(2) Now suppose that $\vec{k}$ is near the Bragg plane that bisects the R.L. vector $\vec{K}_0$, but not near any other Bragg planes, i.e.

$$|\varepsilon_k^0 - \varepsilon_{k-K_0}^0| \leq U \quad \text{but} \quad |\varepsilon_k^0 - \varepsilon_{k-K}^0| \gg U$$
$$\text{for all } \vec{K} \neq 0, \vec{K}_0$$

From (*) we can write

$\vec{K}=0$ (1) $$(\varepsilon - \varepsilon_k^0)\, c_k = U_{K_0}\, c_{k-K_0} + \sum_{K' \neq 0, K_0} U_{K'}\, c_{k-K'}$$

$\vec{K}=\vec{K}_0$ (2) $$(\varepsilon - \varepsilon_{k-K_0}^0)\, c_{k-K_0} = U_{-K_0}\, c_k + \sum_{K' \neq 0, K_0} U_{K'-K_0}\, c_{k-K'}$$

$\vec{K} \neq 0, \vec{K}_0$ (3) $$(\varepsilon - \varepsilon_{k-K}^0)\, c_{k-K} = U_{-K_0}\, c_k + U_{K_0-K}\, c_{k-K_0} + \sum_{K \neq 0, K_0} U_{K'-K}\, c_{k-K'}$$

Now we can say that $(\varepsilon - \varepsilon_{k-K}^0)$ must be greater than $O(U)$ for $\vec{K} \neq 0, \vec{K}_0$ since $(\varepsilon^0 - \varepsilon_{k-K}^0)$ is greater than $O(U)$. So eqn (3) $\Rightarrow$ c_{k-K} must be no bigger than $O(U)$. So the last term on the right in all three equations above is no bigger than $O(U^2)$. Next, $c_k \sim O(1)$ since we start with a free electron of wavevector $\vec{k}$. So from (2) we must conclude that $(\varepsilon - \varepsilon_{k-K_0}^0)\, c_{k-K_0} \sim O(U)$

But $(\varepsilon - \varepsilon^{\circ}_{k-K_0})$ cannot be bigger than $O(U)$ (since the difference is due to the potential U) and c_{k-K} cannot be bigger than $O(1)$.

$\Rightarrow$ only possibility is $c_{k-K_0} \sim O(1)$ and $(\varepsilon - \varepsilon^{\circ}_{k-K_0}) \sim O(U) \Rightarrow (\varepsilon - \varepsilon^{\circ}_{k}) \sim O(U)$ also.

So when $\vec{k}$ is near the Bragg plane bisecting $\vec{K}_0$ (and not near any other Bragg planes) we have

$$c_k \sim c_{k-K_0} \sim O(1)$$
$$c_{k-K} \sim O(U) \quad \text{for all } \vec{K} \neq 0, \vec{K}_0$$
$$(\varepsilon - \varepsilon^{\circ}_{k}) \sim (\varepsilon - \varepsilon^{\circ}_{k-K_0}) \sim O(U)$$

so the energy shift is now $O(U)$ and the scattered wave c_{k-K_0} mixes equally with the original c_k.

This is quite different from case (1) where $\vec{k}$ was not near <u>any</u> Bragg plane and the energy shift was $O(U^2)$

To leading order, the above equations (1), (2), and (3) reduce to a set of two linear equations for c_k and c_{k-K_0}

$$(\varepsilon - \varepsilon_k^0)\, c_k = U_{K_0}\, c_{k-K_0}$$

$$(\varepsilon - \varepsilon_{k-K_0}^0)\, c_{k-K_0} = U_{-K_0}\, c_k$$

[If $\vec{k}$ is near n Bragg planes - that bisect R.L. vectors $\vec{K}_1, \vec{K}_2, \ldots, \vec{K}_n$, we would wind up with $n+1$ equations for $c_k, c_{k-K_1}, c_{k-K_2}, \ldots, c_{k-K_n}$]

We can write the above pair of equations in matrix form:

$$\begin{pmatrix} \varepsilon - \varepsilon_k^0 & -U_{K_0} \\ -U_{-K_0} & \varepsilon - \varepsilon_{k-K_0}^0 \end{pmatrix} \begin{pmatrix} c_k \\ c_{k-K_0} \end{pmatrix} = 0$$

We will have a non trivial solution only when the determinant of the matrix vanishes. This condition determines the two energy eigenvalues $\varepsilon_+, \varepsilon_-$.

