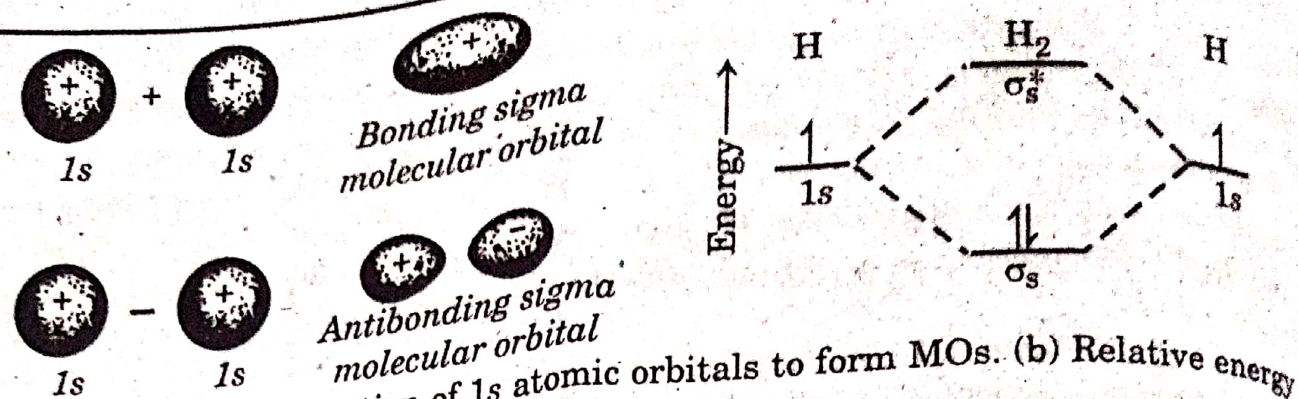


Fig. 2.37. (a) Combination of 1s atomic orbitals to form MOs. (b) Relative energy of σ_{1s} orbitals in H_2 molecule.

ψ_b molecular orbital is formed by the addition of the two 1s orbitals when atomic orbitals of the same sign overlap along the internuclear axes. Such overlap leads to reinforcement of the wave functions in the region between the two nuclei, and ψ_b^2 the probabilily of finding the electron is large between the nuclei, resulting a strong bond between the atoms. The bonding molecular orbital (ψ_b) is in a lower energy state than the average energies of the combining atomic orbitals. The bonding molecular orbitals of the type which are formed from 1s atomic orbitals are denoted as $\sigma(1s)$. ψ_a is formed by the subtraction of the two 1s orbitals, when orbitals of opposite sign overlap, the wave functions interfere with each other in the region between the two nuclei and a node is produced. At the node $\Psi = 0$, and on either side of the node ψ is small, therefore, ψ_a^2 is also small in the region between the nuclei. The repulsive forces will be greater than the attractive forces and therefore, antibonding molecular orbital is at a state of higher energy than the average energies of the component atomic orbitals. The antibonding molecular orbital of this type is denoted by $\sigma^*(1s)$. Both bonding and antibonding molecular orbitals have cylindrical symmetry about the internuclear axis, therefore these orbitals are called σ orbitals and the bonds are called σ bonds.

Conditions for effective combination of atomic orbitals

There are certain conditions for effective combination of atomic orbitals which are described below:

(i) The energies of the AO's combining together must be similar in magnitude or the AO's should have comparable energies. Thus in case of the formation of a homonuclear diatomic molecule of A_2 type, the $1s_a$–AO of the atom A_a will not combine with the $2s_a$ – AO of another atom A_b of the same element, where A_a and A_b are the two atoms of the molecule A_2 since there energies are not equal. Similarly since the energy difference between 2s- and 2p-AO's is too great, they will also not combine. But in case of the formation of heteronuclear diatomic molecule of AB type, such combination may be expected.

