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 \( k \). (Based largely on Stickel's 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 \( k \) is very close to the wave function of a free electron for that same \( k \). For the free electron: \( \Psi^0_k = C_k e^{i \mathbf{k} \cdot \mathbf{r}} \). (The zero superscript means "free")

If we plug into Schrodinger's Eqn, you get \( E = \frac{\hbar^2 k^2}{2m} \). That is:

\[
\frac{-\hbar^2}{2m} \nabla^2 \Psi^0_k + \mathbf{O} \Psi^0_k = \frac{\hbar^2 k^2}{2m} \Psi^0_k
\]

This plane waves have two important properties:

1. They form a "complete set." That is, any wavefunction \( \Psi \) can really be written this way, as we did. (That's the same property that comes from Fourier analysis.)

2. They are orthogonal. That means unless \( k' = k \), when you multiply by \( (\Psi_k)^\dagger \) and integrate, you get zero:

\[
\int (C_k^\dagger C_{k'} e^{i \mathbf{k} \cdot \mathbf{r}})^* (C_k e^{i \mathbf{k} \cdot \mathbf{r}}) \, dV = 0 \quad \text{unless} \quad k = k'
\]

**Step 2:** We consider "nearby free" electrons, that is, some small nonzero potential \( U \).

The \( \Psi_k \)'s will be different, but not very different. Write as an expansion

\[ \Psi_k = \Psi^0_k + \sum_{k'} C_{k'} \Psi^0_{k'} \]

where the \( k' \) wavefunctions are small compared to the original wavefunction.

Plug this into the Schrodinger Eqn:

\[
\frac{-\hbar^2}{2m} \nabla^2 \Psi_k + U(\mathbf{r}) \Psi_k = E \Psi_k
\]

and we get...
\[-\frac{k^2}{2m} \sum \left( V(x) + \sum_{E^0} C_i E^0 \frac{\partial V}{\partial x} \right) + U(x) \left( \sum_{E^0} C_i E^0 \frac{\partial V}{\partial x} \right) = E_k \left( \sum_{E^0} C_i E^0 \right) \]

From the original equation \((E=0)\),
this is \(\frac{1}{2m} \sum \frac{\partial^2 V}{\partial x} \sum_{E^0} E^0 \frac{\partial V}{\partial x} \)
\[= \sum_{E^0} C_i E^0 \frac{\partial V}{\partial x} \]
\[\text{Call this } E_k \text{ (notation 1)} \]

\[E_k \psi_k^0 + \sum_{E^0} C_i \psi_i \left( E_k \psi_k^0 \right) + \sum_{E^0} C_i U(x) \psi_i \]
\[= E_k \psi_k^0 + E_k \sum_{E^0} C_i \psi_i \psi_k^0 \]

It is important to note that each term has six terms.

**Eqn (1)**

We will use Eqn (1) two ways:

1. Multiply by \((\psi_k^0)^*\) and integrate, that produces terms like these:
   
   (a) \(\int (\psi_k^0)^* \psi_k^0 \, dV = 1\)
   
   (b) \(\int (\psi_k^0)^* \psi_k^0 \, dV = 0\)
   
   (c) \(\int (\psi_k^0)^* U(x) \, dV = "U_k^0" \text{ (notation 2)}\)
   
   (d) \(\int (\psi_k^0)^* U(x) \psi_k^0 \, dV = n U_k^0 \text{ (notation 3)}\)

   (e) \(\int (\psi_k^0)^* \psi_k^0 \, dV = 1\)
   
   (f) \(\int (\psi_k^0)^* \psi_k^0 \, dV = 0\)

**Eqn (1)** therefore becomes:

\[E_k^0 + U_k^0 + \sum_{E^0} C_i \psi_i^0 \psi_k^0 = E_k \]

**Eqn (2)**

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

Since the \(C_i\)'s are small, the main correction to the energy is \(U_k^0\):

\[E_k = E_k^0 + U_k^0 \]

