SEM-2 CC-4

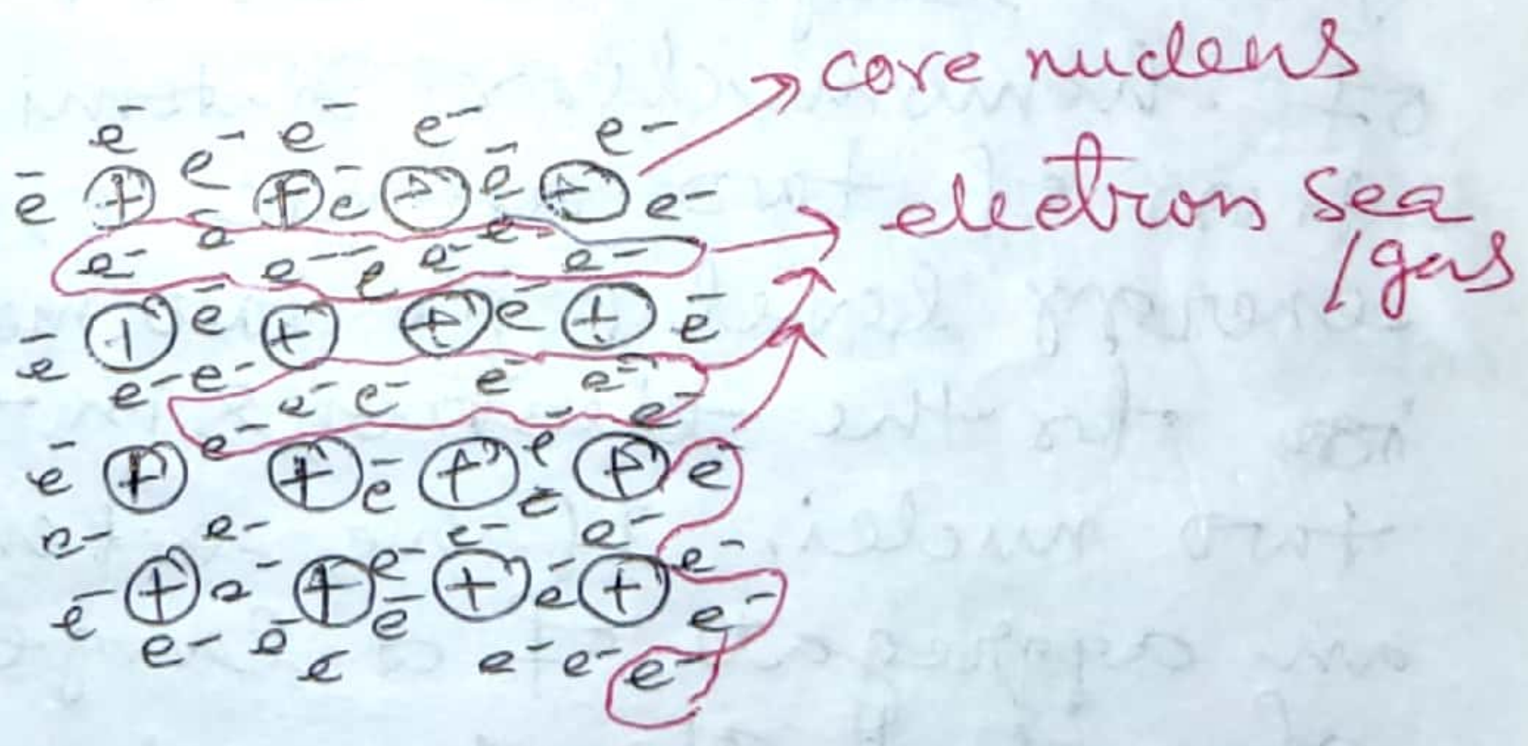
Metallic bonding

Date: 07/03/2020

Metal posses certain distinct features. Explanation of these properties can not done using present bonding theories (like covalent bonding, ionic bonding etc). Several theories have been developed to explain the properties of the metal.

① The electron gas model or electron sea model

This model developed by Scientist Drude and Lorentz. It says that valence electrons of metal in a metallic crystal are not bound to any specific metal nucleus. The positive core form a joint lattice and all the valence electrons occupies their joint field like a gas or sea.

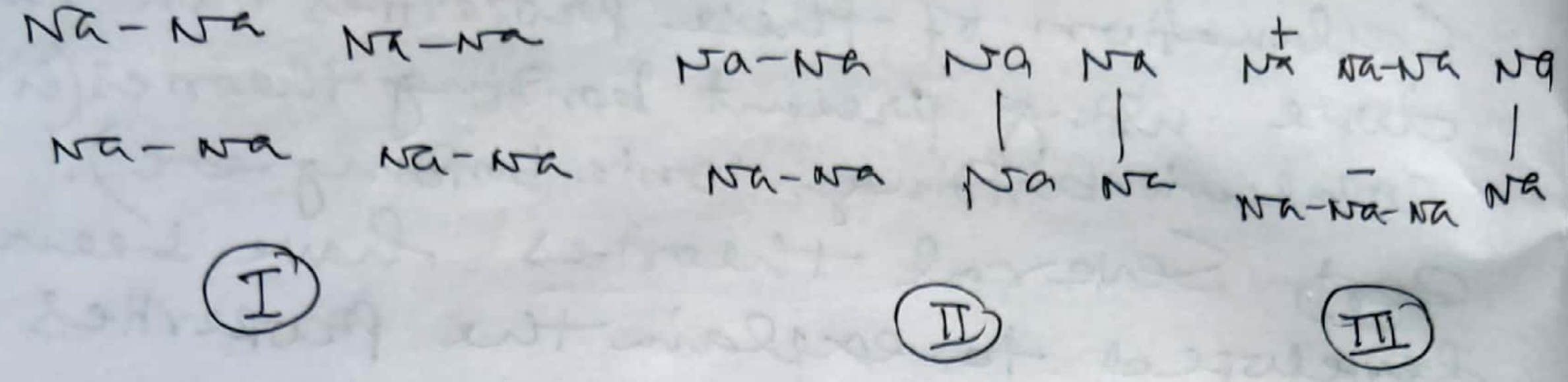


Using this model several properties of metal can explain nicely but it cannot explain the specific heat phenomena properly.

② The valence-bond theory:

This involves resonance of electron pair and one-electron bond among all the nearest atom in a metal in an

aggregate. A few typical examples of such structures involving eight sodium atom is shown below.

