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)

Objectives

- To learn the **tight-binding approximation**.
- To understand the **characteristics of energy band for a 1D TB model**.

Tight-Binding Approximation
(紧束缚近似)

Chapter 4.2: Tight-Binding Model (紧束缚模型)

➢ Tight-Binding Approximation (紧束缚近似)

❖ The tight-binding (TB) approximation states that:

- The valence electrons are **tightly bound to the atom to which they belong**;
- The valence electrons have **limited interactions with** the potentials on the **surrounding atoms**;
- The potentials on the surrounding atoms can be treated as a **perturbation**.

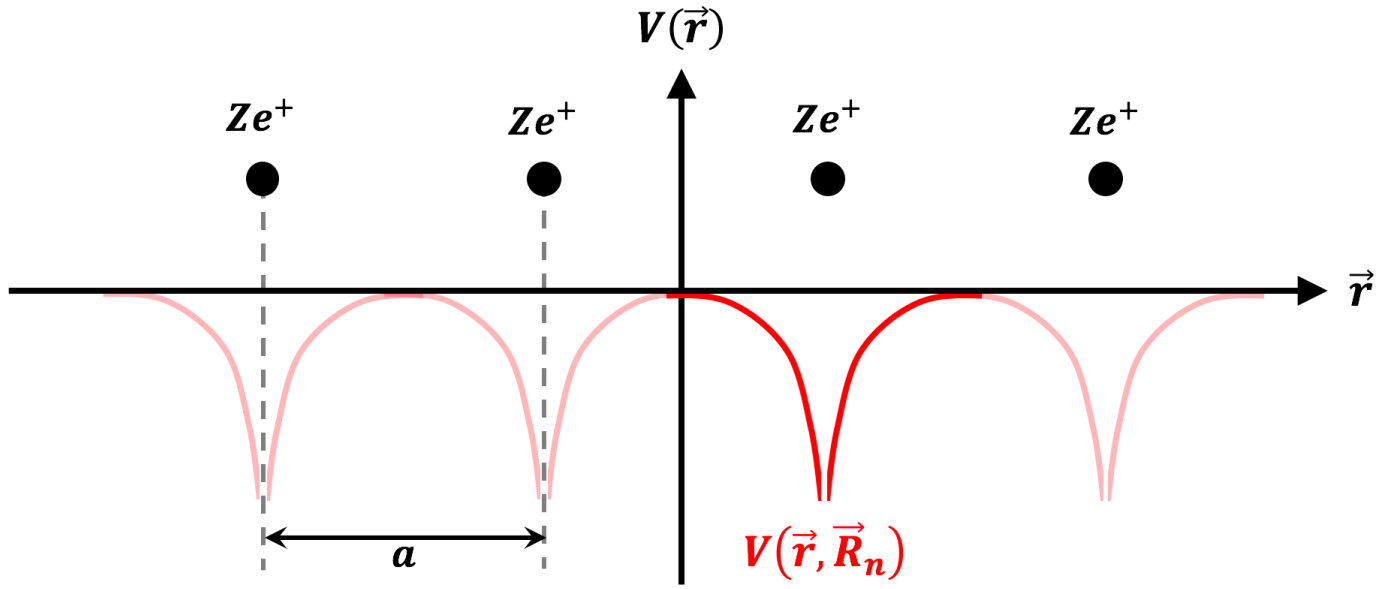
The TB approximation can give a clear picture of how the energy bands of crystals are connected with the energy levels of atoms/molecules!

Chapter 4.2: Tight-Binding Model (紧束缚模型)

➢ Tight-Binding Approximation (紧束缚近似)

❖ The potential of a crystal in the TB approximation:

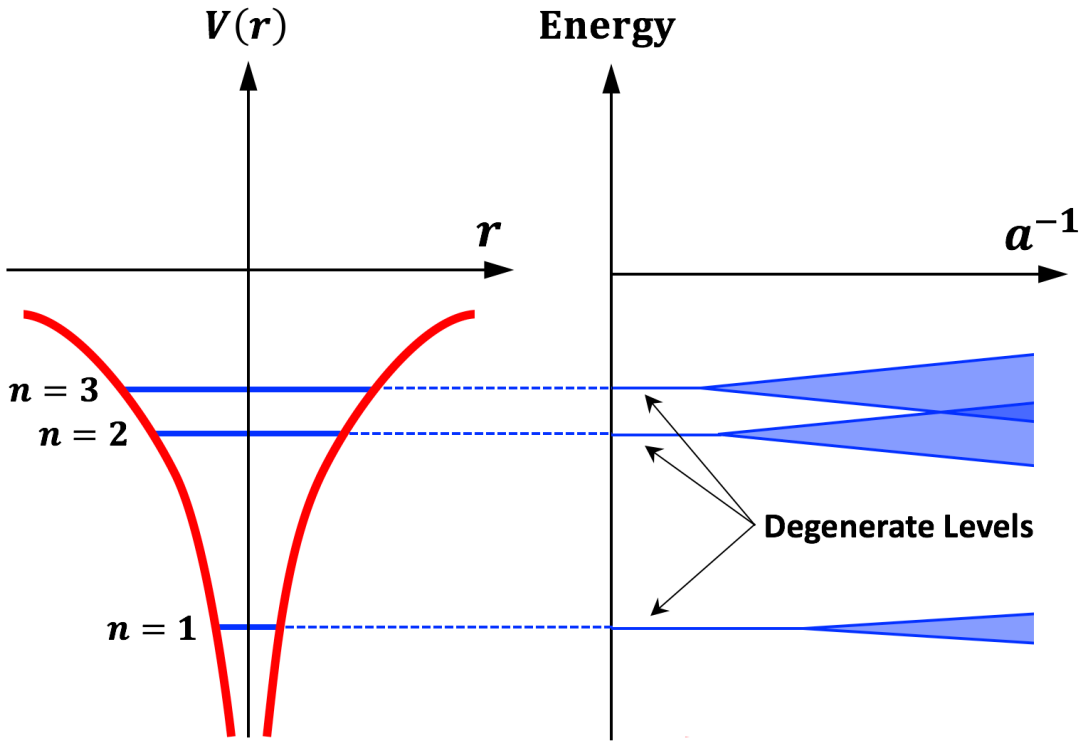
$$V(\vec{r}) = V_0(\vec{r}) + \Delta V(\vec{r}) = \boldsymbol{V}\left(\vec{\boldsymbol{r}}, \vec{R}_{\mathrm{n}}\right) + \left[\boldsymbol{V}(\vec{\boldsymbol{r}}) - \boldsymbol{V}\left(\vec{r}, \vec{R}_{\mathrm{n}}\right)\right]$$



Chapter 4.2: Tight-Binding Model (紧束缚模型)

