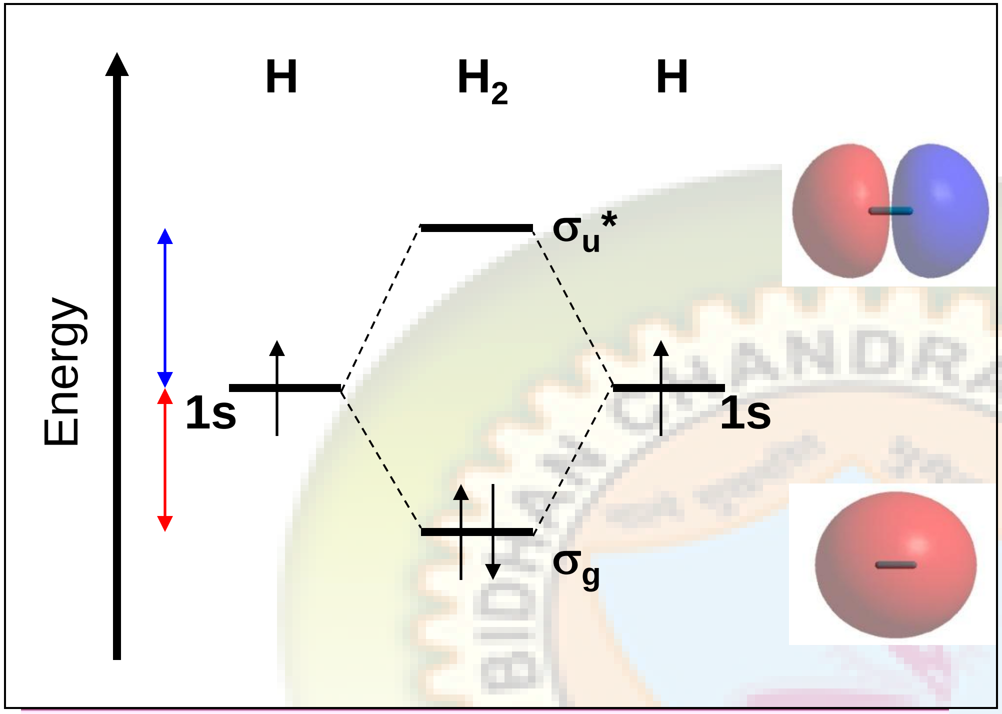
σ^*_u

π^*_g

π_u

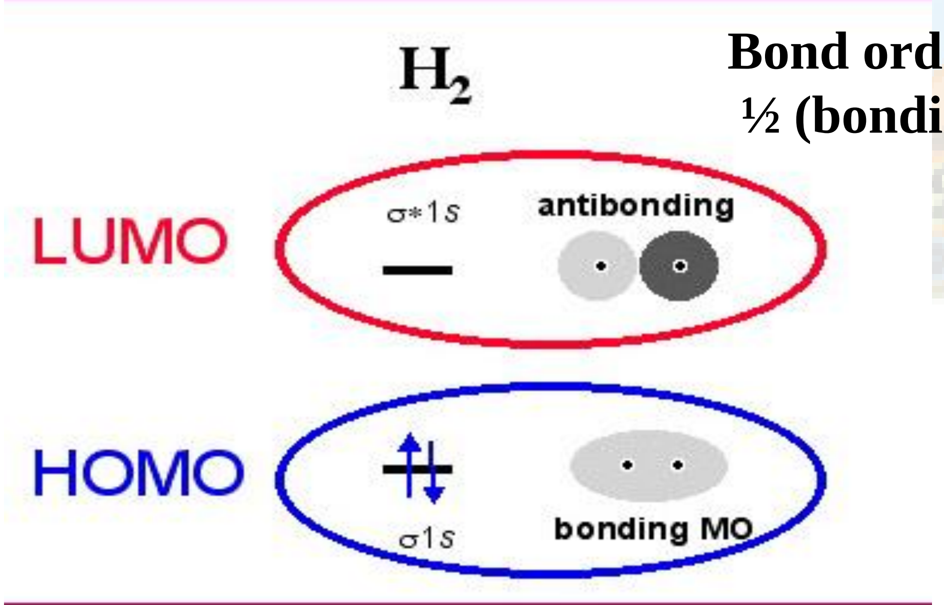
σ_g

First period diatomic molecules



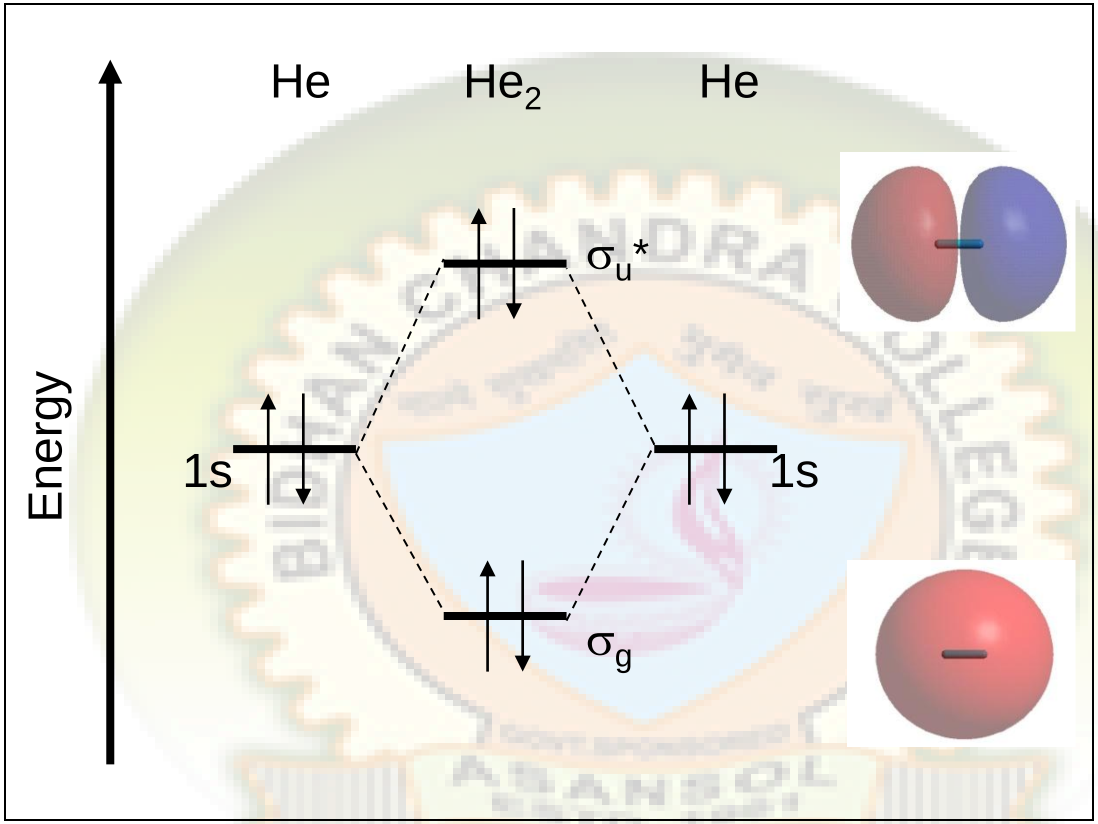
$\sigma 1s^2$

Bond order: 1



Bond order =
½ (bonding electrons – antibonding electrons)

