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THE RELATIVISTIC SHIFT IN THE MÖSSBAUER EFFECT

and

COUPLED SUPERCONDUCTORS

by

B.D.Josephson

Dissertation submitted for the annual election of Fellows

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CONTENTS

PREFACE

Declaration of originality or otherwise.

The work in this dissertation is in general original except where indicated otherwise by references or footnotes.

In part I sections 4,5 and 7 are original, subject to this proviso. Section 1 is an introduction and contains nothing new. Sections 2 and 3 summarise the standard theory required in the later sections, and some details of the treatment may be new, but we have not searched the literature to verify whether this is so. Section 6 summarises the experimental evidence for the theoretical predictions, and is original only in the sense that the information there may not have been previously gathered together in one place. The main source of background information has been Frauenfelder's book on the Mössbauer effect.*

In part II sections 4,5,7,8 and 9 are original. It is also believed that the viewpoint expressed in the introduction is original. Section 2 and the first part of section 3 are a somewhat developed form of lectures given by Dr.P.W.Anderson combined with his 1958 paper, but the way in which the s parameter is defined in section 3 is new. Section 6 is again a development of ideas in Dr. Anderson's 1958 paper.

Acknowledgements.

I should like to thank Dr.W.Marshall for discussions on the work in sections 4 and 5 of part I, and Dr.E.W.Schmid for correspondence which

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* The Mössbauer effect, by H.Frauenfelder, W.A.Benjamin,Inc., New York 1962.

resulted in the investigation of section 7 of part I. As regards part II, I am grateful to Dr.P.W.Anderson for his continued encouragement and for many interesting discussions, and to my supervisor, Professor A.B.Pippard, to whom my interest in the subject of this part is due, for searching comments which led to a better understanding of the unusual physical situations encountered during this investigation.

Finally I should like to thank the State, during the period of the research in part I, and the DSIR during that in part II, for augmenting the scholarship provided by the College.

Part I. THE RELATIVISTIC SHIFT IN THE MÖSSBAUER EFFECT.

1. Introduction.

In 1957 R. L. Mössbauer discovered the phenomenon which is now named after him: when gamma rays areemitted from or absorbed by nuclei in a solid, in a certain fraction of the processes the recoil of the nucleus is taken up by the solid as a whole with no change in its state of vibration. As a result of these processes, the gamma ray spectrum contains a sharply defined peak or peaks whose widths are determined by the lifetime of the excited nuclear state, and may be some orders of magnitude less than those previously thought to be attainable. Mössbauer was able to observe the resonant absorption of a gamma ray emitted from one nucleus by another nucleus in the ground state, and to show that when the source is moved relative to the absorber the absorption is reduced owing to the frequency change produced by the Doppler effect.

By combining the techniques of resonant absorption and use of the Doppler effect to change the frequency, much information has subsequently been obtained, particularly in the fields of nuclear and solid state physics, by the study of nuclear gamma ray spectra. Part I of this dissertation deals with one of the phenomena affecting the spectra, the frequency shift which arises from relativistic effects and can be observed by means of its dependence on temperature. In sections 2 and 3 the parts of the theory of the Mössbauer effect which are relevant to discussion of the relativistic shift are given and sections 4 and 5 deal with the theory of the shift. In section 6 experiments on the relativistic shift are described, and section

7 deals with a difficulty in the classical explanation of the shift which has not been adequately discussed in the literature on the Mössbauer effect.

2. Quantum theory of the Mössbauer effect.

Let ϵ_1, ϵ_2 be the energies of the excited and ground states respectively of a nucleus when it is moving with zero velocity. Let us first consider the decay of a free nucleus, i.e. one not under the action of external forces. In this section we shall ignore the energy broadening due to the finite lifetime of the excited state. The gamma ray energy will not be exactly $\epsilon_1 - \epsilon_2$ in general, since the kinetic energy of the nucleus may change when the gamma ray is emitted. In fact, if the nucleus is originally at rest its kinetic energy will increase, and so the gamma ray energy is less than $\epsilon_1 - \epsilon_2$. Similarly a gamma ray resonantly absorbed by a nucleus at rest must have an energy greater than $\epsilon_1 - \epsilon_2$. Further, if the nucleus is not at rest the gamma ray frequency is shifted in both cases by the Doppler effect, which in this case can be derived from the laws of conservation of momentum and mass-energy. Hence the gamma rays emitted or absorbed by a set of non-interacting nuclei have a continuous spectrum, and the spectra for emission and absorption are shifted relative to each other.

The situation is entirely different for bound nuclei. The simplest model which illustrates the behaviour is that of a nucleus in a potential well. In this case the nucleus, regarded as a point charge, has a discrete set of energy levels $E_1, E_2, \ldots$. The total energy of the system is obtained by adding the internal energy ϵ_1 or ϵ_2. If we neglect the small mass difference

between the excited and ground states, the values of E_i will be the same for the two states. In this case, corresponding to the discrete energy levels there will be a discrete gamma ray spectrum. Moreover, whatever the values of E_i are, there will always be a gamma ray line of energy exactly $\epsilon_1 - \epsilon_2$ corresponding to processes in which the value of E_i is the same for the initial and final states. One would expect an appreciable probability of these 'recoilless' processes if the separation of the potential well energy levels were not too small compared with the change in kinetic energy which would occur for nuclei with the same mean kinetic energy in the absence of the potential well.

We shall now consider the general case of a nucleus embedded in a solid. This is rather more complicated because the motion of the nucleus is correllated with that of the neighbouring atoms. We shall, however, make the approximation that the internal state of the nucleus is not affected by the rest of the solid.* We shall accordingly split up the Hamiltonian into two parts, the first, H_L consisting of the Hamiltonian which would exist if the nucleus were replaced by a point charge of zero spin, and the second, H_N consisting of the internal nuclear energy, its interaction with external and crystalline fields, and the change in energy due to the finite size of the nucleus (the isomer shift). If we again neglect the mass difference between

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* This neglects, for example, the fact that the hyperfine interaction can change the spin of the nucleus. The average interaction is taken into account here by including it in the nuclear energy, but the fluctuations about the average may broaden the energy levels.

the excited and ground states, H_L is independent of the internal state of the nucleus. Our approximation consists in assuming that the eigenfunctions of the total Hamiltonian may be expressed as products of ψ_L, depending only on the centre of gravity of the nucleus, and ψ_N, depending only on the relative coordinates of the particles in the nucleus with respect to its centre of gravity, and that ψ_L and ψ_N are eigenfunctions of H_L and H_N respectively, with eigenvalues E_L and E_N. E_N is the same as what we have previously called ϵ_1 or ϵ_2. Now let the recoil energy R be defined to be the increase in E_L. Then by the conservation of energy, the gamma ray energy is $\epsilon_1-\epsilon_2-R$ for a decay and $\epsilon_1-\epsilon_2+R$ for absorption. We cannot here define a recoilless process to be one in which ψ_L is unchanged, since this would imply that the total momentum of the solid was unchanged, whereas it must change by the amount of the gamma ray momentum.* However, the eigenfunctions of H_L have the form $\psi_L = e^{i\underset{\sim}{K}\cdot\underset{\sim}{R}}\psi_{L0}$, where $\hbar\underset{\sim}{K}$ is the total momentum, $\underset{\sim}{R}$ the centre of gravity of the solid, and ψ_{L0} is a wave function of zero total momentum. The lattice energy is given by

$$E_L = E_{L0} + \frac{\hbar^2 K^2}{2M},$$

where M is the total mass of the solid. A recoilless process can now be defined as one in which $\underset{\sim}{K}$ changes but not ψ_{L0}. For non-interacting nuclei such a process cannot occur since there is no mechanism for the transfer of the recoil among the nuclei, but calculation shows that it has a finite probability in a solid. In such processes E_{L0} is unchanged and R is equal to the change in $\hbar^2K^2/2M$. If the solid is initially at rest this change is of order $1/M$ and is negligible for situations encountered in practice. One is therefore led to the existence of a sharply defined line of energy $\epsilon_1-\epsilon_2$

* I am indebted to R. R. Vierhout for pointing this out.

in the gamma ray spectrum. If the solid is in motion, calculation of the change in $\frac{\hbar^2 K^2}{2M}$ gives the Doppler shift.

3. Classical theory of the Mössbauer effect.

Some features of the Mössbauer effect can be derived from a classical model. The nucleus emitting the gamma ray is replaced by a classical source of electromagnetic waves, of frequency ν , say.* One is then led to the following picture of the Mössbauer effect. First let us suppose that the nucleus oscillates harmonically with a single frequency Ω . Neglecting relativistic effects, the signal perceived by a stationary observer is frequency modulated with modulating frequency Ω about a mean frequency ν , owing to the Doppler effect. The theory of frequency modulation shows that such a signal has frequency compenents $\nu + n\Omega$, for all integral n. In particular, there is a component at the oscillator frequency ν . It can easily be shown that the Fourier transform of a signal frequency modulated in an arbitrary way also has a delta function at its mean frequency, provided that the integral of the deviation from the mean frequency over arbitarily long time intervals is bounded. Consideration of this shows that provided the mean distance between the source and observer does not alter with time, the frequency distribution of the signal seen by the observer has a delta function at the oscillator frequency.

Thus the classical theory explains the existence of the Mössbauer line. However, it does not give all the results of the quantum theory; in partic-

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* The natural linewidth can be taken into account by assuming an exponentially decaying source, but here we shall assume a scource of constant amplitude.

ular it predicts a spectrum which is symmetrical about the Mössbauer line, whereas the real spectrum is assymetric.

4. Quantum theory of the relativistic shift.

The relativistic shift arises from the difference in mass between the excited and ground states, which was neglected in sect. 2. We shall first consider the model of a nucleus in a one dimensional potential well, to indicate qualitatively the results expected. The energy levels of a harmonic well are $(n+\frac{1}{2})\hbar\omega$, where $\omega=\sqrt{F/m}$, F being the force constant and m the nuclear mass. The excited state has a greater mass, and consequently smaller ω. Thus the ~~excited~~ energy levels are all less than the corresponding ones for the ground state. Accordingly the gamma ray energies, both for emission and absorption are reduced, by an amount $(n+\frac{1}{2})\hbar.\Delta\omega$. This is greater for higher energy levels, and so the mean gamma ray energy decreases with increase in temperature. In this model the shift depends on the value of n, and so there is a broadening as well as a shift.

