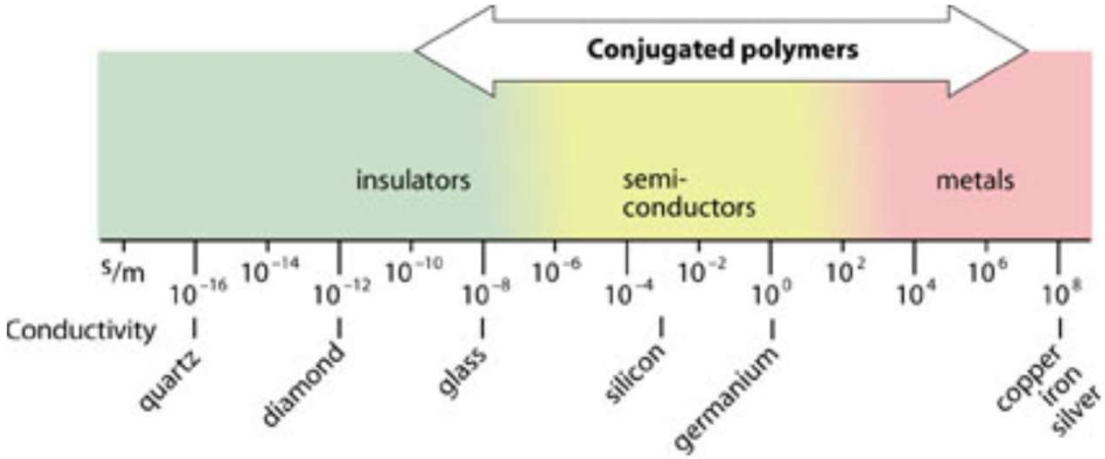
Dept of Phys
M.C. Chang



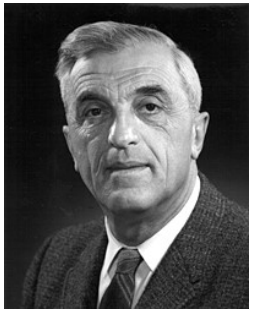
Energy bands

- Nearly-free electron model
- Bloch theorem
- The central equation
- Empty-lattice approximation
- Tight-binding model (see Chap 9)

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

History of band theory

(Ref: chap 4 of 半導體的故事, by 李雅明)



- 1928 – Bloch theory (Ph.D. dissertation under Heisenberg)
- 1929/30 – Peierls
  - nearly-free electron model, diffraction and energy gap
  - electron effective mass
  - a filled band does not conduct
  - hole
  - umklapp process for phonons
- 1930 – Kroenig-Penny model
- 1931 – Wilson explains metal/semiconductor/insulator

Nearly-free electron model

Free electron plane wave

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

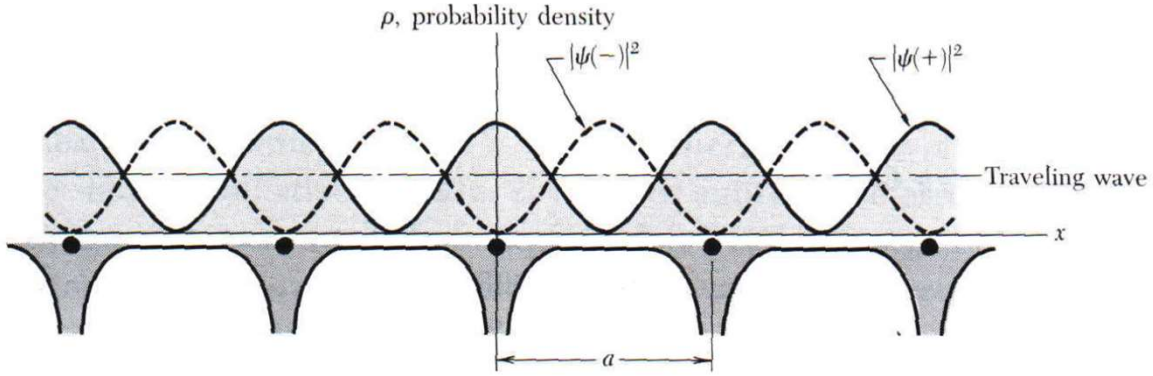
• Consider 1-dim case, when we turn on a lattice potential with period *a*, the electron wave will be Bragg reflected when $k=\pm\pi/a$, which forms two different types of standing wave (Peierls, 1930).

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

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

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

• 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

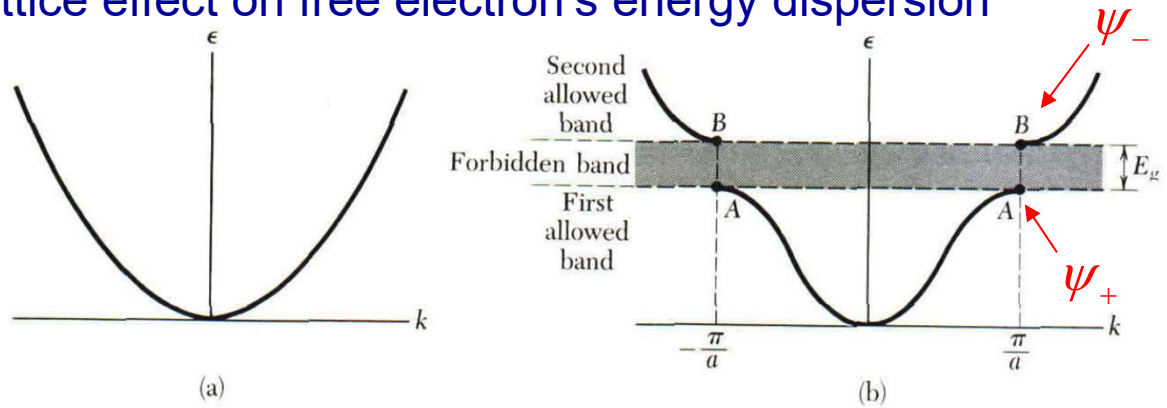
Note: Kittel use *potential energy U* (=e*V*)

$$E_g = \int_0^a dx\left(\rho_- - \rho_+\right)V(x)$$

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

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

• Lattice effect on free electron's energy dispersion

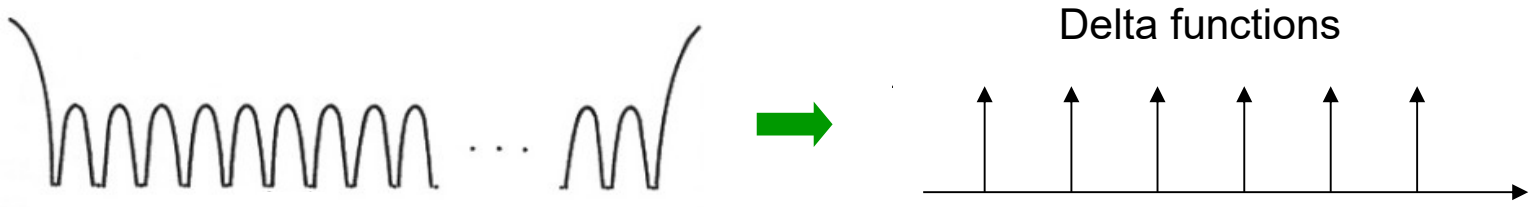


Electron's group velocity is zero near the boundary of the 1st BZ (because of the standing wave).

