Molecular Orbital Theory (MOT)

Major Drawbacks in VBT:

1) VBT assume that each combining species will provide an unpaired electron of opposite spin to form a covalent bond but in case of co-ordinate covalent bond one species provide both electrons.

2) According to the VBT, in O_2 all electrons are paired, so it should be diamagnetic but O_2 is two electron paramagnetic species.

3) In VBT, N_2 contain a triple bond (N≡N) similar to acetylene (HC≡CH). In spite of similarity in bonding, N_2 is very much inert while acetylene is fairly active.

4) VBT can't explain the odd electron bond in a molecule like He_2^+, H_2^+ etc.

Molecular orbital theory (MOT):

- ❖ Molecular orbital theory was proposed and developed mainly by Mulliken, Lennard – Jones and Hückel.

- ❖ In this approach, the skeleton of the molecule with its nuclei in fixed position is first considered then develop molecular orbitals (MOs)

- ❖ The filling electrons to these MOs according to the aufbau principle, Hund's rule and Pauli's exclusion principle.

- ❖ The MOs are polycentric as it has more than one nucleus while the AOs are monocentric as it involves only one nucleus.

- ❖ The MOs are developing from the AOs according to the (i) Linear Combination of Atomic Orbitals (LCAO) method, (ii) United Atom method.

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Important Aspect of LCAO-MOT:

(i) MOs are developed from the skeleton of the molecule containing the nuclei at the fixed position through LCAO method.

(ii) The number of MOs would be equal to the number of AOs involved.

(iii) For an effective combination of AOs they must satisfy the EOS conditions.

   ❖ Energy: The combining wave functions should have comparable energy.

   ❖ Overlap: The AOs representing the electron cloud must undergo overlap appreciably.

   ❖ Symmetry: The lobes of combining AOs must have same symmetry with respect to bond axis.

(iv) Depending upon the overlap integral (S_{AB}), MOs are classified as bonding MO ($S_{AB} > 0$), antibonding MO ($S_{AB} < 0$) and non bonding MO ($S_{AB} = 0$).

(v) After the construction of MOs, electrons are placed to these MOs according to the aufbau principle, Hund's rule and Pauli's exclusion principle.

(vi) The MOs are also defined by four quantum numbers as AOs. 'n' and 'l' are retained from the AOs and spin quantum number have same significance as in atoms. The magnetic quantum number of the MOs are representing by λ and have values $\lambda = -l, -(l-1), ...,0, (l-1), l$. (In diatomic molecule the axis containing the nuclei is taken reference axis.)

For $\lambda = 0$, orbitals are symmetrical around the reference axis and these are called σ-orbitals.

$\lambda = \pm 1$, the orbitals are referred to as π-orbitals and $\lambda = \pm 2$, orbitals are termed as δ-orbitals.

(vii) Based on the symmetry they can be classified as gerade (g) and ungerade (u). The orbitals having centre of symmetry (C_i) are called gerade (g) and lacking of C_i are termed ungerade (u). s and d orbitals are represented by g while p and f orbitals are represented by u.

(viii) The bonding MOs concentrate the electron cloud between the nuclei to stabilize the system while the antibonding orbitals remove the electron cloud from the space between the nuclei to destabilize the system.
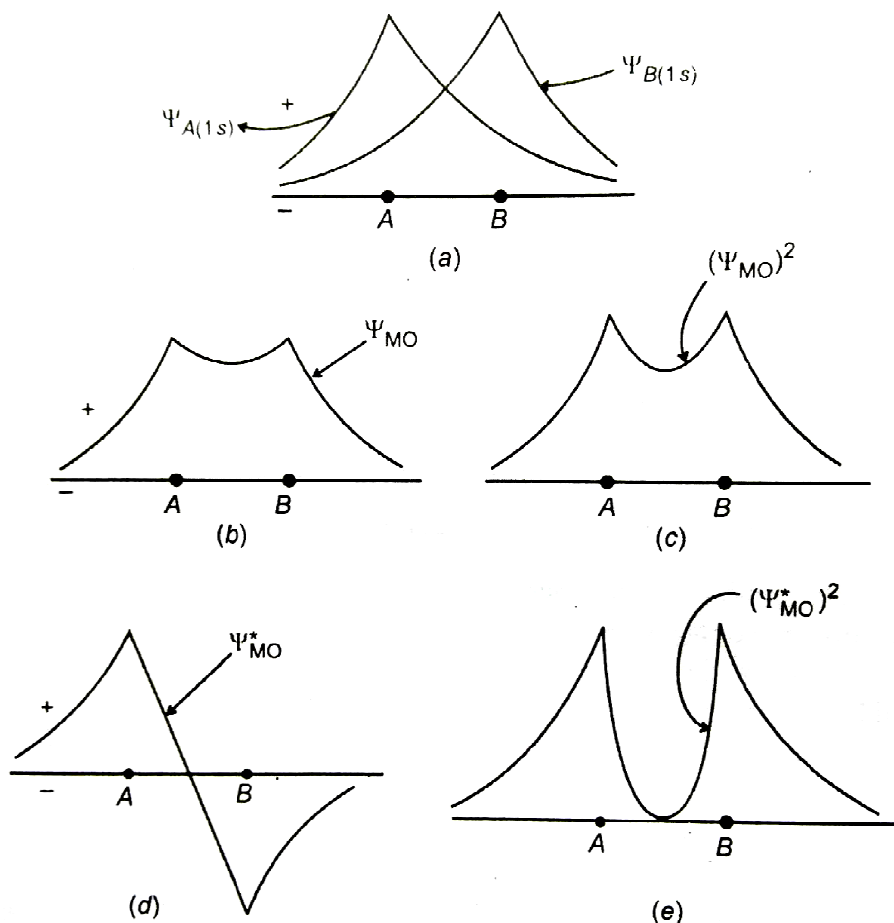
Quantitative representation: (a) wave function of H_A and H_B (b) Ψ_{MO} of H_2^+ (c) Probability of finding electron density in Ψ_{MO} of H_2^+ (d) Ψ^*_{MO} of H_2^+ (e) Probability of finding electron density in Ψ^*_{MO} of H_2^+

(ix) Approximately, the stabilization by the bonding molecular orbital (BMO) is balanced by the destabilization induced by the antibonding molecular orbital (ABMO). That's why the bond order is roughly calculated as,

$$\text{bond order} = \frac{\text{number of electron in BMO} - \text{number of electron in ABMO}}{2}$$

(x) In homonuclear diatomic molecules, both the atomic orbitals contribute equally in forming MO, but in heteronuclear diatomic molecules they contribute unequally.

