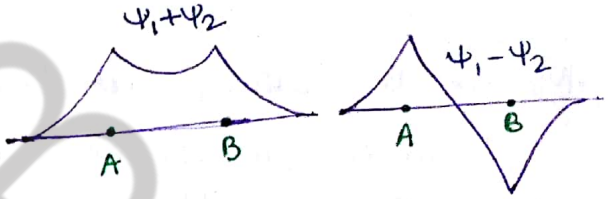
Band Theory of Solids

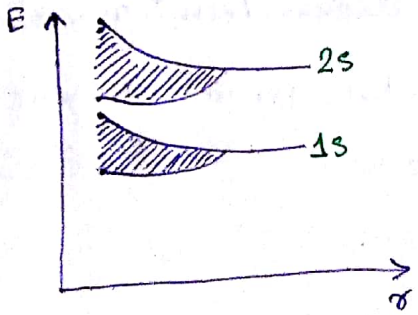
Formation of Energy Bands

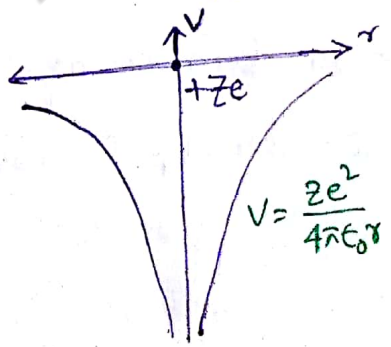
In solids, a periodic potential is formed by the nucleus and other electron cloud. Motion of an electron in periodic potential can be represented by Schrödinger equation, whose solution gives energy states. These states are filled with electrons according to Pauli's exclusion principle & all states are not accessible but bands of energies separated by forbidden energies are possible.

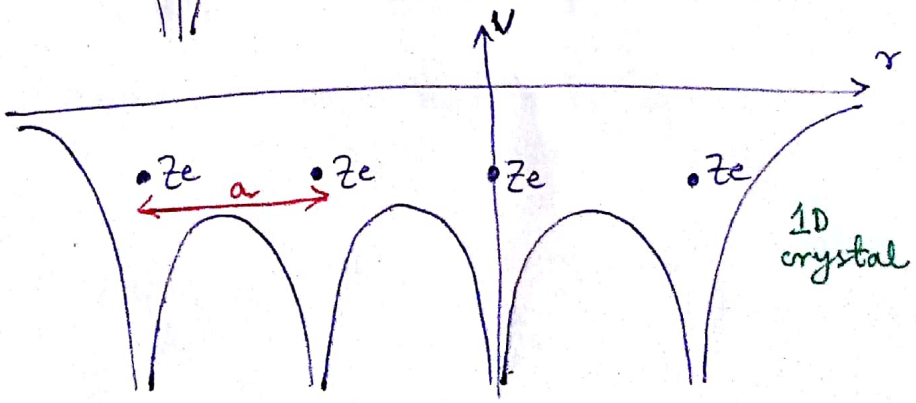
When two atoms are brought close, single energy level splits into a pair of levels. If ψ_1 & ψ_2 are electronic wave functions, then due to overlap, resultant wave function is $(\psi_1 \pm \psi_2)$. For symmetric case, electron can remain midway to A-B but for antisymmetric it cannot, so there is a difference in energy between $(\psi_1+\psi_2)$ & $(\psi_1-\psi_2)$.



Similarly when N no. of atoms are brought together, each energy state splits into N energy states whose separation is very small. These forms quasicontinuous energy band.





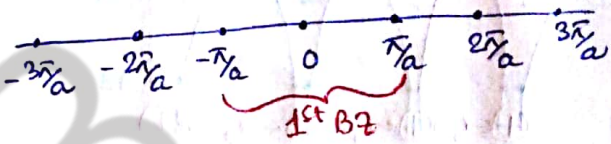


Origin of band structure This can be understood from nearly free electron model where electrons move in a periodic kernel in 1D. Energy of a free electron $E_k = \frac{\hbar^2 k^2}{2m}$ & $\psi_k(x) = e^{ikx}$

Low energy electrons can freely travel as their $\lambda >> a$. High energy electrons almost near to fermi energy have $\lambda \sim a$, & suffer diffraction like X-rays in crystal surface. Electron with deBroglie wavelength λ is brags reflected, $2a\sin\theta = n\lambda$.

or $K = \frac{2\pi}{\lambda}$. after substitution $K = \pm \frac{n\pi}{a\sin\theta}$. For 1D lattice $\theta = \pi/2$ or $K = \pm \frac{n\pi}{a}$.

