

# Chapter 6

## MOLECULES AND SOLIDS

### OBJECTIVES:

- To understand the bonding mechanism, energy states and spectra of molecules
- To understand the cohesion of solid metals using bonding in solids
- To comprehend the electrical properties of metals, semiconductors and insulators
- To understand the effect of doping on electrical properties of semiconductors
- To understand superconductivity and its engineering applications

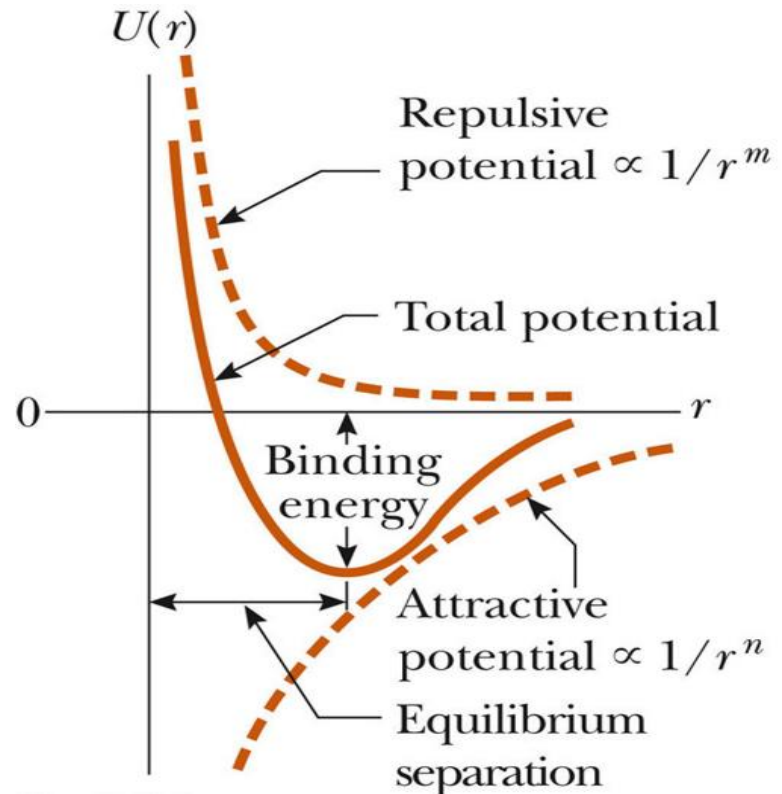
## Molecular bonds

*A stable molecule is expected at a configuration for which the potential energy function for the molecule has its minimum value.*

1. The force between atoms is **repulsive** at very small separation distances.
2. At relatively at larger separations, the force between atoms is **attractive**.

Considering these two features,

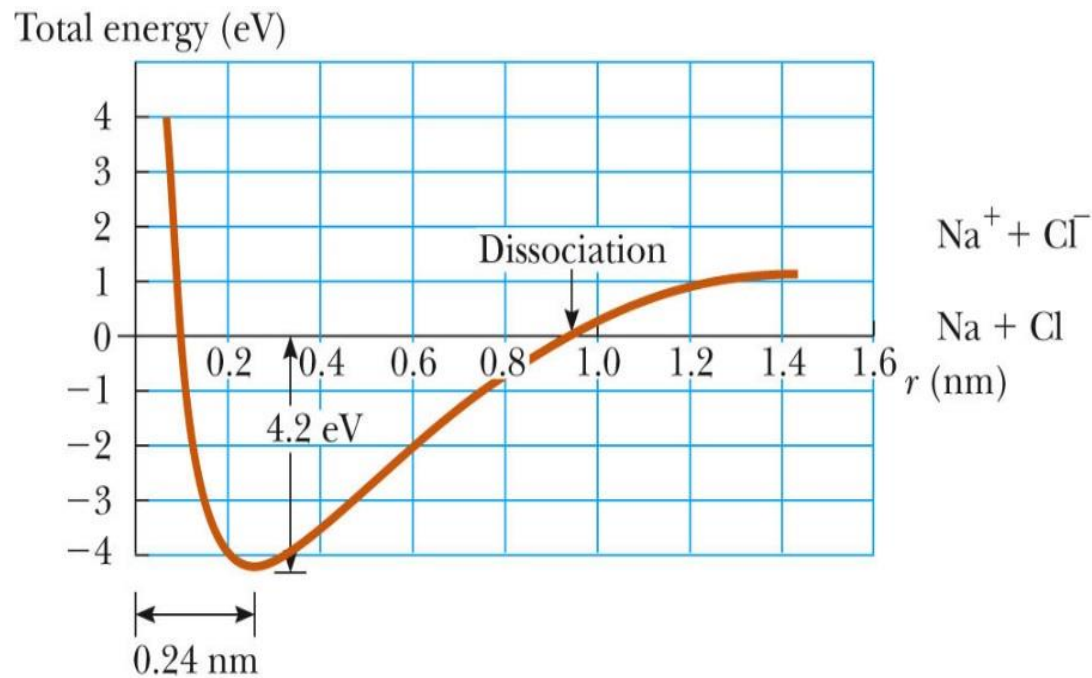
$$U(r) = -\frac{A}{r^n} + \frac{B}{r^m}$$



## Ionic Bonding:

When two atoms combine in such a way that one or more outer electrons are transferred from one atom to the other, the bond formed is called an ionic bond.

