Chapter 06

Chemical Bonding

Atomic Sizes

Definition

The atomic radius means the average distance between the nucleus of the atom and its outermost electronic shell.

Reasons of less precision of radius determination

The radius of an atom cannot be determined precisely due to the following reasons:

(i) There is no sharp boundary of an atom. The probability of finding an electron never becomes exactly zero even at large distances from the nucleus.

(ii) The electronic probability distribution is affected by neighbouring atoms. For this reason, the size of an atom may change from one compound to another.

Techniques for radius measurement

Atomic radii can be determined, by measuring the distances between the centres of adjacent atoms with the help of X-rays or by spectroscopic measurements.

Variation of Atomic Radii in the Periodic Table

Along periods

The atomic radii decrease from left to the right in a period. The decreasing trend in a period is due to:

1. The increase in the nuclear charge. As the nuclear charge increases the pull on the electrons is increased and size of an atom decreases.
2. The shielding effect remains the same from left to right in a period.

Shielding effect/screening effect

The screening effect is also called shielding effect. This is responsible for the decrease in force of attraction of the nucleus for the electrons present in the valence shell.

Decrease of atomic radii in higher periods

The decrease of atomic radii is very prominent in second period, but less in higher periods. The decrease is small when we travel from left to right in transition elements Sc(21)-Zn(30), Y(39)-Cd(48) due to the intervening electrons.

Along groups

The atomic radii increase from top to bottom in a group. The increase in atomic radii in a group is due to:

1. Increase in the number of shells
2. Increase in screening effect

Ionic Radii

Definition

The ionic radius of an ion is the radius of the ion while considering it to be spherical in shape.

Ionic radii of cations and anions

The ionic radius of a cation is smaller than the atomic radius of the element from which it is derived. The ionic radius of an anion is greater than the atomic radius of the corresponding atom.

Examples

The radius of Na atom, for example, reduces from 186 pm to 95 pm after conversion into Na+ ion. The ionic radius of Cl- ion increases from 99 pm to 181 pm. The cationic radius decreases with the increase in the effective nuclear charge on the ion.

Decrease in radius with increasing positive charge

The decrease in radius is larger for divalent ions (Mg^{2+}) and still larger for trivalent ions (Al^{3+}).

Reason

This is due to the reason that with the successive loss of electrons, the nuclear charge attracts the remaining electrons with a greater force.

Increase in radius with increasing negative charge

The increase in the size of the anion is due to the increase in the electron-electron repulsion because of the increase in the valence shell electrons. Greater the amount of negative charge on an atom greater the size of ion.

Trend in the periodic table

The variation of ionic radii in groups and periods has the same trend as for atomic radii. Ionic radius for metals is for positive ions and for elements of group number VA to VII A is for negative ions.

Calculation of ionic radii

Let us consider, the positive and negative ions, which are held together by electrostatic forces of attraction in a crystal lattice. r+ and r- are the values of radii of cation and anion, respectively.

1. Interionic distance

The interionic distance ‘R’ in a crystal lattice is equal to the sum of the cationic radius r+ and the anionic radius r_-

$$R = r_+ + r_-$$

2. Pauling’s study

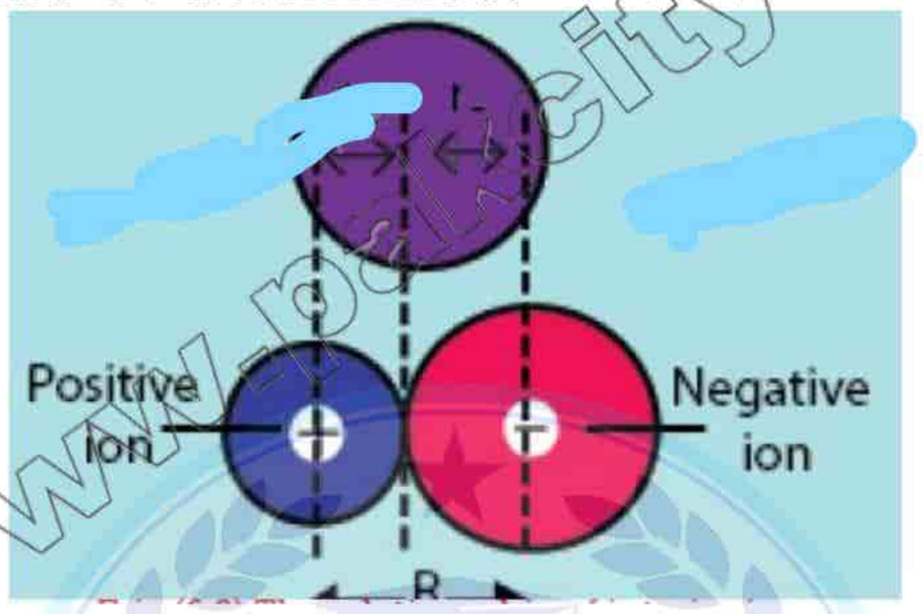
Pauling was able to determine the distance between K+ and Cl- ions in potassium chloride crystal.

$$R = 133\text{pm} + 181\text{ pm} = 314\text{ pm}$$

The ionic radius appeared to be an additive property. Pauling extended this concept to other K^+ salts and calculated the radii of other ions from the relationship:

$$r_- = R - r_+$$

The ionic radii of different cations can also be determined.



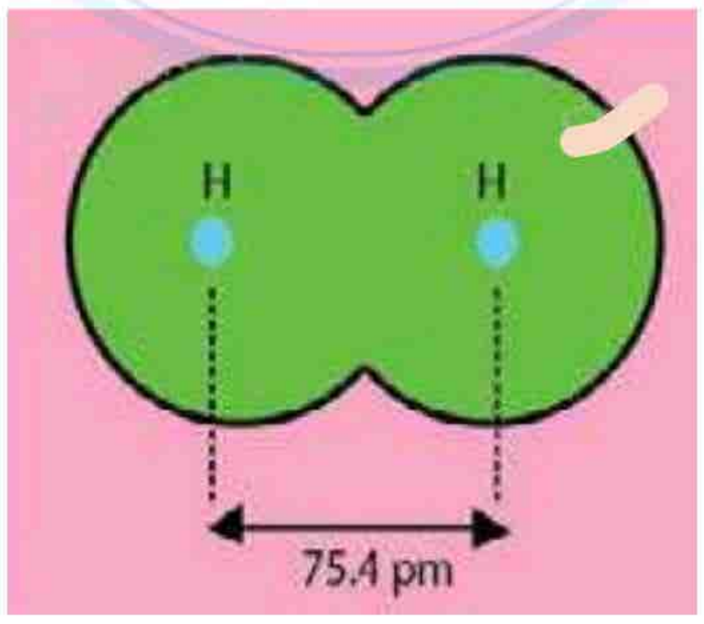
Covalent Radii

Definition

The covalent radius of an element is defined as half of the single bond length between two similar atoms covalently bonded in a molecule.

Example

The covalent radius of hydrogen, for example, is 37.7 pm. It is half of the single bond length (75.4 pm) between the two H atoms in H-H molecule.



Determination of covalent radius

The covalent radius of an atom can be used to determine the covalent radius of another atom. For example, the experimentally determined bond length of C-Cl in CH_3CI is 176.7 pm. The covalent radius of Cl-atom being known as 99.4 pm, that of C-atom can be calculated by subtracting this value from C-Cl bond length. So, the covalent radius of C-atom = 176.7- 99.4 = 77.3 pm.

Variation along periodic table

The variation of covalent radii in groups and periods is almost the same as of atomic radii.

Ionization Energy

Definition

The ionization energy of an element is the minimum energy required to remove an electron from its gaseous atom to form an ion. The process is called ionization.

Example

$$Mg \rightarrow Mg^{+} + e^{-} \qquad \Delta H = 738 kJmol^{-1}$$

Factors Influencing Ionization Energies

Following are the factors influencing ionization energies:

(i) Atomic radius of atom
(ii) Nuclear charge or proton number of the atom
(iii) Shielding effect of inner electrons
(iv) Nature of orbital

Variation in the Periodic Table

Along periods

The ionization energies increase from left to right in a period due to:

1. Increase in the proton number.

This may be explained in terms of the periodicity of the electronic configuration of elements. Each period begins with an element which has one electron in its valence shell and ends with the completion of an electronic shell.

2. Increase in nuclear charge

It leads to a stronger force of attraction between the nucleus and the increasing number of electrons. The stronger force of attraction, ultimately results in difficult removal of electrons.

Along groups

The ionization energy decrease in spite of the increase in proton number or nuclear charge due to:

1. Successive addition of electronic shells

The valence electrons are placed at a larger distance from the nucleus.

2. Effective nuclear charge decreases

As the force of attraction between the nucleus and the outer electron decreases with the increase in distance the electron can be removed more easily or with less energy.

2. Increasing shielding effect

The force of attraction also decreases due to increasing shielding effect of the intervening electrons.

Higher Ionization Energies

The energy required to remove an electron after the removal of first electron is called second ionization energy.

$$Mg \rightarrow Mg^{++} + e^{-} \qquad \Delta H = 1450 kJmol^{-1}$$

Similarly, the energy required to remove third electron after the removal of second one is called the third ionization energy, and it is 7730kJ for Mg.

Reason

Second electron is removed from a positively charged ion rather than a neutral atom. The dominant positive charge holds the electrons more tightly and thus further removal of electrons becomes more difficult.

Ionization energy is index to the metallic character

Ionization energy is an index to the metallic character. The elements having low ionization energies are metals and those having high ionization energies are non-metals. Those with intermediate values are mostly metalloids.

Valency determination

The gaps in the first, second, third and higher ionization energies help us to guess the valency of an element. If, there is sufficient gap between first ionization energy and second one, then the element shows valency of one.

Electron Affinity

Definition

The electron affinity of an atom is the energy released when an electron adds to an empty or partially filled orbital of an isolated gaseous atom in its valence energy level to form an anion having a unit negative charge.

Example

$$Cl(g) + e^- \rightarrow Cl^-(g) \qquad \Delta H = -349 kJmol^{-1}$$

Factors Influencing the Electron Affinity

Following factors influence the electron affinity:

1. Atomic radius
2. Nuclear charge
3. Shielding effect

Variation in the Periodic Table

Along periods

The electron affinities of elements increase from left to right in the periodic table due to:

1. Increase in the nuclear charge.
2. Decrease in atomic radius
3. Constant shielding effect

The alkali metals have the lowest and the halogens have the highest electron affinities.

Along groups

The electron affinities usually decrease from top to bottom due to:

1. Increase in atomic radii
2. Decrease in effective nuclear charge
3. Increase in shielding effect

Exceptions

1. Fluorine has electron affinity less than that of chlorine.

Reason

Fluorine has very small size and seven electrons in 2s and 2p subshells have thick electronic cloud. This thick cloud repels the incoming electron.

2. The elements of group IIA, VA and VIII show abnormally low values in every period of the periodic table. This can be understood from their electronic configurations.

Electronegativity

Definition

The tendency of an atom to attract a shared electron pair towards itself is called its electronegativity.

Factors influencing electronegativity

Following factors influence the electronegativity:

1. Atomic radius
2. Nuclear charge
3. Shielding effect

It is related to the ionization energy and the electron affinity of the element. Thus, fluorine atom is more electronegative than hydrogen atom.

Calculation of electronegativity values

Pauling calculated the electronegativity values of elements from the difference between the expected bond energies for their normal covalent bond and the experimentally determined values. He devised an electronegativity scale on which fluorine is given an arbitrary standard value 4.0. It is the most electronegative element. The electronegativity values of other elements are compared with fluorine.

Units

Electronegativity has no units.

Variation in the Periodic Table

Along periods

The electronegativity of elements increase from left to right in the periodic table due to:

1. Increase in the nuclear charge
2. Decrease in atomic radius
3. Constant shielding effect

Along groups

The electronegativity decreases from top to bottom down the group due to:

1. Increase in atomic radii
2. Decrease in effective nuclear charge
3. Increase in shielding effect

Bond type and electronegativity

The electronegativity differences of the elements can be related to dipole moments and bond energies. The difference in the electronegativity values of the bonded atoms is an index to the polar nature of the covalent bond.

1. When the difference is zero the bond between the two atoms is non-polar.

Thus, all the bonds which are formed between similar atoms are non-polar in character, while those formed between different elements are mostly polar.

2. Elements of widely different electronegativities form ionic bonds.
3. A difference of 1.7 units shows roughly equal contributions of ionic and covalent bonds.

Types of Bonds

Chemical bonds can be classified as:

(i) Ionic bond

(ii) Covalent bond

(iii) Coordinate covalent bond

Ionic Bond

Definition

According to the Lewis theory, ionic bond is formed by the complete transfer of electron or electrons from an atom with low ionization energy to another atom with high electron affinity.

Example

Formation of potassium chloride

Ionization of potassium

The electronic configuration of potassium is:

$$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$$

It may be represented as K (2,8,8,1)

It tends to lose the outermost electron to form K^+ ion.

$$K(2,8,8,1) \rightarrow K^+(2,8,8) + e^- \qquad \Delta H = 419.0\,kJmol^{-1}$$

After the loss of an electron, potassium attains the nearest inert gas configuration of Ar (2,8,8). This is first ionization energy of potassium.

Electron affinity of chlorine

Chlorine atom has the electronic configuration $Is^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$ or Cl (2,8,7). It tends to attain the nearest inert gas configuration of Ar (2,8,8) releasing 348.6 $kJmol^{-1}$ energy. It is the electron affinity of chlorine.

$$:\ddot{\underset{\cdot\cdot}{Cl}}\cdot + e^- \rightarrow :\ddot{\underset{\cdot\cdot}{Cl}}^-: \qquad \Delta H = -349\,kJmol^{-1}$$

The oppositely charged K^+ and Cl^- ions are held together by strong electrostatic force of attraction. The lattice energy of KCl is 690 $kJmol^{-1}$.

Other examples

$$\begin{aligned}
&Ca\ (2,8,8,2) &&\longrightarrow Ca^{2+}\ (2,8,8)+2e^-\\
&Al\ (2,8,3) &&\longrightarrow Al^{3+}\ (2,8)+3e^-\\
&O\ (2,6)+2e^- &&\longrightarrow O^{2-}\ (2,8)\\
&S\ (2,8,6)+2e^- &&\longrightarrow S^{2-}\ (2,8,8)
\end{aligned}$$

Calcium oxide contains ions in the ratio of $Ca^{2+}:O^{2-}$ and its formula is CaO, while in aluminium oxide, Al^{3+} and O^{2-} ions are present in the ratio 2:3. Its formula is Al_2O_3. Similarly, CaS and Al_2S_3 are also ionic compounds to some extent.

Percentage of ionic character

In order to decide the % of ionic nature in a compound note the difference of electronegativity between the bonded atoms.

If the difference is 1.7 or more then the bond is said to be ionic.

Example

NaCl has 72% ionic character.

CsF has 92% ionic character.

There is no bond with 100% ionic character.

Covalent Bond

Definition

According to Lewis and Kossel, a covalent bond is formed by the mutual sharing of electrons between two atoms.

Types of covalent bond

1. Non-polar covalent bond
2. Polar covalent bond

Non-polar covalent bonds

In such bonds, the bonding electron pairs are equally shared and thus bonds are electrically neutral.

Example

In H_2 or Cl_2 molecules, the two electrons forming the covalent bond are equally shared by the two identical atoms having same electronegativities.

$$H:H \quad \text{or} \quad H-H \qquad\qquad :\ddot{\underset{\cdot\cdot}{Cl}}:\ddot{\underset{\times\times}{Cl}}: \quad \text{or}\ Cl{-}{-}{-}Cl$$

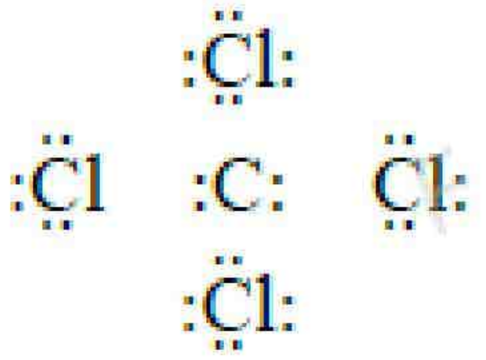
Other examples

F_2, Br_2 and I_2

CCl_4

Reason

This is due to cancellation of all the dipoles of this molecule due to its symmetry. All the C-Cl bonds are polar but molecule is non-polar overall.



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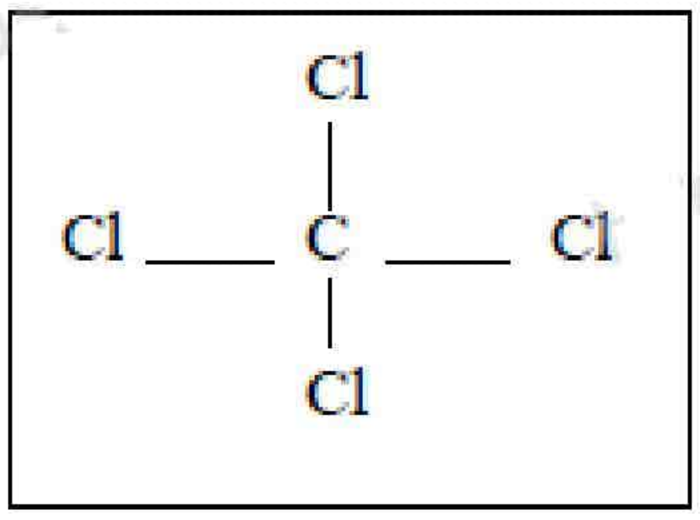


Similar molecular geometry

CH_4, SiH_4, and $SiCl_4$

Polar covalent bond

When two different atoms are joined by a covalent bond, the electron pair is not equally shared between the bonded atoms. The bonding pair of electrons will be displaced towards the more electronegative atom

Examples

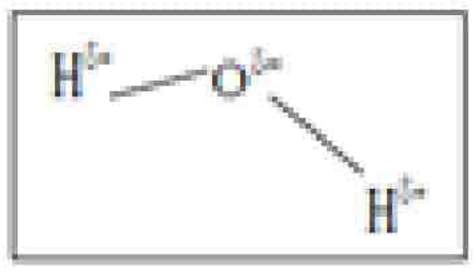
One end of the molecule is partially positive and the other partially negative.