(ii) The charge clouds of the AO's must overlap one another as much as possible, if they are going to combine together to form the MO's. This condition is referred to as the *principle of maximum overlap.*

(iii) The AO's should have the same symmetry about the molecular axis. This condition is known as symmetry condition for the combination of AO's. On the basis of this symmetry condition it is noted that some of the AO's which have comparable energies do overlap, but cannot combine to give MO's. Thus MO's cannot be formed by the overlap of an s-atomic orbital of an atom A and one p-atomic orbital of atom B perpendicular to the molecular axis (either p_x- or p_y. orbital), since the molecular axis is the z-axis. The cause of non-formation of MO's is that the symmetry of s- orbital is not the same as that of p- orbital. Alternatively it can be said that + + overlap is neutralized by the + − overlap or in other words the + − overlap cancels the bonding contribution from the + + overlap.

Thus the following pairs of AO's will not combine to form any MO's, provided that z-axis is assumed to be the molecular axis:

(a) $s-p_z$ pair (b) $s-p_y$ pair (c) p_x-p_y pair (d) p_x-p_z pair (e) p_y-p_z pair.

H_2 molecule has two electrons, both in bonding σ_s orbital and constititue a single covalent bond.

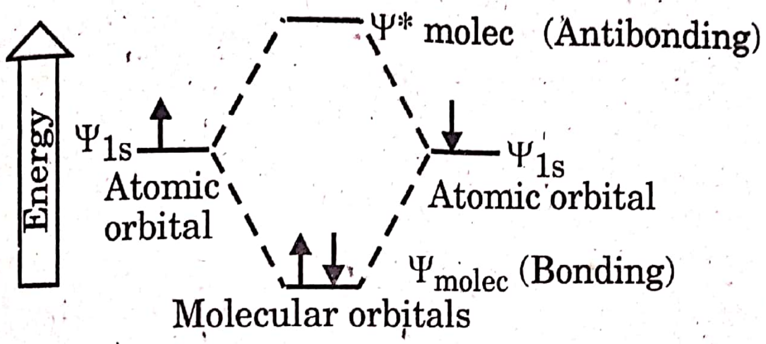


Fig. 2.38. Molecular orbital diagram for H_2 molecule

In molecular orbital theory, the **bond order** is defined as one-half the difference between the numbers of electrons in bonding and in antibonding molecular orbitals (MOs) in a molecule.

$$\text{Bond order} = \frac{\text{No. of electrons in bonding MO} - \text{No. of electrons in antibonding MO}}{2}$$

$$\text{The bond order in } H_2 \text{ molecule} = \frac{2-0}{2} = 1$$

Bond order indicates whether a bond is single, double, triple (or one-half, three halves, fives halves); whereas Lewis theory and Valence bond theory require electron-pair bonds, MO theory accounts quite nicely for one-electron bonds which are known to exist.

Formation of MOs for He_2,

Consider the He_2 molecule which might be formed from two He atoms, each of which furnishes two electrons to the molecule. Thus He_2 molecule will have four electrons, two in the σ_{1s} bonding MO and two in the σ^*_{1s} antibonding MO. As a result of this, the stability gained by two electrons moving to low energy σ_{1s} bonding MO would be lost by the other two electrons moving to the σ^*_{1s} antibonding MO. The result is that no attractive force between He atoms and so He_2 does not exist.

