We now define the Fourier transform and its inverse that is consistent with the allowed wave vectors $\vec{k}$ of the Born - von Karmen boundary conditions

IF
$$\psi(\vec{r}) \equiv \sum_{k} e^{i\vec{k}\cdot\vec{r}} C_k$$

↑ sum over all $\vec{k}$ that obey
Born - von Karman boundary conditions

Then the inverse Fourier transform is

$$C_k = \frac{1}{V} \int_V d^3r \, e^{-i\vec{k}\cdot\vec{r}} \psi(\vec{r})$$

Proof:
$$\frac{1}{V} \int_V d^3r \, e^{-i\vec{k}\cdot\vec{r}} \psi(\vec{r}) = \sum_{k'} C_{k'} \frac{1}{V} \int d^3r \, e^{i(\vec{k'}-\vec{k})\cdot\vec{r}}$$

~~the~~ since both $\vec{k}$ and $\vec{k'}$ satisfy Born - von Karman boundary conditions, we can write

$$\vec{k'} - \vec{k} = \frac{m_1}{N_1} \vec{b}_1 + \frac{m_2}{N_2} \vec{b}_2 + \frac{m_3}{N_3} \vec{b}_3$$

with m_1, m_2, m_3 integers.

Also we can write

$$\vec{r} = x_1 \vec{a}_1 + x_2 \vec{a}_2 + x_3 \vec{a}_3 \qquad 0 \leq x_i \leq N_i$$

since $\vec{r}$ is not in general a BL vector, the x_i are any real values (not necessarily integers)

Now

$$\int_V d^3r = v \int_0^{N_1} dx_1 \int_0^{N_2} dx_2 \int_0^{N_3} dx_3 \qquad \text{since } V = vN$$

$$v = \text{vol primitive cell}$$

and

$$(\vec{k}'-\vec{k})\cdot\vec{r} = 2\pi\left(\frac{m_1}{N_1}x_1 + \frac{m_2}{N_2}x_2 + \frac{m_3}{N_3}x_3\right)$$

So

$$\frac{1}{V}\int d^3r\, e^{i(\vec{k}'-\vec{k})\cdot\vec{r}} = \frac{v}{V}\prod_{i=1}^{3}\left[\int_0^{N_i} dx_i\, e^{2\pi i \frac{m_i}{N_i}x_i}\right]$$

do for example the x_1 integral

$$\int_0^{N_1} dx_1\, e^{2\pi i \frac{m_1 x_1}{N_1}} = \frac{e^{2\pi i m_1} - 1}{\frac{2\pi i m_1}{N_1}}$$

$$= \begin{cases} 0 & m_1 \neq 0 \quad \text{since } m_1 \text{ integer} \\ \\ N_1 & m_1 = 0 \quad (\text{take limit } m_1 \to 0) \end{cases}$$

So

$$\frac{1}{V}\int d^3r\, e^{i(\vec{k}'-\vec{k})\cdot\vec{r}} = \frac{vN_1 N_2 N_3}{V}\delta_{k',k}$$

$$= \delta_{k',k} \qquad \underset{\substack{\text{zero unless} \\ \vec{k}=\vec{k}'}}{\uparrow}$$

So $$\sum_{k'} C_{k'}\frac{1}{V}\int d^3r\, e^{i(\vec{k}'-\vec{k})\cdot\vec{r}} = \sum_{k'} C_{k'}\delta_{k',k} = C_k$$

Bloch's Theorem

Now we prove Bloch's theorem by substituting the Fourier transform in the Schrödinger Equ.

$$-\frac{\hbar^2}{2m} \nabla^2 \psi + U(\vec{r}) \psi = \varepsilon \psi$$

where $U(\vec{r})$ is the ionic potential
and ε is the eigenvalue = electron energy

