

# Review of the previous class

Q1: For electron gas, what is the temperature dependence of specific heat at low temperature ( $\ll$  Fermi temperature)?

A.  $T$

B.  $T^2$

C.  $T^3$

Q2: For electron gas in 1D, what is the temperature dependence of specific heat at low temperature ( $\ll$  Fermi temperature)?

A.  $T$

B.  $T^2$

C.  $T^3$

Q3: For electron gas with a dispersion relation,  $\varepsilon(k) = k^{1/2}$ , what is the temperature dependence of specific heat at low temperature ( $\ll$  Fermi temperature)?

A.  $T$

B.  $T^2$

C.  $T^3$

Q4: Typical Fermi temperature of metals is

A. 100 K

B. 10,000 K

C. 10,000,000 K

# Review of the previous class

Q5: For electron gas, which of the following is largely determined by the ground state ( $T=0$ ) property?

- A. Chemical potential    B. Heat capacity    C. Thermal Expansion

Q6: For electron gas, which of the following is strictly finite temperature property?

- A. Bulk modulus    B. Conductivity    C. Thermal conductivity

Q7: Typical Fermi velocity of metals is NOT  
( $c$ : speed of light,  $v_s$  = velocity of Debye phonon)

- A.  $c/100$     B.  $v_s$     C.  $v_s / 100$

Q8: Current in metals propagates at the

- A. speed of light    B. Fermi velocity    C. drift velocity ( $\sim 1\text{mm/s}$ )



# Lecture 6

## Electrons in Crystal

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Physicists may say “Bragg diffraction.”  
Chemists may say “Chemical bonding.”  
Electrons could not care less.



# Bloch's Theorem

For crystal translation  $T_{\mathbf{R}}$ , the complete basis can be taken as

$$\psi(\mathbf{x}) = \sum_{\mathbf{G}} C(\mathbf{k} + \mathbf{G}) \exp(i(\mathbf{k} + \mathbf{G}) \cdot \mathbf{x})$$

$C$  = complex number,  $\mathbf{G}$  = reciprocal lattice vector

**Bloch's theorem (form 1):**

## Bragg Diffraction Physics

The eigenstates of a periodic Hamiltonian can be chosen so that each eigenstate  $\psi(\mathbf{x})$  satisfies:

$$\psi(\mathbf{x}) = \exp(i\mathbf{k} \cdot \mathbf{x}) u_{n\mathbf{k}}(\mathbf{x}),$$

where  $u_{n\mathbf{k}}(\mathbf{x})$  has the same periodicity as the Hamiltonian, i.e.

$$u_{n\mathbf{k}}(\mathbf{x} + \mathbf{R}) = u_{n\mathbf{k}}(\mathbf{x})$$

for any lattice vector  $\mathbf{R}$  of the Hamiltonian. ( $\hbar\mathbf{k}$  is crystal momentum – NOT true momentum – and  $n$  is symbol for all other quantum numbers – e.g. phonon branch in the case of phonons and band index, spin in the case of electrons)

**Bloch's theorem (form 2):**

The eigenstates of a periodic Hamiltonian can be chosen so that each eigenstate  $\psi(\mathbf{x})$  satisfies:

$$\psi(\mathbf{x} + \mathbf{R}) = \exp(i\mathbf{k} \cdot \mathbf{R}) \psi(\mathbf{x})$$

for any lattice vector  $\mathbf{R}$  of the Hamiltonian.

# Never forget ...

Q1: A potential is periodic with period  $a$  on a ring of length  $L$ .  
Wave vectors associated with the potential are:

- A. integer  $\times 2\pi/a$       B. integer  $\times 2\pi/L$       C. any

Q2: For a phonon excitation on a 1D crystal of period  $a$  and length  $L$ , wave vectors are (within the Born-von-Karman B.C.):

- A. discrete with increment  $2\pi/a$   
B. discrete with increment  $2\pi/L$   
C. continuous

Q3: For electron or neutron on a 1D crystal of period  $a$  and length  $L$ , wave vectors are (within the Born-von-Karman B.C.):

- A. discrete with increment  $2\pi/a$   
B. discrete with increment  $2\pi/L$   
C. continuous

# Properties of Periodic Potential

$$V(x + na) = V(x) \text{ for any integer } n$$

$$\int_0^L dx V(x) \exp(-ikx) = 0 \text{ unless } k = \frac{2\pi}{a} m, m = \text{integer}$$

proof

$$I \equiv \int_0^L dx V(x) \exp(-ikx)$$

$$I * \exp(ikna) \equiv \int_0^L dx V(x) \exp(-ik(x-na)) = \int_{-na}^{L-na} dx V(x+na) \exp(-ikx) = \int_{-na}^{L-na} dx V(x) \exp(-ikx) = I$$

In order for this true for any  $n$ ,  $k = \frac{2\pi}{a} \times \text{integer} \equiv G$  (reciprocal lattice vector)

$$V(x) = \sum_G V_G \exp(iGx), \quad G = \frac{2\pi}{a} m, \quad m = \text{integer}$$

