\[ \varepsilon_k^0 \mathbf{c}_k + \sum_{k'} \mathbf{U}_{k'k} \mathbf{c}_{k-k'} = \varepsilon_k \mathbf{c}_k \]

Apply the above to the wavevector \( \mathbf{k} - \mathbf{k}' \)

\[ \varepsilon_{k'k} \mathbf{c}_{k-k} + \sum_{k'} \mathbf{U}_{k'k} \mathbf{c}_{k-k-k'} = \varepsilon_k \mathbf{c}_{k-k} \]

or relabel the summation vector in the 2nd term

\( \mathbf{k} + \mathbf{k}' \rightarrow \mathbf{k}' \)

\[ \varepsilon_{k-k}^0 \mathbf{c}_{k-k} + \sum_{k'} \mathbf{U}_{k'k} \mathbf{c}_{k-k-k'} = \varepsilon_k \mathbf{c}_{k-k} \]

As \( \mathbf{k} \) in the above varies through the wavevectors in the B.Z., we get a set of linear equations for the Fourier coefficients \( \{ \mathbf{c}_{k-k} \} \) of \( \mathbf{k} \) in B.Z.

Above can be viewed as a matrix eigenvalue problem for the eigenvector \( \{ \mathbf{c}_{k-k} \} \) (viewing \( \mathbf{R} \) as the index of the vector) and \( \varepsilon \) as the eigenvalue.

Solution gives

\[ \Phi(\mathbf{r}) = \sum_k \mathbf{c}_k e^{i(\mathbf{k} \cdot \mathbf{r})} = e^{i\mathbf{K} \cdot \mathbf{r}} \sum_k e^{-i\mathbf{k} \cdot \mathbf{r}} \mathbf{c}_k \]

Define \( \mathbf{U}_k(\mathbf{r}) = \sum_k e^{i\mathbf{k} \cdot \mathbf{r}} \mathbf{c}_{k-k} \)
Then eigenstates have the form

\[ \psi_k(\vec{r}) = e^{iK \cdot \vec{r}} \psi_k(\vec{r}) \]

where \( \psi_k(\vec{r}+\vec{R}) = \psi_k(\vec{r}) \) if \( \psi(\vec{r}) \) is periodic on the B.L.

This is Block's theorem.

If we label the R.L. wavevectors as \( \vec{k}_z \), the Schrödinger equation takes the matrix form

\[
\begin{pmatrix}
E_k^0 & U_{k1} & U_{k2} & U_{k3} & \cdots \\
U_{k1} & E_{k-k1} & U_{k2-k1} & U_{k3-k1} & \cdots \\
U_{k2} & U_{k1-k2} & E_{k-k2} & U_{k3-k2} & \cdots \\
U_{k3} & U_{k1-k3} & U_{k2-k3} & E_{k-k3} & \cdots \\
\vdots & \vdots & \vdots & \vdots & \ddots
\end{pmatrix}
\begin{pmatrix}
C_k \\
C_{k-k1} \\
C_{k-k2} \\
C_{k-k3} \\
\vdots
\end{pmatrix} = \varepsilon
\begin{pmatrix}
C_k \\
C_{k-k1} \\
C_{k-k2} \\
C_{k-k3} \\
\vdots
\end{pmatrix}
\]

Note: Since \( \psi(\vec{r}) \) is a real function,

\[ \psi_{k*}^* = \frac{1}{V} \int d^3r \ e^{-iK \cdot \vec{r}} \psi(\vec{r}) = \psi_{-K} \]

Hence the above matrix is Hermitian since it should be to guarantee it is diagonalizable with real eigenvalues.

If the crystal has inversion symmetry, \( \psi(\vec{r}) = \psi(-\vec{r}) \)

Then

\[ \psi_k = \frac{1}{V} \int d^3r \ e^{-iK \cdot \vec{r}} \psi(\vec{r}) = \frac{1}{V} \int d^3r \ e^{-iK \cdot \vec{r}} \psi(-\vec{r}) = \frac{1}{V} \int d^3r \ e^{iK \cdot \vec{r}} \psi(\vec{r}) = \psi_{-K} = \psi_{k*} \text{ is real} \]
Also, we can assume $U_{k=0} = 0$ due to charge neutrality, since

$$U(r) = \int \frac{d^3r'}{\sqrt{|r-r'|}} \rho(r')$$

$\rho(r')$ is total charge density from all ions and electrons

$$U_{k=0} = \frac{1}{V} \int d^3r' \rho(r') \int d^3r \frac{1}{|r-r'|}$$

independent of $r'$ if using periodic boundary conditions.