(xi) The energy of each MOs can be calculated by solving the appropriate Schrödinger wave equation. For, homonuclear diatomic system energy of the MOs are as
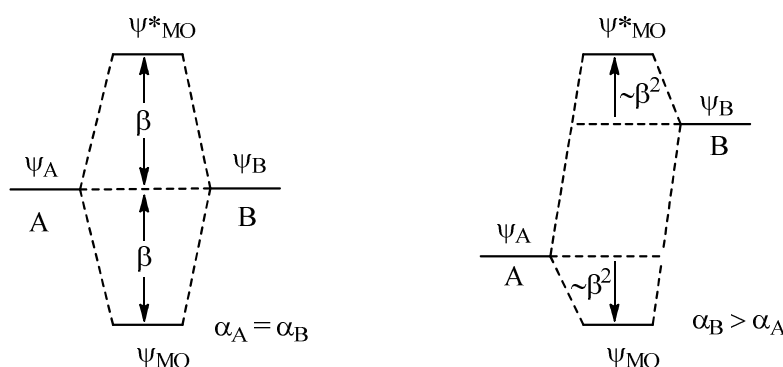
$$E_b = \alpha + \frac{\beta_{AB} - \alpha S_{AB}}{1 + S_{AB}} \qquad E_a = \alpha - \frac{\beta_{AB} - \alpha S_{AB}}{1 - S_{AB}}$$

For, heteronuclear diatomic system energy of the MOs are as

$$E_b = \alpha_A - \frac{(\beta_{AB} - \alpha_A S_{AB})^2}{\alpha_B - \alpha_A} \qquad E_a = \alpha_B + \frac{(\beta_{AB} - \alpha S_{AB})^2}{\alpha_B - \alpha_A}$$

Where, α is Coulomb integral, β_{AB} is resonance integral and S_{AB} is overlapping integral.

(xii) All MOs are normalised. $\int (\Psi_{MO})^2 \, d\tau = 1$ or $\int (\Psi^*_{MO})^2 \, d\tau = 1$ and the corresponding bonding and antibonding MOs are mutually orthogonal i.e. $\int \Psi_{MO} \times \Psi^*_{MO} \, d\tau = 0$


σ, π, δ and φ MOs : σ bond arises by the overlap of '1 lobe + 1 lobe', π bond arises by the overlap of '2 lobes + 2 lobes', δ bond arises by the overlap of '4 lobes + 4 lobes', φ bond arises by the overlap of '6 lobes + 6 lobes'. The s-orbital can only show σ-type interaction; p-orbital can show σ- and π-type interaction, d-orbital can show σ, π and δ-type interaction, f-orbital can show σ, π δ and φ-type interactions.

For the spherically symmetrical s-orbital, the (+) combination gives the sigma bonding molecular orbital (σ-BMO) while the (-) combination gives the sigma antibonding molecular orbital (σ-ABMO). The orbitals like p, d etc which are not spherically symmetrical, in the σ-type interaction, the (+) combination gives the σ-ABMO while the (-) combination gives the σ-BMO; for the π-type interaction the reverse is true.
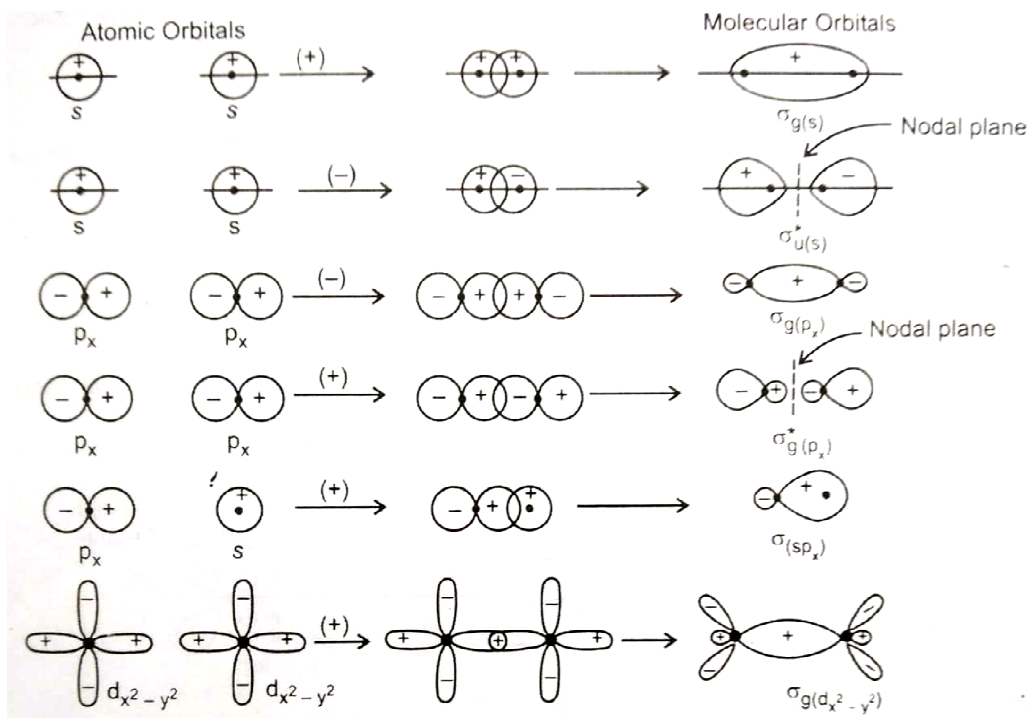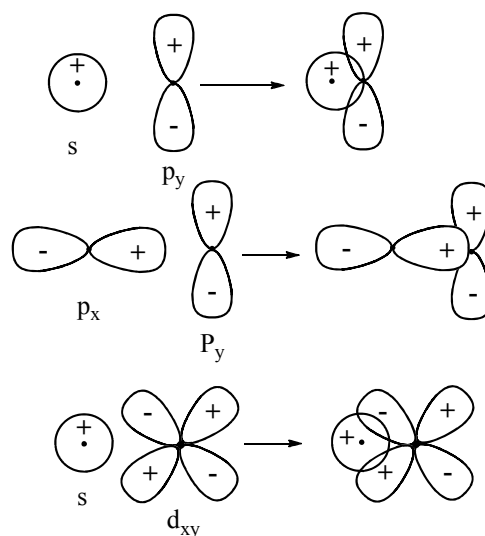
Formation of sigma (σ) type molecular orbitals from atomic orbitals through LCAO
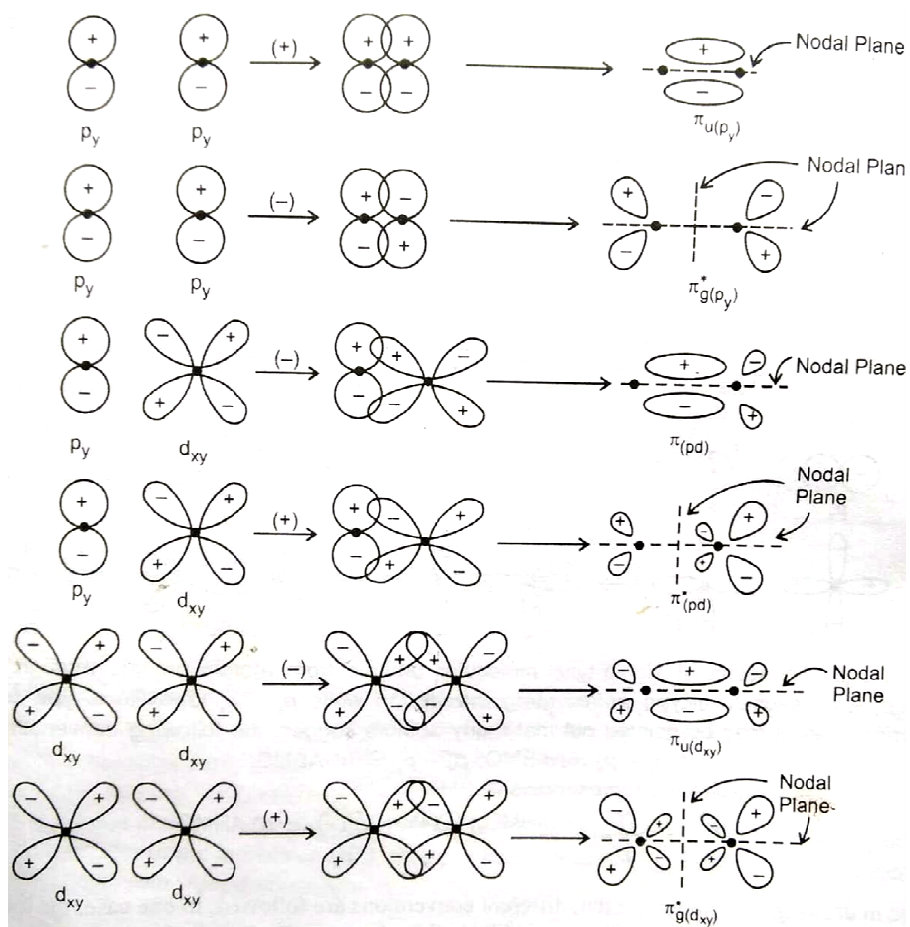
Formation of pi (π) type molecular orbitals from atomic orbitals through LCAO
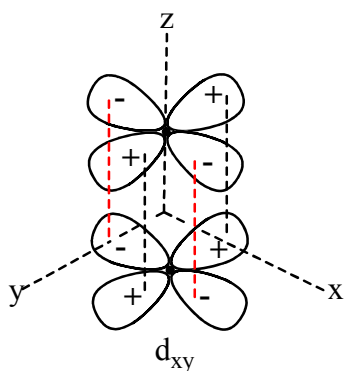
Schematic representation of δ-bonding

