Molecular Orbital Treatment for Homonuclear Diatomic Molecules

(1) Hydrogen molecule, H_2: Hydrogen molecule is formed from $1s^1$ atomic orbitals of two atoms. They give rise to two molecular orbitals σ(1s) and σ*(1s). Both these electron will be in σ(1s) bonding molecular orbital, but with opposite spin. The antibonding molecular orbital remains vacant. The electronic configuration of the molecule is $\sigma(1s^2)\ \sigma^*(1s^0)$.

$$\text{Bond order} = \frac{1}{2}[N_b - N_a] = \frac{[2-0]}{2} = 1.0$$

Since its B.O. is 1.0, so it **exists** and is **stable.**

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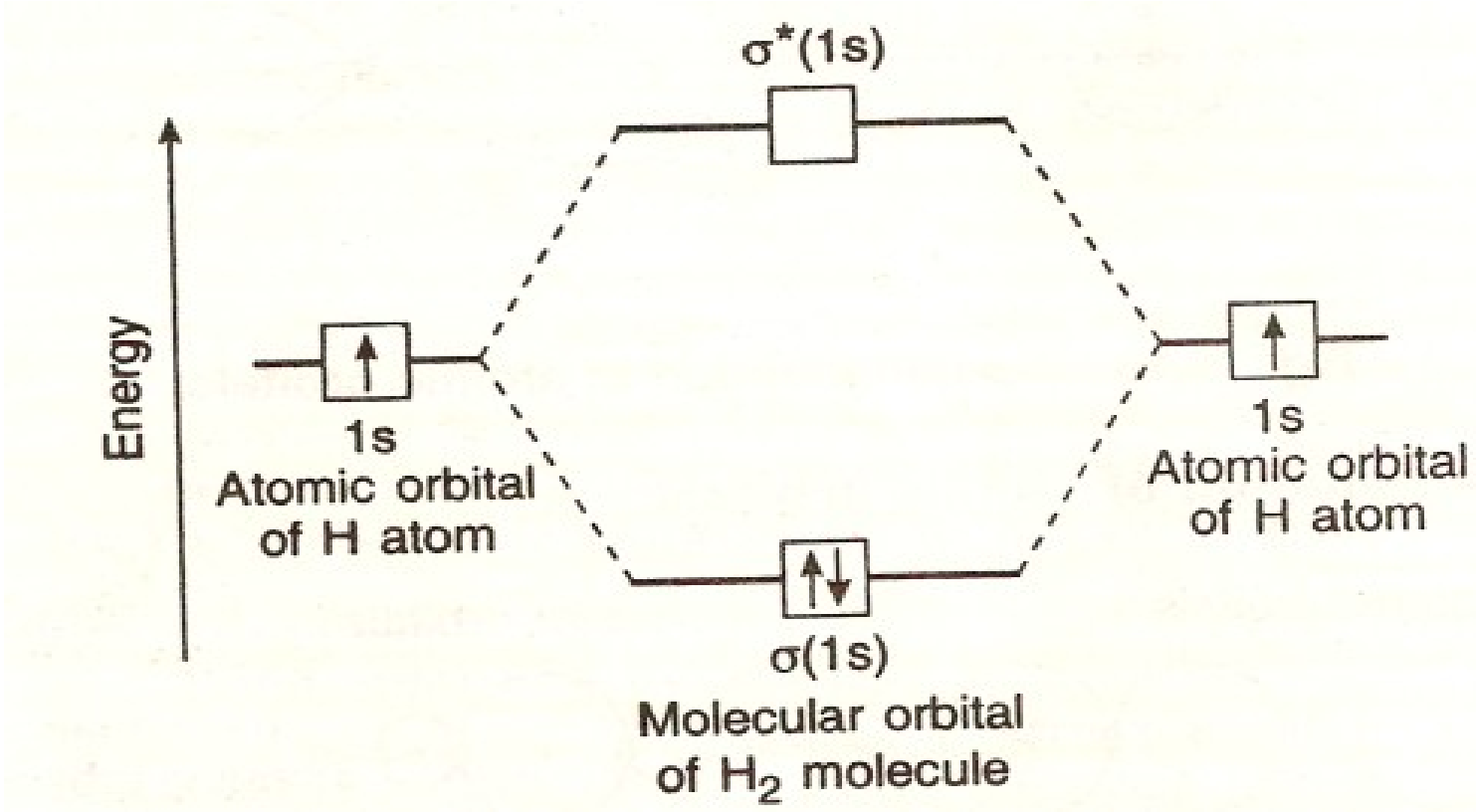
MO Diagram of H2 Molecule:



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(2) Lithium molecule Li_2: Lithium molecule is formed by the overlap between two lithium atoms each having the electronic configuration $1s^2 2s^1$. So, we have total of six electrons which have to be accomodated in 4 molecular orbitals, viz., σ1s, σ*1s, σ2s and σ*2s.

Hence, molecular orbital electronic configuration of Li_2 molecule

$$= \sigma 1s^2\ \sigma^* 1s^2\ \sigma 2s^2 = KK\ \sigma 2s^2$$

Since, the inner shell of filled σ1s and σ *1s molecular orbitals do not contribute to the bonding and is sometimes written as KK which means K-shell is completely filled.