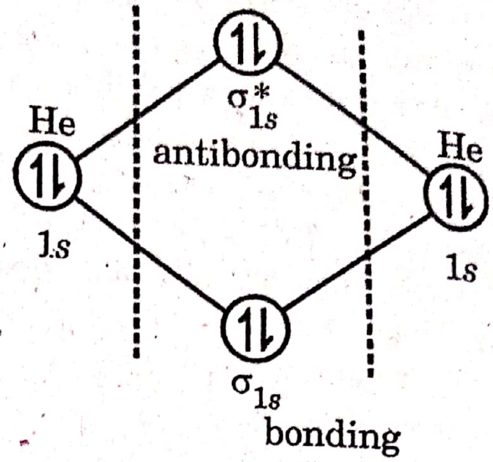


Fig. 2.39. Diagram for the hypothetical for He_2 molecule

$$\text{Bond order in } He_2 = \frac{2-2}{2} = 0$$

Second period elements; Homonuclear diatomic molecules

In the elements of the second period the 1*s*-orbitals are sucked very close to the nuclei, and being so small they overlap to only a small extent, and contribute very little to the bonding energy. The 2s-orbitals extend over as significant region and overlap significantly. Therfore, the molecular orbitals they form play a significant role in the energies of the second period diatomics. We have seen that two Is-orbital can be combined to form two MO : one bonding and one antibonding. The same is true of two 2*s*-orbitals.

In the second period diatomics we also have to allow for the overlap of the 2*p*-orbitals. The combination of two *p* orbitals produces different results depending on which p-orbitals are used. If the x-axis is the internuclear axis, then two $2p_x$ orbitals can overlap properly if they approach each other end to end, to form two MOs: one σ_{2p} bonding orbital with electronic charge built up between the nuclei, and the second σ^*_{2p} antibonding MO with decreased charge density between the nuclei. The bonding and antibonding MOs can be described in terms of wave functions Ψ_b and Ψ_a, respectively, as follows:

$$\Psi_b = \Psi_A(2p_x) + \Psi_b(2p_x) \text{ termed as } \sigma_{2p_x}$$

$$\Psi_a = \Psi_A(2p_x) - \Psi_b(2p_x) \text{ termed as } \sigma^*_{2p_x}$$

Thus Ψ_b is a bonding MO and ψ_a is an antibonding MO.

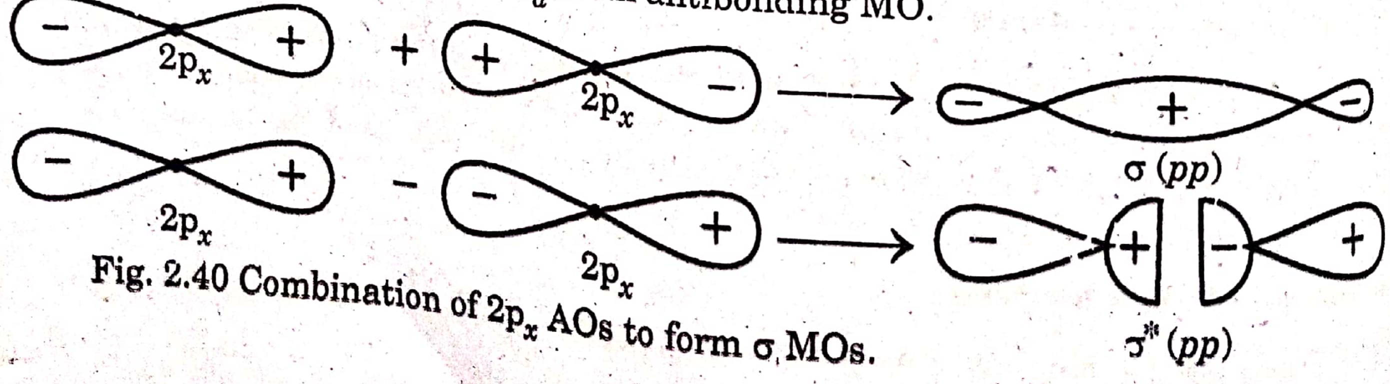


Fig. 2.40 Combination of $2p_x$ AOs to form σ MOs.

