The goal here is to find a method complementary to the Central Equation that will allow us to make statements about how E varies with $\vec{k}$. (Based largely on Stokes' book)

Step 1: We consider free electrons. That is, we will be saying (in Step 2) that the wave function in the crystal for a given $\vec{k}$ is very close to the wavefunction of a free electron for that same $\vec{k}$. For the free electron: $\psi^0_{\vec{k}} = C^0_{\vec{k}} e^{i\vec{k}\cdot\vec{r}}$ (the zero superscripts mean "free")

If you plug into Schroedinger Eqn, you get $E = \frac{\hbar^2 k^2}{2m}$. That is:

$$-\frac{\hbar^2}{2m}\nabla^2\psi^0_{\vec{k}} + 0\,\psi^0_{\vec{k}} = \frac{\hbar^2 k^2}{2m}\psi^0_{\vec{k}}$$

(0 = potential is zero, for free electrons)

These plane waves have two important properties

(1) They form a "complete set." That is, any wavefunction ψ can really be written this way, as we did. (That's the same property sines + cosines have in Fourier analysis.)

(2) They are orthogonal. That means unless $\vec{k}' = \vec{k}$, when you multiply by $(\psi_{k'})^*$ (complex conjugate) and integrate, you get zero:

Proof:
$$\int \left(C^0_{\vec{k}'} e^{i\vec{k}'\cdot\vec{r}}\right)^* \left(C^0_{\vec{k}} e^{i\vec{k}\cdot\vec{r}}\right) dV$$
$$= C^{0*}_{\vec{k}'} C^0_{\vec{k}} \int e^{i(\vec{k}-\vec{k}')\cdot\vec{r}}\, dV$$

$\int e^{i(\vec{k}-\vec{k}')\cdot\vec{r}}\, dV \approx 0$ unless $\vec{k}=\vec{k}'$, since it oscillates up and down rapidly. $= V$ when $\vec{k}=\vec{k}'$

$C^0_{\vec{k}} C^{0*}_{\vec{k}} = |C^0_{\vec{k}}|^2 = \frac{1}{V}$ ← therefore

Step 2: We consider "nearly free" electrons. There is some small nonzero potential U

The $\psi_{\vec{k}}$'s will be different, but not very different. Write as an expansion

$$\psi_{\vec{k}} = \psi^0_{\vec{k}} + \sum_{\vec{k}' \neq \vec{k}} C_{\vec{k}'}\,\psi^0_{\vec{k}'}$$

- $\psi_{\vec{k}}$: new wavefunction for $\vec{k}$
- $\psi^0_{\vec{k}}$: original wavefunction for $\vec{k}$, really has a coefficient slightly less than 1.
- $\sum_{\vec{k}' \neq \vec{k}}$: because we pulled $\vec{k}$ out of summation
- $C_{\vec{k}'}$: small!
- $\psi^0_{\vec{k}'}$: other wavefunction from original $U=0$ situation

Plug this into the Schroedinger Eqn, $-\frac{\hbar^2}{2m}\nabla^2\psi_{\vec{k}} + U(\vec{r})\psi_{\vec{k}} = E_{\vec{k}}\psi_{\vec{k}}$

($E_{\vec{k}}$: Actual energy associated with that wavefunction)

and we get...

$$-\frac{\hbar^2}{2m}\nabla^2\left[\psi_{\vec{k}}^0 + \sum_{\vec{k}'\neq\vec{k}} C_{\vec{k}'}\psi_{\vec{k}'}^0\right] + U(\vec{r})\left[\psi_{\vec{k}}^0 + \sum_{\vec{k}'\neq\vec{k}} C_{\vec{k}'}\psi_{\vec{k}'}^0\right] = E_k\left[\psi_{\vec{k}}^0 + \sum_{\vec{k}'\neq\vec{k}} C_{\vec{k}'}\psi_{\vec{k}'}^0\right]$$

