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

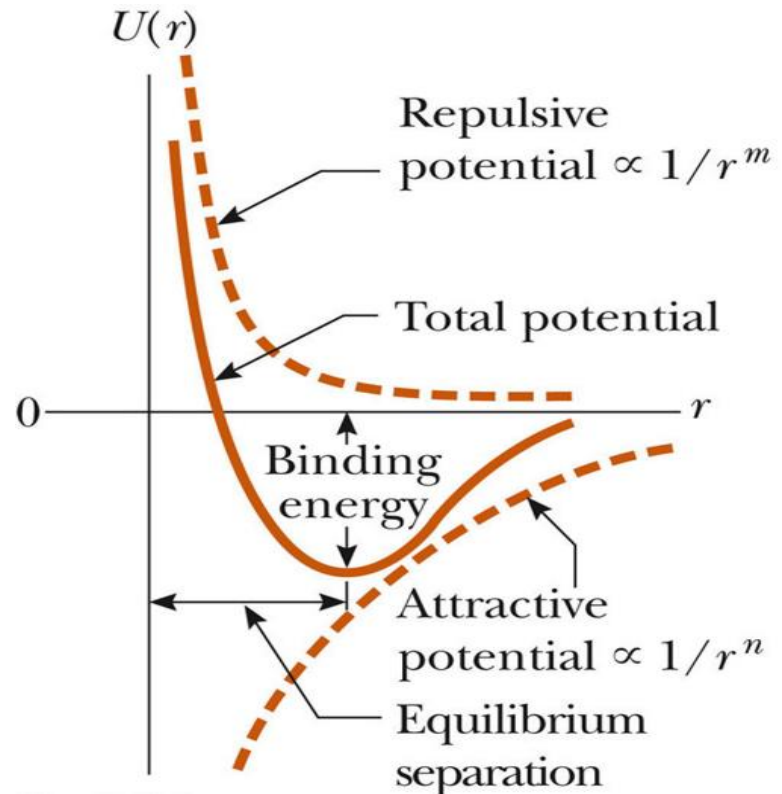- To understand superconductivity and its engineering applications

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 larger separations, the force between atoms is **attractive**.

Considering these two features, (**Lennard–Jones potential**)

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

$U(r)$

Repulsive potential $\propto 1/r^m$

Total potential

0

Binding energy

Attractive potential $\propto 1/r^n$

Equilibrium separation

r

MOLECULAR BONDS – types

✓ Ionic Bonding

✓ Covalent Bonding

✓ Van der Waals Bonding

✓ Hydrogen Bonding

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. Ionic bonds are fundamentally caused by the **Coulomb attraction between oppositely charged ions.**

Example: NaCl
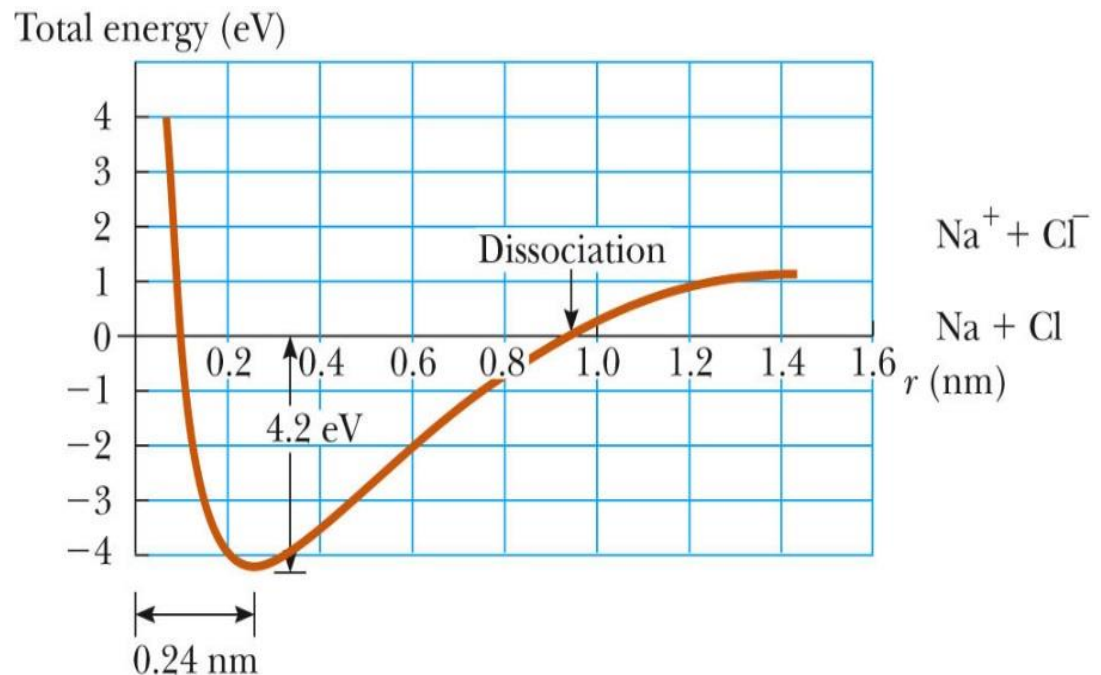
Total energy versus internuclear separation distance for Na⁺ and Cl⁻ ions.

Ionic Bonding:

An ionic bond is formed by electrostatic attraction between oppositely charged ions. Eg, NaCl.

Ionization energy of Na is 5.1 eV. The electron affinity of Cl is 3.7 eV. Thus, the energy required to form Na^+ and Cl^- ions from the neutral atoms is 5.1 – 3.7 = 1.4 eV. This is the total energy of NaCl molecule when the ions infinitely apart. This energy decreases to minimum (–4.2 eV) at the equilibrium separation distance (0.24 nm).

Hence , the dissociation energy of NaCl is 4.2 eV.

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 H_2, F_2, and CO—owe their stability to covalent bonds.
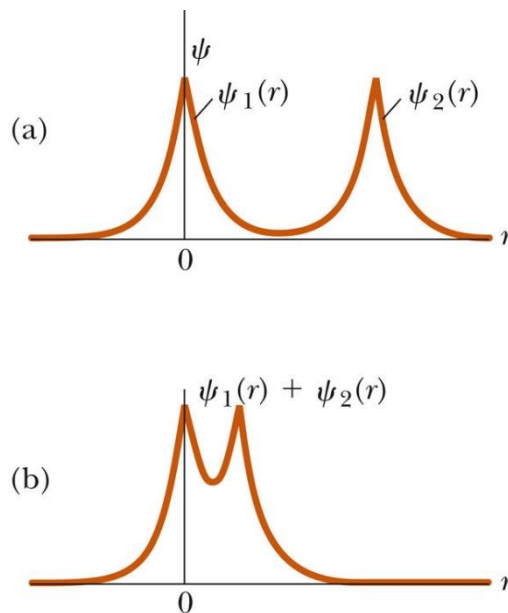
Ground-state wave functions $\psi_1(r)$ and $\psi_2(r)$ for two atoms making a covalent bond. (a) The atoms are far apart, and their wave functions overlap minimally. (b) The atoms are close together, forming a composite wave function $\psi_1(r) + \psi_2(r)$ for the system.

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:**

- **Dipole–induced dipole force**:

- **Dispersion force:**

The first type, called the ***dipole– dipole force***, is an interaction between two molecules each having a permanent electric dipole moment. For example, polar molecules such as HCl have permanent electric dipole moments and attract other polar molecules.

The second type, the ***dipole–induced dipole force***, results when a polar molecule having a permanent electric dipole moment induces a dipole moment in a nonpolar molecule. In this case, the electric field of the polar molecule creates the dipole moment in the nonpolar molecule, which then results in an attractive force between the molecules.

The third type is called the ***dispersion force***, an attractive force that occurs between two nonpolar molecules. Two nonpolar molecules near each other tend to have dipole moments that are correlated in time so as to produce an attractive van der Waals force.

Hydrogen Bonding
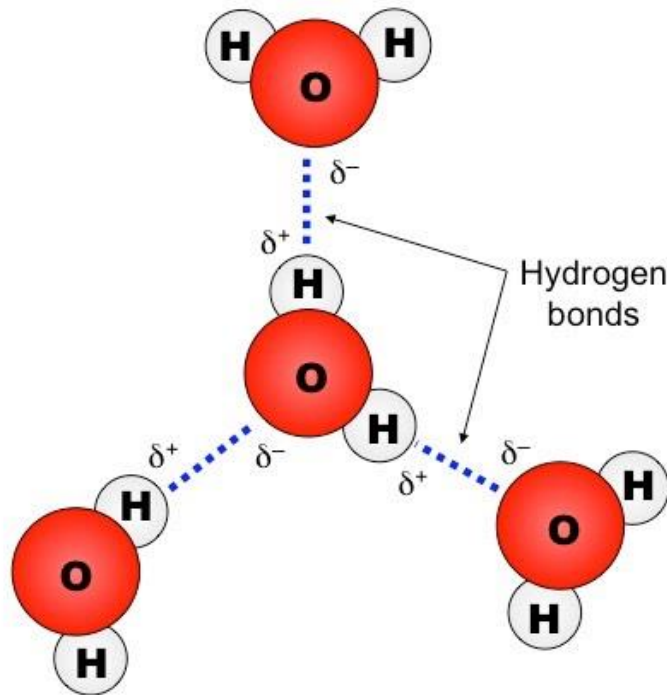
Hydrogen Bonding: A hydrogen bond is a weak electrostatic chemical bond which forms between covalently bonded H-atoms and a strongly electronegative atom with a lone pair of electrons (eg: O, N, F).
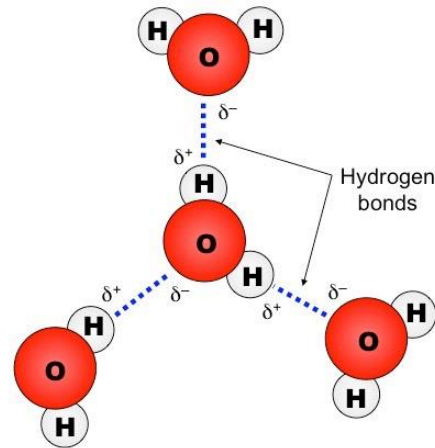
In the two covalent bonds in H_2O, the electrons from the H-atoms are more likely to be found near the O-atom than near the H-atoms. Thus the protons (H-nuclei) are unshielded by electrons and can be attracted to the negative end of another polar molecule (eg: O of H_2O). This way hydrogen bond is formed between two H_2O molecules. This bond is strong enough to form a solid crystalline structure (ice). Similarly, DNA molecules are held together by N–H - - - N hydrogen bonds.

A K^+ ion and a Cl^- ion are separated by a distance of 5.00×10^{-10} m. Assuming the two ions act like point charges, determine

(a) the force each ion exerts on the other and

(b) the potential energy of the two-ion system in electron volts. Coulomb constant is 8.99×10^9 Nm^2C^{-2}
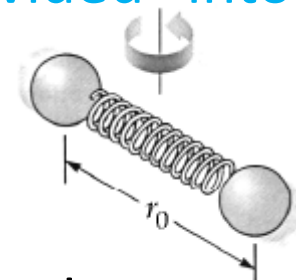
Solution (a)

(a) $\quad F = \dfrac{q^2}{4\pi \epsilon_0 r^2} = \dfrac{\left(1.60 \times 10^{-19}\right)^2 \left(8.99 \times 10^9\right)}{\left(5.00 \times 10^{-10}\right)^2}$ N $= \boxed{0.921 \times 10^{-9} \text{ N}}$ toward the other ion.