➢ Tight-Binding Approximation (紧束缚近似)

❖ The correspondence between energy levels and energy bands:



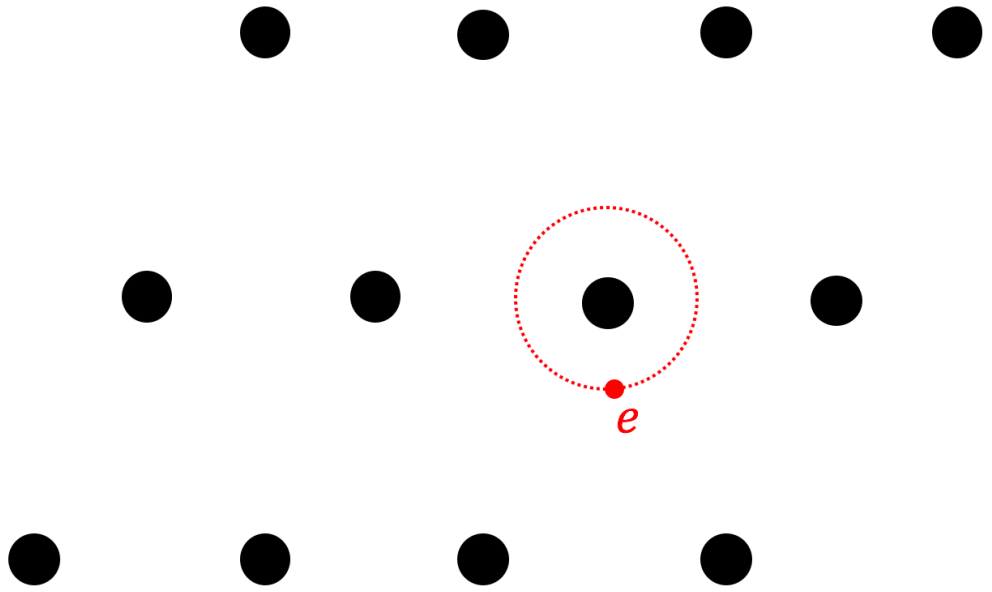
Schematic diagram of the energy levels of an atom (left) and the energy bands of a crystal consisting of the same types of atoms (right). Here, a denotes interatomic distance.

Method of LCAO
(原子轨道线性组合法)

Chapter 4.2: Tight-Binding Model (紧束缚模型)

➢ Method of Linear Combination of Atomic Orbitals (原子轨道线性组合法)

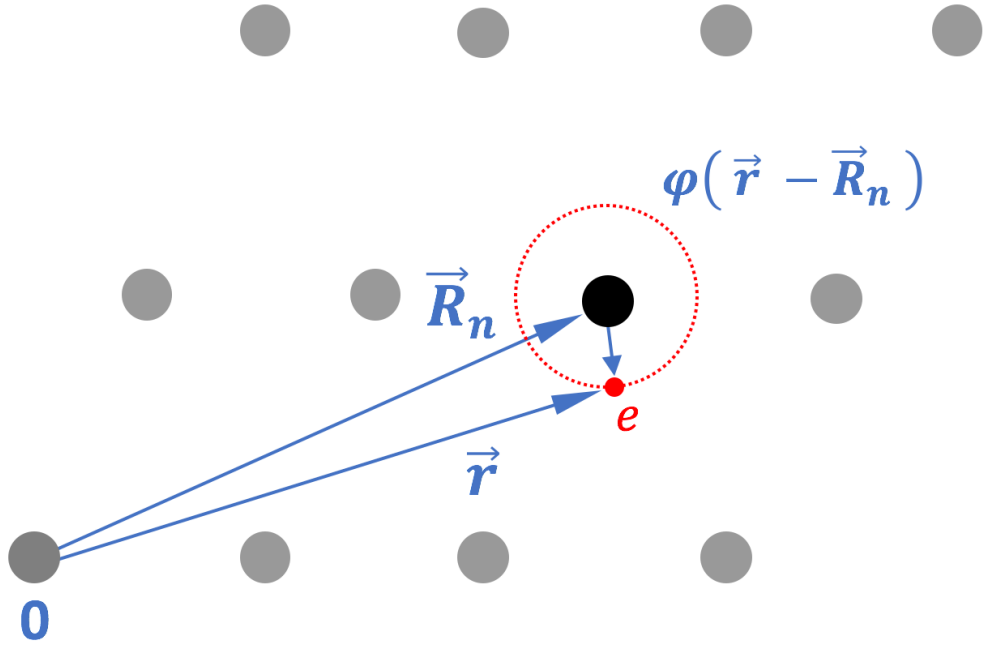
❖ We consider a **3D** monoatomic lattice with $\boldsymbol{N = N_1 N_2 N_3}$ atoms. Each atom has one valence electron with mass $\boldsymbol{m}$**.** The electrons move in the crystal lattice with a periodic potential.



Chapter 4.2: Tight-Binding Model (紧束缚模型)

➢ Method of Linear Combination of Atomic Orbitals (原子轨道线性组合法)

❖ When the **interatomic interactions are fully neglected**, the valence electron of an atom with position $\vec{R}_n = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$ moves only around the isolated atom in its **localized atomic orbital** $\varphi(\vec{r} - \vec{R}_n)$.



Chapter 4.2: Tight-Binding Model (紧束缚模型)

➢ Method of Linear Combination of Atomic Orbitals (原子轨道线性组合法)

❖ The Schrödinger equation for the electron in the **isolated atom** reads:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + \boldsymbol{V}\left(\vec{\boldsymbol{r}} - \vec{\boldsymbol{R}}_{\boldsymbol{n}}\right)\right]\boldsymbol{\varphi}\left(\vec{\boldsymbol{r}} - \vec{\boldsymbol{R}}_{\boldsymbol{n}}\right) = \boldsymbol{\varepsilon}\boldsymbol{\varphi}\left(\vec{\boldsymbol{r}} - \vec{\boldsymbol{R}}_{\boldsymbol{n}}\right)$$

Here, $V\left(\vec{r} - \vec{R}_n\right)$ denotes the **atomic potential** of the atom at $\vec{\boldsymbol{R}}_{\boldsymbol{n}}$ and $\boldsymbol{\varepsilon}$ the energy level of the atomic orbital.

Chapter 4.2: Tight-Binding Model (紧束缚模型)

➢ Method of Linear Combination of Atomic Orbitals (原子轨道线性组合法)

❖ The single-electron Schrödinger equation for the **crystal lattice** reads:

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

Here, $V(\vec{r})$ denotes the **periodic potential** of the lattice and $\boldsymbol{E}$ and $\boldsymbol{\psi}(\vec{\boldsymbol{r}})$ the electron energy and wavefunction in the crystal.

