

vapor pressure to 25 atm, the density increases by about 15% and, at 1.25°K, the sound velocity increases from 237 m/sec to 365 m/sec. From Eq. (36) it follows that this increase in the value of u may be attributed to the rise in E_0 as close packing density is approached. Since ρ varies by such a small amount, it is most reasonable to choose ρ_0 and c to fit the mean experimental values of u and $du/d\rho$. For $c=2.16$ Å and $\rho_0=\frac{1}{2}\rho$, the calculated and measured values of u agree to within a few percent. These values of ρ_0 and c are close to those estimated by Parry and ter Haar² on the basis of the theory of Brueckner and Sawada.¹

IV. CONCLUSIONS

The Padé approximant P_2^2 gives a good qualitative representation of E_0 for all densities and by choice of very plausible values of ρ_0 can be made to give quite

accurate numerical results. To estimate the accuracy of the approximation within the framework of the method itself, it would be necessary to go to sixth-order perturbation theory in order to compare P_3^3 with P_2^2 .

However, the results from fourth-order perturbation theory are sufficiently encouraging to suggest that it would be worthwhile to calculate the energy spectrum in the same way and to introduce the true interaction between helium atoms.

ACKNOWLEDGMENTS

Part of this work was carried out while two of the authors (V.J.E. and J.L.G.) were visitors in the Theoretical Physics Division at A.E.R.E. Harwell, England and they wish to acknowledge the hospitality of Dr. W. Marshall.

Fluxoid Quantization, Pair Symmetry, and the Gap Energy in the Current-Carrying Bardeen-Cooper-Schrieffer State*†

MURRAY PESHKIN

Argonne National Laboratory, Argonne, Illinois

(Received 20 May 1963)

The method of Byers and Yang is extended for application to the current-carrying BCS state by including the magnetic interaction between electrons in the zero-order Hamiltonian. In the case of a thin superconducting ring, the problem is reduced to the zero-current problem by separating out the collective motion. In the general case, this process is not carried out completely, but the symmetry of the BCS state provides enough information to obtain the desired results. When the fluxoid is equal to an integral multiple of $(\pi\hbar c/e)$, the single-particle states occur in pairs which go into each other under reflection about the average electron velocity at each point. A qualitative argument is given to show why this symmetry is necessary for the BCS reduced interaction to have its full effectiveness. The crux of the matter is that in the absence of such symmetry, the Fermi surface is irregular and a substantial fraction of the important states near that surface are unable to participate in a coherent BCS wave function. The Meissner effect is not necessary for the quantization of magnetic flux.

1. INTRODUCTION

THE atomic theory of Bardeen, Cooper, and Schrieffer^{1,2} (BCS) provides a generally satisfactory description of the zero-current state in a superconductor. However, in dealing with the supercurrent state, in which the magnetic interaction between the electrons is of the first importance, it has customarily been necessary to resort to phenomenological methods. The atomic understanding of the zero-resistance, or

persistent-current phenomenon, remains, in this respect, incomplete or at best obscure. Thus, the fact that the trapped flux threading a superconducting ring is quantized in multiples of $(\pi\hbar c/e)$ had to be discovered experimentally,^{3,4} although it is in reality a simple consequence of the BCS theory.

The connection between flux quantization and the BCS theory was first explained by Byers and Yang.⁵ These authors consider a ring superconductor whose thickness is much greater than its penetration depth, so that the Meissner effect is complete. They exclude the surface regions, where the currents actually flow, from

* Work performed under the auspices of the U. S. Atomic Energy Commission.

† This work was reported briefly at the St. Louis Meeting of the American Physical Society [M. Peshkin, *Bull. Am. Phys. Soc.* **8**, 191 (1963)].

¹ J. Bardeen, L. M. Cooper, and J. R. Schrieffer, *Phys. Rev.* **108**, 1175 (1957).

² N. N. Bogoliubov, V. V. Tolmachev, and D. V. Shirkov, *A New Method in the Theory of Superconductivity* (Consultants Bureau, Inc., New York, 1959).

³ B. S. Deaver, Jr., and W. M. Fairbank, *Phys. Rev. Letters* **7**, 43 (1961).

⁴ R. Doll and M. Nabauer, *Phys. Rev. Letters* **7**, 51 (1961).

⁵ N. Byers and C. N. Yang, *Phys. Rev. Letters* **7**, 46 (1961). Similar results were obtained by J. M. Blatt, *Progr. Theoret. Phys. (Kyoto)* **26**, 721 (1961).

their dynamical treatment. In their work, the magnetic effect due to the surface currents is represented by an externally fixed magnetic field of which a flux Φ threads the ring. In this way, they avoid the necessity of describing the supercurrent itself.