Bond order = 1/2 (Nb - Na) = 1/2 (4 - 2) = 1/2 (2 - 0) = 1

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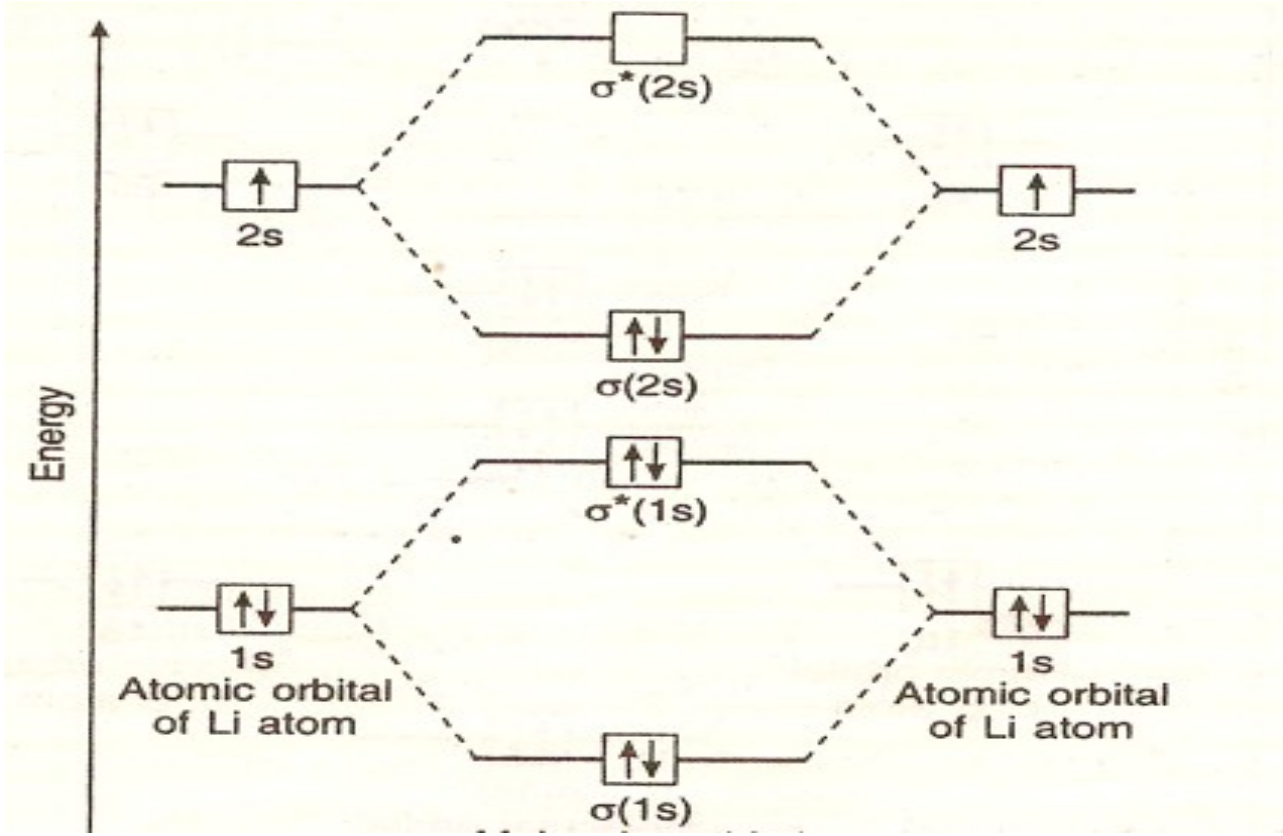

Molecular Orbital Treatment for Homonuclear Diatomic Molecules

(3) Nitrogen Molecule, N_2 : A Nitrogen atom has 2+5=7 electrons. Thus, the N_2 molecule contains 14 electrons. These are arranged as

$$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \begin{cases} \pi\, 2p_y^2 \\ \pi\, 2p_z^2 \end{cases}, \sigma 2p_x^2 .$$

There are eight and two electrons in the bonding molecular orbital respectively.

Bond order of N_2 = ½ (8-2) =3

The N2 molecule is diamagnetic as it has no unpaired electron.

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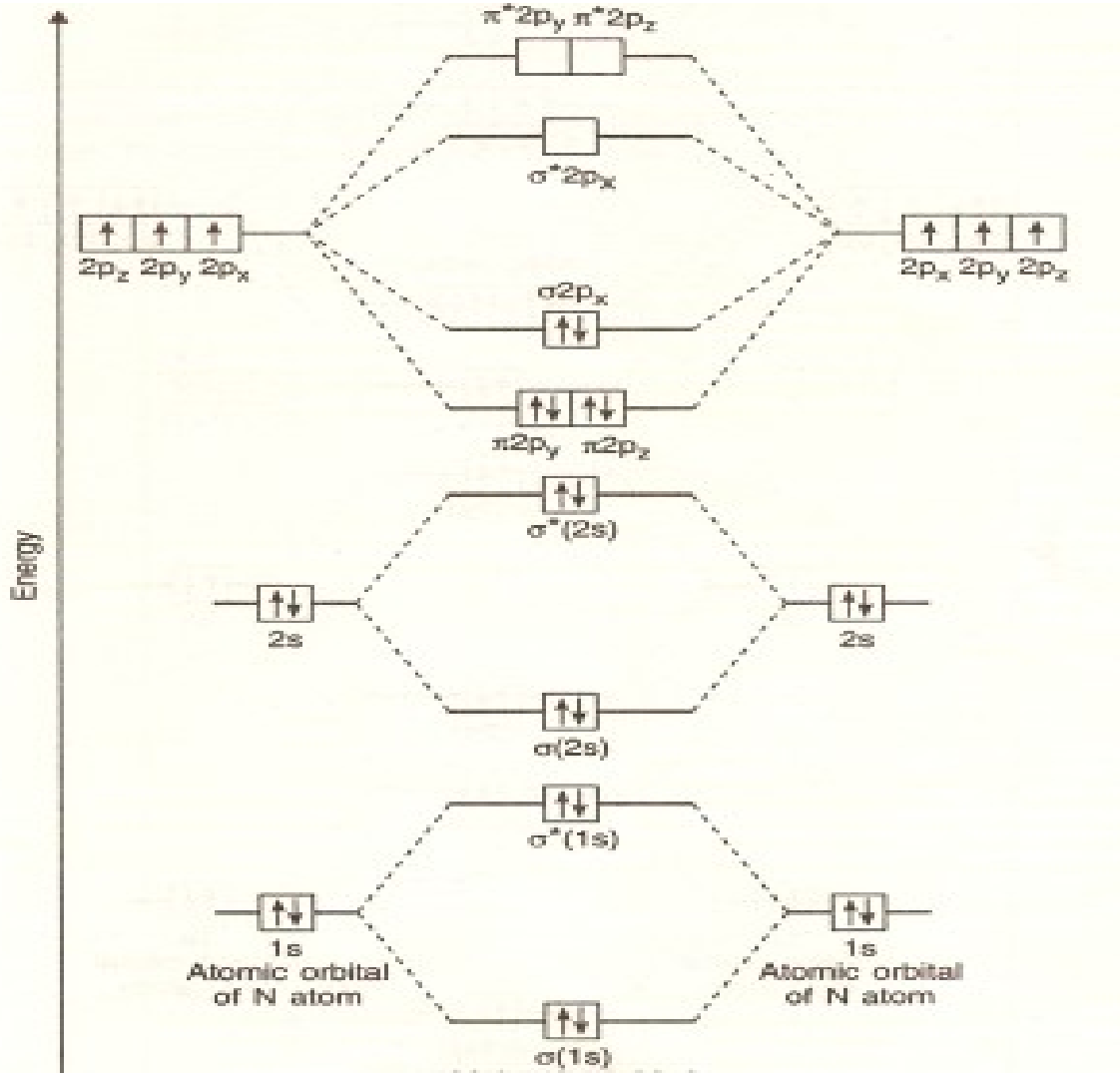

