Wave Functions for Superconducting Electrons

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The observed variation of the transition temperature of mercury with isotopic mass is evidence that the superconducting state arises from interaction of electrons with lattice vibrations. The interaction term which gives scattering of electrons at high temperatures contributes at low temperatures a term to the energy of the system of electrons plus normal modes. Fröhlich has calculated the interaction energy at $T=0°K$ by second-order perturbation theory. The energy is calculated here by taking wave functions of superconducting electrons, which have energies near the Fermi surface, as linear combinations of Bloch functions whose coefficients are functions of coordinates of the normal modes. In an equivalent approximation, Fröhlich's expression for the interaction energy is obtained. When the energy is calculated directly rather than by perturbation theory, modified expressions are obtained for the energy and distribution of electrons in the superconducting state. The criterion for superconductivity is $\hbar/\tau > \sim 2\pi\kappa T$, where τ is the relaxation time for electrons at some high temperature T where τT is constant. It is shown that superconducting electrons have small effective mass.

I. INTRODUCTION

THE isotope effect observed by Reynolds, Serin, Wright, and Nesbitt[1] and by Maxwell[2] is evidence that the superconducting state arises from the interaction of electrons with lattice vibrations rather than from electrostatic interactions between electrons. They found a shift in the transition temperature, T_c, of mercury with isotopic mass, M, such that $M^{\frac{1}{2}}T_c$ is approximately constant, or such that T_c varies directly with the Debye temperature.[3]

The interaction term in the Hamiltonian which gives rise to scattering of electrons and resistance at high temperatures contributes at low temperatures a term to the energy of the system of electrons plus normal modes of vibration. It is possible to make an approximate calculation of the interaction energy on the basis of Bloch theory of metals in which correlations between the positions of electrons which arise from Coulomb forces are neglected. That the Bloch theory works as well as it does in view of the large magnitude of the Coulomb energy is surprising. The theory has a firm empirical foundation in explaining in a qualitative or quantitative way a wide variety of experimental results. An explanation of superconductivity in terms of the Bloch theory would extend its scope to cover nearly all conduction phenomena.

Fröhlich has made a calculation of the interaction energy at $T=0°K$ by an application of perturbation theory.[4] Except for interactions with lattice vibrations, the electrons are treated as free. The interaction terms give no first-order contribution to the energy. Fröhlich calculated the second-order energy. As the energy denominators vanish over part of the range of summation or integration of the second-order energy, it is necessary to take principal values in integrating over the singular regions.

The interaction energy can be interpreted as a self-energy which arises from the virtual emission and absorption of phonons. The operation of the exclusion principle is such as to give a contribution to the self-energy which acts formally like an interaction between electrons in momentum or k-space. The interaction is repulsive when the energies of the electrons are nearly equal and is attractive when the energy difference is larger than the energy of the phonon which connects the two states in the Bloch theory of conductivity.

Fröhlich finds that if the interaction terms are sufficiently large for superconductivity, there exists a state of lower energy than the usual one in which states inside a sphere of radius $k=k_0$ in k-space are occupied and those outside unoccupied. The lower energy state is obtained by taking electrons in a thin outer shell of the usual Fermi distribution and displacing them outward in k-space so as to leave a small gap between an occupied sphere and an occupied concentric spherical shell. This modified distribution has a lower interaction energy and is stable if the energy gained in this way more than compensates for the increase in Fermi energy. This condition gives a criterion for superconductivity.

An approach which appears to be formally quite different from that of Fröhlich has been suggested independently by the author.[5] We shall show here that these two different treatments lead to nearly the same results. They represent different ways of approximating the energy of the same basic Hamiltonian. We have suggested that in the superconducting state the wave functions of electrons which have energies near the Fermi surface, $E=E_0$, are modified by interaction with the normal modes.[5] Wave functions of the superconducting electrons are linear combinations of Bloch functions with energies near $E=E_0$. The coefficients, which are functions of the displacement coordinates of the normal modes, are determined by a modification of the adiabatic theory. The net effect is to lower the energies of those electrons having energies near the

[1] Reynolds, Serin, Wright, and Nesbitt, Phys. Rev. **78**, 487 (1950).
[2] E. Maxwell, Phys. Rev. **78**, 477 (1950); **79**, 173 (1950).
[3] Serin, Reynolds, and Nesbitt, Phys. Rev. **78**, 813 (1950).
[4] H. Fröhlich Phvs. Rev. **79**, 845 (1950).
[5] J. Bardeen, Phys. Rev. **79**, 167 (1950).

Fermi surface. This energy gain is a consequence of the zero-point motion of the ions, and can be interpreted as a lowering of zero-point energy as a result of the interaction between electrons and lattice vibrations.

The mean-square amplitude of a mode with zero-point energy is inversely proportional to the volume over which it extends. It was suggested that as a consequence the lowest energy would be obtained if the modes extended over a distance of the order of 10^{-6} cm, which is about the minimum distance over which the electrons can be localized. However, we shall show here that as a result of the increase in the number of normal modes involved with increase in volume, the interaction energy is independent of the volumes occupied by the normal modes. The distance of $\sim 10^{-6}$ cm thus represents a minimum rather than an optimum value.

