The electronic properties of Metals: quantum mechanical approach

Outline

- Basic assumptions: Born-Oppenheimer and one-electron approximations.
- Intuitive picture for how the energy levels in a solid are formed from those in the atom.
- Calculate the quantum mechanical eigenvalues and wave functions for one electron in some simple potential of all the others and the ions.
- Fill up these eigenvalues using the Fermi-Dirac statistics.

The Born-Oppenheimer principle / the adiabatic approximation

$$H = -\sum_{R_i} \frac{\hbar^2 \nabla_i^2}{2M} - \sum_{r_j} \frac{\hbar^2 \nabla_j^2}{2m_e} + \frac{e^2}{4\pi\epsilon_0} \Big\{ \sum_{R_i \neq R_j} \frac{(Z - Z_V)^2}{|\mathbf{R}_i - \mathbf{R}_j|} + \sum_{r_i \neq r_j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{R_i \neq r_j} \frac{(Z - Z_V)}{|\mathbf{R}_i - \mathbf{r}_j|} \Big\}$$

- We discuss the motions of the electrons and the ions separately. We start out by discussion the electronic states for a fixed lattice of ions in their equilibrium position.

One electron approximation

- Solving the Schrödinger equation for an all-electron wave function in a rigid lattice is still hopeless. We assume an effective one-electron potential.

$$-\frac{\hbar^2\nabla^2}{2m_e}\psi(\mathbf{r}) + U(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

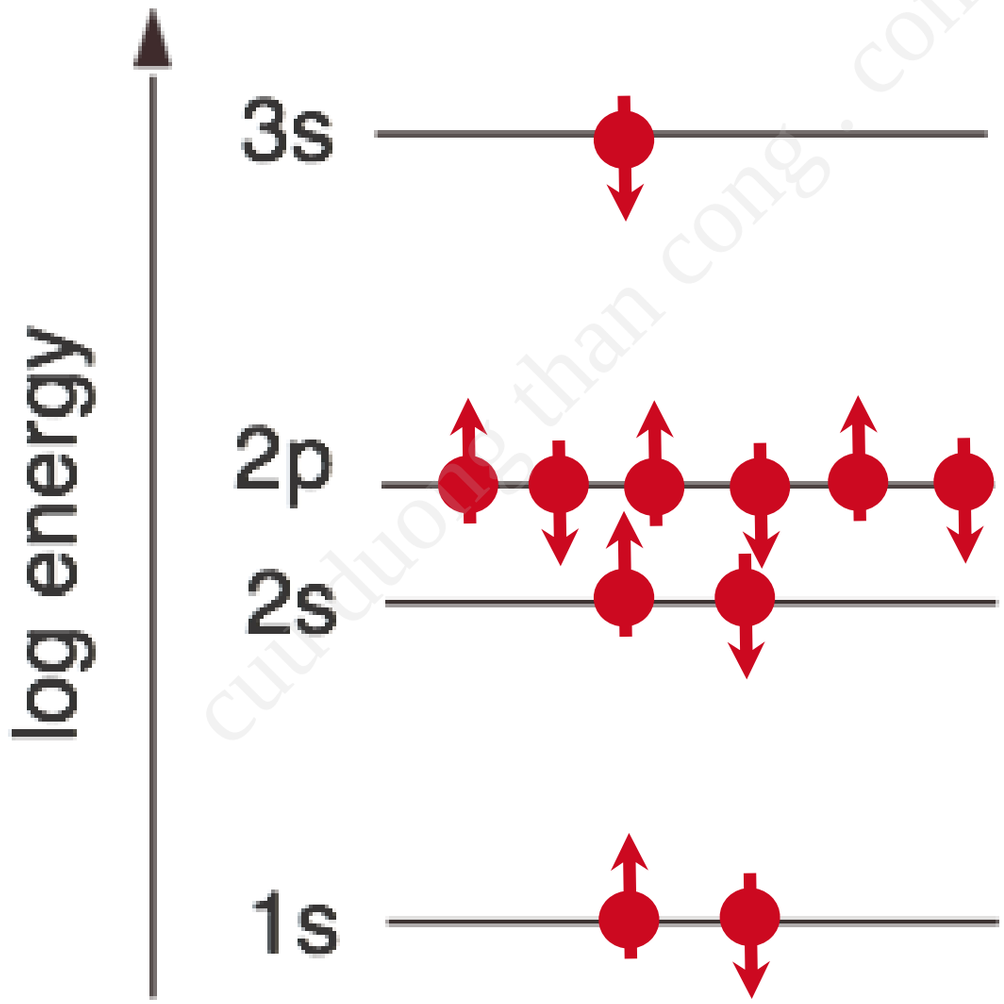
we know for sure that

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

...but not much more

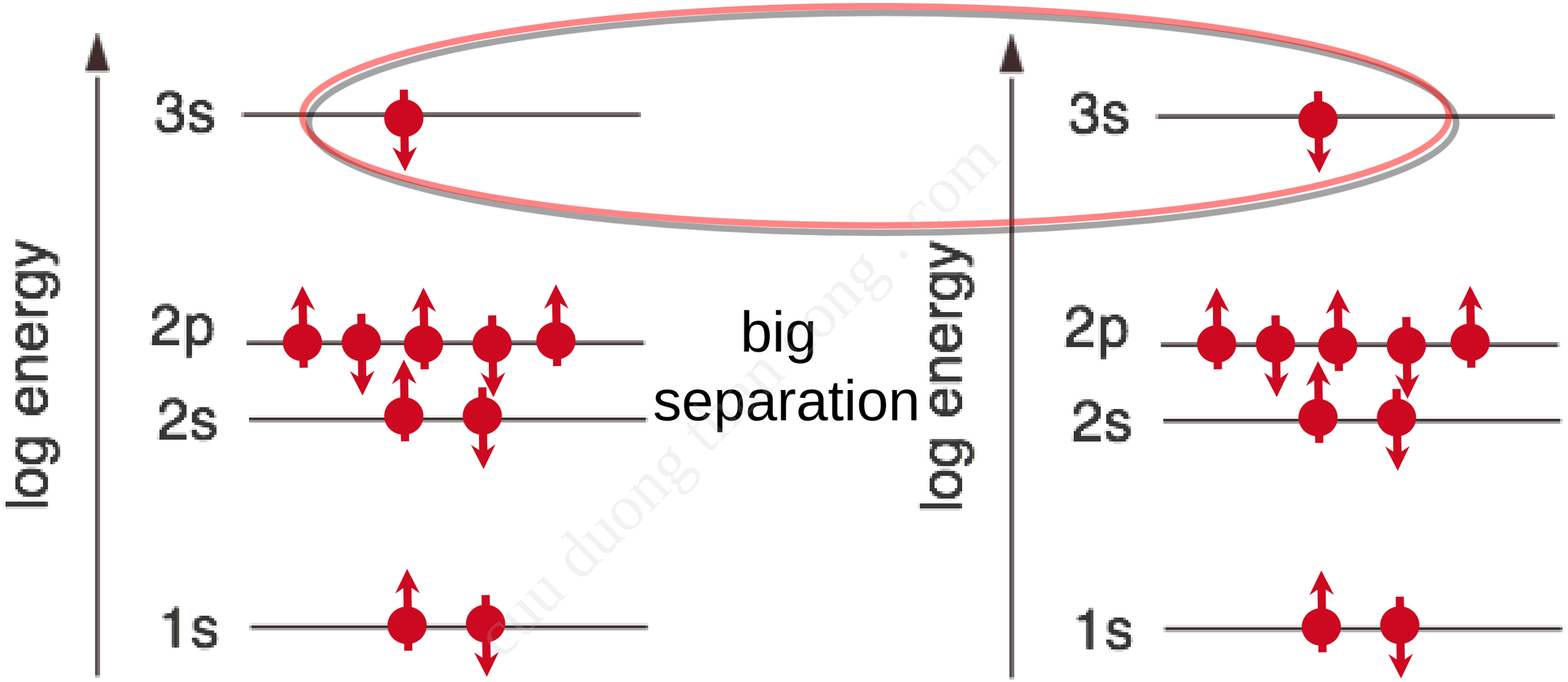
The idea of energy bands: Na

consider one atom of Na: 11 electrons



The idea of energy bands: Na

consider tow Na atoms / a Na_2 molecule: 22 electrons

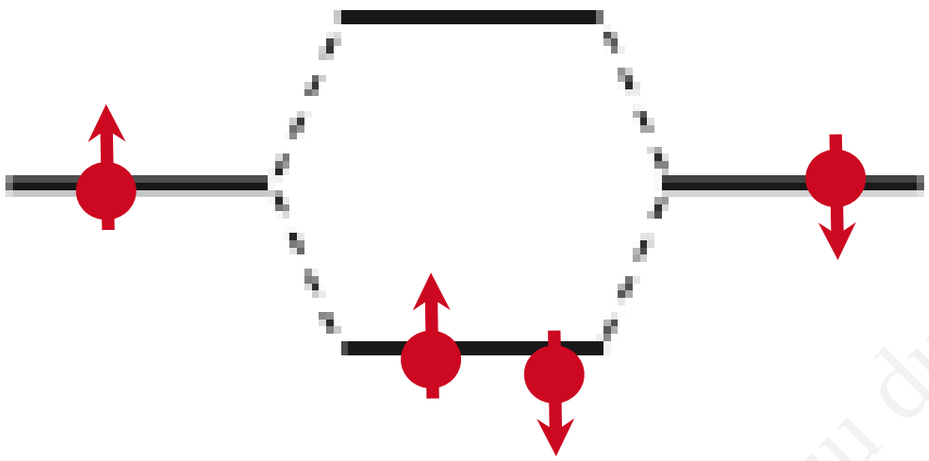


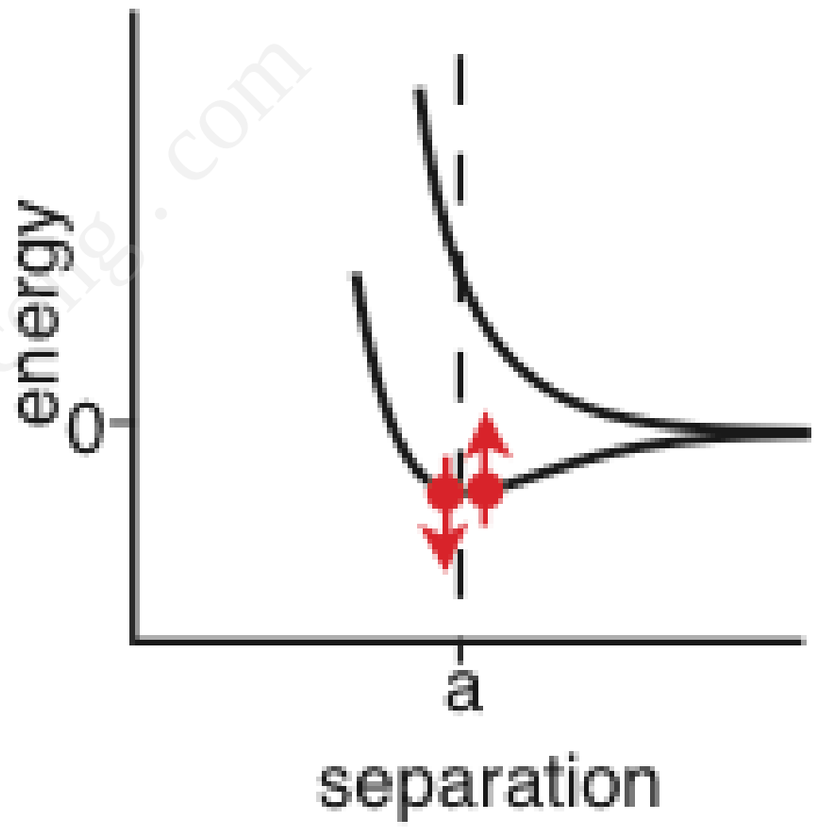
- Focus only on the valence (outer) electrons (3s).
- What happens when we move them together?

The idea of energy bands: Na

consider two Na atoms / a Na_2 molecule: 2 3s electrons

molecular
energy levels
capacity: 2x2=4 electrons





- Levels split up in bonding and anti bonding molecular orbitals and are occupied according to the Pauli principle.
- The distance between the atoms must be such that there is an energy gain.

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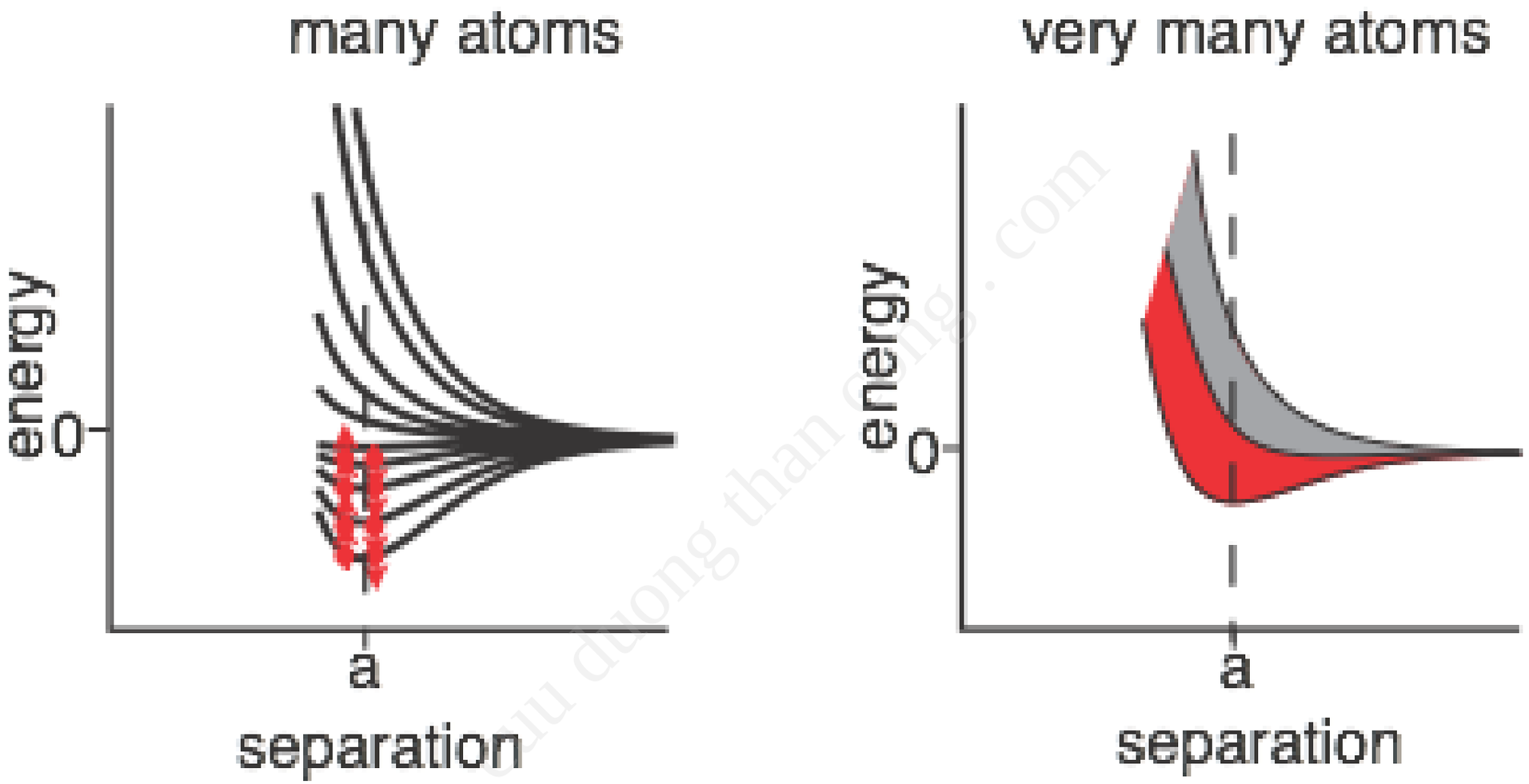
The idea of energy bands: Na

consider many (N) Na atoms (only 3s level)



- N levels with very similar energies, like in a super-giant molecule. We can speak of a “band” of levels.
- Every band has N levels. We can put 2N electrons into it (but we have only N electrons from N Na atoms).

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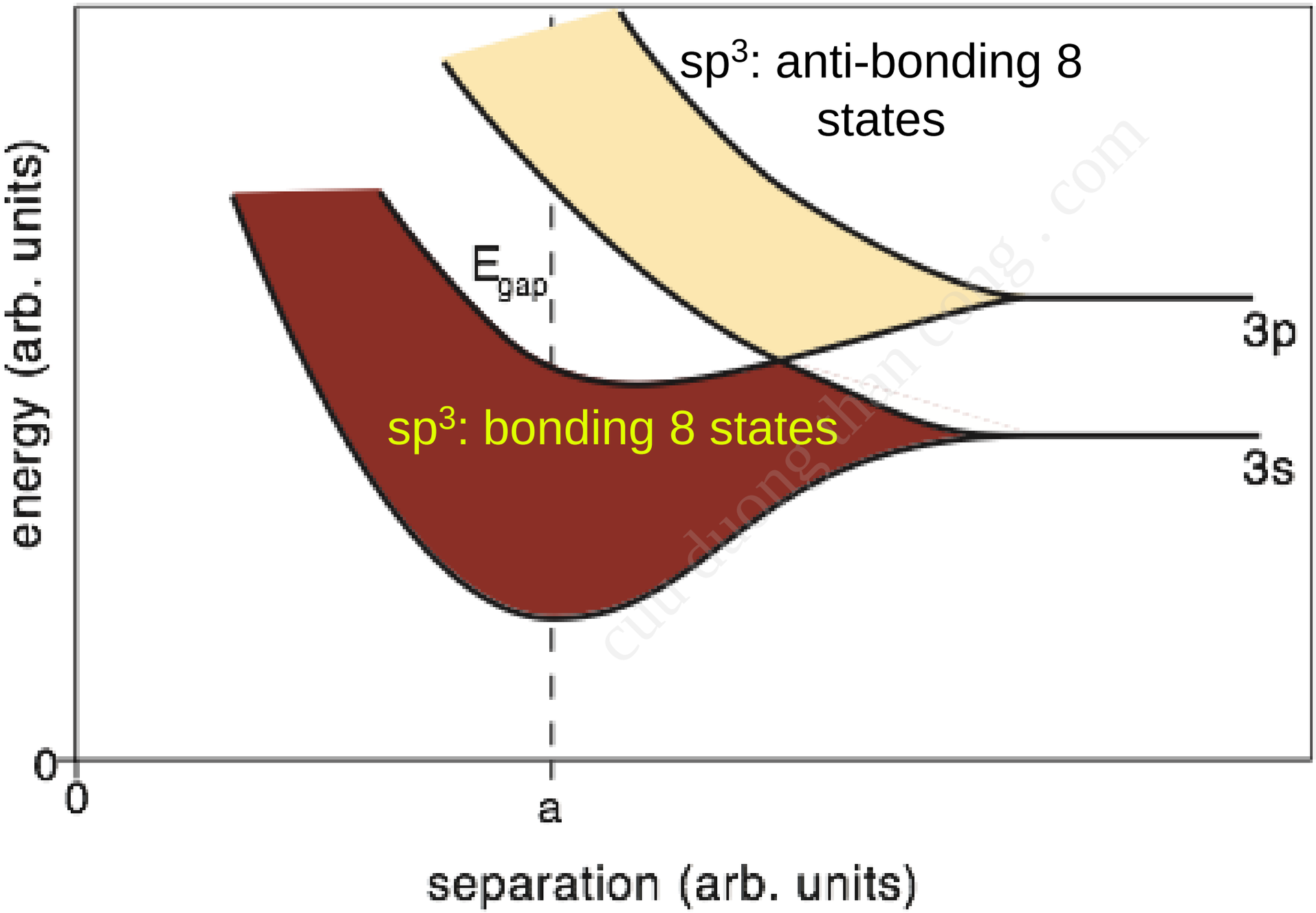
The idea of energy bands: Si or diamond



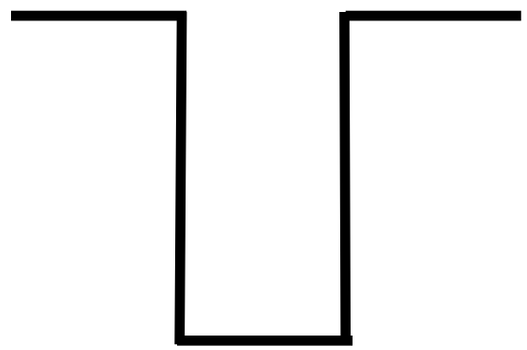
4 electrons per atom
2 atoms per unit cell

8 states per atom
16 states per unit cell

The free electron model

- Completely different approach: consider now free electrons in a box.
- The depth of the box is the minimum potential energy in the solid.

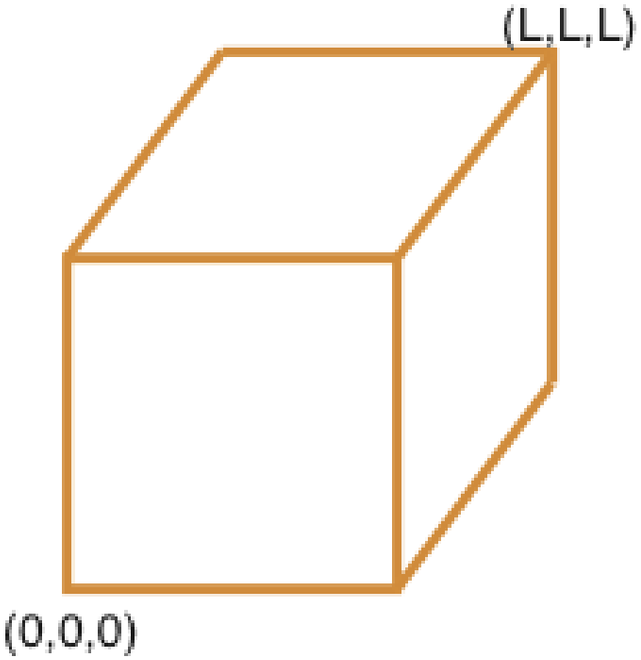
$$-\frac{\hbar^2\nabla^2}{2m_e}\psi(\mathbf{r})+U(\mathbf{r})\psi(\mathbf{r})=E\psi(\mathbf{r})$$



We might just as well require that

$$U(\mathbf{r})=0$$

The free electron model



cube of side length L,

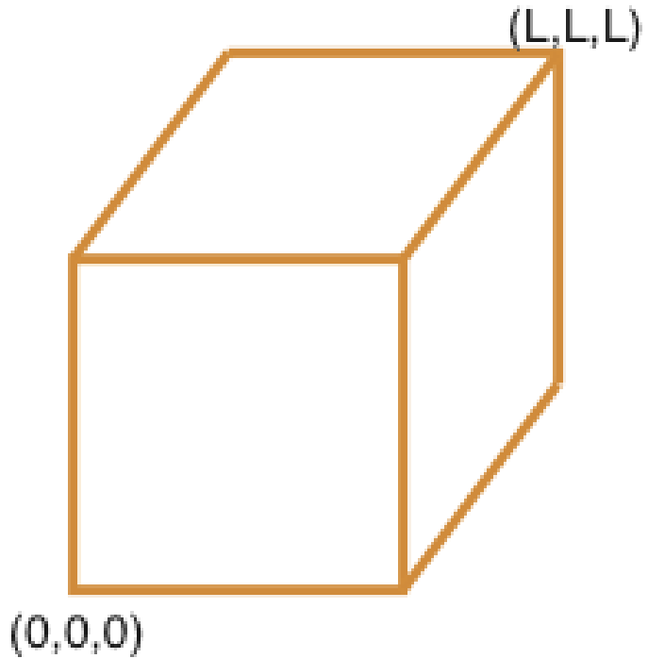
volume of the solid

$$V = L^3$$

electron density *n* and total number of electrons *N*

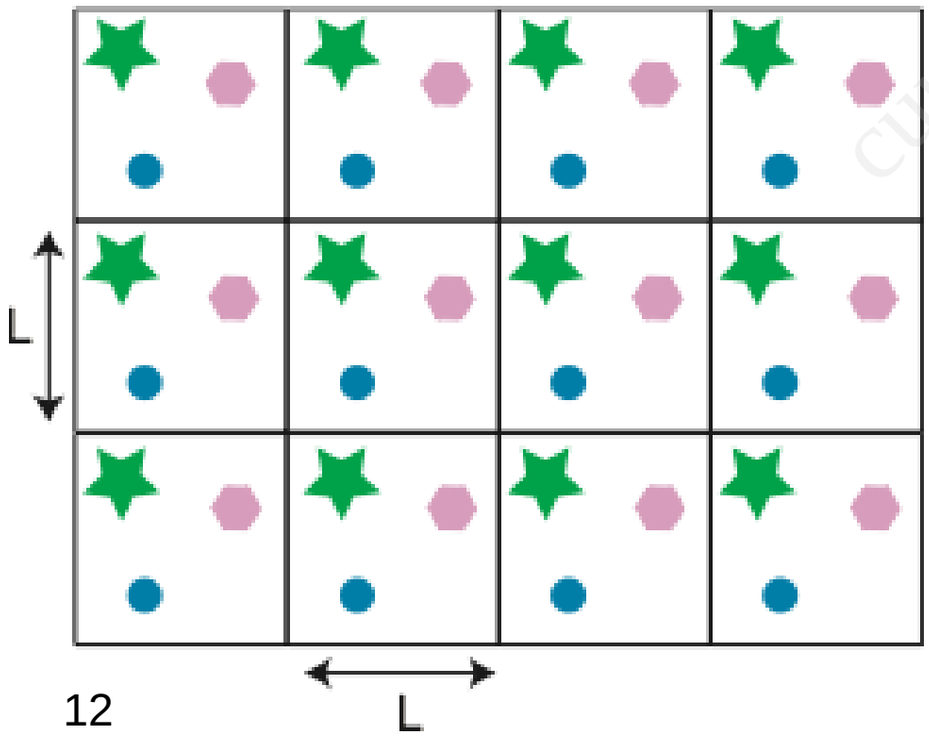
$$n = \frac{N}{V}$$

The free electron model



cube of side length L,
periodic boundary conditions

$$\psi(\mathbf{r}) = \psi(x, y, z) = \psi(x + L, y, z) = \psi(x, y + L, z) = \psi(x, y, z + L)$$



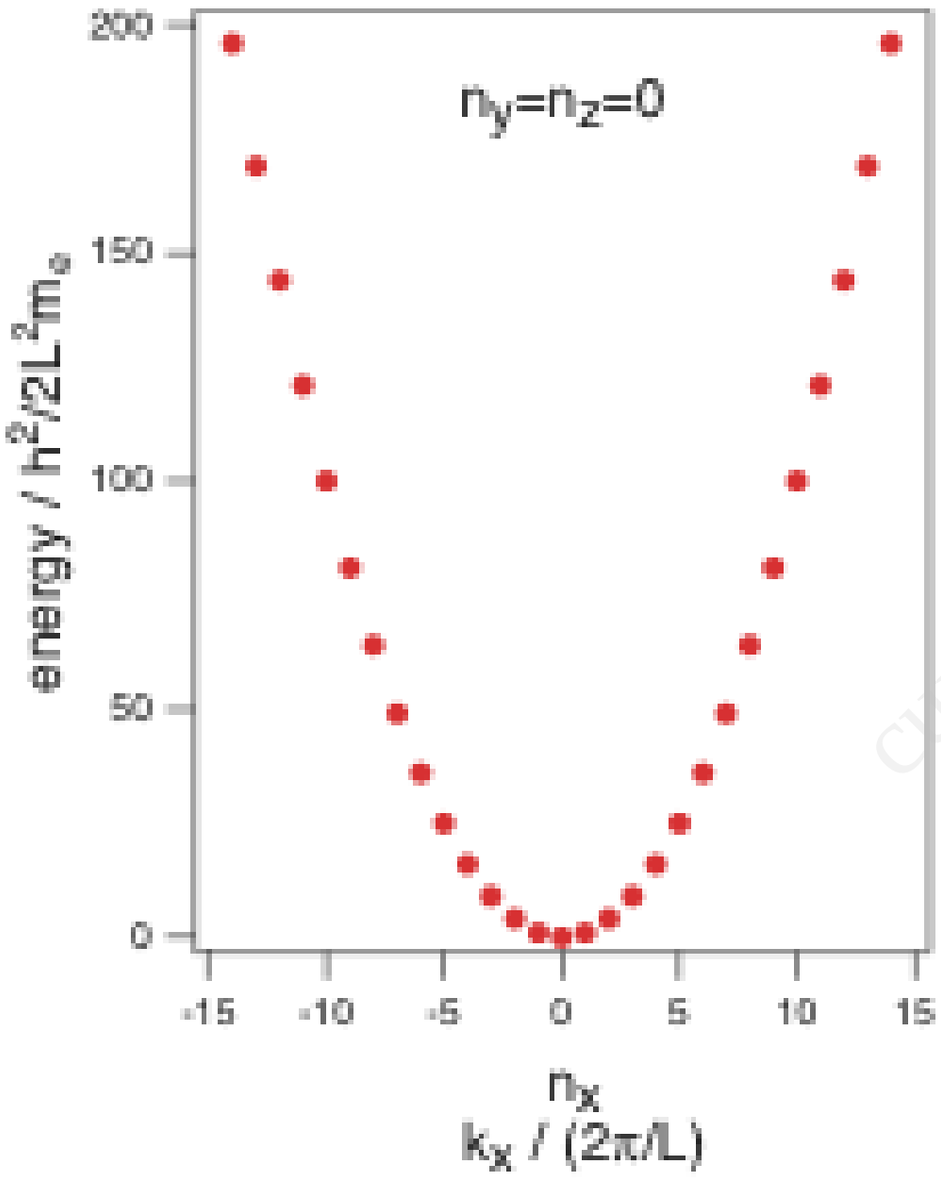
$$\mathbf{k} = (k_x, k_y, k_z) = (\frac{n_x 2\pi}{L}, \frac{n_y 2\pi}{L} \frac{n_z 2\pi}{L})$$

Schrödinger equation

$$-\frac{\hbar^2\nabla^2}{2m_e}\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

solutions

$$\psi(\mathbf{r}) = \frac{1}{\sqrt{V}}e^{i\mathbf{kr}}$$



energy levels

$$E(\mathbf{k}) = \frac{\hbar^2k^2}{2m_e} = \frac{\hbar^2}{2m_e}(k_x^2 + k_y^2 + k_z^2)$$

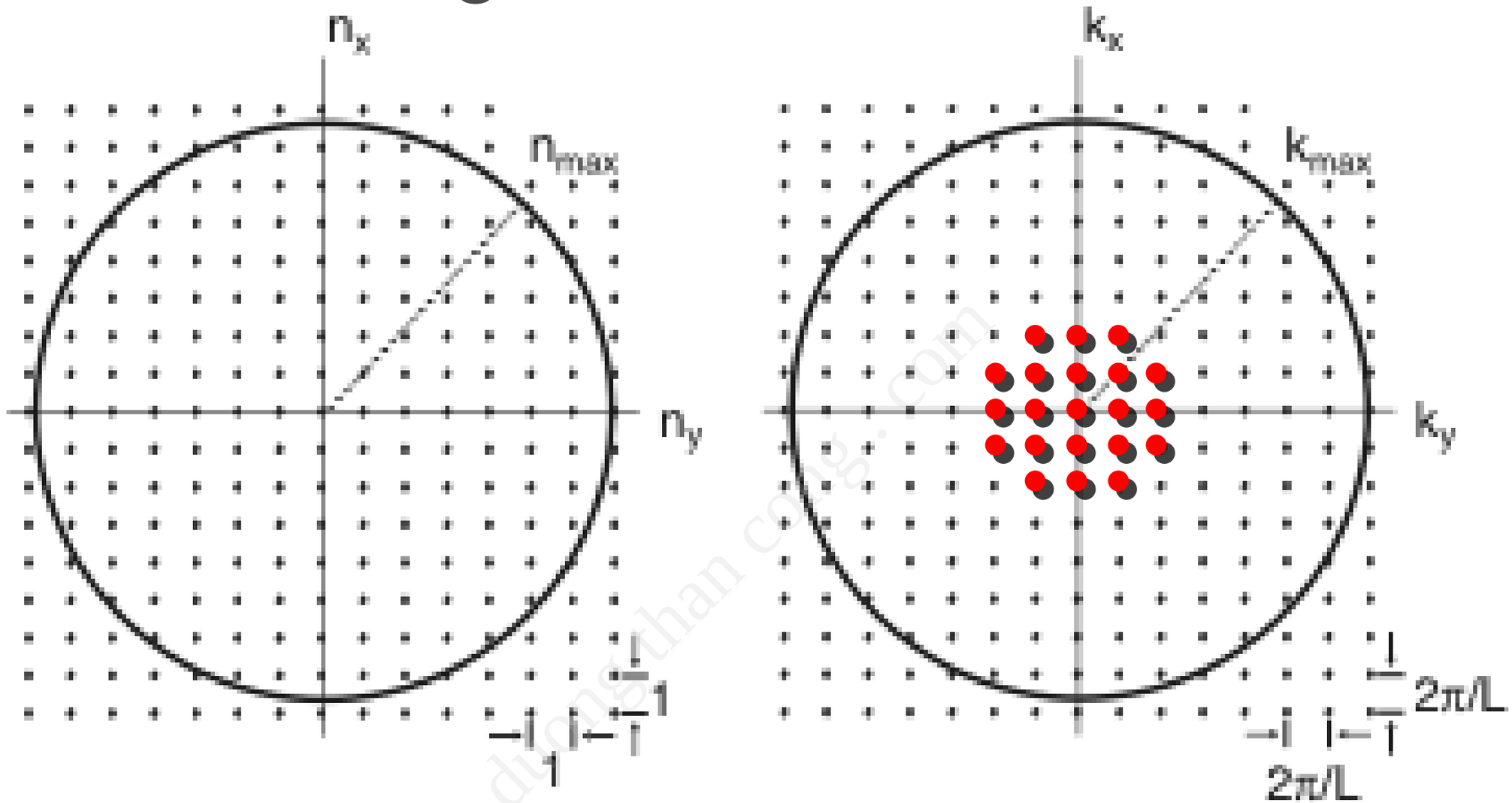
boundary conditions give

$$\mathbf{k} = (k_x, k_y, k_z) = (\frac{n_x 2\pi}{L}, \frac{n_y 2\pi}{L}\frac{n_z 2\pi}{L})$$

order of energy level separation

$$\frac{\hbar^2}{2m_e}\left(\frac{2\pi}{L}\right)^2$$

Filling in the electrons

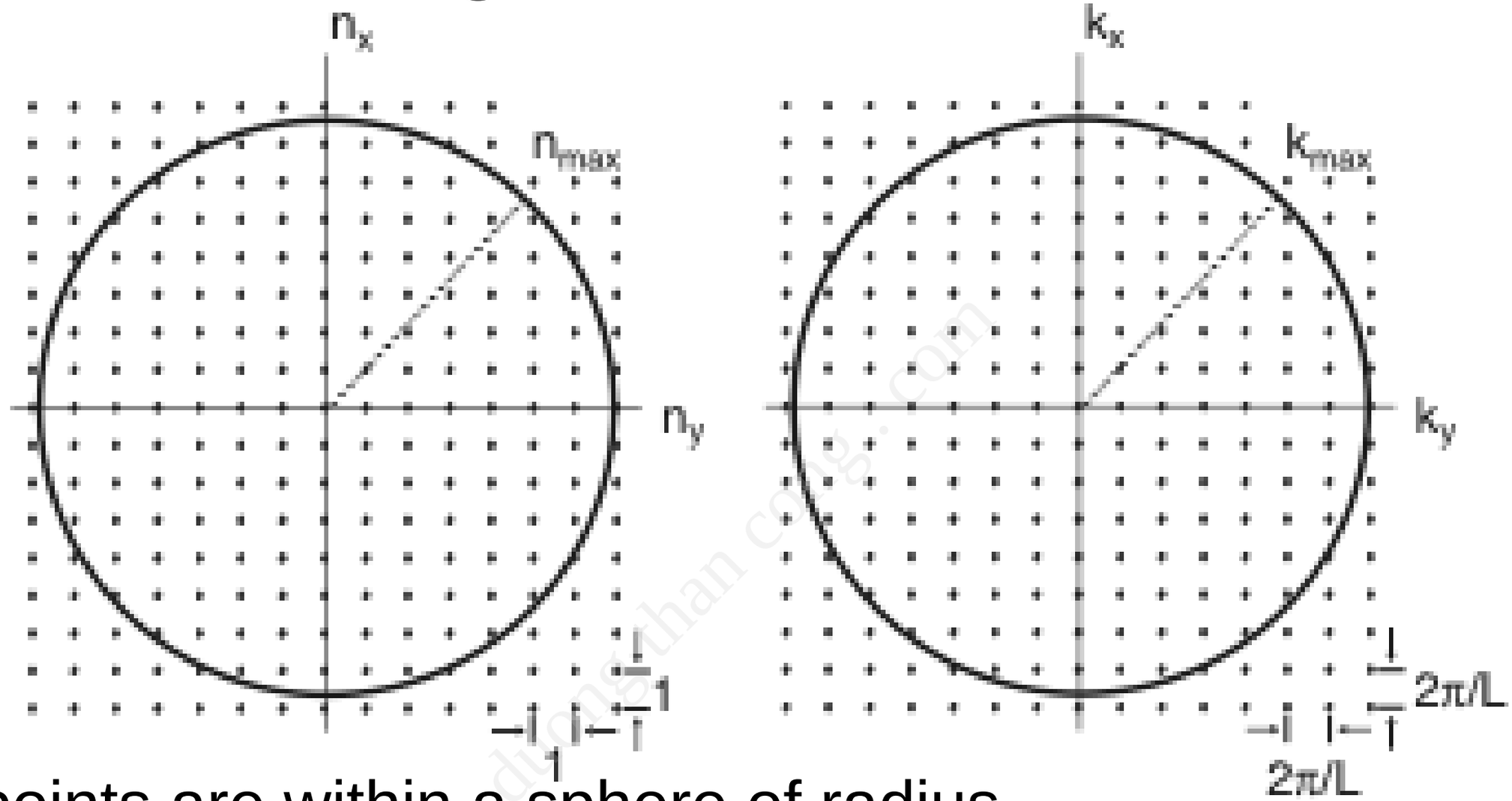


$$\mathbf{k} = (k_x, k_y, k_z) = (\frac{n_x 2\pi}{L}, \frac{n_y 2\pi}{L} \frac{n_z 2\pi}{L})$$

$$E(\mathbf{k}) = \frac{\hbar^2 k^2}{2m_e} = \frac{\hbar^2}{2m_e}(k_x^2 + k_y^2 + k_z^2)$$

2 electrons per k-point. If the electron density is N/V, we have to distribute N electrons on N/2 k-points.

Filling in the electrons



N/2 points are within a sphere of radius

$$\frac{N}{2} = \frac{4}{3}\pi n_{\max}^3 \qquad n_{\max} = \left(\frac{3N}{8\pi}\right)^{1/3}$$

highest occupied energy

$$E_{\max} = \frac{\hbar^2 k_{\max}^2}{2m_e} = \frac{\hbar^2}{2m_e}\left(\frac{2\pi}{L}\right)^2 n_{\max}^2$$

The Fermi energy

highest occupied energy

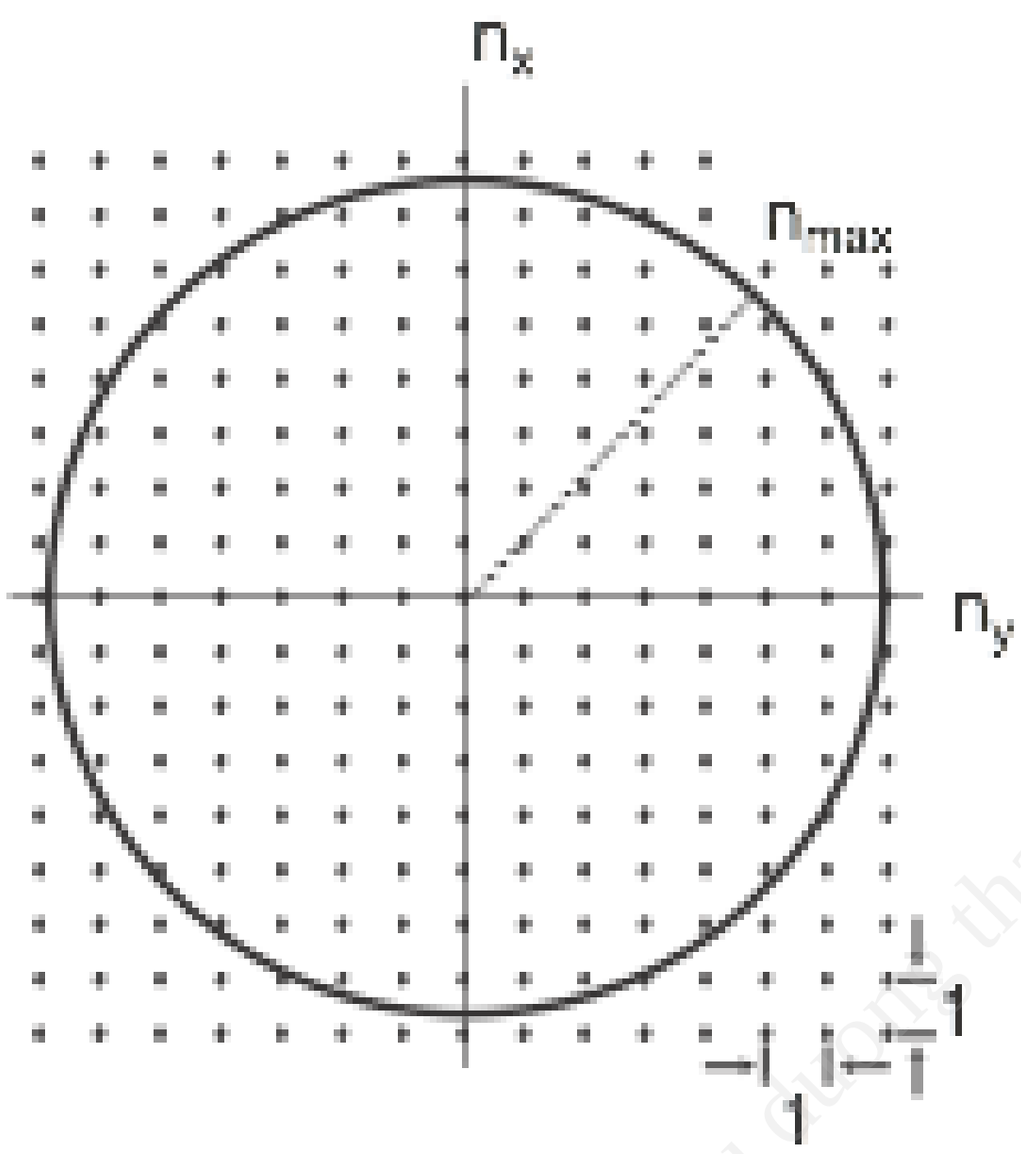
$$E_{\max} = \frac{\hbar^2 k_{\max}^2}{2m_e} = \frac{\hbar^2}{2m_e}\left(\frac{2\pi}{L}\right)^2 n_{\max}^2$$

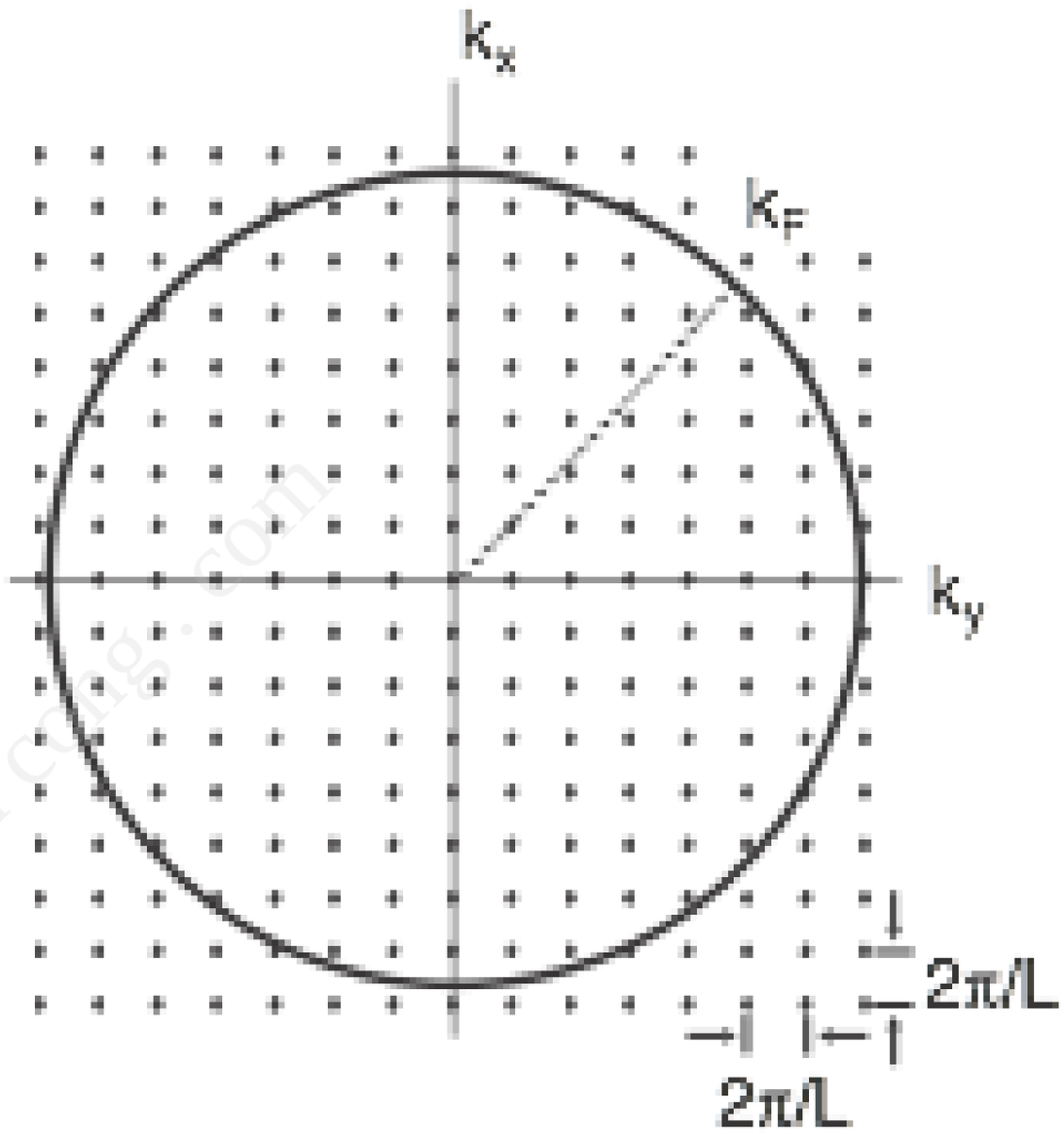
= Fermi energy E_F

with $n_{\max} = \left(\frac{3N}{8\pi}\right)^{1/3}$ and the electron density $n = \frac{N}{V} = \frac{N}{L^3}$

$$E_F = \frac{\hbar^2}{2m_e}(3\pi^2 n)^{2/3} = \frac{\hbar^2 k_F^2}{2m_e}$$

$|\mathbf{k}|_{\max}$ is also called k_F





$$E_{\mathrm{F}} = \frac{\hbar^2 k_{\mathrm{F}}^2}{2m_e} = \frac{\hbar^2}{2m_e}\left(\frac{2\pi}{L}\right)^2 n_{\mathrm{max}}^2$$

The Fermi energy

element	E_F(eV)
Na	3.22
Cu	7.00
Al	11.63

The Fermi velocity

$$\frac{1}{2}m_e v_F^2 = E_F \qquad \text{and} \quad E_F = \frac{\hbar^2}{2m_e}\left(3\pi^2 n\right)^{2/3}$$

$$v_F = \sqrt{\frac{2E_F}{m_e}}$$

- The Fermi velocity does (to first order) not depend on the temperature!

