

# *Fundamentals of Solid State Physics*

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## **Electronic Properties - The Nearly Free Electron Model**

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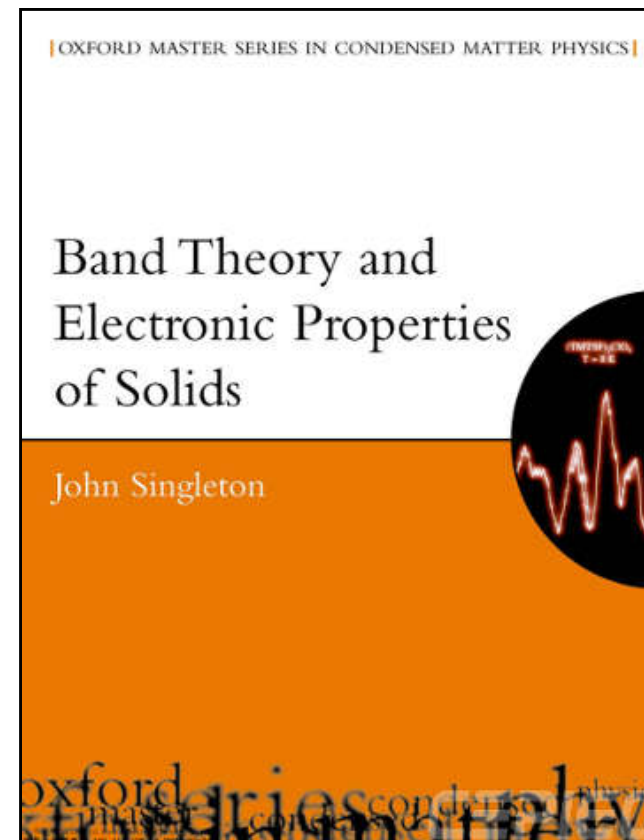
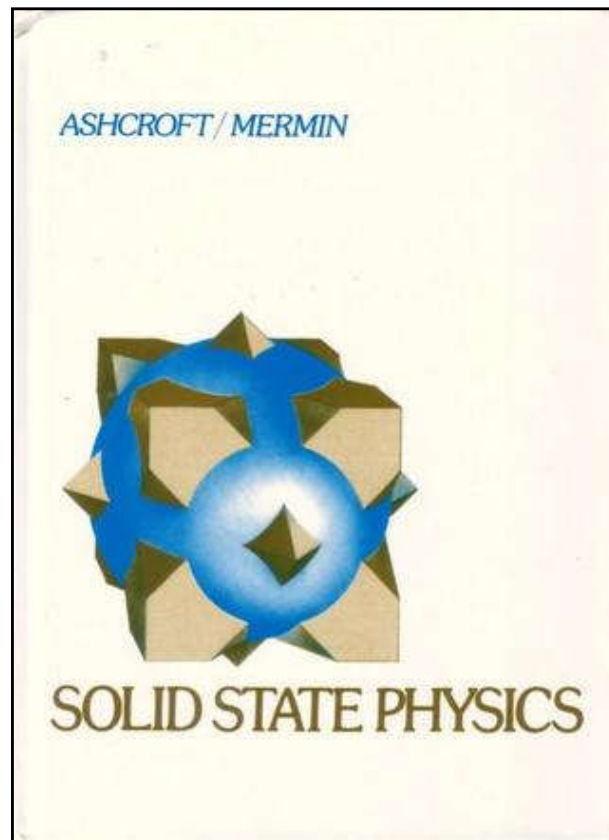


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# Further Reading

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



# Real Electrons in Solids

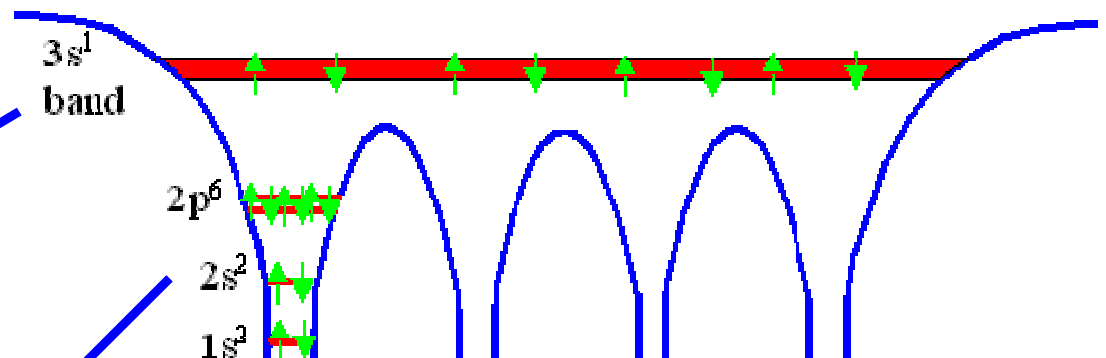
Electrons are in *periodic* potentials

→ **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

**Tight Binding Model**  
"紧束缚"近似



Sodium (Na) [1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup>] 3s<sup>1</sup>

