Fundamentals of Solid State Physics

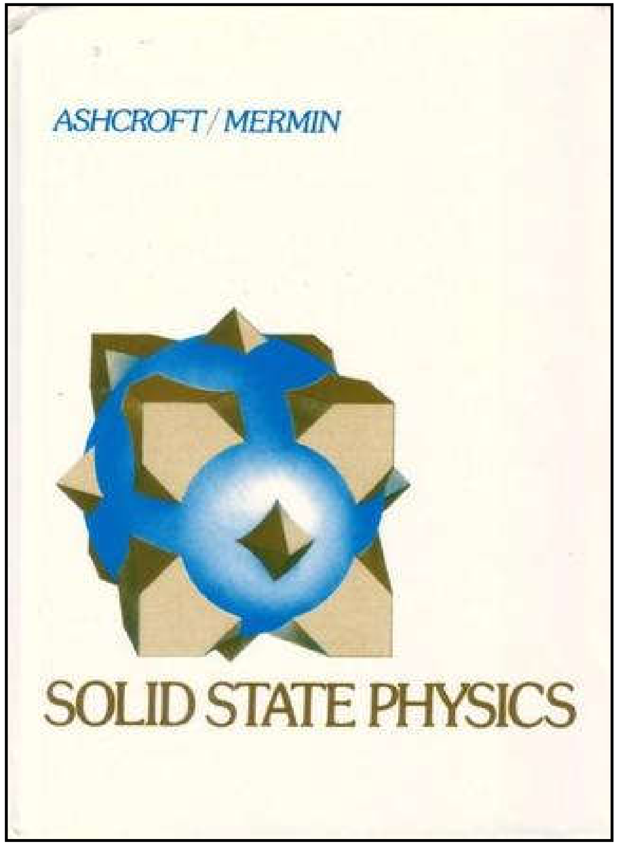
The Nearly Free Electron Model

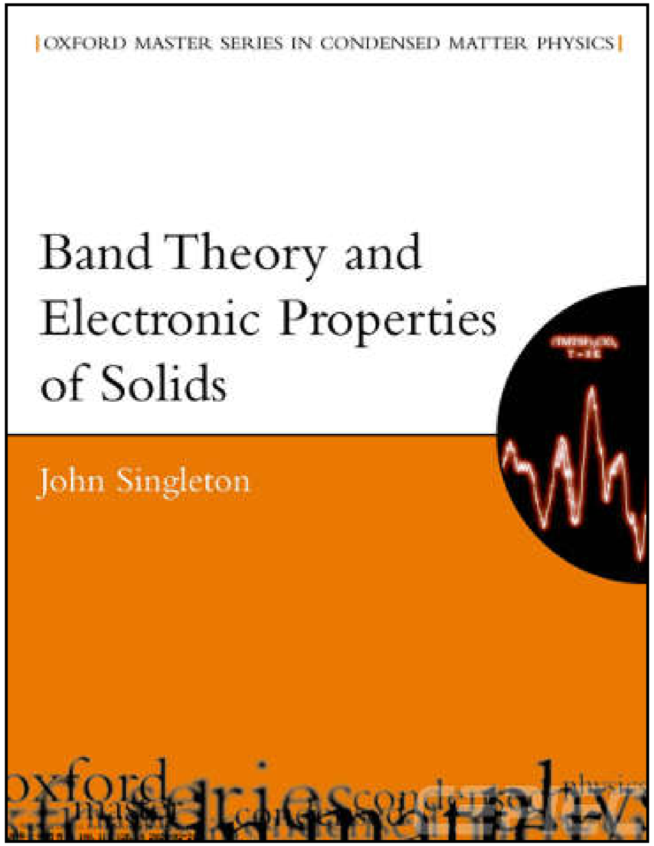
Xing Sheng 盛 兴

Department of Electronic Engineering
Tsinghua University
xingsheng@tsinghua.edu.cn

Further Reading

- **Ashcroft & Mermin, Chapter 9**
- **Singleton, Chapter 3**





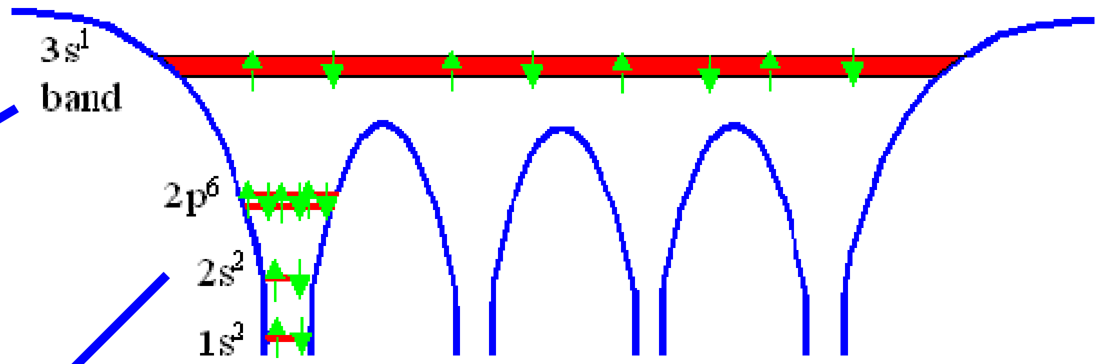
Real Electrons in Solids

Electrons are in *periodic* potentials

Bloch Wave

$$\psi(\mathbf{r}) = \exp(i\mathbf{k}\cdot\mathbf{r})\cdot u_{\mathbf{k}}(\mathbf{r})$$