Schematic representation of non-bonding interaction

δ-Bonding: Two d orbital lying in parallel planes can overlap each other with all four lobes to produce a δ-bonding. The δ-Molecular orbital possesses two nodal planes containing the bond axis and nodal planes are mutually perpendicular. The δ-MOs can arise from the suitable d ± d, f ± f and d ± p_π^*-MO interaction. The magnetic quantum number (λ) of the δ-MOs is ±2.

σ-Bonding: End to end overlap of two lobes of two suitable orbital produce σ-bond. This bond is strong due to better overlap. σ-bond has cylindrical symmetry (C_∞) around the bond axis. It determines the direction of bond. σ-bonding electrons can't participate in delocalization. The magnetic quantum number (λ) of the σ-MOs is zero. σ-MOs, both σ and σ* have no nodal plane containing the internuclear axis.

π-Bonding: Side to side overlap of four lobes of two suitable orbital produce π-bond. This bond is weaker due to poor overlap. π-bond has no C_∞ symmetry so no rotation around bond axis is possible. It has no primary effect in determining the bond direction but it can shorten the bond length. π-bonding electrons being mobile can participate in delocalization. The magnetic quantum number (λ) of the π-MOs is ±1. π-MOs, both π and π* have nodal plane containing the internuclear axis.
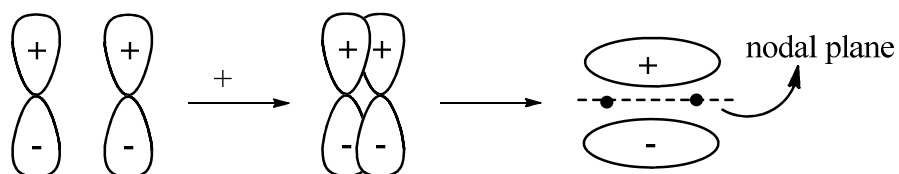
**Simple Molecular Orbital Diagram of Homonuclear Diatomic Molecule**

❖ Here, no interaction between the MOs of same symmetry and no hybridization among the AOs participating in the formation of MOs are considered.

❖ The extent of splitting between the corresponding bonding and antibonding MOs depends on the extent of efficiency of overlapping. In sigma interaction, the better overlapping produces more splitting compared to that in the pi-interaction.

❖ X-axis is considered as bond axis. Therefore, $2p_x$ orbital produces σ-MOs while $2p_y$ and $2p_z$ orbitals produce two sets of π-MOs. The π-MOs are energetically degenerate but mutually perpendicular.

❖ In the MOs, electrons are placed according to the aufbau principal, Hund's rule and Pauli's exclusion principal.

❖ Highest occupied molecular orbital is denoted as HOMO and the lowest unoccupied molecular orbital is termed as LUMO. Both HOMO and LUMO are referred to as frontier molecular orbitals (FMOs). The singly occupied molecular orbital is called SUMO.

❖ Many author named the MOs as follows: $\sigma_g(1s) = 1\sigma_g$; $\sigma^*_u(1s) = 2\sigma^*_u$; $\sigma_g(2s) = 3\sigma_g$; $\sigma^*_u(2s) = 4\sigma^*_u$; $\sigma_g(2p) = 5\sigma_g$; $\pi_u(2p_{y,z}) = 1\pi_u$; $\pi^*_g(2p_{y,z}) = 2\pi^*_g$; $\sigma^*_u(2p_x) = 6\sigma^*_u$

❖ The energy order of the MOs $1\sigma_g < 2\sigma^*_u < 3\sigma_g < 4\sigma^*_u < 5\sigma_g < 1\pi_u < 2\pi^*_g < 6\sigma^*_u$

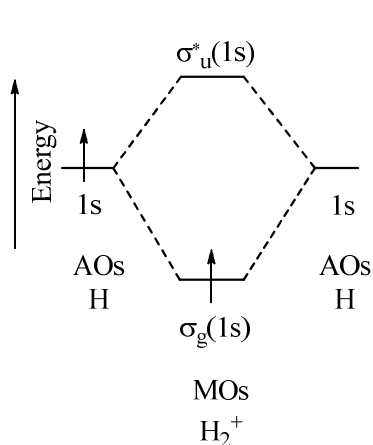**Simple Molecular Orbital diagram**
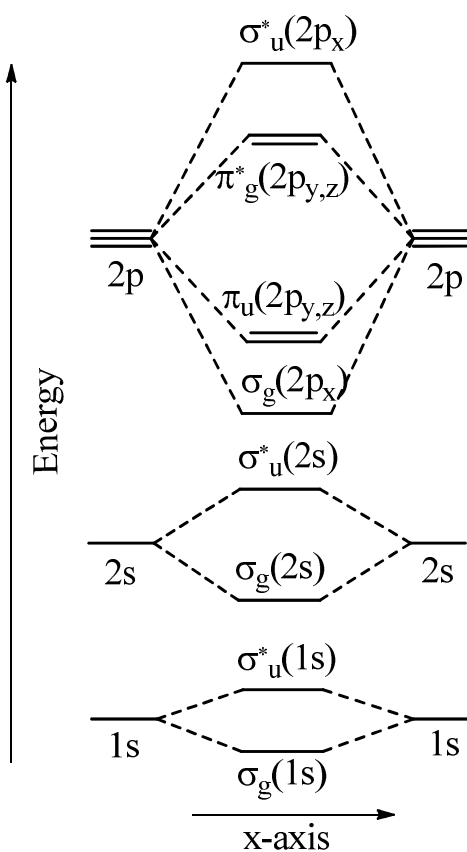
Molecular Orbital Picture of Homonuclear diatomic Molecule

