

## Lecture 9

- Continuing Schrodinger equation for ~~the~~ electrons in periodic potential.

~~the~~ In lecture 8 we started solving the SE in periodic potential by Fourier transform.

$$\psi(\vec{r}) = \sum_{\vec{k}, \vec{G}} \psi_{\vec{k}+\vec{G}} e^{i(\vec{k}+\vec{G}) \cdot \vec{r}} = \sum_{\vec{k}, \vec{G}} U_{\vec{k}}(\vec{G}) e^{i(\vec{k}+\vec{G}) \cdot \vec{r}}$$

We have obtained the following matrix equation for  $U_{\vec{k}}(\vec{G})$ :

$$\left[ \frac{\hbar^2 (\vec{k} + \vec{G})^2}{2m} - E \right] U_{\vec{k}}(\vec{G}) + \sum_{\vec{G}'} U(\vec{G} - \vec{G}') U_{\vec{k}}(\vec{G}') = 0$$

Define the following matrix:

$$H_{\vec{G}, \vec{G}'}(\vec{k}) = \frac{\hbar^2 (\vec{k} + \vec{G})^2}{2m} \delta_{\vec{G}, \vec{G}'} + U(\vec{G} - \vec{G}') =$$

$$= \epsilon_{\vec{k} + \vec{G}} \delta_{\vec{G}, \vec{G}'} + U(\vec{G} - \vec{G}')$$

$$\epsilon_{\vec{k}} = \frac{\hbar^2 \vec{k}^2}{2m}$$

Then we can write the above equation as:

$$\sum_{\vec{G}'} H_{\vec{G}, \vec{G}'} U_{\vec{k}}(\vec{G}') = E U_{\vec{k}}(\vec{G})$$

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Thus ~~our~~ our problem reduces to the eigenvalue problem for the matrix  $H_{\vec{G}, \vec{G}'}$ .

The size of this matrix is infinite. In practical numerical calculations, the matrix is approximated as finite, by removing all matrix elements corresponding to momenta  $\vec{G}'$ , larger than some specific cutoff momentum.

Typically the cutoff momentum is chosen such that  $\frac{\hbar^2 G_c^2}{2m} = \varepsilon(G_c) \gg$  all relevant energy scales in the problem.

Let us now discuss certain important general features of the solution, which are evident without actually solving the problem.

First, clearly  $\vec{k}$  - the first BZ momentum, represents a conserved quantum number.

The eigenstates will thus be labelled by  $\vec{k}$ .

The eigenstates will thus have the following general form:

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

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

Here  $n$  is the index, labelling the different eigenvalues of  $H_{\vec{G}, \vec{G}'}$ .

Index  $n$  is called the band index, for reasons that will become clear soon.

The energy eigenvalues have the form:

$$E = E_n(\mathbf{k}).$$

The important conclusion is that the eigenstates of electron in periodic potential have a very similar form to plane waves, with  $\mathbf{k}$  being the analog of the momentum of a free electron. The important difference is that  $\mathbf{k}$  here is limited to the first BZ, while the free electron momentum is unbounded.

$\mathbf{k}$  is often called the crystal momentum.

$\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} u_{n\mathbf{k}}(\mathbf{r})$  are called

Block functions.

The similarity of  $\psi_{n\mathbf{k}}(\mathbf{r})$  to plane wave states of free electrons explains why electrons are (almost) not scattered by the perfectly periodic crystal potential, they are mostly scattered by the imperfections in it.

To see in more detail what the solutions look like, let us solve the SE in momentum space perturbatively, assuming the periodic potential is weak. For simplicity I will do this ~~in~~ in a one-dimensional case.

$$\left[ \frac{\hbar^2 (k+G)^2}{2m} - E \right] U_k(G) + \sum_{G'} V(G-G') U_k(G') = 0$$

First consider zeroth order of the perturbation theory:  $U=0$ .

$$\left[ \frac{\hbar^2 (k+G)^2}{2m} - E \right] U_k(G) = 0$$

$$E_{Gk} = \frac{\hbar^2 (k+G)^2}{2m} \quad \text{free electron dispersion.}$$

~~$$U_k(G) = \frac{1}{\sqrt{V}} \int_V U_k(x) e^{-iGx} dx$$~~

~~$U_k(G)$~~  Eigenvalues are simply labelled by  $G$  ( $n=G$ )

$$U_{Gk}(G) = \frac{1}{\sqrt{V}} \Rightarrow U_{Gk}(x) = \frac{1}{\sqrt{V}} e^{iGx}$$

$$\psi_{Gk}(x) = \frac{1}{\sqrt{V}} e^{i(k+G)x} \quad \text{usual plane wave}$$

Draw the free electron dispersion as a function of  $\vec{k}$  - momentum in the first Brillouin zone of a ~~periodic~~ periodic potential with period  $a$  (we set its magnitude to zero, but will turn it on later).



