

Electronic Devices  
Semester III EC/TC  
Course Code : 18EC33

**Module 1.**

Bonding forces in solids, energy bands, metals, semiconductors and insulators, direct and indirect semiconductors, electrons and holes, intrinsic and extrinsic materials, conductivity and mobility, drift and resistance, effect of temperature and doping on mobility, Hall effect.

## 1.1 Basic structure of atom

Atom is the smallest indivisible unit. The structure of the Helium atom is shown in Fig 1.1 .

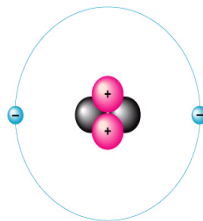


Fig 1.1 Helium atom

## 1.2 Electron Shells

Following points about electrons are useful:

1. Atomic number = number of Electrons
2. Electrons vary in the amount of energy they possess, and they occur at certain energy levels or **electron shells**.
3. The shell may be thought of as an orbit, of the electron around the nucleus.
4. Electron shells determine how an atom behaves when it encounters other atoms
5. Shells are numbered 1,2,3... starting from the one closest to nucleus or K,L,M,....
6. Each shell contains a fixed number of e-
7. In principle a shell can hold  $2n^2$  electrons . So first shell can hold 2, second shell 8, third shell 18 and so on .
8. Since nucleus is positive, the e-s are attracted to it. So the lower shells get filled up first .
9. The e-s in the outermost occupied shell determine the chemical properties of the atom. Its called the valence shell.
10. The outermost shell is stable when it contains 8 e-s.
11. The energy of the electron increases as the shell moves farther from the nucleus.

Examples of e-s in outermost shell are shown in Fig 1.2

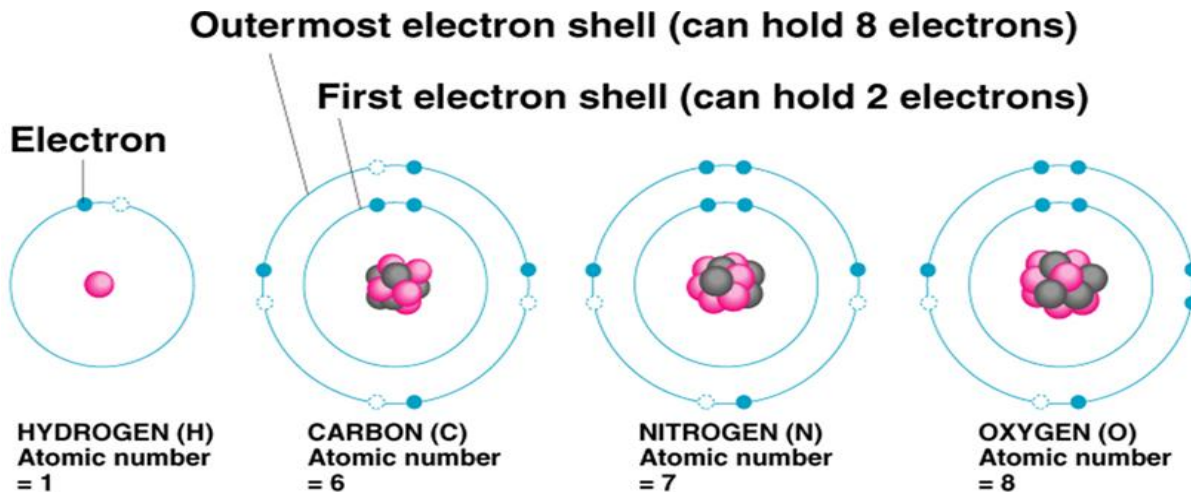


Fig 1.2 : e-s in outermost shell

The rule for stability states that “: Atoms tend to gain or lose electrons to have 8 electrons in the valence band for the atom to be stable.

Consider some examples.

1. What is configuration of N (7)?
  2. Ar (18)?
  3. Ga (31)?
- The number in the bracket indicates the atomic number.

The answer is shown in Fig 1.3

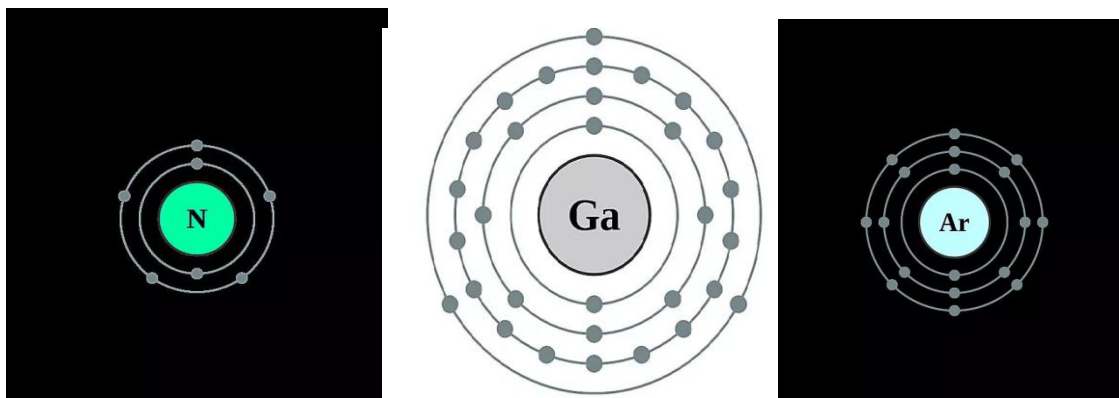


Fig 1.3 : Configuration of different atoms

## 1.4 Periodic-Table

A chart of the **chemical elements** that displays them in rows horizontally in order of increasing atomic number and vertically according to similarity of the **chemical** properties of their atoms. The periodic table is shown in Fig 1.4.

H 1																	He 2																												
Li 3	Be 4	Periodic Table										B 5	C 6	N 7	O 8	F 9	Ne 10																												
Na 11	Mg 12											Al 13	Si 14	P 15	S 16	Cl 17	Ar 18																												
K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36																												
Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54																												
Cs 55	Ba 56	La 57	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	At 85	Rn 86																												
Fr 87	Ra 88	Ac 89	Rf 104	Db 105	Sg 106	Bh 107	Hs 108	Mt 109	Ds 110	Rg 111	Cn 112	Nh 113	Fl 114	Mc 115	Lv 116	Ts 117	Og 118																												
<table border="1"> <tr> <td>Ce 58</td> <td>Pr 59</td> <td>Nd 60</td> <td>Pm 61</td> <td>Sm 62</td> <td>Eu 63</td> <td>Gd 64</td> <td>Tb 65</td> <td>Dy 66</td> <td>Ho 67</td> <td>Er 68</td> <td>Tm 69</td> <td>Yb 70</td> <td>Lu 71</td> </tr> <tr> <td>Th 90</td> <td>Pa 91</td> <td>U 92</td> <td>Np 93</td> <td>Pu 94</td> <td>Am 95</td> <td>Cm 96</td> <td>Bk 97</td> <td>Cf 98</td> <td>Es 99</td> <td>Fm 100</td> <td>Md 101</td> <td>No 102</td> <td>Lr 103</td> </tr> </table>																		Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	Lu 71	Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 99	Fm 100	Md 101	No 102	Lr 103
Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	Lu 71																																
Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 99	Fm 100	Md 101	No 102	Lr 103																																

Fig 1.4 : Periodic Table

## 1.5 Bonding

Two Major Types of Bonding are present between the atoms.

- **Ionic Bonding**
  - forms ionic **compounds**
  - transfer of  $e^-$  takes place.
- **Covalent Bonding**
  - forms **molecules**
  - sharing  $e^-$

Electronegativity is a chemical property which describes how well an atom can attract an electron to itself. Values for electronegativity run from 0 to 4. Electronegativity is used to predict whether a bond between atoms will be ionic or covalent. It can also be used to predict if the resulting molecule will be polar or nonpolar. Electronegativity can be shown by a table as shown in Fig 1.5.

