Physics of Nanomaterials

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Unit (I) Free ele^⊖ theory (qualitative idea) & it's features, Idea of Band structure, Metals, insulators & semiconductors, concept of effective mass, Density of states in Bands, Variation of density of states with energy, Variation of density of states & Band Gap with size of crystal, Electronic structure from Bulk to quantum dot, electronic states in direct & indirect semiconductors Nano-crystals, Excitions in direct & indirect Band Gap semiconductors.

Unit (II) Physics of Reduced dimensional systems & devices: Quantum confinement, electron confinement in 1, 2 & 3-D infinitely Deep square well ptls., Various low dimensional systems: Quantum well structure; Idea of Quantum well structure, Electron wave fun^n & energy in quantum well structure (infinite well approx.), density of states & optical absorption in quantum well, Quantum wires: ele^⊖ wave fun^n & energy, density of states, Quantum dots: ele^⊖ wave fun^n & energy, density of states, Idea of Hetero-junction LED, Quantum well Lasers & Quantum dot lasers, Transistor: Coulomb Blockade & single ele^⊖ Transistor.

Unit (III) Synthesis / Fabrication of Nanomaterials / Nanostructure: Bottom up & Top down approaches

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for synthesis of Nano materials, Synthesis of 0-D nanostructures : Sol Gel process, Synthesis inside Micelles or using Micro emulsions & Growth Termination, Epitaxial Core-Shell nanoparticles, Ball Milling, 1-D nanostructures (Nanowires, nanorods, nanotubes) : Vapor (or solⁿ)-liquid solid (VLS or SLS) growth & size control, electrochemical deposition, Lithography, 2-D nanostructures (Thin Films & quantum wells) : Molecular Beam epitaxy (MBE), MOCVD, cluster Beam evaporation, Ion Beam deposition, chemical Bath deposition technique.

Unit (IV) characterization of Nanostructures : effect of particle size & strain on width of XRD Peaks of nanomaterials, Determination of crystallite Particle size & strain in nanomaterials using Debye Scherrer's Formula & Williamson-Hall's Plot, Transmission eleⁿ Microscopy: Basic principle, Brief idea of Setup, Sample preparation, imaging modes (Dark & Bright Field), selected area eleⁿ diffraction, Photoluminescene (PL) spectroscopy : Basic principle & idea of instrumentation, Shift in PL Peaks with particle size, Determination of alloy composition in Thin Films of compound semiconductors, estimation for width of quantum wells, Raman spectroscopy : Basic principle & idea of instrumentation, variations in Raman spectra of Nanomaterials with particle size, study of Raman spectra of carbon Nanotubes & Graphene.

Unit (I)

Asignment (01)

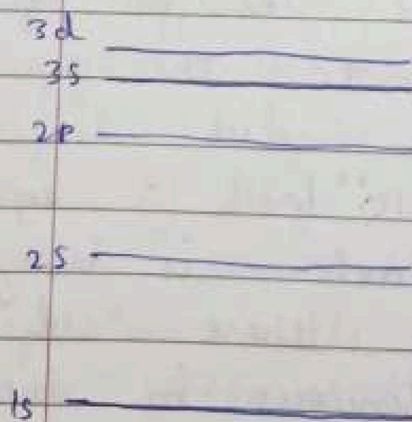
① Describe the band formation in solids. In light of band theory, classify the solids in metals, semiconductors & insulators?

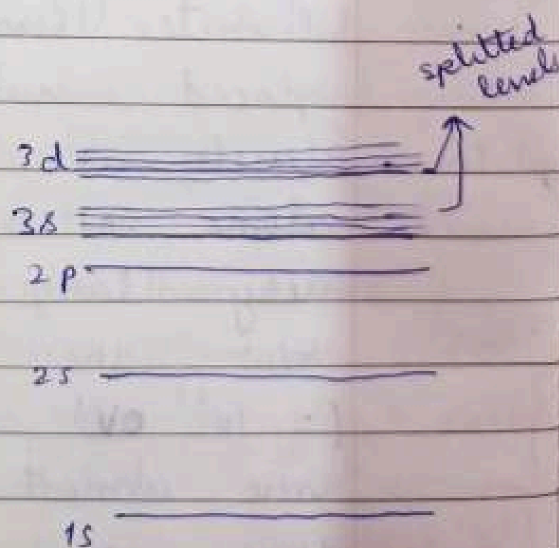
Ans:- We know that electrons in an isolated atom possess discrete energy levels 1s, 2s, 2p, ... etc. These levels are filled with $e^{\ominus}$ in order of increas-ing energy. When these isolated atoms combine to form a solid, they arrange themselves in an orderly pattern, called a crystal. In a crystal, due to periodicity, each atom is in the electrostatic field of neighbouring atoms. The discrete energy levels of individual atoms are no longer valid. Instead, due to interaction b/w atoms, each discrete level splits into closely spaced sub-levels. The no. of sub-levels is equal to the no. of atoms N in the solid. Since N is very large ($N \approx 10^{23}$/cc) ∴ separation b/w these sublevels is very small ($\approx 10^{-23}$ eV). Hence, these sub-levels are almost continuous in energy & thus are said to form energy bands. The first energy level of various atoms constitute the first

energy band, The second energy level form the second energy band & so on. The energy band formed by valence ele$^{\circ}$ of atoms is called the valence band This band is the highest occupied band. The next higher band is known as conduction band & is normally empty. Now, these allowed energy bands are in general separated by regions which have no allowed energy states Such regions are termed as forbidden energy bands or energy gap.

Discrete energy levels for isolated atom

energy levels of atoms in a solid





The splitting of energy levels does

not take place for lower level 1s & 2s because the ele⁻ in these levels are not significantly affected by the presence of other atoms. Further the 2p level does not begin to split until the interatomic separation b/w becomes smaller than actually found in case of sodium. In fact 3s level is the first occupied level to be splitted into sub-levels. In higher energy levels splitting occurs because electronic wave fun overlap significantly to give rise to interaction b/w them.

1) Insulators :-

(I) Insulators are those substances in which the valence band is completely filled with ele⁻ & the conduction band is empty & there is a large forbidden energy gap ($\simeq 5eV$ or more) b/w these two.

(II) Because of this large gap, ele⁻ can not thermally excited easily across this gap from the valence band to the conduction band.

(III) External electric field can not cause any significant current.

(IV) Electrical conductivity of such material

is extremely small & may be regarded as zero under ordinary conditions

(v) NaCl & Diamond are good insulator having forbidden gaps $E_g \simeq 6\,eV$.

(vi) When the temp. of an insulator is raised above room temp. some of the valence e^- may acquire enough energy to cross over to the conduction band giving rise to an extremely small current.

(vii) So resistance of an insulator ↓se slightly with ↑se in temp.

(viii) The resistance of an insulator have -ve temp. coeff. of resistance.

II) Conductors :-

(i) Conductors are those substances in which the bands either overlap or are only partially filled.

(ii) e^- & empty energy states are intermixed within the bands so that e^- can move freely under the influence of an external electric field.

(iii) Metals have high electrical conductivity.

(iv) Their conductivity ↓ses with ↑se in temp.

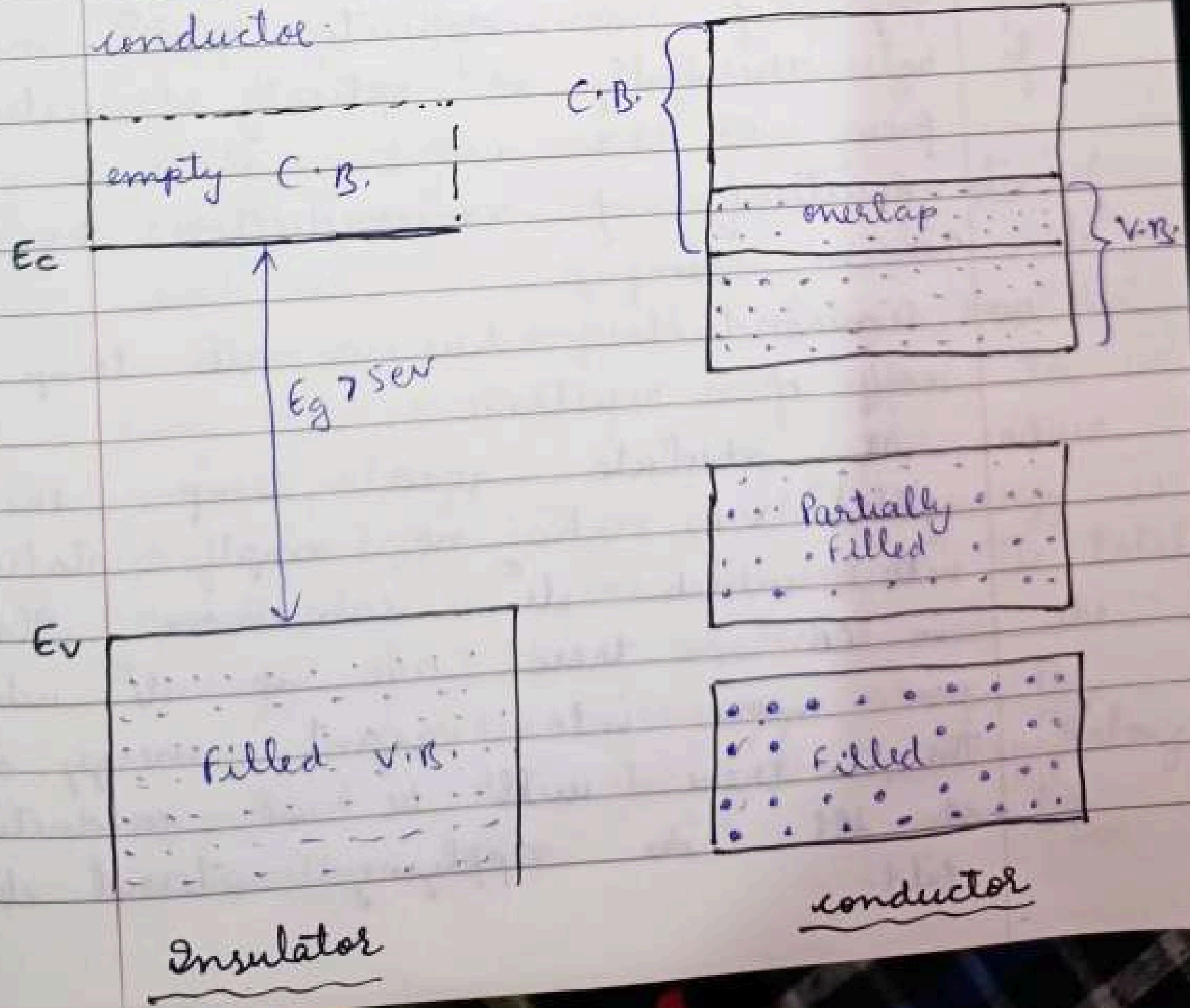
(V) The electrical resis. of metals ↑ses with ↑se in temp. due to increased no. of collisions at higher temp.

(VI) Metals have a +ve temp. coeff. of resistance

(VII) Due to overlapping, the valence band also acts as the conduction band.

eg: $Z = 11$, $Na \rightarrow 1s^2 2s^2 2p^6 3s^1$

Thus, the valence band (formed by 3s level) is only partially filled. On app. of electric field, e^- can freely move into empty states within the same partially filled band. This makes sodium a good conductor.



III) Semiconductors :-

(I) The band structure of semiconductors is similar to that of insulators at absolute zero temp. i.e; a filled V.B. separated from an empty C.B. by forbidden gap which has no allowed energy states.

(II) However, E_g is much smaller in semiconductors than in insulators. e.g:- Si has a band gap of about 1.1eV compares with 6eV for diamond.
Ge has still smaller $E_g = 0.72$ eV

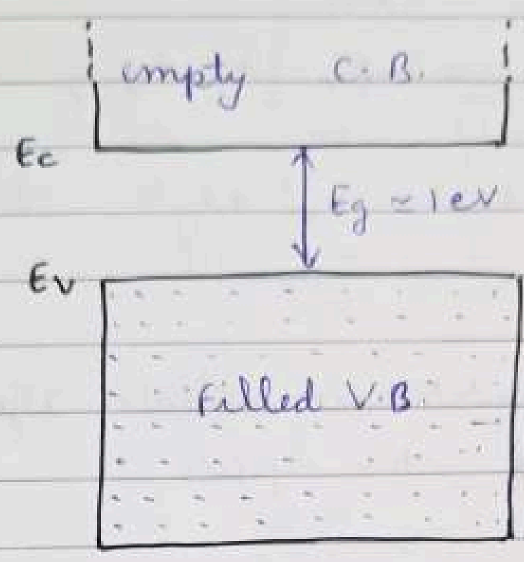
(III) Due to relatively small band gaps of semiconductors, ele⁻ may be thermally or optically excited from V.B. to C.B.

(IV) Resistivity of semiconductors ↓ses with ↑se in temp.

(V) Semiconductor has a -ve temp coeff of resistance.

(VI) At absolute zero temp., the filled V.B. has no empty states into which ele⁻ can move. Also in CB., there are no ele⁻ which can move into vacant energy states. Thus, there will be no conduction at all on applying external electric field.

(vii) Semiconductor behaves like an insulator at absolute zero temp.



② If the energy dispersion relation for a 2D ele$^{\ominus}$ system is given as $\epsilon = \mu \hbar K$ where K is wave vector, for this system find the variation of density of state $g(\epsilon)$ with ϵ.

Ans In a two-dimensional material such as a quantum well, ele$^{\ominus}$ motion is confined along one dir^n (say z) & they are free to move along rest of the two dir^n (x & y). Thus, ele$^{\ominus}$ energy is quantized in one dimension. The total energy of this material is the sum of the energy along the quantised dir^n & the energy along the other two dir^n. It can be

expressed as

$$E = \frac{\hbar^2 k_z^2}{2m} + \frac{\hbar^2 k^2}{2m}$$

$$E = E_n + E_{x,y}$$

where $k^2 = k_x^2 + k_y^2$ & $k_z = \frac{n\pi}{L_z}$

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

Let us now consider the circular area of k- space

$$A_k = \pi k^2$$

hence, along x & y dirⁿ the particle is free to move, therefore due to periodic boundary conditions

$$k_x = \frac{2\pi}{L_x} \; ; \quad k_y = \frac{2\pi}{L_y}$$

area of each mode $= k_x k_y = \frac{(2\pi)^2}{L_x L_y}$

Total no. of modes in the area A_k is given by $= \frac{\text{Total area}}{\text{area of each mode}}$

$$= \frac{\pi k^2}{4\pi^2} L_x L_y$$

$$= \frac{k^2}{4\pi} L_x L_y$$

If the particle be an ele⁻, then there can be two ele⁻ corresponding to

same energy, one with spin up & the other with spin down

∴ Total no. of energy states in the area πk^2 are given by

$$= 2 \times \frac{k^2}{4\pi} L_x L_y = \frac{k^2}{2\pi} L_x L_y$$

No. of states per unit area

$$N = \frac{\text{Total no. of states}}{\text{area}}$$

$$N = \frac{\frac{k^2}{2\pi} L_x L_y}{L_x L_y} = \frac{k^2}{2\pi}$$

∴ density of states

$$g(E) = \frac{dN}{dE} = \frac{d}{dE}(k^2/2\pi)$$

$$g(E) = \frac{k}{\pi}\left(\frac{dk}{dE}\right) \quad (1)$$

$$\because E = \frac{\hbar^2 k^2}{2m} \Rightarrow k = \sqrt{\frac{2m}{\hbar^2}}\, E^{1/2}$$

$$\therefore dk = \sqrt{\frac{2m}{\hbar^2}}\, \frac{1}{2} E^{-1/2}\, dE$$

substituting value of k & dk/dE in (1)

$$\therefore g(E) = \frac{1}{\pi}\sqrt{\frac{2mE}{\hbar^2}} \times \sqrt{\frac{2m}{\hbar^2}} \cdot \frac{1}{2}(E)^{-1/2}$$

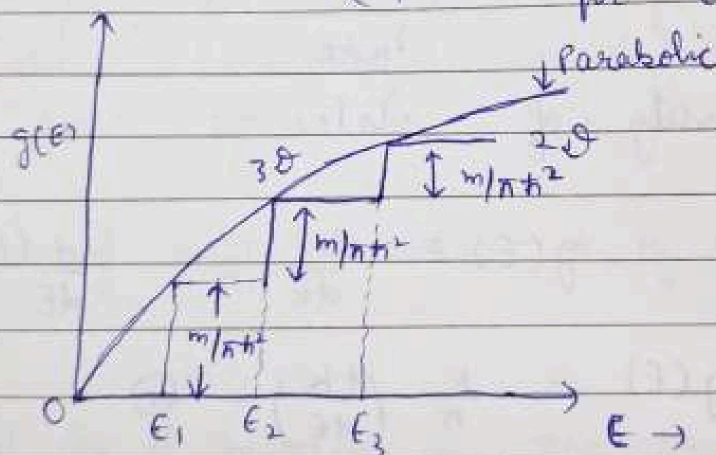
$$\boxed{g(E) = \frac{m}{\pi \hbar^2}} \Rightarrow \boxed{g(E) \propto E^0}$$

This is the energy density of the sub-band for a given k_z (or E_n). For each successive k_z there will be an additional $m/\pi\hbar^2$ term & hence another sub-band.
The density of states is therefore expressed as

$$g(E) = \frac{m}{\pi\hbar^2} \sum_n f(E - E_n)$$

where f is the Heaviside fun^n or unit step fun^n & is given by

$$f(E - E_n) = \begin{cases} 0 & \text{for } E < E_n \\ 1 & \text{for } E > E_n \end{cases}$$



③ Show that effective mass (m^*) of ele$^{\ominus}$ can be represented as

$$m^* = \frac{\hbar^2}{(d^2E/dk^2)}$$

where E & K are energy & wave

vec

Ans Let
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vector respectively.