Diatomic molecules: The bonding in He_2

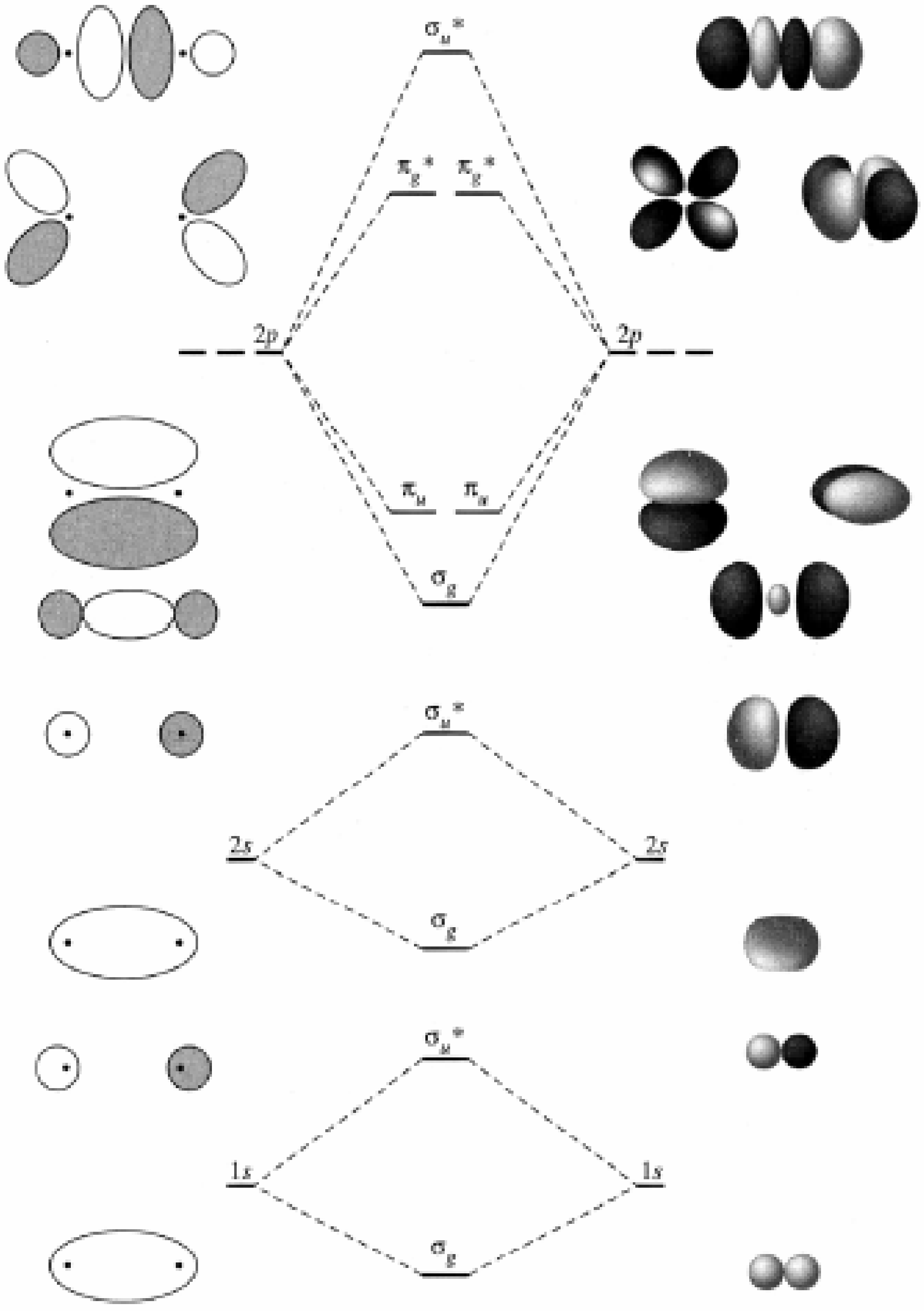


$\sigma 1s^2, \sigma^* 1s^2$

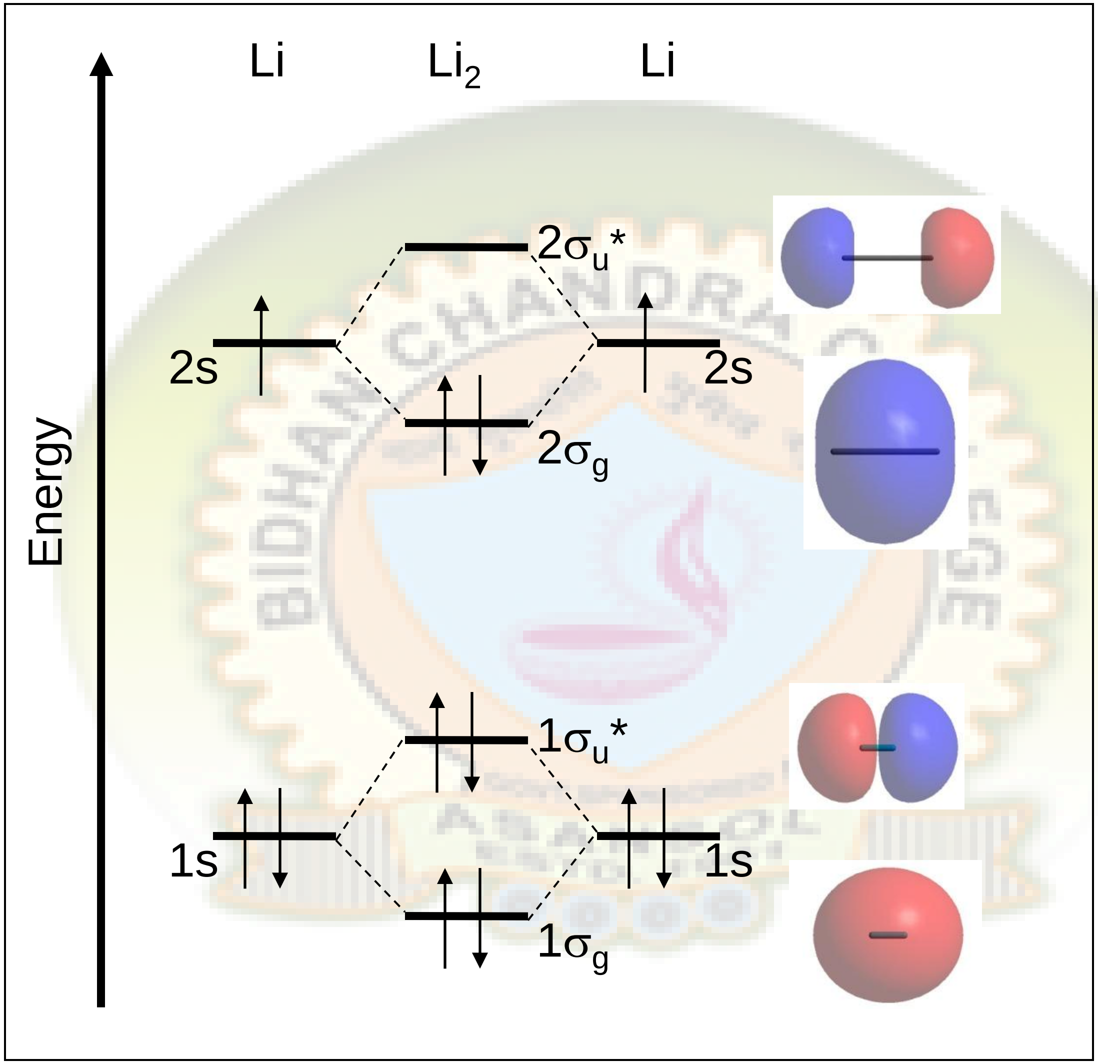
Bond order: 0

Molecular Orbital theory is powerful because it allows us to predict whether molecules should exist or not and it gives us a clear picture of the of the electronic structure of any hypothetical molecule that we can imagine.

