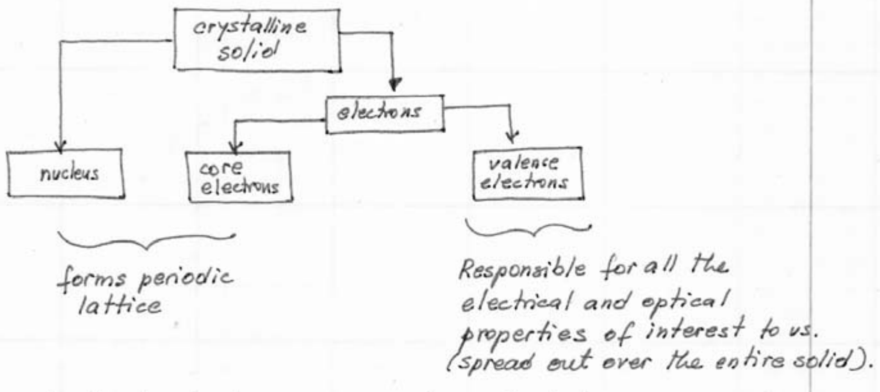
2. Quantum Theory of Electrons in Periodic lattices

- Engineers have usually concerned themselves only with macroscopic description of devices. The complexities of the microscopic world have been hidden in macroscopic parameters like mobility, diffusion coefficient and lifetime.

The miniaturitation of solid-state devices and the advent of superlattices have made possible to control these macroscopic parameters by engineering device structures on a microscopic scale. These novel microstructures are intermediate between:

microscopic (≤ 10 Å)
macroscopic ($\geq 1\,\mu m$)

- The electrical and optical properties of such mesoscopic structures can not be described with macroscopic parameters such as diffusion constant or mobility. Hence, it becomes necessary to understand the operation of a device at a microscopic level.



- To understand electronic properties of solids, we need to describe the behavior of the valence electrons in the presence of the internal forces due to the lattice as well as external forces due to any applied voltage. This is, in general, a many-body problem. Luckily enough, most of the phenomena we are interested in can be described using a one-electron description.

- Classically the position of the electron in an electric field is described by Newton's second law

$$m_0 \frac{d^2 r}{dt^2} = -e E(\vec{r}) = e \nabla \varphi = -\nabla U$$

- Quantum-mechanically, the dynamics of an individual electron is described by the one-electron Schrödinger equation:

$$i\hbar \frac{\partial \Psi_0(\vec r,t)}{\partial t} = -\frac{\hbar^2}{2m_0}\nabla^2\Psi_0(\vec r,t) + V(\vec r,t)\,\Psi_0(\vec r,t)$$

$\Psi_0(\vec r,t)$ = wavefunction of an electron

$|\Psi_0(r,t)|^2 = \Psi_0^*(\vec r,t)\,\Psi_0(\vec r,t)$ = probability density, i.e. probability of a particle being located in a range $\vec r$ to $\vec r + d\vec r$

→ Experimental observables are extracted from averages over the wavefunction. However, one must replace classical quantities with differential operators:

$$\hat r \to r$$
$$\hat p \to \frac{\hbar}{i}\nabla$$
$$\hat E \to i\hbar\frac{\partial}{\partial t}$$

The expectation, or average value, of any observable is then defined as:

$$\langle \hat Q \rangle = \int \Psi^*(\vec r,t)\,\hat Q\,\Psi(\vec r,t)\,d\vec r = \langle|\hat Q|\rangle$$ Dirac notation (inner product)

→ The potential energy term appearing in the SE can be separated into a :

macroscopic part → macroscopic electric field and charge V_E

microscopic part → microscopic electric field due to nearly periodic lattice of ions and the other electrons $U_L(\vec r)$ + fluctuating potential $U_s(\vec r,t)$ representing deviations:

$$V(\vec r,t) = V_E(\vec r,t) + U_L(\vec r) + U_s(\vec r,t)$$

- free electrons
- infinite potential well
- finite potential step
- slowly-varying potential

- Bloch waves
- effective mass concept

Scattering potential from defects and impurities, or it can be caused by phonons that represent vibrations of the ions about their equilibrium position.

