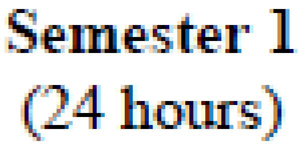
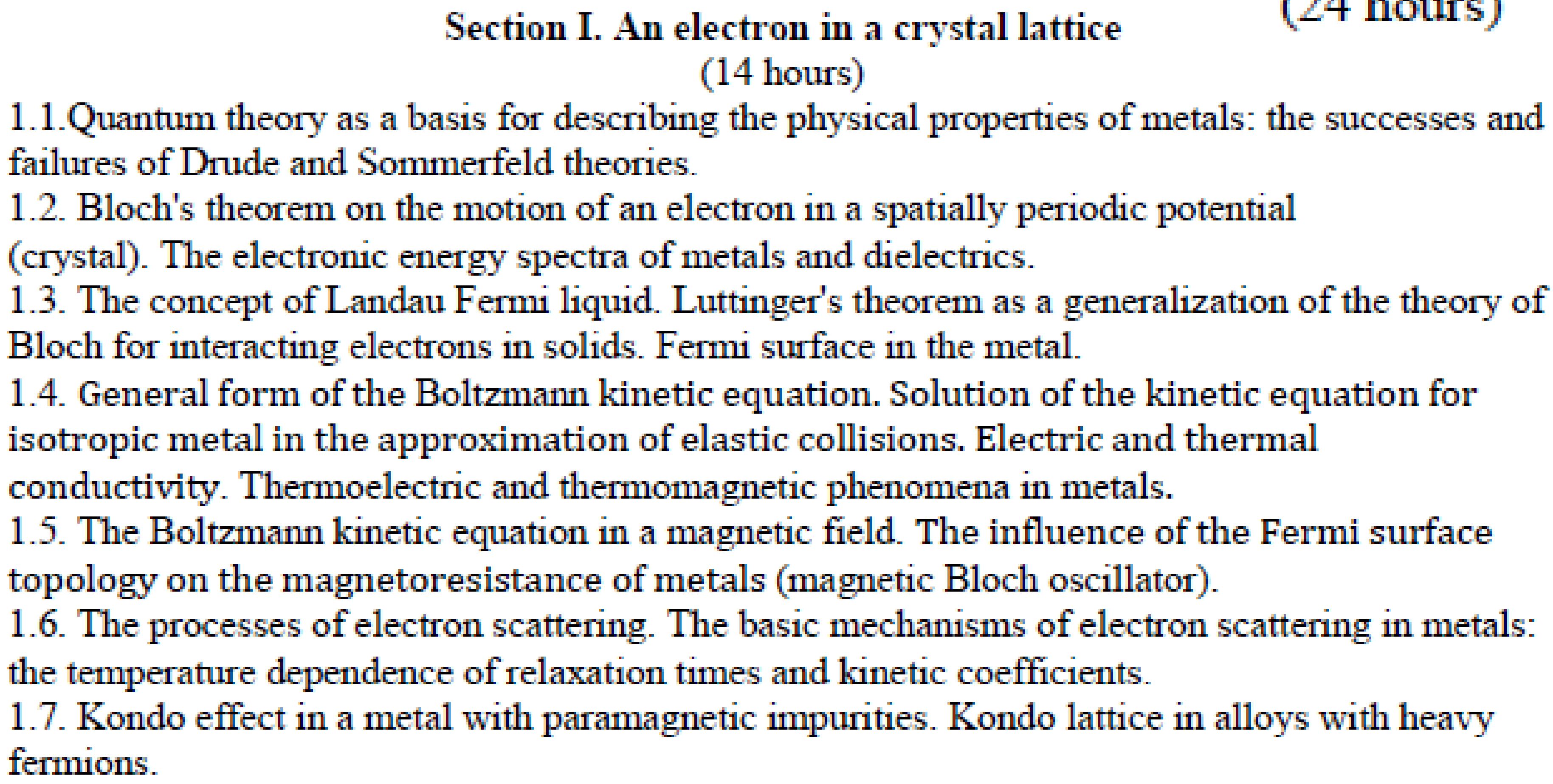
Electron Theory of Metals



Semester 1
(24 hours)



Section I. An electron in a crystal lattice
(14 hours)

1.1.Quantum theory as a basis for describing the physical properties of metals: the successes and failures of Drude and Sommerfeld theories.
1.2. Bloch's theorem on the motion of an electron in a spatially periodic potential (crystal). The electronic energy spectra of metals and dielectrics.
1.3. The concept of Landau Fermi liquid. Luttinger's theorem as a generalization of the theory of Bloch for interacting electrons in solids. Fermi surface in the metal.
1.4. General form of the Boltzmann kinetic equation. Solution of the kinetic equation for isotropic metal in the approximation of elastic collisions. Electric and thermal conductivity. Thermoelectric and thermomagnetic phenomena in metals.
1.5. The Boltzmann kinetic equation in a magnetic field. The influence of the Fermi surface topology on the magnetoresistance of metals (magnetic Bloch oscillator).
1.6. The processes of electron scattering. The basic mechanisms of electron scattering in metals: the temperature dependence of relaxation times and kinetic coefficients.
1.7. Kondo effect in a metal with paramagnetic impurities. Kondo lattice in alloys with heavy fermions.

Section 2. Normal metal in an external magnetic field. Quantum oscillations. (5-10 hours)

Section 3. Other important results without violation of metallic state. (1-4 hours)

Main textbook by A.A. Abrikosov, *Fundamentals of the Theory of Metals*

Topic 1: electrons in crystal (about 3 lectures)

Plan:

1. Some history. Models of Drude and Sommerfeld.
2. Degenerate Fermi gas. Fermi surface and Fermi energy.
3. Electrons in a crystal (periodic lattice potential). Bloch’s wave function.
4. Weak- and strong-coupling approximations for electron interaction with periodic lattice potential. Tight-binding approximation and the model of weakly bounds electrons and their results for electron dispersion in a 3D crystal.

The Drude theory

In 1900 Paul Drude proposed a model of itinerant electrons in the metal. In the model a chaotic thermal motion of the itinerant electrons gained a drift velocity as a result of application of an external electric field $\vec{E}$. So, according to Drude, electrons are accelerated by the electric field, but they dissipate their excess kinetic energy to the lattice during collisions with the ions.

The Drude model rests on the following assumptions:

- Itinerant electrons in the metal form a classical gas, and they are moving through a lattice of static ions. The system as a whole is neutral;
- Electrons do not interact with each other;
- Itinerant electrons participate in the electric current flow and collide with the lattice with a frequency $1/\tau$;
- Electron gas has temperature T.

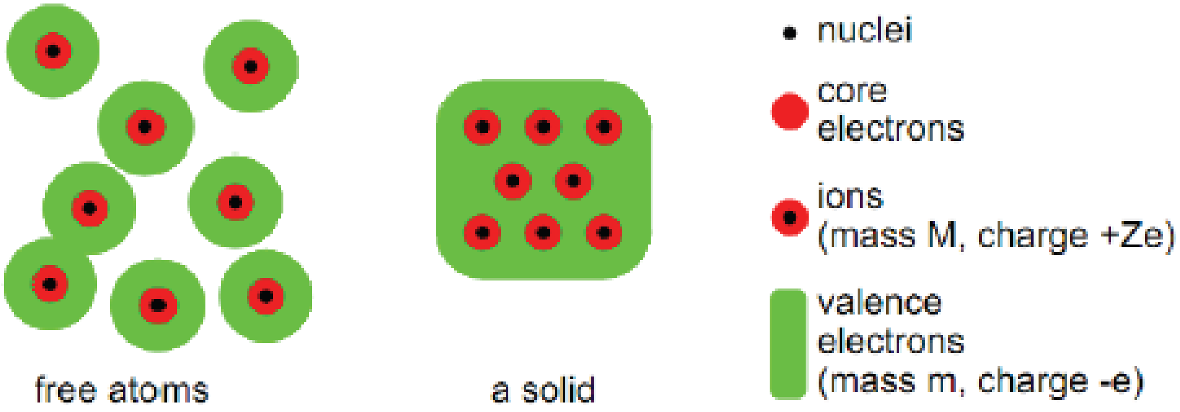


Fig. 1 A sketch of N free atoms merging into a metal. The ions are unchanged during the process where they end up by forming a periodic lattice. The valence electrons leave their host atoms and form an electron gas gluing the ionic lattice together.

Problems of the Drude model

The Drude model is purely classical model, and treats both electrons and ions as solid spheres. **The classical gas model *fails to explain important experimental facts:***

1. The electron specific heat, c_v, is overestimated: measured value is two orders of magnitude less than predicted by the Drude theory.
2. The thermoelectric power, Q, the Seebeck coefficient, is also overestimated: measured value in metals is two orders of magnitude less than predicted by the Drude theory. $S=-\Delta V/\Delta T$.
3. The electron scattering time in metal increases by a few orders of magnitude with decreasing temperature (in pure enough metallic samples), while scattering cross-section of the hard spheres (ions) experienced by classical electrons should stay constant.
4. The Hall coefficient, R_H, is known from experiments to be either positive or negative, while it follows from the Drude model that it should be always negative.

Nevertheless, the Drude formula for conductivity is valid beyond the applicability of the Drude model:

$$\vec{j}(\omega) = \sigma(\omega)\vec{E}(\omega) \qquad \sigma(\omega) = \frac{\sigma_0}{\tau^{-1} - i\omega}; \quad \sigma_0 = \frac{ne^2\tau}{m}$$

Electron transfer in external electric field

Consider motion of electron in an electric field. The second Newton's law in a momentum representation could be written as follows:

$$\frac{d\vec{p}}{dt} = -\frac{\vec{p}}{\tau} - eE \tag{1.1}$$

here the first term models scattering, second – is an electric force. Consider a simple case of electric field consisting of a single harmonic:

$$\vec{p}(t) = \mathrm{Re}\left(\vec{p}(\omega)\cdot \exp\{-i\omega t\}\right); \quad \vec{E}(t) = \mathrm{Re}\left(\vec{E}(\omega)\cdot \exp\{-i\omega t\}\right) \tag{1.2}$$

where Re is the real part of the complex function, and ω is the field frequency. Obviously, Eq. (2) can be substituted now into Eq. (1) and after solving the algebraic equation one finds:

$$-i\omega\vec{p}(\omega) = -\frac{\vec{p}(\omega)}{\tau} - \mathrm{e}\,\vec{E}(\omega) \tag{1.3}$$

Substituting the latter result into Fourier transformed expression for the density of electric current flow, we find:

$$\vec{j}(\omega) = -\frac{ne\vec{p}(\omega)}{m} = \frac{ne^2}{m}\vec{E}(\omega)\frac{1}{\tau^{-1} - i\omega} \tag{1.4}$$

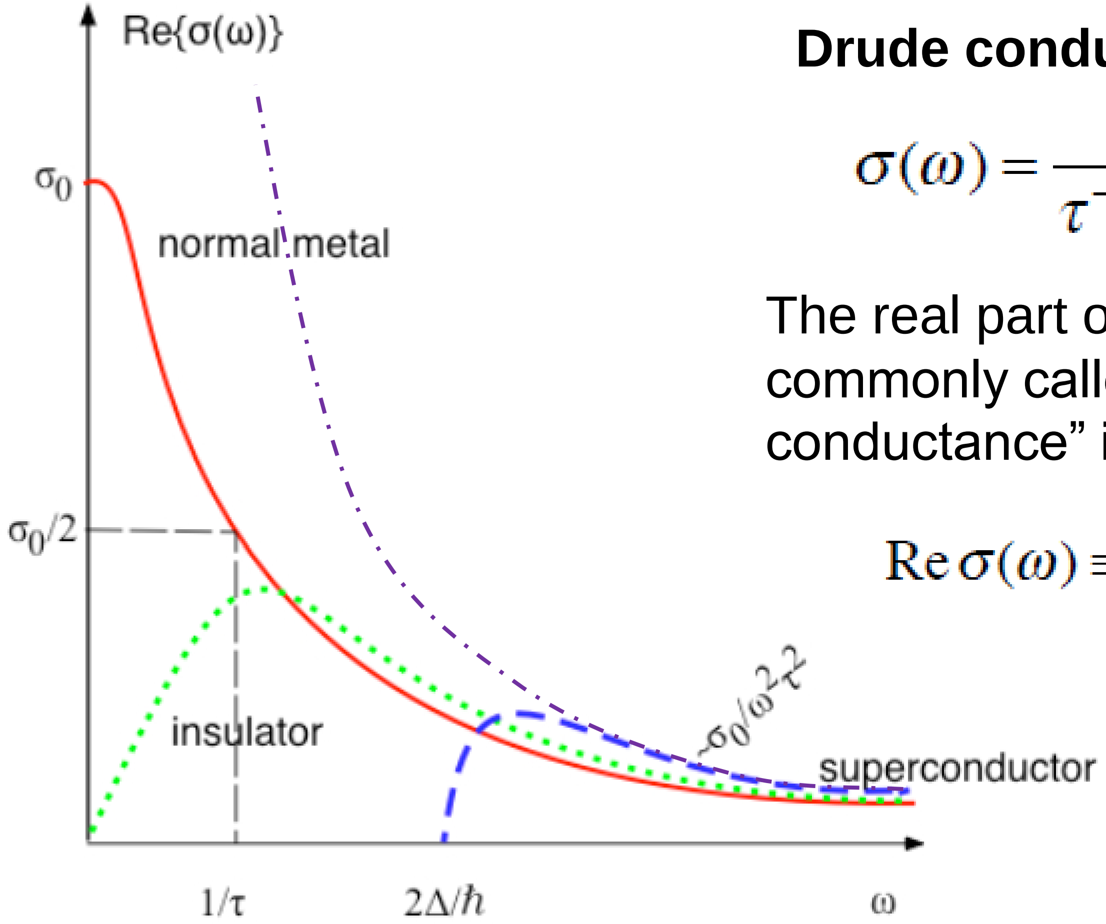
Comparing this result with the Fourier transformed Ohm's law:

$$\vec{j}(\omega) = \sigma(\omega)\vec{E}(\omega) \tag{1.5}$$

one finally obtains the famous Drude's result for the frequency dependent conductivity. Fourier-component of the electron conductivity:

$$\sigma(\omega) = \frac{\sigma_0}{\tau^{-1} - i\omega}; \quad \sigma_0 = \frac{ne^2\tau}{m} \tag{1.6}$$