Ans Let us consider an $ele^{\ominus}$ with wave vector K in the region where external electric field E is present. It's particle velocity v will be equal to the group velocity $d\omega/dK$

i.e.

$$v = \frac{d\omega}{dK} \quad -(1)$$

If ω be the angular freq. of the $ele^{\ominus}$ waves, then its energy

$$E = \hbar\omega \quad -(2)$$

From (1) & (2)

$$v = \frac{1}{\hbar}\frac{dE}{dK} \quad -(3)$$

we consider the hypothetical case in which there is only one $ele^{\ominus}$ in the brillouin zone under consideration. Then, in a time interval dt, $ele^{\ominus}$ energy ↑ses by

$$dE = \text{work done by the electric force}$$
$$= (-eE)\,dx = -eE\,v\,dt \quad -(4)$$

where dx is displacement of $ele^{\ominus}$

during time dt

From ③ & ④

$$dE = -\frac{eE}{\hbar}\left(\frac{dE}{dk}\right) dt$$

$$\therefore \quad \hbar \frac{dk}{dt} = \frac{d(\hbar k)}{dt} = \frac{dp}{dt} = -eE \quad ⑤$$

where $p = \hbar k$ is crystal momentum

on diff. ③ , we get

$$\frac{dv}{dt} = \frac{1}{\hbar}\frac{d}{dt}\left(\frac{dE}{dk}\right) = \frac{1}{\hbar}\frac{d^2E}{dk^2}\frac{dk}{dt}$$

$$= -\frac{eE}{\hbar^2}\left(\frac{d^2E}{dk^2}\right) \quad \text{(using ⑤)}$$

$$-eE = \frac{\hbar^2}{(d^2E/dk^2)} \cdot \frac{dv}{dt} \quad -⑥$$

This eqⁿ is of type

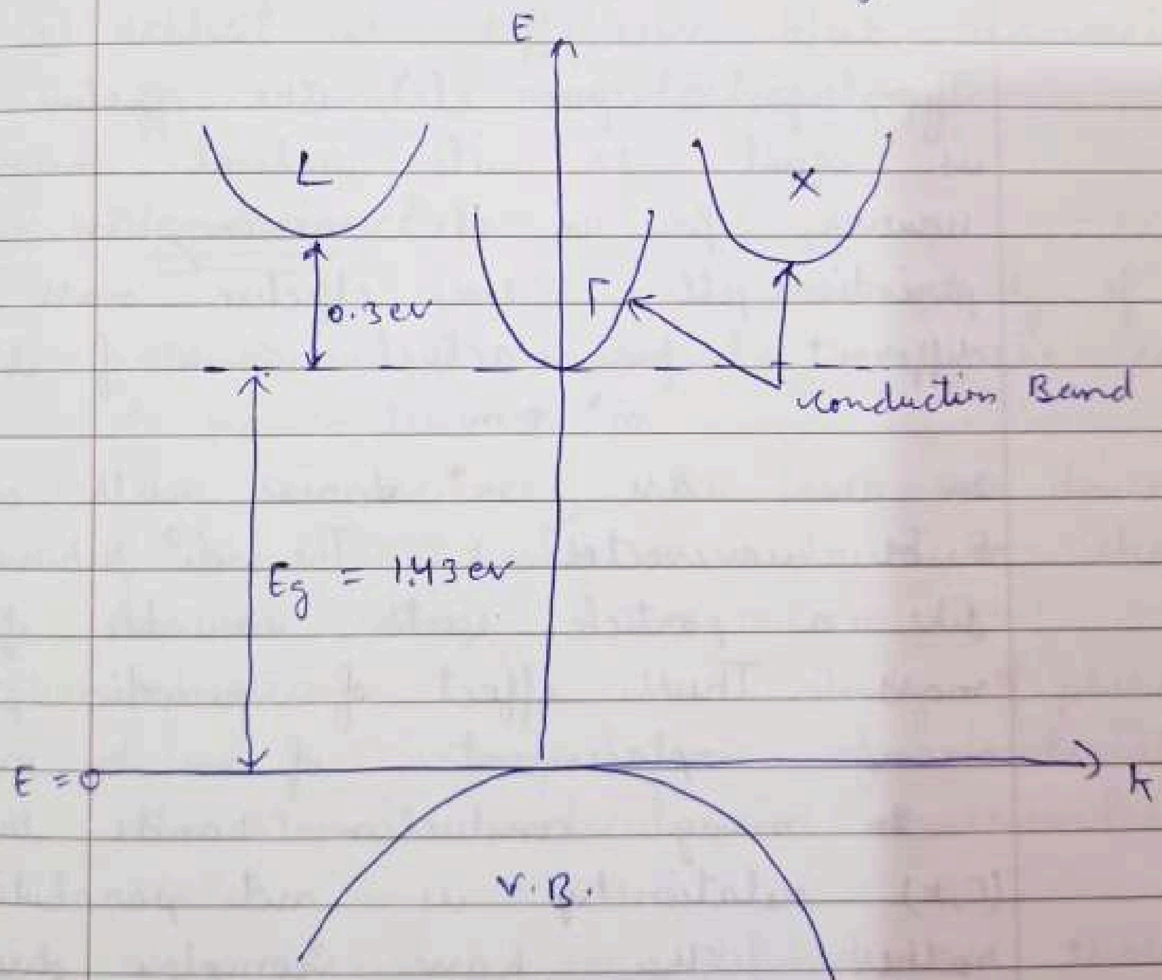
Force = mass × accⁿ

$$\therefore \quad m^* = \frac{\hbar^2}{d^2E/dk^2} \quad ⑦$$

represents the effective mass of an $e^{\ominus}$ in a band with given (E, k) relationship.

$\frac{d^2E}{dk^2}$ ⇒ curvature of band

The shape of the energy bands in three dimensional K- space determines the value of effective mass. The e⁻ effective mass will be smaller in strongly curved bands (eg: Γ) & larger in those bands which have small curvature (eg: L or X)



For a band centred at K=0 (eg Γ), the (E, K) dispersion relation near the minimum is usually parabolic given by

$$E = \frac{\hbar^2 k^2}{2m^*} + E_g \quad -(8)$$

In this case, m^* turns out to be a constant. ||'rly, for a free e^-

$$E = \frac{\hbar^2 k^2}{2m}$$

$$\frac{d^2E}{dk^2} = \frac{\hbar^2}{m}$$

$$m^* = \frac{\hbar^2}{(d^2E/dk^2)} = m$$

Thus, for a free e^- the effective mass is equal to its actual mass. However, for an e^- moving in a periodic ptl., the effective mass is different from actual mass of e^- i.e.

$$m^* \neq m$$

In this case, m^* varies with energy E or wavevector k. The e^- behaves like a particle with variable effective mass. Thus effect of periodic ptl. means replacement of m by m^*.

In many conduction bands the (E,k) relationship is not parabolic, rather they have complex dispersion relation which depend on dir^n^ of e^- transport w.r.t. the principal crystal dir^n^. In such cases, the effective mass is a Tensor quantity. Thus, the e^- near C.B. minima

have +ve values of effective mass where -as ele$^{\ominus}$ near top of V.B. have -ve effective mass.

The effective mass of an ele$^{\ominus}$ in a metal can be determined from cyclotron resonance experiment for most metals

$$\frac{m}{2} \leq m^* \leq 2m$$

(4) What is difference b/w nanoscience and nanotechnology.

Ans:- **Nanoscience :-**

(I) It is the study of structures & materials on the scale of nanometers.

(II) For nanoscience, at least one dimension of the material or structure should lie in range 1 to 100 nm.

(III) Nanoscience is the study of phenomena & manipulation of materials at atomic molecular & macromolecular scales.

(IV) Nanomaterials are defined as those materials which have structured comp. with size less than 100nm in at least one dimension.

(V) In nano-regime properties of nano-materials are quite diffⁿ as compared

to their bulk counterparts.

(VI) Nanostructures can be formed on solid surfaces such as metals, semiconductors & carbon based materials as well as liquids.

(VII) Nanoscience is an emerging area of science & technology today & is the diverse field with very wide applications.

Nanotechnology :-

(i) It is the technology of designing and making functional objects at nanoscale & the science underlying nanotechnology is called nanoscience.

(ii) Nanotechnology as defined, is the manipulation of matter with at least one dimension lying in range 1 to 100 nm.

(iii) Nanotechnology is the design, characterization, production & app^n of structures, devices & systems on nanoscales.

(iv) It may also be defined as the manipulation of matter on an atomic, molecular & supra molecular scale.

(v) It deals with both natural & artifical structures on nanometer scale

(vi) Various field of science such as surface science, organic chemistry, molecular biology, semiconductor phy, microfabrication, molecular engineering etc come under the umbrella of nanotechnology.

(vii) There are 2 basic approaches used in nanotechnology - <u>Top down</u> & <u>bottom up</u>

Top-down methods of making nano-structures require large installation & are quite expensive. They need huge amount of capital to be invested.

Bottom-up approach does not require large installations to be put up & hence is a cost effective method.

⑧ Write fine applications of nano-particles.

Ans:- Nanoparticles are used or being evaluated for use in many fields.

(1) electronics on a nanometer scale, whether made by current Techniques or nanotechnology includes both molecular electronics & electronics and nanoscale device resembling today's semiconductor devices.

(ii) Nanotechnology can help us to move in the dis^n of faster, less costly drug development.

(iii) Medical nanodevices could argument the immune system by finding & disabling unwanted bacteria & viruses.

(iv) Nanodevices could restore artery wall linings to health. This would prevent most heart attacks.

(v) Nanotechnology is also useful for building a better digital brain, where nanomaterials help to device faster microprocessors having endless memory & more energy - efficient.

(vi) Nanomaterials can be used to prepare electrocatalysis for fuel cells & energy storage devices.

⑥ Describe qualitative idea of Drude's free ele$^{\ominus}$ theory of metals.

Ans It is a known fact that ele$^{\ominus}$ revolve in the circular stationary orbits around the nucleus. The +ve charge of the atom is conc. in nucleus. The ele$^{\ominus}$ in outermost orbit are known as valence ele$^{\ominus}$ or conduction ele$^{\ominus}$. In case of metals, these

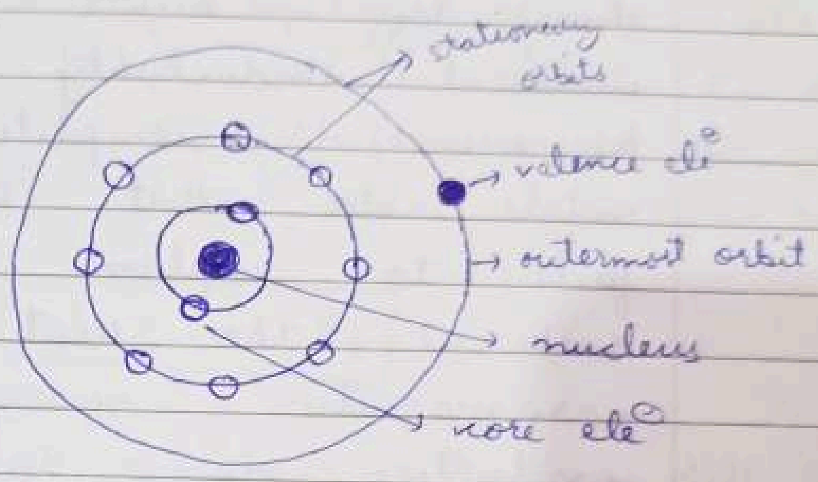
valen the abou of also

atomic structure of $^{23}_{11}$Na

The ins th re el a Th s (a) T a g T (b) -c it

valence ele are loosely bound to the nucleus & they can roam about freely throughout the vol. of crystal. Hence, valence ele are also known as free electrons.

atomic structure of $^{23}_{11}Na$



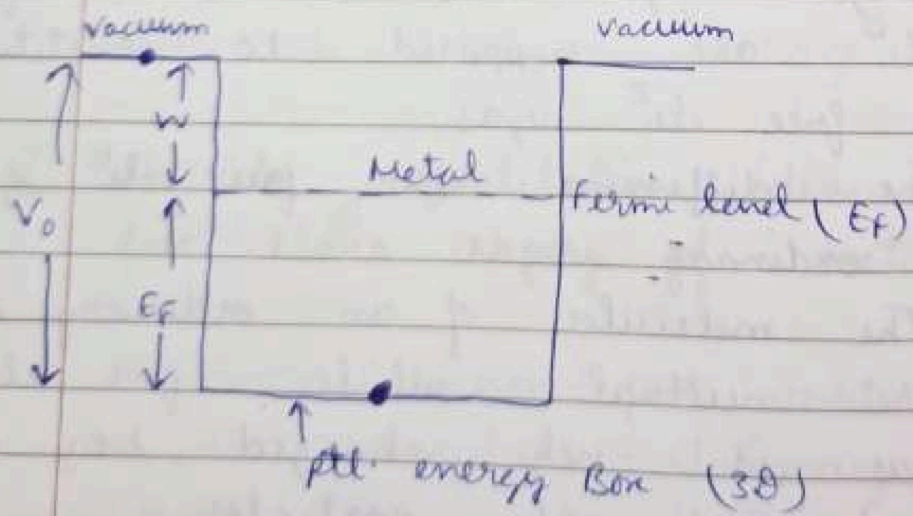
The behaviour of freely moving ele inside the metals is similar to that of atoms or molecules in a perfect gas. Hence, these free ele are supposed to constitute a free ele gas.

The difference b/w free ele gas & ordinary gas are:

(a) The molecules of an ordinary gas are neutral while free ele gas is -vely charged, bcz ele are -vely charged particles.

(b) The conc. of molecules in an ordinary gas is very small as compared to the conc. of ele in a free ele gas.

The classical or Drude Lorentz theory of free e^{-} gas assumes that free e^{-} gas obeys M.B. statistics & explains various prop. of metals such as : validity of ohm's law, high thermal & electrical conductivity of metals (K/σ = const), complete opacity of metals etc. But classical theory fails to explain certain phenomena such as the heat capacity & paramagnetic susceptibility of the conduction e^{-}. Sommerfield explains these char. of an e^{-} gas by treating the problem quantum mechanically using F.D. statistics.



Acc. to Sommerfield, the ptl. energy for an e^{-} in a crystal is periodic. This is because the ptl. energy is caused by the periodically arranged

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the ion cores in lattice through which $ele^{\ominus}$ are moving.
Dia. shows a physical model for metals in which V_0 represents the depth of ptl energy box. At $T = 0K$, all energy levels upto E_f are filled while above E_f are empty. ∴ work required to pull an $ele^{\ominus}$ from metal is given by

$$W = V_0 - E_f$$

where W represents energy diff. b/w an $ele^{\ominus}$ at rest inside metal & one at rest in vacuum & E_f is fermi energy of metal.

⇒ Drude & Lorentz proposed this theory in 1900. Acc. to this theory, the metals containing the free $ele^{\ominus}$ obey the laws of classical mechanics.

Assumption of Drude's Free $ele^{\ominus}$ theory

It based on following postulates.

(i) The valence $ele^{\ominus}$ of atoms are free to move about the whole volume of the metal, like molecules of

a perfect gas in container.

(II) The free $e^{\ominus}$ move in random dir & collide with either +ve ions fixed to the lattice or the other free $e^{\ominus}$. All the collisions are elastic in nature i.e.- there is no loss of energy.

(III) The momentum of free $e^{\ominus}$ obeys the laws of classical kinetic theory of gases.

(IV) The $e^{\ominus}$ velocities in a metal obey classical Maxwell - Boltzmann distribution of velocities.

(V) When the electric field is applied to the metal the free $e^{\ominus}$ are accelerated in dir^n opp. to the dir of applied electric field

(VI) The mutual repulsion among $e^{\ominus}$ is ignored, so that they move in all dir^n with all possible velocities.

(VII) In the absence of field, the energy associated with an $e^{\ominus}$ at temp. T is given by $\frac{3}{2}kT$.
It is related to K.E. eq^n

$$\frac{3}{2}kT = \frac{1}{2}mv_{Th}^2$$

where v_{Th} = thermal velocity

Success of Classical Free e^- Theory

(i) It verifies ohm's law
(ii) It explains electrical conductivity of metals.
(iii) It explains thermal conductivity of metals.
(iv) It derives - Franz law (relation b/w electrical conductivity & thermal conductivity)
(v) also explain optical prop. of metals (opacity of metals)

Drawbacks of Classical Free e^- Theory

(i) It could not explain the photoelectric effect, compton effect & black-body radiation.
(ii) electrical conductivity of semiconductor & insulators could not be explained
(iii) Ferromagnetism could not be explained
(iv) Acc. to classical free e^- theory the specific heat of metals is 4.5R whereas experimental value is given by 3R.
(v) Acc. to classical free e^- theory the electronic specific heat is equal to $\frac{3}{2}R$ while actual value is 0.01 R.
(vi) Widemann Franz law is not valid at low temp.

(VII) It can not explain superconductivity.

⇒ **Density of States :-** The density of states gives the no. of allowed e^- (or holes) states per unit vol. at a given energy level.

OR

The no. of states that the e^- are allowed to occupy per unit vol. per unit energy.

Density :- per unit vol.
State :- allowed solution which satisfy the boundary conditions

why DOS ?

DOS calculations allow one to determine the general distribution of states as a funⁿ of energy & can also determine the spacing b/w the energy bands in semi-conductor.

Applications of DOS

1) Plays an imp. role in the kinetic theory of solids.

