On the Problem of the Molecular Theory of Superconductivity*

F. LONDON
Duke University, Durham, North Carolina
(Received April 25, 1948)

The electrodynamics and thermodynamics of the superconducting state entail quite definite consequences with regard to the stability character of the supercurrents. In contrast to a recent attempt of Heisenberg, superconductivity is characterized in the present paper not as a state of electronic lattice order in ordinary space, but rather as a kind of condensed state in momentum space which implies a long-range order of the momentum vector $p=mv+(e/c)A$ in ordinary space as a consequence of the requirements of quantum kinematics. Indications are that it is most probably the exchange interaction associated with the Coulombian field which is responsible for this condensation in momentum space. Ferromagnetism and superconductivity thus would play the role of two opposite limiting cases of the same effect depending on whether the exchange interaction, competing with the zero-point energy, promotes parallel orientation of the electronic spins or a coordination of the translational momentum in a state of vanishing total spin.

THE appearance of a paper by Heisenberg[1] on superconductivity gives me a welcome occasion to publish a few remarks concerning some related ideas I have nourished for several years but had thought to withhold until I could make a well substantiated contribution to this subject. Since Heisenberg now employs the same interactions that I had in mind but arrives at an entirely different mechanism which, moreover, in my opinion, does not yield superconductivity, it might perhaps be justifiable and even of interest if I briefly develop my viewpoint. Of course, I am quite aware of the necessarily sketchy character of such a discussion.

I. HEISENBERG'S SUPERLATTICE THEORY

Heisenberg's attempt is admittedly not to be considered as a definite solution of the apparently very difficult problem of a molecular theory of superconductivity. He lays stress upon expressing his intention by saying that he wishes to point out a peculiar feature which perhaps characterizes the place in the theory of metals where one might look for an explanation of this phenomenon.

Heisenberg considers—and in this respect we agree with him—the *Coulomb interaction of the electrons* as essential for the establishment of the superconducting state. He assumes the first-order perturbation caused by this interaction to disappear since it is given by the mean value of the interaction potential taken over the unperturbed system, and this mean value disappears if the metal is supposed to be electrically neutral. Accordingly, only the second-order perturbation is regarded as important. It is given by the well-known expression of quantum mechanics:

$$W_2=-\sum_r{}'|H_{0r}|^2/(E_r-E_0). \tag{1}$$

Here H_{0r} is the transition element of the perturbation matrix between the state 0 and the state r and E_0 and E_r the corresponding unperturbed energy values. For two electrons, 1 and 2, of the momenta p_k and p_l in the state 0 and p_m and p_n in the state r the perturbation matrix has the form:

$$\begin{aligned} H_{0r}=(e^2/V^2)\int\int(1/|r_1-r_2| \\ \times\exp\{(2\pi i/h)[(p_m-p_k)r_1 \\ +(p_n-p_l)r_2]\}d\tau_1 d\tau_2 \quad (1') \\ =(4\pi h^2e^2/V|p_n-p_l|^2)\delta(p_k+p_l-p_m-p_n), \end{aligned}$$

where

$$\delta(p)=\begin{cases}1 & \text{for } p=0,\\ 0 & \text{for } p\neq 0.\end{cases}$$

Here we can no longer agree with Heisenberg. The undisturbed state is highly degenerate as a result of the spin and the identity of the electrons. Consequently there might be a first-order effect in spite of the system's being neutral. On the basis of his argument Heisenberg would entirely invalidate his own well-known

* The work reported here was carried out under contract N7onr-455 with the Office of Naval Research.
[1] W. Heisenberg, Zeits. f. Naturkunde **2a**, 185 (1947).

theory of ferromagnetism,[2] since this theory is essentially based on a *first*-order Coulombian perturbation effect in neutral systems, the so-called exchange effect.

Let us, however, first follow Heisenberg's reasoning to its conclusion. A second-order effect is generally due to a perturbation of the eigenfunctions and thus it is surmised that the plane waves of the ordinary theory of metals may not be a suitable starting point. Particularly the states near the surface of the Fermi lake might be greatly disturbed by the presence of the Coulomb interaction. Consequently, it appears preferable to abandon the perturbation method and to start with more suitable wave functions on the basis of the variation method. Heisenberg considers monoelectronic functions in momentum space of the type

$$\psi(p,\vartheta)=\exp[\alpha(\cos\vartheta-1)-\beta(p-P)], \quad (2)$$

where α and β are the parameters to be determined by the minimum principle, P = the limiting momentum of the Fermi distribution, p, ϑ = polar coordinates in momentum space. By this form for the wave function he anticipates a certain range, β^{-1}, of the momentum distribution. This has the consequence that, in ordinary space, he obtains *wave packets* of the *finite* extension βh instead of the usual plane waves of infinite extension in space.

The result is that these localizable wave packets would be arranged best in a kind of space lattice similar to an earlier attempt of Kronig.[3] One may think of a lattice like the *CsCl*-type in which the electrons of opposite spin correspond to the two kinds of ions (see reference 1, Section 2C).

The decisive question is, of course: Why should such a superstructure of electrons, which in itself may appear quite plausible, entail superconductivity? Heisenberg gives an estimate of the different energy contributions in this superstructure from which he infers (reference 1, Eqs. (62), (63), and (64)) that within a certain temperature range $T_1<T<T_0$ an ordered state with a current would be the thermodynamically most stable one, where T_0 is the transition temperature of the superconductor. But for the *lowest temperatures*, $0<T<T_1$, *he obtains a ground state without currents*. He suggests that even at these lowest temperatures, for which a state without macroscopic current is the thermodynamically most stable one, the presence of a "crystal germ" could give rise to a great number of elementary "current threads" of a fixed current strength and direction playing a role similar to that of the Weiss' domains in the theory of ferromagnetism. Normally these threads would be distributed at random and would not give rise to a macroscopic current. But if these current threads could "freeze out" and form a monocrystal, this system might be unable to rid itself of its macrocurrent by collisions with the lattice of the ions. Apparently in virtue of interactions which are not yet explicitly introduced in the theory (surface effects) it is thought that a macrocurrent might be stable or rather metastable after all.