Hydrogen fluoride

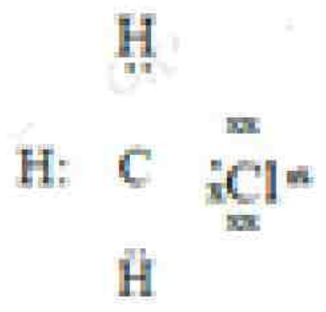
$\mathrm{H{\times}\ddot{F}:}$ or $\mathrm{H^{\delta+}{\times}\,F^{\delta-}}$

Water

$\mathrm{H{\times}\ddot{O}{\times}H}$



Methyl chloride



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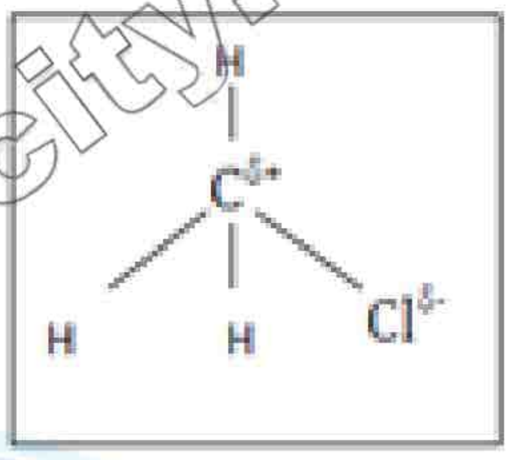
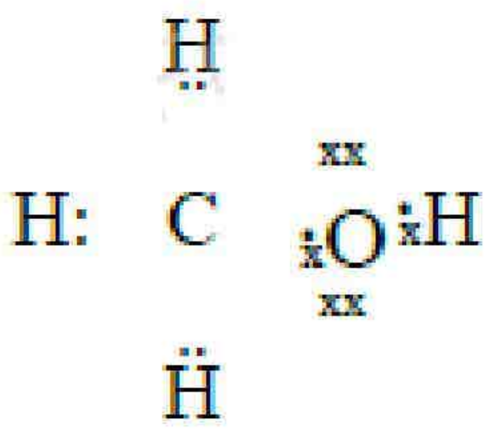


Methanol



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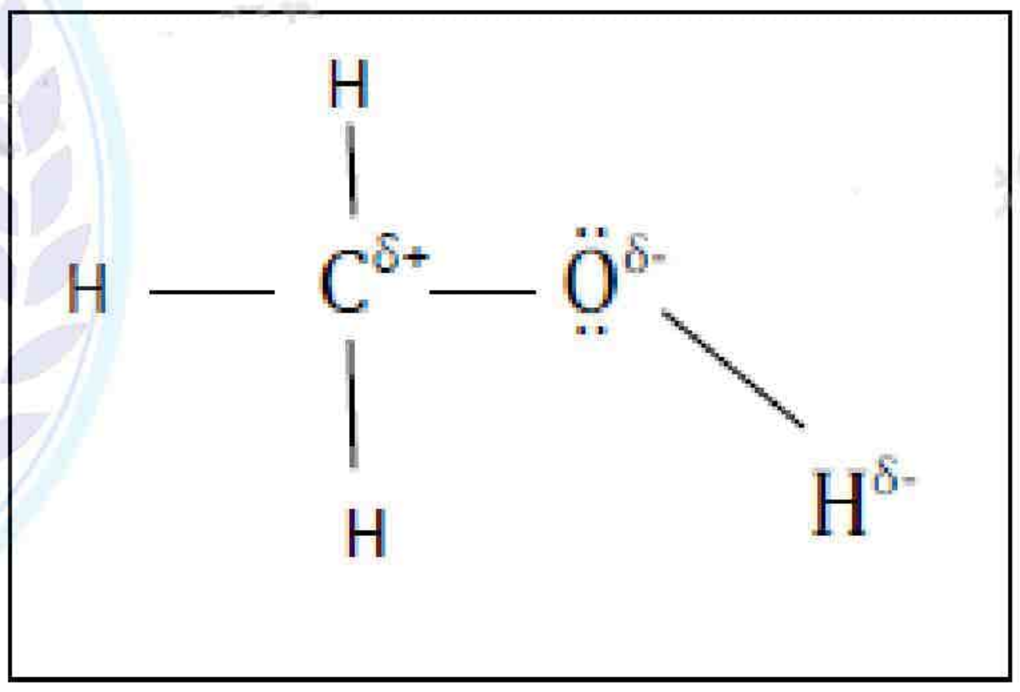


Molecules with double and triple bond

:N:::N: or $:\mathrm{N}\equiv\mathrm{N}:$

$\ddot{\mathrm{O}}::\ddot{\mathrm{O}}$ or $\ddot{\mathrm{O}}=\ddot{\mathrm{O}}$

Carbon dioxide

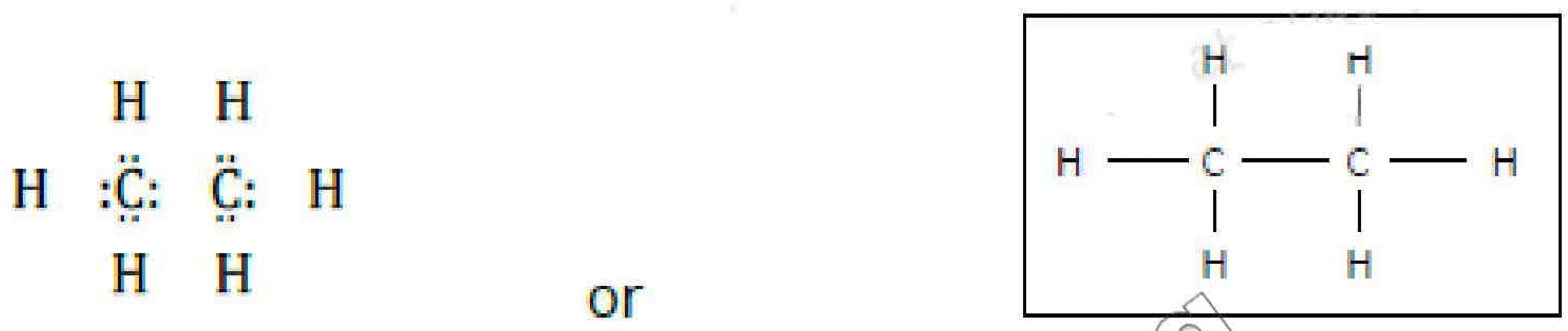
Each bond represents a pair of electrons.

In a double bond (=), two shared pairs and in a triple bond (≡), three shared pairs of electrons are involved.

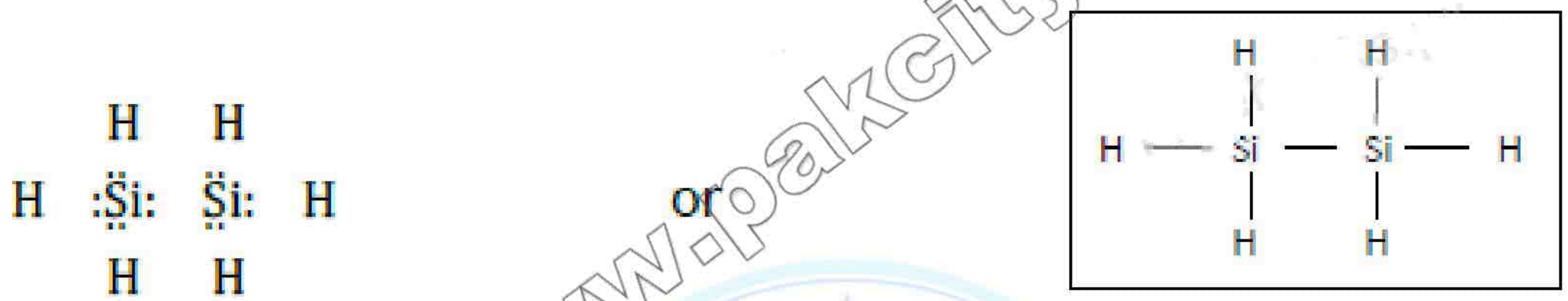
Carbon compounds

Some of the non-metallic atoms, particularly carbon atoms, mutually share their electrons with each other. This leads to the formation of macromolecules. Diamond, graphite and SiC are the best examples of such molecules. Carbon can make single, double and triple covalent bonds in alkanes, alkenes and alkynes.

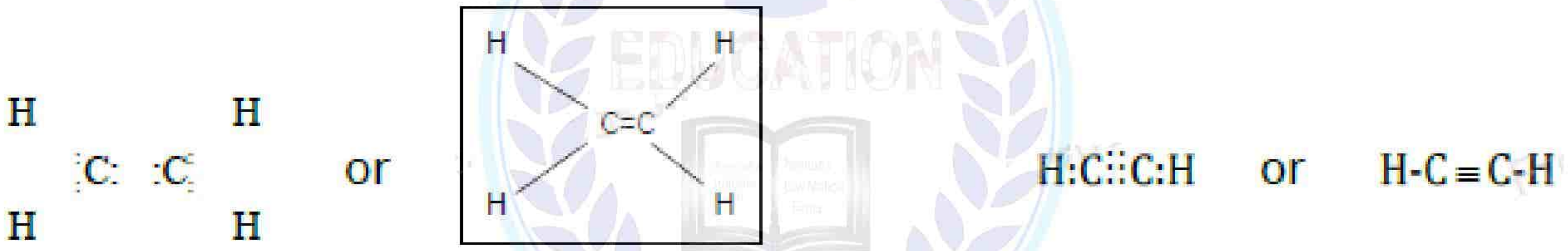
Ethane



Disilane



Ethene and ethyne



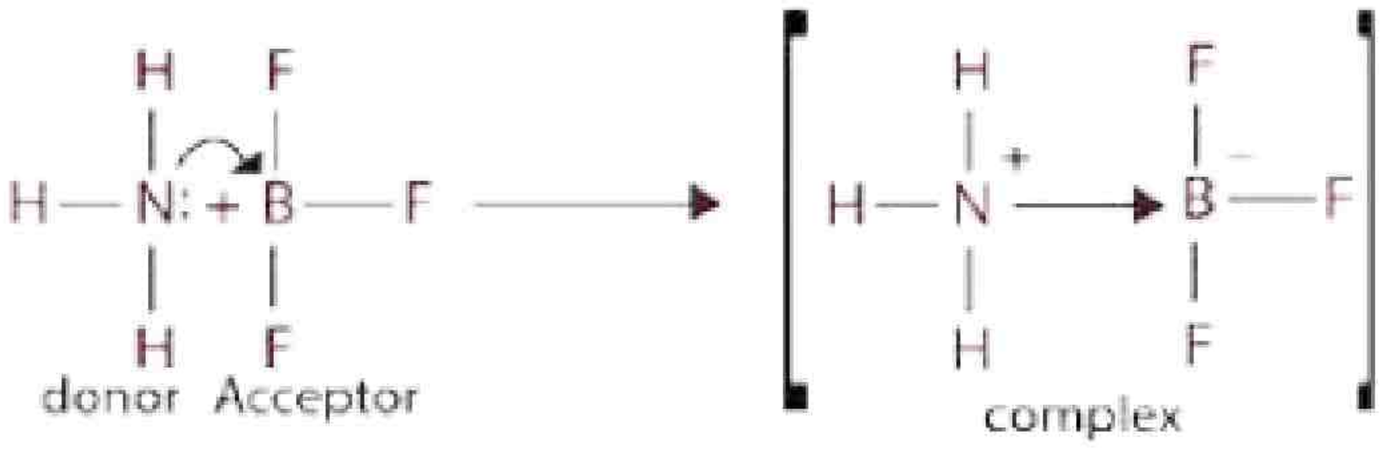
Coordinate Covalent Bond

Definition

A coordinate covalent bond is formed between two atoms when the shared pair of electrons is donated by one of the bonded atoms.

Examples

1. Bond formation between NH_3 and BF_3



NH_3 has three covalent bonds and there is a lone pair of electrons on nitrogen atom. Boron atom in BF_3 is deficient in electrons. The octet of B is not complete in BF_3. Nitrogen can donate the pair of electrons to the acceptor BF_3 and this result in the formation of a coordinate covalent bond.

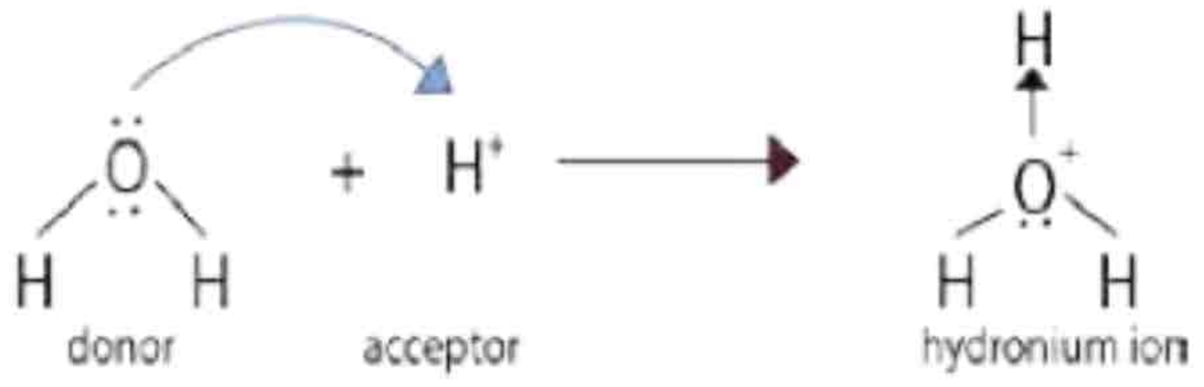
Adduct/complex formation

The complex so produced is overall neutral and charges are indicated on N and B atoms.

In some of the compounds, after the formation of a coordinate covalent bond, the distinction between covalent bond and coordinate bond vanishes.

2. Bond formation between H_2O and H^+

Water donates its electron pair to H+ ion to give $H3O^+$ ion. All the three bonds between oxygen and hydrogen have equal status. Every bond is 33% coordinate covalent and 66% covalent.

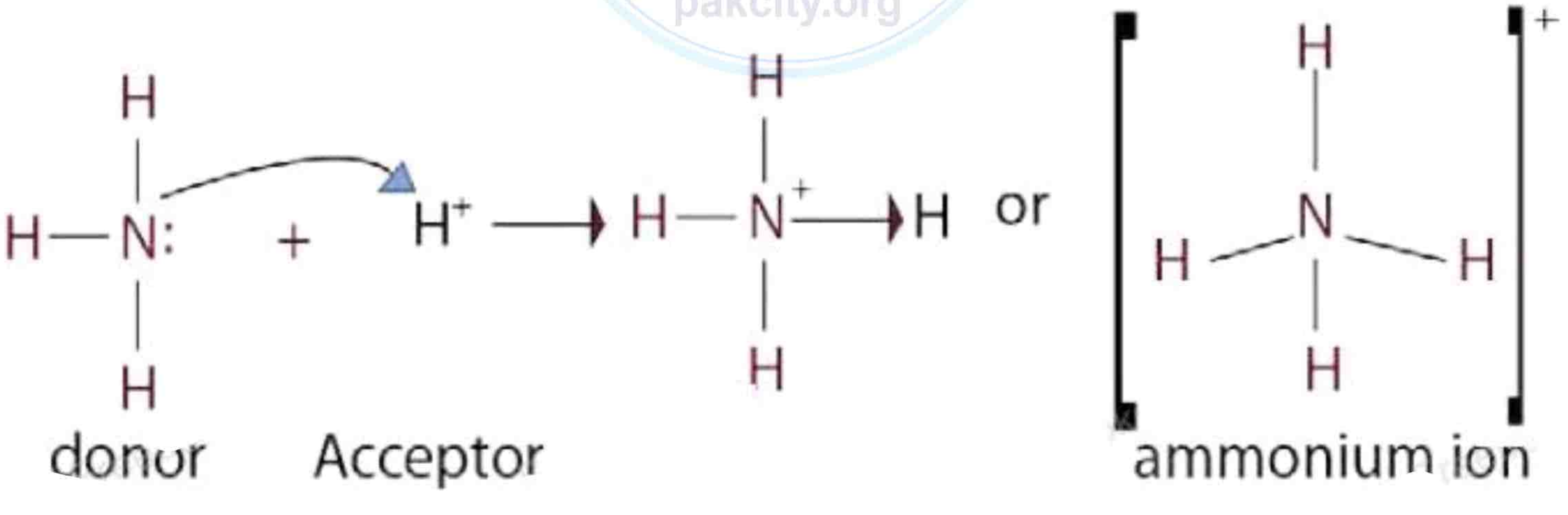


3. Oxonium ion formation

All the alcohols and ethers offer their lone pairs to H^+ to give coordinate covalent bonds. The ions so produced are called oxonium ions.

4. Bond formation between NH_3 and H^+

Ammonia donates its electron pair to H^+ ion to give NH_4^+ ion. All the four bonds behave alike, in NH_4^+ ion.



5. Other examples

(a) All the primary, secondary and tertiary amines like ammonia make such bonds with H^+.
(b) PH_3 combines with H^+ to give PH_4^+ ion called phosphonium ion.
(c) Coordinate covalent bonds are present in HNO_3.
(d) Many oxyacids of halogens, like ($HClO_2$, $HClO_3$, $HClO_4$) have coordinate covalent bonds between chlorine and oxygen.

Valence Shell Electron Pair Repulsion Theory (VSEPR)

Postulates:

1. Both lone pairs as well as the bond pairs participate in determining the geometry of the molecules.
2. All electron pairs remain at maximum distance apart to avoid repulsions.
3. Lone pairs occupy more space than bond pairs because bond pair is attracted by two nuclei whereas lone pair is under the influence of one nucleus.
4. Lone pairs exert greater repulsion forces than bond pairs.
5. The magnitude of repulsions between the electron pairs is of the following order:

lone pair-lone pair>lone pair-bond pair>bond pair-bond pair

These repulsions are called Vander Waals Repulsions.

6. Two electron pairs of double bond and three electron pairs of triple bond occupy more space than one electron pair of single bond.
7. Electron pairs of double bond and single bond are considered as single electron pair in determining the geometry of the molecule.