# Electrons in a Periodic Potential

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

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

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

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

***The Central Equation***

If we know  $V(r)$  →  $C_{\mathbf{k}}, C_{\mathbf{k} \pm \mathbf{G}}, C_{\mathbf{k} \pm 2\mathbf{G}} \dots$   $E_1, E_2, E_3 \dots$

# The Central Equation

We only need to solve it in the first Brillouin zone

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

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

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

# The Central Equation

We only need to solve it in the first Brillouin zone

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

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

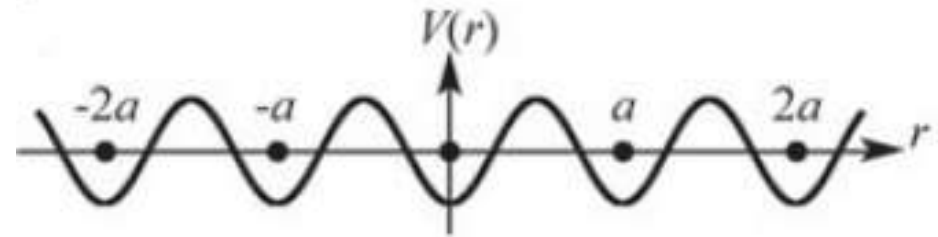
If we know  $V(r)$   $\longrightarrow$

$$E_1(k), E_2(k), E_3(k), \dots$$

# Nearly Free Electron Model

Consider a simple, weak periodic potential ( $V \ll E$ )

