## Rules for LCAOs:

1. The atomic orbitals must be roughly of the same energy.
2. The orbitals must overlap with one another as much as possible.
3. In order to produce bonding and antibonding MOs either the symmetry of the two atomic orbitals must remain unchanged when rotated about the internuclear line or both atomic orbitals must change symmetry in an identical manner.
4. Depending upon the overlap integral ($S_{AB}$) the MOs are classified as BMO ($S_{AB} > 0$), ABMO ($S_{AB} < 0$) and nonbonding MO ($S_{AB} = 0$).
5. All the MOs are normalized

   i.e. $\int \psi_{MO}^2 d\tau = 1$ or $\int (\psi_{MO}^*)^2 d\tau = 1$.

## Rules for Filling Electrons in MOs:

1. The principal quantum number n has the same significance as in atomic orbitals.
2. The subsidiary quantum number l also has the same significance as in atomic orbitals.
3. If magnetic quantum number of atomic orbitals is replaced by a new quantum number $\lambda$:

   $\lambda$ = Quantization of angular momentum

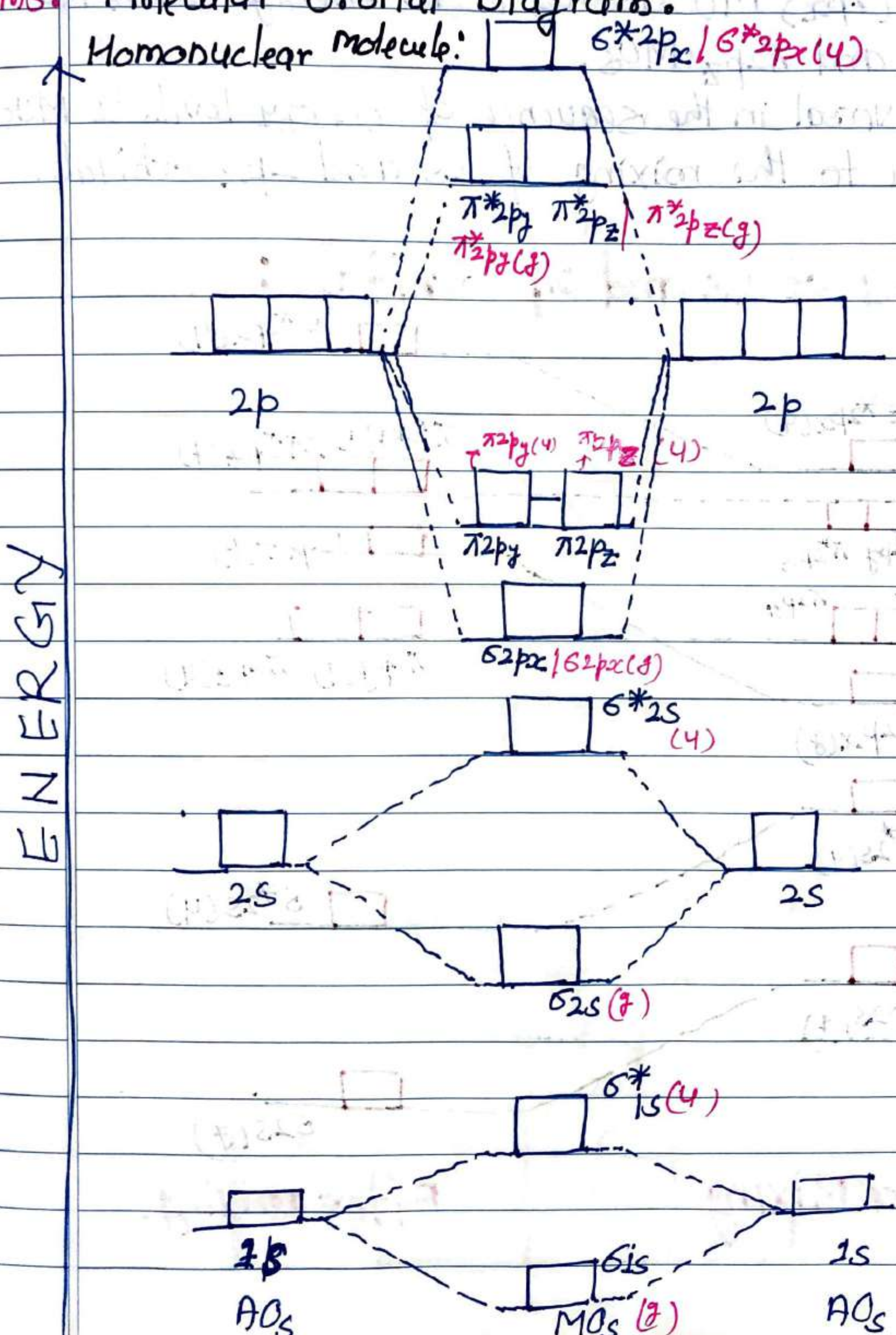
   $\lambda = -l$ to $+l$

λ → 0 σ-orbitals
→ ±1 π-orbitals
→ ±2 δ-orbitals.

