

C H A P T E R

5

The Macroscopic Quantum Model

5.1 INTRODUCTION

As demonstrated in Chapters 2, 3, and 4, a great deal of knowledge about superconductivity can be obtained from the classical model. For example, we not only were able to solve a number of practical engineering problems but also could discern how additional complications, like anisotropy, affected these results. Nevertheless, the model is simply posited to agree with fundamental observations: perfect dc conductivity, the Meissner effect, and the thermodynamic nature of the superconducting transition. In other words, the classical model does not show us how these phenomena are related to each other.

Fritz London had realized this in 1935 and by 1948 was able to show that the London equations could be *derived* from more fundamental ideas if the superelectron fluid were treated as a quantum mechanical entity. This development occurred because London realized that

Superconductivity is an inherently quantum mechanical phenomenon that manifests itself on macroscopic scales.

This is a profound statement. Although quantum mechanics has supplanted Newtonian mechanics as a more appropriate physical theory, we know that over length scales larger than atomic dimensions the classical laws are usually a valid approximation and often more tractable. Superconductivity, however, is like the coherent light emitted from a laser: there simply is no way to account for the phenomenon under classical physics alone. Indeed, it is *precisely because* superconductivity is a macroscopic quantum phenomenon that we observe the “unusual” properties so easily.

We have been able to avoid using quantum mechanics in our models thus far because we have carefully chosen which problems to analyze. This does not imply that only a few select engineering scenarios can be considered by

the London equations; rather we must be careful to include in our models the other properties of superconductors that have no plausible classical explanation. By only considering superconductors in a classical framework, we necessarily leave out aspects that can only be properly treated using quantum mechanics. Our goal, then, is to develop a model of superconductivity that not only reproduces the success of the London equations, but also is consistent with these macroscopic quantum nature of the phenomenon.

To formulate such a model it is, of course, necessary to have a working knowledge of quantum mechanics itself. Consequently, we shall devote a large amount of this chapter to examining those fundamental quantum mechanical issues that have a direct relevance to superconductivity. It should be noted that one of the early goals of quantum mechanics was to provide a theoretical basis for the Rutherford model of a stable atom, which consisted of a positively charged nucleus and negatively charged orbiting electrons. Classically, the orbiting electrons would be accelerating radially as a result of the centripetal forces and, as a result, emit electromagnetic radiation. Thus, under Newtonian mechanics, the electrons would lose energy and eventually spiral into the nucleus. Historically, the explanation as to why this physical model of the atom was stable was one of the first tests of quantum theory. A traditional discussion of quantum physics would be guided with this particular example in mind. Our quantum phenomena of interest are different, however, and we need not feel obligated to follow this usual path. Instead, we will develop some of the concepts of quantum mechanics with the implied objective of modeling supercurrents. This was not how things happened historically, but such an approach will keep us focused on superconductivity.

We therefore introduce the most basic notion of quantum physics, the wave-particle duality of nature, in Section 5.2 and proceed directly to a description of how a single quantum particle moves in Section 5.3. Once we have an understanding of how a single particle moves, we can generalize to how an ensemble moves. The net motion of this ensemble is the supercurrent and it is described in detail in Section 5.4. At this point, we can start to examine superconducting behavior that is manifestly quantum mechanical. Quantization of flux, the topic of Section 5.5, is a natural point to begin such a discussion.

5.2 SCHRÖDINGER'S EQUATION

In 1900 the frequency distribution of the electromagnetic energy radiated by a body at a given temperature was not well understood. In his investigations of this issue, Max Planck found it necessary to abandon the classical notion that an arbitrary amount of energy could be radiated by the body. Instead, Planck obtained the correct frequency distribution by assuming that the body and the electromagnetic field could only exchange energy in certain *discrete* amounts. This simple, though radical, assumption resulted in the first theory of thermal radiation consistent with all available experimental data. At the time, however,

Planck was uncomfortable with such a departure from classical physics and viewed his solution more as a mathematical trick.

Albert Einstein, aware of Planck's work, saw something far more fundamental. In 1905 Einstein postulated that all electromagnetic radiation could be viewed as a collection of *particles* known as photons. This is an extreme departure from the classical notion that radiation is described by an electromagnetic wave. A single photon of a known frequency would thus represent the smallest discrete amount of energy that could be radiated by the heated body. From Einstein's point of view, Planck had not merely proposed a mathematical trick, but in fact uncovered a fundamental characteristic of nature.

In 1924 Louis de Broglie realized that if what had been classically considered a wave could be described in terms of particles, then it is reasonable to expect that what had been classically considered a particle could be described as a wave. He thus proposed the notion of *matter waves* in his doctoral thesis. Although this is a concept totally outside normal experience, it is analogous to using ray optics when studying light. In spite of the fact that we know light is classically wavelike in nature, when working with lenses and mirrors whose dimensions are much greater than the optical wavelength, it is convenient and accurate to neglect the wavelike aspects of light altogether. In this way, we can view Newtonian classical mechanics as a ray optic analog to the more complete picture of de Broglie's matter waves.

Today, there is overwhelming experimental evidence for this *wave-particle duality* in nature. In fact, when quantum mechanics is written in a form that is consistent with Einstein's theory of relativity, the result is one of the most accurate physical theories ever formulated. That the theory predicts things that are occasionally intuitively uncomfortable is a result of our experience based on the *macroscopic* world, where the quantum effects are often small. In these instances, the familiar classical laws of physics, which are a limit of the quantum theory, hold. On the other hand, we sometimes come across phenomena, like superconductivity, where the effects of the wave-particle duality are apparent on the macroscopic scale.

Before we can discuss quantum phenomena quantitatively, however, we must first find the laws that describe the dynamical evolution of a quantum system over space and time. Fortunately in our applications of quantum theory relativistic effects are negligible. We therefore seek the quantum mechanical equivalent of Newton's law. We begin by examining the *Einstein-de Broglie relations*:

$$\mathcal{E} = \hbar\omega \quad (5.1)$$

and

$$\mathbf{p} = \hbar\mathbf{k}. \quad (5.2)$$

Equation 5.1, which was alluded to in Section 3.4, relates the total energy of a quantum particle, $\mathcal{E}$, to the frequency of oscillation, ω . Equation 5.2 relates the

momentum of the quantum particle, p , to the wavevector, k . Notice that this is a vector equation and the magnitude of k is related to the matter wavelength in the usual way:

$$|k| = \frac{2\pi}{\lambda}. \quad (5.3)$$

The constant of proportionality in both these equations is related to *Planck's constant*, h , by

$$\hbar \equiv \frac{h}{2\pi}. \quad (5.4)$$

where $h = 6.6262 \times 10^{-34}$ J-sec. It is because Planck's constant is so small that we tend not to notice quantum effects in the macroscopic world.

The Einstein-de Broglie relations describe *both* the wavelike and the particlelike behavior of quantum systems. In fact, it becomes rather meaningless to make a classical distinction between the two types of behavior. When examining a quantum system, neither type of behavior provides, by itself, a sufficiently accurate description under all circumstances. It is only to help our intuition that we say that a particular experiment is best described by wavelike or particlelike behavior.

To illustrate how the wave-particle duality picture is useful in discerning the physics of a system, consider the electron microscope. This is a device that provides high-resolution pictures at high magnification by exposing the sample to a beam of electrons. To understand the microscope's operating principles, we could concentrate on the particlelike behavior of the electrons. In this case we would discuss how each electron is scattered by its interactions with the sample and how the net result of the large number of electrons scattering in some probabilistic fashion will ultimately produce an image. It is easier, however, to picture the set of electrons as a series of waves and thus invoke our intuition about the operating principle of optical microscopes. An electron microscope can get better resolution at high magnification than an ordinary optical microscope because the wavelength associated with a beam of electrons can be made much smaller than that of visible light. Typically the beam of electrons has been accelerated to a kinetic energy of 10 keV. (Recall that 1 eV is equivalent to 1.6×10^{-19} J.) From Equation 5.2 we see that the wavelength associated with this beam is approximately 0.12 Å, which is far smaller than any wavelength in the visible light regime (~ 4000 – 7000 Å). As a result, an electron microscope is able to provide better resolution of smaller objects than an optical microscope. In this example, then, we see that concentrating on the wavelike nature of the particles provides a more intuitive way of sorting out the relevant physics of the system.

With these ideas in mind, let us find an equation of motion for the simplest quantum system: a free quantum particle; that is, a particle not subjected to any external force. We wish this equation to describe the system's evolution in space

and time $(\mathbf{r}, t)$, but we see from the Einstein-de Broglie relations that it is more natural to describe the evolution in wavevector space and frequency $(\mathbf{k}, \omega)$. As a result, our procedure is as follows. We will first formulate the classical problem in terms of physical quantities that are also natural in quantum mechanics. We see from Equations 5.1 and 5.2 that these natural quantities are $\mathcal{E}$ and $\mathbf{p}$. We then transform the classical expression into a quantum mechanical one using the Einstein-de Broglie relations. Notice that purely quantum mechanical effects will never show up in a classical equation of motion. Thus we have no guarantee that our procedure will yield a correct quantum mechanical equation of motion; we can only determine the validity of the resulting expression through experiment.

We begin by concentrating on the energy of the free particle, $\mathcal{E}$. From classical mechanics, we know that $\mathcal{E}$ of a free particle is just its kinetic energy

$$\mathcal{E} = \frac{1}{2} m (\mathbf{v} \cdot \mathbf{v}), \quad (5.5)$$

where $\mathbf{v}$ is the velocity of the particle and m is its mass. Unfortunately, this relation, as written, is not useful to us because the Einstein-de Broglie relations do not focus on the velocity of a particle. In other words, we must rewrite the right side of Equation 5.5 in terms of $\mathbf{p}$.

Recall that in classical mechanics the motion of a particle is completely specified when we know its initial position and velocity, or alternatively, its initial position and momentum. In other words, classically we can choose our independent variables to be $(\mathbf{r}, \mathbf{v})$ or $(\mathbf{r}, \mathbf{p})$. Indeed, by comparing the classical equation of motion written in terms $(\mathbf{r}, \mathbf{v})$ to that written in terms of $(\mathbf{r}, \mathbf{p})$, we can find the relationship between $\mathbf{p}$ and $\mathbf{v}$. Specifically, since no forces are exerted on the free particle by definition, conservation of momentum requires

$$\frac{d\mathbf{p}}{dt} = 0. \quad (5.6)$$

Alternatively, we could describe the motion of the particle using Newton's law:

$$m \frac{d\mathbf{v}}{dt} = 0. \quad (5.7)$$

By comparing these two expressions, we find

$$\mathbf{p} = m\mathbf{v} \quad (5.8)$$

as our desired expression relating the momentum $\mathbf{p}$ with the *kinematic (or mechanical) momentum* $m\mathbf{v}$.

Rewriting the energy of the free particle in terms of the energy and momentum yields

$$\mathcal{E} = \frac{\mathbf{p} \cdot \mathbf{p}}{2m}. \quad (5.9)$$

Assuming that this classical expression is also valid under quantum mechanics, it transforms under the Einstein-de Broglie relations to be

$$\hbar\omega = \frac{\hbar^2}{2m} (\mathbf{k} \cdot \mathbf{k}) . \quad (5.10)$$

Equation 5.10 relates ω to $\mathbf{k}$ and so this must be the dispersion relation for the matter waves. To obtain the governing relation describing the motion of the quantum particle in terms of space and time, we merely need to work backward from the dispersion relation. Let us *assume* that our quantum particle, which we think of as localized in space, is a superposition of a whole spectrum of matter waves of various amplitudes. Just as in electromagnetism, we can therefore discern the behavior of the system by studying individual plane waves.

Suppose the uniform plane wave

$$\psi = \hat{\psi} e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} \quad (5.11)$$

satisfies the dispersion relation. (Notice that in writing this expression, we have changed notation and now define i to be $\sqrt{-1}$. Unfortunately, harmonic analysis in physics is done under this convention rather than using j , as is done in engineering. At this point, since we are in the domain of physics, it is necessary to make this switch in notation so that the resulting equations will match those found in physics journals and books. The connection between the two conventions is fortunately simple: to go back to the engineering notation, simply replace i with $-j$.) As discussed in Section 4.2, when analyzing dispersion relations of plane waves, the algebraic quantities involving $\mathbf{k}$ and ω translate into terms proportional to space and time derivatives, respectively. In other words, the dispersion relation for the free quantum particle results from the differential equation

$$i\hbar \frac{\partial}{\partial t} \psi = -\frac{\hbar^2}{2m} \nabla^2 \psi, \quad (5.12)$$

as can be verified by direct substitution. This expression, then, is our desired relation describing the evolution of the free quantum particle in space and time.