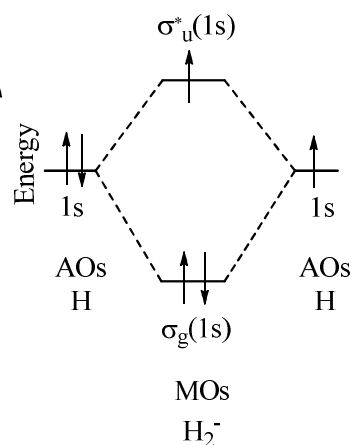**(i) H$_2$, H$_2^+$, H$_2^-$**
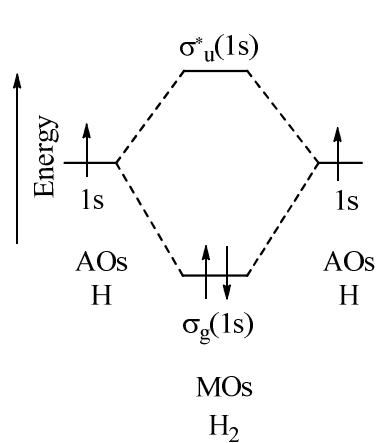
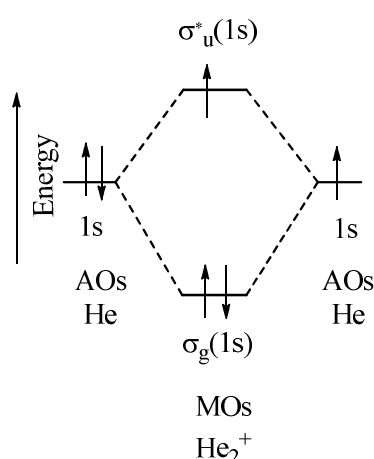Bond order $= \frac{2-0}{2} = 1$ Bond order $= \frac{1-0}{2} = 0.5$ Bond order $= \frac{2-1}{2} = 0.5$

(ii) He_2 , He_2^+

$\sigma^*_u(1s)$

Energy

1s   1s

AOs   AOs
He   He

$\sigma_g(1s)$

MOs
He_2

$\sigma^*_u(1s)$

Energy

1s   1s

AOs   AOs
He   He

$\sigma_g(1s)$

MOs
He_2^+
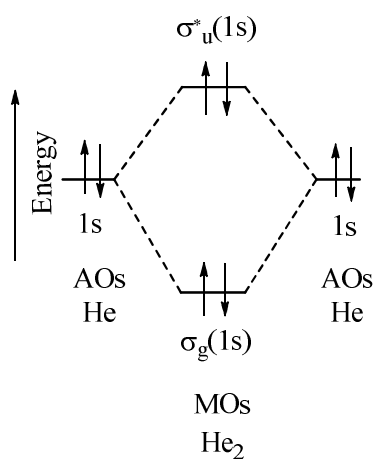
Bond order $= \dfrac{2-2}{2} = 0$ Bond order $= \dfrac{2-1}{2} = 0.5$

➤   It is note that the bond order of H_2^+ and He_2^+ is 0.5, and their bond lengths are 105 and 108 pm respectively.

➤   Bond order of He_2 is zero. Because of this fact non existence of He_2. It is worth mentioning that actually the anti bonding orbital, $\sigma^*_{u(1s)}$ destabilises more than the stabilisation of bonding orbital, $\sigma_{g(1s)}$. If stabilisation of BMO and destabilisation of AMBO is equal then there would be a finite probability of existence of He_2 along with mono atomic He.

(iii) The simple model of MO can't explain the few properties of lighter element mainly lithium to nitrogen in which energy difference between the 2s and 2p orbital is smaller.

➤   Beryllium exists as a mono atomic species as gas phase. But, at very low temperature beryllium exist as diatomic molecule. But this model can't predict the fact.

➤   Experimentally B_2 is paramagnetic but simple MO diagram predicts it is diamagnetic.

➤   Experimentally C_2 is diamagnetic but simple MO diagram predicts it is paramagnetic.

➤   It shows existence of two pi-bonds along with a sigma bond as in acetylene. But, N_2 is inert unlike acetylene.

➤   Ionisation potential of N_2 established that the highest occupied orbital is a σ-orbital while this simple model predicts it is a π-orbital

Therefore some modification of simple MO is required to form MO.

