

NFE model is good for Na, K, Al... etc, in which the lattice potential is only a small perturbation to the electron sea.

## Energy bands (Nearly-free electron model)

- Bragg reflection and energy gap
- Bloch theorem
- The central equation
- Empty-lattice approximation

- For history on band theory, see 半導體的故事, by 李雅明, chap 4

Bloch recalled,

The main problem was to explain how the electrons could sneak by all the ions in a metal so as to avoid a mean free path of the order of atomic distances. Such a distance was much too short to explain the observed resistances, which even demanded that the mean free path become longer and longer with decreasing temperature.

By straight Fourier analysis I found to my delight that the wave differed from the plane wave of free electrons only by a periodic modulation. This was so simple that I didn't think it could be much of a discovery, but when I showed it to Heisenberg he said right away: "That's it!"

$$\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_{\vec{k}}(\vec{r})$$

## Nearly-free electron model

### Free electron plane wave

$$\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}, \quad k_x = n_x \frac{2\pi}{L} \dots \text{etc}$$

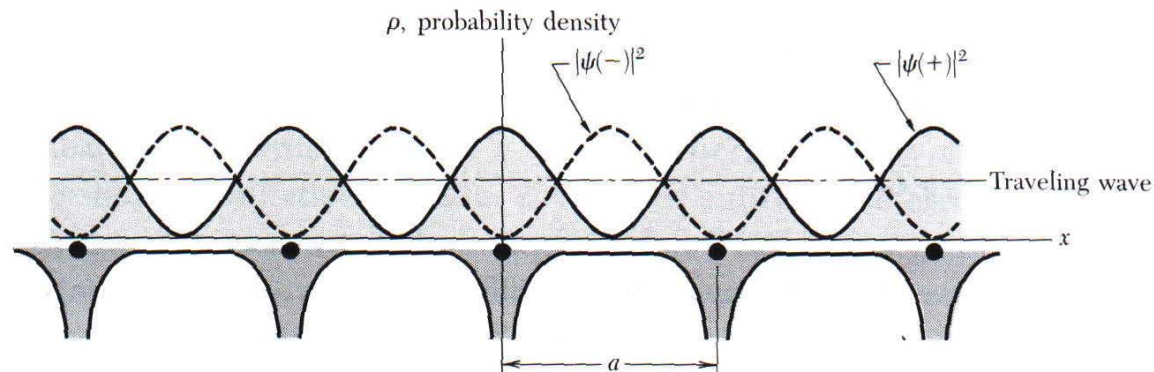
- Consider 1-dim case, when we turn on a lattice potential with period  $a$ , the electron wave will be **Bragg reflected** when  $k = \pm \pi/a$ , which forms two different types of **standing wave**. (Peierls, 1930)

$$\psi_+ = c \left( e^{i\pi x/a} + e^{-i\pi x/a} \right) = \sqrt{\frac{2}{a}} \cos\left(\frac{\pi x}{a}\right),$$

$$\psi_- = c \left( e^{i\pi x/a} - e^{-i\pi x/a} \right) = i\sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right).$$

$$\vec{k} \cdot \hat{G} = \frac{G}{2}$$

- **Density distribution of the two standing waves**



- These 2 standing waves have different electrostatic energies. This is the origin of the energy gap.

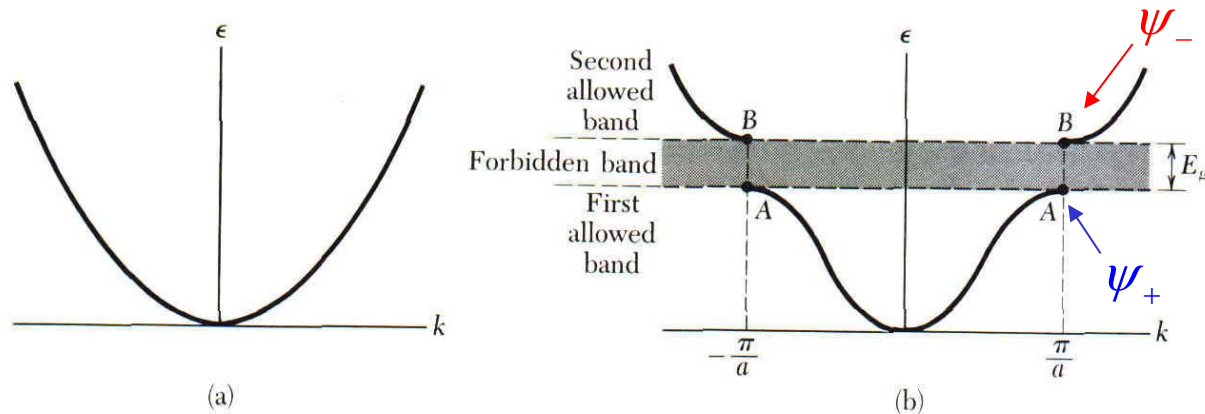
If potential  $V(x)=V\cos(2\pi x/a)$ , then

Note: Kittel use *potential energy*  $U (=eV)$

$$E_g = \int_0^a dx V(x)(-e) (|\psi_-(x)|^2 - |\psi_+(x)|^2)$$

$$= -\frac{2e}{a} V \int_0^a dx \cos\left(\frac{2\pi x}{a}\right) \left( \sin^2 \frac{\pi x}{a} - \cos^2 \frac{\pi x}{a} \right) = eV$$

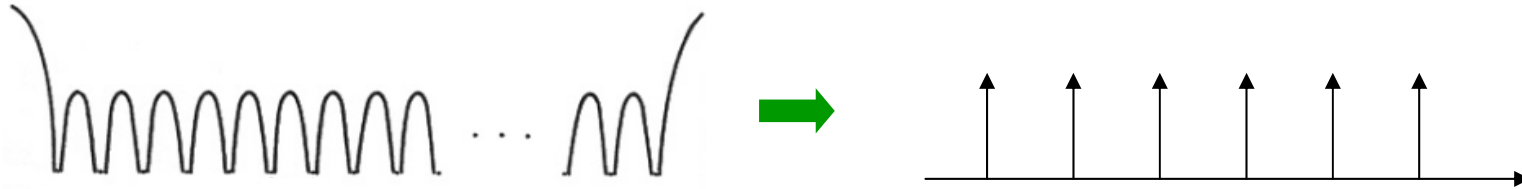
- Lattice effect on free electron's energy dispersion



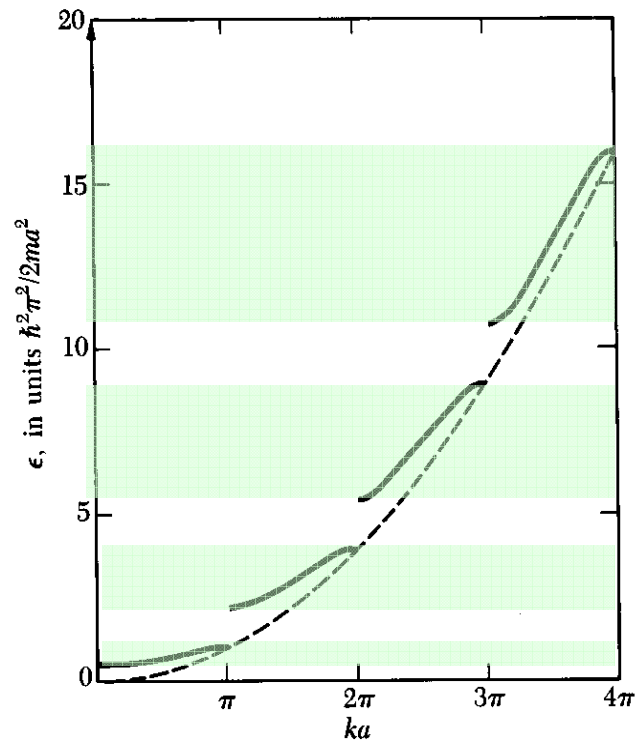
Electron's group velocity is zero near the boundary of the 1st BZ (because of the standing wave).