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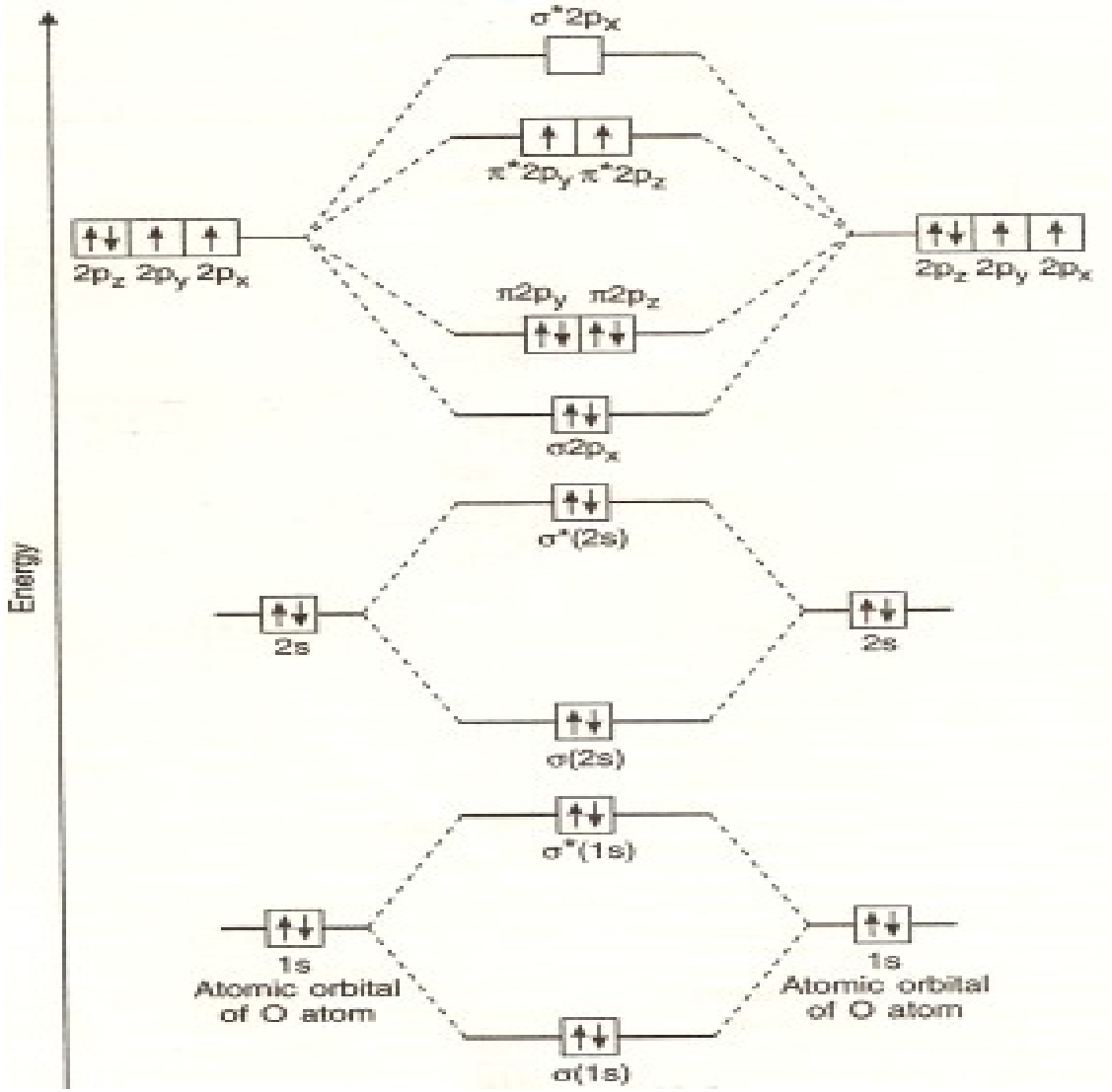
The presence of unpaired electrons in π^*2p_y and π^*2p_z give rise to paramagnetism.