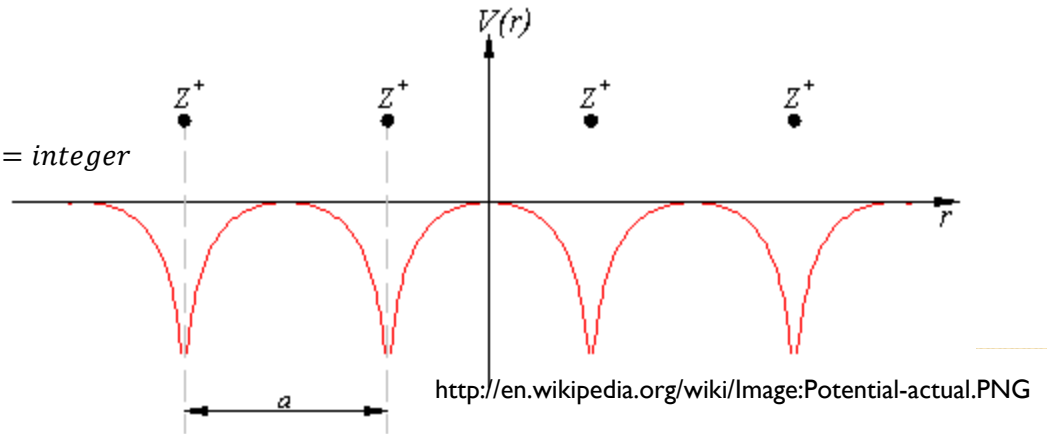
$$V_G = \frac{1}{L} \int_0^L dx V(x) \exp(-iGx)$$

proof (if necessary)

$$\int_0^L dx V(x) \exp(-iG'x) = \sum_G V_G \int_0^L dx \exp(iGx) \exp(-iG'x) = \sum_G V_G L \delta_{G,G'} = LV_{G'}$$

$$V(x) \text{ is real} \rightarrow V_G^* = V_{-G}$$

Hamiltonian is Hermitian in plane wave basis – it should be.



Easy to generalize to 3D

$$V(x) = \sum_G V_G \exp(i\mathbf{G} \cdot \mathbf{x}), \quad \mathbf{G} = p\mathbf{a}^* + q\mathbf{b}^* + r\mathbf{c}^*, \quad p, q, r = \text{integers} \quad \mathbf{a}, \mathbf{b}, \mathbf{c} = \text{real lattice} \quad \mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^* = \text{reciprocal lattice}$$

$$\mathbf{a}^* \cdot \mathbf{a} = \mathbf{b}^* \cdot \mathbf{b} = \mathbf{c}^* \cdot \mathbf{c} = 2\pi, \quad \mathbf{a}^* \cdot \mathbf{b} = \mathbf{a}^* \cdot \mathbf{c} = \mathbf{b}^* \cdot \mathbf{c} = \mathbf{b}^* \cdot \mathbf{a} = \mathbf{c}^* \cdot \mathbf{a} = \mathbf{c}^* \cdot \mathbf{b} = 0$$