When $2p_y$ and $2p_z$ orbitals overlap, they do so in a parallel or sidewise fashion to form MOs which are not symmetrical about the line joining the nuclei. These unsymmetrical combinations are called π orbitals for bonding and π* orbitals for antibonding, but both are weaker than in the σ case because the accumulation of electron density lies away from the optimum positions. There are two MOs of π type and two MOs of π* because there are two pairs of p orbitals that are arranged in a parallel fashion. These MOs obtained from p_y and p_z AOs can be described in terms of wave functions ψ_b and ψ_a as follows:

Combination of two p_y atomic orbitals:

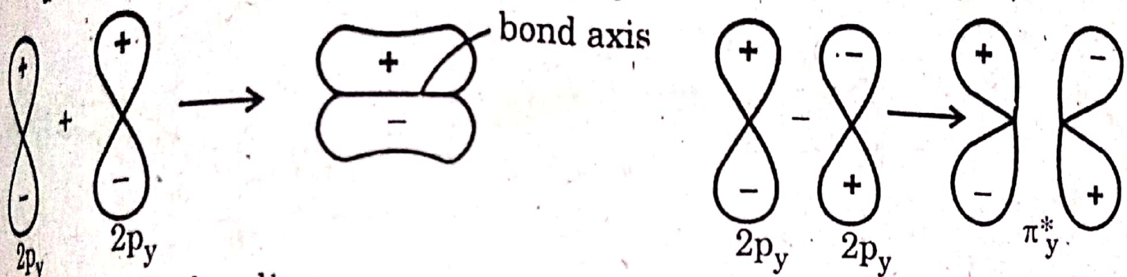
$\psi_b = \psi_A(2p_y) + \psi_B(2p_y)$ termed as π_{2p}, (bonding)

$\psi_a = \psi_A(2p_y) - \psi_B(2p_y)$ termed as $\pi^*_{2p_y}$ (antibonding)

Combination of two p_z atomic orbitals

$\psi_b = \psi_A(2p_z) + \psi_B(2p_z)$ termed as π_{2p_z} (bonding)

$\psi_a = \psi_A(2p_z) - \psi_B(2p_z)$ termed as $\pi^*_{2p_z}$ (antibonding)



(a) π bonding (b) π* Antibondig

Fig. 2.41. Combination of 2p AOs to form π Mos π_{2p_y}

In order to know about the filling of electrons in MOs it is necessary to find out the order of energy levels or stability of their MOs.

The order of increasing energy levels are revealed by spectroscopic data for B_2 through N_2, is as follows:

$$\sigma_{1s} < \sigma^*_{1s} < \sigma_{2s} < \sigma^*_{2s} < \pi_{2p_y} = \pi_{2p_z} < \sigma_{2p_x} < \pi^*_{2p_y} = \pi^*_{2p_z} < \sigma^*_{2p_x}$$

However the relative energy of p_y and p_z orbitals is higher than that of the σ_{2p_x} orbital for O_2, F_2 and (hypothetical) Ne_2.

The change in sequence of MO energies between N_2 and O_2 occurs because the σ_x and σ^*_x MOs actually have some s character, a fact which we had to ignore, when we decided to use the "one AO plus one AO yields two MOs" simplification. The amount of s character in these orbitals decreases as the nuclear charge increases across the period. Because of this the σ_x energy drops below the $\pi_y - \pi_z$ energy at O_2.

The π_{2p_y} and π_{2p_z} bonding and antibonding MOs have the same energy, i.e; they are degenerate.

Li_2 : The electronic configuration of each Li atom (At. No. 3) is $1s^2\,2s^1$. The first shell (K shell) electrons are not involved in the bonding (i.e, as nonbonding electrons). The valence electrons of the two Li atoms are used to populate a new σ_{2s} MO as shown in Fig. 2.42. Representing each of the filled 1s orbitals by K (for a K shell) the electronic configuration of Li_2 can be represented as;

$$2Li\ (1s^2\,2s^1) \longrightarrow Li_2\ [KK\,(\sigma_{2s})^2]$$

The configuration of Li_2 is much like that of H_2, and the bond order which can be determined from the valence electrons only, is equal to $\frac{1}{2}$ (2–0), or 1. With a bond order of 1 the Li_2 molecule is predicted to exist. Neither liquid nor solid Li consists of Li_2 molecules, but diatomic molecules are indeed found in gaseous lithium. The bond energy in Li_2 is 105 kJ mol^{-1}. This is lower than in H_2 (433 kJ mol^{-1}) because of the shielding of the nucleus by the complete K shell in each atom.