Types of Molecules:

Let us consider

A= As central polyvalent atom

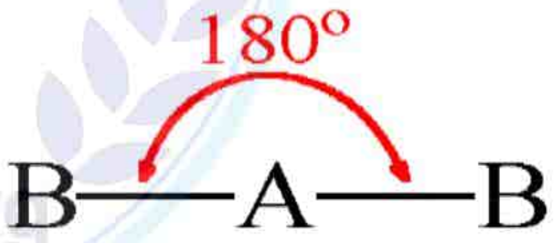
B= Types of atom bonded to A

More than one 'B' type atoms are linked to A to give **AB_2, AB_3, AB_4** type molecules.

1. **AB_2 Type molecules:**

Total electron pairs= 2
Bond pairs= 2
Lone pairs= 0
Geometry= Linear
Angle= 180°

Shape:



Examples: $BeCl_2$, $HgCl_2$

2. **AB_3 Type molecules:**

Total no of electron pair= 3. We can have two sub-types of AB_3 molecules.

a. **AB_3 Type with no lone pair:**

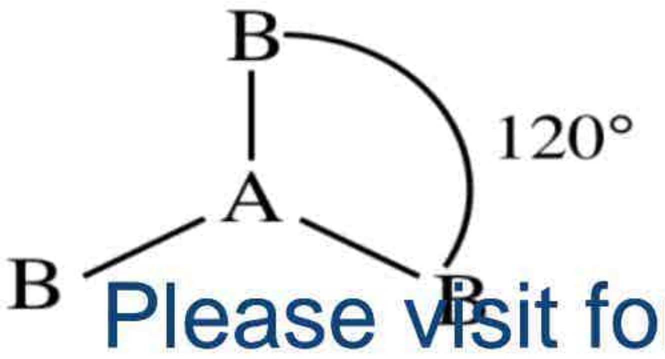
Bond pairs= 3

Lone pairs= 0

Geometry= Trigonal planar

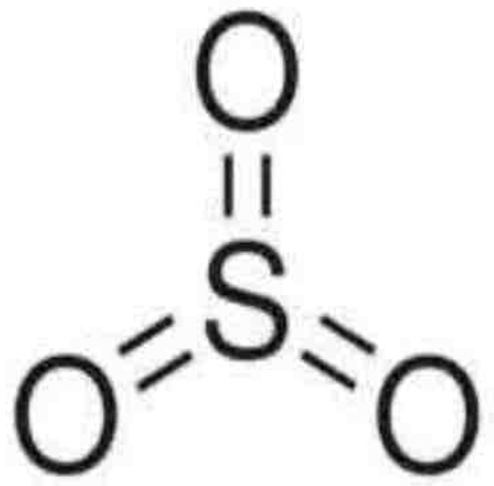
Angle= 120°

Shape:



Example (with single bond): BF_3 **Shape:**

Example (with multiple bond): SO_3



b. **AB$_3$ Type with one lone pair:**

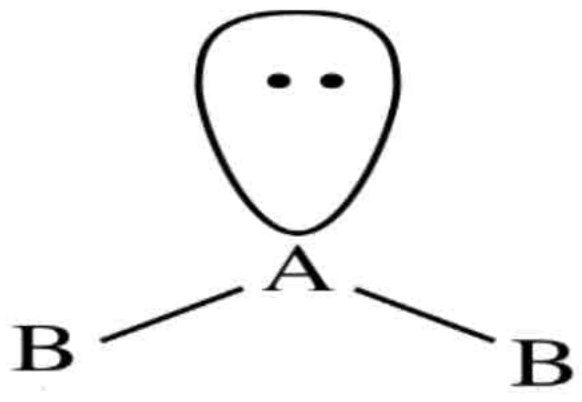
Bond pairs= 2

Lone pairs= 1

Geometry= Bent or angular

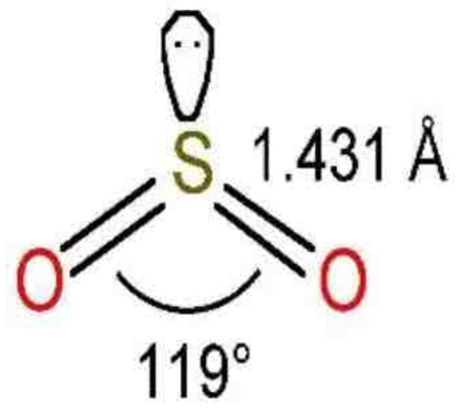
Angle= less than 120°

Shape:



Example (with single bonds): $SnCl_2$

Example (with multiple bond): SO_2



Shape

3. **AB$_4$ Type Molecules:**

Total electron pairs= 4

We can have 3 sub types of AB$_4$ molecules.

a. **AB$_4$ with no lone pair:**

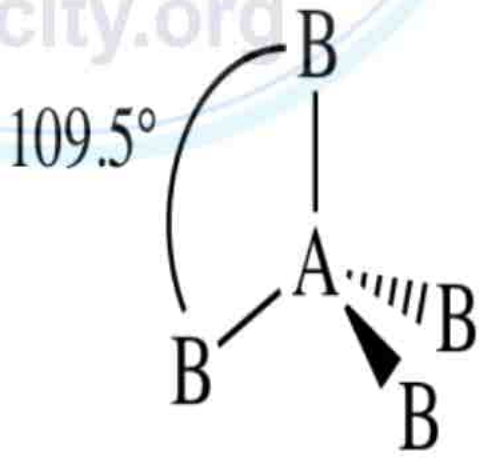
Bond pairs= 4

Lone pairs= 0

Geometry= Tetrahedral

Angle= 109.5°

Shape:



Example: CH_4, BF_3

b. **AB$_4$ type with no lone pair:**

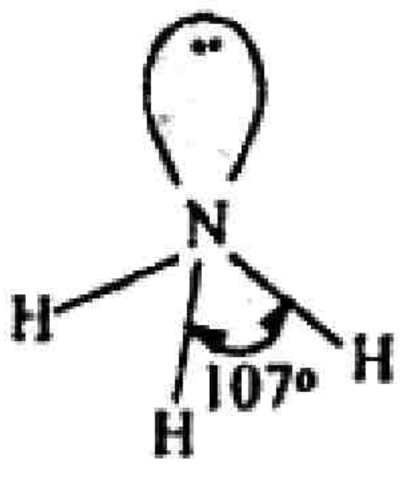
Bond pairs= 3

Lone pairs= 1

Geometry= Trigonal Pyramidal

Angle= less than 109.5°

Shape:



Pyramidal shape

Example: NH_3. Angle is 107.5° in NH_3

c. **AB$_4$ with two lone pairs:**

Bond pairs= 2

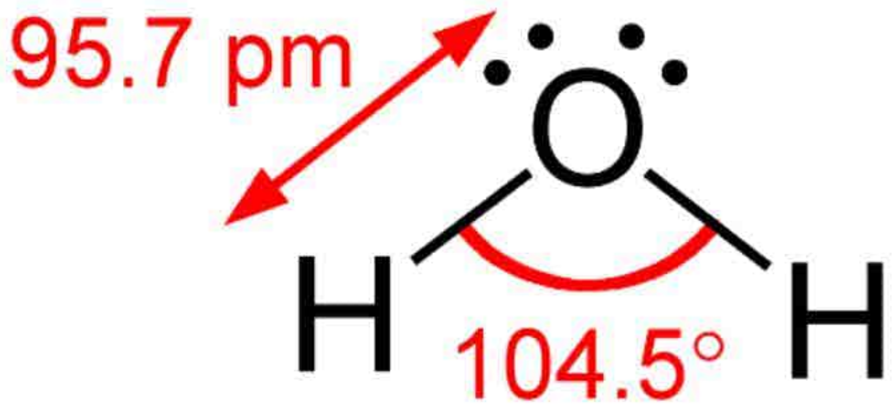
Lone pairs= 2

Geometry= Bent or angular

Angle= less than 109.5°

Shape:

Example: H_2O angle in water is 104.5°



Valence Bond Theory(VBT)

VBT is concerned with both bond formation and the shapes of the molecules.

Main Points:

1. This theory considers molecule as a combination of atoms.
2. According to this, a covalent bond is formed when half-filled orbitals (in valence shell) of two atoms overlap.
3. Pair of electrons (one from each atom) then occupies the overlapped orbital (thus bond formation take place).
4. Larger the overlap stronger is the bond.
5. Direction of the bond is determined by the direction of the overlap.
6. Depending upon the overlap covalent bond can either be σ (sigma) or π (pi).

sigma bond (σ bond):

When two orbitals overlap in such a way that probability of finding an electron is maximum around the line joining the two nuclei it is called sigma bond.

pi bonds (π bond):

When two orbitals overlap in such a way that probability of finding an electron is above and below the inter-nuclear axis it is called pi bond.

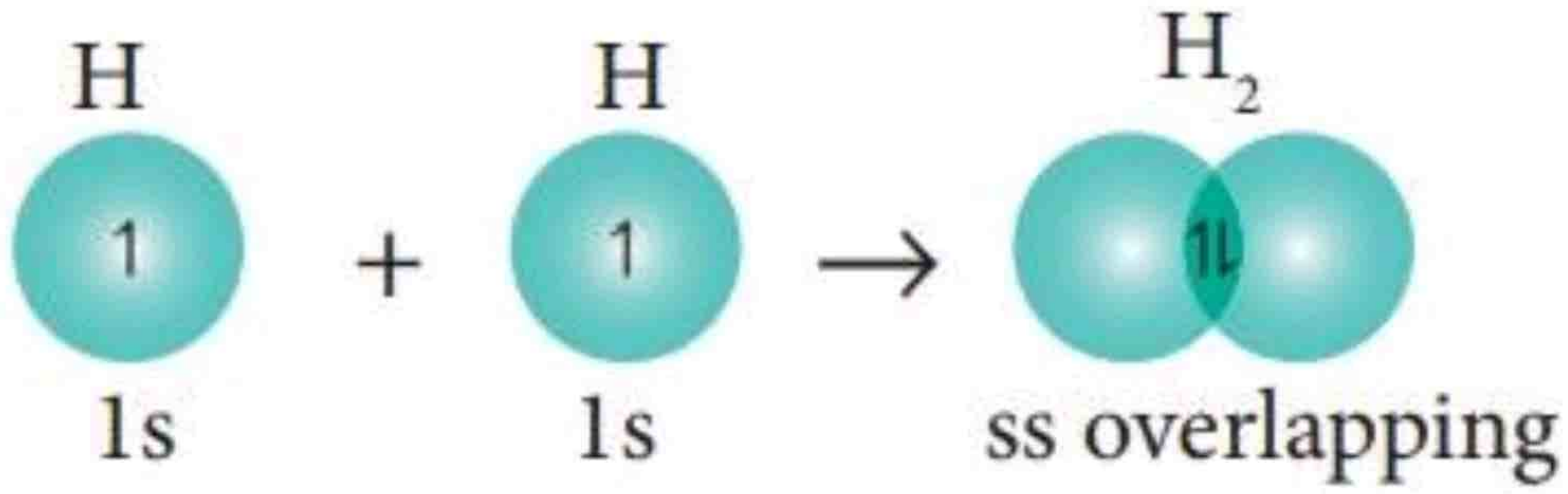
Types of overlaps with examples:

1. s-s overlap:

s-s overlap gives rise to sigma bond

For Example: H_2 molecule

H= $1=1s^1$



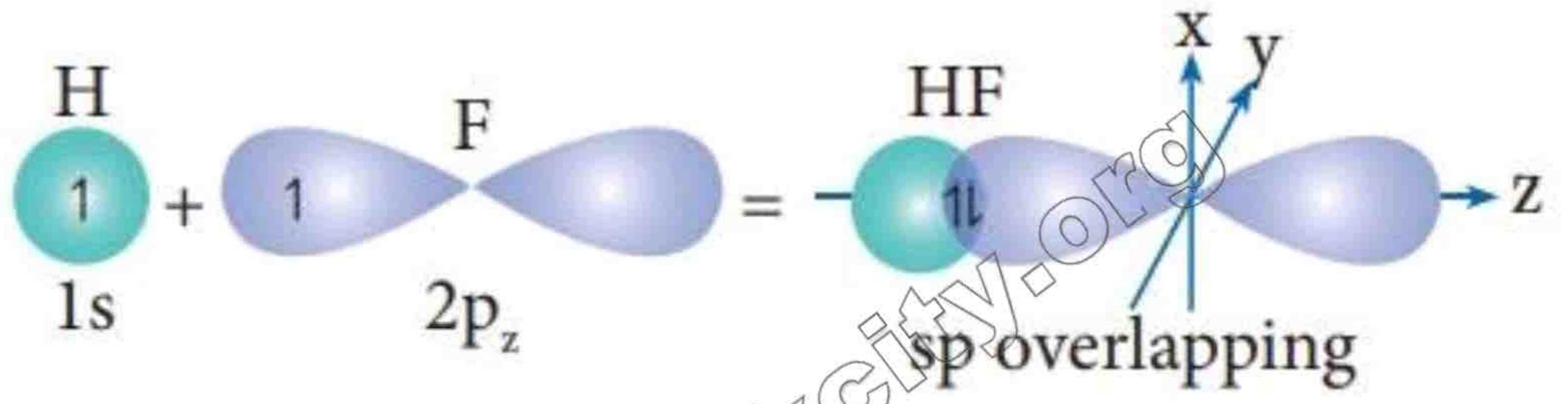
2. s-p overlap:

When s and p orbitals overlap sigma bond is formed.

For example:In HF molecule 1s of H and 2pz of F overlap to form sigma bond

H= 1=$1s^1$

F= 9= $1s^2,2s^2,2p_x^2,2p_y^2,2p_z^1$



3. p-p overlapping:

Type1: When there is a single bond then p-p overlap gives rise to sigma bond.

For example: F_2 molecule (half-filled 2pz orbitals of both fluorine atoms overlap with each other)

F=9=$1s^2,2s^2,2p_x^2,2p_y^2,2p_z^1$

Type 2When there is a double or a triple bond then pi bond is also formed in addition to sigma bond

For example:N_2 molecule

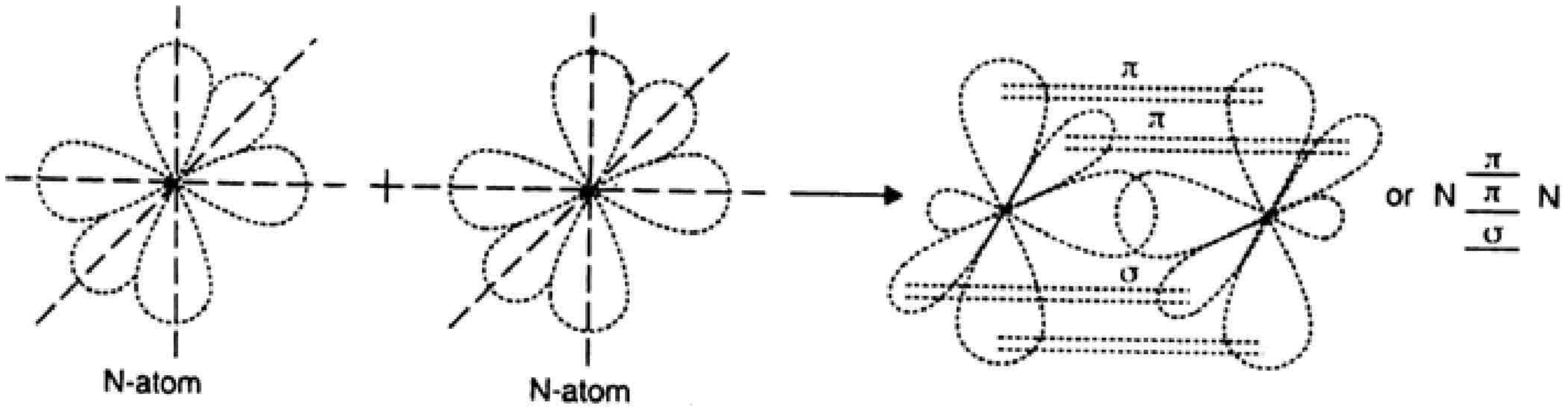
$N_7 = 1s^2,2s^2,2p_x^1,2p_y^1,2p_z^1$

All the three partially filled p orbitals of one N atom overlap with p orbitals of other N atom

- $p_x$overlaps with p_x to form a sigma bond
- p_y overlaps with p_y to form a pi bond

- p_z overlaps with p_z to form a pi bond

Hence, triple covalent bond is formed



Hybridization

Definition

Hybridization is the concept in which atomic orbitals of different energy and shape intermix to form a new set of orbitals of same shape and energy.

OR

According to this, atomic orbitals differing slightly in energy intermix to form new orbitals, which are called hybrid atomic orbitals. They differ from the parent atomic orbitals in shape and possess specific geometry.

Types

There are three basic types of hybridization:

1. sp^3
2. sp^2
3. sp

sp^3 Hybridization

Definition

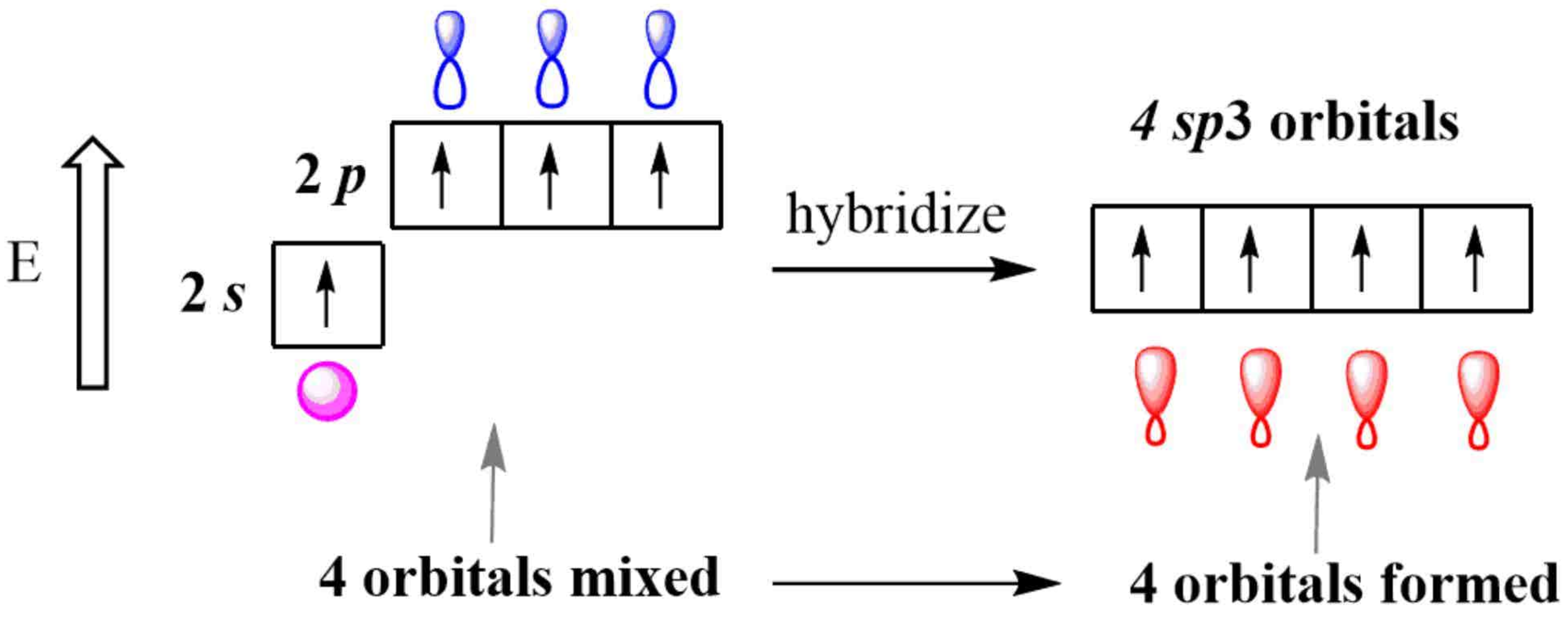
One s and three p orbitals intermix to form a set of four equivalent sp^3 hybrid orbitals.