Solution (b)

(b) $\quad U = \dfrac{-q^2}{4\pi \epsilon_0 r} = -\dfrac{\left(1.60 \times 10^{-19}\right)^2 \left(8.99 \times 10^9\right)}{5.00 \times 10^{-10}}$ J $\approx \boxed{-2.88 \text{ eV}}$

ENERGY STATES AND SPECTRA OF MOLECULES

The energy of an isolated molecule can be divided into four categories:

(1) Electronic energy, due to the interactions between the molecule's electrons and nuclei;

(2) Translational energy, due to the motion of molecule's centre of mass through space;

(3) Rotational energy, due to the rotation of the molecule about its centre of mass; and

(4) Vibrational energy, due to the vibration of the molecule's constituent atoms:

$$E = E_{EL} + E_{TRANS} + E_{ROT} + E_{VIB}$$

The E_{ROT} and E_{VIB} give spectral lines in microwave and the infrared regions of the electromagnetic spectrum, respectively.
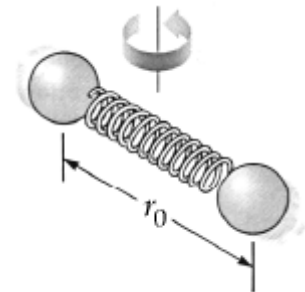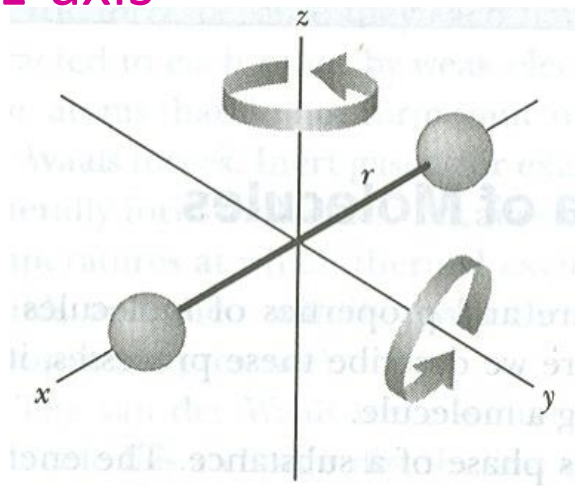
Rotational motion of molecules and Rotational energy
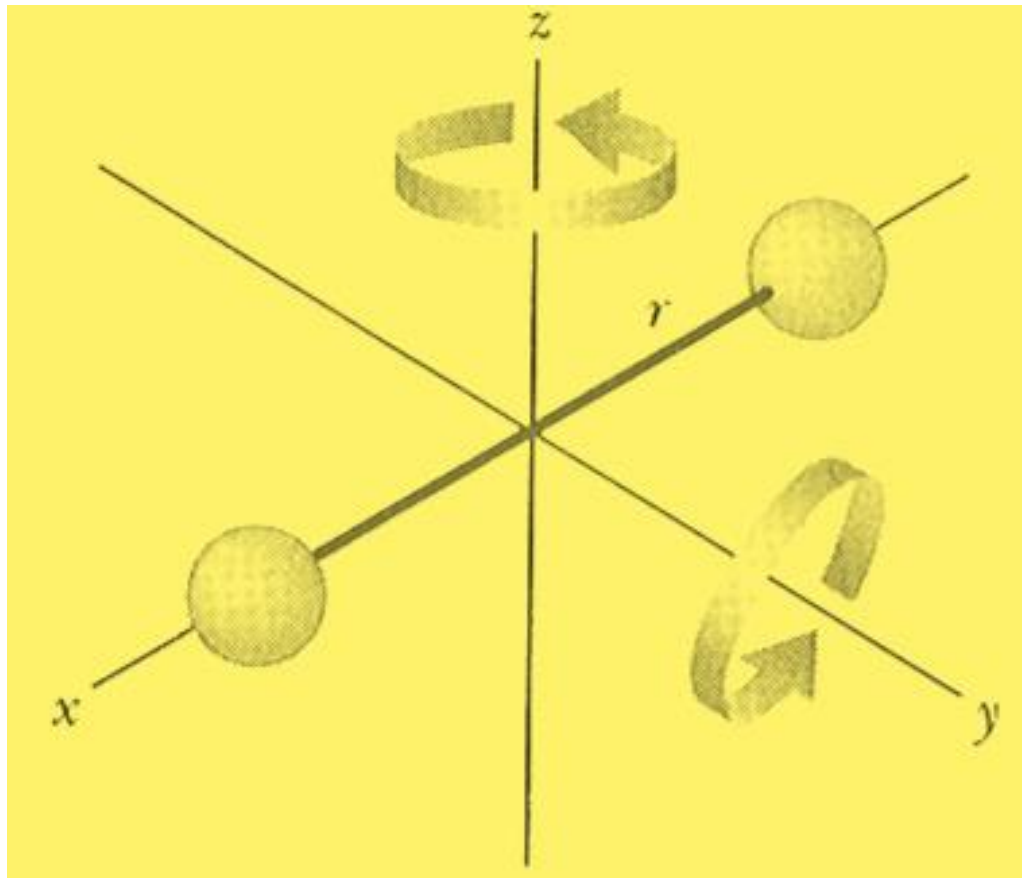
Rotational motion of molecules: A diatomic molecule (m_1, m_2 = masses of the atoms, r = internuclear separation) aligned along an x-axis has only two rotational degrees of freedom, corresponding to rotations about the y- and z-axes.

ω = angular frequency of rotation about y-axis or z-axis

E_{ROT} = rotational kinetic energy of the molecule about that axis

$$E_{ROT} = \tfrac{1}{2} I \omega^2$$

Moment of inertia of the diatomic molecule

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

Reduced mass of the diatomic molecule

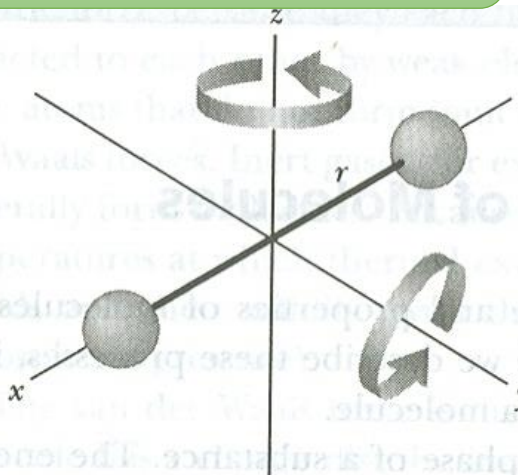$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

Magnitude of the classical angular momentum, $L = I \omega$

Rotational motion of molecules:

Quantized angular momentum of the molecule

$$L = \sqrt{J(J+1)}\ \hbar$$

$J = 0, 1, 2, \ldots$ = rotational quantum number

$$E_{ROT} = \tfrac{1}{2} I \omega^2 = \frac{1}{2I}(I\omega)^2$$

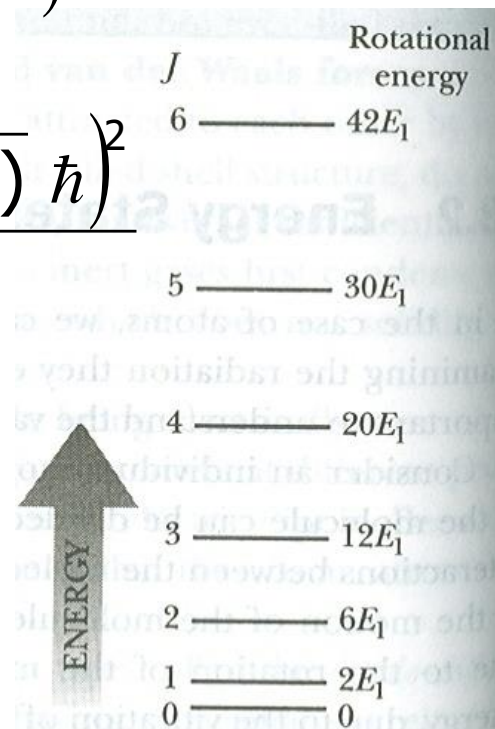$$E_{ROT} = \frac{L^2}{2I} = \frac{\left(\sqrt{J(J+1)}\ \hbar\right)^2}{2I}$$

$$E_{ROT} = \frac{\hbar^2}{2I} J(J+1) \qquad J = 0, 1, 2, \ldots$$

J	Rotational energy
6	$42E_1$
5	$30E_1$
4	$20E_1$
3	$12E_1$
2	$6E_1$
1	$2E_1$
0	0

ENERGY

$$E_1 = \frac{\hbar^2}{2I}$$

The rotational energy of the molecule is quantized and depends on its moment of inertia.

17

Rotational motion of molecules:

Selection rule for rotational transitions: $\Delta J = \pm 1$

Rotational transition photon energies:

$$\Delta E_{ROT} = E_J - E_{J-1} = \frac{\hbar^2}{2I}\left[J(J+1) - (J-1)J\right]$$
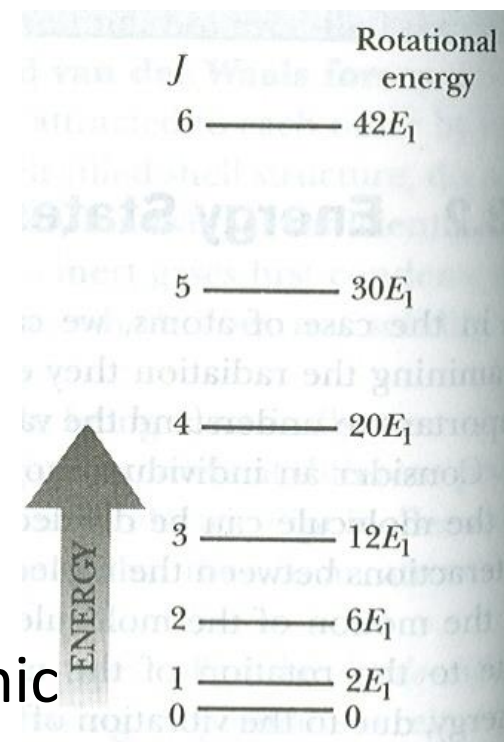
$$h\, f_{ROT} = \Delta E_{ROT} = \frac{\hbar^2}{I}J = \frac{h^2}{4\pi^2 I}J$$

$$J = 1, 2, 3, \ldots$$

$$f_1 = \frac{h}{4\pi^2 I} \qquad f_2 = 2\,f_1, \; f_3 = 3\,f_1, \text{ and so on}$$

These occur in the microwave region.

Quantized rotational energies of a diatomic molecule.

