Second Proof of Bloch's Theorem

$$\psi(\vec{r}) = \sum c_{\vec{q}}\, e^{i\vec{q}\cdot\vec{r}}$$

$$\vec{q} = \sum_{i=1}^{3} \frac{m_i}{N_i}\, \vec{b}_i$$

$$U(\vec{r}) = \sum_{\vec{K}} U_K\, e^{i\vec{K}\cdot\vec{r}}$$

$$U_{\vec{K}} = \frac{1}{V}\int_{\text{cell}} d\vec{r}\, e^{-i\vec{K}\cdot\vec{r}}\, U(\vec{r})$$

$$U_0 = \frac{1}{V}\int_{\text{cell}} d\vec{r}\, U(\vec{r}) = 0$$

$U(\vec{r})$ is real

$$\Rightarrow \quad U_K = \frac{1}{V}\int_{\text{cell}} d\vec{r}\, e^{-i\vec{K}\cdot\vec{r}}\, \underbrace{U(\vec{r})}_{\text{real}}$$

$$* \quad U_{-K} = \frac{1}{V}\int_{\text{cell}} d\vec{r}\, e^{-i(-\vec{K})\cdot\vec{r}}\, U(\vec{r})$$

$$U_{-\vec{K}} = \frac{1}{V}\int_{\text{cell}} d\vec{r}\, e^{+i\vec{K}\cdot\vec{r}}\, U(\vec{r}) = U_{\vec{K}}^*$$

$$U_{-\vec{K}} = U_{\vec{K}}^*$$

Next, assume that crystal has inversion symmetry

$$\Rightarrow \quad U(\vec r) = U(-\vec r)$$

$$\Rightarrow \quad U_{\vec K} = \frac{1}{V}\int_{cell} d\vec r\, e^{-i\vec K\cdot\vec r}\, U(\vec r)$$

$$= \frac{1}{V}\int_{cell} d\vec r\, e^{-i\vec K\cdot\vec r}\, U(-\vec r)$$

$$= \frac{1}{V}\int_{cell} d\vec r\, e^{i\vec K\cdot(-\vec r)}\, U(-\vec r)$$

let $r' = -\vec r$

$\Rightarrow dr' = -d\vec r$

limits of integration $\begin{cases} \vec r : & \vec a \to \vec b \\ \vec r' : & -\vec a \to -\vec b \end{cases}$

$$\int_{-\vec a}^{-\vec b} dr' = -\int_{\vec a}^{\vec b} dr'$$

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

$$U_{\vec K} = U_{\vec K}^{*}$$

$$\Rightarrow \boxed{U_{\vec K} \text{ is } \underline{\text{real}}}$$

i.e. $a + ib = a - ib$

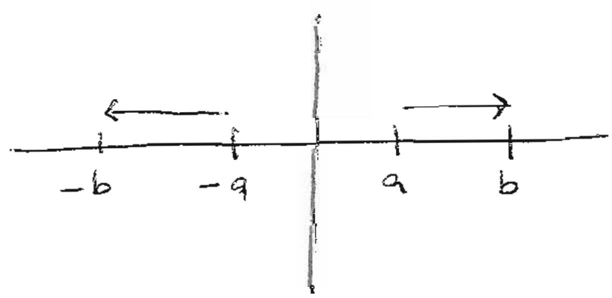
$\Rightarrow ib = -ib$

$\Rightarrow b = -b$

$\Rightarrow 2b = 0$

$\Rightarrow \underline{b = 0}$

and $\therefore$ $a + i(0)$ is <u>real</u>



i.e. $\int_1^2 dr = 1$

$\int_{-1}^{-2} dr = -1$

therefore $$U_{-\vec{K}} = U_{\vec{K}}^{*}$$

and

$$U_{\vec{K}} = U_{K}^{*}$$

$$\Rightarrow \quad U_{\vec{K}} = U_{-\vec{K}} = U_{\vec{K}}^{*}$$ (for crystals with inversion symmetry)

