CHEMICAL BONDING AND MOLECULAR STRUCTURE
BONDING IN SOME HOMONUCLEAR DIATOMIC MOLECULES

Molecular Orbital Configuration of Some Homo-Nuclear Diatomic Species: omonuclear diatomic molecules or ions have two identical atoms linked together. These are A2 type species.

(i) The hydrogen molecule ion, H_2^+: This ion has one hydrogen atom and one H+ ion linked together. Each has Is-orbital Using LACO method two Is-orbitals will combine to give two molecular orbitals. σ(1s) and σ *(1s), the only electron will be accommodated on σ1s. Thus,

$$bond\ order\ for\ H_2^+ = \frac{1}{2}\,(1-0) = \frac{1}{2}$$

H2 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 1s1atomic orbitals of two atoms. The atomic orbitals ($1s^1$) will combine to form two molecular orbitals σ (1s) and σ *(ls). Two electrons are accommodated on σ (1s) and σ **(1s)* remains vacant. Thus,

$$bond\ order\ for\ H_2 = \frac{1}{2}\,(2-0) = 1$$

It is stable and diamagnetic in nature. It has single covalent bond. Its bond dissociation energy is 438 kJ mol^{-1} . The bond length is74 pm.

(iii) The hydrogen molecule ion, He_2^+: It is formed by linking hydrogen atom with hydrogen ion, H-. Both have 1s-orbitals. These will combine to form two molecular orbitals σ (1s) and σ*(1s). These available electrons are accommodated as σ(1s)2 and σ*(1s)1. Thus,

$$bond\ order\ for\ He_2^+ = \frac{1}{2}\,(2-1) = \frac{1}{2}$$

The value of bond order indicates that He2+ can exist but is unstable. The bond dissociation energy is 242 kJ mol^{-1}. It is paramagnetic in nature. Both H2- and He_2^+ have same number of electrons in the antibonding orbitals. Both have same stability, similar bond dissociation energy and similar bond lengths.

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

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(v) Helium molecule, He_2: The electronic configuration of helium atom is $1s^2$. Each helium atom contains 2 electrons, therefore, in He_2 molecule there would be 4 electrons. These electrons will be accommodated in σ1sand σ*1s molecular orbitals leading to electronic configuration:

He_2 : $(\sigma 1s)^2$ $(\sigma^* 1s)^2$ Bond order of He_2 is ½(2 – 2) = 0

He_2 molecule is therefore unstable and does not exist.

Similarly, it can be shown that Be_2 molecule $(\sigma 1s)^2$ $(\sigma^* 1s)^2$ $(\sigma 2s)^2$ $(\sigma^* 2s)^2$ also does not exist.

(vi) Lithium molecule, (Li_2): The electronic configuration of lithium is $1s^2$, $2s^1$. There are six electrons in Li_2. The electronic configuration of Li_2 molecule, therefore, is

Li_2 : $(\sigma 1s)^2$ $(\sigma^* 1s)^2$ $(\sigma 2s)^2$

The above configuration is also written as KK$(\sigma 2s)^2$ where KK represents the closed K shell structure $(\sigma 1s)^2$ $(\sigma^* 1s)^2$.

From the electronic configuration of Li_2 molecule it is clear that there are four electrons present in bonding molecular orbitals and two electrons present in antibonding molecular orbitals. Its bond order, therefore, is ½ (4 – 2) = 1.

It means that Li_2 molecule is stable and since it has no unpaired electrons it should be diamagnetic. Indeed, diamagnetic Li_2 molecules are known to exist in the vapour phase.

(vii) Carbon molecule (C_2): The electronic configuration of carbon is $1s^2\ 2s^2\ 2p^2$. There are twelve electrons in C_2. The electronic configuration of C_2 molecule, therefore, is

$$C_2 : (\sigma 1s)^2 \left(\sigma^* 1s\right)^2 \left(\sigma^* 2s\right)^2 \left(\pi 2p_x^2 = \pi 2p_y^2\right)$$

$$\text{or } KK(\sigma 2s)^2 \left(\sigma^* 2s\right)^2 \left(\pi 2p_x^2 = \pi 2p_y^2\right)$$

The bond order of C_2 is ½ (8 – 4) = 2 and C_2 should be diamagnetic. Diamagnetic C_2 molecules have indeed been detected in vapour phase. It is important to note that double bond in C_2 consists of both pi bonds because of the presence of four electrons in two pi molecular orbitals. In most of the other molecules a double bond is made up of a sigma bond and a pi bond. In a similar fashion the bonding in N_2 molecule can be discussed.