Q: where are the energy gaps when $V(x)=V_1\cos(2\pi x/a)+V_2\cos(4\pi x/a)$?

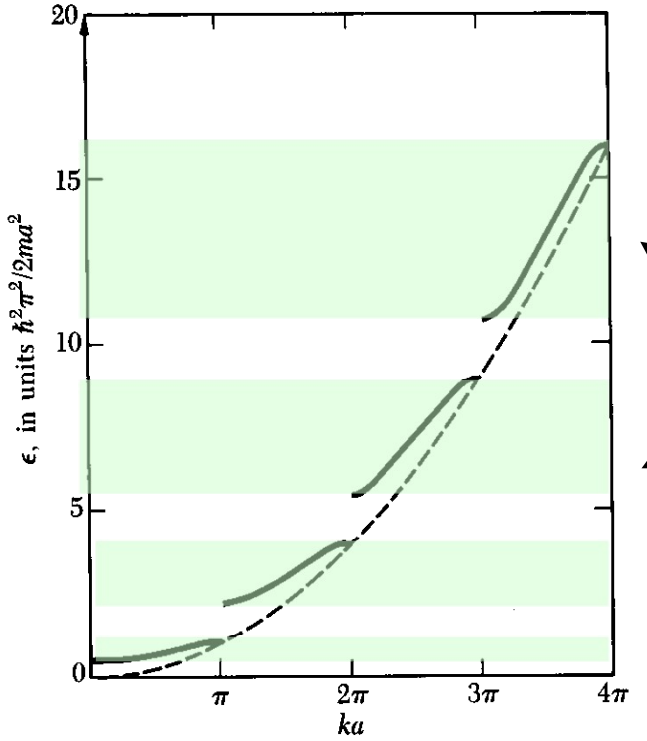
A *solvable* model in 1-dim: The Kroenig-Penny model (1930)

(not a bad model for superlattice)



- Electron energy dispersion calculated from the Schrödinger eq.

(read Kittel if you're interested in this calculation)



Energy bands
(Kittel, p.168)

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

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. … the observed resistances [demands] 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!"

Hoddeson L – Out of the Crystal Maze, p.107

important

Bloch theorem (1928)

The electron states in a periodic potential is of the form

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

- A simple proof for 1-dim (this is basically Bloch's original proof):

$|\Psi(x)|^2$ is the same in each unit cell. ➡ $\Psi(x+a) = C\Psi(x)$, C is a phase

Consider periodic BC,

$$\psi(x+Na) = C^N \psi(x) = \psi(x)$$

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

$$\rightarrow \quad \psi(x+a) = C\psi(x)$$

$$= e^{ika}\psi(x), \quad k \equiv 2\pi \frac{s}{Na}$$

write $\psi_k(x) = e^{ikx} u_k(x)$

then $u_k(x+a) = u_k(x)$

Similar proof applies to higher dimension.

• Schrödinger eq for $\psi_{\vec{k}}$:

Lattice potential

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

Energy eigenstate

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

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

• Schrödinger eq for u_k:

All of the info is in one unit cell.

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

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)

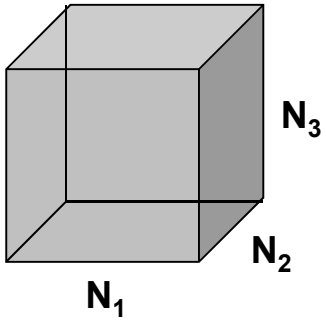
$$\psi_{\vec{k}}(\vec{r}+N_i\vec{a}_i)=\psi_{\vec{k}}(\vec{r}),\quad i=1,2,3$$

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

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

(see chap 2)

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



$$\Delta^3\vec{k}=\frac{\vec{b}_1}{N_1}\cdot\left(\frac{\vec{b}_2}{N_2}\times\frac{\vec{b}_3}{N_3}\right)=\frac{1}{N}\vec{b}_1\cdot(\vec{b}_2\times\vec{b}_3)\qquad N=N_1N_2N_3$$

$$\rightarrow \boxed{\frac{\vec{b}_1\cdot(\vec{b}_2\times\vec{b}_3)}{\Delta^3\vec{k}}=N}$$

$$\frac{\text{Vol of 1st BZ}}{\text{Vol of a k-point}}$$

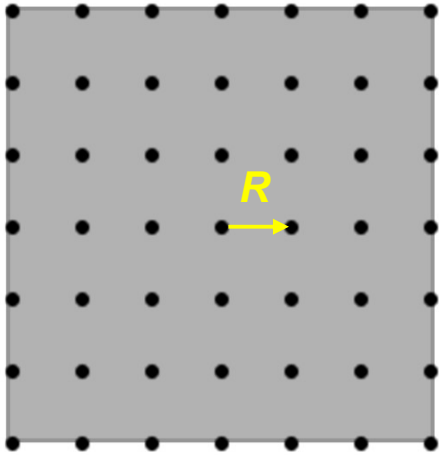
- $\vec{a}_1\cdot(\vec{a}_2\times\vec{a}_3)=v=\frac{V}{N}$,
- $\vec{b}_1\cdot(\vec{b}_2\times\vec{b}_3)=\frac{(2\pi)^3}{v}$,
- $\Delta^3k=\frac{(2\pi)^3}{V}$, as in the free-electron case.

Therefore, there are *N* ***k***-points in a BZ, where
N = total number of unit cells in the crystal.

important

Counting states in *r*-space and *k*-space

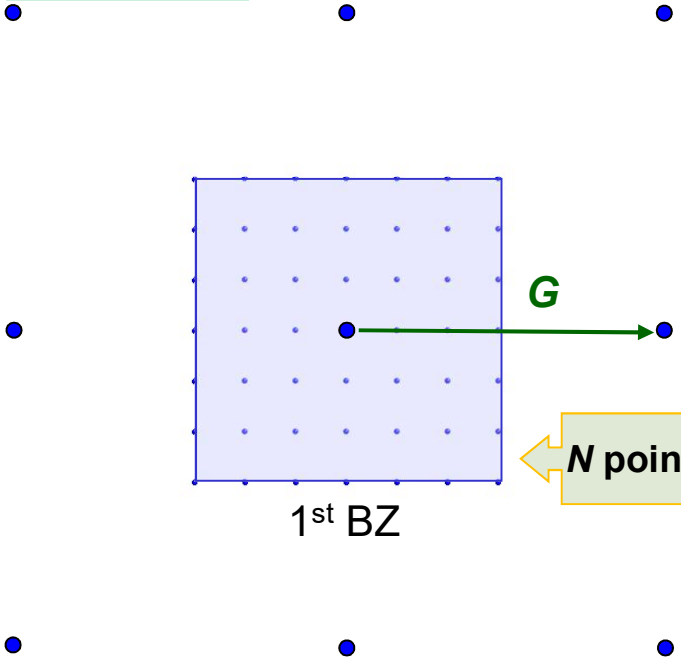
***r*-space** (a crystal with PBC)



***N* points here**

- *N* unit cells (1 atom/cell)
- If each atom contributes *q* valence electrons, then *Nq* electrons in total.