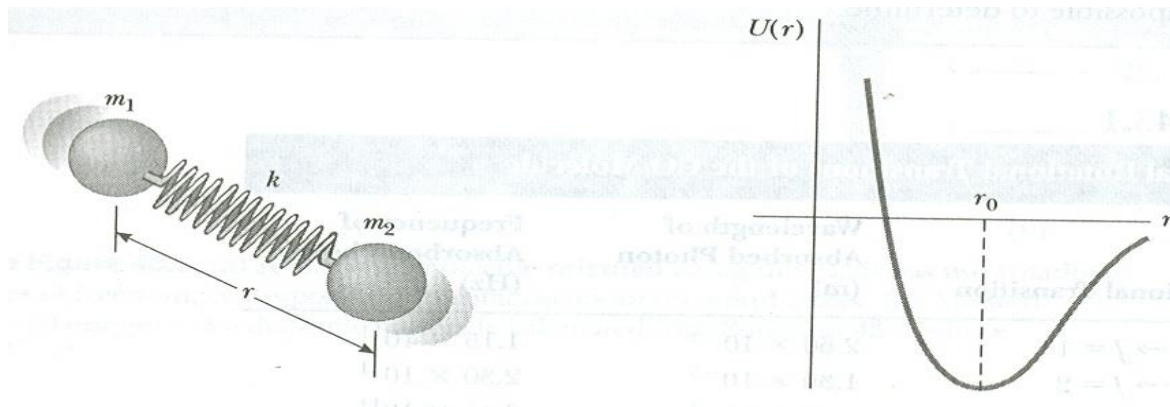|	Rotational energy
J	
6	$42E_1$
5	$30E_1$
4	$20E_1$
3	$12E_1$
2	$6E_1$
1	$2E_1$
0	0

ENERGY

SJ-PROBLEM 43.7:   An HCl molecule is excited to its first rotational energy level, corresponding to $J = 1$. If the distance between its nuclei is $r_o = 0.1275$ nm, what is the angular speed (ω) of the molecule about its centre of mass ?

$m_1 = 1u$ and $m_2 = 35$ u where u is the mass of proton ($= 1.67 \times 10^{-27}$ Kg)

5.69×10^{12} rad/s
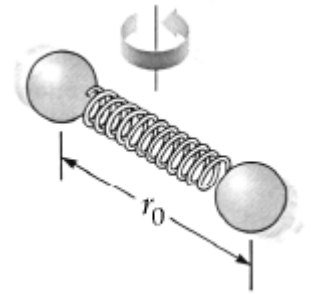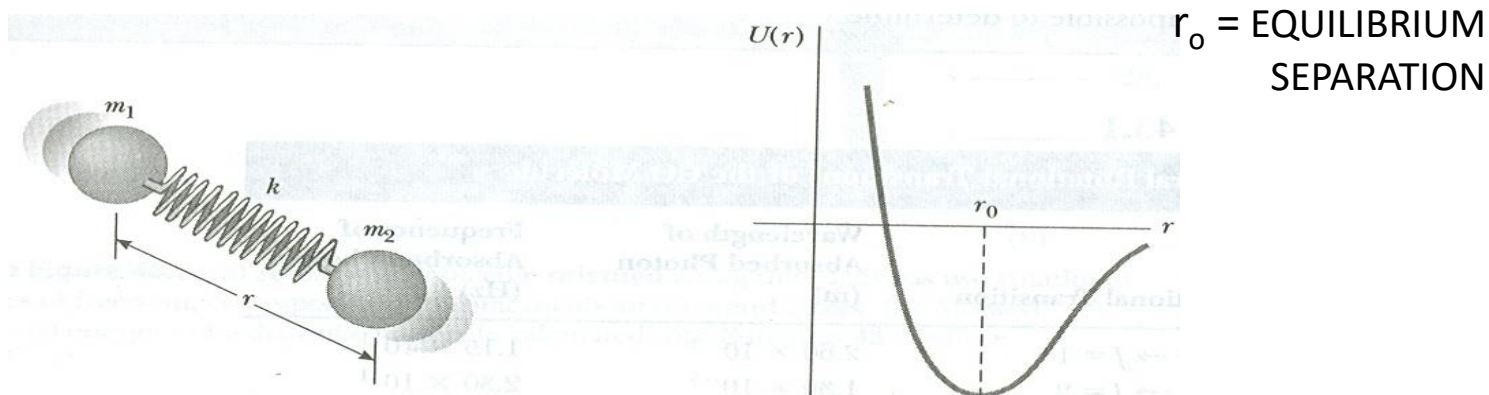
Vibration motion of molecules and Vibrational energy

$$E_{VIB} = \left(v + \tfrac{1}{2}\right)\frac{h}{2\pi}\sqrt{\frac{k}{\mu}} \qquad v = 0, 1, 2, \ldots$$

Vibrational motion of molecules:
Model of a diatomic molecule as a simple harmonic oscillator

Plot of potential energy function for a diatomic molecule

r_o = EQUILIBRIUM SEPARATION

For values of r close to r_o U varies as square of the displacement from equilibrium, like that of a simple harmonic oscillator.

According to classical mechanics, the frequency of vibration is

k = effective spring constant

μ = reduced mass

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

Vibrational motion of molecules:

According to quantum mechanics the vibrational motions are quantized. The allowed vibrational energies of the quantum harmonic oscillator are

$$E_{VIB} = \left(v + \tfrac{1}{2}\right)h\,f \qquad v = 0, 1, 2, \ldots$$

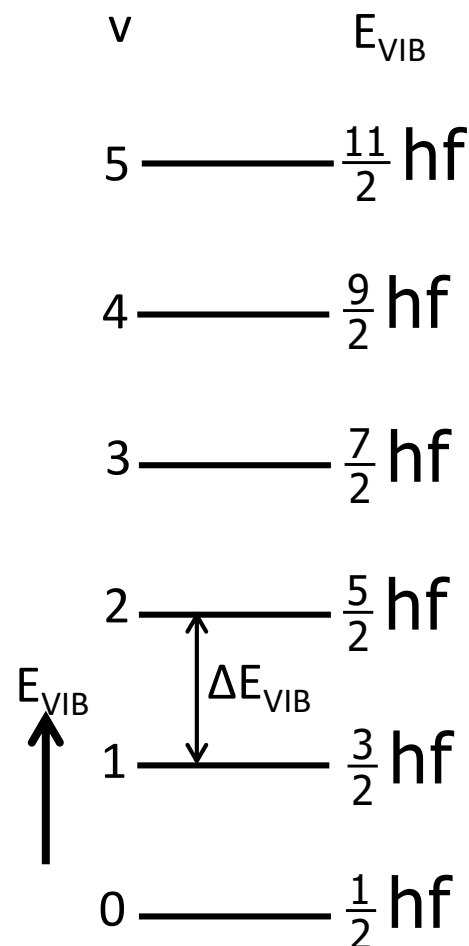v = vibrational quantum number

f = frequency of the oscillator

The lowest vibrational state has the energy = (½) hf.

Substitute $\qquad f = \dfrac{1}{2\pi}\sqrt{\dfrac{k}{\mu}}$

$$E_{VIB} = \left(v + \tfrac{1}{2}\right)\dfrac{h}{2\pi}\sqrt{\dfrac{k}{\mu}} \qquad v = 0, 1, 2, \ldots$$

Selection rule for the allowed vibrational transitions: Δv = ±1

v		E_{VIB}
5	——	$\frac{11}{2}hf$
4	——	$\frac{9}{2}hf$
3	——	$\frac{7}{2}hf$
2	——	$\frac{5}{2}hf$
1	——	$\frac{3}{2}hf$
0	——	$\frac{1}{2}hf$

E_{VIB}

ΔE_{VIB}

Vibrational motion of molecules:
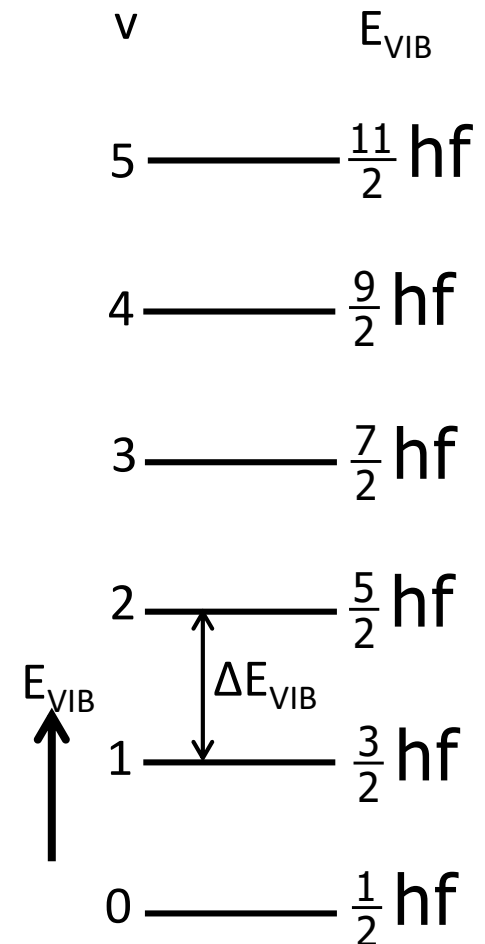
Vibrational transition photon energies:
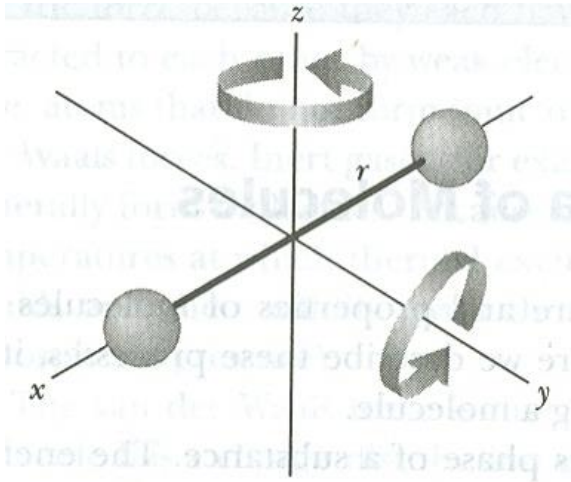
$$\Delta E_{VIB} = \frac{h}{2\pi}\sqrt{\frac{k}{\mu}} = hf$$

f = frequency of the oscillator.

These photons are in infrared region of the spectrum.

