

MODULE-1. ATOMIC AND MOLECULAR

STRUCTURE

ATOMIC ORBITALS DEFINITION- An orbital is a three dimensional space around the nucleus of an atom where the probability of finding the electrons is maximum.

CHARACTERISTIC FEATURES:-

- An **atomic orbital** is a **mathematical function** describing the location and wave-like behaviour of an electron in an **atom**
- Each orbital in an atom is characterized by an unique set of values of the three **quantum numbers** n , ℓ , and m .
- orbital can be occupied by a maximum of two electrons, each with its own projection of **spin**
- The orbitals can be differentiated on the basis of their size, shape or orientation.
- Ψ is a mathematical function which represents the coordinates of an Electron. It also helps to draw the boundary surface diagrams of different orbitals which in turn help to understand the shape of orbitals.
- Ψ^2 represents the probability of finding an electron.

SHAPES OF ORBITALS:- On the basis of surface boundary diagram of orbital they are of four types s, p, d and f (sharp, principle, diffuse and fundamental)

1) Shape of S-orbitals

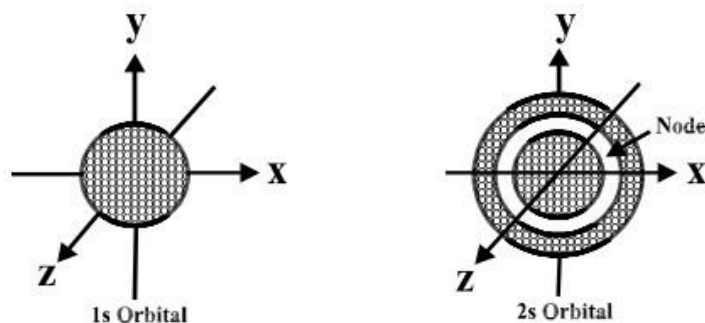


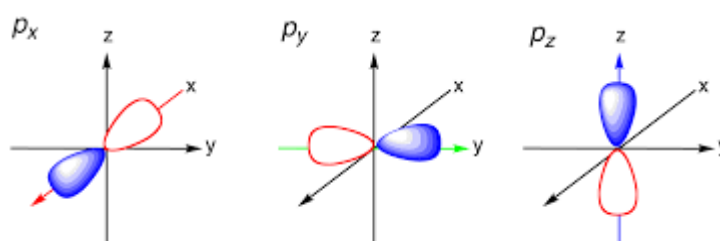
Fig. Shapes of 1s and 2s-orbitals

For s-orbitals, when $l = 0$, the value of m is 0 i.e., there is only one possible orientation. This means that the probability of finding an electron is the same in all directions at a given distance from the nucleus. It should, therefore, be spherical in shape. Hence all s- orbitals are non- directional and spherically symmetrical about the nucleus. The size of an s-orbital depends upon value of the principal quantum number n . Greater the value of ' n ' larger is the size of the orbital.

An important feature of the 2s-orbital is that there is a spherical shell within this orbital where the probability of finding the electron is zero (nearly). This is called a node or nodal surface. In 2s orbital there is one spherical node. The number of nodal

surfaces or nodes in s-orbital of any energy level is equal to $(n-1)$, where n is the principal quantum number.

2) Shape of p-orbitals



The three p orbitals are aligned along perpendicular axes

For p-subshell $l = 1$, there are three values of m namely $-1, 0, +1$. It means that p orbitals can have three possible orientations. These three p-orbitals are equal in energy (degenerate state) but differ in their orientations. Each p-orbital consists of two lobes symmetrical about a particular axis. Depending upon the orientation of the lobes, these are denoted as $2p_x$, $2p_y$ and $2p_z$ accordingly as they are symmetrical about X, Y and Z - axis respectively.

The lines in the figure represents the cross-section of the three dimensional boundary surface of p-orbitals. The boundary surface means the surface which encloses 90 percent of the dots representing the electrons. Two lobes of each p-orbital are separated by a nodal plane (a plane having zero electron density). For example, for $2p_x$ orbital, YZ plane is the nodal plane

Thus, p-orbitals have dumb-bell shape and have directional character. The probability of finding the electron is equal in both the lobes. The p-orbitals of higher energy levels have similar shapes although their size are bigger.