Chapter 4.2: Tight-Binding Model (紧束缚模型)

➢ Method of Linear Combination of Atomic Orbitals (原子轨道线性组合法)

❖ **Perturbation-theory** treatment:

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + \boldsymbol{V}(\vec{\boldsymbol{r}})$$

$$\hat{\boldsymbol{H}} = \hat{\boldsymbol{H}}_{\boldsymbol{0}} + \hat{\boldsymbol{H}}' \qquad \hat{H}_0 = -\frac{\hbar^2}{2m}\nabla^2 + \boldsymbol{V}\left(\vec{\boldsymbol{r}} - \vec{\boldsymbol{R}}_{\boldsymbol{n}}\right)$$

$$\hat{H}' = \boldsymbol{V}(\vec{\boldsymbol{r}}) - \boldsymbol{V}\left(\vec{\boldsymbol{r}} - \vec{\boldsymbol{R}}_{\boldsymbol{n}}\right) \quad \textbf{(Perturbation)}$$

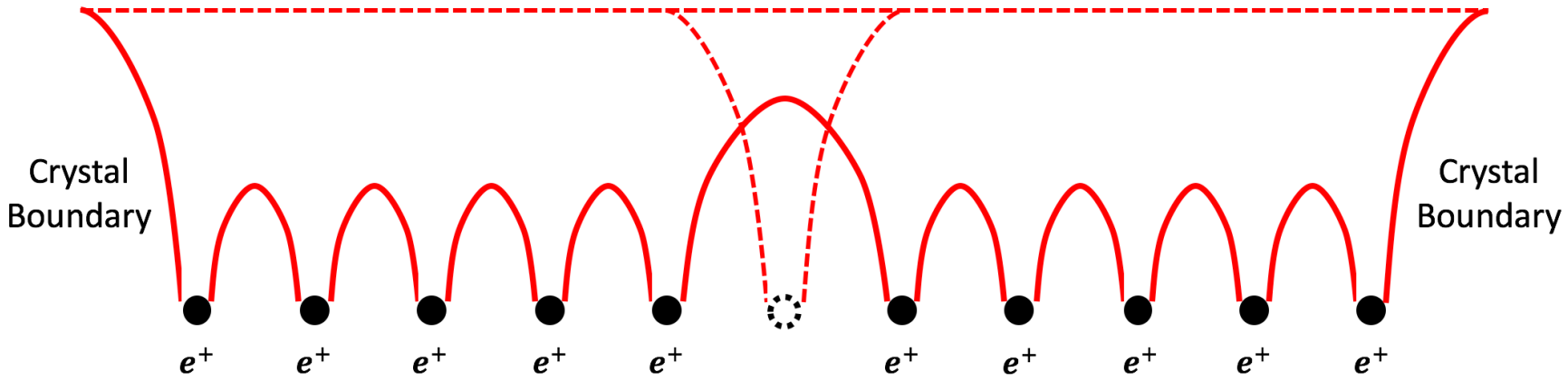
Note that: $\boldsymbol{V}(\vec{\boldsymbol{r}}) = \sum_{\boldsymbol{j}=\boldsymbol{1}}^{\boldsymbol{N}} \boldsymbol{V}\left(\vec{\boldsymbol{r}} - \vec{\boldsymbol{R}}_{\boldsymbol{j}}\right)$.

Chapter 4.2: Tight-Binding Model (紧束缚模型)

➢ Method of Linear Combination of Atomic Orbitals (原子轨道线性组合法)

❖ **Perturbation-theory** treatment:

$$\hat{H}'(\vec{r}) = V(\vec{r}) - V(\vec{r} - \vec{R}_n)$$



Schematic diagram of the perturbation potential $\hat{H}'$

Chapter 4.2: Tight-Binding Model (紧束缚模型)

➢ Method of Linear Combination of Atomic Orbitals (原子轨道线性组合法)

❖ **Perturbation-theory** treatment:

In the zeroth-order approximation:

$$\hat{H}_0\varphi(\vec{r}-\vec{R}_n)=\varepsilon\varphi(\vec{r}-\vec{R}_n)$$

Since the energy level ε is **degenerate** for all the isolated atomic orbitals, we have to apply the **degenerate perturbation theory**.

Chapter 4.2: Tight-Binding Model (紧束缚模型)

➢ Method of Linear Combination of Atomic Orbitals (原子轨道线性组合法)

❖ **Perturbation-theory** treatment:

The wave function of the crystal can be built up by a **linear combination of the atomic orbitals (LCAO)**:

$$\psi(\vec{r}) = \sum_n \alpha_n \varphi\left(\vec{r} - \vec{R}_n\right)$$

Chapter 4.2: Tight-Binding Model (紧束缚模型)

➢ Method of Linear Combination of Atomic Orbitals (原子轨道线性组合法)

❖ **Perturbation-theory** treatment:

It can be expected that the coefficient $\boldsymbol{\alpha_n}$ of the linear combination satisfies:

$$\boldsymbol{\alpha_n = \frac{1}{\sqrt{N}} e^{i\vec{k}\cdot\vec{R}_n}}$$

$$\psi(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} \frac{1}{\sqrt{N}} \sum_n e^{-i\vec{k}\cdot(\vec{r}-\vec{R}_n)} \varphi\left(\vec{r}-\vec{R}_n\right) = e^{i\vec{k}\cdot\vec{r}} u(\vec{r}) \quad \textbf{(Bloch wave)}$$

Chapter 4.2: Tight-Binding Model (紧束缚模型)

➢ Method of Linear Combination of Atomic Orbitals (原子轨道线性组合法)

❖ **Perturbation-theory** treatment:

By applying $\psi(\vec{r})$ to $\vec{H}\psi(\vec{r}) = E\psi(\vec{r})$, it is obtained:

$$\sum_{n} \boldsymbol{\alpha_n} \left[\boldsymbol{\varepsilon} + \hat{\boldsymbol{H}}'(\vec{\boldsymbol{r}})\right] \boldsymbol{\varphi}\left(\vec{\boldsymbol{r}} - \vec{\boldsymbol{R}}_{\boldsymbol{n}}\right) = \boldsymbol{E} \sum_{n} \boldsymbol{\alpha_n}\, \boldsymbol{\varphi}\left(\vec{\boldsymbol{r}} - \vec{\boldsymbol{R}}_{\boldsymbol{n}}\right)$$

Chapter 4.2: Tight-Binding Model (紧束缚模型)

➢ Method of Linear Combination of Atomic Orbitals (原子轨道线性组合法)

❖ **Perturbation-theory** treatment:

Since the interactions between atoms are very weak, it can be approximated that:

$$\int \boldsymbol{\varphi}^*(\vec{\boldsymbol{r}} - \vec{\boldsymbol{R}}_{\boldsymbol{m}})\boldsymbol{\varphi}(\vec{\boldsymbol{r}} - \vec{\boldsymbol{R}}_{\boldsymbol{n}})\mathrm{d}\vec{\boldsymbol{r}} = \boldsymbol{\delta}_{\boldsymbol{mn}}$$

Chapter 4.2: Tight-Binding Model (紧束缚模型)

➢ Method of Linear Combination of Atomic Orbitals (原子轨道线性组合法)

❖ **Perturbation-theory** treatment:

By applying to the Schrödinger equation, we obtain:

$$-\sum_n \alpha_n J\left(\vec{R}_m - \vec{R}_n\right) = (E - \varepsilon)a_m$$

Here, $$-\boldsymbol{J\left(\vec{R}_m - \vec{R}_n\right)} = \int \boldsymbol{\varphi}^*\left(\vec{\xi} - \left(\vec{R}_m - \vec{R}_n\right)\right)\hat{H}'\left(\vec{\xi}\right)\boldsymbol{\varphi}\left(\vec{\xi}\right)\mathrm{d}\vec{\xi}$$

Chapter 4.2: Tight-Binding Model (紧束缚模型)

➢ Method of Linear Combination of Atomic Orbitals (原子轨道线性组合法)

❖ **Perturbation-theory** treatment:

By applying $\boldsymbol{\alpha_n = \frac{1}{\sqrt{N}} e^{i\vec{k}\cdot\vec{R}_n}}$, we end up with the final solutions:

$$E_k = \varepsilon - \sum_s J(\vec{R}_s) e^{-i\vec{k}\cdot\vec{R}_s}$$

$$\psi_k(\vec{r}) = \frac{1}{\sqrt{N}} \sum_n e^{i\vec{k}\cdot\vec{R}_n} \varphi(\vec{r} - \vec{R}_n)$$

$\vec{R}_s = \vec{R}_m - \vec{R}_n$

(the separation between sites m and n)

$\vec{k} = \frac{h_1}{N_1}\vec{b}_1 + \frac{h_2}{N_2}\vec{b}_2 + \frac{h_3}{N_3}\vec{b}_3$

($h_1 h_2 h_3$ are integers)

Chapter 4.2: Tight-Binding Model (紧束缚模型)

➢ Method of Linear Combination of Atomic Orbitals (原子轨道线性组合法)

❖ **Perturbation-theory** treatment:

Since the interactions between atoms are very weak, we can further obtain:

- When $\vec{R}_s = \vec{R}_m - \vec{R}_n = 0$

$$\boldsymbol{J}(\vec{R}_s) = -\int \boldsymbol{\varphi}^*(\vec{\xi})\hat{\boldsymbol{H}}'(\vec{\xi})\boldsymbol{\varphi}(\vec{\xi})\mathrm{d}\vec{\xi} = \boldsymbol{J_0}$$

(called "site energy" 在位能)

- When $\vec{R}_s = \vec{a}$ (neighbors)

$$\boldsymbol{J}(\vec{R}_s) = -\int \boldsymbol{\varphi}^*(\vec{\xi}-\vec{\boldsymbol{a}})\hat{\boldsymbol{H}}'(\vec{\xi})\boldsymbol{\varphi}(\vec{\xi})\mathrm{d}\vec{\xi} = \boldsymbol{J_1}(\vec{\boldsymbol{a}})$$

(called "overlap integral" 交叠积分)

Chapter 4.2: Tight-Binding Model (紧束缚模型)

➢ Method of Linear Combination of Atomic Orbitals (原子轨道线性组合法)

❖ **Perturbation-theory** treatment:

Since the interactions between atoms are very weak, we can further obtain:

$$E_k = \varepsilon - J_0 - \sum_{j=\mathrm{nbs}} J_1(\vec{a}_j)\mathrm{e}^{-i\vec{k}\cdot\vec{a}_j}$$

$$\vec{k} = \frac{h_1}{N_1}\vec{b}_1 + \frac{h_2}{N_2}\vec{b}_2 + \frac{h_3}{N_3}\vec{b}_3 \qquad (h_1 h_2 h_3 \text{ are integers})$$

Chapter 4.2: Tight-Binding Model (紧束缚模型)

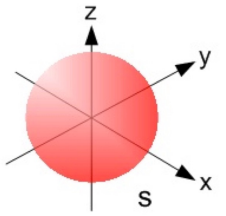
➢ Method of Linear Combination of Atomic Orbitals (原子轨道线性组合法)

❖ **Example:** the energy band of ***s*** **orbitals** in a **simple cubic lattice**.

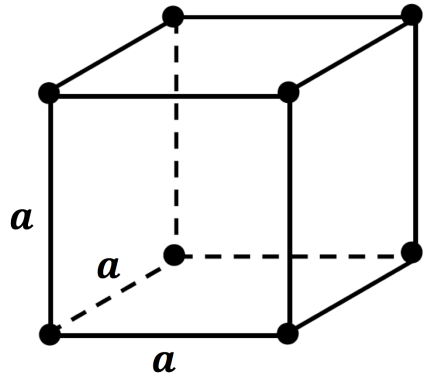
$$E_k = \varepsilon - J_0 - \sum_{j=\text{nbs}} J_1(\vec{a}_j)\mathrm{e}^{-i\vec{k}\cdot\vec{a}_j}$$

For a given site $(0,0,0)$, the coordinates of the 6 neighboring sites:

$$(\pm a, 0,0) \quad (0, \pm a, 0) \quad (0,0, \pm a)$$



s **orbital**



$$\rightarrow \quad E_k = \varepsilon - J_0 - J_1\left(\mathrm{e}^{ik_x a} + \mathrm{e}^{-ik_x a} + \mathrm{e}^{ik_y a} + \mathrm{e}^{-ik_y a} + \mathrm{e}^{ik_z a} + \mathrm{e}^{-ik_z a}\right)$$

$$\rightarrow \quad \boxed{E_k = \varepsilon - J_0 - 2J_1\left(\cos k_x a + \cos k_y a + \cos k_z a\right)}$$

Chapter 4.2: Tight-Binding Model (紧束缚模型)

➢ Method of Linear Combination of Atomic Orbitals (原子轨道线性组合法)

❖ **Example:** the energy band of ***s*** **orbitals** in a **simple cubic lattice**.