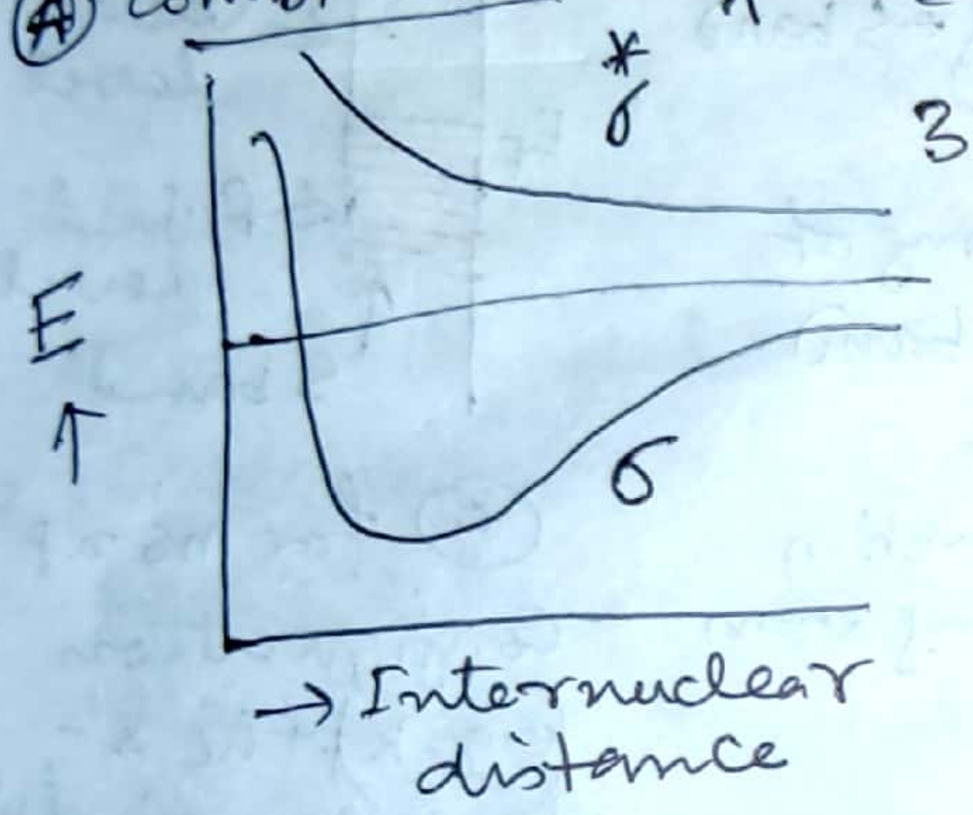


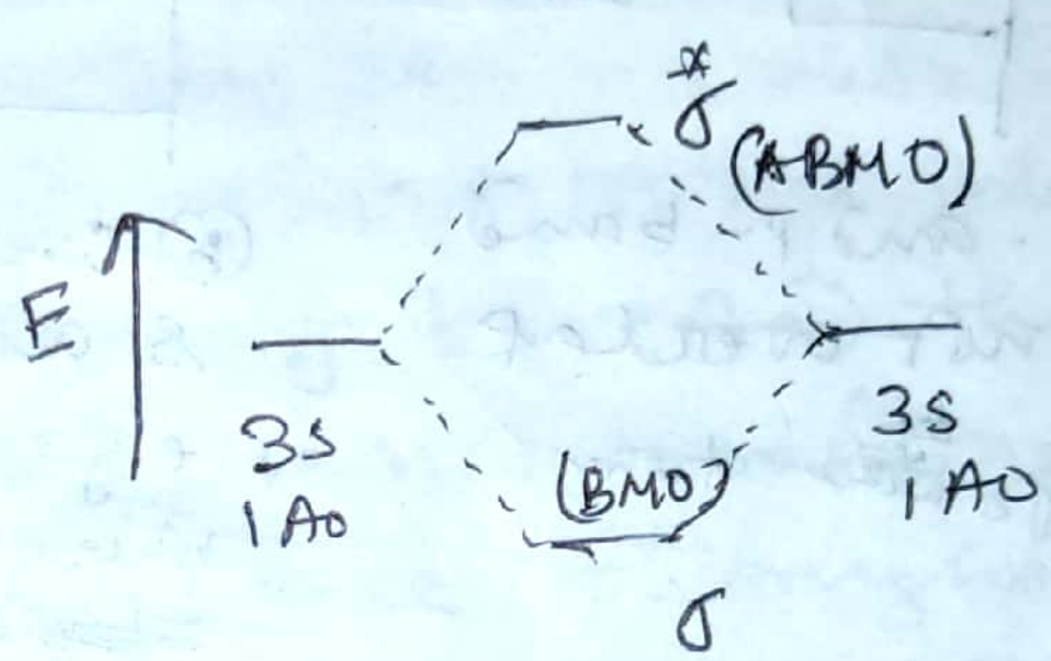
using this ~~model~~ theoretical model metalic properties ~~can~~ is not explain in a straightfoward way. Also ~~the~~ metalic properties in the liquid state cannot be explained ~~by~~ by this theory.

(3) The band theory: ~~It provid~~ It provides most satifactory explanation for various properties of the metal. This theory includes the extension of molecular orbital theory for a large number of atoms. In case of homonuclear diatomic molecule, combination of two atomic orbital produce two energy level (i.e. two molecular orbital) for the electrons in the joint field of two nuclei. If we extend this idea to an aggregate of a large number of (say n) of metal atoms, each offering one orbital for combination with others, there will be a total of n new energy levels (i.e n number of molecular orbitals) these large number of energy levels will be spaced closely; one upon another forming a energy band. The electrons from all the atoms will now enter these energy

levels in a manner similar to the filling of molecular orbital. Following the ~~Aufbau~~ Pauli exclusion principle, these 'n' number of level can accomodate 2n number of electrons. Thus a metal consist of energy bands formed by merging of individual atomic orbitals. In a particular energy band, the topmost levels are fully antibonding in nature and lowest energy levels are fully bonding in nature, and the intermediate levels are of intermediate character.

(A) Combination of two 3s-electron in Na using 3s' atomic orbital



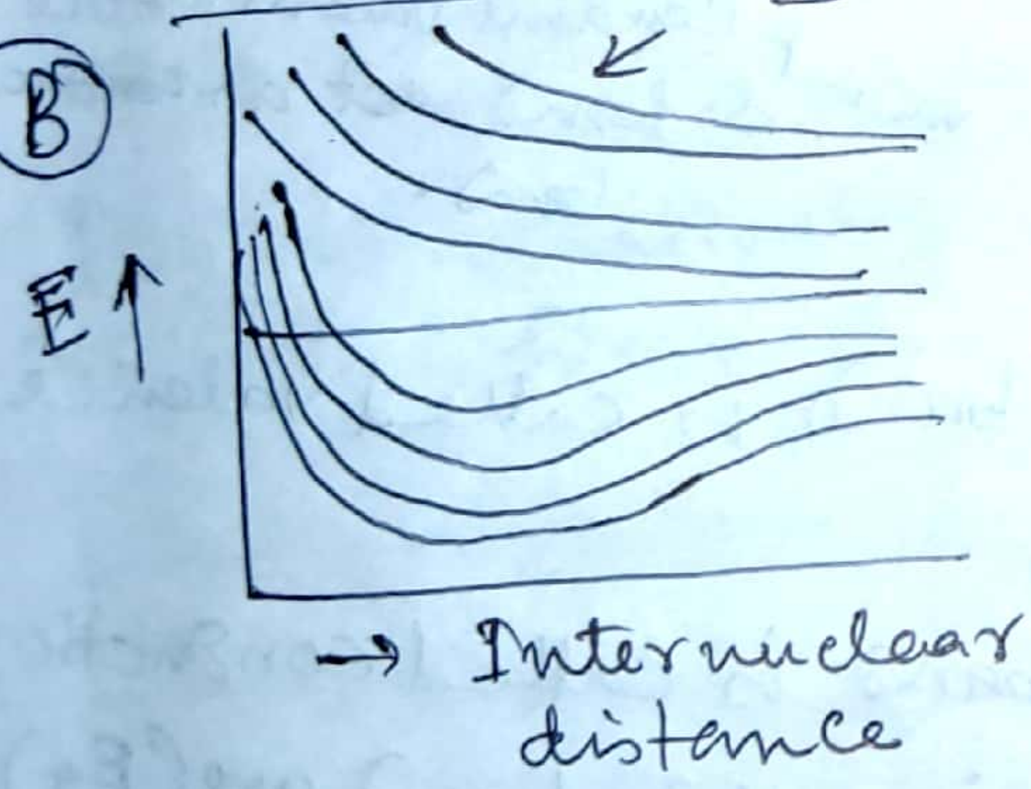


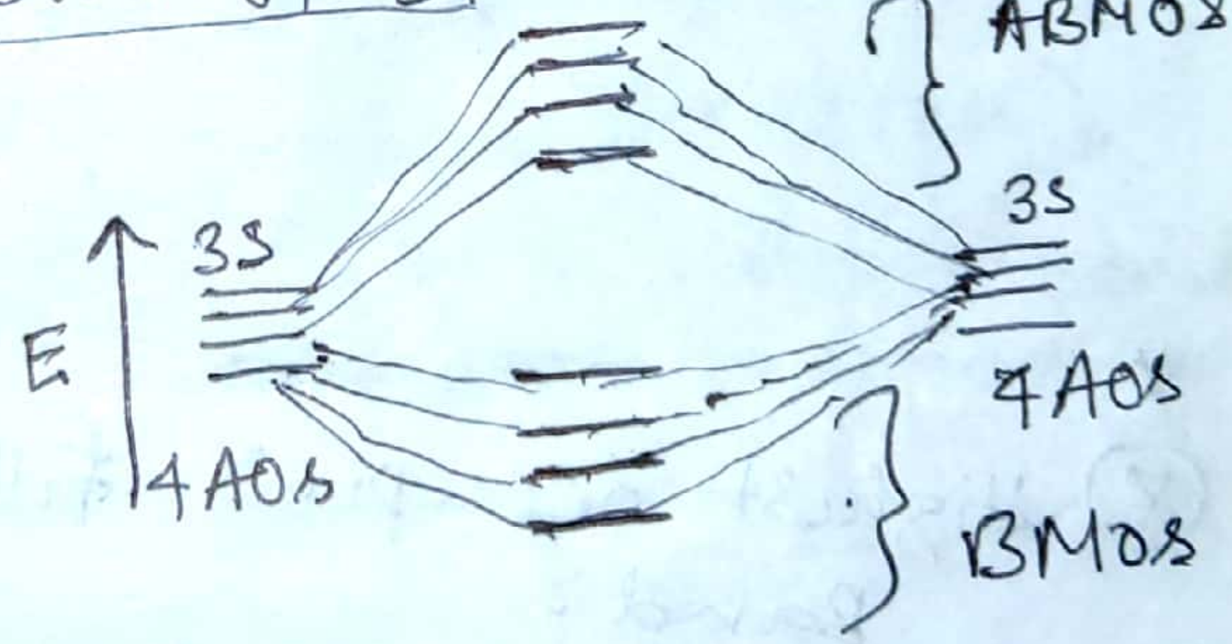
(a)

(b)

Combination of 8 3s-electron of 8 Na-atom:

(B)

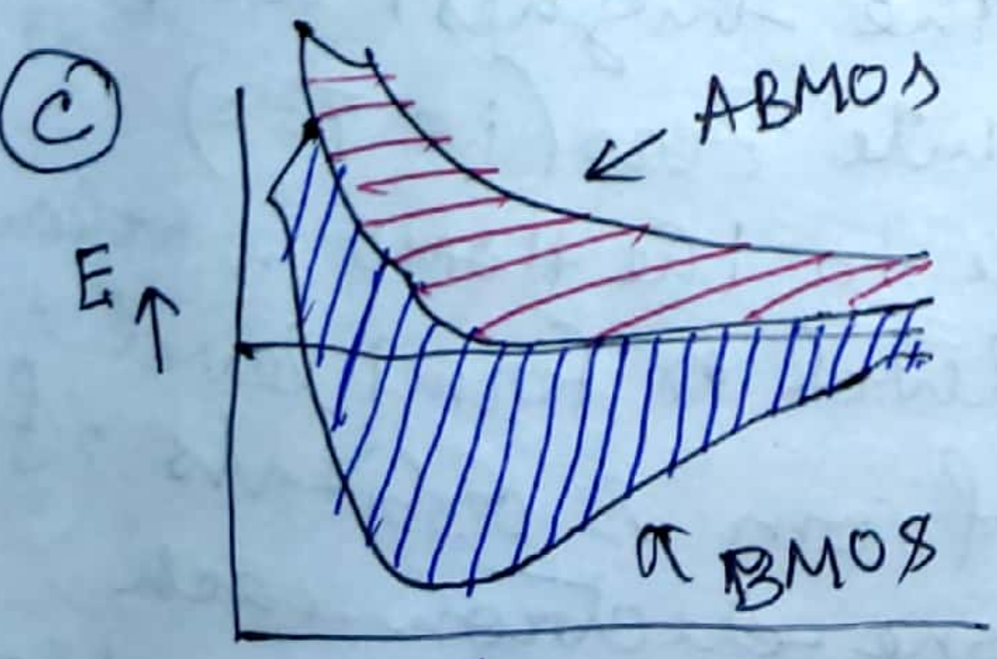




(c)