3) Shape of d-orbitals

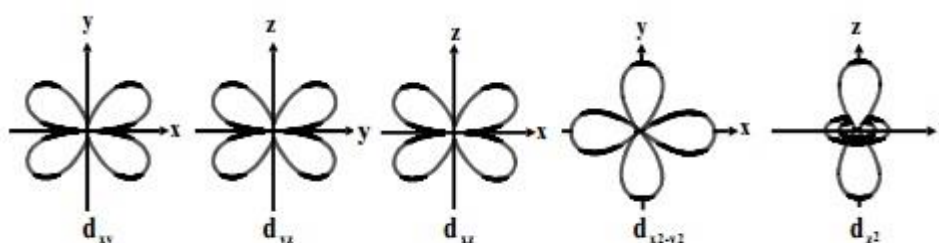


Fig. Shapes of d-orbitals

For d-subshell, $l = 2$, there are five values of m namely $-2, -1, 0, 1, 2$. It means d- orbitals can have five orientations. These are represented by d_{xy} , d_{yz} , d_{zx} , $d_{x^2-y^2}$ and d_{z^2} . The d_{xy} , d_{yz} and d_{zx} orbitals have same shape i.e., clover leaf shape but they lie in XY, YZ and ZX

planes respectively. The d_{z^2} orbital is symmetrical about Z-axis and has a dumb - bell shape with a doughnut shaped electron cloud in the centre. The $d_{x^2-y^2}$ orbital is also clover leaf shaped but its leaves are directed along the X and Y- axis.

The reason for the presence of four lobes in any nd orbital lies in the fact that the d - orbitals have two nodes, and hence two changes in algebraic sign of ψ , which lead to four lobes.

Electronic configuration:- is the standard notation used to describe the electronic structure of an atom. i.e the distribution of electron in various orbitals around nucleus in the ground state of an atom of the elements.

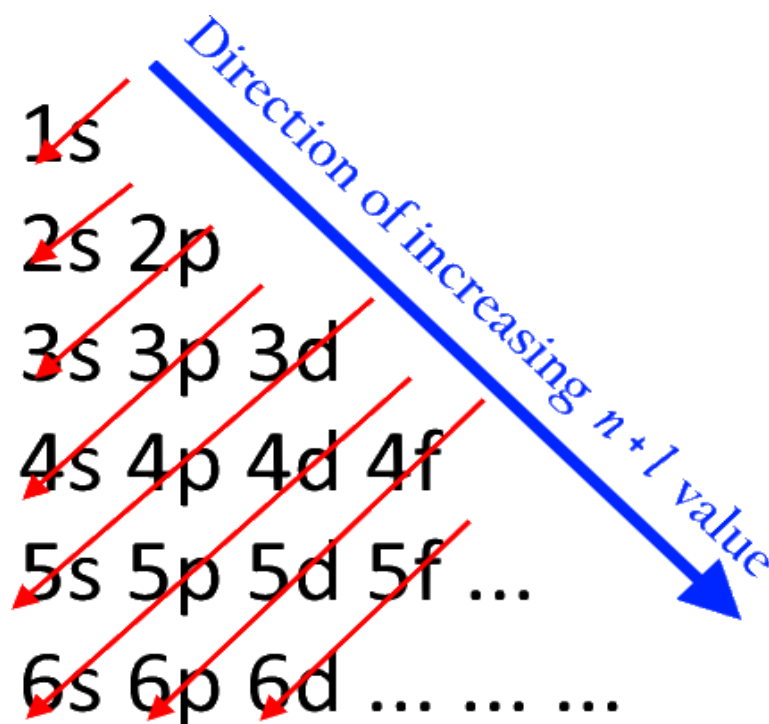
General Rules of Electron Configuration- we must follow a set of three rules: Aufbau Principle, Pauli-Exclusion Principle, and Hund's Rule.

Aufbau Principle

The Aufbau principle dictates that electrons will occupy the orbitals having lower energies before occupying higher energy orbitals. The energy of an orbital is calculated by the sum of the principal and the azimuthal quantum numbers.

According to this principle, electrons are filled in the following order: 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, 7p...

The order in which electrons are filled in atomic orbitals as per the Aufbau principle is illustrated below.



The states crossed by same red arrow have same value. The direction of the red arrow indicates the order of state filling.

There exist many exceptions to the Aufbau principle such as chromium and copper. These exceptions can sometimes be explained by the stability provided by half-filled or completely filled subshells.

Pauli Exclusion Principle- states that a maximum of two electrons, each having opposite spins, can fit in an orbital. This principle can also be stated as “no two electrons in the same atom have the same values for all four quantum numbers”, therefore, if the principal, azimuthal, and magnetic numbers are the same for two electrons, they must have opposite spins.

Hund’s Rule

This rule describes the order in which electrons are filled in all the orbitals belonging to the same subshell having identical energy. For eg. P_x, P_y, P_z , in such cases pairing of electron will not be done until and unless all the subshells were singly filled. In order to maximize the total spin, the electrons in the orbitals that only contain one electron all have the same spin (or the same values of the spin quantum number). And pairing start with electron having opposite spin.