All these four sp^3 hybrid orbitals are degenerate (having equal energy) and are directed at an angle of 109.5^0 in space to give a tetrahedral geometry.

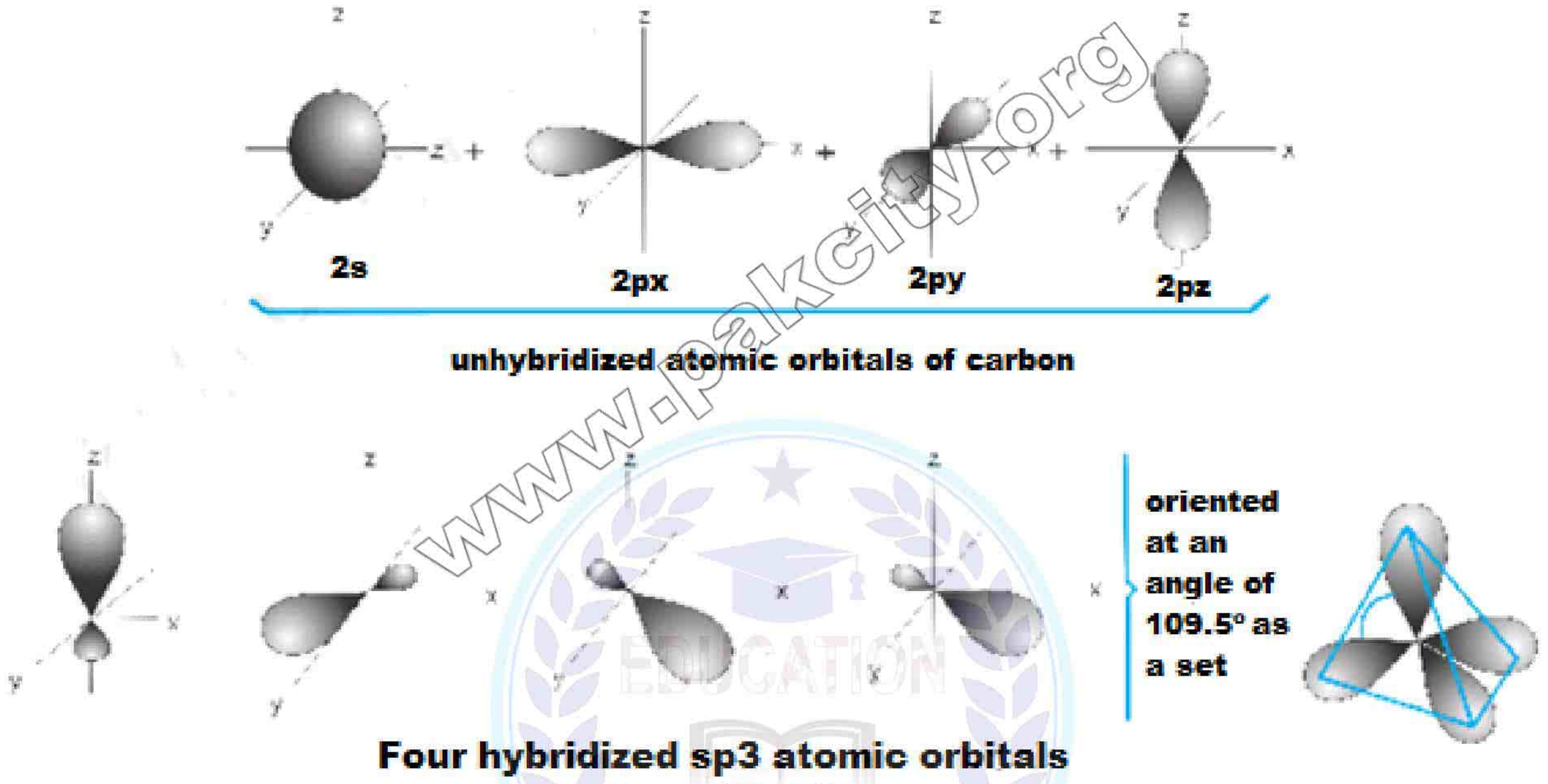
Examples

CH_4, NH_3 and H_2O

Methane



The energies of hybrid orbitals are lower than unhybridized orbitals.



Structure of methane

Explanation of Structure of Methane

Hydrid orbitals: Four sp^3 hybrid orbitals consisting of two lobes formed due to overlap of one s and three p orbitals. Each orbital has one larger lobe and the other smaller lobe.

Overlap of orbitals: Each sp^3 hybrid orbital combines with s orbital of hydrogen to give sp^3-s sigma bonds.

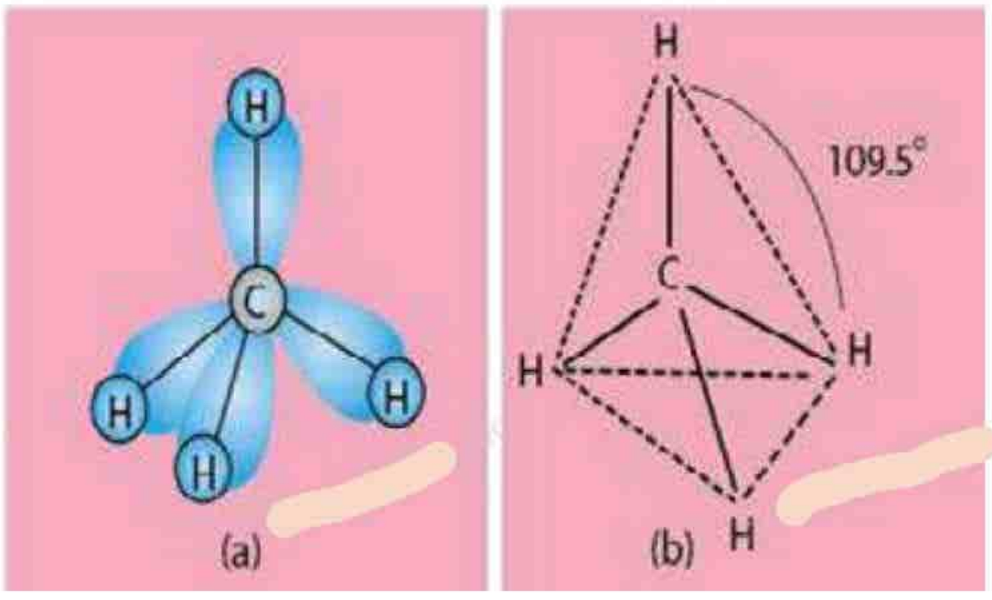
Geometry: Tetrahedral geometry with carbon at center.

Bond angles: Total six bond angles of 109.5°.

Total bonds: Four sigma bonds formed by the overlap of sp^3 hybrid orbitals of carbon with 1s orbitals of four hydrogen atoms.

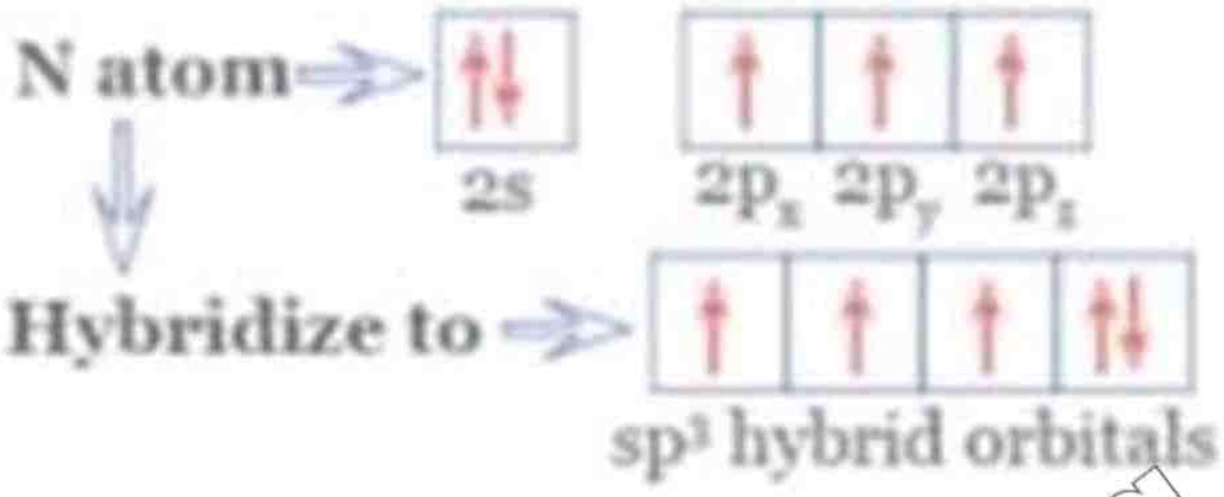
Arrangement of bonds: The four C-H bonds which result from sp^3-s overlap are directed towards the corners of a regular tetrahedron. All the four hydrogen atoms do not lie in the same plane.

Faces, corners, edges: The tetrahedral structure of CH_4 has four faces, four corners and six edges.



Structure of methane

Ammonia



Explanation of Structure of Ammonia

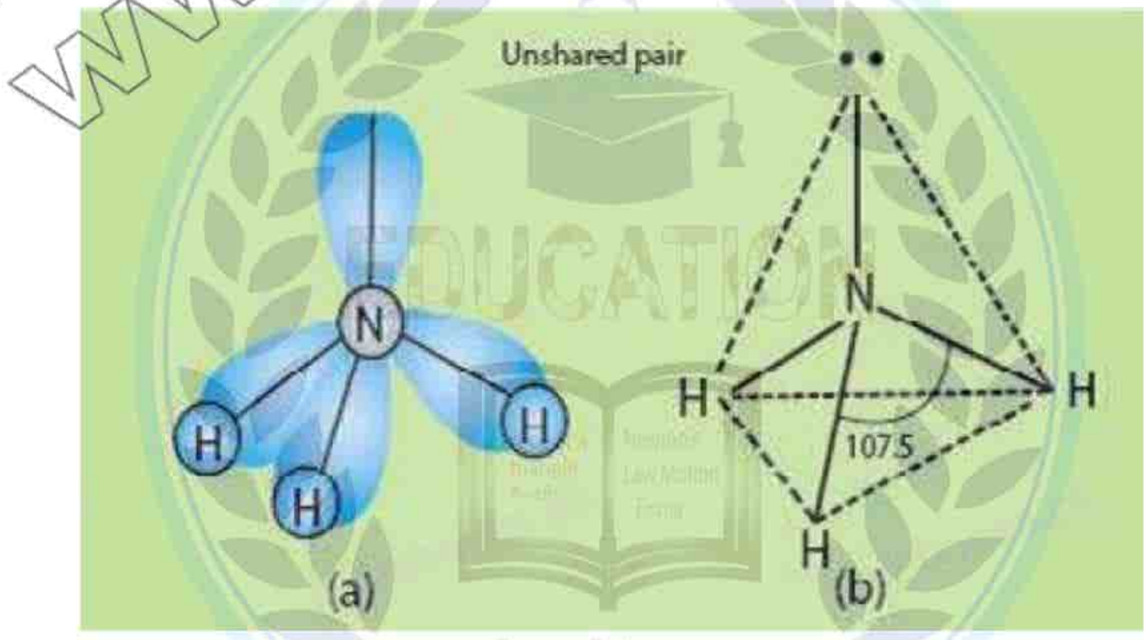
Hybrid orbitals: One s and three p orbitals of nitrogen atom hybridize to form four sp^3 hybrid atomic orbitals.

Overlap of orbitals: Three sp^3 orbitals overlap with three s-orbitals of hydrogen atoms.

Geometry: One corner of the tetrahedron is occupied by lone pair of electrons. The other three corners have single electron. Shape of ammonia is a pyramidal molecule due to repulsion of bond pairs by lone pair of electrons.

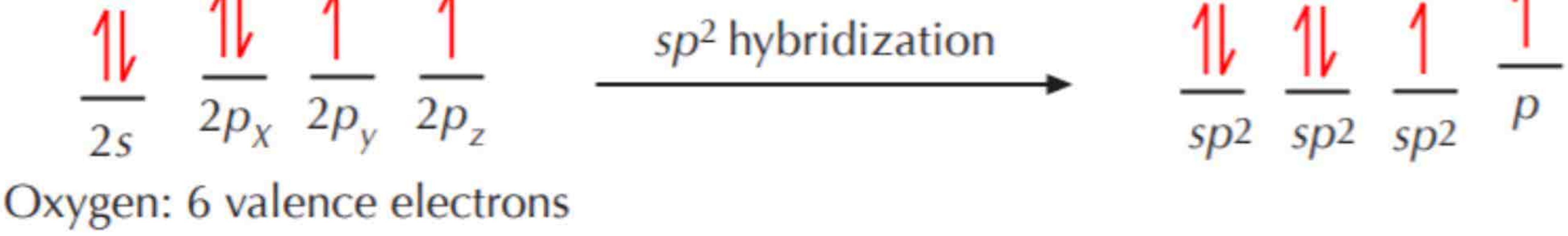
Total bonds: Three sigma bonds formed by sp^3-s orbital overlap.

Bond angle: The bond angle in ammonia is 107.5°.



Structure of ammonia

Water H_2O



Explanation of Structure of Water

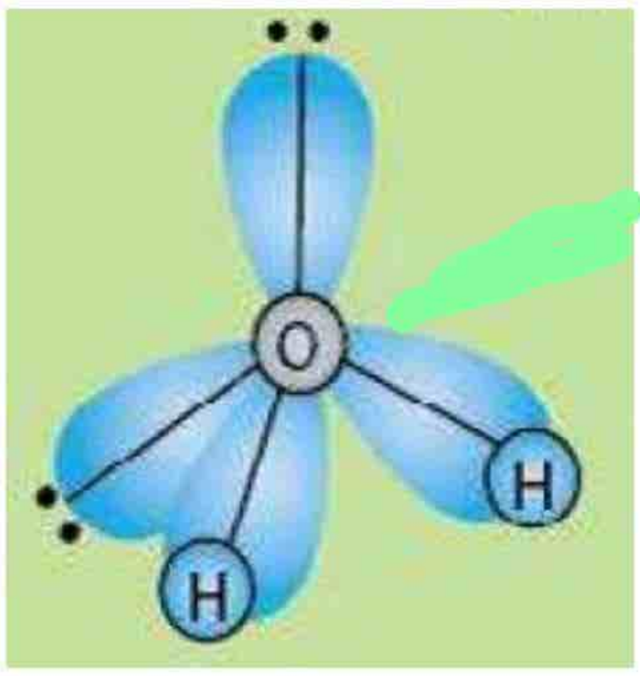
Hybrid orbitals: 2s and three 2p orbitals of oxygen hybridize to form four sp^3 hybrid orbitals.

Overlap of orbitals: The sp^3 orbitals overlap with s orbital of H atoms to form two sigma bonds.

Geometry: The hybrid orbitals will have a tetrahedral arrangement. The two corners of the tetrahedron are occupied by lone pair of electrons and the other two corners by single electron. The molecule of water has bent or angular structure (distorted tetrahedron) because of the repulsion of lone pairs on bond pairs.

Total bonds: Two sigma bonds formed by sp^3-s orbital overlap.

Bond angle: The bond angle in water is 104.5°.



Structure of water

sp^2 hybridization

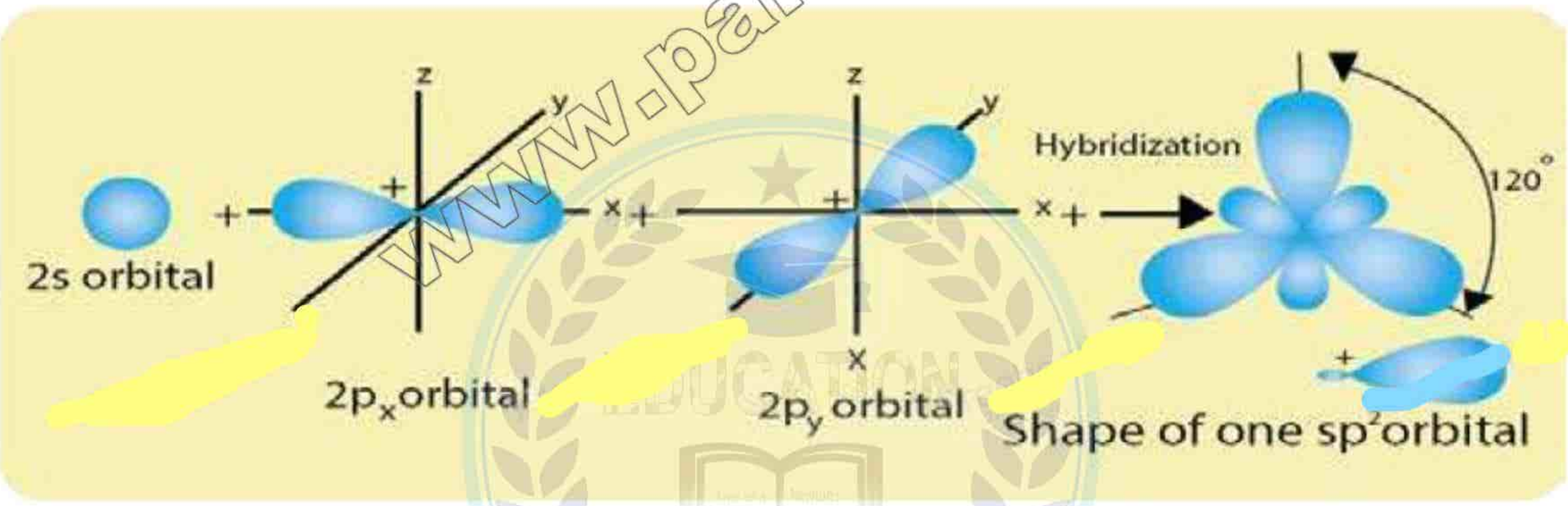
Definition

In sp^2 hybridization, one 's' and two 'p' atomic orbitals of an atom intermix three orbitals called sp^2 hybrid orbitals.