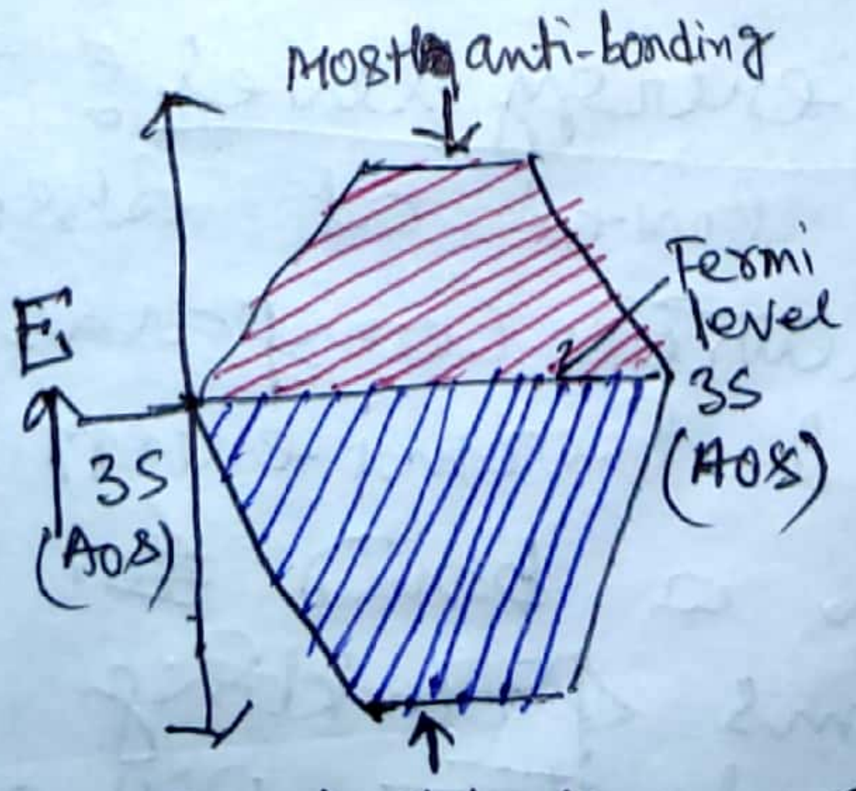
(d)

(C)

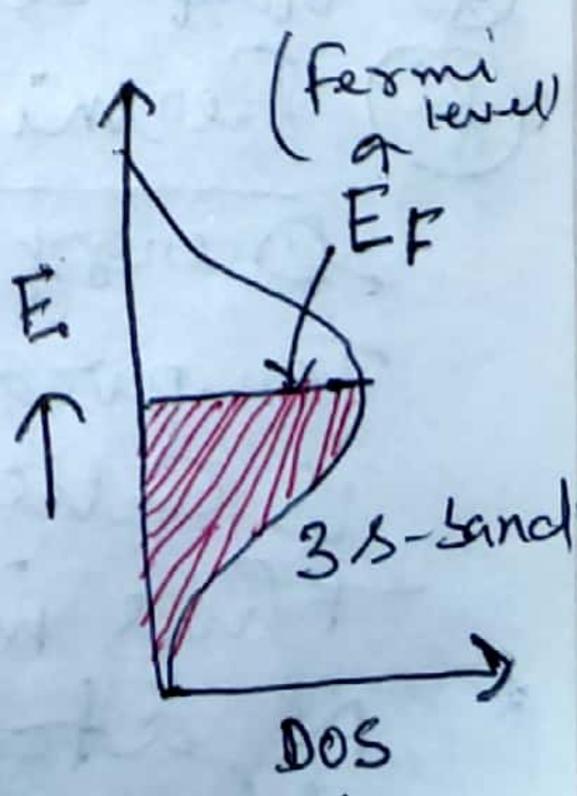


(e)

Interaction atom large number of Na-atoms (say 1 mole)

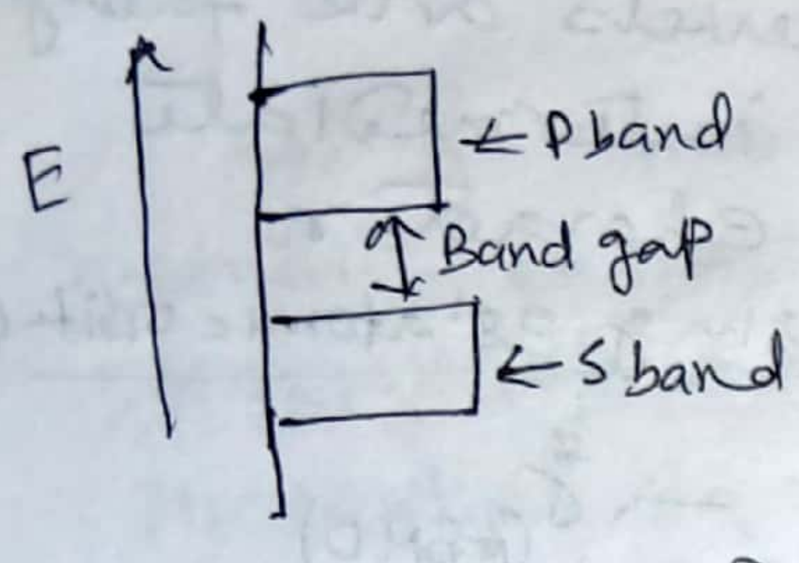


(f) Interaction of large no. of Na-atom

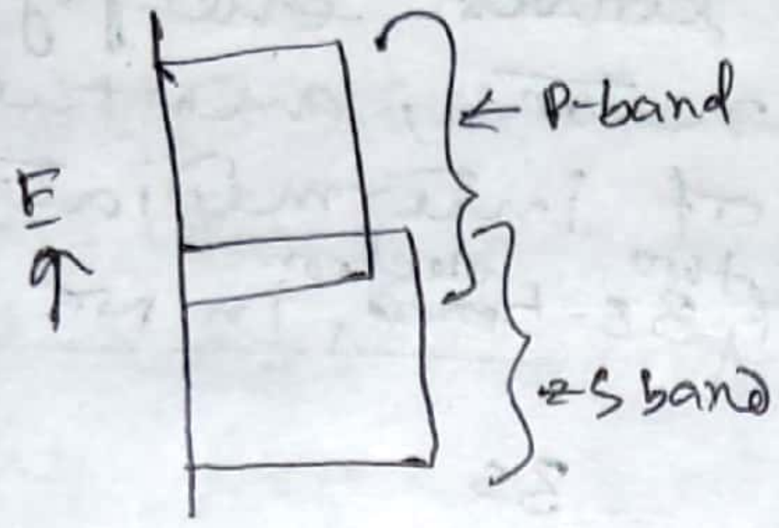


(g) Half-filled 3s-band of Na

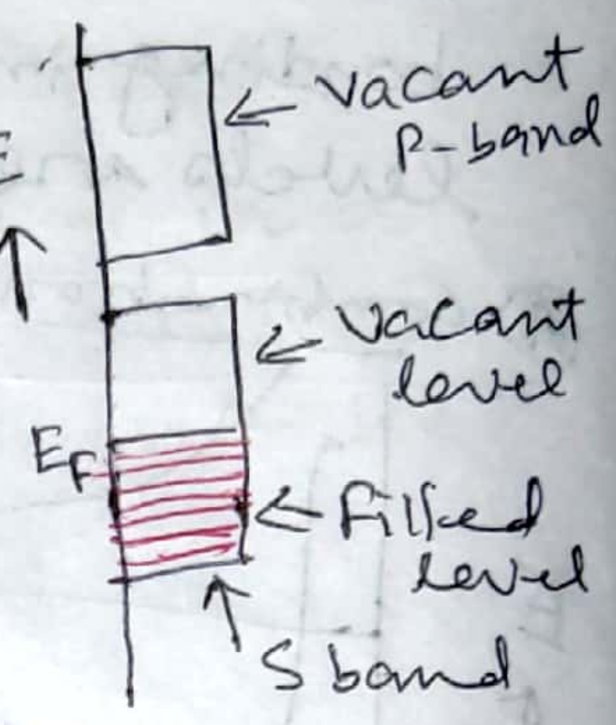
Band width: The band width depends on the degree of overlapping ~~wit~~ which is controlled by the energy difference of the involved atomic orbitals and internuclear seperation. Efficient overlap of the orbitals gives a large band width while inefficient overlap gives a narrow band width.