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



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



$$V_g = V_{-g} = -V_1$$

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

# The Central Equation

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

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



$$E_1, E_2, E_3, \dots$$



# The Central Equation

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

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



$$E_1, E_2, E_3, \dots$$

# The Central Equation

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

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



$$E_1(k), E_2(k)$$

# Energy Diagram

Free electron →

$$V_1 = 0$$

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

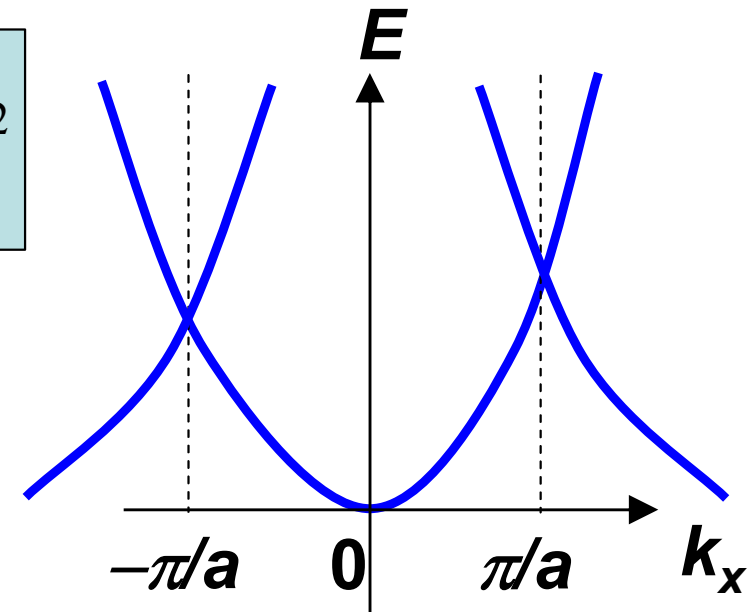
→

$$E = \frac{\hbar^2}{2m} k^2$$

or

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

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



# Energy Diagram

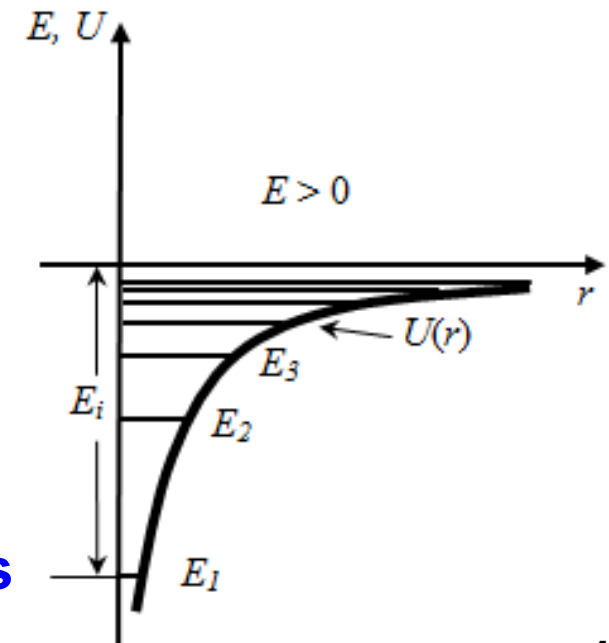
very strong potential  $\longrightarrow$   $V_1 \gg 0$

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

$E$  is constant, independent of  $k$

$$\begin{aligned} &\longrightarrow \boxed{E_+ = V_1} \\ &\boxed{E_- = -V_1} \end{aligned}$$

discrete energy levels  
(atomic orbitals)



# Energy Diagram

Nearly Free electron  $\longrightarrow$

$$V_1 \neq 0$$

and

$$V_1 \ll \frac{\hbar^2}{2m} \left( \frac{\pi}{a} \right)^2$$

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

$\longrightarrow$

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

$$A = \frac{\hbar^2}{2m} k^2$$

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

# Energy Diagram

Nearly Free electron  $\rightarrow$

$$V_1 \neq 0$$

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  $0 < k < \pi/a$

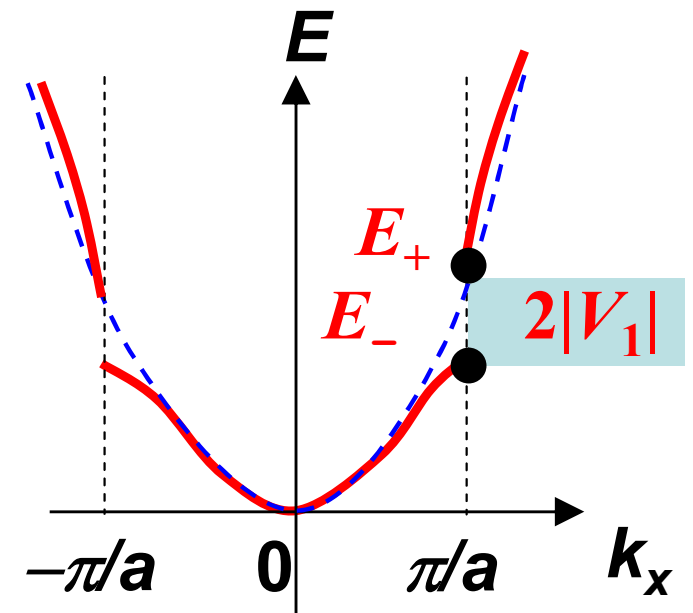
$$E_+ \approx B + |V_1|$$

higher than free electron



$$E_- \approx A - |V_1|$$

lower than free electron



# Energy Diagram

Nearly Free electron  $\rightarrow$

$$V_1 \neq 0$$

and

$$V_1 \ll \frac{\hbar^2}{2m} \left( \frac{\pi}{a} \right)^2$$

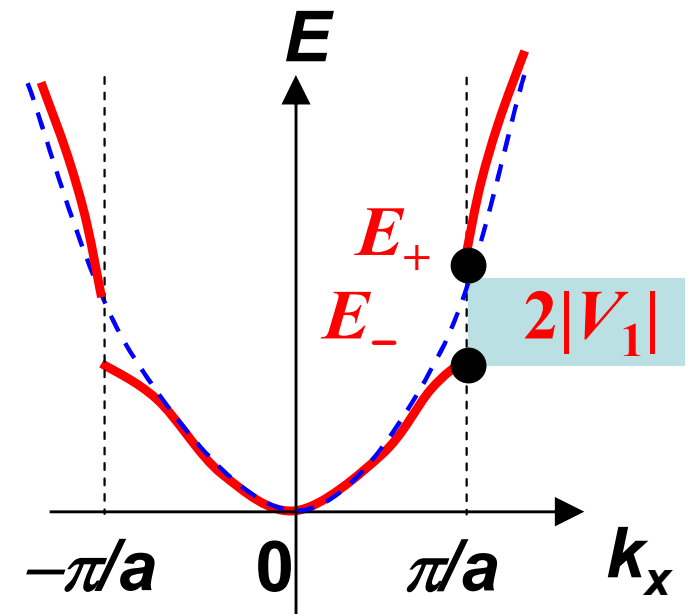
$$\left[ \frac{\hbar^2}{2m} (k - g)^2 - E \right] \left[ \frac{\hbar^2}{2m} k^2 - E \right] - V_1^2 = 0$$