$\vec{a}_1 = a \hat{x}$  - basis vector of the crystal lattice.

$\vec{b}_1 = \frac{1}{a} \hat{x}$  - basis vector of the reciprocal lattice.

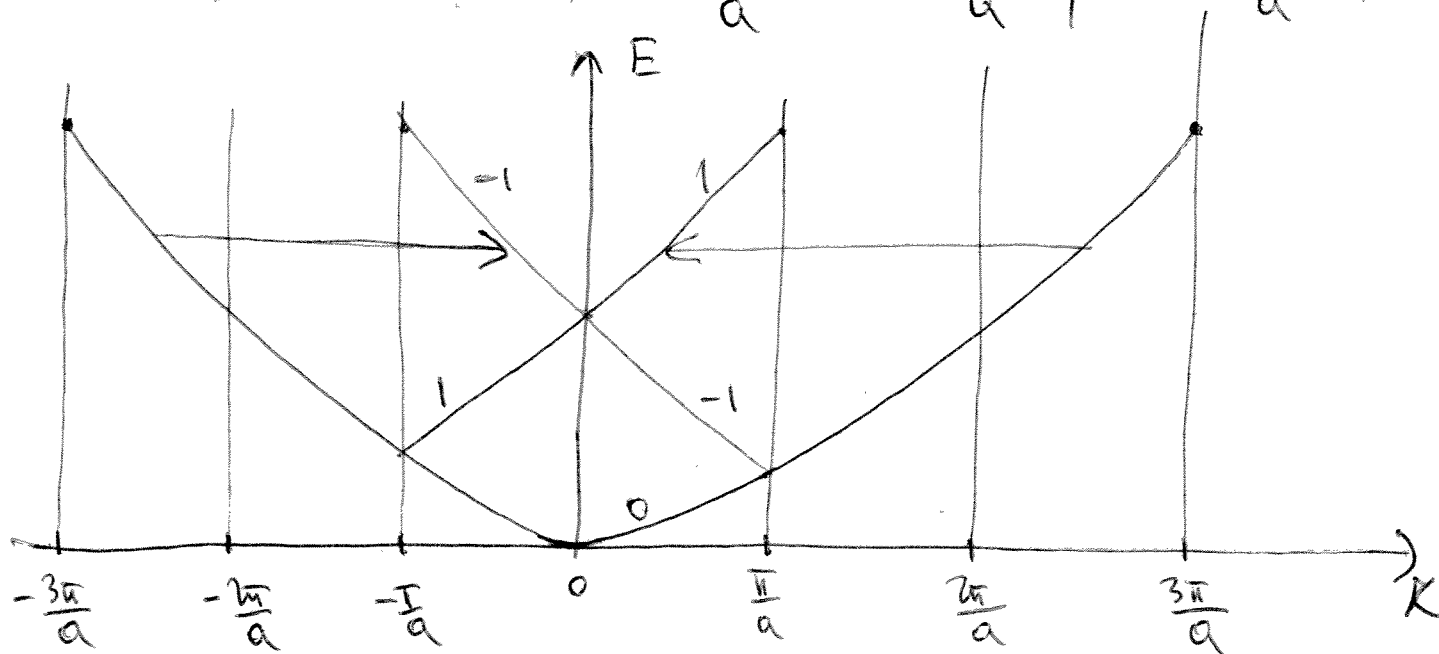
$$\vec{k} = k_1 \vec{b}_1$$

$$k_1 = \frac{2\pi n_1}{N_1}$$

First BZ:

$$-\frac{N_1}{2} \leq n_1 < \frac{N_1}{2}$$

This means that  $-\frac{\pi}{a} \leq k < \frac{\pi}{a}$ ;  $E = \frac{\hbar^2 k^2}{2m}$ .



Now we want to turn on small but nonzero  $V$  and see how the free electron dispersion is modified.