Substitute in the Fourier transforms

$$\psi(\vec{r}) = \sum_k e^{i\vec{k}\cdot\vec{r}} c_k$$

$$U(\vec{r}) = \sum_{k'} e^{i\vec{k}'\cdot\vec{r}} U_{k'}$$

to get

$$\sum_k e^{i\vec{k}\cdot\vec{r}} \frac{\hbar^2 k^2}{2m} c_k + \sum_{k''}\sum_{k'} e^{i(\vec{k}''+\vec{k}')\cdot\vec{r}} U_{k'} c_{k''}$$

$$= \varepsilon \sum_k e^{i\vec{k}\cdot\vec{r}} c_k$$

Now transform summation variable in the 2nd term to $\vec{k} = \vec{k}'' + \vec{k}'$ so $\vec{k}'' = \vec{k} - \vec{k}'$

$$\Rightarrow \sum_k e^{i\vec{k}\cdot\vec{r}} \left[\left(\frac{\hbar^2 k^2}{2m} - \varepsilon\right) c_k + \sum_{k'} U_{k'} c_{k-k'} \right] = 0$$

write $\varepsilon_k^0 \equiv \frac{\hbar^2 k^2}{2m}$

$$\Rightarrow \varepsilon_k^0 \, c_k + \sum_{k'} U_{h'} \, c_{k-k'} = \varepsilon \, c_k$$

Now the ionic potential $U(\vec{r})$ is periodic on the Bravais lattice, i.e.

$$U(\vec{r}+\vec{R}) = U(\vec{r}) \quad \text{for all } \vec{R} \text{ in BL}$$

$\Rightarrow$ the only wave vectors $\vec{k}$ that appear in its Fourier transform are the wavevectors $\{\vec{K}\}$ of the reciprocal lattice.

$$U(\vec{r}+\vec{R}) = \sum_k e^{i k \cdot (\vec{r}+\vec{R})} \, U_k = \sum_k e^{i\vec{k}\cdot\vec{R}} \, e^{i\vec{k}\cdot\vec{r}} \, U_k$$

$$U(\vec{r}) = \sum_k e^{i\vec{k}\cdot\vec{r}} \, U_k$$

these can be equal only if $e^{i\vec{k}\cdot\vec{R}}=1$ for any $\vec{R}$ in BL
$\Rightarrow \vec{k}$ must be a $\vec{K}$ in the R.L.

So the sum on $\vec{k}'$ in above becomes a sum on $\vec{K}$

$$\boxed{\varepsilon_k^0 \, c_k + \sum_K U_K \, c_{k-K} = \varepsilon \, c_k}$$

note: $U_K = \dfrac{1}{V} \displaystyle\int_V d^3 r \; e^{-i\vec{K}\cdot\vec{r}} \, U(\vec{r})$

$$= \dfrac{1}{v} \int_C d^3 r \; e^{-i\vec{K}\cdot\vec{r}} \, U(\vec{r})$$

where C is any primitive all of the B.L. This follows from fact that $U(\vec{r})$ is periodic on the BL

$$\varepsilon_k^0 \, c_k + \sum_{K'} U_{K'} \, c_{k-K'} = \varepsilon \, c_k$$

apply the above to the wave-vector $\vec{k} - \vec{K}$

$$\varepsilon_{k-K}^0 \, c_{k-K} + \sum_{K'} U_{K'} \, c_{k-K-K'} = \varepsilon \, c_{k-K}$$

or relabeling the summation vector in the 2nd term
$$\vec{K} + \vec{K}' \rightarrow \vec{K}'$$

$$\boxed{\varepsilon_{k-K}^0 \, c_{k-K} + \sum_{K'} U_{K'-K} \, c_{k-K'} = \varepsilon \, c_{k-K}}$$

As $\vec{K}$ in the above varies through the wavevectors in the R.L we get a set of linear equations for the Fourier coefficients $\{ c_{k-K} \}$, $\vec{K}$ in RL.

Above can be viewed as a matrix eigenvalue problem for the eigen-vector $\{ c_{k-K} \}$ (viewing $\vec{K}$ as the index of the vector, and ε as the eigenvalue.

Solution gives

$$\psi_k(\vec{r}) = \sum_K e^{i(\vec{k}-\vec{K})\cdot \vec{r}} \, c_{k-K} = e^{i\vec{k}\cdot\vec{r}} \sum_K e^{-i\vec{K}\cdot\vec{r}} \, c_{k-K}$$

Define $u_k(\vec{r}) \equiv \sum_K e^{i\vec{K}\cdot\vec{r}} \, c_{k-K}$

then eigenstates have the form

$$\psi_k(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} \, u_k(\vec{r})$$

where $\quad u_k(\vec{r}+R) = u_k(\vec{r})$ $\quad$ ie $u(\vec{r})$ is periodic
on the B.L.