Full energy level diagram for second row diatomics



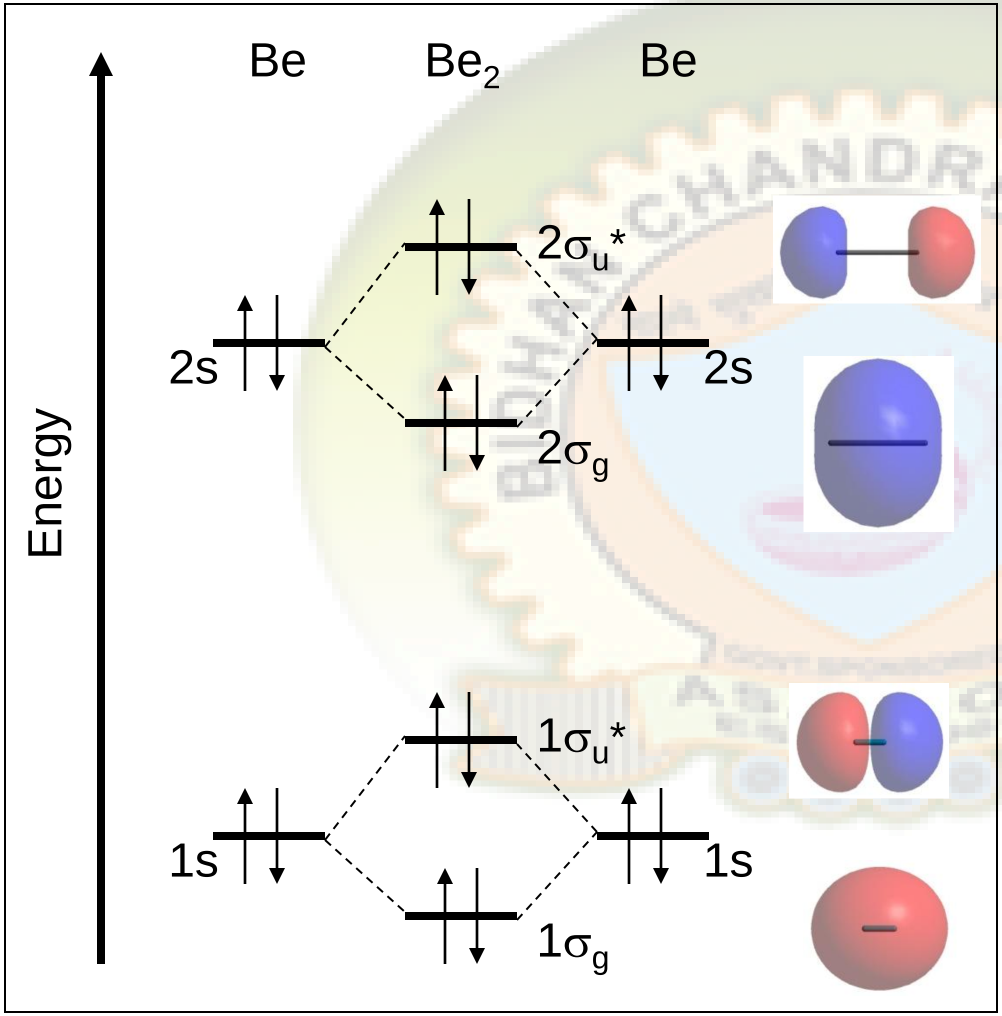
Second period diatomic molecules



$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2$

Bond order: 1

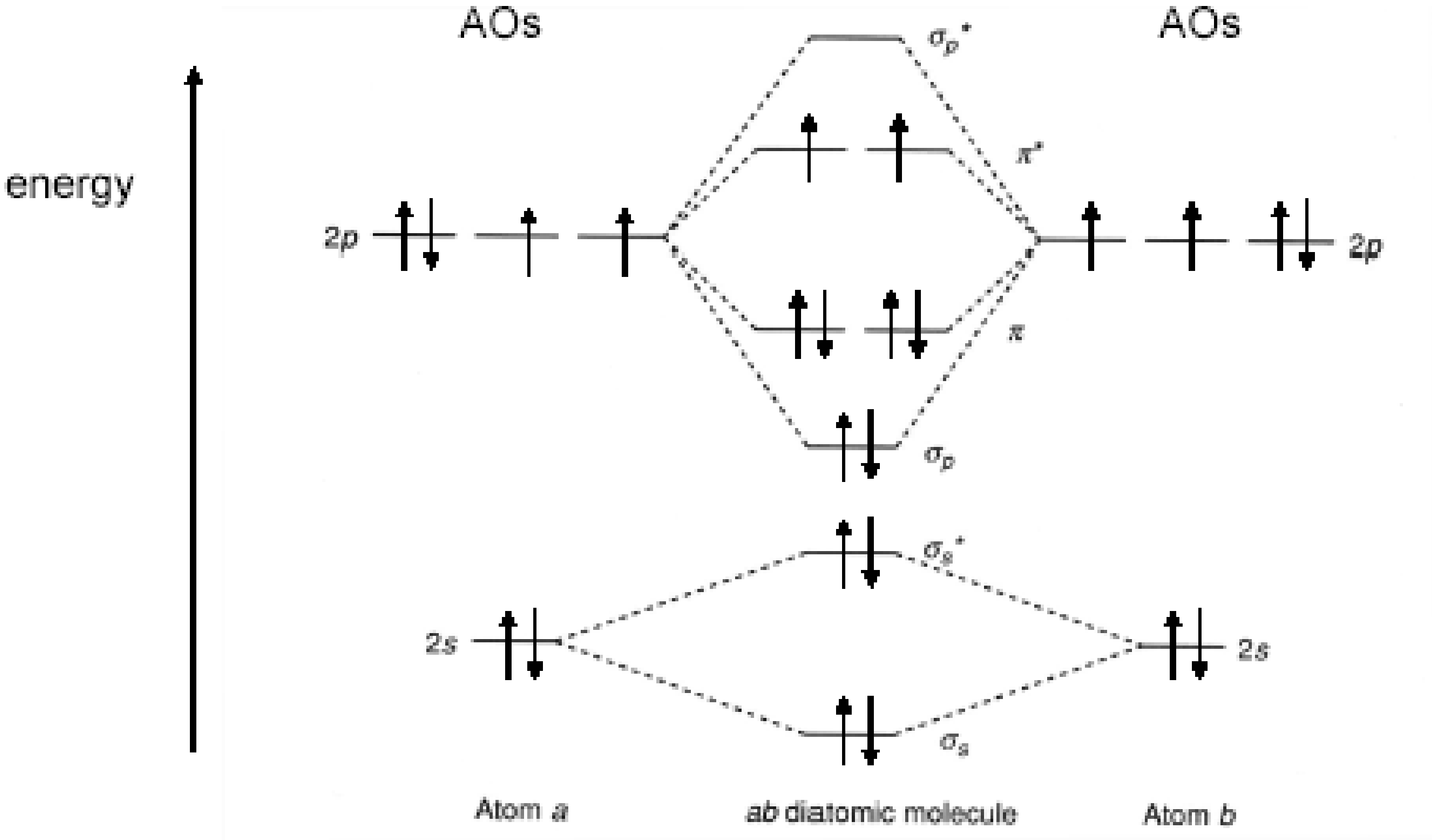
Diatomic molecules: Homonuclear Molecules of the Second Period



