Chapter 9
Electrons in a Weak Periodic Potential

When potential $U = 0$, solutions to Schrodinger's equation are plane waves.

Why? → consider Bloch Theorem

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

If $U = 0$ or constant potential, then

$$u_{n\vec{k}}(\vec{r}) = u_{n\vec{k}}(\vec{r}+\vec{R})$$
$$= \text{constant} = C$$

$$\Rightarrow \psi_{n\vec{k}}(\vec{r}) = \underset{\substack{\uparrow \\ \text{constant}}}{C}\, e^{i\vec{k}\cdot\vec{r}} = \text{plane wave}$$

When potential U is not constant but is weak and periodic, then the general solution is:

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

and

$$\left[\frac{\hbar^2}{2m}(\vec{k}-\vec{K})^2 - \varepsilon\right] c_{\vec{k}-\vec{K}} + \sum_{\vec{K}'} U_{\vec{K}'-\vec{K}}\, c_{\vec{k}-\vec{K}'}$$

In free electron case, all $U_{\vec{K}} = 0$

$$\Rightarrow \quad \left[\frac{\hbar^2}{2m}(\vec{k}-\vec{K})^2 - \mathcal{E}\right] C_{\vec{k}-\vec{K}} = 0$$

or

$$\boxed{\left(\mathcal{E}^{\circ}_{k-K} - \mathcal{E}\right) C_{k-K} = 0}$$

with $\mathcal{E}^{\circ}_{k-K} = \frac{\hbar^2}{2m}(k-K)^2$

for simplicity,
(understand that k's are vectors
K's
etc.
(without always putting $\rightharpoonup$)
vector symbol)

$\Rightarrow$ either $C_{k-K} = 0 \Longrightarrow \psi = 0$ ← trivial solution

or $\underbrace{\mathcal{E} = \mathcal{E}^{\circ}_{k-K}}$

Suppose this is true for only a <u>single</u> value of K

$\Rightarrow$ we get the solutions

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

(showing vector symbols)

But $\mathcal{E} = \mathcal{E}^{\circ}_{k-K}$ could be true for some

set of $K = \{K_1, K_2, \ldots K_m\}$

$$\mathcal{E}^{\circ}_{k-K_1} = \mathcal{E}^{\circ}_{k-K_2} = \mathcal{E}^{\circ}_{k-K_3} = \ldots = \mathcal{E}^{\circ}_{k-K_m}$$

In that <u>degenerate</u> case,

$\Rightarrow$ m independent degenerate solutions

$$\text{total} \quad \psi_k(\vec{r}) = \sum_{K=K_1}^{K_m} c_{k-K_i}\, e^{i(k-K_i)\cdot\vec{r}} \quad \Bigg\} \begin{array}{l}\text{linear combination}\\ \text{of}\\ \text{degenerate}\\ \text{solutions}\end{array}$$

Next, consider non-constant potential

Again we will have 2 cases:

1) non-degenerate case

2) degenerate case

<u>Case 1</u> : non-degenerate

consider fixed k and a particular K_1 such that

$\varepsilon^0_{k-K_1}$ is far from all other ε^0_{k-K}

compared with U

(U is the size of the potential energy variation)

$$\Rightarrow \quad \left| \varepsilon^0_{k-K_1} - \varepsilon^0_{k-K} \right| \gg U \quad \text{for fixed } k \text{ and all } K \neq K_1$$

? What effect does the potential have on the free-electron level where

$$\mathcal{E} = \mathcal{E}^{\circ}_{k-K_1} \quad \text{and} \quad C_{k-K} = 0 \text{ for all } K \neq K_1$$

?

go back to

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

let $K = K_1$

$$\Rightarrow \left(\mathcal{E} - \mathcal{E}^{\circ}_{k-K}\right) C_{k-K} = \sum_{K} U_{K-K_1}\, C_{k-K}$$

(dropped prime on summation index)

We previously defined $U_0 = 0$

$$\Rightarrow U_{K-K_1} = 0 \text{ when } K = K_1$$

Therefore,

$\sum_{K} U_{K-K_1} C_{k-K}$ only has non-zero terms for $K \neq K_1$

Next, start back with the general equations for C_{k-K} and $\mathcal{E}$,

and solve for C_{k-K}

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

$$\left[\varepsilon^\circ_{k-K} - \varepsilon\right] c_{k-K} + \sum_{K'} U_{K'-K}\, c_{k-K'} = 0$$

$$\left[\varepsilon - \varepsilon^\circ_{k-K}\right] c_{k-K} = \sum_{K'} U_{K'-K}\, c_{k-K'}$$

$$= U_{K_1-K}\, c_{k-K_1} + \sum_{K'\neq K_1} U_{K'-K}\, c_{k-K'}$$

$$\Rightarrow \quad c_{k-K} = \underbrace{\frac{U_{K_1-K}\, c_{k-K_1}}{\varepsilon - \varepsilon^\circ_{k-K}}}_{\substack{\text{dominant term} \\ O(U)}} + \underbrace{\sum_{K'\neq K_1} \frac{U_{K'-K}\, c_{k-K'}}{\varepsilon - \varepsilon^\circ_{k-K}}}_{\substack{\text{order of magnitude} \\ \text{smaller} = O(U^2) \\ (= 0 \text{ in case of } U = 0)}}$$

[This assumes that denominator $\varepsilon - \varepsilon^\circ_{k-K} \gg U$]

So, we get that

$$c_{k-K} = \underbrace{\frac{U_{K_1-K}\, c_{k-K_1}}{\varepsilon - \varepsilon^\circ_{k-K}}}_{\text{order} = O(U)} + O(U^2)$$

substitute C_{k-K} into previous expression

$$\Rightarrow \left(\mathcal{E} - \mathcal{E}^{0}_{k-K_1}\right) C_{k-K_1} = \sum_{K} U_{K-K_1} C_{k-K}$$

$$= \sum_{K} U_{K-K_1} \left[\frac{U_{K_1-K}\, C_{k-K_1}}{\mathcal{E} - \mathcal{E}^{0}_{k-K}} + O(U^2) \right]$$

$$\left(\mathcal{E} - \mathcal{E}^{0}_{k-K_1}\right) C_{k-K_1} = \sum_{K} \left[\frac{U_{K-K_1}\, U_{K_1-K}}{\mathcal{E} - \mathcal{E}^{0}_{k-K}} \right] C_{k-K_1} + O(U^3)$$

$$\Rightarrow \quad \mathcal{E} = \mathcal{E}^{0}_{k-K_1} + \sum_{K} \frac{|U_{K-K_1}|^2}{\mathcal{E} - \mathcal{E}^{0}_{k-K}} + O(U^3)$$

let $\mathcal{E}$ = unperturbed $\mathcal{E} = \mathcal{E}^{0}_{k-K_1}$

in the sum

$$\Rightarrow \quad \mathcal{E} = \mathcal{E}^{0}_{k-K_1} + \sum_{K} \frac{|U_{K-K_1}|^2}{\mathcal{E}^{0}_{k-K_1} - \mathcal{E}^{0}_{k-K}} + O(U^3)$$