Equation 5.12 was first proposed by Erwin Schrödinger in 1926, and is thus called Schrödinger's equation. As previously mentioned, we have no a priori reason to guarantee it is the correct governing equation. There is, however, extensive experimental evidence that this is indeed the correct expression for this system. *It should be noted that we have not in any way derived Schrödinger's equation.* This should not be surprising since it is never possible to "derive" a law of nature; after all, Newton did not mathematically derive the classical equations of motion. What we have done, however, is to make a plausibility argument to show the connection between quantum and Newtonian mechanics.

Let us now use a similar argument to develop Schrödinger's equation for a quantum particle under the influence of a potential field that is a function of

position only, $V(\mathbf{r})$. Classically, the energy of the particle is described by the sum of the particle's kinetic and potential energies:

$$\mathcal{E} = \frac{1}{2} m (\mathbf{v} \cdot \mathbf{v}) + V(\mathbf{r}). \quad (5.13)$$

As before, we need to first reexpress this classical equation in terms of the momentum rather than the velocity. We therefore must find a relation between $\mathbf{v}$ and $\mathbf{p}$, similar to Equation 5.6 in the previous example.

Since the potential field is not a function of time, the total energy of the particle is conserved:

$$\frac{d\mathcal{E}}{dt} = 0, \quad (5.14)$$

or specifically,

$$\frac{d}{dt} \left(\frac{1}{2} m (\mathbf{v} \cdot \mathbf{v}) + V(\mathbf{r}) \right) = m\mathbf{v} \cdot \frac{d\mathbf{v}}{dt} + \frac{d}{dt} V(\mathbf{r}) = 0. \quad (5.15)$$

Recall from the chain rule of differentiation that

$$\frac{d}{dt} V(\mathbf{r}) = \frac{\partial}{\partial t} V(\mathbf{r}) + (\mathbf{v} \cdot \nabla) V(\mathbf{r}), \quad (5.16)$$

so Equation 5.15 can be expressed as

$$\mathbf{v} \cdot \left(m \frac{d\mathbf{v}}{dt} + \nabla V \right) = 0, \quad (5.17)$$

since the potential field is independent of time. Since this expression holds for any value of $\mathbf{v}$, we see that

$$m \frac{d\mathbf{v}}{dt} = -\nabla V, \quad (5.18)$$

which is simply Newton's law of motion. The right side of this expression is therefore the force that V exerts on the particle. Since we know from classical mechanics that a force is proportional to a time rate of change of momentum, we see that the left side of Equation 5.18 can be written

$$\frac{d\mathbf{p}}{dt} = -\nabla V. \quad (5.19)$$

Notice that this expression is particularly interesting since it expresses Newton's law only in terms of quantities that are used in writing the energy of the system. Indeed, when the equation of motion can be written in this form, *the term in the time derivative is the canonical momentum, by definition*. In this

case, the canonical momentum is identically equal to the kinematic momentum: $\mathbf{p} = m\mathbf{v}$. In addition, the term in the spatial derivative is the *generalized potential* of the particle, which in this case is simply the applied potential, V .

Having identified the canonical momentum and generalized potential, we find that for this particular example, the energy of the system is

$$\mathcal{E} = \frac{1}{2m} (\mathbf{p} \cdot \mathbf{p}) + V(\mathbf{r}), \quad (5.20)$$

by direct substitution. As before, we assume that this classical expression is valid under quantum mechanics. From the Einstein-de Broglie relations, it therefore becomes

$$\hbar\omega = \frac{\hbar^2}{2m} (\mathbf{k} \cdot \mathbf{k}) + V(\mathbf{r}). \quad (5.21)$$

Unfortunately, we *cannot* treat this expression as a dispersion relation. The reason is that a true dispersion relation is a function of $\mathbf{k}$ and ω *only* and we see that our expression is dependent on $\mathbf{r}$ as a result of the applied potential.

From our previous example, however, we know that Schrödinger's equation for a free particle describes the motion of plane waves in $\mathbf{r}$ - t space. There is no reason to believe that things should be any different when there is an external potential in the problem. As a result, we again assume that Schrödinger's equation is linear and so it is possible to build arbitrary functions by adding together uniform plane waves. We therefore concentrate on how Equation 5.21 describes the space-time evolution of the plane wave given in Equation 5.11. If $\mathbf{k}$ and ω are once again replaced with terms proportional to space and time derivatives, we find that Schrödinger's equation for this case is

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \psi + V(\mathbf{r})\psi. \quad (5.22)$$

As before, this result may be verified by direct substitution.

Let us summarize the steps for formulating the Schrödinger equation from a classical expression:

1. Write the classical equation of motion in terms of the canonical momentum, $\mathbf{p}$, and generalized potential, V :

$$\frac{d\mathbf{p}}{dt} = -\nabla V. \quad (5.23)$$

Indeed, this form identifies the precise expressions for $\mathbf{p}$ and V .

2. Use these quantities to write the energy of the system:

$$\mathcal{E} = \frac{\mathbf{p} \cdot \mathbf{p}}{2m} + V. \quad (5.24)$$

3. Transform the classical expression into a quantum mechanical one by appealing to the Einstein-de Broglie relations. Since Schrödinger's equation is linear, these transformations are

$$\mathcal{E} = h\omega \implies i\hbar \frac{\partial}{\partial t} \quad (5.25)$$

and

$$\mathbf{p} = \hbar \mathbf{k} \implies -i\hbar \nabla. \quad (5.26)$$

These rules are consistent with our two specific examples. More importantly, they can be rigorously derived from a more advanced formulation of classical mechanics. Consequently, we can apply these rules to more general situations.

For example, we need not restrict the applied potential to be conservative (that is, a function independent of time). In fact, Equation 5.22 may be generalized to

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \psi + V(\mathbf{r}, t) \psi. \quad (5.27)$$

This expression is the correct (experimentally verified) general form of Schrödinger's equation. Although we have written a general equation capable of describing the space and time evolution of a system exhibiting wave-particle duality, we are left with the question of the physical interpretation of the function $\psi(\mathbf{r}, t)$. This is the topic of Section 5.3.

5.3 PROBABILITY CURRENTS

In Section 5.2 we saw how Schrödinger's equation governs the evolution of the *wavefunction* ψ in space and time. This wavefunction is somehow descriptive of the quantum system but the connection is not obvious. Indeed, at first glance we might think of the wavefunction as a quantum field, similar to those fields encountered in electromagnetism. This is not the case however. A close look at Schrödinger's equation reveals that ψ cannot be a real scalar function as a result of the factor of i in the expression. This factor represents a phase shift and means that if ψ is a scalar function, it must have *both* real *and* imaginary parts. For a plane wave, this implies

$$\psi = \hat{\psi} e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)}. \quad (5.28)$$

In contrast, electromagnetic fields may be represented as *either* the real *or* imaginary parts of a complex expression. For example, the magnetic field of an electromagnetic wave can be written

$$\mathbf{H} = \text{Re} \left\{ \hat{\mathbf{H}} e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} \right\}. \quad (5.29)$$

Thus, we find that the quantum wavefunction is necessarily a complex quantity. Although this poses no problems with the mathematics of our development, recall that $\hat{\psi}$ was simply thought of as the amplitude of a plane wave. We now see from Schrödinger's equation that the absolute phase of this quantity *cannot* be arbitrary. This is very peculiar; normally when we study plane waves we do not discuss the absolute phase since it does not influence the physics of the problem. Schrödinger's equation, however, seems to suggest that the phase is not arbitrary but rather a *measurable quantity* of physical significance!

To preserve the intuitive notion that the absolute phase of a plane wave should *not* influence the overall physics of a system, Max Born hypothesized in 1927 that the square of the magnitude of the wave function ψ was equal to the *probability* of a quantum mechanical particle to be at the location $\mathbf{r}$ at time t . Stated mathematically we have

$$\wp(\mathbf{r}, t) \equiv |\psi(\mathbf{r}, t)|^2 = \psi^*(\mathbf{r}, t)\psi(\mathbf{r}, t), \quad (5.30)$$

where $\wp$ is the function describing the probability of the location of the particle in space at a certain time. We thus see that the absolute phase of the wavefunction no longer has any experimental significance. In addition, we find that quantum mechanics allows us to predict only the probability of the outcome of an experiment. This is a fundamental difference between quantum mechanics and Newtonian mechanics, which is a deterministic theory. Furthermore, since the particle must exist *somewhere* in space, we know from Equation 5.30 that ψ must also satisfy the *normalization condition*:

$$\int dV \psi^*(\mathbf{r}, t)\psi(\mathbf{r}, t) = 1 \quad (5.31)$$

at all times.

As a result of Born's interpretation of the wavefunction, it is useful to directly determine how $\wp$ evolves in space and time. Let us therefore derive the governing equation for $\wp$ from Schrödinger's equation. We begin by multiplying Equation 5.27 with the complex conjugate of ψ

$$i\hbar\psi^* \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \psi^* \nabla^2 \psi + V\psi^* \psi. \quad (5.32)$$

From this expression, we subtract the complex conjugate of Schrödinger's equation multiplied by ψ :

$$-i\hbar\psi\frac{\partial\psi^*}{\partial t} = -\frac{\hbar^2}{2m}\psi\nabla^2\psi^* + V\psi\psi^* \quad (5.33)$$

to obtain the expression

$$i\hbar\frac{\partial}{\partial t}(\psi\psi^*) = -\frac{\hbar^2}{2m}(\psi^*\nabla^2\psi - \psi\nabla^2\psi^*) . \quad (5.34)$$

Notice that V must be a real quantity since it is the potential associated with the externally applied force. Because any scalar function γ and vector field $\mathbf{C}$ obey the vector identity

$$\nabla \cdot (\gamma\mathbf{C}) = \gamma\nabla \cdot \mathbf{C} + \mathbf{C} \cdot \nabla\gamma \quad (5.35)$$

and $\nabla^2 \equiv \nabla \cdot \nabla$, we can rewrite Equation 5.34 as

$$i\hbar\frac{\partial}{\partial t}(\psi\psi^*) = -\frac{\hbar^2}{2m}(\nabla \cdot (\psi^*\nabla\psi - \psi\nabla\psi^*)) . \quad (5.36)$$

Recognizing the left side of this expression as the time evolution of the probability $\wp(\mathbf{r}, t)$, we find

$$\frac{\partial\wp}{\partial t} = -\nabla \cdot \mathbf{J}_\wp, \quad (5.37)$$

where the *probability current* is defined as

$$\mathbf{J}_\wp \equiv \frac{\hbar}{2im}(\psi^*\nabla\psi - \psi\nabla\psi^*) = \text{Re} \left\{ \psi^* \frac{\hbar}{im} \nabla\psi \right\} . \quad (5.38)$$

Equation 5.37 is our desired relation describing the evolution of the probability of a quantum particle being found at a certain point in space at a certain time. In fact, whereas the normalization condition, Equation 5.31, gave us a *global* constraint on $\wp$, Equation 5.37 gives us a *local* constraint. In other words, the probability of the quantum particle at a certain point cannot change instantaneously, rather it must “flow” in a continuous fashion between two locations. Consequently, it is convenient to define the probability current to help our intuition and make Equation 5.37 look like a “conservation of probability” statement.

Although this relation does bear a great deal of resemblance to the familiar conservation of charge equation from electromagnetic field theory (compare with Equation 2.33), we must remember that *the similarity is mathematical*

only. Whereas the electrical current is a real, physical, measurable quantity, the probability current is a theoretical construct. It is not possible to experimentally measure $\mathbf{J}_p$ for a single particle directly.

Equation 5.38 describes the probabilistic flow of a quantum particle that is subjected to forces that vary in space and time only. It does not, however, describe the situation of central interest for us: that of a *charged* quantum particle in an electromagnetic field. This is because, by its very nature, an electromagnetic field subjects the charged particle to forces that are dependent on the particle's motion. As a result, our previous analysis is not complete. To find $\mathbf{J}_p$ for this scenario, it is necessary to first find the appropriate form of Schrödinger's equation.

In Section 5.2, we saw that if we could express the governing classical equation of motion in the general form

$$\frac{d}{dt}(\text{canonical momentum}) = -\nabla(\text{externally applied potential}), \quad (5.39)$$

we could immediately identify the canonical momentum $\mathbf{p}$ and external potential V , which are used in writing the total energy of the system. This formalism is particularly useful in the present case since the electromagnetic field represents a nonconservative potential making it difficult to formulate energy relationships intuitively. We therefore begin by recognizing that the classical equation of motion for a particle of charge q in an electromagnetic field is Lorentz's law:

$$m \frac{d\mathbf{v}}{dt} = q(\mathbf{E} + (\mathbf{v} \times \mathbf{B})). \quad (5.40)$$

Our first goal in obtaining Schrödinger's equation for this problem is to rewrite Equation 5.40 into the form suggested by Equation 5.39.

