

Propagation in a Crystal Lattice

13-1 States for an electron in a one-dimensional lattice

You would, at first sight, think that a low-energy electron would have great difficulty passing through a solid crystal. The atoms are packed together with their centers only a few angstroms apart, and the effective diameter of the atom for electron scattering is roughly an angstrom or so. That is, the atoms are large, relative to their spacing, so that you would expect the mean free path between collisions to be of the order of a few angstroms—which is practically nothing. You would expect the electron to bump into one atom or another almost immediately. Nevertheless, it is a ubiquitous phenomenon of nature that if the lattice is perfect, the electrons are able to travel through the crystal smoothly and easily—almost as if they were in a vacuum. This strange fact is what lets metals conduct electricity so easily; it has also permitted the development of many practical devices. It is, for instance, what makes it possible for a transistor to imitate the radio tube. In a radio tube electrons move freely through a vacuum, while in the transistor they move freely through a crystal lattice. The machinery behind the behavior of a transistor will be described in this chapter; the next one will describe the application of these principles in various practical devices.

The conduction of electrons in a crystal is one example of a very common phenomenon. Not only can electrons travel through crystals, but other “things” like atomic excitations can also travel in a similar manner. So the phenomenon which we want to discuss appears in many ways in the study of the physics of the solid state.

You will remember that we have discussed many examples of two-state systems. Let's now think of an electron which can be in either one of two positions, in each of which it is in the same kind of environment. Let's also suppose that there is a certain amplitude to go from one position to the other, and, of course, the same amplitude to go back, just as we have discussed for the hydrogen molecular ion in Section 10-1. The laws of quantum mechanics then give the following results. There are two possible states of definite energy for the electron. Each state can be described by the amplitude for the electron to be in each of the two basic positions. In either of the definite-energy states, the magnitudes of these two amplitudes are constant in time, and the phases vary in time with the same frequency. On the other hand, if we start the electron in one position, it will later have moved to the other, and still later will swing back again to the first position. The amplitude is analogous to the motions of two coupled pendulums.

Now consider a perfect crystal lattice in which we imagine that an electron can be situated in a kind of “pit” at one particular atom and with some particular energy. Suppose also that the electron has some amplitude to move into a different pit at one of the nearby atoms. It is something like the two-state system—but with an additional complication. When the electron arrives at the neighboring atom, it can afterward move on to still another position as well as return to its starting point. Now we have a situation analogous not to *two* coupled pendulums, but to an *infinite number* of pendulums all coupled together. It is something like what you see in one of those machines—made with a long row of bars mounted on a torsion wire—that is used in first-year physics to demonstrate wave propagation.

If you have a harmonic oscillator which is coupled to another harmonic oscillator, and that one to another, and so on . . . , and if you start an irregularity in one place, the irregularity will propagate as a wave along the line. The same situation exists if you place an electron at one atom of a long chain of atoms.

13-1 States for an electron in a one-dimensional lattice

13-2 States of definite energy

13-3 Time-dependent states

13-4 An electron in a three-dimensional lattice

13-5 Other states in a lattice

13-6 Scattering by imperfections in the lattice

13-7 Trapping by a lattice imperfection

13-8 Scattering amplitudes and bound states

Usually, the simplest way of analyzing the mechanical problem is not to think in terms of what happens if a pulse is started at a definite place, but rather in terms of steady-wave solutions. There exist certain patterns of displacements which propagate through the crystal as a wave of a single, fixed frequency. Now the same thing happens with the electron—and for the same reason, because it's described in quantum mechanics by similar equations.

You must appreciate one thing, however; the amplitude for the electron to be at a place is an *amplitude*, not a probability. If the electron were simply leaking from one place to another, like water going through a hole, the behavior would be completely different. For example, if we had two tanks of water connected by a tube to permit some leakage from one to the other, then the levels would approach each other exponentially. But for the electron, what happens is amplitude leakage and not just a plain probability leakage. And it's a characteristic of the imaginary term—the i in the differential equations of quantum mechanics—which changes the exponential solution to an oscillatory solution. What happens then is quite different from the leakage between interconnected tanks.