***k*-space**

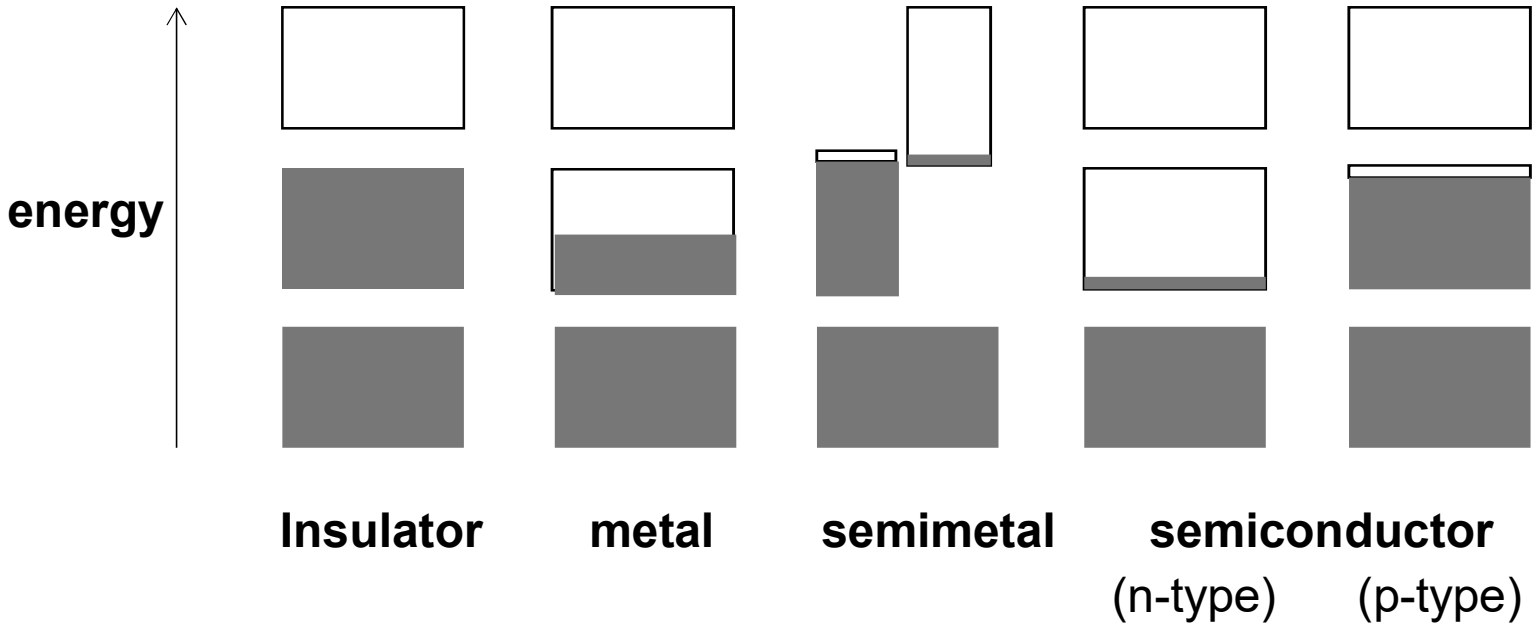


***N* points here**

- Infinite reciprocal lattice points
- *N* ***k***-points in 1st BZ

→ *N* ***k***-points in an energy band

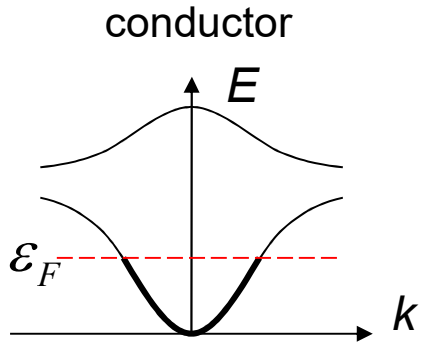
Band theory of solids



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).

∴ each energy band has $2N$ "seats" for electrons.

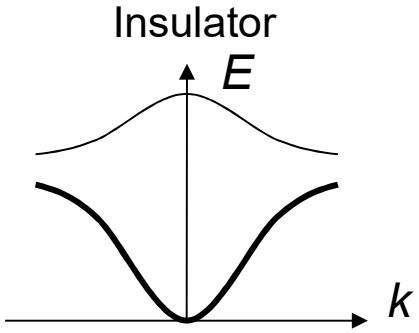


• If a solid has odd number of valence electron per unit cell, then the energy band is half-filled (conductor).

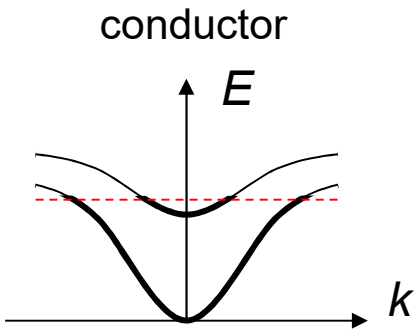
For example, all alkali metals are conductors.

• If a solid has even number of valence electron per unit cell, then the energy band can either be filled or not.

E.g., alkali-earth elements can be conductors or insulators.



Filled band



partially-filled bands

The central equation

Some mathematics before we move on

- Fourier decomposition

If $f(\boldsymbol{r})$ has lattice translation symmetry, that is, $f(\boldsymbol{r})=f(\boldsymbol{r}+\boldsymbol{R})$ for any lattice vector $\boldsymbol{R}$, then it can be expanded as,

$f(\vec{r}) = \sum_{\vec{G}} e^{i\vec{G}\cdot\vec{r}} f_{\vec{G}}$, where $\boldsymbol{G}$ is the reciprocal lattice vector.

(see Chap 2)

- Orthogonal relation

1D $$\int_{cell} dx\, e^{i(G-G')x} = a\delta_{G,G'}$$

3D $$\int_{cell} d^3r\, e^{i(\vec{G}-\vec{G}')\cdot\vec{r}} = v\delta_{\vec{G},\vec{G}'}$$ See A+M, App. D

note: $$\int_{all} d^3r\, e^{i(\vec{k}-\vec{k}')\cdot\vec{r}} = \begin{cases} V\delta_{\vec{k},\vec{k}'} & \text{for discrete } k \\ (2\pi)^3 \delta(\vec{k}-\vec{k}') & \text{for continuous } k \end{cases}$$

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

Schrödinger eq.

