13

Propagation in a Crystal Lattice

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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.

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.

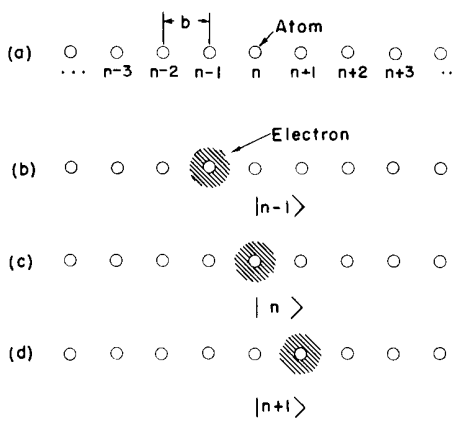

Fig. 13–1. The base states of an electron in a one-dimensional crystal.

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 nth 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

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

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

$$|\,\phi\rangle = \sum_n |\,n\rangle\langle n\,|\,\phi\rangle. \tag{13.1}$$

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).

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

$$|\phi\rangle = \sum_n |n\rangle C_n. \tag{13.2}$$

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:

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

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 nth 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:

$$\begin{aligned}
&\vdots \qquad\qquad\qquad\qquad \vdots \\
i\hbar \frac{dC_{n-1}}{dt} &= E_0 C_{n-1} - AC_{n-2} - AC_n, \\
i\hbar \frac{dC_n}{dt} &= E_0 C_n - AC_{n-1} - AC_{n+1}, \\
i\hbar \frac{dC_{n+1}}{dt} &= E_0 C_{n+1} - AC_n - AC_{n+2}, \\
&\vdots \qquad\qquad\qquad\qquad \vdots
\end{aligned} \tag{13.4}$$

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

$$C_n = a_n e^{-iEt/\hbar}. \tag{13.5}$$

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

$$Ea_n = E_0 a_n - Aa_{n+1} - Aa_{n-1}. \tag{13.6}$$

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

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

and Eq. (13.6) would become

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

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

$$Ea(x_n) = E_0a(x_n) - Aa(x_n + b) - Aa(x_n - b). \tag{13.9}$$

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

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

Then Eq. (13.9) becomes

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

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

$$E = E_0 - Ae^{ikb} - Ae^{-ikb}. \tag{13.12}$$

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

$$E = E_0 - 2A \cos kb. \tag{13.13}$$

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

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

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)

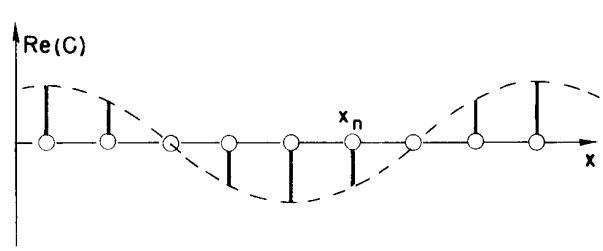

Fig. 13–2. Variation of the real part of C_n with x_n.

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

$$e^{i[kx_n-(E/\hbar)t]}. \tag{13.15}$$

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

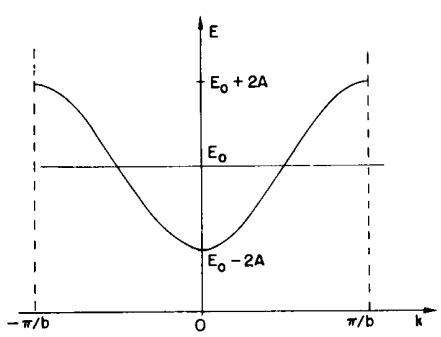

Fig. 13–3. The energy of the stationary states as a function of the parameter k.