Heisenberg claims that from this basis he can derive an equation of the type:[4]

$$(\partial/\partial t)(\Lambda j_s)=E, \quad (3)$$

(reference 1, Eq. (71)) where j_s is the density of the macroscopic supercurrent, E is the electric field strength, and Λ a coefficient characteristic of the superconductor. I have not been able to follow Heisenberg's deduction here. But for the sake of argument let us assume that Eq. (3) can be derived on this basis. In fact an equation of this type has been proposed[5] several times as basis of a macroscopic electrodynamics of superconductivity in the sense of describing *infinite conductivity*. But after the so-called Meissner-Ochsenfeld effect[6] had been discovered it became clear that the assumption of Eq. (3) leads to a great number of current distributions which cannot be realized within superconductors and that one has to introduce a *supplementary restriction* in order to obtain only the currents which actually exist. This restriction can be

[2] W. Heisenberg, Zeits. f. Physik **49**, 619 (1928); see also F. Bloch, Zeits. f. Physik **57**, 545 (1929).

[3] R. de Lar Kronig, Zeits. f. Physik **78**, 744 (1932); **80**, 203 (1932).

[4] Actually Heisenberg obtains an equation somewhat more complicated than (3) (reference 1, Eqs. (70) and (71)) but for the subsequent discussion this is not essential.

[5] B. L. De Haas-Lorentz, Physica **5**, 384 (1925); R. Becker, G. Sauter, and F. Heller, Zeits. f. Physik **85**, 772 (1933).

[6] W. Meissner and R. Ochsenfeld, Naturwiss. **21**, 787 (1933).

written in the form of the following equation:[7]

$$\text{curl}(\Lambda j_s) = -B/c. \quad (4)$$

Heisenberg infers Eq. (4) from Eq. (3) by a purely thermodynamical consideration (reference 1, Section 4b). This proof is, however, dependent on the *assumption* that here one has to deal with a thermodynamical equilibrium state. But this is precisely the assumption which appears not *a priori* justifiable if one considers, as Heisenberg does, superconductivity as the outcome of a "freezing-out" process. Indeed, from Eq. (3) and from Maxwell's $\text{curl}E = -\dot{B}/c$ one infers, taking the curl on both sides of (3), that:

$$(\partial/\partial t)(\text{curl}\Lambda j_s + B/c) = 0, \quad (5)$$

or integrating with respect to time:

$$\text{curl}\Lambda j_s = (B_0 - B)/c. \quad (5')$$

Here B_0 is an arbitrary time independent vector field playing the role of a frozen-in magnetic field, entirely in disagreement with the experimental finding of Meissner and Ochsenfeld, though quite in line with the concept of an infinite conductivity implying the existence of *undercooled* states. Assuming the equation $B_0 = 0$ or Eq. (4) would go beyond the contents of (3); this cannot be inferred on merely thermodynamical grounds, at least not in a case in which one has all reason *not* to accept without proof, the realization of true thermodynamical equilibrium.

Actually, Eq. (4) accounts for a fact which is not yet implied by (3), namely that superconductors are not only *ideal conductors* ($j_s \neq 0$, $E = 0$), but, moreover, *ideal diamagnetics* ($H \neq 0$, $B_0 = 0$). The latter property is not a consequence of the former, nor is the former a consequence of the latter.

We will not expatiate upon the strange feature that according to Heisenberg's theory one would have to distinguish between two temperature intervals ($0 < T < T_1$) and ($T_1 < T < T_0$) of entirely different stability character within the superconducting state ($0 < T < T_0$). While nothing is known which would indicate the existence of such a characteristic temperature T_1, one could perhaps say that T_1 might be lower than all temperatures reached so far.** Thus one may assume that actually one has to deal only with the upper one of the two intervals ($T_1 < T < T_0$).

Turning now to the case $T_1 < T < T_0$ we believe that a state endowed with a current, as the thermodynamically stable one within this temperature interval (reference 1, Eqs. (62), (63), and (64)), would not furnish a satisfactory description of superconductivity as we know it today.

Heisenberg thinks of an *asymmetric distribution* in momentum space, the asymmetry depending on the direction of the current (reference 1, Eq. (58)). That such a model would not be compatible with the facts can be seen readily if one realizes that it would again entail a great number of equivalent equilibrium states which are actually not realized in nature. For instance, an isolated superconducting sphere in thermal equilibrium is free of any current as long as no external field is applied, whereas from Heisenberg's model one would infer that a state with spontaneous current should be stable even in absence of any applied magnetic field.

Suppose superconductivity really were to be interpreted by a great number of different *asymmetric equilibrium states* corresponding to the different current threads, as this is the case with ferromagnetism for the different orientations of the magnetic moment. Then one should expect to find *hysteresis* whenever one tries to change the direction or strength of a supercurrent, say, by changing the direction or strength of an applied magnetic field. Nothing of this kind has ever been observed with superconductors and, indeed, any relaxation effect of this sort would be quite incompatible with all available evidence as to the peculiar mobility by which the supercurrents adjust themselves to the slightest changes of an applied magnetic field. It is true, there are hysteresis effects in superconductors. But they are exclusively confined to the transition into the superconducting state. There is no hysteresis as long as one stays within the limits of the pure superconducting state.

The same criticism also applies to a recent attempt by Born and Cheng.[7a] These authors

[7] F. and H. London, Physica 2, 341 (1935).