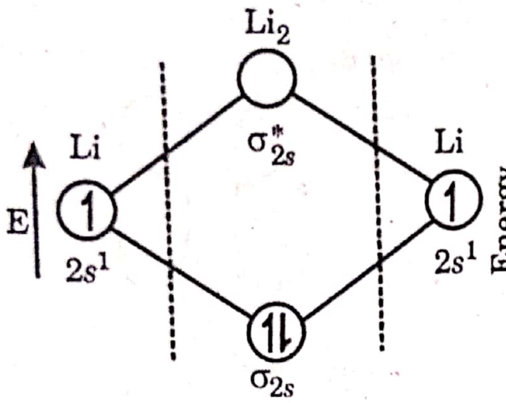


Fig. 2.42. Formation of MOs for Li_2

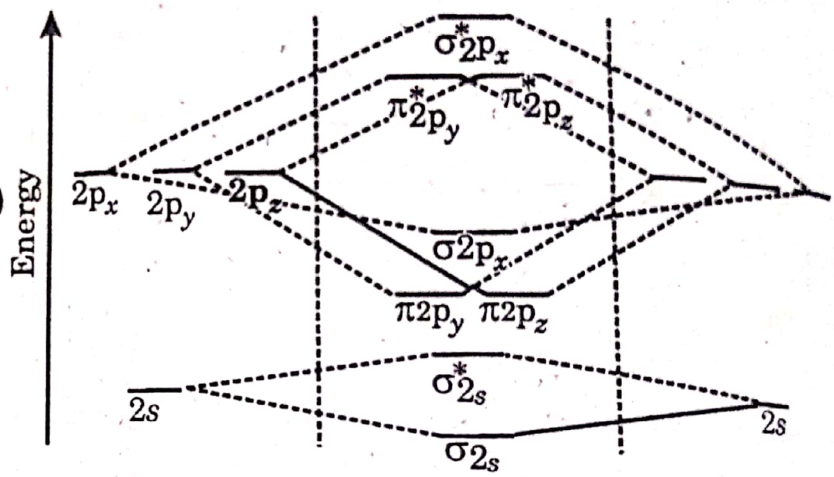


Fig. 2.43. Molecular energies: B_2, C_2 and N_2

N_2 Molecule: The electronic configuration of each nitrogen atom (Z = 7) is $1s^2\,2s^2\,2p_x^1\,2p_y^1\,2p_z^1$. The inner shell (K - shell) electrons do not take part in bonding. Therefore, two 2s and three 2p electrons from each nitrogen atom are to be considered in the bonding interactions. The formation of N_2 proceeds according to the following equation;

$$2N\ (1s^2\,2s^2\,2p^3) \longrightarrow N_2[KK(\sigma_{2s})^2(\sigma^*_{2s})^2\,(\pi_{2p_y})^2\,(\pi_{2p_z})^2\,(\sigma_{2p_x})^2$$

The total number of valence electrons in bonding orbitals is eight and the no. of electrons in antibonding orbital is two. Thus, N_2 has a net excess of six bonding electrons, which corresponds to a bond order of 3 (triple bond).

