

Molecular Orbital Theory**Postulates:**

1. When nuclei of two atoms come close to each other, their atomic orbitals combine leading to the formation of molecular orbitals (MO) and electrons in them belong to the molecule as a whole.
2. The atomic orbitals of same energy and symmetry will combine to form molecular orbitals (MO).
3. The number of molecular orbitals (MOs) formed is equal to the number of atomic orbitals that are combined. The MO thus formed is associated with a definite energy level and the total energy of the molecule is the sum of energies of occupied molecular orbitals.

When two atomic orbitals are combined, one of the resulting MOs is at a lower energy than the original atomic orbitals; this is a bonding orbital (BMO). The other MO is at a higher energy than the original atomic orbitals; this is an antibonding orbital (ABMO).

Difference between a BMO and an ABMO

- a. BMO is formed by addition overlap of atomic orbitals (AO). ABMO is formed by subtraction overlap of AOs.
 - b. BMO has lower energy and hence greater stability than the AOs from which it is formed. ABMO has a higher energy and lower stability than the AOs.
 - c. The electron charge density in between the nuclei is high resulting in lesser repulsion between the nuclei and this causes greater stability of the BMO. In ABMO, the electron charge density is low in between the nuclei which causes greater repulsion and hence destabilizes the ABMO.
4. The atomic orbitals of the atoms in a molecule completely lose their identity after the formation of MOs.
 5. Electrons fill the molecular orbitals in the same way as they fill the atomic orbitals, following the Aufbau principle, Pauli Exclusion Principle and the Hund's rule of maximum multiplicity.

Aufbau principle:

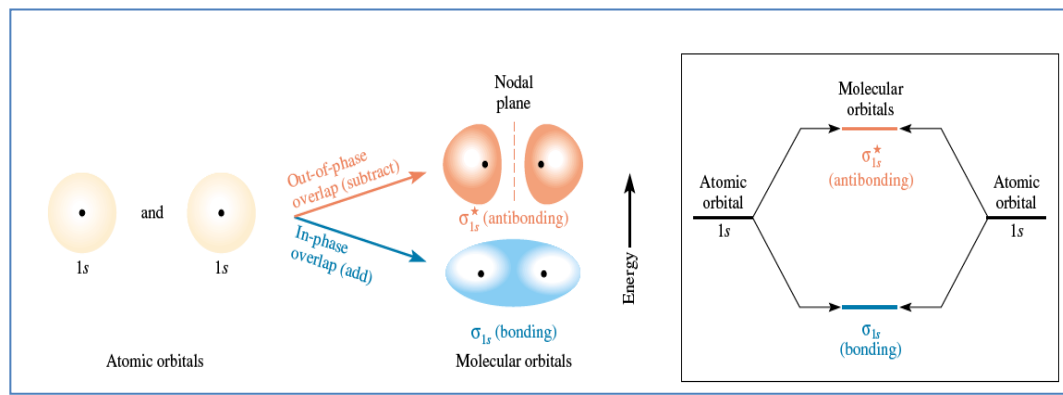
- Orbitals of lowest energy are filled up first.
- Each orbital will hold a maximum of two electrons, provided that they have opposite signs.

Pauli Exclusion Principle

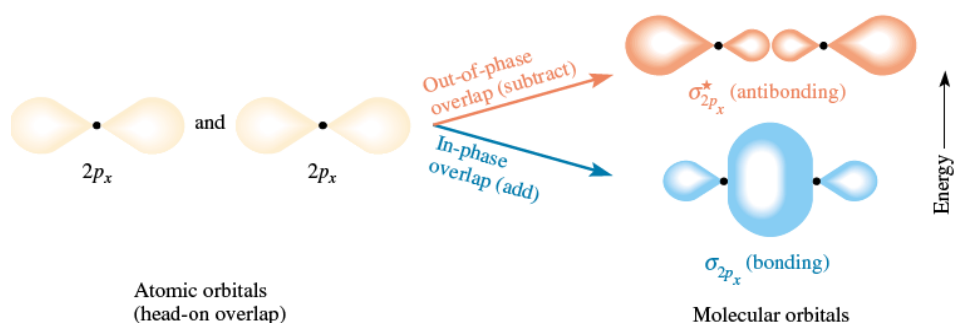
- in a given atom orbital, no two electrons can have all four quantum numbers the same.
- when applied for MO, the principle states that no two electrons in the same molecule can have all four quantum numbers the same.

