Molecular Orbital Theory

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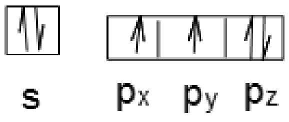
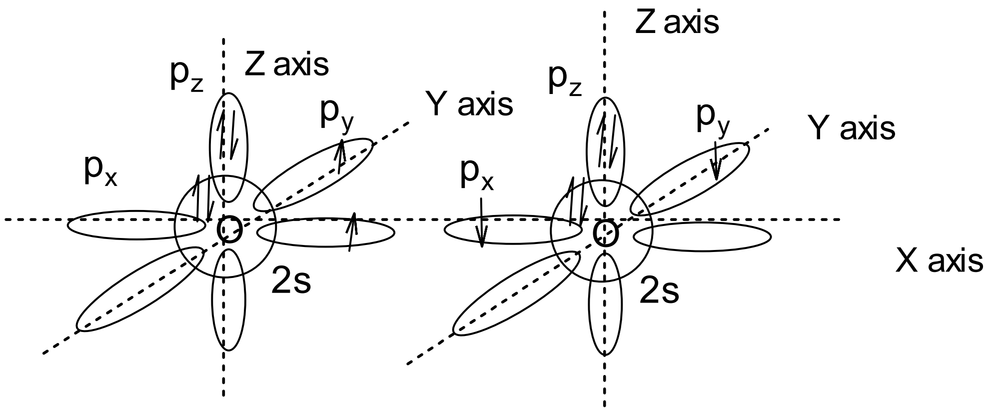
What is the need?

According to the Valence Bond Theory molecular oxygen is formed by the overlap of the atomic orbitals as follows:

$O_8 \longrightarrow 1s^2 /2s^2 \quad 2p^4$

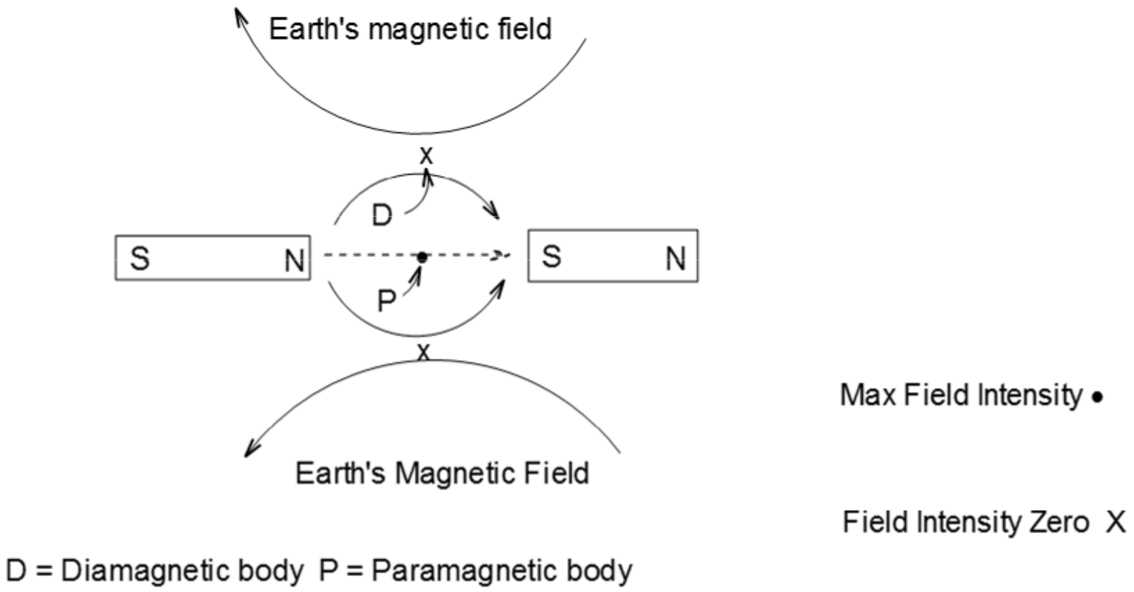


x axis is taken as the bond axis



Here the formation of molecular O_2 $p_x – p_x$ head on orbital and p_y - p_y lateral orbital overlap takes place during. As a result of which all the electrons in O_2 molecule is paired and there is no unpaired electron. But experiments show that molecular oxygen is paramagnetic w.r.t. 2 unpaired electrons. So there is a need to introduce another theory for bonding which is Molecular Orbital Theory (MOT), and it is more improved version of Valence Bond Theory (VBT).

