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

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

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

then the inverse Fourier transform is

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

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

~~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

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

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

Now

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

v = 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

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

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

So

$$\frac{1}{V} \int d^3r \, e^{i(\vec{k}' - \vec{k}) \cdot \vec{r}} = \frac{v N_1 N_2 N_3}{V} \delta_{k',k}$$

$$= \delta_{k',k}$$

zero unless $\vec{k} = \vec{k}'$

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 Schrodinger Eqn.

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

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

$$\Rightarrow \varepsilon_k^0 C_k + \sum_{k'} U_{k'} C_{k-k'} = \varepsilon C_k$$

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

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

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

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

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

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 $\vec{K}$

$$\Rightarrow \boxed{\varepsilon_k^0 C_k + \sum_K U_K C_{k-K} = \varepsilon C_k}$$

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

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

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

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

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

independent of $\vec{r}'$ if using periodic boundary conditions

$$\propto \int d^3r' \rho(\vec{r}') = 0$$ 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.

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

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

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

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

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

As $\vec{K}$ in the above varies through the wavectors in the R.L. we ~~gets~~ get a set of linear equations for the Fourier coefficents $\{c_{k-K}\}$, $\vec{K}$ 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 $\quad u_k(\vec{r}) \equiv \sum_K e^{i\vec{K}\cdot\vec{r}} c_{k-K}$

Then eigenstates have the form

$$\boxed{\begin{aligned} &\psi_k(\vec{r}) = e^{i k\cdot r}\, u_k(\vec{r}) \\ &u_k(\vec{r}+R) = u_k(\vec{r}) \end{aligned}}$$

where (second line) — i.e. $u(\vec{r})$ is periodic on the B.L.

This is <u>Bloch's theorem</u>

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

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

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

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

Hence the above matrix is <u>Hermitian</u> as it should be to guarantee it is diagonalizable with real eigenvalues

Also: If the ~~...~~ crystal has inversion symmetry, i.e. $U(\vec{r}) = U(-\vec{r})$, then

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

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

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

$$\psi_{kn}(\vec{r}) = \sum_K e^{i(\vec{k}-\vec{K})\cdot\vec{r}} \, c_{k-K} \quad \text{with eigenvalue } \varepsilon_n(\vec{k})$$

is the n^{th} eigenvector and eigenvalue of the matrix then ~~ψ_{kn} and~~

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

Therefore the unique states are specified by a wave vector $\vec{q}$ in the 1^{st} 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 1^{st} BZ and $\vec{K}$ is in R.L.)