$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2$

Bond order: 0

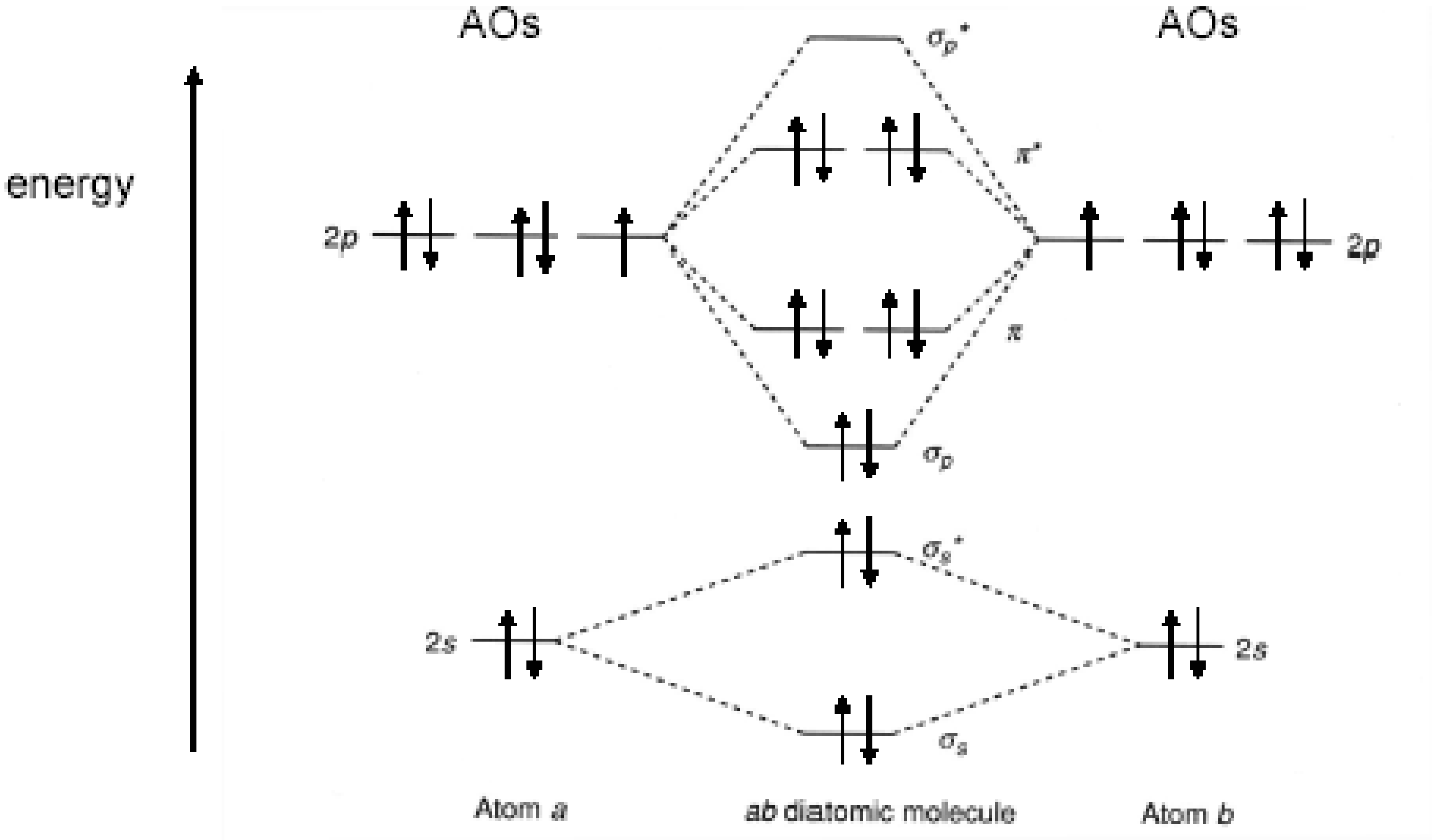
Molecular oxygen



Bond order = 2
2 unpaired electrons –> paramagnetic

Simplified

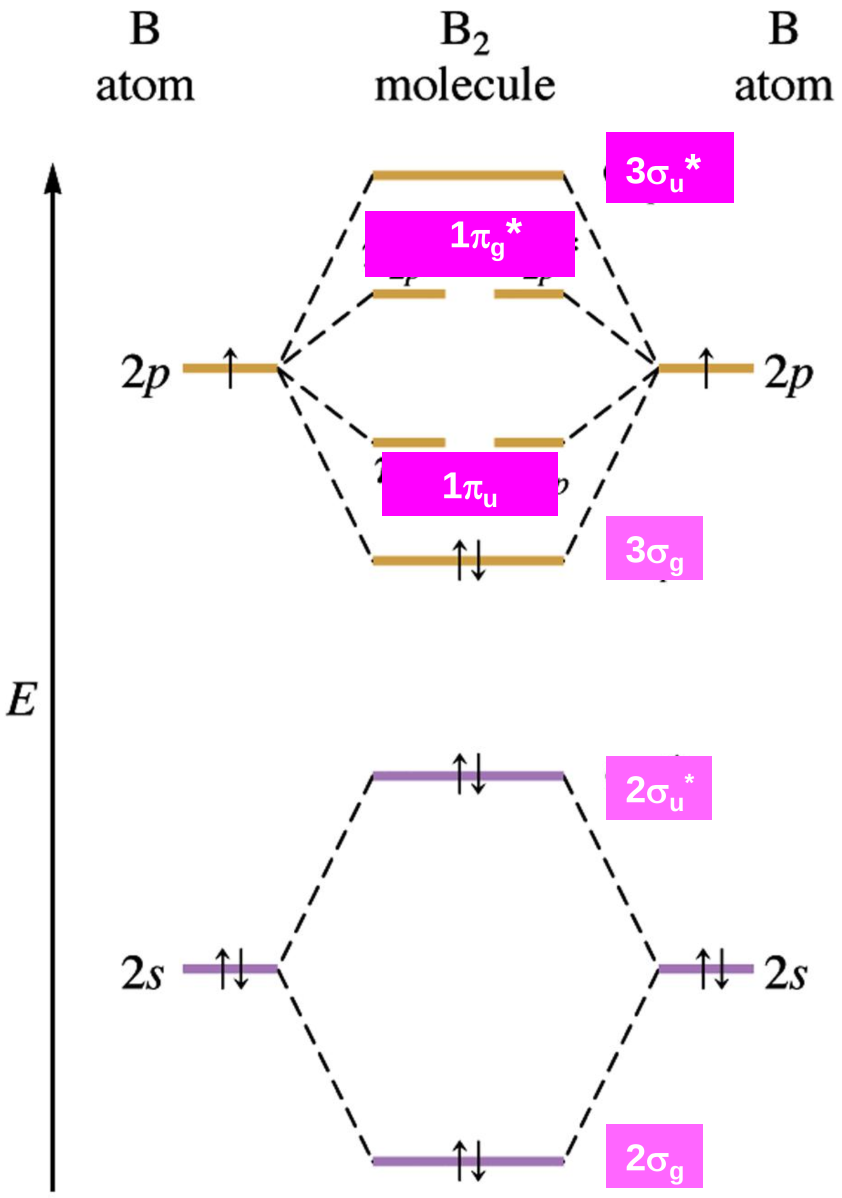
Molecular fluorine



Bond order = 1
0 unpaired electrons –> diamagnetic

Simplified

MO diagram for B_2



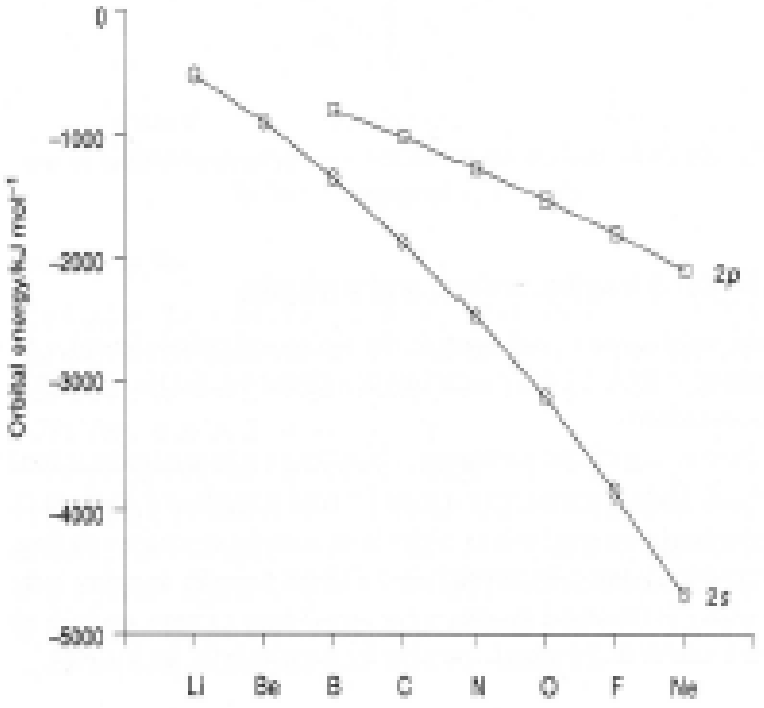
Diamagnetic??

Orbital Mixing

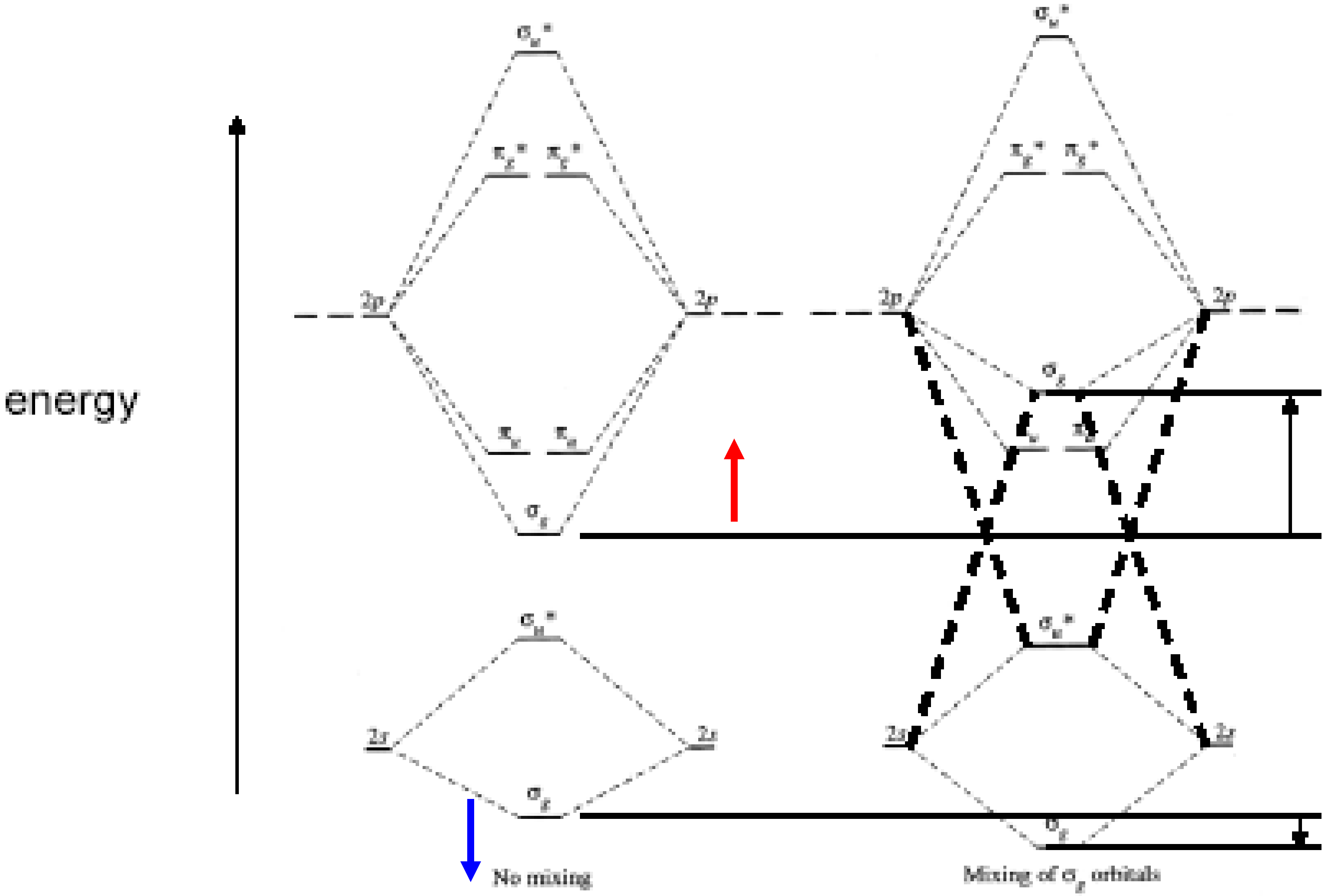
- Orbitals with similar energy interact, if they have the appropriate symmetries
- The σ_{2p} and σ_{2s} orbitals are symmetry related and give rise to two new orbitals, one with higher and one with lower energy

