CHAPTER 2

THE PAIRING THEORY OF SUPERCONDUCTIVITY

In analogy with a free electron gas, normal (N) metals exhibit a single-particle excitation spectrum which, in the limit of a large system, is a continuum starting at zero energy. The degeneracy associated with this spectrum leads to the linear temperature dependence of the electronic specific heat near 0°K, and to the large electrical and thermal conductivities of these materials. In the superconducting (S) phase, the single-particle excitation is radically different from that of normal metals. In superconductors a minimum energy 2Δ, called the energy gap, is required to make a single-particle excitation from the ground state.

2-1 PHYSICAL NATURE OF THE SUPERCONDUCTING STATE

This qualitative difference in the excitation spectra is paralleled by a qualitative difference in the wave functions of the N- and S-phases of metals. In the N-phase, the probability that two single-particle states i and j are simultaneously occupied

is a smoothly varying function of the quantum numbers i and j. For example, in a pure single crystal, the expectation value

$$P_{kk'}{}^{N} = \langle N|n_{k\uparrow}n_{k'\downarrow}|N\rangle \tag{2-1}$$

is a smoothly varying function of $\mathbf{k}$ and $\mathbf{k}'$ (so long as one does not cross the Fermi surface in varying $\mathbf{k}$ or $\mathbf{k}'$). Here $|N\rangle$ represents a typical state in the normal phase and $n_{k\uparrow}$ is the operator which measures the number of electrons in $\mathbf{k}\uparrow$, etc. (see the Appendix). In the superconducting phase,[8] the corresponding probability

$$P_{kk'}{}^{S} = \langle S|n_{k\uparrow}n_{k'\downarrow}|S\rangle \tag{2-2}$$

is also a smoothly varying function of $\mathbf{k}$ and $\mathbf{k}'$ except when $\mathbf{k}$ and $\mathbf{k}'$ are related by the "pairing" condition. This condition states that for a given state $\mathbf{k}$, there exists a single mate $\bar{\mathbf{k}}$ such that the probability $P_{k\bar{k}}{}^{S}$ is larger than $P_{kk'}{}^{S}$ by a finite amount, for all states $\mathbf{k}'$ in the vicinity of $\bar{\mathbf{k}}$. This singular behavior of the two-particle correlation function, which has been stressed by Yang,[39] is no doubt the sort of picture F. London had in mind when he suggested that superconductivity is due to a condensation of the electrons in momentum space.[1] When proper account is taken of residual interactions conventionally neglected in the description of the normal state, these "pairing correlations" leading to superconductivity emerge in a natural manner. Above the superconducting transition temperature, the pairing correlations are broken up by thermal fluctuations and play no important role in the normal phase.

It is essential to realize at the outset that the lowering in energy of the S-phase due to interactions between mates (say $\mathbf{k}\uparrow$ and $\bar{\mathbf{k}}\downarrow$) of a given pair depends critically on the choice of mates ($\mathbf{k}'\uparrow$ and $\bar{\mathbf{k}}'\downarrow$) for other pairs. In fact, the energy gap and most of the observed properties of the superconducting phase would be *absent* were it not for strong correlations *between the pairs*. The reason for the simple BCS model working so well is that in real metals these pair–pair correlations are almost entirely due to Pauli principle restrictions rather than correlations due to true dynamical interactions between the pairs. This fact allows one to treat the system in lowest order as if dynamical interactions

existed *only between mates* of a pair. The pair–pair correlations would then be accounted for by working out this reduced problem consistently with Fermi–Dirac statistics so as to include the crucial Pauli principle correlations between the pairs. We shall call this scheme the pairing (or BCS) approximation.

For a translationally invariant system, we shall see that the pairing $(\mathbf{k}\uparrow, -\mathbf{k}\downarrow)$ of Bloch states leads to the lowest energy of the system. Supercurrent-carrying states are generated by translating this state of the system by an amount $\mathbf{q}/2$ in $\mathbf{k}$-space. The pairing would then be $(\mathbf{k}+\mathbf{q}/2\uparrow, -\mathbf{k}+\mathbf{q}/2\downarrow)$ and the electrons would have a net drift velocity $\mathbf{v}_d = \hbar\mathbf{q}/2m$. More generally, corresponding to each physical system and each state of that system there is a choice of pairing of single-particle states which minimizes the energy (or free energy, at finite temperature). For example, in a superconductor with nonmagnetic impurities present one should pair one-electron states φ_n which include the impurity scattering potential, as Anderson[40] first pointed out. He showed that one should pair a state φ_n and its time-reversed mate $\varphi_n{}^*$ to form the ground state of the system in this case. For a uniform hollow cylinder in the absence of a magnetic field, one would pair the state (n, m, k) with its time-reversed partner $(n, -m, -k)$, where n and m are the radial and azimuthal quantum numbers, respectively, and k is the wave number for motion along the axis of the cylinder. In the presence of a magnetic field, the best pairing depends on the thickness of the cylinder and the strength of the field. For a thickness $d \gg \lambda$ (the penetration depth) one would pair $(n, m+\nu, k)$ with $(n, -m+\nu, k)$ or $(n, m+\nu, k)$ with $(n, -m+\nu+1, k)$ depending on whether the flux trapped in the hole is an even or odd multiple of the flux quantum $hc/2e$, that is, $\nu hc/e$ or $(\nu+\frac{1}{2})hc/e$. As we shall see, these are the only allowed values of the flux trapped within a thick-walled superconducting cylinder. We shall study in detail these various possible pairings in later chapters when we apply the basic theory to physical problems.

While the above "pairing" approximation gives a good account of the single-particle excitation spectrum, there exist

collective modes, such as the plasmons, arising from residual interactions neglected within this approximation. In addition there may be small momentum exciton-like collective modes which lie within the gap. For larger momentum, the exciton states rise above the gap edge and pass into the continuum, thereby becoming heavily damped. The nature of the collective states and their effect on system properties is discussed in Chapter 8.

Also neglected within the simplest pairing approximation are damping effects. In the strong-coupling superconductors, such as lead and mercury, it is essential to include these effects on the same footing as the pairing correlations to obtain a reasonable description of these "bad actors."

The above discussion suggests that the excited states of a superconductor can be represented by a two-fluid model, one for the condensed electrons and one for the excitations. As we mentioned in the introduction, phenomenological two-fluid models (most notably the Gorter–Casimir model[2] and the Ginsburg–Landau model[36]) have played an extremely important role in laying the ground work for our present understanding of superconductivity. While there are important differences between the predictions of the pairing theory and the earlier two-fluid models, the theories share the basic idea that the superfluid electrons (i.e., the strongly correlated pairs in our case) can be described by a local density $\rho_s(\mathbf{r})$ and a local flow velocity $\mathbf{v}_s(\mathbf{r})$. The excited electrons then form an interpenetrating normal fluid which in local thermal equilibrium can be described by the local quantities $\rho_n(\mathbf{r})$ and $\mathbf{v}_n(\mathbf{r})$. As we shall see, the superfluid can only carry out potential flow, that is curl $\mathbf{v}_s(\mathbf{r}) = 0$, a condition emphasized by F. London.[1] (No such restriction holds for the normal fluid.) Many of the observed properties of superconductors can be understood in terms of a two-fluid model having a temperature-dependent energy gap for creating normal fluid (excitations) from the superfluid component.[16c] As we shall see, one can often interpret the results of the microscopic theory in terms of such a model.[9]

2-2 THE ONE-PAIR PROBLEM

To understand the origin and consequence of pairing correlations, it is helpful to consider the problem, first studied by Cooper,[41] of a pair of electrons interacting above a noninteracting Fermi sea of electrons via a velocity-dependent nonretarded two-body potential V. Thus, all but two of the electrons are assumed to be noninteracting. The background electrons enter the total problem only through the Pauli principle by blocking states below the Fermi surface from participating in the remaining two-particle problem. If we measure the kinetic energy ϵ_k relative to its value at the Fermi surface, only states with $\epsilon_k > 0$ are available to the interacting pair of electrons. Since the system is assumed to be translationally invariant and one neglects spin-dependent forces, the center-of-mass momentum $\hbar\mathbf{q}$ of the pair and the total spin S are constants of motion. The orbital wave function of the pair can then be written as

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \varphi_q(\boldsymbol{\rho})e^{i\mathbf{q}\cdot\mathbf{R}} \tag{2-3}$$

where the relative and center-of-mass coordinates are defined by $\boldsymbol{\rho} = \mathbf{r}_1 - \mathbf{r}_2$ and $\mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2)/2$, respectively. The relative coordinate wave function is symmetric for the singlet spin state ($S = 0$) and antisymmetric for the triplet states ($S = 1$). In the limit $\mathbf{q} \to 0$ the relative coordinate problem is spherically symmetric so that $\varphi(\boldsymbol{\rho})$ is an eigenfunction of angular momentum and can be labeled by the angular momentum quantum numbers l and m. For $\mathbf{q} \neq 0$, the component of angular momentum along $\mathbf{q}$ and parity remain good quantum numbers but l is no longer sharp.

For simplicity, we first consider the zero momentum states $\mathbf{q} = 0$, so that ψ can be expanded as

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \varphi(\boldsymbol{\rho}) = \sum_k a_k e^{i\mathbf{k}\cdot\boldsymbol{\rho}} = \sum_k a_k e^{i\mathbf{k}\cdot\mathbf{r}_1} e^{-i\mathbf{k}\cdot\mathbf{r}_2} \tag{2-4}$$

In (2-4), the sum is restricted to the available states ($\epsilon_k > 0$). Since the factors $e^{i\mathbf{k}\cdot\mathbf{r}_1}$ and $e^{-i\mathbf{k}\cdot\mathbf{r}_2}$ can be thought of as single-particle states of momentum $\mathbf{k}$ and $-\mathbf{k}$, we see that the pair wave function is a superposition of configurations in each of which a definite pair state ($\mathbf{k}$, $-\mathbf{k}$) is occupied.

