Inorganic Chemistry

M.S.C. / First Semester

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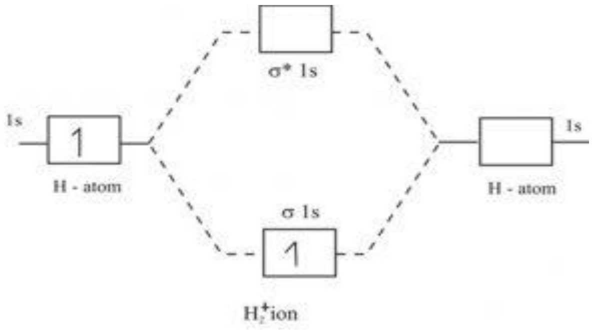
Molecular Orbital Configurations of Some Homonuclear Diatomic Species

Homonuclear diatomic molecules or ions have two identical atoms linked together. These are A_2 type species.

(i) The hydrogen molecule ion , H_2^+ : This ion has one hydrogen atom and one H^+ ion linked together. Each has 1s-orbital. Using LACO method two 1s-orbitals will combine to give two molecular orbitals. σ (1s) and σ*(1s), the only electron will be accommodated on σ (1s)

Thus, bond order for H_2^+ =1/2(1-0) =1/2

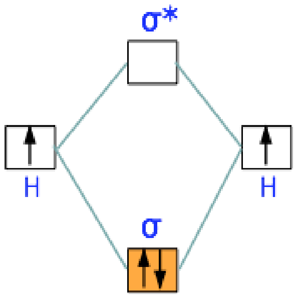
H_2^+ ion can exist but it is unstable. It is paramagnetic in nature. The bond length is 104 pm. Its bond dissociation energy is 269 kJ mol^{-1}.



(ii) The hydrogen molecule, H_2: It is formed from 1s^1 atomic orbitals of two atoms. The atomic orbitals (1s^1) will combine to form two molecular orbitals σ(1s) and σ*(1s) remains vacant.

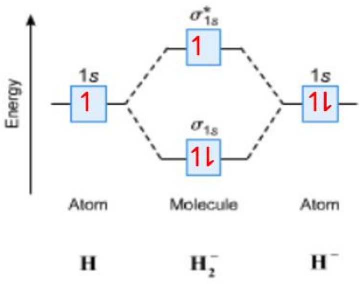
Thus, bond order for H_2 =1/2 (2-0) = 1

It is stable and diamagnetic in nature . It has single covalent bond . Its bond dissociation energy is 438 kJ mol $^{-1}$. The bond length is 74 pm



dihydrogen H_2

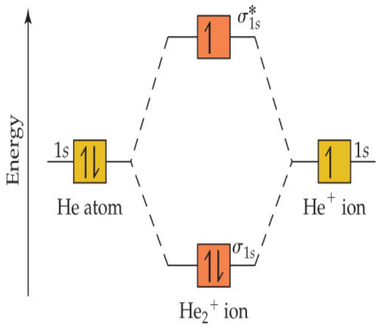
(iii) The hydrogen molecule ion , H_2^{-1} : It is formed by linking hydrogen atom with hydrogen ion , H^{-1}. Both have 1s orbitals. These will combine to form two molecular orbitals σ(ls) and σ*(1s).These available electrons are accommodated as σ(ls)^2 and σ*(1s)^1



Thus , bond order for H_2^{-1}= 1/2 (2-1) = 1/2   It is unstable and paramagnetic in nature

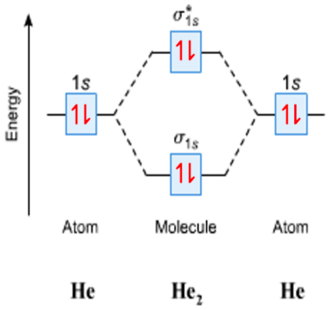
(iv) Helium molecule , He_2^+ : It is formed by linking helium atom with helium ion , He^+ . Both have 1s-orbitals . These will combine to form two molecular orbitals σ(1s) and $\sigma^*(1s)$. Three electrons are accommodated as $\sigma(1s)^2$ and $\sigma^*(1s)^1$.

Thus, bond order for He_2^+ = 1/2 (2-1) = 1/2 .



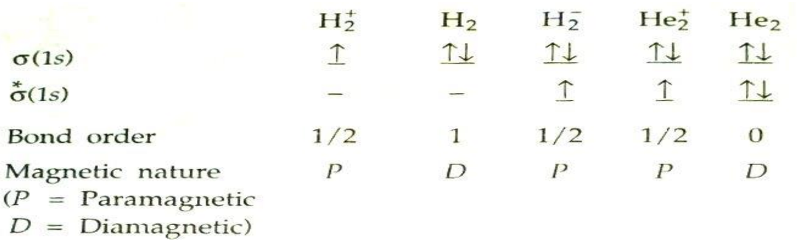
The value of bond order indicates that He_2^+ can exist but is unstable . The bond dissociation energy is 242 kJmol^{-1}.It is paramagnetic in nature . Both H_2^{-1} and He_2^+ have same number of electrons in the antibonding orbitals . Both have same stability , similar bond dissociation energy and similar bond lengths

(v) Helium molecule , He_2: It is formed by linking two helium atoms . Both have 1s-orbitals . These will combine to form two molecular orbitals σ(ls) and $\sigma^*(1s)$. Four available electrons are accommodated as $\sigma(ls)^2$ and $\sigma^*(1s)^2$.