We want now to analyze quantitatively the quantum mechanical situation. Imagine a one-dimensional system made of a long line of atoms as shown in Fig. 13-1(a). (A crystal is, of course, three-dimensional but the physics is very much the same; once you understand the one-dimensional case you will be able to understand what happens in three dimensions.) Next, we want to see what happens if we put a single electron on this line of atoms. Of course, in a real crystal there are already millions of electrons. But most of them (nearly all for an insulating crystal) take up positions in some pattern of motion each around its own atom—and everything is quite stationary. However, we now want to think about what happens if we put an *extra* electron in. We will not consider what the other ones are doing because we suppose that to change their motion involves a lot of excitation energy. We are going to add an electron as if to produce one slightly bound negative ion. In watching what the *one* extra electron does we are making an approximation which disregards the mechanics of the inside workings of the atoms.

Of course the electron could then move to another atom, transferring the negative ion to another place. We will suppose that just as in the case of an electron jumping between two protons, the electron can jump from one atom to the neighbor on either side with a certain amplitude.

Now how do we describe such a system? What will be reasonable base states? If you remember what we did when we had only two possible positions, you can guess how it will go. Suppose that in our line of atoms the spacings are all equal; and that we number the atoms in sequence, as shown in Fig. 13-1(a). One of the base states is that the electron is at atom number 6, another base state is that the electron is at atom number 7, or at atom number 8, and so on. We can describe the n th base state by saying that the electron is at atom number n . Let's say that this is the base state $|n\rangle$. Figure 13-1 shows what we mean by the three base states

$$|n-1\rangle, |n\rangle, \text{ and } |n+1\rangle.$$

Using these base states, any state $|\phi\rangle$ of our one-dimensional crystal can be described by giving all the amplitudes $\langle n|\phi\rangle$ that the state $|\phi\rangle$ is in one of the base states—which means the amplitude that it is located at one particular atom. Then we can write the state $|\phi\rangle$ as a superposition of the base states

$$|\phi\rangle = \sum_n |n\rangle \langle n|\phi\rangle. \quad (13.1)$$

Next, we are going to suppose that when the electron is at one atom, there is a certain amplitude that it will leak to the atom on either side. And we'll take the simplest case for which it can only leak to the nearest neighbors—to get to the next-nearest neighbor, it has to go in two steps. We'll take that the amplitudes for the electron jump from one atom to the next is iA/\hbar (per unit time).

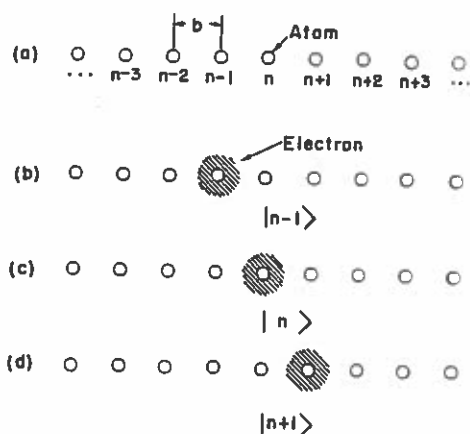


Fig. 13-1. The base states of an electron in a one-dimensional crystal.

For the moment we would like to write the amplitude $\langle n | \phi \rangle$ to be on the n th atom as C_n . Then Eq. (13.1) will be written

$$|\phi\rangle = \sum_n |n\rangle C_n. \quad (13.2)$$

If we knew each of the amplitudes C_n at a given moment, we could take their absolute squares and get the probability that you would find the electron if you looked at atom n at that time.

What will the situation be at some later time? By analogy with the two-state systems we have studied, we would propose that the Hamiltonian equations for this system should be made up of equations like this:

$$i\hbar \frac{dC_n(t)}{dt} = E_0 C_n(t) - A C_{n+1}(t) - A C_{n-1}(t). \quad (13.3)$$

The first coefficient on the right, E_0 , is, physically, the energy the electron would have if it couldn't leak away from one of the atoms. (It doesn't matter what we call E_0 ; as we have seen many times, it represents really nothing but our choice of the zero of energy.) The next term represents the amplitude per unit time that the electron is leaking into the n th pit from the $(n+1)$ st pit; and the last term is the amplitude for leakage from the $(n-1)$ st pit. As usual, we'll assume that A is a constant (independent of t).