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

Keypoint: go to *k*-space to avoid derivatives

$U(\vec{r}+\vec{R})=U(\vec{r}),\quad u_{\vec{k}}(\vec{r}+\vec{R})=u_{\vec{k}}(\vec{r})$ Both are periodic functions

Fourier transform:

1. the lattice potential

$$U(\vec{r})=\sum_{\vec{G}}U_{\vec{G}}e^{i\vec{G}\cdot\vec{r}}$$

G=2π**n**/*a*

2. the wave function

$$u_{\vec{k}}(\vec{r})=\sum_{\vec{G}}C_{\vec{k}}(\vec{G})e^{-i\vec{G}\cdot\vec{r}}$$

k=2π**n**/*L*

unkown

➡ Schröd. eq. in *k*-space

$$\left(\varepsilon^0_{\vec{k}-\vec{G}}-\varepsilon_k\right)C_{\vec{k}}(\vec{G})+\sum_{\vec{G}'}U_{\vec{G}'-\vec{G}}C_{\vec{k}}(\vec{G}')=0,\qquad \varepsilon^0_k\equiv\frac{\hbar^2k^2}{2m}$$

aka. the central eq.

Kittel uses λ_k

Matrix form of the central eq. (in 1D) $G=ng$ ($g\equiv 2\pi/a$)

For a fixed k,

$$\begin{pmatrix} \ddots & & & & & \vdots \\ \varepsilon^0_{k+2g}-\varepsilon_k & U_g & U_{2g} & U_{3g} & U_{4g} & \\ U_{-g} & \varepsilon^0_{k+g}-\varepsilon_k & U_g & U_{2g} & U_{3g} & \\ U_{-2g} & U_{-g} & \varepsilon^0_k-\varepsilon_k & U_g & U_{2g} & \\ U_{-3g} & U_{-2g} & U_{-g} & \varepsilon^0_{k-g}-\varepsilon_k & U_{-g} & \\ U_{-4g} & U_{-3g} & U_{-2g} & U_{-g} & \varepsilon^0_{k-2g}-\varepsilon_k & \\ & & & & \ddots & \vdots \end{pmatrix} \begin{pmatrix} C_k(-2g) \\ C_k(-g) \\ C_k(0) \\ C_k(g) \\ C_k(2g) \\ \vdots \end{pmatrix} = 0$$

- For a given k, there are many eigenvalues ε_{nk}, with eigenvectors $\boldsymbol{C}_{nk}$.
- The eigenvalues $\varepsilon_n(k)$ determine the energy bands.
- The eigenvectors $\{C_{nk}(G), \forall G\}$ determine the Bloch states:

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

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

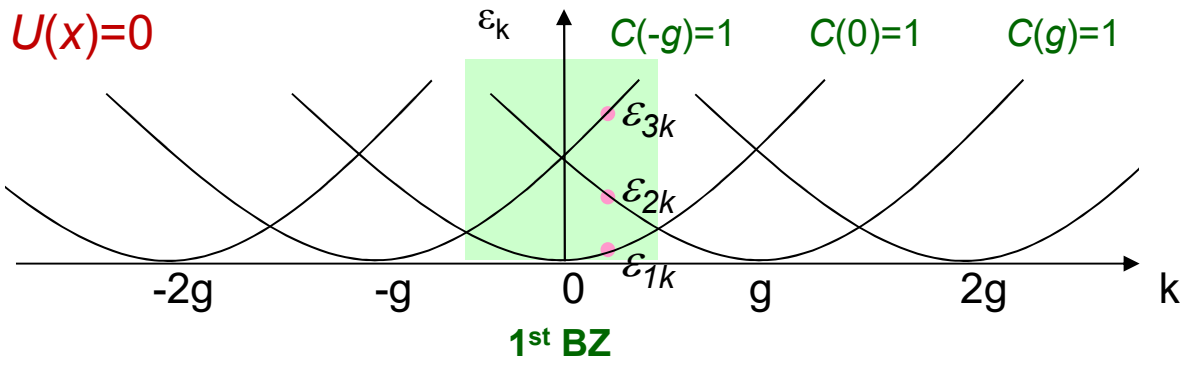
$= U\exp(2\pi ix/a) + U\exp(-2\pi ix/a)$ $(U_g = U_{-g} = U)$

$$\Rightarrow \begin{pmatrix} \ddots & & & & & \vdots \\ \varepsilon^0_{k+2g} - \varepsilon_k & U & 0 & 0 & 0 & C_k(-2g) \\ U & \varepsilon^0_{k+g} - \varepsilon_k & U & 0 & 0 & C_k(-g) \\ 0 & U & \varepsilon^0_k - \varepsilon_k & U & 0 & C_k(0) \\ 0 & 0 & U & \varepsilon^0_{k-g} - \varepsilon_k & U & C_k(g) \\ 0 & 0 & 0 & U & \varepsilon^0_{k-2g} - \varepsilon_k & C_k(2g) \\ & & & & \ddots & \vdots \end{pmatrix} = 0$$

Even though it is an infinite matrix, in practice,

it an be truncated according to the precision desired.

• What are the eigenenergies and eigenstates when U=0?



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

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

- From the central eq., one can see that

$$C_{k+G'}(G+G') = C_k(G)$$

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

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

$$\boxed{\psi_{n,k+G}(x) = \psi_{nk}(x)} \quad \Longleftrightarrow \quad \boxed{\psi_{n,\vec{k}}(\vec{r}+\vec{R}) = e^{i\vec{k}\cdot\vec{R}} \psi_{n,\vec{k}}(\vec{r})}$$

Comparison:

- Bloch energy $\varepsilon_{n,k+G} = \varepsilon_{nk}$ ($\because$ info in the 1st 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).

See Fig in previous page

• 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:

$$\begin{pmatrix} \ddots & & & & & \vdots \\ \varepsilon^0_{k+2g}-\varepsilon_k & U & 0 & 0 & 0 & C_k(-2g) \\ U & \varepsilon^0_{k+g}-\varepsilon_k & U & 0 & 0 & C_k(-g) \\ 0 & U & \varepsilon^0_k-\varepsilon_k & U & 0 & C_k(0) \\ 0 & 0 & U & \varepsilon^0_{k-g}-\varepsilon_k & U & C_k(g) \\ 0 & 0 & 0 & U & \varepsilon^0_{k-2g}-\varepsilon_k & C_k(2g) \\ & & & & \ddots & \vdots \end{pmatrix} = 0$$

cutoff for $k \sim g/2$!