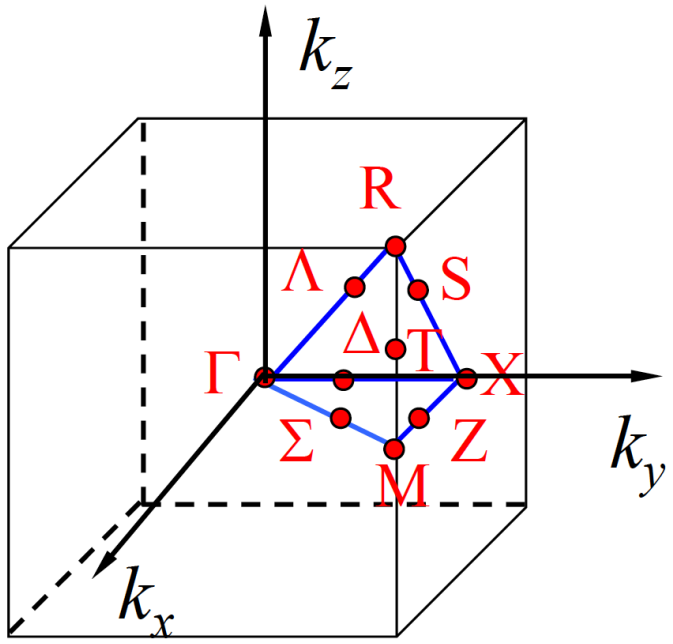
The energy at the high symmetry points in reciprocal space:

$$\Gamma(0,0,0): \quad E(\Gamma) = \varepsilon - J_0 - 6J_1$$

$$\mathrm{X}\left(0,\frac{\pi}{a},0\right): \quad E(\mathrm{X}) = \varepsilon - J_0 - 2J_1$$

$$\mathrm{R}\left(\frac{\pi}{a},\frac{\pi}{a},\frac{\pi}{a}\right): \quad E(\mathrm{R}) = \varepsilon - J_0 + 6J_1$$

$$\mathrm{M}\left(\frac{\pi}{a},\frac{\pi}{a},0\right): \quad E(\mathrm{M}) = \varepsilon - J_0 + 2J_1$$



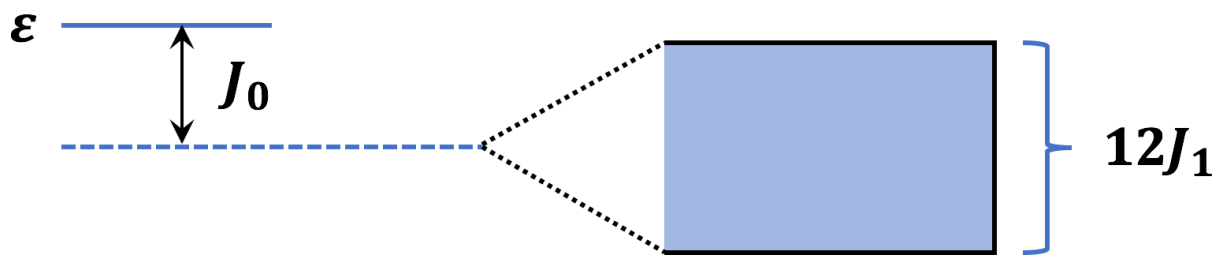
Here, $J_0 > 0$ and $J_1 > 0$

Chapter 4.2: Tight-Binding Model (紧束缚模型)

➢ Method of Linear Combination of Atomic Orbitals (原子轨道线性组合法)

❖ **Example:** the energy band of s **orbitals** in a **simple cubic lattice**.

The band width (带宽): $\Delta E = E(\mathrm{R}) - E(\Gamma) = 12J_1$



The bandwidth is determined by the **magnitude of J_1**, i.e., the overlap integral between neighboring atomic orbitals!

From Energy Levels to Energy Bands
(从能级到能带)

Chapter 4.2: Tight-Binding Model (紧束缚模型)

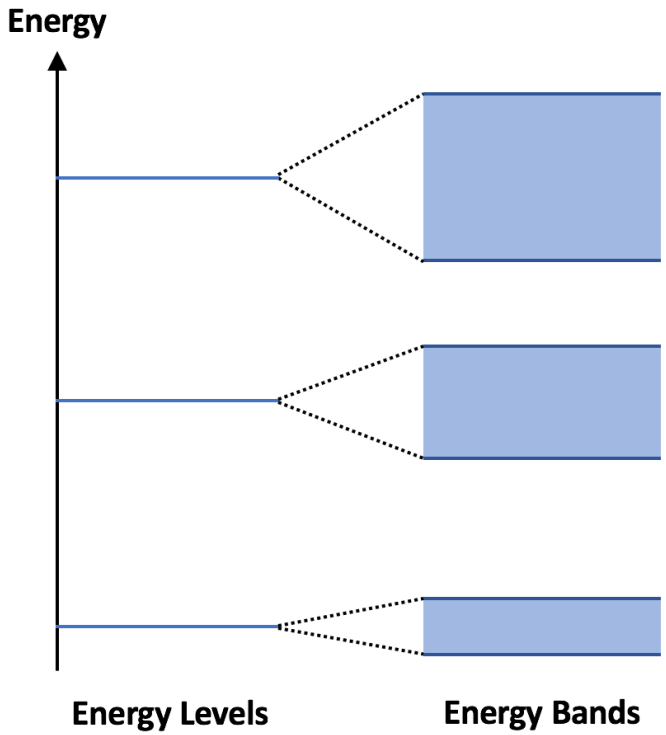
➢ From Energy Levels to Energy Bands (从能级到能带)

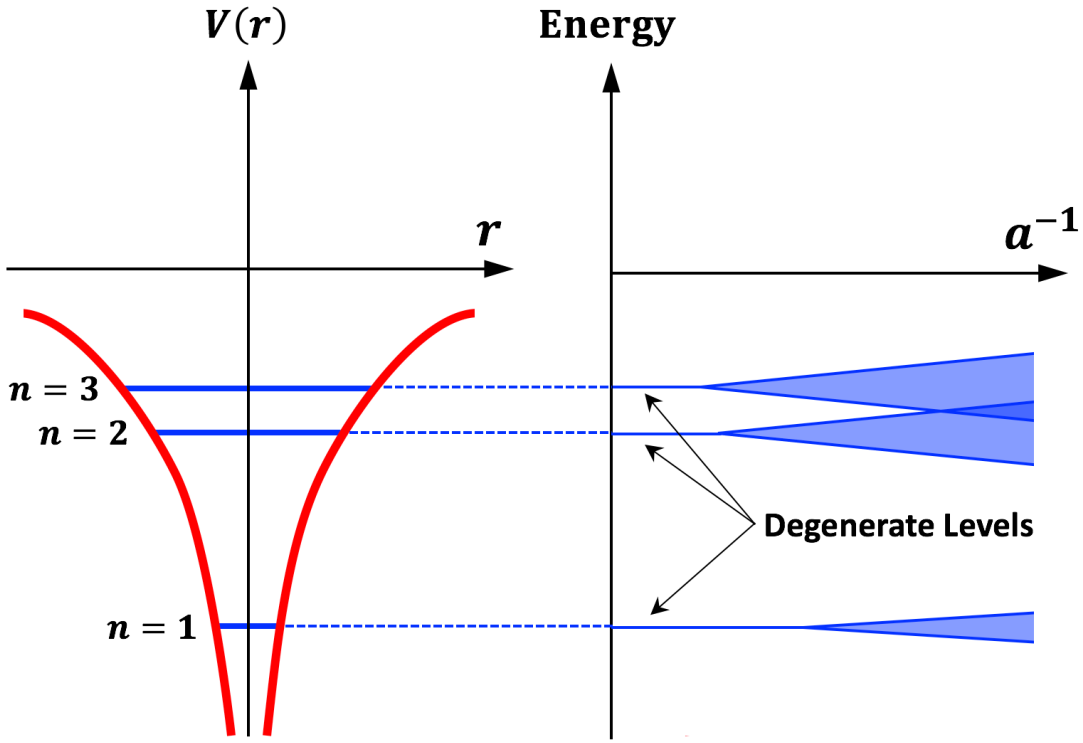
- ❖ From **atomic energy levels** to energy bands:

Chapter 4.2: Tight-Binding Model (紧束缚模型)

➢ From Energy Levels to Energy Bands (从能级到能带)

❖ From **atomic energy levels** to energy bands:

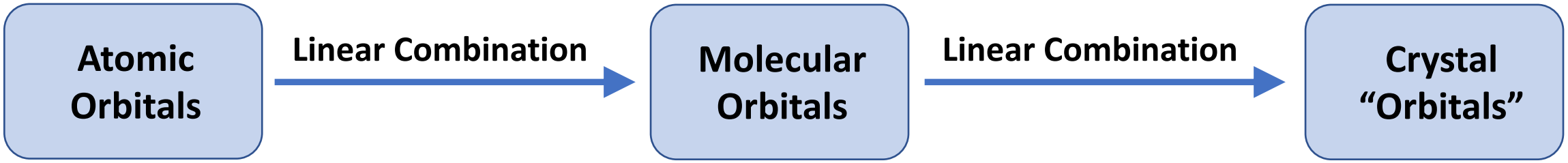




Chapter 4.2: Tight-Binding Model (紧束缚模型)

➢ From Energy Levels to Energy Bands (从能级到能带)

❖ From **molecular energy levels** to energy bands:

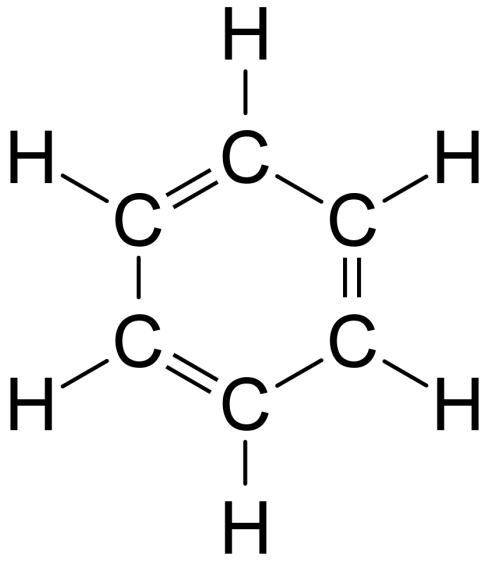


Chapter 4.2: Tight-Binding Model (紧束缚模型)

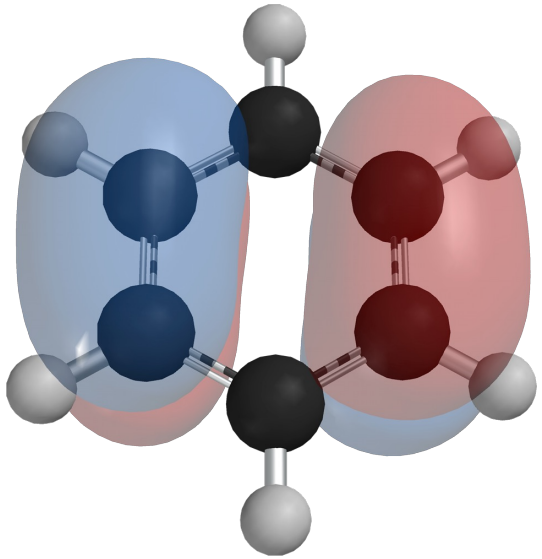
➢ From Energy Levels to Energy Bands (从能级到能带)

❖ From **molecular energy levels** to energy bands:

- **Molecular orbitals (分子轨道)**



The molecular structure of **benzene (苯)**.



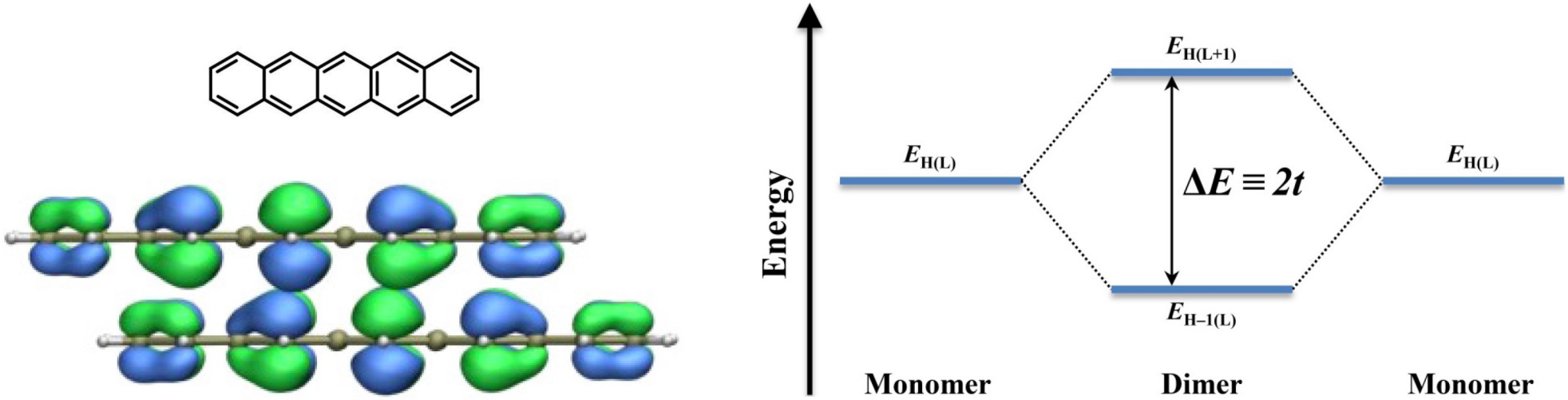
The **highest occupied molecular orbital (HOMO)** of benzene

Chapter 4.2: Tight-Binding Model (紧束缚模型)