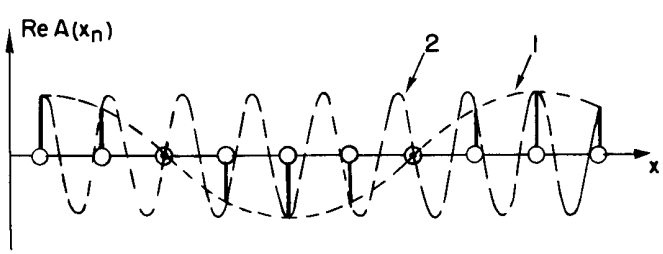

Fig. 13–4. Two values of k which represent the same physical situation; curve 1 is for $k = \pi/4$, curve 2 is for $k = 7\pi/4$.

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

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

and the energy of Eq. (13.13) becomes

$$E = Ak^2b^2. \tag{13.16}$$

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

$$v_{\text{group}} = \frac{d\omega}{dk}; \tag{13.17}$$

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

the same derivation would apply equally well here. An electron state which is a "clump"—namely one for which the C_n vary in space like the wave packet of Fig. 13–5—will move along our one-dimensional "crystal" with the speed v equal to $d\omega/dk$, where $\omega = E/\hbar$. Using (13.16) for E, we get that

$$v = \frac{2Ab^2}{\hbar} k. \tag{13.18}$$

In other words, the electrons move along with a speed proportional to the typical k. Equation (13.16) then says that the energy of such an electron is proportional to the square of its velocity—*it acts like a classical particle.* So long as we look at things on a scale gross enough that we don't see the fine structure, our quantum mechanical picture begins to give results like classical physics. In fact, if we solve Eq. (13.18) for k and substitute into (13.16), we can write

$$E = \tfrac{1}{2} m_{\text{eff}}\, v^2, \tag{13.19}$$

where m_{eff} is a constant. The extra "energy of motion" of the electron in a packet depends on the velocity just as for a classical particle. The constant m_{eff}—called the "effective mass"—is given by

$$m_{\text{eff}} = \frac{\hbar^2}{2Ab^2}. \tag{13.20}$$

Also notice that we can write

$$m_{\text{eff}}\, v = \hbar k. \tag{13.21}$$

If we choose to call $m_{\text{eff}}\, v$ the "momentum," it is related to the wave number k in the way we have described earlier for a free particle.

Don't forget that m_{eff} has nothing to do with the real mass of an electron. It may be quite different—although in real crystals it often happens to turn out to be the same general order of magnitude, about 2 to 20 times the free-space mass of the electron.

We have now explained a remarkable mystery—how an electron in a crystal (like an extra electron put into germanium) can ride right through the crystal and flow perfectly freely even though it has to hit all the atoms. It does so by having its amplitudes going pip-pip-pip from one atom to the next, working its way through the crystal. That is how a solid can conduct electricity.

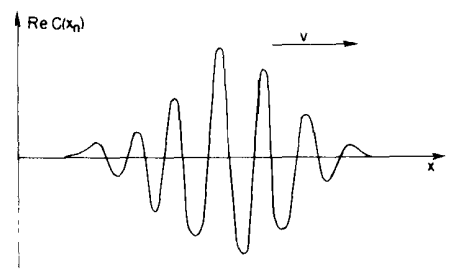

Fig. 13–5. The real part of $C(x_n)$ as a function of x for a superposition of several states of similar energy. (The spacing b is very small on the scale of x shown.)

13–4 An electron in a three-dimensional lattice

Let's look for a moment at how we could apply the same ideas to see what happens to an electron in three dimensions. The results turn out to be very similar. Suppose we have a rectangular lattice of atoms with lattice spacings of a, b, c in the three directions (If you want a cubic lattice, take the three spacings all equal.) Also suppose that the amplitude to leap in the x-direction to a neighbor is $(iA_x/\hbar)$, to leap in the y-direction is $(iA_y/\hbar)$, and to leap in the z-direction is $(iA_z/\hbar)$. Now how should we describe the base states? As in the one-dimensional case, one base state is that the electron is at the atom whose locations are x, y, z, where (x, y, z) is one of the lattice points. Choosing our origin at one atom, these points are all at

$$x = n_x a, \qquad y = n_y b, \qquad \text{and} \qquad z = n_z c,$$

where n_x, n_y, n_z are any three integers. Instead of using subscripts to indicate such points, we will now just use x, y, and z, understanding that they take on only their values at the lattice points. Thus the base state is represented by the symbol $|\,\text{electron at } x, y, z\rangle$, and the amplitude for an electron in some state $|\,\psi\rangle$ to be in this base state is $C(x, y, z) = \langle\text{electron at } x, y, z\,|\,\psi\rangle$.