To accomplish this task, we express the field quantities $\mathbf{E}$ and $\mathbf{H}$ in terms of potentials. Recall from Gauss's magnetic law that the flux density $\mathbf{B}$ can always be written as

$$\mathbf{B} = \nabla \times \mathbf{A}, \quad (5.41)$$

which follows directly from the vector identity

$$\nabla \cdot (\nabla \times \mathbf{C}) = 0. \quad (5.42)$$

In Equation 5.41 $\mathbf{A}$ is a *vector potential* and can be used to write Faraday's law as

$$\nabla \times \left(\mathbf{E} + \frac{\partial \mathbf{A}}{\partial t} \right) = 0. \quad (5.43)$$

Since the curl of the gradient of any single-valued scalar field is zero, Equation 5.43 is equivalent to the statement

$$\mathbf{E} = -\frac{\partial \mathbf{A}}{\partial t} - \nabla \phi, \quad (5.44)$$

where ϕ is a *scalar potential*.

Lorentz's law in terms of these potentials is therefore

$$m \frac{d\mathbf{v}}{dt} = -q \left(\nabla \phi + \frac{\partial \mathbf{A}}{\partial t} - \mathbf{v} \times (\nabla \times \mathbf{A}) \right). \quad (5.45)$$

We now wish to make the form of Equation 5.45 identical to that given in Equation 5.39. Consequently, we need to group all the time derivatives together. From the chain rule of differentiation

$$\frac{d\mathbf{A}}{dt} = \frac{\partial \mathbf{A}}{\partial t} + (\mathbf{v} \cdot \nabla) \mathbf{A}, \quad (5.46)$$

Equation 5.45 becomes

$$\frac{d}{dt} (m\mathbf{v} + q\mathbf{A}) = -q [\nabla \phi - (\mathbf{v} \cdot \nabla) \mathbf{A} - \mathbf{v} \times (\nabla \times \mathbf{A})]. \quad (5.47)$$

From this grouping, Equation 5.47 is close to our desired form and we strongly suspect that the canonical momentum is given by

$$\mathbf{p} = m\mathbf{v} + q\mathbf{A}. \quad (5.48)$$

To verify this is true, however, we must be able to express the right-hand side of Equation 5.47 as the gradient of a scalar function. We thus rewrite it in terms of the canonical momentum:

$$\begin{aligned} \frac{d\mathbf{p}}{dt} &= -q\nabla \phi + \frac{q}{m} (\mathbf{p} \cdot \nabla) \mathbf{A} - \frac{q^2}{m} (\mathbf{A} \cdot \nabla) \mathbf{A} \\ &\quad + \frac{q}{m} \mathbf{p} \times (\nabla \times \mathbf{A}) - \frac{q^2}{m} \mathbf{A} \times (\nabla \times \mathbf{A}). \end{aligned} \quad (5.49)$$

Using the vector identities

$$\mathbf{C} \times (\nabla \times \mathbf{D}) = \nabla(\mathbf{C} \cdot \mathbf{D}) - (\mathbf{C} \cdot \nabla) \mathbf{D} - (\mathbf{D} \cdot \nabla) \mathbf{C} - \mathbf{D} \times (\nabla \times \mathbf{C}) \quad (5.50)$$

and

$$\mathbf{C} \times (\nabla \times \mathbf{C}) = \frac{1}{2} \nabla(\mathbf{C} \cdot \mathbf{C}) - (\mathbf{C} \cdot \nabla) \mathbf{C}, \quad (5.51)$$

we can rewrite Equation 5.49 as

$$\begin{aligned} \frac{d\mathbf{p}}{dt} = & -q\nabla\phi + \frac{q}{m}\nabla(\mathbf{p} \cdot \mathbf{A}) - \frac{q^2}{2m}\nabla(\mathbf{A} \cdot \mathbf{A}) \\ & - \frac{q}{m}(\mathbf{A} \cdot \nabla)\mathbf{p} - \frac{q}{m}\mathbf{A} \times (\nabla \times \mathbf{p}). \end{aligned} \quad (5.52)$$

At this point, recall that we are using the set of independently specified variables $(\mathbf{r}, \mathbf{p})$ to describe the problem. As a result, the spatial derivative of the canonical momentum is identically zero and thus, Equation 5.52 is equivalent to

$$\frac{d\mathbf{p}}{dt} = -\nabla \left(q\phi - \frac{q}{m}\mathbf{p} \cdot \mathbf{A} + \frac{q^2}{2m}\mathbf{A} \cdot \mathbf{A} \right). \quad (5.53)$$

This expression achieves our goal of writing Lorentz's law in the generic form of Equation 5.39.

Let us develop a physical understanding of Equation 5.53. Evidently, the canonical momentum, given by Equation 5.48, is composed of two parts. The first part, $m\mathbf{v}$, is the kinematic momentum and, as we have seen, it is usually associated with the momentum in elementary mechanics. The second part, $q\mathbf{A}$, is called the *field momentum*. This quantity is a direct result of the charge of the particle; any change in the velocity of the particle produces an electromagnetic field that must also be self-consistently considered. In a similar manner, the generalized potential of the problem,

$$V = q\phi - \frac{q}{m}\mathbf{p} \cdot \mathbf{A} + \frac{q^2}{2m}\mathbf{A} \cdot \mathbf{A}, \quad (5.54)$$

is a function not only of space and time but also of the canonical momentum as well. Consequently, the interaction of the externally applied field and the induced current created by the motion of the charged particle is accounted for in a self-consistent fashion. It is emphasized that these results are completely classical in origin, they are not a result of any quantum mechanical effects.

As discussed in Section 5.2, the next step in obtaining Schrödinger's equation is to use the expressions for $\mathbf{p}$ and V to write down the total energy of the system, $\mathcal{E}$. The result is

$$\mathcal{E} = \frac{\mathbf{p} \cdot \mathbf{p}}{2m} + \left(q\phi - \frac{q}{m}\mathbf{p} \cdot \mathbf{A} + \frac{q^2}{2m}\mathbf{A} \cdot \mathbf{A} \right), \quad (5.55)$$

which can be rewritten more compactly as

$$\mathcal{E} = \frac{1}{2m}(\mathbf{p} - q\mathbf{A}) \cdot (\mathbf{p} - q\mathbf{A}) + q\phi. \quad (5.56)$$

Again, this expression is completely classical in origin.

The last step is to translate this classical expression into a quantum mechanical one by using the transformations

$$\mathcal{E} \implies i\hbar \frac{\partial}{\partial t} \quad (5.57)$$

and

$$\mathbf{p} \implies -i\hbar \nabla. \quad (5.58)$$

Thus, we expect the quantum form of Lorentz's law, as expressed by Equation 5.56, to be

$$i\hbar \frac{\partial \psi}{\partial t} = \frac{1}{2m} \left(\frac{\hbar}{i} \nabla - q\mathbf{A} \right)^2 \psi + q\phi\psi, \quad (5.59)$$

and indeed this is the case. Proceeding now as in the beginning of this section, we use Equation 5.59 to find the probability current of a charged quantum particle in an electromagnetic field:

$$\mathbf{J}_\psi = \text{Re} \left\{ \psi^* \left(\frac{\hbar}{im} \nabla - \frac{q}{m} \mathbf{A} \right) \psi \right\}. \quad (5.60)$$

In obtaining this expression, it is important to realize that because ϕ represents a portion of the applied potential field, it is necessarily a real quantity. Equation 5.60 is the relation we sought and in Section 5.4 we see how this expression plays a central role in our quantum mechanical description of superconductivity.

5.4 MACROSCOPIC QUANTUM CURRENTS

As previously mentioned, one of the reasons for the development of quantum mechanics was to explain the stability of the Rutherford model for the atom, consisting of a positively charged nucleus and negatively charged orbiting electrons. Historically, this model was postulated based on Rutherford's *experimental evidence* of the size of an atom. Hence it was a case of developing a physical theory needed to explain an already observed phenomenon. Classically, there was no self-consistent explanation for how the electrons could orbit the nucleus without decaying and having the atom collapse; quantum mechanics provided the necessary framework.

In some sense, the situation for superconductors is similar. In Section 2.5, we saw that our entire notion of superconductivity is built on the hypothesis that the superelectrons do not scatter. This is an assumption that is formulated to "explain" the already observed phenomena of zero dc resistance and the Meissner effect. Although the results of this assumption are consistent with the

experimental evidence, it seems as arbitrary to postulate an infinite scattering time for superelectrons as it does to postulate that the orbiting electrons in an atom can be only in certain discrete radii from the nucleus (as Niels Bohr did in 1913). Schrödinger's equation provided a less arbitrary, and hence better, description of the stable microscopic currents created by the orbiting electrons and thus Fritz London hypothesized that the macroscopic currents in the superconductor might be similarly examined. This is the essence of the *macroscopic quantum model* (MQM) for superconductivity.

Before beginning our study of this model, we should note that the MQM formulation *will not* explain the microscopic origins of superconductivity any better than the classical model. It is therefore natural to ask what are the advantages of the MQM. As we will see, the MQM not only encompasses the classical constitutive relations but also extends them consistently into quantum mechanics. Consequently, the MQM can be used effectively in many problems of engineering interest. In addition, the MQM as postulated from quantum mechanics is related to the Ginzburg-Landau model, discussed in Chapter 10, which is developed along thermodynamic lines of reasoning. This is significant; recall that with the classical model we treated the electromagnetic and thermodynamic properties of the superconductor separately. In contrast, the MQM *necessarily* unites these properties; it is therefore a better model. Finally, because the Ginzburg-Landau (and hence the MQM) model has been shown to be a limiting result of the general microscopic (BCS) model of conventional superconductivity, we are on a better theoretical foundation when discussing the MQM as contrasted to the classical model. As it happens, we obtain all these advantages with only a minimal extra effort in conceptualization.

The central hypothesis behind the MQM can be stated as follows:

There exists a macroscopic quantum wavefunction, $\Psi(\mathbf{r}, t)$, that describes the behavior of the entire ensemble of superelectrons in the superconductor.

The motivation for such an assumption is that it places primary importance on the notion that superconductivity is a *coherent phenomenon* between all the superelectrons. By postulating the existence of $\Psi(\mathbf{r}, t)$ to describe all the superelectrons, we necessarily do not focus on the motions of a single carrier of the supercurrent. This situation is analogous to that found in the quantum description of electromagnetism. Because of wave-particle duality, we envision a photon as a quantum particle of light. Nevertheless, when a large number of these photons act in a coherent fashion (as in a laser), we know that the entire collection of these quantum particles is adequately described in terms of an electromagnetic field. As we shall see, the macroscopic wavefunction is a fieldlike quantity that similarly describes a large collection of coherent superelectrons.

Let us examine the consequences of postulating such a macroscopic wavefunction. We will initially confine our investigation to isotropic materials in order to simplify our calculations. After this special case is understood, the

consequences of the general anisotropic MQM, which is appropriate to use when studying the behavior of anisotropic materials, will be more apparent.

The most straightforward way of proceeding is to compare Ψ with ψ , the wavefunction of the previous two sections that described a *single* quantum particle. Just as ψ is sufficient to describe the microscopic current associated with an electron moving about an atomic nucleus, so too Ψ is sufficient to describe the macroscopic supercurrent $\mathbf{J}_s$ associated with the movement of the entire ensemble of superelectrons.

We saw in Section 5.2 that the square of the magnitude of $\psi(\mathbf{r}, t)$ is interpreted as the probability that the single quantum particle would be located at $\mathbf{r}$ at time t . As a result, the global constraint on the probability (or normalization condition)

$$\int d\nu \psi^*(\mathbf{r}, t) \psi(\mathbf{r}, t) = 1 \quad (5.61)$$

immediately followed. Physically, Equation 5.61 states that a *single* quantum particle existed somewhere in space.

Following this line of reasoning, it is natural to assume that if $\Psi(\mathbf{r}, t)$ is a wavefunction describing the entire ensemble of superelectrons, it satisfies the relation

$$\int d\nu \Psi^*(\mathbf{r}, t) \Psi(\mathbf{r}, t) = N^*. \quad (5.62)$$

Here N^* is the *total number* of superelectrons the macroscopic wavefunction describes. In other words, if all of space is searched, we are guaranteed of finding all the superelectrons. It is tempting to thus interpret the integrand of Equation 5.62 as the *local density* of superelectrons,

$$\Psi^*(\mathbf{r}, t) \Psi(\mathbf{r}, t) = n^*(\mathbf{r}, t). \quad (5.63)$$

Since we envision the superelectrons as discrete entities, there must be a sufficiently large number of them for our interpretation of the local density to make sense. However, the very idea of a macroscopic wavefunction assumes a great number of carriers of supercurrent from the start so that Equation 5.63 is self-consistent with the MQM.