➢ From Energy Levels to Energy Bands (从能级到能带)

❖ From **molecular energy levels** to energy bands:

- **Interaction between molecular orbitals**



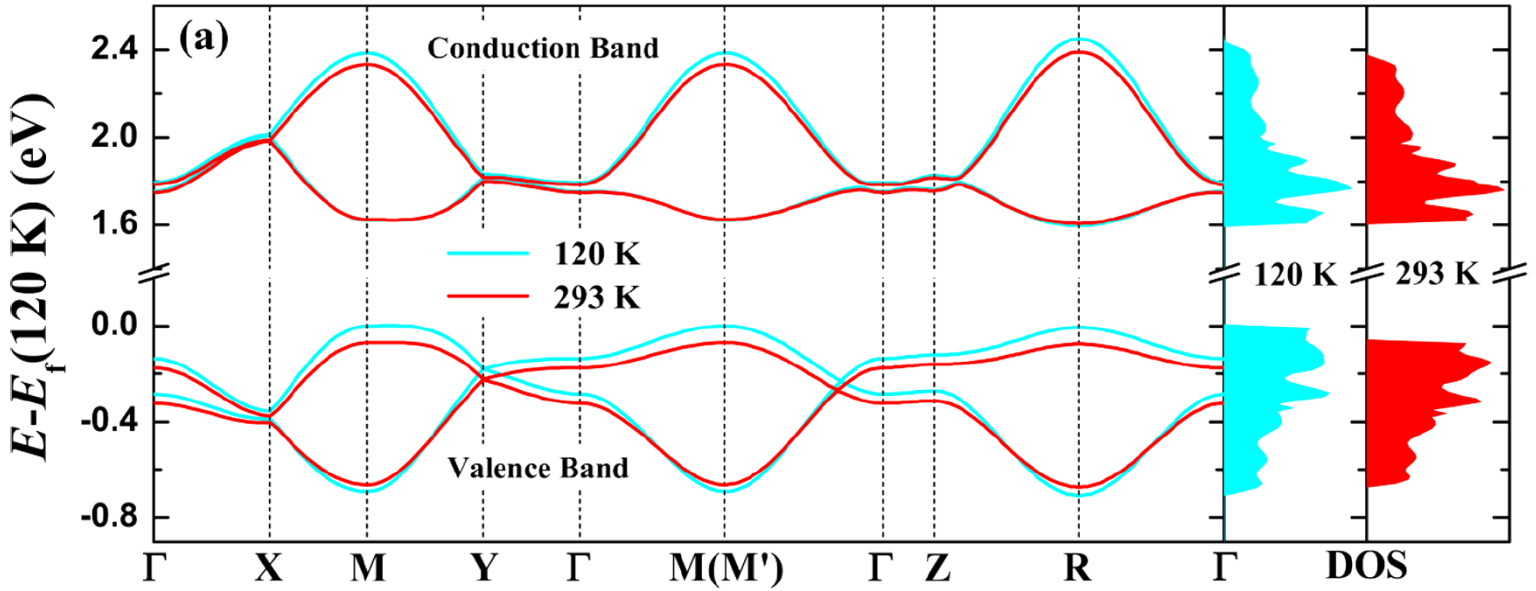
The interaction between the HOMOs of two **pentacene (并五苯)** molecules.

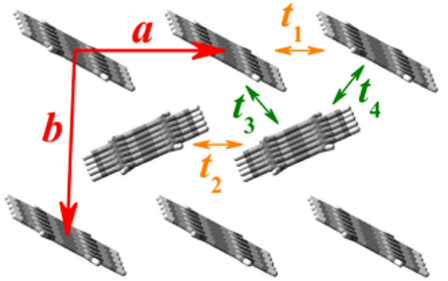
Chapter 4.2: Tight-Binding Model (紧束缚模型)

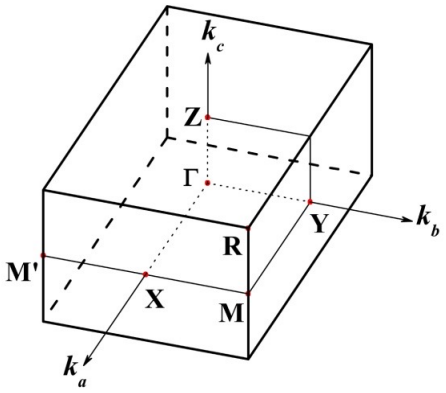
➢ From Energy Levels to Energy Bands (从能级到能带)

❖ From **molecular energy levels** to energy bands:

- Energy band of a **molecular crystal (分子晶体)**







The band structure of pentacene single crystal.

Chapter 4.2: Tight-Binding Model (紧束缚模型)

➢ From Energy Levels to Energy Bands (从能级到能带)

❖ Wannier function (瓦尼尔函数)

In the tight-binding model, the wavefunctions for the electronic states of the energy band are written as a linear combination of the atomic orbitals:

$$\psi_k(\vec{r}) = \frac{1}{\sqrt{N}} \sum_n e^{i\vec{k}\cdot\vec{R}_n} \varphi\left(\vec{r} - \vec{R}_n\right)$$

Chapter 4.2: Tight-Binding Model (紧束缚模型)

➢ From Energy Levels to Energy Bands (从能级到能带)

❖ Wannier function (瓦尼尔函数)

In general, the wavefunctions for any energy band (not only that of the TB model) can be written as a linear combination of the **Wannier functions**:

$$\psi_k(\vec{r}) = \frac{1}{\sqrt{N}} \sum_n e^{i\vec{k}\cdot\vec{R}_n} W(\vec{r} - \vec{R}_n)$$

Chapter 4.2: Tight-Binding Model (紧束缚模型)

➢ From Energy Levels to Energy Bands (从能级到能带)

❖ Wannier function (瓦尼尔函数)

The properties of **Wannier functions**:

$$W(\vec{r}-\vec{R}_n)=\frac{1}{\sqrt{N}}\sum_k e^{-i\vec{k}\cdot\vec{R}_n}\psi_k(\vec{r})$$

$$\int \boldsymbol{W^*(\vec{r}-\vec{R}_m)W(\vec{r}-\vec{R}_n)}\mathrm{d}\vec{\boldsymbol{r}}=\boldsymbol{\delta_{mn}}$$

Chapter 4.2: Tight-Binding Model (紧束缚模型)

➢ From Energy Levels to Energy Bands (从能级到能带)

❖ Wannier function (瓦尼尔函数)

In the tight-binding model, the Wannier functions are just the wavefunctions of the isolated atomic orbitals:

$$W(\vec{r}-\vec{R}_n)=\varphi(\vec{r}-\vec{R}_n)$$

Wannier functions are convenient for dealing with problems associated with the localization (局域化) of wavefunctions!

