A. $MgCl_2$ B. KCl C. CaF_2 D. LiF

Solution: Lattice energy increases with decreasing ionic radii and increases with increasing ionic charge. Since F has smaller ionic radius than Cl and Ca has equal charge (+2) with magnesium, CaF_2 has the highest ionic radii.

Answer: C

8. The correct Lewis structure for Ca_3P_2 is:

A. $Ca_3^{2+}\ [\cdot\ddot{P}\cdot]_2^{3-}$ C. $Ca_2^{3+}\ [\cdot\ddot{P}\cdot]_3^{2-}$

B. $Ca :: P$ D. 3[Ca] 2[$\cdot\ddot{P}\cdot$]

Solution: To attain octet each calcium atom has to lose 2 electrons and each phosphorus atom has to get three electrons

$$3Ca :: + \ 2\cdot\ddot{P}\cdot \longrightarrow Ca_3^{2+}\ [:\ddot{P}:]_2^{3-}$$

Answer: A

3.3 Covalent Bonding

- A covalent bond is a type of bond formed by sharing one or more pairs of electrons between two atoms.
- The covalent bond is the result of the electrostatic attraction between the nuclei of bonding atoms and the electrons shared between them.

1. Lewis structures of covalent bonds

- To draw the Lewis structures of covalent compounds containing any kind of bonds correctly, there following the rules that are given below is very helpful.

i. Predict the skeleton structure

To determine the skeleton structure, follow the guidelines given below.

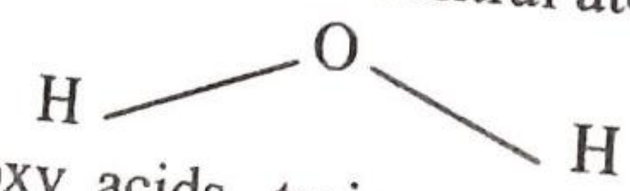
a) The central atom is often the most electro positive element.

Example: C is the central atom in CH_4

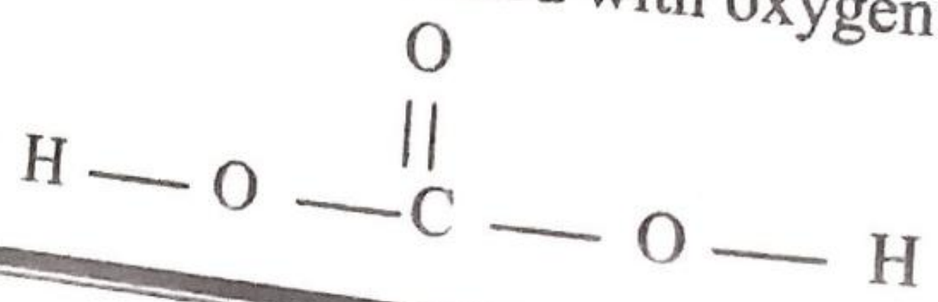
P is the central atom in $POCl_3$

b) Hydrogen atoms always occupy terminal position

Example: O is the central atom in H_2O



c) In oxy acids, terinary acids which contain oxygen, hydrogen atoms are often bonded with oxygen: Example- H_2CO_3



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d) In compounds that have symmetrical formula, it has symmetrical structure. Example hydrogen peroxide H_2O_2

H — O — O — H

e) In a simple binary molecules or poly atomic ions, the central atom usually comes first.

Example – the central atom in NH_4^+ is N and in PO_4^{3-} is P

ii. Determine the total number of valance electrons.

❖ The total valance electron of a molecule can be obtained by adding the valance electrons of each atom.

Example: The total valance electron of CCl_4 is 32, because the valance electron of chlorine atom is 7 and carbon is 4.

4x7+4= 32 e'n

❖ To calculate the total valance electron of poly atomic ions, it is a must to subtract one electron for each positive charge and add one electron for each negative charge.

Example $a)PO_4^{3-}$

Total valence electron = Ve'n of P + 4(ve'n of 0) +3

= 5 + 4 (6) + 3 = 32 e'n

b)NH_4^+

Total valence electron = Ve'n of N + 4(Ve'n of H) -1

= 5 + 4 – 1 = 8 e'n

iii. Make single bond between the central and the terminal atoms.

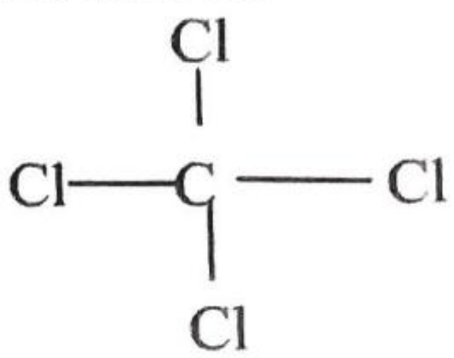
iv. Subtract the bonding electrons from the total valance electrons and distribute them as lone pars around the terminal atoms.

v. Assign any remaining electron as lone pairs around the central atom

vi. If the central atom do not attain octet, use multiple bonds until it attains octet. i.e. During the formation of multiple bond, lone pair electrons should be removed from the terminal atom which forms multiple bond with the central atom.

9. Draw the Lewis structure of CCl_4

i) The central atom is carbon

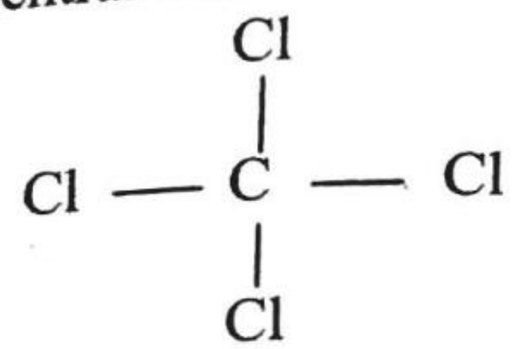


ii) Calculating total valance electron

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$T_{ve'n}$ = Ve'n C + 4 (Valence e'n of Cl)
= 6 + 4 (7) = 32 e'n

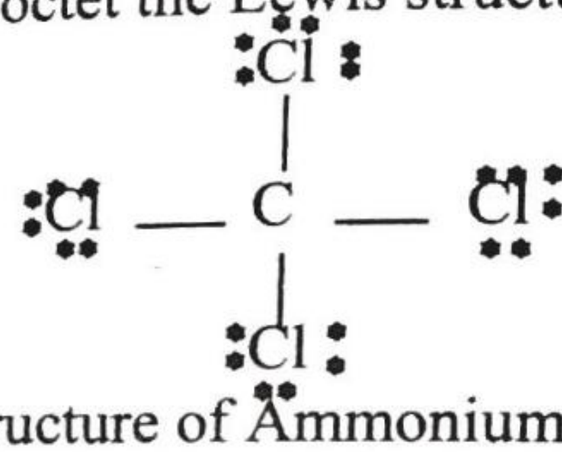
iii) Subtracting the lone pair electrons after forming single bond between the central and terminal atoms.



Lone electrons = 32 – 8 = 24e'n

$\frac{24}{4}$ = 6e'n ⇨ each chlorine atom can get 6 electrons

iv) Since there is no remaining lone pair electrons and the central atom attains octet the Lewis structure of CCl_4 will be

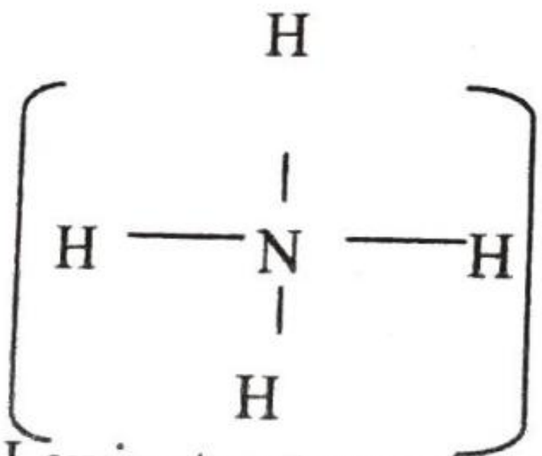


10. Draw the Lewis structure of Ammonium ion, NH_4^+

Valance electron of N is 5 and H is 1

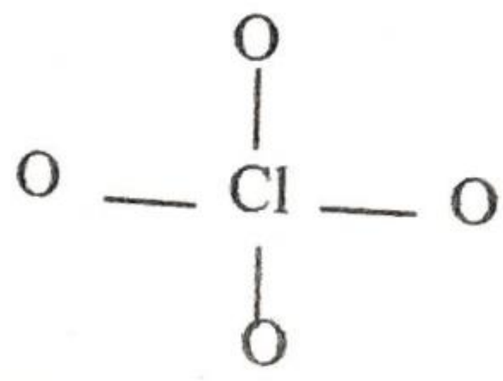
$T_{ve'n}$ = 5+4 (1) -1 = 8e'n

The central atom is N. Therefore the Lewis structure of NH_4^+ is



11. Draw the Lewis structure of Per chlorate ion, ClO_4^-

- The valance electron of Cl is 7 and O is 6
  $T_{ve'n}$ = 7 + 4 (6) +1 = 32e'n
- The central atom is Cl

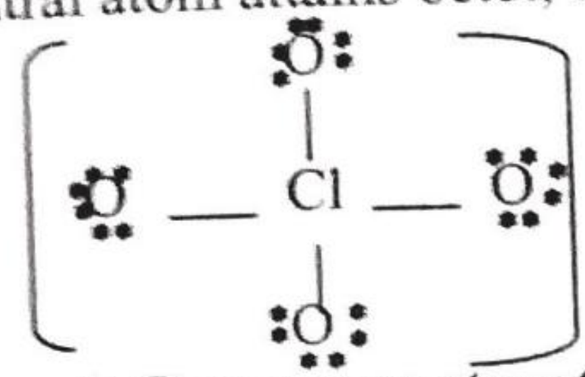


- The lone electrons are 32-8 = 24e'ns

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$\frac{24}{4}$ = 6e`ns for each oxygen atom.