This is **Bloch's theorem**

If we label the R.L. wavevectors as $\vec{K}_i$, the
Schrodinger Eqn takes the matrix form

$$
\begin{pmatrix}
\varepsilon_k^0 & U_{K_1} & U_{K_2} & U_{K_3} & \cdots \\
U_{-K_1} & \varepsilon_{k-K_1}^0 & U_{K_2-K_1} & U_{K_3-K_1} & \\
U_{-K_2} & U_{K_1-K_2} & \varepsilon_{k-K_2}^0 & U_{K_3-K_2} & \\
U_{-K_3} & U_{K_1-K_3} & U_{K_2-K_3} & \varepsilon_{k-K_3}^0 & \\
\vdots & & & & \ddots
\end{pmatrix}
\begin{pmatrix}
c_k \\ c_{k-K_1} \\ c_{k-K_2} \\ c_{k-K_3} \\ \vdots
\end{pmatrix}
= \varepsilon
\begin{pmatrix}
c_k \\ c_{k-K_1} \\ c_{k-K_2} \\ c_{k-K_3} \\ \vdots
\end{pmatrix}
$$

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

$$U_K^* = \frac{1}{V}\int_V d^3r \, e^{i\vec{K}\cdot\vec{r}} \, U(\vec{r}) = U_{-K}$$

Hence the above matrix is **Hermitian** as it should be
to guarantee it is diagonalizable with real eigenvalues

Also: If the ~~~~ crystal has inversion symmetry, ie $U(\vec{r}) = U(-\vec{r})$
Then $\quad U_K = \frac{1}{V}\int_V d^3r \, e^{-i\vec{K}\cdot\vec{r}} \, U(\vec{r}) = \frac{1}{V}\int d^3r \, e^{-i\vec{K}\cdot\vec{r}} \, U(-\vec{r})$

$$= \frac{1}{V}\int d^3r \, e^{i\vec{K}\cdot\vec{r}} \, U(\vec{r}) = U_{-K} = U_K^* \quad \text{is real}$$

Also, we can assume $U_{K=0} = 0$ due to charge neutrality, since

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

$\rho(\vec{r})$ is total charge density from all ions and electrons

$$U_{K=0} = \frac{1}{V} \int d^3r' \, \rho(r') \underbrace{\int d^3r \frac{1}{|\vec{r} - \vec{r}'|}}_{\text{independent of } \vec{r}' \text{ if}}$$

using periodic boundary condition

$$\propto \int d^3r' \rho(\vec{r}') = 0 \qquad \text{if charge neutral}$$

Thus we see that the periodic ionic potential $U(\vec{r})$ only couples wavevectors $\vec{k}$ to the wave vectors $\vec{k}' = \vec{k} - \vec{K}$, with $\vec{K}$ in the RL. These $\vec{k}'$ are just the wave vectors one gets from scattering of the electron off the Bragg planes.

Note: If we let $\vec{k} \to \vec{k} + \vec{k}_0$ in the above matrix equation, the only result is a permutation of the rows and columns since the set
$$\{\vec{k} + \vec{K}\} = \{\vec{k} + \vec{K}_0 + \vec{K}\}$$
since $\vec{K}_0 + \vec{K}$ is vector in the R.L. if both $\vec{K}_0$ and $\vec{K}$ are.