The flux Φ enters the Hamiltonian for free electrons in the deep region, where there is no magnetic field, through the centrifugal term

$$T_C = \frac{1}{2mr^2} \left(l\hbar - \frac{e}{2\pi c} \Phi \right)^2, \quad (1.1)$$

where Φ is expressed in Gaussian units. The integer l is the canonical angular-momentum quantum number.⁶ Byers and Yang consider states of a noninteracting Fermi gas, in which the single-particle states are associated in pairs for which

$$l+l' = q, \quad (1.2)$$

where q is a fixed integer. They show that the energy of the lowest such state depends upon Φ in the manner illustrated in Fig. 1. The heavy curve then gives the lowest states of the type considered, irrespective of the value of q . The minima of the heavy curve occur at the special flux values

$$\Phi = \frac{1}{2}n(2\pi\hbar c/e), \quad (1.3)$$

where n is an integer.

The flux values (1.3) are precisely the ones for which the single-particle states occur in degenerate pairs, which have equal but opposite angular velocities and thus contribute equally to T_C of Eq. (1.1). Byers and Yang assert that the BCS interaction is more effective when the zero-order states are pairwise degenerate than when they are not. It follows that when interaction is included, the minima of the ground-state energy occur for the same flux values (1.3). However, the ripples in the ground-state energy are enhanced by a quantity of the order of magnitude of the BCS gap energy. Surface currents that correspond to the desired flux values (1.3) then lead to an energy for the deep region which is substantially less than the energy for nearby current values. The surface region, whose own energy is negligible, must adjust its current to provide the quantized flux values. Byers and Yang observe that the Meissner effect is an essential ingredient of their theory, since degeneracy is present only if Φ has one of the desired values independently of the radial variable r .

More recently, Bohr and Mottelson⁷ have investigated the stability of the states corresponding to the quantized flux values. These authors give a rough indication of how the method of Byers and Yang may

⁶ The effects of quantization of angular momentum in the presence of a magnetic field from which the electrons are excluded are discussed by M. Peshkin, I. Talmi, and L. J. Tassie, *Ann. Phys. (N. Y.)* **12**, 426 (1961) and by L. J. Tassie and M. Peshkin, *ibid.* **16**, 177 (1961).

⁷ A. Bohr and B. R. Mottelson, *Phys. Rev.* **125**, 495 (1962).

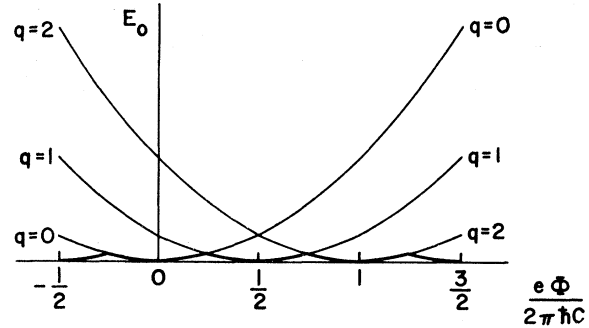


FIG. 1. Lowest energy of a noninteracting Fermi gas made from pairs of states whose total angular momentum (z component) is equal to $q\hbar$, as a function of the enclosed flux Φ . The heavy curve shows the lowest such state irrespective of the value of q .

be used to describe the current-carrying region itself, provided that the superconductor is much thicker than its penetration depth. They introduce, as a perturbation, a self-consistent magnetic field. Even if the wave function is unchanged, it then represents a current-carrying state. Since the flux $\Phi(r)$ out to radius r is not constant, there can be no exact degeneracy of pairs of l values. However, if the superconductor is thick, the Meissner effect guarantees that $\Phi(r)$ is constant over most of the volume. Bohr and Mottelson argue that near-degeneracy is enough to provide the desired minima of the ground-state energy at the appropriate values of the circulating current.

The purpose of the research reported here is to clarify the supercurrent-state relations among flux values, pair degeneracy, the Meissner effect, and the gap energy. In Sec. 2, the method of Byers and Yang is applied to a very thin superconducting ring, where there is no Meissner effect and the current-carrying region is the whole superconductor. The magnetic interaction between electrons is treated exactly by putting it into the zero-order Hamiltonian from the outset. It emerges that the zero-order energy (now magnetic as well as kinetic) is a smooth function of the circulating current, with no preference for any particular flux values. However, for values of the fluxoid⁸ equal to $\frac{1}{2}n(2\pi\hbar c/e)$, the single-particle states appear in pairs which are symmetrically disposed about the average current. That is, each pair contributes equally to the total current and to the total angular momentum. The form of the current-carrying BCS wave function is discussed briefly.

The relation between the gap energy and the symmetry of pairs is discussed in Sec. 3. It is shown that the Fermi surface is rough, more like a golf ball than a sphere, in the absence of pair symmetry with respect to the average angular momentum per particle. A qualitative discussion is given to show that this lack of smoothness of the Fermi surface substantially reduces the effectiveness of the BCS reduced interaction.