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

Truncated form

$$\begin{pmatrix} \varepsilon_k^0 - \varepsilon & U \\ U & \varepsilon_{k-g}^0 - \varepsilon \end{pmatrix} \begin{pmatrix} C(k) \\ C(k-g) \end{pmatrix} = 0$$

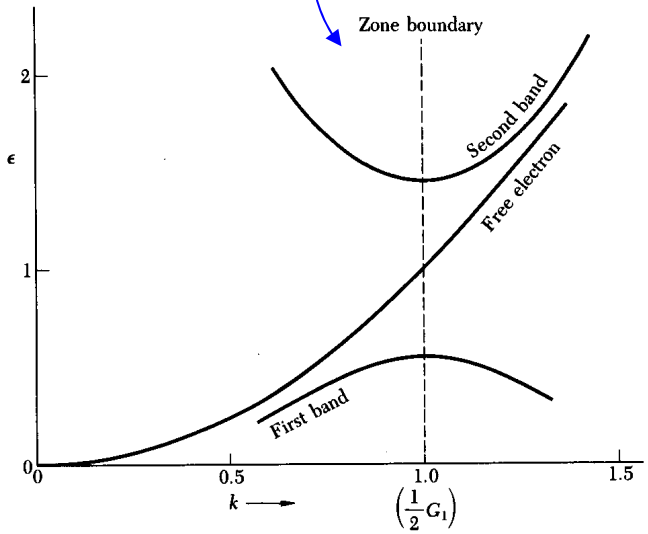
- Energy eigenvalues

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

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

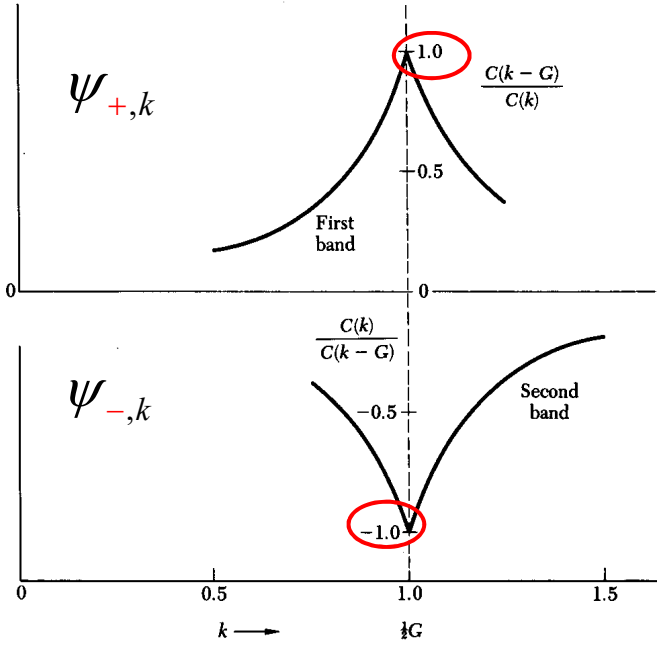
then $\varepsilon_{\pm}(\tilde{k}) = \varepsilon_{g/2}^0 \pm U + \frac{\hbar^2 \tilde{k}^2}{2m}\left(1 \pm \frac{2\varepsilon_{g/2}^0}{U}\right)$

parabola



- Energy eigenstates

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



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

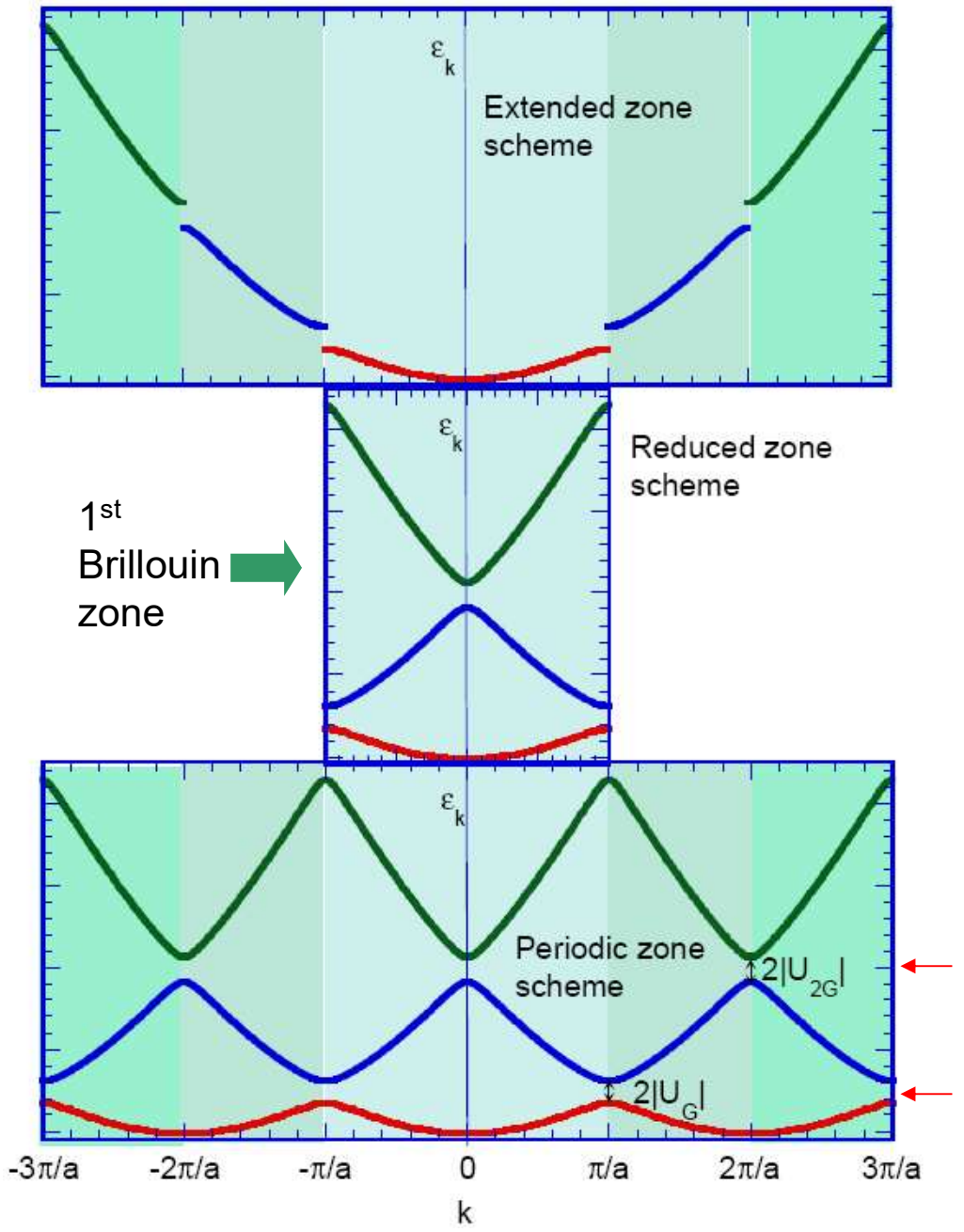
Agree with the diffraction result.