Thus a line representing K values is divided by energy discontinuities into segments of length $\pm \pi/a$ which are the Brillouin zones.

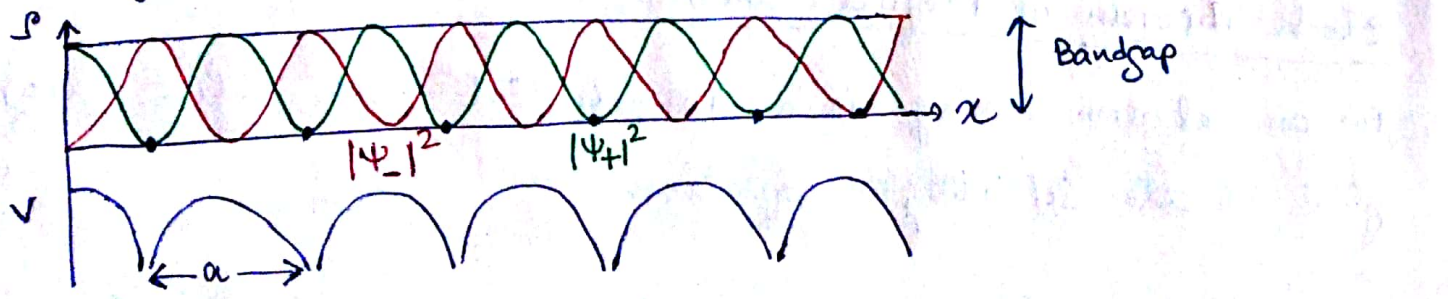


At the boundary $K = \pm \frac{\pi}{a}$, electron wavefunctions are not traveling waves $e^{i\pi x/a}$ & $e^{-i\pi x/a}$ but are standing waves, due to reflection. Two types of standing wave can form

$$\psi_+ = e^{i\pi x/a} + e^{-i\pi x/a} = 2\cos\left(\frac{\pi x}{a}\right) \quad [x \to -x,\ \psi_+ \to \psi_+$$

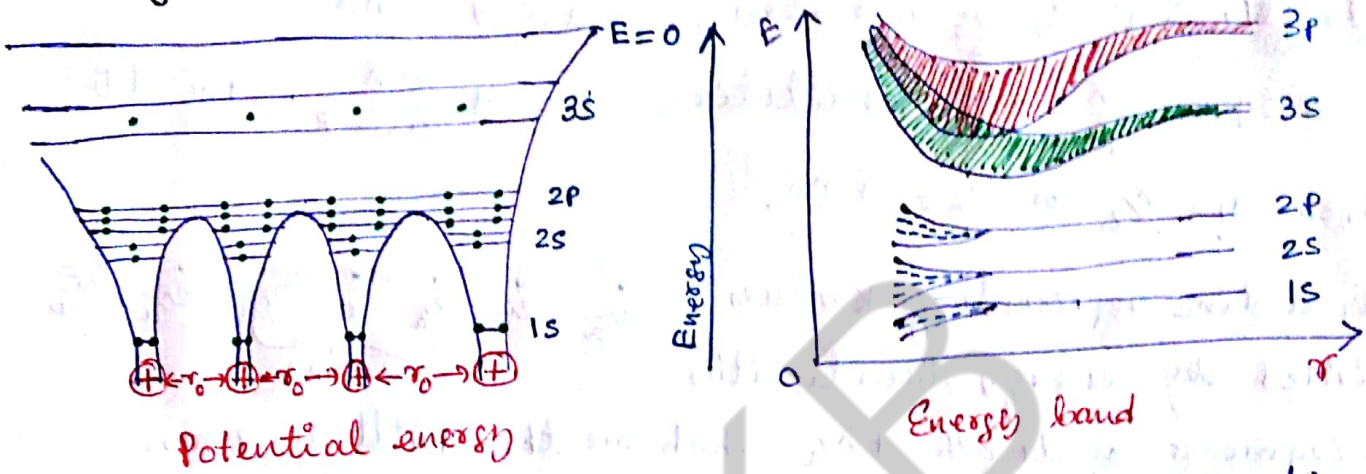
$$\psi_- = e^{i\pi x/a} - e^{-i\pi x/a} = 2i\sin\left(\frac{\pi x}{a}\right). \quad x \to -x,\ \psi_- \to -\psi_-]$$

In quantum mechanics, probability density of electron is $\rho = \psi^*\psi$ and for traveling wave $\psi = e^{\pm ikx}$, $\rho = 1$ so that electron charge density $e|\psi|^2$ = constant. However for standing wave, charge density isn't constant but $e|\psi_+|^2 \propto \cos^2\left(\frac{\pi x}{a}\right)$, $e|\psi_-|^2 \propto \sin^2\left(\frac{\pi x}{a}\right)$



for $x = 0, a, 2a, \cdots$ $\cos^2 \frac{\pi x}{a} = 1$, so its maximum at the kernel core and thus negative electron charge density lowering P.E. of Kernel. for $x = \frac{a}{2}, \frac{3a}{2}, \cdots$, $\sin^2 \frac{\pi x}{a} = 1$, so its maximum in midway between Kernel & increasing the P.E. w.r.t. to travelling wave. So E_g is the difference of two energies.

