Exercise

MULTIPLE TYPE QUESTIONS

1. **Choose the correct option (MCQ).**

i. **The bond energies of F_2, Cl_2, Br_2, and I_2 are 37, 58, 46 and 36kcal respectively. The strongest bond formed is in**

(a)F_2 (b) Cl_2 (c) I_2 (d) Br_2

ii. **The percentage of ionic character of bond between two atoms is calculated from the difference between their**

(a) Ionic (b) Electronegativity (c) Electron affinity (d) ionization energy

iii. **The geometry of PF_5 molecule is**

(a)Planar (b) Square planar (c)Trigonal bipyramidal (d)Tetrahedral

iv. **Sp^3 Hybridization is important in describing the bonding in**

(a)NH_4^+ (b) CCl_4 (c)H_3O^+ (d)AgCl

v. **Greater the dipole moment**

(a)Greater the ionic character (b)Lesser is the polarity

(c)Smaller is the ionic character (d)None

vi. **H-O-H bond in water is 104^0 and not 109.28^0 because of**

(a)High electronegativity of oxygen (b)Bond pair-Bond pair repulsion

(c)Lone pair-lone pair repulsion (d)Lone pair-Bond pair repulsion

vii. **A diatomic molecule has a dipole moment of 1.2D. If its bound distance is 1.0A°. What fraction of electric charge 'e' exist on each atom?**

(a)12% of e (b)18% of e (c)25% of e (d)30% of e

viii. **What is the characteristic of π bond?**

(a)π bond is formed when a sigma bond already exist

(b)π bond is formed from hybrid sp orbitals

(c)π bond is formed by the overlapping of p and/or d orbitals

(d)π bond is formed from lateral overlapping of atomic orbitals

ix. **In the formation of N_2^+ from N_2, the electron is removed from**

(a)σ_{px} orbital (b) σ°_{px} orbital (c) π_{2p} orbital (d) π_{2p} orbital

x. **According to VSEPR theory the most probable shape of the molecule having 4 electron pairs around the central atom is**

(a)Hexagonal (b) Tetragonal (c)Octahedral (d) Linear

<u>Answers</u>

(i)b	**(ii)b**	**(iii)c**	**(iv)b**	**(v)a**
(Vi)d	**(vii)c**	**(viii)b**	**(Ix)a**	**(x)b**

2.

Bond	**Bond energies in kjmol^{-1}**	
X-X	**X=Cl** **242**	**X=I** **151**
H-X (calculated)	**336**	**291**
H-X (observed)	**431**	**299**
Difference	**95**	**08**

(a) Give the reason for the difference in calculates and observed values

(b) Effect of high bond energy on bond length with reason

(c) Ionic character on the basis of bond energies with reason

Ans: (a) Give the reason for the difference in calculates and observed values

The experimentally determined bond energy is significantly greater than the calculated values which means a more stable H-X bond. Electrons are not equally shared between hydrogen and halogen atoms in HX. Since halogen atom is more electronegative, the bonded electron pair is more attracted toward halogen atom; this develop polarity in H-X molecule which produce an additional attractive force. That's why we observe a greater than calculates values.

(b) Effect of high bond energy on bond length with reason

Greater the bond energy lesser will be the bond length and vise versa.

As the electronegativity difference between the bonded atom increases, the strength of additional force increases, this will decrease the bond length, as a result the bond energy increases.

A single bond is longer than a double bond which is longer than the triple bond. The bond energy order is reverse to it.

(c)Ionic character on the basis of bond energies with reason

In HX the electronegativity of X is greater than that of H. so X attracts electrons more towards itself as a result X gets δ^- and H gets δ^+ charge. As a result the ionic character develop between the HX bond. Usually greater the electronegativity difference between two bonded atoms, greater the ionic character and stronger is the bond. Since electronegativity difference in HCl is greater than HI therefore HCl has more ionic character than HI.

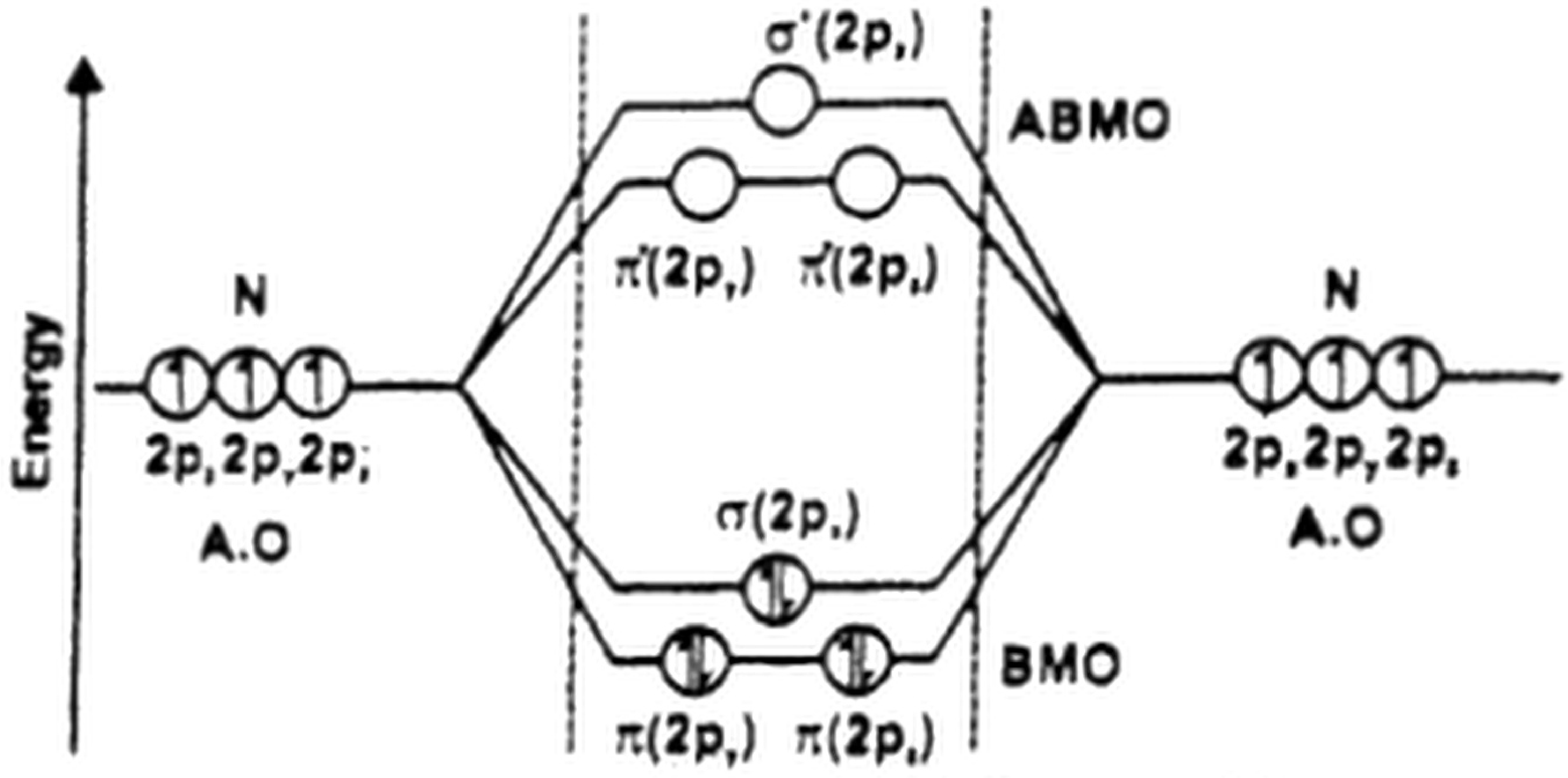
3. Energies of orbitals can be explained by molecular orbital theory. It has been observed that in case of nitrogen molecule $\sigma 2p_x$ is higher in energy than $\pi 2p_y = \pi 2p_z$