(ii) The product of density of states & the prob. distribution fun^n is the no. of occupied states per unit vol. at a given energy level.

(iii) Bulk prop. such as specific heat, paramagnetic susceptibility & other transport phenomena of conductive solids depends on DOS.

Density of states of Fermi Level

The density of states of fermi level is defined as the no. of states per unit energy range.

i.e., $D(E_f) = \frac{dN}{dE_f}$ ①

But $E_f = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3}$ ②

From ②

$$N = \frac{V}{3\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \times E_F^{3/2} \quad ③$$

diff. ③ w.r.t E_F

$$\frac{dN}{dE_f} = \frac{V}{3\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \cdot \frac{3}{2} E_F^{1/2}$$

$$= \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \times E_F^{1/2}$$

So,

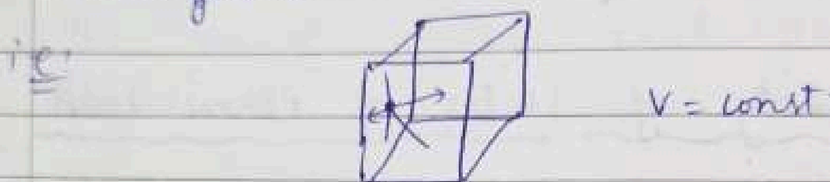
$$\boxed{D(E_F) = \frac{dN}{dE_F} = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{E_F}}$$

Hence, the density of states is proportional to square root of Fermi energy.

⇒ **E-K diagram** (energy - momentum)

Acc to free ele° theory, the potential inside the metal is const throughout.

i.e.



But, accⁿ to Bloch, the ptl inside the metal is not const. instead it is periodic.

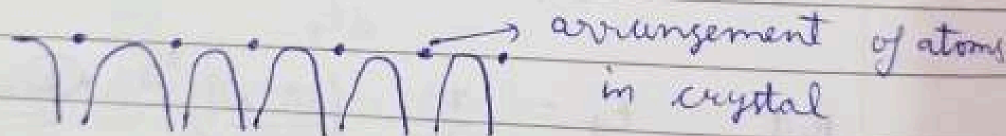


Fig. shows the ptl inside the metal (V = periodic)
hence, the electronic motion inside the metal is

$$\psi_k = u_k e^{ikx}$$

where u_k represents the periodic & e^{ikx} represents the plane wave

Now, to get E-k diagram, we have

to solve schrodinger wave eq^n

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E - V) = 0 \quad (1)$$

$\because$ ψ depends on k, bcz the momentum (k) & ptl (V) both are vary so, E is also vary.

after solving the S.W.E, we get dia. like

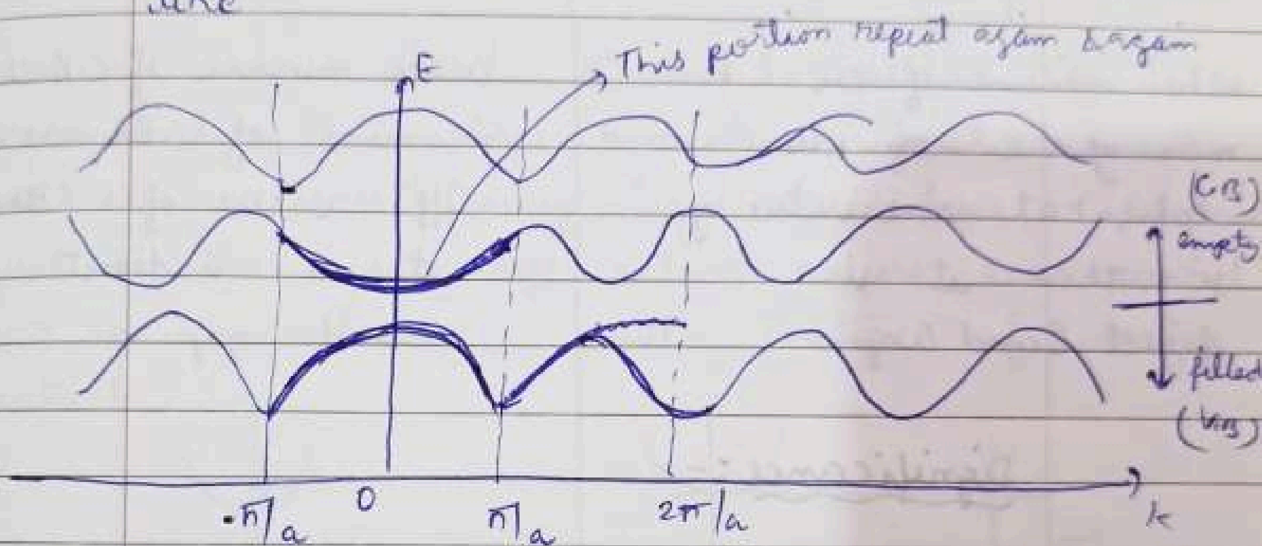
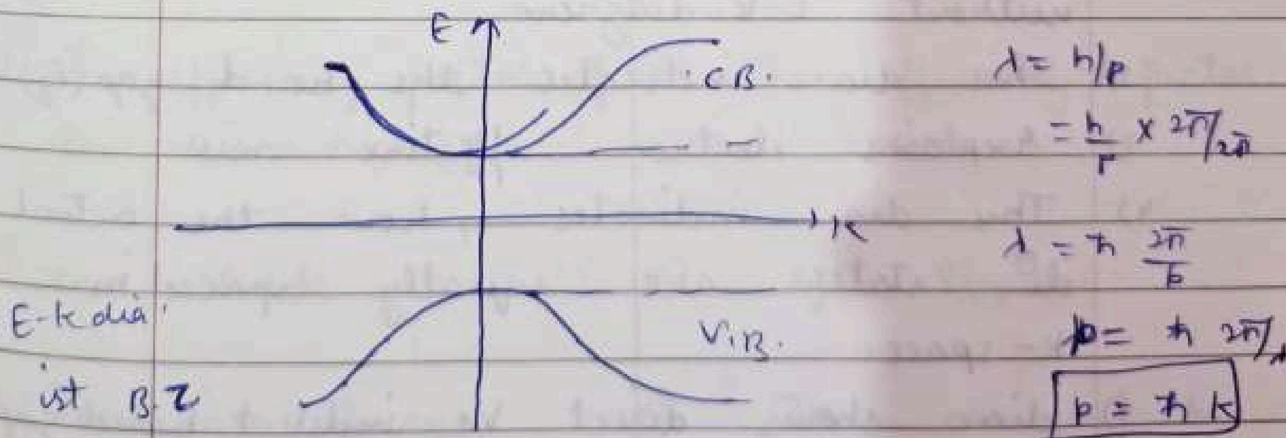


fig. shows electronic motion



$\lambda = h/p$

$= \frac{h}{p} \times 2\pi/2\pi$

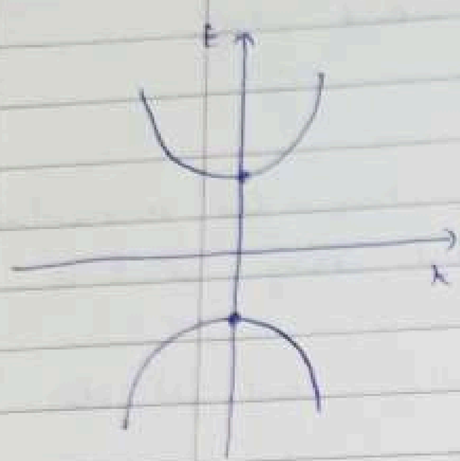
$\lambda = \hbar \frac{2\pi}{p}$

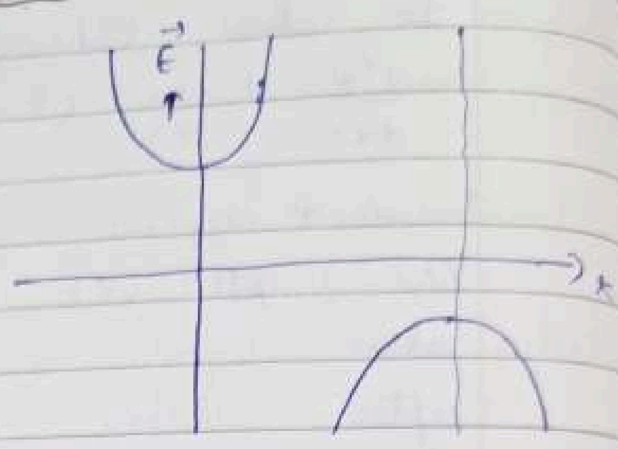
$p = \hbar\, 2\pi/\lambda$

$\boxed{p = \hbar k}$

k = propagation wave vector = $\frac{2\pi}{\lambda}$

⇒ Direct - Indirect Band Gap



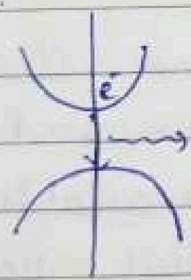
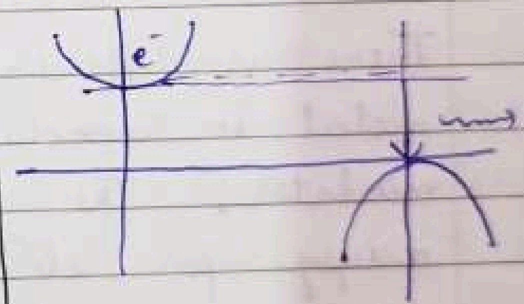


When minima of C.B. & max of V.B. coincides (align) at same value of k, then it is Direct Band Gap.

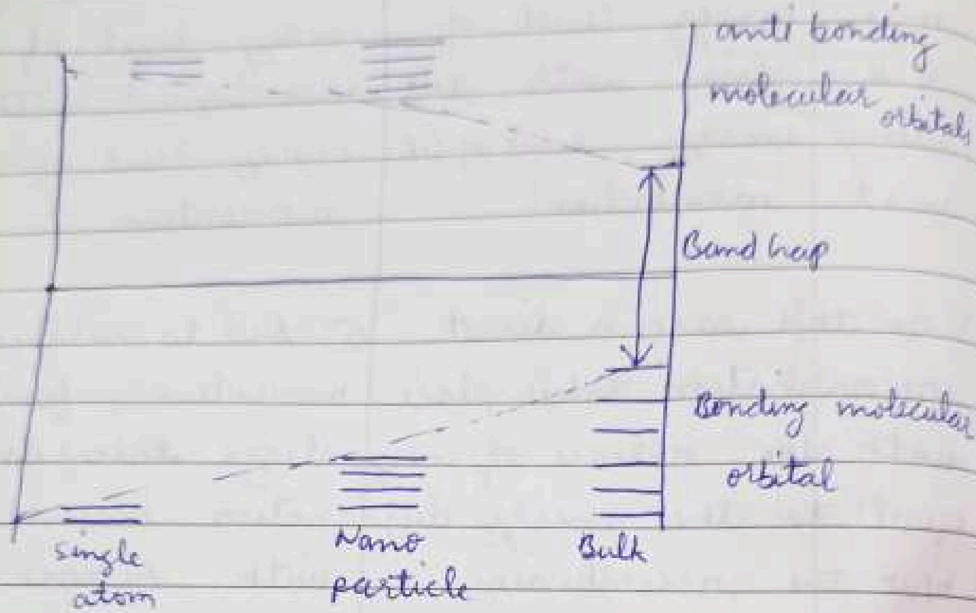
When minima of C.B. & maxima of V.B. are at diff^n value of k, then it is indirect band gap.

Significance :-

1) No theoritical study, experimentation & technological application can take place without E-k diagram.
2) This dia. indicates the band gap (E_g).
3) Explains electron effective mass.
4) This dia. indicates, how the actual ele$^{\ominus}$ states are equally spaced in k-space.
5) dia. shows direct Vs indirect band gap.
6) describle ele$^{\ominus}$ & hole mobility

Direct Band Gap S.C.	Indirect Band Gap S.C.
① A direct band gap S.C. is one in which the max. energy level of V.B. aligns with the min. energy level of C.B. w.r.t momentum.	① A indirect band gap S.C. is one in which the max. energy level of V.B. are misaligned with the min. energy level of C.B. w.r.t momentum.
② In this case, a direct recombination takes place with the release of energy equal to the energy diff. b/w the recombining particles. 	② Due to relative diff. in the momentum, first momenta aligns themselves, a recombi-nation occurs accompanied with release of energy. 
③ The efficiency factor of this is higher.	③ The efficiency factor is lower.
④ eg.- GaAs	④ eg.- Si, Ge
⑤ These are always preffered over indirect band gap for making optical sources.	⑤ They can not be used.

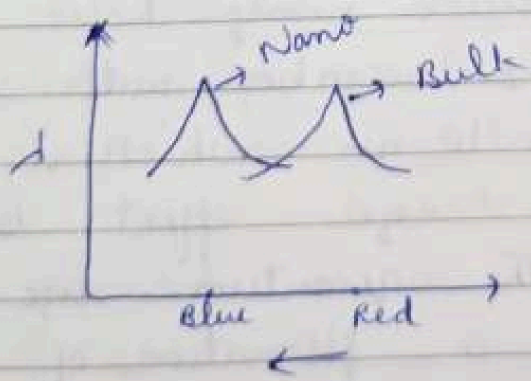
- Variation of Band Gap with size of crystal



There is difference in band structure of metal in conductor, semiconductors & insulators. The region available to occupy for $ele^{\ominus}$ is called Band. The diagram explains the formation of these bands as matter grow from atom or molecule to nanoparticles to bulk matter. In bulk matter band are actually formed by merges of bunch of adjacent energy levels of numerous atoms or molecules. As the particle size gets finer & reaches nanoscale where every particle is made up of finite no. of atoms. The no. of overlapping orbitals or

energy level decreases & width of bands start to narrow. In the extreme case, the single atom or molecule will have very discrete energy level & that can even be represented by a single line. As seen in the diagram the gap b/w C.B & V.B ↑ses as the particle size ↓ses

This explains nano particles have wider band gap then the corresponding bulk matter. Band gap is a region for el⊖. Larger the band gap greater is restriction on the movement of el⊖. Hence, nanoparticles exhibits lower electrical conductivity. There is also shift in absorption spectrum toward low wavelength (λ) i.e.- blue region or ultraviolet region.



Nanosize ZnO and carbon nanotubes can be seen as an example of this concept. Nanosize ZnO have wider band gap & have blue shift in

absorption spectrum. Bulk graphite shows excellent electrical conductivity while as carbon nanotubes show a wider band gap & semiconductor like band width. The energy gap b/w V.B & C.B is of fundamental importance for the properties of solid.

Most of the materials behaviour such as conductivity optical transition or electronic transition depends upon it. Any change of the gap significantly alters the material physics & chemistry.

This occurs when size of the solid is reduced to nanometer length scale. Science of nanometer need to take into account of band gap which is different from bulk.

We consider nanoparticles of metals semiconductor & carbon with size smaller than 10 nm which is a range where size effect become observable. The quantum size effect (QSE) predicts a formation of band gap with decreasing particle size for metals and widening of intrinsic band gap for semiconductors.

Band gap for semiconductor quantum dots is usually well described

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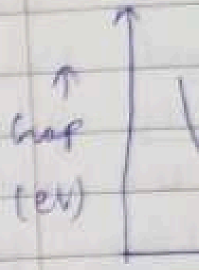
size



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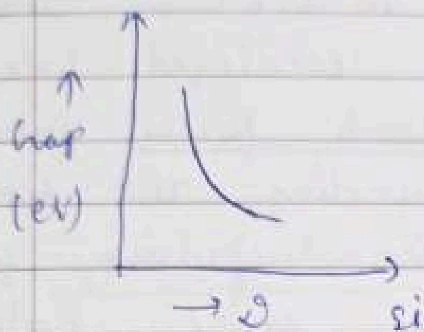
by an extended effective mass approx (EMA). This describe a band gap which gradually ↑se for smaller size particles.

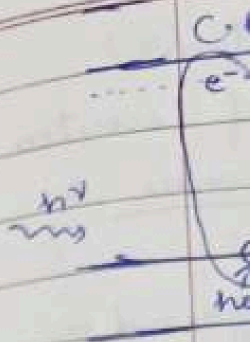


here, dia shows optical band gap energy for Si w.r.t diameter. Electronic properties of material changes drastically as density of states is reduced & by reducing the size of material.

⇒ **exciton**

An exciton is a bound state of an ele⊖ & an ele⊖ hole which are attracted to each other by the electrostatic coulomb force. It is an electrically neutral quasiparticle that exists in insulators, semiconductors & some liquids. The exciton is regarded as an elementary excitation of condensed matter that can transport energy without transporting net electric charge.

