Chap 7

Non-interacting electrons in a periodic potential

- Bloch theorem
- The central equation
- Brillouin zone
- Rotational symmetry

Dept of Phys

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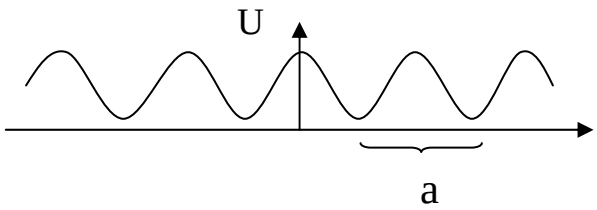
Bloch recalled,

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!"

Lattice Hamiltonian $\left[-\frac{\hbar^2}{2m}\nabla^2 + U(\vec{r})\right]\psi = \varepsilon\psi$

$U(\vec{r}+\vec{R}) = U(\vec{r})$



- Translation operator

$$T_{\vec{R}} = \exp\left(\frac{i}{\hbar}\vec{p}\cdot\vec{R}\right), \qquad \left(T_{\vec{a}_1}, T_{\vec{a}_2}, T_{\vec{a}_3} \text{ mutually commute}\right)$$

- Translation symmetry of the lattice $\rightarrow \left[H, T_{\vec{R}}\right] = 0$

- Simultaneous eigen-states

$$\begin{cases} H\psi_{\alpha\beta} = \varepsilon_\alpha \psi_{\alpha\beta} \\ T_{\vec{R}}\psi_{\alpha\beta} = C_{\vec{R},\beta}\psi_{\alpha\beta} \end{cases}$$

$|\Psi(x)|^2$ is the same in each unit cell

$$\left|C_{\vec{R}}\right| = 1; \quad C_{\vec{R}}C_{\vec{R}'} = C_{\vec{R}+\vec{R}'}$$

$$\Rightarrow C_{\vec{R},\vec{\beta}} = e^{i\vec{\beta}\cdot\vec{R}}$$

$$\therefore \psi_{\alpha\beta}(\vec{r}+\vec{R}) = e^{i\vec{\beta}\cdot\vec{R}}\psi_{\alpha\beta}(\vec{r})$$

Re-label

$$H\psi_{n\vec{k}} = \varepsilon_{n\vec{k}}\psi_{n\vec{k}}$$
$$T_{\vec{R}}\psi_{n\vec{k}} = e^{i\vec{k}\cdot\vec{R}}\psi_{n\vec{k}}$$

Bloch energy, Bloch state

orthogonality

$$\left\langle \psi_{n\vec{k}} \middle| \psi_{n'\vec{k}'} \right\rangle = \delta_{nn'}\delta_{\vec{k}\vec{k}'} \quad [\times V]$$

Bloch theorem (1928)

The electron states in a periodic potential can be written as

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

← Marder's has a factor $\frac{1}{\sqrt{N}}$

where $u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r}+\mathbf{R})$ is a cell-periodic function

Pf: define $u_{n\vec{k}}(\vec{r}) = e^{-i\vec{k}\cdot\vec{r}} \psi_{n\vec{k}}(\vec{r})$

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

$\Rightarrow$ $u_{n\vec{k}}(\vec{r}+\vec{R}) = u_{n\vec{k}}(\vec{r})$.

The cell-periodic part $u_{nk}(x)$ depends on the form of the potential.

- Effective Hamiltonian for u(r)

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

where $\tilde{H}(\vec{k}) \equiv e^{-i\vec{k}\cdot\vec{r}} H e^{i\vec{k}\cdot\vec{r}} = \frac{\hbar^2}{2m}\left(\frac{\nabla}{i} + \vec{k}\right)^2 + U(\vec{r})$

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

important

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

Periodic B.C.
(3-dim case)

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

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

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

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

$N=N_1N_2N_3$

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

$$=\frac{1}{N}\frac{(2\pi)^3}{v},\ \vec{a}_1\cdot(\vec{a}_2\times\vec{a}_3)=v=\frac{V}{N}$$

$$=\frac{(2\pi)^3}{V},\quad \text{as in the free-electron case.}$$

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

Therefore, there are *N* k-points in a unit cell (of reciprocal lattice),

where *N* = total number of primitive cells in the crystal.

important

Fourier decomposition and reciprocal lattice vectors

If f(**r**) has lattice translation symmetry, f(**r**)=f(**r**+**R**), for any lattice vector **R**

[eg. f(**r**) can be the lattice potential], then it can be expanded as,

$$f(\vec{r}) = \sum_{\text{all } \vec{G}} e^{i\vec{G}\cdot\vec{r}} f_{\vec{G}}$$

where **G** is the reciprocal lattice vector.