$$\alpha \int d^3r' \rho(r') = 0$$

if charge neutral

Thus we see that the periodic ionic potential $U(r)$ only couples wavevectors $\bar{k}$ to the wavevectors $k' = \bar{k} - \bar{K}$, with $\bar{K}$ in the RL. These $\bar{k}'$ are just the wavevectors one gets from scattering of the electron off the Bragg planes.
Note: If we let \( \vec{k} \to \vec{k} + \vec{R}_0 \) in the above matrix equation, the only result is a permutation of the rows and columns since the set \( \sum \vec{k} + \vec{R}_0 \vec{3} = \sum \vec{k} + \vec{R}_0 \vec{3} \) since \( \vec{R}_0 + \vec{R} \) is vector in the R.L. if both \( \vec{R}_0 \) and \( \vec{R} \) are.

Hence the eigen vectors and eigenvalues are periodic functions of wavevector with period \( \vec{R}_0 \) given by the R.L. That is, if

\[
\psi_{k,n}(\vec{r}) = \sum_{\vec{K}} e^{-i(\vec{K} \cdot \vec{r})} c_{\vec{k}+\vec{K}} \quad \text{with eigenvalue } \varepsilon_{n,\vec{K}}(\vec{k})
\]

is the \( n^{th} \) eigenvector and eigenvalue of the matrix, then \( \forall \vec{K} \) and

\[
\psi_{k+\vec{K},n}(\vec{r}) = \psi_{k,n}(\vec{r}) \quad \text{periodic in } \vec{K} \to \vec{k} + \vec{K}
\]

\[
\varepsilon_{n,\vec{K}+\vec{R}}(\vec{k}) = \varepsilon_{n,\vec{K}}(\vec{k}) \quad \text{for any } \vec{R} \in \text{R.L.}
\]

Therefore the unique states are specified by a wavevector \( \vec{q} \) in the 1st B.Z. (called the "crystal momentum") and the discrete "band index" \( n \) that labels the different eigenvalues of the above matrix for a given value of \( \vec{q} \).

(all other \( \vec{k} \) values can always be written as \( \vec{k} = \vec{q} + \vec{R} \) where \( \vec{q} \) is in 1st B.Z. and \( \vec{R} \) is in R.L.)
Comment: For free electrons, the energy eigenstates are specified by a wave vector $\mathbf{K}$ that can take a value anywhere in $k$-space. For an electron in a periodic potential, we said eigenstates should be specified by a discrete band index $n$ and a crystal momentum $\mathbf{K}$ that must lie only in the 1st B.Z. But if we take the problem of the periodic potential and let $U \to 0$, we recover the free electron case. So how can these two ways of labeling eigenstates both be valid?

Answer: We can represent even free electron states using the band index $n$ and 1st B.Z. wave vectors as quantum numbers. For any $\mathbf{K}$, anywhere in $k$-space, we can always write $\mathbf{K} = \mathbf{\Gamma} + \mathbf{K'}$ where $\mathbf{\Gamma}$ is a reciprocal lattice vector closest to $\mathbf{K}$ and $\mathbf{K'}$ therefore must be in the 1st B.Z. This follows from the equivalence of all points in the R.L. (since it is a Bravais lattice) and from the definition of the 1st B.Z. as the set of wave vectors closer to the origin than to any other $\mathbf{K}$ in the R.L.
Then for any $\vec{k} = \vec{q} + \vec{K}$ in the $n^{th}$ Brillion Zone,

$$E^0(\vec{k}) = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2 (\vec{q} + \vec{K})}{2m} = E_n(\vec{q})$$

energy at crystal momentu $\vec{q}$ in band index "n". This the band index gives the B.Z., in which the corresponding free electron wave vector $\vec{k}$ lies.

**Ex.** in a 1D B.Z., of lattice constant $a$, R.L. vectors are $\vec{k}_n = \frac{\pi}{a} n$, $n = 0, \pm 1, \pm 2, \ldots$ Bragg planes at $\vec{k} = \frac{\vec{k}_n}{2} = \frac{(\pi/a)}{n}$

representing free electron states by $\frac{\pi}{a}$ in 1st B.Z.