Hund's rule:

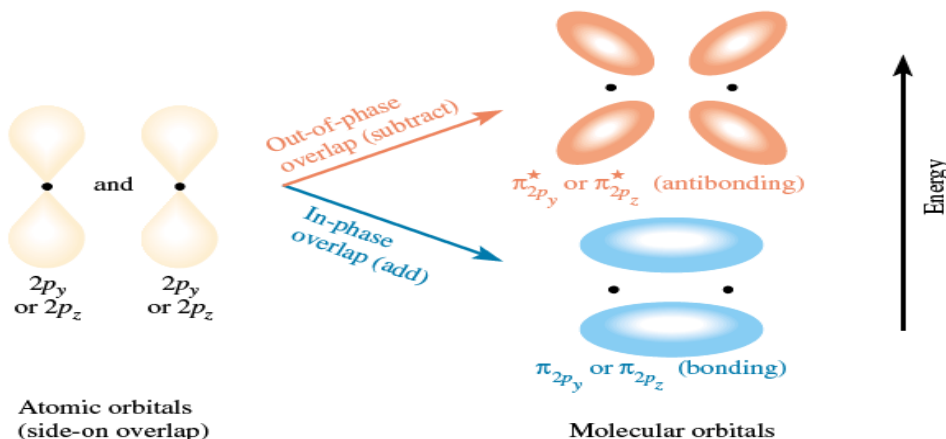
- Several orbitals have the same energy (degenerate orbitals of d, f)
- Electrons will be arranged so as to give maximum number of unpaired spins.



(MO) diagram for the combination of the $1s$ atomic orbitals on two identical atoms (at the left) to form two MOs: a *bonding* orbital, $1s$ (blue), resulting from addition of the $1s$ orbitals. The other is an *antibonding* orbital, $1s^*$ (red), at higher energy resulting from subtraction of the combining $1s$ orbitals. Nuclei are represented by dots.



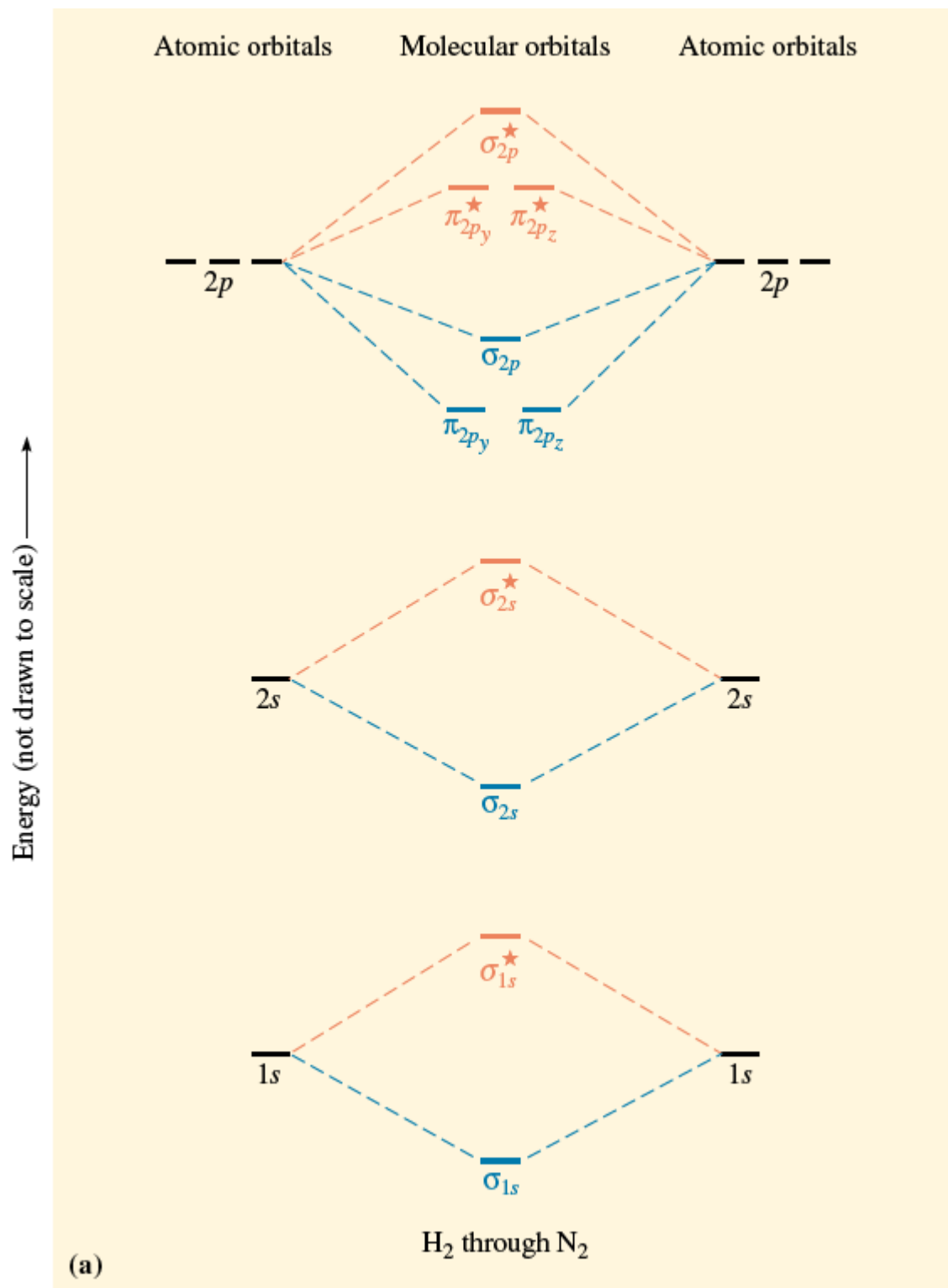
Production of σ_{p_x} and $\sigma^*_{p_x}$ MO by overlap of σ_{p_x} AO on two atoms.