# ELECTRONEGATIVITY

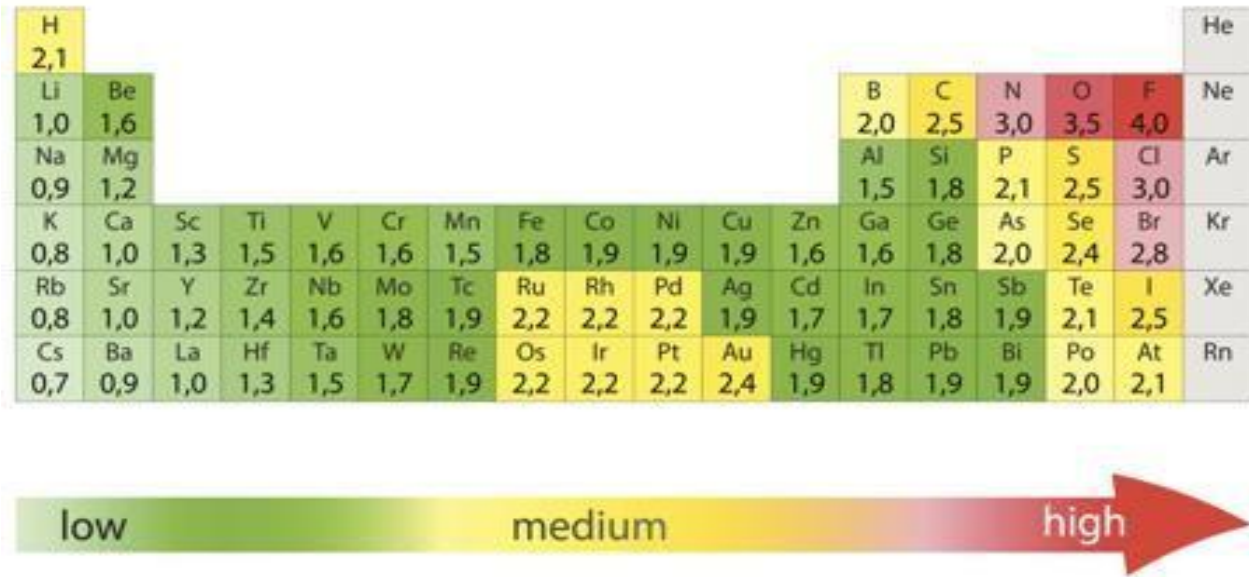
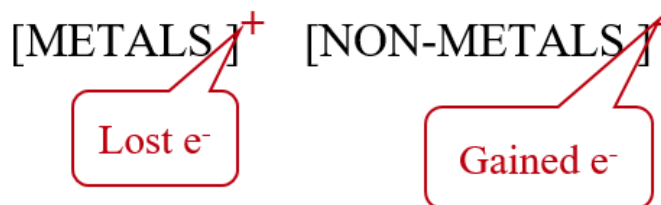


Fig 1.5 Table of Electronegativity

## In ionic bonds:

1. Electrons are transferred between valence shells of atoms
2. Ionic compounds are made of ions, not molecules
3. Ionic compounds are called salts or crystals.

**Always** formed between metals and non-metals



A typical example of an ionic bond is Sodium chloride (NaCl) . The bonding is shown in Fig 1.6.

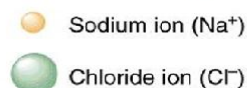
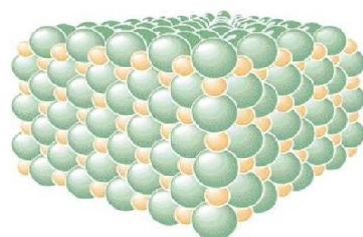
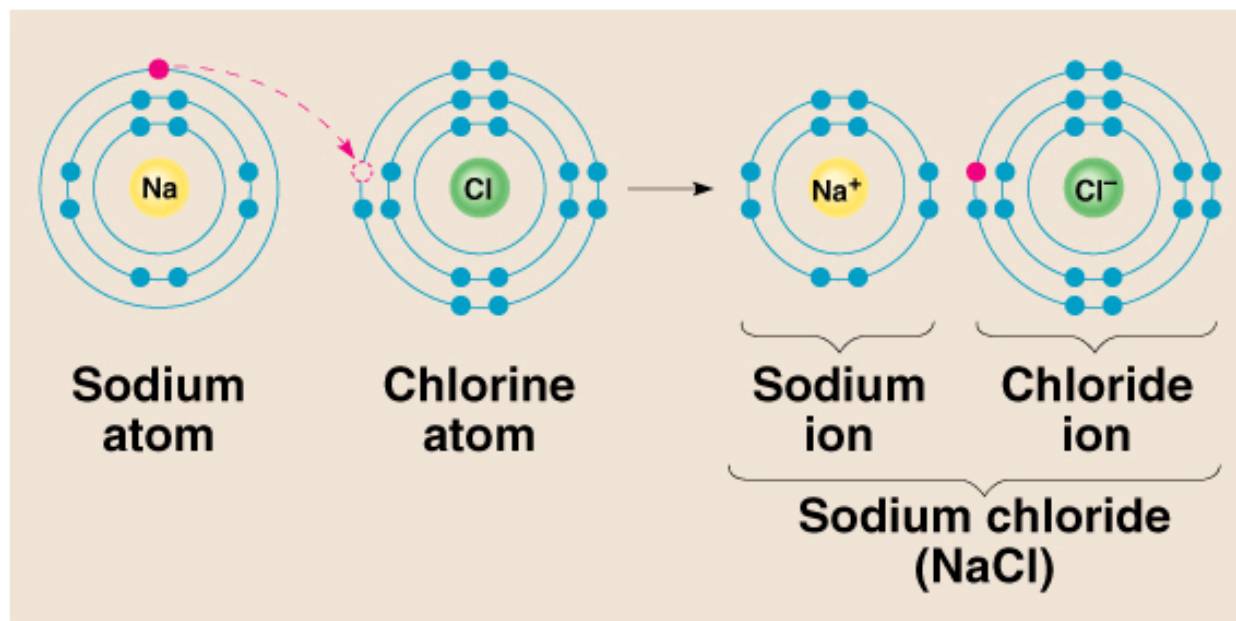


Fig 1.6 : Sodium Chloride

How is the bonding ?

1. Atomic number of sodium is 11. It has one e- in outermost orbit.
2. Atomic number of chlorine is 17. It has seven e-s in outermost orbit.
4. Na becomes (+ve) after giving up electron and Cl becomes (-Ve) after receiving an electron.
5. Each  $\text{Na}^+$  ion exerts attractive force on neighbouring  $\text{Cl}^-$  ions.
6. In the lattice NaCl structure all e-s are tightly bound to the atoms.
7. The outer shells are completely filled and have configurations similar to Ne and Ar. Since there are no loosely bound e-s .NaCl is an insulator.

### Properties of Ionic compounds

1. Hard solid @  $22^\circ\text{C}$

2. High MP temperatures
3. **Non**conductors of electricity in **solid** phase
4. **good** conductors in liquid phase or dissolved in water (aq)
5. Electronegativity is between 1.7 – 4.0
6. Ionic bonds are most often between metals and nonmetals.

### Some Typical Ions with Positive Charges (Cations)

Group 1	Group 2	Group 13
<b>H<sup>+</sup></b>	<b>Mg<sup>2+</sup></b>	<b>Al<sup>3+</sup></b>
<b>Li<sup>+</sup></b>	<b>Ca<sup>2+</sup></b>	
<b>Na<sup>+</sup></b>	<b>Sr<sup>2+</sup></b>	
<b>K<sup>+</sup></b>	<b>Ba<sup>2+</sup></b>	

### Covalent bonds

In covalent bonds pairs of e-s are shared between atoms.

They are formed between non-metal atoms

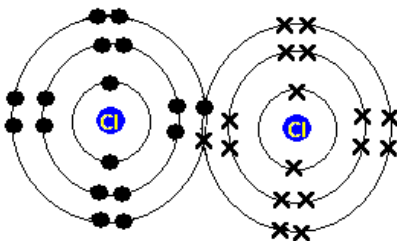
The electronegativity difference of the atoms should be <1.7. They form polyatomic ions.

Some key features are :

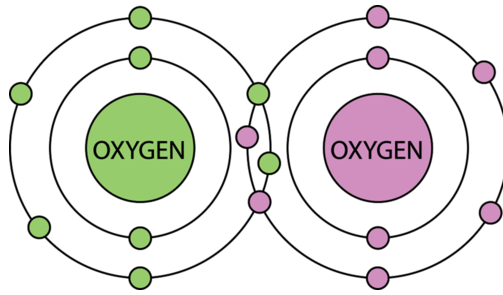
1. Between nonmetallic elements of similar electronegativity.
2. Formed by sharing electron pairs
3. Stable non-ionizing particles, they are not conductors at any state
4. Examples; O<sub>2</sub>, CO<sub>2</sub>, C<sub>2</sub>H<sub>6</sub>, H<sub>2</sub>

Some covalent bonds are shown in Fig 1.7.

### SINGLE covalent bond



### DOUBLE Covalent bond



### TRIPLE Covalent bond

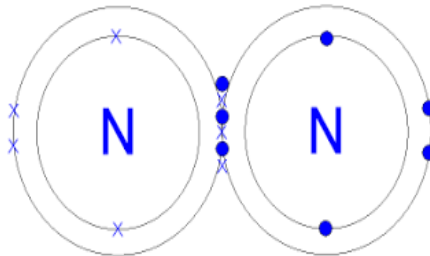


Fig 1.7 : Covalent bonds

In single covalent bond, two e-s are shared, in double 4 e-s are shared and in triple 6 e-s are shared.

There are two kinds of covalent bonds.

Polar covalent: the electrons are shared, but one atom is pulling on the electrons a lot more. The electrons spend more time around that atom.

