June 7

Quantum Mechanics in Periodic Structures (cont.)

In the previous lecture, we studied electron wavefunctions in solids using the very simple tight-binding model. We can get more insight by solving a model Schrödinger equation in 1 dimension with a period potential. A simple example is the *Krönig-Penney model*, with the potential

$$V(x) = \sum_{n=-\infty}^{\infty} v_0 \, \delta(x - na)$$

That is, we wish to solve

$$E\,\varphi(x) = -\frac{\nabla^2}{2m}\varphi(x) + V(x)\,\varphi(x)$$

Away from the delta functions, it is easy to find the general solution to this equation

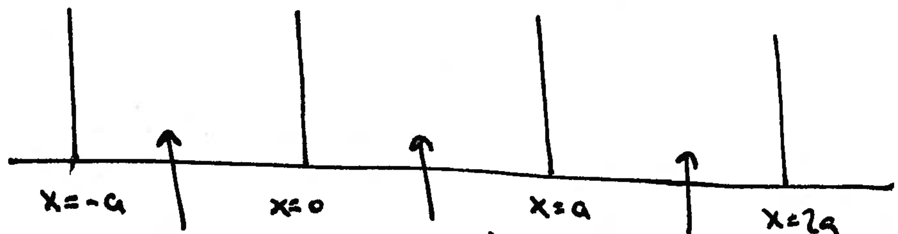
$$\varphi(x) = A e^{ikx} + B e^{-ikx} \qquad E = \frac{k^2}{2m}$$

In our general analysis of the Schrödinger equation in a periodic potential, we saw that each energy eigenstate can also be assigned a definite value of the lattice momentum p such that

$$\varphi(x+a) = e^{ipa}\varphi(x)$$

It is not so obvious what the relationship is between p and k. This will have to emerge from our solution.

However, given p, we can lay out the solution as



$$e^{-ipa}\left(Ae^{ik(x+a)}+Be^{-ik(x+a)}\right) \quad \left(Ae^{ikx}+Be^{-ikx}\right) \quad e^{ipa}\left(Ae^{ik(x-a)}+Be^{-ik(x-a)}\right)$$

THen A and B are determined by the joining conditions across any of the delta functions. At $x = 0$, these conditions are

$$\varphi(x=+\varepsilon) = \varphi(x=-\varepsilon) = \varphi(0)$$

$$-\frac{1}{2m}\left[\frac{d\varphi}{dx}(x=+\varepsilon) - \frac{d\varphi}{dx}(x=-\varepsilon)\right] + v_0\varphi(0) = 0$$

as we discussed for the problem with one delta function earlier in the course. Then

$$A+B = e^{-ipa}\left(Ae^{ika}+Be^{-ika}\right)$$

and

$$-\frac{1}{2m}\left[(ik)(A-B) - ik\,e^{-ipa}\left(Ae^{ika}-Be^{-ika}\right)\right]$$
$$+\, v_0(A+B) = 0$$

From the first equation,

$$A\left(1-e^{i(k-p)a}\right) = -B\left(1-e^{-i(k+p)a}\right)$$

The second equation is then

$$ik\left[A\left(1-e^{i(k-p)a}\right) - B\left(1-e^{-i(k+p)a}\right)\right] = 2mV_0(A+B)$$

Inserting the solution for B, we find

$$2ik\;A\left(1-e^{i(k-p)a}\right) = 2mV_0\left[A - A\frac{\left(1-e^{+i(k-p)a}\right)}{\left(1-e^{-i(k+p)a}\right)}\right]$$

$$2ik\,A\left(1-e^{i(k-p)a}\right)\left(1-e^{-i(k+p)a}\right) = 2mV_0\,A\left[e^{i(k-p)a} - e^{-i(k+p)a}\right]$$

or

$$2ikA\left(1 - e^{-ipa}\left(e^{ika}+e^{-ika}\right) + e^{-2ipa}\right) = 2mV_0\,A\,e^{-ipa}\left(e^{ika}-e^{-ika}\right)$$

$$A\left(\cos pa - \cos ka\right) = \frac{mV_0}{k}\,A\,\sin ka$$

If there is a nontrival solution, $A \neq 0$. Then we must have

$$\cos pa = \cos ka + \frac{mV_0}{k}\sin ka$$

Note that the left-hand side is periodic under

$$p \to p + \frac{2\pi}{a}$$

so this equation only depends on the part of p that is a conserved lattice momentum.

