

Week3-Electronic Band Calculations

ECE 695-O Semiconductor Transport Theory

Fall 2018

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- Nearly Free Electron Model
- Tight-Binding Model

The Periodic Potential-Simple Cubic Case

- In the previous class, we learned that, from Bloch's theorem, the solution of Schrödinger Eq. in a periodic potential has the following form

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

where $u_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) = u_{n\mathbf{k}}(\mathbf{r})$.

- \mathbf{k} can be written as $\mathbf{k}' + \mathbf{K}$ where \mathbf{K} is a reciprocal lattice vector and \mathbf{k}' lies within the first Brillouin zone.
- When band energies are approximated well by free electron energy $\mathcal{E} = \hbar^2 k^2 / 2m$, $\mathcal{E} = \hbar^2 (\mathbf{k}' + \mathbf{K})^2 / 2m$.

$$\mathcal{E}(k_x, k_y, k_z) = \frac{\hbar^2}{2m} \left\{ (k_x + K_x)^2 + (k_y + K_y)^2 + (k_z + K_z)^2 \right\}$$

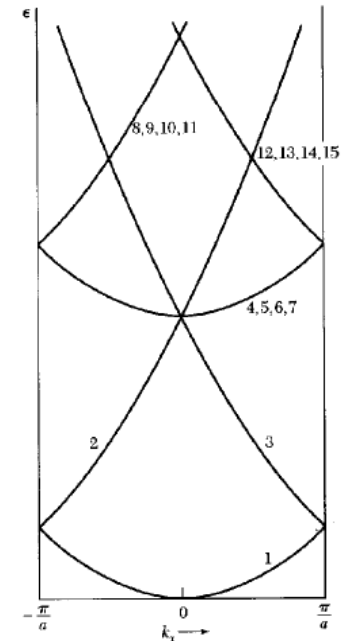
- We can apply this relation to the low-lying free electron bands of a simple cubic lattice [100] direction.

The Periodic Potential-Simple Cubic Case

$$\mathcal{E}(k_x, k_y, k_z) = \frac{\hbar^2}{2m} \left\{ (k_x + K_x)^2 + (k_y + K_y)^2 + (k_z + K_z)^2 \right\}$$

- We can check several low lying bands in this empty lattice with their energy $\mathcal{E}(000)$ at $\mathbf{k}=0$ and $\mathcal{E}(k_x 00)$ along the k_x axis ($\hbar^2/2m = 1$):

Band	$Ga/2\pi$	$\epsilon(000)$	$\epsilon(k_x 00)$
1	000	0	k_x^2
2,3	100, $\bar{1}00$	$(2\pi/a)^2$	$(k_x \pm 2\pi/a)^2$
4,5,6,7	010, 0 $\bar{1}$ 0, 001, 00 $\bar{1}$	$(2\pi/a)^2$	$k_x^2 + (2\pi/a)^2$
8,9,10,11	110, 101, 1 $\bar{1}$ 0, 10 $\bar{1}$	$2(2\pi/a)^2$	$(k_x + 2\pi/a)^2 + (2\pi/a)^2$
12,13,14,15	$\bar{1}10, \bar{1}01, \bar{1}\bar{1}0, \bar{1}0\bar{1}$	$2(2\pi/a)^2$	$(k_x - 2\pi/a)^2 + (2\pi/a)^2$
16,17,18,19	011, 0 $\bar{1}$ 1, 01 $\bar{1}$, 0 $\bar{1}$ $\bar{1}$	$2(2\pi/a)^2$	$k_x^2 + 2(2\pi/a)^2$

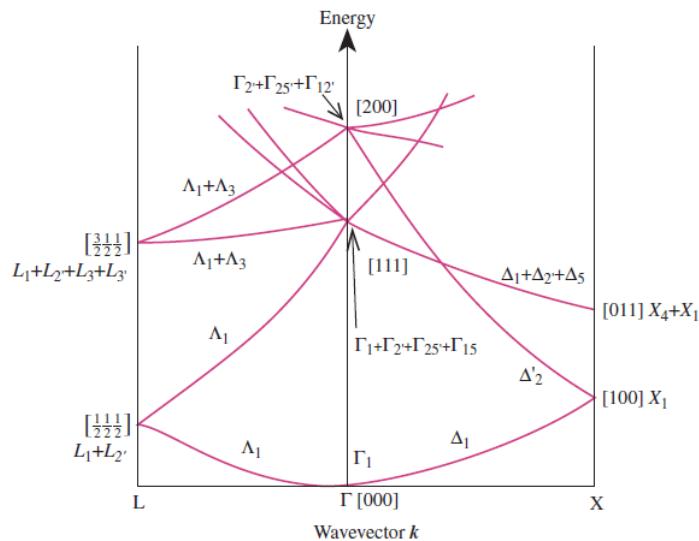


- Yu&Cardona Chap 2.4 contains Zincblende and Diamond cases.