To find the zero-spin eigenstates of the pair, we write Schrödinger's equation as

$$(W - H_0)\psi = V\psi \tag{2-5a}$$

and from (2-4) one has

$$(W - 2\epsilon_k)a_{\mathbf{k}} = \sum_{k'} V_{\mathbf{k}\mathbf{k}'}a_{\mathbf{k}'} \tag{2-5b}$$

where the matrix element $V_{\mathbf{k}\mathbf{k}'}$ is defined by

$$V_{\mathbf{k}\mathbf{k}'} = \langle \mathbf{k}, -\mathbf{k}|V|\mathbf{k}', -\mathbf{k}'\rangle \tag{2-6}$$

In Figure 2-1 a typical scattering process caused by V is illustrated.

While the Schrödinger equation (2-5b) cannot be analytically solved in general, the solution is immediate if $V_{\mathbf{k}\mathbf{k}'}$ is taken to be a factorizable potential $V_{\mathbf{k}\mathbf{k}'} = \lambda w_{\mathbf{k}'}{}^* w_{\mathbf{k}}$. More generally, if the system is isotropic $V_{\mathbf{k}\mathbf{k}'}$ can be expanded into its partial wave components

$$V_{\mathbf{k}\mathbf{k}'} = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} V_l(|\mathbf{k}|, |\mathbf{k}'|) Y_l{}^m(\Omega_{\mathbf{k}}) Y_l{}^{-m}(\Omega_{\mathbf{k}'}) \tag{2-7}$$

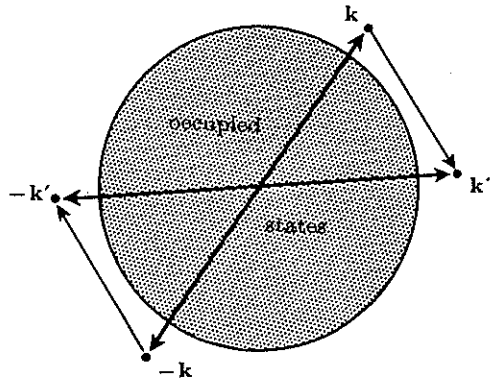

FIGURE 2-1 A typical transition occurring in Cooper's problem in which one pair of electrons interacts above a quiescent Fermi sea. The center-of-mass momentum of the pair is chosen to be zero in this drawing.

and the (l, m) eigenstates of the pair can be determined if V_l is taken to be factorizable,

$$V_l(|\mathbf{k}|, |\mathbf{k}'|) = \lambda_l w_k{}^l w_{k'}{}^{l*} \tag{2-8}$$

In this case we have from (2-5b)

$$(W_{lm} - 2\epsilon_k)a_k = \lambda_l w_k{}^l \sum_{k'} w_{k'}{}^{l*} a_{k'} \tag{2-9a}$$

where

$$a_{\mathbf{k}} = a_k Y_l{}^m(\Omega_{\mathbf{k}}) \tag{2-9b}$$

Equation (2-9a) can be written as

$$a_k = \frac{\lambda_l w_k{}^l C}{W_{lm} - 2\epsilon_k} \tag{2-10a}$$

where the constant C is defined as

$$C = \sum_{k'} w_{k'}{}^{l*} a_{k'} \tag{2-10b}$$

By substituting (2-10a) into the definition (2-10b) one obtains the equation

$$1 = \lambda_l \sum_k |w_k{}^l|^2 \frac{1}{W_{lm} - 2\epsilon_k} \equiv \lambda_l \Phi(W_{lm}) \tag{2-11}$$

determining the energy eigenvalues W_{lm}. If we work in a large but finite box the single-particle energies ϵ_k form a discrete set so that when W passes from below to above $2\epsilon_k$, $\Phi(W)$ jumps from $-\infty$ to ∞. As W moves toward the next higher value of $2\epsilon_k$, $\Phi(W)$ again approaches $-\infty$ and jumps to $+\infty$ as W passes through this higher value. The function $\Phi(W)$ is shown schematically in Figure 2-2. As W passes through the origin to negative values (i.e., the region of bound states) $\Phi(W)$ increases from $-\infty$ to zero as shown. The eigenvalues W_{lm} are given by the intersections of $\Phi(W)$ with the constant function $1/\lambda_l$, as shown for both positive (repulsive) and negative (attractive) λ_l. While the eigenvalues in the continuum are trapped between the unperturbed energies $2\epsilon_k$ and approach the unperturbed energies as the size of the box goes to infinity, a state is bound

split off from the continuum for an attractive l-wave potential, as shown in the figure. For the simple case

$$w_k{}^l = \begin{cases} 1 & 0 < \epsilon_k < \omega_c \\ 0 & \text{otherwise} \end{cases} \tag{2-12a}$$

and $\lambda_l < 0$, the binding energy $|W_{lm}|$ of the pair in the split-off state is given by

$$\frac{1}{|\lambda_l|} = \frac{N(0)}{2} \log \left[\frac{|W_{lm}| + 2\omega_c}{|W_{lm}|} \right] \tag{2-12b}$$

or

$$|W_{lm}| = \frac{2\omega_c}{\exp\left[\dfrac{2}{N(0)|\lambda_l|}\right] - 1} \tag{2-12c}$$

We have assumed the density of states $N(\epsilon_k)$ is slowly varying in the interval $0 < \epsilon_k < \omega_c$ and have approximated it by $N(0)$, the density of single-electron states of one-spin orientation, evaluated at the Fermi surface. From (2-12c) one has for weak coupling $[N(0)|\lambda_l| \ll 1]$

$$|W_{lm}| \cong 2\omega_c \exp\left[-\frac{2}{N(0)|\lambda_l|}\right] \tag{2-13a}$$

while for strong coupling $[N(0)|\lambda_l| \gg 1]$ one obtains

$$|W_{lm}| \simeq N(0)|\lambda_l|\omega_c \tag{2-13b}$$

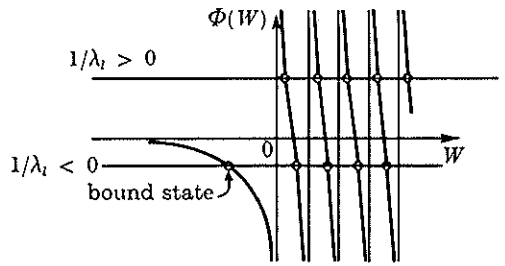

FIGURE 2-2 A plot of the function $\Phi(W)$ [see (2-11)] which determines the eigenenergies in Cooper's one-pair problem. For a repulsive interaction ($\lambda_l > 0$), all states are trapped in the continuum, while for an attractive interaction, a bound state is split off.

From (5-13a) we see that the binding energy is an extremely sensitive function of the coupling strength for weak coupling; however, a bound state exists for arbitrarily weak coupling so long as the potential is attractive near the Fermi surface. This important result was discovered by Cooper,[41] who suggested that the instability of the normal phase, because of pairs of electrons entering this type of bound state, was associated with the occurrence of the superconducting phase.

Earlier work of Schafroth, Blatt, and Butler (SBB)[42] is closely related to Cooper's discussion. Schafroth[43] had suggested that the superconducting state might correspond to a Bose–Einstein condensation of pairs of electrons into localized bound states. An attempt to develop a theory along these lines was made by SBB using what they call the quasi-chemical equilibrium approach for evaluating the partition function of the system. Owing to mathematical difficulties, they were not able to carry out calculations based on their general formulation for any model which exhibited superconducting properties. For a qualitative picture they suggested a model with localized pairs such that the size of the pair bound state is small compared to the average spacing between pairs. The bound pairs would presumably be capable of translational motion relative to the other pairs and one would obtain a continuum of Bose–Einstein excitations above the ground state without an energy gap, in contrast with the pairing theory. If the pairs were indeed well separated they could be treated as independent and Cooper's discussion would be appropriate. It should be pointed out, however, that, subsequent to the work of Bardeen, Cooper, and the author, Blatt and Matsubara extended the Bose condensation approach to give the results of the pairing theory.

Actual superconductors differ in a fundamental manner from a bound pair model in which the pairs are either well separated in space and/or weakly interacting. As we shall see below, there are on the average about one million bound pairs which have their centers of mass falling within the extent of a given pair function. Thus, rather than weakly overlapping pairs, one has just the reverse

limit, very *strongly* overlapping pairs. As we mentioned above, it is surprising that one can meaningfully treat such a system in zero order by including only dynamical interactions between mates of a pair and neglect all but the Pauli principle restrictions when treating interactions between the pairs. It is intended that the discussion below and in the following chapters will help clarify this point.

Returning to the one-pair problem of Cooper, it is interesting to see how the energy of the bound state varies with the center-of-mass momentum $\hbar\mathbf{q}$. If we assume only the s-wave ($l = 0$) part of V is important (as appears to be the case except for the crystalline anisotropy effects), one finds that the binding energy $W(\mathbf{q})$ satisfies

$$1 = |\lambda_0| \sum_{\mathbf{k}} \frac{1}{|W_q| - \epsilon_{\mathbf{k}+\mathbf{q}/2} - \epsilon_{\mathbf{k}-\mathbf{q}/2}} \tag{2-14}$$

where $|\mathbf{k} + \mathbf{q}/2|$ and $|\mathbf{k} - \mathbf{q}/2|$ are required to be greater than k_F, and the sum is to be cut off at $\epsilon_k = \omega_c$. For small q one finds

$$|W_q| = |W_0| - \frac{v_F \hbar q}{2} \tag{2-15}$$

where

$$|W_0| = \frac{2\omega_c}{\left\{\exp\left[\dfrac{2}{N(0)|\lambda_l|}\right] - 1\right\}}$$

as above. Thus, the pair energy increases linearly with the center-of-mass momentum in the limit $\mathbf{q} \to 0$, rather than as q^2, as one might expect. As Cooper pointed out, the drift of the pair with respect to the noninteracting Fermi sea strongly reduces the binding energy of the pair due to the reduced density of low-energy states available to the pair. This effect dominates the q^2 increase of kinetic energy for small q.