Q: where are the energy gaps when  $U(x)=U_1 \cos(2\pi x/a)+U_2 \cos(4\pi x/a)$ ?

A solvable model in 1-dim: The Kronig-Penny model (1930)  
(not a bad model for superlattice)



- Electron energy dispersion calculated from the Schrodinger eq.



Energy bands  
(Kittel, p.168)

## Bloch theorem (1928)

The electron states in a periodic potential is of the form

$$\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_{\vec{k}}(\vec{r}), \text{ where } u_{\vec{k}}(\mathbf{r}+\mathbf{R}) = u_{\vec{k}}(\mathbf{r}) \text{ is a cell-periodic function.}$$

- A simple proof for 1-dim:

$$|\Psi(x)|^2 \text{ is the same in each unit cell. } \longrightarrow \Psi(x+a) = C \Psi(x)$$

$$\text{Consider periodic BC, } \psi(x+Na) = C^N \psi(x) = \psi(x)$$

$$\longrightarrow C = \exp\left(2\pi i \frac{s}{N}\right), \quad s = 0, 1, 2, \dots, (N-1)$$

$$\text{write } \psi_k(x) = \exp\left(2\pi i \frac{s}{Na} x\right) u_k(x), \quad 2\pi \frac{s}{Na} = k$$

$$\text{then } u_k(x+a) = u_k(x)$$

Similar proof can be extended to higher dimensions.

- Schrodinger eq for  $\psi$ :

$$H\psi_{\vec{k}} = \varepsilon_{\vec{k}}\psi_{\vec{k}}, \quad H = \frac{p^2}{2m} + U(\vec{r})$$

Lattice potential

$$\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_{\vec{k}}(\vec{r})$$

$u_{\vec{k}}(\vec{r})$  depends on the form of the periodic lattice potential.

- Schrodinger eq for  $u$ :

$$\tilde{H}(\vec{k})u_{\vec{k}} = \varepsilon_{\vec{k}}u_{\vec{k}} \quad \text{within one unit cell}$$

$10^{23}$  times less effort than the original Schrodinger eq.

where  $\tilde{H}(\vec{k}) \equiv e^{-i\vec{k}\cdot\vec{r}} H e^{i\vec{k}\cdot\vec{r}}$  ← Effective Hamiltonian for  $u_{\vec{k}}(\vec{r})$

$$= \frac{\hbar^2}{2m} \left( \frac{\nabla}{i} + \vec{k} \right)^2 + U(\vec{r})$$

Allowed values of  $k$  are determined by the B.C.

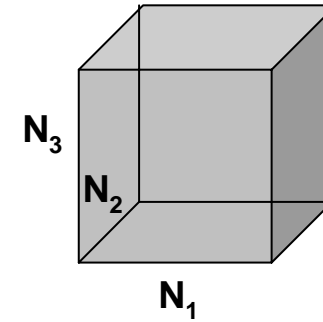
Periodic B.C.  
(3-dim case)

$$\psi_{\vec{k}}(\vec{r} + N_i \vec{a}_i) = \psi_{\vec{k}}(\vec{r}), \quad i=1,2,3$$

$$\rightarrow e^{i\vec{k} \cdot N_i \vec{a}_i} = 1, \quad \forall i$$

$$\rightarrow \vec{k} \cdot N_i \vec{a}_i = 2\pi m_i, \quad m_i \in \mathbb{Z}, \quad \forall i$$

$$\rightarrow \boxed{\vec{k} = \frac{m_1}{N_1} \vec{b}_1 + \frac{m_2}{N_2} \vec{b}_2 + \frac{m_3}{N_3} \vec{b}_3}$$



$$\Delta^3 \vec{k} = \frac{\vec{b}_1}{N_1} \cdot \left( \frac{\vec{b}_2}{N_2} \times \frac{\vec{b}_3}{N_3} \right) = \frac{1}{N} \vec{b}_1 \cdot (\vec{b}_2 \times \vec{b}_3) \rightarrow \boxed{\frac{\vec{b}_1 \cdot (\vec{b}_2 \times \vec{b}_3)}{\Delta^3 \vec{k}} = N}$$

$$N = N_1 N_2 N_3$$

- $\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3) = v = \frac{V}{N},$
- $\vec{b}_1 \cdot (\vec{b}_2 \times \vec{b}_3) = \frac{(2\pi)^3}{v},$
- $\Delta^3 k = \frac{(2\pi)^3}{V},$  as in the free-electron case.

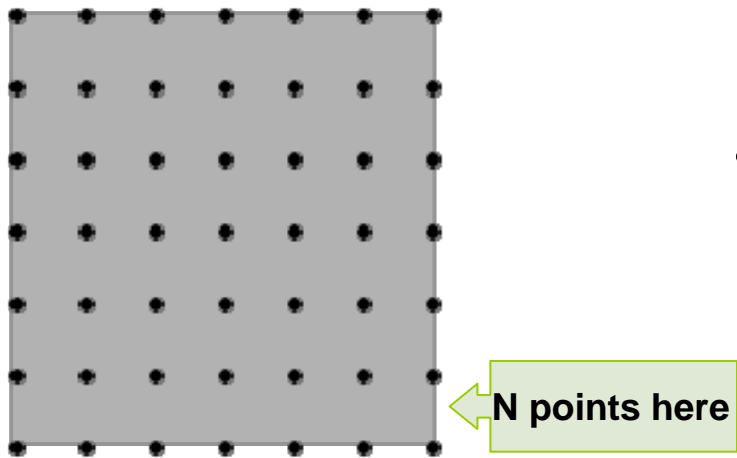
Therefore, there are  $N$   $k$ -points in a BZ (a unit cell in reciprocal lattice), where  $N$  = total number of primitive unit cells in the crystal.



## Countings in r-space and k-space

r-space

a crystal with PBC:



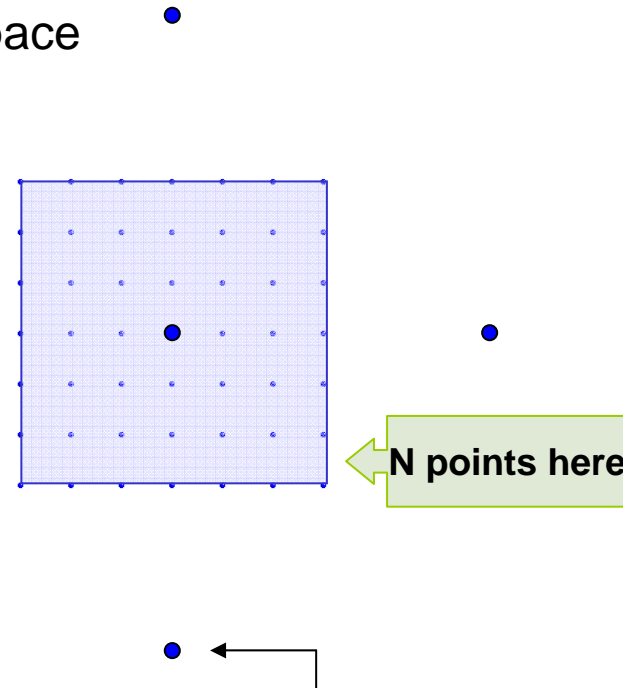
- N unit cells

(N lattice points x 1 atom/point)

- If each atom contributes  $q$  conduction electrons, then  $Nq$  electrons in total.