A general formula can also be found giving the energy shift for a solid. In this case the shift is due to the fact that H_L (sect. 2) is not the same for the excited and ground states of the nucleus. The difference results from the fact that the term $p_i^2/2m_i$ giving the kinetic energy of the nucleus involved in the process contains its mass m_i explicitly. Hence ψ_{L0} and E_{L0} must change during the process. The new values can be derived by regarding the change in H_L as a perturbation. It is necessary to note that since the perturbing term $\sum \frac{p_i^2}{2m_i}$ commutes with the total momentum, if ψ_{L0} is a zero momentum wave function then the new wave function derived by perturbation theory will also be of zero momentum. Applying first order perturbation theory, we obtain

$$\delta E_{LO} = \langle \delta H_L \rangle = \left\langle \delta \frac{p_i^2}{2m_i} \right\rangle$$

$$= -\frac{\delta m_i}{m_i} \left\langle \frac{p_i^2}{2m_i} \right\rangle = -\frac{\delta m_i}{m_i} T_i,$$

where T_i is the expectation value of the kinetic energy of the nucleus. If we neglect the change in $\frac{\hbar^2 K^2}{2M}$, the recoil energy R is just δE_{LO} For an emission process, by the mass-energy relation, $\delta m_i = -E/c^2$, where E is the gamma ray energy. Hence $R = \frac{E}{m_i c^2} T_i$. Similarly for an absorption process, δm_i is E/c^2 and $R = -\frac{E}{m_i c^2} T_i$. In both cases the change in gamma ray energy is

$$\delta E = -\frac{E}{m_i c^2} T_i \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4.1a),$$

and the relative change is

$$\frac{\delta E}{E} = -\frac{T_i}{m_i c^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4.1b).$$

T_i may depend on the initial state of the system, leading to a broadening of the line as well as a shift. This possibility has been considered by Snyder and Wick (1960), who show that the broadening expected in a perfect crystal at a definite temperature is very small. If we neglect the broadening, eqns. 4.1 give the shift as a function of temperature, T_i being now the average kinetic energy of the nucleus at the temperature concerned. The calculation of T_i in the general case is rather complicated, but in two particular cases it can be calculated easily. In the first case, at high temperatures ($T \gg \theta_D$), the classical equipartition theorem holds, and gives the result $T_i = \frac{3}{2} kT$. Hence

$$\frac{\delta E}{E} = -\frac{3}{2} kT / m_i c^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4.2).$$

The temperature coefficent is given by

$$\frac{1}{E} \frac{dE}{dT} = -\frac{3}{2} k / m_i c^2. \quad \ldots\ldots\ldots\ldots\ldots\ldots (4.3)$$

The second case applies when the nucleus is embedded in a lattice of atoms identical to it. Then T_i is simply the mean kinetic energy per atom, and T_i/m_i is the kinetic energy per unit mass. If we also make the approximation of harmonic interatomic forces, then the kinetic energy is half the total lattice

energy. Hence

$$\frac{\delta E}{E} = -\tfrac{1}{2} U_L / c^2 \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4.4)$$

where U_L is the lattice energy per unit mass, and the temperature coefficient is given by

$$\frac{1}{E}\frac{dE}{dT} = -\tfrac{1}{2} C_L / c^2 \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4.5)$$

where C_L is the lattice specific heat per unit mass.

5. Classical theory of the relativistic shift.

The relativistic shift has a very simple interpration on the classical model: it is simply the time dilatation predicted by special relativity. Let us suppose that the proper frequency of the nuclear 'clock' i.e. the frequency in a reference frame stationary with respect to it, is ν . If the velocity of the nucleus relative to the observer is v, the frequency of the clock in the observer's reference frame is $\nu' = \nu\sqrt{1 - v^2/c^2}$. This will not be the same as the frequency seen by the observer, ν_{obs} , owing to the Doppler effect. However, the mean values of ν' and ν_{obs} , taken over a long time interval, will be the same, because the Doppler effect results from the varying phase lag of the signal in passing from the source to the observer, due to the varying distance it has to travel. However, since the mean distance over long periods of time stays constant, these fluctuating phase differences will have no effect on the mean frequency. Since the position of the Mössbauer line depends only on the mean frequency seen by the observer (sect. 3), its shift depends only on the time dilatation, and to first order in v^2 is given by

$$\frac{\delta\nu}{\nu} = -\frac{1}{2}\frac{\overline{v^2}}{c^2} = -\frac{\overline{\frac{1}{2} m_i v^2}}{m_i c^2} = -T_i / m_i c^2,$$

in agreement with eqn. 4.1b. In this case there is no reason why the integral of the deviation of the frequency from its mean value should remain bounded

for arbitrarily long time intervals, since $v^2-\overline{v^2}$ does not have this property. Hence the Mössbauer line is also broadened; however, this is only a second order effect. It could be derived from quantum theory by calculating the perturbation to second order.

This is the most direct method for deriving the relativistic shift from the classical model; other methods lead to some difficulties (sect. 7).

Sherwin (1960) has pointed out that the existence of the shift confirms the reality of Einstein's clock paradox. According to this, if two clocks move from A to B, the first by motion involving accelerations and the second by unaccelerated motion, and the clocks are synchronised at A, then on meeting at B the first clock will be slow compared to the second. Sherwin observes that if we have two nuclei, the first in a solid at a high temperature and the second in a solid at a low temperature, these play the roles of the two clocks in the clock paradox.

6. Experiments on the relativistic shift.

The relativistic shift was first observed, though it was not realised at the time, in the experiment carried out by Cranshaw et. al. (1960) to observe the gravitational red-shift. They measured the frequency shift between a source and absorber at different heights, and noticed that the fluctuations between results on different runs were appreciably greater than could be explained as statistical fluctations. In the case of the particular nucleus used, Fe^{57}, the relative shift is $2.2\times10^{-15}/^{\circ}C$ at room temperature, and later measurements revealed fluctuating temperature differences between source and absorber of the order of $0.5^{\circ}C$, sufficient to explain the fluctuations in measured shift. Later Cranshaw and Schiffer (unpublished) checked the shift

more directly by cooling the absorber to liquid nitrogen temperature, thus producing a comparatively large and easily measured shift. Meanwhile the relativistic shift had been discovered independently by Pound and Rebka (1960), who showed that its temperature dependence for Fe^{57} agreed with (4.4). A similar result for Sn^{119} was obtained by Boyle et. al. (1960).

7. Is the relativistic shift a second order Doppler effect?

Pound and Rebka (1960) proposed the following explanation of the relativistic shift. The Doppler shift can be expanded as a power series in v, the velocity of the source. The terms of first order have no effect on the Mössbauer line, since $\overline{v}$ is zero. However, $\overline{v^2}$ is not zero, and it is the second order term, proportional to the mean kinetic energy, which is the relativistic shift. E.W. Schmid has pointed out (private communication) that this does not appear to give the right result in the general case. In this section we shall show how the inconsistency can be resolved.

Suppose, as in sect. 5, that the nuclear frequency is ν measured by an observer moving with the nucleus, and ν_{obs} as seen by the stationary observer. Let v be the velocity of the nucleus, and θ the angle between its velocity and the line joining it to the stationary observer, as seen in the stationary reference frame. For simplicity we suppose θ constant. According to special relativity (Einstein 1907),

$$\nu_{obs} = \frac{\nu\sqrt{1-v^2/c^2}}{1-(v/c)\cos\theta}.$$

To second order in v,

$$\nu_{obs} = \nu\left\{1 - \tfrac{1}{2}\frac{v^2}{c^2} + \frac{v}{c}\cos\theta + \frac{v^2}{c^2}\cos^2\theta\right\}$$

$$= \nu\left\{1 + \frac{v}{c}\cos\theta + \tfrac{1}{2}\frac{v^2}{c^2}\cos 2\theta\right\} \quad \ldots\ldots\ldots\ldots\ldots (7.1)$$

The frequency of the Mössbauer line as seen by the observer is

$$\overline{\nu_{obs}} = \nu\left\{1 + \tfrac{1}{2}\frac{\overline{v^2}}{c^2}\cos 2\theta\right\} \qquad (7.2)$$

since $\overline{v} = 0$.

However, the correct expression for the frequency is, by sect. 5,

$$\overline{\nu} = \nu\left\{1 - \tfrac{1}{2}\frac{\overline{v^2}}{c^2}\right\}.$$

This agrees with (7.2) only when $\theta = 90^0$; i.e. transverse oscillation of the nucleus. The explanation is as follows. In deriving (7.2) from (7.1) the time average was taken. However, the time occurring on the left side of (7.1) is the time when the signal reaches the observer, and on the right side the time when it leaves the nucleus. These are not the same, and so the process of time averaging is not justified. The above considerations indicate that the relativistic shift cannot be regarded as a straightforward second order Doppler shift. The correct result can be obtained by the reasoning of section 5.

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Part II. COUPLED SUPERCONDUCTORS.

1. Introduction.

When a metal becomes superconducting, remarkable changes occur in its properties, the most striking being the flow of currents without resistance and the exclusion of magnetic fields from the interior of the metal. Thanks to the recent theories of Bardeen, Schrieffer and Cooper (1957) and other workers these phenomena are now fairly well understood, and are known to result from a type of long range order extending throughout the superconductor. If the superconducting metal is cut into two pieces these properties are lost, even if the pieces are reconnected by a wire of normal metal; a magnetic field can penetrate into the normal metal joining them, while it is impossible to make a current flow from one piece to the other without the continuous expenditure of energy. Clearly the two pieces no longer cooperate together in the way necessary to produce the characteristic behaviour of a single superconductor. If, however, they are pressed together into direct contact the original behaviour is restored and the two pieces behave like one.

It is natural to ask whether there can be any behaviour of two superconductors intermediate between those characteristic of complete separation and of complete union, in which the two parts influence each other a certain amount, but not enough to exhibit the phenomena of superconductivity to their full extent. This question is of particular interest in view of the experiments now being carried out involving tunnelling through a barrier layer between superconductors (Nicol et. al. 1960, Giaever 1960) and conduction between two superconductors separated by a thin normal layer,

(Smith et. al. 1961). In addition, a superconductor in the intermediate state consists of a complicated domain structure of normal and superconducting regions, and the superconducting regions might be expected to influence each other to some extent. In the case of tunnelling there has previously been no valid theoretical treatment of the case when both sides of the barrier are superconducting, and the experimentally demonstrated absence in the formula for the tunnelling current of the coherence factors, shown by Bardeen, Cooper and Schrieffer (1957) to occur in calculations involving superconductors, has not been explained.

It is to the resolution of these questions that this part of the dissertation is devoted. We shall see that if two superconductors influence each other slightly, not only do they exhibit to a restricted extent the properties of a single superconductor, but they also show several new properties, which are perhaps no less remerkable.

In sections 2 and 3 the theory of broken symmetry, its application to superconductivity and the definition of the phase operator are described. Using these ideas the mathematical formalism necessary to deal with coupled superconductors is derived in sections 4 and 5. In section 6 Anderson's analogy between a superconductor and a rotating body, which proves helpful to seeing the physics behind the mathematics, is developed further. In section 7, as a preliminary to dealing with coupled superconductors we discuss the properties of a system consisting of two completely non-interacting superconductors, and in section 8, the main body of the work, the properties of coupled superconductors are derived. Finally, in section 9 we apply a modified form of the perturbation theory methods of Cohen, Falicov and Phillips, in conjunction with the mathematical techniques developed in sections 4 and 5, to calculate the magnitude of the effects in tunnelling.

2. Broken symmetry and restricted canonical ensembles.

Anderson (1961-2) has considered the feature of 'broken symmetry' which occurs in many calculations of the self-consistent field type and is generally associated with phase transitions. Much of the succeeding discussion can best be understood against the background of these ideas, and so we shall outline the relevant features in this section.

