Lecture 23 (Griffiths, chapter 5.3.2).

Kronig-Penney Model of Solid.
Hill Equation.
Floquet-Bloch Theorem.
Dirac Comb.
Band Structure.

As usual, few (one) of the loosely bound outermost valence electrons in each atom become detached and roam around throughout the material subject to the combined potential of the entire crystal.

The essence of a Kronig-Penney model is as follows. Each of those electrons in a lattice sees a periodic array of potential wells due to the forces exerted on the electrons by the regularly spaced positively charged essential stationary nuclei, see figure below. As in the free electron model (that we considered last lecture) electrons are also subject to some boundary conditions and the Pauli Exclusion Principle.

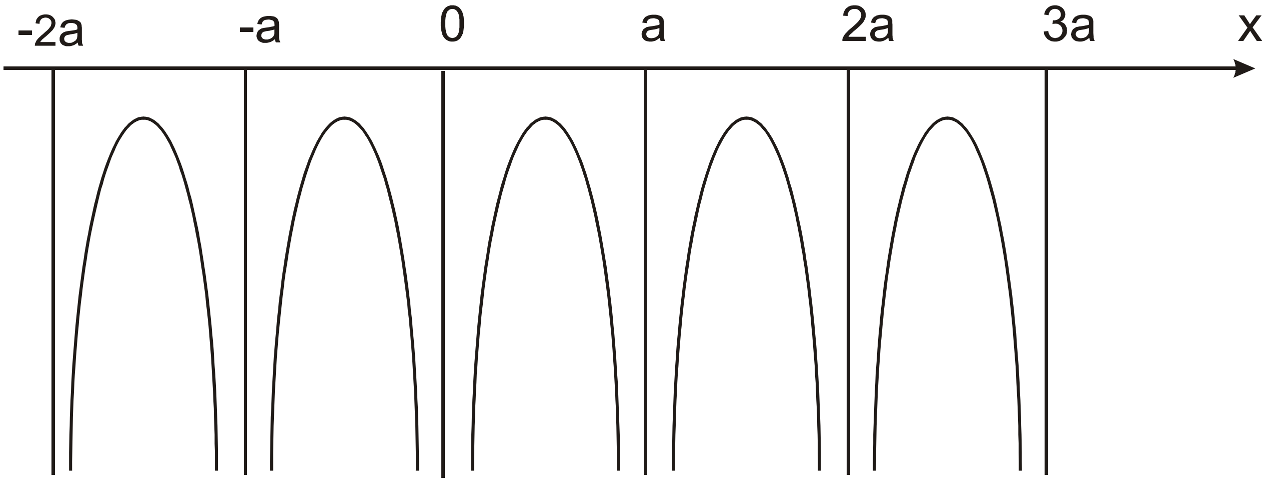

Figure 1

The qualitative behavior of electrons is dictated to a remarkable degree by the fact that the potential is periodic. The actual shape is relevant only to the finer details. Therefore, it is reasonable to consider the simplest possible model of a periodic potential – a one-dimensional Dirac comb.

But let me start from the Schrödinger equation for arbitrary periodic potential:

$$\frac{d^2\psi(x)}{dx^2}+\frac{2m}{\hbar^2}\left[E-V(x)\right]\psi(x)=0\,, \qquad V(x)=V(x+a)\,. \qquad (23.1)$$

Using the notation $f(x) \equiv \frac{2m}{\hbar^2}\left[E - V(x)\right]$, we obtain

$$\frac{d^2\psi(x)}{dx^2} + f(x)\psi(x) = 0, \quad f(x) = f(x+a). \tag{23.2}$$

Equation (23.2) is a so-called **Hill equation**. According to **Floquet-Bloch theorem**, its general solution can be represented as a superposition of two **Bloch waves**

$$\psi(x) = C_1F_1(x)\exp(i\mu_1 x) + C_2F_2(x)\exp(i\mu_2 x), \tag{23.3}$$

where

$$F_{1,2}(x) = F_{1,2}(x+a), \qquad \mu_2 = -\mu_1. \tag{23.4}$$

In general, the parameter $\mu \equiv \mu_1$ is complex. It follows immediately that both Bloch waves, $\psi_{1,2}(x) = F_{1,2}(x)\exp(i\mu_{1,2}x)$, satisfy condition

