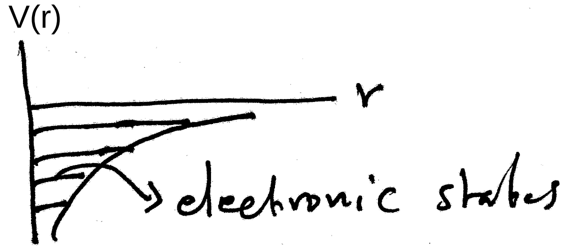
Chapter 7

Non-interacting electrons in a periodic potential

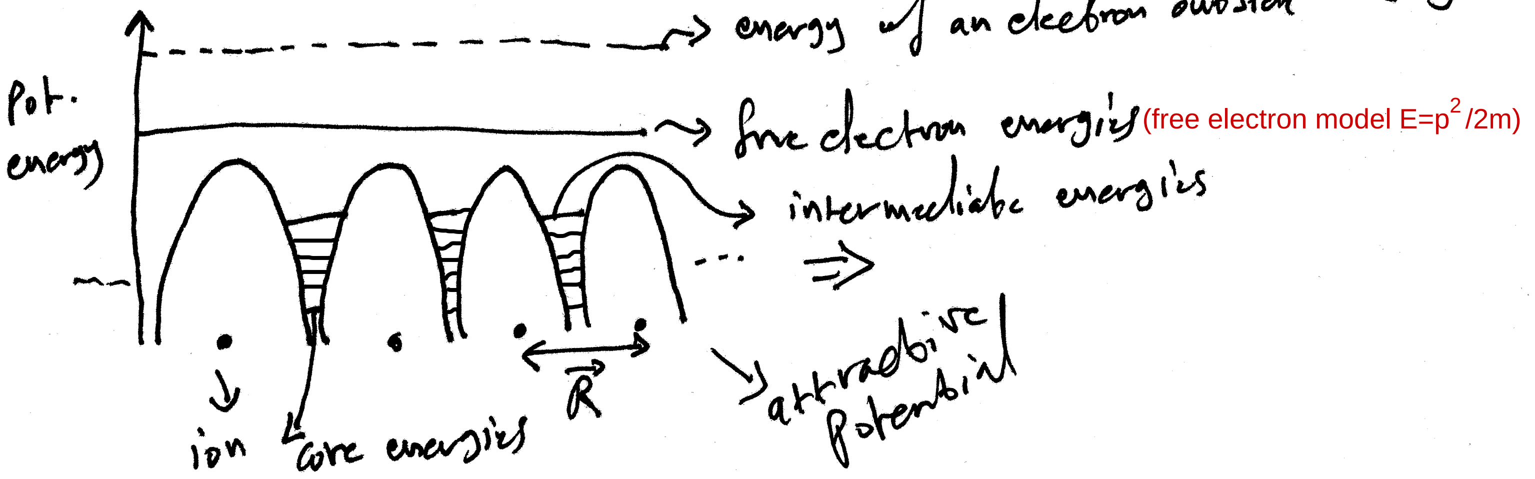
- So far, we have discussed the free electron model, where we ignored both periodic potential of the ions in the crystal and the el-el interactions. Let us discuss the influence of the periodic potential on electronic states. Here we consider a periodic potential $U(\vec{r})$ that has the underlying lattice periodicity of the ions. i.e

$$U(\vec{r}+\vec{R}) = U(\vec{r}) \, ; \quad \text{for all translational vectors } \vec{R} \text{ in the Bravais lattice}$$

Recall that for an electron trapped in the potential well of a positive ion, the potential energy is given by $V = -k_e \frac{Ze^2}{r}$ that can be represented by



- Now putting ions together to form a crystal, we get



Translational symmetry and Bloch's theorem

due to the translational symmetry of the periodic potential, the many electron problem ($\sim 10^{23}/cm^3$) can be reduced to a single electron moving in this periodic potential, so the single electron Hamiltonian H is $H = \frac{P^2}{2m} + U(\vec{r})$.

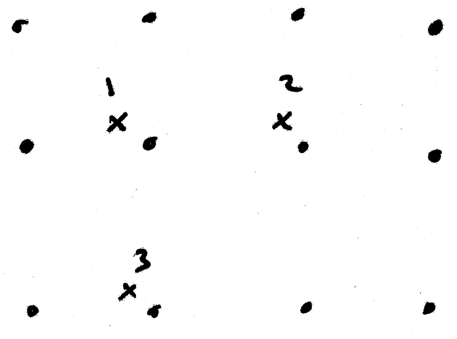
if we denote the single electron wave function by $\psi(\vec{r})$, then the schrodinger eq^n takes the form

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r}) + U(\vec{r})\,\psi(\vec{r}) = \mathcal{E}\,\psi(\vec{r})$$

Now how to solve this eq^n to obtain $\psi(\vec{r})$ and $\mathcal{E}$?

now since $U(\vec{r})$ is Periodic; i.e

$U(1) = U(2) = U(3)$ --- and due to translational symmetry, we expect



$$|\psi(1)|^2 = |\psi(2)|^2 = |\psi(3)|^2$$

i.e $|\psi(r)|^2$ is the same at equivalent positions

but this does not imply that $\psi(\vec{r}) \overset{?}{=} \psi(\vec{r}+\vec{R})$

in fact $\psi(\vec{r}) \neq \psi(\vec{r}+\vec{R})$, they are related by a phase factor i.e $\psi(\vec{r}+\vec{R}) = e^{i\theta(\vec{R})}\psi(\vec{r})$

where $\theta(\vec{R})$ is real

This form satisfies

$$|\psi(\vec{r}+\vec{R})|^2 = |\psi(\vec{r})|^2$$

let us see how to find the phase factor $e^{i\theta}$?

the translational operator $\hat{T}_R$ is defined as $\hat{T}_R \psi(\vec{r}) = \psi(\vec{r}+\vec{R})$

Now consider first an infinitesimal translation of $\delta\vec{R}$, so that

$$\hat{T}_{\delta\vec{R}}\psi(\vec{r}) = \psi(\vec{r}+\delta\vec{R})$$

$$\approx \psi(\vec{r}) + \delta\vec{R}\cdot\vec{\nabla}_r\psi(r) + ---$$

Taylor series expansion about $\vec{r}$

$$= \psi(\vec{r}) + i\vec{k}\cdot\delta\vec{R}\,\psi(\vec{r})$$

$$= [1 + i\vec{k}\cdot\delta\vec{R}]\psi(\vec{r}) \; ;$$

where

$$\vec{p} = \frac{\hbar}{i}\vec{\nabla}_r$$

$$\Rightarrow \vec{\nabla}_r = \frac{i\vec{p}}{\hbar} = i\vec{k}$$

$\vec{k}$: wave number of electron

Now for finite translation of

$\vec{R} = N\delta\vec{R}$; $N \to \infty$, we get

$$\hat{T}_{\vec{R}} = \lim_{N\to\infty}[T(\delta\vec{R})]^N$$

where the finite translation $\vec{R}$ can be represented as a successive infinitesimal translations of $N\delta\vec{R}$

so $\hat{T}_{\vec{R}} = \lim_{N\to\infty}\left[1 + i\frac{\vec{k}\cdot\vec{R}}{N}\right]^N$; now $i\frac{\vec{k}\cdot\vec{R}}{N} \ll 1$

$1 + x \approx e^x$, when $x \ll 1$

$$\approx \left[e^{i\frac{\vec{k}\cdot\vec{R}}{N}}\right]^N = e^{i\vec{k}\cdot\vec{R}}$$

so $\boxed{\psi(\vec{r}+\vec{R}) = e^{i\vec{k}\cdot\vec{R}}\psi(\vec{r})}$ Bloch's theorem --- (1)

Now when $T_{\vec{R}}$ applied on $H\psi(\vec{r})$, we get

$$T_{\vec{R}} H \psi(\vec{r}) = H(\vec{r}+\vec{R})\,\psi(\vec{r}+\vec{R})$$; but $H(\vec{r}+\vec{R}) = H(\vec{r})$ invariant under translation

$$= H(\vec{r})\,\psi(\vec{r}+\vec{R})$$

$$= H\; T_{\vec{R}}\,\psi(r)$$

$\Rightarrow T_R H = H T_R \Rightarrow \hat{H}$ and $\hat{T}_{\vec{R}}$ commute

an alternative way to show that is (see problem 1 in HW#5)

$$[T_R, H] = [\,e^{i\vec{k}\cdot\vec{R}}, H] = [\,e^{i\frac{\vec{p}\cdot\vec{R}}{\hbar}}, \frac{p^2}{2m} + U(\vec{r})]$$

Now $[e^{i\frac{\vec{p}\cdot\vec{R}}{\hbar}}, \frac{p^2}{2m}] = 0$ as $[x, f(x)] = 0$

and $$[T_{\vec{R}}, U(\vec{r})]\psi(r) = T_R\big(U(\vec{r})\psi(r)\big) - U(\vec{r})\,T_{\vec{R}}\,\psi(\vec{r})$$

$$= U(\vec{r}+\vec{R})\,\psi(\vec{r}+\vec{R}) - U(\vec{r})\,\psi(\vec{r}+\vec{R})$$

$$= 0$$, as $U(\vec{r}+\vec{R}) = U(\vec{r})$

So since $\hat{H}$ and $\hat{T}_{\vec{R}}$ commute, then it is possible to find simultaneous eigen states of both $\hat{H}$ and $\hat{T}_{\vec{R}}$. the commutation of the two operators indicates that we need two quantum numbers to fully determine the wave function i.e $\psi_{nk}(\vec{r})$; i.e for each allowed k value, there are n bands associated with it. (to be discussed latter)

k: for translation $\hat{T}$
n: energy $\hat{H}$

furthermore, the translation operators corresponding to translation through different lattice vectors commute; i.e $[T_R, T_{R'}]=0$

proof: $[T_R, T_{R'}]\psi(r) = (T_R T_{R'} - T_{R'} T_R)\psi(r)$

$$= T_R\,\psi(\vec r+\vec R') - T_{R'}\,\psi(\vec r+\vec R)$$

$$= \psi(\vec r+\vec R'+\vec R) - \psi(\vec r+\vec R+\vec R') = 0 \checkmark$$

- <u>An alternative form of Bloch's theorem</u>

We have seen that we need two quantum numbers $(\vec k, n)$ to fully describe the electronic wave function $\psi_{n\vec k}$ with an energy eigenvalues of $\mathcal{E}_n(\vec k)$ or $\mathcal{E}_{n\vec k}$.

we know that for free electron model $\psi \sim e^{i\vec k\cdot\vec r}$; now with adding periodic potential $U(\vec r)$, Bloch proposed that the solution is still plane waves but modulated by a periodic function $u_{\vec k}(\vec r)$

$$\psi_{n\vec k}(\vec r) = e^{i\vec k\cdot\vec r}\,u_{n\vec k}(\vec r) \quad ; \text{where } u_{n\vec k}(\vec r) = u_{nk}(\vec r+\vec R)$$

↓ periodic with periodicity of the lattice $\vec R$

↓ called "Bloch functions"

of course, the first Bloch's form can be derived from the second form

$$\psi_{nk}(\vec r+\vec R) = e^{i\vec k\cdot(\vec r+\vec R)}\,u_{nk}(\vec r+\vec R) = e^{i\vec k\cdot\vec R}\,\underbrace{e^{i\vec k\cdot\vec r}\,u_{nk}(\vec r)}_{\psi_{nk}(\vec r)} = e^{i\vec k\cdot\vec R}\,\psi_{nk}(\vec r)$$

now let us normalize bloch functions $\psi_{nk}(\vec{r})$, where

$\psi_{nk}(\vec{r})$ is normalized over the volume of the sample V

$U_{nk}(\vec{r})$ " " " " " " the unit cell Ω

where $V = N\Omega$, assuming the sample is composed of N unit cells, each of volume Ω, so

using $\int_{\Omega} U^*_{nk}(\vec{r})\, U_{nk}(\vec{r})\, d^3r = 1$, we get

$$1 = \int_V \psi^*_{nk}(\vec{r})\, \psi_{nk}(\vec{r})\, d^3r = A^2 \int_V e^{-i\vec{k}\cdot\vec{r}}\, e^{i\vec{k}\cdot\vec{r}}\, U^*_{nk}(r)\, U_{nk}(r)\, d^3r$$

Assuming $\psi_{nk}(\vec{r}) = A e^{i\vec{k}\cdot\vec{r}}\, U_{nk}(r)$

$$1 = A^2 \int_V U^*_{nk}(r)\, U_{nk}(r)\, d^3r$$

$$= A^2 N \underbrace{\int_{\Omega} U^*_{nk}(r)\, U_{nk}(r)\, d^3r}_{=1} = A^2 N \Rightarrow A = \frac{1}{\sqrt{N}}$$

$$\Rightarrow \psi_{nk}(\vec{r}) = \frac{1}{\sqrt{N}}\, e^{i\vec{k}\cdot\vec{r}}\, U_{nk}(\vec{r})$$; with $\int_{\Omega} |u|^2 d^3r = 1$

or $1 = A^2 N \Omega = A^2 V$, then $A = 1/\sqrt{V}$

$$\psi_{nk}(\vec{r}) = \frac{1}{\sqrt{V}}\, e^{i\vec{k}\cdot\vec{r}}\, U_{nk}(\vec{r})$$; with $\int_{\Omega} |u|^2 d^3r = \Omega$

where always $\int_V |u|^2 d^3r = N \int_{\Omega} |u|^2 d^3r$

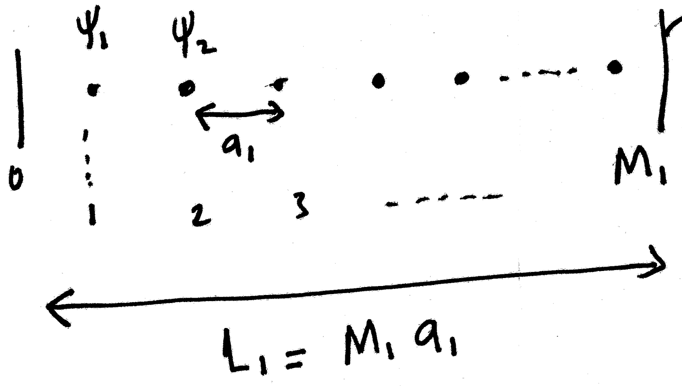
Now the question is what are the allowed values of $\vec{k}$? ← Bloch wave vector

for cubic crystal ($V=L^3$), we can use the previous values for the wave vectors of the free electrons; i.e $\vec{k} = \frac{2\pi}{L}(l_x, l_y, l_z)$ when l_x, l_y, l_z are integers.

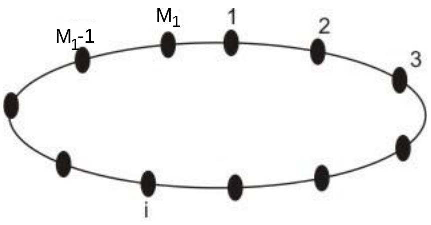
$e^{ik_x L}=1$, periodic BCs as done in chapter 6

however, for non-cubic crystals, let us find the appropriate Boundary conditions that yield the correct values of $\vec{k}$. consider a crystaline solid of finite size which has the same shape as the primitive unit cell of the Bravais lattice but with dimensions: $L_1 = M_1 a_1$; $L_2 = M_2 a_2$; and $L_3 = M_3 a_3$. the solid then contains $M = M_1 M_2 M_3$ unit cells (lattice points).

let us focus on the $\vec{a}_1$ direction



each lattice point represents a unit cell



Note that $\psi_2 = e^{ik_1 a}\psi_1$; so not Periodic over one unit cell, but ψ is Periodic over the size of the crystal; i.e if we wrap the 1D crystal into the shape of a circle, then

$$\psi_{k_x}(x+L_1) = \psi_{k_x}(x)$$

$$\Rightarrow \psi_{k_x}(x+M_1 a_1) = \psi_{k_x}(x)$$

now we know that from Bloch theorem that

$$\psi_{k_x}(x+L_1) = e^{ik_xL_1}\psi_{k_x}(x) \equiv \psi_{k_x}(x) \Rightarrow e^{ik_xL_1} = 1$$

or $\cos(k_xL_1) = 1$

$\Rightarrow k_xL_1 = 2\pi m_1$; m_1 is integer

$$k_x = \frac{2\pi m_1}{L_1} = \frac{2\pi}{M_1 a_1} m_1 = \frac{2\pi}{a_1}\frac{m_1}{M_1} = b_1\frac{m_1}{M_1}$$

where $m_1 = 0, 1, 2, \ldots, M_1-1$, we get the similarly along the $\vec{a}_2$ and $\vec{a}_3$ directions, we get the B.Cs, that allowed values of k consistent with B.Cs, that takes the form $\vec{k} = \frac{m_1}{M_1}\vec{b}_1 + \frac{m_2}{M_2}\vec{b}_2 + \frac{m_3}{M_3}\vec{b}_3$; where $\vec{b}_1, \vec{b}_2, \vec{b}_3$ are the primitive vectors of the Reciprocal lattice that satisfies $\vec{b}_i \cdot \vec{a}_j = 2\pi\delta_{ij}$.

in general; $\vec{k} = \sum_{l=1}^{3}\frac{m_l}{M_l}\vec{b}_l$; $0 \leq m_l < M_l$

$m_1 : 0, 1, 2, \ldots M_1-1$
$m_2 : 0, 1, 2, \ldots M_2-1$
$m_3 : 0, 1, 2, \ldots M_3-1$

since $M_l \gg 1$, the $\vec{k}$-vectors form a dense set of point in reciprocal space.

to avoid over-counting, $\vec{k}$ is usually chosen to be in the 1st B.Z. So there are $M = M_1M_2M_3$ allowed $\vec{k}$'s in the first B.Z, which is the same as the number of unit cells in the direct crystal lattice
(or LPs)

Crystal momentum:

for free electrons (with $U(\vec r)=0$), $\hat{\vec p}$ and $\hat H = \frac{\hat p^2}{2m}$ commute, hence $\psi_k(\vec r)$ is a simultaneous eigenfunctio of both $\hat H$ and $\hat p$ with an eigenvalues of ε and $\hbar k$ with $\hbar\vec k$ being the momentum of the electron. But for Bloch electrons, $[\hat p, \hat H] \neq 0$; i.e with

$$\hat p = -i\hbar\nabla \Rightarrow \hat p\,\psi_{nk}(\vec r) = -i\hbar\vec\nabla\psi_{nk}(\vec r)$$

$$= -i\hbar\vec\nabla\left(e^{i\vec k\cdot\vec r}u_{nk}(\vec r)\right)$$

$$= \hbar\vec k\,\psi_{nk}(\vec r) + e^{i\vec k\cdot\vec r}(-i\hbar)\vec\nabla u_{nk}(\vec r)$$

so $\psi_{nk}(\vec r)$ is Not an eigenstate of $\hat p$. So $\hbar\vec k$ is usually called the crystal momentum but the electron momentum.