(a) Draw energy diagram for nitrogen molecule

(b) Give reason why than $\sigma 2p_x$ is greater than $\pi 2p_y$

Ans:

(a) Draw energy diagram for nitrogen molecule



Molecular orbitals energy level diagram of N_2

(b) Give reason why than $\sigma 2p_x$ is greater than $\pi 2p_y$

In above diagram it is shown that the energy of $\sigma 2p_x$ is higher than 2py = 2pz. This indicates that the σ-bond of nitrogen is more reactive than its π-bond. We have seen in the energy order of $N_2 \sigma_2 p_x$ is higher in energy than $\pi 2p_y = \pi 2p_z$ molecular orbitals. This reversal is due to mixing of 2x and $2p_x$ atomic orbitals

Explanation:

Actually the energy difference of 2s and 2p atomic orbitals is small, there is a possibility of mixing of these orbitals (hybridization of A.O) as a result σ2s and σ^0 2s MO do not retain pure s-character.

Similarly, $\sigma 2p_x$ and $\sigma^0 2p_x$ MO's do not have pure p-character. All the four MO's acquire sp-character. Due to this mixing, their energies change in such a way that MOs σ2s and $\sigma^0$2s become more stable and lower in energy. MOs as σ2p and $\sigma^0$2p become less stable and are raised in energy. Since $\pi 2p_y = \pi 2p_z$ remain unchanged. $\sigma 2p_x$ is raised to such an extent that it become higher in energy than the π-bonds

Examples:

But O_2 and F_2 do not do so. The reason is high energy difference of their 2s and 2p i.e. 1595 kj/mole and 2078kj/mole foro_2 and F_2respectively. The values are 554kj/mole for Br, 846kj/mole for carbon and 1195 kj/mole for N_2 and these energy differences have been calculated by spectroscopic techniques.

Q4. Carbon can make a bond with hydrogen to form ethyne. Bond energy of C-H is same although 2s and 2p orbitals are involved which have difference in energies

(a) Explain the formation of ethyne molecule on the basis of hybridization

(b) Draw a diagram of ethyne molecule

Ans. Hybridization;

Hybridization is the process of mixing of atomic orbitals of different shapes and energies to give the hybrid orbitals of same energy and shape.

2s and 2p orbitals of carbon do not make the bond directly this is because of hybridization theory.

(a) Explain the formation of ethyne molecule on the basis of hybridization

One 2s and one 2p orbitals of carbon atom intermix to give two sp hybrid orbitals. The 2p, and 2p, orbitals remain unhybridized. Each sp hybrid orbitals contains one electron. The two sp hybrid orbitals are directed along a straight line at an angle of 180° between them. The two unhybridized p orbitals which are perpendicular to each other are also perpendicular to the plane of the two sp hybrid orbitals. Thus each carbon atom possesses two sp hybrid orbitals and two pure p-atomic orbitals. Each C-atom undergoes sp-s overlap with one H-atoms and sp-sp overlap with other carbon atom to form two σ-bonds.

The two half-filled P orbitals of two carbon atoms overlap sideways to form two π-bonds. Thus ethyne molecule contains one σ-bond and two π-bonds between two carbon atoms and two carbon-hydrogen σ-bonds. The electronic clouds of two π-bonds merge into each other to form cylindrical shaped π-electron cloud.

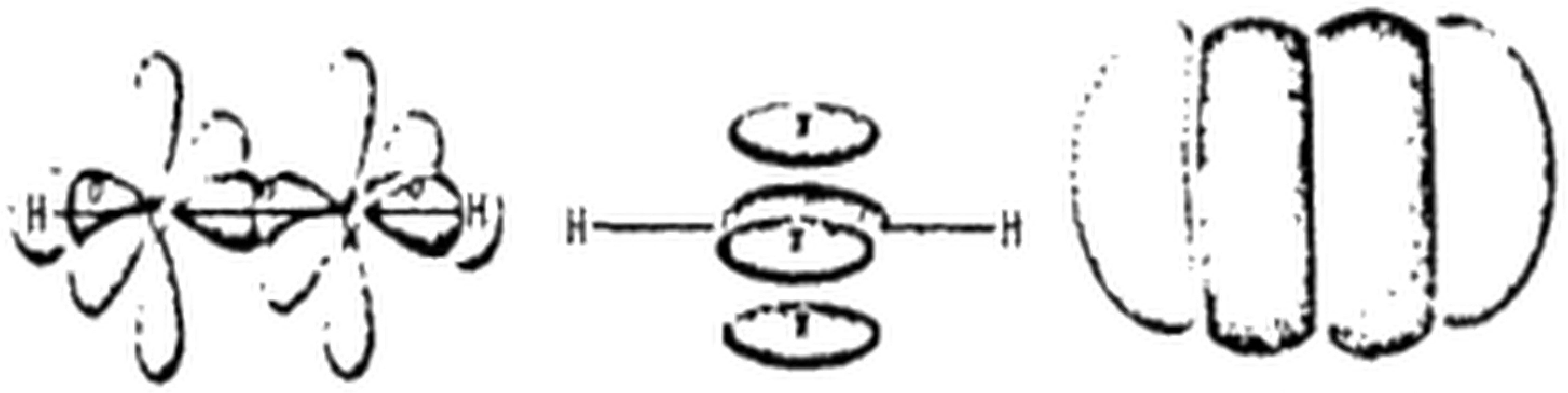
Structure of Ethyne, (HC≡CH)