$$V_G^* = V_{-G}$$

# Effect of Periodic Potential on Plane Wave Basis

$$\phi_k(x) = \exp(ikx), \quad k = \frac{2\pi}{L} \times \text{integer} \quad (\text{Born - von Karman B.C.})$$

$$H = \frac{p^2}{2m} + V(x)$$

$$\langle \phi_{k'} | H | \phi_k \rangle = \langle \phi_{k'} | V | \phi_k \rangle = \int_0^L dx \exp(i(k - k')x) V(x) \quad \text{for } k \neq k'$$

$$V(x) = \sum_G V_G \exp(iGx), \quad G = \frac{2\pi}{a} m, \quad m = \text{integer}$$

$$\langle \phi_{k'} | H | \phi_k \rangle = \sum_G V_G \int_0^L dx \exp(i(G + k - k')x)$$

$$G + k - k' = \frac{2\pi}{a} \times \text{integer} + \frac{2\pi}{L} \times \text{integer} = \frac{2\pi}{L} \times \text{integer} \quad \text{Period} = \frac{L}{\text{integer}}$$

$$\langle \phi_{k'} | H | \phi_k \rangle = 0 \quad \text{unless } k - k' = G \quad (\text{any reciprocal lattice vector})$$

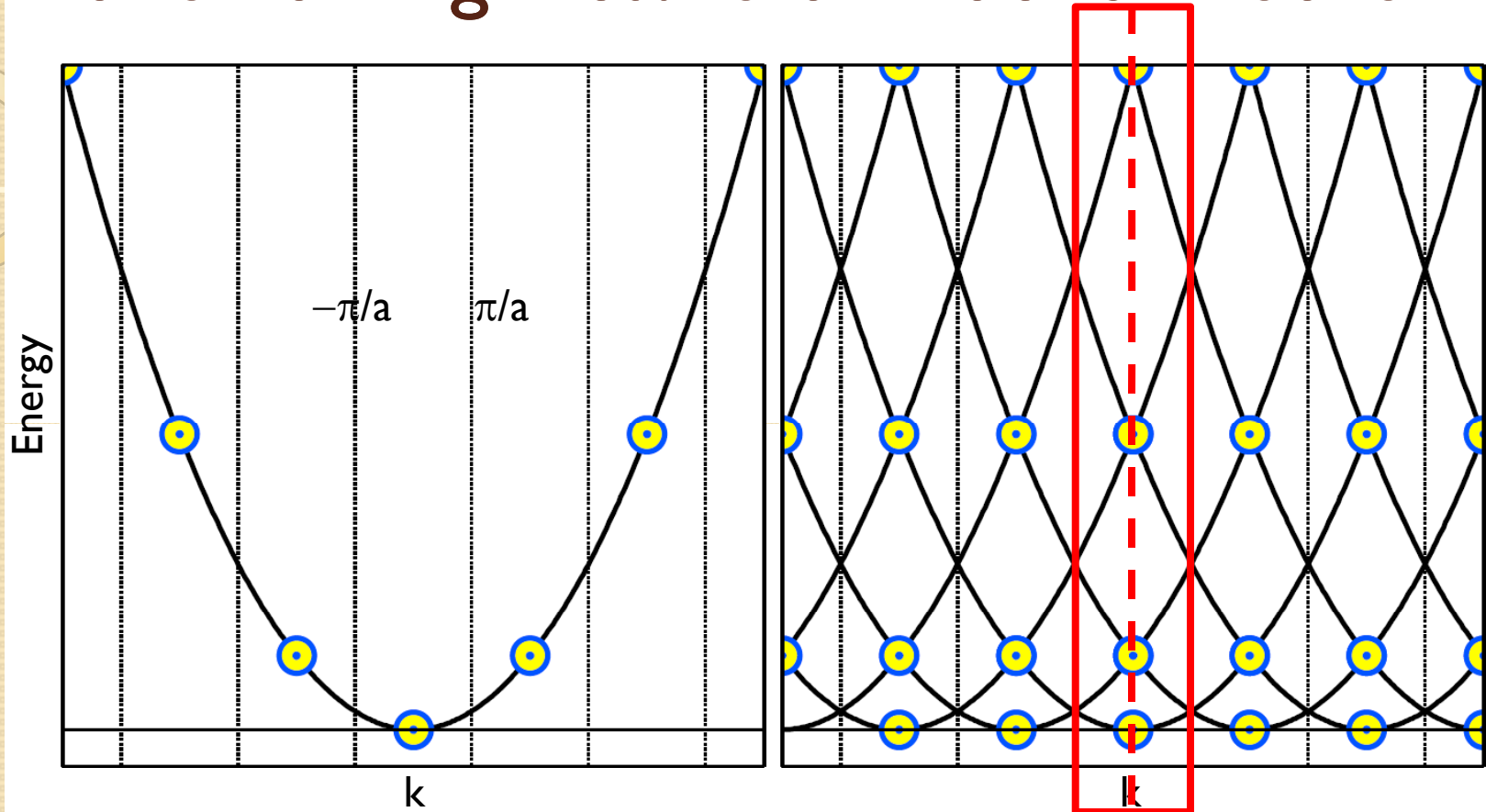
$$\psi_k(x) = \sum_G C(k + G) \exp(i(k + G)x) = \exp(ikx) u_k(x)$$