4. The spin quantum is the same as for atomic orbitals and may have values of ±½.

The Energies of MOs obtained by the overlap of 1s, 2s and 3, 2p Orbitals of two Atoms: Molecular Orbital Diagram:

Homonuclear molecule:

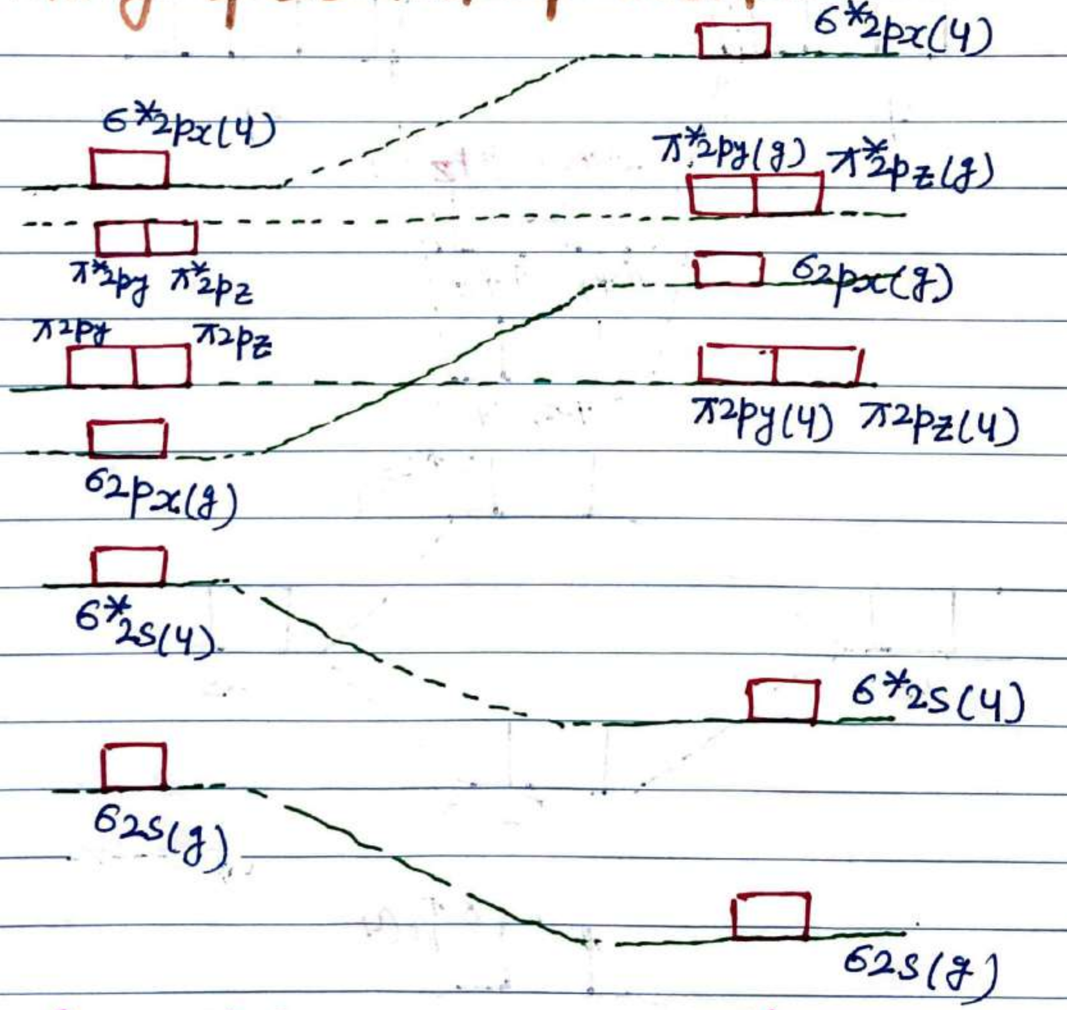


Spectroscopic studies have revealed that the above sequence of energy levels of MOs are not correct for all molecules.