Q: why do we need to consider only 1st B.Z ?

This question should be discussed after next section (Fourier analysis)

$$\psi_{n\vec k}(\vec r) = \sum_{K}\psi(\vec k-\vec K)\,e^{i(\vec k-\vec K)\cdot\vec r}$$

so $\psi_{n,\vec k+\vec K'}(\vec r) = \sum_{K}\psi(\vec k+\vec K'-\vec K)\,e^{i(\vec k+\vec K'-\vec K)\cdot\vec r}$; let $K'' = K - K'$

$$= \sum_{K''}\psi(\vec k-\vec K'')\,e^{i(\vec k-\vec K'')\cdot\vec r}$$; K'' is dumy

$$= \psi_{n\vec k}$$

hence ⇒ the energy eigenvalue of the state $\psi_{n\vec k}(\vec r)$ is the same as that of $\psi_{n\vec k+K}(\vec r)$ ⇒ $\varepsilon_{n\vec k} = \varepsilon_{n\vec k+\vec K}$

$$\varepsilon_n(\vec k) = \varepsilon_n(\vec k+\vec K)$$

Fourier analysis of Bloch theorem:

because $U(\vec{r})$ is periodic for all lattice vectors $\vec{R}$, then it can be represented (expanded) into plane waves with wavevectors that are reciprocal lattice wavevectors only.

i.e $U(\vec{r}) = \sum_{\vec{K}} \underset{\overset{\downarrow}{U(\vec{K})}}{U_K}\, e^{i\vec{K}\cdot\vec{r}}$; since $U(\vec{r})$ is real, then $U_{-K} = U_K^*$

i.e $U(-K) = U^*(K)$

(see problem 2 in HW#5)

to find $U(K)$, multiply by $e^{-i\vec{K}'\cdot\vec{r}}$ and integrate over d^3r (total volume)

$$\int_V d^3\vec{r}\, U(\vec{r})\, e^{-i\vec{K}'\cdot\vec{r}} = \sum_K U(K) \underbrace{\int d^3\vec{r}\, e^{i(\vec{K}-\vec{K}')\cdot\vec{r}}}_{V\,\delta_{K,K'}}$$

where, $\int_0^L dx\, e^{-ik'x} e^{ikx} = L\delta_{k,k'}$ | $= V \sum_K U(K)\, \delta_{K,K'}$ $= V\, U(K')$

let $K' \to K$, then

$$U(K) = U_K = \frac{1}{V}\int_V d^3\vec{r}\, U(\vec{r})\, e^{-i\vec{K}\cdot\vec{r}}$$

$$= \frac{1}{V}\, N \int_\Omega d^3\vec{r}\, U(\vec{r})\, e^{-i\vec{K}\cdot\vec{r}} = \frac{1}{\Omega}\int_{\underset{\overset{\downarrow}{\text{unit cell}}}{\Omega}} d^3\vec{r}\, U(\vec{r})\, e^{-i\vec{K}\cdot\vec{r}}$$

$V = N\Omega$

similarly, $\psi(\vec{r})$ can be expanded into plane waves (Fourier components) as

$\psi(\vec{r}) = \frac{1}{V}\sum_q \psi(q)\, e^{i\vec{q}\cdot\vec{r}}$; with $\psi(q) = \int_V d^3\vec{r}\, \psi(\vec{r})\, e^{-i\vec{q}\cdot\vec{r}}$

Now the expansion coefficients $\psi(q)$ in the bloch functions are found by substituting the fourier series of $U(\vec r)$ and $\psi(\vec r)$ into the schrodinger equation

$$H\psi(\vec r) = \varepsilon\,\psi(\vec r) \Rightarrow (H-\varepsilon)\,\psi(\vec r)=0 \Rightarrow \left(\frac{p^2}{2m}+U(r)-\varepsilon\right)\psi(\vec r)=0$$

$$\Rightarrow\left[-\frac{\hbar^2\nabla_r^2}{2m}+U(\vec r)-\varepsilon\right]\psi(\vec r)=0$$

$$\Rightarrow\left[-\frac{\hbar^2\nabla_r^2}{2m}+U(\vec r)-\varepsilon\right]\frac{1}{V}\sum_{q'}\psi(q')\,e^{i\vec q'\cdot\vec r}=0$$

now $\nabla_r^2\sum_{q'}\psi(q')\,e^{i\vec q'\cdot\vec r} = \sum_{q'} -(q')^2\,\psi(q')\,e^{i\vec q'\cdot\vec r}$

so
$$\frac{1}{V}\sum_{q'}\left(\frac{\hbar^2 q'^2}{2m}-\varepsilon+U(\vec r)\right)\psi(q')\,e^{i\vec q'\cdot\vec r}=0$$

$$\frac{1}{V}\sum_{q'}\left(\varepsilon^0_{q'}-\varepsilon+U(\vec r)\right)\psi(q')\,e^{i\vec q'\cdot\vec r}=0$$

$$\frac{1}{V}\sum_{q'}\left[(\varepsilon^0_{q'}-\varepsilon)\,e^{i\vec q'\cdot\vec r}+U(\vec r)\,e^{i\vec q'\cdot\vec r}\right\}\psi(q')=0$$

$$\frac{1}{V}\sum_{q'}\left[(\varepsilon^0_{q'}-\varepsilon)\,e^{i\vec q'\cdot\vec r}+\sum_{K}U_K\,e^{i(\vec K+\vec q')\cdot\vec r}\right\}\psi(q')=0$$

now multiply by $e^{-i\vec q\cdot\vec r}$ and integrate over V $\int_V d^3\vec r$

$$\frac{1}{V}\sum_{q'}\left[\int_V(\varepsilon^0_{q'}-\varepsilon)\,e^{i(\vec q'-\vec q)\cdot\vec r}\,d^3\vec r+\sum_{K}U_K\int_V d^3\vec r\,e^{i(\vec K+\vec q'-\vec q)\cdot\vec r}\right\}\psi(q')=0$$

$$\frac{1}{V}\sum_{q'}\left[(\varepsilon^0_{q'}-\varepsilon)\underbrace{\int_V e^{i(\vec q'-\vec q)\cdot\vec r}\,d^3\vec r}_{V\,\delta_{q,\,q'}}+\sum_{K}U_K\underbrace{\int_V e^{i(\vec K+\vec q'-\vec q)\cdot\vec r}\,d^3\vec r}_{V\,\delta_{q,\,K+q'}}\right\}\psi(q')=0$$

$$\sum_{q'} (\varepsilon^0_{q'} - \varepsilon)\,\psi(q')\,\delta_{\vec q,\vec q'} + \sum_{K} U_K \sum_{q'} \delta_{\vec q,\vec K+\vec q'}\,\psi(q') = 0$$

$$(\varepsilon^0_q - \varepsilon)\,\psi(\vec q) + \sum_K U_K\,\psi(\vec q - \vec K) = 0 \qquad \Big\} \Rightarrow K + q' = q \;\Rightarrow\; \vec q\,' = \vec q - \vec K$$

relabel $K \to K'$ $\Rightarrow$

Schrodinger eqn in reciprocal space

$$(\varepsilon^0_q - \varepsilon)\,\psi(\vec q) + \sum_{K'} U_{K'}\,\psi(\vec q - \vec K') = 0 \quad ----- \quad (2)$$

This is the central equation. it represents ∞ infinite # of equations that can be solved to find the coefficients $\psi(\vec q)$. practically, $\vec k$ is chosen to be in the 1st BZ (reduce zone), and when $\vec k$ happens to be outside 1st BZ, it can be carried back into the 1st BZ by subtracting a suitable reciprocal lattice vector $\vec q \to \vec k - \vec K$, where $\vec k$ is in the first BZ. equation (2) reads now

$$\left[\frac{\hbar^2}{2m}(\vec k - \vec K)^2 - \varepsilon\right]\psi(\vec k - \vec K) + \sum_{K'} U_{K'}\,\psi(\vec k - \vec K - \vec K') = 0$$

$$\Rightarrow \psi(\vec k - (\vec K + \vec K')) = \psi(\vec k - \vec K'')$$

$$\left[\frac{\hbar^2}{2m}(\vec k - \vec K)^2 - \varepsilon\right]\psi(\vec k - \vec K) + \sum_{K''} U_{K''-K}\,\psi(k - K'') = 0 \quad \text{where } K'' = \underbrace{K + K'}$$

the sum is also reciprocal lattice vector

relabel $K'' \to K'$

$$\left[\frac{\hbar^2}{2m}(\vec k - \vec K)^2 - \varepsilon\right]\psi(\vec k - \vec K) + \sum_{K'} U_{K'-K}\,\psi(k - K') = 0 \quad ---- \quad (2)$$

and for $\vec k$ to be in 1st B.Z $\vec q \to \vec k - \vec K$

Now $\psi(\vec r) = \frac{1}{V}\sum_q \psi(q)\, e^{i\vec q\cdot\vec r}$

$$= \frac{1}{V}\sum_K \underbrace{\psi(\vec k - \vec K)}\, e^{i(\vec k - \vec K)\cdot\vec r}$$

These coefficients are obtained by solving eqn (2)

Note that using the second form of Bloch theorem

$\psi_k(\vec{r}) = \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{r}} u_k(\vec{r})$, the last form of $\psi(\vec{r})$ can be written as

$$\psi_k(\vec{r}) = \frac{1}{V} e^{i\vec{k}\cdot\vec{r}} \underbrace{\sum_{\vec{K}} \psi(\vec{k}-\vec{K}) e^{-i\vec{K}\cdot\vec{r}}}_{u_k(r) \text{ which is periodic}} \quad --- (3)$$

Note: can also be written as $\psi(\vec{k}+\vec{K}) e^{i(\vec{k}+K}$

a part from this factor

so ← check

$$u_k(\vec{r}+\vec{R}) = \sum_{K} \psi(k-K) e^{-i\vec{K}\cdot(\vec{r}+\vec{R})} = \sum_{K} \psi(k-K) e^{-i\vec{K}\cdot\vec{R}} e^{-i\vec{K}\cdot\vec{r}}$$

$$= e^{-i\vec{K}\cdot\vec{R}} \sum_{K} \psi(k-K) e^{-i\vec{K}\cdot\vec{r}} = e^{-i\vec{K}\cdot\vec{R}} u_k(r)$$

see page 8 in lecture notes of chapter 3...

but $e^{-i\vec{K}\cdot\vec{R}} = 1 \Rightarrow$ so $u_k(\vec{r}+\vec{R}) = u_k(\vec{r})$

- for a fixed value of $\vec{k}$, equation (2) represents an infinite set of coupled equations that can be used to find the coefficients $\psi(\vec{k}-\vec{K})$ and the eigenvalues for each $E_n(\vec{k})$ or $E_{n\vec{k}}$; where n is a band index. i.e for each k in 1st B.Z, there are many bands associated with it labeled by $\underline{\underline{n}}$, so wave functions and eigenvalues are labeled as $\psi_{nk}(\vec{r})$ and E_{nk}. practically, eqn (2) can be written in a matrix form with

practically, eqn 2 is truncated to finite number of terms

$$K, K' = 0, \pm K_1, \pm K_2, \pm K_3, ---$$
$$= 0, +K_1, -K_1, +K_2, -K_2, +K_3, -K_3, ---$$

So taking $K, K' = 0, \pm K_1$ will produce 3×3 matrix

" " $= 0, \pm K_1, \pm K_2$, ---- 5×5 " , and so on

You can also take 2×2, 4×4. However, bigger matrix, Results are more accurate

- let us try $K, K' = 0, -K_1, +K_1$

$\boxed{K=0} \Rightarrow K' = 0, -K_1, +K_1$

$$\left(\frac{\hbar^2k^2}{2m} - \varepsilon\right)\psi(k) + U_0\,\psi(k) + U_{K_1}\psi(k-K_1) + U_{-K_1}\psi(k+K_1) = 0 \quad \text{---} (1)$$

$\boxed{K=-K_1} \Rightarrow K' = 0, -K_1, +K_1$

$$\left(\frac{\hbar^2}{2m}(k+K_1)^2 - \varepsilon\right)\psi(k+K_1) + U_{K_1}\psi(k) + U_{2K_1}\psi(k-K_1) + U_0\,\psi(k+K_1) = 0 \quad \text{---} (2)$$

$\boxed{K=+K_1} \Rightarrow K' = 0, -K_1, +K_1$

$$\left(\frac{\hbar^2}{2m}(k-K_1)^2 - \varepsilon\right)\psi(k-K_1) + U_{-K_1}\psi(k) + U_0\,\psi(k-K_1) + U_{-2K_1}\psi(k+K_1) = 0 \quad \text{---} (3)$$

$$\begin{pmatrix} \frac{\hbar^2k^2}{2m} - \varepsilon + U_0 & U_{-K_1} & U_{K_1} \\ U_{K_1} & \frac{\hbar^2}{2m}(k+K_1)^2 - \varepsilon + U_0 & U_{2K_1} \\ U_{-K_1} & U_{-2K_1} & \frac{\hbar^2}{2m}(k-K_1)^2 - \varepsilon + U_0 \end{pmatrix} \begin{pmatrix} \psi(k) \\ \psi(k+K_1) \\ \psi(k-K_1) \end{pmatrix} = 0 \quad \text{---} (4)$$