If $|W_0|$ is imagined to be of order kT_c, (2-15) shows that the pair would have lost most of its binding energy when

$$q \sim \frac{k_B T_c}{\hbar v_F} \sim \frac{k_B T_c}{E_F} k_F \sim 10^{-4} k_F \sim 10^4 \text{ cm}^{-1} \tag{2-16}$$

This number is roughly numerically equal to the reciprocal of

Pippard's coherence length $\xi_0 \sim 10^{-4}$ cm,[33] about which we shall have more to say. If one calculates the pair function $\varphi(\rho)$ from (2-4) and (2-10a) one finds the size of the bound state is of order ξ_0. Thus, one would be required to have an extremely small density of bound pairs if an isolated pair model were to be appropriate. In fact, the density would be so small that the predicted N–S energy difference at zero temperature would be many orders of magnitude too small to agree with experiment.

Thus far we have considered only the singlet spin state of the bound pair. If there is a strong attractive odd l potential, the triplet state will have the largest binding energy and one might expect the pairing in the superconducting state to be in a triplet state. There is no experimental evidence to support other than singlet pairing at present.

In closing this section we emphasize that the single-pair model exhibits a continuous spectrum above the ground state, without an energy gap.

2-3 LANDAU'S THEORY OF A FERMI LIQUID

Looking back at Cooper's argument, one might raise several objections to the conclusion that the bound state in the two-particle problem has anything to do with the occurrence of superconductivity. For example, one knows that Coulomb and phonon interactions between electrons in the normal state lead to a correlation energy of order one electron-volt per electron,[44] compared with the negligibly small binding energy $W \simeq 10^{-4}$ ev of a bound pair. Is it not possible that the strong correlations between all the electrons in the normal state will necessarily lead to fluctuations which break up the weakly bound state of a given pair of electrons? In addition, even if such a bound state could exist in a metal, would not the strong overlap of the pairs required to fit the observed condensation energy lead to interactions which would destroy the concept of bound pairs?

In answering the first objection, it is important to recognize that Landau's theory of a Fermi liquid[45] gives a good account of the low-lying single-particle excitations of the normal state. In

this theory, the excited states of a normal metal are placed in one-to-one correspondence with those of a free-electron gas. In Landau's theory, one asserts that the essential effect of the interactions between the electrons in the normal state of a metal is to shift the effective mass of an electron (now called a "quasi-particle") by an amount which is observed to be of order 10 to 50 per cent. An important feature of the theory is that a quasi-particle, as opposed to a "bare" electron, is a stable excitation in the immediate vicinity of the Fermi surface (at sufficiently low temperature). There is, however, a coupling between quasi-particles which arises from interactions neglected within this Fermi liquid approximation. This residual coupling leads to superconductivity.

The basis for Landau's theory has been extensively investigated and one knows that the theory is correct in all orders of perturbation theory[46] starting from the noninteracting system. The theory no doubt has a wider range of validity than that of the perturbation series itself, although its exact limitations are not known at present. Empirically, Landau's theory works very well in the normal state.

The remarkably small energy difference between the normal and superconducting states of a metal (10^{-8} ev per electron) strongly suggests that there is only a subtle shift of the electron–electron correlations between the two states. Since Landau's theory gives a good account of the normal state, it is reasonable to use the complete set of wave functions given by this theory as a basis for constructing the wave functions of the superconducting state. This procedure is particularly appealing because the superconducting wave functions primarily involve normal state configurations in which quasi-particle excitations are present only near the Fermi surface. However, these are just the configurations which are best described by the Landau theory. Therefore, Cooper's result is to be understood in the sense that his two-particle problem is actually a two-quasi-particle problem.

A difficulty with the above approach is that one knows little about the interaction between quasi-particles in the normal phase

from an experimental point of view. While the quasi-particle's effective mass involves the forward scattering amplitude of two quasi-particles, the effective mass also involves band-structure effects which are difficult to estimate accurately. More important is the fact that one needs the interaction for finite momentum and energy transfer so that one is forced to estimate the interaction theoretically. While this problem is not completely settled at present, it appears that one understands the essential features of the interaction, the remaining complications arising primarily from detailed crystalline effects (see Chapter 7).

In regard to the second objection mentioned above, it is true that the simple picture of bound pairs of electrons forming the ground state of the superconductor is impaired by their great overlap. Nevertheless there remains the strongly correlated occupancy of a given quasi-particle state (say $\mathbf{k}\uparrow$) with its mate (say $-\mathbf{k}\downarrow$) as in Cooper's problem. Interactions between quasi-particles which tend to break up this correlated occupancy are presumably already included in Landau's description of the normal state. Thus a simplified model in which one includes pairing correlations between otherwise noninteracting quasi-particles is not at the outset an unreasonable starting point. It is this point of view Bardeen, Cooper, and the author took in constructing the microscopic theory of superconductivity.

2-4 THE PAIRING APPROXIMATION

We saw above that for a translationally invariant normal system carrying no current, the $\mathbf{q} = 0$ pair state is the most unstable, in the sense that it is the pair with the largest binding energy W. In Chapter 7 a time-dependent treatment of the normal state instability is given and one finds the greatest growth rate is for $\mathbf{q} = 0$ pairs, in agreement with Cooper's result. Thus it is natural to solve the reduced problem in which interactions are considered only between electrons of opposite momentum. One hopes that the resolution of the strongest instability will modify the system so as to remove the $\mathbf{q} \neq 0$ pair instabilities as well. This is exactly what happens. We restrict our attention to pairing electrons of opposite spin orientation.

We shall use the formalism of second quantization to describe the interacting electron system; this scheme is reviewed in the Appendix. The creation and destruction operators for electrons of wavevector $\mathbf{k}$ and z-component of spin s ($\uparrow$ or $\downarrow$) are denoted by c_{ks}^{+} and c_{ks}, respectively. They satisfy the usual Fermi anticommutation rules. The Hamiltonian for the reduced problem of the $\mathbf{q} = 0$ pairs is

$$H_{\text{red}} = \sum_{ks} \epsilon_k n_{ks} + \sum_{kk'} V_{k'k} b_{k'}^{+} b_k \tag{2-17}$$

where the pairing matrix element $V_{k'k}$ is given by

$$V_{k'k} = \langle k', -k' | V | k, -k \rangle \tag{2-18}$$

and the operator b_k^{+} creates a pair of electrons in the single-particle states $k\uparrow$ and $-k\downarrow$, that is,

$$\begin{aligned} b_k^{+} &= c_{k\uparrow}^{+} c_{-k\downarrow}^{+} \\ b_k &= c_{-k\downarrow} c_{k\uparrow} \end{aligned} \tag{2-19}$$

This type of Hamiltonian forms the basis of the theory of superconductivity proposed by Bardeen, Cooper, and the author.[8] Further argument for concentrating on these particular interactions in describing the ground state and the low-lying excited states are given in the original paper by Bardeen, Cooper, and the author and in a review article by Bardeen and the author.[9] There it is argued, on the basis of phase-space considerations as well as effects due to the antisymmetry of the wave functions, that the $\mathbf{q} = 0$ pair state should be macroscopically occupied in cases where the superfluid momentum density is zero (although $\mathbf{v}_s$ need not be zero in the presence of magnetic fields). We expect the matrix element $V_{k'k}$ to be predominantly negative near the Fermi surface for superconductivity to occur. As we shall see in Chapter 7, this attraction is due to the ions overscreening the Coulomb repulsion, thereby reversing the sign of the effective interaction. While (2-17) is written in terms of bare single-particle operators c_{ks}, the reduced Hamiltonian can be formally viewed as a model Hamiltonian describing residual interactions ($V_{k'k}$) between the quasi-particles in the normal phase as discussed above. Since the pairing correlations constitute a fractional change of only $\sim 10^{-8}$ in the total correlation energy of a metal, it is clear that this more

liberal interpretation of H_{red} must be adopted. When the quasi-particle picture of the normal phase excitations is insufficient, as in lead and mercury, other techniques must be used in treating the superconducting phase (see Chapters 6 and 7). Note that the form of H_{red} depends upon the choice of pairing, as discussed in Section 2-1.

Since the pairing interaction maintains the pairing condition, it follows that the eigenstates of H_{red} can be labeled by those states $\mathbf{k}$, s which are occupied, their mates $-\mathbf{k}$, $-\mathbf{s}$ being unoccupied. This labeling of states leads to a one-to-one correspondence of the eigenstates of H_{red} with the eigenstates of a noninteracting Fermi gas (or the normal state). As we shall see, if excitations happen to be in states $\mathbf{k}\uparrow$ *and* $-\mathbf{k}\downarrow$, special care must be taken so that these configurations are properly orthogonal to the ground-state wave function.

It is clear that if V is attractive, the ground state of H_{red} has no pair state $(\mathbf{k}\uparrow, -\mathbf{k}\downarrow)$ occupied by a single electron. In this case the operator $n_{k\uparrow} + n_{-k\downarrow}$ can be replaced by $2b_k{}^+ b_k$ that is, twice the pair occupation number. The reduced Hamiltonian is then

$$H_{\text{red}}{}^0 = \sum_k 2\epsilon_k b_k{}^+ b_k + \sum_{k,k'} V_{k'k} b_{k'}{}^+ b_k \qquad (2\text{-}20)$$

It might be argued that eigenstates of $H_{\text{red}}{}^0$ follow immediately by forming new operators B_n which are linear combinations of the b_k's such that H_{red} is of the form $\sum_n \tilde{\epsilon}_n B_n{}^+ B_n$. This argument is incorrect. If the operators b_k and $b_k{}^+$ described true Bose particles (rather than pairs of fermions) the B_n's and $B_n{}^+$'s would also describe Bose particles and the ground state would be formed by placing all the bosons in the lowest state. Rather, one finds by direct calculation the commutation relations

$$[b_k, b_{k'}{}^+] = 0 \qquad \text{for } \mathbf{k} \neq \mathbf{k}' \qquad (2\text{-}21a)$$

$$[b_k, b_{k'}{}^+] = 1 - (n_{k\uparrow} + n_{-k\downarrow}) \qquad \text{for } \mathbf{k} = \mathbf{k}' \qquad (2\text{-}21b)$$

and

$$[b_k, b_{k'}] = 0 = [b_k{}^+, b_{k'}{}^+] \qquad (2\text{-}21c)$$

These are not of the form required by Bose–Einstein statistics. The factor $(n_{k\uparrow} + n_{-k\downarrow})$ in (2-21b) represents the effect of the

Pauli principle acting on the individual electrons forming the pair. Perhaps it is simplest to view the "pairon" operators b_k and $b_k{}^+$ as satisfying Bose–Einstein statistics for $\mathbf{k} \neq \mathbf{k}'$ and satisfying the Pauli principle $b_k{}^{+2} = 0 = b_k{}^2$ for $\mathbf{k} = \mathbf{k}'$. It is the latter relation which ruins a simple Bose gas picture.[47]

In attempting to find a variational estimate of the ground-state energy and wave function of H_{red}, the author tried to adapt the intermediate coupling approximation of Tomonaga, familiar in the coupled meson–nucleon problem and the polaron problem.[48, 49] In these problems one assumes that successive bosons (mesons or phonons) are emitted into the *same* orbital state (about the proton or the electron, respectively). The form of the orbital state φ and the weight A_N of the $N/2$ boson state are then determined by minimizing the system energy. Lee, Low, and Pines[49a] simplified the procedure for the polaron by assuming what is equivalent to a parameterized form for the weights A_N. Their wave function, after a canonical transformation has been made to eliminate the electron's coordinate from the problem, is

$$|\psi_0\rangle \alpha \prod_k e^{g_k(a_k{}^+ + a_{-k})}|0\rangle \qquad (2\text{-}22)$$

where the a^+'s are phonon creation operators. The function g_k is essentially the Fourier transform of the orbital wave function φ of the phonons surrounding the electron.