**Eqn (2)** still holds to first order.

2. To complete the story, we need to know the \(C_i\)'s
   Multiply Eqn (1) by \((\psi_k^0)^*\) and integrate. That produces terms like:
   \(\int \psi_k^0 \psi_k^0 \psi_k^0 \psi_k^0 \, dV = \sum_{E^0} C_i \psi_i \psi_k^0 \psi_k^0 \psi_k^0 \psi_k^0 \)
   This is summation, \(\sum_{E^0} \psi_i \psi_k^0 \psi_k^0 \psi_k^0 \psi_k^0 \)
(a) $\int (g_k^0)^* (g_k^0) \, dV = 0$

(b) $\int (g_k^0)^* (g_{k'}^0) \, dV = \text{nonzero only when } k'' = k'$
   (one term in summation)
   In that case $\omega = 1$

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

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

(e) $\int (f_k^0)^* (f_k^0) \, dV = 0$

(f) $\int (f_k^0)^* (f_{k'}^0) \, dV = \text{nonzero only when } k'' = k'$
   and $\omega = 1$

Eqn (1) therefore becomes

$$C_k \approx E_k + U_{k'' k'} + \sum_{k'' k'} C_{k'' k'} U_{k'' k'} = E_k C_k$$

much smaller than...

approximate this as $E_k$

Solve for $C_k'$:

$$C_k' \approx \frac{U_{k'' k'}^*}{E_k - E_k^0}$$

now rename $k''$ as $k''$

$$C_k' \approx \frac{U_{k' k''}^*}{E_k - E_k^0} \quad \text{Eqn (3)}$$

Plug Eqn (3) into Eqn (2)

$$F_k = E_k^0 + U_{k' k''} + \sum_{k' + k'' = k} \frac{U_{k' k''} U_{k'' k'}}{E_k - E_k^0} \quad \text{Eqn (4)}$$

So, if we know the potential $U(k)$, we can in principle calculate
the $U_{k' k''}$-type integrals for each $k'$ (and $k''$), and
know how $E$ vs $k'$ deviates from the free electron energies $\frac{p_{k'}^2 m}{2}$
Step 3: Analyze this very important result, Eqn (4)

**First order**

\[ U_{kk'} = \int_C |C_k|^2 e^{i \mathbf{k} \cdot \mathbf{r}} \mathbf{e} \cdot dV \]

\[ = \int_C U(\mathbf{r}) \cdot \left[ C_k^* \right]^2 \mathbf{e} \cdot e^{i \mathbf{k} \cdot \mathbf{r}} \mathbf{e} \cdot dV \]

\[ = \frac{1}{V} \int_C U(\mathbf{r}) \cdot dV \]

Since \( \mathbf{U} \) doesn't depend on \( \mathbf{k} \), only \( \mathbf{k} \).

So, in first order, a non-zero \( \mathbf{U} \) just shifts the whole bands up or down by some amount.

**Second order**

Same sort of integral but with \( \mathbf{k} \cdot \mathbf{r} \)

\[ U_{kk'}^{(2)} = \frac{1}{V} \int_C U(\mathbf{r}) \cdot e^{i (\mathbf{k} + \mathbf{k'}) \cdot \mathbf{r}} \mathbf{e} \cdot dV \]

Consider what happens when \( \mathbf{r} \rightarrow \mathbf{r} + \mathbf{R}_{\text{ellec/vec}} \)

Let \( \mathbf{r}' = \mathbf{r} + \mathbf{R}_{\text{ellec/vec}} \)

\[ U_{kk'}^{(2)} = \frac{1}{V} \int_C U(\mathbf{r}') \cdot e^{i (\mathbf{k} + \mathbf{k'}) \cdot \mathbf{r}'} \mathbf{e} \cdot dV' \]

\[ = e^{i (\mathbf{k} + \mathbf{k'}) \cdot \mathbf{R}_{\text{ellec/vec}}} \frac{1}{V} \int_C U(\mathbf{r}) \cdot e^{i (\mathbf{k} + \mathbf{k'}) \cdot \mathbf{r}} \mathbf{e} \cdot dV' \]

\[ \downarrow \]

Must = 1!

\[ \Rightarrow \left[ \mathbf{k} + \mathbf{k}' = \mathbf{g} \right] \] 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 \( \mathbf{k} \) in Eqn (4)

above just has to be done for \( \mathbf{k} \)'s separated from the \( \mathbf{k} \) of interest by a R.L.V.
Step 4: The special case of the B, 2, edge.