Differences between Orbit and Orbitals	
Orbit	Orbitals
An orbit is the simple planar representation of an electron.	An orbital refers to the dimensional motion of an electron around the nucleus in a three-dimensional motion.
It can be simply defined as the path that gets established in a circular motion by revolving the electron around the nucleus	An orbital can simply be defined as the space or the region where the electron is likely to be found the most.
The shape of molecules cannot be explained by an orbit as they are non-directional by nature.	The shapes of the molecules can be found out as they are directional by nature.
An orbit that is well-defined goes against the Heisenberg principle.	An ideal orbital agrees with the theory of Heisenberg’s Principles.

Quantum Numbers

To completely describe an electron in an atom, four quantum numbers are needed: energy (n), angular momentum (ℓ), magnetic moment (m_ℓ), and spin (m_s).

Principal Quantum Number (n)

The first quantum number describes the electron shell, or energy level, of an atom. The value of n ranges from 1 to the shell containing the outermost electron of that atom. This number gives the distance between the electron and the nucleus. The average distance increases with

n, thus quantum states with different principal quantum numbers are said to belong to different shells.

Azimuthal Quantum Number (l)

The second quantum number, known as the angular or orbital quantum number, describes the subshell and gives the magnitude of the orbital angular momentum through the relation. $\ell = 0$ is called an s orbital, $\ell = 1$ a p orbital, $\ell = 2$ a d orbital, and $\ell = 3$ an f orbital. The value of ℓ ranges from 0 to $n - 1$ because the first p orbital ($\ell = 1$) appears in the second electron shell ($n = 2$), the first d orbital ($\ell = 2$) appears in the third shell ($n = 3$), and so on. In chemistry, this quantum number is very important since it specifies the shape of an atomic orbital and strongly influences chemical bonds and bond angles.

Magnetic Quantum Number (m)

The magnetic quantum number describes the energy levels available within a subshell and yields the projection of the orbital angular momentum along a specified axis. The values of m_ℓ range from $-\ell$ to ℓ , with integer steps between them. The s subshell ($\ell = 0$) contains one orbital, and therefore the m_ℓ of an electron in an s subshell will always be 0. The p subshell ($\ell = 1$) contains three orbitals (in some systems depicted as three “dumbbell-shaped” clouds), so the m_ℓ of an electron in a p subshell will be -1 , 0 , or 1 . The d subshell ($\ell = 2$) contains five orbitals, with m_ℓ values of -2 , -1 , 0 , 1 , and 2 . The value of the m_ℓ quantum number is associated with the orbital orientation.

Spin Projection Quantum Number (s)

The fourth quantum number describes the spin (intrinsic angular momentum) of the electron within that orbital and gives the projection of the spin angular momentum (s) along the specified axis. the values of m_s range from $-s$ to s , where s is the spin quantum number, an intrinsic property of particles. An electron has spin $s = \frac{1}{2}$, consequently m_s will be \pm , corresponding with spin and opposite spin. Each electron in any individual orbital must have different spins because of the Pauli Exclusion Principle; therefore an orbital never contains more than two electrons.

For example, if $n = 3$ and $l = 2$ in an atom, the possible values of the magnetic quantum number are -2 , -1 , 0 , $+1$, and $+2$.

Azimuthal Quantum Number ($l = n-1$)	Value Corresponding Orbitals ($2l + 1$)	Number of Possible Values of m_l
0 ('s' subshell)	$2 \cdot 0 + 1 = 1$	0
1 ('p' subshell)	$2 \cdot 1 + 1 = 3$	-1, 0, and 1
2 ('d' subshell)	$2 \cdot 2 + 1 = 5$	-2, -1, 0, 1, and 2

The total number of orbitals in a given subshell is a function of the 'l' value of that orbital. It is given by the formula $(2l + 1)$. For example, the '3d' subshell ($n=3$, $l=2$) contains 5 orbitals

($2 \times 2 + 1$). Each orbital can accommodate 2 electrons. Therefore, the 3d subshell can hold a total of 10 electrons.

Molecular orbital theory

The Molecular Orbital Theory (MOT) is a theory on chemical bonding developed by F. Hund and R. S. Mulliken to describe the structure and properties of different molecules. The valence-bond theory failed to adequately explain how certain molecules contain two or more equivalent bonds whose bond orders lie between that of a single bond and that of a double bond, such as the bonds in resonance-stabilized molecules. This is where the molecular orbital theory proved to be more powerful than the valence-bond theory.

Molecular orbital theory was proposed to explain following facts:

- The formation of chemical bonds.
- Relative bond strength.
- Magnetic behaviour of the molecules.