$$u_k(x + na) = u_k(x)$$

$$\psi_k(x + na) = \exp(ikna) \psi_k(x)$$

Another proof of Bloch's theorem  
Easily generalized to 3D  
(other quantum numbers such as spin are implicit)

# Zone Folding Picture of Bloch's Theorem



Procedure to solve for any crystal potential (not only for weak potential)

1. Start from plane wave
2. Fold the free electron band to the first Brillouin zone
3. Solve the block matrix of  $H$  for states along a vertical line

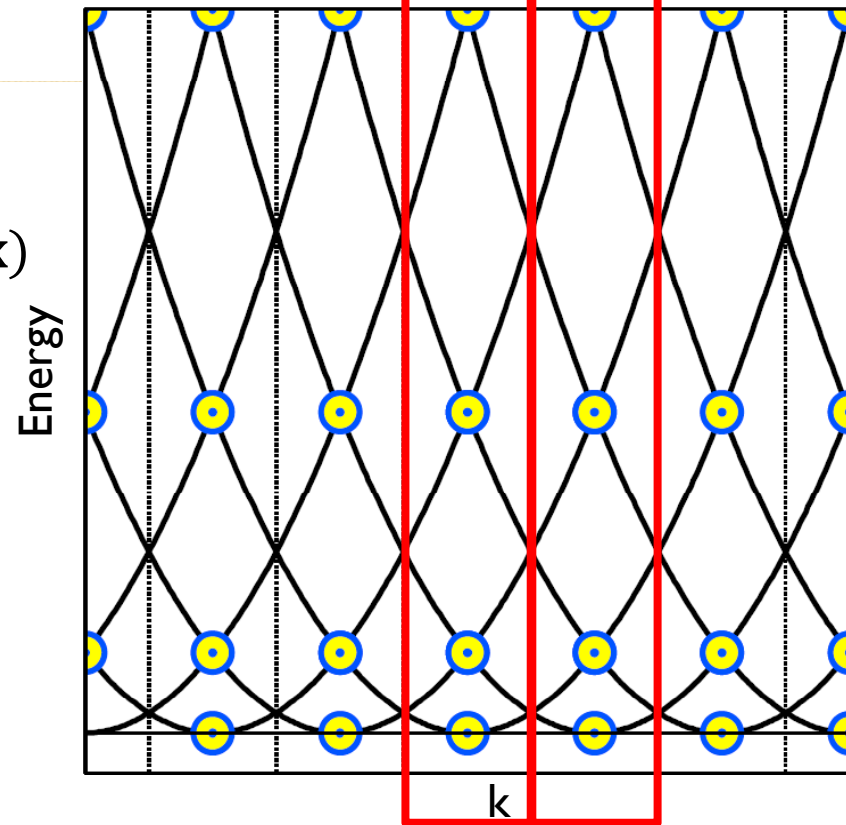
**VERY IMPORTANT**

# Crystal Momentum

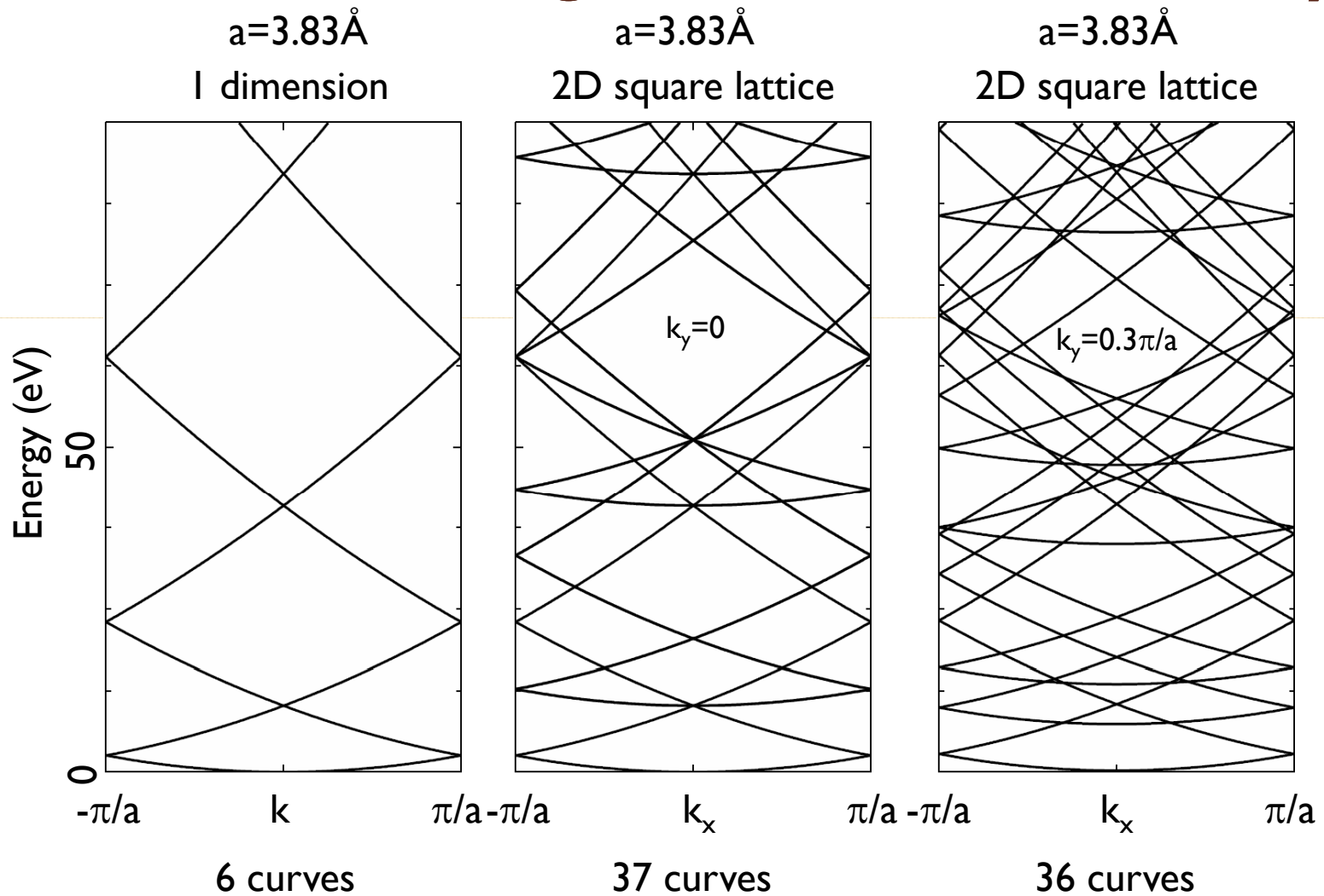
- Just like in phonon case, the wave vector  $\mathbf{k}$  is ambiguous up to any reciprocal lattice vector

$$\psi_{\mathbf{n}\mathbf{k}}(\mathbf{x} + \mathbf{R}) = \exp(i\mathbf{k} \cdot \mathbf{R}) \psi_{\mathbf{n}\mathbf{k}}(\mathbf{x})$$

Eigen-value of lattice translation  
 $\mathbf{k}$  is “**crystal momentum**”  
ambiguous up to  $\mathbf{G}$

