21

The Schrödinger Equation in a Classical Context: A Seminar on Superconductivity

21-1 Schrödinger's equation in a magnetic field

This lecture is only for entertainment. I would like to give the lecture in a somewhat different style—just to see how it works out. It's not a part of the course—in the sense that it is not supposed to be a last minute effort to teach you something new. But, rather, I imagine that I'm giving a seminar or research report on the subject to a more advanced audience, to people who have already been educated in quantum mechanics. The main difference between a seminar and a regular lecture is that the seminar speaker does not carry out all the steps, or all the algebra. He says: "If you do such and such, this is what comes out," instead of showing all of the details. So in this lecture I'll describe the ideas all the way along but just give you the *results* of the computations. You should realize that you're not supposed to understand everything immediately, but believe (more or less) that things would come out if you went through the steps.

All that aside, this is a subject I *want* to talk about. It is recent and modern and would be a perfectly legitimate talk to give at a research seminar. My subject is the Schrödinger equation in a classical setting—the case of superconductivity.

Ordinarily, the wave function which appears in the Schrödinger equation applies to only one or two particles. And the wave function itself is not something that has a classical meaning—unlike the electric field, or the vector potential, or things of that kind. The wave function for a single particle *is* a "field"—in the sense that it is a function of position—but it does not generally have a classical significance. Nevertheless, there are some situations in which a quantum mechanical wave function *does* have classical significance, and they are the ones I would like to take up. The peculiar quantum mechanical behavior of matter on a small scale doesn't usually make itself felt on a large scale except in the standard way that it produces Newton's laws—the laws of the so-called classical mechanics. But there are certain situations in which the peculiarities of quantum mechanics can come out in a special way on a large scale.

At low temperatures, when the energy of a system has been reduced very, very low, instead of a large number of states being involved, only a very, very small number of states near the ground state are involved. Under those circumstances the quantum mechanical character of that ground state can appear on a macroscopic scale. It is the purpose of this lecture to show a connection between quantum mechanics and large-scale effects—not the usual discussion of the way that quantum mechanics reproduces Newtonian mechanics on the average, but a special situation in which quantum mechanics will produce its own characteristic effects on a large or "macroscopic" scale.

I will begin by reminding you of some of the properties of the Schrödinger equation.† I want to describe the behavior of a particle in a magnetic field using the Schrödinger equation, because the superconductive phenomena are involved with magnetic fields. An external magnetic field is described by a vector potential, and the problem is: what are the laws of quantum mechanics in a vector potential? The principle that describes the behavior of quantum mechanics in a vector potential is very simple. The amplitude that a particle goes from one place to another along a certain route when there's a field present is the same as the amplitude that it would go along the same route when there's no field, multiplied by the exponential of the line integral of the vector potential, times the electric charge divided by Planck's constant[1] (see Fig. 21-1):

$$\langle b \,|\, a \rangle_{\text{in } \boldsymbol{A}} = \langle b \,|\, a \rangle_{A=0} \cdot \exp\left[\frac{iq}{\hbar} \int_a^b \boldsymbol{A} \cdot d\boldsymbol{s}\right]. \tag{21.1}$$

It is a basic statement of quantum mechanics.

Now without the vector potential the Schrödinger equation of a charged particle (nonrelativistic, no spin) is

$$-\frac{\hbar}{i} \frac{\partial \psi}{\partial t} = \hat{\mathcal{H}}\psi = \frac{1}{2m}\left(\frac{\hbar}{i}\boldsymbol{\nabla}\right) \cdot \left(\frac{\hbar}{i}\boldsymbol{\nabla}\right)\psi + q\phi\psi, \tag{21.2}$$

† I'm not really reminding you, because I haven't shown you some of these equations before; but remember the spirit of this seminar.

[1] Volume II, Section 15-5.

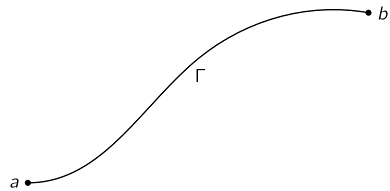

Fig. 21-1. The amplitude to go from a to b along the path Γ is proportional to $\exp\bigl[(iq/\hbar)\int_a^b \boldsymbol{A}\cdot d\boldsymbol{s}\bigr]$.

where ϕ is the electric potential so that $q\phi$ is the potential energy.† Equation (21.1) is equivalent to the statement that in a magnetic field the gradients in the Hamiltonian are replaced in each case by the gradient minus $q\boldsymbol{A}$, so that Eq. (21.2) becomes

$$-\frac{\hbar}{i}\frac{\partial\psi}{\partial t}=\hat{\mathcal{H}}\psi=\frac{1}{2m}\biggl(\frac{\hbar}{i}\boldsymbol{\nabla}-q\boldsymbol{A}\biggr)\cdot\biggl(\frac{\hbar}{i}\boldsymbol{\nabla}-q\boldsymbol{A}\biggr)\psi+q\phi\psi, \tag{21.3}$$

This is the Schrödinger equation for a particle with charge q moving in an electromagnetic field $\boldsymbol{A},\phi$ (nonrelativistic, no spin).

To show that this is true I'd like to illustrate by a simple example in which instead of having a continuous situation we have a line of atoms along the x-axis with the spacing b and we have an amplitude $-K$ for an electron to jump from one atom to another when there is no field.‡ Now according to Eq. (21.1) if there's a vector potential in the x-direction $A_x(x,t)$, the amplitude to jump will be altered from what it was before by a factor $\exp[(iq/\hbar)\,A_xb]$, the exponent being $iq/\hbar$ times the vector potential integrated from one atom to the next. For simplicity we will write $(q/\hbar)A_x\equiv f(x)$, since A_x, will, in general, depend on x. If the amplitude to find the electron at the atom "n" located at x is called $C(x)\equiv C_n$, then the rate of change of that amplitude is given by the following equation:

$$\begin{aligned}-\frac{\hbar}{i}\frac{\partial}{\partial t}C(x)=E_0C(x)&-Ke^{-ibf(x+b/2)}C(x+b)\\&-Ke^{+ibf(x-b/2)}C(x-b).\end{aligned} \tag{21.4}$$

† Not to be confused with our earlier use of ϕ for a state label!

‡ K is the same quantity that was called A in the problem of a linear lattice with no magnetic field. See Chapter 13.

There are three pieces. First, there's some energy E_0 if the electron is located at x. As usual, that gives the term $E_0C(x)$. Next, there is the term $-KC(x+b)$, which is the amplitude for the electron to have jumped backwards one step from atom "$n+1$," located at $x+b$. However, in doing so in a vector potential, the phase of the amplitude must be shifted according to the rule in Eq. (21.1). If A_x is not changing appreciably in one atomic spacing, the integral can be written as just the value of A_x at the midpoint, times the spacing b. So $(iq/\hbar)$ times the integral is just $ibf(x+b/2)$. Since the electron is jumping backwards, I showed this phase shift with a minus sign. That gives the second piece. In the same manner there's a certain amplitude to have jumped from the other side, but this time we need the vector potential at a distance $(b/2)$ on the other side of x, times the distance b. That gives the third piece. The sum gives the equation for the amplitude to be at x in a vector potential.

Now we know that if the function $C(x)$ is smooth enough (we take the long wavelength limit), and if we let the atoms get closer together, Eq. (21.4) will approach the behavior of an electron in free space. So the next step is to expand the right-hand side of (21.4) in powers of b, assuming b is very small. For example, if b is zero the right-hand side is just $(E_0-2K)C(x)$, so in the zeroth approximation the energy is E_0-2K. Next comes the terms in b. But because the two exponentials have opposite signs, only even powers of b remain. So if you make a Taylor expansion of $C(x)$, of $f(x)$, and of the exponentials, and then collect the terms in b^2, you get

$$
\begin{aligned}
-\frac{\hbar}{i}\,\frac{\partial C(x)}{\partial t} &= E_0C(x)-2KC(x)\\
&\quad -Kb^2\{C''(x)-2if(x)C'(x)-if'(x)C(x)-f^2(x)C(x)\}. \qquad (21.5)
\end{aligned}
$$

(The "primes" mean differentiation with respect to x.)

Now this horrible combination of things looks quite complicated. But mathematically it's exactly the same as

$$
-\frac{\hbar}{i}\,\frac{\partial C(x)}{\partial t}=(E_0-2K)C(x)-Kb^2\biggl[\frac{\partial}{\partial x}-if(x)\biggr]\biggl[\frac{\partial}{\partial x}-if(x)\biggr]C(x). \qquad (21.6)
$$

The second bracket operating on $C(x)$ gives $C'(x)$ plus $if(x)C(x)$. The first bracket operating on these two terms gives the C'' term and terms in the first derivative of $f(x)$ and the first derivative of $C(x)$. Now remember that the solutions for zero magnetic field[2] represent a particle with an effective mass m_{eff} given by

$$Kb^2 = \frac{\hbar^2}{2m_{\text{eff}}}.$$

If you then set $E_0 = -2K$, and put back $f(x) = (q/\hbar)A_x$, you can easily check that Eq. (21.6) is the same as the first part of Eq. (21.3). (The origin of the potential energy term is well known, so I haven't bothered to include it in this discussion.) The proposition of Eq. (21.1) that the vector potential changes all the amplitudes by the exponential factor is the same as the rule that the momentum operator, $(\hbar/i)\boldsymbol{\nabla}$ gets replaced by

$$\frac{\hbar}{i}\boldsymbol{\nabla} - q\boldsymbol{A},$$

as you see in the Schrödinger equation of (21.3).

