

UNIT-1

BONDS TO BANDS

Introduction to quantum chemistry – Motion of a quantum mechanical particle in one dimension (time- independent) – Schrödinger wave equation for hydrogen atom (No derivation) – Physical meaning of wave function - Angular and radial wave functions and probability densities – Quantum numbers – Principal, azimuthal, spin and magnetic quantum numbers – Wave functions and orbital shapes - s,p,d,f - LCAO-MO of H₂ – Band theory of solids: Conductors, semi-conductors and superconductors – Role of As and Ga doping on band structures.

1.1 INTRODUCTION

In this chapter, we shall give an overview of the properties of solids and how quantum mechanics helps us to understand these properties. In the solid state, a material at a given temperature and pressure has a well definite shape. The forces of interaction between the atoms in the solid must be strong and the bonds between them are stable under existing conditions. In subsections, we used quantum mechanics to understand how these bonds are formed. We have considered the crystalline solids, in which the bonds allow the formation of regular arrays of atoms within the solid. In other subsections, we give an introductory treatment of energy bands and the band theory of solids to explain the electrical conductivity and why some solids are conductors, whereas others are semiconductors or insulators.

Most important among these is the idea of a bond, and the use of frontier-orbital arguments. Interpretative constructs, such as the density of states, the decomposition of these densities and crystal orbital overlap population, allow a

Bonds to Bands

recovery of bonds, a finding of the frontier orbitals that control structure and reactivity in extended systems as well as discrete molecules.

1.2 ELECTROMAGNETIC WAVE

Electromagnetic wave or radiation is a wave that consists of oscillating electric and magnetic fields which is characterized by wavelength λ and frequency ν (number of oscillations per second). The wavelength and frequency of the wave is related to velocity c ($3 \times 10^8 \text{ ms}^{-1}$) of the wave by $c = \lambda\nu$

1.3 BLACK BODY RADIATION

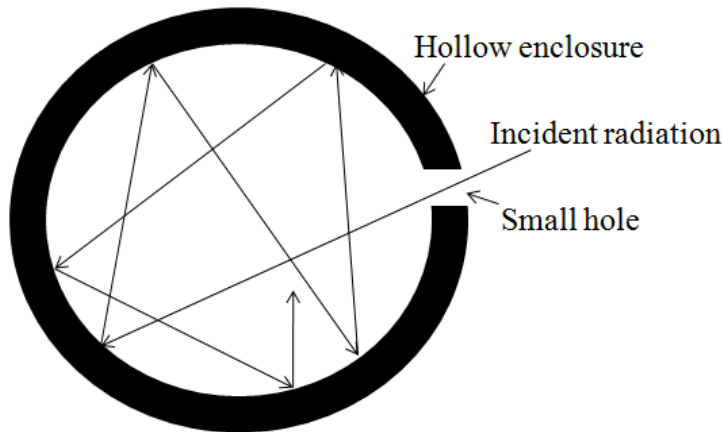


Fig 1.1 Black body radiation

An ideal black body is an object that absorbs all the radiations falling on it. A hollow enclosure or chamber having a small hole is an appropriate black body because it absorbs all the radiation entering it due repeated reflections inside the enclosure. The radiation emitted from such a black body is called black body radiation. A perfect absorber is also a perfect emitter of radiation. The intensity of the total radiation emitted per unit surface area from a black body depends on temperature T and is independent of the nature of the solid.

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1.3.1 Laws of Radiation

The radiation emitted by a heated body is explained by the laws of radiation.

1.3.1.1 Wien's law

The wavelength λ_m corresponding to the maximum energy density $\rho(\nu)d\nu$ is inversely proportional to the temperature T.

$$\lambda_m \propto \frac{1}{T}$$

$$\lambda_m = \frac{b}{T}$$

$$\lambda_m T = b$$

where b is called Wien's constant and value of b is 2897 microkelvin.

1.3.1.2 Rayleigh-Jean's law

Rayleigh derived an equation for the distribution of energy density called the Rayleigh-Jean's law

$$\rho(\nu)d\nu = \frac{8\pi\nu^2}{c^3} K_B T d\nu$$

where $\rho(\nu)d\nu$ is the energy density and K_B is the Boltzmann constant ($1.38 \times 10^{-23} \text{ JK}^{-1}$).

1.3.1.3 Planck's law of radiation

Max Planck derived an expression for energy density of a black body radiation called as Planck's radiation law and is given by

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$$\rho(\nu)d\nu = \frac{8\pi h\nu^3}{c^3} \frac{1}{(e^{(h\nu/K_B T)} - 1)} d\nu$$

Planck introduced a constant h known as Planck's constant (value of $h = 6.626 \times 10^{-34} \text{Js}$). He proposed the Planck's quantum theory based on energy quantization to explain the black body radiation.

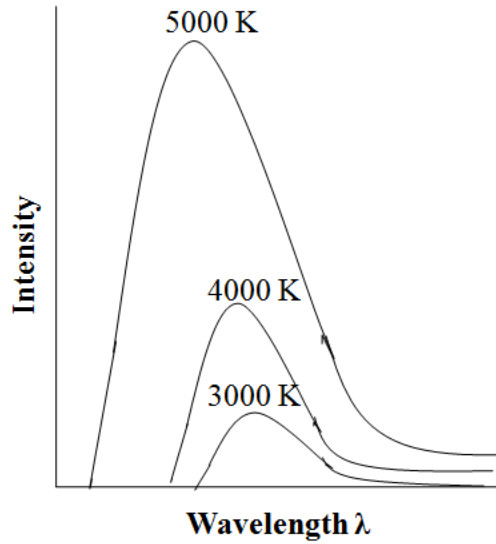


Fig 1.2 Planck's law of black body radiation

The black body emits radiation in a wide spectrum of wavelengths. The distribution of energy of emitted radiation over different frequencies is called as energy density and is given by $\rho(\nu)d\nu$. At any temperature T , the energy density $\rho(\nu)d\nu$ increases with increase in ν , reaches a maximum and then drops to zero. With increase in T , the maximum of curve shifts to higher frequency (i.e) shorter wavelength side.

Planck's quantum theory of radiation

According to this theory

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1. Energy is absorbed or emitted in the form of discrete sets of small bundles of energy known as quanta.
2. Each quantum is associated with certain amount of energy $E = h\nu$, where h is Planck constant and ν is the frequency of radiation.
3. A body can emit or absorb energy only in integral multiples of quantum (i.e) $1h\nu, 2h\nu, 3h\nu, \dots, nh\nu$.

1.4 PHOTOELECTRIC EFFECT

In 1905, based on the Planck's idea of energy quantization, Albert Einstein discovered law of the photoelectric effect. According to photoelectric effect, when a light photon of a certain frequency ν strikes the surface of metal, electrons are emitted from the metal. The photon transfers its energy $h\nu$ to the electrons and this is used to overcome the binding energy (ω) and to increase kinetic energy $\left(\frac{1}{2}m\nu^2\right)$ of the emitted electrons.

$$h\nu = \omega + \frac{1}{2}m\nu^2$$

since $\omega = h\nu_0$, where ν_0 is the threshold frequency

$$h\nu = h\nu_0 + \frac{1}{2}m\nu^2$$

$$\frac{1}{2}m\nu^2 = h\nu - h\nu_0$$

$$\frac{1}{2}m\nu^2 = h(\nu - \nu_0)$$

This equation is called the Einstein photoelectric equation

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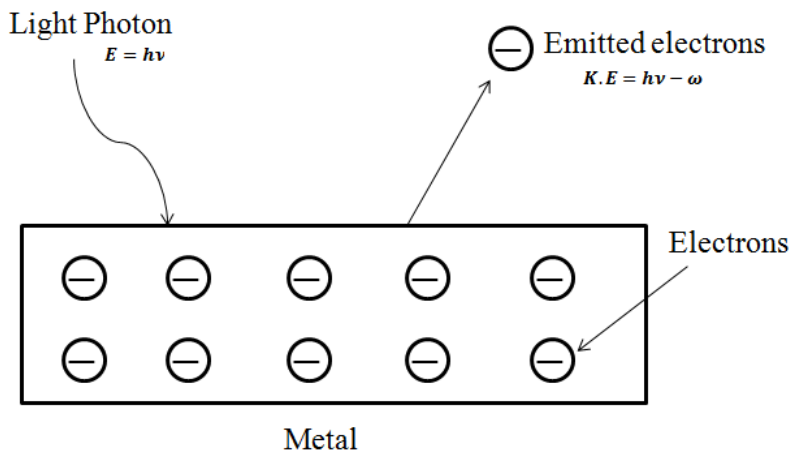


Fig 1.3 Photoelectric effect

Observations

1. Light with minimum frequency called the threshold frequency ν_0 is necessary to cause emission of electron by photoelectric effect. (If $\nu < \nu_0$ there is no photoelectric effect)
2. Kinetic energy of emitted electrons is directly proportional to frequency and independent of intensity of incident radiation.

1.5 WAVE – PARTICLE DUALITY OF ELECTRON – de BROGLIE’S HYPOTHESIS

Louis de Broglie in 1924 proposed that the quantization of energy of an atom can be explained only when electrons exhibit wave-particle dual behaviour. This hypothesis was verified through electron diffraction experiment by Davisson and Germer. The electrons produce diffraction patterns similar to light waves when passed through a nickel crystal which confirms the wave nature of electrons. de Broglie hypothesis can be derived by using Einstein’s energy mass relationship

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$$E = mc^2 \quad (1)$$

where c is velocity of photon and m is mass of photon.

According to Planck, the energy of photon is quantized which inherently possess the duality nature of particle, since energy of photon E is a particle property and frequency ν is a wave property.

$$E = h\nu \quad (2)$$

Thus from equations (1) and (2)

$$h\nu = mc^2 \Rightarrow \nu = \frac{mc^2}{h}$$

In wave theory of light, the frequency ν and wavelength λ is related to each other by the equation $\nu\lambda = c$

Therefore,

$$\lambda = \frac{c}{\nu} = \frac{ch}{mc^2} = \frac{h}{mc} = \frac{h}{p}$$

where p is the momentum of the photon $p = mc$

de Broglie proposed that the wavelength or frequency of electron similar to the photon is related to the momentum of the electron

$$\lambda = \frac{h}{mc} \text{ or } \frac{h}{p}$$

where λ = wavelength of electron, m = mass of electron, p = momentum of electron, h = Planck's constant.

de Broglie hypothesis of wave-particle duality is applicable to all subatomic particles such as neutrons, protons etc.

Bonds to Bands

1.6 HEISENBERG'S UNCERTAINTY PRINCIPLE

Heisenberg stated that “it is not possible, even in principle to measure both position and momentum of an electron simultaneously”. This is known as Heisenberg uncertainty principle. Mathematically it is expressed as

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$$

Where Δx is the uncertainty in position of the electron, Δp is the uncertainty in momentum of the electron and h is the Planck's constant. If the position of an electron is determined with high accuracy then its momentum becomes uncertain. Similarly, if the momentum of the electron is measured precisely then its position will be uncertain. This principle holds good only for microscopic particles however, it does not apply to larger bodies (i.e) both momentum and position can be determined accurately at the same time.

1.7 THEORY OF WAVE MOTION

The de Broglie, Heisenberg uncertainty principle and electron diffraction experiments established the dual nature of electrons as particle as well as wave. A particle is localized and it cannot be present in more than one place at same time whereas wave cannot be localized at a point and varies from a point to point in space. In order to insight the behaviour of electrons it is necessary to understand the characteristics of wave motion.

1.7.1 Classical Waves and Wave Equation

Consider the wave motion in vibration of a string, the vertical displacement of string from its mean position and is called the amplitude of wave or vibration. This amplitude is a function of position (x) and time (t) and denoted as $\Psi(x,t)$.

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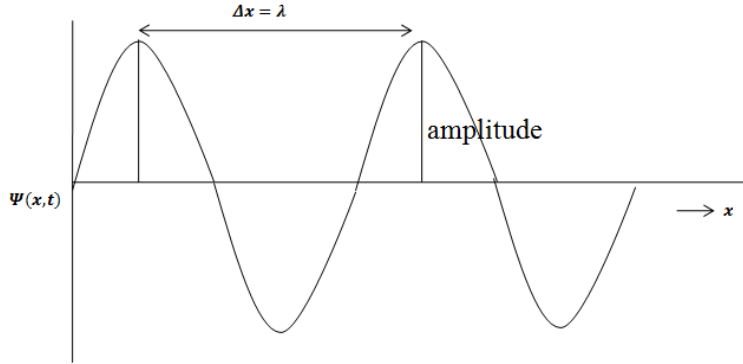


Fig 1.4 Classical wave

Here the wave makes same amplitude at regular intervals of Δx which is λ the wavelength of the wave. The velocity of wave c is given by λ/t , the frequency ν (number of waves per unit time) will be $c = \lambda/t \Rightarrow 1/t = c/\lambda \Rightarrow \nu = c/\lambda$ and the wave number (number of waves per unit distance) will be $\bar{\nu} = 1/\lambda$. The periodic nature of $\Psi(x, t)$ propose the sine or cosine function of x and t where x is position coordinate and t is time coordinate. The expression for wave function is obtained by solving the equation of the wave motion which is not in the scope of this book

$$\frac{\partial^2 \Psi}{\partial x^2} = \frac{1}{c^2} \frac{\partial^2 \Psi}{\partial t^2} \quad (1)$$

where $\Psi = \Psi(x, t)$. By applying separation of variables method, function $\Psi(x, t)$ is separated into a product of two functions

$$\Psi(x, t) = \Psi(x) \cdot \Phi(t) \quad (2)$$

where $\Psi(x)$ is a function of x only and $\Phi(t)$ is a function of t only. Substituting equation (2) in (1) and dividing by $\Psi(x) \cdot \Phi(t)$ on both sides gives

$$\frac{c^2}{\Psi} \cdot \frac{\partial^2 \Psi}{\partial x^2} = \frac{1}{\Phi} \cdot \frac{\partial^2 \Phi}{\partial t^2} \quad (3)$$

Bonds to Bands

The left hand side of equation (3) depends only on x and right hand side depends only on t however both sides are equal and are equated to a constant $-k^2$

$$\frac{c^2}{\Psi} \cdot \frac{\partial^2 \Psi}{\partial x^2} = \frac{1}{\Phi} \cdot \frac{\partial^2 \Phi}{\partial t^2} = -k^2 \quad (4)$$

Thus two equations are obtained from equation (4)

$$\frac{\partial^2 \Psi}{\partial x^2} = -\frac{k^2}{c^2} \Psi \quad (5)$$

$$\frac{\partial^2 \Phi}{\partial t^2} = -k^2 \Phi \quad (6)$$

Here equation (5) is the time-independent wave equation called as amplitude equation.

The general solutions for equations (5) and (6) are

$$\Psi(x) = A \sin\left(\frac{kx}{c}\right) + B \cos\left(\frac{kx}{c}\right) \quad (7)$$

$$\Phi(t) = C \sin(kt) + D \cos(kt) \quad (8)$$

where A,B,C and D are arbitrary constants.

The other solutions of equation (5) are

$$\Psi(x) = A \exp\left(\pm \frac{2\pi i x}{\lambda}\right) \quad (9)$$

These exponential functions are expressed in trigonometric functions as

$$\exp(\pm i k x) = \cos k x \pm i \sin k x \quad (10)$$

Bonds to Bands

1.7.2 Stationary Waves

Waves expressed by the equation (5) are called running waves in which Ψ is a function of time. However, electron waves in atoms and molecules are stationary waves in which Ψ does not change with time. A classical example of such wave is the wave in a vibrating string clamped at two ends.