This concern that enough superelectrons exist to allow the concept of a local density to be meaningful is identical to that found in fluid mechanics. Although we know that all fluids are made of discrete atoms or molecules, it is convenient to describe a local aggregation of the discrete entities with a continuous function; namely, the local fluid density. It is therefore not surprising that the total collection of superelectrons are often referred to as a quantum mechanical “charged superfluid.”

The analogy to fluid mechanics is powerful in developing an intuition about the MQM. Instead of a wavefunction describing events in terms of probabilities for a single particle, we are now considering so many quantum particles that

we have a wavefunction describing the *actual location* of some subset of this ensemble. As a result, the local constraint on Ψ analogous to Equation 5.37 is not a “flow of probability” but rather a “flow of particles”—*which is nothing more than a physical current*. Following Equation 5.60, we therefore immediately write the macroscopic quantum current density (or the supercurrent density as we have previously called it) consistent with the MQM for a superconductor in an electromagnetic field:

$$\mathbf{J}_s = q^* \text{Re} \left\{ \Psi^* \left(\frac{\hbar}{im^*} \nabla - \frac{q^*}{m^*} \mathbf{A} \right) \Psi \right\}. \quad (5.64)$$

Notice it is necessary to multiply the ensemble probability current, which describes a particle flux, by the charge of a superelectron to obtain an electrical current density.

Equation 5.64 can be expressed in a more useful form. By virtue of our assumptions for $\Psi(\mathbf{r}, t)$, it is consistent that the macroscopic wavefunction obeys a Schrödingerlike equation for the ensemble in an electromagnetic field:

$$i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}, t) = \frac{1}{2m^*} \left(\frac{\hbar}{i} \nabla - q^* \mathbf{A}(\mathbf{r}, t) \right)^2 \Psi(\mathbf{r}, t) + q^* \phi(\mathbf{r}, t) \Psi(\mathbf{r}, t). \quad (5.65)$$

Intuitively, we can envision the form of this equation as equivalent to the sum of the individual energies associated with each particle in a field, Equation 5.59. Because of the phase factor i in Equation 5.65, the macroscopic wavefunction, like the microscopic one, is a complex quantity. Therefore $\Psi(\mathbf{r}, t)$ is of the form

$$\Psi(\mathbf{r}, t) = \sqrt{n^*(\mathbf{r}, t)} e^{i\theta(\mathbf{r}, t)}, \quad (5.66)$$

where θ is a real function representing the phase of the complex number. By writing the macroscopic wavefunction in this manner, we have guaranteed that the square of its magnitude will yield the local density of superelectrons. Substituting this expression into our relation describing the supercurrent, Equation 5.64, yields the *supercurrent equation*

$$\mathbf{J}_s = q^* n^*(\mathbf{r}, t) \left(\frac{\hbar}{m^*} \nabla \theta(\mathbf{r}, t) - \frac{q^*}{m^*} \mathbf{A}(\mathbf{r}, t) \right). \quad (5.67)$$

Written in this form, the local velocity associated with the supercurrent, $\mathbf{v}_s$, is identified as the quantity in parentheses

$$\mathbf{v}_s \equiv \frac{\hbar}{m^*} \nabla \theta(\mathbf{r}, t) - \frac{q^*}{m^*} \mathbf{A}(\mathbf{r}, t). \quad (5.68)$$

Equation 5.67 is deceiving in its simplicity. It states that the supercurrent $\mathbf{J}_s$, *which can be experimentally measured*, is related to only the phase of the macroscopic wavefunction and the vector potential; *neither of which can be directly determined from experiment*. After all, θ is the absolute phase of a

wavefunction, so it can have no direct physical meaning. Moreover, because any single-valued scalar field, γ , satisfies

$$\nabla \times (\nabla \gamma) = 0, \quad (5.69)$$

we know that for an arbitrary scalar function χ ,

$$\mathbf{B} = \nabla \times \mathbf{A} = \nabla \times (\mathbf{A} + \nabla \chi). \quad (5.70)$$

Thus there exist an infinite number of vector potentials that will describe the correct magnetic flux! As a result, although θ and $\mathbf{A}$ were initially introduced as a matter of *mathematical* convenience, Equation 5.67 seems to imply that these quantities are *physically* measurable, which is not the case.

To overcome this dilemma, we recognize that the relationship between the phase of the wavefunction and the vector potential is *not* arbitrary but, in fact, fixed. In this way, we can measure the supercurrent and still not be able to experimentally determine θ and $\mathbf{A}$. In other words, we demand that Equation 5.67 be independent of the specific choice of the vector potential $\mathbf{A}$. The specific form of $\mathbf{A}$ is sometimes referred to as the gauge, and hence we desire to make the supercurrent equation *gauge invariant*.

Mathematically, the concept of gauge invariance is straightforward. Suppose we define a new vector potential $\mathbf{A}'$ as

$$\mathbf{A}' \equiv \mathbf{A} + \nabla \chi. \quad (5.71)$$

We see from Equation 5.70 that this new potential is an equally valid description of the original magnetic flux density. In addition, the new vector potential must also describe the original electric field. As a result, we define a new scalar potential ϕ' so that the electric field is written

$$\mathbf{E} = -\frac{\partial \mathbf{A}'}{\partial t} - \nabla \phi'. \quad (5.72)$$

Comparing this expression to that written in terms of the original potentials (Equation 5.44), we see that the two scalar potentials are related by

$$\phi' \equiv \phi - \frac{\partial \chi}{\partial t}. \quad (5.73)$$

We can therefore separately specify the spatial and temporal dependences of the arbitrary scalar function χ to generate new sets of vector and scalar potentials that still describe the original magnetic and electric fields.

We should be able to rewrite Equation 5.65 in terms of these new potentials:

$$i\hbar \frac{\partial}{\partial t} \Psi'(\mathbf{r}, t) = \frac{1}{2m^*} \left(\frac{\hbar}{i} \nabla - q^* \mathbf{A}'(\mathbf{r}, t) \right)^2 \Psi'(\mathbf{r}, t) + q^* \phi'(\mathbf{r}, t) \Psi'(\mathbf{r}, t), \quad (5.74)$$

where $\Psi'(\mathbf{r}, t)$ is the new macroscopic wavefunction associated with the potentials. As before, this new macroscopic wavefunction has the form

$$\Psi'(\mathbf{r}, t) = \sqrt{n^*(\mathbf{r}, t)} e^{i\theta'(\mathbf{r}, t)}. \quad (5.75)$$

Notice that the magnitude of Ψ' is the same as that of Ψ because both wavefunctions describe the same physical situation and hence both must describe the same local density of superelectrons:

$$\Psi'^*(\mathbf{r}, t)\Psi'(\mathbf{r}, t) = \Psi^*(\mathbf{r}, t)\Psi(\mathbf{r}, t) = n^*(\mathbf{r}, t). \quad (5.76)$$

Moreover, when expressed in terms of the new variables, the supercurrent

$$\mathbf{J}_s = q^* n^* \left(\frac{\hbar}{m^*} \nabla \theta' - \frac{q^*}{m^*} \mathbf{A}' \right), \quad (5.77)$$

must be the same as expressed in Equation 5.67 since it is an experimentally measurable quantity. The only way for this condition to be satisfied is if

$$\theta' = \theta + \frac{q^*}{\hbar} \chi, \quad (5.78)$$

and thus the relationship between the two macroscopic wavefunctions becomes

$$\Psi'(\mathbf{r}, t) = \Psi(\mathbf{r}, t) e^{i(q^*/\hbar)\chi}. \quad (5.79)$$

We see that the same scalar function χ changes the form of *both* $\mathbf{A}$ and θ . Hence the supercurrent always has a precise value that can be experimentally measured regardless of the gauge chosen. Now that we know our equations are gauge invariant, we need not concern ourselves with the issue explicitly.

Equation 5.67 is the most general form for the supercurrent in an isotropic superconductor since it includes the possibility that the local superelectron density is constant in neither space nor time. In fact, if the assumed form of Ψ is substituted into Equation 5.65, the imaginary portion of the result yields

$$\nabla \cdot \mathbf{J}_s = - \frac{\partial}{\partial t} (q^* n^*) = - \frac{\partial}{\partial t} \rho_s, \quad (5.80)$$

which is nothing more than conservation of charge. It is consistent with the free superelectron fluid model, however, to assume the local density n^* is constant. This approximation is true in many practical situations where the local fluctuations in density for a superelectron fluid in equilibrium are on length and time scales that are too small to be of engineering interest. We will normally use the MQM under this limiting case.

To demonstrate that the MQM is consistent with the conclusions reached using the classical model, it is necessary and sufficient to show that *both* the first and second London equations are direct consequences of the supercurrent

equation in this limit of constant n^* . We therefore reintroduce the isotropic London coefficient Λ (Equation 2.132), into Equation 5.67:

$$\Lambda \mathbf{J}_s = - \left(\mathbf{A}(\mathbf{r}, t) - \frac{\hbar}{q^*} \nabla \theta(\mathbf{r}, t) \right). \quad (5.81)$$

By taking the curl of this expression, we find

$$\nabla \times (\Lambda \mathbf{J}_s) = -\nabla \times \mathbf{A} = -\mathbf{B}, \quad (5.82)$$

and the second London equation (Equation 3.6), is immediately recovered.

The calculation to obtain the first London equation is a bit more involved. We first take the partial derivative with respect to time of Equation 5.81. Rearranging terms yields

$$\frac{\partial}{\partial t} (\Lambda \mathbf{J}_s) = - \left[\frac{\partial \mathbf{A}}{\partial t} - \frac{\hbar}{q^*} \nabla \left(\frac{\partial \theta}{\partial t} \right) \right]. \quad (5.83)$$

Of course, the problem is we have not found an expression for the time dependence of the phase of the macroscopic wavefunction yet. However, if we remember our assumption that n^* is constant in space and time, the real part of the Schrödingerlike equation (Equation 5.65) is

$$-\hbar \frac{\partial \theta}{\partial t} = \frac{1}{2n^*} \Lambda \mathbf{J}_s^2 + q^* \phi. \quad (5.84)$$

This expression is known as the *energy-phase relationship*. Substituting it into Equation 5.83 yields

$$\frac{\partial}{\partial t} (\Lambda \mathbf{J}_s) = \mathbf{E} - \frac{1}{n^* q^*} \nabla \left(\frac{1}{2} \Lambda \mathbf{J}_s^2 \right), \quad (5.85)$$

where the relationship between the electric field and the potentials was previously established by Equation 5.44.

This expression is *nearly* the same as the first London equation described in Section 2.5. There is an extra term in this expression, however, which we can identify as proportional to the gradient of the kinetic energy of the super-electrons. At first, we might guess that this extra term is a result of purely quantum mechanical effects so that our previous classical derivation would not produce it. If the term were a result of a quantum effect though, it would contain Planck's constant and we see that this is not the case. Therefore, we must determine why Equation 5.85 is not consistent with our previous statement of the first London equation, Equation 2.131.

We consequently try to cast Equation 5.85 in a more familiar form. From the vector identity

$$\mathbf{C} \times (\nabla \times \mathbf{C}) = \frac{1}{2} \nabla (\mathbf{C} \cdot \mathbf{C}) - (\mathbf{C} \cdot \nabla) \mathbf{C} \quad (5.86)$$

and the second London equation, Equation 5.85 can be written as

$$\frac{\partial}{\partial t} (\Lambda \mathbf{J}_s) + \frac{1}{n^* q^*} (\mathbf{J}_s \cdot \nabla) (\Lambda \mathbf{J}_s) = \mathbf{E} + \frac{1}{n^* q^*} (\mathbf{J}_s \times \mathbf{B}). \quad (5.87)$$

We now appeal to the convective (or total) time derivative that we introduced in Equation 5.16:

$$\frac{d}{dt} (\Lambda \mathbf{J}_s) = \frac{\partial}{\partial t} (\Lambda \mathbf{J}_s) + (\mathbf{v}_s \cdot \nabla) (\Lambda \mathbf{J}_s). \quad (5.88)$$

Using the fact that $\mathbf{J}_s = n^* q^* \mathbf{v}_s$, we then find that Equation 5.87 reduces to

$$m^* \frac{d\mathbf{v}_s}{dt} = q^* \mathbf{E} + q^* \mathbf{v}_s \times \mathbf{B}. \quad (5.89)$$

Thus we find that from Lorentz's law and the second London equation, we obtain the nonlinear first London equation! As a result, *Equation 5.85* must be the correct form of the expression that describes the phenomenon of zero dc resistance in superconductors. That we needed the second London equation in deriving the first London equation is an indication that the Meissner effect is a bit more fundamental in the physics of superconductivity than the phenomenon of zero dc resistance. Of course these remarks hold for the classical model of superconductivity as well. In fact, had we not neglected the magnetic portion of Lorentz's law when deriving the first London equation in Section 2.5, there would be no inconsistency now.