when  $k = \pi/a$

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



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

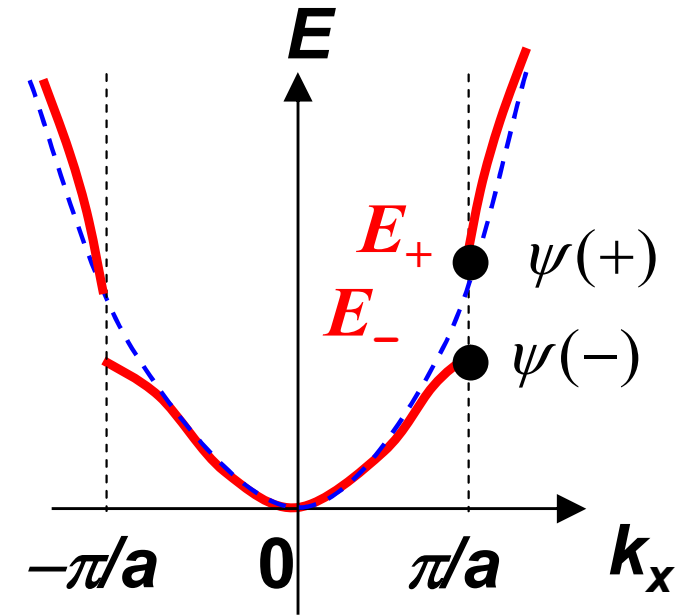


**Band Gap!**

# 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  $k = \pi/a$

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



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

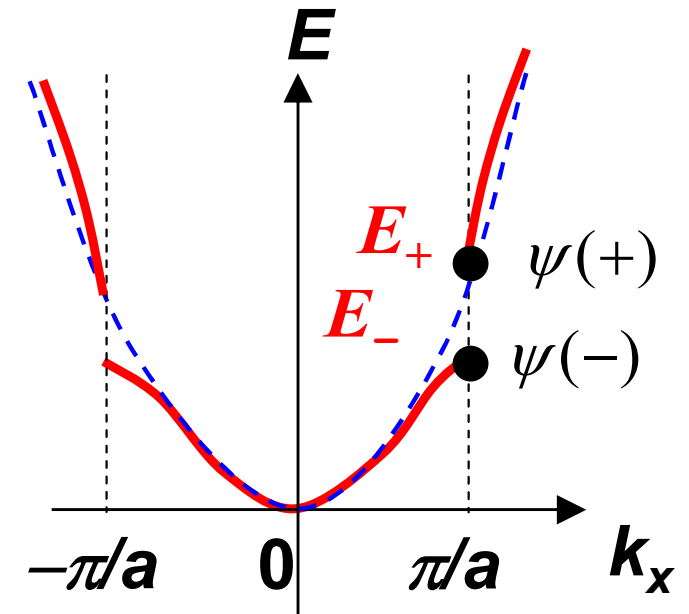
$$|\psi(-)|^2 \sim \cos^2(\pi x / a)$$



# 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  $k = \pi/a$

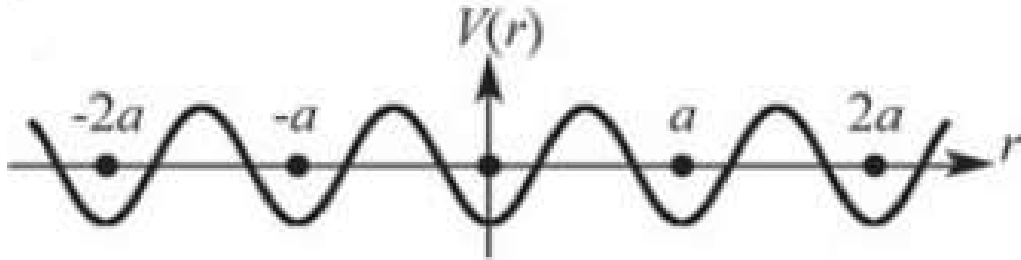
$$E_+ \left( k = \frac{\pi}{a} \right) = \frac{\hbar^2}{2m} \left( \frac{\pi}{a} \right)^2 + |V_1|$$