It has been observed that in case of homonuclear diatomic molecules of second row elements of the periodic table upto $N_2$ (viz. $Li_2$, $Be_2$, $B_2$, $C_2$, $N_2$) the $\sigma(2p_x)$ MO is higher in energy than the $\pi 2p_y$ and $\pi 2p_z$ MOs.

The reversal in the sequence of energy levels of MOs is due to the mixing of 2s and $2p_x$ orbitals.

## Mixing of 2s and 2p orbitals :




Before Mixing　　　　After mixing

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We know that $\sigma_{2s}$ and $\sigma^*_{2s}$ MOs are formed by the combination of 2s AOs of two atoms while $\sigma_{2p_x}$ and $\sigma^*_{2p_x}$ MOs are formed by the combination of $2p_x$ AOs of the two atoms.

However, if the energy differences between 2s and 2p AOs are small, there is a possibility of mixing of MOs of $\sigma_{2s}$ and $\sigma_{2p_x}$ as they are of the same symmetry and $\sigma^*_{2s}$ and $\sigma^*_{2p_x}$ as they are also of the same symmetry with the result that the $\sigma_{2s}$ and $\sigma^*_{2s}$ MOs do not retain the pure s character and the $\sigma_{2p_x}$ and $\sigma^*_{2p_x}$ MOs do not retain the pure p-character. Infact all the four MOs acquire a mixed character. Due to this s-p mixing, the energies of all the four orbitals change in such a way that the resulting MOs $\sigma_{2s}$ and $\sigma^*_{2s}$ which also contain some p character, become more stable and are thus lowered in energy whereas the MOs $\sigma_{2p_x}$ and $\sigma^*_{2p_x}$ which contain some s character also now become less stable and are thus raised in energy.

→ Since $\pi_{2p}$ orbitals are not involved in mixing the energies of $\pi_{2p_y}$ and $\pi_{2p_z}$ MOs remain unchanged.

Q. How is it that the mixing of $\sigma_{2s}$ and $\sigma_{2p_x}$ and $\sigma^*_{2s}$ and $\sigma^*_{2p_x}$ occurs in case of second row elements upto nitrogen and not in case of oxygen and fluorine?

Difference in the energies of 2s and $2p_x$ AOs of II$^{nd}$ row elements.

| Atoms | Li | Be | B | C | N | O | F |
|---|---|---|---|---|---|---|---|
| $(\Delta E_{2p-2s})$ $kJ\,mol^{-1}$ | 178 | 262 | 449 | 510 | 570 | 1430 | 1970 |

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## Rules for Filling Electrons in MOs:

1. The MO with lowerst energy is filled first.
2. The maximum number of electrons in a molecular orbital cannot exceed two and the two electrons must be of opposite spin
3. If there are two or more MOs at the same energy level, pairing of electrons will occur only after each orbital of the same energy has one electron.

## Bond Order:

No. of covalent bond present in a molecule is called as B.O.

$$B.O. = \frac{\text{No. of } \bar{e}\text{ns in BMOs} - \text{No. of } \bar{e}\text{ns in ABMO}}{2}$$

## Energy levels Order of MOs for $Li_2$, $Be_2$, $B_2$, $C_2$ and $N_2$:

$\sigma_{1s} > \sigma^*_{1s} > \sigma_{2s} > \sigma^*_{2s} > \pi_{2p_y} = \pi_{2p_z} > \sigma_{2p_x} > \pi^*_{2p_y} = \pi^*_{2p_z} > \sigma^*_{2p_x}$

Energy order →

## Energy levels Order of MOs for heavier elements beyond nitrogen:

$\sigma_{1s} > \sigma^*_{1s} > \sigma_{2s}, \sigma^*_{2s} > \sigma_{2p_x} > \frac{\pi_{2p_y}}{\pi_{2p_z}} > \frac{\pi^*_{2p_y}}{\pi^*_{2p_z}} > \sigma^*_{2p_x}$

