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.

\[
|E_k^0 - E_{\vec{k}-\vec{k}_0}| \leq U \quad \text{but} \quad |E_k^0 - E_{\vec{k}-\vec{k}_0}| > U \\
\text{for all} \; \vec{k} \neq 0, \vec{k}_0
\]

From (1) we can write

\[
\vec{k} = 0 \quad (1) \quad (E - E_{\vec{k}_0}) C_k = \sum_{k' \neq 0, \vec{k}_0} U_{\vec{k}_0} C_{k-\vec{k}_0} + \sum_{k' \neq 0, \vec{k}_0} U_{\vec{k}_0} C_{k'-\vec{k}_0}
\]

\[
\vec{k} = \vec{k}_0 \quad (2) \quad (E - E_{\vec{k}_0}) C_{\vec{k}_0} = \sum_{k' \neq 0, \vec{k}_0} U_{\vec{k}_0} C_{k-\vec{k}_0} + \sum_{k' \neq 0, \vec{k}_0} U_{\vec{k}_0} C_{k'-\vec{k}_0}
\]

\[
\vec{k} \neq 0, \vec{k}_0 \quad (3) \quad (E - E_{\vec{k}-\vec{k}_0}) C_{\vec{k}_0} = \sum_{k' \neq 0, \vec{k}_0} U_{\vec{k}_0} C_{k-\vec{k}_0} + \sum_{k' \neq 0, \vec{k}_0} U_{\vec{k}_0} C_{k'-k_0}
\]

Now we can say that \( (E - E_{\vec{k}-\vec{k}_0}) \) must be greater than \( o(U) \) for \( \vec{k} \neq 0, \vec{k}_0 \) since \( (E - E_{\vec{k}-\vec{k}_0}) \) is greater than \( o(U) \). So eqn (3) \( \Rightarrow C_{\vec{k}_0} \) 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, \( C_{\vec{k}_0} \sim o(1) \) since we start with a free electron of wave vector \( \vec{k}_0 \). So from (2) we must conclude that

\[
(E - E_{\vec{k}-\vec{k}_0}) C_{\vec{k}-\vec{k}_0} \sim o(U)
\]
But \( (\varepsilon - \varepsilon_k - \varepsilon_0) \) cannot be bigger than \( O(1) \)
(since the difference is due to the potential \( V \))
and \( C_{k-k} \) cannot be bigger than \( O(1) \).

\[ \Rightarrow \text{only possibility is } C_{k-k_0} \sim O(1) \text{ and } (\varepsilon - \varepsilon_k - \varepsilon_0) \sim O(1) \Rightarrow (\varepsilon - \varepsilon_k) \sim O(1) \text{ also.} \]

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

\[ C_k \sim C_{k-k_0} \sim O(1) \]
\[ C_{k-k} \sim O(1) \text{ for all } \vec{k} \neq 0, \vec{k}_0 \]
\[ (\varepsilon - \varepsilon_k) \sim (\varepsilon - \varepsilon_k - \varepsilon_0) \sim O(1) \]

so the energy shift is now \( O(1) \)
and the scattered wave \( C_{k-k_0} \) mixes equally
with the original \( C_k \).

This is quite different from case \( 0 \) where \( \vec{k} \) was not near any Bragg plane and the energy shift was \( O(V^2) \).
To leading order, the above equations (1), (2), and (3) reduce to a set of two linear equations for $c_k$ and $c_{k-k_0}$

\[(E - \varepsilon_{k_0}^0) c_k = U_{k_0} c_{k-k_0}\]

\[(E - \varepsilon_{k-k_0}^0) c_{k-k_0} = U_{-k_0} c_k\]

If $k$ is near $n$ Bragg planes that bisect $k$ vectors $\bar{k}_1, \bar{k}_2, \ldots, \bar{k}_n$, 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:

\[
\begin{pmatrix}
E - \varepsilon_{k_0}^0 & -U_{k_0} \\
-U_{-k_0} & E - \varepsilon_{k-k_0}^0
\end{pmatrix}
\begin{pmatrix}
c_k \\
c_{k-k_0}
\end{pmatrix} = 0
\]