Note $U_{-K_0} = U_{K_0}^*$ so above matrix is Hermitian, as it must be.

$$\Rightarrow \quad (\varepsilon - \varepsilon_k^0)(\varepsilon - \varepsilon_{k-K_0}^0) = |U_{K_0}|^2$$

$$\varepsilon^2 - \varepsilon(\varepsilon_k^0 + \varepsilon_{k-K_0}^0) + \varepsilon_k^0 \varepsilon_{k-K_0}^0 - |U_{K_0}|^2 = 0$$

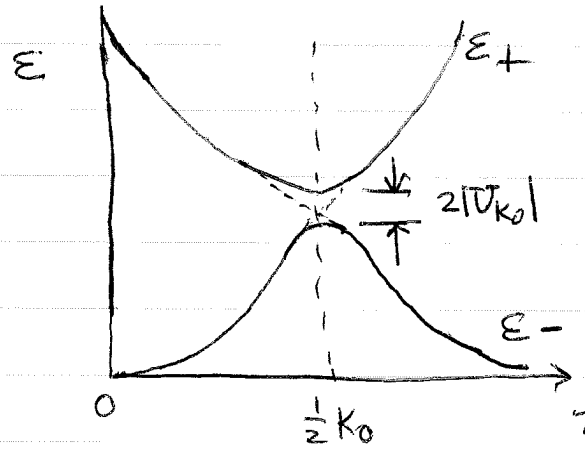
$$\varepsilon_\pm = \frac{\varepsilon_k^0 + \varepsilon_{k-K_0}^0}{2} \pm \sqrt{\frac{(\varepsilon_k^0 + \varepsilon_{k-K_0}^0)^2}{4} - \varepsilon_k^0 \varepsilon_{k-K_0}^0 + |U_{K_0}|^2}$$

$$(*) \quad \varepsilon_\pm = \frac{\varepsilon_k^0 + \varepsilon_{k-K_0}^0}{2} \pm \sqrt{\left(\frac{\varepsilon_k^0 - \varepsilon_{k-K_0}^0}{2}\right)^2 + |U_{K_0}|^2}$$

when $\vec{k}$ is exactly on a Bragg plane, $\varepsilon_k^0 = \varepsilon_{k-K_0}^0$

$$\varepsilon_\pm = \varepsilon_k^0 \pm |U_{K_0}|$$

gives jump $\Delta\varepsilon = \varepsilon_+ - \varepsilon_- = 2|U_{K_0}|$ at Bragg plane



energy dispersion relation from (*)

$k_\parallel = \vec{k} \cdot \hat{K}_0$

From (*) one can show that $\vec{v}_k = \frac{1}{\hbar}\frac{\partial \varepsilon}{\partial \vec{k}}$ has a vanishing component in the direction of $\vec{K}_0$ when $\vec{k}$ lies exactly on the Bragg plane - reasonable as $\vec{k}$ on Bragg plane $\Rightarrow$ we have a standing wave in $\hat{K}_0$ direction.

We can also consider the eigenvectors. ~~Exactly on~~ When $\vec{k}$ is exactly on a Bragg plane and $\varepsilon_\pm = \varepsilon_k^0 \pm |U_{k_0}|$ with $\varepsilon_k^0 = \varepsilon_{k+k_0}^0$ the matrix equation for the two degenerate states is:

$$\begin{pmatrix} \pm|U_{k_0}| & -U_{k_0} \\ -U_{-k_0} & \pm|U_{k_0}| \end{pmatrix} \begin{pmatrix} c_k \\ c_{k-k_0} \end{pmatrix} = 0$$

write $U_{k_0} = |U_{k_0}| e^{i\varphi}$ φ is phase of complex U_{k_0}
Above is then

$$|U_{k_0}| \begin{pmatrix} \pm 1 & -e^{i\varphi} \\ -e^{-i\varphi} & \pm 1 \end{pmatrix} \begin{pmatrix} c_k \\ c_{k-k_0} \end{pmatrix} = 0$$