Thus equation (5) may be expressed as

$$\frac{\partial^2 \Psi}{\partial x^2} = -\frac{4\pi^2}{\lambda^2} \Psi \quad (11)$$

From classical waves we know that

$$\frac{k}{c} = \frac{2\pi}{\lambda c}$$
$$\therefore k = \frac{2\pi}{\lambda}$$

Equation (7) becomes

$$\Psi(x) = A \sin\left(\frac{2\pi x}{\lambda}\right) + B \cos\left(\frac{2\pi x}{\lambda}\right) \quad (12)$$

Hence the wave does not vibrate at the ends $x = 0$ and $x = L$ and this is called as boundary conditions.

The first boundary condition $x = 0$, Ψ becomes 0 from equation (12) and B becomes zero

$$0 = A \sin\left(\frac{2\pi}{\lambda} \cdot 0\right) + B \cos\left(\frac{2\pi}{\lambda} \cdot 0\right) = B \quad (13)$$

The second boundary condition on equation (13) is $x = L$ and $B = 0$, $\therefore \Psi$ becomes 0

Bonds to Bands

$$0 = A \sin\left(\frac{2\pi}{\lambda} \cdot L\right) \quad (14)$$

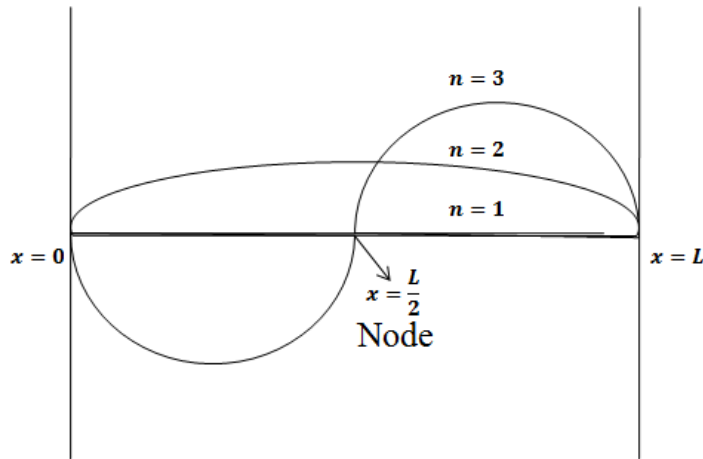


Fig 1.5 Stationary wave - Vibration in clamped string

Equation (14) is satisfied when

1. $A = 0$, but Ψ becomes zero everywhere and for all values of x which is not acceptable.
2. $\frac{2\pi}{\lambda} \cdot L = n\pi$, where $n = 0, \pm 1, \pm 2, \pm 3 \dots$ or $\lambda = \frac{2L}{n}$ and is acceptable.

The solution of the wave equation is $\Psi = A \sin \frac{n\pi x}{L}$ where A is maximum amplitude of the wave. The equation becomes zero at boundary conditions and integral number of half wavelength between the clamped ends of the string. The points where Ψ becomes zero is called node.

Bonds to Bands

For example when $n = 0$, $\Psi = 0$ everywhere, when $n = 1$, $\Psi = 0$ only at $x = 0$ and $x = L$, and there is no node, when $n = 2$, Ψ becomes zero at $x = L/2$ which is a node, for $n = 3$, Ψ becomes zero at $x = L/3$ and $2L/3$ thus two nodes are present and so on.

1.7.3 Schrodinger Equation for Particle Waves

Erwin Schrodinger proposed that if electrons have both particle and wave behaviour the equation of wave motion can be applied to them. He used the time-independent wave equation to explain the particle wave. For an electron of wavelength λ moving along x-coordinate,

$$\frac{\partial^2 \Psi}{\partial x^2} = -\frac{4\pi^2}{\lambda^2} \Psi \quad (15)$$

From de Broglie relationship, $\lambda = \frac{h}{mv}$ and substituting in equation gives

$$\begin{aligned} \frac{\partial^2 \Psi}{\partial x^2} &= -\frac{4\pi^2 m^2 v^2}{h^2} \Psi = -\frac{8\pi^2 m T \Psi}{h^2} \\ \frac{\partial^2 \Psi}{\partial x^2} &= -\frac{8\pi^2 m (E - V)}{h^2} \Psi \end{aligned} \quad (16)$$

$$\frac{\partial^2 \Psi}{\partial x^2} = -\frac{8\pi^2 m (E - V)}{h^2} \Psi \quad (17)$$

where $\Psi = \Psi(x)$, T is kinetic energy, V is potential energy and E is total energy of the electron ($E=T+V$). This is known as Schrodinger equation for particle (electron) of mass m moving in one dimensional motion. For three dimensional motion, the equation will be a partial differential equation with three coordinates x, y and z .

Bonds to Bands

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = -\frac{8\pi^2 m(E - V)}{h^2} \psi \quad (18)$$

1.7.4 Conditions for Acceptable Wave Function

The conditions for an acceptable wave function Ψ are

1. It must be finite.
2. It must be single-valued at all points.
3. It must be continuous.

If these three conditions are obeyed then the function Ψ is called a well-behaved wave function.

1.7.5 Motion of Quantum Mechanical Particle

The quantum mechanical particle such as electrons in atoms and molecules can execute translational, rotational and vibrational motion. However, the common type of motion is translational or linear when they move freely.

For linear motion of free particle which is not affected by any force or potential barrier and free to move in limitless space, the equation (17) becomes Schrodinger equation for free particle and is given by

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 mE}{h^2} \psi = 0 \quad (19)$$

Here potential energy V is a constant and assumed to be zero since the free particle is not subjected to any potential barrier.

Bonds to Bands

1.7.5.1 Particle in one dimensional box

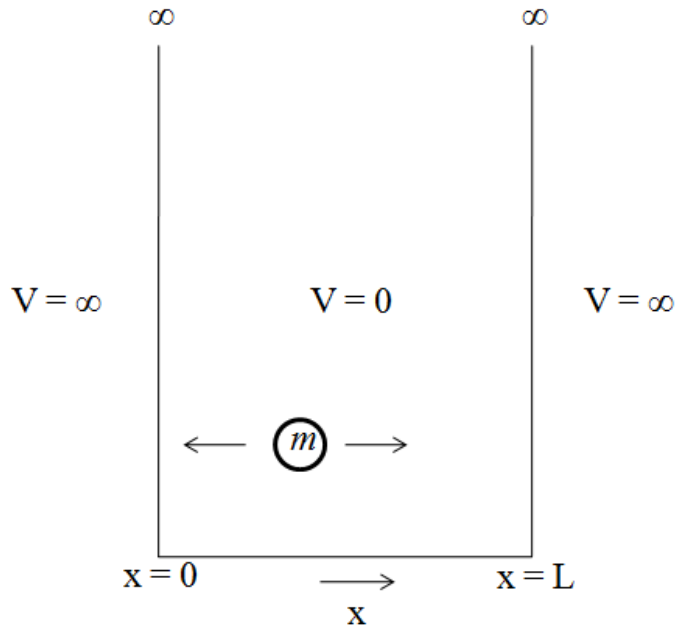


Fig 1.6 Particle in one dimensional box of length L

Consider a particle is moving in a limited space like bounded electrons in atoms and molecules serves as particle in a box model. If the limited space is a one dimensional box of length L with infinite high walls at the two ends, the particle is not subjected to any force inside the box where potential energy $V = 0$ and outside the box it is infinity thus $V = \infty$.

Hence the potential energy is discontinuous (high at $x=0$ and $x=L$ and inside the box is zero), thus the Schrodinger equation should be considered inside and outside the box separately.

The Schrodinger equation outside the box (where $V = \infty$) will be

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$$\frac{\partial^2 \Psi}{\partial x^2} + \frac{8\pi^2 m(E - \infty)}{h^2} \Psi = 0 \quad (20)$$

$$-\frac{h^2}{8\pi^2 m} \frac{\partial^2 \Psi}{\partial x^2} + \infty \Psi = E \Psi \quad (21)$$

The Schrodinger equation inside the box $0 \leq x \leq L$ (where $V = 0$)

$$\frac{\partial^2 \Psi}{\partial x^2} + \frac{8\pi^2 m(E - 0)}{h^2} \Psi = 0 \quad (22)$$

$$-\frac{h^2}{8\pi^2 mE} \frac{\partial^2 \Psi}{\partial x^2} = E \Psi \quad (23)$$

The probability of finding a particle outside the box, (i.e) $\Psi^2 = 0$ due the large potential energy ($V = \infty$) present in these regions $x < 0$ and $x > L$ and thus $\Psi = 0$. Since Ψ must be continuous (i.e) it cannot rise and fall suddenly, thus Ψ must be zero at $x = 0$ and $x = L$. This is the boundary condition for this system.

The Schrodinger equation inside the box is written as

$$\frac{\partial^2 \Psi}{\partial x^2} + k^2 \Psi = 0 \quad (24)$$

$$k^2 = \frac{8\pi^2 mE}{h^2} \quad (25)$$

Equation (24) is satisfied by well behaved functions such as $\sin kx$, $\cos kx$, e^{ikx} and e^{-ikx} .

Wave function and Energy of the particle

The wave function is described either in terms of real form such as $\sin kx$ and $\cos kx$ and complex forms such as e^{ikx} and e^{-ikx} .

The general solution of real form of wave function is given as

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$$\Psi = A \sin kx + B \cos kx \quad (26)$$

where A and B are arbitrary constants. The values of A, B and k are determined by applying boundary conditions to equation (26)

i. At $x = 0$, Ψ becomes 0

$$0 = A \sin (k \cdot 0) + B \cos (k \cdot 0)$$

Thus $B = 0$ and hence $\Psi = A \sin kx$ for all values of x

ii. At $x = L$, Ψ becomes 0

$$0 = A \sin (k \cdot L) + 0 \cos (k \cdot L)$$

$$\text{Thus } 0 = A \sin kL$$

This expression is satisfied if either $A = 0$ or $kL = n\pi$.

Case 1: If $A = 0$, $B = 0$, then Ψ becomes 0 everywhere which not acceptable.

Case 2: Thus $kL = n\pi$ or $k = n\pi/L$ where n is an integer (1,2,3...) but not zero (if $n = 0$, Ψ becomes 0)

The wave function and energy of the particle in one dimensional box is given as

$$\Psi = A \sin \frac{n\pi x}{L} \quad (27)$$

$$E = \frac{k^2 \hbar^2}{8\pi^2 m} = \frac{n^2 \hbar^2}{8mL^2} \quad (28)$$

Quantization

In the energy equation (28), the terms \hbar , m and L are constants and energy E depends only on integer n . Thus energy is quantized (i.e) have discrete set of values

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and the integer n is a quantum number. Hence a particle confined to move in a limited space and its energy is quantized.

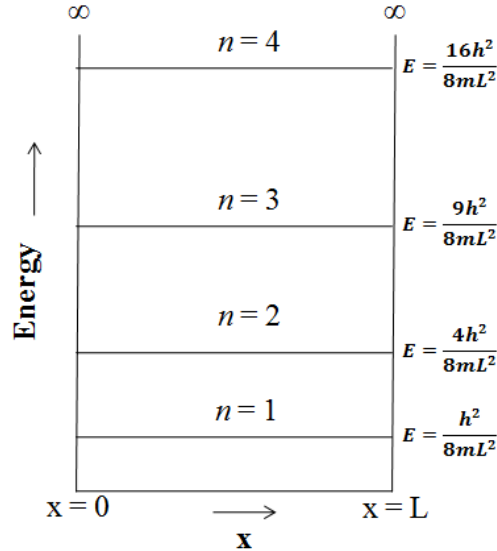


Fig 1.7 Energy levels for particle in one dimensional box

Energy levels

The Figure 1.7 shows the quantization of energy of a particle in one dimensional box. The allowed energy levels are drawn as horizontal lines which shows that for a value of n , energy E does not change with position x of the particle.

The lowest energy level E_1 is not zero but $\frac{h^2}{8mL^2}$ ($n = 1$) and is also called the “zero point energy”. The energy E depends on n^2 which shows that increase in n , increases the spacing between energy levels

$$\Delta E = E_{n+1} - E_n = [(n+1)^2 - n^2]E_1 = (2n+1)E_1$$

Since E is proportional to $\frac{1}{L^2}$

Bonds to Bands

Case 1: When the box is small the energy spacing (ΔE) is greater (i.e) the quantization is pronounced.

Case 2: When the box is wider, ΔE decreases and in limiting case of $L \rightarrow \infty$ (free particle) the quantization vanishes.

Similarly ΔE is also proportional to $\frac{1}{m}$ thus for macroscopic system (large m) the energy levels are closely spaced and there is no quantization.

Value of A

The value A is determined by the normalization of wave function which is given by

$$\int_0^L \Psi^2 dx = \int_0^L A^2 \sin^2 \frac{n\pi x}{L} dx = 1$$

$$\text{we know that } \sin^2 x = \frac{(1 - \cos 2x)}{2}$$

$$\int_0^L A^2 \sin^2 \frac{n\pi x}{L} dx = \frac{A^2}{2} \int_0^L \left(1 - \cos \frac{2n\pi x}{L}\right) dx = 1$$

$$\frac{A^2}{2} \left\{ [x]_0^L - \left[\frac{\sin 2n\pi x/L}{2n\pi/L} \right]_0^L \right\} = 1$$

$$\frac{A^2 L}{2} = 1$$

$$A = \sqrt{\frac{2}{L}}$$

Thus the normalized wave function is $\Psi = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}$

Bonds to Bands

1.7.5.2 Physical meaning of wave function Ψ - Probability density

In Schrodinger wave equation, Ψ is not a physically observable quantity and does not have any direct physical meaning. However it is used to explain all the observable physical quantities and this function is known as wave function. The physical interpretation of square of wave function Ψ^2 is a measure of the probability of finding a particle in specified small volume of space. Ψ^2 is considered if Ψ is real function and $\Psi\Psi^*$ is considered when Ψ is complex and Ψ^* is its complex conjugate but the product $\Psi\Psi^*$ is always real.

The normalized wave function is used to calculate the probability density (i.e) the probability of finding the particle at different points in the one dimensional box. The probability density is given as

$$\psi^2 = \frac{2}{L} \sin^2 \frac{n\pi x}{L}$$

varying between 0 and $\frac{2}{L}$. The probability of particle in a box has maximum probability at certain points depending on value of n and is given as

$$P = \int_a^b \psi^2 dx = \frac{2}{L} \int_a^b \sin^2 \frac{n\pi x}{L} dx$$

- i. For $n = 1$, the maximum probability $\left(\frac{2}{L}\right)$ occurs at $x = \frac{L}{2}$
- ii. For $n = 2$, the maximum probability occurs at $x = \frac{L}{4}$ and $x = \frac{3L}{4}$ on both side of the middle point and is zero at $x = \frac{L}{2}$ and so on.

The probability will never be negative and these curves are always symmetric about the reflection plane at the middle of the box.

Bonds to Bands

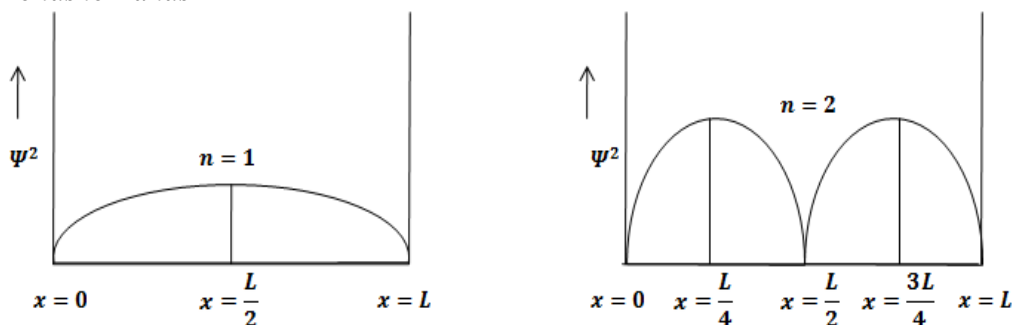


Fig 1.8 Probability density curves of particle in one dimensional box for $n = 1$ and $n = 2$ energy levels

1.7.5.3 Schrodinger equation for hydrogen atom

Hydrogen atom is a two particle system which contains one electron (of mass m and charge $-e$) and one proton (nucleus of mass M and charge $+Ze$). Consider x_1, y_1, z_1 and x_2, y_2, z_2 as the Cartesian coordinates for the proton and electron respectively which are separated by a distance r . Since the proton mass is very much greater than electron, the reduced mass calculated will be considered as the mass of the electron.