Integers label correspondingly sections of the curves in the two equivalent representations.

can translate the section of curve in $n^{th}$ B.Z. back into 1st B.Z. by subtracting appropriate $\vec{k}$ from $\vec{k}$.
Because $\mathbf{k}$ enters the matrix equation as a parameter via the terms $E_{\mathbf{k}+\mathbf{k}}$, we expect that the eigenvalues $E_n(\mathbf{k})$ are smooth continuous functions of $\mathbf{k}$.

Because $E_n(\mathbf{k})$ is periodic in $\mathbf{k}$, $E_n(\mathbf{k}+\mathbf{k}) = E_n(\mathbf{k})$, we expect that $E_n(\mathbf{k})$ has a maximum and a minimum and varies continuously between them. This is why $E_n(\mathbf{k})$ is referred to as an energy band.

Since $\varphi_{\mathbf{k}
\mathbf{n}}(\mathbf{r}) = \sum \psi_{\mathbf{k}} \exp(-i\mathbf{k}\cdot\mathbf{r})$ is no longer a pure plane wave, $\varphi_{\mathbf{k}
\mathbf{n}}$ is not an eigenstate of momentum. This is reasonable since with the periodic potential turned on the system no longer has translational invariance. However, the system does have invariance in translations by B.L. vectors $\mathbf{K}$. This is why $\varphi_{\mathbf{k}
\mathbf{n}}$ mixes only wavevectors related to $\mathbf{k}$ by $\mathbf{k}' = \mathbf{k} - \mathbf{K}$ for $\mathbf{K}$ in B.L. Because of this difference, $\mathbf{k}$ is called the "crystal momentum" -- it is not the true momentum. In collisions, the crystal momentum of an electron is "conserved" modulo a B.L. vector $\mathbf{K}$.
Because $\Psi_{kn}(\vec{k})$ and $E_n(\vec{k})$ are periodic in $k$-space, the states $\vec{k}$ and $\vec{k} + \vec{K}$ are not physically different. Nevertheless, it is sometimes convenient to represent states by a $\vec{k}$ that is not in the 1st BZ. This must often be done when one wants to make closer analogy to free electrons. One therefore has three commonly used schemes for representing band structure. We illustrate these in 1D.

**Reduced Zone Scheme:** restrict $\vec{k}$ to 1st BZ for all energy bands $n$.

**Repeated Zone Scheme:** show all values of $\vec{k}$, with $E_n(\vec{k})$ periodic in $\vec{k}$. 

\[ \begin{align*}
\text{Reduced Zone scheme} & : \text{ restrict } \vec{k} \text{ to 1st BZ for all energy bands } n \\
\text{Repeated Zone scheme} & : \text{ show all values of } \vec{k}, \text{ with } E_n(\vec{k}) \text{ periodic in } \vec{k}
\end{align*} \]
Extended Zone scheme: show energy bad \( n \) using \( \mathbf{k} \) vectors in \( n \) th BZ.

Note: However one represents the band structure, distinct each band contains only \( N \) allowed values of \( \mathbf{k} \) consistent with the Born-von Karman boundary conditions \( \Rightarrow \) each band can contain \( 2N \) electron states (2 for spin up \( \uparrow \) and \( \downarrow \))

\( N = \# \) sites in crystal \( (= \# \) cons if we have a single \( \mathbf{BZ} \) and not a lattice with \( \mathbf{a} \) basis) \( \)

\( \nu \)

If one computes the expectation of velocity in a Bloch electron state, one finds

\[
\tilde{\mathbf{v}}_n(\mathbf{k}) = \langle \Phi_n (\mathbf{k}) | \frac{i}{\hbar} \hat{\mathbf{V}} | \Phi_n (\mathbf{k}) \rangle = \int d^3 r \frac{\nabla \Phi^*_n (\mathbf{r}) \cdot \nabla \Phi_n (\mathbf{r})}{\hbar} \\
= \frac{1}{\hbar} \tilde{\mathbf{V}}_n(\mathbf{k})
\]

\( \langle \tilde{\mathbf{v}}_n(\mathbf{k}) \rangle \) looks just like group velocity, but an exact result gradient with respect to \( \mathbf{k} \)

\( \hat{\mathbf{V}}_n(\mathbf{k}) \)

proof follows.