2.1 Bloch Theorem (Floquet's Theorem)

The Bloch theorem is a mathematical statement regarding the form of the one-electron wavefunction for a perfectly periodic equation.

Consider the differential equation

$$\frac{d^2\psi}{dx^2} + f(x)\psi(x) = 0 \qquad \text{where } f(x+a) = f(x)$$

with general solution:

$$\psi(x) = A g(x) + B h(x)$$

Since $f(x+a) = f(x)$, $g(x+a)$ and $h(x+a)$ are also solutions to the above equation, which can be expressed as:

$$\begin{aligned} g(x+a) &= \alpha_1 g(x) + \alpha_2 h(x) \\ h(x+a) &= \beta_1 g(x) + \beta_2 h(x) \end{aligned}$$

Therefore:

$$\begin{aligned} \psi(x+a) &= A[\alpha_1 g(x) + \alpha_2 h(x)] + B[\beta_1 g(x) + \beta_2 h(x)] = \\ &= (A\alpha_1 + B\beta_1) g(x) + (A\alpha_2 + B\beta_2) h(x) = \lambda\psi(x) \\ &= \lambda A g(x) + \lambda B h(x) \end{aligned}$$

This leads to:

$$\left.\begin{aligned} (\alpha_1 - \lambda)A + B\beta_1 &= 0 \\ \alpha_2 A + (\beta_2 - \lambda)B &= 0 \end{aligned}\right\}$$

solutions to this equations are λ_1 and λ_2

$$\lambda_1 = e^{ik_1 a}, \quad \lambda_2 = e^{ik_2 a}$$

We now define:

$$u_{K_1}(x) = e^{-ik_1 x}\psi(x)$$

$$u_{K_2}(x) = e^{-iK_2 x}\psi(x)$$

Then:

$$\begin{aligned} u_{K_1}(x+a) &= e^{-ik_1(x+a)}\psi(x+a) = e^{-ik_1 x - ik_1 a}\Lambda_1\psi(x) \\ &= e^{-ik_1 x} e^{-ik_1 a} e^{ik_1 a}\psi(x) = e^{-ik_1 x}\psi(x) = u_{K_1}(x) \end{aligned}$$

The function u_{K_1} is periodic with period a. Therefore:

$$\psi(x) = e^{ik_1 x} u_{K_1}(x)$$

The result that all one-electron wavefunctions for periodic potentials can be written as:

$$\psi(x) = \underset{\substack{\nearrow \\ \text{plane-wave} \\ \text{component}}}{e^{ikx}} \; \underset{\substack{\nwarrow \\ \text{cell periodic part}}}{u_k(x)}$$

is known as Bloch theorem.

Note: if periodic boundary conditions are imposed in a one-dimensional crystal of N-atoms, then, if the wavefunction is to be single-valued, we must have:

$$\psi(x+Na) = e^{ik(x+Na)} u_k(x+Na) = e^{ikx} u_k(x) e^{ikNa} = e^{ikx} u_k(x)$$

which gives: $e^{ikNa} = e^{i2\pi n} \Rightarrow k_n = \frac{2\pi}{Na} n = \frac{2\pi}{L} n$

Now, if N is large, there will be many allowed values of k and it may be regarded as forming a quasi-continuum range of values.

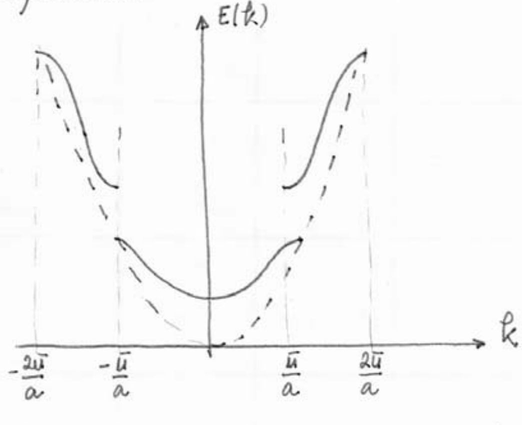
- For 3D systems:

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

n = band index

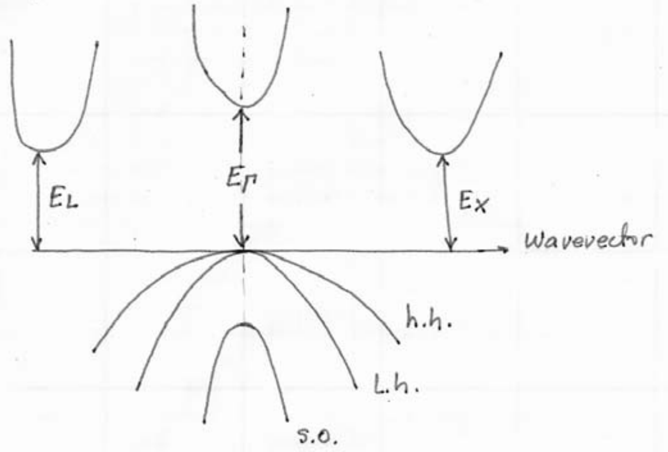
2.2 Kronig-Penney model

For the case of infinite periodic one-dimensional potential (square-well) one can arrive at exact solutions to the Schrödinger equation.



- For large energies, the allowed bands are very large and the forbidden bands are very narrow.
- The curve $E(k)$ always has a zero slope at the edges of the allowed bands.
- $\hbar k$ is defined as a crystal momentum and in many cases the dynamical behavior of the electron in a crystal lattice with respect to the crystal momentum is similar to that of a free particle with respect to the real momentum.

Using different methods for energy band-structure calculation, one can arrive at the energy bands, i.e. the $E(k)$ vs. k relation for arbitrary material. The model band structure used in simple analysis is given below.



2.3. Crystal momentum and effective mass

- If the function $u_k(x)$ is a constant, $\psi(x) = e^{ikx}$ corresponds to a perfectly free electron of momentum $p = \pm\hbar k$ whose energy is

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

- We now consider the motion of an electron in the crystal under the influence of an applied electric field. The group velocity associated with the "electron wavepacket" is given by:

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

- Suppose now that the electron is acted upon by an external electric field $\mathbf{E}$ which leads to energy increase

$$dE = \frac{dE}{dk}\,dk = -e\mathbf{E}\,dx = -e\mathbf{E}\,v_g\,dt = -e\mathbf{E}\,\frac{1}{\hbar}\frac{dE}{dk}\,dt$$

which leads to:

$$dk = -\frac{e}{\hbar}\mathbf{E}\,dt \quad \text{or} \quad \hbar\frac{dk}{dt} = -e\mathbf{E} = F$$

This equation tells us that the time rate of change of crystal momentum equals the force $-eE$. It is thus the analogue of Newton's law showing that the crystal momentum of the electron in a periodic lattice changes under the influence of an applied field. the same way does the true momentum of free electron in vacuum.

- Differentiating the expression for v_g with respect to time gives:

$$\frac{dv_g}{dt} = \frac{1}{\hbar}\frac{d}{dt}\left(\frac{dE}{dk}\right) = \frac{1}{\hbar}\frac{d}{dk}\left(\frac{dE}{dk}\right)\frac{dk}{dt} = \frac{1}{\hbar}\frac{d^2E}{dk^2}\left(-\frac{e}{\hbar}\right)\mathcal{E} = \frac{F}{m^*}$$

where the effective mass is given by:

$$\frac{1}{m^*} = \frac{1}{\hbar^2}\frac{d^2E}{dk^2}$$

or, in general, the effective mass tensor is: $\frac{1}{m_{ij}} = \frac{1}{\hbar^2}\frac{\partial^2 E}{\partial k_i \partial k_j}$

→ If the energy E is a parabolic function of k, then the effective mass will be constant.

→ If $E(k)$ vs. k is not parabolic, then the mass will be a function of the energy (hyperbolic band model)

→ To summarize, to a first approximation, the entire effect of the periodic crystal potential is to replace the free electron mass with an effective mass.

