Chapter 4

Electron Band Theory
(电子能带理论)

Outline

- **Chapter 4.1** Nearly-Free-Electron Model (近自由电子模型)
- **Chapter 4.2** Tight-Binding Model (紧束缚模型)
- **Chapter 4.3** Square-Potential-Well Model (方势阱模型)
- **Chapter 4.4** Conductors & Nonconductors (导体与非导体)

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- **Chapter 4.4** Conductors & Nonconductors (导体与非导体)

Objectives

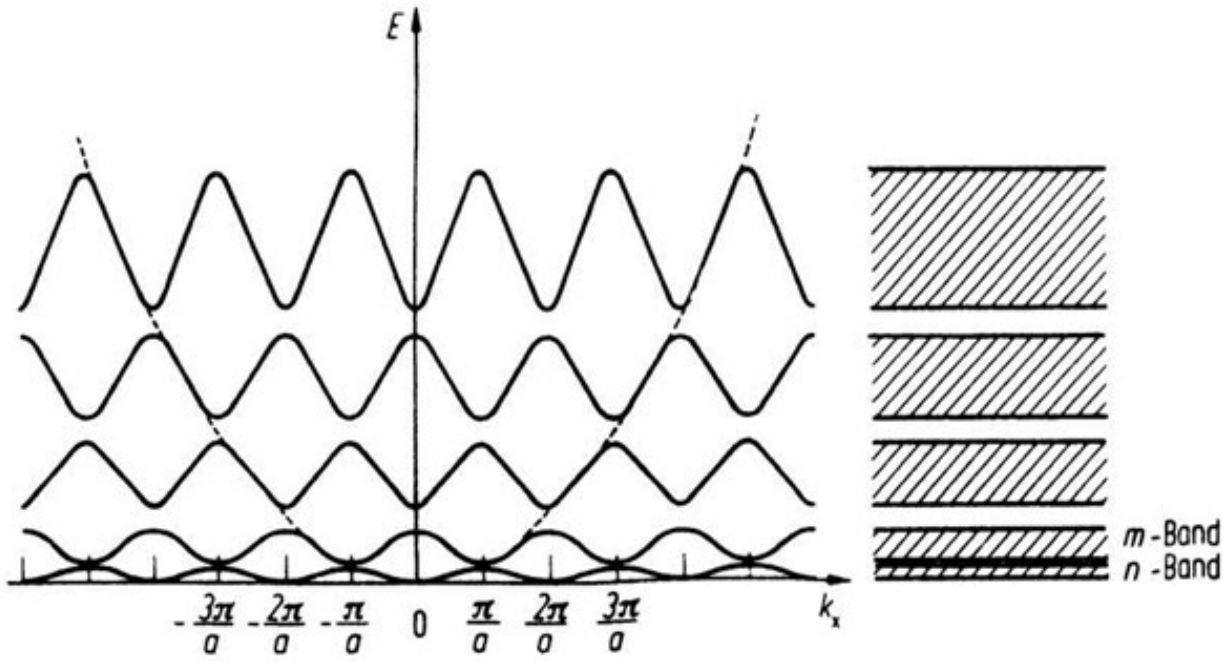
- To learn the **approximations** made for band theory.
- To understand the **Bloch theorem**.
- To understand the **origin of energy bands and band gaps.**

Band Theory in Solids
(固体能带理论)

Chapter 4.1: Nearly-Free-Electron Model (近自由电子模型)

➢ Band Theory in Solids (固体能带理论)

❖ The band theory represents a **fundamental theory** of the quantum-mechanical description of how electrons are present in the (periodic) potential of solids.

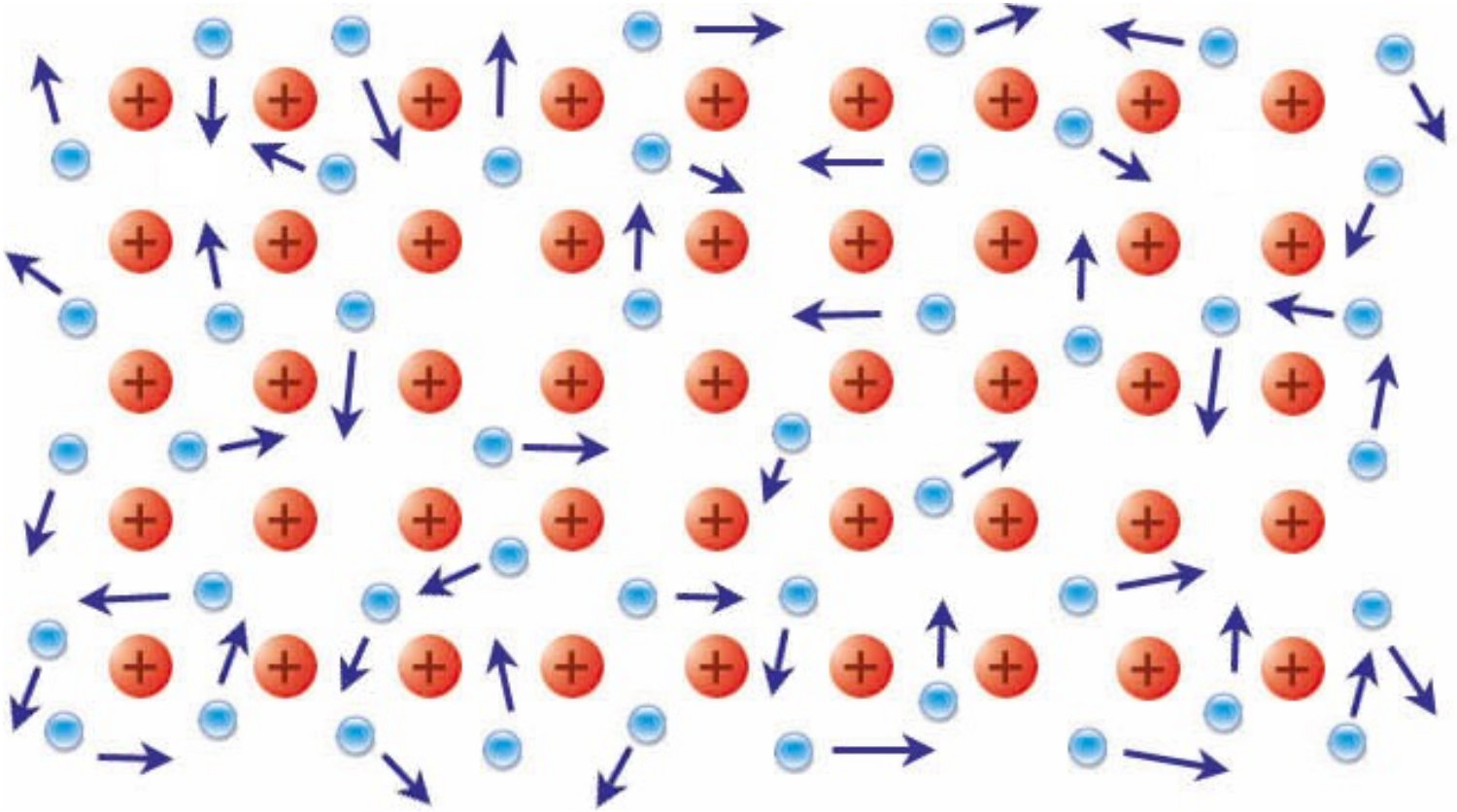


Schematic diagram of the electron band of a periodic lattice in reciprocal space.

Chapter 4.1: Nearly-Free-Electron Model (近自由电子模型)

➢ Band Theory in Solids (固体能带理论)

❖ The quantum-mechanical description of a crystal:



Schematic diagram of the electron motion in a crystal.

Chapter 4.1: Nearly-Free-Electron Model (近自由电子模型)

➢ Band Theory in Solids (固体能带理论)

❖ The quantum-mechanical description of a crystal:

- The Hamiltonian of a crystal with $\boldsymbol{N}$ atoms (each atom consists of $\boldsymbol{Z}$ valence electrons with mass $\boldsymbol{m}$ and one atomic core with $\boldsymbol{Ze}$ positive charges and mass $\boldsymbol{M}$) reads:

$$\hat{H} = \underbrace{-\sum_{n=1}^{N}\frac{\hbar^2}{2M}\nabla_n^2}_{\text{Kinetic energy of cores}} + \underbrace{\frac{1}{2}\sum_{n,m(n\neq m)}^{N}\frac{1}{4\pi\varepsilon_0}\frac{(Ze)^2}{|\vec{R}_n-\vec{R}_m|}}_{\text{Potential energy between cores}} \underbrace{-\sum_{i=1}^{NZ}\frac{\hbar^2}{2m}\nabla_i^2}_{\text{Kinetic energy of electrons}} + \underbrace{\frac{1}{2}\sum_{i,j(i\neq j)}^{NZ}\frac{1}{4\pi\varepsilon_0}\frac{e^2}{|\vec{r}_i-\vec{r}_j|}}_{\text{Potential energy between electrons}} \underbrace{-\sum_{i=1}^{NZ}\sum_{n=1}^{N}\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{|\vec{r}_i-\vec{R}_n|}}_{\text{Potential energy between electrons and cores}}$$

$$= \hat{T}_{\text{lat}} + \hat{V}_{\text{lat}} + \hat{T}_{\text{ele}} + \hat{V}_{\text{e-e}} + \hat{V}_{\text{e-l}}$$

Chapter 4.1: Nearly-Free-Electron Model (近自由电子模型)

➢ Band Theory in Solids (固体能带理论)

❖ The quantum-mechanical description of a crystal:

- The stationary Schrödinger equation of the crystal reads:

$$\hat{H}\psi(\vec{r},\vec{R}) = E\psi(\vec{r},\vec{R})$$

Here, E and $\psi(\vec{r},\vec{R})$ denote the eigen-energy and eigen-wavefunction, respectively.

It is almost impossible to solve such a "many-body" (多体) Schrödinger equation without any approximation!

Chapter 4.1: Nearly-Free-Electron Model (近自由电子模型)

➢ Band Theory in Solids (固体能带理论)

❖ The band theory is essentially an **approximate theory** used to obtain the **electronic structures (电子结构)** of a crystal.

❖ The **fundamental approximations** adopted in the band theory include:

- ❑ **Adiabatic Approximation (绝热近似)**
- ❑ **Mean-Field Approximation (平均场近似)**
- ❑ **Periodic-Potential Approximation (周期势近似)**

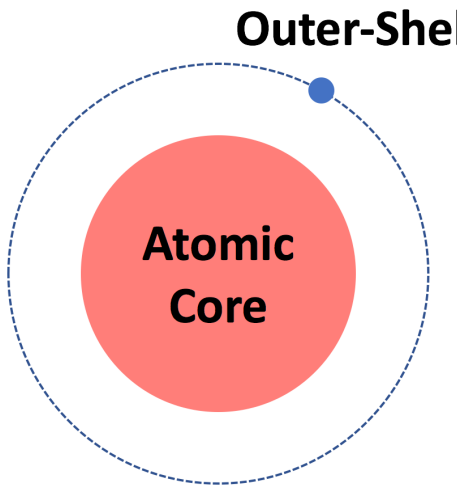
Chapter 4.1: Nearly-Free-Electron Model (近自由电子模型)

➢ Band Theory in Solids (固体能带理论)

❑ Adiabatic Approximation (绝热近似)

- The motion of valence electrons (outer-shell electrons) and atomic cores is separable.
- The electrons move much faster than the atomic cores such that the atomic cores can be regarded as remaining **"static"** during the motion of electrons.

$$\psi(\vec{r},\vec{R}) = \psi_{\mathrm{ele}}(\vec{r})\psi_{\mathrm{lat}}(\vec{R})$$



➢ Band Theory in Solids (固体能带理论)

❑ Adiabatic Approximation (绝热近似)

- As a result, the "many-body" Schrödinger equation is reduced to a **"many-electron" (多电子)** Schrödinger equation:

$$\hat{H}_{\text{ele}}\psi_{\text{ele}}(\vec{r}) = E\psi_{\text{ele}}(\vec{r})$$

$$\hat{H}_{\text{ele}} = -\sum_{i=1}^{NZ}\frac{\hbar^2}{2m}\nabla_i^2 + \frac{1}{2}\sum_{i,j(i\neq j)}^{NZ}\frac{1}{4\pi\varepsilon_0}\frac{e^2}{|\vec{r}_i-\vec{r}_j|} - \sum_{i=1}^{NZ}\sum_{n=1}^{N}\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{|\vec{r}_i-\vec{R}_n|}$$

$$= \hat{T}_{\text{ele}} + \hat{V}_{\text{e-e}} + \hat{V}_{\text{e-l}}$$

Chapter 4.1: Nearly-Free-Electron Model (近自由电子模型)

➢ Band Theory in Solids (固体能带理论)

❑ Adiabatic Approximation (绝热近似)

- The consequence of the adiabatic approximation:

“Many-body” Problem → **“Many-electron” Problem**

Chapter 4.1: Nearly-Free-Electron Model (近自由电子模型)

➢ Band Theory in Solids (固体能带理论)

❑ Mean-Field Approximation (平均场近似)

- The Coulomb interactions between a single electron and the rest electrons are approximated by a time-independent **"mean field" (平均场)**:

$$\hat{V}_{\mathrm{e-e}} = \frac{1}{2}\sum_{i,j(i\neq j)}^{NZ}\frac{1}{4\pi\varepsilon_0}\frac{e^2}{\left|\vec{r}_i-\vec{r}_j\right|} \approx \sum_{i=1}^{NZ}\left\langle\hat{V}_{\mathrm{e-e}}(\vec{r}_i)\right\rangle$$

$$\rightarrow \quad \boxed{\hat{H}_i = -\frac{\hbar^2}{2m}\nabla_i^2 + \left\langle\hat{V}_{\mathrm{e-e}}(\vec{r}_i)\right\rangle - \sum_{n=1}^{N}\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{\left|\vec{r}_i-\vec{R}_n\right|}} \qquad \hat{H}_{\mathrm{ele}} = \sum_{i=1}^{NZ}\hat{H}_i$$

➢ Band Theory in Solids (固体能带理论)

❑ Mean-Field Approximation (平均场近似)

- As a result, the "many-electron" Schrödinger equation is reduced to a **"single-electron" (单电子)** Schrödinger equation, which can be applied to all the electrons:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + \hat{V}(\vec{r})\right]\psi(\vec{r}) = E\psi(\vec{r})$$

$$\hat{V}(\vec{r}) = \left\langle \hat{V}_{\mathrm{e-e}}(\vec{r}) \right\rangle - \sum_{n=1}^{N} \frac{1}{4\pi\varepsilon_0} \frac{Ze^2}{\left|\vec{r} - \vec{R}_n\right|}$$

- The mean-field approximation is also called **single-electron approximation (单电子近似)** or **Hartree-Fock approximation (哈特里-福克近似)**!