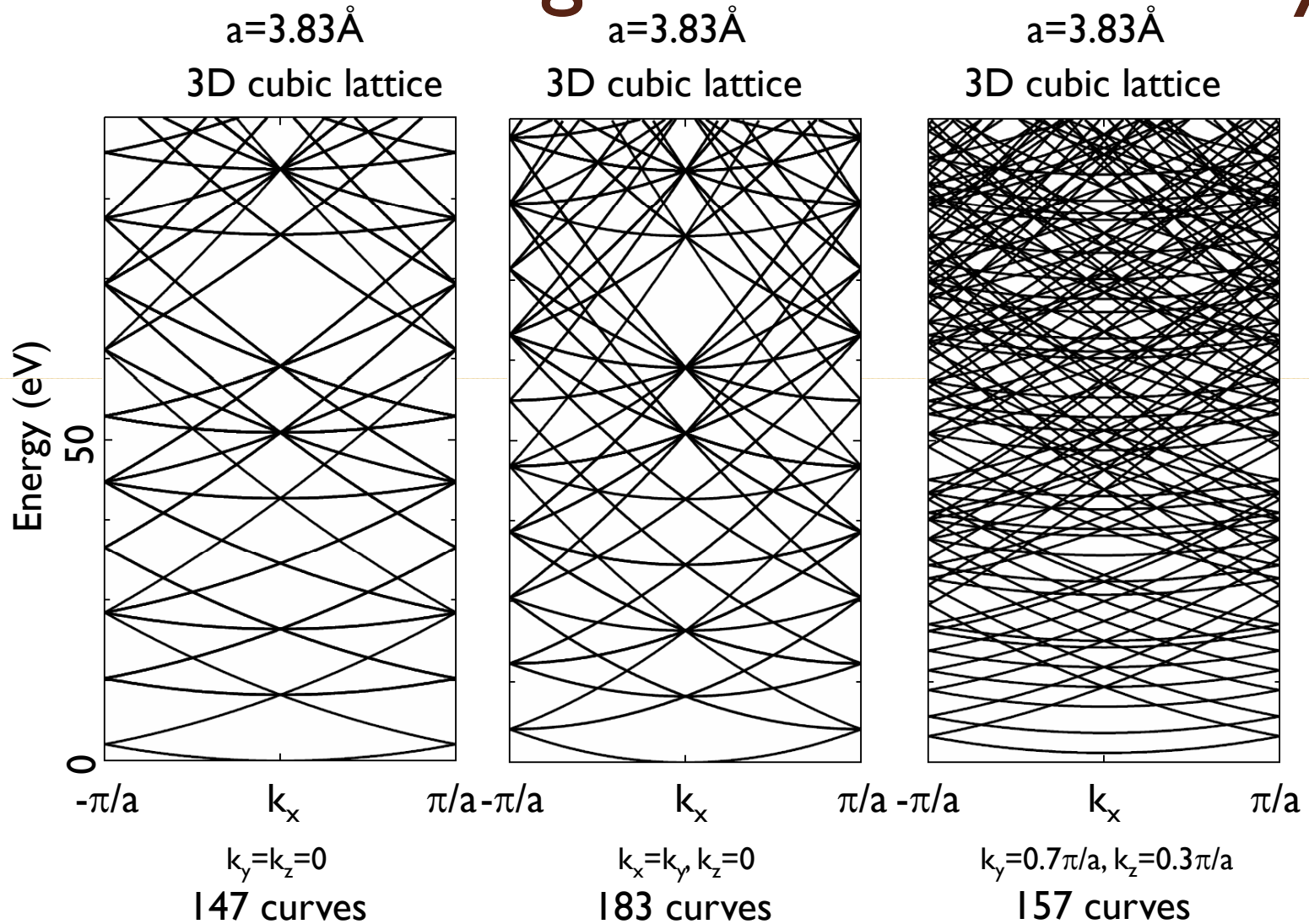


# Zone-Folding and dimensionality



This is what makes the scattering, such as photoelectric effect, possible in crystal, while it may not be possible in free space (homework).

# Zone-Folding and dimensionality



# Curves  $\sim A^D$ , for a given energy range (0 – 100 eV here; with  $A = 5-6$ )

# Equation of Motion ( $\infty \times \infty$ )

$$H = \frac{p^2}{2m} + V(x) = \frac{p^2}{2m} + \sum_G V(G) \exp(iGx)$$

$$\psi_k(x) = \sum_{G'} C(k + G') \exp(i(k + G')x)$$

$$H\psi_k(x) = \sum_{G'} \lambda_{k+G'} C(k + G') \exp(i(k + G')x) + \sum_{G,G'} V(G) \exp(iGx) C(k + G') \exp(i(k + G')x)$$

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

$$H\psi_k(x) = \sum_{G'} \lambda_{k+G'} C(k + G') \exp(i(k + G')x) + \sum_{G,G'} V(G) C(k + G') \exp(i(k + G + G')x)$$

$$= \sum_{G'} \lambda_{k+G'} C(k + G') \exp(i(k + G')x) + \sum_{G,G'} V(G) C(k + G' - G) \exp(i(k + G')x)$$

$$= \sum_{G'} \left[ \lambda_{k+G'} C(k + G') + \sum_G V(G) C(k + G' - G) \right] \exp(i(k + G')x)$$

$\infty \times \infty$  matrix !

$$H\psi_k(x) = E\psi_k(x) = E \sum_{G'} C(k + G') \exp(i(k + G')x)$$

$$\lambda_{k+G'} C(k + G') + \sum_G V(G) C(k + G' - G) = EC(k + G')$$

$$(\lambda_{k+G'} - E)C(k + G') + \sum_G V(G) C(k + G' - G) = 0$$

$$(\lambda_k - E)C(k) + \sum_G V(G) C(k - G) = 0$$

$$\begin{bmatrix} V(1) & \lambda_{k-G} & V(2) & V(3) & \dots \\ V(2) & \lambda_k - E & V(1) & V(2) & \dots \\ \dots & V(2) & V(1) & \lambda_{k+G} & \dots \end{bmatrix} \begin{bmatrix} C(k-G) \\ C(k) \\ C(k+G) \\ \vdots \end{bmatrix} = 0$$

# Toy Problem (Kronig-Penney)

$$V(x) = Aa \sum_{n=1}^N \delta(x - na)$$

$$V(G) = \frac{1}{L} \int_0^L dx V(x) \exp(-iGx) = \frac{1}{L} Aa \sum_{n=1}^N \exp(-iGna), \quad G = \text{integer} \times \frac{2\pi}{a}$$

$$V(G) = \frac{1}{L} AaN = \frac{AL}{L} = A$$

$$1 = - \sum_{n=-\infty}^{\infty} \frac{A}{\lambda_{k-2\pi n/a} - E}$$

$N \rightarrow \infty$

$$(\lambda_k - E)C(k) + A \sum_{n=-\infty}^{\infty} C\left(k - \frac{2\pi n}{a}\right) = 0$$

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

$$\cot(x) = \sum_{n=-\infty}^{\infty} \frac{1}{n\pi + x}$$

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

a bit of math

$$f(k) \equiv \sum_{n=-\infty}^{\infty} C\left(k - \frac{2\pi n}{a}\right)$$

$$C(k) = -\frac{Af(k)}{\lambda_k - E}$$

$$\frac{\hbar^2}{2mA} = - \sum_{n=1}^N \frac{1}{\left(k - \frac{2\pi n}{a}\right)^2 - K^2} = \frac{a^2 \sin(Ka)}{4Ka(\cos(ka) - \cos(Ka))}$$

$$f\left(k - \frac{2\pi m}{a}\right) = f(k), \quad m = \text{any integer}$$

$$f(k) = \sum_{n=-\infty}^{\infty} C\left(k - \frac{2\pi n}{a}\right) = \sum_{n=-\infty}^{\infty} -\frac{Af(k)}{\lambda_{k-2\pi n/a} - E}$$