The Salient features of the molecular orbital theory are listed below:

- The molecular orbitals are created because of the overlapping of the atomic orbitals. The atomic orbitals merge with each other to form the molecular orbitals.
- The electrons of the molecules fill the new energy states of the molecular orbitals, similar to filling up of the energy states of the atomic orbitals.
- The probability of finding the distribution of electrons around the nuclei of a molecule is given by the molecular orbital.
- The two atomic orbitals which combine to form the molecular orbital should possess energy values of similar orientation. For eg. 1S orbital can only combine with 1S not with 2S or 2P.
- The number of molecular orbitals created are equal to the number of combining atomic orbitals.
- The shape of the molecular orbitals depends on the shape of the atomic orbitals.

Linear Combination of Atomic Orbitals (LCAO)- Molecular orbitals can generally be expressed through a linear combination of atomic orbitals (LCAO).

Conditions for Linear Combination of Atomic Orbitals: The conditions that are required for the linear combination of atomic orbitals are as follows:

- **Same Energy of Combining Orbitals-** The atomic orbitals combining to form molecular orbitals should have comparable energy. This means that 2p orbital of an atom can combine with another 2p orbital of another atom but 1s and 2p cannot combine together as they have appreciable energy difference.
- **Same Symmetry about Molecular Axis-** The combining atoms should have the same symmetry around the molecular axis for proper combination; otherwise, the electron density will be sparse. For e.g. all the sub-orbitals of 2p have the same energy but still, 2p_x orbital of an atom can only combine with a 2p_x orbital of another atom

but cannot combine with $2p_x$ and $2p_y$ orbital as they have a different axis of symmetry. In general, the z -axis is considered as the molecular axis of symmetry.

- **Proper Overlap between Atomic Orbitals-** The two atomic orbitals will combine to form molecular orbital if the overlap is proper. Greater the extent of overlap of orbitals, greater will be the nuclear density between the nuclei of the two atoms.

Types of Molecular Orbitals: - According to the molecular orbital theory, there exist three primary types of molecular orbitals that are formed from the linear combination of atomic orbitals. An atomic orbital is an electron wave; the waves of the two atomic orbitals may be in phase or out of phase. Suppose Ψ_A and Ψ_B represent the amplitude of the electron wave of the atomic orbitals of the two atoms A and B.

- **Bonding Molecular Orbitals** - When the two waves are in phase so that they add up and amplitude of the wave is $\Phi = \Psi_A + \Psi_B$. The probability of finding the electron in the internuclear region of the bonding molecular orbital is greater than that of combining atomic orbitals. The electrons present in the bonding molecular orbital result in the attraction between the two atoms so they have lower energy and hence has greater stability than that of the combining atomic orbitals. They are represented by σ , π , and δ .
- **Anti Bonding Molecular Orbitals-** when the two waves are out of phase, the waves are subtracted from each other so that the amplitude of the new wave is $\Phi' = \Psi_A - \Psi_B$. The probability of finding the electron in the internuclear region decreases in the anti-bonding molecular orbitals. The electrons present in the anti-bonding molecular orbital result in the repulsion between the two atoms so have higher energy and lower stability than that of the combining atomic orbitals. They are formed by the subtractive effect of the atomic orbitals. They are represented by σ^* , π^* , δ^* . The lowering of the energy of bonding molecular orbital than the combining atomic orbital is called stabilization energy and similarly increase in energy of the anti-bonding molecular orbitals is called destabilization energy.
- **Non-Bonding Molecular Orbitals-** In the case of non-bonding molecular orbitals, due to a complete lack of symmetry in the compatibility of two bonding atomic orbitals, the molecular orbitals formed have no positive or negative interactions with each other. These types of orbitals do not affect the bond between the two atoms.