Chapter 4.1: Nearly-Free-Electron Model (近自由电子模型)

➢ Band Theory in Solids (固体能带理论)

❑ Mean-Field Approximation (平均场近似)

- The consequence of the mean-field approximation:

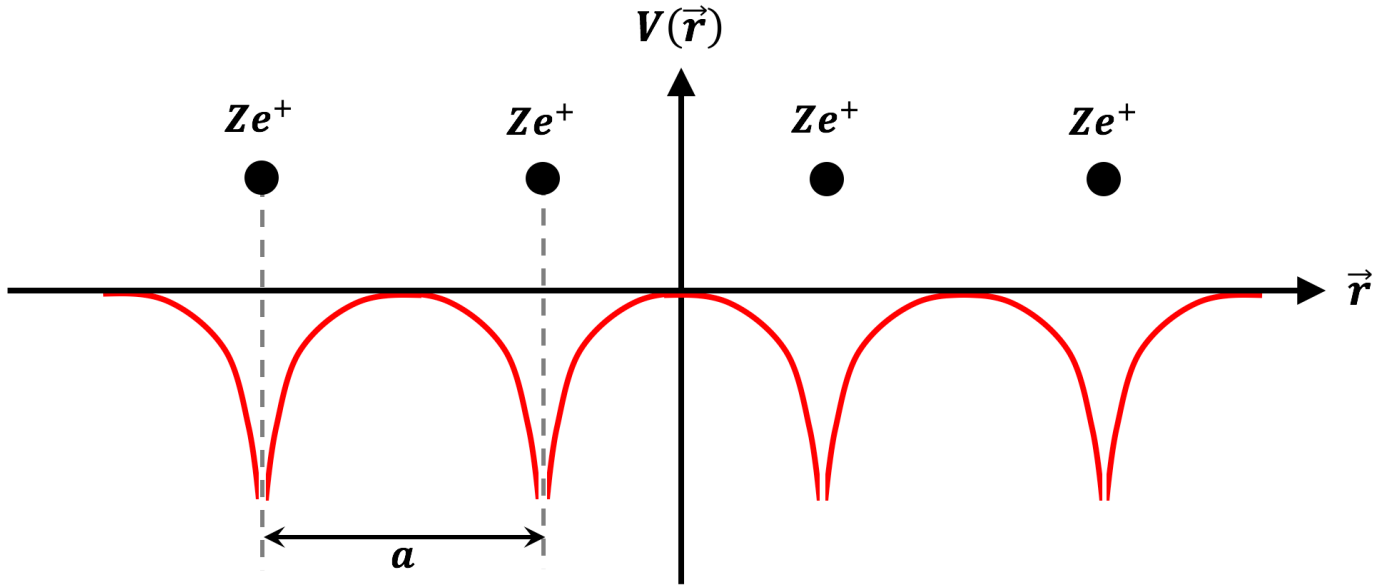
“Many-electron” Problem → **“Single-electron” Problem**

Chapter 4.1: Nearly-Free-Electron Model (近自由电子模型)

➢ Band Theory in Solids (固体能带理论)

❑ Periodic-Potential Approximation (周期势近似)

- The potential experienced by the electrons is **periodic in space** and has a **translational symmetry (平移对称性)** the same as that of the lattice:



Schematic diagram of periodic potential.

Chapter 4.1: Nearly-Free-Electron Model (近自由电子模型)

➢ Band Theory in Solids (固体能带理论)

❑ Periodic-Potential Approximation (周期势近似)

- The potential experienced by the electrons is **periodic in space** and has a **translational symmetry (平移对称性)** the same as that of the lattice:

$$\hat{V}(\vec{r} + \vec{R}_n) = \hat{V}(\vec{r})$$

$\vec{R}_n$ denotes any lattice vector in real space.

Chapter 4.1: Nearly-Free-Electron Model (近自由电子模型)

➢ Band Theory in Solids (固体能带理论)

❑ Periodic-Potential Approximation (周期势近似)

- The consequence of the periodic-potential approximation:

“Single-electron” Problem → **Making Use of the Bloch Theorem.**

Chapter 4.1: Nearly-Free-Electron Model (近自由电子模型)

➢ Band Theory in Solids (固体能带理论)

❖ Based on the three approximations mentioned above, the electronic structures of the crystal can be obtained by solving the following **single-electron Schrödinger equation**:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + \hat{V}(\vec{r})\right]\psi(\vec{r}) = E\psi(\vec{r})$$

$$\hat{V}(\vec{r} + \vec{R}_n) = \hat{V}(\vec{r})$$

The "single-electron" Schrödinger equation represents the starting point of the band theory!

Bloch Theorem
(布洛赫定理)

Chapter 4.1: Nearly-Free-Electron Model (近自由电子模型)

➢ Bloch Theorem (布洛赫定理)

❖ The Bloch theorem states that, for a periodic lattice potential $\hat{V}(\vec{r}+\vec{R}_n)=\hat{V}(\vec{r})$, the solution $\psi(\vec{r})$ to the Schrödinger equation satisfies:

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

Here, $\vec{k}$ denotes a **wave vector (波矢).**

This suggests that a phase factor of $e^{i\vec{k}\cdot\vec{R}_n}$ is added to the wave function when it is spatially translated by a lattice vector of $\vec{R}_n$.

Chapter 4.1: Nearly-Free-Electron Model (近自由电子模型)

➢ Bloch Theorem (布洛赫定理)

❖ According to the Bloch theorem, the wave function $\psi(\vec{r})$ can be written as:

$$\boldsymbol{\psi}(\vec{\boldsymbol{r}}) = \mathrm{e}^{i\vec{\boldsymbol{k}}\cdot\vec{\boldsymbol{r}}}\boldsymbol{u}(\vec{\boldsymbol{r}})$$

Here, $\boldsymbol{u}(\vec{\boldsymbol{r}})$ denotes a periodic function:

$$\boldsymbol{u}\left(\vec{\boldsymbol{r}} + \vec{\boldsymbol{R}}_{\boldsymbol{n}}\right) = \boldsymbol{u}(\vec{\boldsymbol{r}})$$

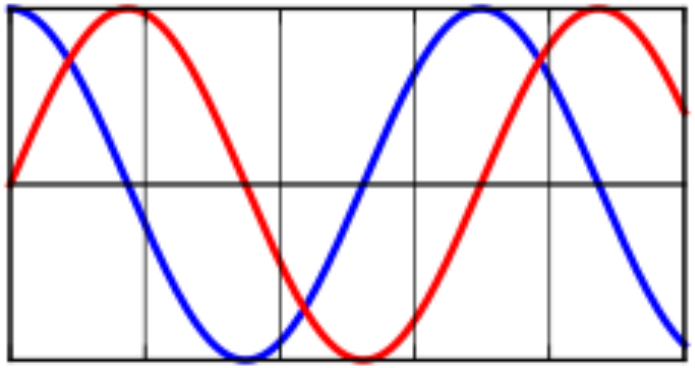
❖ The wave function $\boldsymbol{\psi}(\vec{\boldsymbol{r}})$ is also called **Bloch function (布洛赫函数)** or **Bloch wave (布洛赫波).**

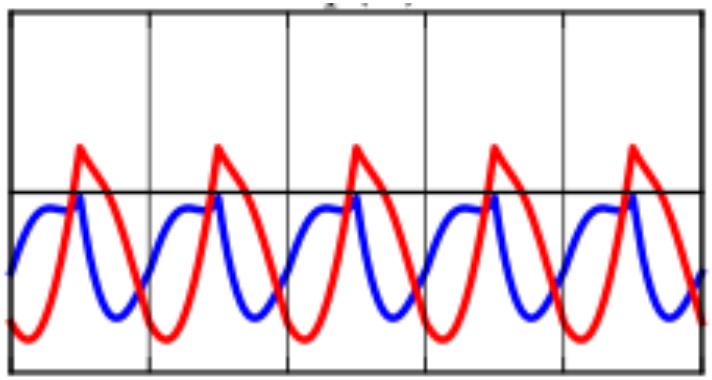
Chapter 4.1: Nearly-Free-Electron Model (近自由电子模型)

➢ Bloch Theorem (布洛赫定理)

❖ Examples of Bloch function:

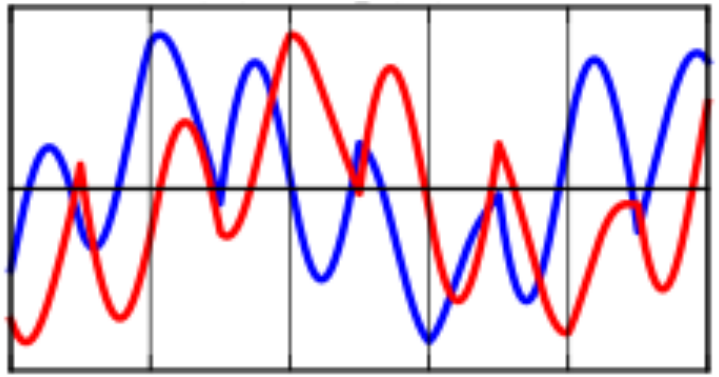
$e^{i\vec{k}\cdot\vec{r}}$





$u(\vec{r})$

$\psi(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}u(\vec{r})$

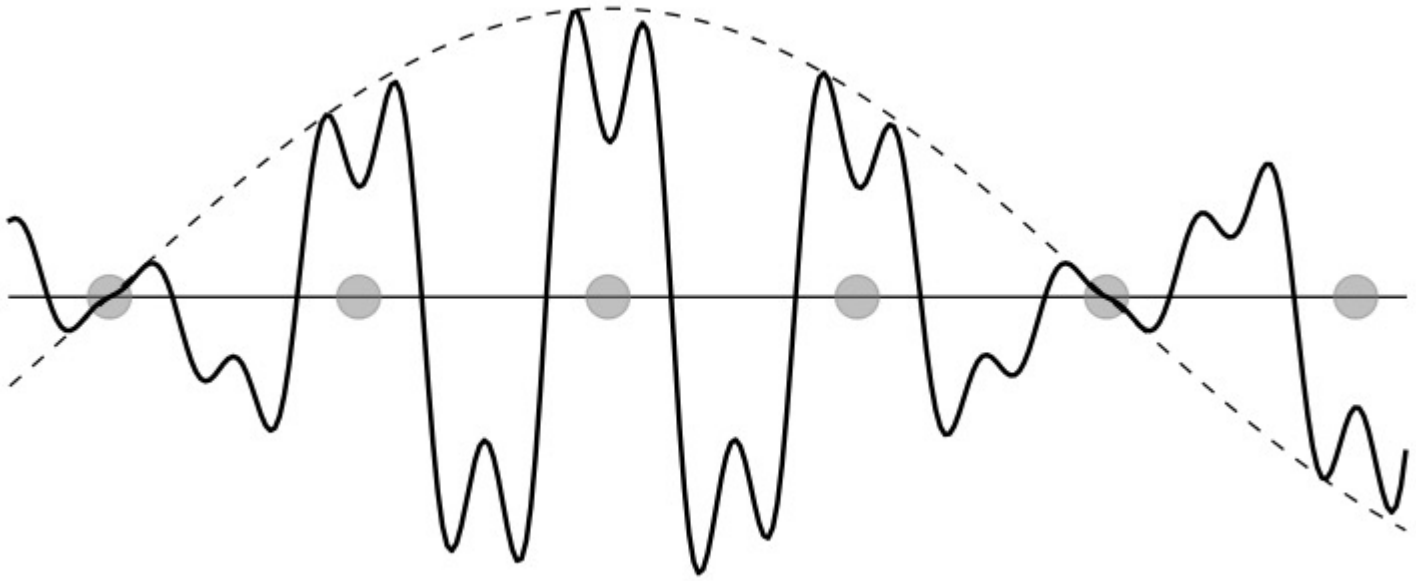


Real part

Imaginary part

➢ Bloch Theorem (布洛赫定理)

❖ Examples of Bloch function:



Schematic diagram of the real part of a Bloch function in a 1D lattice.