<u>Schrodinger Eq.</u>

$$H\Psi = \left(-\frac{\hbar^2}{2m}\vec{\nabla}^2 + U(\vec{r})\right)\Psi = \varepsilon\Psi$$

$$\Psi(\vec{r}) = \sum_{q} c_q \, e^{i\vec{q}\cdot\vec{r}}$$

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

$$-\frac{\hbar^2}{2m}\vec{\nabla}^2\Psi = \vec{\nabla}^2 \sum_{q} c_q e^{i\vec{q}\cdot\vec{r}} = -\frac{\hbar^2}{2m} \sum_{q} -q^2 c_q e^{i\vec{q}\cdot\vec{r}}$$

$$= \sum_{q} \frac{\hbar^2}{2m} q^2 c_q e^{i\vec{q}\cdot\vec{r}}$$

$$U\Psi = \left(\sum_{K} U_{\vec{K}} e^{i\vec{K}\cdot\vec{r}}\right)\left(\sum_{q} c_q e^{i\vec{q}\cdot\vec{r}}\right)$$

$$= \sum_{Kq} U_{\vec{K}} c_q e^{i(\vec{K}+\vec{q})\cdot\vec{r}} = \sum_{K\vec{q}'} U_{\vec{K}} c_{q'-K} e^{i\vec{q}'\cdot\vec{r}}$$

$$= \sum_{\vec{K}'\vec{q}} U_{\vec{K}'} c_{q-K'} e^{i\vec{q}\cdot\vec{r}} = \sum_{\vec{q}} e^{i\vec{q}\cdot\vec{r}} \sum_{\vec{K}'} U_{\vec{K}'} c_{q-\vec{K}'}$$

$$\Rightarrow H\psi = \sum_{\vec q} \frac{\hbar^2}{2m} q^2 c_{\vec q}\, e^{i\vec q\cdot\vec r} + \sum_{\vec q} e^{i\vec q\cdot\vec r} \sum_{\vec K'} U_{\vec K'} c_{\vec q-\vec K'} = \mathcal{E}\psi$$

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

plane waves satisfying Born-von Karman are an orthogonal set

$\Rightarrow$ for all $\vec q$,

$$\boxed{\left(\frac{\hbar^2}{2m} q^2 - \mathcal{E}\right) c_{\vec q} + \sum_{\vec K'} U_{\vec K'} c_{\vec q-\vec K'} = 0}$$

let $\vec q = \vec k - \vec K$

$\vec k$ is in 1^{st} B.Z.

$$\Rightarrow \left(\frac{\hbar^2}{2m}(\vec k-\vec K)^2 - \mathcal{E}\right) c_{\vec k-\vec K} + \sum_{\vec K'} U_{\vec K'} c_{\vec k-\vec K-\vec K'} = 0$$

$$K' \rightarrow K' - K$$

$$\Rightarrow \left(\frac{\hbar^2}{2m}(\vec k-\vec K)^2 - \mathcal{E}\right) c_{\vec k-\vec K} + \sum_{\vec K'} U_{\vec K'-K}\, c_{\vec k-\vec K'} = 0$$

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

$$\longrightarrow \quad \psi_{\vec k}(\vec r) = \sum_{\vec K} c_{\vec k-\vec K}\, e^{i(\vec k-\vec K)\cdot\vec r}$$

i.e. $c_{\vec q}$ takes on only values like

$c_{\vec k-\vec K}$, $c_{\vec k-\vec K''}$

where $\vec K$, $\vec K'$, $\vec K''$ are all reciprocal lattice vectors

$$\Rightarrow \psi_{\vec k}(\vec r) = e^{i\vec k\cdot\vec r}\left(\sum_{\vec K} c_{\vec k-\vec K}\, e^{-i\vec K\cdot\vec r}\right)$$

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

Bloch wavefunction

$$\underbrace{u_{\vec k}(\vec r) = \sum_{\vec K} c_{\vec k-\vec K}\, e^{-i\vec K\cdot\vec r}}_{\text{periodic function}}$$

$$u(\vec r) = u(\vec r+\vec R)$$

Some Points Regarding Bloch's Theorem

in Bloch case

$$\vec{k} \not\propto \vec{p}$$

eigenstates of H are not simultaneous eigenstates of p

because, H is not completely translationally invariant in the presence of a non-constant potential

