THE KRONIG-PENNEY MODEL

Metals generally have a crystalline structure, that is, the ions are arranged in a way that exhibits a spatial periodicity. This periodicity has an effect on the motion of the free electrons in the metal, and this effect is exhibited in the simple model that we will now discuss.

The periodicity will be built into the potential, for which we require that

$$V(x + a) = V(x) \tag{5-95}$$

Since the kinetic energy term $-(\hbar^2/2m)(d^2/dx^2)$ is unaltered by the change $x \rightarrow x + a$, the whole *Hamiltonian is invariant under displacements by a.* For the case of zero potential, when the solution corresponding to a given energy $E = \hbar^2k^2/2m$ is

$$\psi(x) = e^{ikx} \tag{5-96}$$

the displacement yields

$$\psi(x + a) = e^{ik(x+a)} = e^{ika}\psi(x) \tag{5-97}$$

that is, the original solution multiplied by a phase factor, so that

$$|\psi(x + a)|^2 = |\psi(x)|^2 \tag{5-98}$$

The observables will therefore be the same at x as at $x + a$, that is, we cannot tell whether we are at x or at $x + a$. In our example we shall also insist that $\psi(x)$ and $\psi(x + a)$ differ only by a phase factor, which need not, however, be of the form e^{ika}.

[7]This can be justified for the potentials shown in Fig. 5.15. Our approximate expressions for transmission probabilities are not applicable to delta function potentials.

We digress briefly to discuss this requirement more formally. The invariance of the Hamiltonian under a displacement $x \to x + a$ can be treated formally as follows. Let D_a be an operator whose rule of operation is that

$$D_a f(x) = f(x + a) \tag{5-99}$$

The invariance implies that

$$[H, D_a] = 0 \tag{5-100}$$

We can find the eigenvalues of this operator by noting that

$$D_a \psi(x) = \lambda_a \psi(x) \tag{5-101}$$

together with

$$D_{-a} D_a f(x) = D_a D_{-a} f(x) = f(x) \tag{5-102}$$

implies that $\lambda_a \lambda_{-a} = 1$, so that λ_a must be of the form $e^{\sigma a}$. Consider now a simultaneous eigenfunction of H and D_a, $\psi(x)$ and define

$$u(x) = e^{-\sigma x} \psi(x) \tag{5-103}$$

Then

$$\begin{aligned} D_a u(x) &= u(x + a) = e^{-\sigma(x+a)} D_a \psi(x) \\ &= e^{-\sigma(x+a)} e^{\sigma a} \psi(x) \\ &= e^{-\sigma x} \psi(x) = u(x) \end{aligned} \tag{5-104}$$

Thus $u(x)$ is a periodic function of a obeying

$$u(x + a) = u(x) \tag{5-105}$$

and $\psi(x) = e^{\sigma x} u(x)$. If we now take into account that square integrability requires that the real part of σ must vanish, we get the condition that a simultaneous eigenfunction of H and D_a must be of the form

$$\psi(x) = e^{ix \operatorname{Im} \sigma} u(x) \tag{5-106}$$

with $u(x) = u(x + a)$. It is convenient to write $\operatorname{Im}\sigma = \phi/a$. This statement, known as *Bloch's theorem*, was first used by F. Bloch in the context of quantum mechanics, but it is also known in the mathematical literature as Floquet's theorem.

To simplify the algebra, we will take a series of repulsive delta-function potentials,

$$V(x) = \frac{\hbar^2}{2m} \frac{\lambda}{a} \sum_{n=-\infty}^{\infty} \delta(x - na) \tag{5-107}$$

Away from the points $x = na$, the solution will be that of the free-particle equation, that is, some linear combination of $\sin kx$ and $\cos kx$ (we deal with real functions for simplicity). Let us assume that in the region R_n defined by $(n - 1)\, a \leq x \leq na$, we have

$$\psi(x) = A_n \sin k(x - na) + B_n \cos k(x - na) \tag{5-108}$$

and in the region R_{n+1}, defined by $na \leq x \leq (n + 1)\, a$ we have

$$\psi(x) = A_{n+1} \sin k[x - (n + 1)\, a] + B_{n+1} \cos k[x - (n + 1)\, a] \tag{5-109}$$