Note that $U^*_{K_1} = U_{-K_1}$ and $U^*_{2K_1} = U_{-2K_1}$

or $U_{K1} = U^*_{-K1}$

$U_{2K1} = U^*_{-2K1}$

also the diagonal elements are given by

$\frac{\hbar^2}{2m}(\vec{k} - \vec{K})^2 - \varepsilon + U_0$; where $K = 0, -K_1, +K_1$,

empty lattice approximation: (ELA)

also called zero-th order perturbation, meaning that the potential $U(\vec{r})$ is infinitly weak such that it can be neglected; i.e $U(\vec{r}) \rightarrow 0$. in this case all elements of U_K vanish leaving the matrix (H) diagonal with 3 dispersion relations $\varepsilon_q = \frac{\hbar^2 q^2}{2m}$, where q can always be brought to 1st B.Z by using $\vec{q} = \vec{k} + \vec{K}$;

with $K = \frac{2\pi}{a} n$; $n = 0, \pm 1, \pm 2, ---$ for 1D lattice

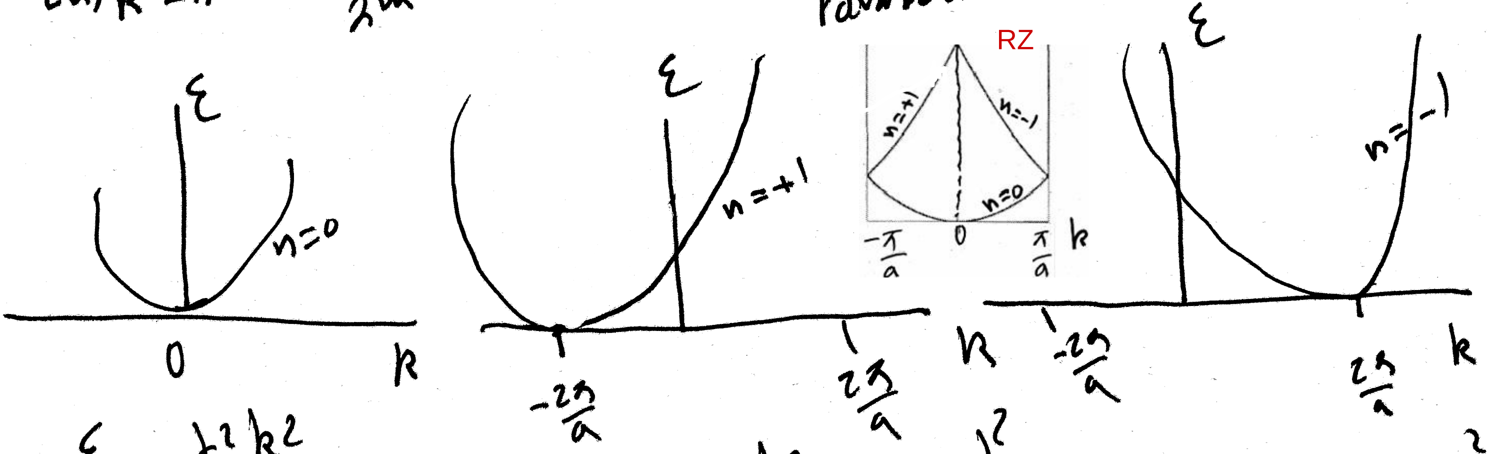
so $\varepsilon_{n,\vec{k}} = \frac{\hbar^2 k^2}{2m}$; for $K = 0$; i.e with $n = 0$

$\varepsilon_{n,\vec{k}+\vec{K}} = \frac{\hbar^2}{2m}(k+K)^2$; for $K = \frac{2\pi}{a}$; $n = +1$

Parabola centered at $\vec{K} = -\frac{2\pi}{a}$

and $\varepsilon_{n,\vec{k}-\vec{K}} = \frac{\hbar^2}{2m}(k-K)$; for $K = -\frac{2\pi}{a}$; $n = -1$

Parabola centered at $K = \frac{2\pi}{a}$



$\varepsilon_{nk} = \frac{\hbar^2 k^2}{2m}$

$K = 0$

$\varepsilon_{n,\vec{k}+\vec{K}} = \frac{\hbar^2}{2m}\left(k + \frac{2\pi}{a}\right)^2$

$K = \frac{2\pi}{a}$

$\varepsilon_{n,\vec{k}-\vec{K}} = \frac{\hbar^2}{2m}\left(k - \frac{2\pi}{a}\right)^2$

$K = -\frac{2\pi}{a}$

the band structure of empty lattice model can be derived directly from the central equation

$$\left[\frac{\hbar^2}{2m}(k-K)^2-\varepsilon\right]\psi(k-K)+\sum_{K'}U_{K'-K}\,\psi(k-K')=0$$

, now for empty lattice model $(U=0)$ ⇒ the eqn reads now

$$\left[\frac{\hbar^2}{2m}(k-K)^2-\varepsilon\right]\psi(k-K)=0$$

, but $\psi(k-K)\neq 0$ ⇒

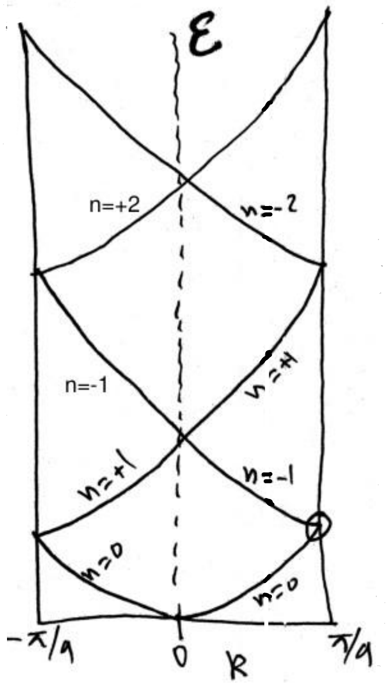
$$\frac{\hbar^2}{2m}(k-K)^2-\varepsilon=0 \Rightarrow \varepsilon=\frac{\hbar^2}{2m}(k-K)^2$$

now the reciprocal lattice vector $\vec{K}=\frac{2\pi}{a}n$, $n=0,\pm1,\pm2,----$

⇒ writing $\varepsilon=\frac{\hbar^2}{2m}\left(k+\frac{2\pi}{a}n\right)^2$, $n=0,\pm1,\pm2,---$

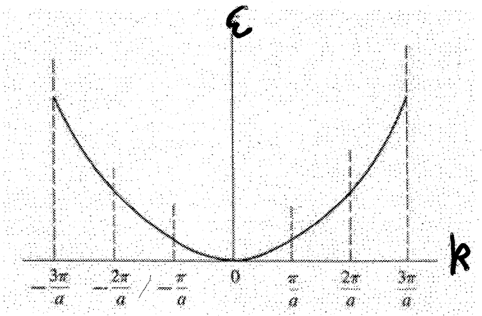
$\therefore$ $\varepsilon=\frac{\hbar^2}{2m}\left(k+\frac{2\pi}{a}n\right)^2$; $n=0,\pm1,\pm2,---$

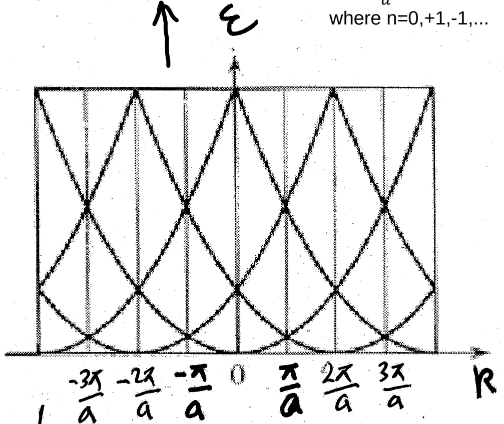
usually, the band structure is represented by 3 schemes:
extended, repeated, and reduced as shown

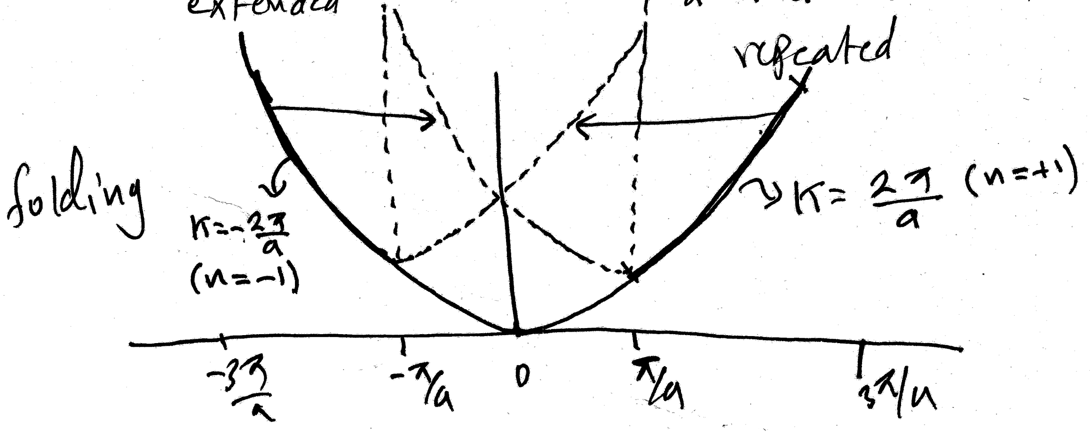


Reduced

parabolas centered at $K=\frac{2\pi}{a}n$
where n=0,+1,-1,...







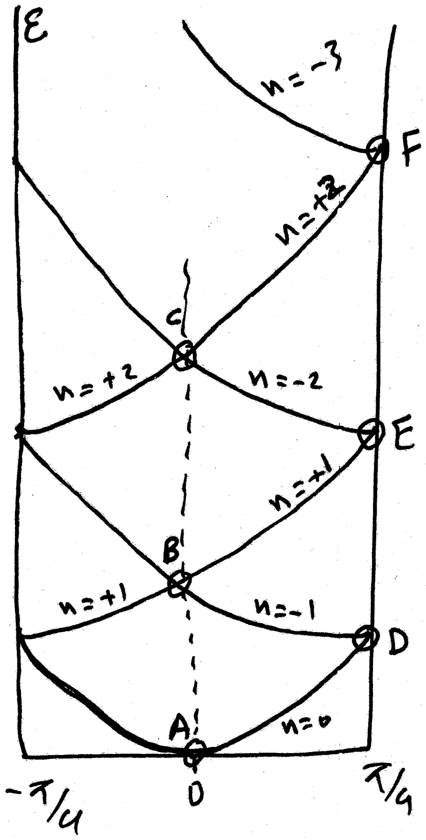
to plot energy bands of ELA, see page 22 of this lecture notes

Extended Zone: free electron parabola over all k-space

Repeated Zone: " " " repeated in each Brillouin Zone

reduced Zone: All bands folded into the 1^{st} B.Z $[-\frac{\pi}{a}, \pi/a]$

let us find some values on the reduced zone for the 1D lattice



i) at $k=0$, $\Rightarrow \mathcal{E}_n = \frac{\hbar^2}{2m}\left(k + \frac{2\pi}{a}n\right)^2$

$$= \frac{\hbar^2}{2m}\left(\frac{2\pi}{a}n\right)^2$$

for $n=0 \Rightarrow \mathcal{E}_0 = 0$, point A in figure

for $n=\pm1 \Rightarrow \mathcal{E}_{\pm1} = \frac{\hbar^2}{2m}\left(\frac{2\pi}{a}\right)^2 = \frac{2\pi^2\hbar^2}{ma^2}$ point B

$\Rightarrow$ the two bands have same energy (degenerate)

for $n=\pm2$, $\mathcal{E}_{\pm2} = \frac{\hbar^2}{2m}\left(\frac{4\pi}{a}\right)^2 = 4\,\frac{2\pi^2\hbar^2}{ma^2}$ point C -- and so on

$\Rightarrow$ degenerate $(0,1,4,--)$ in unit of $\frac{2\pi^2\hbar^2}{ma^2}$

ii) at $k = \pi/a \Rightarrow \mathcal{E}_n = \frac{\hbar^2}{2m}\left(\frac{\pi}{a} + \frac{2\pi n}{a}\right)^2 = \frac{\hbar^2}{2m}\left(\frac{\pi(1+2n)}{a}\right)^2$

for $n=0 \Rightarrow \mathcal{E}_0 = \frac{\hbar^2\pi^2}{2ma^2}$, for $n=-1 \Rightarrow \mathcal{E}_{-1} = \frac{\hbar^2\pi^2}{2ma^2} = \mathcal{E}_0$

because the two bands $(n=0, n=-1)$ intersect at point D

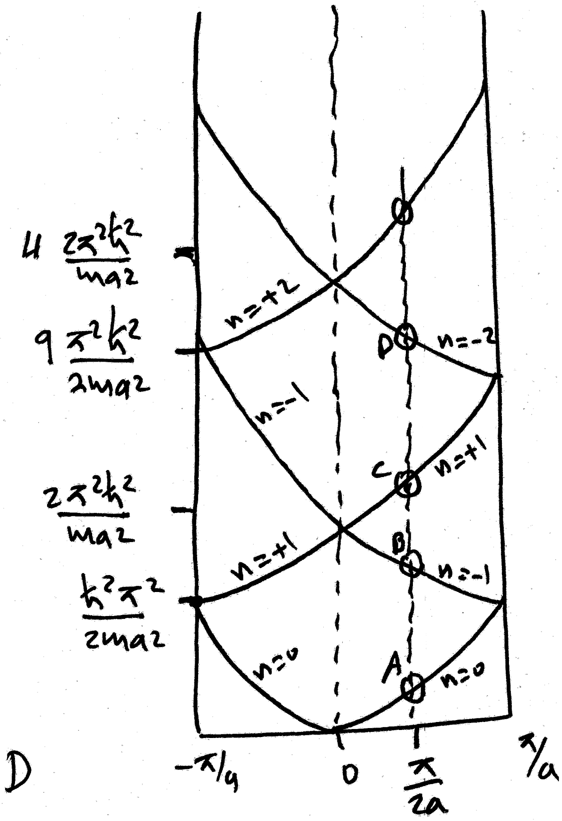
and for $n=+1$ and $n=-2 \Rightarrow \mathcal{E}_{+1} = \mathcal{E}_{-2} = 9\,\frac{\pi^2\hbar^2}{2ma^2}$ again, the two bands $(n=+1, n=-2)$ intersect at point E.

for $n=+2$ and $n=-3 \Rightarrow \mathcal{E}_{+2} = \mathcal{E}_{-3} = 25\,\frac{\pi^2\hbar^2}{2ma^2}$ point F

$\Rightarrow (1,9,25,--)$ in unit of $\frac{\pi^2\hbar^2}{2ma^2}$

iii) $k = \pi/2a \Rightarrow \varepsilon_n = \frac{\hbar^2}{2m}\left(\frac{\pi}{2a} + \frac{2\pi}{a}n\right)^2$

$$= \frac{\hbar^2}{2m}\left(\frac{\pi(1+4n)}{2a}\right)^2$$



for $n=0 \Rightarrow \varepsilon_0 = \frac{\hbar^2}{2m}\left(\frac{\pi}{2a}\right)^2$ point A

for $n=-1 \Rightarrow \varepsilon_{-1} = \frac{\hbar^2}{2m}\left(\frac{3\pi}{2a}\right)^2$ point B

for $n=+1 \Rightarrow \varepsilon_{+1} = \frac{\hbar^2}{2m}\left(\frac{5\pi}{2a}\right)^2$ point C

for $n=-2 \Rightarrow \varepsilon_{-2} = \frac{\hbar^2}{2m}\left(\frac{7\pi}{2a}\right)^2$ point D

and so on.

The eigenstates are plane waves $\psi_{nk}(x) = e^{i(k+\frac{2\pi}{a}n)x}$

- at $k=0, n=0 \Rightarrow \psi_{0,0}(x) = 1$ = constant wavefunction
- at $k=\pi/a$, there are two degenerate bands ($n=0, n=-1$) having the same energy $\frac{\hbar^2\pi^2}{2ma^2}$; the eigenstates are

$n=0, \ \psi_{0,\pi/a}(x) = e^{i\frac{\pi}{a}x}$

$n=-1, \ \psi_{-1,\pi/a}(x) = e^{i(\pi/a - \frac{2\pi}{a})x} = e^{-i\frac{\pi}{a}x}$

- at $k=0$, again the two bands ($n=+1, n=-1$) are degenerate

$\Rightarrow \psi_{+1,0}(x) = e^{i\frac{2\pi}{a}x}, \quad \psi_{-1,0}(x) = e^{-i\frac{2\pi}{a}x}$, and so on

Note that there is a degeneracy at $k=\pm\pi/a$; both $k=+\frac{\pi}{a}$ and $k=-\frac{\pi}{a}$ are equivalent, so let us work on $k=+\pi/a$ only. So at $k=+\frac{\pi}{a}$, the two bands $n=0$ and $n=-1$ have same energy. Similarly at $k=0$, the two bands $n=+1$ and $n=-1$ are degenerate.

The number of allowed k-states in each band, n, of the FBZ for 1D lattice is N (to be shown latter in page 22 of this lecture notes)

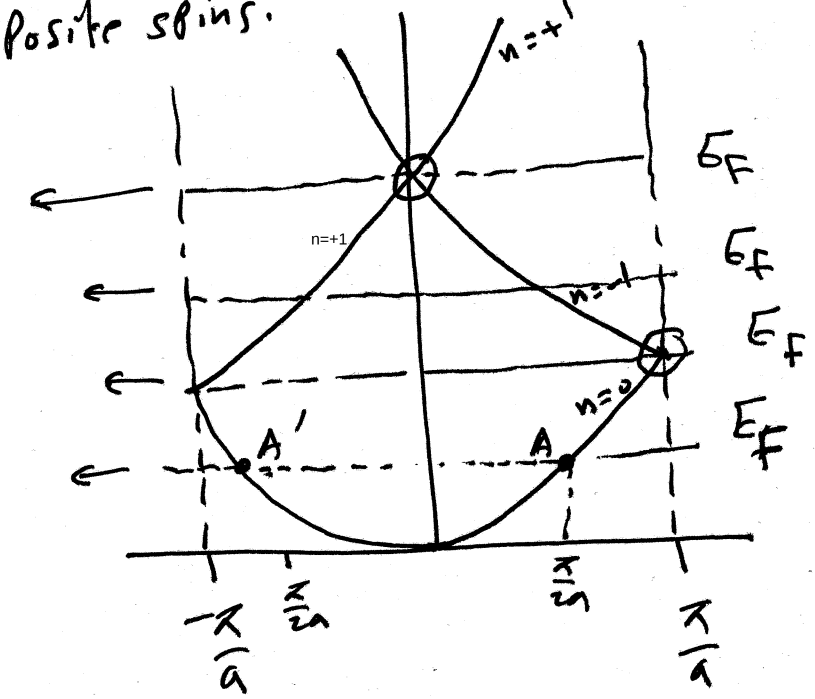
- Note that assuming, there is 1e/unit cell, then the $n=0$ band is half-filled, meaning the fermi level is as shown in the figure. Recall that each state can be filled with two electrons with opposite spins.

first two bands are filled 4e/cell

$n=0$ is filled and ½ of $n=1$ are filled 3e/cell

1st band is filled 2e/cell

1st band is ½ filled 1e/cell



- Note that if the # of electrons/cell is even we always hit the degeneracy points $k=\pm\pi/a$
- Note that the points A and A' have a trivial degeneracy due to time reversal, which we don't consider as a real degeneracy. We see that E_F of the $n=0$ band is

$$E_F=\frac{\hbar^2}{2m}\left(\frac{\pi}{2a}\right)^2$$ w.r.t the bottom of the band.