Optical conductivity in the Drude theory. Its comparison in metals, insulators and superconductors



Drude conductivity

$$\sigma(\omega) = \frac{\sigma_0}{\tau^{-1} - i\omega}; \quad \sigma_0 = \frac{ne^2\tau}{m}$$

The real part of the expression above, commonly called as "optical conductance" is readily obtained:

$$\mathrm{Re}\,\sigma(\omega) \equiv \sigma'(\omega) = \frac{\sigma_0}{1+(\omega\tau)^2}$$

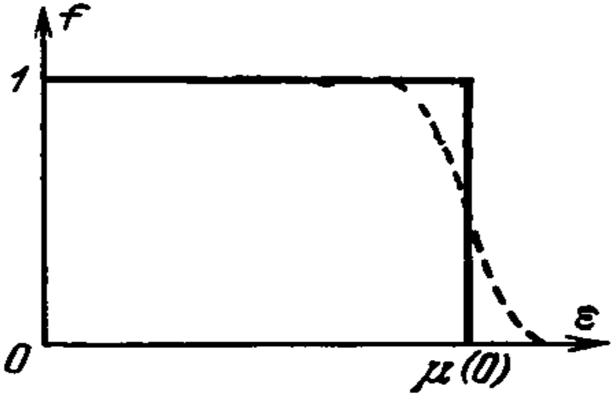
Fig.2 The curves for "optical conductance": solid line – normal metal in the Drude theory; dashed line – superconductor with the gap Δ; dotted line – insulator.

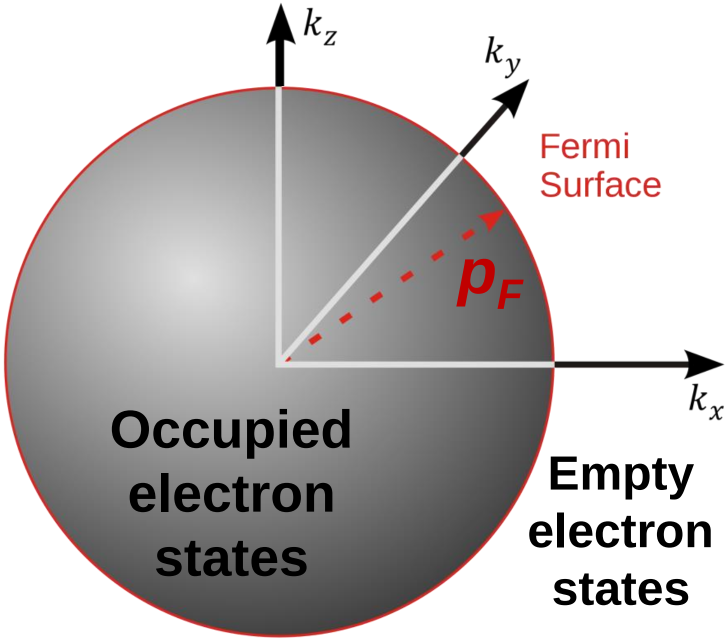
Fermi gas of free electrons.
Sommerfeld theory of metals.

Free electron dispersion relation: $E=p^2/2m$

Fermi distribution function

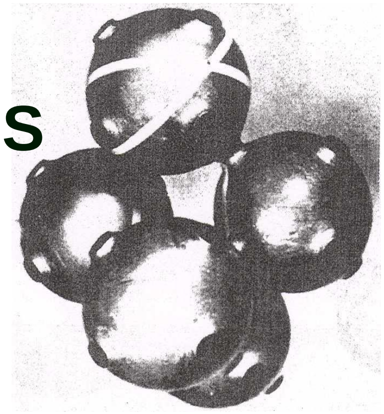
$$f=\left[e^{(\varepsilon-\mu)/T}+1\right]^{-1}.$$





Fermi surface, separating occupied ($E<E_F$) and empty ($E>E_F$) electron states in 3D space), in a free electron gas is a sphere of radius p_F in momentum space.

In crystals the FS (Fermi surface) is not a sphere:



FS of gold

The number of quantum states in the interval $d^3p = dp_x\,dp_y\,dp_z$ is equal to

$$dN=V\frac{d^3p}{(2\pi\hbar)^3}$$

Appendix: derivation of Fermi distribution from the Gibbs distribution (Landau&Lifshitz, Vol .5, Sec. 53)

The statistical sum is the sum over all energy levels with

$$Z \equiv \sum_n e^{-E_n/T} = \mathrm{tr}\, \exp\left(-\hat{H}/T\right)$$

The free energy at fixed particle number is given by the logarithm of statistical sum:

$$F = -T \log \sum_n e^{-E_n/T}$$

Thermodynamic potential for a variable number of particles and fixed chemical potential μ

$$\Omega = -T \log \sum_N \left[e^{\mu N/T} \sum_n e^{-E_{nN}/T} \right]$$

For a given quantum state k in Ω there is only a sum over particle numbers n_k:

$$\Omega_k = -T \log \sum_{n_k} \left(e^{(\mu-\varepsilon_k)/T}\right)^{n_k}$$

For fermions n_k may be only 0 or 1:

$$\Omega_k = -T \log\left(1 + e^{(\mu-\varepsilon_k)/T}\right).$$

Statistical average of particle number n_k is given by the partial derivative:

$$\overline{n_k} = -\frac{\partial \Omega_k}{\partial \mu} = \frac{e^{(\mu-\varepsilon_k)T}}{1 + e^{(\mu-\varepsilon_k)/T}} = \frac{1}{e^{(\varepsilon_k-\mu)/T} + 1}\,.$$

Sommerfeld theory of metals.

In 1927 Arnold Sommerfeld applied Fermi–Dirac statistics to the Drude model of electrons in metals, thus considering ideal Fermi gas with Fermi surface (Drude-Sommerfeld model). This enabled him to solve the unresolved problems of the Drude theory. Namely, the Pauli exclusion principle, that leads to the famous Fermi-step distribution of fermions in the ideal Fermi gas, leads to a drastic decrease of the fraction of electrons that can absorb heat and this explains the two orders of magnitude difference between classical and quantum results for the electron specific heat and thermo-power (Seebeck coefficient):

$$c_V = \frac{\pi^2}{2}\left(\frac{k_B T}{\varepsilon_F}\right) n k_B \qquad Q = -\frac{c_V}{3ne} = -\frac{\pi^2}{6}\left(\frac{k_B T}{\varepsilon_F}\right)\frac{k_B}{e}$$

where ε_F is the Fermi energy, and n is density of the Fermi gas.

In both formulas above, the Fermi gas model brings extra small factor $k_B T/\varepsilon_F$ that multiplies, essentially, the Drude's results. **Another achievement of the Sommerfeld's theory of metals was exact derivation of the *Lorenz number* in the *Wiedemann-Franz law*, which is in excellent agreement with experiments:**

$$\frac{\kappa}{\sigma T} = \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2 \longleftarrow$$

Lorenz number

Here κ is the thermal conductance of the electron gas, e is electron charge (modulus) and k_B is the Boltzmann constant.

Appendix: derivation of heat capacity of Fermi gas (1)

The energy of Fermi gas is given by a sum over all states with the weight of their filling factor:

$$E = 2\int \varepsilon(\boldsymbol{p})\, f\, d^3\boldsymbol{p}\,\frac{V}{(2\pi\hbar)^3},$$ where $f = [\mathrm{e}^{(\varepsilon-\mu)/T}+1]^{-1}$.

Heat capacity is the derivative of energy as function of temperature:

$$C = V^{-1}\left(\frac{\partial E}{\partial T}\right)_V = 2\int \varepsilon(\boldsymbol{p})\,\frac{\partial f}{\partial T}\,\frac{\mathrm{d}^3\boldsymbol{p}}{(2\pi\hbar)^3}.$$

$$\frac{\partial f}{\partial T} = T^{-1}\,\frac{\mathrm{e}^{(\varepsilon-\mu)/T}}{(\mathrm{e}^{(\varepsilon-\mu)/T}+1)^2}\left(\frac{\varepsilon-\mu}{T}+\frac{\mathrm{d}\mu}{\mathrm{d}T}\right) = -\frac{\partial f}{\partial \varepsilon}\left(\frac{\varepsilon-\mu}{T}+\frac{\mathrm{d}\mu}{\mathrm{d}T}\right),$$

where $$\frac{\partial f}{\partial \varepsilon} = -T^{-1}\,\frac{\mathrm{e}^{(\varepsilon-\mu)/T}}{(\mathrm{e}^{(\varepsilon-\mu)/T}+1)^2} = -(4T)^{-1}\cosh^{-2}\left(\frac{\varepsilon-\mu}{2T}\right)$$

The derivative dμ/dT can be taken from the identity

$$\frac{\partial}{\partial T}\frac{N}{V} = -2\int \frac{\partial f}{\partial \varepsilon}\left(\frac{\varepsilon-\mu}{T}+\frac{\mathrm{d}\mu}{\mathrm{d}T}\right)\frac{\mathrm{d}^3\boldsymbol{p}}{(2\pi\hbar)^3} = 0$$

and the integrals over d^3p are expressed via the integrals over the Fermi surface *S* and ε:

$$\int \cdots \mathrm{d}^3\boldsymbol{p} = \int \cdots \mathrm{d}\varepsilon \int \frac{\mathrm{d}S}{v}.$$

Here we used $d\varepsilon = v dp$, because $v_i = \partial\varepsilon/\partial p_i$

Appendix: derivation of heat capacity of Fermi gas (2)

Using the identities:

$$\int \frac{\partial f}{\partial \varepsilon}\, d\varepsilon = -1 \quad \text{and} \quad \int (\varepsilon-\mu)^2 \frac{\partial f}{\partial \varepsilon}\, d\varepsilon = -(4T)^{-1} \int_{-\infty}^{\infty} \frac{z^2\, dz}{\cosh^2(z/2T)} = -\frac{\pi^2 T^2}{3}.$$

for arbitrary but smooth function

$$F(\varepsilon) = F(\mu) + (\varepsilon-\mu)F'(\mu) + \tfrac{1}{2}(\varepsilon-\mu)^2 F''(\mu) + \cdots$$

we obtain the integral

$$\int F(\varepsilon)\frac{\partial f}{\partial \varepsilon}\, d\varepsilon \approx -F(\mu) - \tfrac{1}{6}\pi^2 T^2\, F''(\mu).$$

Then the integrals

$$C = -2\int \varepsilon \frac{\partial f}{\partial \varepsilon}\left(\frac{\varepsilon-\mu}{T} + \frac{d\mu}{dT}\right)\frac{d^3p}{(2\pi\hbar)^3}, \quad \frac{\partial}{\partial T}\frac{N}{V} = -2\int \frac{\partial f}{\partial \varepsilon}\left(\frac{\varepsilon-\mu}{T} + \frac{d\mu}{dT}\right)\frac{d^3p}{(2\pi\hbar)^3} = 0$$

give

$$C = \mu\nu(\mu)\frac{d\mu}{dT} + \tfrac{1}{3}\pi^2 T \frac{d}{d\mu}(\mu\nu(\mu)), \quad \text{and} \quad \frac{d}{dT}\left(\frac{N}{V}\right) = \nu(\mu)\frac{d\mu}{dT} + \tfrac{1}{3}\pi^2 T \frac{d\nu(\mu)}{d\mu} = 0.$$