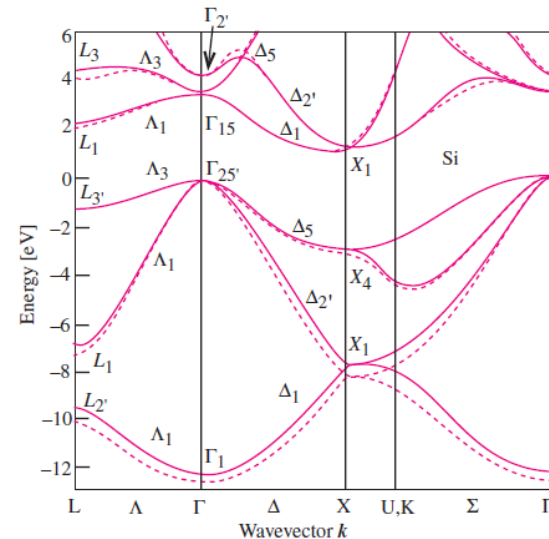
The Periodic Potential-Diamond

- Yu&Cardona Chap 2.4 contains Zincblend and Diamond cases.

Empty Lattice Model for Diamond Crystal



Si band structure



Perturbation Theory

- The degenerate energy states near (the first Brillouin) zone boundary requires perturbative treatment.
- Perturbation theory is an approximation method in quantum mechanics.
- The aim is to find the solution of a *perturbed* system using the known solution of a *unperturbed* system.

$$H_0 \psi_{i0} = \mathcal{E}_{i0} \psi_{i0}$$

H_0 : unperturbed Hamiltonian

ψ_{i0} : known eigenstate

\mathcal{E}_{i0} : known eigenvalue


Perturbed system (by H')

$$(H_0 + H')\psi = \mathcal{E}\psi$$

$$\psi = \sum a_i \psi_{i0}$$

(↑ The new states are linear combination of known states)

Perturbation Theory(2)

$$(H_0 + H')\psi = \varepsilon\psi \qquad \psi = \sum a_i \psi_{i0}$$


$$\Rightarrow (H_0 + H') \sum a_i \psi_{i0} = \varepsilon \sum a_i \psi_{i0}$$

(↑ If you think about the enumeration of i, this is actually a vector.)

- If we consider inner product,

$$\begin{aligned} \int d^3r \psi_{i0}^* (H_0 + H') \sum_j a_j \psi_{j0} &= \int \varepsilon \underbrace{\sum_j a_j \psi_{i0}^* \psi_{j0}}_{= \varepsilon \sum_j a_j \delta_{ij}} d^3r \\ &= \sum_j \int d^3r a_j \psi_{i0}^* H_0 \psi_{j0} + \sum_j \int d^3r a_j \psi_{i0}^* H' \psi_{j0} \\ &= \sum_j a_j \varepsilon_{j0} \delta_{ij} + \sum_j a_j \underbrace{\int d^3r \psi_{i0}^* H' \psi_{j0}}_{(\equiv H'_{ij})} \end{aligned}$$

:orthogonality of eigenvectors

Perturbation Theory(3)

$$\Rightarrow \sum_j a_j \epsilon_{j0} \delta_{ij} + \sum_j a_j H'_{ij} = \epsilon \sum_j a_j \delta_{ij}$$

$$\Rightarrow \sum_j a_j (\epsilon_{j0} - \epsilon) \delta_{ij} + \sum_j a_j H'_{ij} = 0$$

$$\Rightarrow \sum_j a_j [H'_{ij} - (\epsilon - \epsilon_{j0}) \delta_{ij}] = 0$$

- We can write down this in a matrix form.

