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ONLINE STUDY RESOURCE

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Coordinate Covalent Bond

1. The coordinate covalent bond is a special type of covalent bond in which shared pair of electrons between two atoms is contributed by one of the atoms only.
2. The atom which contributes the electron pair for sharing is called electron pair donor and the atom that accepts the electron pair for sharing is referred to as electron pair acceptor. The coordinate bond is shown by an arrow, pointing from donor atom to acceptor atom.
3. An atom to act as a donor must have atleast one lone pair in its valence shell.

Eg. ; NH_3 H_2O ; SF_4

one lone pair two lone pairs one lone pair

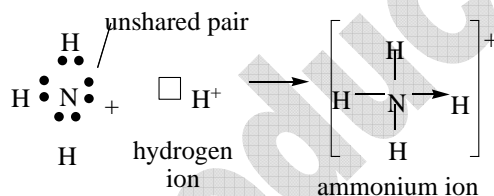
4. An atom to act as an acceptor must have an empty orbital to accommodate the accepted lone pair of electrons.

Eg. $[\text{H}^+]$ $[\text{BF}_3]$ $[\text{AlCl}_3]$

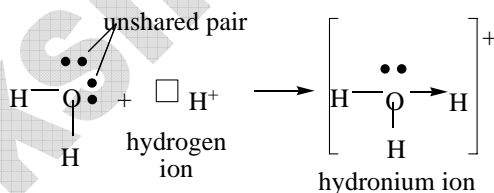
Empty orbital empty orbital empty orbital

5. Compounds containing unshared pair of electrons readily form dative covalent bonds. For example, when ammonia is mixed with gaseous hydrogen chloride, white clouds of ammonium chloride are formed.

i) The reaction involves the formation of a dative bond between N atom in NH_3 containing lone pair and H^+ ion from HCl .

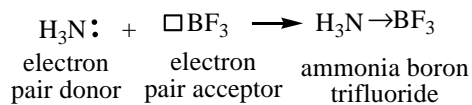


ii) A similar reaction occurs and hydronium ion is formed when hydrogen chloride dissolves in water

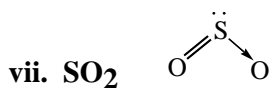
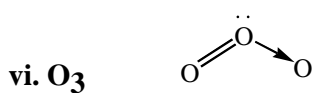
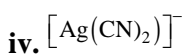
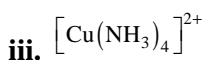


Note; once a dative bond is formed, it is indistinguishable from a covalent bond. The only difference between the two is mode of formation.

iii.) A dative bond is formed between ammonia and boron trifluoride because N in NH_3 has lone pair of electrons while boron in BF_3 has only six electrons in the valence shell. sp^3 hybrid orbital of N having a lone pair overlaps the vacant p-orbital of boron.



Some other examples for Co-ordinate covalent bond



6: During dative bond formation both shape and hybridisation of Acceptor molecule changes but in case of donor molecule only shape changes.

7: All donors act as Lewis bases and acceptors act as Lewis acids.

8: In a hydrated cation, the bond between water molecule and cation is dative bond. Every water molecule involves in one dative bond only.

Example:



9. The bond between ligand and metal atom (or) metal ion in complex compounds is dative bond.

Example:

i. $[Cu(NH_3)_4]SO_4$ contains 4 dative bonds.

ii. $[Ni(H_2O)_6]Cl_2$ contains 6 dative bonds.

10. The total number of covalent bonds and dative bonds made by an atom is known as its covalency

Ex:

I. Covalency of Nitrogen in NO_3^- ion is 4.

Ii. Covalency of sulphur in SO_4^{2-} ion is 6.

Iii. Covalency of Oxygen in H_3O^+ ion is 3.

11. All complex compounds (except Metal carbonyls), Ammonium salts, Alkali metal isocyanides etc contain Ionic, Covalent and Dative bonds.

12. Complexes like $CuSO_4 \cdot 5H_2O$, $MgSO_4 \cdot 7H_2O$ contain Ionic, Covalent, Hydrogen bond and Dative bonds

13. The properties of coordinate compounds are intermediate between the properties of ionic and covalent compounds.

a. Coordinate compounds exist as gases, liquids and solids under ordinary conditions.

b. The melting and boiling points of coordinate compounds are higher than those of covalent and lower than those of ionic substances.

c. They are less soluble in polar solvents like water, but readily soluble in non polar solvents like benzene and carbon tetra chloride.

d. They are as stable as covalent compounds.

e. Like covalent compounds, coordinate compounds are poor conductors of electricity. They undergo molecular reactions which are slow.

f. The dative bond is a strong bond with directional nature.