B.O. of O2 = ½ (8-4) = 2

Molecular Orbital Treatment for Homonuclear Diatomic Molecules



Molecular Orbital Treatment for Homonuclear Diatomic Molecules

The electronic configuration, bond order and magenatic character of O_2^-, O_2^+ and O_2^{2-}

Species	Electronic configuration	Bond order	Magnetic behaviour
O_2^+	$kk\ \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_x^2 \left[\pi 2p_y^2, \pi 2p_z^2\right] \left[\pi^* 2p_y^1, \pi^* 2p_z^0\right]$	$\frac{(8-3)}{2} = 2.5$	Paramagnetic
O_2^-	$kk\sigma 2s^2 \sigma^* 2s^2 \sigma 2p_x^2 \left[\pi 2p_y^2, \pi 2p_z^2\right] \left[\pi^* 2p_y^2, \pi^* 2p_z^1\right]$	$\frac{(8-5)}{2} = 1.5$	Paramagnetic
O_2^{2-}	$kk\sigma 2s^2 \sigma^* 2s^2 \sigma 2p_x^2 \left[\pi 2p_y^2, \pi 2p_z^2\right] \left[\pi^* 2p_y^2, \pi^* 2p_z^2\right]$	$\frac{(8-6)}{2} = 1$	Diamagnetic

Molecular Orbital Treatment For Heteronuclear Diatomic Molecules

(1) <u>Nitric oxide molecule, NO:</u> The nitrogen atom has 2 + 5 = 7 electrons and the oxygen atom has 2 + 6 = 8 electrons, making 15 electrons in the molecule. The order of energy levels of the various MO's are the same as for homonuclear diatomic molecules heavier than C_2.

The arrangement is :

$$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2, \begin{cases} \pi 2p_y^2 \\ \pi 2p_z^2 \end{cases}, \begin{cases} \pi^* 2p_y^1 \\ \pi^* 2p_z^0 \end{cases}$$

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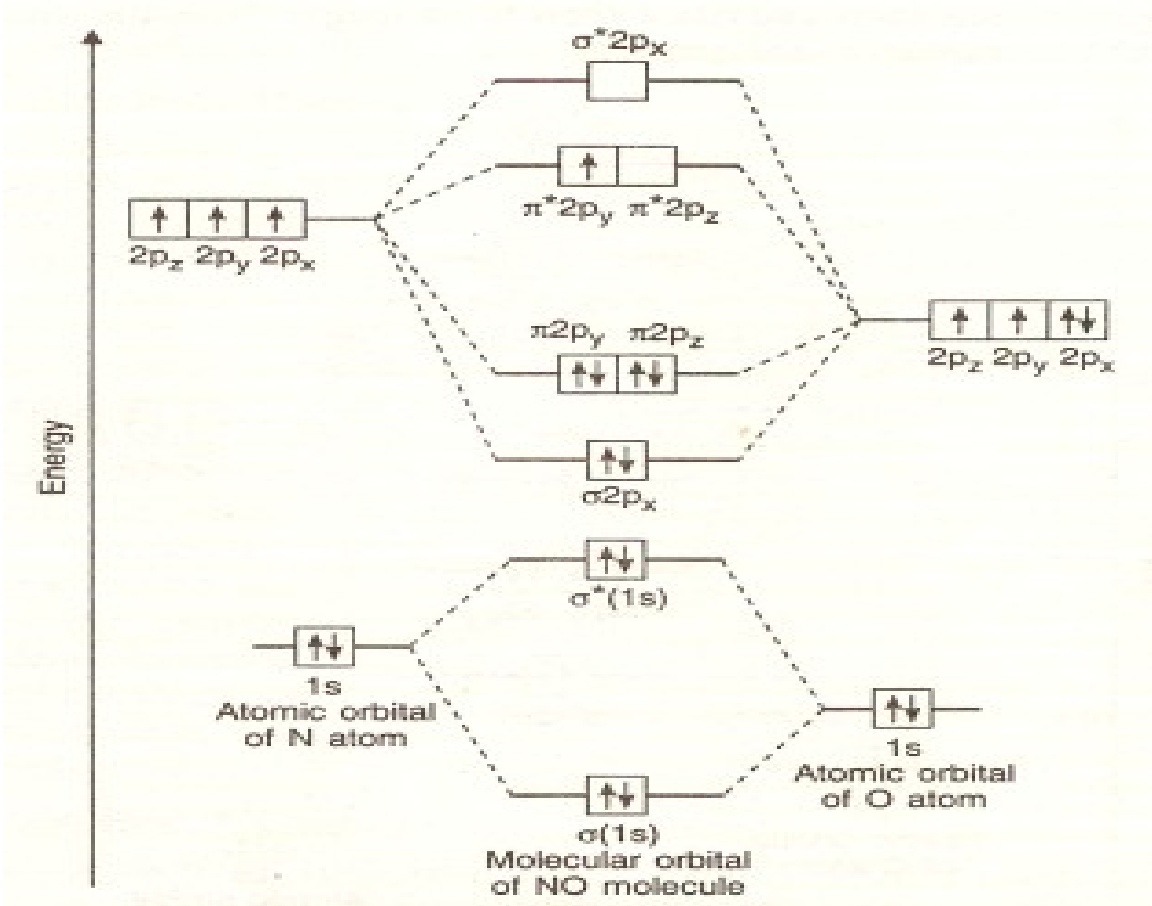
Molecular Orbital Treatment For Heteronuclear Diatomic Molecules

The molecule is **paramagnetic,** since it contain an unpaired electron in π*2py or π*2pz orbital.