In hydrogen atom two types of motions are involved i) translational motion of hydrogen atom as a whole and ii) the internal motion of electron and nucleus relative to each other. The Schrodinger equation involving these motions is

$$\hat{H}\Psi_T = E_T\Psi_T$$

where \hat{H} is Hamiltonian operator, $\Psi_T = \Psi(x_1, y_1, z_1, x_2, y_2, z_2)$ and E_T is the total wave function and total energy (translational energy and internal energy) of the hydrogen

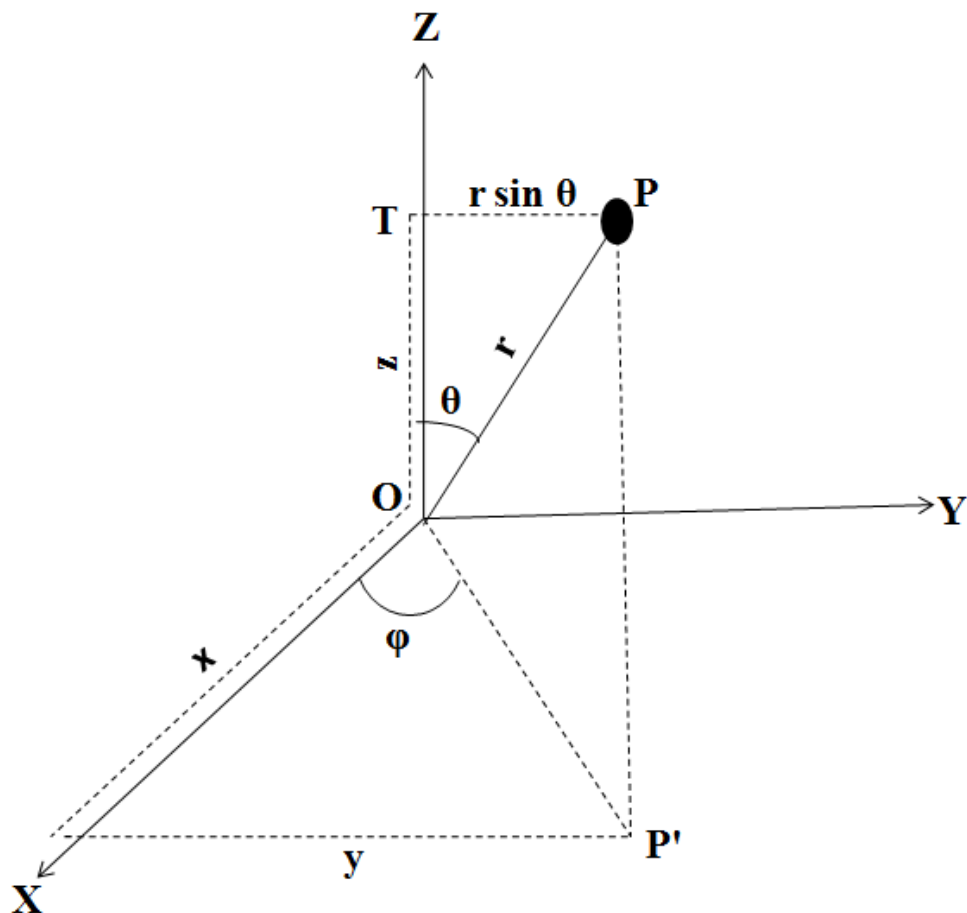


Fig 1.9 Relationship between Cartesian and spherical coordinates

atom. The spatial rotation of electron around the nucleus (containing proton) can be explained by two angular variables ϕ (azimuthal angle) and θ (zenith angle) and radial distance r from the nucleus.

The Schrodinger equation of hydrogen atom is

$$\hat{H}(r, \theta, \phi)\Psi(r, \theta, \phi) = E\Psi(r, \theta, \phi)$$

Bonds to Bands

The hydrogen atom Hamiltonian ($\hat{H} = T + V$) contains kinetic energy operator T in terms of spherical coordinates and spherically symmetrical potential energy. The potential energy is given by

$$V = \frac{Ze^2}{(4\pi\epsilon_0)r}$$

The Cartesian coordinates are converted to spherical coordinates in terms of radius r and angle ϕ measured between 0 to 2π and angle θ measured between 0 to π . The relationship between x , y and z and r , θ and ϕ is given as

$$\begin{aligned} PT = OP' &= r \sin \theta \\ x &= OP' \cos \phi = r \sin \theta \cos \phi \\ y &= OP' \sin \phi = r \sin \theta \sin \phi \\ z &= OT = r \cos \theta \end{aligned}$$

Thus the time-independent Schrodinger equation for hydrogen atom

$$\left\{ \frac{h^2}{8\pi^2m} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] - \frac{ze^2}{4\pi\epsilon_0 r} \right\} \Psi(r, \theta, \phi) = E \Psi(r, \theta, \phi)$$

This equation can be separated into spherical harmonic function $Y(\theta, \phi)$ and radial function $R(r)$ by using product wave function.

$$\Psi(r, \theta, \phi) = R(r) \cdot Y(\theta, \phi)$$

Here the spherical harmonic functions give the information about the position of electron around the proton and the radial function $R(r)$ tells the distance of electron from the proton. The energy term E_n and the solution for $R(r)$ and $Y(\theta, \phi)$ depends only on one quantum number n (principal quantum number). However, the other three quantum numbers are necessary for proper description of complete wave function.

$$E_n = \frac{me^4}{8\epsilon_0^2 h^2 n^2}$$

1.8 QUANTUM NUMBERS

Bonds to Bands

Four quantum numbers are necessary to define an orbital. The combination of these four quantum numbers of electrons in an atom is described by a wave function satisfied by Schrodinger equation. The quantum numbers are used to account for the electronic configuration of an electron in an atom and the probable position of electron in an atom.

The quantum numbers explain the shells, subshell, orbitals and spin of electrons. The four quantum numbers are

1. Principal quantum number (n)

The principal quantum number characterizes the principal electron shell which decides the energy of an electron and the probable position of the electron from the nucleus. Thus n describes the size of the orbital and energy level in which the electron is placed. The larger the value of n , larger is the size of orbital which show that the electron is at longer distance from the nucleus. When $n = 1$, it belongs to first principal shell (ground state) and lowest energy level. When electron absorb energy it is excited to the higher principal shells ($n = 2, 3, 4, \dots$). Thus n takes integral values $1, 2, 3, \dots, \infty$ except zero since when $n = 0$, the energy of atom becomes zero and the atom doesn't exists. The value of n describes the shells K, L, M, N.... in the atom.

2. Azimuthal quantum number (l)

The azimuthal quantum number or orbital quantum number characterize the shape of the orbital and the subshell to which electron belong to. Each l value indicates subshell which is designated as s, p, d, f . Each subshell corresponds to unique shape. It also determines the number of angular nodes of the orbital which will be equal to the number of l values. The value of l is subshell to which electrons belong to and it depends on n values and can have integral values from 0 to $n-1$. Thus

$$l = 0, 1, 2, \dots (n-1).$$

3. Magnetic quantum number (m_l)

Bonds to Bands

The magnetic quantum number represents the number of orbitals and orientation of orbitals in a subshell. The value of m_l is based on the value of l and can have a total of $(2l+1)$ values. Thus magnetic quantum number has values as $m_l = -l, \dots, 0, \dots, +l$

Table 1.1 l and m_l value for s, p, d, f subshells

Subshell	l value	m_l value
s	0	0
p	1	-1, 0, +1
d	2	-2, -1, 0, +1, +2
f	3	-3, -2, -1, 0, +1, +2, +3

Table 1.2 Total number of orbitals in subshells

Principal quantum number (n)	Subshell corresponding to azimuthal quantum number (l)	Magnetic quantum number (m_l)	Name of the subshell orbital	Total number of orbital in subshells
$n = 1, 2, 3, \dots$	s ($l=0$)	$m_l = 0$	s	1
	p ($l = 1$)	$m_l = 0$	p_z	3
		$m_l = \pm 1$	p_x	
			p_y	
	d ($l = 2$)	$m_l = 0$	d_{z^2}	5
		$m_l = \pm 1$	d_{xz}	
			d_{yz}	
		$m_l = \pm 2$	d_{xy}	
			$d_{x^2-y^2}$	
		$m_l = 0$	f_{z^3}	

Bonds to Bands

Principal quantum number (n)	Subshell corresponding to azimuthal quantum number (l)	Magnetic quantum number (m_l)	Name of the subshell orbital	Total number of orbital in subshells
	$f \ (l = 3)$	$m_l = \pm 1$	f_{xz^2}	7
			f_{yz^2}	
		$m_l = \pm 2$	f_{xyz}	
			$f_{z(x^2-y^2)}$	
		$m_l = \pm 3$	$f_{x(x^2-3y^2)}$	
			$f_{y(3x^2-y^2)}$	

4. Spin quantum number (m_s)

The spin quantum number refers the direction of spin of an electron in an orbital. The direction of spin can be clockwise ($m_s = + \frac{1}{2}$) or anticlockwise ($m_s = - \frac{1}{2}$).

1.9 ASSIGNING ELECTRONS TO ORBITALS

Three set of rules govern the filling of electrons in the orbital. They are

1. Aufbau principle

Aufbau principle states that the electrons in an atom occupy the orbital of lowest energy before filling the higher energies. Thus electrons are filled in increasing order of energy

$$1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, \dots$$

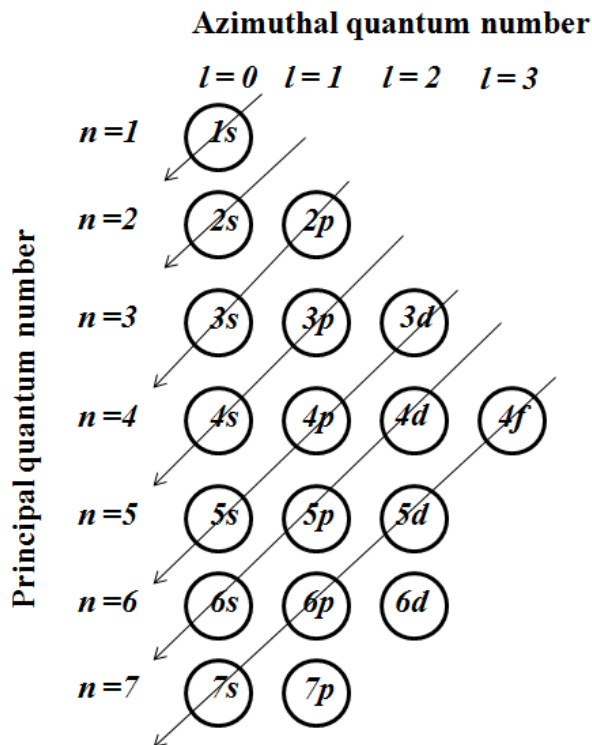


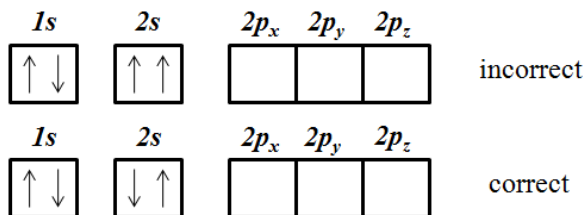
Fig 1.10 Aufbau principle

2. *Pauli-Exclusion principle*

It states that no two electrons in the same atom can have all the four quantum number the same. The electrons in each orbital have three quantum numbers n , l and m_l same but the fourth quantum number m_s will be different. Thus a single orbital can accommodate a maximum of two electrons with opposite spin. The s -orbital can accommodate 2 electrons, p -orbital can hold till 6 electrons (each 3 orbitals hold 2 electrons), the five d -orbitals can accommodate 10 electrons and seven f -orbitals can hold 14 electrons.

Bonds to Bands

For Beryllium, the electronic configuration is $1s^2, 2s^2$

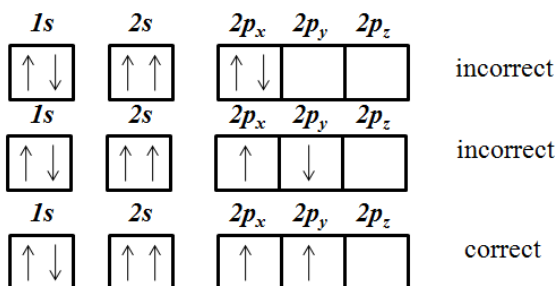


The two electrons in $2s$ orbital ($2s^2$) have $n = 2$, $l = 0$, $m_l = 0$
however m_s will be $+\frac{1}{2}$ and $-\frac{1}{2}$ represented by \uparrow and \downarrow

3. Hund's rule

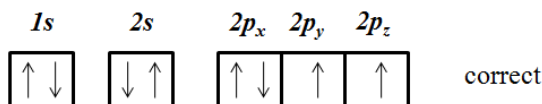
According to Hund's rule, every orbital in a subshell should be filled with at least one electron before pairing of electrons takes place. Further the electrons in singly filled orbitals of subshell have the same spin.

For Carbon, the electronic configuration is $1s^2, 2s^2, 2p^2$



Electrons in orbitals of same subshell have same spin

For Oxygen, the electronic configuration is $1s^2, 2s^2, 2p^4$



Thus pairing of electrons occurs only after all orbitals in subshell is at least filled with one electron

Bonds to Bands

1.10 ANGULAR AND RADIAL WAVE FUNCTIONS

Thus the complete wave function of hydrogen-like atoms is given as

$$\Psi_{nlm}(r, \theta, \varphi) = R_{nl}(r)Y_{lm}(\theta, \varphi)$$

Each wave function has two parts the radial wave function $R_{nl}(r)$ and angular wave function (spherical harmonics) $Y_{lm}(\theta, \varphi)$. The radial wave function depends on the quantum numbers n and l whereas the angular wave function depends on only l and m . The radial wave function describes the size of the atomic orbital (i.e) the distance between the electron and nucleus. The angular wave function describes the shape of the atomic orbital. The real forms of radial and angular wave functions and complete wave function for s and p orbitals of hydrogen atom ($Z = 1$ and $a_0 = 1$) is given below

Table 1.31 Radial, Angular wave function and complete wave function of s and p orbitals

Quantum numbers n, l, m	Radial wave function (R_{nl})	Angular wave function (Y_{lm})	Complete wave function (Ψ_{nlm})
$n=1, l=0, m=0$	$R_{10} = 2e^{-r}$	$Y_{00} = \frac{1}{\sqrt{4\pi}}$	$\Psi_{1s} = \Psi_{100} = \frac{1}{\sqrt{\pi}}e^{-r}$
$n=2, l=0, m=0$	$R_{20} = \frac{1}{2\sqrt{2}}(2-r)e^{-r/2}$	$Y_{00} = \frac{1}{\sqrt{4\pi}}$	$\Psi_{2s} = \Psi_{200} = \frac{1}{4\sqrt{2\pi}}(2-r)e^{-r/2}$
$n=2, l=1, m=+1$	$R_{21} = \frac{1}{2\sqrt{6}}re^{-r/2}$	$Y_{1+1} = \sqrt{\frac{3}{4\pi}}\sin\theta\cos\varphi$	$\Psi_{2px} = \Psi_{21+1} = \frac{1}{4\sqrt{2\pi}}re^{-r/2}\sin\theta\cos\varphi$
$n=2, l=1, m=-1$	$R_{21} = \frac{1}{2\sqrt{6}}re^{-r/2}$	$Y_{1-1} = \sqrt{\frac{3}{4\pi}}\sin\theta\sin\varphi$	$\Psi_{2py} = \Psi_{21-1} = \frac{1}{4\sqrt{2\pi}}re^{-r/2}\sin\theta\sin\varphi$
$n=2, l=1, m=0$	$R_{21} = \frac{1}{2\sqrt{6}}re^{-r/2}$	$Y_{10} = \sqrt{\frac{3}{4\pi}}\cos\theta$	$\Psi_{2pz} = \Psi_{210} = \frac{1}{4\sqrt{2\pi}}re^{-r/2}\cos\theta$

Bonds to Bands

1.11 WAVE FUNCTION OF ATOMIC ORBITALS AND ORBITAL SHAPES

The wave function $\Psi(r, \theta, \phi)$ of hydrogen atom is known as atomic orbitals. Atomic orbital is a wave function that explains the behavior of an electron in atom or region of space. Orbital of different systems varies only with nuclear charge Z . The probability of finding an electron in atom is described by Ψ^2 (square of wave function of atomic orbital).