Nearly Free Electron Model
"近自由"近似



Sodium (Na) [$1s^2$ $2s^2$ $2p^6$] $3s^1$

Tight Binding Model
"紧束缚"近似

Electrons in a Periodic Potential

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r})+V(\mathbf{r})\cdot\psi(\mathbf{r})=E\psi(\mathbf{r})$$

$$\psi(\mathbf{r})=\sum_{\mathbf{k}}C_{\mathbf{k}}\exp(i\mathbf{k}\cdot\mathbf{r})$$

$$V(\mathbf{r})=\sum_{\mathbf{G}}V_{\mathbf{G}}\exp(i\mathbf{G}\cdot\mathbf{r})$$

$$\rightarrow\quad\left(\frac{\hbar^2k^2}{2m}-E\right)C_{\mathbf{k}}+\sum_{\mathbf{G}}V_{\mathbf{G}}C_{\mathbf{k}-\mathbf{G}}=0$$

The Central Equation

If we know *V(r)* $\rightarrow$ $C_{\mathbf{k}},C_{\mathbf{k}\pm\mathbf{G}},C_{\mathbf{k}\pm2\mathbf{G}}\cdots$ $E_1,E_2,E_3\ldots$

The Central Equation

We only need to solve it in the first Brillouin zone

$$
\begin{pmatrix}
\ddots & \cdots & \cdots & \cdots & \ddots \\
\cdots & \frac{\hbar^2}{2m}(k-g)^2 - E & V_{-g} & V_{-2g} & \cdots \\
\cdots & V_g & \frac{\hbar^2}{2m}k^2 - E & V_{-g} & \cdots \\
\cdots & V_{2g} & V_g & \frac{\hbar^2}{2m}(k+g)^2 - E & \cdots \\
\ddots & \cdots & \cdots & \cdots & \ddots
\end{pmatrix}
\begin{pmatrix}
\vdots \\
C_{k-g} \\
C_k \\
C_{k-g} \\
\vdots
\end{pmatrix}
= 0
$$

$V_{G=0}$ is a constant (the ground level energy)
here we assume $V_{G=0} = 0$

$$\boxed{g = \frac{2\pi}{a}}$$

The Central Equation

We only need to solve it in the first Brillouin zone

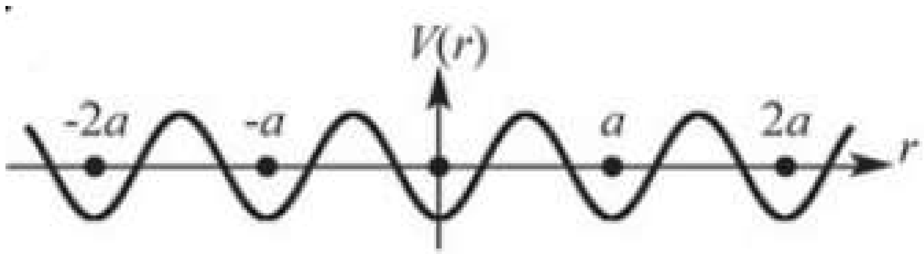
$$\det\begin{pmatrix} \ddots & \cdots & \cdots & \cdots & \iddots \\ \cdots & \frac{\hbar^2}{2m}(k-g)^2 - E & V_{-g} & V_{-2g} & \cdots \\ \cdots & V_g & \frac{\hbar^2}{2m}k^2 - E & V_{-g} & \cdots \\ \cdots & V_{2g} & V_g & \frac{\hbar^2}{2m}(k+g)^2 - E & \cdots \\ \iddots & \cdots & \cdots & \cdots & \ddots \end{pmatrix} = 0$$

$$\boxed{g = \frac{2\pi}{a}}$$

If we know *V(r)* $\longrightarrow$ $\boxed{E_1(k), E_2(k), E_3(k), \ldots}$

Nearly Free Electron Model

Consider a simple, weak periodic potential (*V* << *E*)



$$V = -2V_1 \cos\left(\frac{2\pi}{a}x\right) = -2V_1 \cos(gx) = -V_1(e^{igx} + e^{-igx})$$

$$V(\mathbf{r}) = \sum_{\mathbf{G}} V_{\mathbf{G}} \exp(i\mathbf{G}\cdot\mathbf{r})$$

$$\rightarrow \quad V_g = V_{-g} = -V_1$$

$$V_{2g} = V_{-2g} = V_{3g} = V_{-3g} = \ldots = 0$$

The Central Equation

$$\det\begin{pmatrix} \ddots & \cdots & \cdots & \cdots & \ddots \\ \cdots & \frac{\hbar^2}{2m}(k-g)^2 - E & -V_1 & 0 & \cdots \\ \cdots & -V_1 & \frac{\hbar^2}{2m}k^2 - E & -V_1 & \cdots \\ \cdots & 0 & -V_1 & \frac{\hbar^2}{2m}(k+g)^2 - E & \cdots \\ \ddots & \cdots & \cdots & \cdots & \ddots \end{pmatrix} = 0$$

$$\boxed{g = \frac{2\pi}{a}}$$

$$\rightarrow \boxed{E_1, E_2, E_3 \ldots}$$

The Central Equation

$$\det \begin{pmatrix} \ddots & \cdots & \cdots & \cdots & \ddots \\ \cdots & \frac{\hbar^2}{2m}(k-g)^2 - E & -V_1 & 0 & \cdots \\ \cdots & -V_1 & \frac{\hbar^2}{2m}k^2 - E & -V_1 & \cdots \\ \cdots & 0 & -V_1 & \frac{\hbar^2}{2m}(k+g)^2 - E & \cdots \\ \ddots & \cdots & \cdots & \cdots & \ddots \end{pmatrix} = 0$$