Energy order →

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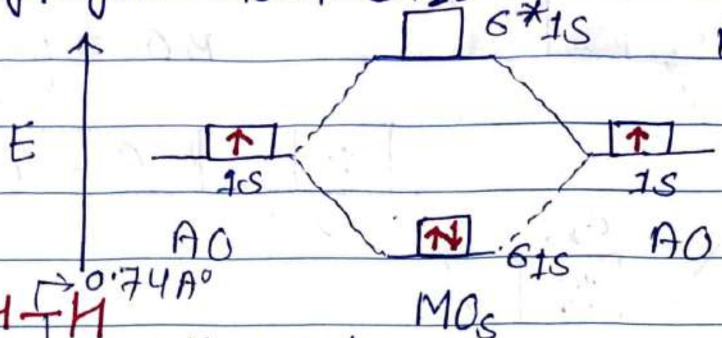
Hydrogen Molecule ($H_2$):




$B.O = \frac{2-0}{2}$

$B.O. = 1$

$H_2$ molecule

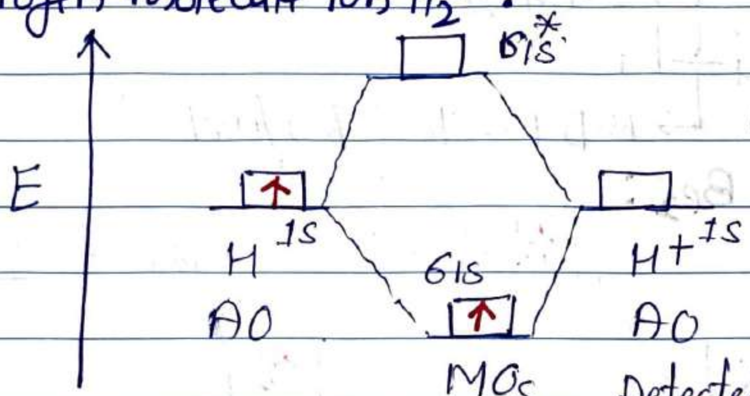
H—H

diamagnetic.

H—H → 0.74 A°

→ B.D.E = 458 kJ mol⁻¹

Hydrogen molecule ion $H_2^+$ :




$B.O = \frac{1-0}{2}$

$B.O = 1/2$

No real existence.

Detected spectroscopically when an electric discharge is passed through hydrogen gas under reduced pressure.

$H_2^+$

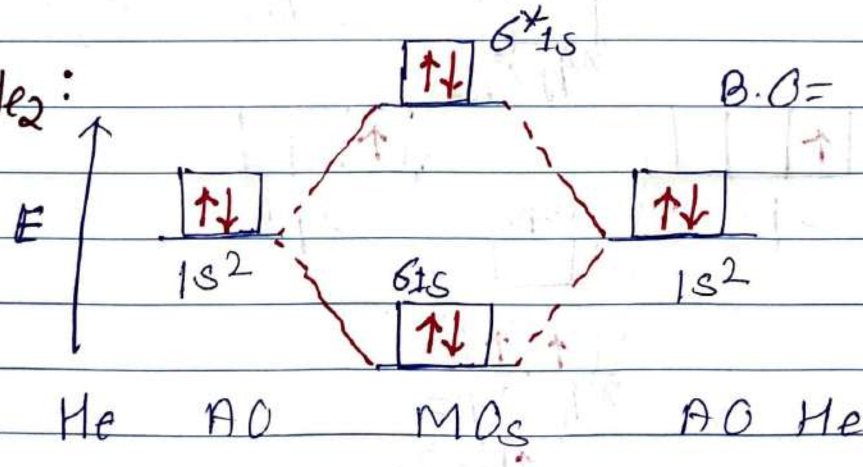
~~$H-H^+$~~

$B.O = \frac{1}{2}$

$B.D.E = 255$ kJ mol⁻¹

$B.L. = 1.06$ A°

$He_2$ :




$B.O = \frac{2-2}{2} = 0$

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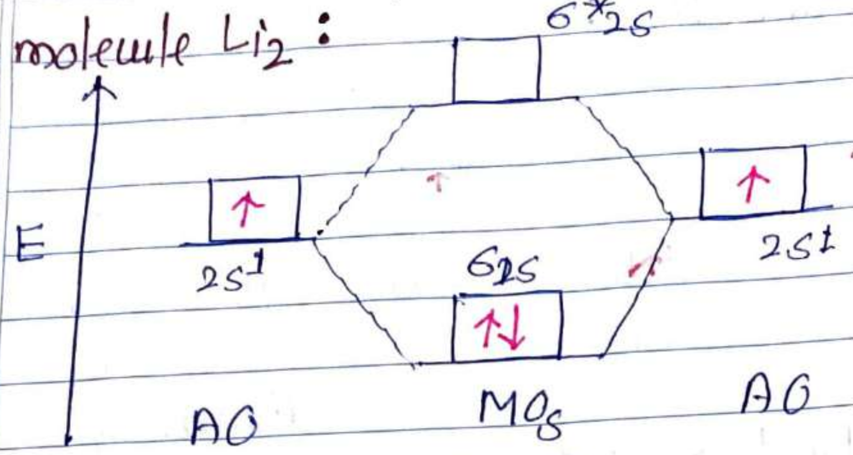
Lithium molecule $Li_2$ : $1s^2 2s^1$