From the original Schrodinger Eqn ($U=0$), this $= \frac{\hbar^2 k^2}{2m} \times \psi_{\vec{k}}^0$ → call this E_k^0 (Notation 1)

similarly, each of these produces an $\frac{\hbar^2 k'^2}{2m}$ term,

$$= \sum_{\vec{k}'\neq\vec{k}} C_{\vec{k}'} E_{\vec{k}'}^0 \psi_{\vec{k}'}^0$$

$$\underbrace{E_k^0 \psi_{\vec{k}}^0}_{(a)} + \sum_{\vec{k}'\neq\vec{k}} \underbrace{C_{\vec{k}'} E_{\vec{k}'}^0 \psi_{\vec{k}'}^0}_{(b)} + \underbrace{U(\vec{r})\psi_{\vec{k}}^0}_{(c)} + \sum_{\vec{k}'\neq\vec{k}} \underbrace{C_{\vec{k}'} U(\vec{r})\psi_{\vec{k}'}^0}_{(d)} = \underbrace{E_k\psi_{\vec{k}}^0}_{(e)} + \underbrace{E_k \sum_{\vec{k}'\neq\vec{k}} C_{\vec{k}'}\psi_{\vec{k}'}^0}_{(f)} \qquad \text{Eqn (1)}$$

important eqn with six terms, labeled (a) through (f)

We'll use Eqn (1) two ways.

(1) Multiply by $(\psi_{\vec{k}}^0)^*$ and integrate. That produces effects like these:

(a) $\int (\psi_{\vec{k}}^0)^* (\psi_{\vec{k}}^0)\, dV = 1$

(b) $\int (\psi_{\vec{k}}^0)^* (\psi_{\vec{k}'}^0)\, dV = 0$

(c) $\int (\psi_{\vec{k}}^0)^* U(\vec{r}) (\psi_{\vec{k}}^0)\, dV =$ "$U_{\vec{k}\vec{k}}$" (notation 2)

(d) $\int (\psi_{\vec{k}}^0)^* U(\vec{r}) (\psi_{\vec{k}'}^0)\, dV =$ "$U_{\vec{k}\vec{k}'}$" (Notation 3)

(e) $\int (\psi_{\vec{k}'}^0)^* (\psi_{\vec{k}'}^0)\, dV = 1$

(f) $\int (\psi_{\vec{k}'}^0)^* (\psi_{\vec{k}''}^0)\, dV = 0$

Eqn (1) therefore becomes

$$E_k^0 + U_{\vec{k}\vec{k}} + \sum_{\vec{k}'\neq\vec{k}} C_{\vec{k}'} U_{\vec{k}\vec{k}'} = E_k \qquad \text{Eqn (2)}$$

I.e., new energy = old energy + stuff.

Since the $C_{\vec{k}'}$'s are small, the main correction to the energy is $U_{\vec{k}\vec{k}}$:

$$E_k = E_k^0 + U_{\vec{k}\vec{k}}$$

Eqn (2) still, to first order.

(2) To complete the story, we need to know the $C_{\vec{k}'}$'s

Multiply Eqn (1) by $(\psi_{\vec{k}''}^0)^*$ and integrate. That produces terms like:

↳ an arbitrary term in summation, $\vec{k}'' \neq \vec{k}$

(a) $\int (\psi_{k''}^{\circ})^* (\psi_{k}^{\circ}) \, dV = 0$

(b) $\int (\psi_{k''}^{\circ})^* (\psi_{k'}^{\circ}) \, dV =$ nonzero only when $k'' = k'$ (one term in summation) In that case $= 1$

(c) $U_{k''k}$

(d) sum of $U_{k''k'}$ terms

(e) $\int (\psi_{k'',1}^{\circ})^* (\psi_{k}^{\circ}) \, dV = 0$

(f) $\int (\psi_{k''}^{\circ})^* (\psi_{k'}^{\circ}) \, dV =$ nonzero only when $k'' = k'$, and then $= 1$

Eqn (1) therefore becomes

$$C_{k''} E_{k''}^{\circ} + U_{k''k} + \underbrace{\sum_{k' \neq k} C_{k'} U_{k''k'}}_{\text{much smaller than } U_{k''k}, \text{ so toss out}} = \underbrace{E_k C_{k''}}_{\text{Approximate this as } E_k^{\circ}}$$

Solve for $C_{k''}$:

$$C_{k''} \approx \frac{U_{k''k}}{E_k^{\circ} - E_{k''}^{\circ}}$$

Now rename k'' as k'

$$\boxed{C_{k'} \approx \frac{U_{k'k}}{E_k^{\circ} - E_{k'}^{\circ}}} \qquad \text{Eqn (3)}$$

Plug Eqn (3) into Eqn (2)

$$\boxed{E_k = E_k^{\circ} + U_{kk} + \sum_{k' \neq k} \frac{U_{k'k} U_{kk'}}{E_k^{\circ} - E_{k'}^{\circ}}} \qquad \text{Eqn (4)}$$

zeroth order — first order correction — second order correction

So, if we know the potential $U(r)$, we can in principle calculate the $U_{kk'}$-type integrals for each k (and k'), and know how E vs k deviates from the free electron energies $\frac{\hbar^2 k^2}{2m}$