At room temperature most molecules have vibrational energies corresponding to the v = 0 state because the spacing between vibrational states is much greater than the thermal energy ($k_B T$) at room temperature (~ 25 meV).

v E_{VIB}
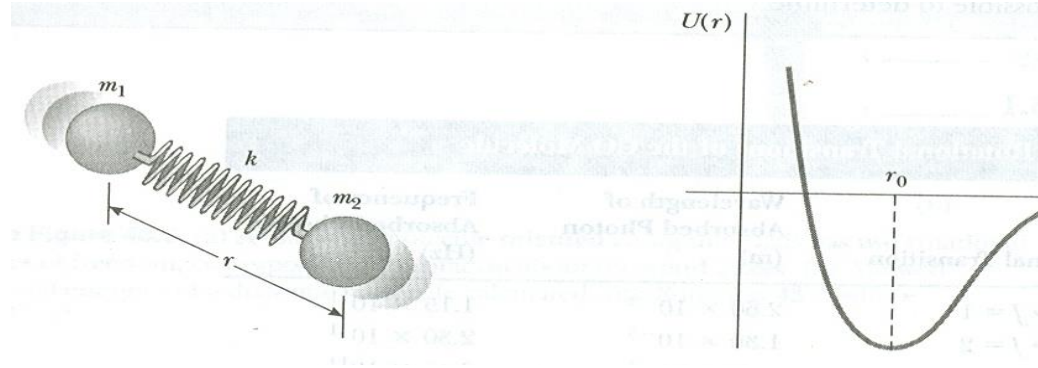
5 ———— $\frac{11}{2}hf$

4 ———— $\frac{9}{2}hf$

3 ———— $\frac{7}{2}hf$

2 ———— $\frac{5}{2}hf$

ΔE_{VIB}

E_{VIB} 1 ———— $\frac{3}{2}hf$

0 ———— $\frac{1}{2}hf$

$$E_{ROT} = \frac{\hbar^2}{2\,I}\, J(J+1) \qquad J = 0, 1, 2, \ldots$$

$$E_{VIB} = \left(v + \tfrac{1}{2}\right)\frac{h}{2\pi}\sqrt{\frac{k}{\mu}} \qquad v = 0, 1$$

SJ-EXAMPLE 43.2:   Vibration of the CO molecule:
The frequency of photon that causes $v = 0$ to $v = 1$ transition
in the CO molecule is 6.42 x 10^{13} Hz.   Ignore any changes in
the rotational energy.

(A) Calculate the force constant k for   this molecule.
(B) What is the maximum
classical amplitude of vibration for this molecule
in the $v = 0$ vibrational state ?

Atomic masses of C and O are 12 u and 16 u , respectively

v E_{VIB}

5 ——— $\frac{11}{2}hf$

4 ——— $\frac{9}{2}hf$

3 ——— $\frac{7}{2}hf$

2 ——— $\frac{5}{2}hf$

E_{VIB} ΔE_{VIB}

1 ——— $\frac{3}{2}hf$

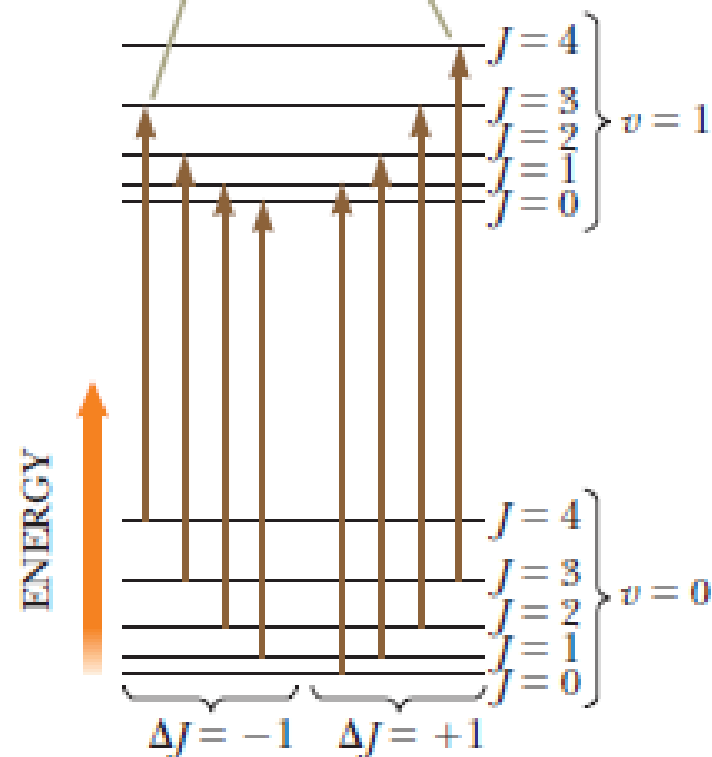0 ——— $\frac{1}{2}hf$

25
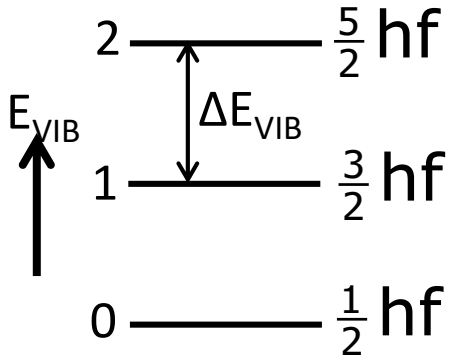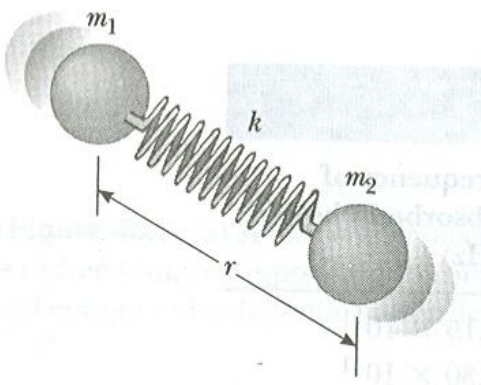
ENERGY STATES AND SPECTRA OF MOLECULES

In general a molecule vibrates and rotates simultaneously. So, for a molecule the total energy is the sum of its vibrational energy and rotational energy

vibrational energy

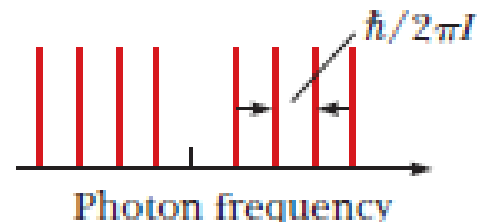rotational energy

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

The transitions obey the selection rule $\Delta J = \pm 1$ and fall into two sequences, those for $\Delta J = +1$ and those for $\Delta J = -1$.

$J=4$
$J=3$
$J=2$
$J=1$
$J=0$
$v=1$

ENERGY

$J=4$
$J=3$
$J=2$
$J=1$
$J=0$
$v=0$

$\Delta J = -1$ $\Delta J = +1$

a

$\hbar/2\pi I$

Photon frequency

EXPECTED LINES IN THE ABSORPTION SPECTRUM OF A DIATOMIC MOLECULE

ABSORPTIVE TRANSITIONS BETWEEN V = 0 AND V = 1 VIBRATIONAL STATES OF A DIATOMIC MOLECULE WITH CONDITION ΔJ = ±1
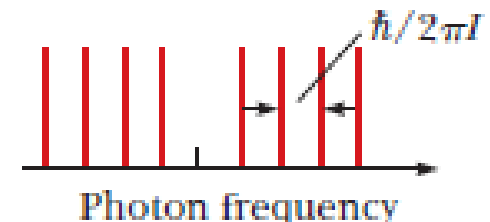
WHEN A MOLECULE ABSORBS A PHOTON OF FREQ (f), THE VIBRATIONAL QUANTUM NUMBER V INCREASES BY ONE UNIT WHILE ROTATIONAL QUANTUM NUMBER J EITHER INCREASES OR DECREASES BY ONE UNIT.

SO, MOLECULAR SPECTRUM CONSISTS OF TWO GROUPS OF LINES.

The transitions obey the selection rule $\Delta J = \pm 1$ and fall into two sequences, those for $\Delta J = +1$ and those for $\Delta J = -1$.
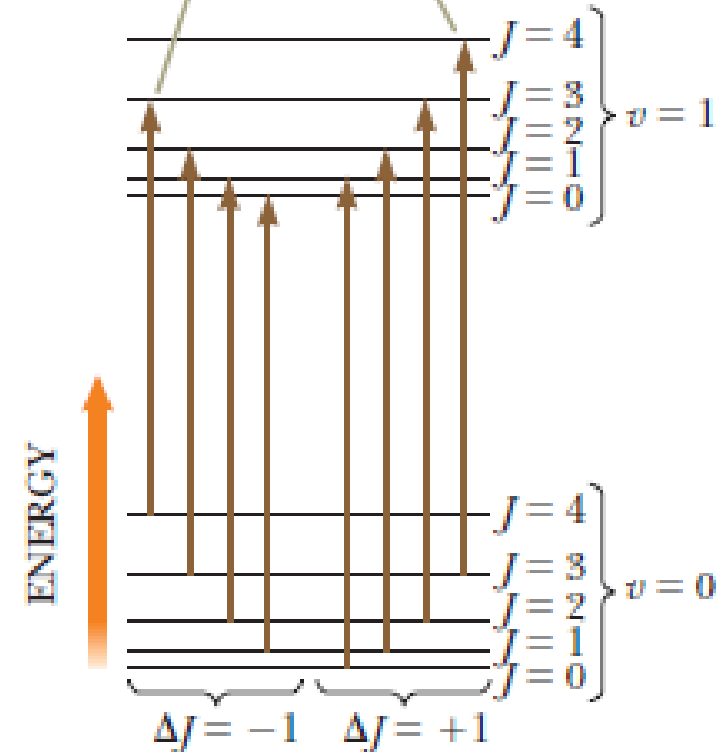
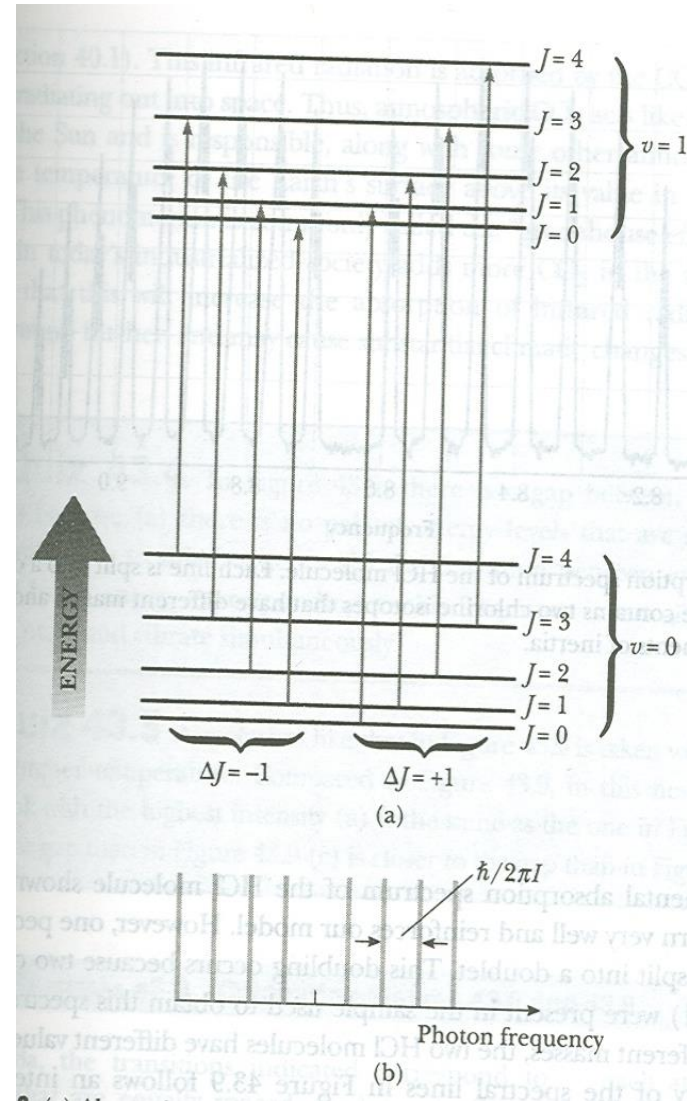Molecular spectra:

The energies of the absorbed photon of freq 'f':

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

(transition between J and J+1)

$$J = 0, 1, 2, \ldots \quad (\Delta J = +1)$$

J = rotational quantum number of the initial state.