$$\text{Bond order} = \frac{\text{No. of } e^- \text{ in bonding MOs} - \text{No. of } e^- \text{ in antibonding MOs}}{2}$$

$$= \frac{8-2}{2} = \frac{6}{2} = 3$$

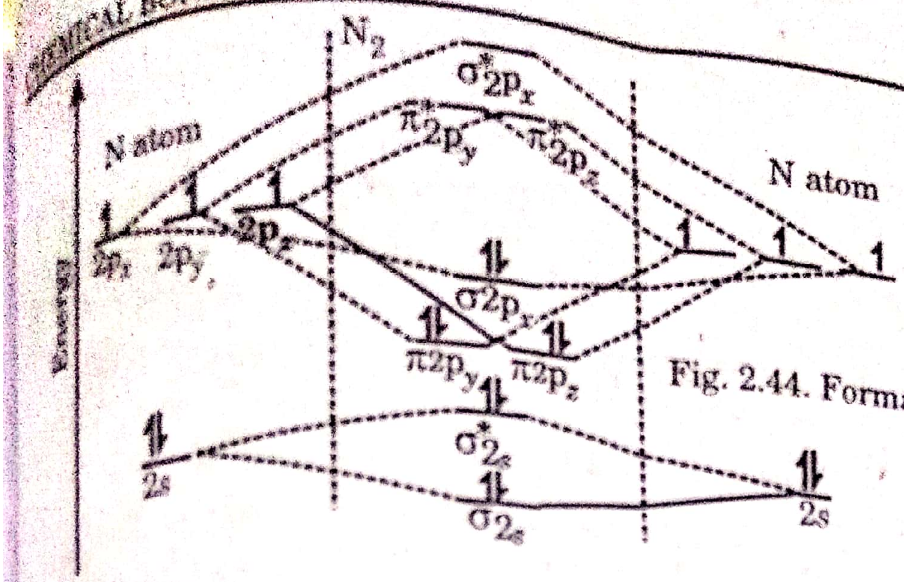


Fig. 2.44. Formation of N_2 molecule

N_2 is very stable since it has the largest excess of bonding over antibonding electrons. Magnetic measurements confirm that all electrons are paired in N_2 : it is not paramagnetic. The six electrons in the π_{2p_y}, π_{2p_z} and σ_{2p_x} orbitals correspond to the six electrons shown in the Lewis structure : N ::: N:

O_2 Molecule. The electronic configuration of each O atom (Z = 8) is $1s^2, 2s^2, 2p_x^2, 2p_y^1, 2p_z^1$. The K-shell electrons do not take part in bonding. Therefore, two 2s and four electrons from each oxygen atom are to be considered in the bonding interactions. The formation of O_2 proceeds according to the following equation:

$$2O\,(1s^2, 2s^2, 2p^4) \longrightarrow O_2[KK(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p_x})^2(\pi_{2p_y})^2(\pi_{2p_z})^2(\pi^*_{2p_y})^1(\pi^*_{2p_z})^1$$

The O_2 molecule contains two electrons more than N_2 molecule and these electrons must go into the degenerate antibonding π^*_{2p} (i.e. $\pi^*_{2p_y}$ and $\pi^*_{2p_z}$) molecular orbitals according to **Hund's rule.**

The total number of valence electrons in bonding orbitals is eight, and the number of electrons in antibonding orbitals is four. Thus O_2 has a net excess of four bonding electrons, which corresponds to a bond order of 2.

O_2 molecule has **two** unpaired electrons, even though the total number of electrons is even. Thus the paramagnetism of O_2 is explained.

The lower bond order of O_2 than N_2 is consistent with the fact that O_2 has a smaller bond energy and a longer bond length than does N_2.

The MO theory readily accounts for the observed magnetic and bond characteristics.