The way in which the typical superconducting properties follow from the model is not yet completely clear and our explanation differs from that of Fröhlich.[4] In our picture, the superconducting electrons with energies near the Fermi surface have a small effective mass, of the order of kT_c/E_0, and this leads to a perfect diamagnetism according to the theories of Landau and of Peierls.[5] A model of a gas of non-interactinge lectrons of small effective mass leads to a theory of the London type.[5a] Fröhlich's explanation is based more on a persistent current idea. He finds current carrying states that are metastable in that it requires energy to remove a single electron or group of electrons in such a way as to reduce the current, although the lowest state, which is the one described above, has zero net current.[5b]

Whether or not a metal becomes superconducting depends on the magnitude of the electron-lattice interaction terms. As the same interaction terms enter into the theory of high temperature resistivity, the criterion for superconductivity can be expressed in terms of the resistivity or in terms of the relaxation time associated with the resistivity. The approximate criterion which we obtain below is similar to but somewhat more restrictive than the one derived earlier by Fröhlich.[4] It may be expressed in either of the following ways: A metal is superconducting if

$$\rho n > 10^6,$$

where ρ is the room temperature resistivity expressed in e.s.u. and n is the number of valence electrons per cc, or what amounts to the same thing, if

$$\hbar/\tau > \sim 2\pi\kappa T,$$

where τ is the relaxation time for the conduction electrons at the high temperature T. As τT is constant at high temperatures, the criterion is really independent of T. It should be noted that the superconducting metals are just those for which the electron-lattice interaction is so strong that the usual perturbation theory treatment for calculating high temperature resistivity begins to break down. The above criterion holds in nearly all cases except for the transition metals which are not expected to be superconducting in any case.

This paper is concerned primarily with the energy of the lowest state of pure metals and so should give the energy difference at $T=0$. We shall not be concerned with the thermodynamics of the superconducting state nor with the nature of the transition from the normal state. Except for some estimates of effective mass, we shall not attempt to show here how the typical superconducting properties follow from the model.

II. THE HAMILTONIAN

We consider a metal of volume V in which there are N_A atoms and $n=\nu N_A$ conduction electrons. The Hamiltonian is the sum of three terms corresponding to the electrons, the lattice displacements, and the interaction between them:

$$H=H_e+H_L+H_I. \tag{2.1}$$

The first term, H_e, is the Hamiltonian for the electrons with ions in their equilibrium positions. We shall neglect correlation effects and assume that each electron moves in the periodic field $U(x)$ of the lattice. Then

$$H_e=\Sigma_i H_{ei} \quad i=1, 2, \cdots n, \tag{2.2}$$

where

$$H=-(\hbar^2/2m)\Delta_i+U(x_i) \tag{2.2a}$$

and x_i represents the coordinates of the ith electron. The wave functions of H_{ei} are the Bloch functions $\psi_k(x_i)$ with energy ϵ_k:

$$H_{ei}\psi_k(x_i)=\epsilon_k\psi_k(x_i). \tag{2.3}$$

The wave functions of H_e are products of Bloch functions.

The Hamiltonian for the lattice, H_L, can be expressed in the form:

$$H_L=\Sigma_r\left\{-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial q_r{}^2}+\tfrac{1}{2}K_r q_r{}^2\right\}, \quad r=1, 2, \cdots 3N_A, \tag{2.4}$$

where μ is proportional to the mass of the atoms, the exact value depending on how the displacement coordinate, q_r, is defined. The force constant, K_r, can be expressed in terms of the angular frequency, ω_r, of the mode:

$$K_r=\mu\omega_r{}^2. \tag{2.5}$$

We shall be concerned only with the N_A longitudinal modes which interact with the electrons.

The interaction terms are linear in the displacements, and we shall indicate this explicitly by taking

$$H_I=\Sigma_{i,r}V_r(x_i)q_r. \tag{2.6}$$

[5a] *Added in proof.* In a paper submitted for publication in the Physical Review we show that the London phenomenological equations for superconductivity follow as a limiting case when the effective mass is so small that the Landau-Peierls theory yields a diamagnetic susceptibility $<-\frac{1}{4}\pi$, and also that the method of effective mass may be applied to wave functions for superconducting electrons as derived in the present paper.

[5b] *Added in proof.* Fröhlich has abandoned this explanation. See the comments added in proof to his paper (reference 4).

The interaction terms give the matrix elements

$$\mathfrak{M}_{kk'}=\int \psi_k^* V_r(x)\psi_{k'}d\tau \tag{2.7}$$

which vanish except for a normal mode with wave vector κ_r such that

$$k'=k\pm\kappa_r+K_n, \tag{2.8}$$

where K_n is a lattice vector of the reciprocal lattice space. This selection rule is well known from the theory of metals.[6] Since we have indicated q_r explicitly, $\mathfrak{M}_{kk'}$ differs from the usual $M_{kk'}$ by a factor q_r. We shall define:

$$|M_{kk'}|^2=(q_{kk'}^2)_{\text{Av}}|\mathfrak{M}_{kk'}|^2, \tag{2.9}$$

where $q_{kk'}$ is the coordinate of the normal mode which connects k and k'. The average is over the zero-point wave function of the normal mode.

III. WAVE FUNCTIONS FOR THE SYSTEM OF ELECTRONS PLUS NORMAL MODES

An approximate wave function for the system may be constructed as follows. The wave function for the electrons is taken to be a product of functions $\varphi_i(x_i, q_r)$ each of which depends on the coordinates of a single electron, x_i, and which depends parametrically on the coordinates of the normal modes, q_r. This product is multiplied by a product of functions $Q_r(q_r)$ for the normal modes:

$$\Psi=\Pi_i\varphi_i(x_i, q_r)\cdot\Pi_r Q_r(q_r). \tag{3.1}$$

In the lowest energy state the functions Q_r are the harmonic oscillator functions for zero-point energy, $\frac{1}{2}\hbar\omega_r$.