Step 3 Analyze this very important result, Eqn (4)

First order $U_{\vec{k}\vec{k}} = \int (\psi_{\vec{k}}^{0})^{*}\, u(\vec{r})\, (\psi_{\vec{k}}^{0})\, dV$

$= \int u(\vec{r}) \underbrace{|C_k^{(0)}|^2}_{=\frac{1}{V}} \underbrace{e^{-i\vec{k}\cdot\vec{r}}\, e^{i\vec{k}\cdot\vec{r}}}_{=1}\, dV$

$U_{\vec{k}\vec{k}} = \frac{1}{V}\int u(\vec{r})\, dV$

↳ doesn't depend on $\vec{k}$!

So, to first order, a non-zero U just shifts entire bands up or down by some amount.

Second order Same sort of integral, but with $\vec{k}' \neq \vec{k}'$

$U_{\vec{k}\vec{k}'} = \frac{1}{V}\int u(\vec{r})\, e^{i(\vec{k}'-\vec{k})\cdot\vec{r}}\, dV$

Consider what happens when $\vec{r} \to \vec{r} + \vec{R}$ ↳ a lattice vector

Let $\vec{r}' = \vec{r} - \vec{R}$

$U_{\vec{k}\vec{k}'} = \frac{1}{V}\int \underbrace{u(\vec{r}'+\vec{R})}_{=u(\vec{r}')}\, e^{i(\vec{k}'-\vec{k})\cdot(\vec{r}'+\vec{R})}\, dV'$

$= e^{i(\vec{k}'-\vec{k})\cdot\vec{R}} \underbrace{\frac{1}{V}\int u(\vec{r}')\, e^{i(\vec{k}'-\vec{k})\cdot\vec{r}'}\, dV'}_{\text{equals } U_{\vec{k}\vec{k}'}}$

↓

must = 1!

$\therefore \boxed{\vec{k}'-\vec{k} = \vec{G}}$ a reciprocal lattice vector

This means you only get a 2nd order contribution from electron states at the same reduced-zone k values.

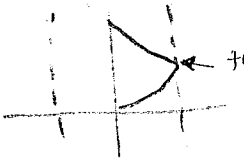
I.e., the sum over $\vec{k}$ in eqn (4) above just has to be done for $\vec{k}$'s separated from the $\vec{k}$ of interest by a R.L.V.

Step 4 The special case of the B.Z. edge

In Eqn 4, $E_k = E_k^0 + U_{\vec{k}\vec{k}} + \sum_{\vec{k}' = \vec{k}+\vec{G}} \frac{U_{\vec{k}\vec{k}'} U_{\vec{k}'\vec{k}}}{E_k^0 - E_{k'}^0}$

a serious problem occurs when $E_k^0 = E_{k'}^0$. Denominator = 0!

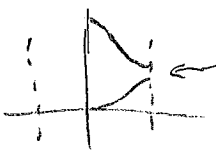
This is the case at zone edges



You have to solve this a different way,

using "Degenerate Perturbation Theory"

The results show (1) a band gap opens up and (2) the slope of E vs k goes to 0.



Conceptually, this is related to Bragg scattering: the condition where $\vec{k}' = \vec{k} + \vec{G}$ and $E_k = E_{k'}$ is just the same as elastic phonon scattering studied in chapter 2. So, you can think of the two results occurring as the electron waves at the BZ boundary get Bragg reflected back and form a standing wave which doesn't transmit energy. (Again, compare to phonon standing waves at BZ edge as studied in Chapter 3.)

Back to the math: As in Step 2,

$$\psi_{\vec{k}} = \psi_{\vec{k}}^0 + \underbrace{\sum_{\vec{k}' \neq \vec{k}} C_{\vec{k}'} \psi_{\vec{k}'}^0}$$

Ignore all of the terms in summation except the one that has the same energy as $\psi_{\vec{k}}^0$.

Recognize that this term can be very significant, so we'd better not say it's coefficient is small. Nor that the $\psi_{\vec{k}}^0$ coefficient is about equal to 1.