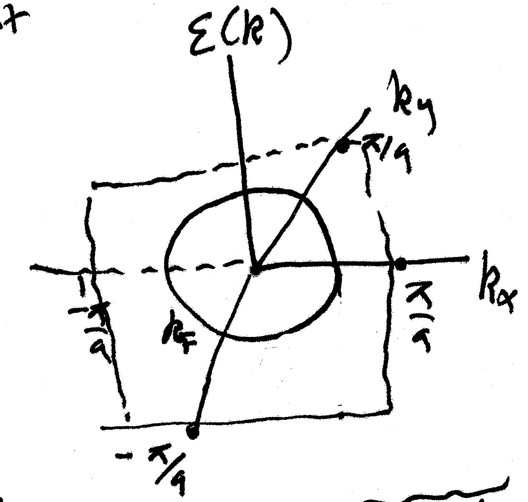
calculated over one unit cell

Now for 1D lattice with 1e/cell, the density n is $n=\frac{N}{a}$; but $N=1 \Rightarrow n=\frac{1}{a} \Rightarrow E_F=\frac{\hbar^2\pi^2}{8m}n^2$

here n is density not band index

$E_F \propto n^2$

$E=\frac{\hbar^2k^2}{2m}$, E_F occurs at $k=\frac{\pi}{2a}$, then for 2D lattice with spacing a, the 1st B.Z is a square, so assuming 1e/cell, a circle with radius k_F will be filled; i.e half of the 1st B.Z will be filled ⇒ area of circle = half area of square of side 2Pi/a



$$\pi k_F^2 = \frac{1}{2}\left(\frac{2\pi}{a}\right)^2 = \frac{1}{2}\,\frac{4\pi^2}{a^2} \Rightarrow k_F^2 = \frac{2\pi}{a^2}$$

$$\Rightarrow E_F = \frac{\hbar^2}{2m}k_F^2 = \frac{\hbar^2}{2m}\,\frac{2\pi}{a^2} = \frac{\hbar^2\pi}{ma^2} \;;$$

n = N/A

n = 1/a^2

Fermi surface is a circle with radius k_F

$$\Rightarrow E_F = \frac{\hbar^2\pi}{m}n \Rightarrow E_f \propto n$$

The number of allowed k-states in each band, n, of the FBZ for 2D square lattice is N (to be shown latter in page 23 of this lecture notes)

for 3D, lattice with spacing a, the 1st B.Z is a cube and for the n=0 band, half of the 1st B.Z will be filled so

$$\frac{4}{3}\pi k_F^3 = \frac{1}{2}\left(\frac{2\pi}{a}\right)^3 \Rightarrow k_F^3 = \frac{3\pi^2}{a^3},\; k_F = \left(\frac{3\pi^2}{a^3}\right)^{1/3}$$

$$\Rightarrow E_F = \frac{\hbar^2}{2m}k_F^2 = \frac{\hbar^2}{2m}\left(\frac{3\pi^2}{a^3}\right)^{2/3} \;; \quad n = \frac{1}{a^3}$$ = N/V

$$= \frac{\hbar^2}{2m}(3\pi^2)^{2/3}\, n^{2/3} \Rightarrow E_F \propto n^{2/3}$$

Fermi surface is a sphere with radius k_F

Note that for empty lattice approximation (free electron model), we have $H_0 = -\frac{\hbar^2\nabla^2}{2m}$ and $U(\vec{r}) = 0$

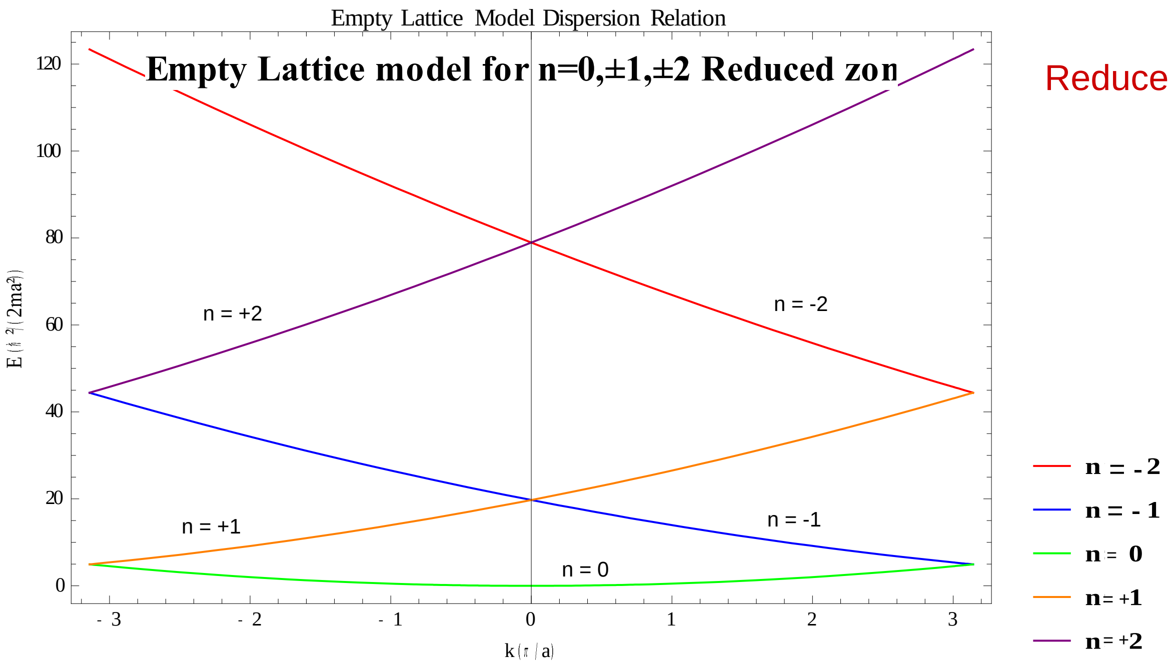
⇒ $\mathcal{E}_k^0$ energy eigenvalue

- now adding a constant potential, to H_0, will only shift the energy states up or down, so it can be still called (no gaps) free electron model; $H = H_0 + \underline{U_c}$ → constant; i.e with some scalling we can subtract U_c or make it zero

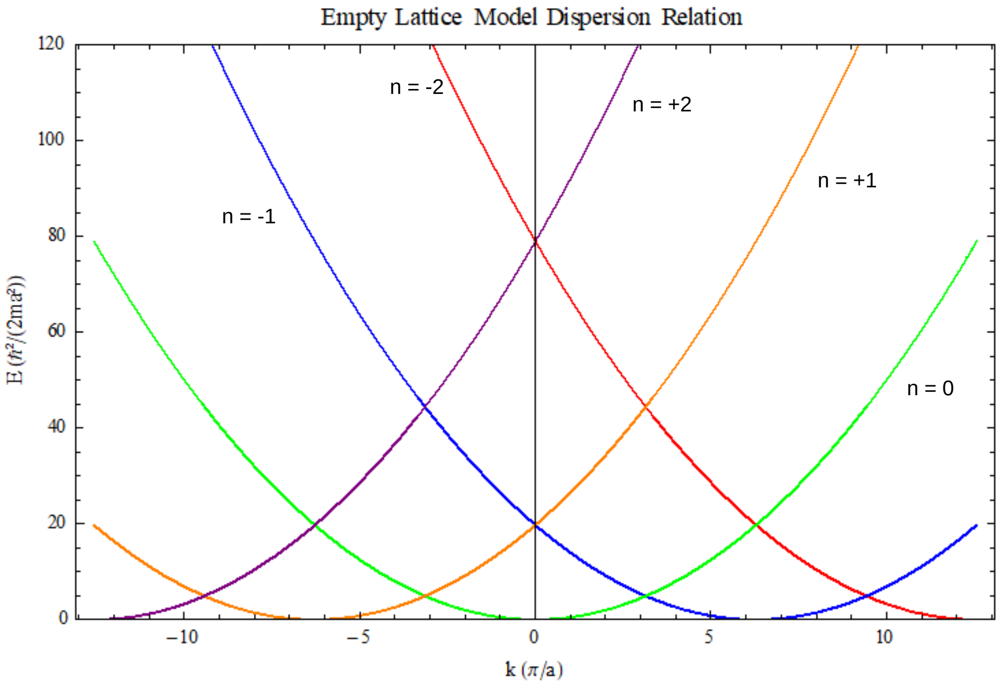
Mathematica code for band structure calculation of the Empty Lattice Model (ELM)

```
(*Define parameters*)ℏ = 1; (*Reduced Planck constant*)m = 1; (*Electron mass*)a = 1;
(*Lattice constant*)(*Define the dispersion relation for the empty lattice model*)
ELM[n_, k_] := (ℏ^2 / (2 m)) * (k + (2 π / a) * n) ^2;

(*Plot the dispersion relation for the first few bands*)
Plot[{ELM[-2, k], ELM[-1, k], ELM[0, k], ELM[1, k], ELM[2, k]}, {k, -π / a, π / a}, PlotRange → {0, 120},
 Frame → True, FrameLabel → {"k (π/a)", "E (ℏ²/(2ma²))"},
 PlotLegends → {"n = -2", "n = -1", "n = 0", "n = 1", "n = 2"}, PlotStyle → {Red, Blue, Green, Orange, Purple},
 PlotLabel → "Empty Lattice Model Dispersion Relation"]
```



Reduced zone



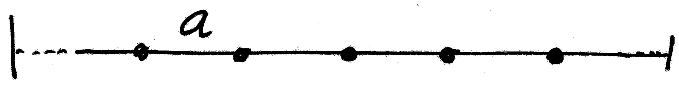
Extended Zone

to make this plot, just change the range of k above as

{k, -4π/a, -4π/a}

Number of states in the 1st Brillouin Zone (B.Z)

a) 1D Solid of N monoatomic atoms with spacing a



$L_x = Na$; N: # of atoms or # of unit cells

the total # of distinct k-states in the 1^{st} B.Z is determined by quantization of k-values and Periodic boundary conditions

$\Psi_k(x) = U_k(x) e^{ik_x x}$; bloch theorem, with $U_k(x)$ is Periodic

$\Rightarrow \Psi_k(0) = \Psi_k(L_x) \Rightarrow U_k(0) = U_k(L) e^{ik_x L}$; but $U_k(0) = U_k(L)$

$\Rightarrow e^{ik_x L_x} = 1 \Rightarrow \cos k_x L_x = 1 \Rightarrow k_x L_x = 2\pi n$; $n = 1, 2, 3, —$

$\Rightarrow k_x = \frac{2\pi}{L_x} n$ with $\Delta k_x = \frac{2\pi}{L_x}$

the density of states in k-space $D(k)dk$ is the # of states between k and k+dk, where

$D(k) = \frac{1}{\Delta k_x} = \frac{1}{2\pi / L_x} = \frac{L_x}{2\pi} = \frac{Na}{2\pi}$ = constant, meaning states are uniformaly distributed (equally spaced) in k-space. now the # of allowed k-states within the 1^{st} B.Z can be found in two ways

i) $N_s = \frac{\text{width of } 1^{s} \text{ B.Z}}{\Delta k_x} = \frac{2\pi / a}{2\pi / L_x} = \frac{L_x}{a} = N$

ii) by direct integration of $D(k)$ over $\{-\pi/a, \pi/a\}$

$$\Rightarrow N_s = \int_{-\pi/a}^{\pi/a} D(k)\, dk = \frac{L_x}{2\pi}\int_{-\pi/a}^{\pi/a} dk = \frac{L_x}{2\pi}\left[\frac{2\pi}{a}\right] = \frac{L_x}{a} = N$$

Note that while $D(k)$ is uniform in k-space, the energy density of states $D(\varepsilon)$ is not constant because $\varepsilon(k)$ depends nonlinearly on k, for example 1D free particle $\varepsilon(k) \propto k^2$

b) in 2D

$$D(k) = \frac{1}{\Delta^2\vec{k}} = \frac{1}{\Delta k_x \Delta k_y} = \frac{1}{\left(\frac{2\pi}{L_x}\right)\left(\frac{2\pi}{L_y}\right)} = \frac{L_x L_y}{(2\pi)^2} = \frac{A}{(2\pi)^2} \quad ; \quad A: \text{area}$$

$$N_s = \int D(k)\, d^2k = \frac{A}{(2\pi)^2}\underbrace{\int d^2k}_{}$$ elemental area in reciprocal space $= \left(\frac{2\pi}{a}\right)^2$ → area of primitive cell

$$= \frac{A}{(2\pi)^2}\left(\frac{2\pi}{a}\right)^2 = \frac{A}{a^2} = N$$

c) in 3D

$$D(k) = \frac{1}{\Delta^3\vec{k}} = \frac{1}{\Delta k_x \Delta k_y \Delta k_z} = \frac{1}{\left(\frac{2\pi}{L_x}\right)\left(\frac{2\pi}{L_y}\right)\left(\frac{2\pi}{L_z}\right)} = \frac{L_x L_y L_z}{(2\pi)^3} = \frac{V}{(2\pi)^3}$$

$$\Rightarrow N_s = \int D(k)\, d^3k = \frac{V}{(2\pi)^3}\underbrace{\int d^3k}_{}$$ elemental volume in reciprocal space (volume of primitive cell) $= \left(\frac{2\pi}{a}\right)^3$

$$= \frac{V}{(2\pi)^3}\frac{(2\pi)^3}{a^3} = \frac{V}{a^3} = N$$

---

the DOS in energy space $D(\varepsilon)$ can be derived from $D(k)$ using

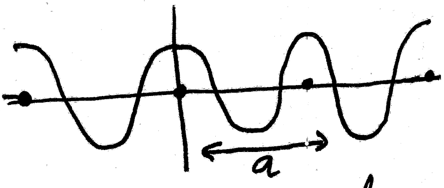
$$D(\varepsilon) = D(k)\left|\frac{dk}{d\varepsilon}\right| \cdot \underbrace{(\text{degeneracy factor})}_{}$$

in 1D = 4
in 2D = 1
3D = 1

Now let us add Periodic Potential (cosine Potential) and see how energy $\varepsilon(k)$ and eigenstates are affected. We will see that a band gaps will be developed at zone boundaries and a standing waves will be formed between zone boundaries.