N.B. Paramagnetic body (indicative of presence of unpaired electron) is that body which when kept in magnetic field moves into the region of higher intensity side, whereas, diamagnetic body(indicative of the fact that all electrons are paired)is that body which when kept into the magnetic field moves into the region of lower intensity side.



Basic Points of MOT

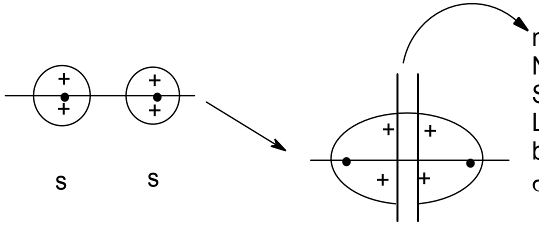
1. Atomic orbitals (A.O.s/a.o.s) combine to form molecular orbitals (M.O.s/m.o.s). The number of m.o.s formed is equal to the number of a.o.s combined.

2. During the combination *Symmetry Adapted Linear Combination* rule (SALC) or *Linear Combination of Atomic Orbital* (LCAO) rule must be followed.

3. When two a.o.s combine two m.o.s are formed – one is of lower energy than either of the two a.o.s and it is called bonding m.o. and the other one is of higher energy than either of the two a.o.s and it is called antibonding m.o. When a.o.s combine with same sign of the wave function of their lobes, bonding m.o. results and when a.o.s combine with opposite signs of the wave function of their lobes, antibonding m.o.results.

4. M.O. pictures:-

Head on interaction



s s

A.O. A.O.

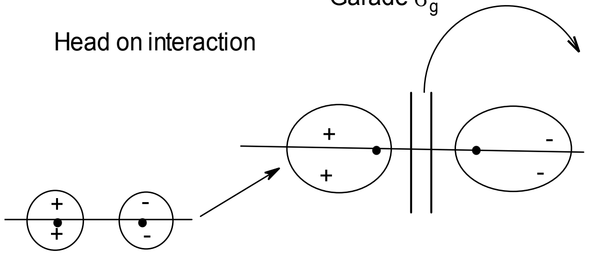
σ or σ_b

Garade σ_g

more electron density between two nuclei;
Nu-Nu repulsion is less;
Stability high;
Lower energy;
bonding m.o.;
σ type

Bonding M.O.

Head on interaction



less electron density between the two nuclei;
Nu-Nu repulsion is more;
less stability;
higher energy;
antibonding m.o.;

σ type

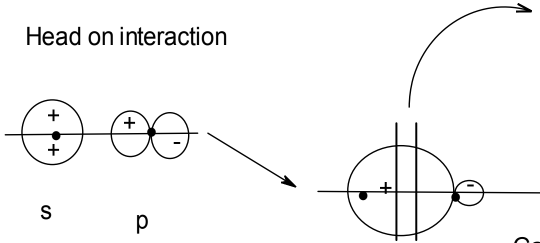
s s

A.O. A.O.

σ_a or σ^*

Ungarade σ_u

Head on interaction



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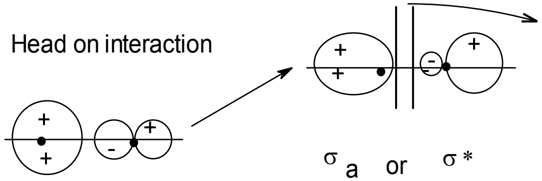
A.O. A.O.