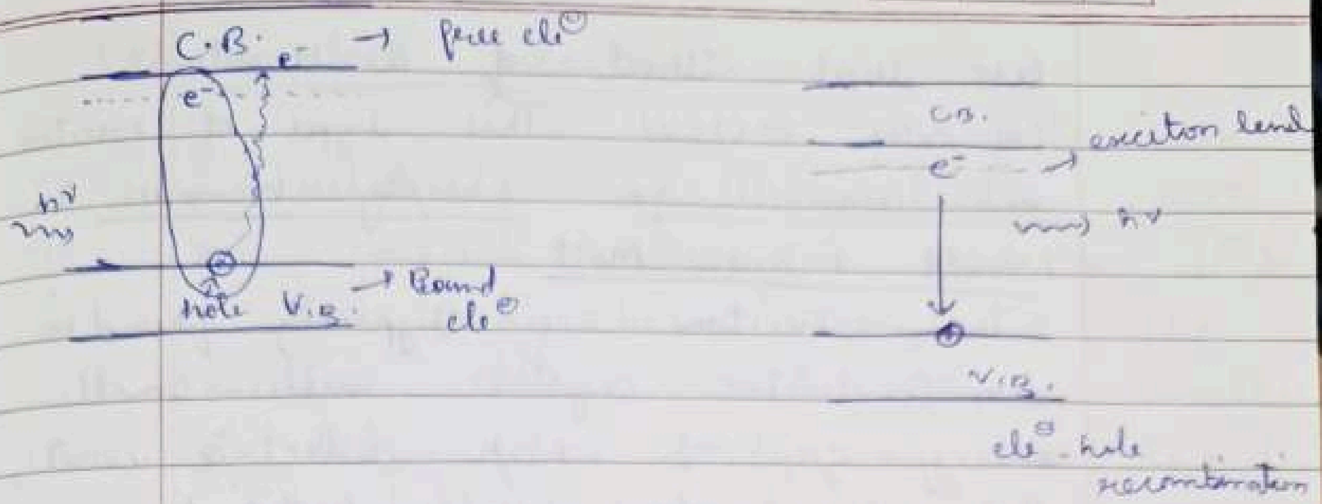
An exciton can form when a material absorbs a photon of higher energy than it's band gap. This



excites an $e^{\ominus}$ from V.B. into C.B. In turn, this leaves behind a +vely charged $e^{\ominus}$ hole (an abstraction for the location from which an $e^{\ominus}$ was moved) The $e^{\ominus}$ in C.B. is then less attracted to this localized hole due to repulsive coulomb forces from large no. of $e^{\ominus}$ surrounding the hole & excited $e^{\ominus}$. These repulsive forces provide a stabilizing energy balance. Consequently, the exciton has slightly less energy than the unbound $e^{\ominus}$ & hole.

Some excitons are intrinsically unstable w.r.t decays into a free $e^{\ominus}$ & free hole. All excitons are unstable against the ultimate recombination process in which the $e^{\ominus}$ drops into the hole.

The $e^{\ominus}$ & hole may have either ‖'el or anti-‖'el spins. The spins are coupled by the exchange interaction, giving rise to exciton fine structure. In periodic lattices, the properties of an exciton show momentum (K-vector) dependence.



Types of exciton

1) Wannier - Mott exciton
11) Frenkel exciton

(1) Wannier - Mott exciton :-

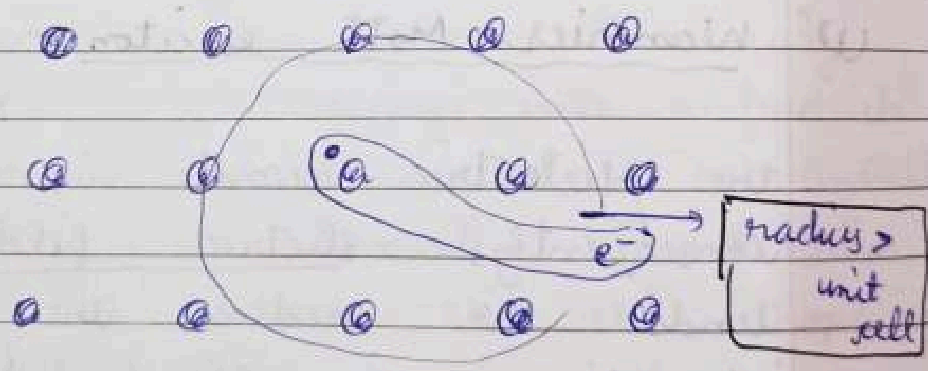
In semiconductor the dielectric const. is generally large. consequently, electric field screening Tends to reduce the coulomb interaction b/w ele & holes. The result is WME, which has radius larger than the lattice spacing.

Small effective mass of ele that is typical of semiconductors also favors large exciton radii. As a result, The effect of the lattice ptl. can be incorporated into the effective masses of ele & hole.

Because of lower masses & the screened coulomb interaction, B.E. is usually much

less that that of a H-atom (of order 0.01eV). This type of exciton was named for Gregory Wannier & Nevill Francis Mott.

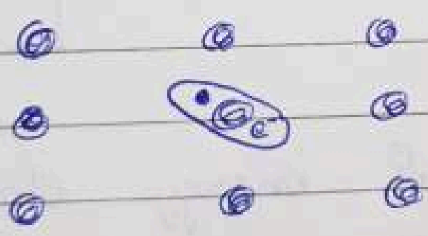
This excitons are typically found in semiconductor crystals with small energy gaps & high dielectric const, but have also been identified in liquids, such as liquid xenon. They are also known as large excitons.



→ Inorganic semiconductor (Si, Ge)
→ B.E less than ≃ 0.01 eV
→ avg ele⊖-hole pair separation is large as compared to lattice const.

(ii) Frenkel exciton :-

In materials with a relatively small dielectric const, the coulomb interaction b/w an e^{-} & a hole may be strong & the excitons thus tend to be small, of the same order as the size of unit cell. Molecular excitons may even be entirely located on the same molecule, as in fullerenes. This Frenkel exciton named after Yakov Frenkel, has a typical B.E. on the order of 0.1 to 1ev.

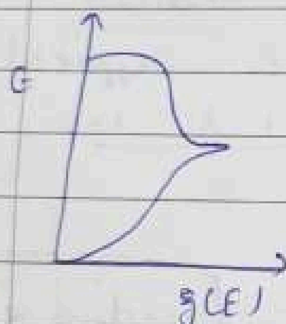


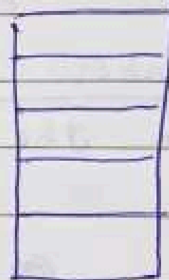
radius < unit cell

→ small exciton
→ bound atom
→ organic semiconductor (hat)

→ Variation of density of states with size of crystal

In a crystalline solid energy & vol. density of electronic state changes across energy bands. Generally a no. of energy levels which corresponds to electronic wave fun^n in the crystal in the central region of the band are very large.





energy band

The no. of $e^{\ominus}$ energy states per unit vol. over the energy interval $E \rightarrow E + dE$ are called density of states and defined as $g(E)\,dE$.
where $g(E)$ = density of states

Thus, no. of states per unit vol. upto some energy E is given as

$$N_v(E) = \int_0^E g(E)\, dE \quad (1)$$

The expression for density of states for a 3D crystal is given as

$$g(E)_{3D} = \frac{1}{2\pi^2}\left(\frac{2m^*}{\hbar^2}\right)^{3/2}(E - E_{pot})^{1/2}$$

where m^* = e^- effective mass in a band.
E_{pot} = ptl energy, which may be conduction band edge or V.B. edge energy E_c or E_v resp.

For 2D structure such as quantum well, the confinement of carriers in 1 dirⁿ results in the formation of quantum states for motion in that dirⁿ. therefore, the density of states for 2D structure is modified & can be expressed as

$$g(E)_{2D} = \frac{m^*}{\pi\hbar^2}\sum_i H(E - E_i)$$

where $H(E-E_i)$ is called heaviside funⁿ. It takes the value of zero when $E < E_i$ & 1 when $E > E_i$

i.e.- $$H(E-E_i) = \begin{cases} 0 & E < E_i \\ 1 & E > E_i \end{cases}$$

E_i = i^{th} energy level within 2D quantum well.

For 1D structure like quantum wire, motion of charge carriers are allowed

only in 1 dirⁿ & other two dirⁿ are quantised. The density of states in 1D given as

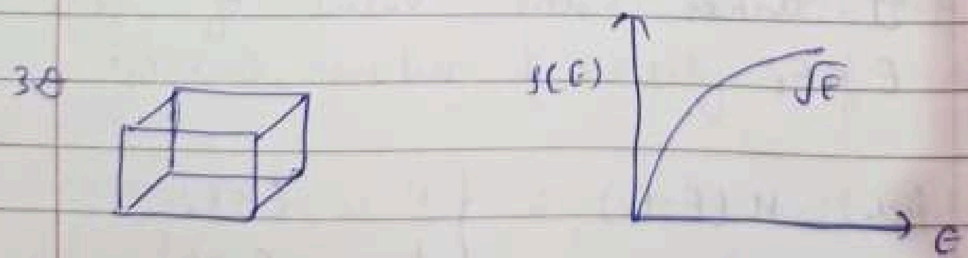
$$g(E)_{1D} = \frac{1}{\pi}\left(\frac{2m^*}{\hbar^2}\right)^{1/2} \sum_i n_i \frac{H(E-E_i)}{(E-E_i)^{1/2}}$$

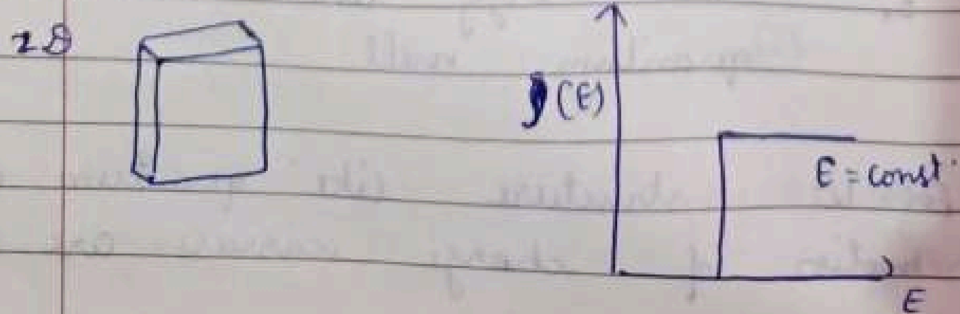
where $H(E-E_i)$ = Heaviside funⁿ
n_i = degeneracy factor

For 0-D structure like quantum dot, all 3 dirⁿ are quantised & expression for density of states is

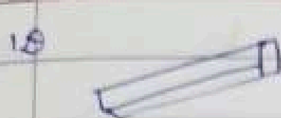
$$g(E)_{0D} = \sum_i 2\,\delta(E-E_i)$$

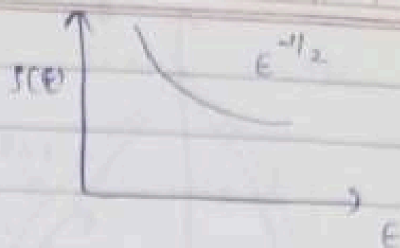
Density of states for 3D, 2D, 1D & 0D for electronic system is given as



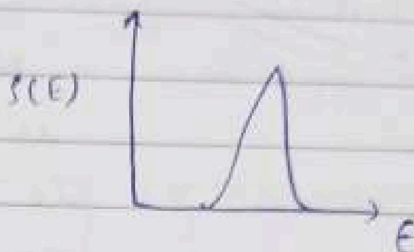


1D





0D



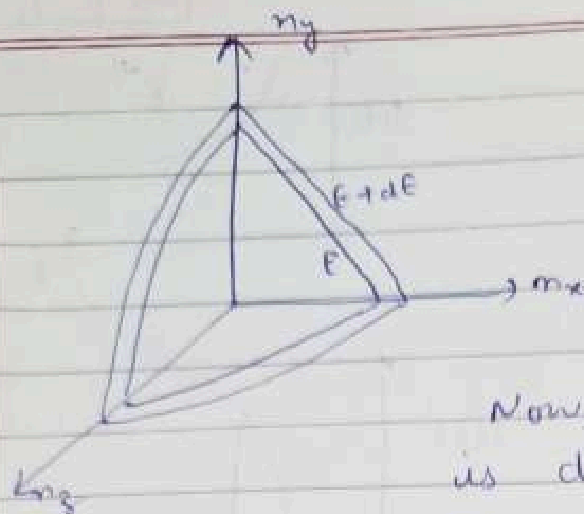
As the size ↓ses from bulk to nanoscale, bandgap ↑ses & density of states ↓ses.

⇒ <u>Variation of D(E) with energy</u>

Total no. of available energy states per unit energy range is called density of energy states ~~Z(E)~~ Z(E) at energy E. No. of energy states with a particular value of E depends upon how many combination of quantum no. results in the same value of n as

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

For this purpose we construct a space of points represented by n_x, n_y & n_z each pt. with integer value of coordinates represent an energy state



Now, radius vector n is draw from origin to a pt n_x, n_y, n_z in space as shown

All points of the sphere with radius n will have same energy. In this space, every integer specifies a state i.e. a unit cube contain exactly one state. Thus the no. of states in any vol. is equal to numerical value of the vol. expressed with units of cube of lattice parameter.

vol. of sphere of radius n is given as

$$V = \frac{4}{3}\pi n^3$$

since value of n_x, n_y & n_z are restricted to be +ve. All energy states will be in the octant of sphere i.e $\frac{1}{8th}$ of vol. of sphere.

So, no of available states within sphere is equal to $\frac{1}{8}\left(\frac{4}{3}\pi n^3\right)$

||'ly, no. of energy states with sphere of radius $(n+dn)$ is given as

$$= \frac{1}{8}\left[\frac{4}{3}\pi (n+dn)^3\right]$$

The no. of energy states within E & E + dE i.e. in energy interval dE is given as

$$Z(E)\,dE = \frac{1}{8}\left[\frac{4}{3}\pi (n+dn)^3\right] - \frac{1}{8}\left(\frac{4}{3}\pi n^3\right)$$

$$= \frac{\pi}{6}\left[(n+dn)^3 - n^3\right]$$

$$= \frac{\pi}{6}\left[n^3 + dn^3 + 3n^2 dn + 3n dn^2 - n^3\right]$$

$$Z(E)\,dE = \frac{\pi}{6}\left[dn^3 + 3n^2\,dn + 3n\,dn^2\right]$$

Since, dn is small $\rightarrow dn^2$ & dn^3 neglected

$$Z(E)\,dE = \frac{\pi}{6}(3n^2 dn) = \frac{\pi}{2} n^2 dn$$

$$\boxed{Z(E)\,dE = \frac{\pi}{2} n(n\,dn)} \quad -(1)$$

we know $E = \frac{n^2 h^2}{8mL^2}$, $n^2 = \frac{8mL^2 E}{h^2}$ (2)

$$\therefore n = \frac{2\sqrt{2}L}{h}(mE)^{1/2} \quad (3)$$

on diff (ii) $2n\,dn = \frac{8mL^2}{h^2} dE$

$$\boxed{dn = \frac{4mL^2}{n h^2} dE} \quad (4)$$

Put value of n & dn, we get

$$Z(E)\,dE = \frac{\pi}{2}\frac{2\sqrt{2}L(mE)^{1/2}}{h} \times \frac{4mL^2}{h^2}dE$$

$$Z(E)\,dE = \frac{\sqrt{2}\,4\pi\, m^{3/2}L^3}{h^3}E^{1/2}\,dE$$

$$Z(E)\,dE = \frac{\pi}{4}\left(\frac{8mL^2}{h^2}\right)^{3/2}E^{1/2}\,dE \quad (5)$$

Pauli's exclusion principle permits 2 e^- in each state.

∴ no. of energy levels actually available are

$$Z(E)\,dE = \frac{\pi}{2}\left(\frac{8mL^2}{h^2}\right)^{3/2}E^{1/2}\,dE \quad (6)$$

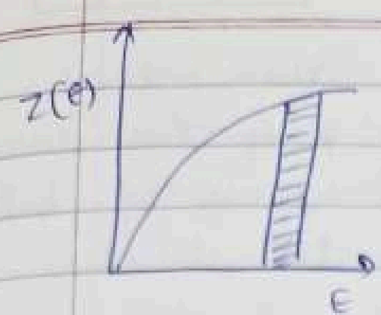
Thus, no. of energy states ↑ses as a funⁿ of energy. Also energy states ↑ses with ↑ses in crystal vol.

$$Z(E)\,dE = \frac{\pi}{2}\left(\frac{8m}{h^2}\right)^{3/2}L^3E^{1/2}\,dE \quad (7)$$

as $L^3 = V$

$$\frac{Z(E)\,dE}{\text{vol.}} = \frac{\pi}{2}\left(\frac{8m}{h^2}\right)^{3/2}E^{1/2}\,dE \quad (8)$$

$L^2 dE$



Thus, no of energy states present in unit vol. having energy value laying b/w energy E & $E + dE$ called energy density of energy states is obtained by putting $L^3 = V = 1$ & given by eqⁿ (8).

(5)

⇒ <u>Electronic structure from bulk to quantum dot</u>

2 dE

In small nanocrystals (i.e.- nanomaterials), the electronic energy levels are not continuous as in the bulk but are discrete, because of the confinement of the electronic wave funⁿ to the physical dimensions of the particles. This phenomena is called quantum confinement & therefore nanocrystals are also referred to as quantum dots.

(6)

For a semiconductor particle, quantum confinement occurs when the nano-crystal radius become comparable to the exciton Bohr radius. The <u>confinement leads to a transition from continuous to discrete energy levels</u>. When materials are so small that they lie in the quantum

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states
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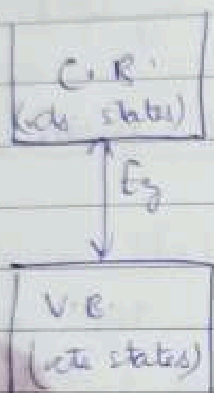
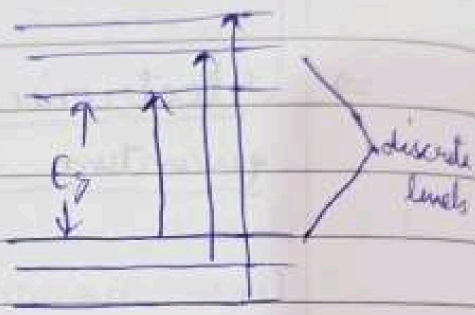
confinement regime, then their electronic & optical properties deviate substantially from those of bulk materials. The discrete structure of energy states leads to a discrete absorption spectrum from a nanostructure.