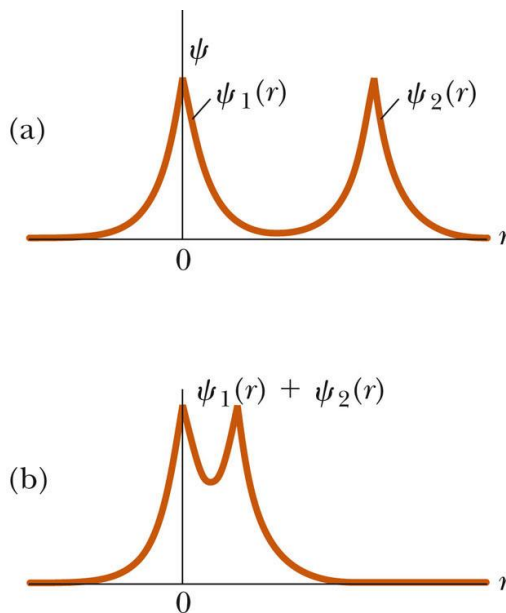
### Example: NaCl



*Total energy versus internuclear separation  
distance for  $\text{Na}^+$  and  $\text{Cl}^-$  ions.*

## Covalent Bonding:

A covalent bond between two atoms is one in which electrons supplied by either one or both atoms are shared by the two atoms. Many diatomic molecules such as  $\text{H}_2$ ,  $\text{F}_2$ , and  $\text{CO}$ —owe their stability to covalent bonds.



*Ground-state wave functions  $\psi_1(r)$  and  $\psi_2(r)$  for two atoms making a covalent bond. (a) The atoms are far apart, and their wave functions overlap minimally. (b) The atoms are close together, forming a composite wave function  $\psi_1(r) + \psi_2(r)$  for the system.*

**Van der Waals Bonding:** Because of the dipole electric fields, two molecules can interact such that there is an attractive force between them.

There are three types of van der Waals forces.

**Dipole– dipole force:** An interaction between two molecules each having a permanent electric dipole moment.

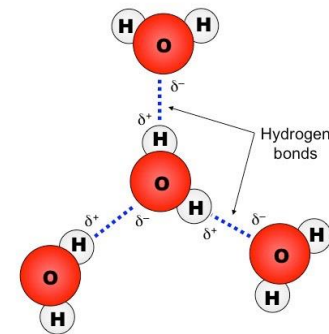
**Dipole–induced dipole force:** A polar molecule having a permanent electric dipole moment induces a dipole moment in a nonpolar molecule.

**Dispersion force:** An attractive force that occurs between two nonpolar molecules.

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## Hydrogen Bonding:

A hydrogen atom in a given molecule can also form a second type of bond between molecules called a **hydrogen bond**.



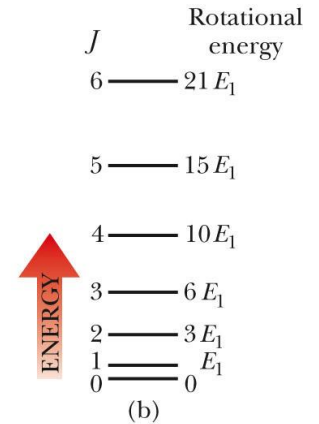
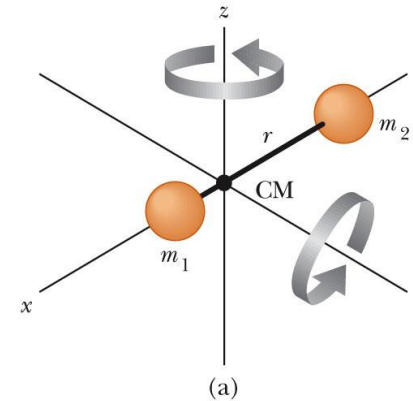
# Energy States and Spectra of Molecules

$$E = E_{\text{el}} + E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}}$$

## Rotational Motion of Molecules

$$E_{\text{rot}} = \frac{1}{2} I \omega^2$$

$$I = \left( \frac{m_1 m_2}{m_1 + m_2} \right) r^2 = \mu r^2 \quad \mu = \frac{m_1 m_2}{m_1 + m_2}$$



$$L = \sqrt{J(J+1)} \hbar \quad J = 0, 1, 2, \dots$$

$$E_{\text{rot}} = E_J = \frac{\hbar^2}{2I} J(J+1) \quad J = 0, 1, 2, \dots$$

$$E_{\text{photon}} = \frac{\hbar^2}{I} J = \frac{h^2}{4\pi^2 I} J \quad J = 1, 2, 3, \dots$$

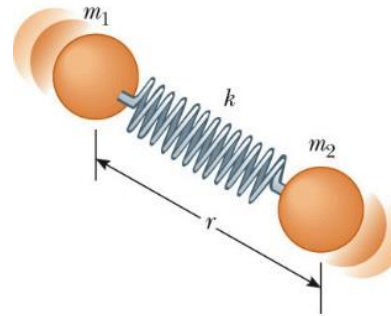
# Vibrational Motion of Molecules

$$f = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

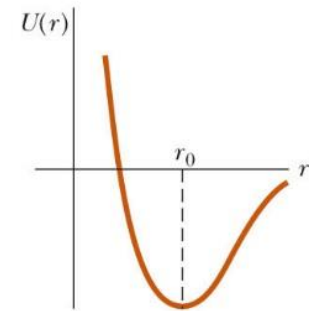
$$E_{\text{vib}} = \left( v + \frac{1}{2} \right) hf \quad v = 0, 1, 2, \dots$$

$$E_{\text{vib}} = \left( v + \frac{1}{2} \right) \frac{h}{2\pi} \sqrt{\frac{k}{\mu}} \quad v = 0, 1, 2, \dots$$