21-2 The equation of continuity for probabilities

Now I turn to a second point. An important part of the Schrödinger equation for a single particle is the idea that the probability to find the particle at a position is given by the absolute square of the wave function. It is also characteristic of the quantum mechanics that probability is conserved in a local sense. When the probability of finding the electron somewhere decreases, while the probability of the electron being elsewhere increases (keeping the total probability unchanged), something must be going on in between. In other words, the electron has a continuity in the sense that if the probability decreases at one place and builds up at another place, there must be some kind of flow between. If you put a wall, for example, in the way, it will have an influence and the probabilities will not be the same. So the conservation of probability alone is not the complete statement of the conservation law, just as the conservation of energy alone is not as deep and important as the *local* conservation of energy.[3] If energy is disappearing, there must be a flow of energy to correspond. In the same way, we would like to find a "current" of probability such that if there is any change in the probability density (the probability of being found in a unit volume), it can be considered as coming from an inflow or an outflow due to some current. This

[2] Section 13-3.
[3] Volume II, Section 27-1.

current would be a vector which could be interpreted this way—the x-component would be the net probability per second and per unit area that a particle passes in the x-direction across a plane parallel to the yz-plane. Passage toward $+x$ is considered a positive flow, and passage in the opposite direction, a negative flow.

Is there such a current? Well, you know that the probability density $P(\boldsymbol{r},t)$ is given in terms of the wave function by

$$P(\boldsymbol{r},t) = \psi^*(\boldsymbol{r},t)\psi(\boldsymbol{r},t). \tag{21.7}$$

I am asking: Is there a current $\boldsymbol{J}$ such that

$$\frac{\partial P}{\partial t} = -\boldsymbol{\nabla}\cdot\boldsymbol{J}? \tag{21.8}$$

If I take the time derivative of Eq. (21.7), I get two terms:

$$\frac{\partial P}{\partial t} = \psi^*\,\frac{\partial\psi}{\partial t} + \psi\,\frac{\partial\psi^*}{\partial t}. \tag{21.9}$$

Now use the Schrödinger equation—Eq. (21.3)—for $\partial\psi/\partial t$; and take the complex conjugate of it to get $\partial\psi^*/\partial t$—each i gets its sign reversed. You get

$$\begin{aligned}\frac{\partial P}{\partial t} = -\frac{i}{\hbar}\biggl[&\psi^*\,\frac{1}{2m}\biggl(\frac{\hbar}{i}\,\boldsymbol{\nabla}-q\boldsymbol{A}\biggr)\cdot\biggl(\frac{\hbar}{i}\,\boldsymbol{\nabla}-q\boldsymbol{A}\biggr)\psi + q\phi\psi^*\psi\\ &-\psi\,\frac{1}{2m}\biggl(-\frac{\hbar}{i}\,\boldsymbol{\nabla}-q\boldsymbol{A}\biggr)\cdot\biggl(-\frac{\hbar}{i}\,\boldsymbol{\nabla}-q\boldsymbol{A}\biggr)\psi^* - q\phi\psi\psi^*\biggr].\end{aligned} \tag{21.10}$$

The potential terms and a lot of other stuff cancel out. And it turns out that what is left can indeed be written as a perfect divergence. The whole equation is equivalent to

$$\frac{\partial P}{\partial t} = -\boldsymbol{\nabla}\cdot\biggl\{\frac{1}{2m}\,\psi^*\biggl(\frac{\hbar}{i}\,\boldsymbol{\nabla}-q\boldsymbol{A}\biggr)\psi + \frac{1}{2m}\,\psi\biggl(-\frac{\hbar}{i}\,\boldsymbol{\nabla}-q\boldsymbol{A}\biggr)\psi^*\biggr\}. \tag{21.11}$$

It is really not as complicated as it seems. It is a symmetrical combination of ψ^* times a certain operation on ψ, plus ψ times the complex conjugate operation on ψ^*. It is some quantity plus its own complex conjugate, so the whole thing is real—as it ought to be. The operation can be remembered this way: it is just the momentum operator $\hat{\boldsymbol{\mathcal{P}}}$ minus $q\boldsymbol{A}$. I could write the current in Eq. (21.8) as

$$\boldsymbol{J}=\frac{1}{2}\biggl\{\psi^*\biggl[\frac{\hat{\boldsymbol{\mathcal{P}}}-q\boldsymbol{A}}{m}\biggr]\psi+\psi\biggl[\frac{\hat{\boldsymbol{\mathcal{P}}}-q\boldsymbol{A}}{m}\biggr]^*\psi^*\biggr\}. \tag{21.12}$$

There is then a current $\boldsymbol{J}$ which completes Eq. (21.8).

Equation (21.11) shows that the probability is conserved locally. If a particle disappears from one region it cannot appear in another without something going on in between. Imagine that the first region is surrounded by a closed surface far enough out that there is zero probability to find the electron at the surface. The total probability to find the electron somewhere inside the surface is the volume integral of P. But according to Gauss's theorem the volume integral of the divergence $\boldsymbol{J}$ is equal to the surface integral of $\boldsymbol{J}$. If ψ is zero at the surface, Eq. (21.12) says that $\boldsymbol{J}$ is zero, so the total probability to find the particle inside can't change. Only if some of the probability approaches the boundary can some of it leak out. We can say that it only gets out by moving through the surface—and that is local conservation.

21-3 Two kinds of momentum

The equation for the current is rather interesting, and sometimes causes a certain amount of worry. You would think the current would be something like the density of particles times the velocity. The density should be something like $\psi\psi^*$, which is o.k. And each term in Eq. (21.12) looks like the typical form for the average-value of the operator

$$\frac{\hat{\boldsymbol{\mathcal{P}}}-q\boldsymbol{A}}{m}, \tag{21.13}$$

so maybe we should think of it as the velocity of flow. It looks as though we have two suggestions for relations of velocity to momentum, because we would also think that momentum divided by mass, $\hat{\boldsymbol{\mathcal{P}}}/m$, should be a velocity. The two possibilities differ by the vector potential.

It happens that these two possibilities were also discovered in classical physics, when it was found that momentum could be defined in two ways.[4] One of them is

[4] See, for example, J. D. Jackson, *Classical Electrodynamics*, John Wiley and Sons, Inc., New York (1962), p. 408.

called "kinematic momentum," but for absolute clarity I will in this lecture call it the "mv-momentum." This is the momentum obtained by multiplying mass by velocity. The other is a more mathematical, more abstract momentum, some times called the "dynamical momentum," which I'll call "p-momentum." The two possibilities are

$$mv\text{-momentum} = m\boldsymbol{v}, \tag{21.14}$$

$$p\text{-momentum} = m\boldsymbol{v} + q\boldsymbol{A}. \tag{21.15}$$

It turns out that in quantum mechanics with magnetic fields it is the p-momentum which is connected to the gradient operator $\hat{\boldsymbol{\mathcal{P}}}$, so it follows that (21.13) is the operator of a velocity.

I'd like to make a brief digression to show you what this is all about—why there must be something like Eq. (21.15) in the quantum mechanics. The wave function changes with time according to the Schrödinger equation in Eq. (21.3). If I would suddenly change the vector potential, the wave function wouldn't change at the first instant; only its rate of change changes. Now think of what would happen in the following circumstance. Suppose I have a long solenoid, in which I can produce a flux of magnetic field ($\boldsymbol{B}$-field), as shown in Fig. 21-2. And there is a charged particle sitting nearby. Suppose this flux nearly instantaneously builds up from zero to something. I start with zero vector potential and then I turn on a vector potential. That means that I produce suddenly a circumferential vector potential $\boldsymbol{A}$. You'll remember that the line integral of $\boldsymbol{A}$ around a loop is the same as the flux of $\boldsymbol{B}$ through the loop.[5] Now what happens if I suddenly turn on a vector potential? According to the quantum mechanical equation the sudden change of $\boldsymbol{A}$ does not make a sudden change of ψ; the wave function is still the same. So the gradient is also unchanged.

But remember what happens electrically when I suddenly turn on a flux. During the short time that the flux is rising, there's an electric field generated whose line integral is the rate of change of the flux with time:

$$\boldsymbol{E} = -\frac{\partial \boldsymbol{A}}{\partial t}. \tag{21.16}$$

That electric field is enormous if the flux is changing rapidly, and it gives a force on the particle. The force is the charge times the electric field, and so

[5] Volume II, Chapter 14, Section 14-1.