We shall illustrate the theory by considering a particular example, an isotropic ferromagnetic system. If one calculates the ground state of such a system by the Hartree-Fock method, one obtains a state in which all the spins are aligned in a definite direction. This state has the property that it is not invariant under all the transformations which leave the Hamiltonian invariant, in particular, rotations. The same feature occurs in the grand canonical ensemble obtained by having a distribution of excitations given by the usual statistical mechanical formulae for non-interacting particles. We shall call an ensemble obtained in this way a restricted canonical ensemble, since it does not contain all the states of the true grand canonical ensemble, which must have all the symmetries of the Hamiltonian.

From any restricted canonical ensemble others may be obtained by applying the transformations which leave the Hamiltonian invariant. Under these transformations the self-consistent field will transform in a well defined manner, and there will exist a set of parameters $\{a\}$ as a function of which theself-consistent field in any particular ensemble can be expressed. For example, in the ferromagnetism case the direction cosines of the direction of magnetization determine the self-consistent field. Similarly, in a solid six parameters suffice to specify the mean lattice position, which determines, for example, the self-consis tent field in which the electrons move. In all cases

the parameters may be treated as classical variables, since they depend on the mean properties of a large number of particles and are subject only to insignificant quantum-mechanical and statistical fluctuations. More precisely, corresponding to the parameters $\{a\}$ there exists a set of quantum-mechanical operators $\{A\}$ such that if N is the number of particles in the system, the restricted ensemble specified by $\{a\}$ consists of states which are, to order $\sqrt{(1/N)}$, eigenfunctions of the operators A with eigenvalues a. One feature associated with restricted ensembles is the existence of collective excitations, which can be thought of as due to processes which change the values of the ensemble parameters, whereas the quasi-particle excitations leave the parameters unchanged. For example, in a solid rotations of the solid as a whole are collective excitations.

3. Broken symmetry in superconductors and the S operators.

A loss of symmetry of the kind considered in the previous section occurs in the random phase approximation (RPA) treatment of superconductors (Anderson 1958). In this theory it is assumed that if k,k' are states between which pairing occurs in superconductors (Bardeen et. al. 1957) then the operators $a_k^\dagger a_{k'}^\dagger$ and $a_k a_{k'}$, which respectively create and destroy a pair of electrons in these states, have non-zero expectation values.* This assumption allows superconductivity to be treated by the use of self-consistent field methods. Before describing these we note two simplifying assumptions which are usually made, mainly in order to simplify the notation. These are that the system is invariant under time reversal and under rotations in spin space. These assumptions will not materially affect any of the succeeding

* Here and in the following we shall use Roman letters for electron operators and Greek letters for quasi-particle operators.

arguments except where it is explicitly stated. If the assumption of time-reversal symmetry is made, then the paired states k,k' are time reversed states k,-k. Under the assumption of invariance under rotations in spin space the convention can be made that states not preceeded by and not preceeded by a minus sign have spin up and spin down respectively. The following self-consistent field parameters can then be defined:

$$\overline{n_k} = \langle a_k^+ a_k \rangle, \quad \overline{n_{-k}} = \langle a_{-k}^+ a_{-k} \rangle, \quad \overline{b_k} = \langle a_{-k} a_k \rangle, \quad \overline{b_k}^* = \langle a_k^+ a_{-k}^+ \rangle \qquad (3.1).$$

The next step in the RPA treatment is to write down the commutators of single-electron creation and destruction operators with the Hamiltonian and to linearize them with the use of the RPA. The Bogoliubov operators

$$\begin{aligned} \alpha_{k0}^+ &= u_k a_k^+ - v_k a_{-k} \\ \alpha_{k1}^+ &= u_k a_{-k}^+ + v_k a_k \\ \alpha_{k0} &= u_k a_k - v_k a_{-k}^+ \\ \alpha_{k1} &= u_k a_{-k} + v_k a_k^+ \end{aligned} \qquad (3.2)$$

($u_k^2 + v_k^2 = 1$) are then found by solving the equations

$$[H, \alpha_k^+] = \epsilon_k \alpha_k^+, \quad [H, \alpha_k] = -\epsilon_k \alpha_k \qquad (3.3),$$

which give u_k and v_k in terms of the $\overline{b}$'s and $\overline{n}$'s. Owing to our assumption of time-reversal symmetry the $\overline{b}$'s are real and so u_k and v_k can be chosen to be real. Finally the $\overline{b}$'s and $\overline{n}$'s are found in terms of the u_k and v_k for an ensemble containing a Fermi-Dirac distribution of the quasi-particles thus defined.*

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*This differs from Anderson's treatment in two ways; firstly he wishes to derive the collective excitations and so works with operator pairs, and secondly he considers only the ground state. However, the treatment sketched here is a valid method for finding the quasi-particle operators at a finite temperature, provided that energies are measured relative to the Fermi energy

The ensemble defined in this way is a restricted canonical ensemble. To see this, let us consider the effect of the transformation which changes the phases of wave functions with different numbers of electrons relative to each other. More precisely, it is the transformation obtained by multiplying the state vectors by the unitary operator $e^{iN\theta}$, where N is the total number of electrons and θ an arbitrary real constant. The matrix elements of H with respect to the new states are the same as before, since H commutes with N. The effect of the transformation on the self-consistent field parameters (3.1) is

$$\bar{n}_k \rightarrow \bar{n}_k, \ \bar{n}_{-k} \rightarrow \bar{n}_{-k}, \ \bar{b}_k \rightarrow e^{2i\theta}\bar{b}_k, \ \bar{b}_k^* \rightarrow e^{-2i\theta}\bar{b}_k^* \qquad (3.4).$$

Since the $\bar{b}_k$ are not invariant under the transformation, the ensemble derived from the RPA solution is not invariant, and so is a restricted ensemble. As indicated in sect. 2. other restricted canonical ensembles may be obtained from a given one, in this case by applying the operator $e^{iN\theta}$ to the state vectors.

We now turn to the problem of finding a parameter s to label the restricted ensembles. To do this let us take a particular solution of the RPA equations to be the ensemble s=1. If the Hamiltonian is time-reversal symmetric the solution with real b_k, which gives an ensemble with time reversal symmetry, should be chosen in order that the symmetry may be maintained in the succeeding manipulations. From (3.4) we see that the self-consistent field parameters for the ensemble obtained by applying the operator $e^{iN\theta}$ involve θ only through the expression $e^{2i\theta}$, and this we shall take to define s. s thus always has unit amplitude. As in sect. 2, we shall suppose that there exists an operator

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(Bogoliubov 1958), so that the conventional statistical mechanical treatment shall be valid.

S such that a typical state in the ensemble s is (to order $1/\sqrt{N}$) an eigenfunction of S with eigenvalue s, and hence an eigenfunction of $S^\dagger$ with eigenvalue s^*. We shall see in sect. 4 that in superconductivity it is the operator S rather than the parameter s which has a simple physical significance.

4. Generalised operators in superconductors.

Since the Bogoliubov operators depend on the self-consistent field parameters they can be good quasi-particle operators in only one ensemble. While in most calculations in superconductivity theory the correct results can be obtained by averaging over a single restricted ensemble, in problems involving two superconducting regions it is necessary to consider a general restricted ensemble (cf. sections 7 and 8). The appropriate generalised forms of the Bogoliubov operators can be derived in the following way. Let A be a good quasi-particle operator for the ensemble s=1. Now let the canonical transformation generated by the operator $e^{iN\theta}$ be applied to both the state vectors and the operators. This changes the ensemble s=1 into the ensemble $s=e^{2i\theta}$, and A into a new operator A_θ. Since a canonical transformation leaves matrix elements unchanged, A_θ is a good quasi-particle operator for the ensemble $s=e^{2i\theta}$. It is then necessary to express A_θ in terms of s instead of θ. Since s is the eigenvalue of S, if in this form s is replaced by the operator S, the resultant operator will be a good quasi-particle operator for all ensembles. Applying the transformation to the Bogoliubov operators (3.2) we obtain

$$\left.\begin{aligned}
(\alpha_{k0}^+)_\theta &= u_k e^{i\theta} a_k^+ - v_k e^{-i\theta} a_{-k} \\
(\alpha_{k1}^+)_\theta &= u_k e^{i\theta} a_{-k}^+ + v_k e^{-i\theta} a_k \\
(\alpha_{k0})_\theta &= u_k e^{-i\theta} a_k - v_k e^{i\theta} a_{-k}^+ \\
(\alpha_{k1})_\theta &= u_k e^{-i\theta} a_{-k} + v_k e^{i\theta} a_k^+
\end{aligned}\right\} \qquad \ldots\ldots\ldots\ldots (4.1)$$

However, these operators cannot be expressed in terms of $s=e^{2i\theta}$, but since we have not yet used any formulae which depend on their phases, we may multiply (4.1) by $e^{\pm i\theta}$ and replace $e^{2i\theta}$ and $e^{-2i\theta}$ by S and $S^\dagger$ respectively, obtaining

$$\left.\begin{aligned}
\alpha^\dagger_{ek0} &= u_k a^\dagger_k - v_k S^\dagger a_{-k} \\
\alpha^\dagger_{hk0} &= u_k S a^\dagger_k - v_k a_{-k} \\
\alpha^\dagger_{ek1} &= u_k a^\dagger_{-k} + v_k S^\dagger a_k \\
\alpha^\dagger_{hk1} &= u_k S a^\dagger_{-k} + v_k a_k \\
\alpha_{ek0} &= u_k a_k - v_k S a^\dagger_{-k} \\
\alpha_{hk0} &= u_k S^\dagger a_k - v_k a^\dagger_{-k} \\
\alpha_{ek1} &= u_k a_{-k} + v_k S a^\dagger_k \\
\alpha_{hk1} &= u_k S^\dagger a_{-k} + v_k a^\dagger_k
\end{aligned}\right\} \quad \ldots\ldots\ldots \quad (4.2)$$

The quasi-particle energies will be the same as in the Bogoliubov theory:

$$\left.\begin{aligned}
[H, \alpha_{eks}] &= \epsilon_{ks} \alpha^\dagger_{eks} \\
[H, \alpha_{hks}] &= \epsilon_{ks} \alpha^\dagger_{hks} \\
[H, \alpha_{eks}] &= -\epsilon_{ks} \alpha_{eks} \\
[H, \alpha_{hks}] &= -\epsilon_{ks} \alpha_{hks}
\end{aligned}\right\} \quad \ldots\ldots\ldots \quad (4.3)$$

(4.2) may be inverted to express electron operators in terms of quasi-particle operators:

$$\left.\begin{aligned}
a^\dagger_k &= u_k \alpha^\dagger_{ek0} + v_k \alpha_{hk1} \\
a^\dagger_{-k} &= u_k \alpha^\dagger_{ek1} - v_k \alpha_{hk0} \\
a_k &= u_k \alpha_{ek0} + v_k \alpha^\dagger_{hk1} \\
a_{-k} &= u_k \alpha_{ek1} - v_k \alpha^\dagger_{hk0}
\end{aligned}\right\} \quad \ldots\ldots\ldots \quad (4.4)$$

We next consider quasi-particle occupation number operators. These may be defined by the equivalent expressions:

$$\nu_{ks} = \alpha^\dagger_{eks} \alpha_{eks} = \alpha^\dagger_{hks} \alpha_{hks} \quad \ldots\ldots\ldots \quad (4.5)$$

both of which reduce to the Bogoliubov expressions for the s=1 ensemble.

