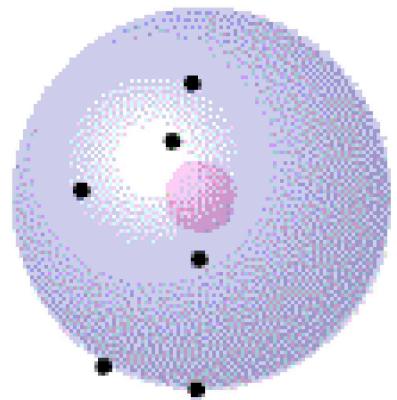


# **ATOMIC STRUCTURE**

## **SEM I**

- ATOMIC ORBITALS, ORBITAL SHAPES, ELECTRONIC CONFIGURATION, MOT, BONDING & ANTIBONDING ORBITALS, MO DIAGRAMS OF Be<sub>2</sub>, O<sub>2</sub>, CO, NO, THEIR BOND ORDER, MAGNETIC PROPERTIES



# Where did it all begin?

The word “atom” comes from the Greek word “*atomos*” which means *indivisible*.

The idea that all matter is made up of atoms was first proposed by the Greek philosopher **Democritus** in the 5th century B.C.

**Democritus**

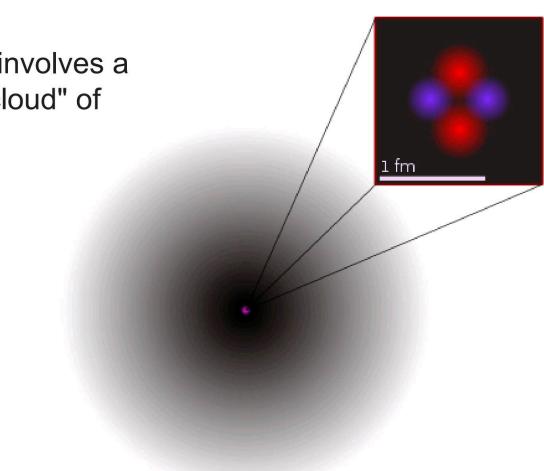


## ATOM:



- Every matter consists of basic entities called elements.
- Each element is composed of smallest particles called 'ATOM'.
- Atom- the name is derived from Greek language **Atomos** means 'Not to be cut'.

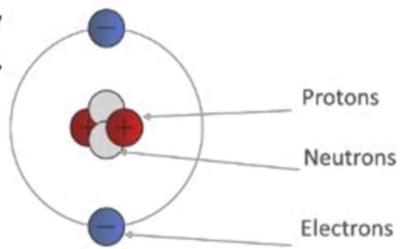
The current model of the sub-atomic structure involves a dense nucleus surrounded by a probabilistic "cloud" of electrons



$$1 \text{ \AA} = 100 \text{ pm}$$

## Atomic structure

- Atom consists of positively charged **NUCLEUS** at the centre and negatively charged **Electrons** revolving around it.
- Radius of an atom –  $10^{-10}$  m.
- Radius of the nucleus –  $10^{-15}$  m.
- Nucleus consists of Protons and Neutrons together called Nucleons.
- Most of the mass of an Atom is possessed by Nucleus.



# Discovery of subatomic particles

- Plum pudding model
- The colloquial nickname "plum pudding" was soon attributed to Thomson's model as the distribution of electrons within its positively charged region of space reminded many scientists of raisins, then called "plums", in the common English dessert, plum pudding
- First proposed by J. J. Thomson in 1904, soon after the discovery of the electron, but before the discovery of the atomic nucleus



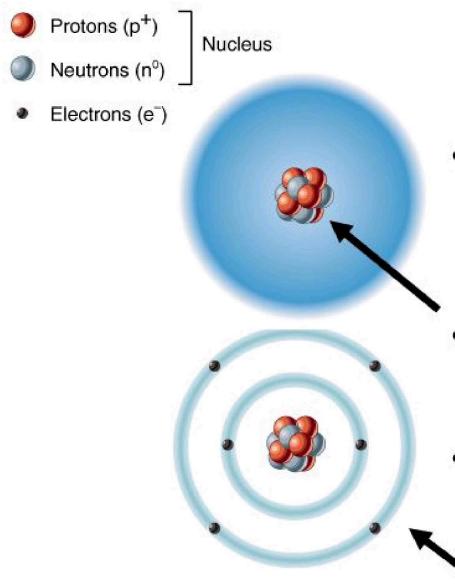
## SUBPARTICLES IN AN ATOM

ELECTRONS

PROTONS

NEUTRONS

# Structure of Atoms

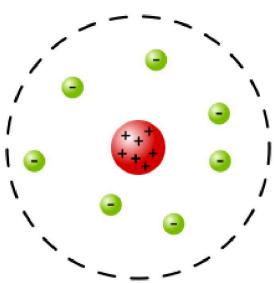


- Atoms are the smallest units of matter that retain the properties of an element
- Atoms consist of 3 types of subatomic particles
  - protons, neutrons and electrons
- Nucleus contains protons (p<sup>+</sup>) & neutrons (neutral charge)
- Electrons (e<sup>-</sup>) surround the nucleus as a cloud (electron shells are designated regions of the cloud)

# THOMSON MODEL

Thomson showed that cathode rays were composed of previously unknown negatively charged particles (now called electrons), which he calculated must have bodies much smaller than atoms and a very large charge-to-mass ratio.

Rutherford's new model for the atom, based on the experimental results, contained new features of a relatively **high central charge concentrated into a very small volume** in comparison to the rest of the atom and with this central volume also containing the bulk of the atomic mass of the atom. This region would be known as the "nucleus" of the atom.

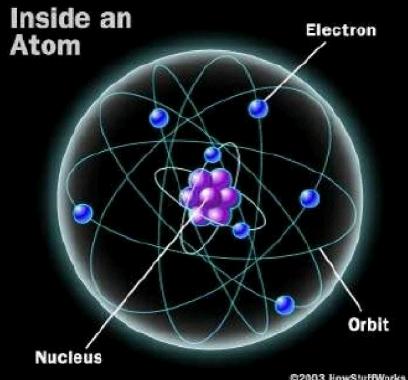


## RUTHERFORD'S MODEL

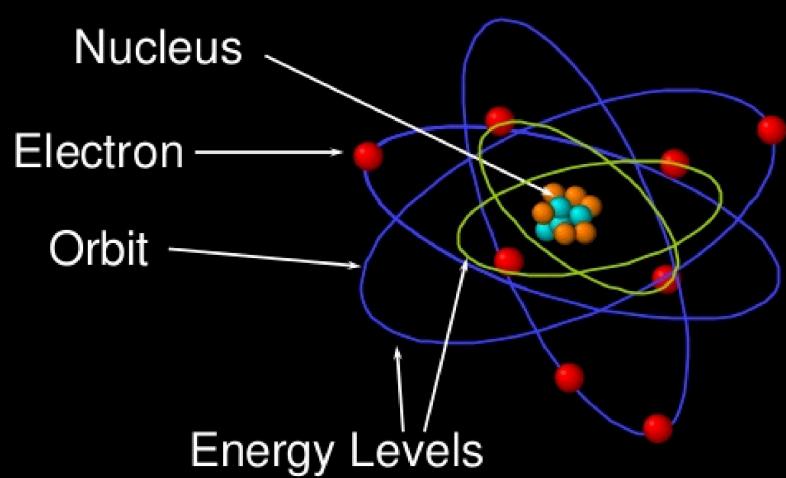
- Rutherford overturned Thomson's model in 1911 with his well-known [gold foil experiment](#) in which he demonstrated that the atom has a tiny and heavy nucleus. Rutherford designed an experiment to use the [alpha particles](#) emitted by a radioactive element as probes to the unseen world of atomic structure. If Thomson was correct, the beam would go straight through the gold foil. Most of the beams went through the foil, but a few were deflected.
-

## Atomic Models

- This model of the atom may look familiar to you. This is the Bohr model. In this model, the nucleus is orbited by electrons, which are in different energy levels.
  - A model uses familiar ideas to explain unfamiliar facts observed in nature.
    - A model can be changed as new information is collected.

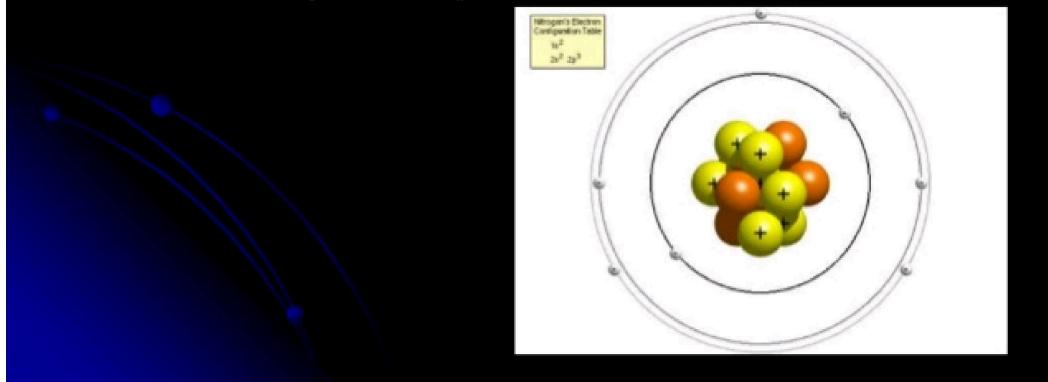


## Bohr's Model



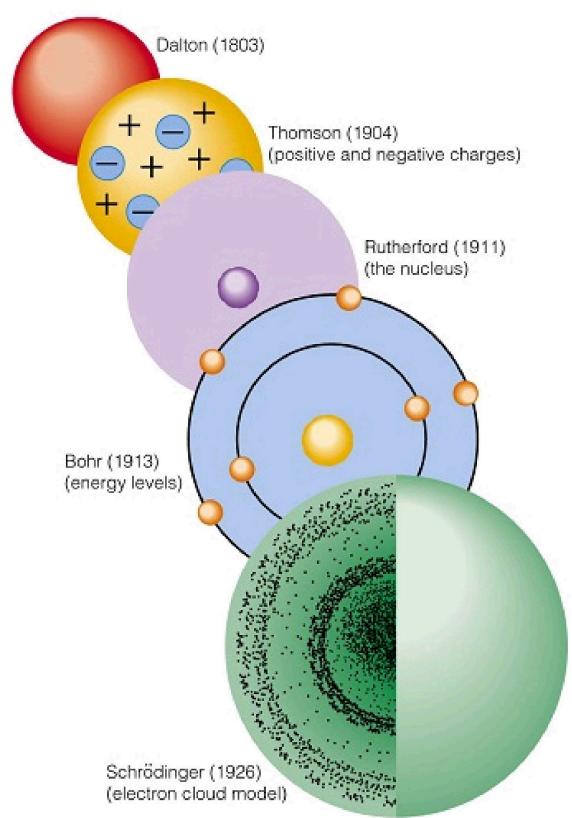
## Bohr's Model = planets

- Has been called **planetary model**
  - Energy levels occupied by **electrons** are like **orbits of planets at different distances from the sun (nucleus)**



## Bohr's Model

- Modified Rutherford's model in 1913
- Proposed that each electron has a certain amount of energy
  - Helped electron move around nucleus
- Electrons move around nucleus in region called **energy levels**
- Energy levels surround nucleus in rings, like layers of onion



<b>Differences between Orbit and Orbitals</b>	
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 defined as the path that gets established in a circular motion by revolving the electron around the nucleus	An orbital can be defined as the space or region where the electron is most likely to be found.
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.
A well-defined orbit goes against the Heisenberg principle.	An ideal orbital agrees with the theory of Heisenberg's Principles

## DRAWBACKS OF BOHR'S ATOMIC MODEL

- Objections were being made on Bohr's atomic model about:
  - the movement of electrons in 3D space
  - spectra of poly electronic atoms.
- Bohr's atomic model failed to justify these objections.

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## Erwin Rudolf Schrödinger

- In 1926, **Erwin Rudolf Schrödinger**, gave the idea that of wave motion of electron
- Nobel Prize in Physics in 1933



## Schrödinger Equation

- He formulated an equation called "the Schrödinger equation", in which electrons are treated as moving with wave like motion in 3D space around the nucleus.
- The solution of Schrödinger Equation gave a set of numerical values.

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## “The Quantum Numbers”

- Explained the arrangement and movement of electrons, spectral lines of poly electronic atoms and gave an acceptable model of an atom.



## Quantum Numbers

- ◎ According to Heisenberg's Uncertainty Principle, it is not possible to give the exact position of an electron and its energy at the same time.
- ◎ But the **probability** of finding an electron in an orbital of given energy can be determined.

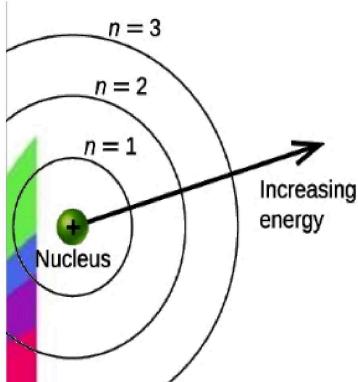
# The 4 Quantum Numbers - An Electron's Address

- Principal Quantum Number ( $n$ )
  - Specifies the main energy level (orbit)
- Azimuthal Quantum Number ( $\lambda$ )
  - Information about the sub energy level (orbital)
- Magnetic Quantum Number ( $m$ )
  - Spatial orientations of an orbital
- Spin Quantum Number ( $s$ )
  - Spin movement of electrons

## Principal Quantum Number

- ◎ main **energy level** of an orbital.
- ◎ Indicates the relative size of the orbital
- ◎ an increase in n also means increase in the energy of the electron in the orbital.  
 $n = 1, 2, 3, \dots$

## Principal Quantum Number (n)



- Size & Energy of an orbit/shell
- $n = 1, 2, 3, 4, \dots$
- Greater value of n represents Bigger orbits with high energies
- Distance from the nucleus also increases.