In Eqn 4, \( E_k = E_k^0 + \sum_{E_k'} \frac{U_{kE} U_{kE'}}{E_k^0 - E_{k'}^0} \)

A serious problem occurs when \( E_k^0 = E_{k'}^0 \). Denominator \( = 0! \)

This is the case at zone edges.

\[ \text{These two } k's \text{ have some energy.} \]

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 \( E_v \) vs. \( k_x \) goes to 0.

(The math is done below.)

Conceptually, this is related to Bragg scattering: the condition where \( k_x' = k_x + G \) and \( E_k = E_{k'} \) is just the same as elastic phonon scattering studied in Chapter 2. So you can think of these 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,

\[ Y_k = Y_k^0 + \sum_{E_k'} \frac{E_k', E_k'}{E_k^0 - E_{k'}^0} \]

Diagonalize all of the terms in summation except the one that has the same energy as \( Y_k \).

Recognize that this term can be very significant, so we'd better not say it's coefficient is small. Nor that the \( Y_k^0 \) coefficient is about equal to it.
So now we have

\[ \psi_k = C_k \psi_{k^0} + C_{k'} \psi_{k'} \]

Plug this into Schrödinger Eqn as in Step 2 above

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

\[ C_k \psi_{k^0} + C_{k'} \psi_{k'} = C_k \psi_{k^0} + C_{k'} \psi_{k'} \]

Eqn (1) analog

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

1. Multiply by \((\psi_{k^0})^*\) and integrate.

2. Multiply by \((\psi_{k'})^*\) and integrate.

That gives us

1. \( C_k E_{k^0} + C_{k'} U_{kk^0} + C_{k'} U_{kk'} = C_k E_k \)

2. \( C_{k'} E_{k'} + C_k U_{kk'} + C_k U_{kk^0} = C_{k'} E_k \)

Written as a matrix equation:

\[
\begin{pmatrix}
E_{k^0} + U_{kk^0} - E_k & U_{kk^0} \\
U_{kk^0} & E_{k'} + U_{kk^0} - E_k
\end{pmatrix}
\begin{pmatrix}
C_k \\
C_{k'}
\end{pmatrix}
= 0
\]

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

\[
(E_{k^0} + U_{kk^0} - E_k)(E_{k'} + U_{kk^0} - E_k) - U_{kk^0}^2 = 0
\]

Solve for \( E_k \) (skipping several lines of algebra)

\[
E_k = E_{k^0} \pm \frac{\sqrt{1 - \frac{U_{kk^0}}{E_{k^0} - E_{k'}}^2}}{2}
\]

But we've already specified that \( E_k = E_{k^0} \).
Therefore, the two energy values become

\[ (\text{upper}) \; E^+_k = E^{0}_k + U^{\alpha\alpha}_k + |U^{\alpha\beta}_k|^2 \]
\[ (\text{lower}) \; E^-_k = E^{0}_k + U^{\alpha\alpha}_k - |U^{\alpha\beta}_k|^2 \]

Eqn. (5)

Gap between the two is:

\[ \Delta E = 2 |U^{\alpha\beta}_k| \]

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

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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 \( \Delta E = 2 |U^{\alpha\beta}_k| \)

\[ = 2 \int (\psi^*_k \cdot \mathbf{U} \cdot \psi_k) \, dV \]

3. Near the zone edge, \( k = k_{\text{min}} + \Delta k \), the energy dependence is parabolic:

\[ E^{\pm}_k = E^{\pm}_k + C_1 \Delta k^2 \]

\[ E^{\pm}_k = E^{\pm}_k - C_2 \Delta k^2 \]