- Since the central atom attains octet, the Lewis structure of is:

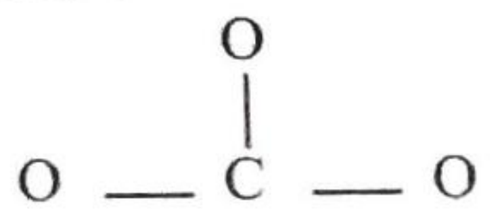


2. Resonance structures

Resonance Structures–are different bonding arrangements for the same molecule. Each structure in the resonance is known as resonance hybrids. There are some important points about resonance structure. These are:

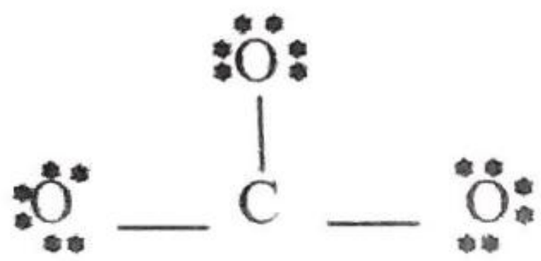
- ☞ The double bonds are delocalized or the electrons never belong to a single atom.
- ☞ They differ only in the positions of their electron pairs.
- ☞ Double–headed arrows are usually used to show bond delocalization over two or more positions.
- ☞ Double-headed arrows does not mean the molecule changes back and forth from one structure to the other but it means the actual structure of the molecule is intermediate between these structures.
- ☞ The actual molecule, that is, the resonance hybrid is more stable (has lower energy) than any of the contributing structures.

12. The Lewis structure of Carbonate ion CO_3^{2-}
    - The valance electron of carbon is 4
    - The valance electron of oxygen is 6
      Tve'n = 4 + 6(3) + 2 = 24e'n
    - The central atom is C



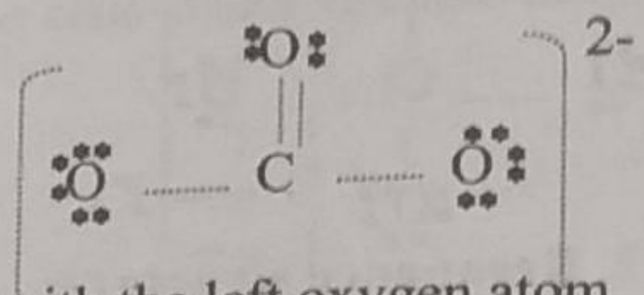
- The total lone electrons are 24-6=18e'n

$\frac{18}{3}$ = 6e'ns for each oxygen atom

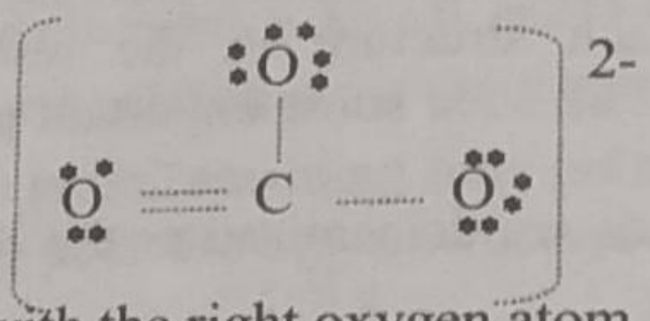


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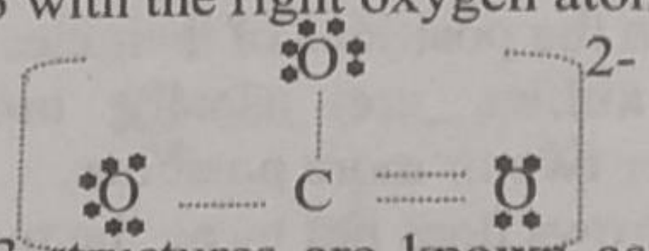
The central atom does not attain octet. Therefore, there must be a multiple bond between the central and one of the terminal atoms
Possibility 1 with the upper oxygen atom



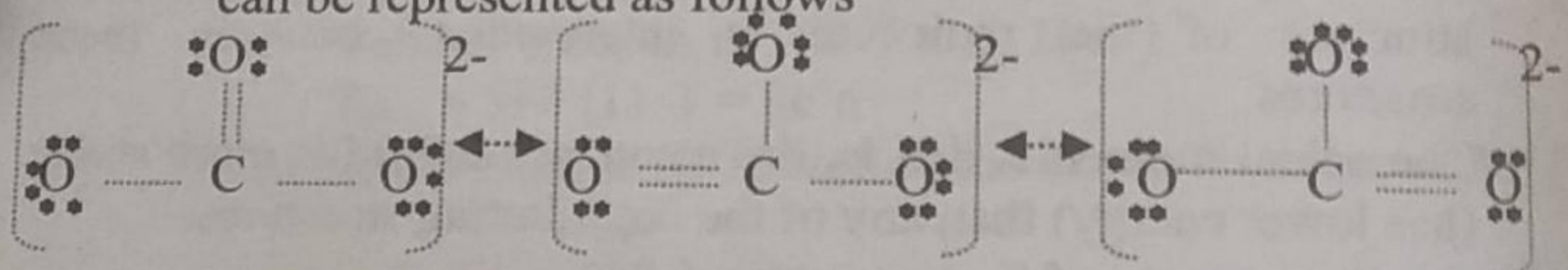
- Possibility 2, with the left oxygen atom



- Possibility 3 with the right oxygen atom



- The above 3 structures are known as **Resonance hybrids** and can be represented as follows



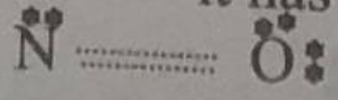
3. Exceptions to the octet rule

❖ Although the octet rule can be used to predict the structural formulas for many molecules, there are some exceptions.

A. **Less than Octet:** When atoms of group IIA and IIIA elements appear as central atom, they will have valance electron less than eight. Example: $BeCl_2$, BCl_3 BF_3 $AlCl_3$, AlF_3

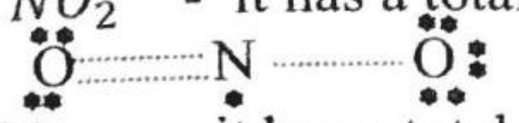
B. **More than octet:** Some atoms that are found beyond group IIA of the periodic table sometimes form bonds that give them more than an octet of electrons. This is because they have vacant 3d orbitals. Example, PCl_5 , SF_6, $XeCl_4$ . . . .