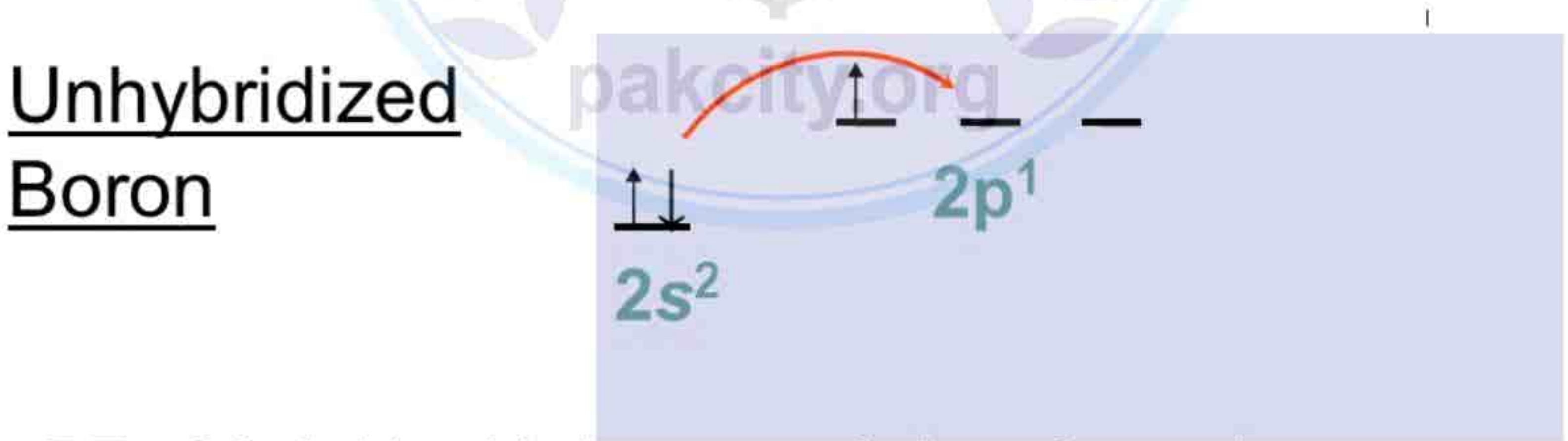
Examples

BF_3

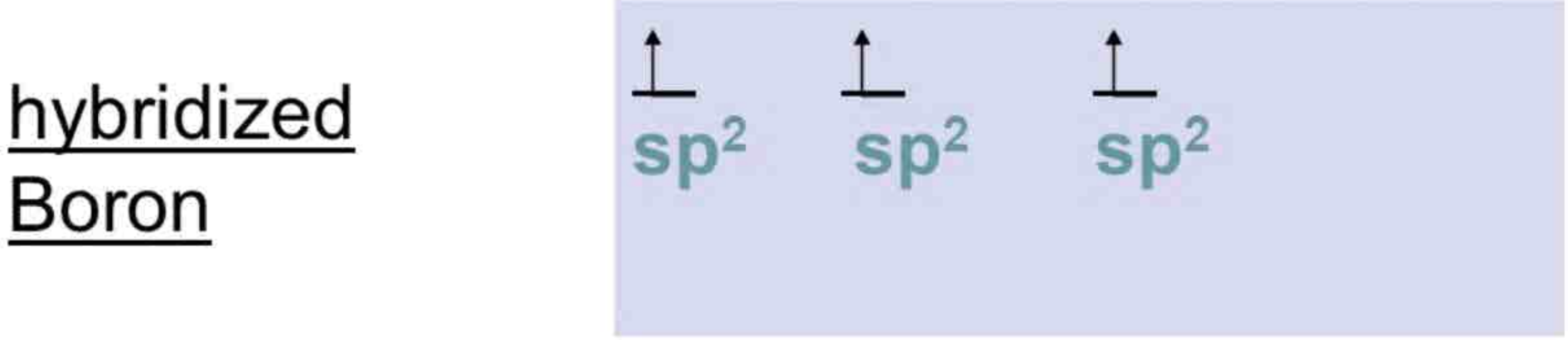
Ethene (ethylene)



Boron Trifluoride

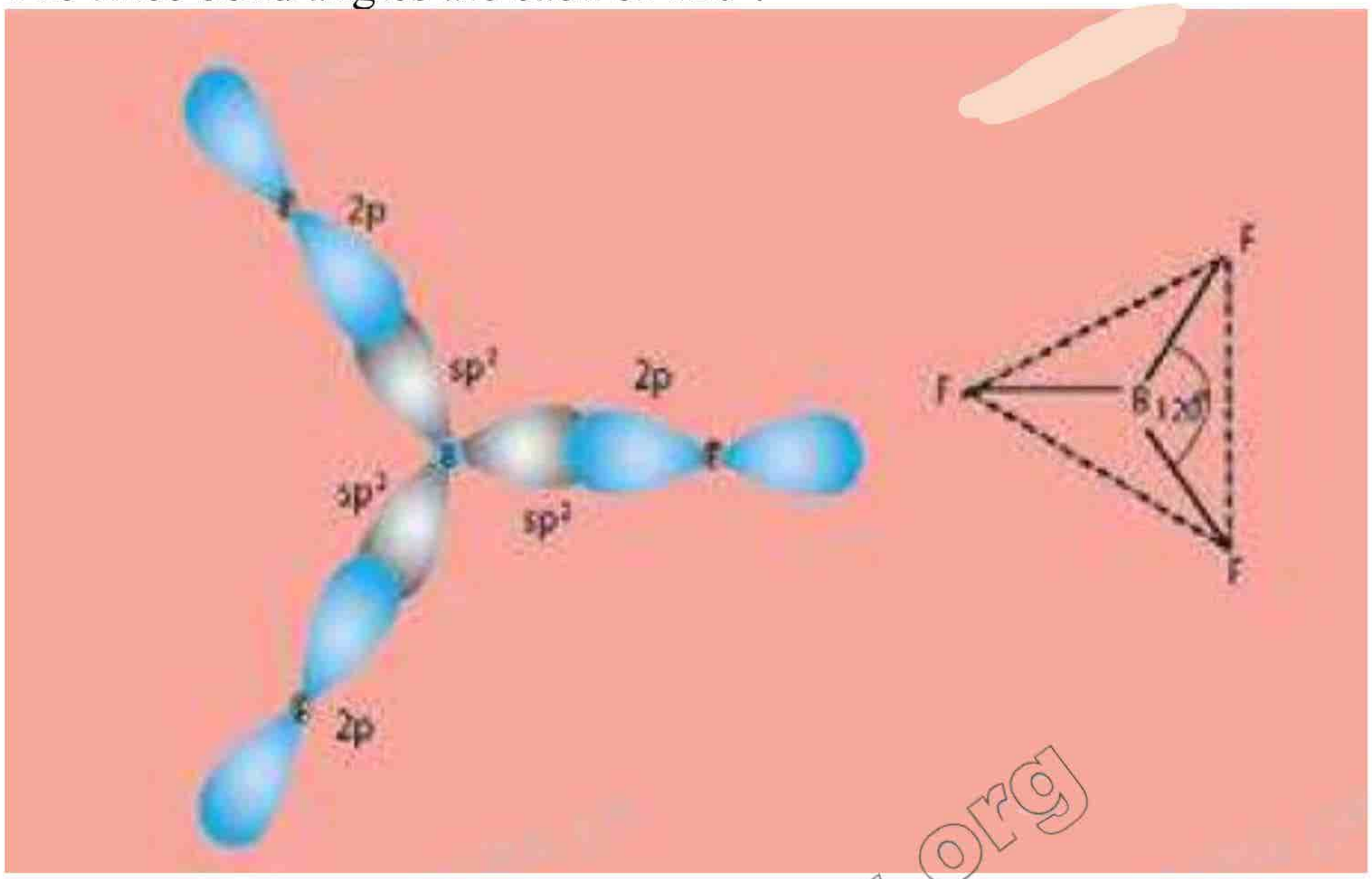


For BF_3, 3 hybrid orbitals are needed, so 3 atomic orbitals are required as follows: $(s + p + p) = sp^2$



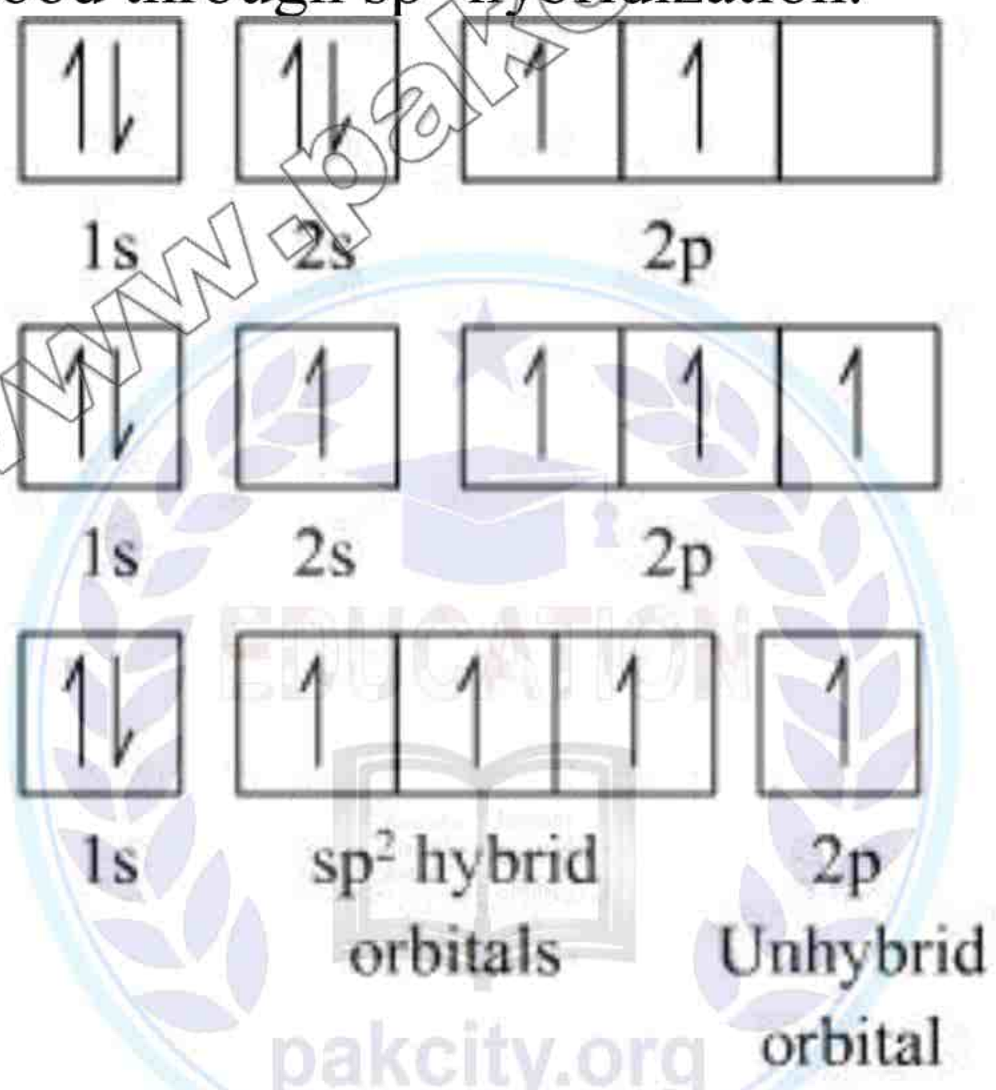
Explanation of Structure of BF_3

Hybrid orbitals: One s and two 2p atomic orbitals of boron overlap to form three sp^2 hybrid orbitals.
Overlap of orbitals: BF_3 is formed by the overlap of three half-filled sp^2 hybrid orbitals of boron with $2p_z$ orbitals of three fluorine atoms.
Geometry: The structure is triangular planar.
Total bonds: Three bonds formed by sp^2-$2p_z$ orbital overlap.
Bond angle: The three bond angles are each of 120°.



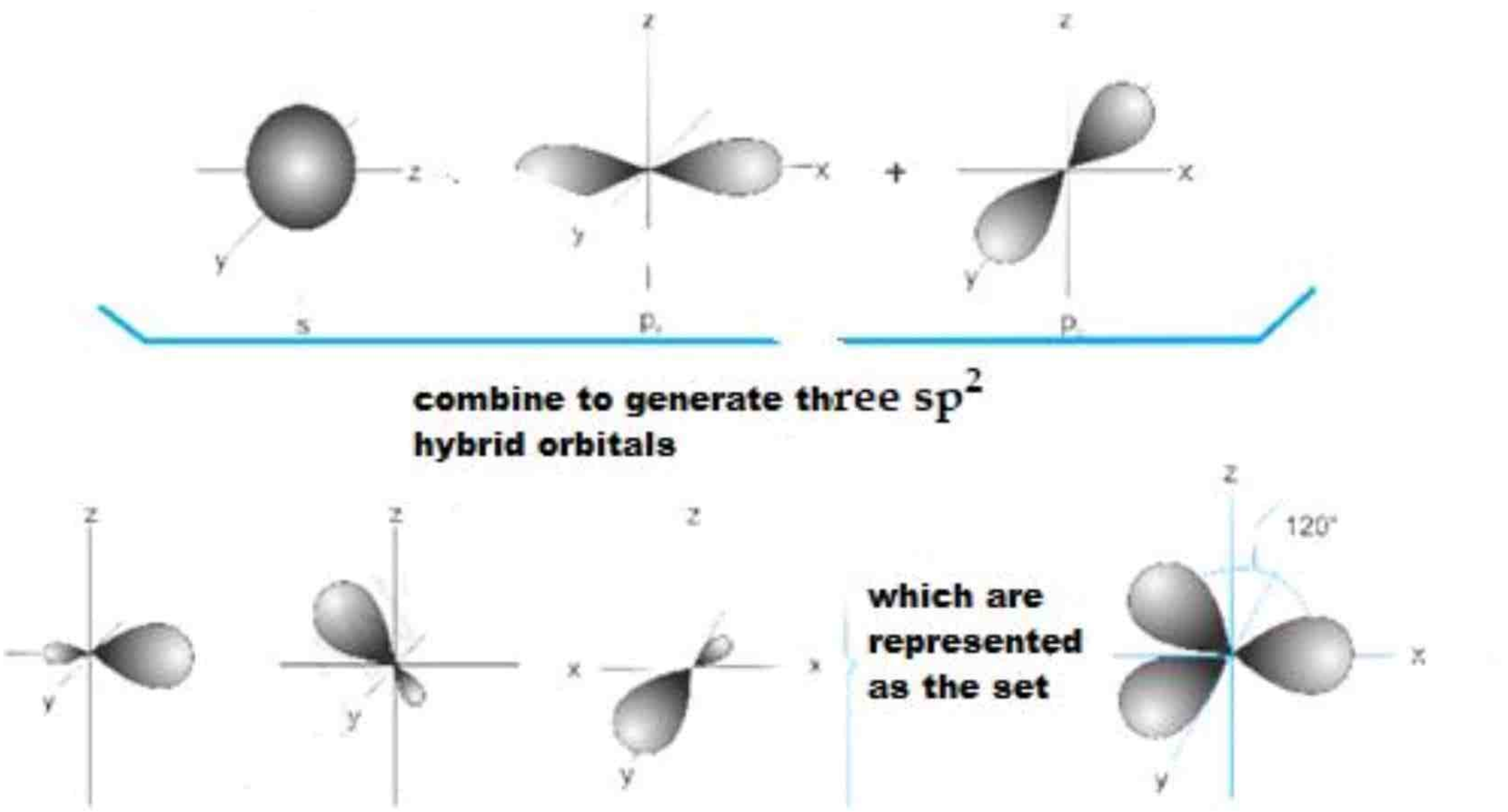
Ethene $H_2C=CH_2$ /Ethylene

The structure of alkenes can be understood through sp^2 hybridization.

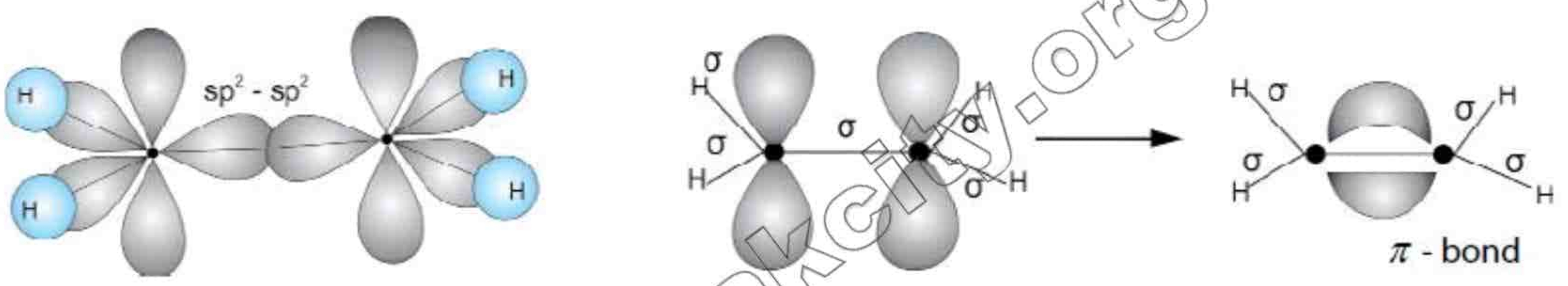


Explanation of Structure of ethene

Hybrid orbitals: Three sp^2 hybrid orbitals formed by one s and two 2p orbitals of carbon.
Unhybridized orbitals: The unhybridized $2p_z$ orbital will remain perpendicular to the hybridized orbitals.
Overlap of orbitals: sp^2 hybrid orbital of each carbon overlaps to give sp^2-sp^2 sigma bond and the other two sp^2 orbitals overlap with 1s orbitals of hydrogen to give sp^2-s sigma bonds. The unhybridized $2p_z$ orbitals overlap sideways to give a π-bond.
Geometry: Trigonal planar.
Bond angle: The bond angle between any two sp^2 hybrid orbitals is 120°.