We shall now derive various commutation relations. Firstly, since the multiplication of state vectors by $e^{iN\theta}$ multiplies s by $e^{2i\theta}$(by definition of s), it follows that $e^{-iN\theta}Se^{iN\theta}=e^{2i\theta}S$. Differentiating with respect to θ and putting $\theta=0$, we obtain

$$\left.\begin{aligned}[S,N] &= 2S \\ [S^\dagger,N] &= -2S^\dagger\end{aligned}\right\} \quad \ldots\ldots\ldots\ldots (4.6)$$

Hence

The states of the s=1 ensemble are those in which the occupation numbers corresponding to the Bogoliubov operators (3.2) have definite values, and so application of a Bogoliubov operator to one of these states produces another state in the same ensemble. It follows that if a generalised quasi-particle operator is applied to a state in any restricted ensemble it produces a state in the same ensemble, i.e. it does not alter the value of s. Hence the generalised quasi-particle operators commute with S and $S^\dagger$,

$$\left.\begin{aligned}&[\alpha^\dagger_{eks},S^\dagger]=[\alpha^\dagger_{hks},S^\dagger]=[\alpha_{eks},S^\dagger]=[\alpha_{hks},S^\dagger] \\ =\ &[\alpha^\dagger_{eks},S]=[\alpha^\dagger_{hks},S]=[\alpha_{eks},S]=[\alpha_{hks},S]=0\end{aligned}\right\} \quad (4.7)$$

and
$$[\nu_{ks},S^\dagger]=[\nu_{ks},S]=0 \quad \ldots\ldots\ldots (4.8).$$

From (4.6) and(4.8), S leaves quasi-particle occupation numbers unchanged but reduces the total number of electrons by two. It can therefore be interpreted as the operator which removes a bound pair of electrons.* Similarly $S^\dagger$ creates a bound pair.

Since S is a classical variable, (sect. 2)

$$[S^\dagger,S]=0 \quad \ldots\ldots\ldots (4.9)$$

to order $1/\sqrt{N}$. This may be compared with the commutation relations for a boson state macroscopically occupied. In that case $[\alpha^\dagger,\alpha]=1$, while $\alpha^\dagger\alpha=N$,

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* In the theory of Gor'kov (1958) it is the operator which changes $|N+2\rangle$ into $|N\rangle$.

and α^+, α may be regarded as commuting (Bogoliubov et. al. 1959).

We next derive commutation relations between N and the quasi-particle operators. From (4.2) and (4.6) we obtain

$$\begin{aligned} [N, \alpha^+_{eks}] &= \alpha^+_{eks} \\ [N, \alpha^+_{hks}] &= -\alpha^+_{hks} \\ [N, \alpha_{eks}] &= -\alpha_{eks} \\ [N, \alpha_{hks}] &= \alpha_{hks} \end{aligned} \qquad (4.10).$$

Thus e and h creation operators respectively increase and decrease N by one, and vice versa for destruction operators. This is analogous to the behaviour of electron and hole operators, and is the reason for the nomenclature used.

Any relation satisfied by Bogoliubov operators may be extended to a relation between generalised quasi-particle operators by applying the canonical transformation generated by $e^{iN\theta}$, thus producing a relation between θ operators, (4.1), replacing the θ operators by generalised quasi-particle operators, and expressing any power of $e^{i\theta}$ left over in terms of S or $S^\dagger$ operators. In this way we can obtain the relations

$$\left.\begin{aligned} \alpha^+_{eks} &= S^\dagger \alpha^+_{hks} \\ \alpha^+_{hks} &= S\, \alpha^+_{eks} \\ \alpha_{eks} &= S \alpha_{hks} \\ \alpha_{hks} &= S^\dagger \alpha_{eks} \end{aligned}\right\} (4.11),$$

$$\left.\begin{aligned} &[\alpha^+_{eks}, \alpha_{ek's'}]_+ = [\alpha^+_{hks}, \alpha_{hk's'}] = \delta_{kk'}\delta_{ss'} \\ &[\alpha^+_{eks}, \alpha_{hk's'}]_+ = \delta_{kk'}\delta_{ss'} S^\dagger \\ &[\alpha^+_{hks}, \alpha_{ek's'}]_+ = \delta_{kk'}\delta_{ss'} S \\ &\text{and all other anticommutators are zero,} \end{aligned}\right\} (4.12)$$

$$\left.\begin{aligned} \alpha^+_{eks}\alpha_{hks} &= S^\dagger \nu_{ks} \\ \alpha^+_{hks}\alpha_{eks} &= S\, \nu_{ks} \end{aligned}\right\} (4.13).$$

Finally we note the formula for the Hamiltonian in the quasi-particle approximation:

$$H = \sum_{k,s} \nu_{ks}\, \epsilon_{ks} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.14).$$

5. The effect of a change in the origin of energy.

The treatment of sections 3 and 4 is valid only when energies are measured relative to the Fermi energy. However, the only effect of changing the origin of energy will be on the Hamiltonian and on the evolution of the system with time. If the origin of energy is changed so that the Fermi energy becomes λ, the only effect on the Hamiltonian is to add the term λN, changing (4.14) into

$$H = \sum_{k,s} \nu_{ks}\, \epsilon_{ks} + \lambda N \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5.1).$$

Using (4.3), (4.5), (4.6), (4.8), (4.10) and (4.12), we deduce

$$\left.\begin{aligned} [H, \alpha^{+}_{eks}] &= (\epsilon_{ks} + \lambda)\, \alpha^{+}_{eks} \\ [H, \alpha^{+}_{hks}] &= (\epsilon_{ks} - \lambda)\, \alpha^{+}_{hks} \\ [H, \alpha_{eks}] &= (-\epsilon_{ks} - \lambda)\, \alpha_{eks} \\ [H, \alpha_{hks}] &= (-\epsilon_{ks} + \lambda)\, \alpha_{hks} \end{aligned}\right\} \quad (5.2)$$

$$\left.\begin{aligned} [H, S^{+}] &= 2\lambda S^{+} \\ [H, S] &= -2\lambda S \end{aligned}\right\} \quad (5.3)$$

From these equations it is seen that the generalised operators remain good quasi-particle operators with an arbitrary energy origin, in contrast to the Bogoliubov operators.

We shall impose the requirement that the relations expressing the self-consistent field in terms of s must not involve ~~time~~ the time explicitly. This defines the time dependence of s, and from (5.3) it is seen that s has imaginary exponential time dependence with frequency $2\lambda/\hbar$. This time dependcan be regarded as due to the generation of collective excitations by the perturbing term λN added to the Hamiltonian.

6. The analogy between a superconductor and a rotating solid.

Our conclusions concerning the physical significance of the above considerations can be better understood if the properties of a familiar system, which is closely analogous to a superconductor, are kept in mind. This is that of a solid constrained by frictionless forces to rotate about a fixed axis (cf. Anderson 1958). In such a system the component of angular momentum about the axis is constant and quantised to values $m\hbar$ (neglecting complications due to spin). This follows from symmetry properties, just as the conservation of total charge, Ne, does in any system of electrons. However, in a solid there is also a variable φ, whose existence is due instead to broken symmetry, describing the orientation of the solid. The single-valued $e^{i\varphi}$ corresponds closely to the parameter s in superconductors. To continue the analogy, corresponding to the states in superconductors which have the same quasi-particle distribution but different total number of electrons, are states of a solid which are identical apart from their angular momentum (cf. states of a molecule which have all their quantum numbers equal except the rotational ones), and can to a good approximation be obtained from each other by applying the operators $e^{\pm i\varphi}$ (cf. the operators $S, S^\dagger$ in the superconducting case). States with a definite φ are superpositions of these states with definite phases, just like the states of the restricted ensembles in a superconductor.

To complete the analogy we note that what corresponds to the k Fermi energy of the superconductor is the angular velocity of the rotating body, since both determine the frequency with which the classical variable rotates, while the angular momentum of the rotating body corresponds to the number of

of electrons in the superconductor, as noted above.

7. Physical significance of the S operator.

In this section we shall consider various questions concerning the physical interpretation and consequences of the preceeding theory, and in particular the existence of the S operator and restricted ensembles.*

In the first place we shall discuss the question of whether it is actually possible to do an experiment to observe the value of s. Some light is thrown on this by the fact that S does not commute with N. This implies that any observation of s, the eigenvalue of S, cannot be performed without changing N, the number of electrons in the system. Hence it is not possible to determine s simply by subjecting the superconductors to electromagnetic fields, for example. A complementary fact is that the result of any observation which does not alter the value of N is independent of s, and calculations can be done just as well with a restricted ensemble (as in the usual Bogoliubov/RPA methods) as with the true grand canonical ensemble. This is because one can transform any one restricted ensemble into any other one by applying an operator $e^{iN\theta}$, which does not alter the matrix elements of any operator which commutes with N. The analogous property in the case of the rotating solid is that its internal properties are independent of its orientation, owing to the symmetry of the Hamiltonian.

Next we may note that if somehow we manage to observe the value of s, the system is left in a state which is a superposition with definite phase relations of states with different values of N. Wick et. al. (1952) have

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* cf. Wick et. al. (1952).

suggested that such states do not exist, and that systems with an indefinite number of electrons can be described only by density matrices.* However Anderson (private communication) has disputed this on grounds connected with the basic postulates of quantum mechanics. Another relevant point is that s can be caused to change merely by altering the absolute potential of the system. Whether the absolute potential has any meaning is another question beset by philosophical difficulties. We shall therefore not discuss further the problem of a single superconductor, but go on to the case of two superconductors.

In the first place we shall consider a system composed of two entirely seperate subsystems l and r, each containing a superconducting region. The total number of electrons N will be the sum of the numbers in the two regions N_l and N_r, and the Hamiltonian H the sum of two Hamiltonians H_l and H_r. There will be two pair operators S_l, S_r (and ensemble parameters s_l, s_r) since the self-consistent field equations do not connect self-consistent field parameters in different regions. Commutation relations for two operators in the same region will be the same as for a single region, while two operators in different regions commute or anticommute according to the number of fermion operators they contain. It is easily seen that while S_l and S_r do not commute with N, $S_l^\dagger S_r$ and $S_r^\dagger S_l$ do commute with N but not with N_l or N_r. Their expectation values $s_l^* s_r$ and $s_r^* s_l$ depend on the phase difference between s_l and s_r. By similar arguments to those used in the case of a single superconductor we arrive at the following conclusions:

(a). The phase difference can be measured (in theory, at any rate) without adding electrons to the whole system, but not without allowing electrons to pass from one region to the other.

* Note added in proof. The argument of Wick et. al. does not in fact apply to superpositions of states differing from each other by an even number of electrons, such as those occurring in superconductivity theory.

(b) If a quantity can be observed without allowing electrons to pass from one region to the other, its value is independent of the phase difference, but a quantity whose measurement necessitates allowing electrons to pass from one region to the other may depend on the phase difference.

(c) States in which there is a definite phase difference, i. e. eigenstates of $S_l^\dagger S_r$ must be states in which the numbers of electrons in the two regions are indefinite, but since $S_l^\dagger S_r$ commutes with N they can contain a definite total number of electrons, and so no difficulties of principle are involved.