Example:  $H_2O$ , shown in Fig 1.8.

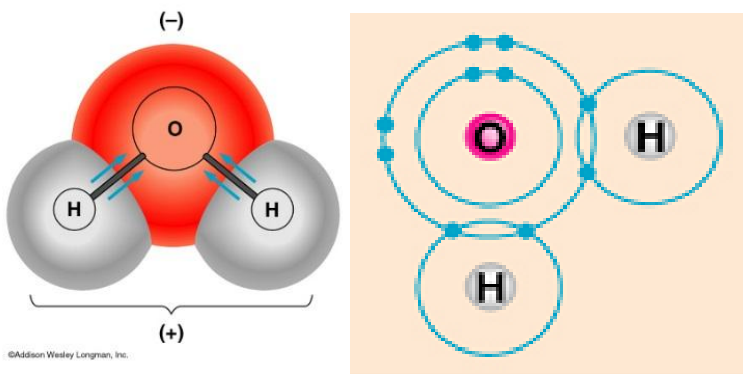


Fig 1.8 : Water molecule, polar covalent bond

Water is a *polar molecule* because oxygen is more electronegative than hydrogen, and therefore electrons are pulled closer to oxygen.

The other type is Nonpolar covalent: the electrons are evenly shared between the two atoms.

Example:  $H_2$  or  $Cl_2$



- 1) Covalent compounds generally have much **lower melting and boiling points** than ionic compounds.
- 2) Covalent compounds are **soft** (compared to ionic compounds)
- 3) **Covalent compounds tend to be more flammable than ionic compounds.**  
There are exceptions to this rule!
- 4) **Covalent compounds don't conduct electricity in water.**

### **Metallic bonds**

1. Bonds formed in metals. Holds the atoms strongly.
2. There is a cloud of electrons around the atoms.
3. Good conductors of electricity

Example : Na, Fe, Al, Cu etc.

The outer shell is partially filled, usually by no more than 3 electrons. They have a low ionization potential. Hence, the valence electrons can be delocalized throughout the metals. Delocalized electrons are not associated with a particular nucleus of a metal, instead, they are free to move throughout the whole crystalline structure forming a "sea" of electrons. The electrons and the positive ions in the metal have a strong attractive force between them. This holds the lattice structure together, as shown in Fig 1.8. Therefore, metals often have a high melting or boiling points. Metals exhibit properties such as malleability, ductility, conduction of heat and electricity, lustrous etc.

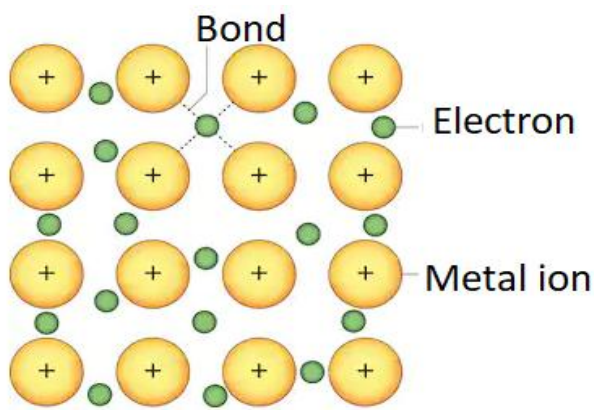


Fig 1.8 : Metallic bonds

## 1.6 Energy Bands

- When isolated atoms are brought together to form solid, interactions occur between neighboring atoms forming bonds.
- The forces of attractions and repulsion between the atoms will find a balance at the proper atomic spacing for the particular crystal.
- The changes that occur in the e- energy, give rise to different electrical properties of solids.
- In solids the molecules are so closely arranged that the electrons of the atoms of the molecules, tend to move into the orbitals of neighbouring atoms. Hence, the electron orbitals overlap.
- Instead of discrete energy levels, the energy levels overlap to form a band of levels. These set of energy levels, that are closely packed are called Energy Bands.
- Pauli's Exclusion principle says that no two electrons in an interacting system have the same orbital configuration. Therefore the band consists of a number of closely spaced energy levels.
- The discrete energy levels of isolated atoms are split into new levels belonging to the pair, rather than the individual atoms.

### 1.6.1 Concept of Shells and Sub-shells

- Each of the allowed electron orbits is assigned a Principal quantum number  $n$  (1,2,3...) or the letters (K,L, M...). 1(K) is closest to nucleus.
- All the orbitals that have the same value of  $n$  belong to a shell.
- Inside each shell there may be sub-shells corresponding to different rate of rotations, orientation and spin of the electrons.
- The angular momentum quantum number,  $l$ , describes the shape of the orbital, is associated with the angular momentum of the electron and tells which sub-shells are present in the principal quantum number. It divides the shells into sub-shells.  $l$  has values from 0 to  $n-1$ .
- There are four different sub-shells - s, p, d, f. s is spherical; p has three orbitals, along x,y,z axis. s has lowest energy and f has highest energy
- Each subshell can hold a maximum number of electrons :
- s- 2 ; p - 6; d- 10; f - 14.
- The shell number is equal to number of possible subshells. So shell 1 (K) can have only one subshell namely 1s. Similarly we have 2s,2p; 3s,3p and 3d and so on
- Each subshell has number of orbitals. Orbital is region of space where an e- can be found. Only two e-s are possible per orbital

How do we know the electronic structure of an atom?

Three RULES determine the structure.

RULE 1: Lowest energy orbitals fill first. Filling Pattern would be 1s, 2s, 2p, 3s, 3p, ... Fig 1.8 helps to know the relative energy levels of the orbitals.

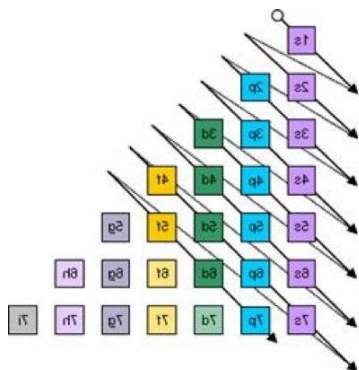


Fig 1.8 : Energy levels of orbitals

RULE 2 : Pauli's Exclusion Principle : Only two e-s are permitted per orbital, with opposite spins. Two e-s with opposite spins in same orbital are said to be paired.

RULE 3: Hund's rule : Most stable arrangement of e-s in a subshell is when the maximum number of unpaired e-s exist, possessing same spin directions.

Example :

1. Chlorine – 17 -  $1s^2 2s^2 2p^6 3s^2 3p^5$

2. How many unpaired e-s are present in Oxygen atom ?

Oxygen has 6 valence e-s –  $2s^2 2p^4$ .

So e-s fill  $P_x, P_y, P_z$  (Hund's rule) and then again  $P_x$ . So there are two unpaired e-s.

### 1.7 Schrodinger Wave Equation for Electron

In it electron is described as a three dimensional wave in the electric field of a positively charged nucleus. The probability of finding an electron at any point around the nucleus can be determined by the help of Schrodinger wave equation which is,

$$\nabla^2 \Psi + (8\pi^2 m / h^2) (E - V) \Psi = 0$$

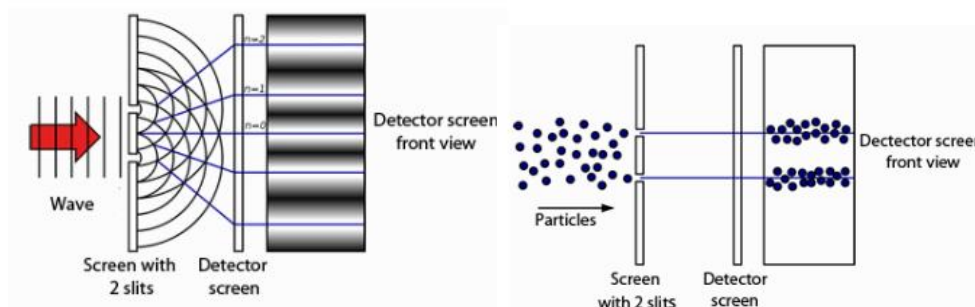
$h$  – Planck's constant,  $E$  – Total energy,  $V$  – potential energy and  $\Psi$  – amplitude of wave,  $\nabla^2$  – Laplacian Operator,  $m$  – mass of e-

It is only the particle that is modelled as a wave. Their charge is a particle. Meaning, the position of the e- is represented as a wave but once the e- is found, all of its charge will be in that location.

“Schizophrenic Behaviour” .....

De –Borglie Postulated that not only light but also atomic particles have wave-particle duality!!

The wave and particle natures are shown in Fig 1.9.