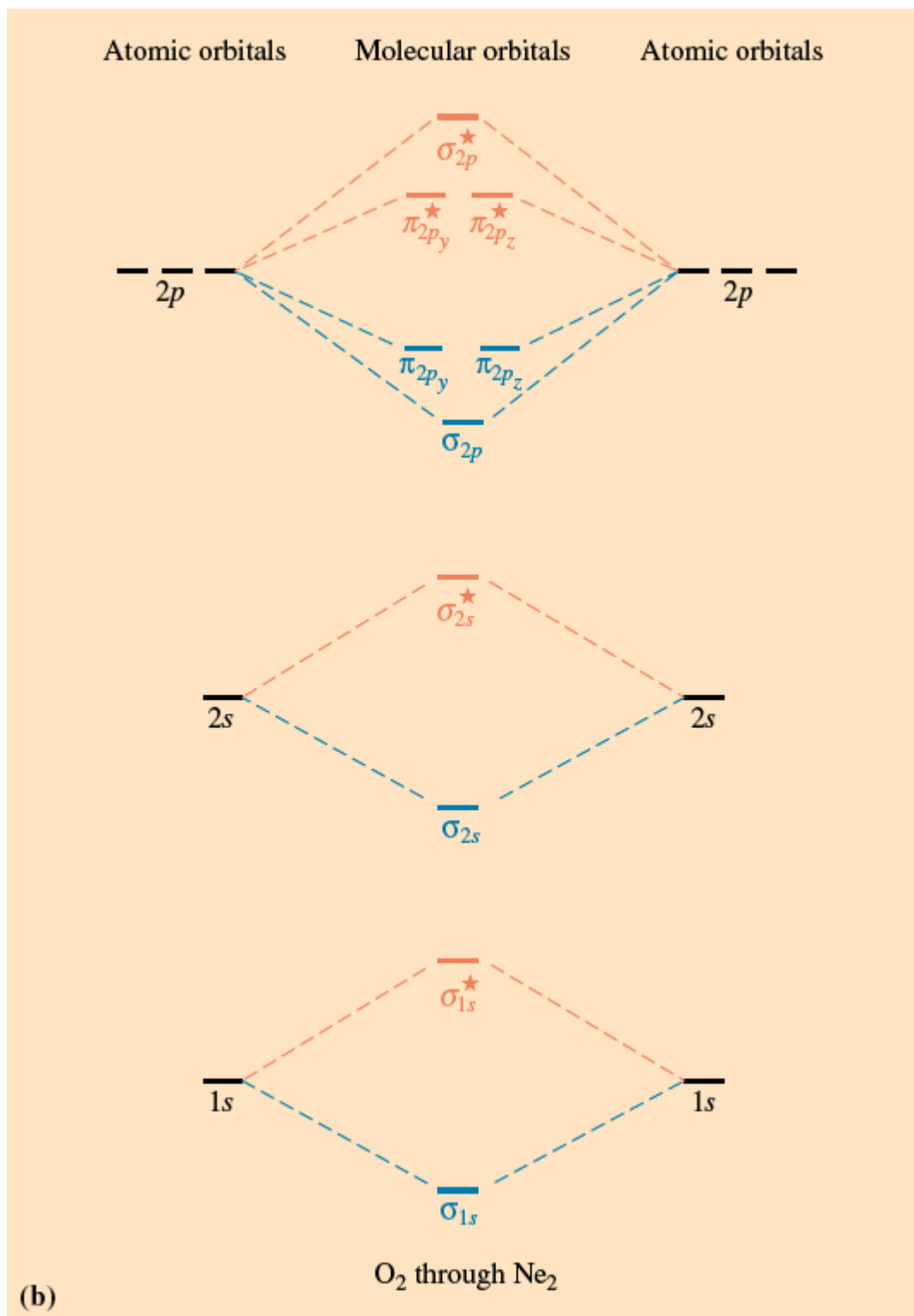
The Π_{2p} and Π^*_{2p} MO from overlap of one pair of $2p$ AO (for instance, $2p_y$ orbitals)