$\nearrow$ period $= \frac{2\pi}{(2\pi/a)} = a$

Example: $U(x) = 2V_0 \cos \frac{2\pi}{a} x$; the Potential has periodicity of underlaying 1D lattice (a). V_0 is the strength of the cosine potential.



starting from the central equation

$$\left[\frac{\hbar^2}{2m}(k-K)^2-\varepsilon\right]\psi(k-K) + \sum_{K'} U_{K'-K}\,\psi(k-K') = 0 \text{ , and}$$

knowing that as a good approximation, it is enough to mix two Reciprocal lattice vectors $(\vec{K_1}, \vec{K_2})$ surrounding the k-point that we want to find $\varepsilon(k)$ at that point. This works for most practical 1D, 2D, 3D crystals

$$\text{at } K = K_1 \Rightarrow \left[\frac{\hbar^2}{2m}(k-K_1)^2-\varepsilon\right]\psi(k-K_1) + \sum_{K'} U_{K'-K_1}\,\psi(k-K') = 0 \qquad K' = K_1, K_2$$

$$\Rightarrow \left[\frac{\hbar^2}{2m}(k-K_1)^2-\varepsilon\right]\psi(k-K_1) + U_0\,\psi(k-K_1) + U_{K_2-K_1}\,\psi(k-K_2) = 0$$

$$\Rightarrow \left[\frac{\hbar^2}{2m}(k-K_1)^2+U_0-\varepsilon\right]\psi(k-K_1) + U_{K_2-K_1}\,\psi(k-K_2) = 0 \quad \text{--} \ (1)$$

similarly

at $K = K_2$ $\Rightarrow \left[\frac{\hbar^2}{2m}(k-K_2)^2 - \mathcal{E}\right]\psi(k-K_2) + \sum_{K'} U_{K'-K_2}\,\psi(k-K') = 0$

$K' = K_1, K_2$

$$\Rightarrow \left[\frac{\hbar^2}{2m}(k-K_2)^2 - \mathcal{E}\right]\psi(k-K_2) + U_0\,\psi(k-K_2) + U_{K_1-K_2}\,\psi(k-K_1) = 0$$

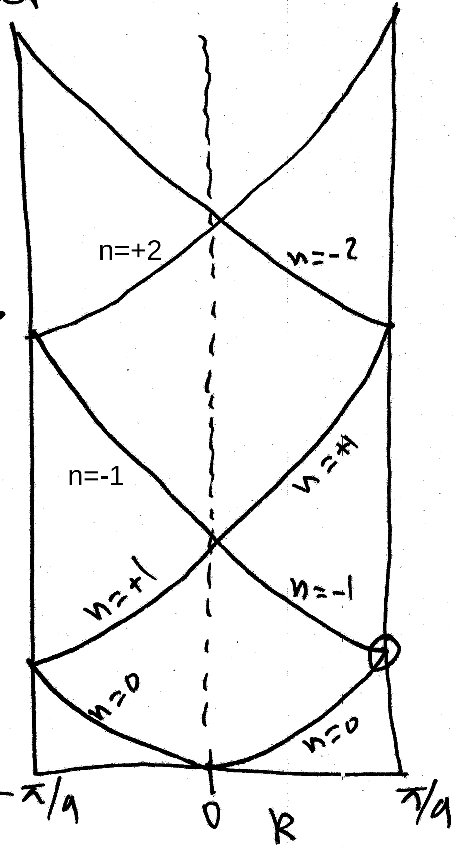
$$\Rightarrow \left[\frac{\hbar^2}{2m}(k-K_2)^2 + U_0 - \mathcal{E}\right]\psi(k-K_2) + U_{K_1-K_2}\,\psi(k-K_1) = 0 \quad \text{----- (2)}$$

equations (1) and (2) can be written in matrix form as

$$\begin{bmatrix} \frac{\hbar^2}{2m}(k-K_1)^2 + U_0 - \mathcal{E} & U_{K_2-K_1} \\ U_{K_1-K_2} & \frac{\hbar^2}{2m}(k-K_2)^2 + U_0 - \mathcal{E} \end{bmatrix} \begin{bmatrix} \psi(k-K_1) \\ \psi(k-K_2) \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix} \quad \text{--(3)}$$

Now $U(x)$ is real $\Rightarrow U_{-K} = U_K^{*} = U_K \Rightarrow U_{K_1-K_2} = U_{-(K_2-K_1)} = U^{*}_{K_2-K_1}$ $= U_{K2-K1}$

- how to pick up $\vec{K}_1, \vec{K}_2$: several options. The best one is to select two vectors that surround the point k at we wish to find energy eigenvalue at.
- let us solve eqn (3) at the point $k = \frac{\pi}{a}$. we see at $k = \pi/a$, the two bands $n=0$ and $n=-1$ that correspond to $K_1 = 0$ and $K_2 = -\frac{2\pi}{a}$ are good choice. sometimes, plugging in K_1 and K_2 in eqn 3 is confusing due to sign conversion. so instead of using $\frac{\hbar^2}{2m}(\vec{k}-\vec{K}_1)^2$ or $\frac{\hbar^2}{2m}(\vec{k}+\vec{K}_1)^2$, I would



prefere to use $\frac{\hbar^2}{2m}\left(k+\frac{2\pi}{a}n\right)^2$; $n=0,\pm1,\pm2,\ldots$

based on this conversion, eqn 3 goes to

$$\begin{bmatrix} \frac{\hbar^2}{2m}\left(k+\frac{2\pi}{a}n_1\right)^2+U_0-\mathcal{E} & U_{K_2-K_1} \\ U^*_{K_2-K_1} & \frac{\hbar^2}{2m}\left(k+\frac{2\pi}{a}n_2\right)^2+U_0-\mathcal{E} \end{bmatrix}\begin{bmatrix}\psi(k-K_1)\\ \psi(k-K_2)\end{bmatrix}=\begin{bmatrix}0\\0\end{bmatrix}$$

at $k=\pi/a$ and using $n_1=0$ and $n_2=-1$, we have --(4)

$$\begin{bmatrix} \frac{\hbar^2\pi^2}{2ma^2}+U_0-\mathcal{E} & U_{-\frac{2\pi}{a}} \\ U^*_{-\frac{2\pi}{a}} & \frac{\hbar^2\pi^2}{2ma^2}+U_0-\mathcal{E} \end{bmatrix}\begin{pmatrix}\psi(k-K_1)\\ \psi(k-K_2)\end{pmatrix}=\begin{pmatrix}0\\0\end{pmatrix} \quad --(5)$$

need to find $U_{-\frac{2\pi}{a}}$; from $U_K(\vec{r})=\frac{1}{\Omega}\int_\Omega d^3\vec{r}\, U(\vec{r})\, e^{-i\vec{K}\cdot\vec{r}}$

↳ over unit cell

in 1D $\Rightarrow$ $U_K(x)=\frac{1}{a}\int_0^a dx\, U(x)\, e^{-iKx}$

$$\Rightarrow U_{-\frac{2\pi}{a}}=\frac{1}{a}\int_0^a dx\ 2V_0\cos\frac{2\pi}{a}x\ e^{+i\frac{2\pi}{a}x},$$

using $\cos x=(e^{ix}+e^{-ix})/2$, we get

$$U_{-\frac{2\pi}{a}}=\frac{V_0}{a}\int_0^a dx\left[e^{i\frac{2\pi}{a}x}+e^{-i\frac{2\pi}{a}x}\right\}e^{+i\frac{2\pi}{a}x}$$

$$=\frac{V_0}{a}\int_0^a dx\left\{1+e^{+i\frac{4\pi}{a}x}\right\}=\frac{V_0}{a}\left[x+\frac{e^{+i\frac{4\pi}{a}x}}{\left(+i\frac{4\pi}{a}\right)}\right]_0^a$$

$$=\frac{V_0}{a}\left[a+\frac{a}{4\pi i}e^{+4\pi i}-\frac{a}{4\pi i}\right\} ;$$

$$U_{-\frac{2\pi}{a}} = \frac{V_0}{a}\left[a + \frac{a}{4\pi i} e^{i4\pi} - \frac{a}{4\pi i}\right] = \frac{V_0}{a}\left[a + \frac{a}{4\pi i} - \frac{a}{4\pi i}\right] = V_0$$

where $e^{i4\pi} = 1$ $\Rightarrow U_{-\frac{2\pi}{a}} = U^{*}_{-\frac{2\pi}{a}} = V_0$ as V_0 is real

similarly $U_0 = \frac{1}{a}\int_0^a dx\, 2V_0 \cos\frac{2\pi}{a}x = \frac{2V_0}{a}\int_0^a \cos\frac{2\pi}{a}x \, dx$

$=$ Zero, as we integrate $\cos\frac{2\pi}{a}x$ over its Period $\frac{2\pi}{2\pi/a} = a$

we see that $U_{\pm\frac{2\pi}{a}}$ is the only Fourier components that survive for this potential, i.e

$$U_{\pm\frac{4\pi}{a}} = U_{\pm\frac{6\pi}{a}} = U_{\pm\frac{8\pi}{a}} = \cdots = 0 .$$

there is another way to find the non-vanishing Fourier components

$U(x) = \sum_{K} U_K e^{iKx}$, with $K = \frac{2\pi}{a}n$; $n = 0, \pm 1, \pm 2, \ldots$

$$= \sum_n U_{\frac{2\pi}{a}n} e^{i\frac{2\pi}{a}nx}$$

$$= U_0 + U_{\frac{2\pi}{a}} e^{i\frac{2\pi}{a}x} + U_{-\frac{2\pi}{a}} e^{-i\frac{2\pi}{a}x} + U_{+\frac{4\pi}{a}} e^{i\frac{4\pi}{a}x} + U_{-\frac{4\pi}{a}} e^{-i\frac{4\pi}{a}x}$$

$$+ U_{\frac{6\pi}{a}} e^{i\frac{6\pi}{a}x} + U_{-\frac{6\pi}{a}} e^{-i\frac{6\pi}{a}x} + \cdots \quad \cdots (*)$$

but $U(x) = 2V_0 \cos\frac{2\pi}{a}x = 2V_0 \frac{e^{i\frac{2\pi}{a}x} + e^{-i\frac{2\pi}{a}x}}{2}$

$$= V_0 e^{i\frac{2\pi}{a}x} + V_0 e^{-i\frac{2\pi}{a}x} \quad \cdots (**)$$

by comparing equations (*) and (* *), we find

$U_0 = 0$, $U_{\frac{2\pi}{a}} = V_0$, $U_{-\frac{2\pi}{a}} = V_0$, and the rest components vanish, i.e $U_{\pm\frac{4\pi}{a}} = U_{\pm\frac{6\pi}{a}} = \dots = 0$,

Now equation (5) becomes

$$\begin{bmatrix} \frac{\hbar^2\pi^2}{2ma^2} - \varepsilon & V_0 \\ V_0 & \frac{\hbar^2\pi^2}{2ma^2} - \varepsilon \end{bmatrix} \begin{bmatrix} \psi(k-K_1) \\ \psi(k-K_2) \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}$$

these two equations have a solution when

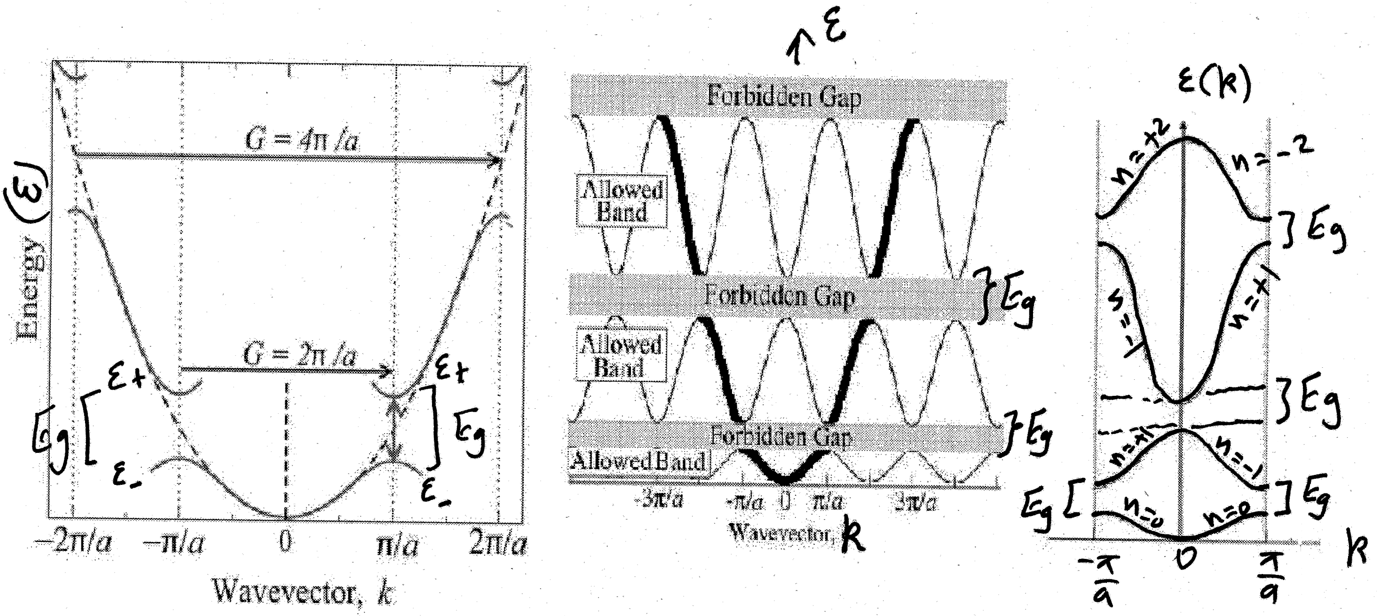
$$\begin{vmatrix} \frac{\hbar^2\pi^2}{2ma^2} - \varepsilon & V_0 \\ V_0 & \frac{\hbar^2\pi^2}{2ma^2} - \varepsilon \end{vmatrix} = 0$$

$$\Rightarrow \left(\frac{\hbar^2\pi^2}{2ma^2} - \varepsilon\right)^2 - V_0^2 = 0 \Rightarrow \left(\frac{\hbar^2\pi^2}{2ma^2} - \varepsilon\right)^2 = V_0^2$$

$$\Rightarrow \frac{\hbar^2\pi^2}{2ma^2} - \varepsilon = \pm V_0 \quad \Rightarrow \varepsilon = \frac{\hbar^2\pi^2}{2ma^2} \pm V_0$$

$$\Rightarrow \varepsilon_+ = \frac{\hbar^2\pi^2}{2ma^2} + V_0 \quad \text{and} \quad \varepsilon_- = \frac{\hbar^2\pi^2}{2ma^2} - V_0$$

$$\Rightarrow E_g = \Delta\varepsilon = \varepsilon_+ - \varepsilon_- = 2V_0$$



$\Rightarrow \varepsilon_+ = \frac{\hbar^2\pi^2}{2ma^2} + V_0$ and $\varepsilon_- = \frac{\hbar^2\pi^2}{2ma^2} - V_0 \Rightarrow \Delta\varepsilon = E_g = \varepsilon_+ - \varepsilon_- = 2V_0$

$n=0$ band is pushed down by V_0 and $n=-1$ band is pushed up by V_0 creating a gap of $2V_0$ at $k=\pi/a$.

same bandgap is obtained at $k=-\pi/a$ when mixing the bands $n=0$ and $n=+1$

now what are the eigenstates corresponding to ε_+ and ε_-

$$\psi(\vec{r}) = \frac{1}{V}\sum_{K}\psi(\vec{k}-\vec{K})\,e^{i(\vec{k}-\vec{K})\cdot\vec{r}}$$

in 1D $\psi(x) = \frac{1}{L}\sum_{K}\psi(k-K)\,e^{i(k-K)x}$

rewrite in terms of band index, n. $\vec{k}-\vec{K} \rightarrow k + \frac{2\pi}{a}n$ $\quad n = 0, \pm1, \pm2 \ldots$

$$\Rightarrow \psi(x) = \frac{1}{L}\sum_{n=0,-1}\psi\left(k+\frac{2\pi}{a}n\right)e^{i\left(k+\frac{2\pi}{a}n\right)x} \quad ; \quad \text{at } k = \pi/a$$

$$= \frac{1}{L}\left[\psi(\pi/a)\,e^{i\frac{\pi}{a}x} + \psi(-\pi/a)\,e^{-i\frac{\pi}{a}x}\right]$$

Need to find $\psi(\pi/a)$ and $\psi(-\pi/a)$

Now

c) for $\mathcal{E}_+$, substitute $\mathcal{E}_+$ into eq^n (5), we get with $U_0 = 0$ and $U_{\frac{2\pi}{a}} = V_0$, $\mathcal{E}_+ = \frac{\hbar^2\pi^2}{2ma^2} + V_0$

$$\begin{bmatrix} \frac{\hbar^2\pi^2}{2ma^2} - \mathcal{E}_+ & V_0 \\ V_0 & \frac{\hbar^2\pi^2}{2ma^2} - \mathcal{E}_+ \end{bmatrix} \begin{bmatrix} \psi(\pi/a) \\ \psi(-\pi/a) \end{bmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

$$\begin{bmatrix} -V_0 & V_0 \\ V_0 & -V_0 \end{bmatrix} \begin{bmatrix} \psi(\pi/a) \\ \psi(-\pi/a) \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}$$

$\Rightarrow -V_0\,\psi(\pi/a) + V_0\,\psi(-\pi/a) = 0$ $\Rightarrow \psi(-\pi/a) = \psi(\pi/a)$

$\psi(\pi/a)$ is arbitrary, set it to 1 $\Rightarrow \psi(\pi/a) = 1$, then $\psi(-\pi/a) = 1$

$$\Rightarrow \psi^+(x) = \frac{1}{L}\left[\psi(\pi/a)\,e^{i\frac{\pi}{a}x} + \psi(-\pi/a)\,e^{-i\frac{\pi}{a}x}\right]$$

$$= \frac{1}{L}\left\{e^{i\frac{\pi}{a}x} + e^{-i\frac{\pi}{a}x}\right\} = \frac{2}{L}\cos\frac{\pi}{a}x$$

let us normalize $\psi^+(x) = \frac{2A}{L}\cos\frac{\pi}{a}x$; A : normalizabic constant

$$\Rightarrow \int_0^L |\psi^+|^2 dx = 1 \quad \Rightarrow \frac{4A^2}{L^2}\underbrace{\int_0^L \cos^2\left(\frac{\pi}{a}x\right)dx}_{\frac{L}{2}} = 1$$

$$\Rightarrow \frac{4A^2}{L^2}\frac{L}{2} = 1 \Rightarrow A = \sqrt{\frac{L}{2}}$$

$$\Rightarrow \psi^+(x) = \frac{2}{L}\sqrt{\frac{L}{2}}\cos\frac{\pi}{a}x = \sqrt{\frac{2}{L}}\cos\frac{\pi}{a}x$$