$B.O. = \left(\frac{2-0}{2}\right)$

**B.O. = 1**

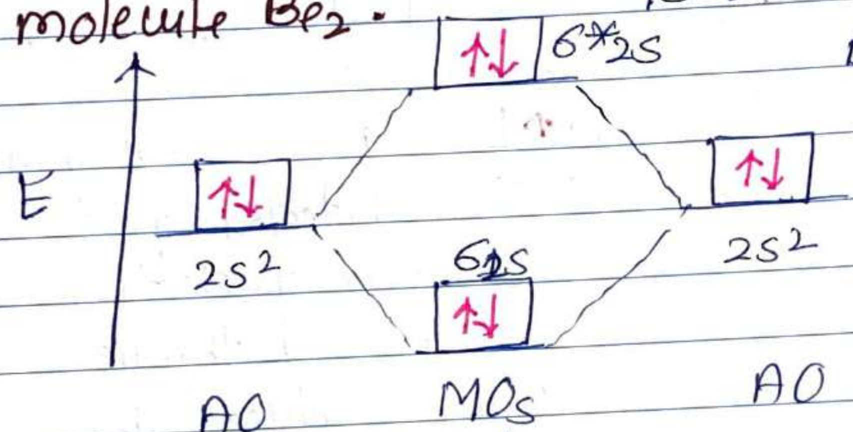



Li—Li → 2.67 A°

→ B.D.E. = 105 kJ/mol

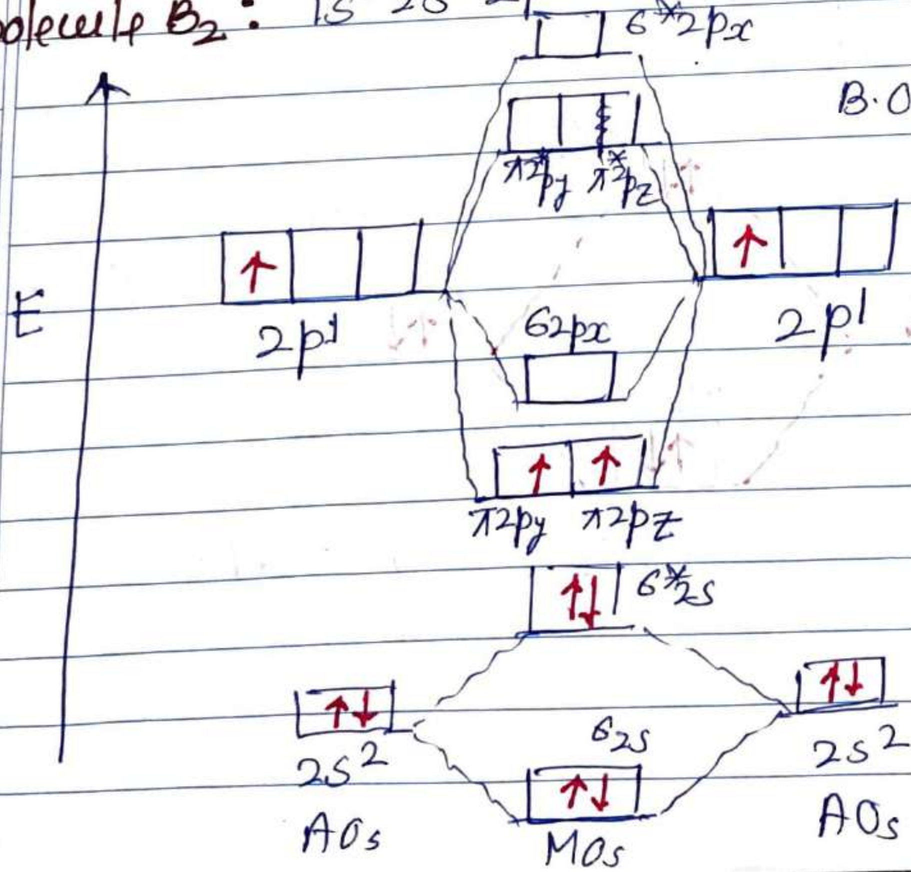
Beryllium molecule $Be_2$ : $1s^2 2s^2$

$B.O. = \frac{2-2}{2} = 0$




Boron molecule $B_2$ : $1s^2 2s^2 2p^1$

$B.O = \frac{4-2}{2} = 1$



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for $C_2$ molecule $1s^2 2s^2 2p^2$