(a) S- and P- band do not overlap e.g. ~~bi atom~~



(b) Overlapping of S- and P- band e.g in Ca where interaction ~~bta~~ among atom are stronger



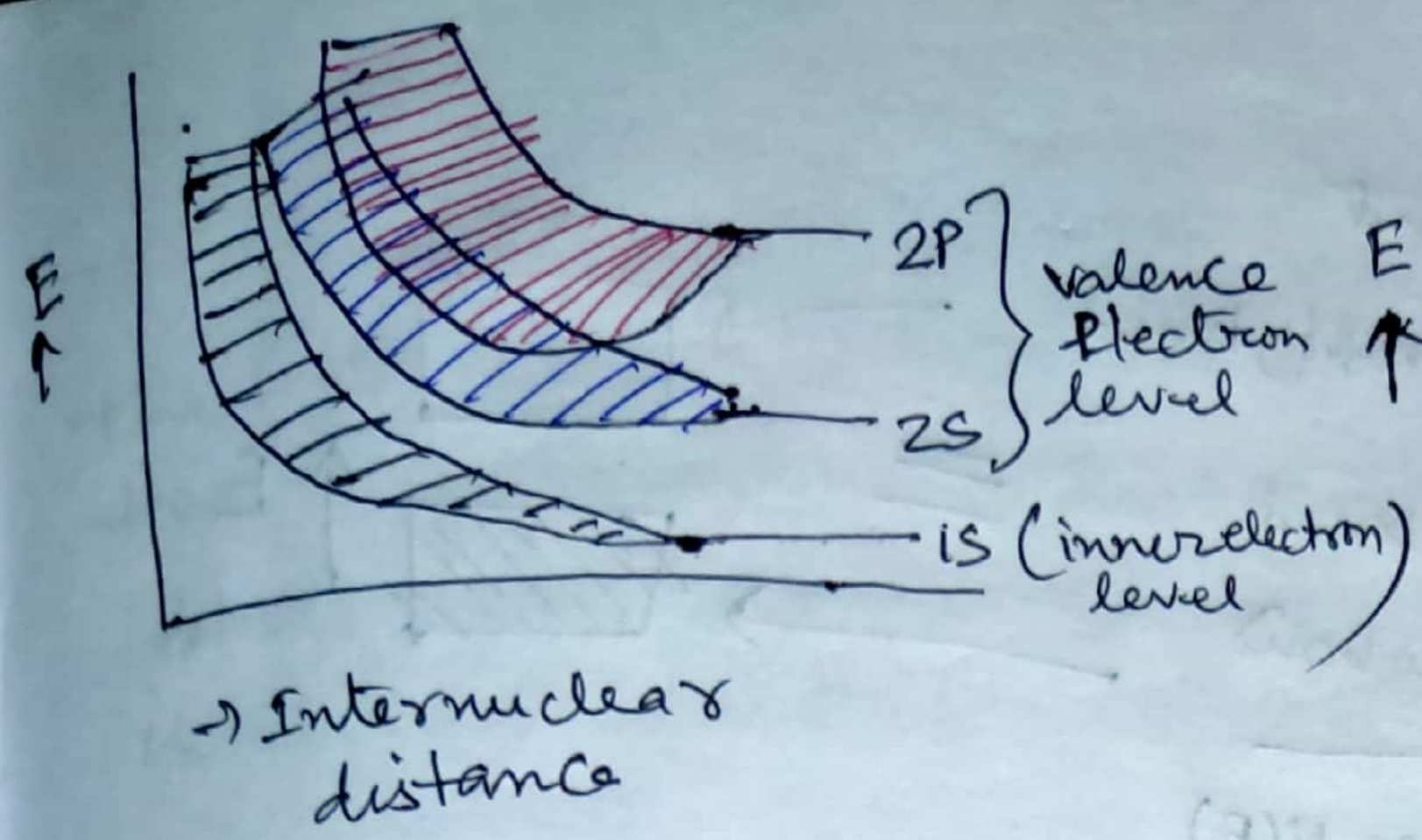
(c) for $ns^1 np^0$ configuration (e.g. K), the S-band remain just half filled and P-band remains vacant. Here vacant S-band act as conducting band.

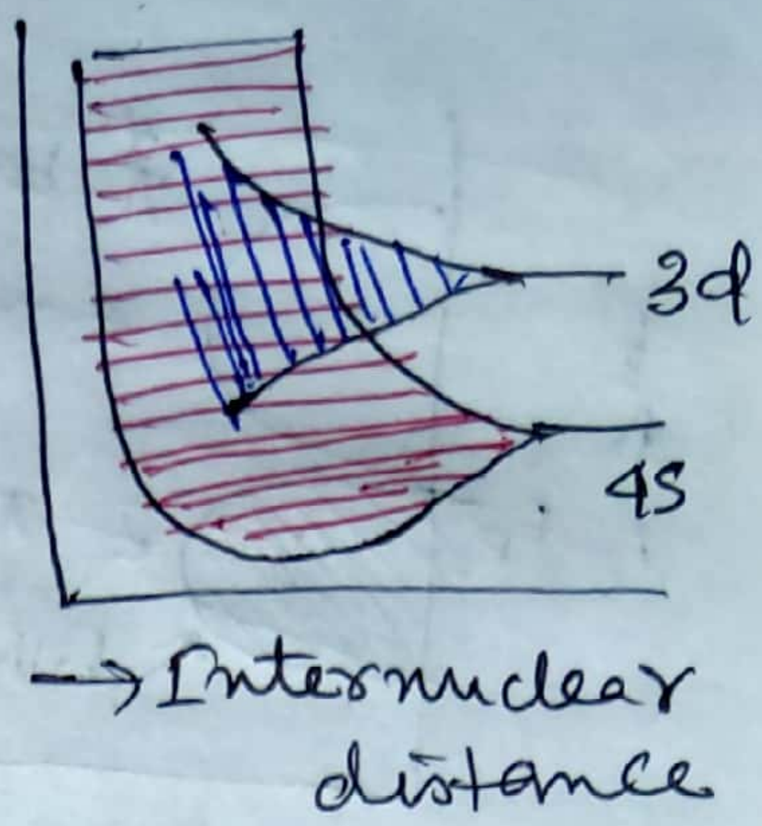
(*) Highest occupied filled band is called valence Band.

(*) lowest unoccupied band is called conduction band.

(*) Gap between two bands is called band gap (E_g)

(*) **Fermi energy level**: The highest occupied energy level at absolute zero (i.e $T=0$) Temperature, Comparable to the HOMO in molecule is called Fermi energy level or Fermi level. Thus in a band ~~for~~ from S orbitals of N atoms providing one electron each, the N electron will occupy the lower N/2 energy level and Fermi level lies ~~at~~ close to the Centre of the band.