For a full description of the behavior of any state $|\phi\rangle$, we would have one equation like (13.3) for every one of the amplitudes C_n . Since we want to consider a crystal with a very large number of atoms, we'll assume that there are an indefinitely large number of states—that the atoms go on forever in both directions. (To do the finite case, we will have to pay special attention to what happens at the ends.) If the number N of our base states is indefinitely large, then also our full Hamiltonian equations are infinite in number! We'll write down just a sample:

$$\begin{aligned} & \vdots & & \vdots \\ i\hbar \frac{dC_{n-1}}{dt} &= E_0 C_{n-1} - A C_{n-2} - A C_n, \\ i\hbar \frac{dC_n}{dt} &= E_0 C_n - A C_{n-1} - A C_{n+1}, \\ i\hbar \frac{dC_{n+1}}{dt} &= E_0 C_{n+1} - A C_n - A C_{n+2}, \\ & \vdots & & \vdots \end{aligned} \quad (13.4)$$

13-2 States of definite energy

We could study many things about an electron in a lattice, but first let's try to find the states of definite energy. As we have seen in earlier chapters this means that we have to find a situation in which the amplitudes all change at the same frequency if they change with time at all. We look for solutions of the form

$$C_n = a_n e^{-iEt/\hbar}. \quad (13.5)$$

The complex number a_n tell us about the non-time-varying part of the amplitude to find the electron at the n th atom. If we put this trial solution into the equations of (13.4) to test them out, we get the result

$$E a_n = E_0 a_n - A a_{n+1} - A a_{n-1}. \quad (13.6)$$

We have an infinite number of such equations for the infinite number of unknowns a_n —which is rather petrifying.

All we have to do is take the determinant . . . but wait! Determinants are fine when there are 2, 3, or 4 equations. But if there are a large number—or an infinite number—of equations, the determinants are not very convenient. We'd better just try to solve the equations directly. First, let's label the atoms by their

positions; we'll say that the atom n is at x_n and the atom $(n + 1)$ is at x_{n+1} . If the atomic spacing is b —as in Fig. 13-1—we will have that $x_{n+1} = x_n + b$. By choosing our origin at atom zero, we can even have it that $x_n = nb$. We can rewrite Eq. (13.5) as

$$C_n = a(x_n)e^{-iEt/\hbar}, \quad (13.7)$$

and Eq. (13.6) would become

$$Ea(x_n) = E_0a(x_{n+1}) - Aa(x_{n+1}) - Aa(x_{n-1}). \quad (13.8)$$

Or, using the fact that $x_{n+1} = x_n + b$, we could also write

$$Ea(x_n) = E_0a(x_n) - Aa(x_n + b) - Aa(x_n - b). \quad (13.9)$$

This equation is somewhat similar to a differential equation. It tells us that a quantity, $a(x)$, at one point, (x_n) , is related to the same physical quantity at some neighboring points, $(x_n \pm b)$. (A differential equation relates the value of a function at a point to the values at infinitesimally nearby points.) Perhaps the methods we usually use for solving differential equations will also work here; let's try.

Linear differential equations with constant coefficients can always be solved in terms of exponential functions. We can try the same thing here; let's take as a trial solution

$$a(x_n) = e^{ikx_n}. \quad (13.10)$$

Then Eq. (13.9) becomes

$$Ee^{ikx_n} = E_0e^{ikx_n} - Ae^{ik(x_n+b)} - Ae^{ik(x_n-b)}. \quad (13.11)$$

We can now divide out the common factor e^{ikx_n} ; we get

$$E = E_0 - Ae^{ikb} - Ae^{-ikb}. \quad (13.12)$$

The last two terms are just equal to $(2A \cos kb)$, so

$$E = E_0 - 2A \cos kb. \quad (13.13)$$

We have found that for *any* choice at all for the constant k there is a solution whose energy is given by this equation. There are various possible energies depending on k , and each k corresponds to a different solution. There are an infinite number of solutions—which is not surprising, since we started out with an infinite number of base states.

Let's see what these solutions mean. For each k , the a 's are given by Eq. (13.10). The amplitudes C_n are then given by

$$C_n = e^{ikx_n}e^{-(i/\hbar)Et}, \quad (13.14)$$

where you should remember that the energy E also depends on k as given in Eq. (13.13). The *space dependence* of the amplitudes is e^{ikx_n} . The amplitudes oscillate as we go along from one atom to the next.