Energy bands in Sodium crystal



Potential energy

Energy band

Valence orbital overlap for 3s orbital to form quasi continuous energy band. Empty 3p level also spreads, so as 2s & 2p with decrease of r. When $r = r_0 = 0.367$ nm, 3s & 3p states overlap.

In metals, band overlap happens but in other materials they are separated by a band gap E_g & the energy of highest filled level is Fermi energy E_F. At 0K, levels upto E_F is filled & those above are empty. Using Pauli's principle, each s-band having N atoms can accomodate 2N electrons. If highest s-band is fully filled then electron drift using external force is stopped & such solids are called insulators.

Bloch Theorem or Floquet's theorem

For an electron moving in a 1D potential with $V(x) = V(x+a)$ is given by the Schrödinger equation

$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}[E - V(x)]\psi = 0$. Bloch theorem stats that the solution of the Schrödinger equation for a periodic potential is

$$\boxed{\psi(x) = e^{\pm ikx} u_k(x)}$$ where $u_k(x) = u_k(x+a)$. which are plane waves $e^{\pm ikx}$ modulated by $u_k(x)$ with the periodicity of the lattice. $\psi(x)$ is the Bloch wave or Bloch function.

Proof of Bloch's theorem

If $f(x)$ and $g(x)$ are two real, independent solution of Schrödinger equation $\psi(x) = Af(x) + Bg(x)$. As $V(x) = V(x+a)$, $f(x+a)$ and $g(x+a)$ are also solutions.

$$\therefore f(x+a) = \alpha_1 f(x) + \alpha_2 g(x), \quad g(x+a) = \beta_1 f(x) + \beta_2 g(x).$$

$$\psi(x+a) = Af(x+a) + Bg(x+a)$$
$$= (A\alpha_1 + B\beta_1) f(x) + (A\alpha_2 + B\beta_2) g(x)$$
$$= \lambda A f(x) + \lambda B g(x) = \lambda \psi(x). \text{ where we have}$$

chosen $A\alpha_1 + B\beta_1 = \lambda A$, $A\alpha_2 + B\beta_2 = \lambda B$. with λ a constant.

Now this gives nonzero values of A and B if determinant of coefficient is zero $\begin{vmatrix} \alpha_1 - \lambda & \beta_1 \\ \alpha_2 & \beta_2 - \lambda \end{vmatrix} = 0$ or $\lambda^2 - (\alpha_1 + \beta_2)\lambda + \alpha_1\beta_2 - \alpha_2\beta_1 = 0$ ——— (1)

[[As $f(x)$ & $g(x)$ are solution of Schrödinger equation,

$\left\{\frac{d^2f(x)}{dx^2} + \frac{2m}{\hbar^2}[E - V(x)]f(x) = 0\right\}$, $\left\{\frac{d^2g(x)}{dx^2} + \frac{2m}{\hbar^2}[E - V(x)]g(x)\right\} = 0$

$g(x)\times$ ↑ Substract ↑ $\times f(x)$

$$f(x)\frac{d^2g(x)}{dx^2} - g(x)\frac{d^2f(x)}{dx^2} = 0 \text{ or } f(x)\frac{dg(x)}{dx} - g(x)\frac{df(x)}{dx} = \text{constant} = W(x)$$

wronskian

$$\therefore W(x+a) = f(x+a)\frac{dg(x+a)}{dx} - g(x+a)\frac{df(x+a)}{dx}$$
$$= f(x+a)\left[\beta_1\frac{df(x)}{dx} + \beta_2\frac{dg(x)}{dx}\right] - g(x+a)\left[\alpha_1\frac{df(x)}{dx} + \alpha_2\frac{dg(x)}{dx}\right]$$

$= [\alpha_1 f(x) + \alpha_2 g(x)]\left[\beta_1 \frac{df(x)}{dx} + \beta_2 \frac{dg(x)}{dx}\right] - [\beta_1 f(x) + \beta_2 g(x)]\left[\alpha_1 \frac{df(x)}{dx} + \alpha_2 \frac{dg(x)}{dx}\right]$