Pf: Fourier expanson,

$$f(\vec{r}) = \sum_{\vec{k}} e^{i\vec{k}\cdot\vec{r}} f(\vec{k})$$

$$f(\vec{r}+\vec{R}) = \sum_{\vec{k}} e^{i\vec{k}\cdot\vec{R}} e^{i\vec{k}\cdot\vec{r}} f(\vec{k}) = f(\vec{r}).$$

Therefore, $e^{i\vec{k}\cdot\vec{R}} = 1$ for $\forall\, \vec{R}$ ➡

$$\vec{k} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3 = \vec{G}_{hkl} \qquad \forall\, h,k,l$$

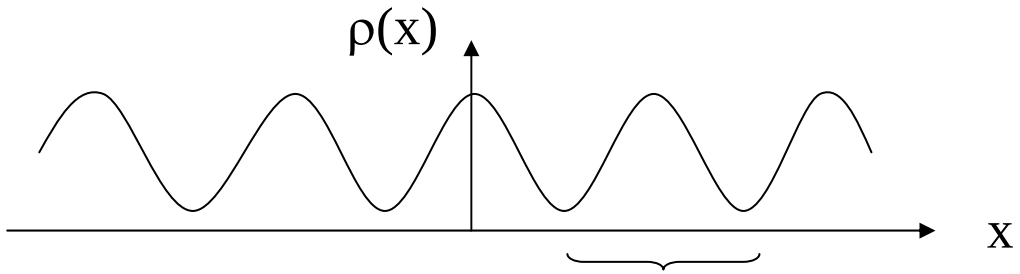
The expansion above is ***very*** general, it applies to

- all types of Bravais lattice (e.g. bcc, fcc, tetragonal, orthorombic...)
- in every dimension (1, 2, and 3)

All you need to do is find out the reciprocal lattice vectors **G**

A simple example:

electron density (or potential, or cell-periodic function) of a 1-dim lattice



$$\vec{a}_1 = a\hat{x},$$

$$\rightarrow \quad \vec{b}_1 = (2\pi / a)\hat{x}$$

$$\vec{G}_n = n\vec{b}_1,$$

$$\vec{G}_n \cdot \vec{r} = (n\vec{b}_1)\cdot(x\hat{x}) = (2\pi n / a)x$$

$$\therefore \rho(x) = \sum_n e^{i(2\pi n/a)x}\rho_n$$

important

Some useful formulas (for electrons in a lattice box)

1D

$$\delta(k) = \frac{L}{2\pi}\delta\left(\frac{k}{2\pi/L}\right)$$

$$\rightarrow \frac{L}{2\pi}\delta_{k,0}$$

$$\therefore \quad L\delta_{k,0} \leftrightarrow 2\pi\delta(k)$$

3D

$$\delta(\vec{k}) = \frac{L_x L_y L_z}{(2\pi)^3}\delta\left(\frac{k_x}{2\pi/L_x}\right)\delta\left(\frac{k_x}{2\pi/L_y}\right)\delta\left(\frac{k_x}{2\pi/L_z}\right)$$

$$\rightarrow \frac{V}{(2\pi)^3}\delta_{\vec{k},0}$$

$$\therefore \quad V\delta_{\vec{k},0} \leftrightarrow (2\pi)^3\,\delta(\vec{k})$$

$$\sum_{k\in 1\text{st BZ}} e^{ik\cdot na} = N\delta_{n,0}$$

$$\sum_{n} e^{ik\cdot na} = N\delta_{k,0}$$

$$\sum_{\vec{k}\in 1\text{st BZ}} e^{i\vec{k}\cdot\vec{R}} = N\delta_{\vec{R},0}$$

$$\sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} = N\delta_{\vec{k},0}$$

Restrict k to the 1st BZ,
Cf. Marder, App A.4

$$\int_{cell} dx\, e^{iGx} = a\delta_{G,0}$$

$$\int_{cell} d^3r\, e^{i\vec{G}\cdot\vec{r}} = v\delta_{\vec{G},0}$$

A+M, App. D

note: $$\int_{all} d^3r\, e^{i\vec{k}\cdot\vec{r}} = \begin{cases} V\delta_{\vec{k},0} & \text{for discrete } k \\ (2\pi)^3\,\delta(\vec{k}) & \text{for continuous } k \end{cases}$$

important

How do we determine $u_k(\boldsymbol{x})$ from the potential $U(\boldsymbol{x})$?

Schrodinger equation

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

Keypoint: go to *k*-space to simplify the calculation

Fourier transform

1. the lattice potential

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

G=2 π **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=2 π **n**/L

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

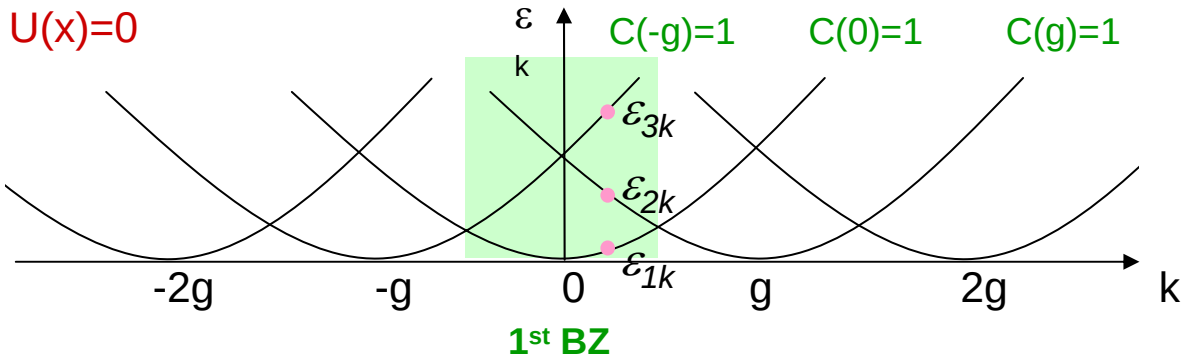
$$\left(\varepsilon^0_{\vec{k}-\vec{G}}-\varepsilon_k\right)C_{\vec{k}}(\vec{G})+\sum_{\vec{G}'}U_{\vec{G}'-\vec{G}}C_{\vec{k}}(\vec{G}')=0,\quad \varepsilon^0_k\equiv\frac{\hbar^2k^2}{2m}$$

Matrix form of the central eq. (in 1D) G=ng (g=2 π /a)

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

for a particular k

- For a given k, there are many eigen-energies ε_{nk}, with eigen-vectors $\boldsymbol{C}_{nk}$.