Thus, bond order for Hey = 1/2(2-2) = 0

Hence, there can be no possibility for the existence of He_2 molecule



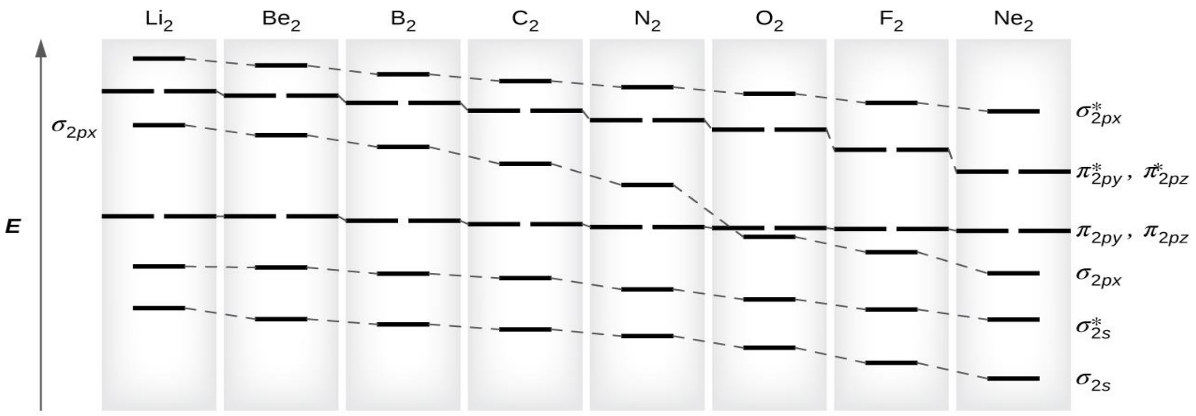
	H_2^+	H_2	H_2^-	He_2^+	He_2
σ(1s)	↑	↑↓	↑↓	↑↓	↑↓
$\overset{*}{\sigma}(1s)$	–	–	↑	↑	↑↓
Bond order	1/2	1	1/2	1/2	0
Magnetic nature (P = Paramagnetic D = Diamagnetic)	P	D	P	P	D

The Diatomic Molecules of the Second Period

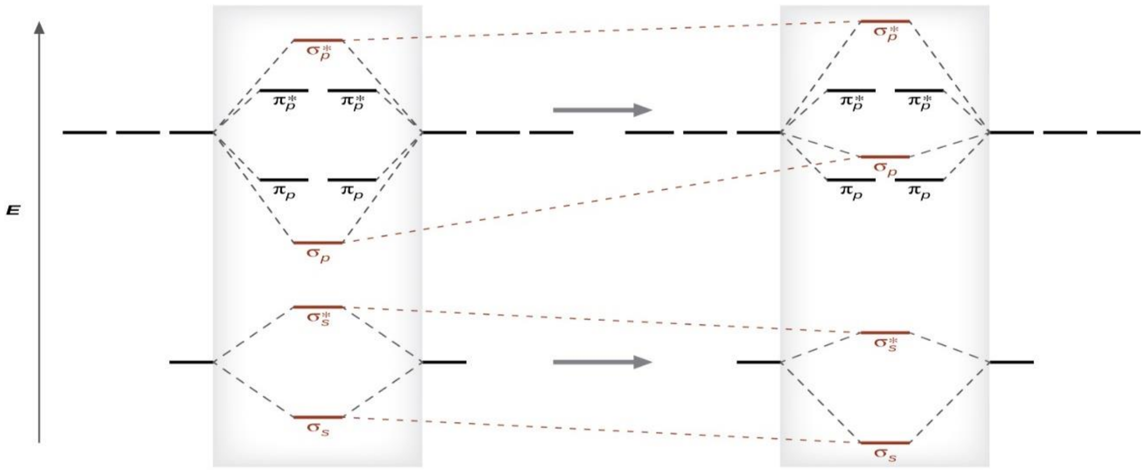
Eight possible homonuclear diatomic molecules might be formed by the atoms of the second period of the periodic table: Li_2, Be_2, B_2, C_2, N_2, O_2, F_2, and Ne_2. However, we can predict that the Be_2 molecule and the Ne_2 molecule would not be stable. We can see this by a consideration of the molecular electron configurations

We predict valence molecular orbital electron configurations just as we predict electron configurations of atoms. Valence electrons are assigned to valence molecular orbitals with the lowest possible energies. Consistent with Hund’s rule, whenever there are two or more degenerate molecular orbitals, electrons fill each orbital of that type singly before any pairing of electrons takes place.

As we saw in valence bond theory, σ bonds are generally more stable than π bonds formed from degenerate atomic orbitals. Similarly, in molecular orbital theory, σ orbitals are usually more stable than π orbitals. However, this is not always the case. The MOs for the valence orbitals of the second period are shown in Figure below. Looking at Ne_2 molecular orbitals, we see that the order is consistent with the generic diagram shown in the previous section. However, for atoms with three or fewer electrons in the *p* orbitals (Li through N) we observe a different pattern, in which the σ_p orbital is higher in energy than the π_p set. Obtain the molecular orbital diagram for a homonuclear diatomic ion by adding or subtracting electrons from the diagram for the neutral molecule.



