

Theory of Semiconductor Devices (반도체 소자 이론)

Lecture 7

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Nearly Free Electron Model

- When the *kinetic energy* of the electrons is **large** compared to the periodic energy of the lattice, the behavior of the electrons can be approximated by **nearly free electron wavefunctions**.
- Although often considered a *pedagogical* exercise, with the advent of **pseudopotential** theory [J. C. Phillips and L. Kleinman, *Phys. Rev.* 116, 287 (1959)] this method has become important in the calculation of semiconductor energy bands.
- In the nearly free electron model , **gaps occur** in allowed electron energy values for the following **reasons**.
 - Traveling electron waves **reflected from adjacent atoms interfere constructively** to produce standing waves. Some of these standing waves pile up charge **at the atomic sites**, where their energy is lowered, while other standing waves pile up charge **between atomic sites**, where their energy is increased over the free-electron values. This **shift in energy between the standing-wave states** produces an **energy gap**.

Nearly Free Electron Model

- Let us consider a **Bloch electron** with a wavefunction given by (2.10) and (2.11).
- From (1.9) the **periodic** part of the wavefunction can be expanded in a **Fourier series** with reciprocal lattice vector, \mathbf{K} , as index:

$$\psi_{\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{k}\cdot\mathbf{r})u_{\mathbf{k}}(\mathbf{r}) \quad (2.10)$$

$$u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r} + \mathbf{R}) \quad (2.11)$$

$$u_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{K}} A_{\mathbf{K}} \exp(i\mathbf{K}\cdot\mathbf{r}) \quad (2.45)$$

where

$$A_{\mathbf{K}} = \frac{1}{\Omega} \int_{\Omega} u_{\mathbf{k}}(\mathbf{r}) \exp(-i\mathbf{K}\cdot\mathbf{r}) d\mathbf{r} \quad (2.46)$$

- The **wavefunction** then has the form

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{K}} A_{\mathbf{K}} \exp[i(\mathbf{k} + \mathbf{K})\cdot\mathbf{r}] \quad (2.47)$$

- The one-electron **Schrödinger equation** (2.1) is then

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + U(\mathbf{r}) - \mathcal{E} \right] \sum_{\mathbf{K}} A_{\mathbf{K}} \exp[i(\mathbf{k} + \mathbf{K})\cdot\mathbf{r}] = 0 \quad (2.48)$$

or

$$\sum_{\mathbf{K}} \left[\frac{\hbar^2}{2m} (\mathbf{k} + \mathbf{K})^2 + U(\mathbf{r}) - \mathcal{E} \right] A_{\mathbf{K}} \exp[i(\mathbf{k} + \mathbf{K})\cdot\mathbf{r}] = 0 \quad (2.49)$$

Nearly Free Electron Model

- Multiplying on the left by $(1/\Omega) \exp [-i(\mathbf{k} + \mathbf{K}') \cdot \mathbf{r}]$, where \mathbf{K}' is another [reciprocal lattice vector](#) and integrating over a primitive unit cell, (2.49) becomes

$$\frac{1}{\Omega} \sum_{\mathbf{K}} A_{\mathbf{K}} \int_{\Omega} \left[\frac{\hbar^2}{2m} (\mathbf{k} + \mathbf{K})^2 + U(\mathbf{r}) - \mathcal{E} \right] \exp [i(\mathbf{K} - \mathbf{K}') \cdot \mathbf{r}] d\mathbf{r} = 0 \quad (2.50)$$

- But

$$\frac{1}{\Omega} \int_{\Omega} \exp [i(\mathbf{K} - \mathbf{K}') \cdot \mathbf{r}] d\mathbf{r} = \delta_{\mathbf{K}, \mathbf{K}'} \quad (2.51)$$

where the Kronecker delta is

$$\delta_{\mathbf{K}, \mathbf{K}'} = \begin{cases} 1 & \text{for } \mathbf{K} = \mathbf{K}' \\ 0 & \text{for } \mathbf{K} \neq \mathbf{K}' \end{cases} \quad (2.52)$$