The Fermi velocity

$$\frac{1}{2}m_e v_F^2 = E_F$$

$$v_F^2 = \frac{2E_F}{m_e}$$

element	E_F(eV)	v_F(ms^{-1})
Na	3.22	1.07 10^6
Al	11.63	2.02 10^6
Cu	7.00	1.57 10^6

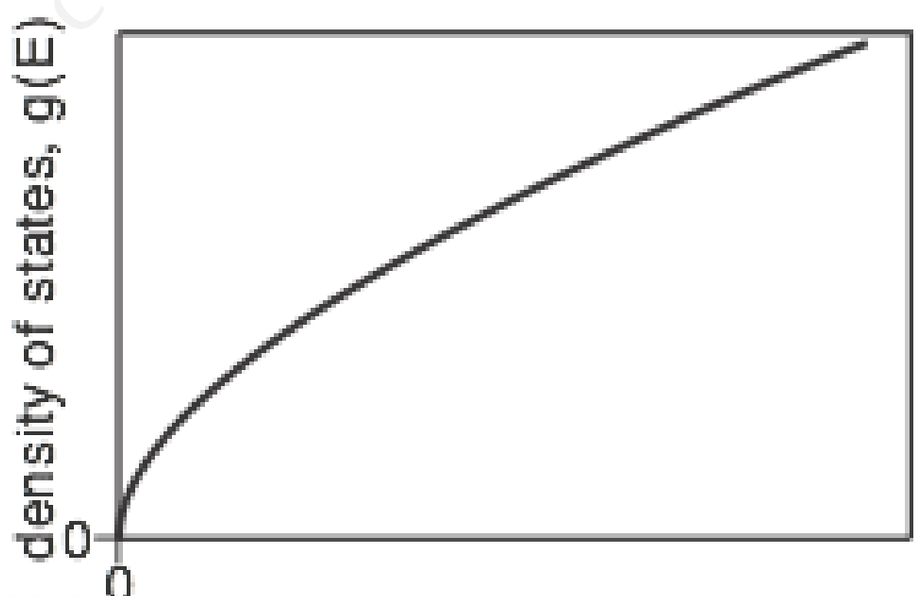
The density of states: free electrons

We can now calculate the density of states.

we have $$E(N) = \frac{\hbar^2}{2m_e}\left(\frac{3\pi^2 N}{V}\right)^{2/3}$$

$$N(E) = \frac{V}{3\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{3/2} E^{3/2}$$

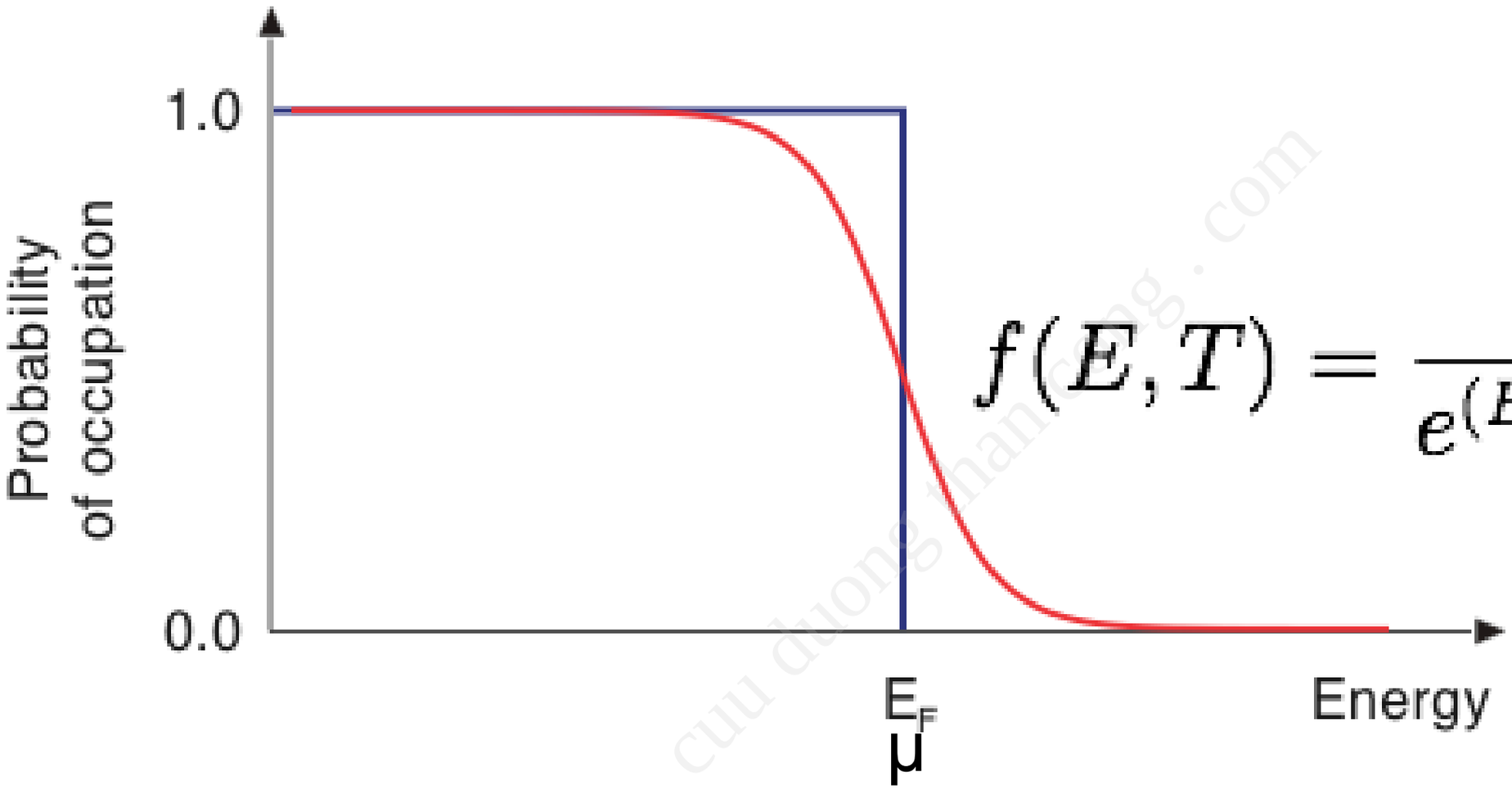
$$g(E)dE = \frac{dN}{dE}dE = \frac{V}{2\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{3/2} E^{1/2}dE$$



The Fermi-Dirac distribution

- How are the electronic states populated at finite temperature?

The Fermi-Dirac distribution



$$f(E,T) = \frac{1}{e^{(E-\mu)/k_B T} + 1}$$

- At T=0 all the states are filled up to the highest occupied state. This state is called the Fermi energy E_F. It is equal to the chemical potential μ at T=0.

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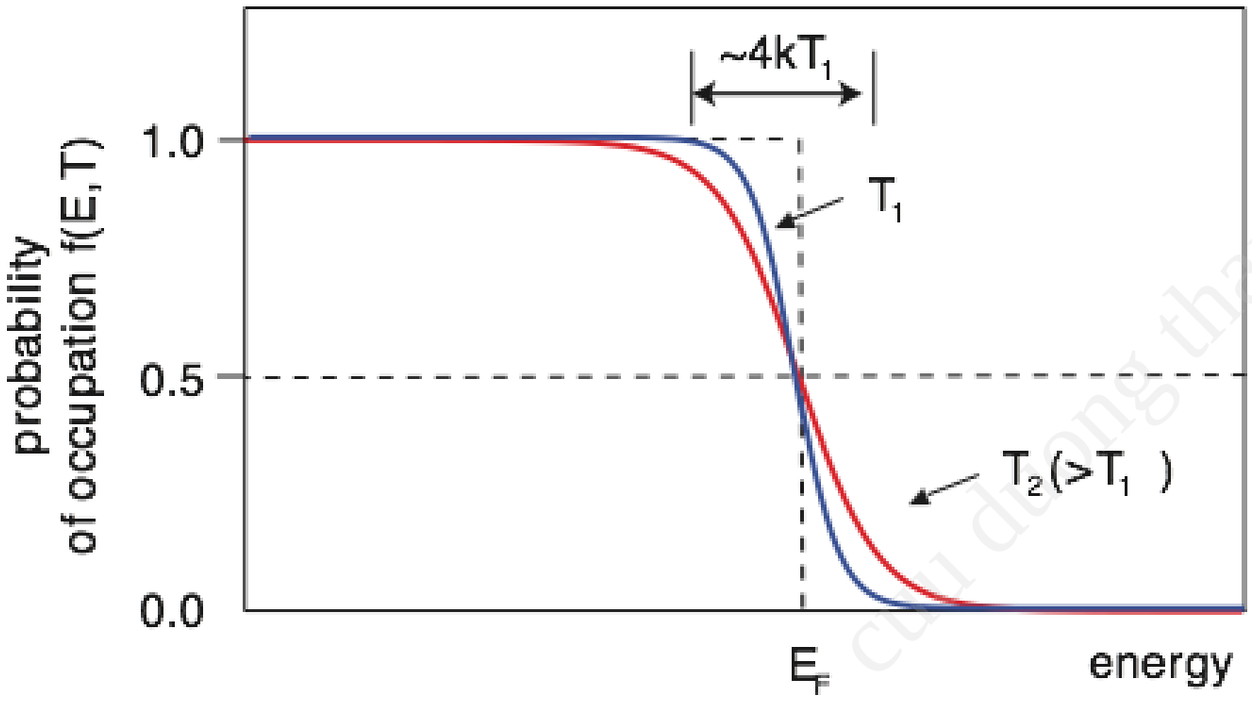
The Fermi-Dirac distribution



$$f(E,T) = \frac{1}{e^{(E-E_F)/k_BT}+1}$$

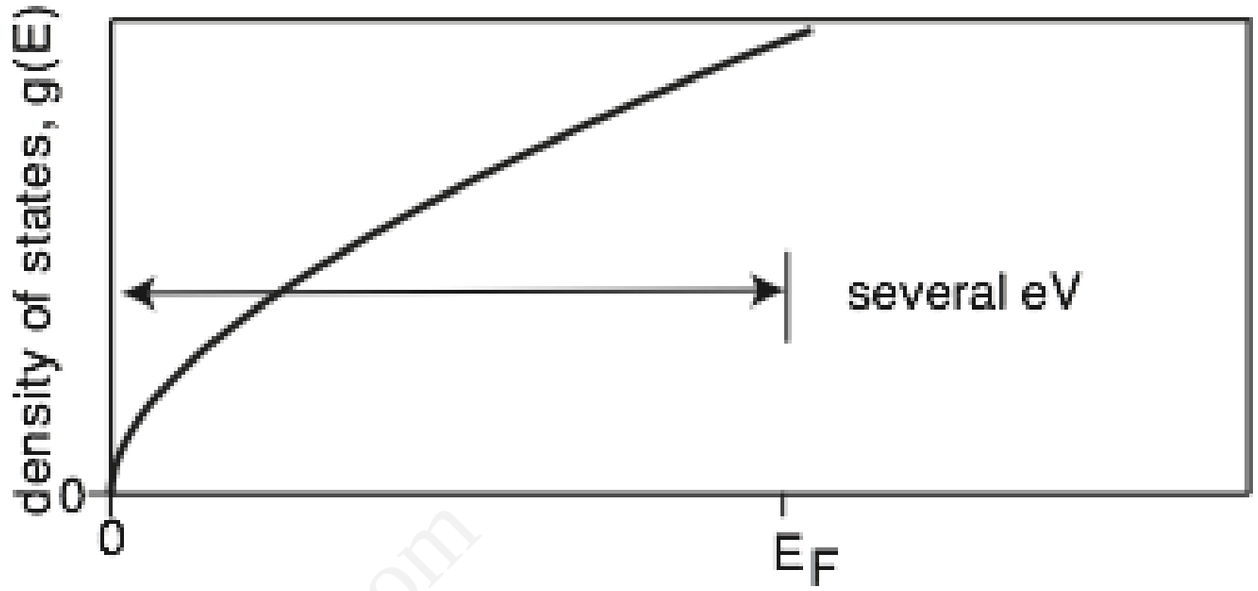
$$k_BT\ln[\frac{1}{f(E,T)}-1] = E - E_F$$

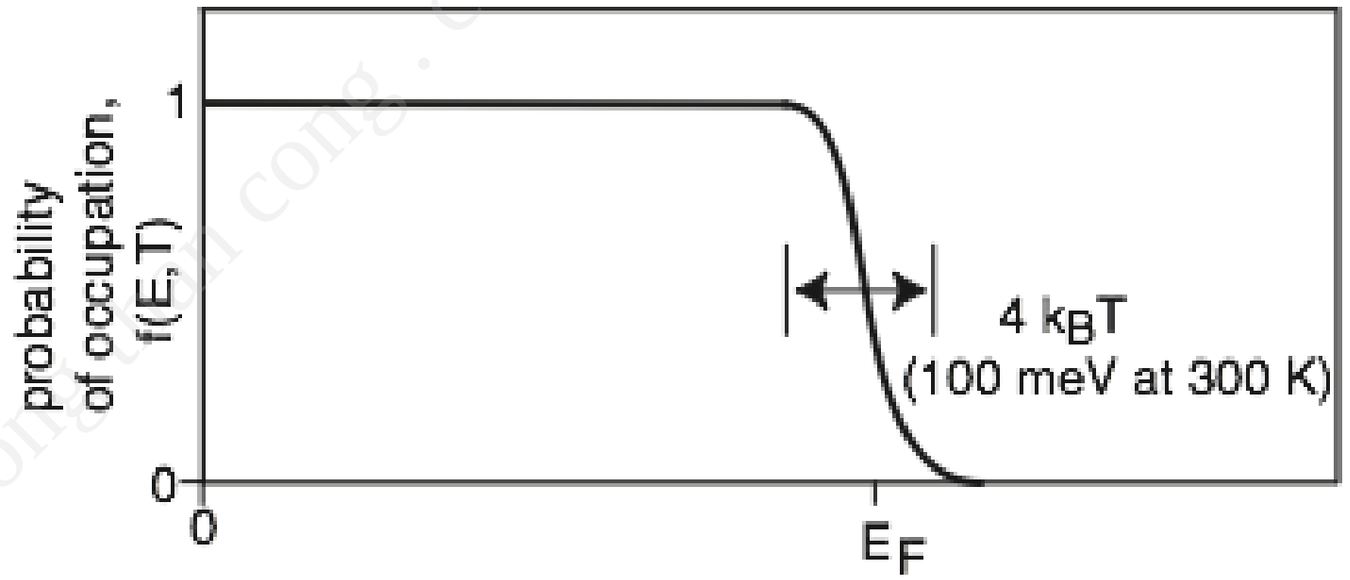
$$k_BT\ln[\frac{1}{0.1}-1] = 2.2k_BT$$

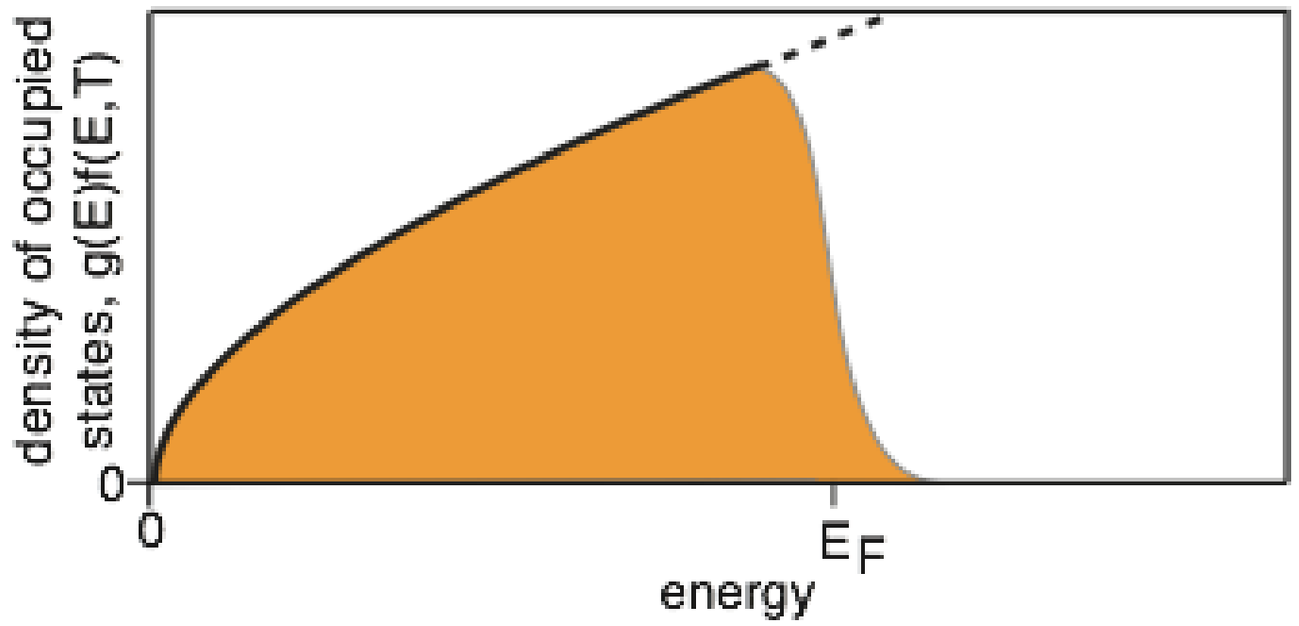
$$k_BT\ln[\frac{1}{0.9}-1] = -2.2k_BT$$

Occupation of the states at finite T

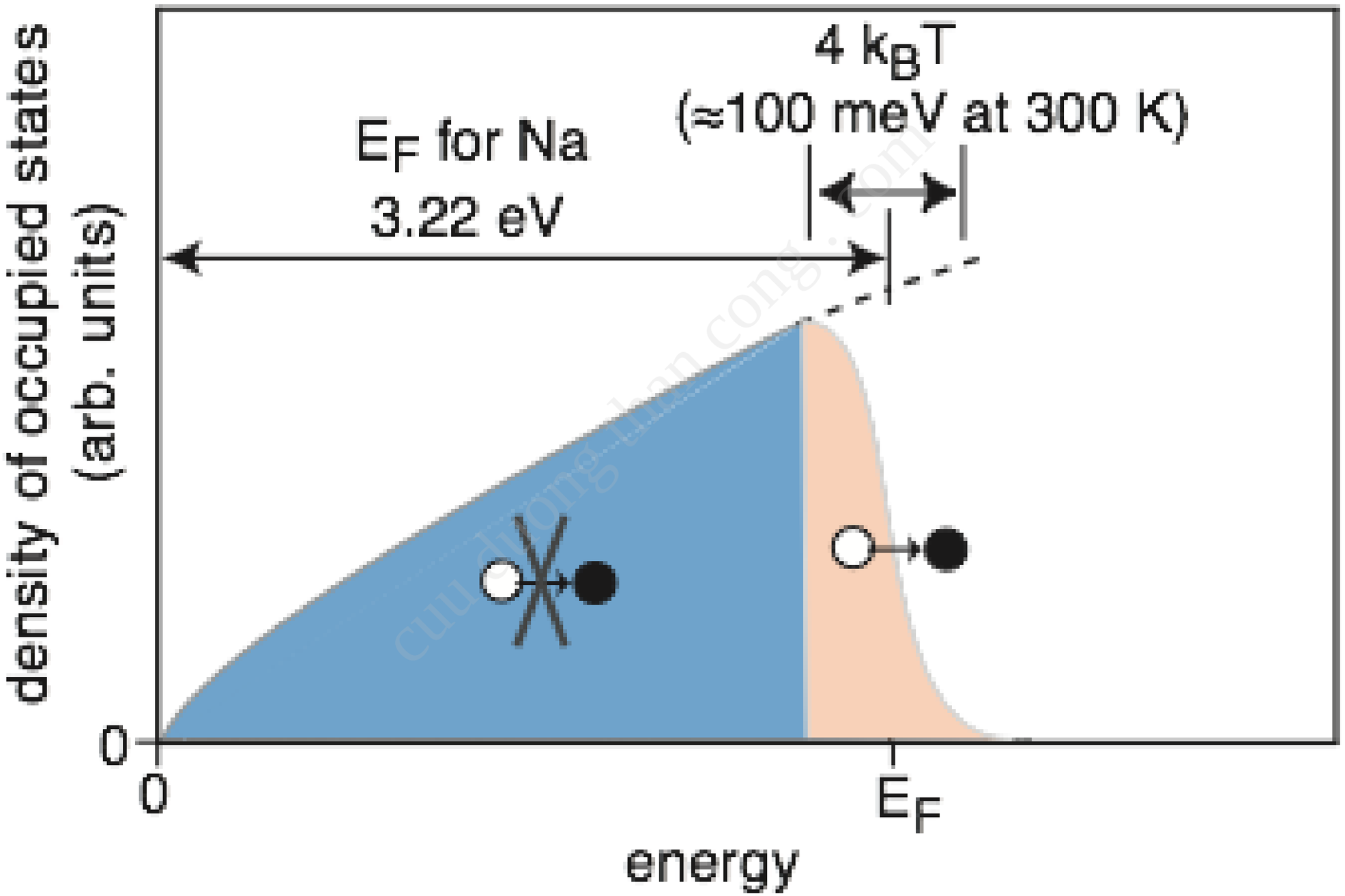
$$f(E,T) = \frac{1}{e^{(E-\mu)/k_B T} + 1}$$



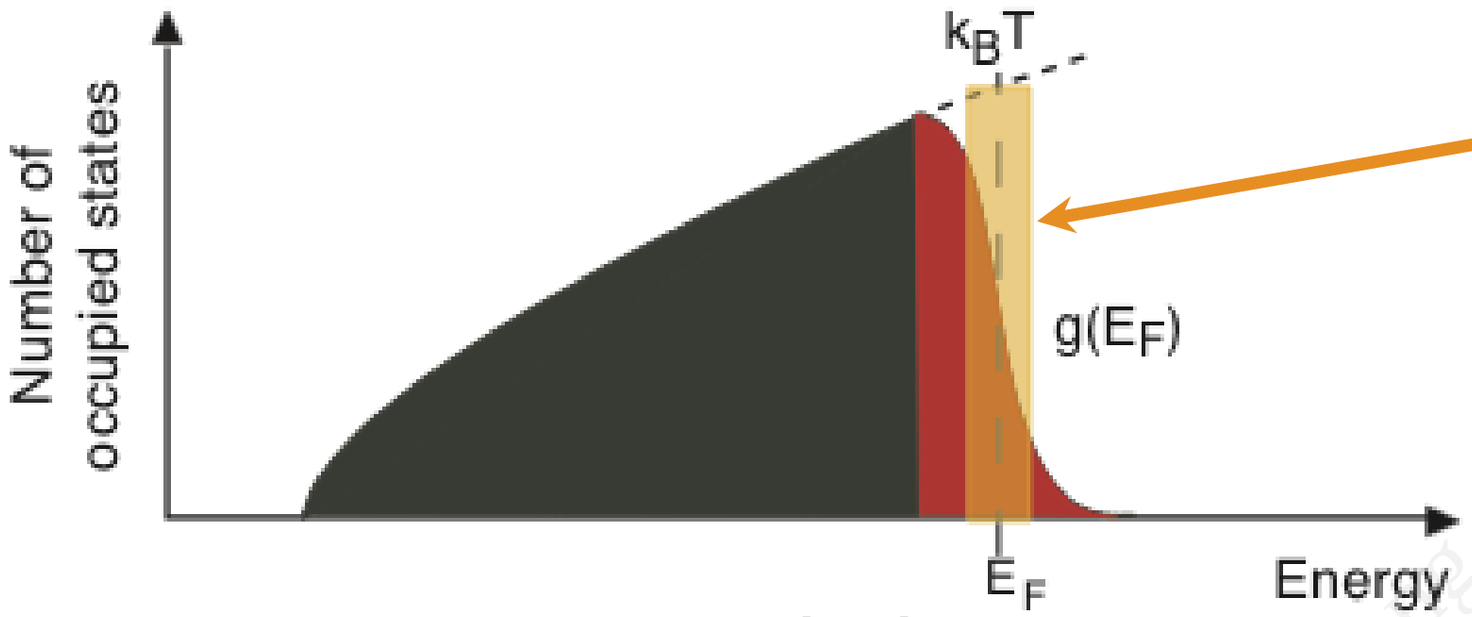




The ‘Fermi trap’ effect



Heat capacity of the electrons: estimate



$$k_B T g(E_F)$$

Their mean energy is

$$< E >= \frac{3}{2} k_B T g(E_F) k_B T$$

and the heat capacity

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V = 3 k_B^2 T g(E_F)$$

The result of this sloppy calculation is quite similar to the correct result which is

$$C_V = \frac{\pi^2}{3} k_B^2 T g(E_F)$$

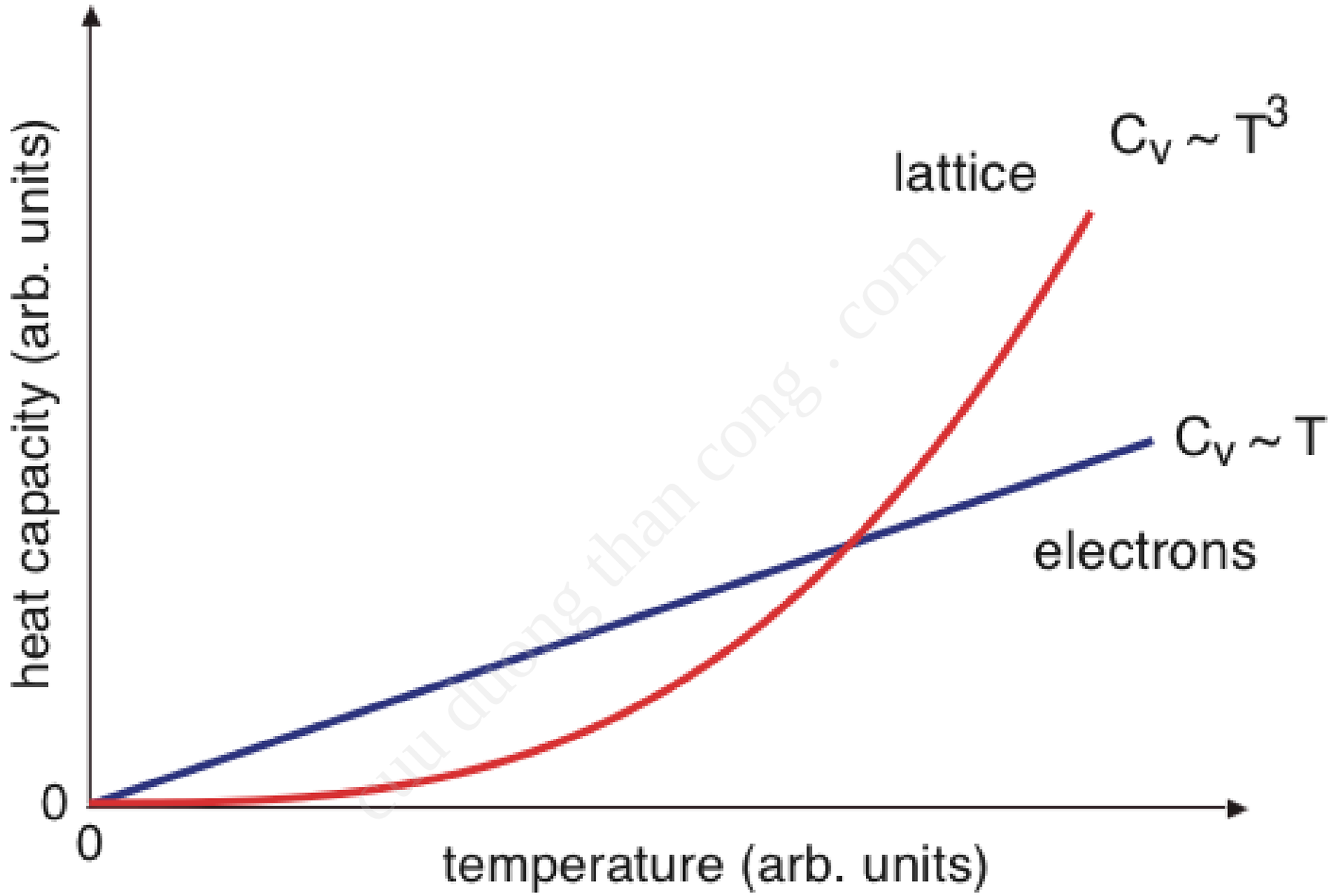
Comparison of the Dulong-Petit law to experiment

	77 K (JK^{-1})	273 K (JK^{-1})
classical value	24.9	24.9
copper	12.5	24.3
aluminium	9.1	23.8
gold	19.1	25.2
lead	23.6	26.7
iron	8.1	24.8
sodium	20.4	27.6
silicon	5.8	21.8

values of one mole of substance

- At high temperatures the Dulong-Petit law works quite well, also for metals.

Heat capacity of a metal: lattice + electrons



- two contributions: lattice and electrons
- electrons unimportant at high T but dominating at sufficiently low T

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Thermal conduction by electrons

very similar to the phonon expression

mean free path
similar to phonons (?)

heat capacity
0.01 of phonon
value

$$\kappa = \frac{1}{3} v_t^2 \tau c_v = \frac{1}{3} \lambda v_t c_v$$

velocity, at least 1000 times
larger than for phonons

Free electron quantum version of Wiedemann Franz

$$\frac{\kappa}{\sigma} = LT \qquad \kappa = \frac{1}{3} v_t^2 \tau c_v \qquad \sigma = \frac{n e^2 \tau}{m_e}$$

We must use the Fermi velocity and the correct heat capacity for the electrons. We know (almost) all this.

we get...

$$\frac{\kappa}{\sigma} = \frac{\pi^2}{3} \frac{k_B^2}{e^2} T = LT$$

so that L = 2.45 10^{-8} Watt Ω K^{-2}

The Wiedemann Franz law: Drude model

estimated thermal conductivity
(from a classical ideal gas)

$$\kappa = \frac{1}{3} v_t^2 \tau c_v$$

$$\sigma = \frac{n e^2 \tau}{m_e}$$

$$\frac{\kappa}{\sigma} = \frac{3}{2}\frac{k_B^2}{e^2} T = LT$$

but now we have

$$\frac{\kappa}{\sigma} = \frac{\pi^2}{3}\frac{k_B^2}{e^2} T = LT$$

Comparison of the Lorenz number to experimental data

at 273 K

metal	10^{-8} Watt Ω K^{-2}
Ag	2.31
Au	2.35
Cd	2.42
Cu	2.23
Mo	2.61
Pb	2.47
Pt	2.51
Sn	2.52
W	3.04
Zn	2.31

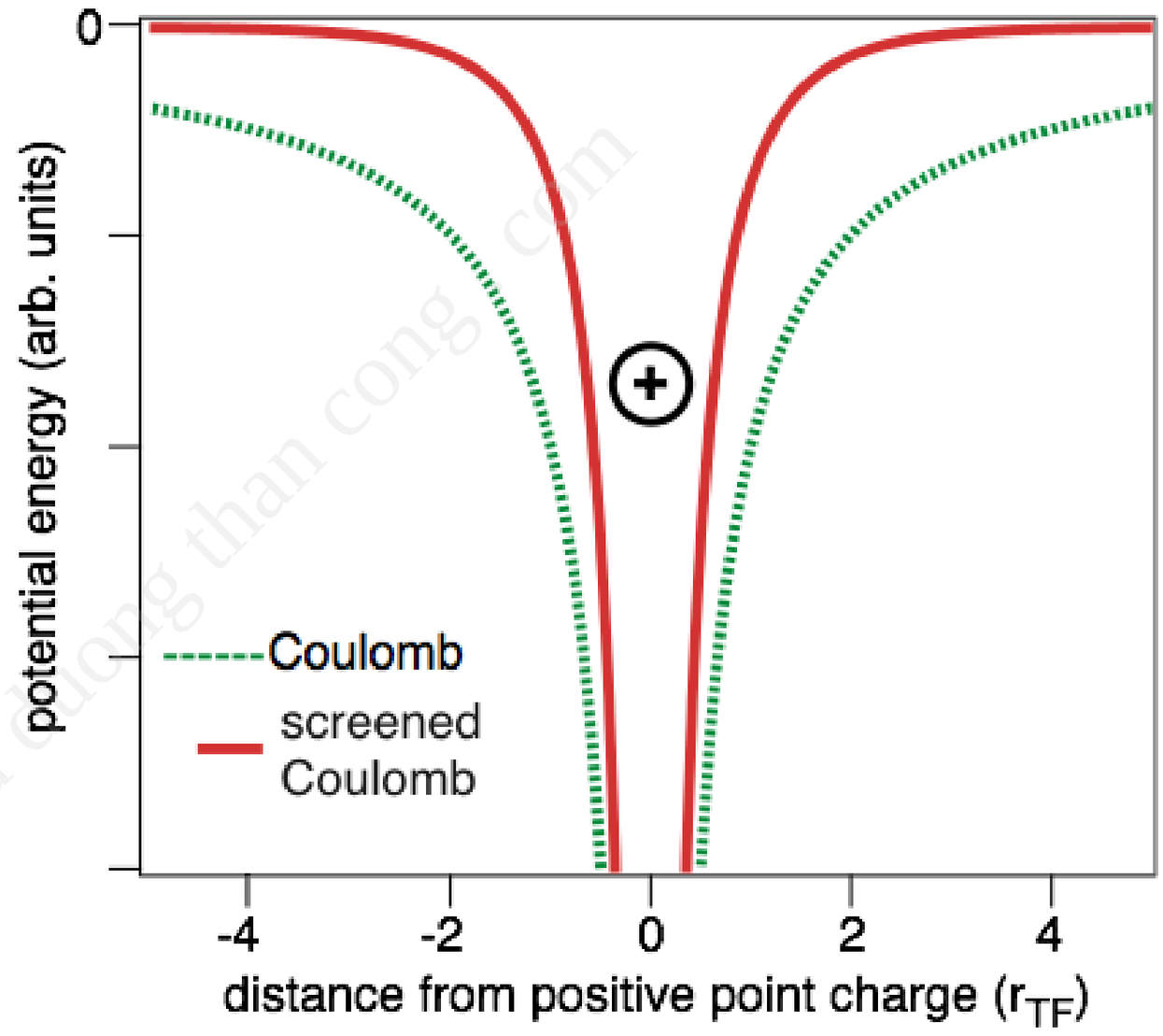
$$\frac{\kappa}{\sigma} = \frac{\pi^2}{3}\frac{k_B^2}{e^2}T = LT$$

L = 2.45 10^{-8} Watt Ω K^{-2}

Screening in Metals

positive point charge in vacuum

$$\phi_0(r) = \frac{1}{4\pi\epsilon_0}\frac{q}{r}$$

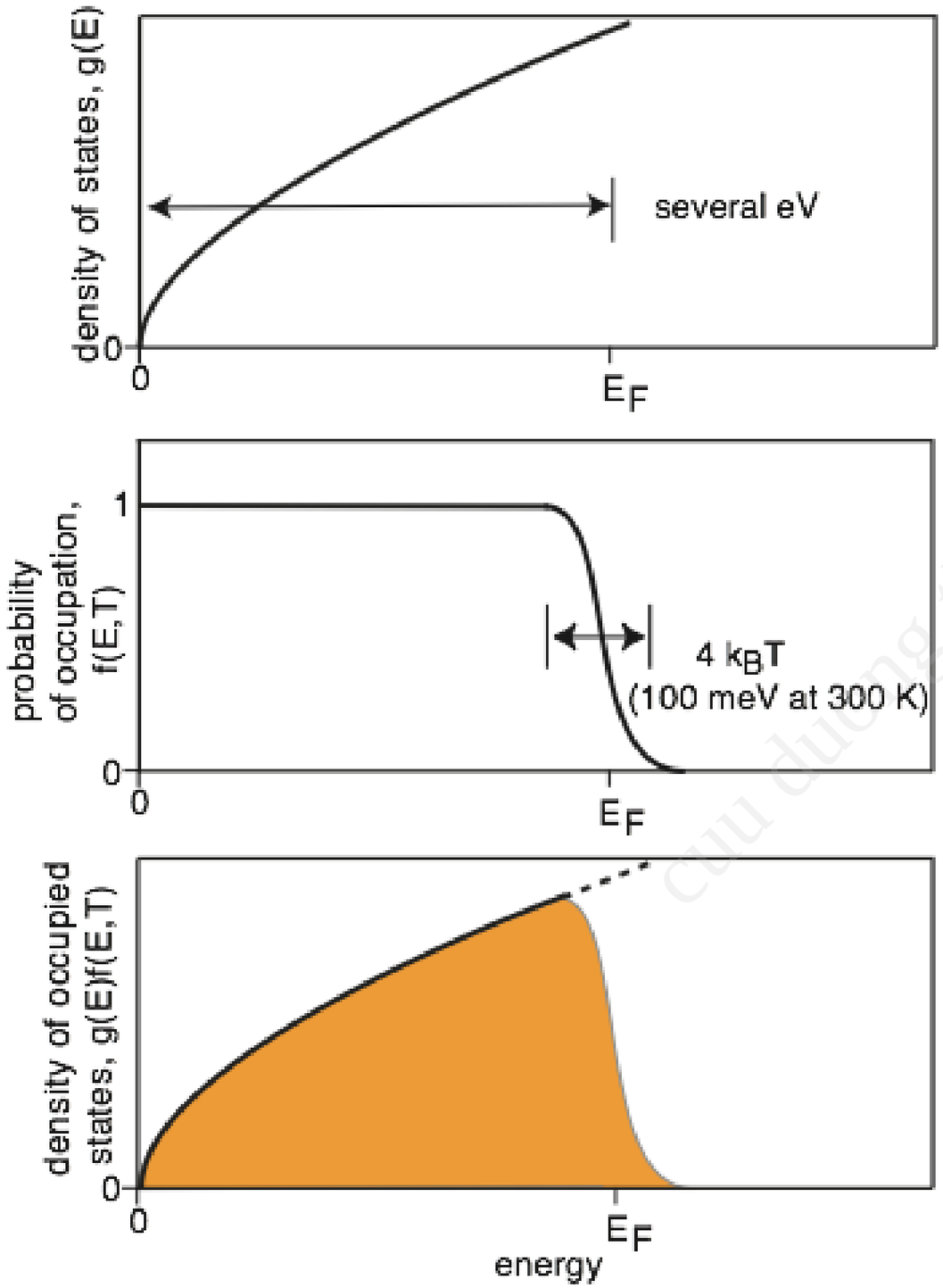


positive point charge in a metal

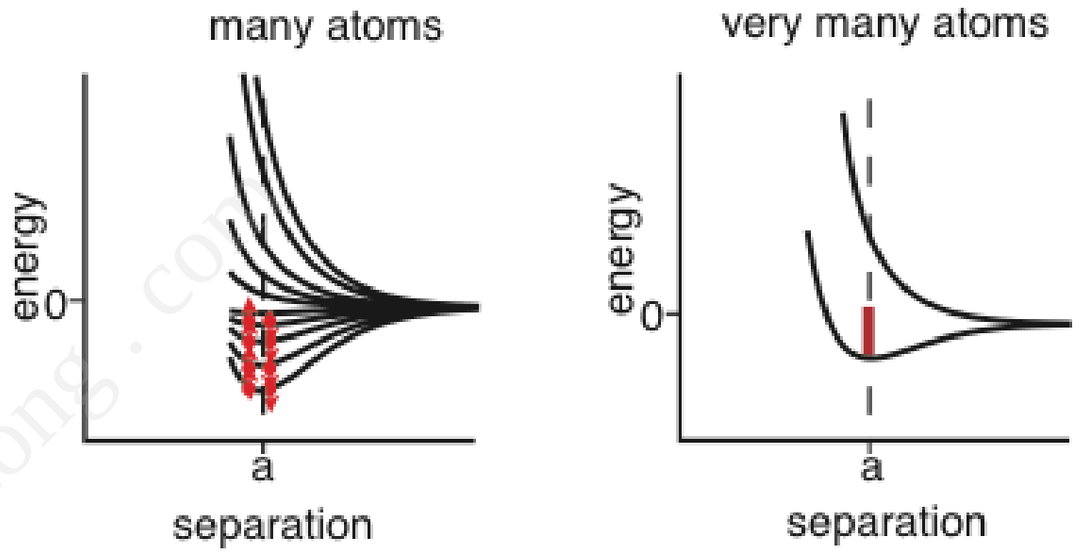
$$\phi(r) = \frac{1}{4\pi\epsilon_0}\frac{q}{r}e^{-r/r_{\mathrm{TF}}}$$