(d) $s_l^* s_r$ has time dependence $e^{-2i(\lambda_l-\lambda_r)t/\hbar} = e^{-2ieVt/\hbar}$, where V is the potential difference. Hence all quantities dependent on the phase difference oscillate with frequency 2eV/h. It is mainly on account of this fact that the Bogoliubov/RPA theory cannot cope with the present situation.

The question of absolute potential does not arise in this case. Nevertheless the system does exhibit the paradoxical behaviour discussed by Aharonov and Bohm (1959), that its behaviour can be affected by the existence of electric fields through which no electrons are able to pass. To see this, suppose that the phase difference is measured at a time t_1. The phase differ- at a later time t_2 will depend on the integrated value of the potential difference between the regions over the interval between t_1 and t_2. This potential difference implies the existence of electric fields in the space between the regions. However, it is necessary to allow electrons to pass through this field only at t_1 and t_2, when the measurements of phase difference are being made, and not during the intervening time.

It should be noted that the initial phase difference existing when the two regions first become superconducting is completely uncertain, in the quantum-mechanical sense, but once it has been measured its future value

can be predicted if the potential difference is known (eventually statistical and quantum-mechanical fluctuations will make the phase difference uncertain again until another observation is made).

8. The properties of coupled superconductors.

8.1. Introduction.

In section 7 we saw that the physical consequences of the existence of the s parameters are connected with processes in which electrons can be transferred from one region to the other. We shall therefore now consider the possibilities that can occur when a small amount of electron transfer is possible, i.e. there is weak coupling between the two subsystems. An example of this is a system containing two superconductors between which tunnelling is possible. Another example of coupling occurs when two superconducting regions are joined by a normal region, though here the coupling is very strong, since electron transfer is not inhibited by a potential barrier. This coupling can be expressed mathematically by adding a transfer term H_T to the Hamiltonian. In the case of tunneling one normally assumes that H_T is composed of terms like $T_{lr} a_l^\dagger a_r$, representing transfer of an electron from a state r in one region to a state l in the other. The situation is more complicated in the case of superconductors joined by a normal region, since there is a time lag between the disappearance of an electron from one superconductor and its reappearance in the other. The unit of time which one would expect to be relevant in superconductors is Planck's constant divided by the energy gap, i.e. $\sim 10^{-11}$ sec. For example this is the length of time for which a virtual state obtained by exciting a pair of quasi-particles can exist. In this time an electron travels a coherence length. Hence electron tunnelling

can be treated as an instantaneous process, but electron transfer between two superconductors separated by a normal region of thickness comparable with or greater than a coherence length can not.

8.2. General properties of coupled superconductors.

We shall now consider some general features of the behaviour of coupled superconductors, in the first place by considering the analogous system of two interacting rotating bodies. To give a concrete picture of the interaction, we may suppose that the bodies are magnetised and that the interaction is magnetic. Corresponding to the current passing from one region to the other, which is proportional to the rate of transfer of electrons, is the couple between the two solids, which is equal to the rate of transfer of angular momentum. The analogy to current being fed into one region and out of the other by an external source is the application of equal and opposite couples to the two solids, and the analogy to the potential difference between the regions is the difference in the angular velocities of the solids.

In the case of the rotating solids, there are two types of contribution to the couple between them. The first is a dissipative kind (eddy currents, etc.), which exists only when the solids have different angular velocities, and tends to make their angular velocities the same. The second, the direct interaction between the magnetic moments, is non-dissipative and produces a steady couple when the solids have the same angular velocity, and its existence is intimately connected with the broken symmetry, which picks out a definite direction in each solid. If one replaces the words 'solid', 'couple' and 'angular velocity' by 'region','current' and 'potential' respectively, one is immediately struck by the analogy with ohmic currents and supercurrents.

The causes of ohmic currents are well known, and will not be discussed further here. The second contribution arises from the fact that the rate of transfer of quanta depends on the phase difference between the classical variables, and we shall now consider possible causes of this in the case of superconductivity.* One way in which the phase difference could enter is through the operation of coherence factors.# These arise from interference between the two processes $k_1 \rightarrow k_2$ and $-k_2 \rightarrow -k_1$ (Bardeen, Cooper and Schrieffer 1957), and the phase difference between the matrix elements which have to be added would depend on the phase difference between the s parameters in the two regions, if k_1 and k_2 were states in different regions. It is at first sight surprising that these two processes should interfere, since they involve electron transfer in opposite directions. This paradoxical result is due to the fact that any knowledge of the phase difference necessarily implies a lack of knowledge of the numbers of electrons in the two regions, and so wave functions with this property must be used to demonstrate the interference. To take the simplest possible example, if the initial state is $a\psi_{N_1,N_2} + b\psi_{N_1+2,N_2-2}$, where ψ_{lm} is a state with l electrons in one region and m in the other, operation of the transfer term in the Hamiltonian produces a state containing the term $(aT_{\leftarrow} + bT_{\rightarrow})\psi_{N_1+1,N_2-1}$, where $T_{\leftarrow}$, $T_{\rightarrow}$ are the coefficients of the terms in H_T which transfer electrons in the two directions. It is clear that in this circumstance interference between the two processes can occur, and that the phase depends on the phase difference between a and b.

The other main cause of dependence of the current on the phase difference is the possibility of transfer of a bound pair from one region to the other.

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* Detailed calculations in the case of tunnelling are performed in section 9.

Contrast Bardeen (1961), whose arguments we find unconvincing.

In mathematical form, if at t=0 the system is in a state ψ, at a later time there is a finite probability that the system will be in the state $S_l^+ S_r \psi$, in which a pair has been transferred from region r to region l. To explore the consequences of this, we shall simplify the model by supposing that this is the only possible process. We shall also make the approximation that it takes place instantaneously. The process is in fact a second order one, since it involves the transfer of two electrons, and the energies of the intermediate state differ from the initial and final state energies by an amount of the order of the energy gap. Hence the effective time for the process is that mentioned earlier, h divided by the energy gap, and the approximation should be valid if the phase difference varies only slightly in that time, i.e. if the potential difference is small compared to the voltage corresponding to the gap energy.

We shall therefore assume $H_T = M S_l^+ S_r + M^* S_r^+ S_l$ . . . . (8.2.1).

The current from region l to region r is therefore

$$J = e\dot{N}_r = ie/\hbar\,[H_l + H_r + H_T, N_r] = ie/\hbar\,[H_T, N_r]$$
$$= -2ie/\hbar\,(M S_l^+ S_r - M^* S_r^+ S_l), \text{ by (4.6).}$$

If the two regions are restricted ensembles, we deduce that

$$\langle J \rangle = -2ie/\hbar\,(M s_l^* s_r - M^* s_r^* s_l) \quad . \quad . \quad . \quad . \quad . \quad (8.2.2)$$

This shows explicitly the dependence of the current on the phase difference. An unusual feature is that the current is linear in the matrix element, whereas one normally thinks of the probability of a process in quantum mechanics as being proportional to its square. However, in the usual situation in which one calculates transition probabilities there are a large number of states with small occupation numbers, whereas here we are dealing with a transition between just two states, whose occupation numbers are large. The

same feature is apparent in the analogy of the rotating solids. The transfer of angular momentum may be regarded as due to the virtual emission of a photon by one solid followed by its absorption by the other, and the matrix element is thus proportional to the product of their magnetic moments. The couple between the solids is also proportional to their product, and is therefore linear in the matrix element.

This linear dependence of the currents on the matrix element is very important to the question of their possible observation in tunnelling. If T is a typical matrix element for single electron transfer, the matrix element for transfer of pairs will be proportional to $|T|^2$, since it is a second order process. Hence the pair current is also proportional to $|T|^2$. The normal quasi-particle current is proportional to $|T|^2$ as well, since the usual perturbation theory applies to it. Hence the pair current is proportional to the quasi-particle current, and not to its square, as might be thought. If it were proportional to its square it would be extremely small, since the tunnelling probability for even a single quasi-particle is very small in the specimens normally used. We shall suppose that a similar expression to (8.2.2) holds even when pair transfer is not instantaneous.

8.3. Supercurrents, DC and AC.

As in the case of coupled rotating solids, there are two possible types of behaviour, depending on whether the potential difference between the regions is zero or non-zero. We shall first consider the case of zero potential difference. In that case the phase difference remains constant with time and a supercurrent given by (8.2.2) flows. This current is due to the transfer of bound pairs from one region to the other. Assuming there to be no other contributions to the current when the potential difference is zero, there is a

maximum current, $J_c = 4|M|e/\hbar$ . . . . . (8.3.1)

which can be carried in this way.* Analogously, in the case of the coupled rotating solids, there is a maximum couple which can be transmitted from one to the other without allowing relative rotation. If equal and opposite couples of less than the maximum are applied to the solids, they will rotate until the couple which they exert on each other becomes equal to the applied couple. Similarly, if current less than the critical value is fed into a system of two coupled superconductors, initially a potential difference will be set up, which will cause the phase difference to change until the supercurrent becomes equal to the current fed in.

Coupling between the two regions so as to allow a supercurrent to pass between them can be achieved in practice by placing them in contact. Supercurrents have also been observed between two superconductors with a thin normal region in between (Smith et. al. 1961). The calculation of section 9 indicates that it may also be possible to observe supercurrents in tunnelling.

Now we consider the case when there is a finite potential difference between the two regions. In that case $s_l^* s_r$ oscillates with frequency $\nu = 2eV/h$, and so by (8.2.2) the current also oscillates with this frequency,# and has amplitude $4|M|e/\hbar = J_c$. There is in this case no DC pair current, to first order in M (though there will be the usual dissipative quasi-particle current), and this can be attributed to the fact that the process of

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* It is possible that M may depend on J, the current flowing from one region to the other. However, if J_c is small the variation in M when $|J| < J_c$ can be neglected. We shall therefore ignore this complication, though it is the dominant effect in determining the critical current in bulk superconductors.

$1\,\mu V$ corresponds to 483.6 Mc/s, and $\simeq$ 1 Gc/s to 2.068 μV.

transfer of a bound pair from one region to the other no longer conserves energy. However, the process of transfer is possible if a photon of the correct frequency is emitted, and this emission can be regarded as radiation produced oy the oscillating supercurrents. The explanation as a pair transfer process with photon emission does not require the assumption of definite phase relationships between the two regions. Since photons have a continuous energy distribution conventional perturbation theory applies, and leads to a rate of photon emission proportional to $|M|^2$. This agrees with the interpretation in terms of oscillating currents proportional to $|M|$, since the number of photons radiated by an oscillating current is proportional to the square of its amplitude.

The energy of the emitted photons comes from the transfer of pairs through the potential difference, and in order to maintain the system in a steady state the energy must be supplied from a current source. The two-superconductor system is in fact a direct DC to AC converter. The conversion is a spontaneous emission process, rather than one of stimulated emission as in a maser.