Continuity of the wave function implies that $(x = na)$

$$-A_{n+1} \sin ka + B_{n+1} \cos ka = B_n \tag{5-110}$$

and the discontinuity condition (5-13) here reads

$$kA_{n+1} \cos ka + kB_{n+1} \sin ka - kA_n = \frac{\lambda}{a} B_n \tag{5-111}$$

A little manipulation yields

$$\begin{aligned} A_{n+1} &= A_n \cos ka + (g \cos ka - \sin ka)\, B_n \\ B_{n+1} &= (g \sin ka + \cos ka)\, B_n + A_n \sin ka \end{aligned} \tag{5-112}$$

where $g = \lambda/ka$.

The requirement from Bloch's theorem that

$$\psi(x + a) = e^{i(x+a)\mathrm{Im}\,\sigma}\, u(x + a) = e^{i\phi}\, e^{ix\mathrm{Im}\,\sigma}\, u(x) = e^{i\phi}\, \psi(x) \tag{5-113}$$

implies that

$$\psi(R_{n+1}) = e^{i\phi}\, \psi(R_n) \tag{5-114}$$

This is satisfied if

$$\begin{aligned} A_{n+1} &= e^{i\phi} A_n \\ B_{n+1} &= e^{i\phi} B_n \end{aligned} \tag{5-115}$$

When this is inserted into (5-113), we find a consistency condition that reads

$$(e^{i\phi} - \cos ka)(e^{i\phi} - g \sin ka - \cos ka) = \sin ka(g \cos ka - \sin ka)$$

that is,

$$e^{2i\phi} - e^{i\phi}(2 \cos ka + g \sin ka) + 1 = 0$$

Multiplication by $e^{-i\phi}$ gives

$$\cos \phi = \cos ka + \tfrac{1}{2} g \sin ka \tag{5-116}$$

If we take periodic boundary conditions for our "crystal" so that

$$\psi(R_{n+N}) = \psi(R_n) \tag{5-117}$$

then it follows from (5-114) that $e^{iN\phi} = 1$, that is,

$$\phi = \frac{2\pi}{N} m \qquad m = 0, \pm 1, \pm 2, \ldots \tag{5-118}$$

We used square integrability to show that σ had to be imaginary. If the x-values do not extend to infinity, then we would require that $(e^{\sigma a})^N = 1$, which again would imply that $\sigma a = i\phi$, a pure imaginary number.

We denote ϕ by qa, where q is the wave number of an electron in a box of length Na, with periodic boundary conditions and without any potential, that is, without any ions present. Thus (5-116) should be rewritten in the form

$$\cos qa = \cos ka + \tfrac{1}{2}\lambda \frac{\sin ka}{ka} \tag{5-119}$$

This is a very interesting result, because the left side is always bounded by 1, that is, there are restrictions on the possible ranges of the energy $E = \hbar^2 k^2/2m$ that depend on the parameters of our "crystal." Figure 5-19 shows a plot of the function $\cos x + \lambda \sin x/2x$ as a function of $x = ka$. The horizontal line represents the bounds on $\cos qa$, and the regions of x, for which the curve lies outside the strip, are forbidden regions. Thus there are *allowed energy bands* separated by regions that are forbidden. Note that the onset of a forbidden band corresponds to the condition

$$qa = n\pi \qquad n = \pm 1, \pm 2, \pm 3, \ldots \tag{5-120}$$

This, however, is just the condition for Bragg reflection with normal incidence. The existence of energy gaps can be understood qualitatively. In first approximation the electrons are free, except that there will be Bragg reflection when the waves reflected from successive atoms differ in phase by an integral number of 2π, that is, when (5-120) is satisfied. These reflections give rise to standing waves, with even and odd waves of the form $\cos \pi x/a$ and $\sin \pi x/a$, respectively. The energy levels corresponding to these standing waves are degenerate. Once the attractive interaction between the electrons and the positively charged ions at $x = ma$ (m integer) is taken into account, the even states, peaked at the ion location will move down in energy, and the odd states, peaked in between, will move up in energy. Thus the energy degeneracy is split at $k = n\pi/a$ and this leads to energy gaps, as shown in Fig. 5-19.