As before, the amplitudes $C(x, y, z)$ may vary with time. With our assumptions, the Hamiltonian equations should be like this:

$$i\hbar \frac{dC(x, y, z)}{dt} = E_0C(x, y, z) - A_xC(x + a, y, z) - A_xC(x - a, y, z) - A_yC(x, y + b, z) - A_yC(x, y - b, z) - A_zC(x, y, z + c) - A_zC(x, y, z - c). \quad (13.22)$$

It looks rather long, but you can see where each term comes from.

Again we can try to find a stationary state in which all the C's vary with time in the same way. Again the solution is an exponential:

$$C(x, y, z) = e^{-iEt/\hbar}e^{i(k_xx+k_yy+k_zz)}. \quad (13.23)$$

If you substitute this into (13.22) you see that it works, provided that the energy E is related to k_x, k_y, and k_z in the following way:

$$E = E_0 - 2A_x \cos k_xa - 2A_y \cos k_yb - 2A_z \cos k_zc. \quad (13.24)$$

The energy now depends on the *three* wave numbers k_x, k_y, k_z, which, incidentally, are the components of a three-dimensional vector $\boldsymbol{k}$. In fact, we can write Eq. (13.23) in vector notation as

$$C(x, y, z) = e^{-iEt/\hbar}e^{-i\boldsymbol{k}\cdot\boldsymbol{r}} \quad (13.25)$$

The amplitude varies as a complex *plane wave* in three dimensions, moving in the direction of $\boldsymbol{k}$, and with the wave number $k = (k_x^2 + k_y^2 + k_z^2)^{1/2}$.

The energy associated with these stationary states depends on the three components of $\boldsymbol{k}$ in the complicated way given in Eq. (13.24). The nature, of the variation of E with $\boldsymbol{k}$ depends on relative signs and magnitudes of A_x, A_y, and A_z. If these three numbers are all positive, and if we are interested in small values of k, the dependence is relatively simple.

Expanding the cosines as we did before to get Eq. (13.16), we can now get that

$$E = E_{\min} + A_xa^2k_x^2 + A_ybk_y^2 + A_zck_z^2. \quad (13.26)$$

For a simple cubic lattice with lattice spacing a we expect that A_x and A_y and A_z would be equal—say all are just A—and we would have just

$$E = E_{\min} + Aa^2(k_x^2 + k_y^2 + k_z^2),$$

or

$$E = E_{\min} + Aa^2k^2. \quad (13.27)$$

This is just like Eq. (13.16). Following the arguments used there, we would conclude that an electron packet in *three* dimensions (made up by superposing many states with nearly equal energies) also moves like a classical particle with some effective mass.

In a crystal with a lower symmetry than cubic (or even in a cubic crystal in which the state of the electron at each atom is not symmetrical) the three coefficients A_x, A_y, and A_z are different. Then the "effective mass" of an electron localized in a small region *depends on its direction of motion.* It could, for instance, have a different inertia for motion in the x-direction than for motion in the y-direction. (The details of such a situation are sometimes described in terms of an "effective mass tensor.")

13–5 Other states in a lattice

According to Eq. (13.24) the electron states we have been talking about can have energies only in a certain "band" of energies which covers the energy range from the minimum energy

$$E_0 - 2(A_x + A_y + A_z)$$

to the maximum energy

$$E_0 + 2(A_x + A_y + A_z).$$

Other energies are possible, but they belong to a different class of electron states. For the states we have described, we imagined base states in which an electron is placed on an atom of the crystal in some particular state, say the lowest energy state.

