Some Remarks on the Quantum Theory of the Superconductive State

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AFTER many unsuccessful attempts to understand the mechanism of superconductivity on the basis of the quantum theory of electronic conduction in metals a new way of regarding the whole problem was opened up when F. London[1] introduced his phenomenological description of the magnetic behavior of superconductors, especially the Meissner effect. In fact, this phenomenological theory, which after essential contributions by M. v. Laue[2] seems to cover the general electromagnetic experience about superconductivity, reducing the problem to the study of a set of linear differential equations for the electromagnetic field in a superconductive medium obtained from Maxwells equations by the introduction of a current-density vector proportional to the magnetic vector potential, lends itself quite naturally to suggestions as to the quantum theoretical background of the phenomena in question. First of all it follows from the considerations of London and v. Laue that in order to arrive at a general interpretation of superconductivity we need only fix our attention on the behavior of an infinite homogeneous medium. Moreover, as pointed out by London himself, a characteristic term in the wave mechanical current-density formula—we shall call it the London current—is just proportional to the vector potential, the factor of proportionality being of the right order of magnitude. Ordinarily, however, this term is almost completely cancelled by the rest of the current-density—the gradient current—a fact already illustrated by Bohr's[3] well-known proof of the absence of any diamagnetism of the electrons in a metal on classical theory and corresponding to the weak diamagnetism derived by L. Landau on quantum theory.

It is characteristic of the London theory that it describes a case of magnetic action on matter depending linearly on the field where the concept of magnetic permeability does not apply. As shown in an earlier paper[4] such a state of things is just what may be considered the general case on quantum theoretical perturbation theory applied to a system of electrons in a magnetic field. Introducing the wave functions perturbed by an arbitrary magnetic field, which in part may be due to the electrons themselves, into the wave mechanical current-density formula we arrive at an expression which in general is not proportional to, but still linear in the magnetic vector potential. Thus by means of the ordinary relation between current and magnetic field a linear integro-differential equation for the magnetic vector potential is obtained, which may be taken as the basis for the calculation of the magnetic properties of the electron system in question as far as non-linear effects may be neglected. In the paper mentioned it was further shown that there will be no contribution to the gradient current from transition possibilities corresponding to two occupied electron states, a full electron band contributing thus only to the London current. That this has something to do with superconductivity is made still more plausible by the fact that there will also be no contribution to the main part of the gradient current from transition possibilities corresponding to an occupied and an empty state belonging to the same value of the wave number vector but with mutually orthogonal wave functions such as would occur with a full s band and a partially filled p band in the approximation starting from atomic wave functions. In the present paper we shall arrive at similar but more precise results from the more general starting point of an arbitrary distribution

[1] F. London, *Une conception nouvelle de la supraconductibilite* (Hermann et Cie, 1934).
[2] M. v. Laue, Ann. d. Physik **42**, 65 (1942); Zeits. f. Physik **118**, 445 (1941); **120**, 578 (1943).
[3] N. Bohr, *Metallernes Elektronteori* (Copenhagen, 1911).
[4] O. Klein, Arkiv för mat., astr. och fysik, N:o 12, **31A** (1944); referred to in the following as I.

of the electrons of a band with respect to the energy. Thus from the theorem mentioned it follows that the gradient current due to the presence of a magnetic field will be determined from the conditions at the surface of such a band provided that it is without holes as will be the case at the absolute zero of temperature. Since the gradient current will contain the energy differences between neighboring filled and empty states as denominators, we see that its value will be particularly small if the surface of the Fermi distribution lies at a point where the energy changes comparatively rapidly with momentum as at the boundary of a Brillouin zone or more generally at a place where the density of states with respect to energy is particularly small. This now entails that the part of the specific heat which is due to the electrons and proportional to the absolute temperature will also be small, which agrees well with the observation that such a term is lacking in the specific heat of the superconductive state.

The considerations just sketched, which would seem to form a step towards a quantum theory of the superconductive state, are quite in line with the view which London himself has taken towards the problem. Thus his suggestion of a comparatively large energy difference between the lowest and the next electron band entailing a vanishingly small perturbation of the lowest state is very close to the considerations of this note if by state we mean the whole full electron band. For a closer study to which we shall now proceed it is more practical, however, to regard the separate wave functions of the single electron states as is always done in the Hartree-Fock treatment of the many-electron problem, and these are by no means negligibly disturbed by a magnetic field.