This is a standing wave that gets reflected at $k = \pm\pi/a$ (Bragg reflection)

ii) for $\varepsilon_- = \frac{\hbar^2\pi^2}{2ma^2} - V_0$, we have

$$\begin{bmatrix} \frac{\hbar^2\pi^2}{2ma^2} - \varepsilon_- & V_0 \\ V_0 & \frac{\hbar^2\pi^2}{2ma^2} - \varepsilon_- \end{bmatrix} \begin{bmatrix} \psi(\pi/a) \\ \psi(-\pi/a) \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}$$

$$\begin{bmatrix} V_0 & V_0 \\ V_0 & V_0 \end{bmatrix} \begin{bmatrix} \psi(\pi/a) \\ \psi(-\pi/a) \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix} \Rightarrow V_0\,\psi(\pi/a) + V_0\,\psi(-\tfrac{\pi}{a}) = 0$$

$$\Rightarrow \psi(-\pi/a) = -\psi(\pi/a)$$

set $\psi(\pi/a) = 1 \Rightarrow$ then $\psi(-\pi/a) = -1$

$$\Rightarrow \psi^-(x) = \frac{1}{L}\left\{ \psi(\pi/a)\, e^{i\pi/a\, x} + \psi(-\pi/a)\, e^{-i\pi/a\, x} \right\}$$

$$= \frac{1}{L}\left[e^{i\pi/a\, x} - e^{-i\pi/a\, x} \right\} = \frac{2i}{L} \sin\frac{\pi}{a}x$$

normalize $\psi^-(x) = \frac{2iA}{L}\sin\frac{\pi}{a}x$, $\int_0^L |\psi^-|^2 dx = 1$

with $\psi^{-*}(x) = -\frac{2iA}{L}\sin\frac{\pi}{a}x$

$$\Rightarrow \frac{4A^2}{L}\underbrace{\int_0^L \sin^2\frac{\pi}{a}x\, dx}_{\frac{L}{2}} = 1 \Rightarrow A = \sqrt{\frac{2}{L}}$$

$$\Rightarrow \psi^-(x) = \sqrt{\frac{2}{L}}\; i \sin\frac{\pi}{a}x$$, again this is a standing wave.

for this cosine potential, all band gaps are identical having same magnitude of $2V_0$, even at $k = 0$

in summary, the Potential $U(x) = 2V_0 \cos \frac{2\pi}{a} x$ creates band gaps at zone boundaries $k = \pm \frac{\pi}{a} n$; $n = 1, 2, 3, 4, ..$ The Potential has a Period of a and its reciprocal lattice vectors are $K = 0, \pm \frac{2\pi}{a}, \pm \frac{4\pi}{a}, ---$. However, only $K = \pm \frac{2\pi}{a}$ is relevant as the $U(x)$ has a non-zero Fourier component only at $\pm \frac{2\pi}{a}$ i.e $U_{\frac{2\pi}{a}} = U_{-\frac{2\pi}{a}} = V_0$ and the rest Fourier componen vanish. to find the band gap as specific k, we can mix only two Reciprocal lattice vectors that differes by $\pm \frac{2\pi}{a}$, for example $K_1 = 0$ and $K_2 = +\frac{2\pi}{a}$ or $K_1 = 0$ and $K_2 = -\frac{2\pi}{a}$. to find the band gap at k value outside the 1^{st} B.Z, fold it to the 1^{st} B.Z and find the equivalent Point. for example, to find E_g at $k = \frac{3\pi}{a}$, fold it to 1^{st} B.Z by subtracting suitable Reciprocal lattice vector

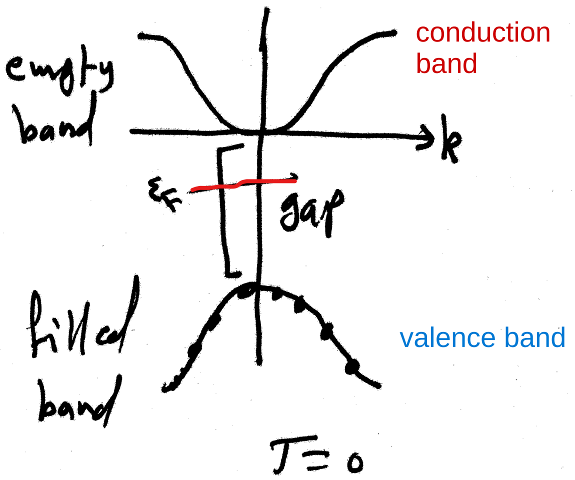
$$\frac{3\pi}{a} - \frac{2\pi}{a} = +\frac{\pi}{a} \quad \text{or} \quad \frac{3\pi}{a} - \frac{4\pi}{a} = -\frac{\pi}{a},$$

so the band gap at $k = \frac{3\pi}{a}$ is the same as that gaps at $k = \pm \pi/a$.

Metals, Insulators, and semiconductors:

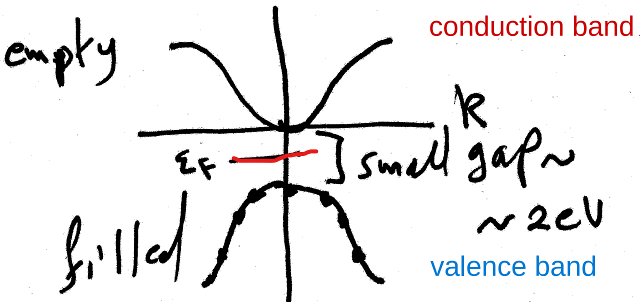
Insulator: completely filled bands separated by completely empty bands by a large gap

- Fermi level in the gap, so $D(\varepsilon_F) = 0 \Rightarrow$ No conduction



Semiconductor: completely filled bands separated by completely empty bands by a small gap

- Fermi level in the gap, so at $T=0$, $D(\varepsilon_F) = 0$, No conduction

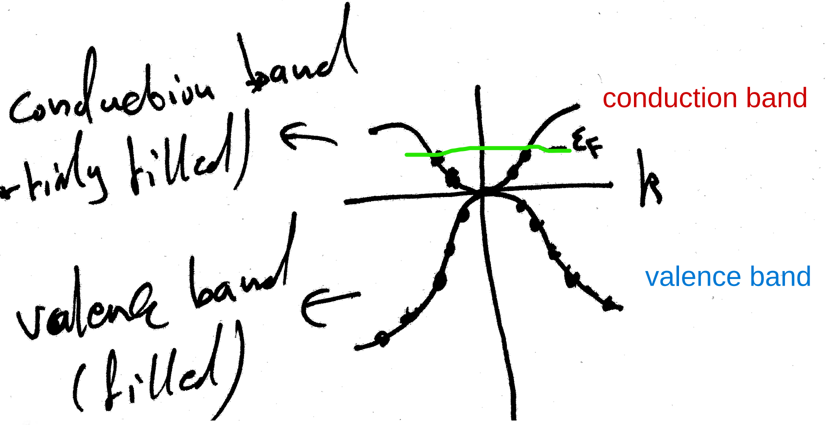


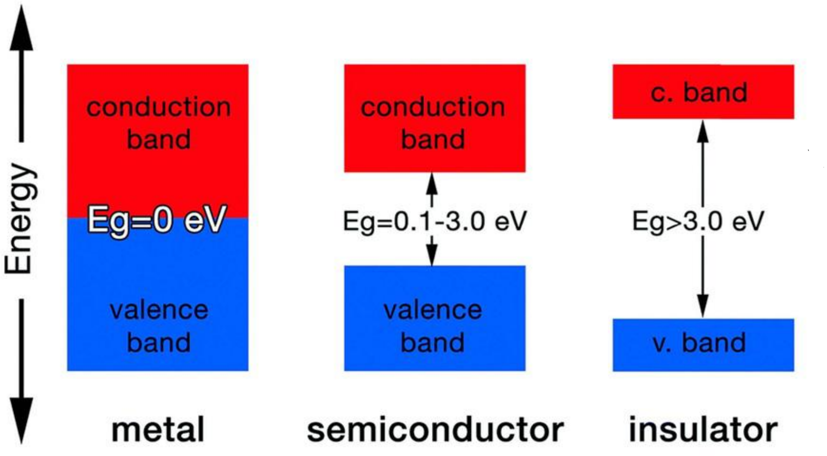
at RT, Fermi level is shifted up to conduction ban by thermal energy k_B T

typical size of band gap in semiconductors is around 1 eV

Metal: highest occupied band is partially filled with no gap

- Fermi level is in the conduction band, so $D(\varepsilon_F)$ is large, so there is a good conduction





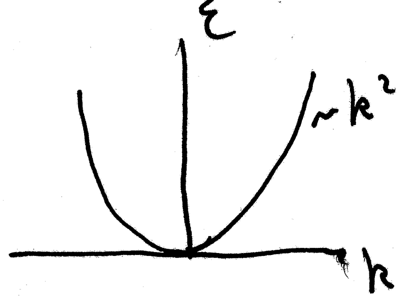
Velocity of Bloch electron in the state $(n,\vec{k})$ $\vec{v}_n(\vec{k})$

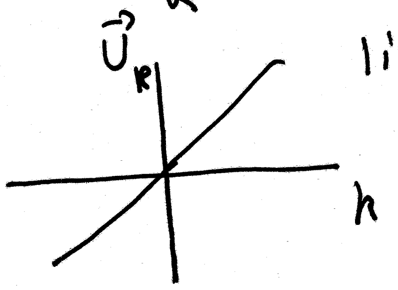
for an electron with $\psi_{n\vec{k}}(\vec{r})$ and $\varepsilon_n(\vec{k})$, the velocity is given by $\vec{v}_n(\vec{k}) = \frac{1}{\hbar}\vec{\nabla}_{\vec{k}}\varepsilon_n(\vec{k})$; $\vec{\nabla}_k$: gradient w.r.t $\vec{k}$

for free electron ($U(r)=0$), we have

$\psi \sim e^{i\vec{k}.\vec{r}}$ and $\varepsilon(\vec{k}) = \frac{\hbar^2 k^2}{2m}$, $\vec{p} = \hbar\vec{k}$

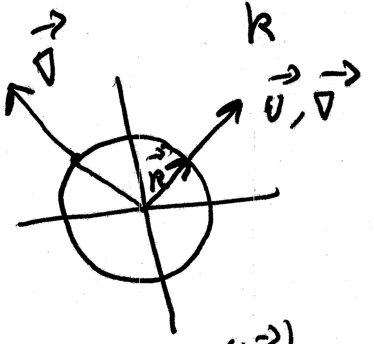
so $\vec{v}(\vec{k}) = \frac{1}{\hbar}\nabla_k\varepsilon(\vec{k}) = \frac{1}{\hbar}\frac{2\hbar^2\vec{k}}{2m} = \frac{\hbar\vec{k}}{m}$





linear $\vec{v} \propto \vec{k}$

$\vec{v}$ in direction of $\vec{k}$



But for solids with $U(r) \neq 0$

the formula $\vec{v}_n(\vec{k}) = \frac{1}{\hbar}\nabla_k\varepsilon_n(k)$ is not-trivial ?!!

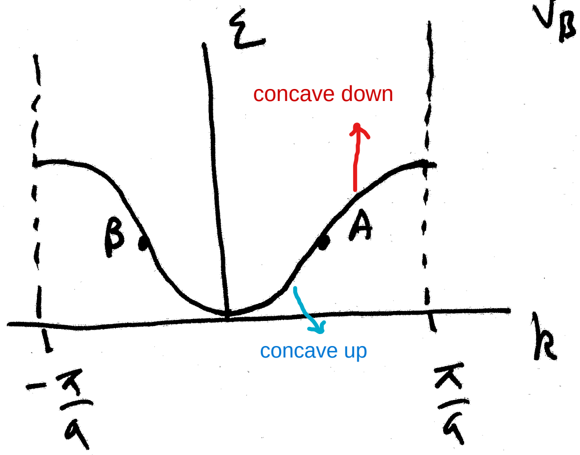
from QM, $\psi_{nk}(\vec{r})$ has time dependence of $e^{-i\frac{\varepsilon_n(\vec{k})}{\hbar}t} \sim e^{-i\omega_n(\vec{k})t}$

so $\vec{v}_n(\vec{k}) = \vec{\nabla}\left(\frac{1}{\hbar}\varepsilon_n(\vec{k})\right) \approx \vec{\nabla}\omega_n(k)$

$\equiv$ group velocity

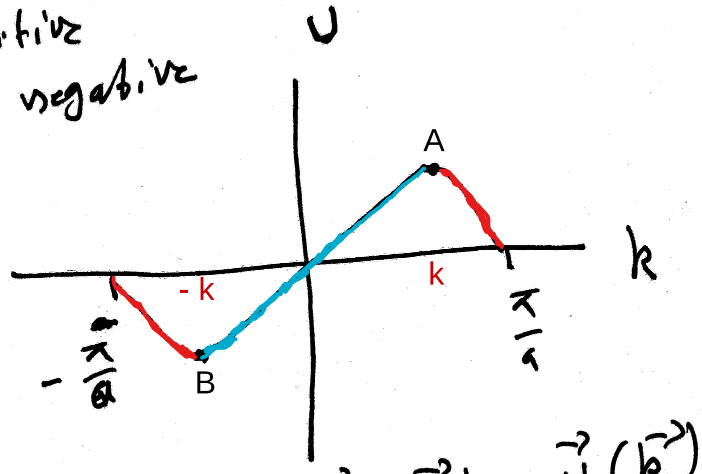
Note that direction of $\vec{v}_n(\vec{k})$ is in direction of $\underbrace{\vec{\nabla}_k\varepsilon_n(k)}$ which is perpendicular to a constant energy surface.

for 1D system with weak potential, let us take the lowest energy band $n=0$, and see the behavior of $\vec{v}_n(\vec{k})$



$v_A \rightarrow$ positive

$v_B \leftarrow$ negative



Note that $\vec{v}(-\vec{k}) = -\vec{v}(\vec{k})$

the last sentence means that completely filled band has zero total electron velocity

Van Hove singularities!

the general definition of DOS is

$$D(\varepsilon) = \frac{2}{(2\pi)^d} L^d \int dk^d \, \delta(\varepsilon - \varepsilon_k)$$: factor 2 for spin

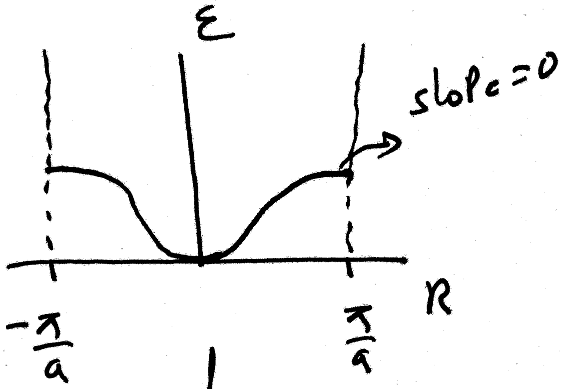
for a particular band n in 1D lattice, we have

$$D_n(\varepsilon) = \frac{2L}{2\pi} \int_0^\infty dk \, \delta(\varepsilon - \varepsilon_k) = \frac{L}{\pi} \int_0^\infty \frac{d\varepsilon_k}{|d\varepsilon_k/dk|} \delta(\varepsilon - \varepsilon_k)$$

$$= \frac{L}{\pi} \frac{1}{|d\varepsilon_k/dk|}\Big|_{\varepsilon_k = \varepsilon}$$

; there is an aditional factor 2, comes from $\varepsilon_{-k} = \varepsilon_k$ in 1D but this time

Note that at $k = \pm \frac{\pi}{a}$, zone-edge, $\frac{d\varepsilon_k}{dk} = 0$, so $D_n(\varepsilon)$ diverges. this is called van Hove singularity.