σ_b or σ

Garade σ_g

Head on interaction



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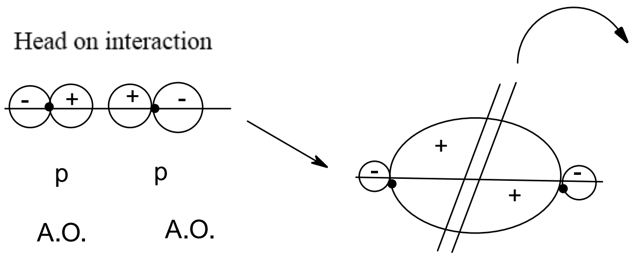
Head on interaction



more electron density between two nuclei;
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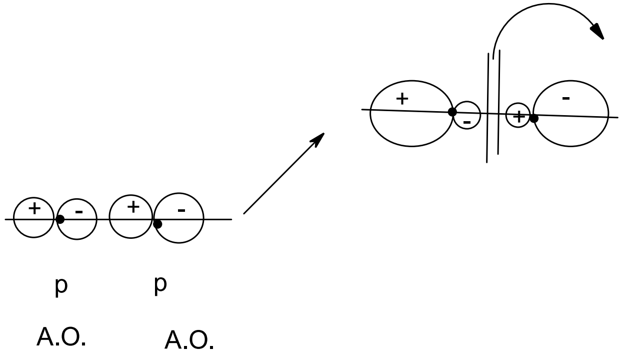
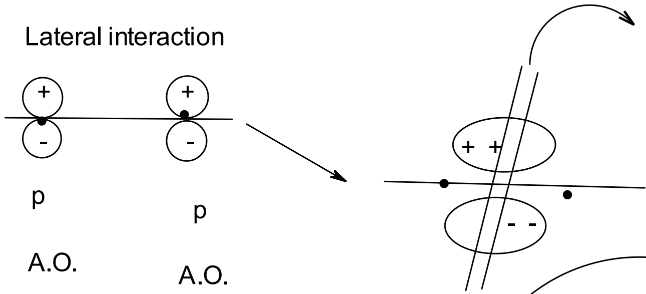
σ_b or σ ; Garade σ_g



less electron density between the two nuclei;
Nu-Nu repulsion is more;
less stability;
higher energy;
antibonding m.o.;

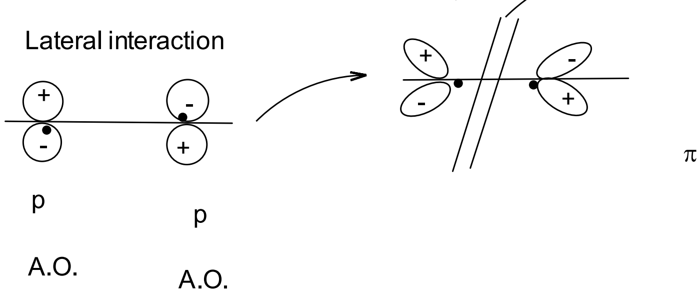
Lateral interaction



more electron density in the region between the two nuclei;Nu-Nu repulsion is low; stability; bonding m.o. π type

π or π_b or πu ; ungarade type

Lateral interaction



Less electron density in the region between the two nuclei: Nu-Nu repulsion is more; Less stability; antibonding m.o. π type

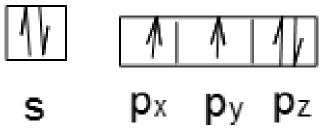
π^* or πa or πg ; garade type

Note: an orbital is said to have garade configuration if we start from any point of any lobe of the orbital and proceed through the centre of gravity of the orbital to the point just diametrically opposite to the initial point and we reach to the same sign of the wave function on the orbital lobe; similarly, an orbital is said to have ungarade configuration if we start from any point of any lobe of the orbital and proceed through the centre of gravity of the orbital to the point just diametrically opposite to the initial point and we reach to the opposite sign of the wave function on the orbital lobe.

The electrons are adde to these m.o.s obeying basic principles such as a) Auf Bau principle – lower energy m.o.s are given electrons first then higher energy m.o.s b) Hund's rule- electrons tend to remain unpaired as long as m.o.s of equal energies are available and c) Pauli's exclusion principle- there can be maximum two electron in an m.o.