$p = \frac{\hbar}{i}\vec{\nabla}$

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

$$H = H(\vec{r})$$

$$p\psi = \frac{\hbar}{i}\vec{\nabla}\psi_{n\vec{k}} = \frac{\hbar}{i}\vec{\nabla}\left(e^{i\vec{k}\cdot\vec{r}}u_{n\vec{k}}(\vec{r})\right)$$

$$= \frac{\hbar}{i}\left(i\vec{k}e^{i\vec{k}\cdot\vec{r}}u_{n\vec{k}} + e^{i\vec{k}\cdot\vec{r}}\vec{\nabla}u_{n\vec{k}}(\vec{r})\right)$$

$$= \hbar\vec{k}\,\psi_{n\vec{k}}(\vec{r}) + e^{i\vec{k}\cdot\vec{r}}\frac{\hbar}{i}\vec{\nabla}u_{n\vec{k}}(\vec{r})$$

$$\neq C \times \psi_{n\vec{k}}(\vec{r})$$

because although $\hbar\vec{k}$ is a constant times ψ, the second term is not

but <u>if</u> $\vec{\nabla}u_{n\vec{k}}(\vec{r}) = 0 \Rightarrow u_{n\vec{k}}(\vec{r}) =$ constant in space

$$\Rightarrow p\psi = \hbar\vec{k}\psi$$

$$\Rightarrow \vec{p} = \hbar\vec{k}$$

but <u>not</u> in general.

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

$\vec{k}$ can always be confined to a convenient primitive cell, such as the 1st B.Z., because if $\vec{k}'$ is <u>not</u> in (e.g.) the 1st B.Z., then

$$\vec{k} = \vec{k}' - \vec{K} \quad \underline{\text{is}} \text{ in the 1st B.Z.}$$

where $\vec{K}$ is some recip. lat. vector

if $\vec{k}'$ → Bloch wave vector

then $\vec{k}$ → Bloch wave vector, since

$$\psi(\vec{r}+\vec{R}) = e^{i\vec{k}'\cdot\vec{R}}\,\psi(\vec{r})$$

$$= e^{i(\vec{k}+\vec{K})\cdot\vec{R}}\,\psi(\vec{r})$$

$$\underline{\psi(\vec{r}+\vec{R}) = e^{i\vec{k}\cdot\vec{R}}\,\psi(\vec{r})}\ \underbrace{e^{i\vec{K}\cdot\vec{R}}}_{=1}$$

Start again with Schrodinger Eq.

$$H\Psi = \left(-\frac{\hbar^2}{2m}\vec{\nabla}^2 + U(\vec{r})\right)\Psi = \mathcal{E}\Psi$$

$$\text{let } \Psi = e^{i\vec{k}\cdot\vec{r}}u(\vec{r})$$

$$\vec{\nabla}^2\Psi = -k^2\Psi + e^{i\vec{k}\cdot\vec{r}}\vec{\nabla}^2 u(\vec{r})$$

$$\Rightarrow -\frac{\hbar^2}{2m}\left(-k^2 u(\vec{r}) + \vec{\nabla}^2 u(\vec{r})\right)\left(e^{i\vec{k}\cdot\vec{r}}\right) = \mathcal{E}\,u(\vec{r})\left(e^{i\vec{k}\cdot\vec{r}}\right)$$
$$+ U(\vec{r})u(\vec{r})\left(e^{i\vec{k}\cdot\vec{r}}\right)$$

$$\Rightarrow \frac{\hbar^2}{2m}\left(-\vec{\nabla}^2 + \vec{k}^2\right)u_{\vec{k}}(\vec{r}) + U(\vec{r})\,u_{\vec{k}}(\vec{r}) = \mathcal{E}_{\vec{k}}\,u_{\vec{k}}(\vec{r})$$

$$\Rightarrow \left(\frac{\hbar^2}{2m}\left(\frac{1}{i}\nabla + \vec{k}\right)^2 + U(\vec{r})\right)u_{\vec{k}}(\vec{r}) = \mathcal{E}_{\vec{k}}\,u_{\vec{k}}(\vec{r})$$

since $\vec{\nabla}\vec{k} = 0$

$$\Rightarrow H_{\vec{k}}\,u_{\vec{k}}(\vec{r}) = \mathcal{E}_{\vec{k}}\,u_{\vec{k}}(\vec{r})$$