→ The nonparabolicity is often described by a relation of the form

$$E(1+\alpha E) = \frac{\hbar^2 k^2}{2m^*}$$

which for the group velocity gives:

$$v_g = \frac{1}{\hbar}\frac{dE}{dk} = \frac{1}{\hbar}\frac{1}{dk/dE}$$

Since:

$$k = \frac{\sqrt{2m^*}}{\hbar}\sqrt{E+\alpha E^2}$$

we get:

$$v_g = \frac{1}{\cancel{\hbar}}\,\frac{1}{\frac{\sqrt{2m^*}}{\cancel{\hbar}}\,\frac{1}{2}\,(E+\alpha E^2)^{-1/2}}\cdot(1+2\alpha E)^{-1}$$

$$= \frac{2}{\sqrt{2m^*}}\,[E(1+\alpha E)]^{1/2}\,(1+2\alpha E)^{-1} =$$

$$= \frac{2}{\sqrt{2m^*}}\,\frac{\hbar k}{\sqrt{2m^*}}\,\frac{1}{1+2\alpha E} = \frac{2\hbar k}{2m^*}\,\frac{1}{1+2\alpha E} = \frac{\hbar k/m^*}{1+2\alpha E}$$

To summarize;

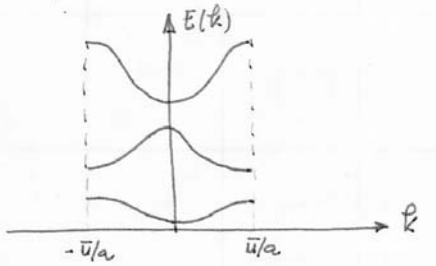
$v_g = \frac{\hbar k}{m^*}\,\frac{1}{1+2\alpha E}$ for non-parabolic (hyperbolic) bands.

2.4 Reduced zone representation; electrons and holes

- The condition that led to the allowed and forbidden energy bands in the Kronig-Penney model is:

$$-1 \le \cos(ka) \le 1$$

which suggests that for values $k' = k + n\frac{2\pi}{a}$, it leads to the same condition, i.e. the assignment for values of k is not unique. Therefore, one can translate any of the curves by $n\frac{2\pi}{a}$ and still satisfy the above condition. By doing this transformation we arrive at the REDUCED ZONE REPRESENTATION of the energy versus propagation constant relationship.



Bloch wavefunctions satisfy the Bragg reflection condition at points $k = n\pi/a$ where

$$v_g = \frac{1}{\hbar}\frac{dE}{dk} = 0$$

(standing wave pattern)

- The current density from a given band is then given by:

$$\vec{J} = -e n_0 \vec{v} \qquad \text{average velocity } \vec{v} = \frac{1}{n_0 V}\sum_i \vec{v}_i$$

number of electrons per unit volume belonging to the band

$$\vec{J} = -e n_0 \frac{1}{n_0 V}\sum_i \vec{v}_i = -\frac{e}{V}\sum_i \vec{v}_i$$

Important remarks:

(a) In a completely filled band or completely empty band the current is identically zero

(b) If we have perfectly periodic potential, an electron in an occupied band will undergo Zener oscillations. Scattering processes prevent the Zener oscillation behavior from ever occuring in practice.

- For a band that contains small number of electrons, the current obtained when a small voltage is applied is obtained by summing the velocityes of all the electrons in the band.
- If the band is nearly full, there will be very few empty states, the current is best expressed by writting it in a form:

$$J = -\frac{e}{V}\sum_i v_i = -\frac{e}{V}\left[\overset{0}{\cancel{\sum_j \vec{v}_j}} - \sum_K v_K\right] = \frac{e}{V}\sum_K v_K = -\frac{(-e)}{V}\sum_K v_K$$

sum over all occupied velocity states

sum over all velocity states

sum over unoccupied velocity states (positive charges)

Since the unoccupied states will always be at the top of the band where $1/m^* = \frac{1}{\hbar^2}\frac{d^2E}{dk^2} < 0$ (concave) and since the charge is negative, it can be considered as a positive particle of positive mass that is accelerated in the direction of the field. Therefore, almost full band may be regarded as involving a relatively small number of positive charges which we call holes. The velocity and momenta of the holes are those corresponding to the unoccupied states in the band.