Chapter 4.1: Nearly-Free-Electron Model (近自由电子模型)

➢ Bloch Theorem (布洛赫定理)

❖ Proof of the Bloch theorem:

We first define **translation symmetry operators $\hat{T}_j$ (平移对称算符)**:

$$\hat{T}_j f(\vec{r}) = f(\vec{r} + \vec{a}_j) \quad (j = 1,2,3)$$

→ Commutation relations: $[\hat{T}_i, \hat{T}_j] = 0 \qquad [\hat{T}_i, \hat{H}] = 0 \quad (i, j = 1,2,3)$

→ Common eigen-functions: $\psi \quad \rightarrow \quad \hat{H}\psi = E\psi \qquad \hat{T}_j\psi = \lambda_j\psi$

→ Periodic boundary condition: $\psi(\vec{r}) = \psi(\vec{r} + N_j\vec{a}_j) = \hat{T}_j^{N_j}\psi(\vec{r}) = \lambda_j^{N_j}\psi(\vec{r}) \rightarrow \lambda_j^{N_j} = 1$

Chapter 4.1: Nearly-Free-Electron Model (近自由电子模型)

➢ Bloch Theorem (布洛赫定理)

❖ Proof of the Bloch theorem:

For integers l_j: $\lambda_j = \mathrm{e}^{i2\pi\frac{l_j}{N_j}} = \mathrm{e}^{i\vec{k}\cdot\vec{a}_j}$ $\vec{k} = \frac{l_1}{N_1}\vec{b}_1 + \frac{l_2}{N_2}\vec{b}_2 + \frac{l_3}{N_3}\vec{b}_3$

$$\psi(\vec{r}+\vec{R}_n) = \hat{T}_1^{N_1}\hat{T}_2^{N_2}\hat{T}_3^{N_3}\psi(\vec{r}) = \lambda_1^{N_1}\lambda_2^{N_2}\lambda_3^{N_3}\psi(\vec{r}) = \mathrm{e}^{i\vec{k}\cdot(N_1\vec{a}_1+N_2\vec{a}_2+N_3\vec{a}_3)}\psi(\vec{r})$$

$$\boxed{\psi(\vec{r}+\vec{R}_n) = \mathrm{e}^{i\vec{k}\cdot\vec{R}_n}\psi(\vec{r})}$$

Note:

The wave vector $\vec{k}$ represents the quantum number of translation symmetry operators!

Chapter 4.1: Nearly-Free-Electron Model (近自由电子模型)

➢ Bloch Theorem (布洛赫定理)

Felix Bloch 布洛赫
(1905-1983)
Swiss Physicist

❖ The founder of electron band theory in solids (1928).

❖ Winner of the Nobel Prize for physics in 1952 (shared with Edward M. Purcell) for “the development of new ways for nuclear magnetic precision measurements”.

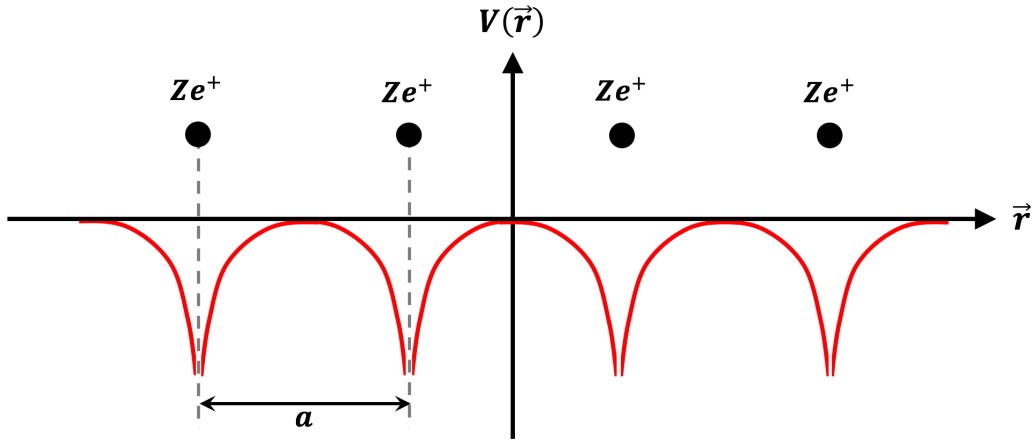
Models of Periodic Potential
(周期势模型)

Chapter 4.1: Nearly-Free-Electron Model (近自由电子模型)

➢ Models of Periodic Potential (周期势模型)

❖ There are two approaches to understand the periodic potential in limiting cases:

$$V(\vec{r}+\vec{R}_n)=V(\vec{r})$$



❑ **Nearly-Free-Electron Model (近自由电子模型):** In the limit of **free electron (自由电子极限)**

❑ **Tight-Binding Model (紧束缚模型):** In the limit of **binding electron (束缚电子极限)**

Chapter 4.1: Nearly-Free-Electron Model (近自由电子模型)

➢ Models of Periodic Potential (周期势模型)

❖ There are two approaches to understand the periodic potential in two limiting cases:

$$V(\vec{r}) = V_0(\vec{r}) + \Delta V(\vec{r})$$

Solvable part (可解部分)

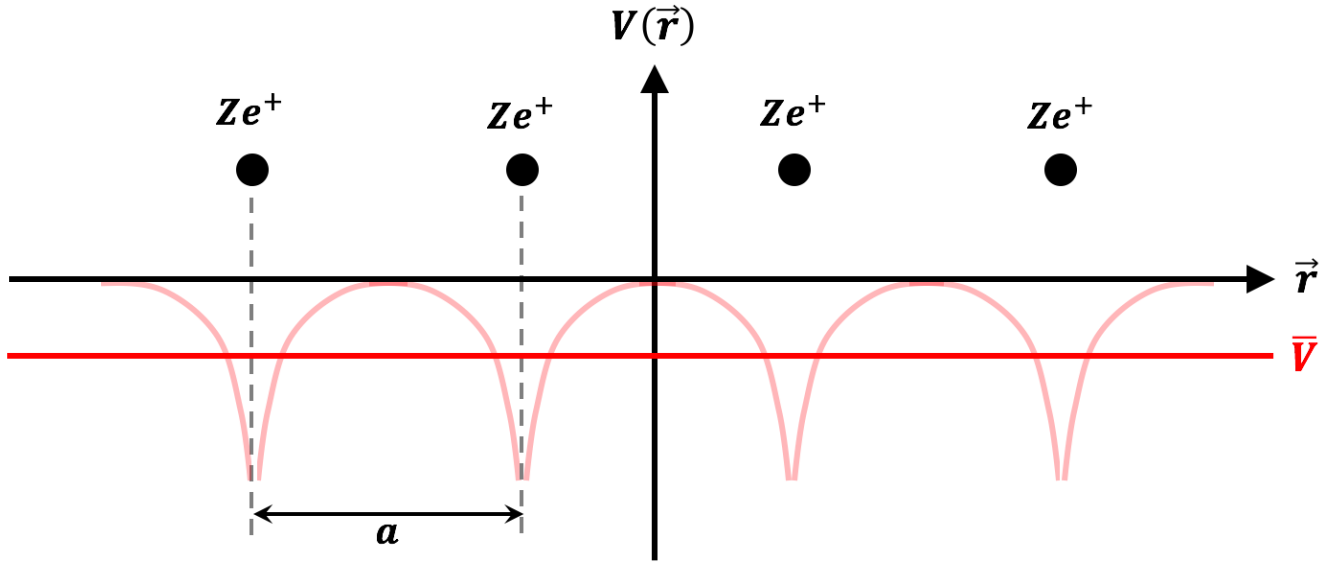
Perturbation part (微扰部分)

Chapter 4.1: Nearly-Free-Electron Model (近自由电子模型)

➢ Models of Periodic Potential (周期势模型)

❑ Nearly-Free-Electron Model (近自由电子模型)

$$V(\vec{r}) = V_0(\vec{r}) + \Delta V(\vec{r}) = \overline{V} + [V(\vec{r}) - \overline{V}]$$

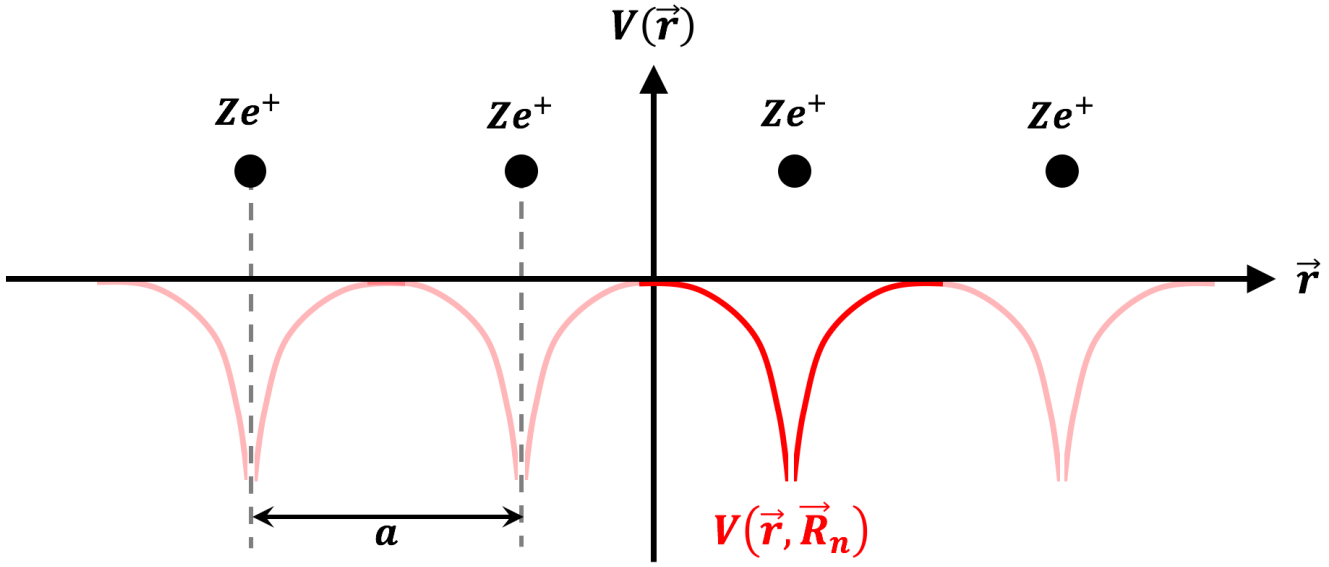


Chapter 4.1: Nearly-Free-Electron Model (近自由电子模型)

➢ Models of Periodic Potential (周期势模型)

❑ Tight-Binding Model (紧束缚模型)

$$V(\vec{r}) = V_0(\vec{r}) + \Delta V(\vec{r}) = \boldsymbol{V}\left(\vec{\boldsymbol{r}}, \vec{R}_{\mathrm{n}}\right) + \left[\boldsymbol{V}(\vec{\boldsymbol{r}}) - \boldsymbol{V}\left(\vec{r}, \vec{R}_{\mathrm{n}}\right)\right]$$



Nearly-Free-Electron Model in 1D
(一维近自由电子模型)

Chapter 4.1: Nearly-Free-Electron Model (近自由电子模型)

➢ Nearly-Free-Electron Model in 1D (一维近自由电子模型)

❖ We consider a **1D** monoatomic lattice with a periodic potential $\boldsymbol{V(x)}$ and $\boldsymbol{N}$ atoms; each atom consists of $\boldsymbol{Z}$ valence electrons with mass $\boldsymbol{m}$.

