



volume per allowed wavevector in $\vec{k}$ -space is the volume of the parallelepiped formed by the vectors $\frac{\vec{b}_i}{N_i}$

$$= \frac{\vec{b}_1 \cdot (\vec{b}_2 \times \vec{b}_3)}{N_1 N_2 N_3} = \frac{(2\pi)^3}{N (\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3))}$$

$$= \frac{(2\pi)^3}{vN} = \frac{(2\pi)^3}{V} \quad \begin{matrix} V = vN \\ = \text{total volume BL} \end{matrix}$$

where $v = \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)$ is the volume of the primitive cell of the B.L. and $\frac{(2\pi)^3}{v}$ is the volume of the primitive cell of the R.L.

Note: volume per allowed wavevector $\frac{(2\pi)^3}{V}$ is same as we had for free electrons.

Number of allowed $\vec{k}$ values in any primitive cell of the R.L. is

$$\frac{\left[\frac{(2\pi)^3}{v} \right]}{\left[\frac{(2\pi)^3}{vN} \right]} = N \quad \text{number of wvs in BL}$$

Number of allowed $\vec{k}$ values in any primitive cell of the R.L., for example the 1st BZ, is N

$\Rightarrow$ # electron states in 1st BZ is $2N$ (2 from spin = ± 1)
 $\Rightarrow$ when valence $z=1$, ground state occupies half the states of 1st BZ

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

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

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

then the inverse Fourier transform is

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

Proof:

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

~~the~~ since both $\vec{k}$ and $\vec{k}'$ satisfy Born-von Karmen 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

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

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

Now

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

$v = \text{vol primitive cell}$

and

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

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

do for example the x_1 integral

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

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

So

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

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

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

Bloch's Theorem

Now we prove Bloch's Theorem by substituting the Fourier transform in the Schrödinger Eqn.

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

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

Substitute in the Fourier transforms

$$\psi(\vec{r}) = \sum_{\vec{k}} e^{i\vec{k} \cdot \vec{r}} c_{\vec{k}}$$

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

to get

$$\begin{aligned} \sum_{\vec{k}} e^{i\vec{k} \cdot \vec{r}} \frac{\hbar^2 k^2}{2m} c_{\vec{k}} + \sum_{\vec{k}''} \sum_{\vec{k}'} e^{i(\vec{k}'' + \vec{k}') \cdot \vec{r}} U_{\vec{k}'} c_{\vec{k}''} \\ = \epsilon \sum_{\vec{k}} e^{i\vec{k} \cdot \vec{r}} c_{\vec{k}} \end{aligned}$$

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

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

$$\text{write } \epsilon_k^0 = \frac{\hbar^2 k^2}{2m}$$

$$\Rightarrow \epsilon_k^0 c_k + \sum_{k'} U_{k'} c_{k-k'} = \epsilon c_k$$

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 wave vectors $\{\vec{K}\}$ of the reciprocal lattice.

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

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

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 $\vec{K}$

$$\Rightarrow \boxed{\epsilon_k^0 c_k + \sum_{\vec{K}} U_{\vec{K}} c_{k-\vec{K}} = \epsilon c_k}$$

$$\begin{aligned} \underline{\text{note:}} \quad U_{\vec{K}} &= \frac{1}{V} \int_V d^3r \, e^{-i\vec{K} \cdot \vec{r}} U(\vec{r}) \\ &= \frac{1}{v} \int_C d^3r \, e^{-i\vec{K} \cdot \vec{r}} U(\vec{r}) \end{aligned}$$

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

$$\epsilon_k^0 c_k + \sum_{k'} U_{k'} c_{k-k'} = \epsilon c_k$$

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

$$\epsilon_{k-k}^0 c_{k-k} + \sum_{k'} U_{k'} c_{k-k-k'} = \epsilon c_{k-k}$$

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

$$\epsilon_{k-k}^0 c_{k-k} + \sum_{k'} U_{k'-k} c_{k-k'} = \epsilon c_{k-k}$$

As $\vec{k}$ in the above varies through the wavevectors in the R.L. we ~~get~~ ^{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

$$\psi(\vec{r}) = \sum_{\vec{k}} e^{i(\vec{k}-\vec{k}') \cdot \vec{r}} c_{k-k} = e^{i\vec{k} \cdot \vec{r}} \sum_{\vec{k}} e^{-i\vec{k}' \cdot \vec{r}} c_{k-k}$$

$$\text{Define } u(\vec{r}) \equiv \sum_{\vec{k}} e^{i\vec{k} \cdot \vec{r}} c_{k-k}$$

then eigenstates have the form

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

where $u_{\vec{k}}(\vec{r} + \vec{R}) = u_{\vec{k}}(\vec{r})$ i.e. $u(\vec{r})$ is periodic on the B.L.

This is Bloch's theorem

If we label the R.L. wavevectors as $\vec{K}_2$, the Schrodinger Eqn takes the matrix form

$$\begin{pmatrix} E_{\vec{k}}^0 & U_{\vec{k}_1} & U_{\vec{k}_2} & U_{\vec{k}_3} & \dots \\ U_{-\vec{k}_1} & E_{\vec{k}-\vec{k}_1}^0 & U_{\vec{k}_2-\vec{k}_1} & U_{\vec{k}_3-\vec{k}_1} & \\ U_{-\vec{k}_2} & U_{\vec{k}_1-\vec{k}_2} & E_{\vec{k}-\vec{k}_2}^0 & U_{\vec{k}_3-\vec{k}_2} & \\ U_{-\vec{k}_3} & U_{\vec{k}_1-\vec{k}_3} & U_{\vec{k}_2-\vec{k}_3} & E_{\vec{k}-\vec{k}_3}^0 & \\ \vdots & & & & \ddots \end{pmatrix} \begin{pmatrix} c_{\vec{k}} \\ c_{\vec{k}-\vec{k}_1} \\ c_{\vec{k}-\vec{k}_2} \\ c_{\vec{k}-\vec{k}_3} \\ \vdots \end{pmatrix} = E \begin{pmatrix} c_{\vec{k}} \\ c_{\vec{k}-\vec{k}_1} \\ c_{\vec{k}-\vec{k}_2} \\ c_{\vec{k}-\vec{k}_3} \\ \vdots \end{pmatrix}$$

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

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

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

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

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

$$= \frac{1}{V} \int_V d^3r e^{i\vec{k} \cdot \vec{r}} U(\vec{r}) = U_{-\vec{k}} = U_{\vec{k}}^* \text{ is real}$$

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

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

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

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

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

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.

Note: If we let $\vec{k} \rightarrow \vec{k} + \vec{K}_0$ 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 eigen vectors and eigenvalues are periodic functions of wave vector with periodicity given by the R.L. That is, if

$$\psi_{k,n}(\vec{r}) = \sum_{\vec{k}} e^{i(\vec{k} - \vec{k}_0) \cdot \vec{r}} c_{\vec{k} - \vec{k}_0} \quad \text{with eigenvalue } E_n(\vec{k})$$

is the n^{th} eigenvector and eigenvalue of the matrix then $\psi_{k,n}$ and

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

Therefore the unique states are specified by a wave vector $\vec{g}$ 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 $\vec{g}$.

(all other $\vec{k}$ values can always be written as $\vec{k} = \vec{g} + \vec{K}$ where $\vec{g}$ is in 1st BZ and $\vec{K}$ is in R.L.)