C. **Molecules with an odd number of valence electrons:** A molecule that has an odd number of electrons cannot follow the octet rule.
Example: NO – it has a total of 11 valance electrons

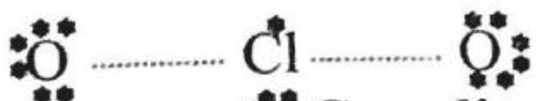


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NO_2 - it has a total of 17 valance electrons



ClO_2 –it has a total of 19 valance electrons

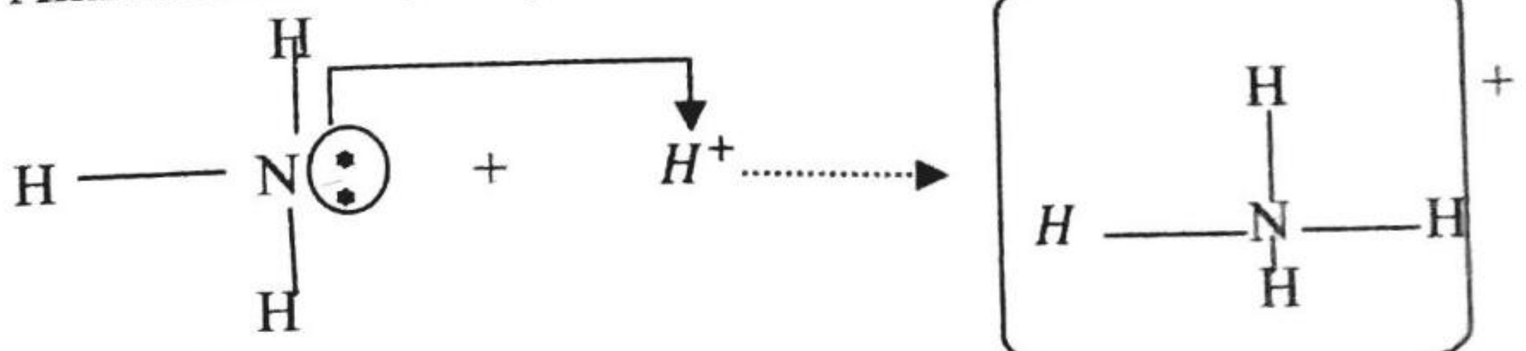


4. Coordinate covalent bond

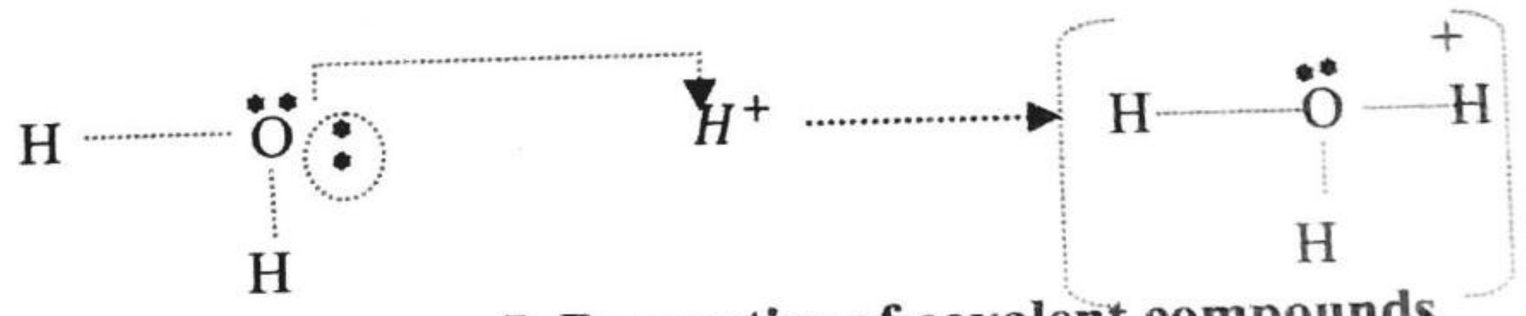
- It is also known as **dative bond** or **donor – acceptor bond**.
- **A coordinate covalent bond** is a type of covalent bond in which the shared electrons are donated by one of the combining atoms

Example: Formation of ammonium ion, NH_4^+ and hydronium ion H_3O^+ to understand the fundamental concept of coordinate covalent bond.

- Ammonium ion, NH_4^+



- Hydronium ion,



5. Properties of covalent compounds

- Generally covalent compounds are aggregates of discrete molecules. There is no ion in covalent compounds.
- Since the intermolecular force of attraction that holds the molecules together is weak, most covalent molecule exist in liquid and gaseous state.
- Generally, covalent molecules have low meltingz and boiling point. This is due to the weak intermolecular force of attraction, which results in a need for a lower energy to separate the molecules.
- Polar covalent molecules have higher melting point and boiling point than nonpolar molecules since they have relatively strong intermolecular force of attraction.
- They are neither hard nor brittle.

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- Polar covalent compounds can conduct electricity because they have partial charges.

6. Polar and nonpolar bonds in covalent molecules

- Though covalent bonds are formed by sharing of electrons between two atoms, the shared electrons might not be evenly distributed between them.
- Based on the distribution of electrons among the two atoms, covalent bonds can be classified in to polar and nonpolar bonds.

A. **Polar bonds**: are bonds which are formed by unequal distribution of shared electrons.

- This unequal distribution of the shared electrons is due to the electro negativity difference between the combining atoms.
- The bonding electrons spent much of their time near to the most electro negative element and as a result the atom will have a partial negative charge (δ^-).
- On the other hand, the less electro negative element will have a partial positive charge (δ^+).
- Let us consider HF molecule. Since flourine has high electro negativity than hydrogen, it attracts much of the electron to it's side and form partial negative charge (δ^-) while hydrogen form partially positive charge (δ^+)



Fig 3.3 distribution of bonding electrons in HF molecule

- Covalent molecules which possesses polar covalent bonds are often polar.
- HCl, HF, HBr, HI, CO, NO,H_2S , H_2O are some examples of polar molecules.
- In general, the polarity of molecules is measured by dipole moment (μ).
- It is the magnitude of the separated charges multiplied by the distance q.

$$\mu = q\ x\ d$$

- Some covalent molecules which possess polar bonds, but the dipole moment of the molecule will be 0 and therefore the

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molecule will be non polar. $CO_2, BCl_3, BF_3, CCl_4, CF_4$ are some examples of non polar molecules possessing polar bonds.

B. **Non polar bonds**: are covalent bonds formed when the bonding electrons are equally distributed between the combining atoms.

☞ These bonds are formed when the combining atoms have exactly equal values of electronegativity as happened in homonuclear diatomic molecules like O_2, H_2, N_2.

3.4 Inter molecular forces in covalent compounds

- Intra-molecular forces like ionic and covalent bond can determine the chemical property of the substance.
- Intermolecular forces are relatively weak forces formed due to the attraction between ions and molecules and can affect the properties of these substances.
- There are many kinds of intermolecular forces which exist between covalent molecules. But the most important are;

1. Dipole – dipole forces

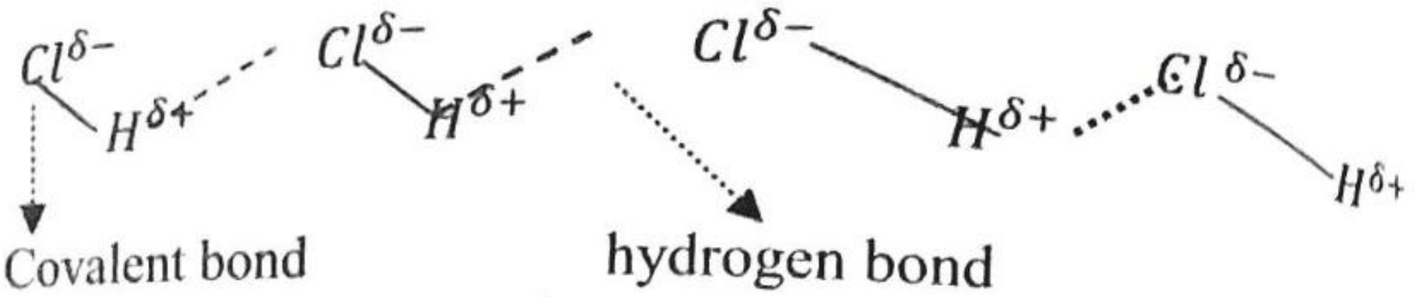
- Polar molecules have a small partial positive charge at one end of the molecule and an equal negative charge at the other end.
- Attractions between opposite charges of neighboring permanent dipoles are called **dipole-dipole attractive forces**.
- Polar molecules, generally, have higher melting point, boiling point, heat of fusion and vaporization than the corresponding non polar molecules of comparable mass. For example, both butanal ($CH_3CH_2\,CH_2COH$) and n-pentane ($CH_3CH_2\,CH_2CH_2\,CH_3$) have comparable molar mass, but the boiling point of butanal (74.8°C) is greater than the boiling point of n-pentane(36°C). This is due to the existence of dipole-dipole forces within butanal molecules.

2. Hydrogen bonding

- The partial charges on atoms in a molecule are particularly large if one of the atoms in the covalent bond is hydrogen and the other atom is fluorine, oxygen, nitrogen and chlorine (the most electronegative elements).
- The large partial charges in covalent molecules containing these elements result in strong electrostatic attraction between the partial negative charge of hydrogen atom of one molecule and the partial negative charge of the most electro negative element

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(F, O, and N) of the other molecule. This attraction force is known as **Hydrogen bond**.