For an infinite medium including the sources of the imposed magnetic field with no unperturbed current-density of the electrons, the integro-differential equation mentioned above will take the form

$$-\Delta A(r)+\frac{4\pi\epsilon^2}{mc^2}\rho(r)A(r)-\int\theta(r,r')\cdot A(r')dr' = -\Delta A_0(r). \quad (1)$$

Here $A(r)$ denotes the total vector potential at a point in space with the coordinate vector r, $A_0(r)$ the corresponding potential of the field due to other sources than the electrons considered, $-\epsilon$ the charge, m the mass of the electron, and c the vacuum velocity of light. Further $\rho(r)$ is the electron number density at the point in question and dr' a volume element at the integration point r', the integration being carried out over all space. The nucleus $\theta(r, r')$ is, in general, a tensor but degenerates in important cases approximately into a scalar, and it follows from the well-known theorem of Bloch that for a crystalline medium it may be written in the following way

$$\theta(r,r')=(2\pi)^{-\frac{3}{2}}\sum_\tau K_\tau(r-r')e^{i\tau\cdot r}, \quad (2)$$

where τ is any whole number vector corresponding to the lattice periodicity. Similarly we may put

$$\rho(r)=\sum_\tau \rho_\tau e^{i\tau\cdot r}, \quad (3)$$

where $\rho_0=N$ represents the average number of electrons per unit volume. Further we shall use Fourier expansions of the functions $K_\tau(r)$, namely

$$K_\tau(r)=(2\pi)^{-\frac{3}{2}}\int K_\tau(k)e^{ik\cdot r}dk. \quad (4)$$

Here dk denotes a volume element in wave number space. Thus we may replace the integro-differential Eq. (1) by the following system of linear equations

$$k^2A(k)+\sum_\tau g_\tau(k-\tau)\cdot A(k-\tau)=k^2A_0(k), \quad (5)$$

with

$$g_\tau(k)=\frac{4\pi\epsilon^2}{mc^2}\rho_\tau-K_\tau(k). \quad (6)$$

In the case of free electrons only $g_0(k)$ differs from 0 and is for any spherically symmetrical distribution of the electrons in k space equal to a scalar. Therefore we shall expect that for the more loosely bound electron of a metallic medium as are in all probability responsible for superconductivity the g_τ, $\tau\neq 0$ may be treated as small quantities and that in a first survey of the subject they may be neglected altogether. In this way we obtain the following solution of (5)

$$A(k)=\frac{k^2}{k^2+g_0(k)}A_0(k). \quad (7)$$

If now $g_0(k)$ takes a finite positive value for

$k=0$, we see that for k-values fulfilling the condition $|k| \ll [g_0(0)]^{\frac{1}{2}}$, $A(k)$ will practically vanish. This means that there will be a Meissner effect, a magnetic field being able to penetrate the matter in question only to a depth of the order of magnitude $1/[g_0(0)]^{\frac{1}{2}}$. In the special case where $K_0(0)$ vanishes we have only a London current and here

$$g_0(0)=\kappa^2=\frac{4\pi\epsilon^2}{mc^2}N. \tag{8}$$

κ is the reciprocal length characteristic of London's suggestion as to the interpretation of his theory.

Let now $\psi_k(r)$ be an electronic function corresponding to the energy $E(k)$. Then according to the theorem of Bloch we may write

$$\psi_k(r)=\frac{1}{V^{\frac{1}{2}}}\sum_\tau u_\tau(k)e^{i(\tau+k)\cdot r}. \tag{9}$$

V is a volume of periodicity which is later taken to be infinitely large. Since all the functions $\psi_k(r)$ are to be normalized with respect to this volume the following relation will hold

$$\sum_\tau |u_\tau(k)|^2=1. \tag{10}$$

Assuming further such symmetry to hold that $u_\tau(k)$ is independent of the sign of the whole number vector τ, then from the considerations in I, we obtain the following expression for $K_0(k)$

$$K_0(k)=\sum_{k_0}\frac{4\pi\epsilon^2}{mc^2V}\left\{(2k_0+k)k\frac{|\sum_\tau u_\tau^*(k_0)u_\tau(k_0+k)|^2}{\frac{2m}{\hbar^2}[E(k_0+k)-E(k_0)]}\right.$$
$$\left.-(2k_0-k)k\frac{|\sum_\tau u_\tau^*(k_0)u_\tau(k_0-k)|^2}{\frac{2m}{\hbar^2}[E(k_0-k)-E(k_0)]}\right\} \tag{11}$$

where the summation with respect to k_0 is to be carried out over all the electrons present in the band in question, and where $(2k_0+k)k_0$ means the tensor formed by multiplication of the two vectors $2k_0+k$ and k_0. On account of (10) the sum with respect to τ in the numerator may for small k values be replaced by unity.