We now have

$$\begin{aligned} \sum_{\mathbf{K}} A_{\mathbf{K}} \left[\frac{\hbar^2}{2m} (\mathbf{k} + \mathbf{K})^2 - \mathcal{E} \right] \delta_{\mathbf{K}, \mathbf{K}'} \\ = - \frac{1}{\Omega} \sum_{\mathbf{K}} A_{\mathbf{K}} \int_{\Omega} U(\mathbf{r}) \exp [i(\mathbf{K} - \mathbf{K}') \cdot \mathbf{r}] d\mathbf{r} \end{aligned} \quad (2.53)$$

Nearly Free Electron Model

or

$$\begin{aligned}
 A_{\mathbf{K}'} \left[\mathcal{E} - \frac{\hbar^2}{2m} (\mathbf{k} + \mathbf{K}')^2 \right] \\
 = \frac{1}{\Omega} \sum_{\mathbf{K}} A_{\mathbf{K}} \int_{\Omega} U(\mathbf{r}) \exp [i(\mathbf{K} - \mathbf{K}') \cdot \mathbf{r}] d\mathbf{r} \quad (2.54)
 \end{aligned}$$

Since from (2.9) $U(\mathbf{r})$ is periodic in \mathbf{R} , we can **expand** it in a Fourier series **with reciprocal lattice vector, \mathbf{K}''** , as index:

$$U(\mathbf{r}) = \sum_{\mathbf{K}''} B_{\mathbf{K}''} \exp (i\mathbf{K}'' \cdot \mathbf{r}) \quad (2.55)$$

where

$$B_{\mathbf{K}''} = \frac{1}{\Omega} \int_{\Omega} U(\mathbf{r}) \exp (-i\mathbf{K}'' \cdot \mathbf{r}) d\mathbf{r} \quad (2.56)$$

- Using (2.55) in (2.54), we obtain

$$\begin{aligned}
 A_{\mathbf{K}'} \left[\mathcal{E} - \frac{\hbar^2}{2m} (\mathbf{k} + \mathbf{K}')^2 \right] \\
 = \frac{1}{\Omega} \sum_{\mathbf{K}} \sum_{\mathbf{K}''} A_{\mathbf{K}} B_{\mathbf{K}''} \int_{\Omega} \exp [i(\mathbf{K} - \mathbf{K}' + \mathbf{K}'') \cdot \mathbf{r}] d\mathbf{r} \quad (2.57)
 \end{aligned}$$

Nearly Free Electron Model

But just as in (2.51),

$$\frac{1}{\Omega} \int_{\Omega} \exp [i(\mathbf{K} - \mathbf{K}' + \mathbf{K}'') \cdot \mathbf{r}] d\mathbf{r} = \delta_{\mathbf{K}, \mathbf{K}' - \mathbf{K}''} \quad (2.58)$$

where

$$\delta_{\mathbf{K}, \mathbf{K}' - \mathbf{K}''} = \begin{cases} 1 & \text{for } \mathbf{K} = \mathbf{K}' - \mathbf{K}'' \\ 0 & \text{for } \mathbf{K} \neq \mathbf{K}' - \mathbf{K}'' \end{cases} \quad (2.59)$$

- Thus (2.57) becomes

$$\begin{aligned} A_{\mathbf{K}'} \left[\mathcal{E} - \frac{\hbar^2}{2m} (\mathbf{k} + \mathbf{K}')^2 \right] &= \sum_{\mathbf{K}} \sum_{\mathbf{K}''} A_{\mathbf{K}} B_{\mathbf{K}''} \delta_{\mathbf{K}, \mathbf{K}' - \mathbf{K}''} \\ &= \sum_{\mathbf{K}''} A_{\mathbf{K}' - \mathbf{K}''} B_{\mathbf{K}''} \end{aligned} \quad (2.60)$$

which, with a change of notation, gives us

$$A_{\mathbf{K}} \left[\mathcal{E} - \frac{\hbar^2}{2m} (\mathbf{k} + \mathbf{K})^2 \right] = \sum_{\mathbf{K}'} A_{\mathbf{K} - \mathbf{K}'} B_{\mathbf{K}'} \quad (2.61)$$

- Equation (2.61) is an exact expression relating the **Fourier coefficients** $A_{\mathbf{K}}$ for the expansion of the **Bloch function** $u(\mathbf{r})$ to the **Fourier coefficients** $B_{\mathbf{K}}$ for the expansion of the **effective one-electron lattice potential energy** $U(\mathbf{r})$.