If you have an atom in empty space, and add an electron to make an ion, the ion can be formed in many ways. The electron can go on in such a way as to make the state of lowest energy, or it can go on to make one or another of many possible "excited states" of the ion each with a definite energy above the lowest energy. The same thing can happen in a crystal. Let's suppose that the energy E_0 we picked above corresponds to base states which are ions of the lowest possible energy. We could also imagine a new set of base states in which the electron sits near the nth atom in a different way—in one of the excited states of the ion—so that the energy E_0 is now quite a bit higher. As before there is some amplitude A (different from before) that the electron will jump from its excited state at one atom to the same excited state at a neighboring atom. The whole analysis goes as before, we find a band of possible energies centered at a higher energy. There can, in general, be many such bands each corresponding to a different level of excitation.

There are also other possibilities. There may be some amplitude that the electron jumps from an excited condition at one atom to an unexcited condition at the next atom. (This is called an interaction between bands.) The mathematical theory gets more and more complicated as you take into account more and more bands and add more and more coefficients for leakage between the possible states. No new ideas are involved, however; the equations are set up much as we have done in our simple example.

We should remark also that there is not much more to be said about the various coefficients, such as the amplitude A, which appear in the theory. Generally they are very hard to calculate, so in practical cases very little is known theoretically about these parameters and for any particular real situation we can only take values determined experimentally.

There are other situations where the physics and mathematics are almost exactly like what we have found for an electron moving in a crystal, but in which the "object" that moves is quite different. For instance, suppose that our original crystal—or rather linear lattice—was a line of neutral atoms, each with a loosely bound outer electron. Then imagine that we were to remove one electron. Which atom has lost its electron? Let C_n now represent the amplitude that the electron *is missing* from the atom at x_n. There will, in general, be some amplitude $iA/\hbar$ that the electron at a neighboring atom—say the $(n - 1)$st atom—will jump to the nth leaving the $(n - 1)$st atom without its electron. This is the same as saying that there is an amplitude A for the "missing electron" to jump from the nth atom to the $(n - 1)$st atom. You can see that the equations will be exactly the same—of course, the value of A need not be the same as we had before. Again we will get the same formulas for the energy levels, for the "waves" of probability which move through the crystal with the group velocity of Eq. (13.18), for the effective mass, and so on. Only now the waves describe the behavior of the *missing electron*—or "hole" as it is called. So a "hole" acts just like a particle with a certain mass m_{eff}. You can see that this particle will appear to have a positive charge. We'll have some more to say about such holes in the next chapter.

As another example, we can think of a line of identical *neutral* atoms one of which has been put into an excited state—that is, with more than its normal ground state energy. Let C_n be the amplitude that the nth atom has the excitation. It can interact with a neighboring atom by handing over to it the extra energy and returning to the ground state. Call the amplitude for this process $iA/\hbar$. You can see that it's the same mathematics all over again. Now the object which moves is called an *exciton*. It behaves like a neutral "particle" moving through the crystal, carrying the excitation energy. Such motion may be involved in certain biological

processes such as vision, or photosynthesis. It has been guessed that the absorption of light in the retina produces an "exciton" which moves through some periodic structure (such as the layers in the rods we described in Chapter 36, Vol. 1; see Fig. 36–5) to be accumulated at some special station where the energy is used to induce a chemical reaction.

13–6 Scattering from imperfections in the lattice

We want now to consider the case of a single electron in a crystal which is not perfect. Our earlier analysis says that perfect crystals have perfect conductivity —that electrons can go slipping through the crystal, as in a vacuum, without friction. One of the most important things that can stop an electron from going on forever is an imperfection or irregularity in the crystal. As an example, suppose that somewhere in the crystal there is a missing atom; or suppose that someone put one wrong atom at one of the atomic sites so that things there are different than at the other atomic sites. Say the energy, E_0 or the amplitude A could be different. How would we describe what happens then?