- when U(x) $\neq$0, for a particular k, u_{nk} is a linear combination of plane waves, with coefficients $\boldsymbol{C}_{nk}$: $u_{nk}(x)=\sum_G C_{nk}(G)e^{-iGx}$

Also valid in higher dim

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

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

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

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

• Bloch energy $\varepsilon_{n,k+G} = \varepsilon_{nk}$

Example.

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

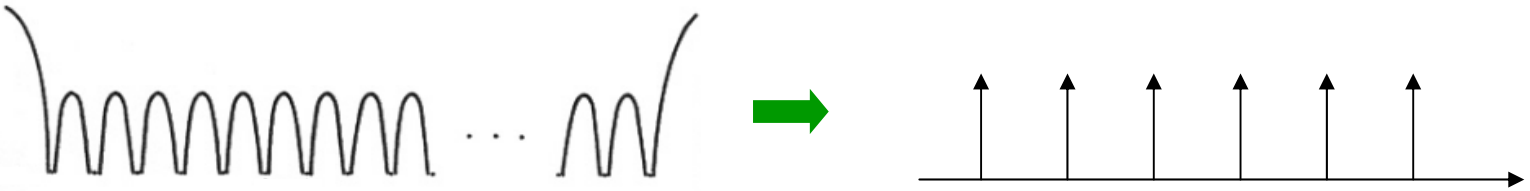
$= U \exp(2\pi ix/a) + U \exp(-2\pi ix/a)$ $(U_g = U_{-g} = U)$

Matrix form of the central eq.

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

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

(not a bad model for superlattice)



$$U(x) = A\,a\sum_s \delta(x - sa) = \sum_n U_n e^{iG_n x} = U_0 + 2\sum_{n>0} U_n \cos G_n x$$

$$U_n = \frac{1}{a}\int_{-a/2}^{a/2} dx\, U(x)\, e^{-iG_n x} = A$$

$$\left(\varepsilon^0_{k-ng} - \varepsilon_k\right) C_n + \sum_m U_{m-n} C_m = 0$$

$$\Rightarrow C_n = \frac{A}{\varepsilon_k - \varepsilon^0_{k-ng}} \sum_m C_m$$

$$\Rightarrow 1 = \sum_n \frac{A}{\varepsilon_k - \varepsilon^0_{k-ng}}$$

$$\frac{\hbar^2}{2mA} = \sum_n \frac{1}{K^2 - \left(k - \frac{2\pi n}{a}\right)^2}, \quad K^2 \equiv \frac{2m\varepsilon_k}{\hbar^2}$$

$$= \frac{1}{2K}\sum_n \left(\frac{1}{K + k - \frac{2\pi n}{a}} + \frac{1}{K - k + \frac{2\pi n}{a}} \right)$$

$$= \frac{a}{4K}\left[\cot\left(K + k\right)\frac{a}{2} + \cot\left(K - k\right)\frac{a}{2} \right]$$