8.4. The effect on supercurrents of thermal fluctuations and electrostatic energy.

The existence of the supercurrents discussed in 8.3 depends on the phases of the two regions being locked together by the coupling. It is clear that if the coupling is small enough the locking together of phases will be destroyed by thermal fluctuations. We may derive a criterion for the occurrence of phase locking by noting that (8.2.1) expresses the interaction energy as a function of the phase difference, and shows that it varies between the limits $\pm 2|M|$. An excitation energy $4|M|$ is thus required to enable the phases to rotate freely relative to each other, and in order that this should not be caused by thermal fluctuations, we must have

$$4|M| \gg kT \quad \ldots\ldots\ldots\ldots \quad (8.4.1).$$

In terms of the critical current (eqn. 8.3.1),

$$J_c \gg ekT/\hbar \quad \ldots\ldots\ldots\ldots \quad (8.4.2).$$

Putting $T \sim 1^{\circ}K$, this gives $J_c \gg 2\times10^{-8}A$. The lifetime of the supercurrent would be expected to increase exponentially with increase in $|M|$, and so for supercurrents to last for macroscopic time intervals it should be sufficient to have $J_c > 1\mu A$. If J_c, as defined by (8.3.1), is less than $0.5\mu A$, steady supercurrents with zero potential difference should not occur, but J_c still has significance as the amplitude of the oscillatory currents occuring at a non-zero potential difference.

Another factor which must be considered as possibly limiting the occurrence of supercurrents is that of electrostatic energy. This has the effect of inhibiting the transfer of pairs from one region to the other, and tending to prevent the locking of phases, which requires pair transfer. Since the energy gained by matching phases is $2|M|$, and the energy required to transfer a pair of electrons is $2e^2/C$, where C is the capacitance between the regions, the condition for phase matching to be favoured is $\frac{2e^2}{C} \ll 2|M|$ ..... (8.4.3). Since the condition $4|M| \gg kT$ must also be satisfied, this will be so provided that $e^2/C < \frac{1}{4}kT$, i.e. $C > 4e^2/kT \sim 10^{-2}$pF.for $T=1^{\circ}K$. It is clear from this that the effect of the electrostatic energy is normally negligible compared with that of thermal fluctuations.

8.5. <u>Interaction of supercurrents with radiation: induced superconductivity.</u>

We shall now investigate the phenomena that can occur when external electromagnetic radiation is present in the system. We shall regard the effect of the radiation as simply producing oscillations in the potential difference between the regions. Since the rate of change of phase difference is propor-

tional to the potential difference, the pair current will no longer have constant frequency but will be frequency modulated. If the mean potential difference is V, and the frequency of the incident radiation is ν, the pair current will have Fourier components of frequency $|2eV/h \pm n\nu|$ (n integral). Radiation of this frequency can then be emitted. Quantum-mechanically, the process consists of the transfer of a pair from one region to the other, with absorption or stimulated emission of quanta of the incident radiation, and emission of another photon to make up the energy difference.

In a similar manner to the situation in the absence of radiation, different behaviour results when 2eV is an exact multiple of $h\nu$. In that case the pair current has a zero frequency component, which will depend on the phase relationships between the incident radiation and the s parameters. Thus the mean current can take on a range of values while the potential difference remains at $nh\nu/2e$. In other words, the DC characteristic has a portion of zero slope resistance at a non-zero voltage. The width of this portion depends on the intensity of the incident radiation. This phenomenon can be regarded as superconductivity induced by the radiation, and is due to pair transfer accompanied by the absorption or stimulated emission of photons. It might form the basis of a means of measuring h/e *, or of accurate stabilisation of very small voltages.

8.6. Spatial distribution of supercurrents.

We have so far been concerned only with the total supercurrent and not with its distribution in space. To investigate this, we shall idealise the situation by supposing that the two regions have a common interface S, which is to be regarded as composed of pairs of points, one on each side. The

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* Suggested by Professor A. B. Pippard.

transfer of electrons is then regarded as the annihilation of an electron at a point on one side with the simultaneous creation of an electron at the corresponding point on the other side, i.e.

$$H_T = \sum_s \int_S \{ T_p a_s^+(P_l) a_s(P_r) + T_p^* a_s^+(P_r) a_s(P_l) \} dS$$

where s is a spin index and l and r label points on the two sides of S. The second order matrix element M for pair transfer is given by summing the contributions to it over each pair of points at which the electrons can cross, and is proportional to

$$\sum_{s,s'} \int_{P \in S} \int_{P' \in S} \int_{t'=-\infty}^{\infty} T_p T_{p'} F_l^*(P,s,t;P',s',t') F_r(P,s,t;P',s',t') dt'$$

where F_l, F_r are the Gor'kov functions (1958) which give the matrix elements for destruction of pairs on the two sides. We have integrated over only one time variable in order to obtain a finite result. We shall now make the approximation of putting

$$F(P,s,t;P',s',t') = \begin{cases} \frac{1}{\sqrt{2}} \delta(P,P') \delta(t,t') \psi(P,t) & \text{if } s \neq s', \\ 0 & \text{if } s = s'; \end{cases}$$

this is equivalent to neglecting spatial variation over a coherence length, and making the same assumption as before about about the rapidity of changes with time. ψ is the 'effective superconducting wave function'. We then obtain

$$M = \int m(P) dS \qquad (8.6.1)$$

where

$$m(P) \propto T_p^2 \psi_l^*(P) \psi_r(P) \qquad (8.6.2).$$

Hence, from (8.2.2) the total supercurrent is proportional to

$$\int_S \{ -2iek (T_p^2 \psi_l^*(P) \psi_r(P) s_l^* s_r - T_p^{*2} \psi_r^*(P) \psi_l(P) s_r^* s_l) \} dS$$

Therefore, assuming that the current density at any point depends only on quantities in the neighbourhood of that point, the supercurrent density is

$$j = j_1 s_l^* s_r + j_1^* s_r^* s_l \qquad (8.6.3)$$

where

$$j_1 \propto -2iek T_p^2 \psi_l^*(P) \psi_r(P) \qquad (8.6.4).$$

If time-reversal symmetry exists in the absence of a magnetic field, then j_1 must be pure imaginary everywhere, since time reversal changes $j \to -j$, $s_1 \to s_1^*$ and $s_r \to s_r^*$. Similarly, from the invariance of H_T under time reversal it follows that m must be real.

8.7. Effects of magnetic fields.

To investigate the effects of magnetic fields we shall make use of the result (Keller and Zumino 1961) that the change in phase of ψ round a closed curve in a superconductor is equalnto the fluxoid through it divided by $\hbar c/2e$.* Let Pand Q be two points in S, and C be a curve obtained by going from P to Q in region 1 and back again in region r, and let Φ be the fluxoid through C. In the result quoted, the phase change in ψ in going from one superconductor to the other must not be included, but only the sum of the phase changes which occur on traversing the portions of the curve which lie in one superconductor only. Therefore

$$\begin{aligned}\Phi/(\hbar c/2e) &= \{\phi(Q_1) - \phi(P_1)\} + \{\phi(P_r) - \phi(Q_r)\} \\ &= \{\phi(Q_1) - \phi(Q_r)\} - \{\phi(P_1) - \phi(P_r)\} \\ &= \Delta\phi(Q) - \Delta\phi(P),\end{aligned}$$

where ϕ is the phase angle of ψ and $\Delta\phi$ its change in crossing S. Hence from from (8.6.4) the difference in phase between the values of j_1 at P and Q is equal to $\Phi/(\hbar c/2e)$. We see that the effect of a magnetic field is to cause the phase of j_1 to vary over S. The consequences of this depend on the amount of coupling between the regions and the strength of the magnetic field. In the first place, let us suppose that the coupling is so weak that the supercurrents induced do not appreciably affect the field. In this case a sufficiently large magnetic field will cause the ~~phase of~~ critical ~~value of~~

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* I am indebted to Dr. P.W.Anderson for pointing out the connection between phases and fluxoids.

the supercurrent to be reduced, owing to the variation of phase of j_1 over S. This will start to happen when the fluxoid through the curve becomes of the order of a flux quantum hc/2e. If the superconducting regions are sufficiently thick to prevent the field penetrating right through them, the curve C can be drawn so that it is in a region of zero supercurrent, and then the only contribution to the fluxoid comes from the flux inside C, and this can be calculated from knowledge of the penetration depth of the superconductors.* If one assumes a penetration depth of 10^{-5} cm., and the dimensions of S to be of the order of $1mm^2$, one arrives at a relevant field of the order of 0.1gauss.

An interesting situation occurs when S consists of two seperated regions which are so small that j_1 can be taken to have constant phase in each one. This might occur, for example, if two specimens of the type used in tunnelling experiments were connected in parallel. In that case the curve C would be a curve encircling the hole between the two parts of the circuit which were in parallel. In this situation the total supercurrent is a periodic function of the flux through the hole, the unit of periodicity being the flux quantum hc/2e, beaause J_1 is effectively the sum of two terms, which vary in relative phase as the flux is changed. This is very similar to the situation pointed out by Aharonov and Bohm (1961, 1959), involving interference of electrons which can travel along two different paths, between which there is some magnetic flux. In that case the diffraction pattern has periodicity in the flux with period hc/e; in our case the unit is hc/2e instead, since the interference is between pairs, which have charge 2e.

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* Note that it is only fields tangential to the interface which are important. Trapped flux going straight from one region to the other has no effect on the phase of j_1.

We shall now consider what can happen when the coupling between the regions is sufficiently strong for the supercurrents to have an appreciable effect on the magnetic field. We shall for simplicity consider only the case when the total supercurrent from one region to the other is zero, i.e. when no external current is fed into the system. There will still be currents across the interface, as can be seen from eqn. (8.6.3), since the phase of j_1 is not constant in the presence of a magnetic field. These currents are diamagnetic currents of the same type as those encountered in bulk superconductors, and tend to screen out the magnetic field from the region between the superconductors. More light is thrown on this by eqns. (8.2.1) and (8.6.1), which show that the coupling energy is proportional to $|M|$, and that this is greatest when m has the same phase everywhere, i.e. when the field is excluded. For sufficiently small fields the gain in coupling energy resulting from exclusion of the field is greater than the magnetic energy required to do so. From this criterion one deduces a critical field given by

$$H_c^2 = j_c h/ed \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8.7.1),$$

where d is the thickness of the layer of penetration of the field when it is not excluded, and j_c is the critical supercurrent density. Taking $d=2\times10^{-5}$ cm., this gives

$$H_c = 0.05\sqrt{j_c} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8.7.2)$$

where H_c is in gauss and j_c in amps/cm^2.

The effective distance D to which the field penetrates between the regions is given by the relation $H_c/D = 4\pi j_c/c$, which follows from Maxwell's equations under the assumption of exponential decay with depth, and yields the result

$$D^2 = hc^2/16\pi^2 j_c ed. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8.7.3).$$

Again putting $d=2\times10^{-5}$ cm., this gives

$D=0.04/\sqrt{j_c}$ cm. . . . . (8.7.4),

where j_c is in amps/cm^2.

8.8. Summary.

Summarising the results of this section, it can be said that if two superconductors are coupled together strongly enough to overcome the effects of thermal fluctuations, they show to a limited extent the characteristic properties of a single superconductor, in particular the exclusion of magnetic fields and supercurrents. If, however, a finite potential difference exists between the superconductors, these properties are lost and oscillatory ones take their place.

