Proof of momentum theorem:

Note first that
\[ \hat{P}_p = -i \hbar \hat{\nabla} \cdot \cdot \cdot \]

Consider
\[ E_n(\vec{k} + \vec{q}) = E_n(\vec{k}) + \vec{q} \cdot \hat{\nabla}_k E_n(\vec{k}) \]
\[ + O(q^2) \]

Now consider
\[ H \psi_{n\vec{k}}(\vec{r}) = E_n(\vec{k}) \psi_{n\vec{k}}(\vec{r}) \]
\[ H(e^{i\vec{k} \cdot \vec{\rho}} u_{n\vec{k}}(\vec{r})) = E_n(\vec{k}) e^{i\vec{k} \cdot \vec{\rho}} u_{n\vec{k}}(\vec{r}) \]
\[ H = -\frac{\hbar^2}{2m} \nabla^2 + U(\vec{r}) \]

Now consider
\[ \nabla^2(e^{i\vec{k} \cdot \vec{\rho}} u_{n\vec{k}}(\vec{r})) = \nabla \cdot \left[ i \hbar e^{i\vec{k} \cdot \vec{\rho}} u_{n\vec{k}}(\vec{r}) \right] \]
\[ + e^{i\vec{k} \cdot \vec{\rho}} \nabla u_{n\vec{k}}(\vec{r}) \]
\[ = -k^2 e^{i\vec{k} \cdot \vec{\rho}} u_{n\vec{k}}(\vec{r}) + 2i \vec{k} \cdot e^{i\vec{k} \cdot \vec{\rho}} \nabla u_{n\vec{k}}(\vec{r}) \]
\[ + e^{i\vec{k} \cdot \vec{\rho}} \nabla^2 u_{n\vec{k}}(\vec{r}) \]
\[ = e^{i\vec{k} \cdot \vec{\rho}} (\nabla + i \vec{k})^2 u_{n\vec{k}}(\vec{r}) \]
The Schrödinger equation becomes

\[ -\frac{i\hbar^2}{2m} \left( \vec{\nabla} + i\vec{k} \right)^2 \psi_{nk}(\vec{r}) + U(\vec{r})\psi_{nk}(\vec{r})e^{i\vec{k} \cdot \vec{r}} = E_{nk} e^{i\vec{k} \cdot \vec{r}} \psi_{nk}(\vec{r}) \]

or

\[ H(\vec{k}) \psi_{nk}(\vec{r}) = E_{nk} \psi_{nk}(\vec{r}) \]

where

\[ H(\vec{k}) = -\frac{i\hbar^2}{2m} (\vec{\nabla} + i\vec{k})^2 + U(\vec{r}) \]

Then

\[ H(\vec{k} + \vec{q}) = -\frac{i\hbar^2}{2m} (\vec{\nabla} + i\vec{k} + i\vec{q})^2 + U(\vec{r}) \]

\[ = H(\vec{k}) - \frac{i\hbar^2}{m} \vec{q} \cdot (\vec{\nabla} + i\vec{k}) + O(q^2) \]

"perturbation"

Hence

\[ E_{nk, \vec{k} + \vec{q}} \approx E_{nk, \vec{k}} + \int \psi_{nk}^*(\vec{r}) \left( -\frac{i\hbar^2}{m} \vec{q} \cdot (\vec{\nabla} + i\vec{k}) \right) \psi_{nk}(\vec{r}) d^3r \]

Using the well-known 1st order perturbation theory result

\[ E_{nk, \vec{k} + \vec{q}} \approx E(\vec{k}) + \vec{q} \cdot \nabla_k E_{nk}(\vec{k}) \]

This last integral can be written

\[ \int \psi_{nk}^*(\vec{r}) \left( -\frac{i\hbar^2}{m} \vec{q} \cdot \vec{\nabla} \right) \psi_{nk}(\vec{r}) d^3r \]
Proof:
\[ \int \psi_{nk}(\vec{r}) \left( -\frac{i\hbar}{m} \nabla \right) \psi_{nk}(\vec{r}) \, d^3r \]
\[ = \int e^{-i\frac{\hbar^2}{2m}\nabla^2} \left( e^{i\frac{\hbar^2}{2m}\nabla^2} \psi_{nk}(\vec{r}) \right) \, d^3r \]
\[ = \int e^{-i\frac{\hbar^2}{2m}\nabla^2} \left( \nabla + i\frac{\hbar^2}{2m} \psi_{nk}(\vec{r}) \right) \, d^3r \]
\[ \text{(using chain rule)} \]
QED.