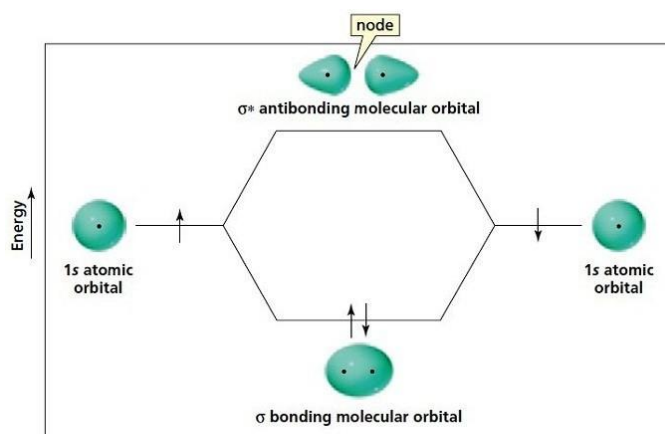


Fig. No. Energies of BMO and ABMO

Difference between Bonding molecular orbital and Anti bonding molecular orbital

Bonding molecular orbital	Anti Bonding molecular orbital
Molecular orbitals formed by the additive effect of the atomic orbitals is called bonding molecular orbitals	Molecular orbitals formed by the subtractive effect of atomic is called anti-bonding molecular orbitals
These are formed by the combination of + and + and – with – part of the electron waves	These are formed by the overlap of + with – part.
Probability of finding the electrons is more in the case of bonding molecular orbitals	Probability of finding electrons is less in antibonding molecular orbitals. There is also a node between the anti-bonding molecular orbital between two nuclei where the electron density is zero.
The electron density, in the bonding molecular orbital in the internuclear region, is high. As a result, the nuclei are shielded from each other and hence the repulsion is very less.	The electron density in the antibonding molecular orbital in the internuclear region is very low and so the nuclei are directly exposed to each other. Therefore the nuclei are less shielded from each other.
The bonding molecular orbitals are represented by σ , π , δ .	The corresponding anti-bonding molecular orbitals are represented by σ^* , π^* , δ^* .

Difference Between Sigma and Pi bond	
Sigma Bond (σ)	Pi Bond (π)
During sigma bond formation overlapping orbitals can either be one hybrid orbital and a single pure orbital, or two pure orbitals and two hybrid orbitals.	During pi bond formation overlapping orbitals must be two unhybridized orbitals.
Sigma bonds are known to exist independently and allow free rotation.	Pi-bonds must always exist along with sigma bond and the rotation is restricted.
Sigma bonds are stronger bonds.	Pi bonds are usually less powerful compared to sigma bonds.

Sigma bonds are formed first when atoms interact.	Pi bonds between two atoms are formed after sigma bonds are formed between them.
During the bonding between two given atoms, Only one sigma bond is formed.	Here two pi bonds can exist between two atoms.
Sigma bonds are known to have cylindrical charge symmetry around the axis of the bond.	No symmetry exists in pi bonds.
Atoms with sigma bonds can be highly reactive.	Atoms with pi bonds are not as reactive in nature when compared to those with only sigma bonds.
Sigma bond can be used to determine the shapes of molecules.	Pi bond cannot be used for the same purpose.

Bond Order

It may be defined as the half of difference between the number of electrons present in the bonding orbitals and the antibonding orbitals that is,

$$\text{Bond order (B.O.)} = (\text{No. of electrons in BMO} - \text{No. of electrons in ABMO}) / 2$$

Those with positive bonding order are considered stable molecule while those with negative bond order or zero bond order are unstable molecule.

Significance of Bond Order

- If value of bond order is positive, it indicates a stable molecule and if the value is negative or zero, it means that the molecule is unstable.
- The stability of a molecule is measured by its bond dissociation energy. But the bond dissociation energy is directly proportional to the bond order. Greater the bond order, greater is the **bond dissociation energy**.
- Bond order is inversely proportional to the bond length. The higher the bond order value, smaller is the bond length. **For Example** the bond length in nitrogen molecule is shorter than in oxygen molecule
- Magnetic character - If all the electrons in the molecule of a substance are paired, the substance is diamagnetic (repelled by the magnetic field). On the other hand, if there are unpaired electrons in the molecule, the substance is paramagnetic (attracted by the magnetic field).

Magnetic Behaviour: If all the molecular orbitals in species are spin paired, the substance is diamagnetic. But if one or more molecular orbitals are singly occupied it is paramagnetic.

SOME EXAMPLES OF HOMONUCLEAR DIATOMIC MOLECULES

HYDROGEN MOLECULE: A hydrogen molecule contains two bonding electrons and no antibonding electrons.

$$\text{Bond order in H}_2 = (2-0)/2 = 1$$

Because the bond order for the H–H bond is equal to 1, the bond is a single bond.

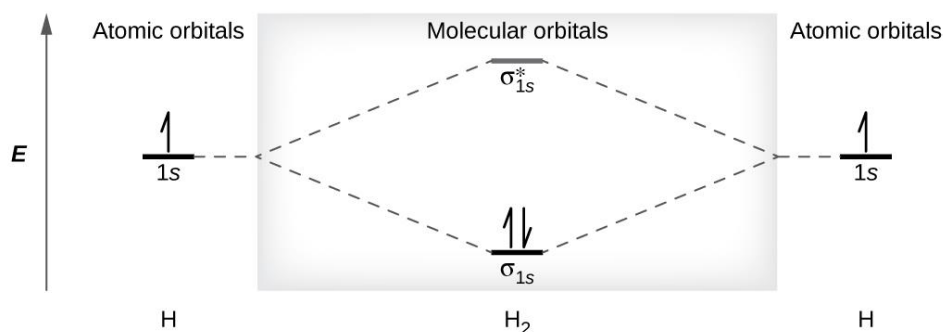


Figure: The molecular orbital energy diagram predicts that H₂ will be a stable molecule with lower energy than the separated atoms.