Total bonds: One sp^2-sp^2 sigma bond and two sp^2-s sigma bonds. One $2p_z$-$2p_z$ π-bond.



Structure of ethene

sp Hybridization

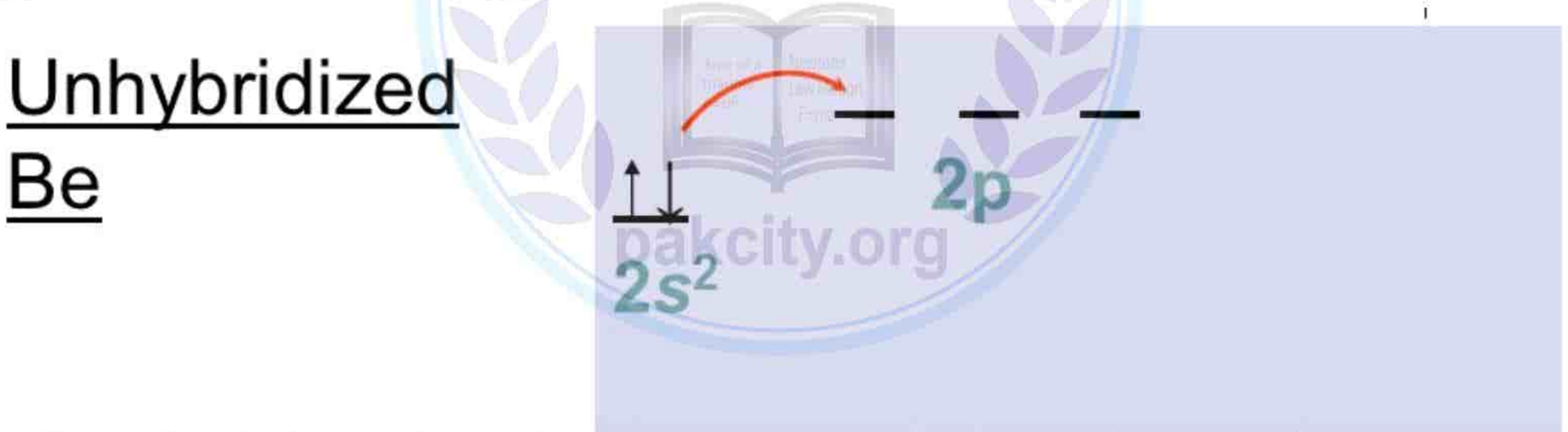
Definition

In sp hybridization, one ‘s’ and one ‘p’ orbitals intermix to form two sp-hybrid orbitals called sp hybrid orbitals.

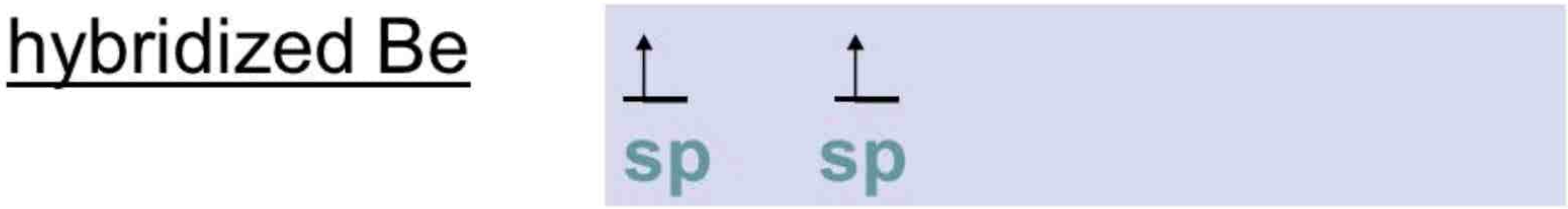
Examples

Ethylene, $BeCl_2$

Beryllium Dichloride



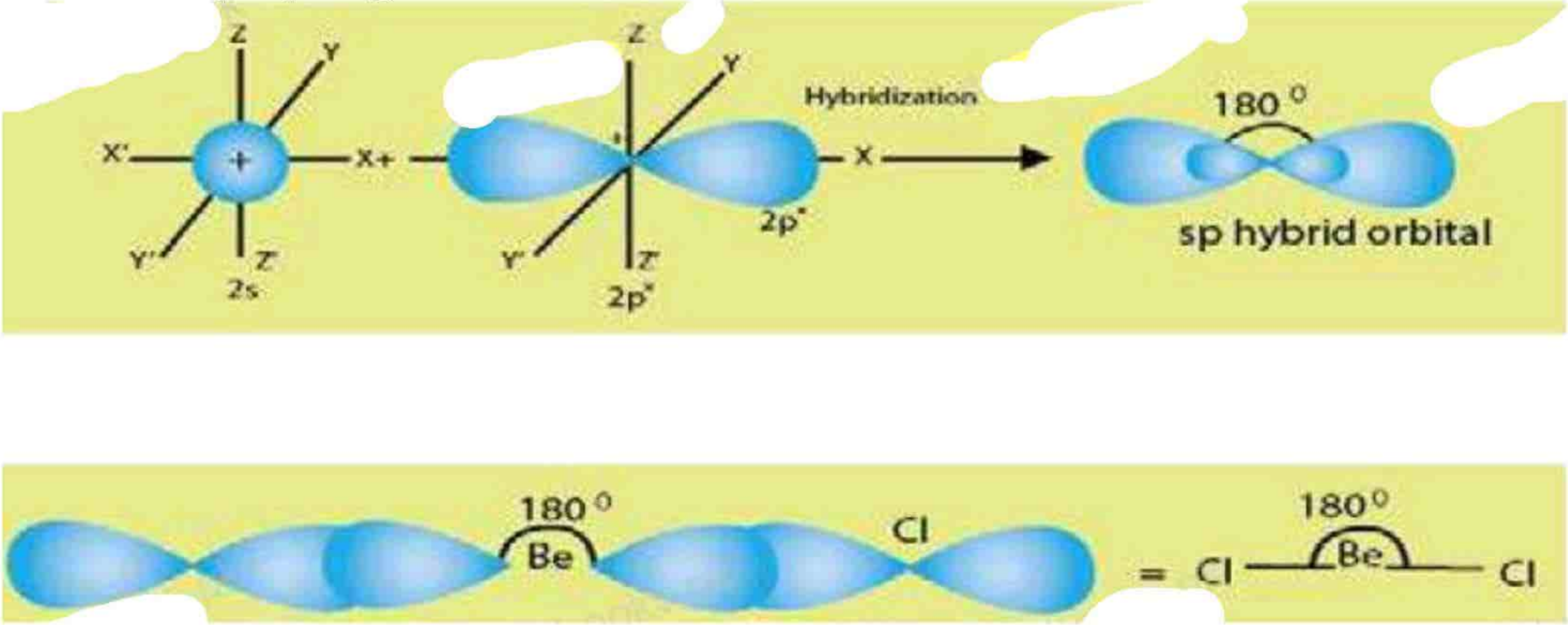
For $BeCl_2$, 2 hybrid orbitals are needed, so 2 atomic orbitals are required as follows: (s + p) = sp



Explanation of Structure of $BeCl_2$

- **Hybrid orbitals:** One s and one p orbital of Be overlap to give two sp hybrid orbitals.

- **Overlap of orbitals:** Two sp hybrid orbitals of Be atom overlap with the half-filled $3p_z$-orbitals of chlorine atoms.
- **Geometry:** Linear shape.
- **Total bonds:** Two sp-$3p_z$ sigma bonds.



Structure of Beryllium dichloride

- **Bond angle:** The Cl-Be-Cl bond angle is 180°.

Ethyne ($HC\equiv CH$) Acetylene

Hybrid orbitals: One 2s and one 2p orbitals of the carbon atom mix together to give rise to two degenerate sp hybridized atomic orbitals.

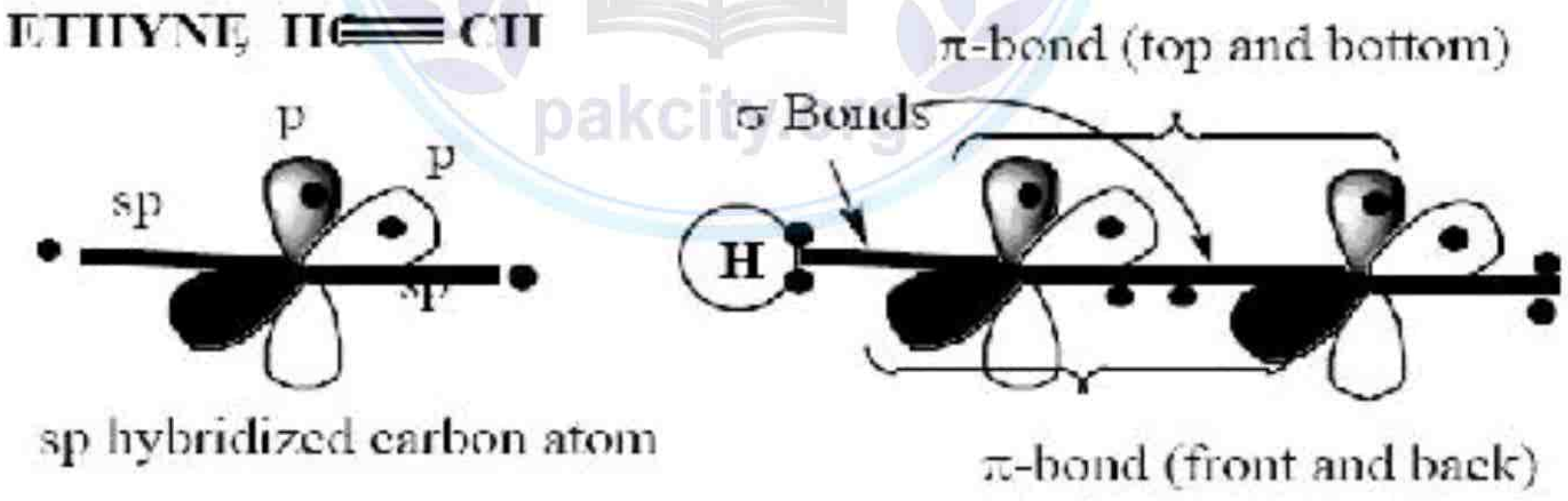
Unhybridized orbitals: The unhybridized 2py and 2pz orbitals are perpendicular to the hybridized orbitals.

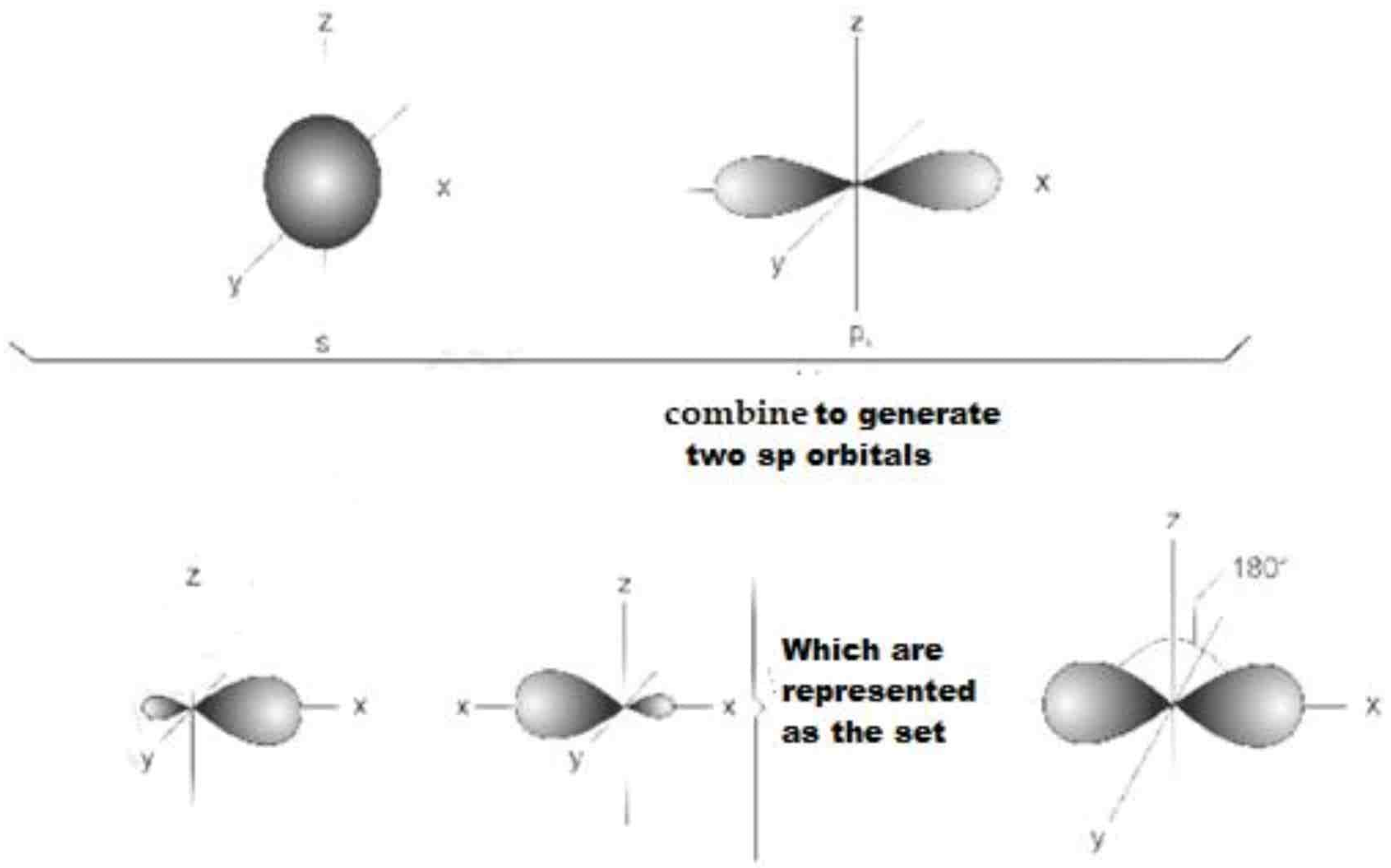
Overlap of orbitals: Two sp hybridized carbon atoms join together to form a sigma bond by sp-sp overlap. The other sp orbital forms a sigma bond with 1s orbital of hydrogen atom. The two unhybridized p orbitals on each carbon atom overlap sideways give two π -bonds.

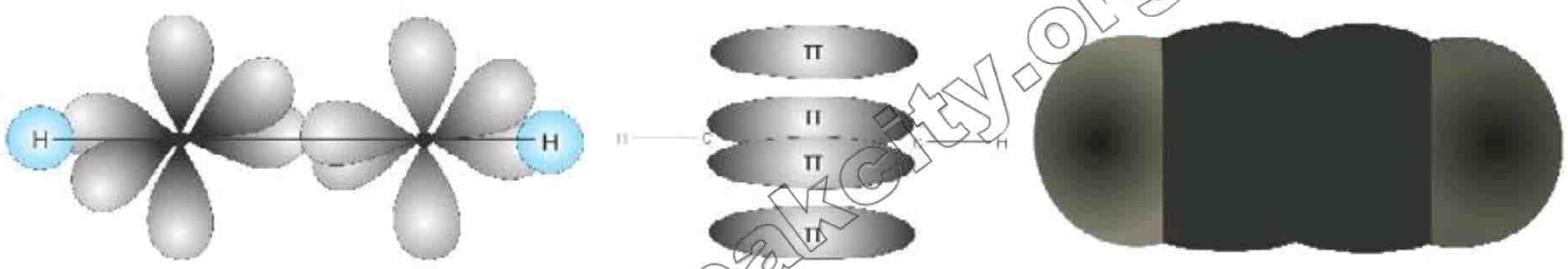
Geometry: Linear shape.

Total bonds: One sp-sp sigma bond and two sp-s sigma bonds. Two, $2p_y$-$2p_y$ and $2p_z$-$2p_z$, π-bonds.

Bond angles: These orbitals have a bond angle of 180°.