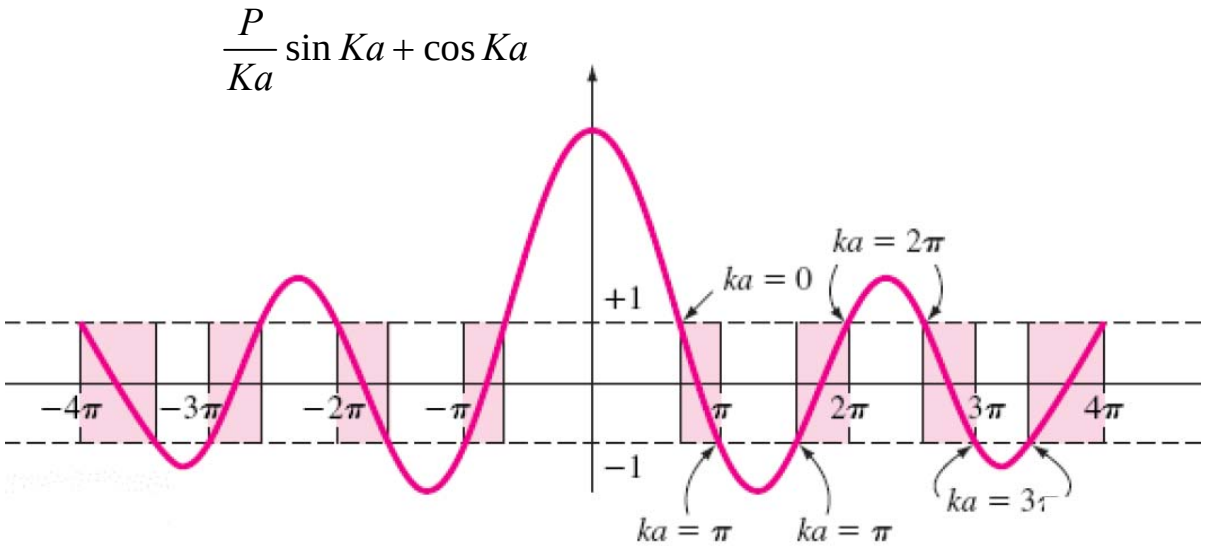
$$\sum_n \frac{1}{x + n\pi} = \cot x$$

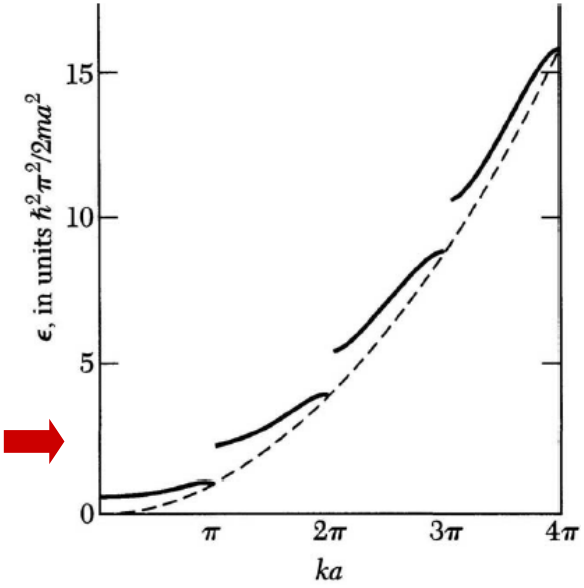
...

$$\Rightarrow \frac{\hbar^2}{2mA} = \frac{a}{2K}\frac{\sin Ka}{\cos ka - \cos Ka}$$

$$\Rightarrow \frac{P}{Ka}\sin Ka + \cos Ka = \cos ka \qquad \left(P = \frac{mAa^2}{\hbar^2}\right)$$

K has a real solution when





$$\varepsilon_k = \varepsilon_{n,k'+G} \quad (k' \in \text{1st BZ})$$
$$= \varepsilon_{n,k'}$$

Sometimes it is convenient to extend the domain of *k* with the following requirement

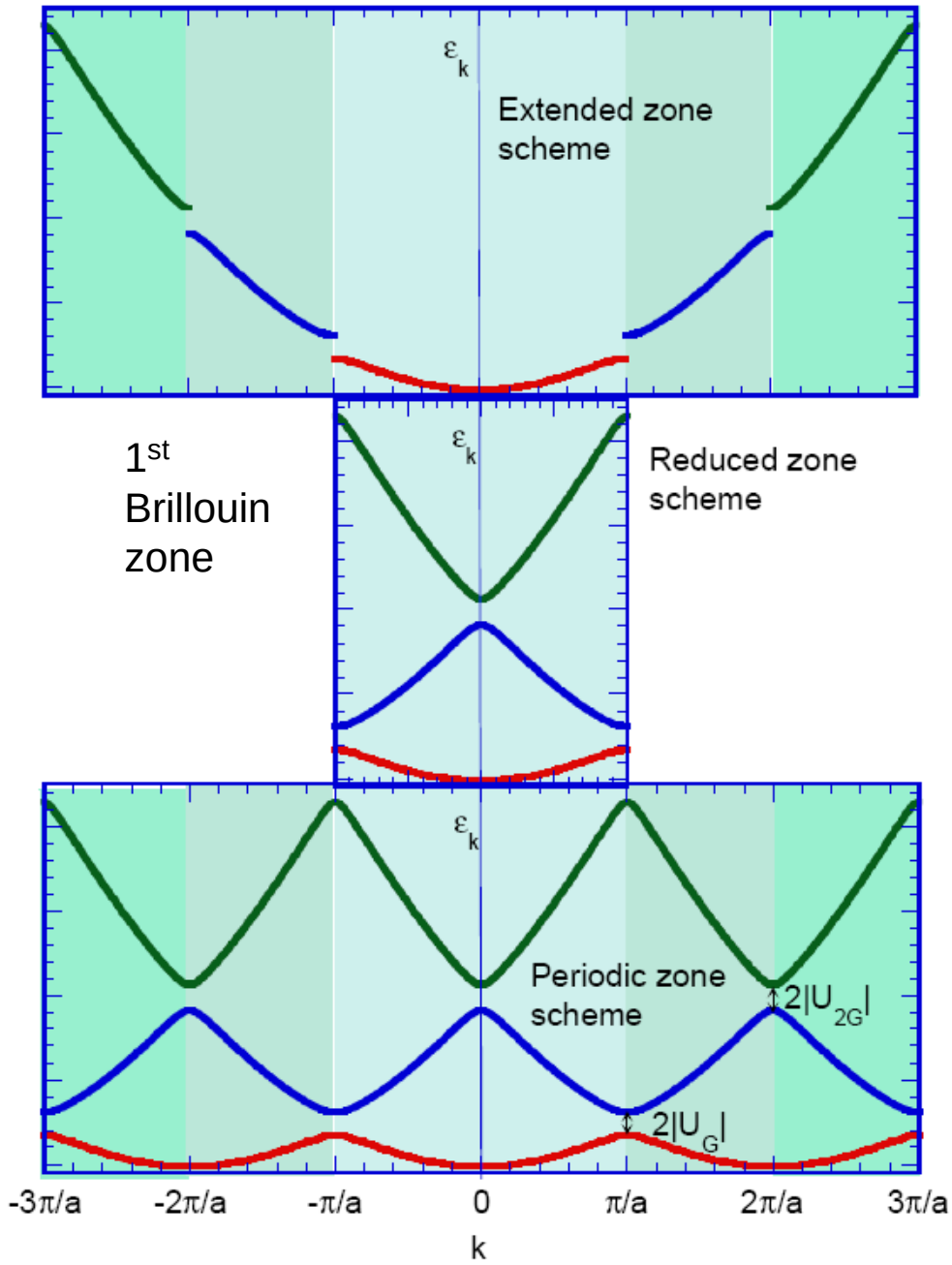
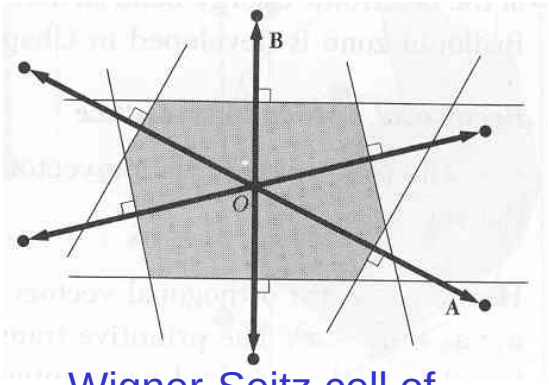