ADJACENT SPECTRAL LINES ARE SEPARATED BY FREQUENCY:

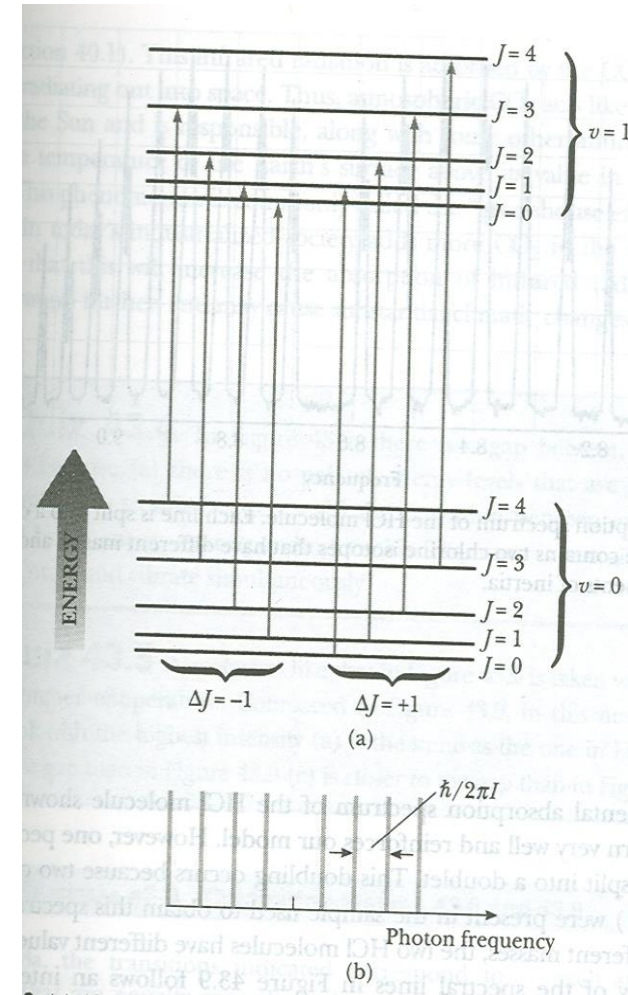$$\Delta f = \frac{\hbar}{2\pi I}$$

28

Molecular spectra:

The energies of the absorbed photon of freq 'f':

$$\Delta E = hf - \frac{\hbar^2}{I} J$$

(transition between J and J-1)
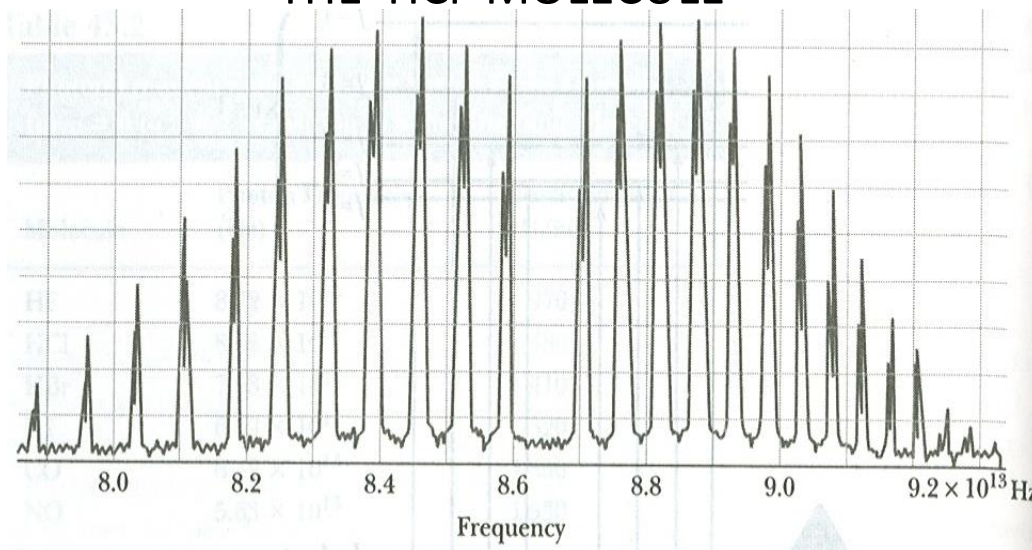
$$J = 1, 2, 3, \ldots \qquad (\Delta J = -1)$$

ADJACENT SPECTRAL LINES ARE SEPARATED BY FREQUENCY:

$$\Delta f = \frac{\hbar}{2\pi I}$$

29

Molecular spectra:

ABSORPTION SPECTRUM OF
THE HCl MOLECULE

THE DOUBLET IN EACH PEAK IS DUE TO THE TWO ISOTOPES OF Cl. Because the isotopes have different masses, the two HCl molecules have different values of I.

The number of molecules in an excited rotational state (n) is given by:

$$n = n_0 e^{\dfrac{-\hbar^2 J(J+1)}{2Ik_BT}}$$

$$Intensity \propto (2J+1)e^{\dfrac{-\hbar^2 J(J+1)}{2Ik_BT}}$$

n_o is the number of molecules in J=0 state

Bonding in Solids

- **Ionic Solids**

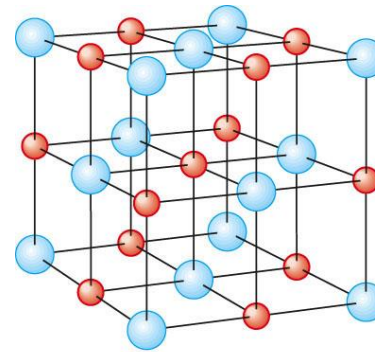- **Covalent Solids**

- **Metallic Solids**
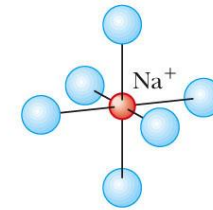
Bonding in Solids

Ionic Solids:

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

(a)   (b)   (c)

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

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

U_o is called the **ionic cohesive energy** of the solid
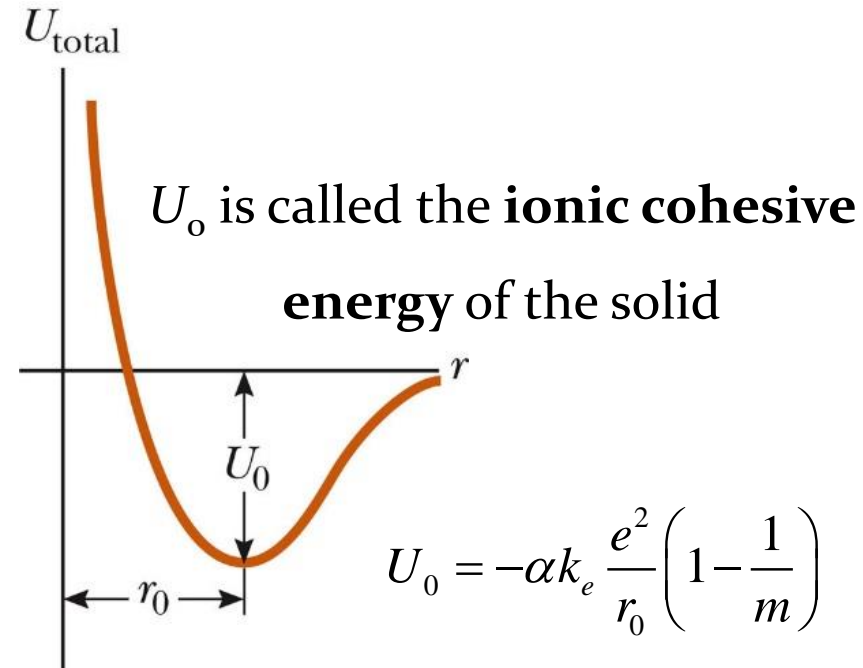
$$U_0 = -\alpha k_e \frac{e^2}{r_0}\left(1 - \frac{1}{m}\right)$$
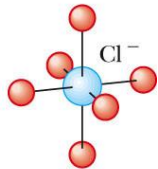
The ionic cohesive energy of a solid is the energy required to separate the solid into a collection of isolated positive and negative ions.

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.*

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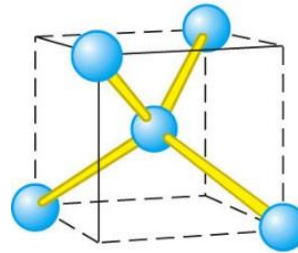
(a)
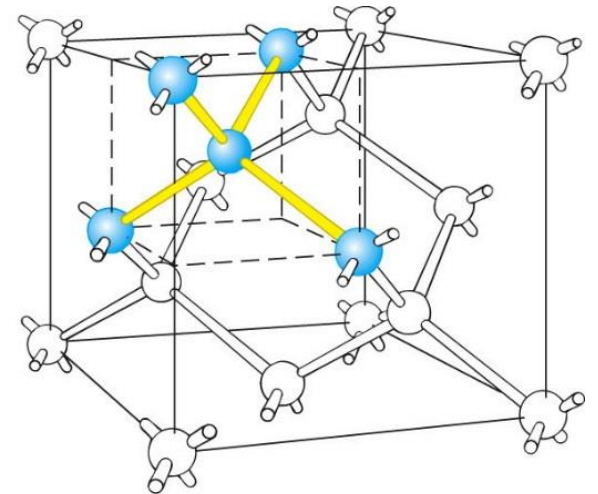
(b)

Free-Electron Theory of Metals

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.
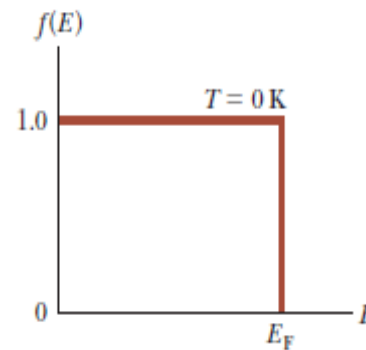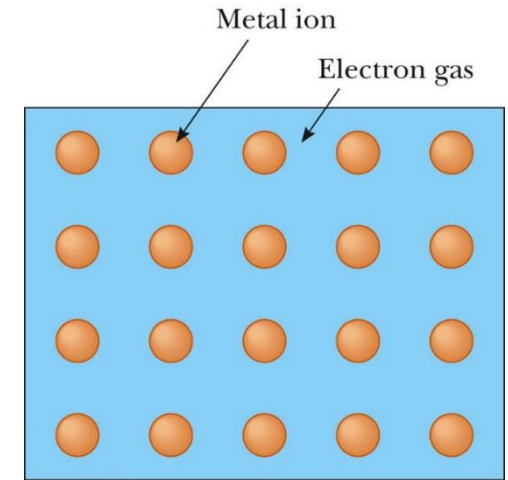
- Probability of occupation of a particular energy state by an electron in a solid is given by the Fermi-Dirac distribution function :

$$f(E) = \cfrac{1}{\exp\left(\cfrac{E - E_F}{kT}\right) + 1}$$
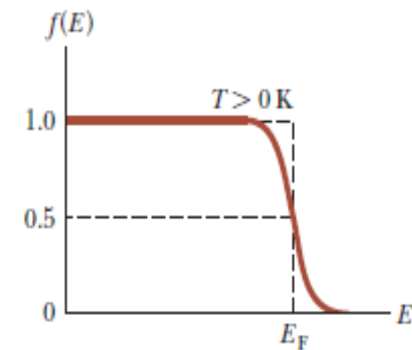
DERIVATION OF DENSITY-OF-STATES FUNCTION g(E):