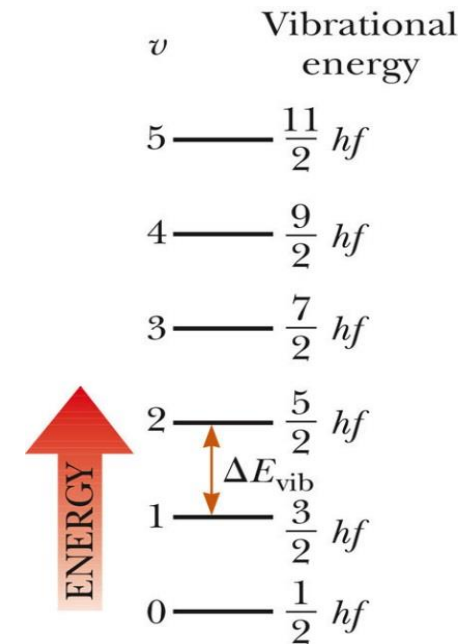
$$E_{\text{photon}} = \Delta E_{\text{vib}} = \frac{h}{2\pi} \sqrt{\frac{k}{\mu}}$$



(a)



(b)

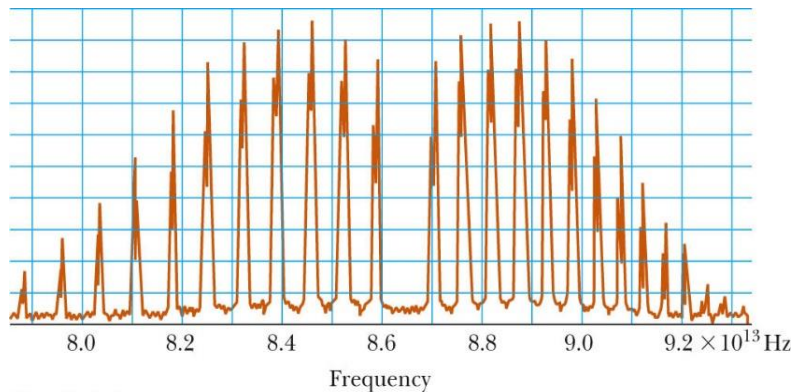
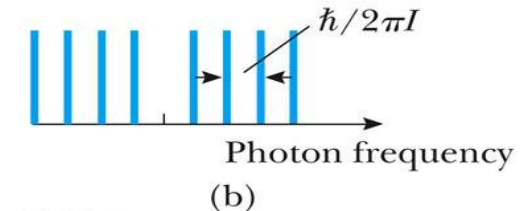
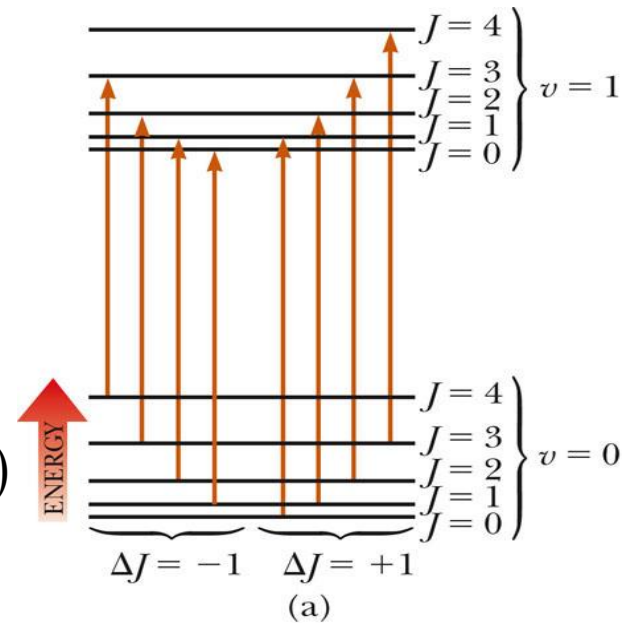


# Molecular Spectra

$$E = \left( v + \frac{1}{2} \right) hf + \frac{\hbar^2}{2I} J(J+1)$$

$$E_{\text{photon}} = \Delta E = hf + \frac{\hbar^2}{I} (J+1) \quad J = 0, 1, 2, \dots \quad (\Delta J = +1)$$

$$E_{\text{photon}} = \Delta E = hf - \frac{\hbar^2}{I} J \quad J = 1, 2, 3, \dots \quad (\Delta J = -1)$$



$$n = n_0 e^{\frac{-\hbar^2 J(J+1)}{2Ik_B T}}$$

$$\text{Intensity} \propto (2J + 1) e^{\frac{-\hbar^2 J(J+1)}{2Ik_B T}}$$

*Experimental absorption spectrum of the HCl molecule*



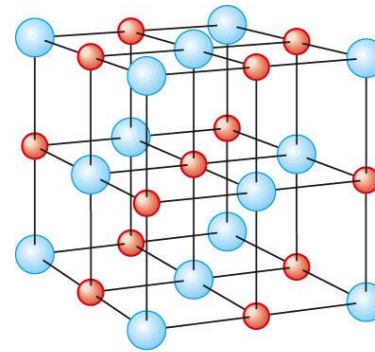
# Bonding in Solids

## Ionic Solids:

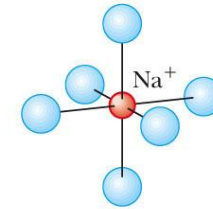
$$U_{\text{attractive}} = -\alpha k_e \frac{e^2}{r}$$

where  $\alpha$  is a dimensionless number known as the **Madelung constant**. The value of  $\alpha$  depends only on the particular crystalline structure of the solid ( $\alpha = 1.747$  for the NaCl structure).