$$g = \frac{2\pi}{a}$$

$$\rightarrow \boxed{E_1, E_2, E_3 \ldots}$$

The Central Equation

$$\begin{vmatrix} \frac{\hbar^2}{2m}(k-g)^2 - E & -V_1 \\ -V_1 & \frac{\hbar^2}{2m}k^2 - E \end{vmatrix} = 0$$

$$\rightarrow \boxed{\left[\frac{\hbar^2}{2m}(k-g)^2 - E\right]\left[\frac{\hbar^2}{2m}k^2 - E\right] - V_1^2 = 0}$$

$$\rightarrow \boxed{E_1(k), E_2(k)}$$

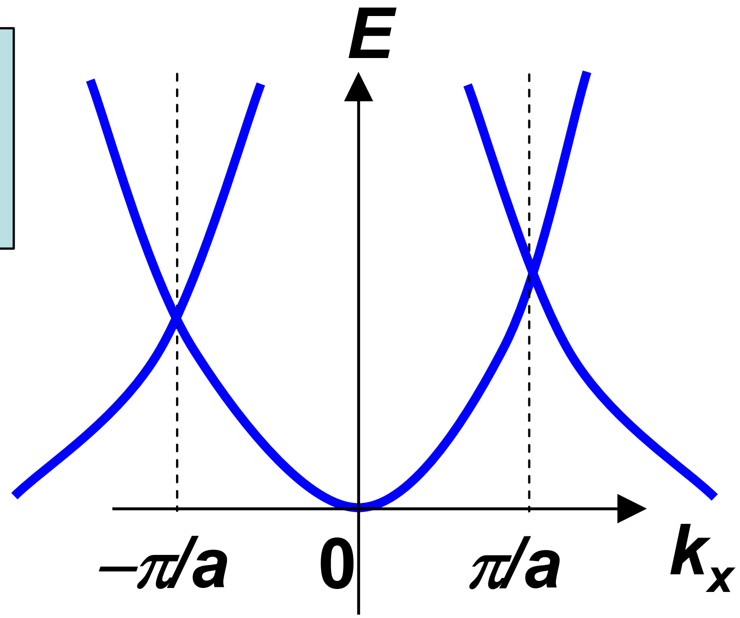
Energy Diagram

Free electron → $\boxed{V_1 = 0}$

$$\left[\frac{\hbar^2}{2m}(k-g)^2 - E\right]\left[\frac{\hbar^2}{2m}k^2 - E\right] - V_1^2 = 0$$

→ $\boxed{E = \frac{\hbar^2}{2m}k^2}$ **or** $\boxed{E = \frac{\hbar^2}{2m}(k-g)^2}$

$$\boxed{E\left(k = \frac{\pi}{a}\right) = \frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2}$$



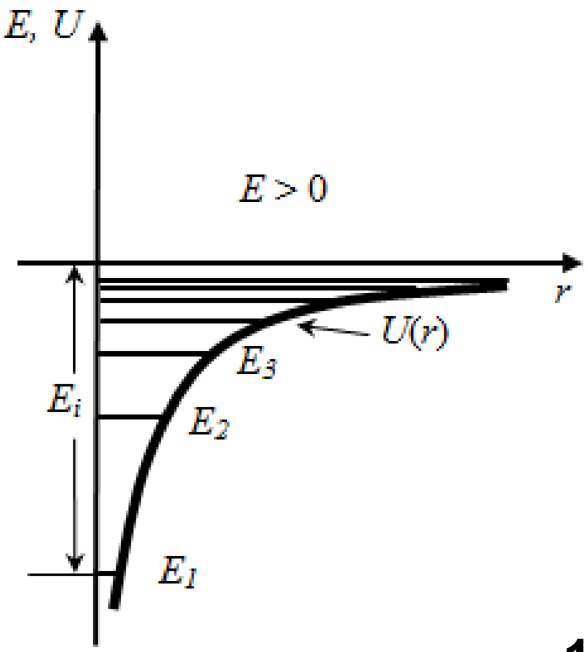
Energy Diagram

very strong potential → $\boxed{V_1 >> 0}$

$$\left[\frac{\hbar^2}{2m}(k-g)^2 - E\right]\left[\frac{\hbar^2}{2m}k^2 - E\right] - V_1^2 = 0$$

E **is constant, independent of** ***k***

→ $\boxed{E_+ = V_1}$ $\boxed{E_- = -V_1}$



discrete energy levels
(atomic orbitals)

Energy Diagram

Nearly Free electron → $V_1 \neq 0$ **and** $V_1 \ll \frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2$

$$\left[\frac{\hbar^2}{2m}(k-g)^2 - E\right]\left[\frac{\hbar^2}{2m}k^2 - E\right] - V_1^2 = 0$$

→ $$E_\pm = \frac{(A+B) \pm \sqrt{(A-B)^2 + 4V_1^2}}{2}$$

$$A = \frac{\hbar^2}{2m}k^2 \qquad B = \frac{\hbar^2}{2m}(k-g)^2$$

Energy Diagram

Nearly Free electron → $\boxed{V_1 \neq 0}$ **and** $\boxed{V_1 \ll \frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2}$

$$\left[\frac{\hbar^2}{2m}(k-g)^2 - E\right]\left[\frac{\hbar^2}{2m}k^2 - E\right] - V_1^2 = 0$$