This switch in orbital ordering occurs because of a phenomenon called **s-p mixing**. s-p mixing does not create new orbitals; it merely influences the energies of the existing molecular orbitals. The σ_s wavefunction mathematically combines with the σ_p wavefunction, with the result that the σ_s orbital becomes more stable, and the σ_p orbital becomes less stable Figure below. Similarly, the antibonding orbitals also undergo s-p mixing, with the σ_{s*} becoming more stable and the σ_{p*} becoming less stable.



s-p mixing occurs when the *s* and *p* orbitals have similar energies. When a single *p* orbital contains a pair of electrons, the act of pairing the electrons raises the energy of the orbital. Thus the 2*p* orbitals for O, F, and Ne are higher in energy than the 2*p* orbitals for Li, Be, B, C, and N. Because of this, O_2, F_2, and N_2 only have negligible s-p mixing (not sufficient to change the energy ordering), and their MO diagrams follow the normal pattern. All of the other period 2 diatomic molecules do have s-p mixing, which leads to the pattern where the σ_p orbital is raised above the π_p set.

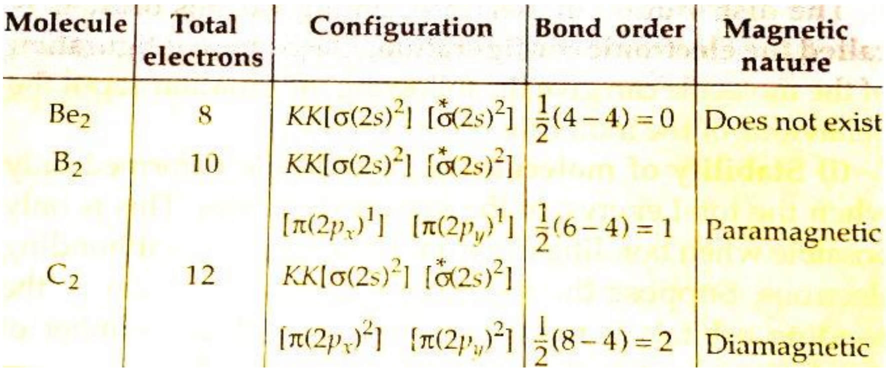
(vi) Lithium molecule, (Li_2): The electronic configuration of lithium atom (Z=3) is $1s^2\ 2s^1$ Thus , total number of electrons in Li_2 molecule would be 6. The electronic configuration of Li_2 molecule may be written as $\sigma(1s)^2\ \sigma^*(1s)^2\ \sigma(2s)^2$.This may be written as KK[$\sigma(2s)^2$]. Where KK represents fully filled inner K shells in two atoms, i.e., [$\sigma(1s)^2$][$\sigma^*(1s)^2$] . These are also called non - bonding orbitals.

It is clear from the electronic configuration of Li_2 molecule that there are 4 bonding electrons and 2 antibonding electrons .

Bond order = $N_b - N_a/2 = 4-2/2 = 1$

Thus, Li_2 molecule is stable . It has one single sigma bond. The bond dissociation energy is 110 kJ mol^{-1} and the bond length is 265 pm . As it has no unpaired electron, it is diamagnetic in nature. Li_2 molecules are found to exist in vapour state

(vii) Be_2,B_2 and C_2 molecules: The electronic configurations along with bond orders and magnetic nature of these molecules are given below :



Molecule	Total electrons	Configuration	Bond order	Magnetic nature
Be_2	8	$KK[\sigma(2s)^2]\ [\overset{*}{\sigma}(2s)^2]$	$\frac{1}{2}(4-4)=0$	Does not exist
B_2	10	$KK[\sigma(2s)^2]\ [\overset{*}{\sigma}(2s)^2]$ $[\pi(2p_x)^1]\ \ [\pi(2p_y)^1]$	$\frac{1}{2}(6-4)=1$	Paramagnetic
C_2	12	$KK[\sigma(2s)^2]\ [\overset{*}{\sigma}(2s)^2]$ $[\pi(2p_x)^2]\ \ [\pi(2p_y)^2]$	$\frac{1}{2}(8-4)=2$	Diamagnetic

The bond in B_2 is weak π bond . The bond dissociation energy is 290 kJ mol^{-1} and bond length is 159 pm . C_2 molecule has double bond consisting both the π bonds as 4 electrons are present in pi molecular orbitals. Generally, in most of the molecules , the double bond consists of one sigma and one pi bond like Li_2 a molecules , C_2 molecule also exist in vapour state.

Comparison of stabilities of H_2 , Li_2 and B_2

The three molecules, *i.e.*, H_2, Li_2 and B_2 possess the same value or bond order (*i.e.*,1) but their stabilities are different. H_2 molecule has maximum stability out of these molecules

This can be explained as follows :

1- Li - Li bond length is much larger than H - H bond length
2- The overlapping of 2s-2s atomic orbitals in lithium is less effective than the overlapping of 1s-1s atomic orbitals in hydrogen
3- Li_2 molecule has two electrons in antibonding orbital while H_2 , has no electrons in the antibonding orbital

4- In Li_2 molecule , the electrons in σ(2s) molecular orbital are shielded by inner σ(1s) electrons . Thus, there is less attraction between electrons in σ(2s) and the nuclei

Because of above reasons , Li_2 is less stable than H_2

Boron atom is smaller in size than Li atom and the B_2 molecule has 6 electrons in the bonding orbitals while Li_2 molecule has four electrons in the bonding orbitals . Hence , B_2 is more stable than Li_2