The electronic configuration of carbon in ground and excited states is as follow;

$_6C$ (ground state) = $1s^2$, $2s^2$, $2p_x^1$, $2p_y^1$, $2p_z$

$_6C$ (excited state) =$1s^2$, $2s^2$, $2p_x^1$, $2p_y^1$, $2p_z^1$

$_6C$ (hybridized state) =$1s^2$, $(2sp)^1$,$(2sp)^1$, $2p_y^1$, $2p_z^1$



formation of σ bonds formation of π bonds space-filling model

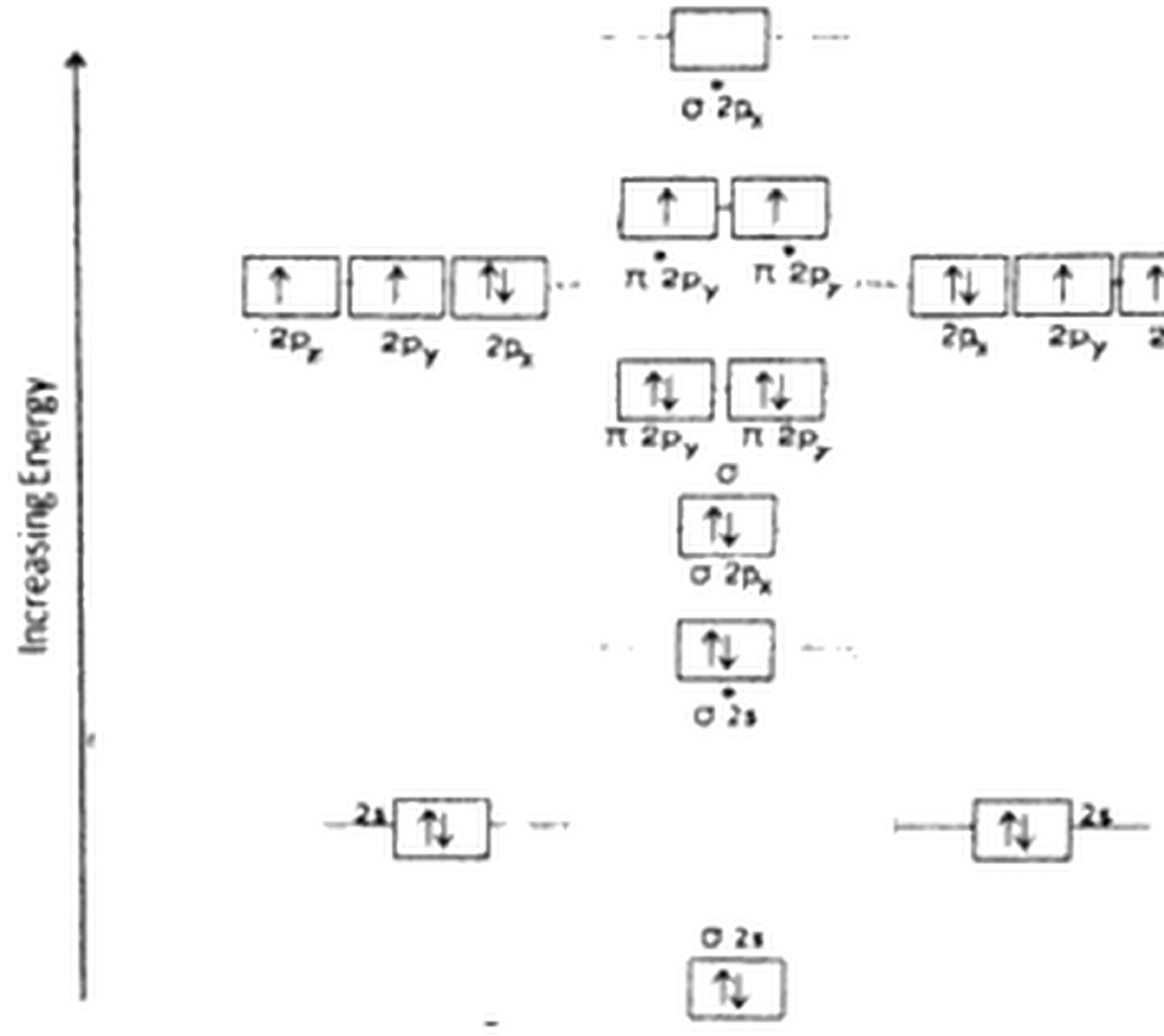
H—C≡C—H

Structure of Ethyne (CH ≡CH)

4. **How does molecular orbital theory explain the paramagnetic character of O_2 , O_2^{2+} and O_2^{2-} species?**

Ans: Paramagnetic character of O_2 :