** Indeed H. Hoppe in a recent paper, Ann. d. Phys. 1, 405 (1947), comes to the conclusion that $T_1 = 0$.

[7a] M. Born and K. C. Cheng, Nature 161, 968 (1948).

again propose an asymmetric momentum distribution (in this case arranged in certain "pockets" of the Brillouin zones) in order to account for different permanent currents in the superconductor. In reality there are no permanent currents but at best permanent magnetic fluxes and these occur exclusively in multiply connected superconducting regions.

It is true that some "frozen-in" magnetic fields are frequently found in simply connected superconductors; but they are, according to all evidence, generally to be attributed to non-equilibrium structures, to porous superconducting regions with non-superconducting inclusions, etc. They can be entirely eliminated by using very pure material and monocrystals. This is at least the interpretation which has been widely accepted and has found its general expression in Gorter and Casimir's thermodynamics[8] and in the electrodynamical equations (3) and (4). One may, of course, question whether these thermodynamics and electrodynamics are the last word concerning the macroscopic interpretation of superconductivity. But Heisenberg does not question this, and we certainly would not expect the macroscopic theory to be so fundamentally wrong.

Supplement to Section I

After conclusion of the present paper I received a copy of a manuscript of a paper, "Ueber das elektrodynamische Verhalten der Supraleiter," kindly sent to me by Professor W. Heisenberg. In this new paper Heisenberg withdraws his previous thermodynamical proof of the Meissner effect criticized above. However, now he even undertakes to prove Eq. (4) and the Meissner effect by considering only the action of the *classical Lorentz force*. This again is only possible by way of an assumption which anticipates what actually is the main point to be proven, namely, that case (A), applying the magnetic field after the superconducting state has been established, leads to the same velocity distribution as case (B) in which the magnetic field is applied already in the normal state and the transition into the superconducting state is done while the external field is kept constant. Heisenberg actually considers only the first case (A) and obtains our Eq. (4). However, it is by no means trivial; on the contrary, it would just be the task of a molecular theory of superconductivity to show why the two cases, A and B, lead to the same result.

[8] C. J. Gorter and H. Casimir, Physica 1, 306 (1934).

II. CONCLUSIONS FROM THE ELECTRODYNAMICS OF THE SUPERCONDUCTOR

Before one undertakes to develop a molecular theory of superconductivity it might be well to see how far the electrodynamics as expressed by Eqs. (3) and (4) already allows one to draw conclusions as to the kind of stability and the type of order realized in the superconducting state. Here we have partly to repeat, partly to supplement, remarks which were published about 13 years ago.[9] Their meaning will perhaps become clearer now when they are discussed in connection with Heisenberg's attempt.

A. Gauge Invariance and Superconductor Potential

We introduce the mean momentum field $\bar{p}_s$ of the superelectrons, defined as

$$\bar{p}_s=(m_s/n_se)j_s+(e/c)A, \tag{6}$$

where m_s is the effective mass of the superelectrons, n_s their number per cm^3 and A the vector potential of the magnetic field ($B=\mathrm{curl}A$). We may then write Eq. (4) simply in the form

$$\mathrm{curl}\bar{p}_s=0, \tag{4'}$$

if we assume

$$m_s/n_s=\Lambda e^2. \tag{7}$$

Accordingly we may express the vector $\bar{p}_s$ as the gradient of a scalar χ

$$\bar{p}_s=\mathrm{grad}\chi. \tag{8}$$

This χ, which we may call the "superconductor potential," is ***only defined within the superconductor*** and, hence, ***needs not be single-valued*** in multiply connected superconductors.

The vector potential A is not uniquely defined by the magnetic induction B. It can be replaced, as is well known, by an equivalent A' connected with A by a "gauge transformation" of the form

$$A'=A+\mathrm{grad}k, \tag{9}$$

[9] F. London, Proc. Roy. Soc. **A152**, 24 (1935). See also "Une conception nouvelle de la supraconductibilité," Actualités Scientifiques et Industrielles **458** (1937).

where k is an arbitrary continuous scalar with continuous first and second derivatives. Since k, in contrast to χ, is defined to be free of singularities in *whole* space it has always to be *single-valued.*

If we postulate the supplementary condition

$$\mathrm{div} A = 0 \quad (10)$$

for A and for all equivalent A', then k has to fulfill the equation:

$$\nabla^2 k = 0. \quad (11)$$

From (9) it follows also that $\bar{p}_s$ is not entirely determined by the definition (6). But the difference $\bar{p}_s - (e/c)A$ has a well defined meaning. If A is transformed according to (9), then p_s has to be transformed likewise by

$$\bar{p}_s' = \bar{p}_s + (e/c)\,\mathrm{grad} k. \quad (12)$$

We may add that, correspondingly, in quantum-mechanics any wave function $\psi(r_1, r_2 \cdots r_\alpha \cdots r_N)$ which obeys a Schrödinger equation with the vector potential A is equivalent to a ψ' which is defined by

$$\psi' = \psi \exp[(2\pi ie/hc)\textstyle\sum_\alpha k(r_\alpha)], \quad (13)$$

and which fulfills the corresponding Schrödinger equation with A'.

It is possible and convenient to chose a *standard value* for the vector potential with respect to the superconductor. We may, for instance, always chose A so that on the surface of the superconductor

$$A_\perp = 0. \quad (14)$$

Indeed, if we had originally another vector potential A' which did not fulfill (14), it would be connected with A by a transformation of the type of Eq. (9)

$$A' = A + \mathrm{grad} k$$

with Eq. (11)

$$\nabla^2 k = 0,$$

where, according to (14), k has to fulfill the boundary condition

$$(\mathrm{grad} k)_\perp = A_\perp'. \quad (14')$$

From well-known theorems of potential theory it follows that there is just one single-valued solution k within the superconductor which satisfies (11) and (14′). Accordingly, for a given magnetic field B there is just one standard vector potential A which, by the way, is defined so as to disappear for $B=0$.