Thus, the order of stability is $H_2 > B_2 > Li_2$

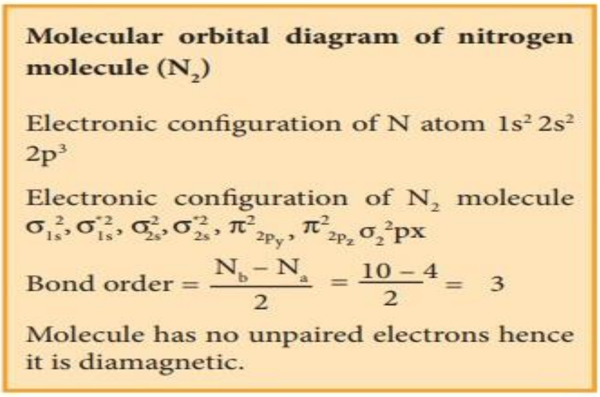
(viii) Nitrogen molecule(N_2) : The electronic configuration of nitrogen is $1s^2\ 2s^2\ 2p^3$ In nitrogen molecule , there are 14 electrons of which 4 are in the K shell and are non-bonding. Each atom contributes four atomic orbitals and thus the molecule consists of 8 molecular orbitals. Then ten electrons are alloted to molecular orbitals as follows

$$KK\ \sigma(2s)^2\ \sigma^*(2s)^2\ \pi(2p_x)^2\ \pi(2p_y)^2\ \pi(2p_z)^2$$

where KK denotes the closed K shell structure $\sigma(1s)^2\ \sigma^*(1s)^2$

Bond order =1/2(8-2) =3 or = ½(10-4) = 3

Thus, nitrogen molecule has three bonds, one sigma and two pi so can be writing electron configuration of N_2 molecule as $(\sigma_{1s}^{b})^2\ (\sigma_{1s}^{*})^2\ (\sigma_{2s}^{b})^2(\sigma_{1s}^{*})^2(\sigma_{2px}^{b})^2\ (\pi_{2py,z}^{b})^4$ .The molecule is diamagnetic. It has high bond dissociation energy (945kJ mol^{-1}) and bond length is 110 pm .



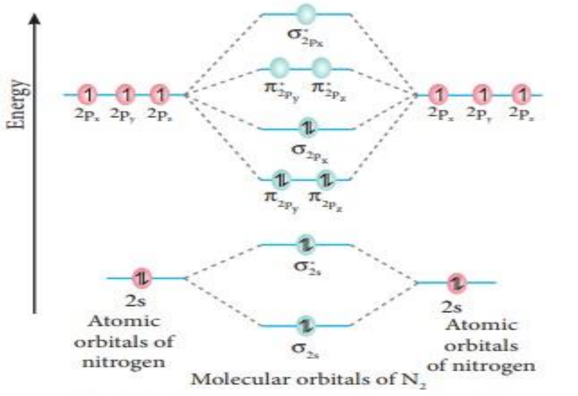
Molecular orbital diagram of nitrogen molecule (N_2)

Electronic configuration of N atom $1s^2\,2s^2\,2p^3$

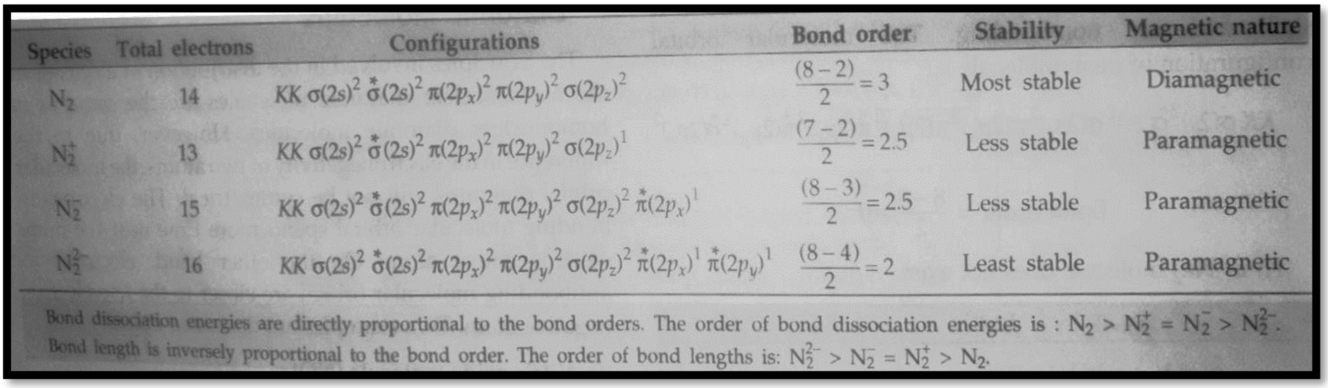
Electronic configuration of N_2 molecule $\sigma_{1s}^{2}, \sigma_{1s}^{*2}, \sigma_{2s}^{2}, \sigma_{2s}^{*2}, \pi^2_{2p_y}, \pi^2_{2p_z}\ \sigma_2{}^2px$

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{10-4}{2} = 3$$

Molecule has no unpaired electrons hence it is diamagnetic.