HELIUM MOLECULE: Two helium atoms do not combine to form a dihelium molecule, the hypothetical electron configuration of He₂ as $(\sigma 1s)^2(\sigma^* 1s)^2$. Helium exists as discrete atoms rather than as diatomic molecules. The bond order in a hypothetical dihelium molecule would be zero.

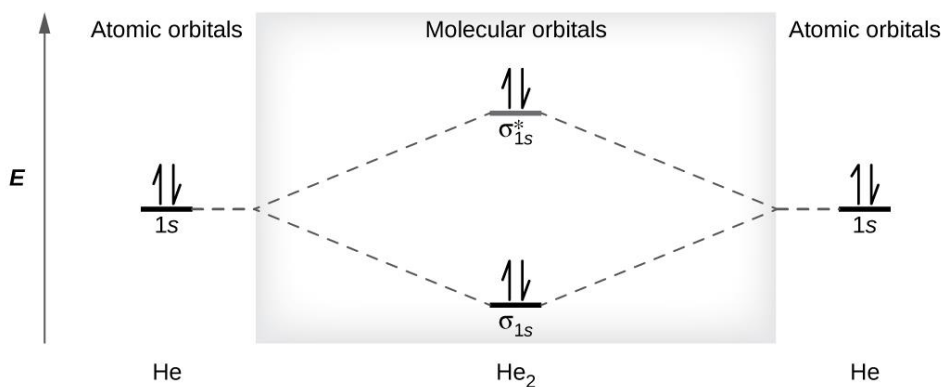


Figure: The molecular orbital energy diagram predicts that He₂ will not be a stable molecule, since it has equal numbers of bonding and antibonding electrons.

$$\text{Bond order in He}_2 = (2-2)/2 = 0$$

A bond order of zero indicates that no bond is formed between two atoms.

BERYLLIUM MOLECULE:

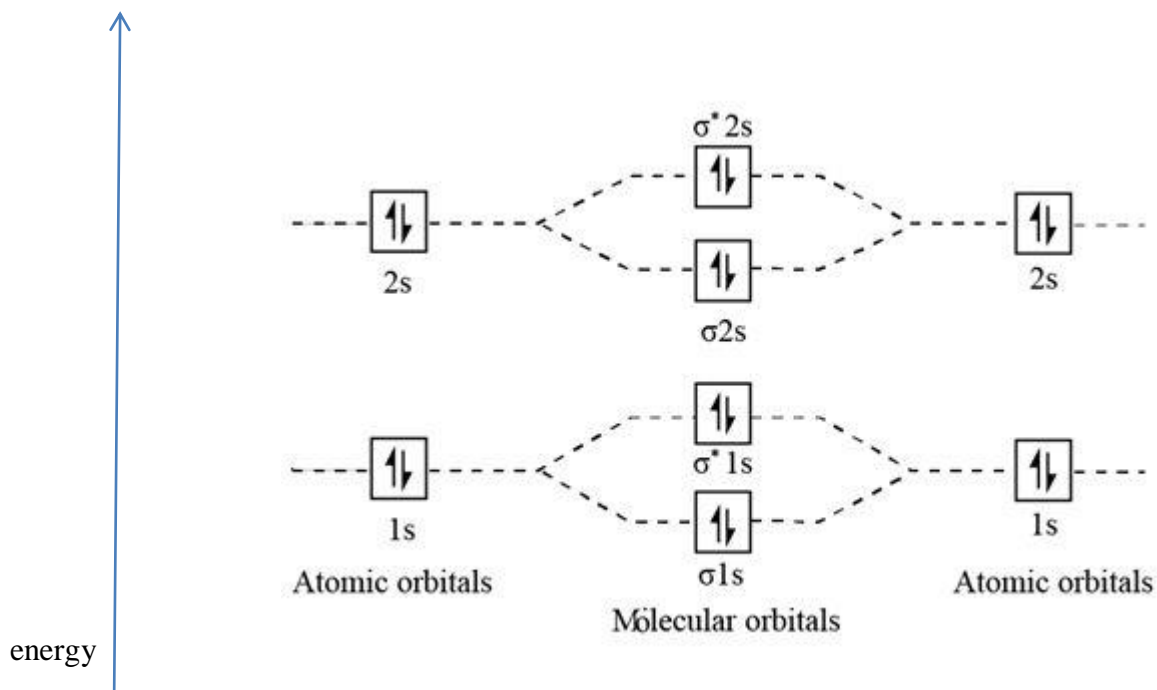


Figure: The molecular orbital energy diagram predicts that Be_2 will not be a stable molecule, since it has equal numbers of bonding and antibonding electrons.

$$\text{Bond order in } \text{Be}_2 = (4-4)/2 = 0$$

A bond order of zero indicates that no bond is formed between two atoms.