We mean that, in space, the amplitude goes as a *complex* oscillation—the *magnitude* is the same at every atom, but the phase at a given time advances by the amount (ikb) from one atom to the next. We can visualize what is going on by plotting a vertical line to show just the real part at each atom as we have done in Fig. 13-2. The envelope of these vertical lines (as shown by the broken-line curve)

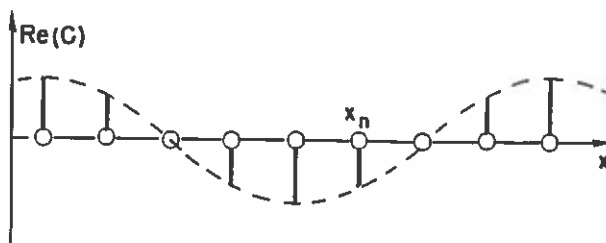


Fig. 13-2. Variation of the real part of C_n with x_n .

is, of course, a cosine curve. The imaginary part of C_n is also an oscillating function, but is shifted 90° in phase so that the absolute square (which is the sum of the squares of the real and imaginary parts) is the same for all the C 's.

Thus if we pick a k , we get a stationary state of a particular energy E . And for any such state, the electron is equally likely to be found at every atom—there is no preference for one atom or the other. Only the phase is different for different atoms. Also, as time goes on the phases vary. From Eq. (13.14) the real and imaginary parts propagate along the crystal as waves—namely as the real or imaginary parts of

$$e^{i(kx_n - (E/\hbar)t)} \quad (13.15)$$

The wave can travel toward positive or negative x depending on the sign we have picked for k .

Notice that we have been assuming that the number k that we put in our trial solution, Eq. (13.10), was a real number. We can see now why that must be so if we have an infinite line of atoms. Suppose that k were an imaginary number, say ik' . Then the amplitudes a_n would go as $e^{k'x_n}$, which means that the amplitude would get larger and larger as we go toward large x 's—or toward large negative x 's if k' is a negative number. This kind of solution would be O.K. if we were dealing with line of atoms that ended, but cannot be a physical solution for an infinite chain of atoms. It would give infinite amplitudes—and, therefore, infinite probabilities—which can't represent a real situation. Later on we will see an example in which an imaginary k does make sense.

The relation between the energy E and the wave number k as given in Eq. (13.13) is plotted in Fig. 13-3. As you can see from the figure, the energy can go from $(E_0 - 2A)$ at $k = 0$ to $(E_0 + 2A)$ at $k = \pm\pi/b$. The graph is plotted for positive A ; if A were negative, the curve would simply be inverted, but the range would be the same. The significant result is that any energy is possible within a certain range or "band" of energies, but no others. According to our assumptions, if an electron in a crystal is in a stationary state, it can have no energy other than values in this band.

According to Eq. (13.10), the smallest k 's correspond to low-energy states— $E \approx (E_0 - 2A)$. As k increases in magnitude (toward either positive or negative values) the energy at first increases, but then reaches a maximum at $k = \pm\pi/b$, as shown in Fig. 13-3. For k 's larger than π/b , the energy would start to decrease again. But we do not really need to consider such values of k , because they do not give new states—they just repeat states we already have for smaller k . We can see that in the following way. Consider the lowest energy state for which $k = 0$. The coefficient $a(x_n)$ is the same for all x_n . Now we would get the same energy for $k = 2\pi/b$. But then, using Eq. (13.10), we have that

$$a(x_n) = e^{i(2\pi/b)x_n}.$$

However, taking x_0 to be at the origin, we can set $x_n = nb$; then $a(x_n)$ becomes

$$a(x_n) = e^{i2\pi n} = 1.$$

The state described by these $a(x_n)$ is physically the same state we got for $k = 0$. It does not represent a different solution.

As another example, suppose that k were $\pi/4b$. The real part of $a(x_n)$ would vary as shown by curve 1 in Fig. 13-4. If k were seven times larger ($k = 7\pi/4$), the real part of $a(x_n)$ would vary as shown by curve 2 in the figure. (The complete

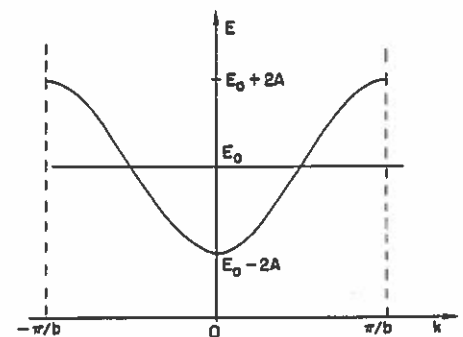


Fig. 13-3. The energy of the stationary states as a function of the parameter k .