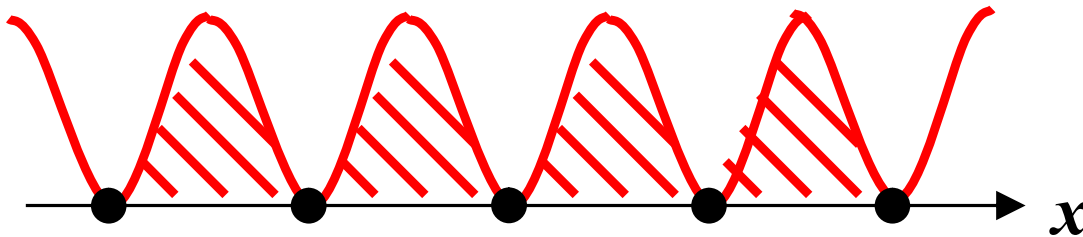
$$\psi(+) \sim i \sin(\pi x / a)$$

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

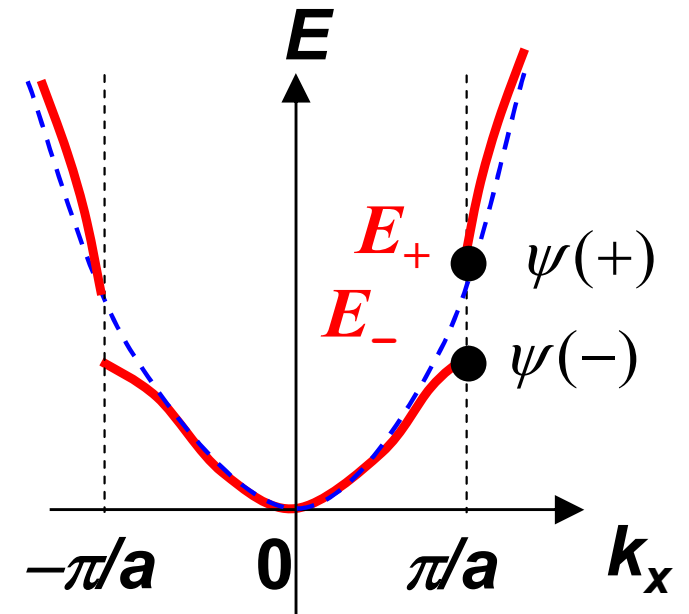
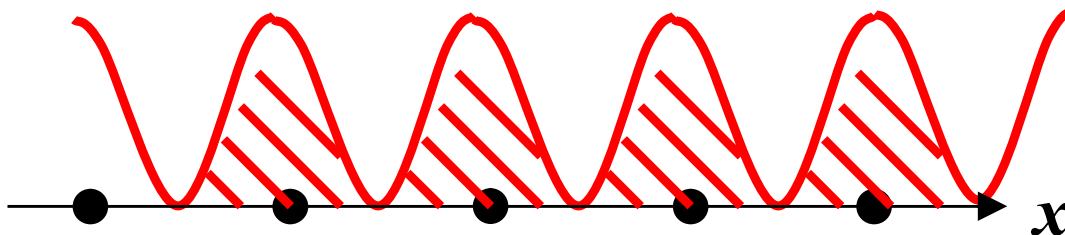
# The Origin of Band Gap