Each φ_i is assumed to be normalized so that

$$\int \varphi_i^*\varphi_i d\tau=1 \tag{3.2}$$

for all values of the q_r. This relation, when differentiated with respect to q_r, gives the real part of

$$\int \varphi_i^*(\partial\varphi_i/\partial q_r)d\tau=0, \tag{3.3}$$

and by a second differentiation:

$$-\int \varphi_i^*(\partial^2\varphi_i/\partial q_r^2)d\tau=\int|\partial\varphi_i/\partial q_r|^2 d\tau. \tag{3.4}$$

These well-known relations are useful in calculating the contribution of the terms $(-\hbar^2/2\mu)(\partial^2/\partial q_r^2)$ to the energy. Equation (3.3) implies that cross terms of the form

$$\varphi_i^*\varphi_j^*(\partial\varphi_i/\partial q_r)(\partial\varphi_j/\partial q_r)$$

vanish on integration. Equation (3.4) is used in calculation the contribution of φ_i to the kinetic energy of the ions.[7]

The functions φ_i can be expressed as a linear combination of Bloch functions in which the coefficients are functions of the q's:

$$\varphi_i=\Sigma_k a_k(q)\psi_k. \tag{3.5}$$

The normalization condition requires that

$$\Sigma_k|a_k|^2=1. \tag{3.6}$$

The wave function, φ_i, makes the following contribution to the energy:

$$E_i=\{\Sigma_k\epsilon_k|a_k|^2+\Sigma_{kk'}a_k^*q_{kk'}\mathfrak{M}_{kk'}a_{k'}$$
$$+\Sigma_{kk'}a_{k'}^*q_{kk'}\mathfrak{M}_{k'k}a_k+(\hbar^2/2\mu)\Sigma_{k,r}|\partial a_k/\partial q_r|^2\}_{\text{Av}}, \tag{3.7}$$

where the first term comes from H_e, the second and third from the interaction terms, and the last from the kinetic energy of the ions after making use of (3.3). The whole expression is averaged over the normal modes.

The total energy is obtained by summing (3.7) over all occupied states of the electrons and adding the energies of the normal modes. It is, of course, necessary to take the exclusion principle into account in calculating the energy of the electrons. If the φ_i are orthogonal, each such state can be occupied by two electrons of opposite spin.

To get a non-vanishing contribution from the interaction terms, a_k and $a_{k'}$ must have opposite parity. Thus if a_k is an even function of $q_{kk'}$, $a_{k'}$ must be an odd function or at least have an odd part. This suggests taking φ_i of the form

$$\varphi_i=N(\psi_k+\Sigma_{k'}b_{k'}q_{kk'}\psi_{k'}) \tag{3.8}$$

where N is a normalization factor chosen to satisfy (3.2):

$$N=(1+\Sigma b_{k'}^2 q_{kk'}^2)^{-\frac{1}{2}}, \tag{3.9}$$

and the $b_{k'}$ are constant factors to be chosen to make the energy a minimum. The normal coordinate $q_{kk'}$ is that for the mode which connects the states k and k'.

The calculation of the energy by using (3.8) for φ_i in (3.7) is straightforward. The only term which requires discussion is that involving $|\partial a_k/\partial q_r|^2$. We shall show that terms arising from derivatives of the normalization factor give a negligible contribution. We have

$$\Sigma_{k'}\int|\partial\varphi_i/\partial q_{kk'}|^2 d\tau$$
$$=\Sigma_{k'}\{N^{-2}|\partial N/\partial q_{kk'}|^2+N^2 b_{k'}^2\}$$
$$=\Sigma_{k'}(q_{kk'})^{-2}\{(N^2 b_{k'}^2 q_{kk'}^2)^2+N^2 b_{k'}^2 q_{kk'}^2\}. \tag{3.10}$$

[6] See, for example, N. F. Mott and H. Jones, *Properties of Metals and Alloys* (Oxford University Press, Oxford, 1936), or F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940).

[7] A simpler treatment, which leads to the same final results, could be made if it were assumed that each q_r is contained in no more than one φ_i. This would allow an immediate separation of the equation into parts which depend only on the coordinates of a single electron and the normal modes with which it interacts.

Since

$$\Sigma N^2 b_{k'}{}^2 q_{kk'}{}^2 < 1, \tag{3.11}$$

and since the sum is over a large number of positive terms,

$$\Sigma (q_{kk'})^{-2} (N^2 b_{k'}{}^2 q_{kk'}{}^2)^2 \ll \Sigma (q_{kk'})^{-2} (N^2 b_{k'}{}^2 q_{kk'}{}^2), \tag{3.12}$$

and we shall neglect it in comparison.

The last term of (3.7) then reduces to

$$(\hbar^2/2\mu)\Sigma_{k'} N^2 b_{k'}{}^2. \tag{3.13}$$

The mean square amplitude of a mode with zero-point energy is such that the mean potential energy is one-half the total energy, $\frac{1}{2}\hbar\omega_r$, or

$$\tfrac{1}{2} K_r (q_r{}^2)_{\text{Av}} = \tfrac{1}{4}\hbar\omega_r. \tag{3.14}$$

Thus

$$[\hbar^2/2\mu(q_r{}^2)]_{\text{Av}} = (\hbar K_r/\mu\omega_r) = \hbar\omega_r, \tag{3.15}$$

since $K_r/\mu = \omega_r{}^2$. With use of (3.15), (3.13) becomes:

$$\Sigma \hbar\omega_{kk'} N^2 b_{k'}{}^2 (q_{kk'}{}^2)_{\text{Av}}. \tag{3.16}$$