Modification of Molecular Orbital Energy diagram
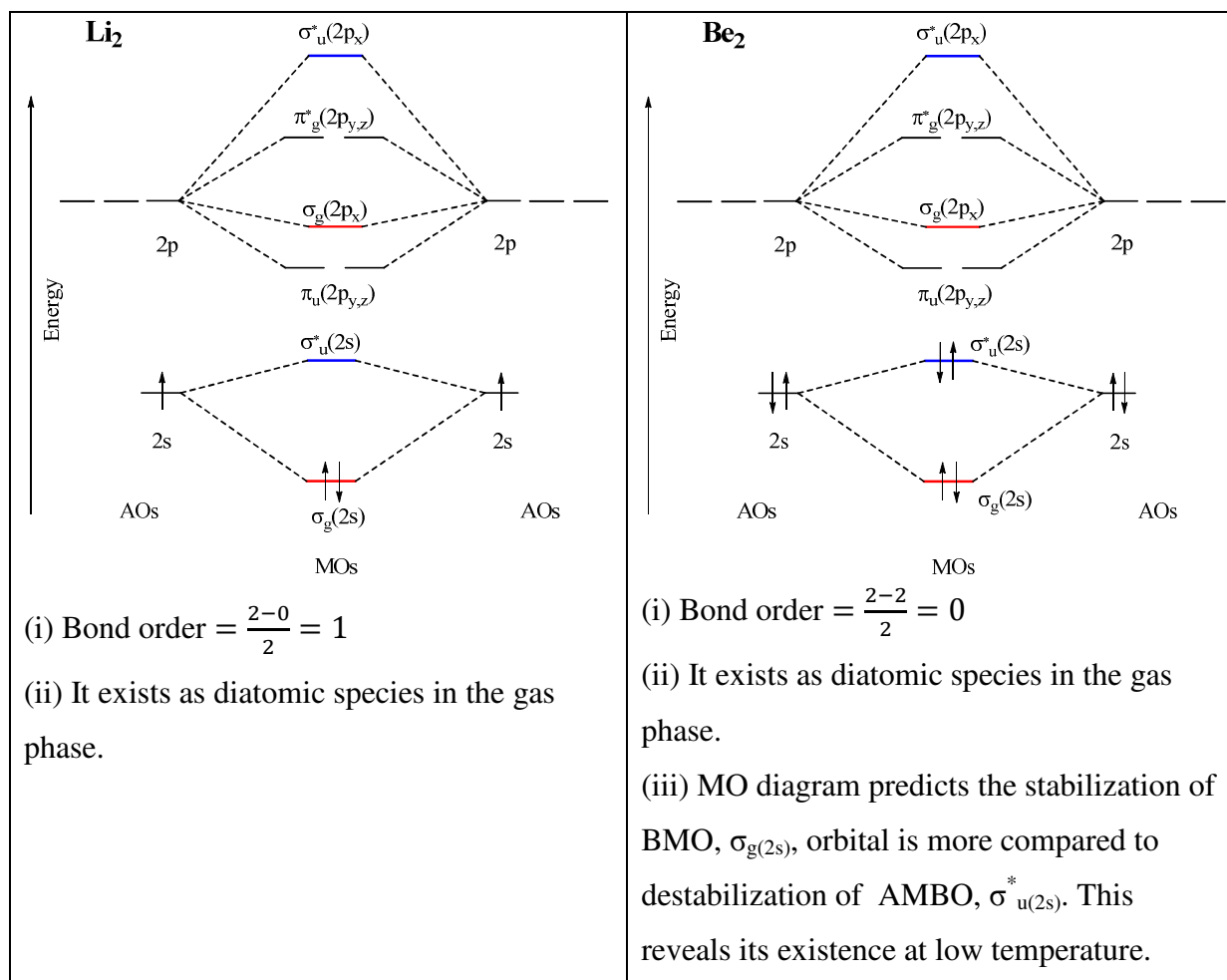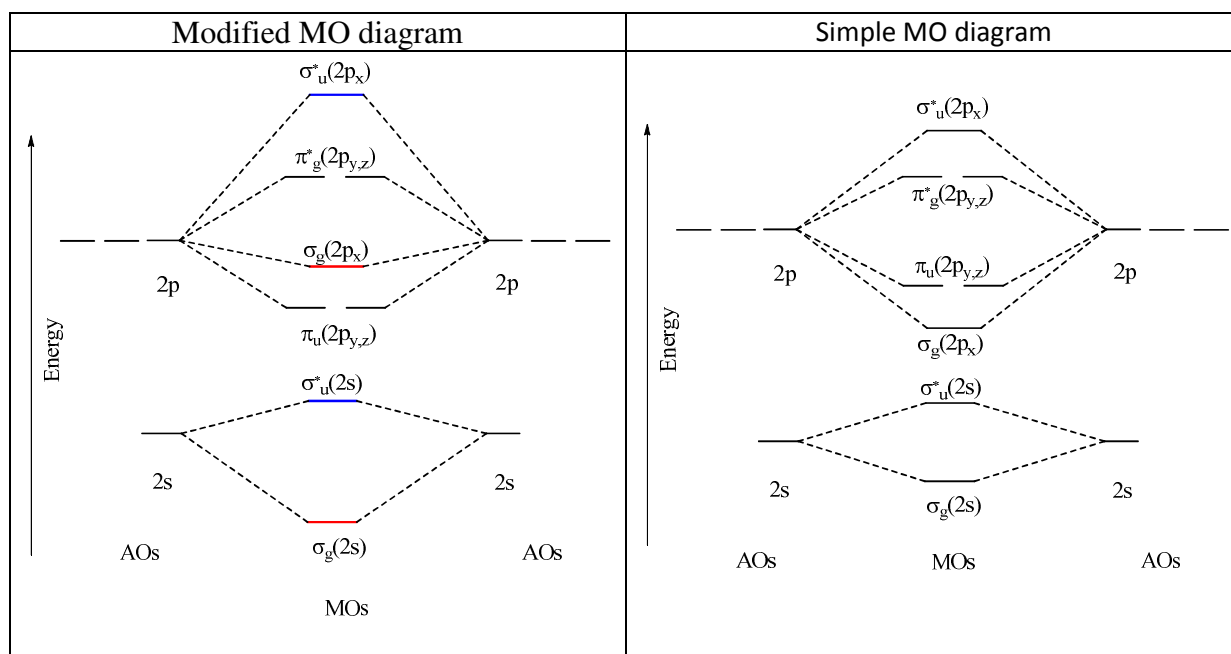
The modification can be attained in two possible ways:

(i) Incorporation of symmetry interaction (i.e. noncrossing rule) among the molecular orbitals obtained in simple treatment. According to the quantum mechanics, two orbitals of the same symmetry mutually repel resulting the lower energy orbital become more stabilized and higher energy orbitals becomes more destabilized. If we considered the simple MO diagram, the pair $\sigma_{g(2s)}$ - $\sigma_{g(2px)}$ and $\sigma^*_{u(2s)} - \sigma^*_{u(2px)}$ interact to each other. As a result, the energy of $\sigma_{g(2s)}$ and $\sigma^*_{u(2s)}$ is lower down and the energy of $\sigma_{g(2px)}$ and $\sigma^*_{u(2px)}$ is increased. This type interaction becomes prominent when the energy difference of 2s and 2p orbital is smaller. As we go lithium to neon the energy difference of these two orbital increases as shown below.

2nd period	Li	Be	B	C	N	O	F	Ne
$E_{2p} \sim E_{2s}$ (eV)	1.8	2.8	4.5	5.3	6.0	15.0	20.5	26.7
3rd period	Na	Mg	Al	Si	P	S	Cl	Ar
$E_{3p} \sim E_{3s}$ (eV)	2.0	2.6	4.5	5.2	5.5	9.8	11.5	13.5

Therefore, this type of symmetry interaction is quite important for N_2 and lighter molecule. For highly electronegative atom like O and F, the 2s lie far below of 2p orbitals and do not interact significantly. In fact, simple MO diagram is quite appropriate for O_2 and F_2 molecule.

(ii) Participation of hybrid orbitals (mixing of s and p-orbitals) instead of pure atomic orbitals for generating the molecular orbitals.

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Modified MO diagram for Li_2 to N_2

Modified MO diagram	Simple MO diagram

Li_2

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

(ii) It exists as diatomic species in the gas phase.

Be_2

(i) Bond order $= \frac{2-2}{2} = 0$

(ii) It exists as diatomic species in the gas phase.

(iii) MO diagram predicts the stabilization of BMO, $\sigma_{g(2s)}$, orbital is more compared to destabilization of AMBO, $\sigma^{*}_{u(2s)}$. This reveals its existence at low temperature.

B₂

$\sigma^*_u(2p_x)$

$\pi^*_g(2p_{y,z})$

$\sigma_g(2p_x)$

2p

2p

Energy

$\pi_u(2p_{y,z})$

$\sigma^*_u(2s)$

2s

2s

AOs

AOs

$\sigma_g(2s)$

MOs

(i) Bond order $= \dfrac{4-2}{2} = 1$

(ii) It contains two unpaired electron. So it is paramagnetic.

C₂

$\sigma^*_u(2p_x)$

$\pi^*_g(2p_{y,z})$

$\sigma_g(2p_x)$

2p

2p

Energy

$\pi_u(2p_{y,z})$

$\sigma^*_u(2s)$

2s

2s

AOs

AOs

$\sigma_g(2s)$

MOs

(i) Bond order $= \dfrac{6-2}{2} = 2$

(ii) It is diamagnetic.

N₂

$\sigma^*_u(2p_x)$

$\pi^*_g(2p_{y,z})$

$\sigma_g(2p_x)$

2p

2p

Energy

$\pi_u(2p_{y,z})$

$\sigma^*_u(2s)$

2s

2s

AOs

AOs

$\sigma_g(2s)$

MOs

i) Bond order $= \dfrac{8-2}{2} = 3$

(ii) HOMO is $\sigma_{g(2px)}$. Therefore, ionisation energy is higher than the expected.