Bulk



Nanostructure
(quantum dot)

A quantum confined structure is one in which the motion of the e^- & holes are confined in one or more dirⁿ by ptl. barriers. If the charge carriers are confined along one dirⁿ & delocalized (i.e. free) in other two dirⁿ, then the resultant structure is a quantum well. When the confinement occurs in 2D & the carriers are delocalized in the remaining 3rd dirⁿ, then the resultant structure is a quantum wire or nanowire. A quantum dot may have shape of a

tiny cube, a short cylinder or a sphere with nanometer dimensions & exhibits confinement in all three dir^n. There is no ~~delocalized~~ delocalization in this case.

eg.-

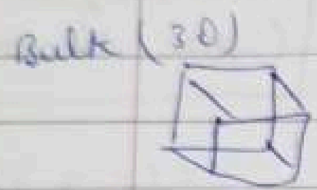
Quantum structure	Confinement dimensions	Delocalization (free dimensions)
01. Bulk conductor	0	3 (x, y, 3)
02. Quantum well/ Superlattices	1 (3)	2 (x, y)
03. Quantum wire	2 (x, y)	1 (3)
04. Quantum dot/ Nanocrystals	3 (x, y, 3)	0

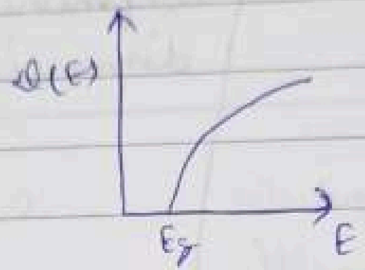
As more no. of dimensions is confined, more discrete energy levels can be found i.e.- carrier movement is strongly confined in a given dimension.

Nanostructure	Representation
Quantum well	particle in 1D box
Quantum wire	particle in 2D box
quantum dot	particle in 3D box

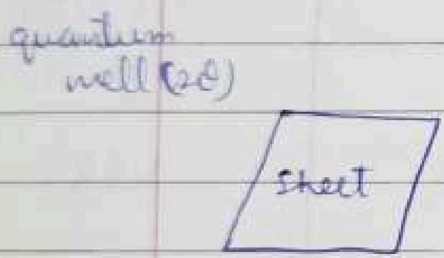
The density of states D(E) determines the various electronic & other properties. Thus, the nature of the dimensionality & of the confinement associated with a particular nanostructure have a noticeable effect on it's properties

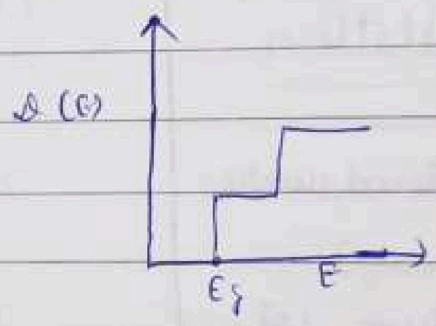
Bulk (3D)



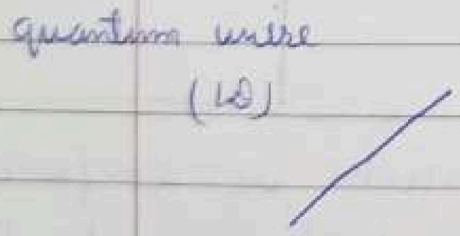


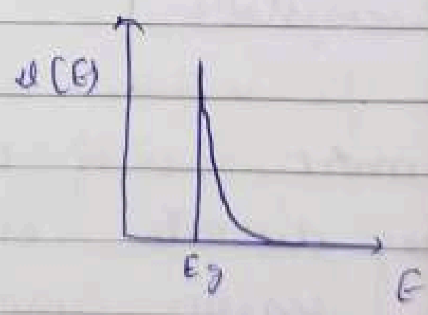
quantum well (2D)



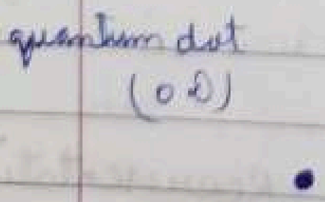


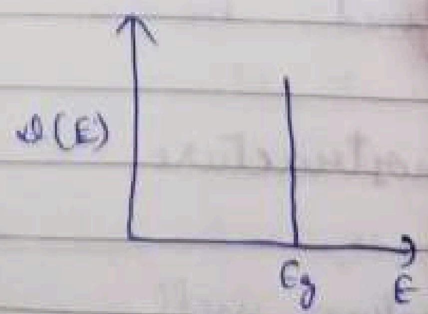
quantum wire (1D)





quantum dot (0D)





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⇒ Electronic states in Direct & Indirect Semiconductor Nanocrystal

When quantitative calculations are made of band structures, a single ele$^{\ominus}$ is assumed to travel through a perfectly periodic lattice. The wave fun^n of the ele$^{\ominus}$ is assumed to be in the form of a plane wave moving, eg:- in x dir^n with propagation const K, also called a wave vector. The space dependent wave fun^n for the ele$^{\ominus}$ is

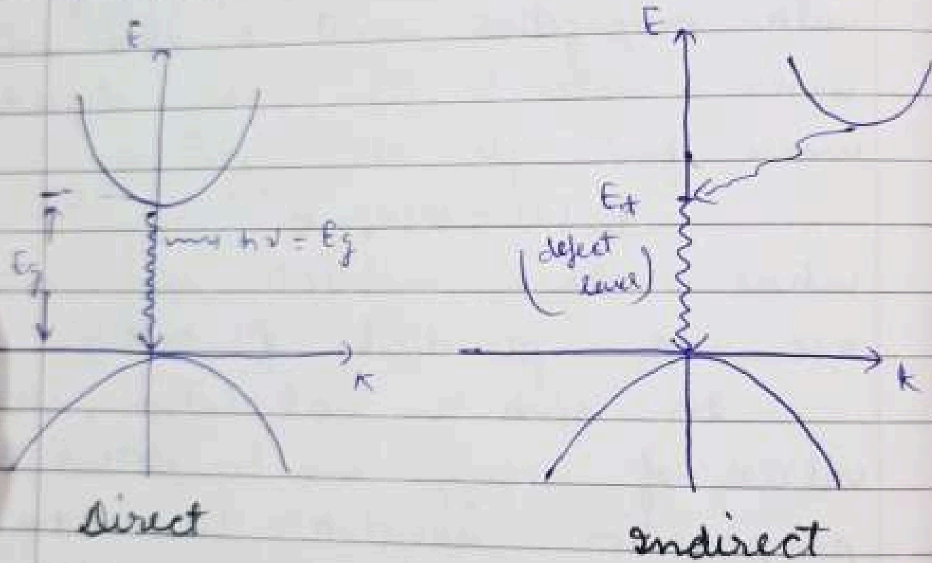
$$\psi_K(x) = U(K_x, x)\, e^{iK_x x}$$

where $U(K_x, x)$ modulates the wave fun^n acc. to periodicity of lattice.

In such a calculation, allowed values of energy can be plotted Vs the propagation const K. Since the periodicity of most lattices is different in various dir^n. The E-K dia. must be plotted for various crystal dir^n & the full relationship b/w E & K is a complex surface which should be visualized in 3D.

The band structure of GaAs has a min. in C.B. & max. in V.B. for the same K value (K=0). On the other hand, Si has it's V.B. max at a diff^n value of K than it's C.B. min.

Thus an $e^{\ominus}$ making a smallest energy transition from C.B to V.B in GaAs can do so without a change in k value on the other hand, a transition from min pt. in Si C.B to max pt. of V.B. requires some change in k. Thus, there are two classes of semiconductor energy bands :- direct & indirect



Direct Indirect

In a direct semiconductor such as GaAs, an $e^{\ominus}$ in the C.B. can fall to an empty state in V.B., giving off the energy difference Eg as a photon of light.

On the other hand, an $e^{\ominus}$ in C.B. min. of an indirect semiconductor such as Si cannot fall directly to V.B. max but must undergo a momentum change as well as changing

its ene... which ... energy ... to ... emitted ... is inclu... ... can be ... output ... emitte... made ... band - ... materia... defect

its energy. In an indirect transition which involves a change in k, the energy is generally given up as heat to the lattice rather than as an emitted photon. This diff. b/w direct & indirect band structure is very imp for deciding which semiconductor can be used in devices requiring light output. eg:- semiconductor light emitters & lasers generally must be made of materials capable of direct band-to-band transitions or of indirect materials with vertical transitions b/w defect states.

Test

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(8) (1) Define density of states and study the variation of it with energy & band gap of crystal.

Ans:- The density of states gives the no. of allowed electronic (or holes) states per unit vol. at a given energy level
OR The total no. of available electronic states per unit energy interval is known as density of states.
It is denoted by $g(E)$ & given as

$$g(E) = \frac{dn}{dE} \quad -(1)$$

where dn = no. of electronic state present in energy range E to $E + dE$

Acc. to free $e^{\ominus}$ theory of metals, each energy level contains two electronic states, one with up spin & other with down spin.

$\therefore \quad g(E) = 2 \times \frac{dn}{dE} \quad -(2)$

$\because \quad E = \frac{\hbar^2}{2m}\left(\frac{n\pi}{L}\right)^2 \quad (3)$

$\therefore \quad \frac{dE}{dn} = \frac{\hbar^2}{2m} 2n\frac{\pi}{L} \cdot \frac{\pi}{L} = \frac{n\pi^2\hbar^2}{mL^2}$

$\because \hbar = \frac{h}{2\pi}$

$\therefore \quad \frac{dE}{dn} = \frac{n\pi^2 h^2}{4\pi^2 mL^2}$

$$\boxed{\frac{dE}{dn} = \frac{nh^2}{4mL^2}} \Rightarrow \frac{dn}{dE} = \frac{4mL^2}{nh^2}$$

Put in (i)

$$\therefore g(E) = 2 \times \frac{4mL^2}{nh^2} = \frac{8mL^2}{nh^2}$$

$$g(E) = \frac{8mL^2}{h^2} \times \frac{1}{n} \quad \text{—(*)}$$

from (i) we have

$$E = \frac{\hbar^2}{2m}\left(\frac{n\pi}{L}\right)^2 = \frac{n^2\pi^2}{L^2}\frac{h^2}{4\pi^2 \times 2}$$

$$E = \frac{n^2h^2}{8mL^2} \Rightarrow n^2 = \frac{8mL^2E}{h^2}$$

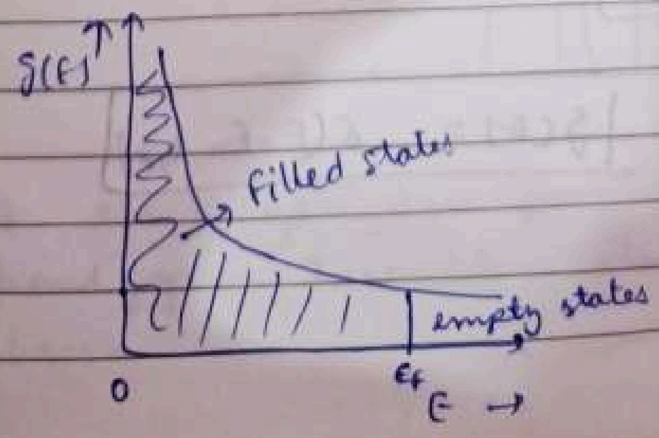
$$n^2 = \frac{8mEL^2}{h^2} \Rightarrow \frac{1}{n^2} = \frac{h^2}{8mL^2E}$$

$$\frac{1}{n} = \left(\frac{h^2}{8mL^2E}\right)^{1/2} \quad \text{Put in (*)}$$

$$\therefore g(E) = \frac{8mL^2}{h^2} \times \frac{h}{(8mE)^{1/2} L}$$

$$g(E) = \sqrt{8m}\,\frac{L}{h\sqrt{E}} = \frac{4L}{h}\sqrt{\frac{m}{2E}}$$

i.e.- $\boxed{g(E) \propto \frac{1}{\sqrt{E}}}$



above dia shows the variation of $g(E)$ with energy E & indicates that all energy levels upto E_f are filled with e^{-}.

→ The expression for density of states for a 3D crystal is given as

$$g(E) = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}(E)^{1/2}$$

For 2D

$$g(E) = \frac{m}{\pi\hbar^2}\sum_n \Theta(E-E_n)$$

where Θ is Heaviside fcn^n

i.e:-

$$\Theta(E-E_n) = \begin{cases} 0 & \text{for } E < E_n \\ 1 & \text{for } E > E_n \end{cases}$$

For 1D

$$g(E) = \sqrt{\frac{2m}{\pi^2\hbar^2}}\sum_{n,l}\frac{1}{\sqrt{E-E_{n,l}}}\Theta(E-E_{nl})$$

For 0D

$$g(E) = \delta(E-E_{n,l,p})$$

Density for

3D

2D

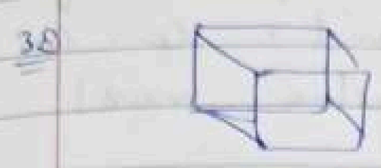
1D

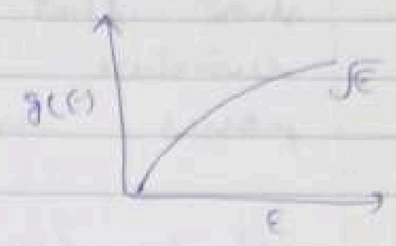
0D

i.e. v

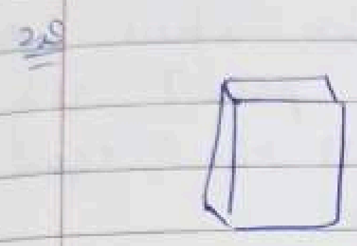
Density of states for 3D, 2D, 1D & 0D for electronic states is given as

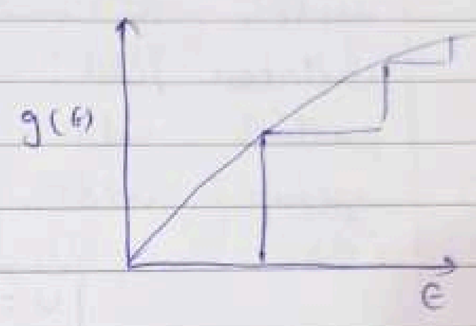
3D



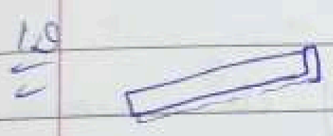


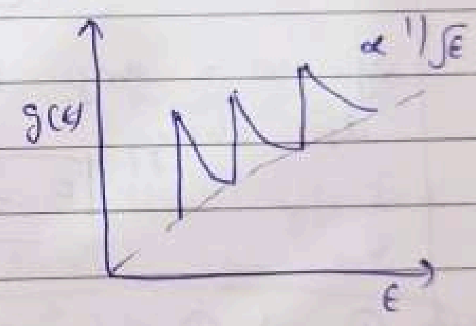
2D



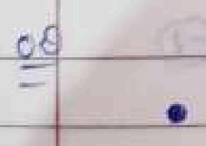


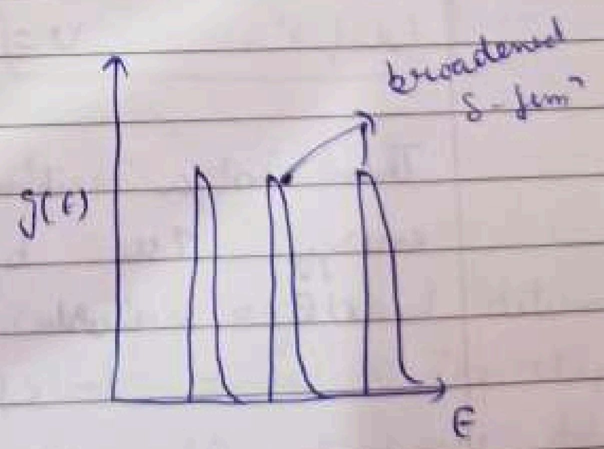
1D





0D





i.e. As the size ↓ses from bulk to nanoscale band gap ↑ses & density of states ↓ses.

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8

(7) what is effective mass of particle in crystal ? obtain expression for it & show that it depends upon curvature of band. Can an e⁻ posses -ve effective mass?