The expression for the energy obtained by using (3.8) in (3.7) can be simplified considerably by setting:

$$c_k{}^2 = (N^2)_{\text{Av}}, \quad c_{k'}{}^2 = (N^2 q_{kk'}{}^2)_{\text{Av}} b_{k'}{}^2. \tag{3.17}$$

With use (3.16) for the last term, Eq. (3.7) becomes (with neglect of the small difference between $(N^2)_{\text{Av}} \times (q_{kk'}{}^2)_{\text{Av}}$ and $(N^2 q_{kk'}{}^2)_{\text{Av}}$):

$$E_k = c_k{}^2 \epsilon_k + \Sigma c_{k'}{}^2 (\epsilon_{k'} + \hbar\omega_{kk'}) + \Sigma c_k M_{kk'} c_{k'} + \Sigma c_{k'} M_{k'k} c_k. \tag{3.18}$$

We have replaced $(q_{kk'}{}^2)_{\text{Av}}{}^{\frac{1}{2}} \mathfrak{M}_{kk'}$ by $M_{kk'}$ (see Eq. (2.9)). The c's are subject to the normalization condition

$$c_k{}^2 + \Sigma_{k'} c_{k'}{}^2 = 1. \tag{3.19}$$

The variational problem gives the following set of equations for the c's

$$c_k \epsilon_k + \Sigma c_{k'} M_{k'k} = E_k c_k, \tag{3.20a}$$

$$c_{k'}(\epsilon_{k'} + \hbar\omega_{kk') } + c_k M_{kk'} = E_k c_{k'}. \tag{3.20b}$$

If the $c_{k'}$ are determined by second-order perturbation theory, we have

$$c_{k'} = c_k M_{kk'}/(\epsilon_k - \epsilon_{k'} - \hbar\omega_{kk'}), \tag{3.21}$$

and the second-order contribution to the energy is

$$\Delta E_k = \Sigma_{k'} |M_{kk'}|^2/(\epsilon_k - \epsilon_{k'} - \hbar\omega_{kk'}). \tag{3.22}$$

If this contribution is summed over all $\boldsymbol{k}$ for the occupied states, the total change is

$$\Delta W = 2\Sigma_k \Sigma_{k'} |M_{kk'}|^2/(\epsilon_k - \epsilon_{k'} - \hbar\omega_{kk'}). \tag{3.23}$$

The factor 2 accounts for the fact that each state can be occupied by two electrons. Because of the exclusion principle, the states $\boldsymbol{k}'$ must be normally unoccupied. Thus if f_k is the probability that a state $\boldsymbol{k}$ is occupied and $(1-f_{k'})$ the probability that $\boldsymbol{k}'$ is unoccupied, the energy becomes

$$\Delta W = 2\Sigma_k \Sigma_{k'} \frac{|M_{kk'}|^2 f_k (1-f_{k'})}{\epsilon_k - \epsilon_{k'} - \hbar\omega_{kk'}}, \tag{3.24}$$

where the sum is now over *all* values of $\boldsymbol{k}$ and $\boldsymbol{k}'$.

This expression can be obtained directly from the original Hamiltonian (2.1), and is the one which Fröhlich[4] used to calculate the self-energy of the electrons as a result of interaction with the phonon field.

It will be noted that the energy denominators are small and the perturbation procedure breaks down when

$$|\epsilon_k - \epsilon_{k'} - \hbar\omega_{kk'}| < \sim |M_{kk'}|. \tag{3.25}$$

Fröhlich integrated over these singular regions by taking principal parts. We shall follow a different method which we believe gives a better insight into the superconducting states.

IV. WAVE FUNCTIONS FOR SUPERCONDUCTING ELECTRONS

The exclusion principle imposes severe restrictions on the wave functions. For each linear combination of the type (3.8) which yields a low energy state there is an orthogonal state using the same Bloch functions which has higher than normal energy. In order to get a net decrease in energy of the electrons, it is necessary to include twice as many Bloch states as there are electrons to be accommodated so that only the low energy states need be occupied. This is possibly only if the initial states have energies within the order of Δ of the Fermi surface, where Δ is the decrease in energy resulting from the electron-lattice interaction terms.

We shall construct wave functions for the superconducting electrons for the state corresponding to $T = 0°\text{K}$ by taking $\boldsymbol{k}$-values which lie in the energy range between E_0 and $E_0 + \epsilon_1$ and $\boldsymbol{k}'$ values which lie between $E_0 - \epsilon_1$ and E_0. The wave functions for $\epsilon_k < E_0 - \epsilon_1$ are taken to be the usual Bloch functions. The energy ϵ_1 will be determined below to make the total energy a minimum and is approximately equal to Δ for the superconducting wave functions. This configuration is similar to that which Fröhlich obtained by displacing a spherical shell of electrons outward from the boundary of the Fermi distribution. Our calculation of the energy differs from his in that we do not use perturbation theory and the questionable procedure of an integration over singularities by taking principal parts is avoided.

In the superconducting state, the interaction is so large that (3.25) is satisfied for $\boldsymbol{k}'$ such that $E_0 - \epsilon_1 < \epsilon_{k'} < E_0$. There are terms in the energies of both the normal and superconducting states which come from ϵ_1 interaction with unoccupied states of higher energy and which contribute terms proportional to M^2 to the self-energy. Since these latter terms do not differ much between the normal and superconducting states we shall omit them from calculations of the energy difference.