The application of this physical idea to superconductivity is complicated by several features. First, the "pairon" operators do not truly satisfy Bose statistics and, second, the number of electrons is a definite number N_0 in our system, rather than being a probability distribution $|A_N|^2$ of finite width about the value N_0. The author tried to describe the ground state of H_{red} by

$$|\psi_0\rangle \alpha \prod_k e^{g_k b_k{}^+}|0\rangle = \prod_k (1 + g_k b_k{}^+)|0\rangle \qquad (2\text{-}23)$$

where we have used the fact that $b_k{}^{+2} = 0$ in expanding out the exponential. The normalization integral is easily seen to be

$$\langle\psi_0|\psi_0\rangle = \prod_k (1 + |g_k|^2) \qquad (2\text{-}24)$$

so that

$$|\psi_0\rangle = \prod_k \frac{1 + g_k b_k^+}{(1 + |g_k|^2)^{1/2}} |0\rangle \tag{2-25}$$

is a properly normalized state. By expanding out the infinite product one sees that $|\psi_0\rangle$ has a nonvanishing amplitude for all even numbers of electrons, 0, 2, 4, ... However, by choosing g_k appropriately the mean number of particles described by $|\psi_0\rangle$ can be adjusted to be the required number N_0. As in the grand canonical ensemble, one can show that the width of the distribution is of order $N_0^{1/2}$ so that particle number fluctuations cause no difficulty in a large system.

Since we want to minimize the ground-state energy subject to the constraint

$$\langle\psi_0|N_{op}|\psi_0\rangle \equiv \langle\psi_0| \sum_{ks} n_{ks}|\psi_0\rangle = N_0 \tag{2-26}$$

we use the Lagrange multiplier scheme and minimize

$$\delta W = \delta\langle\psi_0|H_{red} - \mu N_{op}|\psi_0\rangle = 0 \tag{2-27}$$

On combining (2-20) and (2-27) one finds the quantity to be minimized is[8]

$$W = \sum_k 2(\epsilon_k - \mu)v_k^2 + \sum_{k,k'} V_{k'k} u_k v_k u_{k'} v_{k'} \tag{2-28}$$

where u_k and v_k are defined by

$$u_k = \frac{1}{(1 + g_k^2)^{1/2}} \tag{2-29a}$$

and

$$v_k = \frac{g_k}{(1 + g_k^2)^{1/2}} \tag{2-29b}$$

thus

$$u_k^2 + v_k^2 = 1 \tag{2-29c}$$

We have assumed phases are chosen so that $V_{k'k}$ and g_k are real quantities. On minimizing W one finds

$$u_k^2 = \frac{1}{2}\left(1 + \frac{\epsilon_k - \mu}{E_k}\right) \tag{2-30a}$$

$$v_k^2 = \frac{1}{2}\left(1 - \frac{\epsilon_k - \mu}{E_k}\right) \tag{2-30b}$$

and

$$u_k v_k = \frac{\Delta_k}{2E_k} \tag{2-30c}$$

where E_k is defined by

$$E_k = +[(\epsilon_k - \mu)^2 + \Delta_k^2]^{1/2} \tag{2-30d}$$

As we shall see, E_k turns out to be the energy required to create a quasi-particle of momentum $\mathbf{k}$ in the superconducting state. The "energy-gap" parameter Δ_k satisfies the integral equation

$$\Delta_k = -\sum_{k'} V_{kk'} \frac{\Delta_{k'}}{2E_{k'}} \tag{2-30e}$$

One must simultaneously solve (2-30e) and the constraint condition

$$\langle\psi_0|N_{op}|\psi_0\rangle = 2\sum_k v_k^2 = N_0 \tag{2-31}$$

to determine Δ_k and μ. If the single-particle energy ϵ_k is measured relative to the Fermi energy in the normal state, μ is just the shift of the chemical potential between the normal and superconducting states. For a system possessing particle-hole symmetry in the vicinity of the Fermi surface, one finds $\mu = 0$. In general, this is an excellent approximation and we shall assume $\mu = 0$ in solving for Δ_k. Once the energy-gap equation (2-30e) is solved, one can obtain the energy difference $W_N - W_S$ between the N- and S-states by inserting the expressions for u_k and v_k back into (2-28). An explicit solution of (2-30e) is easily obtained if $V_{kk'}$ is approximated by the s-wave potential

$$V_{kk'} \equiv \begin{cases} -V < 0 & \text{for } |\epsilon_k| \text{ and } |\epsilon_{k'}| < \omega_c \\ 0 & \text{otherwise} \end{cases} \tag{2-32}$$

so that $V_{kk'}$ is attractive in a shell of width $2\omega_c$ centered at the Fermi surface. In this case one finds

$$\Delta_k = \begin{cases} \Delta_0 & \text{for } |\epsilon_k| < \omega_c \\ 0 & \text{otherwise} \end{cases} \tag{2-33}$$

where

$$\Delta_0 = \frac{\omega_c}{\sinh\left[\frac{1}{N(0)V}\right]} \simeq 2\omega_c \exp\left[-\frac{1}{N(0)V}\right] \tag{2-34}$$

The right-hand equality holds in the weak-coupling limit $N(0)V \gtrsim \frac{1}{4}$. By substituting this result into the expression for the ground-state energy (2-28) and subtracting the ground-state energy of the normal phase (i.e., the unperturbed Fermi sea in this model) one finds the condensation energy

$$W_N - W_S = \frac{1}{2} N(0)\, \Delta_0{}^2 \cong 2N(0)\omega_c{}^2 \exp\left[-\frac{2}{N(0)V}\right] \quad (2\text{-}35)$$

Since thermodynamics[4] gives the relation

$$W_N - W_S = \frac{H_0{}^2}{8\pi} \quad (2\text{-}36)$$

where H_0 is the critical magnetic field for destroying superconductivity at zero temperature, we find

$$H_0 = 2[\pi N(0)]^{1/2}\, \Delta_0 \quad (2\text{-}37)$$

By using experimental values of $N(0)$ and Δ_0 one finds values of H_0 which are in reasonably good agreement with experiment.[9, 16]

We note that the condensation energy (2-35) is not an analytic function of the coupling constant $N(0)V$ so that a perturbation treatment starting from the normal phase could not give this result unless one sums an infinite number of graphs of a selected class.[50]

Returning to the ground-state wave function (2-23), we would expect on the basis of the Tomonaga scheme that the projection of $|\psi_0\rangle$ onto the N-particle space would lead to a function (in the coordinate representation) of the form

$$\langle r_1, s_1; r_2, s_2; \cdots r_N, s_N|\psi_0\rangle \equiv \psi_{0N}$$
$$= \mathscr{A}\varphi(\mathbf{r}_1 - \mathbf{r}_2)\chi_{12}\varphi(\mathbf{r}_3 - \mathbf{r}_4)\chi_{34}\cdots\varphi(\mathbf{r}_{N-1} - \mathbf{r}_N)\chi_{N-1,N} \quad (2\text{-}38)$$

The function φ is the relative coordinate wave function of a pair (*the same function for all pairs*) and χ_{ij} is corresponding spin function $\uparrow(i)\downarrow(j)$. Thus within the pairing approximation all pairs are in the *same* state in the ground-state wave function. The operator $\mathscr{A}$ in (2-38) antisymmetrizes the entire function.

This result, first noted by Dyson, can be obtained by taking the inner product of $|\psi_0\rangle$ with the basis vector

$$|\mathbf{r}_1, s_1; \mathbf{r}_2, s_2; \cdots \mathbf{r}_N, s_N\rangle = \psi_{s_1}{}^+(\mathbf{r}_1)\psi_{s_2}{}^+(\mathbf{r}_2)\cdots\psi_{s_N}{}^+(\mathbf{r}_N)|0\rangle$$

and expanding the ψ^+'s in terms of the creation operators $c_{ks_i}{}^+$ by

$$\psi_{s_i}{}^+(\mathbf{r}_i) = \sum_k e^{-i\mathbf{k}\cdot\mathbf{r}_i} c_{ks_i}{}^+ \quad (2\text{-}39)$$

The N-particle state (2-38) has been discussed by Blatt[51a] in the case where φ is a general function of $\mathbf{r}_1$ and $\mathbf{r}_2$. This generalization corresponds to considering pairings between states other than $\mathbf{k}\uparrow$ and $-\mathbf{k}\downarrow$.