Thus
\[ \vec{V}_k \, E_n(\vec{k}) = \frac{\hbar}{m} \left( -i\frac{\hbar^2}{m} \nabla \right) \ln k \]
\[ = \frac{\hbar}{m} \langle n\vec{k} | \hat{p}_\parallel \ln k \rangle \]
\[ = \frac{\hbar}{m} \langle n\vec{k} | \hat{v}_{\text{op}} \ln k \rangle \]

or
\[ \langle n\vec{k} | \hat{v}_{\text{op}} \ln k \rangle = \frac{\hbar}{m} \vec{V}_k \, E_n(\vec{k}) \]
QED.

Free electron case: \[ E_n(\vec{k}) = \frac{\hbar^2 k^2}{2m} \]
\[ \hat{V} = \frac{\hbar k}{m} \]

E.g. in 1d: \[ v \sim \frac{1}{k} \frac{\partial E_n(\vec{k})}{\partial k} \]

Near bottom of band (for Kronig-Penney \[ A(k) \approx A(\vec{K}) \] model)
\[ E_n(\vec{k}) \sim A k^2, \quad v_{\eta}(\vec{k}) \sim 2Ak \]
So \( \alpha \) to \( k \) but with different "effective mass"
Fermi surface

Levels are filled up to some maximum energy called Fermi energy (at $T = 0$) $E_F$.

The surface $\sqrt{E_n(k)} = E_F$ is a 2d surface in $k$-space.

Can extend through several bands.
Can have filled, empty, or partially filled bands.

If even # of elecs. per primitive cell, can have filled bands $\Rightarrow$ no Fermi surface.

E.g. C, Si, Ge 8 elecs/cell.
At 4 fitted bands:

Zn 4 elecs per cell but metal (overlapping bands)
An example: Free electron band structure

\[ E(\mathbf{k}) = \frac{\hbar^2 k^2}{2m} \]

Surfaces of constant energy are

\[ E_n (\mathbf{k}) = E = \frac{\hbar^2 k^2}{2m*} \]

spheres

Fermi surface would be a sphere in k-space.

Another example:

\[ E_n (\mathbf{k}) = \sum_i A_i k_i^2 \]

Surfaces of constant energy are ellipsoids

In some cases, the surfaces of const. energy can touch the Brillouin zone boundary. They are then called open BZ energy surfaces and they really extend through all space.

Note periodicity of band structure:

\[ E_{n,k+\mathbf{K}} = E_{nk} \]

\[ \psi_{n,k+\mathbf{K}} (\mathbf{r}) = \psi_{n,k} (\mathbf{r}). \]

Total volume \( V \) of \( \mathbf{k} \)-space occupied by electrons below Fermi energy is \( \frac{2n^* \pi^2 \mathbf{k}^2}{3} \)

where \( n^* = \text{vol. of 1st zone} \)

and \( n^* \) is the \# of valence electrons per atom.
How about density of states?

\[ g(E) \, dE = \# \text{ of electron states per unit vol. between } E \text{ and } E + dE \]

E.g., free electron states

\[ E(k) = \frac{\hbar^2 k^2}{2m} \quad \text{or} \quad k = \sqrt{\frac{2mE}{\hbar^2}} \]

Surface of constant energy is \( |k| = \text{const} \) or \( k^2 = \text{const} \).

i.e., a sphere

\# of states between \( E \) and \( E + dE \) is determined by vol. of \( k \)-space between \( k \) and \( k + dk \), where

\[ k + dk = \sqrt{\frac{2m(E + dE)}{\hbar^2}} = \sqrt{\frac{2mE}{\hbar^2}} + \frac{1}{2} \sqrt{\frac{2m}{\hbar^2}} E^{-\frac{1}{2}} dE \]

or

\[ dk = \frac{1}{2} \sqrt{\frac{2m}{\hbar^2}} E^{-\frac{1}{2}} dE \]

The \# of states in this shell is

\[ 4\pi k^2 \, dk \cdot \frac{V}{4\pi^3} \]

\[ = \frac{V}{4\pi^3} \cdot \frac{1}{2} \left( \frac{2m}{\hbar^2} \right)^{\frac{3}{2}} E^{-\frac{1}{2}} \left( \frac{2mE}{\hbar^2} \right)^{\frac{1}{2}} \right) dE \]

\[ = \frac{V}{8\pi^3} \left( \frac{2m}{\hbar^2} \right)^{\frac{3}{2}} E^{\frac{1}{2}} dE \]