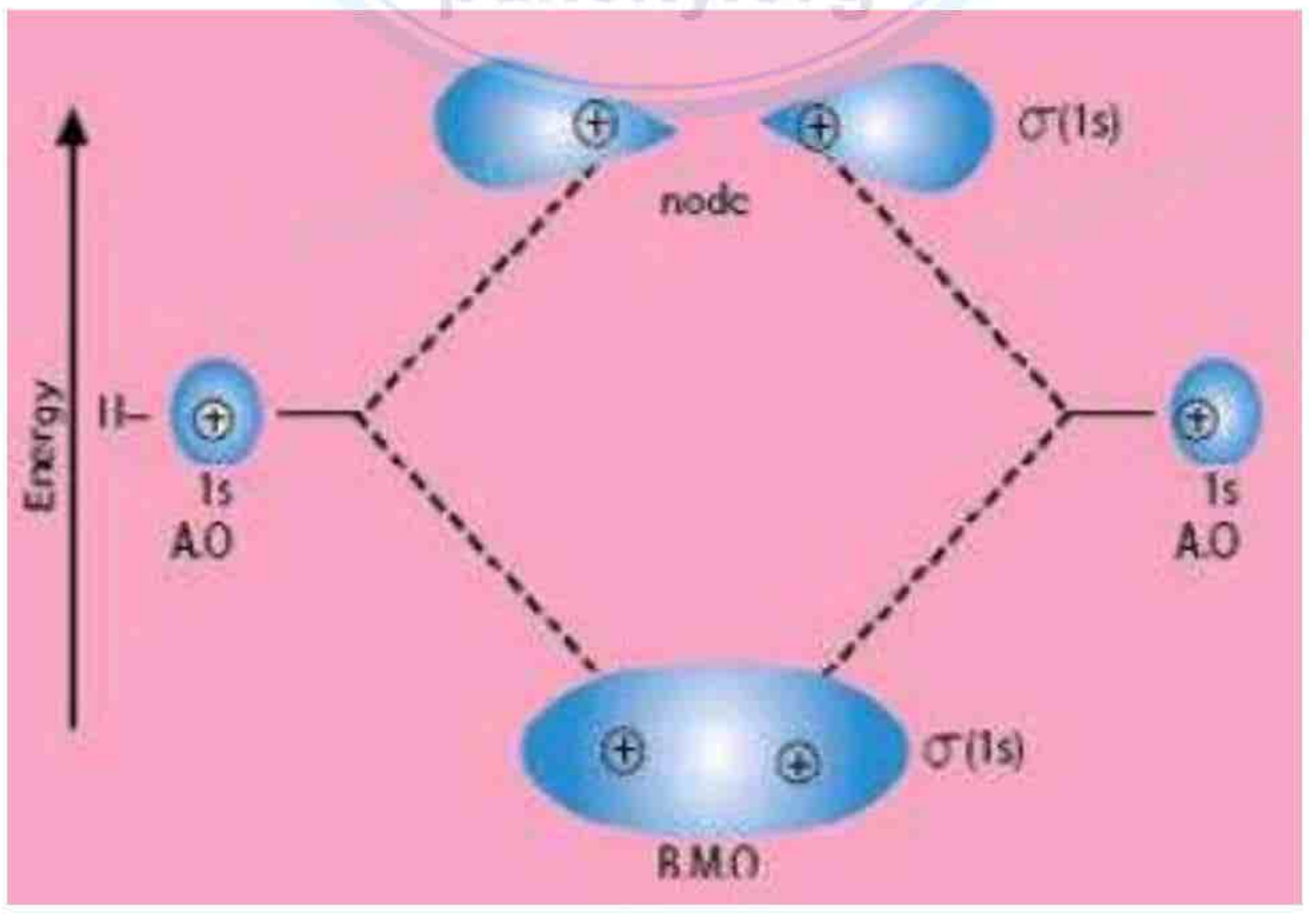


Formation of σbonds Formation of π bonds Space filling model

Molecular Orbital Theory

Postulates

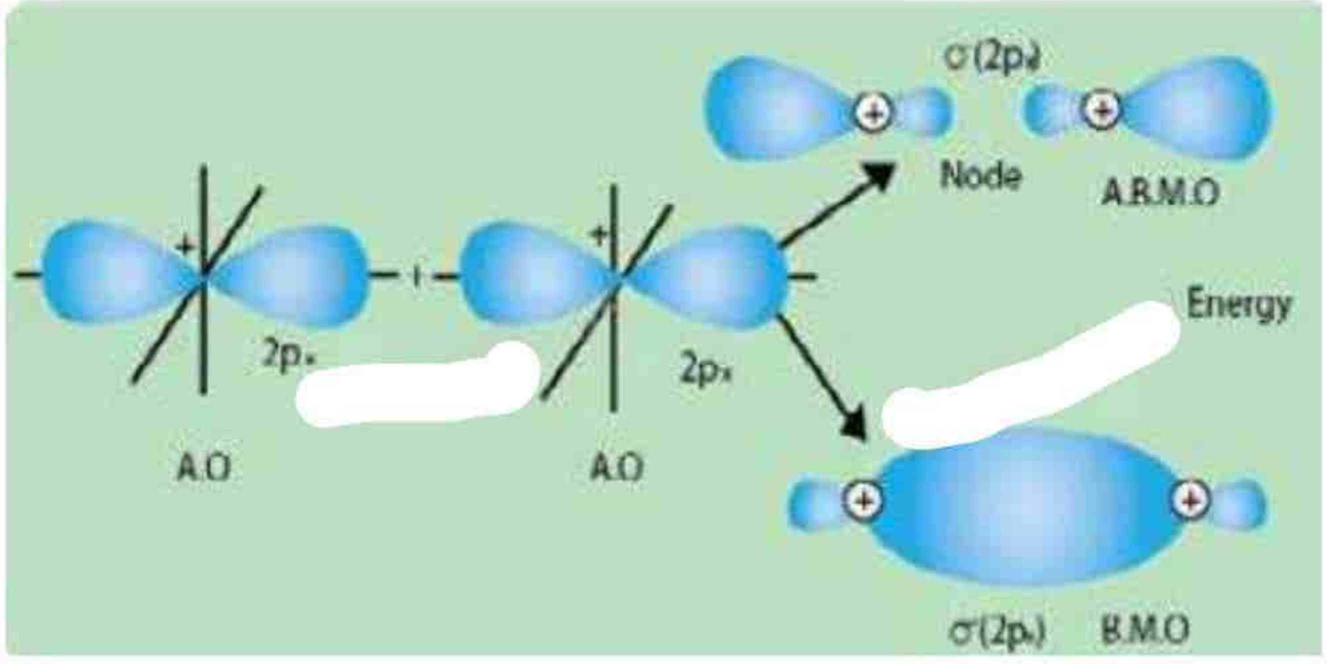
1. It considers the whole molecule as a single unit.
2. It assumes that the atomic orbitals of the combining atoms overlap to form new orbitals called molecular orbitals which are characteristic of the whole molecule.
3. Two atomic orbitals, after overlapping, form two molecular orbitals which differ in energy. One of them, having lower energy, is called bonding molecular orbital while the other having higher energy is called anti-bonding molecular orbital.



4. The bonding molecular orbital is symmetrical about the axis joining the nuclei of the bonded atoms (molecular axis). It is designated as sigma (σ) bonding molecular orbital while the antibonding molecular orbital, is called σ^*.
5. The filling of electrons into the molecular orbitals takes place according to the Aufbau principle, Pauli's exclusion principle and Hund's rule.
6. Overalapping of orbitals occurs in two ways:

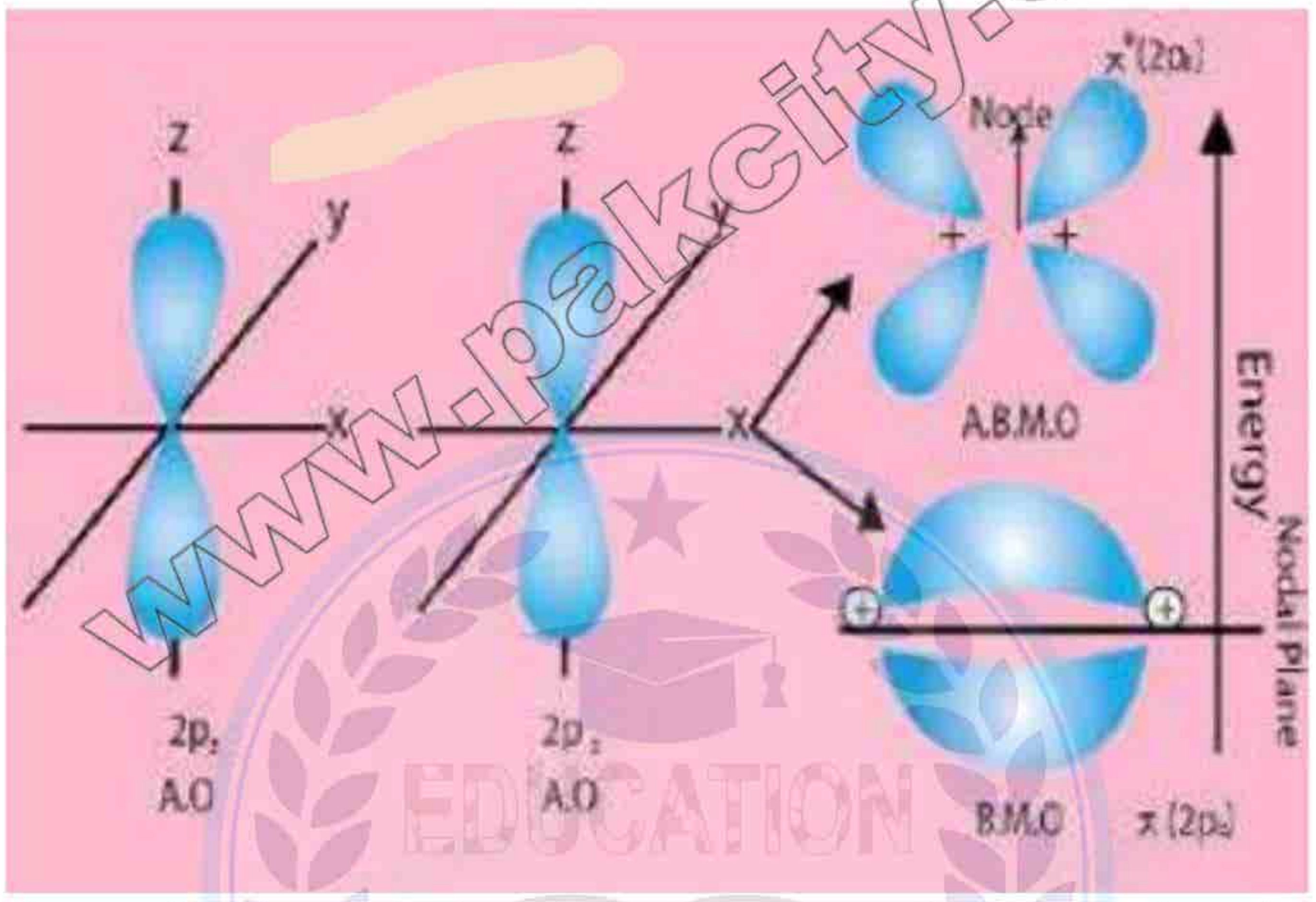
(a) Head on Approach

The p-orbitals of the two atoms approach along the same axis (i.e. p_x axis). This combination of the atomic orbitals gives rise to σ (2px) bonding and σ^* (2px) anti-bonding molecular orbitals. Both are symmetrical about the nuclear axis.



(b) Sideways Approach

When the axes of two p-orbitals (i.e p_y or p_z orbitals) are parallel to each other, they interact to form molecular orbitals.

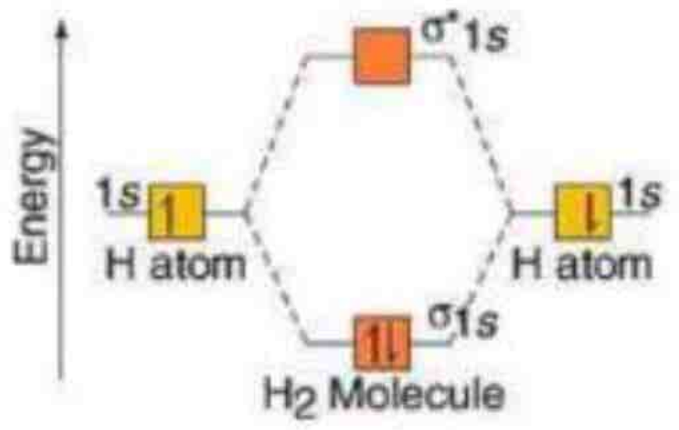


7. The bonding molecular orbitals π ($2p_y$) or π ($2p_z$) have zero electron density on the nuclear axis (called the nodal plane). The electron density is uniformly distributed above and below the nodal plane.
8. The anti-bonding molecular orbitals π^* ($2p_y$) and π^* ($2p_z$) have the least electron density in the π inter-nuclear region. Since the 2py and 2pz atomic orbitals are degenerate, the p molecular orbitals i.e. π (2py) and π (2pz) are also degenerate. So, are also the π^*(2py) and π^*(2pz) molecular orbitals.
9. Overall six molecular orbitals (three bonding and three anti-bonding) are formed from two sets of 2p atomic orbitals.
10. The bond formed as a result of linear overlap is σ bond, while that formed as a result of sideways overlap is called a p (pi) bond.
11. There are three bonding molecular orbitals, the p-orbitals overlap can lead to the formation of at the most three bonds: one sigma and two π-bonds.
12. The number of bonds formed between two atoms after the atomic orbitals overlap is called the bond order and is taken as half of the difference between the number of bonding electrons and anti-bonding electrons.

$$\text{Bond order} = \frac{\text{No. of electrons in the B.M.O} - \text{No. of electrons in the A.B.M.O}}{2}$$

MOT Diagram of Hydrogen Molecule

Bond order $= \frac{2-0}{2} = 1$



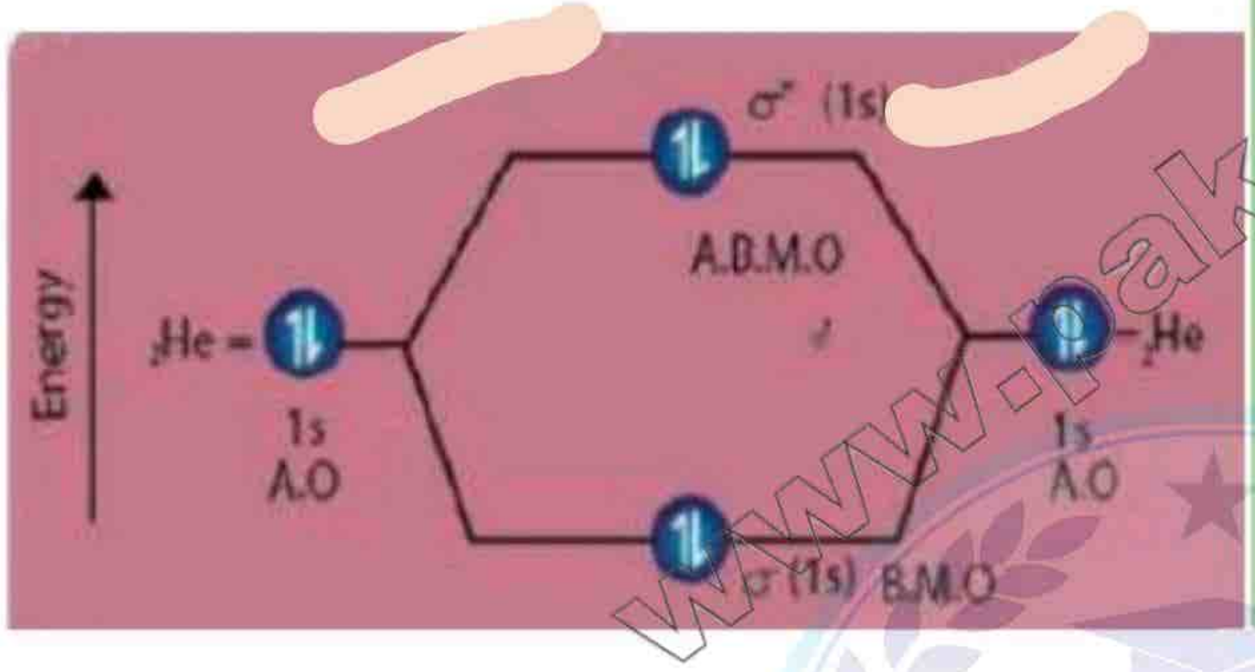
MOT Diagram of He, N_2 and O_2

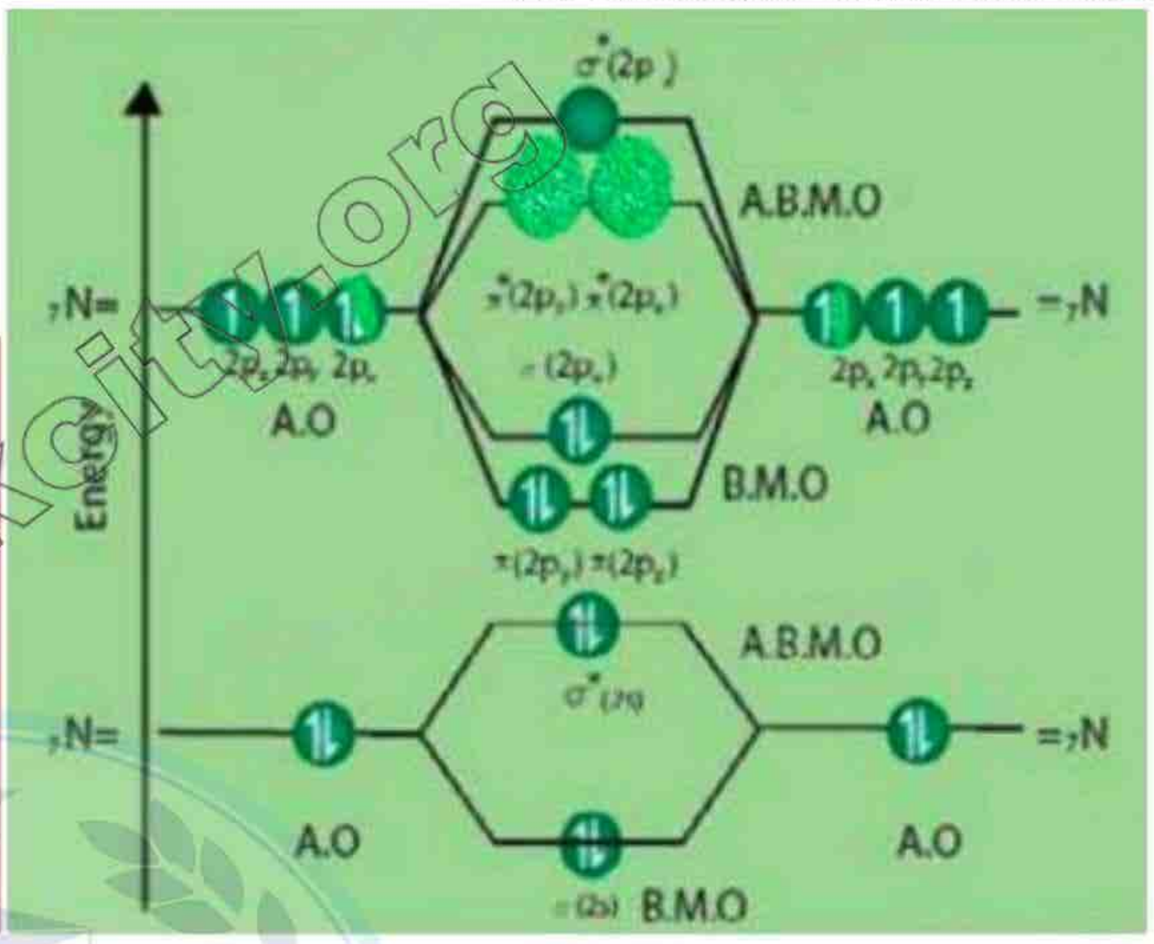
Helium

Nitrogen (diamagnetic, repelled by the magnetic field)

Triple bond :one sigma and two π bonds.
The bond dissociation energy=941kJmol^{-1}.
Six electrons enter into three outermost bonding orbitals.
No electrons enter into anti-bonding orbitals.