$= (\alpha_1\beta_2 - \alpha_2\beta_1)\left[f(x)\frac{dg(x)}{dx} - g(x)\frac{df(x)}{dx}\right] = (\alpha_1\beta_2 - \alpha_2\beta_1)\, W(x)$

But $W(x+a) = W(x) =$ constant, $\therefore$ $\underline{\alpha_1\beta_2 - \alpha_2\beta_1 = 1}$]]

Eq. ① becomes, $\underline{\lambda^2 - (\alpha_1 + \beta_2)\lambda + 1 = 0}$. Here $\alpha_1 + \beta_2$ is a function of energy E & we have two roots λ_1 & λ_2 or two functions $\psi_1(x)$ and $\psi_2(x)$ with $\psi_1(x+a) = \lambda\psi(x)$ & $\lambda_1\lambda_2 = 1$.

Special cases $(\alpha_1 + \beta_2)^2 < 4$, $\lambda^2 - (\alpha_1+\beta_2)\lambda + 1 = 0$ have complex roots, & conjugate to each other. $\lambda = e^{\pm ika}$

$\psi(x+a) = e^{\pm ika}\psi(x)$ which is of the Bloch form $\psi(x) = e^{\pm ikx}u_k(x)$

$= e^{\pm ik(x+a)}u_k(x+a) = e^{\pm ika}e^{\pm ikx}u_k(x+a) = e^{\pm ika}\psi(x)$

$= \lambda\psi(x)$ Bloch theorem hence proved.

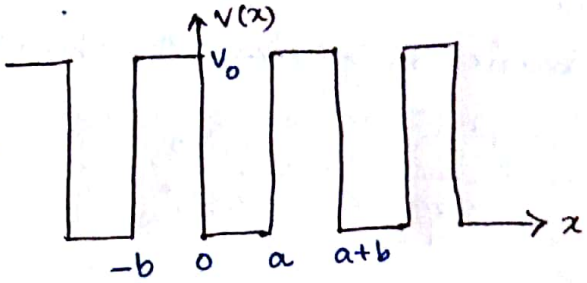
Special cases $(\alpha_1 + \beta_2)^2 > 1$, $\lambda^2 - (\alpha_1+\beta_2)\lambda + 1 = 0$ have real roots

$\lambda_1 = e^{\mu a}$, $\lambda_2 = e^{-\mu a}$, μ = real. & & corresponding Schrödinger equation, $\psi_1(x) = e^{\mu x}u(x)$, $\psi_2(x) = e^{-\mu x}u(x)$

Although mathematically valid, these are forbidden wavefunctions as they're not bounded. at $\pm\infty$, both diverge.

The allowed roots $e^{\pm ika}$ and forbidden roots $e^{\pm\mu a}$ are functions of $(\alpha_1 + \beta_2)$ and hence energy. So energy spectrum of electron moving in periodic potential consists of allowed & forbidden energy regions orbands.

Kronig-Penny Model [Energy spectrum of electron consists of a allowed energy bands separated by forbidden region]



In free electron theory the assumption is valence electrons see zero potential but this isn't true with ionic & covalent bond as electrons are localized near the nuclei, that gives periodically varying potential.

whose solution from Schrödinger equation is very hard.

Instead Kronig & Penny solved it using simpler 1D potential of sharp ~~end~~ edge with periodicity a+b.

$V = 0, \quad 0 < x < a$

$= V_0, \quad -b < x < 0$

whose Schrödinger equation is

$$\frac{d^2\psi}{dx^2} + \underbrace{\frac{2m}{\hbar^2}E}_{\alpha^2}\psi = 0, \quad 0 < x < a$$

$$\frac{d^2\psi}{dx^2} + \underbrace{\frac{2m}{\hbar^2}(E - V_0)}_{\beta^2}\psi = 0, \quad -b < x < 0 \qquad \text{— (1)}$$

$V(x) = V(x + a + b)$

According to Bloch theorem, solution of wave equation for periodic potential will be plane wave modulated by the lattice periodicity. $\psi(x) = u_k(x)\, e^{ikx}$ with $u_k(x) = u_k(x + a + b)$.