The quantized energy of a particle (mass m) in a **one dimensional box** of (length L) are

$$E_n = \frac{h^2}{8\,m\,L^2}\,n^2 = \frac{\hbar^2\pi^2}{2\,m\,L^2}\,n^2 \qquad , \quad n = 1, 2, 3, \ldots$$

For a free-electron (mass m) in a metal cube of side L (three-dimensional box), the quantized energies are

$$E_n = \frac{\hbar^2\pi^2}{2\,m\,L^2}\left(n_x^2 + n_y^2 + n_z^2\right) \qquad n_x, n_y, n_z = \text{quantum numbers.}$$

Energy equation in 3D-box can be written as

$$n_x^2 + n_y^2 + n_z^2 = \frac{E}{E_o} = n^2$$

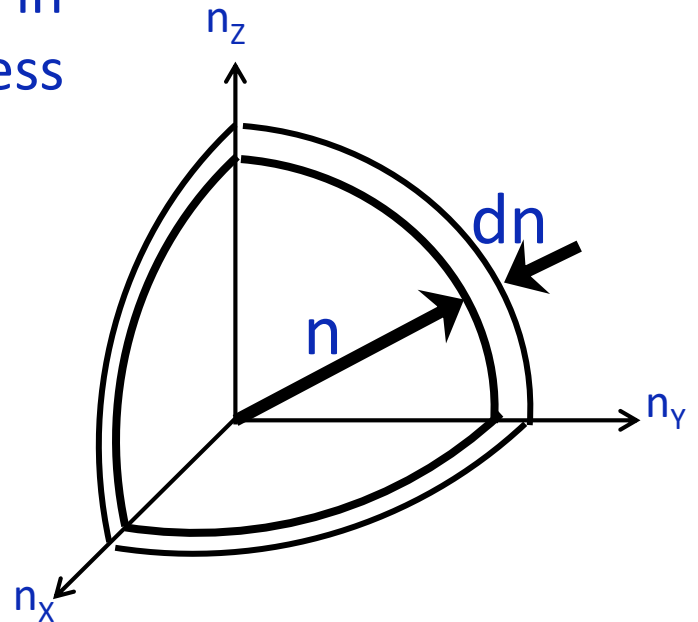where $E_o = \dfrac{\hbar^2 \pi^2}{2\,m\,L^2}$

and $n = \sqrt{\dfrac{E}{E_o}}$

This is the equation of a sphere of radius n. Thus, **the number of allowed energy states** having energies between E and E+dE is equal to the number of points in a spherical shell of radius n and thickness dn.

$G(E)dE = (\tfrac{1}{8})(4\pi n^2 dn) = (\tfrac{1}{2})\pi n^2 dn$

G(E) is the total number of states.

Since all the n_x, n_y, n_z can have positive values only in an octant of the three-dimensional space.

$$g(E) = \frac{G(E)}{V}$$

Replacing n by $\sqrt{\dfrac{E}{E_o}}$, G(E) dE= $(½)\boldsymbol{\pi}$n²dn

$$G(E)\, dE = \tfrac{1}{2}\,\pi \left(\frac{E}{E_o}\right) d\left[\left(\frac{E}{E_o}\right)^{\frac{1}{2}}\right]$$

d($E^{1/2}$) = (½)$E^{-1/2}$ dE

$$G(E)\ dE = \tfrac{1}{2}\,\pi \left(\frac{E}{E_o}\right) E_o^{-\frac{1}{2}}\,\tfrac{1}{2}\,E^{-\frac{1}{2}}\ dE = \tfrac{1}{4}\,\pi\,E_o^{-\frac{3}{2}}\,E^{\frac{1}{2}}\ dE$$

$$G(E)\ dE = \tfrac{1}{4}\,\pi \left(\frac{\hbar^2\pi^2}{2mL^2}\right)^{-\frac{3}{2}} E^{\frac{1}{2}}\ dE$$

Substituting for E_0

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

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

$$g(E)\,dE \;=\; \frac{4\sqrt{2}\,\pi\,m^{3/2}}{h^3}\,E^{1/2}\,dE \qquad \because \quad \hbar = \frac{h}{2\pi}$$

To consider the spin states, each particle-in-a-box state should be multiplied by 2.

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

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

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

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

AN EXPRESION FOR FERMI ENERGY OF A METAL AT ZERO K

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

Where n_e is the number of electrons per unit volume:

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 equal to the product of the number of allowed states and the probability that a state is occupied:
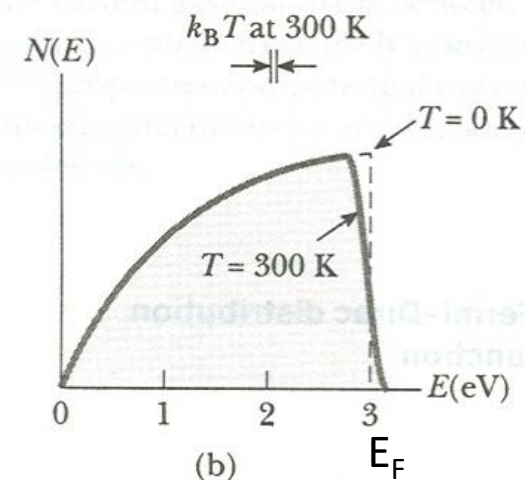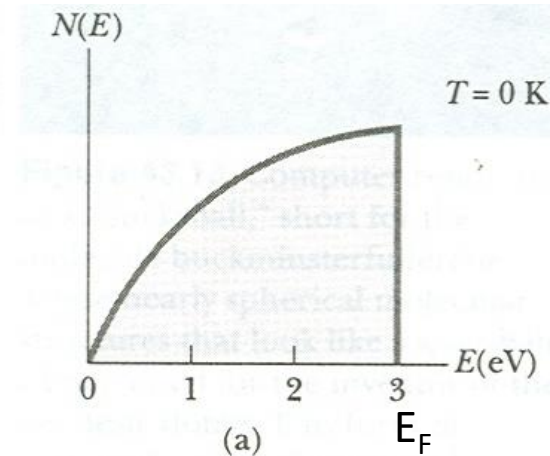
i.e N(E) dE= g(E) f(E)dE

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

The number of electrons per unit volume:

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

$$n_e\ =\ \frac{8\sqrt{2}\ \pi\ m^{3/2}}{h^3}\ \int_0^{E_F}\ \frac{E^{1/2}\ dE}{\exp\left(\dfrac{E-E_F}{k\ T}\right)\ +\ 1}$$

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

$$\therefore \text{ At } T = 0, \quad n_e = \frac{8\sqrt{2}\,\pi\,m^{3/2}}{h^3} \int_0^{E_F} E^{1/2}\, dE$$

$$n_e = \frac{8\sqrt{2}\,\pi\,m^{3/2}}{h^3} \left(\tfrac{2}{3}\right) E_F^{3/2} = \frac{16\sqrt{2}\,\pi\,m^{3/2}}{3\,h^3} E_F^{3/2}$$

→ FREE-ELECTRON DENSITY IN A METAL AT ZERO K

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

→ FERMI ENERGY OF A METAL AT ZERO K

The average energy of a free-electron in a metal at zero K is

$$E_{AV} = \tfrac{3}{5} E_F$$

At zero K, all levels below E_F are filled with electrons and all levels above E_F are empty. At 300 K, a very small fraction of the free electrons are excited above E_F.

SJ-PROBLEM 43.31: Calculate the energy of a conduction electron in silver at 800 K, assuming the probability of finding an electron in that state is 0.950. The Fermi energy is 5.48 eV at this temperature.

Solution:

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

$$f(E) = \left[\exp\left(\frac{E - E_F}{kT}\right) + 1\right]^{-1} = 0.950$$

$$\exp\left(\frac{E - E_F}{kT}\right) = \frac{1}{0.950} - 1 = 0.0526 \qquad \frac{E - E_F}{kT} = \ln(0.0526)$$

= -2.94 J

$$E - E_F = -2.94\frac{\left(1.38 \times 10^{-23}\right)(800)\ \text{J}}{1.60 \times 10^{-19}\ \text{J/eV}} = -0.203\ \text{eV} \ \text{ or } \ \boxed{E = 5.28\ \text{eV}}.$$

Show that the average kinetic energy of a conduction electron in a metal at zero K is

$$E_{AV} = \tfrac{3}{5} E_F$$

Suggestion: In general, the average kinetic energy is

$$E_{AV} = \frac{1}{n_e} \int E\, N(E)\, dE$$

where the density of particles

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

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

Solution:

$$E_{AV} = \frac{1}{n_e} \int E\, N(E)\, dE$$

$N(E) = 0$ for $E > E_F$;.

Since $f(E)=1$ for $E<E_F$ and $f(E)=0$ for $E>E_F$, we can take

$$N(E) = CE^{1/2} = \frac{8\sqrt{2}\pi\, m_e^{3/2}}{h^3}E^{1/2}$$

Since

$$E_{AV} = \frac{1}{n_e}\int E\, N(E)\, dE$$

$$E_{av} = \frac{1}{n_e}\int_0^{E_F} CE^{3/2}\, dE = \frac{C}{n_e}\int_0^{E_F} E^{3/2}\, dE = \frac{2C}{5n_e}E_F^{5/2}.$$

$$But \quad n_e = \frac{2}{3}\,\frac{8\sqrt{2}\,\pi\, m^{3/2}}{h^3}\, E_F^{3/2}$$

$$\frac{C}{n_e} = \frac{3}{2}E_F^{-3/2}$$

$$E_{av} = \left(\frac{2}{5}\right)\left(\frac{3}{2}E_F^{-3/2}\right)E_F^{5/2} = \boxed{\frac{3}{5}E_F}.$$

SJ-PROBLEM 43.35: (a) Consider a system of electrons confined to a three-dimensional box. Calculate the ratio of the number of allowed energy levels at 8.50 eV to the number at 7.00 eV. (b) Copper has a Fermi energy of 7.0 eV at 300 K. Calculate the ratio of the number of occupied levels at an energy of 8.50 eV to the number at Fermi energy. Compare your answer with that obtained in part (a). Solution:

(a) The density-of-states at energy E .