6. The order of energy of molecular orbitals

In simple homonuclear diatomic molecules (H_2 , He_2 , Li_2 , Be_2 , B_2 , C_2 , N_2) the order is



$(\sigma_{1s}), (\sigma_{1s}^*), (\sigma_{2s}), (\sigma_{2s}^*), (\pi_{2p_y}) = (\pi_{2p_z}), (\sigma_{2p}), (\pi_{2p_y}^*) = (\pi_{2p_z}^*), (\sigma_{2p}^*)$



For diatomic molecules like O_2 , F_2 and hypothetical Ne_2 , the order is (σ_{1s}) , (σ_{1s}^*) , (σ_{2s}) , (σ_{2s}^*) , (σ_{2p_x}) , $(\pi_{2p_y}) = (\pi_{2p_z})$, $(\pi_{2p_y}^*) = (\pi_{2p_z}^*)$, $(\sigma_{2p_x}^*)$

7. Bond order and stability:

If N_b represents the number of electrons present in the BMO and N_a the number of electrons present in the ABMO.

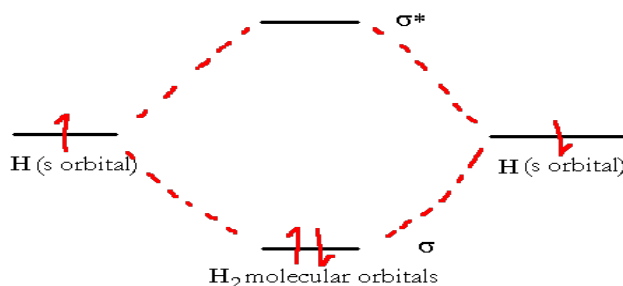
$$\text{Then Bond Order (BO)} = \frac{[\text{BMO} - \text{ABMO}]}{2}$$

- If $\text{BO} > 1$; i.e $\text{BMO} > \text{ABMO}$; then the molecule is stable
- If $\text{BO} < 1$; then the molecule is unstable
- If $\text{BO} = 0$; the molecule is unstable.
- For diatomic molecules, the stability is directly proportional to the bond order. Thus a molecule with a bond order 3 is more stable than a molecule with a bond order 2.
- Bond length is found to be inversely proportional to the bond order. Greater the bond order, shorter is the bond length.