The orbital function φ in (2-38) is given by

$$\varphi(\boldsymbol{\rho}) = \sum_k g_k e^{i\mathbf{k}\cdot\boldsymbol{\rho}} \quad (2\text{-}40)$$

thus g_k is the Fourier transform of $\varphi(\boldsymbol{\rho})$, as stated above. While there is a formal similarity between (2-38) and the wave function for a condensed Bose–Einstein gas of pairs of electrons with opposite spin, the antisymmetrization operator $\mathscr{A}$ is all important in real superconductors. In fact, the (unnormalized) ground state of the noninteracting Fermi gas can be written in this form with

$$g_k = \begin{cases} 1 & |k| < k_f \\ 0 & |k| \gtrless k_f \end{cases} \quad (2\text{-}41)$$

so that antisymmetrization removes the correlations between opposite spin electrons implied by φ in this case. In the superconducting state g_k differs from (2-41) only for values of $\mathbf{k}$ in the immediate vicinity of the Fermi surface. This difference is reflected in a long-range tail of $\varphi(\boldsymbol{\rho})$ which increases the probability of two antiparallel spin electrons being near each other out to a range $\xi_0 \equiv \hbar v_F/\pi\Delta_0 \sim 10^{-4}$ cm, that is, Pippard's coherence length. As we mentioned above, this quasi-bound state has such a long range in space that on the average about 10^6 other pairs have their centers of mass in this region. [In this estimate electrons deep within the Fermi sea have not been counted since they behave essentially as if the material were in the normal phase.] Thus an isolated pair picture has little meaning here.

2-5 QUASI-PARTICLE EXCITATIONS

To find the excited states of the BCS reduced Hamiltonian (2-17) we consider adding an electron to the system in the state $\mathbf{p}\uparrow$ (its mate $-\mathbf{p}\downarrow$ being empty). The only effect of this process is to block the pair state ($\mathbf{p}\uparrow$, $-\mathbf{p}\downarrow$) from participating in the pairing interaction (due to the Pauli principle). Since $-\mathbf{p}\downarrow$ is assumed to be empty, the electron in $\mathbf{p}\uparrow$ cannot be scattered out of this state, due to the form of the pairing interaction (2-20). Of course, residual interactions not explicitly included in H_{red} will allow this process to take place; however, these interactions appear to have a small effect on the excitation spectrum (since they are implicitly included in the quasi-particles of the normal state).

The quasi-particle energy is defined to be the total excitation energy of the system when the extra electron is added to the system. From (2-28) we see that by deleting the pair state ($\mathbf{p}\uparrow$, $-\mathbf{p}\downarrow$), the energy of the interacting pairs is increased by

$$-2\epsilon_p v_p^2 - 2\Big[\sum_{k'} V_{pk'} u_{k'} v_{k'}\Big] u_p v_p \tag{2-42}$$

To this we must add the single-particle energy ϵ_p of the added electron. The total excitation energy is given by

$$\epsilon_p[1 - 2v_p^2] + 2\Delta_p u_p v_p \tag{2-43}$$

where we have used the gap equation (2-30e) to simplify the interaction energy term. If we use the results (2-30) for u_k and v_k (with $\mu = 0$), we find the excitation energy

$$W_{p\uparrow} - W_0 = \frac{\epsilon_p^2}{E_p} + \frac{\Delta_p^2}{E_p} = E_p \tag{2-44}$$

Thus, the parameter E_p defined by (2-30c) is just the energy required to create a quasi-particle in state $\mathbf{p}\uparrow$. A plot of E_p vs. $\mathbf{p}$ is given in Figure 2-3. The minimum energy required to add an electron to the system is $\Delta_{k_f} \equiv \Delta_0 \sim 10^{-3} - 10^{-4}$ ev. In principle the chemical potential μ should be shifted a small amount to ensure $\langle N\rangle = N_0 + 1$ in the excited state; however, this correction has negligible effect in a large system.

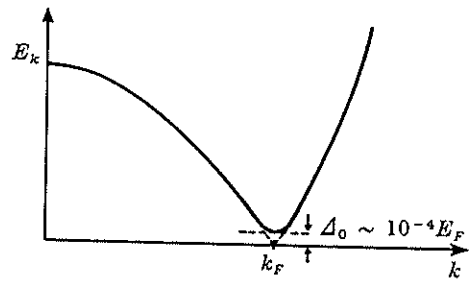

FIGURE 2-3 The quasi-particle energy E_k in the superconducting state plotted as a function of the wavevector $\mathbf{k}$. The energy $E_k = (\epsilon_k^2 + \Delta_k^2)^{1/2}$ differs from the corresponding energy $|\epsilon_k|$ of the normal state only in the vicinity of the Fermi surface. The energy gap observed in experiments which do not inject or withdraw electrons from the system is $2\Delta_0$, a minimum energy Δ_0 being required to create each quasi-particle produced in a one-electron transition. Note: All energies are measured with respect to the Fermi energy.

In the above calculation, nothing has been said about $\mathbf{p}$ being above (or below) the Fermi surface. Since the pairing interactions smooth out the jump in the single-particle occupation numbers $\langle n_k\rangle$ in the normal phase at the Fermi surface, as shown in Figure 2-4, there is a finite probability of being able to add an electron to the system in a state p below the Fermi surface. The excitation energy is positive in this case as it is for $|\mathbf{p}| > p_f$. In an analogous way one can calculate the energy required to remove an electron in the state $\mathbf{p}\uparrow$ from the ground state. One again finds the energy $E_p(>0)$ regardless of whether $|\mathbf{p}|$ is greater or less than the Fermi momentum.

Therefore, the minimum energy required to create a single-particle-like excitation from the superconducting ground state is $2\Delta_0$, Δ_0 for removing an electron from one state and Δ_0 for placing it in another state.

It is important to realize that the states created by *adding* an electron to $|\psi_{0N}\rangle$ in state $\mathbf{p}\uparrow$ or *removing* an electron from state $-\mathbf{p}\downarrow$ in $|\psi_{0N}\rangle$ are *identical* within the pairing approximation except that the number of superfluid pairs in the two states differs by unity. If instead of $|\psi_{0N}\rangle$ we work with the state $|\psi_0\rangle$

(2-23), which represents an ensemble of ground-state wave functions averaged over systems with $\cdots N-2, N, N+2\cdots$ particles, these two states generated by $c_{p\uparrow}^{+}$ and by $c_{-p\downarrow}$ are truly identical, aside from a normalization factor. This result is established by noting that

$$\begin{aligned} c_{p\uparrow}^{+}|\psi_0\rangle &= c_{p\uparrow}^{+}\prod_k (u_k + v_k b_k^{+})|0\rangle \\ &= u_p c_{p\uparrow}^{+}\prod_{k\neq p}(u_k + v_k b_n^{+})|0\rangle \qquad (2\text{-}45a) \\ &\equiv u_p|\psi_{p\uparrow}\rangle \end{aligned}$$

and

$$\begin{aligned} c_{-p\downarrow}|\psi_0\rangle &= c_{-p\downarrow}\prod_k (u_k + v_k b_k^{+})|0\rangle \\ &= -v_p c_{p\uparrow}^{+}\prod_{k\neq p}(u_k + v_k b_k^{+})|0\rangle \qquad (2\text{-}45b) \\ &= -v_p|\psi_{p\uparrow}\rangle \end{aligned}$$

where $|\psi_{p\uparrow}\rangle$ is the normalized one-quasi-particle state

$$|\psi_{p\uparrow}\rangle = c_{p\uparrow}^{+}\prod_{k\neq p}(u_k + v_k b_k^{+})|0\rangle \qquad (2\text{-}46)$$

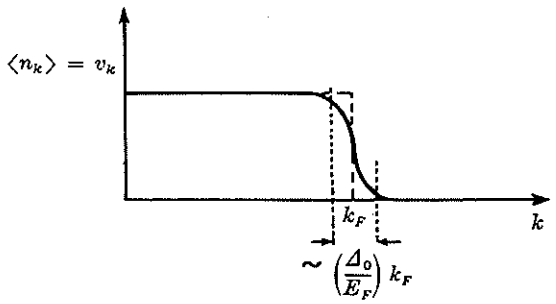

FIGURE 2-4 A plot of the average occupation number $\langle n_k\rangle$ of the Bloch states in the superconducting state if one makes a single-particle model for the normal state. The occupation number in the normal state, shown here as 1 for $k < k_F$ and 0 for $k > k_F$, is also rounded due to normal state interactions, although a discontinuity of $\langle n_k\rangle$ presumably remains. The "smearing" of the Fermi surface by the pairing correlations occurs only over a range $\sim 10^{-4}k_F$ about the Fermi surface.

An important mathematical simplification occurs if one considers the linear combination

$$\gamma_{p\uparrow}^{+} = u_p c_{p\uparrow}^{+} - v_p c_{-p\downarrow} \qquad (2\text{-}47a)$$

of the two equivalent operators. From (2-45) we see that $\gamma_{p\uparrow}^{+}$ applied to $|\psi_0\rangle$ creates the normalized state $|\psi_{p\uparrow}\rangle$,

$$\gamma_{p\uparrow}^{+}|\psi_0\rangle = |\psi_{p\uparrow}\rangle \qquad (2\text{-}47b)$$

The orthogonal combination

$$\gamma_{-p\downarrow} = u_p c_{-p\downarrow} + v_p c_{p\uparrow}^{+} \qquad (2\text{-}48a)$$

when applied to $|\psi_0\rangle$ leads to the null-state vector (not to be confused with the vacuum $|0\rangle$)

$$\gamma_{-p\downarrow}|\psi_0\rangle = 0 \qquad (2\text{-}48b)$$

The relations (2-47a) and (2-48a), and their Hermitian conjugates

$$\gamma_{p\uparrow} = u_p c_{p\uparrow} - v_p c_{-p\downarrow}^{+} \qquad (2\text{-}49a)$$

$$\gamma_{-p\downarrow}^{+} = u_p c_{-p\downarrow}^{+} + v_p c_{p\uparrow} \qquad (2\text{-}49b)$$

were introduced independently by Bogoliubov[52] and by Valatin.[53] These relations are known as the B–V transformation. As the notation suggests $\gamma_{p\uparrow}^{+}$ and $\gamma_{-p\downarrow}^{+}$ create quasi-particles in states $p\uparrow$ and $-p\downarrow$, respectively, while $\gamma_{p\uparrow}$ and $\gamma_{-p\downarrow}$ destroy quasi-particles in these states. Thus one has the relations

$$\gamma_{p\uparrow}^{+}|\psi_0\rangle = |\psi_{p\uparrow}\rangle \qquad (2\text{-}50a)$$

$$\gamma_{-p\downarrow}^{+}|\psi_0\rangle = |\psi_{-p\downarrow}\rangle \qquad (2\text{-}50b)$$

$$\gamma_{p\uparrow}|\psi_0\rangle = 0 \qquad (2\text{-}50c)$$

$$\gamma_{-p\downarrow}|\psi_0\rangle = 0 \qquad (2\text{-}50d)$$

The last two relations are equivalent to the statement that $|\psi_0\rangle$ is the vacuum state for quasi-particles. It follows by direct computation that the quasi-particle operators satisfy Fermi–Dirac statistics:

$$\{\gamma_{ps}, \gamma_{p's'}^{+}\} = \delta_{pp'}\,\delta_{ss'} \qquad (2\text{-}51a)$$

$$\{\gamma_{ps}, \gamma_{p's'}\} = \{\gamma_{ps}^{+}, \gamma_{p's'}^{+}\} = 0 \qquad (2\text{-}51b)$$

and can be thought of as leading to excitations that form a weakly interacting Fermi gas.