- Since hydrogen bonds are much stronger than dipole -dipole forces, liquids which contain hydrogen bonds have high boiling point than liquids containing dipole-dipole forces of comparable mass. For example, the boiling point of 1-propanol ($CH_3\ CH_2\ CH_2\ OH$) with molecular mass of 60 is 97°C which is higher than the boiling point of propanal ($CH_3\ CH_2COH$)(56°C) with molecular mass of 58 .

Hydrogen bond and the unique properties of water

- Hydrogen bond is responsible for much of the exceptional properties of water.

i. Water expands, when cooled into solid. When water molecules are cooled dawn, hydrogen bonding traps the molecule in to a rigid hexagonal structure that aligns water molecule in such a way as to create huge gaps between the molecules. This makes ice less dense than water and this is the reason why ice floats over water.
ii. Because of hydrogen bond, water has high heat of vaporization, strong surface tension, high specific heat and viscous.
iii. Water has relatively high boiling and freezing point because of hydrogen bond.

3. **Landon force (Dispersion force)**
   - It is a weak inter-molecular force which exists in all covalent molecules but significant in non-polar molecules.
   - London forces result from the attraction of the positively charged nucleus of one atom for the electron cloud of an adjacent atom in another molecule.
   - In general, London forces are formed by the electrostatic attraction between induced dipoles. How?

A. The electrons are distributed around the nucleus. A symmetrical, spherical atom has no separation of charges.

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B. At any time, however, such an atom can lose its spherical shape and become a temporary dipole
C. A temporary dipole can distort the electron cloud of a symmetrical atom and induce a dipole in it

- London forces exist between all particles (atoms, ions, and molecules) whether they are polar or non polar. But, the forces are influential only in non polar compounds.
- The strength of London forces is dependent on the molecular mass and molecular size of the substance.
  - As molecular mass increases, number of electrons also increases, thus, strength of London force also increases. For example, the strength of London force in I_2 is much greater than Cl_2 because the molecular mass of iodine is greater than chlorine.
  - As the molecular size of the substance increases, they can easily be distorted to give induced dipoles. Therefore, strength of London force increases. For example, the boiling point of n-butane is much greater than the boiling point of 2- methyl propane, though they have equal molecular mass. This is because the size of 2-methyl propane is less than the size of n-butane due to the branching in its structure, and therefore the strength of the London force decreases.

Confidence building problem 2

13. Which of the following is true about resonance structures?
    A. They have different arrangement of atoms
    B. Double-headed arrows does not mean the molecule changes back and forth from one structure to the other
    C. The actual molecule is more stable (has lower energy) than any of the contributing structures.
    D. A and B

    Solution: In molecules that have resonance structures, the actual molecule, that is, the resonance hybrid is more stable (has lower energy) than any of the contributing structures.

    Answer: C
14. Which one of the following is a nonpolar molecule with polar bond?
    A) N_2 B) H_2S C) BF_3 D) NH_3

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Solution: CH_4 and N_2 are non-polar molecules. The bond in N_2 is non-polar however the bonds (B-F) in BF_3 are polar. Therefore, BF_3 is a non-polar molecule with polar bonds.

Answer: C

15. Which of the following statements about intermolecular interactions is incorrect?
    A. Dispersion interaction are greater for Xe than for He.
    B. Dipole-dipole interactions are greater for CF_4 than for H_2O.
    C. Individual hydrogen bonds are stronger for HF than for HCl.
    D. H_2O boils at a higher temperature than H_2S because of hydrogen bonding

Solution: CF_4 is non-polar but H_2O is polar. Thus, dipole-dipole interactions are greater for CF_4 than for H_2O.

Answer: B

16. Assume that all are in liquid phase. Which among the following has the highest boiling point?

A. Ar B. Cl_2 C. CH_4 D. Br_2

Solution: All are nonpolar molecules. Therefore, the intermolecular force of attraction is London force. The magnitude of London force increases, as molecular mass increases. The molecular mass of Br_2 is higher than the rest of molecules. Therefore, it has the highest boiling point.

Answer: D

17. Which of the following does not contain any dative bond

a. NH_4F b. H_3O^+ c.$NaBF_4$ d. none

Solution: All molecules contain coordinate covalent (dative) bond.

Answer: D

18. Which of the following has zero dipole moment

a. PH_3 b. PH_4 c. CH_4 d. CH_2Cl_2

Solution: Non-polar molecules have zero dipole moment.

Answer: C

19. Which one of the following has least polarity in bond?

a. H-F b. H–Cl c. H–O d. C–S

Solution: Polar bonds are formed due to the difference in the electronegativity of the bonded atoms. As the difference increase the bond becomes more polar. Since sulfur has the lowest electronegativity, C-S has the least polarity.

Answer: D

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3.5 Molecular Geometry

- The valance shell electron pair repulsion (VSEPR) theory states that valance shell electron pairs are arranged around the central atom in such a way that there is a maximum separation and therefore minimum repulsion among electron pairs.
- According to VSEPR theory, ***a single bond, a double bond a triple bond or an unshared pair of electrons is considered to be a single region of high electron density***. Moreover, according to the theory ***each valance shell pair of electron on an atom is significant and the repulsion among valence shell pairs of electrons determines the shapes of molecules***.
- The repulsion forces between the valance shell electron pairs are of three types. These are Lone pair-Lone pair (LP-LP), Bonding pair - Lone pair (BP – LP), and Bonding pair – Bonding pair (BP – BP). Many measurements of bond angles of known geometries of molecules proved that lone pairs of electrons require more space than the bonding pairs. Therefore, the magnitude of the repulsive forces can be generalized as

  LP – LP≫ LP – BP≫BP – BP
- To better understand the concept, let us consider the shape of water molecule. Water molecule has two lone pair electrons at the central oxygen atom. Therefore, all the three types of repulsion forces exist. Since the LP – LP repulsion is much stronger than the other two repulsion forces, the bonding orbitals get closer.



- The VSEPER theory which is used to predict the geometries of molecules is based on the following basic assumptions:
  1. If there is lone pair at the central atom, the arrangement of electron pairs and molecular geometry are not the same. This is because the greater repulsion forces between lone pairs of electrons can cause distortion in the structure.
  2. The electron – electron repulsion in triple bonds are greater than double bonds and double bonds are greater than single bonds. Therefore, triple bonds can cause much distortion than double and single bonds.

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3. If the molecule contains atoms which have significant difference in their electro negativity, the electrons in the bond distorted toward the more electro negative atom. As a result, the repulsion between the bonding pair and other electron – pairs in the molecule will decrease because of the decrease in the electron density near the central atom.

❖ Though the VSEPR theory does not apply in all circumstances, it does explain a wide variety of molecular shapes. Let's take a close look at the most common geometries. **In our discussion A represents central atom, X represents terminal atom** and E **represents lone pairs**

1. **LINEAR**:- In a linear molecule the atoms are connected in straight line with bond angle of 180^0. All molecules that contain only 2 atoms (diatomic molecules) are linear $O_2, N_2, Cl_2, HCl, HF, HI$ are some examples. Besides to these substances, all molecules of Ax_2 type are also linear in geometry. Some of the examples are $CO_2, BeCl_2, CS_2$ $e.t.c.$
2. **TRIGONAL PLANAR:-** Molecules with trigonal planar shape has a trigonal, flat shape. In such molecules the central atom is bonded to three other atoms and has no unshared pairs of electron. The molecules with planar shape are characterized by AX_3 and bond angle 120^0. **Examples-** BF_3,BC_3, NO_3^- - - - -
3. **TETRAHEDRAL** – In molecules with tetrahedral shape the atoms are arranged in three dimensions and has bond angle of 109.5^0. Some of the examples are $CH_4, CCl_4, NH_4^+, SO_4^{2-}$ the molecules are usually represented by AX_4.
4. **PYRAMIDAL** – Pyramidal molecule has a central atom that is bonded to three other atoms and has one unshared pair of valence electron. This shape is also known as trigonal pyramidal. Such molecules are characterized by AX_3E. The bond angle of thus geometry is about 107.3^0. Ammonia, NH_3 is a good example of such geometry.
5. **V- Shaped or Angular** – This geometry is formed by compounds which have either Ax_2E or $Ax_2\ E_2$ form.
   a. A molecule which is bonded with two atoms and one lone pair at the central atom (AX_2 E type) can form V-shaped or Angular shape. The bond angle decreases due to the strong repulsion of

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the lone pairs to the bonding pair electrons. Example: $PbCl_2, SnBr_2, O_3$ etc

b. Molecules which contain a central atom bonded with two other atoms and have two lone pairs of electrons can Havel V-Shaped or angular shape. Such molecules are usually represented by AX_2E_2. Due to the strong repulsions between the lone pairs the bond angle decrease to 104.5^0.Example: H_2O, H_2S

❖ The table given below can summarize the difference in molecular geometries due to the repulsion of electron pairs even for similar set of electron arrangement.