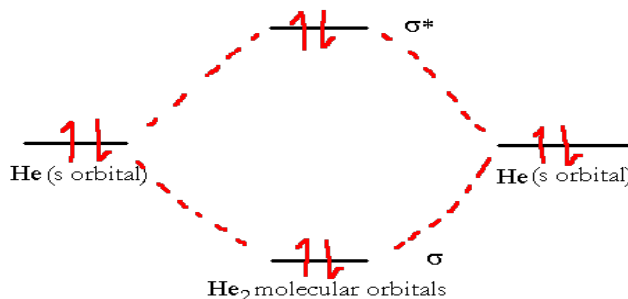
8. Diamagnetic and paramagnetic nature of the molecules

If all the electrons in the molecule are paired, it is diamagnetic in nature.

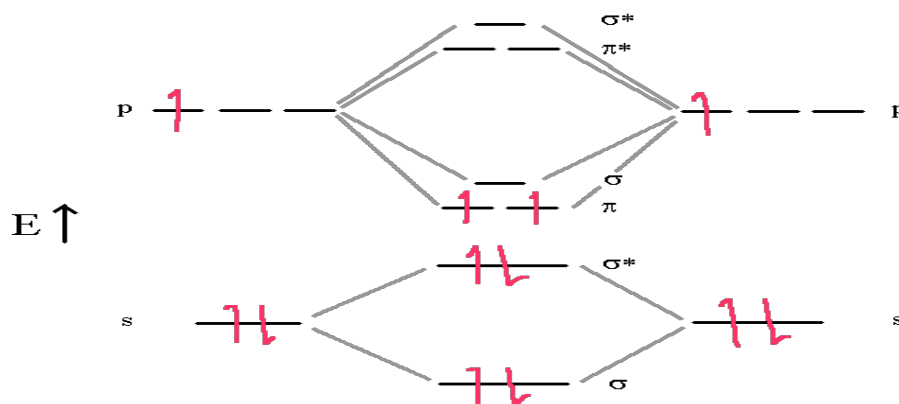
On the other hand, if the molecule has some unpaired electrons, it is paramagnetic in nature.

Molecular orbital diagrams of homonuclear diatomic molecules**1. H_2** 

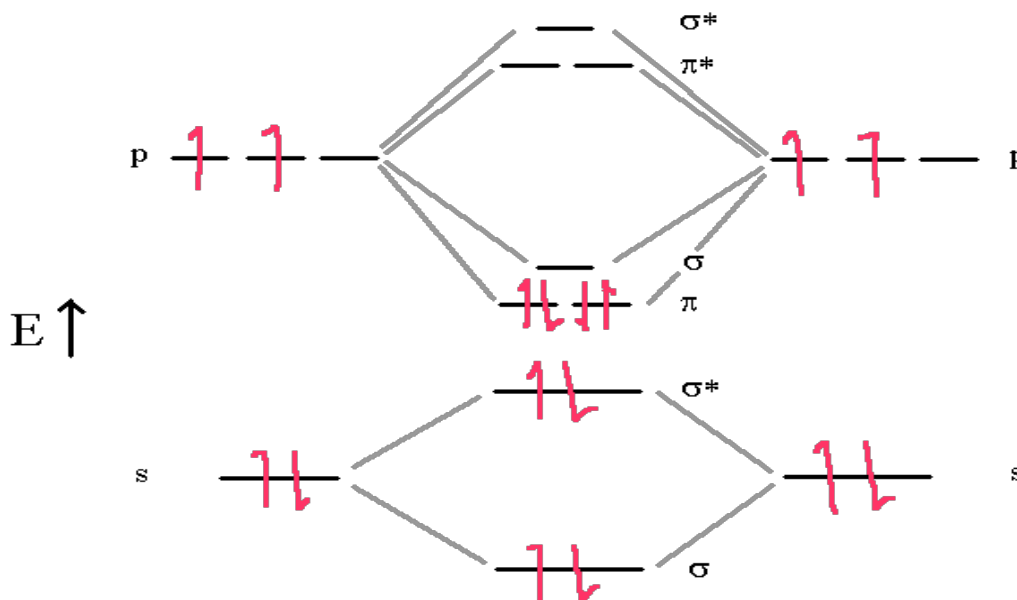
- The Molecule H_2 has an electron configuration $(\sigma_{1s})^2$.
- Bond order = $[\text{bonding electrons} - \text{Anti-bonding electrons}]/2 = 2/2 = 1$.