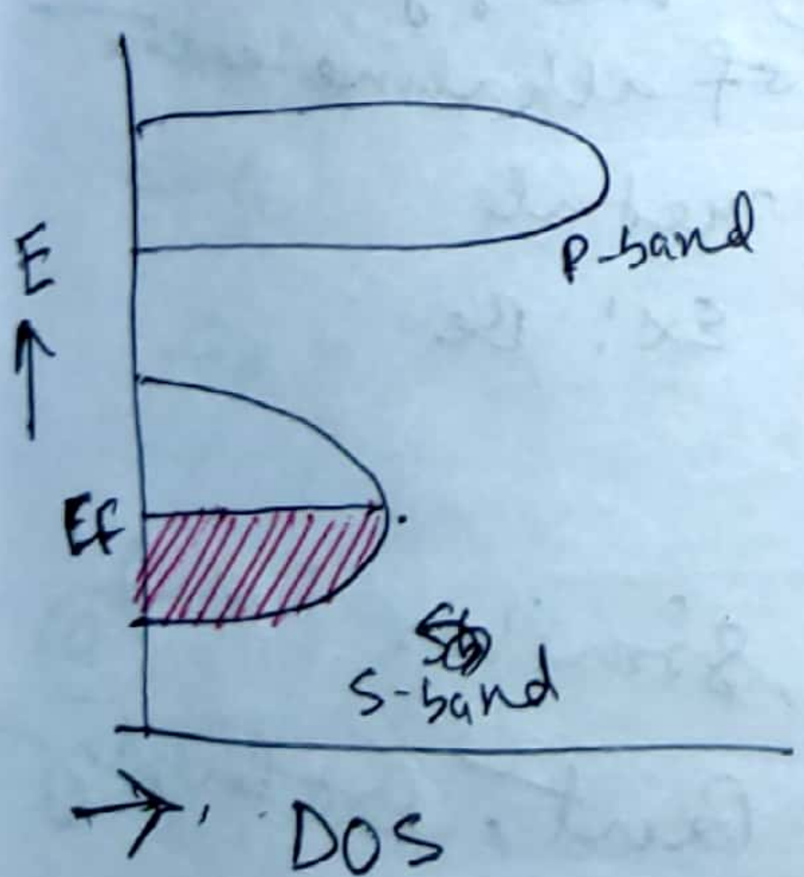


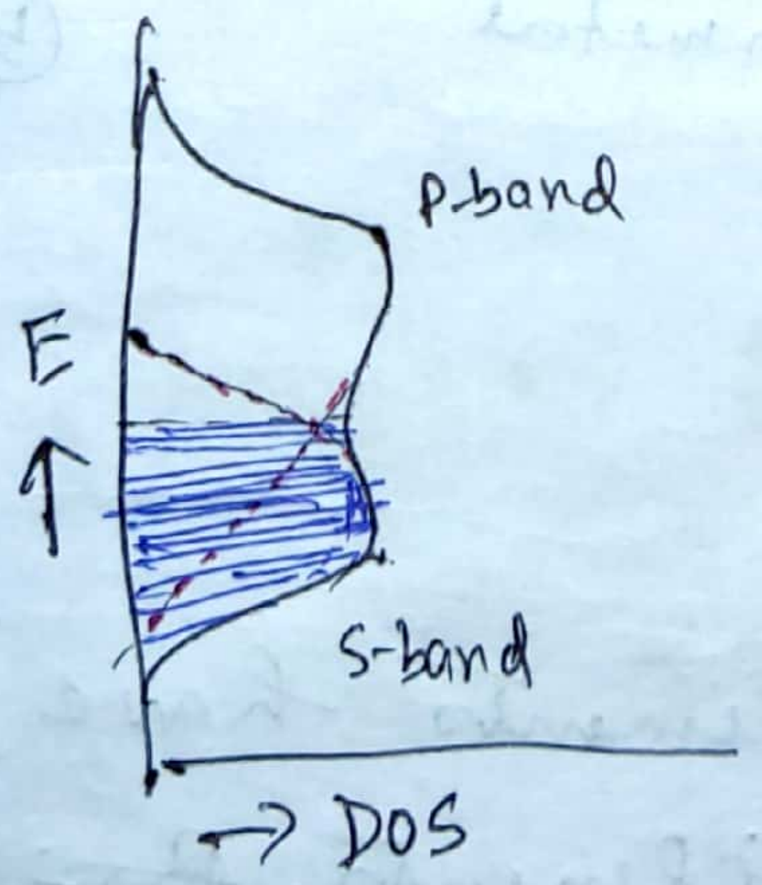


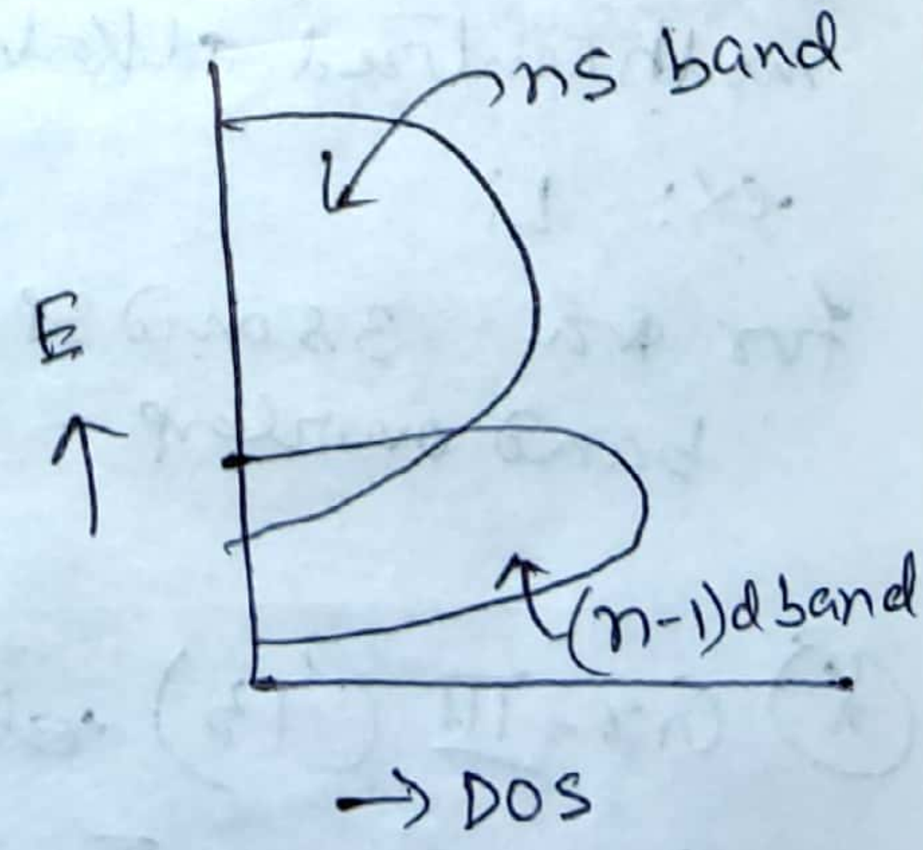
Density of states (DOS) in an energy band:

The number of energy levels per unit energy increment gives the measure of density of states. Thus DOS denotes the number of energy state per unit volume in the interval of E and E+dE. It may be noted that particular energy band is not uniformally packed. i.e. DOS is not same throughout the band. In three dimension, the centre of the band is most heavily populated (i.e DOS maximum) while the edges (both the top most and lowest) are poorly populated (DOS is less).

DOS is relatively higher in a narrow band. DOS is much higher for d-band in comparison to s- and p-band.



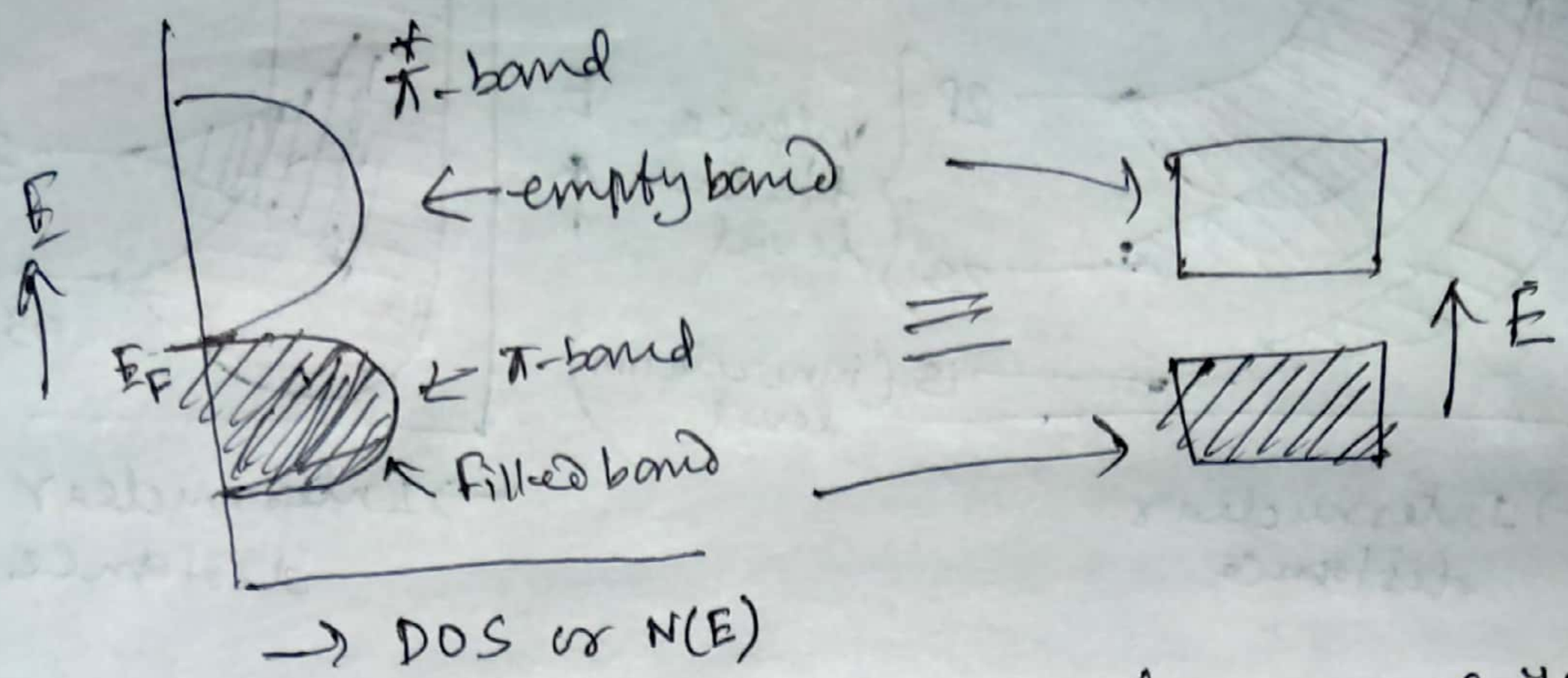




(a) DOS of of Na metal.

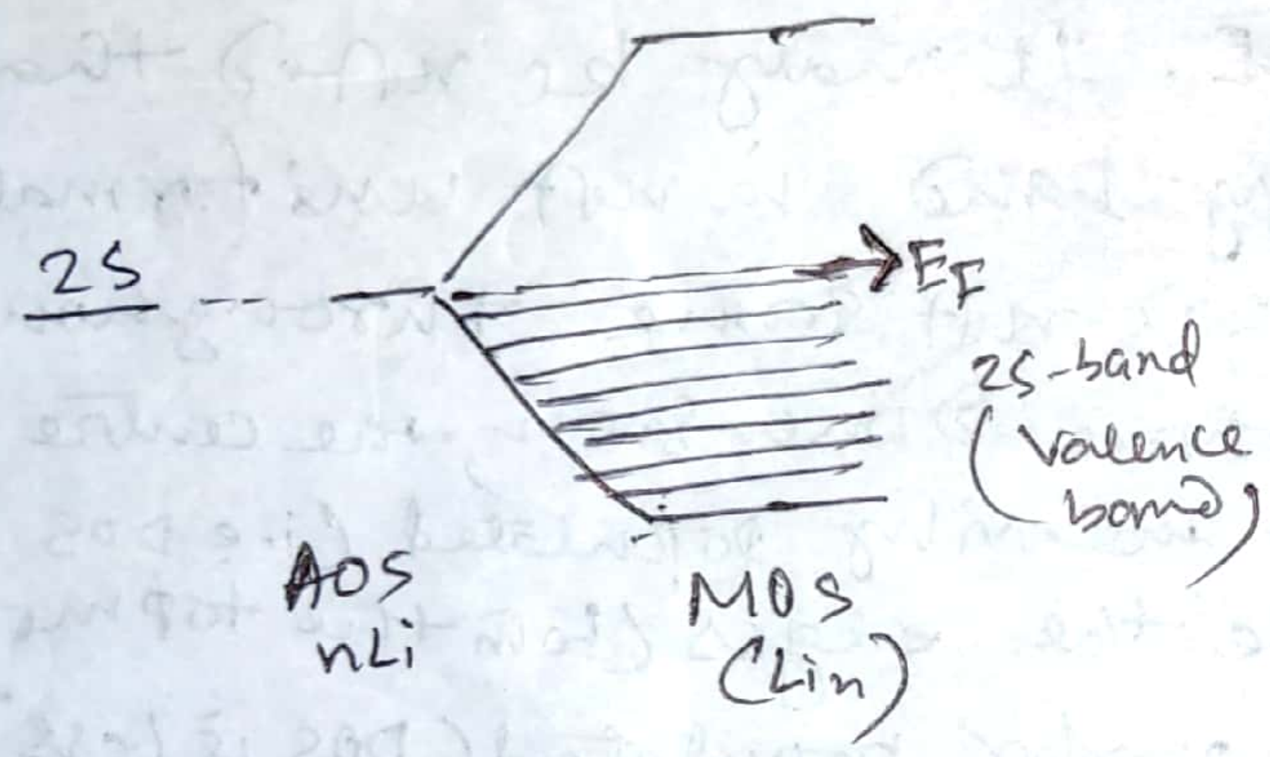
(b) DOS of Ca metal with mixing of filled s-band and vacant p-band