$\frac{2-2}{2} = 0$

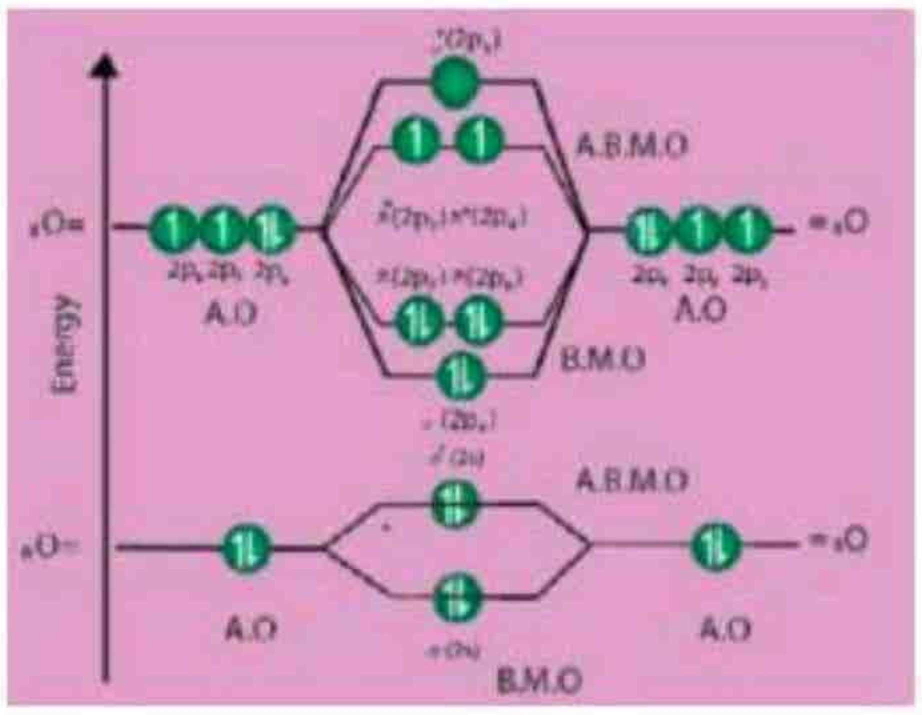




$\sigma(1s^2)<\sigma^*(1s^2)<\sigma(2s^2)<\sigma^*(2s^2)<\pi(2p^2{}_y)=\pi(2p^2{}_z)<\sigma(2p^2{}_x)<\pi^*(2p_y)=\pi^*(2p_z)<\sigma^*(2p_x)$

$\frac{6-0}{2}=\frac{6}{2}=3$

Oxygen (paramagnetic gets attracted by magnetic field in liquid state)



$$\sigma(1s)^2 < \sigma^*(1s)^2 < \sigma(2s)^2 < \sigma^*(2s)^2 < \sigma(2p_x) < \pi(2p_y)^2 = \pi(2p_z)^2 < \pi^*(2p_y)^1 = \pi_z^*(2p_z)^1 < \sigma^* 2p_x$$

$$\text{Bond order} = \frac{6-2}{2} = 2$$

It corresponds to a double bond.
This is consistent with the large bond energy of 496kJ mol^{-1} of oxygen molecule.

Dipole Moment

Definition

The dipole moment (μ) is defined as the product of the electric charge (q) and the distance between the positive and negative centres (r).

Formula Applied

$$\mu = q \times r$$

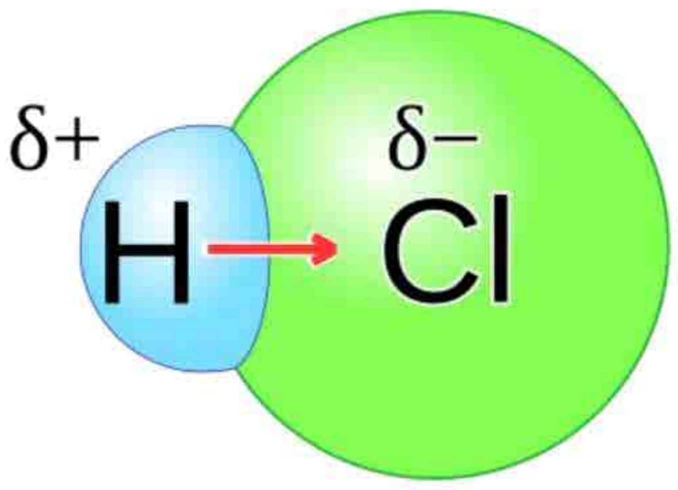
Vector quantity

The dipole moment is a vector quantity which has a magnitude as well as a direction.

Example

In HCl the molecule becomes polar due to the electronegativity difference.

The separation of positive and negative charges on the molecule is called a dipole and the molecule is said to have a dipole moment.



The dipole moments of HF, HCl, HBr. HI, CO, NO, etc. are directed from electropositive ends to electronegative ends.

Units

The dipole moments are measured in Debye (D) units.

Measurement of Dipole Moment

Let us consider a hypothetical molecule (A^*—B^-), or a unit negative charge separated from a unit positive charge by distance r = 100 pm (1 Å).

The dipole moment of such a molecule can be calculated by multiplying the distance 100pm to charge of one electron or proton.

$$\mathbf{1.6\ x10^{-19}C\ m = (1.6022x10^{-19}C)\ x\ (100x10^{-12}m) = 1.6022x10^{-29}\ mC}$$

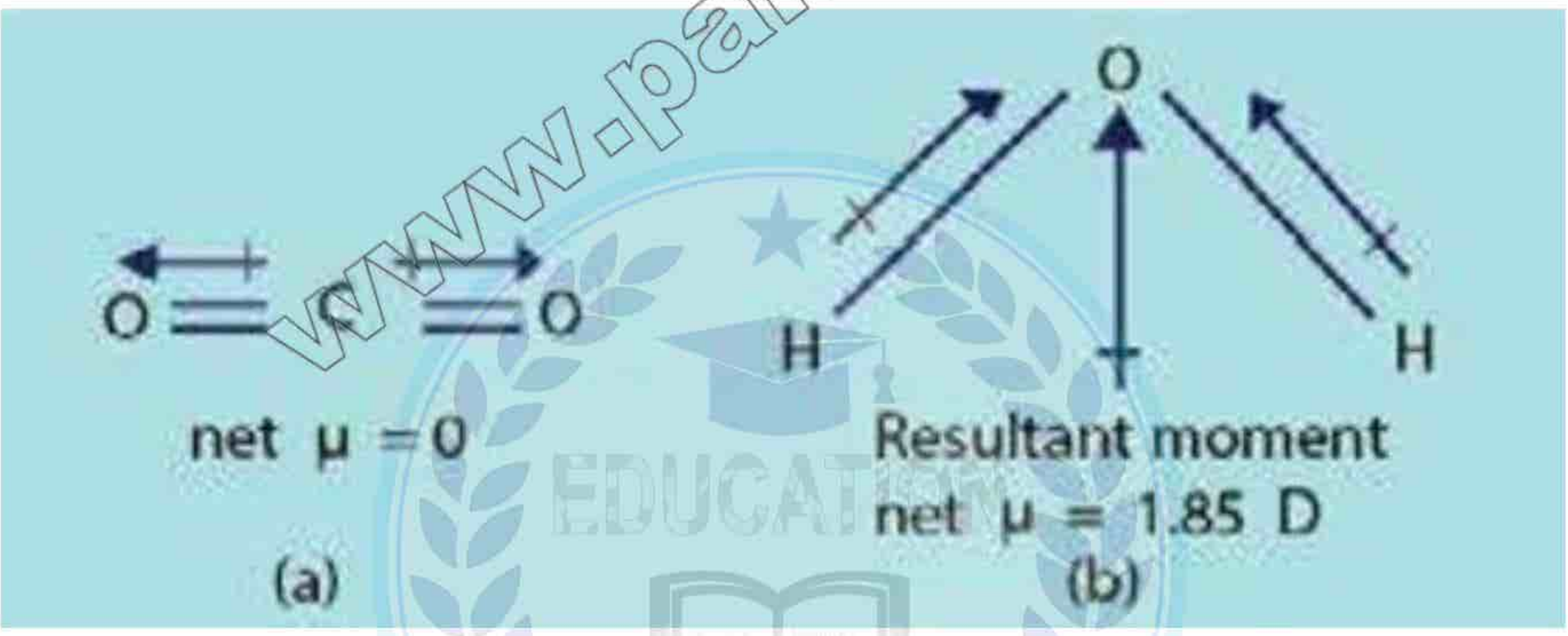
Another unit of dipole moment is Debye. The equivalence of Debye and mC is 1 D = $3.336x10^{-30}$mC. So, the dipole moment of the above system in Debye units is:

$$= \frac{1.6022\,x\,10^{-29}mC}{3.336x\,10^{-30}mC} = 4.8\ D$$

If the molecule is polyatomic and contains two or more dipoles, then the net dipole moment is the resultant of the vector addition of the individual bond moments.

Examples

Examples of CO_2 and H_2O are:



Dipole Moments and Molecular Structures

Information about the molecular structure

Dipole moment provides two types of information about the molecular structure:

(i) Percentage ionic character of a bond

(ii) Angles between the bonds or the geometry of molecules

(1) Percentage ionic character

For this purpose, we should know the actual dipole moment μ_{obs} of the molecule and actual bond length. The dipole moment of 100% ionic compound is represented as μ_{ionic}.

$$\%\text{age of ionic character} = \frac{\mu_{obs}}{\mu_{ionic}} x100$$

(2) Bond Angles or the Geometry of Molecules

Dipole moment of water

The dipole moment of water is 1.85 D which **ruled out its linear structure**.

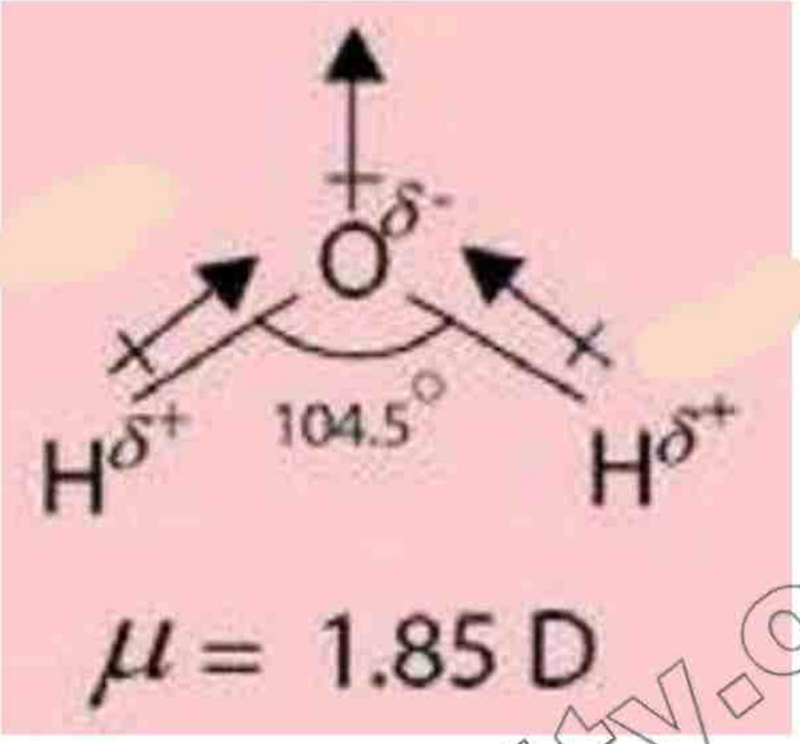
The calculations show that water has an angular structure with a bond angle 104.5° between the two O-H bonds.

A linear H_2O molecule (H-O-H) would have **zero dipole moment**.

Other examples

H_2S and SO_2

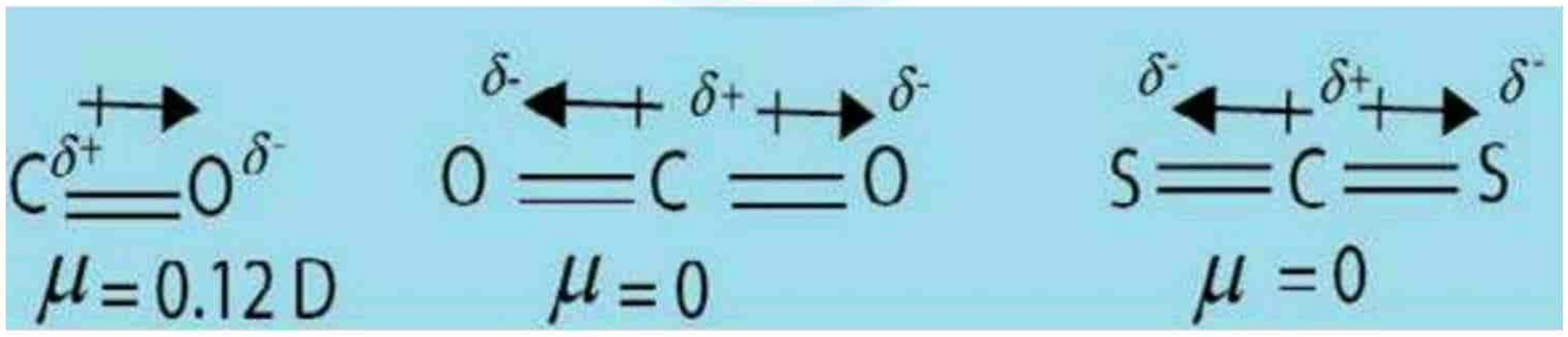
The triatomic molecules H_2S or SO_2 etc. are also bent like H_2O.



CO, CO_2 and CS_2

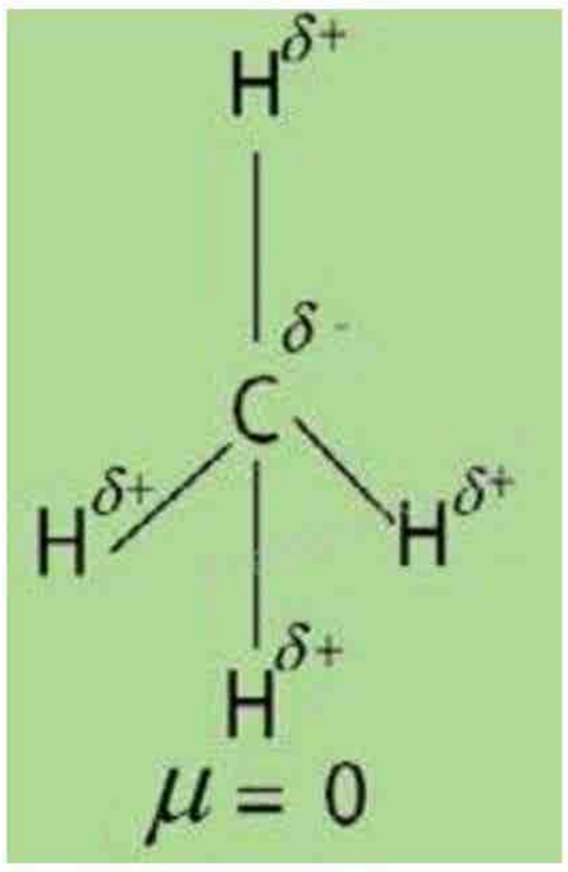
CO has a dipole moment while CO_2 does not have any.

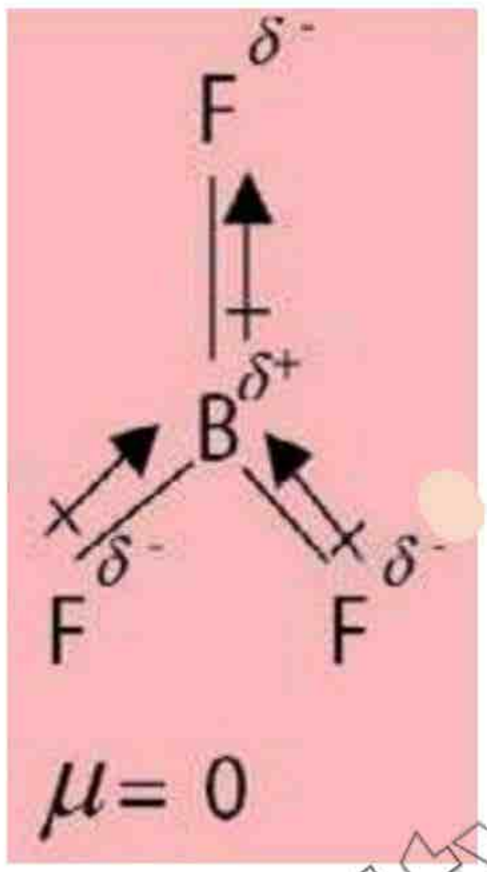
The reason is that CO_2 has **a linear structure**, where the dipoles being equal and opposite, cancel out each other's effect. Similarly, CS_2 has **zero dipole moment**.



BF_3, $AlCl_3$, CH_4, SiH_4 and CCl_4

Symmetrical triangular planar molecules of BF_3, $AlCl_3$ and perfectly tetrahedral molecules like CH_4, SiH_4, CCl_4 also **have zero dipole moments**.





This is all due to the cancellation of individual bond moments.

Important long questions from past papers

1. Write note on ionic bond OR covalent bond OR coordinate covalent bond.
2. Write the main postulates of VSEPR theory and explain the structure of Ammonia on the basis of this theory.
3. Explain sp hybridization.
4. Explain sp^3hybridization.
5. What is sp^2 hybridization.
6. Explain the molecular orbital structure of N_2 and O_2 molecules on the basis of MOT.
7. Explain important points of Molecular orbital theory.
8. Define ionization energy. Write factors affecting it and trends in the periodic table.
9. Define electron affinity. Name the factors affecting it and trends in the periodic table.
10. Discuss the valence bond theory. How are the sigma and pi bonds formed?
11. Define dipole moment. Give its units. How is it used to determine the geometry of molecule? Give an example.