The Kronig-Penney model has some relevance to the theory of metals, insulators, and semiconductors if we take into account the fact (to be studied later) that energy levels occupied by electrons cannot accept more electrons. Thus a metal may have an energy band partially filled. If an external field is applied, the electrons are accelerated, and if there are momentum states available to them, the electrons will occupy the momentum states under the influence of the electric field. Insulators have completely filled bands, and an electric field cannot accelerate

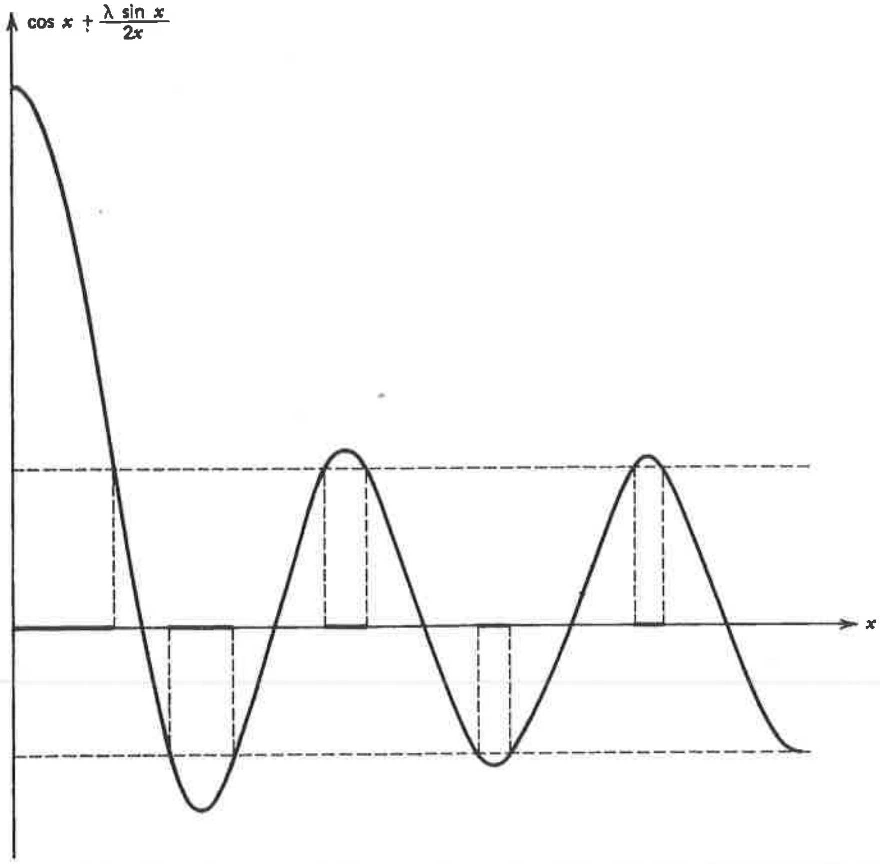

Figure 5-19. Plot of cos x + $(\lambda/2)(\sin x/x)$ as a function of x. The horizontal lines represent the bounds ± 1. The regions of x for which the curve lines outside the strip are forbidden.

electrons, since there are no neighboring empty states. If the electric field is strong enough, the electrons can "jump" across a forbidden energy gap and go into an empty allowed energy band. This corresponds to the breakdown of an insulator. The semiconductor is an insulator with a very narrow forbidden gap. There, small changes of conditions, such as a rise in temperature, can produce the "jump" and the insulator becomes a conductor.