Proceeding now to the calculation of $K_0(0)$ according to the theorem mentioned above we need only consider a thin surface layer at the boundary of the Fermi distribution corresponding to those electronic states which with a given small k-vector combine with states outside the occupied region of wave number space. The thickness l of this layer at a given point k_0 is seen to be equal to the projection of k on the normal to the boundary which will be a surface of constant energy, and the number of states within a volume element of this surface layer corresponding to the element of area dS will be $[2V/(2\pi)^3]l\cdot dS$. Further we have with sufficient accuracy for the energy difference in the denominator of (11)

$$E(k_0+k)-E(k_0)=k\cdot\nabla E=l\cdot|\nabla E|,$$

where ∇E is the gradient of E as a function of k_0. Thus the contribution to $K_0(0)$ from the volume element in question will be

$$\frac{\epsilon^2}{\pi^2mc^2}\frac{(k_0)k_0dS}{(m/\hbar^2)|\nabla E|},$$

and it follows

$$K_0(0)=\frac{\epsilon^2}{\pi^2mc^2}\int\frac{dS(k_0)k_0}{(m/\hbar^2)|\nabla E|}, \tag{12}$$

where now we have written k for the wave number vector at the integration point, the integration being extended over the whole boundary surface, which by the way need not be simply connected. Hereby the first term of (11) contributes to that part of the integral where the vector k forms an acute angle with the direction of ∇E while the second term gives rise to the rest of the integral.

We see immediately that $K_0(0)$ will tend to be small when the energy gradient is large at the surface. Thus for instance at a zone boundary of a perfect crystal the gradient will become infinite, so that such a surface will give no contribution at all to $K_0(0)$. To get a clearer idea of the orders of magnitude involved we shall apply (12) to the case where E is a function of the magnitude of the vector k only and does not depend on its direction. Here the surfaces of constant energy are spheres, and we have $|\nabla E|=E'(|k|)$ and $dS=k^2d\Omega$ where $d\Omega$ is an element of solid angle. We put

$$\alpha(|k|)=\frac{m}{\hbar^2}\cdot\frac{E'(|k|)}{|k|} \tag{13}$$

and get thus

$$K_0(0)=\frac{\epsilon^2|k^2|}{\pi^2mc^2\alpha}\int\frac{(k)kd\Omega}{|k|}.$$

Since all the non-diagonal terms of the tensor vanish at the integration over the sphere and the diagonal terms become all equal to $|k^2|/3$ and since

$$|k|^3/3\pi^2=N \tag{14}$$

is the number of electrons per unit volume we obtain with the notation of formula (8)

$$K_0(0)=\kappa^2/\alpha. \tag{15}$$

For free electrons we see that $\alpha=1$ and as soon as $E'(|k|)$ is greater than the corresponding quantity for free electrons α will be greater than 1 and thus $K_0(0)<\kappa^2$. Comparing with formula (6) we verify first of all that for free electrons the London term is completely cancelled by $K_0(0)$ and, moreover, we see that for $\alpha>1$ there will be a positive $g_0(0)$ which lies between 0 and κ^2.

In most practical cases, for instance when the medium is polycrystalline, the tensor $(k)k$ appearing in the general formula (12) may as in the case just treated be replaced by its average scalar $k^2/3$. Then we may still retain the simple form of Eq. (14) if we introduce the following generalized definition of α, which contains the earlier definition (13) as a special case, namely

$$\alpha=\frac{m}{\hbar^2}\frac{\int\frac{k\cdot\nabla E}{|\nabla E|}dS}{\int\frac{k^2}{|\nabla E|}dS}, \tag{16}$$

and the general conclusions drawn from (15) will still be valid.