Hence the eigenvectors and eigenvalues are periodic functions of wavevector with periodicity given by the R.L. That is, if

$$\psi_{\vec{k},n}(\vec{r}) = \sum_{K} e^{i(\vec{k} - \vec{K}) \cdot \vec{r}} c_{k-K} \qquad \text{with eigenvalue } \varepsilon_n(\vec{k})$$

is the nth eigenvector and eigenvalue of the matrix then ~~then matrix~~

$$\psi_{k+K, n}(\vec{r}) = \psi_{k,n}(\vec{r}) \left.\begin{array}{r} \\ \end{array}\right\} \begin{array}{l} \text{periodic in} \\ \vec{k} \to \vec{k} + \vec{K} \\ \text{for any } \vec{K} \text{ in R.L.} \end{array}$$

$$\varepsilon_n(\vec{k} + \vec{K}) = \varepsilon_n(\vec{k})$$

Therefore the unique states are specified by a wavevector $\vec{q}$ in the 1st BZ (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 $\vec{k} = \vec{q} + \vec{K}$ where $\vec{q}$ is in 1st BZ and $\vec{K}$ is in R.L.)

<u>Comment</u> — For free electrons the energy eigenstates are specified ~~by~~ by a wave vector $\vec{k}$ that can take a value <u>anywhere</u> 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 $\vec{q}$ that must lie only in the 1st BZ. 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?

<u>Answer</u>: We can represent even free electron states using the band index n and 1st BZ $\vec{q}$ as quantum numbers. For any $\vec{k}$, anywhere in k-space, we can always write $\vec{k} = \vec{q} + \vec{K}$ where $\vec{K}$ is ~~the~~ a unique R.L. vector closest to $\vec{k}$ and $\vec{q}$ 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 BZ as the set of wave vectors closer ~~closest~~ to the origin than to any other $\vec{K}$ in the R.L.

Then for any $\vec{k} = \vec{q} + \vec{K}$ in the nth Brillouin Zone

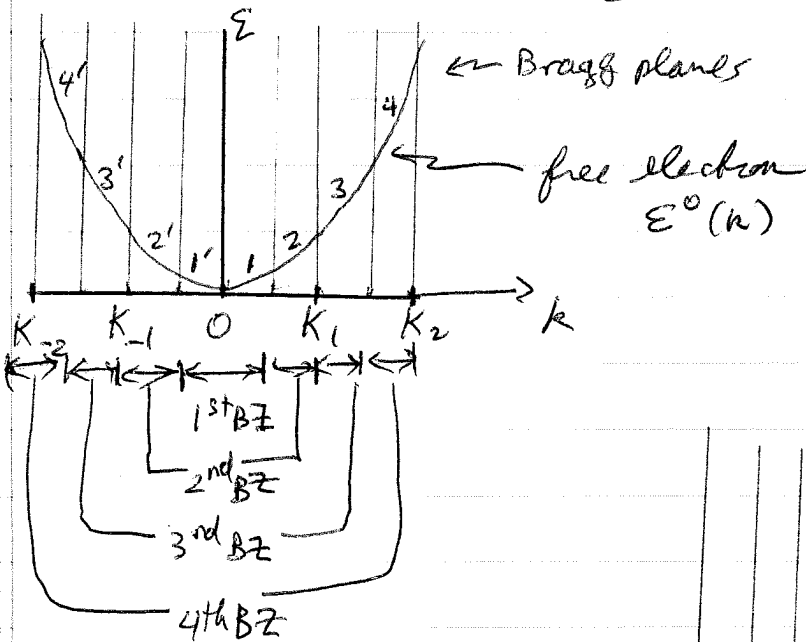write $\varepsilon^0(\vec{k}) = \dfrac{\hbar^2 k^2}{2m} = \dfrac{\hbar^2 (\vec{q} + \vec{K})}{2m} = \varepsilon_n(\vec{q})$

↗ energy at crystal momentum $\vec{q}$
in band index "n"

Thus the band index gives the B.Z. in which the corresponding free electron wave vector $\vec{k}$ lies.

Ex: in a 1D B.L. of lattice constant a
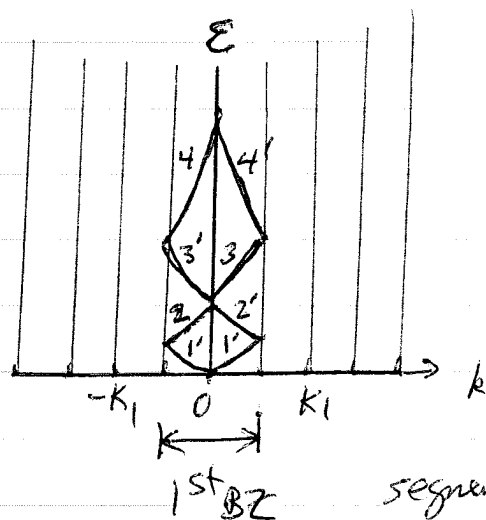R.L. vectors are $K_n = \left(\dfrac{2\pi}{a}\right) n$, $n = 0, \pm 1, \pm 2, \ldots$
Bragg planes at $k = \dfrac{K_n}{2} = \left(\dfrac{\pi}{a}\right) n$