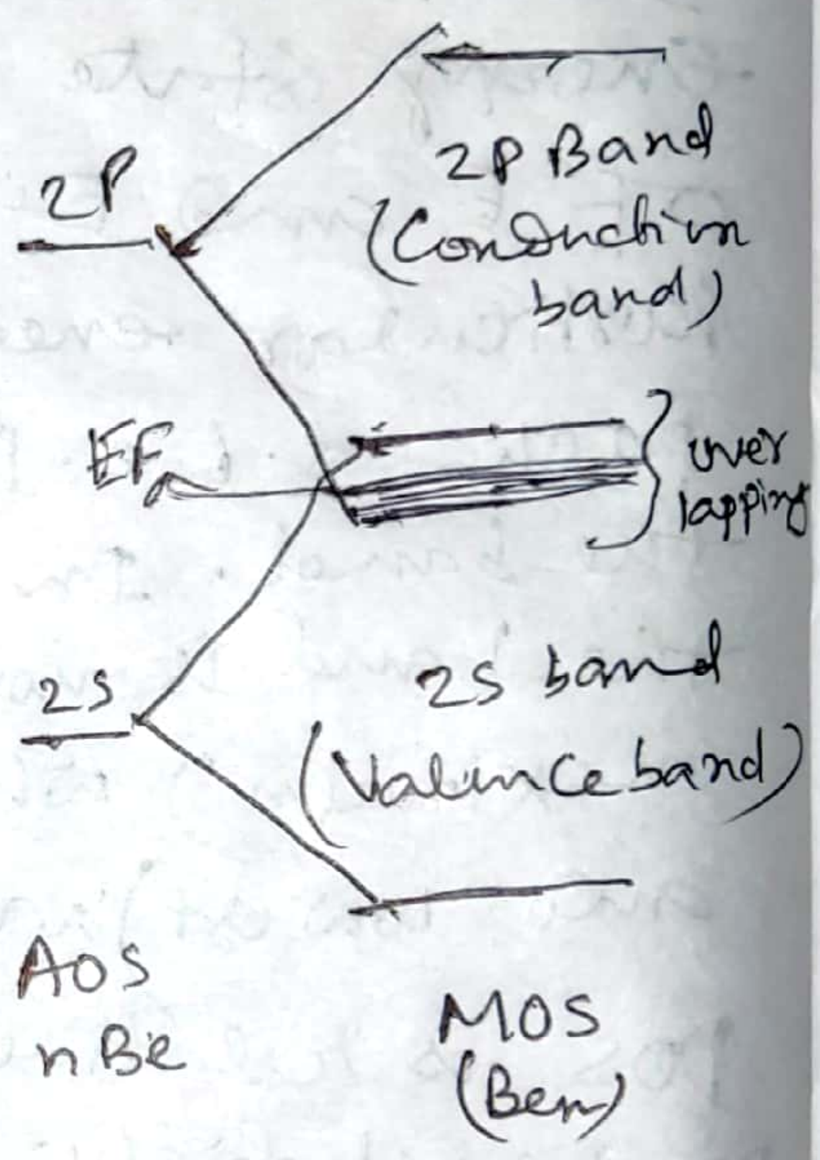
(c) Overlapping (n-1) d band and ns band in transition metal. Relative position of d and s band depends on d^n configuration.



(a) DOS of a typical semimetal (e.g. graphite)

Band Structure:



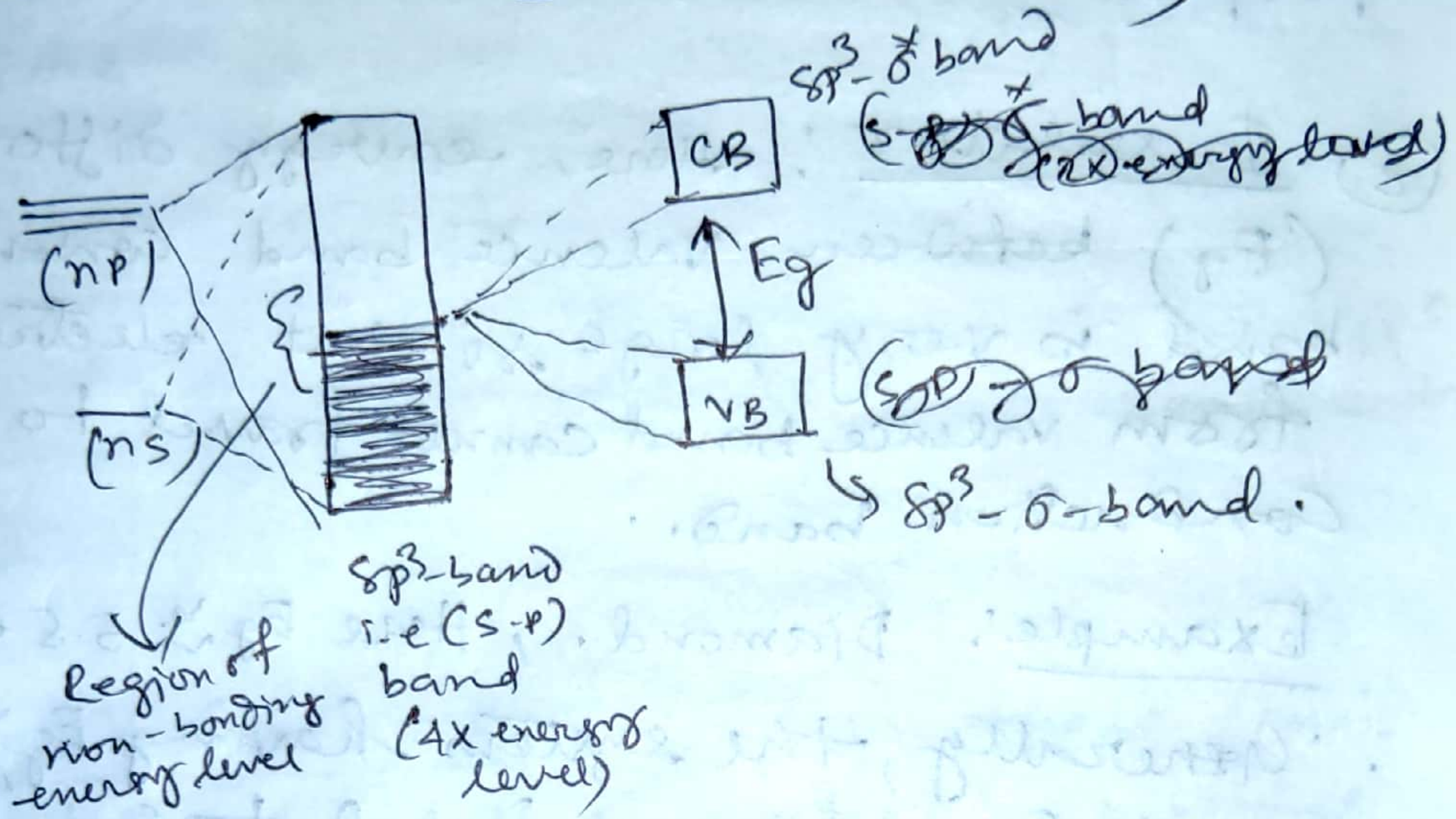


(a) Energy Band of multicentred alkali metal
ex: Li
for wa 3s and 3p band overlap

(b) Energy band of alkaline earth metal
Ex: Be

(*) Gr-III (13) elements have similar band like Gr.-I elements. ~~But~~ But, probably the filled ns band and partially filled np band overlap.

For Gr.- IV (14) elements (e.g. C, Si, Ge, Sn) the s-p band (say sp^3 hybrid) split into two bands where lower band is called BMOs (valence band) and higher band is called ABMOs (conduction band).



The energy gap decrease in the sequence C > Si > Ge

(*) Depending on the electrical conductivity solid's can be classified as conductor, insulator, semiconductor or semimetals. This conduction behaviour can be explained in terms of Band theory.

(a) Conductor: The substance in which the highest valence band is partially filled or the conduction band valence band are overlapping are described as conductors. Here E_g is zero.

Example: Na, K, Li; coinage metal (Cu, Ag, Au)

- Such metal one valence electron on each atom provides a half filled conduction band.

(b) Semimetals: In such cases, $E_g = 0$, but the junction of conduction and valence band DOS $= 0$.

Example: graphite, Bismuth, antimony and arsenic also shows semimetallic properties.

(c) Insulator: Here, energy difference (E_g) between valence band conduction band is very large so that electrons from valence band cannot travel to the conduction band.

Example: Diamond, Here $E_g \simeq 5.5$ eV

Generally, the system having $E_g > 3$ eV are referred to as insulators.

(d) Semiconductors: The substance which have electrical conductivity in between metal and insulator are called semiconductors.