Nearly Free Electron Model

- Formally, we *could* now solve this problem by taking **self-consistent expressions** for $U(\mathbf{r})$ and $u(\mathbf{r})$ and determining the coefficients $A_{\mathbf{K}}$ and $B_{\mathbf{K}}$, from (2.46), (2.56), and (2.61) in an iterative fashion.
- We can obtain *approximate* analytical solutions, however, by taking certain *assumptions* regarding the *relative sizes* of the various coefficients.
- The **simplest** assumption to make is that only the terms for \mathbf{K} and \mathbf{K}' equal to zero are **important**. This assumption just leads to **free-electron solutions**.
- The **next simplest** assumption is that only the terms for \mathbf{K} and \mathbf{K}' equal to zero and \mathbf{K} equal to \mathbf{K}' are **important**.
- Under this assumption we obtain two equations for the coefficients from (2.61):

$$\begin{aligned}
 A_0 \left[\mathcal{E} - \frac{\hbar^2}{2m} \mathbf{k}^2 \right] &= A_0 B_0 + A_{-\mathbf{K}} B_{\mathbf{K}} && \text{for } \mathbf{K} = 0 \\
 A_{\mathbf{K}} \left[\mathcal{E} - \frac{\hbar^2}{2m} (\mathbf{k} + \mathbf{K})^2 \right] &= A_0 B_{\mathbf{K}} + A_{\mathbf{K}} B_0 && \text{for } \mathbf{K} = \mathbf{K}'
 \end{aligned} \tag{2.62}$$

Nearly Free Electron Model

- For simplicity we have ignored the degenerate $-\mathbf{K}'$ term in each of these equations. If you wish to include them, simply replace every B_K in the rest of the analysis by $2 B_K$.
- Since from (2.46) and (2.56) $A_{-K} B_K = A_K B_{-K}$, we can put this coupled set of equations in the matrix form

$$\begin{bmatrix} \mathcal{E} - \mathcal{E}_0 & -B_{-K} \\ -B_K & \mathcal{E} - \mathcal{E}_K \end{bmatrix} \begin{bmatrix} A_0 \\ A_K \end{bmatrix} = 0 \quad (2.63)$$

where

$$\mathcal{E}_0 \equiv \frac{\hbar^2 \mathbf{k}^2}{2m} + B_0 \quad \text{and} \quad \mathcal{E}_K \equiv \frac{\hbar^2 (\mathbf{k} + \mathbf{K})^2}{2m} + B_0 \quad (2.64)$$

- Note that \mathcal{E}_0 and \mathcal{E}_K have the form of free-electron energies in a constant potential energy B_0 and correspond to the first two terms in the wavefunction (2.47),

$$\psi_{\mathbf{k}}(\mathbf{r}) = A_0 \exp(i\mathbf{k} \cdot \mathbf{r}) + A_K \exp[i(\mathbf{k} + \mathbf{K}) \cdot \mathbf{r}] \quad (2.65)$$

- To keep the coefficients of the wavefunction expansion, A_0 and A_K , from vanishing identically, the determinant of the matrix in (2.63) must be zero.