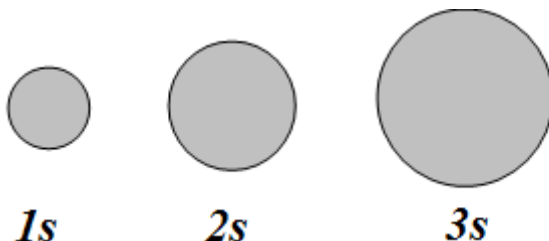
1.11.1 Orbital Shapes

Each orbital is represented by a number and a letter where the number (1, 2, 3, ...) indicates the energy level of the electron in the atom and letter (s, p, d, f) denotes the shape of the orbital. From the solution of Schrodinger wave equation, diagrammatic representation of shapes of atomic orbitals is drawn using the boundary surface diagrams.

A boundary surface diagram is a boundary surface for an orbital represented in a space where the value of probability density Ψ^2 is a constant.

1. s-orbital

Boundary surface diagram of s -orbital is spherical with nucleus at the center. All the s -orbitals $1s, 2s, 3s, \dots$ are spherically symmetrical but their size and energy increases with increase in principal quantum number (n) values ($1s < 2s < 3s \dots$).



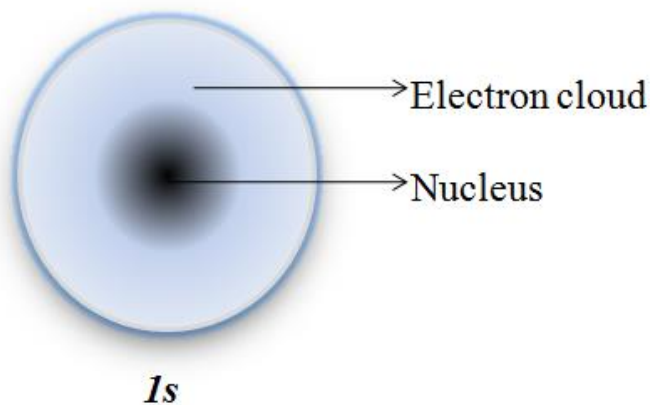
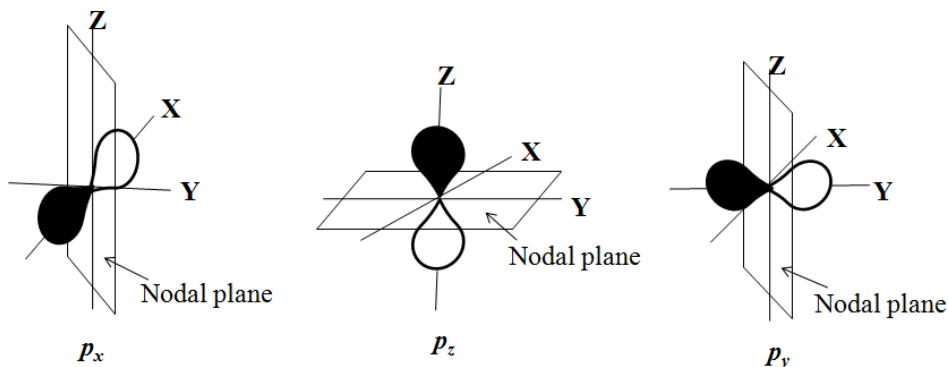


Fig 1.11 Boundary surface diagram of s -orbital

2. p -orbital

Boundary surface diagram of p -orbital show two lobes on either side of plane passing through the center of the nucleus called nodal plane that bisects the two lobes. Unlike s -orbital, the p -orbital has three orientations that are designated as p_x , p_y and p_z which lie on x , y , z axes which are mutually perpendicular to each other.

These three p -orbitals have same energy, size and shape. The size and energy of the p -orbital increase with increase in n values ($2p < 3p < 4p \dots$).



Bonds to Bands

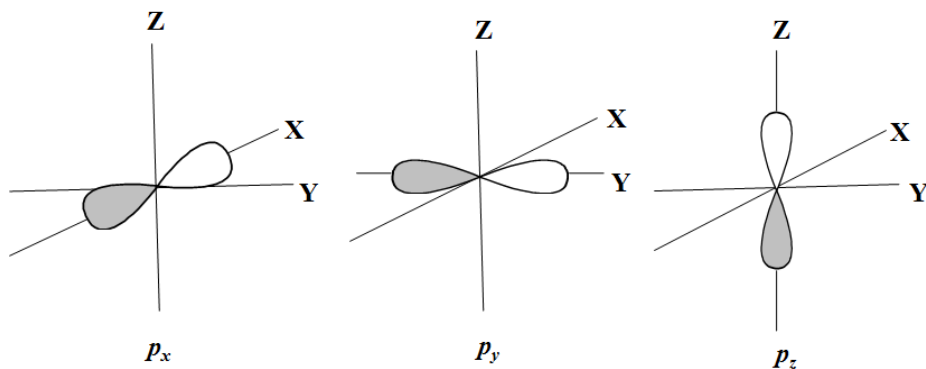
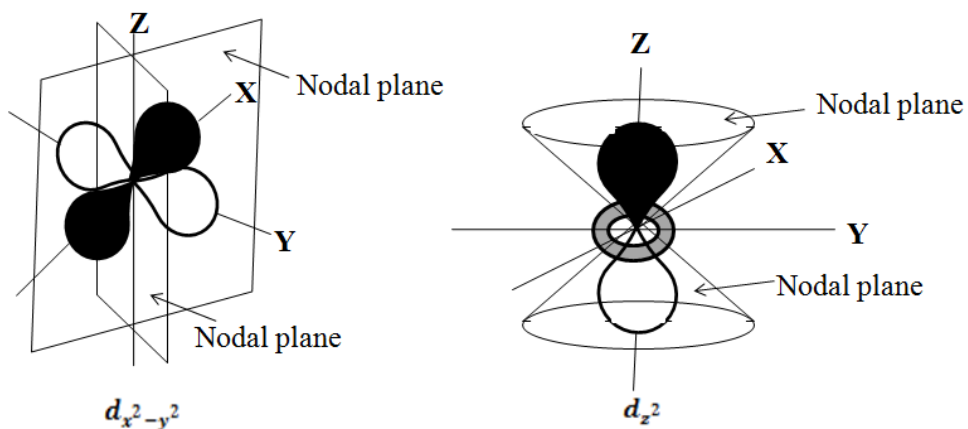


Fig 1.12 Nodal planes and Boundary surface diagram of p- orbitals

3. *d-orbital*

Boundary surface diagram of four of the five *d*-orbitals (d_{xz} , d_{yz} , d_{xy} , $d_{x^2-y^2}$) consists of four lobes arranged in a plane which is intersected by two perpendicular nodal planes.



Bonds to Bands

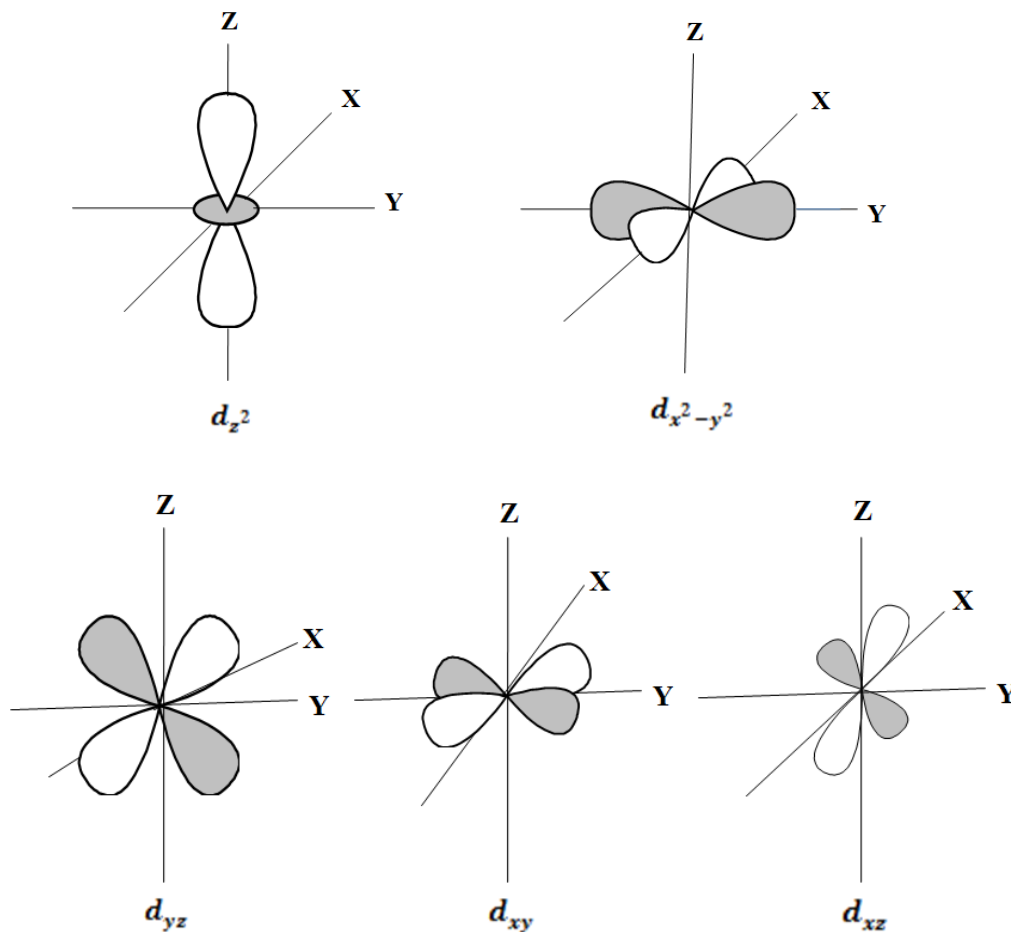


Fig 1.13 Nodal planes and Boundary surface diagram of d -orbitals

The fifth d -orbital d_{z^2} shows two lobes in the z -axis and a doughnut of electron density in the xy plane. However, the energy of all five d -orbitals is the same. The size and energy of d -orbitals increase with an increase in n values ($3d < 4d < 5d \dots$).

Bonds to Bands

4. f-orbital

When $n = 4$ and $l = 3$, the subshell consists of seven f-orbitals. The boundary surface diagrams show that each f-orbital has three nodal surfaces and thus their shapes are complex and difficult to represent by simple diagram.

1.12 THEORY OF BOND FORMATION

Two theories which explain the bond formation are

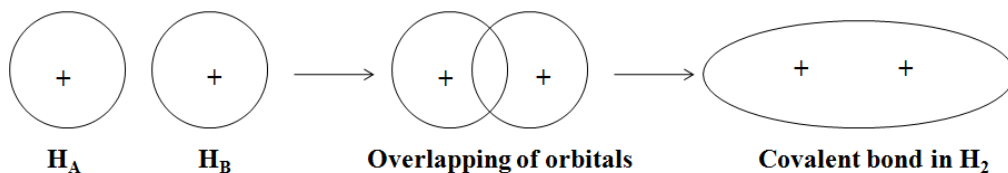
1. Valence bond theory
2. Molecular orbital theory

1.12.1 Valence Bond Theory (VB Theory)

Valence bond theory explains the formation of covalent bonds in molecules based on the number of valence electrons and does not consider the other electrons in the atom. The VB theory is based on the concept of atomic orbital overlap. Atomic orbital overlap is the interaction of two atomic orbitals of two atoms followed by sharing of electrons of atoms.

Salient features of Valence bond theory

1. According to this theory covalent bonds are formed between atoms that are sufficiently closer and can overlap their atomic orbitals.
2. Covalent bond is formed by a pair of electrons shared by two atoms.
3. Lone pair of electrons does not involve in bond formation.



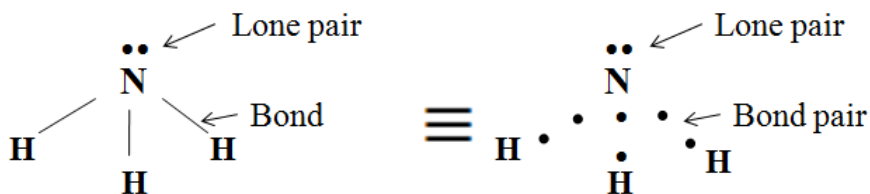
Bonds to Bands

Formation of covalent bond in H_2 molecule

Consider two hydrogen atoms H_A and H_B which are far away from each other. Each hydrogen atom contains one electron in 1s atomic orbital. When the two hydrogen atoms come closer there is overlap of these two 1s atomic orbitals resulting in the covalent bonding. Now the electron in H_A can revolve around nuclei of H_B and vice versa. Thus after bond formation the two electrons lose their identity and cannot distinguish which electron belong to H_A and H_B . The two electrons can move into orbitals of two atoms. These electrons are equally shared between the orbitals and form a covalent bond.

- ❖ Pairing of electrons results in decrease of energy of the system
- ❖ This leads to the formation of bond between the atoms which produce a molecule
- ❖ It increases the stability of the system, thus a molecule of hydrogen is more stable than two hydrogen atoms
- ❖ The atoms involved in the bond formation attain stable electronic configuration (Noble gas configuration)
- ❖ A pair of electrons shared by two atoms creates a covalent bond
- ❖ ***Bond pair and Lone pair:***

A pair of electrons between two bonded atoms constituting the bond is known as bond pair and pair of electrons which does not involve in bonding is known as lone pair.

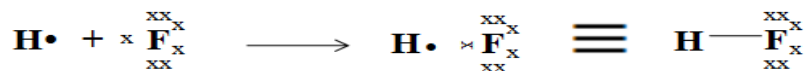


Bonds to Bands

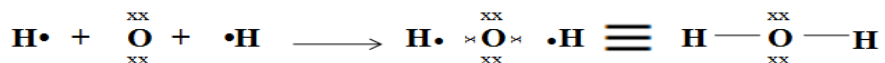
- ❖ Atom may contain non-bonding electron pair (i.e) a pair of valence electrons present on a bonded atom which does not involve in bonding. For example, NH_3 contains three bond pair and one non-bonding electron pair (lone pair) and water has two bond pair and two lone pairs.

VB theory to some molecules

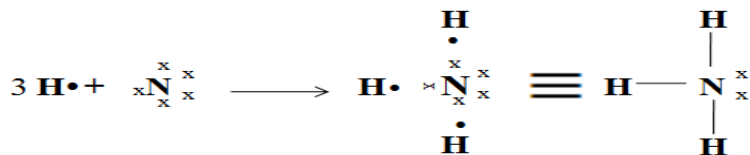
1. **HF:** In HF molecule, singly filled 1s orbital of H atom overlap with singly filled 2p orbital of F to form H – F covalent bond. The three lone pair of electrons remains as non-bonding electron pair on F atom.



2. **H₂O:** In H₂O molecule, O atom contains two singly filled 2p orbitals which overlap with singly filled 1s orbital of each H atom to form two O – H bonds. Two lone pair of electrons is present as non-bonding electron pair on O atom.