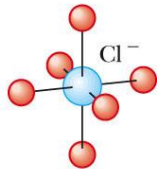
$$U_{\text{total}} = -\alpha k_e \frac{e^2}{r} + \frac{B}{r^m}$$



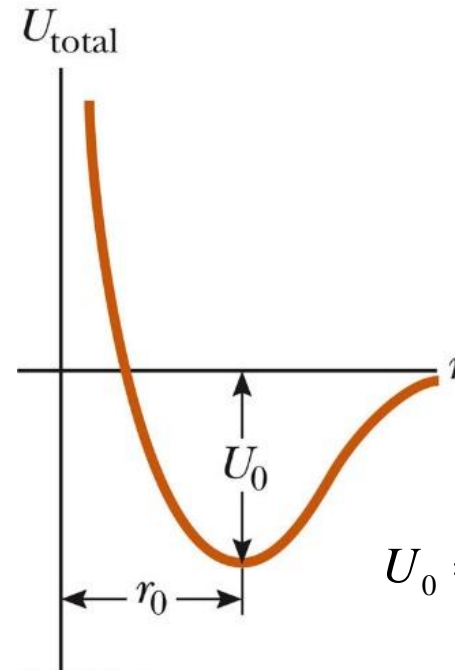
(a)



(b)



(c)



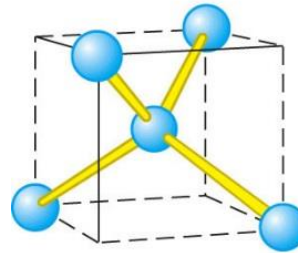
$$U_0 = -\alpha k_e \frac{e^2}{r_0} \left( 1 - \frac{1}{m} \right)$$

$U_0$  is called the **ionic cohesive energy** of the solid

## Covalent Solids:

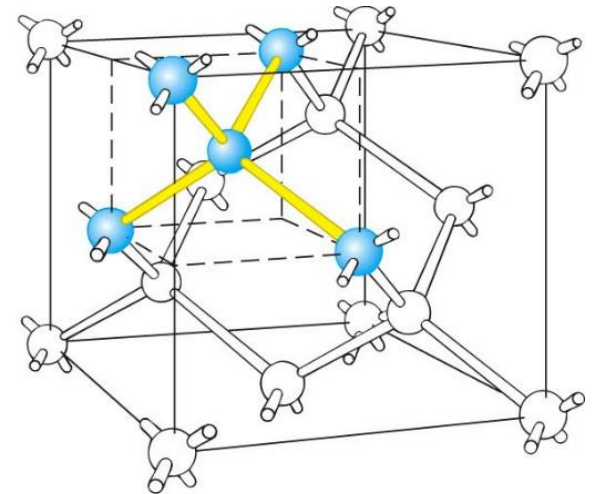
- Solid carbon, in the form of diamond, is a crystal whose atoms are covalently bonded.
- In the diamond structure, each carbon atom is covalently bonded to four other carbon atoms located at four corners of a cube

(a) *Each carbon atom in a diamond crystal is covalently bonded to four other carbon atoms so that a tetrahedral structure is formed.*



(a)

(b) *The crystal structure of diamond, showing the tetrahedral bond arrangement*



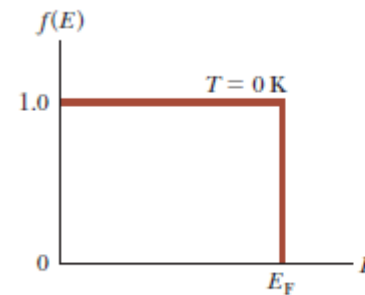
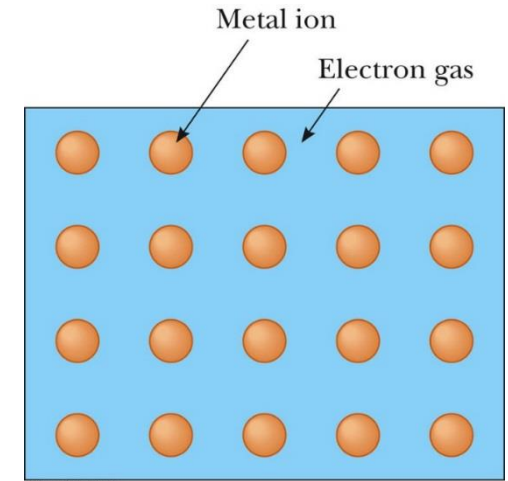
(b)

# Free-Electron Theory of Metals

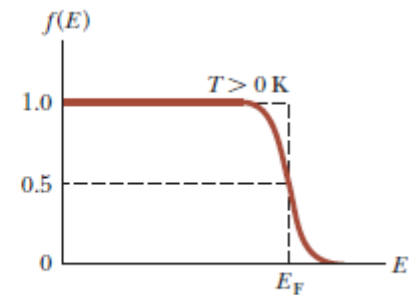
## Metallic Solids:

- **Free-electron** → free to move through the metal but are trapped within a three-dimensional box formed by the metal surfaces.
- Probability of occupation of a particular energy state by an electron in a solid is given by the Fermi-Dirac distribution function :

$$f(E) = \frac{1}{\exp\left(\frac{E - E_F}{kT}\right) + 1}$$



(a)



(b)