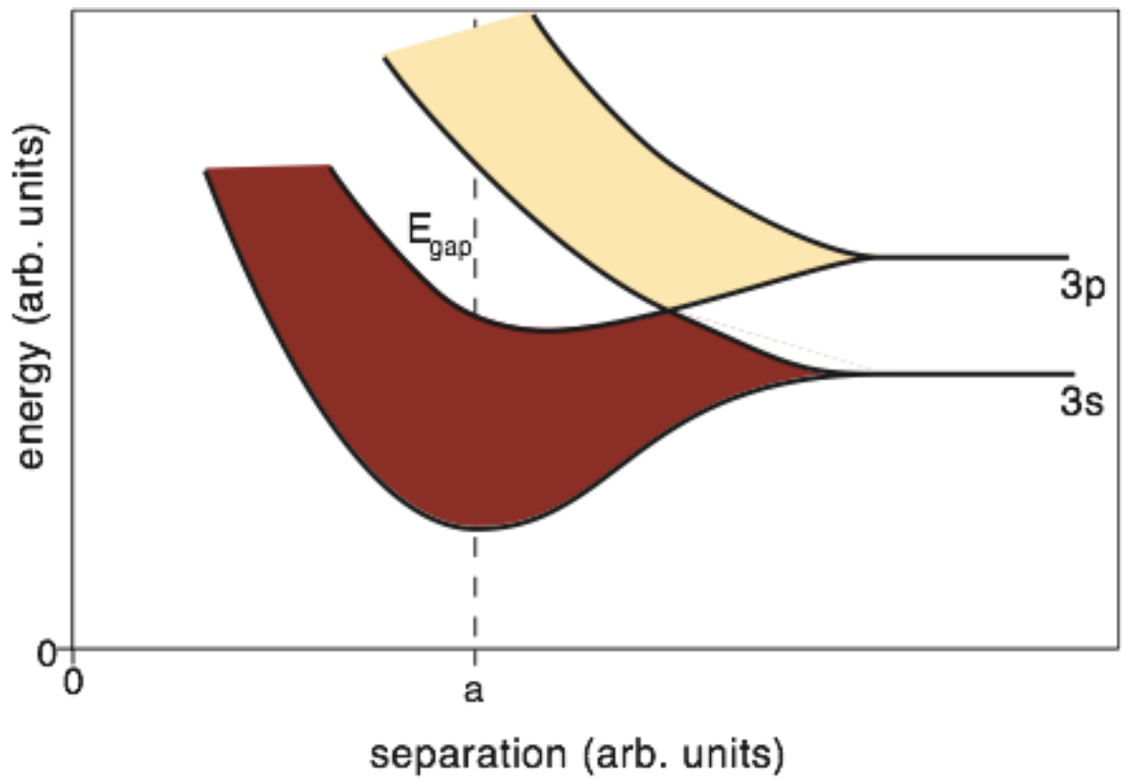
Thomas-Fermi screening length $r_{\mathrm{TF}} = \sqrt{\frac{V\epsilon_0}{e^2 g(E_F)}}$

free electron model



naive band picture





Bloch waves

Schrödinger equation for a periodic potential $U(\mathbf{r}) = U(\mathbf{r}+\mathbf{R})$

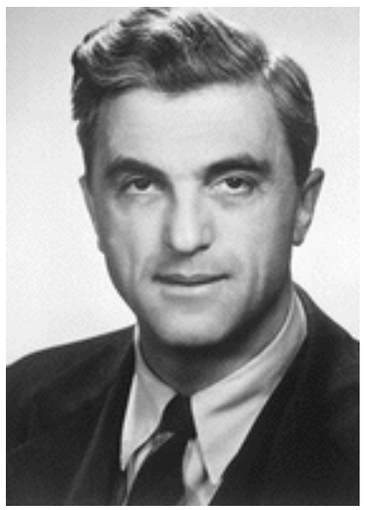
$$-\frac{\hbar^2\nabla^2}{2m_e}\psi(\mathbf{r}) + U(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

solutions have the form of **Bloch waves**

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

plane wave

lattice-periodic function



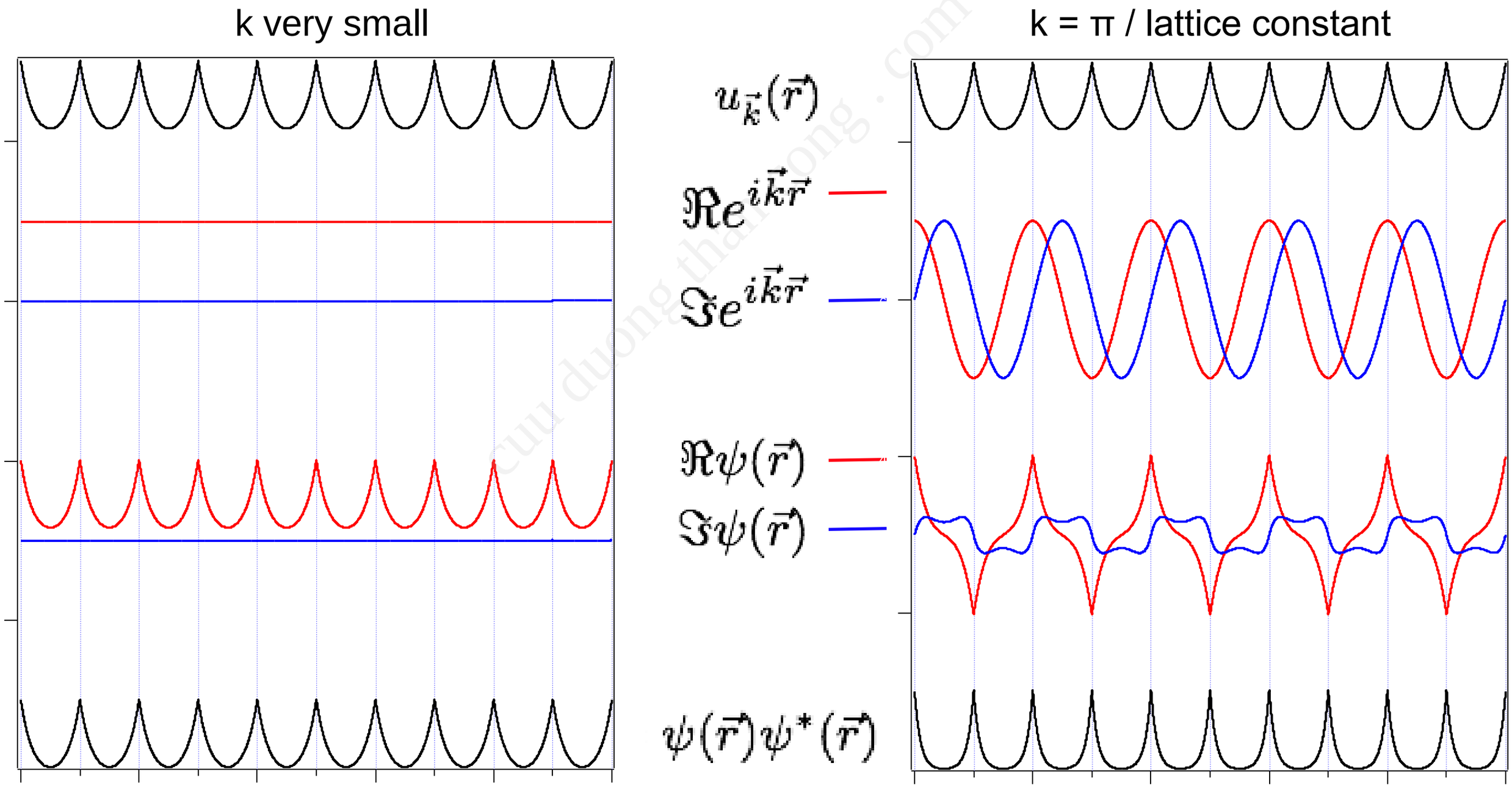
Felix Bloch, Nobel 1952

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

examples of Bloch waves

$$\psi(\vec{r}) = u_{\vec{k}}(\vec{r}) e^{i\vec{k}\vec{r}} \qquad u_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r} + \vec{R})$$

we assume that $u_{\vec{k}}(\vec{r})$ does not depend on $\vec{k}$



periodic boundary conditions

crystal with cubic unit cell, side length *a*, *N* units in each direction

$$\mathbf{k} = (k_x, k_y, k_z) = (\frac{n_x 2\pi}{Na}, \frac{n_y 2\pi}{Na} \frac{n_z 2\pi}{Na})$$

$$= \frac{n_x 2\pi}{Na}\hat{\mathbf{x}} + \frac{n_y 2\pi}{Na}\hat{\mathbf{y}} + \frac{n_z 2\pi}{Na}\hat{\mathbf{z}}$$

$$= \frac{n_x}{N}\mathbf{b}_1 + \frac{n_y}{N}\mathbf{b}_2 + \frac{n_z}{N}\mathbf{b}_3$$

general crystal structure, *N* units in each direction

$$\mathbf{k} = \frac{n_x}{N}\mathbf{b}_1 + \frac{n_y}{N}\mathbf{b}_2 + \frac{n_z}{N}\mathbf{b}_3$$

$$\{\mathbf{G}\} \subset \{\mathbf{k}\}$$

Proof of Bloch's theorem

$$-\frac{\hbar^2\nabla^2}{2m_e}\psi(\mathbf{r}) + U(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

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

$$U_{-\mathbf{G}} = U_{\mathbf{G}}^*$$

$$\psi(\mathbf{r}) = \sum_{\mathbf{k}} c_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}}$$

kinetic energy term

$$-\frac{\hbar^2\nabla^2}{2m_e}\psi(\mathbf{r}) = \sum_{\mathbf{k}} \frac{\hbar^2 k^2}{2m_e} c_{\mathbf{k}} e^{i\mathbf{k}\mathbf{r}}$$

potential energy term

$$U(\mathbf{r})\psi(\mathbf{r}) = \left(\sum_{\mathbf{G}} U_{\mathbf{G}} e^{i\mathbf{G}\mathbf{r}}\right)\left(\sum_{\mathbf{k}} c_{\mathbf{k}} e^{i\mathbf{k}\mathbf{r}}\right) = \sum_{\mathbf{k}\mathbf{G}} U_{\mathbf{G}} c_{\mathbf{k}} e^{i(\mathbf{G}+\mathbf{k})\mathbf{r}} = \sum_{\mathbf{k}'\mathbf{G}} U_{\mathbf{G}} c_{\mathbf{k}'-\mathbf{G}} e^{i\mathbf{k}'\mathbf{r}}$$

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

Schrödinger equation in new form

$$\sum_{\mathbf{k}} e^{i\mathbf{k}\mathbf{r}} \left\{ \left(\frac{\hbar^2 k^2}{2m_e} - E \right) c_{\mathbf{k}} + \sum_{\mathbf{G}} U_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}} \right\} = 0$$

every term has to vanish

$$\left(\frac{\hbar^2 k^2}{2m_e} - E \right) c_{\mathbf{k}} + \sum_{\mathbf{G}} U_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}} = 0$$

a set of equations for every **k** in the first Brillouin zone

For example, if $U_{\mathbf{G}'} \neq 0$ in the first equation, we will also have

$$\left(\frac{\hbar^2 (|\mathbf{k}-\mathbf{G}'|^2}{2m_e} - E \right) c_{\mathbf{k}-\mathbf{G}'} + \sum_{\mathbf{G}} U_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}'-\mathbf{G}} = 0$$

a set of equations for every **k** in the first Brillouin zone

$$\left(\frac{\hbar^2 k^2}{2m_e} - E\right) c_{\mathbf{k}} + \sum_{\mathbf{G}} U_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}} = 0$$

$$\left(\frac{\hbar^2 (|\mathbf{k} - \mathbf{G}'|^2}{2m_e} - E\right) c_{\mathbf{k}-\mathbf{G}'} + \sum_{\mathbf{G}} U_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}'-\mathbf{G}} = 0$$

and so on....

$$\psi(\mathbf{r}) = \sum_{\mathbf{k}} c_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} \longrightarrow \psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}} e^{i(\mathbf{k}-\mathbf{G})\mathbf{r}}$$

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} \left(\sum_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}} e^{-i\mathbf{G}\mathbf{r}}\right)$$

use periodicity of the lattice

$$\psi(\mathbf{r}) = \sum_{\mathbf{k}} c_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} \qquad U(\mathbf{r}) = \sum_{\mathbf{G}} U_{\mathbf{G}} e^{i\mathbf{G}\mathbf{r}}$$

$$U_{-\mathbf{G}} = U_{\mathbf{G}}^{*}$$

Schrödinger equation in new form

$$\sum_{\mathbf{k}} e^{i\mathbf{k}\mathbf{r}} \left\{ \left(\frac{\hbar^2 k^2}{2m_e} - E \right) c_{\mathbf{k}} + \sum_{\mathbf{G}} U_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}} \right\} = 0$$

every term has to vanish

$$\left(\frac{\hbar^2 k^2}{2m_e} - E \right) c_{\mathbf{k}} + \sum_{\mathbf{G}} U_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}} = 0 \qquad \psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} \left(\sum_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}} e^{-i\mathbf{G}\mathbf{r}} \right)$$

Symmetry of Bloch functions

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}} e^{i(\mathbf{k}-\mathbf{G})\mathbf{r}}$$

shift by a reciprocal lattice vector gives the same

$$\psi_{\mathbf{k}+\mathbf{G}'}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}+\mathbf{G}'} e^{i(\mathbf{k}-\mathbf{G}+\mathbf{G}')\cdot\mathbf{r}} = \sum_{\mathbf{G}''} c_{\mathbf{k}-\mathbf{G}''} e^{i(\mathbf{k}-\mathbf{G}'')\cdot\mathbf{r}}$$

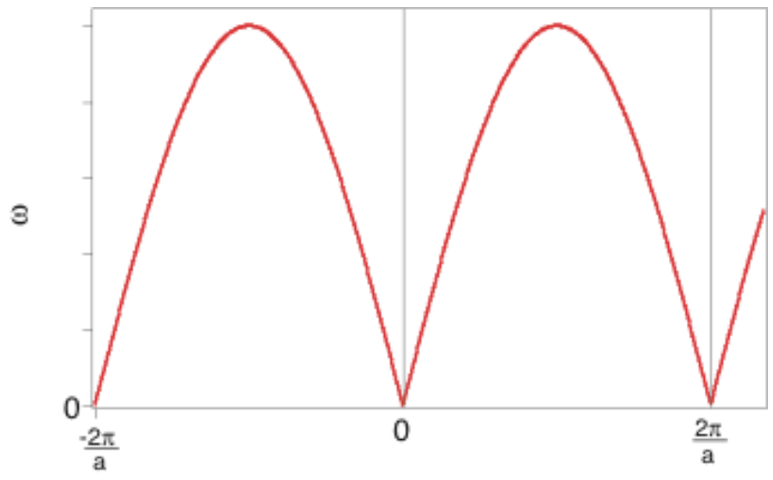
$$\mathbf{G}'' = \mathbf{G} - \mathbf{G}'$$

so

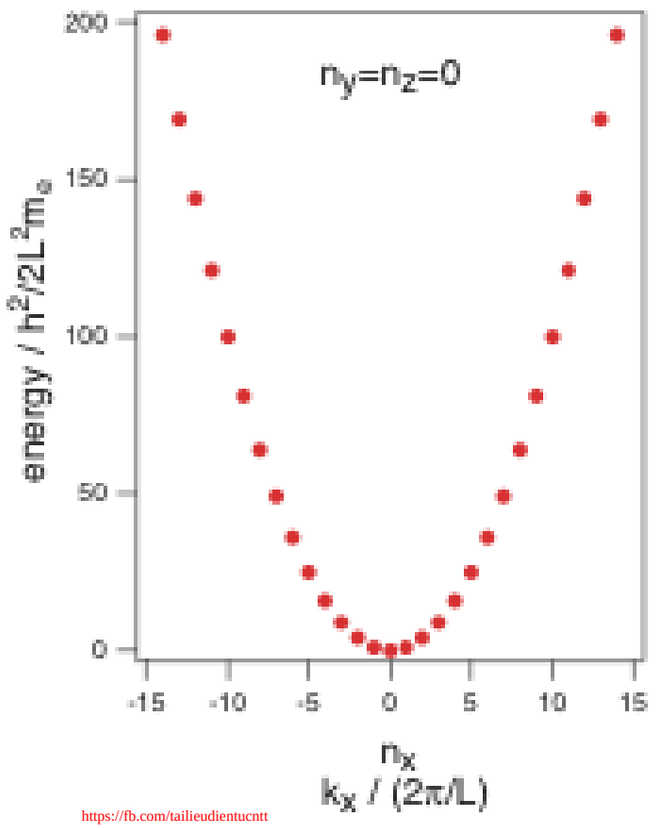
$$\psi_{\mathbf{k}+\mathbf{G}'} = \psi_{\mathbf{k}}(\mathbf{r})$$

$$E(\mathbf{k}+\mathbf{G}') = E(\mathbf{k})$$

phonons



free electron

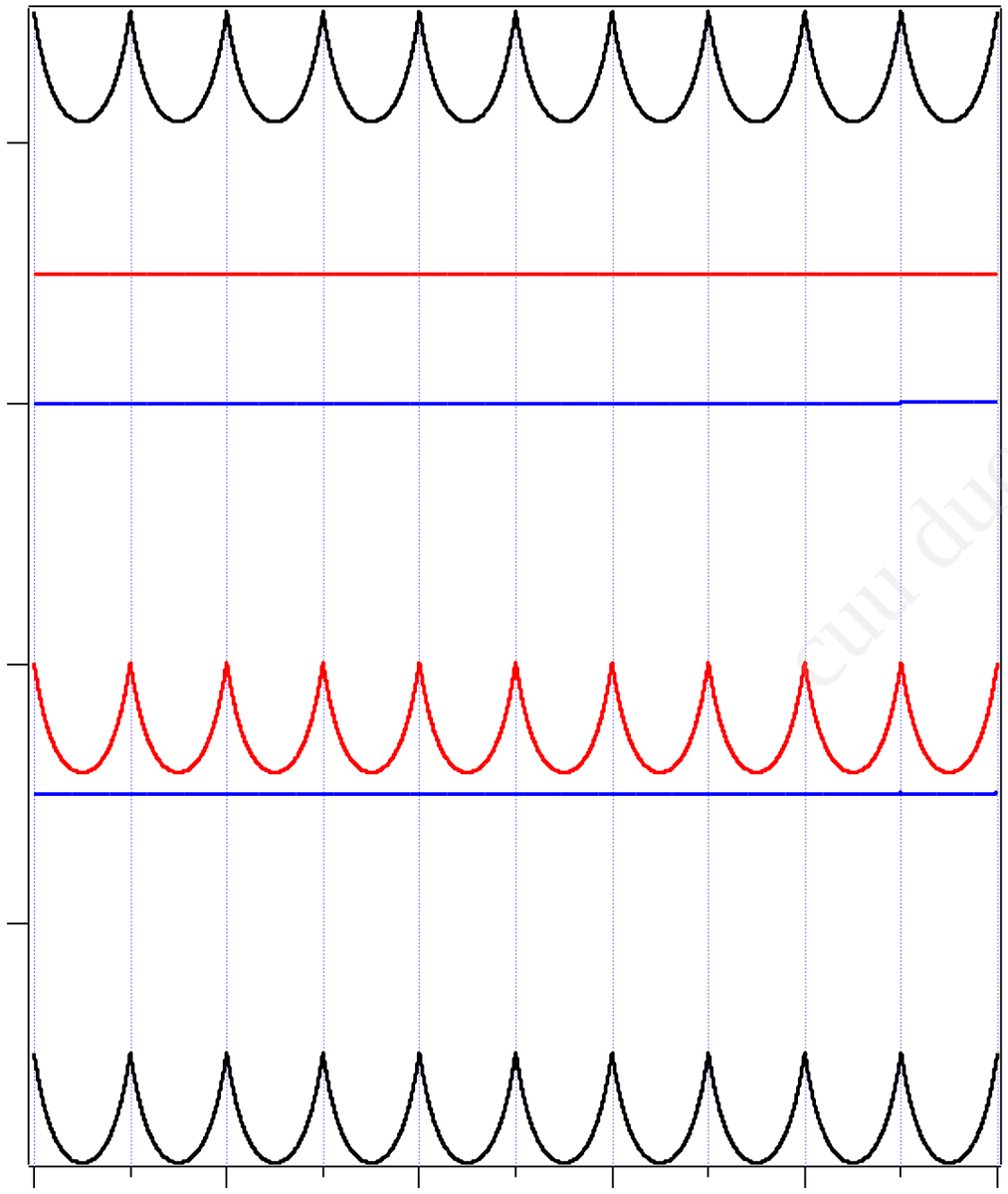


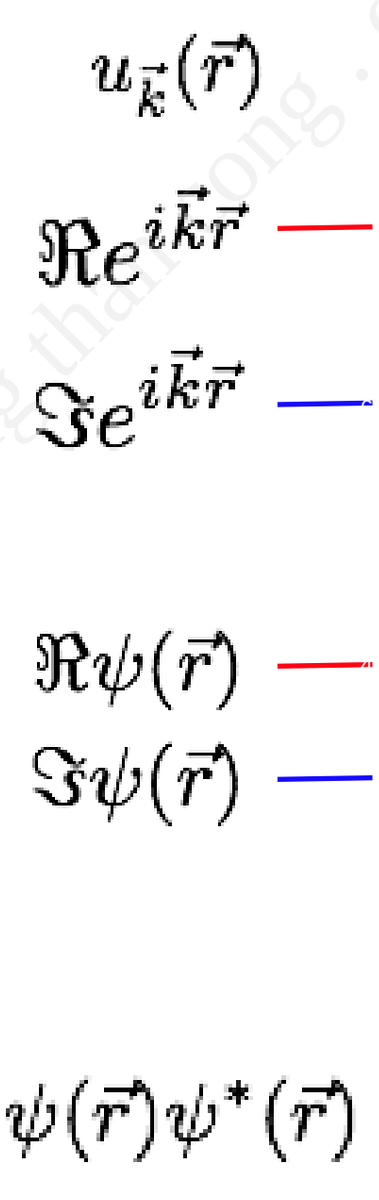
periodicity of Bloch waves

$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r})$ does NOT have lattice periodicity

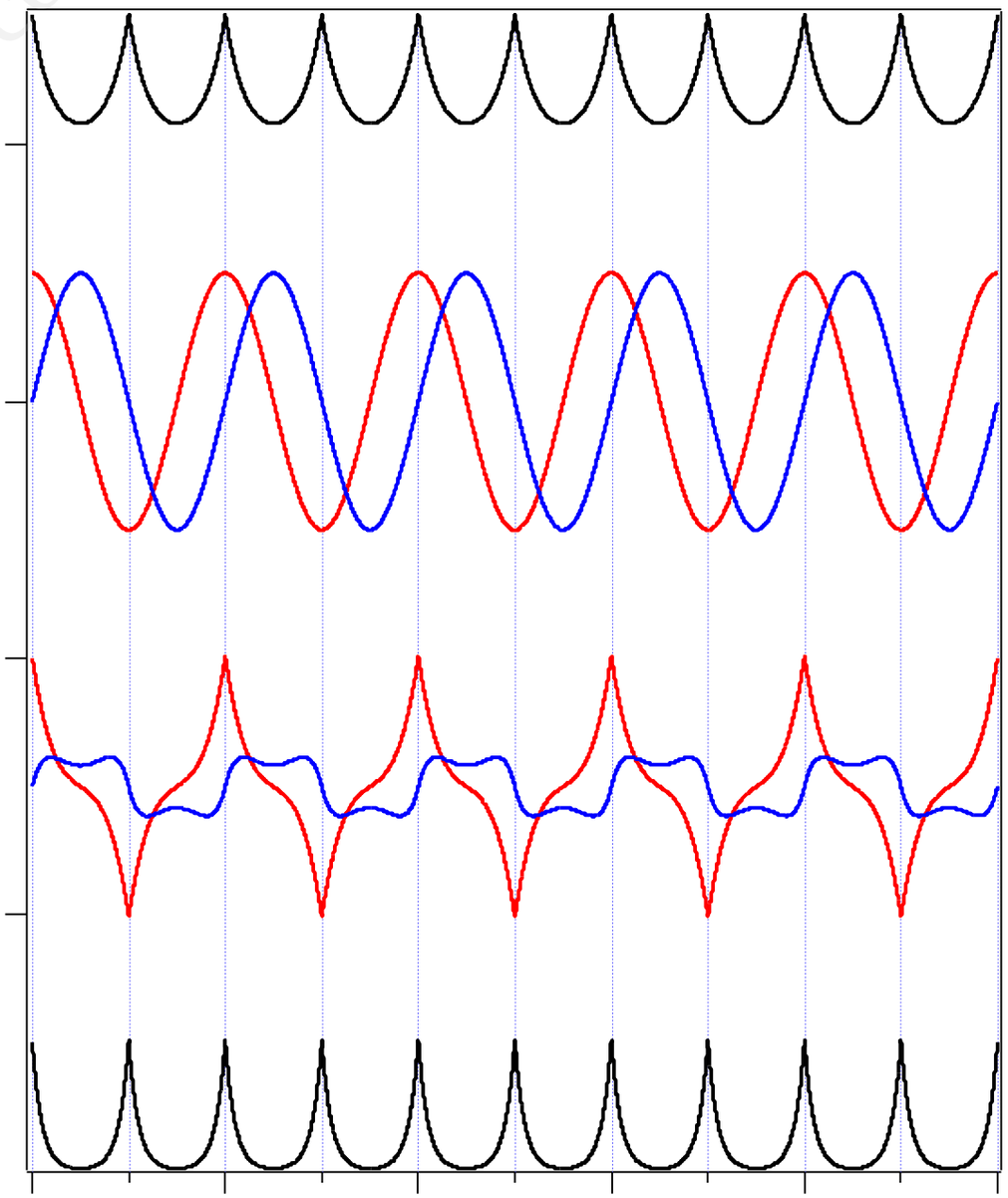
$\psi_{\mathbf{k}}(\mathbf{r})\psi^*_{\mathbf{k}}(\mathbf{r})$ does have lattice periodicity

k very small





k = π / lattice constant



Nearly free electrons in one dimension

real space lattice

reciprocal space lattice

$$g = 2\pi/a$$

$$U(x) = \sum_n U_n e^{ingx} = U_{-1} e^{-ix2\pi/a} + U_1 e^{ix2\pi/a} = U\left(e^{-ix2\pi/a} + e^{ix2\pi/a}\right)$$

so U has only U_1 and U_{-1} and we call both U

Schrödinger equation for one k is

$$\left(\frac{\hbar^2 k^2}{2m_e} - E\right) c_k + \sum_g U_g c_{k-g} = \left(\frac{\hbar^2 k^2}{2m_e} - E\right) c_k + U c_{k-g} + U c_{k+g} = 0$$

solutions

$$\psi_k(x) = \sum_g c_{k-g} e^{i(k-g)x}$$

General Strategy

$$H\psi(x) = E\psi(x)$$

$$\psi(x) = \sum_k c_k \phi_k(x)$$

multiply from the left with $\phi^*_{k'}$
and integrate over all *x*

$$\int \phi^*_{k'} H \psi(x) dx = E \int \phi^*_{k'} \psi(x) dx = E c_{k'}$$

gives

$$\sum_k V_k c_k = E c_{k'}$$

Generate one of these equations for every k.

Explicit calculation

$$-\frac{\hbar^2}{2m_e}\frac{\partial^2}{\partial x^2}\psi_k(x)+U(x)\psi_k(x)=E\psi_k(x)$$

$$U(x)=Ue^{-igx}+Ue^{igx}$$

assume that

$$\psi_k(x)=e^{i(k-g)x}c_{k-g}+e^{ikx}c_k+e^{i(k+g)r}c_{k+g}$$

calculate

$$\int_L e^{-ikx}H\psi_k(x)dx=\int_L e^{-ikx}\left(-\frac{\hbar^2}{2m_e}\frac{\partial^2}{\partial x^2}\psi_k(x)+U(x)\psi_k(x)\right)dx=\int_L e^{-ikx}E\psi_k(x)dx$$

$$=c_kE$$

gives

$$\left(\frac{\hbar^2k^2}{2m_e}-E\right)c_k+Uc_{k-g}+Uc_{k+g}=0$$

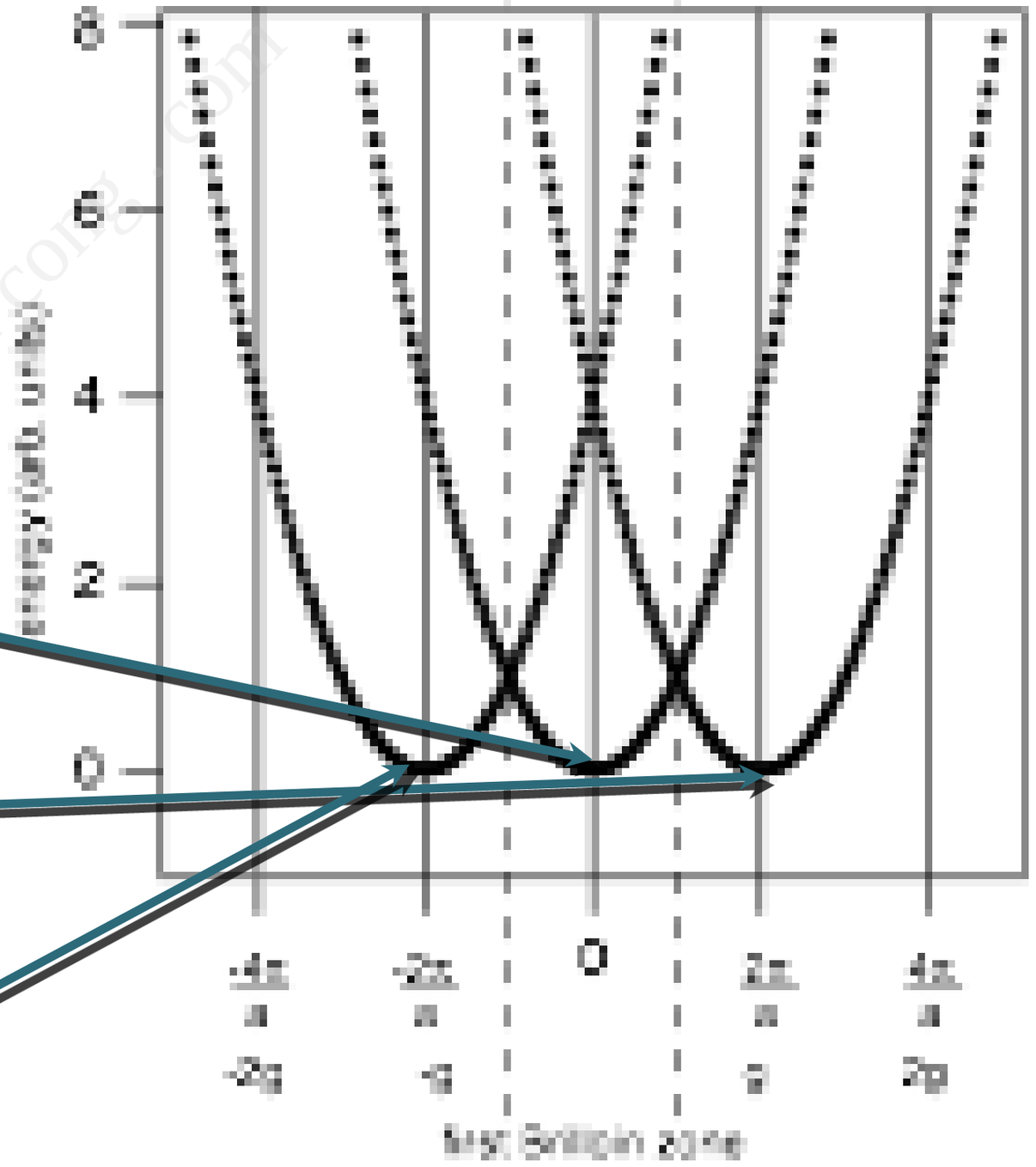
3 equations

very small U

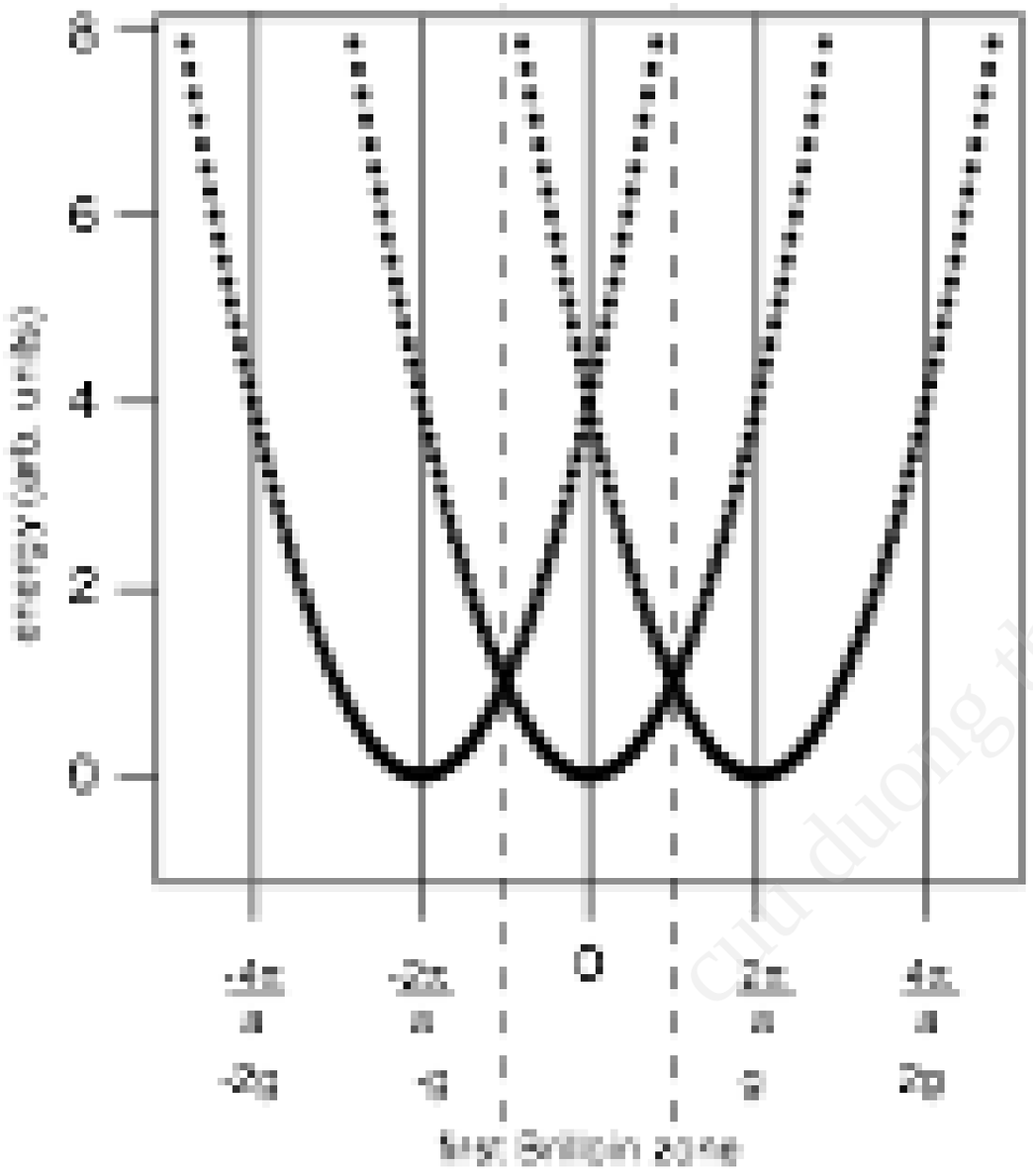
$$\left(\frac{\hbar^2 k^2}{2m_e} - E\right) c_k + U c_{k-g} + U c_{k+g} = 0$$

$$\left(\frac{\hbar^2 (k-g)^2}{2m_e} - E\right) c_{k-g} + U c_k = 0$$

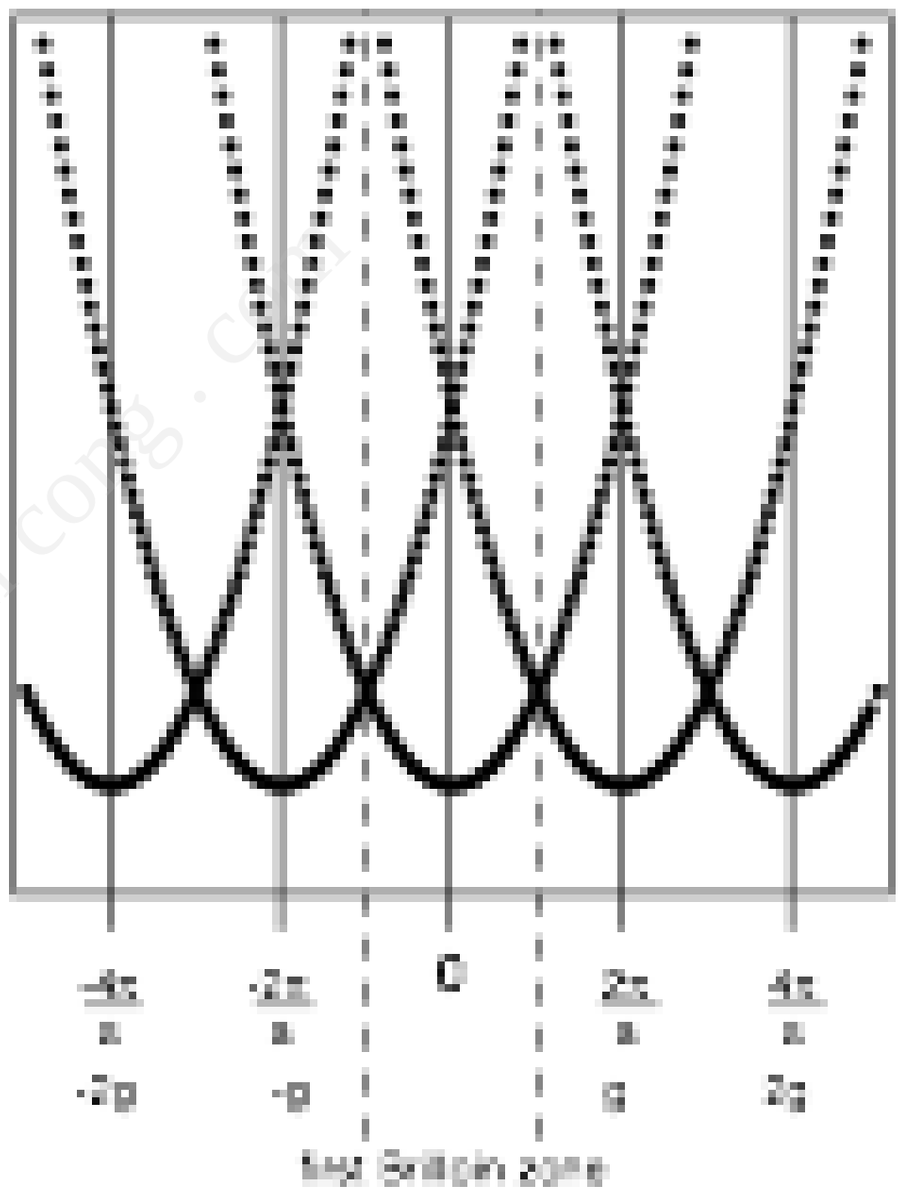
$$\left(\frac{\hbar^2 (k+g)^2}{2m_e} - E\right) c_{k+g} + U c_k = 0$$



3 equations, very small U



5 equations, very small U



bottom line: free electrons plus symmetry $E(\mathbf{k}+\mathbf{G}') = E(\mathbf{k})$

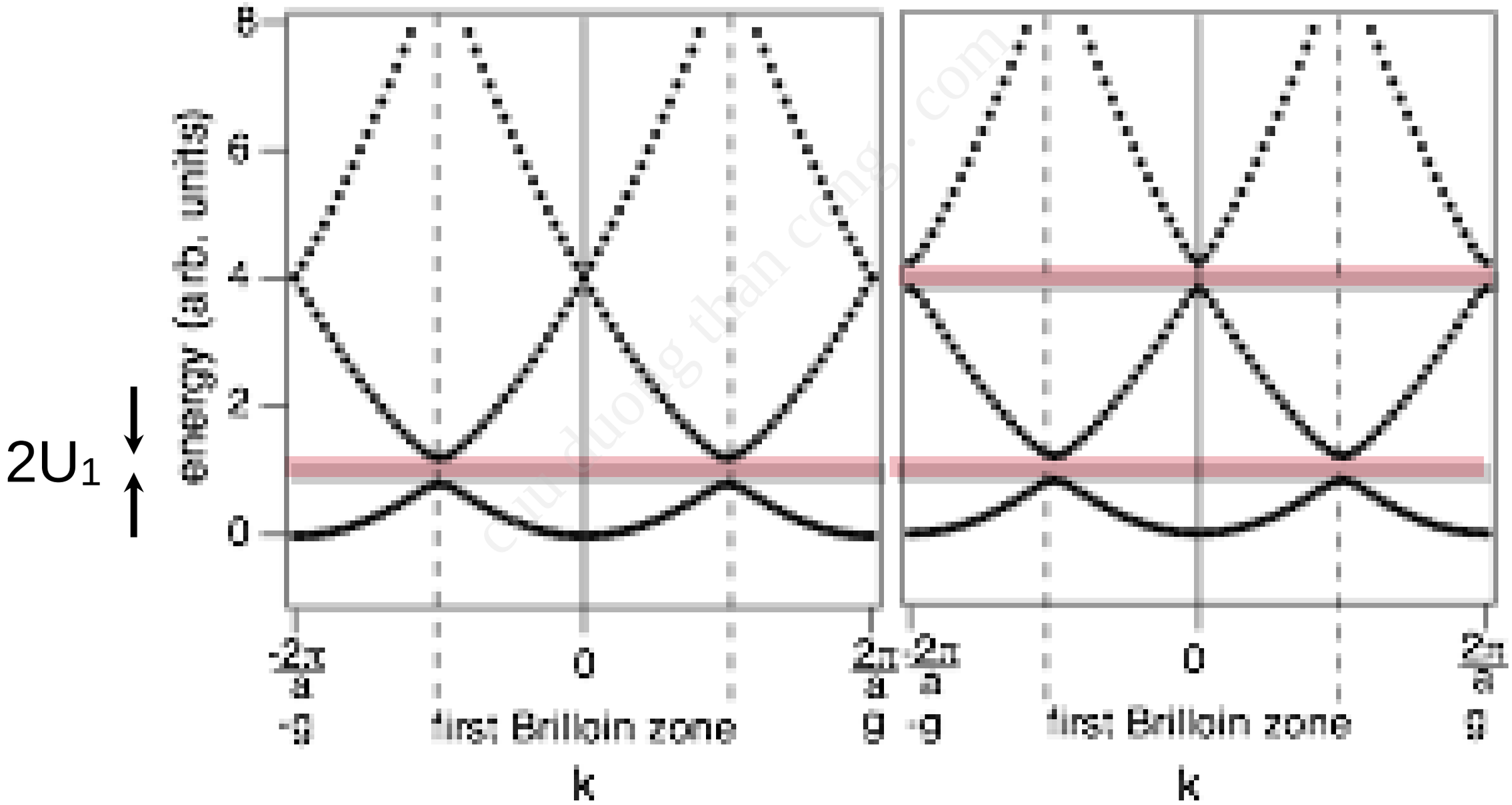
Potential of finite size

$$U(x) = \sum_n U_n e^{ingx}$$

$U_1 = U_{-1}^* > 0$

$U_1 = U_{-1}^* > 0$

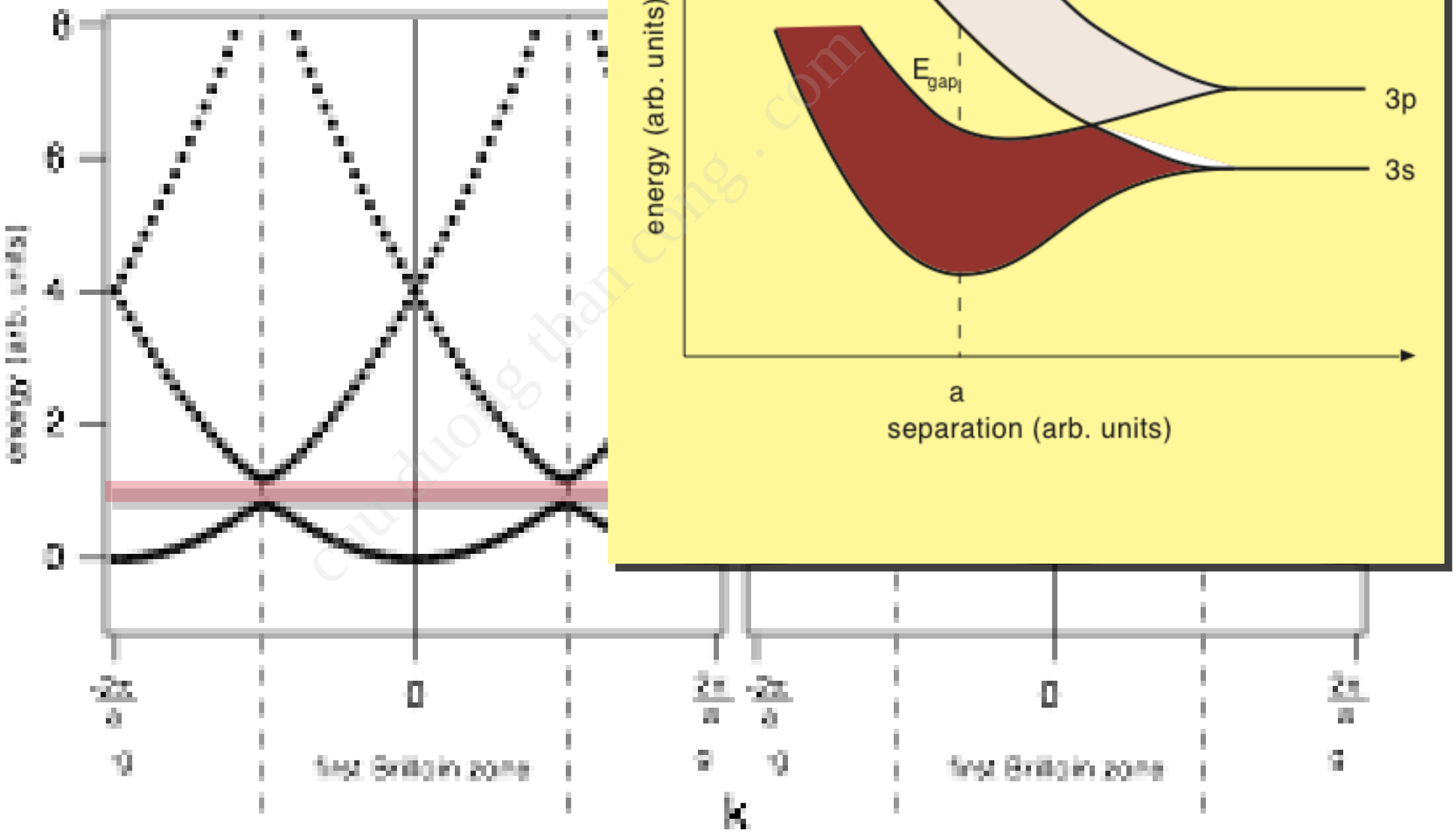
$U_2 = U_{-2}^* > 0$



opening of absolute band gaps!