OXYGEN MOLECULE:

Electronic configuration: $\sigma 1s, \sigma^* 1s, \sigma 2s, \sigma^* 2s, \sigma 2p_z, [\pi 2p_x = \pi 2p_y], [\pi^* 2p_x = \pi^* 2p_y], \sigma^* 2p_z$

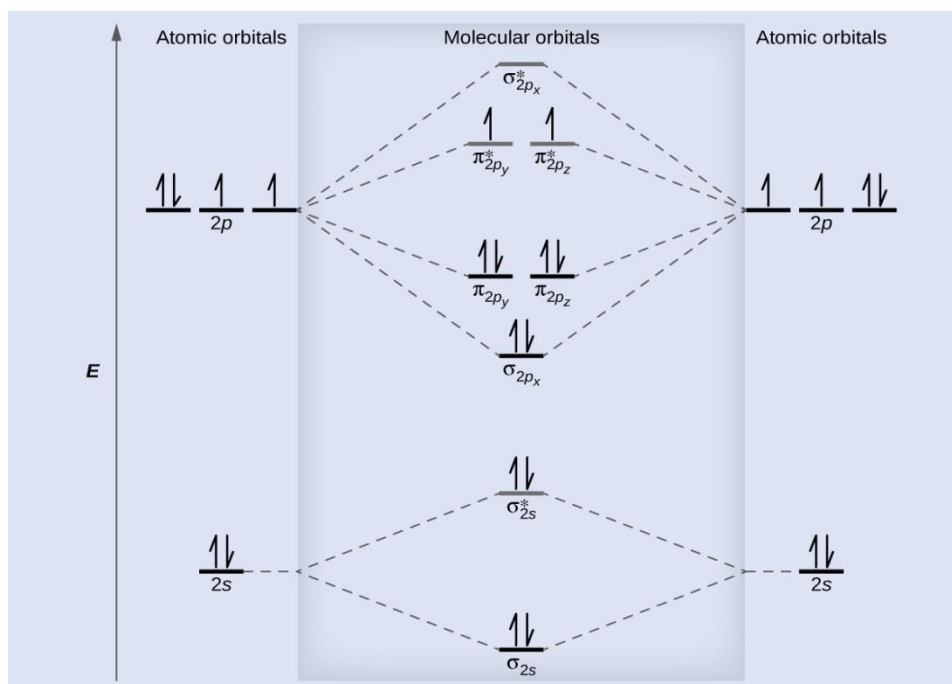


Figure: The molecular orbital energy diagram for O_2 predicts two unpaired electrons.

Oxygen is paramagnetic due to the presence of two unpaired electrons in the $(\pi_{2py}, \pi_{2pz})^*$ molecular orbitals.

$$\text{Bond order in O}_2 = (8-4)/2 = 2$$

Because the bond order for the O-O bond is equal to 2, the bond is a double bond.

SOME EXAMPLES OF HETERONUCLEAR DIATOMIC MOLECULES

NO – formed by the overlapping of two different atoms of N & O.

N = $1s^2, 2s^2, 2p^3$ & O = $1s^2, 2s^2, 2p^4$ total of 15 electrons.

Electronic configuration: $\sigma 1s, \sigma^* 1s, \sigma 2s, \sigma^* 2s, \sigma 2p_z, [\pi 2p_x = \pi 2p_y], [\pi^* 2p_x = \pi^* 2p_y], \sigma^* 2p_z$