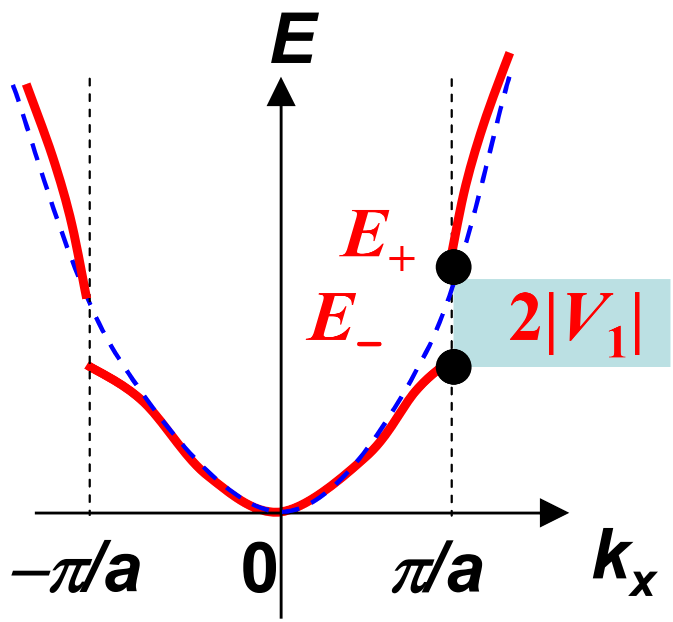
when $0 < k < \pi/a$

→ $\boxed{E_+ \approx B + |V_1|}$

higher than free electron

$\boxed{E_- \approx A - |V_1|}$

lower than free electron



Energy Diagram

Nearly Free electron → $V_1 \neq 0$ **and** $V_1 \ll \frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2$

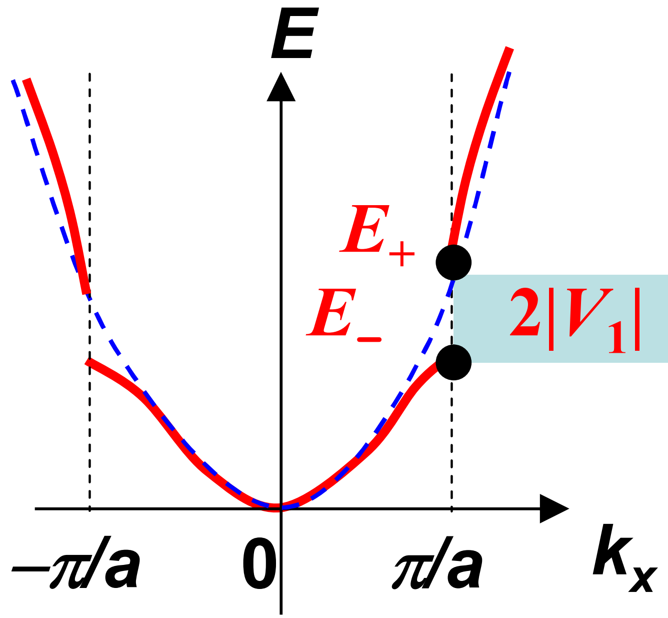
$$\left[\frac{\hbar^2}{2m}(k-g)^2 - E\right]\left[\frac{\hbar^2}{2m}k^2 - E\right] - V_1^2 = 0$$

when $k = \pi/a$

→

$$E_+\left(k=\frac{\pi}{a}\right) = \frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2 + |V_1|$$

$$E_-\left(k=\frac{\pi}{a}\right) = \frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2 - |V_1|$$

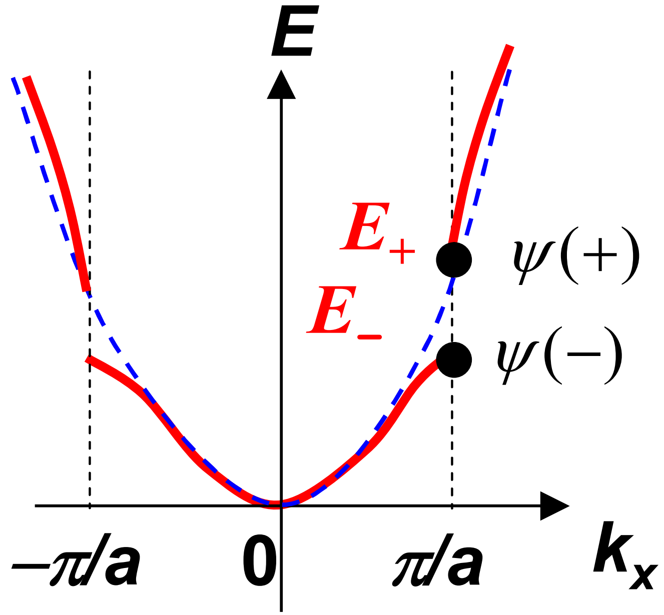


Band Gap!

Energy Diagram

$$\begin{pmatrix} \frac{\hbar^2}{2m}(k-g)^2 - E & -V_1 \\ -V_1 & \frac{\hbar^2}{2m}k^2 - E \end{pmatrix} \begin{pmatrix} C_{k-g} \\ C_k \end{pmatrix} = 0$$

$$\psi = C_{k-g}\exp[i(k-g)x] + C_k \exp[ikx]$$



when $k = \pi/a$

$$E_-\left(k = \frac{\pi}{a}\right) = \frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2 - |V_1| \quad \rightarrow$$