(iv) Since HOMO is $\sigma_{g(2px)}$, a sigma MO and LUMO is $\pi^*_{g(2py,z)}$. Thus, it is difficult to remove an electron from HOMO and acceptance of an electron in LUMO is also energetically unfavourable. That's why N₂ is inert.

(v) For the same reason N₂ can't acts as a good ligand.
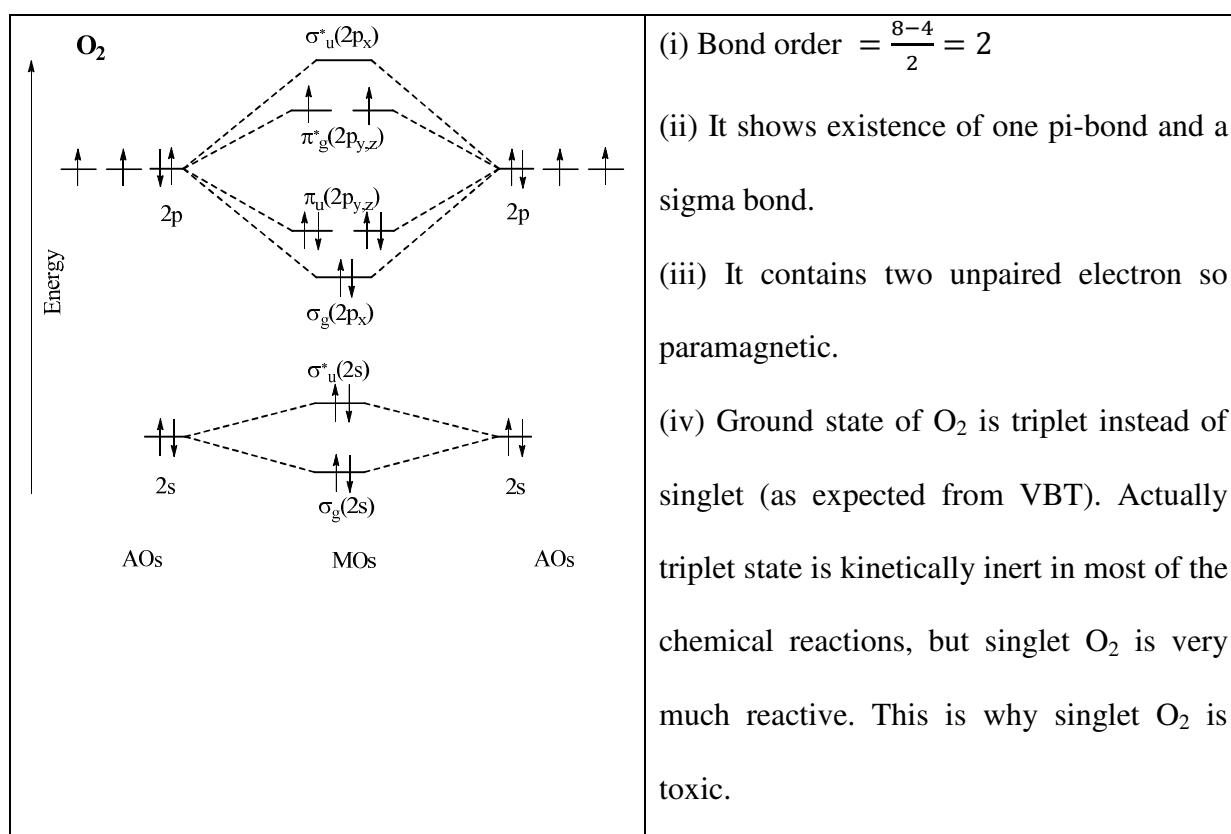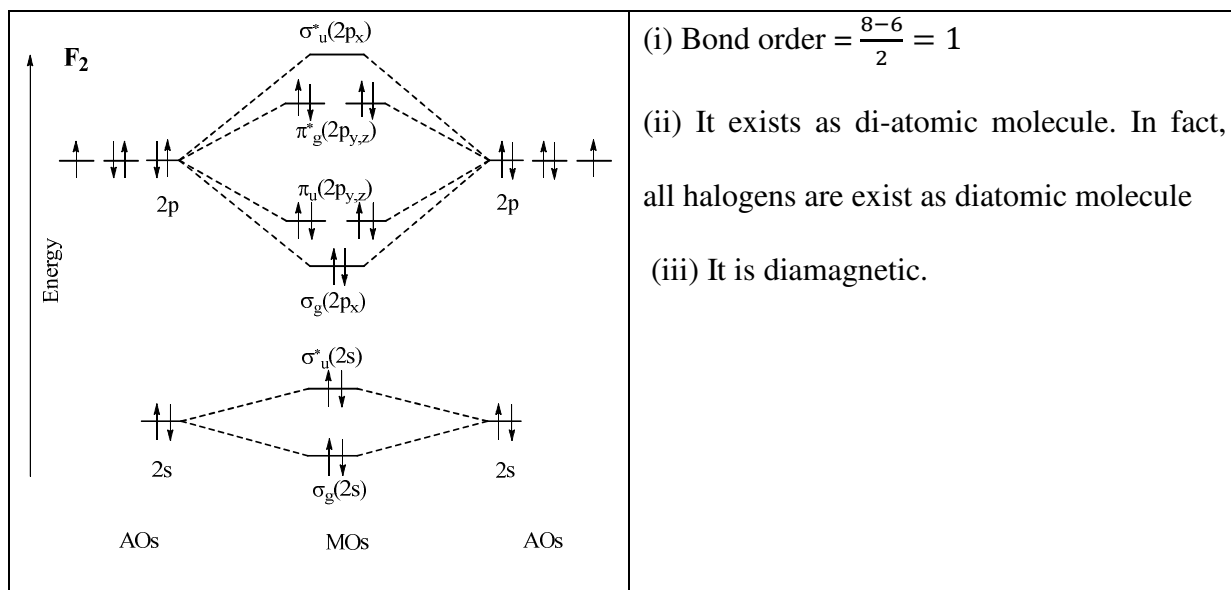
Comparison of ionisation energy of atomic nitrogen and molecular nitrogen:

It is observed that the first ionisation energy of the atomic nitrogen is less than that of the molecular nitrogen. $IE(N_2) = 1503$ kJ mol^{-1} > $IE(N) = 1402$ kJ mol^{-1}. In case of N_2, the electron is to be removed from HOMO, a BMO (σ_g) which is comparatively more stable than the corresponding AO of atomic nitrogen. This is why, N_2 requires higher energy for ionisation.