⁸ F. London, *Superfluids* (Dover Publications, Inc., New York, 1961), Vol. I.

The case of a superconductor of arbitrary thickness is considered in Sec. 4. There no detailed treatment is attempted. However, it is demonstrated that quantization of the fluxoid is exactly equivalent to symmetry of pairs with respect to the local average electron velocity. In this section, it is assumed that the magnetic interaction is approximated by a self-consistent field, but not that it is a small perturbation.

Consideration is limited to the ground state throughout. The electron spin is ignored except in Sec. 4.

2. PAIRING MODEL IN A THIN RING

Let N spinless electrons move in a long cylindrical shell of radius a . The thickness of the shell is supposed to be negligible compared with all other lengths of interest, but still great enough to accommodate many nodes in the radial wave functions. An externally fixed magnetic field in the direction of the cylinder (z) axis threads the cylinder, the flux being Φ_e . The electrons are at first supposed to be free particles, except that their motion is influenced by Φ_e and by the flux Φ_s induced by the circulation of other electrons. In calculating Φ_s , cylindrical symmetry is maintained by smearing the charge of each electron uniformly over the surface of the cylinder. This smearing is only a convenience. It would result from the self-consistent field approximation even if it were not a feature of the original model.

The classical Hamiltonian for the zero-order model described, the irrelevant radial and axial variables being neglected, is

$$\mathcal{H}_0 = \frac{1}{2ma^2} \sum_k \left[L_k - \frac{e}{2\pi c} (\Phi_e + \Phi_s) \right]^2 + \frac{N\gamma}{2ma^2} \left(\frac{e\Phi_e}{2\pi c} \right)^2. \quad (2.1)$$

The canonical orbital angular momentum of the k th electron has its z component equal to L_k . The positive constant γ , defined by

$$\gamma = mc^2/\sigma e^2, \quad (2.2)$$

where σ is the number of electrons per unit length of cylinder and m is the effective mass of the electron, has magnitude unity or less in practical cases.

The external flux Φ_e enters Hamiltonian (2.1) as a number. However, the induced flux Φ_s must be regarded as a function of the dynamical variables L_k . This function can be determined from the Maxwell equation

$$\nabla \times \mathbf{B} = 4\pi \mathbf{j}/c, \quad (2.3)$$

which in the cylindrical case becomes

$$\Phi_s = 2\pi a^2 (\sigma e/Nc) \sum_k \omega_k. \quad (2.4)$$

The angular velocity ω_k of the k th electron is given by

$$\omega_k = \frac{1}{ma^2} \left[L_k - \frac{e}{2\pi c} (\Phi_e + \Phi_s) \right]. \quad (2.5)$$

Equations (2.4) and (2.5) may be combined to give the "source equation"

$$\frac{e\Phi_s}{2\pi c} = \frac{1}{N(1+\gamma)} \sum_k \left[L_k - \frac{e\Phi_e}{2\pi c} \right], \quad (2.6)$$

which is now taken as the formal definition of the symbol Φ_s in the Hamiltonian (2.1).

That \mathcal{H}_0 is indeed the correct Hamiltonian for the model described, with Φ_s defined by Eq. (2.6), may be verified by using

$$\omega_k = \partial \mathcal{H}_0 / \partial L_k \quad (2.7)$$

to derive (2.5). The first term of (2.1) is then seen to represent the sum of the kinetic energies of the electrons, while the second term represents the energy in the induced magnetic field. This magnetic term contains spurious diagonal contributions introduced by squaring expression (2.6) for Φ_s . These spurious terms result only in a self-interaction of each electron and might be summarized by a negligible shift in the effective mass m .

The zero-order Hamiltonian (2.1) describes an independent-particle model in the formal sense that each L_k is a constant of the motion, so that the eigenfunctions are antisymmetrized products

$$\psi_0 = \mathcal{A} \prod_k \{ \exp(i l_k \theta_k) \}. \quad (2.8)$$

However, the angular velocity ω_k of the k th electron depends upon the canonical variables L_j of all the electrons. This feature has important consequences for the available states of motion of the "free" electrons.

The simplest model of a superconductor at zero temperature is constructed by taking the Hamiltonian

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}', \quad (2.9)$$

where the BCS reduced interaction \mathcal{H}' represents the indirect electron-electron interaction through vibrations of the crystal lattice. This residual interaction is assumed to be a scalar quantity, so that it preserves the net angular momentum (z component) of an interacting pair of electrons. The principal effect of the residual interaction is known from the work of BCS, at least in the zero-current state with $\Phi_e = 0$. It becomes energetically advantageous to replace the zero-order ground state (2.8) by the zero-current N -particle BCS state $\psi_{\text{BCS}}(0)$. The latter state is made up of correlated pairs of single-particle states, so chosen that opposite values of the angular-momentum quantum number are always paired with each other.