9. Calculation of tunnelling currents.

We now turn to the calculation of the tunnelling current between two superconductors. The method we use is a modification of the perturbation treatment of Cohen et. al. (1962) for the case when only one region is superconducting, and is in the spirit of the Goldstone perturbation theory (1957). This is based on the interaction picture, i.e. the evolution of operators with time depends on the Hamiltonian without tunnelling:

$$\dot{A} = i/\hbar\,[H_l + H_r, A] \quad . \quad . \quad . \quad . \quad (9.1)$$

while the evolution of state vectors depends only on the small tunneling term:

$$\dot{\psi} = -i/\hbar\, H_T \psi \quad . \quad . \quad . \quad . \quad . \quad (9.2)$$

This gives the same time dependence of the physically important matrix elements as the more usual Schrödinger and Heisenberg pictures. In order to avoid difficulties resulting from the use of Fourier transforms of functions which do not tend to zero at infinitely distant times, one normally multiplies H_T by $e^{\epsilon t}$, where ϵ is a small positive constant which is allowed to tend to

zero. In the following calculation we shall always put ϵ equal to zero as soon as it is possible to do so without affecting the subsequent evaluations. We must now consider the appropriate initial conditions. Since we wish to calculate the oscillating currents as well as the steady ones we suppose that at $t=-\infty$ the system consists of two independent restricted canonical ensembles, which are then allowed to interact.

The point of using the interaction picture is that in it quasi-particle and pair operators have the simple imaginary exponential time dependance, as follows from equations (5.2),(5.3) and (9.1). These neglect quasi-particle interactions which complicate the time dependence, but these interactions should not affect the tunnelling current. If, however, we had used the Heisenberg picture part of the time dependence would have arisen from the tunnelling term in the Hamiltonian and could not have been ignored.

The mean tunnelling current is given by

$$J(t)=ie/\hbar\frac{d}{dt}\langle N_r\rangle=ie/\hbar\langle[H_1+H_r+H_T,N_r]\rangle,$$

(since the formula for the time derivative of expectation values involves the total Hamiltonian)

$$=ie/\hbar\langle[H_T,N_r]\rangle=ie/\hbar\sum_k p_k\langle k(t)|[H_T,N_r]|k(t)\rangle$$

where p_k is the weight of state k in the ensemble.

To calculate J(t) to second order in H_T, k(t) needs to be known to first order. Integrating (9.2) we obtain to first order

$$|k(t)\rangle=(1-i/\hbar\int_{-\infty}^{t}e^{\epsilon t'}H_T(t')dt)|k(-\infty)\rangle=(1-i/\hbar E(t))|k(-\infty)\rangle$$

where $E(t)=\int_{-\infty}^{t}e^{\epsilon t'}H_T(t')dt$. . . . . (9.3)

Hence $J(t)=ie/\hbar\sum_k p_k\langle k(-\infty)|\{1+i/\hbar E(t)\}[H_T,N_r]\{1-i/\hbar E(t)\}|k(-\infty)\rangle$

$$=e/\hbar^2\langle[[H_T,N_r],E]\rangle. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9.4)$$

where the expectation value is with respect to the ensemble at $t=-\infty$ and higher order terms have been omitted.

We shall assume that the system has time-reversal symmetry and symmetry with respect to rotations in spin space, with the same convention as in section 3 concerning the direction of spin of a state. Time-reversal symmetry plays an essential part in the succeeding argument, but the assumption of symmetry under rotations in spin space is made only in order to demonstrate the essential features of the calculation without becoming involved in the complications of generalising the RPA theory to pairing with general time-reversed states.* Results which are essentially the same are obtained if this is done. Taking this assumption and the discussion of (8.1) into account, we can write H_T in the form

$$H_T=\sum_{l,r}(T_{lr}a_l^\dagger a_r+T_{-l,-r}a_{-l}^\dagger a_{-r}+T_{rl}a_r^\dagger a_l+T_{-r,-l}a_{-r}^\dagger a_{-l}) \quad .. \quad .. \quad .. \quad .. (9.5)$$

where as usual l and r distinguish states on the two sides. Since H_T is Hermitean and has time reversal symmetry,

$$T_{rl}=T_{lr}^* \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (9.6)$$

$$T_{-l,-r}=T_{lr}^* \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (9.7)$$

From (9.5),

$$[H_T,N_r]=\sum_{l,r}(T_{lr}a_l^\dagger a_r+T_{-l,-r}a_{-l}^\dagger a_{-r}-T_{rl}a_r^\dagger a_l-T_{-r,-l}a_{-r}^\dagger a_{-l}) \quad .. \quad .. \quad .. \quad (9.8)$$

If H_T is expressed in terms of quasi-particle operators, each term has exponential time dependence and the integration necessary to evaluate E can be performed immediately. If (9.8) is also expressed in terms of quasi-particle operators and the resulting expressions substituted into (9.4), the expression

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* In particular, notational difficulties arise from the fact that double application of the time reversal transformation to a fermion operator changes its sign. The assumption neccessary in the general case to ensure that all contributions to the supercurrent at absolute zero are in phase is that $\langle a_k^\dagger (Ta_k)^\dagger\rangle$ is positive for all states k, where T is the time reversal transformation.

for J reduces to terms consisting of the expectation values of products of four quasi-particle operators at time t, two in each region, with respect to the restricted ensemble at $t=-\infty$, when the regions are independent. The only such products with non-zero expectation values are of the form $\alpha^{+}_{fl}\alpha_{fl}\alpha^{+}_{fr}\alpha_{fr}$ where each f can be either an e or an h. Their expectation values can be obtained in terms of the mean occupation numbers by using (4.5), (4.12) and (4.13).

We shall now give the formulae obtained by following this procedure and outline the intermediate stages of the calculation.

Substituting (4.4) into (9.5) we obtain

$$H_T = \sum_{l,r}\{T_{lr}(u_l u_r \alpha^{+}_{el0}\alpha_{er0} + u_l v_r \alpha^{+}_{el0}\alpha^{+}_{hr1} + v_l u_r \alpha_{hl1}\alpha_{er0} + v_l v_r \alpha_{hl1}\alpha^{+}_{hr1}) + T_{-l,-r}(u_l u_r \alpha^{+}_{el1}\alpha_{er1} - u_l v_r \alpha^{+}_{el1}\alpha^{+}_{hr0} - v_l u_r \alpha_{hl0}\alpha_{er1} + v_l v_r \alpha_{hl0}\alpha^{+}_{hr0})\}$$

$+$ Hermitean conjugate terms (h.c.) .. ..(9.9)

The calculation of E(t) (eqn. 9.3) involves the evaluation of integrals such as

$$\int_{-\infty}^{t} e^{\epsilon t'}\alpha^{+}_{el0}(t')\alpha_{er0}(t')dt' = \alpha^{+}_{el0}(0)\alpha_{er0}(0)\int_{-\infty}^{t} e^{\{\epsilon+i(\lambda_l+\epsilon_l-\lambda_r-\epsilon_r)/\hbar\}t'}dt'$$
$$= \alpha^{+}_{el0}(0)\alpha_{er0}(0)e^{\{\epsilon+i(\lambda_l+\epsilon_l-\lambda_r-\epsilon_r)/\hbar\}t}\Big/\{\epsilon+i(\lambda_l+\epsilon_l-\lambda_r-\epsilon_r)/\hbar\}$$
$$= -i\hbar\,\alpha^{+}_{el0}(t)\alpha_{er0}(t)\Big/(eV+\epsilon_l-\epsilon_r-i\eta)$$

where $\eta=\hbar\epsilon$, and gives the result

$$E = i\hbar\sum_{l,r}\{T_{lr}\left(\frac{u_l u_r}{eV+\epsilon_l-\epsilon_r-i\eta}\alpha^{+}_{el0}\alpha_{er0} + \frac{u_l v_r}{eV+\epsilon_l+\epsilon_r-i\eta}\alpha^{+}_{el0}\alpha^{+}_{hr1} + \frac{v_l u_r}{eV-\epsilon_l-\epsilon_r-i\eta}\alpha_{hl1}\alpha_{er0} + \frac{v_l v_r}{eV-\epsilon_l+\epsilon_r-i\eta}\alpha_{hl1}\alpha^{+}_{hr1}\right) + T_{-l,-r}\left(\frac{u_l u_r}{eV+\epsilon_l-\epsilon_r-i\eta}\alpha^{+}_{el1}\alpha_{er1} - \frac{u_l v_r}{eV+\epsilon_l+\epsilon_r-i\eta}\alpha^{+}_{el1}\alpha^{+}_{hr0} - \frac{v_l u_r}{eV-\epsilon_l-\epsilon_r-i\eta}\alpha_{hl0}\alpha_{er1} + \frac{v_l v_r}{eV-\epsilon_l+\epsilon_r-i\eta}\alpha_{hl0}\alpha^{+}_{hr0}\right)\} + \text{h.c.} \quad \ldots(9.10)$$

Substituting (4.4) into (9.8) we obtain

$$[H_T, N_r] = \sum_{l,r} \{ T_{lr}(u_l u_r \alpha^\dagger_{el0}\alpha_{er0} + u_l v_r \alpha^\dagger_{el0}\alpha^\dagger_{hr1} + v_l u_r \alpha_{hl1}\alpha_{er0} + v_l v_r \alpha_{hl1}\alpha^\dagger_{hr1})$$
$$T_{-l,-r}(u_l u_r \alpha_{el1}^\dagger \alpha_{er1} - u_l v_r \alpha^\dagger_{el1}\alpha^\dagger_{hr0} - v_l u_r \alpha_{hl0}\alpha_{er1} + v_l v_r \alpha_{hl0}\alpha_{hr0})\} - \text{h.c.} \quad \ldots (9.11)$$