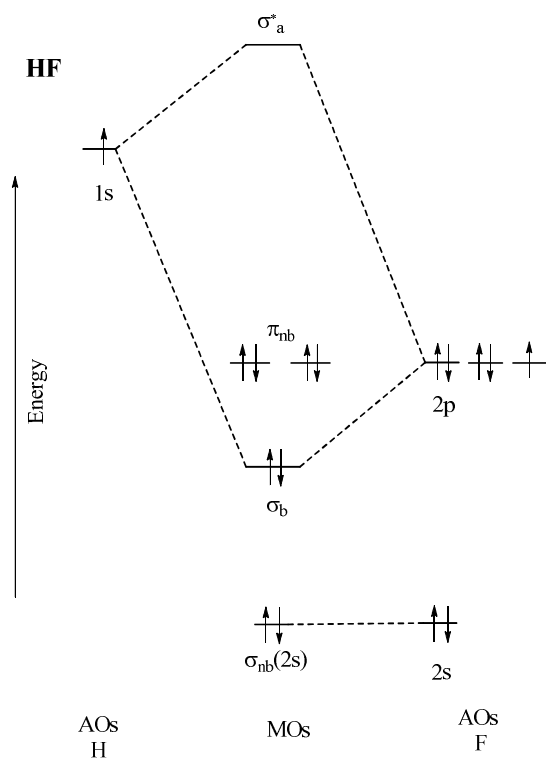|	
O₂ $\sigma^*_u(2p_x)$ $\pi^*_g(2p_{y,z})$ 2p 2p $\pi_u(2p_{y,z})$ $\sigma_g(2p_x)$ $\sigma^*_u(2s)$ 2s 2s $\sigma_g(2s)$ Energy AOs MOs AOs	(i) Bond order $= \dfrac{8-4}{2} = 2$ (ii) It shows existence of one pi-bond and a sigma bond. (iii) It contains two unpaired electron so paramagnetic. (iv) Ground state of O_2 is triplet instead of singlet (as expected from VBT). Actually triplet state is kinetically inert in most of the chemical reactions, but singlet O_2 is very much reactive. This is why singlet O_2 is toxic.

Comparison of ionisation energy of atomic oxygen and molecular oxygen:

It is observed that the first ionisation energy of the atomic oxygen is higher than that of the molecular oxygen. $IE(O) = 1314$ kJ mol^{-1} > $IE(O_2)$ 1164 kJ mol^{-1}. In case of O_2, the electron is to be removed from HOMO (i.e. SOMO), an ABMO (π^*_g) which is destabilized compared to the outermost AO of oxygen atom. This is why, O_2 requires less energy for its ionisation.

$\sigma^*_u(2p_x)$ **F₂** 2p $\pi^*_g(2p_{y,z})$ $\pi_u(2p_{y,z})$ 2p $\sigma_g(2p_x)$ $\sigma^*_u(2s)$ 2s $\sigma_g(2s)$ 2s AOs MOs AOs	(i) Bond order $= \frac{8-6}{2} = 1$ (ii) It exists as di-atomic molecule. In fact, all halogens are exist as diatomic molecule (iii) It is diamagnetic.

Molecular Orbital diagram of heteronuclear diatomic molecules

HF

(i) Bond order $= \dfrac{2-0}{2} = 1$

(ii) All the occupied energy levels remain predominantly on the fluorine atom and it is expecting the HF molecule to be polar with a partial negative charge on fluorine atom.
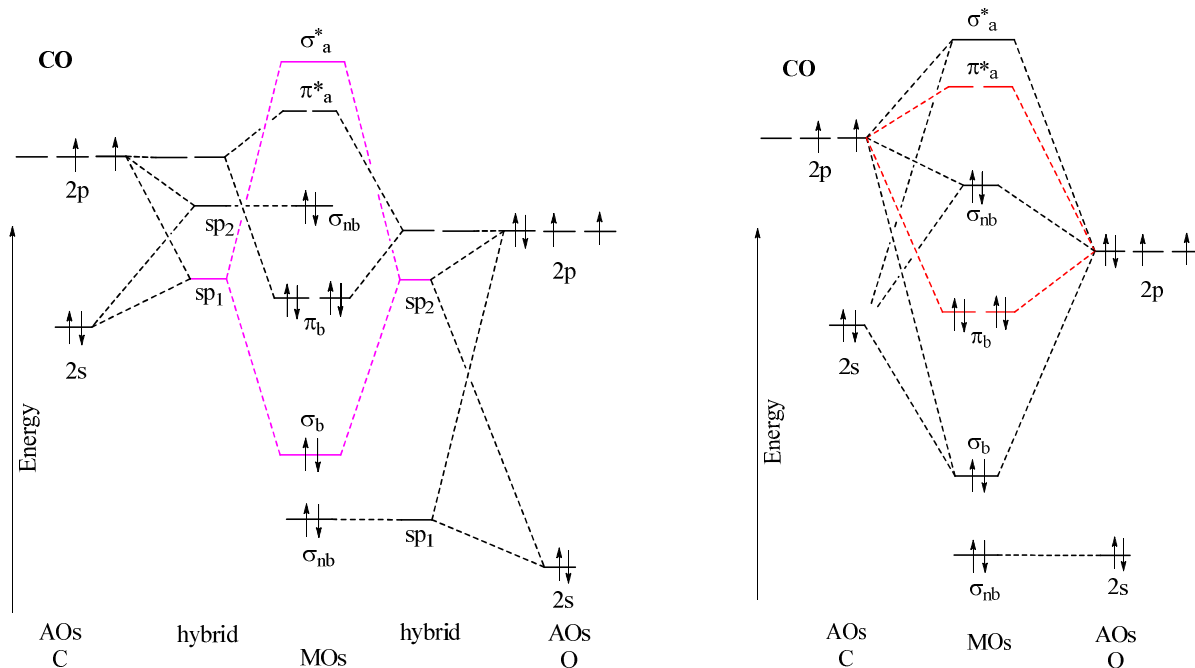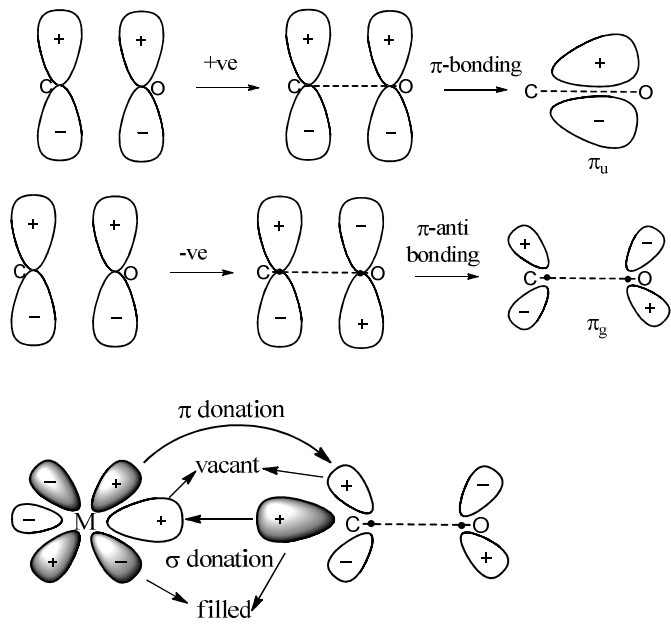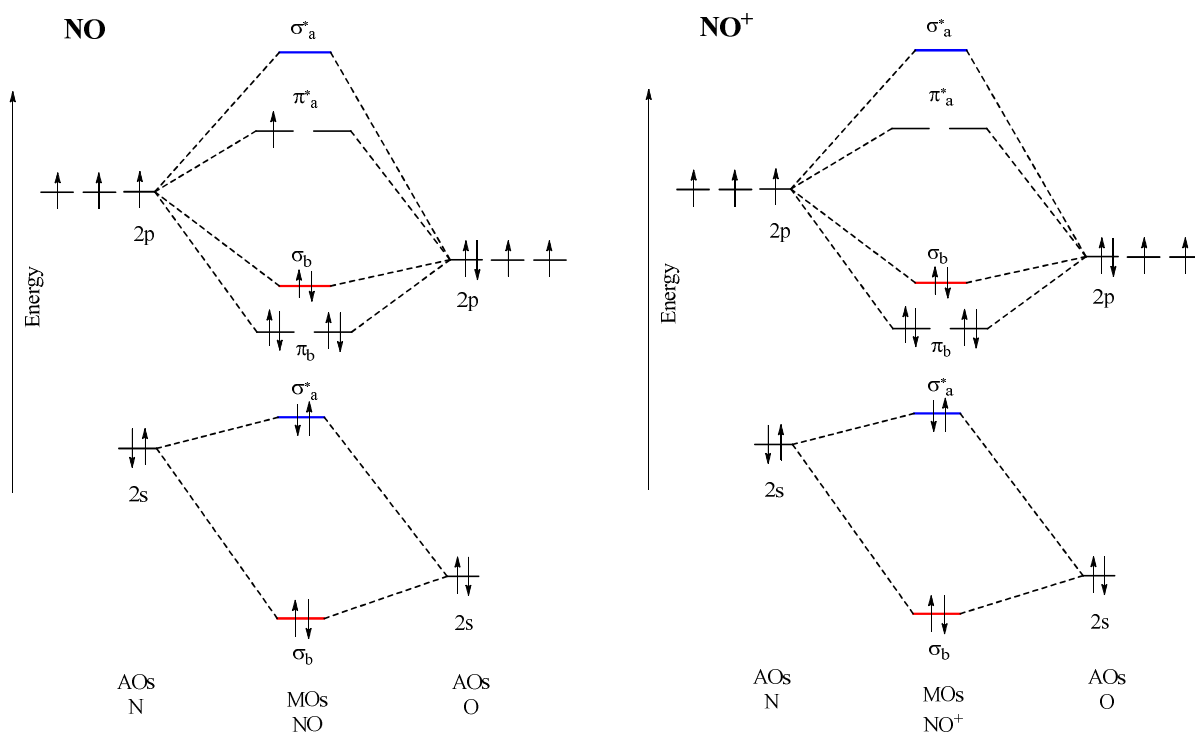
(i) Bond order $= \frac{6-0}{2} = 3$