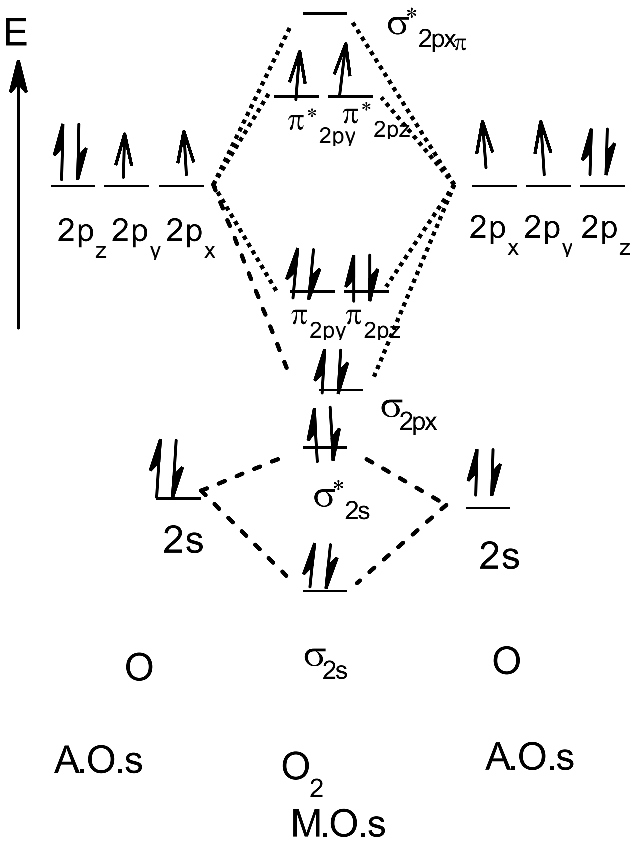
On the basis of the above mentioned postulates we can draw the m.o. diagram for the molecular O_2 as follows:

$O_8 \longrightarrow 1s^2 /2s^2 \quad 2p^4$



x axis is taken as the bond axis

6x2=12 electrons are to be fed into the m.o.s (we assume that inner core electrons do not participate in m.o. formation. Even if we consider inner core orbitals there is no change in the overall results.)



Thus we see that there are two unpaired electrons in the tw antibonding π^* orbitals.
Bond Order = (no. of electrons in the bonding level- no of electrons in the antibonding levels)/2 = (8-4)/2 = 2

We can also show the m.o. of O_2 (12e) with the help of linear scheme m.o diagram: $\sigma_{2s}^{2} < \sigma_{2s}^{*\,2} < \sigma_{2px}^{2} < \pi_{2py}^{2} = \pi_{2pz}^{2} < \pi_{2py}^{*\,1} = \pi_{2pz}^{*\,1} < \sigma_{2px}^{*}$; Proceeding exactly in the same way, we can write the m.o. diagram for O_2^+(11e): $\sigma_{2s}^{2} < \sigma_{2s}^{*\,2} < \sigma_{2px}^{2} < \pi_{2py}^{2} = \pi_{2pz}^{2} < \pi_{2py}^{*\,1} = \pi_{2pz}^{*} < \sigma_{2px}^{*}$; one unpaired electron and B.O. = (8-3)/2 = 2.5, then for O_2^-(13e): $\sigma_{2s}^{2} < \sigma_{2s}^{*\,2} < \sigma_{2px}^{2} < \pi_{2py}^{2} = \pi_{2pz}^{2} < \pi_{2py}^{*\,2} = \pi_{2pz}^{*\,1} < \sigma_{2px}^{*}$; one unpaired electron and B.O. = (8-5)/2 = 1.5 and finally for O_2^{2-}(14e): $\sigma_{2s}^{2} < \sigma_{2s}^{*\,2} < \sigma_{2px}^{2} < \pi_{2py}^{2} = \pi_{2pz}^{2} < \pi_{2py}^{*\,2} = \pi_{2pz}^{*\,2} < \sigma_{2px}^{*}$; no unpaired electron and B.O. = (8-6)/2 = 1.0

In a similar way we can draw the M.O. diagram for N_2:

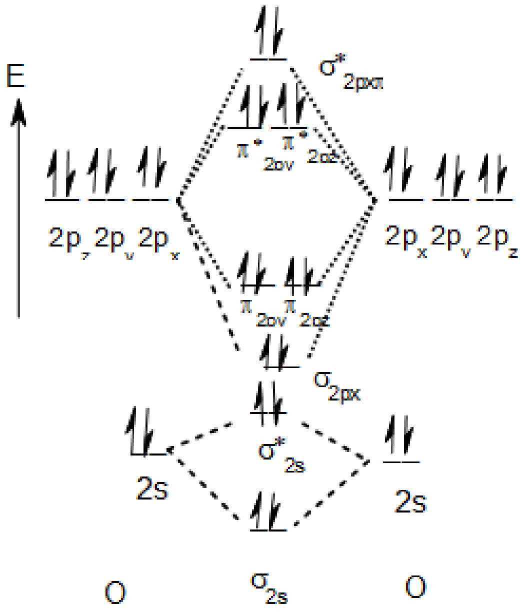
$N_7 \rightarrow 1s^2/2s^2\ 2p^3$ So 5e in the outermost shell, now we have to add 10 e in the m.o.