Fig from Dr. Suzukis' note (SUNY@Albany)

First Brillouin zone for 2D reciprocal lattice

$$\varepsilon_{n,\vec{k}+\vec{G}} = \varepsilon_{n,\vec{k}}$$

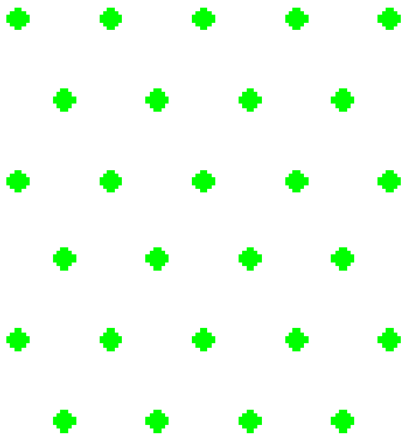
$$\psi_{n,\vec{k}+\vec{G}}(\vec{r}) = \psi_{n,\vec{k}}(\vec{r})$$



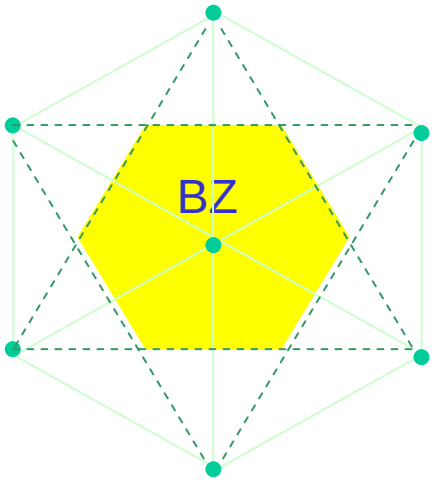
Wigner-Seitz cell of
the reciprocal lattice