$$\Rightarrow \quad \pm c_{k-k_0} = e^{-i\varphi} c_k$$

$$c_{k-k_0} = \pm e^{-i\varphi} c_k$$

so the two eigenvectors are $\sim \begin{pmatrix} 1 \\ e^{-i\varphi} \end{pmatrix}$ and $\begin{pmatrix} 1 \\ -e^{-i\varphi} \end{pmatrix} = \begin{pmatrix} c_k \\ c_{k-k_0} \end{pmatrix}$
These are orthonormal as necessary

$$\begin{pmatrix} c_k^* & c_{k-k_0}^* \end{pmatrix} \begin{pmatrix} c_k \\ c_{k-k_0} \end{pmatrix} = 1 - e^{i\varphi} e^{-i\varphi} = 0$$

and correspond to wavefunctions as we saw in our introductory discussion:

$$\psi_1 = e^{i\vec{k}\cdot\vec{r}} + e^{-i\varphi} e^{i(\vec{k}-\vec{k}_0)\cdot\vec{r}}$$

$$\psi_2 = e^{i\vec{k}\cdot\vec{r}} - e^{-i\varphi} e^{i(\vec{k}-\vec{k}_0)\cdot\vec{r}}$$

ψ_2 has π phase shift with respect to ψ_1

Velocity and constant energy surface at a Bragg plane

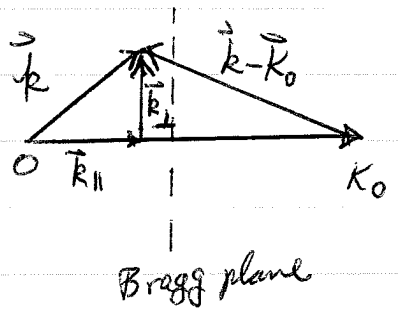
$$\vec{v}_n(\vec{k}) = \frac{1}{\hbar}\frac{\partial \varepsilon_n(\vec{k})}{\partial \vec{k}}$$

$\Rightarrow$ normal vector to a constant energy surface, $\varepsilon_n(\vec{k}) = \varepsilon_0$ constant, points in direction of $\vec{v}_n(\vec{k})$.

In the <u>weak potential approximation</u> for $\vec{k}$ near a Bragg plane bisecting R.L. vector $\vec{K}_0$ we had

$$\varepsilon_\pm = \frac{\varepsilon^0_k + \varepsilon^0_{k-K_0}}{2} \pm \sqrt{\left(\frac{\varepsilon^0_k - \varepsilon^0_{k-K_0}}{2}\right)^2 + |U_{K_0}|^2}$$

Write $\vec{k} = \vec{k}_\parallel + \vec{k}_\perp$, $\vec{k} - \vec{K}_0 = \vec{k}_\parallel - \vec{K}_0 + \vec{k}_\perp$ with $\vec{k}_\parallel$ the component of $\vec{k}$ parallel to $\vec{K}_0$



We can then write $\varepsilon_\pm$ as functions of $k_\parallel$ and $k_\perp$

$$\varepsilon_\pm = \frac{\hbar^2}{2m}\frac{(k_\parallel^2 + k_\perp^2) + (k_\parallel^2 + K_0^2 - 2k_\parallel K_0 + k_\perp^2)}{2}$$

$$\pm \sqrt{\left(\frac{\hbar^2}{2m}\right)^2\left(\frac{K_0^2 - 2k_\parallel K_0}{2}\right)^2 + |U_{K_0}|^2}$$