for N_2(10e): $\sigma_{2s}^2 < \sigma_{2s}^{*2} < \sigma_{2px}^2 < \pi_{2py}^2 = \pi_{2pz}^2 < \pi_{2py}^* = \pi_{2pz}^* < \sigma_{2px}^*$; no unpaired electron and B.O. = (8-2)/2 = 3.0 and for N_2^+(9e): $\sigma_{2s}^2 < \sigma_{2s}^{*2} < \sigma_{2px}^2 < \pi_{2py}^2 = \pi_{2pz}^1 < \pi_{2py}^* = \pi_{2pz}^* < \sigma_{2px}^*$; one unpaired electron and B.O. = (7-2)/2 = 2.5

Thus we see that $O_2 \rightarrow O_2^+ + e$ is a favourable process as the electron is lost from the antibonding orbital and bond order is increasing whereas $N_2 \rightarrow N_2^+ + e$ is not a favourable process as the electron is lost fro the bonding level and B.O. is decreasing.

Q: Why is Ne_2 molecule not formed?

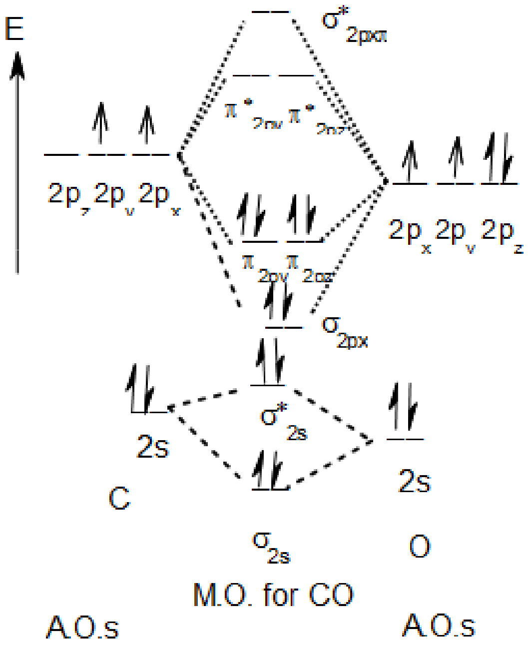
The answer may be given in terms of M.O. theory.



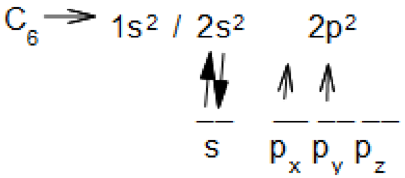
Each Ne has 8e in the outermost shell
We account for 16e in the m.o.s

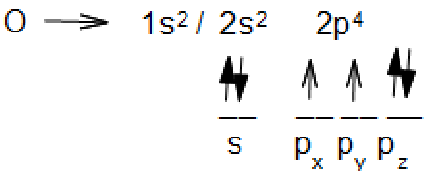
B.O. = (8-8)/2 = 0
So Ne_2 does not exist.

Now we can extend our idea to form the m.o. diagram for some heteronuclear diatomic molecules like CO, NO, HCl etc. We will also consider their VB picture. Let us consider CO.