Potential of finite size

$U_1 = U_{-1} > 0$



opening of absolute band gaps!

Potential of finite size

$$U(x) = \sum_n U_n e^{ingx}$$

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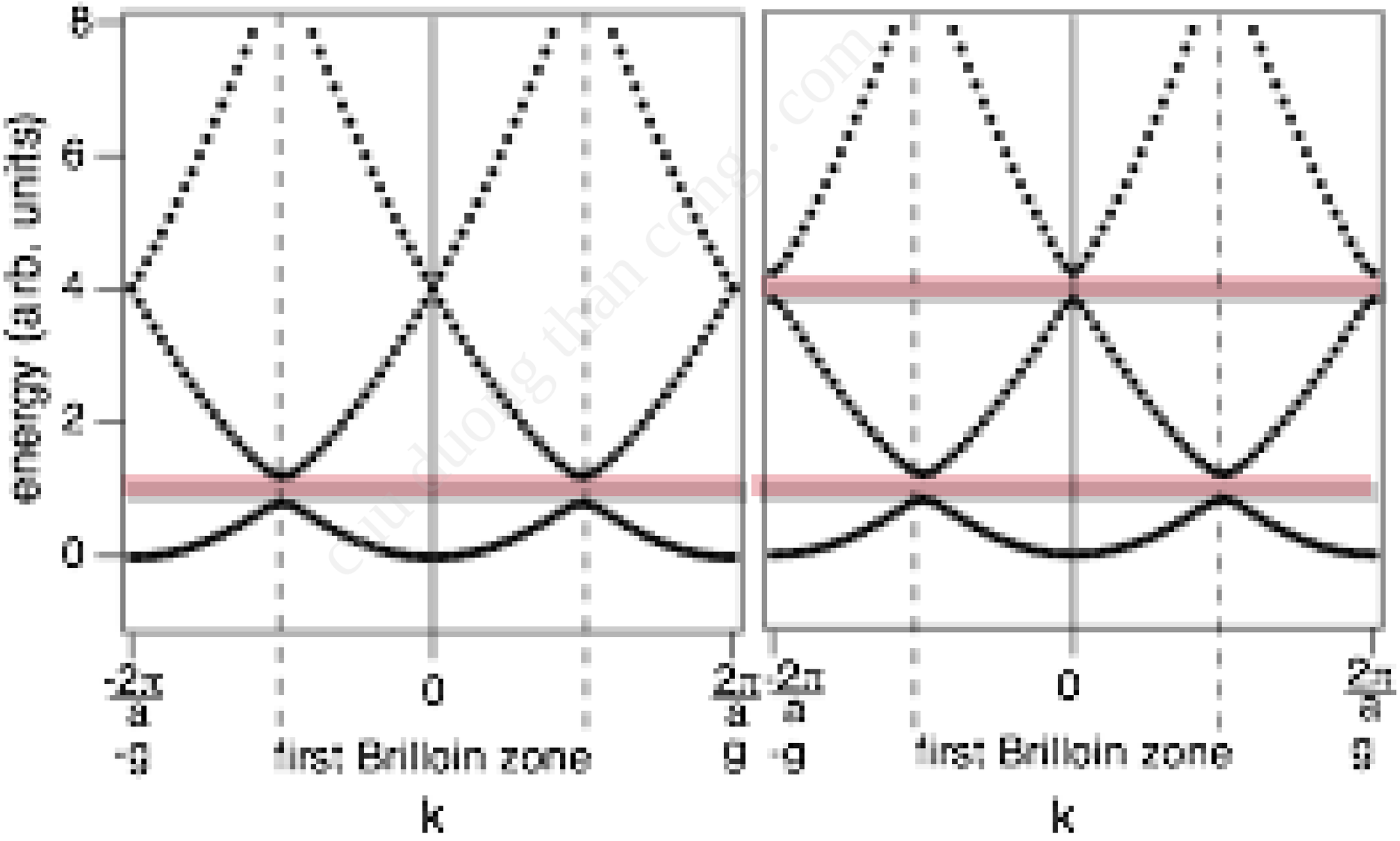
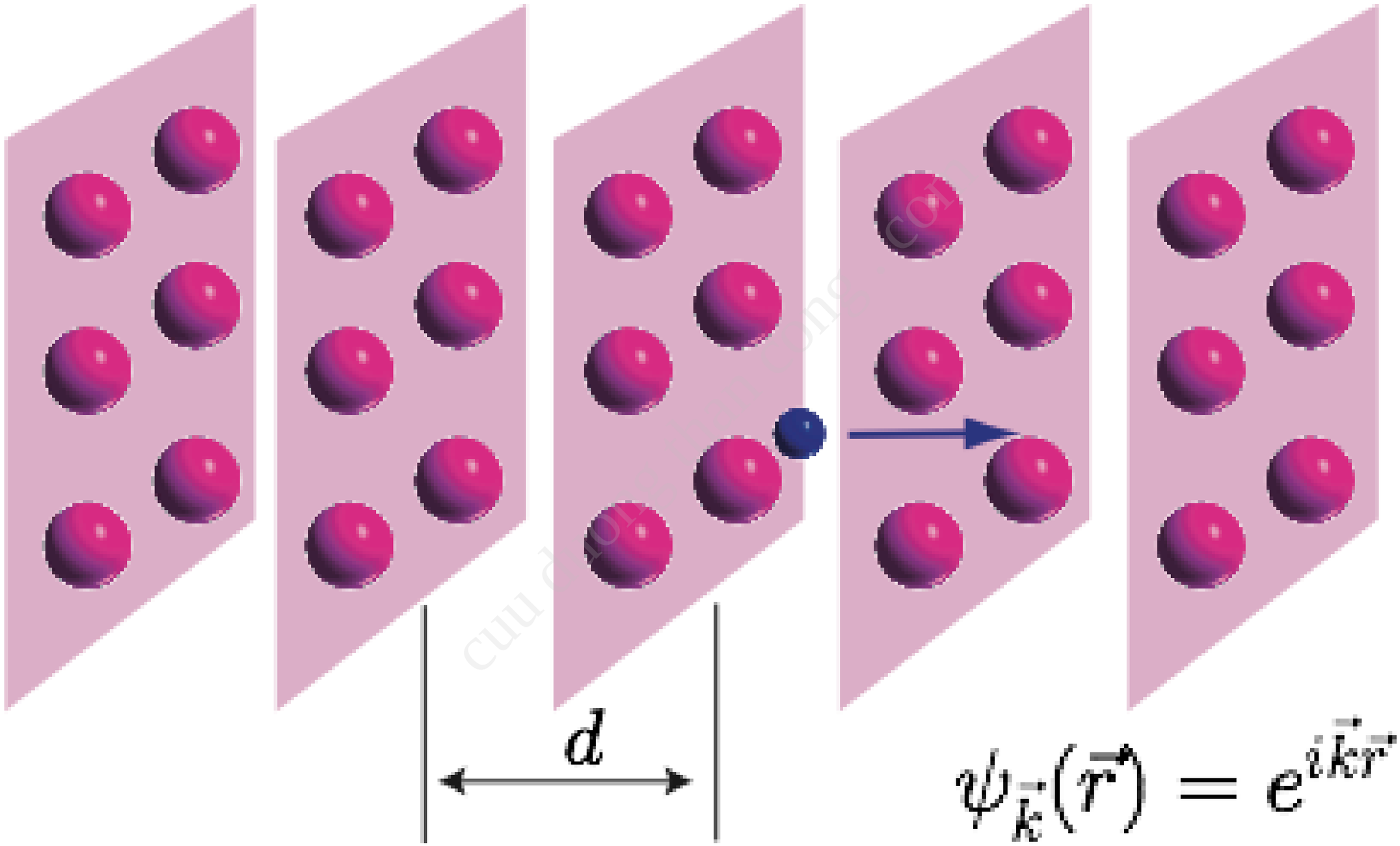


opening of absolute band gaps!

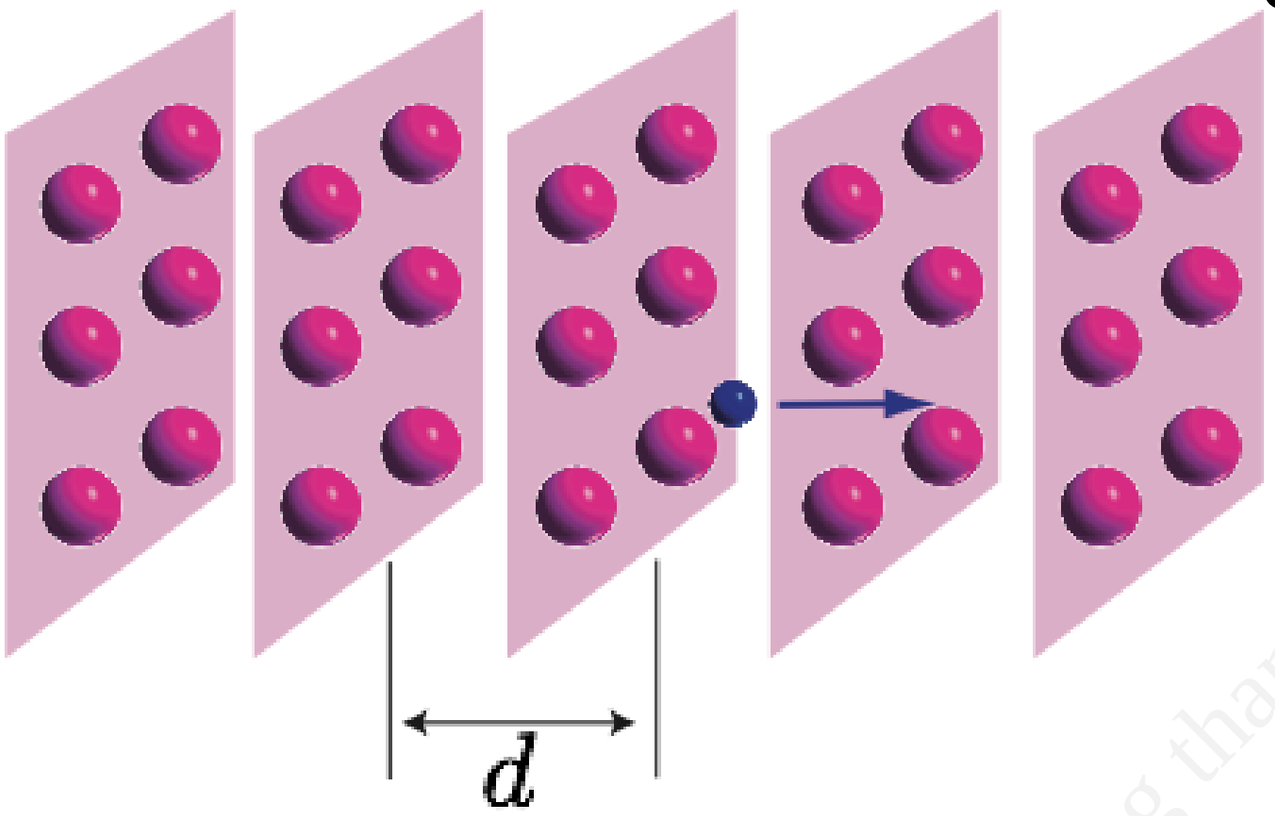
A qualitative argument: Bragg-reflection for nearly free electrons



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

electron traveling perpendicular to crystal planes

Bragg-reflection for nearly free electrons



consider only one direction (x)

free electron wave function

$$\psi(r) = e^{ikr}$$

with a de Broglie wavelength

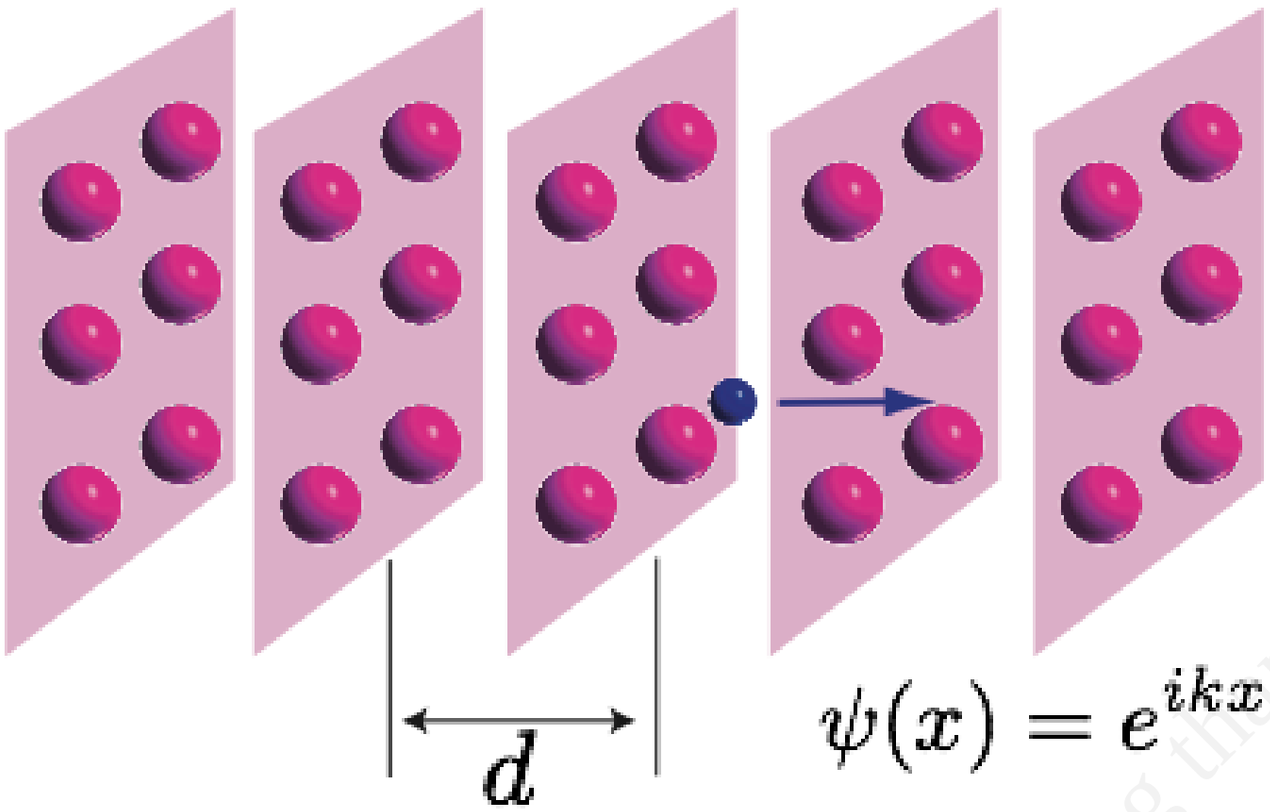
$$k = \frac{2\pi}{\lambda} \qquad \lambda = \frac{2\pi}{k}$$

Bragg condition $n\lambda = n\frac{2\pi}{k} = 2d\sin\Theta$ with $\theta = 90°, -90°$

this gives a Bragg condition for electron waves:

$$k = \pm\frac{n\pi}{d}$$

Bragg-reflection for nearly free electrons



Bragg condition for electron waves:

$$k = \pm \frac{n\pi}{d}$$

Bragg reflection results in standing, not traveling electron waves

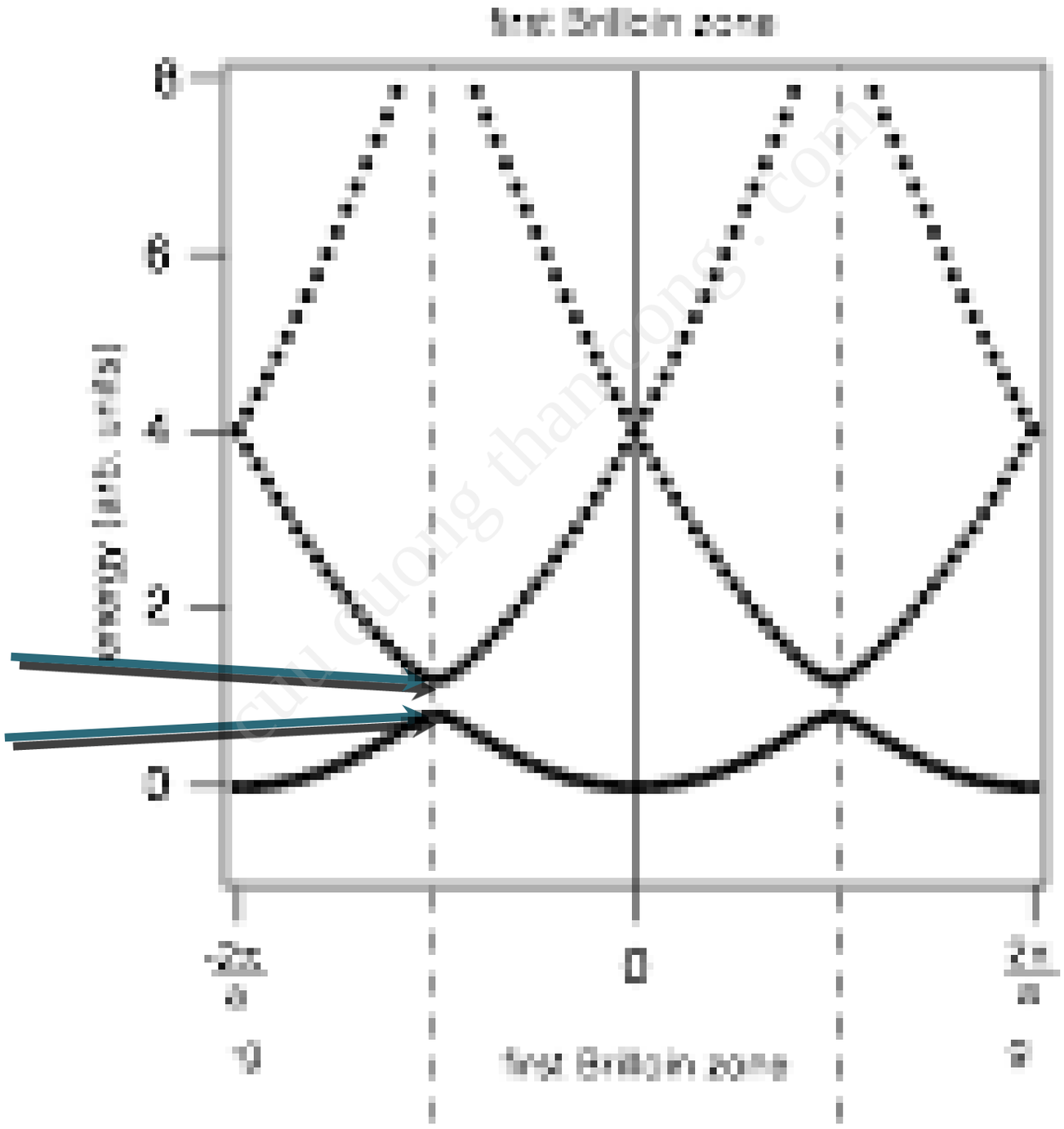
in general: $\psi(x) \propto e^{ikx} + Ae^{-ikx}$ with $|A| = 1$

$$\Psi(+) = \exp(i\frac{\pi}{d}x) + \exp(-i\frac{\pi}{d}x) = 2\cos(\frac{\pi}{d}x)$$

$$\Psi(-) = \exp(i\frac{\pi}{d}x) - \exp(-i\frac{\pi}{d}x) = 2i\sin(\frac{\pi}{d}x)$$

Group velocity of the Bloch electrons

$$v_g = \frac{d\omega(k)}{dk} = \frac{1}{\hbar}\frac{dE(k)}{dk}$$



$v_g = 0$

Gap opening for nearly free electrons

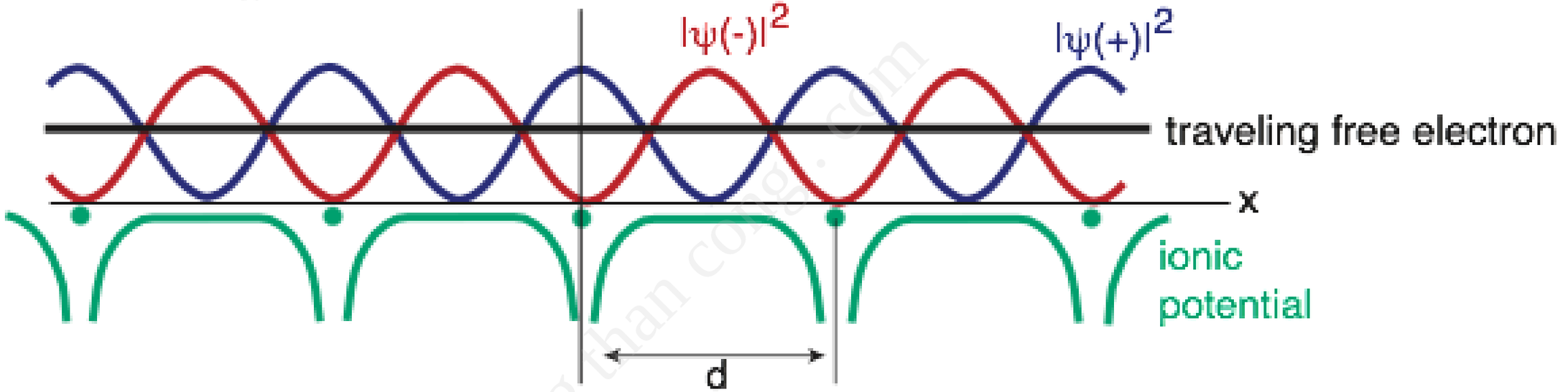
$$\Psi(-) = 2i\sin(\frac{\pi}{d}x)$$

$$\Psi(+) = 2\cos(\frac{\pi}{d}x)$$

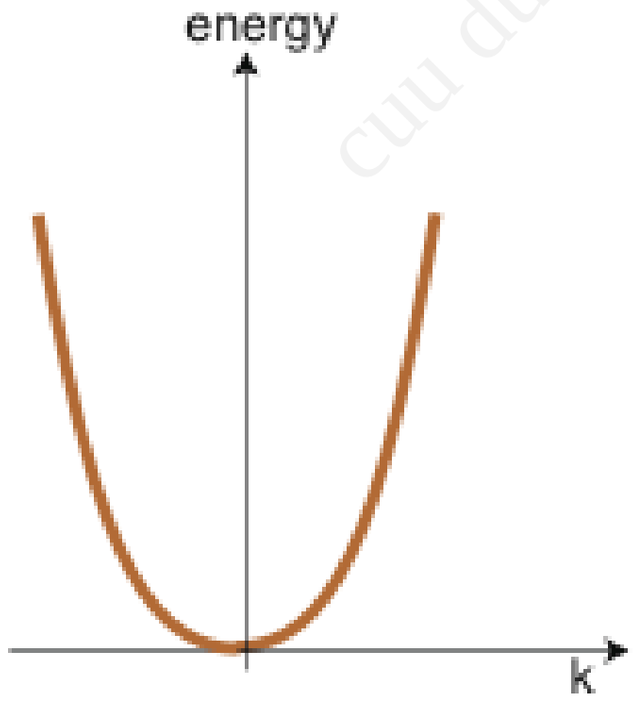
probability density

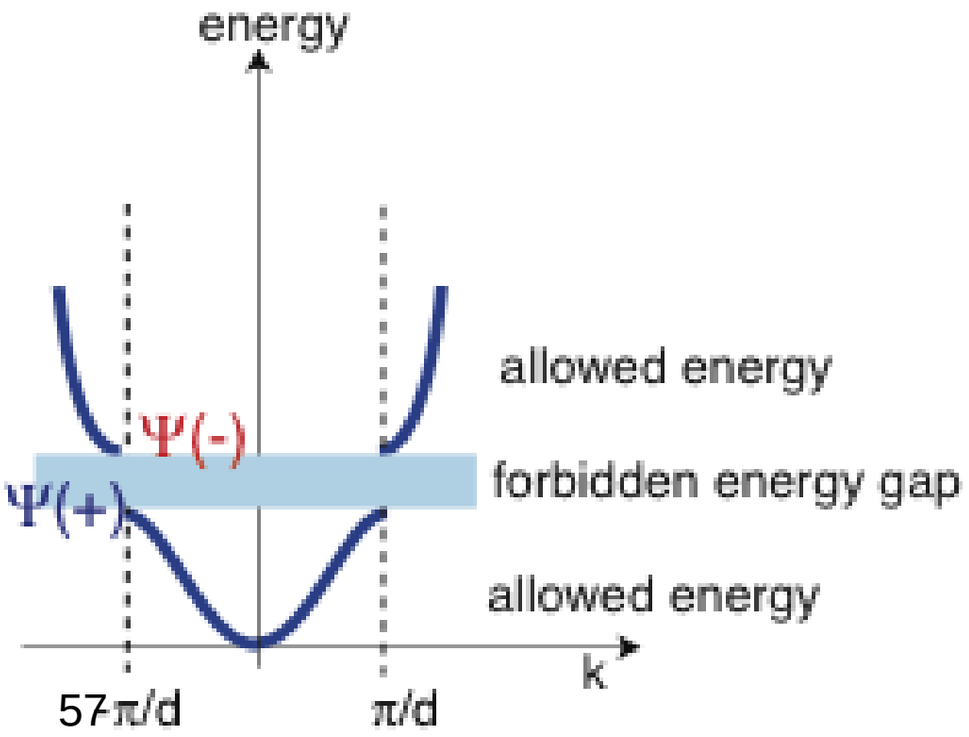
$$|\Psi(-)|^2 = 4\sin^2(\frac{\pi}{d}x)$$