Wave behavior

Particle Behavior

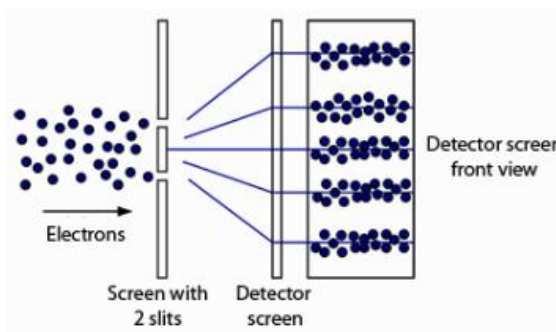


Fig 1.9 Electron behavior

So what does it mean if electrons are represented as waves??

- ✓ The atomic orbital is a wave function which describes how electron is distributed around the nucleus.
- ✓ Molecular orbital (MO) is a wave function is the distribution of the electron over all the nuclei of a molecule.
- ✓ If MO is large near an atom, there is a high probability of finding e- near it. If it is zero there is no chance of finding e- there.
- ✓ In Linear combination of atomic orbitals (LCAO) approximation, each MO is constructed from a superposition of atomic orbitals belonging to the atoms in the molecule.
- ✓ The size of the contribution of an orbital from a particular atom indicates the probability that the electron will be found on that atom.

- ✓ The actual shape of the molecular orbital (and indirectly its energy) is a reflection of the extent to which the individual atomic orbitals interfere with one another either constructively or destructively.

### 1.7.1 Linear Combination of Atomic Orbitals (LCAO)

- A **linear combination of atomic orbitals** or **LCAO** is a superposition of atomic orbitals .

Conditions for effective linear combination of atomic orbitals:

- The combining atomic orbitals should have same or nearly same energy
- The atomic orbitals should have the same symmetry about the molecular axis

Superposition of two orbitals are of two types :

#### 1. Bonding Orbital

The amplitudes of the two atomic orbitals interfere constructively with one another. So there is an enhanced amplitude between the two nuclei. As a result, any electron that occupies this molecular orbital has a high probability of being found between the two nuclei, and its energy is lower than when it is confined to either atomic orbital alone.

#### 2. Anti bonding orbital

Taking the difference of the two atomic orbitals, however, results in destructive interference in the inter-nuclear region where the amplitude of one orbital is subtracted from the other. This destructive interference is complete on a plane midway between the nuclei, and hence there is a nodal plane—i.e., a plane of zero amplitude—between the nuclei. Any electron that occupies this orbital is excluded from the inter-nuclear region, and its energy is higher than it would be if it occupied either atomic orbital.

The orbitals are shown in Fig 1.10. The orbitals in Hydrogen atom are shown in Fig 1.11.

## Linear Combination of Atomic Orbitals (LCAO) Form Molecular Orbitals (MO) = Hybridization

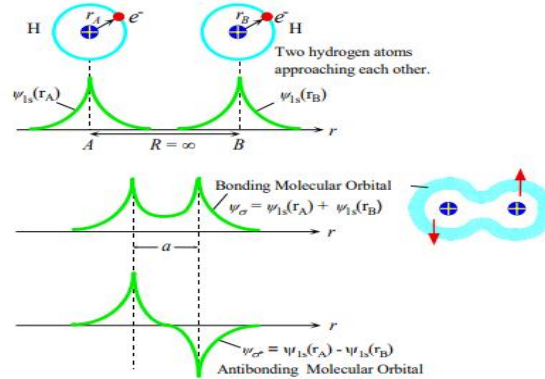
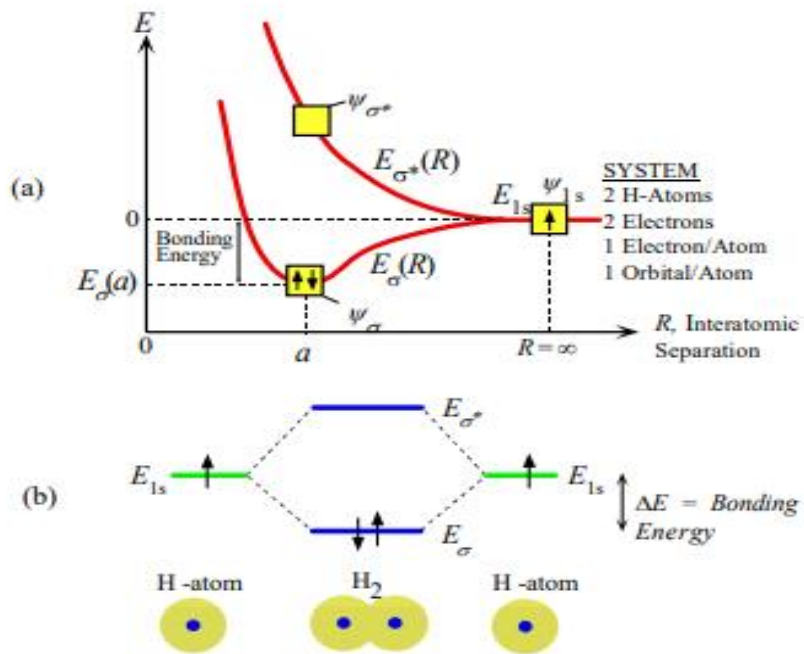


Fig. 4.1: Formation of molecular orbitals, bonding and antibonding ( $\psi_{\sigma}$  and  $\psi_{\sigma^*}$ ) when two H atoms approach each other. The two electrons pair their spins and occupy the bonding orbital  $\psi_{\sigma}$ .

From *Principles of Electronic Materials and Devices, Second Edition*, S.O. Kasap (© McGraw-Hill, 2002) <http://Materials.USask.ca>

Fig 1.10 : Bonding and anti-bonding orbitals.



1.11 : Orbitals in Hydrogen atom.

### 1.7.2 : Energy bands

- ❖ If instead of 2 e-s we bring N e-s together N atoms, we get N distinct LCAO, and N closely spaced energy levels in a band.

- ❖ When two atoms are far apart they have similar electronic structures, But when they come close, the electron waves overlap.
- ❖ The exclusion principle dictates that no two electrons in a given interacting system may have the same quantum state
- ❖ So there must be at most one electron per level after there is a splitting of the discrete energy levels of the isolated atoms into new levels belonging to the pair rather than to individual atoms.

Consider SILICON whose Electronic structure is  $1s^2 2s^2 2p^6 3s^2 3p^2$

If we consider  $N$  atoms, there will be  $2N$ ,  $2N$ ,  $6N$ ,  $2N$ , and  $6N$  available states of type  $1s$ ,  $2s$ ,  $2p$ ,  $3s$ , and  $3p$ , respectively. As the interatomic spacing decreases, these energy levels split into bands, beginning with the outer ( $n = 3$ ) shell. As the " $3s$ " and " $3p$ " bands grow, they merge into a single band composed of a mixture of energy levels.

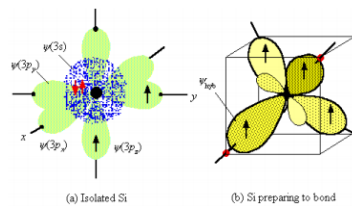


Fig 1.12 : Orbitals in Si

1. The  $3s$  orbital and three  $3p$  orbitals are perturbed and form 4, hybridized orbitals as shown in Fig 1.12.
2. These are directed towards tetrahedron.
3. Each orbital takes one valence electron

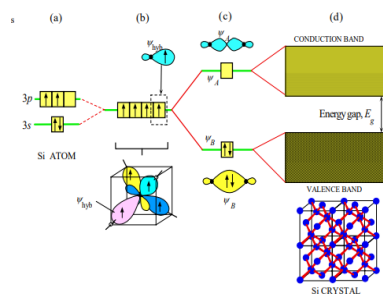


Fig 1.13 : Energy bands in Si

The four orbitals of neighboring atoms overlap to form bonding orbital (full) and anti-bonding orbital (empty) in lattice structure the bonding orbitals form valence band ( $4N$  states) and the anti-bonding orbitals form conduction band ( $4N$  states) as shown in Fig 1.13.

Electron distribution in  $N$  silicon atoms

- Lower  $1s$  band has  $2N$  e-s.

- 2s band has  $2N$  e-s and 2p band has  $6N$  e-s.
- The  $4N$  states of the third orbital (originally two in 3s and two in 3p) will occupy either valence band or conduction band.
- At 0 K, every state in valence band will be filled.
- The energy difference between the valence band and conduction band is called **Forbidden Gap**.