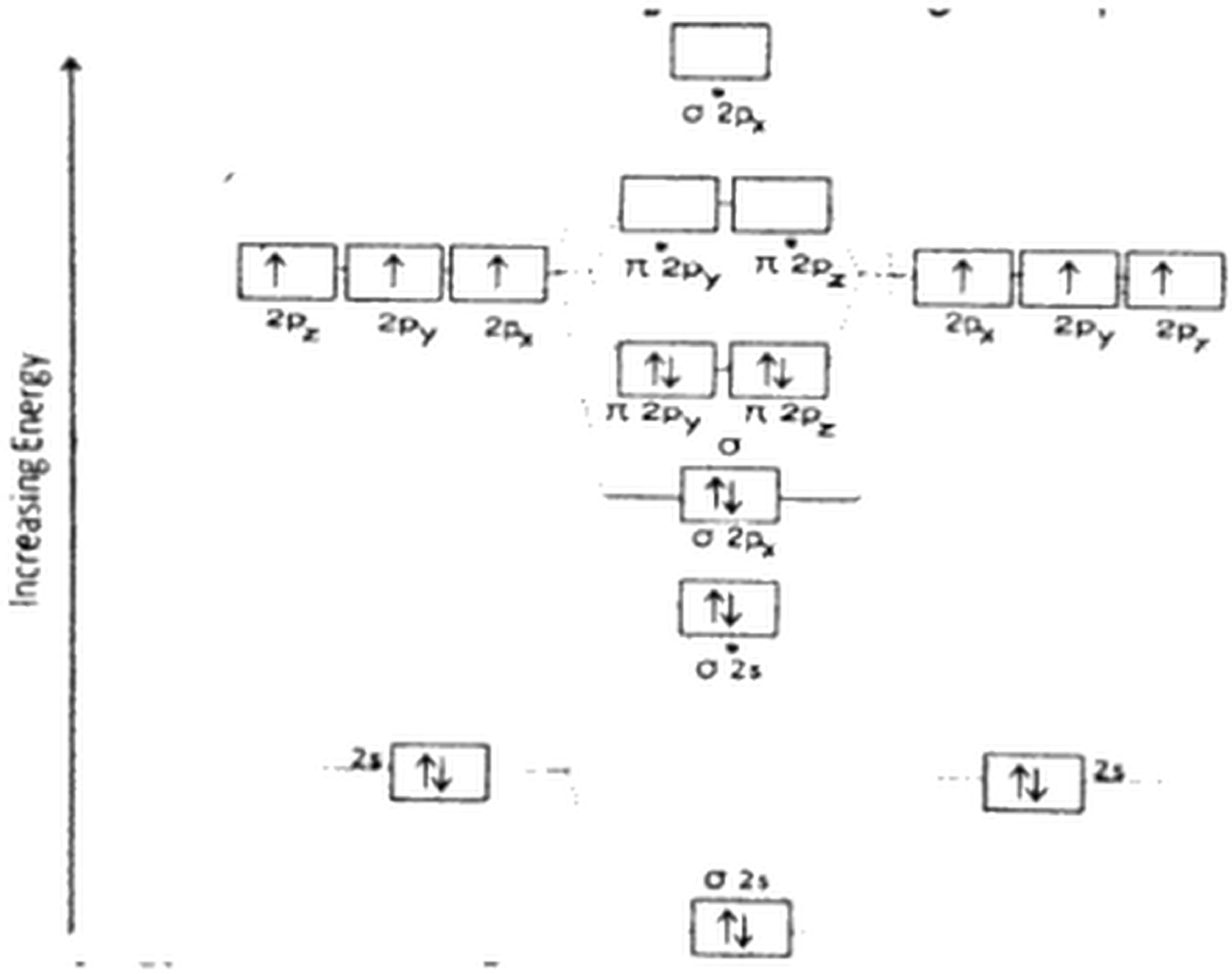
According to molecular orbital theory, the energy diagram of O_2 contain two unpaired electrons in anti-bonding due to which O_2 shows paramagnetic behavior.



Paramagnetic character of O_2^{2+}

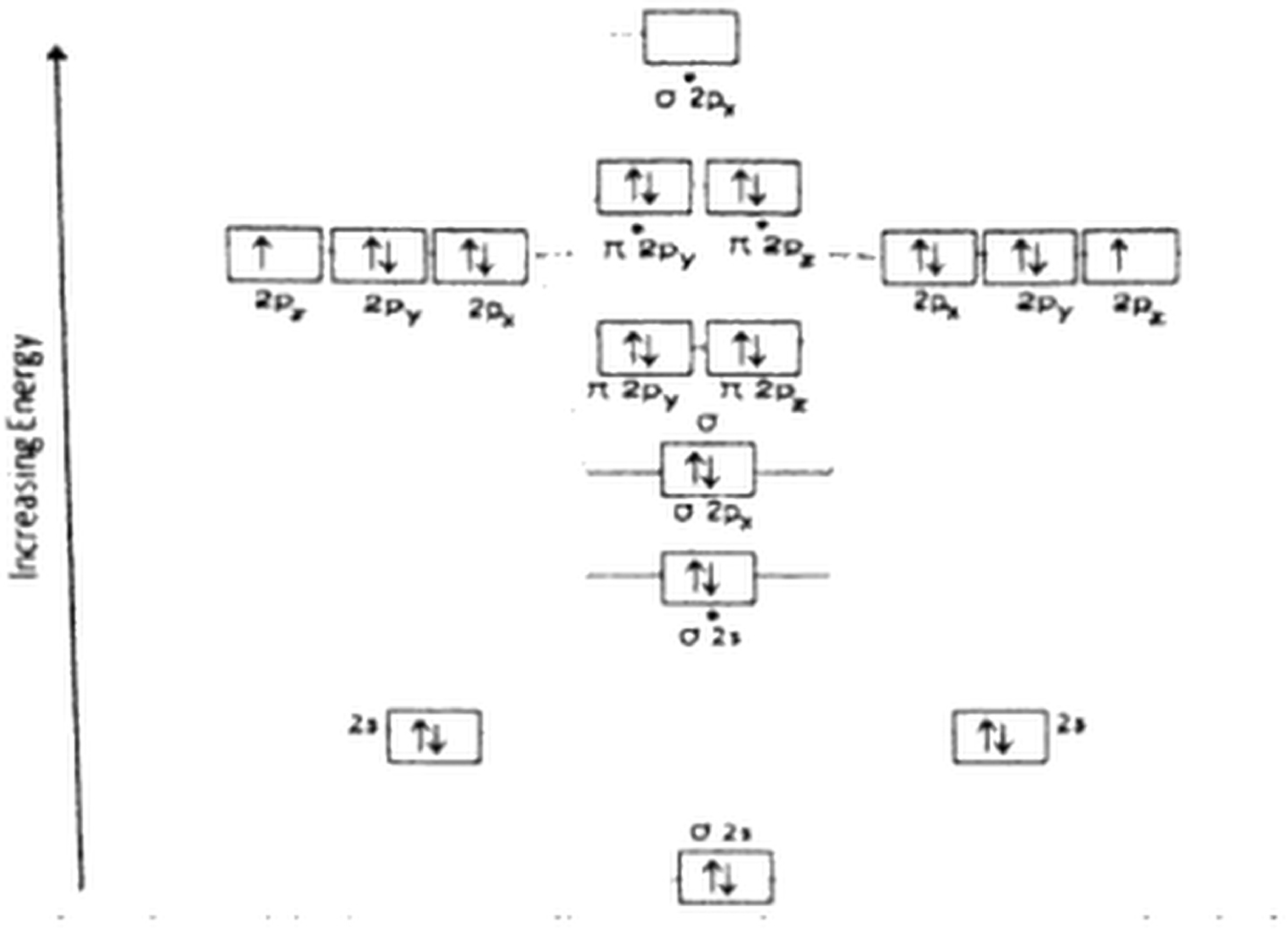
Molecular orbital energy diagram for O_2^{2+} is as follows:

In this MO energy diagram, there is no unpaired electrons in anti-bonding molecular orbitals. This indicates that O_2^{2-} is a diamagnetic specie.