If we assume that $\epsilon_k \simeq \epsilon_{k'} + \hbar\omega_{kk'}$, Eq. (3.20b) gives

$$c_{k'} = c_k M_{kk'}/\Delta, \tag{4.1}$$

where Δ is the energy difference $E_k - \epsilon_k$. Substitution of this value into (3.20a) gives

$$\Delta^2 = \Sigma_{k'} |M_{kk'}|^2, \tag{4.2}$$

or

$$\Delta = (\Sigma_{k'} |M_{kk'}|^2)^{\frac{1}{2}}. \tag{4.3}$$

The wave function of the superconducting state is then

$$\varphi_k = N(\psi_k \pm \Delta^{-1} \Sigma_{k'} \mathfrak{M}_{kk'} q_{kk'} \psi_{k'}). \tag{4.4}$$

Normalization requires that the average value of N^2 be $\frac{1}{2}$. The negative signs apply to the low energy state and the positive to the high energy state; the energies being

$$E_k = \epsilon_k \pm \Delta. \tag{4.5}$$

The number of states k' in the sum depends on the spread of the energies $\epsilon_{k'} + \hbar\omega_{kk'}$ about ϵ_k. It is reasonable to take an energy spread of the order of Δ and we shall include only those k' which satisfy:

$$\epsilon_k - \epsilon_{k'} - \Delta < \hbar\omega_{kk'} < \epsilon_k - \epsilon_{k'} + \Delta. \tag{4.6}$$

Criterion for Superconductivity

The criterion for superconducivity is obtained from the condition that (4.6) be satisfied for most k' in the gap between the occupied sphere and the occupied spherical shell.[7a] One can then use (4.3) and (4.5) for the energies and Δ is proportional to the first power of $M_{kk'}$. Since the average value of $\epsilon_k - \epsilon_{k'}$ is ϵ_1, and since ϵ_1 is approximately equal to Δ, the k' which satisfy (4.6) are such that

$$\hbar\omega_{kk'} < 2\Delta. \tag{4.7}$$

The value of $\omega_{kk'}$ is proportional to $|k - k'|$ which in turn depends on the angle, θ, between k and k'. If ω_m is the maximum value[8] corresponding to $\theta = 180°$,

$$\hbar\omega_{kk'} = \hbar\omega_m \sin\tfrac{1}{2}\theta. \tag{4.8}$$

It is convenient to use

$$x = \sin\tfrac{1}{2}\theta \tag{4.9}$$

as a measure of the angle between k and k'. According to (4.7), the limiting value of x is

$$x_1 = 2\Delta/\hbar\omega_m. \tag{4.10}$$

We shall now evaluate Δ from (4.2), taking those k' in the sum which satisfy (4.7) and assuming that $|M_{kk'}|^2$ depends on the angle between k and k' and thus on x. The total number of k' states in volume V in the energy range, ϵ_1 is

$$\epsilon_1 V N(E_0), \tag{4.11}$$

where $N(E_0)dE$ is the number of states per unit volume in the range dE at the Fermi surface. In integrating over angles the factor $\sin\theta d\theta$ becomes $4xdx$. The sum (4.2) is given approximately by an integration over x between 0 and x_1:

$$\Delta^2 = 2\epsilon_1 V N(E_0) \int_0^{x_1} [M(x)]^2 x dx. \tag{4.12}$$

Since $\epsilon_1 \simeq \Delta$, this equation can be simplified to:

$$\Delta = 2VN(E_0) \int_0^{x_1} [M(x)]^2 x dx. \tag{4.13}$$

This is an implicit equation for Δ. The upper limit x_1 is $2\Delta/\hbar\omega_m$ or unity, whichever is the smaller.

The criterion for the existence of the superconducting state is that (4.13) have a solution other than $\Delta = 0$. With reasonable assumptions regarding the dependence of M on x, the right-hand side has an upward curvature until x_1 is almost equal to its maximum value of unity. If there is a solution, it must occur for x_1 close to unity. Thus we must have (see Eq. (4.7)):

$$a = 2VN(E_0) \int_0^1 [M(x)]^2 x dx > \tfrac{1}{2}\hbar\omega_m. \tag{4.14}$$

As in the previous work,[4,5] an estimate of the average value of the matrix element can be obtained from the resistivity at high temperatures. When this is done, (4.14) gives a criterion similar to, but more restrictive than that of Fröhlich.[4]

The criterion may be expressed most simply in terms of the relaxation time associated with high temperature conductivity. The expression for the relaxation time, τ, in terms of the matrix element $(M_{kk'})_T$ for high temperatures is given by[9]

$$\hbar/\tau = \pi V N(E_0) \int_0^{\pi} [M_T(\theta)]^2 (1 - \cos\theta) \sin\theta d\theta. \tag{4.15}$$

The high temperature matrix element corresponds to an

[7a] *Added in proof.* The criterion may be derived in a simple way as follows. The energy corresponding to (4.4) is:

$$E_k = \tfrac{1}{2}\epsilon_k + \tfrac{1}{2}(\epsilon_{k'} + \hbar\omega_{kk'}) - \Delta.$$

In order to have a net decrease in energy it is necessary that the superconducting states have a lower energy than the Bloch states they replace. The energy difference is on the average:

$$(E_k - \epsilon_{k'})_{Av} = \tfrac{1}{2}(\epsilon_k - \epsilon_{k'})_{Av} + \tfrac{1}{2}(\hbar\omega_{kk'})_{Av} - \Delta$$
$$= \tfrac{1}{2}\epsilon_1 + \tfrac{1}{2}(\hbar\omega_{kk'})_{Av} - (a\epsilon_1)^{\frac{1}{2}}.$$

It follows from (4.3) that Δ^2 is proportional to the number of states k' and thus to ϵ_1. The factor a is given by (4.14). The right-hand side is lowest for $\epsilon_1 = a$ and is negative only if

$$a > (\hbar\omega_{kk'})_{Av}.$$

This criterion is equivalent to (4.17) which was derived from the condition (4.6).