$$\psi_1(x+a) = \lambda_1\psi_1(x), \qquad \psi_2(x+a) = \lambda_2\psi_2(x), \tag{23.5}$$

where $\lambda_1 = e^{i\mu_1 a}$, $\lambda_2 = e^{i\mu_2 a}$; and $\lambda_2 = 1/\lambda_1$ since $\mu_2 = -\mu_1$. The virtue of Floquet-Bloch theorem is that we need only solve the Schrödinger equation within a single period (say, on the interval $0 \le x < a$); recursive application of equation (23.5) generates solution everywhere else.

Now let me impose some restrictions (I wouldn't call this by boundary conditions) on a general solution (23.3). We imagine that the length of the crystal Na is very large $(N \sim 10^{23})$, i.e. in fact infinite. Therefore, it is reasonable to expect the probability density to vary in the same way as the potential, i.e.

$$|\psi(x+a)|^2 = |\psi(x)|^2. \tag{23.6}$$

From this condition we have two possible sets of solutions:

$$C_2 = 0, \qquad \mu_1 = \frac{2\pi}{Na}n, \quad n = 0,\ \pm1,\ \pm2,\ \ldots; \tag{23.7a}$$

or

$$C_1 = 0, \qquad \mu_2 = \frac{2\pi}{Na}n, \quad n = 0,\ \pm1,\ \pm2,\ \ldots. \tag{23.7b}$$

Therefore, in infinite (very large) crystal the solutions of the Schrödinger equation are two independent Bloch waves, $\psi_{1,2}(x) = F_{1,2}(x)\exp(i\mu_{1,2}x)$, (not their superposition) with necessarily real μ, see (23.7); remember that $\mu_2 = -\mu_1 \equiv -\mu$.

Now, suppose the periodic potential consists of a long string of delta-functions (the Dirac comb):

$$V(x) = -\alpha \sum_{j=-\infty}^{j=+\infty} \delta(x - ja), \quad \alpha > 0. \tag{23.8}$$

Let me find the two Bloch wave. In the region $ja < x < (j+1)\,a$ each of them can be represented as

$$\psi(x) = A_j\, e^{ik(x-na)} + B_j\, e^{-ik(x-na)};$$

and in the region $(j-1)\,a < x < j\,a$ as

$$\psi(x) = A_{j-1}\, e^{ik(x-(j-1)a)} + B_{j-1}\, e^{-ik(x-(j-1)a)}.$$

According to Floquet theorem $\psi(ja) = \lambda \psi((j-1)\,a)$, $\psi'(ja) = \lambda \psi'((j-1)a)$. As a result, $A_{j-1} = A_j / \lambda$, $B_{j-1} = B_j / \lambda$. At $x = ja$, $\psi(x)$ must be continuous and its derivative suffers a discontinuity proportional to the strength of the delta function (see Griffiths, pp. 71-72) . Therefore,

$$\frac{A_j}{\lambda} e^{ika} + \frac{B_j}{\lambda} e^{-ika} = A_j + B_j \ ,$$

$$i\,k\left(A_j - B_j\right) - i\,k\left(\frac{A_j}{\lambda} e^{ika} - \frac{B_j}{\lambda} e^{-ika}\right) = -\frac{2m\alpha}{\hbar^2}\left(A_j + B_j\right).$$

From this system we obtain quadratic equation for λ (two values of λ correspond to the two Bloch waves)

$$\lambda^2 - 2f(E)\,\lambda + 1 = 0, \qquad f(E) = \cos ka - \frac{m\alpha^2}{\hbar^2 k} \sin ka. \tag{23.9}$$

First, we can see that $\lambda_1 \lambda_2 = 1$. This is the expected result, see Floquet theorem. Second, we can see that $\lambda_1 + \lambda_2 = 2f(E)$. Taking into account that $\lambda_{1,2} = e^{\pm i\mu a}$, we obtain

$$\cos(\mu\, a) = \cos ka - \frac{m\alpha}{\hbar^2 k} \sin ka. \tag{23.10}$$

This is a so-called dispersion equation for the parameter μ. Introducing notation $\varphi \equiv \mu\, a$, where φ is called Bloch phase, $z \equiv k\, a$, $\beta \equiv m\alpha\, a / \hbar^2$, we finally arrived at

$$\cos\,\varphi = \cos\,z - \frac{\beta}{z} \sin\,z. \tag{23.11}$$

The constant β is a dimensionless measure of the strength of the delta function. In Figure 2 I plotted $\cos\varphi(k)$ for the case $\beta = 7$.