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

$$\text{and } u_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r} + \vec{R})$$

$$\underbrace{H_{\vec{k}}\, u_{\vec{k}}(\vec{r}) = \mathcal{E}_{\vec{k}}\, u_{\vec{k}}(\vec{r})}$$

eigenvalue problem

restricted to a single primitive cell of the crystal

(due to boundary condition)

$\Rightarrow$ ~~discrete~~ infinite, discrete set of eigenvalues, with band index n

$$\Rightarrow \quad u_{n\vec{k}}(\vec{r})$$

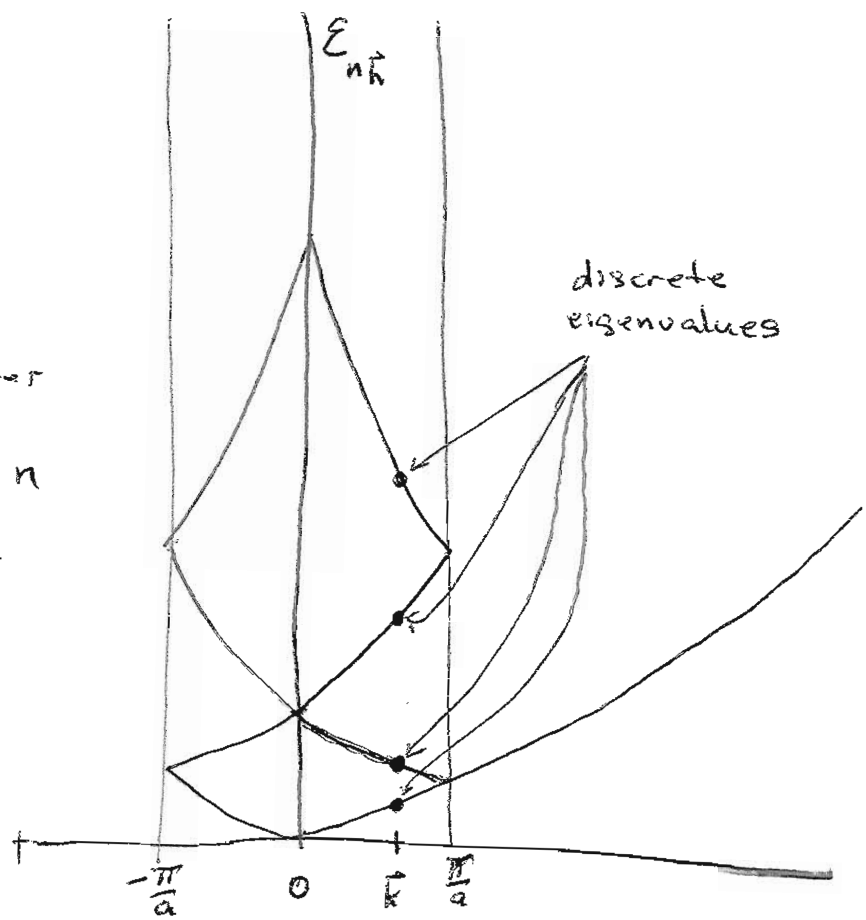
band index

n is related simply to the various harmonics of $\vec{k}$

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

for this Hamiltonian, $\vec{k}$ is simply a continuous parameter

$\Rightarrow$ each energy level for a given n will vary continuously with $\vec{k}$



The above graph is arrived at also by considering periodicity of ψ with $\vec{K}$

$$\Rightarrow \quad \psi_{n,\vec{k}+\vec{K}}(\vec{r}) = \psi_{n\vec{k}}(\vec{r})$$

$$\text{and} \quad \mathcal{E}_{n,\vec{k}+\vec{K}} = \mathcal{E}_{n\vec{k}}$$

$\Rightarrow$ family of continuous functions $\mathcal{E}_{n\vec{k}}$ or $\mathcal{E}_n(\vec{k})$

$\mathcal{E}_{n\vec{k}}$ has periodicity of the reciprocal lattice

The information on these functions is called the <u>band structure</u> of the solid

for every n, $\mathcal{E}_{n\vec{k}}$ is called an energy <u>band</u> (or $\mathcal{E}_n(\vec{k})$)