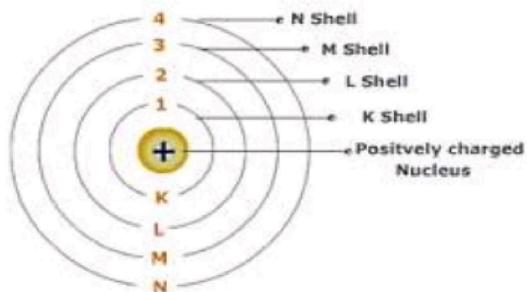
## Principle Quantum Number (n)

Total No. of Electrons in an orbit =  $2n^2$

Value of n	Name of Shell	Total No. of Electrons $2n^2$	
$n=1$	K	$2(1)^2 =$	2
$n=2$	L	$2(2)^2 =$	8
$n=3$	M	$2(3)^2 =$	18
$n=4$	N	$2(4)^2 =$	32

## Bohr's Model of the Atom

- The special orbits known as discrete orbits of electron are allowed inside an atom. These orbits or shells are represented by the letters K,L,M,N,..... Or the numbers , $n=1,2,3,4,\dots$



## Bohr's Model of the Atom

Each orbit can hold a specific maximum number of electrons An easy way to calculate the total number of electrons that can be held by a given energy level is to use the formula  $2 \cdot n^2$

	Shell	maximum no: of electrons
1	- K	$2 \cdot 1^2 = 2$
2	- L	$2 \cdot 2^2 = 8$
3	- M	$2 \cdot 3^2 = 18$
4	- N	$2 \cdot 4^2 = 32$

## Azimuthal Quantum Number

◎ also called Angular Momentum Number

◎ defines the shape of the orbital.

◎ values range from 0 to n-1.

$$\ell = n - 1$$

### Azimuthal Quantum Number ( $\lambda$ )

○ Each energy level is divided into sub levels.

○  $\lambda$  defines the shape of sub energy level/orbital

$\lambda$	Sub level	Name	No. of electrons
0	s	Sharp	2
1	p	Principal	6
2	d	Diffused	10
3	f	Fundamental	14

## Azimuthal Quantum Number

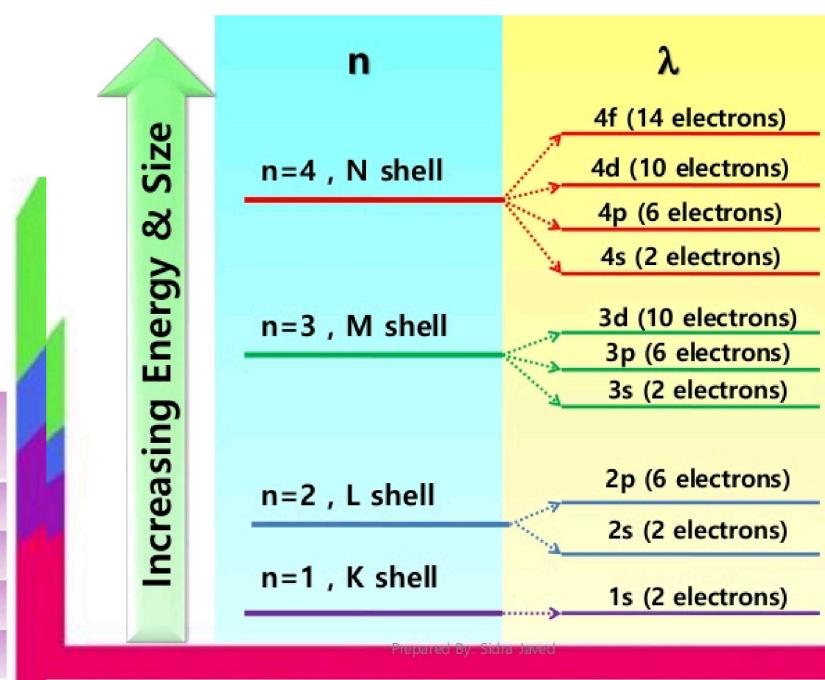
$\ell$	Sublevel	Orbital Shape
0	sharp - s	spherical
1	principal - p	dumbbell-shaped
2	diffused - d	cloverleaf
3	fundamental - f	too complex

## Relationship between $n$ & $\lambda$

$$\lambda = 0 \rightarrow (n-1)$$

Orbit	$n$	$\lambda$	Orbitals	No. of electrons
K	1	0	1s	2
L	2	0, 1	2s, 2p	$2+6=8$
M	3	0, 1, 2	3s, 3p, 3d	$2+6+10=18$
N	4	0, 1, 2, 3	4s, 4p, 4d, 4f	$2+6+10+14=32$

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## Magnetic Quantum Number (m)

- Explains the effect of an orbital in magnetic field i.e. the orientation of an orbital
- Orbitals split up into **degenerate orbitals** (having same energy & size) in a magnetic field
- Each degenerate orbital can hold up to 2 electrons

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### Magnetic Quantum Number, $m_l$

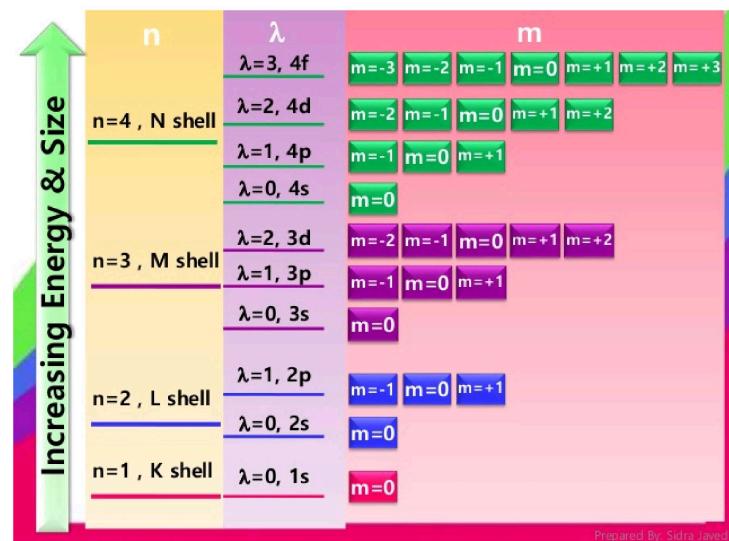
- ◎ describes the orientation of the orbital in space.
- ◎ values are  $-l$  to  $+l$
- ◎ values per sublevel =  $2l + 1$ .

## Relationship between $\lambda$ & m

$$m = -\lambda \rightarrow 0 \rightarrow +\lambda$$

$\lambda$	m	Degenerate orbitals	No. of electrons
$\lambda = 0, s$	0	1	2
$\lambda = 1, p$	-1, 0, +1	3	$2+2+2 = 6$
$\lambda = 2, d$	-2, -1, 0, +1, +2	5	$2+2+2+2+2 = 10$
$\lambda = 3, f$	-3, -2, -1, 0, +1, +2, +3	7	$2+2+2+2+2+2+2 = 14$

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### Sublevel and Capacity of Each Main Energy Level

Main Energy Level	No. of Sublevel	Identity of Sublevels	No. of Orbitals ( $n^2$ )	Max. No. of Electrons ( $2n^2$ )
1	1	1s	1	2
2	2	2s 2p	1 3	2 6
3	3	3s 3p 3d	1 3 5	2 6 10
4	4	4s 4p 4d 4f	1 3 5 7	2 6 10 14

### Magnetic Quantum Number, $m_l$

◎describes the orientation of the orbital in space.

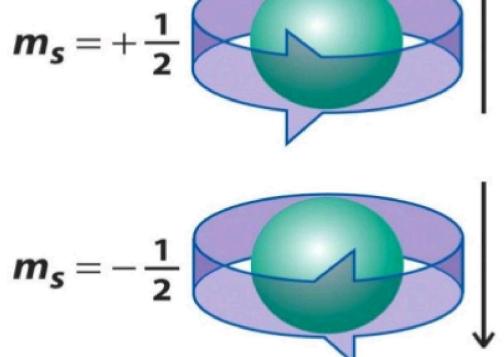
◎values are  $-l$  to  $+l$

◎values per sublevel =  $2l + 1$ .

## Spin Quantum Number (s)

- Direction of spin of an electron
- Electron which rotates around the nucleus also rotates around its own axis
- This is called self rotation
- Either Clockwise (50%) or anticlockwise (50%)
- $s = -1/2$  ( $\uparrow$ ) for clockwise
- $s = +1/2$  ( $\downarrow$ ) for anticlockwise

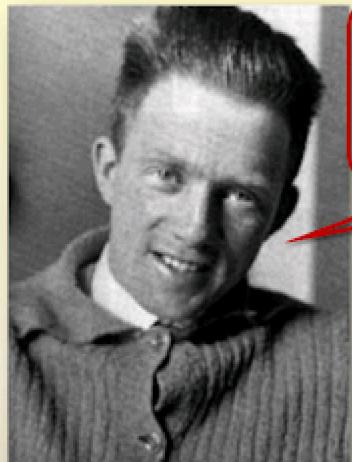
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Spin of electron  
Associated with magnetic field

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## Heisenberg Uncertainty Principle



Werner  
Heisenberg

"One cannot simultaneously determine both the position and momentum of an electron."

The more certain you are about where the electron is, the less certain you can be about where it is going.

The more certain you are about where the electron is going, the less certain you can be about where it is.

## **THREE PRINCIPLES TO LOCATE ELECTRONS**

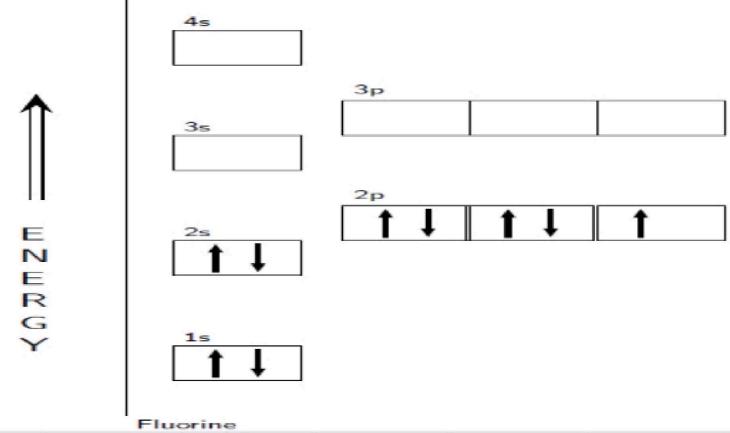
APPLYING THE 3 PRINCIPLES, THE LOCATION OF  
THE ELECTRONS CAN EASILY BE PREDICTED



## THE AUFBAU PRINCIPLE

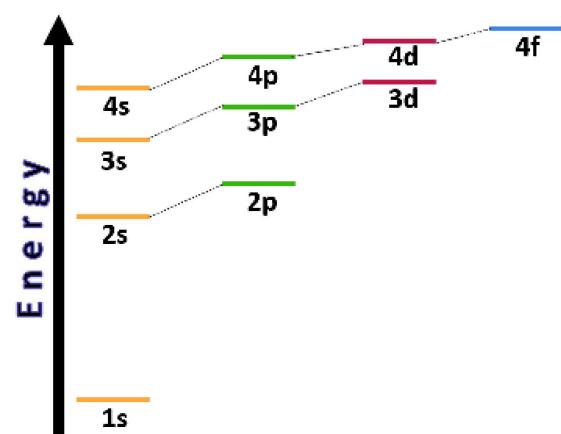
- Comes from the German word, “**aufbauen**” which means “**to build up**”.
- States that “**Electrons are added one at a time to the lowest energy orbitals available until all the electrons of the atoms are counted for.**”

## THE AUFBAU PRINCIPLE

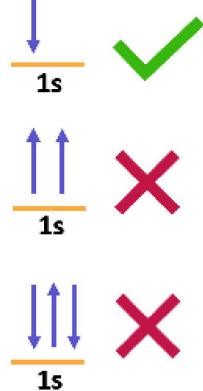


## Aufbau Principle Rules

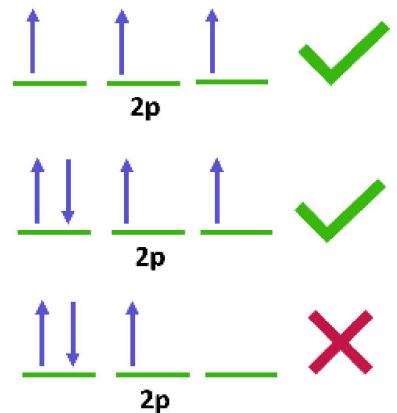
1. Fill orbitals by energy



2. Up to two electrons per orbital



3. Filling degenerate orbitals



# What is the Aufbau Principle?

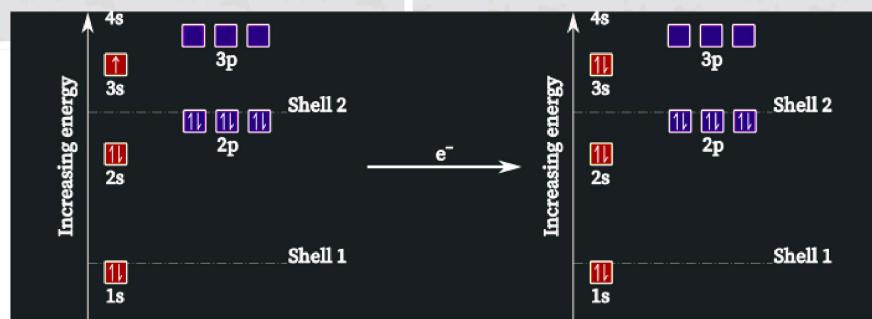
1. Orbitals are filled from lowest energy to highest energy.
2. An orbital can hold up to two electrons. The two electrons will have opposite spins.
3. If two or more orbitals have the same energy (degenerate), one electron goes into each orbital before electrons are paired. Each of the electrons in the half-filled orbital have the same spin. Once half-filled, the electrons can be paired with opposite spins.