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.
\[(E - E_h^0) (E - E_{k-k_0}) = |U_{k_0}|^2\]

\[E^2 - E(E_k^0 + E_{k-k_0}) + E_h^0 E_{k-k_0} - |U_{k_0}|^2 = 0\]

\[E_{\pm} = \frac{E_k^0 + E_{k-k_0}}{2} \pm \sqrt{\left(\frac{E_k^0 + E_{k-k_0}}{2}\right)^2 - E_h^0 E_{k-k_0} + |U_{k_0}|^2}\]

\[(*)\]

\[E_{\pm} = \frac{E_k^0 + E_{k-k_0}}{2} \pm \sqrt{\left(\frac{E_k^0 - E_{k-k_0}}{2}\right)^2 + |U_{k_0}|^2}\]

when \(\vec{k}\) is exactly on a Bragg plane, \(E_h^0 = E_{k-k_0}\)

\[E_{\pm} = E_k^0 \pm |U_{k_0}|\]

gives jump \(\Delta E = E_+ - E_- = 2|U_{k_0}|\) at Bragg plane

From \((*)\) one can show that \(\vec{E}_h = \frac{1}{h} \frac{2E}{\partial k}\) has

a vanishing component in the direction of \(\vec{k}\)

when \(\vec{k}\) lies exactly on the Bragg plane

reasonable as \(\vec{k}\) on Bragg plane yields a standing wave in \(\vec{k}_0\) direction.
We can also consider the eigenvectors. Exactly when \( \mathbf{T} \) is exactly on a Bragg plane and 
\[ E_{\pm} = E_{k}^{0} \pm |U_{k}| \] 
with \( E_{k}^{0} = E_{k+k_{0}}^{0} \) the matrix equation for the two degenerate states \( c_{k} \) and \( c_{k-k_{0}} \)

\[
\begin{pmatrix}
\pm |U_{k}| & -U_{k} \\
-U_{k} & \pm |U_{k}|
\end{pmatrix}
\begin{pmatrix}
c_{k} \\
c_{k-k_{0}}
\end{pmatrix} = 0
\]

write \( U_{k_{0}} = |U_{k_{0}}| e^{i\varphi} \) \( \varphi \) in plane of complex \( U_{k_{0}} \)
Above is then

\[
|U_{k_{0}}|
\begin{pmatrix}
\pm 1 & -e^{i\varphi} \\
-e^{-i\varphi} & \pm 1
\end{pmatrix}
\begin{pmatrix}
c_{k} \\
c_{k-k_{0}}
\end{pmatrix} = 0
\]

\[ \Rightarrow \pm c_{k-k_{0}} = e^{-i\varphi} c_{k} \]
\[ c_{k-k_{0}} = \pm e^{-i\varphi} c_{k} \]
so the two eigenvectors are \( \sim (1) \) and \( (1) \)

These are orthonormal as necessary

\[
\frac{c_{k}}{c_{k-k_{0}}} = 1 - e^{i\varphi} - e^{-i\varphi} = 0
\]

and correspond to wave functions as we saw

\[ \psi_{1} = e^{-ik_{-} \mathbf{r}} + e^{i\varphi} e^{i(k_{-} - k_{0}) \cdot \mathbf{r}} \]

\[ \psi_{2} = e^{-ik_{-} \mathbf{r}} - e^{i\varphi} e^{i(k_{-} - k_{0}) \cdot \mathbf{r}} \]

\( \psi_{2} \) has \( \pi \) phase shift (or \( \psi_{2} \) is rotated to \( \psi_{1} \))
Velocity and constant energy surface at a Bragg plane

\[ \mathbf{V}_n (\mathbf{k}) = \frac{1}{\hbar} \frac{\partial \mathbf{E}_n (\mathbf{k})}{\partial \mathbf{k}} \]

\( \mathbf{n} \) normal vector to a constant energy surface,

\( \mathbf{E}_n (\mathbf{k}) = \mathbf{E}_0 \) constant, points in direction of \( \mathbf{V}_n (\mathbf{k}) \).