$$\psi(-) \sim \cos(\pi x / a)$$

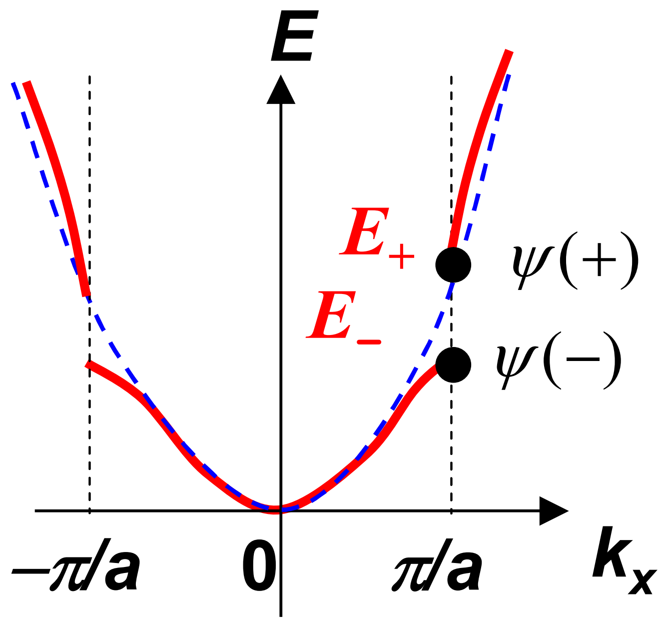
$$|\psi(-)|^2 \sim \cos^2(\pi x / a)$$

Homework 5.3

Energy Diagram

$$\begin{pmatrix} \frac{\hbar^2}{2m}(k-g)^2 - E & -V_1 \\ -V_1 & \frac{\hbar^2}{2m}k^2 - E \end{pmatrix} \begin{pmatrix} C_{k-g} \\ C_k \end{pmatrix} = 0$$

$$\psi = C_{k-g} \exp[i(k-g)x] + C_k \exp[ikx]$$



when $k = \pi/a$

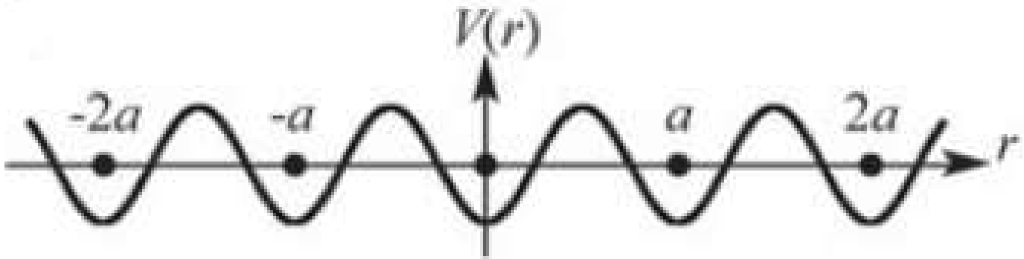
$$E_+\left(k = \frac{\pi}{a}\right) = \frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2 + |V_1| \rightarrow$$