2. He_2 

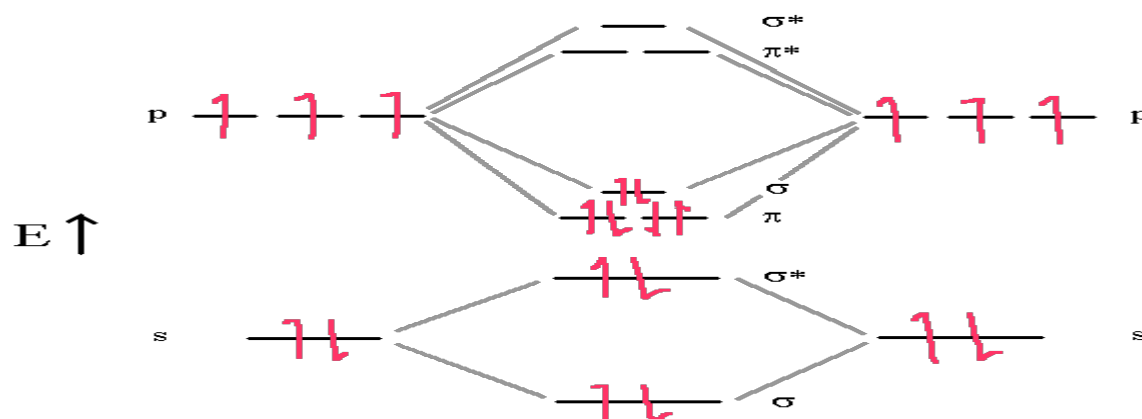
- The MO electronic configuration is $(\sigma_{1s})^2(\sigma_{1s}^*)^2$, i.e., one bonding orbital having 2 electrons and one antibonding orbital having 2 electrons.
- Bond order = $[2-2]/2 = 0$
- Thus the He_2 molecule does not exist.

3. B_2 

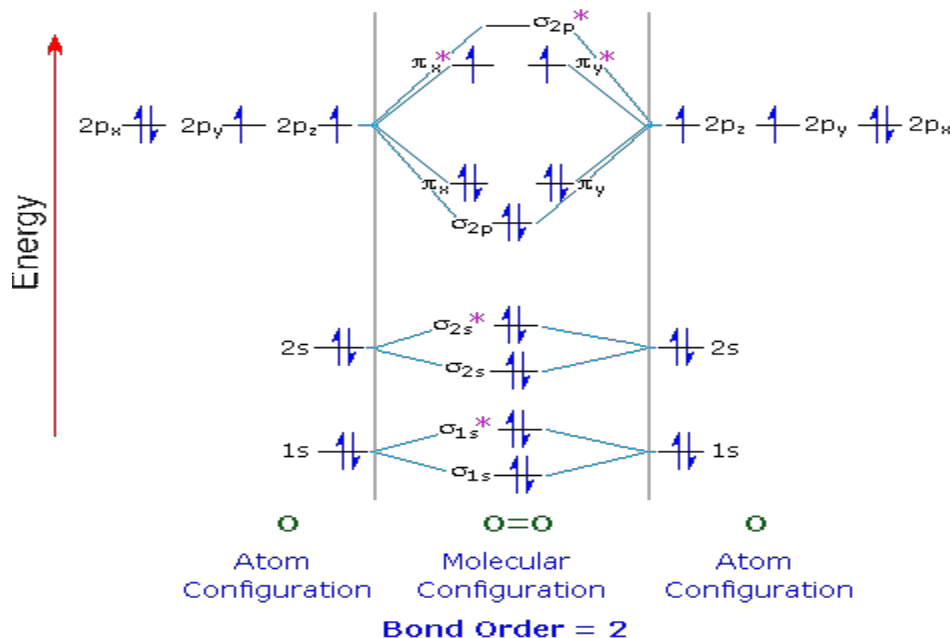
- Atomic Number of B = 5; Number of electrons in Boron molecule = 10
- The MO electronic configuration is $(\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2(\sigma^* 2s)^2[(\pi 2p_y)^1(\pi 2p_z)^1]$, **$\pi 2p$ orbitals have lower energy than $\sigma 2p_x$ orbital.**
- Since the π_{2py} , π_{2pz} orbitals are degenerate (identical energy) Hund's rule applies and each orbital is singly filled.
- The inner shell does not participate in bonding. Stability occurs due to filling of π_{2p} orbitals
- Bond order = $[6-4]/2 = 1$; hence B_2 exists