The last condition gives

$$\frac{d\mu}{dT} = -\tfrac{1}{3}\pi^2 T \frac{\nu'(\mu)}{\nu(\mu)}, \quad \textbf{and} \quad \mu(T) = \mu(0) - \tfrac{1}{6}\pi^2 T^2 \frac{\nu'(\mu)}{\nu(\mu)}$$

where $\nu(\varepsilon)$ is the density of states (DoS), and $\nu(\mu)$ is DoS at the Fermi level

Finally, for the heat capacity we obtain

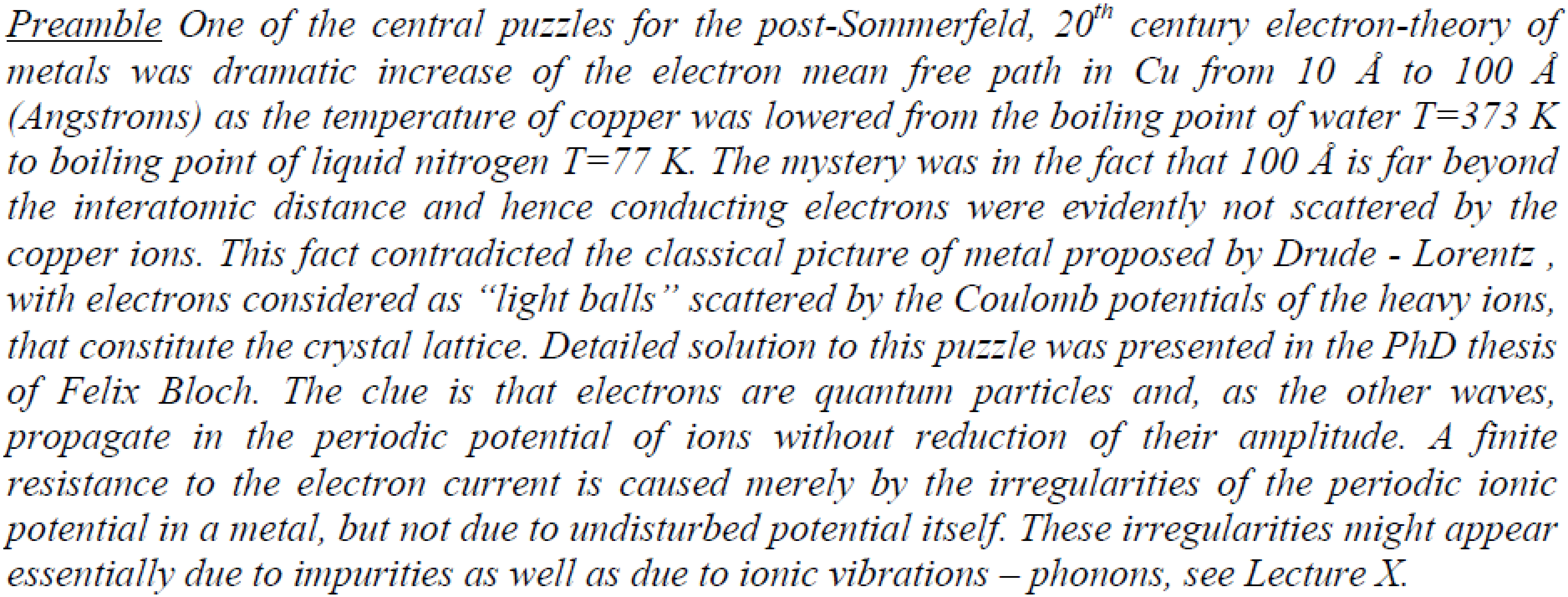
$$\boxed{C = \tfrac{1}{3}\pi^2\, T\nu(\mu).}$$

Problems of Sommerfeld model

Nevertheless, disregard of electron-electron and electron-lattice interactions left the following problems unresolved within the framework of Sommerfeld model:

1. The Hall coefficient, R_H, is known from experiments to be either positive or negative, while it still follows even from Sommerfeld model that it should be always negative; besides, the model cannot explain not vanishing value and magnetic field dependence of the magnetoresistence.
2. Besides the linear term in the specific heat experimentally one finds a cubic term as well, which has different sign and the significantly different order of magnitude than high temperature corrections to Sommerfeld calculation.
3. The sign of the Seebeck coefficient is known from experiments to be either positive or negative, while it follows from Sommerfeld model that it should be always negative.
4. Why there exist insulators which have valence electrons while in atomic state, and how the number of conducting (itinerant) electrons is determined in the metals built from elements of variable valences?
5. How to explain temperature dependence of the resistivity at low temperatures and deviations from the Wiedemann-Franz law?

Electrons in a crystalline lattice



Preamble One of the central puzzles for the post-Sommerfeld, 20th century electron-theory of metals was dramatic increase of the electron mean free path in Cu from 10 Å to 100 Å (Angstroms) as the temperature of copper was lowered from the boiling point of water T=373 K to boiling point of liquid nitrogen T=77 K. The mystery was in the fact that 100 Å is far beyond the interatomic distance and hence conducting electrons were evidently not scattered by the copper ions. This fact contradicted the classical picture of metal proposed by Drude - Lorentz , with electrons considered as "light balls" scattered by the Coulomb potentials of the heavy ions, that constitute the crystal lattice. Detailed solution to this puzzle was presented in the PhD thesis of Felix Bloch. The clue is that electrons are quantum particles and, as the other waves, propagate in the periodic potential of ions without reduction of their amplitude. A finite resistance to the electron current is caused merely by the irregularities of the periodic ionic potential in a metal, but not due to undisturbed potential itself. These irregularities might appear essentially due to impurities as well as due to ionic vibrations – phonons, see Lecture X.

In fact, the quantum-mechanical problem of an electron in a periodic 3D potential is complicated, and the result may strongly differ from the free-electron model, because the electrons are strongly scattered by the wave vectors of 3D periodic modulation.

Energy bands

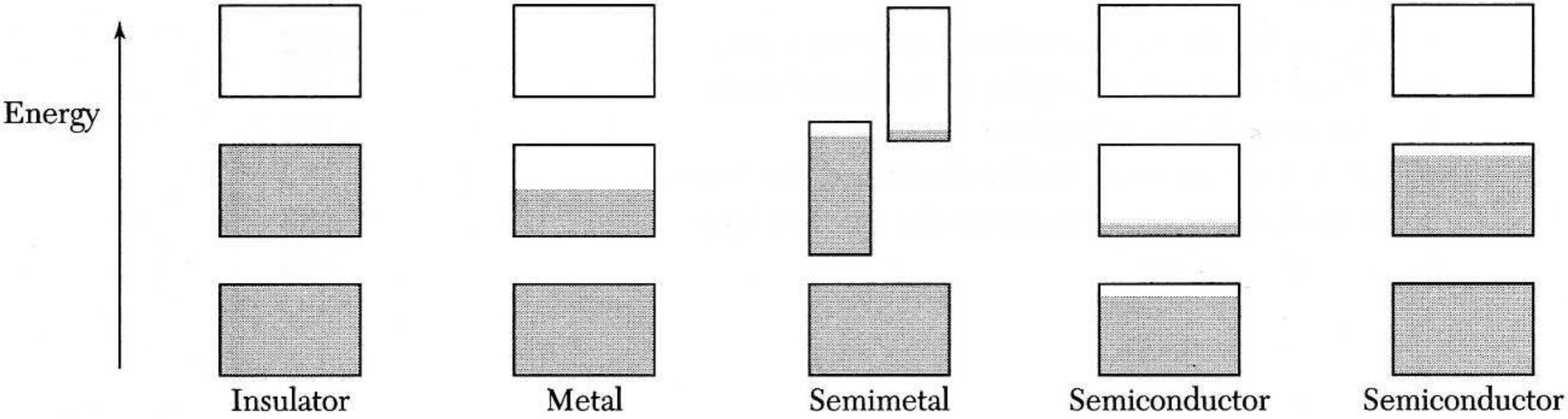
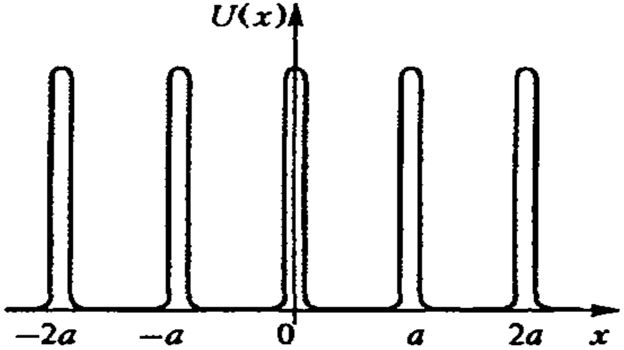


Figure 1 Schematic electron occupancy of allowed energy bands for an insulator, metal, semimetal, and semiconductor. The vertical extent of the boxes indicates the allowed energy regions; the shaded areas indicate the regions filled with electrons. In a **semimetal** (such as bismuth) one band is almost filled and another band is nearly empty at absolute zero, but a pure **semiconductor** (such as silicon) becomes an insulator at absolute zero. The left of the two semiconductors shown is at a finite temperature, with carriers excited thermally. The other semiconductor is electron-deficient because of impurities.

Electron in a 1D crystalline lattice



Problem in a quantum mechanics:
a particle in a one-dimensional (1D) periodic potential (ideal crystal) $U = \alpha \sum_{n=-\infty}^{\infty} \delta(x-na)$

The general solution is $\Psi = A_n \exp\{ik(x-na)\} + B_n \exp\{-ik(x-na)\}$,

where $k = \sqrt{2mE/\hbar^2}$. From $\Psi(x+a) = \mu\Psi(x)$, => $A_{n-1} = \frac{A_n}{\mu}$, $B_{n-1} = \frac{B_n}{\mu}$.

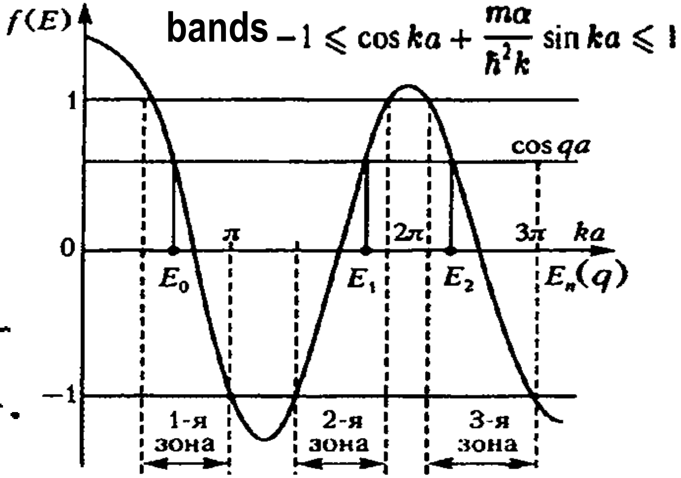
From sewing of wave functions $A_n + B_n = \exp\{ika\}A_{n-1} + \exp\{-ika\}B_{n-1}$,

at $x=na$ we get $\left(1+\frac{2im\alpha}{\hbar^2 k}\right)A_n - \left(1-\frac{2im\alpha}{\hbar^2 k}\right)B_n = \exp\{ika\}A_{n-1} - \exp\{-ika\}B_{n-1}$.

This system of equations gives:

$$\mu^2 - 2\mu f(E) + 1 = 0,$$

$$f(E) \equiv \cos ka + \frac{m\alpha}{\hbar^2 k}\sin ka,$$


bands $-1 \leqslant \cos ka + \frac{m\alpha}{\hbar^2 k}\sin ka \leqslant 1$

Electron dispersion is given by the equation:

$$\cos qa = \cos\sqrt{\frac{2ma^2E_n}{\hbar^2}} + m\alpha\frac{1}{(2m\hbar^2E_n)^{1/2}}\sin\sqrt{\frac{2ma^2E_n}{\hbar^2}}.$$

Kronig-Penney periodic potential

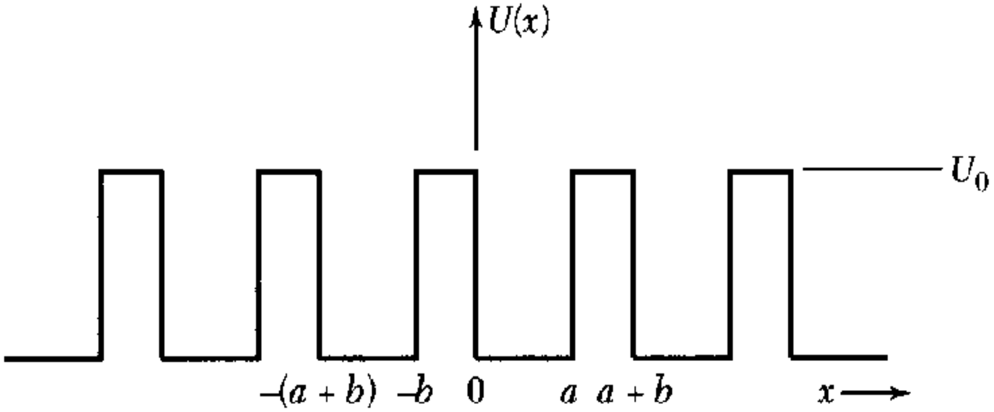


Figure 4 Square-well periodic potential as introduced by Kronig and Penney.