3. **NH₃:** In NH₃ molecule, N atom contains three singly filled 2p orbitals which overlap with singly filled 1s orbital of each H atom to form three N – H bonds. One lone pair of electrons is present as non-bonding electron pair on N atom.



Types of orbital overlap

Bonds to Bands

Depending on the types of atomic orbital involve in bonding, different types of bonds are possible.

1. **σ bond:** A covalent bond formed by end-to-end or head-to-head overlap of atomic orbitals of two atoms such as overlap of $s - s$, $s - p_x$, $p_x - p_x$ atomic orbitals is called a σ bond.
2. **π bond:** When p orbitals of two atoms approach along and have a lateral overlap such as overlap of $p_z - p_z$ or $p_y - p_y$ atomic orbitals is called a π bond.

Success of VB theory

1. It successfully explains the covalent bond formation in molecules by using concept of atomic orbital overlap.
2. According to this theory electron pairing results in decrease of energy of the system which contributes to stability of the system.
3. It also explains the geometries of many covalent molecules.
4. It clearly depicts the strength of σ bond and π bond.
5. Application of VB theory has lead to development of stereochemistry of carbon compounds.

Limitations of VB theory

1. This theory ignores the electrons other than the valence electrons.
2. It does not explain the partial ionic character of bonds.
3. It does not explain the bond formation in complex multi-atom molecules.
4. It cannot account for coordinate bond in which one atom donates both the electrons required for bond formation.
5. It does not explain the bond formation in molecules like H_2^+ and He_2^+ which involves sharing of single electron.

Bonds to Bands

1.12.2 Linear Combination of Atomic Orbitals – Molecular Orbitals (LCAO-MO)

In the VB theory even after the formation of the molecule, the atomic orbitals remain as such and retain their identity with respect to their atoms.

In the MO theory, after the formation of the molecule, the valence electrons lose their identity and they no longer belong to individual atoms but belong to molecule as a whole.

Salient features of Molecular Orbital theory

1. According to MO theory the atomic orbitals (AO) of the atoms combine to form new orbitals known as molecular orbitals (MO).
2. Molecular orbitals are described by wave functions based on quantum chemistry.
3. Overlapping of two AO results in formation of two MO (i.e) one bonding MO and one antibonding MO.

Wave function

1. Every atom can possess full set of s, p, d, f orbitals but not all of them will have electrons
2. The space where there is more probability of finding electrons is called atomic orbital.
3. The representation of AO is called electron probability density diagram which show the most probable distribution of electron cloud around the nuclei.
4. Each AO is described by a wave function.
5. For example wave function of $1s$ and $2p$ orbital is shown below where r is the distance between electron and nucleus.

Bonds to Bands

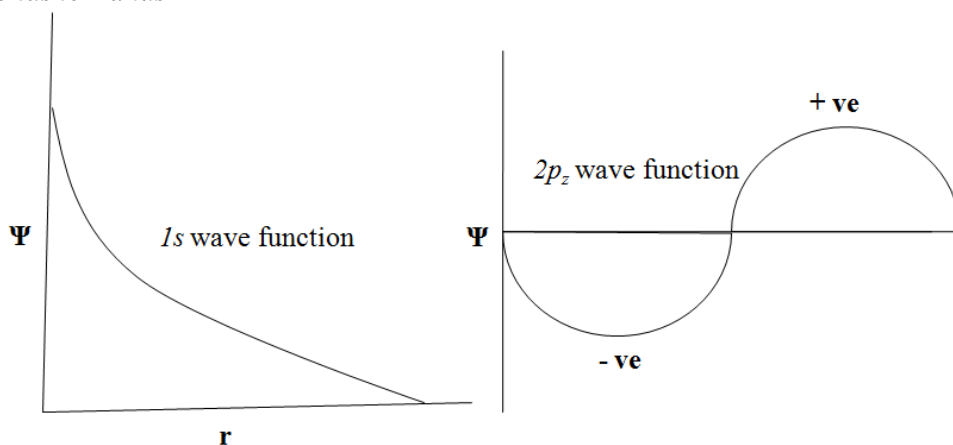


Fig 1.14 wave function of $1s$ orbital and $2p$ orbital

- ❖ The wave function of the $1s$ orbital is always positive sign (above the reference axis)
- ❖ The wave function of $2p$ orbital is sometimes positive sign (above the axis) and sometimes negative (below the axis). Thus changes sign from positive to negative.
- ❖ The above fact is represented as electron probability density diagram (AO) with + or – sign. These two sign indicates the relative probabilities and – sign does not show that the probability is negative.
- ❖ The probability density diagram describes the shape of the atomic orbital. Shapes of $1s$ orbital and $2p_z$ orbital are shown below.

Bonds to Bands

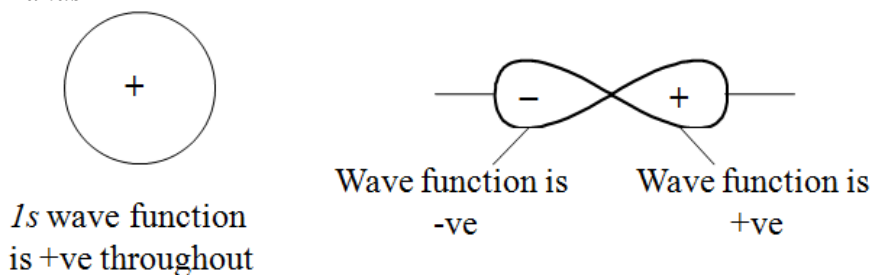


Fig 1.15 Probability density diagram of 1s orbital and 2p orbital

Combination of wave function: Bonding and Antibonding molecular orbitals

Two waves can overlap in two different ways to form bonding molecular orbital or antibonding molecular orbital. The overlap of the positive part of one AO with positive part of another AO and negative part of one AO with negative part of another AO reinforces and produce a larger wave known as bonding molecular orbital. Similarly the overlap of the positive of one AO with the negative part of another AO results in destruction of wave and produces an antibonding molecular orbital.

1.12.2.1 LCAO – MO of H_2

Molecular orbital is described by wave function similar to atomic orbital. The wave function of MO is obtained by Linear combination of atomic orbitals method. This concept can be explained by considering hydrogen molecule H_2 . Hydrogen molecule has two hydrogen atoms H_A and H_B whose atomic orbitals are described by wave function ϕ_A and ϕ_B . These two atomic orbitals overlap (i.e) $\phi_A \pm \phi_B$ and produce a new wave function known as molecular orbital. Such algebraic sum of functions is called as linear combination.

Bonds to Bands

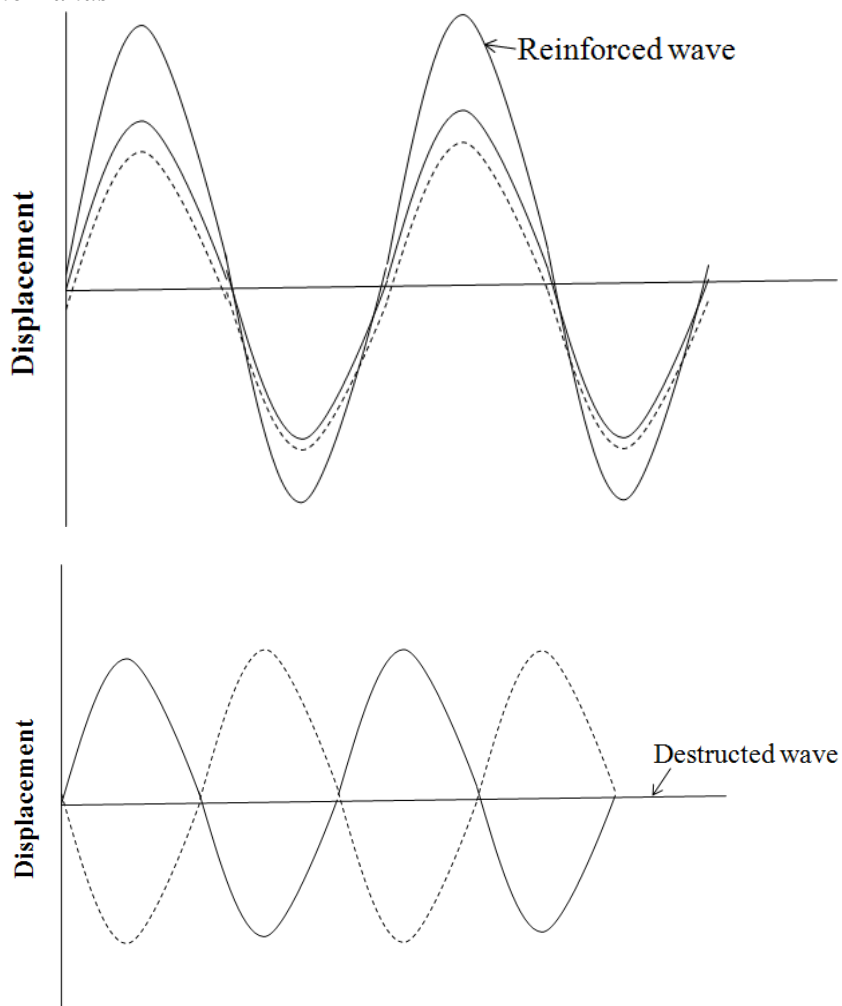


Fig 1.16 Formation of bonding and antibonding molecular orbital by reinforcement and destruction of two AO waves

The two normalized LCAO wave functions are

$$\Psi_b = N_b(\varphi_A + \varphi_B) \quad (1)$$

$$\Psi_a = N_a(\varphi_A - \varphi_B) \quad (2)$$

Bonds to Bands

Where Ψ_b and Ψ_a are wave function, N_b and N_a are Normalization constant of bonding and antibonding molecular orbitals respectively. The numerical value of N_b and N_a was calculated to be 0.71 ($\sim \sqrt{1/2}$). The energy of LCAO-MO's Ψ_b and Ψ_a is represented as E_b and E_a and is given as

$$E_b = \frac{\int \Psi_b \hat{H} \Psi_b d\tau}{\Psi_b \Psi_b d\tau} = \frac{N_b^2 \int (\varphi_A + \varphi_B) \hat{H} (\varphi_A + \varphi_B)}{1} \quad (3)$$

$$E_b = N_b^2 \left(\int \varphi_A \hat{H} \varphi_A d\tau + \int \varphi_A \hat{H} \varphi_B d\tau + \int \varphi_B \hat{H} \varphi_A d\tau + \int \varphi_B \hat{H} \varphi_B d\tau \right) \quad (4)$$

Where \hat{H} is the Hamiltonian operator (total energy operator). Substituting the integrals with symbols

$$Q_A = \int \varphi_A \hat{H} \varphi_A d\tau \quad (5)$$

$$Q_B = \int \varphi_B \hat{H} \varphi_B d\tau \quad (6)$$

$$\beta = \int \varphi_A \hat{H} \varphi_B d\tau = \int \varphi_B \hat{H} \varphi_A d\tau \quad (7)$$

Since both the atoms A and B are H atom, $Q_A = Q_B = Q$ and the energy equation (4) becomes

$$E_b = 2N_b^2(Q + \beta) \quad (8)$$

Similarly

$$E_a = 2N_a^2(Q - \beta) \quad (9)$$

Here integral Q represents the energy of an electron in the orbital φ_A or φ_B that is equal to the ground state energy of hydrogen atom. The integral β represents the energy of interaction between the orbitals φ_A and φ_B . It is called exchange integral and is inherently negative. Thus an electron occupying bonding MO, Ψ_b is more stable and

Bonds to Bands

an electron in Ψ_a is less stable than electron in a pure atomic orbital, ϕ_A or ϕ_B . The actual energy of stabilization and destabilization is obtained by substituting Normalization constant N_a and N_b ($N_a = N_b = \sqrt{1/2}$) in equation (8) and (9).

$$E_b = (Q + \beta) \quad (10)$$

$$E_a = (Q - \beta) \quad (11)$$

This is depicted in the energy level diagram as

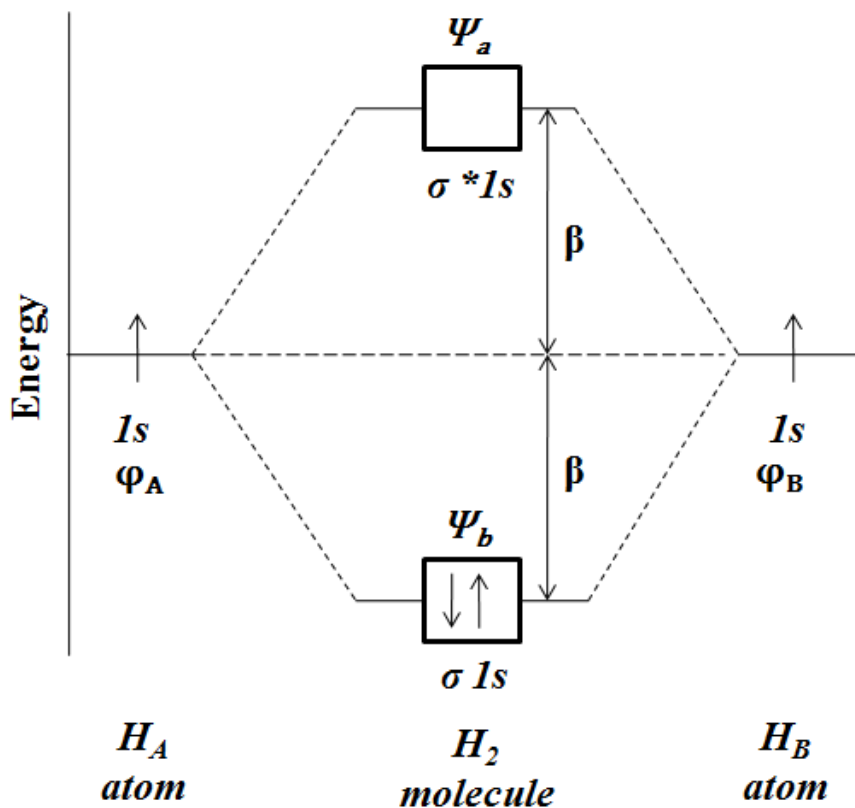


Fig 1.17 Energy level diagram for formation of bonding and antibonding MO of H_2 molecule

Bonds to Bands

As the bonding and antibonding orbitals are formed, the AO overlap, energy changes occur. The formation of the bonding MO (Ψ_b) decreases the energy and that of antibonding MO (Ψ_a) increases the energy.

- The energy of the bonding MO is lower than that of antibonding MO.
- The energy difference between AO and bonding MO is called stabilization energy and it is denoted as β .
- The energy difference between AO and antibonding MO is denoted as β .
- Each MO can accommodate two electrons with opposite spins similar to AO.
- The energy of each electron is decreased by β and hence the total reduction in energy of the system is 2β . This denotes the bond energy.
- This reduction in energy is the driving force for bond formation.
- When two AO of H atoms combine, it forms lower energy bonding MO which is designated as $\sigma 1s$ and higher energy antibonding MO which is designated as $\sigma^* 1s$.
- The two electrons each from AO of H atom occupy the lower energy bonding MO with opposite spins.
- In homonuclear diatomic molecule such as H_2 molecule, each H atom has an electron and they occupy the lower energy MO $\sigma 1s$. Hence the MO configuration for H_2 is $\sigma 1s^2$.