Type of the Molecule	Bonding pairs of electron	Lone pairs of electron	Electron pair Arrangement	Molecular Geometry
AX_2	2	0	Linear	Linear
Ax_2E	2	1	Trigonal planar	Angular
Ax_3	3	0	Trigonal planar	Triangle planar
Ax_4	4	0	Tetrahedral	Tetrahedral
Ax_3E	3	1	Tetrahedral	Trigonal pyramid
Ax_2E_2	2	2	Tetrahedral	Angular(Vshape)
Ax_5	5	0	Trigonalbipyramid	Trigonalbipyramid
Ax_4E	4	1	Trigonalbipyramid	Seesaw
Ax_3E_2	3	2	Trigonalbipyramid	T-shaped
Ax_2E_3	2	3	Trigonalbipyramid	Linear
Ax_6	6	0	Octahedral	Octahedral
Ax_5E	5	1	Octahedral	Square pyramidal
Ax_4E_2	4	2	Octahedral	Square Planar

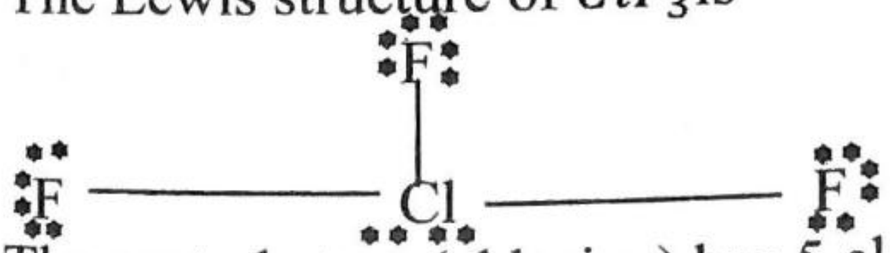
Table 3.1 Molecular geometries based on VSEPR theory

20. Use VSEPR theory to predict the shape of the following molecules or molecular ions.

a. ClF_3 b. PBr_5 c. ICl_2^- d. NO_3^-

Solution a) ClF_3

The Lewis structure of ClF_3 is



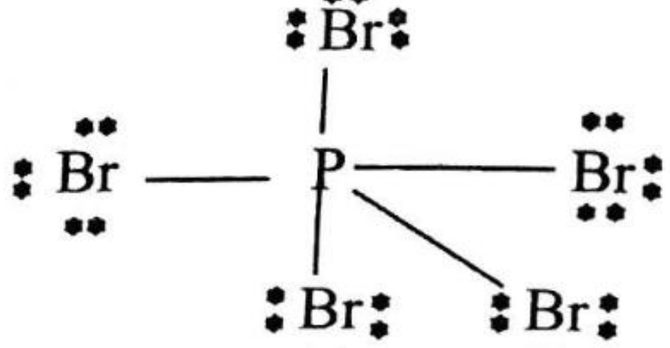
- The central atom (chlorine) has 5 electron pairs- 3 bonding pairs and 2 lone pair.

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- Since chlorine has 5 electron pairs the electron set arrangement is Trigonalbipyramid.
- Since chlorine has 3 bonding pairs and 2 lone pair it is Ax_3E_2 type molecule. Therefore, the molecule has sesaw geometry.

b) PBr_5

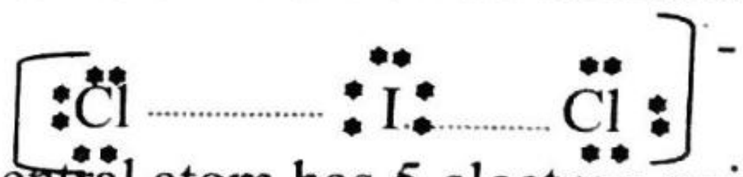
- The Lewis structure of the molecule is



- The central atom phosphorus has 5 electron pairs. Thus, the electron set arrangement is trigonal bi pyramidal
- Since the central atom has no lone pair, the molecule has similar electron set arrangement and molecular geometry (shape)

c) ICl_2^-

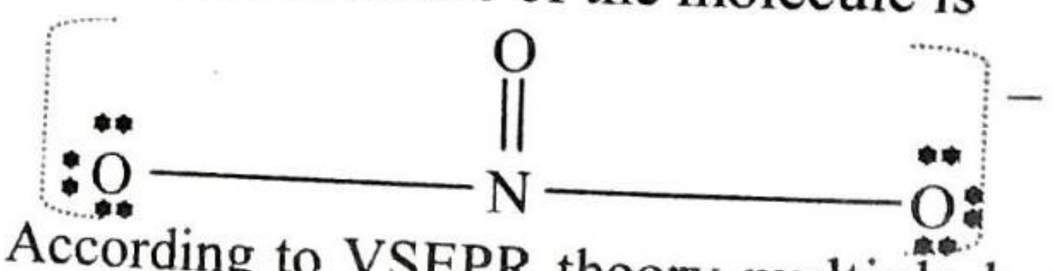
- The Lewis structure of the molecule is



- The central atom has 5 electron pairs. Therefore, the electron set arrangement is trigonal pyramid
- Since the central atom has 2 bonding and 3 lone pairs of electrons the molecule has AX_2E_3 and has Linear shape with a bond angle of 180^0

d. NO_3^-

- The Lewis structure of the molecule is



- According to VSEPR theory multiple bonds are counted as one pair. Therefore the central atom has 3 bonding pairs arranged in trigonalplanr.
- Since there is no lone pair at the central atom, the molecule has a form AX_3. Therefore it has Trigonal planar geometry

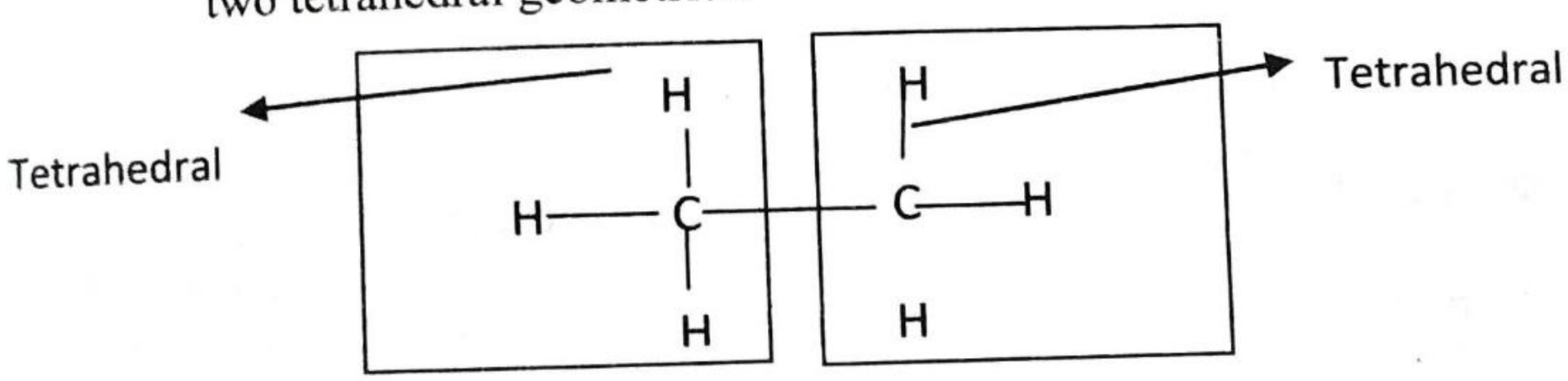
Molecular geometry and dipole moment

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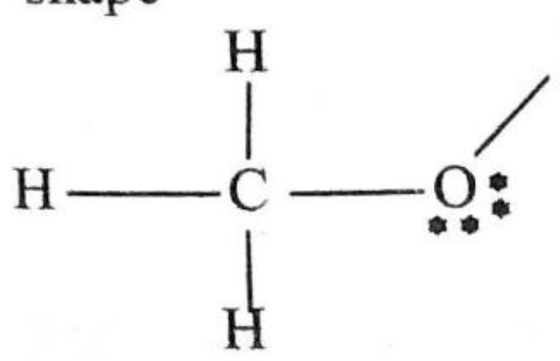
Type of the molecule	Molecular Geometry	Dipole Moment
Ax	Linear	Usually non-zero
AX_2	Linear	Zero
$Ax_2E(Ax_2E_2)$	Angular (v-shaped)	Usually non-zero
Ax_3	Trigonal planar	Zero
Ax_3E	Trigonal pyramidal	Usually non-zero
Ax_3E_2	T-shaped	Usually non-zero
Ax_4	Tetrahedral	Zero
Ax_4E_2	Square planar	Zero
Ax_5	Trigonal bi pyramidal	Zero
Ax_5E	Square pyramidal	Usually non-zero
Ax_6	Octahedral	Zero

N.B. The molecular shapes of molecules with more than one central atom can be different in different part of the molecule.