However, there is a problem solving the equation near $k = 0$. At $k = 0$, the right-hand side of the equation equals

$$1 + mv_0 a > 1$$

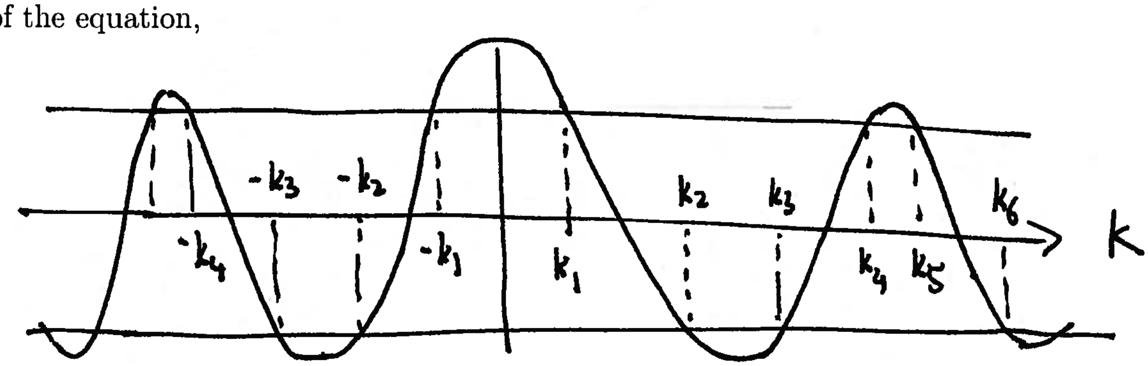
so that there is no solution for real p. However, if p is complex, then the factor

$$(e^{ipa})^n$$

will blow up as $n \to \infty$ or as $n \to -\infty$. So, there is a continuum-normalizable wavefunction only when

$$\left| \cos ka + \frac{mv_0}{k} \sin ka \right| \le 1$$

Now we can see the form of the general solution if we graph the right-hand side of the equation,



There are *no* energy eigenstates for

$$E < \frac{k_1^2}{2m}$$

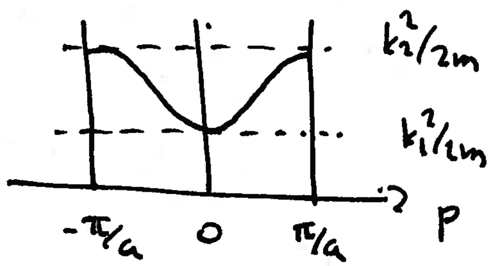
corresponding to

$$-k_1 < k < k_1$$

At $k = \pm k_1$, the value of p is $p = 0$. At

$$k = \pm k_2 \qquad , \qquad p = \pm \frac{\pi}{a}$$

So the two segments $(-k_2, -k_1)$ and (k_1, k_2) together form an energy band



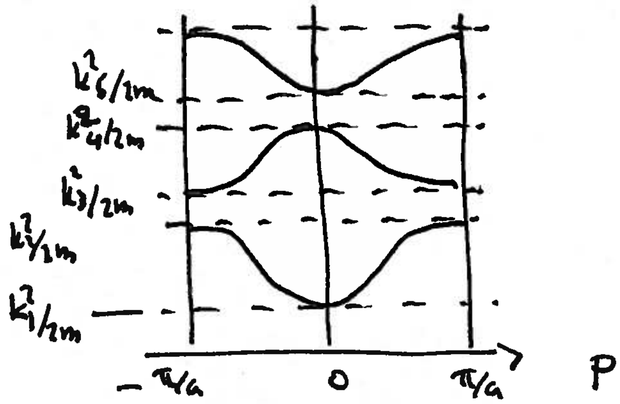
The next band begins at

$$k = \pm k_3 \qquad E = \frac{k_3^2}{2m} \qquad p = \pm \frac{\pi}{a}$$

and extends to

$$k = \pm k_4 \qquad E = \frac{k_4^2}{2m} \qquad p = 0$$

In all, we have energy levels



The band gaps become smaller as $|k| \to \infty$, since the $\sin ka$ term has a coefficient proportional to $1/k$.