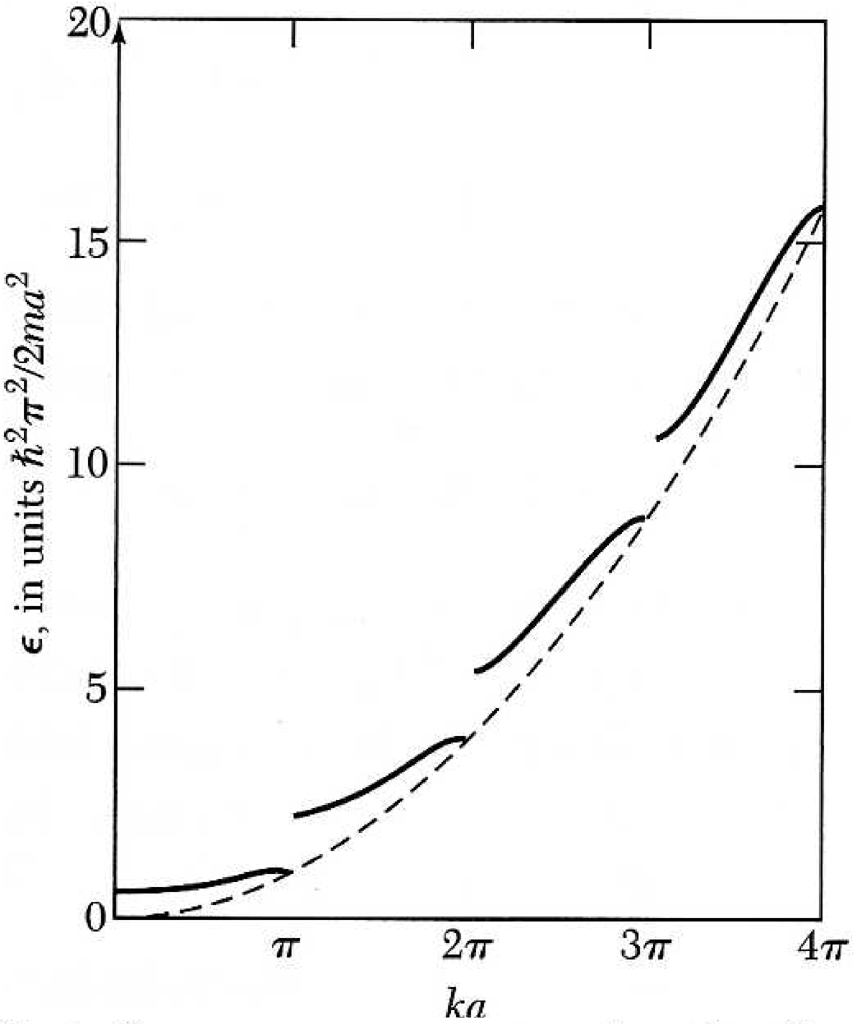
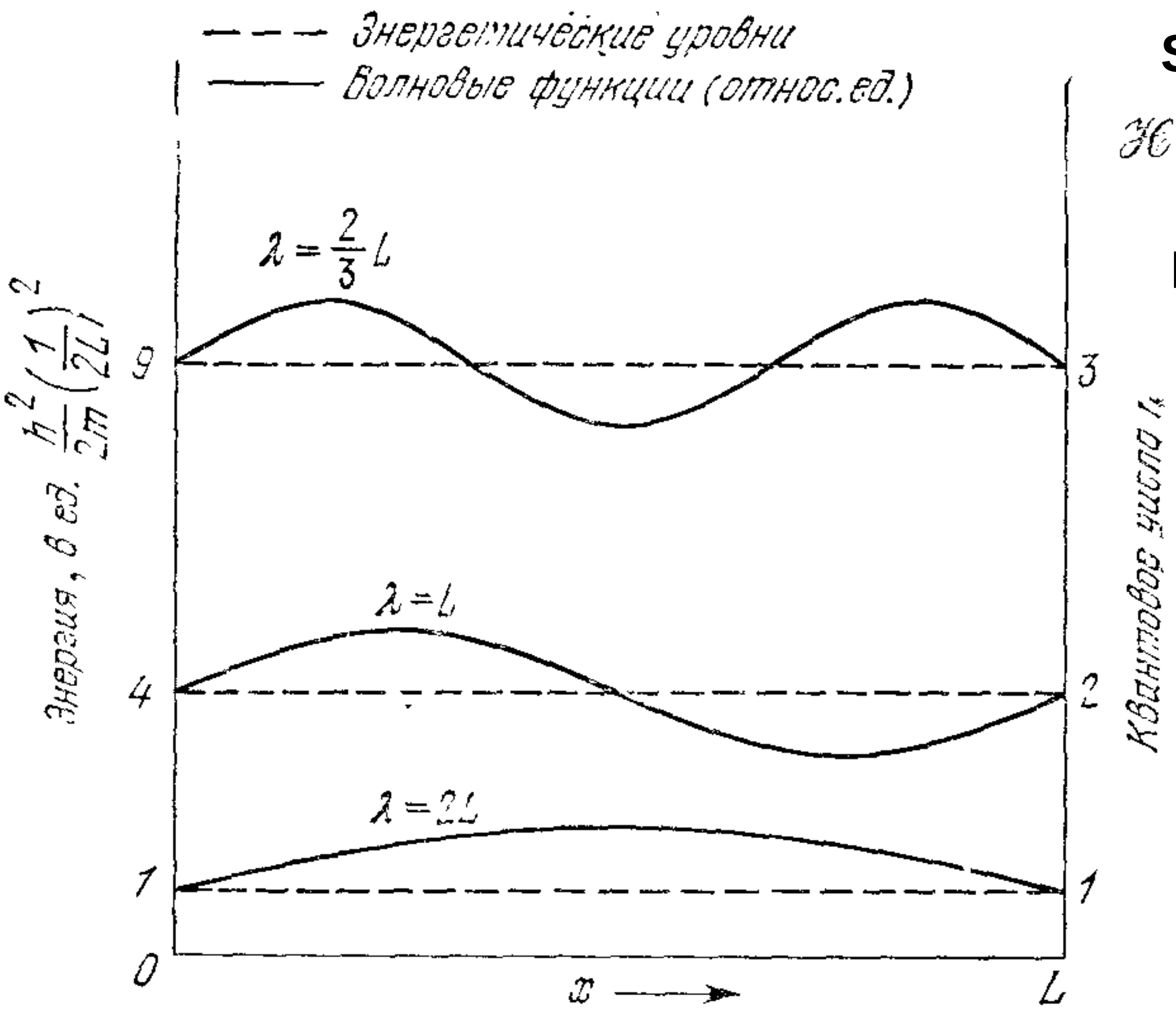


Figure 6 Plot of energy vs. wavenumber for the Kronig-Penney potential, with $P = 3\pi/2$. Notice the energy gaps at $ka = \pi, 2\pi, 3\pi \ldots$.

Energy levels in a rectangular potential well



Schrodinger equation

$$\mathcal{H}\psi_n = -\frac{\hbar^2}{2m}\frac{d^2\psi_n(x)}{dx^2} = \varepsilon_n\psi_n,$$

Boundary conditions:

$$\psi_n(0) = 0, \quad \psi_n(L) = 0,$$

Solution:

Wave functions:

$$\psi_n = A\sin\left(\frac{n\pi}{L}x\right),$$

Energy levels:

$$\varepsilon_n = \frac{\hbar^2}{2m}\left(\frac{n\pi}{L}\right)^2$$

Each energy level forms an electron band

Electrons in a crystalline lattice. Bloch's theorem.

Periodic crystalline potential $U(\mathbf{r}+\mathbf{a}_n)=U(\mathbf{r})$, where

$\mathbf{a}_n=n_1\mathbf{a}_1+n_2\mathbf{a}_2+n_3\mathbf{a}_3$, a_i – lattice constants, n_i – integers.

The Schrödinger equation $-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r})+U(\mathbf{r})\,\psi(\mathbf{r})=\varepsilon\psi(\mathbf{r})$.
has an important property:

if $\psi(r)$ is a solution, than $\psi(r+a_n)$ is also a solution with the same energy

If this level is non-degenerate,* than $\boxed{\psi(\mathbf{r}+\mathbf{a}_n)=C\psi(\mathbf{r}),}$ where $C=e^{i\varphi}$

Thus the wave functions in a crystal are $\psi_p(\vec{r}+\vec{a}_n)=\exp\{i\vec{p}\cdot\vec{a}_n/\hbar\}\psi_p(\vec{r})$

Vector $\vec{p}$ is called quasi-momentum

The Bloch's theorem:

$\psi_p(\vec{r})=\exp\{i\vec{p}\cdot\vec{r}/\hbar\}u(\vec{r})$, where $u(\vec{r}+\vec{a}_n)=u(\vec{r})$ is periodic

An essence of the Bloch's function is that it does not decay no matter how big is the sample, thus making finite probability for a conduction electron to propagate through the whole crystal without decay of the current, unlike a classical particle that would be able to move only diffusively, being scattered by the ions. This important result is in the root of the notion of coherent electronic bands found in metals.

Appendices (1)

*** If the level is degenerate, than $\psi_\mu(\boldsymbol{r}+\boldsymbol{a}_n)=\sum_\nu C_{\mu\nu}\psi_\nu(\boldsymbol{r})$.**

Orthogonality + normalization of wave functions requires

$\int \psi_\mu^*(\boldsymbol{r})\,\psi_\nu(\boldsymbol{r})\,\mathrm{d}V=\delta_{\mu\nu}$, **or** $\sum_\eta C_{\mu\eta}^* C_{\nu\eta}=\delta_{\mu\nu}$ **=>** $C_{\mu\nu}$ **is a unitary matrix, and can be diagonalized.**

Then the eigenvalues $|C|^2=1$ **or** $C=e^{i\varphi(a_n)}$

Quasi-momentum and reciprocal space

The Bloch's theorem:

$\psi_p(\vec{r}) = \exp\{i\vec{p}\cdot\vec{r}/\hbar\}u(\vec{r})$, **where** $u(\vec{r}+\vec{a}_n) = u(\vec{r})$ **is periodic function.**