Ans Let us consider an e⁻ with wave vector K in region where external electric field E is present. It's particle velo v will be equal to group velo $d\omega/dk$

i.e.-

$$\boxed{v = \frac{d\omega}{dK}} \quad (1)$$

If ω = ang. freq. of e⁻ waves, its energy

$$\boxed{E = \hbar\omega} \quad (2)$$

from (1) & (2)

$$v = \frac{1}{\hbar}\frac{dE}{dK} \quad (3)$$

Then in a time interval dt, e⁻ energy ↑ses by

dE = work done by electric force

$= (-eE)\,dx = -eE\,v\,dt \quad (4)$

where dx = displacement of e⁻ during time dt

$$\therefore \quad dE = \frac{-eE}{\hbar}\left(\frac{dE}{dk}\right)dt$$

$$\therefore \quad \hbar\frac{dk}{dt} = \frac{d(\hbar k)}{dt} = \frac{dP}{dt} = -eE \quad (5)$$

diff. (3)

$$\frac{dv}{dt} = \frac{1}{\hbar}\frac{d}{dt}\left(\frac{dE}{dk}\right) = \frac{1}{\hbar}\frac{d^2E}{dk^2}\frac{dk}{dt}$$

$$= \frac{-eE}{\hbar^2}\left(\frac{d^2E}{dk^2}\right)$$

eq^n (5) ⇒

$$-eE = \left(\frac{\hbar^2}{d^2E/dk^2}\right)\frac{dv}{dt} \quad (6)$$

This eq^n is of type

Force = mass × acc^n

It is known as the effective mass of e^- & denoted by m^*

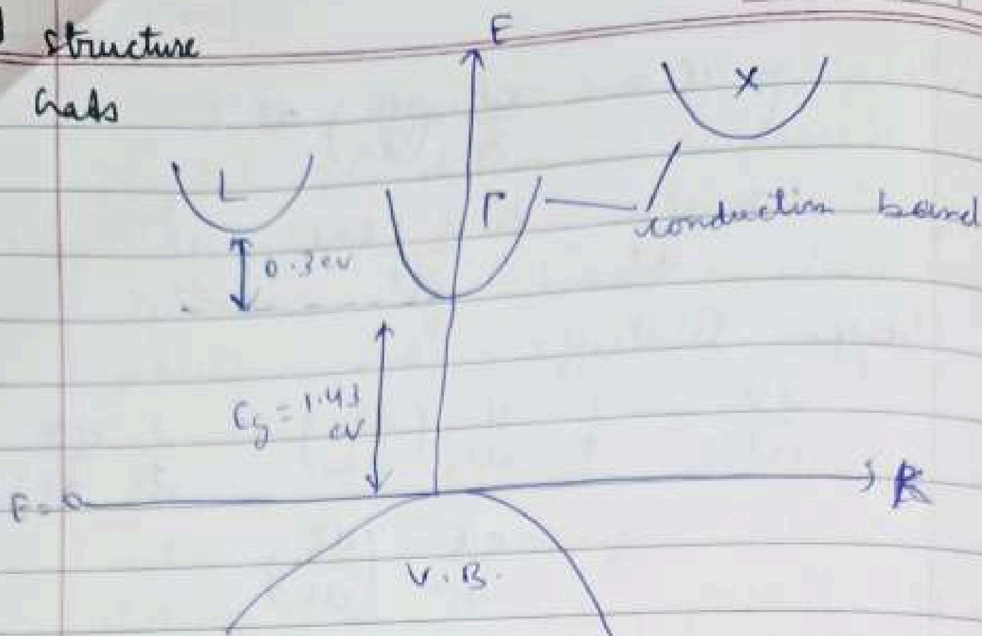
i.e.-

$$\boxed{m^* = \frac{\hbar^2}{d^2E/dk^2}} \quad (7)$$

$$\frac{d^2E}{dk^2} = \text{curvature of band}$$

Hence, the curvature of band determines the e^- effective mass. The slope of energy bands in 3D k-space determines the value of effective mass.

Band structure of GaAs



For a band structure at $K=0$, E-K dispersion relⁿ near the min. is usually parabolic & given by

$$E = \frac{\hbar^2 k^2}{2m^*} + E_g \quad -⑧$$

||'rly for free e⁻

$$E = \frac{\hbar^2 k^2}{2m} \Rightarrow \frac{d^2E}{dk^2} = \frac{\hbar^2}{m}$$

$$\therefore m^* = \frac{\hbar^2}{d^2E/dk^2} = m$$

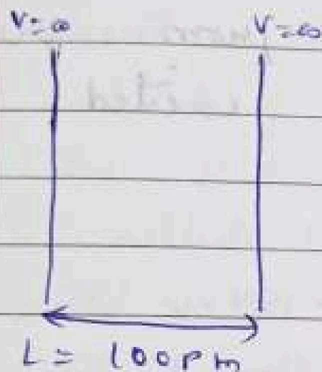
For free e⁻, the effective mass is equal to it's actual mass.

From dia. the curvature d^2E/dk^2 is +ve at C.B. minima but it is -ve at V.B. max. Thus, e⁻ ~~near~~ near

C.B. minima have +ve value of effective mass whereas near top of V.B. have -ve value of effective mass

③ An ele$^{\ominus}$ confined in 1D infinite deep ptl. energy wall of width of l = 100 pm.

(i) what is smallest amt of energy that ele$^{\ominus}$ have?



$\because$ $E_n = \frac{n^2h^2}{8mL^2}$

$\because$ smallest energy → ground state ⇓ $n=1$

$\therefore$ $E = \frac{1^2h^2}{8mL^2} = \frac{h^2}{8mL^2}$

$E = \frac{(6.67\times10^{-34})^2}{8\times9.1\times10^{-31}\times(100\times10^{-12})^2}$ $\because 1pm = 10^{-12}m$

$E = \frac{44.4889\times10^{-68}}{72.8\times10^{-31}\times10^{4}\times10^{-24}}$

$E = \frac{44.4889\times10^{-68}}{72.8\times10^{-51}} = \frac{44.4889\times10^{-68+51}}{72.8}$

$E = \frac{44.4889\times10^{-17}}{72.8} = 0.61111126\times10^{-17}$

$= 6.111\times10^{-18}$ J

$\because$ 1 eV = 1.6×10^{-19} J

$\therefore$ energy in eV = $\frac{6.111 \times 10^{-18}}{1.6 \times 10^{-19}}$

$E = 3.8194 \times 10^{1}$

$\boxed{E = 38.194 \text{ eV}}$ Ans

(ii) How much energy is transferred to e^{-} if it is to make a quantum jump from ground state to second excited state.

For ground state $n = 1$

$E_1 = 38.194$ eV

2nd excited state $\Rightarrow n = 3$

$$E_3 = \frac{n^2 h^2}{8mL^2} = \frac{9 \times 44.4889 \times 10^{-68}}{72.8 \times 10^{-51}}$$

$$E_3 = \frac{400.4001 \times 10^{-68+51}}{72.8}$$

$$E_3 = 5.500 \times 10^{-17} = 55.0 \times 10^{-18} \text{ J}$$

$$E_3 = \frac{55 \times 10^{-18}}{1.6 \times 10^{-19}} = 34.375 \times 10^{1}$$

$\boxed{E_3 = 343.75 \text{ eV}}$

$\therefore$ energy transferred to e^{-} = $E_3 - E_1$

$= 343.75 - 38.194$

$= 305.556$ eV Ans

(8)

(5) assumptions of classical free $ele^{\ominus}$ theory of Drude - Lorentz free theory. explains complete opacity & high lustre on basis of this theory. what are failure of this theory.

→ Assumptions:

(1) The valence $ele^{\ominus}$ of atoms are free to move about the whole vol. of metal like molecule of a perfect gas in container.
(2) The free $ele^{\ominus}$ move in random dir^n & collide with either +ve ions fixed to lattice or other free $ele^{\ominus}$. All collisions are elastic in nature i.e.- there is no loss of energy.
(3) The mom. of free $ele^{\ominus}$ obeys laws of classical kinetic theory of gases.
(4) The $ele^{\ominus}$ velo in metal obey classical MB distribution of velo.
(5) when electric field is applied to metal free $ele^{\ominus}$ are acc^n in opp. dir^n to the dir^n of applied electric field.
(6) The mutual repulsion among $ele^{\ominus}$ is ignored so that they move in all dir^n with all possible velo.
(7) In absence of field, energy associ-ated with an $ele^{\ominus}$ at temp. T

is given by $\frac{3}{2}KT$.
It is related to K.E eqn

$$\frac{3}{2}KT = \frac{1}{2}mv_{TH}^2$$

V_{TH} = thermal velo.

Success of classical free e^- Theory

1. verifies ohm's law
2. It explains electrical conductivity of metals
3. It explains thermal conductivity of metals
4. It derives Franz law (relation b/w electrical conductivity & thermal conductivity.
5. also explain optical prop. of metals (opacity of metals)

Drawbacks / Failures

1. It could not explain photoelectric effect, compton effect & black body radiation
2. Electrical conductivity of semiconductor & insulators could not be explained.
3. ferromagnetism could not be explain.
4. Wiedemann Franz law is not valid at low temp.
5. It can not explain superconductivity.

⑥ ...
$\frac{3}{2}$

(6) Acc. to classical free e^{-} theory the electronic specific heat is equal to $\frac{3}{2}R$ while actual value is $0.01R$

Unit = 02

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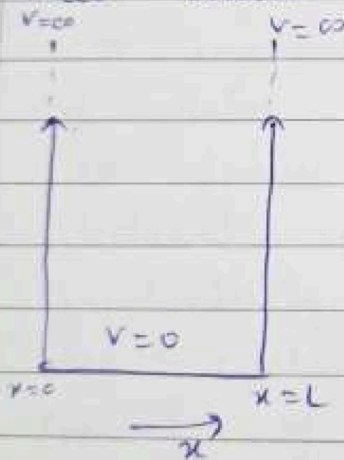
Electron confinement in 1-D infinitely deep square well potentials

Let us now discuss the problem of Q.C along one dirⁿ. It is same as the problem of particle in 1D box. In a quantum well (2D structure), particles are confined to a thin sheet of thickness L along x-dirⁿ by infinite ptl barriers, which create a quantum well shown below



In real systems, this confinement is due to electrostatic ptl. (generated by external electrodes, doping, strain, impurities etc) the presence of interfaces b/w diffⁿ materials; the presence of surfaces; or a combination of these agents. The ptl. funⁿ is

$$V(x) = \begin{cases} 0 & \text{for } 0<x<L \\ \infty & \text{for } x \leq 0 \;\&\; x \geq L \end{cases} \quad (1)$$

The ele$^{\ominus}$ is confined to remain always within the ptl. box & wave funⁿ ψ of the ele$^{\ominus}$ corresponding to energy E is determined from S.W.E as

or ele$^{\ominus}$ wave... structure (...

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(1)

$x \geq L$

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→ Eleⁿ wave funⁿ & energy in Quantum well structure (infinite well approximation)

$$\frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2}\psi = 0 \quad (2)$$

where E = K.E of eleⁿ

The general solⁿ of above eqⁿ is

$$\psi(x) = A\sin Kx + B\cos Kx \quad (3)$$

where A & B are const. to be determined from the boundary condition and

$$K = \sqrt{2mE/\hbar^2} \quad (4)$$

Boundary conditions are (due to continuity of ψ)

$\psi = 0$ at $x = 0$ & $\psi = 0$ at $x = L$ (5)

∴ Putting $\psi(x) = 0$ when $x = 0$ in (3)

$$\psi(0) = B \Rightarrow \boxed{B = 0} \quad (6)$$

Now, use $\psi(x = L) = 0$

(3) ⇒ $\psi(L) = A\sin K.L = 0$

$A \neq 0$ (otherwise $\psi(x) = 0 \; \forall \; x$)

hence, $\sin KL = 0 \Rightarrow \sin KL = \sin n\pi$

$$\Rightarrow \boxed{K = \frac{n\pi}{L}} \quad (7)$$

where $n = 1, 2, 3, \ldots$

∴ (3) for the allowed wave funⁿ becomes

$$\psi_n(x) = A\sin\left(\frac{n\pi}{L}\right)x \quad (8)$$

Evaluate A

normalize wave funⁿ $\psi_n(x)$ for which

$$\int_0^L \psi_n^*(x)\, \psi_n(x)\, dx = 1$$

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

using $\sin^2\theta = \frac{1-\cos 2\theta}{2}$

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

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

(second term = 0)

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

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

Put in ⑧

$$\therefore \boxed{\psi_n(x) = \sqrt{\frac{2}{L}} \sin\frac{n\pi x}{L}} \quad (9)$$

The allowed energy values or eigen values can be obtained from ④ & ⑦

$$k = \frac{n\pi}{L} = \sqrt{2mE/\hbar^2} \Rightarrow \frac{2mE}{\hbar^2} = \frac{n^2\pi^2}{L^2}$$

or

$$\boxed{E_n = E = \frac{n^2\pi^2\hbar^2}{2mL^2}} \quad (10)$$

are the discrete energy states of the particle within quantum region. However, outside the well region particle energies are continuous. Here, n = principal quantum no.

$$\therefore E_{n+1} - E_n = \frac{[(n+1)^2 - n^2]\pi^2 \hbar^2}{2mL^2}$$

$$= \frac{(n^2 + 1 + 2n - n^2)\pi^2 \hbar^2}{2mL^2}$$

$$E_{n+1} - E_n = \frac{(2n+1)\pi^2 \hbar^2}{2mL^2}$$

$$\boxed{E_{n+1} - E_n \propto \frac{1}{L^2}} \quad \& \quad \boxed{E_{n+1} - E_n \propto (2n+1)}$$

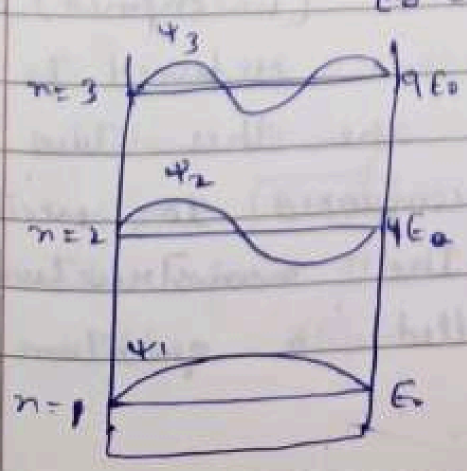
As the dimension (= L) of the energy well ↑ses, the spacing b/w discrete energy levels ↓ses. In the infinite crystal (i.e. bulk) a cts. occur.

* Above analysis shows that confinement of particle motion leads to discreteness or quantization of particle energies. The spacing b/w energy levels ↑ses principal quantum no. n ↑ses.

Zero Point energy

The lowest energy (for $n=1$) in the above case is

$$E_0 = \frac{\pi^2 \hbar^2}{2mL^2} \neq 0$$



The energy E_0 is called the zero pt energy or confinement energy. Its origin lies in the Heisenberg's uncertainty principle.

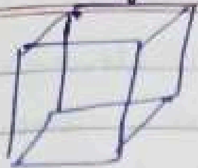
Since, the particle is constrained within a finite region, the variability in its position has an upper bond i.e. uncertainty in its position is finite whose max. value can be L.

∴ uncertainty in particle's momentum can not be zero, the particle must contain some energy in this lowest state. The zero-pt energy ↑ses with ↓ses in the width of the well.

⇒ Quantum well structure

It is a 2-D nanostructure in which there is confinement along one dir^n & particle is free to move in other 2 dir^n (i.e. in a plane). Particle possess discrete (or quantized) energies associated with the confinement dimensions. Particle energies are its along the other two (unconfined) dimensions. If one dimension is reduced to the nanorange while the other two dimensions remain large compared to exciton Bohr radius, then the nanostructure so obtained is called a quantum well.

Rectangular Nanostructure



Bulk material (3D)

well (2D)

Optical absorption in Quantum well

The quantum well looks like an artificial model but has little application in the real world. Although an infinitely deep well cannot be made, it is simple now a days to grow structure that are close to ideal finite wells but in practice the infinitely deep well is often used as an approximation bcz it's results are so simple.

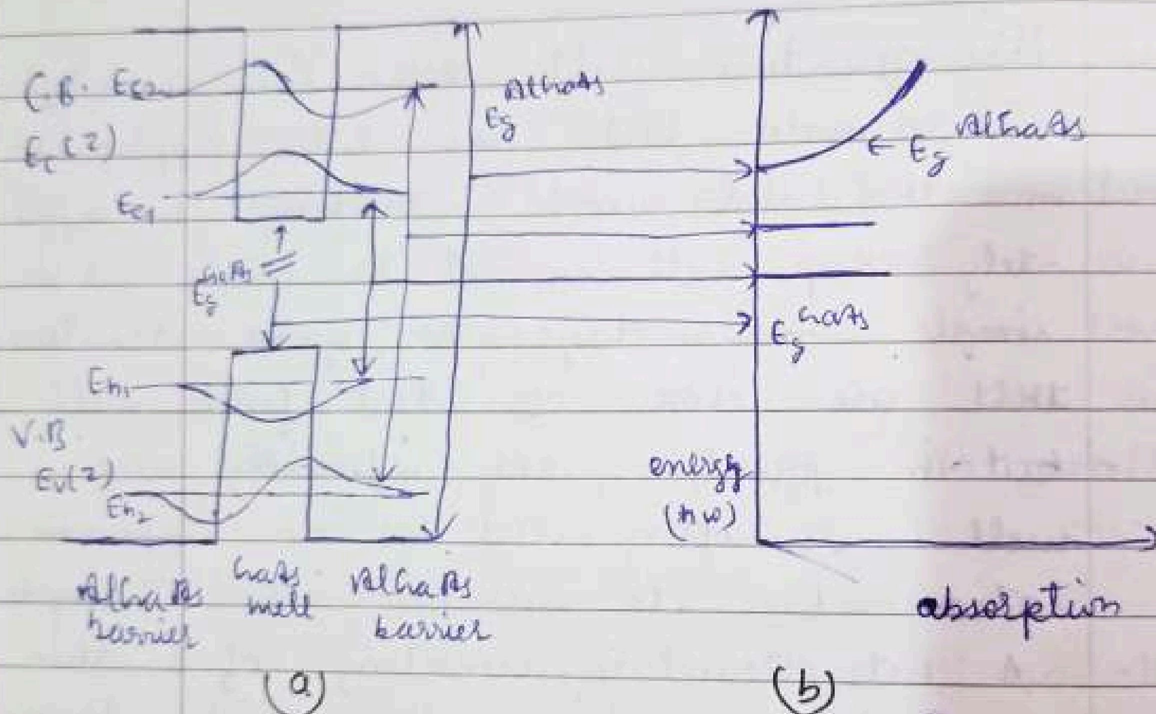
A heterostructure consisting of a thin sandwich of GaAs b/w thick layers of AlGaAs provides a simple quantum well shown below (AlGaAs really means an alloy such as $Al_{0.3}Ga_{0.7}As$, but the abbrevation is universal).