Li : 200 kJ/mol

F: 2500 kJ/mol



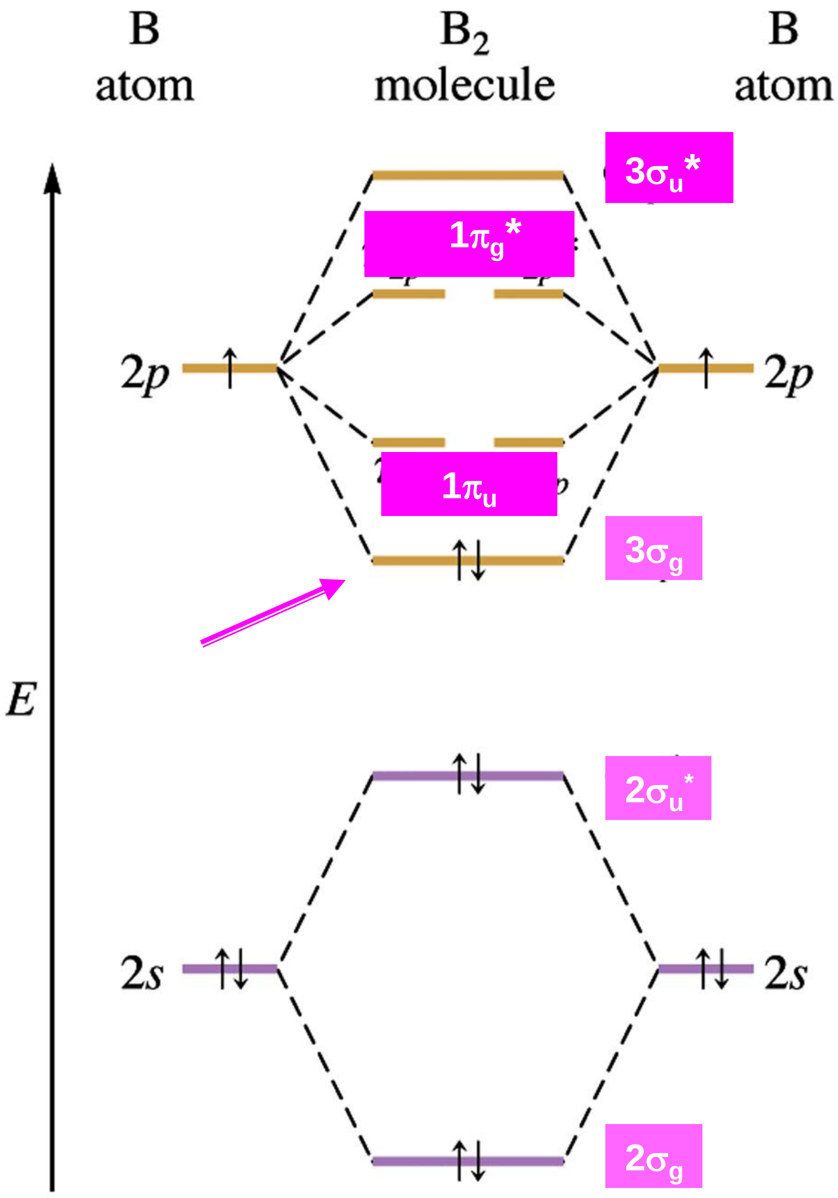
Effect of orbital mixing

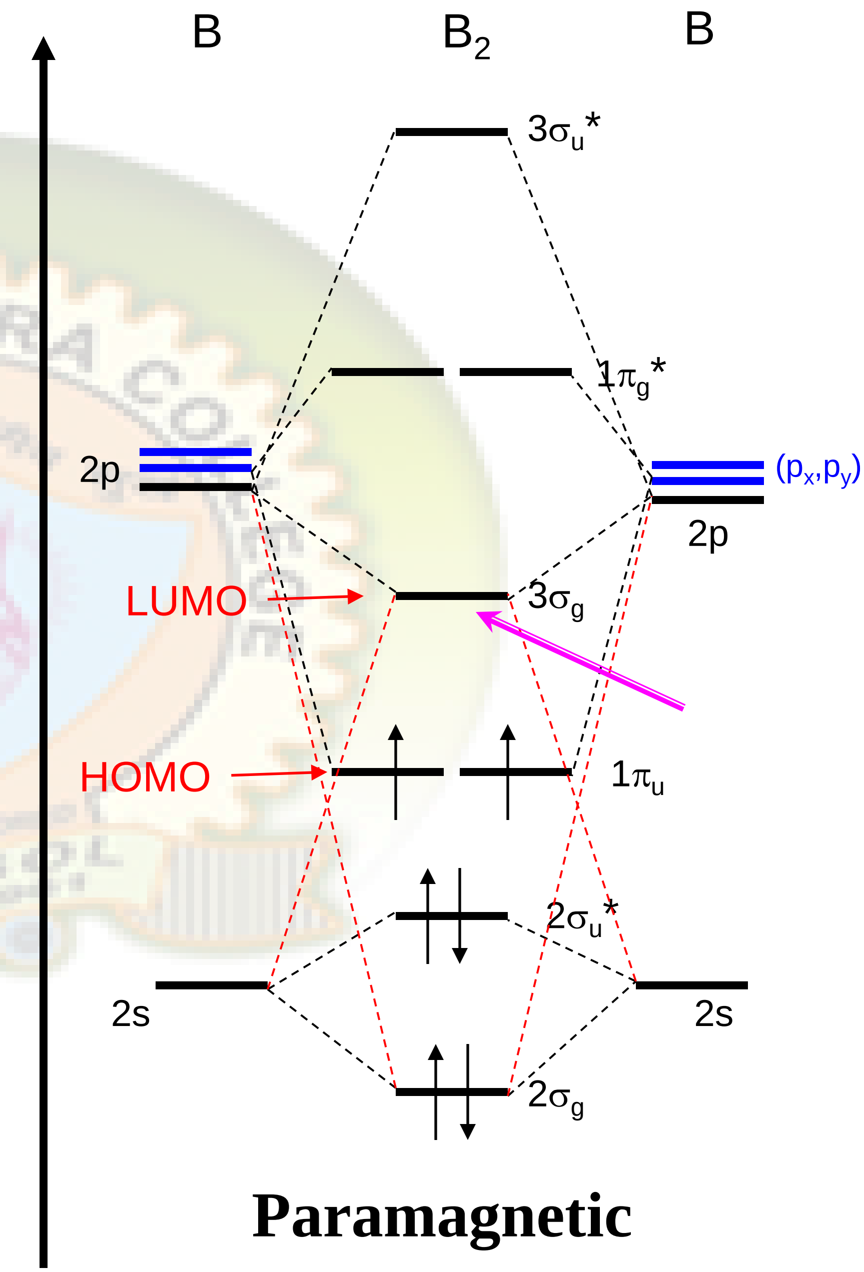


Same symmetry, energy mix-

the one with higher energy moves higher and the one with lower energy moves lower