❖ The single-electron Schrödinger equation reads:

$$\boldsymbol{\hat{H}\psi(x) = E\psi(x)}$$

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + V(x) \qquad V(x + R_n) = V(x) \qquad R_n = na$$

Chapter 4.1: Nearly-Free-Electron Model (近自由电子模型)

➢ Nearly-Free-Electron Model in 1D (一维近自由电子模型)

❖ Assuming that **the fluctuations of the periodic potential in space are small**, $\boldsymbol{V(x)}$ can be expanded in terms of **Fourier series (傅里叶级数)**:

$$\boldsymbol{V(x)} = \sum_{\boldsymbol{n=0}}^{\boldsymbol{N-1}} \boldsymbol{V_n} \mathbf{e}^{\boldsymbol{i}\frac{2\pi}{a}nx} = \bar{\boldsymbol{V}} + \sum_{\boldsymbol{n=1}}^{\boldsymbol{N-1}} \boldsymbol{V_n} \mathbf{e}^{\boldsymbol{i}\frac{2\pi}{a}nx}$$

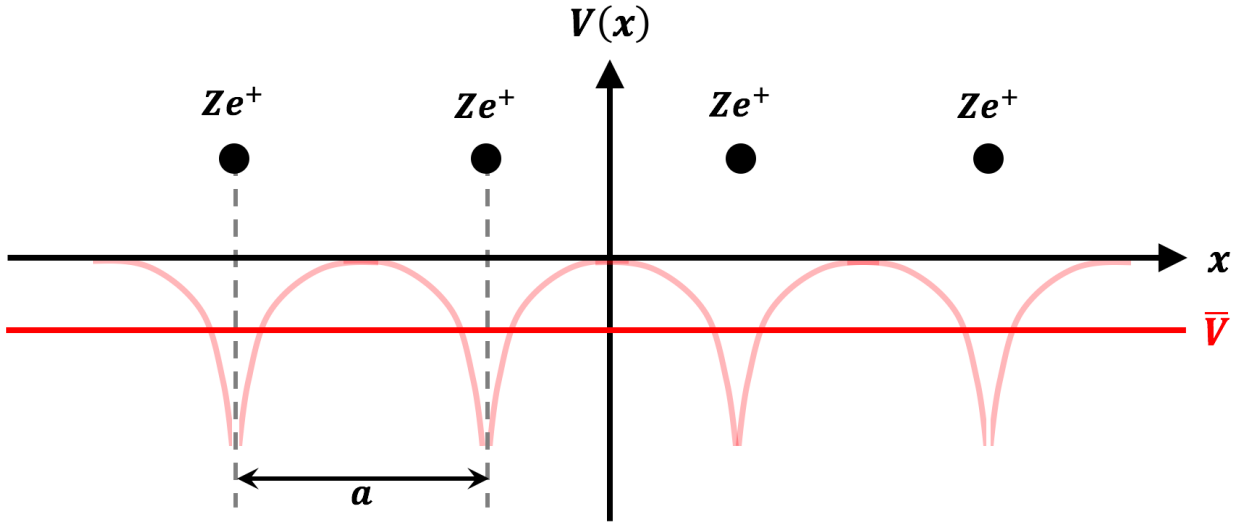
$$V_n = \frac{1}{Na}\int_0^{Na} \mathrm{e}^{-i\frac{2\pi}{a}nx} V(x)\mathrm{d}x$$

Chapter 4.1: Nearly-Free-Electron Model (近自由电子模型)

➢ Nearly-Free-Electron Model in 1D (一维近自由电子模型)

❖ Assuming that **the fluctuations of the periodic potential in space are small**, $V(x)$ can be expanded in terms of **Fourier series (傅里叶级数)**:

$$\bar{V} = V_0 = \frac{1}{Na}\int_0^{Na} V(x)\mathrm{d}x$$



Chapter 4.1: Nearly-Free-Electron Model (近自由电子模型)

➢ Nearly-Free-Electron Model in 1D (一维近自由电子模型)

❖ In the spirit of **perturbation theory (微扰理论)**, we obtain:

$$\widehat{\boldsymbol{H}} = \widehat{\boldsymbol{H}}_{\boldsymbol{0}} + \widehat{\boldsymbol{H}}' \qquad \widehat{H}_0 = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \bar{V} \qquad \widehat{\boldsymbol{H}}' = \boldsymbol{V}(\boldsymbol{x}) - \bar{\boldsymbol{V}} = \Delta \boldsymbol{V}(\boldsymbol{x})$$

$$\boldsymbol{E} = \boldsymbol{E}^{(\boldsymbol{0})} + \boldsymbol{E}^{(\boldsymbol{1})} + \boldsymbol{E}^{(\boldsymbol{2})} + \cdots$$

$$\boldsymbol{\psi} = \boldsymbol{\psi}^{(\boldsymbol{0})} + \boldsymbol{\psi}^{(\boldsymbol{1})} + \boldsymbol{\psi}^{(\boldsymbol{2})} + \cdots$$

$E^{(n)}$ and $\psi^{(n)}$ denote the ***n*-th order terms (*n* 阶项)** of the eigen-energy and eigen-wavefunction, respectively.

Chapter 4.1: Nearly-Free-Electron Model (近自由电子模型)

➢ Nearly-Free-Electron Model in 1D (一维近自由电子模型)

❖ In the **zeroth-order approximation (零级近似)**, we obtain a system of **free electrons** moving in a constant potential $\bar{V}$:

$$\hat{H}_0\psi^{(0)}(x) = E^{(0)}\psi^{(0)}(x) \qquad \hat{H}_0 = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \bar{V}$$

$$\psi_k^{(0)}(x) = \frac{1}{\sqrt{Na}}e^{ikx} \qquad \int_0^{Na} \psi_k^{(0)*}(x)\psi_{k'}^{(0)}(x)\,dx = \delta_{kk'}$$

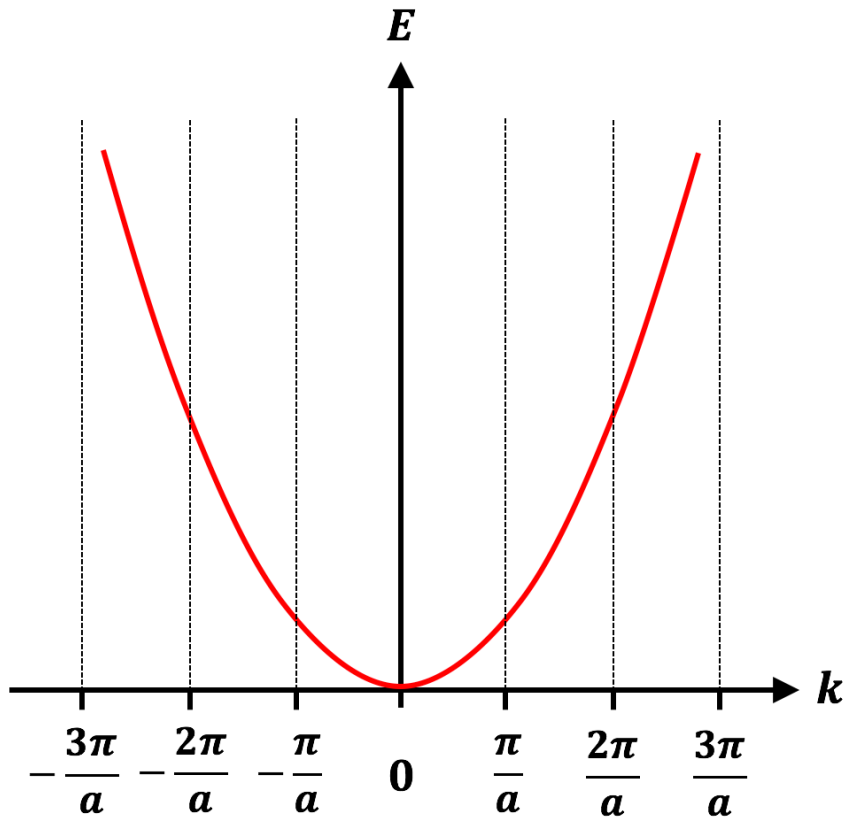
$k = n\frac{2\pi}{Na}$ $\quad n = 0, \pm1, \pm2, \cdots$ (as a result of the **periodic boundary condition**)

Chapter 4.1: Nearly-Free-Electron Model (近自由电子模型)

➢ Nearly-Free-Electron Model in 1D (一维近自由电子模型)

❖ In the **zeroth-order approximation (零级近似)**, we obtain a system of **free electrons** moving in a constant potential $\bar{V}$:

$$E_k^{(0)} = \frac{\hbar^2 k^2}{2m} + \bar{V}$$



This is also called the free-electron approximation (自由电子近似) or empty lattice approximation (空格子近似)!

Chapter 4.1: Nearly-Free-Electron Model (近自由电子模型)

➢ Nearly-Free-Electron Model in 1D (一维近自由电子模型)

❖ The first-order correction to energy (能量的一级修正):

$$E_k^{(1)} = \langle k|\Delta V|k\rangle = \langle k|V|k\rangle - \bar{V} = 0$$

Here, $|\boldsymbol{k}\rangle = \boldsymbol{\psi}_{\boldsymbol{k}}^{(\boldsymbol{0})}(\boldsymbol{x})$ and $\langle \boldsymbol{k}|\boldsymbol{V}|\boldsymbol{k}\rangle = \int_{\boldsymbol{0}}^{\boldsymbol{Na}} \left|\boldsymbol{\psi}_{\boldsymbol{k}}^{(\boldsymbol{0})}(\boldsymbol{x})\right|^{\boldsymbol{2}} \boldsymbol{V}(\boldsymbol{x})\mathbf{d}\boldsymbol{x} = \frac{\boldsymbol{1}}{\boldsymbol{Na}} \int_{\boldsymbol{0}}^{\boldsymbol{Na}} \boldsymbol{V}(\boldsymbol{x})\mathbf{d}\boldsymbol{x} = \bar{\boldsymbol{V}}$

The first-order correction to energy is exactly zero!

➢ Nearly-Free-Electron Model in 1D (一维近自由电子模型)

❖ The first-order correction to wavefunction (波函数的一级修正):

$$\psi_k^{(1)}(x) = \sum_{k' \neq k} \frac{\langle k'|\Delta V|k\rangle}{E_k^{(0)} - E_{k'}^{(0)}} \psi_{k'}^{(0)} = \frac{1}{\sqrt{Na}} \mathrm{e}^{ikx} \sum_{n=1}^{N-1} \frac{V_n}{\frac{\hbar^2}{2m}\left[k^2 - \left(k + n\frac{2\pi}{a}\right)^2\right]} \mathrm{e}^{i\frac{2\pi}{a}nx}$$

where $\boldsymbol{V_n}$ denotes the ***n*th Fourier coefficient** of $V(x)$:

$$V_n = \frac{1}{Na}\int_0^{Na} \mathrm{e}^{-i\frac{2\pi}{a}nx} V(x)\mathrm{d}x = \frac{1}{a}\int_0^{a} \mathrm{e}^{-i\frac{2\pi}{a}nx} V(x)\mathrm{d}x$$

Chapter 4.1: Nearly-Free-Electron Model (近自由电子模型)

➢ Nearly-Free-Electron Model in 1D (一维近自由电子模型)

❖ The first-order correction to wavefunction (波函数的一级修正):

The **interaction between states $|k\rangle$ and $|k'\rangle$** as a result of the periodic potential:

$$\langle k'|\Delta V|k\rangle = \langle k'|[V(x) - \bar{V}]|k\rangle = \langle k'|V(x)|k\rangle = \begin{cases} V_n & \text{when } k' = k + n\frac{2\pi}{a} \\ 0 & \text{when } k' \neq k + n\frac{2\pi}{a} \end{cases}$$

The interaction between $|k\rangle$ and $|k'\rangle$ is nonzero only when $k' = k + n\frac{2\pi}{a}$

Chapter 4.1: Nearly-Free-Electron Model (近自由电子模型)

➢ Nearly-Free-Electron Model in 1D (一维近自由电子模型)

❖ The second-order correction to energy (能量的二级修正):

$$E_k^{(2)} = \sum_{k' \neq k} \frac{|\langle k'|\Delta V|k\rangle|^2}{E_k^{(0)} - E_{k'}^{(0)}} = \sum_{n=1}^{N-1} \frac{|V_n|^2}{\frac{\hbar^2}{2m}\left[k^2 - \left(k + n\frac{2\pi}{a}\right)^2\right]}$$

It is important to note that $E_k^{(2)}$ diverges ($\rightarrow 0$) when $k = -n\frac{\pi}{a}$

Chapter 4.1: Nearly-Free-Electron Model (近自由电子模型)

➢ Nearly-Free-Electron Model in 1D (一维近自由电子模型)