So

\[ g(E) = \frac{1}{8\pi^3} \left( \frac{2m}{\hbar^2} \right)^{\frac{3}{2}} E^{\frac{1}{2}} \]

for free electrons

\[ (E > 0) \quad = 0 \quad \text{if } E < 0 \]
**General formula:**

\[ g_n(E) = \text{dos of } n\text{th band} = ? \]

**Method:** Calculate vol. of \( k \)-space between the surfaces \( E_n(k) = E \) and \( E_n(k) = E + dE \) (in 1\textsuperscript{st} zone)

Multiply by \( \frac{1}{4\pi^3} \) (dos in \( k \)-space per unit vol)

Then

\[ g_n(E)dE = \frac{1}{4\pi^3} \int_{V'} d^3k \]

where \( V' \) is shell between \( E_n(k) = E \) and \( E_n(k) = E + dE \)

There is a formula for this, derived from below:

\[ \int_{V'} d^3k = \int_{S_n(E)} dS \cdot dk(k) \]

Now

\[ E + dE = E + \hat{v}_k E \cdot \hat{k} = E + |\hat{v}_k|E \hat{k} \text{ \( dE \) \since \( \hat{v}_k \) \parallel \text{ to surface } E_n(k) = E} \]
[This is a standard result of the calculus of several variables: the gradient is perpendicular to the contours of const. E]

[This is because the component of $\hat{\nabla}_k E$ along the tangent to the surface of const. E is zero: E doesn't change along those two directions.]

So $E + dE = E + |\nabla_k E| d\kappa(\kappa)$

and $dE = |\nabla_k E_n(\kappa)| d\kappa(\kappa)$

Thus $\int_V d^3k = \int S_{n(E)} dS \frac{dE}{|\nabla_k E_n(\kappa)|}$

and $g_n(E) dE = \frac{1}{4\pi^2} \int_{S_{n(E)}} dS \frac{1}{|\nabla_k E_n(\kappa)|}$

$$g_n(E) = \sqrt{\frac{1}{4\pi^3}} \int_{S_{n(E)}} dS \frac{1}{|\nabla_k E_n(\kappa)|}$$

Very useful (discussed later)

Exercise: use this formula to get free electron DOS.

Some general properties

$E_n(\kappa)$ is periodic in $k$-space

$E_n(\kappa) = E_n(\kappa + \kappa)$
"Critical pts."

Since $E_n(k)$ periodic in $k^0$, generally bounded above and below, it must oscillate.

Then there must be places where
\[ \nabla_k^2 E_n(k) = 0 \]

There are four types of points depending these singularities are integrable in 3d.

$g_n(E)$ is finite.

But there are 4 types of singularities, depending on second derivatives.

Matrix of second derivatives has components
\[ \left( \frac{\partial^2 E_n(k)}{\partial k_i \partial k_j} \right)_{k = k_0} \]

3 eigenvalues since 3x3 Hermitian matrix.

1. All three positive
   Band minimum

2. All three negative
   Band maximum

3 and 4) one neg, two positive
   Saddle points

4. one pos, two neg
Typical đồ looks like this:

\[ g_n(E) \]

\[ \alpha (E - E_{\text{min}}) \]

\[ \alpha (E_{\text{max}} - E)^{\frac{1}{2}} \]

\[ \text{Band min} \quad \text{Band max} \quad E \]

saddle pts:

These are called "Van Houwelingen singularities."

\[ |\frac{dg_n}{dE}| \to \infty \] at these pts.

There must be at least one min. and one max. in each band.

Example: near bottom of band

\[ E(k) = E(k_0) + \frac{1}{2} \sum_{i,j=1}^{3} A_{ij} (k_i - k_0_i)(k_j - k_0_j) \]

\[ = E(k_0) + \frac{1}{2} \sum_{\alpha=1}^{3} \lambda_{\alpha} (k - k_0)_{\alpha}^2 \]

in a coordinate system where \( \frac{\partial}{\partial x^\alpha} A_{ij} \) is diagonal;

\( \lambda_{\alpha} \) is the diagonal component one of the six eigenvalues of the matrix \( A_{ij} \).
Weak periodic potential:

Band structure determined by

\[ \Sigma \left( \frac{\hbar^2}{2m} |\mathbf{k} + \mathbf{k}'|^2 - E \right) \psi_R(k) \]

\[ + \sum_{k'} U_{R-k'} \psi_{k'}(\mathbf{k}) = 0 \]

Where we write \( \psi_k(\mathbf{k}) = \sum_{\mathbf{k}'} \psi_{\mathbf{k}'}(\mathbf{k}) e^{i(k+k') \cdot \mathbf{r}} \)

General solution: diagonalize large matrix \( H(k) \)

Whose matrix elements are

\[ H_{kk'}(\mathbf{k}) = \frac{\hbar^2}{2m} |\mathbf{k} + \mathbf{k}'|^2 \delta_{k, k'} + U_{R-k'} \]

D. Consider only \( k \) in first B.Z. This is called the empty lattice band structure.

Case I: \( U_{R-k'} = 0 \)

\( H \) is diagonal and eigenvalues are just plane waves \( \frac{\hbar^2}{2m} |\mathbf{k} + \mathbf{k}'|^2 \) with eigenstates

\[ e^{i(k+k') \cdot \mathbf{r}} \]

\( \frac{1}{\sqrt{V}} e^{i(k+k') \cdot \mathbf{r}} \) (if normalized in volume \( V \)).

Case II. \( U_{R-k'} \) is weak, but no two free-electron states at Bloch vector \( k \) are nearly degenerate.
Recall result of second-order non-degenerate perturbation theory: if $H = H_0 + V$

$$E_n = E_{n0} + \langle n | V | n \rangle + \sum_{n' \neq n} \frac{|\langle n | V | n' \rangle|^2}{E_n - E_{n'}} + o(U^3)$$

where $H_0 | n \rangle = E_{n0} | n \rangle$

For present case, we get

$$E_R^2 = \frac{\hbar^2}{2m} |K + \vec{R}|^2 + U_0$$

$$+ \sum_{K' \neq K} \frac{|U_{K' - R}|^2}{E_K^0 - E_{K'}^0}$$

where $E_K^0 = \frac{\hbar^2}{2m} |K + \vec{R}|^2$

and $U_0 = U_{K - R'}$ with $\vec{R'} = \vec{R}$

Valid for small $|U_{K - R'}|$ ($|U_{K - R'}| \ll E_K^0 - E_{K'}^0$)

Special case: 1d bands

Case III. $U_{K - R'}$ is small real but two free plane waves are nearly degenerate.
For example, suppose that at wave number $k$, the two plane waves

$$\frac{k^2}{2m} |\mathbf{K} + \mathbf{K}'|^2$$

and

$$\frac{k^2}{2m} |\mathbf{K} - \mathbf{K}'|^2$$

are nearly degenerate (but only those two).

Then we can just consider a $2 \times 2$ submatrix of $H(k)$ involving these two plane waves, and diagonalize directly, i.e. we only solve the two coupled eqs.

$$
\begin{pmatrix}
\frac{k^2}{2m} |\mathbf{K} + \mathbf{K}'|^2 - E & 0 \\
0 & \frac{k^2}{2m} |\mathbf{K} - \mathbf{K}'|^2 - E \\
\end{pmatrix}
\begin{pmatrix}
c_{K} \mathbf{c} (\mathbf{K}) \\
c_{K'} \mathbf{c} (\mathbf{K}') \\
\end{pmatrix} = 0
$$

 energy levels determined by solving

$$
\begin{vmatrix}
\frac{k^2}{2m} |\mathbf{K} + \mathbf{K}'|^2 - E & U_{K-K'}^2 \\
U_{K-K'}^2 & \frac{k^2}{2m} |\mathbf{K} - \mathbf{K}'|^2 - E \\
\end{vmatrix} = 0
$$
\[ E^2 - \left( E_K(\vec{k}) + E_{K'}(\vec{k}') \right) E + E_K(\vec{k}) E_{K'}(\vec{k}') - \left| U_{K,K'} \right|^2 = 0 \]

where \[ E_K(\vec{k}) = \frac{\hbar^2}{2m} \left| \vec{k} + \vec{P} \right|^2 \]

\[ E = \frac{1}{2} \left( E_K(\vec{k}) + E_{K'}(\vec{k}') \right) \pm \sqrt{\left( E_K(\vec{k}) - E_{K'}(\vec{k}') \right)^2 + 4 \left| U_{K,K'} \right|^2} \]