For example, consider ethane C_2H_6. The molecule has two central atoms (the two carbon atoms) each of them has no lone pair and is Ax_4type. Therefore ethane molecule is shaped like two tetrahedral geometries.



Example: Methanol (CH_3OH). The molecule has two central atoms (oxygen and carbon). If we consider carbon atom it has four bonding pairs and has no lone pair. Therefore, the molecule has tetrahedral shape at carbon. The oxygen atom has 2 bonding pairs and 2 lone pairs. Therefore the molecule at oxygen is V-shape



(structure of methanol)

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Solution: The strength of metallic bond increase as the number of electrons in the delocalized sea of electrons (valence electrons) increases. The strength of metallic bond also increases with decreasing atomic size (as the atoms are closely packed). Down a given group valence electrons remains constant but atomic size increases. Thus, strength of metallic bond decreases.

Answer: C

3.7 Chemical Bonding Theories

- There are two modern chemical bonding theories which use quantum mechanics. These are
  1. Valence Bond Theory (VBT)
  2. Molecular orbital theory (MOT)

3.7.1 Valence Bond Theory (VBT)

- In valence bond theory (VBT), a covalent bond is regarded as a bond formed when an electron in atomic orbital on one atom pairs its spin with that of an electron in an atomic orbital on another atom.
  - This overlapping of orbitals pulls the combining atoms together because the electrons in the orbitals begin to move about both atoms and attracted to both nuclei at the same time.
  - Thus, the strength of the bond between any two atoms generally depends on the extent of overlap between the two orbitals.
  - The greater the extent of overlap in the orbitals results in a greater bond strength between the two atoms.
  - The way in which the orbitals overlap can result in different covalent bonds.

1. Sigma (δ) and pi(π)bonds

- When two atomic orbitals overlap along the intermolecular axis the resulting localized bond is called **sigma bond(δ)**.
- s-s and s-p always overlap along the nuclear axis (head- to-head) fashion to form sigma bond.
- Sigma bond has a cylindrical shape about the bond axis. They have high electron density in between the bonded nuclei (see fig 3.7)



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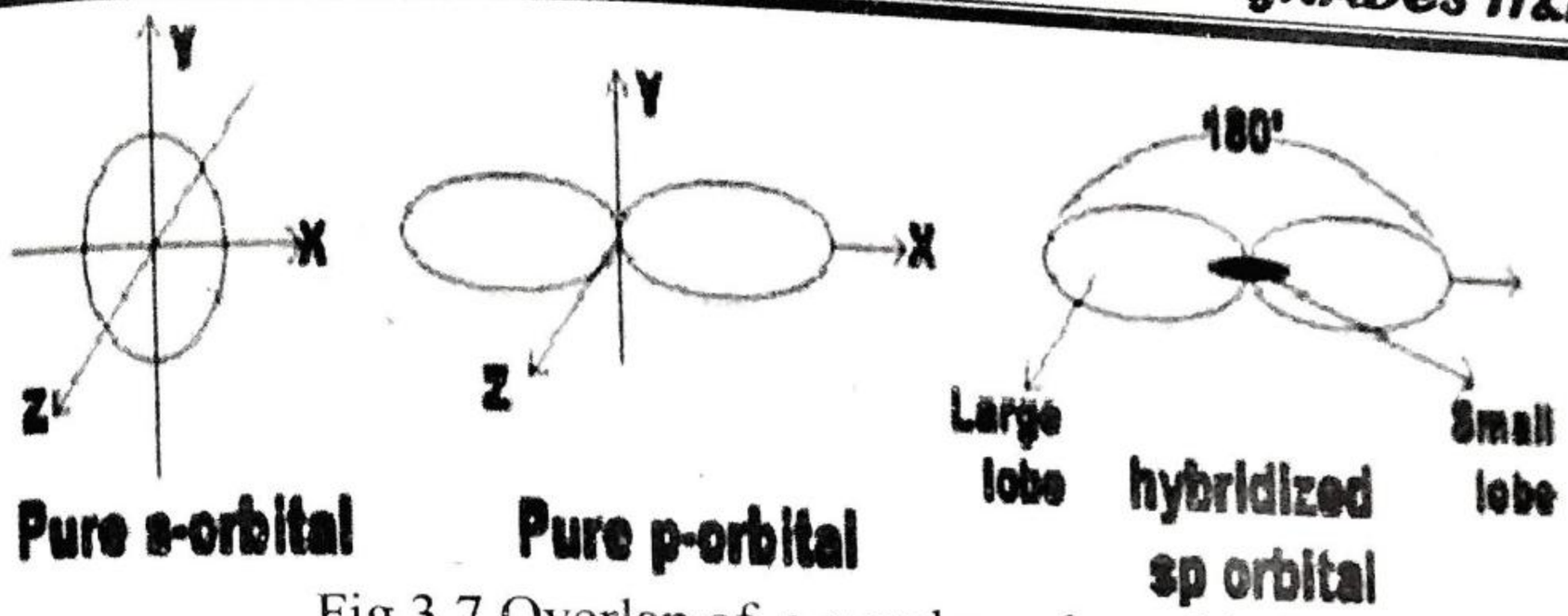


Fig 3.7 Overlap of s-s and s and p orbitals

- A Pi (π) bond is formed by the side wise overlap of two parallel P orbitals.
- Pi bonds are usually formed by the two parallel P orbitals after the formation of strong δ bond.
- However, the sidewise overlap of P orbitals do not give as strong bond as along the axis overlap of two orbitals.

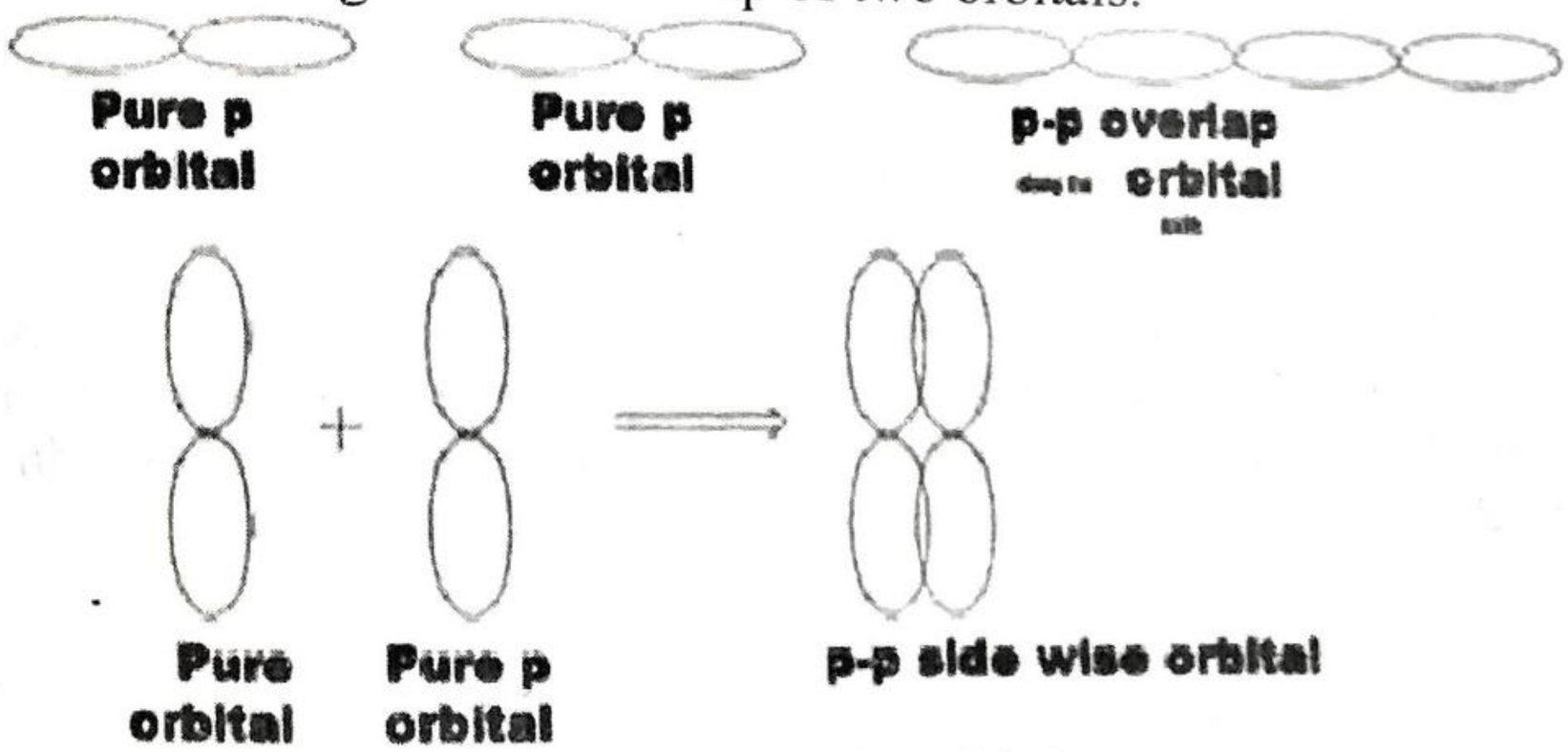


Fig. 3.8 overlap of two 2p orbitals

Summary about overlap of orbitals and sigma and Pi bonds

- *S-S, S-P and P-P overlap along the orbital axis form sigma bond.*
- *Sidewise overlaps of P-P orbitals form Pi bonds.*
- *Single bonds have only one sigma bond.*
- *Duble bonds have one sigma and one pi bonds*
- *Triple bonds have one sigma and two Pi bonds.*