By substituting $\psi(x)$ in equation (1) and substituting the boundary condition: $(u_1)_{x=0} = (u_2)_{x=0}$ $\quad (u_1)_{x=a} = (u_2)_{x=b}$

$$\left(\frac{du_1}{dx}\right)_{x=0} = \left(\frac{du_2}{dx}\right)_{x=0} \qquad \left(\frac{du_1}{dx}\right)_{x=a} = \left(\frac{du_2}{dx}\right)_{x=b}$$

one gets four equations & to get nonzero coefficients the 4×4 determinant vanishes. From that K-P obtained,

$$\frac{\beta^2 + \alpha^2}{2\alpha\beta} \sinh \beta b \sin \alpha a + \cosh \beta b \cos \alpha a = \cos k(a + b)$$

To simplify K-P considered when $V_0 \to \infty$ and $b \to 0$, $V_0 b$ is finite or potential barriers become δ-functions. $V_0 b$ is known as barrier strength. As $b \to 0$, $\sinh \beta b \to \beta b$, $\cosh \beta b \to 1$ and

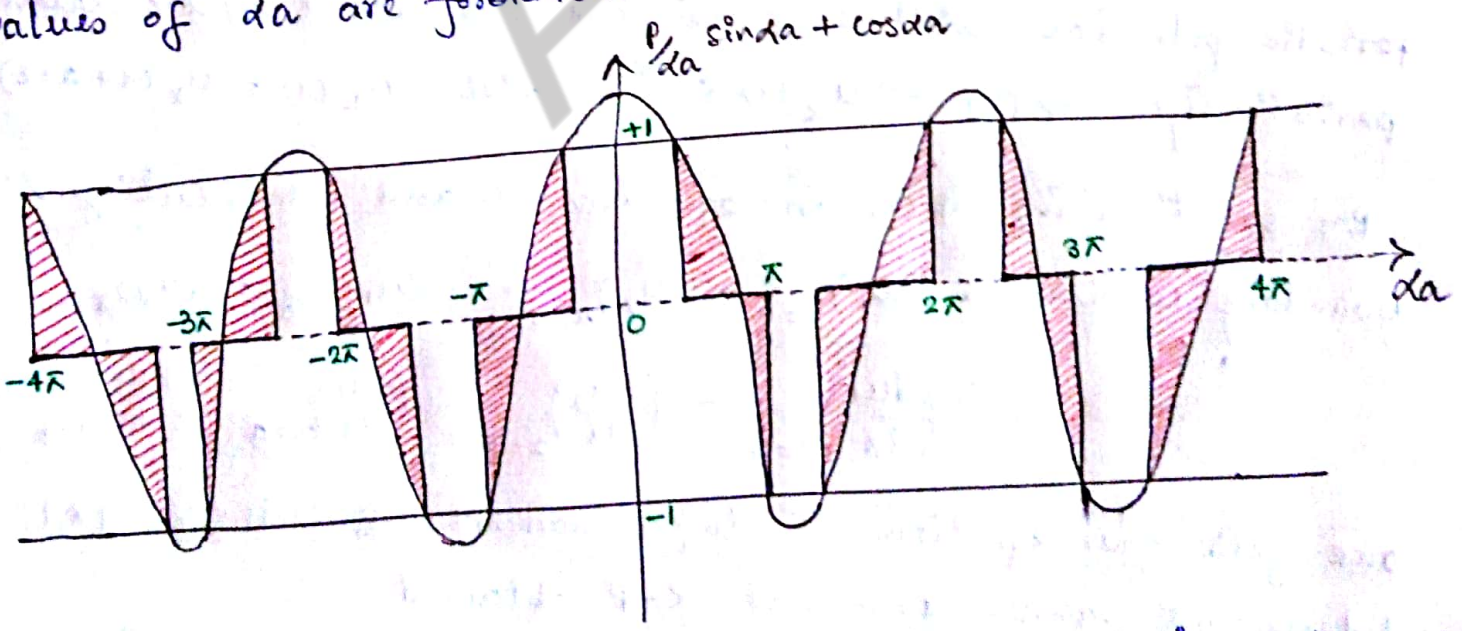
$$\frac{\beta^2 + \alpha^2}{2\alpha\beta} = \frac{mV_0}{\alpha\beta\hbar^2} \quad \therefore \quad \frac{mV_0 b}{\alpha\hbar^2} \sin\alpha a + \cos\alpha a = \cos ka$$

$$\therefore \boxed{P \frac{\sin\alpha a}{\alpha a} + \cos\alpha a = \cos ka} \quad \text{where } P = \frac{mV_0 ab}{\hbar^2}$$

when P is increased, the area of potential barrier is increased and the electron is bound more strongly to a potential well. $P \to 0$ means barrier is very weak & the electrons become free electron

$$\therefore \lim_{P \to 0}, \quad \alpha a = ka \quad \therefore \quad \alpha^2 = k^2 = \frac{2mE}{\hbar^2} \quad \therefore E = \frac{\hbar^2 k^2}{2m}$$