$\sigma 1s^2 \; \sigma^* 1s^2 \; \sigma 2s^2 \; \sigma^* 2s^2 \; \pi 2p_y^2 \; \pi 2p_z^2 \; \sigma 2p_x^0$

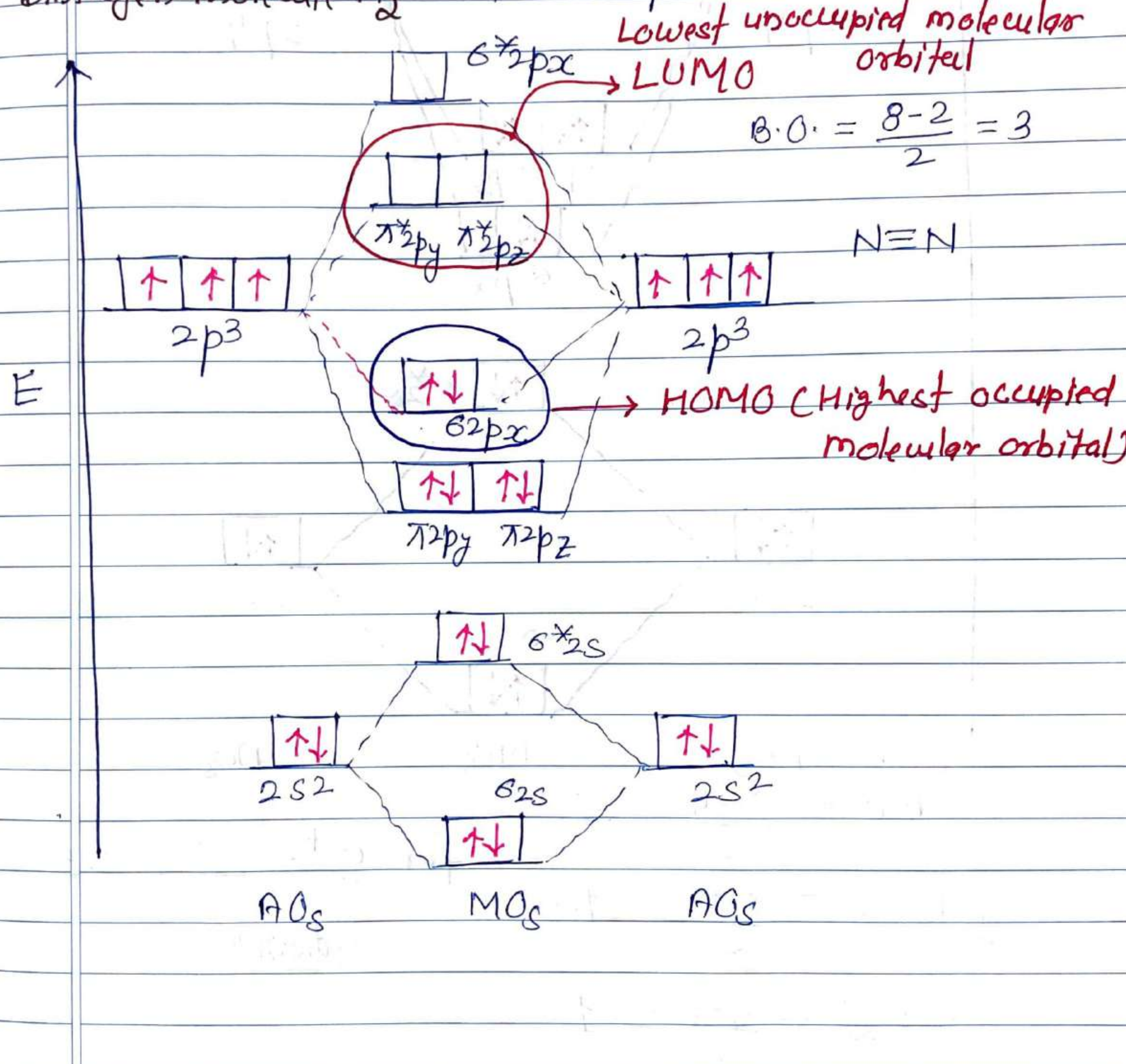
$$B.O = \frac{8-4}{2} = \frac{4}{2} = 2$$