In the weak potential approximation, for \( \mathbf{k} \) near a Bragg plane directly R.L. vector \( \mathbf{k}_0 \), we had

\[ \mathbf{E}_\pm = \frac{\mathbf{E}_k^0 + \mathbf{E}_{k-k_0}^0}{2} \pm \sqrt{\left( \frac{\mathbf{E}_k^0 - \mathbf{E}_{k-k_0}^0}{2} \right)^2 + |\mathbf{U}_{k_0}|^2} \]

Write \( \mathbf{k} = \mathbf{k}_\parallel + \mathbf{k}_\perp \), \( \mathbf{k} - \mathbf{k}_0 = \mathbf{k}_\parallel - \mathbf{k}_0 + \mathbf{k}_\perp \),

with \( \mathbf{k}_\parallel \) the component of \( \mathbf{k} \) parallel to \( \mathbf{k}_0 \).

We can then write \( \mathbf{E}_\pm \) as functions of \( k_\parallel \) and \( k_\perp \)

\[ \mathbf{E}_\pm = \frac{\hbar^2}{2m} \left( \frac{k_\parallel^2 + k_\perp^2}{2} + \left( \frac{k_\parallel^2 + k_0^2 - 2k_\parallel k_0 + k_\perp^2}{2} \right) \right) \]

\[ \pm \sqrt{\left( \frac{\hbar^2}{2m} \right)^2 \left( \frac{k_0^2 - 2k_\parallel k_0}{2} \right)^2 + |\mathbf{U}_{k_0}|^2} \]
one can then show that

\[ \frac{\partial \varepsilon \pm}{\partial k_{\parallel}} = 0 \quad \text{as} \quad k_{\parallel} \to \frac{k_0}{2}, \quad \text{i.e. when} \quad \mathbf{R} \quad \text{lies exactly on the Bragg plane,} \]

\[ \frac{\partial \varepsilon \pm}{\partial k_{\parallel}} = \frac{h^2}{2m} \left( 2k_{\parallel} - k_0 \right) \pm \frac{1}{2} \left( \frac{h^2}{2m} \right)^2 \left( k_0^2 - 2k_{\parallel}k_0 \right) \left( -2k_{\parallel} \right) \frac{1}{\sqrt{\left( \frac{h^2}{2m} \right)^2 \left( \frac{k_0^2 - 2k_{\parallel}k_0}{2} \right)^2 + \left( \mathbf{\tilde{R}} \right)^2}} \]

= 0 \quad \text{when} \quad k_{\parallel} = \frac{k_0}{2} \]

⇒ velocity of electron exactly at Bragg plane
is always in a direction lying within the Bragg plane
- the component of \( \mathbf{v} \) (k) parallel to \( \mathbf{R}_0 \), i.e. perpendicular to the Bragg plane, vanishes

⇒ constant energy surface must intersect Bragg plane perpendicularly

1st BZ
2D square B.L.

constant energy surface for free electrons

these results are only for the weak potential approx
Bend structure and ground state in weak potential approximation

Free electron energy spectrum is \( \varepsilon_k = \frac{\hbar^2 k^2}{2m} \).

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 \( \varepsilon_0 = \frac{\hbar^2 (\vec{q} + \vec{K})^2}{2m} \) as a function of \( \vec{q} \) in 1st BZ. This gives a separate curve for each RL vector \( \vec{K} \), and this gives \( \varepsilon_0 \) 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 Bravais plane). In one dimension, the result looks like below:

\[ k = \frac{2\pi}{a}, \quad \varepsilon_k = \frac{\hbar^2 k^2}{2m} \]

---

Extended zone

Heavy lines are for \( \vec{q} + \vec{K} \) with \( 0 \leq \vec{q} \leq \frac{\vec{K}}{2} \) - positive half 1st BZ