## LIMITATION

The Aufbau principle works very well for the ground states of the atoms for the first 18 elements, then decreasingly well for the following 100 elements.

## PAULI EXCLUSION PRINCIPLE

- Proposed by **Wolfgang Pauli**.
- States that “**no two electrons can occupy the same quantum state simultaneously in an atom.**”



## PAULI EXCLUSION PRINCIPLE

1. An orbital can hold a maximum of 2 electrons:  
A small rectangular box contains two arrows, one pointing up and one pointing down, representing two electrons in an orbital.
2. The 2 electrons can occupy the same orbital if they spin in opposite directions.
3. Electrons are said to be paired.

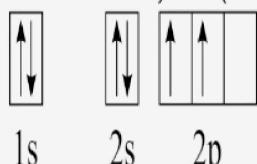


## HUND'S RULE

- States that “**when electrons occupy orbitals of equal energy, one electron enters each orbital until all the orbitals contain one electron with parallel spins. Second electrons then add to each orbital pairing the spins of the first electron.**”

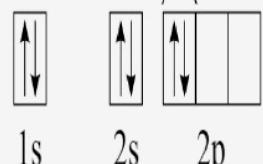
## HUND'S RULE

no electron-electron repulsion  
equals lower energy



correct

electron-electron repulsion  
equals higher energy



incorrect

Example of Hund's rule: Orbital diagram for carbon, showing the correct application of Hund's Rule.

---

## Electron Configuration Diagrams

### Aufbau Principle:

Electrons will occupy the lowest energy level orbital that will receive it.

### Pauli Exclusion Principle:

No two electrons within an atom may have an identical set of all four quantum numbers..

### Hund's Rule:

Electrons will occupy all empty orbitals in a subshell with single electrons having parallel spins before entering half-filled orbitals.



## ELECTRONIC CONFIGURATION OF SELECTED ELEMENTS

ELEMENT	TOTAL ELECTRONS	ORBITAL DIAGRAM			ORBITAL NOTATION
		1s	2s	2p	
H	1	↑			1s <sup>1</sup>
Li	3	↑↓	↑		1s <sup>2</sup> , 2s <sup>1</sup>
N	7	↑↓	↑↓	↑↑↑	1s <sup>2</sup> , 2s <sup>2</sup> , 2p <sup>3</sup>
O	8	↑↓	↑↓	↑↓↑	1s <sup>2</sup> , 2s <sup>2</sup> , 2p <sup>4</sup>
Ne	10	↑↓	↑↓	↑↓↑↓↑↓	1s <sup>2</sup> , 2s <sup>2</sup> , 2p <sup>6</sup>

## Orbital Diagrams

- We often represent an orbital as a square and the electrons in that orbital as arrows.
- The direction of the arrow represents the spin of the electron.



Unoccupied orbital

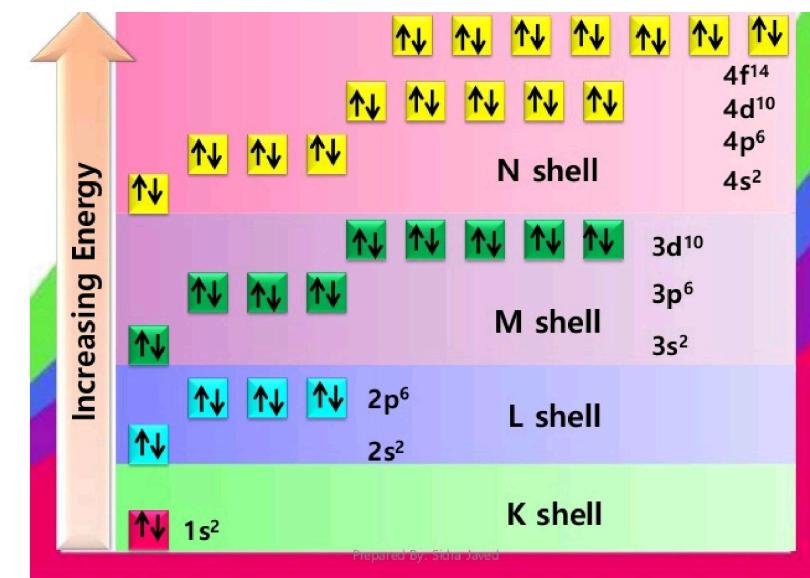


Orbital with 1 electron



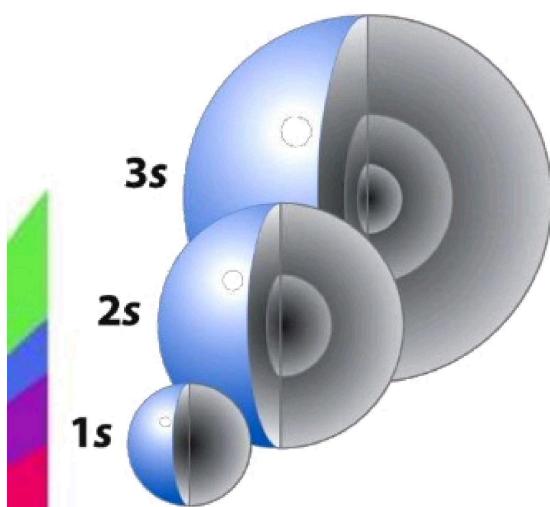
Orbital with 2 electrons

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## Electron Cloud



A cloud showing the probability of finding the electron in terms of charged cloud around the nucleus is called Electron Cloud.

## Key aspects of Bohr's model

- Electrons move around the nucleus at stable orbits without emitting radiation.
- Electron in one of these stable orbit has a definite energy.
- Energy is radiated only when electrons make transitions from high energy orbit to a low energy orbit.

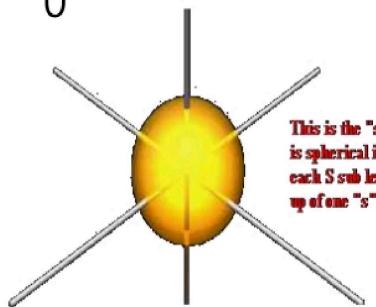
### Atomic Orbitals: s, p, d, f

- Atomic orbitals are regions of space where the probability of finding an electron about an atom is highest.
  - s orbital → spherical shape
  - p orbital → dumb-bell shape
  - d orbital → clover leaf shape
  - f orbital → double clover leaf

## s orbital - spherically symmetric

$\lambda = 0$  and  $m =$

0

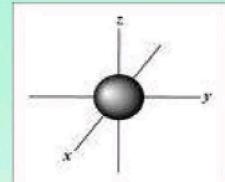


This is the "s" orbital it  
is spherical in shape  
each S sub level is made  
up of one "s" orbital

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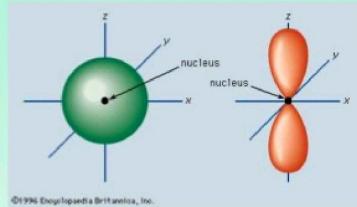
### S- orbital

- Spherical shape with the nucleus at its center



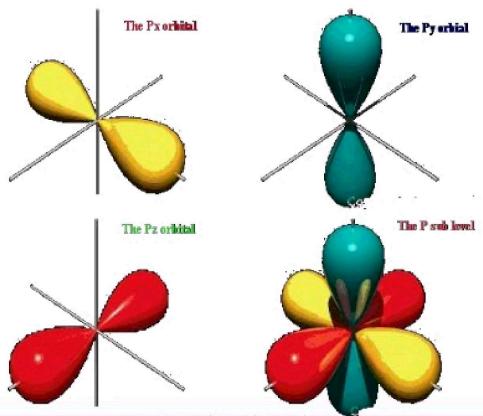
P-orbital

- “dumb-bell shape”



**p orbital - dumbbell shaped**

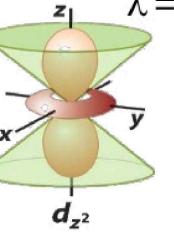
$$\lambda = 1 \quad m = -1, 0, +1$$



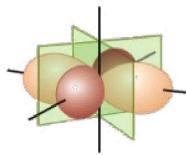
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## **d orbital shapes**

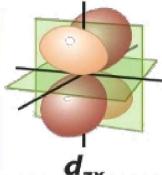
$\lambda = 2 \quad m = -2, -1, 0, +1, +2$



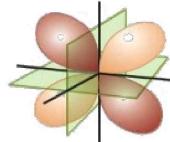
$d_{z^2}$



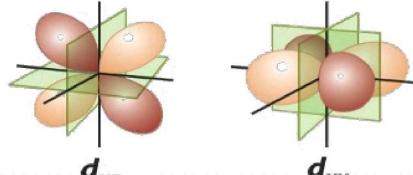
$d_{x^2-y^2}$



$d_{zx}$



$d_{yz}$



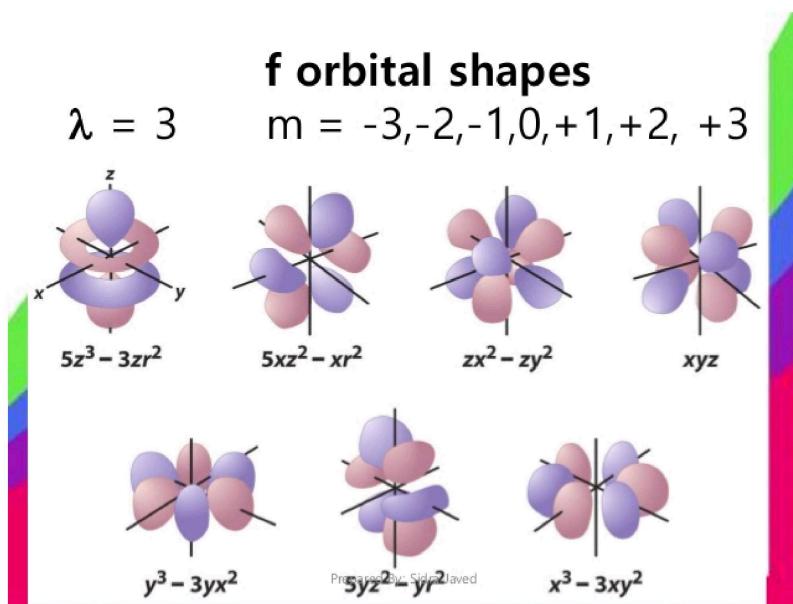
$d_{xy}$

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## f orbital shapes

$\lambda = 3$

$m = -3, -2, -1, 0, +1, +2, +3$



Prepared By Sidiq Javed

# DUAL NATURE OF ELECTRON

- **Wave-like properties:**

- Electrons do not orbit a nucleus in the manner of a planet orbiting the Sun, but instead exist as standing waves. Thus the lowest possible energy an electron can take is similar to the fundamental frequency of a wave on a string. Higher energy states are similar to harmonics of that fundamental frequency.
- The electrons are never in a single point location, though the probability of interacting with the electron at a single point can be found from the electron's wave function. The electron's charge acts like it is smeared out in space in a continuous distribution, proportional at any point to the squared magnitude of the electron's wave function.

- **Particle-like properties:**

- The number of electrons orbiting a nucleus can only be an integer.
- Electrons jump between orbitals like particles. For example, if one photon strikes the electrons, only one electron changes state as a result.
- Electrons retain particle-like properties such as: each wave state has the same electric charge as its electron particle. Each wave state has a single discrete spin (spin up or spin down) depending on its superposition.

# ORBITAL

An **orbital** is a three dimensional description of the most likely location of an electron around an atom.

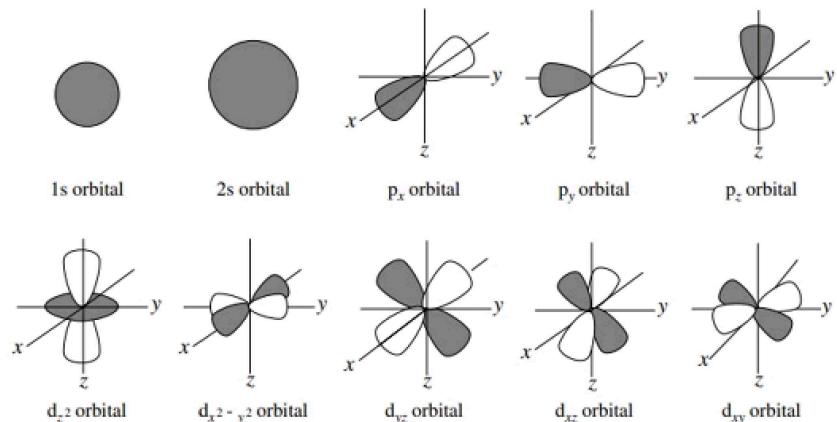


Figure 1.1 Depiction of s, p, and d atomic orbitals.

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## Electron Configuration Diagrams

### Aufbau Principle:

Electrons will occupy the lowest energy level orbital that will receive it.