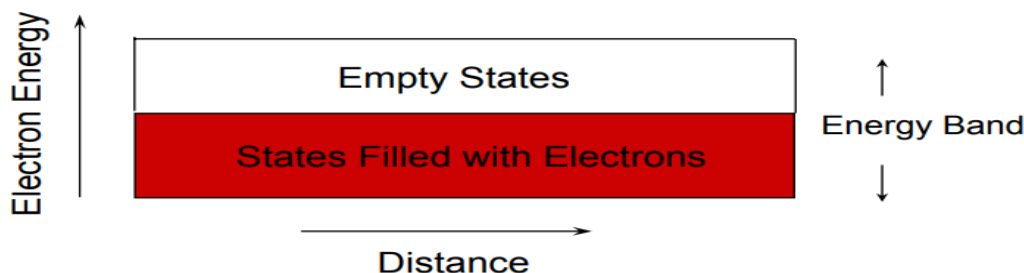
### 1.8 Metals, Insulators and Semiconductors

- An energy band is a range of allowed electron energies.
- Every solid has its own characteristic energy band structure
- The band structure is responsible for the electrical characteristics
- We have valence band and conduction band
- The energy gap in between is the forbidden gap.
- Charges experience acceleration in presence of electric field.
- Electrons will move in a direction opposite to the direction of the applied electric field (Remember, positive charges accelerate in the direction of the electric field)

*In order for a material to be conductive, both free electrons and empty states must be available.*

#### Metals

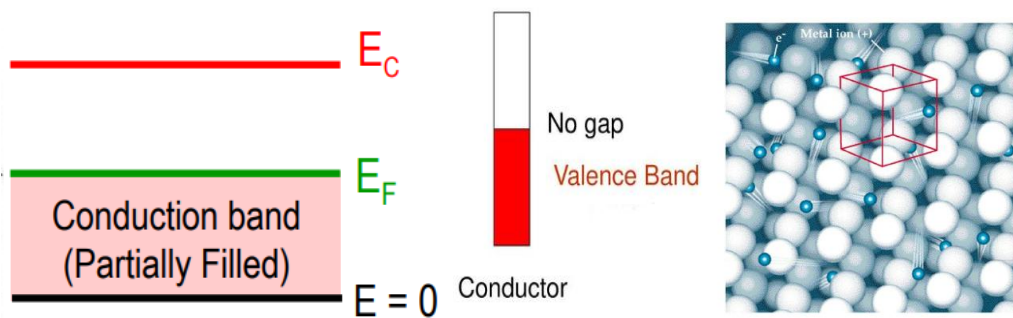
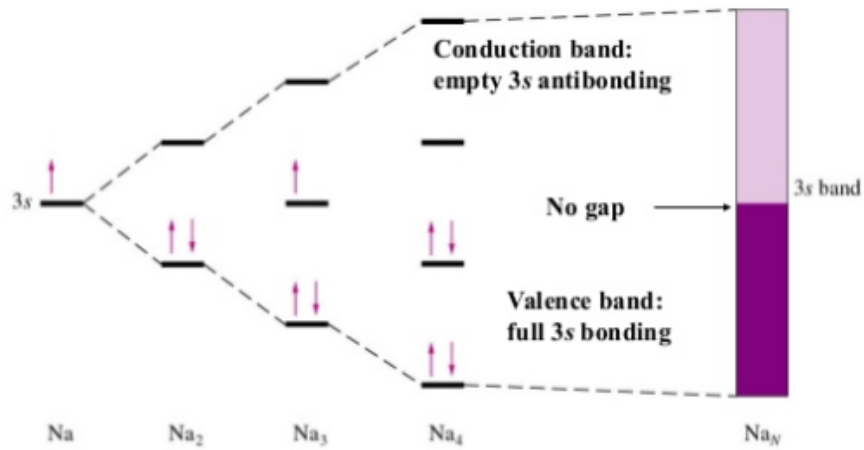
- ❖ The energy band in a metal is only partially filled with electrons.
- ❖ Metals have overlapping valence and conduction bands



For an electron to become free to conduct, it must be promoted into an empty available energy state. For metals, these empty states are adjacent to the filled states. Generally, energy supplied by an electric field is enough to stimulate electrons into an empty state. Hence, metals are said to have high conductivity. In metals the Fermi level is defined as the top most occupied energy level. Also defined as the energy level from where one can remove an electron with minimum Energy.

Consider example of Na.

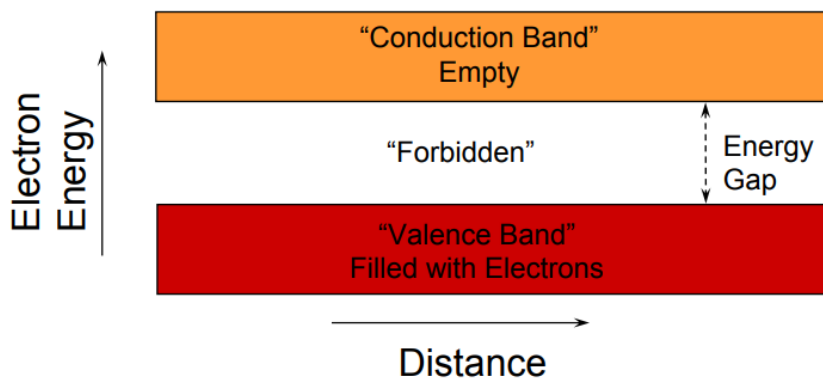




### Insulator

The valence band and conduction band are separated by a large ( $> 4\text{eV}$ ) energy gap, which is a “forbidden” range of energies. Electrons must be promoted across the energy gap to conduct, but the energy gap is large. So small electric fields are not sufficient to transfer the e-s from valence band to conduction band.

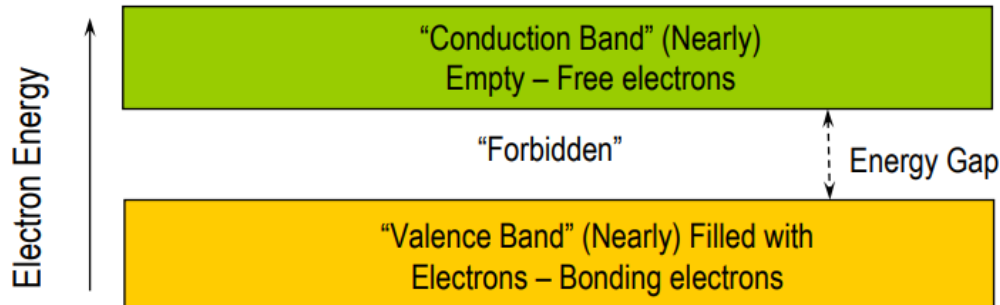
When the electric field is very large, then the insulation “**breaks down**” and starts conducting.



At  $T = 0$ , lower valence band is filled with electrons and upper conduction band is empty, leading to zero conductivity. At  $T > 0$ , electrons are usually NOT thermally “excited” from valence to conduction band, leading to zero conductivity.

## Semiconductors

The energy gap is  $< 2$  eV.



They belong to group IV in the periodic table. Semiconductors have resistivities in between those of metals and insulators. Elemental semiconductors (Si, Ge) are perfectly covalent; by symmetry electrons shared between two atoms are to be found with equal probability in each atom.

1. If relatively few e-s reside in an otherwise empty band, plenty of unoccupied energy states are available into which e-s can move. If we consider Si, valence band is completely full at 0K. And conduction band is empty. Since VB is full, no empty states. So no e-s transfer. Since conduction band is empty, no charge transport here also. Hence, Si has high resistivity.
2. Semiconductors at 0K have same structure as insulators – a filled valence band and empty conduction band, both separated by a band gap, which does not have any allowed states. However, this band gap is lesser than in an insulator.
3. In Si band gap is 1.1 eV.
4. Since band gap is low, e-s can be transferred from lower energy valence band by thermal or optical energy.
5. At room temp, Si will have significant number of e-s excited thermally into conduction band, whereas in an insulator (gap  $> 4$  eV) negligible e-s in conduction band.

### 1.9 Direct and indirect semiconductors

With the particle-wave nature of e-s the likelihood of finding an e- at a particular location is described by a wave equation. The wave equation for an e-s assumed to move in the x direction is given by

$$\psi_{\mathbf{k}}(x) = U(\mathbf{k}_x, x) e^{j\mathbf{k}_x x}$$

$k_x$  is the wave vector or propagation constant.  $U(\mathbf{k}, x)$  Modulates wave function according to periodicity of lattice. The **propagation constant  $k$  (also called wave vector)** of a sinusoidal electromagnetic wave is a measure of the change undergone by the amplitude and phase of the wave as it propagates in a given direction.

The wave vector (or  $k$  vector) of a plane wave is a vector which points in the direction in which the wave propagates.. Its magnitude is the wave number as defined by wave number

$$K=2\pi/\lambda$$

where  $\lambda$  is the wavelength in the medium. The value of allowed energy can be plotted Vs  $k$ . The periodicity of the lattice structure is different in various directions. So the actual plot of  $(E,K)$  is a 3D one.