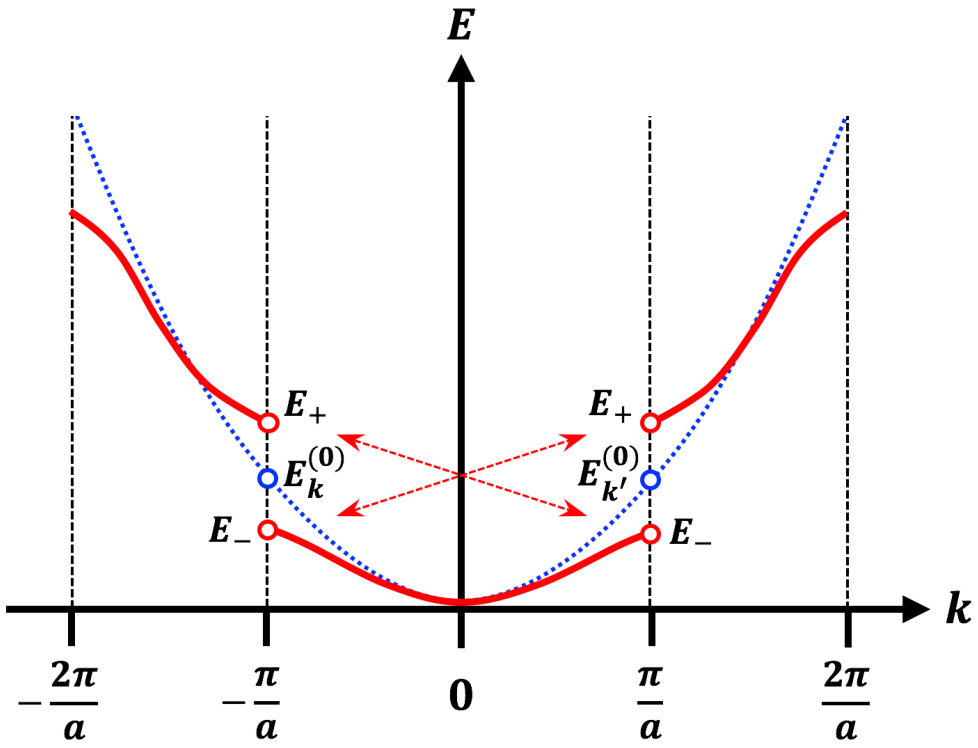
❖ The second-order correction to energy (能量的二级修正):

$$E_+ = \frac{1}{2}\left[\left(E_k^{(0)} + E_{k'}^{(0)}\right) + \sqrt{\left(E_k^{(0)} - E_{k'}^{(0)}\right)^2 + 4|V_n|^2}\right]$$

$$E_- = \frac{1}{2}\left[\left(E_k^{(0)} + E_{k'}^{(0)}\right) - \sqrt{\left(E_k^{(0)} - E_{k'}^{(0)}\right)^2 + 4|V_n|^2}\right]$$

When $\boldsymbol{k} = -\boldsymbol{n}\dfrac{\boldsymbol{\pi}}{\boldsymbol{a}}$ and $\boldsymbol{k'} = \boldsymbol{n}\dfrac{\boldsymbol{\pi}}{\boldsymbol{a}}$

Degenerate perturbation theory (简并微扰论).



Chapter 4.1: Nearly-Free-Electron Model (近自由电子模型)

➢ Nearly-Free-Electron Model in 1D (一维近自由电子模型)

❖ The solutions to the Schrödinger equation:

$$\psi_k(x) = \frac{1}{\sqrt{Na}} e^{ikx} \left\{ 1 + \sum_{n=1}^{N-1} \frac{V_n}{\frac{\hbar^2}{2m}\left[k^2 - \left(k + n\frac{2\pi}{a}\right)^2\right]} \mathrm{e}^{i\frac{2\pi}{a}nx} \right\}$$

(up to the 1st order)

$$E_k = \begin{cases} E_k^{(0)} + \sum_{n=1}^{N-1} \frac{|V_n|^2}{\frac{\hbar^2}{2m}\left[k^2 - \left(k + n\frac{2\pi}{a}\right)^2\right]} & \textbf{when } \boldsymbol{k \neq -n\frac{\pi}{a}} \\ \frac{1}{2}\left[\left(E_k^{(0)} + E_{k'}^{(0)}\right) \pm \sqrt{\left(E_k^{(0)} - E_{k'}^{(0)}\right)^2 + 4|V_n|^2}\right] & \textbf{when } \boldsymbol{k = -n\frac{\pi}{a}, k' = n\frac{\pi}{a}} \end{cases}$$

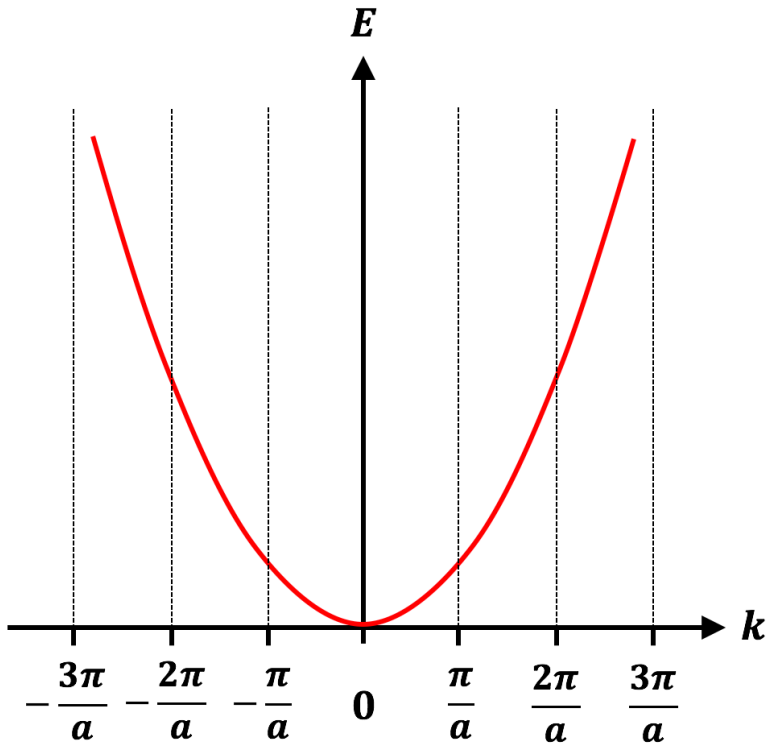
(up to the 2nd order)

Note that $\psi_k(x + na) = e^{ikna}\psi_k(x)$ (Bloch theorem)!

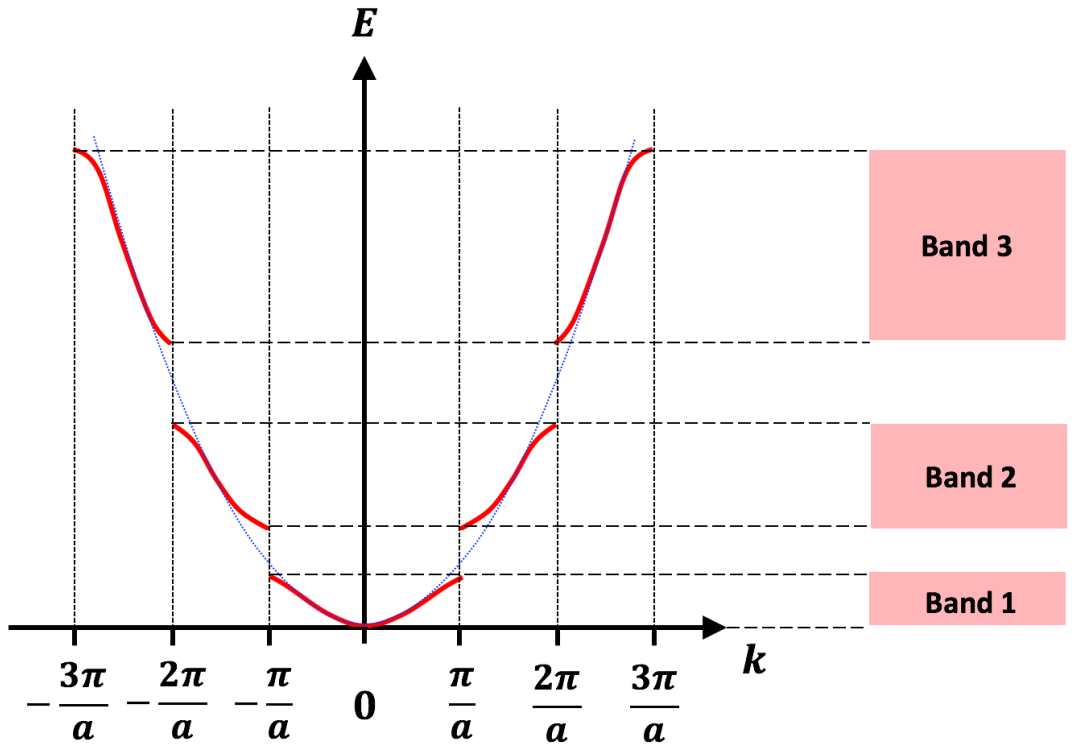
Chapter 4.1: Nearly-Free-Electron Model (近自由电子模型)

➢ Nearly-Free-Electron Model in 1D (一维近自由电子模型)

❖ Energy bands (能带):



The energy dispersion of **free electron.**



The energy dispersion of **nearly-free electron.**

Chapter 4.1: Nearly-Free-Electron Model (近自由电子模型)

➢ Nearly-Free-Electron Model in 1D (一维近自由电子模型)

❖ Energy bands (能带):

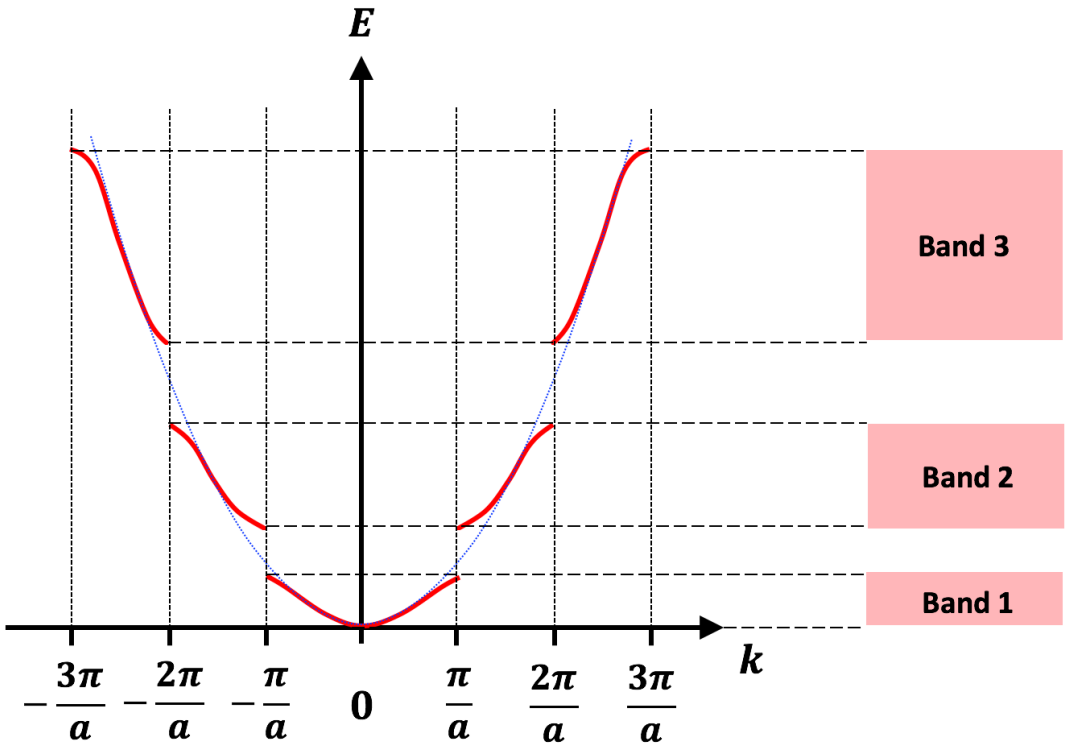
$$\boldsymbol{k = n\frac{2\pi}{Na}\ (n = 0, \pm 1, \pm 2, \cdots)}$$

Band 1: $-\frac{\pi}{a} \le k < \frac{\pi}{a}$ **(1st BZ)**

Band 2: $\frac{\pi}{a} \le |k| < \frac{2\pi}{a}$ **(2nd BZ)**

Band 3: $\frac{2\pi}{a} \le |k| < \frac{3\pi}{a}$ **(3rd BZ)**

…



The energy dispersion of **nearly-free electron.**

Chapter 4.1: Nearly-Free-Electron Model (近自由电子模型)

➢ Nearly-Free-Electron Model in 1D (一维近自由电子模型)

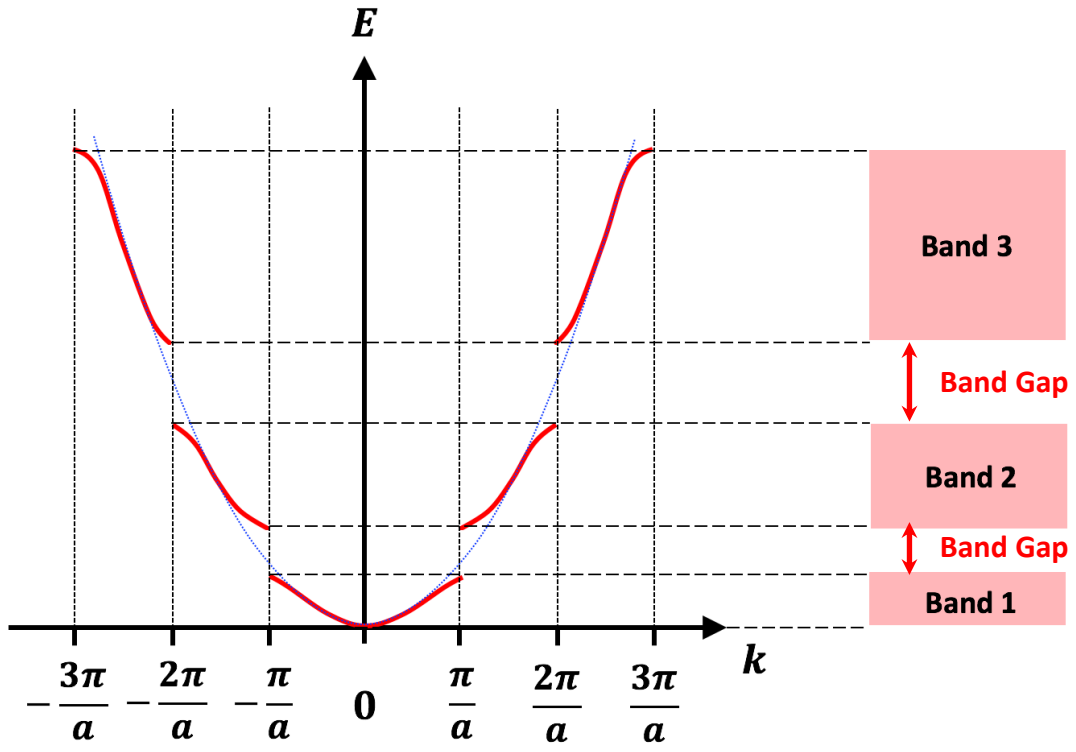
❖ Band gaps (带隙):

$$E_{\text{gap}} = E_+ - E_- = 2|V_n|$$

When $\boldsymbol{k = n\frac{\pi}{a}}$ $(\boldsymbol{n = \pm 1, \pm 2, \cdots})$

Here, $V_n = \frac{1}{a}\int_0^a \mathrm{e}^{-i\frac{2\pi}{a}nx} V(x)\mathrm{d}x$

No electronic states within the band gaps!