In these case E_g is not too high. E_g values generally lie in between 1-3 eV

Semiconductor

- Elemental: Si, Ge
- Compound:
  - III-V (13-15): GaAs, GaP
  - II-VI (12-16): CdS,
  - IV-IV (14-16): SiC

Semiconductors

- Intrinsic
  (Here Semiconductor behaviour is inherent in nature)
  e.g. Ge
- Extrinsic or doped
  (Here Semiconductor behaviour is imposed by deliberate addition of impurities)
  - n-type Semiconductor
  - p-type Semiconductor

Extrinsic Semiconductor: In these Semiconductor; a small amount of impurities called ~~dopant~~ dopant, is added deliberately to a pure sample of intrinsic Semiconductor. This is why this type of Semiconductor is called extrinsic or doped Semiconductor. The method of addition of an impurity is called doping. Depending on the nature of impurity, the extrinsic Semiconductor can be classified as n-type and p-type.

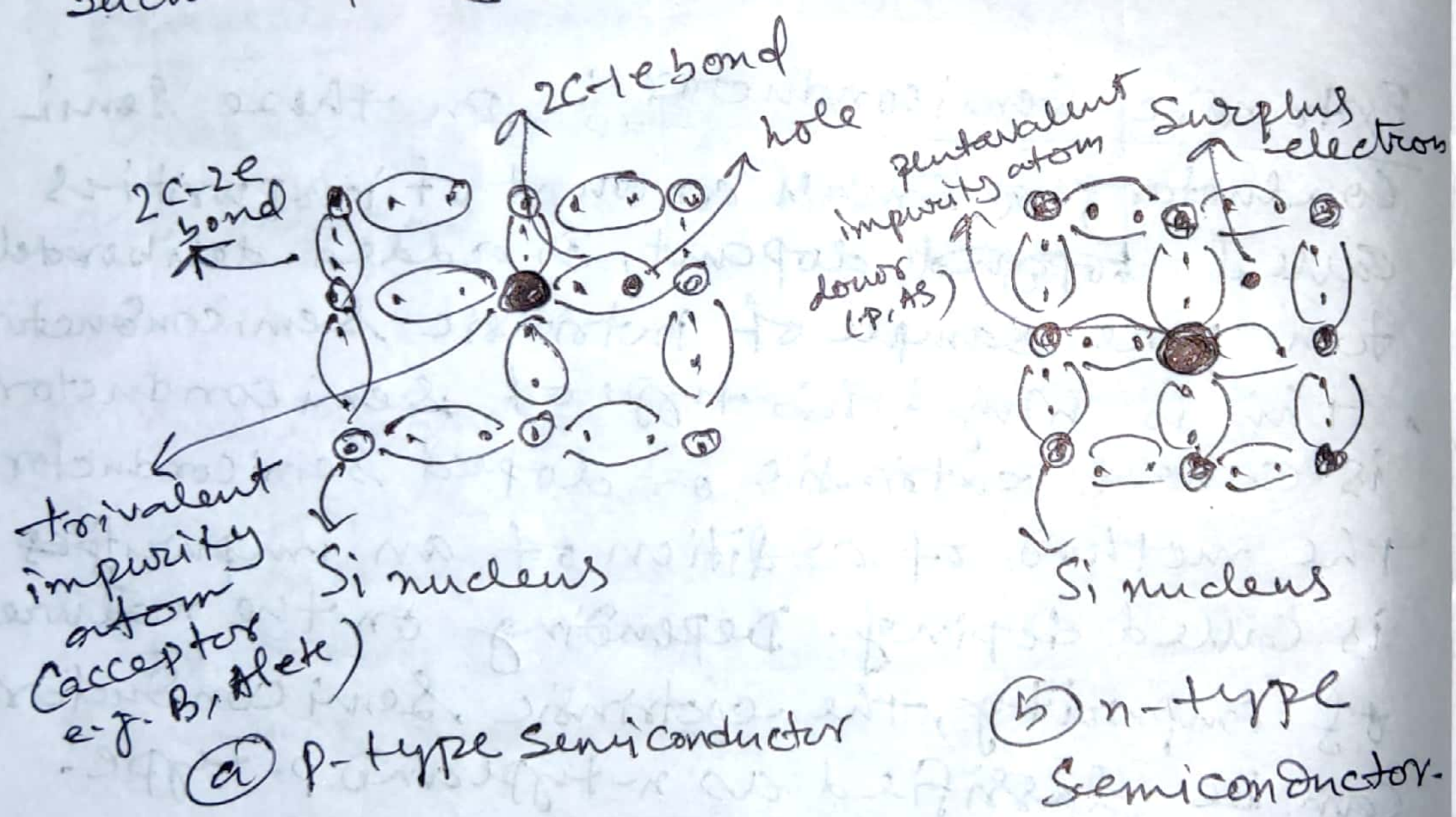
n-type Semiconductor: Addition of group-15 elements (e.g. As or Sb); with 5 valence electrons) to gr.-14 Semiconductors, (e.g. Ge) produce an n-type Semiconductor. These impurities place a filled energy ~~band~~ level just below an empty band (i.e CB band). Electrons from the ~~impurities~~ impurities can be easily excited to the

band. Hence the conductivity results the flow of electrons and hence it is called a negative or n-type semiconductor.

When gr-V (15) elements ~~doped~~ doped in gr-IV (14) semiconductor, the gr-V elements utilise its four electron out of five valence electron to bind tetrahedrally with the neighbouring Si or Ge-atoms.

Thus, the fifth electron on each impurities atom remain unbound and these are loosely held. this fifth electron is almost free and it can be easily ionised to give the electrons into the conduction band (CB).

Such impurity atoms are called donor atom



(a) p-type semiconductor

(b) n-type semiconductor.

Example of n-type semiconductor:

P, As, Sb doped Si or Ge

~~P-type~~

The conductivity $\sigma = e n_d \mu_e$

$n_d \rightarrow$ no. of donor atom.

p type Semiconductor:

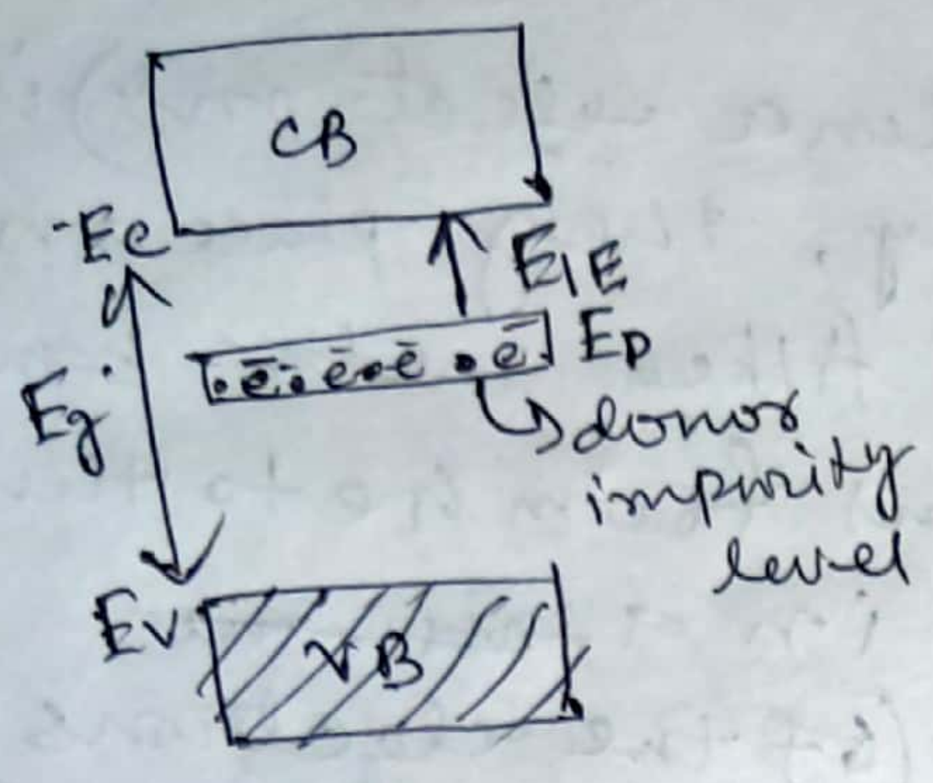
When Ga or In (3 valence electrons) is added to Ge as impurity, they place an empty band just above a filled ~~meta~~ band. (VB): passage of electrons from Ge to these empty bands results in a ~~[illegible]~~ number of vacant site (of the electrons) on Ge and renders it positively charged. the vacant sites are called positive holes. ~~Aj~~ Adjacent electrons move to fill these positive holes, creating further positive holes behind them. In effect, there is a migration of the positive hole and p-type semiconductor is obtained.

Example: Doping of B, Al, Ga, In to Ge or Si results p-type semiconductor.