Consequently, $\bar{p}_s$ is uniquely determined by the current j_s according to (5). Summarizing, we then may say that under stationary conditions the vector $\bar{p}_s$ fulfills the following equations: Within the superconductor:

$$\mathrm{curl}\bar{p}_s = 0, \quad \text{(equivalent to (4))} \quad (4')$$

$$\mathrm{div}\bar{p}_s = 0, \quad \text{(because of (10) and of the continuity equation for } j_s) \quad (10')$$

and at its boundary:

$$\bar{p}_{s\perp} = (m_s/n_s e) j_{s\perp}. \quad \text{(equivalent to (14))} \quad (14'')$$

For a simply connected superconductor these equations have one unique solution, provided $j_{s\perp}$ is given on its whole surface. Especially for an isolated superconductor ($j_{s\perp}=0$) this solution is well known to be

$$\bar{p}_s = 0. \quad (15)$$

For a multiply connected superconductor the solution of (4′) (13) (14″) is not uniquely determined unless the line integrals

$$\oint_{(k)} \bar{p}_s \cdot ds = (e/c)\phi_k, \quad (16)$$

taken along a curve within the superconductor around every hole, k, are given. The quantities ϕ_k are approximately identical with the fluxes through those holes and at the same time defined as the moduli of the, in this case, multivalued superconductor potential χ:

$$\phi_k = \int_{(k)} (A + \Lambda c j_s) \cdot ds = \int\!\!\int_{(k)} B \cdot dS + \Lambda c \oint_{(k)} j_s \cdot ds$$

$$= (e/c) \oint_{(k)} \mathrm{grad}\chi \cdot ds = (e/c)\langle\chi\rangle_k.$$

By $\langle\chi\rangle_k$ we denote the modulus of χ, i.e., the increase of χ, when being continued once around the hole k. From the differential equations (3) and (4) it follows that the ϕ_k are constant in time and independent of the path, insofar as the path (k) embraces the hole k just once. In general, the line integral $\Lambda c \oint j_s \cdot ds$ is negligible compared with the surface integral $\int\!\int B \cdot dS$.

B. Long-Range Order of the Momentum Vector

Equation (15) does not necessarily say that there is no current in a simply connected isolated superconductor. In a magnetic field the momentum vector is not necessarily parallel nor is it proportional to the current vector; according to (4′) we may express (15) in the following way:

$$(c/e)\bar{p}_s \equiv \Lambda c j_s + A = 0,$$

or

$$j_s = -A_s/\Lambda c. \qquad (15')$$

This means that there is a well defined current in a magnetic field and no current in the absence of any magnetic field. In addition, we have the equation of Maxwell's theory (we neglect the displacement current and assume as magnetic permeability $\mu = 1$:

$$\text{curl curl} A = (4\pi/c)j. \qquad (17)$$

It can be shown that in a simply connected isolated superconductor Eqs. (15′) and (17) uniquely determine the current by the field in infinity as a kind of surface current located within a layer of the very small depth of $c(4\pi\Lambda)^{\frac{1}{2}}$ behind the surface of the superconductor.

Compare Eq. (15′) with the behavior of an isolated ordinary conductor in a magnetic field: In the absence of an electric field there is no ordinary current; hence we have, in contrast to (15′), in a normal conductor:

$$j_n = 0, \qquad (18)$$

and instead of (15):

$$\bar{p}_n = (e/c)A. \qquad (19)$$

The latter is a very simple consequence[10] of the fact that the Hamiltonian $\mathcal{H}$ of free electrons in a magnetic field is given by:

$$\mathcal{H} = (p - (e/c)A)^2/2m. \qquad (20)$$

Hence a superconductor is distinguished from a normal conductor by the feature that something prevents the momentum $\bar{p}_s$ from assuming the local value of $(e/c)A$ and, hence, from minimizing the kinetic energy expression (20). We may characterize the superconducting state by saying that n_s electrons per cm^3 maintain a kind of *long-distance order with respect to their momentum vector p*, quite comparable to the ferromagnetic state, in which case it is the electronic angular momentum which is maintained over long distance by a cooperative order-disorder mechanism.

We have chosen the standard vector potential in such a way (Eq. (14)) that for the isolated simply connected superconductor it is especially the value $\bar{p}_s = 0$ which is maintained by the long range order over the whole body. In general we can only say that the long-range order is expressed by the Eq. (4′), $\text{curl}\bar{p}_s = 0$. For a straight wire of constant cross section, which is fed at its ends by a current, this still means simply $\bar{p}_s = \text{constant}$ over the whole diameter and length of the wire whereas the current is very inhomogeneously distributed over the cross section and is appreciable only near the surface.

Thus, summarizing this paragraph we may say that the long-range order characteristic of the superconducting state concerns, according to Eq. (4), the *momentum vector p* rather than the elementary current threads assumed by Heisenberg.

C. The Stability Character of the Supercurrents

According to the macroscopic electrodynamics, superconductivity is described in such a way that an isolated simply connected superconductor has no current unless an external magnetic field is applied. For a given applied field there exists just *one* current distribution.[11] It is true, at first sight it looks as if one could easily conceive of a situation of lower energy, for instance a state in which in an applied magnetic field *no* current would be present. However, such a state is not provided for by the differential equations (3) and (4) of the superconducting state although it would have less electromagnetic and kinetic energy than the existing state with current. The stability of the unique realizable state appears here to be of a quite similar character as it was the case in the older quantum theory of Bohr, where it also was still possible to imagine nonexisting states lower than the ground state, and the stability of the ground state had to be formally accepted from the mere *absence* of such

[10] As long as one can disregard quantum effects this (Eq. (19)) simply follows from the fact that the distribution function, $f(\mathcal{H})$, is an even function of the components of the vector $p-(e/c)A$. Hence $\int (p-(e/c)A)f(\mathcal{H})dp$, the integral over an odd function, must disappear.