The energy dispersion of **nearly-free electron.**

Chapter 4.1: Nearly-Free-Electron Model (近自由电子模型)

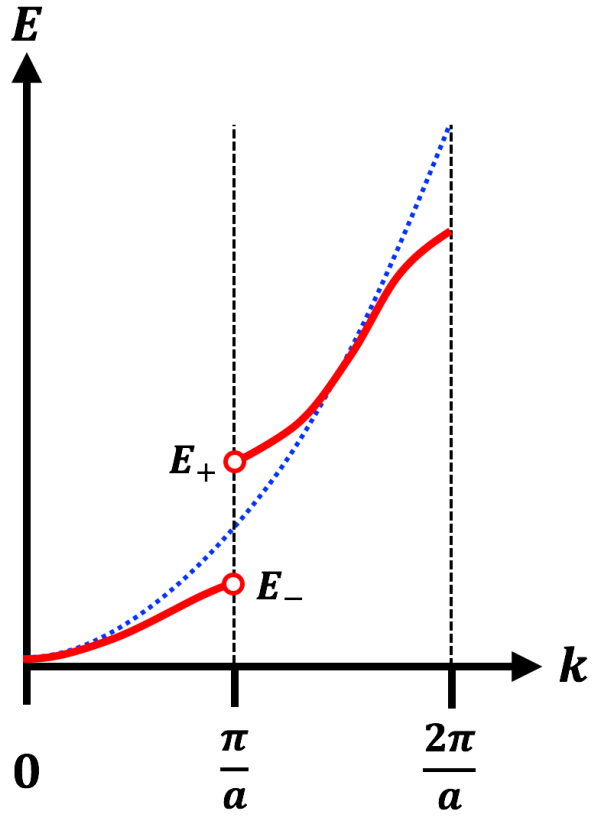
➢ Nearly-Free-Electron Model in 1D (一维近自由电子模型)

❖ The physical origin of band gaps (带隙的物理来源):

Standing waves (驻波) at the boundary of BZs:

$$\psi_+ = \sqrt{\frac{2}{Na}}\cos\left(\frac{\pi}{a}x\right)$$

$$\psi_- = i\sqrt{\frac{2}{Na}}\sin\left(\frac{\pi}{a}x\right)$$

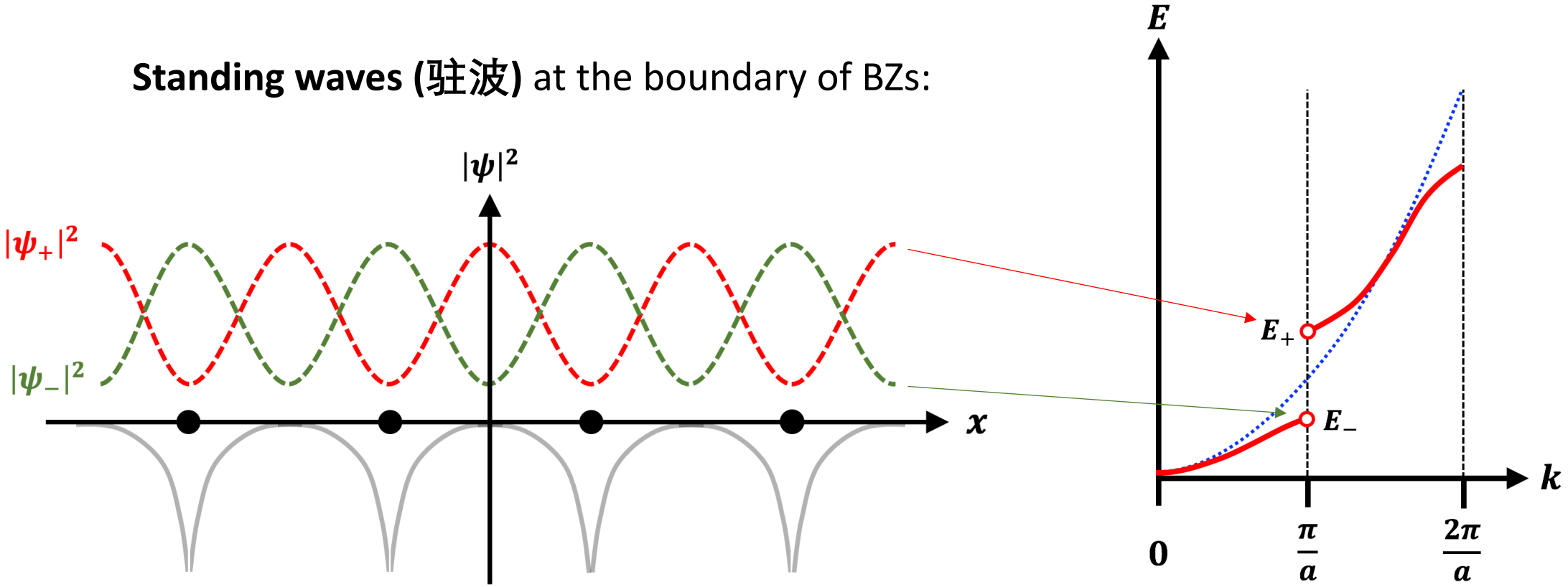


Chapter 4.1: Nearly-Free-Electron Model (近自由电子模型)

➢ Nearly-Free-Electron Model in 1D (一维近自由电子模型)

❖ The physical origin of band gaps (带隙的物理来源):

Standing waves (驻波) at the boundary of BZs:



Chapter 4.1: Nearly-Free-Electron Model (近自由电子模型)

➢ Nearly-Free-Electron Model in 1D (一维近自由电子模型)

❖ The physical origin of band gaps (带隙的物理来源):

The band gaps essentially result from **Bragg reflection (布拉格反射)** at the boundary of Brillouin zones!

The **Bragg condition (布拉格条件)**:

$$\left.\begin{aligned} \boldsymbol{2a = n\lambda} \\ \lambda = \frac{2\pi}{|k|} \end{aligned}\right\} \quad \boxed{|\boldsymbol{k}| = \boldsymbol{n}\frac{\boldsymbol{\pi}}{\boldsymbol{a}} \quad (\boldsymbol{n} = \mathbf{1}, \mathbf{2}, \mathbf{3}, \cdots)}$$

Chapter 4.1: Nearly-Free-Electron Model (近自由电子模型)

➢ Nearly-Free-Electron Model in 1D (一维近自由电子模型)

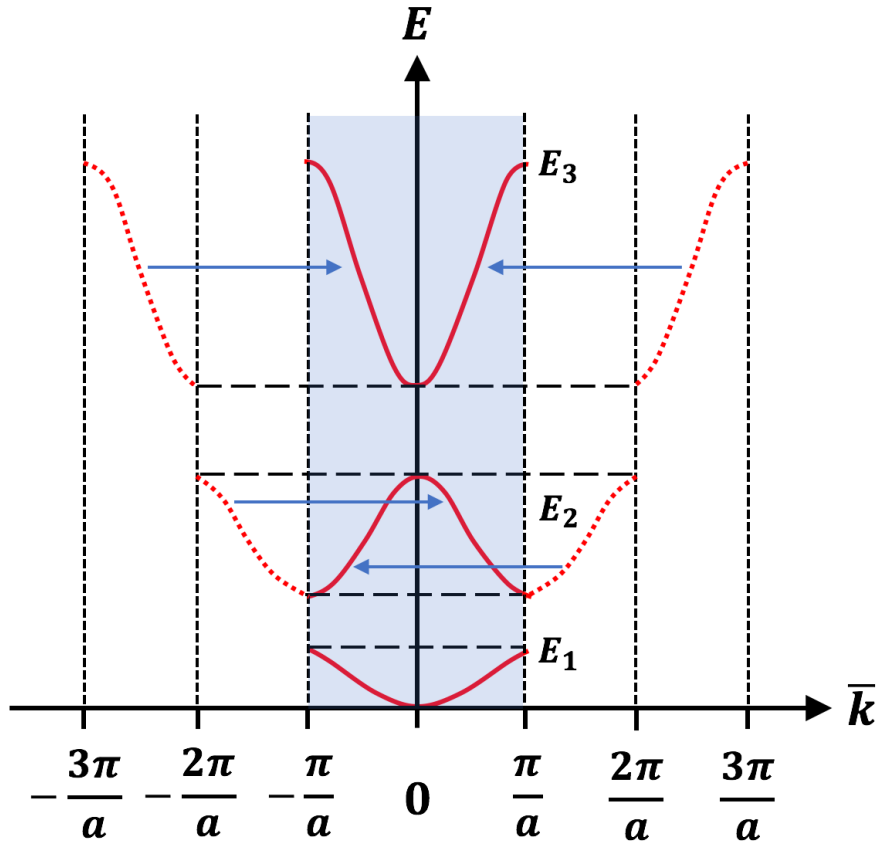
❖ Energy bands in the **reduced Brillouin zone (简约布里渊区):**

The **reduced wave vectors (简约波矢):**

$$-\frac{\pi}{a} \le \bar{k} < \frac{\pi}{a} \quad \text{or} \quad -\frac{\pi}{a} < \bar{k} \le \frac{\pi}{a}$$

The relation between k and $\bar{k}$:

$$k = \bar{k} + n\frac{2\pi}{a} \quad (n = 0, \pm 1, \pm 2, \cdots)$$



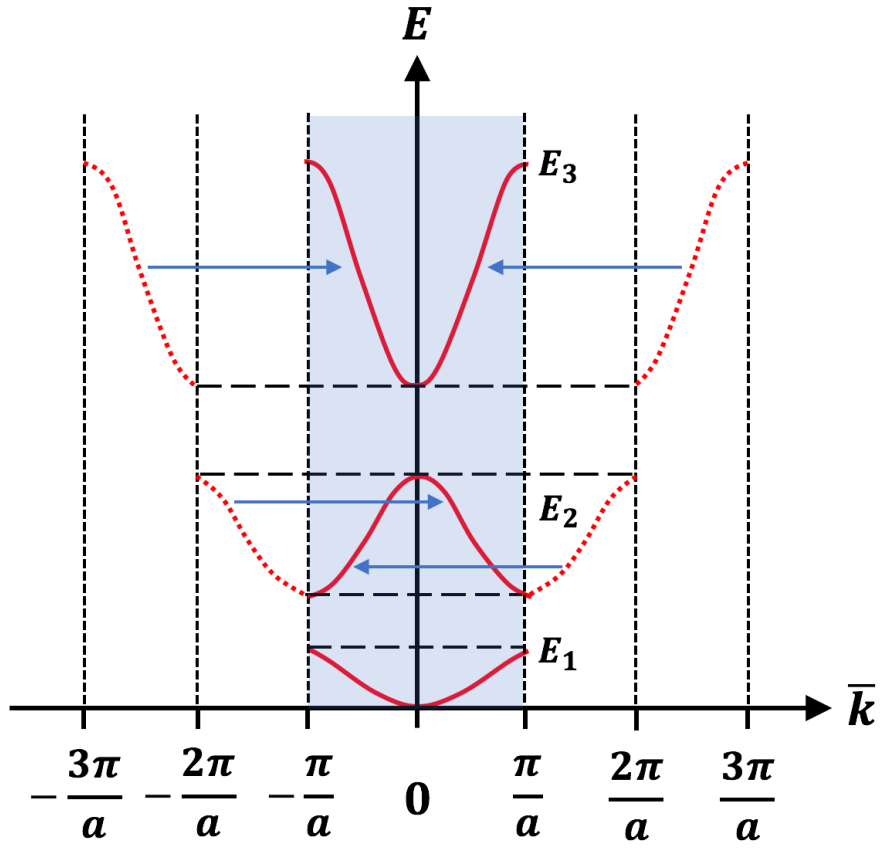
Chapter 4.1: Nearly-Free-Electron Model (近自由电子模型)