3 ways to plot the energy bands:

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

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

$$(k = k' \pm ng)$$



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

Kittel, p.225 (Chap 9)

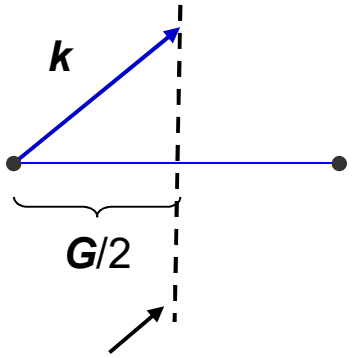
Fig from Dr. Suzukis' note (SUNY@Albany)

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

- 0^{th} order approx.: empty lattice ($U(\boldsymbol{r})=0$)
- 1^{st} order approx.: energy gap opened by Bragg reflection

Laue diffraction 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:

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

(a parabolic surface)

- Free electron in empty lattice:

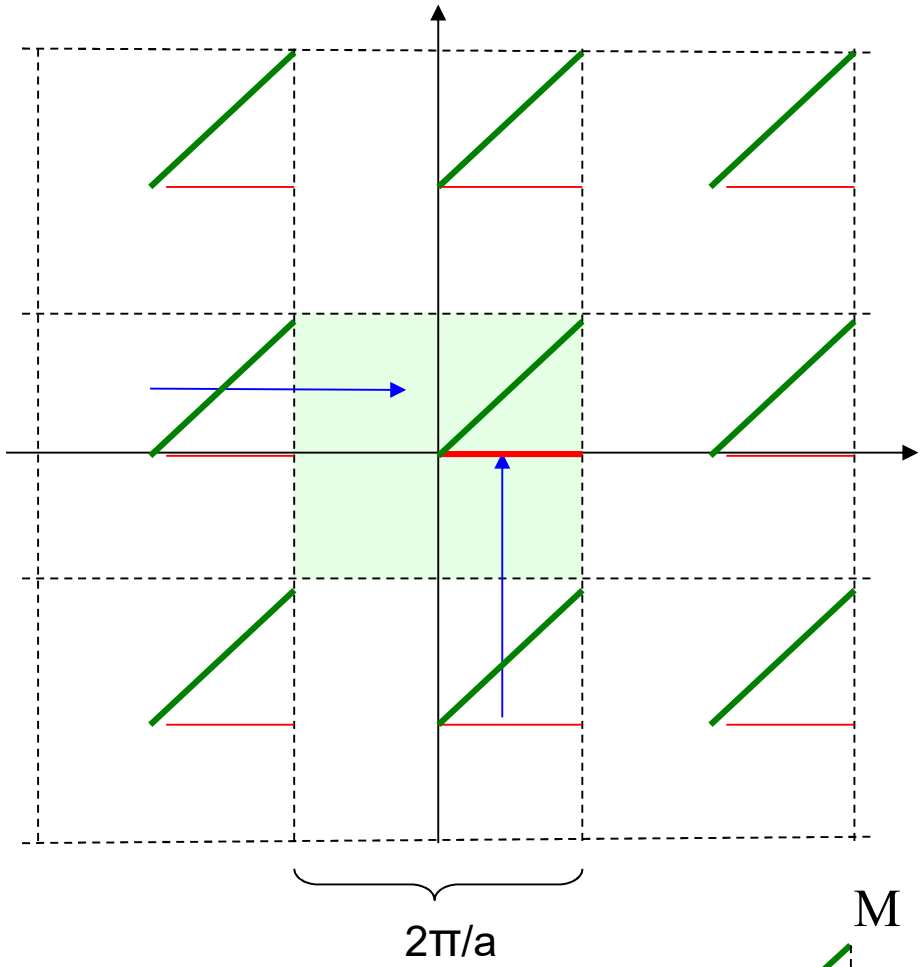
$$\varepsilon_{\mathbf{k}} = \varepsilon_{n\mathbf{k}'} = \frac{\hbar^2 \left(\mathbf{k}' + \mathbf{G}\right)^2}{2m}$$

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

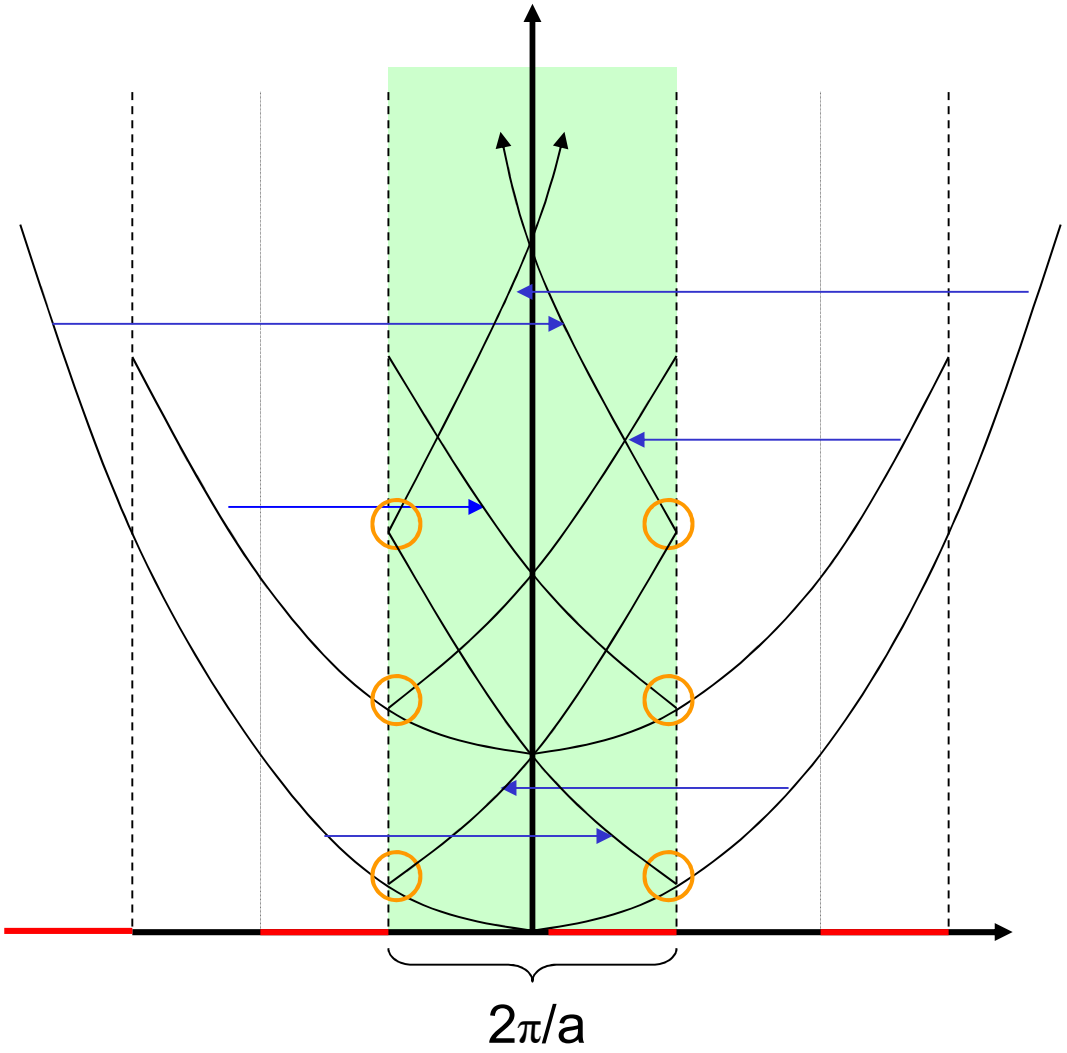
$$\mathbf{k}' \in 1^{st}\, BZ$$

How to fold a parabolic surface back to the first BZ?