2. Hybridization

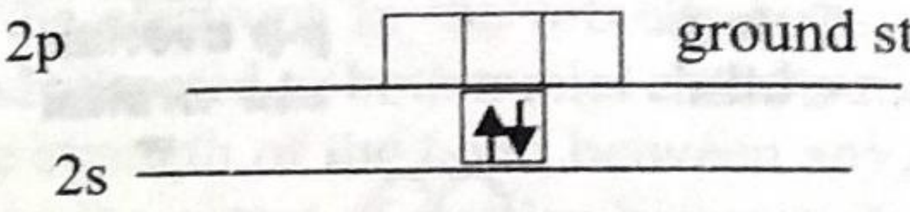
- Hybridization is the mixing of two or more atomic orbitals to yield two or more identical hybrid orbitals.

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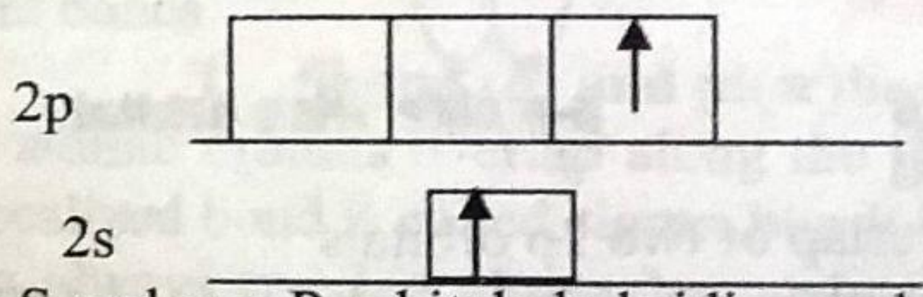
- ❖ Hybrid orbitals of an atom have a combination of the properties of the atomic orbitals that are mixed to form them.
- ❖ The number of the new hybrid orbitals is equal to the number of atomic orbitals that are combined to form them. For example, the mixing of one s and one p orbitals in any atom yield two SP hybrid orbitals.
- ❖ The concept of hybridization is also used to explain the shape of molecules. But, it fails to give reason why the molecule has this geometry.

sp hybrid orbitals

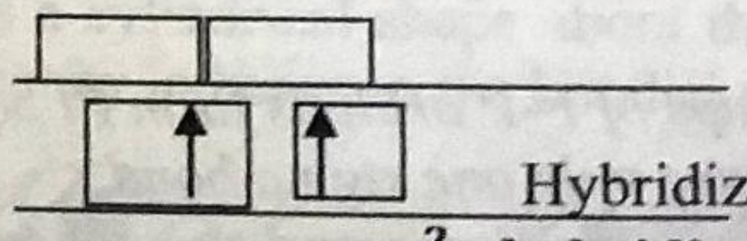
- ❖ SP hybrid orbitals are formed by the mixing of one S and one p orbitals. Some example of compounds involve SP hybridization are BeX_2, CdX_2 where x= F, Cl, Br, I
  Example: the formation of hybrid bonds in BeF_2
- The ground state valence electron configuration of beryllium atom is



- As fluorine atoms approach the beryllium atom the energy released from them make one of the electrons in S orbital to excite in to an empty P orbital. This results in the formation of two bonding orbitals, each with one electron.



- These one S and one P orbitals hybridize and form two identical SP hybrid orbitals



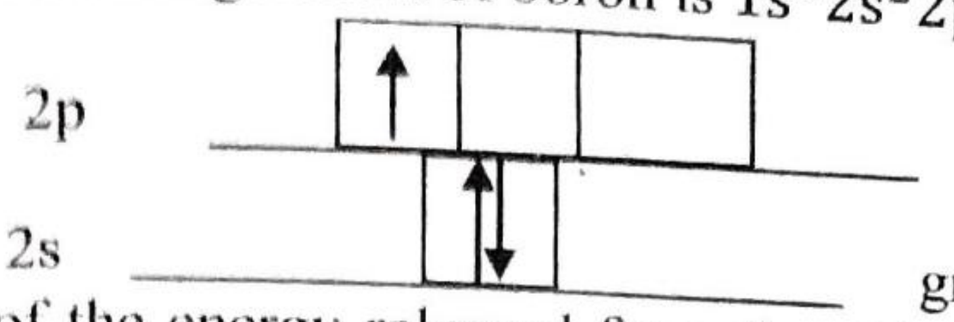
sp^2 hybridization

- ❖ sp^2 hybridization is formed by the overlap of one s and two p orbitals.
- ❖ Three identical sp^2 hybrid orbitals are formed from the hybridization of one s and two p orbitals.

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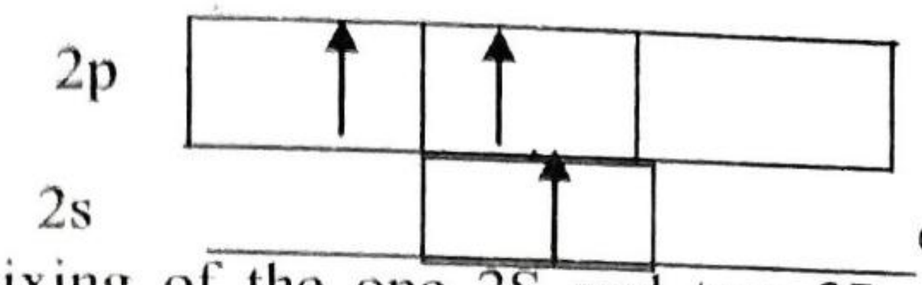
Example: boron tri chloride (BCl_3)

- The electron configuration of boron is $1s^2 2s^2 2p^1$



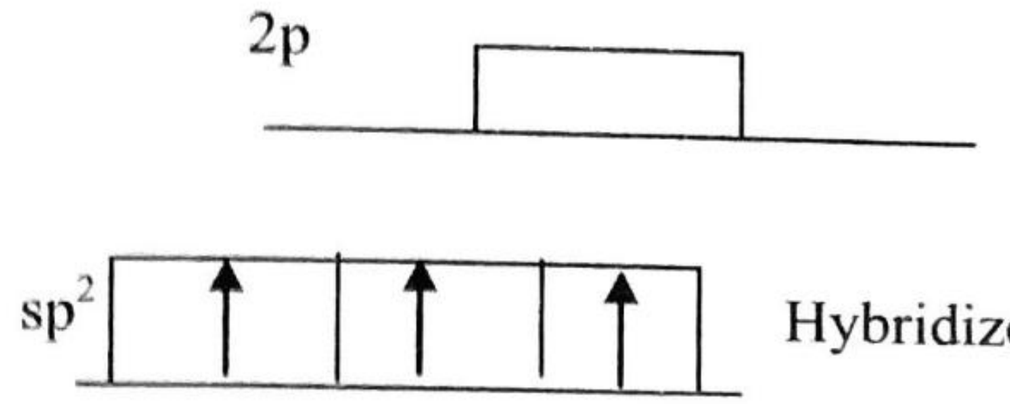
ground state

- Because of the energy released from the chlorine atoms one of the 2s electrons jump to empty p orbitals.



excited state

- By the mixing of the one 2S and two 2P orbitals three identical SP^2hybrid orbitals are formed with 33.33% S character and 66.67% P character.



Hybridized state of boron

sp^3 Hybridization

- sp^3Hybridization is formed by mixing of one s and three p orbitals.
- Four identical sp^3hybrid orbitals are formed.
- sp^3hybrid orbitals which has 75% P character and 25% s characters.
- Example: methane (CH_4) molecule involves sp^3 hybridization.
- SP^3 hybridization can also explain the bond formation in molecule which contain lone pairs like Ax_3E and Ax_2E type.