As $\cos ka$ is bound between $+1$ and -1, LHS should take values of αa for which it lies between $+1$ & -1. $\therefore$ Such αa represent wave like solutions $\psi(x) = e^{ikx} u_k(x)$. Other values of αa are forbidden.



as $ka \to [0, \pi]$, $\cos ka \to [+1, -1]$ allowed boundaries $\cos ka = \pm 1$

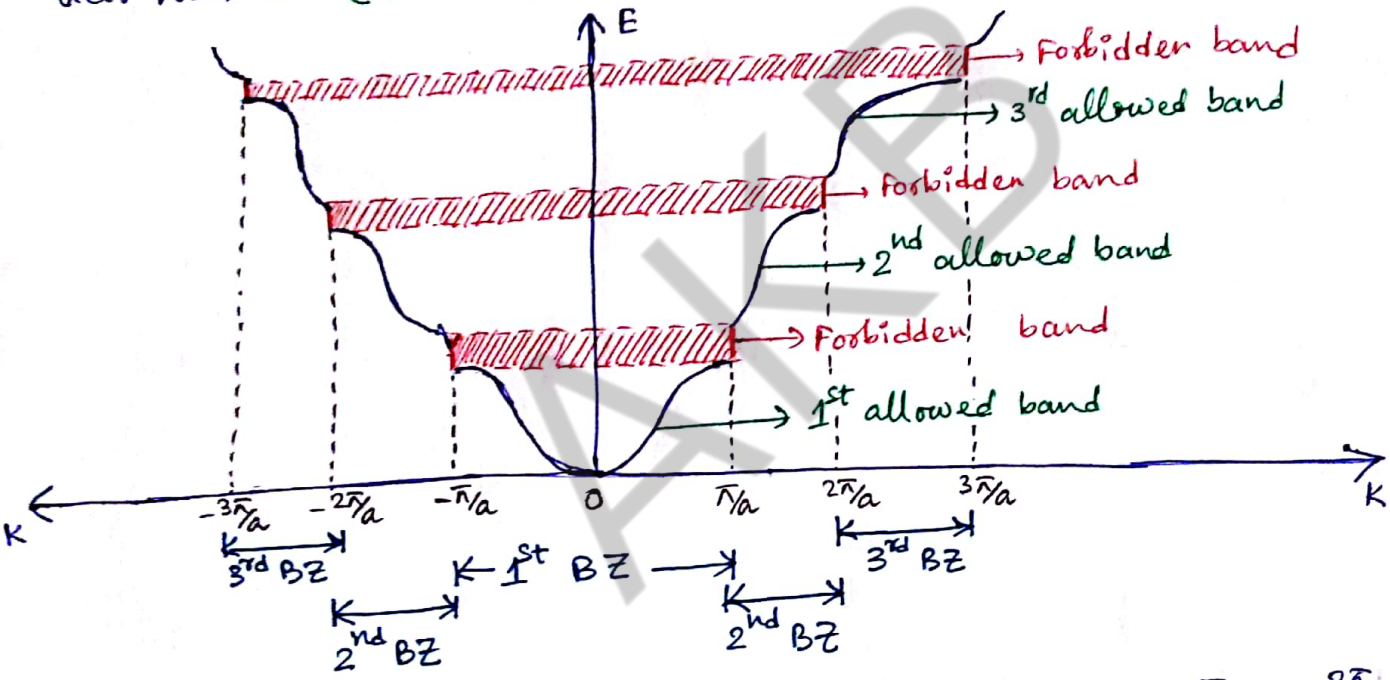
$\therefore ka = n\pi$ or $k = \frac{n\pi}{a}$.

As αa increases, $P\frac{\sin \alpha a}{\alpha a}$ decreases, so the width of allowed energy bands ~~decrease~~ increases & forbidden energy regions become narrower. As P increases, width of allowed energy bands decreases and for $P \to \infty$, they are infinitely thin & independent of k.

for $P \to \infty$, allowed αa are points, $\alpha a = \pm n\pi$

$$\text{or } \alpha^2 = \frac{n^2\pi^2}{a^2} = \frac{2mE}{\hbar^2} \quad \therefore E = \frac{n^2\pi^2\hbar^2}{2ma^2} \neq E(k)$$

Energy level is discrete & the electron is completely bound to their nuclei. (line spectrum) for $P = 0$ (quasi-continuous)