← Bragg planes

← free electron $\varepsilon^0(k)$

$4'$ $3'$ $2'$ $1'$ 1 2 3 4

K_{-2} K_{-1} O K_1 K_2 → k

1st BZ
2nd BZ
3rd BZ
4th BZ

can translate the section of curve in n^{th} BZ back into 1st BZ by subtract appropriate K from $\vec{k}$

representing free → electron states by $\vec{q}$ in 1st BZ. Integers label corresponding sections of the curves in the two equivalent representations

ε

4 $4'$
$3'$ 3
2 $2'$
$1'$ $1'$

$-K_1$ O K_1 → k

1st BZ

segments of curve labeled n or n' came from the nth BZ of free electrons

<u>Comments:</u>
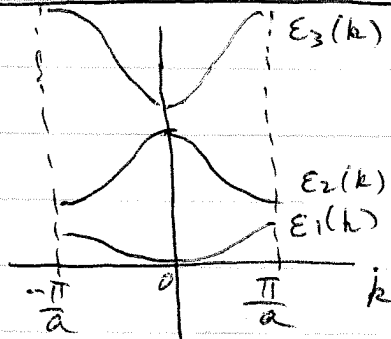
① Because $\vec{k}$ enters the matrix equation as a parameter via the terms ε^k_{k+K}, we expect that the eigenvalues $\varepsilon_n(\vec{k})$ are smooth continuous functions of $\vec{k}$.

② Because $\varepsilon_n(\vec{k})$ is periodic in $\vec{k}$, $\varepsilon_n(\vec{k}+\vec{K}) = \varepsilon_n(\vec{k})$, we ~~expect~~ ^{must have} that $\varepsilon_n(\vec{k})$ has a maximum and a minimum and varies continuously between them. This is why $\varepsilon_n(\vec{k})$ is refered to as an energy band
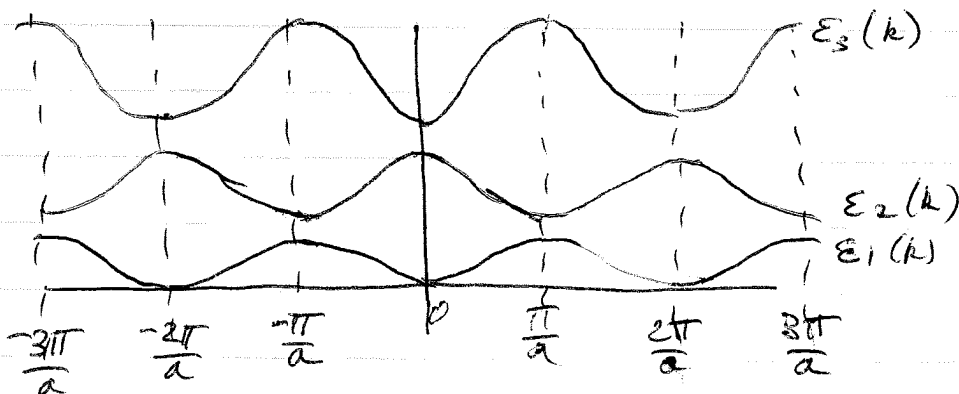
③ Since $\psi_{kn}(\vec{r}) = \sum_{k} e^{i(k-K)\cdot\vec{r}} c_{k-K}$ is no longer a pure plane wave, ψ_{kn} is <u>NOT</u> an eigenstate of momentum. This is reasonable since with the periodic potential turned on the system no longer has translational invariance. However the system does have invariance in translations by B.L. vectors $\vec{R}$. This is why ψ_{kn} mixes only wave vectors related to $\vec{k}$ by $\vec{k}' = \vec{k} - \vec{K}$ for $\vec{K}$ in R.L. Because of this ~~difference~~, $\vec{k}$ is called the "crystal momentum" — it is not the true momentum. In collisions, the <u>crystal</u> ~~true~~ momentum of an electron is ~~only~~ "conserved" modulus a R.L. vector $\vec{K}$.