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



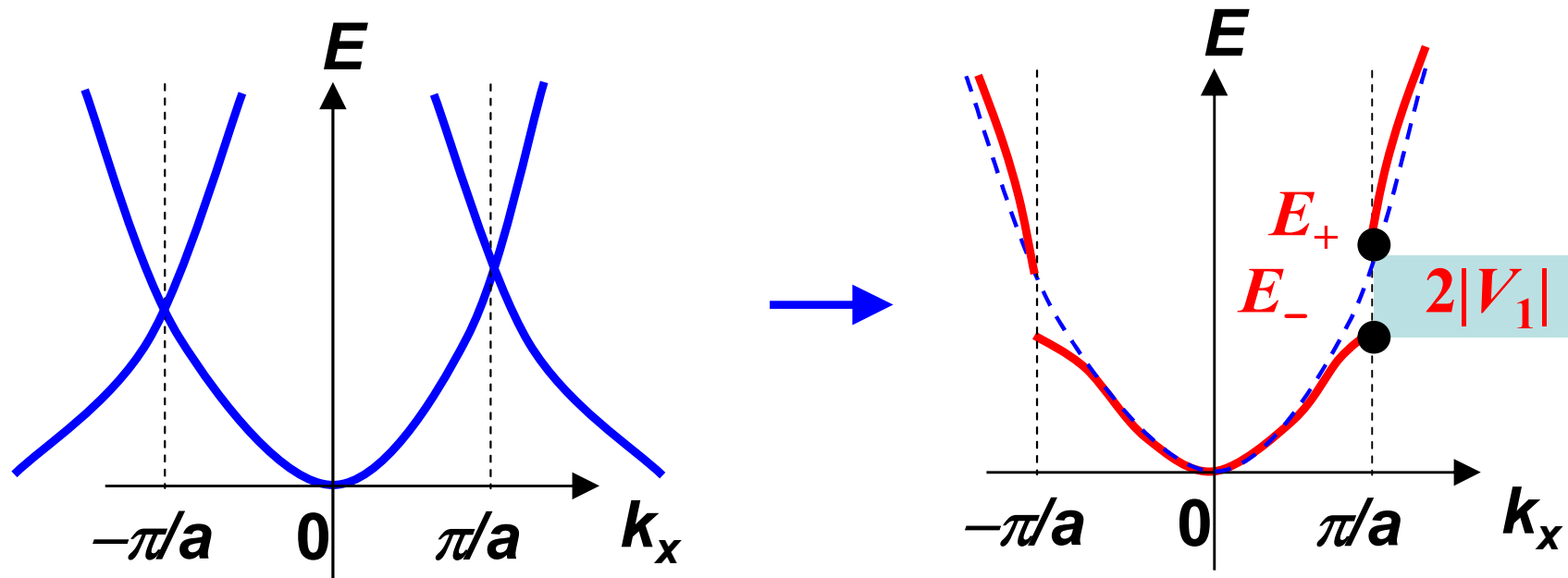
$$|\psi(-)|^2 \sim \cos^2(\pi x / a)$$



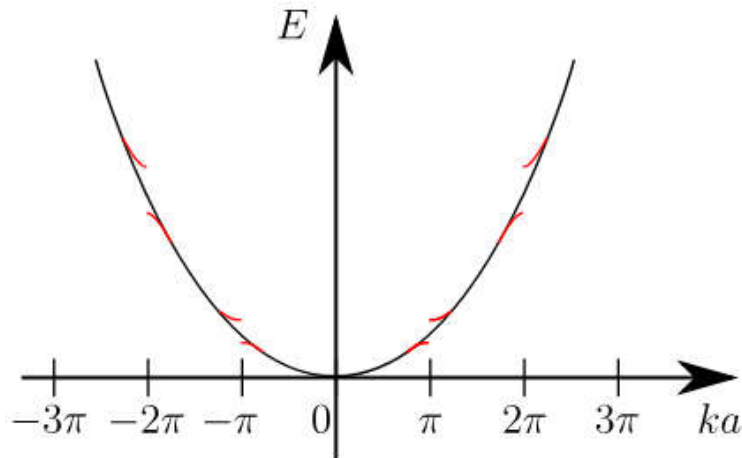
**Two wavefunctions  
have different  
probability  
distributions in the  
lattice**

# The Origin of Band Gap

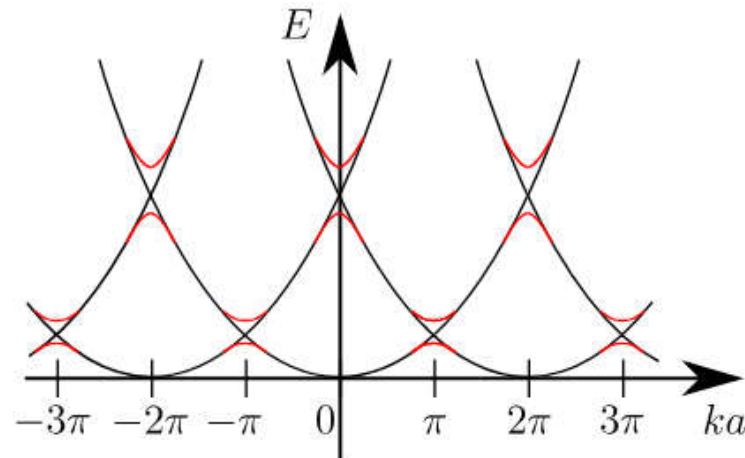
- The periodic potential perturbs the band of free electrons
- Another view: two electrons cannot occupy the same state (Pauli exclusion principle), the overlapped part has to be separated and repel each other