Light lines are for \( \vec{q} + \vec{K} \) with \( -\frac{\vec{K}}{2} \leq \vec{q} \leq 0 \) - negative half 1st BZ

In reduced zone plots, the number label the BZ that the band came from in the extended zone plot.
In 1-D the bands do not overlap if
\[
\max_{\vec{q}} E_n(\vec{q}) < \min_{\vec{q}} E_{n+1}(\vec{q}) \quad n \text{ is band index}
\]

When \( \max_{\vec{q}} E_n(\vec{q}) \) and \( \min_{\vec{q}} E_{n+1}(\vec{q}) \) 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 eigenstate to get the lowest total energy many electron state consistent with the Pauli exclusion principle.

From Born-van-Kasen boundary conditions we know that in a BL with \( N \) sites, there are \( N \) allowed \( \vec{k} \) vectors in any primitive cell of the BZ, \( \Rightarrow \) \( N \) allowed \( \vec{q} \) vectors in the 1st BZ and hence \( 2N \) allowed electron states in each energy band (factor of 2 from spin \( \uparrow \) or spin \( \downarrow \) 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 \( Z \). i.e. each BL site contributes \( Z \) conduction electrons
In 1-D, since energy bands do not overlap:

1. If \( Z = 2m \) is even, then we completely fill up the lowest \( m \) bands and all other bands are completely empty.

2. If \( Z = 2m+1 \) is odd, then we completely fill up the lowest \( m \) bands, and the \((m+1)\)st band is \( \frac{1}{2} \) filled. All higher bands are completely empty.

**Case 1: \( Z \) even:** Material is an insulator.

At low \( T \) in equilibrium, bands are completely filled or completely empty \( \Rightarrow \) there is an energy gap \( E_g \) between the most energetic electron and the lowest unoccupied electron state (i.e., the first excited state)

\[
E_g = \min_{q} \varepsilon_{n+1}(q) - \max_{q} \varepsilon_{n}(q)
\]

\( \Rightarrow \) Unless electrons somehow receive an energy \( \geq E_g \), they cannot scatter - no available empty states offer an energy to scatter to! We will soon see that a filled band can carry no current.

\( \Rightarrow \) material is an insulator provided \( k_B T \leq E_g \) and \( E_{EL} \leq E_g \) where \( E_{EL} \) is the mean free path.

When \( k_B T \geq E_g \), the equilibrium state will have some electrons, with density \( n \approx e^{-E_g/k_B T} \), excited over the gap \( E_g \) from the top of the \( m = \frac{3}{2} \) band into the bottom of the \((m+1)\)st band.
band. Now these electrons at bottom of M band at top of W band will have nearly empty states they can scatter into. Applying an E field will scatter electrons and create a non-equilibrium distribution that carries a finite current.

\[
\begin{align*}
\text{kT} \ll E_g & \Rightarrow \text{insulator} \\
\text{kT} \gg E_g & \Rightarrow \text{semiconductor - carries density } \sim e^{-E_g/kT}
\end{align*}
\]

**Case 2**  
\[ Z \text{ odd } \]: Material is a metal  
The highest band containing electrons is partially (half) filled at \( T=0 \).

\[
\Rightarrow \text{ at any } T \text{ there are empty states nearby in energy scattered into more energetic states to the most energetic electrons at } E_F.
\]

There is no energy gap. When apply electric field \( E \) one will set up a non-equilibrium distribution carrying a current.

So for 1-D weak potential, \[ Z \text{ odd } \Rightarrow \text{metal} \]  
\[ Z \text{ even } \Rightarrow \text{insulator} \]

This was a consequence of the non-overlapping bands.

But in 2-D or 3-D (or even perhaps 1-D when potential is NOT weak) bands can overlap.
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.

This \( Z \) even need not be an insulator—we might have more than one partially filled band containing the most energetic electrons at \( E_F \) and \( \Rightarrow \) metal.

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 single Hubbard model is often used (the Hubbard model is simple to state, but very difficult to solve!)