Nearly Free Electron Model

Since $B_{-K}B_K = B_K^*B_K = B_K^2$ for crystals with **inversion symmetry**, we obtain a **quadratic equation** for the energy of the electrons,

$$\mathcal{E}^2 - (\mathcal{E}_0 + \mathcal{E}_K)\mathcal{E} + (\mathcal{E}_0\mathcal{E}_K - B_K^2) = 0 \quad (2.66)$$

which has the solutions

$$\mathcal{E}^\pm = \frac{1}{2}(\mathcal{E}_0 + \mathcal{E}_K) \pm \frac{1}{2}[(\mathcal{E}_0 - \mathcal{E}_K)^2 + 4B_K^2]^{1/2} \quad (2.67)$$

- By comparing (2.67) with (2.64) and (2.65), we see that the states with energy \mathcal{E}_0 and \mathcal{E}_K are combined into **two states** ψ^+ and ψ^- with energies \mathcal{E}^+ and \mathcal{E}^- by the **energy perturbation** B_K .

- We can examine these **nearly free electron** bands most simply for \mathbf{k} in the **direction of \mathbf{K}** . The **lowest-lying band** is obtained for $\mathbf{K} = 0$ in (2.67) and looking at \mathcal{E}^- for \mathbf{k} near zero. This gives us

$$\mathcal{E}^- = \frac{h^2\mathbf{k}^2}{2m} \quad (2.68)$$

so the \mathcal{E}^- versus \mathbf{k} is **parabolic near $\mathbf{k} = 0$** .

- At the zone boundary, $\mathbf{k} = \frac{1}{2}\mathbf{K}$, and for $\mathbf{K} = -\mathbf{K}$, we have, from (2.67),

$$\mathcal{E}^\pm = \mathcal{E}_0 \pm |B_K| \quad (2.69)$$

Nearly Free Electron Model

- Thus we see that at the zone boundary the energy of the ψ^- state is *lower* than the free-electron energy by $|B_K|$, and the energy of the ψ^+ state is *higher* by $|B_K|$. It is evident, then, that the periodic lattice potential has created an *energy gap* of magnitude $2 |B_K|$ between these two states.

- In Fig. 2.7 the higher-energy bands are shown inside the first Brillouin zone and also outside. The bands outside are referred to as an *extended zone scheme*. They tend to show more clearly how the nearly free electron bands are perturbed from the free-electron parabola with discontinuities at the zone boundaries.

- Note that because of this perturbation, K is no longer a band index.