Main point is that the eigenstates of an electron in a periodic potential, although they are not eigenstates of momentum, nevertheless have a
well defined, generally finite, value for their average velocity. Therefore, in spite of the interaction of the electron with the periodic potential, the electron in its eigenstate moves with a steady velocity even if no net force (for example from an electric field) is applied to it. This is in contrast to Drude's classical picture in which collisions between the electron and the ions served to randomize any initial electron velocity on the collision time scale $\tau$. The reason Drude's picture does not hold in because of the wave nature of the electron and its coherent scattering off the ions.
A nonperturbative proof for $\overrightarrow{V}_k = \frac{1}{\hbar} \frac{\partial E_k}{\partial \overrightarrow{k}}$

The Bloch function is known to be of the form [ignore bond index]

$$\overrightarrow{U}_k(\overrightarrow{x}) = e^{i\overrightarrow{k} \cdot \overrightarrow{x}} U_k(x)$$

where $U_k(x)$ is periodic in the Bravais lattice and satisfies

$$H_k U_k = E_k U_k$$

where

$$H_k = \frac{\hbar^2}{2m} \left( \frac{1}{i} \overrightarrow{v} + \overrightarrow{k} \right)^2 + U(\overrightarrow{x})$$

Note that $H_k$ is Hermitian for any $\overrightarrow{k}$.

Suppose $U_k(x)$ is normalized as

$$\int_{\Omega} |U_k|^2 d^3x = 1$$

where $\Omega$ is a primitive cell.

From (2) we have

$$\frac{\partial U_k}{\partial \overrightarrow{k}} H_k U_k = E_k \frac{\partial U_k^*}{\partial \overrightarrow{k}} U_k$$

Taking complex conjugate of eq. (4) yields [using $H_k^* = H_{-k}$]

$$\frac{\partial U_k}{\partial \overrightarrow{k}} H_{-k} U_k^* = E_k \frac{\partial U_k^*}{\partial \overrightarrow{k}} U_k^*$$

Adding (4) and (5) and integrating over the primitive cell $\Omega$ we get

$$E_k \frac{\partial}{\partial \overrightarrow{k}} \int_{\Omega} |U_k|^2 d^3x = \int_{\Omega} \left[ \frac{\partial U_k^*}{\partial \overrightarrow{k}} H_k U_k + \frac{\partial U_k}{\partial \overrightarrow{k}} H_{-k} U_k^* \right] d^3x$$

(6)
Since $H_{\bar{K}K}$ is Hermitian,

$$
\int_{\Omega} \frac{\partial u_{\bar{K}}^*}{\partial \bar{K}} H_{\bar{K}K} u_{\bar{K}} d^3x = \left[ \int_{\Omega} u_{\bar{K}} H_{\bar{K}K} \frac{\partial u_{\bar{K}}^*}{\partial \bar{K}} d^3x \right]^* = \int_{\Omega} u_{\bar{K}}^* H_{\bar{K}K} \frac{\partial u_{\bar{K}}}{\partial K} d^3x \tag{7}
$$

Thus, (3), (6) and (7) together imply

$$
\int_{\Omega} \left[ \frac{\partial u_{\bar{K}}^*}{\partial \bar{K}} H_{\bar{K}K} u_{\bar{K}} + u_{\bar{K}}^* H_{\bar{K}K} \frac{\partial u_{\bar{K}}}{\partial K} \right] d^3x = 0 \tag{8}
$$

However, (1) and (3) directly imply

$$
\mathcal{E}_{\bar{K}} = \int_{\Omega} u_{\bar{K}}^* H_{\bar{K}K} u_{\bar{K}} d^3x \tag{9}
$$

Differentiate eq. (7) with respect to $\bar{K}$ and exploit (8) we have

$$
\frac{\partial \mathcal{E}_{\bar{K}}}{\partial \bar{K}} = \int_{\Omega} u_{\bar{K}}^* \frac{\partial H_{\bar{K}K}}{\partial \bar{K}} u_{\bar{K}} d^3x
\begin{aligned}
&= \frac{\hbar^2}{m} \int_{\Omega} u_{\bar{K}}^* \left( \frac{1}{i} \nabla + \bar{K} \right) u_{\bar{K}} d^3x \\
&= \frac{1}{m} \int_{\Omega} \psi_{\bar{K}}^* \left( \frac{\hbar}{i} \nabla \right) \psi_{\bar{K}} d^3x = -V_{\bar{K}}
\end{aligned}
$$

or

$$
\frac{1}{\hbar} \frac{\partial \mathcal{E}_{\bar{K}}}{\partial \bar{K}} = \frac{1}{m} \int_{\Omega} \psi_{\bar{K}}^* \left( \frac{\hbar}{i} \nabla \right) \psi_{\bar{K}} d^3x = -V_{\bar{K}}
$$