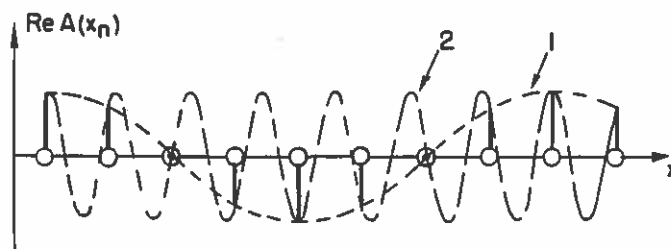


Fig. 13-4. Two values of k which represent the same physical situation; curve 1 is for $k = \pi/4$, curve 2 is for $k = 7\pi/4$.

cosine curves don't mean anything, of course; all that matters is their values *at the points* x_n . The curves are just to help you see how things are going.) You see that both values of k give the same amplitudes at all of the x_n 's.

The upshot is that we have all the possible solutions of our problem if we take only k 's in a certain limited range. We'll pick the range between $-\pi/b$ and $+\pi/b$ —the one shown in Fig. 13-3. In this range, the energy of the stationary states increases uniformly with an increase in the magnitude of k .

One side remark about something you can play with. Suppose that the electron cannot only jump to the nearest neighbor with amplitude iA/\hbar , but also has the possibility to jump in one direct leap to the *next nearest* neighbor with some other amplitude iB/\hbar . You will find that the solution can again be written in the form $a_n = e^{ikx_n}$ —this type of solution is universal. You will also find that the stationary states with wave number k have an energy equal to $(E_0 - 2A \cos kb - 2B \cos 2kb)$. This shows that the shape of the curve of E against k is not universal, but depends upon the particular assumptions of the problem. It is not always a cosine wave—it's not even necessarily symmetrical about some horizontal line. It is true, however, that the curve always repeats itself outside of the interval from $-\pi/b$ to π/b , so you never need to worry about other values of k .

Let's look a little more closely at what happens for small k —that is, when the variations of the amplitudes from one x_n to the next are quite slow. Suppose we choose our zero of energy by defining $E_0 = 2A$; then the minimum of the curve in Fig. 13-3 is at the zero of energy. For small enough k , we can write that

$$\cos kb \approx 1 - k^2 b^2 / 2,$$

and the energy of Eq. (13.13) becomes

$$E = Ak^2 b^2. \quad (13.16)$$

We have that the energy of the state is proportional to the square of the wave number which describes the spatial variations of the amplitudes C_n .

13-3 Time-dependent states

In this section we would like to discuss the behavior of states in the one-dimensional lattice in more detail. If the amplitude for an electron to be at x_n is C_n , the probability of finding it there is $|C_n|^2$. For the *stationary* states described by Eq. (13.12), this probability is the same for all x_n and does not change with time. How can we represent a situation which we would describe roughly by saying an electron of a certain energy is localized in a certain region—so that it is more likely to be found at one place than at some other place? We can do that by making a superposition of several solutions like Eq. (13.12) with slightly different values of k —and, therefore, slightly different energies. Then at $t = 0$, at least, the amplitude C_n will vary with position because of the interference between the various terms, just as one gets beats when there is a mixture of waves of different wavelengths (as we discussed in Chapter 48, Vol. I). So we can make up a "wave packet" with a predominant wave number k_0 , but with various other wave numbers near k_0 .†

In our superposition of stationary states, the amplitudes with different k 's will represent states of slightly different energies, and, therefore, of slightly different frequencies; the interference pattern of the total C_n will, therefore, also vary with time—there will be a pattern of "beats." As we have seen in Chapter 48 of Volume I, the peaks of the beats [the place where $|C(x_n)|^2$ is large] will move along in x as time goes on; they move with the speed we have called the "group velocity." We found that this group velocity was related to the variation of k with frequency by

$$v_{\text{group}} = \frac{d\omega}{dk}; \quad (13.17)$$

† Provided we do not try to make the packet too narrow.