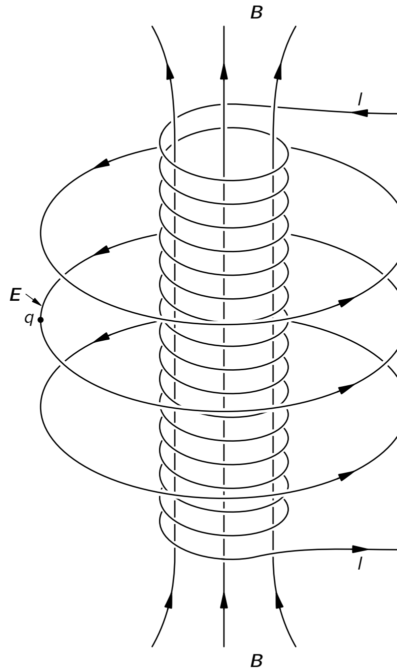

Fig. 21-2. The electric field outside a solenoid with an increasing current.

during the build up of the flux the particle obtains a total impulse (that is, a change in $m\boldsymbol{v}$) equal to $-q\boldsymbol{A}$. In other words, if you suddenly turn on a vector potential at a charge, this charge immediately picks up an mv-momentum equal to $-q\boldsymbol{A}$. But there is something that isn't changed immediately and that's the difference between $m\boldsymbol{v}$ and $-q\boldsymbol{A}$. And so the sum $\boldsymbol{p} = m\boldsymbol{v} + q\boldsymbol{A}$ is something which is not changed when you make a sudden change in the vector potential. This quantity $\boldsymbol{p}$ is what we have called the p-momentum and is of importance in classical mechanics in the theory of dynamics, but it also has a direct significance in quantum mechanics. It depends on the character of the wave function, and it is the one to be identified with the operator

$$\hat{\boldsymbol{\mathcal{P}}} = \frac{\hbar}{i}\,\boldsymbol{\nabla}.$$

21-4 The meaning of the wave function

When Schrödinger first discovered his equation he discovered the conservation law of Eq. (21.8) as a consequence of his equation. But he imagined incorrectly that P was the electric charge density of the electron and that $\boldsymbol{J}$ was the electric current density, so he thought that the electrons interacted with the electromagnetic field through these charges and currents. When he solved his equations for the hydrogen atom and calculated ψ, he wasn't calculating the probability of anything—there were no amplitudes at that time—the interpretation was completely different. The atomic nucleus was stationary but there were currents moving around; the charges P and currents $\boldsymbol{J}$ would generate electromagnetic fields and the thing would radiate light. He soon found on doing a number of problems that it didn't work out quite right. It was at this point that Born made an essential contribution to our ideas regarding quantum mechanics. It was Born who correctly (as far as we know) interpreted the ψ of the Schrödinger equation in terms of a probability amplitude—that very difficult idea that the square of the amplitude is not the charge density but is only the probability per unit volume of finding an electron there, and that when you do find the electron some place the entire charge is there. That whole idea is due to Born.

The wave function $\psi(\boldsymbol{r})$ for an electron in an atom does not, then, describe a smeared-out electron with a smooth charge density. The electron is either here, or there, or somewhere else, but wherever it is, it is a point charge. On the other hand, think of a situation in which there are an enormous number of particles in exactly the same state, a very large number of them with exactly the same wave function. Then what? One of them is here and one of them is there, and the probability of finding any one of them at a given place is proportional to $\psi\psi^*$. But since there are so many particles, if I look in any volume $dx\,dy\,dz$ I will generally find a number close to $\psi\psi^*\,dx\,dy\,dz$. So in a situation in which ψ is the wave function for each of an enormous number of particles which are all in the same state, $\psi\psi^*$ *can* be interpreted as the density of particles. If, under these circumstances, each particle carries the same charge q, we can, in fact, go further and interpret $\psi^*\psi$ as the density of *electricity*. Normally, $\psi\psi^*$ is given the dimensions of a probability density, then ψ should be multiplied by q to give the dimensions of a charge density. For our present purposes we can put this constant factor into ψ, and take $\psi\psi^*$ itself as the electric charge density. With this understanding, $\boldsymbol{J}$ (the current of probability I have calculated) becomes directly the electric current density.

So in the situation in which we can have very many particles in exactly the same state, there is possible a new physical interpretation of the wave functions. The charge density and the electric current can be calculated directly from the wave functions and the wave functions take on a physical meaning which extends into classical, macroscopic situations.

Something similar can happen with neutral particles. When we have the wave function of a single photon, it is the amplitude to find a photon somewhere. Although we haven't ever written it down there is an equation for the photon wave function analogous to the Schrödinger equation for the electron. The photon equation is just the same as Maxwell's equations for the electromagnetic field, and the wave function is the same as the vector potential $\boldsymbol{A}$. The wave function turns out to be just the vector potential. The quantum physics is the same thing as the classical physics because photons are noninteracting Bose particles and many of them can be in the same state—as you know, they *like* to be in the same state. The moment that you have billions in the same state (that is, in the same electromagnetic wave), you can measure the wave function, which is the vector potential, directly. Of course, it worked historically the other way. The first observations were on situations with many photons in the same state, and so we were able to discover the correct equation for a single photon by observing directly with our hands on a macroscopic level the nature of wave function.

Now the trouble with the electron is that you cannot put more than one in the same state. Therefore, it was long believed that the wave function of the Schrödinger equation would never have a macroscopic representation analogous to the macroscopic representation of the amplitude for photons. On the other hand, it is now realized that the phenomena of superconductivity presents us with just this situation.

21-5 Superconductivity

As you know, very many metals become superconducting below a certain temperature[6]—the temperature is different for different metals. When you reduce the temperature sufficiently the metals conduct electricity without any resistance. This phenomenon has been observed for a very large number of metals but not for all, and the theory of this phenomenon has caused a great deal of difficulty. It

[6] First discovered by Kamerlingh-Onnes in 1911; H. Kamerlingh-Onnes, Comm. Phys. Lab., Univ. Leyden, Nos. 119, 120, 122 (1911). You will find a nice up-to-date discussion of the subject in E. A. Lynton, *Superconductivity*, John Wiley and Sons, Inc., New York, 1962.

took a very long time to understand what was going on inside of superconductors, and I will only describe enough of it for our present purposes. It turns out that due to the interactions of the electrons with the vibrations of the atoms in the lattice, there is a small net effective *attraction* between the electrons. The result is that the electrons form together, if I may speak very qualitatively and crudely, bound pairs.

Now you know that a single electron is a Fermi particle. But a bound pair would act as a Bose particle, because if I exchange both electrons in a pair I change the sign of the wave function twice, and that means that I don't change anything. A pair *is* a Bose particle.

The energy of pairing—that is, the net attraction—is very, very weak. Only a tiny temperature is needed to throw the electrons apart by thermal agitation, and convert them back to "normal" electrons. But when you make the temperature sufficiently low that they have to do their very best to get into the absolutely lowest state; then they do collect in pairs.

I don't wish you to imagine that the pairs are really held together very closely like a point particle. As a matter of fact, one of the great difficulties of understanding this phenomena originally was that that is not the way things are. The two electrons which form the pair are really spread over a considerable distance; and the mean distance between pairs is relatively smaller than the size of a single pair. Several pairs are occupying the same space at the same time. Both the reason why electrons in a metal form pairs and an estimate of the energy given up in forming a pair have been a triumph of recent times. This fundamental point in the theory of superconductivity was first explained in the theory of Bardeen, Cooper, and Schrieffer,[7] but that is not the subject of this seminar. We will accept, however, the idea that the electrons do, in some manner or other, work in pairs, that we can think of these pairs as behaving more or less like particles, and that we can therefore talk about the wave function for a "pair."

Now the Schrödinger equation for the pair will be more or less like Eq. (21.3). There will be one difference in that the charge q will be twice the charge of an electron. Also, we don't know the inertia—or effective mass—for the pair in the crystal lattice, so we don't know what number to put in for m. Nor should we think that if we go to very high frequencies (or short wavelengths), this is exactly the right form, because the kinetic energy that corresponds to very rapidly varying wave functions may be so great as to break up the pairs. At finite

[7] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, *Phys. Rev.* **108**, 1175 (1957).

temperatures there are always a few pairs which are broken up according to the usual Boltzmann theory. The probability that a pair is broken is proportional to $\exp(-E_{\text{pair}}/kT)$. The electrons that are not bound in pairs are called "normal" electrons and will move around in the crystal in the ordinary way. I will, however, consider only the situation at essentially zero temperature—or, in any case, I will disregard the complications produced by those electrons which are not in pairs.