➢ Nearly-Free-Electron Model in 1D (一维近自由电子模型)

❖ Energy bands in the **reduced Brillouin zone (简约布里渊区):**

To specify an electronic state in the reduced Brillouin zone (1st BZ), one has to:

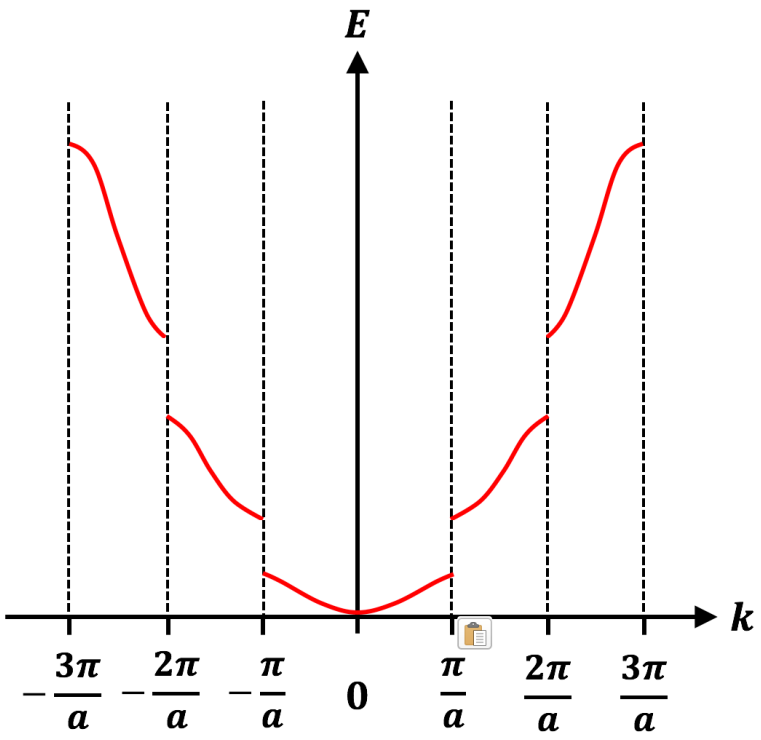
1) label the **band number ($E_1, E_2, \cdots$)** that the state belongs to;
2) identify the **reduced wave vector $\bar{k}$** of the state.



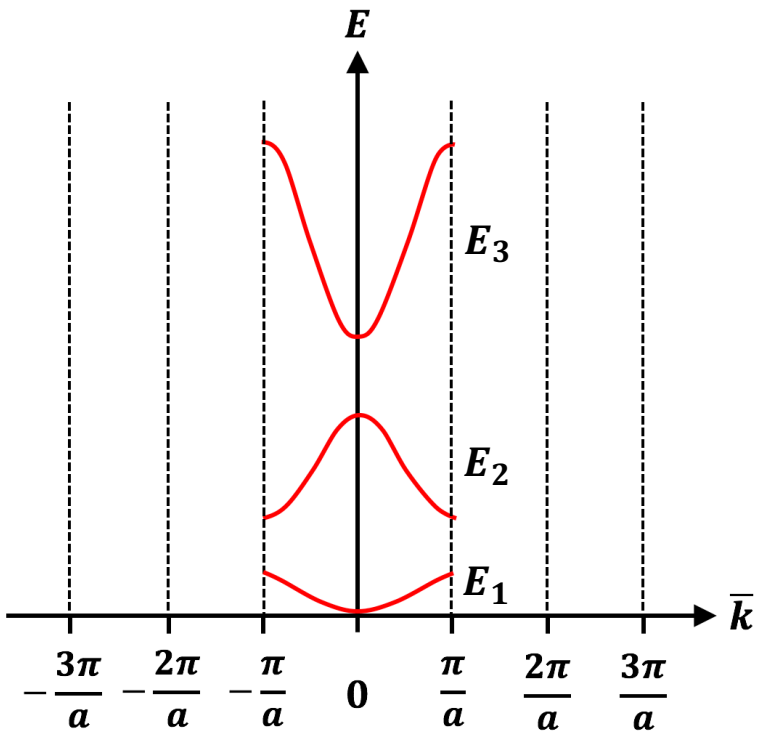
Chapter 4.1: Nearly-Free-Electron Model (近自由电子模型)

➢ Nearly-Free-Electron Model in 1D (一维近自由电子模型)

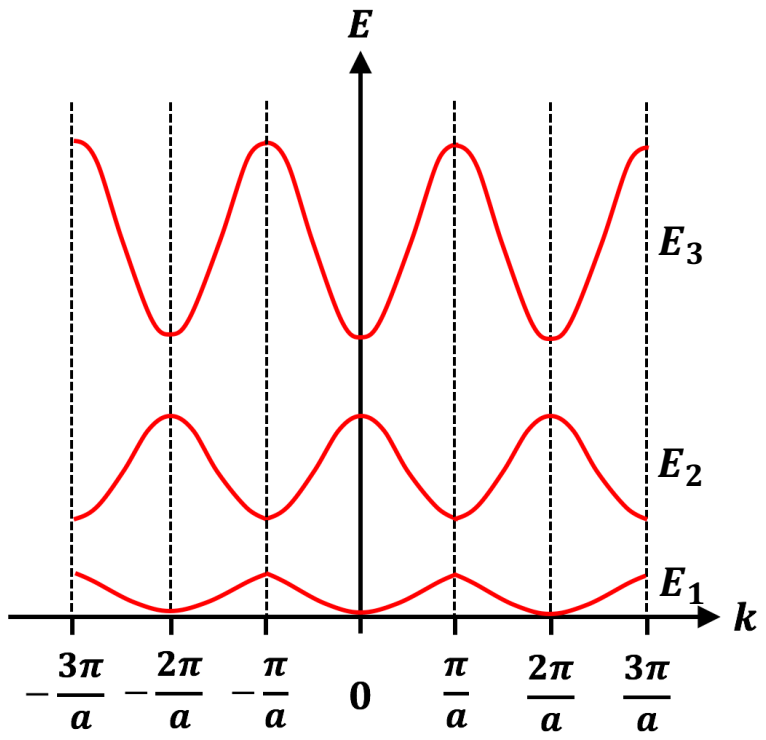
❖ Three ways of presenting energy bands:



Extended diagram (扩展图)



Reduced diagram (简约图)



Periodic diagram (周期图)

Chapter 4.1: Nearly-Free-Electron Model (近自由电子模型)

➢ Nearly-Free-Electron Model in 1D (一维近自由电子模型)

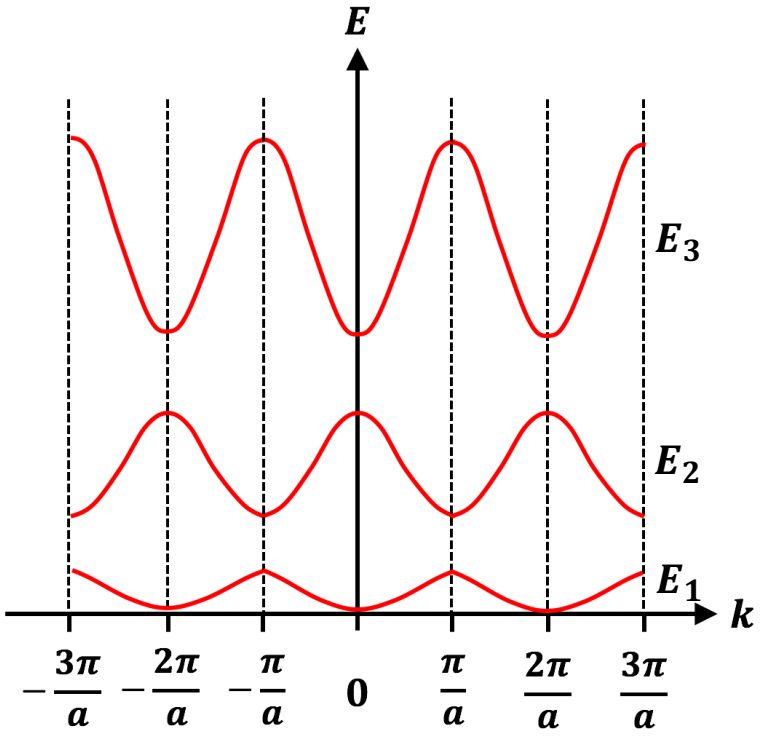
❖ The symmetry of energy bands:

$$E_n(k) = E_n(-k)$$

$$E_n(k) = E_n(k + G_m)$$

$$E_n(k) = E_n(\hat{\alpha}k)$$

Here, $G_m = m\frac{\pi}{a}$ $(m = \pm 1, \pm 2, \cdots)$ denotes a reciprocal vector and $\hat{\alpha}$ a point-symmetry operator.



Periodic diagram (周期图)

Nearly-Free-Electron Model in 3D
(三维近自由电子模型)

Chapter 4.1: Nearly-Free-Electron Model (近自由电子模型)

➢ Nearly-Free-Electron Model in 3D (三维近自由电子模型)

❖ Similar methods can be applied to the case of 3D NFE model.

❖ **The single-electron Schrödinger equation:**

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]\psi(\vec{r}) = E\psi(\vec{r})$$

$$V(\vec{r}+\vec{R}_m) = V(\vec{r}) \qquad \vec{R}_m = m_1\vec{a}_1 + m_2\vec{a}_2 + m_3\vec{a}_3$$

$$V(\vec{r}) = \sum_n V_n e^{i\vec{G}_n\cdot\vec{r}} = \overline{V} + \sum_{n\neq 0} V_n e^{i\vec{G}_n\cdot\vec{r}} \qquad \vec{G}_n = n_1\vec{b}_1 + n_2\vec{b}_2 + n_3\vec{b}_3$$

Chapter 4.1: Nearly-Free-Electron Model (近自由电子模型)

➢ Nearly-Free-Electron Model in 3D (三维近自由电子模型)

❖ The **zeroth-order solutions**:

$$\psi_{\vec{k}}^{(0)} = \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{r}} \qquad E_{\vec{k}}^{(0)} = \frac{\hbar^2 k^2}{2m} + \bar{V}$$

$$\vec{k} = \frac{l_1}{N_1}\vec{b}_1 + \frac{l_2}{N_2}\vec{b}_2 + \frac{l_3}{N_3}\vec{b}_3$$

Chapter 4.1: Nearly-Free-Electron Model (近自由电子模型)

➢ Nearly-Free-Electron Model in 3D (三维近自由电子模型)

❖ The **higher-order corrections**:

$$\boldsymbol{\psi}_{\vec{k}}^{(1)} = \sum_{\vec{k}' \neq \vec{k}} \frac{\langle \vec{k}' | \Delta \boldsymbol{V} | \vec{k} \rangle}{\boldsymbol{E}_{\vec{k}}^{(0)} - \boldsymbol{E}_{\vec{k}'}^{(0)}} \boldsymbol{\psi}_{\vec{k}'}^{(0)} \qquad \boldsymbol{E}_{\vec{k}}^{(2)} = \sum_{\vec{k}' \neq \vec{k}} \frac{\left| \langle \vec{k}' | \Delta \boldsymbol{V} | \vec{k} \rangle \right|^2}{\boldsymbol{E}_{\vec{k}}^{(0)} - \boldsymbol{E}_{\vec{k}'}^{(0)}}$$

$$\langle \vec{k}' | \Delta V | \vec{k} \rangle = \langle \vec{k}' | V(\vec{r}) | \vec{k} \rangle = \frac{1}{v} \int_{\mathrm{pc}} \mathrm{e}^{-i\vec{G}_n \cdot \vec{r}} V(\vec{r}) \mathrm{d}\vec{r} = V_n \qquad \vec{\boldsymbol{k}}' - \vec{\boldsymbol{k}} = \vec{\boldsymbol{G}}_{\boldsymbol{n}}$$

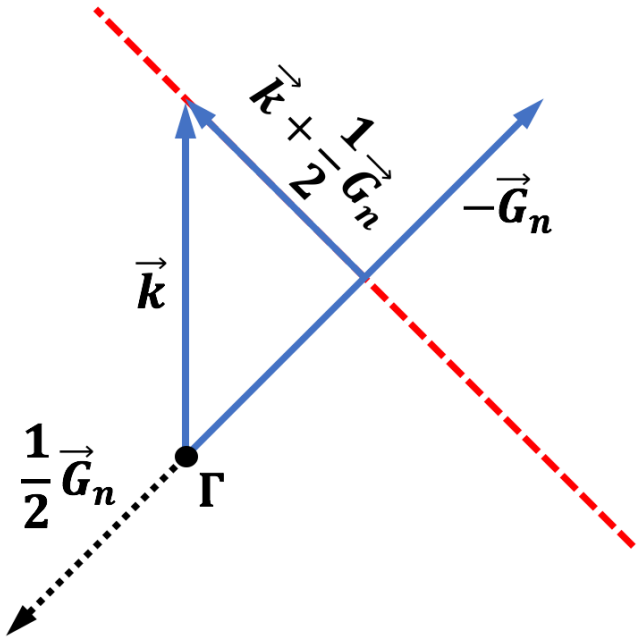
Here, v denotes the volume of a **primitive cell (pc)** and the integral is performed within a **pc**.