The terms with non-zero expectation value in the commutator of (9.11) and (9.10) are of two distinct types:

$$[\alpha^\dagger_{el0}\alpha_{er0}, \alpha^\dagger_{er0}\alpha_{el0}] = \alpha^\dagger_{el0}\alpha_{er0}\alpha^\dagger_{er0}\alpha_{el0} - \alpha^\dagger_{er0}\alpha_{el0}\alpha^\dagger_{el0}\alpha_{er0}$$
$$= \alpha^\dagger_{el0}\alpha_{el0}\alpha_{er0}\alpha^\dagger_{er0} - \alpha_{el0}\alpha^\dagger_{el0}\alpha^\dagger_{er0}\alpha_{er0}$$
$$= \nu_{l0}(1-\nu_{r0}) - (1-\nu_{l0})\nu_{r0} \qquad \text{from (4.5) and (4.12)},$$
$$= \nu_{l0} - \nu_{r0}.$$

$$\text{and } [\alpha^\dagger_{el0}\alpha_{er0}, \alpha_{hl0}\alpha^\dagger_{hr0}] = \alpha^\dagger_{el0}\alpha_{er0}\alpha_{hl0}\alpha^\dagger_{hr0} - \alpha_{hl0}\alpha^\dagger_{hr0}\alpha^\dagger_{el0}\alpha_{er0}$$
$$= -\alpha^\dagger_{el0}\alpha_{hl0}\alpha_{er0}\alpha^\dagger_{hr0} + \alpha_{hl0}\alpha^\dagger_{el0}\alpha^\dagger_{hr0}\alpha_{er0}$$
$$= -\nu_{l0}S_l^\dagger(1-\nu_{r0})S_r + (1-\nu_{l0})S_l^\dagger \nu_{r0} S_r$$

from (4.12) and (4.13),

$$= -(\nu_{l0} - \nu_{r0}) S_l^\dagger S_r.$$

Substituting (9.10) and (9.11) into (9.4), and using (9.6) and (9.7) we obtain

$$J = \frac{-ie}{\hbar}\sum_{l,r}|T_{lr}|^2\Big[\frac{u_l^2 u_r^2(\overline{\nu_{l0}} - \overline{\nu_{r0}})}{eV+\epsilon_l-\epsilon_r-i\eta} + \frac{u_l^2 v_r^2(-1+\overline{\nu_{l0}}+\overline{\nu_{r1}})}{eV+\epsilon_l+\epsilon_r-i\eta} + \frac{v_l^2 u_r^2(1-\overline{\nu_{l1}}-\overline{\nu_{r0}})}{eV-\epsilon_l-\epsilon_r-i\eta} + \frac{v_l^2 v_r^2(-\overline{\nu_{l1}}+\overline{\nu_{r1}})}{eV-\epsilon_l+\epsilon_r-i\eta}$$
$$+ u_l v_l u_r v_r S_l^* S_r\Big\{\frac{\overline{\nu_{l0}} - \overline{\nu_{r0}}}{eV+\epsilon_l-\epsilon_r-i\eta} + \frac{1-\overline{\nu_{l0}}-\overline{\nu_{r1}}}{eV+\epsilon_l+\epsilon_r-i\eta} + \frac{-1+\overline{\nu_{l1}}+\overline{\nu_{r0}}}{eV-\epsilon_l-\epsilon_r-i\eta} + \frac{-\overline{\nu_{l1}}+\overline{\nu_{r1}}}{eV-\epsilon_l+\epsilon_r-i\eta}\Big\}\Big]$$
$$+ \text{h.c. \& r.s.} \quad \ldots \quad (9.12)$$

where r.s. denotes terms obtained by reversing spins, i.e. interchanging 0 and 1 in the spin suffixes. This can be written in the form

$$J = J_0 + J_1 s_1^* s_r + J_1^* s_r^* s_1 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (9.13).$$

J_0 is the DC component of the current at a finite voltage, while the other terms are the phase-dependent terms discussed in (8.2), which have no DC component except at zero voltage. Since $\frac{1}{A-i\eta} = P\frac{1}{A} + \pi i \delta(A)$, (P=principal value), J_0, which consists of terms derived from the first row of (9.12), can be written as

$$J_0 = \frac{2\pi e}{\hbar} \sum_{l,r} |T_{lr}| \{ u_l^2 u_r^2 (\overline{\nu_{l0}} - \overline{\nu_{r0}}) \delta(eV + \epsilon_l - \epsilon_r) + u_l^2 \nu_r^2 (-1 + \overline{\nu_{l0}} + \overline{\nu_{r1}}) \delta(eV + \epsilon_l + \epsilon_r)$$
$$+ \nu_l^2 u_r^2 (1 - \overline{\nu_{l1}} - \overline{\nu_{r0}}) \delta(eV - \epsilon_l - \epsilon_r) + \nu_l^2 \nu_r^2 (-\overline{\nu_{l1}} + \overline{\nu_{r1}}) \delta(eV - \epsilon_l + \epsilon_r) \}$$
$$+ \text{r.s.} \quad \ldots (9.14)$$

(9.14) can be cast into a form in which u_k and v_k do not appear, as in the case considered by Cohen et. al. (1962). To do this one notes that reflection about the Fermi surface leaves T, ϵ and $\overline{\nu}$ unchanged, to a good approximation, but changes u_k^2 into $1-u_k^2$ and v_k^2 into $1-v_k^2$, so that one can omit the factors u_k^2 and v_k^2 in (9.14) if the region of integration over both l and r is confined to one side of the Fermi surface in each term. If one then defines single-electron energies and occupation numbers by the relations

$$E_k = \begin{cases} \lambda_k - \epsilon_k, & |k| < k_F \\ \lambda_k + \epsilon_k, & |k| > k_F \end{cases} \quad (9.15)$$

$$n_{k0} = \begin{cases} 1 - \nu_{k1}, & |k| < k_F \\ \nu_{k0}, & |k| > k_F \end{cases} \quad (9.16)$$

then (9.14) reduces to

$$J_0 = \frac{2\pi e}{\hbar} \sum_{l,r} |T_{lr}|^2 (\overline{n_{l0}} - \overline{n_{r0}}) \delta(E_{l0} - E_{r0}) + \text{r.s.} \quad \ldots\ldots (9.17)$$

This is the same as the result expected on the single-electron picture, the probabilities of tunnelling from the state l0 to the state r0 and vice versa being $\overline{n}_{l0}\,\overline{(1-n_{r0})}\,|T_{lr}|^2\,\delta(E_{l0}-E_{r0})$ and $\overline{n_{l0}(1-n_{r0})}\,\frac{2\pi}{\hbar}\,|T_{lr}|^2\,\delta(E_{l0}-E_{r0})$

and $\overline{n_{r0}(1-n_{e0})}\ \frac{2\pi}{\hbar}|T_{er}|^2\delta(E_{e0}-E_{r0})$ respectively.

This our formula for the DC component of the current agrees with that obtained from the single electron picture. However, the latter model is devoid of physical reality, since it effectively assumes that quasi-particles suddenly change from electrons to holes at the Fermi surface, with a corresponding discontinuity in single-electron energies(eqn. 9.15). This excludes, for example, processes in which a quasi-particle outside the Fermi surface on one side crosses the barrier and becomes a quasi-particle inside the Fermi surface on the other side. The wrong value for the current would be obtained in general if the discontinuity in properties were supposed to take place elsewhere than on the Fermi surface. In a superconductor quasi-particles in fact change continuously from electrons to holes in a region near the Fermi surface, and our eqn. (9.14) reflects the lack of any discontinuity.

We shall now consider the phase-dependent currents. J_1 is equal to the coefficient of $s_1^* s_r$ in the second row of (9.12) plus reversed spin terms, and can be decomposed into delta function and principal value parts. In analsing it we shall assume that $u_k v_k$ is always positive. Its reality follows from time-reversal symmetry, and consideration of the RPA equations shows that it can be taken as positive for all k if a suitably averaged matrix element for electron-electron interactions, $V_{k,-k;k',-k'}$, is negative, i.e. essentially the same as the condition for superconductivity itself, though it might be violated over a small part of the Fermi surface.*

The delta function part of J_1 has a very similar structure to J_0, and can be considered as the correction to J_0 for coherence effects. With the above assumption about $u_k v_k$, it can be seen that when s_1 and s_r are in phase the

* Note added in proof: $u_k v_k$ can change sign only if the energy gap becomes zero at some point on the Fermi surface.

contribution to the current from the tunnelling of quasi-particles (the first and fourth terms of 9.12) is increased and the contribution from creation and destruction of pairs of quasi particles, one on each side, (the second and third terms of 9.12) is decreased. The principal value part of J_1 is due to the tunnelling of pairs, is zero when s_l and s_r are in phase, and has the typical form of a second order matrix element.

We shall now consider what remains of J_1 at zero voltage, when the delta function terms cancel. J_1 then reduces to

$$-\frac{2ie}{\hbar}\sum_{l,r} s_l |T_{lr}|^2 u_l v_l u_r v_r \left(P\frac{\bar{v}_{l0}-\bar{v}_{r0}}{\epsilon_l-\epsilon_r} + P\frac{1-\bar{v}_{l0}-\bar{v}_{r1}}{\epsilon_l+\epsilon_r}\right) + r.s.$$

At absolute zero, $\bar{v}=0$, so only the second term contributes, and all contributions to it are in phase. At finite temperatures the second term becomes less in magnitude, and the critical supercurrent is further reduced by the first term (since $\bar{v}$ is a decreasing function of ϵ).

Finally we shall calculate the tunnelling supercurrent at absolute zero, using the following quantities derived from the BCS theory:

$$uv = \tfrac{1}{2}\frac{\Delta}{\epsilon}$$

$$\frac{dN}{d\epsilon} = \begin{cases} 2\frac{\epsilon}{\sqrt{(\epsilon^2-\Delta^2)}}N, & \epsilon > \Delta \\ 0, & \epsilon < \Delta \end{cases}$$

where Δ is half the full energy gap and N, assumed constant, is the density of states in the normal metal. The factor 2 arises from the fact that ϵ is positive for states on both sides of the Fermi surface. We shall replace $|T_{lr}|^2$ by M, an averaged value over all pairs of states of given energies, and neglect its dependence on energy. The critical supercurrent J_c ($=2|J_1|$) is then given by

$$J_c = \frac{4e}{\hbar} M N_l N_r \Delta_l \Delta_r \int_{\Delta_l}^{\infty} d\epsilon_l \int_{\Delta_r}^{\infty} d\epsilon_r \frac{1}{(\epsilon_l+\epsilon_r)\sqrt{(\epsilon_l^2-\Delta_l^2)}\sqrt{(\epsilon_r^2-\Delta_r^2)}}$$

$$= \frac{4e}{\hbar} M N_l N_r \Delta_l \Delta_r \int_{\Delta_l}^{\infty} \frac{d\epsilon_l}{\sqrt{(\epsilon_l^2-\Delta_l^2)}} \int_{\Delta_r}^{\infty} \frac{d\epsilon_r}{(\epsilon_l+\epsilon_r)\sqrt{(\epsilon_r^2-\Delta_r^2)}}$$

$$= \frac{4e}{\hbar} M N_l N_r \Delta_l \Delta_r \int_{\Delta_l}^{\infty} \frac{d\epsilon_l \cosh^{-1}(\epsilon_l/\Delta_r)}{\sqrt{(\epsilon_l^2-\Delta_l^2)}\sqrt{(\epsilon_r^2-\Delta_r^2)}} \quad (\text{assuming } \Delta_l \geq \Delta_r)$$

$$= \frac{4e}{\hbar} M N_\ell N_r \Delta_\ell \Delta_r \int_{\cosh^{-1}(\Delta_\ell/\Delta_r)}^{\infty} \frac{t\,dt}{\sqrt{(\Delta_r^2 \cosh^2 t - \Delta_\ell^2)}} \quad (\text{putting } \epsilon_\ell = \Delta_r \cosh t) \qquad \ldots (9.18)$$

In the case when $\Delta_\ell = \Delta_r = \Delta$, this can be converted immediately into a standard integral:

$$J_c = \frac{4e}{\hbar} M N_\ell N_r \Delta \int_0^{\infty} t \operatorname{cosech} t\,dt = \frac{\pi^2 e M N_\ell N_r \Delta}{\hbar} \qquad \ldots (9.19)$$

Comparing this with the formula for the current flowing when the metals are in the normal state, $J = \frac{2\pi e}{\hbar} M N_\ell N_r V$, we see that the critical supercurrent at absolute zero is equal to the current flowing in the normal state at a voltage equal to $\pi/4$ times the full energy gap.

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