Free $e^{\ominus}$ have energy $$E_0(k) = \frac{\hbar^2 k^2}{2m}$$

$e^{\ominus}$ in a semiconductor live in C.B., which changes their energy in two ways. **First**, energy must be measured from the bottom of the band E_c rather than from zero.

Second. $ele^{\ominus}$ behaves as though their mass is $m_0 m_e$ where the effective mass $m_e = 0.067$ in GaAs

$$\therefore \boxed{E_c(k) = E_c + \frac{\hbar^2 k^2}{2 m_0 m_e}}$$



The sandwich acts like a quantum well because E_c is higher in AlGaAs than in GaAs & the diff. ΔE_c provide the barrier that confines the $ele^{\ominus}$. Typically, $E_c \simeq 0.2 - 0.3\,eV$ viz not large. However we shall approx. it as infinite to find the energy levels in a well of width 'a'.

&

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2ma^2}$$ shows that

the energy of bound states, labelled with n_e is

$$E_{c,n_e} = E_c^{GaAs} + \frac{n_e^2 \pi^2 \hbar^2}{2 m_0 m_e a^2}$$

we could measure these energy levels by shining light on the sample & determining which freq. were absorbed. A photon is absorbed by exciting an e^- from a lower level to a higher one. & the energy of photons matches the diff. in electronic energy levels. We might therefore hope to see absorption at a freq. given by

$\hbar\omega = E_{C2} - E_{C1}$.

Unfortunately, this is difficult expt. & a different technique is usually used. Semiconductors have energy levels in other bands. The most imp. of these is the V.B. which lies below C.B. The top of this is at E_v & the band curves downward as a funⁿ of K giving

$$E_v(K) = E_v - \frac{\hbar^2 K^2}{2 m_0 m_e}$$

which contains another effective mass m_h ($m_h = 0.5$ in GaAs).

The C.B. & V.B. are separated by an energy called band gap i.e. $E_g = E_C - E_V$.

their effective ... ntum ... aAs ... provide ... large ... els in ... at

Again, there is a quantum well bcz E_v is at a diff^n level in GaAs well as AlGaAs barriers. The energies of the bound states are

$$E_{v,n_h} \approx E_v^{GaAs} - \frac{n_h^2 \pi^2 \hbar^2}{2 m_0 m_h a^2}$$

Everything is 'upside down' in V.B. as shown above.

The V.B. is completely full & C.B. completely empty, in a pure semiconductor at 0 temp. Optical absorption must therefore lift an ele⊖ from V.B into C.B.

In a bulk sample of GaAs this can occur provided that $\hbar\omega > E_g^{GaAs}$. 11'ly, we need $\hbar\omega > E_g^{AlGaAs}$. This process leaves behind an empty state or hole in V.B.

Now, look at quantum well. Although the well is of GaAs, absorption cannot start at $\hbar\omega = E_g^{GaAs}$, bcz the states in well are quantized. The lowest energy at which absorption can occur is given by diff. $E_{e1} - E_{h1}$ b/w the lowest state in well in C.B. & the lowest state in the well in V.B. Absorption can occur at

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higher energies by using other ite & the strongest transitions occur b/w corresponding state in two band. so, net $n_e = n_h = n$

∴ strong absorption occurs at freq.

$$\hbar \omega_n = E_{en} - E_{hn} = \left(E_c^{GaAs} + \frac{n_e^2 \pi^2 \hbar^2}{2 m_e m_0 a^2} \right) - \left(E_v^{GaAs} - \frac{n_h^2 \pi^2 \hbar^2}{2 m_0 m_h a^2} \right)$$

$$= E_g^{GaAs} + \frac{n^2 \pi^2 \hbar^2}{2 m_0 a^2} \left(\frac{1}{m_e} + \frac{1}{m_h} \right) \quad - (*)$$

The energies look like those in a quantum well where the effective mass is m_{eh} given by

$$1/m_{eh} = \frac{1}{m_e} + \frac{1}{m_h}$$

This is called the <u>optical effective mass</u>.

If the wells really were infinitely deep, there would be an infinite series of lines with freq. given by (*)
The barriers in the semiconductors are finite, & absorption occur in AlGaAs barriers ∀ freq. where $\hbar\omega > E_g^{AlGaAs}$
The resulting spectrum shown above (b) assuming that there are two bound states in both C.B. & V.B. no absorption

is possible for $\hbar\omega < E_g^{GaAs}$ & there is a its band of absorption for $\hbar\omega > E_g^{AlGaAs}$. B/w these two freq. lie two discrete lines produced by transitions b/w states in quantum well. The width of well can be inferred from the energy of these lines if effective masses are known.

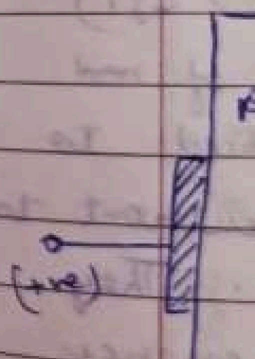
⇒ **Quantum Wires :-**

It is a 1-D nanostructure in which there is confinement along two dirⁿ & particle is free to move in the third dirⁿ. Particle has discrete energies associated with these 2 dirⁿ of confinement & its along the third (unconfined) dirⁿ. If 2 dimensions is reduced to the nanorange, keeping third one is large then the resulting nanostructure is called a quantum wire.

[Further from Book pg no. 69 - 70]

⇒ **Quantum Dot :-**

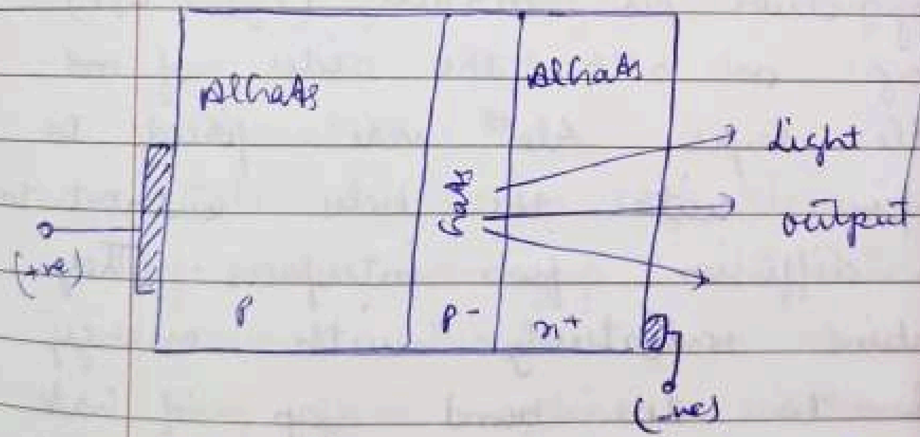
The extreme case in which confinement of the particle occurs in all the dirⁿ, results in a 0-D nanostructure, called quantum dot.



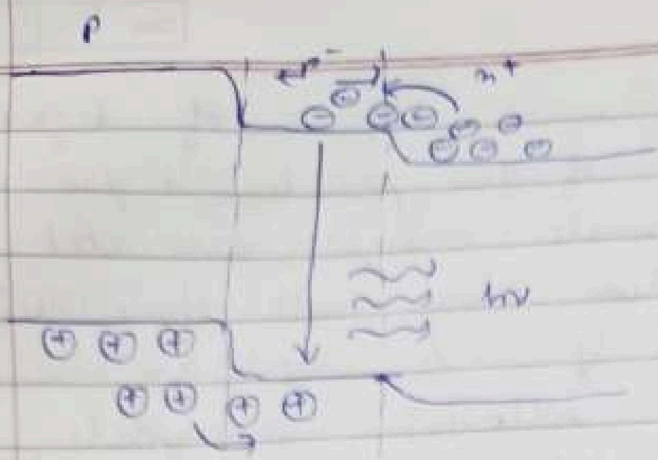
In this case, the no of degree of freedom of the particle is zero. Particle has discrete energies associated with its motion along all three dir.
Example of 0D objects are - nanoparticles, clusters, colloids, nanocrystals, fullerenes.
Quantum dots are composed of several to a few thousand atoms.

(Further from book pg no 73)

⇒ Double Heterojunction LED (DH-LED)



The above dia depicts heterojunction LED structure. As shown, it is GaAs/AlGaAs based double heterojunction LED. Thin layer of GaAs is sandwiched b/w two layers of AlGaAs.
GaAs is lightly doped & has narrower bandgap (E_{g_1}) of about 1.43 eV. AlGaAs layers have wider bandgap (E_{g_2}) of about 2.1 eV.



when forward bias is applied through its top & bottom contacts, ele⊖ are jumped / injected from highly doped (n^+) AlGaAs layer to central active (P^-) GaAs layer.

The injected ele⊖ are trapped within the middle layer due to double heterojunction ptl barriers ($E_{g_2} > E_{g_1}$) existing on both the sides of middle layer. Ele⊖ are forced to recombine with the holes without too much diffusion from interfaces. They recombine radiatively with energy equal to the band gap of GaAs.

As recombination b/w ele⊖ & holes is limited to narrower central part, internal quantum efficiency of such LED is higher compare to single junction LED.

Moreover, GaAs & AlGaAs are lattice matched. Hence, surface density will be very smaller. In addition, emitted

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photons from active region is not absorbed by top and bottom AlGaAs layers due to $E_{g_2} > E_{g_1}$ condition.
Due to above reasons, overall performance of DHLED improves.

Benefits / Advantages of DHLED

i) It offers higher efficiency with low to high radiance compare to simple homojunction (p-n^+) LED type.

ii) Emitting wavelength of GaAs / AlGaAs based DHLEDs range approx. b/w 0.8 to 0.9 μm ~~In~~ If InP / InGaAsP based LEDs are used for long wavelength radiation b/w 0.93 - 1.65 μm due to min. signal attenuation.

iii) Both n- region & p- region are made out of wide bandgap materials. Hence, there is no absorption in these regions. They form optical windows.

iv) n- region & p- region can be highly doped.

v) Injected e^- & holes are confined in a very narrow active region (quantum well) where, $n^* p$ product is extremely high. Hence, radiative recombination rate (R) is also high.

→ Drawbacks / Disadvantage

1) These LEDs are useful at low temp.
11) It comes from very small ptl barrier which ele encounters (in C.B) when it reaches p-side of the junction.
111) There is complexity involved during growth process.

Quantum well Laser

It may be viewed as sandwiches consisting of a layer of material with small bandgap embeded between two layers of material with a larger bandgap. Such a double heterostructure confines carriers into the small bandgap material, Thus realizing in the growth dirn, the "particle in a box".

Quantum well (QW) technology allows the crystal growers for the first time to control the range, depth & arrangement of quantum mechanical ptl wells. This can be used not only to demonstrate examples of elementary quantum mechanics, but to make a powerful new laser, a quantum well laser. To build a lower dimensional material deliberately, squeezing one

side of a 3-D plane until it is no thicker than one ele$^{\ominus}$ wavelength traps ele$^{\ominus}$ in a 2-D plane.

In 2-D, the so-called density of states, becomes quantised. ele$^{\ominus}$ are not readily confined to physical barriers. To trap ele$^{\ominus}$, one need only sandwich a material, typically a crystalline semiconductor, filled with low energy ele$^{\ominus}$, b/w two slices of semiconductor with higher energy ele$^{\ominus}$.

Any ele$^{\ominus}$ in the lower energy slice will be confined, unable to cross the barrier b/w the two diff^{n} semiconductors if the barrier is sufficiently ~~(unable to cross the barrier b/w the two diff^{n} semiconductors)~~ thick. The interface where the two semiconductor crystals meet is known as a heterojunction (junction b/w 2 dissimilar semiconductor materials with diff^{n} bandgaps)

In turn heterostructure are formed from multiple heterojunctions. The energy of the ele$^{\ominus}$ in these semiconductors is outlined by the band theory. Valence ele$^{\ominus}$ determine some of material's properties, especially chemical ones but they do not contribute to current flow because they are fairly tightly

bound to atom. To conduct electricity e^- must be in a higher energy band known as the C.B. In metals many of e^- normally occupy this band enabling conduction of electric current.

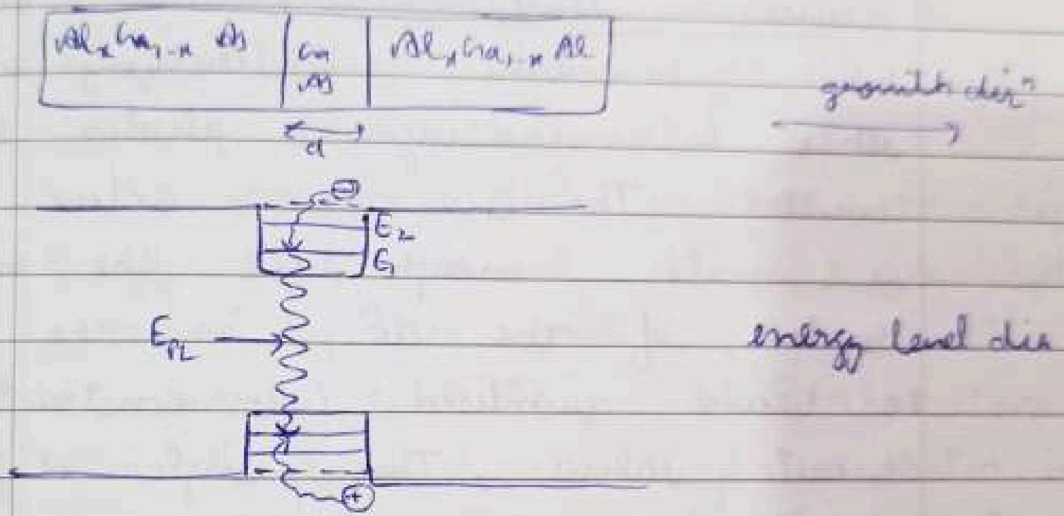
Semiconductors, on the other hand, can be made to conduct by introducing impurities called dopants that deposit e^- into C.B. e^- can also be introduced by illuminating the e^- semiconductor, which promotes e^- to C.B. from V.B. The energy needed to drive an e^- from V.B. to C.B. is the bandgap energy (measured in eV)

These structures can be grown by molecular beam epitaxy or chemical vapour deposition (CVD) with control of the layer thickness down to monolayer (i.e. single atom thick layers).

MBE machine is an ultrahigh vacuum chamber which allows layers of atoms to be deposited as thin as 0.2 nm on a heated semiconductor substrate. Their aim was to create a quantum well, viz made by depositing a very thin layer of lower bandgap material b/w layers of higher bandgap material.

In the dia. shown below, The

GaAs has smaller band gap than $Al_xGa_{1-x}As$ & forms not only a quantum well for C.B. $e^{\ominus}$, it also forms a quantum well for V.B. holes; so that carriers are confined in this layer.



The idea was to trap $e^{\ominus}$ in lower bandgap semiconductor, GaAs e.g. which has bandgap energy of 1.5eV. The $e^{\ominus}$ would be unable to cross the heterojunction barrier into the layers of AlGaAs which has bandgap of 3.1 eV. If GaAs, the actual quantum well was just tens of atomic layers ~ 30 nm, quantum effects would then be observed. i.e. $e^{\ominus}$ has a substantial prob. of passing through, tunneling into the high bandgap material.

In the last decade the imp.

of the quantum well laser has grown steadily until the point where today, it is preferred to most semiconductor lasers. The only significant difference b/w an ordinary semiconductor laser & a quantum well laser is in the relative size of each device's active region, where the e^{-} & holes recombine, neutralizing each other & causing a photon to be emitted. The QW laser's active region is small enough for the energy level of the e^{-} in the well to become quantised i.e. constructed to discrete values. This single diff. brings about a major advantage; a QW laser radiates light very efficiently powered by much less current than a conventional semiconductor laser.

As a result, semiconductors that operate on the principle of quantum confinement dissipate far less heat. This feature combined with the small physical size of the lasers, means that the devices can be packed tightly together to form arrays are more reliable & can operate at higher temp.

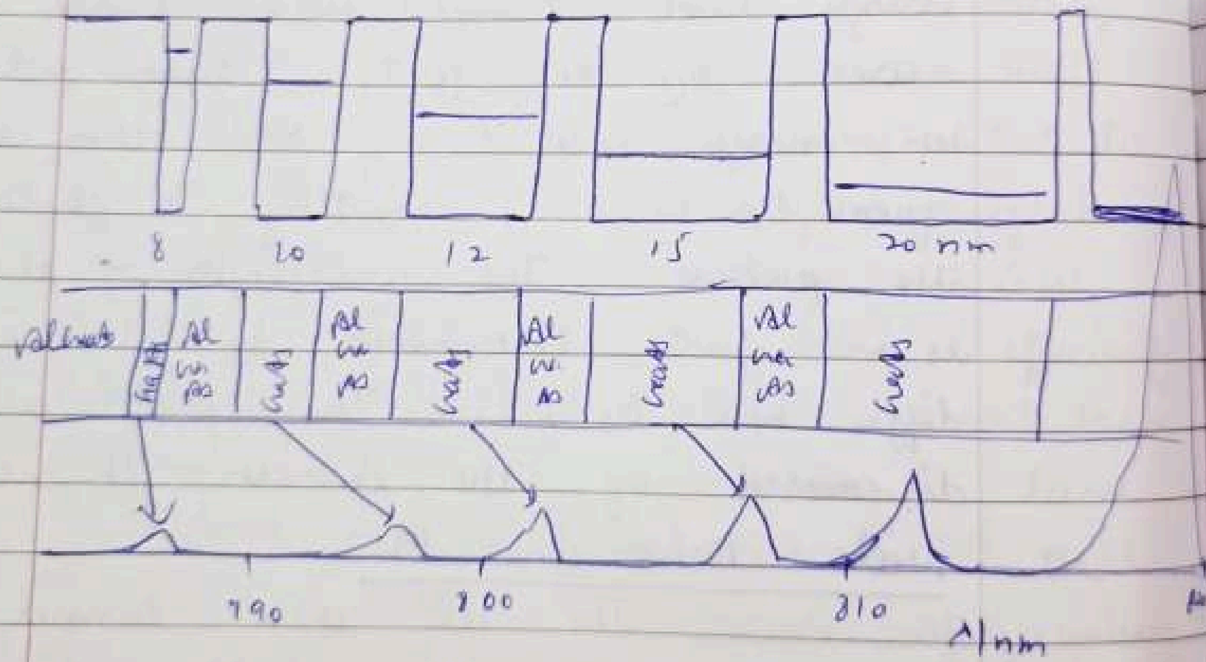
How does this transfer to laser technology?