2D square lattice's reciprocal lattice

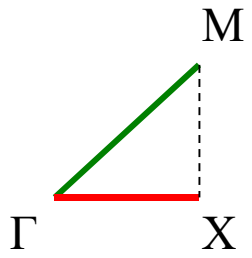


Folded parabola along ΓX (reduced zone scheme)



- There would be energy gaps at BZ boundaries because of the Bragg reflection

- The folded parabola along ΓM is different



- Usually we plot only major directions. For 2D square lattice, they are ΓX, XM, MΓ

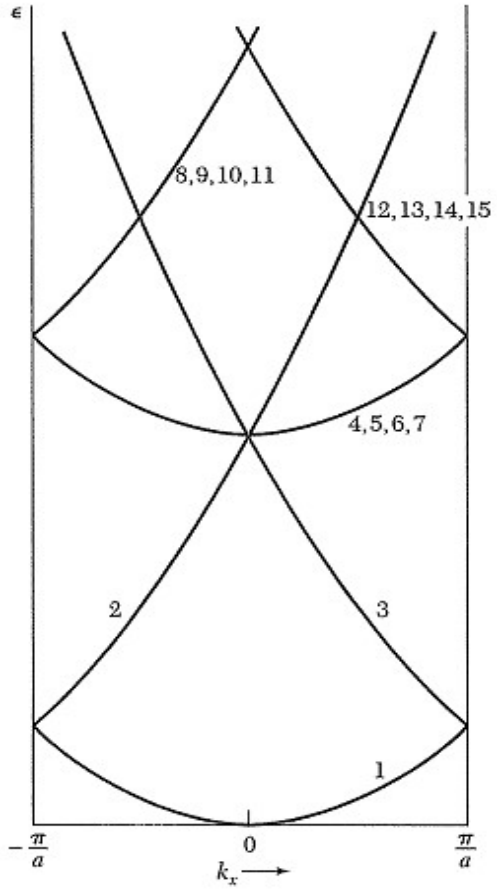
Empty Lattice in 3D

Simple cubic lattice

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

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

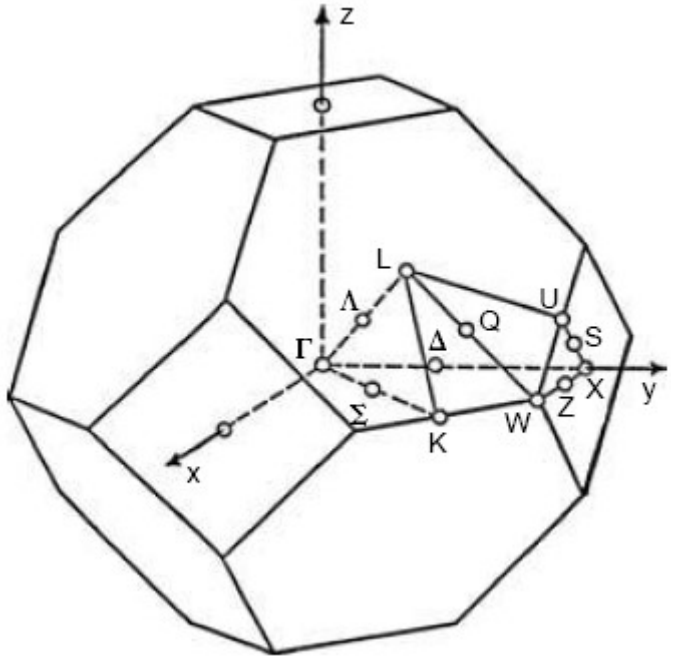
$$\mathbf{k}' \in 1^{st}\, BZ$$

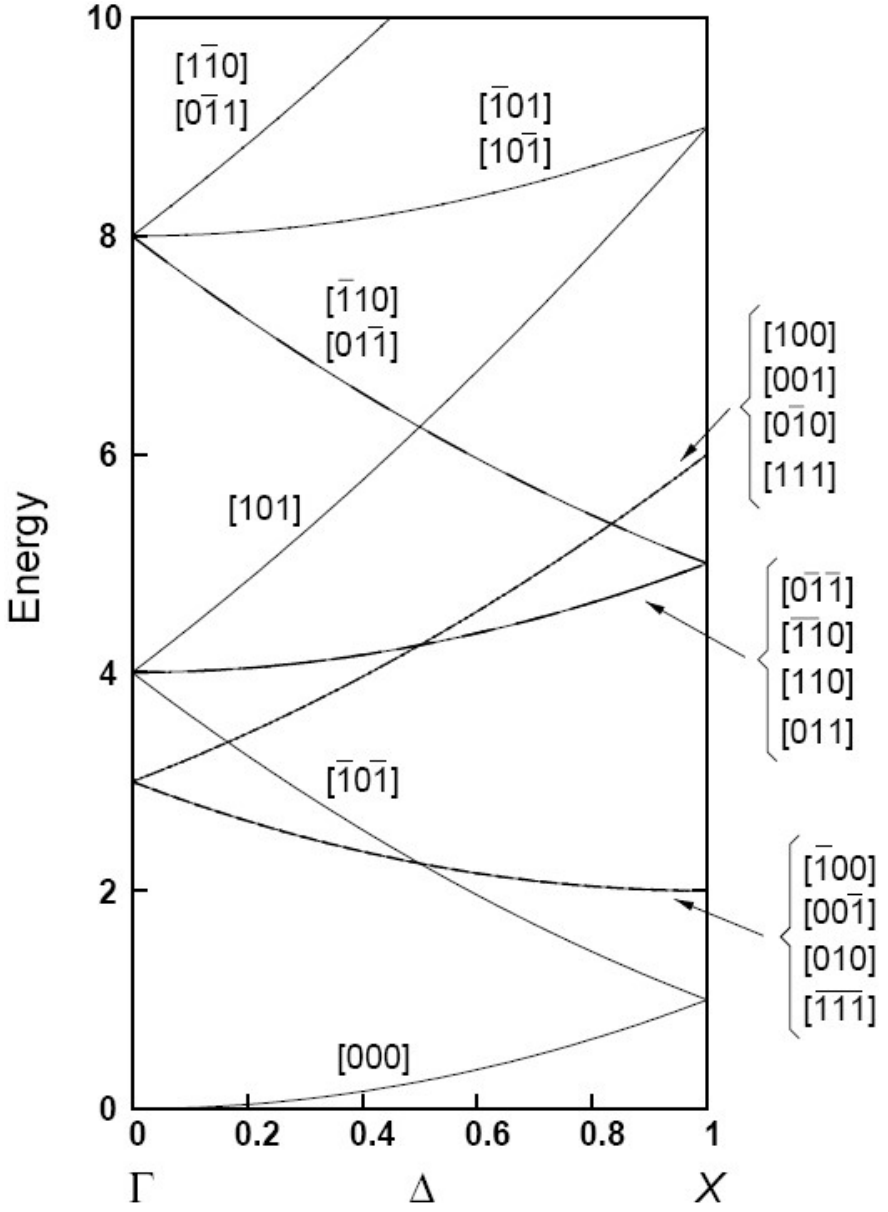


Band	$Ga/2\pi$	$\epsilon(000)$	$\epsilon(k_x 00)$
1	000	0	k_x^2