one can then show that

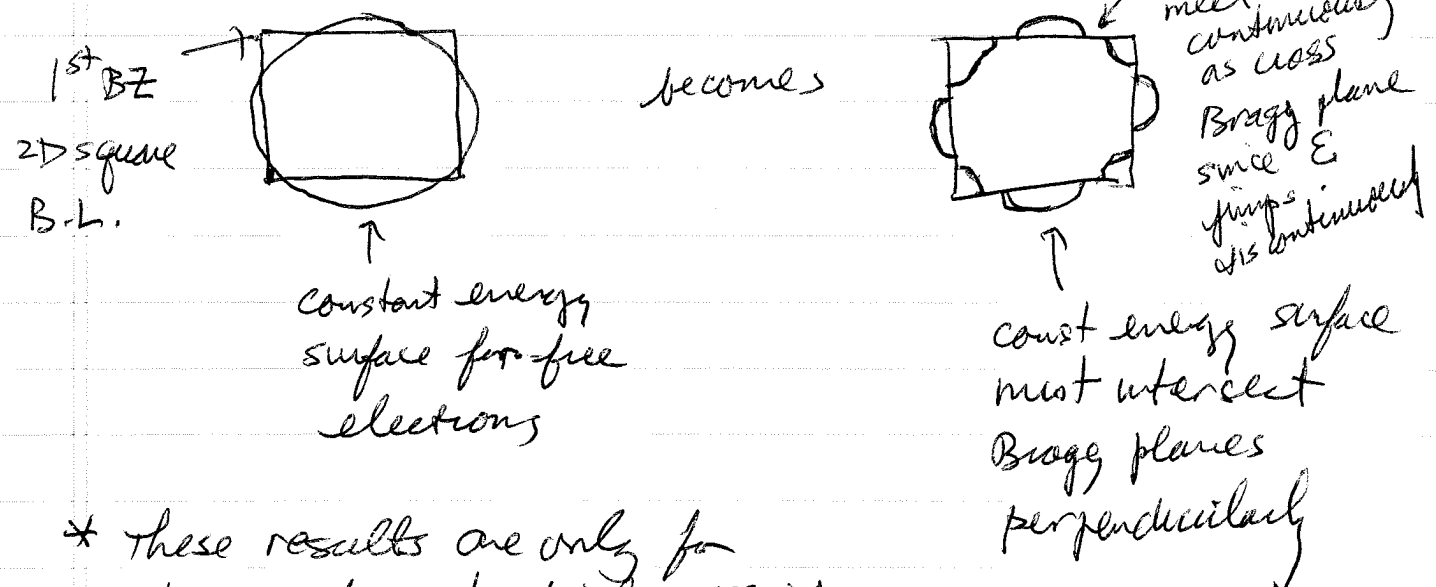
$\frac{\partial \mathcal{E}_\pm}{\partial k_{||}} \to 0$ as $k_{||} \to \frac{K_0}{2}$, ie when $\vec{k}$ lies exactly on the Bragg plane.

$$\frac{\partial \mathcal{E}_\pm}{\partial k_{||}} = \frac{\hbar^2}{2m}(2k_{||} - K_0) \pm \frac{\frac{1}{2}\left(\frac{\hbar^2}{2m}\right)^2 (K_0^2 - 2k_{||}K_0)(-2k_{||})}{\sqrt{\left(\frac{\hbar^2}{2m}\right)^2 \left(\frac{K_0^2 - 2k_{||}K_0}{2}\right)^2 + |U_{K_0}|^2}}$$

$= 0$ when $k_{||} = \frac{K_0}{2}$

$\Rightarrow$ velocity of electron exactly at Bragg plane is always in a direction lying within the Bragg plane — the component of $\vec{v}_n(k)$ parallel to $\vec{K}_0$, ie perpendicular to the Bragg plane, vanishes