Q: what if there are  $p$  atoms per lattice point?

k-space



- Infinite reciprocal lattice points
- N  $k$ -points in 1<sup>st</sup> BZ
- N  $k$ -points in an energy band

## Difference between conductor and insulator (Wilson, 1931)

- There are  $N$   $k$ -points in an energy band, each  $k$ -point can be occupied by two electrons (spin up and down).

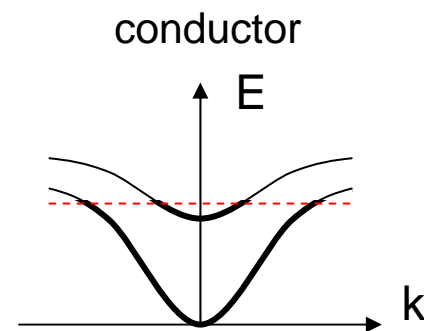
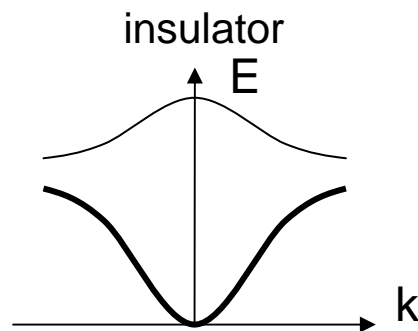
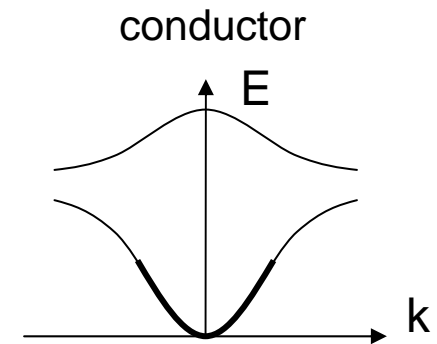
$\therefore$  each energy band has  $2N$  “seats” for electrons.

- If a solid has **odd** number of valence electron per primitive cell, then the energy band is **half-filled** (conductor).

For example, all alkali metals are conductors.

- If a solid has **even** number of valence electron per primitive cell, then the energy band **might be filled** (if filled, then insulator).

E.g., alkali earth elements can be conductor or insulator.



## I. FUNCTION WITH LATTICE TRANSLATION SYMMETRY

In Chap 2, we have lattice systems with discrete translation symmetry. Physical quantity such as the distribution of charge density,  $n(\mathbf{r})$ , is invariant under lattice translation,

$$\underline{n(\mathbf{r} + \mathbf{R}) = n(\mathbf{r})}, \quad (1)$$

where  $\mathbf{R}$  is any given lattice vector. Such a function can be Fourier decomposed as

$$n(\mathbf{r}) = \sum_{\mathbf{G}} n_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}}, \quad (2)$$

where  $G$  is the reciprocal lattice vector. For a simple cubic lattice with lattice constant  $a$ ,  $\mathbf{G} = \frac{2\pi}{a}(n_x, n_y, n_z)$ , where  $n_{x,y,z}$  are integers.

The set of exponentials,  $\{e^{i\mathbf{G}\cdot\mathbf{r}}\}$ , satisfy the orthogonal relation,

$$\langle \mathbf{G}' | \mathbf{G} \rangle \equiv \int_{\text{cell}} d^3r e^{-i\mathbf{G}'\cdot\mathbf{r}} e^{i\mathbf{G}\cdot\mathbf{r}} = v\delta_{\mathbf{G},\mathbf{G}'}. \quad (3)$$

The integration is over a unit cell with volume  $v$ . As a result, this set of exponentials can be considered as a set of independent basis vectors, and the function  $n(\mathbf{r})$  can be considered as a vector in an infinite-dimensional vector space (the Hilbert space).

Applying the orthogonal relation to Eq. (2), we can evaluate the coefficient of expansion,

$$n_{\mathbf{G}} = \frac{1}{v} \int_{\text{cell}} d^3r n(\mathbf{r}) e^{-i\mathbf{G}\cdot\mathbf{r}}. \quad (4)$$

Obviously, if  $n(\mathbf{r}) = 0$ , then  $n_{\mathbf{G}} = 0$  for  $\forall \mathbf{G}$ . This also implies that, if

$$\sum_{\mathbf{G}} g_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}} = \sum_{\mathbf{G}} h_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}}, \quad (5)$$

then

$$g_{\mathbf{G}} = h_{\mathbf{G}} \text{ for } \forall \mathbf{G}. \quad (6)$$

To prove it, one simply put the two summations on the same side of the equation and identify  $g_{\mathbf{G}} - h_{\mathbf{G}}$  as  $n_{\mathbf{G}}$ . Eq. (6) merely reflects the fact that the basis vectors,  $\{e^{i\mathbf{G}\cdot\mathbf{r}}\}$ , are linearly independent.

How do we determine  $u_{\vec{k}}(\mathbf{r})$  from lattice potential  $U(\mathbf{r})$ ?

Schrodinger equation 
$$\left[ \frac{(\vec{p} + \hbar\vec{k})^2}{2m} + U(\vec{r}) \right] u_{\vec{k}}(\vec{r}) = \varepsilon_{\vec{k}} u_{\vec{k}}(\vec{r})$$

Keypoint: go to  $k$ -space to avoid derivatives and simplify the calculation

Fourier transform

1. the lattice potential

$$U(\vec{r}) = \sum_{\vec{G}} U_{\vec{G}} e^{i\vec{G}\cdot\vec{r}} \quad \mathbf{G} = 2\pi \mathbf{n}/a$$

2. the wave function

$$u_{\vec{k}}(\vec{r}) = \sum_{\vec{G}} C_{\vec{k}}(\vec{G}) e^{-i\vec{G}\cdot\vec{r}} \quad \mathbf{k} = 2\pi \mathbf{n}/L$$

→ Schrod. eq. in  $k$ -space  
aka. the central eq.

$$\left( \varepsilon_{\vec{k}-\vec{G}}^0 - \varepsilon_{\vec{k}} \right) C_{\vec{k}}(\vec{G}) + \sum_{\vec{G}'} U_{\vec{G}'-\vec{G}} C_{\vec{k}}(\vec{G}') = 0, \quad \varepsilon_{\vec{k}}^0 \equiv \frac{\hbar^2 k^2}{2m}$$