Write the SE in matrix notation:

$$\sum_{G'} H_{GG'} U_k(G') = E U_k(G)$$

$$H_{GG'} = \sum_{k+G} \delta_{GG'} + V(G-G')$$

$$E_{k+G} = \frac{\hbar^2 (k+G)^2}{2m}$$

$$V(\vec{G}) = \frac{1}{\mathcal{R}} \int_{\text{unit cell}} d\vec{r} U(\vec{r}) e^{-i\vec{G} \cdot \vec{r}}$$

$\mathcal{R} = \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)$  - volume of the unit cell.

In our 1D case  $V(G) = \frac{1}{a} \int_0^a dx U(x) e^{-iGx}$

Note that  $V(G=0)$  can always be taken to be zero:

$$V(0) = \frac{1}{a} \int_0^a U(x) dx - \text{simple average value of the potential.}$$

This just gives an overall constant shift of the energy of the electrons and can be ignored.

Thus  $V(G-G')$  are not zero only in the off-diagonal elements of the matrix  $H_{GG'}$ .

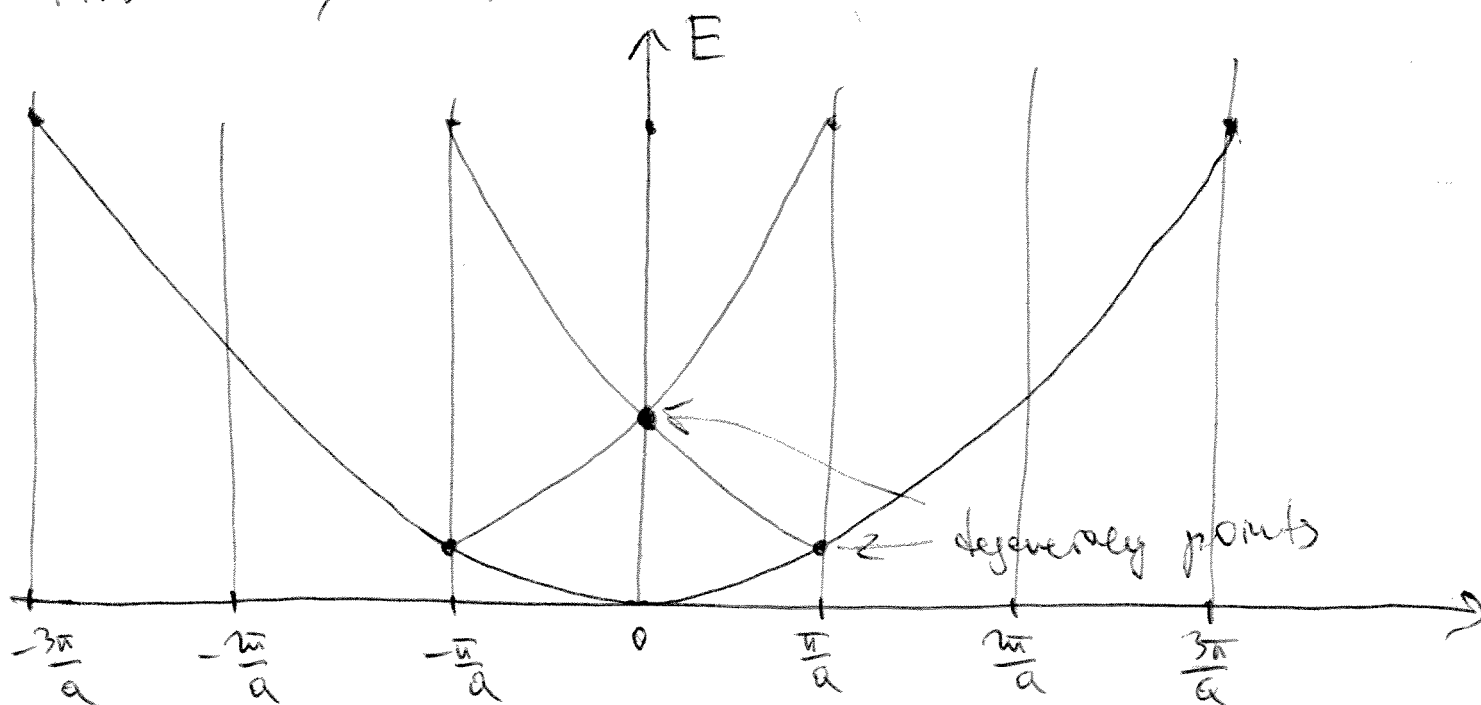
$$\sum_{G'G} H_{GG'} U_k(G') = E U_k(G)$$

At zeroth order ~~the~~  $E = E_{G+k} = \epsilon_{k+G}$  - the matrix is diagonal and the eigenvalues are simply the diagonal matrix elements.