$$\psi(+) \sim i \sin(\pi x / a)$$

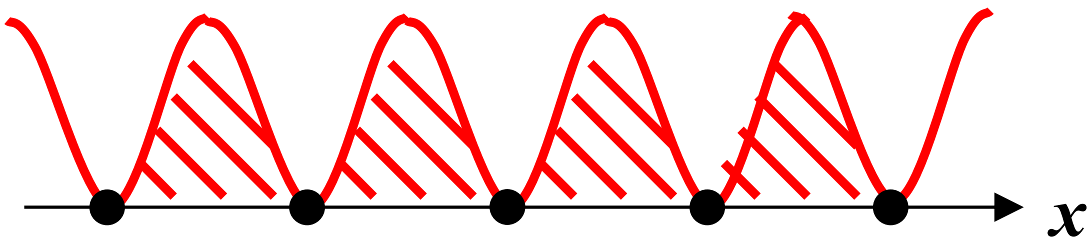
$$|\psi(+)|^2 \sim \sin^2(\pi x / a)$$

Homework 5.3

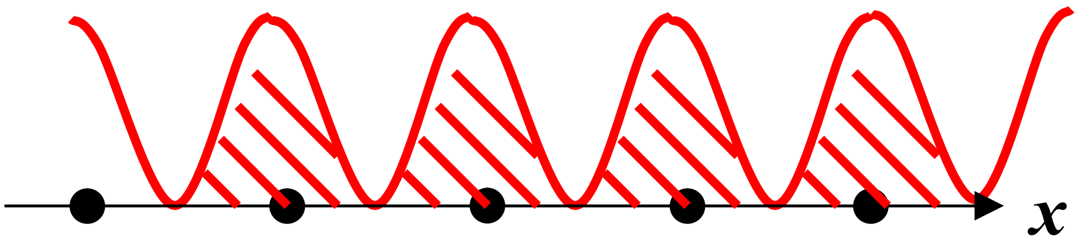
The Origin of Band Gap

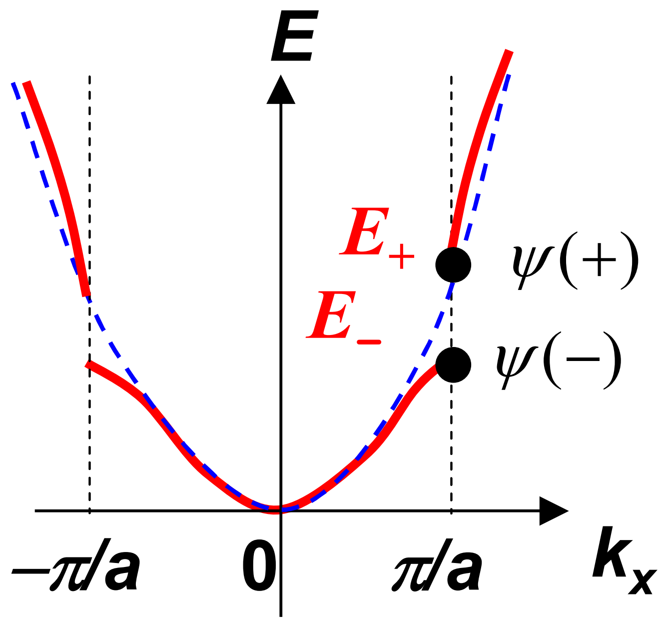


$$|\psi(+)|^2 \sim \sin^2(\pi x / a)$$



$$|\psi(-)|^2 \sim \cos^2(\pi x / a)$$

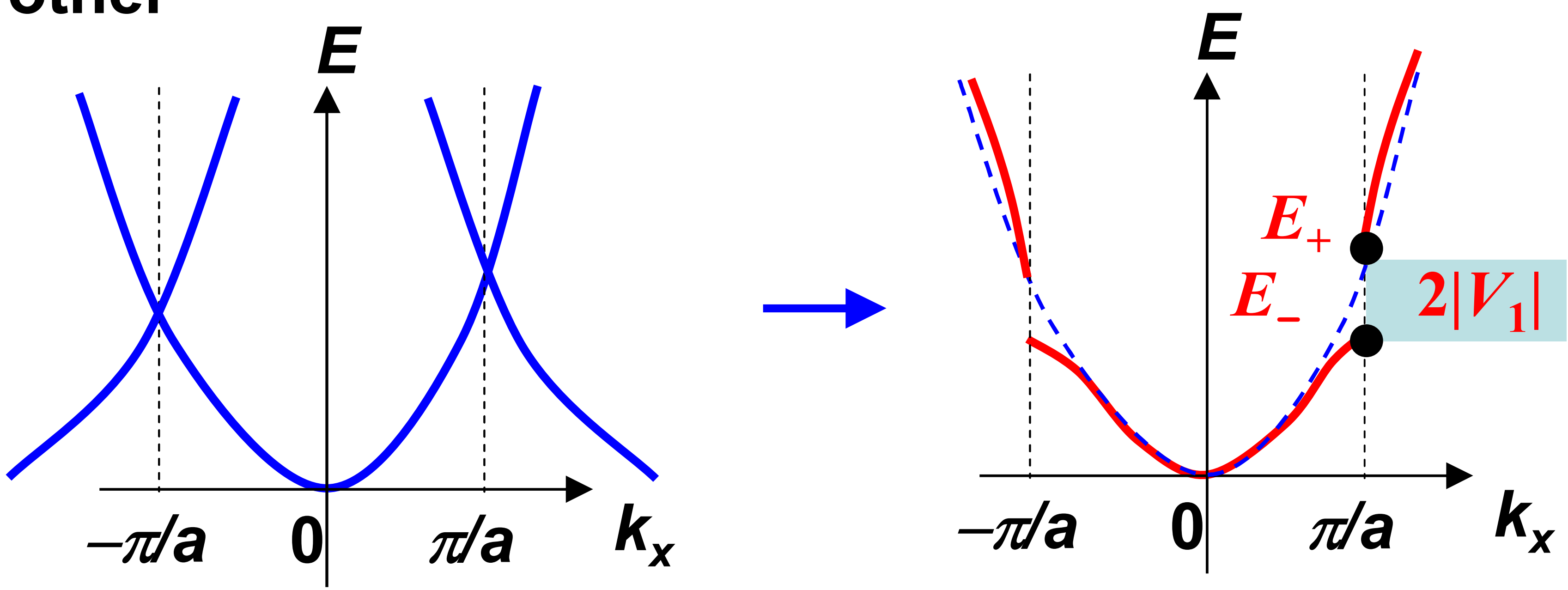




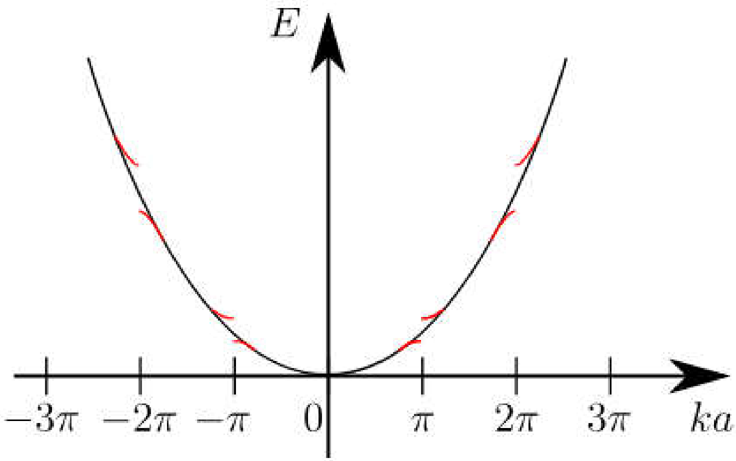
Two wavefunctions have different probability distributions in the lattice