## Density of states:

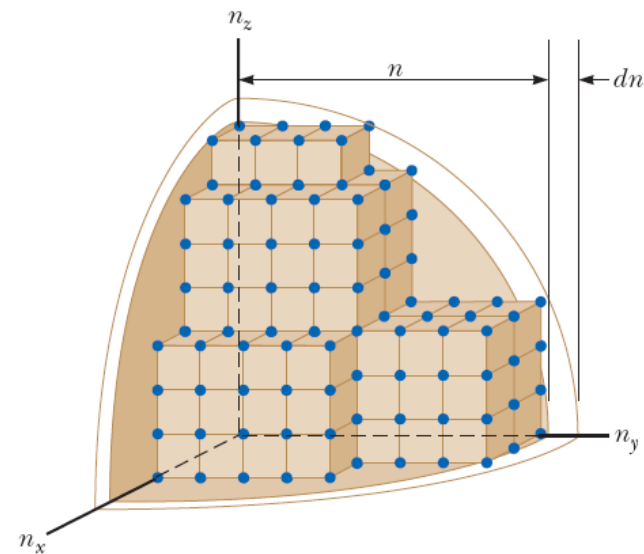
The quantized energy of a particle of mass  $m$  in a one dimensional box of length  $L$

$$E_n = \frac{h^2}{8 m L^2} n^2 = \frac{\hbar^2 \pi^2}{2 m L^2} n^2$$

In three dimension

$$E_n = \frac{\hbar^2 \pi^2}{2 m L^2} (n_x^2 + n_y^2 + n_z^2)$$

$$n_x^2 + n_y^2 + n_z^2 = n^2$$



Number of states from  $E$  to  $E+dE$  is

$G(E) dE = (1/8)(4\pi n^2 dn)$  and it can be shown that

$$G(E) dE = \frac{\sqrt{2}}{2} \frac{m^{3/2} L^3}{\pi^2 \hbar^3} E^{1/2} dE, \quad L^3 = V$$

$g(E) = \frac{G(E)}{V}$  is the number of states per unit volume [v in normal space] per unit energy range

$$g(E) dE = \frac{8\sqrt{2} \pi m^{3/2}}{h^3} E^{1/2} dE$$

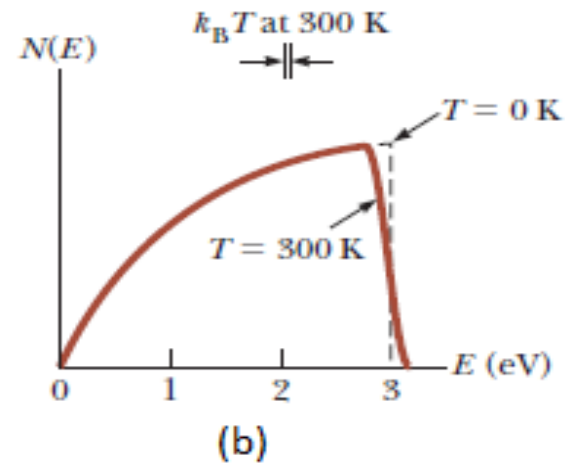
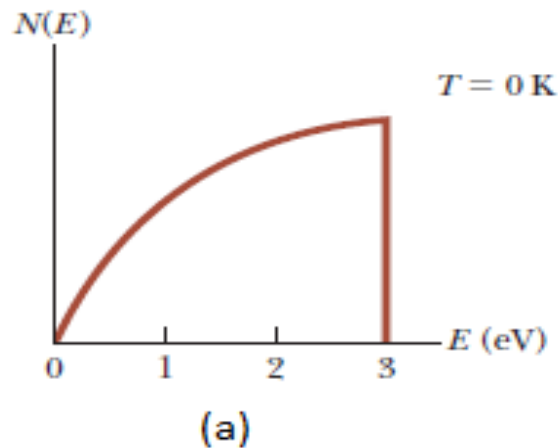
For derivation, refer study material

**$g(E)$  is called the density-of-states function.**

For a metal in thermal equilibrium, the number of electrons per unit volume,  $N(E) dE$ , that have energy between  $E$  and  $E+dE$  is

$$N(E)dE = g(E)f(E)dE$$

$$N(E) dE = \frac{8\sqrt{2} \pi m^{3/2}}{h^3} \frac{E^{1/2} dE}{\exp\left(\frac{E - E_F}{k T}\right) + 1}$$



The number of electrons per unit volume:

$$n_e = \int_0^{\infty} N(E) dE$$

At  $T = 0$ ,  $f(E) = 1$  for  $E < E_F$  and  $f(E) = 0$  for  $E > E_F$ .

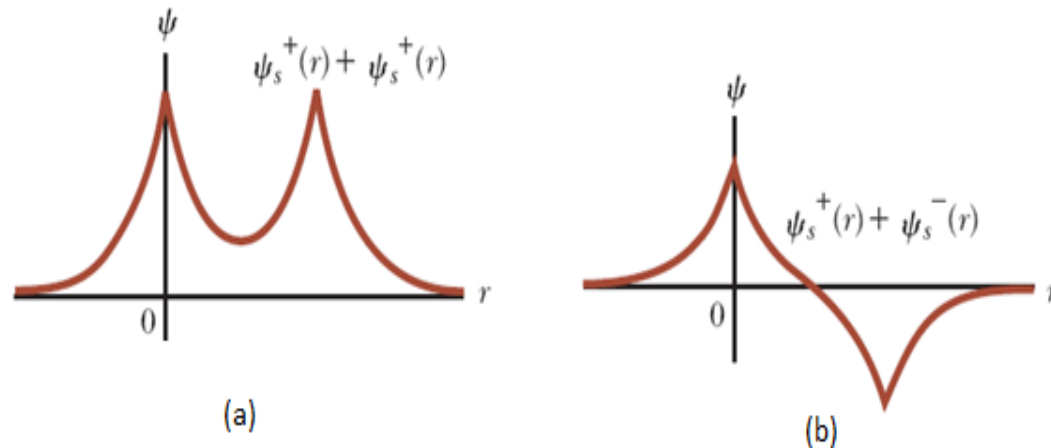
$$n_e = \frac{16\sqrt{2} \pi m^{3/2}}{3 h^3} E_F^{3/2}$$