**1.9.1 Direct Semiconductors** : Here, the minimum of the conduction band and the Maximum of valence band occur for same value of  $k$  as shown in Fig 1.14. Ex : GaAs. Thus an e- making a smallest energy transition from the conduction band to valence band without a change in  $k$  value. In the process it gives out energy. **Used for LEDs, Laser**

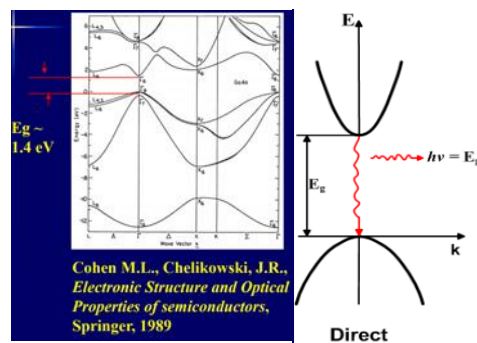


Fig 1.14 : Direct semiconductors

### 1.9.2 : Indirect semiconductor

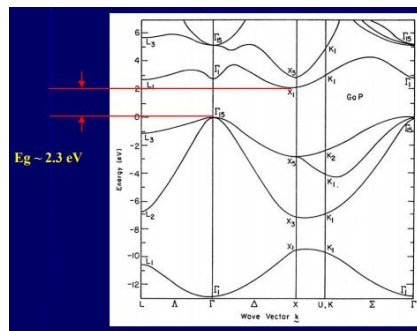


Fig 1.15 : Indirect Semiconductors

In IndirectSemiconductors the minimum of the conduction band does not occur at the same  $k$  value as the valence band maximum , as shown in Fig 1.15. An electron promoted to the conduction band requires a change of its momentum to make the transition to the valence band (typ. occurs via

lattice vibrations. Ex Si, Ge) .When an electron in the CB min. falls to an empty state in the VB max. it falls first to defect state ( $E_t$ ) within the band gap, giving off energy difference as heat with a change in  $k$  value and then it falls to the VB max., giving off energy difference  $E_t$  as a photon of light without a change in  $k$  (or  $p$ ) value. Here both momentum and Energy of  $e^-$  change with Change in  $k$ .(Fig 1.16)

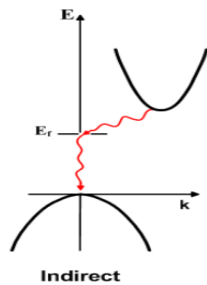


Fig 1.16 : Change in state of  $e^-$

## 1.10 Electrons and Holes

### 1.10.1 Intrinsic and Extrinsic Semiconductors

In metals there are a number of free  $e^-$ s that can move easily under influence of an electric field. In semiconductor, at 0K the valence band is completely filled and the conduction band is empty. As temperature is increased a few  $e^-$ s receive enough of thermal energy and get excited across the bandgap and move to conduction band. So we have

- A few  $e^-$ s in the otherwise empty conduction band
- A few unoccupied states in the valence band. This empty state (energy level) in valence band is called HOLE.

The  $e^-$  in the conduction band and the hole in the valence band , created by transition of  $e^-$  from VB to CB are called “ electron-hole” pair. [EHP] as shown in Fig 1.17

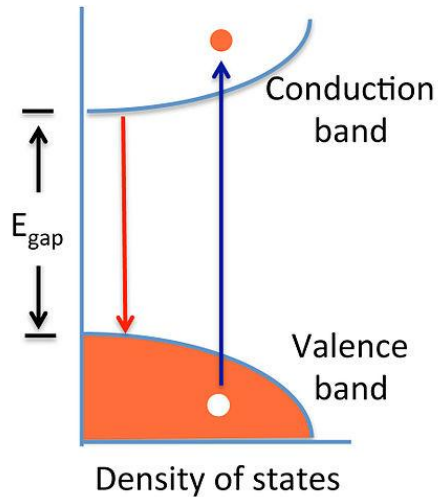


Fig 1.17 : EHP

When the VB is completely filled an electron  $j$  with wave vector  $k_j$  is matched by another  $e^- j'$  with wave vector  $-k_j$ , as shown in Fig 1.18.

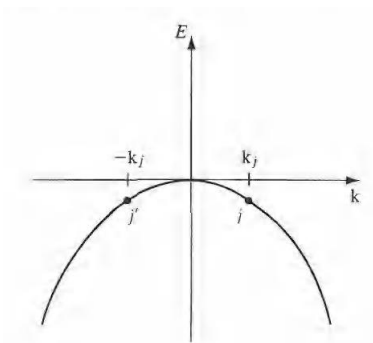


Fig 1.18 : Filled VB

The two  $e^-$ s have opposite momenta. So net current is zero, unless one of the  $e^-$ s is removed.

In a filled band with  $N$   $e^-$ /cm<sup>3</sup>, the current density is given by, where  $v$  is velocity.

$$J = (-q) \sum_i^N v_i = 0$$

Now if we create a hole by removing the  $j$ th  $e^-$ , the current density is sum of all  $e^-$ s minus the contribution of  $j$ th  $e^-$ .

$$J = (-q) \sum_i^N v_i - (-q)v_j$$

The first term is zero. So current density is  $+qv_p$

So the current density due to the creation of a hole is same as a positive charge  $q$ . Hence the hole can be viewed as a positive particle with the same charge as electron. But remember it is not a particle at all. It's simply an empty energy state. But it is customary to treat holes as positive charges with positive mass. In pure Si for example there are  $10^{10}$  EHP/cm<sup>3</sup> at room temp. The e-s in the conduction band are surrounded by a large number of unoccupied states, in which they are free to move. Thus in semiconductor we have

- e-s in conduction band which can contribute to current (they move opposite to the direction of E field)
- Holes in valence band which also contribute to current. They move in same direction as E field (since their effect is same as that of a +ve

Since holes have opposite charge, hole energy increases opposite to the electron energy. Therefore, holes seeking lowest energy are on top of the VB and e-s in conduction band are at the bottom of CB, as shown in Fig 1.19.

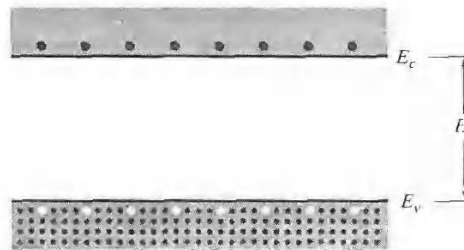


Fig 1.19

- Electron energies increase going up, while hole energies increase going down.
- Electron and hole wave vectors point in opposite directions and these charge carriers move opposite to each other.
- An  $(E, K)$  is a function of the energy (potential + Kinetic) Vs the wave vector which depends on the crystal direction. This is drawn at a particular point in space.
- The bottom of CB corresponds to zero KE and hence gives only PE. For holes the top of VB is zero KE.

### 1.10.2 Intrinsic semiconductor

A perfect semiconductor without any lattice defects is called an intrinsic semiconductor. There are no charge carriers at 0K. At higher temps EHPs are generated which are the only charge carriers. Qualitatively it's like breaking the covalent bond in the crystal lattice. The energy required to break the bond is the Band gap energy. The e-s and holes are not localized as shown, but spread over the lattice spacings as shown in Fig 1.20

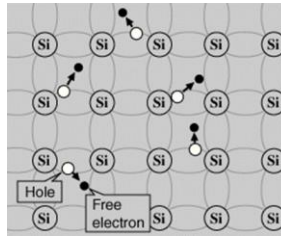


Fig 1.20 : e-s and holes in lattice structure

The Fermi level lies in the middle of the Band gap. Since here we have only EHP, the number of e-s 'n', in the conduction band is equal to the number of holes 'p' in the valence band.

$$n = p = n_i$$

- ❖ At a particular temp, the concentration is  $n_i$ , called the **intrinsic carrier concentration**. It depends on the band gap and temperature.
- ❖ **Recombination** takes place when an e- from CB makes a transition to VB (either direct or indirect).
- ❖ For a steady carrier concentration, the rate of recombination of EHPs must be same as their generation.
- ❖ If temperature is changed,  $n = p = n_i$  a new equilibrium sets in. At any temp

$$r_i = g_i$$

$$r_i = \alpha_r n_0 p_0 = \alpha_r n_i^2 = g_i$$

### How do intrinsic semiconductors conduct?

Under applied field the electrons (thermally excited into the conduction band) can move using the vacant states in the conduction band. Holes move in the opposite direction in the valence band. This conductivity is low, as the number of e-s excited are very less. The conductivity is a function of the temperature.

### Extrinsic Semiconductor

The process of mixing an impurity with semiconductor is called **Doping**. An extrinsic semiconductor is a semiconductor doped by a specific impurity which is able to deeply modify its electrical properties, making it suitable for electronic applications (diodes, transistors, etc.) or optoelectronic applications (light emitters and detectors). Impurity is called **Dopant**.

- When a crystal is doped such that the equilibrium carrier concentrations  $n_0$  and  $p_0$  are different from the intrinsic carrier concentration  $n_i$  the material is said to be *extrinsic*.