$E = \frac{\hbar^2 k^2}{2m}$ will now have discontinuities at $k = \pm\frac{\pi}{a}, \pm\frac{2\pi}{a}, \pm \cdots$

These k values define the 1st, 2nd, 3rd, ... etc Brillouin zones (BZ)

The curves (bands) are horizontal & at bottom & top, parabolic near top & bottom with curvature in opposite direction, within a band, energy is periodic in k. as $\cos\left(k + \frac{2\pi n}{a}\right)a = \cos ka$ &

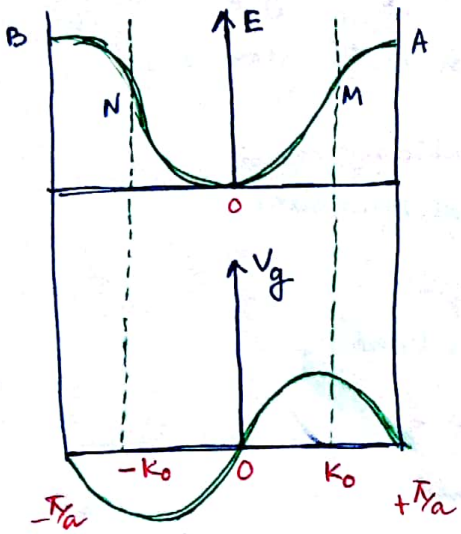
$P\frac{\sin \alpha a}{\alpha a} + \cos \alpha a = \cos ka$ eqn. remains same.

Variation of Energy & velocity with wavevector

According to deBroglie an electron moving with a velocity v is equivalent to a wave packet moving with group velocity = particle velocity $v_g = \frac{d\omega}{dK}$. As energy of particle is $E = \hbar\omega$ or $\omega = \frac{E}{\hbar}$

$\therefore v_g = \frac{d\omega}{dk} = \frac{1}{\hbar}\frac{dE}{dK}$. Now we have for free electron $E = \frac{\hbar^2 K^2}{2m}$.

or $\frac{dE}{dK} = \frac{\hbar^2}{m}K$, $\therefore v_g = \frac{1}{\hbar}\frac{dE}{dK} = \frac{\hbar}{m}K = \frac{p}{m}$.



From band theory $E \not\propto K^2$ but varies as shown. Curve is symmetric about OE axis with points of inflexion at M & N where $\frac{dE}{dK}$ = maximum, so as v (as $v = \frac{1}{\hbar}\frac{dE}{dK}$). At points A, O, B slope $\frac{dE}{dK} = 0$ Similarly variation of v shows that at $K = 0, \pm\frac{\pi}{a}$ velocity of electron is zero. So the velocity is zero at bottom & top of Brillouin zone. At ~~if~~ inflexion point $\pm K_0$ velocity is maximum (free electron velocity)

Effective mass of an electron

The electrons in a crystal are not free but interact with the periodic potential of the lattice. So effective mass is introduced so that that can be taken as free carriers of charge (electron or hole) in our calculation.

If electron moves distance dx by electric field $\mathcal{E}$ in dt time, then $dE = e\mathcal{E}\,dx = e\mathcal{E}v\,dt$ where $v = \frac{dx}{dt}$ = velocity

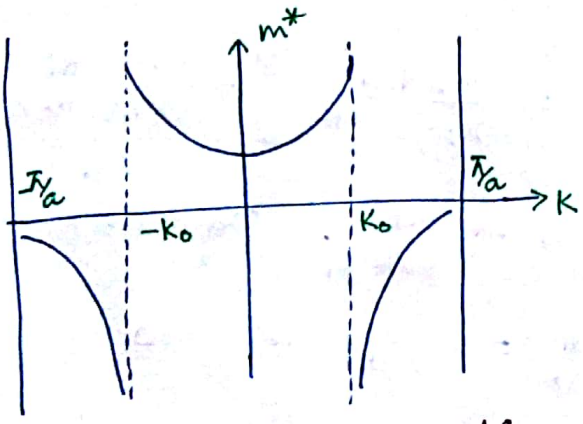
Now $v = \frac{1}{\hbar}\frac{dE}{dK}$ $\therefore dE = \frac{e\mathcal{E}}{\hbar}\frac{dE}{dK}dt$ or $\frac{dK}{dt} = \frac{e\mathcal{E}}{\hbar}$