4. C_2 

- Atomic Number of C = 6; Number of electrons in C_2 molecule = 12
- The MO electronic configuration is $(\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2(\sigma^* 2s)^2[(\pi 2p_y)^2(\pi 2p_z)^2]$
- Bond order = $[8-4]/2 = 2$; hence C_2 exists

5. N₂

- Atomic Number of N = 7; Number of electrons in N₂ molecule = 14
- The MO electronic configuration is $(\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2(\sigma^* 2s)^2[(\pi 2p_y)^2(\pi 2p_z)^2](\sigma 2p_x)^2$
- The inner shell do not participate in bonding, the bonding and antibonding 2s orbitals cancel each other, so only one $\sigma 2p_x$ and 2 $\pi 2p$ orbitals remain giving a
- Bond order = $[10-4]/2 = 3$; hence 3 bonds exist in N₂ molecule

O₂

- Atomic Number of O = 8; Number of electrons in O₂ molecule = 16
- The MO electronic configuration is $(\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2(\sigma^* 2s)^2[(\pi 2p_y)^2(\pi 2p_z)^2](\sigma 2p_x)^2[(\pi^* 2p_y)^1(\pi^* 2p_z)^1]$

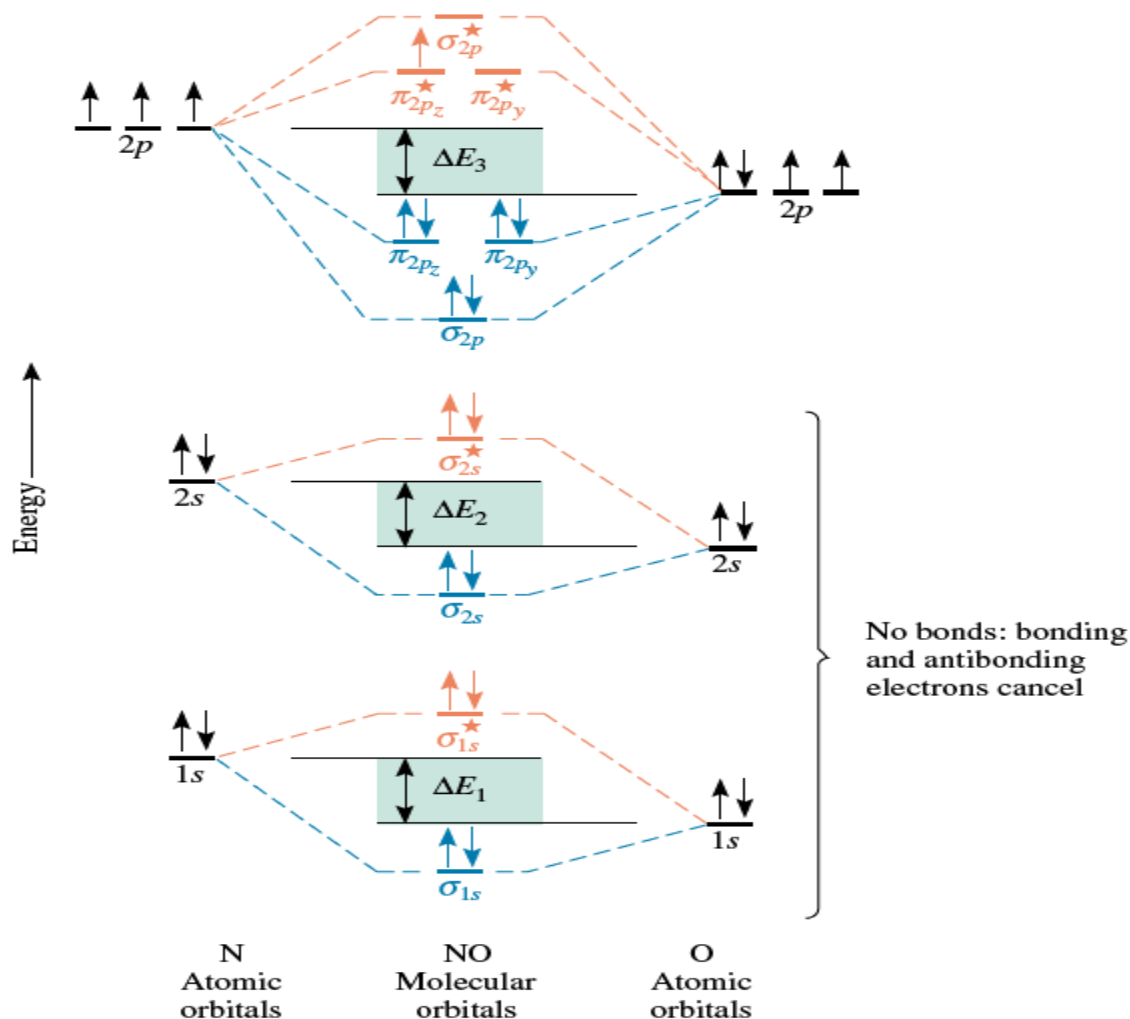
- The antibonding π^*_{2py} and π^*_{2pz} orbitals are singly occupied in accordance to Hund's rule.
- Unpaired electrons give rise to paramagnetism. Since there are two unpaired electrons with parallel spins, this explains why oxygen is paramagnetic.
- Bond order = $[10-6]/2 = 2$; hence a double bonds exist in O_2 molecule