Bonds to Bands

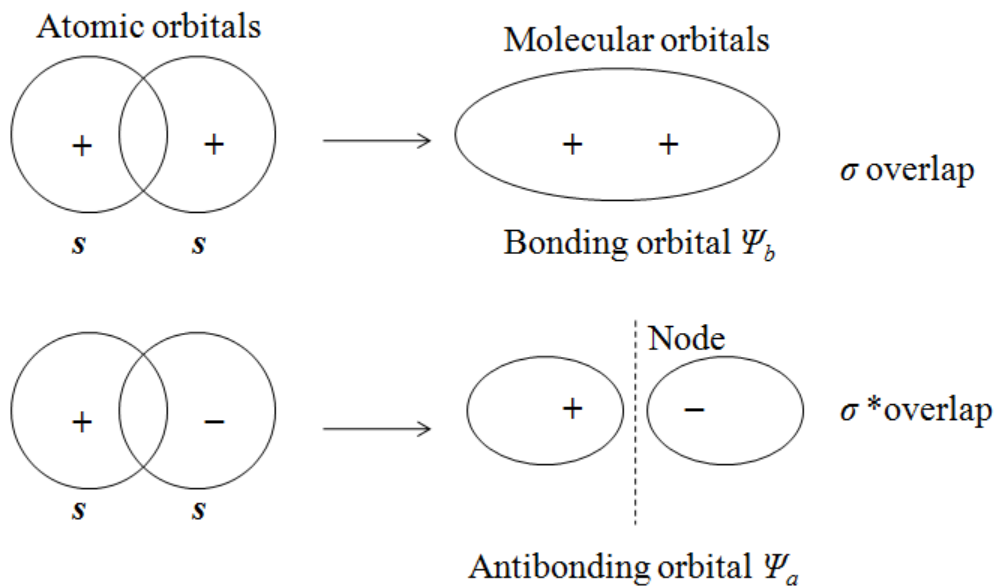


Fig 1.18 Combination of $s - s$ atomic orbitals to form bonding and antibonding molecular orbitals

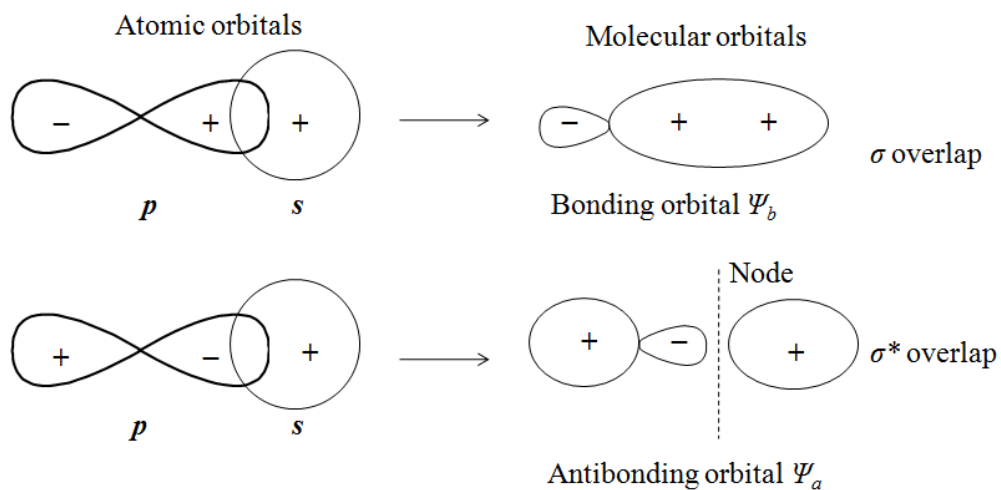


Fig 1.19 Combination of $s - p$ atomic orbitals to form bonding and antibonding molecular orbitals

Bonds to Bands

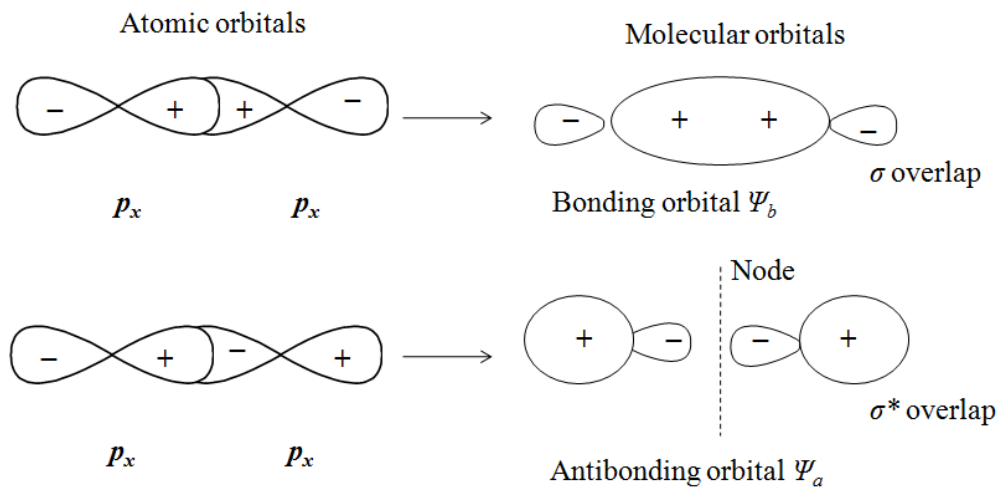


Fig 1.20 Combination of $p_x - p_x$ atomic orbitals to form bonding and antibonding molecular orbitals

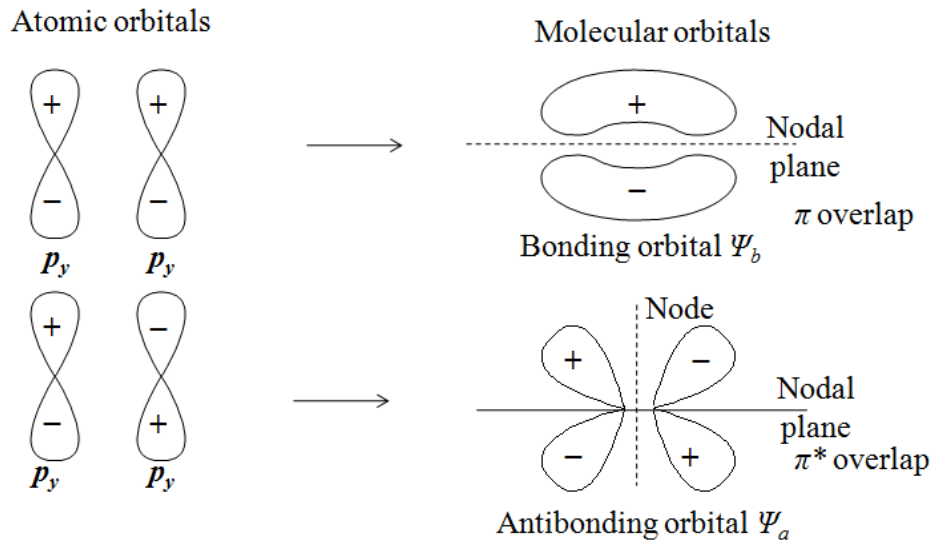


Fig 1.21 Combination of $p_y - p_y$ atomic orbitals to form bonding and antibonding molecular orbitals

Bonds to Bands

1.13 BAND THEORY

Band theory is a quantum model which gives an insight about the possible energies of electrons in the solids in order to understand the electrical and optical properties of solids. It is the molecular orbital theory of covalent bands extended to solids. A single atom has discrete energy states or energy levels of electrons, however in the case of assembly of atoms, situation is somewhat different. Like when two atoms come closer, their atomic orbitals get overlapped to form new orbits called molecular orbitals (bonding and antibonding). When large number of atoms are in close association as in case of solids, the discrete nature of energy levels of atoms vanishes and there are formation of large number of energy levels having close energy differences, which in the other sense can be called a band of energy levels or energy bands.

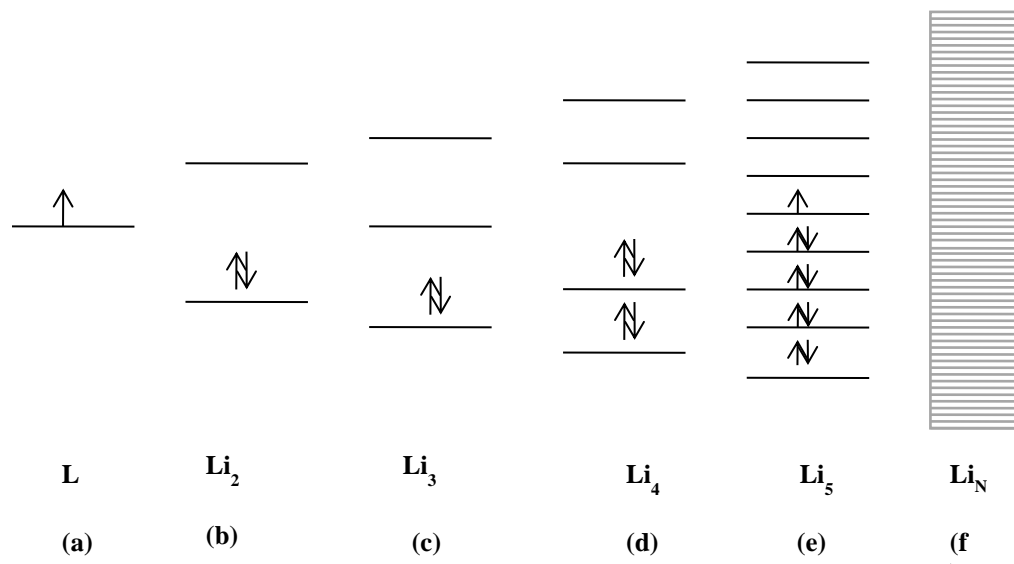


Illustration of band theory: (a) single Li-atom with one 2s-valence electron, (b) Li₂ with two M.O., one filled and one vacant, (c) Li₃ with three M.O., (d) Li₄ with four M.O., (e) Li₉ with nine M.O., half-filled, (f) Li_N with a band of N M.O.

Bonds to Bands

In order to understand band theory of solids, let us imagine the construction of lithium metal by adding Li-atoms one at a time, forming Li^2 then Li^3 , Li^4 , Li^5 and so on, until we have Li^N , where N is a very large number of the order of 10^{20} .

Electrons in the solids having allowed energies belong to the allowed energy bands. The allowed energy bands can be separated by forbidden band to which the electron energy in the solid does not belong. The allowed energy bands are of two types called valence band and conduction band. In a solid, valence band and conduction band can be separated by a forbidden band as in case of semiconductors and insulators. Hence the solids have three types of energy bands which are valence band, forbidden band and conduction band.

Salient features of band theory:

1. Solids are made up of giant molecules, in which a very large number of spherical atoms are arranged in a regular close-packed pattern in the form of crystals.
2. When the atoms are brought together in solids, the atomic orbitals of the valence shells 'interact' forming molecular orbitals.
3. During interaction between these atoms, they influence each other and constitute one single system of electrons while the inner shells remain intact and are not affected.
4. The individual energies within an energy band are so-close together and considered to be continuous. Consequently, an electron in a solid crystal can occupy any of these large number of energy level, within the band. Thus, a **band** is a *group of infinitesimally energy levels in a solid/crystal*.

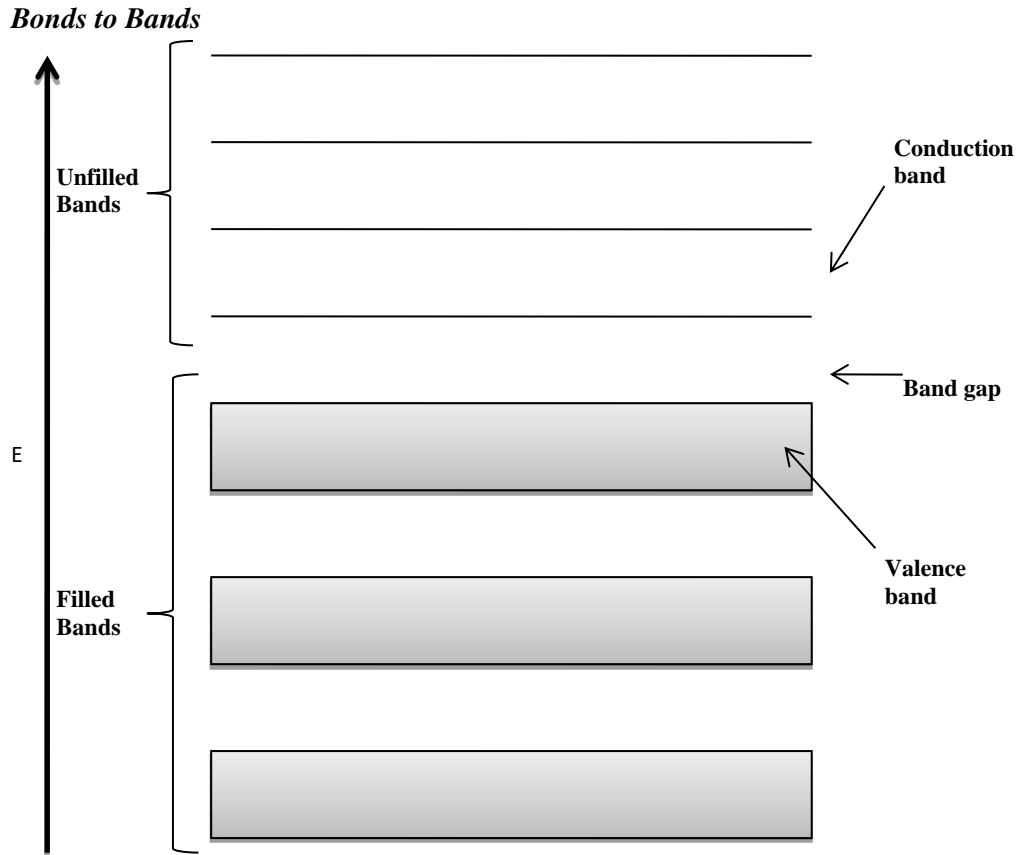


Fig 1.22 Energy bands in solids

Depending upon the composition of a solid/crystal, the bands are of three types.

1. Valence band:

Valence band is the band of energy levels occupied by the valence electrons. It is lowest in energy among three types of bands. Valence band is generally fully filled in insulators, however in case of conductors valence band is partially filled by electrons. This band is below the forbidden band and valence electrons are present in this band. In conductors valence electrons are free to move in this band and are easily transferred into the conduction band without giving any external energy.

Bonds to Bands

2. Conduction band:

The next permitted band, above the valence band, is called the conduction band and the electrons occupying this band are called conduction electrons. It is the band of orbitals in which electrons are present which have been jumped from the valence band. It is higher in energy than the valence band and forbidden band. Electrons in this band have enough energy to move freely and if some external force is applied in the form potential difference across the ends of solid, electrons flow in a particular direction which we called the flow of charge or electric current. This band is responsible for the conduction of electricity.

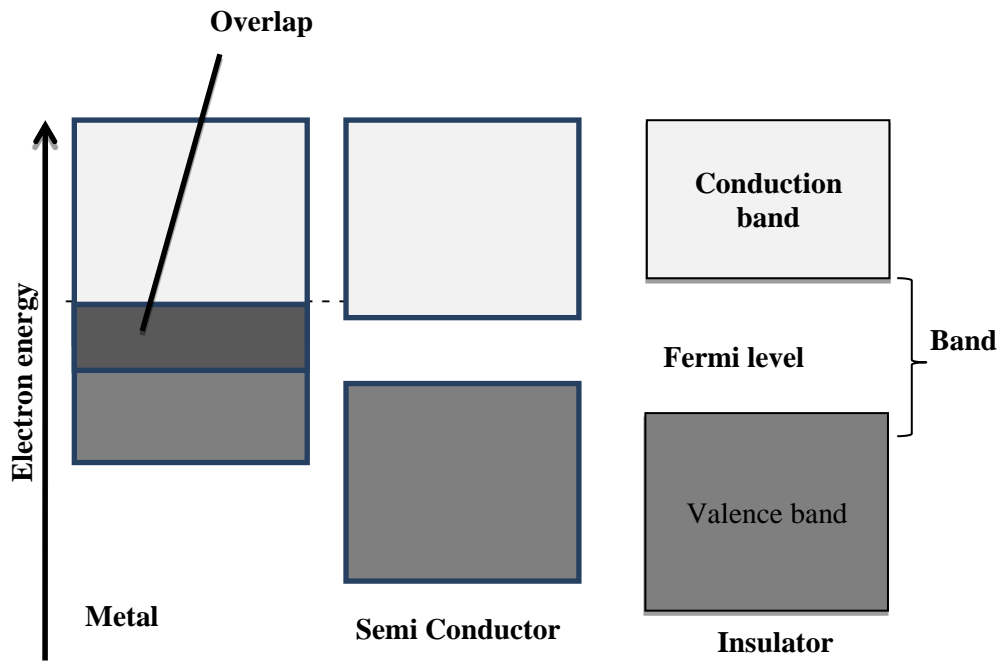


Fig 1.23 Valence, conduction and forbidden (band gap) in solids

On the basis of presence of forbidden band gap energy and band gap size, solids can be distinguished into three types namely conductors, insulators and semi-conductors.