Molecular Orbital Treatment For Heteronuclear Diatomic Molecules

(2) <u>NO+ and NO- Ions:</u> The electronic configuration, bond order and magnetic character of these ions are :

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NO^+	$kk\ \sigma(2s^2), \sigma^*2s^2\sigma(2p_x)^2, \begin{cases}\pi 2p_y^2 \\ \pi 2p_z^2\end{cases}$	$\frac{8-2}{2}=3$	Diamagnetic
NO^-	$kk\ \sigma(2s^2)\sigma^*2s^2, \sigma(2p_x)^2 \begin{cases}\pi(2p_y)^2 \\ \pi(2p_z)^2,\end{cases} \begin{cases}\pi^*(2p_y)^1 \\ \pi^*(2p_z)^1\end{cases}$	$\frac{(8-4)}{2}=2$	Paramagnetic

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(3) <u>Carbon monoxide molecule, CO:</u> The carbon atom has 2 + 4 = 6 electrons and the O atom has 2 + 6 = 8 electrons, so the CO molecule contains 14 electrons. The order is the same as for light atoms like C.

$$\sigma 1s^2, \sigma^* 2s^2, \sigma 2s^2, \sigma^* 2s^2, \overline{\begin{cases} \pi 2p_y^2 \\ \pi 2p_z^2 \end{cases}}, \sigma 2p_x^2$$

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Hence Molecule exists with a triple bond.

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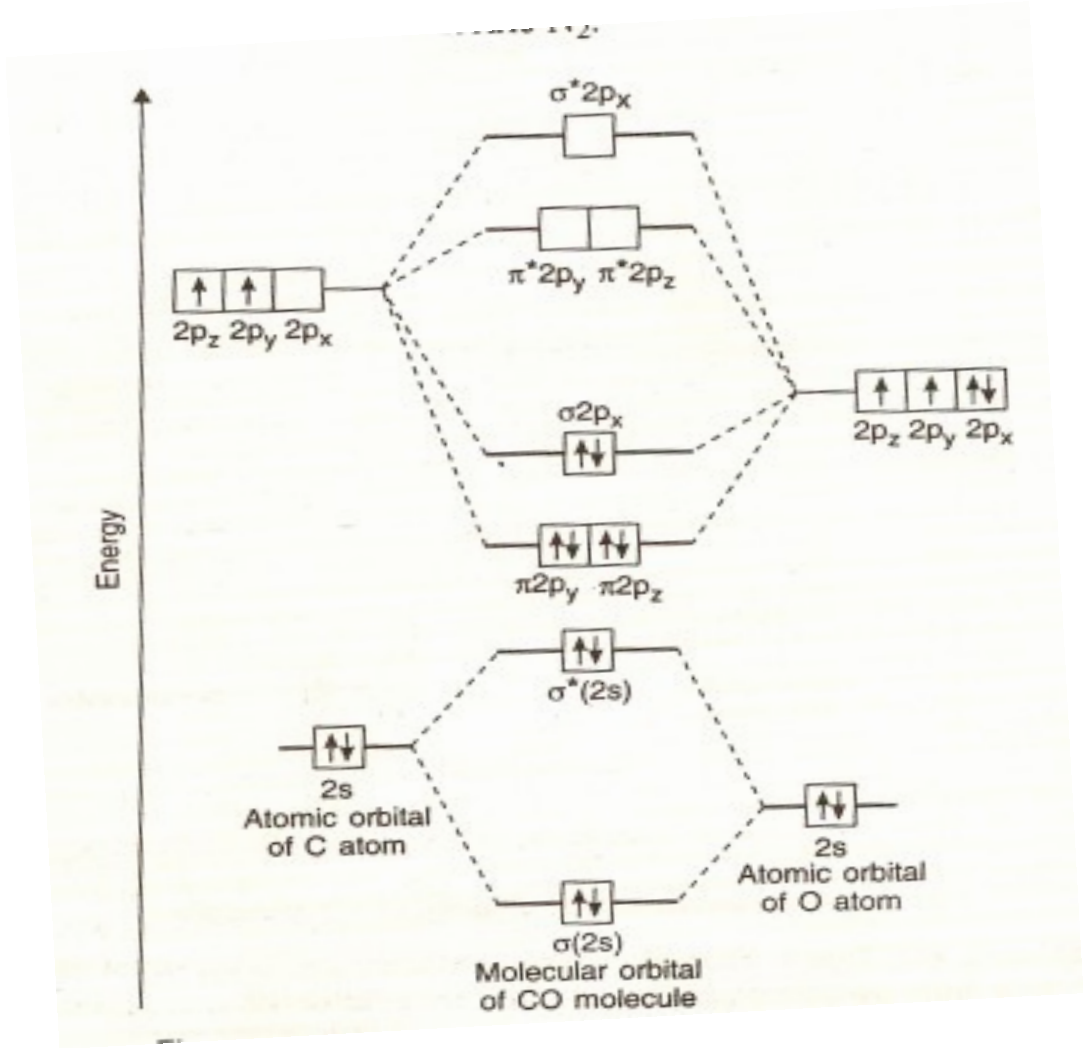