(ii) HOMO is σ_{nb} orbital and LUMO is π_a^* orbital.

(iii) Lower dipole moment of CO can be explained by MO diagram. HOMO is σ_{nb} orbital, which is mainly a $2p_x$ orbital of carbon. Therefore, in CO there is finite electron density on carbon due to presence of lone pair. This lone pair of electron on carbon predominates over the bond pair of electron localized towards oxygen due to higher electronegativity. This give rise to lower dipole moment and negative end of dipole lies on carbon.

(iv) CO binds the metal ion trough carbon rather than more electronegative oxygen. MO diagram of CO predicting that HOMO (σ_{nb}) and LUMO (π_a^*) both orbitals are enriching with carbon orbital (2p) character. During bond formation with the metal ion, CO donates electrons of σ_{nb} (HOMO) form an σ bond and it is reinforced by strong π-bond through accepting electron to vacant π_a^*(LUMO). Thus, CO acts as a good σ donor and π acceptor through its carbon end. So, in CO, carbon is ligating atom not the oxygen atom.

NO

σ*ₐ

π*ₐ

2p

σ_b

2p

π_b

σ*ₐ

2s

2s

σ_b

AOs
N

MOs
NO

AOs
O

Energy

NO⁺

σ*ₐ

π*ₐ

2p

σ_b

2p

π_b

σ*ₐ

2s

2s

σ_b

AOs
N

MOs
NO⁺

AOs
O

Energy

(i) Bond order $= \frac{8-3}{2} = 2.5$

(ii) It is paramagnetic. The unpaired electron is present in the anti bonding orbital (π_a^*), which is delocalized over the whole molecule, though the π_a^* orbital possess more weightage of p-orbital of nitrogen. Since, the unpaired electron is not localized on a particular atom, it is reluctant to form dimer.

(iii) The HOMO (actually SOMO) is π_a^* whose energy is higher than that of AOs of nitrogen and oxygen. This is why, ionisation energy of NO is less than that of both nitrogen and oxygen. The first IP values (kJ mol⁻¹) of NO, N and O are: 894, 1402 and 1314 respectively. For this reason, NO readily lose this antibonding electron to form NO⁺.

(iv) The bond order of NO⁺ is $\frac{8-2}{2}$ =3. This is why, N-O bond length in NO⁺ (106 pm) is shorter than that in NO (113 pm).

(v) Like, CO and CN-, NO+ can acts as π acid ligand.

(vi) HOMO is σ_b and LUMO is π_a^*.

(v) In NO$^+$, σ donation occur through σ$_b$ (HOMO) orbital and π acceptance through vacant π_a^*(LUMO) orbital. Thus, NO$^+$ acts as a π-acid ligand. The positive charge on the ion will favour π acceptance but at the same time it will reduce the efficiency as an σ donation. The higher electronegativity of nitrogen compared to carbon will make NO$^+$ a stronger π acid ligand.

(vi) π acidity order is NO$^+$ > CO > CN$^-$ and σ donation order CN$^-$ > CO > NO$^+$
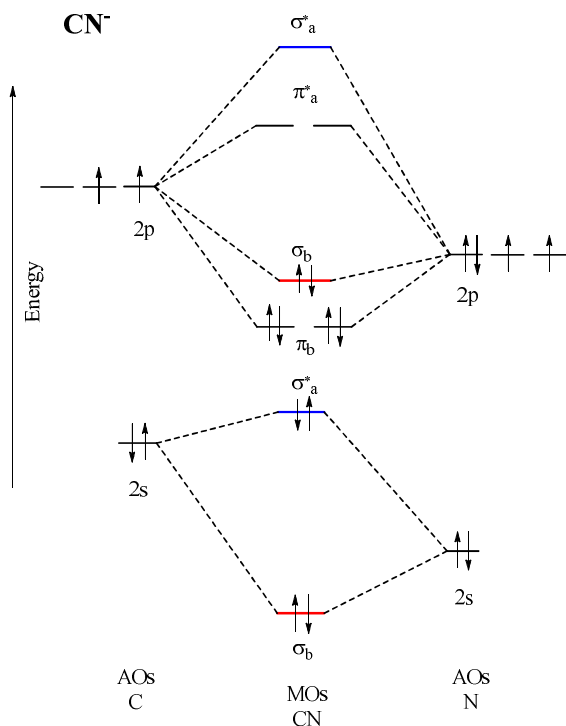
(i) Bond order $= \frac{8-2}{2} = 3$

(ii) The CN⁻ is isoelectronic with CO, NO⁺, N₂ (10 valence electrons).

(iii) Like CO and NO⁺, it acts as π-acid ligand.

(iv) HOMO is σ_b and LUMO is π_a^*.

(v) CN⁻ donates electrons of σ_b (HOMO) to form an σ bond and takes back the electron by to vacant π_a^*(LUMO) to form π-bond. Thus, CN⁻ acts as a π-acid ligand. The negative charge on the ion will favour σ donation but at the same time it will reduce the efficiency as a π acceptor. The lower electronegativity of nitrogen compared to oxygen will make CN- a poorer π acid ligand.

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