Since electron pairs are bosons, when there are a lot of them in a given state there is an especially large amplitude for other pairs to go to the same state. So nearly all of the pairs will be locked down at the lowest energy in *exactly the same state*—it won't be easy to get one of them into another state. There's more amplitude to go into the same state than into an unoccupied state by the famous factor $\sqrt{n}$, where $n-1$ is the occupancy of the lowest state. So we would expect all the pairs to be moving in the same state.

What then will our theory look like? I'll call ψ the wave function of a pair in the lowest energy state. However, since $\psi\psi^*$ is going to be proportional to the charge density ρ, I can just as well write ψ as the square root of the charge density times some phase factor:

$$\psi(\boldsymbol{r}) = \rho^{1/2}(\boldsymbol{r})e^{i\theta(\boldsymbol{r})}, \tag{21.17}$$

where ρ and θ are real functions of $\boldsymbol{r}$. (Any complex function can, of course, be written this way.) It's clear what we mean when we talk about the charge density, but what is the physical meaning of the phase θ of the wave function? Well, let's see what happens if we substitute $\psi(\boldsymbol{r})$ into Eq. (21.12), and express the current density in terms of these new variables ρ and θ. It's just a change of variables and I won't go through all the algebra, but it comes out

$$\boldsymbol{J} = \frac{\hbar}{m}\biggl(\boldsymbol{\nabla}\theta - \frac{q}{\hbar}\,\boldsymbol{A}\biggr)\rho. \tag{21.18}$$

Since both the current density and the charge density have a direct physical meaning for the superconducting electron gas, both ρ and θ are real things. The phase is just as observable as ρ; it is a piece of the current density $\boldsymbol{J}$. The *absolute* phase is not observable, but if the gradient of the phase is known everywhere, the phase is known except for a constant. You can define the phase at one point, and then the phase everywhere is determined.

Incidentally, the equation for the current can be analyzed a little nicer, when you think that the current density $\boldsymbol{J}$ is *in fact* the charge density times the velocity of motion of the fluid of electrons, or $\rho\boldsymbol{v}$. Equation (21.18) is then equivalent to

$$m\boldsymbol{v} = \hbar\,\boldsymbol{\nabla}\theta - q\boldsymbol{A}. \tag{21.19}$$

Notice that there are two pieces in the mv-momentum; one is a contribution from the vector potential, and the other, a contribution from the behavior of the wave function. In other words, the quantity $\hbar\,\boldsymbol{\nabla}\theta$ is just what we have called the p-momentum.

21-6 The Meissner effect

Now we can describe some of the phenomena of superconductivity. First, there is no electrical resistance. There's no resistance because all the electrons are collectively in the same state. In the ordinary flow of current you knock one electron or the other out of the regular flow, gradually deteriorating the general momentum. But here to get one electron away from what all the others are doing is very hard because of the tendency of all Bose particles to go in the same state. A current once started, just keeps on going forever.

It's also easy to understand that if you have a piece of metal in the superconducting state and turn on a magnetic field which isn't too strong (we won't go into the details of how strong), the magnetic field can't penetrate the metal. If, as you build up the magnetic field, any of it were to build up inside the metal, there would be a rate of change of flux which would produce an electric field, and an electric field would immediately generate a current which, by Lenz's law, would oppose the flux. Since all the electrons will move together, an infinitesimal electric field will generate enough current to oppose completely any applied magnetic field. So if you turn the field on after you've cooled a metal to the superconducting state, it will be excluded.

Even more interesting is a related phenomenon discovered experimentally by Meissner.[8] If you have a piece of the metal at a high temperature (so that it is a normal conductor) and establish a magnetic field through it, and then you lower the temperature below the critical temperature (where the metal becomes a superconductor), *the field is expelled.* In other words, it starts up its own current—and in just the right amount to push the field out.

We can see the reason for that in the equations, and I'd like to explain how. Suppose that we take a piece of superconducting material which is in one lump.

[8] W. Meissner and R. Ochsenfeld, *Naturwiss.* **21**, 787 (1933).

Then in a steady situation of any kind the divergence of the current must be zero because there's no place for it to go. It is convenient to choose to make the divergence of $\boldsymbol{A}$ equal to zero. (I should explain why choosing this convention doesn't mean any loss of generality, but I don't want to take the time.) Taking the divergence of Eq. (21.18), then gives that the Laplacian of θ is equal to zero. One moment. What about the variation of ρ? I forgot to mention an important point. There is a background of positive charge in this metal due to the atomic ions of the lattice. If the charge density ρ is uniform there is no net charge and no electric field. If there would be any accumulation of electrons in one region the charge wouldn't be neutralized and there would be a terrific repulsion pushing the electrons apart.† So in ordinary circumstances the charge density of the electrons in the superconductor is almost perfectly uniform—I can take ρ as a constant. Now the only way that $\nabla^2\theta$ can be zero everywhere inside the lump of metal is for θ to be a constant. And that means that there is no contribution to $\boldsymbol{J}$ from p-momentum. Equation (21.18) then says that the current is proportional to ρ times $\boldsymbol{A}$. So everywhere in a lump of superconducting material the current is necessarily proportional to the vector potential:

$$\boldsymbol{J} = -\rho\,\frac{q}{m}\,\boldsymbol{A}. \tag{21.20}$$

Since ρ and q have the same (negative) sign, and since ρ is a constant, I can set $-\rho q/m = -$(some positive constant); then

$$\boldsymbol{J} = -(\text{some positive constant})\boldsymbol{A}. \tag{21.21}$$

This equation was originally proposed by London and London[9] to explain the experimental observations of superconductivity—long before the quantum mechanical origin of the effect was understood.

Now we can use Eq. (21.20) in the equations of electromagnetism to solve for the fields. The vector potential is related to the current density by

$$\nabla^2\boldsymbol{A} = -\frac{1}{\epsilon_0 c^2}\,\boldsymbol{J}. \tag{21.22}$$

† Actually if the electric field were too strong, pairs would be broken up and the "normal" electrons created would move in to help neutralize any excess of positive charge. Still, it takes energy to make these normal electrons, so the main point is that a nearly uniform density ρ is highly favored energetically.

[9] F. London and H. London, *Proc. Roy. Soc.* (London) **A149**, 71 (1935); *Physica* **2**, 341 (1935).

If I use Eq. (21.21) for $\boldsymbol{J}$, I have

$$\nabla^2 \boldsymbol{A} = \lambda^2 \boldsymbol{A}, \tag{21.23}$$

where λ^2 is just a new constant;

$$\lambda^2 = \rho \frac{q}{\epsilon_0 mc^2}. \tag{21.24}$$

We can now try to solve this equation for $\boldsymbol{A}$ and see what happens in detail. For example, in one dimension Eq. (21.23) has exponential solutions of the form $e^{-\lambda x}$ and $e^{+\lambda x}$. These solutions mean that the vector potential must *decrease* exponentially as you go from the surface into the material. (It can't increase because there would be a blow up.) If the piece of metal is very large compared to $1/\lambda$, the field only penetrates to a thin layer at the surface—a layer about $1/\lambda$ in thickness. The entire remainder of the interior is free of field, as sketched in Fig. 21-3. This is the explanation of the Meissner effect.

How big is the distance λ? Well, remember that r_0, the "electromagnetic radius" of the electron (2.8×10^{-13} cm), is given by

$$mc^2 = \frac{q_e^2}{4\pi\epsilon_0 r_0}.$$

Also, remember that q in Eq. (21.24) is twice the charge of an electron, so

$$\frac{q^2}{\epsilon_0 mc^2} = \frac{8\pi r_0}{q_e}.$$

Writing ρ as $q_e N$, where N is the number of electrons per cubic centimeter, we have

$$\lambda^2 = 8\pi N r_0. \tag{21.25}$$

For a metal such as lead there are about 3×10^{22} atoms per cm^3, so if each one contributed only one conduction electron, $1/\lambda$ would be about 2×10^{-6} cm. That gives you the order of magnitude.