Kittel  
uses  $\lambda_{\vec{k}}$

Matrix form of the central eq. (in 1D)

$$G=ng \quad (g \equiv 2\pi/a)$$

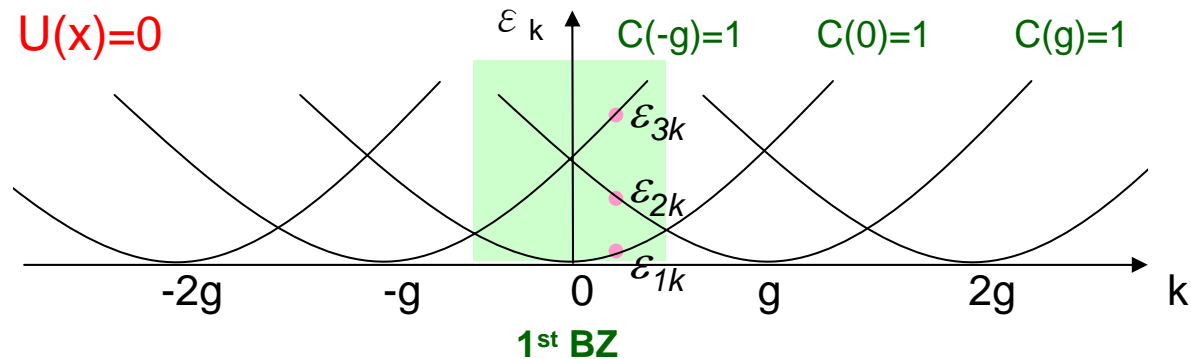
$$\begin{matrix} \ddots & & & & & & \vdots \\ \left( \begin{array}{ccccc} \varepsilon_{k+2g}^0 - \varepsilon_k & U_g & U_{2g} & U_{3g} & U_{4g} \\ U_{-g} & \varepsilon_{k+g}^0 - \varepsilon_k & U_g & U_{2g} & U_{3g} \\ U_{-2g} & U_{-g} & \varepsilon_k^0 - \varepsilon_k & U_g & U_{2g} \\ U_{-3g} & U_{-2g} & U_{-g} & \varepsilon_{k-g}^0 - \varepsilon_k & U_{-g} \\ U_{-4g} & U_{-3g} & U_{-2g} & U_{-g} & \varepsilon_{k-2g}^0 - \varepsilon_k \end{array} \right) \begin{pmatrix} C_k(-2g) \\ C_k(-g) \\ C_k(0) \\ C_k(g) \\ C_k(2g) \\ \vdots \end{pmatrix} = 0 & \leftarrow & \text{for a particular } k \end{matrix}$$

- For a given  $k$ , there are many eigen-values  $\varepsilon_{nk}$  with eigen-vectors  $\mathbf{C}_{nk}$ .
- The eigenvalues  $\varepsilon_n(k)$  determines the energy band.
- The eigenvectors  $\{C_{nk}(G), \forall G\}$  determines the Bloch states.

Example:  $U(x) = 2U \cos 2\pi x/a$

$$\begin{matrix} \ddots & & & & & & \vdots \\ \left( \begin{array}{ccccc} \varepsilon_{k+2g}^0 - \varepsilon_k & U & 0 & 0 & 0 \\ U & \varepsilon_{k+g}^0 - \varepsilon_k & U & 0 & 0 \\ 0 & U & \varepsilon_k^0 - \varepsilon_k & U & 0 \\ 0 & 0 & U & \varepsilon_{k-g}^0 - \varepsilon_k & U \\ 0 & 0 & 0 & U & \varepsilon_{k-2g}^0 - \varepsilon_k \end{array} \right) \begin{pmatrix} C_k(-2g) \\ C_k(-g) \\ C_k(0) \\ C_k(g) \\ C_k(2g) \\ \vdots \end{pmatrix} = 0 \end{matrix}$$

- What are the eigen-energies and eigen-states when  $U=0$ ?



- when  $U(x) \neq 0$ , for a particular  $k$ ,  $u_{nk}$  is a linear combination of plane waves, with coefficients  $C_{nk}$ :

$$u_{nk}(x) = \sum_G C_{nk}(G) e^{-iGx}$$

- From the central eq., one can see that  $C_{k+G'}(G+G') = C_k(G)$

$$u_{nk}(x) = \sum_G C_{nk}(G) e^{-iGx}$$

$$\Rightarrow u_{n,k+G}(x) = e^{-iGx} u_{nk}(x)$$

$$\psi_{n,k+G}(x) = \psi_{nk}(x)$$

$$\psi_{n,\vec{k}}(\vec{r} + \vec{R}) = e^{i\vec{k} \cdot \vec{R}} \psi_{n,\vec{k}}(\vec{r});$$

$$\psi_{n,\vec{k} + \vec{G}}(\vec{r}) = \psi_{n,\vec{k}}(\vec{r})$$

- Bloch energy  $\epsilon_{n,k+G} = \epsilon_{nk}$  ( $\because$  info in the 1<sup>st</sup> BZ is enough)

## Approximation of the central equation

- The Bloch state  $\psi_{nk}(x) = \sum_G C_{nk}(G) e^{i(k-G)x}$

is a superposition of ...  $\exp[i(k-g)x]$ ,  $\exp[ikx]$ ,  $\exp[i(k+g)x]$  ...

- If  $k \sim 0$ , then the most significant component of  $\psi_{1k}(x)$  is  $\exp[ikx]$  (little superposition from other plane waves).
- If  $k \sim g/2$ , then the most significant components of  $\psi_{1k}(x)$  and  $\psi_{2k}(x)$  are  $\exp[i(k-g)x]$  and  $\exp[ikx]$ , others can be neglected.

Truncation:

$$\begin{array}{cccccc}
 \ddots & & & & & \vdots \\
 \left( \begin{array}{cccccc}
 \varepsilon_{k+2g}^0 - \varepsilon_k & U & 0 & 0 & 0 & \\
 U & \varepsilon_{k+g}^0 - \varepsilon_k & U & 0 & 0 & \\
 0 & U & \boxed{\varepsilon_k^0 - \varepsilon_k} & U & 0 & \\
 0 & 0 & U & \varepsilon_{k-g}^0 - \varepsilon_k & U & \\
 0 & 0 & 0 & U & \varepsilon_{k-2g}^0 - \varepsilon_k & \\
 & & & & \ddots & 
 \end{array} \right)
 \begin{array}{c}
 \left( \begin{array}{c}
 C_k(-2g) \\
 C_k(-g) \\
 \boxed{C_k(0)} \\
 \boxed{C_k(g)} \\
 C_k(2g) \\
 \vdots
 \end{array} \right) = 0
 \end{array}
 \end{array}
 \quad \text{cutoff for } k \sim g/2!$$



## Energy levels near zone boundary $k \sim g/2$

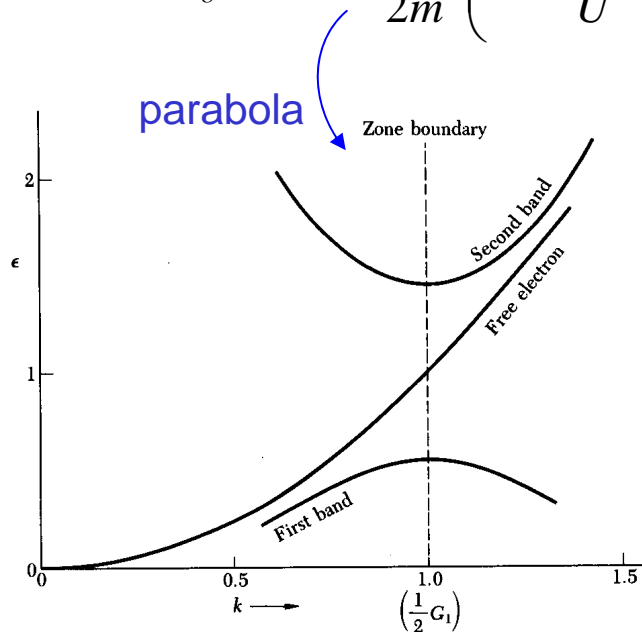
- Cut-off form of the central eq. 
$$\begin{pmatrix} \varepsilon_k^0 - \varepsilon & U \\ U & \varepsilon_{k-g}^0 - \varepsilon \end{pmatrix} \begin{pmatrix} C(k) \\ C(k-g) \end{pmatrix} = 0$$

- Energy eigenvalues

$$\varepsilon_{\pm}(k) = \frac{1}{2}(\varepsilon_k^0 + \varepsilon_{k-g}^0) \pm \frac{1}{2} \sqrt{(\varepsilon_k^0 - \varepsilon_{k-g}^0)^2 + (2U)^2}$$