TB Model vs NFE Model
(紧束缚模型与近自由电子模型对比)

Chapter 4.2: Tight-Binding Model (紧束缚模型)

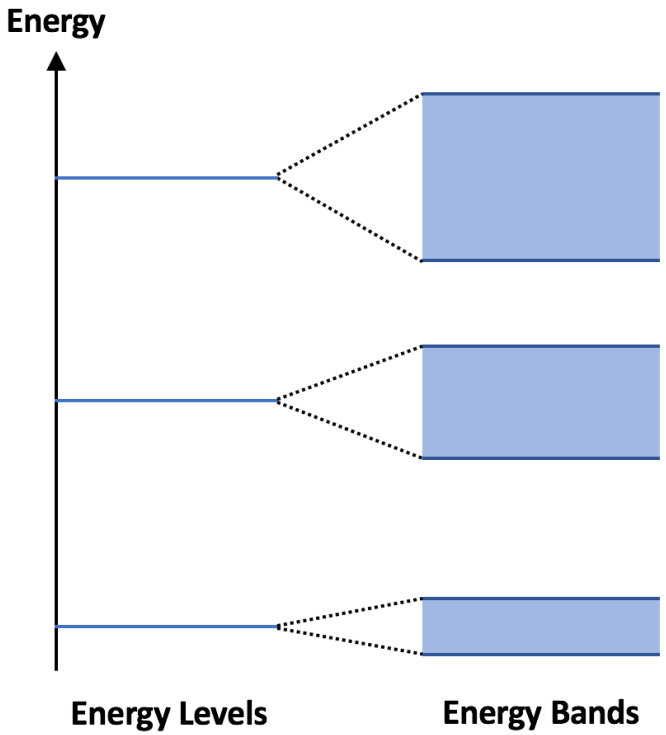
➢ TB Model vs NFE Model

Tight-Binding Model	Nearly-Free-Electron Model
Electrons are tightly bound to nuclei;	Electrons are nearly free;
Wave functions are linear combination of atomic orbitals;	Wave functions are approximated by plane waves;
Energy bands are formed as a result of interactions between atomic levels.	Energy bands are formed as a result of band gaps opened up at the boundary of Brillouin zones.

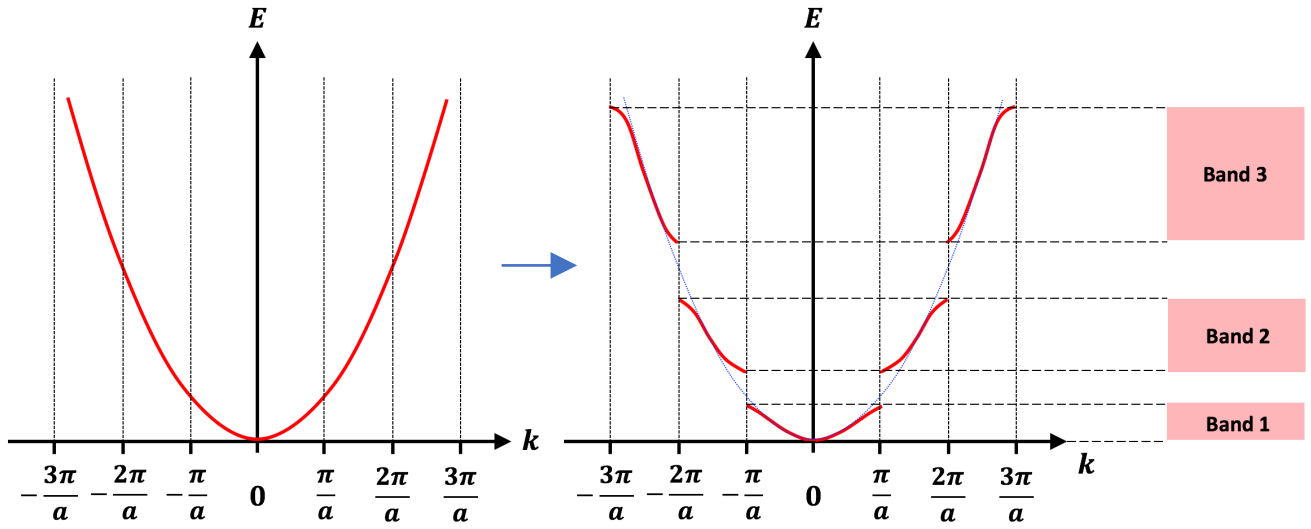
Chapter 4.2: Tight-Binding Model (紧束缚模型)

➢ TB Model vs NFE Model

TB Model



NFE Model



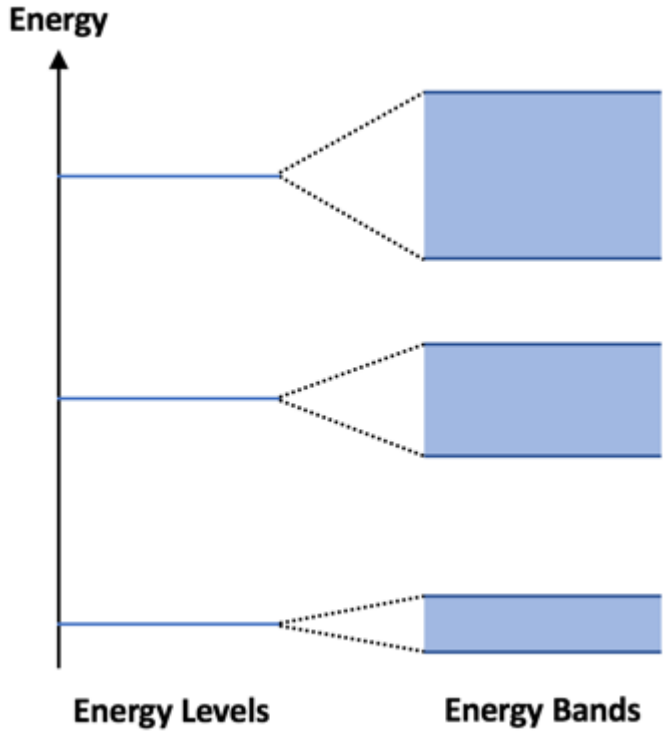
Summary (总结)

Chapter 4.2: Tight-Binding Model (紧束缚模型)

➢ Summary

- ❖ Tight-Binding Approximation
- ❖ Linear Combination of Atomic Orbitals (LCAO)

  Degenerate Perturbation Theory
- ❖ From Energy Levels to Energy Bands



Chapter 4.2: 课后作业

考虑一维单原子链（原子间距为a, 链长为Na）, 对于原子的s能级, 利用紧束缚模型, 求:

1. 原子链能带的色散关系$E(k)$;
2. 能带的态密度$g(E)$;
3. 能带的宽度.

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