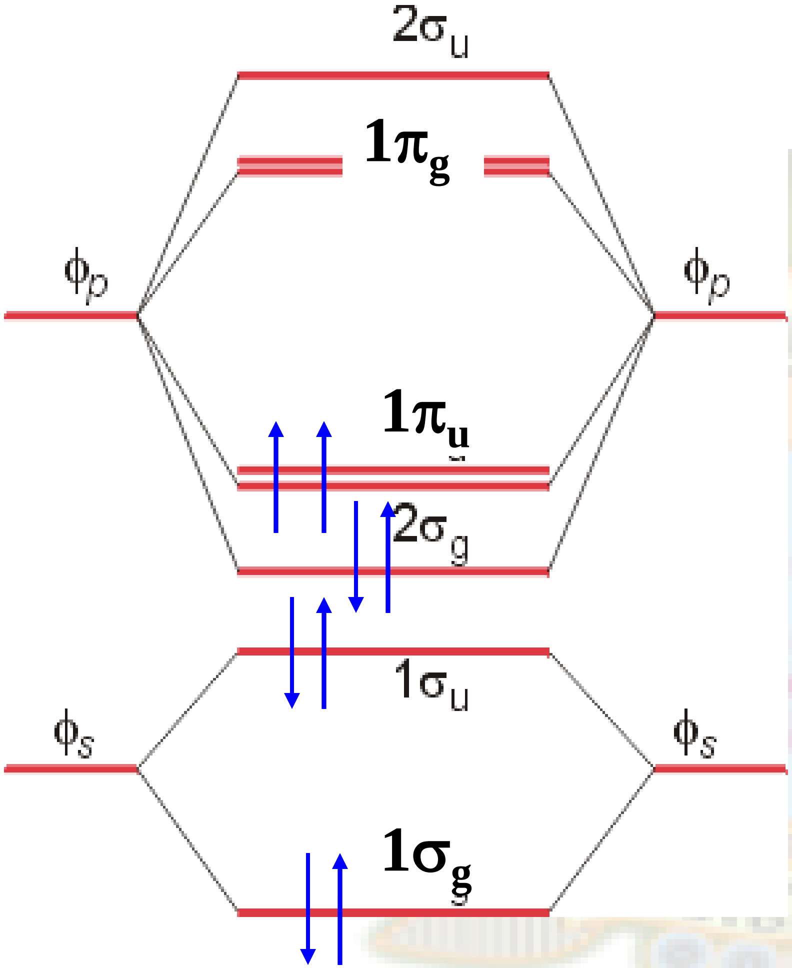
MO diagram for B_2

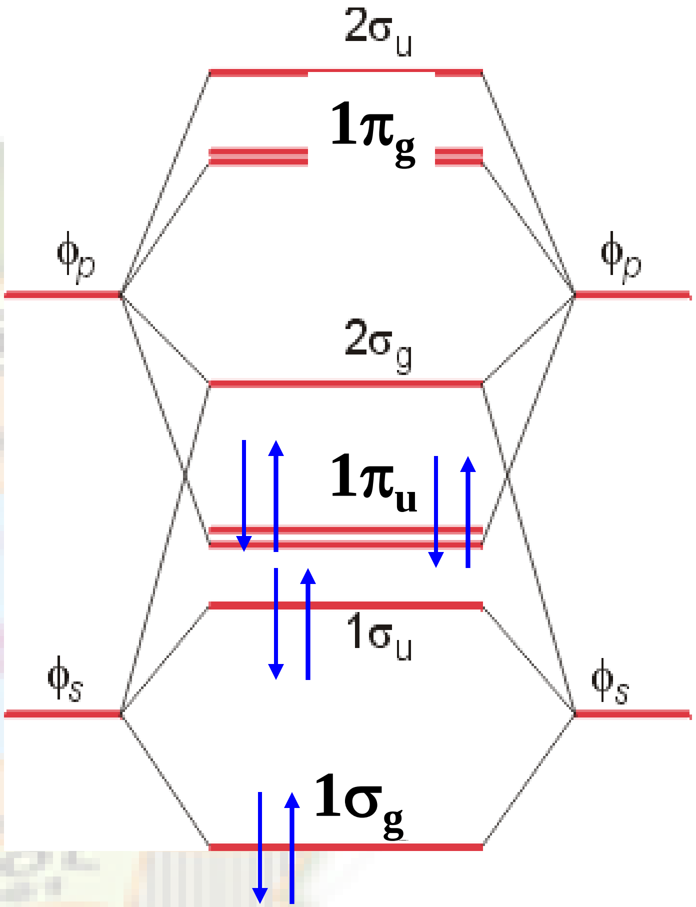




Paramagnetic

C_2

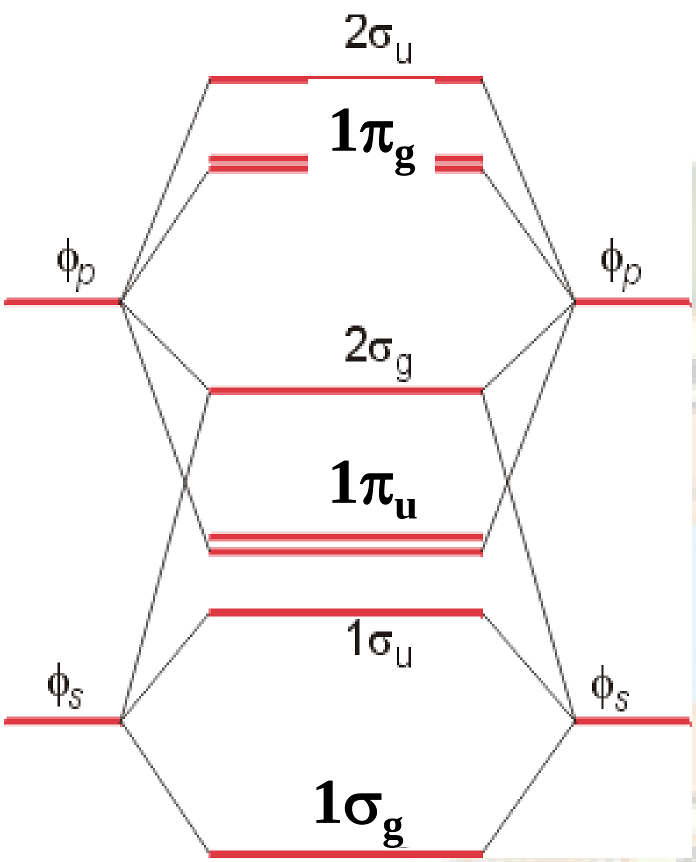




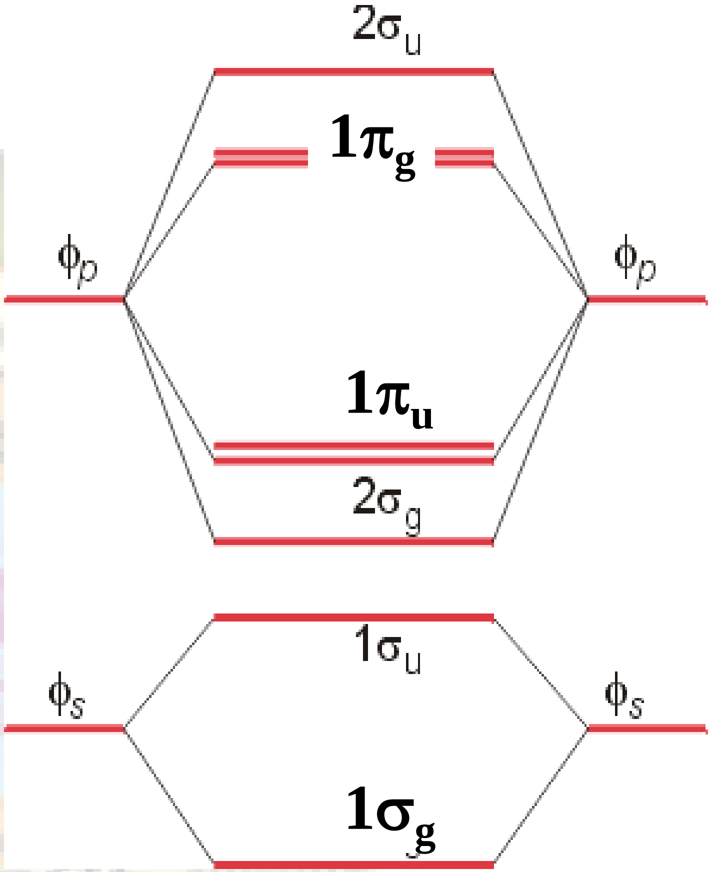
Para~~m~~agnetic ?