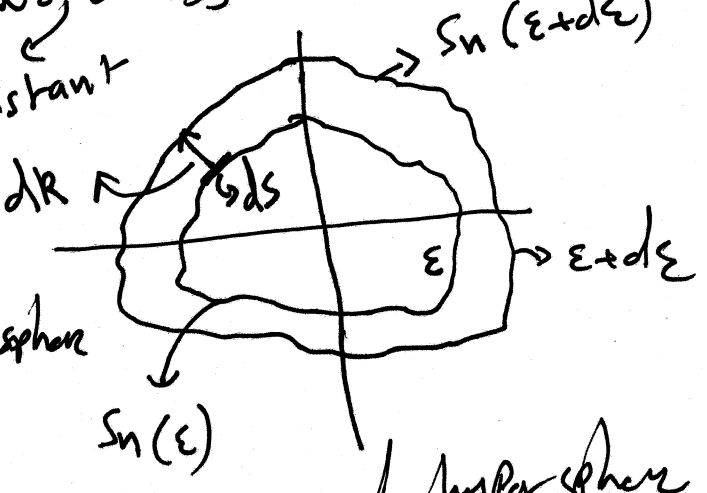
- Now the total density of states is given by

$D(\varepsilon) = \sum_n D_n(\varepsilon)$; sum over all available bands

for spin

$$= \frac{\overset{\nwarrow}{2}L^d}{(2\pi)^d}\int d^dk\,\delta(\varepsilon - \varepsilon_{nk}) \quad \cdots (5)$$

; where d^dk is an element of volume in d-dimensional k-space. so let us see how can we convert this integral over energy. the DOS is the # of states in the energy range $\varepsilon \to \varepsilon + d\varepsilon$ or the # of allowed k-values between ε and $\varepsilon + d\varepsilon$. now consider two constant energy surfaces separated by $d\varepsilon$. Now



$$d^dk = ds^{d-1}\,dk^1 \equiv \underset{\text{shortly}}{\underline{ds\,dk}}$$

↓
volume of d-dimensional hypersphere
↳ elemental

ds: elemental surface area of d-dimensional hypersphere

dk: perpendicular distance between the two energy surfaces so eq^n 5 reads

$$D(\varepsilon) = \frac{2L^d}{(2\pi)^d}\int ds\, dk\, \delta(\varepsilon-\varepsilon_k)$$

$$= \frac{2L^d}{(2\pi)^d}\underbrace{\int ds}_{\swarrow}\quad \underbrace{\int \frac{d\varepsilon}{|d\varepsilon/dk|}\,\delta(\varepsilon-\varepsilon_k)}_{\frac{1}{|\nabla_k \varepsilon_k|}\ \to} \quad --- \quad (6)$$

surface area of a d-dimensional hypersphere (in Marder called $\int d\Sigma$)

calculated at $\varepsilon = \varepsilon_k$ at the constant energy surface

now the surface area of a d-dimensional hypersphere with radius k is given by $= \dfrac{2\pi^{d/2}}{\Gamma(d/2)}\,k^{d-1}$

$$\text{so } D(\varepsilon) = \frac{2L^d}{(2\pi)^d} \times \frac{2\pi^{d/2}\,k^{d-1}}{\Gamma(d/2)} \times \frac{1}{|\nabla \varepsilon_k|}$$

let us test this result for 3D, 2D, and 1D system of free electrons where $\varepsilon_k = \dfrac{\hbar^2 k^2}{2m}$

$$\frac{\partial \varepsilon_k}{\partial k} = \nabla\varepsilon = \frac{\hbar^2}{m}k$$

$\underline{\underline{3D}}$: $$D(\varepsilon) = \frac{2V}{(2\pi)^3}\,\frac{2\pi^{3/2}}{\Gamma(3/2)}\,\frac{k^2}{\frac{\hbar^2}{m}k} \quad ; \quad \Gamma(3/2) = \frac{\sqrt{\pi}}{2}$$

d=3

$$= \frac{2V}{(2\pi)^3}\,\frac{2\pi^{3/2}}{\sqrt{\pi}/2}\cdot k \cdot \frac{m}{\hbar^2} \quad ; \quad k = \left(\frac{2m\varepsilon}{\hbar^2}\right)^{1/2}$$

$$\Rightarrow D(\varepsilon) = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\varepsilon^{1/2}$$ ✓

2D: $D(\varepsilon) = \frac{2A}{(2\pi)^2}\cdot\frac{2\pi}{\Gamma(1)}\,\frac{k}{\frac{\hbar^2}{m}k} = \frac{Am}{\pi\hbar^2}$ ✓ ; $\Gamma(1)=1$

d=2

1D: $D(\varepsilon) = \frac{2L}{2\pi}\,\frac{2\pi^{1/2}}{\Gamma(1/2)}\,\frac{1}{\frac{\hbar^2}{m}k} = \frac{L}{\pi}\,\frac{2\sqrt{\pi}}{\sqrt{\pi}}\,\frac{m}{\hbar^2}\,\frac{1}{k}$

d=1

$$= \frac{2L}{\pi}\,\frac{m}{\hbar^2}\,\frac{1}{k} \quad ; \quad k = \left(\frac{2m}{\hbar^2}\right)^{1/2}\varepsilon^{1/2}$$

$$= \frac{2L}{\pi}\,\frac{m}{\hbar^2}\,\frac{1}{\left(\frac{2m}{\hbar^2}\right)^{1/2}\varepsilon^{1/2}} = \frac{L}{\pi}\,\frac{2m}{\hbar^2}\,\frac{1}{\left(\frac{2m}{\hbar^2}\right)^{1/2}\varepsilon^{1/2}}$$

$$= \frac{L}{\pi}\left(\frac{2m}{\hbar^2}\right)^{1/2}\varepsilon^{-1/2}$$

$$= \frac{L}{\pi\hbar}\sqrt{\frac{2m}{\varepsilon}}$$ ✓

---

useful math relations:

$\Gamma(n) = (n-1)!$; $\Gamma(n+1) = n\,\Gamma(n)$; $\Gamma\left(\frac{n}{2}+1\right) = \left(\frac{n}{2}\right)!$

$= \frac{n}{2}\,\Gamma\left(\frac{n}{2}\right)$

n:	$-3/2$	$-1/2$	$1/2$	1	$3/2$	2	$5/2$
$\Gamma(n)$:	$\frac{4\sqrt{\pi}}{3}$	$-2\sqrt{\pi}$	$\sqrt{\pi}$	1	$\frac{\sqrt{\pi}}{2}$	1	$\frac{3\sqrt{\pi}}{4}$

effective mass of Bloch electrons:

$v_g = \frac{1}{\hbar}\frac{\partial \varepsilon}{\partial k}$ group velocity

now $\vec{p} = \hbar \vec{k} \Rightarrow \frac{d\vec{p}}{dt} = \hbar \frac{d\vec{k}}{dt}$

$$\vec{F} = \hbar \frac{d\vec{k}}{dt}$$

$$\frac{d\vec{v}_g}{dt} = \frac{1}{\hbar}\frac{\partial^2 \varepsilon}{\partial \vec{k}^2}\frac{\partial \vec{k}}{\partial t} = \frac{1}{\hbar^2}\frac{\partial^2 \varepsilon}{\partial \vec{k}^2} \times \vec{F}$$

$$\Downarrow$$

$$\vec{a} = \frac{1}{\hbar^2}\frac{\partial^2 \varepsilon}{\partial k^2}\vec{F} \;;$$

define $\frac{1}{m^*} = \frac{1}{\hbar^2}\frac{\partial^2 \varepsilon}{\partial k^2}$

$\Rightarrow \vec{a} = \frac{\vec{F}}{m^*} \Rightarrow \vec{F} = \underset{\substack{\downarrow \\ \text{effective mass}}}{m^*}\vec{a}$

in general $m^* = m^*(\vec{k})$

- for free electron $\varepsilon = \frac{\hbar^2 k^2}{2m} \Rightarrow \frac{\partial \varepsilon}{\partial k} = \frac{\hbar^2}{m}k$

$$\frac{\partial^2 \varepsilon}{\partial k^2} = \frac{\hbar^2}{m}$$

$$\Rightarrow \frac{1}{m^*} = \frac{1}{\hbar^2}\frac{\hbar^2}{m} = \frac{1}{m}$$

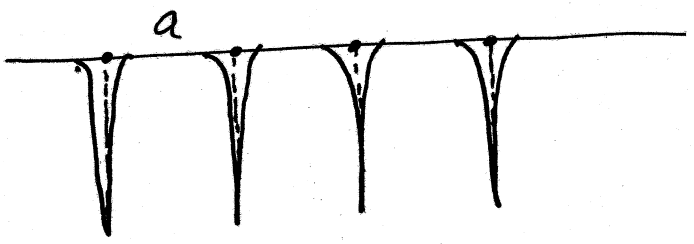
$$\Rightarrow \underline{m^* = m}$$

- in unit of m_e, m^* could be in the range $0.01 m_e \rightarrow$ more than $\underline{1000 m_e}$ in heavy fermion materials

7.2.6 Kronig-Penney Model:

consider a 1D lattice with spacing a, and suppose that in each unit cell there is a delta function potential given by $U(x) = U_0 a\,\delta(x)$; U_0 has a dimension of energy and determines the strength of the delta potential.

$$U_K = \frac{1}{a}\int_{\text{unit cell}} dx\, e^{-iKx}\, U(x)$$



$$= \frac{U_0 a}{a}\underbrace{\int_a dx\, e^{-iKx}\,\delta(x)}_{1} = U_0$$

using $\int_{-\infty}^{\infty} dx\, f(x)\,\delta(x-0) = f(0)$

$U_0 < 0$

$L = Na$;

N: # of LPs or atoms

instead of integrating over unit cell, U_K can be calculated over the whole 1D lattice

$$U_K = \frac{1}{L}\int_L \sum_R \delta(x-R)\, e^{-iKx}\, dx$$; where $U(x) = U_0 a \sum_R \delta(x-R)$

$R = na$

where R is reciprocal lattice vectors

$$\Rightarrow U_K = \frac{U_0 a}{L}\sum_R \int_L e^{-iKx}\,\delta(x-R)\,dx = \frac{U_0 a}{L}\sum_R e^{-iKR}$$

but $e^{-iKR} = e^{-i\frac{2\pi}{a}na} = e^{-i2\pi n} = 1$

$$\Rightarrow U_K = \frac{U_0 a}{L}\sum_R 1 = \frac{U_0 a N}{L} = \frac{U_0 \cancel{L}}{\cancel{L}} = U_0$$ as obtained before

Now the central eq^n over one unit cell reads

$$(\varepsilon_q^0 - \varepsilon)\,\psi(q) + \sum_K U_K\, \psi(q-K) = 0$$; with $U_K = U_0$

$$\left(\varepsilon_q^{(0)} - \varepsilon\right)\psi(q) + U_0 \underbrace{\sum_{K} \psi(q-K)}_{Q_q} = 0$$

$$\left(\varepsilon_q^{0} - \varepsilon\right)\psi(q) + U_0 Q_q = 0$$, to solve this in the 1st B.Z. let $q = k - K$

$$\Rightarrow \left(\varepsilon_{k-K}^{0} - \varepsilon\right)\psi(k-K) + U_0 Q_{k-K} = 0$$

$$\psi(k-K) + \frac{U_0}{\varepsilon_{k-K}^{(0)} - \varepsilon} Q_{k-K} = 0$$, this is done for one unit cell; to do it for the whole crystal, we sum over all $\vec{K}$, reciprocal lattice vectors

$$\sum_{K} \psi(k-K) + U_0 \sum_{K} \frac{Q_{k-K}}{\varepsilon_{k-K}^{(0)} - \varepsilon} = 0$$

but from the definition of $Q_q = \sum_K \psi(q-K)$, we have

$$Q_k = \sum_{K} \psi(k-K) = \sum_{K'} \psi(k-K')$$

relabel only

, Now $Q_{k-K} = \sum_{K'} \psi(k-K-K')$

$$= \sum_{K''} \psi(k-K'') ;$$

relabel where $K'' = K + K'$

$$= \sum_{K} \psi(k-K)$$

$$= Q_k$$

$$\therefore Q_{k-K} = Q_k$$

$$Q_k + U_0 \sum_{K} \frac{Q_k}{\varepsilon_{k-K}^{(0)} - \varepsilon} = 0$$

$$Q_k + U_0 Q_k \sum_{K} \frac{1}{\varepsilon_{k-K}^{(0)} - \varepsilon} = 0$$

$$\left[1 + U_0 \sum_{K} \frac{1}{\varepsilon_{k-K}^{(0)} - \varepsilon}\right] Q_k = 0$$

but $Q_k \neq 0$

$$\Rightarrow 1+U_0\sum_{K}\frac{1}{\varepsilon^{(0)}_{k-K}-\varepsilon}=0 \quad\Rightarrow \sum_{K}\frac{1}{\varepsilon^{(0)}_{k-K}-\varepsilon}=-\frac{1}{U_0}$$

the last eq^n is nothing but Schrodinger eq^n in reciprocal space. It can be solved numerically. let us make the eq^n dimensionless by introducing the dimensionless quantities $\tilde{\varepsilon}$ and $\tilde{U}_0$.

Now $\varepsilon^{(0)}_{k-K}=\frac{\hbar^2}{2m}(\vec{k}-\vec{K})^2$; $\vec{K}=\frac{2\pi}{a}n$; $K_0=\frac{2\pi}{a}$ for $n=1$ and let $k=\frac{2\pi}{a}f$; f is dimensionless number

$$\Rightarrow \sum_{K}\frac{1}{\frac{\hbar^2}{2m}\left(\frac{2\pi}{a}f-\frac{2\pi}{a}n\right)^2-\varepsilon}=-\frac{1}{U_0}$$

$$\sum_{n}\frac{1}{\frac{\hbar^2(2\pi)^2}{2ma^2}(f-n)^2-\varepsilon}=-\frac{1}{U_0}$$

$$\Rightarrow \frac{1}{\frac{\hbar^2(2\pi)^2}{2ma^2}}\sum_{n}\frac{1}{(f-n)^2-\frac{\varepsilon}{\frac{\hbar^2(2\pi)^2}{2ma^2}}}=-\frac{1}{U_0}$$

$$\Rightarrow \sum_{n}\frac{1}{(f-n)^2-\frac{\varepsilon}{\frac{\hbar^2(2\pi)^2}{2ma^2}}}=-\frac{1}{U_0}\,\frac{\hbar^2(2\pi)^2}{2ma^2}$$

let $\tilde{\varepsilon}=\varepsilon\Big/\frac{\hbar^2(2\pi)^2}{2ma^2}$ and $\tilde{U}_0=\frac{U_0}{\frac{\hbar^2(2\pi)^2}{2ma^2}}$

$$\Rightarrow \boxed{\sum_{n}\frac{1}{(f-n)^2-\tilde{\varepsilon}}=-\frac{1}{\tilde{U}_0}}$$

dimensionless eq^n that can be solved numerically where both $\tilde{\mathcal{E}}$ and $\tilde{U}_0$ are measured in units of $\frac{\hbar^2}{2m}\left(\frac{2\pi}{a}\right)^2 = \frac{\hbar^2 K_0^2}{2m}$

$\Rightarrow \sum_n \frac{1}{(f-n)^2-\tilde{\mathcal{E}}} = -\frac{1}{\tilde{U}_0}$, $S_k(\tilde{\mathcal{E}}) = -\frac{1}{\tilde{U}_0}$; where $S_k(\tilde{\mathcal{E}}) = \sum_K \frac{1}{(f-n)^2-\tilde{\mathcal{E}}}$

$S_k(\tilde{\mathcal{E}}) = -\frac{1}{\tilde{U}_0}$; let us solve this eq^n at $k=0, \pi/a$, and for $\tilde{U}_0$= -0.1 ,-10.0

c) $k=0$

poles of $S_k(\varepsilon)$ occurs when $(f-n)^2 \cdot\cdot - \varepsilon = 0$

Band structure for 1 D solid of spacing a (Kronig - Penney Model)

Mathematica code for solving equation 7.89 in Marder textbook

```
In[1186]:=

sum[b_?NumericQ] := Sum[1/(n^2-b), {n, -Infinity, Infinity}]; (*Define the sum[b] for k=0*)
equation[b_] := sum[b] == 10;                    (*Define the equation:sum[b]=10 for Uo=-0.1*)
plot1 = Plot[{10, 0.1, sum[b]}, {b, 0, 10}, ImageSize → 900, TicksStyle → Large,
  AxesLabel → {Style["ε", Bold, 25], Style["Sum", Bold, 25]}]   (*Plot the sum and solutions for Uo=-0.1 and -10*)
```