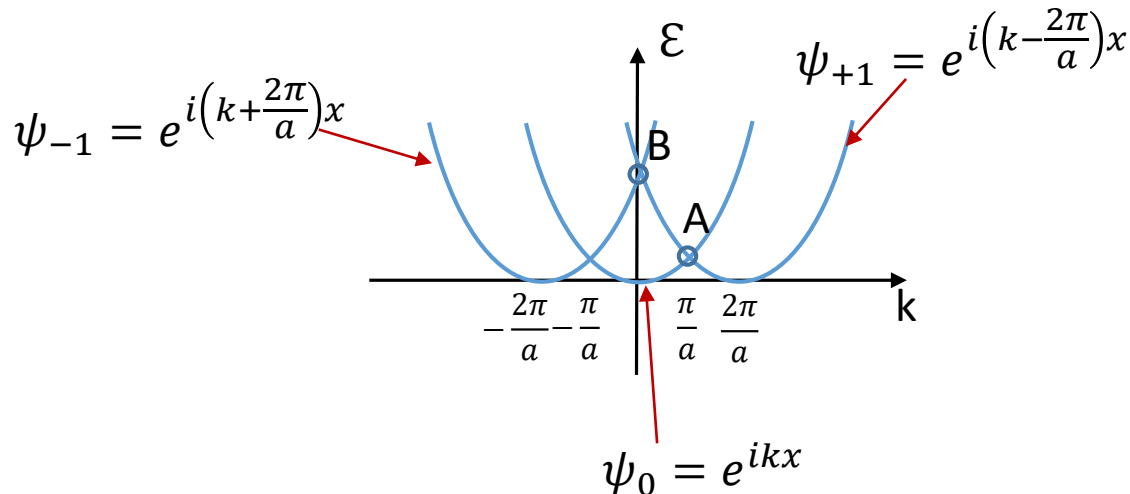
$$\begin{bmatrix} H'_{11} - (\epsilon - \epsilon_{10}) & H'_{12} & H'_{13} & \cdots \\ H'_{21} & H'_{22} - (\epsilon - \epsilon_{20}) & H'_{23} & \cdots \\ H'_{31} & H'_{32} & H'_{33} - (\epsilon - \epsilon_{30}) & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix} \begin{pmatrix} a_1 \\ a_2 \\ a_3 \\ \vdots \end{pmatrix} = 0$$

- Non-trivial solution can be found by solving $\det[H'] = 0$.
- For 1st order perturbation theory, only need to calculate block diagonalized part.

Application to Periodic Potential

- We can apply the perturbation theory to the weak periodic potential.
- As a demonstration, we go back to the simple 1D case.

$$H = -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} \right) \quad \leftarrow \text{Empty Lattice}$$



$$H' = V(x)$$

$$V(x) = V(x + a)$$

- Here, we have to know the range of interest. For example, consider ψ_0 and ψ_{+1} only for A.
- Consider ψ_{+1} and ψ_{-1} only for B.

Application to Periodic Potential(2)

- For a generalized case, we have two wave functions:

$$\psi_{10} = \frac{1}{\sqrt{V}} e^{ikx}$$

$$\psi_{20} = \frac{1}{\sqrt{V}} e^{i(k-K)x}$$

($1/\sqrt{V}$ is normalization factor)

$$H_0 \psi_{10} = \mathcal{E}_{10} \psi_{10}$$

$$H_0 \psi_{20} = \mathcal{E}_{20} \psi_{20}$$

$$\mathcal{E}_{10} = \frac{\hbar^2 k^2}{2m} = \mathcal{E}_k$$

$$\mathcal{E}_{20} = \frac{\hbar^2 (k-K)^2}{2m} \equiv \mathcal{E}_{k-K}$$

- Then we have a 2x2 matrix:

$$\begin{vmatrix} H'_{11} - (\mathcal{E} - \mathcal{E}_{10}) & H'_{12} \\ H'_{21} & H'_{22} - (\mathcal{E} - \mathcal{E}_{20}) \end{vmatrix} = 0$$

Application to Periodic Potential(3)

- We can evaluate each matrix element:

$$H'_{11} = \frac{1}{V} \int e^{-i\mathbf{k}\cdot\mathbf{r}} V(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{r}} d^3r = \frac{1}{V} \int V(\mathbf{r}) d^3r = 0$$

This does not need to be zero but it should be a constant.
Do you remember we defined like this when we were proving Bloch's theorem?