### Pauli Exclusion Principle:

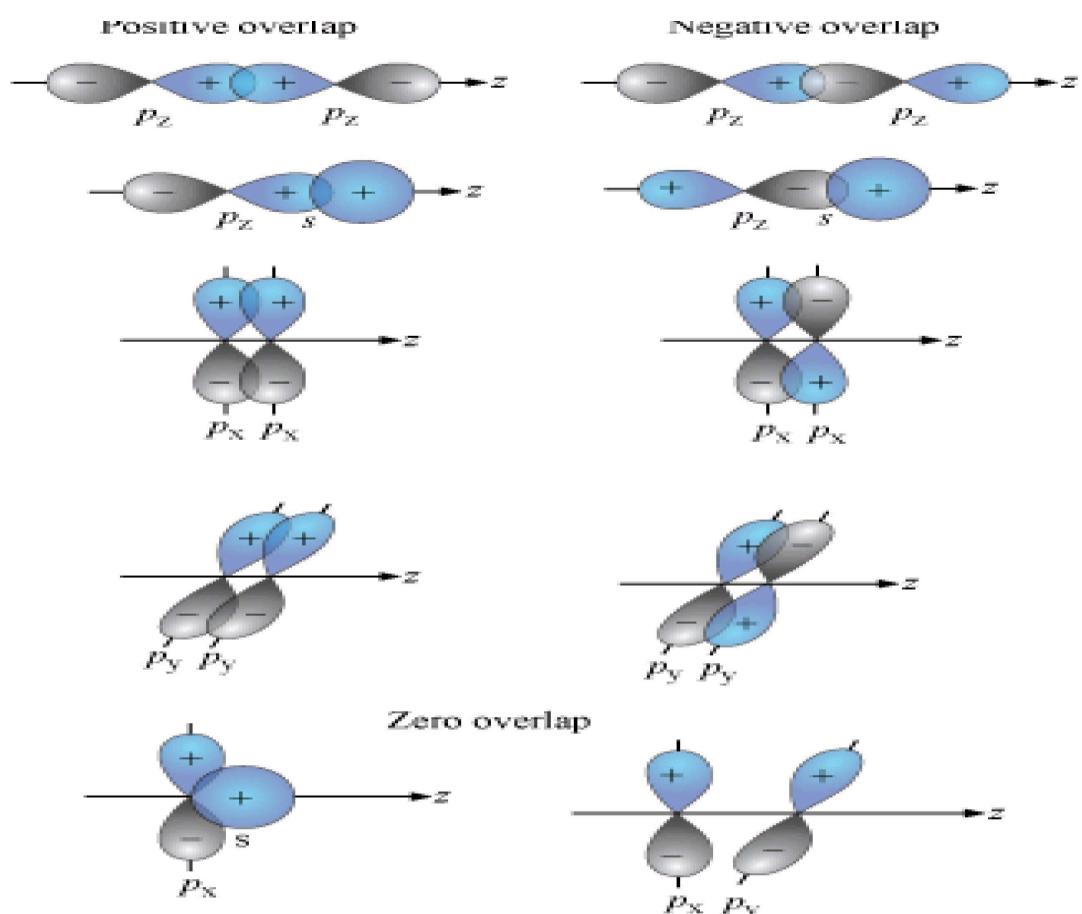
No two electrons within an atom may have an identical set of all four quantum numbers..

### Hund's Rule:

Electrons will occupy all empty orbitals in a subshell with single electrons having parallel spins before entering half-filled orbitals.



← Aufbau diagram



# MOLECULAR ORBITAL THEORY

- MULLIKEN DEVELOPED THIS THEORY.
- IT EXPLAINS: FORMATION OF CHEMICAL BOND
- RELATIVE BOND STRENGTHS
- DIAMAGNETIC OR PARAMAGNETIC NATURE OF MOLECULES.

# MOT

- The atomic orbitals merge with each other to form the molecular orbital. 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.

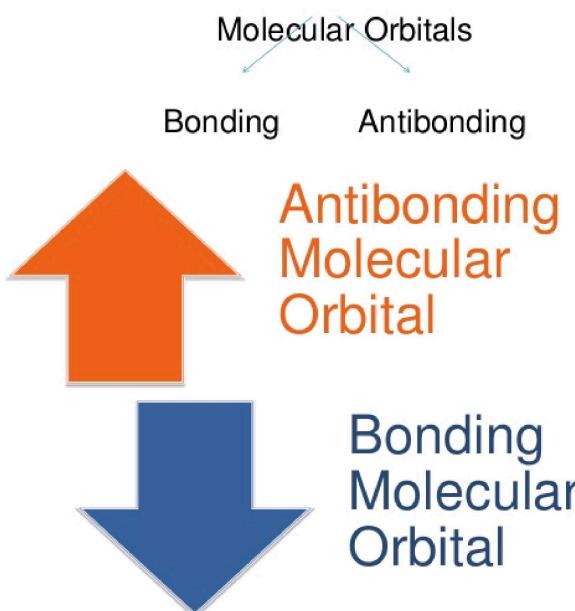
## INTRODUCTION

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- MOT - initially developed by Robert S. Mullikan.
  - the bonding between atoms is described.
  - provides answers to more complex questions.
  - allows one to predict the distribution of electrons
- And this in turn can help predict molecular properties such as shape, magnetism, and Bond Order.

## PRINCIPLES OF MOT

- In molecules, atomic orbitals combine to form molecular orbitals which surround the molecule.

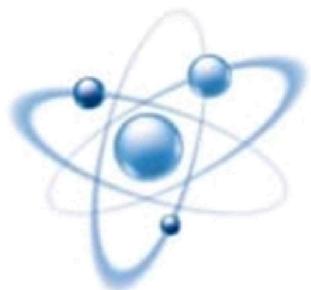


- Molecular bonds have lower potential energy than in separate atomic orbitals.
- Thus, electrons prefer to stay in a molecular bond.



Equal no. of orbitals	Order of Energy
Principles	
Atomic orbitals of like energies.	Following both the <a href="#">Pauli exclusion principle</a> and <a href="#">Hund's rule</a>

- Molecular bonds have lower potential energy than in separate atomic orbitals.
- Thus, electrons prefer to stay in a molecular bond.



# Molecular Orbital Theory

- Atomic orbitals mix together and make:
  - Bonding Orbitals  
Electrons in these orbitals help hold atoms near each other
  - Antibonding Orbitals  
Electrons in these orbitals push atoms apart from each other
  - Nonbonding Orbitals (*kind of like lone pairs*)  
Electrons in these orbitals have no effect on bonding
- Molecular Orbitals can:
  - be Sigma or Pi  $\Sigma$
  - be spread over multiple atoms

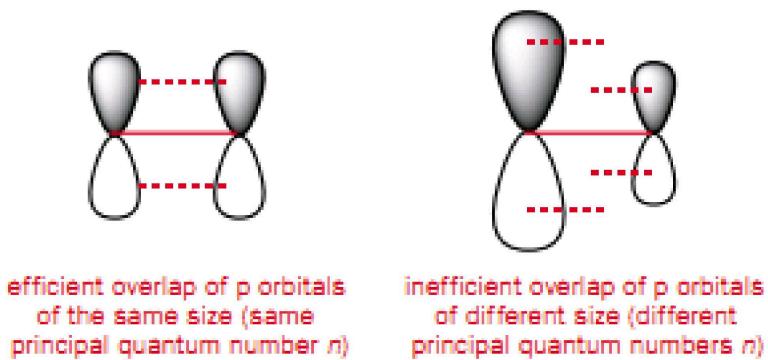
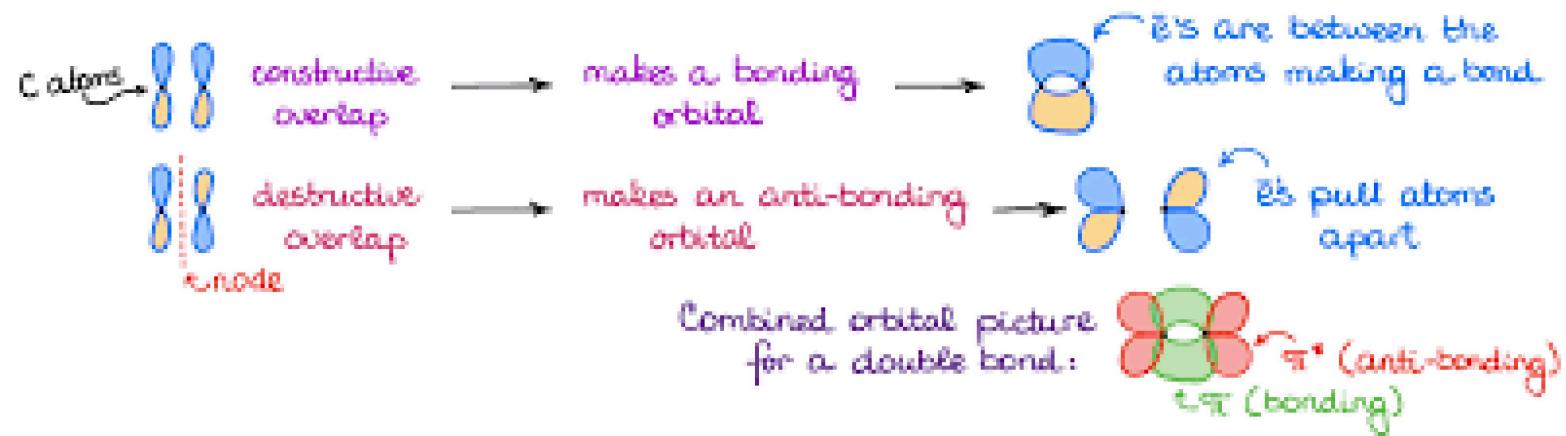
### DIFFERENCE BETWEEN BONDING AND ANTIBONDING MOLECULAR ORBITALS

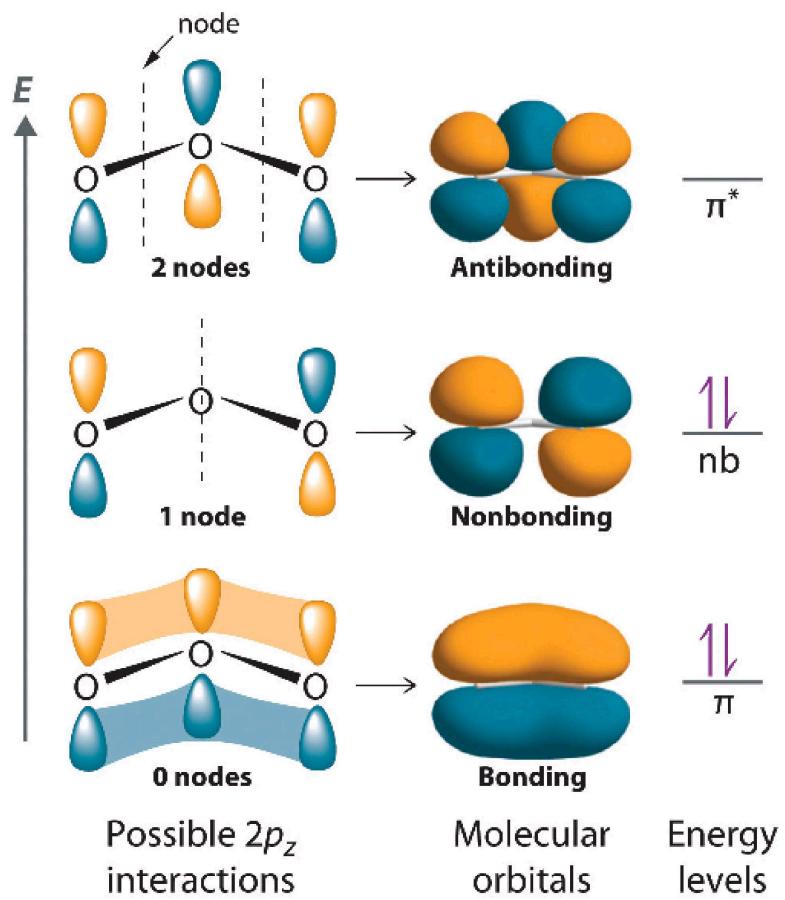
Bonding MO	Antibonding MO
<p>1. It is formed by <b>addition</b> overlap of atomic orbitals.</p> <p>2. The wave function of a bonding MO is given by <math>\Psi_{(MO)} = \Psi_A + \Psi_B</math></p> <p>3. Its formation takes place when the lobes of atomic orbitals have <b>same signs</b>.</p> <p>4. The energy of bonding MO is <b>lower</b> than that of atomic orbitals from which it is formed.</p> <p>5. The electron density is <b>high</b> in the region between the nuclei of bonded atoms.</p> <p>6. Every electron in bonding MO contributes towards the <b>attractive force</b>.</p>	<p>1. It is formed by <b>subtraction</b> overlap of atomic orbitals.</p> <p>2. The wave function of an antibonding MO is given by <math>\Psi^*_{(MO)} = \Psi_A - \Psi_B</math></p> <p>3. Its formation takes place when the lobes of atomic orbitals have <b>different signs</b>.</p> <p>4. The energy of antibonding MO is <b>higher</b> than that of atomic orbitals from which it is formed.</p> <p>5. The electron density is <b>low</b> in the region between the nuclei of bonded atoms.</p> <p>6. Every electron in antibonding contributes towards <b>repulsive force</b>.</p>

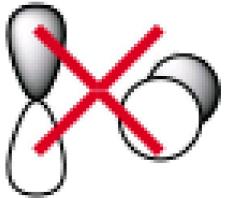
## Difference between Sigma and Pi molecular orbitals:

TABLE DIFFERENCE BETWEEN SIGMA AND PI MOLECULAR ORBITALS

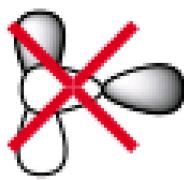
Sigma ( $\sigma$ ) MO	Pi ( $\pi$ ) MO
1. It is formed by head to head overlapping of atomic orbitals.	1. It is formed by the sidewise overlapping of $p_y$ or $p_x$ atomic orbitals.
2. The overlap is along internuclear axis.	2. The overlap is perpendicular to internuclear axis.
3. As a result of this strong bond is formed.	3. As a result of this weak bond is formed.
4. This orbital is symmetrical to rotation about the line joining the two nuclei.	4. This orbital is not symmetrical to rotation about the line joining the two nuclei.
5. The region of overlap is greater.	5. The region of overlap is lesser.