⑨ Because $\psi_{kn}(\vec{r})$ and $\varepsilon_n(\vec{k})$ 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 is most often 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
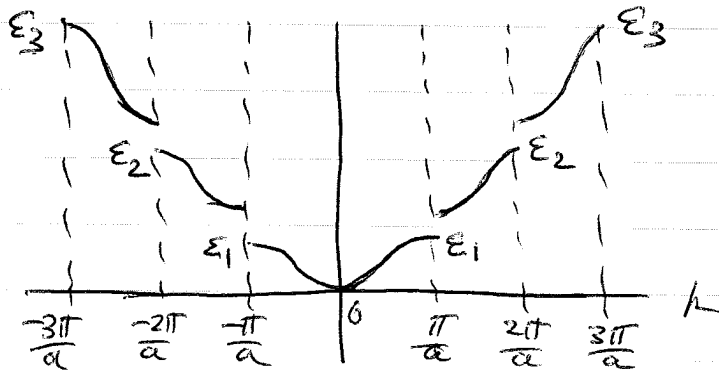
Reduced zone scheme : restrict $\vec{k}$ to 1st BZ for all energy bands n

$\varepsilon_3(k)$

$\varepsilon_2(k)$

$\varepsilon_1(k)$

$-\dfrac{\pi}{a}$ 0 $\dfrac{\pi}{a}$ k

Repeated zone scheme : show all values of $\vec{k}$, with $\varepsilon_n(\vec{k})$ periodic in $\vec{k}$

$\varepsilon_3(k)$

$\varepsilon_2(k)$

$\varepsilon_1(k)$

$-\dfrac{3\pi}{a}$ $-\dfrac{2\pi}{a}$ $-\dfrac{\pi}{a}$ 0 $\dfrac{\pi}{a}$ $\dfrac{2\pi}{a}$ $\dfrac{3\pi}{a}$

Extended Zone scheme : show energy band n
~~#~~ using $\vec{k}$ vectors in n th BZ.

Note: However one represents the band structure,
each band contains only N ~~the~~ distinct allowed
values of $\vec{k}$ consistent with the Born - von Karman
boundary conditions. $\Rightarrow$ each band can contain
$2N$ electron states   (2 for spin $\uparrow$ or $\downarrow$)
$N = \#$ ~~ions~~ primitive cells in crystal ($= \#$ ions if we have a simple
                                  BL and **not** a lattice with a basis)

⑤ If one computes the expectation of velocity
    in a Bloch ~~std~~ electron state, one finds

$$\vec{v}_n(\vec{k}) = \langle \psi_{nk} | \frac{\hbar}{i} \vec{\nabla} | \psi_{nk} \rangle = \int d^3r \; \psi_{nk}^*(\vec{r}) \frac{\hbar}{i} \vec{\nabla} \psi_{nk}(\vec{r})$$

$$= \frac{1}{\hbar} \vec{\nabla}_k \, \varepsilon_n(\vec{k}) \qquad \leftarrow \text{ looks just like group}$$
velocity, but is exact result
for expectation
value of $\vec{v}$
in eigenstate

↑ gradient with respect to $\vec{k}$

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 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 τ. The reason Drude's picture does not hold is because of the wave nature of the electron and its phase coherent scattering off the ions.

A nonperturbative proof for $\boxed{\vec{V}_{\vec{k}} = \frac{1}{\hbar}\frac{\partial \mathcal{E}_{\vec{k}}}{\partial \vec{k}}}$

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

$$\psi_{\vec{k}}(\vec{x}) = e^{i\vec{k}\cdot\vec{x}}\, u_{\vec{k}}(\vec{x})$$

where $u_{\vec{k}}(\vec{x})$ is periodic in the Bravais lattice and satisfies

$$H_{\vec{k}}\, u_{\vec{k}} = \mathcal{E}_{\vec{k}}\, u_{\vec{k}} \qquad\qquad \text{---(1)}$$

where

$$H_{\vec{k}} = \frac{\hbar^2}{2m}\left(\frac{1}{i}\nabla + \vec{k}\right)^2 + U(\vec{x}) \qquad\qquad (2)$$

Note that $H_{\vec{k}}$ is Hermitian for any $\vec{k}$.