[11] M. von Laue, Nach. d. Akad. der Wiss., Göttingen Math. Phys. Chem. Abt., 86 (1946).

lower states, excluded by the quantum conditions. Indeed, Eq. (4) has very much the *character of a quantum condition*, we called it a "supplementary restriction" and we shall see presently to what implications this will lead.

Summing up we may say that in the case of the isolated simply connected superconductor the currents are stable—not because they are "frozen out" but rather because in the given applied field there is *no other current provided for*, not even zero current.

The case of a multiply connected superconductor, say a ring, requires special consideration. In this case the occurrence of a permanent current is not dependent on an applied magnetic field. The field maintaining the current may here be furnished by the current itself. But such a ring current does not represent a state of minimum free energy. The state in which the ring has no current has, of course, less energy if no external field is applied. Nevertheless, the state with current has a kind of *macroscopic metastability*. The quantities (16)

$$\phi_k = (c/e)\oint_{(k)} p_s\cdot ds = \iint_{(k)} B\cdot dS + c\int \Lambda j_s\cdot ds$$

are constant in time as a consequence of (3) and (4). It requires a *finite* change of the macroscopic variables, e.g., heating above the transition temperature or the application of a magnetic field stronger than the threshold field, in order to release the free energy locked in by the ring.

It is clear from this remark that it makes little sense to speak of the stability of a single current element. One has to consider the system as a whole including the entire external field and its sources. In fact, each current element has its kinetic energy $\Lambda j_s^2/2$ which has its minimum for $j_s=0$. Nevertheless, a state $j_s\neq 0$ can be entirely stable if it is the only one compatible with the external applied field and with the boundary conditions.

III. QUANTUM-MECHANICAL DESCRIPTION OF SUPERCONDUCTIVITY

In the preceding section we have shown that it is the quantity p_s rather than the current j_s which in the superconducting state appears to be held in a kind of long-range order.

The problem of superconductivity is accordingly reduced to finding the mechanism which at sufficiently low temperature enforces the establishment of this kind of order. Before we come to this point it will be well to recall that Eq. (15) and, for multiply connected superconductors, the general Eq. (8) describe a very characteristic situation if they are expressed in the language of quantum mechanics.

It is well known that in non-relativistic quantum mechanics, which at any rate should be competent for explaining superconductivity, the density of the electric current at the point R in space for a state represented by the wave function in multidimensional configuration space $\psi(r_1, r_2, \cdots r_\alpha, \cdots r_N)$ is given by:

$$j(R) = \sum_\alpha \int \{(he/4\pi i m)[\psi^* \operatorname{grad}_\alpha\psi - \psi \operatorname{grad}_\alpha\psi^*] - (e^2/mc)A(R)\psi\psi^*\}\,\delta_{R\alpha}d\tau. \quad (21)$$

Here $\delta_{R\alpha}$ is the three-dimensional Dirac function $\delta(R-r_\alpha)$. The integration is to be extended over the whole $3N$-dimensional configuration space; $\operatorname{grad}_\alpha$ is the operator $(\partial/\partial x_\alpha, \partial/\partial y_\alpha, \partial/\partial z_\alpha)$.

A. Simply Connected Isolated Superconductor

If one substitutes plane waves distributed over a Fermi distribution into the expression (21) the terms with the gradients cancel by reason of symmetry. The sum

$$\sum_\alpha \int \psi\psi^*\delta_{R\alpha}d\tau = n(R) \quad (22)$$

is the particle number per cm³. Hence we obtain

$$j(R) = -(e^2/mc)n(R)A(R). \quad (23)$$

This is identical with Eq. (15′) or, hence, Eq. (15), provided that $n(R)$ is a function sufficiently smooth to be replaced by its "coarse-grained" mean value. In fact, for plane waves $n(R)$ is exactly constant.

To be sure, the plane waves are not eigenfunctions of free electrons in a magnetic field. In reality the eigenfunctions of free electrons do depend very definitely on the magnetic field. What happens is well known: the plane waves coil up and transmute into a kind of wave packets of cylindric shape, the axes oriented parallel to the field. These eigenfunctions closely correspond to the corkscrew orbits of the classical motion of free electrons in a magnetic field. In thermal equilibrium they arrange in such a way that Eq. (19),

$$\bar{p}=(e/c)A(R),$$

is very nearly fulfilled. As we have seen, for classical mechanics this equation is exactly fulfilled. In quantum mechanics the uncertainty relation entails a little difficulty as p cannot be exactly prescribed at a given point in space R. The result is the appearance of the diamagnetism of free electrons first calculated by Landau.[12] But this is a very small effect and may be discarded here.

However the electrons in the superconducting state are certainly not to be considered as free; they have a lower energy than in the normal state, realizable at the same temperature in a strong magnetic field. If $H_c(T)$ is the so-called magnetic threshold field, which limits the superconducting state, the free energy difference per cm^3 between the normal state and the superconducting state is given by

$$F_s-F_n=-H_c^2/8\pi. \quad (24)$$

The existence of an energy difference clearly indicates that the superelectrons have yielded to some interaction. Hence there is no reason to expect them to behave like the coiling wave functions of free electrons in a magnetic field.