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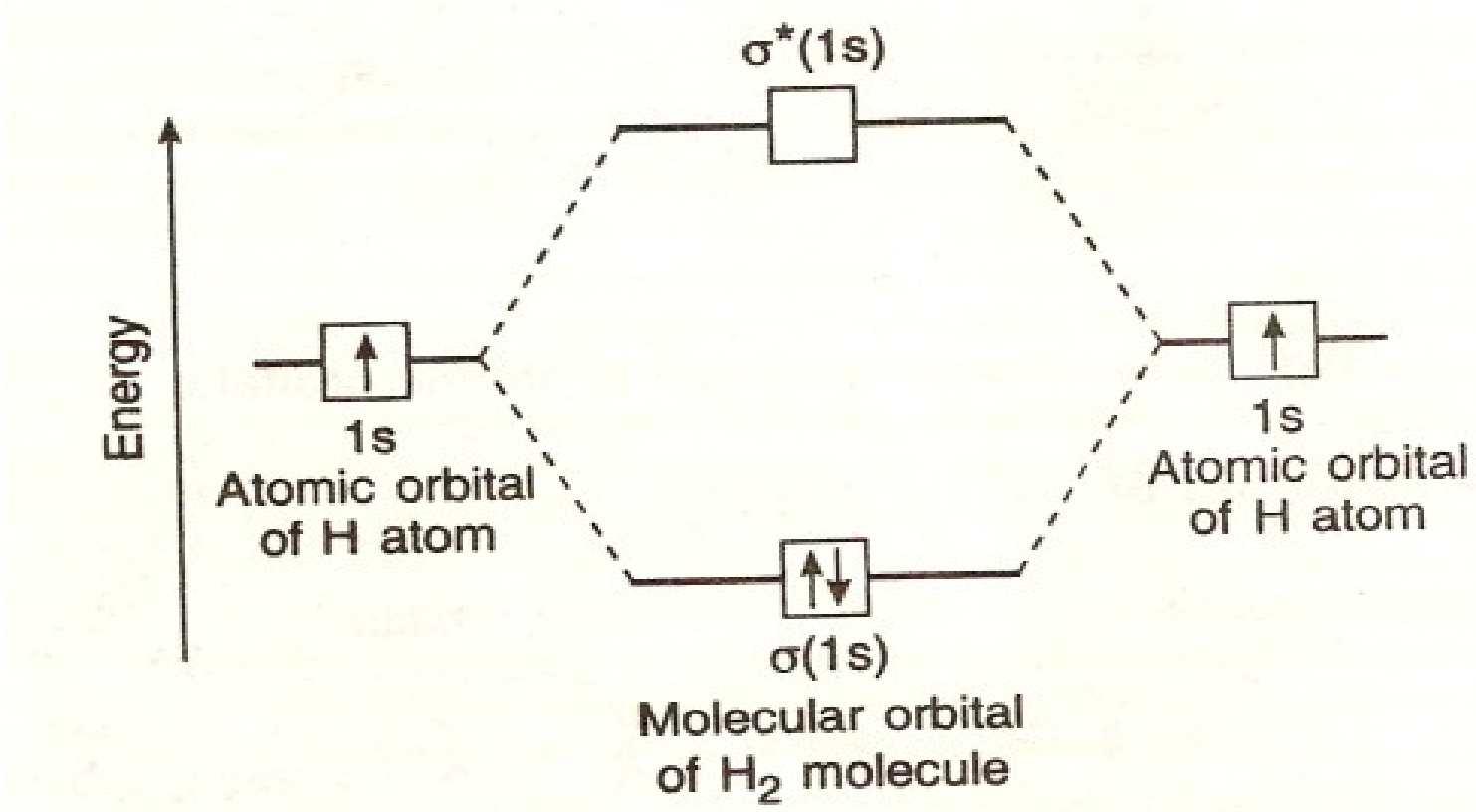

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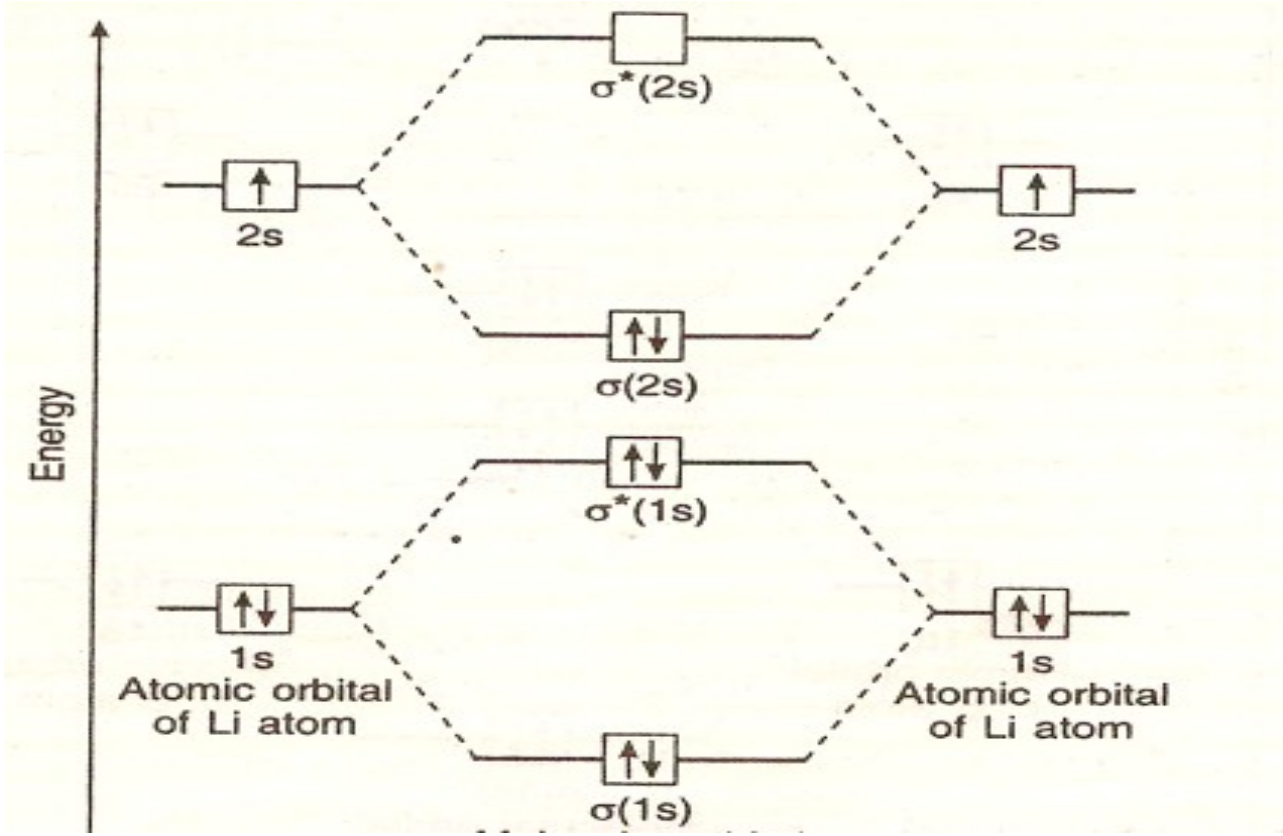