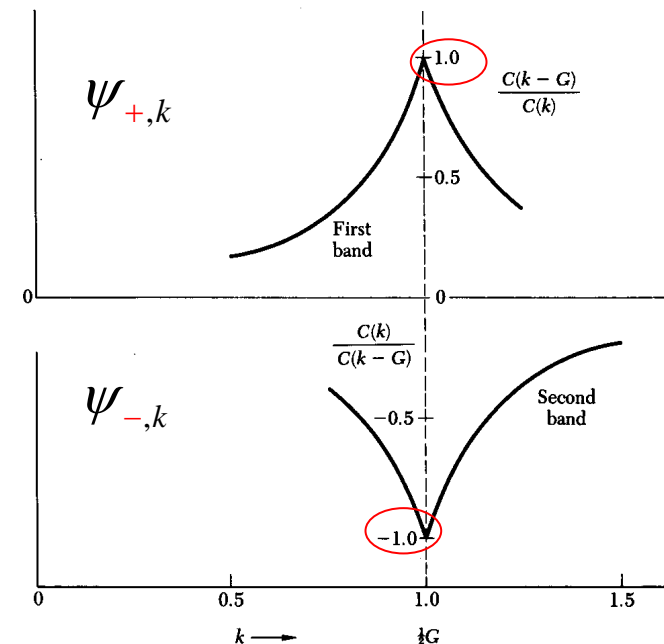
define  $\tilde{k} = k - \frac{g}{2}$

then 
$$\varepsilon_{\pm}(\tilde{k}) = \varepsilon_{g/2}^0 \pm U + \frac{\hbar^2 \tilde{k}^2}{2m} \left( 1 \pm \frac{2\varepsilon_{g/2}^0}{U} \right)$$



- Energy eigenstates

$$\psi_{\pm k}(x) = C_{\pm}(k)e^{ikx} + C_{\pm}(k-g)e^{i(k-g)x}$$



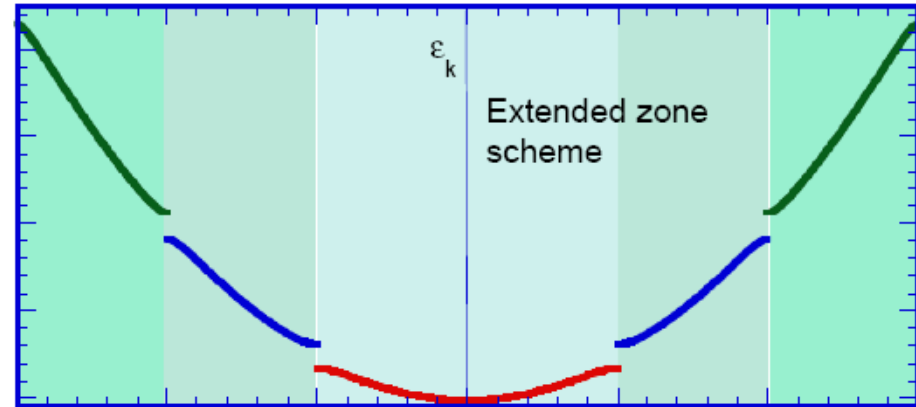
$$\Rightarrow \psi_{\pm, \frac{g}{2}}(x) \approx \begin{cases} \cos(\pi x / a) \\ \sin(\pi x / a) \end{cases}$$

3 ways to plot the energy bands:

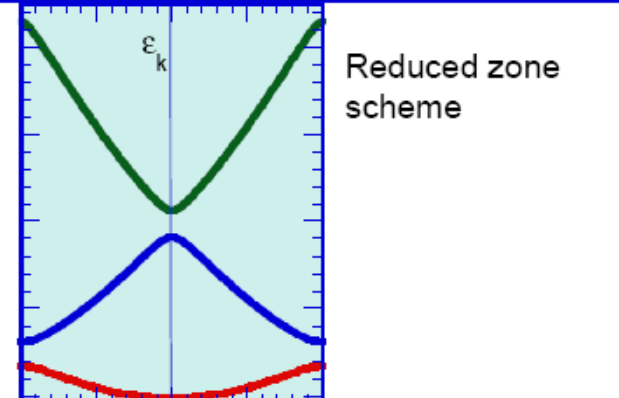
$$(k' \in 1\text{st BZ})$$

$$\varepsilon_{n,k'} \rightarrow \varepsilon_k$$

$$(k = k' + G)$$



1st Brillouin zone →



Sometimes it is convenient to repeat the domains of  $k$

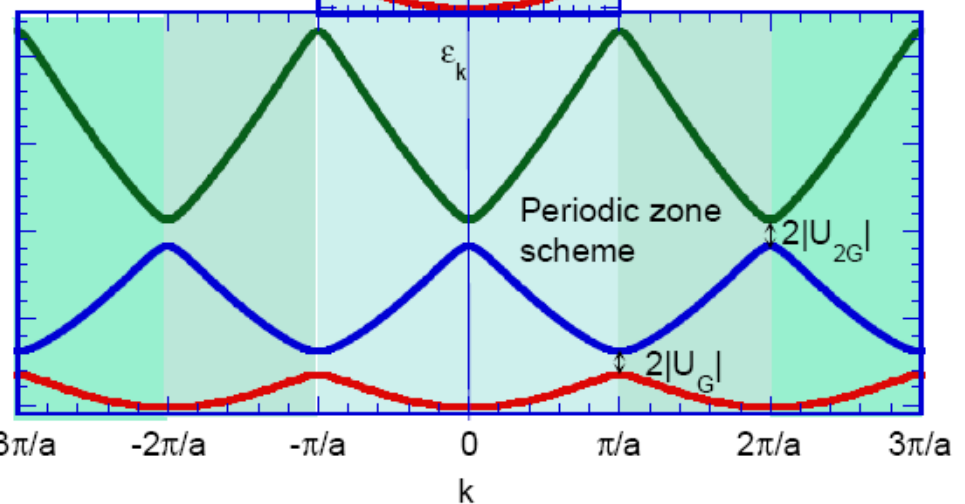


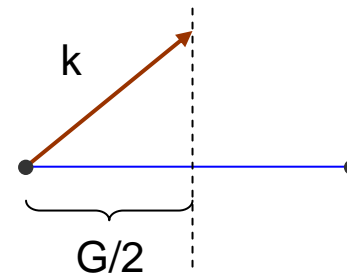
Fig from Dr. Suzukis' note (SUNY@Albany)

## Nearly-free-electron model in 2-dim (energy bands)

- 0<sup>th</sup> order approx.: **empty lattice** ( $U(r)=0$ )
- 1<sup>st</sup> order approx.: energy gap opened by Bragg reflection

Laue condition

$$\vec{k} \cdot \hat{G} = \frac{G}{2}$$



→ Bragg reflection whenever  $k$  hits the BZ boundary

## “Empty lattice” in 2D

- Free electron in vacuum:

$$\varepsilon_{\mathbf{k}} = \frac{\hbar^2 \mathbf{k}^2}{2m}$$

- Free electron in empty lattice:

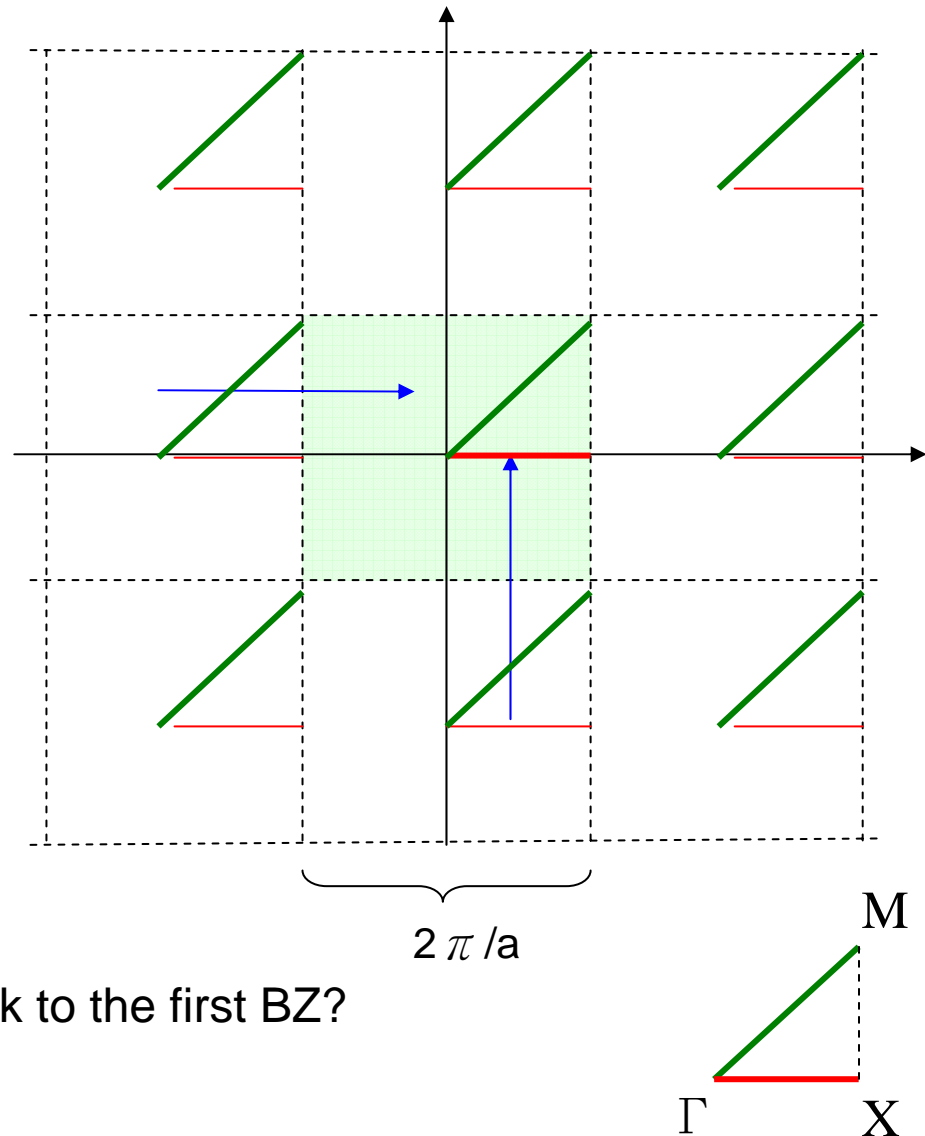
$$\varepsilon_{\mathbf{k}} = \varepsilon_{n\mathbf{k}'} = \frac{\hbar^2 (\mathbf{k}' + \mathbf{G})^2}{2m}$$

$$\mathbf{k} = \mathbf{k}' + \mathbf{G}$$

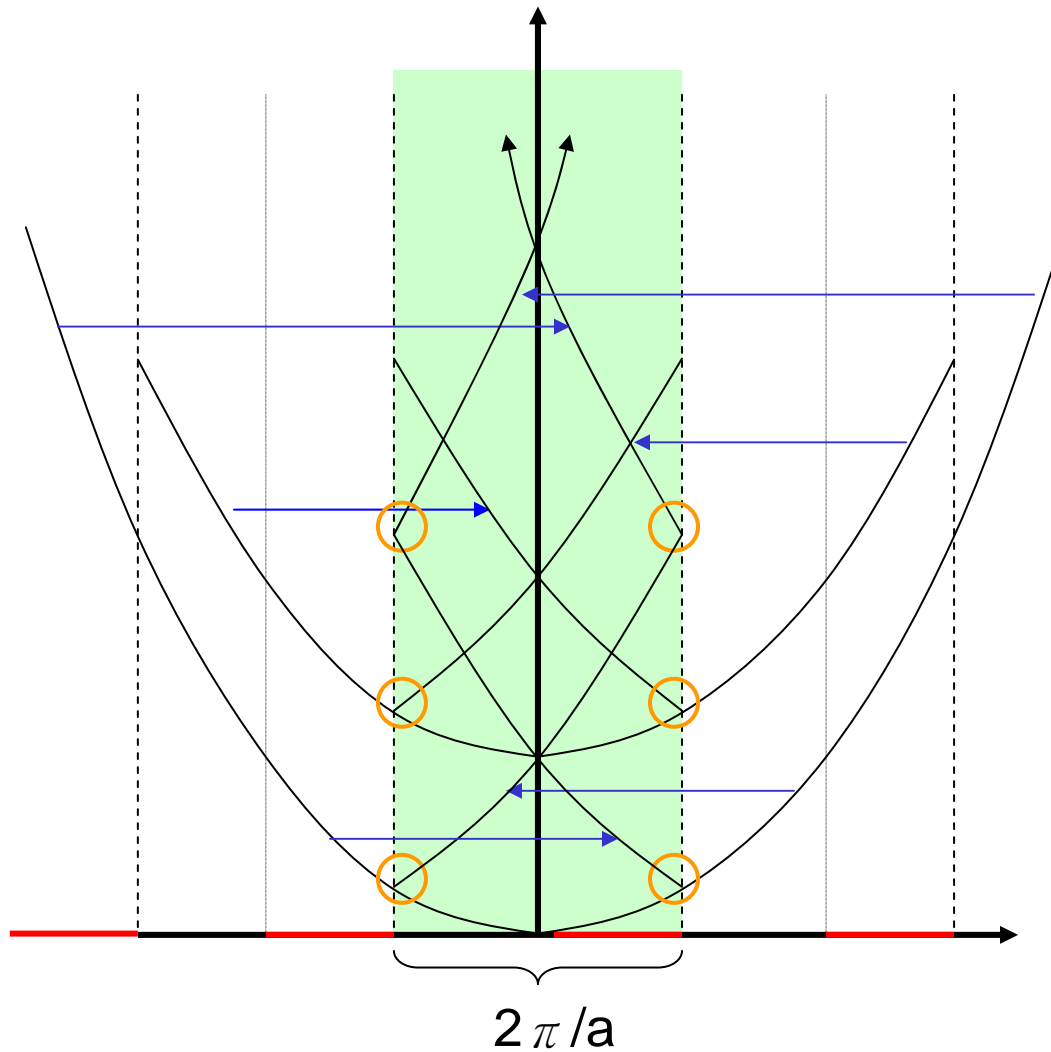
$$\mathbf{k}' \in 1^{st} \text{ BZ}$$

- How to fold a parabolic “surface” back to the first BZ?