$$\frac{P \sin(Ka)}{Ka} + \cos(Ka) = \cos(ka)$$

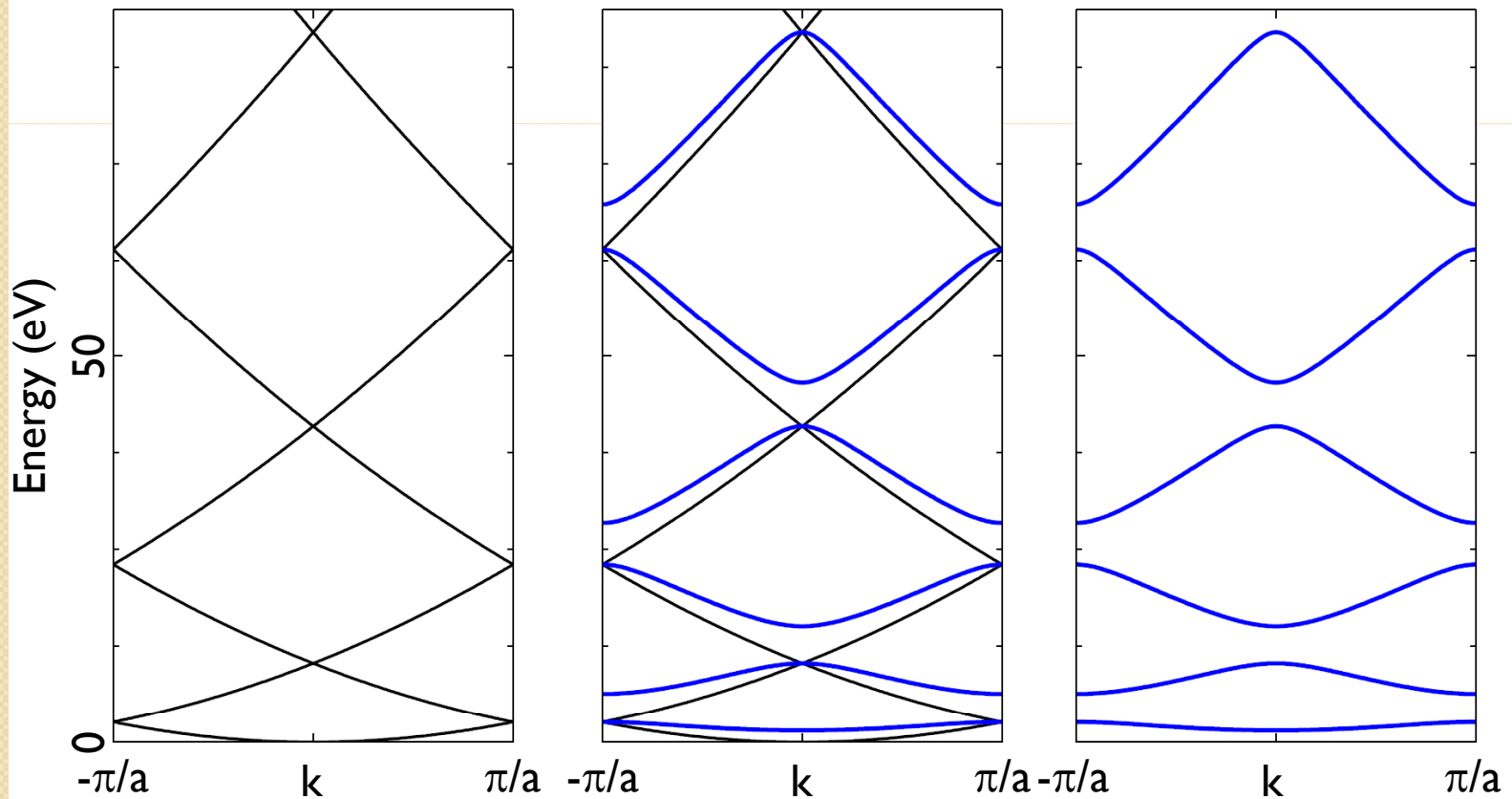
$$P = \frac{mAa^2}{2\hbar^2}$$

# Toy Problem (Kronig-Penney)

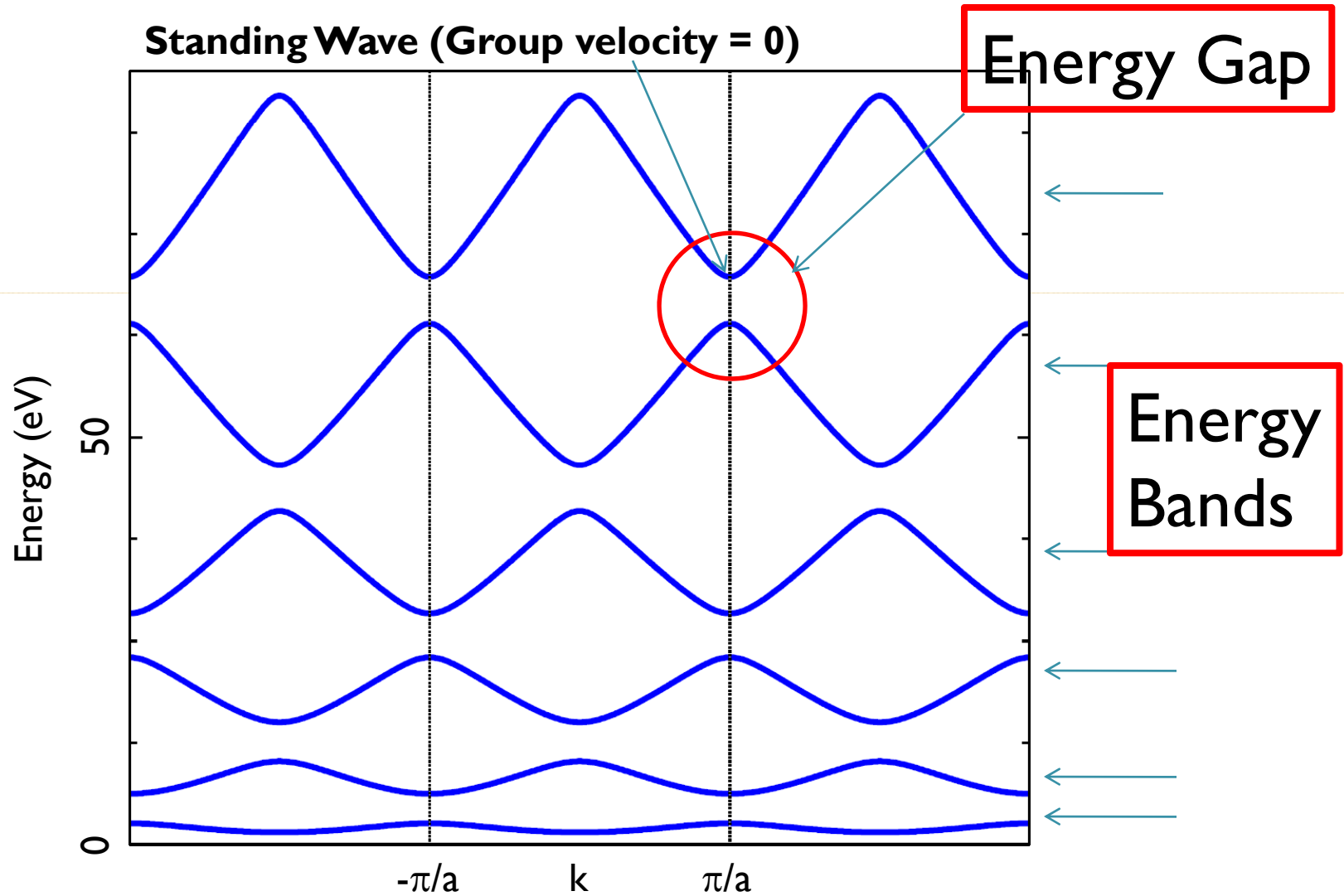
$$\frac{P \sin(Ka)}{Ka} + \cos(Ka) = \cos(ka)$$

$$P = \frac{m A a^2}{2 \hbar^2}$$

$$a = 3.83 \text{ \AA}$$
$$P = 6$$



# Toy Problem (Kronig-Penney)



# Reminder

Consider a