We are now faced with an embarrassing situation: are all our previous results incorrect since we used an incomplete form of the first London equation? Fortunately the answer is no. Our problem solving techniques have bypassed any calculation where the neglected term would have been significant. *However, this good fortune does not imply that we may always neglect the nonlinear term in the first London equation.* On the contrary, occasionally it plays an important role.

Nonetheless, let us now demonstrate why previously solved problems in earlier chapters are consistent with the correct (nonlinear) form of the first London equation. This is most easily done by separating the problems in three categories: MQS, EQS, and those involving both magnetic and electric fields.

Recall that whenever we solved an MQS problem, the slab in a magnetic field for example, we never even used the first London equation. The electric fields were not of zeroth-order importance and they were found from Faraday's law *after* the magnetic fields and associated currents were calculated. Since we

did not calculate corrections to the original supercurrent distributions, the first London equation was not invoked and all the MQS examples were correctly solved.

For EQS problems the issues are more subtle. In these cases, we did use the first London equation and it is important to see why our linearized form did not cause errors. Equation 5.85 reduces to Equation 2.131 when

$$|\mathbf{E}| \gg \left| \frac{1}{n^* q^*} \nabla (\Lambda \mathbf{J}_s^2) \right|. \quad (5.90)$$

If we assume that changes in spatial distributions occur over length scales ℓ this statement implies

$$|\mathbf{E}| \gg |\mathbf{v}_s| \left| \frac{\Lambda \mathbf{J}_s}{\ell} \right|. \quad (5.91)$$

By a similar dimensional analysis for the second London equation, we find that

$$\left| \frac{\Lambda \mathbf{J}_s}{\ell} \right| \sim |\mathbf{B}|. \quad (5.92)$$

As a result, the solutions to previous EQS problems are correct as long as

$$|\mathbf{E}| \gg |\mathbf{v}_s| |\mathbf{B}|. \quad (5.93)$$

This condition is not surprising; it is consistent with the assumption we made in Section 2.5 to neglect the magnetic portion of Lorentz's law when we derived the first London equation.

Of course, Equation 5.93 is not always justified. If there is a significant spatial variation in the motion of the superelectrons, a nontrivial magnetic field can be created. This magnetic field can then successfully compete with the applied electric field to alter the distribution of the supercurrent flow. In other words, the only true EQS superconducting problems are those in which the geometry does not vary too rapidly (as defined by Equation 5.91). As it happens, the problems studied in previous sections where the electric field is dominant are in this category.

Suppose, however, that *both* magnetic and electric fields are important, as in the cases of electromagnetics or energy analysis. It is fortuitous that our previous analysis with the linearized form of the first London equation *still* holds. There are two reasons for this. First, the spatial distribution of the electric field inside a superconductor is usually determined by Faraday's law as was discussed in Section 4.2. Since Faraday's law involves the curl of $\mathbf{E}$, we find that the added correction term in the nonlinear first London equation (the gradient of a scalar function) will not affect our previous results! The second reason that our previous results hold stems from the way in which we examined Poynting's theorem. Recall from Section 3.5 that we only examined

energy distributions over finite volumes. In other words, we exclusively based our interpretations on an integral rather than differential formulation. Because of this viewpoint, Poynting's theorem, as given by Equation 3.97, and all the conclusions based on it are still correct.

Let us examine this second issue further. In expressing the first London equation as we did in Chapter 2, we treated the supercurrent as a field quantity, like $\mathbf{E}$ or $\mathbf{B}$. Thus if we use our linearized expression (Equation 2.131), we might think that the local power density associated with the supercurrent is

$$\mathbf{E} \cdot \mathbf{J}_s = \frac{\partial}{\partial t} \left(\frac{1}{2} \Lambda \mathbf{J}_s^2 \right), \quad (5.94)$$

which is *not true*. The supercurrent is not a field as such, it is a flux of charged matter. As a result, there is power associated with *both* its kinetic *and* field momenta. This is merely another way of expressing the fact that the canonical momentum of a charged particle, as given by Equation 5.48, is the quantity that is conserved in physical processes. Using the full form of the first London equation (Equation 5.85), we find

$$\mathbf{E} \cdot \mathbf{J}_s = \frac{d}{dt} \left(\frac{1}{2} \Lambda \mathbf{J}_s^2 \right), \quad (5.95)$$

which is the proper local power density. Of course, if we look at an integral formulation of Poynting's theorem, Equation 3.97, this difference is no longer apparent.

Let us generalize the MQM to an anisotropic superconductor as promised earlier. As we saw in Section 3.6, a matrix describing the mass of a superelectron can be used to account for anisotropic superconductivity. Consequently, it is not difficult to generalize the Schrödingerlike equation for the macroscopic wavefunction:

$$i\hbar \frac{\partial \Psi}{\partial t} = \frac{1}{2} \left(\frac{\hbar}{i} \nabla - q^* \mathbf{A} \right)^T \overline{\mathbf{m}^*}^{-1} \left(\frac{\hbar}{i} \nabla - q^* \mathbf{A} \right) \Psi + q^* \phi \Psi \quad (5.96)$$

as well as the definition of the macroscopic quantum current:

$$\mathbf{J}_s = q^* \text{Re} \left\{ \Psi^* \overline{\mathbf{m}^*}^{-1} \left(\frac{\hbar}{i} \nabla - q^* \mathbf{A} \right) \Psi \right\}. \quad (5.97)$$

Using the general form of the macroscopic wavefunction Ψ given in Equation 5.66, we arrive at an expression for the macroscopic quantum current in an anisotropic superconductor:

$$\mathbf{J}_s = q^* n^*(\mathbf{r}, t) \overline{\mathbf{m}^*}^{-1} (\hbar \nabla \theta(\mathbf{r}, t) - q^* \mathbf{A}(\mathbf{r}, t)), \quad (5.98)$$

which can also be written

$$\bar{\bar{\mathbf{A}}}\mathbf{J}_s = - \left(\mathbf{A}(\mathbf{r}, t) - \frac{\hbar}{q^*} \nabla \theta(\mathbf{r}, t) \right). \quad (5.99)$$

Moreover, under the assumption that n^* is a constant everywhere, the first and second London equations for the anisotropic case are readily obtained:

$$\frac{\partial}{\partial t} (\bar{\bar{\mathbf{A}}}\mathbf{J}_s) = \mathbf{E} - \frac{1}{n^* q^*} \nabla \left(\frac{1}{2} \mathbf{J}_s^T \bar{\bar{\mathbf{A}}}\mathbf{J}_s \right) \quad (5.100)$$

and

$$\nabla \times (\bar{\bar{\mathbf{A}}}\mathbf{J}_s) = -\mathbf{B}. \quad (5.101)$$

Not surprisingly, the forms of these equations are quite similar to those for the isotropic superconductor. Indeed, the mathematical details of the derivations follow closely to those used in the isotropic case.

We have found that the MQM self-consistently unites both London equations into a unifying macroscopic quantum supercurrent. This check on the self-consistency of our classical reasoning is only the beginning of the power of the MQM. In Section 5.5 we use the MQM to analyze superconducting phenomena that have *no classical analog at all*.

Before finishing this section, however, let us briefly examine how quantum mechanics affects our description of the normal electrons. For us, the primary result of this description is that *the Drude model developed in Section 2.5 still gives the correct conductivity*. The quantum mechanical description, however, shows that each carrier in the normal electron gas has a background speed associated with it. In other words, when no currents are applied or induced in the material at zero temperature, each electron moves in random directions with a *Fermi velocity*, v_F . Notice that in spite of the fact that each electron is moving at the same *speed*, there is no net motion of the electron gas under these conditions because the *direction* of each carrier is random. Of course, the carrier velocity we associate with currents is the *net* speed of the electron gas.

The Fermi velocity provides a way to translate some of our limiting criteria from a temporal viewpoint into a spatial one. For example, since the average time between each scattering event is τ_{tr} , the intrinsic average distance between scattering events, known as the *mean free path* ℓ_{tr} , is

$$\ell_{tr} = v_F \tau_{tr}. \quad (5.102)$$

For instance, we found in Section 2.5 that the scattering time in copper is approximately $\tau_{tr} \approx 2.4 \times 10^{-14}$ seconds. Since the Fermi velocity is typically on the order of 10^7 m/s, we therefore know that each conduction electron in copper travels about $0.24 \mu\text{m}$ between scattering events. Moreover, recall that we could approximate the conductivity of a material to be nondispersive for

frequencies satisfying $\omega\tau_{tr} \ll 1$. Since the Fermi velocity is typically a tenth of the speed of light, the temporal based criterion translates into the spatial based criterion

$$10\ell_{tr} \ll \lambda_{em}, \quad (5.103)$$

where λ_{em} is the electromagnetic wavelength in the material. In other words, if the wavelength is so large as to encompass many scattering sites, the motion of the electron is most affected by the scattering events rather than the changing electromagnetic field. As a result, the overall conduction in the material will not be sensitive to a change in frequency and it is valid to approximate the conductivity as nondispersive.

Finally, the randomness of the direction of the normal electrons' motion is also reflected in their quantum mechanical description. The ensemble of the normal electrons can also be described by a wavefunction; this wavefunction, however, is not coherent in phase as is the macroscopic wavefunction of the superelectrons. Therefore, no simple macroscopic wavefunction, analogous to $\Psi(\mathbf{r}, t)$, is found for the normal state.

5.5 FLUX QUANTA

Thus far, we have demonstrated that the MQM is consistent with the constitutive laws for superconductivity we previously deduced using classical reasoning. We now would like to examine the *quantum mechanical* consequences of the model. To simplify the discussion, we will assume that the superconducting media is homogeneous, as is typically done when using the MQM. In addition, we will assume that the superconducting material is isotropic. (Our argument, however, will hold for anisotropic materials as well and can be obtained by replacing Λ with $\bar{\Lambda}$.)

We begin with the supercurrent equation written in terms of Λ :

$$\Lambda \mathbf{J}_s = - \left(\mathbf{A}(\mathbf{r}, t) - \frac{\hbar}{q^*} \nabla \theta(\mathbf{r}, t) \right). \quad (5.104)$$

Suppose we integrate this expression about a closed contour C . From Stokes's theorem (Equation 2.35) we know

$$\oint_C \mathbf{A} \cdot d\mathbf{l} = \int_S (\nabla \times \mathbf{A}) \cdot d\mathbf{s} = \int_S \mathbf{B} \cdot d\mathbf{s}, \quad (5.105)$$

where S is the surface defined by the contour C and $\mathbf{B}$ is the magnetic flux density associated with the vector potential. Equation 5.104 can therefore be written as

$$\oint_C (\Lambda \mathbf{J}_s) \cdot d\mathbf{l} + \int_S \mathbf{B} \cdot d\mathbf{s} = \frac{\hbar}{q^*} \oint_C \nabla \theta \cdot d\mathbf{l}. \quad (5.106)$$

Let us evaluate the integral on the right side of this expression. We know from vector calculus that the integral of the gradient of a scalar function along the path defined by points $\mathbf{r}_a$ and $\mathbf{r}_b$ is

$$\int_{\mathbf{r}_a}^{\mathbf{r}_b} \nabla \theta \cdot d\mathbf{l} = \theta(\mathbf{r}_b, t) - \theta(\mathbf{r}_a, t). \quad (5.107)$$

Thus it would seem when $\mathbf{r}_b \rightarrow \mathbf{r}_a$ such that a closed path is formed, this integral is zero. In general this is not true, however, because the *specific value* of the phase of Ψ is not well defined. Indeed, there exist an *infinite number* of possible values of the phase since for integer values of n

$$\Psi(\mathbf{r}, t) = \sqrt{n^*} e^{i(\theta_p + 2\pi n)} \quad (5.108)$$

all give the same value for Ψ . Thus we find that although the macroscopic wavefunction is always well defined, the phase of Ψ ,

$$\theta(\mathbf{r}, t) = \theta_p(\mathbf{r}, t) + 2\pi n, \quad (5.109)$$

is not. The phase can only be specified to within modulo 2π of its *principal value* θ_p , which has the restricted range $-\pi$ to π . Since θ_p is a single-valued function, we find that

$$\oint_C \nabla \theta \cdot d\mathbf{l} = \lim_{\mathbf{r}_b \rightarrow \mathbf{r}_a} (\theta(\mathbf{r}_b, t) - \theta(\mathbf{r}_a, t)) = 2\pi n. \quad (5.110)$$

From this analysis, Equation 5.106 becomes

$$\oint_C (\Lambda \mathbf{J}_s) \cdot d\mathbf{l} + \int_S \mathbf{B} \cdot d\mathbf{s} = n\Phi_o, \quad (5.111)$$

where n has been replaced by $-n$ with no loss of generality and Φ_o represents a *flux quantum* defined as

$$\Phi_o \equiv \frac{2\pi\hbar}{|q^*|} = \frac{h}{|q^*|}. \quad (5.112)$$

By definition, the flux quantum is necessarily a positive quantity. Let us explore the consequences of this expression.