$b = \tilde{\varepsilon}$

poles occurs when $n^2 - \varepsilon = 0$,

$\varepsilon = \pm 1, \pm 2, \pm 3, \ldots \ldots$

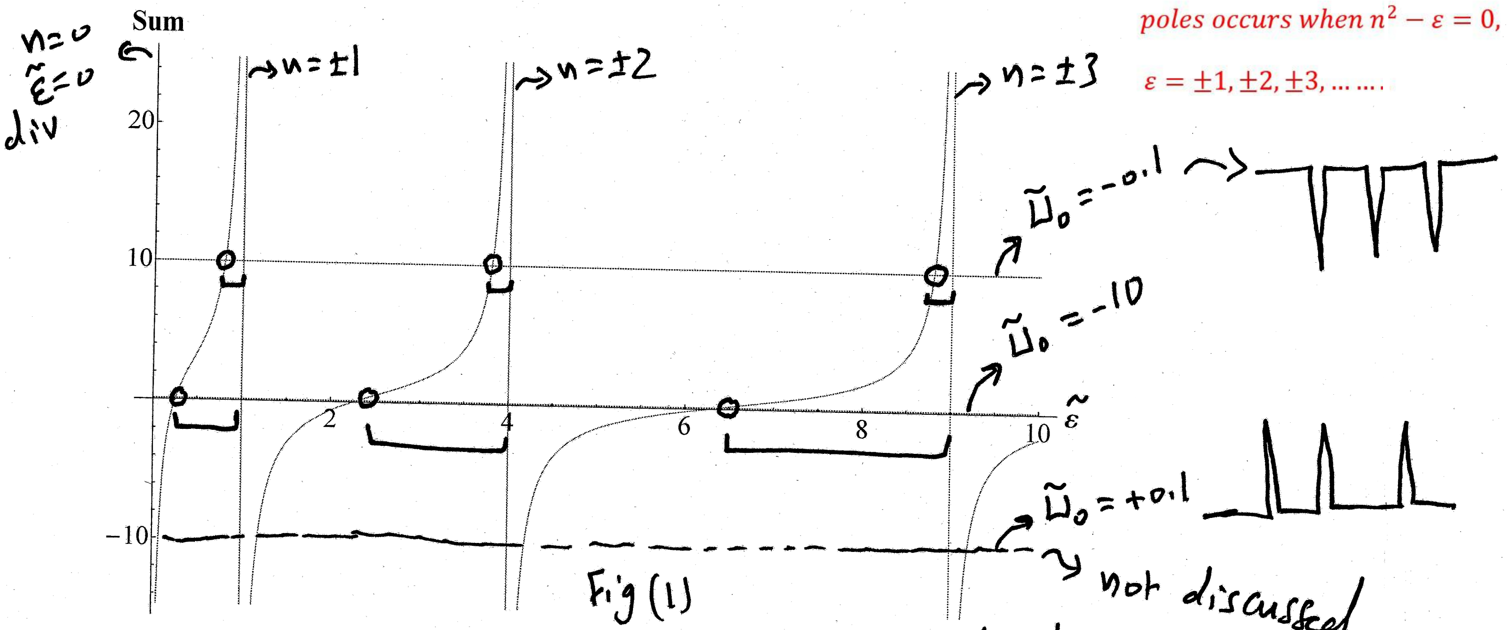


Fig (1)

the solution is the intersection points of the two curves $S_k(\mathcal{E})$ and $-1/\tilde{U}_0$ that are represented by circles. each circle represents $\mathcal{E}_-$ and the energy interval from $\mathcal{E}_-$ to the next vertical line is half of the gap.

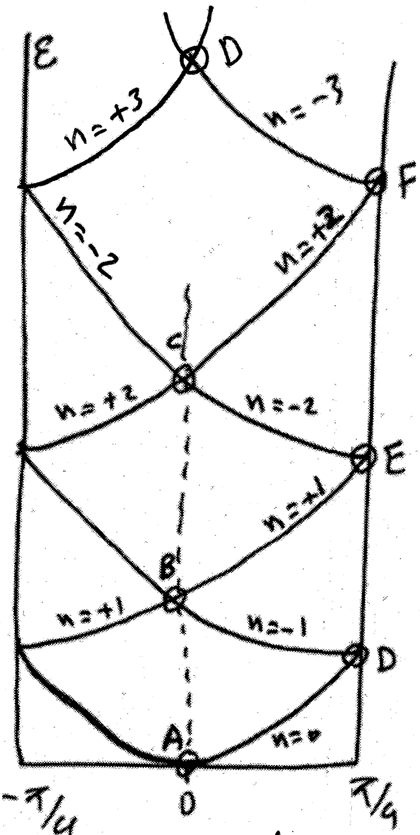
- for very weak potential $\left(-\frac{1}{\tilde{U}_0} \to \infty\right)$ and there, the $-\frac{1}{\tilde{U}_0}$ horizontal line intersects the vertical band lines $n = \pm 1, \pm 2, ---$, recovering the free electron model with energies $\tilde{\mathcal{E}}_1 = 1$, $\tilde{\mathcal{E}}_2 = 4$, $\tilde{\mathcal{E}}_3 = 9$, ---

poles occur at 1, 4, 9, ...

i.e $\varepsilon_1 = \tilde{\varepsilon}_1 \frac{\hbar^2 k_0^2}{2m} = (1)\frac{\hbar^2 (2\pi)^2}{2ma^2} = \frac{2\pi^2\hbar^2}{ma^2}$ Point B

$\varepsilon_2 = \tilde{\varepsilon}_2 \frac{\hbar^2 k_0^2}{2m} = (4)\frac{\hbar^2 (2\pi)^2}{2ma^2} = 4\,\frac{2\pi^2\hbar^2}{ma^2}$ Point C

and so on ----



Fig(2)

- now for weak potential ($\tilde{U}_0 = -0.1$), a band gaps are created at $n = \pm 1, \pm 2, \pm 3$---- with lower energies

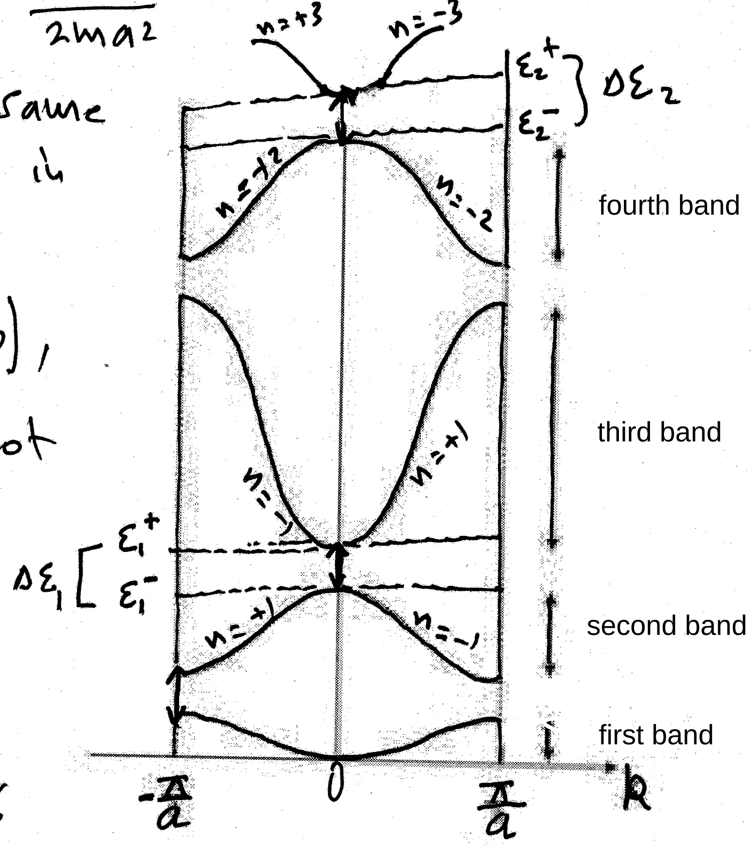
$\tilde{\varepsilon}_1^- = 0.8$, $\tilde{\varepsilon}_2^- = 3.8$, $\tilde{\varepsilon}_3^- = 8.8$, so

$\tilde{\varepsilon}_1^+ = 1.2$, $\tilde{\varepsilon}_2^+ = 4.2$, $\tilde{\varepsilon}_3^+ = 9.2$

$\Rightarrow \Delta\varepsilon = \tilde{\varepsilon}^+ - \tilde{\varepsilon}^- = 0.4$ in unit $\frac{\hbar^2 (2\pi)^2}{2ma^2}$

all gaps are equal (i.e have same magnitude) at $k=0$ as shown in Fig(1)

- for strong potential ($\tilde{U}_0 = -10$), the created band gaps are not uniform in size as shown in Fig(1), with lower energies



Fig(3)

$\tilde{\varepsilon}_1^- = 0.25$, $\tilde{\varepsilon}_2^- = 2.3$, $\tilde{\varepsilon}_3^- = 6.4$, so

$\tilde{\varepsilon}_1^+ = 1 + 0.75 = 1.75$, $\tilde{\varepsilon}_2^+ = 4 + 1.7 = 5.7$, $\tilde{\varepsilon}_3^+ = 9 + 2.6 = 11.6$

$$\Rightarrow \left.\begin{aligned} \Delta\tilde{\varepsilon}_1 &= 1.75 - 0.25 = 1.5 \\ \Delta\tilde{\varepsilon}_2 &= 5.7 - 2.3 = 3.4 \\ \Delta\tilde{\varepsilon}_3 &= 11.6 - 6.4 = 5.2 \end{aligned}\right\}$$

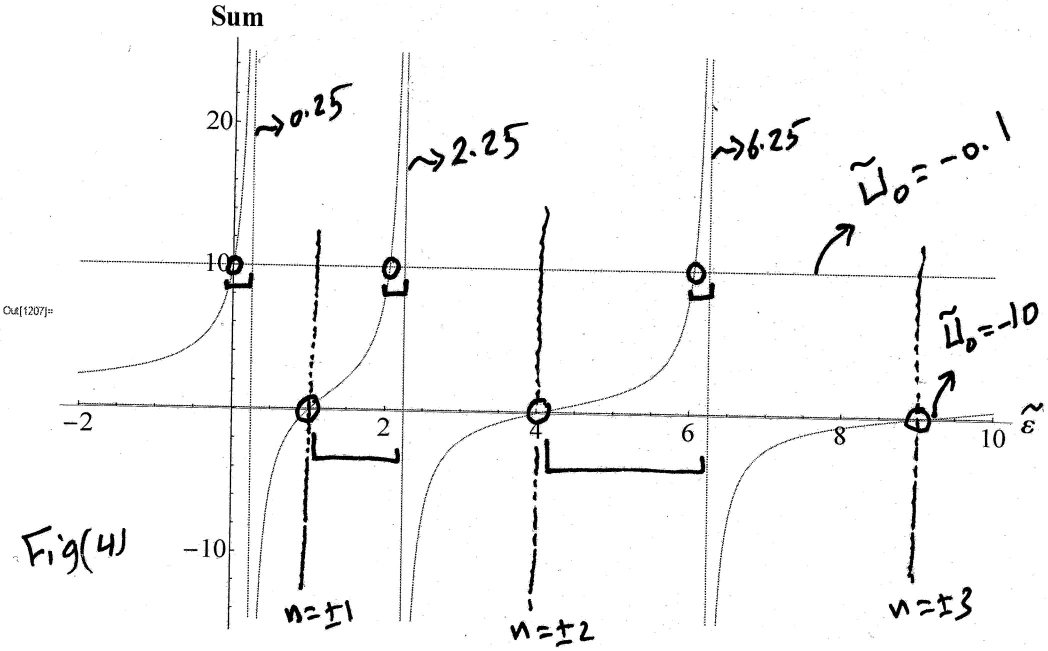
energy levels are shifted differently under the application of strong potential

ii) $k = \pi/a$

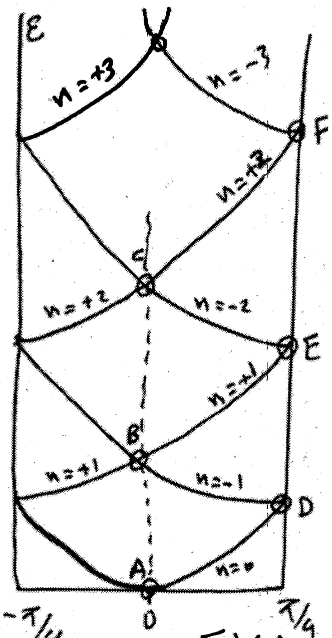
```
In[1205]:= sum[b_?NumericQ] := Sum[1 / ((0.5 - n) ^2 - b), {n, - Infinity, Infinity}];
 equation[b_] := sum[b] == 10; (*Define the equation:sum[b]=10*)
 Plot4 = Plot[{10, 0.1, sum[b]}, {b, -2, 10}, ImageSize → 900, TicksStyle → Large,
   AxesLabel → {Style["ε", Bold, 25], Style["Sum", Bold, 25]}] (*Plot the sum and solutions *)
```

$b = \tilde{\varepsilon}$

Out[1207]=



Fig(4)



Fig(5)

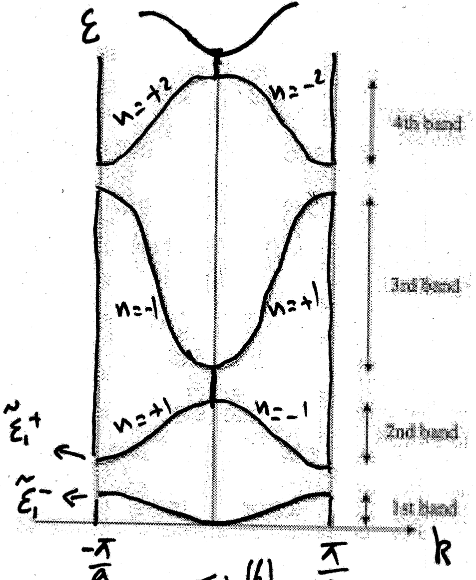
Now we have $\sum_n \frac{1}{(\frac{1}{2}-n)^2 - b} = -\frac{1}{\tilde{U}_0}$, and

the poles occur at $b = (1/2 - n)^2$

$n = 1 \Rightarrow b = (1/2 - 1)^2 = 0.25$

$n = 2 \Rightarrow b = (1/2 - 2)^2 = \frac{9}{4} = 2.25$

$n = 3 \Rightarrow b = (1/2 - 3)^2 = \frac{25}{4} = 6.25$



Fig(6)

Now for very weak potential $(-\frac{1}{\tilde{U}_0} \to \infty)$, the $(-\frac{1}{\tilde{U}_0})$ horizontal line intersects the new poles at 0.25, 2.25, 6.25, --- and so on

No band gaps created and the energies are

$$\varepsilon_1 = 0.25 \frac{\hbar^2 (2\pi)^2}{2ma^2} = \frac{\hbar^2 \pi^2}{2ma^2} \quad \text{Point D}$$

$$\varepsilon_2 = 2.25 \frac{\hbar^2 (2\pi)^2}{2ma^2} = \frac{9}{4} \frac{\hbar^2 4\pi^2}{2ma^2} = 9 \frac{\hbar^2 \pi^2}{2ma^2} \quad \text{Point E}$$

$$\varepsilon_3 = 6.25 \frac{\hbar^2 (2\pi)^2}{2ma^2} = \frac{25}{4} \frac{\hbar^2 4\pi^2}{2ma^2} = 25 \frac{\hbar^2 \pi^2}{2ma^2} \quad \text{Point F}$$

consistent with earlier values obtained for Empty lattice model for weak potential ($\tilde{U}_0 = -0.1$), a band gaps are created as shown in Fig (4) and the lower edge of band energies are shown by an open circles at the intersection points and given by

$\tilde{\varepsilon}_1^- = 0$, $\tilde{\varepsilon}_2^- = 2$, $\tilde{\varepsilon}_3^- = 6$ with gaps being measured w.r.t / new poles, so

$\tilde{\varepsilon}_1^+ = 0.25 + 0.25 = 0.5$, $\tilde{\varepsilon}_2^+ = 2.25 + 0.25 = 2.5$, $\tilde{\varepsilon}_3^+ = 6.25 + 0.25 = 6.5$

$\Delta\tilde{\varepsilon}_1 = \tilde{\varepsilon}_1^+ - \tilde{\varepsilon}_1^- = 0.5$, $\Delta\tilde{\varepsilon}_2 = 0.5$, $\Delta\tilde{\varepsilon}_3 = 0.5$

all band gaps have same size ($\Delta\tilde{\varepsilon} = 0.5$) and comparable to those gabs created at $k = 0$ ($\Delta\tilde{\varepsilon} = 0.4$)

- for strong potential ($\tilde{U}_0 = -10$), a band gaps created with different sizes at zone boundaries. the lower edge of the bands read

$\tilde{\varepsilon}_1^- = 1$, $\tilde{\varepsilon}_2^- = 4$, again gaps are measured w.r.t new poles located at (2.25 and 6.25), so

$\tilde{\varepsilon}_1^+ = 2.25 + 1.25 = 3.5$, $\tilde{\varepsilon}_2^+ = 6.25 + 2.25 = 8.5$

$\Rightarrow$ $\Delta\tilde{\varepsilon}_1 = 3.5 - 1 = 2.5$, $\Delta\tilde{\varepsilon}_2 = 8.5 - 4 = 4.5$

gaps are not uniform in size and also different from those gaps created at $k = 0$ under the same applied potential ($\tilde{U}_0 = -10$). In conclusion, the Kronig-Penney model is good for understanding how periodic potentials lead to formation of energy bands in solids, allowing to interprete many electronic properties of real materials.