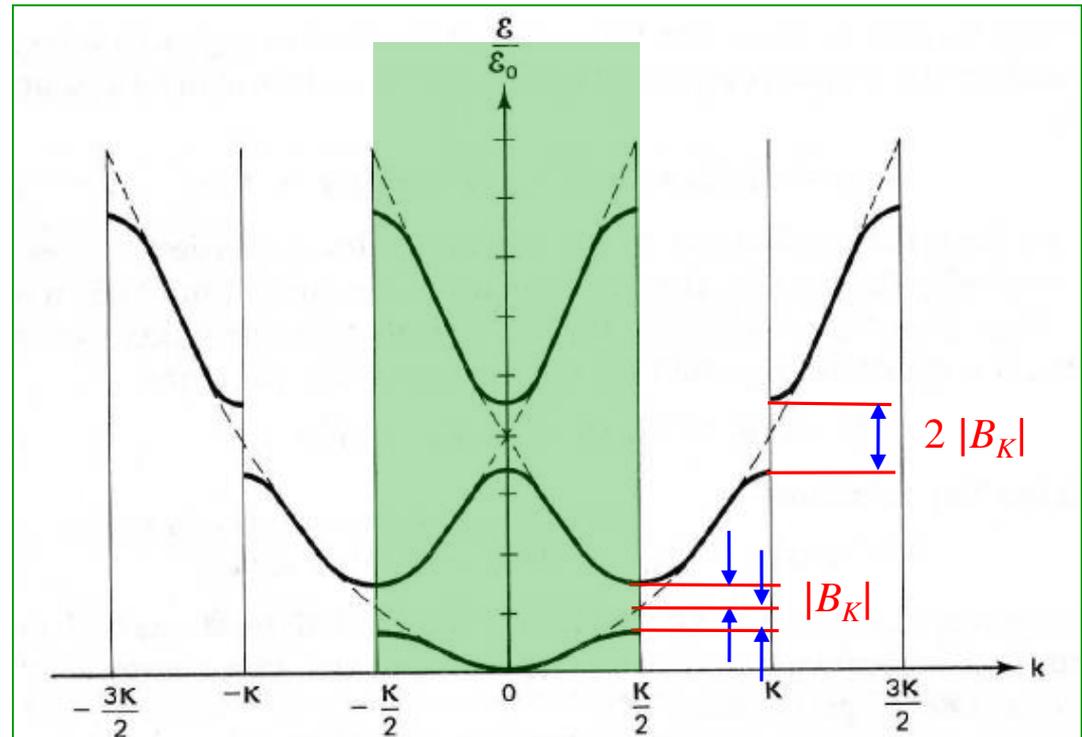


Figure 2.7 Nearly free electron energy bands for k in the direction of K . The dashed line shows the parabolic free-electron \mathcal{E} versus k dependence. The higher-lying bands outside the first Brillouin zone is referred to as an extended zone scheme; $\mathcal{E}_0 = (\hbar^2/2m)(\frac{1}{2}K)^2 + B_0$.

Nearly Free Electron Model

- It is interesting to examine the wavefunctions that correspond to these energy bands. From (2.65) the wavefunctions at the zone boundary are

$$\psi(r) = A_0 \exp(i\frac{1}{2}\mathbf{K}\cdot\mathbf{r}) + A_K \exp(-i\frac{1}{2}\mathbf{K}\cdot\mathbf{r}) \quad (2.70)$$

The ratio of the coefficients can be obtained from (2.62) and (2.64) as

$$\frac{A_K}{A_0} = \frac{B_K}{\mathcal{E} - \mathcal{E}_K} \quad (2.71)$$

or using (2.67) ,

$$\frac{A_K}{A_0} = \frac{2B_K}{(\mathcal{E}_0 - \mathcal{E}_K) \pm [(\mathcal{E}_0 - \mathcal{E}_K)^2 + 4B_K^2]^{1/2}} \quad (2.72)$$

- At the zone boundary $\mathcal{E}_0 = \mathcal{E}_K$, and

$$\frac{A_K}{A_0} = \mp \frac{B_K}{|B_K|} \quad (2.73)$$

- Let us **assume** that B_K is **negative**. This corresponds to a periodic potential that is negative in the neighborhood of each atom and thus tends to attract electrons. Then

Nearly Free Electron Model

- Then

$$\begin{aligned}\psi^-(r) &= A_0[\exp(i\frac{1}{2}\mathbf{K}\cdot\mathbf{r}) + \exp(-i\frac{1}{2}\mathbf{K}\cdot\mathbf{r})] \\ &= 2A_0 \cos(\frac{1}{2}\mathbf{K}\cdot\mathbf{r})\end{aligned}\tag{2.74}$$

and

$$\psi^+(r) = 2A_0i \sin(\frac{1}{2}\mathbf{K}\cdot\mathbf{r})\tag{2.75}$$

- Therefore, we find that **the periodic potential has converted the traveling electron plane waves of (2.65) into the standing waves of (2.74) and (2.75) at the zone boundaries.** This corresponds to Bragg reflection of the electrons.

- If we determine the electron charge density for these two standing waves, as indicated in Fig.

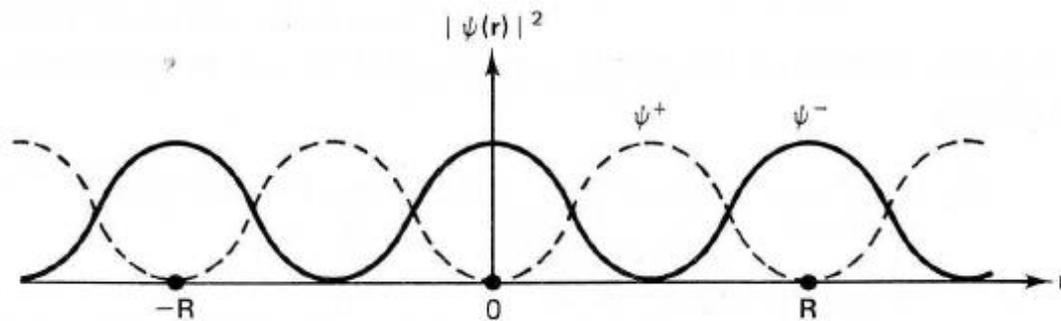


Figure 2.8 Distribution of electron charge density in direct space for \mathbf{r} in the direction of \mathbf{R} , the direct lattice vectors, for values of \mathbf{k} at the zone boundaries in reciprocal space.