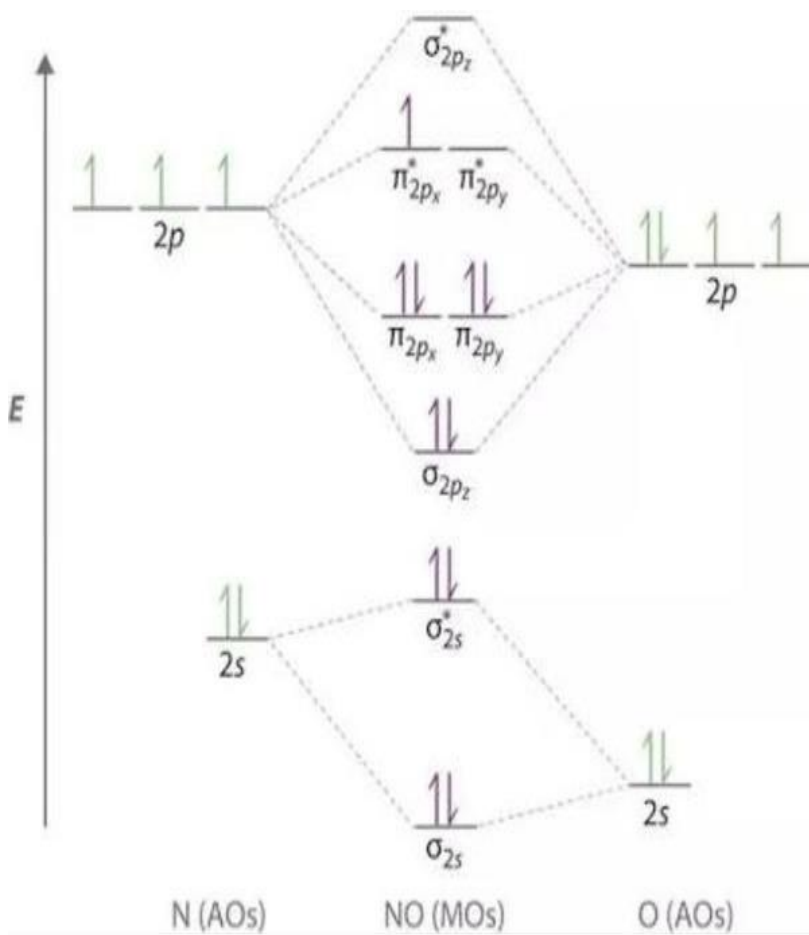


Figure: The molecular orbital energy diagram for NO predicts one unpaired electron.

$$\text{Bond order in NO} = (8-3)/2 = 2.5$$

It is paramagnetic due to the presence of one unpaired electron in the $(\pi_{2py})^*$ molecular orbitals.

CO – formed by the overlapping of two different atom of C & O.

C = $1s^2, 2s^2, 2p^2$ & O = $1s^2, 2s^2, 2p^4$ total of 14 electrons.

Electronic configuration: $\sigma 1s, \sigma^* 1s, \sigma 2s, \sigma^* 2s, \sigma 2p_z, [\pi 2p_x = \pi 2p_y], [\pi^* 2p_x = \pi^* 2p_y], \sigma^* 2p_z$

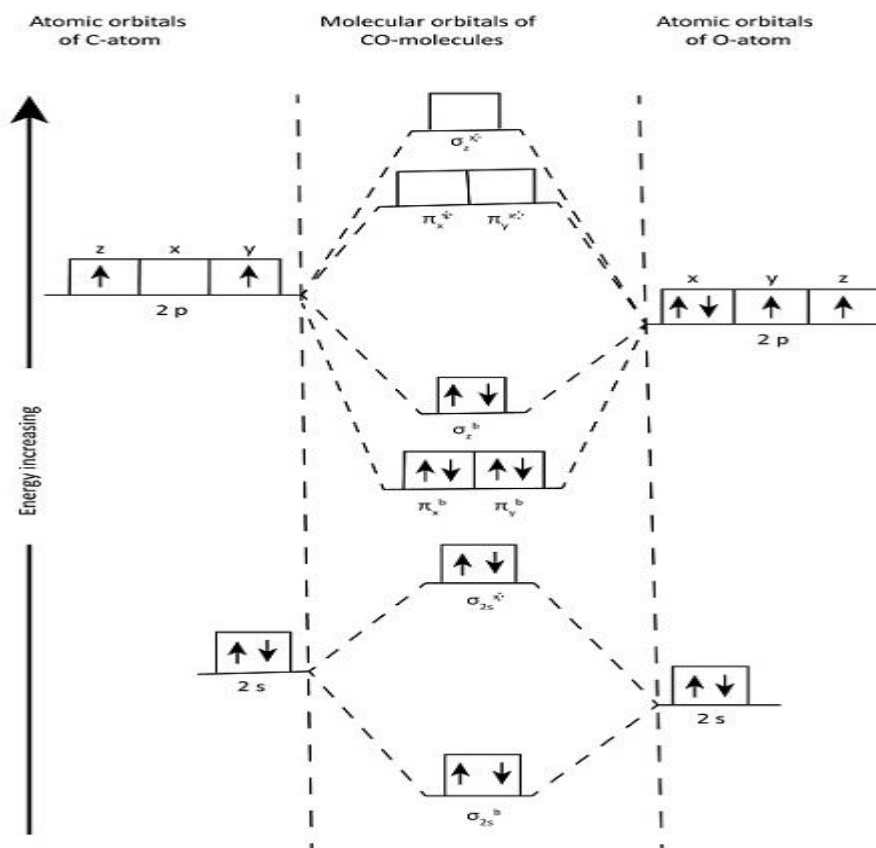


Figure: The molecular orbital energy diagram for CO predicts all paired electrons.

$$\text{Bond order in CO} = \frac{(8-2)}{2} = 3$$

It is Diamagnetic due to the presence of all paired electrons in the molecular orbitals.