Example 5.5.1: Consider the closed contour shown in Figure 5.1a, where the surface S defined by the contour is in a simply connected bulk superconducting region. Recall that we evaluate the closed contour integrals in Equation 5.111 by imagining a line integration between the two points $\mathbf{r}_a$ and $\mathbf{r}_b$ taken in the limit where $\mathbf{r}_b \rightarrow \mathbf{r}_a$. Since Equation 5.111 holds for all contours, we can examine the particular case when the size of the contour is shrunk to zero length. In this case, both integrals vanish (assuming that there are no singularities in

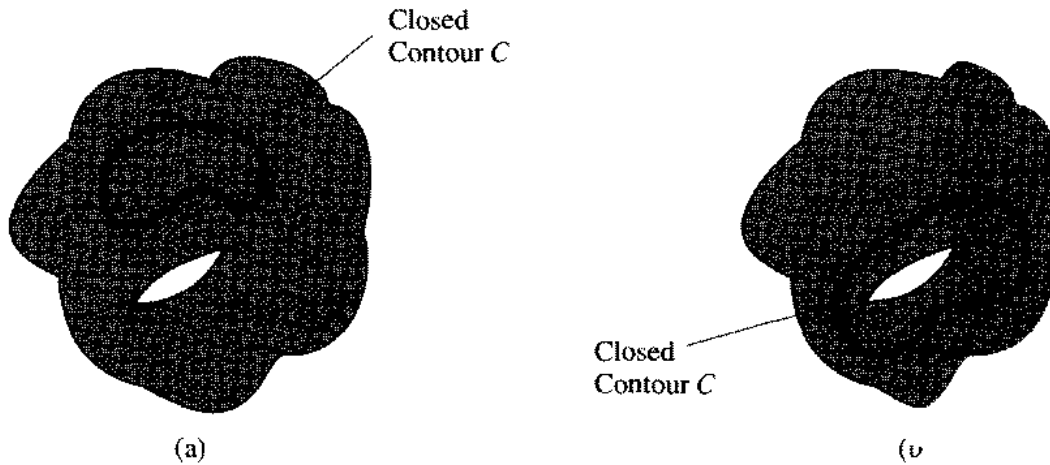


Figure 5.1 Possibilities for a closed contour within a superconducting medium: (a) The path is in a simply connected bulk superconducting region. (b) The path is in a multiply connected region.

the supercurrents or flux densities), and we find that $n = 0$ in the simply connected superconducting region. This is expected because the $n = 0$ condition immediately yields the integral form of the second London equation which is the constitutive relation for simply connected regions.

Example 5.5.2: The situation is very different if the closed path is in a multiply connected region as illustrated in Figure 5.1b. Notice that the surface S now covers both superconducting *and* normal regions. Thus when we close the line integral by applying the limit $r_b \rightarrow r_a$, we have built some “memory” into the path: we specifically know that the nonsuperconducting region was enclosed. In other words, the phases at the points r_a and r_b are now distinct. Consequently, although the principal value of the two phases is necessarily the same, the difference between the two phases is $2\pi n$.

The left-hand side of Equation 5.111 is known as a *fluxoid* and hence, this expression is a statement of *fluxoid quantization*. Notice that any externally applied flux, generated by either fields or currents, is not necessarily quantized; the flux created by any induced supercurrents must also be included in the calculation. That the total amount of flux passing through a multiply connected superconductor cannot be arbitrary but instead a discrete number of fundamental flux quanta is totally beyond the bounds of classical theory; indeed the issue never came up when we examined the multiply connected superconducting cylinder classically in Section 3.2.

Let us now reexamine Example 3.2.3 to see how the result differs when we use the MQM. Recall that the problem consisted of finding the field distribution around a hollow superconducting cylinder with a thick wall. By “thick,” we mean that the wall thickness is much greater than a penetration depth λ and so the bulk approximation is valid. Clearly, the analysis will not change when

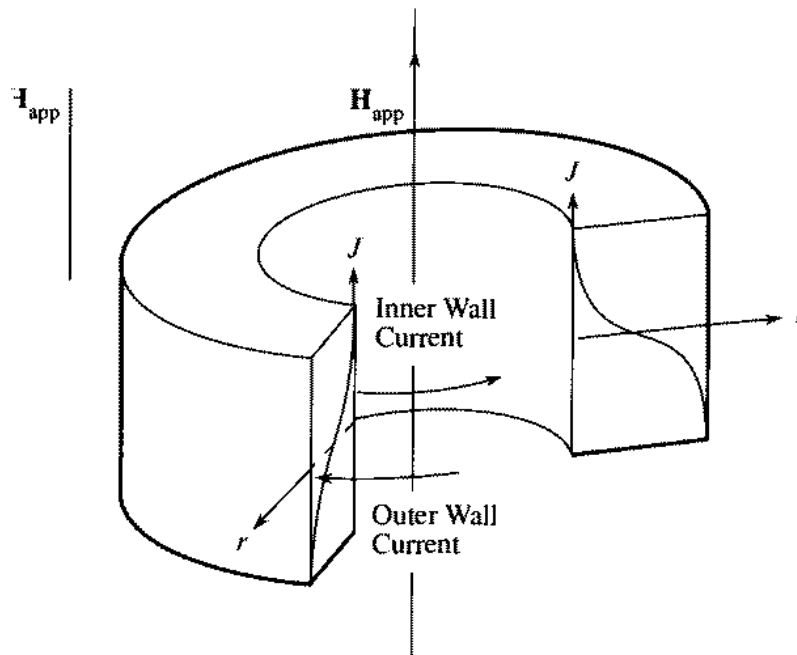
we apply the external field *after* the superconductor has been cooled below the critical temperature: there is never any flux that threads the cylinder under these conditions.

The problem is more interesting for the case when the external field is applied *before* the cylinder undergoes the superconducting transition. As previously discussed, when the cylinder becomes superconducting, a current flows on the outer surface to expel the applied B from the bulk material. In addition, another current flows in the opposite direction on the inner surface to maintain the applied field in the free space region as required by Ampère's law. So far, these general ideas hold for both the classical model and the MQM.

The differences occur when we examine the details of the actual trapped flux. In the classical case, the currents flowing on the inner surface are constrained only by Ampère's law. In fact, when the applied field is removed, the only affect of the superconducting material is to support these currents without any dissipation. Hence, classically we could trap an *arbitrary* amount of flux in the cylinder by simply varying the intensity of the initial applied field.

This is not the case when the MQM is used to solve the problem. In addition to Ampère's law, the induced supercurrents must also satisfy the fluxoid quantization condition represented by Equation 5.111. As illustrated in Figure 5.2, if we choose a closed contour deep within the thick wall, $J_s \approx 0$, the MQM reveals that

$$\int_S \mathbf{B} \cdot d\mathbf{s} = n\Phi_0. \quad (5.113)$$



Detail showing the fine distribution of the induced supercurrent in a hollow superconducting cylinder with a thick wall.

In other words, if we were to remove the applied field, the total flux trapped in the cylinder, which includes contributions from the flux density penetrating the superconductor as well as that found in the free space region, is *always* a discrete number of quanta irrespective of the initial value of the applied field. Thus the MQM predicts that the trapped flux is quantized under such conditions.

We can therefore test the validity of the MQM by trying to *experimentally measure* this flux quantization. In 1961, two sets of researchers, B. S. Deaver and W. M. Fairbank in the United States and R. Doll and M. Näbauer in Germany, in fact performed the experiment we have just outlined. In these experiments, the “hollow cylinder” was made by coating a nonsuperconducting thin filament with a superconducting layer; the former pair of researchers electroplated tin on copper wire while the latter evaporated lead onto a quartz fiber. The reason for using a small cylinder cross section is clear if we look at the magnitude of Φ_o as defined by Equation 5.112. Since we expect the charge of the superelectron to be that of the order of a normal electron, we find $\Phi_o \sim 1 \times 10^{-15} \text{ T-m}^2$; very small indeed! To observe discrete flux quanta, it is easier to limit the area of the loop rather than to try to produce extremely tiny flux densities.

Once the applied field is removed, the flux trapped inside the loop may be measured in a variety of ways: Deaver and Fairbank chose to vibrate the cylinder rapidly in the axial direction and measure the resulting rf signal via a pair of coils while Doll and Näbauer suspended their sample orthogonal to the cylinder’s axis and observed the torsion created when the trapped flux interacted with another external field. The results of both experiments were essentially identical and convincing: although the samples were cooled in a number of applied field strengths, the net flux trapped occurred only in quantized steps (see Figure 5.3). Also, as one would expect from our formulation, the results did not change when the direction of the applied field was reversed. The two sets of researchers demonstrated experimentally the limitations of a purely classical approach to superconductivity.

There are additional observations that can be made from the data. First, the precise value of a single flux quantum can be obtained. The data indicates that

$$\Phi_o = \frac{h}{2e} = 2.07 \times 10^{-15} \text{ T-m}^2, \quad (5.114)$$

where e is the magnitude of the charge associated with an electron. If we compare this result with our definition of Φ_o (Equation 5.112), we arrive at the important conclusion

$$|q^*| = 2e. \quad (5.115)$$

Here, then, is *experimental evidence* that the superelectron carries twice the charge of a normal one. Historically, this result provided the first experimental proof of the existence of Cooper pairs, which were crucial in the

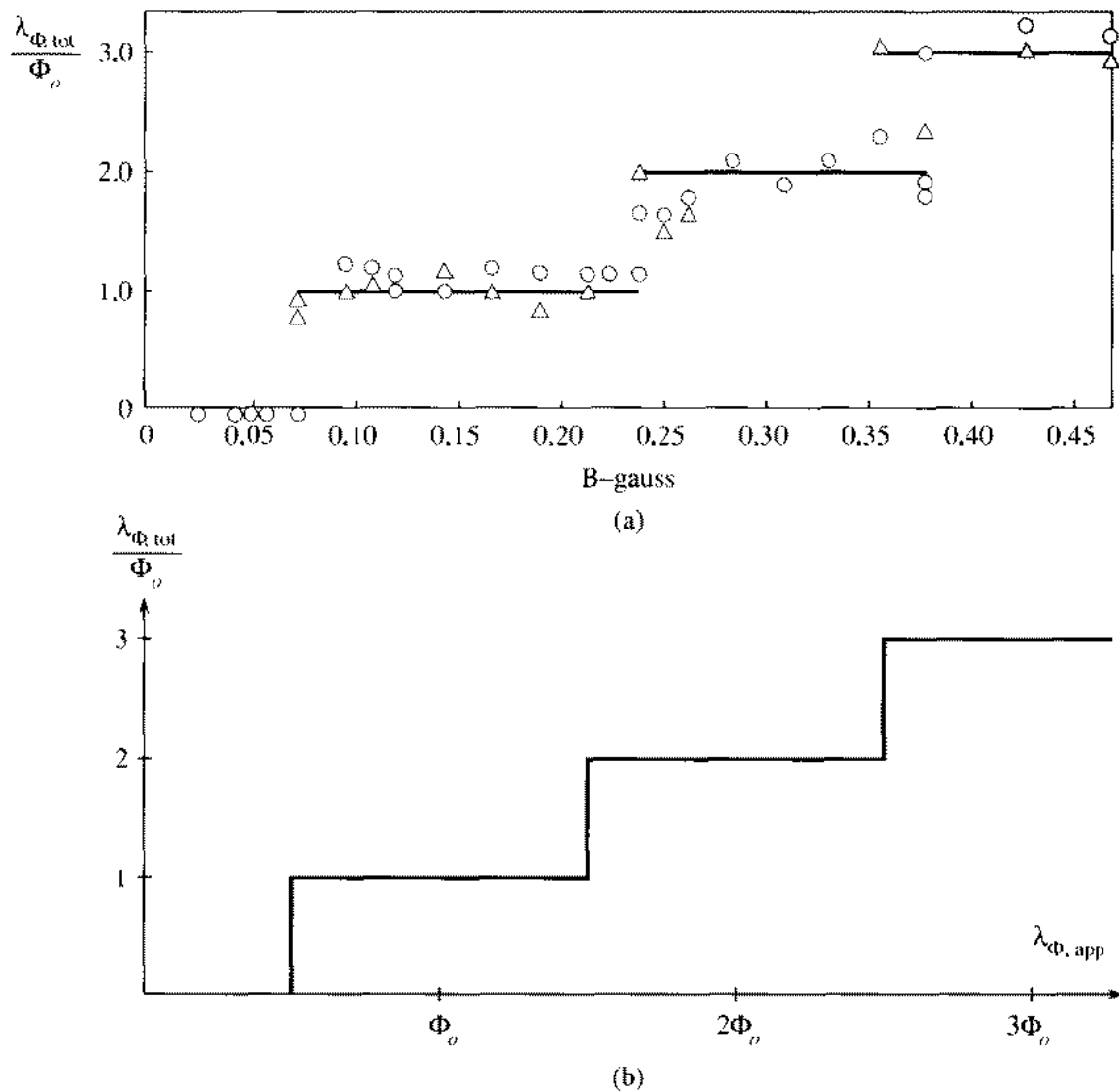


Figure 5.3 Flux trapped in hollow cylinder. (a) Experimental evidence of flux quanta measured by Deaver and Fairbank. The results from Doll and Näbauer are essentially identical. (b) Idealized form of the data. Source: B. S. Deaver and W. M. Fairbank, "Experimental Evidence for Quantized Flux in Superconducting Cylinders," *Physical Review Letters*, Vol. 7, 1961.

microscopic model of superconductivity proposed by John Bardeen, Leon Cooper, and Robert Schrieffer in 1957.