These results fit into a more general theory of differential equations with periodic coefficient functions. Consider, for example, the case of a second-order linear differential equation for $\phi(x)$ with coefficient functions of period a. If we specify the values

$$(\phi(0),\ \phi'(0))$$

at $x = 0$, we can integrate the equation and compute these values at $x = a$. The relation can be written

$$\begin{pmatrix} \phi(a) \\ \phi'(a) \end{pmatrix} = T \begin{pmatrix} \phi(0) \\ \phi'(0) \end{pmatrix}$$

Then

$$\begin{pmatrix} \phi(2a) \\ \phi'(2a) \end{pmatrix} = T^2 \begin{pmatrix} \phi(0) \\ \phi'(0) \end{pmatrix}$$

and so forth. The eigenvector of the matrix T, with eigenvalue e^{λ} gives a solution of the form

$$\phi(x) = e^{\lambda(x/a)}\ \eta(x)$$

where $\eta(x)$ is a periodic function. More generally all solutions to a linear differential equation with periodic coefficient can be written as a linear combination of such solutions of this type, periodic up to a factor; this is *Floquet's theorem.*

For two solutions of the Schrödinger equation $\phi_1(x)$ and $\phi_2(x)$, it is not difficult to show that the *Wronskian*

$$W = \phi_1(x)\phi_2'(x) - \phi_1'(x)\phi_2(x)$$

is constant. From this is follows that

$$\det T = 1$$

Then the solutions that are periodic up to a factor come in pairs. Often, the exponent λ is imaginary.

$$\lambda = i\alpha$$

However, as we change the energy for the same potential, λ can cross over and become real. In this case, there are no wavefunctions that are continuum-normalizable. We have seen exactly this happen in the Krönig-Penney model; now we see that it is a general phenomenon. The values of the energy for which λ is real give the gaps between energy bands.

There is one more simple problem that is useful for understanding energy bands. This is the theory of a free Schrödinger particle perturbed by a weak periodic potential. In this problem, we start with a free particle with the energy-momentum relation

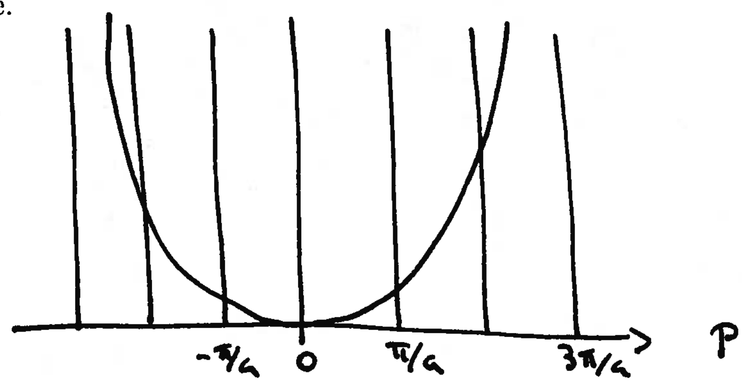
$$E = \frac{p^2}{2m}$$

A periodic potential can be written in a Fourier representation as

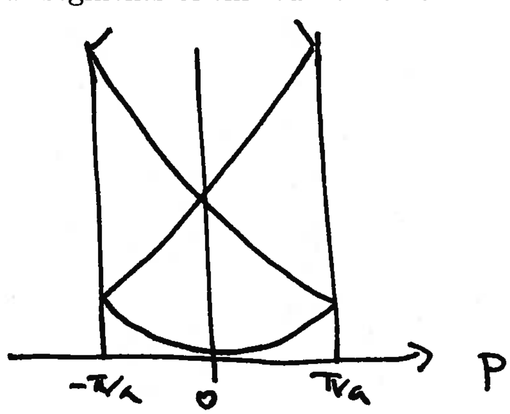
$$V(x) = \sum_n e^{i\frac{2\pi}{a}nx} V_n$$

That is, the nonzero Fourier components are associated with momenta on the reciprocal lattice. Perturbing with these elements induces changes in momentum by reciprocal lattice vectors.

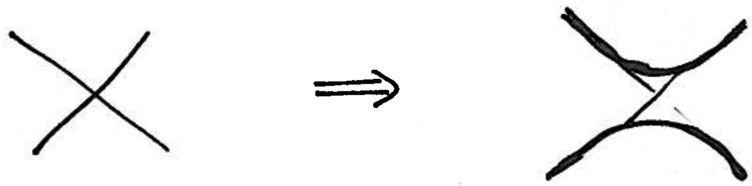
To begin the analysis, draw the energy-momentum relation as a function of p and consider the projection from the full momentum p to a lattice momentum that lies in the Brillouin zone.