(ix) N_2^+, N_2^- and N_2^{2-} ions: The configurations of N_2^+, N_2^- and N_2^{2-} ions along with their bond orders, stability and their magnetic character are tabulated below:



Species	Total electrons	Configurations	Bond order	Stability	Magnetic nature
N_2	14	$KK\ \sigma(2s)^2\ \overset{*}{\sigma}(2s)^2\ \pi(2p_x)^2\ \pi(2p_y)^2\ \sigma(2p_z)^2$	$\frac{(8-2)}{2}=3$	Most stable	Diamagnetic
N_2^+	13	$KK\ \sigma(2s)^2\ \overset{*}{\sigma}(2s)^2\ \pi(2p_x)^2\ \pi(2p_y)^2\ \sigma(2p_z)^1$	$\frac{(7-2)}{2}=2.5$	Less stable	Paramagnetic
N_2^-	15	$KK\ \sigma(2s)^2\ \overset{*}{\sigma}(2s)^2\ \pi(2p_x)^2\ \pi(2p_y)^2\ \sigma(2p_z)^2\ \overset{*}{\pi}(2p_x)^1$	$\frac{(8-3)}{2}=2.5$	Less stable	Paramagnetic
N_2^{2-}	16	$KK\ \sigma(2s)^2\ \overset{*}{\sigma}(2s)^2\ \pi(2p_x)^2\ \pi(2p_y)^2\ \sigma(2p_z)^2\ \overset{*}{\pi}(2p_x)^1\ \overset{*}{\pi}(2p_y)^1$	$\frac{(8-4)}{2}=2$	Least stable	Paramagnetic

Bond dissociation energies are directly proportional to the bond orders. The order of bond dissociation energies is : $N_2 > N_2^+ = N_2^- > N_2^{2-}$.
Bond length is inversely proportional to the bond order. The order of bond lengths is: $N_2^{2-} > N_2^- = N_2^+ > N_2$.

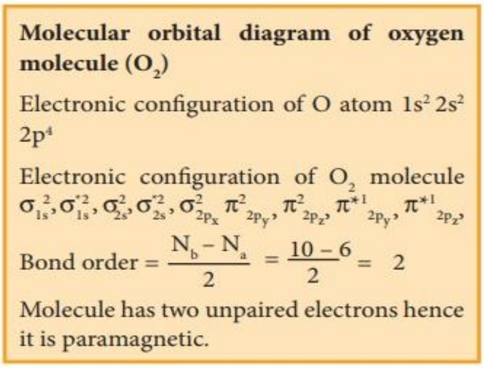
(x) Oxygen molecule : The electronic configuration of oxygen is $1s^2\ 2s^2\ 2p^4$ In oxygen molecule , there are 16 electrons of which 4 are in the K shell and are non-bonding . Each atom contributes four atomic orbitals and thus, the molecule consists of 8 molecular orbitals. The 12 electrons are alloted to molecular orbitals as follows:

$$KK\ \sigma(2s)^2\ \sigma^*(2s)^2\ \sigma(2p_z)^2\ \pi(2p_x)^2\ \pi(2p_y)^2\ \pi^*(2p_x)^1\ \pi^*(2p_y)^1$$

Note : $\sigma(2p_z)$ is filled first and then $\pi(2p_x)$ and $\pi(2p_y)$ molecular orbitals are filled

Bond order =1/2(8-4)= 2

The oxygen molecule has two bonds (one sigma and one pi). The last two molecular orbitals are singly occupied hence the molecule is paramagnetic in nature. The molecule is stable. The bond dissociation energy is 497 kj mol^{-1} and bond length 121 pm.



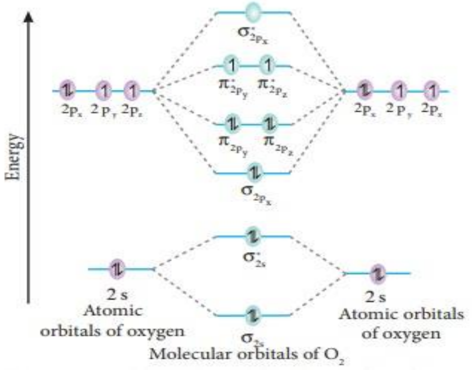
Molecular orbital diagram of oxygen molecule (O_2)

Electronic configuration of O atom $1s^2\ 2s^2\ 2p^4$

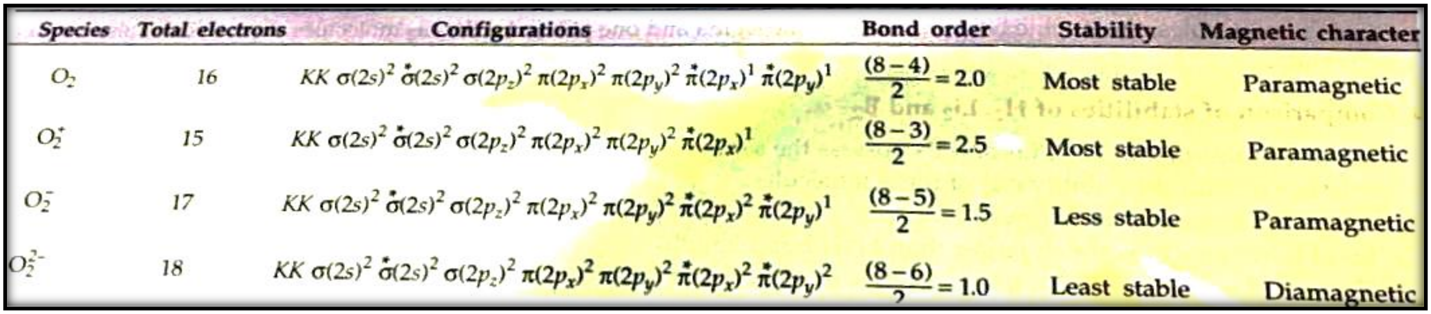
Electronic configuration of O_2 molecule $\sigma_{1s}^2, \sigma_{1s}^{*2}, \sigma_{2s}^2, \sigma_{2s}^{*2}, \sigma_{2p_x}^2\ \pi^2_{2p_y}, \pi^2_{2p_z}, \pi^{*1}_{2p_y}, \pi^{*1}_{2p_z},$

Bond order = $\frac{N_b - N_a}{2} = \frac{10-6}{2} = 2$

Molecule has two unpaired electrons hence it is paramagnetic.