Diamagnetic

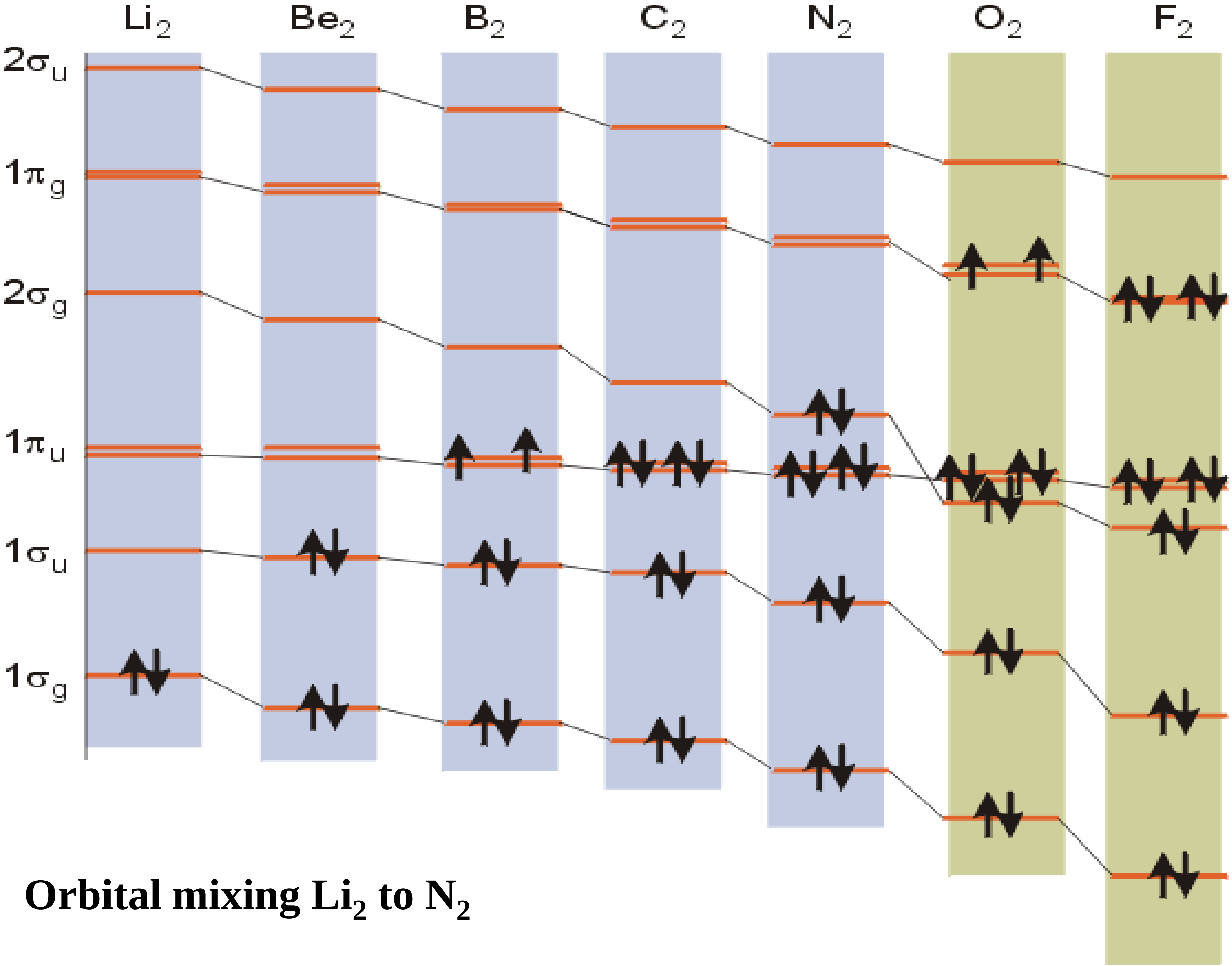
General MO diagrams



Li_2 to N_2

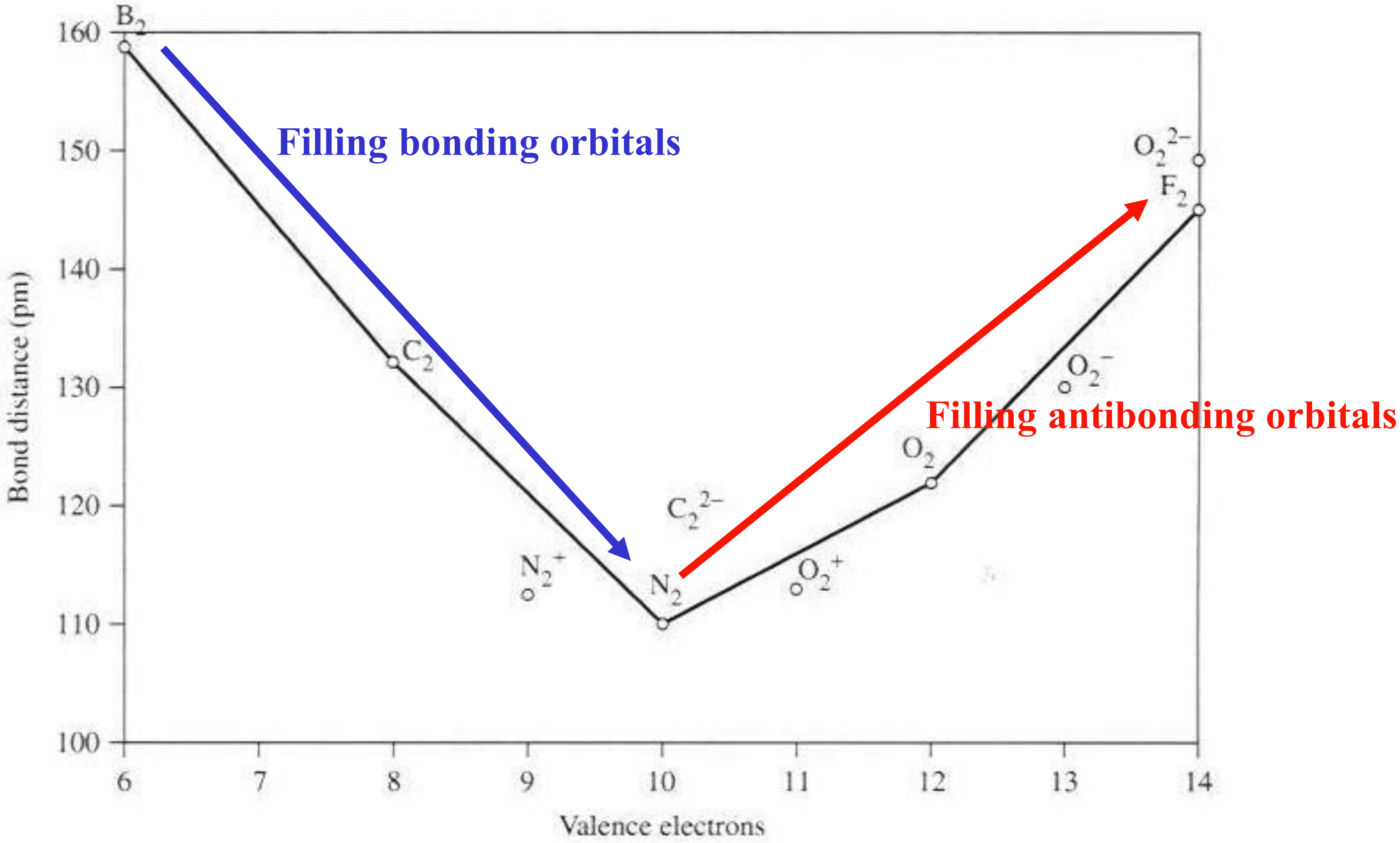


O_2 and F_2



Orbital mixing Li$_2$ to N$_2$

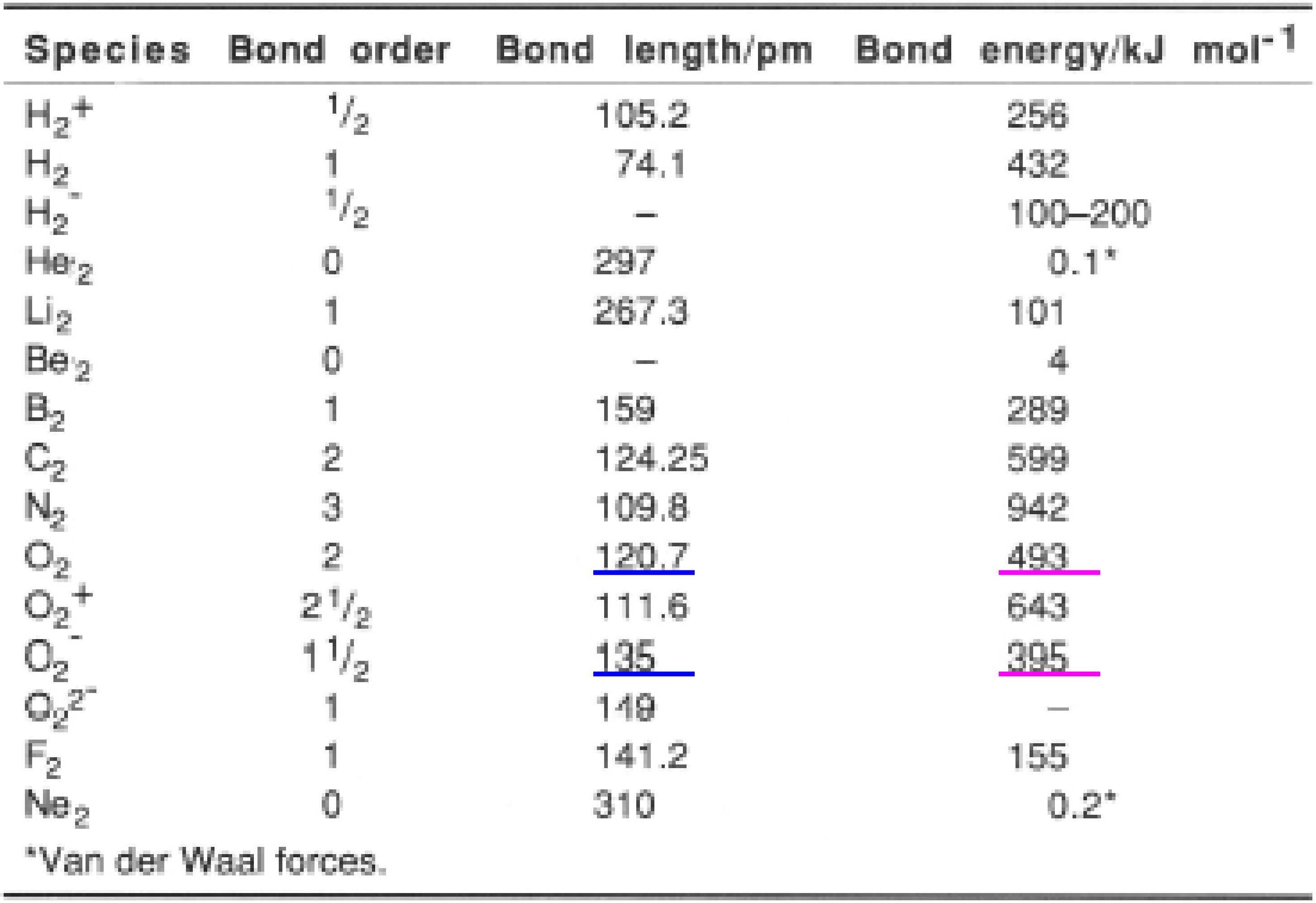
Bond lengths in diatomic molecules



Filling bonding orbitals

Filling antibonding orbitals

Bond Order vs. Bond Length & Energy



Species	Bond order	Bond length/pm	Bond energy/kJ mol^{-1}
H_2^+	$^1/_2$	105.2	256
H_2	1	74.1	432
H_2^-	$^1/_2$	–	100–200
He_2	0	297	0.1*
Li_2	1	267.3	101
Be_2	0	–	4
B_2	1	159	289
C_2	2	124.25	599
N_2	3	109.8	942
O_2	2	120.7	493
O_2^+	$2\,^1/_2$	111.6	643
O_2^-	$1\,^1/_2$	135	395
O_2^{2-}	1	149	–
F_2	1	141.2	155
Ne_2	0	310	0.2*

*Van der Waal forces.

Summary

From a basis set of N atomic orbitals, N molecular orbitals are constructed. In Period 2, N=8.

The eight orbitals can be classified by symmetry into two sets: 4 σ and 4 π orbitals.

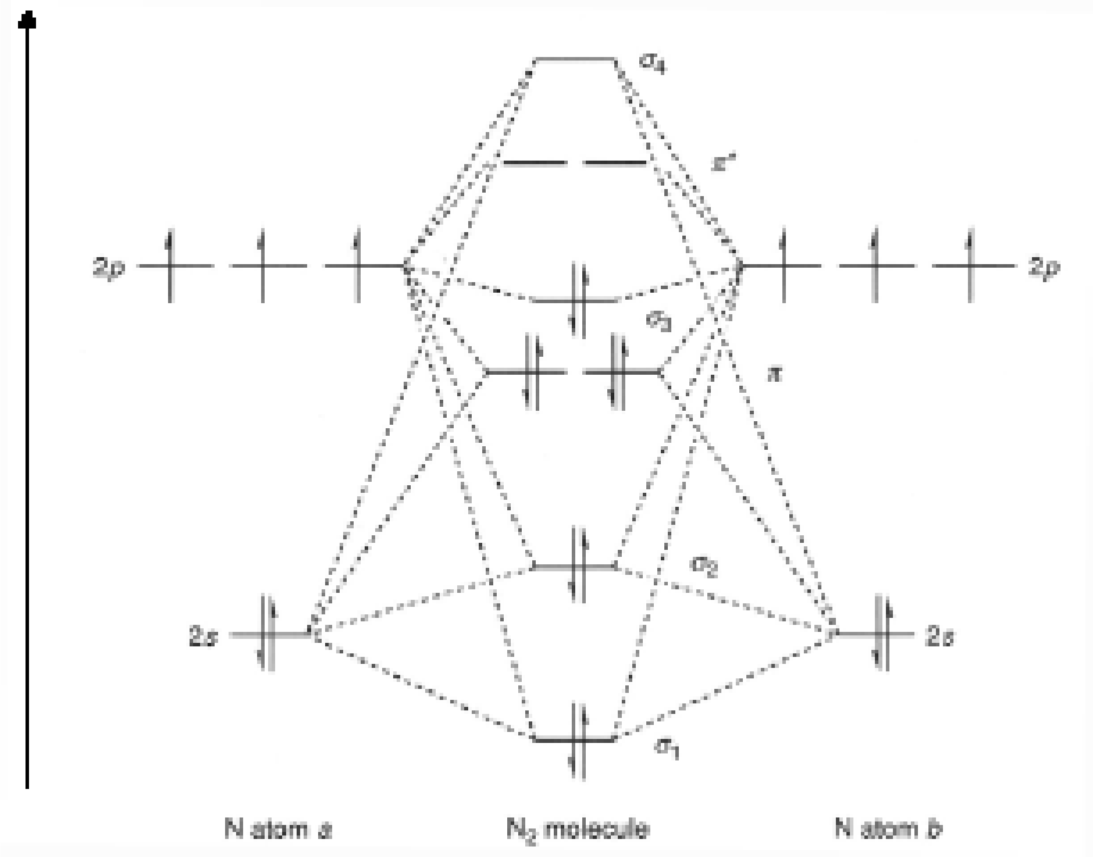
The four π orbitals from one doubly degenerate pair of bonding orbitals and one doubly degenerate pair of antibonding orbitals.

The four σ orbitals span a range of energies, one being strongly bonding and another strongly antibonding, with the remaining two σ orbitals lying between these extremes.

To establish the actual location of the energy levels, it is necessary to use absorption spectroscopy or photoelectron spectroscopy.