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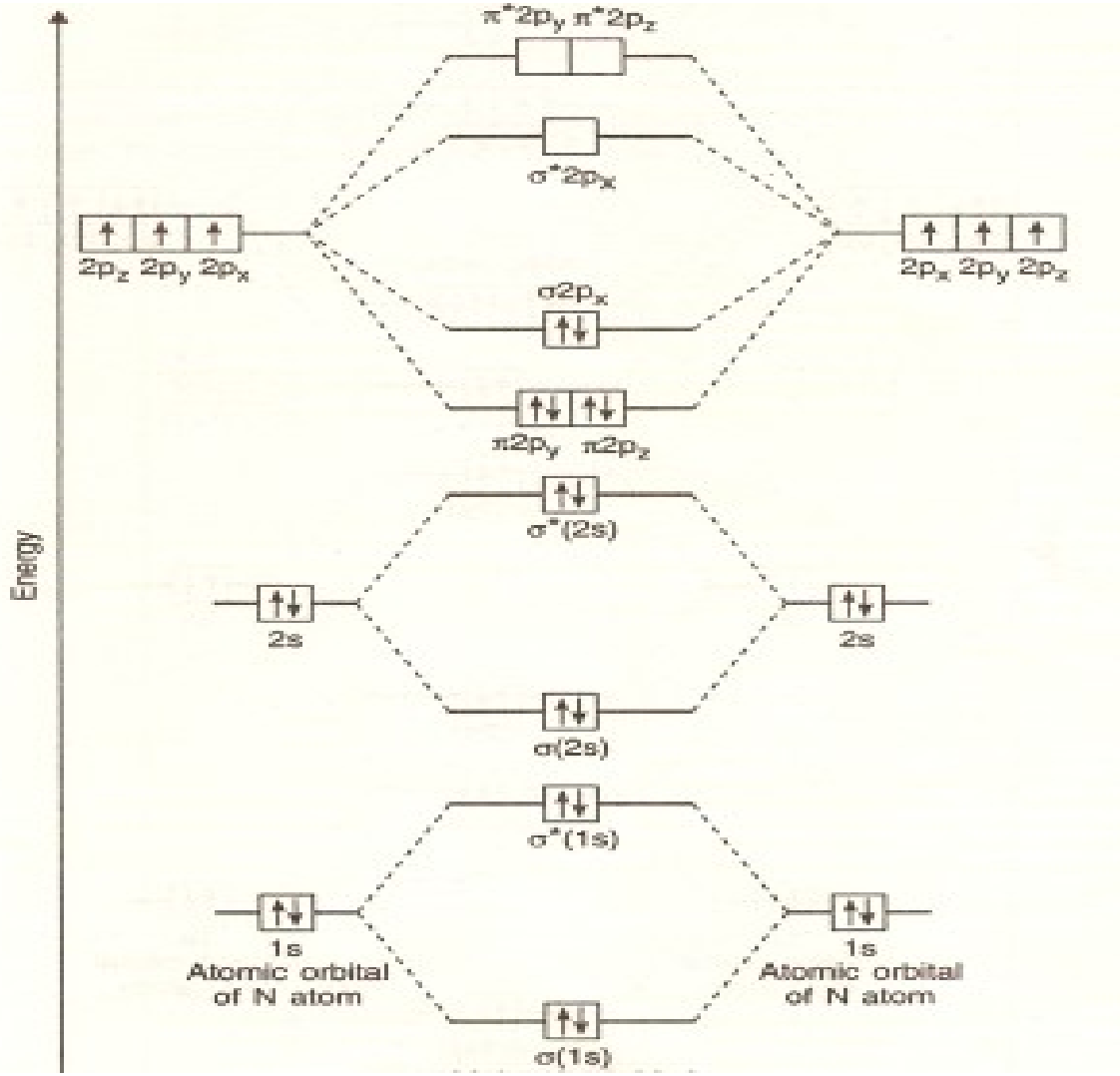