(i) **O_2^+, O_2^- and O_2^{2-} ions** : The configurations of O_2^+, O_2^- and O_2^{2-} ions along with their bond orders , stability and their magnetic character are tabulated ahead :



Species	Total electrons	Configurations	Bond order	Stability	Magnetic character
O_2	16	$KK\ \sigma(2s)^2\ \overset{*}{\sigma}(2s)^2\ \sigma(2p_z)^2\ \pi(2p_x)^2\ \pi(2p_y)^2\ \overset{*}{\pi}(2p_x)^1\ \overset{*}{\pi}(2p_y)^1$	$\frac{(8-4)}{2} = 2.0$	Most stable	Paramagnetic
O_2^+	15	$KK\ \sigma(2s)^2\ \overset{*}{\sigma}(2s)^2\ \sigma(2p_z)^2\ \pi(2p_x)^2\ \pi(2p_y)^2\ \overset{*}{\pi}(2p_x)^1$	$\frac{(8-3)}{2} = 2.5$	Most stable	Paramagnetic
O_2^-	17	$KK\ \sigma(2s)^2\ \overset{*}{\sigma}(2s)^2\ \sigma(2p_z)^2\ \pi(2p_x)^2\ \pi(2p_y)^2\ \overset{*}{\pi}(2p_x)^2\ \overset{*}{\pi}(2p_y)^1$	$\frac{(8-5)}{2} = 1.5$	Less stable	Paramagnetic
O_2^{2-}	18	$KK\ \sigma(2s)^2\ \overset{*}{\sigma}(2s)^2\ \sigma(2p_z)^2\ \pi(2p_x)^2\ \pi(2p_y)^2\ \overset{*}{\pi}(2p_x)^2\ \overset{*}{\pi}(2p_y)^2$	$\frac{(8-6)}{2} = 1.0$	Least stable	Diamagnetic

The bond dissociation energies and stability are in the given order: $O_2^+ > O_2 > O_2^- > O_2^{2-}$ The bond lengths are in the given order : $O_2^{2-} > O_2^- > O_2 > O_2^+$

(ii) **Fluorine molecule**: Electronic configuration of F-atom (Z=9) is $1s^2 2s^2 2p^5$.Total number of electrons in F_2 molecule is 18 of which 4 are in K shell and are non-bonding. Each atom contributes four atomic orbitals. The 14 electrons are alloted to molecular orbitals as follows:

$$KK\ \sigma(2S)^2\ \sigma^*(2S)^2\ \sigma(\ 2p_z)^2\ \pi(2p_x)^2\ \pi(2p_y)^2\ \pi^*(2p_x)^2\ \pi^*(2p_y)^2$$

Bond order =1/2(8-6)=1

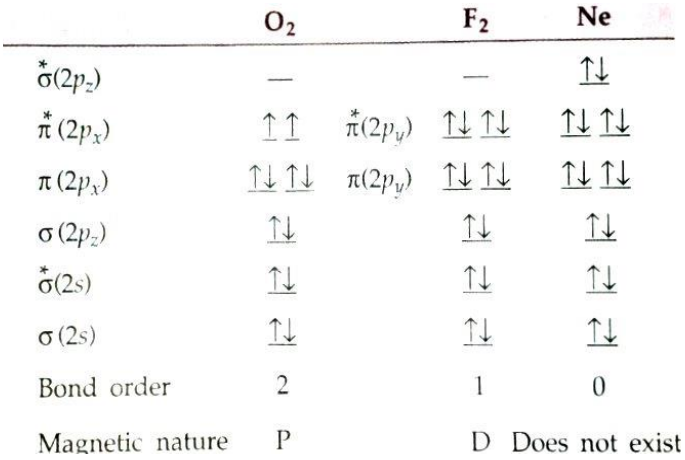
F_2 molecule has one single bond. The molecule is diamagnetic as no unpaired electron is present in the molecule. The bond dissociation energy is 159 kJ mol^{-1} and bond length is 143 pm

(iii) **Neon molecule (Ne_2):** The electronic configuration of neon atom is $1s^2 2s^2 2p^6$. In Ne_2 molecule 20 electrons are present , out of which four electrons are in K shell and are non-bonding . The molecular orbital configuration of neon molecule is:

$KK\ \sigma(2S)^2\ \sigma^*(2S)^2\ \sigma(2p_z)^2\ \pi(2p_x)^2\ \pi(2p_y)^2\ \pi^*(2p_x)^2\ \pi^*(2p_y)^2\ \sigma^*(2p_z)^2$

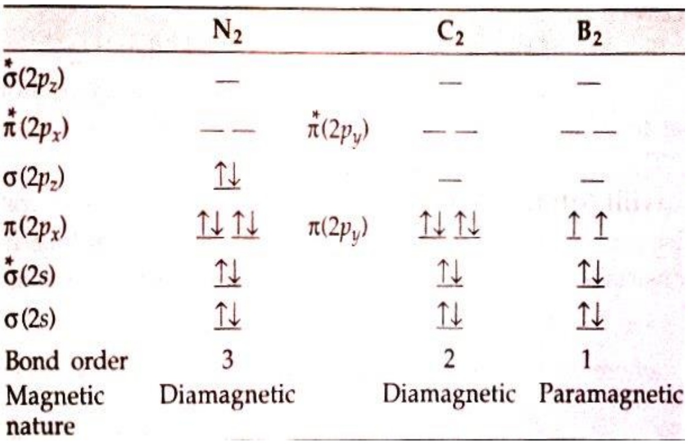
Bond order = ½(8-8)= 0

Thus, Ne_2 molecule does not exist.