Ex: Hexagonal lattice

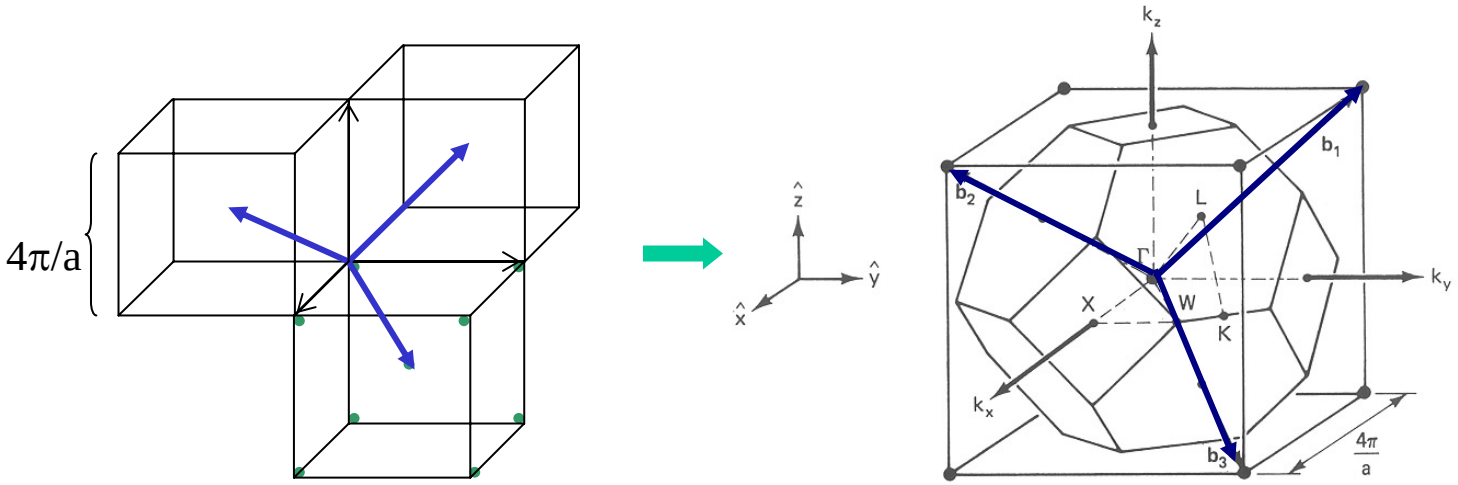
direct lattice



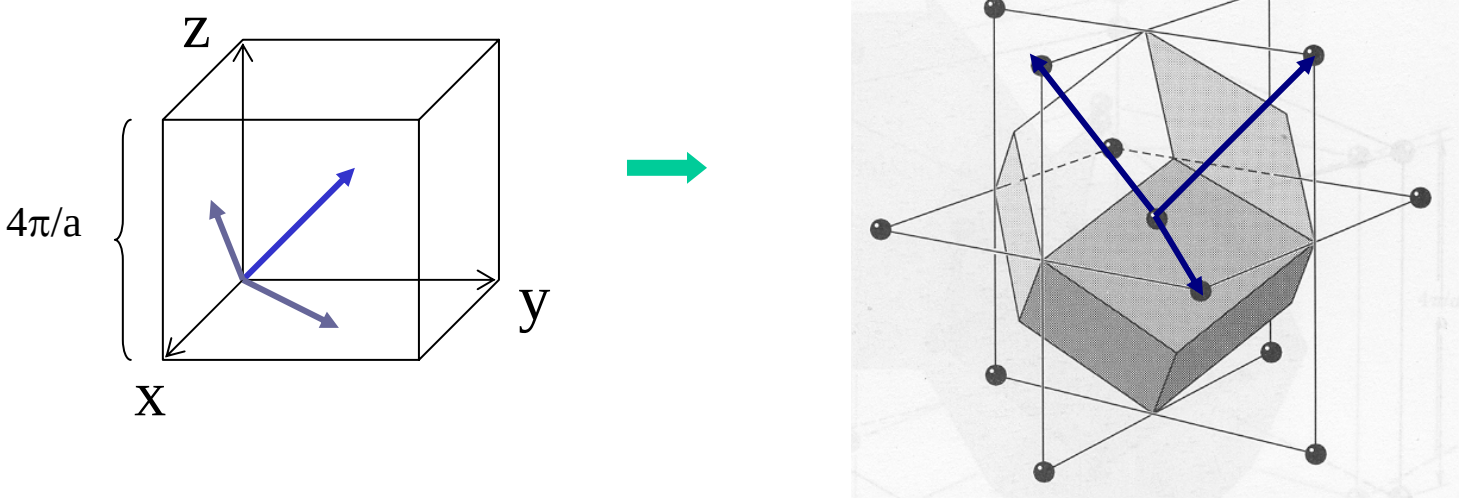
reciprocal lattice



The first BZ of FCC lattice (its reciprocal lattice is BCC lattice)



The first BZ of BCC lattice (its reciprocal lattice is FCC lattice)



Momentum and velocity of an electron in a Bloch state

- momentum

Not a momentum eigen-state

$$\frac{\hbar}{i}\nabla\psi_{nk} = \hbar\vec{k}\psi_{nk} + e^{i\vec{k}\cdot\vec{r}}\frac{\hbar}{i}\nabla u_{nk}$$

Crystal (quasi)-momentum

$$\psi_{nk}(x) = \sum_G C_{n,k-G} e^{i(k-G)x}$$

∴ for a Bloch state with crystal momentum ħk, the actual momentum can have, with various probabilities, an infinity of values.

- velocity

$$\vec{v}_n(\vec{k}) = \frac{\hbar}{m}\left\langle\psi_{nk}\left|\frac{1}{i}\nabla\right|\psi_{nk}\right\rangle$$

$$= \frac{\hbar}{m}\left\langle u_{nk}\left|\frac{1}{i}\nabla + \vec{k}\right|u_{nk}\right\rangle$$

$$= \left\langle u_{nk}\left|\frac{\partial\tilde{H}(\vec{k})}{\hbar\partial\vec{k}}\right|u_{nk}\right\rangle$$

$$= \frac{\partial\varepsilon_n(\vec{k})}{\hbar\partial\vec{k}}$$

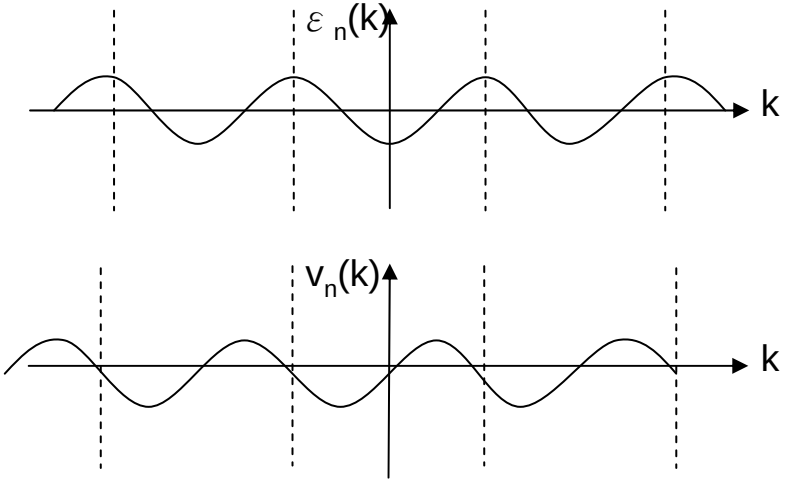
~ group velocity

$$\tilde{H}(\vec{k}) = e^{-i\vec{k}\cdot\vec{r}} H e^{i\vec{k}\cdot\vec{r}}$$

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

$$\tilde{H}(\vec{k})\left|u_{nk}\right\rangle = \varepsilon_n(\vec{k})\left|u_{nk}\right\rangle$$

- In a perfect lattice, the motion is unhindered
- velocity is zero at Brillouin zone boundary



A. Wilson (1932)

… Bloch, in showing that tightly bound electrons could in fact move through the lattice, had "proved too much"—that all solids should be metals. Were insulators simply very poor conductors? However, implicit in Peierls's papers on the Hall effect lay the clue, not carried further by Peierls, that a filled band would carry no current.