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

Hence the ratio required is.

$$\frac{g(8.50 \text{ eV})}{g(7.00 \text{ eV})} = \frac{C(8.50)^{1/2}}{C(7.00)^{1/2}} = \boxed{1.10}.$$

$$N(E) = \frac{8\sqrt{2}\,\pi\,m^{\frac{3}{2}}}{h^3}\,\frac{E^{\frac{1}{2}}}{\exp\left(\dfrac{E-E_F}{kT}\right)+1}$$

$$N(E) = \frac{CE^{\frac{1}{2}}}{\exp\left(\dfrac{E-E_F}{k_b T}\right)+1}$$

Hence, the required ratio is

$$\frac{N(8.50\ \text{eV})}{N(7.00\ \text{eV})} = \frac{(8.50)^{1/2}}{(7.00)^{1/2}}\left[\frac{e^{(7.00-7.00)/k_B T}+1}{e^{(8.50-7.00)/k_B T}+1}\right].$$

At $T = 300$ K, $k_B T = 4.14\times10^{-21}$ J $= 0.025\,9$ eV,

$$\frac{N(8.50\ \text{eV})}{N(7.00\ \text{eV})} = \frac{(8.50)^{1/2}}{(7.00)^{1/2}}\left[\frac{2.00}{e^{(1.50)/0.025\,9}+1}\right].$$

And

$$\frac{N(8.50\ \text{eV})}{N(7.00\ \text{eV})} = \boxed{1.55\times10^{-25}}.$$

Comparing this result with that from part (a), we conclude that very few states with $E > E_F$ are occupied.

Band Theory of Solids

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.
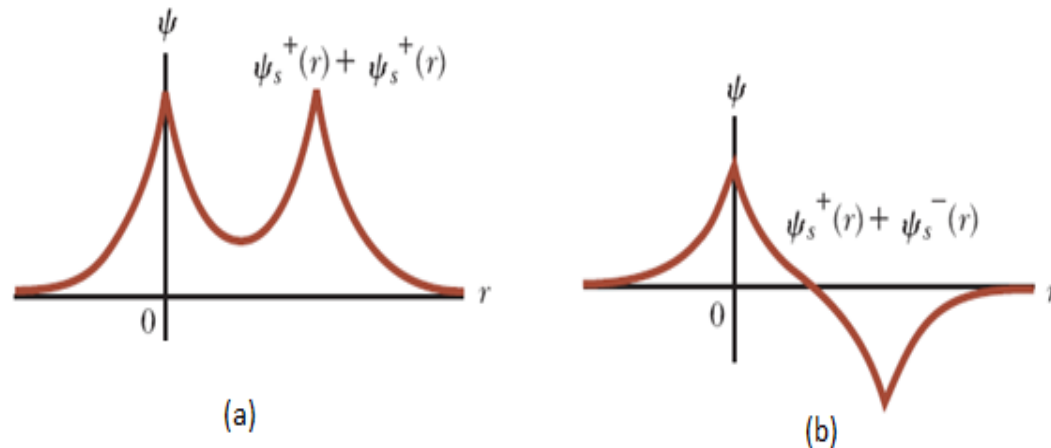
The wave functions of two atoms combine to form a composite wave function : a) symmetric-symmetric
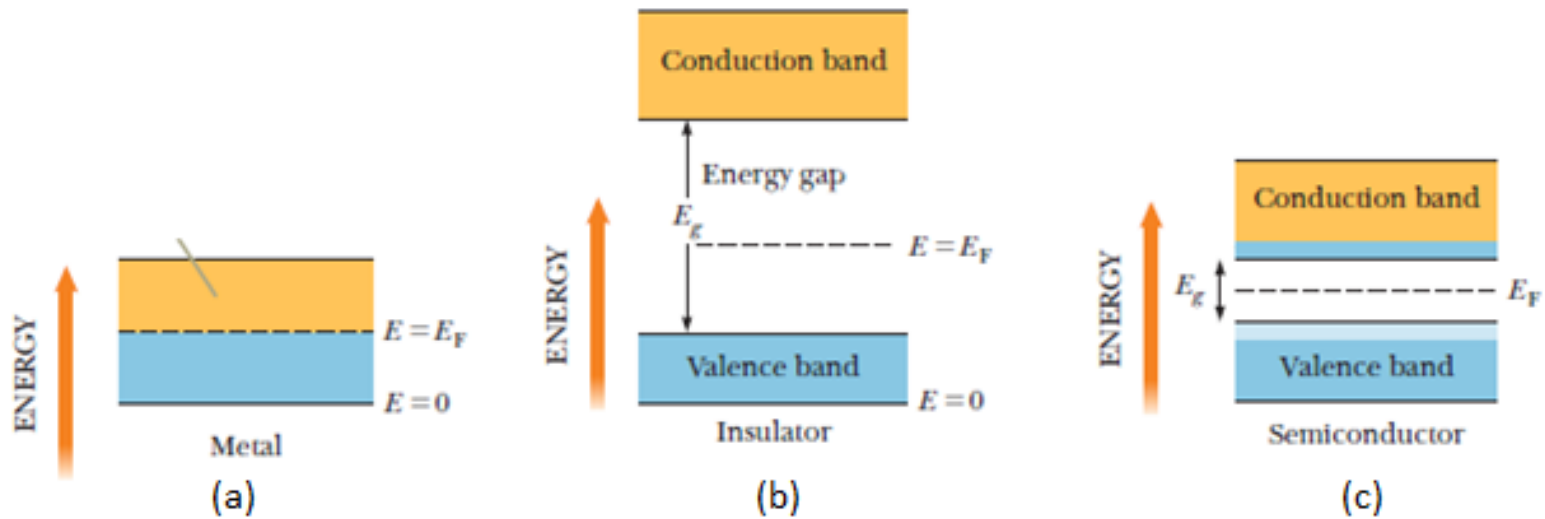
b) symmetric-antisymmetric
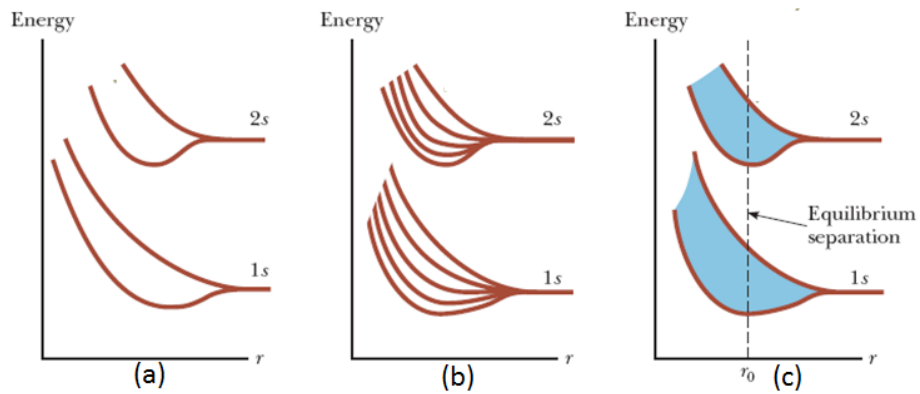
Splitting of 1s and 2s levels
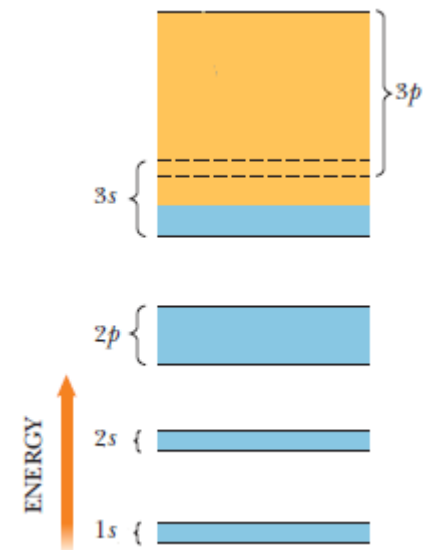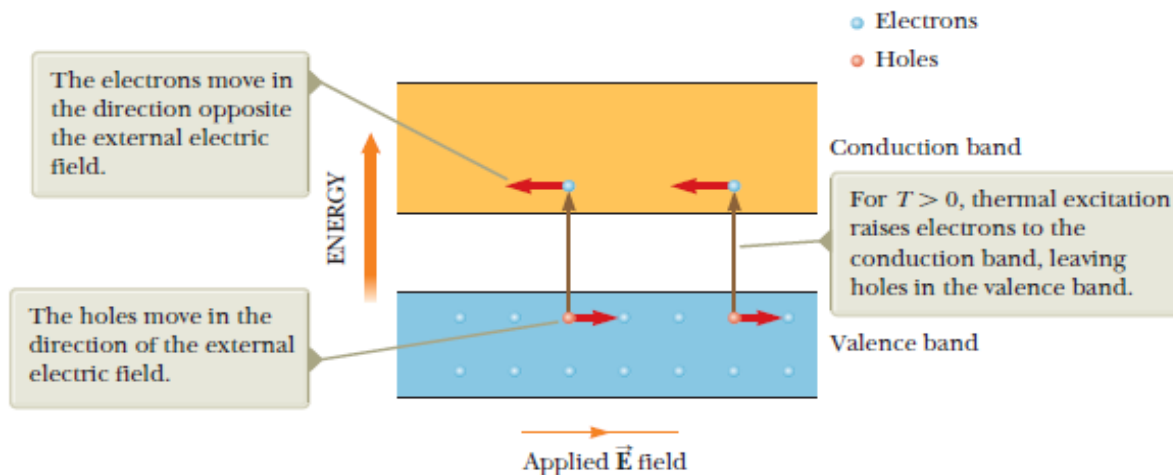

Energy bands of a sodium crystal

Electrical Conduction in Metals, Insulators and Semiconductors

a) Metals

b) Insulators

c) Semiconductors

- Semiconductors

The charge carriers in a semiconductors are electrons and holes.

The electrons move in the direction opposite the external electric field.

The holes move in the direction of the external electric field.

Electrons
Holes

Conduction band

For $T > 0$, thermal excitation raises electrons to the conduction band, leaving holes in the valence band.