So, now we have

$$\psi_{\vec{k}} = C_{\vec{k}}\psi^0_{\vec{k}} + C_{\vec{k}'}\psi^0_{\vec{k}'}$$

Plug this into Schrodinger Eqn as in Step 2 above

$$-\frac{\hbar^2}{2m}\nabla^2\left[C_{\vec{k}}\psi^0_{\vec{k}} + C_{\vec{k}'}\psi^0_{\vec{k}'}\right] + U(\vec{r})\left[C_{\vec{k}}\psi^0_{\vec{k}} + C_{\vec{k}'}\psi^0_{\vec{k}'}\right] = E_k\left[C_{\vec{k}}\psi^0_{\vec{k}} + C_{\vec{k}'}\psi^0_{\vec{k}'}\right]$$

$$C_{\vec{k}}E^0_k\psi^0_{\vec{k}} + C_{\vec{k}'}E^0_{k'}\psi^0_{\vec{k}'} + C_{\vec{k}}U(\vec{r})\psi^0_{\vec{k}} + C_{\vec{k}'}U(\vec{r})\psi^0_{\vec{k}'} = C_{\vec{k}}E_k\psi^0_{\vec{k}} + C_{\vec{k}'}E_k\psi^0_{\vec{k}'}$$

Eqn (1) analog

We do the same two things we did to Eqn back in Step 2, pg 2

(1) Multiply by $(\psi^0_{\vec{k}})^*$ and integrate.

(2) Multiply by $(\psi^0_{\vec{k}'})^*$ and integrate.

That gives us

(1) $C_{\vec{k}}E^0_k + C_{\vec{k}}U_{\vec{k}\vec{k}} + C_{\vec{k}'}U_{\vec{k}\vec{k}'} = C_{\vec{k}}E_k$

(2) $C_{\vec{k}'}E^0_{k'} + C_{\vec{k}}U_{\vec{k}'\vec{k}} + C_{\vec{k}'}U_{\vec{k}'\vec{k}'} = C_{\vec{k}'}E_k$ ($U_{\vec{k}'\vec{k}'} = U_{\vec{k}\vec{k}}$)

Written as a matrix equation:

$$\begin{pmatrix} E^0_k + U_{\vec{k}\vec{k}} - E_k & U_{\vec{k}\vec{k}'} \\ U_{\vec{k}\vec{k}'} & E^0_{k'} + U_{\vec{k}\vec{k}} - E_k \end{pmatrix}\begin{pmatrix} C_{\vec{k}} \\ C_{\vec{k}'} \end{pmatrix} = 0$$

for non-zero solutions, force $\det(\ ) = 0$

$$\left(E^0_k + U_{\vec{k}\vec{k}} - E_k\right)\left(E^0_{k'} + U_{\vec{k}\vec{k}} - E_k\right) - U^2_{\vec{k}\vec{k}'} = 0$$

Solve for E_k (skipping several lines of algebra)

$$E_k = E_{k\text{-ave}} + U_{\vec{k}\vec{k}} \pm \sqrt{\frac{1}{4}E^2_{k\,\text{diff}} + U^2_{\vec{k}\vec{k}'}}$$

$E_{k\text{-ave}} \rightarrow \frac{E^0_k + E^0_{k'}}{2}$; $E_{k\,\text{diff}} \rightarrow E^0_{k'} - E^0_k$

But we've already specified that $E^0_k = E^0_{k'}$!

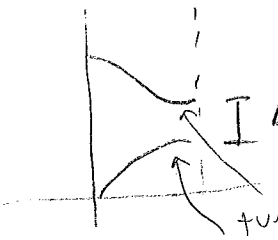
Therefore the two energy values become

$$\text{(upper)}\quad E_k^+ = E_k^0 + U_{\vec{k}\vec{k}} + |U_{\vec{k}\vec{k}'}|$$
$$\text{(lower)}\quad E_k^- = E_k^0 + U_{\vec{k}\vec{k}} - |U_{\vec{k}\vec{k}'}|$$

Eqn (5)

Gap between the two is

$$\Delta E = 2|U_{\vec{k}\vec{k}'}|$$



turns out... (a bit more work) that the bands approach the gap region in a parabolic fashion.

What did we learn?

① Away from the zone edge degeneracy
- to first order, all energies for various k's get shifted up/down the same amount
- to second order, differences occur, but they only depend on higher bands at the same k-value (reduced zone scheme)

② At zone edge, a gap opens up with $\Delta E = 2U_{\vec{k}\vec{k}'}$
$= 2\int (\psi_{k'}^0)^* U(\vec{r}) (\psi_{k}^0)\, dV$

③ Near the zone edge, $k = k_{\text{zone edge}} + \Delta k$, the energy dependence is parabolic: $E_{\text{upper}} = E_k^+ + C_1 \Delta k^2$
$E_{\text{lower}} = E_k^- - C_2 \Delta k^2$