It is intended that the main points of this paper, which are qualitative in character, should not depend upon the detailed structure of the BCS state. Nevertheless, it is interesting and helpful to consider that structure as well. For present purposes, the most useful formal expression for the N -electron $\psi_{\text{BCS}}(0)$ is that

given by Blatt⁹:

$$\psi_{\text{BCS}}(0) = (\sum_l g_l a_l^\dagger a_{-l}^\dagger)^{\frac{1}{2}N} \psi_{\text{vac}}. \quad (2.10)$$

Here, ψ_{vac} represents the zero-electron state, a_l^\dagger creates an electron with angular momentum $l\hbar$, and the coefficients g_l may be regarded as variational parameters. The energy of this BCS state is lower than that of the lowest zero-order state (2.8) by an amount equal to the zero-temperature energy gap.

In considering the current-carrying state, it is useful to introduce the fluxoid quantum number \bar{l} defined by

$$\bar{l}\hbar = N^{-1} \sum_k L_k \quad (2.11)$$

$$= (e/2\pi c) [\Phi_e + (1+\gamma)\Phi_s]. \quad (2.12)$$

Because \mathcal{H}' is assumed to be a scalar quantity, \bar{l} is an exact constant of the motion. For large N , it is capable of nearly continuous variation.

In terms of the fluxoid, the zero-order Hamiltonian (2.1) can be written in the form

$$\mathcal{H}_0 = \mathcal{H}_c(\bar{l}) + \mathcal{H}_c(\bar{l}, \Phi_e), \quad (2.13)$$

where

$$\mathcal{H}_c(\bar{l}) = (2ma^2)^{-1} \sum_k [L_k - \bar{l}\hbar]^2, \quad (2.14)$$

$$\mathcal{H}_c(\bar{l}, \Phi_e) = \frac{1}{2ma^2} \frac{N\gamma}{1+\gamma} \left(\bar{l}\hbar - \frac{e\Phi_e}{2\pi c} \right)^2 \quad (2.15a)$$

$$= \frac{N\gamma(1+\gamma)}{2ma^2} \left(\frac{e\Phi_e}{2\pi c} \right)^2. \quad (2.15b)$$

The collective term $\mathcal{H}_c(\bar{l}, \Phi_e)$ now contains the magnetic energy plus the kinetic energy of the collective motion in the supercurrent. This term is identical to the energy of N particles having charge e , mass m , and angular momentum $\bar{l}\hbar$, except for the nearly continuous variation of \bar{l} . The internal term $\mathcal{H}_c(\bar{l})$ contains the remaining kinetic energy, that is, the energy of motion relative to the average motion. Equation (2.14) for $\mathcal{H}_c(\bar{l})$ should properly include the radial and axial kinetic energies.

The great simplicity of the thin-ring case derives from the feature that \mathcal{H}_c depends upon the constant \bar{l} alone. Consequently, \mathcal{H}_c has no influence upon the wave function; the only role of \mathcal{H}_c is to increase the energy of the current-carrying state by the amount indicated in Eqs. (2.15). The zero-order ground state $\psi_0(\bar{l})$ is determined by $\mathcal{H}_c(\bar{l})$ alone, and the BCS state $\psi_{\text{BCS}}(\bar{l})$ by $\mathcal{H}_c(\bar{l}) + \mathcal{H}'$. The thin-ring problem thus appears formally to be similar to the deep-region problem considered by Byers and Yang, except that the fluxoid $\bar{l}\hbar$ must be substituted for the flux. There is, however, an important difference. The variables L_k are no longer independent, but must obey the constraint (2.11). It is precisely this constraint that gives rise to the "quantization" phenomenon in the thin-ring case.

For integral or half-integral values of the fluxoid (favored values), the single-particle states occur in

⁹ J. M. Blatt, Progr. Theoret. Phys. (Kyoto) 23, 447 (1960).

pairs whose radial and axial quantum numbers are equal and whose l_k values are symmetrically disposed about \bar{l} , i.e.,

$$l_k - \bar{l} = -(l_{k'} - \bar{l}). \quad (2.16)$$

Except in the zero-current case, these partner states do not have opposite angular velocities. Instead, the average angular velocity

$$\frac{1}{2}(\omega_k + \omega_{k'}) = \frac{1}{ma^2} \left(\bar{l}\hbar - \frac{e\Phi_e}{2\pi c} \right) \quad (2.17)$$

of each pair accounts for $2/N$ of the total circulating current. The partner states are nevertheless degenerate in the sense that they contribute equally to $\mathcal{H}_c(\bar{l})$. The zero-order ground state is therefore obtained by filling the single-particle states in pairs, so that each occupied state is the partner of another occupied state. The constraint (2.11) is automatically satisfied, and the Fermi surface is the usual constant-energy ellipsoid.