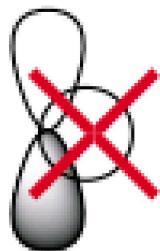




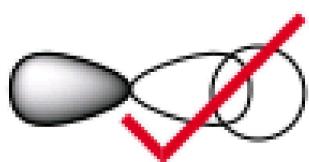
p<sub>z</sub> and p<sub>x</sub>



p<sub>z</sub> and p<sub>y</sub>



p and s  
(side-on)

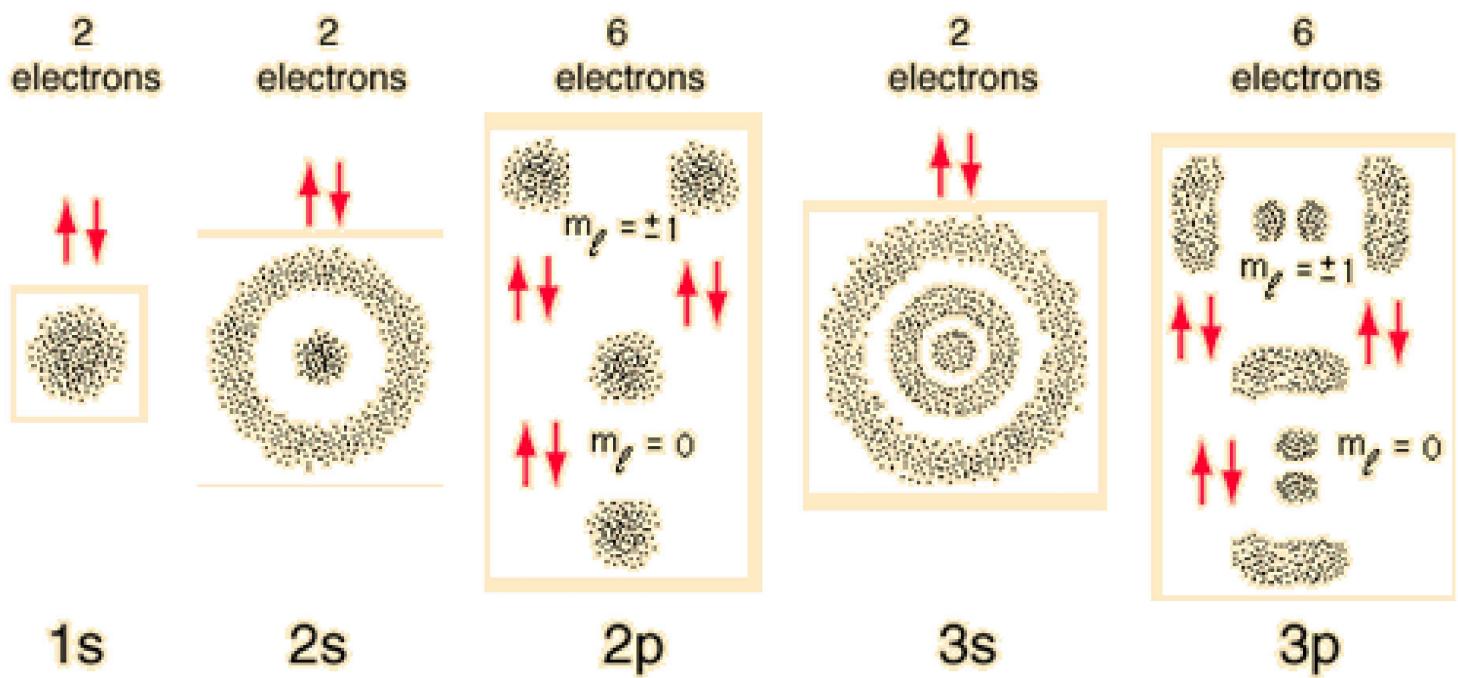


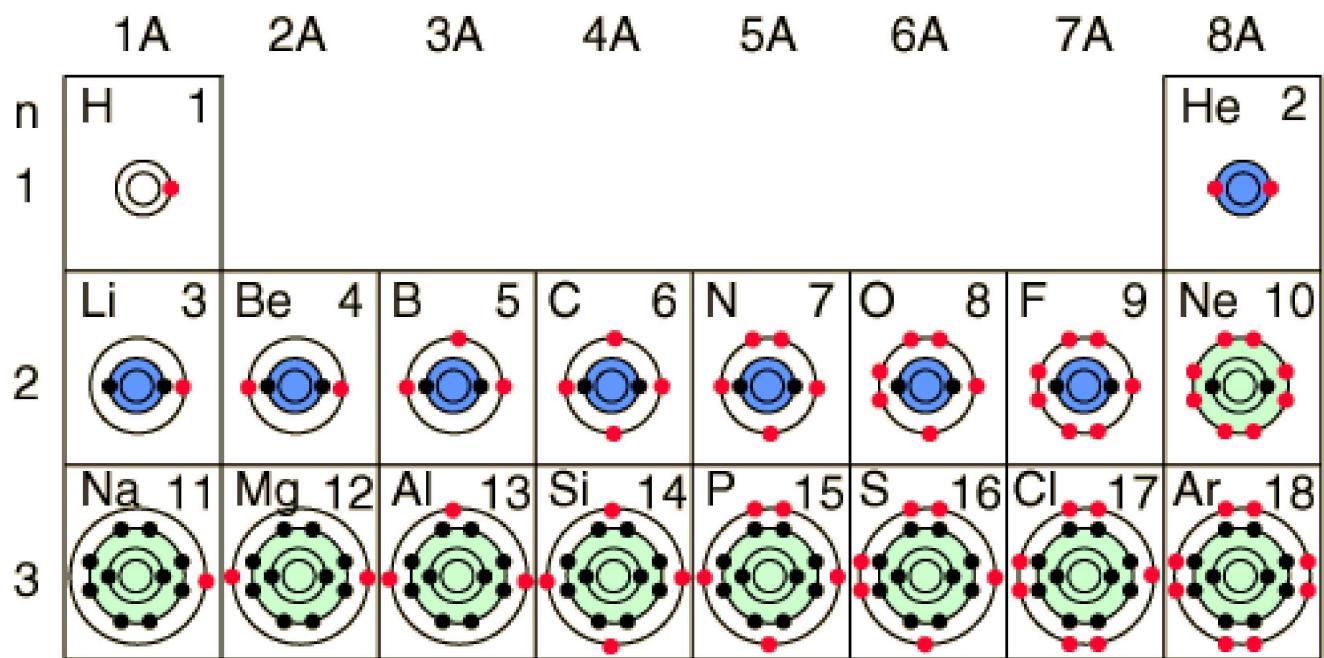
p and s  
(end-on)

however, s and p orbitals  
can overlap end-on

these two p orbitals cannot combine because they are perpendicular to each other

here any constructive overlap is cancelled out by equal amounts of destructive overlap







- The key features of the molecular orbital theory are listed below.
- The total number of molecular orbitals formed will always be equal to the total number of atomic orbitals offered by the bonding species.
- There exist different types of molecular orbitals viz; bonding molecular orbitals, anti-bonding molecular orbitals, and non-bonding molecular orbitals. Of these, anti-bonding molecular orbitals will always have higher energy than the parent orbitals whereas bonding molecular orbitals will always have lower energy than the parent orbitals.
- The electrons are filled into molecular orbitals in the increasing order of orbital energy (from the orbital with the lowest energy to the orbital with the highest energy).
- The most effective combinations of atomic orbitals (for the formation of molecular orbitals) occur when the combining atomic orbitals have similar energies.

## Molecular Orbital Theory

- Properties of molecular orbitals
  - The number of molecular orbitals (MOs) formed is equal to the number of atomic orbitals combined.
  - Of the two MOs formed when two atomic orbitals are combined, one is a bonding MO (lower energy) and one is an antibonding MO (higher energy).
  - In the ground state, electrons enter the lowest energy MO available.
  - Pauli Exclusion Principle is obeyed: a maximum of two electrons may be contained in a single MO.
  - Hund's rule is obeyed: in the ground state, electrons enter degenerate orbitals singly before pairing up.

If two nuclei are positioned at equilibrium distance, the electron are added and they will go in to molecular orbitals.

## POSTULATES

- Each molecular orbital is given by a wave function  $\Psi$  known as **molecular orbital wave function**.
- $\Psi^2$  represents to **probability density or total electron charge density**.
- Each wave function ( $\Psi$ ) is associated with a set of quantum no which determines the energy and the shape of the orbitals.
- Each wave function ( $\Psi$ ) is associated with certain amount of energy and total amount of energy is sum of energies of occupied molecular orbitals.
- The number of molecular orbitals (MOs) formed is always equal to the number of atomic orbitals combined.
- Filling of orbitals takes place accordingly to **HUND's rule, PAULI's principle and as that of Aos.**

## APPROXIMATION OF MOs

For approximation of correct MO, though there are several methods let's do accordingly with Liner Combination of Atomic Orbitals (LCAO)

### Liner Combination of Atomic Orbitals (LCAO)

#### **Conditions for LCAO-**

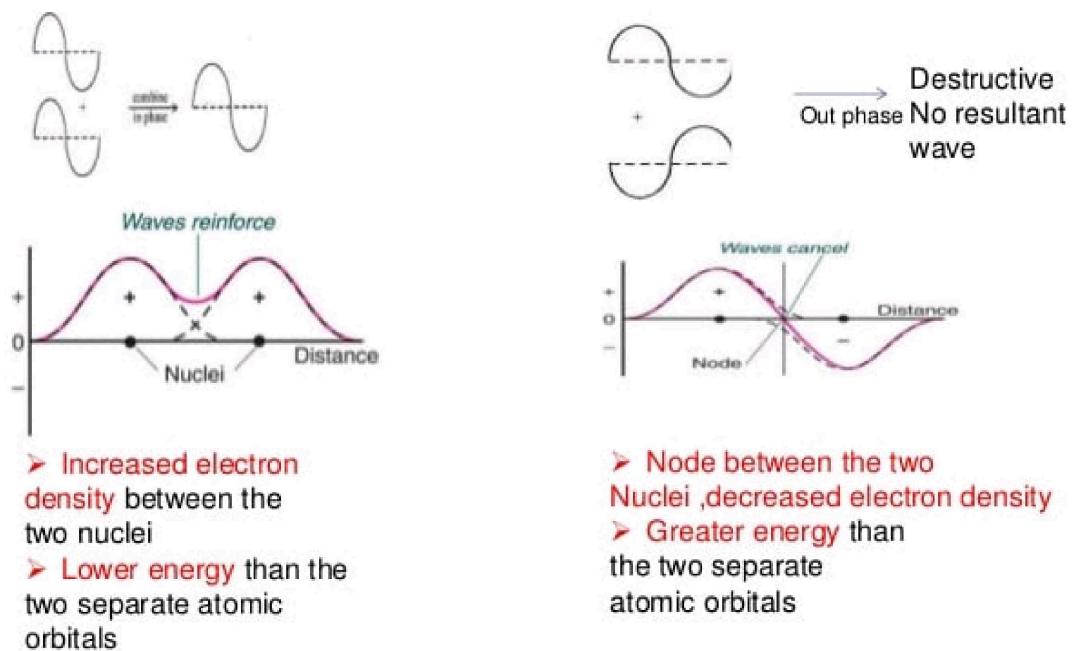
- Atomic orbital's must be roughly of the **same energy**. Atomic orbitals with differing energies or the wrong spatial orientation (orthogonal) do not combine, and are called non-bonding orbitals.
- The orbital must overlap one another as much as possible- i.e. atoms must be **close enough for effective overlapping**.
- In order to produce bonding and anti bonding MOs, either the **symmetry of two atomic orbital must be same** or when rotated about the internuclear line both atomic orbital's must change symmetry in identical manner.



$$\Psi_{AB} = N(\Psi_A + \Psi_B)$$

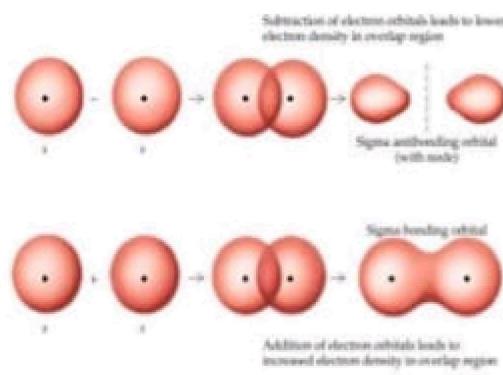
$$\Psi^2_{AB} = (\Psi_A^2 + \Psi_B^2 + 2 \Psi_A \Psi_B)$$