Evidently, according to (21), it would be sufficient to show that in the superconducting state, as a result of those interactions, the eigenfunctions would resist coiling when brought into a magnetic field and, in fact, simply stay exactly as they are without magnetic field, i.e., as if they were frozen in. Although this would be by no means the only way of obtaining the result (23) we will here consider this possibility somewhat more closely. It means precisely the opposite of the mechanism proposed by Heisenberg: we would expect sharp wave packets in momentum space, sharp even in the presence of a magnetic field, provided the field is smaller than the threshold field. In ordinary space the wave functions would be very widely extended, just as the plane waves fill the whole available volume. Heisenberg, on the other hand, suggests a certain relative localizability in ordinary space, a super lattice, and, correspondingly, some diffusedness of the momentum distribution as described by the wave function (2). According to our concept the long-distance order of the momentum vector would be due to the wide extension of the individual quantum state, as each plane-wave eigenfunction represents a constant momentum vector throughout the whole volume. We would have one single symmetric quantum state for a simply connected isolated superconductor at 0°A. while Heisenberg proposes a continuum of asymmetric states.

[12] L. Landau, Zeits. f. Physik **64**, 629 (1930).

B. Superconducting Ring

Thus far we have only considered an isolated, simply connected superconductor. In order to discuss the case in which an actual transfer of electricity is brought forward it is simplest to consider the case of a superconducting ring. In a ring the superconductor potential may have a modulus and we have, in general, to deal with Eq. (8) or

$$\bar{p}_s=\Lambda e j_s+(e/c)A=\text{grad}\chi, \quad (8')$$

where the modulus of χ describes the flux possibly locked in by the ring.

In this case it is instructive formally to divide the magnetic field B and its vector potential A into two parts:

$$B=B_0+B_1, \quad (25)$$

$$A=A_0+A_1, \quad (26)$$

in such a way that the total flux of B and the total flux of B_0 are the same, but B_0 is chosen so as to disappear entirely in the material of the ring. For sake of illustration one may imagine B_0 caught inside a hollow cylindric superconductor which has been put into the hole of the ring. Although B_0 is supposed to disappear within the material, the vector potential, A_0, will not vanish there. This simply follows from the fact that on a closed path located entirely within the material

$$\oint A_0\cdot ds=\int\int B_0\cdot dS\neq 0.$$

Since $\text{curl}A_0=0$ within the material, we may write

$$A_0=\text{grad}\nu, \quad (27)$$

where ν has to be a multivalued function whose modulus $\langle\nu\rangle$ is just equal to the flux of B_0,

$$\langle\nu\rangle \equiv \oint \mathrm{grad}\nu\cdot ds = \int\int B_0\cdot dS.$$

In addition ν has to fulfill the equations

$$\nabla^2\nu = 0 \quad \text{in the interior,}$$

and

$$(\mathrm{grad}\nu)_\perp = 0 \quad \text{on the surface.}$$

By these conditions gradν is uniquely determined within the whole ring. Correspondingly, if $\psi_0(r_1, r_2\cdots r_N)$ is the wave function of the super-electrons in the ring without flux, we have to write, according to (13),

$$\psi = \psi_0 \exp[2\pi i(e/hc)\textstyle\sum_\alpha \nu(r_\alpha)] \qquad (28)$$

for the wave function embracing the field B_0, even though no magnetic field is yet in the material itself. This transformation $\psi_0 \rightarrow \psi$ as expressed by Eq. (28) is, evidently, quite generally valid for any ring-shaped quantum-mechanical system which embraces a magnetic flux in such a way as not to touch the flux itself. We now add the field B_1, supposed to be so small as not to destroy superconductivity, and we further assume that now, as well as before, the superconducting state is characterized by that peculiar rigidity of the wave function in a weak magnetic field. Then we may substitute the ψ of Eq. (28) in the expression for the current (21) and obtain:

$$j = -(ne^2/mc)A_1 = (1/\Lambda c)(\mathrm{grad}\nu - A). \quad (29)$$

This is exactly the relation (8′) for the ring if we put $(e/c)\nu = \chi$. It would accordingly be sufficient to prove this particular rigidity in momentum space for a conveniently shaped, simply connected, isolated superconductor. The properties of the ring, and presumably also those of an open superconducting wire which is fed at its ends, would then follow automatically.

Obviously, the state represented by (28) is not identical with ψ_0; it is a metastable excited state which is entirely determined by the flux of B. We see the requirement that ψ be single-valued imposes to the moduli of ν and to the fluxes ϕ a quantum condition,

$$(e/c)\langle\nu\rangle = (e/c)\phi = \oint p_s ds = Kh,$$

where K has to be an integer.

C. The Superconductor as a Quantum Mechanism of Macroscopic Scale

Summarizing the preceding discussion we may say that the long-range order of the momentum vector $\bar{p}$, implied by the macroscopic electrodynamics (IIB) offers a peculiar possibility of reducing superconductivity to a particularly simple quantum-mechanical model: If the momentum vector statistics of at least a fraction of the electrons is *sharp*, or else forms a sharp lattice in momentum space, the wave function has to be spread, according to the uncertainty relation, over a wide volume in ordinary space, and if, moreover, this fraction of the electronic wave function remains essentially unchanged in a magnetic field ($<H_c$), then Eq. (4) follows from (21). If this interpretation should prove correct, then the characteristic stability and mobility of the supercurrents would be understood at the same time, *viz.*, as the outcome of a quantum-mechanical possibility to which we already have referred (IIC) when we characterized Eq. (4) as something like a *quantum-mechanical restriction:* In a simply connected, isolated superconductor, for instance, all possible currents would be represented by the adiabatic transformations of one single quantum state and would be entirely determined by the *macroscopic boundary conditions*, *viz.*, by the orientation and strength of this applied magnetic field in large distance: There is exactly *one* single current distribution for each applied magnetic field, very much the same as this is the case, say, for the ground state of a diamagnetic atom. Correspondingly, one has stability (absence of dissipation) of this current because there is no state with another current provided for in the given magnetic field. The macroscopic, i.e., electrodynamical, boundary conditions coincide here with the boundary conditions which determine the quantum state. Hence one may also say this interpretation characterizes the superconductor as a pure quantum mechanism of macroscopic scale.