Vector $\vec{p}$ is called quasi-momentum

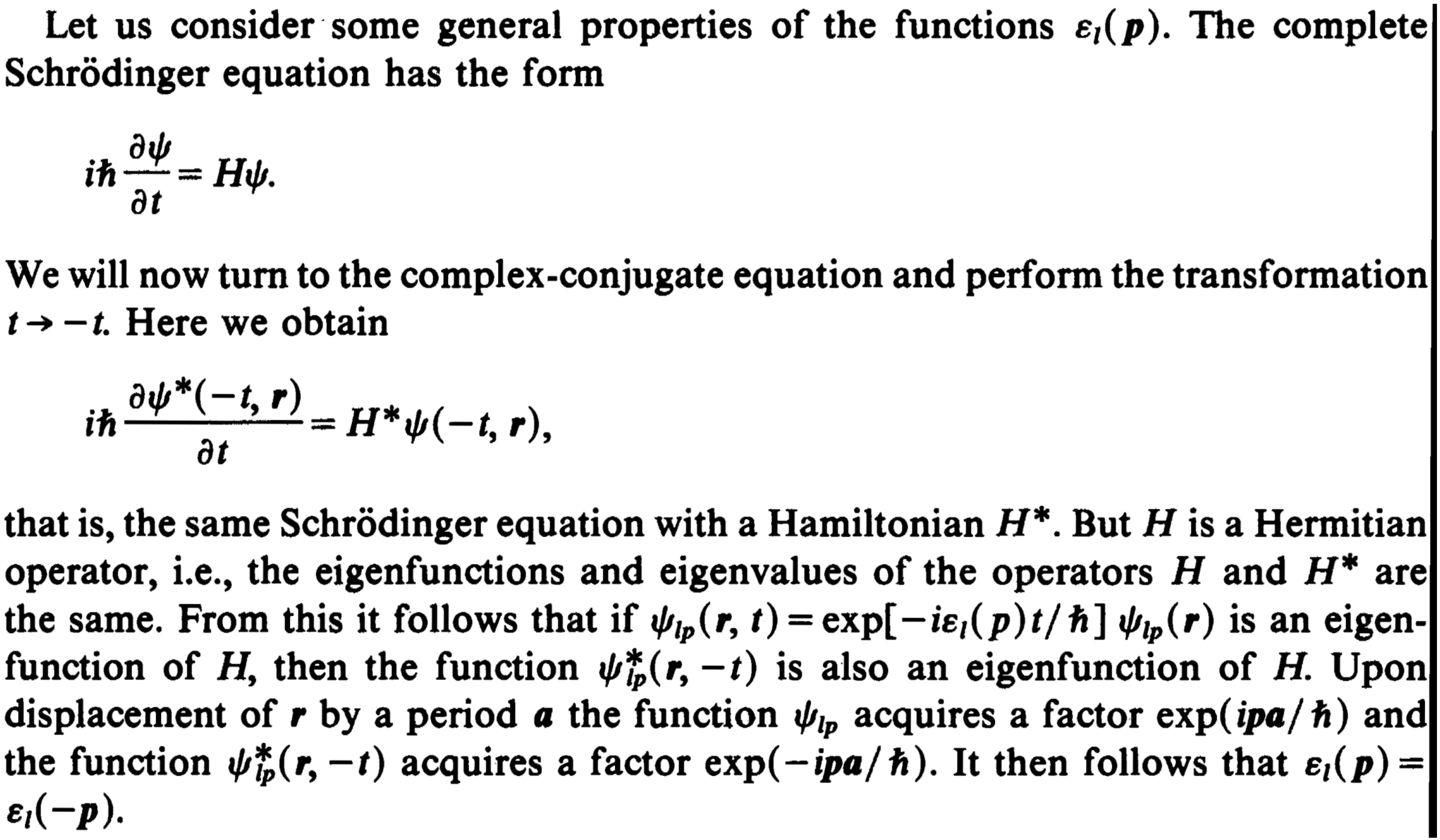
It is easy to see that this vector has been defined ambiguously. Namely, if to $\boldsymbol{p}$ we add the vector $\hbar\boldsymbol{K}$, which satisfies the condition $\boldsymbol{K}\boldsymbol{a}_n = 2\pi m$ for any lattice period $\boldsymbol{a}_n$ (where m is an integer), we will obtain the same coefficients $C(\boldsymbol{a}_n)$. The equations $\boldsymbol{K}\boldsymbol{a}_n = 2\pi m$ are satisfied by an infinite system of vectors, all of which may be written in the following form: $\boldsymbol{K} = q_1\boldsymbol{K}_1 + q_2\boldsymbol{K}_2 + q_3\boldsymbol{K}_3$.
Here q_i are integers and $\boldsymbol{K}_i$ are the smallest noncoplanar vectors $\boldsymbol{K}\boldsymbol{a}_n = 2\pi m$.

These reciprocal lattice vectors K_i are given by

$$\vec{K}_1 = \frac{2\pi[\vec{a}_2\times\vec{a}_3]}{(\vec{a}_1\cdot[\vec{a}_2\times\vec{a}_3])};\vec{K}_2 = \frac{2\pi[\vec{a}_3\times\vec{a}_1]}{(\vec{a}_1\cdot[\vec{a}_2\times\vec{a}_3])};\vec{K}_3 = \frac{2\pi[\vec{a}_1\times\vec{a}_2]}{(\vec{a}_1\cdot[\vec{a}_2\times\vec{a}_3])}$$

They come from the Fourier transform of the periodic crystal potential and give the scattering wave vectors of this periodic potential.

General properties of electron dispersion: ε(p)=ε(-p)



Let us consider some general properties of the functions $\varepsilon_l(\boldsymbol{p})$. The complete Schrödinger equation has the form

$$i\hbar\frac{\partial\psi}{\partial t} = H\psi.$$

We will now turn to the complex-conjugate equation and perform the transformation $t \to -t$. Here we obtain

$$i\hbar\frac{\partial\psi^*(-t, \boldsymbol{r})}{\partial t} = H^*\psi(-t, \boldsymbol{r}),$$

that is, the same Schrödinger equation with a Hamiltonian H^*. But H is a Hermitian operator, i.e., the eigenfunctions and eigenvalues of the operators H and H^* are the same. From this it follows that if $\psi_{lp}(\boldsymbol{r}, t) = \exp[-i\varepsilon_l(p)t/\hbar]\,\psi_{lp}(\boldsymbol{r})$ is an eigenfunction of H, then the function $\psi^*_{lp}(\boldsymbol{r}, -t)$ is also an eigenfunction of H. Upon displacement of $\boldsymbol{r}$ by a period $\boldsymbol{a}$ the function ψ_{lp} acquires a factor $\exp(i\boldsymbol{pa}/\hbar)$ and the function $\psi^*_{lp}(\boldsymbol{r}, -t)$ acquires a factor $\exp(-i\boldsymbol{pa}/\hbar)$. It then follows that $\varepsilon_l(\boldsymbol{p}) = \varepsilon_l(-\boldsymbol{p})$.

Electron dispersion ε(p) is a periodic function of p

Let us draw from some reciprocal lattice point all ***K***-vectors that connect it with the other lattice points. Then, we draw planes perpendicular to each of these vectors and dividing them in half. These planes will cut out a certain figure in the space of the reciprocal lattice which has the shape of a polyhedron. It is not difficult to see that such a polyhedron possesses all the required properties and may therefore be taken as the region of specification of the quasimomentum ***p***. It is called the Brillouin zone. Figure 1 shows examples of Brillouin zones for the face-centred cubic (a) and body-centered cubic (b) lattices.

Electron dispersion *ε(p)* , i.e. the dependence of energy on electron quasi-momentum, is a periodic function of *p* with periods given by reciprocal lattice vectors *K*. Usually, it is defined in one Brillouin zone.

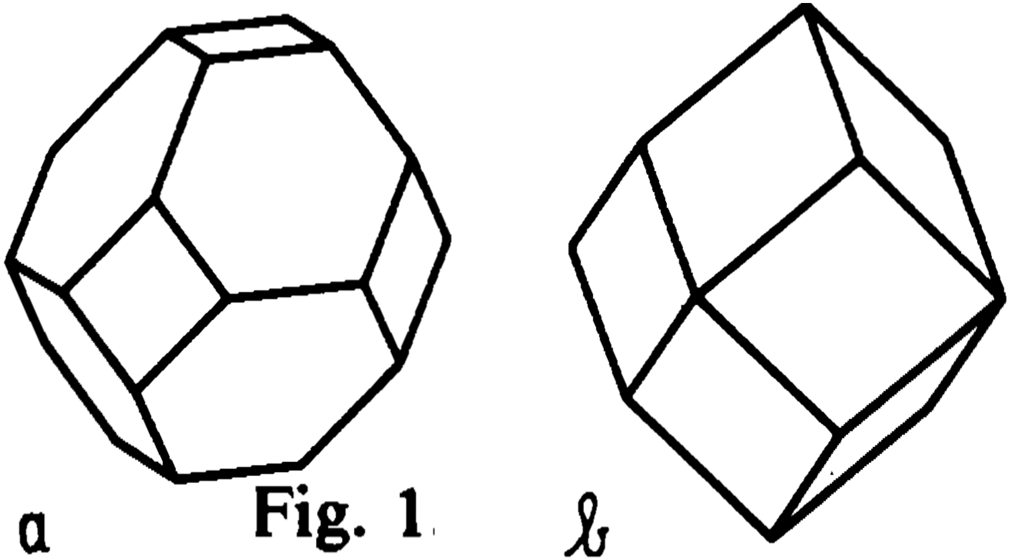


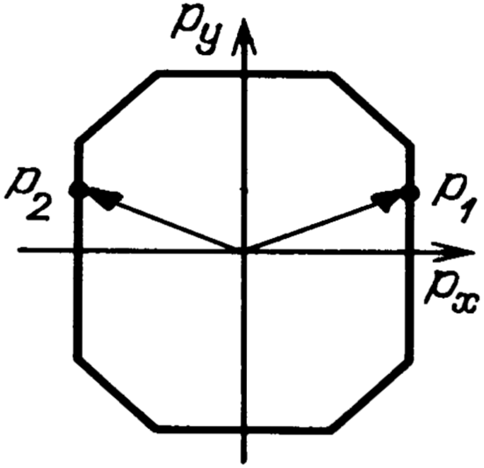
Fig. 1

Electron dispersion ε(p) is a crystal

As a rule, the crystal lattices of metals exhibit high symmetry. This gives rise to certain properties of the function $\varepsilon_l(\boldsymbol{p})$. Suppose, for example, that the symmetry plane perpendicular to the axis p_x passes through the point $\boldsymbol{p}=0$. If there exist faces of the Brillouin zone perpendicular to the p_x axis, then $\varepsilon_l(\boldsymbol{p})$ as functions of p_x must have extrema on these faces. Indeed, let us single out the points of these faces, $\boldsymbol{p}_1$ and $\boldsymbol{p}_2$, which are symmetric with respect to the symmetry plane (fig. 2). They differ by a reciprocal lattice period (multiplied by $\hbar$). Therefore, at these points

Electron energy ε(p) is a periodic function of momentum p, =>

$$\varepsilon_l(\boldsymbol{p}_1)=\varepsilon_l(\boldsymbol{p}_2), \qquad \frac{\partial\varepsilon_l(\boldsymbol{p}_1)}{\partial p_x}=\frac{\partial\varepsilon_l(\boldsymbol{p}_2)}{\partial p_x}.$$



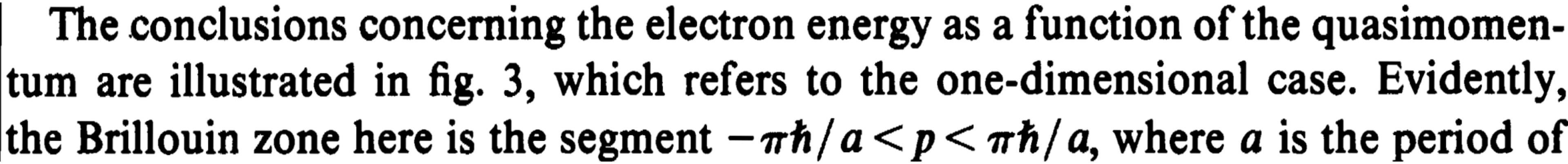
From the mirror symmetry with respect to p_x plane also

$$\frac{\partial\varepsilon_l(\boldsymbol{p}_1)}{\partial p_x}=-\frac{\partial\varepsilon_l(\boldsymbol{p}_2)}{\partial p_x}.$$

Hence $\dfrac{\partial\varepsilon_l(\boldsymbol{p}_1)}{\partial p_x}=0$ **and** $\left(\dfrac{\partial\varepsilon_l}{\partial p_x}\right)_{p_x=0}=0.$

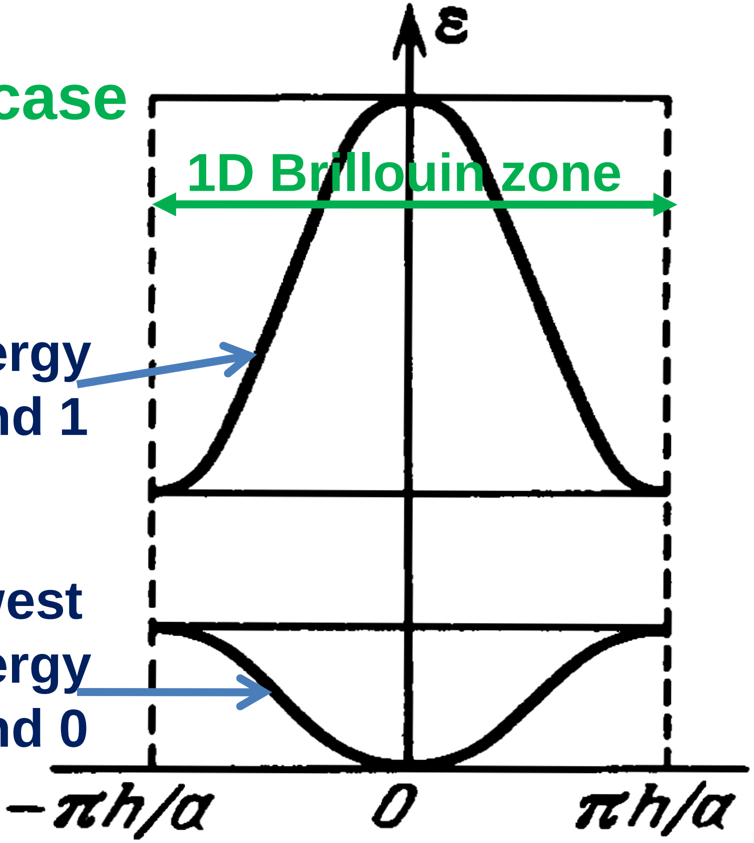
Thus, we arrive at the conclusion that for symmetrical lattices, as a rule, there are extrema of the functions $\varepsilon_l(\boldsymbol{p})$ in the center of the Brillouin zone or at its boundaries.