It is important to remember that the γ and γ^+'s must operate on the ensemble-averaged states, e.g., $|\psi_0\rangle$, not on the N-particle projection of these states $|\psi_{0N}\rangle$. If one thinks of $\gamma_{p\uparrow}{}^+$ as acting on an N-particle state, it would appear that a quasi-particle is a linear combination of a particle and a hole. This is *not* correct. In the N-particle system a quasi-particle of momentum $\mathbf{p}$ and spin s is nothing more than an electron definitely occupying the state $\mathbf{p}$, s with its mate $-\mathbf{p}$, $-s$ being definitely empty. In configuration space, the $N+1$ particle wave function corresponding to $|\psi_{p\uparrow}\rangle$ is

$$\psi_{p\uparrow}(\mathbf{r}_1, s_1; \cdots \mathbf{r}_{N+1}, s_{N+1}) = \mathscr{A}\varphi'(\mathbf{r}_1 - \mathbf{r}_2)\chi_{12}\varphi'(\mathbf{r}_3 - \mathbf{r}_4)\chi_{34}\cdots \varphi'(\mathbf{r}_{N-1} - \mathbf{r}_N)\chi_{N-1,N}\exp(i\mathbf{p}\cdot\mathbf{r}_{N+1})\uparrow_{N+1} \quad (2\text{-}52)$$

where $\varphi'(\rho)$ is given by (2-40) with the term $\mathbf{k} = \mathbf{p}$ deleted. For some purposes it is convenient to discuss the excitation in terms of the empty state $-\mathbf{p}$, $-s$ and call the excitation a "hole." In other cases one prefers to concentrate on the occupied state $\mathbf{p}$, s. The wave function for the pair state $(\mathbf{p}\uparrow, -\mathbf{p}\downarrow)$ is the same in either case regardless of the words used to describe it. However, one must keep in mind that the number of superfluid pairs differs by unity in the two descriptions of the same state.

An excited state having quasi-particles in $\mathbf{k}_1 s_1$, $\mathbf{k}_2 s_2 \cdots \mathbf{k}_n s_n$ is given by

$$|\psi_{k_1 s_1, k_2 s_2, \cdots k_n s_n}\rangle = \gamma_{k_1 s_1}{}^+ \gamma_{k_2 s_2}{}^+ \cdots \gamma_{k_n s_n}{}^+ |0\rangle \quad (2\text{-}53)$$

The excitation energy is $E_{k_1 s_1} + E_{k_2 s_2} + \cdots E_{k_n s_n}$. The Bogoliubov–Valatin operators have the important property that the excited state

$$|\psi_{p\uparrow, -p\downarrow}\rangle = \gamma_{p\uparrow}{}^+ \gamma_{-p\downarrow}{}^+ |\psi_0\rangle \quad (2\text{-}54)$$

is orthogonal to the ground state. This is not true if one generates the excitations by applying $c_{p\uparrow}{}^+ c_{p\downarrow}{}^+$ to $|\psi_0\rangle$. In the original BCS treatment these doubly excited pair states (called "real" pairs as opposed to the "virtual" pairs occurring in the ground state) were treated separately and were represented by the factor

$$(v_p - u_p b_p{}^+) \quad (2\text{-}55)$$

in the wave function. However, this is just the factor one obtains by expressing the γ^+'s in (2-54) in terms of the c and c^+'s and simplifying the factors involving $b_p{}^+$ in the wave function.

It has been shown by several groups[54] that for H_{red} the variational solutions for $|\psi_0\rangle$ and the quasi-particle spectrum are exact in the limit of a large system so long as the number of excitations present is small compared to the number of electrons participating in the pairing interactions. In the next section we shall see how these results are generalized to finite temperature where the latter condition is not satisfied.

2-6 LINEARIZED EQUATIONS OF MOTION

In the original work of Bardeen, Cooper, and the author a complete discussion of the thermodynamic properties of the superconducting state was carried out within the pairing approximation. As for $T = 0$, their treatment of the system described by H_{red} is exact in the limit of large volume. In agreement with experiment, they obtained a second-order phase transition at T_c and an exponentially vanishing electronic specific heat for $T \lesssim \frac{1}{2}T_c$. For a discussion of this work and its comparison with experiment, the reader is referred to the original BCS paper[8] and to a review article by Bardeen and the author.[9]

Rather than repeating the BCS finite-temperature treatment, we would like to illustrate an alternative procedure based on a linearization of the equations of motion for the single-particle operators $c_{p\uparrow}{}^+$ and $c_{-p\downarrow}$. The discussion follows closely a treatment given by Valatin,[55] and leads to results identical to those of BCS.

To fix ideas, we begin with the reduced Hamiltonian (2-24)

$$H_{\text{red}} = \sum_{k,s} \epsilon_k n_{ks} + \sum_{k,k'} V_{k'k} b_{k'}{}^+ b_k \quad (2\text{-}17)$$

(although, owing to our approximations, the scheme gives essentially the same results if the full two-body interaction is considered). The basic idea is to find eigenoperators, say $\mu_\alpha{}^+$ and μ_β, which satisfy

$$[H_{\text{red}}, \mu_\alpha{}^+] = \Omega_\alpha \mu_\alpha{}^+ \quad (2\text{-}56a)$$

and the Hermitian conjugate relation

$$[H_{\text{red}}, \mu_\beta] = -\Omega_\beta \mu_\beta \tag{2-56b}$$

where the Ω's are positive quantities. It follows that the eigenoperators $\mu_\alpha{}^+$ and μ_β create and destroy excitations of the system since by applying the operator equation (2-56b) to the ground state $|\psi_0\rangle$ of H_{red} we find

$$[H_{\text{red}}, \mu_\alpha{}^+]|\psi_0\rangle = (H_{\text{red}} - W_0)\mu_\alpha{}^+|\psi_0\rangle = \Omega_\alpha \mu_\alpha{}^+|\psi_0\rangle \tag{2-57}$$

Thus $|\psi_\alpha\rangle \equiv \mu_\alpha{}^+|\psi_0\rangle$ is an eigenstate of H_{red} with excitation energy Ω_α. In an analogous manner one finds that μ_β lowers the energy of the system by Ω_β, from which it follows that the ground state (or the excitation vacuum) satisfies

$$\mu_\beta|\psi_0\rangle = 0 \tag{2-58}$$

for all β. Operators which approximately satisfy (2-56) presumably give an approximate description of the excitations. Except in extremely simple systems, the exact operators $\mu_\alpha{}^+$ can neither be found nor are of great interest since physically interesting probes (i.e., external fields, injected particles, etc.) create complicated superpositions of such excitations (see Chapter 5).

Suppose we try to find an operator which adds a quasi-particle of momentum $\mathbf{p}$ and spin $\uparrow$ to the ground state of H_{red}. The simplest fermion operator which will add this momentum and spin to the system is $c_{p\uparrow}{}^+$, so we try

$$[H_{\text{red}}, c_{p\uparrow}{}^+] = \epsilon_p c_{p\uparrow}{}^+ + \sum_{k'} V_{k'p} b_{k'}{}^+ c_{-p\downarrow} \tag{2-59}$$

In the absence of the interaction $c_{p\uparrow}{}^+$ satisfies (2-56a) with the excitation energy $\Omega_\alpha = \epsilon_p$. The "excitation" energy is just the energy required to add an electron to the system in state $\mathbf{p}$. In the presence of V, $c_{p\uparrow}{}^+$ is no longer an eigenoperator. In fact we must go out of the operator subspace of $c_{k\uparrow}{}^+$ and include products of the forms c^+cc in constructing $\mu_\alpha{}^+$. When this more complicated guess for $\mu_\alpha{}^+$ is commuted with H_{red}, still higher order polynomials in c^+ and c appear. In most cases the series continues on to infinite order, just as the series of equations determining the Green's functions, which are discussed in Chapter 5. To obtain a tractable problem we must cut off the chain at a certain order by approximating the commutators. Whether the termination is meaningful clearly depends on the physics of the problem. Fortunately, the interactions in H_{red} are sufficiently simple that one can cut off the series by including in a sense only a linear combination of c and c^+.