$$|\Psi(+)|^2 = 4\cos^2(\frac{\pi}{d}x)$$



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



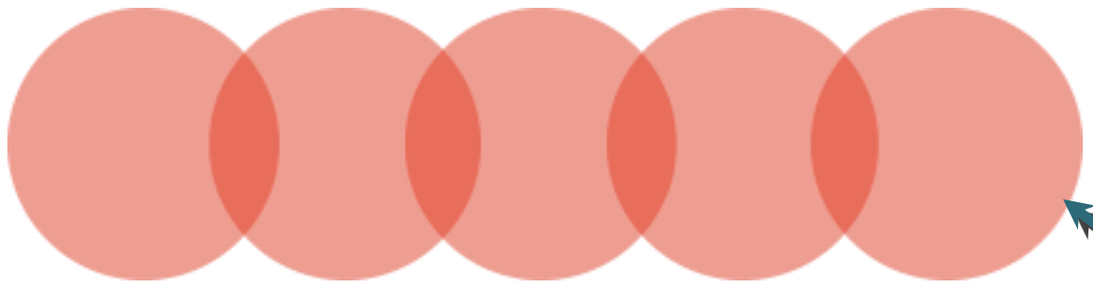


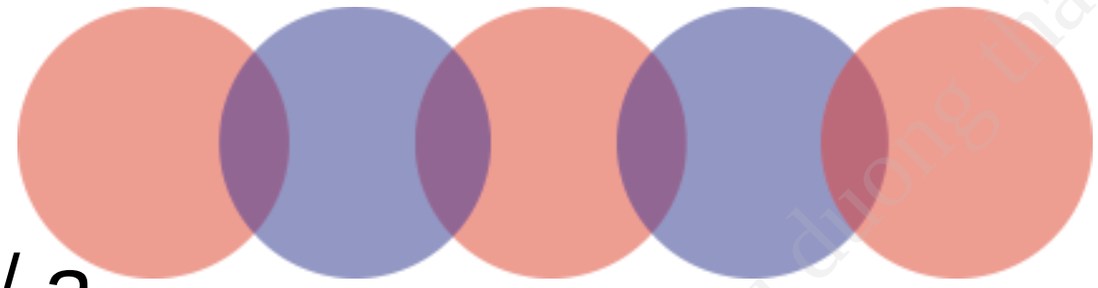
...yet another point of view

ion cores

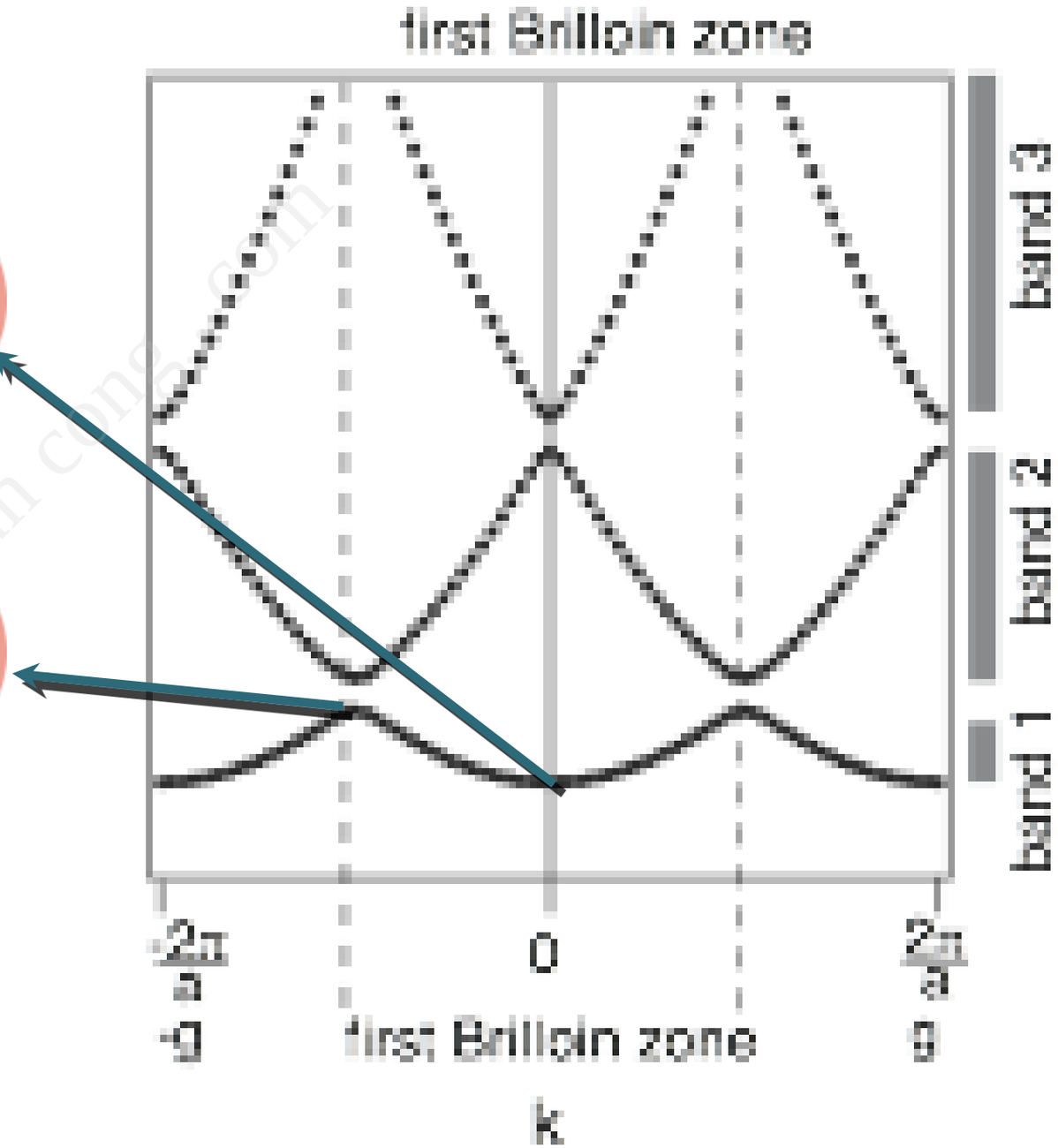
a

k=0





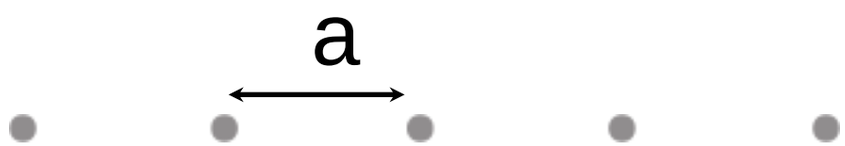
k=π / a



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

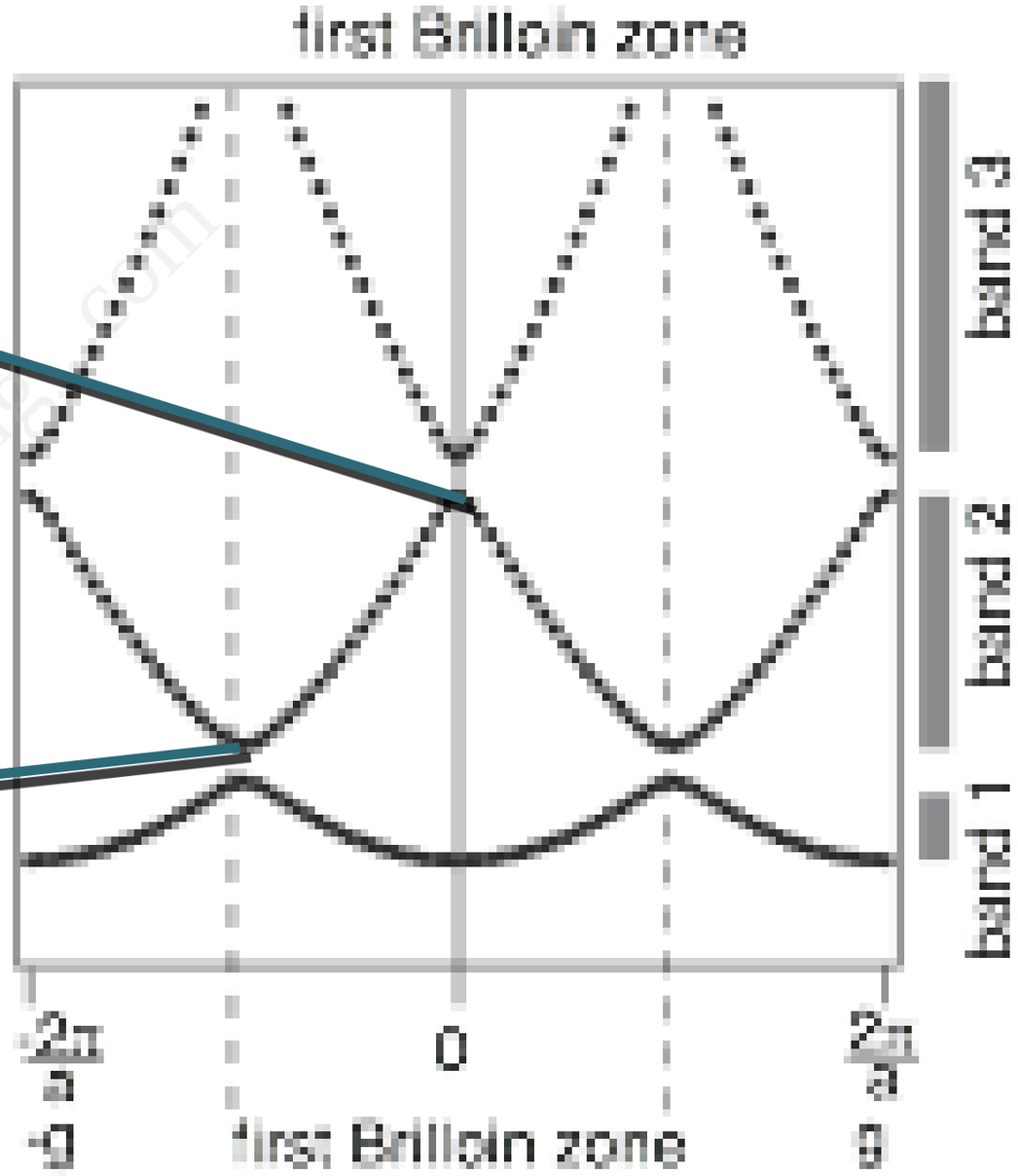
...yet another point of view

ion cores



k=0

k=π / a



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

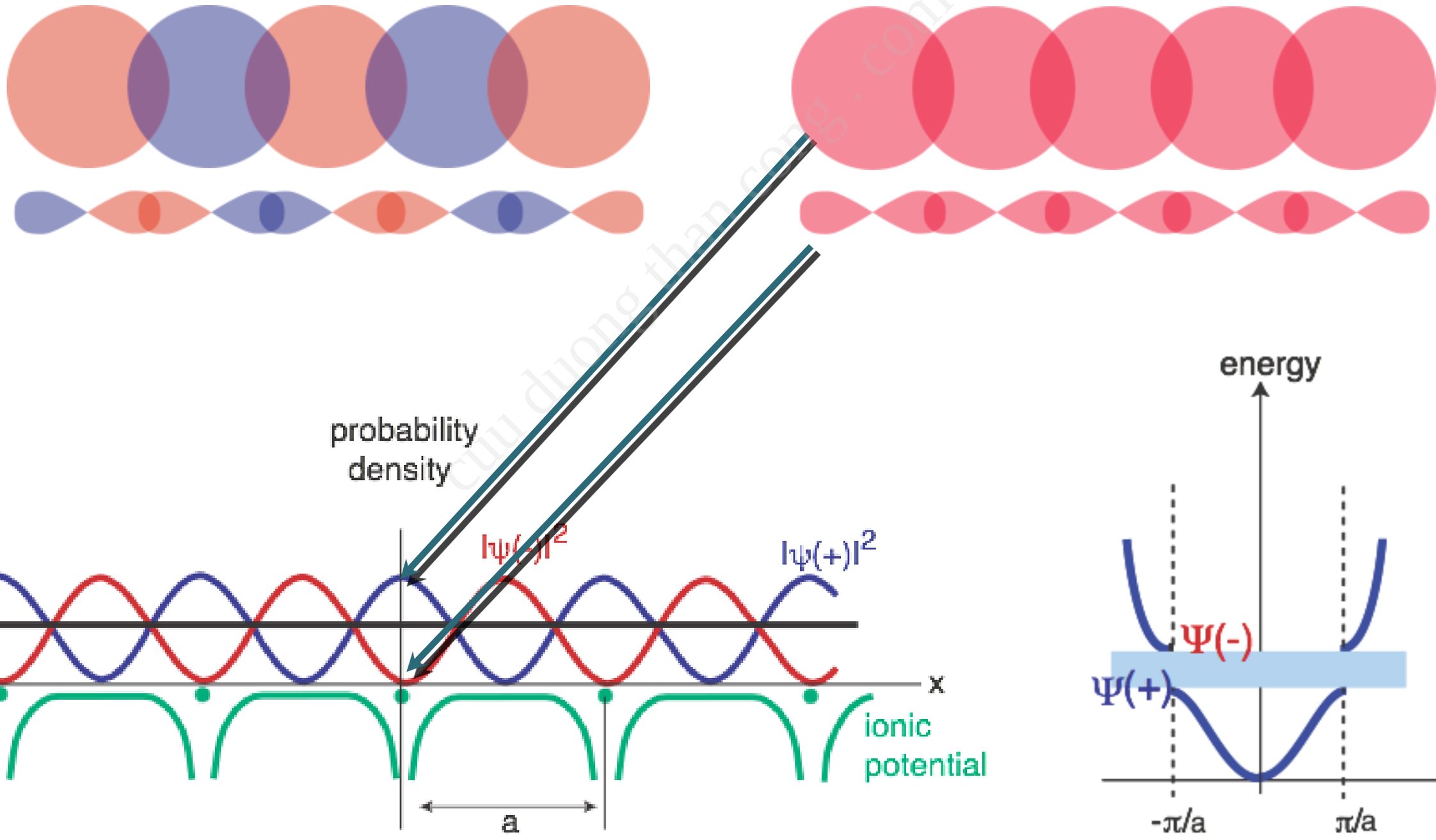
ion cores

a

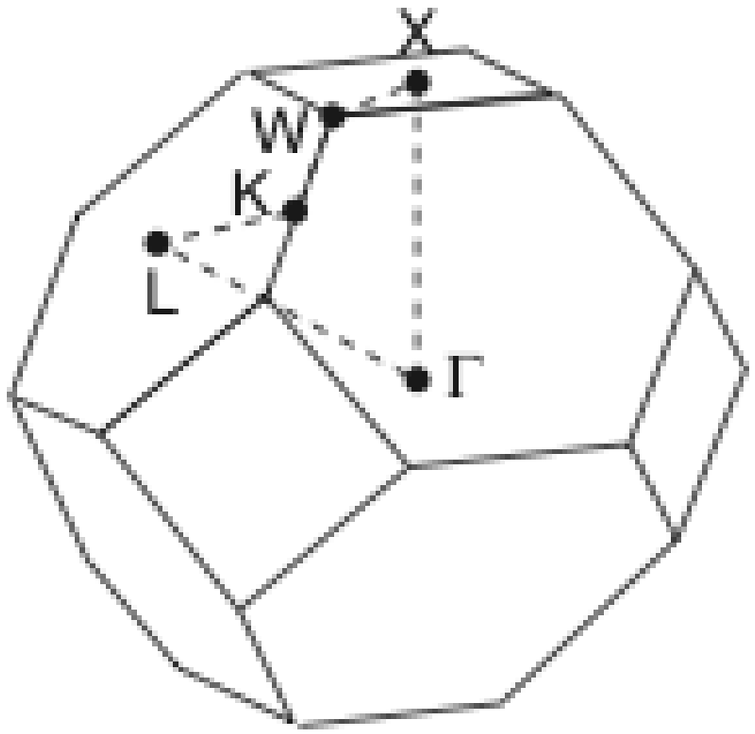
k=π / a

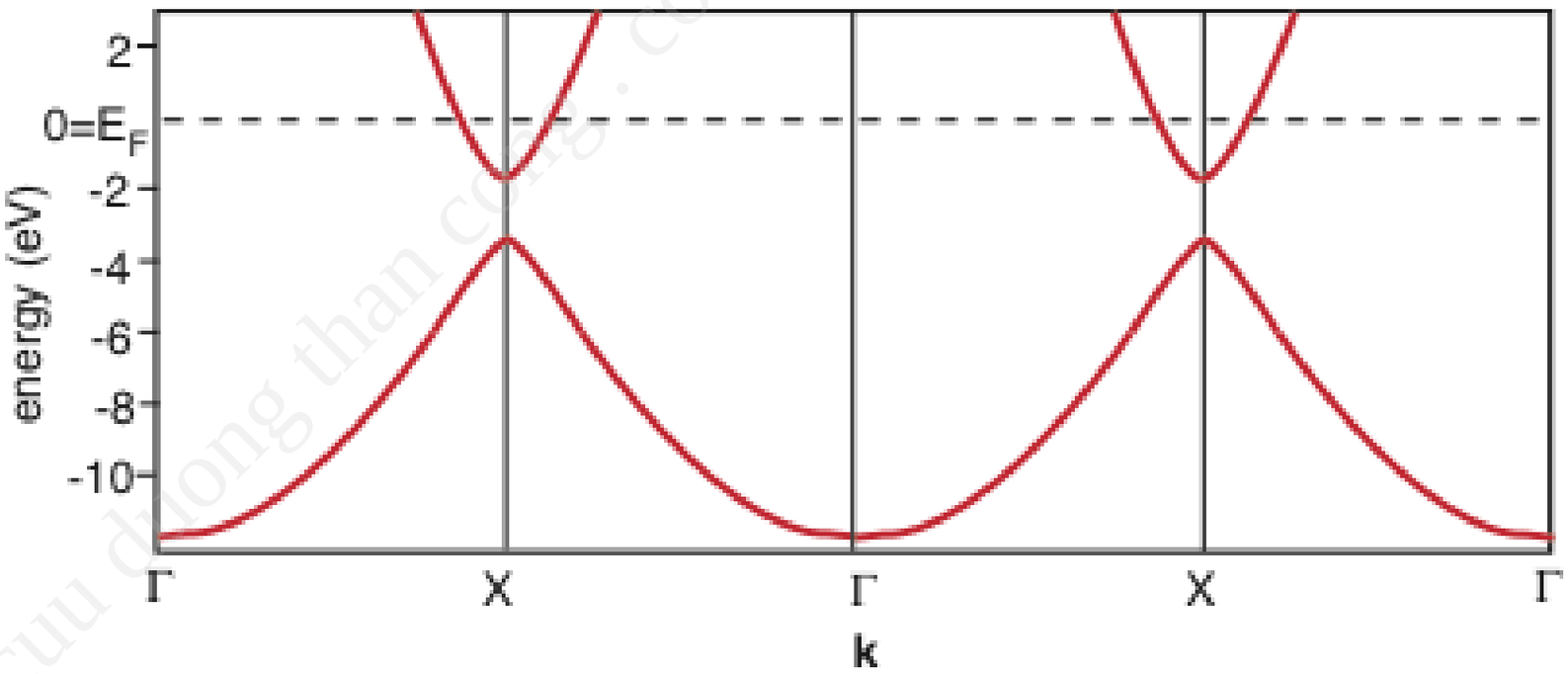
$\Psi(x)$

$|\Psi(x)|^2$

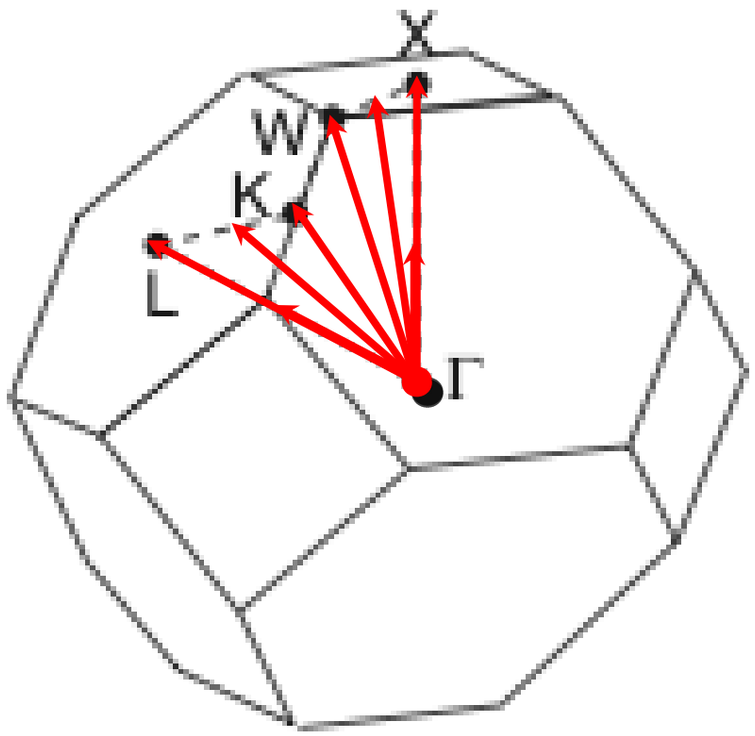


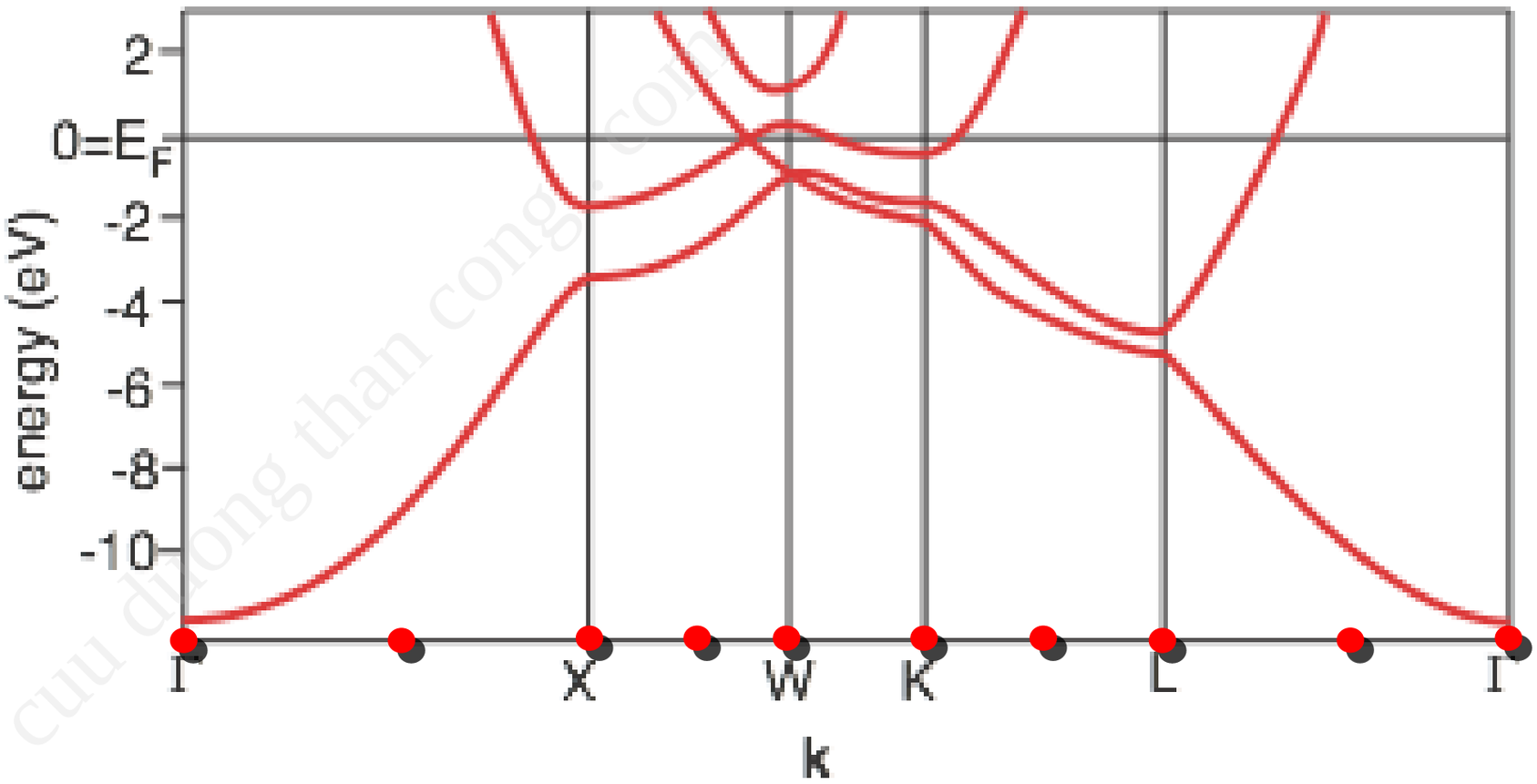
Band structures of real materials: Al



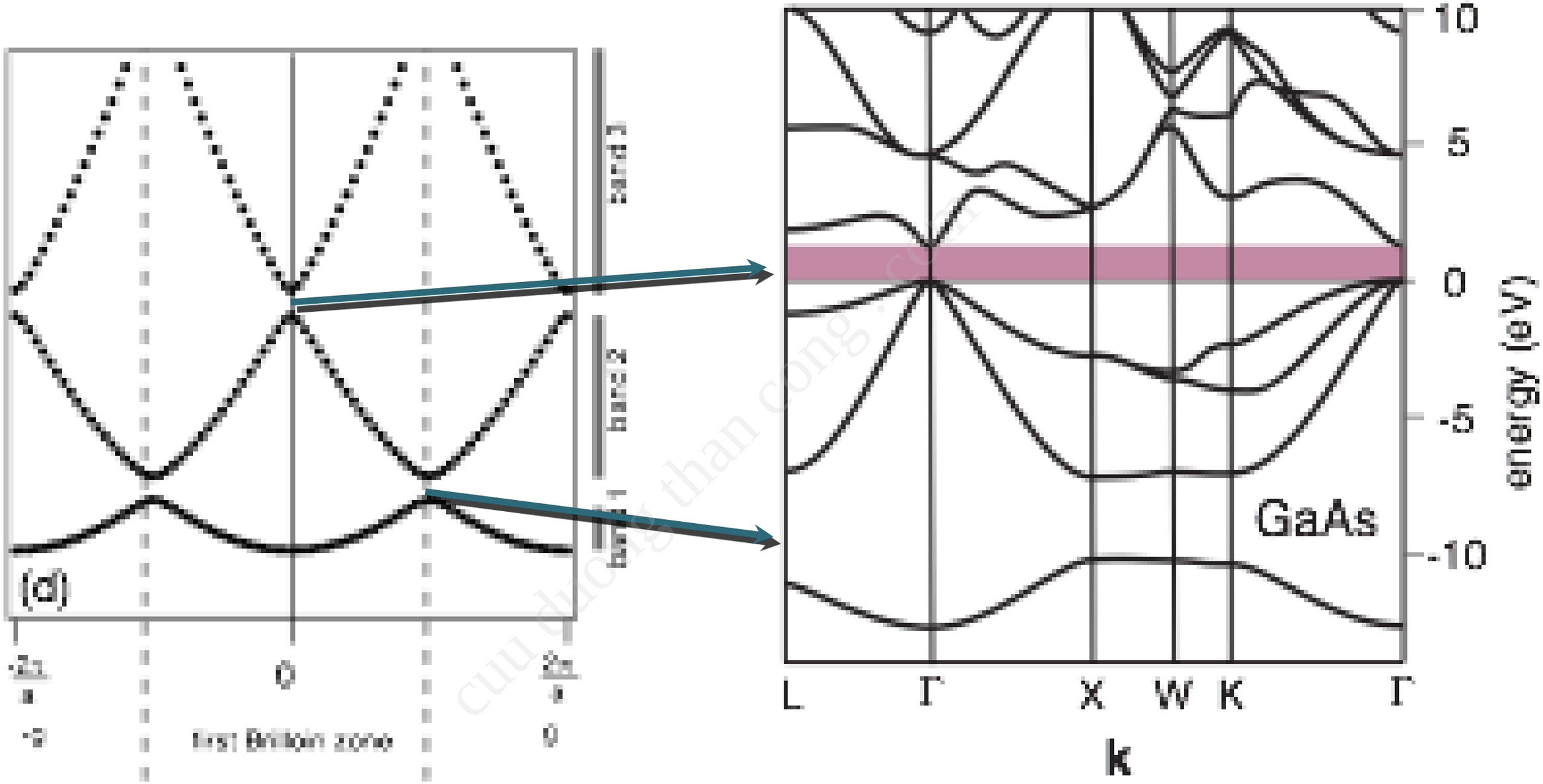


Band structures of real materials: Al

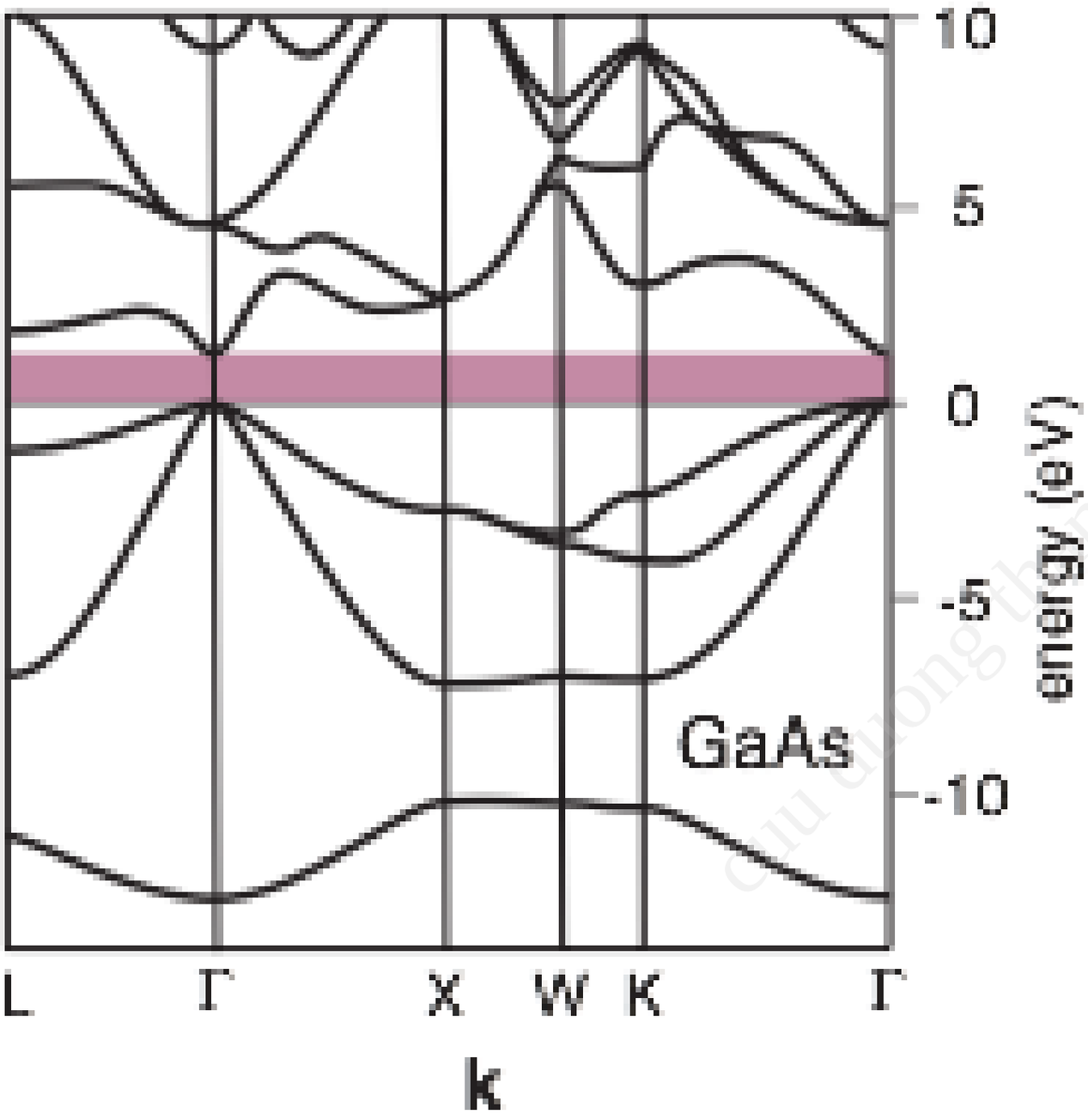


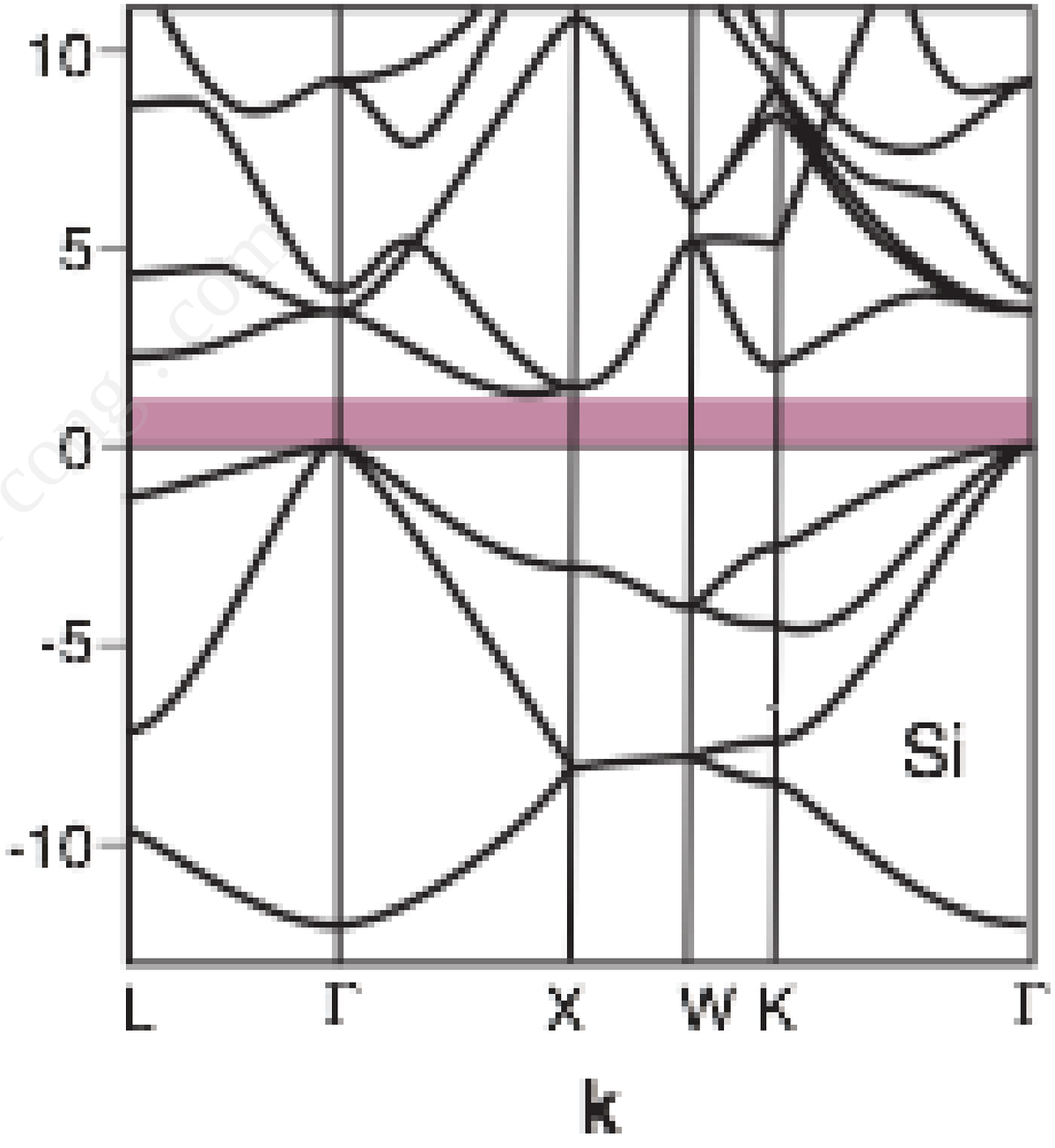


Band structures of real materials: Si and GaAs

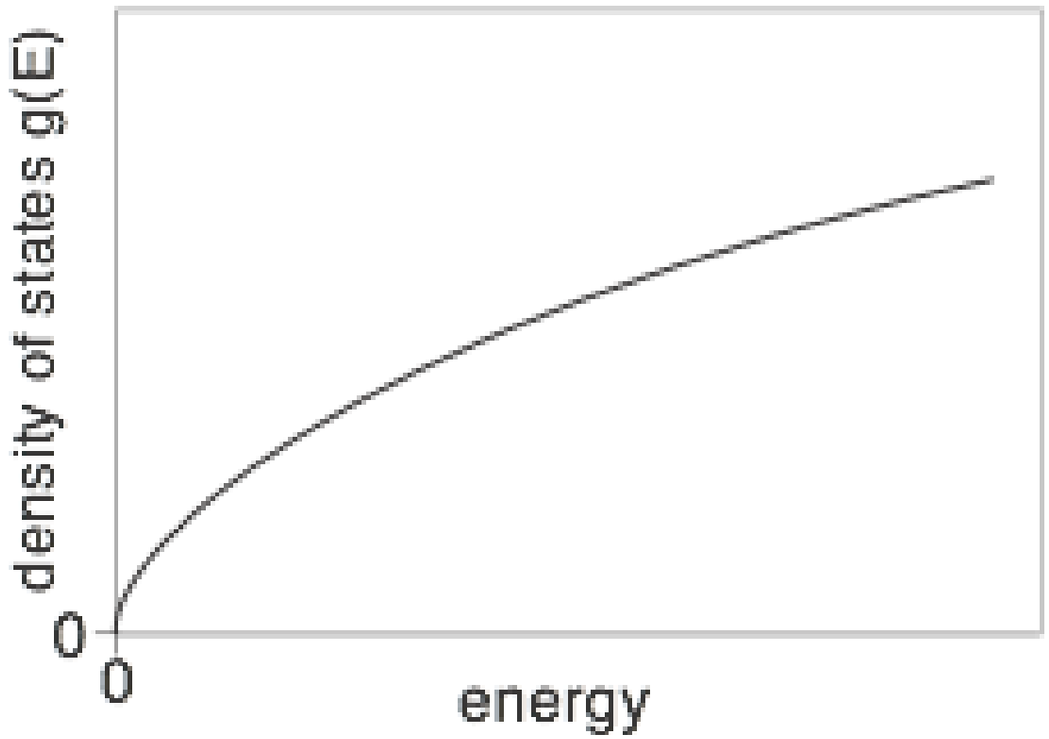


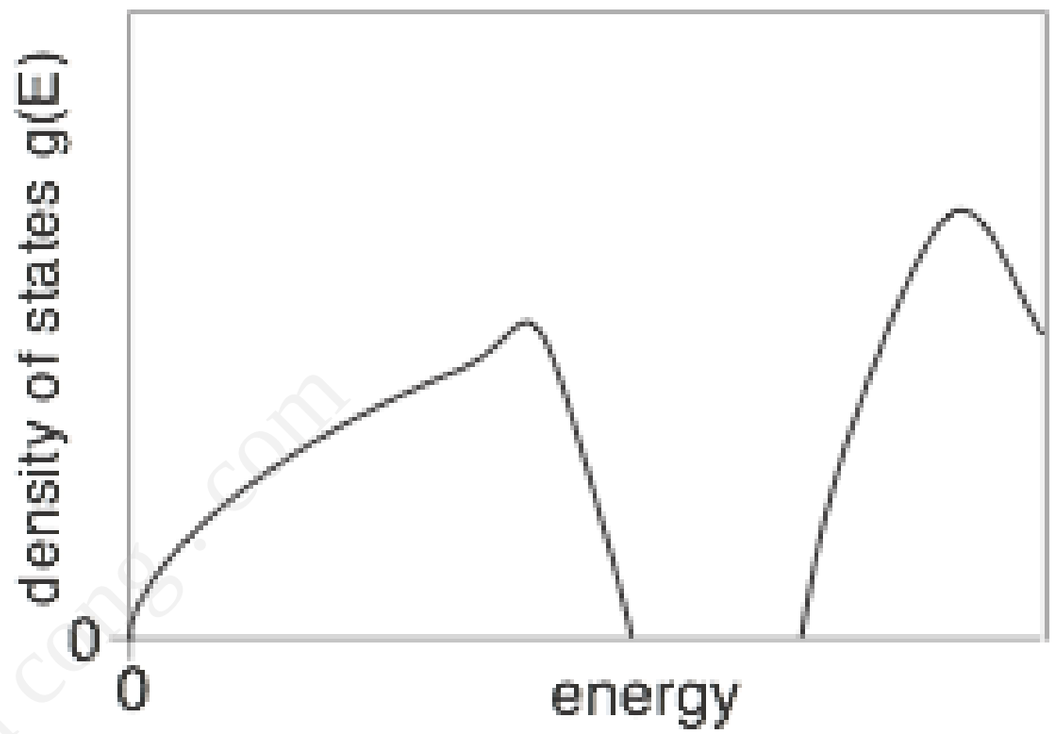
Band structures of real materials: Si and GaAs

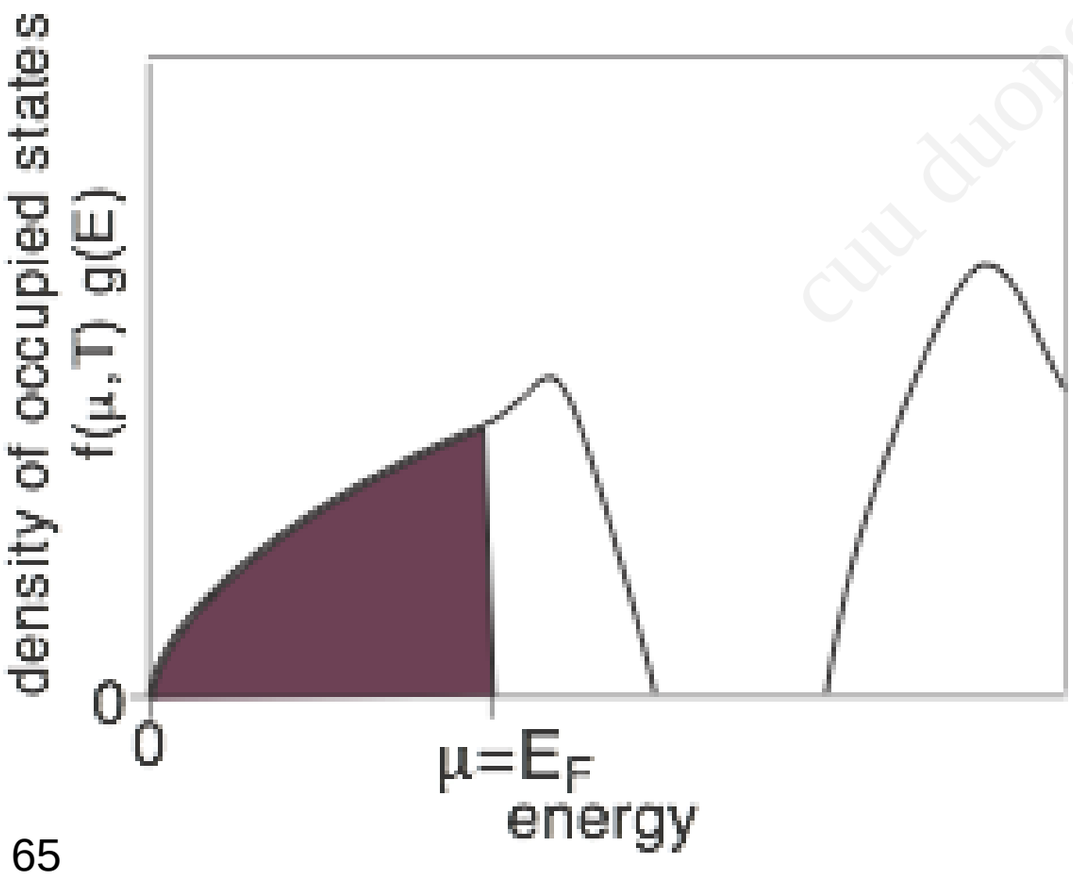


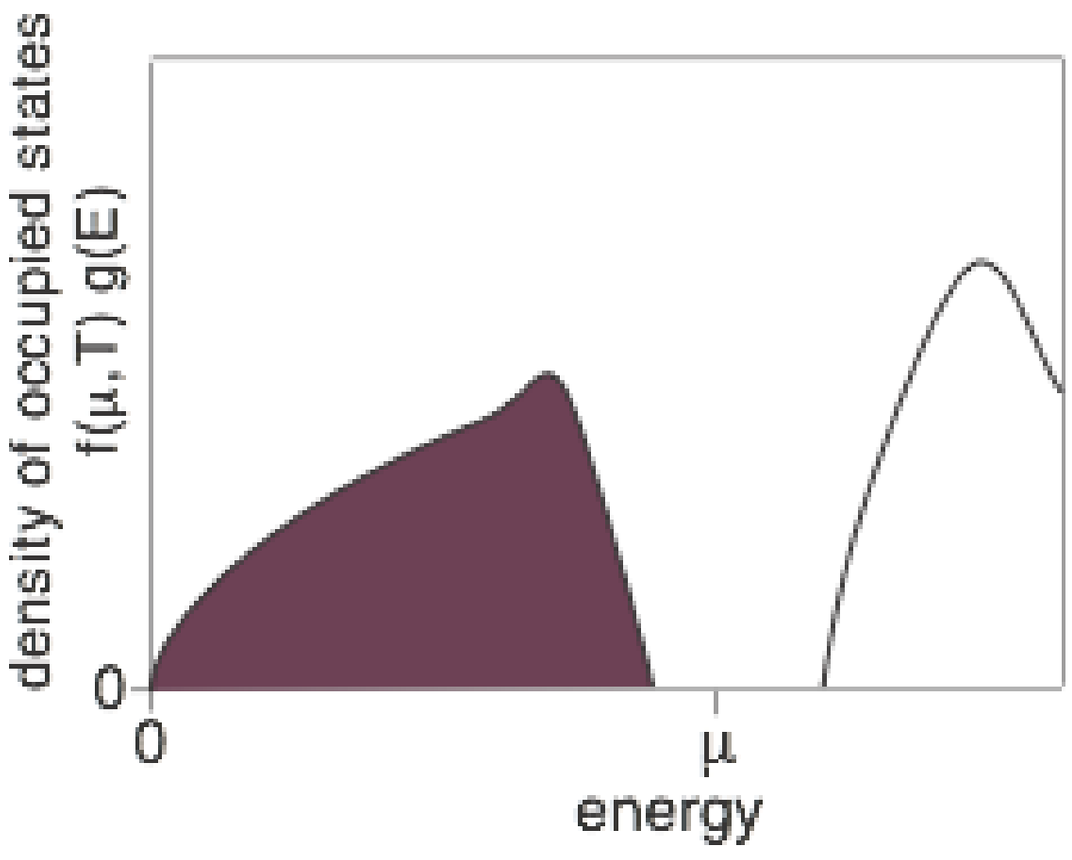


Metals and insulators / semiconductors

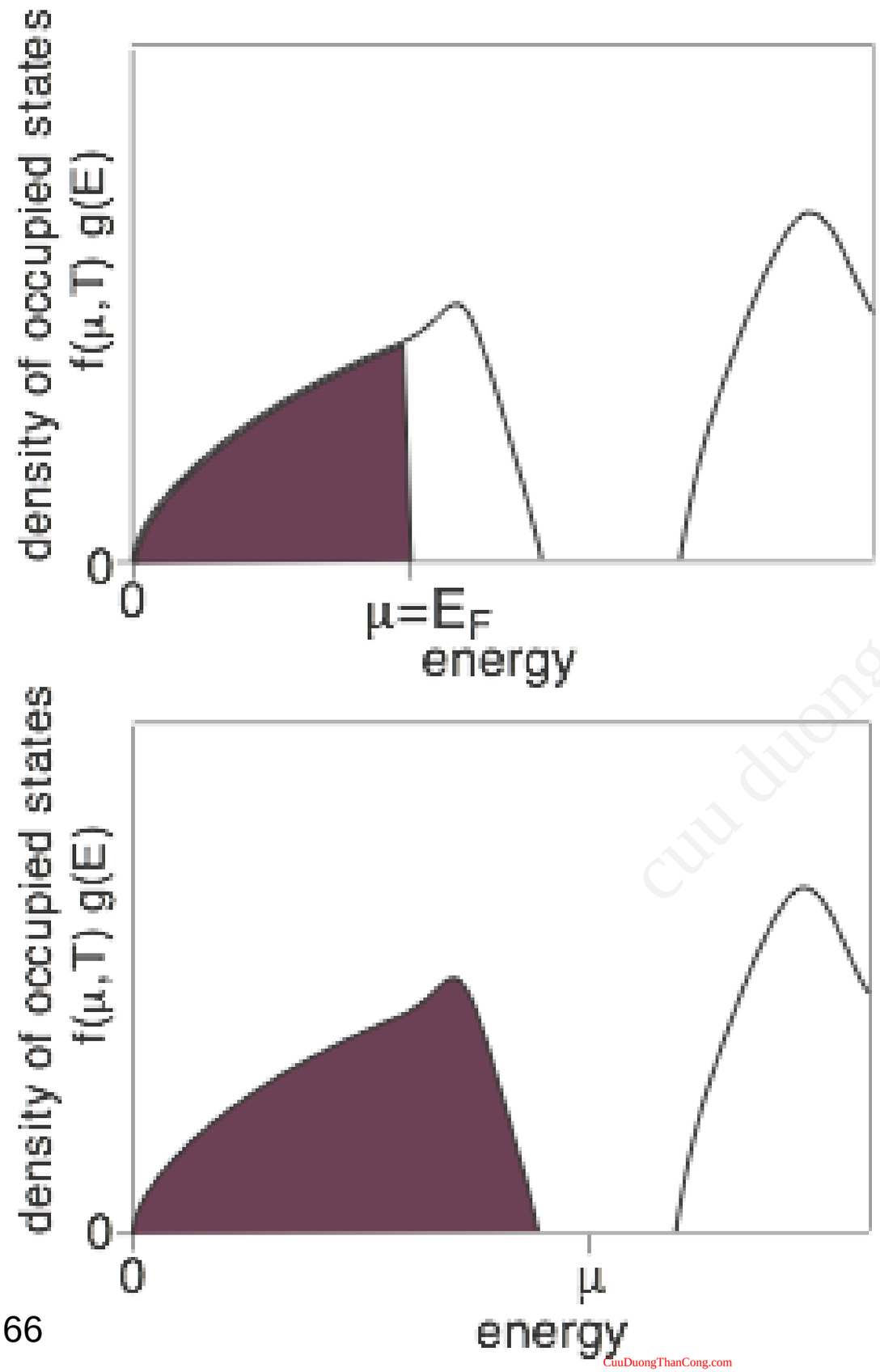






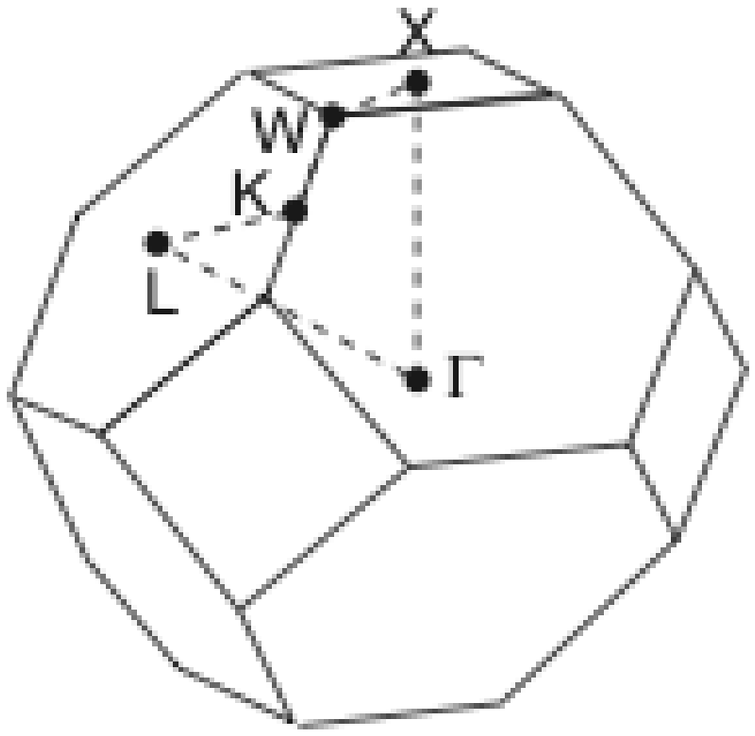


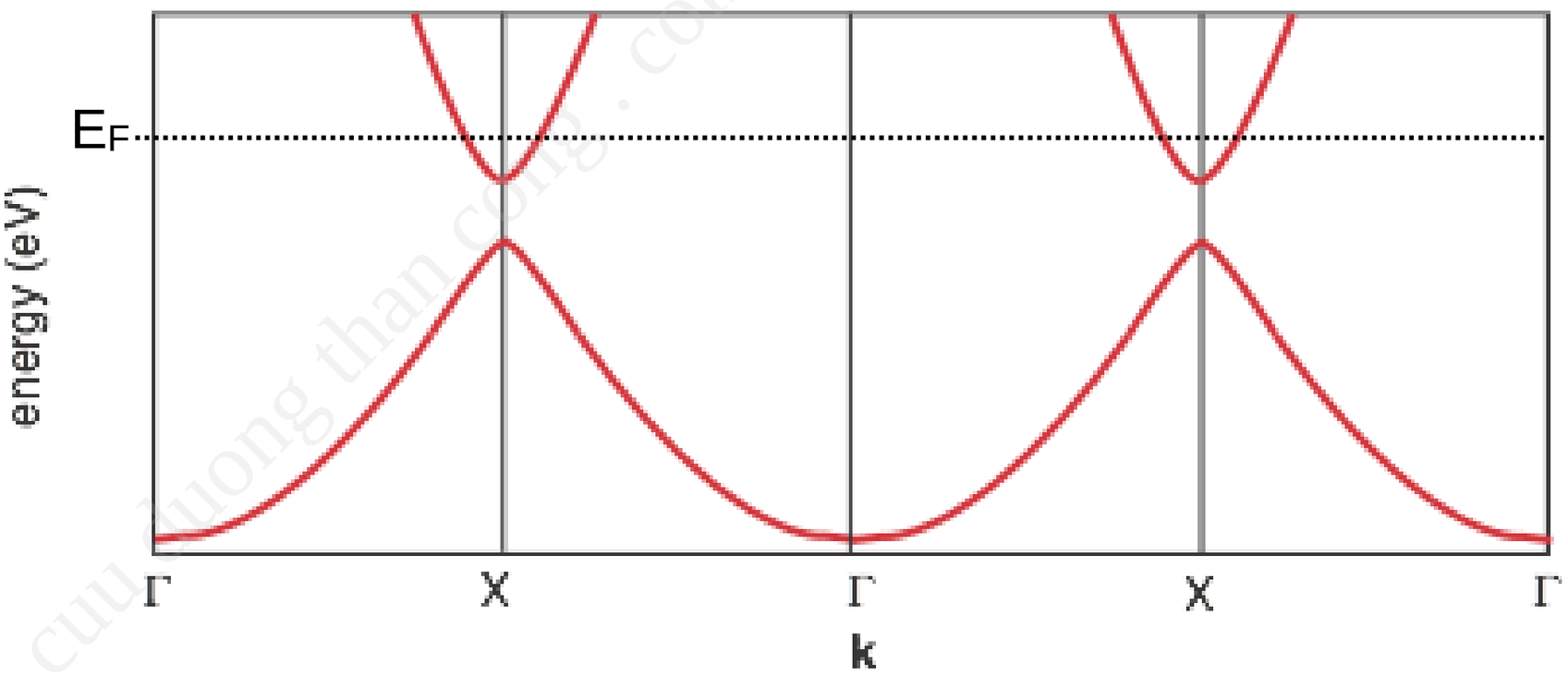
Metals and insulators / semiconductors



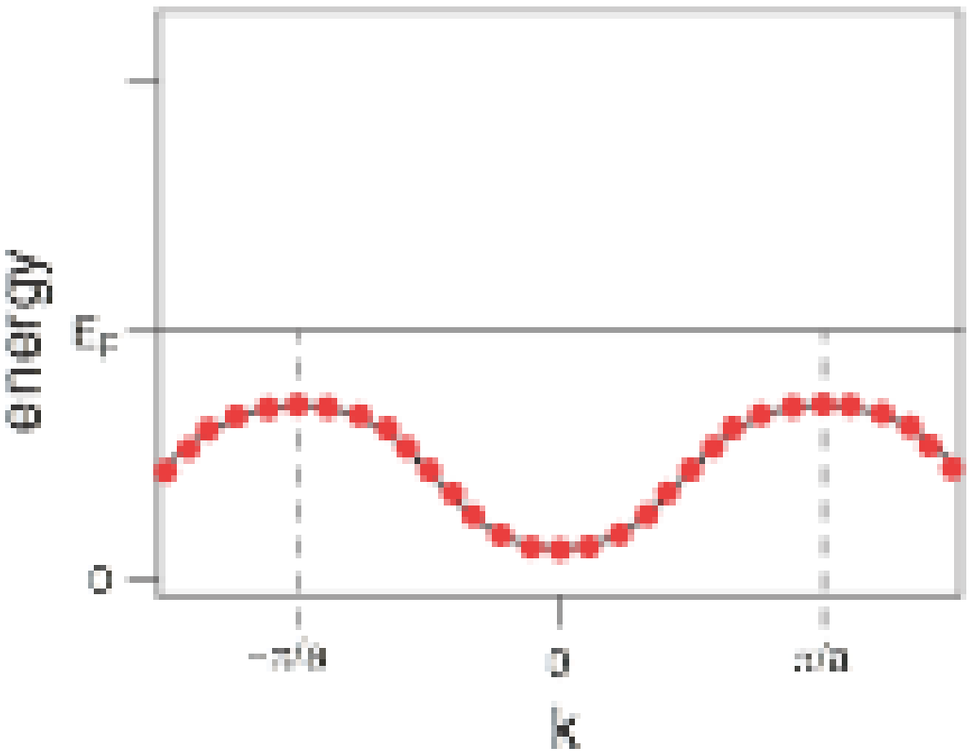
- A metal has a finite density of states at the chemical potential (Fermi energy).
- A semiconductor must have an absolute gap in its band structure (only necessary criterion, not sufficient).
- The number of electrons per unit cell must be such that all the bands are exactly filled up to this gap.

metal or semiconductor?