Electron dispersion ε(p) is a crystal (2)



The conclusions concerning the electron energy as a function of the quasimomentum are illustrated in fig. 3, which refers to the one-dimensional case. Evidently, the Brillouin zone here is the segment $-\pi\hbar/a < p < \pi\hbar/a$, where a is the period of

1D case



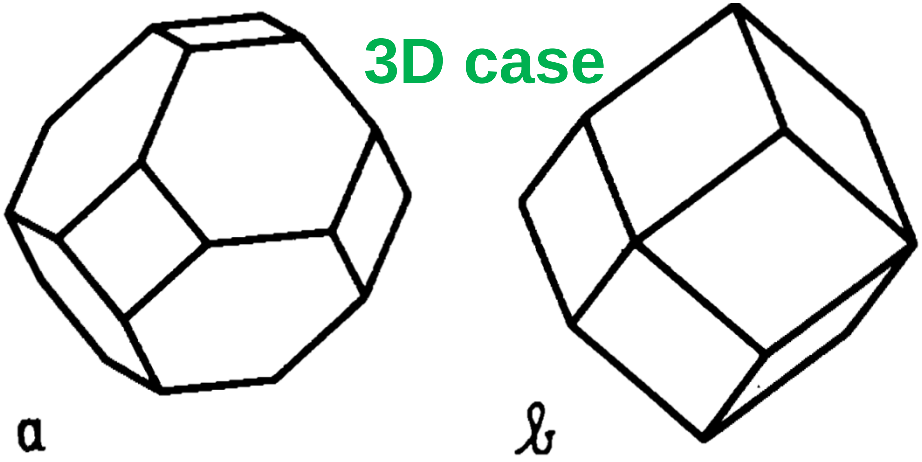
1D Brillouin zone

energy band 1

lowest energy band 0

Fig. 3

3D case



3D Brillouin zones of face centered (a) and body-centered (b) crystals.

See more illustrations in wikipedia.

Typical notation: Γ-point usually denotes the center of Brillouin zone

Approximation of weakly bound electrons

(nearly free electron model)

We use the perturbation theory (iteration procedure). In the zeroth order we take isotropic free electron gas with dispersion ε(p)=$p^2/2m$, spherical Fermi surface. Its wave functions are the plane waves $L^{-1/2}\,e^{ipx/\hbar}$.

In the first approximation we include the periodic scattering potential $U(x)=\sum_n U_n\, e^{2\pi inx/a}$ with matrix elements: $U(p,p')=L^{-1}\int U(x)\, e^{-i(p-p')x/\hbar}\, dx$

These matrix elements are nonzero only if $p-p'=2\pi n\hbar/a$, i.e. in 3D only for scattering by any linear combination of reciprocal lattice vectors *K*.

We denote $U(p,p')=U_n$. In the first order in U(x) the energy correction to ε(p)=$p^2/2m$ is diagonal matrix element *U(p,p)=const*. This constant energy correction does not change the dependence ε(p).

In the second order in U(x) the energy correction to ε(p) is

$$\varepsilon^{(2)}(p)=\sum_{n\neq 0}\frac{|U_n|^2}{\varepsilon^{(0)}(p)-\varepsilon^{(0)}(p-2\pi n\hbar/a)}$$

This energy correction is large if the denominator is small, i.e. when ε(p)≈ ε($p-2\pi n\hbar/a$). This happens when $p\approx\pi n\hbar/a$, i.e. at the Brillouin-zone boundary. Then one must use perturbation theory for degenerate states.

Perturbation theory for degenerate states, applied to electrons in crystal lattice

Suppose that the sought-for wave function has the form $\psi = A_1\psi_1 + A_2\psi_2$, where ψ_1 corresponds to the first state and ψ_2 to the second. Substituting this expression into the Schrödinger equation $H\psi = \varepsilon\psi$, we find

$$A_1(\varepsilon_1 - \varepsilon)\psi_1 + U(A_1\psi_1 + A_2\psi_2) + A_2(\varepsilon_2 - \varepsilon)\psi_2 = 0,$$

where $\varepsilon_1 = p^2/2m$ and $\varepsilon_2 = p'^2/2m$. Multiplying by ψ_1^* and then by ψ_2^*, integrating and using the orthogonality of ψ_1 and ψ_2, we obtain

$$A_1(\varepsilon_1 - \varepsilon + U_0) + U_nA = 0, \qquad U_n^* A_1 + (\varepsilon_2 - \varepsilon + U_0)A_2 = 0.$$

The eigenvalues are found from the vanishing condition of the determinant of this homogenous linear system (the constant U_0 is incorporated into ε):

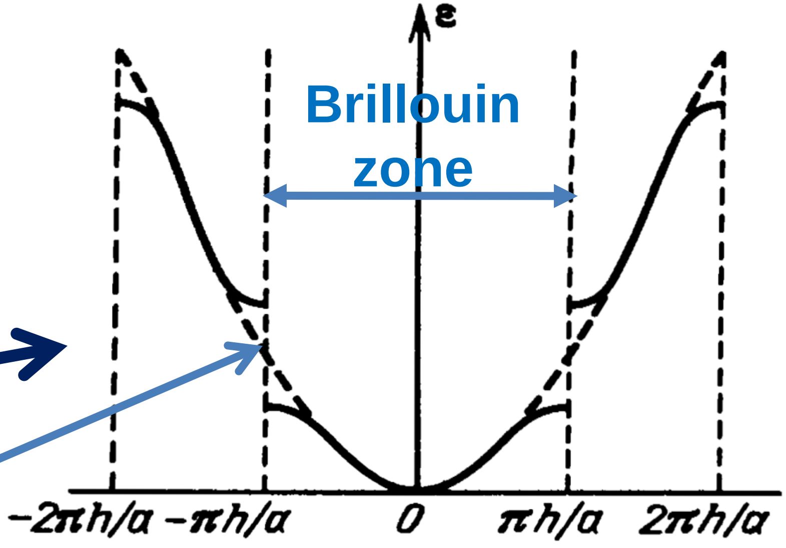
$$\varepsilon^2 - (\varepsilon_1 + \varepsilon_2)\varepsilon + \varepsilon_1\varepsilon_2 - |U_n|^2 = 0.$$

This equation has two solutions:

$$\boxed{\varepsilon = (\tfrac{1}{2})(\varepsilon_1 + \varepsilon_2) \pm [(\tfrac{1}{4})(\varepsilon_1 - \varepsilon_2)^2 + |U_n|^2]^{1/2}.}$$

This result for 1D electron dispersion (for energy spectrum) is shown in Fig.

Energy gap at the edges of Brillouin zone



The model of weakly bound electrons in 3D crystal

The crystal-lattice potential $U(\mathbf{r}) = \sum_{\mathbf{K}} U_{\mathbf{K}}\, e^{i\mathbf{K}\mathbf{r}}$,

where $\mathbf{K}$ are the periods of the reciprocal lattice.

The second-order perturbation theory in 3D gives

$$\varepsilon^{(2)}(p) = \sum_{K} \frac{|U_K|^2}{\varepsilon^{(0)}(p) - \varepsilon^{(0)}(p-K)}$$

This correction is small except regions where $\varepsilon^{(0)}(\mathbf{p}) = \varepsilon^{(0)}(\mathbf{p} - \hbar\mathbf{K})$.

Perturbation theory for degenerate states (in the first order in U_K) gives

$$\varepsilon(\mathbf{p}) = (\tfrac{1}{2})[\varepsilon^{(0)}(\mathbf{p}) + \varepsilon^{(0)}(\mathbf{p} - \hbar\mathbf{K})] \pm [(\tfrac{1}{4})(\varepsilon^{(0)}(\mathbf{p}) - \varepsilon^{(0)}(\mathbf{p} - \hbar\mathbf{K}))^2 + |U_{\mathbf{K}}|^2]^{1/2}. \qquad (1)$$

To obtain this, we need to solve the Schrodinger equation $\hat{H}\psi = E\psi$,

where

$$\hat{H} = \begin{pmatrix} \varepsilon^{(0)}(p) & U_K \\ U_K & \varepsilon^{(0)}(p-K) \end{pmatrix} \quad \text{and} \quad \psi = \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = \begin{pmatrix} \psi(p \approx K/2) \\ \psi(p \approx -K/2) \end{pmatrix}$$

Diagonalization of this matrix goes via the calculation of the determinant: It gives the eigenvalues in Eq. (1) as the solutions of quadratic equation:

$$\begin{vmatrix} \varepsilon^{(0)}(p) - \varepsilon & U_K \\ U_K & \varepsilon^{(0)}(p-K) - \varepsilon \end{vmatrix} = 0$$

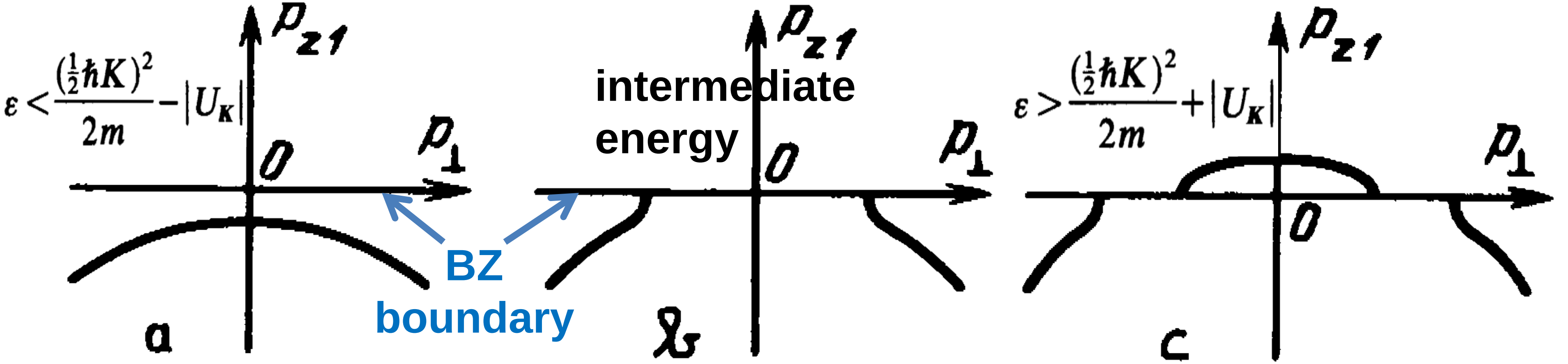
The analysis of electron dispersion in 3D crystal in the approximation of weak coupling to lattice

Perturbation theory for degenerate states (in the first order in U_K) gives

$$\varepsilon(\boldsymbol{p}) = (\tfrac{1}{2})[\varepsilon^{(0)}(\boldsymbol{p}) + \varepsilon^{(0)}(\boldsymbol{p} - \hbar\boldsymbol{K})] \pm [(\tfrac{1}{4})(\varepsilon^{(0)}(\boldsymbol{p}) - \varepsilon^{(0)}(\boldsymbol{p} - \hbar\boldsymbol{K}))^2 + |U_{\boldsymbol{K}}|^2]^{1/2}.$$

Let us choose the axis p_z along $\hbar K$ and introduce a new variable, $p_{z1} = p_z - \frac{1}{2}\hbar K$. Substituting $\varepsilon^{(0)} = p^2/2m$ into (1.42) and using the new variables, we find that

the electron dispersion near the BZ boundary is $$\varepsilon(\boldsymbol{p}) = \frac{[p_\perp^2 + p_{z1}^2 + (\frac{1}{2}\hbar K)^2]}{2m} \pm \left[\left(\frac{p_{z1}\hbar K}{2m}\right)^2 + |U_K|^2\right]^{1/2}$$



intermediate energy

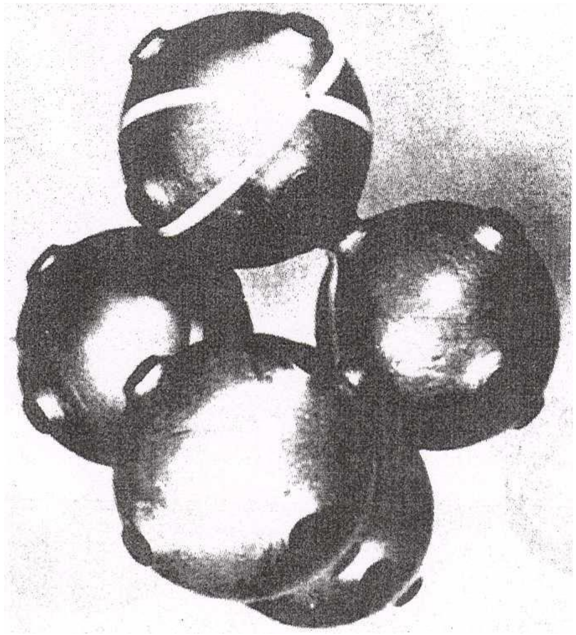
BZ boundary

Figure illustrates the surface ε=const near the boundary of Brillouin zone (BZ)

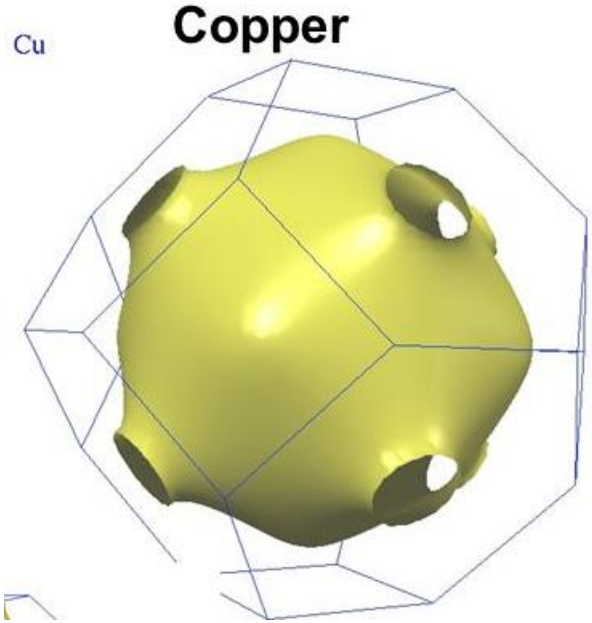
Electron velocity $v_z = \partial\varepsilon/\partial p_z = 0$ ⊥ to the boundaries of Brillouin zone (BZ) => strong Bragg reflections from the BZ boundaries.