For integral values of \bar{l} , the zero-order ground state is obtained from that for $\bar{l}=0$ simply by replacing each l_k by $l_k + \bar{l}$. The internal part of the kinetic energy is unchanged by this transformation. The collective part of the energy is given by the constant $\mathcal{H}_c(\bar{l}, \Phi_e)$ of Eqs. (2.15). For half-integral values of \bar{l} , the Fermi surface is slightly different; but the internal part of the kinetic energy is unchanged except for (Fermi) surface terms which become unimportant in the limit of large N .

The current-carrying BCS state for favored values of \bar{l} is formally the same as the zero-current state of Byers and Yang, again under substitution of the fluxoid for the flux. The interaction Hamiltonian \mathcal{H}' is assumed to be insensitive to small changes in the flux values. Then, for integral \bar{l} ,

$$\psi_{\text{BCS}}(\bar{l}) = \psi_{\text{BCS}}(0) \prod_k \{ \exp(i\bar{l}\theta_k) \}, \quad (2.18a)$$

or in the field-theoretic notation

$$\psi_{\text{BCS}}(\bar{l}) = (\sum_l g_l a_l^\dagger a_{-l+2\bar{l}}^\dagger)^{\frac{1}{2}N} \psi_{\text{vac}}. \quad (2.18b)$$

For half-integral \bar{l} , the new pairing scheme of Byers and Yang must be used. The coefficients g_l in Eq. (2.18b) are changed slightly, but for large N the gap energy is the same. In either case,

$$E_{\text{BCS}}(\bar{l}) = E_{\text{BCS}}(0) + \mathcal{H}_c(\bar{l}, \Phi_e), \quad (2.19)$$

where the last term is the kinetic plus magnetic energy of the supercurrent.

For unfavored values of the fluxoid, the single-particle states no longer appear in symmetric pairs. For large N , this change has negligible effect on the internal kinetic energy, which is changed by only a surface term. The energy which accounted for the ripple in the heavy curve of Fig. 1 appears here in the collective term. Then, for each Φ_e , the zero-order energy is a quadratic function of \bar{l} ; its minimum appears when $\Phi_s = 0$, not necessarily at one of the favored values of \bar{l} . In contrast to the behavior for the thick ring, the

kinetic energy alone does not account for the fluxoid quantization phenomenon.

Now let it be assumed that the effect of the residual interaction \mathcal{H}' is sensitive to the occurrence of the single-particle states in pairs which are symmetric about \bar{l} , so that the BCS gap energy is substantially reduced when such symmetry is lacking. A qualitative argument supporting this assumption is given in Sec. 3, below. Then the ground-state energy for favored values of the fluxoid is lower than that for unfavored values by an amount comparable with the BCS gap energy. This result restores the phenomenon of the flux quantization in a thin ring. In Fig. 2, the energy $E_{\text{BCS}}(\bar{l})$ of the current-carrying ground state is displayed as a function of the induced flux Φ_s for two representative values of Φ_s . The parabolic behavior comes from the collective term in the Hamiltonian. The ripple arises from the variation of the gap energy with \bar{l} . Its amplitude is consequently comparable with the gap energy. The Φ_s dependence of $E_{\text{BCS}}(\bar{l})$ for various favored \bar{l} may be read off Fig. 1 by substituting $2\bar{l}$ for q and Φ_s for Φ . In this case, the amplitude of the ripple in the lowest state is just equal to the variation of the combined kinetic and magnetic energies since the BCS gap has its full strength for all values of Φ_s . It should be noted that in an actual experiment wherein Φ_s is varied at near-zero temperature, the system would maintain fixed \bar{l} so that its energy would be parabolic in Φ_s and would not follow the heavy line of Fig. 1.

This result, that the fluxoid should be quantized in a thin ring, was first obtained by Blatt,¹⁰ using a Bose gas model, and by Bardeen¹¹ with the Ginzburg-Landau theory. As each of the $\frac{1}{2}N$ bosons is given charge $2e$, and they all have the same quantum number l_b in the ground state, their energy is given by

$$\mathcal{H}_b = \frac{N}{ma^2} \frac{\gamma}{1+\gamma} \left(\frac{1}{2} l_b \hbar - \frac{e\Phi_s}{2\pi c} \right)^2. \quad (2.20)$$

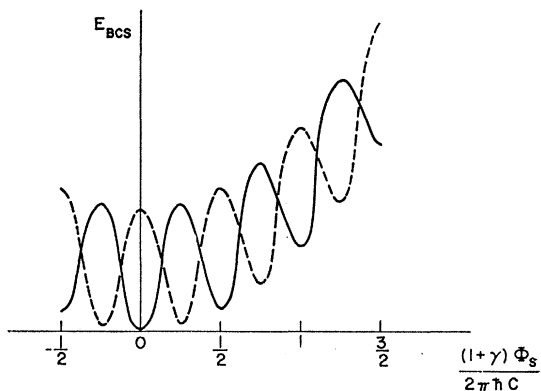


FIG. 2. Current-carrying ground-state energy E_{BCS} as a function of the induced flux Φ_s . The solid curve is for external flux Φ_s equal to zero. The dashed curve is for $(e\Phi_s/2\pi\hbar c) = -\frac{1}{4}$.