MOLECULAR ORBITAL THEORY (proposed by Hund-Mulliken)

1. According to this theory the atomic orbitals combine to form the molecular orbitals.
2. The number of molecular orbitals formed is equal to the number of atomic orbitals involved and they belong to the molecule.
3. The molecular orbitals are formed by LCAO method (linear combination of atomic orbitals) *i.e.* by addition or subtraction of wave functions of individual atoms thus

$$\Psi_{MO} = \Psi_A \pm \Psi_B$$

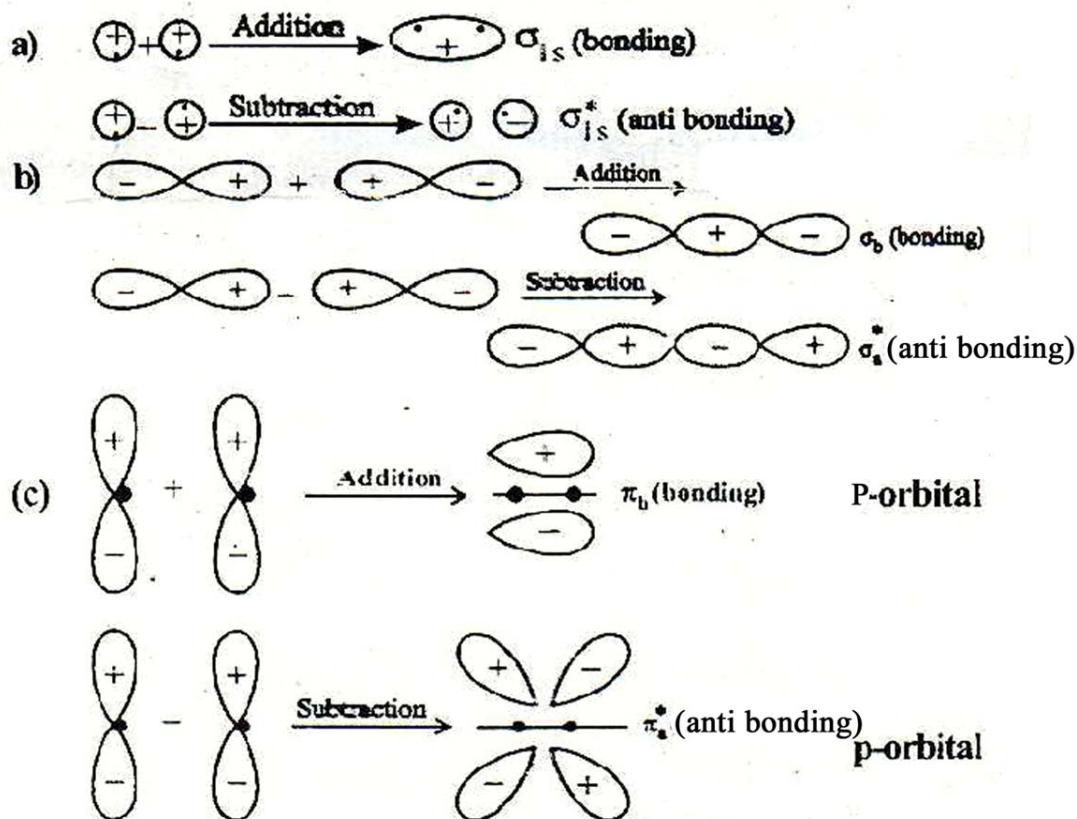
$$\Psi_b = \Psi_A + \Psi_B$$

$$\Psi_a = \Psi_A - \Psi_B$$

Ψ_b = bonding molecular orbital

Ψ_a = Anti bonding molecular orbital

4. The order of energies of molecular orbitals is bonding orbitals < Non-bonding orbitals < Anti-bonding orbitals.
5. Molecular orbitals with lower energy than atomic orbitals are bonding molecular orbitals and those with higher energy is anti-bonding molecular orbital and which are not involved in bonding are called non-bonding orbitals.
6. Molecular orbital of lower energy is known as bonding molecular orbital and of higher energy is known as antibonding molecular orbital.
7. Aufbau rule, Pauli's exclusion principle and Hund's rule are applicable to molecular orbitals, during the filling of electrons
8. Their shape is governed by the shape of atomic orbitals.