Paramagnetic character of O_2^{2-}

Molecular orbital theory of O_2^{2-} is as follows



In this molecular orbital energy diagram, there is no unpaired electrons in anti-bonding molecular orbitals. This indicates that O_2^{2-} is a diamagnetic specie.

Q6. The melting points, boiling points, heat of vaporization and heats of sublimation of electrovalent-compounds are higher as compared with those of covalent-compounds. Explain.

Ans: The force of attraction between electrovalent compounds (ionic compounds) are electro static forces of attraction which are strong forces as compare to Vander Waals forces of attractions (present in covalent compounds) which are less stronger forces due to which the melting points, boiling points, heat of vaporization and heats of sublimation of electrovalent-compounds are higher as compared with those of covalent-compounds.

7. The dipole moment of HCl is 1.03D and the distance between atoms is 127 pm calculate the percentage ionic character of the HCl bond.

(Ans. 16.9%)

Ans: Bond length = r = 127pm = 1.27×10^{-10} m

$q = 1.6022 \times 10^{-19}$ C

$\mu_{ionic} = q \times r$

$1D = 3.366 \times 10^{-30}$ Cm

Dipole moment of a molecule = charge × distance

$\mu_{ionic} = (1.6022 \times 10^{-19}\ C)(1.27 \times 10^{-10}\ m)$

$= 2.034 \times 10^{-29}$ mC

To convert it into Debye, we divide it by 3.336×10^{-30}

$$\mu_{ionic} = \frac{2.034 \times 10{-}29\ mC}{3.366 \times 10{-}30\ Cm}$$

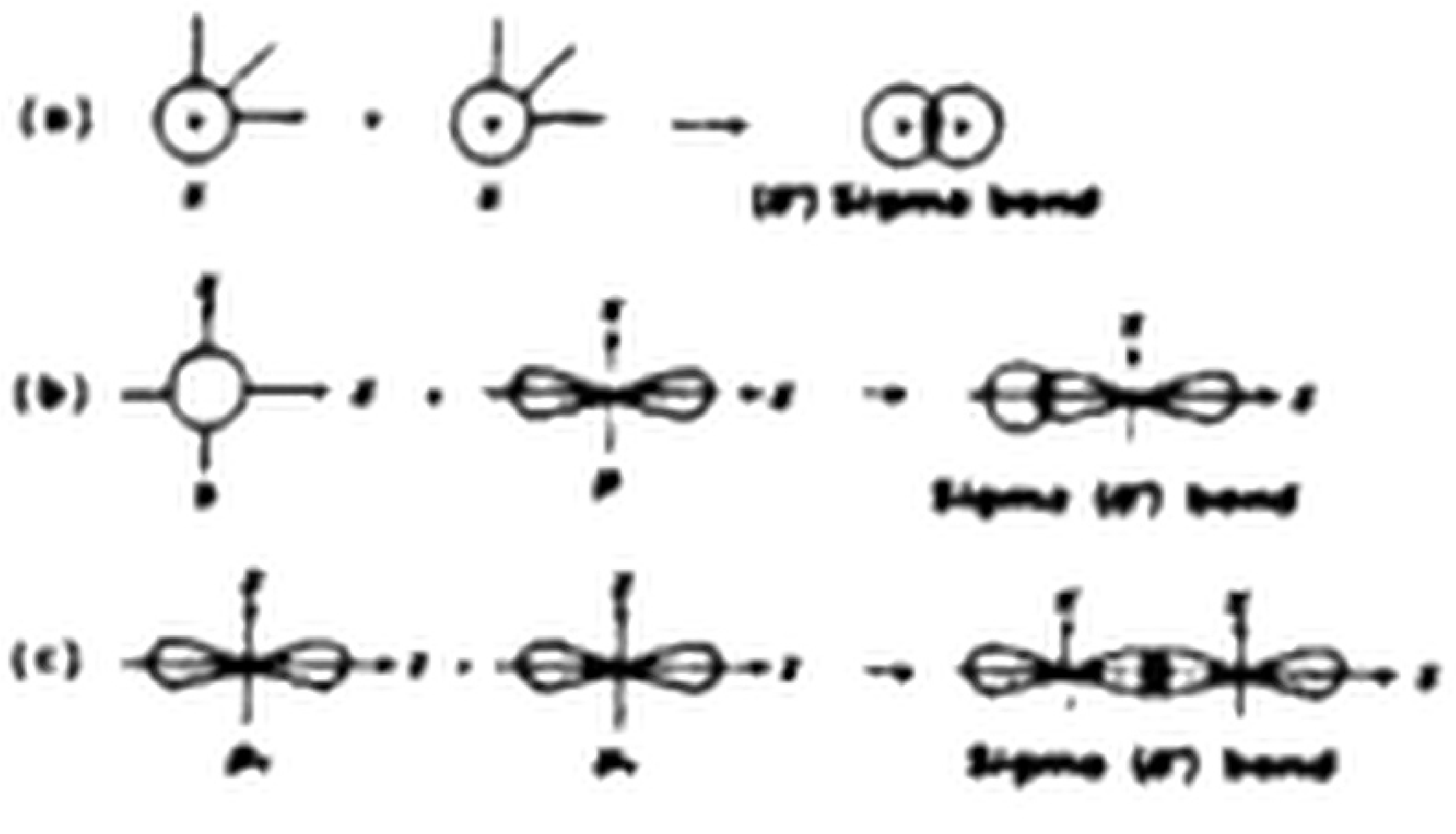
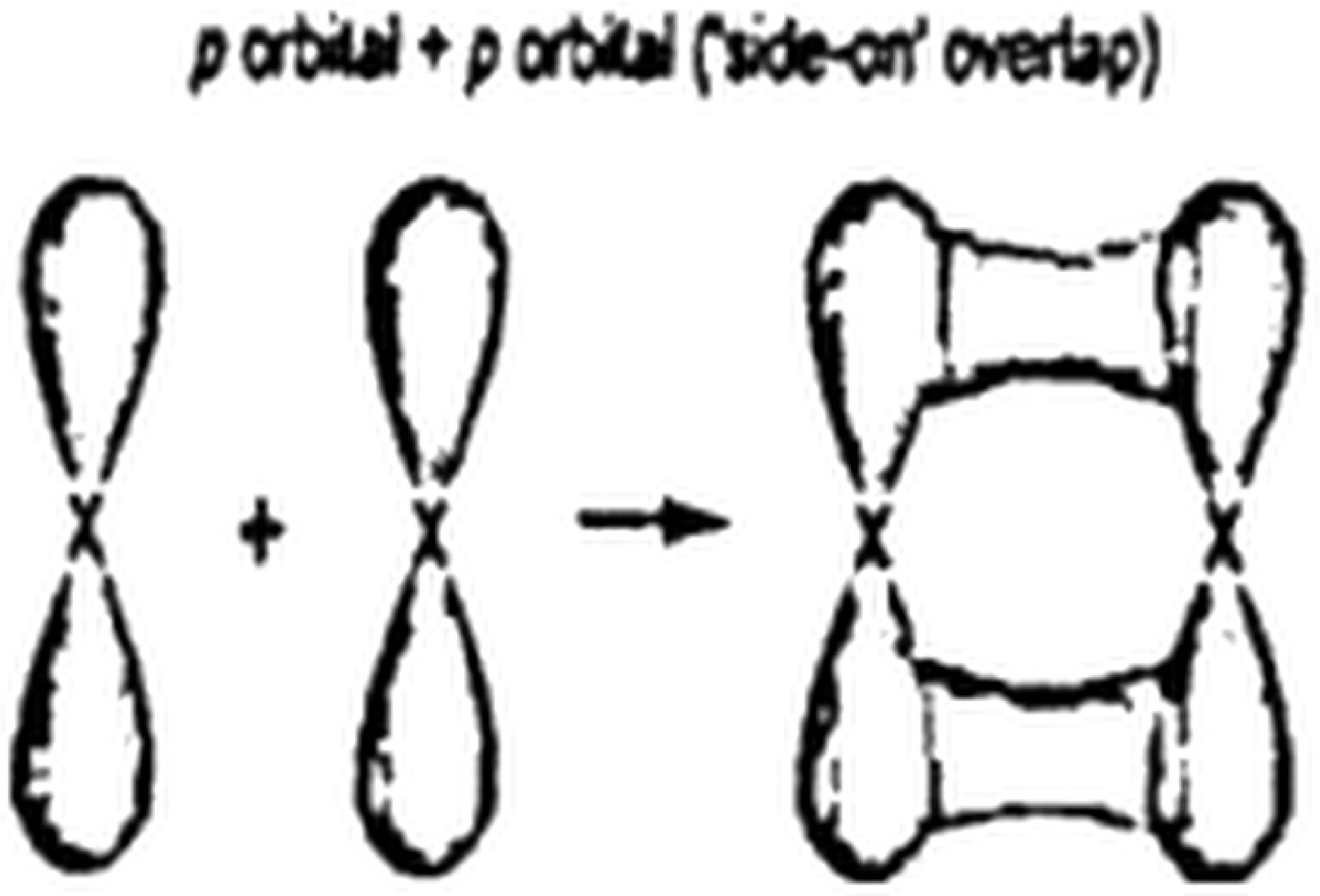
= 6.0995 Debye