¹⁰ J. M. Blatt, Phys. Rev. Letters 7, 82 (1961).

¹¹ J. Bardeen, Phys. Rev. Letters 7, 162 (1961).

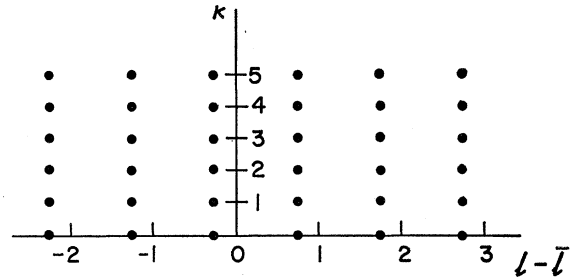


FIG. 3. Allowed values of the radial or axial quantum number κ and the angular momentum difference $l-\bar{l}$, for $\bar{l}=\frac{1}{4}$. The energy of the single-particle state is proportional to the square of the distance from its representative point to the origin. The third axis is not shown.

In this case, integral and half-integral values of $\frac{1}{2}l_b$ are the only ones allowed, while in the BCS theory the corresponding values of \bar{l} are merely favored energetically. In either case, the fluxoid $[\Phi_s + (1+\gamma)\Phi_s]$ is effectively quantized in units of $(\pi\hbar c/e)$. The two models also share the feature that quantum jumps from one favored current value to another are forbidden because the transition involves changing the state of every particle. In fact, any model which constructs the supercurrent state from pairs that are symmetric under reflection about the local average velocity gives the same result for the fluxoid. This point is pursued in Sec. 4, below.

3. SYMMETRY AND THE GAP ENERGY

That the BCS gap energy should respond sensitively to minute changes in the flux values is at first sight surprising. A qualitative argument will now be given to show that this phenomenon is unavoidable in the BCS theory. The crux of the argument is that small variations in the Fermi surface, whose effect on the kinetic energy is negligible, may be decisive for the interaction energy because the interaction is concentrated at the Fermi surface.

Suppose it is desired to construct the zero-order ground state for $\bar{l}=\frac{1}{4}$. The lattice of available single-particle states is illustrated in Fig. 3. The vertical scale, which is indexed by the radial or axial quantum number κ , is adjusted to make the single-particle contribution to the internal kinetic energy proportional to the square of the distance from the lattice point to the origin. The third axis is not shown in Fig. 3. For $\bar{l}=\frac{1}{4}$, as for all unfavored values of \bar{l} , there is no pair symmetry about \bar{l} . The occupation scheme for the zero-order ground state is indicated schematically in Fig. 4, where the horizontal lines connect occupied states. Each horizontal line corresponds to a radial or axial quantum number κ . Half of the horizontal lines (right lines) have equally many occupied states on the two sides of the vertical axis, but nevertheless stick out further to the right. The left lines have an extra state on the left side. In this

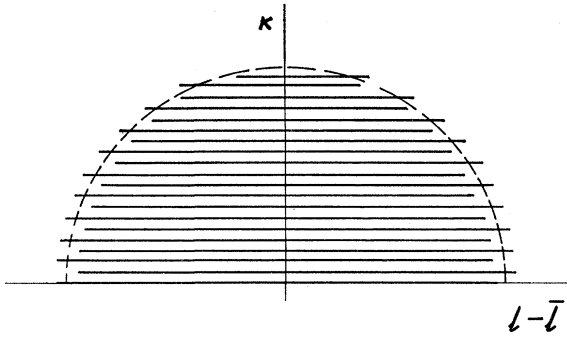


FIG. 4. Occupation scheme of the ground state for noninteracting electrons with $l = \frac{1}{4}$. Horizontal lines connect representative points (see Fig. 3) of occupied states. The dashed semicircle represents the nearest sphere to the Fermi surface.

way, the constraint (2.11) is obeyed. It is easy to estimate that the effect of the Fermi surface irregularity upon the internal kinetic energy is of order $N^{-\frac{1}{2}}$ times that energy. It is a typical surface effect.