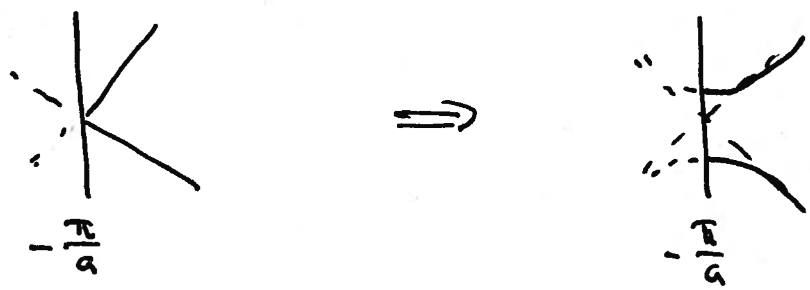
Anticipating that the final spectrum will depend on the lattice momentum component of p, I will move the various segments of this curve into the Brillouin zone.



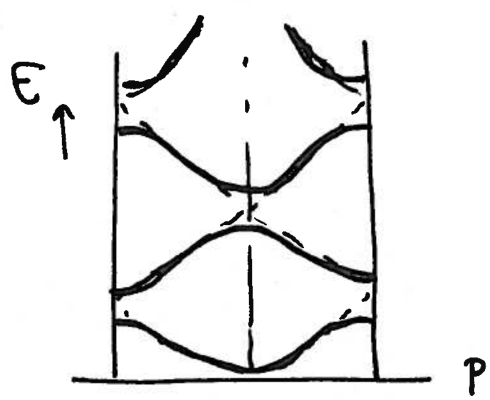
Where the lines cross, we have degenerate states with the same value of the lattice momentum. At the moment, these states have different values of the full momentum, but the full momentum will not be conserved when we turn on the potential. Then these states will mix with one another and split in energy



This splitting will also smooth the cusps at the boundaries of the Brillouin zone, so that the energies will become analytic, periodic functions of the lattice momentum, as required.



The final result is a spectrum of energies

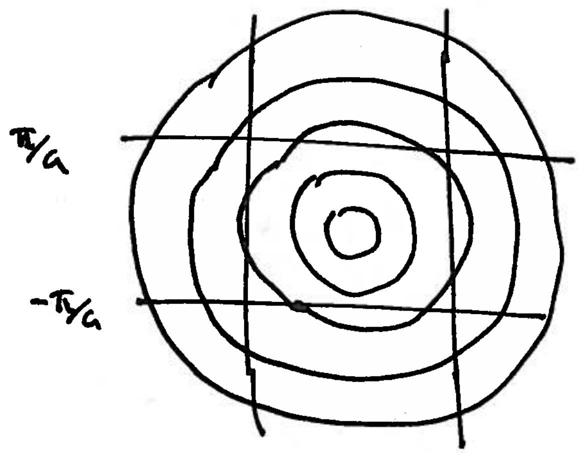


very similar to the ones that we found in the previous two examples.

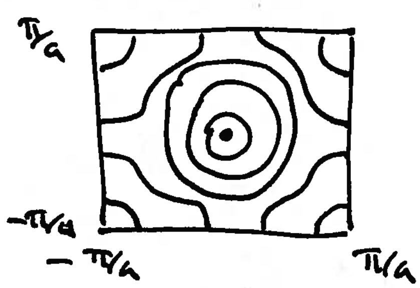
This perturbation of a free-particle spectrum is the easiest of the examples to generalize to higher dimensions. Consider, then, the case of a particle in 2 dimensions in a weak periodic potential. For a square lattice, the Brillouin zone is the square

$$-\frac{\pi}{a} < p^1, p^2 < \frac{\pi}{a}$$

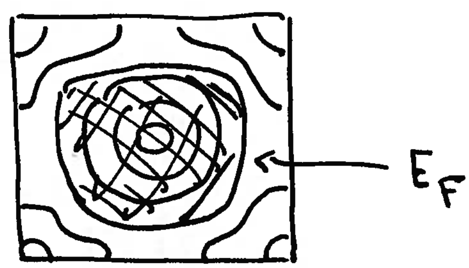
When $V = 0$, the contours of constant energy $E(p)$ are



Consider first the contours already in the Brillouin zone. When we turn on the periodic potential, these contours will be smoothed into periodic curves.