### An analogy of atomic wave functions.

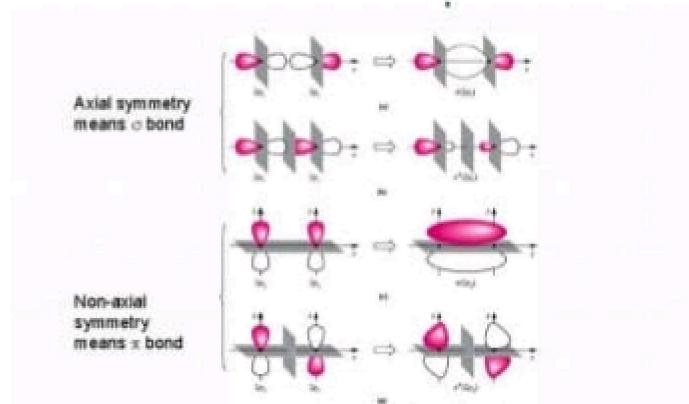


## PICTORIAL REPRESENTATION OF AOs TO FORM MOs

### COMBINATION OF S ORBITALS

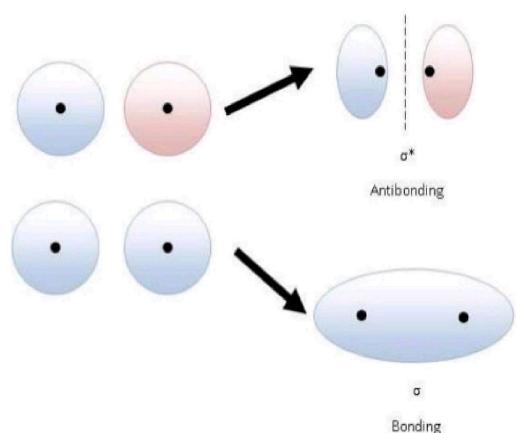
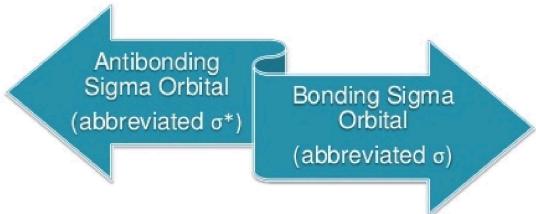


### COMBINATION OF P ORBITALS



## SIGMA BONDS ( $\sigma$ )

- They are symmetrical about the axis



## Rules for Combining Atomic Orbitals

1. The number of molecular orbitals = the number of atomic orbitals combined.
2. The strength of the bond depends upon the degree of orbital overlap.

## Period 2 Diatomic Molecules

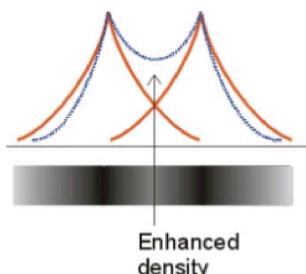
For the second period, assume that, due to a better energy match, *s* orbitals combine with *s* orbitals, and *p* orbitals combine with *p* orbitals.

The symmetry of *p* orbitals permits end-on-end overlap along the bond axis, or side-by-side overlap around, but not along, the internuclear axis.

## Localized Electron Model

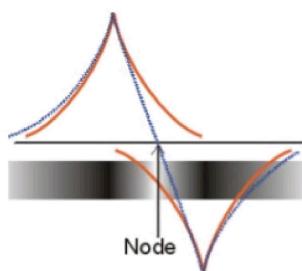
- Good for explaining molecular shapes;
- Two singly occupied orbitals from separate atoms form  $\sigma$ -overlaps.
- Electron pairs occupy overlap area to form  $\sigma$ -bonds;
- Two types of covalent bonds may be formed:
  1.  $\sigma$  -bond: orbitals overlap along internuclear axis
  2.  $\pi$  -bond: side-to-side overlap of orbitals perpendicular to the internuclear axis

## Molecular Orbital Theory



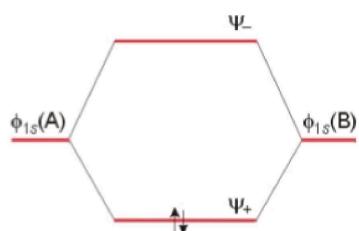
The bonding orbital results in increased electron density between the two nuclei, and is of lower energy than the two separate atomic orbitals.

## Molecular Orbital Theory

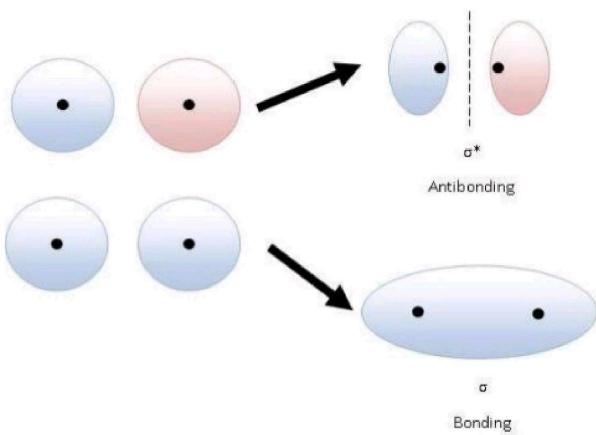


The antibonding orbital results in a node between the two nuclei, and is of greater energy than the two separate atomic orbitals.

## Molecular Orbital Theory



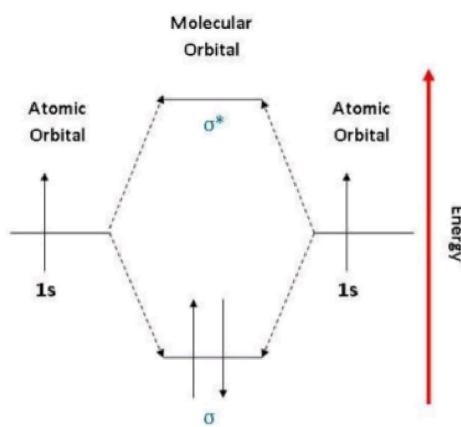
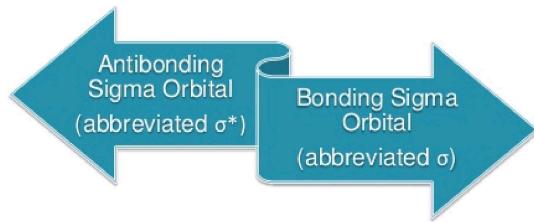
The result is an energy level diagram with the bonding orbital occupied by a pair of electrons. The filling of the lower molecular orbital indicates that the molecule is stable compared to the two individual atoms.



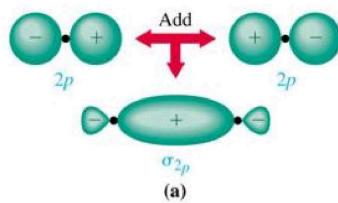
## SIGMA BONDS ( $\sigma$ )

□ They are symmetrical about the axis

□

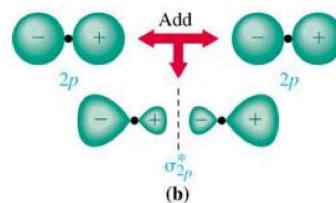


## Molecular orbitals of the second period elements



(a) The addition of two  $2p$  orbitals, in phase, along the internuclear axis to form a  $\sigma_{2p}$  MO.

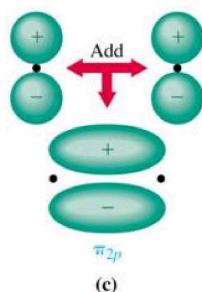
Electron density is located between the nuclei leading to bond formation.



(b) The addition of two  $2p$  orbitals, out of phase, forming a  $\sigma^*_{2p}$  MO.

This orbital has a nodal plane perpendicular to the internuclear axis (as do all antibonding orbitals!)

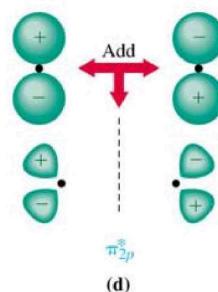
## Molecular orbitals of the second period elements



(c)

(c) The addition of two  $2p$  orbitals, in phase, perpendicular to the internuclear axis to form a  $\pi_{2p}$  MO.

Electron density is located between the nuclei contributing to multiple bond formation.

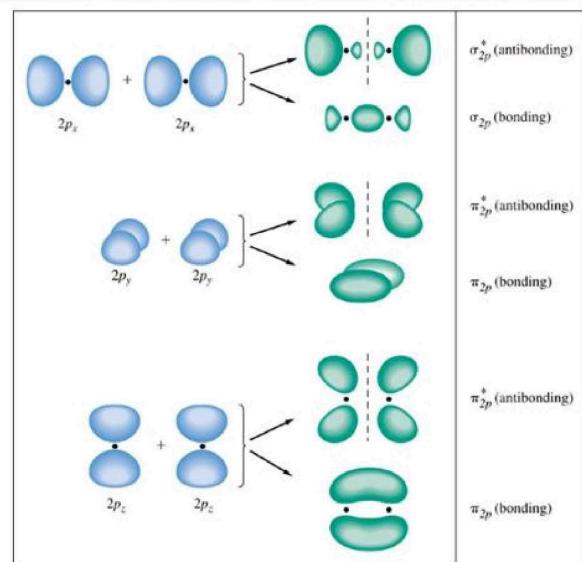


(d)

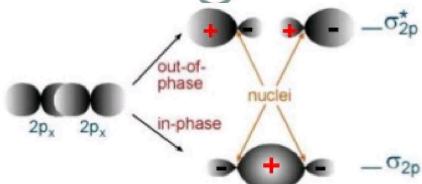
(d) The addition of two  $2p$  orbitals, out of phase, forming a  $\pi_{2p}^*$  MO.

This orbital also has a nodal plane perpendicular to the internuclear axis (as do all antibonding orbitals!)

## Molecular orbitals of the second period elements

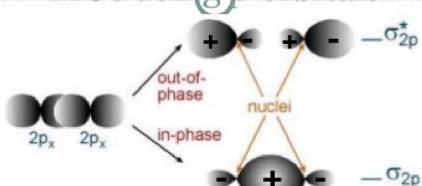


### MOs using $p$ orbitals



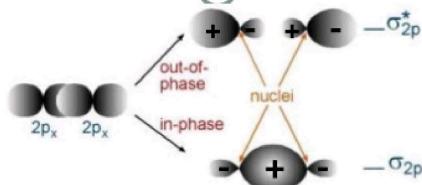
With the  $x$  axis as the bond axis, the  $p_x$  orbitals may combine constructively or destructively. The result is a  $\sigma$  bonding orbital and a  $\sigma$  anti-bonding orbital.

### MOs using $p$ orbitals



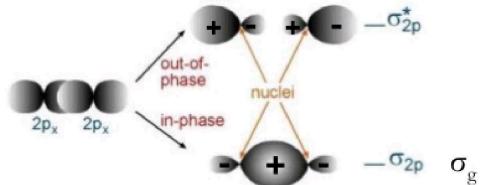
The designation  $\sigma$  indicates symmetric electron density around the internuclear ( $x$ ) axis. The + and - signs indicate the sign of the wave function, and not electrical charges.

### MOs using $p$ orbitals

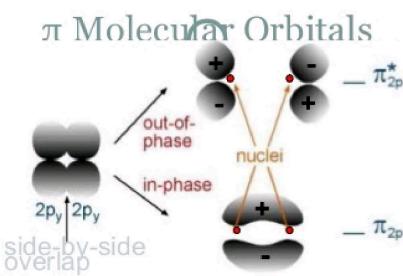


Some texts will use the symmetry designations of  $g$  (gerade) or  $u$  (ungerade) instead of indicating

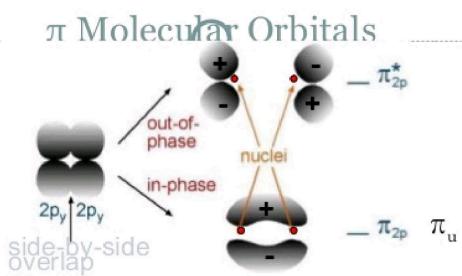
### MOs using $p$ orbitals



For these orbitals, the bonding orbital is *gerade*, or symmetric around the bond axis.

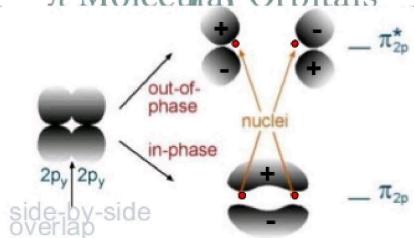


The orbital overlap side-by-side is less than that of overlap along the bond axis (end-on-end). As a result, the bonding orbital will be higher in energy than the previous example.



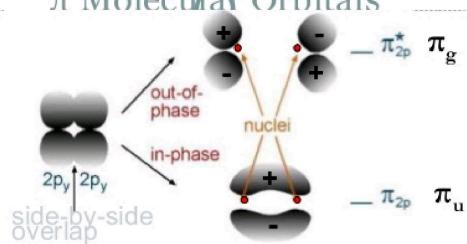
Some texts use the subscripts *g* and *u* instead of bonding and anti-bonding. In this example, the

### $\pi$ Molecular Orbitals



$\pi$  orbitals are asymmetric with respect to the bond axis. There is electron density surrounding the bond axis, with a node along the internuclear axis.

### $\pi$ Molecular Orbitals



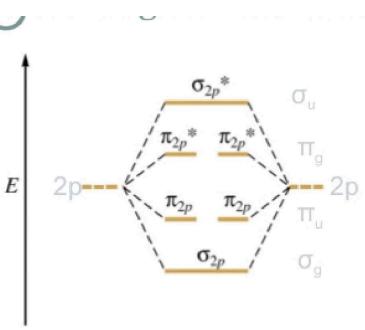
The anti-bonding orbital is *gerade*, or symmetric about a center of symmetry.