By taking matrix elements of (2-59) between the N-particle ground state $|0, N\rangle$ and the $N+1$ particle state $|p\uparrow, N+1\rangle$ with one quasi-particle present in state $p\uparrow$, we have

$$\begin{aligned}(\Omega_{p\uparrow} - \epsilon_p)&\langle p\uparrow, N+1|c_{p\uparrow}{}^+|0, N\rangle \\ &= \sum_{\alpha, k'} V_{k'p}\langle p\uparrow, N+1|c_{-p\downarrow}|\alpha, N+2\rangle\langle\alpha, N+2|b_{k'}{}^+|0, N\rangle\end{aligned} \tag{2-60}$$

where the sum is over the eigenstates of the $N+2$ particle system. If we measure all energies relative to the chemical potential, $\mu = \lim_{n/N\to 0}(W_{0,N+n} - W_{0,N})/n$, where $n \gg 1$, $\Omega_{p\uparrow}$ is the energy required to add a quasi-particle in $\mathbf{p}\uparrow$ to $|0, N\rangle$. We argue that for a large system the intermediate state sum is given by retaining only the $N+2$ particle ground state. It is not that the matrix elements of $b_{k'}{}^+$ for all other α are small compared to the one for $\alpha = 0$, but as we shall see the matrix element of $c_{-p\downarrow}$ entering the equation is small when the $\alpha \neq 0$ matrix element of $b_{k'}{}^+$ is large, and therefore the product is negligible. Thus (2-60) becomes

$$(\Omega_p - \epsilon_p)F_p = \sum_k V_{kp} B_k G_p \tag{2-61}$$

where

$$F_p = \langle p\uparrow, N+1|c_{p\uparrow}{}^+|0, N\rangle \tag{2-62a}$$

$$G_p = \langle p\uparrow, N+1|c_{-p\downarrow}|0, N+2\rangle \tag{2-62b}$$

$$B_k = \langle 0, N+2|b_k{}^+|0, N\rangle \tag{2-62c}$$

Another relation between F and G can be obtained by taking the matrix element of $(H_{\text{red}}, c_{-p\downarrow})$ between the states $|0, N+2\rangle$ and $|p\uparrow, N+1\rangle$. If the intermediate state sum is again replaced by the single term $\alpha = 0$, one finds

$$(\Omega_p + \epsilon_p)G_p = \sum_k V_{kp} B_k F_p \tag{2-63}$$

where we have chosen phases so that all quantities are real. The secular equation for (2-61) and (2-63) is

$$\begin{vmatrix} \Omega_p - \epsilon_p & \Delta_p \\ \Delta_p & \Omega_p + \epsilon_p \end{vmatrix} = \Omega_p^2 - \epsilon_p^2 - \Delta_p^2 = 0 \qquad (2\text{-}64)$$

where the parameter Δ_p is defined by

$$\Delta_p = -\sum_k V_{kp} B_k \qquad (2\text{-}65)$$

(The matrix element B_k is still to be determined.) From equation (2-64) we find the (positive) excitation energy Ω_p of the state $|p\uparrow, N+1\rangle$ is given by

$$\Omega_p = +(\epsilon_p^2 + \Delta_p^2)^{1/2} \equiv E_p \qquad (2\text{-}66)$$

The negative energy root $-E_p$ corresponds to the process in which a quasi-particle in the time-reversed state $-\mathbf{p}\downarrow$ is destroyed. The eigenoperators $\mu_\alpha^+ \equiv \gamma_{p\uparrow}^+$ and $\mu_\beta \equiv \gamma_{-p\downarrow}$ corresponding to the positive and negative energy solutions are of the form

$$\gamma_{p\uparrow}^+ = u_p c_{p\uparrow}^+ - v_p c_{-p\downarrow} R^+ \qquad (2\text{-}67a)$$

and

$$\gamma_{-p\downarrow} = u_p c_{-p\downarrow} + v_p R c_{p\uparrow}^+ \qquad (2\text{-}67b)$$

The operator R^+ transforms a given state in an N-particle system into the corresponding state in the $N+2$ particle system; thus

$$R^+|0, N\rangle = |0, N+2\rangle \qquad (2\text{-}68)$$

and

$$R^+|k, s; N\rangle = |k, s; N+2\rangle$$

while

$$R|0, N+2\rangle = |0, N\rangle, \text{ etc.}$$

By inserting the eigenvalues back into (2-61) or (2-63) and requiring that the γ^+ and γ's satisfy Fermi anticommutation relations it follows that u_p and v_p are given by

$$u_p^2 = \frac{1}{2}\left(1 + \frac{\epsilon_p}{E_p}\right) \qquad (2\text{-}69a)$$

$$v_p^2 = \frac{1}{2}\left(1 - \frac{\epsilon_p}{E_p}\right) \qquad (2\text{-}69b)$$

$$u_p v_p = \frac{\Delta_p}{2E_p} \qquad (2\text{-}69c)$$

The formal similarity between these results and those of the last section is complete if we require that $|0, N\rangle$ be the ground state of the system, that is,

$$\gamma_{p\uparrow}|0, N\rangle = 0 \qquad (2\text{-}70a)$$

and

$$\gamma_{-p\downarrow}|0, N\rangle = 0 \qquad (2\text{-}70b)$$

Thus, the γ^+'s create noninteracting fermion excitations from the "vacuum state" $|0, N\rangle$.

By inverting (2-67a), (2-67b), and their Hermitian conjugates to solve for the c-operators in terms of the γ's, one finds from the definition of B_k (2-62c) the relation

$$B_k = u_k v_k = \frac{\Delta_k}{2E_k} \qquad (2\text{-}71)$$

On combining this result with the definition of Δ_p (2-65) we find an equation determining the parameter Δ_p:

$$\Delta_p = -\sum_k V_{kp} \frac{\Delta_k}{2E_k} \qquad (2\text{-}72)$$

which is just the energy-gap equation (2-30e). Thus the excitation energies are identical in the two approaches and the quasi-particle operators differ only by the presence of R.[56]

As in the BCS treatment, it is straightforward to generalize these results to finite temperature. The only change is that instead of the ground state $|0, N\rangle$ appearing one has a typical state $|T, N\rangle$ excited at the temperature T. All goes through as above except for the relation (2-71). For $T \neq 0$ one has

$$B_k = \langle T, N+2|b_k^+|T, N\rangle = \frac{\Delta_k}{2E_k}(1 - f_{k\uparrow} - f_{-k\downarrow}) \qquad (2\text{-}73)$$

where f_{ks} is the expectation value of the quasi-particle occupation number $\gamma_{ks}^+\gamma_{ks}$ in the state $|T, N\rangle$. Since the quasi-particles are essentially independent fermions (whose properties change

slowly with temperature) f_{ks} is given by the Fermi distribution function

$$f_{ks} = \frac{1}{e^{\beta E_k} + 1} \qquad (E_k > 0) \tag{2-74}$$

and

$$B_k = \frac{\Delta_k}{2E_k} \tanh \frac{\beta E_k}{2} \tag{2-75}$$

By inserting this result into (2-65) we obtain the finite-temperature BCS gap equation

$$\Delta_p = -\sum_k V_{kp} \frac{\Delta_k}{2E_k} \tanh \frac{\beta E_k}{2} \tag{2-76}$$

This finite-temperature treatment of the pairing theory is entirely equivalent to the BCS treatment, which, as we mentioned above, gives an exact account of the system described by the reduced Hamiltonian (in the limit of large volume). If V_{kp} is approximated by (2-32), Δ_k is again of the form (2-33) where $\Delta_0(\beta)$ satisfies

$$\frac{1}{N(0)V} = \int_0^{\omega_c} \frac{d\epsilon}{(\epsilon^2 + \Delta_0^2)^{1/2}} \tanh \left[\frac{\beta}{2}(\epsilon^2 + \Delta_0^2)^{1/2}\right] \tag{2-77}$$

As T increases from zero, Δ_0 decreases as shown in Figure 2-5, vanishing at the transition temperature T_c. Thus, T_c is given by

$$\frac{1}{N(0)V} = \int_0^{\omega_c} \frac{d\epsilon}{\epsilon} \tanh \left[\frac{\epsilon}{2k_B T_c}\right] \tag{2-78}$$

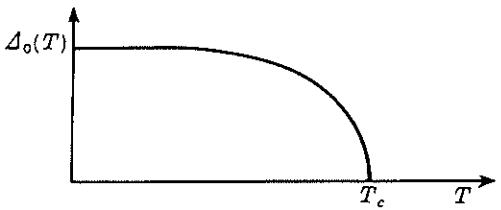

FIGURE 2-5 A plot of the temperature dependence of the energy-gap parameter $\Delta_0(T)$. Note that Δ_0 vanishes with infinite slope as $T \to T_c$, leading to the second-order phase transition.

In the weak-coupling limit this gives

$$k_B T_c = 1.14\omega_c \exp\left[-\frac{1}{N(0)V}\right] \tag{2-79}$$

so that the ratio $2\Delta_0(T = 0)/k_B T_c$ is 3.52 in this limit. While this ratio is in reasonably good agreement with experiment for weak-coupling superconductors,[9,16] the ratio is too small to account for the observed ratio for lead and mercury. It now appears that temperature-dependent damping effects account for the discrepancy.[57]

The free energy of the superconducting state

$$F_s = W_s - TS \tag{2-80}$$

can be obtained by calculating the expectation value of H_{red} with respect to the typical state $|T, N\rangle$ and using the standard expression

$$S = -2k_B \sum_k \{f_k \log f_k + (1 - f_k) \log (1 - f_k)\} \tag{2-81}$$

for the entropy of the quasi-particle (normal) fluid, where f_k is given by (2-74). The energy W_s is easily seen to be[8]

$$W_s = 2\sum_k |\epsilon_k| \left[f_k + \frac{1}{2}\left(1 - \frac{|\epsilon_k|}{E_k}\right) \tanh \frac{\beta E_k}{2}\right] + \sum_k \frac{\Delta_k^2}{2E_k} \tanh \frac{\beta E_k}{2} + 2 \sum_{|k| < k_F} \epsilon_k \tag{2-82}$$

The bulk critical magnetic field $H_c(T)$ is given by

$$\frac{H_c^2}{8\pi} = F_N(T) - F_S(T) \tag{2-83}$$

where the free energy of the normal state $F_N(T)$ is given by (2-80), (2-81), and (2-82) with $\Delta_k = 0$. H_0 is plotted in Figure 2-6 for the potential (2-32). The electronic specific heat can be calculated from

$$c_{es} = 2k_B \beta^2 \sum_k f_k(1 - f_k) \left[E_k^2 + \frac{\beta}{2} \frac{d\,\Delta_k^2}{d\beta}\right] \tag{2-84}$$

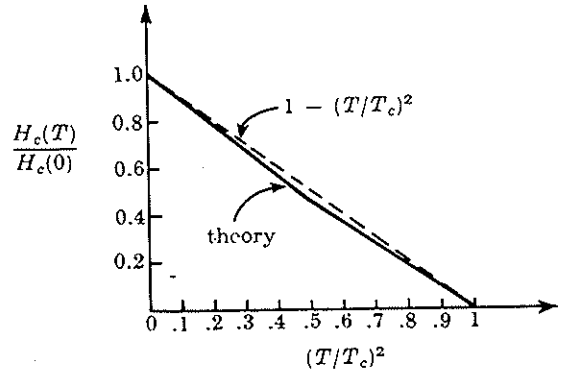

FIGURE 2-6 A plot of the critical magnetic field versus temperature.

and is plotted in Figure 2-7. The jump of the electronic-specific heat at T_c is due to Δ^2 being proportional to $(T_c - T)$ near T_c so that the derivative in (2-84) is discontinuous at T_c.