Bonds to Bands

A. Conductors:

In conductors there is zero band gap energy. Valence band and conduction band are overlapped. So the electrons in the valence band can easily move into conduction band. Presence of large number of free electrons in the conduction band results in the flow of electric current. Metals have zero band gap energy. So the electrons in the valence band are free to move into the conduction band without gaining any additional energy and hence they are good conductors of electricity.

B. Insulators:

Insulators have large band gap energy and band gap size. It is difficult for an electron from a valence band to gain energy and move into conduction band. Absence of free electrons in the conduction band of insulators restricts the flow of electric current in insulators. So the insulators are poor conductors of electricity. The conductivity of insulators is 24 orders of magnitude less than conductors.

C. Semiconductors:

Semiconductors have small band gap energy and band gap width. The band gap in semiconductors is approximately 1 eV and it is possible for an electron in the conduction band to gain this small amount of energy and enter into conduction band to have some conductivity. Conductivity of semiconductors is between that of insulators and conductors which is about 4-16 orders of magnitude less than conductors. It is further possible for the semiconductors to decrease or tailor this band gap energy, which find its useful applications in electronics and photoelectronics. Semiconductors are being used in the electronic devices such as radios, computers, mobile phones, televisions, automobiles, amplifiers. Semiconductors are being used in the formation of integrated circuits, transistors, diodes, photovoltaic cells etc.

Bonds to Bands

Examples of semiconductors include silicon, germanium, antimony, boron, tellurium, selenium etc.

Type of semiconductors

Semiconductors are classified into two types as:

i. Intrinsic semiconductors.

Intrinsic semiconductors are extremely pure (above 99.9999% pure) elements like silicon, germanium and selenium, having four valence electrons in their atoms and their forbidden gap energy is about 1 eV. These metals have crystalline structures, in which each atom forms four covalent bonds by sharing with four neighbouring atoms. In such semiconductors, the energy gap is so small (about 1 eV) that even at ordinary temperature, there are many valence electrons, which possess sufficient energy to jump across the forbidden gap to conduction band. Intrinsic semiconductors are also called undoped semiconductors.

ii. Extrinsic semiconductors.

Extrinsic semiconductor are basically intrinsic semiconductors, whose conducting properties have been improved by adding extremely small amounts of specific substitutional impurities called doping agent or dopants. The addition of doping agent reduces the energy gap (E_g), thereby allowing more electrons to flow from valence band to the empty conduction band. Usually, 1 part of doping agent is added to 10⁶ parts of parent element (Si, Ge, etc.). By appropriate doping, the conductivity of an intrinsic semiconductor may be increased by 10,000 times. Dopants added to the extrinsic semiconductor gives desired electrical and optical properties to the semiconductor.

Based on the nature of the doping agent added, the extrinsic semiconductors are of following two classes:

Bonds to Bands

Doping

Doping is a process of adding an impurity to the semiconductor in order to modulate the properties and obtain the desired electrical, optical and structural properties of the semiconductor. The impurity added to the semiconductor is called dopant.

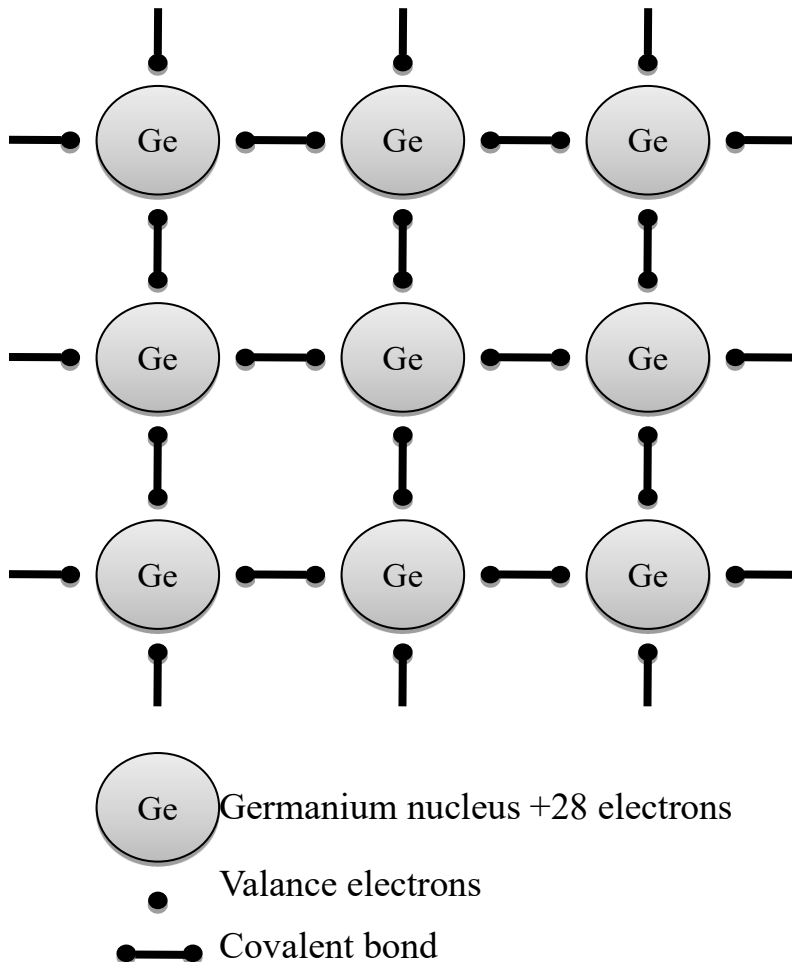


Fig 1.24 Intrinsic semiconductor

Bonds to Bands

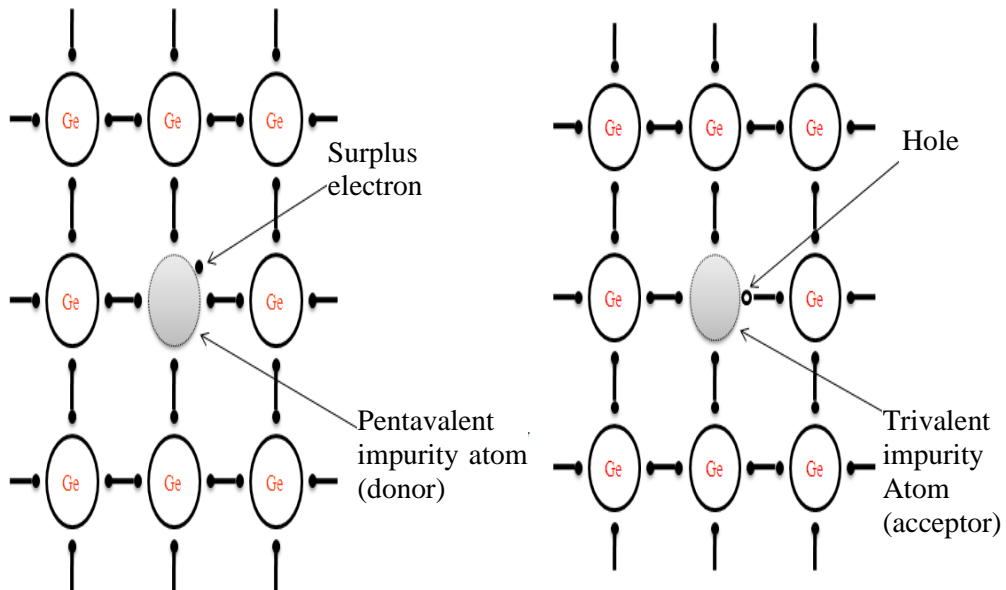


Fig 1.25 Extrinsic semiconductor

Dopants are of two types which include n-type and p-type dopants. Generally doping is done to increase the conductivity of semiconductors. Doping increases the charge carriers that results in the increased electrical conductivity of semiconductor. Higher the increase in the number of charge carriers in the semiconductor higher is its electrical conductivity.

Doping atoms occupy the lattice positions of the semiconductor. They increase the number of charge carriers of the semiconductor in the form of electrons and holes.

Electrons are negatively charged but the holes attain the positive charge. Generally group III and group V elements of periodic table are extensively used as dopants.

Bonds to Bands

Types of Extrinsic semiconductor:

1. n-type semiconductor :

It is an excess negatively charged electrons containing semiconductor and obtained by adding extremely small quantity of a pentavalent element impurity like phosphorus, arsenic or antimony to pure intrinsic semiconductor crystal lattice like silicon, germanium, tellurium etc.

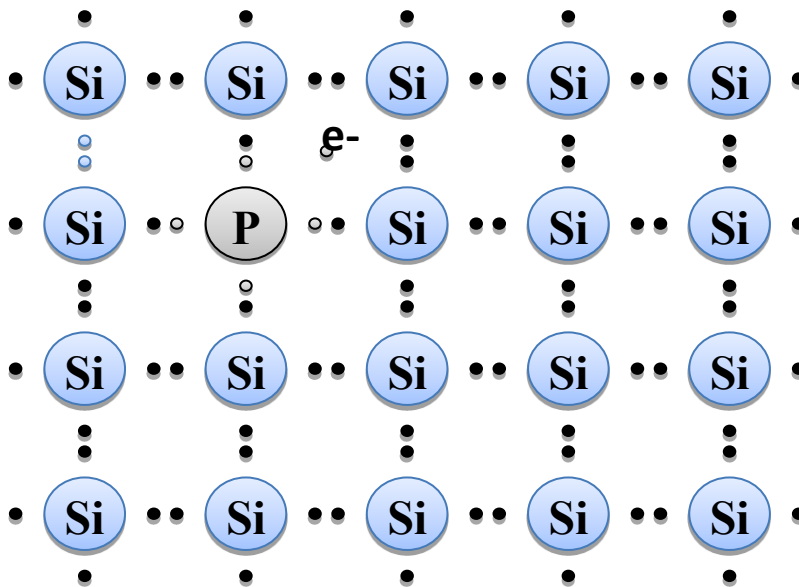


Fig 1.26 n-type semiconductor

Conduction Process: The doping atom forms four covalent bonds with the surrounding four Si atoms of intrinsic semiconductor with the help of four of its five valence electrons, while the fifth excess electron remains loosely bound to the donor atom. This loosely bound excess electron is easily excited from the valence band to the conduction band, when an electric field is applied. Thus, conduction is due to movement of excess electrons present in an n-type semiconductor. In other words, the electrical conductivity of an n-type semiconductor is dependent only on the number of

Bonds to Bands

free or excess electrons present in the conduction band. This results in the increase of negatively charged electrons and hence n-type semiconductor is formed. Here n stands for negative charge or sign. Increase of charge carriers in the form of negatively charged electrons increases the electrical conductivity of semiconductor.

2. p-type semiconductor :

It is an excess positively charged holes containing semiconductor and is obtained by adding an extremely small quantity of trivalent element like boron, aluminum to the pure intrinsic semiconductor crystal lattice like silicon, germanium, etc.

Conduction process: All the three valence electrons present in the trivalent doping agent (an acceptor atom) form three covalent bonds with the surrounding three of the four atoms, thereby one bond in one of the four surrounding Ge atoms is left incomplete. This gives rise to a positive hole. The positive hole so formed in the crystal lattice conduct current, when electric field is applied. During this type of conduction process, a hole travels to an adjacent atom by acquiring an electron and re-establishing a new covalent bond, by breaking an existing covalent bond in the adjacent atom and creating a new hole of it. In this way, holes are filled by electrons from one atom to another and creating new holes in sequence in the crystal lattice.

The movement of holes through the crystal of a p-type extrinsic semiconductor is nothing but movement of a positive electric charge. Holes carry the current by accepting electrons and move in the opposite direction to that of electrons during the flow of electric current.

Thus, in such a semiconductor, the positively charged holes are in excess and the only charge-carriers during conduction.

Bonds to Bands

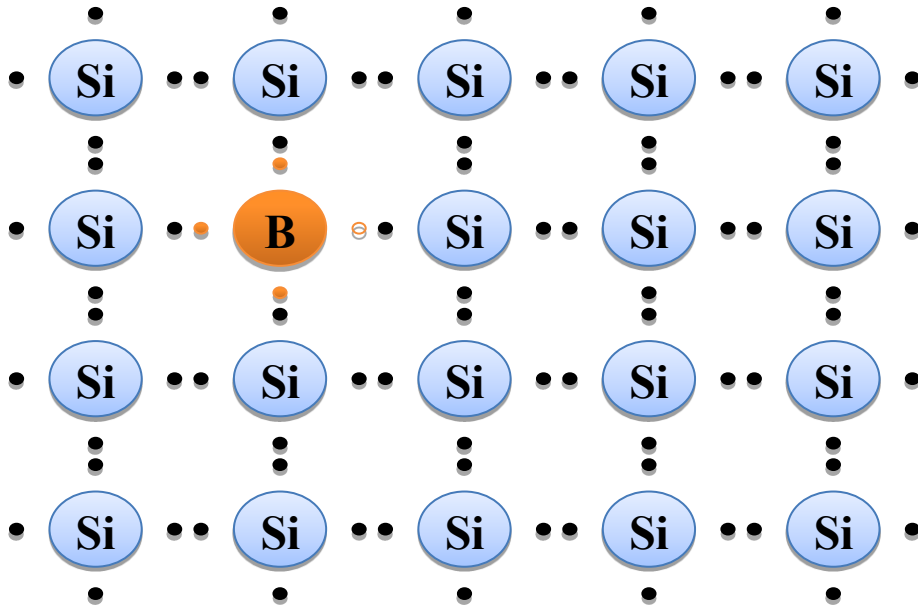


Fig 1.27 p-type semiconductor

Role of Arsenic doping on Silicon:

Arsenic is a group V element or pentavalent. It is doped with silicon semiconductor to form n-type semiconductor. Arsenic atom enters into lattice position of silicon atom and bonds covalently with four silicon atoms. The fifth electron of arsenic is free to move in the semiconductor which results in the increase of charge carriers and hence conductivity of semiconductor. Not only with silicon, arsenic can also be doped with other semiconductors.