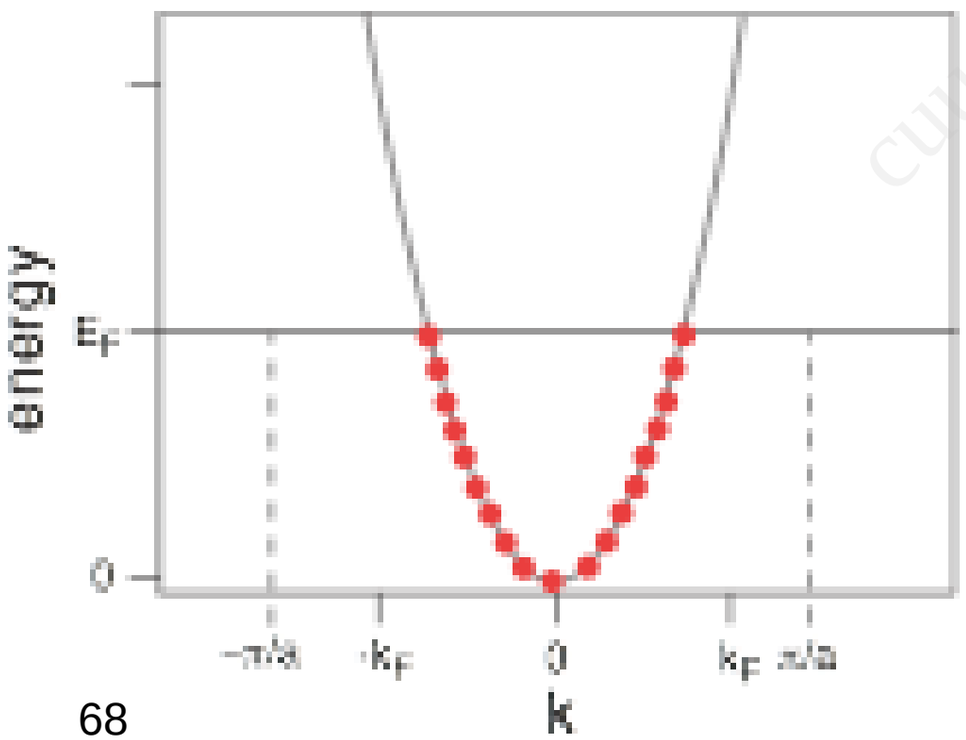
filling the bands - electron counting



N unit cells -> N possible (different) k values

$$k = \frac{2\pi}{aN} n$$

2N possible states per band and k-point (because of spin)

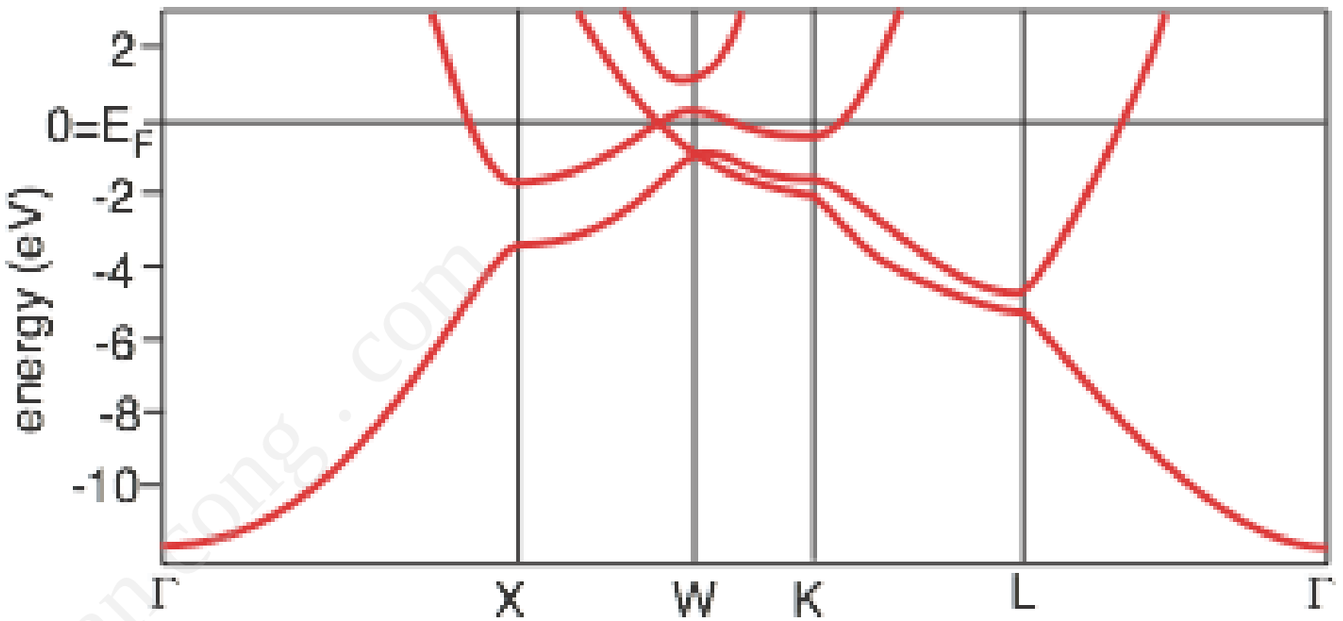


2 valence electrons per unit cell fill one band

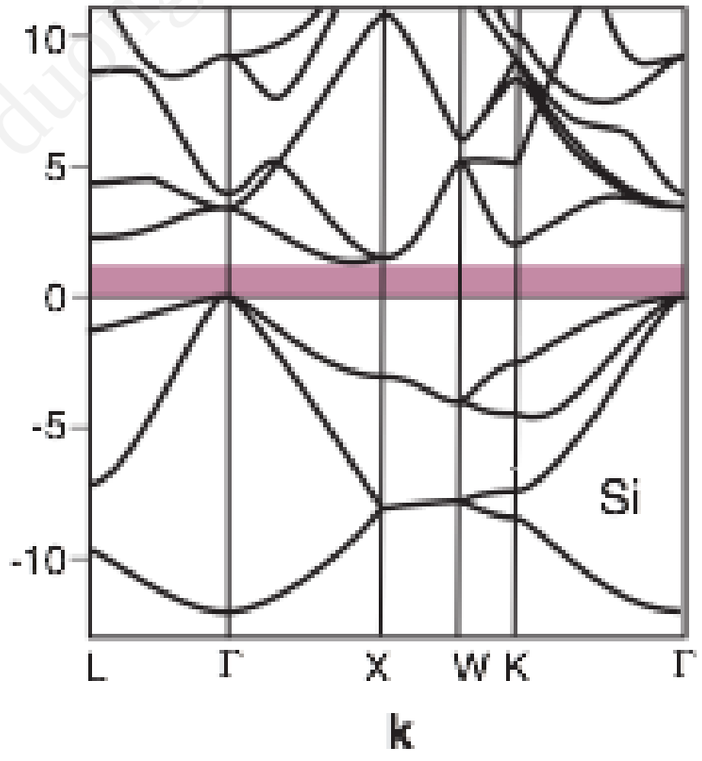
An odd number of valence electrons per unit cell results in a metal

electron counting: examples

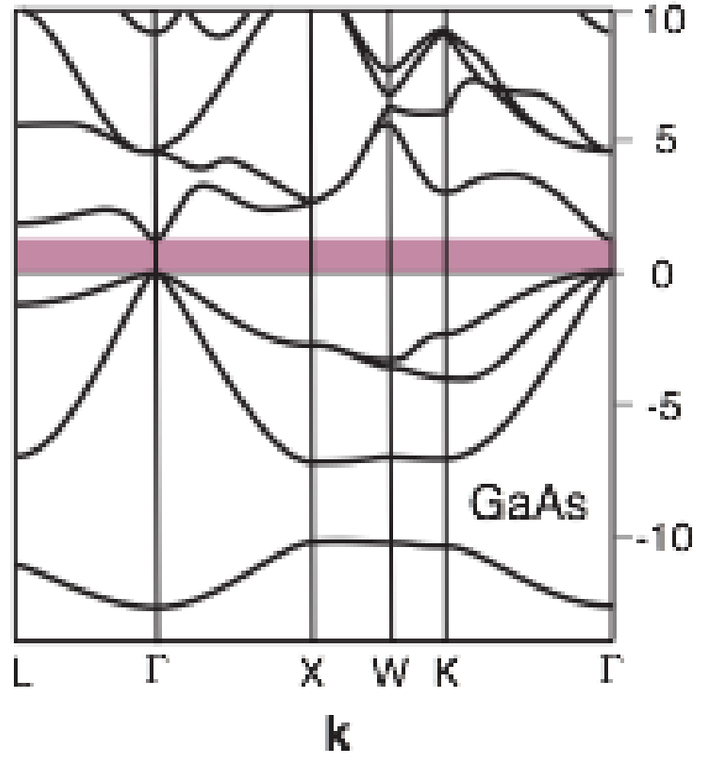
Al: fcc,
1 atom per unit cell,
3 electrons per atom
metal



Si: fcc,
2 atoms per unit cell,
4 electrons per atom
semiconductor

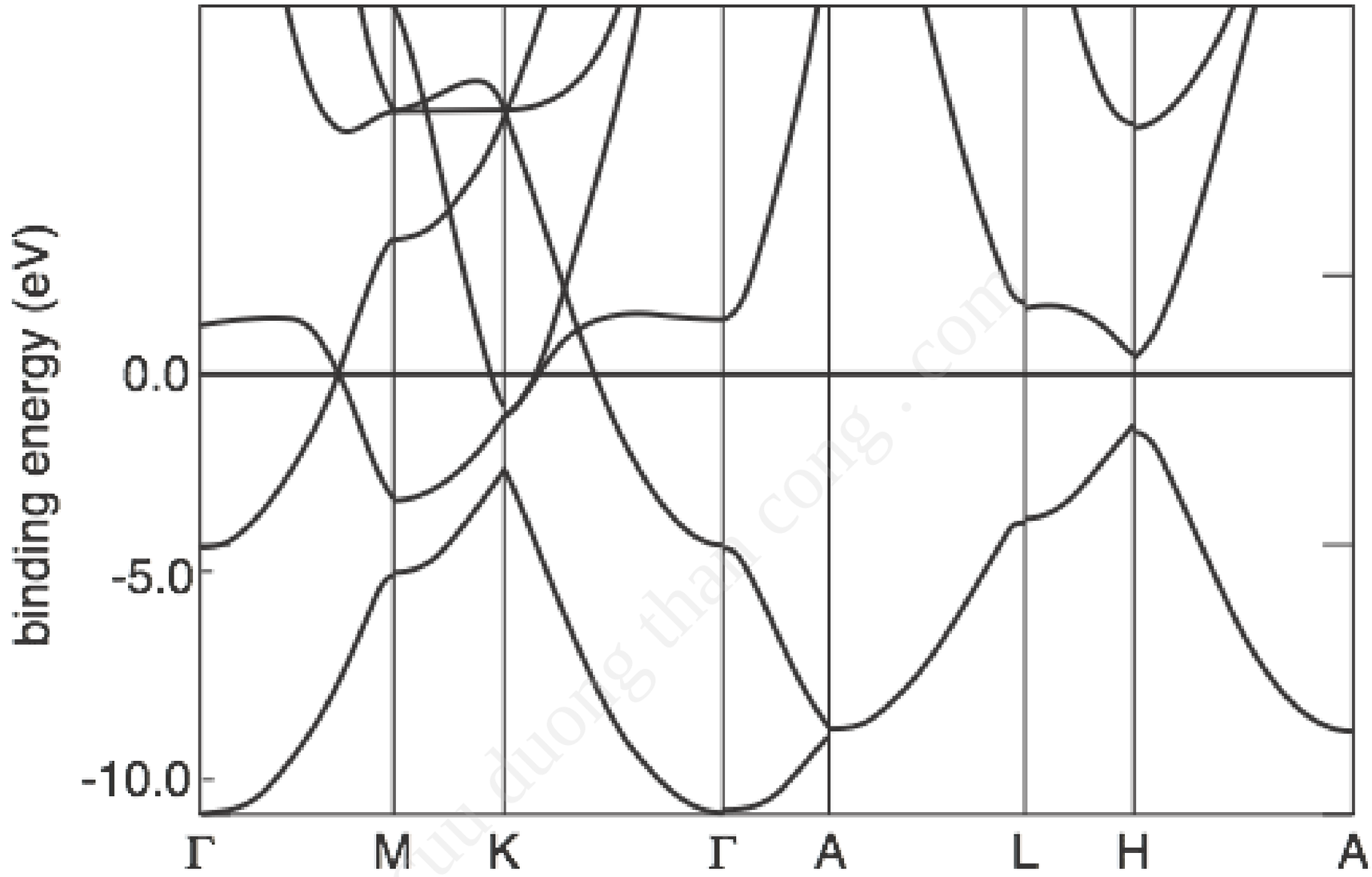


8=4+4



8=3+5

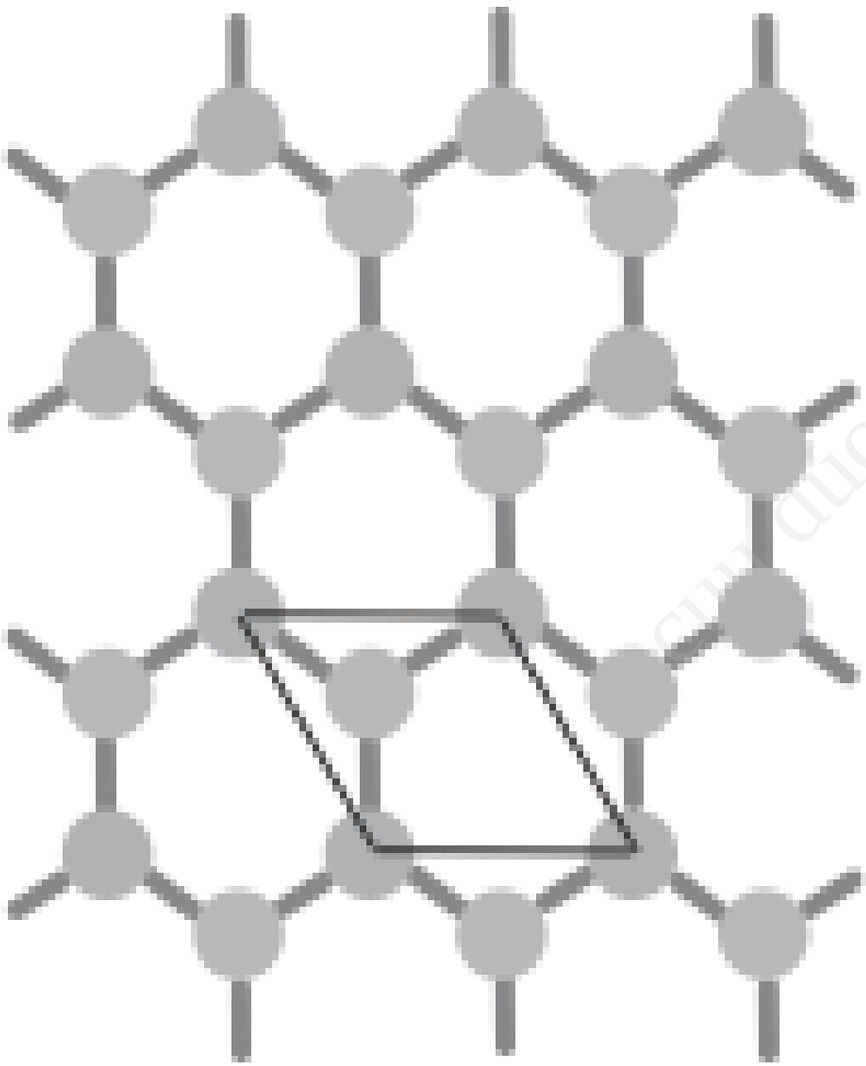
Electron counting



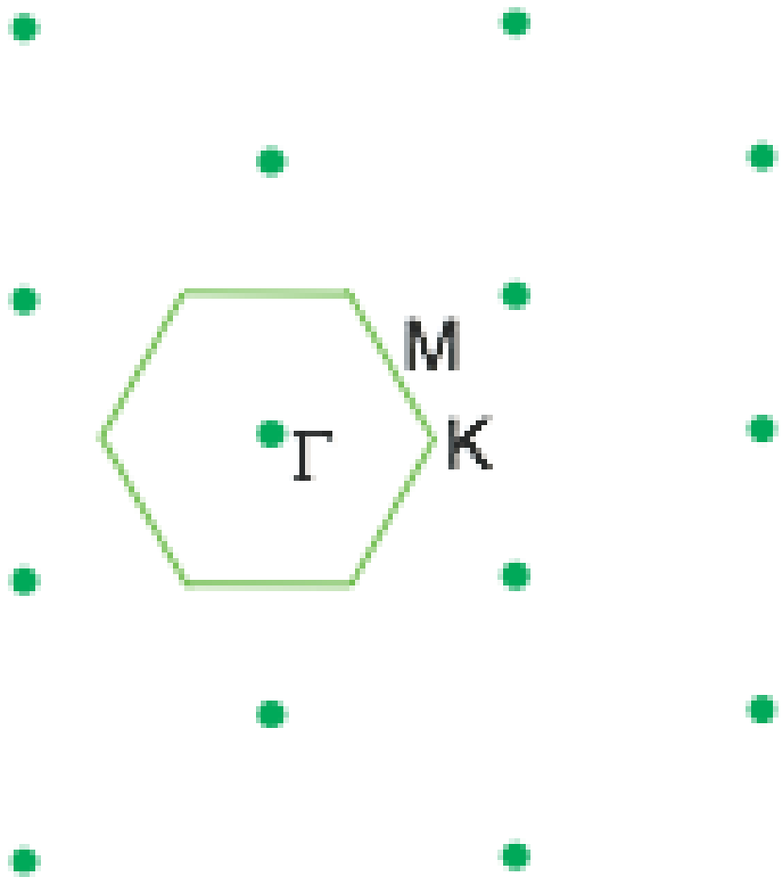
- example 3: Be, hcp structure, 2 atoms per unit cell, 4 valence electrons per unit cell, METAL.

semimetals: graphene, structure

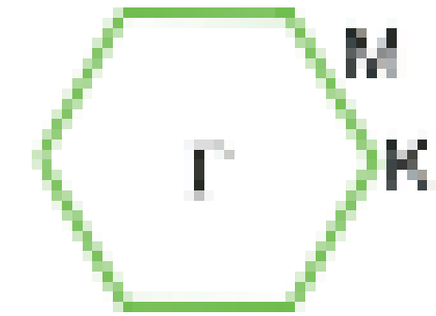
real space structure
primitive unit cell

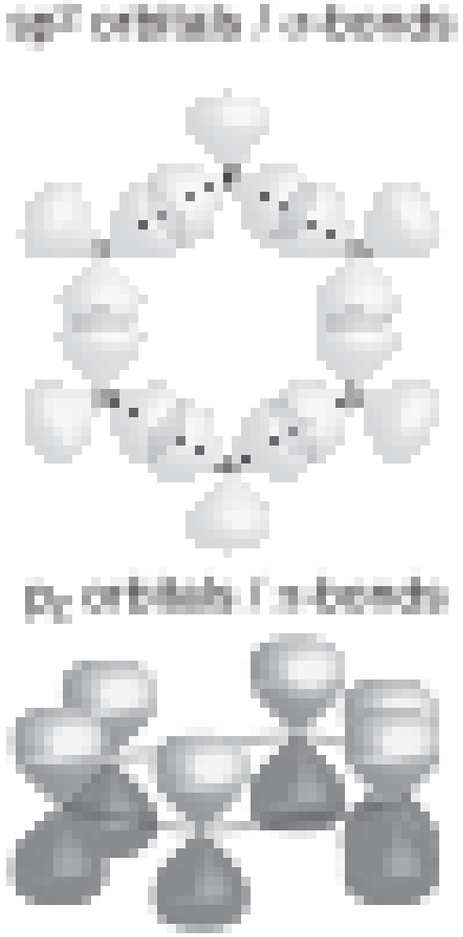


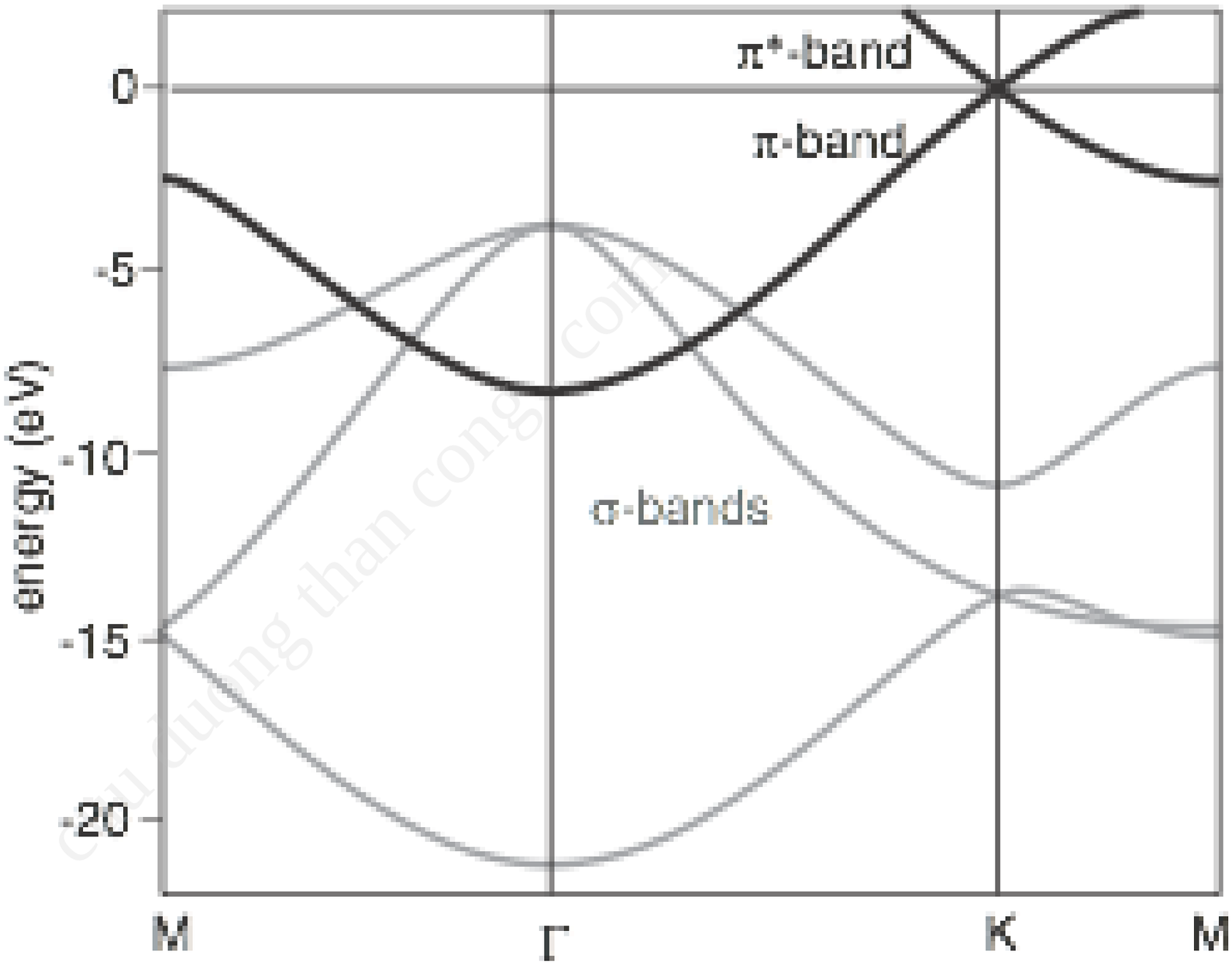
reciprocal space structure
Brillouin zone



semimetals: graphene, band structure





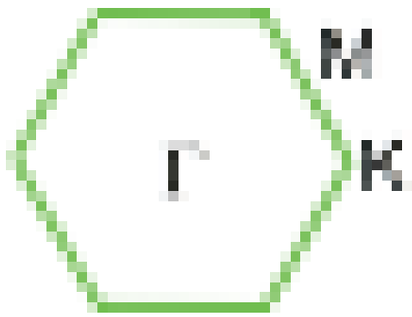


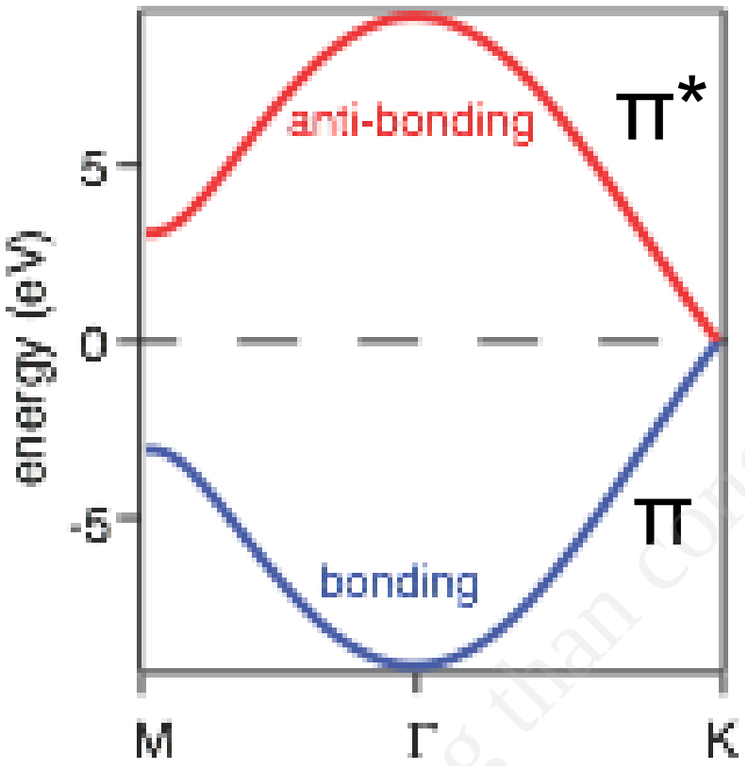
4 electrons per atom, 2 atoms per cell -> 8 electrons per cell, 4 occupied bands

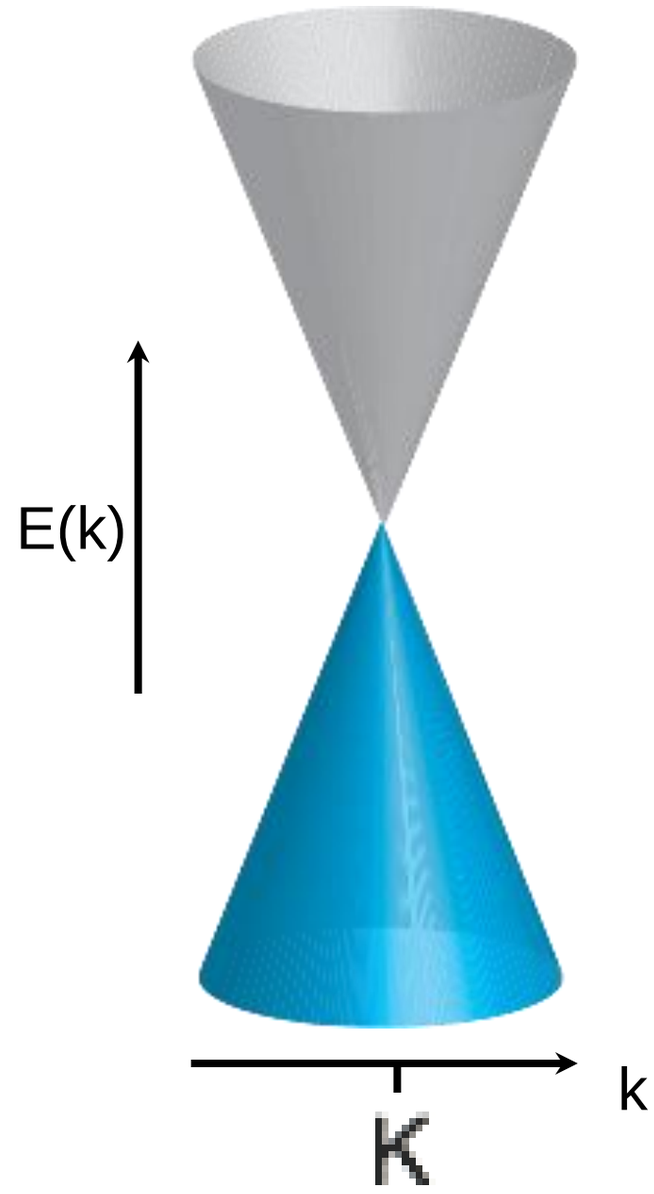
sp^2: 6 states per atom, 12 states per unit cell, 6 σ states, 6 σ* states (not shown)

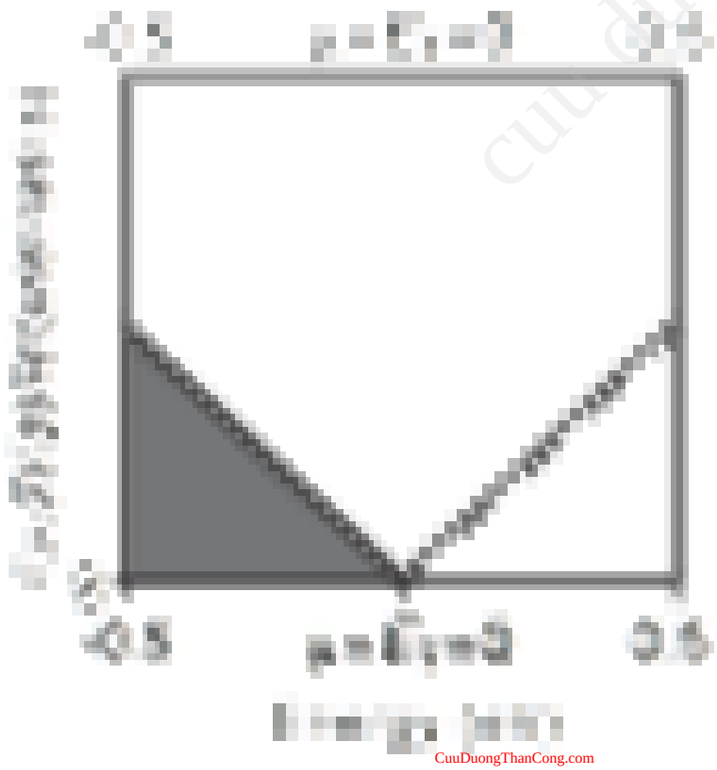
p_z orbitals: 2 states per atom, 4 states per unit cell, 2 π states, 2 π* states

SMALL LETTER PIUnicode: U+03C0, UTF-8: CF 80band









Dirac cone
linear dispersion
group velocity 10^6 ms^{-1}
linear g(E)

The quantum number **k**: crystal momentum

- **k** has both an interpretation as wave vector and (three) quantum numbers.
- It is tempting to interpret ħ**k** as the electron's momentum but this is wrong

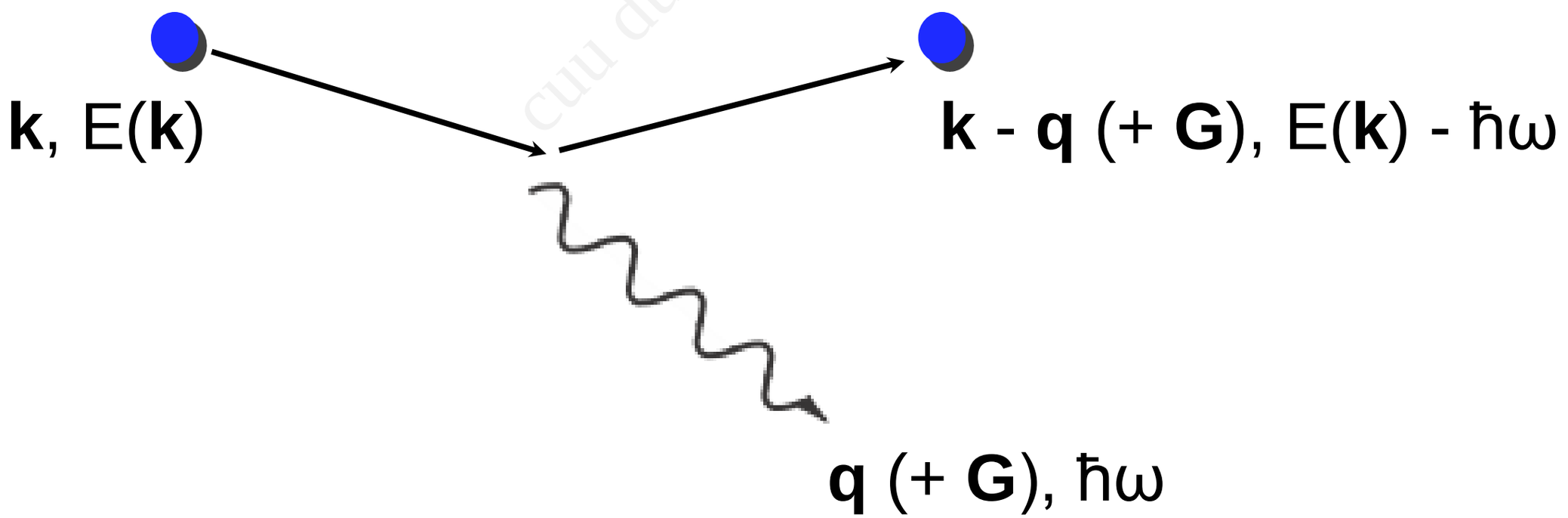
$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} u_{\mathbf{k}}(\mathbf{r})$$

$$-i\hbar\nabla\psi_{\mathbf{k}}(\mathbf{r}) = \hbar\mathbf{k}\psi_{\mathbf{k}}(\mathbf{r}) - e^{i\mathbf{k}\mathbf{r}} i\hbar\nabla u_{\mathbf{k}}(\mathbf{r})$$

The quantum number **k**: crystal momentum

- But ħ**k** is still useful. It is called the “crystal momentum”

example: scattering of electron by phonon



Transport properties

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

- Localised electrons must be described as packages of Bloch waves.
- Bloch electrons travel through the (perfect) crystal without any scattering at all.

Classical motion in an electric field

kinetic energy change with time

$$\frac{dE}{dt} = \frac{dE}{dv}\frac{dv}{dt} = -e\mathcal{E}v$$

$$E = \frac{1}{2}m_e v^2$$

$$\frac{dE}{dv} = m_e v$$

$$m_e \frac{dv}{dt} = -e\mathcal{E}$$

$$\frac{dv}{dt} = -\frac{e}{m_e}\mathcal{E}$$

kinetic energy change with time (Bloch electron)

$$\frac{dE}{dt} = \frac{dE}{dk}\frac{dk}{dt}$$

$$\frac{dE}{dt} = -e\mathcal{E}v_g \qquad \frac{dE}{dk} = \hbar\frac{d\omega}{dk} = \hbar v_g$$

$$-e\mathcal{E}v_g = \hbar v_g \frac{dk}{dt}$$

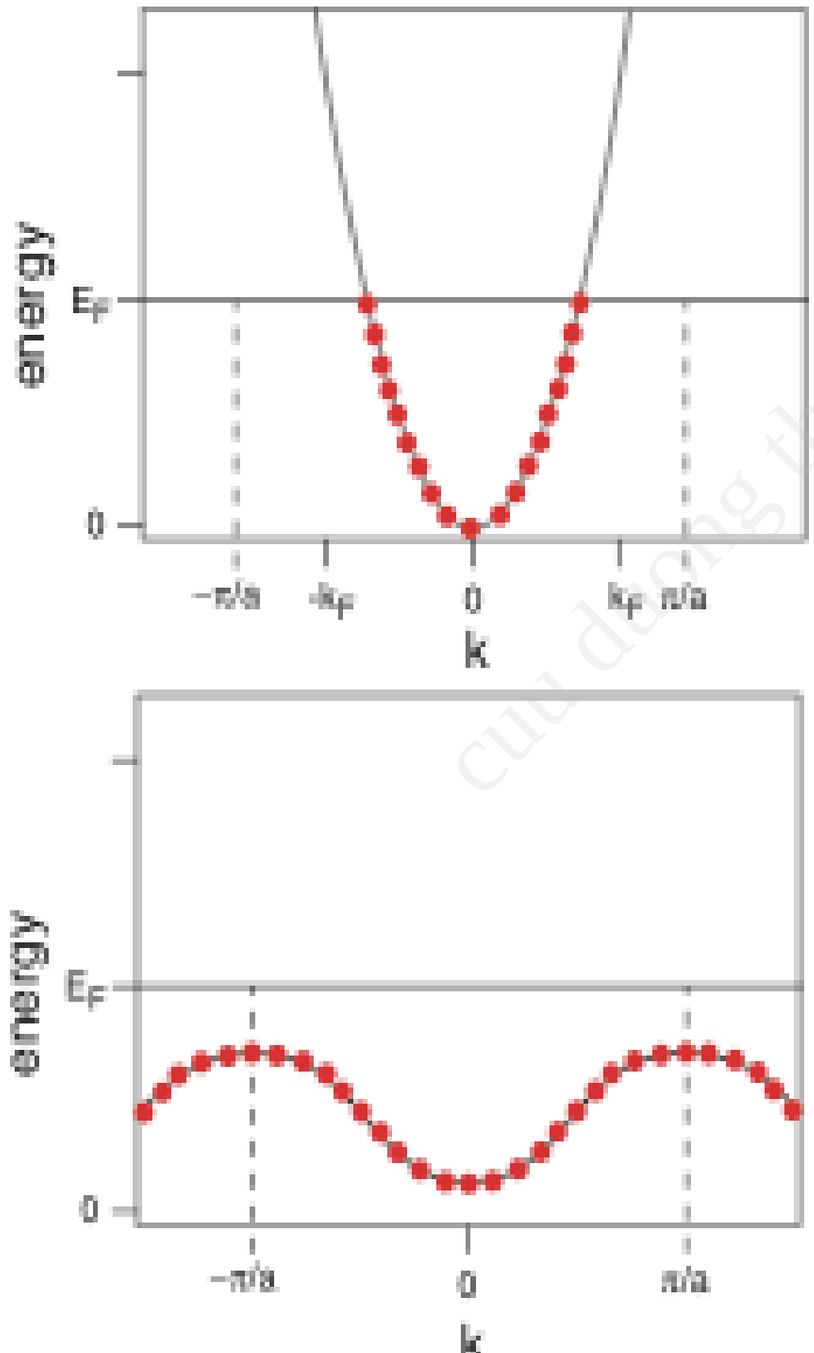
equation of motion in k-space!

$$\hbar\frac{dk}{dt} = -e\mathcal{E}.$$

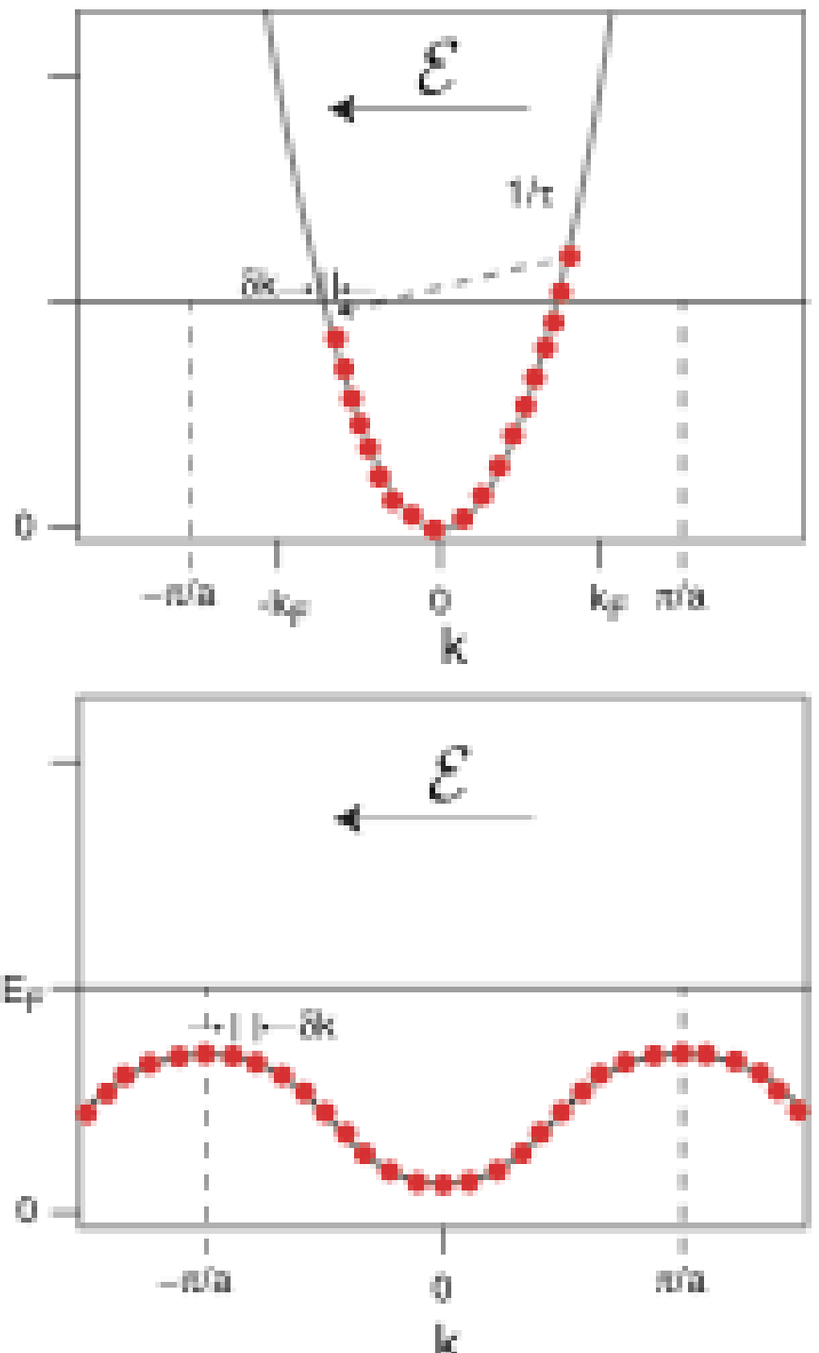
equation of motion $$\hbar \frac{dk}{dt} = -e\mathcal{E}.$$

remember also $$v_g = \frac{1}{\hbar}\frac{dE}{dk}$$

no field



finite field



Typical size of δk

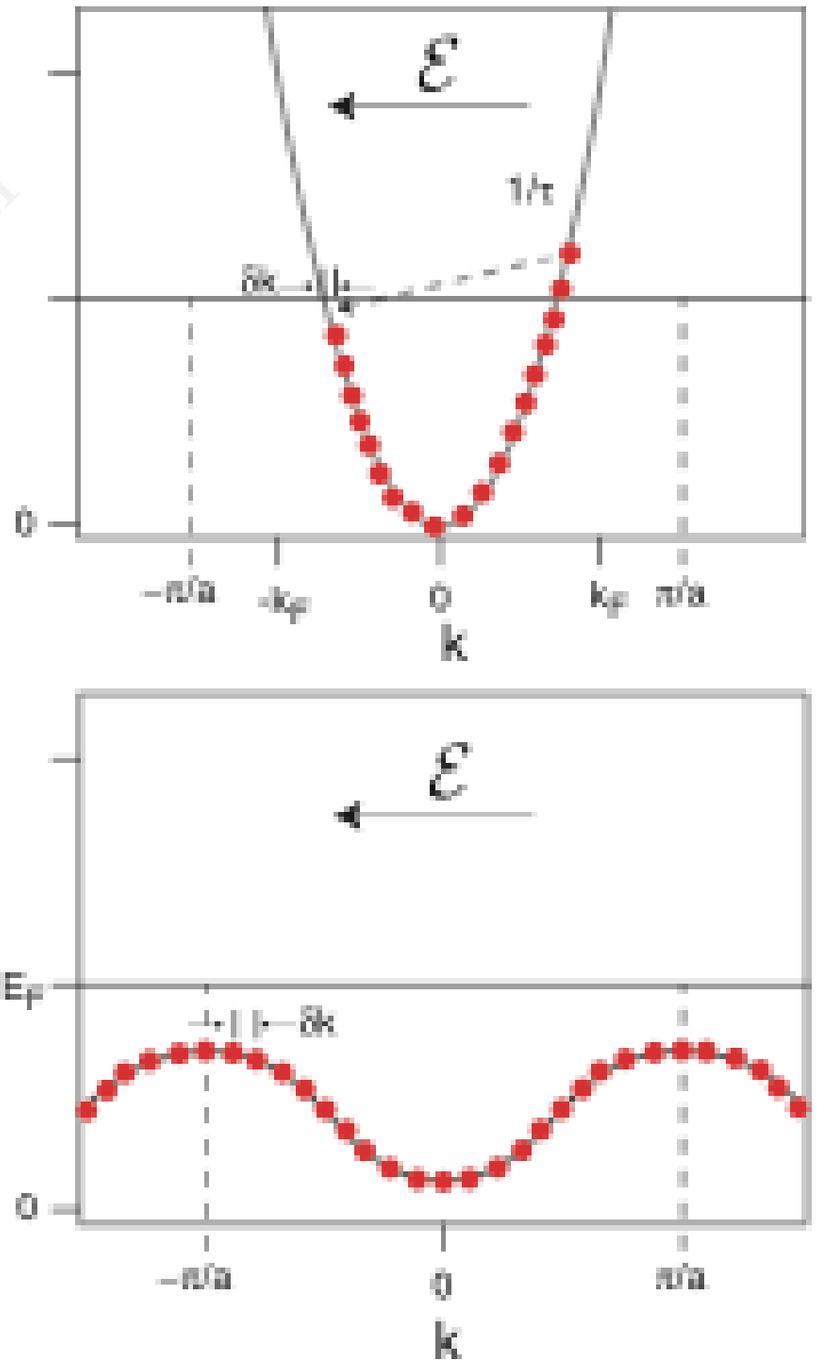
$$\mathcal{E} = 10^2 \mathrm{V m}^{-1}$$

$$\tau = 10^{-14} \mathrm{s}$$

$$\delta k = e\mathcal{E}\tau/\hbar \approx 10^4 \mathrm{m}^{-1}$$

$$1/a \approx 10^{10} \mathrm{m}^{-1}$$

finite field



group velocity of an electron

$$v_g = \frac{d\omega(k)}{dk} = \frac{1}{\hbar}\frac{dE(k)}{dk}$$

acceleration

$$a = \frac{dv_g}{dt} = \frac{1}{\hbar}\frac{d}{dt}\frac{dE(k)}{dk} = \frac{1}{\hbar}\frac{d^2E(k)}{dk^2}\frac{dk}{dt}$$

$$a = -\frac{1}{\hbar^2}\frac{d^2E(k)}{dk^2}e\mathcal{E}.$$

$$\hbar\frac{dk}{dt} = -e\mathcal{E}.$$

and with $$m^* = \hbar^2\left(\frac{d^2E(k)}{dk^2}\right)^{-1}$$

$$m^*a = -e\mathcal{E}$$

The effective mass is essentially the inverse curvature of the band.