## Molecular Orbital Theory

### Difference between Bonding and Antibonding molecular orbitals

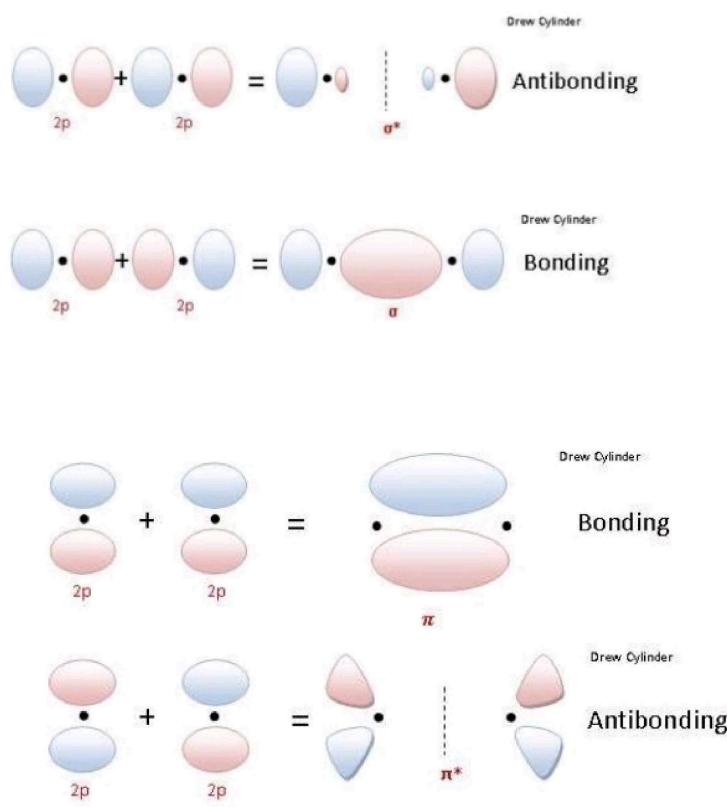
Bonding MO	Antibonding MO
It is formed by <b>addition overlap</b> of atomic orbitals.	It is formed by <b>subtraction overlap</b> of atomic orbitals.
The wave function of a bonding MO is given by $\Psi_{(MO)} = \Psi_A + \Psi_B$	The wave function of an antibonding MO is given by $\Psi^*_{(MO)} = \Psi_A - \Psi_B$
Its formation takes place when the <b>lobes of atomic orbitals have same signs.</b>	Its formation takes place when the <b>lobes of atomic orbitals have different signs.</b>
The <b>energy of bonding MO is lower</b> than that of atomic orbitals from which it is formed.	The <b>energy of antibonding MO is higher</b> than that of atomic orbitals from which it is formed.
The <b>electron density is high</b> in the region between the nuclei of bonded atoms.	The <b>electron density is low</b> in the region between the nuclei of bonded atoms.
Every electron in bonding MO <b>contributes towards the attractive force.</b>	Every electron in antibonding <b>contributes towards repulsive force.</b>

This is a molecular orbital energy level diagram for the  $p$  orbitals. Note that the  $\sigma$  bonding orbital is lowest in energy due to the greater overlap end-on-end.



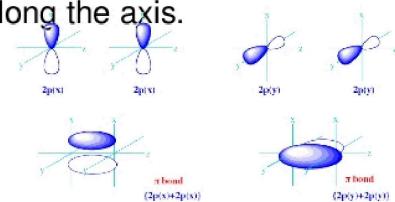
### Molecular Orbital Diagrams

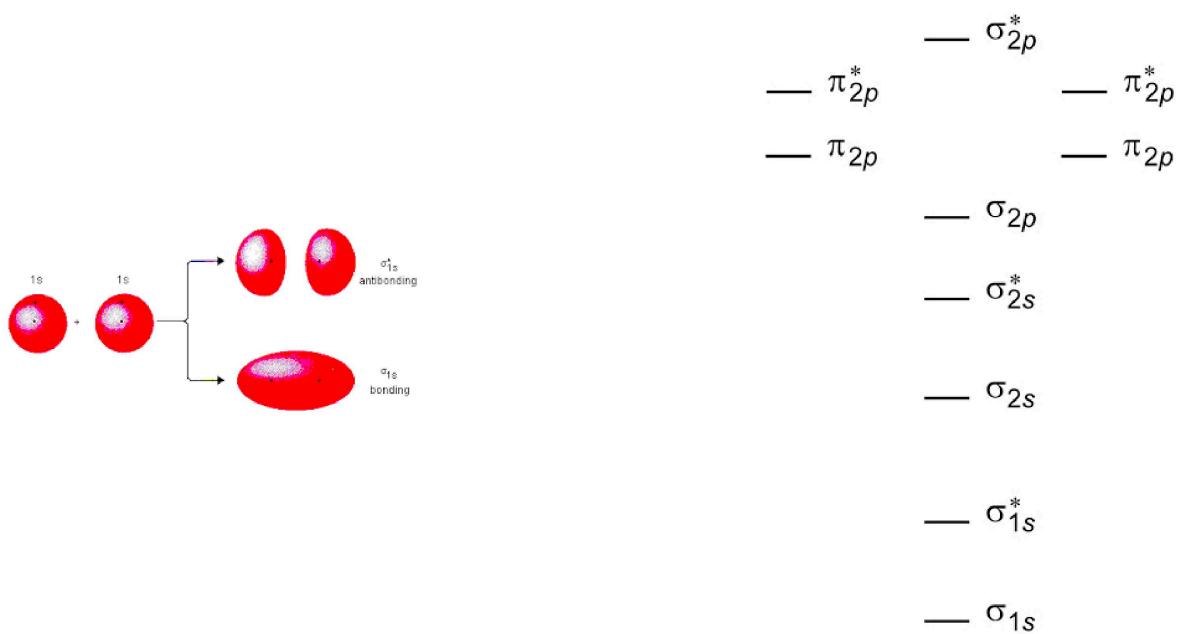
1. Electrons preferentially occupy molecular orbitals that are lower in energy.
2. Molecular orbitals may be empty, or contain one or two electrons.
3. If two electrons occupy the same molecular orbital, they must be spin paired.
4. When occupying degenerate molecular orbitals, electrons occupy separate orbitals with parallel spins before pairing.



## PI BONDS ( $\pi$ )

- The pi bonding bonds as a side to side overlap, which then causes there to be no electron density along the axis, but there is density above and below the axis.





## DETERMINING BOND ORDER

- Bond Order indicates the strength of the bond. The higher the Bond Order, the stronger the bond.

$$\text{Bond Order} = \frac{1}{2}(a-b)$$

where, a = number of  $e^-$  in bonding Molecular Orbitals

b = number of  $e^-$  in antibonding Molecular Orbitals.

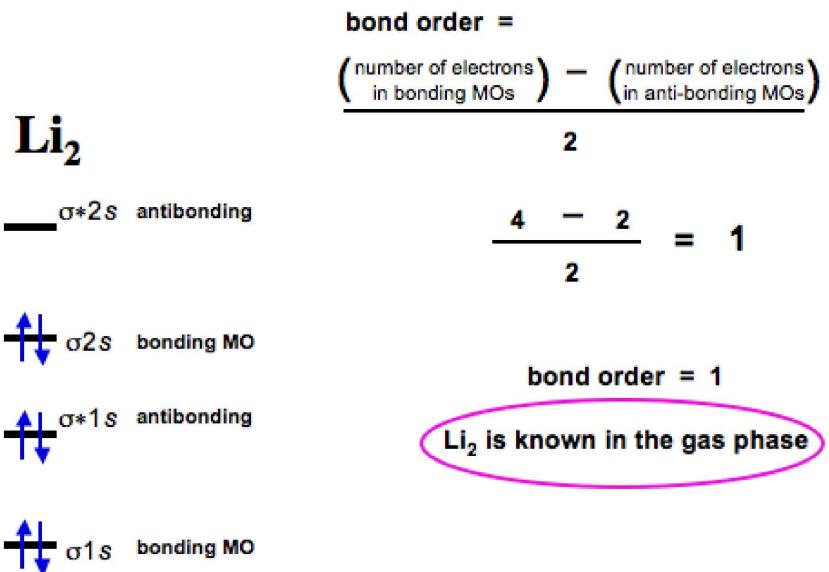
## STABILITY OF THE MOLECULE

- If the Bond Order is Zero, then no bonds are produced and the molecule is not stable (for example  $\text{He}_2$ ).
- If the Bond Order is 1, then it is a single covalent bond.
- The higher the Bond Order, the more stable the molecule is.

## Molecular Orbital Theory

- A stable molecular species is one that has more electrons in bonding MOs than in antibonding MOs.
- Previously, we had stated that for a single bond, the bond order (B.O.) = 1, for a double bond B.O. = 2, etc...we may now formally define this in terms of MOs.
- Bond order: one-half the difference between the numbers of electrons in bonding and in antibonding molecular orbitals in a covalent bond.

$$\text{Bond Order} = \frac{\# e^- \text{ in bonding MOs} - \# e^- \text{ in antibonding MOs}}{2}$$

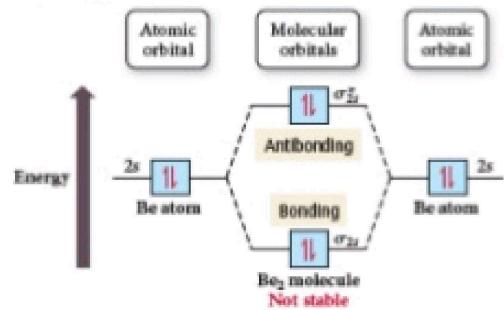


## Molecular Orbital Theory

### Beryllium molecule

The ground state electronic configuration of Be ( $Z = 3$ ) is  $1s^2 2s^2$

- The four valence electrons of  $\text{Be}_2$  occupy **one bonding MO** and **one antibonding MO**.
- The ground state electronic configuration  $\text{Be}_2$  is  $\sigma_g(1s)^2 \sigma_u^*(1s)^2 \sigma_g(2s)^2 \sigma_u^*(2s)^2$  MOs.
- It suggested that  $\text{Be}_2$  is **diamagnetic** in nature.
- The **bond order is 0** and we predict that  $\text{Be}_2$  should not be stable.



## Need for MO Theory



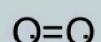
Valence bond theory fails to explain the bonding in many simple molecules.

The oxygen molecule has a bond length and strength consistent with a double bond, and it contains two unpaired electrons.

## Need for MO Theory

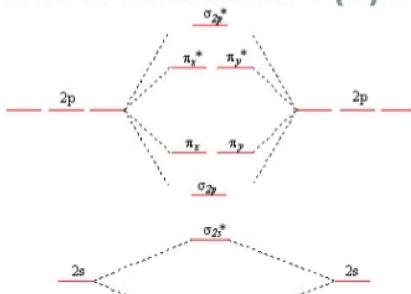


Valence bond theory predicts the double bond, but not the paramagnetism of oxygen.

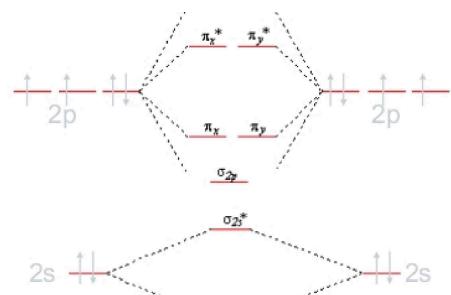


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## Molecular Orbital Diagrams

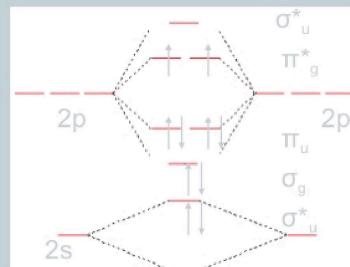


For  $O_2$ , there will be a total of 12 valence electrons that must be placed in the diagram.



For  $O_2$ , there will be a total of 12 valence electrons that must be placed in the diagram.

## MO Diagram

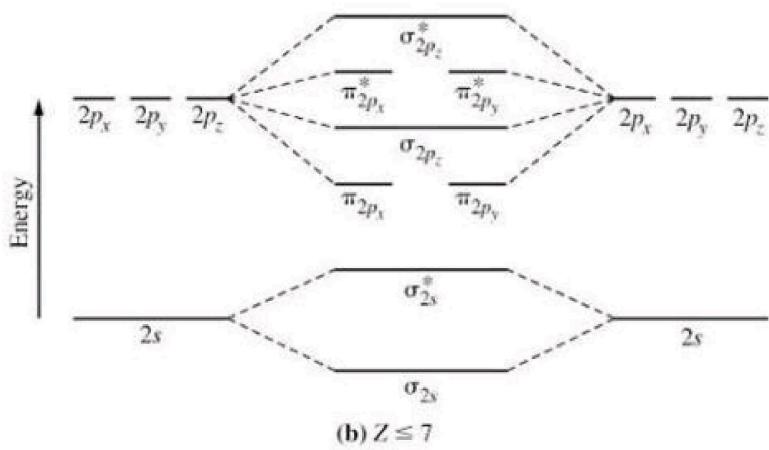


The molecular orbital diagram for oxygen shows two unpaired electrons, consistent with experimental data.

## Molecular orbitals of the second period elements

For diatomics of the second period elements with  $Z = 7$  or less, the energy difference between the  $s$  and  $p$  orbitals is small, and both produce regions of electron density between the nuclei (through  $\sigma_{2s}$  and  $\sigma_{2p}$  MOs). This leads to mixing of the  $\sigma_{2s}$  and  $\sigma_{2p}$  MOs.