$H'_{22} = 0$ with the same reason.

$$H'_{12} = \frac{1}{V} \int e^{-i\mathbf{k}\cdot\mathbf{r}} V(\mathbf{r}) e^{i(\mathbf{k}-\mathbf{K})\cdot\mathbf{r}} d^3r$$

$$= \frac{1}{V} \int V(\mathbf{r}) e^{-i\mathbf{K}\cdot\mathbf{r}} d^3r \quad \longrightarrow \quad \text{This is } \mathbf{K}\text{th coefficient of Fourier transform of the potential } V$$

$$\equiv V_{\mathbf{K}}$$

$$H'_{21} = \frac{1}{V} \int e^{-i(\mathbf{k}-\mathbf{K})\cdot\mathbf{r}} V(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{r}} d^3r = \frac{1}{V} \int V(\mathbf{r}) e^{i\mathbf{K}\cdot\mathbf{r}} d^3r = V_{-\mathbf{K}} = V_{\mathbf{K}}^*$$

because our potential is always real

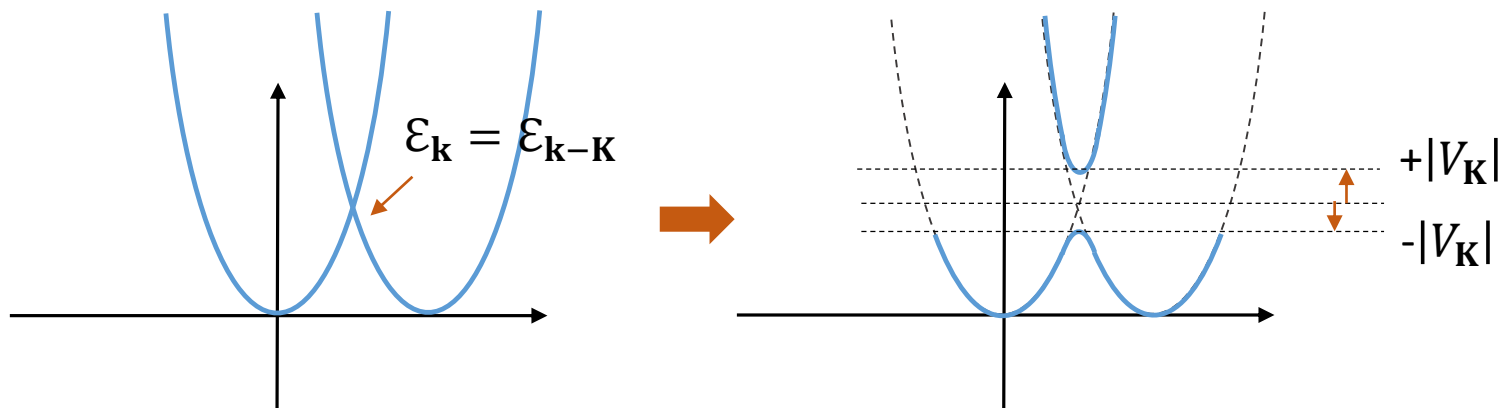
Application to Periodic Potential(4)

- So we have

$$\begin{vmatrix} H'_{11} - (\varepsilon - \varepsilon_{\mathbf{k}}) & H'_{12} \\ H'_{21} & H'_{22} - (\varepsilon - \varepsilon_{\mathbf{k}-\mathbf{K}}) \end{vmatrix} = \begin{vmatrix} \varepsilon_{\mathbf{k}} - \varepsilon & V_{\mathbf{K}} \\ V_{\mathbf{K}}^* & \varepsilon_{\mathbf{k}-\mathbf{K}} - \varepsilon \end{vmatrix} = 0$$

$$\Rightarrow \varepsilon = \frac{1}{2}(\varepsilon_{\mathbf{k}} + \varepsilon_{\mathbf{k}-\mathbf{K}}) \pm \sqrt{\left(\frac{\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}-\mathbf{K}}}{2}\right)^2 + |V_{\mathbf{K}}|^2}$$

- When $\varepsilon_{\mathbf{k}} = \varepsilon_{\mathbf{k}-\mathbf{K}}$ like at the zone boundary, $\varepsilon = \frac{1}{2}(\varepsilon_{\mathbf{k}} + \varepsilon_{\mathbf{k}-\mathbf{K}}) \pm |V_{\mathbf{K}}|$



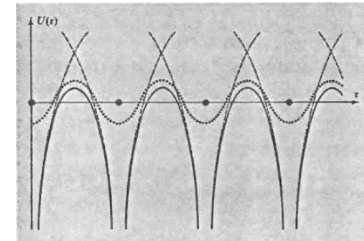
Tight-binding Model

- Tight-binding model is also called linear combination of atomic orbital (LCAO)
- In tight-binding model, we use atomic wave functions as a known system and apply perturbation theory.