Example: NH_3 is AX_3E type molecule.

sp^3d Hybridization

- This type of hybridization is formed by the mixing of one S, three P and one d orbitals.
- Molecules which have an expanded octet (the valence electron of the central atom is greater than 8 can have this kind of hybridization.

Example: Phosphorus penta fluoride (PF_5)

sp^3d^2 hybridization

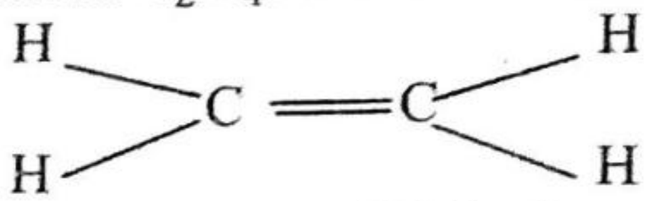
- This type of hybridization is formed by the mixing of one S, three P and two d orbitals. **Example: SF_6**

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Multiple bonds and hybridization

a. Compounds Containing Double bonds

Example: Ethene C_2H_4. The Lewis structure of the molecule is



- Since there are 3 regions of high electron density around each carbon atom, VSEPR theory tell us that each carbon is at the center of a trigonal plane with a bond angle of 120^0.
  - Therefore, we know that each doubly-bonded carbon atom is SP^2 hybridized with one electron in each SP^2 hybrid orbital and one electron in the $2p_z$ orbital which is perpendicular to the plane of the three sp^2 hybrid orbitals.

b. Compounds containing triple bond

Example: Ethyne (C_2H_2); H—C≡C—H

- According to the VSEPR theory there are two regions of high electron density around each carbon atom.
  - Therefore the molecule has liner geometry with a bond angle of 180^0 and each carbon atom has sp hybridization

- Generally, the hybrid state of the central atom in a simple covalent molecule or poly atomic ion can be predicted by using the general formula given below
- For simple molecules $\frac{1}{2}[V+G]$
- For cations and anions $\frac{1}{2}[V+G\pm a]$

Where, V=number of monovalent atoms or groups attached to the central atom, G=number of outer shell electrons in ground state of the central atom, a= magnitude of the charge on cataion or anion

- The hybrid state of the central atom is related with the calculated X as follows

X	2	3	4	5	6	7
Hybrid state	Sp	Sp^2	Sp^3	Sp^3d	Sp^3d^2	Sp^3d^2

- For example, let us consider the hybridization of the following

$PF_5 = \frac{1}{2}[5+5] = 5$, thus sp^3d $\quad ClO_3^- = 1/2[0+7+1] = 4$, thus sp^3

$NH_4^+ = 1/2[4+5-1] = 4$, thus, sp^3

Confidence building problems 4

25. What is the orbital hybridization of the oxygen atom in Cl_2O?

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A. Sp B. sp^2 C. sp^3 D. sp^2d

Solution: For simple molecules

$$\frac{1}{2}[V + G]$$

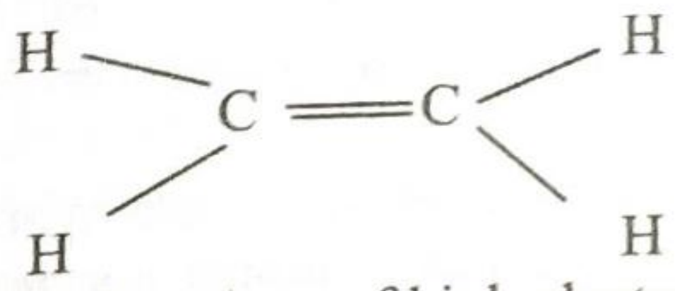
$Cl_2O = \frac{1}{2}[2 + 6] = 4$, thus the hybridization is sp^3

Answer: C

26. The hybridization of each carbon in C_2F_4 and acetylene is in the order of:

A. sp^2, sp b.sp^2, sp^2 c. sp^3, sp d.sp, sp^3

Solution: The Lewis structure of the molecule is



Since there are 3 regions of high electron density around each carbon atom, each carbon is at the center of a trigonal plane with a bond angle of 120^0. Therefore, each doubly-bonded carbon atom is sp^2 hybridized.

Answer: B

27. Number of δ and π bonds respectively in

$$CH_3{-}C{\equiv}C-CH_2{-}CH=CH_2$$

A) 13 and 2 B) 10 and 4 C) 13 and 3 D) 11 and 3

Solution: single bonds contain δ-bond. Double bonds contain 1- δ and 1 π bond triple bond contains 1- δ and 2- π bonds. Therefore, the substance contains $13{-}\delta$ and 3 π bonds.

Answer: C

28. When the hybridization state of carbon atom changes from sp to sp^2 the angle between the hybridized orbital:

A) Remains constant C) Decreases considerably

B) Increases gradually D) Cannot be determined

Solution: Sp hybridization occurs in molecules that have linear (180^0) arrangement. SP^2 hybridization occurs in molecules that have planar electron arrangement (120^0).

Answer: C

29. Which of the following hybrid orbital is favoring the formation of trigonal bipyramidal?

A. Sp^3d B. sp^3 C. sp^3d^2 D. sp^3d^3

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Solution: Sp^3d hybridization favors the formation of trigonal bipyramidal geometry.

Answer: A

3.7.2 The Molecular Orbital theory

- Molecular orbital theory postulates the combination of atomic orbitals of different atoms to form molecular orbitals, so that electrons in them belong to the molecule as a whole.
- It gives better descriptions of electron cloud distributions and magnetic properties than valence bond theory.

Bonding and Anti bonding Orbitals

- As hybrid orbitals are thought as mixtures of their component orbitals in valence bond theories, molecular orbitals are used in molecular orbital theory.
- As two atomic orbitals combine to produce two hybrid orbitals, so do two atomic orbitals from two separate atoms produce two molecular orbitals.

Bonding Molecular orbitals

- result from the addition of the atomic orbitals overlap.
- they have a region of high electron density between the nuclei.
- These orbitals have an energy level lower than either of the atomic orbitals
- the molecule is more stable than its constituents (atoms).
- They are denoted by δ or π.

Anti-bonding orbitals

- are orbitals resulting from the subtraction of the atomic orbitals that overlap.
- the electron densities is concentrated away from the region between the two nuclei or have a region of zero electron density between the nuclei.
- As a result, the two nuclei repel each other.
- Thus, the antibonding orbitals have higher energy than either of the atomic orbitals.
- Generally, these orbitals are denoted by δ^* or π^*.

N.B. Sigma and Pi bonds are shared pair of electron whereas sigma and Pi orbitals are molecular orbitals that may or may not be occupied by electrons.

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Sigma (δ) and Pi (π) Molecular Orbitals

- **Sigma (δ) molecular orbitals**: are formed by the combination of either two S orbitals or by the head to head combination of two P-orbitals along the x-axis.
  - From the combination of the two s orbitals bonding sigma orbital (δ_s) and anti bonding sigma orbital (δ_s^*) are formed and from the head to head combination of two p orbitals the x axis bonding sigma orbitals (δP_x) and anti bonding sigma orbitals ($\delta\rho_x^*$) are formed.
- **Pi (π) Molecular Orbitals**: are formed when the two P orbitals overlap sidewise.
  - The Pi(π) molecular orbitals contain two p orbitals oriented at right angles.
  - The bonding Pi orbitals are $\pi\rho_y$ and $\pi\rho_z$ and the anti bonding Pi orbitals π_{py}^* and πp_z^*. $\pi\rho_y$ and $\pi\rho_z$ have the same energy and $\pi\rho_y$ * and $\pi\rho_z$ *have also the same energy.

Molecular Electron Configuration of Diatomic molecules

- In order to write the electron configuration of simple diatomic molecules, it is important to apply Aufabu, Hunds and Pauli exclusion principles.
  - **Aufbau (building up) principle** states that electrons are put in to orbitals in the order of increasing orbital energy; the lowest energy orbitals are filled before electrons are placed in higher energy orbitals.
  - **Pauli Exclusion Principle** states that an orbital can hold a maximum of 2 electrons and if there are two electrons in the orbital they must have opposite (paired) spins.
  - **Hunds rule** states that when filling degenerate orbitals other than s, electrons are placed in individual orbitals before they are paired up
- In simple diatomic molecules the order of energy of the molecular orbital
  A) For molecules whose total number of electrons (the sum of the electrons of the two atoms) is greater than 14.

$$\delta_{1s},\delta_{1s}^*\ \delta_{2s}\ \delta_{2s}^*\ \delta_{2px}\ \begin{cases}\pi_{2py}\\ \pi_{2pz}\end{cases}\ \begin{cases}\pi_{2py}^*\\ \pi_{2pz}^*\end{cases}\ \delta 2\rho_x^*$$

Increasing energy

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