In addition to the quantized phenomenon, Deaver and Fairbank noted a pattern in their data. They found that the experimental evidence suggests the minimum applied field to trap n flux quanta in the cylinder is $2n - 1$ times greater than the minimum field to trap a single quantum unit. Hence, two, three, and four flux quanta can be trapped when the applied flux is respectively three, five, and seven times the minimum required to obtain the original flux quantum.

This observation has a consistent interpretation under the MQM. From fluxoid quantization, we know that the total flux threading the cylinder, $\lambda_{\Phi, \text{tot}}$, is quantized:

$$\lambda_{\Phi, \text{tot}} = n\Phi_o = \lambda_{\Phi, \text{app}} + \Delta\lambda_{\Phi}, \quad (5.116)$$

where $\lambda_{\Phi, \text{app}}$ is the trapped flux that would be obtained from a classical analysis of the problem and $\Delta\lambda_{\Phi}$ is the additional flux needed to maintain the quantized effect. Since our cylinder has thick walls, we can appeal to the bulk approximation and model the system in lumped form. As a result, the net inductance of the loop is L , and so the additional persistent current needed to maintain quantization, Δi , is

$$\Delta i = \frac{\Delta\lambda_{\Phi}}{L} = \frac{n\Phi_o - \lambda_{\Phi, \text{app}}}{L}. \quad (5.117)$$

A plot of Equation 5.117 (shown in Figure 5.4), however, shows that there are a seemingly *infinite* number of possible Δi for a given $\lambda_{\Phi, \text{app}}$ that will satisfy the MQM. How does the cylinder “decide” the number of Φ_o to trap?

The answer can be found by examining the energy of the system. As previously stated, when the cylinder is cooled below the superconducting transition temperature, currents flow on both the inner and outer surfaces to maintain the proper flux distribution. However, the superconducting cylinder responds in a manner that is consistent not only with the MQM but also with the principle that the system will equilibrate to its lowest energy state. Because there is an energy associated with any circulating current, the cylinder will equilibrate as

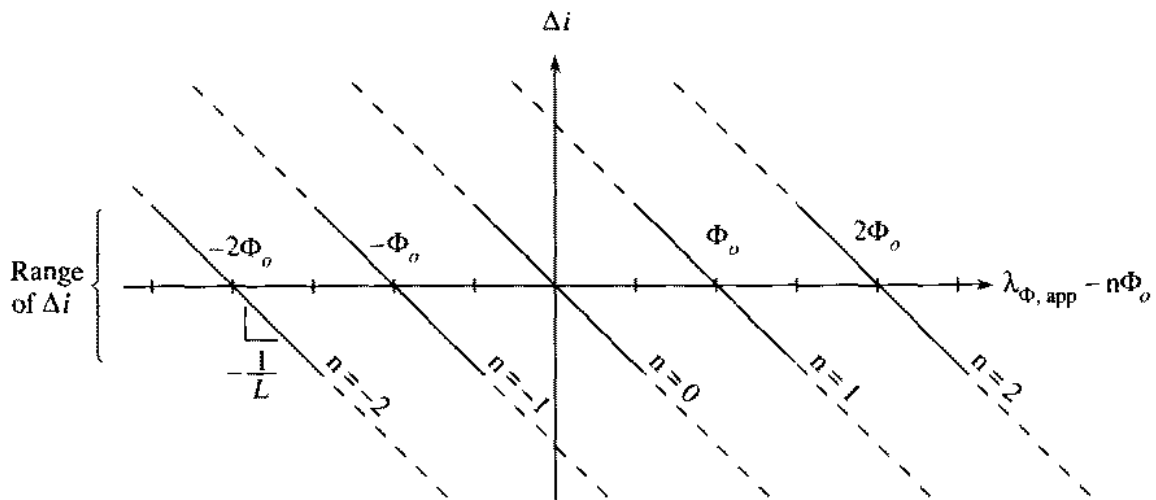


Figure 5.4 The additional supercurrent induced to maintain fluxoid quantization has many possible values for a given applied flux. The system chooses the lowest current necessary, however, and so actually Δi only falls within the range indicated.

it is cooled below T_c by minimizing the extra current needed to produce an integral number of flux quanta. The small extra current induced for quantization will either strengthen the amount of flux linked by the loop if $\lambda_{\Phi,app}$ is not strong enough, or, by flowing in the opposite direction, repel a small portion of the applied flux if it is too great. As is illustrated in Figure 5.4, the maximum magnitude of the additional current is therefore

$$|\Delta i|_{\max} = \frac{\Phi_o}{2L}. \quad (5.118)$$

Physically, this maximum is reached when the applied flux differs from an integral number of quanta by $\Phi_o/2$. The same magnitude of current induced in the cylinder can produce a half-flux quantum to either increase or decrease the net flux quanta trapped to be integral.

If we now return to Equation 5.117, we see that the minimum $\lambda_{\Phi,app}$ required to produce $n\Phi_o$ occurs when the contribution of Δi is greatest and flows in a direction to increase the net flux. Replacing Δi by its maximum value (Equation 5.118) shows that this minimum applied flux has a value

$$\lambda_{\Phi,app}|_{\min} = (2n - 1) \frac{\Phi_o}{2} \quad (5.119)$$

and we recover the $2n - 1$ pattern observed by Deaver and Fairbank. Physically, we see that this pattern allows the superconductor to supply the minimum amount of energy (in terms of Δi) while still maintaining fluxoid quantization.

We have thus demonstrated how the MQM not only recovers all our previous results obtained by applying the London equations, but also is consistent with the quantized nature of superconductivity that is observed experimentally. This is just the beginning. In Chapter 6, we shall see how the MQM allows us to model those properties of a superconductor that would be difficult, if not impossible, to account for in classical terms.

5.6 SUMMARY

In this chapter, we extended our concepts of superconductivity from a classical theory to a quantum one. In quantum mechanics, the wave-particle duality of nature is explicit and it is therefore possible to encounter such nonclassical ideas as matter waves or “particles” of light (photons). As a direct consequence of this duality, Schrödinger’s equation for a single quantum particle in a scalar potential (Equation 5.27) describes the dynamical evolution of a probability amplitude $\psi(\mathbf{r}, t)$. The physical interpretation of this function is that the square of its magnitude is the *probability* that the particle will be at a specific place $\mathbf{r}$ at a certain time t . To describe the motion of this probability distribution in space-time, we found it intuitively appealing to think in terms of a probability

current. Moreover, we were able to extend these concepts when the applied potentials were not conservative as in the case of an electromagnetic field.

Because we envision superconductivity as a coherent phenomenon between all the superelectrons, however, it is convenient to describe the entire ensemble of carriers with a single macroscopic wavefunction

$$\Psi(\mathbf{r}, t) = \sqrt{n^*(\mathbf{r}, t)} e^{i\theta(\mathbf{r}, t)}.$$

As a result, the form of the equation governing the entire ensemble subjected to an electromagnetic field is similar to Schrödinger's equation for a single particle:

$$i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}, t) = \frac{1}{2m^*} \left(\frac{\hbar}{i} \nabla - q^* \mathbf{A}(\mathbf{r}, t) \right)^2 \Psi(\mathbf{r}, t) + q^* \phi(\mathbf{r}, t) \Psi(\mathbf{r}, t).$$

That we may assign a single wavefunction for the entire motion of the superelectrons is the fundamental hypothesis behind the macroscopic quantum model of superconductivity (MQM).

The MQM is relatively easy to use since many insights gained from the single particle wavefunction translate naturally into equivalent statements involving the ensemble wavefunction. For example, since Ψ describes the entire collection of superelectrons, the square of its magnitude is now the probability of finding all the carriers at a specific place at a specific time. However, this is just another way of describing the local density of the superelectrons in space and time, $n^*(\mathbf{r}, t)$. As shown above, we self-consistently reflect this physics in the expression of Ψ itself. Moreover, it is often convenient to model the local density as constant in space and time. In these instances, the dependence of the macroscopic wavefunction on $\mathbf{r}$ and t is contained entirely within the phase θ .

More importantly, the MQM provides an extension of the concept of probability currents. Since Ψ describes many particles, the flow of probability for the entire ensemble is equivalent to the flow of the macroscopic supercurrent, $\mathbf{J}_s$, as given in Equation 5.67 for the case of an isotropic superconductor:

$$\mathbf{J}_s = q^* n^*(\mathbf{r}, t) \left(\frac{\hbar}{m^*} \nabla \theta(\mathbf{r}, t) - \frac{q^*}{m^*} \mathbf{A}(\mathbf{r}, t) \right),$$

or equivalently,

$$\Lambda \mathbf{J}_s = - \left(\mathbf{A}(\mathbf{r}, t) - \frac{\hbar}{q^*} \nabla \theta(\mathbf{r}, t) \right).$$

This relation, the supercurrent equation, is of primary importance in the MQM and, of course, it can be extended to describe anisotropic media as well. Its time derivative yields the first London equation

$$\frac{\partial}{\partial t} (\Lambda \mathbf{J}_s) = \mathbf{E} - \frac{1}{n^* q^*} \nabla \left(\frac{1}{2} \Lambda \mathbf{J}_s^2 \right)$$

that self-consistently includes the effects of the magnetic field created by the motion of the carriers. The curl of the supercurrent equation returns the second London equation, included here for completeness:

$$\nabla \times (\Lambda \mathbf{J}_s) = -\mathbf{B}.$$

Finally, when the supercurrent equation is integrated around a path in a multiply connected region, we obtain

$$\oint_C (\Lambda \mathbf{J}_s) \cdot d\mathbf{l} + \int_S \mathbf{B} \cdot d\mathbf{s} = n\Phi_0,$$

which is a statement of fluxoid quantization. By measuring the value of the flux quantum Φ_0 , the concept that the superelectron is in reality a Cooper pair is experimentally confirmed. Once again, it is emphasized that extending this discussion to anisotropic materials is not difficult. Indeed, the previous four relations can be used for anisotropic superconductors if Λ is replaced by $\bar{\Lambda}$.

References for Chapter 5

As noted in Section 5.1, the way in which quantum mechanics is developed in this chapter is for the sole purpose of motivating the macroscopic quantum model of superconductivity. Consequently, it may appear that much of quantum mechanics is based on heuristic arguments. In fact, this is far from the case, but to explore the subject rigorously requires a deeper understanding of *classical* mechanics. There is a formal way of obtaining Newtonian mechanics through the principle of least action. Briefly stated, this means that a classical object moves along a trajectory to minimize a certain abstract quantity called the "action." The problem of solving Newton's law therefore reduces to finding this path of least action using a branch of mathematics known as variational calculus. An excellent, short account of the principle of least action and variational calculus is contained in Chapter 19 of Volume II of *The Feynman Lectures on Physics* by R. P. Feynman, R. B. Leighton, and M. Sands (Addison-Wesley, 1964). Although brief, the chapter contains nearly all the essential physical ideas behind this formalism of classical mechanics. A more detailed description of this material, as well as its philosophical implications in both classical and quantum mechanics, can be found in *Variational Principles in Dynamics and Quantum Theory* written by W. Yourgrau and S. Mandelstam (Dover, 1979). The rigorous details of canonical momenta and generalized potentials that we have omitted are described in a very readable manner in this book.

The formalism of quantum mechanics is, in fact, directly based on this formal way of doing classical mechanics. Again, we have obtained the basic ideas of this approach without much rigor. To become truly proficient in the ideas of quantum mechanics requires a more detailed study of the material. In Volume I of *The Feynman Lectures on Physics*, an elementary, but appealing, introduction to quantum phenomena is given: Chapter 37 covers the notions of wave-particle duality and probability amplitudes, while Chapter 38 considers some of the elementary implications of the Einstein-de Broglie relations. These accounts are particularly helpful since they concentrate on the ideas rather than the mathematics involved in a quantum mechanical description of nature.