Known system: $\left(-\frac{\hbar^2}{2m} \nabla^2 + \underset{\substack{\uparrow \\ \text{atomic potential}}}{V(\mathbf{r})} \right) \underset{\substack{\uparrow \\ \text{atomic wave function}}}{\phi(\mathbf{r})} = \epsilon_0 \phi(\mathbf{r})$

- We have a new system with periodic potential:

$$U(\mathbf{r}) = \sum_j V(\mathbf{r} - \mathbf{R}_j)$$



- The new system is

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + U(\mathbf{r}) \right) \psi(\mathbf{r}) = \left\{ \overbrace{-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r})}^{H_0} + \overbrace{(U(\mathbf{r}) - V(\mathbf{r}))}^{H'} \right\} \psi(\mathbf{r}) = \epsilon \psi(\mathbf{r})$$

Tight-binding Model(2)

- The perturbed solution is a linear combination of unperturbed system:

$$\psi(\mathbf{r}) = \sum_j c_j \phi(\mathbf{r} - \mathbf{R}_j)$$

There should be orbital index for the higher band since there are additional types of atomic wave functions (s, p, d, ...)

$$\sum_{jn} c_{jn} \phi_n(\mathbf{r} - \mathbf{R}_j)$$

- Here, $c_j = e^{i\mathbf{k} \cdot \mathbf{R}_j}$ to satisfy Bloch's theorem $\psi(\mathbf{r} + \mathbf{R}_j) = e^{i\mathbf{k} \cdot \mathbf{R}_j} \psi(\mathbf{r})$.
- Then,

$$\psi(\mathbf{r}) = \sum_j e^{i\mathbf{k} \cdot \mathbf{R}_j} \phi(\mathbf{r} - \mathbf{R}_j)$$

Tight-binding Model(3)

- We apply the perturbation theorem in a similar manner:

$$\int \phi^*(\mathbf{r})(H_0 + H') \sum_j e^{i\mathbf{k} \cdot \mathbf{R}_j} \phi(\mathbf{r} - \mathbf{R}_j) d^3r = \int \phi^*(\mathbf{r}) \mathcal{E} \sum_j e^{i\mathbf{k} \cdot \mathbf{R}_j} \phi(\mathbf{r} - \mathbf{R}_j) d^3r$$

$$\begin{aligned} \mathcal{E}_0 \int \phi^*(\mathbf{r}) \sum_j e^{i\mathbf{k} \cdot \mathbf{R}_j} \phi(\mathbf{r} - \mathbf{R}_j) d^3r + \int \phi^*(\mathbf{r}) H' \sum_j e^{i\mathbf{k} \cdot \mathbf{R}_j} \phi(\mathbf{r} - \mathbf{R}_j) d^3r \\ = \mathcal{E} \int \phi^*(\mathbf{r}) \sum_j e^{i\mathbf{k} \cdot \mathbf{R}_j} \phi(\mathbf{r} - \mathbf{R}_j) d^3r \end{aligned}$$

$$\mathcal{E} = \mathcal{E}_0 + \frac{\sum_j e^{i\mathbf{k} \cdot \mathbf{R}_j} \int \phi^*(\mathbf{r}) [U(\mathbf{r}) - V(\mathbf{r})] \phi(\mathbf{r} - \mathbf{R}_j) d^3r}{1 + \underbrace{\sum_{j \neq 0} \int \phi^*(\mathbf{r}) \phi(\mathbf{r} - \mathbf{R}_j) e^{i\mathbf{k} \cdot \mathbf{R}_j} d^3r}_{\text{Integration with all except for itself: usually small}}}$$

Integration with all except for itself: usually small

Tight-binding Model(4)

$$\varepsilon \cong \varepsilon_0 - \beta - \sum_{j \neq 0} \gamma(\mathbf{R}_j) e^{i\mathbf{k} \cdot \mathbf{R}_j}$$

$$\beta \equiv - \int \phi^*(\mathbf{r}) [U(\mathbf{r}) - V(\mathbf{r})] \phi(\mathbf{r}) d^3r$$

$$\gamma(\mathbf{R}_j) \equiv - \int \phi^*(\mathbf{r}) [U(\mathbf{r}) - V(\mathbf{r})] \phi(\mathbf{r} - \mathbf{R}_j) d^3r$$

- The overlap integral between second nearest neighbors are small.
- Thus, usually we need to consider only the nearest neighbors.
- Ex) 4 ϕ s for tetrahedral bonding (sp³) in a diamond or zincblend crystal.