Specifically, when \( E_K(\vec{k}) = E_{K'}(\vec{k}') \), we get

\[ E = \frac{1}{2} \left( E_K(\vec{k}) + E_{K'}(\vec{k}') \right) \pm \left| U_{K,K'} \right| \]

so the degeneracy is split by \( 2 \left| U_{K,K'} \right| \)

This splitting

E.g. Suppose \( \vec{K} = \vec{0} \). Then we need

\[ E_{\vec{K}} = \frac{\hbar^2}{2m} \left| \vec{k} \right|^2 = \frac{\hbar^2}{2m} \left| \vec{k} + \vec{P} \right|^2 \]

for degeneracy, or \( \hbar^2 = \left| \vec{k} + \vec{P} \right|^2 \)

This occurs at the faces of the first B.Z., since we know that those faces bisect a vector \( \vec{k} \) drawn from the origin.
Any point on this face satisfies \( |\vec{r}|^2 = |\vec{k} - \vec{K}|^2 \) for some \( \vec{K} \).

One face of first B.Z.

Thus, bands are split all along face of first zone.

Splitting is approximately \( 2|\vec{U}_R| \).

Near pt. where two planes intersect (B.Z. edge) three plane waves, almost degenerate.

Near B.Z. corner, four plane waves nearly degenerate.

Must diagonalize a \( 4 \times 4 \) matrix to get splittings.

Illustration: 1 dimension.

Let repeat dist. be \( a \).

So, \( \phi \) allowed \( K \)'s are \( \frac{2\pi}{a} n \), \( n = 0, \pm 1, \pm 2, ... \).

1st B.Z. runs from \( -\frac{\pi}{a} \) to \( \frac{\pi}{a} \).

If there is no potential, the plane wave states are

\[
\frac{\hbar^2}{2m} \left( k + \frac{2\pi n}{a} \right)^2 - \frac{\pi}{a} < k < \frac{\pi}{a}
\]
"Empty-lattice band structure"

If we turn on a weak periodic potential \( U(x) \),

it has Fourier components

\[
U_n(x) = \frac{1}{2a} \int_{-a}^{a} e^{-i \pi n x / a} U(x) \, dx
\]

\[
= \frac{1}{2a} \int_{-a}^{a} e^{-i \pi n x / a} U(x) \, dx
\]

\( \equiv U_n \)

The band structure in the presence of this weak potential looks like that below:
Notice the presence of "band repulsion" near bands that were crossing "repel" in presence of perturbation.

Wave function near \( k = \frac{\pi}{a} \) for third two bands.

If \( U = 0 \) the states are (un-normalized)

\[
e^{ikx} \text{ and } e^{i(kx - \frac{2\pi}{a})x}
\]

at \( k = \frac{\pi}{a} \), each \( \Psi \) has energy \( \frac{\hbar^2 \pi^2}{2m(a)^2} \)

If \( U \neq 0 \) the energies become

approximately \( \frac{\hbar^2 \pi^2}{2m(a)^2} + |U| \) at \( k = \frac{\pi}{a} \)

and the wave functions become

\[
\frac{1}{\sqrt{2}} (e^{ikx} - e^{i(kx - \frac{2\pi}{a})x}) \text{ for upper state}
\]
What about wave functions? We have
\[
\left[ \frac{\hbar^2}{2m} k^2 - E(k) \right] c_0(k) + U_1(k) c_0(k) = 0
\]

So, \[ c_1(k) = \frac{E(k) - \frac{\hbar^2 k^2}{2m}}{U_1(k)} c_0(k) \]

If \( k = \frac{\pi}{a} \) and \( \alpha \), then for the lower state,
\[ c_1(k) = \frac{\frac{\hbar^2 k^2}{2m} - |U_1(k)| - \frac{\hbar^2 k^2}{2m}}{U_1(k)} c_0(k) \]
\[ = - \frac{U_1(k) c_0(k)}{U_1(k)} \]

If \( U_1(k) < 0 \), then \[ c_1(k) = c_0(k) \]

and eigenstate of lower band is proportional to
\[ \phi \propto e^{i k x} + e^{i (k - \frac{2\pi}{a}) x} \]
\[ \propto \cos \frac{\pi}{a} x \]

Upper band is \( \sin \frac{\pi}{a} x \).
Notice in 1D that if system has even # of electrons per primitive cell, there is a band gap between first filled and first empty state.