C=C

→ B.L. = 1.31 A°

→ B.D.E = 628 kJ/mol

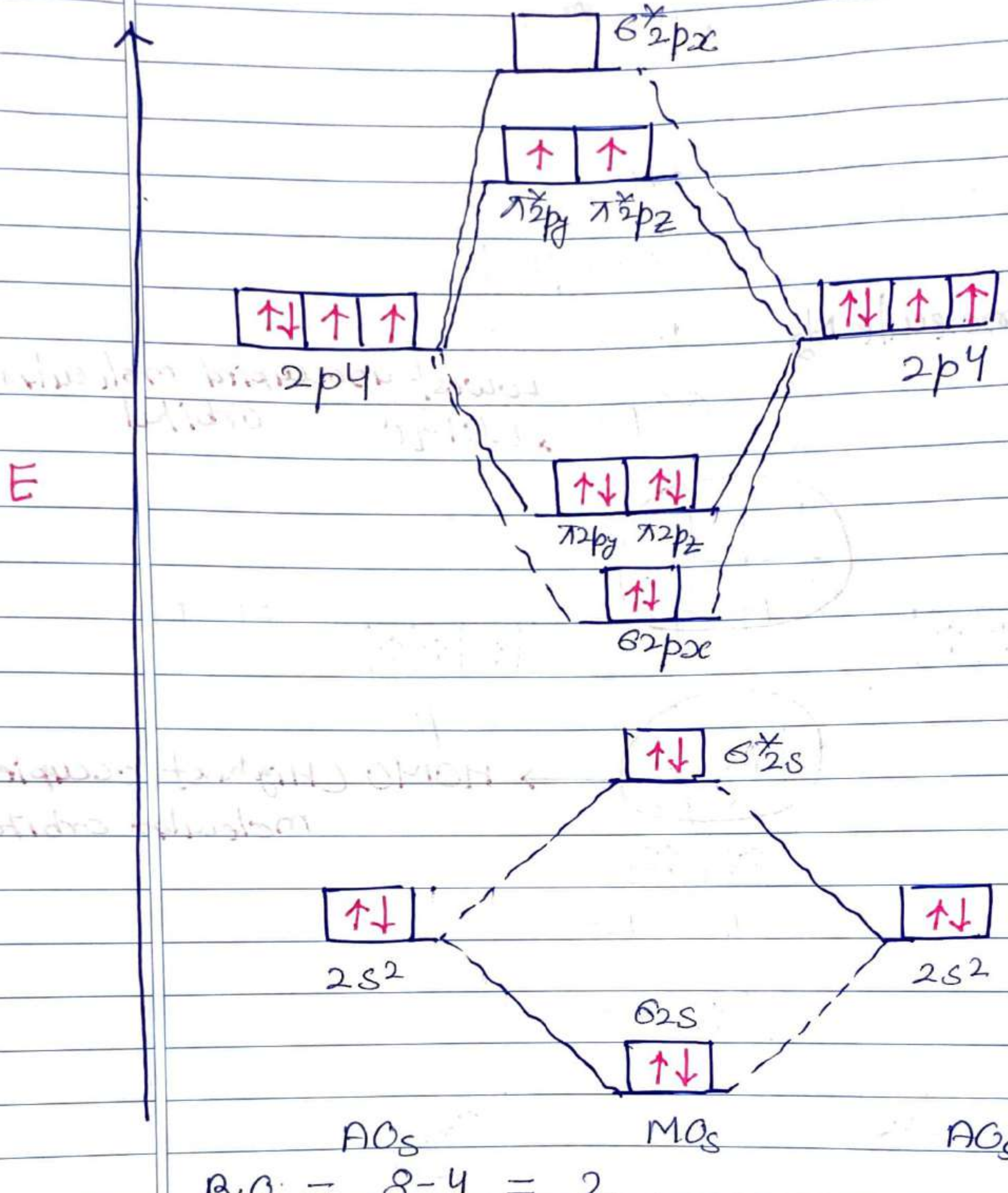
Dinitrogen molecule $N_2$ $1s^2 2s^2 2p^3$