To achieve laser action, two conditions have to be met. Ist, the higher energy level say E_2 must have a large no of e^- than the lower viz E_1. This condition is known as <u>population inversion</u> & ensures that the light is amplified rather than attenuated.

In operation, e^- pumped to a high energy level tunnel into & are captured by the first two wells i.e. energy level E_2. The e^- then drop from E_2 to E_1, emitting a photon in the process. The wavelength of photon is in fact determined by the energy diff. b/w E_2 & E_1. This fact was discovered by the Danish Physicist <u>Niels Bohr in 1913.</u>

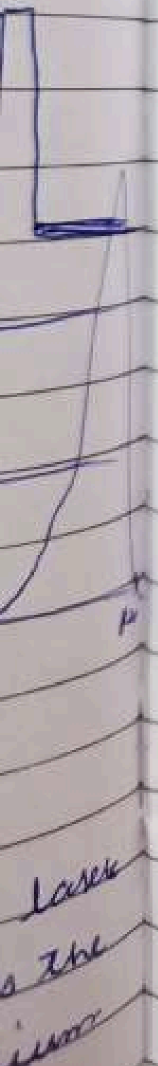
The e^- then tunnel into the third quantum well where they drop to before tunneling out of the laser & exiting the three well structure. Each successive active region is at a lower energy than the one before it, so that the active regions are like steps in a staircase. In b/w the active

regions are injector / relaxation regions, which collect the $e^{\ominus}$ coming out at one active region & pass them on to the next, lower energy one. All the active & injector regions are engineered to allow $e^{\ominus}$ to move efficiently from the top of the staircase to the bottom. The end results is that a single $e^{\ominus}$ passing through laser emits not one but 25 photons.



⇒ <u>Quantum dot laser</u>

A quantum dot laser is a semiconductor laser which uses the quantum dots as the active medium. In quantum dot lasers, dots play an important role.



Construction :-

The top p-metal layer has a GaAs contact layer Immediately below it, there are a pair of two µm thick $Al_{0.85}Ga_{0.15}As$ cladding layers that surround a 190 nm thick waveguide made up of $Al_{0.05}Ga_{0.95}As$ in b/w p-metal & n-substrate. Here the waveguide plays a role of conducting the emitted light to the exit ports at the edges of the structure. The waveguide is a 30 nm thick GaAs region & centered in This region are 12 monolayers of $In_{0.5}Ga_{0.5}As$ quantum dots with a density of 1.5×10^{10} cm^2

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Working:-

1) The $e^{\ominus}$ hole recombination causes the emission of laser light
2) By varying the length & width, the laser light with particular wavelength will be emitted.
3) A particular wavelength of 1.32 μm viz in the near infrared region can be produced.
4) The faces of the layer were coated with high reflectively material (ZnSe) where the light is reflected back & forth to increase the stimulated emission & in turn the laser emission is enhanced.

Advantages:-

1) Broad spectrum with a specific wavelength of light emission can be obtained by changing dot size.
2) operates even at high frequencies.
3) It is an efficient laser.
4) Gain is 2 to 3 times more than the quantum well.

Disadvantages:-

1) It is very difficult to form high quality dots (uniform size & higher density)

7) difficult to manufacture

Applications :-

i) They are used in medicine

ii) used in display technologies, spectroscopy & telecommunications

iii) used in optical transmission system & optical LANs

⇒ **Coulomb Blockade**

In semiconductor devices, the mag. of current is reduced as the feature size of device reduces. A typical semiconductor device utilizes many ele$^{\ominus}$ e.g. there can be $10^{11}-10^{12}$ ele$^{\ominus}$ in $1cm^2$ area of typical MOSFET device. If the device size is too small then a single ele$^{\ominus}$ may be involved in device application. Change of one elementary charge is small nanometric system has a measurable effect in their electrical & transport properties. This phenomena is called Coulomb Blockade.

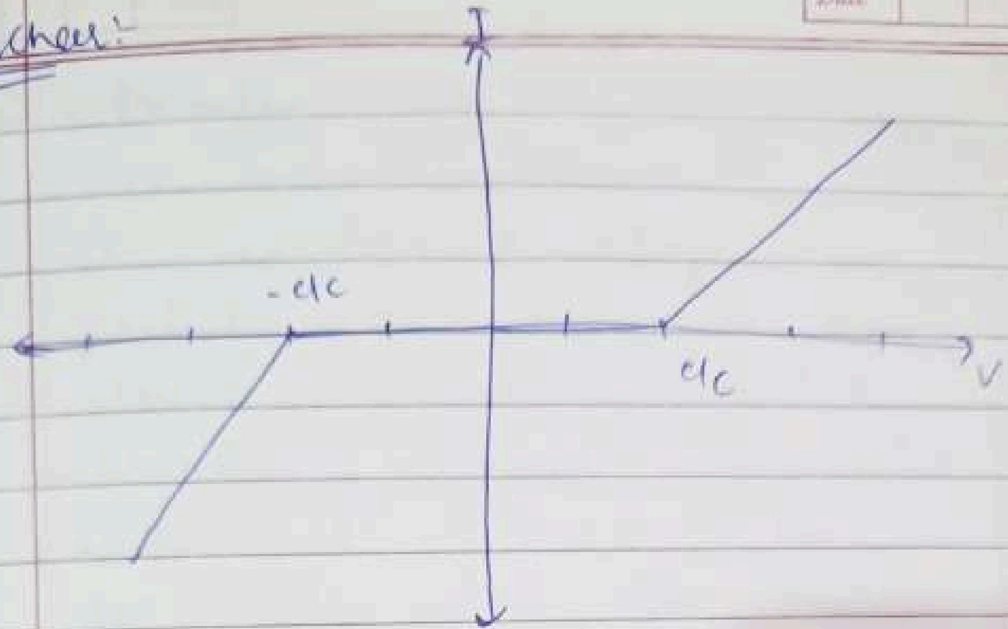
Consider a quantum dot structure, connected to ele$^{\ominus}$ reservoir at each side by ptl barriers. The energies of quantum dot when the no. of ele$^{\ominus}$ in the dot is N, is changed in amount of

single unit charges. If we want to change no N of $e^{\ominus}$ in dot by adding just one $e^{\ominus}$, then $e^{\ominus}$ will have to tunnel from left reservoir into the dot

This is done by using a ptl energy supply eV to $e^{\ominus}$ by using a vol. source. If the charge in quantum dot is Q & their capacitance C, then ptl energy is $Q^2/2C$.

Thus, an energy of at least $e^2/2C$ need to be provided to $e^{\ominus}$ & for $e^{\ominus}$ to enter the dot, vol. must be raised to atleast $e/2C$ i.e.- the $e^{\ominus}$ can't tunnel if the vol. is $|V| = e/2C$. The vol. range b/w $-e/2C$ & $e/2C$ where current can not go through the dot is called coulomb blockade.

I-V char:

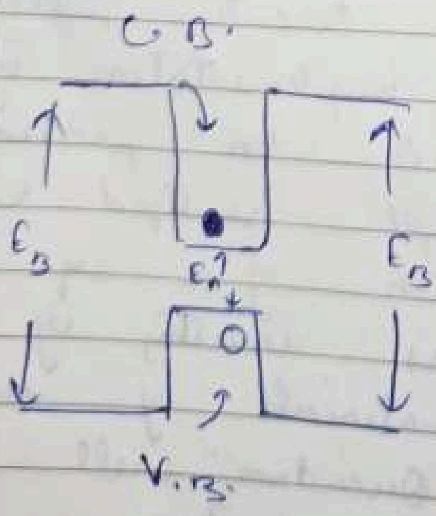


Repeated tunnelling of a single e^- produces what is known as coulomb staircase.

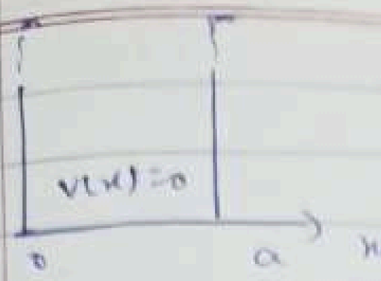
② **Quantum well:-** It is a 2D nanostructure in which there is confinement along one dirn & particle is free to move in other 2 dirn. Particle posses discrete energies associated with confinement dim. Particle energies are its along the other two dimensions.

The term "well" refers to a semiconductor region that is grown to posses a lower energy, so that it acts as a trap for ele$^{\ominus}$ & holes. These wells are called as quantum wells because such semiconductor regions are only a few atomic layers thick. Quantum wells are real-world implementation of the particle in 1.D box problem. They are expt. realized by epitaxial growth of a seq of ultrathin layers consisting of semi-conducting materials of varying composition. Quantum well are formed in semiconductors by having a material like Ga As sandwiched b/w 2 layers of a material

with a wider band gap like AlAs.
These structures can be grown by molecular beam epitaxy (MBE) or CVD (chemical vapour deposition) with control of layer thickness down to monolayers.
Two dissimilar semiconductors with diffⁿ band gap can be joined to form a heterojunction. If a thin layer of narrower band gap material A is sandwiched b/w 2 layers of wider band gap material B then we get a double heterojunction. If the layer A is sufficiently thin then such a structure is called a single quantum well.



~~Quan~~ Infinite Ptl. well



Consider quantum well (2D) structure particles are confined to a thin sheet of thickness 'a' along x-dir by infinite well which creates a quantum well.

ptl. funⁿ is

$$V(x) = \begin{cases} 0 \; ; & 0 < x < a \\ \infty \; ; & x \le 0 \text{ or } x \ge a \end{cases}$$

S.W.E. in ptl. well region where

$V(x) = 0$

$$\therefore \; -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi$$

$$\frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2}\psi = 0$$

$$\Rightarrow \boxed{\frac{d^2\psi}{dx^2} + k^2\psi = 0} \quad (1) \qquad k^2 = \frac{2mE}{\hbar^2}$$

$$k = \sqrt{\frac{2mE}{\hbar^2}}$$

$\therefore$ boundary conditions are

$$\psi(0) = \psi(a) = 0$$

$\therefore$ Solⁿ of (1) is

$$\psi(x) = A\sin kx + B\cos kx$$

$\because \psi(0) = 0$

$$\Rightarrow 0 = 0 + B\cos k(0)$$

$$\Rightarrow \boxed{B = 0}$$

$\therefore \psi(x) = A \sin kx$

Now $\because \psi(a) = 0$

$\therefore 0 = A \sin ka$ $\quad \because A \neq 0$

$\Rightarrow \sin ka = \sin n\pi$

$\Rightarrow ka = n\pi \Rightarrow k = \frac{n\pi}{a}$

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

$\therefore$ Sol^n is

$$\psi(x) = A \sin \frac{n\pi}{a} x \quad -②$$

using Normalization condition

$$\int_0^a \psi^* \psi \, dx = 1$$

$$\Rightarrow \int_0^a A^* A \sin^2 \frac{n\pi}{a} \, dx = 1$$

$$\Rightarrow A = \sqrt{\frac{2}{a}}$$

$$\therefore \psi(x) = \sqrt{\frac{2}{a}} \sin \frac{n\pi}{a} x \quad ③$$

$$\because k^2 = \frac{2mE}{\hbar^2} \Rightarrow \frac{n^2\pi^2}{a^2} = \frac{2mE}{\hbar^2}$$

$$\therefore E = \frac{n^2\pi^2\hbar^2}{2ma^2} = \frac{n^2h^2}{8ma^2} \quad ④$$

these are discrete energy states

of particle within quantum well region

→ outside the well region particle energies are continuous.

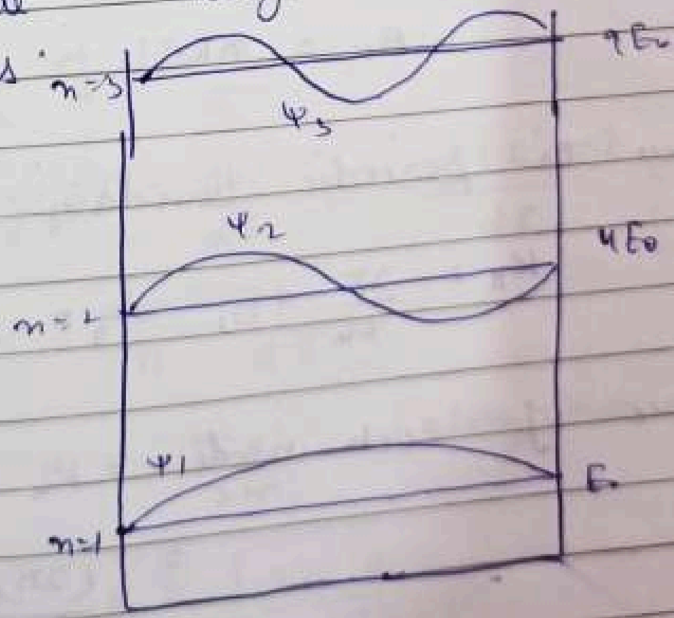
$$E_{n+1} - E_n = \frac{\left((n+1)^2 - n^2\right)\pi^2\hbar^2}{2ma^2}$$

$$= \frac{(2n+1)\pi^2\hbar^2}{2ma^2}$$

$$E_{n+1} - E_n \propto \frac{1}{a^2} \quad \&$$

$$E_{n+1} - E_n \propto (2n+1)$$

as the dim. 'a' ↑ses, the spacing b/w discrete energy level ↓ses. In a infinite crystal a continuum occurs.



Zero pt. energy.

$$E_0 = \frac{\pi^2\hbar^2}{2ma^2} \neq 0$$

Density of states in 2D / Quantum well

∵ In Quantum well, $e^{\ominus}$ motion is confined along 1 Dirⁿ & free to move along rest of 2 dirⁿ

$$\therefore E = \frac{\hbar^2 k_z^2}{2m} + \frac{\hbar^2 k^2}{2m}$$

$$E = E_n + E_{x,y}$$

here, $e^{\ominus}$ is confined in z-dirⁿ

$$k^2 = k_x^2 + k_y^2$$

$$k_z = \frac{n\pi}{L_z} \quad ; n = 1, 2, 3, \ldots$$

Let us consider circular area of k-space

$$A_k = \pi k^2$$

due to periodic boundary condition

$$k_x = \frac{2\pi}{L_x}, \quad k_y = \frac{2\pi}{L_y}$$

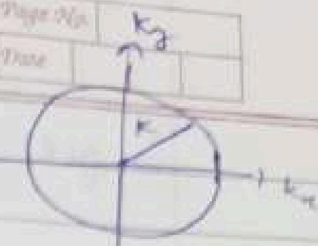
∴ area of each mode $= k_x k_y$

$$= \frac{(2\pi)^2}{L_x L_y}$$

∴ Total no of modes in area A_k

$$= \frac{\text{Total area}}{\text{area of each mode}} = \frac{\pi k^2}{(2\pi)^2 / L_x L_y}$$

$$= \frac{k^2}{4\pi} L_x L_y$$



2 e^- can have same energy, one with spin up & other with spin down.

$\therefore$ Total no. of energy states in area πk^2 =

$$2 \times \frac{k^2}{4\pi} L_x L_y = \frac{k^2}{2\pi} L_x L_y$$

no. of states per unit area

$$N = \frac{\text{Total no. of states}}{\text{area}}$$

$$= \frac{\frac{k^2}{2\pi} L_x L_y}{L_x L_y} = \frac{k^2}{2\pi}$$

$\therefore$ density of states

$$g(E) = \frac{dN}{dE} = \frac{d(k^2/2\pi)}{dE} = \frac{1}{2\pi} 2k \frac{dk}{dE}$$

$$g(E) = \frac{k}{\pi} \frac{dk}{dE}$$

$\because$ $E = \frac{\hbar^2 k^2}{2m}$ (along free dir^n)

$$\therefore \quad k = \sqrt{\frac{2mE}{\hbar^2}}$$

$$\therefore \quad dk = \sqrt{\frac{2m}{\hbar^2}} \frac{1}{2} E^{-1/2} dE$$

$$\frac{dk}{dE} = \frac{1}{2}\sqrt{\frac{2m}{\hbar^2}} E^{-1/2}$$

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$$\therefore g(E) = \frac{1}{\pi}\left(\frac{2mE}{\hbar^2}\right)^{1/2} \times \left(\frac{2m}{\hbar^2}\right)^{1/2} \frac{1}{2} E^{-1/2}$$

$$\boxed{g(E) = \frac{m}{\pi\hbar^2}}$$

$\therefore$ in general

$$\boxed{g(E) = \frac{m}{\pi\hbar^2} \sum_n \Theta(E - E_n)}$$

where Θ = Heaviside fun^n

i.e.:- $\Theta(E - E_n) = \begin{cases} 1 & ; \quad E < E_n \\ 0 & ; \quad E > E_n \end{cases}$

The resulting DOS for a quantum well is a staircase