First order correction:

$$E_{Gk} \approx \epsilon_{k+G} + U_{G-G} = \epsilon_{k+G} \quad \text{— no first order correction the free electron dispersion.}$$

Thus, generally, corrections to free-electron dispersion occur only at order  $U^2$  which are small at small  $U$ . These corrections can be ignored everywhere, except at degeneracy points, where different branches of the free electron dispersion, reduced to the first BZ, cross.



Consider one such point at  $E_{k=\frac{\pi}{a}} = E_{\frac{\pi}{a}} - \epsilon = E - \frac{\pi}{a}$

$G = \frac{2\pi}{a}$  — the smallest nonzero reciprocal lattice vector.

Clearly at small  $V$  we can examine each point of degeneracy separately.

$$\sum_{G G'} U_{GG'} U_k(G') = E U_k(G)$$

Let  $G = \frac{2\pi}{a} n$ . Consider  $n = -1, 0, 1$

$$H = \begin{pmatrix} E_{k-\frac{2\pi}{a}} & U(-\frac{2\pi}{a}) & U(-\frac{4\pi}{a}) \\ U(\frac{2\pi}{a}) & E_k & U(-\frac{2\pi}{a}) \\ U(\frac{4\pi}{a}) & U(\frac{2\pi}{a}) & E_{k+\frac{2\pi}{a}} \end{pmatrix}$$

$$U(x) = \sum_G U(G) e^{iGx} \quad \text{is real} \Rightarrow$$

$$\Rightarrow U^*(x) = \sum_G U^*(G) e^{-iGx} = U(x) = \sum_G U(G) e^{iGx}$$

$$\text{Thus } U(-G) = U^*(G)$$

$$H = \begin{pmatrix} E_{k-\frac{2\pi}{a}} & U^*(\frac{2\pi}{a}) & U^*(\frac{4\pi}{a}) \\ U(\frac{2\pi}{a}) & E_k & U(\frac{2\pi}{a}) \\ U(\frac{4\pi}{a}) & U(\frac{2\pi}{a}) & E_{k+\frac{2\pi}{a}} \end{pmatrix}$$



This  $H$  is hermitian, as it should be.

If we are interested in what happens near the degeneracy point  $k = \frac{\pi}{a}$ , where  $\epsilon_k$  is degenerate with  $\epsilon_{k-\frac{\pi}{a}}$ , can consider only the upper left  $2 \times 2$  block of the matrix.

$$H = \begin{pmatrix} \epsilon_{k-\frac{\pi}{a}} & U^*\left(\frac{\pi}{a}\right) \\ U\left(\frac{\pi}{a}\right) & \epsilon_k \end{pmatrix}$$

Diagonalize  $H$ :

$$\det(H - IE) = \det \begin{pmatrix} \epsilon_{k-\frac{\pi}{a}} - E & U^*\left(\frac{\pi}{a}\right) \\ U\left(\frac{\pi}{a}\right) & \epsilon_k - E \end{pmatrix} =$$

$$= (\epsilon_k - E)(\epsilon_{k-\frac{\pi}{a}} - E) - |U\left(\frac{\pi}{a}\right)|^2 =$$

$$= E^2 - E(\epsilon_k + \epsilon_{k-\frac{\pi}{a}}) + \epsilon_k \epsilon_{k-\frac{\pi}{a}} - |U\left(\frac{\pi}{a}\right)|^2 = 0$$

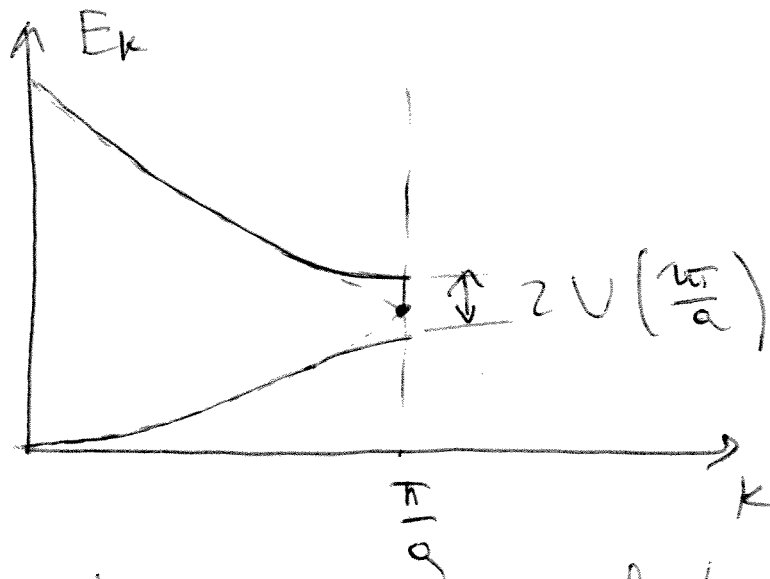
The solutions are:

$$E_k = \frac{\epsilon_k + \epsilon_{k-\frac{\pi}{a}}}{2} \pm \sqrt{\left(\frac{\epsilon_k - \epsilon_{k-\frac{\pi}{a}}}{2}\right)^2 + |U\left(\frac{\pi}{a}\right)|^2}$$

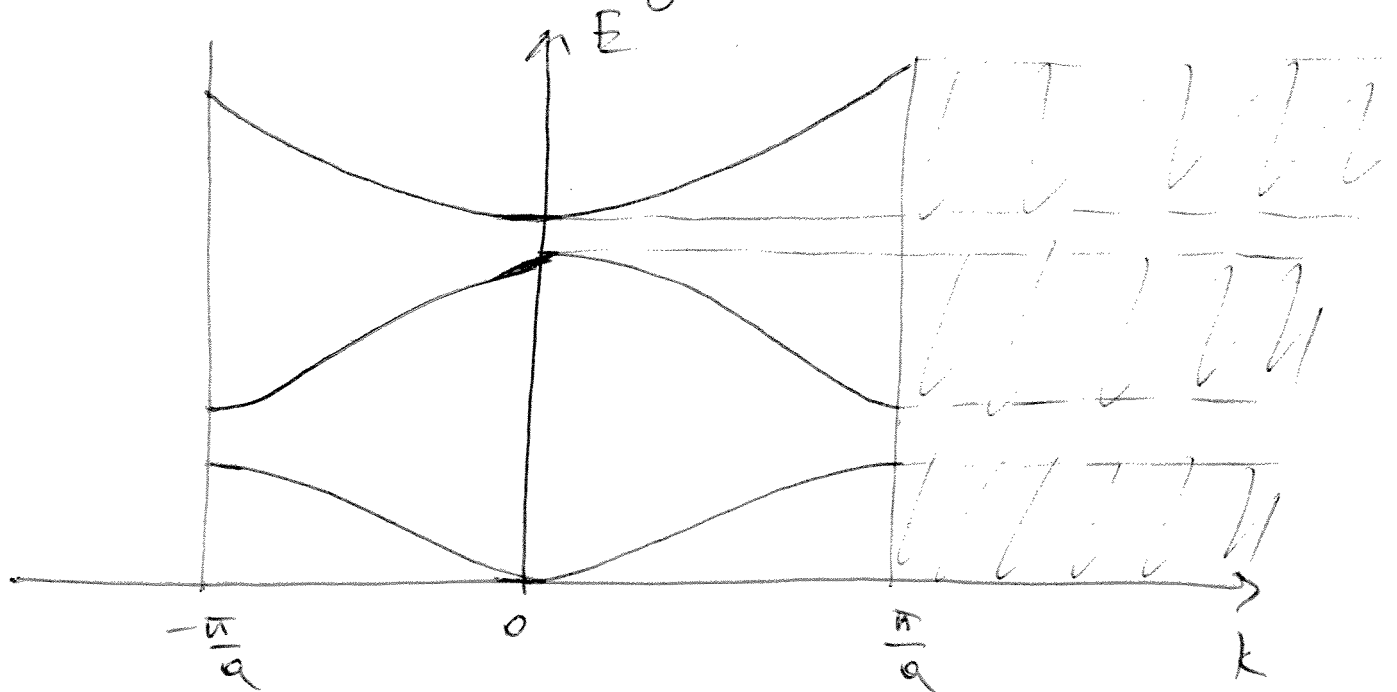
Exactly at the degeneracy point we have:

$$\epsilon_k = \epsilon_{\frac{\pi}{a}} = \epsilon_{\frac{\pi}{a} - \frac{\pi}{a}}$$

"  $E_{\frac{\pi}{a}} = \varepsilon_{\frac{\pi}{a}} \pm \left| V\left(\frac{\pi}{a}\right) \right|$  - the degeneracy is lifted. <sup>10</sup>



The dispersion of the electron in periodic potential then has the following general form:



Allowed values of  $E$  form bands.

Intervals of forbidden values are called bandgaps.