Chapter 4.1: Nearly-Free-Electron Model (近自由电子模型)

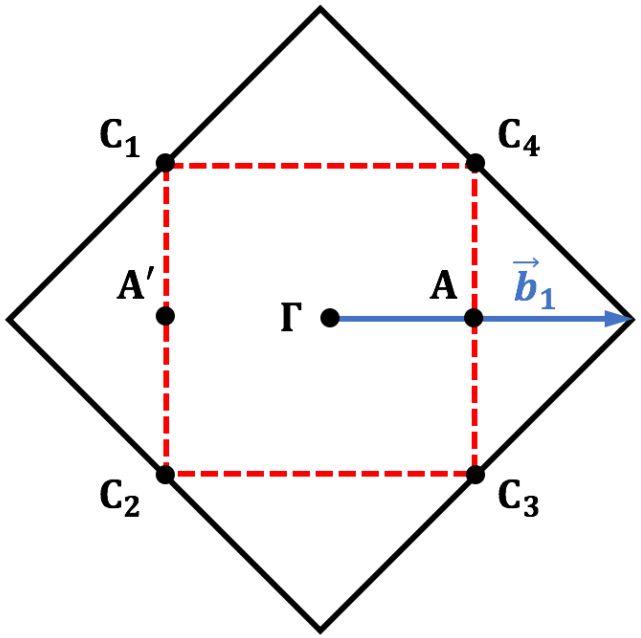
➢ Nearly-Free-Electron Model in 3D (三维近自由电子模型)

❖ **Band gaps** open up at the **boundary of Brillouin zones**:

$$\vec{G}_n \cdot \left(\vec{k} + \frac{1}{2}\vec{G}_n\right) = 0$$



Equations for the boundary of BZs



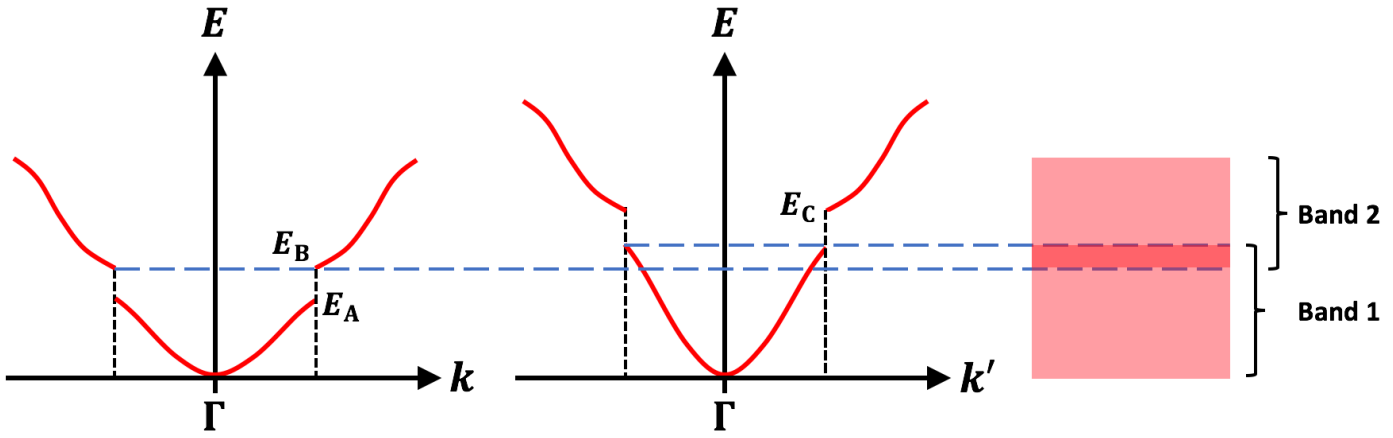
An example of simple cubic BZ

Chapter 4.1: Nearly-Free-Electron Model (近自由电子模型)

➢ Nearly-Free-Electron Model in 3D (三维近自由电子模型)

❖ **Band gaps** open up at the **boundary of Brillouin zones**:

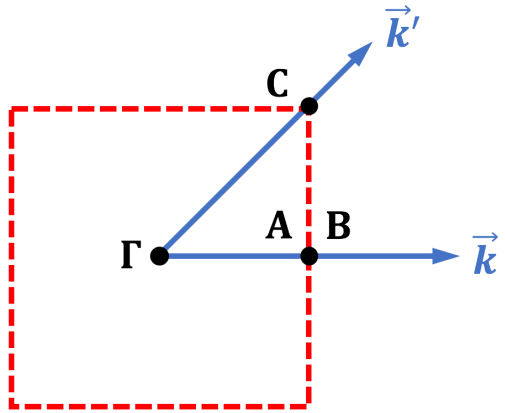
In some **special cases**, while band gaps open up along different directions, the overall band gap may not be observed!



Band dispersion along $\Gamma \rightarrow A$.

Band dispersion along $\Gamma \rightarrow C$.

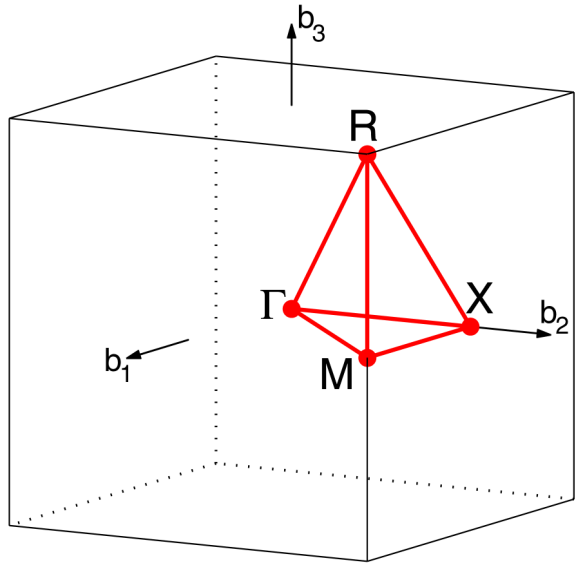
No overall band gap!



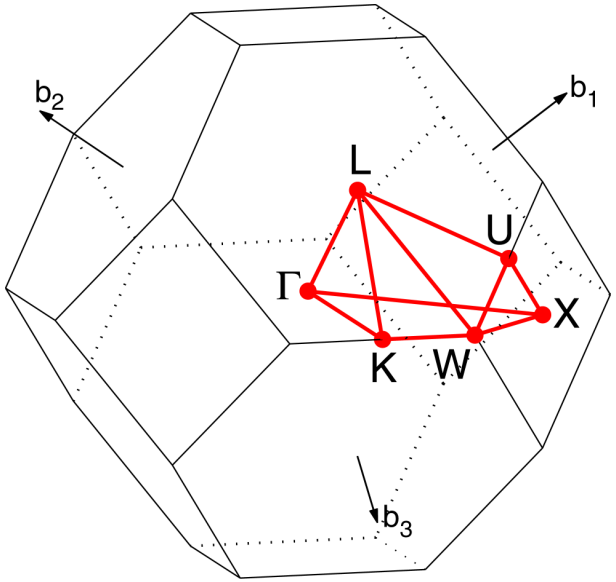
Chapter 4.1: Nearly-Free-Electron Model (近自由电子模型)

➢ Nearly-Free-Electron Model in 3D (三维近自由电子模型)

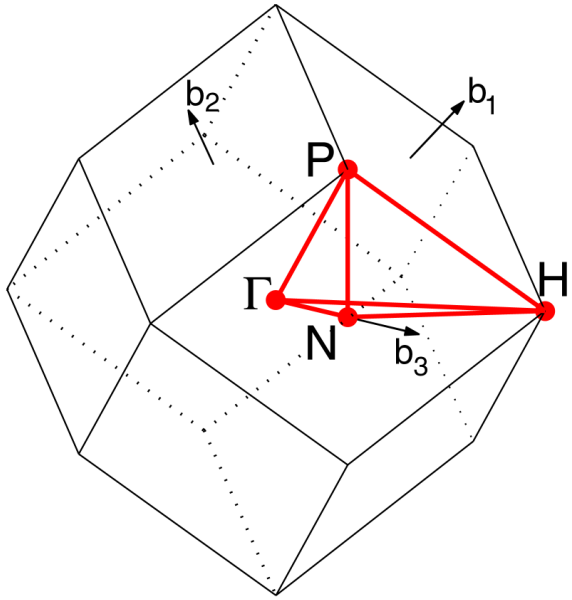
❖ The **reduced Brillouin zone (1st Brillouin zone)** in 3D:



Simple cubic



Body-centered cubic



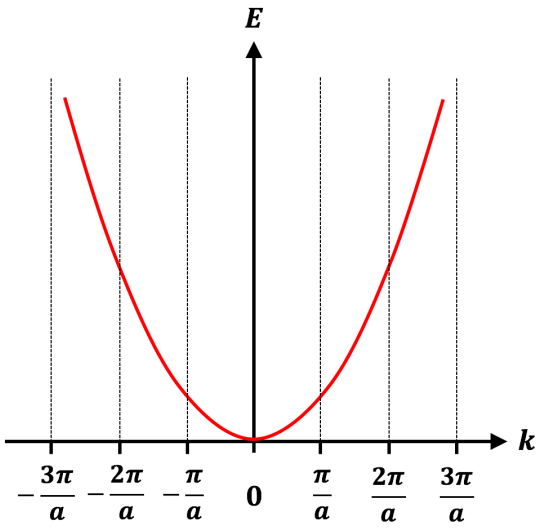
Face-centered cubic

Summary (总结)

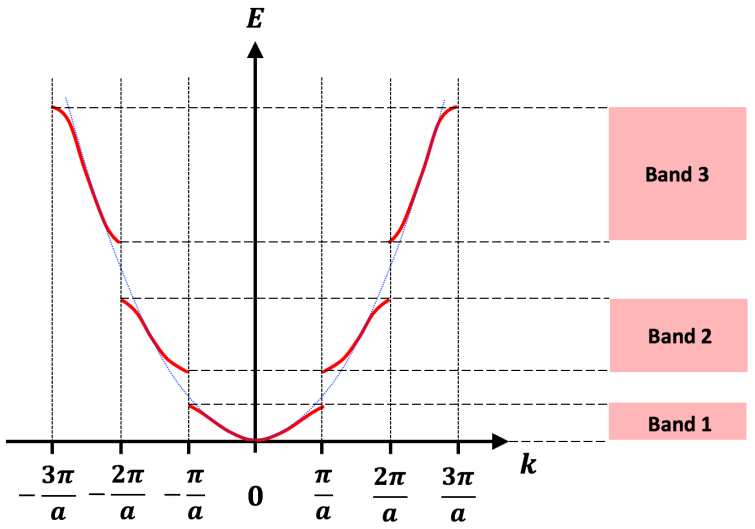
Chapter 4.1: Nearly-Free-Electron Model (近自由电子模型)

➢ Summary

- ❖ **Electronic energy bands** are formed as a result of the periodic potential of crystals.
- ❖ **Band gaps** open up at the **boundary of Brillouin zones** as a result of **Bragg reflection**.
- ❖ **No electronic states** are allowed within the **band gaps**.



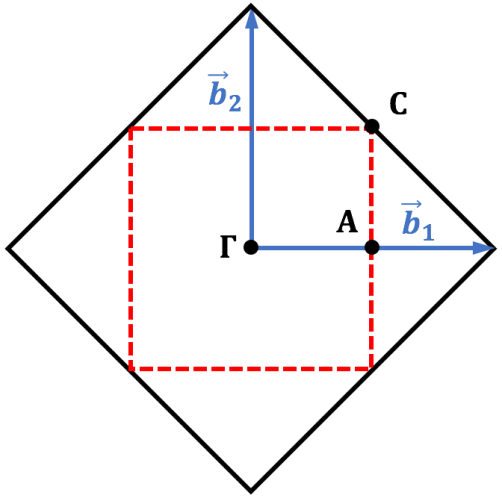
Quasi-continuous **energy levels** (准连续**能级**)



A series of **energy bands** (一系列**能带**)

Chapter 4.1: 课后作业

1. 对于边长为a的二维正方晶格，证明：
自由电子在第一布里渊区边界（如右图所示）C点处的动能是A点处动能的2倍。



2. 对于一维近自由电子模型，$k = \pm\frac{2\pi}{a}$状态简并微扰的能量为E_+和E_-，求出对应的波函数ψ_+和ψ_-，并说明它们都代表驻波。（假设$V_n = V_n^*$）

提交时间： 4月10日之前

提交方式： 手写（写明姓名学号）后拍照，通过本班课代表统一提交电子版