Hamiltonian for two states  $|0\rangle, |1\rangle$  interacting with each other

$$\begin{bmatrix} 0 & V \\ V^* & 0 \end{bmatrix}$$

$$V = |V| \exp(i\delta)$$

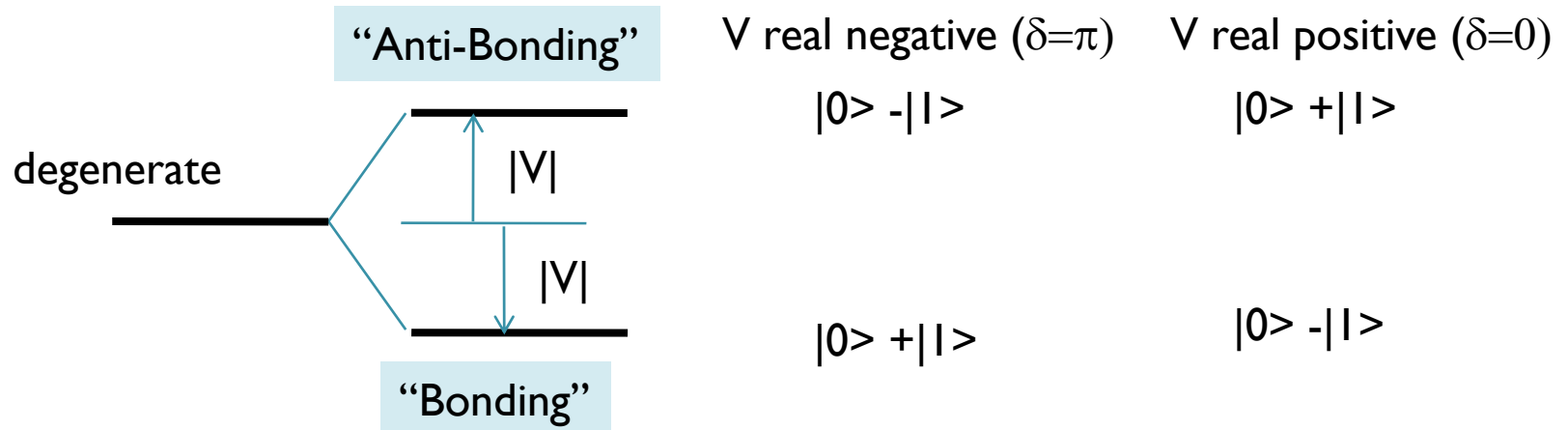
Eigen-values =  $\pm |V|$

Equal parts of  $|0\rangle$  and  $|1\rangle$

Eigen-state =  $|0\rangle - \exp(-i\delta)|1\rangle$ , for Eigen-value =  $-|V|$  (ground state)