To actually solve quantum problems, however, one would like a more mathematically oriented text. There are many books available on quantum mechanics, but three in particular are especially useful when approaching the subject for the first time. *Principles of Quantum Mechanics* by R. Shankar (Plenum, 1980) provides a nice blend of physical concepts with mathematics. In particular, all the ideas behind canonical momenta, Schrödinger's equation, probability currents, and the like, are given a reasonable treatment in Chapters 4 and 5. A second book, *Quantum Mechanics* written by C. Cohen-Tannoudji, B. Diu, and F. Laloë (Wiley, 1977), is well suited for a self-study of the subject. The total size of the two volumes is immense but this is because nearly all of the mathematics is shown in great detail. Moreover, the text is highly modular and need not be read entirely in sequence. Finally, *Introductory Quantum Mechanics* by R. L. Liboff (Holden-Day, 1980) is a more concise text that approaches the subject from a traditional point of view. All these books contain enough worked examples and problems to help the reader practice using the concepts of quantum mechanics.

With regards to the MQM, Section E of Volume I of F. London's book, *Superfluids* (Dover, 1961), contains a lucid discussion of this approach by the inventor himself. Moreover, this section is of historical interest, as London predicts fluxoid quantization. It is interesting to note that since he did not anticipate the existence of Cooper pairs, his predicted value of Φ_0 is too large by a factor of two. *The Feynman Lectures on Physics* (Volume III, Chapter 21) also contains a description of the MQM. Finally, the first experimental measurements of the flux quantum are described in the two papers discussed in Section 5.5. The complete references are: (a) B. S. Deaver and W. M. Fairbank, "Experimental Evidence for Quantized Flux in Superconducting Cylinders," *Physical Review Letters* **7**, 43 (1961); and (b) R. Doll and M. Näbauer, "Experimental Proof of Magnetic Flux Quantization in a Superconducting Ring," *Physical Review Letters* **7**, 51 (1961).

Problems

Problem 5.1 (Wave-Particle Duality): Show that the de Broglie wavelength of a 10 keV beam of electrons is indeed $0.12 \text{ \AA}$ as claimed in Section 5.2. (Assume that the energy of the electrons is purely kinetic.) What is the energy of a beam of photons with the same wavelength? What is the de Broglie wavelength of a beam of thermally excited neutrons at $T = 300 \text{ K}$? (Recall that the thermal energy of a particle is given by $\mathcal{E} = \frac{3}{2}k_B T$, where k_B is Boltzmann constant.) The rest mass of a neutron, M_n , is approximately $1.7 \times 10^{-27} \text{ kg}$. Comment on why thermally excited neutrons are useful for probing the structure of crystals.

Problem 5.2 (Time Independent Schrödinger Equation): Assume that the wavefunction of a quantum particle can be written in the variable separable form

$$\psi(\mathbf{r}, t) = \hat{\psi}(\mathbf{r})T(t),$$

where T is a function of time only.

a. Show that

$$T(t) \propto e^{-i(E_0/\hbar)t}$$

(where $\mathcal{E}_o$ is the energy of the particle) and so the wavefunction becomes

$$\psi(\mathbf{r}, t) = \hat{\psi}(\mathbf{r}) e^{-i(\mathcal{E}_o/\hbar)t}.$$

- b. Show that when the wavefunction has the form given in part (a), it satisfies the *time independent Schrödinger equation*:

$$\mathcal{E}_o \hat{\psi}(\mathbf{r}) = -\frac{\hbar^2}{2m} \nabla^2 \hat{\psi}(\mathbf{r}) + V(\mathbf{r}) \hat{\psi}(\mathbf{r}).$$

When the quantum particle has a definite energy $\mathcal{E}_o$, it will satisfy this relation.

Problem 5.3 (Particle in a Box): Consider the situation where a particle of mass m has its motion constrained by a “box.” In other words, the particle can only move in the region from $x = 0$ to $x = a$. The particle is not subjected to any other potentials or constraints. As a result, the particle neither loses energy to nor receives energy from the walls of the box when it bounces off them.

- What is the possible time independent values of the particle’s energy under *classical* mechanics?
- What is the probability of finding the particle at the point x' (where $0 \leq x' \leq a$) under *classical* mechanics? Recall that the probability of a continuous variable, like x , implies that the particle lies in the interval $x + dx$.
- Solve part (a) under *quantum* mechanics. (Hint: Review Problem 5.2 for a statement of the time independent Schrödinger equation.)
- Solve part (b) under *quantum* mechanics.
- Discuss the limiting conditions for the quantum mechanical problem to appear classical.

Problem 5.4 (Tunneling Through a Barrier): Consider the time independent potential energy profile shown in Figure P5.1. Such a barrier is characteristic of an insulator

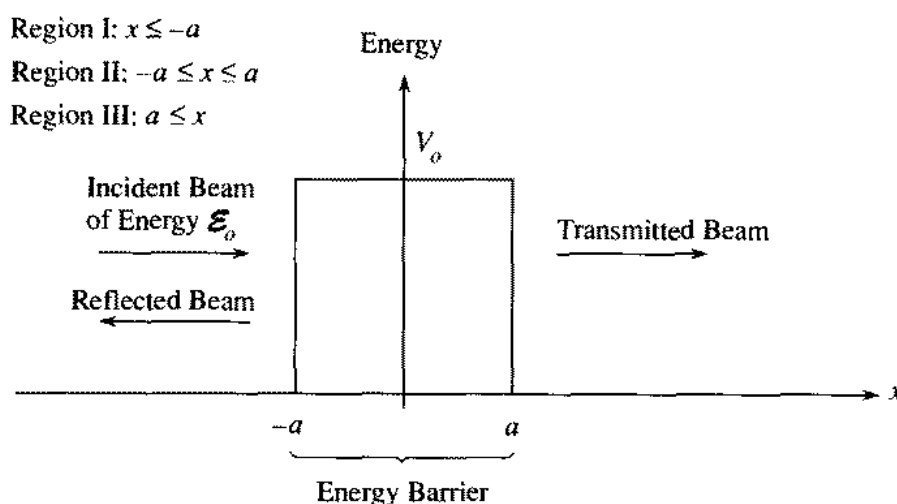


Figure P5.1 A Potential Barrier for the Incident Particles

sandwiched between two metallic conductors. Suppose a beam of electrons (a current) is incident on the barrier from the left. The energy of the beam is $\mathcal{E}_o$ where $\mathcal{E}_o < V_o$.

- a. Sketch the force associated with this potential. How does this force tend to push particles that are incident on the barrier?
- b. Treating the beam of electrons as a *classical* entity, find the ratio of the transmitted current to the incident current. (The transmitted current is that part of the beam that passes through the barrier.)

The answer obtained in part (b) is *not* observed experimentally. The reason is that the incident current beam is a *quantum mechanical* entity. We will assume that the energy of the beam of electrons is a constant. In other words, the particles will have a definite energy $\mathcal{E}_o$ whether they are in regions I, II, or III. Let us therefore solve this problem using the time independent Schrödinger equation (review Problem 5.2).

- c. Assume that the wavefunction of the incident particles is of the form

$$\psi_{\text{in}} = \hat{\psi}_{\text{in}} e^{i[\mathbf{k}_I \cdot \mathbf{r} - (\mathcal{E}_o/\hbar)t]}.$$

Since the quantum particles can “bounce” off the potential barrier and be reflected, the *total* wavefunction in region I is

$$\psi_I = \hat{\psi}_{\text{in}} e^{i[\mathbf{k}_I \cdot \mathbf{r} - (\mathcal{E}_o/\hbar)t]} + \hat{A} e^{-i[\mathbf{k}_I \cdot \mathbf{r} + (\mathcal{E}_o/\hbar)t]},$$

where $\hat{A}$ is the complex constant associated with the reflected wavefunction and will be determined by the boundary conditions. Write expressions for the wavefunctions in the other two regions, ψ_{II} and ψ_{III} . Find $\mathbf{k}_I$, $\mathbf{k}_{\text{II}}$, and $\mathbf{k}_{\text{III}}$ in terms of $\mathcal{E}_o$ and V_o . Leave the amplitudes of the waves as constants to be determined by the boundary conditions. Discuss the wavefunction in region II (the region of the potential) by comparing it to evanescent waves in electromagnetism. (Hint: Remember that $\mathcal{E}_o < V_o$.)

- d. In quantum mechanics, it is assumed that the wavefunction is continuous everywhere. What boundary condition does this imply across an interface? (Use the standard notation that the interface separates regions 1 and 2.)
- e. We can use the boundary condition from part (d) to deduce a second boundary condition on the wavefunction. Assuming that the external potential across the interface changes no more rapidly than a step (as is often the case), integrate the one-dimensional Schrödinger's equation to show that

$$\frac{\partial \psi_1}{\partial x} = \frac{\partial \psi_2}{\partial x}$$

across the interface.

- f. Use the boundary conditions found in parts (d) and (e) to solve for the complex constants obtained in part (c).
- g. Find the ratio of the transmitted current to the incident current. (Do not confuse the incident current with the *total* current in region I, which includes both incident and reflected parts.) How does the quantum mechanical result differ from the

classical one obtained in part (b)? (The quantum mechanical particles are said to have *tunneled* through the energy barrier.)

Problem 5.5: Prove Equation 5.60.

Problem 5.6: Starting with the second London equation and Lorentz's law, obtain the nonlinear first London equation. Notice that it is not necessary to use quantum mechanics to obtain this result.

Problem 5.7: In this problem, assume that the local density of the superfluid $n^*(\mathbf{r}, t)$ is *not* a constant in either space or time. Show that the imaginary part of the Schrödingerlike equation (Equation 5.65) is

$$\frac{\partial n^*}{\partial t} = -\nabla \cdot (n^* \mathbf{v}_s) .$$

Interpret this result physically. Multiply both sides of this relation by q^* and physically interpret the result. What is the constraint on $\mathbf{v}_s$ when n^* is a constant in both space and time?

Problem 5.8: Prove the energy-phase relationship (Equation 5.84) under the condition that the superelectron fluid density is constant in space and time.

Problem 5.9: The Bohr-Sommerfeld rule of quantization requires that

$$\oint_C \mathbf{p} \cdot d\mathbf{l} = nh ,$$

where $\mathbf{p}$ is the canonical momentum

$$\mathbf{p} = m\mathbf{v} + q\mathbf{A} .$$

n is an integer, and h is Planck's constant.

- Show that applying this quantization rule to the superelectron fluid immediately yields the statement of fluxoid quantization (Equation 5.111).
- Show that for the superfluid

$$\frac{d\mathbf{p}}{dt} = -\nabla \left(\frac{1}{2} m^* (\mathbf{v}_s \cdot \mathbf{v}_s) + q^* \phi \right) ,$$

where ϕ is the scalar potential needed to describe the electric field. (Hint: Use the nonlinear first London equation.) Show that this expression implies that the quantization does not change in time:

$$\frac{d}{dt} (n\Phi_0) = 0 .$$

Problem 5.10 (The London Gauge): As is well known from vector calculus, a vector is not completely specified until *both* its divergence and curl are known. As a result,

although the curl of the vector potential is defined ($\nabla \times \mathbf{A} = \mathbf{B}$), we are still free to specify its divergence. As with MQS problems, it is sometimes convenient to define

$$\nabla \cdot \mathbf{A}_L = 0,$$

which is known as the *London gauge*. (We will use the subscript “L” to remind us that we are specifying the gauge.) In addition, the London gauge is defined so that

$$\mathbf{A}_L \cdot \mathbf{n} = 0$$

where $\mathbf{n}$ is the normal to the superconducting surface.

- a. Suppose we pick a vector potential, $\mathbf{A}'_L$, which satisfies the bulk condition

$$\nabla \cdot \mathbf{A}'_L = 0$$

but *not* the boundary condition. As discussed in Section 5.4, we can transform $\mathbf{A}'_L$ into $\mathbf{A}_L$ via the relation

$$\mathbf{A}'_L = \mathbf{A}_L + \nabla \chi.$$

Find the appropriate bulk and boundary conditions on the scalar function χ .

- b. As shown in part (a), we can always adjust the vector potential to become $\mathbf{A}_L$. As a result, show that the phase in the London gauge satisfies the condition

$$\nabla^2 \theta_L = 0$$

in the bulk, and

$$\nabla \theta_L \cdot \mathbf{n} = \left(\frac{q^*}{\hbar} \Lambda \mathbf{J}_s \right) \cdot \mathbf{n}$$

at the boundary. (Assume that n^* is constant in space and time.) Show that $\nabla \theta_L$ is completely specified *within a simply connected region*.

- c. Argue that if the superconductor is isolated so that

$$\mathbf{J}_s \cdot \mathbf{n} = 0$$

everywhere on the boundary, the result of the London gauge is

$$\Lambda \mathbf{J}_s = -\mathbf{A}_L.$$

Notice that this expression is only valid in simply connected regions as discussed in part (b).