M.O. for CO



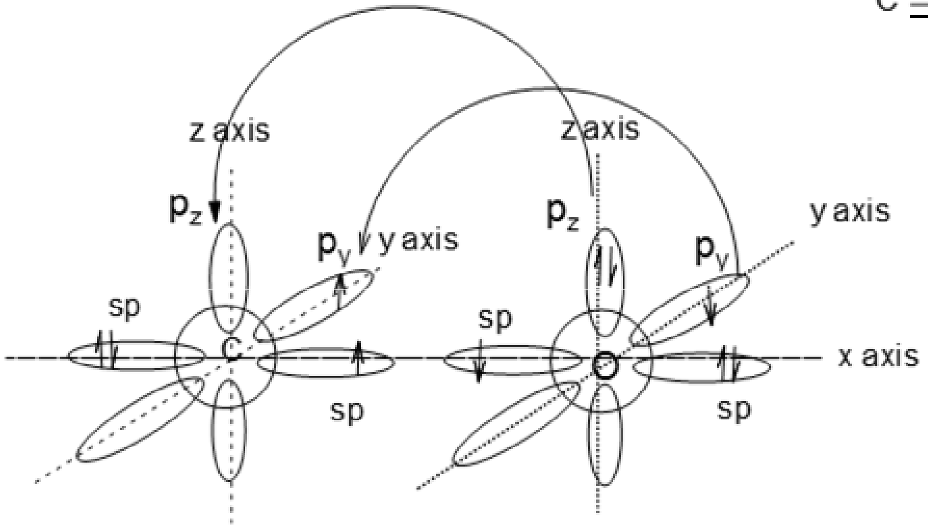


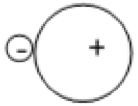
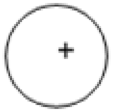
As O is Smaller in size than C, the energy of 2s and 2p of O is lower than those of C; The total no. of electrons that are to be filled in the m.o.s are 10(4 for C and 6 for O); Bond Order = (8-2)/2 = 3.0

Now let us consider the V.B. picture of CO

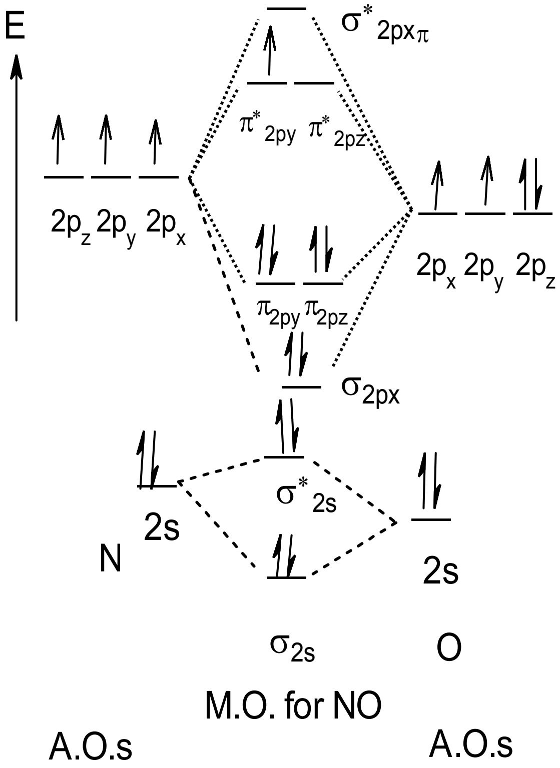
A dative bond is formed by the overlap of filled $2p_z$ orbital of O and empty $2p_z$ orbital of C in addition to the two normal covalent bonds formed by the overlap of singly filled sp hybrid orbital and $2p_y$ of each of C and O: here also the effective bond order is 3.0