Molecular Nitrogen

- According to calculations the σ_g orbital is higher in energy than the two π_{2p} orbitals:



Bond order = 3
no unpaired electrons –> diamagnetic

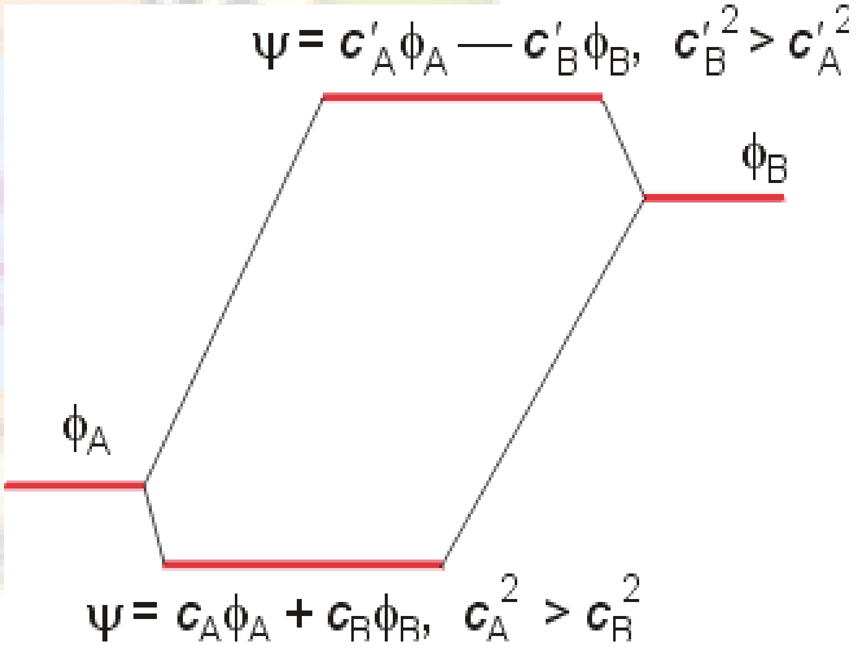
Hetronuclear diatomics

- The contributions to the MO from each of the atoms is unequal
  - $\psi = c_A\phi(A) + c_B\phi(B) + \ldots\ldots$
- The more electronegative atom contributes strongly to the bonding orbital
- The less electronegative atom contributes strongly to the anti-bonding orbital
  - gives rise to polarity

Distance between b-MO and AO

Heteronuclear Diatomics….

- **The energy level diagram is not symmetrical.**
  - **The bonding MOs are closer to the atomic orbitals which are lower in energy.**
  - **The antibonding MOs are closer to those higher in energy.**



c – extent to which each atomic orbitals contribute to MO

If $c_A > c_B$ the MO is composed principally of ϕ_A

HF

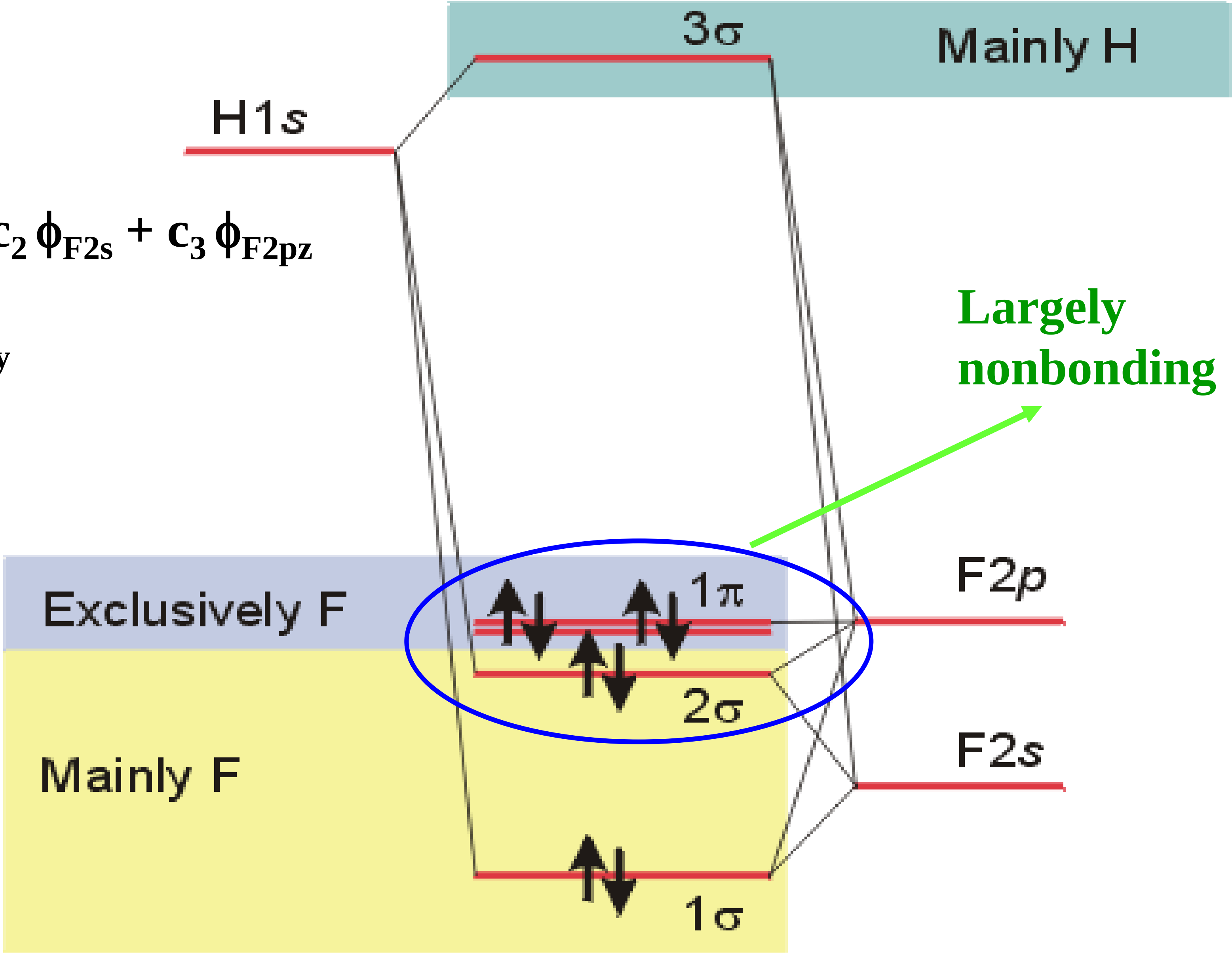
1s	1
2s, 2p	7

$$\psi = c_1\,\phi_{H1s} + c_2\,\phi_{F2s} + c_3\,\phi_{F2pz}$$

$2p_x$ and $2p_y$

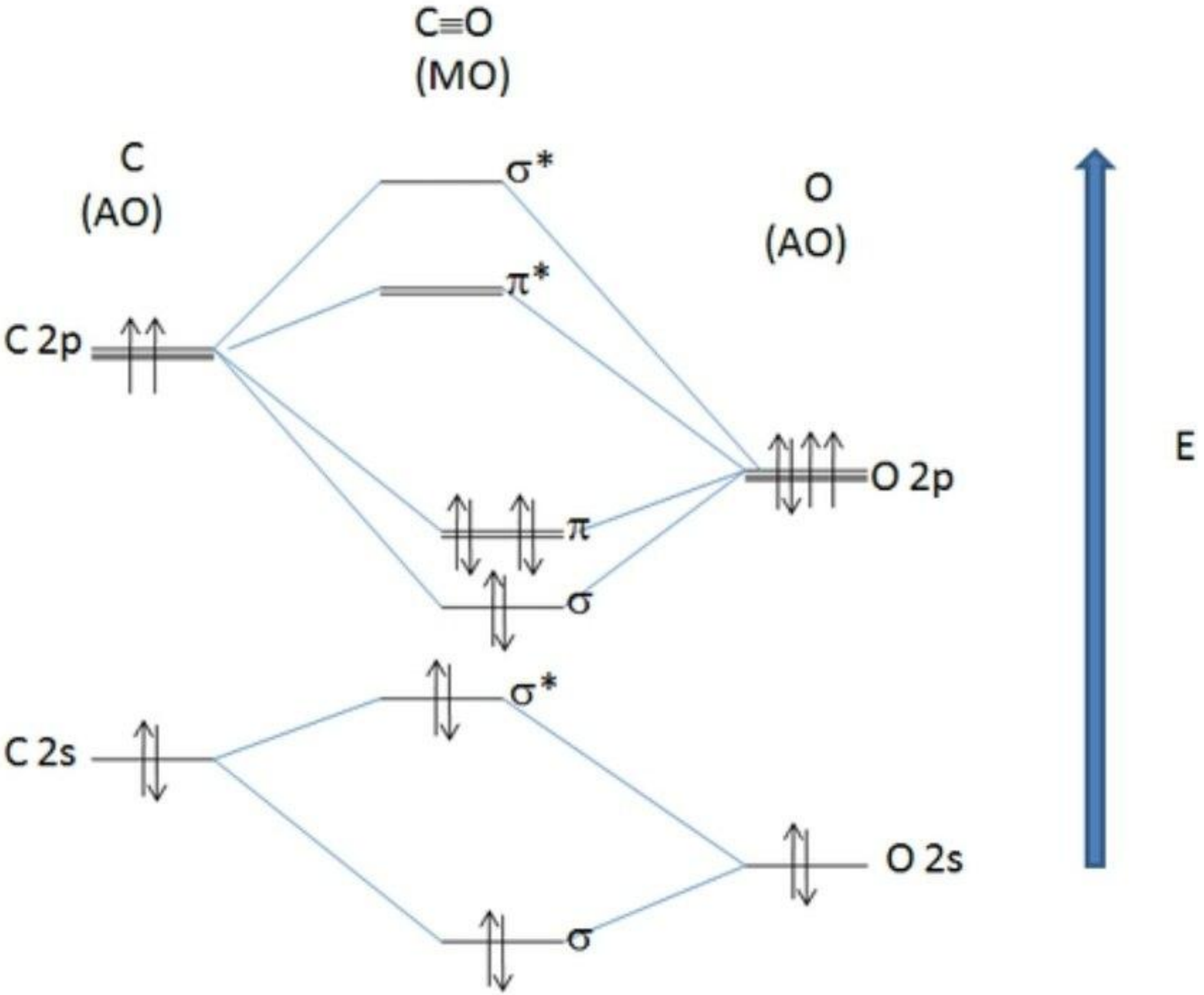
$1\sigma^2\ 2\sigma^2 1\pi^4$

Polar



Largely nonbonding

MO of carbon monoxide:



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