21-7 Flux quantization

The London equation (21.21) was proposed to account for the observed facts of superconductivity including the Meissner effect. In recent times, however,

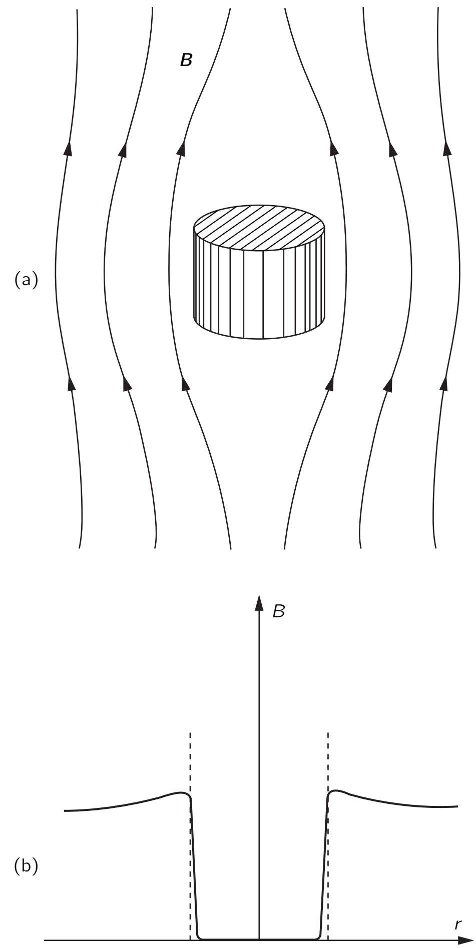

Fig. 21-3. (a) A superconducting cylinder in a magnetic field; (b) the magnetic field B as a function of r.

there have been some even more dramatic predictions. One prediction made by London was so peculiar that nobody paid much attention to it until recently. I will now discuss it. This time instead of taking a single lump, suppose we take a *ring* whose thickness is large compared to $1/\lambda$, and try to see what would happen if we started with a magnetic field through the ring, then cooled it to the superconducting state, and afterward removed the original source of $\boldsymbol{B}$. The sequence of events is sketched in Fig. 21-4. In the normal state there will be a

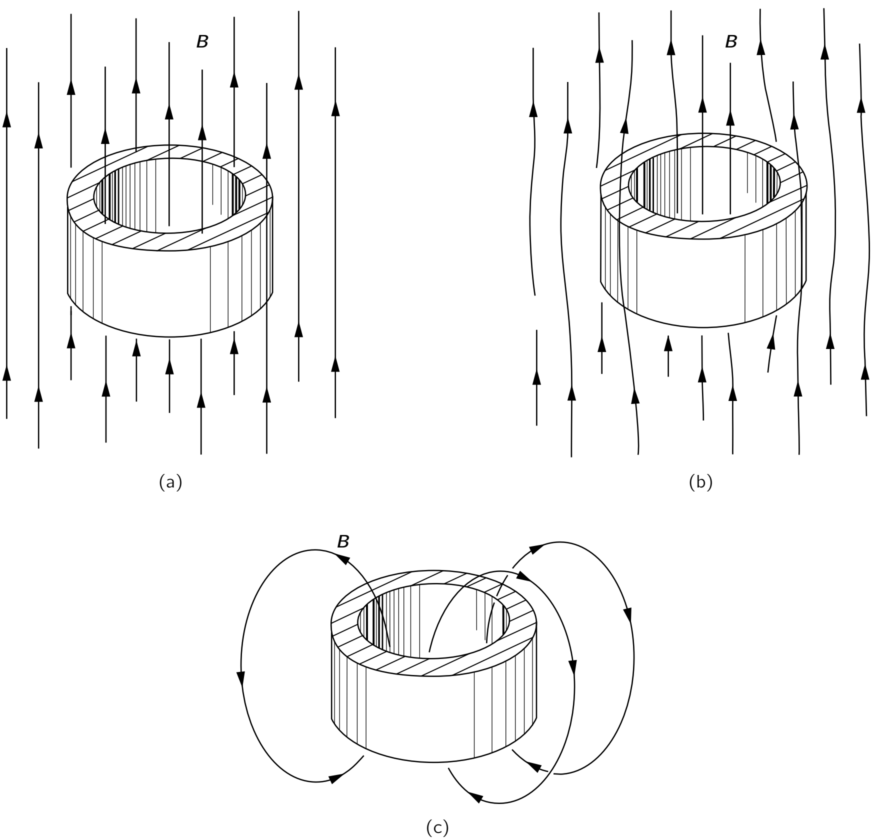

Fig. 21-4. A ring in a magnetic field: (a) in the normal state; (b) in the superconducting state; (c) after the external field is removed.

field in the body of the ring as sketched in part (a) of the figure. When the ring is made superconducting, the field is forced outside of the *material* (as we have just seen). There will then be some flux through the hole of the ring as sketched in part (b). If the external field is now removed, the lines of field going through the hole are "trapped" as shown in part (c). The flux Φ through the center can't decrease because $\partial\Phi/\partial t$ must be equal to the line integral of $\boldsymbol{E}$ around the ring, which is zero in a superconductor. As the external field is removed a super current starts flowing around the ring to keep the flux through the ring a constant. (It's the old eddy-current idea, only with zero resistance.) These currents will, however, all flow near the surface (down to a depth $1/\lambda$), as can be shown by the same kind of analysis that I made for the solid block. These currents can keep the magnetic field out of the body of the ring, and produce the permanently trapped magnetic field as well.

Now, however, there is an essential difference, and our equations predict a surprising effect. The argument I made above that θ must be a constant in a solid block *does not apply for a ring*, as you can see from the following arguments.

Well inside the body of the ring the current density $\boldsymbol{J}$ is zero; so Eq. (21.18) gives

$$\hbar\,\boldsymbol{\nabla}\theta = q\boldsymbol{A}. \tag{21.26}$$

Now consider what we get if we take the line integral of $\boldsymbol{A}$ around a curve Γ, which goes around the ring near the center of its cross-section so that it never gets near the surface, as drawn in Fig. 21-5. From Eq. (21.26),

$$\hbar \oint \boldsymbol{\nabla}\theta \cdot d\boldsymbol{s} = q \oint \boldsymbol{A} \cdot d\boldsymbol{s}. \tag{21.27}$$

Now you know that the line integral of $\boldsymbol{A}$ around any loop is equal to the flux

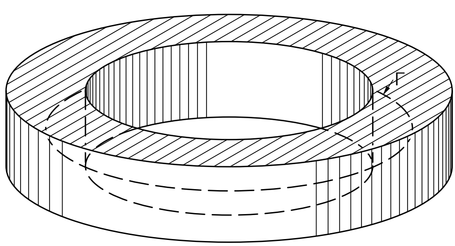

Fig. 21-5. The curve Γ inside a superconducting ring.

of $\boldsymbol{B}$ through the loop

$$\oint \boldsymbol{A}\cdot d\boldsymbol{s}=\Phi.$$

Equation (21.27) then becomes

$$\oint \boldsymbol{\nabla}\theta\cdot d\boldsymbol{s}=\frac{q}{\hbar}\,\Phi. \tag{21.28}$$

The line integral of a gradient from one point to another (say from point 1 to point 2) is the difference of the values of the function at the two points. Namely,

$$\int_1^2 \boldsymbol{\nabla}\theta\cdot d\boldsymbol{s}=\theta_2-\theta_1.$$

If we let the two end points 1 and 2 come together to make a closed loop you might at first think that θ_2 would equal θ_1, so that the integral in Eq. (21.28) would be zero. That would be true for a closed loop in a simply-connected piece of superconductor, but it is not necessarily true for a ring-shaped piece. The only physical requirement we can make is that *there can be only one value of the wave function for each point.* Whatever θ does as you go around the ring, when you get back to the starting point the θ you get must give the same value for the wave function

$$\psi=\sqrt{\rho}e^{i\theta}.$$

This will happen if θ changes by $2\pi n$, where n is any integer. So if we make one complete turn around the ring the left-hand side of Eq. (21.27) must be $\hbar\cdot 2\pi n$. Using Eq. (21.28), I get that

$$2\pi n\hbar=q\Phi. \tag{21.29}$$

The trapped flux must always be an integer times $2\pi\hbar/q$! If you would think of the ring as a classical object with an ideally perfect (that is, infinite) conductivity, you would think that whatever flux was initially found through it would just stay there—any amount of flux at all could be trapped. But the quantum-mechanical theory of superconductivity says that the flux can be zero, or $2\pi\hbar/q$, or $4\pi\hbar/q$, or $6\pi\hbar/q$, and so on, but no value in between. It must be a multiple of a basic quantum mechanical unit.

London[10] predicted that the flux trapped by a superconducting ring would be quantized and said that the possible values of the flux would be given by

[10] F. London, *Superfluids*; John Wiley and Sons, Inc., New York, 1950, Vol. I, p. 152.

Eq. (21.29) with q equal to the electronic charge. According to London the basic unit of flux should be $2\pi\hbar/q_e$, which is about 4×10^{-7} gauss $\cdot$ cm^2. To visualize such a flux, think of a tiny cylinder a tenth of a millimeter in diameter; the magnetic field inside it when it contains this amount of flux is about one percent of the earth's magnetic field. It should be possible to observe such a flux by a sensitive magnetic measurement.

In 1961 such a quantized flux was looked for and found by Deaver and Fairbank[11] at Stanford University and at about the same time by Doll and Näbauer[12] in Germany.

In the experiment of Deaver and Fairbank, a tiny cylinder of superconductor was made by electroplating a thin layer of tin on a one-centimeter length of No. 56 (1.3×10^{-3} cm diameter) copper wire. The tin becomes superconducting below 3.8°K while the copper remains a normal metal. The wire was put in a small controlled magnetic field, and the temperature reduced until the tin became superconducting. Then the external source of field was removed. You would expect this to generate a current by Lenz's law so that the flux inside would not change. The little cylinder should now have magnetic moment proportional to the flux inside. The magnetic moment was measured by jiggling the wire up and down (like the needle on a sewing machine, but at the rate of 100 cycles per second) inside a pair of little coils at the ends of the tin cylinder. The induced voltage in the coils was then a measure of the magnetic moment.