$C \equiv O$

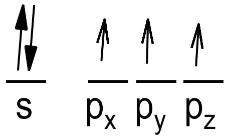


A hybrid orbital is  is equivalent to 

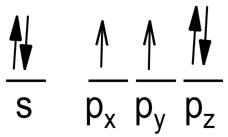
we don't show the negative lobes



$N_7 \longrightarrow 1s^2 \,/\, 2s^2 \quad 2p^3$



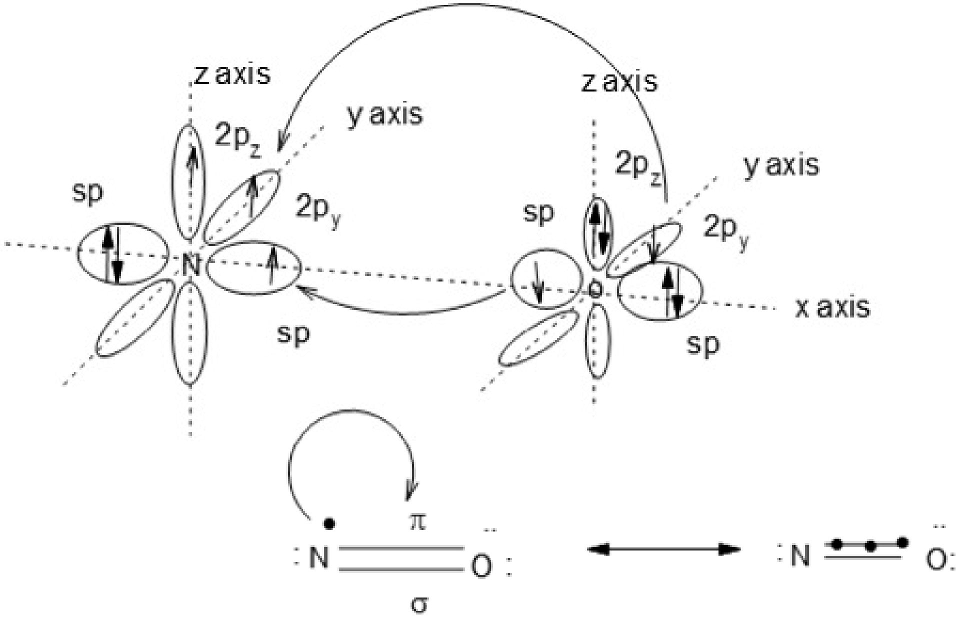
$O \longrightarrow 1s^2 / \; 2s^2 \quad 2p^4$



As O is Smaller in size than N, the energy of 2s and 2p of O is lower than those of N; The total no. of electrons that are to be filled in the m.o.s are 11(5 for N and 6 for O); Bond Order = (8-3)/2 = 2.5

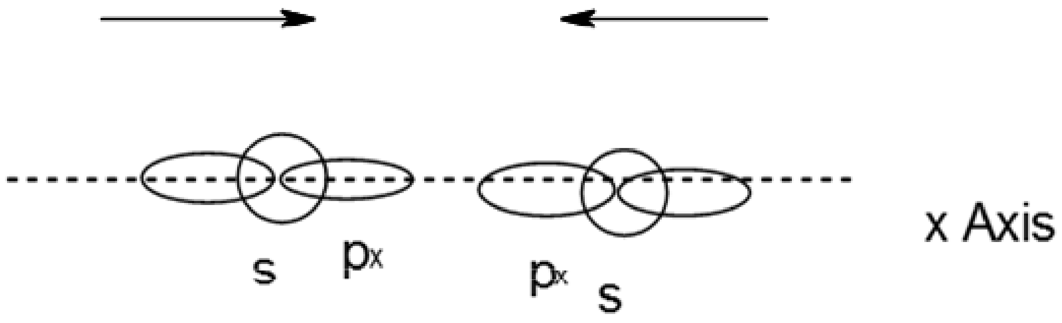
As the odd electron is present in high energy $\pi*$ orbital, it can easily be lost and in NO^+ bond order is increased, stability is increased. That is why NO loses electron very easily even if it is formed by the combination of two very much electronegatve elements (O and N). Ionization Energy of Hg is 10.43 eV/atom and that of NO is 9.23eV/molecule. This indicates that NO is more prompt in giving up an electron that Hg, the later being regarded as metal.

We can show the VB picture of NO to indicate why the bond order is being considered as 2.5



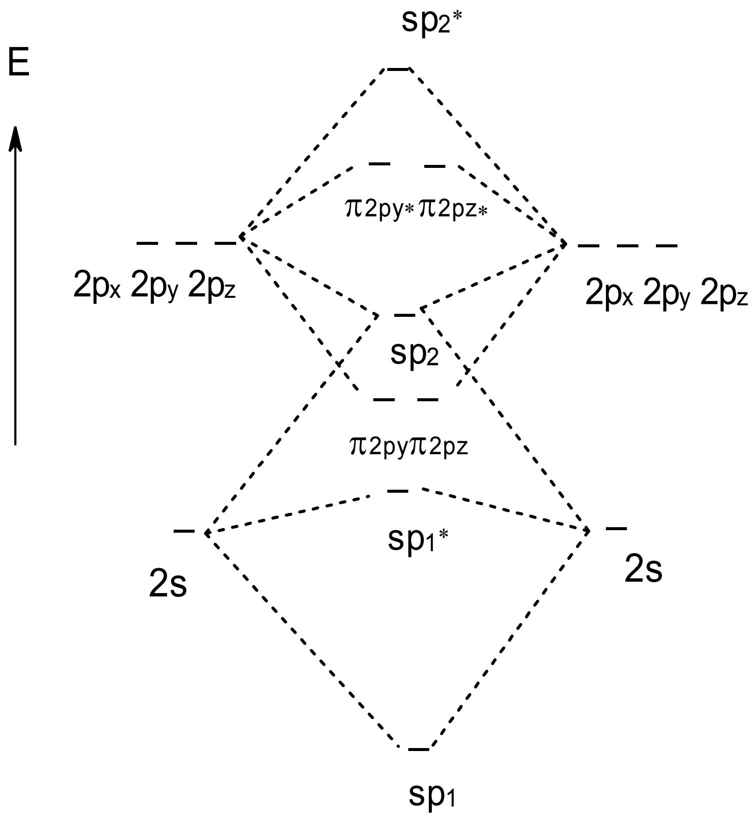
Here the odd electron may sometimes be the part of three electron bond and then the effective bond order is 2.5