$\Rightarrow$ constant energy surface must intersect Bragg plane perpendicularly



* these results are only for the weak potential approx

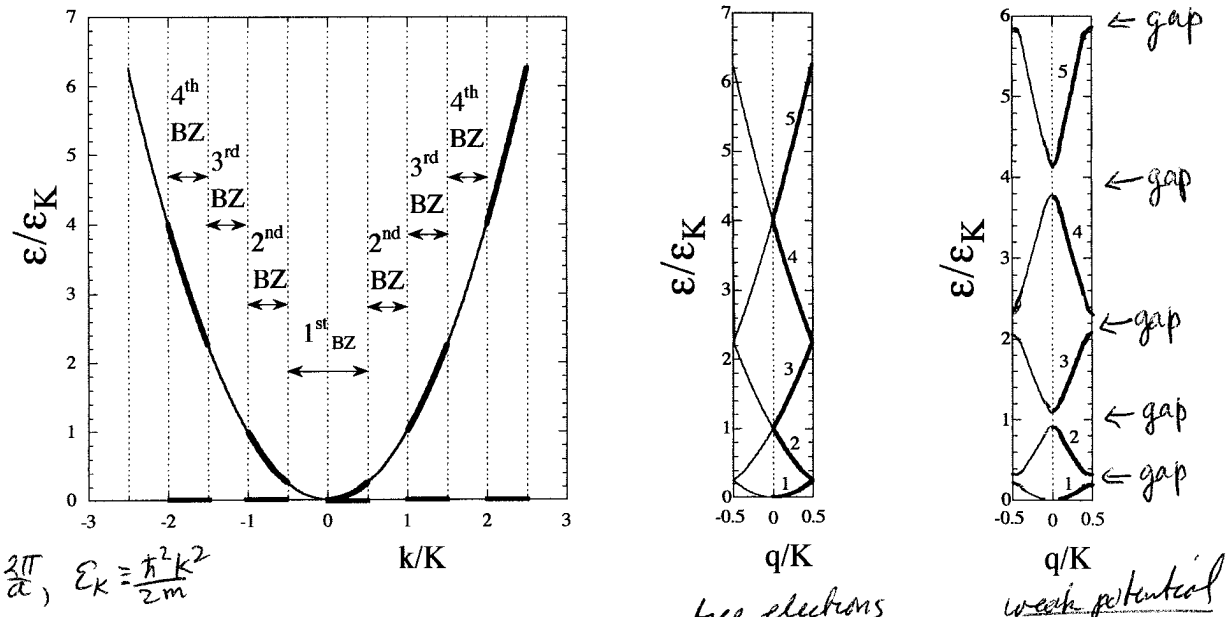
Band structure and ground state in weak potential approximation

Free electron energy spectrum is $\varepsilon_k^0 = \frac{\hbar^2 k^2}{2m}$

To represent the free electron energy spectrum in the "reduced zone" scheme, for each wavevector $\vec{k}$ we write

$$\vec{k} = \vec{q} + \vec{K}$$

where $\vec{q}$ is in the 1st BZ and $\vec{K}$ is in R.L. This decomposition is unique. We then plot $\varepsilon_k^0 = \hbar^2(\vec{q}+\vec{K})^2/2m$ as a function of $\vec{q}$ in 1st BZ. This gives a separate curve for each RL vector $\vec{K}$, and thus gives ε_k^0 represented as separate bands in the reduced zone scheme. When a weak potential is turned on, energy gaps are introduced wherever the free electron bands have a degeneracy (the degeneracies will occur when $\vec{q}+\vec{K}$ lies on a Bragg plane). In one dimension, the result looks like below:



$k = \frac{2\pi}{a}$, $\varepsilon_K = \frac{\hbar^2 k^2}{2m}$

extended zone — free electrons — reduced zone — weak potential

heavy lines are for $q+K$ with $0 \le q \le \frac{K}{2}$ – positive half 1st BZ

light lines are for $q+K$ with $-\frac{K}{2} \le q \le 0$ – negative half 1st BZ

In reduced zone plots, the numbers label the BZ that the band came from in the extended zone plot.

In 1-D the bands do not overlap ie

$$\max_{\vec{q}} \varepsilon_n(\vec{q}) < \min_{\vec{q}} \varepsilon_{n+1}(\vec{q})$$ n is band index

When $\max \varepsilon_n(\vec{q})$ and $\min \varepsilon_{n+1}(\vec{q})$ occur at the same value of $\vec{q}$, we say there is a direct gap. When they occur at different $\vec{q}$, we say there is an indirect gap.

Ground state in 1-D weak potential

To construct the ground state one fills up the lowest energy single electron eigenstates to get the lowest total energy many electron state consistent with the Pauli exclusion principal.