It is impossible to write a BCS wave function of the form (2.18b) for $l = \frac{1}{4}$ because that form can give only the favored values of l , due to the quantization of angular momentum. To get $l = \frac{1}{4}$, it is necessary to have at least two different pairing schemes. The most attractive way to do this is to pair single-particle states symmetrically about the center of each horizontal line in Fig. 4. Then the average angular momentum per electron for right lines is $\frac{1}{2}\hbar$. That for left lines is zero. Formally, this scheme is given by

$$\psi_{\text{BCS}}(\frac{1}{4}) = (\sum_{\kappa l^R} g_{\kappa l} a_{\kappa l}^\dagger a_{\kappa, -l+1}^\dagger)^{\frac{1}{2}N} \times (\sum_{\kappa l^L} g_{\kappa l} a_{\kappa l}^\dagger a_{\kappa, -l}^\dagger)^{\frac{1}{2}N} \psi_{\text{vac}}, \quad (3.1)$$

where \sum^R is restricted to values of κ that correspond to right lines in Fig. 4 and \sum^L is restricted to left-line values. Because of the angular-momentum conservation, \mathcal{H}' does not connect pairs of states on right lines with pairs on left lines. Consequently, the state (3.1) represents two coexisting BCS systems. The total number of interactions is half that for favored values of l , and the BCS gap energy must be reduced by about the same factor.

Although wave function (3.1), thought of as a trial function, is a special one, the qualitative argument appears to be general. The only single-particle states that contribute importantly to the interaction energy are the ones nearest to the Fermi surface. Any scheme that pairs electrons so that all interacting pairs have the same net angular momentum necessarily misses one of the electrons nearest to the Fermi level in about half of the pairs.

4. SYMMETRY AND THE FLUXOID

When the superconductor is permitted to have arbitrary thickness and shape, the supercurrent state is not necessarily related to the zero-current state by the mere addition of the collective motion, as it was in

Eq. (2.18a). The important simplicity of the thin ring, that the collective term in the Hamiltonian is a constant of the motion, is missing in the general case. The collective term influences the zero-order internal wave function in a current-dependent way. The matrix elements of the residual interaction accordingly depend upon the current. In more graphic terms, the correlated pairs are polarized by the magnetic and centrifugal forces.

Nevertheless, it is possible to see in a very general way that symmetry of the BCS state with respect to the local collective velocity at every point is equivalent to the choice of the favored values for the fluxoid, properly defined.

Let $\rho(\mathbf{x})$ and $\mathbf{u}(\mathbf{x})$ represent the average density and the average velocity of electrons near point \mathbf{x} , in a current-carrying BCS state. The average current so defined serves as the source of an induced vector potential

$$\mathbf{A}_e(\mathbf{x}) = (e/c) \int |\mathbf{x} - \mathbf{y}|^{-1} \rho(\mathbf{y}) \mathbf{u}(\mathbf{y}) d\mathbf{y}. \quad (4.1)$$

The total vector potential $\mathbf{A}(\mathbf{x})$ is given by

$$\mathbf{A}(\mathbf{x}) = \mathbf{A}_e(\mathbf{x}) + \mathbf{A}_s(\mathbf{x}), \quad (4.2)$$

where the choice of gauge for the external $\mathbf{A}_e(\mathbf{x})$ is irrelevant.

In the self-consistent-field approximation, the velocity operator for the k th electron is given by

$$m \mathbf{v}_k(\mathbf{x}_k) = \mathbf{p}_k - (e/c) \mathbf{A}(\mathbf{x}_k). \quad (4.3)$$

It is now assumed that the BCS state is unchanged by the symmetry operation¹²

$$\begin{aligned} \mathbf{x}_k &\rightarrow \mathbf{x}_k, \\ \boldsymbol{\sigma}_k &\rightarrow -\boldsymbol{\sigma}_k, \\ \mathbf{v}_k(\mathbf{x}_k) - \mathbf{u}(\mathbf{x}_k) &\rightarrow -[\mathbf{v}_k(\mathbf{x}_k) - \mathbf{u}(\mathbf{x}_k)]. \end{aligned} \quad (4.4)$$

In terms of the canonical momenta, the last of Eqs. (4.4) reads

$$\mathbf{p}_k \rightarrow -\mathbf{p}_k + 2(e/c) \mathbf{D}(\mathbf{x}_k), \quad (4.5)$$

where

$$(e/c) \mathbf{D}(\mathbf{x}) = m \mathbf{u}(\mathbf{x}) + (e/c) \mathbf{A}(\mathbf{x}). \quad (4.6)$$