[8] Assuming that "Umklapp" processes of Peierls are not involved. Transitions through large angles may result from such processes (see J. Bardeen, Phys. Rev. 52, 688 (1937)). The values of $\hbar\omega_{kk'}$ for large angles would then be smaller than those given by (4.8), and the criterion for superconductivity somewhat less restrictive.

[9] N. F. Mott and H. Jones reference 6, Eq. (48), p. 262.

energy κT in a vibrational mode while the low temperature matrix element corresponds to zero-point energy $\frac{1}{2}\hbar\omega_{kk'}$. Thus

$$M_T^2=(2\kappa T/\hbar\omega_{kk'})M^2=(2\kappa T/\hbar\omega_m)(M^2/x)$$

with change of the variable of integration from θ to x, (4.15) becomes:

$$\hbar/\tau=16\pi(\kappa T/\hbar\omega_m)VN(E_0)\int_0^1[M(x)]^2x^2dx. \quad (4.16)$$

Except for an extra factor of x, the integral in (4.16) is the same as that in (4.14), so that we can express a in terms of τ. We shall assume for simplicity that the angular dependence is such that the extra factor of x gives an extra factor of $\frac{1}{2}$ on integration. We may then write (4.14) in the form

$$a=(\hbar\omega_m/4\pi\kappa T)(\hbar/\tau)>\tfrac{1}{2}\hbar\omega_m \quad (4.17)$$

The criterion for superconductivity is then:

$$\hbar/\tau>\sim 2\pi\kappa T. \quad (4.18)$$

As $1/\tau$ is proportional to T at high temperatures, relation (4.18) is independent of T. It indicates that a large interaction between electrons and lattice vibrations is required for superconductivity. The interaction must be so large, in fact, that the usual theory of conductivity based on perturbation theory and variation of constants begins to break down. The assumption that the wave functions are Bloch functions only weakly coupled to the vibrations is not a good approximation even for the normal state of the superconducting metals.

TABLE I. Test of the approximate criterion for superconductivity: $10^{-6}\rho n>1$.

Normal	ν	$10^{16}\rho$(e.s.u.) 293°K	$10^{-22}n/\text{cm}^3$	$10^{-6}\rho n$
Li	1	0.10	4.7	0.47
Na	1	0.054	2.56	0.14
K	1	0.079	1.33	0.105
Rb	1	0.15	1.1	0.165
Cs	1	0.22	0.85	0.185
Cu	1	0.018	8.5	0.15
Ag	1	0.018	5.9	0.11
Au	1	0.025	6.3	0.16
Be	2	0.04	24.5	0.97
Mg	2	0.045	8.6	0.39
Ca	2	0.05	4.7	0.24
Sr	2	0.35	3.6	1.25
Ba	2	0.72	3.2	2.3
Superconducting				
La	3	0.68	8.1	5.5
Ti	4	0.50	23	11.5
Zr	4	0.48	17	8.5
Hf	4	0.39	17	6.6
Th	4	0.12	12	1.44
V	5	0.20	34	6.8
Nb	5	0.28	27.5	7.7
Ta	5	0.17	27	4.6
Zn	2	0.065	13.2	0.86
Cd	2	0.09	10	0.90
Hg	2	0.30	8.5	2.5
Al	3	0.03	18	0.54
Ga	3	0.45	15	6.8
In	3	0.10	11.5	1.15
Tl	3	0.18	10.5	1.9
Sn	4	0.13	15	1.95
Pb	4	0.24	13	3.1

The criterion (4.18) can be expressed in terms of the room-temperature resistivity, ρ, if we use the free-electron formula:[6]

$$\sigma=1/\rho=ne^2\tau/m, \quad (4.19)$$

where n is the number of valence electrons per unit volume. For $T=20°\text{C}=293°\text{K}$, (4.18) becomes

$$n\rho>2\pi m\kappa T/he^2\sim 10^6 \text{ (e.s.u.)}, \quad (4.20)$$

The value 10^6 applies if ρ is expressed in e.s.u. and would be about 10^{18} if ρ is in practical units.[10] Except for the transition metals, (4.20) is valid for practically all cases (Table I). None of the monovalent metals satisfy (4.20). Since the transition metals have narrow energy bands, one would not expect to get much energy gain by taking linear combinations corresponding to the superconducting states. A large effective mass should be used in (4.20). Thus they are not expected to be superconducting.

Energy of the Superconducting State

We shall suppose that the criterion for superconductivity is satisfied so that practically all $\boldsymbol{k}'$ in the energy range ϵ_1 satisfy (4.6) and may be included in the sum (4.2). The energy Δ^2 is then given by (4.12) with $x_1=1$. Using the definition of a in (4.14), we have

$$\Delta^2=\epsilon_1 a. \quad (4.21)$$

The difference in energy between the superconducting and normal states is

$$W_s-W_n=2N(E_0)\epsilon_1(\epsilon_1-\Delta). \quad (4.22)$$

The factor $2N(E_0)\epsilon_1$ is the number of superconducting electrons, counting both spin states, and $\epsilon_1-\Delta$ is the average energy difference per electron.