2.5. Dynamics of electrons in two and three-dimensional lattices

We can generalize in a rather straigtforward way the concepts introduced in the previous section for 2D and 3D systems:

- Group velocity:

$$\vec{v}_g = \frac{1}{\hbar}\nabla_K E \qquad \nabla_K \text{ (gradient operator in the } k\text{-space)}$$

- Effective mass tensor:

$$\frac{d\vec{v}_g}{dt} = \frac{1}{\hbar}\frac{d}{dt}\nabla_K E \quad , \quad \nabla_K E = \underbrace{\frac{\partial E}{\partial k_x}}_{A_x}\vec{i}_x + \underbrace{\frac{\partial E}{\partial k_y}}_{A_y}\vec{i}_y + \underbrace{\frac{\partial E}{\partial k_z}}_{A_z}\vec{i}_z$$

Then: $$\frac{\partial}{\partial t}A_i = \frac{\partial A_i}{\partial k_x}\frac{\partial k_x}{\partial t} + \frac{\partial A_i}{\partial k_y}\frac{\partial k_y}{\partial t} + \frac{\partial A_i}{\partial k_z}\frac{\partial k_z}{\partial t}$$

$$= (\nabla_K A_i)\cdot\frac{d\vec{k}}{dt}$$

The vector $\frac{d\vec{A}}{dt}$ can thus be written as: $\frac{d\vec{A}}{dt} = \underbrace{(\nabla_K \vec{A})}_{\text{tensor}}\cdot\underbrace{\frac{d\vec{k}}{dt}}_{\text{vector}}$

Therefore:

$$\frac{dv_g}{dt} = \frac{1}{\hbar}\nabla_K(\nabla_K E)\cdot\frac{d\vec{k}}{dt} = \frac{1}{\hbar^2}\nabla_K(\nabla_K E)\cdot\underbrace{\vec{F}} = \left(\frac{1}{m^*}\right)\vec{F}$$

where the effective mass tensor is: $\frac{1}{m^*} = \frac{1}{\hbar^2}\nabla_K(\nabla_K E)$

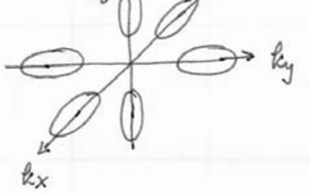
The elements of this tensor are:

$$\left(\frac{1}{m^*}\right)_{\alpha\beta} = \frac{1}{\hbar^2}\frac{\partial^2 E}{\partial k_\alpha \partial k_\beta} \quad \Rightarrow \left(\frac{1}{m^*}\right)_{\alpha\beta} = \left(\frac{1}{m^*}\right)_{\beta\alpha}$$

- The constant energy surfaces will, in general, for the conduction band be given by:

$$\frac{\hbar^2 k_x^2}{2m_x} + \frac{\hbar^2 k_y^2}{2m_y} + \frac{\hbar^2 k_z^2}{2m_z} = E$$

Silicon → ellipsoidal constant energy surfaces in the first Brilloin zone



GaAs → simple spherical constant energy surface centered at the Γ-point

- Valence bands exhibit warped constant energy surfaces:

$$E \approx \frac{\hbar^2 k^2}{2m_0}\left[A \pm \left(B^2 + \frac{C^2}{6}\right)^{1/2}\right] \quad \text{small } k$$

$$E \approx a k^2 [1 \mp g(\theta,\varphi)] \quad \begin{matrix} - \text{ heavy} \\ + \text{ light} \end{matrix}$$

$$g(\theta,\varphi) = [b^2 + c^2(\sin^4\theta \cos^2\phi \sin^2\phi + \sin^2\theta \cos^2\theta]^{1/2}$$

$$a = \frac{\hbar^2 |A|}{2m_0}, \quad b = \frac{|B|}{|A|}, \quad c = \frac{|c|}{|A|}$$