To be specific, we will return to the one-dimensional case and we will assume that atom number "zero" is an "impurity" atom and has a different value of E_0 than any of the other atoms. Let's call this energy $(E_0 + F)$. What happens? When an electron arrives at atom "zero" there is some probability that the electron is scattered backwards. If a wave packet is moving along and it reaches a place where things are a little bit different, some of it will continue onward and some of it will bounce back. It's quite difficult to analyze such a situation using a wave packet, because everything varies in time. It is much easier to work with steady-state solutions. So we will work with stationary states, which we will find can be made up of continuous waves which have transmitted and reflected parts. In three dimensions we would call the reflected part the scattered wave, since it would spread out in various directions.

We start out with a set of equations which are just like the ones in Eq. (13.6) except that the equation for $n = 0$ is different from all the rest. The five equations for $n = -2, -1, 0, +1$, and $+2$ look like this:

$$\begin{aligned}
&\vdots \qquad\qquad\qquad \vdots \\
Ea_{-2} &= E_0a_{-2} - Aa_{-1} - Aa_{-3}, \\
Ea_{-1} &= E_0a_{1-} - Aa_{0} - Aa_{-2}, \\
Ea_0 &= (E_0 + F)a_0 - Aa_1 - Aa_{-1}, \\
Ea_1 &= E_0a_1 - Aa_2 - Aa_0, \\
Ea_2 &= E_0a_2 - Aa_3 - Aa_1, \\
&\vdots \qquad\qquad\qquad \vdots
\end{aligned} \tag{13.28}$$

There are, of course, all the other equations for $|n|$ is greater than 2. They will look just like Eq. (13.16).

For the general case, we really ought to use a different A for the amplitude that the electron jumps to or from atom "zero," but the main features of what goes on will come out of a simplified example in which all the A's are equal.

Equation (13.10) would still work as a solution for all of the equations except the one for atom "zero"—it isn't right for that one equation. We need a different solution which we can cook up in the following way. Equation (13.10) represents a wave going in the positive x-direction. A wave going in the negative x-direction would have been an equally good solution. It would be written

$$a(x_n) = e^{-ikx_n}.$$

The most general solution we could have taken for Eq. (13.6) would be a com-

bination of a forward and a backward wave, namely

$$a_n = \alpha e^{ikx_n} + \beta e^{-ikx_n}. \tag{13.29}$$

This solution represents a complex wave of amplitude α moving in the $+x$-direction and a wave of amplitude β moving in the $-x$-direction.

Now take a look at the set of equations for our new problem—the ones in (13.28) together with those for all the other atoms. The equations involving a_n's with $n \leq 1$ are all satisfied by Eq. (13.29), with the condition that k is related to E and the lattice spacing b by

$$E = E_0 - 2A \cos kb. \tag{13.30}$$

The physical meaning is an "incident" wave of amplitude α approaching atom "zero" (the "scatterer") from the left, and a "scattered" or "reflected" wave of amplitude β going back toward the left. We do not loose any generality if we set the amplitude α of the incident wave equal to 1. Then the amplitude β is, in general, a complex number.

We can say all the same things about the solutions of a_n for $n \geq 1$. The coefficients could be different, so we would have for them

$$a_n = \gamma e^{ikx_n} + \delta e^{-ikx_n}, \qquad \text{for} \qquad n \geq 1. \tag{13.31}$$

Here, γ is the amplitude of a wave going to the right and δ a wave coming from the right. We want to consider the *physical* situation in which a wave is originally started only from the left, and there is only a "transmitted" wave that comes out beyond the scatterer—or impurity atom. We will try for a solution in which $\delta = 0$. We can, certainly, satisfy all of the equations for the a_n except for the middle three in Eq. (13.28) by the following trial solutions.

$$\begin{aligned} a_n \ (\text{for } n < 0) &= e^{ikx_n} + \beta e^{-ikx_n}, \\ a_n \ (\text{for } n > 0) &= \gamma e^{ikx_n}. \end{aligned} \tag{13.32}$$

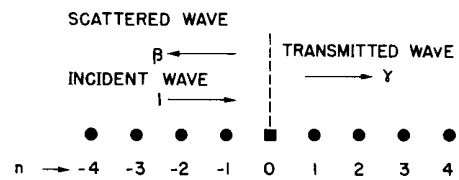

Fig. 13–6. Waves in a one-dimensional lattice with one "impurity" atom at $n = 0$.