The Origin of Band Gap

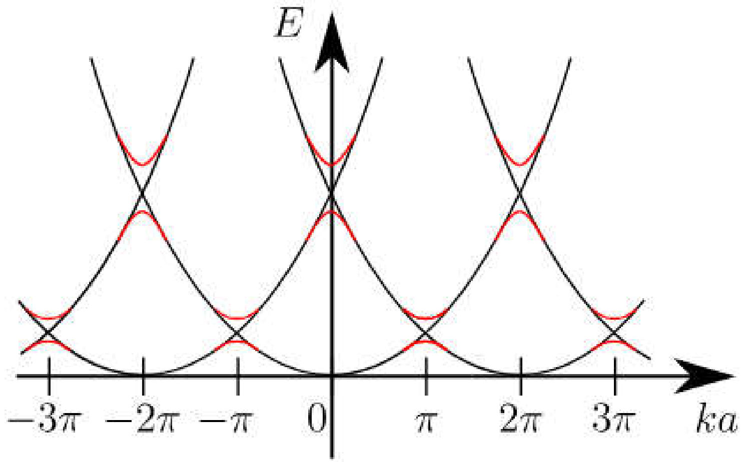
- **Mathematical view: The periodic potential perturbs the wavefunction of free electrons**
- **Physical view: two electrons cannot occupy the same state (Pauli exclusion principle), the overlapped part has to be separated and repel each other**