## 2D square lattice’s reciprocal lattice

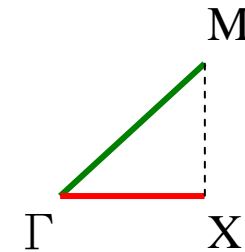


Folded parabola along  $\Gamma X$  (reduced zone scheme)



- In reality, there are energy gaps at BZ boundaries because of the Bragg reflection

- The folded parabola along  $\Gamma M$  is different



- Usually we only plot the major directions, for 2D square lattice, they are  $\Gamma X$ ,  $XM$ ,  $M\Gamma$

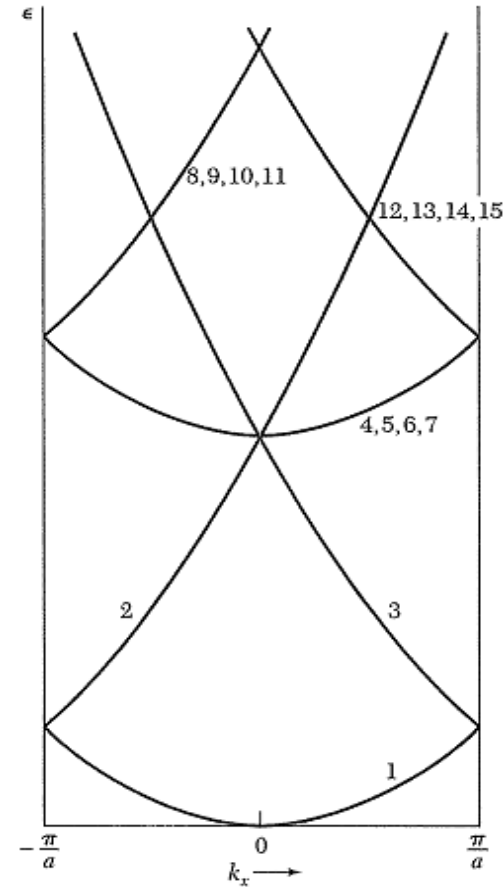
## Empty Lattice in 3D

Simple cubic lattice

$$\varepsilon_{\mathbf{k}} = \varepsilon_{n\mathbf{k}'} = \frac{\hbar^2 (\mathbf{k}' + \mathbf{G})^2}{2m}$$

$$\mathbf{k} = \mathbf{k}' + \mathbf{G}$$

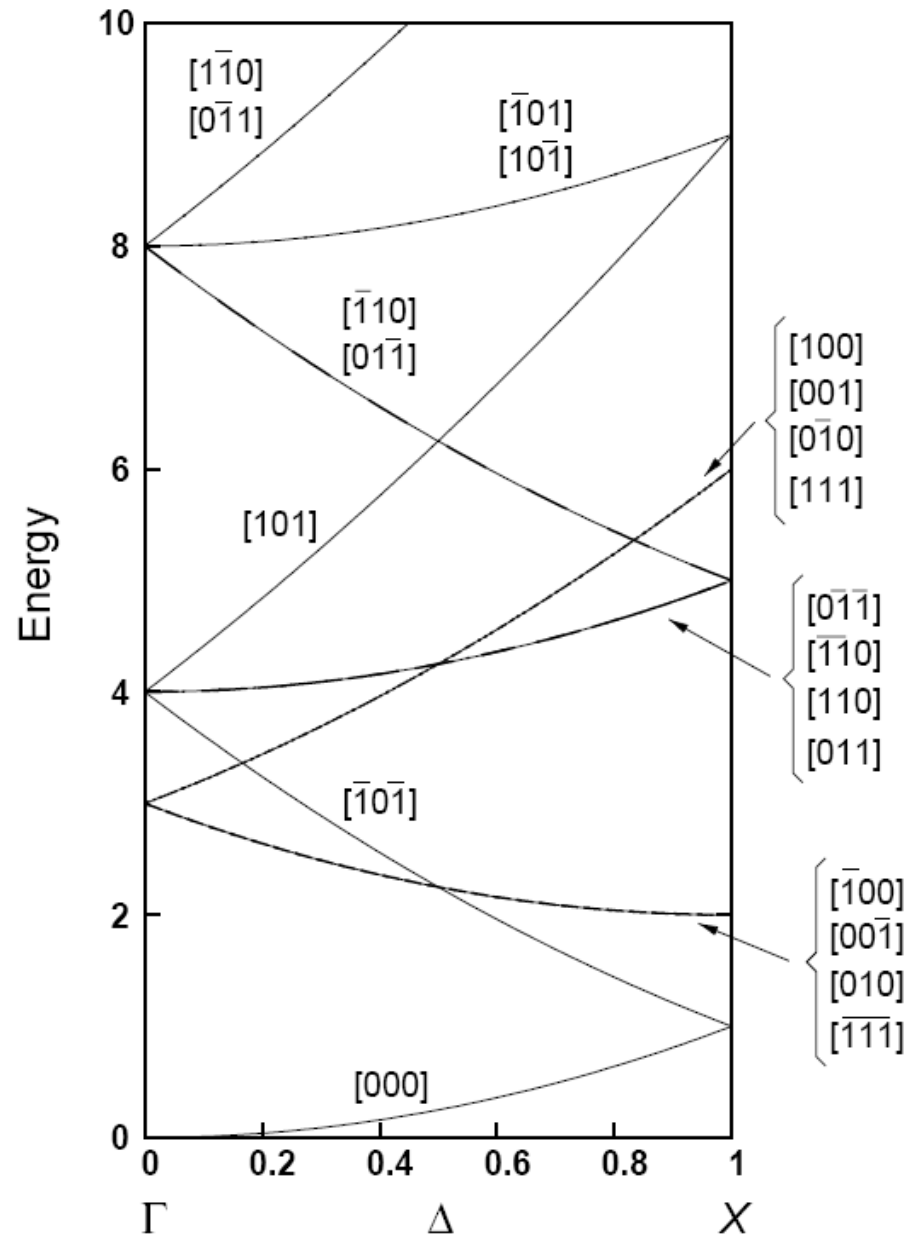
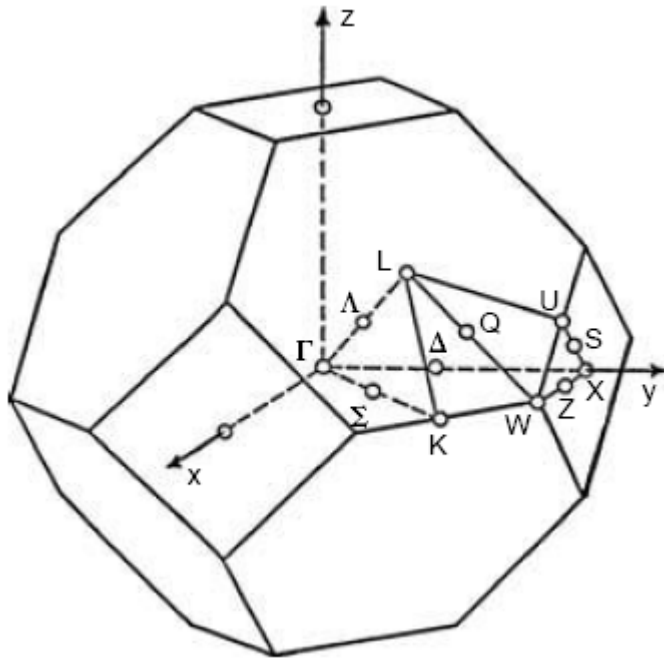
$$\mathbf{k}' \in 1^{st} \text{ BZ}$$



Band	$Ga/2\pi$	$\varepsilon(000)$	$\varepsilon(k_x, 00)$
1	000	0	$k_x^2$
2,3	100, $\bar{1}00$	$(2\pi/a)^2$	$(k_x \pm 2\pi/a)^2$
4,5,6,7	010, $0\bar{1}0$ , 001, $00\bar{1}$	$(2\pi/a)^2$	$k_x^2 + (2\pi/a)^2$
8,9,10,11	110, $10\bar{1}$ , $1\bar{1}0$ , $10\bar{1}$	$2(2\pi/a)^2$	$(k_x + 2\pi/a)^2 + (2\pi/a)^2$
12,13,14,15	$\bar{1}10$ , $\bar{1}01$ , $\bar{1}\bar{1}0$ , $\bar{1}0\bar{1}$	$2(2\pi/a)^2$	$(k_x - 2\pi/a)^2 + (2\pi/a)^2$
16,17,18,19	011, $0\bar{1}1$ , $01\bar{1}$ , $0\bar{1}\bar{1}$	$2(2\pi/a)^2$	$k_x^2 + 2(2\pi/a)^2$