Suppose $u_{\vec{k}}(\vec{x})$ is normalized as

$$\int_{\Omega} |u_{\vec{k}}|^2 d^3\vec{x} = 1 \qquad\qquad (3)$$

where Ω is a primitive cell

From (2) we have

$$\frac{\partial u_{\vec{k}}^*}{\partial \vec{k}} H_{\vec{k}}\, u_{\vec{k}} = \mathcal{E}_{\vec{k}}\, \frac{\partial u_{\vec{k}}^*}{\partial \vec{k}} u_{\vec{k}} \qquad\qquad (4)$$

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

$$\frac{\partial u_{\vec{k}}}{\partial \vec{k}} H_{-\vec{k}}\, u_{\vec{k}}^* = \mathcal{E}_{\vec{k}}\, \frac{\partial u_{\vec{k}}}{\partial \vec{k}} u_{\vec{k}}^* \qquad\qquad (5)$$

Adding (4) and (5) and integrating over the primitive cell Ω we get

$$\mathcal{E}_{\vec{k}} \frac{\partial}{\partial \vec{k}} \int_{\Omega} |u_{\vec{k}}|^2 d^3\vec{x} = \int_{\Omega}\left[\frac{\partial u_{\vec{k}}^*}{\partial \vec{k}} H_{\vec{k}}\, u_{\vec{k}} + \frac{\partial u_{\vec{k}}}{\partial \vec{k}} H_{-\vec{k}}\, u_{\vec{k}}^* \right] d^3\vec{x}$$

$$(6)$$

Since $H_{-\vec{k}}$ is Hermitian,

$$\int_{\Omega} \frac{\partial u_{\vec{k}}}{\partial \vec{k}} H_{-\vec{k}} u_{\vec{k}}^* \, d^3\vec{x} = \left[\int_{\Omega} u_{\vec{k}} H_{-\vec{k}} \frac{\partial u_{\vec{k}}^*}{\partial \vec{k}} \, d^3\vec{x} \right]^*$$

$$= \int_{\Omega} u_{\vec{k}}^* H_{\vec{k}} \frac{\partial u_{\vec{k}}}{\partial \vec{k}} \, d^3\vec{x} \qquad (7)$$

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

$$\int_{\Omega} \left[\frac{\partial u_{\vec{k}}^*}{\partial \vec{k}} H_{\vec{k}} u_{\vec{k}} + u_{\vec{k}}^* H_{\vec{k}} \frac{\partial u_{\vec{k}}}{\partial \vec{k}} \right] d^3\vec{x} = 0 \qquad (8)$$

However, (1) and (3) directly imply

$$\mathcal{E}_{\vec{k}} = \int_{\Omega} u_{\vec{k}}^* H_{\vec{k}} u_{\vec{k}} \, d^3\vec{x} \qquad (9)$$

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

$$\frac{\partial \mathcal{E}_{\vec{k}}}{\partial \vec{k}} = \int_{\Omega} u_{\vec{k}}^* \frac{\partial H_{\vec{k}}}{\partial \vec{k}} u_{\vec{k}} \, d^3\vec{x}$$

$$= \frac{\hbar^2}{m} \int_{\Omega} u_{\vec{k}}^* \left(\frac{1}{i} \nabla + \vec{k} \right) u_{\vec{k}} \, d^3\vec{x}$$

or

$$\frac{1}{\hbar} \frac{\partial \mathcal{E}_{\vec{k}}}{\partial \vec{k}} = \frac{1}{m} \int_{\Omega} \psi_{\vec{k}}^* \left(\frac{\hbar}{i} \nabla \right) \psi_{\vec{k}} \, d^3\vec{x} = \vec{V}_{\vec{k}}$$