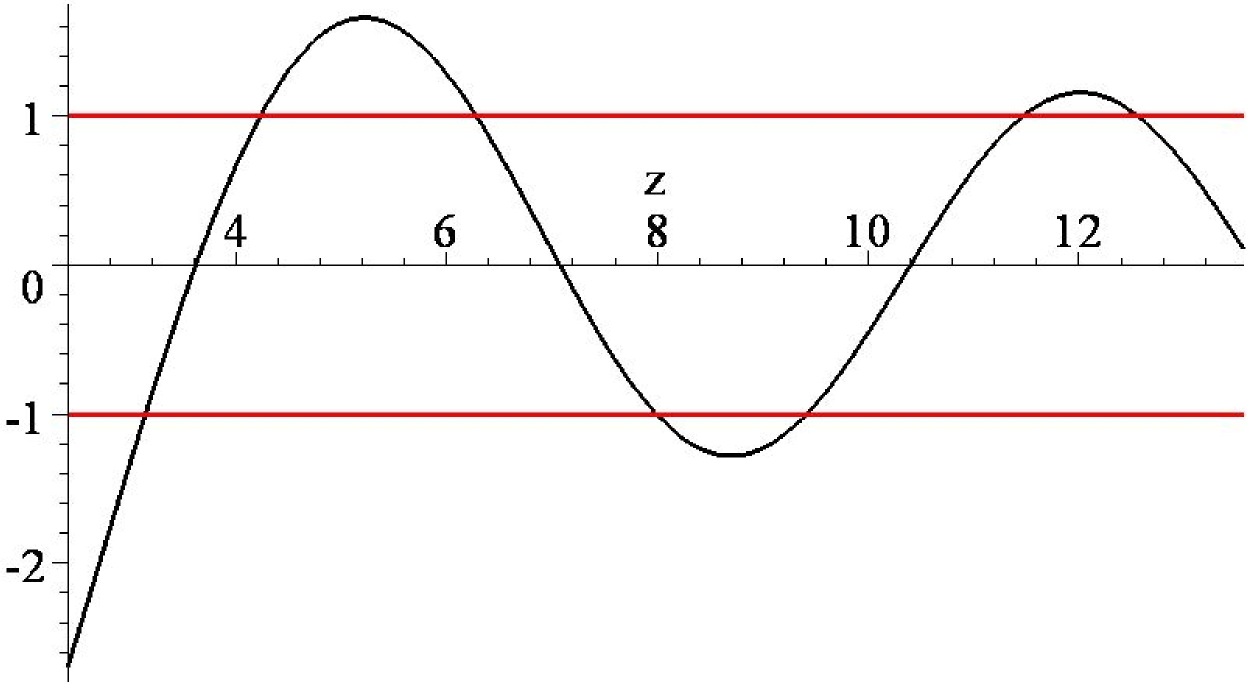

Figure 2

We have a set of forbidden and allowed bands:

allowed bands, when $-1 \le \cos\varphi \le 1$,

forbidden bands (band gaps), when $|\cos\varphi| \ge 1$.

In very large (infinite) crystals the parameter μ is necessarily real. Therefore, the Bloch phase $\varphi \equiv \mu a$ is necessarily real as well. Hence, electrons can be located only in allowed bands. Within an allowed band there are N (very large number of atoms) allowed single-particle discrete states; remember that in infinite crystals $\mu a = 2\pi n / N$. Because of the Pauli exclusion principle, each of those states can hold only two electrons. If each atom has one valence electron, the first allowed band will be half-filled. If each atom has two valence electrons, those atoms completely fill the first band. When a band is just filled, the system should be an insulator. When a ban is partly filled, the system should be a good conductor.