A filled band does not carry current (Peierls, 1929)

- Electric current density

$$\vec{j} = \frac{1}{V} \sum_{\text{filled } \vec{k}} (-e\vec{v}) = -e \int \frac{d^3k}{(2\pi)^3} \frac{1}{\hbar} \frac{\partial \varepsilon_n(\vec{k})}{\partial \vec{k}}$$

- Inversion symmetry, $\varepsilon_n(k) = \varepsilon_n(-k)$

→ electrons with momenta $\hbar k$ and $-\hbar k$ have opposite velocities

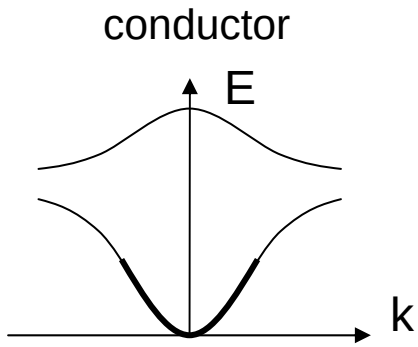
→ no net current in equilibrium

→ a filled band carries no current even in an external field

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.



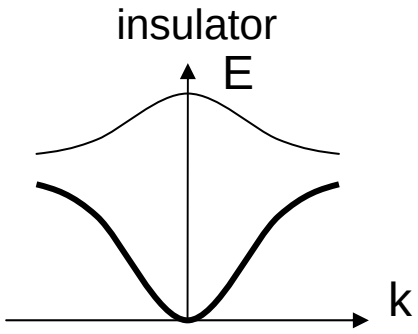
• If a solid has odd number of valence electron per primitive cell, then the energy band is half-filled (conductor).

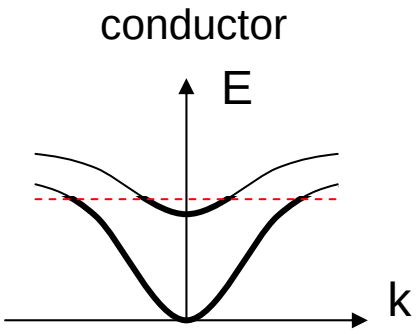
For example, all alkali metals are conductors

• If a solid has even number of valence electron per primitive cell, then the energy band is filled (insulator).

Wilson recalls Bloch's reply after hearing his arguments:

"No, it's quite wrong, quite wrong, quite wrong, not possible at all."





A nearly-filled band

• "charge" of a hole:

$$\vec{j} = -\frac{e}{V}\sum_{\text{filled }\vec{k}} \vec{v}$$

$$= -\frac{e}{V}\left(\sum_{\vec{k}\in 1\text{st BZ}} \vec{v} - \sum_{\text{unfilled }\vec{k}} \vec{v}\right)$$

$$= +\frac{e}{V}\sum_{\text{unfilled }\vec{k}} \vec{v}$$

∴ unoccupied states behave as +e charge carriers

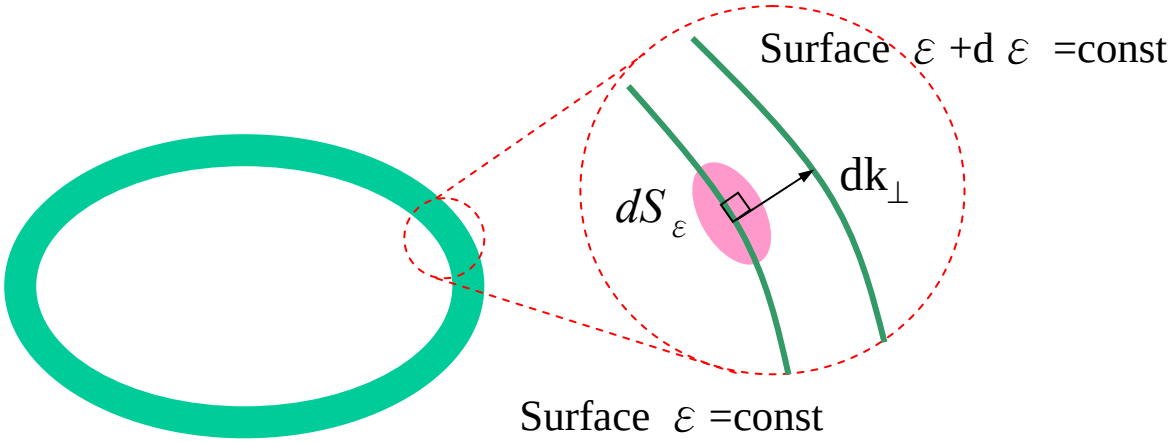
• "momentum" of a hole:

If an electron of wavevector k_0 is missing, then the sum over filled k, $\sum k = -k_0$.