The situation we are talking about is illustrated in Fig. 13–6.

By using the formulas in Eq. (13.32) for a_{-1} and a_{+1}, the three middle equations of Eq. (13.28) will allow us to solve for a_0 and also for the two coefficients β and γ. So we have found a complete solution. Setting $x_n = nb$, we have to solve the three equations

$$\begin{aligned} (E - E_0)\{e^{ik(-b)} + \beta e^{-ik(-b)}\} &= -A\{a_0 + e^{ik(-2b)} + \beta e^{-ik(-2b)}\}, \\ (E - E_0 - F)a_0 &= -A\{\gamma e^{ikb} + e^{ik(-b)} + \beta e^{-ik(-b)}\}, \\ (E - E_0)\gamma e^{ikb} &= -A\{\gamma e^{ik(2b)} + a_0\}. \end{aligned} \tag{13.33}$$

Remember that E is given in terms of k by Eq. (13.30). If you substitute this value for E into the equations, and remember that $\cos x = \frac{1}{2}(e^{ix} + e^{-ix})$, you get from the first equation that

$$a_0 = 1 + \beta; \tag{13.34}$$

and from the third equation that

$$a_0 = \gamma. \tag{13.35}$$

These are consistent only if

$$\gamma = 1 + \beta \tag{13.36}$$

This equation says that the transmitted wave (γ) is just the original incident wave (1) with an added wave (β) equal to the reflected wave. This is not always true, but happens to be so for a scattering at one atom only. If there were a clump of impurity atoms, the amount added to the forward wave would not necessarily be the same as the reflected wave.

We can get the amplitude β of the reflected wave from the middle equation of Eq. (13.33); we find that

$$\beta = \frac{-F}{F - 2iA \sin kb}. \tag{13.37}$$

We have the complete solution for the lattice with one unusual atom.

You may be wondering how the transmitted wave can be "more" than the incident wave as it appears in Eq. (13.34). Remember, though, that β and γ are complex numbers and that the number of particles (or rather, the probability of finding a particle) in a wave is proportional to the absolute square of the amplitude. In fact, there will be "conservation of electrons" only if

$$|\beta|^2 + |\gamma|^2 = 1. \tag{13.38}$$

You can show that this is true for our solution.

13–7 Trapping by a lattice imperfection

There is another interesting situation that can arise if F is a negative number. If the energy of the electron is lower at the impurity atom (at $n = 0$) than it is anywhere else, then the electron can get caught on this atom. That is, if $(E_0 + F)$ is below the bottom of the band at $(E_0 - 2A)$, then the electron can get "trapped" in a state with $E < E_0 - 2A$. Such a solution cannot come out of what we have done so far. We can get this solution, however, if we permit the trial solution we took in Eq. (13.15) to have an imaginary number for k. Let's set $k = i\kappa$ Again, we can have different solutions for $n < 0$ and for $n > 0$. A possible solution for $n < 0$ might be

$$a_n \text{ (for } n < 0) = ce^{+\kappa x_n}. \tag{13.39}$$

We have to take a plus sign in the exponent; otherwise the amplitude would get indefinitely large for large negative values of n. Similarly, a possible solution for $n > 0$ would be

$$a_n \text{ (for } n > 0) = c'e^{-\kappa x_n}. \tag{13.40}$$

If we put these trial solutions into Eq. (13.28) all but the middle three are satisfied provided that

$$E = E_0 - A(e^{\kappa b} + e^{-\kappa b}). \tag{13.41}$$

Since the sum of the two exponential terms is always greater than 2, this energy is below the regular band, and is what we are looking for. The remaining three equations in Eq. (13.28) are satisfied if $c = c'$ and if κ is chosen so that

$$A(e^{\kappa b} - e^{-\kappa b}) = -F. \tag{13.42}$$

Combining this equation with Eq. (13.41) we can find the energy of the trapped electron; we get

$$E = E_0 - \sqrt{4A^2 + F^2}. \tag{13.43}$$

The trapped electron has a unique energy—located somewhat below the conduction band.