Transformation (4.4) is achieved by the antiunitary operation

$$\psi \rightarrow \prod_k \left\{ \left[\exp\left(\frac{2ie}{\hbar c} \int^{\mathbf{x}_k} \mathbf{D}(\mathbf{x}) \cdot d\mathbf{x}\right) \right] (i\boldsymbol{\sigma}_{y_k}) \right\} \psi^*, \quad (4.7)$$

where ψ^* is the complex conjugate and $\boldsymbol{\sigma}_{y_k}$ is the Pauli matrix $\boldsymbol{\sigma}_y$, which acts to reverse the spin of the k th electron. However, Eq. (4.7) makes sense only if the resulting ψ is a single-valued function of all the \mathbf{x}_k , i.e.,

¹² This assumption follows from the self-consistent-field approximation of replacing $\mathbf{A}(\mathbf{x})$ in \mathcal{H}_0 by its average value.

if the line integral about each closed path obeys

$$\oint \mathbf{D}(\mathbf{x}) \cdot d\mathbf{x} = n\pi\hbar c/e, \quad (4.8)$$

where n is an integer. This is just the condition that the fluxoid¹³

$$\Phi_0 = \oint [\mathbf{A}(\mathbf{x}) + (mc/e)\mathbf{u}(\mathbf{x})] \cdot d\mathbf{x} \quad (4.9)$$

associated with each closed curve must have the favored values

$$\Phi_0 = \frac{1}{2}n(2\pi\hbar c/e). \quad (4.10)$$

Peshkin and Tobocman¹⁴ prove that favored values of the flux are necessary and sufficient for the existence of the desired symmetry operation (4.4) in the zero-current case. Their proof, which will not be repeated here, may be generalized to the current-carrying case by substitution of $\mathbf{D}(\mathbf{x})$ for their $\mathbf{A}(\mathbf{x})$ and of the fluxoid for their flux F .

This requirement of favored values of the fluxoid in a thick ring applies to any model that is constructed symmetrically in the sense described. It was first noted by Keller and Zumino¹⁵ in the case of the Ginzburg-Landau model. It applies equally to the Bose gas model, which is known to lead to the London equation with a quantized inhomogeneous term.¹⁶ It is quite trivial to demonstrate that the additional term results in the favored values of the fluxoid.

5. CONCLUSIONS

The method of Byers and Yang has been generalized to discuss the current-carrying BCS state in a ring superconductor. The procedure is simply to treat the magnetic interaction between the electrons properly, by introducing it into the Hamiltonian from the outset. In the case of a very thin superconducting ring, the problem can be carried through completely because the collective motion separates and does not influence the

¹³ This definition of the fluxoid reduces to the more usual one, which involves the average current instead of the average velocity, if the density is assumed to be constant.

¹⁴ M. Peshkin and W. Tobocman, *Phys. Rev.* **127**, 1865 (1962).

¹⁵ J. B. Keller and B. Zumino, *Phys. Rev. Letters* **7**, 164 (1961).

¹⁶ H. J. Lipkin, M. Peshkin, and L. J. Tassie, *Phys. Rev.* **126**, 116 (1962).

internal structure of the supercurrent. In the general case, this feature is lacking. Nevertheless, it is possible to obtain the principal conclusions from the symmetry features of the theory, without actually producing the current-carrying wave function.

Inclusion of the current-carrying electrons in the dynamical treatment results in several minor generalizations of the conclusions of Byers and Yang. The important symmetry property of the BCS state is the symmetry of paired single-particle states in the local rest frame of the supercurrent at each point. In the current-carrying state, this symmetry is different from the condition of zero-order degeneracy. The approximate argument of Bohr and Mottelson (discussed in Sec. 2) is made exact by this result. The conclusions of those authors, therefore, do not need the assumption of a thick superconductor.

Symmetry with respect to the average current is equivalent to quantized values of the fluxoid rather than the flux. In the zero-current case, the two quantities are, of course, equal. A somewhat surprising result of the quantization of the fluxoid instead of the flux is that the Meissner effect is not necessary for quantization of magnetic flux. The symmetry principle that governs the effectiveness of the interaction applies equally well with or without the Meissner effect.

The results given here do not depend upon the reasonable, but not universally valid¹⁷ assumption that the density of conduction electrons should be uniform. However, in the absence of uniformity, it is essential that the fluxoid be defined in terms of the average velocity of the electrons instead of the average current.

The remarkable sensitivity of the BCS gap energy to minute changes in the magnetic flux can be understood qualitatively in terms of the shape of the Fermi surface. For unfavored values of the fluxoid, the single-particle states do not appear in symmetric pairs, and the Fermi surface becomes rough. It is impossible to construct the usual BCS coherent wave function from states lying close to such a rough surface without sacrificing a substantial fraction of all the interacting pairs.

ACKNOWLEDGMENTS

The work presented here owes much to conversations which I have enjoyed with F. Coester, with H. J. Lipkin, and with J. R. Schrieffer.

¹⁷ F. Bloch and H. E. Rorschach, *Phys. Rev.* **128**, 1697 (1962).