%age of ionic character = $\frac{\mu(obs)}{\mu(calc)} \times 100 = \frac{1.03}{6.0995} \times 100 = 16.88\%$

So the percentage ionic character of HCl is 16.88%

8. How would you distinguish between sigma and pi bond?

Ans:

Sigma bond(σ)	Pi bond (π)
It is formed by bead on overlap of atomic orbitals	It is formed by sideways overlap of atomic orbitals
In this case the maximum electron density is symmetrically distributed around bond axis	In this case the electron density is unsymmetrically distributes around the line joining to nuclei
The probability of finding an electron is maximum at the region between two nuclei	The probability of finding an electron is minimum at the region between two nuclei. It is present above and below bond axis
It is the first bond formed between two atoms	It is the bond formed after sigma bond
Maximum number of sigma bond is one	Thy can be or two in number
The orbital that make sigma bond  Formation of a sigma bond due to (a) The s - s overlap (b) The s - p overlap (c) The p_x - p_x overlap	The orbital that can make Pi bond 

Note:

a. In case of pi bond formation which is over a covalent bond, the electron density is greatest above and below the line joining the two nuclei and this is also called nodal plane.

b. Only pure, parallel, co-planner, half filled p-orbitals on adjacent atoms can form a π bond.

c. Only one bond in any multiple bonds can be a sigma bond, the remaining bonds are pi bonds.

d. In case of hybridization, the overlapping of any hybrid-orbitals always produces a sigma (σ) bond.

9. Arrange the following species in order of increasing stability

Li_2 , Li_2^+ , Li_2^-

Justify your choice with molecular orbital theory.