Fermi-surface in weak-coupling regime

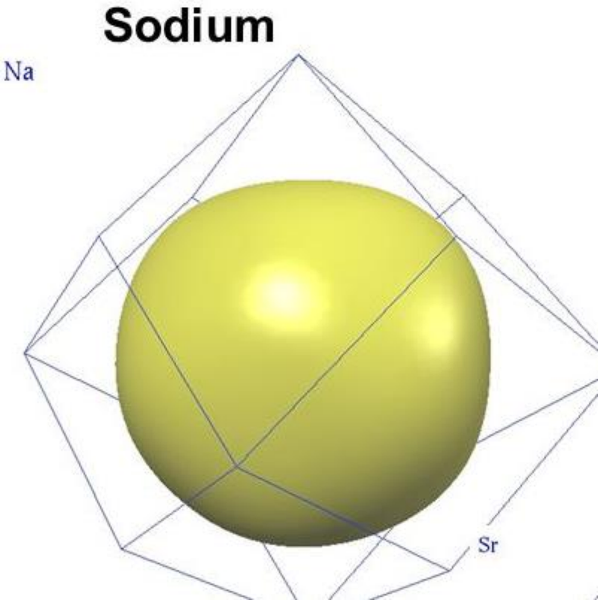
Fermi-surface – surface $\varepsilon(p)=\mu=E_F$ in the momentum space. In the weak-coupling regime it deviates from a sphere mainly only at the boundaries of Brillouin zone.



Fermi surface of gold



Copper



Sodium

Tight-binding approximation.

(derivation from Ch. Kittel, Introduction to Solid State Physics, 8th edition)

Bloch wave function
$$\psi_{\mathbf{k}}(\mathbf{r}) = N^{-1/2} \sum_j \exp(i\mathbf{k}\cdot\mathbf{r}_j)\varphi(\mathbf{r}-\mathbf{r}_j)$$

The electron energy is
$$\langle \mathbf{k}|H|\mathbf{k}\rangle = N^{-1}\sum_j \sum_m \exp[i\mathbf{k}\cdot(\mathbf{r}_j-\mathbf{r}_m)]\,\langle\varphi_m|H|\varphi_j\rangle \;,$$

where $\varphi_m \equiv \varphi(\mathbf{r}-\mathbf{r}_m)$.

Writing $\boldsymbol{\rho}_m = \mathbf{r}_m - \mathbf{r}_j$, $\langle \mathbf{k}|H|\mathbf{k}\rangle = \sum_m \exp(-i\mathbf{k}\cdot\boldsymbol{\rho}_m)\int dV\,\varphi^*(\mathbf{r}-\boldsymbol{\rho}_m)H\varphi(\mathbf{r})$

Keeping only $\int dV\,\varphi^*(\mathbf{r})H\varphi(\mathbf{r}) = -\alpha \;;\quad \int dV\,\varphi^*(\mathbf{r}-\boldsymbol{\rho})H\varphi(\mathbf{r}) = -\gamma \;;$

we have the first-order energy, provided $\langle\mathbf{k}|\mathbf{k}\rangle = 1$:

$$\boxed{\langle \mathbf{k}|H|\mathbf{k}\rangle = -\alpha - \gamma\sum_m \exp(-i\mathbf{k}\cdot\boldsymbol{\rho}_m) = \epsilon_{\mathbf{k}}}$$

Tight-binding approximation: transfer integral

Energy spectrum

$$\langle \mathbf{k}|H|\mathbf{k}\rangle = -\alpha - \gamma \sum_m \exp(-i\mathbf{k}\cdot\boldsymbol{\rho}_m) = \epsilon_\mathbf{k}$$

For two hydrogen atoms the direct calculation of overlap energy gives

$$\gamma(\mathrm{Ry}) = 2(1+\rho/a_0)\exp(-\rho/a_0) \quad \text{where} \quad a_0 = \hbar^2/me^2.$$

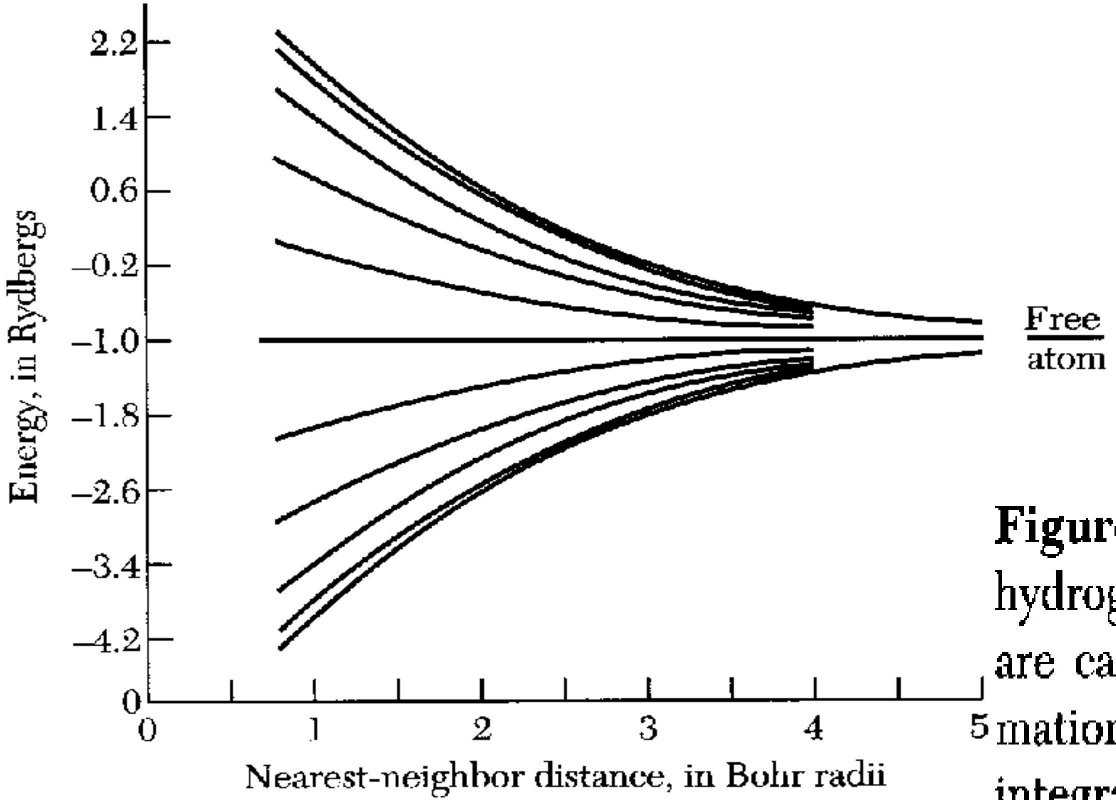


Figure 17 The 1s band of a ring of 20 hydrogen atoms; the one-electron energies are calculated in the tight-binding approximation with the nearest-neighbor overlap integral of Eq. (9).

Tight-binding approximation. Wannier functions

(derivation from A.A. Abrikosov, Fundamentals of the theory of metals)

the Schrödinger equation is $-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}+\sum_n U(x-na)\,\psi(x)=\varepsilon\psi(x)$

Its exact solution are the Bloch waves: $\psi_p(x)=e^{ipx/\hbar}u_p(x)$

The Wannier functions are defined as a Fourier transform of Bloch waves: $w_n(x)=N^{-1/2}\sum_p e^{-ipna/\hbar}\,\psi_p(x)$

The Wannier functions $w_n(x)$ are located near n-th ion in the crystal.
If the Bloch waves were plane waves e^{ipx}, the Wannier function would be a δ–function: $w_n(x)=\delta(x-na)$. Now $w_n(x)=w(x-na)$ and satisfy eq.

$$\sum_n\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+U(x-na)\right)e^{ipna/\hbar}w_n(x)+\sum_n h(x)\,e^{ipna/\hbar}w_n(x)=\varepsilon(p)\sum_n e^{ipna/\hbar}w_n(x),$$

where $h(x)=V(x)-U(x-na)$ acts as small perturbation, because the product $U(x-ma)\,w_n(x)$ with $n\neq m$, is small

In the zeroth approximation, neglecting this term $h(x)$, $w_n(x)$ equals to the wave function of isolated atom $w^{(0)}=\varphi(x)$ and satisfies Schrodinger equation with energy $\varepsilon^{(0)}(p)=\varepsilon_0$ equal to the energy level of isolated atom

Tight-binding approximation (1)

for electron dispersion in a crystal

Assuming that $w = w^{(0)} + w^{(1)}$, we find equation on $w^{(1)}$:

$$\sum_n \left(-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + U(x-na) - \varepsilon_0 \right) w^{(1)}\,\mathrm{e}^{ipna/\hbar}$$
$$= [\varepsilon(p) - \varepsilon_0] \sum_n \mathrm{e}^{ipna/\hbar} w_n^{(0)}(x) - \sum_n h(x)\,\mathrm{e}^{ipna/\hbar} w_n^{(0)}(x).$$

This is a linear equation for $w^{(1)}$ with a right-hand side. According to the general rule, such an equation has a solution only if the right-hand side is orthogonal to the solution of the corresponding reduced equation with the same boundary conditions. These conditions consist of the vanishing of w at ±∞. From this it follows that the corresponding solution of the reduced equation is just $w(x)$ in the zeroth approximation, i.e., $\varphi(x)$. From the orthogonality condition we deduce that

$$\varepsilon(p) - \varepsilon_0 = \frac{\sum_n h(n)\,\mathrm{e}^{ipna/\hbar}}{\sum_n I(n)\,\mathrm{e}^{ipna/\hbar}},$$

where

$$h(n) = \int \varphi^*(x)\,h(x)\,\varphi(x-na)\,\mathrm{d}x,$$
$$I(n) = \int \varphi^*(x)\,\varphi(x-na)\,\mathrm{d}x.$$

Tight-binding approximation (results)

In 1D case the electron dispersion ε(p) is given by

$$\varepsilon(p)-\varepsilon_0=\frac{\sum\limits_n h(n)\,\mathrm{e}^{ipna/\hbar}}{\sum\limits_n I(n)\,\mathrm{e}^{ipna/\hbar}},$$

where

$$h(n)=\int \varphi^*(x)\,h(x)\,\varphi(x-na)\,\mathrm{d}x,$$

$$I(n)=\int \varphi^*(x)\,\varphi(x-na)\,\mathrm{d}x.$$

Here $h(x)=V(x)-U(x-na)=\sum\limits_{m\neq n}U\left(x-ma\right)$

and φ(x) are the electron wave functions on isolated ions.