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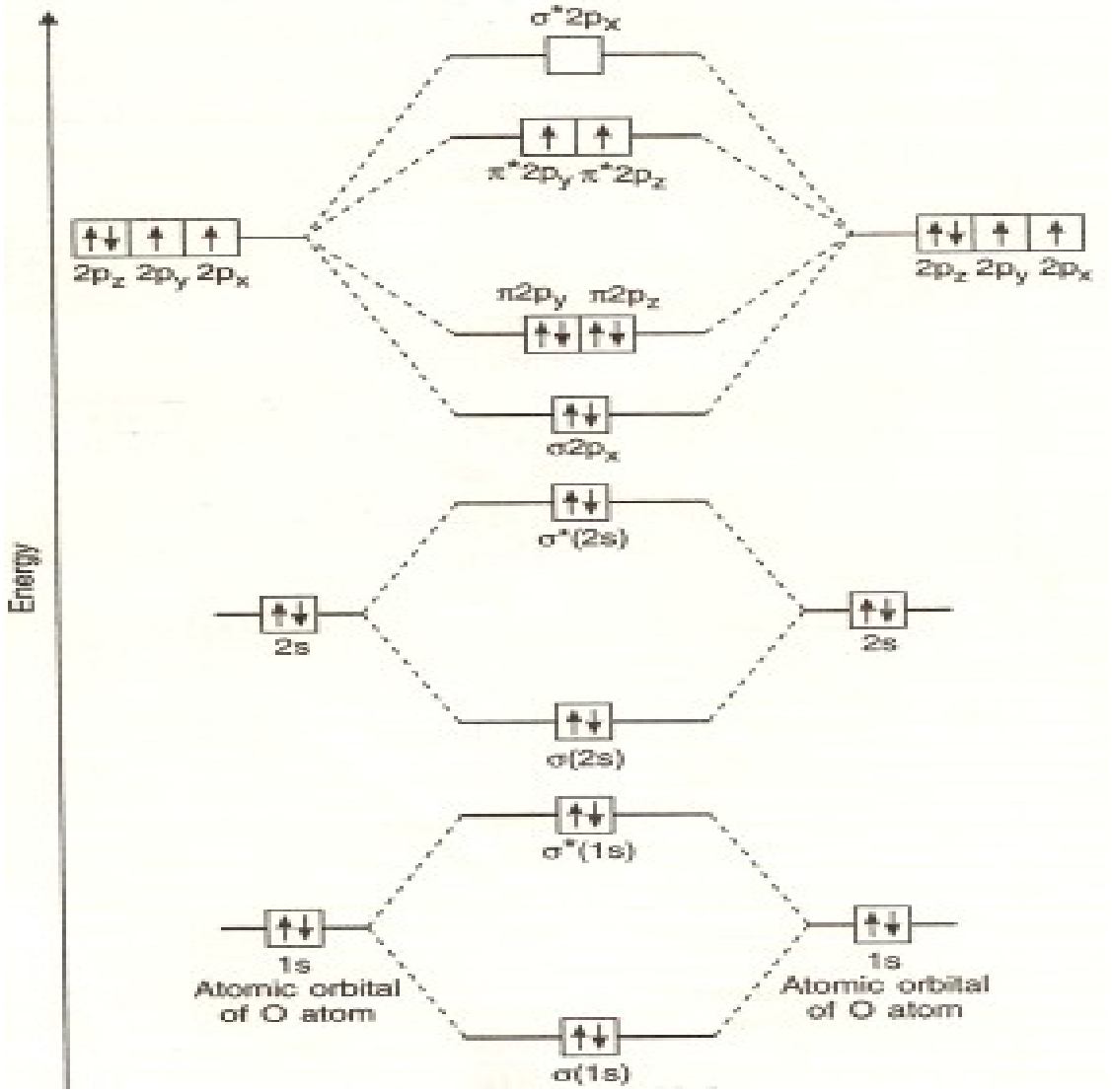

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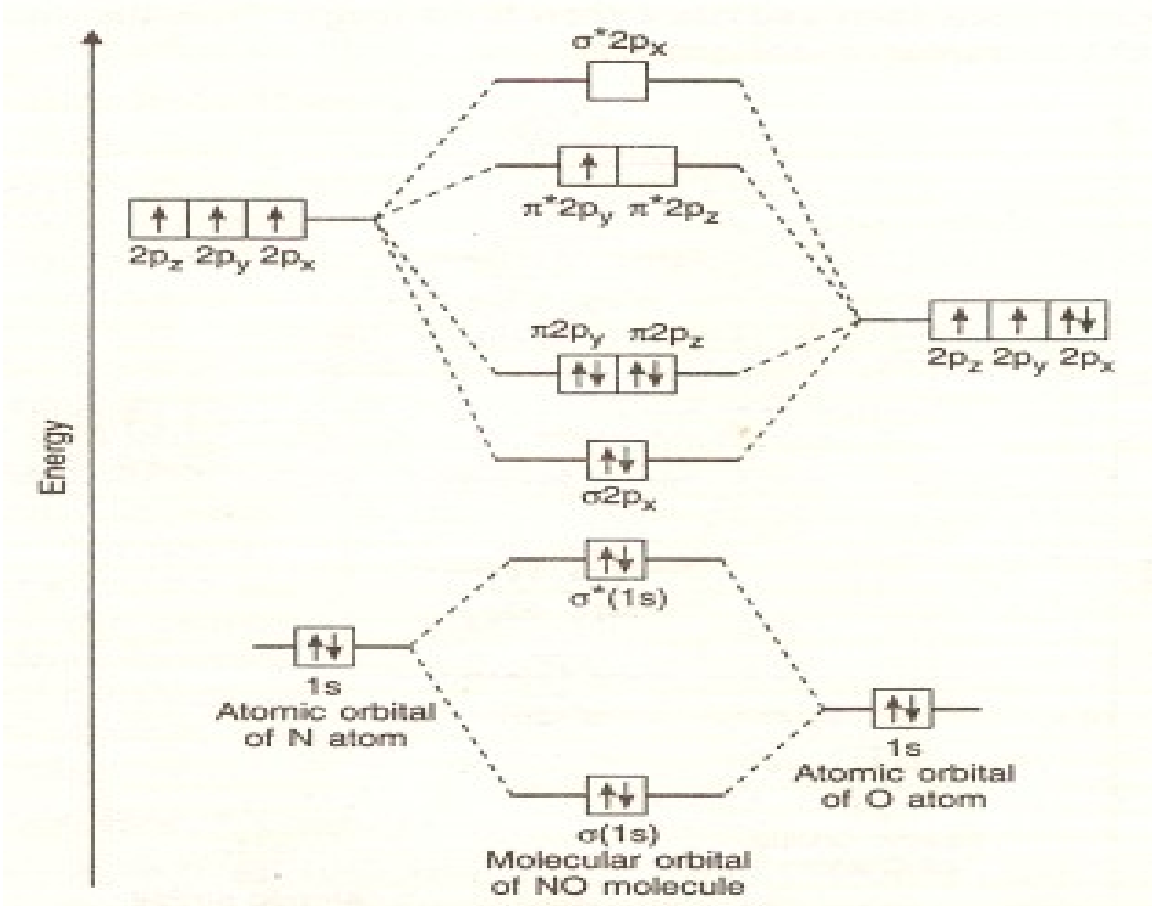

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