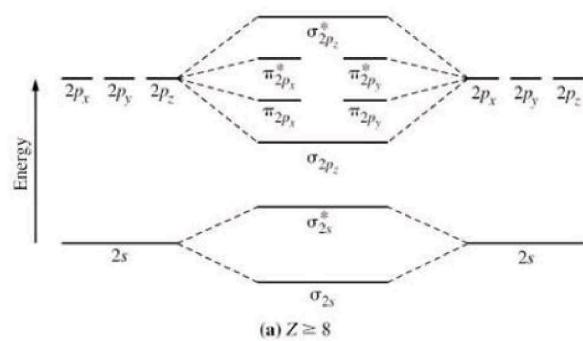
This leads to the following molecular orbital energy level scheme.



## Molecular orbitals of the second period elements

For diatomics of the second period elements with  $Z = 8$  or greater, the energy difference between the  $s$  and  $p$  orbitals is large, and little  $s$  and  $p$  orbital mixing takes place.

This leads to the following molecular orbital energy level scheme.



## Molecular orbitals of the second period elements

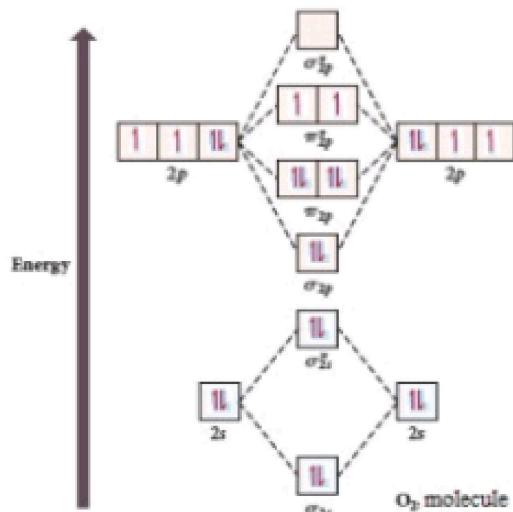
$2p^*$	□	□	↑↓			
$2p^* \ 2p^*$	↑↓	↑↓	↑↓	↑↓	↑↓	
$2p \ 2p$	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓
$2p$	↑↓	↑↓	↑↓			
$2s^*$	↑↓	↑↓	↑↓			
$2s$	↑↓	↑↓	↑↓			
Bond order	2	1	0			
Magnetism	Para-magnetic	Di-magnetic	-			

O<sub>2</sub>      F<sub>2</sub>      Ne<sub>2</sub>

## Molecular Orbital Theory

**O<sub>2</sub> molecule**

- The electronic configuration of oxygen is **1s<sup>2</sup>2s<sup>2</sup>2p<sup>4</sup>**
- The ground electronic configuration of O<sub>2</sub> molecule, therefore, is -  
 $\sigma(1s)^2 \sigma^*(1s)^2 \sigma(2s)^2 \sigma^*(2s)^2 \sigma(2p_z)^2 \pi^*(2p_x)^2 \pi^*(2p_y)^1 \pi^*(2p_y)^1$ .
- O<sub>2</sub> molecule should be paramagnetic.
- From the electronic configuration of O<sub>2</sub> molecule, it is clear that **ten electrons are present in bonding molecular orbitals** and **six electrons are present in antibonding molecular orbitals**.
- Its bond order, therefore, is =  $\frac{1}{2}(10 - 6) = 2$ .



O<sub>2</sub> MOLECULE : ATOMIC NO.=8

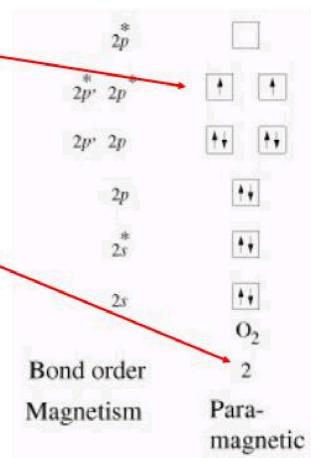
1s<sub>2</sub>,2s<sub>2</sub>, 2p<sub>4</sub> & 1s<sub>2</sub>,2s<sub>2</sub>,2p<sub>4</sub>

- BOND ORDER=  $8-4/2=2$
- $10 - 6 =4 /2=2$
- O-O IS DOUBLE BOND
- O=O IS MOLECULE
- PARAMAGNETIC DUE TO 2 UNPAIRED ELECTRONS

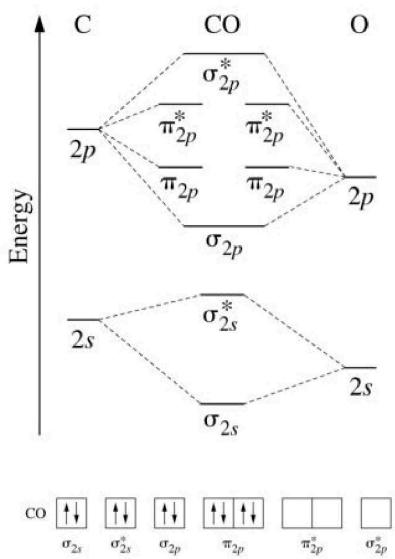
## Molecular Orbital Theory

- A special look at  $O_2$

- Experimentally,  $O_2$  is paramagnetic.
- The experimentally determined bond length of  $O_2$  is consistent with double bond character.
- Molecular orbital theory explains both observations! (FINALLY!)



### Molecular Orbital Theory - Heteronuclear diatomic molecules



For heterodiatomics, the energy of the bonding orbital is closer to that of the more electronegative atom and energy of the antibonding orbital is closer to that of the less electronegative atom.

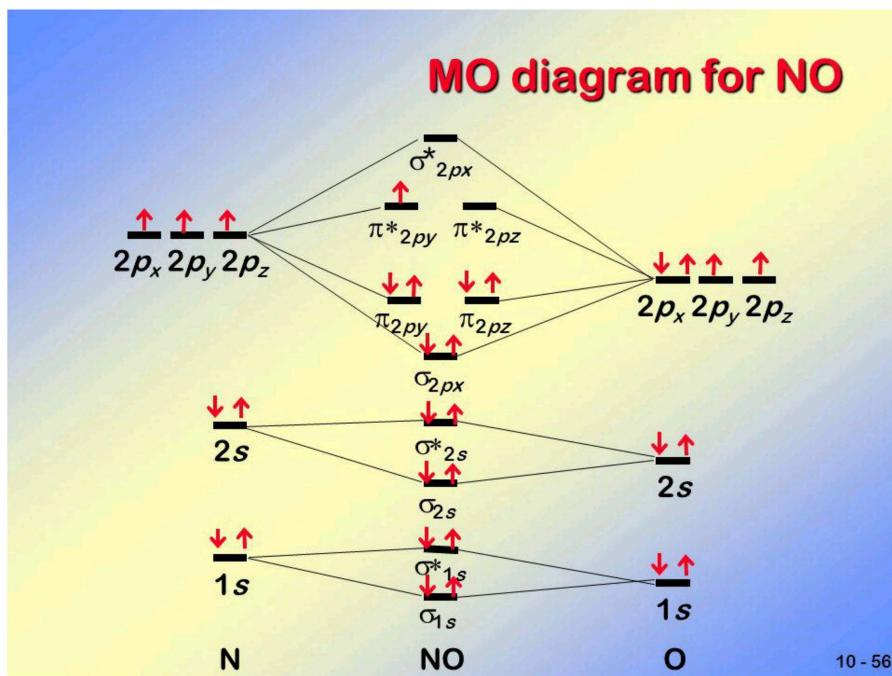
The atoms involved must not be too far apart so that the order of the energy levels is not too different than that of the homodiatics.

When deciding what MO energy level diagram to use, if either of the atoms is O or F, use the splitting pattern for  $Z \geq 8$ .

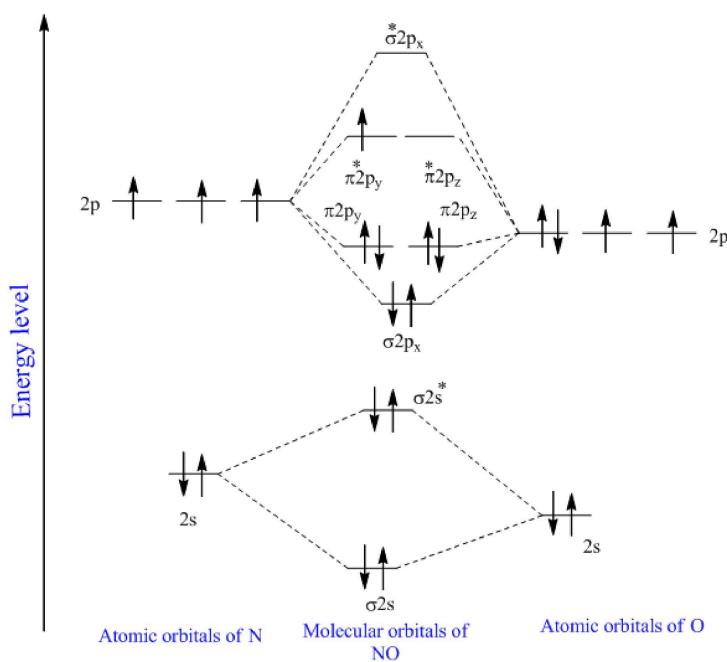
## NO MOLECULE :: BO =3

- N=7=1s2,2s2,2p3
- O=8= 1s2,2s2,2p4
- For bond order consider only orbital 2 and not both.
- BOND ORDER=  $(8- 3 )/2= 2.5$  ==Almost 3
- MOLECULE IS PARAMAGNETIC

# DRAW THIS WAY



# DRAW FULL DIAGRAM OF ALL ATOMIC ORBITALS STARTING FROM 1S

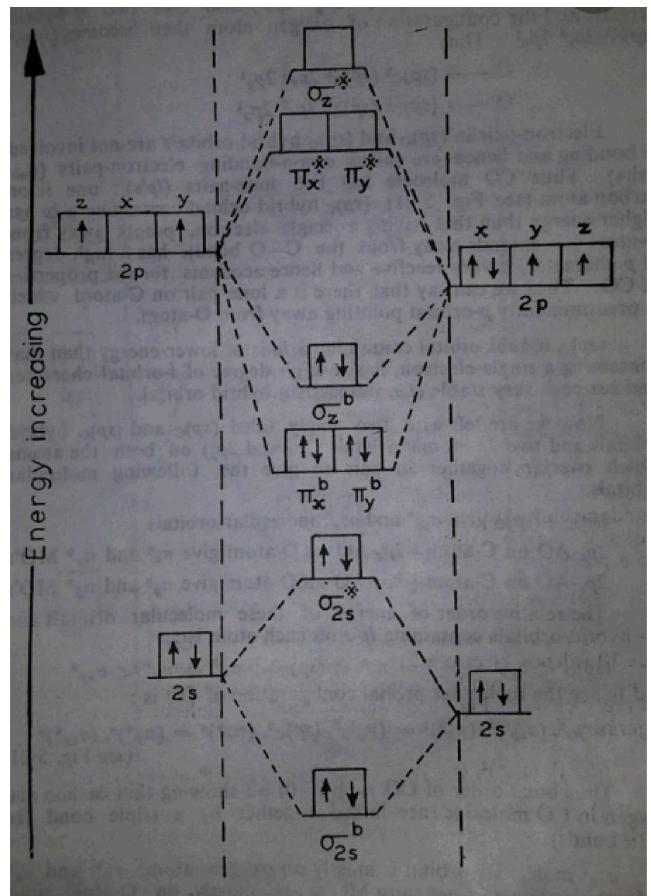


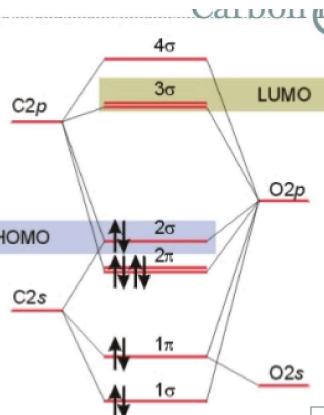
## CO MOLECULE

- C=6=1s<sub>2</sub>,2s<sub>2</sub>,2p<sub>2</sub>
- O=8= 1s<sub>2</sub>,2s<sub>2</sub>,2p<sub>4</sub>
- For bond order consider ALL BONDING & ANTIBONDING ORBITAL ELECTRONS
- BOND ORDER=  $(8-2)/2 = 3$
- Since there is no unpaired electron in Antibonding orbital, molecule is **diamagnetic**

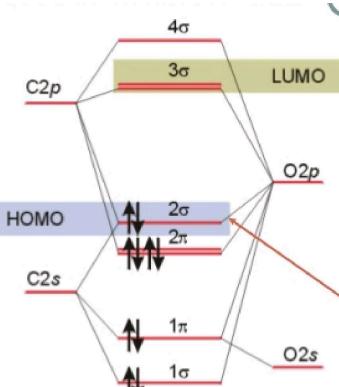
# CO MOLECULE

- BOND ORDER=  $=8-2=6/2=3$





In carbon monoxide, the bonding orbitals reside more on the oxygen atom, and the anti-bonding orbitals reside more on the carbon atom.



CO is a highly reactive molecule with transition metals. Reactivity typically arises from the highest occupied molecular orbital (HOMO), when donating electrons.



When acting as an electron pair acceptor, the lowest unoccupied molecular orbital (LUMO), is significant.

## ***Limitations of Molecular Orbital Model***

- 1. MO diagrams are complex.**
- 2. MO diagrams are difficult for molecules with more than two atoms.**
- 3. No prediction of geometry**



Every good conversation starts with good  
listening.

Thankyou verymuch for ur patient listening.