When the experiment was done by Deaver and Fairbank, they found that the flux was quantized, *but that the basic unit was only one-half as large as London had predicted.* Doll and Näbauer got the same result. At first this was quite mysterious,† but we now understand why it should be so. According to the Bardeen, Cooper, and Schrieffer theory of superconductivity, the q which appears in Eq. (21.29) is the charge of a *pair* of electrons and so is equal to $2q_e$. The basic flux unit is

$$\Phi_0 = \frac{\pi\hbar}{q_e} \approx 2 \times 10^{-7} \text{ gauss} \cdot \text{cm}^2 \tag{21.30}$$

or one-half the amount predicted by London. Everything now fits together, and

† It has once been suggested by Onsager that this might happen (see Deaver and Fairbank, Ref. 11), although no one else ever understood why.

[11] B. S. Deaver, Jr., and W. M. Fairbank, *Phys. Rev. Letters* **7**, 43 (1961).
[12] R. Doll and M. Näbauer, *Phys. Rev. Letters* **7**, 51 (1961).

the measurements show the existence of the predicted purely quantum-mechanical effect on a large scale.

21-8 The dynamics of superconductivity

The Meissner effect and the flux quantization are two confirmations of our general ideas. Just for the sake of completeness I would like to show you what the complete equations of a superconducting fluid would be from this point of view—it is rather interesting. Up to this point I have only put the expression for ψ into equations for charge density and current. If I put it into the complete Schrödinger equation I get equations for ρ and θ. It should be interesting to see what develops, because here we have a "fluid" of electron pairs with a charge density ρ and a mysterious θ—we can try to see what kind of equations we get for such a "fluid"! So we substitute the wave function of Eq. (21.17) into the Schrödinger equation (21.3) and remember that ρ and θ are real functions of x, y, z, and t. If we separate real and imaginary parts we obtain then two equations. To write them in a shorter form I will—following Eq. (21.19)—write

$$\frac{\hbar}{m}\,\boldsymbol{\nabla}\theta-\frac{q}{m}\,\boldsymbol{A}=\boldsymbol{v}. \tag{21.31}$$

One of the equations I get is then

$$\frac{\partial\rho}{\partial t}=-\boldsymbol{\nabla}\cdot\rho\boldsymbol{v}. \tag{21.32}$$

Since $\rho\boldsymbol{v}$ is first $\boldsymbol{J}$, this is just the continuity equation once more. The other equation I obtain tells how θ varies; it is

$$\hbar\,\frac{\partial\theta}{\partial t}=-\frac{m}{2}\,v^2-q\phi+\frac{\hbar^2}{2m}\left\{\frac{1}{\sqrt{\rho}}\,\nabla^2(\sqrt{\rho})\right\}. \tag{21.33}$$

Those who are thoroughly familiar with hydrodynamics (of which I'm sure few of you are) will recognize this as the equation of motion for an electrically charged fluid if we identify $\hbar\theta$ as the "velocity potential"—except that the last term, which should be the energy of compression of the fluid, has a rather strange dependence on the density ρ. In any case, the equation says that the rate of change of the quantity $\hbar\theta$ is given by a kinetic energy term, $-\frac{1}{2}mv^2$, plus a potential energy term, $-q\phi$, with an additional term, containing the factor $\hbar^2$, which we could call a "quantum mechanical energy." We have seen that inside a superconductor ρ is kept very uniform by the electrostatic forces, so this term can almost certainly be neglected in every practical application provided we have only one superconducting region. If we have a boundary between two superconductors (or other circumstances in which the value of ρ may change rapidly) this term can become important.

For those who are not so familiar with the equations of hydrodynamics, I can rewrite Eq. (21.33) in a form that makes the physics more apparent by using Eq. (21.31) to express θ in terms of $\boldsymbol{v}$. Taking the gradient of the whole of Eq. (21.33) and expressing $\boldsymbol{\nabla}\theta$ in terms of $\boldsymbol{A}$ and $\boldsymbol{v}$ by using (21.31), I get

$$\frac{\partial \boldsymbol{v}}{\partial t} = \frac{q}{m}\left(-\boldsymbol{\nabla}\phi - \frac{\partial \boldsymbol{A}}{\partial t}\right) - \boldsymbol{v}\times(\boldsymbol{\nabla}\times\boldsymbol{v}) - (\boldsymbol{v}\cdot\boldsymbol{\nabla})\boldsymbol{v} + \boldsymbol{\nabla}\frac{\hbar^2}{2m^2}\left(\frac{1}{\sqrt{\rho}}\nabla^2\sqrt{\rho}\right). \tag{21.34}$$

What does this equation mean? First, remember that

$$-\boldsymbol{\nabla}\phi - \frac{\partial \boldsymbol{A}}{\partial t} = \boldsymbol{E}. \tag{21.35}$$

Next, notice that if I take the curl of Eq. (21.31), I get

$$\boldsymbol{\nabla}\times\boldsymbol{v} = -\frac{q}{m}\,\boldsymbol{\nabla}\times\boldsymbol{A}, \tag{21.36}$$

since the curl of a gradient is always zero. But $\boldsymbol{\nabla}\times\boldsymbol{A}$ is the magnetic field $\boldsymbol{B}$, so the first two terms can be written as

$$\frac{q}{m}(\boldsymbol{E} + \boldsymbol{v}\times\boldsymbol{B}).$$

Finally, you should understand that $\partial\boldsymbol{v}/\partial t$ stands for the rate of change of the velocity of the fluid at a point. If you concentrate on a particular particle, its acceleration is the *total* derivative of $\boldsymbol{v}$ (or, as it is sometimes called in fluid dynamics, the "comoving acceleration"), which is related to $\partial\boldsymbol{v}/\partial t$ by[13]

$$\left.\frac{d\boldsymbol{v}}{dt}\right|_{\text{comoving}} = \frac{\partial \boldsymbol{v}}{\partial t} + (\boldsymbol{v}\cdot\boldsymbol{\nabla})\boldsymbol{v}. \tag{21.37}$$

This extra term also appears as the third term on the right side of Eq. (21.34).

[13] See Volume II, Section 40-2.

Taking it to the left side, I can write Eq. (21.34) in the following way:

$$m\,\frac{d\boldsymbol{v}}{dt}\bigg|_{\text{comoving}} = q(\boldsymbol{E}+\boldsymbol{v}\times\boldsymbol{B}) + \boldsymbol{\nabla}\frac{\hbar^2}{2m^2}\left(\frac{1}{\sqrt{\rho}}\,\nabla^2\sqrt{\rho}\right). \tag{21.38}$$

We also have from Eq. (21.36) that

$$\boldsymbol{\nabla}\times\boldsymbol{v} = -\frac{q}{m}\,\boldsymbol{B}. \tag{21.39}$$

These two equations are the equations of motion of the superconducting electron fluid. The first equation is just Newton's law for a charged fluid in an electromagnetic field. It says that the acceleration of each particle of the fluid whose charge is q comes from the ordinary Lorentz force $q(\boldsymbol{E}+\boldsymbol{v}\times\boldsymbol{B})$ plus an additional force, which is the gradient of some mystical quantum mechanical potential—a force which is not very big except at the junction between two superconductors. The second equation says that the fluid is "ideal"—the curl of $\boldsymbol{v}$ has zero divergence (the divergence of $\boldsymbol{B}$ is always zero). That means that the velocity can be expressed in terms of velocity potential. Ordinarily one writes that $\boldsymbol{\nabla}\times\boldsymbol{v}=0$ for an ideal fluid, but for an *ideal charged fluid in a magnetic field*, this gets modified to Eq. (21.39).

So, Schrödinger's equation for the electron pairs in a superconductor gives us the equations of motion of an electrically charged ideal fluid. Superconductivity is the same as the problem of the hydrodynamics of a charged liquid. If you want to solve any problem about superconductors you take these equations for the fluid [or the equivalent pair, Eqs. (21.32) and (21.33)], and combine them with Maxwell's equations to get the fields. (The charges and currents you use to get the fields must, of course, include the ones from the superconductor as well as from the external sources.)

Incidentally, I believe that Eq. (21.38) is not quite correct, but ought to have an additional term involving the density. This new term does not depend on quantum mechanics, but comes from the ordinary energy associated with variations of density. Just as in an ordinary fluid there should be a potential energy density proportional to the square of the deviation of ρ from ρ_0, the undisturbed density (which is, here, also equal to the charge density of the crystal lattice). Since there will be forces proportional to the gradient of this energy, there should be another term in Eq. (21.38) of the form: (const) $\boldsymbol{\nabla}(\rho-\rho_0)^2$. This term did not appear from the analysis because it comes from the interactions between particles, which I neglected in using an independent-particle approximation. It is, however, just the force I referred to when I made the qualitative statement that electrostatic forces would tend to keep ρ nearly constant inside a superconductor.