The reader is referred to the literature[9, 16] for a detailed discussion of the thermodynamic properties of the system.

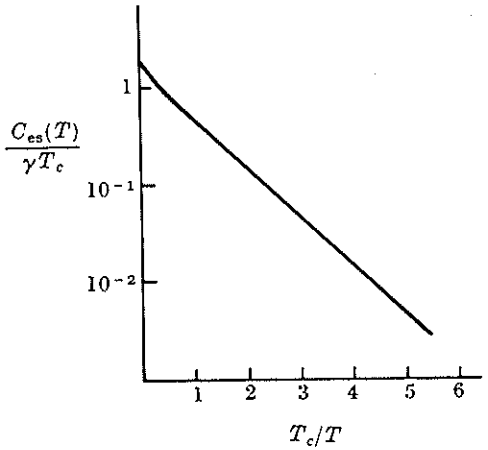

FIGURE 2-7 A plot of the electronic-specific heat as a function of T_c/T.

2-7 CONCLUDING REMARKS

Before closing this chapter we would like to make a few remarks.

1. While there is a formal similarity between the ground state (2-38) of H_{red} and a condensed Bose–Einstein gas, the analogy must be used with care due to the strong overlap of the pair functions. As a result of this overlap the excitation spectrum in real metals exhibits an energy gap rather than a continuous spectrum characteristic of a Bose gas. If the treatment is extended to include the interactions neglected in H_{red} and one assumes all interactions to be of short range, a continuous boson spectrum, starting at zero energy appears in the energy gap corresponding to density fluctuations in the electron system. In real metals these low-lying boson modes are pushed up to the plasmon energy ($\sim 10^4 \times 2\Delta_0$) due to the long-range Coulomb interaction between electrons so that there are no low-lying boson modes except for dressed lattice vibrations (phonons) in cases of physical interest.[58]

2. The discussion in this chapter has emphasized states for which the momentum density of the superfluid is zero, i.e., the pairing $(k\uparrow, -k\downarrow)$ was treated. If the Hamiltonian of the electron system were Galilean-invariant, states with finite superfluid momentum could be formed by translating the zero-momentum eigenfunction by an amount $\mathbf{q}/2$ in momentum space. The transformed wave function would be

$$\exp\left(\frac{i}{2}\sum_{j=1}^{N}\mathbf{q}\cdot\mathbf{r}_j\right)\psi_0(\mathbf{r}_1s_1, \mathbf{r}_2s_2, \ldots \mathbf{r}_Ns_N)$$
$$= \mathcal{A}\varphi(\mathbf{r}_1 - \mathbf{r}_2)\exp\left[\frac{i\mathbf{q}\cdot(\mathbf{r}_1 + \mathbf{r}_2)}{2}\right]\uparrow_1\downarrow_2$$
$$\times \cdots\varphi(\mathbf{r}_{N-1} - \mathbf{r}_N)\exp\left[\frac{i\mathbf{q}\cdot(\mathbf{r}_{N-1} + \mathbf{r}_N)}{2}\right]\uparrow_{N-1}\downarrow_N \quad (2\text{-}85)$$

so that the "center-of-mass" wave function of a pair would go from the $\mathbf{q} = 0$ state to the plane wave state of momentum $\mathbf{q}$. For states involving mass flow of this sort, a condensed Bose gas picture may be helpful; however, one must be cautious in using

this picture in detailed calculations. In particular since the fixed ions will create a magnetic field in the moving frame, the function φ will change its form. Also, if the wavevector $\mathbf{q}$ varies appreciably over a coherence length ξ_0 the separation into center-of-mass and relative coordinates is of questionable value.

3. We have concentrated on singlet spin pairing with φ being an s-state in the absence of crystal anisotropy. The problems of triplet spin pairing and $l \neq 0$ orbital states have been treated by a number of authors[59] and we refer the reader to the literature for a discussion of these questions. In addition, pairing of states other than Bloch functions can be easily handled, since the basic scheme does not rely on the form of the states being paired.

4. In Section 2-2 we saw that not only the $\mathbf{q} = 0$ pairs are unstable if we consider fluctuations about the normal state, but the $q \neq 0$ pairs are also unstable. In Chapter 8 we investigate the stability of the ground state $|\psi_0\rangle$ given by the pairing approximation. As mentioned above, there are no unstable pair fluctuations about this state. This result is due to the finite energy required to create from the superfluid the quasi-particles which one tries to bind together by the residual interactions.

5. In Section 2-6 we stated that the matrix element $\langle \alpha, N+2|b_k{}^+|0, N\rangle$ is large not only for the $N+2$ particle ground state $|0, N+2\rangle$ but that there is another state α giving a large matrix element. Specifically, the two-quasi-particle state $|k\uparrow, -k\downarrow, N+2\rangle$ gives

$$|\langle k\uparrow, -k\downarrow, N+2|b_k{}^+|0, N\rangle| = u_k{}^2 = \frac{1}{2}\left(1 + \frac{\epsilon_k}{E_k}\right) \tag{2-86}$$

compared to the matrix element

$$|\langle 0, N+2|b_k{}^+|0, N\rangle| = u_k v_k = \frac{\Delta_k}{2E_k} \tag{2-87}$$

which we retained. For $\mathbf{k}$ on the Fermi surface, both of matrix elements are equal to $1/(2)^{1/2}$. However, the matrix element $\langle p\uparrow, N+1|c_{-p\downarrow}|k\uparrow, -k\downarrow, N+2\rangle$ which multiplies (2-86) in (2-60) is zero since $c_{-p\downarrow}$ does not affect the quasi-particles in $k\uparrow$ and $-k\downarrow$. On the other hand, the matrix element $\langle p\uparrow, N+1|c_{-p\downarrow}|0, N+2\rangle$ which multiplies (2-87) in (2-60) is equal to $-v_p$ which is $1/(2)^{1/2}$ for $\mathbf{p}$ on the Fermi surface. Therefore we are justified in retaining the single term $\alpha = 0$ in the intermediate state sum.

6. While the ground-state wave function $|\psi_0\rangle$ [see (2-25)] represents an ensemble average of ground-state wave functions $|\psi_{0N}\rangle$ for systems having an even number of electrons,

$$|\psi_0\rangle = \sum_{N(\text{even})} A_N|\psi_{0N}\rangle \tag{2-88}$$

we can obtain $|\psi_{0N}\rangle$ from $|\psi_0\rangle$ if A_N is arranged to be of the form $|A_N|e^{iN\varphi}$. Then

$$|\psi_0{}^\varphi\rangle = \sum_{N(\text{even})} |A_N|e^{iN\varphi}|\psi_{0N}\rangle \tag{2-89}$$

and

$$|A_{N'}|\,|\psi_{0N'}\rangle = \frac{1}{2\pi}\int_0^{2\pi} e^{-iN'\varphi}|\psi_0{}^\varphi\rangle\, d\varphi \tag{2-90}$$

By our choice of phases (2-32) is just $|\psi_0{}^0\rangle$ so that $|\psi_0{}^\varphi\rangle$ is given by

$$|\psi_0{}^\varphi\rangle = \prod_k (u_k + e^{2i\varphi}v_k b_k{}^+)|0\rangle \tag{2-91}$$

that is, a factor of $e^{i\varphi}$ is contributed by each creation operator c^+. Therefore the normalized N' particle ground state is given by

$$|\psi_{0N'}\rangle = \frac{1}{2\pi|A_{N'}|}\int_0^{2\pi} e^{-iN'\varphi}\prod_k (u_k + e^{2i\varphi}v_k b_k{}^+)|0\rangle\, d\varphi \tag{2-92}$$

where the amplitude of the N' particle state is given by

$$|A_{N'}|^2 = \frac{1}{2\pi}\int_0^{2\pi} e^{-iN'\varphi}\prod_k (u_k{}^2 + e^{2i\varphi}v_k{}^2)\, d\varphi \tag{2-93}$$

The probability $|A_{N'}|^2$ is sharply peaked about the average number N_0, having a width[60] of the order of $N_0{}^{1/2}$. The fact that the average energy $\langle\psi_0{}^\varphi|H_{\text{red}}|\psi_0{}^\varphi\rangle$ is independent of φ should not be interpreted as a degeneracy of the ground state of a physical N particle system. Since the $N-2$, N, $N+2, \ldots$ particle systems are completely independent, the average energy of these

systems should be independent of the relative phase of their wave functions.

For a large system, whether the physical system has an even or an odd total number of electrons makes no difference in its macroscopic properties; thus the wave functions above apply for any N. The situation is distinctly different for pairing correlations in atomic nuclei, where these differences lead to the well-known even–odd effects.[61]

CHAPTER 3

APPLICATIONS OF THE PAIRING THEORY

Since the BCS theory was originally proposed, attempts to justify the pairing correlations basic to the theory have proceeded along two lines. The first approach has been to apply the BCS theory to a wide variety of phenomena in superconductors and check the theoretical predictions of the pairing approximation against experiment. The second approach has been to treat by various approximate methods the residual interactions neglected within the pairing scheme, hoping to show that these residual interactions introduce no major change in the predicted properties of the system. Both approaches have enjoyed considerable success. Owing to the remarkably good agreement between the pairing theory and a broad class of experimentally observed phenomena, it would appear that the first approach has successfully established the validity of the pairing concept upon which the theory is based.[9, 16]

3-1 JUSTIFICATION OF THE PAIRING HYPOTHESIS

In this chapter we shall follow the first approach and review the calculation of a number of system properties within the pairing