We shall find the value of ϵ_1 which makes W_s a minimum. With use of (4.21), we have

$$W_s-W_n=2N(E_0)(\epsilon_1^2-a^{\frac{1}{2}}\epsilon_1^{\frac{1}{2}}). \quad (4.23)$$

Setting

$$\partial(W_s-W_n)/\partial\epsilon_1\sim 2\epsilon_1-3/2a^{\frac{1}{2}}\epsilon_1^{\frac{1}{2}}=0,$$

we find

$$\epsilon_1=(9/16)a, \quad (4.24)$$

and

$$\Delta=(3/4)a. \quad (4.25)$$

The minimum value of W_s-W_n is then

$$W_s-W_n=-(27/128)N(E_0)a^2$$
$$=-(27/128)N(E_0)(\hbar\omega_m/4\pi\kappa T)^2(\hbar/\tau)^2. \quad (4.26)$$

[10] Fröhlich's criterion is approximately $\rho n\nu^{\frac{1}{2}}>0.2\times 10^6$, where ν is the valency. This criterion is less restrictive than ours and is not in as good agreement with observation. Compare Table I with the corresponding table in reference 4.

The second expression is obtained by using (4.17) for a. A very similar expression would have been found if we had used (4.4) for the wave functions and calculated the energy from the Hamiltonian instead of using (4.2).[10a]

The energy difference is usually determined from the critical field, H_c, at $T=0$:

$$W_s-W_n=-H_c^2/8\pi. \tag{4.27}$$

From (4.26) and (4.27), we find

$$H_c=(27\pi N(E_0)/16)^{\frac{1}{2}}(\hbar^2\omega_m/4\pi\kappa T\tau). \tag{4.28}$$

The free-electron model gives[6]

$$N(E_0)=mk_0/2\pi^2\hbar^2, \tag{4.29}$$

where k_0 is the maximum value of k in the Fermi distribution:

$$k_0=(3\pi^2 n)^{\frac{1}{3}}. \tag{4.30}$$

Equation (4.28) gives values for H_c which are too large, as does the corresponding expression of Fröhlich.[4] For example, approximate values for lead, taking 3 valence electrons per atom, are:

$$\rho=2.2\times10^{-17}\text{ e.s.u. at }273^\circ\text{K},$$
$$n=1.3\times10^{23}\text{ electrons/cm}^3,$$
$$\hbar\omega_m\sim10^{-14}\text{ ergs},\quad 1/\tau\sim ne^2\rho/m\sim7\times10^{14}\text{ sec.}^{-1},$$
$$k_0\sim1.6\times10^8\text{ cm}^{-1},\quad N(E_0)\sim8\times10^{33},$$

which give $H_c\sim3000$ oersteds as compared with the observed value of 800. Values are even higher for lighter elements with larger values of $\hbar\omega_m$.

Our calculations undoubtedly overestimate the energy, and the free-electron approximation is probably poor for most of the superconducting metals. Even when these factors are taken into consideration, the theoretical values of H_c appear to be too large. It is believed that the difficulty is not so much in the calculations and model for the superconducting state as for the normal state. The criterion (4.18) indicates that the Bloch functions are probably not sufficiently good wave functions for the normal states of superconducting metals. A theory of transition phenomena would require a good model for both superconducting and normal states.

The expression for a (Eq. (4.14)) is similar to the expression for the energy change, ΔE, estimated in the earlier publication[5] from the adiabatic approximation and is what would have been obtained there if account had been taken of the increase in the number of interactions with increase in volume. The number of interactions is equal to p as there defined, and the expression for ΔE (Eq. (4)) should be multiplied by p. This makes ΔE independent of the volume, V, but the expression then gives values which are about an order of magnitude larger than most values of κT_c.

[10a] *Added in proof.* It probably would have been better to have used this method which involves replacing $\epsilon_1-\Delta$ in (4.22) with $\frac{1}{2}\epsilon_1+\frac{1}{2}(\hbar\omega_{kk'})_{Av}-\Delta$. This procedure leads to a larger value for the energy difference, W_s-W_n when a is larger compared with $(\hbar\omega_{kk'})_{Av}$.

The calculation given in the present paper shows that the pure adiabatic approximation is not valid. Terms coming from $\int|\partial\varphi_i/\partial q_r|^2 d\tau$ give an increase in Fermi energy which reduces the average energy change per superconducting electron, but it still appears to be larger than κT_c for most elements.

The expressions for the energy change are consistent with the isotope effect. Since $\hbar\omega_m$ varies as $M^{-\frac{1}{2}}$ and τ is independent of isotopic mass, H_c, and thus T_c should vary as $M^{-\frac{1}{2}}$, in agreement with experiment.[3]

Non-Symmetric Distributions; Effective Mass

According to Eqs. (4.24) and (4.25) the average energy difference, $\Delta-\epsilon_1$, between the normal and superconducting states per superconducting electron is $\Delta/4$. The energy difference is large only for a symmetric distribution in k-space corresponding to zero net current. Let us imagine a distribution displaced in k-space by a small vector $\boldsymbol{k}_1$ corresponding to an average momentum $\hbar\boldsymbol{k}_1$ per electron. If the displacement $\boldsymbol{k}_1$ changes the Fermi energy of electrons near the Fermi surface by an amount of the order of Δ, the condition (4.6) for the linear combinations will be valid only for a small number of the $\boldsymbol{k}'$ states and the energy difference between the superconducting and normal states will be small. From this we can estimate the change in superconducting energy with $\boldsymbol{k}_1$ and thus estimate the effective mass of electrons in the superconducting state.