	O_2		F_2	Ne
$\overset{*}{\sigma}(2p_z)$	—		—	↑↓
$\overset{*}{\pi}(2p_x)$	↑ ↑	$\overset{*}{\pi}(2p_y)$	↑↓ ↑↓	↑↓ ↑↓
$\pi(2p_x)$	↑↓ ↑↓	$\pi(2p_y)$	↑↓ ↑↓	↑↓ ↑↓
$\sigma(2p_z)$	↑↓		↑↓	↑↓
$\overset{*}{\sigma}(2s)$	↑↓		↑↓	↑↓
$\sigma(2s)$	↑↓		↑↓	↑↓
Bond order	2		1	0
Magnetic nature	P		D	Does not exist

Molecular occupancy of homonuclear diatomic molecules of O_2 , F_2 and Ne_2



	N_2		C_2	B_2
$\overset{*}{\sigma}(2p_z)$	—		—	—
$\overset{*}{\pi}(2p_x)$	— —	$\overset{*}{\pi}(2p_y)$	— —	— —
$\sigma(2p_z)$	↑↓		—	—
$\pi(2p_x)$	↑↓ ↑↓	$\pi(2p_y)$	↑↓ ↑↓	↑ ↑
$\overset{*}{\sigma}(2s)$	↑↓		↑↓	↑↓
$\sigma(2s)$	↑↓		↑↓	↑↓
Bond order	3		2	1
Magnetic nature	Diamagnetic		Diamagnetic	Paramagnetic

Molecular occupancy of homonuclear diatomic molecules of B_2, C_2 and N_2

Structures of Heteronuclear Diatomic Molecules

The principles involved in the distribution of electrons in the heteronuclear diatomic molecules are the same as in homonuclear diatomic molecules. However, due to the difference in the electronegativity of two atoms, the molecular orbital diagrams will not be symmetrical. The electrons in bonding molecular orbital spend more time near the more electronegative atom. On the other hand, electrons in antibonding molecular orbital are closer to the less electro negative atom. Two examples are discussed below:

(i) Nitric oxide molecule (NO): Total valence electrons = 5 + 6 = 11

The distribution of the electrons in various molecular orbitals of NO molecule is done in the following manner:

$KK\ \sigma(2S)^2\ \sigma^*(2S)^2\ \sigma(2p_z)^2\ \pi(2p_x)^2\ \pi(2p_y)^2\ \pi^*(2p_x)^1$

Bond order =1/2 (8-3) = 2.5

The presence of one unpaired electron makes the molecule less stable. It is paramagnetic in nature.

Configuration of NO^+ (Valence electrons =10)

$KK\ \sigma(2S)^2\ \sigma^*(2S)^2\ \sigma(2p_z)^2\ \pi(2p_x)^2\ \pi(2p_y)^2$

Bond order =1/ 2 (8-2) = 3

Configuration of NO^- (Valence electrons = 12)

$KK\ \sigma(2S)^2\ \sigma^*(2S)^2\ \sigma(2p_z)^2\ \pi(2p_x)^2\ \pi(2p_y)^2\ \pi^*(2p_x)^1\ \pi^*(2p_y)^1$

Bond order =1/ 2 (8 - 4) = 2

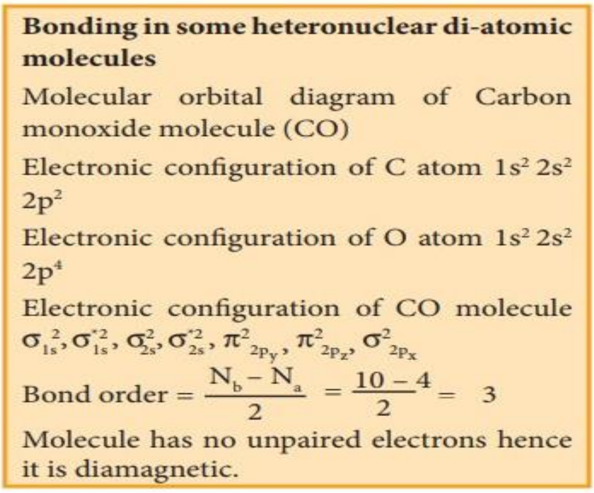
(i) **Carbon monoxide molecule (CO):** Total valence electrons = 4 + 6 = 10

The distribution of electrons in various molecular orbitals of CO molecule is done in the following manner:

$KK\ \sigma(2S)^2\ \sigma^*(2S)^2\ \pi(2p_x)^2\ \pi(2p_y)^2\ \sigma(2p_z)^2$

Bond order =1/2(8–2) = 3

It represents one sigma bond and two pi-bonds . The molecule is stable and diamagnetic in nature.