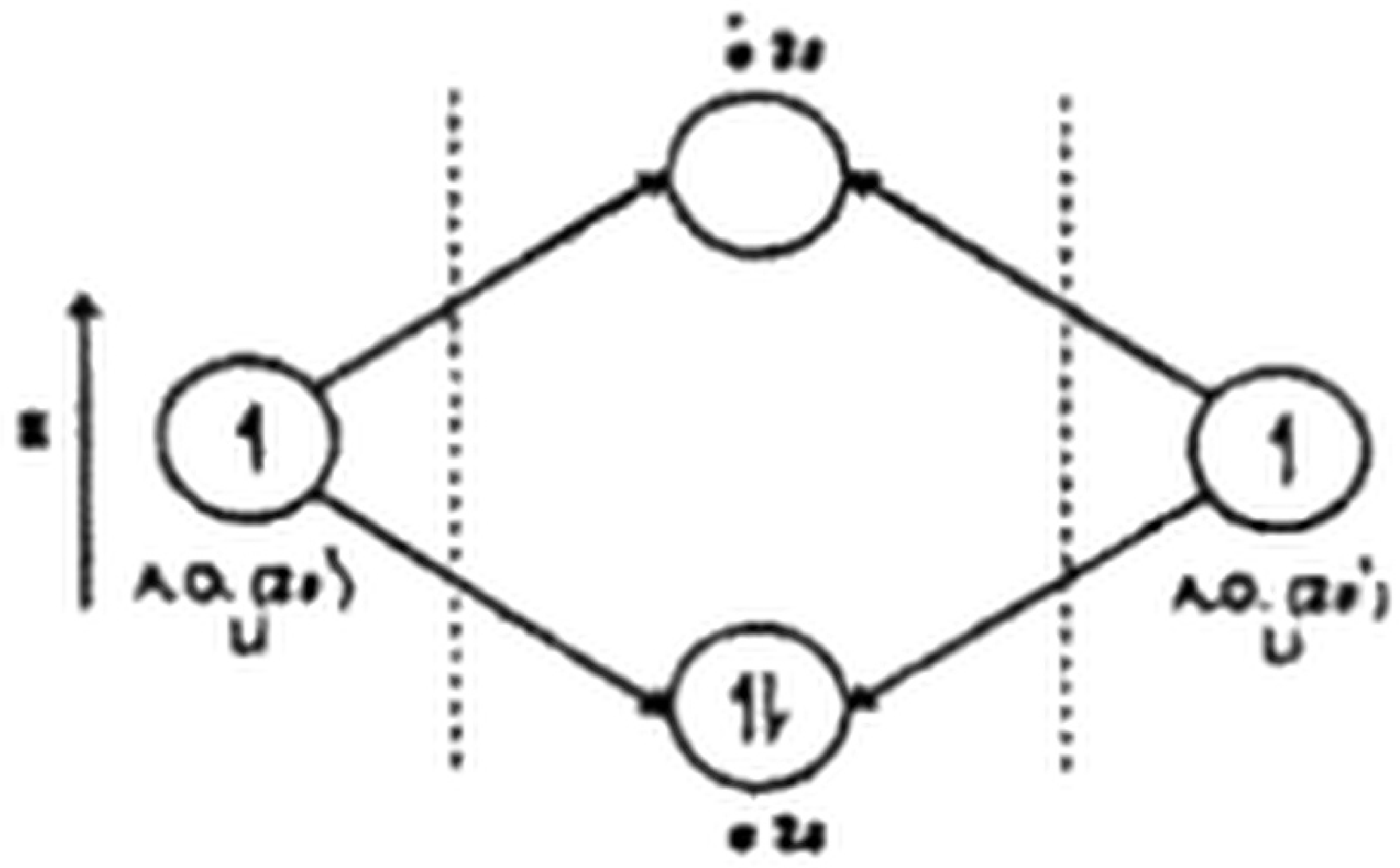
Ans: Lithium Molecule Li_2 :

Li = $1s^2$,$2s^1$

i. The molecular orbital diagram of Li_2 is given below.

ii. As there is no electron is present in σ*2s so the bond order will be.

Bond order = $\frac{2-0}{2}$ = 1



(molecular energy level diagram of Li_2)

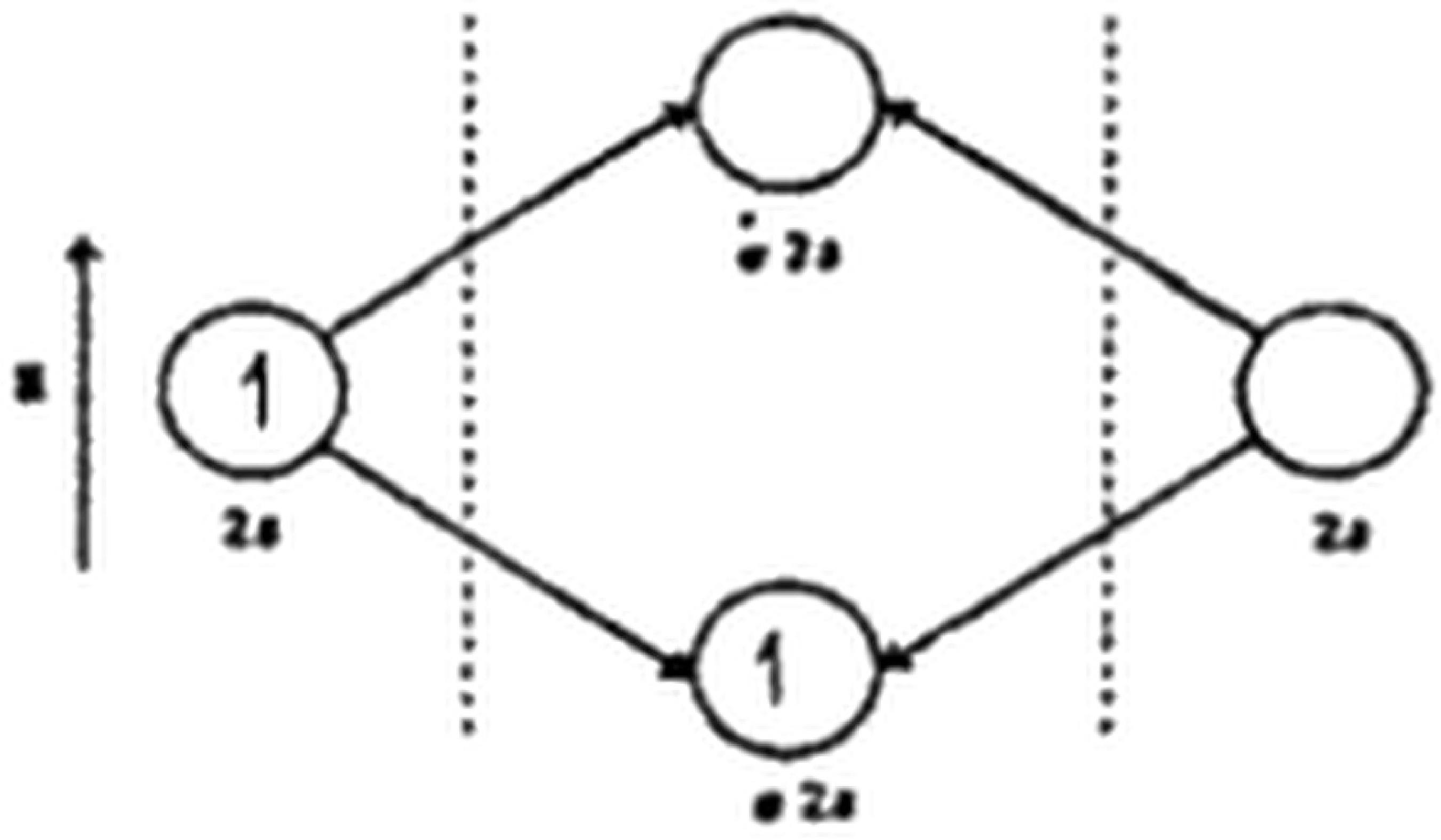
Lithium (Li_2^+) ion:

I. The molecular orbital diagram of Li_2^+ is shown below

II. One electron is present in σ2s orbital

III. The antibonding molecular orbitals σ*2s is empty

IV. Thus its bond order is = $\frac{1-0}{2}$ = 0.5



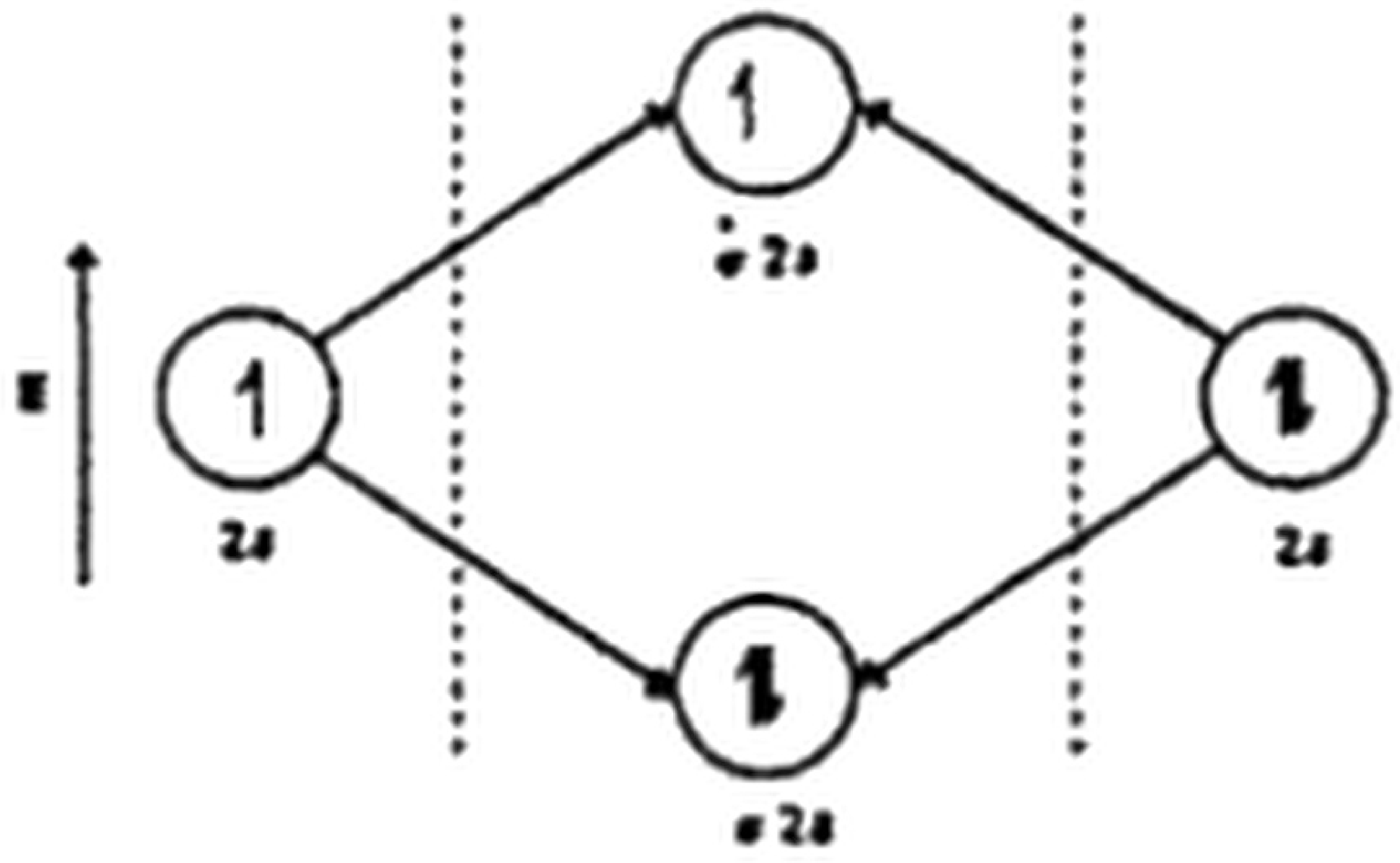
Lithium (Li_2^-) ion:

I. The molecular orbital diagram of Li_2^- is shown below

II. two electrons is present in σ2s orbital

III. The antibonding molecular orbitals σ*2s contain one electron

IV. Thus its bond order is = $\frac{2-1}{2}$ = 0.5



Conclusion:

From the bond orders it is concluded that of Li_2 has greater bond order than those of Li_2^- and Li_2^+ ions, therefore, it has stronger bonding and it is more stable than Li_2^- and Li_2^+ ions. Li_2^- and Li_2^+ ions have same bond order, therefore, they have almost equal stability.

But Li_2^- has more electrons in high energy antibonding orbitals than Li_2^+

Thus, Li_2^+ ion is more stable than Li_2^- and ion.

Therefore, increasing order of stability is $Li_2^- < Li_2^+ < Li_2$

10. A double bond is stronger than a single bond and a triple bond is weaker than a

double bond.

Ans: A single bond consists of a sigma electron could (orbital) which in itself is the strongest type of bonding

But, when we create a double you are adding a pi orbital (which is weaker than sigma orbital), since the pi orbital is being added to an existing sigma orbital it logically follows that it will be a stronger one (pi and sigma > Sigma), the effect of the pi orbital will be strengthening the overall bond (double bond) but also shortening the distance between then atoms which means shorter bond.

Triple bond on the other hand adds another pi orbital to the existing sigma and pi orbitals making the triple bond weaker than a double bond

The shrinkage of the multiple bonds is due to the presence of extra π electrons (two π) electrons in the case of a double bond and four π electrons in case of triple bond which makes a triple bond is weaker than a double bond.) between the two nuclei, which exert additional attraction on both the nuclei bringing them closer to each other

Therefore, double bond is stronger than a single bond and a triple bond is weaker than a double bond