This would be the situation at absolute zero. For a finite temperature there are, of course, excitations to be expected. Below the transition temperature, however, a kind of phase equilibrium will be established between the normal and superconducting electrons, two phases, interpenetrating each other in any volume element of ordinary space but separated in momentum space. Only a fraction of the formerly superconducting charges will still be connected with the magnetic field by a relation like (4) and their number n_s will be subject to thermal fluctuations, while other degrees of freedom, the lattice vibrations, will be excited. These excitations cannot serve, however, to dissipate the supercurrent, since the latter would still be connected with the magnetic field as before by Eq. (4) except that n_s will undergo thermal fluctuations around a certain mean value. This is quite comparable with the situation in a diamagnetic molecule, which is also unable to get rid of its diamagnetic current by transitions between its vibrational and rotational states. This is not because these degrees of freedom would be entirely uncoupled from the electronic motion, which is not true, but because in all these states practically the *same* diamagnetic current is maintained by the magnetic field. Of course, there will be fluctuations of this current, as the diamagnetism will not be quite the same in the different vibrational and rotational states; and in the case of the superconductor, there will be current fluctuations in addition, because of the fluctuations of the number n_s. But these fluctuations would vary around a *mean value* of the current density, which is the quantity which appears as j_s in (4); they would not open an opportunity for a transition to a non-diamagnetic state.

We have now to investigate whether a mechanism of this kind can be found among the accepted interactions between electrons in metals.

IV. THE EXCHANGE EFFECT OF THE COULOMBIAN INTERACTION

In Section I we have referred to the exchange effect of the Coulomb interaction playing the basic role in the theory of ferromagnetism. In the case of $p_m = p_l$ and $p_n = p_k$ the matrix element (1′) represents the so-called exchange integral of free electrons,

$$I_{kl} = 4\pi h^2 e^2 / V|p_k - p_l|^2, \quad (31)$$

corresponding to two states which differ only insofar as two electrons have exchanged their momenta. These two states have the same unperturbed energy. Hence one has a highly degenerate system and in the theory of ferromagnetism one deals with the secular equation defined by these matrix elements. The solutions of this secular problem give the first-order perturbation of the energy. In actual fact, up to the present time no one has succeeded in solving this secular problem rigorously. So far it has been possible only to determine the series of *energy mean values* of those groups of states which have the *same total spin s*. With this simplified energy spectrum the statistics have been worked out in a magnetic field. How far this procedure can be justified we do not know.

The exchange integral (31) is evidently always *positive*. In the case of two electrons with parallel spins it is to be multiplied by a factor -1 in order to give the first-order approximation of the energy and by a factor $+1$ for antiparallel spins. This favors ferromagnetism. Nevertheless, ferromagnetism does not necessarily follow from this model, as was already shown by Bloch,[2] since in order to have parallel spins the electrons in question must have different momenta (Pauli principle) and this may require more kinetic energy than can be gained as exchange energy.

For the mean value of the exchange energy of the group of states which have the total spin s one obtains the following expression:

$$\bar{E}_{\text{exch}}(s, n) = -2 \sum_{\alpha<\beta} I_{\alpha\beta} - \sum_{\alpha, k} I_{\alpha k} - \frac{4s(s+1) + n(n-4)}{2n(n-1)} \sum_{k<l} I_{kl}, \quad (32)$$

where the Greek indices refer to doubly occupied electronic states and Latin indices to singly occupied ones. n is the number of singly occupied states. I_{kl} is given by Eq. (31). The kinetic energy is, of course, given by

$$E_{\text{kin}} = (1/m)\sum_\alpha p_\alpha^2 + (1/2m)\sum p_k^2 \quad (33)$$

Bloch[2] determined as condition for ferromagnetism of this model the inequality

$$(N/V)^{-\frac{1}{3}} > (3/4\pi)^{\frac{1}{3}}(1+2^{-\frac{1}{3}})h^2/5me^2 \quad (34)$$

or

$$N/V < 10^{22} \text{ cm}^{-3},$$

where N/V is the number of electrons per cm^3. Unless this inequality is fulfilled the lowest state of the system has $s = 0$.

True, this model has to be taken with several grains of salt, and indeed it is too crude to give correct conditions for the appearance of ferromagnetism. In fact, it has been improved in many respects particularly by taking account of the lattice structure. Still a closer study of this simple mechanism might be of interest. The general behavior of the exchange integral (31) and the negative factors with which it is multiplied in Eq. (32) show that even in a case in which the exchange interaction is not strong enough to bring the system into a ferromagnetic state this interaction still has the character of a kind of *attraction in momentum space*. All terms in (32) are negative and proportional to $(p_k - p_l)^{-2}$.

One could understand that a mutual attraction in momentum space might bring forward a kind of condensation, something like a solid state in that space, i.e., a state which not only has a relatively sharp momentum distribution (which would not mean anything particular as any Fermi distribution of the ordinary plane waves of free electrons would show this character) but which, moreover, would *maintain* its sharpness with respect to p even in the presence of a not too strong magnetic field. As shown in III a state of this kind would be just sufficient for bringing forth superconductivity.

Hence, all this boils down to the question of whether the exchange effect of the Coulomb field actually entails such a condensation in momentum space as suspected. This is a very difficult question which cannot be answered without entering into a special investigation, which would go beyond the scope of the present paper. Here we shall point only to a few indications which seem to speak in favor of our conjecture, but, as the same time, show that relying on the mean value formula (32), so instructive for discussing ferromagnetism, will most probably be insufficient for solving the problem in question.