Alternatively speaking, a hole with wavevector k_h (= $-k_0$). is produced.

important

DOS for a Bloch band ε_{nk}



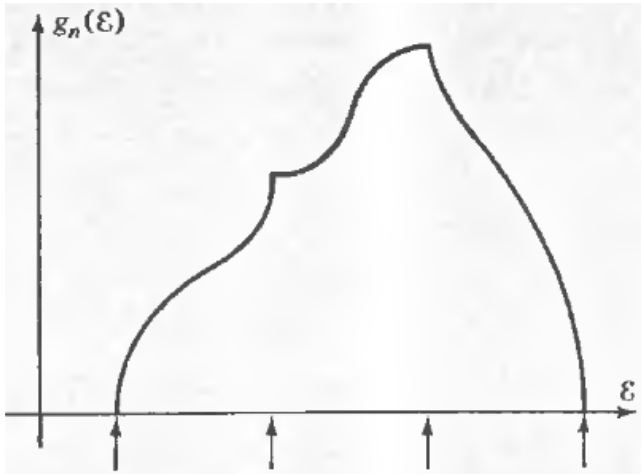
$$D(\varepsilon)d\varepsilon = \left(\frac{L}{2\pi}\right)^3 \int_{Shell} d^3k$$

$$d^3k = dS_\varepsilon dk_\perp$$

$$d\varepsilon = \left|\nabla_{\vec{k}}\varepsilon\right| dk_\perp$$

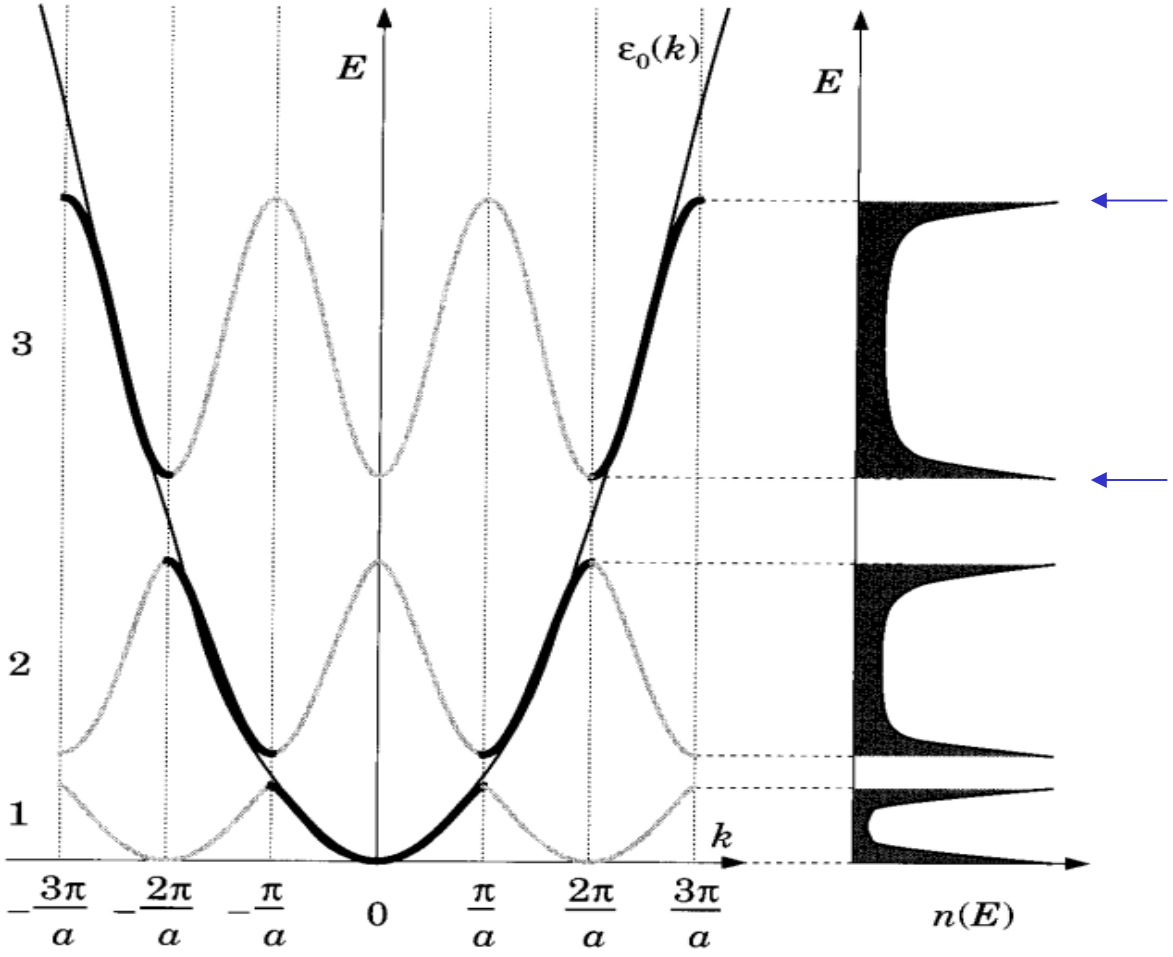
$$\therefore d^3k = dS_\varepsilon \frac{d\varepsilon}{\left|\nabla_{\vec{k}}\varepsilon\right|}$$

$$\Rightarrow D(\varepsilon) = \left(\frac{L}{2\pi}\right)^3 \int \frac{dS_\varepsilon}{\left|\nabla_{\vec{k}}\varepsilon\right|}$$



If $v_k = \left|\nabla_{\vec{k}}\varepsilon\right| = 0$, then there is "van Hove singularity" (1953)

For example, DOS of 1D energy bands



Van Hove singularity