FERMI ENERGY OF A METAL AT ZERO K

$$E_F(0) = \frac{h^2}{2m} \left( \frac{3n_e}{8\pi} \right)^{2/3}$$

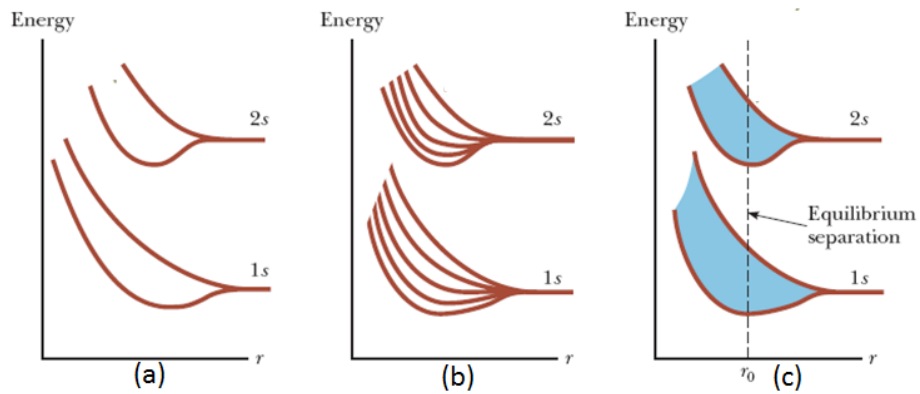
## Band Theory of Solids

- The wave functions of two atoms combine to form a composite wave function for the two-atom system when the atoms are close together.
- Thus, each energy level of an atom splits into two close energy levels when the wave functions of the two atoms overlap.

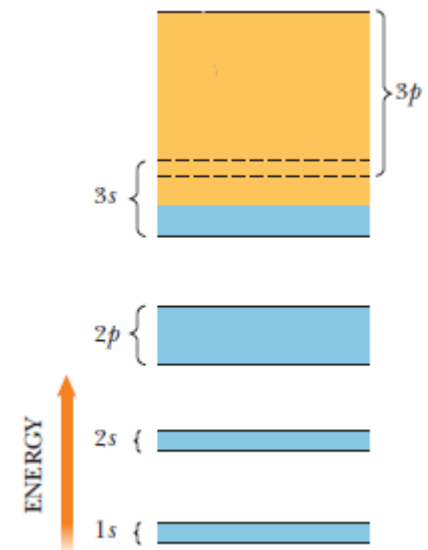


*The wave functions of two atoms combine to form a composite wave function : a) symmetric-symmetric  
b) symmetric-antisymmetric*