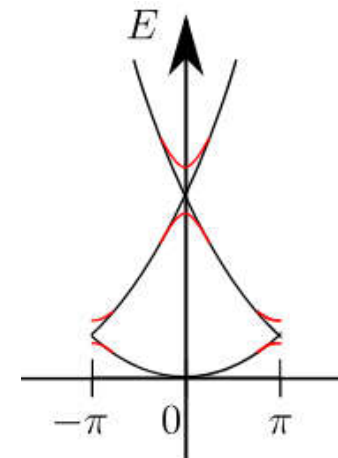
# Band Structure / Diagram 能带图



**extended zone /  
band structure**  
扩展布里渊区

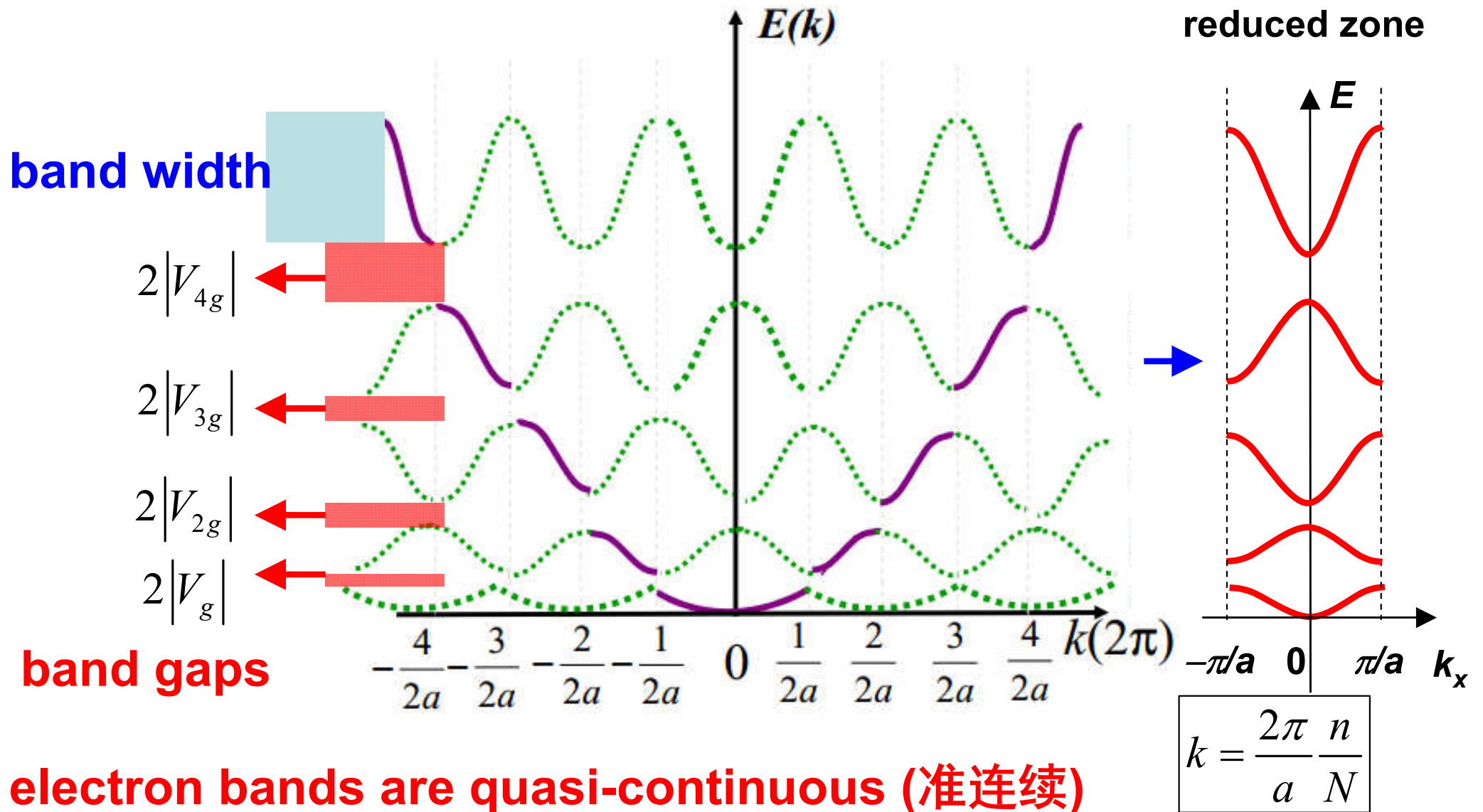


**repeated zone /  
band structure**  
周期性布里渊区

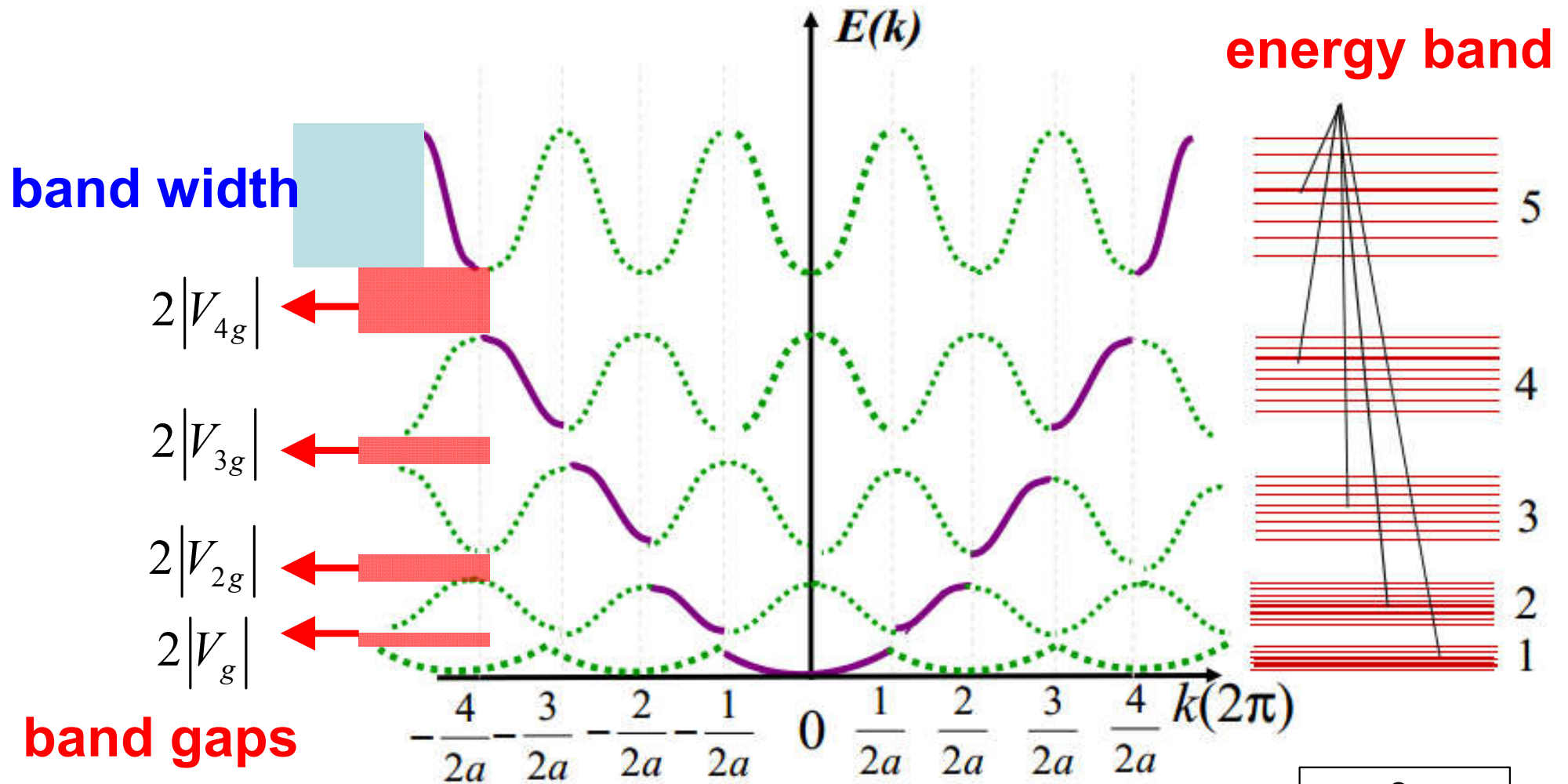


**reduced zone /  
band structure**  
简约布里渊区

# Band Structure / Diagram



# Band Structure / Diagram



electron bands are quasi-continuous (准连续)

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

$$n = 0, \pm 1, \pm 2, \dots \quad 23$$

***Thank you for your attention***