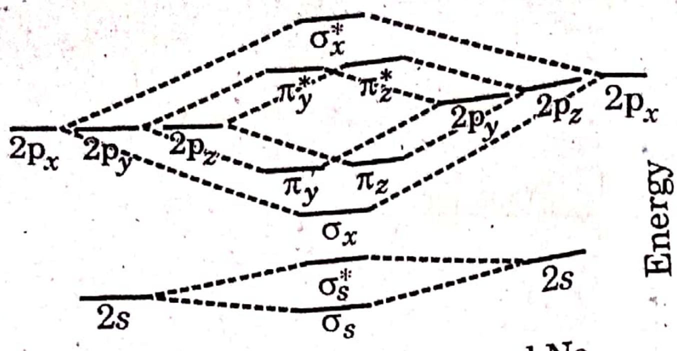


Fig. 2.45. MO energies: O_2, F_2 and Ne_2

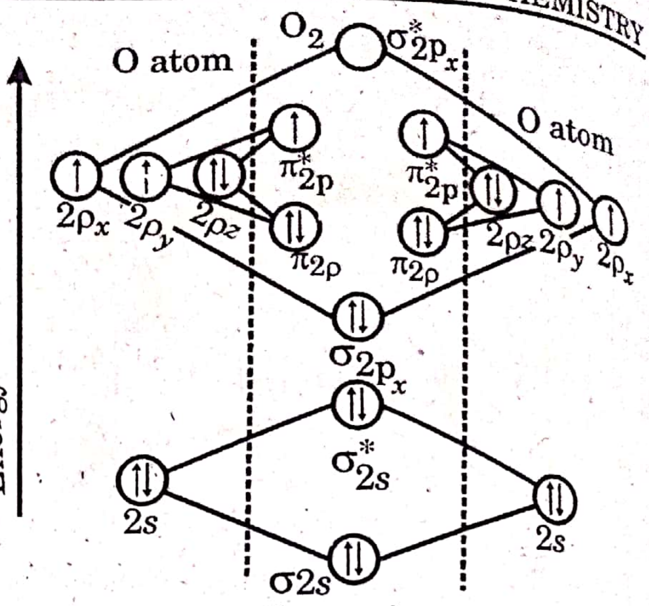


Fig. 2.46 Formation of O_2 molecule.

F_2 molecule. The addition of two more electrons to the O_2 configuration gives the orbital population of F_2. Note that these two electrons must go into the two degenerate antibonding (π^*_{2p} (*i.e.*, ($\pi^*_{2p_y}$ and $\pi^*_{2p_z}$) orbitals. Since the antibonding π^*_{2p} orbitals are both filled, the bond order in F_2 is only 1. The effective F–F bonding is provided by a σ bond due to the two electrons present in the σ_{2p} MO. All the other electrons in bonding MOs are cancelled by those in corresponding antibonding MOs. The electronic configuration in F_2 molecule is;

$$F_2\ [KK\,(\sigma_{2s})^2(\sigma^*_{2s})(\sigma_{2p_x})^2(\pi_{2p_y})^2(\pi_{2p_z})^2(\pi^*_{2p_y})^2(\pi^*_{2p_z})^2$$

Cl_2 and Br_2 have analogous structures. Chlorine has its K- and L- -shells and Bromine has its, K, L and M shells full or non-bonding.

Example 2.2: Would you expect Be_2 and Ne_2 exist as stable molecules?

Solution: A stable diatomic molecule must have an excess of bonding over antibonding electrons. The electronic configuration of Be_2 and Ne_2 are;

$$Be_2\ :\ KK\ (\sigma_{2s})^2\ (\sigma^*_{2s})^2$$

$$Ne_2\ :\ KK\ (\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p_x})^2(\pi_{2p_y})^2(\pi_{2p_z})^2(\pi^*_{2p_y})^2(\pi^*_{2p_z})^2(\sigma^*_{2p_x})^2$$

Both Be_2 and Ne_2 have equal numbers of bonding and antibonding electrons and a bond order of zero. They do not exist as stable molecules. Indeed Be_2 and Ne_2 have never been observed

2.16 HETERONUCLEAR DIATOMIC MOLECULES

Diatomic molecules having different atoms are called **heteronuclear.** The difference in electronegativities in these molecules causes the MO energy spacings to be different from those in homonuclear diatomics.