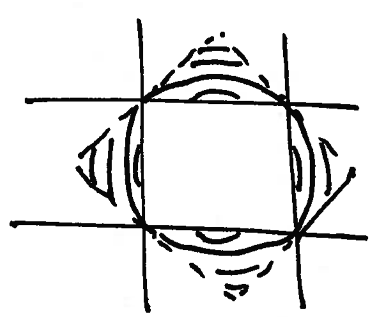


A half-filled band will correspond to the level occupancy

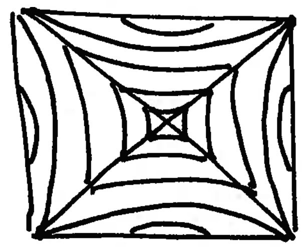


with a distinct one-dimensional *Fermi surface.*

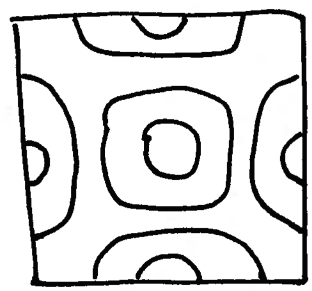
Next, consider the contours just outside the Brillouin zone in the original picture, in particular, those contours in the region



which is called the *second Brillouin zone.* By translations by a lattice momentum, we can bring these points into the (first) Brillouin zone



Then smoothing gives the picture

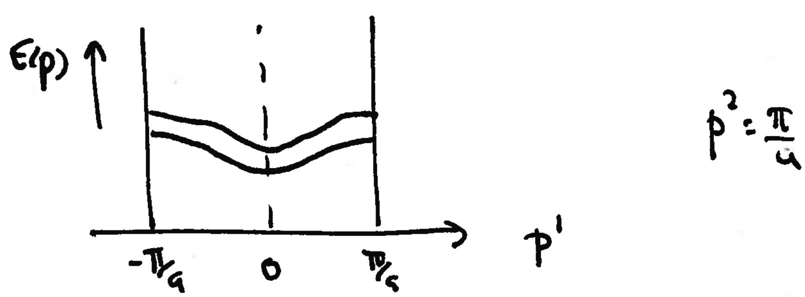


with a band gap on the boundary of the zone separating this band from the one below, and with the energies of state *increasing* from the points

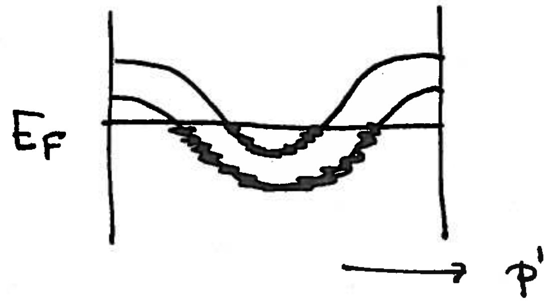
$$\left(0,\ \pm\frac{\pi}{a}\right) \qquad\qquad \left(\pm\frac{\pi}{a},\ 0\right)$$

to the center of the zone.

Along the wall of the zone at $p^2 = \pi/a$, the two energy bands have the form

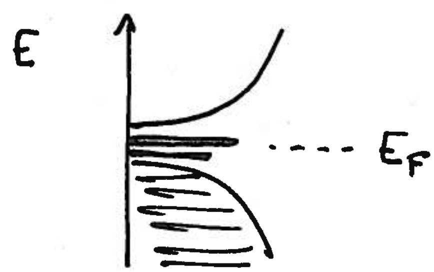


Now it is possible that, if we add electrons to a density that would completely fill the lower band, a more energetically preferred configuration would be



for which the system would be a metal. In general, it is necessary to understand the 3-dimensional structure of the electron energy bands to predict whether a given solid will be a metal or an insulator.

There are intermediate situations between metal and insulator. In Germanium, there are distinct filled and unfilled bands, but the band gap is so small that it can be bridged by a thermal fluctuation. In Silicon, it is possible add impurities that insert states into the energy gap, and these can form tight-binding bands in the gap



These materials are *semiconductors*. The manipulation of their properties provides the main technology behind modern electronic devices.

There is much, much more to learn about electrons in solids. But I hope that these lectures have given you an introduction to this important practical use of quantum mechanics.