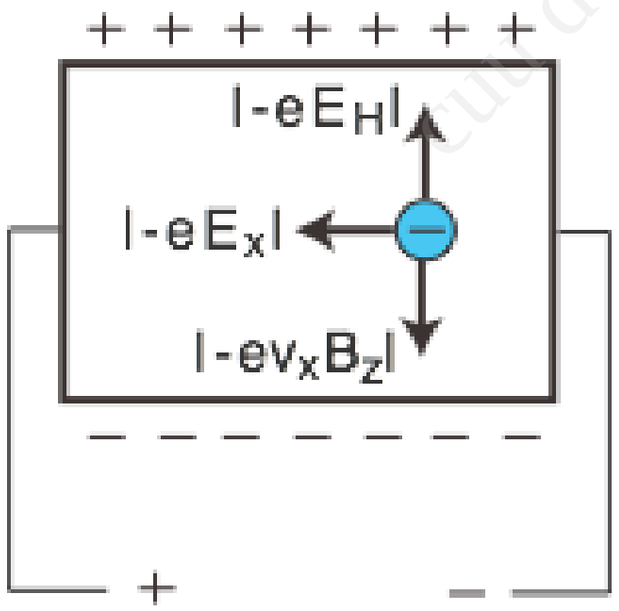
Negative effective mass

and with $$m^* = \hbar^2 \left(\frac{d^2 E(k)}{dk^2} \right)^{-1}$$

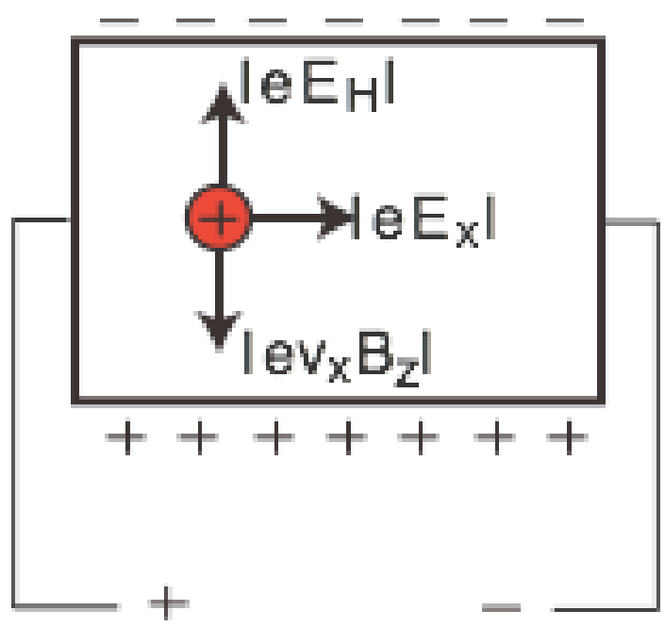
$$m^* a = -e\mathcal{E}$$

$$m^* = \hbar^2 \left(\frac{d^2 E(k)}{dk^2} \right)^{-1} < 0$$

$$-|m^*|a = -e\mathcal{E}$$



$$|m^*|a = e\mathcal{E}$$



perfect lattice

Bloch waves propagate freely

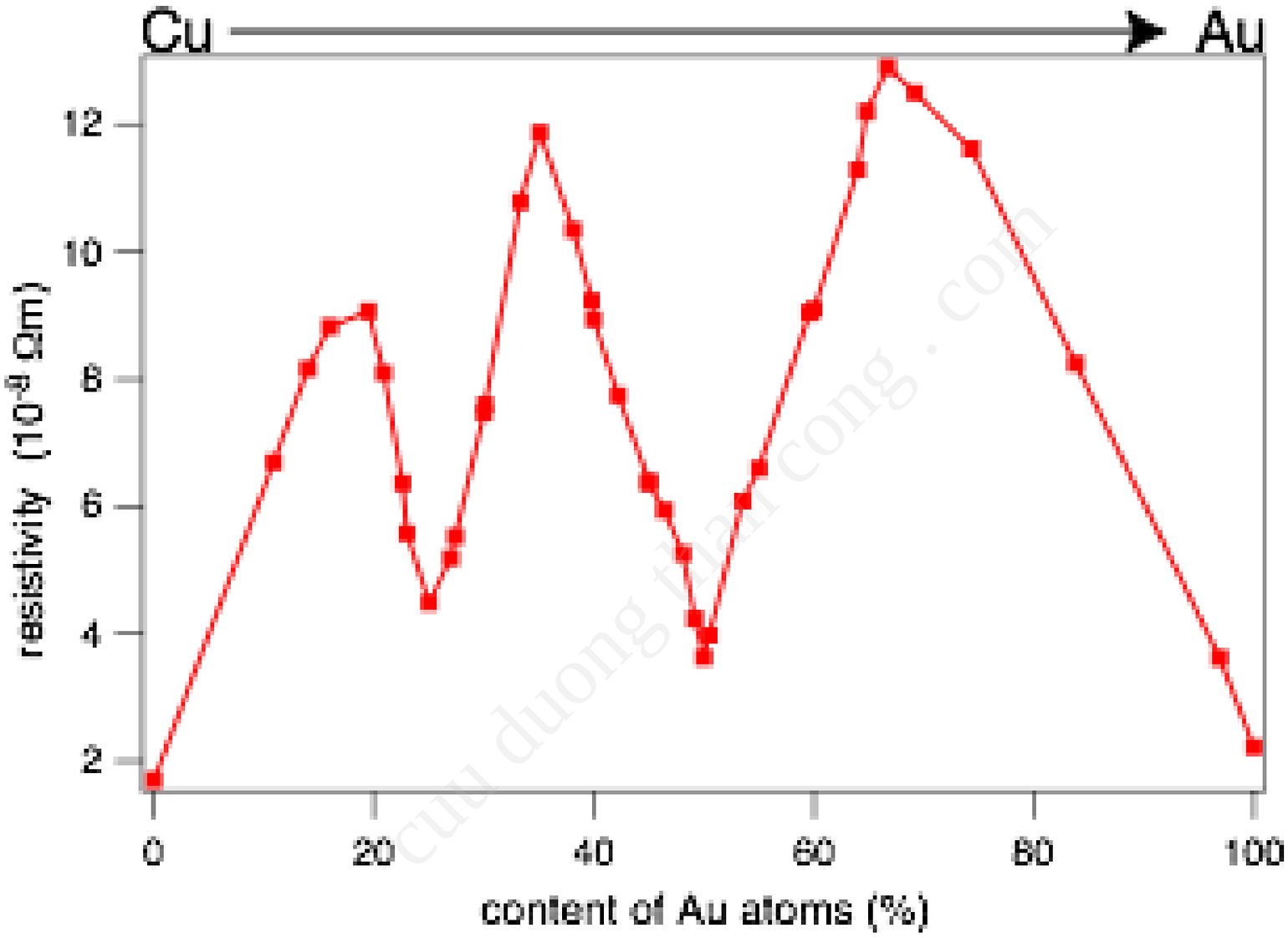
$$\psi_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r})e^{i\vec{k}\vec{r}}$$

causes of scattering / finite resistance

- Any kind of deviation from the perfect lattice
- Point defects, extended defects, vacancies, substitutional atoms in the lattice....
- Thermal vibrations (like static distortions on the electron’s time scale)

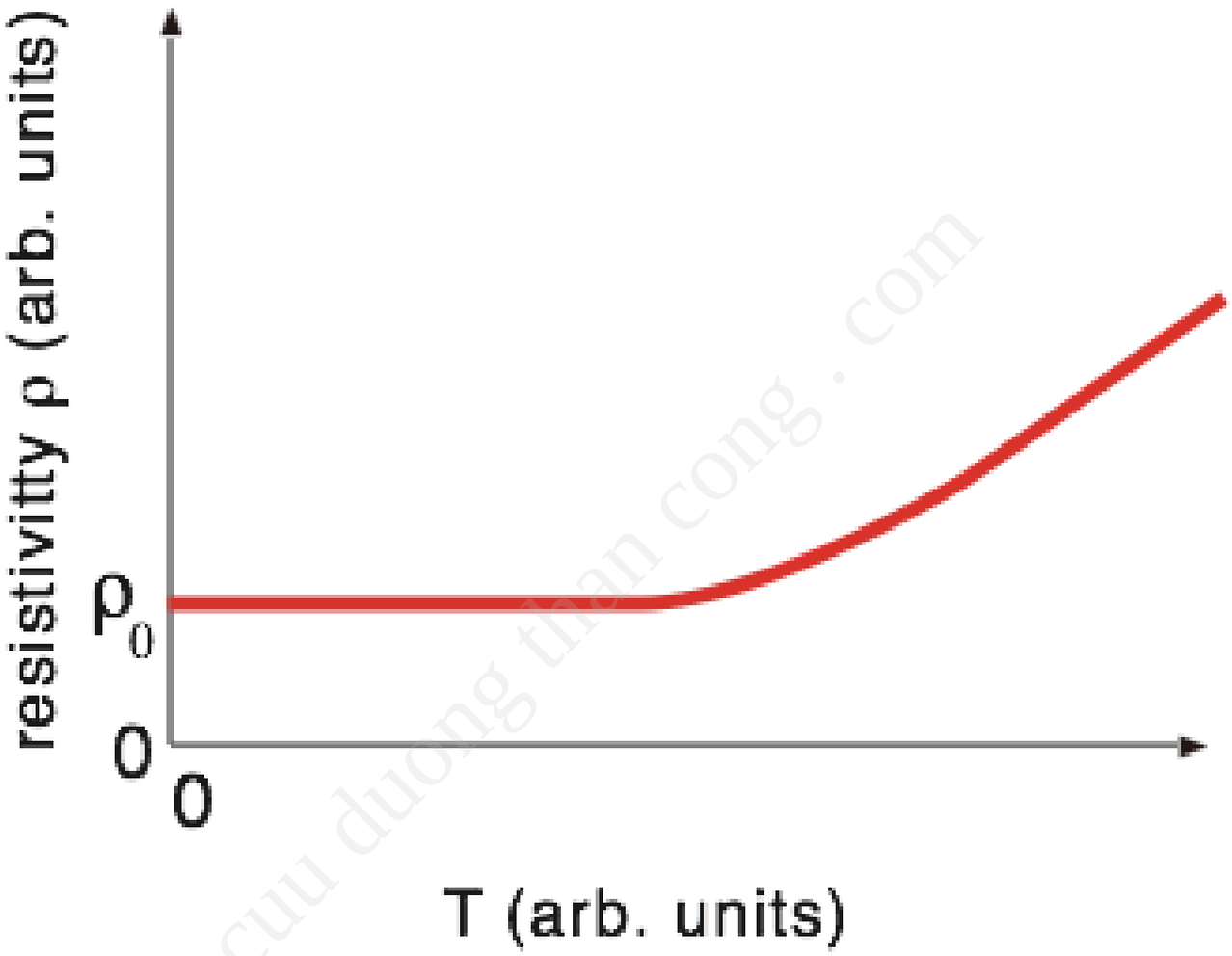
give rise to relaxation time τ

Failures of the Drude model: electrical conductivity of an alloy



- The resistivity of an alloy should be between those of its components, or at least similar to them.
- It can be much higher than that of either component.

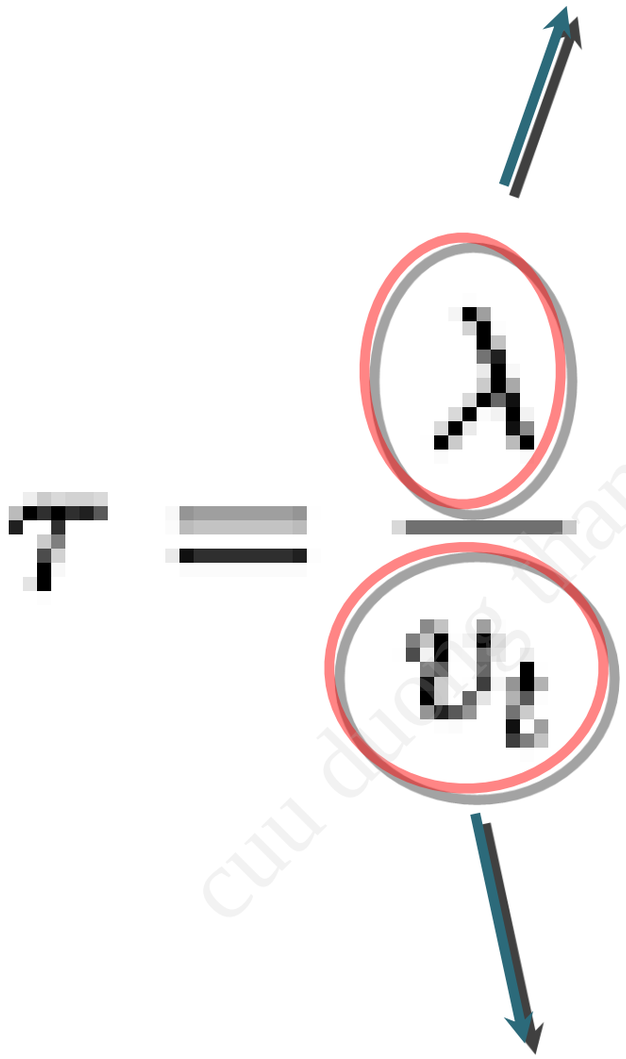
Temperature-dependence of the resistivity



- At higher temperatures the resistivity increases because of stronger lattice vibrations / more phonons to scatter from.
- At low temperature the resistivity saturates because of the defects and impurities.

Modified Drude formula

mean free path by lattice imperfections



(average) velocity at the Fermi level

Modified Drude formula

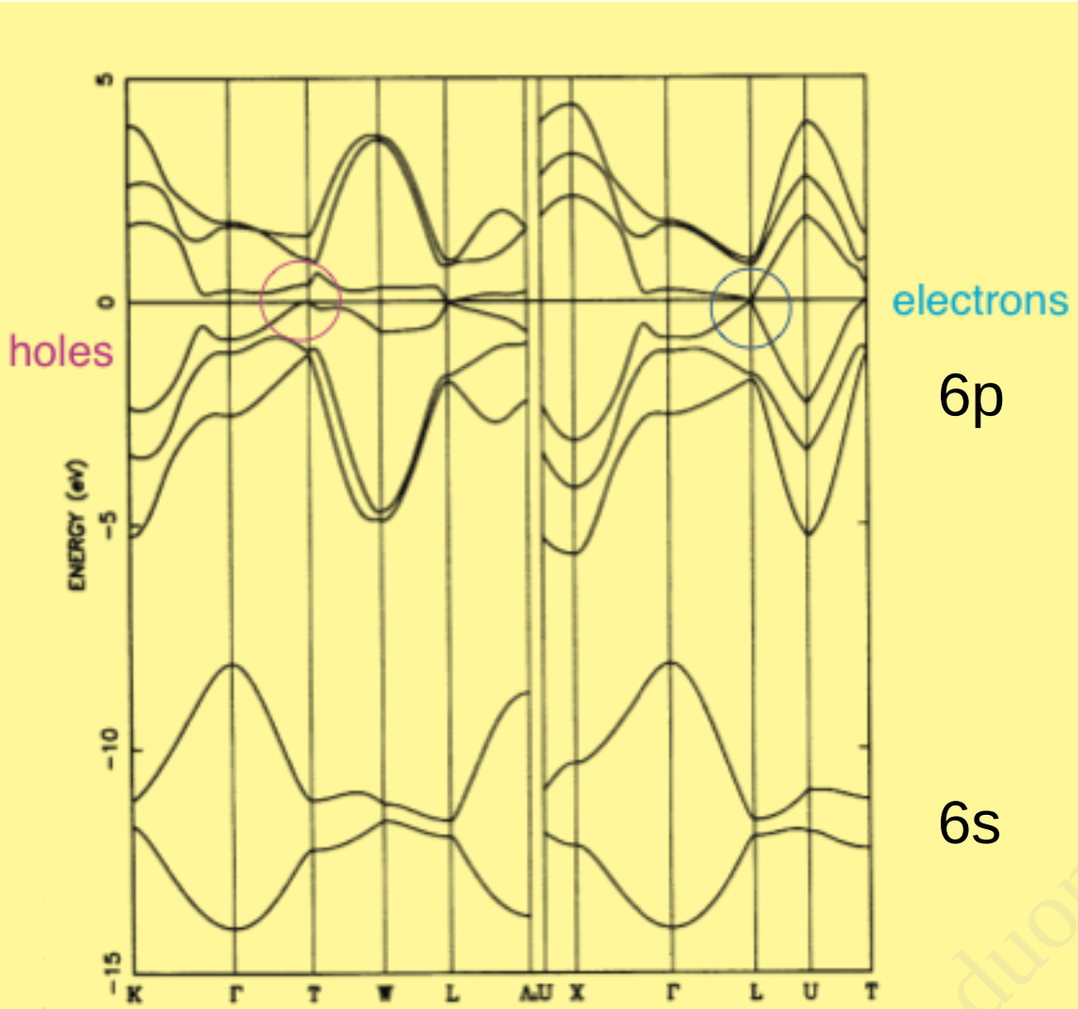
electron density from partially filled bands

$$\sigma = \frac{ne^2\tau}{m^*}$$

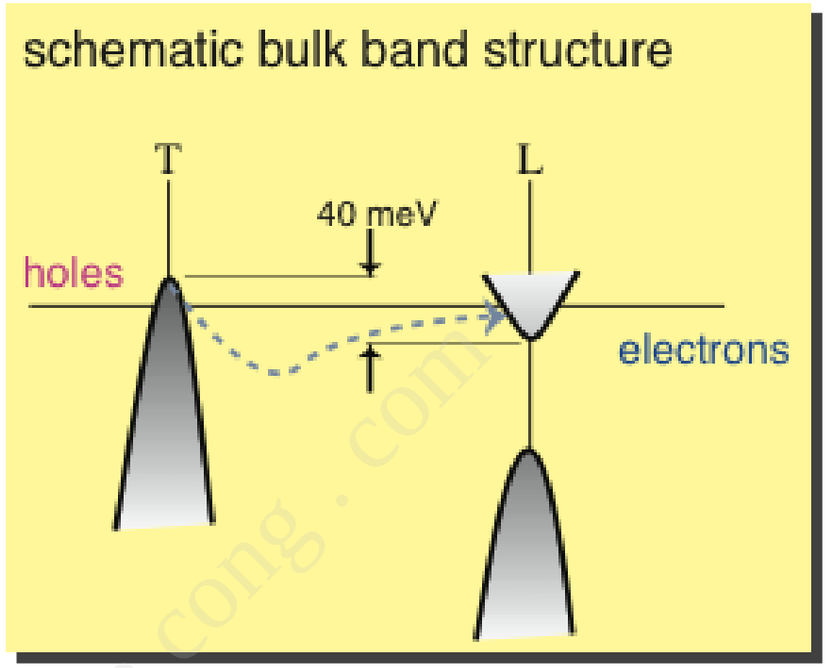
still relaxation time

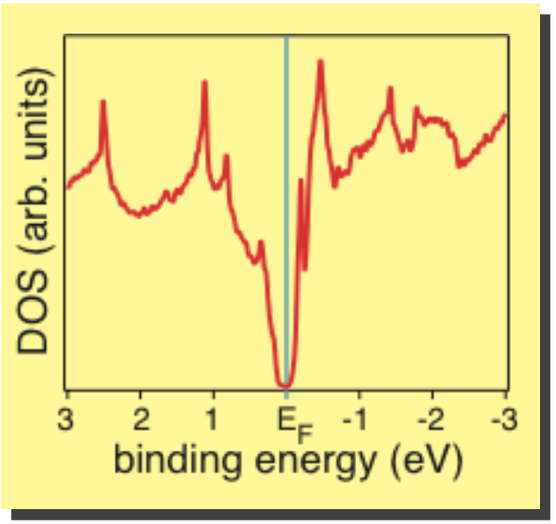
(average) effective mass of those electrons

Electronic structure of Bi



tight-binding calculation, Liu and Allen, PRB 52, 1566 (1995)



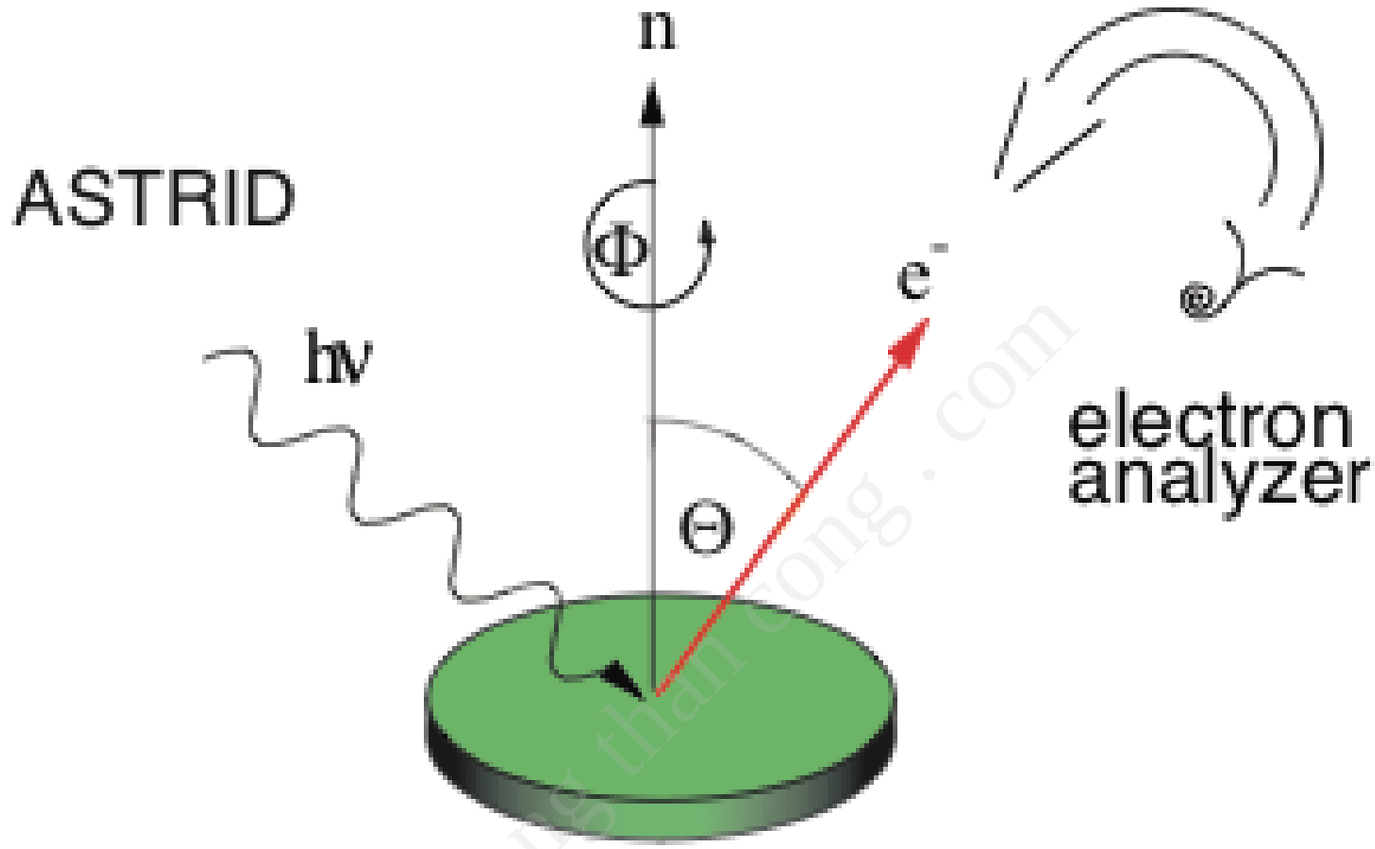


- almost an insulator
- small energy scales and small effective masses
- strong spin-orbit interaction but two electrons per band.

$$R_H = \frac{-1}{ne}$$

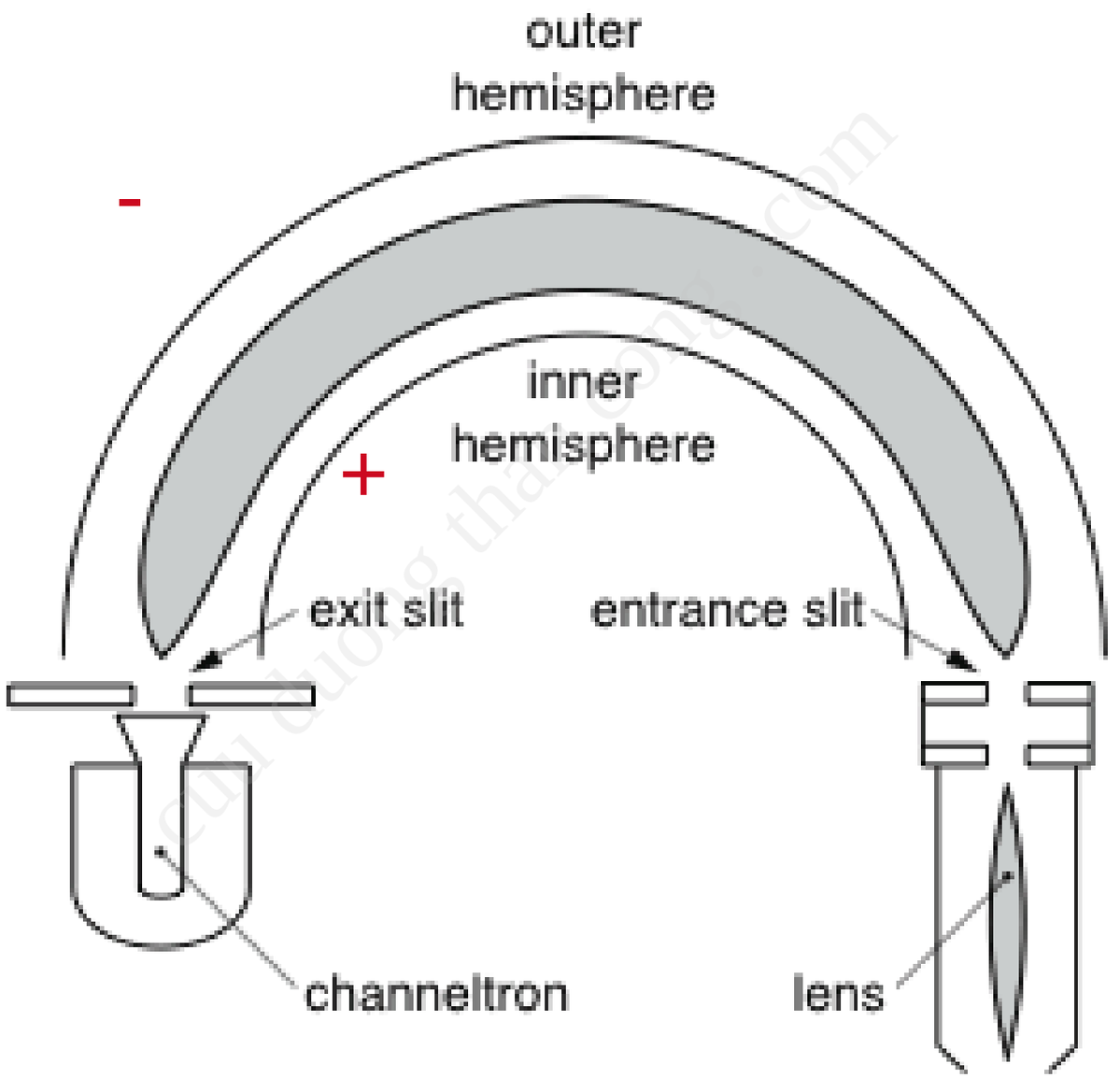
Focus on photoemission

Angle-resolved photoemission (ARPES)

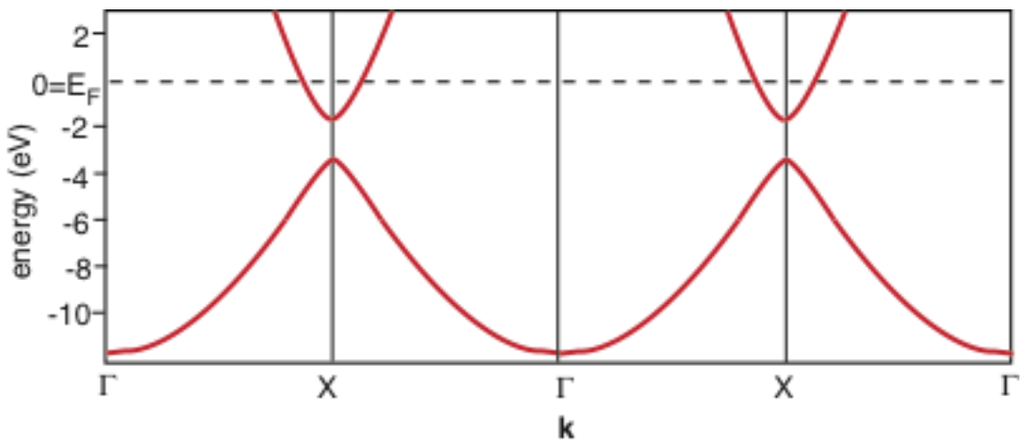


- Measure the energy and emission angle of the photoemitted electrons outside the surface.
- Calculate the energy and the k-vector outside the surface.
- Infer the energy and the k-vector inside the solid, i.e. the bands.

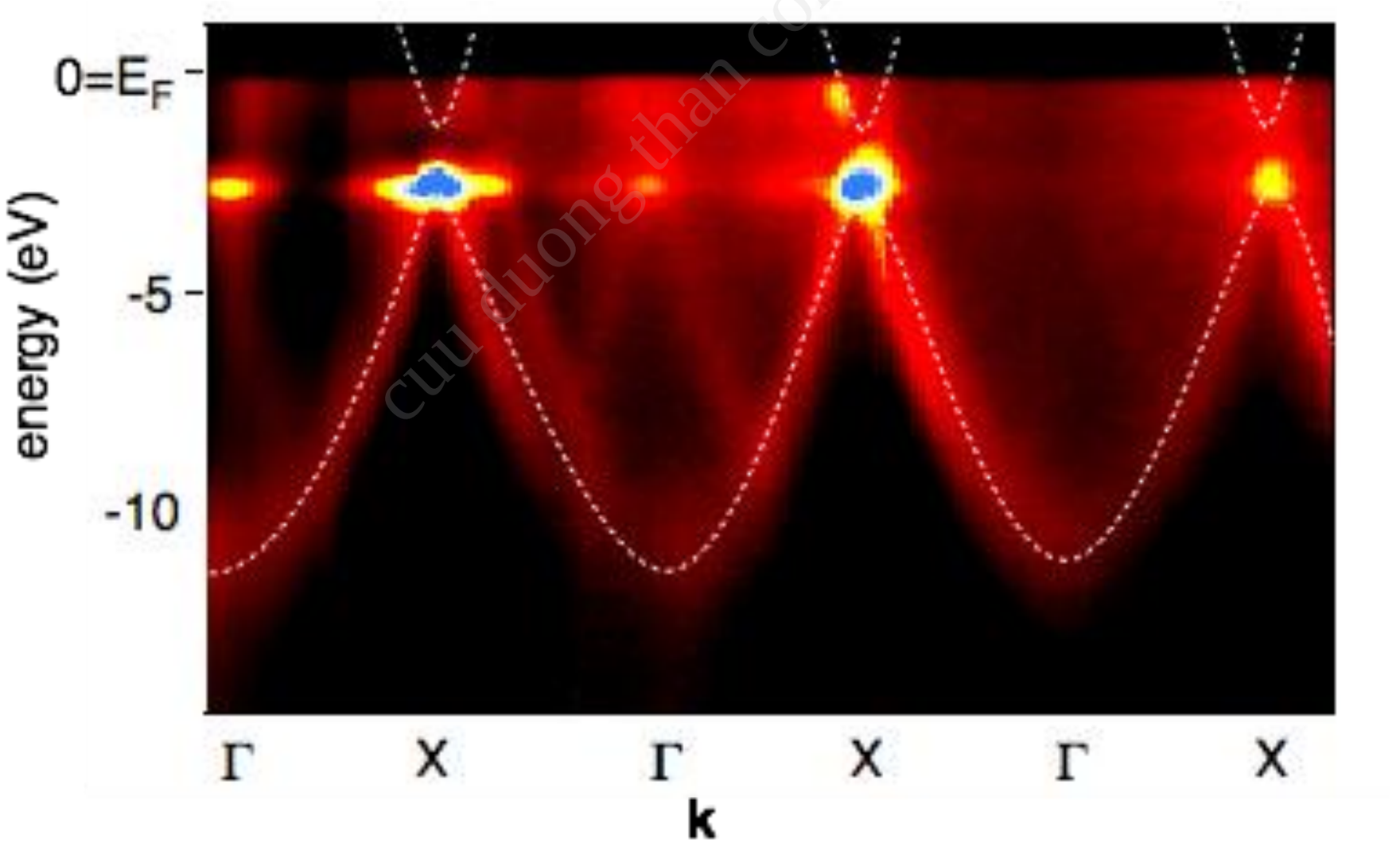
electron analyzers: hemispherical analyzer



Band structure of Al

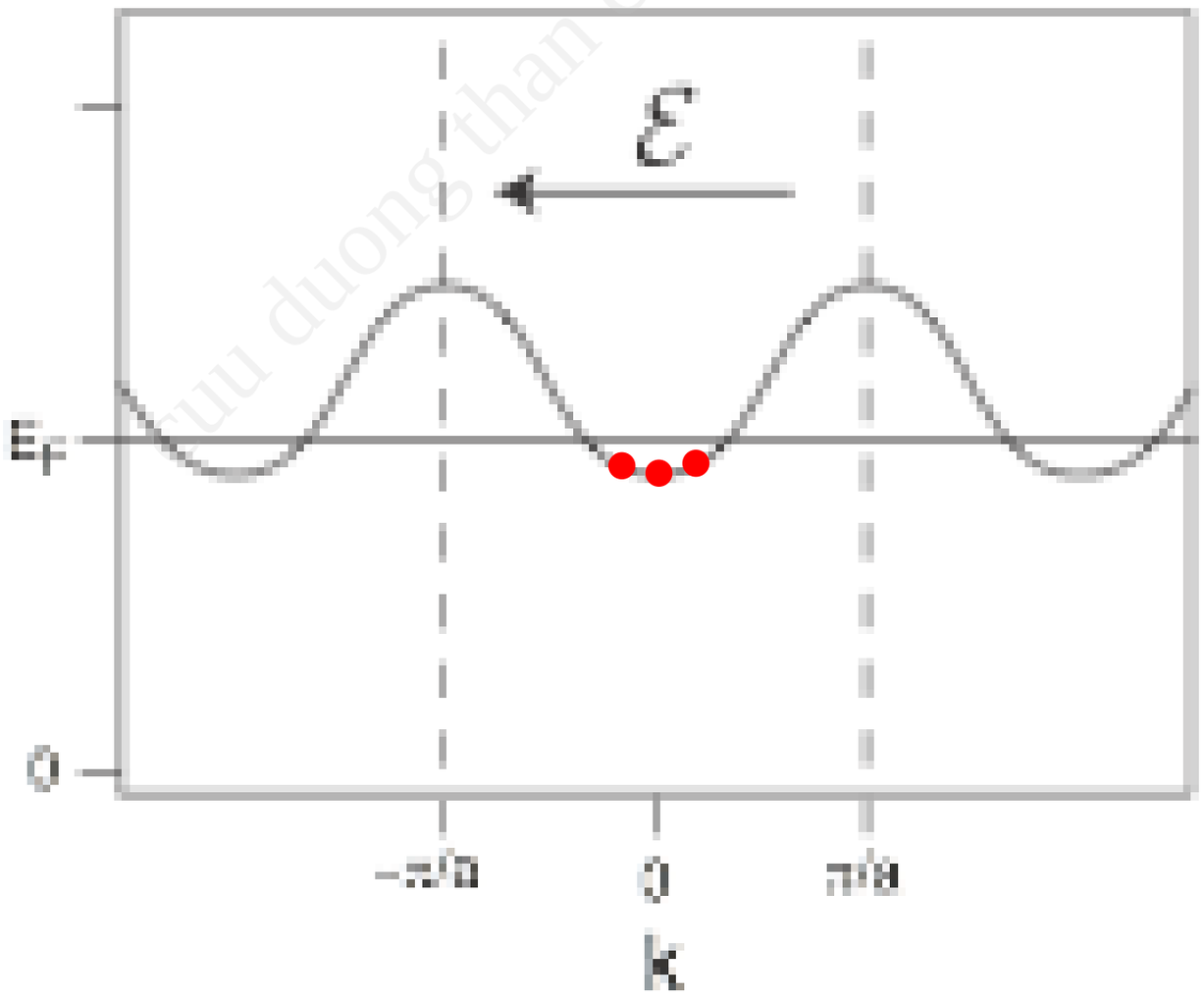


measure E, **k** outside the solid
deduce E(**k**) inside the solid



Bloch oscillations

$$\hbar \frac{dk}{dt} = -e\mathcal{E}.$$



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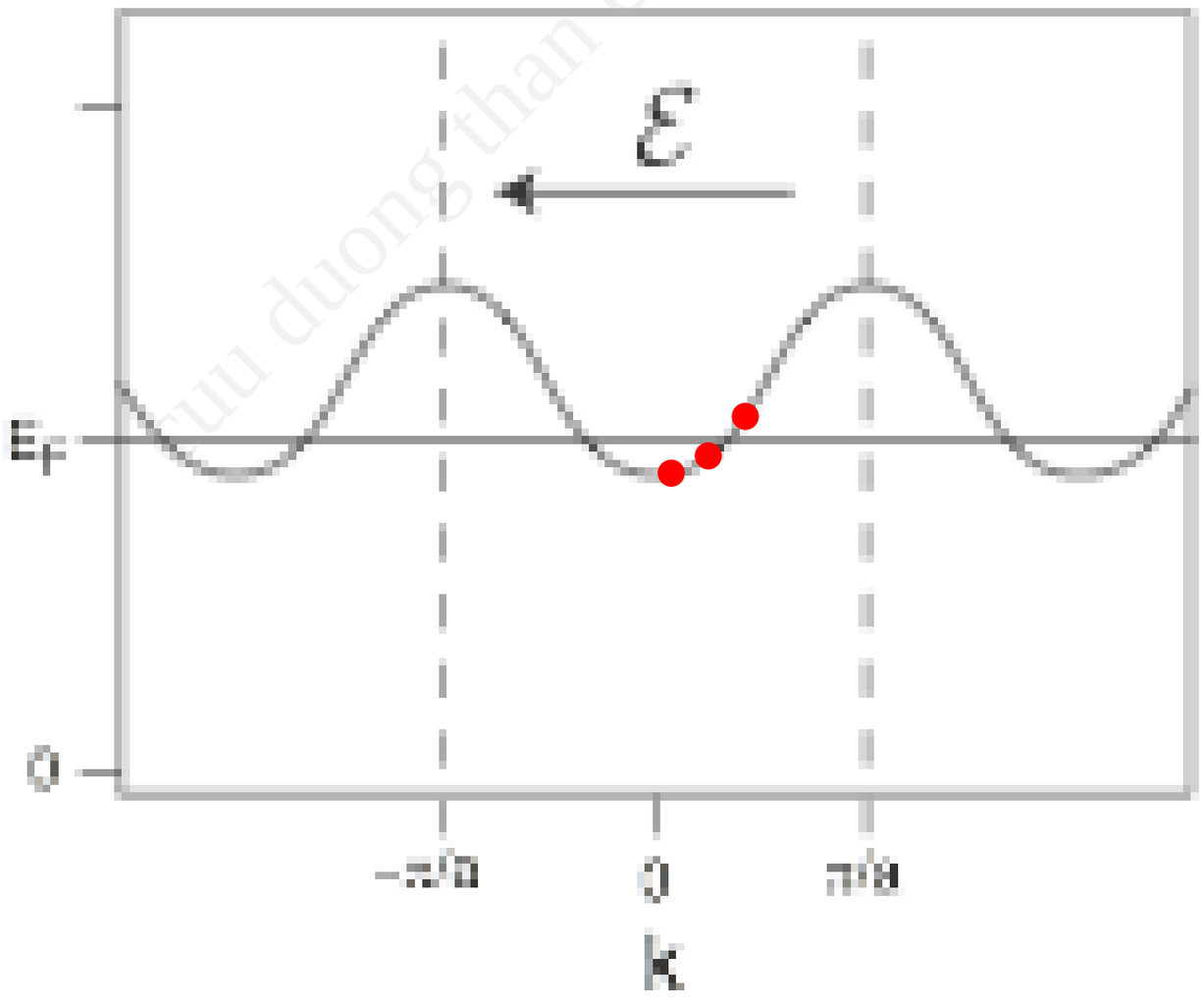