Molecular Orbitals for First- and Second-Period (Row) Diatomic Molecules^a

	H ₂	He ₂ ^c	Li ₂ ^b	Be ₂ ^c	B ₂ ^b	C ₂ ^b	N ₂		O ₂	F ₂	Ne ₂ ^c
Increasing energy (not to scale)											
σ^*_{2p}	—	—	—	—	—	—	—		—	—	$\uparrow\downarrow$
π^*_{2py} π^*_{2pz}	—	—	—	—	—	—	—		\uparrow \uparrow	$\uparrow\downarrow$ $\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow\downarrow$
σ_{2p}	—	—	—	—	\uparrow \uparrow	$\uparrow\downarrow$ $\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow\downarrow$	π_{2py}, π_{2pz}	$\uparrow\downarrow$ $\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow\downarrow$
π_{2py} π_{2pz}	—	—	—	—	\uparrow \uparrow	$\uparrow\downarrow$ $\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow\downarrow$	σ_{2p}	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$
σ^*_{2s}	—	—	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$		$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$
σ_{2s}	—	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$		$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$
σ^*_{1s}	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$		$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$
σ_{1s}	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$		$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$
Paramagnetic?	no	no	no	no	yes	no	no		yes	no	no
Bond order	1	0	1	0	1	2	3		2	1	0
Observed bond length (Å)	0.74	—	2.67	—	1.59	1.31	1.09		1.21	1.43	—
Observed bond energy (kJ/mol)	436	—	110	9	≈270	602	945		498	155	—

^aElectron distribution in molecular orbitals, bond order, bond length, and bond energy of homonuclear diatomic molecules of the first- and second-period elements. Note that nitrogen molecules, N_2 , have the highest bond energies listed; they have a bond order of three. The species C_2 and O_2 , with a bond order of two, have the next highest bond energies.

^bExists only in the vapor state at elevated temperatures.

Molecular orbital diagrams of heteronuclear diatomic molecules1. **NO**

MO energy level diagram for nitrogen oxide, NO, a slightly polar heteronuclear diatomic molecule

- Atomic Number of N = 7; Atomic Number of O = 8; Number of electrons in NO = 15
- The MO electronic configuration is $(\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_x)^2[(\pi 2p_y)^2(\pi 2p_z)^2][(\pi^* 2p_y)^1(\pi^* 2p_z)^0](\sigma^* 2p_x)$
- The AO of oxygen, the more electronegative element, are a little lower in energy than the corresponding AOs of nitrogen, the less electronegative element.
- Bond order = $[10-5]/2 = 2.5$; hence NO is stable.
- NO is paramagnetic since it contains one unpaired electron.

2. CO

- Atomic Number of C = 6; Atomic Number of O = 8; Number of electrons in CO = 14
- The MO electronic configuration is
 $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 [(\pi 2p_y)^2 (\pi 2p_z)^2] (\sigma 2p_x)^2 (\sigma^* 2s)^2$
- The AO of oxygen are a little lower in energy than the corresponding AOs of Carbon, the less electronegative element.
- Bond order = $[10-4]/2 = 3$; thus CO contains a triple bond.
- CO is diamagnetic because there are no unpaired electrons.