Notice that the amplitudes we have in Eq. (13.39) and (13.40) do *not* say that the trapped electron sits right on the impurity atom. The probability of finding the electron at nearby atoms is given by the square of these amplitudes. For one particular choice of the parameters it might vary as shown in the bar graph of Fig. 13–7. The probability is greatest for finding the electron on the impurity atom. For nearby atoms the probability drops off exponentially with the distance from the impurity atom. This is another example of "barrier penetration." From the point-of-view of classical physics the electron doesn't have enough energy to get away from the energy "hole" at the trapping center. But quantum mechanically it can leak out a little way.

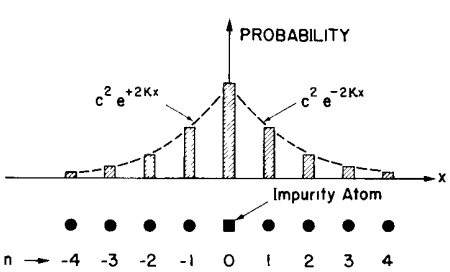

Fig. 13–7. The relative probabilities of finding a trapped electron at atomic sites near the trapping impurity atom.

13–8 Scattering amplitudes and bound states

Finally, our example can be used to illustrate a point which is very useful these days in the physics of high-energy particles. It has to do with a relationship between scattering amplitudes and bound states. Suppose we have discovered—through experiment and theoretical analysis—the way that pions scatter from protons. Then a new particle is discovered and someone wonders whether maybe it is just a combination of a pion and a proton held together in some bound state (in an analogy to the way an electron is bound to a proton to make a hydrogen atom). By a bound state we mean a combination which has a lower energy than the two free-particles.

There is a general theory which says that a bound state will exist at that energy at which the scattering amplitude becomes infinite if extrapolated algebraically (the mathematical term is "analytically continued") to energy regions outside of the permitted band.

The physical reason for this is as follows. A bound state is a situation in which there are only waves tied on to a point and there's no wave coming in to get it started, it just exists there by itself. The relative proportion between the so-called "scattered" or created wave and the wave being "sent in" is infinite. We can test this idea in our example. Let's write our expression Eq. (13.37) for the scattered amplitude directly in terms of the energy E of the particle being scattered (instead of in terms of k). Since Equation (13.30) can be rewritten as

$$2A \sin kb = \sqrt{4A^2 - (E - E_0)^2},$$

the scattered amplitude is

$$\beta = \frac{-F}{F - i\sqrt{4A^2 - (E - E_0)^2}}. \tag{13.44}$$

From our derivation, this equation should be used only for real states—those with energies in the energy band, $E = E_0 \pm 2A$. But suppose we forget that fact and extend the formula into the "unphysical" energy regions where $|E - E_0| > 2A$. For these unphysical regions we can write†

$$\sqrt{4A^2 - (E - E_0)^2} = i\sqrt{(E - E_0)^2 - 4A^2}.$$

Then the "scattering amplitude," whatever it may mean, is

$$\beta = \frac{-F}{F + \sqrt{(E - E_0)^2 - 4A^2}}. \tag{13.45}$$

Now we ask: Is there any energy E for which β becomes infinite (i.e., for which the expression for β has a "pole")? Yes, so long as F is negative, the denominator of Eq (13.45) will be zero when

$$(E - E_0)^2 - 4A^2 = F^2,$$

or when

$$E = E_0 \pm \sqrt{4A^2 + F^2}.$$

The minus sign gives just the energy we found in Eq. (13.43) for the trapped energy.

What about the plus sign? This gives an energy *above* the allowed energy band. And indeed there is another bound state there which we missed when we solved the equations of Eq. (13.28). We leave it as a puzzle for you to find the energy and amplitudes a_n for this bound state.

The relation between scattering and bound states provides one of the most useful clues in the current search for an understanding of the experimental observations about the new strange particles.

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† The sign of the root to be chosen here is a technical point related to the allowed signs of κ in Eqs. (13.39) and (13 40). We won't go into it here.