Now $\hbar K = p$ or $\hbar\frac{dK}{dt} = \frac{dp}{dt} = f = e\mathcal{E}$

Now $a = \frac{dv}{dt} = \frac{1}{\hbar}\frac{d^2E}{dk\,dt} = \frac{1}{\hbar}\frac{d^2E}{dk^2}\frac{dk}{dt} = \frac{1}{\hbar}\frac{d^2E}{dk^2}\frac{F}{\hbar}$

or $\frac{a}{F} = \frac{1}{\hbar^2}\frac{d^2E}{dK^2} = \frac{1}{m^*}$ (using $F = m^*a$)

$\therefore m^* = \frac{\hbar^2}{\frac{d^2E}{dK^2}}$. The ratio of rest mass of free electron m to effective mass in crystal in K-state is $f_K = \frac{m}{m^*} = \frac{m}{\hbar^2}\frac{d^2E}{dK^2}$ which determines the extent to which electron can be thought free. Results of free electron theory can be applied to Band theory with m replaced by m^*.



$E_F = \frac{\hbar^2}{2m^*}\left(\frac{3N}{8\pi V}\right)^{2/3}$

Valence & Conduction band ; Forbidden band

The highest filled energy band which includes electrons shared in covalent bonds or electrons transferred in ionic bonds is known as valence band, denoted by E_V. When the number of valence electrons in one atom is less than the number of electrons to fill the outer orbit of other atom in solid, valence electrons are free to move to form free electron gas. A band of energy from 0 to E_F is formed known as conduction band, denoted by E_C. The forbidden energy region where no electron can remain between E_V & E_C is the forbidden band, denoted by E_g.

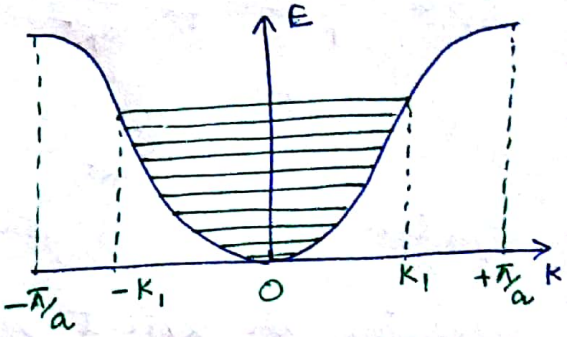
We can distinguish conductors (metals), insulators, semiconductors on the basis of band theory. $f_K = \frac{m}{m^*} = \frac{m}{\hbar^2}\frac{d^2E}{dK^2}$ that measures how much electrons can take part in electric conduction.

Now for a 1-D lattice of periodicity L, $\psi(x+L) = \psi(x)$

$\therefore e^{ik(x+L)}u_k(x+L) = e^{ikx}u_k(x)$

Because of periodicity $u_k(x+L) = u_k(x)$

$\therefore e^{ik(x+L)} = e^{ikx}$ or $K = \frac{2\pi n}{L}$ or $dK = \frac{2\pi}{L} dn$, $dn = \frac{L}{2\pi} dK$



dn is the number of possible states between K & K+dK. Since two electrons occupy each state, effective no. of free electrons in stated region is

$$N_{eff} = 2\int_{-K_1}^{K_1} f_K \, dn = 2\int_{-K_1}^{K_1} \frac{m}{\hbar^2} \frac{d^2E}{dK^2} \frac{L}{2\pi} dK$$

$$= \frac{mL}{\pi\hbar^2}\int_{-K_1}^{K_1} \frac{d^2E}{dK^2} dK = \frac{2mL}{\pi\hbar^2}\int_{0}^{K_1} \frac{d^2E}{dK^2} dK = \frac{2mL}{\pi\hbar^2}\left[\frac{dE}{dK}\right]_0^{K_1} = \frac{2mL}{\pi\hbar^2}\left(\frac{dE}{dK}\right)_{K_1}$$

as $\frac{dE}{dK}$ at $K=0 = 0$. So N_{eff} depends on $\left(\frac{dE}{dK}\right)_{K_1}$. When the band is completely full so atop the band $\frac{dE}{dK} = 0$ $\therefore N_{eff} = 0$.

CW Dispersion relation for a 1D crystal of lattice constant a is $E(K) = E_0 - \alpha - 2\beta \cos ka$ where E_0, α, β constants. Find out the effective mass of the electron at the bottom & top of the band.

We know $m^* = \frac{\hbar^2}{\frac{d^2E}{dK^2}} = \frac{\hbar^2}{2\beta a^2 \cos ka}$

Atop the band $\cos ka = \cos\pi = -1$, bottom of band, $\cos ka = \cos 0 = 1$

$\therefore m^*_{top} = -\frac{\hbar^2}{2\beta a^2}$, $m^*_{bottom} = \frac{\hbar^2}{2\beta a^2}$