9. π_{2p_x} and π_{2p_y} has one nodal plane, whereas $\pi_{2p_x}^*$ and $\pi_{2p_y}^*$ has two nodal planes.
10. For most of the molecules or ions, σ_{2p_z} has higher energy than π_{2p_x} and π_{2p_y} because the difference between the 2s and 2p atomic energy levels is small and as a result σ_{2s} and σ_{2p} are so close that the electrons present in them repel and raise the energy of σ_{2p} above π molecular orbitals
11. The increasing order of relative energies of M.O having less than or equal to 14 electrons.
 $\sigma_{1s} < \sigma_{1s}^* < \sigma_{2s} < \sigma_{2s}^* < \pi_{2p_z} = \pi_{2p_y} < \sigma_{2p_x}$
 $< \pi_{2p_z}^* = \pi_{2p_y}^* < \sigma_{2p_x}^*$
 for more than 14 electrons ____
 $\sigma_{1s} < \sigma_{1s}^* < \sigma_{2s} < \sigma_{2s}^* < \sigma_{2p_x} < \pi_{2p_z} = \pi_{2p_y} <$
 $\pi_{2p_z}^* = \pi_{2p_y}^* < \sigma_{2p_x}^*$
12. If N_b is the number of electrons occupying bonding orbitals and N_a the number of antibonding orbitals, then
 (i) The molecule is stable if N_b is greater than N_a

(ii) The molecule is unstable if N_b is less than N_a .

13. The electronic configuration and the bond order in case of simple diatomic molecules can be obtained by filling the molecular orbitals by applying Aufbau principle and Hunds rule etc.
14. **BOND ORDER:** The relative stability of a molecule can be determined on the basis of bond order. It is defined as the number of covalent bonds in a molecule. It is equal to one half of the difference between the number of electrons in the bonding and antibonding molecular orbitals.

$$B.O = \frac{1}{2}[\text{Number of bonding electrons} - \text{Number of antibonding electrons}]$$

$$= \frac{N_b - N_a}{2}$$

The bond orders of 1, 2 or 3 correspond to single, double or triple bond. But bond order may be fractional in some cases.

The magnetic properties of molecules can also be ascertained

E.g1: Hydrogen molecule (H_2)-

Total number of electrons = 2, filling in molecular orbitals we have $\sigma_{1s}^2 < \sigma_{1s}^{*0}$

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

Hence there is a single bond between two hydrogen atoms and due to absence of unpaired electrons it is diamagnetic

E.g. 2: Helium molecule [He_2] –

The total number of electrons = 4 and filling in molecular orbitals we have $\sigma_{1s}^2 < \sigma_{1s}^{*2}$

$$\text{Bond order} = \frac{1}{2}[2-2] = 0, \text{ molecule can not exist}$$

E.g. 3: Nitrogen molecule [N_2] -

The total number of electrons = 14 and filling in molecular orbitals we have

$$\sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \left\{ \pi_{2p_z}^2 \right\} \left\{ \pi_{2p_y}^2 \right\} \sigma_{2p_x}^2$$

$$\text{Bond order} = \frac{1}{2}[10-4] = 3, \text{ It is diamagnetic}$$

E.g4; Oxygen molecule [O_2] -

Total number of electrons = 16 and electronic configuration is

$$\sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \sigma_{2p_x}^2 \left\{ \pi_{2p_z}^2 \right\} \left\{ \pi_{2p_y}^2 \right\} \left\{ \pi_{2p_z}^{*1} \right\} \left\{ \pi_{2p_y}^{*1} \right\} \sigma_{2p_x}^*$$

$$\text{Bond order} = 1/2[10-6]=2$$

As shown by electronic configuration the molecule contains two unpaired electrons, hence it is paramagnetic in nature

E.g5: [O₂⁺] ion: its electronic configuration is

$$\sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \sigma_{2p_x}^2 \left\{ \begin{matrix} \pi_{2p_z}^2 \\ \pi_{2p_y}^2 \end{matrix} \right\} \left\{ \begin{matrix} \pi_{2p_z}^{*1} \\ \pi_{2p_y}^{*1} \end{matrix} \right\} \sigma_{2p_x}^*$$

Bond order=1/2[10-5]=2.5 ,it is paramagnetic.

15. Relative order of stabilities of is

$$N_2 > N_2^+ > N_2^- > N_2^{2-}.$$

16. As bond length is inversely proportional to bond order, bond lengths will be in the order
 $N_2^{2-} > N_2^- = N_2^+ > N_2.$

17. **The bond lengths of O₂ and ions are in the order**

$$O_2^{2-} > O_2^- > O_2 > O_2^+.$$

18. **The dissociation energy of O₂ molecule and its ions are in the order:** $O_2^+ > O_2 > O_2^- > O_2^{2-}.$

19. **Isoelectronic species have the same shape and same bond order.**

E.g. Both CO and NO⁺ have bond order 3.