The displacement $\boldsymbol{k}_1$ which gives a change in Fermi energy Δ is such that

$$\Delta\sim\hbar^2k_0k_1/m,$$

or

$$k_1\sim m\Delta/\hbar^2k_0. \tag{4.31}$$

The effective mass, m_e, in the superconducting state can be estimated by equating $\hbar^2k_c^2/2m_e$ to the energy difference $\Delta/4$. This gives

$$\Delta/4\sim\hbar^2k_1^2/2m_e=(\hbar^2/2m_e)(m\Delta/\hbar^2k_0)^2, \tag{4.32}$$

from which we get

$$m_e\sim(2\Delta m/\hbar^2k_0^2)m\sim(\Delta/E_0)m, \tag{4.33}$$

which is of the order of 10^{-4} or 10^{-3} m.

As the diamagnetic susceptibility varies as $(m/m_e)^2$ according to Peierls' modification[11] of the Landau theory, a value of $m_e\sim10^{-3}$m is sufficiently small to make $\chi<-1/4\pi$, which suggests that when this condition is fulfilled the "superconducting state" is a

[11] R. Peierls, Zeits. f. Physik **80**, 763 (1933). Peierls' formula may be expressed in the following way. The contribution to the susceptibility of electrons in a given Brillouin zone which contains n_z electrons and is filled to an energy E_z, measured from the bottom of the zone, is $\chi_z=-(m/m_e)^2n_z\mu^2/2E_z$, where $\mu=e\hbar/2mc$. The number of Brillouin zones required to accomodate all electrons with energies within $\sim E_z$ of the Fermi surface, E_0, is the order of (nE_z/n_zE_0), where n is the total number of electrons per unit volume. The total susceptibility is thus of the order $\chi_z=-(m/m_e)^2n\mu^2/2E_0$, or the order of $(m/m_e)^2$ times Landau's expression. As Landau's expression gives values of the order of 10^{-7}, it is necessary to have $m/m_e>\sim10^{-3}$ to have a perfect diamagnetic.

perfect diamagnetic. To get a complete theory of the superconducting properties it would be necessary to re-examine the problem for the situation in which the magnetic field is confined to a thin surface layer corresponding to the penetration depth of the London theory.[5a]

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Angular Distribution of the $Al^{27}(d, \alpha)Mg^{25}$ Reaction and Energy Levels in Mg^{25}†

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The energy distribution and angular dependence of the alpha-particle groups from the nuclear reaction $Al^{27}(d, \alpha)Mg^{25}$ have been investigated. A magnetically analyzed beam of 11.1 Mev deuterons was used. Eleven alpha-particle groups were measured, corresponding to ten excited levels in Mg^{25} at 0.57, 0.96, 1.63, 1.97, 2.74, 3.36, 4.01, 4.81, 5.48, and 5.95 Mev. The ground state Q-value for the reaction was found to be 6.58 ± 0.03 Mev, giving a value for the mass difference Al^{27}–Mg^{25} of 1.99626 ± 0.00003 mass units. The intensities of all the groups, with the exception of Q_2, show marked dependence on the angle of measurement. The average spacing of the levels in Mg^{25} is 0.6 Mev, and is nearly constant over the range studied.

I. INTRODUCTION

An excited level in Mg^{25} was first observed by McMillan and Lawrence,[1] from the $Al^{27}(d, \alpha)Mg^{25}$ reaction. Two groups of alpha-particles were found with an energy difference corresponding to an excited level at 0.7 Mev. Pollard, Sailor, and Wyly,[2] using 3.79 Mev deuterons, observed two additional groups showing three excited levels in the Mg^{25} nucleus. French and Treacy[3] repeated these measurements with 0.93 Mev deuterons, using an ionization chamber to count the alpha-particles and found five groups.

The present investigation of the $Al^{27}(d, \alpha)Mg^{25}$ reaction was undertaken to measure the angular distribution of the alpha-particle groups and to search for groups corresponding to states of higher excitation made feasible by the use of the 11-Mev deuteron beam of the Indiana University Cyclotron.

II. METHOD AND APPARATUS

The deuteron beam was led through a four-inch diameter, evacuated tube from the target chamber of the cyclotron to a magnetic analyzer situated outside the water shielding tanks; a distance of fifteen feet.

The analyzer magnet was constructed using a rectangular yoke with a cross section sixteen inches square. The pole pieces were made in the form of a truncated wedge with a gap of 2.0 inches. The lids of the magnet vacuum chamber are of one-half inch iron, leaving a net gap of one inch. The magnet coils require about one kilowatt of power to produce a maximum field of 12,000 Gauss. A field of 10,635 gauss was sufficient to deflect the 11-Mev deuteron beam through 56°. The current in the coils is supplied by a motor generator, and the use of an electronic stabilizer enables the current to be held constant within 0.2 percent. The magnetic field is measured with a flip coil and ballistic galvanometer, calibrated against a standard mutual inductance.

Scattering of the beam in the analyzer chamber is prevented by the use of suitable diaphragms to define the beam. Adjustable slits are placed at the entrance to the analyzer chamber and in the tube leading to the reaction chamber to define the beam to the target.

The magnetic analyzer was calibrated with alpha-particles of polonium and thorium active deposit. The source was placed on the axis of the beam tube, ten feet from the analyzer. A proportional counter located behind the focal slit was then used to count the alpha-particles as the magnetic field was varied. Alpha-particles from Po, ThC and ThC′ were used to give three points on the energy *versus* magnetic field curve at energies of 5.3, 6.05, and 8.78 Mev respectively. A linear relation was obtained between the alpha-particle energy and the square of the magnetic field. The energy of the deuteron beam striking the target could then be determined by using the relation:

$$E_D = (He\rho)^2/2mc^2,$$

where m is the deuteron mass, e is the charge, c is the velocity of light, and H is the magnetic field required to focus the deuteron beam of energy E_D on the target slit. ρ is the effective radius of curvature in the analyzer and was found equal to 64.1 cm from the alpha-particle

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