### What effect does impurity have on energy levels?

- When impurities or lattice defects are introduced into an otherwise perfect crystal, additional levels are created in the energy band structure, usually within the band gap. Based on the impurity we have two types of extrinsic semiconductors

### 1.10.3 n –type semiconductor

The dopant is a group V element such as P, As, Sb .These are pentavalent. Since it is pentavalent, there are 5 e-s in the outer most orbit. 4 of these bond with 4 Si atoms, and the fifth is loosely bound to the parent atom. the extra unbonded electron is practically free with an Energy level near the conduction band . The impurity atoms are called **Donor atoms**, since they donate e-s. (fig 1.21)

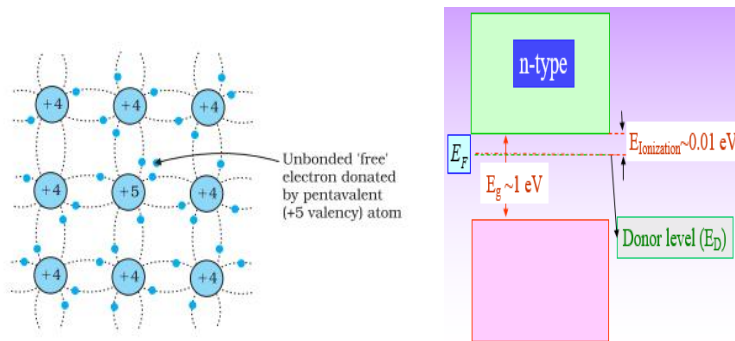


Fig 1.21 : n-type semiconductor

So what happens?

1. The energy level of the donor e-s, are just below the conduction band.
2. Ionization Energy required to move an electron from the Donor level to conduction band,  $E_{\text{ionization}} < E_g$ .
3. Even at RT large fraction of the donor electrons are excited into the conduction band.
4. Electrons in the conduction band are the majority charge carriers. There are still a few holes in the VB, due to the e-s which have been excited thermally to CB.
5. The fraction of the donor level electrons excited into the conduction band is much larger than the number of electrons excited from the valence band.



6. *Law of mass action*: States that the product of number of electrons in the conduction band and the number of holes in the valence band is constant at a fixed temperature and is independent of amount of donor and acceptor impurity added  $(n_e)^{\text{conduction band}} \times (n_h)^{\text{valence band}} = \text{Constant}$

The number of holes is very small in an n-type semiconductor

8. Unlike intrinsic semiconductors, Number of electrons  $\neq$  Number of holes

### 1.10.4 p-type semiconductor

A p-type semiconductor is created when trivalent elements (B, G, In, Al) are used to dope pure semiconductors, like Si and Ge. When a trivalent atom takes the place of a Si atom, three of its electrons bond with three neighboring Si atoms. However, there is no electron to bond with the fourth Si atom. This leads to a hole or a vacancy between the trivalent and the fourth silicon atom. This hole initiates a jump of an electron from the outer orbit of the atom in the neighborhood creating a hole at the site from where the electron jumps. A hole is now available for conduction. (remember though that it's e- which moves). The impurity is called ACCEPTOR. (Fig 1.22)

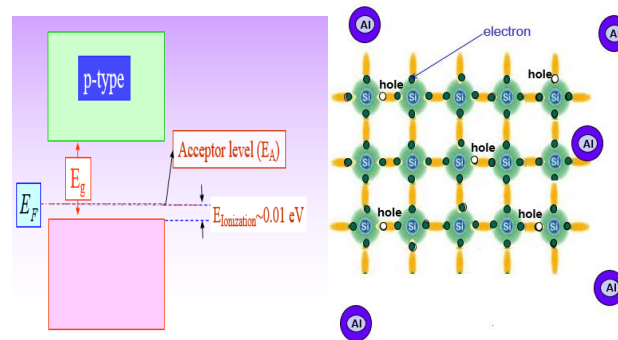


Fig 1.22 : p-type semiconductor

1. At 0K the holes are bound to the dopant atom
2. As T increases the holes gain thermal energy and break away from the dopant atom and are available for conduction
3. The level of the bound holes are called the **acceptor level** (which can accept an electron) and acceptor level is close to the valance band.
4. Holes are the majority charge carriers. Intrinsically excited electrons (in the CB) are small in number
5. The number of holes made available by the dopant atoms is independent of the ambient temperature and primarily depends on the doping level.
- 6.. Number of electrons  $\neq$  Number of holes

Generally, the column V donor levels lie approximately 0.01 eV below the conduction band in Ge, and the column III acceptor levels lie about 0.01 eV above the valence band. In Si the usual donor and acceptor levels lie about 0.03-0.06 eV from a band edge.

### What are majority and minority carriers?

In extrinsic semiconductors, the carrier which is large in number is called majority carrier and the one which is less is called minority carrier. In n-type : e-s are majority and holes are minority. In p-type, holes are majority and e-s are minority.

### 1.11 Conductivity and mobility

The charge carriers in a solid are in constant motion, even at thermal equilibrium. At room temperature, for example, the thermal motion of an individual electron may be visualized as random scattering from lattice vibrations, (Fig 1.23) impurities, other electrons, and defects. Since scattering is random, the net motion for a group of  $n$  e-/cm<sup>3</sup> is zero.

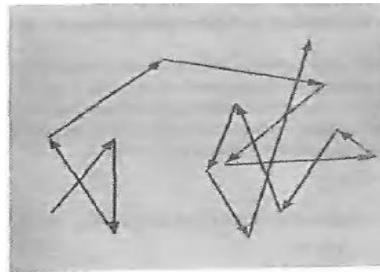


Fig 1.23 : Random scattering of e-s

A single e- may not return to its starting place in a finite time. However if a large number of e-s are considered, there is no preferred direction of flow, and hence net current is zero. When an electric field is applied each e-, experiences a force  $-qE$ . The e- accelerate in a direction opposite to the direction of the field. If the field  $E_x$  is applied in the x direction, then each e- experiences a force  $-qE_x$ . This force is too small for a significant change in the random movement. However, when a large number of e-s are taken, there is a net motion of the group in the  $-x$  direction. Now if the total momentum of the group (x component) is  $\rho_x$ , then the rate of change of the momentum is the force. If we assume  $n$  e-s then the total force is given by  $-nqE_x$ . Therefore

$$-nqE_x = \frac{d\rho_x}{dt}. \quad (\text{Eq1})$$

The net acceleration is just balanced in steady state by the decelerations of the collision processes. Thus, while the steady field  $E_x$  does produce a net momentum  $\rho_x$ , the net rate of change of momentum when collisions are included must be zero in the case of steady state current flow.

Now consider  $N_0$  e-s at time  $t=0$  and  $N(t)$  the number of e-s that have not undergone any collision at time  $t$ . Now the rate of decrease in  $N(t)$  at time  $t$  is proportional to the number left unscattered at  $t$ . Therefore,

$$\frac{-dN(t)}{dt} = \frac{N(t)}{\tau}. \text{ (Eq2)}$$

$\tau$  is called the **mean free time**. It is the average time before a randomly picked electron makes its next collision. As collisions are random, it does not depend on the elapsed time since prior collision. Eq(2) is a first order differential equation whose solution is given by

$$N(t) = N_0 e^{-t/\tau}. \text{ (Eq3)}$$

To find the total rate of momentum change from collisions, we must investigate the collision probabilities. If the collisions are truly random, there will be a constant probability of collision at any time for each electron. With the definition of Mean free time between collisions, the probability that the e- has a collision in a time dt, is given by dt/ $\tau$ . The differential change in momentum is given by,

$$d\rho_x = -\rho_x \frac{dt}{\tau}$$

And the rate of change of momentum due to decelerating effect is given by

$$\frac{d\rho_x}{dt} = \frac{-\rho_x}{\tau}$$

Now in steady state, sum of acceleration and deceleration is zero.

$$\frac{-\rho_x}{\tau} - nqEx = 0.$$

The **average momentum per electron** is

$$\frac{-\rho_x}{n} = -\tau qEx. \text{ (Eq4)}$$

we can calculate the average velocity of an electron and it is equal to

$$\langle V_x \rangle = -\tau qEx/m^* \text{ (Eq5)}$$

( $m^*$  is the effective mass).

Actually, the individual electrons move in many directions by thermal motion during a given time period, but (Eq5) tells us the net drift of an average electron in response to the electric field. The drift speed described is usually much smaller than the random speed due to the thermal motion. The **current density** because of this drift velocity is given by

$J_x = -qn\langle v_x \rangle$			
ampere	coulomb	electrons	cm
$\frac{\quad}{\text{cm}^2}$	$\frac{\quad}{\text{electron}}$	$\frac{\quad}{\text{cm}^3}$	$\frac{\quad}{\text{s}}$

Substituting for the drift velocity  $\langle V_x \rangle$  we get

$$J_x = \frac{\tau n q^2}{m^*} E_x \quad (\text{Eq6})$$

We see that the current density is proportional to the Electric Field. This is **Ohm's Law**. Simply written,

$$J_x = \sigma E_x \quad (\text{Eq7})$$

$$\text{Conductivity } \sigma = \frac{\tau n q^2}{m^*} = n q \mu_n \quad (\text{Eq 8}) \text{ ----unit is } \Omega\text{cm}^{-1}$$

Mobility of e-,  $\mu_n = q\tau/m^*$ . From (Eq5) this is also equal to  $\langle V_x \rangle / E_x$  (ratio of drift velocity to Electric field). A lighter particle has higher mobility. Mobility describes the ease with which electrons drift in the material. Mobility is a very important quantity in characterizing semiconductor materials and in device development.