21-9 The Josephson junction

I would like to discuss next a very interesting situation that was noticed by Josephson[14] while analyzing what might happen at a junction between two superconductors. Suppose we have two superconductors which are connected by a thin layer of insulating material as in Fig. 21-6. Such an arrangement is now called a "Josephson junction." If the insulating layer is thick, the electrons can't get through; but if the layer is thin enough, there can be an appreciable quantum mechanical amplitude for electrons to jump across. This is just another example of the quantum-mechanical penetration of a barrier. Josephson analyzed this situation and discovered that a number of strange phenomena should occur.

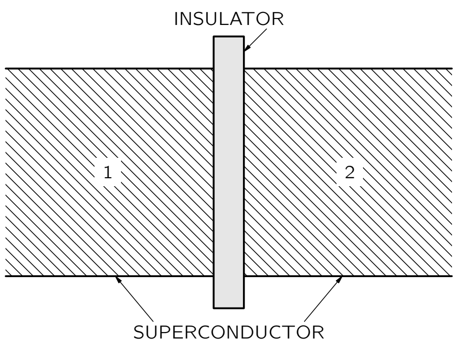

Fig. 21-6. Two superconductors separated by a thin insulator.

In order to analyze such a junction I'll call the amplitude to find an electron on one side, ψ_1, and the amplitude to find it on the other, ψ_2. In the superconducting state the wave function, ψ_1 is the common wave function of all the electrons on one side, and ψ_2 is the corresponding function on the other side. I could do this problem for different kinds of superconductors, but let us take a very simple situation in which the material is the same on both sides so that the junction

[14] B. D. Josephson, *Physics Letters* **1**, 251 (1962).

is symmetrical and simple. Also, for a moment let there be no magnetic field. Then the two amplitudes should be related in the following way:

$$i\hbar\,\frac{\partial\psi_1}{\partial t} = U_1\psi_1 + K\psi_2,$$

$$i\hbar\,\frac{\partial\psi_2}{\partial t} = U_2\psi_2 + K\psi_1.$$

The constant K is a characteristic of the junction. If K were zero, these two equations would just describe the lowest energy state—with energy U—of each superconductor. But there is coupling between the two sides by the amplitude K that there may be leakage from one side to the other. (It is just the "flip-flop" amplitude of a two-state system.) If the two sides are identical, U_1 would equal U_2 and I could just subtract them off. But now suppose that we connect the two superconducting regions to the two terminals of a battery so that there is a potential difference V across the junction. Then $U_1 - U_2 = qV$. I can, for convenience, define the zero of energy to be halfway between, then the two equations are

$$\begin{aligned} i\hbar\,\frac{\partial\psi_1}{\partial t} &= \frac{qV}{2}\,\psi_1 + K\psi_2, \\ i\hbar\,\frac{\partial\psi_2}{\partial t} &= -\frac{qV}{2}\,\psi_2 + K\psi_1. \end{aligned} \tag{21.40}$$

These are the standard equations for two quantum mechanical states coupled together. This time, let's analyze these equations in another way. Let's make the substitutions

$$\begin{aligned} \psi_1 &= \sqrt{\rho_1}e^{i\theta_1}, \\ \psi_2 &= \sqrt{\rho_2}e^{i\theta_2}, \end{aligned} \tag{21.41}$$

where θ_1 and θ_2 are the phases on the two sides of the junction and ρ_1 and ρ_2 are the density of electrons at those two points. Remember that in actual practice ρ_1 and ρ_2 are almost exactly the same and are equal to ρ_0, the normal density of electrons in the superconducting material. Now if you substitute these equations for ψ_1 and ψ_2 into (21.40), you get four equations by equating the real and imaginary parts in each case. Letting $(\theta_2 - \theta_1) = \delta$, for short, the result is

$$\begin{aligned}\dot{\rho}_1 &= +\frac{2}{\hbar}\,K\sqrt{\rho_2\rho_1}\sin\delta,\\ \dot{\rho}_2 &= -\frac{2}{\hbar}\,K\sqrt{\rho_2\rho_1}\sin\delta,\end{aligned} \tag{21.42}$$

$$\begin{aligned}\dot{\theta}_1 &= -\frac{K}{\hbar}\sqrt{\frac{\rho_2}{\rho_1}}\cos\delta - \frac{qV}{2\hbar},\\ \dot{\theta}_2 &= -\frac{K}{\hbar}\sqrt{\frac{\rho_1}{\rho_2}}\cos\delta + \frac{qV}{2\hbar}.\end{aligned} \tag{21.43}$$

The first two equations say that $\dot{\rho}_1 = -\dot{\rho}_2$. "But," you say, "they must both be zero if ρ_1 and ρ_2 are both constant and equal to ρ_0." Not quite. These equations are not the whole story. They say what $\dot{\rho}_1$ and $\dot{\rho}_2$ would be *if there were no extra electric forces* due to an unbalance between the electron fluid and the background of positive ions. They tell how the densities would *start* to change, and therefore describe the kind of current that would begin to flow. This current from side 1 to side 2 would be just $\dot{\rho}_1$ (or $-\dot{\rho}_2$), or

$$J = \frac{2K}{\hbar}\sqrt{\rho_1\rho_2}\sin\delta. \tag{21.44}$$

Such a current would soon charge up side 2, *except* that we have forgotten that the two sides are connected by wires to the battery. The current that flows will not charge up region 2 (or discharge region 1) because currents will flow to keep the potential constant. These currents from the battery have not been included in our equations. When they are included, ρ_1 and ρ_2 do not in fact change, but the current across the junction is still given by Eq. (21.44).

Since ρ_1 and ρ_2 do remain constant and equal to ρ_0, let's set $2K\rho_0/\hbar = J_0$, and write

$$J = J_0\sin\delta. \tag{21.45}$$

J_0, like K, is then a number which is a characteristic of the particular junction.

The other pair of equations (21.43) tells us about θ_1 and θ_2 We are interested in the difference $\delta = \theta_2 - \theta_1$ to use Eq. (21.45); what we get is

$$\dot{\delta} = \dot{\theta}_2 - \dot{\theta}_1 = \frac{qV}{\hbar}. \tag{21.46}$$

That means that we can write

$$\delta(t) = \delta_0 + \frac{q}{\hbar}\int V(t)\,dt, \tag{21.47}$$

where δ_0 is the value of δ at $t = 0$. Remember also that q is the charge of a pair, namely, $q = 2q_e$. In Eqs. (21.45) and (21.47) we have an important result, the general theory of the Josephson junction.

Now what are the consequences? First, put on a DC voltage. If you put on a DC voltage, V_0, the argument of the sine becomes $(\delta_0 + (q/\hbar)V_0 t)$. Since $\hbar$ is a small number (compared to ordinary voltage and times), the sine oscillates rather rapidly and the net current is nothing. (In practice, since the temperature is not zero, you would get a small current due to the conduction by "normal" electrons.) On the other hand if you have *zero* voltage across the junction, you can get a current! With no voltage the current can be any amount between $+J_0$ and $-J_0$ (depending on the value of δ_0). But try to put a voltage across it and the current goes to zero. This strange behavior has recently been observed experimentally.[15]

There is another way of getting a current—by applying a voltage at a very high frequency in addition to a DC voltage. Let

$$V = V_0 + v\cos\omega t,$$

where $v \ll V$. Then $\delta(t)$ is

$$\delta_0 + \frac{q}{\hbar}\,V_0 t + \frac{q}{\hbar}\,\frac{v}{\omega}\sin\omega t.$$

Now for Δx small,

$$\sin(x + \Delta x) \approx \sin x + \Delta x\cos x.$$

Using this approximation for $\sin\delta$, I get

$$J = J_0\biggl[\sin\Bigl(\delta_0 + \frac{q}{\hbar}\,V_0 t\Bigr) + \frac{q}{\hbar}\,\frac{v}{\omega}\sin\omega t\cos\Bigl(\delta_0 + \frac{q}{\hbar}\,V_0 t\Bigr)\biggr].$$

The first term is zero on the average, but the second term is not if

$$\omega = \frac{q}{\hbar}\,V_0.$$

[15] P. W. Anderson and J. M. Rowell, *Phys. Rev. Letters* **10**, 230 (1963).

There should be a current if the AC voltage has just this frequency. Shapiro[16] claims to have observed such a resonance effect.

If you look up papers on the subject you will find that they often write the formula for the current as

$$J = J_0 \sin\left(\delta_0 + \frac{2q_e}{\hbar}\int \boldsymbol{A}\cdot d\boldsymbol{s}\right), \tag{21.48}$$

where the integral is to be taken across the junction. The reason for this is that when there's a vector potential across the junction the flip-flop amplitude is modified in phase in the way that we explained earlier. If you chase that extra phase through, it comes out as given above.