From Born-von Karman boundary conditions we know that in a BL with N sites, there are N allowed $\vec{k}$ vectors in any primative cell of the R.L. $\Rightarrow$ N allowed $\vec{q}$ vectors in the 1st BZ and hence 2N allowed electron states in each energy band (factor of 2 from spin ↑ or spin ↓ for each $\vec{q}$)

$\Rightarrow$ each energy band can hold 2 electrons per Bravais lattice site

Assume for simplicity we have a crystal structure with one ion at each BL site, with valence Z. ie each BL site contributes Z conduction electrons

In 1-D, since energy bands do not overlap:

① If $Z = 2m$ is <u>even</u>, then we completely fill up the lowest m bands and all other bands are completely empty

② If $Z = 2m+1$ is <u>odd</u>, then we completely fill up the lowest m bands, and the $(m+1)^{st}$ band is 1/2 filled. All higher bands are completely empty.

<u>case ① Z even</u>: material is an <u>insulator</u>

At low T in equilibrium, bands are completely filled or completely empty ⇒ there is an energy gap ε_g between the most energetic electron and the lowest unoccupied electron state (ie the first excited state)

$$\varepsilon_g = \min_q \varepsilon_{n+1}(q) - \max_q \varepsilon_n(q)$$

⇒ Unless electrons somehow receive an energy $\gtrsim \varepsilon_g$, they cannot scatter - no nearby empty states nearby in energy to scatter to! We will soon see that a filled band can carry no current

⇒ material is an insulator provided $k_B T \lesssim \varepsilon_g$ and $eEl \lesssim \varepsilon_g$ where l is the mean free path

When $k_B T \gtrsim \varepsilon_g$, the equilibrium state will have some electrons, with density $\sim e^{-\varepsilon_g / k_B T}$ excited over the gap ε_g from the top of the $m = Z/2$ band into the bottom of the $m+1$

band. Now these electrons at bottom of m+1 band at at top of m band will have nearby empty states they can scatter into. Apply an $\vec{E}$ field will scatter electrons and create a non equilibrium distribution that carries a finite current.

$$\Rightarrow \begin{cases} k_B T \ll \mathcal{E}_g \Rightarrow \text{insulator} \\ k_B T \gtrsim \mathcal{E}_g \Rightarrow \underline{\text{semiconductor}} - \text{carrier density} \sim e^{-\mathcal{E}_g/k_B T} \end{cases}$$

<u>case ② Z odd</u> : Material is a metal

The highest band containg electrons is partially (half) filled at $T=0$,

$\Rightarrow$ at any T there are empty states nearby in energy ~~to scatter into~~ ~~over energy gap~~ to the most energetic electrons at $\mathcal{E}_F$. There is no energy gap. When apply electric field $\vec{E}$ one will set up a non-equilibrium distribution carry a current

So for 1-D weak potential, Z odd $\Rightarrow$ metal
Z even $\Rightarrow$ insulator

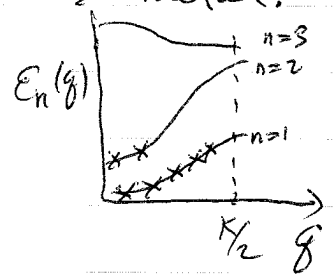
This was a consequence of the non-overlaping bands.

But in 2-D or 3-D (or even perhaps 1-D when potential is NOT weak) bands <u>can</u> coverlap,

ie we may have the case that

$$\max_{q} \varepsilon_n(q) > \min_{q} \varepsilon_{n+1}(q)$$

In such a case, as one constructs the ground state, one will start to fill up the $n+1$ band before one has completely filled the n band. Thus Z even need not be an insulator - we might have more than one partially filled band containing the most energetic electrons at E_F $\Rightarrow$ metal.



when bands overlap, can have several partially filled bands before completely filling a given band

However, we still would expect that if a material is an insulator, it must have only completely filled bands and completely empty bands (so no scattering possible). Since each filled band holds 2 electrons per Bravais lattice site, we would still expect Z must be even.

Thus we would expect that Z even is a necessary but not sufficient condition to have an insulator.

But it turns out that even this is not always true. While most insulators do have Z even, it was known in 1940's that some transition metal oxides, such as NiO and CoO, have Z odd but are still insulators!

Such materials, where Z is odd but material is an insulator, are called Mott insulators. It is believed that in these cases strong electron-electron interactions are responsible for the effect, invalidating the conclusions of the independent electron approximation that is the basis of band theory. To study such problems the simple Hubbard model is often used (the Hubbard model is simple to state, but very difficult to solve!)