Bonds to Bands

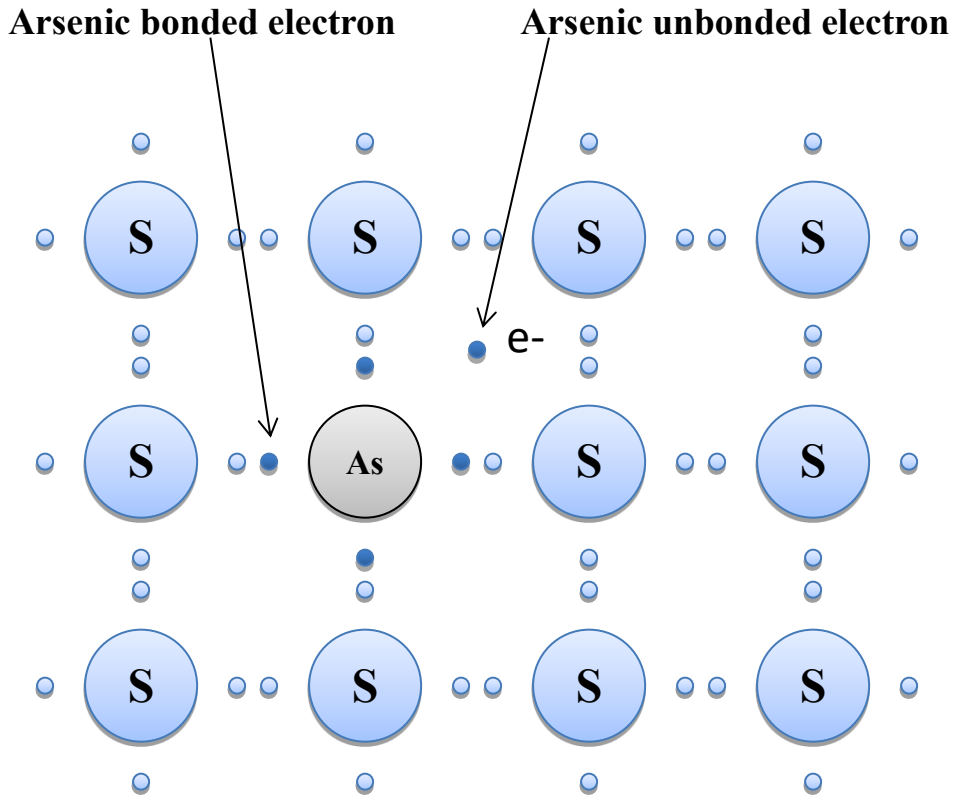


Fig 1.28 Doping of arsenic with silicon

Role of Gallium doping on Silicon:

Gallium belongs to third group of periodic table. It is trivalent element. It can be doped with silicon to form p-type semiconductor. It has only three valence electrons in its outer most shell. In the lattice structure, it is surrounded by four silicon atoms and hence creating electron deficient sites called holes. These holes are ready to accept the electrons and increase the electrical conductivity of semiconductor. Germanium can also be doped with gallium to form p-type semiconductor.

Bonds to Bands

1.14 SUPERCONDUCTORS

Ordinary metals conduct electricity and their specific conductivity is around $10^6 \text{ ohm}^{-1}\text{cm}^{-1}$. It has been found that for a number of metals and alloys, the electrical resistance disappears abruptly and completely at temperatures, a few degrees above absolute zero. Low temperature research has led to the discovery of an amazing phenomenon of superconductivity.

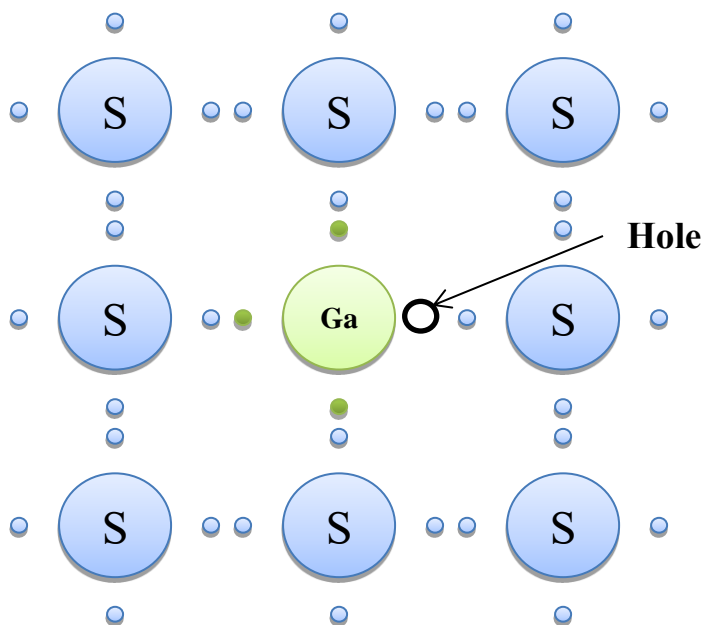


Fig 1.29 Doping of gallium with silicon

Superconductors are materials *which conduct electricity without any electrical resistance*. The maximum temperature, in which a superconducting material exhibits superconductivity, is called its critical temperature (T_c). Materials in superconducting state become diamagnetic and are repelled by magnets. The phenomenon of superconductivity was first observed by Heiki Kammerlingh Onnes, a Dutch physicist in 1913 and found that mercury became superconducting at 4K (at boiling point of liquid helium).

Bonds to Bands

This astonishing work earned him the 1973 Nobel Prize in physics. Thereafter in 1986 scientists Karl Muller and Johannes Bednorz developed superconductors by cooling oxide of copper, lanthanum and barium to 40 degrees Kelvin, greater than zero degree Kelvin as was thought to be required for the material to be a superconductor. Decades after, superconductors have been developed at 164 degrees Kelvin under high pressure.

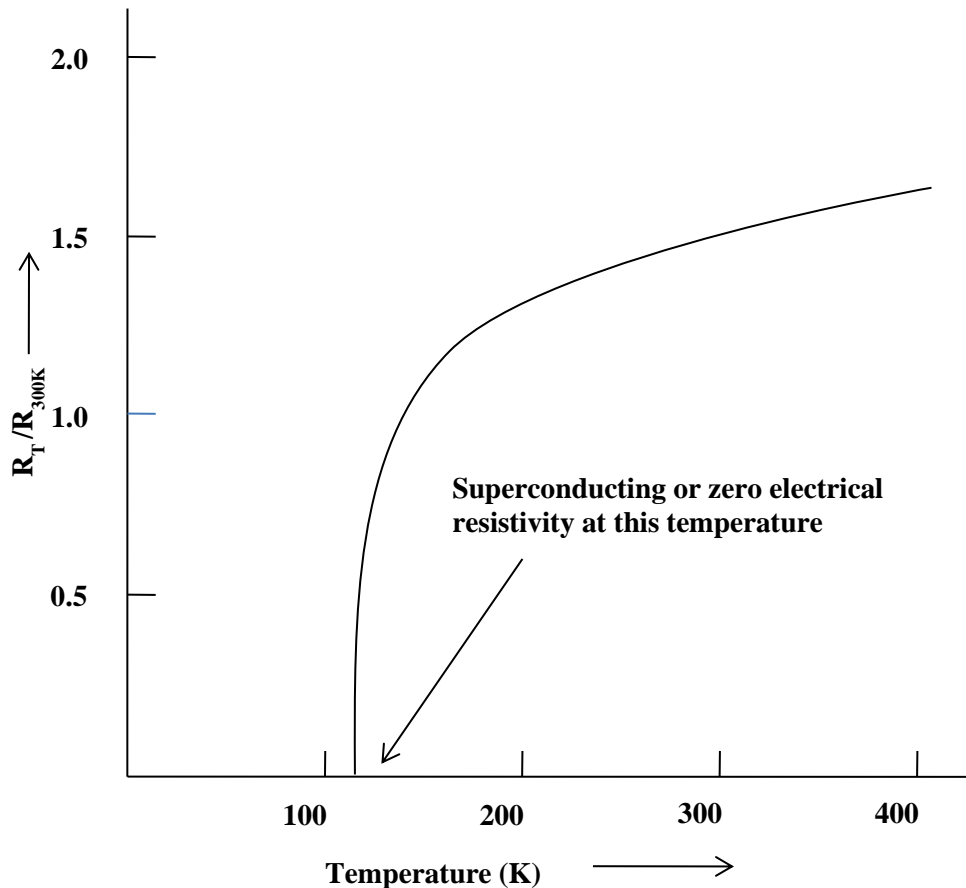


Fig 1.30 **Electrical resistivity on going to zero absolute in a superconducting material.**

Bonds to Bands

Properties of superconductors:

1. They possess greater resistivity than other elements at room temperature.
2. The transition temperature for different isotopes of a superconductive element decreases with the atomic mass of the isotope.
3. On adding impurity to a superconducting element, the critical temperature is lowered.
4. During transition, neither thermal expansion nor elastic properties change.
5. In superconducting state, all electromagnetic effects disappear.
6. When a low magnetic field is applied to a superconductor and it is cooled to low temperature below its transition temperature, then the superconductor expels all magnetic flux. This is known as **Meissner** effect.

High temperature superconductors:

In 1986, George Bednorz and Alexmuller found that an oxide of La, Ba and Cu lose its resistance around 35 K. In 1987, Paul Chu and Wu Jr reported that a ceramic compound, $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ ($y \leq 0.5$) is superconducting upto 100K. This compound is also known as 1: 2: 3 compound, due to its Y: Ba: Cu stoichiometry.

Preparation of 1: 2: 3 compound:

0.750 g of yttrium oxide (Y_2O_3), 2.622 g of barium carbonate (BaCO_3) and 1.1581 g of cupric oxide (CuO) is taken in a mortar and grind the mixture to fine powder with the help of pestle. Then, transfer the powder to a porcelain crucible and place it in a furnace maintained at 920-930 °C for about 10-12 hours. Allow the mixture to cool gradually in the furnace itself and the mixture absorbs the requisite amount of oxygen from the atmosphere. When the temperature of the furnace becomes about 1000 °C, the crucible is taken out and cooled in air. The resulting compound is 1: 2: 3

Bonds to Bands

having composition $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ and exhibits superconductivity well above 77K. The structure of 1: 2: 3 compound is similar to mineral perovskite (CaTiO_3) structure.

Applications of superconductivity:

The phenomenon of superconductivity has many applications such as:

1. Superconducting magnets capable of generating high fields with low power consumptions are being employed in scientific tests and research equipments.
2. They are also used for magnetic resonance imaging (MRI) in the medical field as a diagnostic tool.
3. It is used as a magnet for high-energy particle accelerators.
4. It is used as a memory or storage elements in computers.
5. It is used in high-speed magnetically levigated trains.
6. It is used in high-speed switching and signal transmission for computers.

Solved Problems

1. When a radiation of wavelength 500 nm strikes a metal surface, electrons are emitted from the surface of a metal. The kinetic energy for one electron emitted from the metal is $1 \times 10^{-19}\text{J}$. Calculate the minimum energy required to remove an electron from a metal (binding energy).

Solution:

Wavelength $\lambda = 500 \text{ nm}$

Incident radiation energy

$$E = h\nu = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{500 \times 10^{-9}} = 3.975 \times 10^{-19} \text{ J}$$

Bonds to Bands

$$h\nu = \omega + \frac{1}{2}m\nu^2$$

The minimum energy required to remove an electron from a metal is

$$\omega = h\nu - \frac{1}{2}m\nu^2 = (3.975 \times 10^{-19}) - (1 \times 10^{-19}) = 2.975 \times 10^{-19}J$$

2. Calculate the wavelength of an electron having velocity $6 \times 10^6 \text{ ms}^{-1}$ and mass $9.1 \times 10^{-31} \text{ Kg}$.

Solution: The wavelength of an electron

$$\begin{aligned}\lambda &= \frac{h}{p} = \frac{h}{mv} = \frac{6.626 \times 10^{-34}Js}{(9.1 \times 10^{-31}Kg) \times (6 \times 10^6ms^{-1})} \\ &= 1.2 \times 10^{-9} m \text{ or } 1.2 nm\end{aligned}$$

3. Calculate the uncertainty in position for a ball of mass 0.2 Kg moving with a speed of 10 ms^{-1} is measured at an accuracy of 1%.

Solution: The momentum of the ball is given by

$$p = m\nu = 0.2 Kg \times 10ms^{-1} = 2 Kg.ms^{-1}$$

Thus uncertainty in momentum is calculated from momentum and % of accuracy

$$\Delta p = 2 \times 0.01 = 0.02 Kg.ms^{-1}$$

$$\Delta x = \frac{h}{\Delta p} = \frac{6.626 \times 10^{-34}Js}{0.02 Kg.ms^{-1}} = 3.31 \times 10^{-32}m \quad \because 1J = 1Kg.m^2$$

Bonds to Bands

4. Calculate the zero point energy of an electron of mass $9.1 \times 10^{-31} \text{Kg}$ in one dimensional box of length 1\AA .

Solution: The energy of electron in one dimensional box is

$$E = \frac{n^2 h^2}{8mL^2} = \frac{n^2 \times (6.626 \times 10^{-34} \text{Js})^2}{8 \times (9.1 \times 10^{-31} \text{Kg}) \times (1 \times 10^{-10} \text{m})^2}$$
$$= n^2 \times 4.16 \times 10^{-20} \text{Js}^2$$

The zero point energy is the lowest energy level or first energy level

$$E_1 = 1^2 \times 4.18 \times 10^{-20} \text{Js}^2$$

5. Calculate the energy difference between E_4 and E_3 for an electron in a one dimensional box of length 12\AA .

Solution: The energy of electron in one dimensional box is

$$E = \frac{n^2 h^2}{8mL^2} = \frac{n^2 \times (6.626 \times 10^{-34} \text{Js})^2}{8 \times (9.1 \times 10^{-31} \text{Kg}) \times (12 \times 10^{-10} \text{m})^2} = n^2 \times 4.16 \times 10^{-20} \text{Js}^2$$

The electron in lowest energy level or first energy level

$$E_1 = 1^2 \times 4.18 \times 10^{-20} \text{Js}^2$$

$$\Delta E = E_4 - E_3 = (2n + 1)E_1 = (6 + 1) \times 4.16 \times 10^{-20}$$
$$= 2.912 \times 10^{-20} \text{Js}^2 \text{ or Watt second}$$

6. Determine the value of A in wave function of particle in one dimensional box of length L and find out the normalized wave function of it by normalization method.

Solution: The value A is determined by the normalization of wave function which is given by

Bonds to Bands

$$\int_0^L \Psi^2 d\tau = \int_0^L A^2 \sin^2 \frac{n\pi x}{L} dx = 1$$

$$\text{we know that } \sin^2 x = \frac{(1 - \cos 2x)}{2}$$

$$\int_0^L A^2 \sin^2 \frac{n\pi x}{L} dx = \frac{A^2}{2} \int_0^L \left(1 - \cos \frac{2n\pi x}{L}\right) dx = 1$$

$$\frac{A^2}{2} \left\{ [x]_0^L - \left[\frac{\sin 2n\pi x/L}{2n\pi/L} \right]_0^L \right\} = 1$$

$$\frac{A^2 L}{2} = 1$$

$$A = \sqrt{\frac{2}{L}}$$

Thus the normalized wave function is $\Psi = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}$

Questions:

Part-A

1. What is a black body radiation?
2. Recall Rayleigh-Jean's Law.
3. What is Planck's law of radiation?
4. Summarize the photoelectric effect.

Bonds to Bands

5. How is kinetic energy of emitted electrons related to frequency and intensity of incident light?
6. Tell de Broglie's hypothesis.
7. Define Heisenberg's Uncertainty principle.
8. What are the conditions for acceptable wave functions?
9. Define zero point energy for 1D box.
10. What happens to spacing of energy levels when length of one dimensional box increases?
11. Outline the wave function and energy for a particle in 1D box.
12. What is probability density?
13. List out the types of quantum numbers.
14. Define Aufbau principle.
15. Explain Pauli's exclusion principle.
16. Define Hund's rule.
17. Draw the structure of p-orbitals.
18. Determine the number of orbitals in d subshell.
19. Compare the bonding and antibonding molecular orbitals.
20. Explain conductors, semiconductors and insulators with a neat diagram.
21. What are super conductors? Give example.
22. Differentiate between n-type and p-type semiconductor.
23. List out the properties of superconductors.
24. List out the applications of superconductors.
25. Define Meissner effect.

Bonds to Bands

Part-B

1. Elaborate the LCAO-MO method in the formation of hydrogen molecule.
2. Formulate the Schrodinger wave equation for a particle in one dimensional box and determine the wave function and energy of the particle.
3. Determine the value of A in the wave function of particle in 1D box by Normalization method.
4. Outline the time-independent Schrodinger equation of hydrogen atom using ϕ and θ .
5. Explain the various shapes of atomic orbitals with neat sketch.
6. Summarize the significance of four quantum numbers.
7. Explain band theory of solids with neat diagram.
8. Discuss the various types of semiconductors with suitable examples.
9. Explain the role of doping of arsenic and gallium on silicon with neat diagram.
10. Write a note on superconductor with suitable example.

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