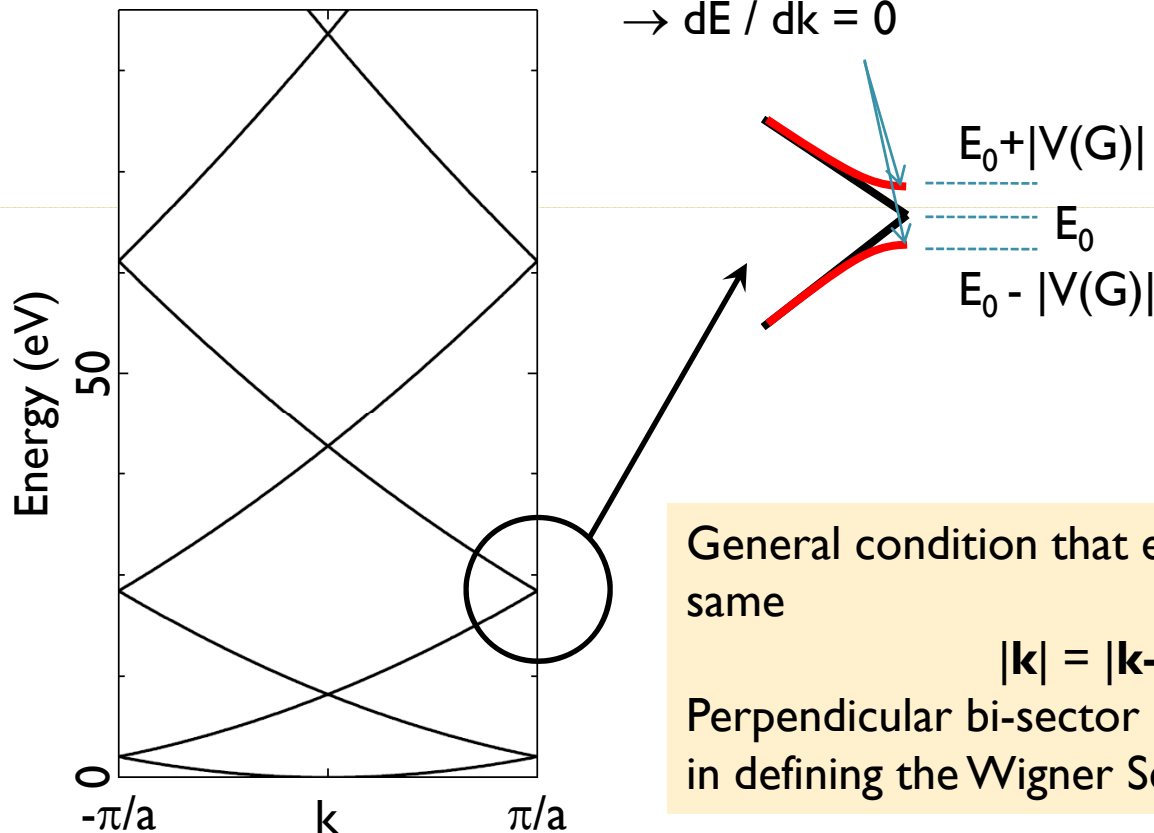
$|0\rangle + \exp(i\delta)|1\rangle$ , for Eigen-value =  $|V|$  (excited state)

Up to a normalization factor ( $1/\sqrt{2}$ )



# In the limit of weak potential

At  $k=\pi/a$ , wave function is equal mix of  $k$  and  $k+\mathbf{G}$   
→ Standing Wave (group velocity = 0)  
→  $dE / dk = 0$

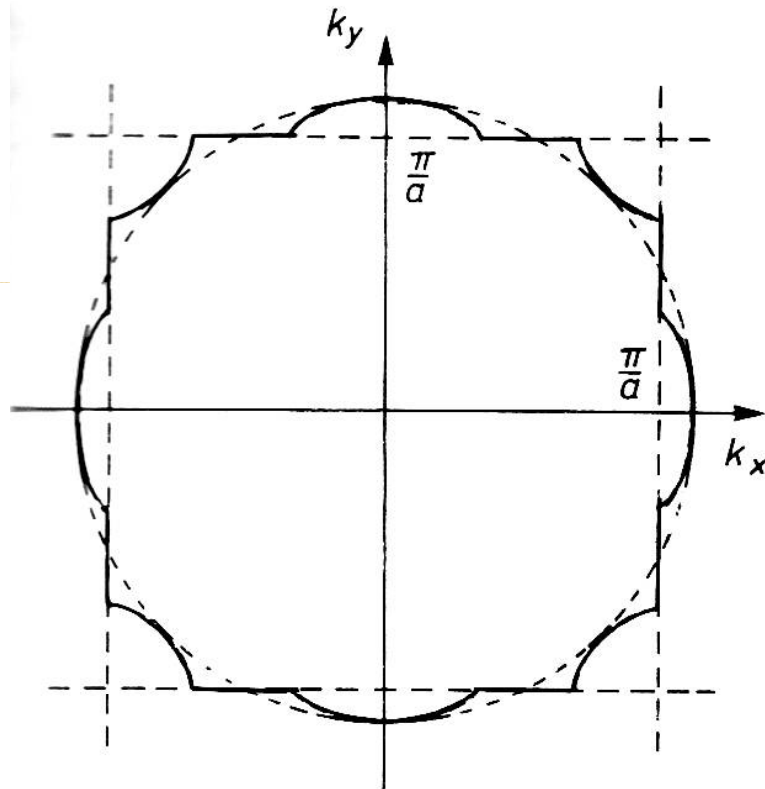


General condition that energies are the same

$$|\mathbf{k}| = |\mathbf{k}-\mathbf{G}|$$

Perpendicular bi-sector planes that we used in defining the Wigner Seitz Cell!

# Change in the Fermi Surface



Gradient of  $E(k)$  is parallel to the BZ face, i.e. the group velocity perpendicular to the BZ face is zero. (homework)

Constant energy contour intersects BZ at right angle

H&H, Figure 4.5

# Metals, Insulator, Semi-conductors, Semi-metals

No band gap,      Gap > 1 eV,      Gap < 1 eV,      No Gap  
Partially filled bands      All bands filled      Small number of e's and holes

To entirely fill a band, need 2 electrons per unit cell. Bands can also overlap.

Wilson's rule: metal if an odd number of free electrons per unit cell