### What is effective mass?

When responding, e.g., to external forces, the effective mass determines how quickly a particle will accelerate. It can be either heavier or lighter than the true mass of an electron. It will be different for different energy bands. We can say,  $m^* = \frac{1}{3} \left( \frac{1}{m_l} + \frac{2}{m_t} \right)$ ;  $m_l$  = mass in longitudinal direction;  $m_t$  = mass in transversal direction.

#### 1.11.1 Mobility of holes

For any particle a general definition of mobility is the ratio of drift velocity to the Electric field. Its inversely proportional to the effective mass  $m^*$ . Its unit is  $\text{m}^2/\text{v.s}$ . The ability of a hole to move, in the presence of applied electric field is called hole mobility. Its given by  $\mu_p = v_p / E$ .  $v_p$  is the drift velocity of holes. Since the effective mass of holes is greater than that of e-s, they have a lower mobility.

#### 1.11.2 Conductivity in a semiconductor

In the presence of an electric field, electrons and hole both drift, but in opposite directions. Since charges are opposite, both currents flow in the same direction. The conductivity due to each depends on

- How many carriers there are (n or p) [ n for negative, p for positive]
- How easily can the carriers move (mobility  $\mu_n$  and  $\mu_p$ )

Conductivity of a semiconductor is

$$S = qn\mu_n + qp\mu_p$$

The current density is then given by

$$J = \sigma E_x \text{ (we are still considering } E \text{ in the } x \text{ direction). This is the drift current.}$$

1. The direction of conventional current is the direction of flow of positive charges.

2. Holes flow along the direction of E. Hence they create a current in the direction of E (as holes are similar to positive charges)
3. e-s drift in a direction opposite to E. However, since e- has negative charge, the current due to this is also in the direction of E.
4. Hence, the drift current of both e-s and holes is along the direction of applied field E.
5. The drift current is constant through out the bar.

### Effect of temperature and doping on mobility

In a semiconductor, both mobility and carrier concentration are temperature dependent. conductivity as a function of temperature is expressed by:

$$\sigma = q(\mu_n(T)n(T) + \mu_p(T)p(T) )$$

There are two basic types of scattering mechanisms that influence the mobility of electrons and holes:

- lattice scattering
- impurity scattering.

### Lattice scattering

In lattice scattering a carrier moving through the crystal is scattered by a vibration of the lattice, resulting from the temperature. The frequency of such scattering events increases as the temperature increases, since the thermal agitation of the lattice increases. Hence, mobility decreases as temperature increases. This is important in intrinsic semiconductors.

### Impurity scattering

This phenomenon is important for doped semiconductors.

Impurity scattering is caused by crystal defects such as ionized impurities. At lower temperatures, carriers move more slowly, so there is more time for them to interact with charged impurities. As a result, as the temperature decreases, **impurity scattering increases**, and the **mobility decreases**. This is just the opposite of the effect of lattice scattering. (fig 1.24)

### Thus with increase in temperature

- Lattice scattering increases and mobility decreases
- Impurity scattering decreases and mobility increases

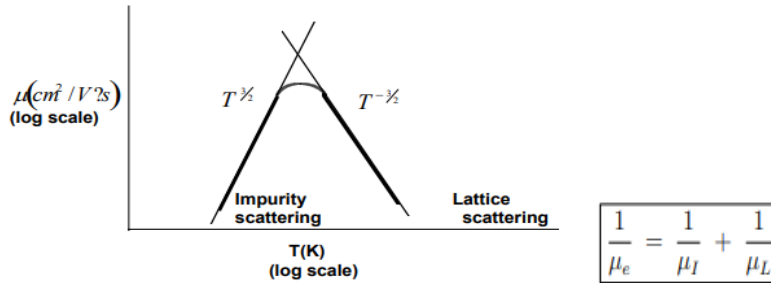


Fig 1.24 : Scattering

The scattering with lower Mobility dominates.

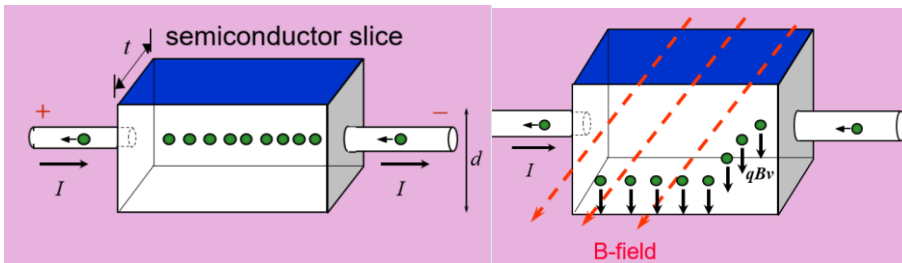
**Effect of doping on mobility**

With increase in doping levels the mobility decreases since the Impurity scattering increases.

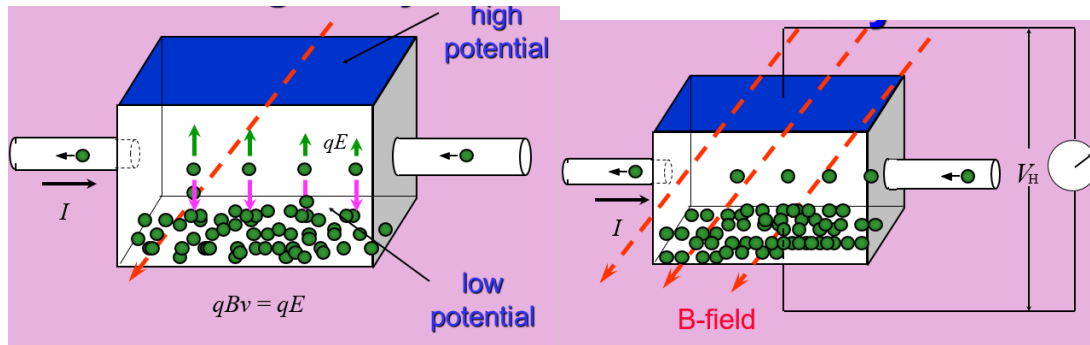
**1.12 Hall Effect**

Discovered by Edwin Hall in 1879. The Hall effect is the production of a voltage difference (called the Hall Voltage) across a current carrying conductor, in the presence of a magnetic field. The generated voltage is perpendicular to both the current and the magnetic field.

Lorentz Force equation,  $\mathbf{F} = q(\mathbf{E} + \mathbf{v} \times \mathbf{B})$ ;  $v$  is velocity. Refer Fig 1.25



Without Magnetic Field (a) When Magnetic field is applied in z axis (b)



(c) E field produced along y axis (d) Hall voltage is produced

Fig 1.25 Hall effect

Assume current is in x axis . Then E is produced along y axis.

To maintain a steady flow  $E_y = v_x B_z$ . The E field is created when the magnetic field shifts the electrons (holes) . In the figure, we have considered the direction of current I. This is same as the hole drift direction. So we can analyze the **p-type**. The establishment of the electric field is called the Hall Effect and the potential difference is called the Hall Voltage. The voltage is given by

$$V = Ew; \text{ where } w \text{ is the width.}$$

Now for holes, the current density is given by (derived earlier)

$$J_x = qp_0 \langle v_x \rangle$$

We get the velocity  $\langle v_x \rangle = J_x / qp_0$ .

Substituting this in the equilibrium equation we get

$$E_y = \frac{J_x}{qp_0} B_z = R_H J_x B_z ; R_H = \frac{1}{qp_0}$$

We see that the Hall Field is proportional to product of current density and magnetic flux density. The constant of proportionality is called the **Hall coefficient**  $R_H$ .

The above relationship gives a method to determine hole concentration, from measurement of Hall voltage  $V_{AB}$  in the presence of a known magnetic field.

$$p_0 = \frac{1}{qR_H} = \frac{J_x B_z}{qE_y} = \frac{\left(\frac{I_x}{wt}\right) B_z}{q \left(\frac{V_{AB}}{w}\right)} = \frac{I_x B_z}{qtV_{AB}}$$

All the quantities on RHS are measurable. Hence Hall effect can be used to determine the carrier concentration accurately. The mobility is the ratio of the Hall coefficient to the resistivity.

$$\mu_p = R_H / \rho$$

### For an n-type semiconductor

A negative value of q is used for electrons, and the Hall voltage  $V_{AB}$  and Hall coefficient  $R_H$  are negative. In fact, measurement of the sign of the Hall voltage is a common technique for determining if an unknown sample is p-type or n-type.