We shall write formula (12) in still another form which is useful in connection with the problem of the specific heat of the superconductive state. For this purpose we introduce a quantity $\nu(k)$ defining the number of states per unit energy range, unit area of the corresponding surface of constant energy and unit volume, so that

$$N(E)=\int\nu(k)dS, \tag{17}$$

the integral being extended over the whole surface of energy E is the usual density of states. Since there are—apart from spin—$dk/(2\pi)^3$ states per unit volume in the element dk of wave number space, we see that

$$\nu(k)=\frac{1}{8\pi^3|\nabla E|}. \tag{18}$$

Instead of (12) we may thus write

$$K_0(0)=\frac{8\pi\epsilon^2\hbar^2}{m^2c^2}\int\nu(k)(k)kdS,$$

or if we replace the tensor $(k)k$ by its average scalar $\frac{1}{3}k^2$

$$K_0(0)=N(E)\frac{8\pi\epsilon^2\hbar^2}{3m^2c^2}\langle k^2\rangle_{\text{Av}}, \tag{19}$$

where we have put

$$\langle k^2\rangle_{\text{Av}}=\frac{1}{N(E)}\int k^2\nu(k)dS. \tag{20}$$

Since $\langle k^2\rangle_{\text{Av}}$ will in general not differ much from the corresponding quantity in a spherically symmetrical distribution, where it is determined from the number N by means of (14), this formula may be useful in judging the relationship between the lack of a temperature proportional term in the specific heat—the magnitude of which is determined by $N(E)$—and superconductivity.

It should be pointed out that the results of the above considerations, although derived for a perfect lattice, are rather insensitive towards aperiodic perturbations as long as the electronic wave functions retain their general resemblance with the wave functions of free electrons. This is of importance in connection with the superconductive properties of alloys or otherwise imperfect crystals.

Before ending this note we shall make a general remark regarding the compatibility of London's theory of the superconductive state with present electronic physics. Thus from the theorem of Bohr mentioned above it follows that any attempt to derive the London theory by means of considerations based on classical physics must necessarily fail. On the other hand the fact that Planck's quantum of action does not appear in the formulae of London would also seem to exclude a quantum theoretical explanation of the

theory and would thus throw doubt on the validity of the considerations put forward in this note. Without entering more deeply into this puzzling problem we shall briefly show how the behavior of free electrons in magnetic fields may throw some light on the paradox in question. Thus for a spherically symmetrical distribution of free electrons of energy E it follows from the formulae developed in I that with the notations used in the present note

$$g_0(k)=\frac{\kappa^2}{2}f(\xi),$$

where

$$\xi=\frac{2}{\hbar|k|}(2mE)^{\frac{1}{2}},$$

and

$$f(\xi)=1-\tfrac{1}{2}\left(\xi-\frac{1}{\xi}\right)\log\frac{1+\xi}{|1-\xi|}.$$

Now for small ξ-values, i.e. when $E\ll\hbar^2k^2/8m$, $f(\xi)\sim 2$, so that $g_0(k)$ tends towards the London value κ^2. Transforming the equations for the vector potential back to ordinary space we see that the nucleus of the space integral which thus determines the field in terms of the given imposed field will be less and less influenced, the smaller the value of E, by the parts of the k space where the condition $E\ll\hbar^2k^2/8m$ is not fulfilled. Letting E tend towards zero with the value of κ fixed we arrive thus at the London equation in the limit. Now it is true, as pointed out in I, that because of the Pauli exclusion principle we cannot with real electrons let E diminish without a corresponding decrease of κ, κ^2 being proportional to the number of electrons per unit volume. But with particles obeying the Bose-Einstein statistics the condition mentioned would be fulfilled when the temperature is sufficiently low. We see thus how in an extreme quantum theoretical case—the de Broglie wavelength concerned being very large compared to the dimensions within which the field varies appreciably—the Planck constant gradually disappears from the formulae, which at the same time retain their non-classical form. In the other extreme case, where the energy of the electrons is very large the Planck constant likewise falls out in agreement with Bohr's theorem, since $f(\xi)\to 0$ when $\xi\to\infty$. In a Fermi distribution at the absolute zero of temperature there will always be electrons with low energies present which explains the deviation of Landau's formula of the magnetic susceptibility of an electron gas from Bohr's theorem. Here, too, we have the remarkable case of a quantum effect formula without Planck's constant.[5]

[5] A closer study of the behavior of free electrons in magnetic and electric fields is under preparation by J. Lindhard.