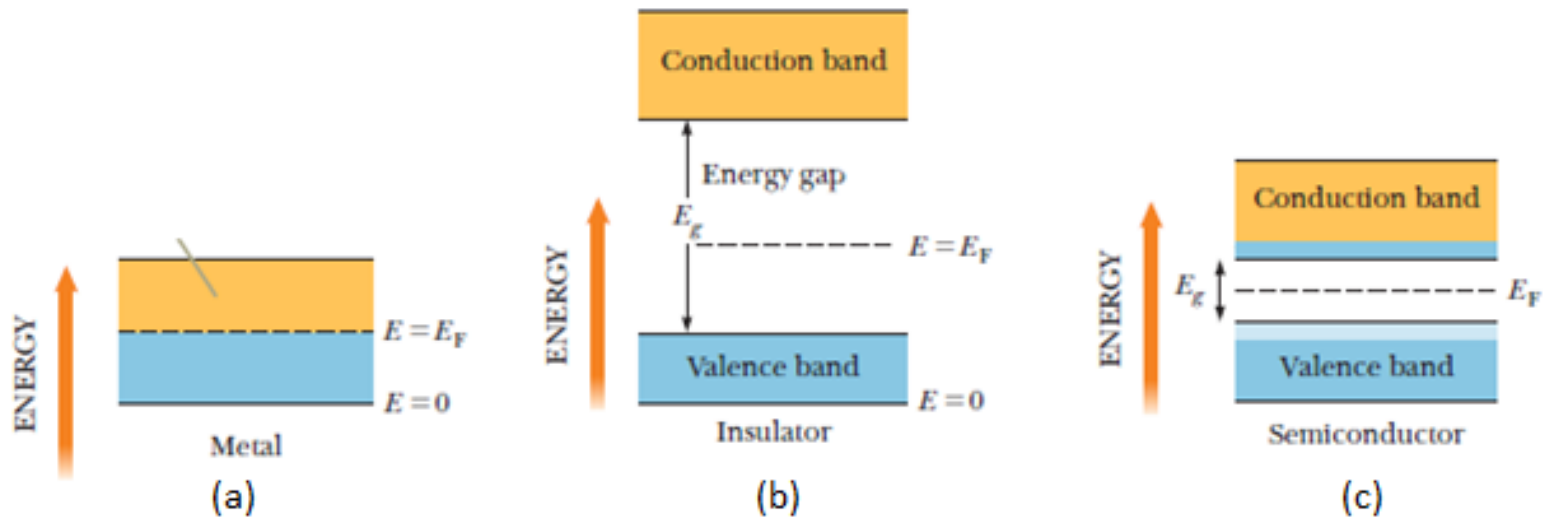
Splitting of 1s and 2s levels



Energy bands of a sodium crystal

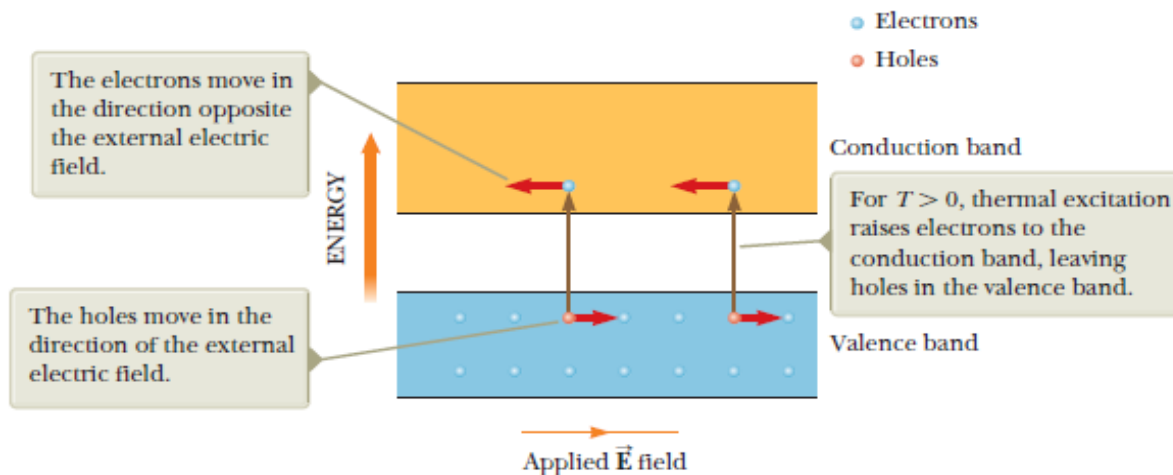
# Electrical Conduction in Metals, Insulators and Semiconductors

- a) Metals
- b) Insulators
- c) Semiconductors



- Semiconductors

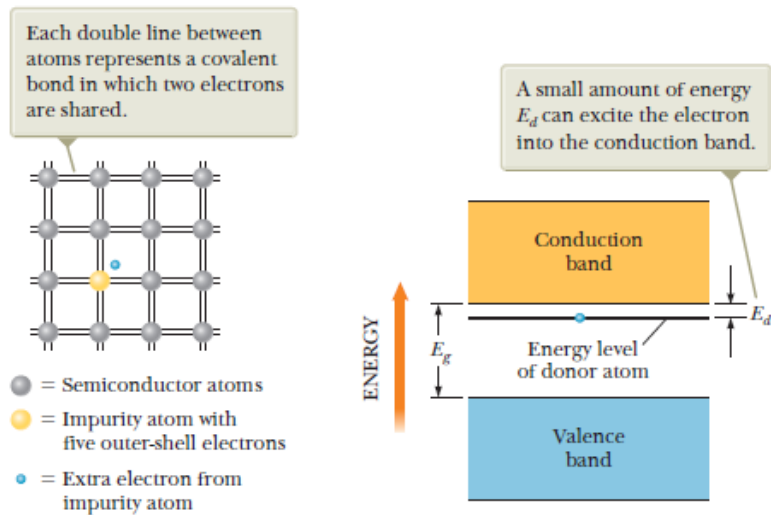
The charge carriers in a semiconductors are electrons and holes.



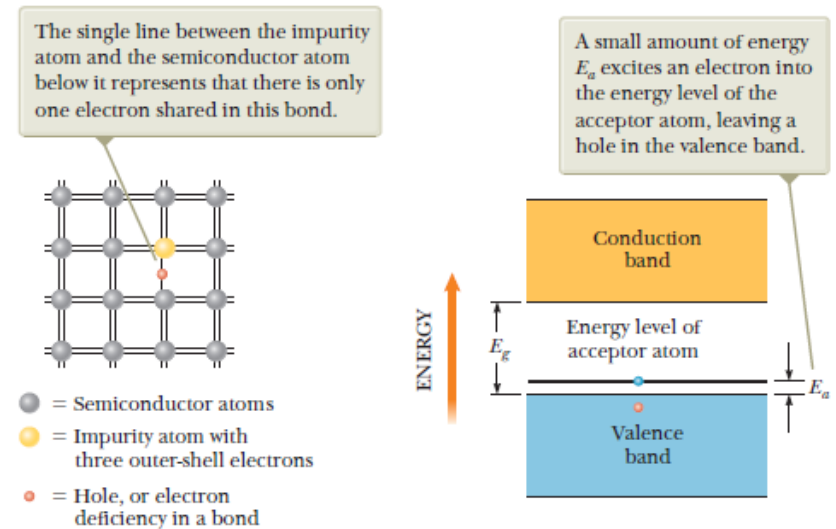
*Energy-Gap Values for Some Semiconductors*

Crystal	$E_g$ (eV)	
	0 K	300 K
Si	1.17	1.14
Ge	0.74	0.67
InP	1.42	1.34
GaP	2.32	2.26
GaAs	1.52	1.42
CdS	2.58	2.42
CdTe	1.61	1.56
ZnO	3.44	3.2
ZnS	3.91	3.6