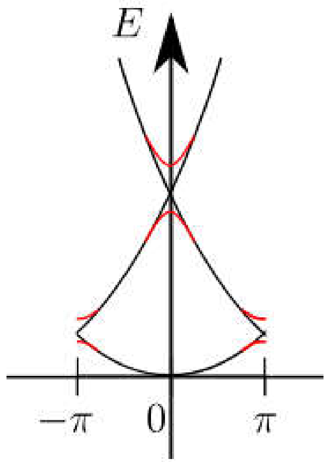
Band Structure / Diagram 能带图



extended zone / band structure
扩展布里渊区



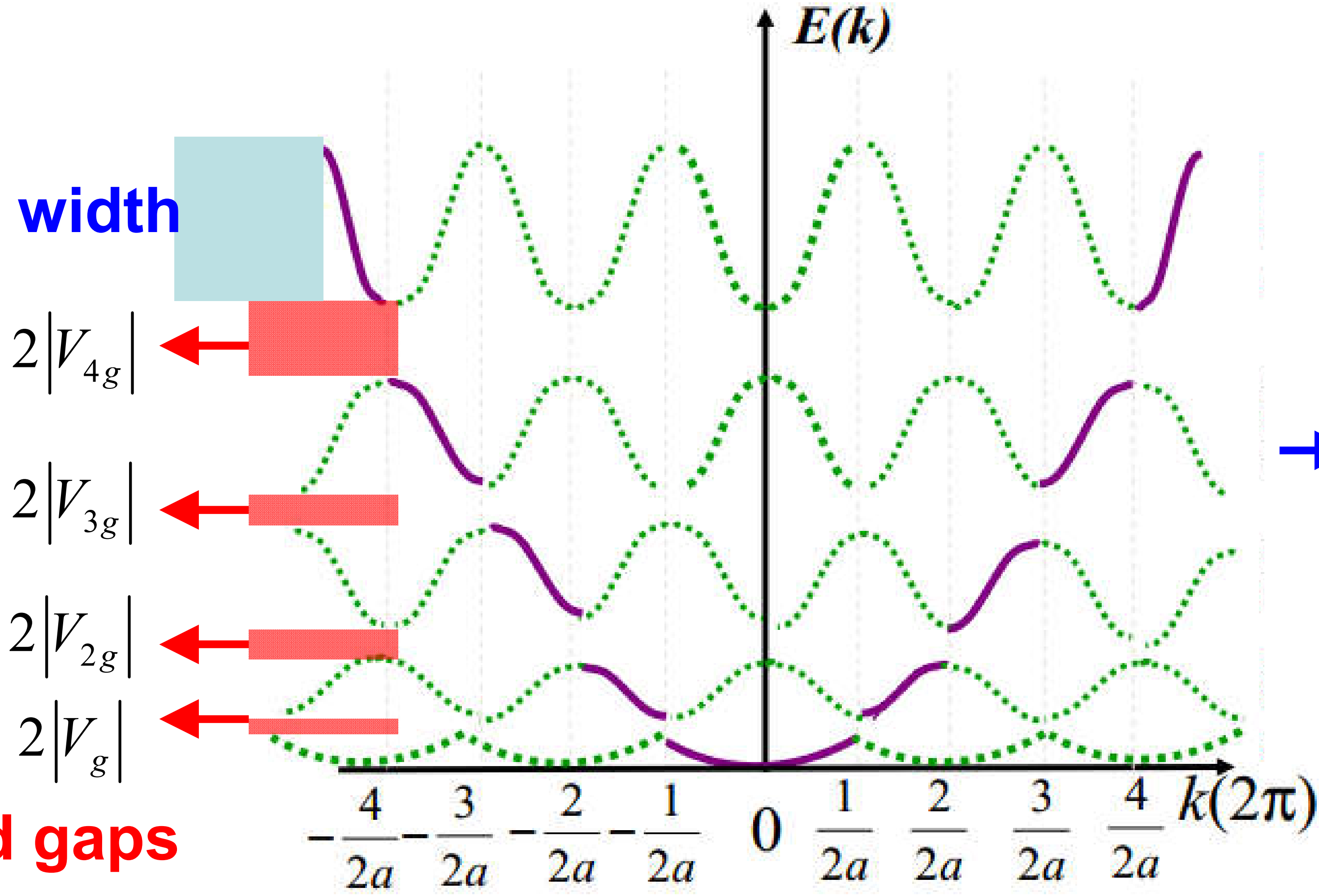
repeated zone / band structure
周期性布里渊区



reduced zone / band structure
简约布里渊区

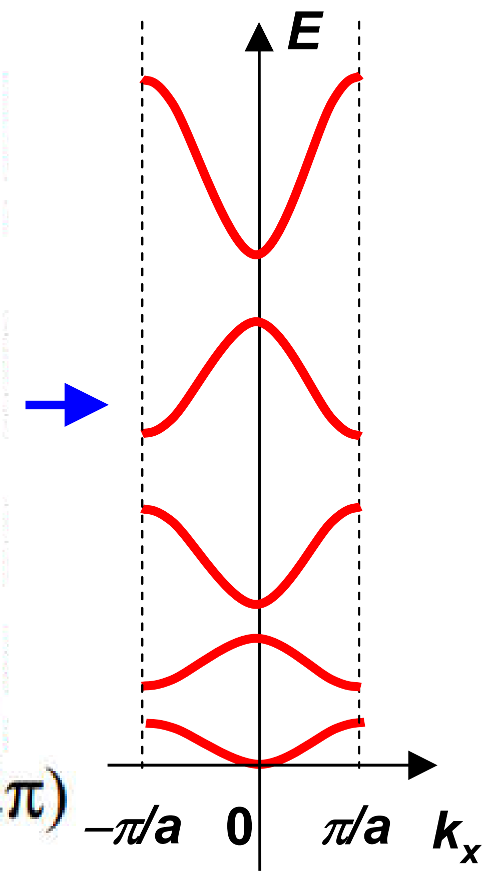
Band Structure / Diagram

band width



band gaps

reduced zone



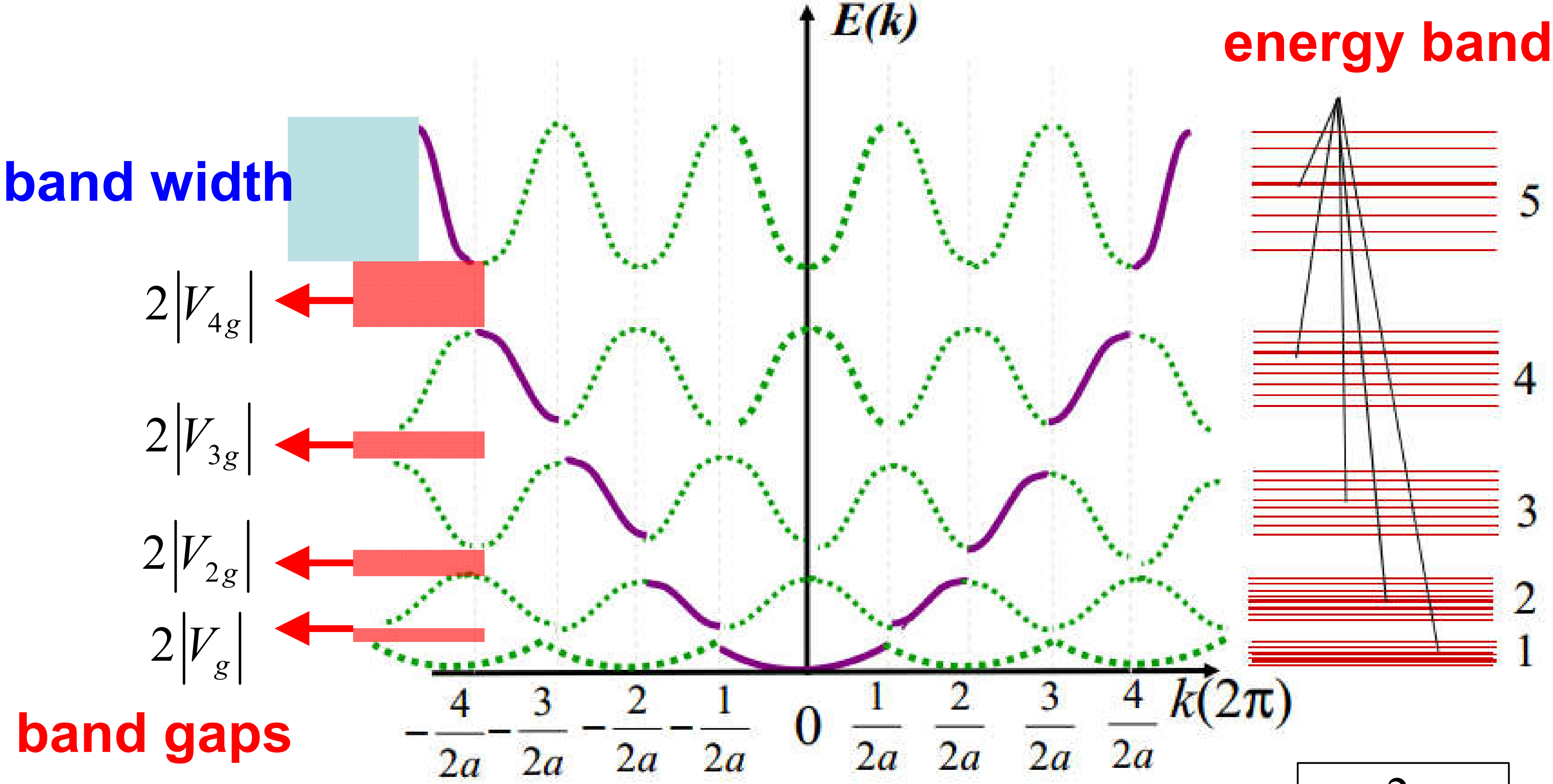
$$k = \frac{2\pi}{a}\frac{n}{N}$$

$$n = 0, \pm 1, \pm 2, \ldots$$

electron bands are quasi-continuous (准连续)

Q: how many states are there in each band?

Band Structure / Diagram



$$k = \frac{2\pi}{a}\frac{n}{N}$$

$$n = 0, \pm 1, \pm 2, \ldots$$

electron bands are quasi-continuous (准连续)

Q: how many states are there in each band?

Thank you for your attention