Valence band

Applied $\vec{E}$ field

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
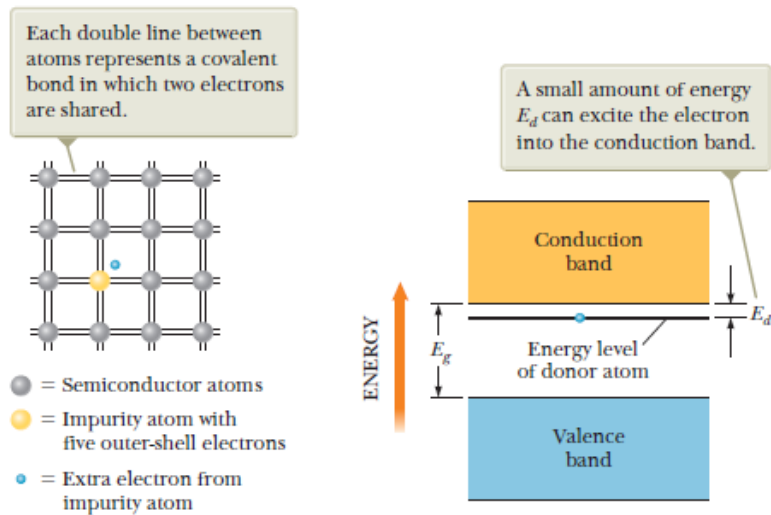
n-type semiconductor
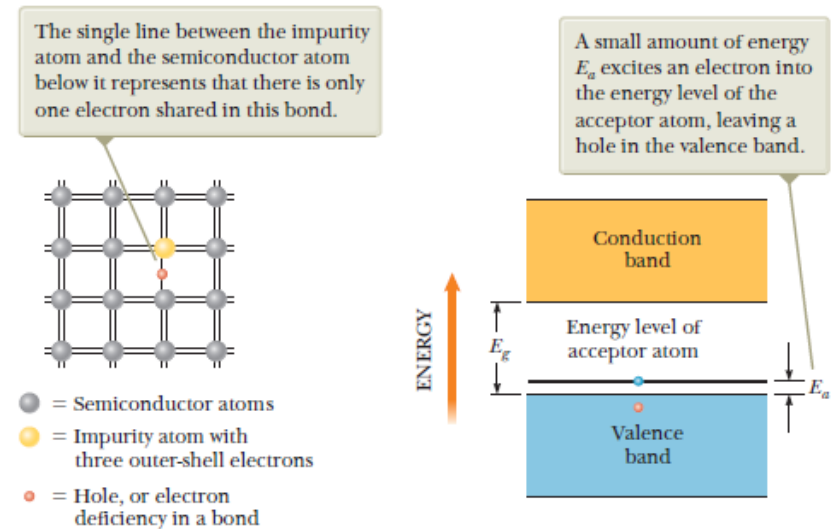
p-type semiconductor
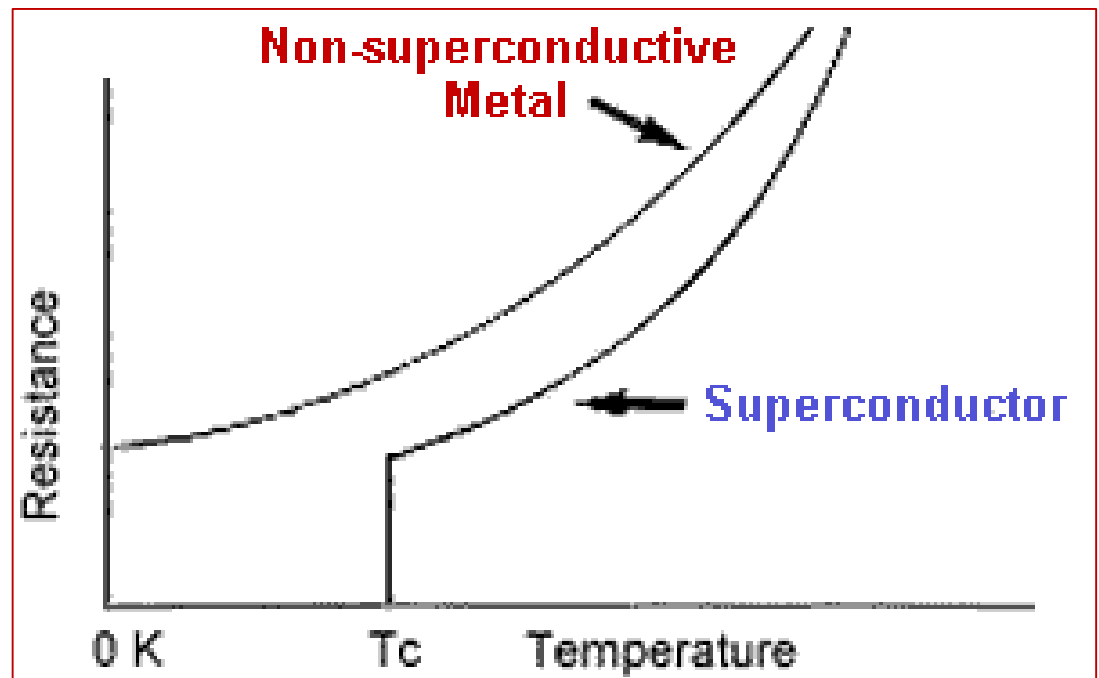
Superconductivity-Properties and Applications

# 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.

$T > T_c$

$T < T_c$

I
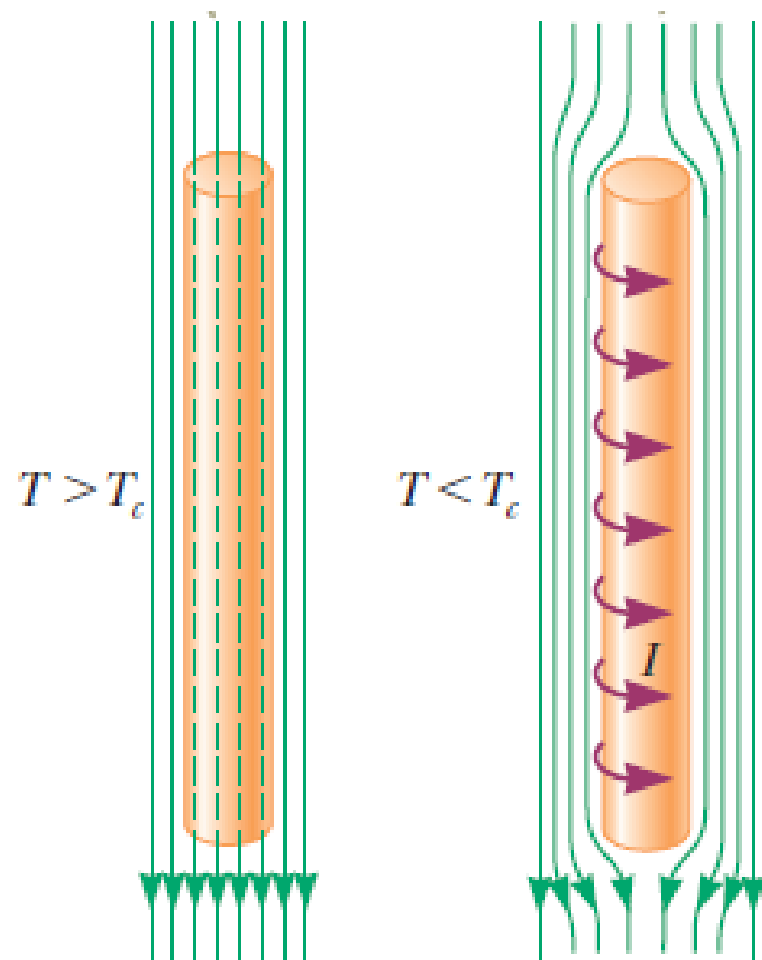
BCS Theory:

- 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

A light-emitting diode (LED) made of the semiconductor GaAsP emits red light (λ= 650nm). Determine the energy-band gap E_g in the semiconductor.
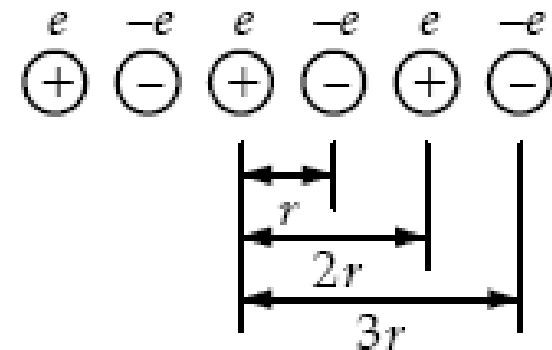
Ans: 1.91 eV

$$E_g = \frac{hc}{\lambda} = 1.91\ eV$$

SJ-PROBLEM 43.25: Consider a one-dimensional chain of alternating positive and negative ions. Show that the potential energy associated with one of the ions and its interactions with the rest of this hypothetical crystal is

$$U(r) = -k_e \alpha \frac{e^2}{r}$$

where the Madelung constant is $\alpha = 2\ln 2$ and r is the inter-ionic spacing.

Hint: Use the series expansion

$$\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \dots$$

$$U = -\frac{k_e e^2}{r} - \frac{k_e e^2}{r} + \frac{k_e e^2}{2r} + \frac{k_e e^2}{2r} - \frac{k_e e^2}{3r} - \frac{k_e e^2}{3r} + \frac{k_e e^2}{4r} + \frac{k_e e^2}{4r} - \dots$$

$$= -\frac{2k_e e^2}{r}\left(1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \dots\right)$$

But, $\ln(1+x) = \cancel{x} - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \dots$ (x=1)

so, $U = -\frac{2k_e e^2}{r}\ln 2$, or $\boxed{U = -k_e \alpha \frac{e^2}{r} \text{ where } \alpha = 2\ln 2}$.

SJ-PROBLEM 43.39: Most solar radiation has a wavelength of 1 μm or less. What energy gap should the material in solar cell have in order to absorb this radiation ? Is silicon (E_g= 1.14 eV) appropriate ?

solution:

If $\lambda \le 1.00 \times 10^{-6}$ m, then photons of sunlight have energy

$$E \ge \frac{hc}{\lambda_{max}} = \frac{\left(6.626 \times 10^{-34}\ \text{J}\cdot\text{s}\right)\left(3.00 \times 10^{8}\ \text{m/s}\right)}{1.00 \times 10^{-6}\ \text{m}}\left(\frac{1\ \text{eV}}{1.60 \times 10^{-19}\ \text{J}}\right) = 1.24\ \text{eV} .$$

Thus, the energy gap for the collector material should be

Eg ≤ 1.24 eV. Since Si has an energy gap Eg ≈ 1.14 eV, it will absorb radiation of this energy and

greater. Therefore, Si is acceptable as a material for a solar collector.

Estimate the band gap energy of the semiconductor in the infrared LED (wavelength = 1.0 µm) of a typical TV-remote control.

Solution:

The energy of the photons given by $E = hc/\lambda$ therefore the energy of the photons from the remote control is

$E = hc/\lambda = 1.24$ eV

Niobium metal becomes a super conductor when cooled below 9K. Its superconductivity is destroyed when the surface magnetic field exceeds 0.100T. Determine the maximum current a 2.00 mm diameter Niobium wire can carry and remain super conducting, in the absence of any external magnetic field. $\mu_0=4\pi\times10^{-7}$ Hm^{-1}

$$B = \frac{\mu_0 I}{2\pi r}$$

$$B_{max} = \frac{\mu_0 I_{max}}{2\pi r}$$

$$I_{max} = \frac{2\pi r B_{max}}{\mu_0} = 500\ A$$

SJ-PROBLEM 43.47: Determine the current generated in a superconducting ring of niobium metal 2.00 cm in diameter when a 0.0200-T magnetic field directed perpendicular to the ring is suddenly decreased to zero. The inductance of the ring is 3.10×10^{-8} H.

Solution:

By Faraday's and Lenz law

$$\frac{\Delta \Phi_B}{\Delta t} = L \frac{\Delta I}{\Delta t} = A \frac{\Delta B}{\Delta t}.$$

$$\Delta I = \frac{A(\Delta B)}{L} = \frac{\pi (0.010\,0 \text{ m})^2 (0.020\,0 \text{ T})}{3.10 \times 10^{-8} \text{ H}} = \boxed{203 \text{ A}}.$$