2,3	$100,\bar{1}00$	$(2\pi/a)^2$	$(k_x \pm 2\pi/a)^2$
4,5,6,7	$010,0\bar{1}0,001,00\bar{1}$	$(2\pi/a)^2$	$k_x^2 + (2\pi/a)^2$
8,9,10,11	$110,101,1\bar{1}0,10\bar{1}$	$2(2\pi/a)^2$	$(k_x + 2\pi/a)^2 + (2\pi/a)^2$
12,13,14,15	$\bar{1}10,\bar{1}01,\bar{1}\bar{1}0,\bar{1}0\bar{1}$	$2(2\pi/a)^2$	$(k_x - 2\pi/a)^2 + (2\pi/a)^2$
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

1st Brillouin zone:

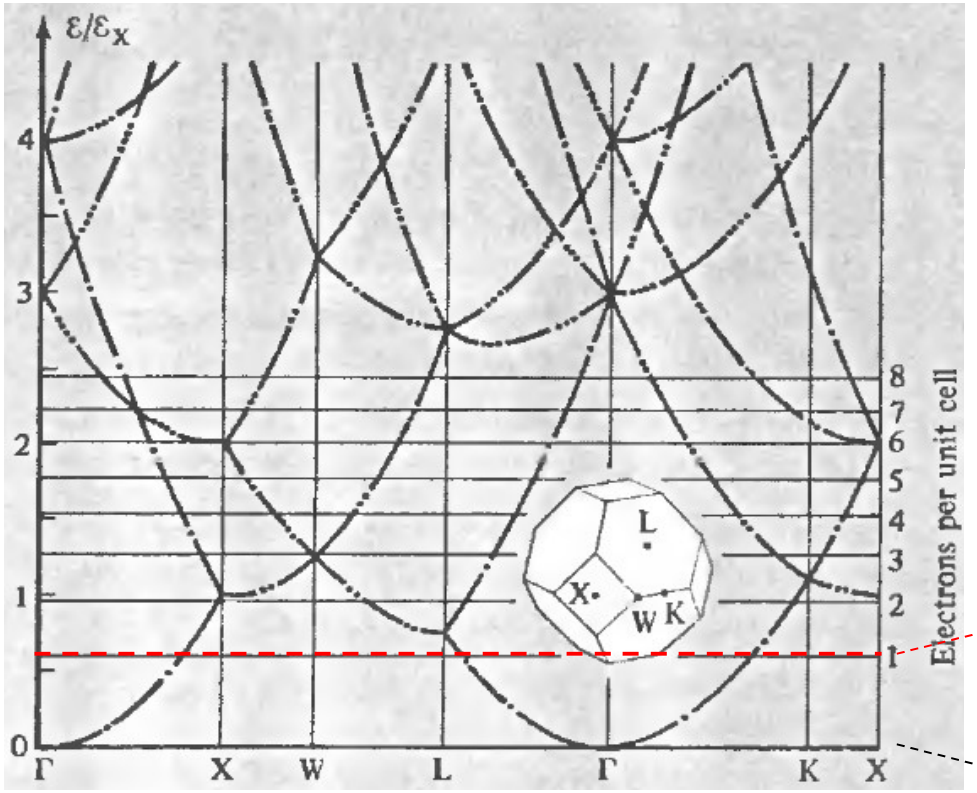




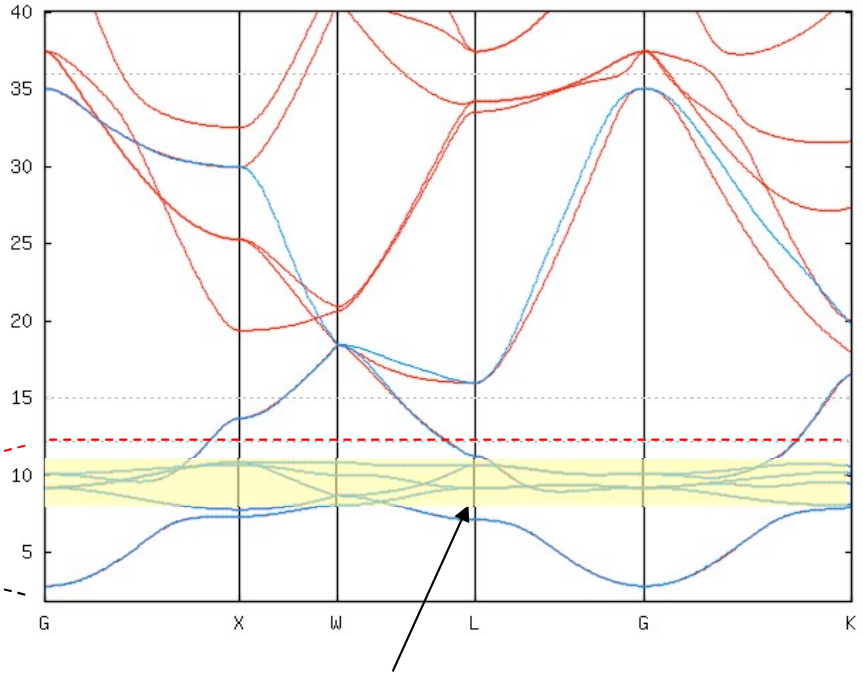
Energy bands for empty FCC lattice along the Γ-*X* direction.

Comparison with real band structure

The energy bands for "empty" FCC lattice



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



d bands

lampx.tugraz.at/~hadley/ss1/empty/empty.php

From Dr. J. Yates's ppt