2.8, we find that the charge for ψ^- is concentrated near the sites or atoms in the direct lattice, while the charge for ψ^+ is concentrated between atoms.

Nearly Free Electron Model

- We conclude, then, that the energy gap is caused by the potential well (B_K negative) at the atoms, which attracts the charge of ψ^- (lowers its energy) and repulses the charge of ψ^+ (raises its energy).
- Because of this position dependence, the ψ^- state is said to be "s-like," in analogy to atomic s-levels, which do not vanish at the ion, and the ψ^+ state is referred to as "p-like," since its charge vanishes at the atoms.
- With the nearly free electron model we have developed the concept of *allowed* and *forbidden* energy bands.
- In a relatively simple manner, two other very important properties of electrons in a periodic potential can also be obtained from this model. Since \mathcal{E}_0 is about equal to \mathcal{E}_K near the zone boundary, we can approximate the term in square brackets in (2.67) by

$$(1 + x)^{1/2} \approx 1 + \frac{1}{2}x$$

or

$$\mathcal{E}^{\pm} \approx \frac{1}{2}(\mathcal{E}_0 + \mathcal{E}_K) \pm |B_K| \left[1 + \frac{1}{2} \left(\frac{\mathcal{E}_0 - \mathcal{E}_K}{2|B_K|} \right)^2 \right] \quad (2.76)$$

Nearly Free Electron Model

- Using (2.64) and $\mathbf{k} \approx \pm \frac{1}{2}\mathbf{K}$ near a boundary, (2.76) can be put in the form

$$\mathcal{E}^{\pm} \approx B_0 \pm |B_K| + \frac{\hbar^2 \mathbf{k}^2}{2m^*} \quad (2.77)$$

where

$$m^* = \frac{m}{1 \pm \hbar^2 \mathbf{K}^2 / m |B_K|} \quad (2.78)$$

- Equations (2.77) and (2.78) show us that the electron energies **near the zone boundaries** have an approximately parabolic dependence on wavevector in a manner **similar to free electrons**.
- The Bloch electrons, however, behave as though they have **mass different from the free-electron mass**.
- This behavior is characterized by an **effective mass, m^*** , as given in (2.78).
- Equation (2.78) also shows us that the effective mass for ψ^- states near the top of the lowest-lying band in Fig. 2.7 is **negative**, while the effective mass for ψ^+ states near the bottom of the next-highest band is **positive**.

Nearly Free Electron Model

- The concept of an electron in a periodic potential energy having an effective mass different from its free mass should not be surprising.
- We found in Section 2.1 that the wavevector, \mathbf{k} , is *not proportional* to the real electron momentum which takes into account the response of the electron to **external forces** and the **internal forces due to the periodic potential**. It reflects only the **response of the electron to external forces**.
- The response of the electron to the **periodic potential energy of the crystal is accounted for with the effective mass, m^*** , which can be **greater or smaller** than the free mass, m .
- A **negative effective mass** for an electron simply means that in the process of increasing its \mathbf{k} vector under the influence of an external force, the **momentum transfer** from the crystal to the electron is **larger** than and in the **opposite direction** to the applied external force. We consider the effects of external forces in more detail in Chapter 5.

$$\mathbf{p}\psi_{\mathbf{k}}(\mathbf{r}) = \hbar\mathbf{k}\psi_{\mathbf{k}}(\mathbf{r}) + \exp(i\mathbf{k}\cdot\mathbf{r}) \frac{\hbar}{i} \frac{\partial}{\partial \mathbf{r}} u_{\mathbf{k}}(\mathbf{r})$$