As of now we have not considered the s-p interaction. The m.o. diagram is based on the interaction of 2s with 2s and $2p_x$ with $2p_x$ orbitals (considering x-axis as bond axix). But when two such orbitals approach each other then there is every possibility that’s-s, s-p, p-s and p-p interaction. So 4 m.o. results. The m.o. diagram may be modified considering s-p interaction.



Now we will draw the m.o. diagram for O_2 molecule and for hypothetical B_2 considering sp interaction. ($B_5 \rightarrow 1s^2 / 2s^2 2p^1$ hence, 3e in the outermost shell and for B_2 we have to count 6e in the m.o.s)

M.O. without sp interaction



Linear Scheme:

$\sigma sp1 < \sigma sp1^{*} < \pi 2py = \pi 2pz < \sigma sp2 < \pi^{*}{}_{2py} \pi^{*}{}_{2pz} < \sigma^{*}{}_{sp2}$

Thus for O_2 we add 12 e as

$\sigma sp1^{2} < \sigma sp1^{*\ 2} < \pi 2py^{2} = \pi 2pz^{2} < \sigma sp2^{2} < \pi^{*}{}_{2py}{}^{1} \pi^{*}{}_{2pz}{}^{1} < \sigma^{*}{}_{sp2}$

and we see the same result is coming out.

B.O. = 2.0 and no. of unpaired e = 2

But for hypothetical B_2 molecule we add 6 e as

$\sigma sp1^{2} < \sigma sp1^{*\ 2} < \pi 2py^{\ 1} = \pi 2pz^{1} < \sigma sp2 < \pi^{*}{}_{2py} \pi^{*}{}_{2pz} < \sigma^{*}{}_{sp2}$

The result is no. of unpaired e's are 2

If we do not consider the sp interaction for B_2 the arrangement of electrons will look like the following: $\sigma_{2s}^2 < \sigma_{2s}^{*2} < \sigma_{2px}^2 < \pi_{2py} = \pi_{2pz} < \pi_{2py}^* = \pi_{2pz}^* < \sigma_{2px}^*$; thus we see that the results differ. Here we see that there is no unpaired electron. Experimentally it has been found that B_2 has 2 unpaired electrons. So, for B_2 we need to consider the sp interaction while there is no problem if we do not consider sp interaction for O_2. Hence we arrive at the conclusion that for some we must consider sp interaction while for others we may or may not consider the sp interaction. Now the question is that for which elements we have to consider the sp interaction positively and why?

Let us consider the second period elements:

	Li_3	Be_4	B_5	C_6	N_7	O_8	F_9	Ne_{10}
Electronic config.$1s^2$	$2s^1$	$2s^2$	$2s^22p^1$	$2s^22p^2$	$2s^22p^3$	$2s^22p^4$	$2s^22p^5$	$2s^22p^6$

Energy Gap between 2s and 2p: for Li 200 kJ mol^{-1} ------------------------------For F 2500 kJ mol^{-1}

As we go from left to right the gap between 2s and 2p orbitals increases. In the region from Li to C the gap between 2s and 2p is very low and s has more chance to interact with p and we must consider the sp interaction, but for N to Ne the gap between 2s and 2p is sufficiently high and s has less opportunity to interact with p and we may or may not consider the sp interaction. So is the case with the third period.