Empty FCC lattice

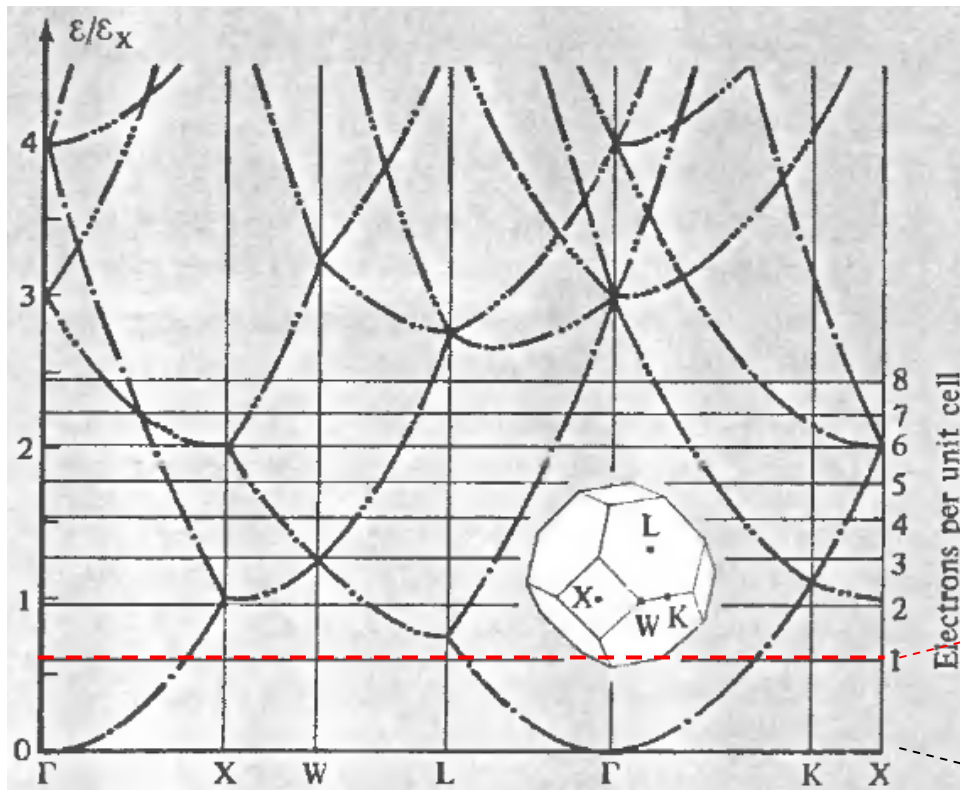
1<sup>st</sup> Brillouin zone:



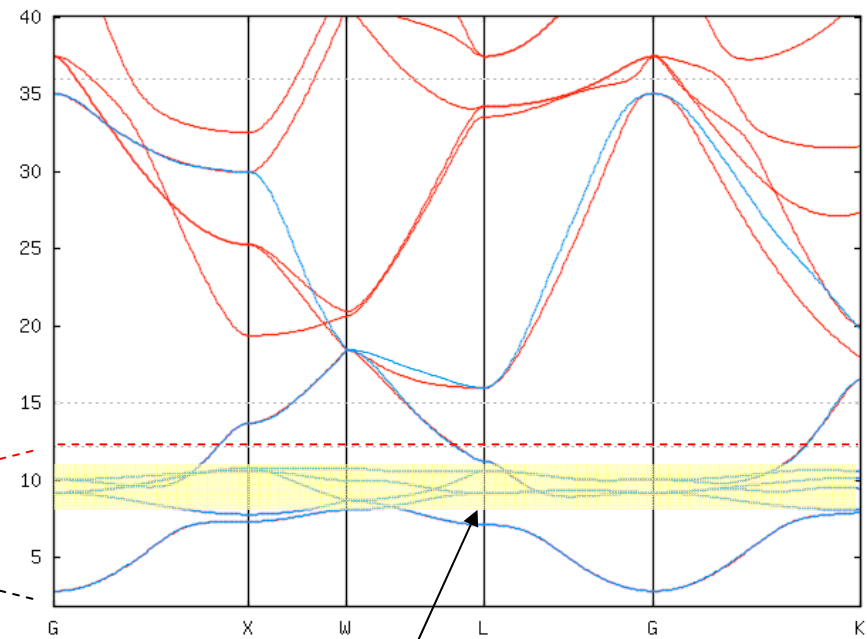
Energy bands for empty FCC lattice along the  $\Gamma$ - $X$  direction.

## Comparison with real band structure

The energy bands for  
“empty” FCC lattice



Actual band structure for  
copper (FCC,  $3d^{10}4s^1$ )



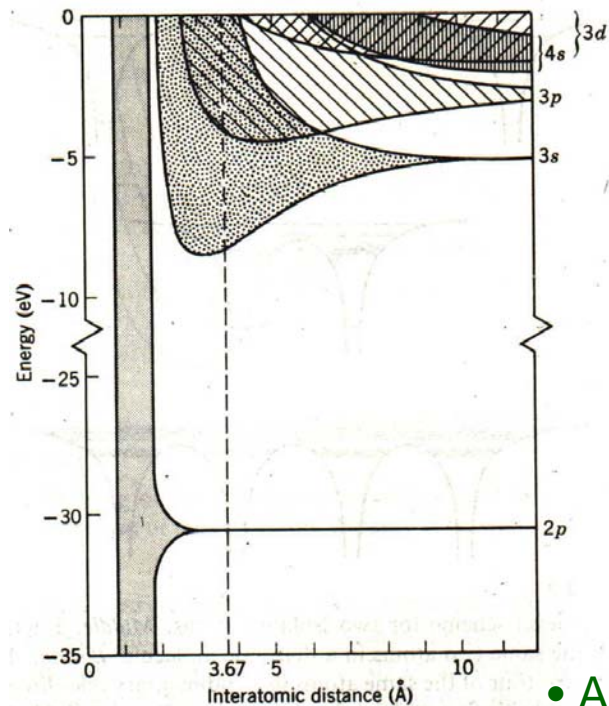
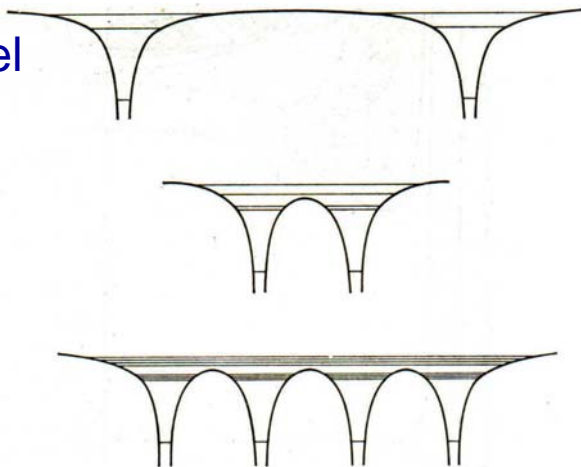
d bands

From Dr. J. Yates's ppt



# Origin of energy bands - an opposite view

Tight binding model  
(details in chap 9)



- Covalent solid

- d-electrons in transition metals

- Alkali metal

- noble metal