Finally, I would like to describe a very dramatic and interesting experiment which has recently been made on the interference of the currents from each of two junctions. In quantum mechanics we're used to the interference between amplitudes from two different slits. Now we're going to do the interference between two junctions caused by the difference in the phase of the arrival of the currents through two different paths. In Fig. 21-7, I show two different junctions, "a" and "b", connected in parallel. The ends, P and Q, are connected to our electrical instruments which measure any current flow. The external current,

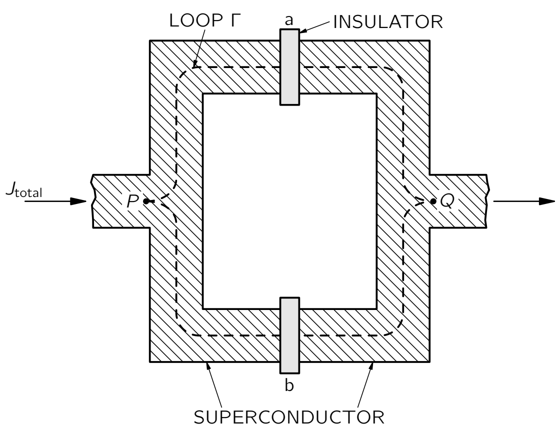

Fig. 21-7. Two Josephson junctions in parallel.

[16] S. Shapiro, *Phys. Rev. Letters* **11**, 80 (1963).

J_{total}, will be the sum of the currents through the two junctions. Let J_{a} and J_{b} be the currents through the two junctions, and let their phases be δ_{a} and δ_{b}. Now the phase difference of the wave functions between P and Q must be the same whether you go on one route or the other. Along the route through junction "a", the phase difference between P and Q is δ_{a} plus the line integral of the vector potential along the upper route:

$$\Delta\text{Phase}_{P\to Q} = \delta_{\text{a}} + \frac{2q_e}{\hbar}\int_{\text{upper}} \boldsymbol{A}\cdot d\boldsymbol{s}. \tag{21.49}$$

Why? Because the phase θ is related to $\boldsymbol{A}$ by Eq. (21.26). If you integrate that equation along some path, the left-hand side gives the phase change, which is then just proportional to the line integral of $\boldsymbol{A}$, as we have written here. The phase change along the lower route can be written similarly

$$\Delta\text{Phase}_{P\to Q} = \delta_{\text{b}} + \frac{2q_e}{\hbar}\int_{\text{lower}} \boldsymbol{A}\cdot d\boldsymbol{s}. \tag{21.50}$$

These two must be equal; and if I subtract them I get that the difference of the deltas must be the line integral of $\boldsymbol{A}$ around the circuit:

$$\delta_{\text{b}} - \delta_{\text{a}} = \frac{2q_e}{\hbar}\oint_{\Gamma} \boldsymbol{A}\cdot d\boldsymbol{s}.$$

Here the integral is around the closed loop Γ of Fig. 21-7 which circles through both junctions. The integral over $\boldsymbol{A}$ is the magnetic flux Φ through the loop. So the two δ's are going to differ by $2q_e/\hbar$ times the magnetic flux Φ which passes between the two branches of the circuit:

$$\delta_{\text{b}} - \delta_{\text{a}} = \frac{2q_e}{\hbar}\,\Phi. \tag{21.51}$$

I can control this phase difference by changing the magnetic field on the circuit, so I can adjust the differences in phases and see whether or not the total current that flows through the two junctions shows any interference of the two parts. The total current will be the sum of J_{a} and J_{b}. For convenience, I will write

$$\delta_{\text{a}} = \delta_0 + \frac{q_e}{\hbar}\,\Phi, \qquad \delta_{\text{b}} = \delta_0 - \frac{q_e}{\hbar}\,\Phi.$$

Then,

$$J_{\text{total}} = J_0\left\{\sin\left(\delta_0 + \frac{q_e}{\hbar}\,\Phi\right) + \sin\left(\delta_0 - \frac{q_e}{\hbar}\,\Phi\right)\right\}$$
$$= 2J_0\sin\delta_0\cos\frac{q_e\Phi}{\hbar}. \tag{21.52}$$

Now we don't know anything about δ_0, and nature can adjust that anyway she wants depending on the circumstances. In particular, it will depend on the external voltage we apply to the junction. No matter what we do, however, $\sin\delta_0$ can never get bigger than 1. So the *maximum* current for any given Φ is given by

$$J_{\text{max}} = 2J_0\left|\cos\frac{q_e}{\hbar}\,\Phi\right|.$$

This maximum current will vary with Φ and will itself have maxima whenever

$$\Phi = n\,\frac{\pi\hbar}{q_e},$$

with n some integer. That is to say that the current takes on its maximum values where the flux linkage has just those quantized values we found in Eq. (21.30)!

The Josephson current through a double junction was recently measured[17] as a function of the magnetic field in the area between the junctions. The results are shown in Fig. 21-8. There is a general background of current from various effects we have neglected, but the rapid oscillations of the current with changes in the magnetic field are due to the interference term $\cos q_e\Phi/\hbar$ of Eq. (21.52).

One of the intriguing questions about quantum mechanics is the question of whether the vector potential exists in a place where there's no field.[18] This experiment I have just described has also been done with a tiny solenoid between the two junctions so that the only significant magnetic $\boldsymbol{B}$ field is inside the solenoid and a negligible amount is on the superconducting wires themselves. Yet it is reported that the amount of current depends oscillatorily on the flux of magnetic field inside that solenoid even though that field never touches the wires—another demonstration of the "physical reality" of the vector potential.[19]

I don't know what will come next. But look what can be done. First, notice that the interference between two junctions can be used to make a sensitive

[17] Jaklevic, Lambe, Silver, and Mercereau, *Phys. Rev. Letters* **12**, 159 (1964).
[18] Jaklevic, Lambe, Silver, and Mercereau, *Phys. Rev. Letters* **12**, 274 (1964).
[19] See Volume II, Chapter 15, Section 15-5.

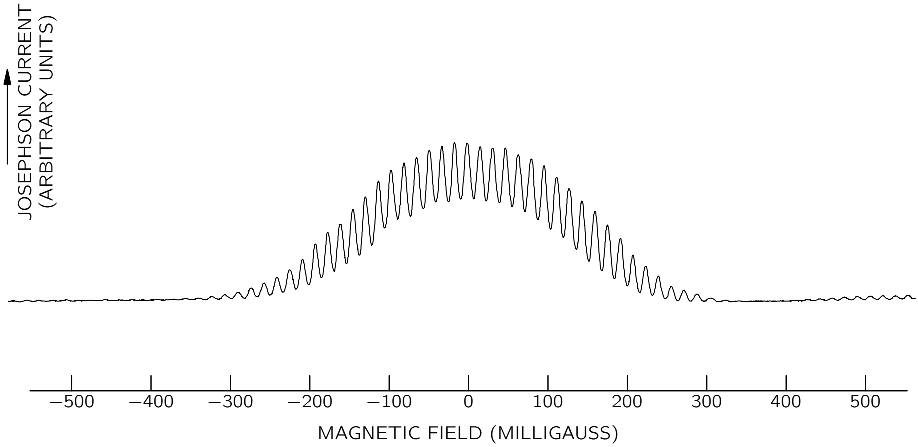

Fig. 21-8. A recording of the current through a pair of Josephson junctions as a function of the magnetic field in the region between the two junctions (see Fig. 21-7). [This recording was provided by R. C. Jaklevic, J. Lambe, A. H. Silver, and J. E. Mercereau of the Scientific Laboratory, Ford Motor Company.]

magnetometer. If a pair of junctions is made with an enclosed area of, say, 1 mm^2, the maxima in the curve of Fig. 21-8 would be separated by 2×10^{-6} gauss. It is certainly possible to tell when you are 1/10 of the way between two peaks; so it should be possible to use such a junction to measure magnetic fields as small as 2×10^{-7} gauss—or to measure larger fields to such a precision. One should be able to go even further. Suppose for example we put a set of 10 or 20 junctions close together and equally spaced. Then we can have the interference between 10 or 20 slits and as we change the magnetic field we will get very sharp maxima and minima. Instead of a 2-slit interference we can have a 20- or perhaps even a 100-slit interferometer for measuring the magnetic field. Perhaps we can predict that the measurement of magnetic fields will—by using the effects of quantum-mechanical interference—eventually become almost as precise as the measurement of wavelength of light.

These then are some illustrations of things that are happening in modern times—the transistor, the laser, and now these junctions, whose ultimate practical applications are still not known. The quantum mechanics which was discovered in 1926 has had nearly 40 years of development, and rather suddenly it has begun to be exploited in many practical and real ways. We are really getting control of nature on a very delicate and beautiful level.

I am sorry to say, gentlemen, that to participate in this adventure it is absolutely imperative that you learn quantum mechanics as soon as possible. It was our hope that in this course we would find a way to make comprehensible to you at the earliest possible moment the mysteries of this part of physics.