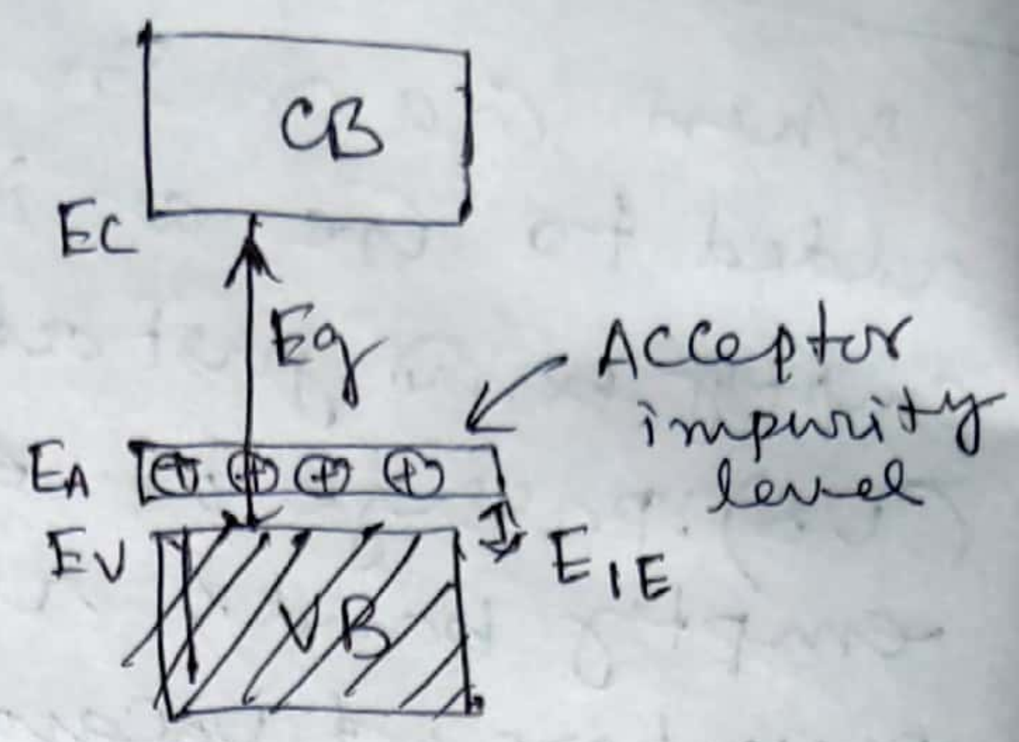
When B-atom ~~doped~~ substituted one Si-atom, then the B-atom binds with three Si-atom through normal 2c-1e bond while it binds with the fourth Si through an electron deficient 2c-1e bond. the electron deficient 2c-1e bond is equivalent to a positive hole signifying the missing of electron. The ~~[illegible]~~ number of positive holes is the ~~[illegible]~~ number of impurity atoms doped. the positive holes remain in a level called impurity acceptor level close to the VB of Ge. positive holes in the VB are the majority carrier of electricity.

Conductivity $\sigma_p = e n_a \mu_h$

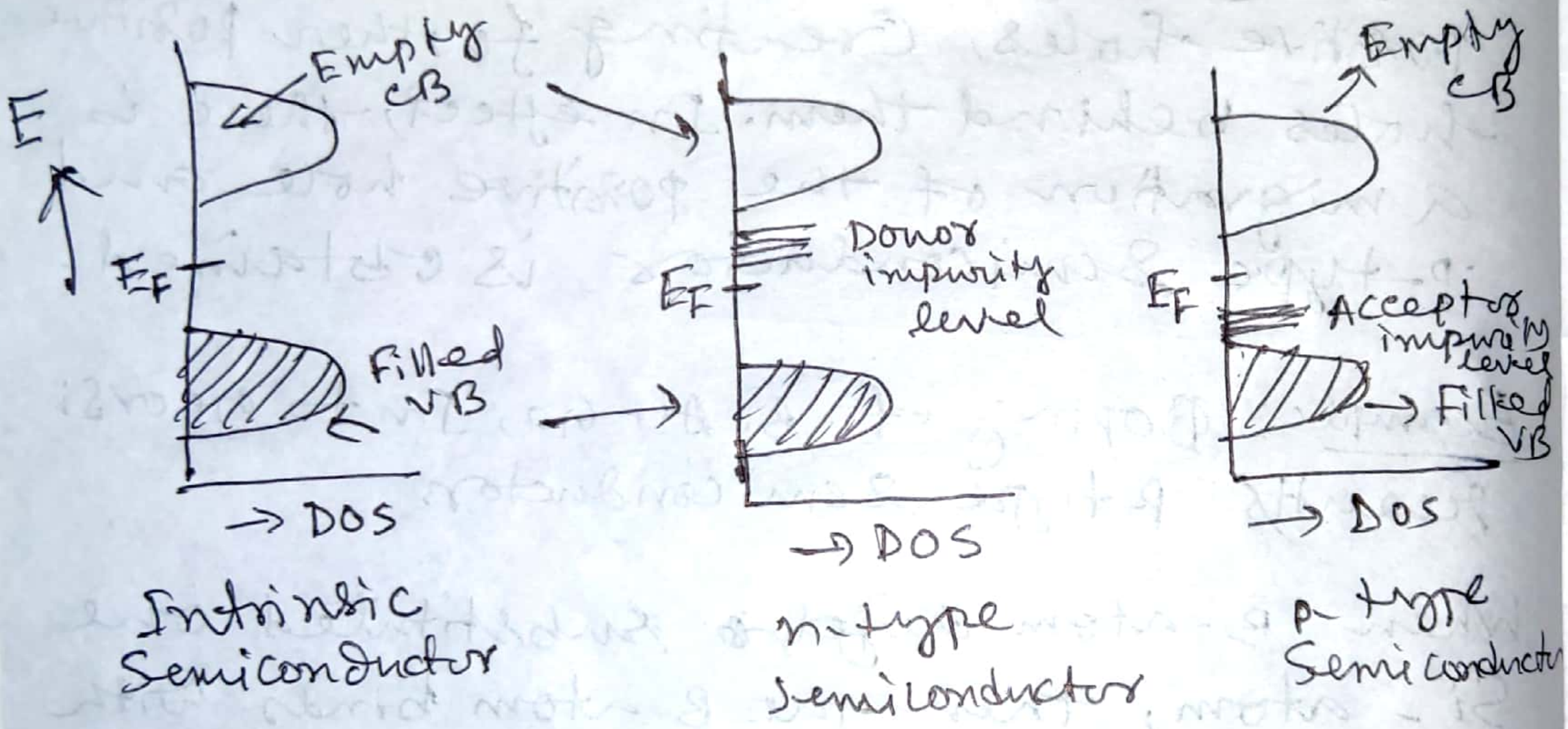
$n_a \rightarrow$ no. of acceptor atom.



n-type Semiconductor



p-type Semiconductor

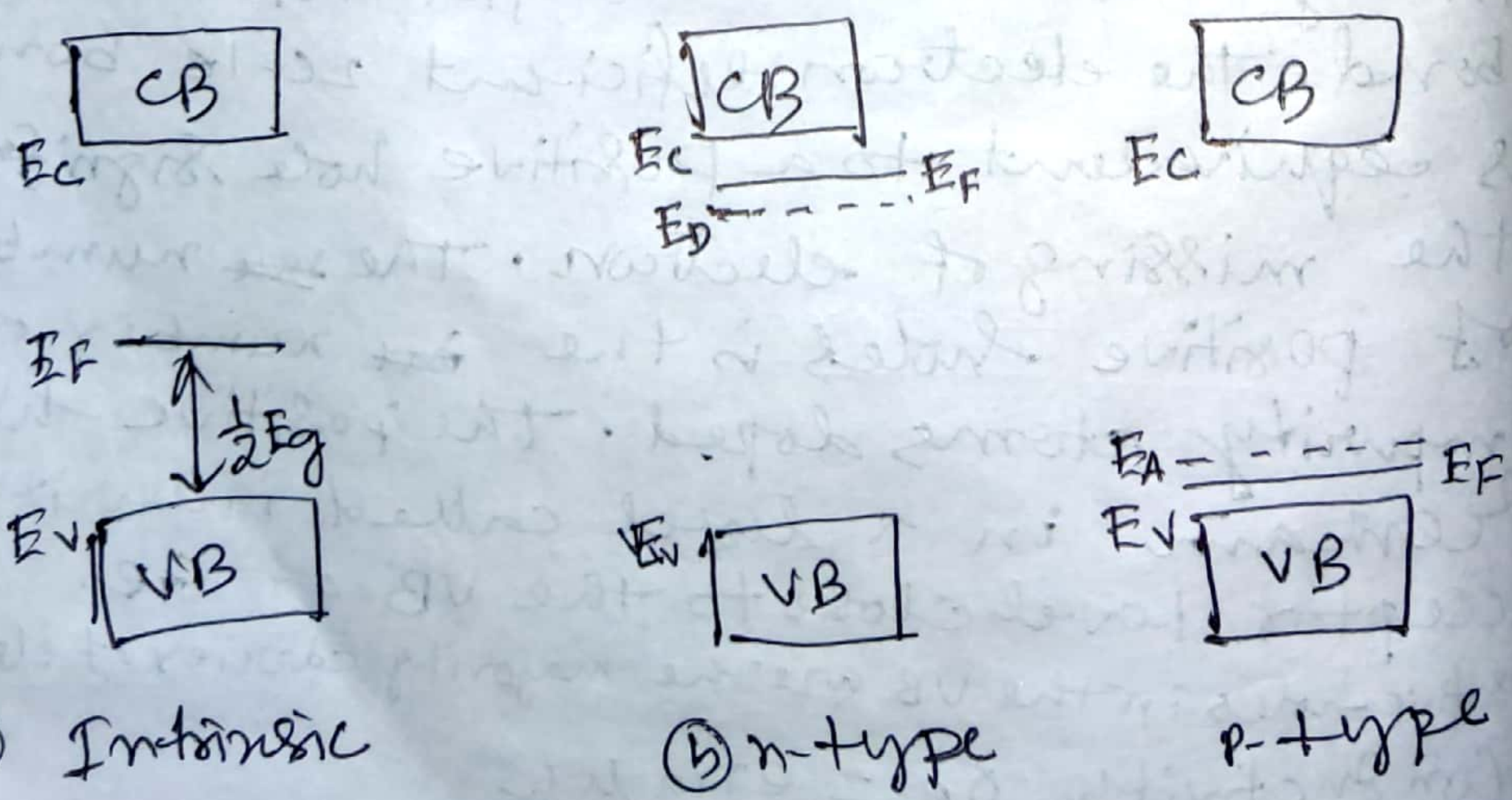


Intrinsic Semiconductor

n-type Semiconductor

p-type Semiconductor

Position of Fermi level for extrinsic semiconductor



(a) Intrinsic (b) n-type p-type