- Semiconductors
  - ✓ Intrinsic semiconductor
  - ✓ Doped Semiconductors → n-type and p-type



n-type semiconductor

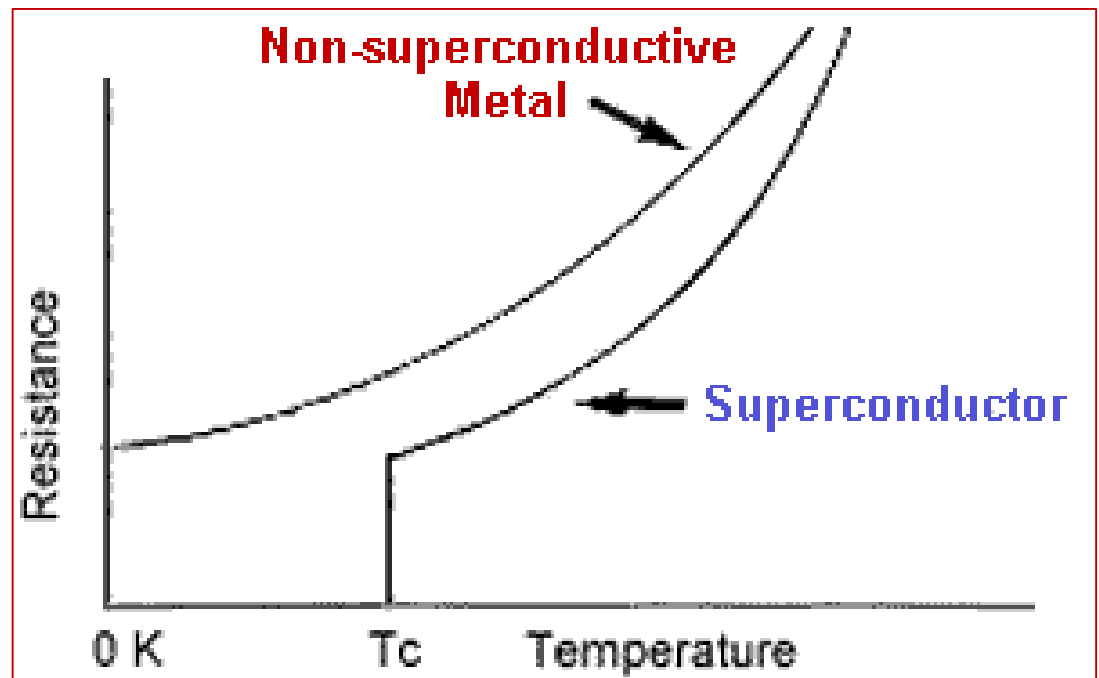


p-type semiconductor

# Superconductivity-Properties and Applications

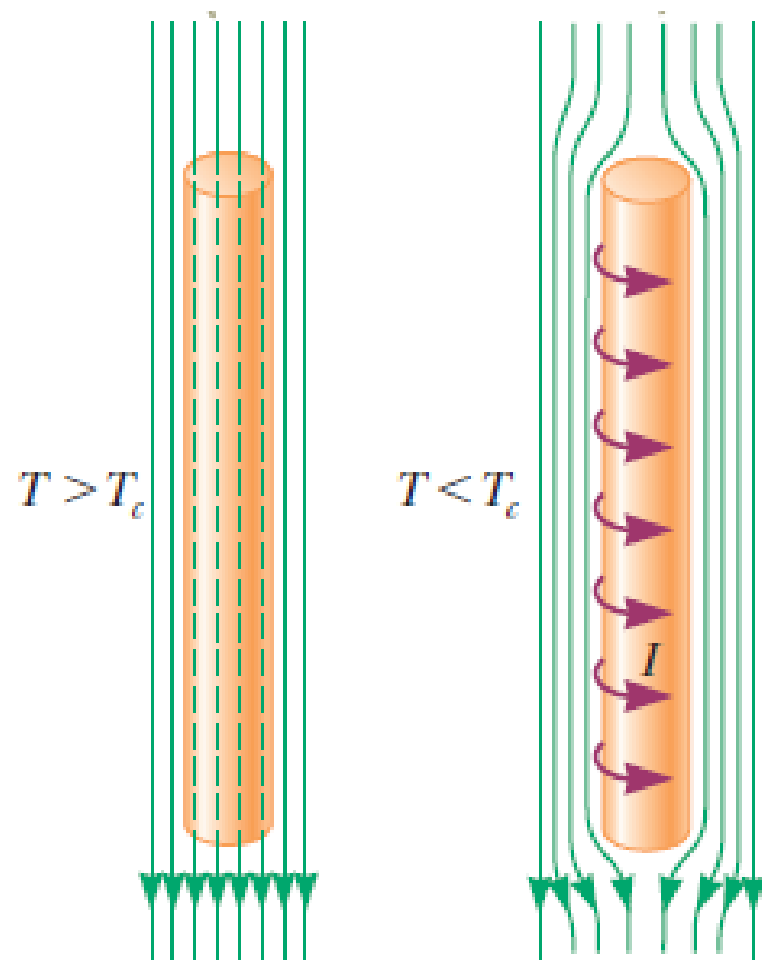
Superconductors are the materials whose electrical resistance ( $R$ ) decreases to zero below a certain temperature  $T_C$  called the critical temperature.

( $T_C = 4.2$  K for Hg).



**Meissner effect** : Exclusion of magnetic flux from the interior of superconductors when their temperature is decreased below the critical temperature.

- A superconductor expels magnetic fields by forming surface currents.
- Surface currents induced on the superconductor's surface produce a magnetic field that exactly cancels the externally applied field inside the superconductor.



## BCS Theory:

- Cooper pair - behaves like a particle with integral spin (Bosons)
- Bosons do not obey Pauli's exclusion principle – hence they can be in same quantum state at low temperature
- Collision with lattice atoms is origin of resistance. But Cooper pair can't give up energy as they are in ground state.
- Cooper pair can't gain energy – due to energy gap
- Hence no interaction and no resistance

## Applications:

- To produce high field
- Magnetic resonance imaging (MRI)
- Magnetic levitation
- Lossless power transmission