$$B.O. = \frac{8-2}{2} = 3$$

N≡N

Oxygen molecule $O_2$ O $1s^2 2s^2 2p^4$




$B.O = \frac{8-4}{2} = 2$

for $O_2^+ = \frac{8-3}{2} = 2.5$ ↳ dioxygenyl

for $O_2^- = \frac{8-5}{2} = 1.5$ superoxide

for $O_2^{2-} = \frac{8-6}{2} = 1$ ↳ peroxide

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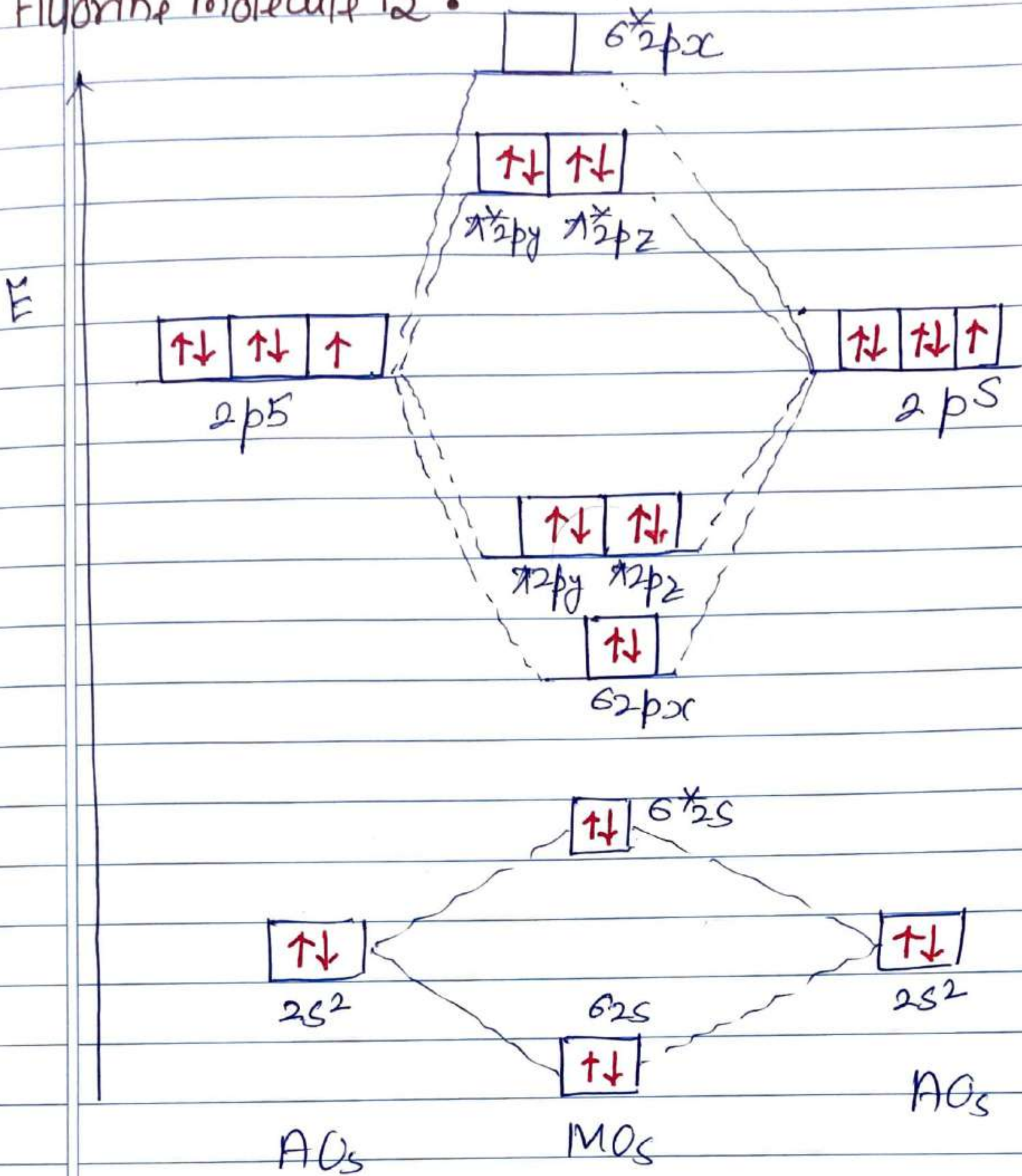
Fluorine molecule $F_2$ : $1s^2 2s^2 2p^5$




$$B.O. = \frac{8-6}{2} = 1$$