That superconductivity occurs at much lower temperatures than ferromagnetism does in no way exclude the possibility that both phenomena might be due to the same kind of interaction. In fact, this difference as to the characteristic temperature is just what one would expect. In the case of ferromagnetism the gain of internal energy is of the order of the *total exchange energy* itself as the parallel orientation of the spins entails, in (32), an increase of the factor $[4s(s+1)+n(n-4)]/2n(n-1)$ from $\frac{1}{2}$ to 1; in addition, it decisively affects the number of states which are doubly occupied. On the other hand, if in the superconducting state the electrons arrange themselves only more closely in momentum space without much change of orientation of their spins, then only a *very small fraction* of the original exchange energy can be released as only a minute diffusedness in the momentum distribution near the surface of the Fermi lake is removed by the condensation in question.

Let us now consider N free electrons in a volume V distributed over an entirely degenerated Fermi distribution of which the maximum momentum p_0 is given by

$$(8\pi/3)p_0^3 V = Nh^3. \quad (35)$$

On the basis of Eqs. (31) and (32) it is not difficult to calculate the total exchange energy of a single electron of the momentum p in the field of the N other electrons as function of p and p_0. The result is well known[13] to be given by

$$E_{\text{exch}}(p) = -(2p_0 e^2/h)\{1+[(p_0^2-p^2)/2pp_0] \times \ln[(p+p_0)/|p-p_0|]\}. \quad (36)$$

The function (36) has for $p=p_0$ a logarithmically infinite derivative and the components of the so-called mass tensor

$$m_{xy} = (\partial^2 E/\partial p_x \partial p_y)^{-1} \quad (37)$$

vanish there as $|p-p_0|$.

A *vanishing effective mass*, as this is expressed by (36) and (37), would imply a finite acceleration by an infinitely small force. Obviously, this is a rather formal result which may only serve to indicate that in the neighborhood of the top of the Fermi distribution the electrons behave very "quantum-mechanically:" The smaller the mass the greater the quantum effects. Accordingly, the familiar mixed procedure, customary in the electronic theory of metals, *viz.*, of first calculating energy bands in p-space (Brillouin zones) and then applying classical mechanics on wave packets is certainly not feasible here if we wish to calculate the behavior of these electrons in a magnetic field.

It is further noteworthy that the formula for the magnetic susceptibility χ of the so-called

[13] P. A. M. Dirac, Proc. Camb. Phil. Soc. 26, 376 (1930).

Landau-Peierls diamagnetism,[14] which in the case $E=E(|p|)$ can be written simply in the form,

$$\chi=-(e^2/18\pi hc^2)(E'+2pE'')_{p\to p_0}, \qquad (38)$$

would give, in the present case, an *infinite diamagnetic susceptibility*. Also, this result is entirely formal and nothing but an indication that here again an extreme effect is to be expected. It would be necessary to calculate the simultaneous effect of exchange interaction and magnetic field from the beginning and it would presumably be decisive to take account of the effect of the magnetic reaction field produced by the diamagnetic currents, as the resultant field in the interior of the superconductor would be almost zero. One has here to keep in mind that superconductivity is not correctly described by any value of the magnetic susceptibility alone. Hence, one would not be satisfied by calculating the total magnetization only. It would be necessary to consider the current distribution in all detail.

The *level density* at the top of the Fermi distribution would, according to (36), just disappear, though only as feebly as $1/\ln|p-p_0|$. This indicates that in the interaction field (36) the eigenfunctions near the top are less easily deformed (IIIA) by an external magnetic field than those of free electrons would be, since the spacing of the energy levels (E_0-E_k) is decisive for the first-order perturbations of the eigenfunctions:

$$\psi=\psi_0+\sum_k{}'[H_{0k}/(E_0-E_k)]\psi_k,$$

where ψ_k are the so-called "right" eigenfunction of "zero" order.

However, it can be anticipated that it will require a better approximation than the one given by the mean value formula of the energy spectrum, at least the exact solution of the first-order secular problem but possibly even a still better approximation which considers the electronic correlation effect more appropriately. The logarithmic singularity of $\partial E/\partial p$ (Eq. (36)) is apparently just too weak to cause a phase transition at a finite temperature. This can be learned from an investigation by Sampson and Seitz[15] who studied the effect of (36) on the magnetic susceptibility of Li and Na on the basis of the so-called Bardeen integral equation. These authors showed that the exchange effect as given by (36) would yield only a small contribution to the magnetic susceptibility proportional to $\ln(e^2p_0/hkT)$ and would not entail the appearance of a discontinuity of the specific heat or a sudden condensation at a finite temperature. However, Sampson and Seitz themselves make several reservations as to the competence of their approximation method and come to the conclusion that even for their very limited aims "the problem of the electron-electron correlations has.not yet been solved with sufficient completeness to say accurately to which extent the minimum of the energy level density would be influenced by their effect."

[14] R. Peierls, Zeits. f. Physik **80**, 763 (1933).
[15] J. B. Sampson and F. Seitz, Phys. Rev. **58**, 633 (1940).

CONCLUSION

Thus we come to the conclusion that the problem of the molecular theory of superconductivity has not always been posed quite properly. We tried to show that on the basis of the electrodynamics and thermodynamics of the superconductor one can draw quite definite conclusions with regard to the stability character of the supercurrents. In contrast to earlier attempts our discussion led us to characterize superconductivity, not as a state of electronic lattice order, as this was proposed by Kronig and quite recently by Heisenberg, but rather as a kind of condensed state in momentum space implying a long-range order of the momentum vector in ordinary space, presumably as an outcome of the requirements of quantum kinematics. We assembled indications which suggest that it is most probably the exchange interaction associated with the Coulomb field of the electrons which is responsible for this "condensation in momentum space." Ferromagnetism and superconductivity would then be considered as two opposite limiting cases of the same effect, depending on whether the exchange interaction competing with the zero-point energy promotes parallel orientation of the electronic spins or a coordination of the translational momentum in a state of vanishing total spin. However, it had to be left to the future to decide whether or not this suggestion can be substantiated by a rigorous theory.