In tight binding approximation the overlap of functions φ(x) on adjacent ions is very small, => $h(1)>>h(2)$ .. and $I(0)=1>>I(1)>>I(2)$. Hence, we may keep only $I(0)$, $I(1)$ and $h(1)$ (since $h(0)=0$). Then we obtain the 1D electron dispersion given by

$$\varepsilon-\varepsilon_0=h(0)+2[h(1)-h(0)\;I(1)]\cos\left(\frac{pa}{\hbar}\right)$$

In simplest 3D case:

$$\varepsilon-\varepsilon_0=\frac{\sum\limits_n h(n)\,\mathrm{e}^{ipa_n/\hbar}}{\sum\limits_n I(n)\,\mathrm{e}^{ipa_n/\hbar}}$$

and for the cubic crystal lattice, with basic vectors

$$a_n=(\pm\tfrac{1}{2}a,\pm\tfrac{1}{2}a,\pm\tfrac{1}{2}a)$$

the electron dispersion is very different from free e^-:

$$\varepsilon-\varepsilon_0=h(0)+8[h(1)-h(0)\;I(1)]\times\cos\left(\frac{p_xa}{2\hbar}\right)\cos\left(\frac{p_ya}{2\hbar}\right)\cos\left(\frac{p_za}{2\hbar}\right)$$

Electron dispersion in the tight-binding approximation (isotropic 3D case)

Energy spectrum

$$\boxed{\langle \mathbf{k}|H|\mathbf{k}\rangle = -\alpha - \gamma \sum_m \exp(-i\mathbf{k}\cdot\boldsymbol{\rho}_m) = \epsilon_{\mathbf{k}}}$$

For a simple cubic structure the nearest-neighbor atoms are at

$$\boldsymbol{\rho}_m = (\pm a,0,0)\ ;\quad (0,\pm a,0)\ ;\quad (0,0,\pm a)\ , \quad \Rightarrow$$

the electron dispersion is

$$\epsilon_{\mathbf{k}} = -\alpha - 2\gamma(\cos k_x a + \cos k_y a + \cos k_z a)$$

For the fcc structure with eight nearest neighbors,

$$\epsilon_{\mathbf{k}} = -\alpha - 8\gamma \cos \tfrac{1}{2}k_x a \cos \tfrac{1}{2}k_y a \cos \tfrac{1}{2}k_z a$$

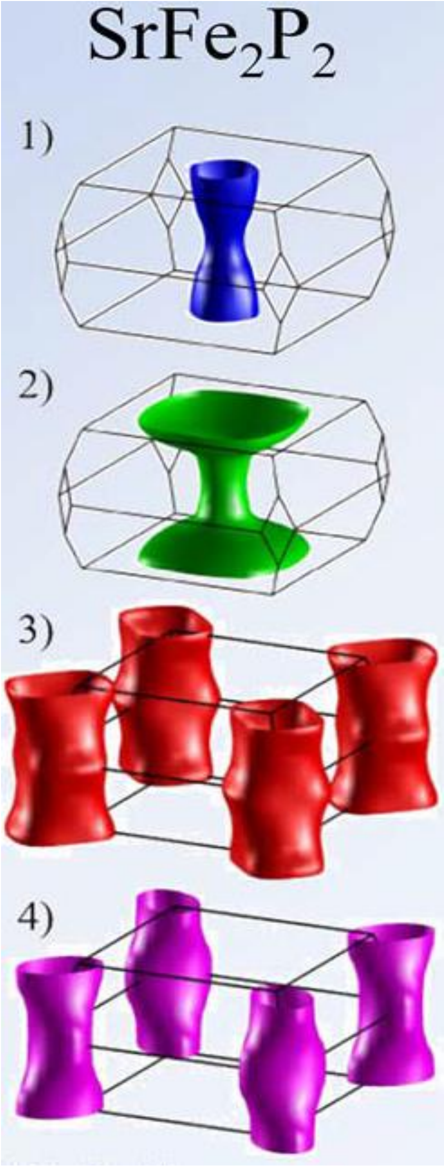
Fermi-surface in the tight-binding regime (anisotropic case)

Quasi-2D electron dispersion:

$\varepsilon(p)=\varepsilon_{||}(p_{||})+2t_z \cos(p_z d/\hbar)$,

$2t_z< E_F$, $\varepsilon_{||}(p_{||}) \approx p_{||}^2/2m_{||}$.

Fermi-surface:

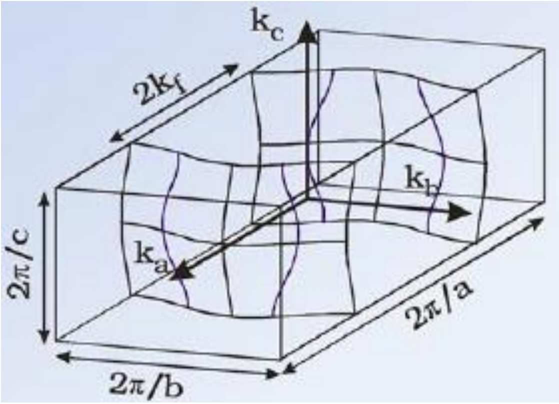


Quasi-1D electron dispersion:

$\varepsilon(p)=\varepsilon_x(p_x)+2t_y \cos(p_y d/\hbar)$
$+2t_z \cos(p_z d/\hbar)$,

$t_y,t_z<< E_F$, $\varepsilon_x(p_x) \approx p_x^2/2m_x$.

Fermi-surface:

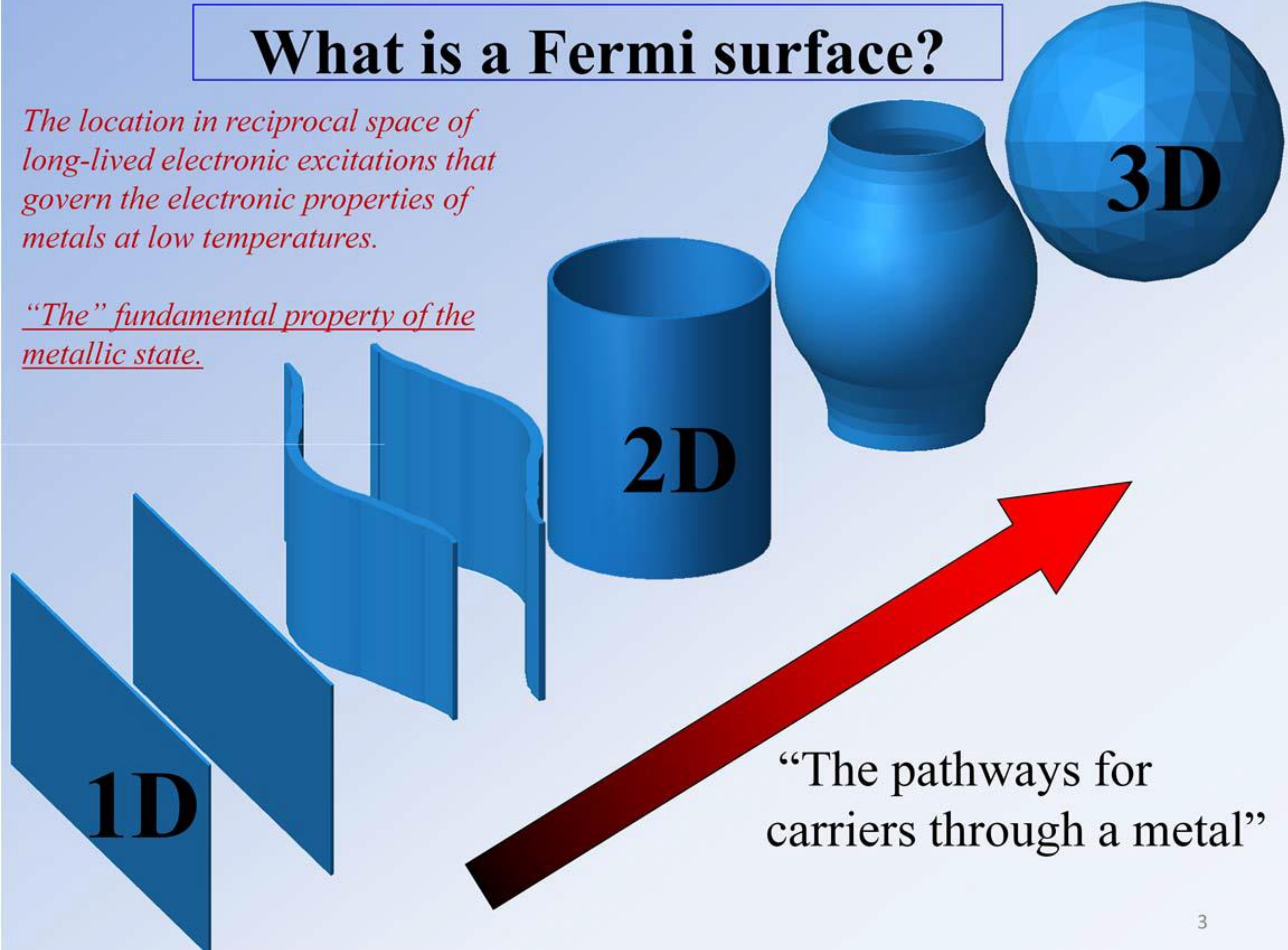


organic metals,

What is a Fermi surface?

The location in reciprocal space of long-lived electronic excitations that govern the electronic properties of metals at low temperatures.

<u>"The" fundamental property of the metallic state.</u>

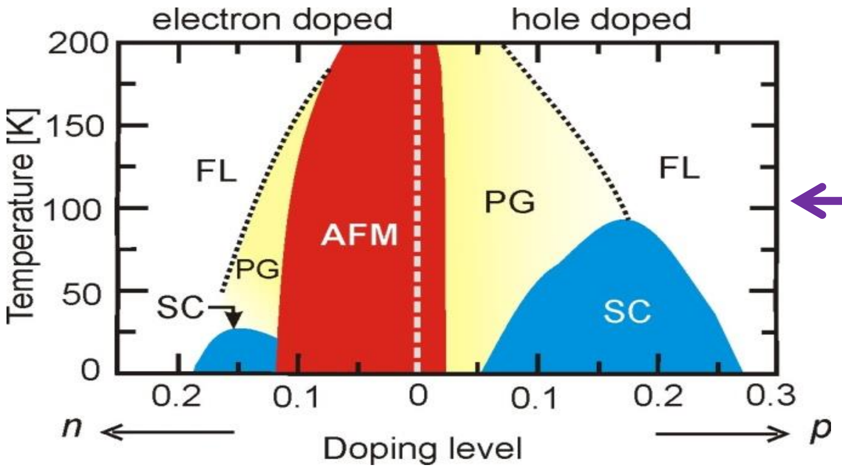


"The pathways for carriers through a metal"

Fermi-surface reconstruction in electron-doped cuprate superconductors

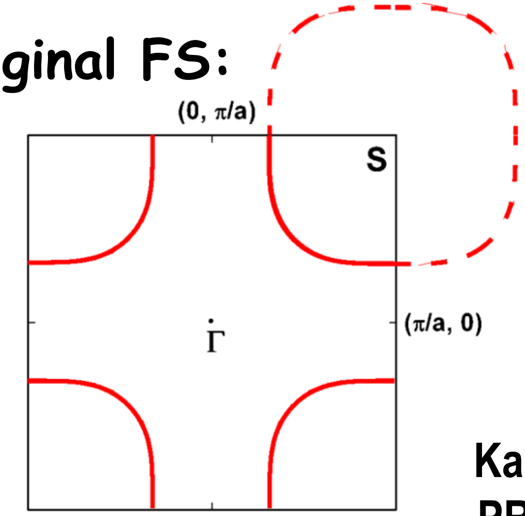
$Nd_{2-x}Ce_xCuO_4$

(NCCO)



Phase diagram of cuprate high-Tc superconductors

Original FS:

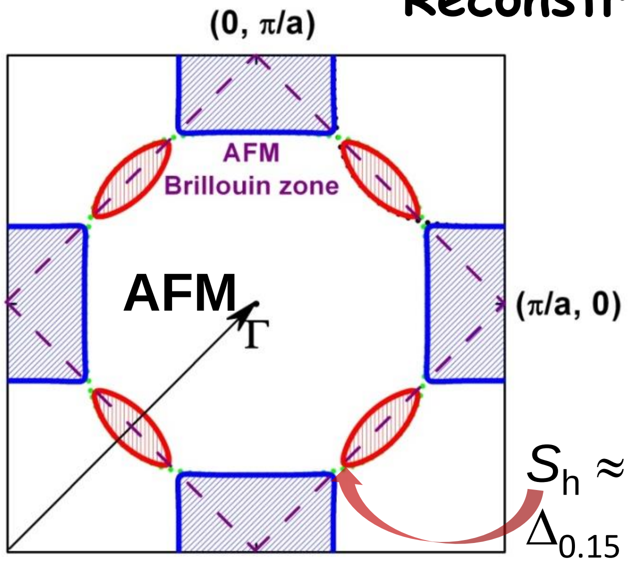


$n = 0.17$

$S_h = 41.5\%$ of S_{BZ}

T. Helm, M. Kartsovnik et al., PRL 103, 157002 (2009)

Reconstructed FS:



$S_h \approx 1.1\%$ of S_{BZ};

$\Delta_{0.15} \approx 64$ meV;

$\Delta_{0.16} \approx 36$ meV

$n = 0.15$ and 0.16