The general conditions for the most effective combination of atomic orbitals in a molecule are as follows:-

The AOs involved should: (i) have similar energies; (ii) overlap as much as possible; and have the same symmetry with respect to the x (i.e. internuclear) axis.

In a heteronuclear molecule AB the choice of AOs for combination is guided by information from atomic spectroscopy. The molecular wave function ψ obtained by the linear combination of 1s-orbitals, on two dissimilar atoms can be written as;

$$\psi = C_A \, 1s_A + C_B \, 1s_B$$

Where the weighting coefficients are unequal. The electron distribution is given by the square of this wave function;

$$\psi^2 = C_A^2(1s_A)^2 + C_B^2(1s_B)^2 + 2C_AC_B(1s_A)(1s_B)$$

If C_B^2 is greater than C_A^2 there is a greater probability of finding the electron in the orbital of atom B than in that of atom A.

Let us now apply the MO theory to explain the bonding in heteronuclear diatomic molecules such as HF. The electronic configuration of H and F atoms are;

H $1s^1$ F $1s^2 2s^2 2p^5$

Combinations of the hydrogen 1s orbital with the inner-shell orbital 1s or even the 2s orbital of F can be ruled out, because the energies of these orbitals of F are much too low. The 2p orbitals of F have suitable energy and they are involved in bond formation. Let us consider which of the 2p orbitals is able to overlap more effectively with H (1s) AO so as to form available MO.

The MO are classified into σ and π type. The hydrogen 1s orbital is of σ type in the context of molecular symmetry and so can combine with the 2p orbital of the F atom, if we take the molecular (internuclear) axis as the x-axis, The $2p_y$ and $2p_z$ orbitals are of π type, and so do not take part in the bonding because there are no hydrogen orbitals of π type except at very high energy. The $2p_x$ atomic orbital of F combines with 1s atomic orbital of H to form an effective σ-bond overlap as shown in Fig. 2.47.

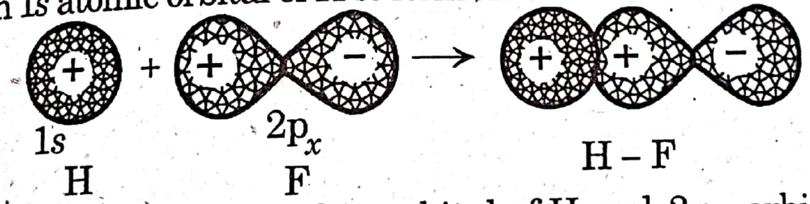


Fig. 2.47 Combination of 1s-orbital of H and $2p_x$ orbital of F to form HF.

On the other hand, if $2p_y$ or $2p_z$ orbitals of F overlap with 1s atomic orbital of H broadside on, the overlap from the positive lobe will be counterbalanced by the negative lobe as shown in Fig. 2.48. It may be now concluded that only $2p_x$ atomic orbital is responsible for the bond formation between H and F.

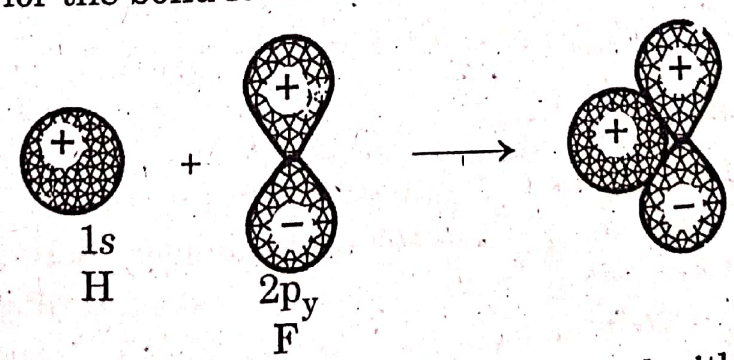


Fig. 2.48. Vanishing of the overlap by H (1s) orbital with F($2p_y$) orbital