Bonding in some heteronuclear di-atomic molecules

Molecular orbital diagram of Carbon monoxide molecule (CO)

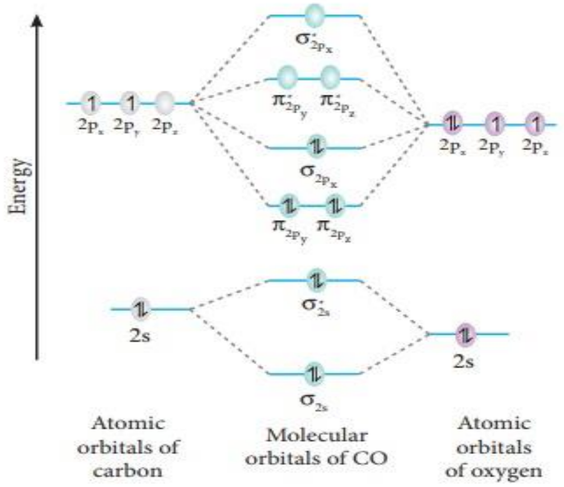
Electronic configuration of C atom $1s^2\ 2s^2\ 2p^2$

Electronic configuration of O atom $1s^2\ 2s^2\ 2p^4$

Electronic configuration of CO molecule $\sigma_{1s}^2, \sigma_{1s}^{*2}, \sigma_{2s}^2, \sigma_{2s}^{*2}, \pi^2_{2p_y}, \pi^2_{2p_z}, \sigma^2_{2p_x}$

Bond order $= \frac{N_b - N_a}{2} = \frac{10-4}{2} = 3$

Molecule has no unpaired electrons hence it is diamagnetic.



(ii) **CN^- ion:** Total number of valence electrons = 10

The configuration of CN^- ion is :

$KK\ \sigma(2S)^2\ \sigma^*(2S)^2\ \pi(2p_x)^2\ \pi(2p_y)^2\ \sigma(2p_z)^2$

Bond order =1/2(8–2) = 3

The ion is stable and diamagnetic in nature.

(iii) BN molecule: Total number of valence electrons = 8

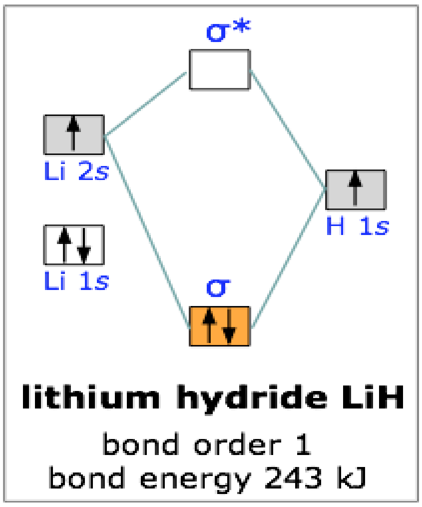
The configuration of BN molecule is:

$KK\ \sigma(2S)^2\ \sigma^*(2S)^2\ \pi(2p_x)^2\ \pi(2p_y)^2$

Bond order = 1/2(6-2) = 2

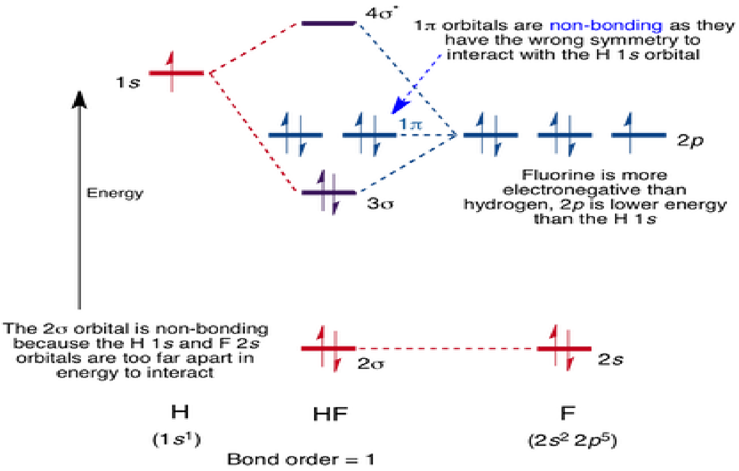
The molecule is stable and diamagnetic in nature.

(iiv) Lithium Hydride Molecular



Molecular Orbital Diagram for the HF Molecule

Interaction occurs between the 1s orbital on hydrogen and the 2p orbital in fluorine causing the formation of a sigma-bonding and a sigma-antibonding molecular orbital, as shown below.



Comparison of Valence Bond Theory and Molecular Orbital Theory

Points of resemblance

(i) For the covalent bond formation, orbital overlap is necessary in both the theories.
(ii) The orbitals responsible for overlapping must have nearly same energies and proper orientation according to both the theories.
(iii) According to both the theories, the electron density is high in the region between the atomic nuclei.
(iv) Both the theories account for the directional nature of the bond.
(v) Both the theories predict the non - existence of He_2 and Ne_2 molecules.
(vi) Both the theories are approximate.

Points of difference

(i) In valence bond theory, atomic orbitals of the combing atoms do not lose their individual character to a great extent but in molecular orbital theory atomic orbitals of the combining atoms lose their identity and new molecular orbitals come into existence.
(ii) According to valence bond theory electron density increases in the region of overlap while in molecular orbital theory, there is increase as well as decrease in electron density in the region of orbital overlap.

(iii) In valence bond theory, resonance plays its part while in molecular orbital theory resonance has no role to play.

(iv) Mathematically, valence bond theory is quite easy to apply while molecular orbital theory is difficult to apply.

(v) Valence bond theory does not explain paramagnetic nature of O_2 molecule while molecular orbital theory explains the paramagnetic behavior of O_2 molecule.

(vi) Valence bond theory fails to explain the existence of H_2^+ ion while molecular orbital theory explains the existence of H_2^+ ion.