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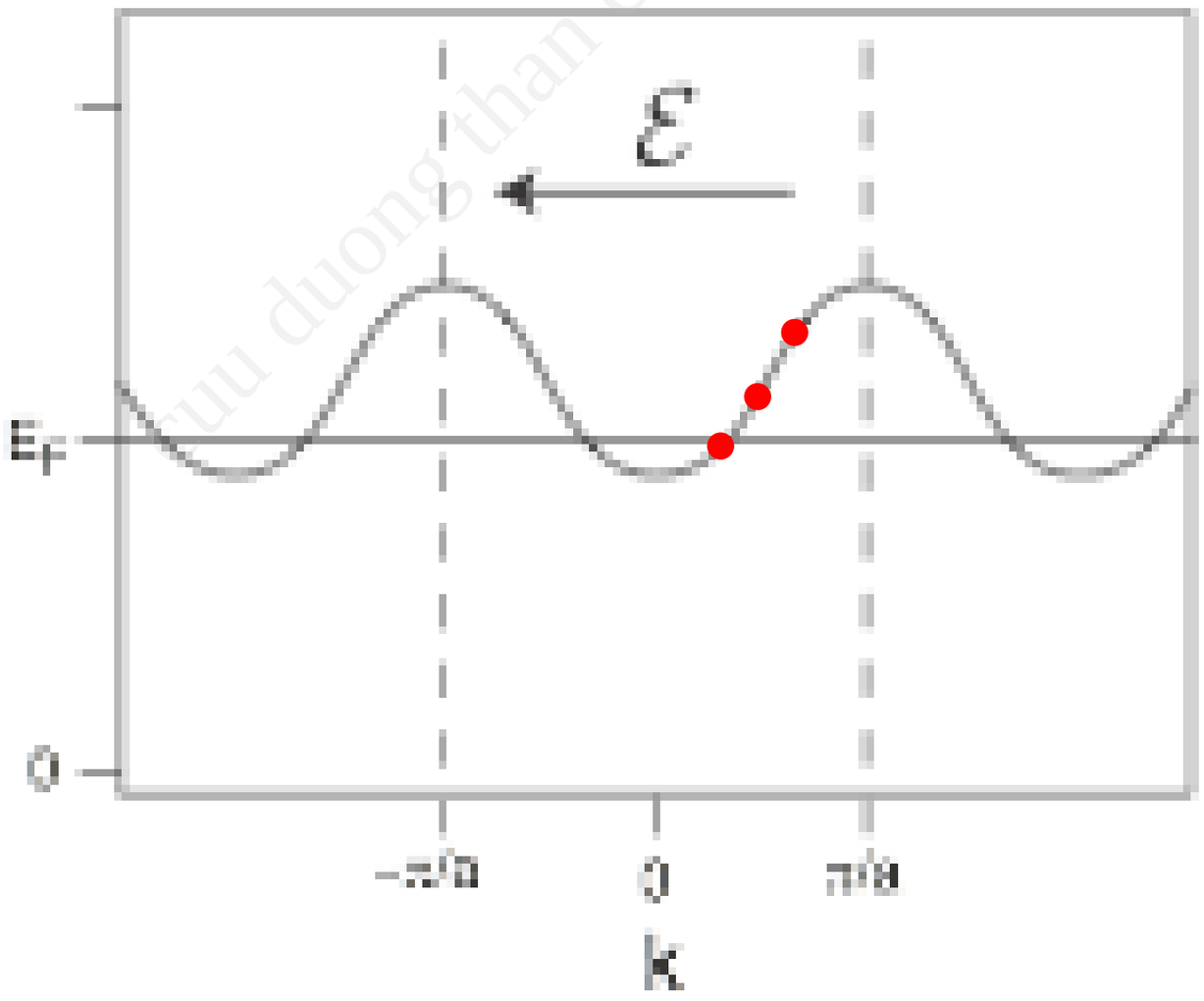

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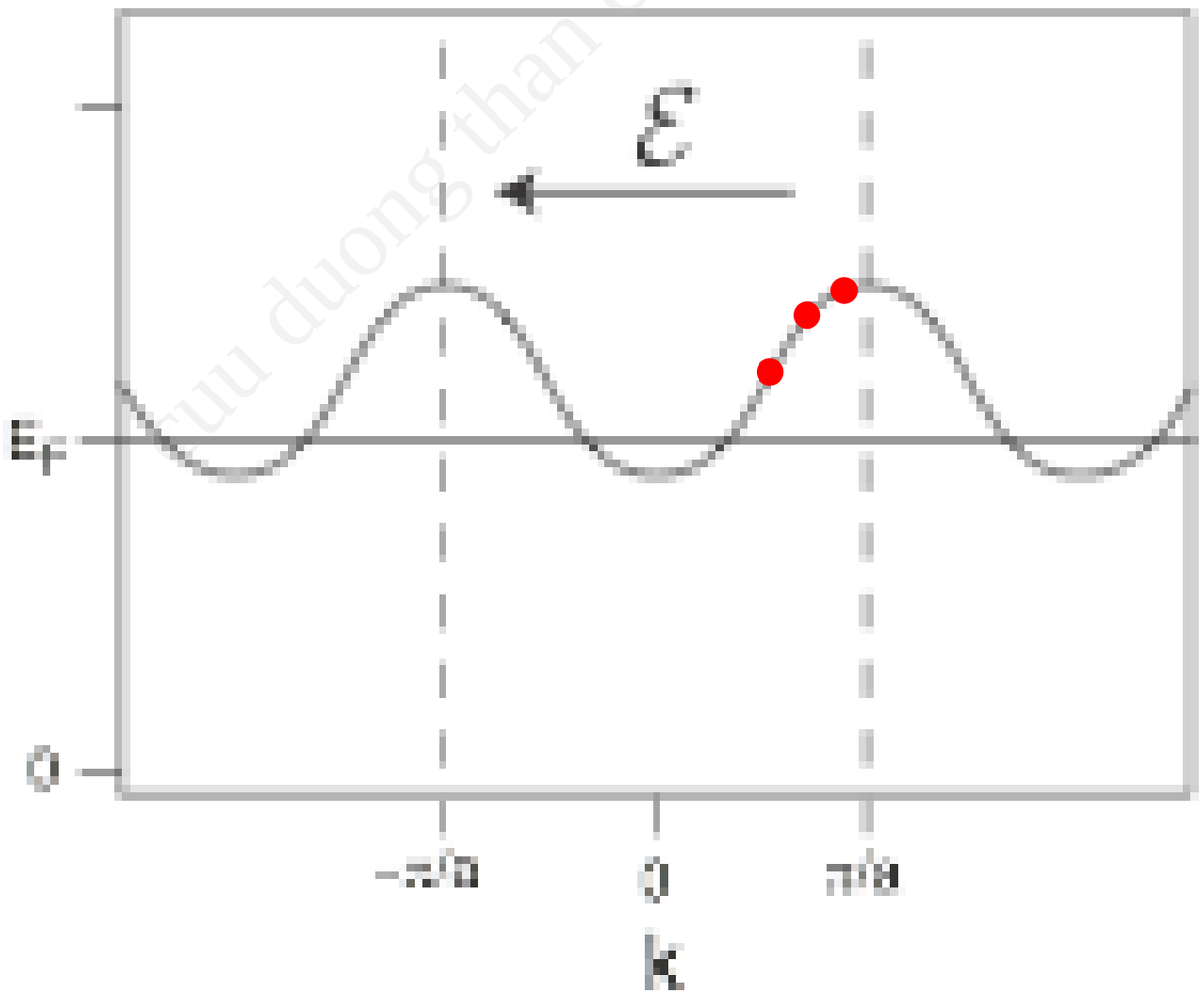

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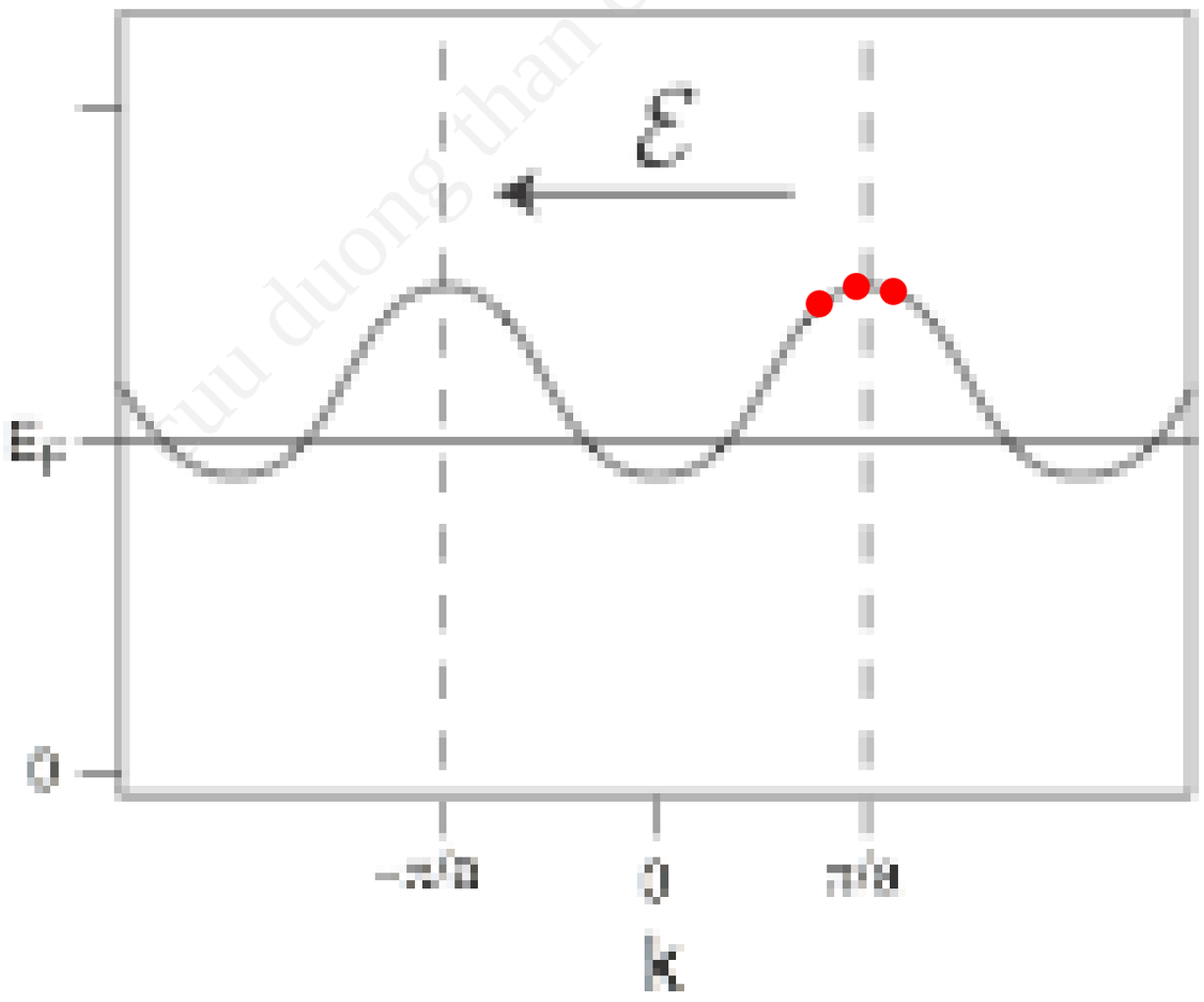

Bloch oscillations

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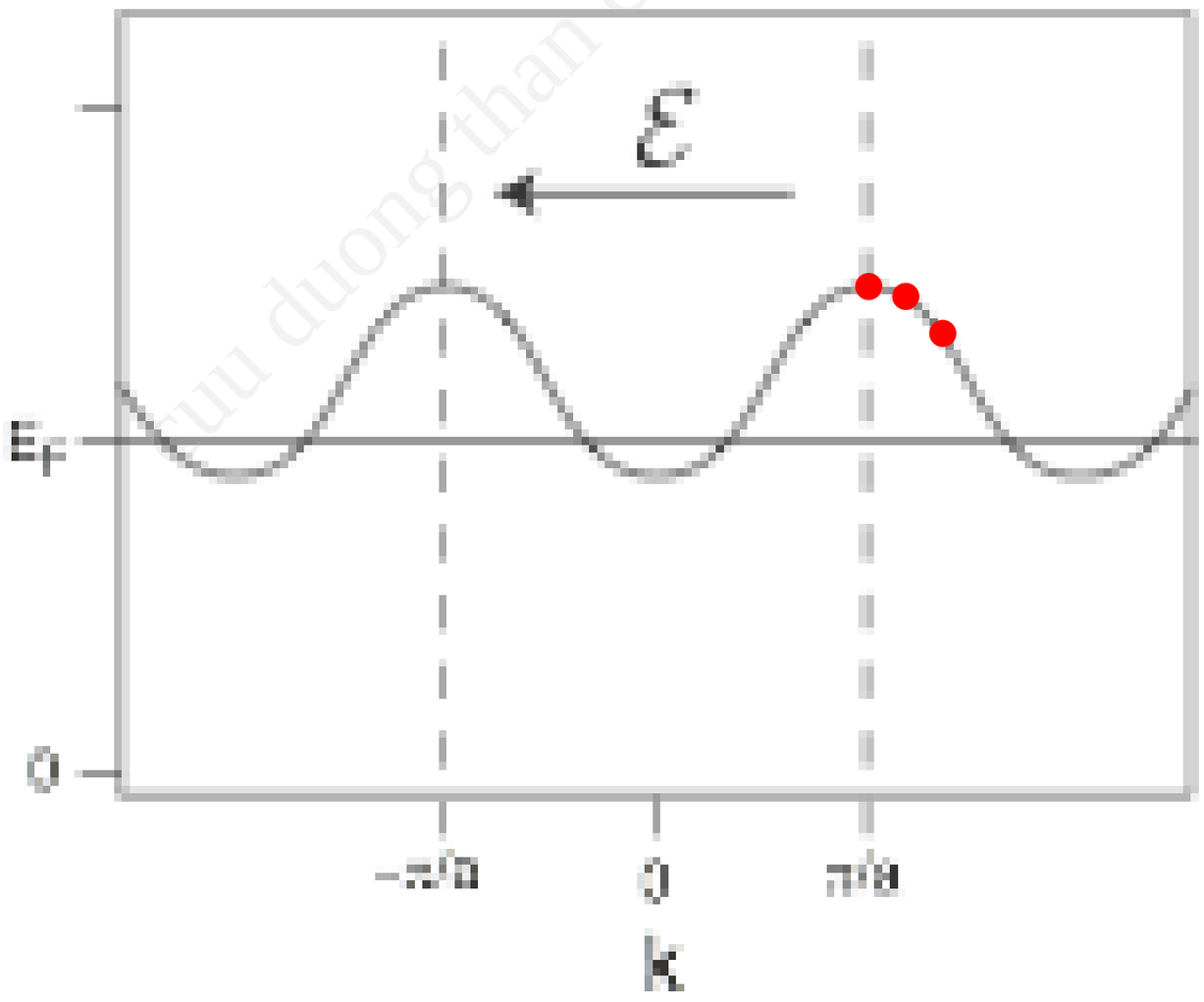
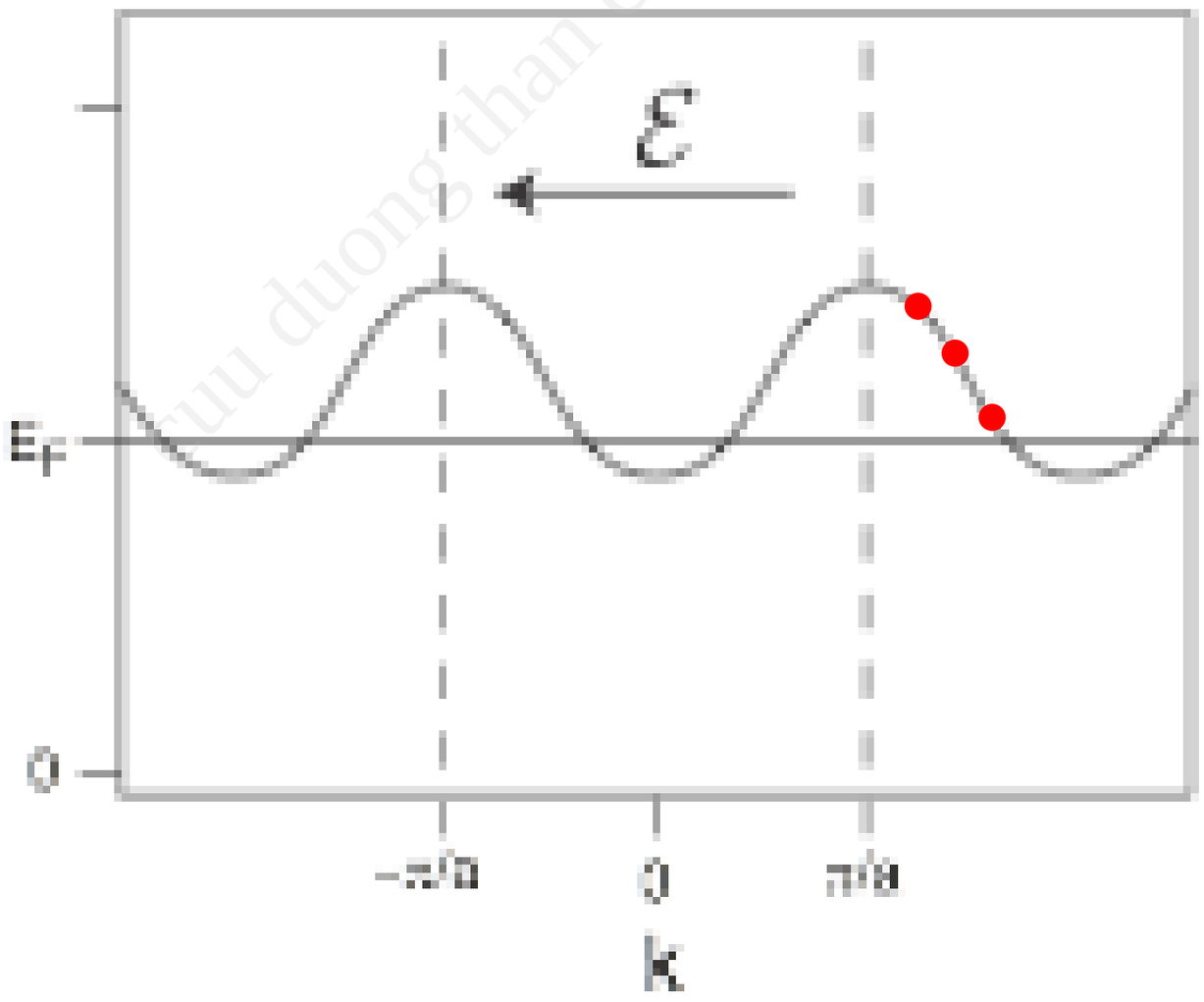


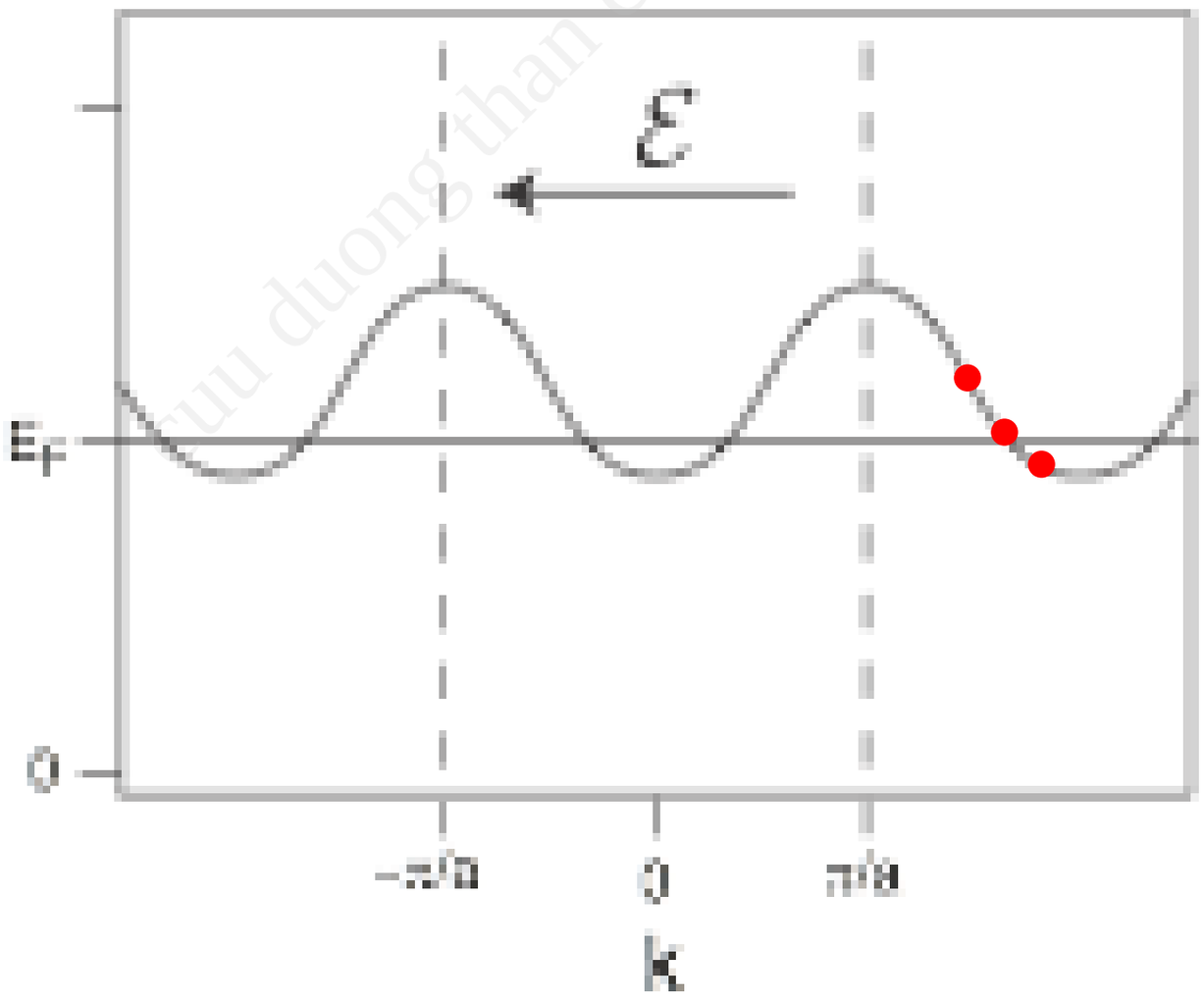
Bloch oscillations

$$\hbar \frac{dk}{dt} = -e\mathcal{E}.$$



Bloch oscillations

$$\hbar \frac{dk}{dt} = -e\mathcal{E}.$$



Bloch oscillations

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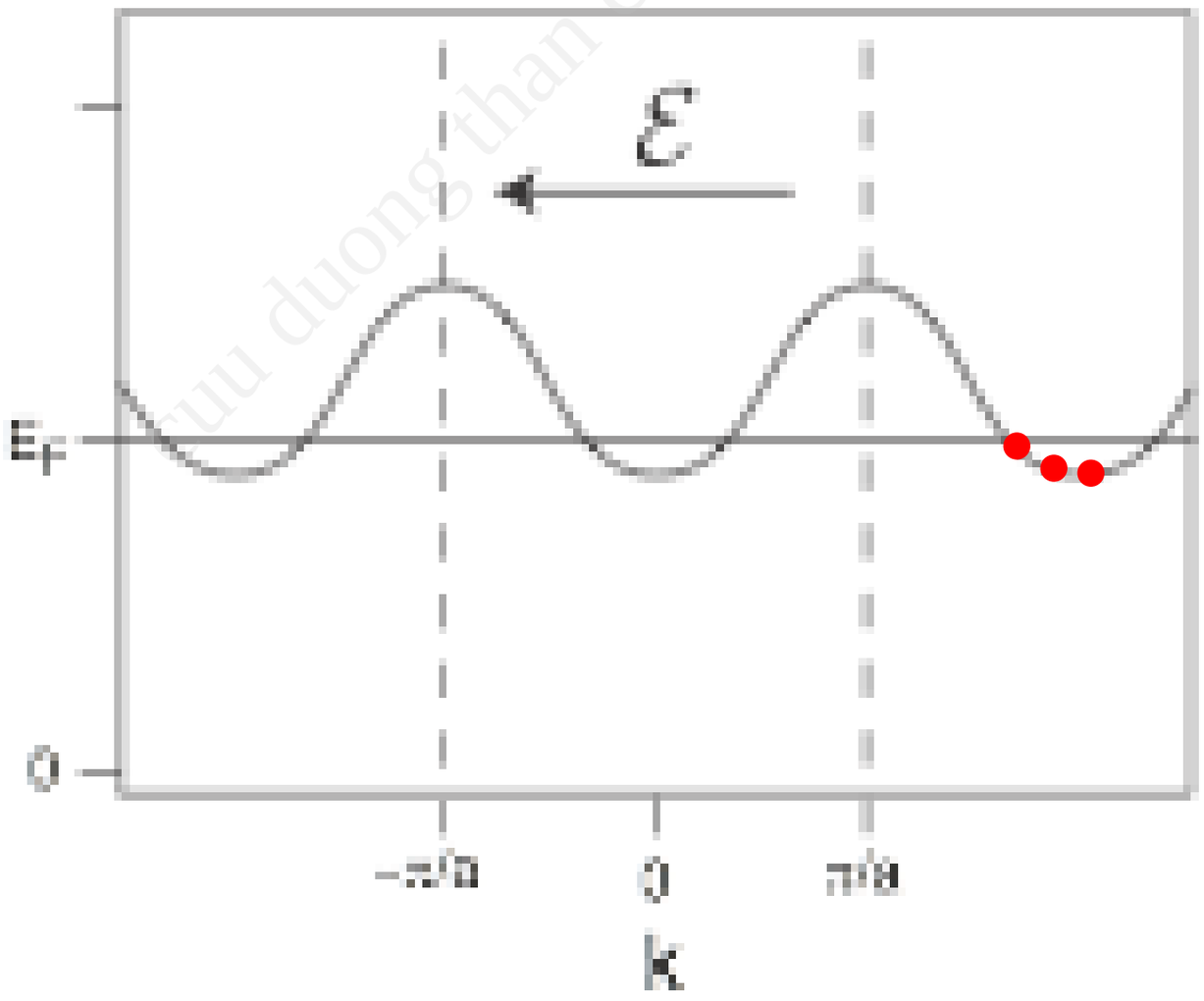

Bloch oscillations

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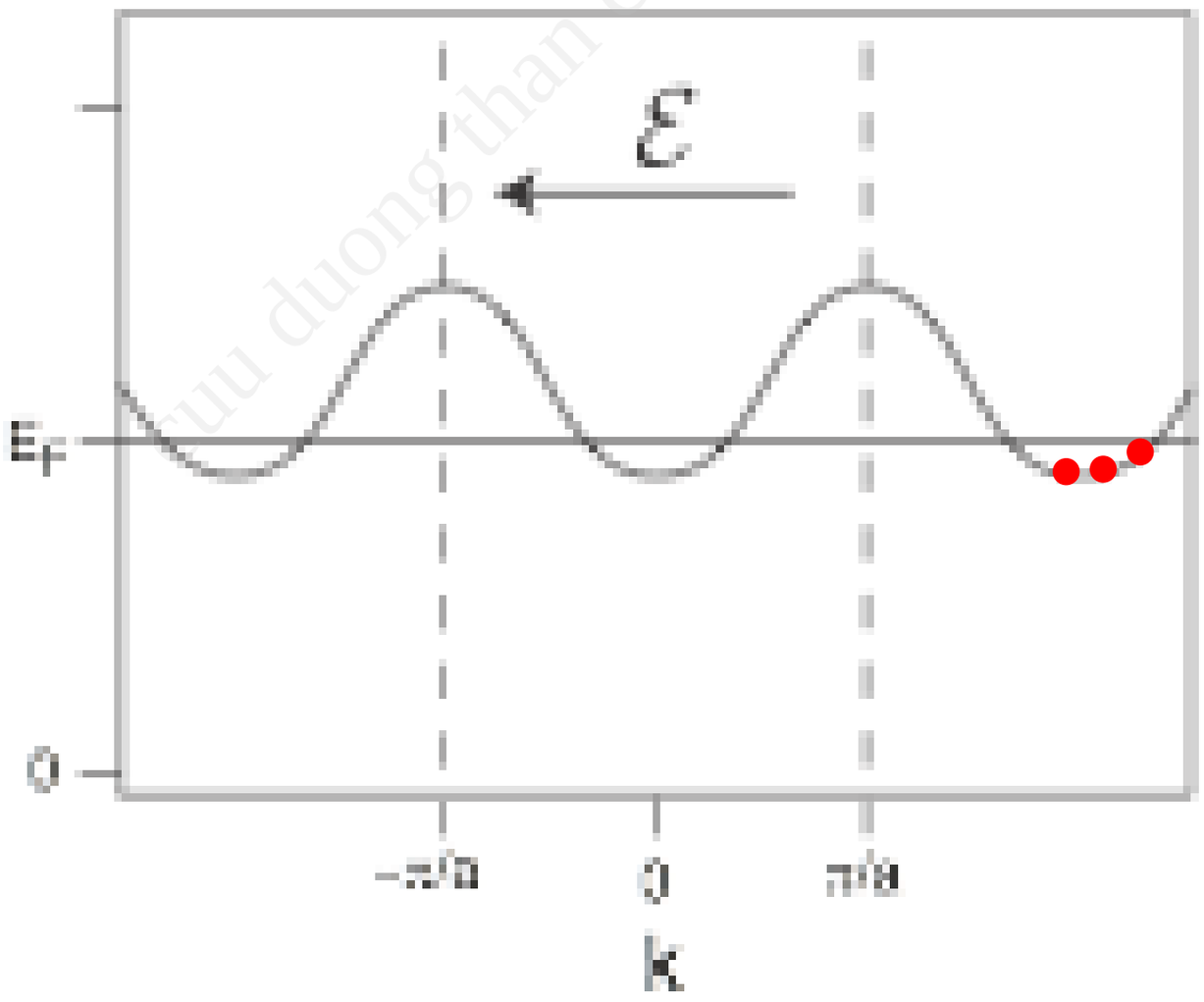
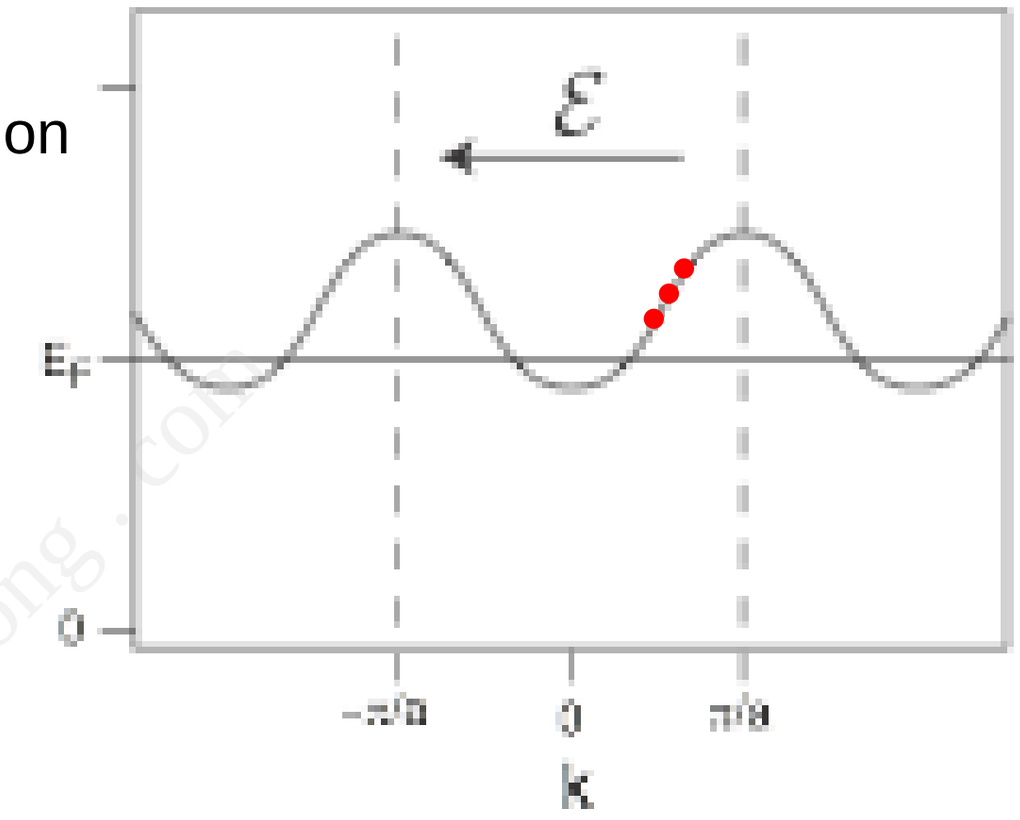


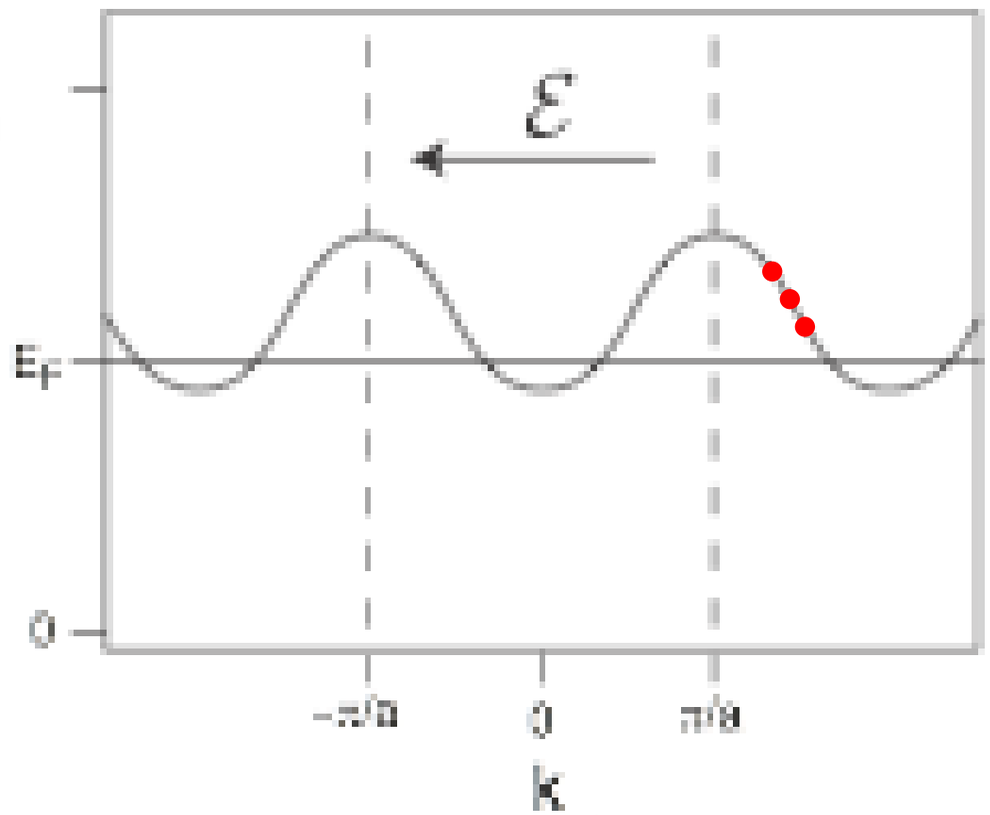
Bloch oscillations

positive group velocity
e move against field direction



$$\hbar \frac{dk}{dt} = -e\mathcal{E}.$$

negative group velocity
e move in field direction



- we get an AC current for a DC field!

Bloch oscillations

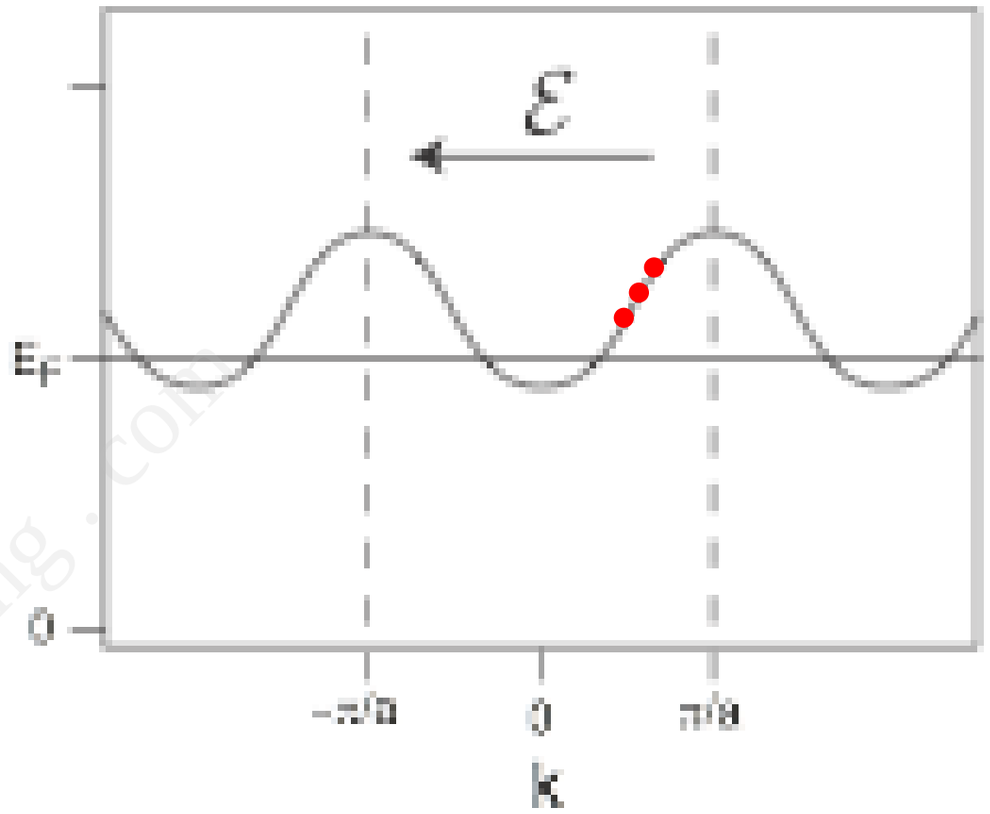
periodicity of the AC oscillation

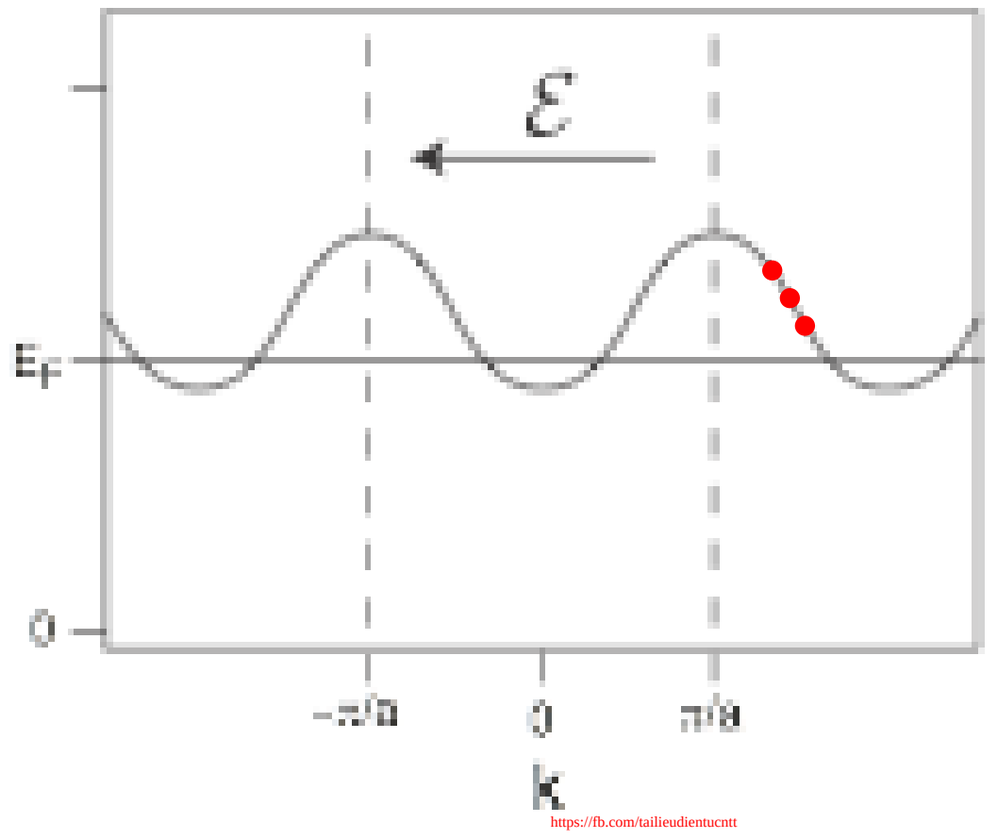
$$\hbar \frac{dk}{dt} = -e\mathcal{E}$$

how long does it take to change k by 2π/a?

$$\frac{2\pi}{a} = \Delta k = \frac{e\mathcal{E}\tau}{\hbar}$$

$$\tau = \frac{h}{e\mathcal{E}a}$$





with high field we can get 10^{-11} s or so
too long compared to typical relaxation times
possible solutions: artificial periodic structures
with larger lattice constant a